Supporting Information

for

Benzo[1,2-*b*:6,5-*b′*]dithiophene(dithiazole)-4,5-Dione Derivatives: Synthesis, Electronic Properties, Crystal Packing and Charge Transport

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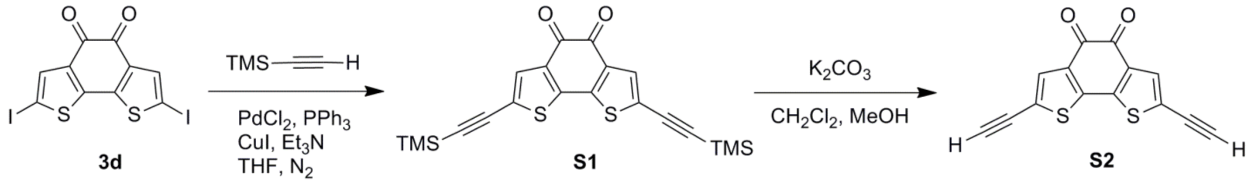
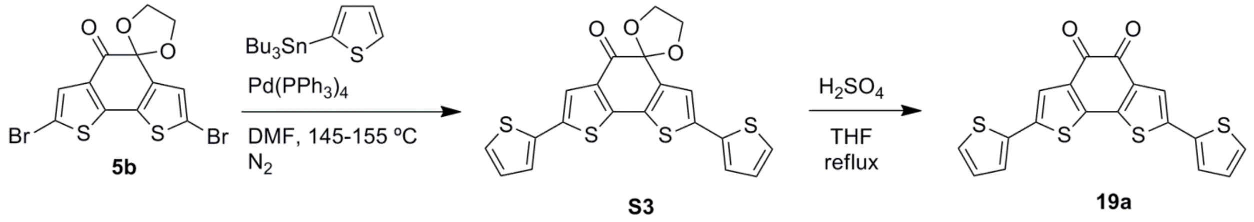
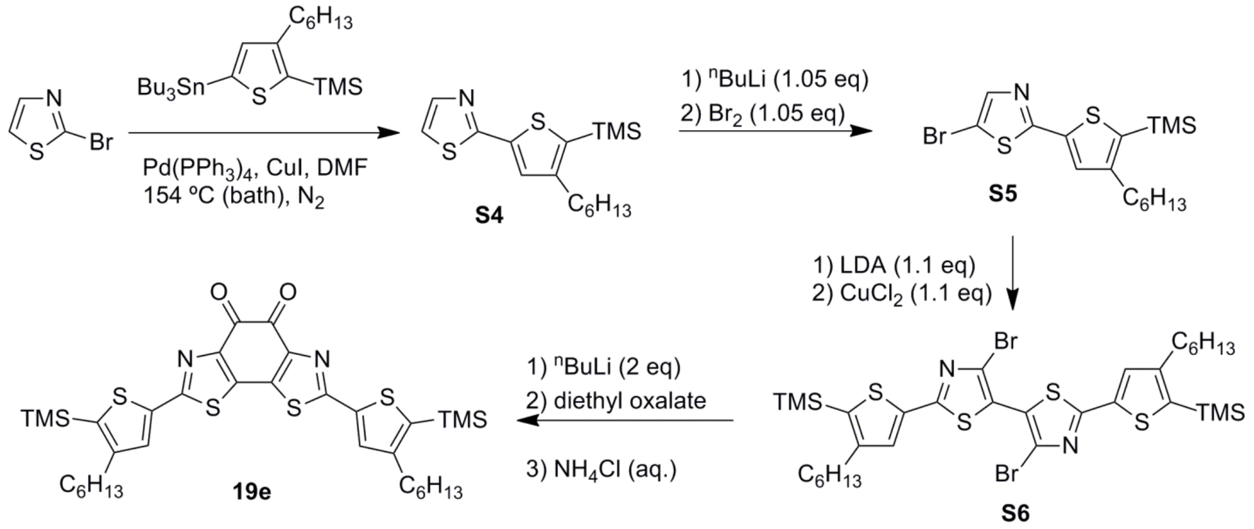


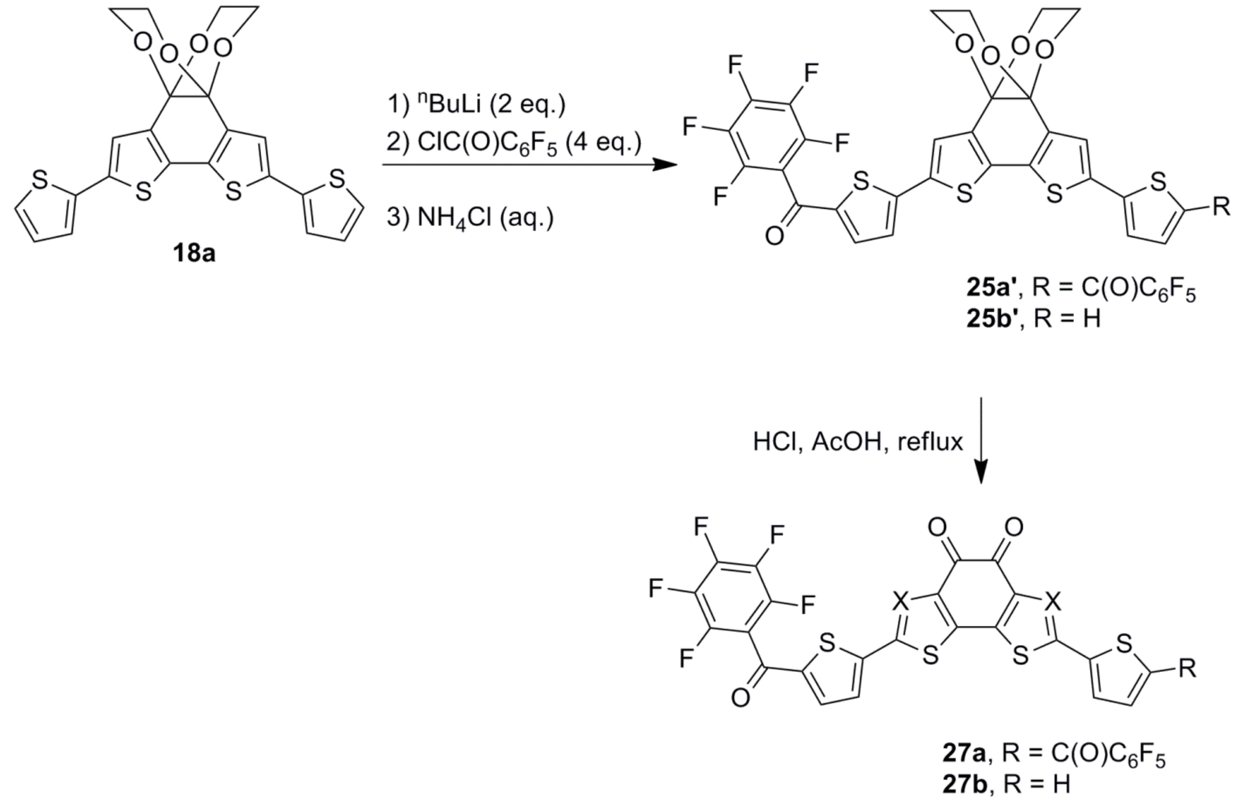
Scheme S1. **Sonogashira coupling of 2,7-diiodo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (3d) and preparation of 2,7-bis-ethynyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione.**



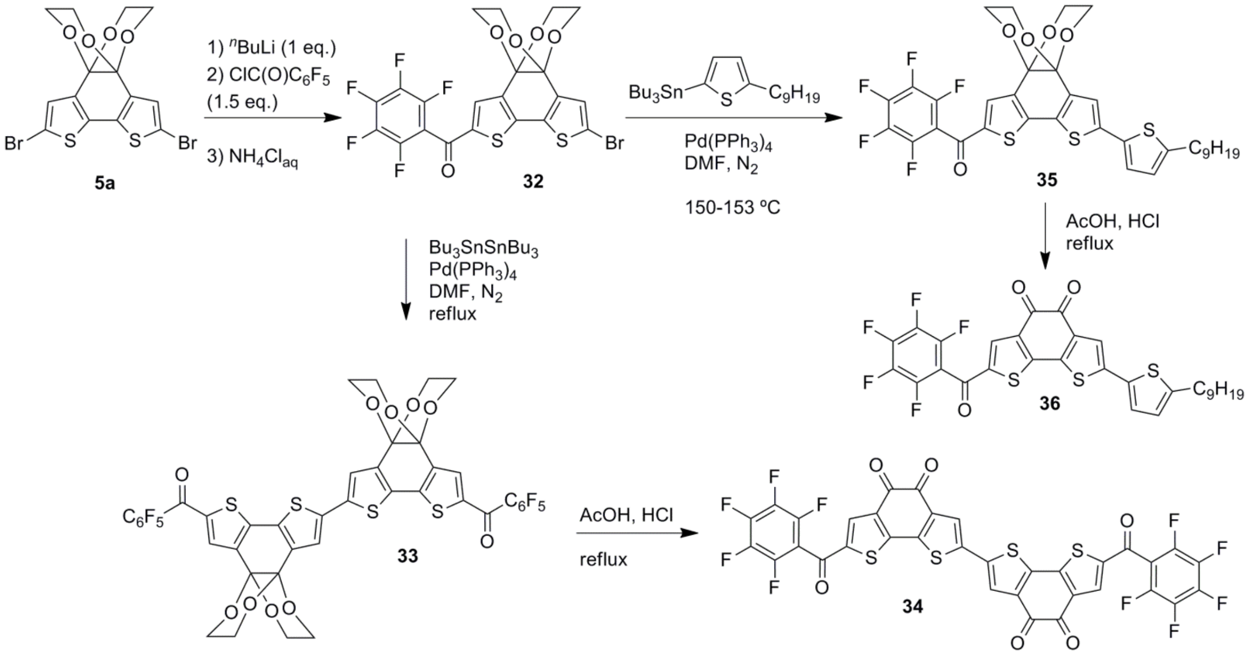
Scheme S2. Alternative synthesis of 2,7-bis-(thiophene-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19a).



Scheme S3. Preparation of 2,7-bis-(4-n-hexyl-5-trimethylsilyl-thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (19e).



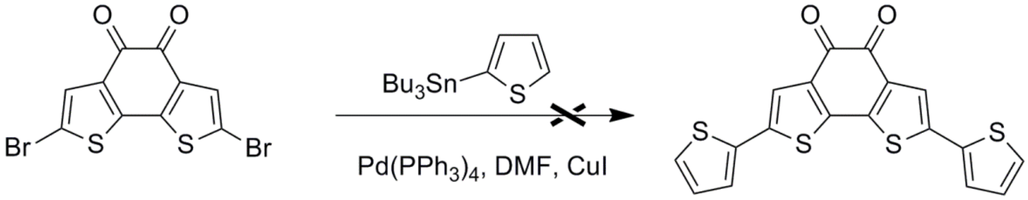
Scheme S4. Preparation of 27a,b from 18a.



Scheme S5. Preparation of target molecules 34 and 36.

1. *Stille coupling*

The Stille coupling of 2,7-dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**3c**) and 2,7-diiodo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**3d**) with two different thienyl stannanes was attempted (Scheme S6 and S7), and the major products isolated from both reactions were not expected ones. Mass spectrometry analysis of the product of the Stille coupling of 2,7-diiodo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**3d**) (Scheme S7) suggested that the Stille coupling was accompanied by the nucleophilic attack of the butyl group of tri-*n*-butylstannyl derivative on one of the carbonyl groups of the diketone bridge (Figure S2). UV-vis absorption spectra of the main product (Figure S3) has a band structure similar to the intermediate **20**, which has one of the carbonyl groups protected, and that provides further support for the side reaction at the dicarbonyl group.



Scheme S6. Attempted Stille coupling of 2,7-dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (3c) with 2-tri-*n*-butylstannylthiophene.

2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**3c**) (0.25 mmol, 0.094 g), thienyl stannane (2.2 eq., 0.55 mmol, 0.21 g), CuI (0.03 mol%, 0.0075 mmol, 1.4 mg) and Pd(PPh_3)$_4$ (10 mol%, 0.025 mmol, 0.029 g) were mixed in an oven-dried two-neck flask equipped with magnetic stirbar, nitrogen inlet and septum. Anhydrous DMF (10 mL) was added under nitrogen atmosphere and the reaction mixture was stirred overnight at room temperature. TLC analysis (dichloromethane as eluant) showed the presence of a new spot and starting unreacted dibromide **3c**. The mixture was heated up to 60 ºC, and the color changed from reddish-brown to bright yellow (a product is expected to be dark in color (green or blue). TLC analysis showed complete consumption of the starting dibromide, and the reaction mixture was cooled to room temperature, treated with water and diethyl ether, and brown organic phase was separated. The aqueous phase was extracted with diethyl ether, and combined organic phases were dried over $MgSO_4$. The solvent was removed by rotary evaporation and the crude product was obtained as soft brown matter. This crude compound was purified by the column chromatography (silica gel, dichloromethane as eluant). Fractions with the major product were combined, the solvents were removed, and the product was analyzed by ^{1}H NMR (Figure S1). Too many peaks were detected in the aromatic region, which indicated that the desired product was not obtained, and the symmetry of the molecule is broken. UV-vis absorption spectrum did not show the wide weak absorption at 400-900 nm part of the spectrum, which provided evidence that the diketone moiety of the molecule was not present in the major isolated product.

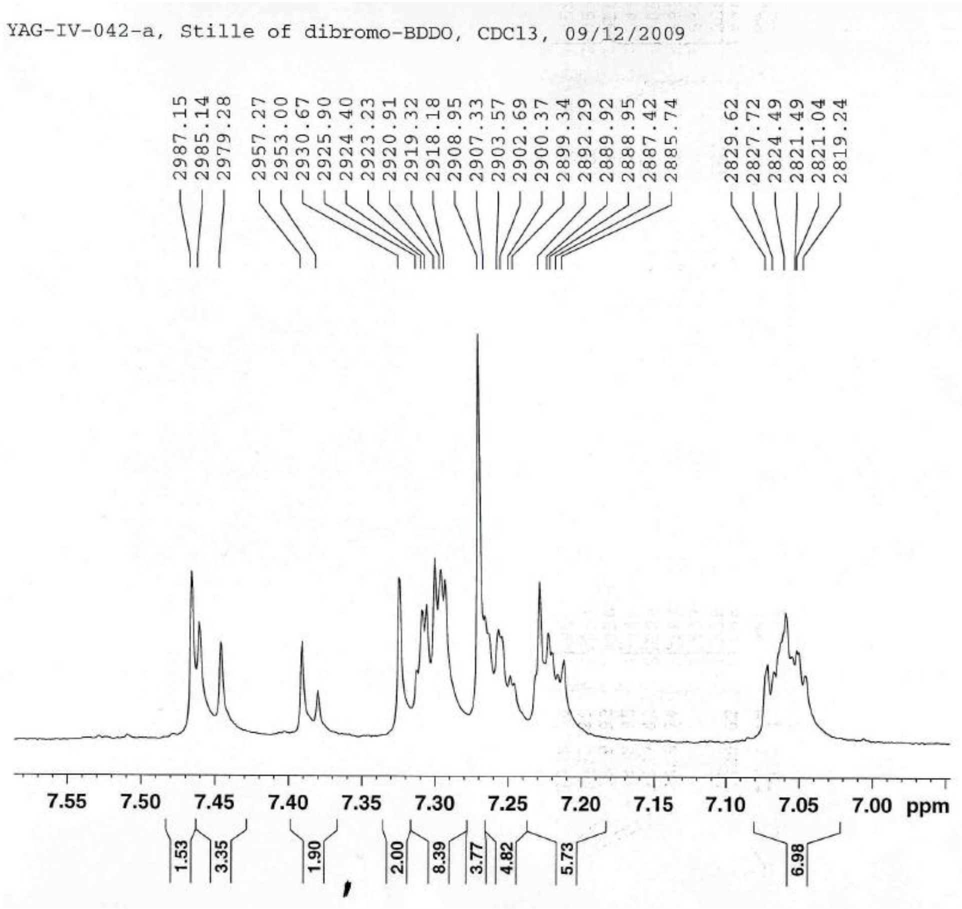
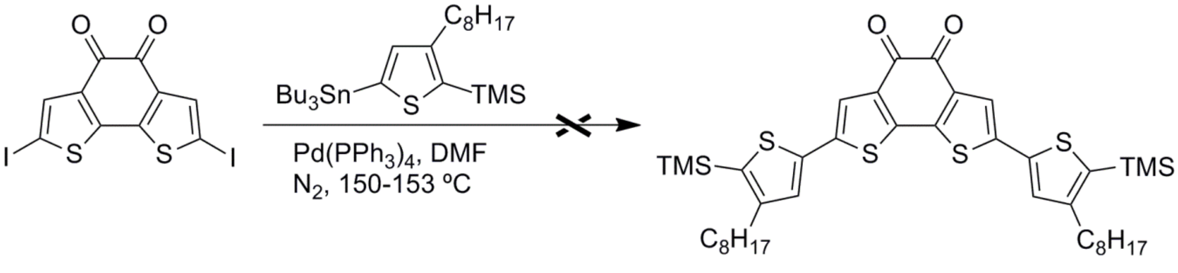


Figure S1. Aromatic region of ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the major product of the Stille coupling of 2,7-dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (3c) and thienyl stannane.



Scheme S7. Attempted Stille coupling of 2,7-diiodo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (3c) with 2-tri-*n*-butylstannyl-4-*n*-octyl-5-trimethylsilylthiophene.

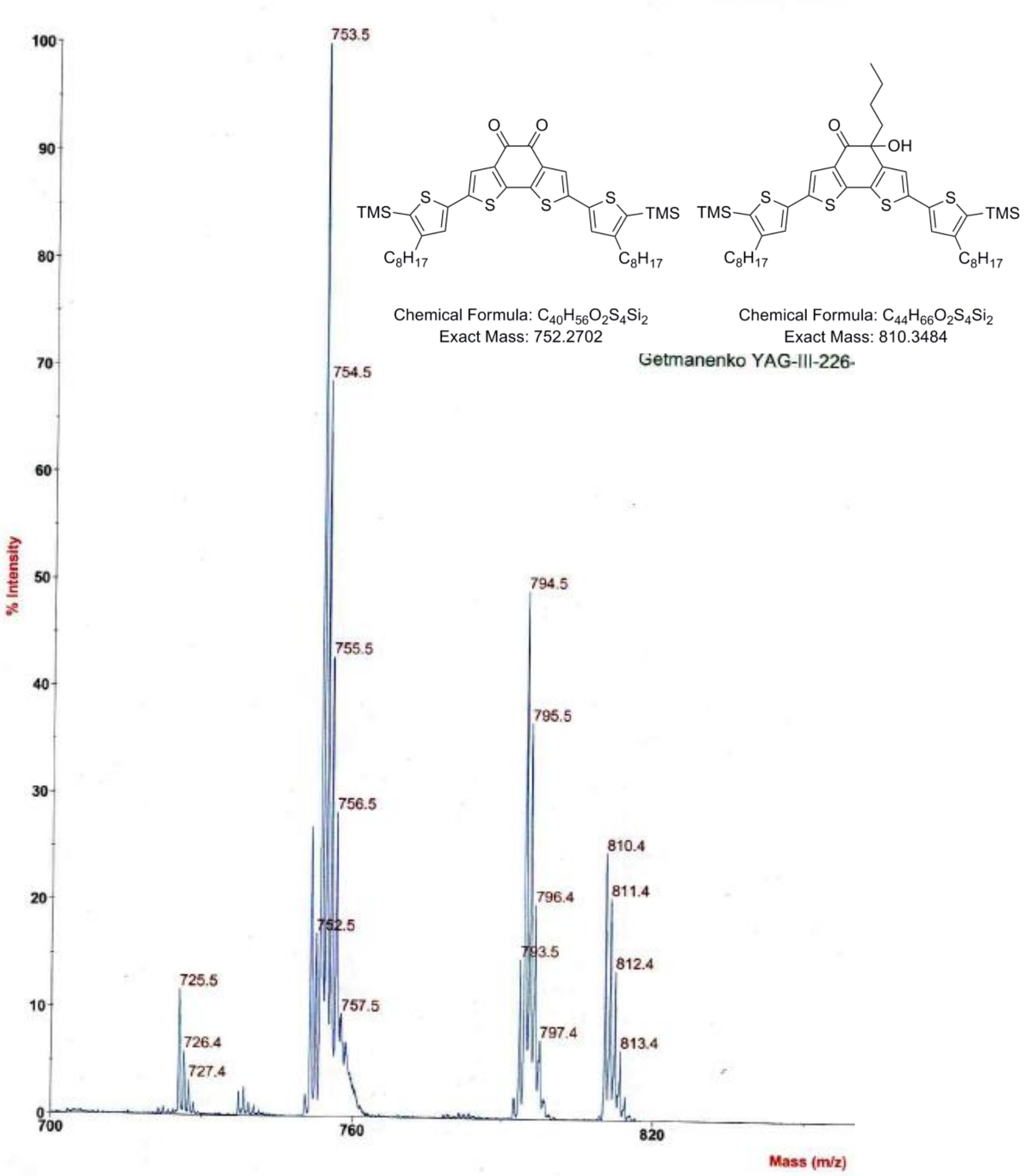


Figure S2. MS analysis of the major product of the Stille coupling of 2,7-diiodo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (3d) and 2-trimethylsilyl-3-*n*-octyl-5-tri-*n*-butylstannylthiophene.

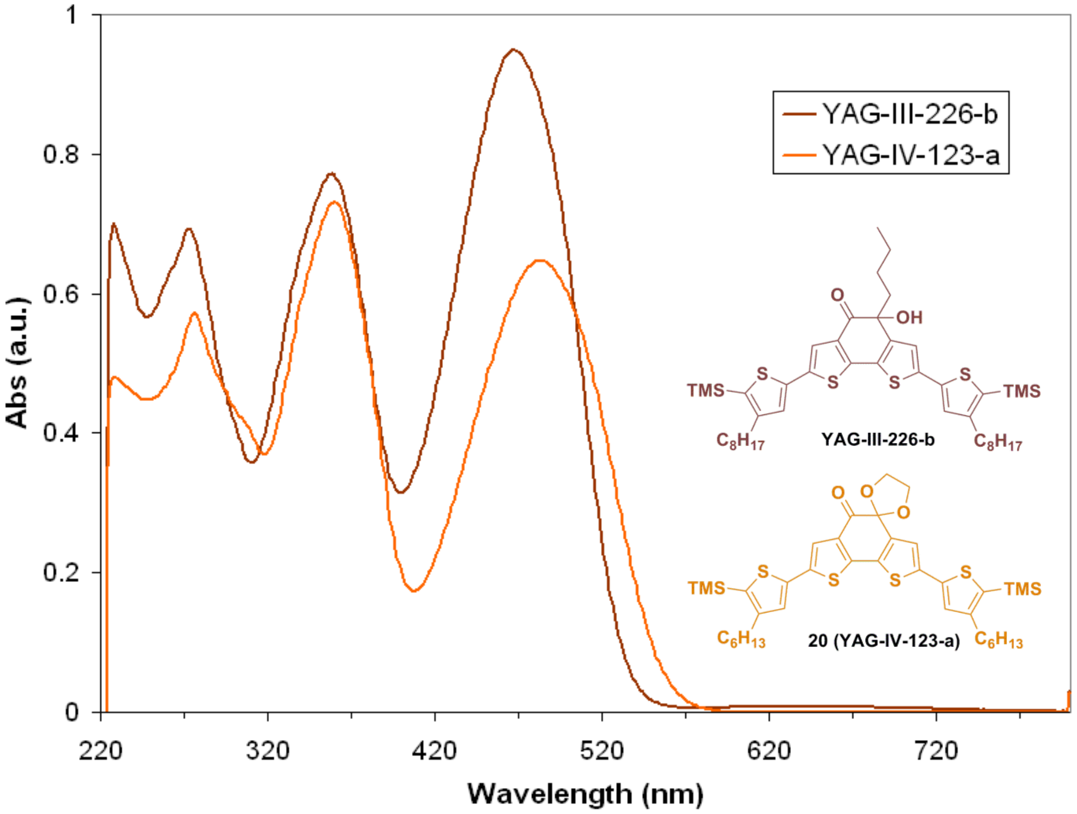
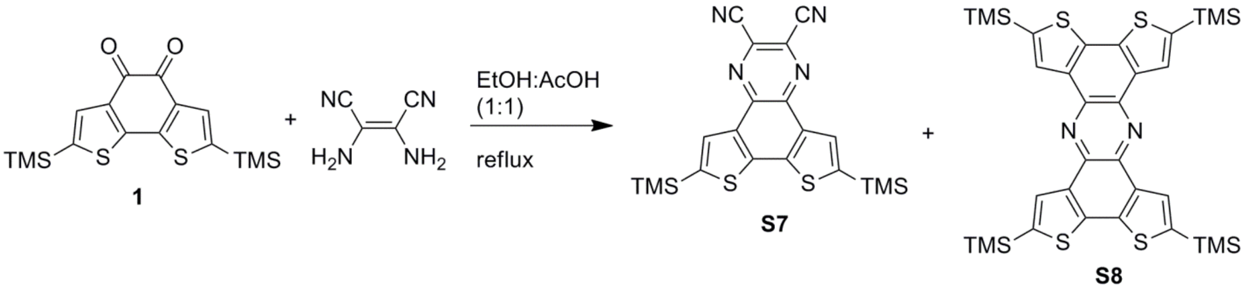


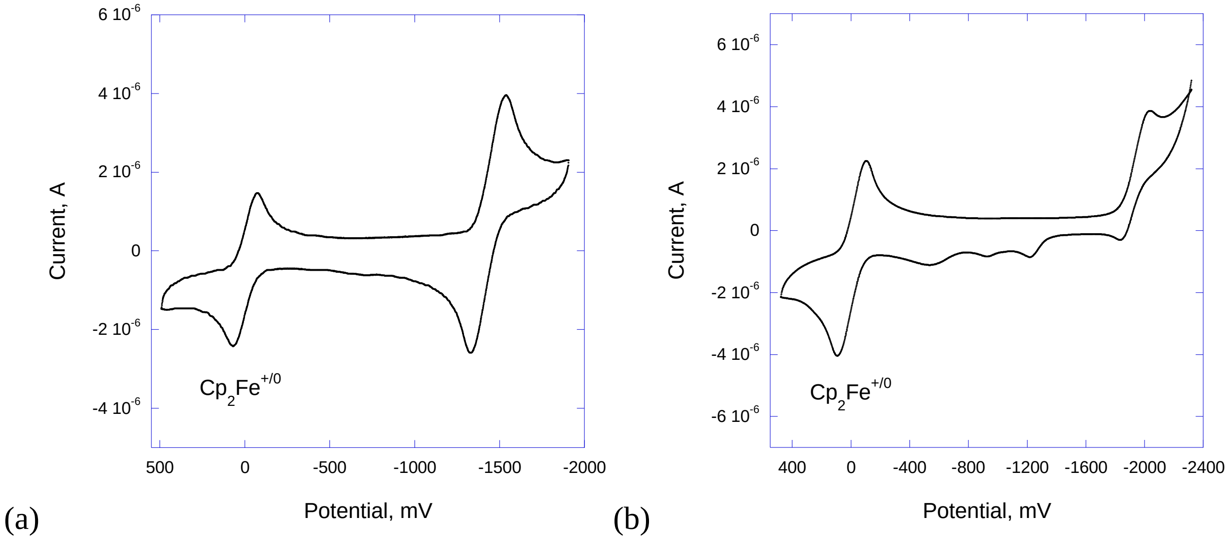
Figure S3. UV-vis absorption spectra of product of the problematic Stille coupling of 2,7-diiodo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (3d) and 2-trimethylsilyl-3-*n*-octyl-5-tri-*n*-butylstannylthiophene and similarly structured intermediate 20.

2. Condensation of 2,7-bis-trimethylsilyl-benzo[1,2-b:6,5-b']dithiophene-4,5-dione with diamine

2,7-Bis-trimethylsilyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**1**) was tested in the condensation with diaminomaleonitrile, a diamine bearing two strong electron-withdrawing cyano groups. Under the conditions used (ethanol:acetic acid) two major products, 6,9-bis(trimethylsilyl)dithieno[3,2-*f*:2',3'-*h*]quinoxaline-2,3-dicarbonitrile (**S7**) (11% yield) and 2,5,9,12-tetrakis(trimethylsilyl)tetrathieno[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazine (**S8**) (25% yield), were isolated (Scheme S8).



Scheme S8. Condensation of 2,7-bis-trimethylsilyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (1) with diaminomaleonitrile.



(a) (b)

Figure S4. CV analyses (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV rate) of *(a)* 6,9-bis(trimethylsilyl)dithieno[3,2-*f*:2',3'-*h*]quinoxaline-2,3-dicarbonitrile (S7): $E_{1/2}^{0/1-}$ = -1.43 V (partially reversible) and *(b)* 2,5,9,12-tetrakis(trimethylsilyl)tetrathieno[3,2-*a*:2',3'-*c*:3'',2''-*h*:2''',3'''-*j*]phenazine (S8): $E_{1/2}^{0/1-}$ = -1.93 V (partially reversible).

Despite the presence of two cyano-groups in the desired product **S7** the reduction potential ($E_{1/2}^{0/1-}$ = -1.43 V vs. Cp_2Fe) is shifted in the negative direction in comparison with the parent compound, 2,7-bis-trimethylsilyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione **1**[1] ($E_{1/2}^{0/1-}$ = -1.09 V vs. Cp_2Fe), and, as a result, less attractive for the construction of materials with potential air stable operation in *n*-channel OFET.

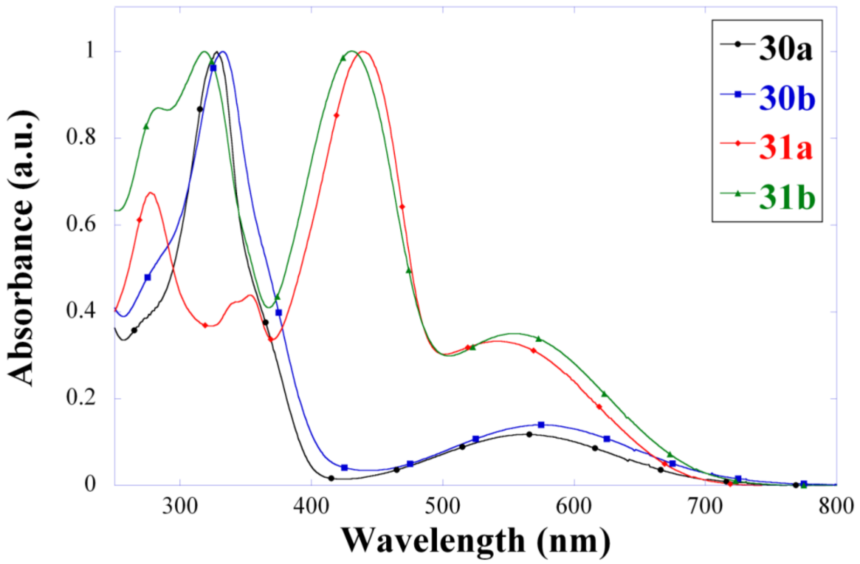


Figure S5. Normalized UV-vis absorption spectra of 4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one derivatives 30a,b and 31a,b.

2. Single crystal X-ray analysis

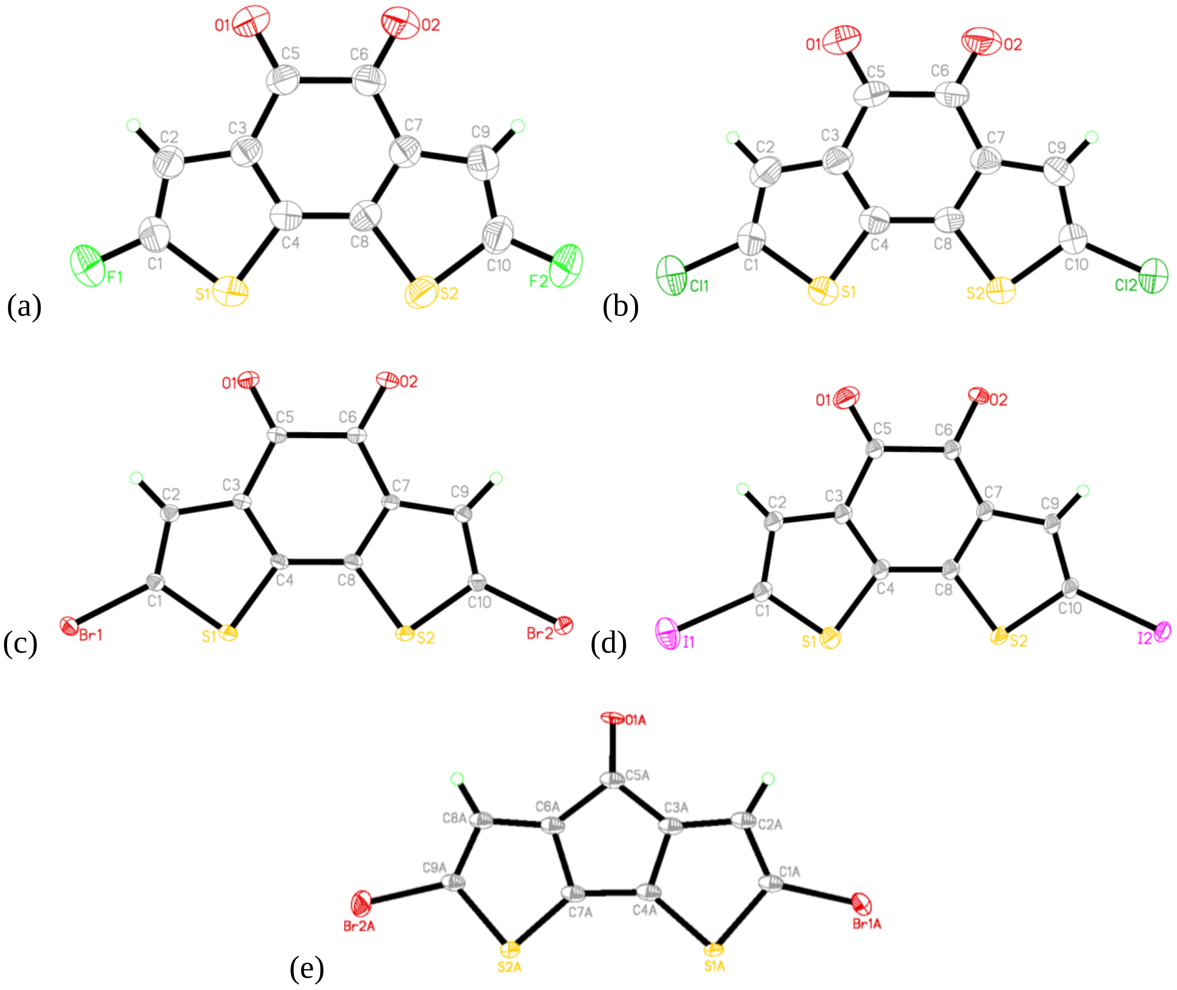


Figure S6. ORTEP drawing of 3a (a), 3b (b), 3c (c), 3d (d) and 8b (molecule A) with numbering scheme (50% probability level, hydrogen atoms drawn arbitrary small).

The dibromo-substituted monocarbonyl compound **8b** (Figure S6 (e)) crystallizes in the orthorhombic $P2_12_12_1$ space group with four independent molecules labeled A, B, C, and D in the asymmetric unit (Figure S7). Similar to **3a-3d**, in **8b** all four molecules are characterized by nearly planar tricyclic cores as evidenced by the dihedral angles between the thiophene rings (Supporting Information, Table S1).

The crystal packing is driven by the presence of the carbonyl group involved into the tri-center S···O···S bonding pattern similar to the previously reported 2,5-bis(triisopropylsilyl)-7*H*-cyclopenta[1,2-*d*:4,3-*d'*]bis(thiazole)-7-one.[1] Through these S···O contacts the two ribbons with the A-D-A-D and B-C-B-C molecules' sequence are generated, O(1D)···S(2A) = 2.926, O(1D)···S(1A) = 2.962; O(1A)···S(1D)(0.5-*x*, -1-*y*, *z*-0.5) = 2.912; O(1A)···S(2D)(0.5-*x*, -1-*y*, *z*-

0.5) = 2.908 Å; O(1C)···S(2B) = 2.934; O(1C)···S(1B) = 2.905, O(1B)···S(1C)(0.5-x, -2-y, z-0.5) = 2.931; O(1B)···S(2C)(0.5-x, -2-y, z-0.5) = 2.919 Å. Both ribbons are nearly planar as the dihedral angles between the average planes through the molecules inside the ribbons indicate, angle A/D = 0.18(23)° and angle B/C = 4.22(21)° (Figure S7). By means of Br···Br and CH···Br short contacts the ribbons are interconnected into corrugated layer that is extended parallel to the *bc* plane (Figure S7 (c)). The extent of the layer's corrugation is roughly defined by the dihedral angle between the mean planes through the adjacent ribbons which is equal to 60.25°. The antiparallel layers stack along the shortest crystallographic *a* axis with two layers per unit cell, and meet by their monocarbonyl fragments. The crystal packing is strengthened by the S···O contacts which act perpendicular to the layer plane (Figure S7 (c)).

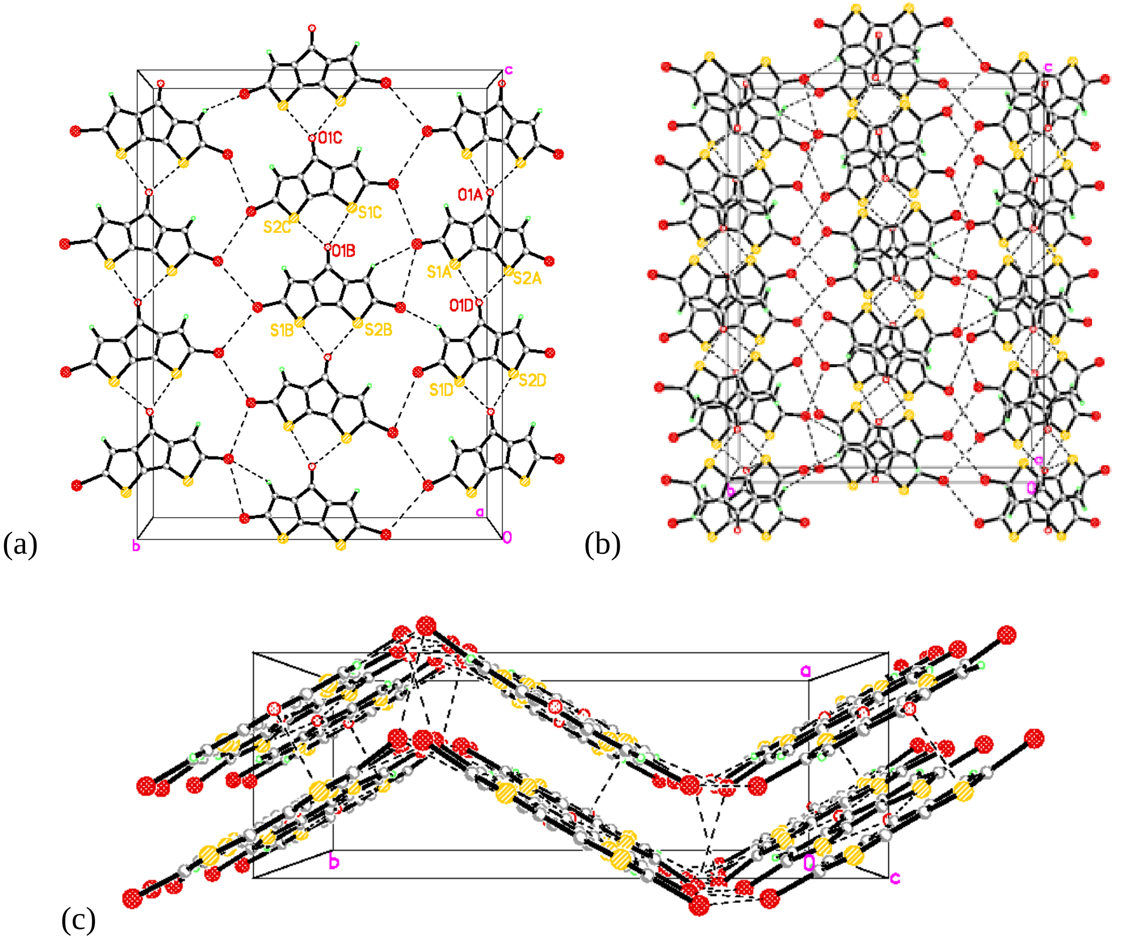


Figure S7. Fragments of crystal packing in 8b: (a) Fragment of layer built of two ribbons interlinked *via* Br···Br and CH···Br contacts: Br(1A)···Br(2B) = 3.849; B(1A)···Br(1C)(0.5-*x*, -2-*y*, *z*-0.5) = 3.777; Br(1A)···Br(1D)(*x*-0.5, -1.5-*y*, -1-*z*) = 3.808; B(1A)···Br(1D)(0.5+*x*, -1.5-*y*, -1-*z*) = 3.885; Br(1B)···Br(2A)(*x*, *y*-1, *z*) = 3.793; Br(1B)···Br(2D)(*x*, *y*-1, *z*) = 3.733, Br(1C)···Br(2C)(-*x*, *y*-0.5, -0.5-*z*) = 4.165; Br(1C)···Br(2C)(1-*x*, *y*-0.5, -0.5-*z*) = 3.980;

Br(1D)···Br(2C) = 3.860 Å; (b) Fragments of two antiparallel layers showing the overlapping areas; (c) side view of two layers showing the S···O contacts.

The ORTEP drawings for the carbonyl-protected dihalides **5-7** are shown in Figure S8. Compound **5** crystallizes in the tetragonal *P*4/*ncc* space group with half a molecule per asymmetric unit. The molecule resides on a two-fold axis that passes through the middles of C(4)-C(4)* and C(5)-C(5)* bonds. Compounds **6** and **7** crystallize in the triclinic *P*-1 and monoclinic $P2_1/n$ space groups, respectively, with one molecule per asymmetric units. The Csp^3-Csp^3 bridges in **5-7** provide the tricyclic core distortion from planarity evidenced by the increased (in comparison with **3a-3d**) dihedral angles between the thiophene rings ranging from 9.87(9)° in **6** to 14.97(12)° in **7**.

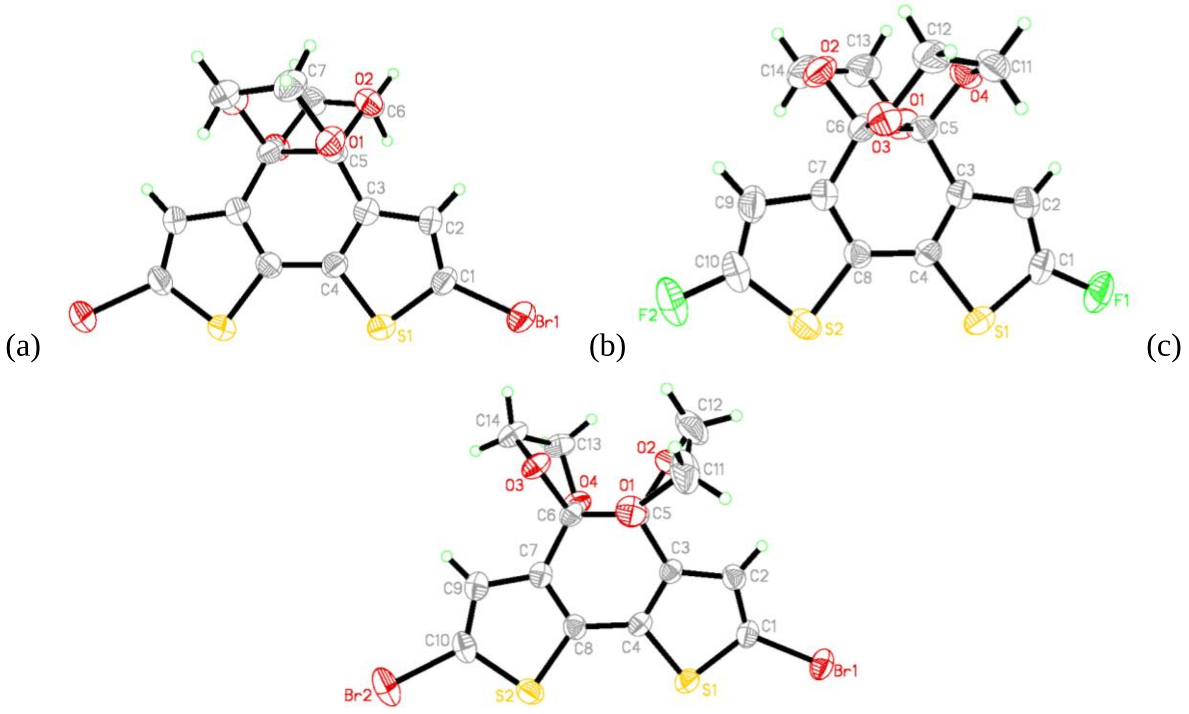


Figure S8. ORTEP drawing of 5a (a), 6 (b) and 7 (c) (50% probability level, hydrogen atoms drawn arbitrary small).

The bulky and flexible dioxolane ketone-protected groups preclude the co-facial stacks formation and, contrary to **3a-3d**, in **5-7** (Figure S8) the molecules related by the inversion centers form the antiparallel stacks along the shortest crystallographic axes with the overlapping areas decreasing from **5a** to **7**. The most effective stacking with the largest overlapping area between the neighbouring molecules and the shortest interplanar spacing of 3.842 Å is observed in **5a** (Figure S8). Between the stacks the halogen-based interactions exist (Figure S10).

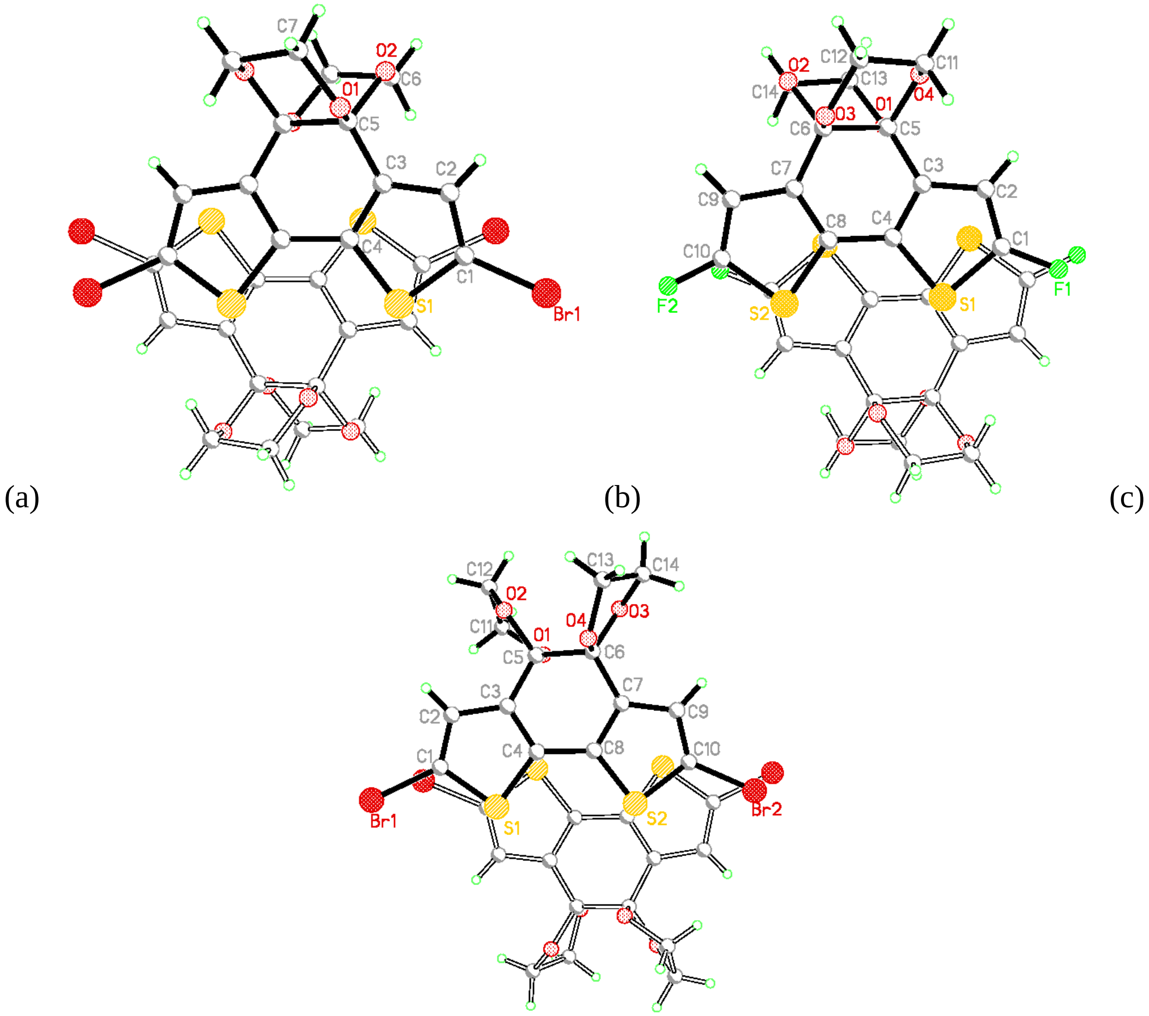


Figure S9. The overlapping patterns in projection on the molecules shown by solid lines in 5a (a), 6 (b), and 7 (c).

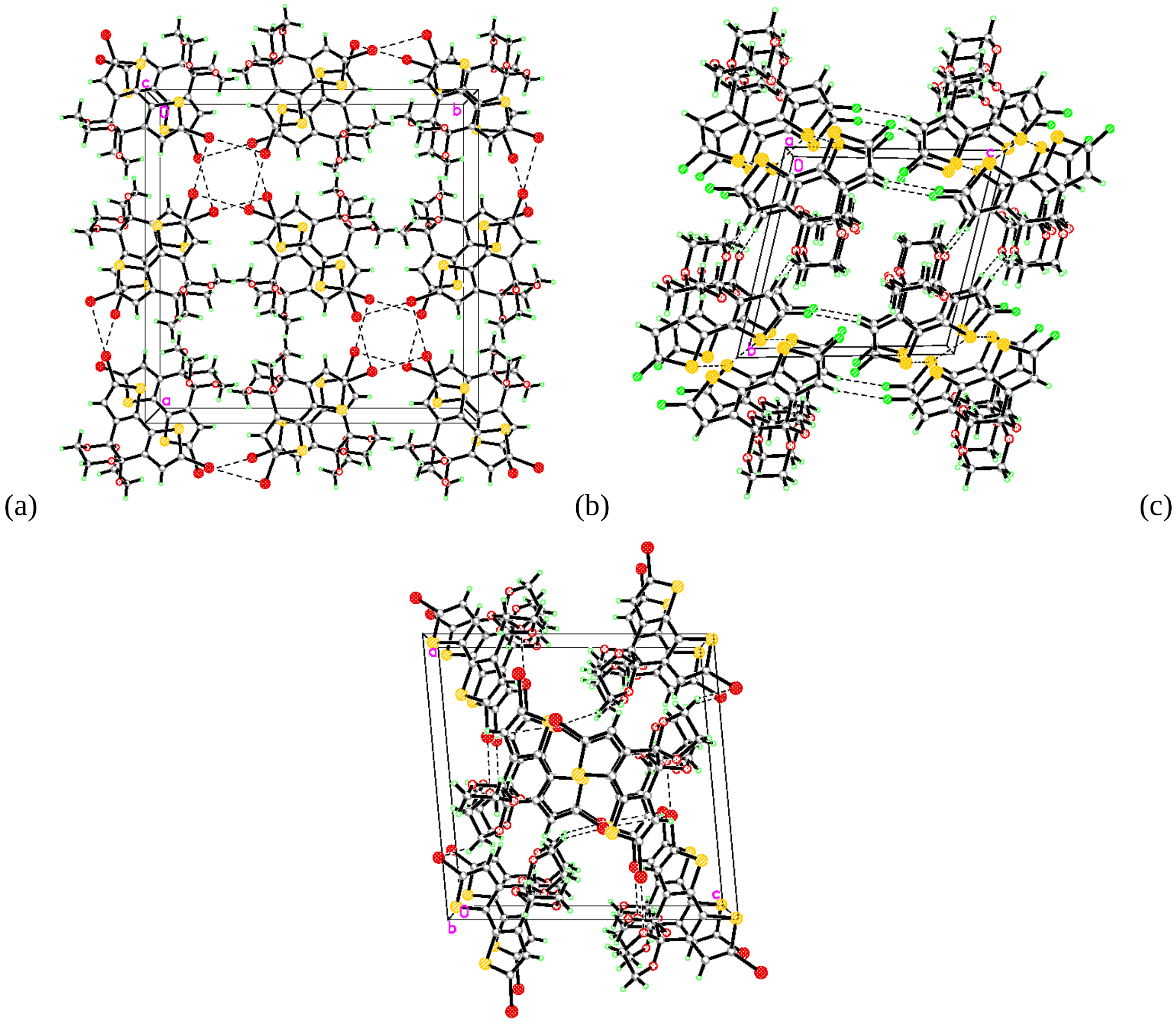


Figure S10. The fragments of crystal packing shown along the stacking direction in 5a: (a) Br(1)…Br(1)(0.5-y, x, z) = 3.582; Br(1)…Br(1)(y, 0.5-x, z) = 3.582 Ǻ; in 6: (b) C(9)…F(1)(x, y, z+1) = 3.401 Ǻ; in 7: (c) C(14)…Br(2)(2.5-x, 0.5+y, 0.5-z) = 3.787; Br(1)…O(4)(1.5-x, 0.5+y, 0.5-z) = 3.005 Ǻ.

Compound **9a** crystallizes in the monoclinic space groups *P*2/*c*. The molecule **9a** resides on the 2-fold axis passing through the middles of the C(4)-C(4)* and C(5)-C(5)* bonds. Although the bulky di-oxolane substituents prevent the close co-facial stacks, the molecules translated along the shortest crystallographic *a* axis (Table S3) are self-associated into ribbons *via* short F···F contacts F(2)···F(5)(*x*-1, *y*, *z*) = 2.791 Ǻ between the pentafluorinated rings displayed in the parallel planes. The antiparallel ribbons are combined into corrugated layers *via* short O(1)···F(3)(-*x*, 1-*y*, 1-*z*) = 2.883 Ǻ contacts (Figures S11 and S12).

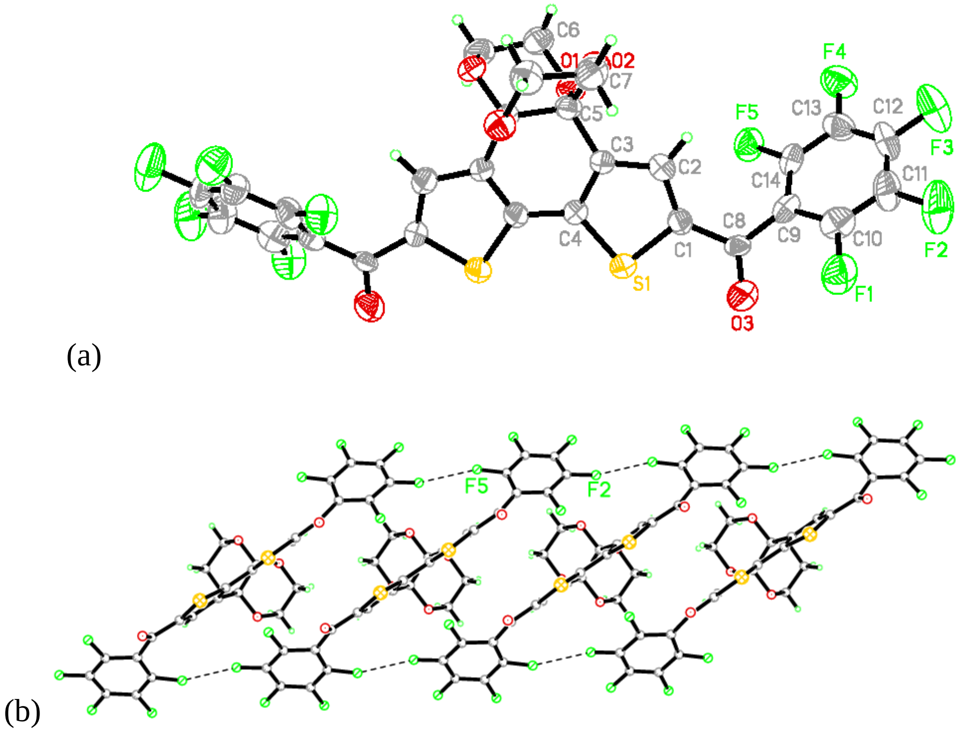


Figure S11. ORTEP drawing (a) and self-association patterns (b) in 9a.

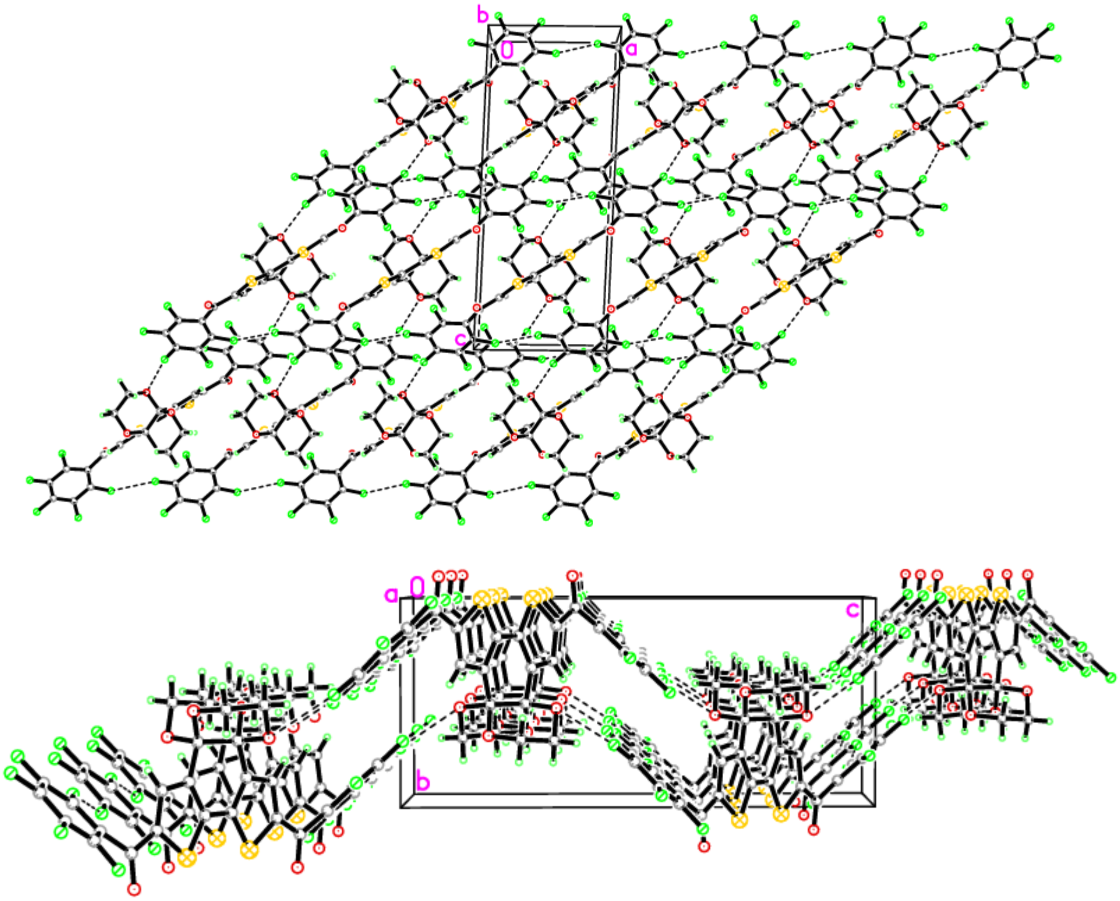
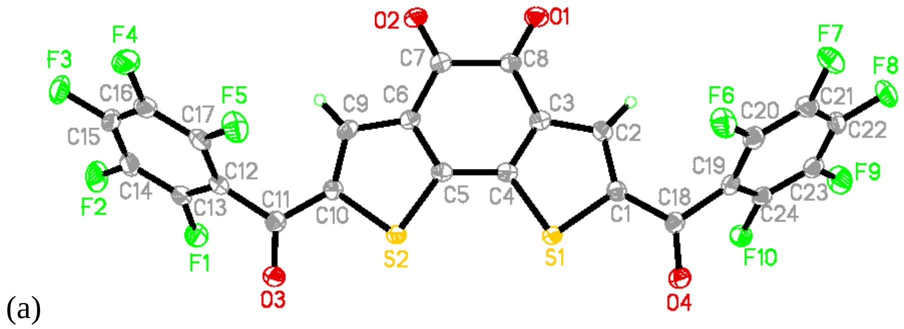


Figure S12. Fragments of layers in 9a.



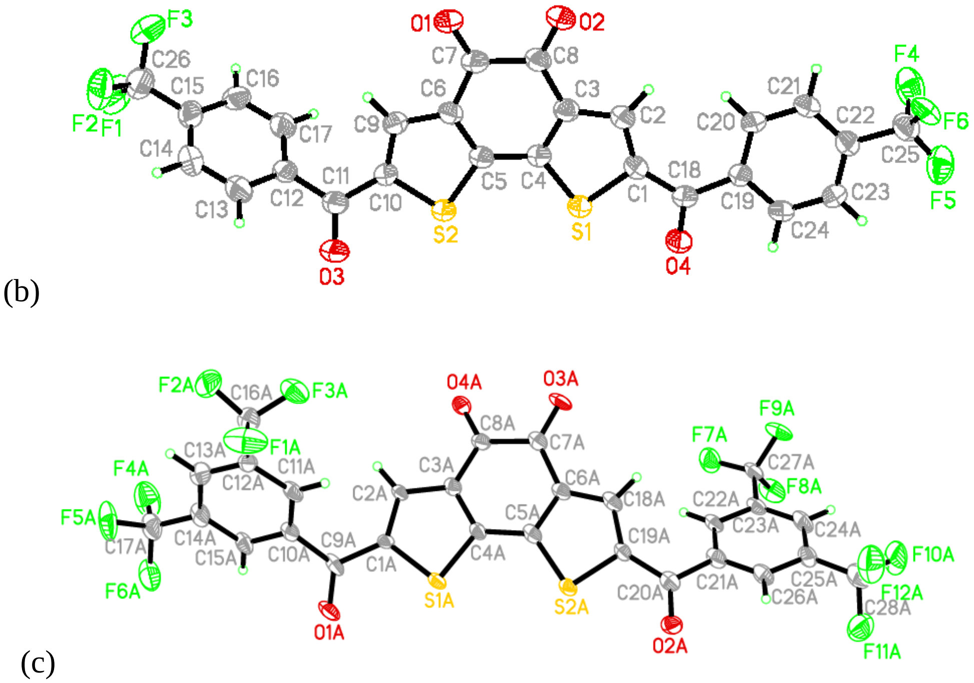


Figure S13. ORTEP drawings for 10a (a), 10c (b), 10d (c) (50% probability level, hydrogen atoms drawn arbitrary small). For 10d of three independent molecules labeled A, B, C only molecule A is shown. Only one of three disordered positions is shown for fluorine atoms in 10c.

Compounds **16a** and **16c** crystallize in the same monoclinic *P*2_1/c space group with two independent molecules A and B in the asymmetric unit of **16a** and one molecule in **16c** (Figure S14). The molecular structures of these ketone-protected bis-thiazole derivatives do not differ essentially from their bis-thiophene analog **9a**. Similar to **9a** the molecules have the butterfly shapes with the non-planar tricyclic core (Table S1).

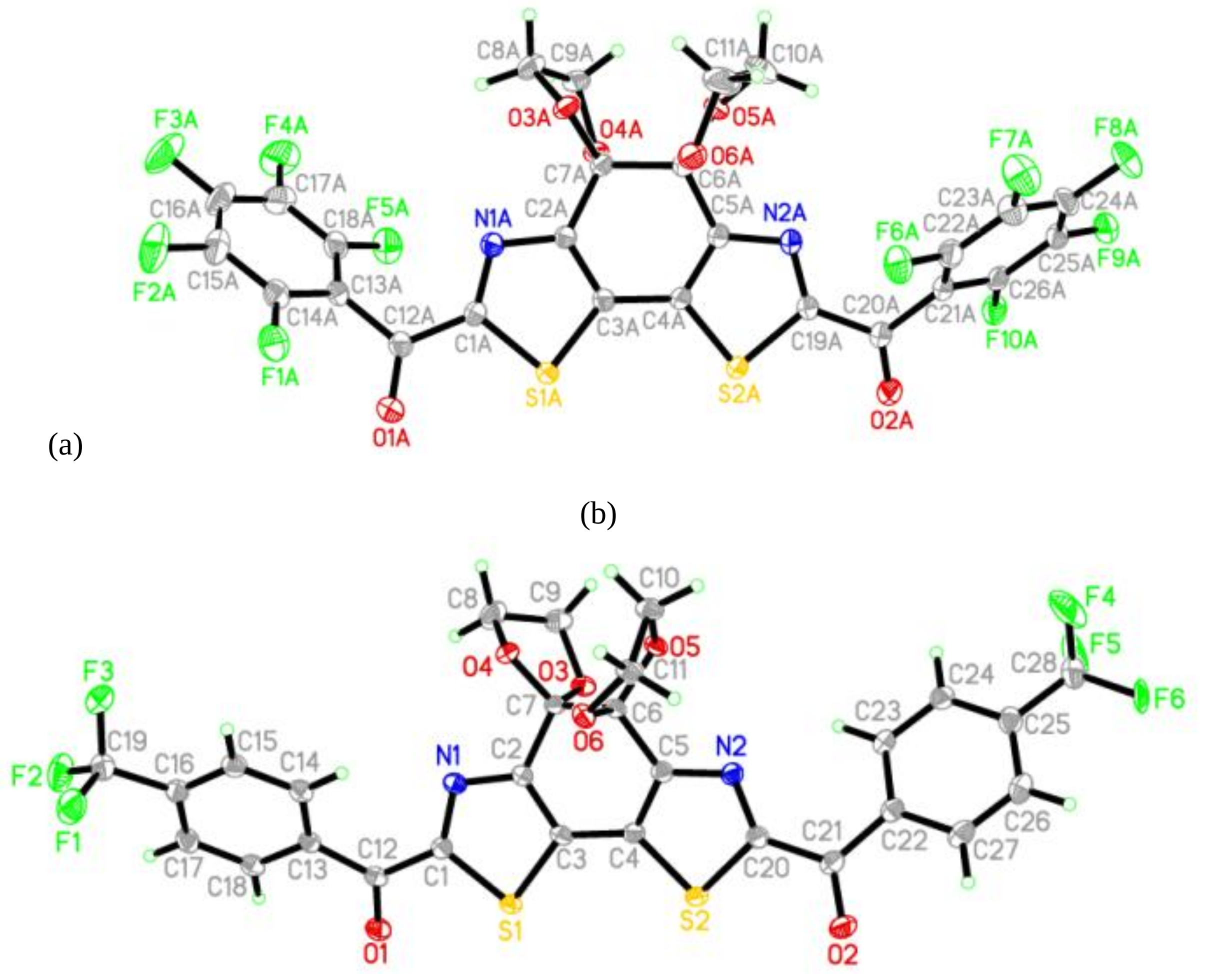


Figure S14. (a) ORTEP drawing for 16a (a) and 16c (b) with numbering scheme (50% probability level, hydrogen atoms drawn arbitrary small). Only molecule A of two crystallographically different molecules is shown for 16a.

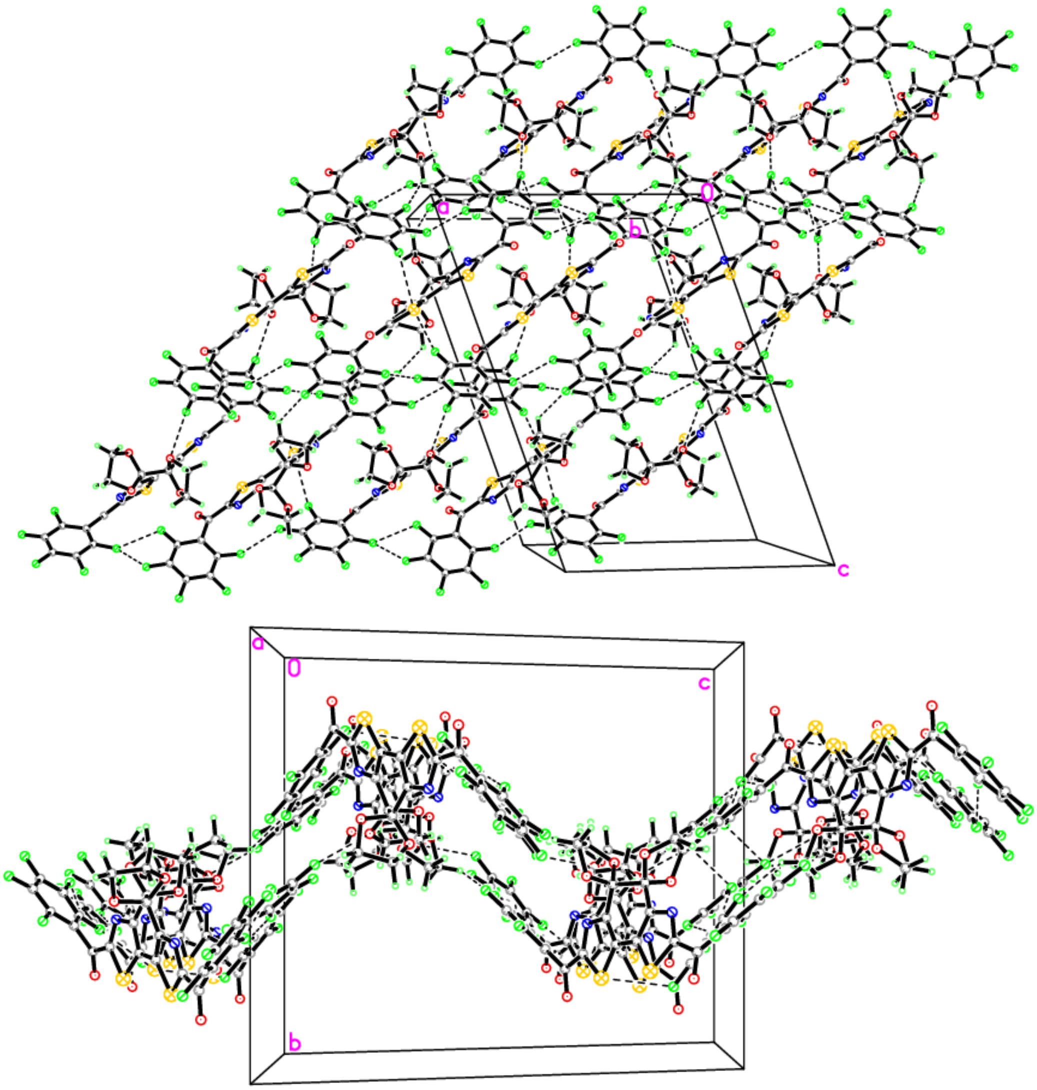


Figure S15. Fragments of layers 16a: top and side views.

The packing patterns in **16a** (Figure S15) reproduce **9a** as far as the molecules form the -A-B-A-B- infinite chains along the crystallographic *a* direction and the short F···F contacts act between the neighbouring molecules in the chain and between the chains generating the layer similar to **9a** (Figures S12). In **16c** the molecules related by the two-fold screw axis form the dimers overlapping by the thiazole rings. The dihedral angle between the tricyclic cores in the dimer is 5.95 º, the separations between the centroids of the overlapping thiazole rings are 3.783 and 4.103 Å. The dimers are associated into H-bonded chain *via* weak CH···O contacts (Figure S16).

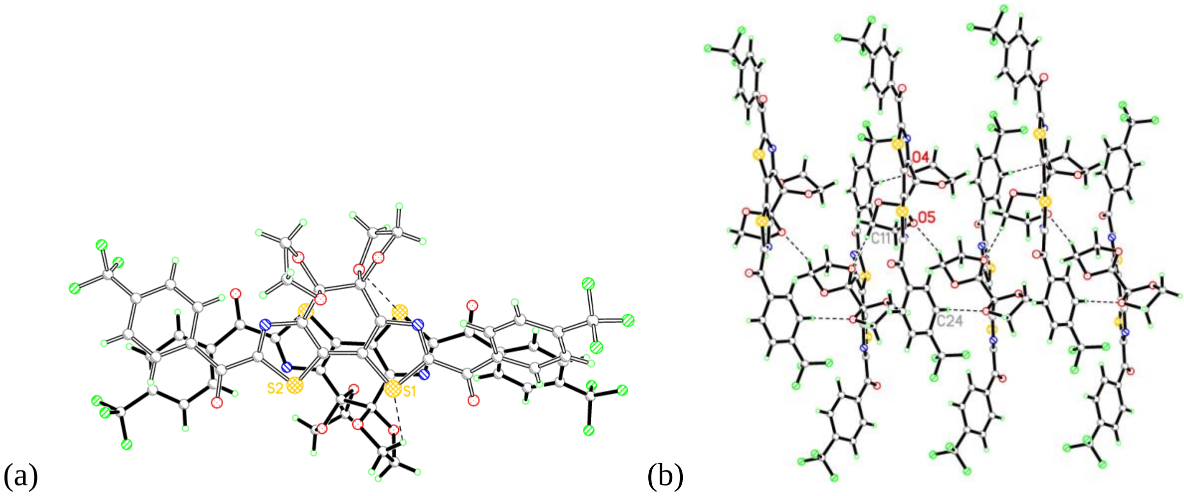
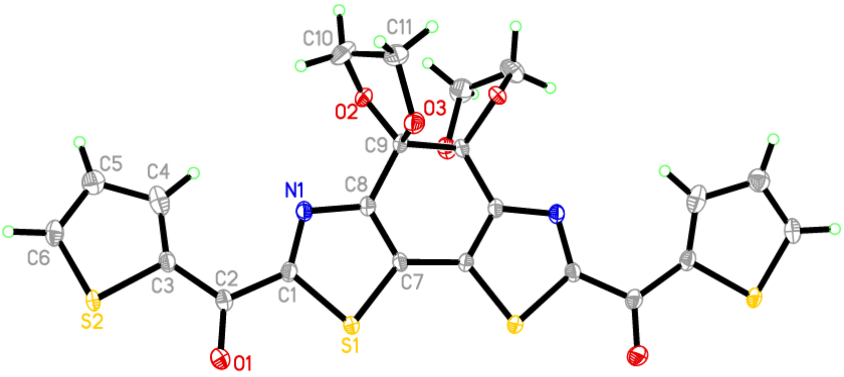
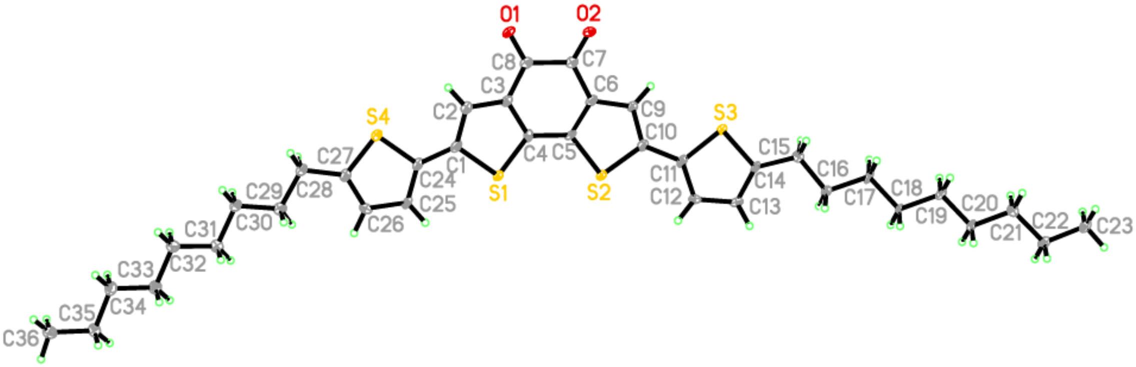


Figure S16. Fragments of crystal packing in 16c: (a) overlapping pattern in the dimer in 16c; (d) fragment of ribbon in 16c.

ORTEP drawings for **16d**, **19b, 19d, 24** and **26b** are shown in Figure S17. Compound **16d** crystallizes in the monoclinic *C*2/*c* space group with half a molecule per asymmetric unit. The molecule resides on a two-fold axis which passes through the middles of C(7)-C(7)* and C(9)-C(9)* bonds. Compounds **24** and **26b** crystallize in the monoclinic space groups $P2_1/c$ and *C*2/*c*, respectively with one molecule per asymmetric units. The substitution of the phenyl rings by the thiopnene rings results in the flattaning of **16d** as well as **19d**, **24** and **26b** molecules with the extended conjugation systems as it is evidenced from the reduced values of the dihedral angles between the tricyclic cores and the attached thiophene rings in these compounds Table S1).


C10
C11
O2
O3
C9
C5
C4
N1
C8
C6
C3
C2
C1
C7
S2
S1
O1

(a)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C9
S4
S3
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C10
C15
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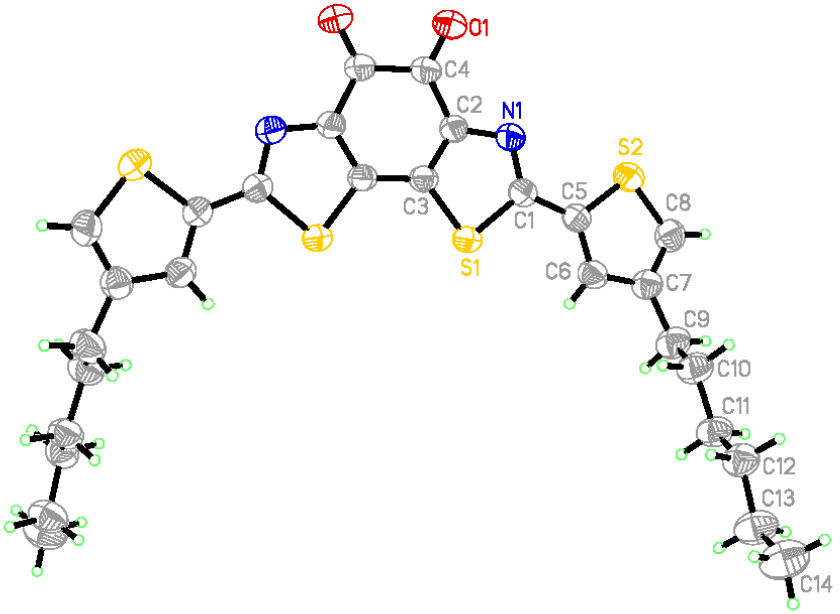
C1
C11
C16
C28
C29
S1
S2
C14
C12
C17
C18
C25
C13
C20
C30
C26
C19
C22
C23
C31
C21
C32
C33
C34
C35
C36

(b)


O1
C4
C2
N1
S2
C5
C8
C3
C1
S1
C6
C7
C9
C10
C11
C12
C13
C14

(c)

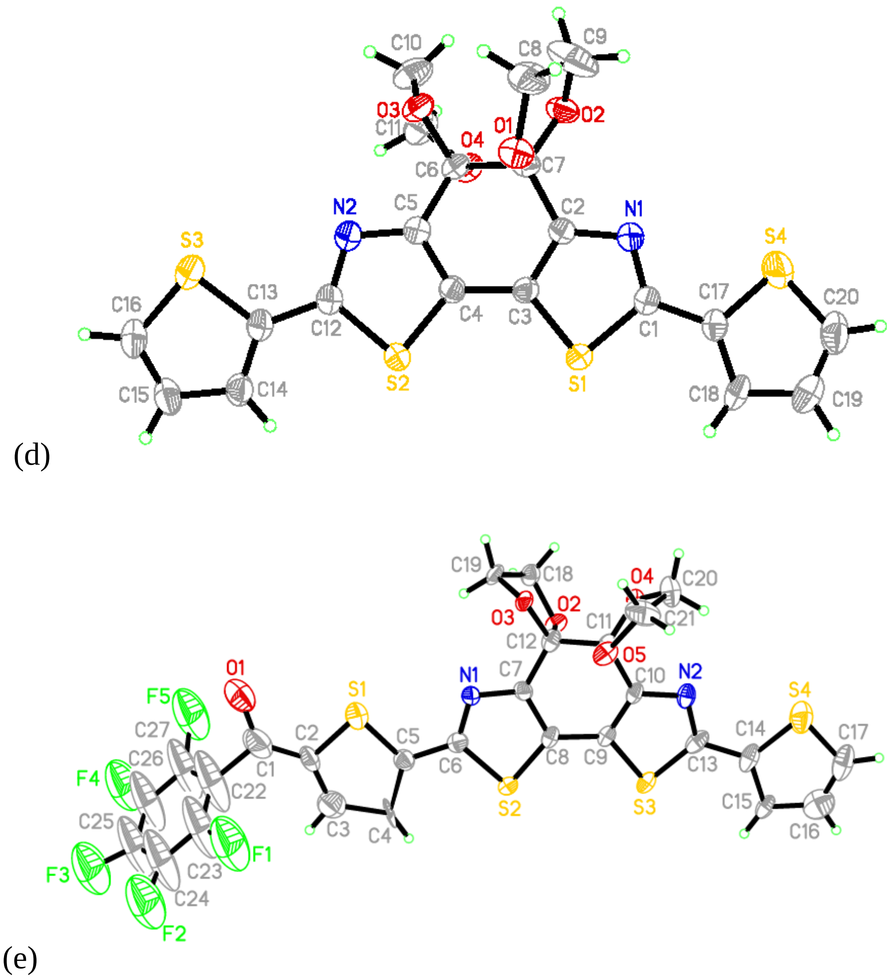
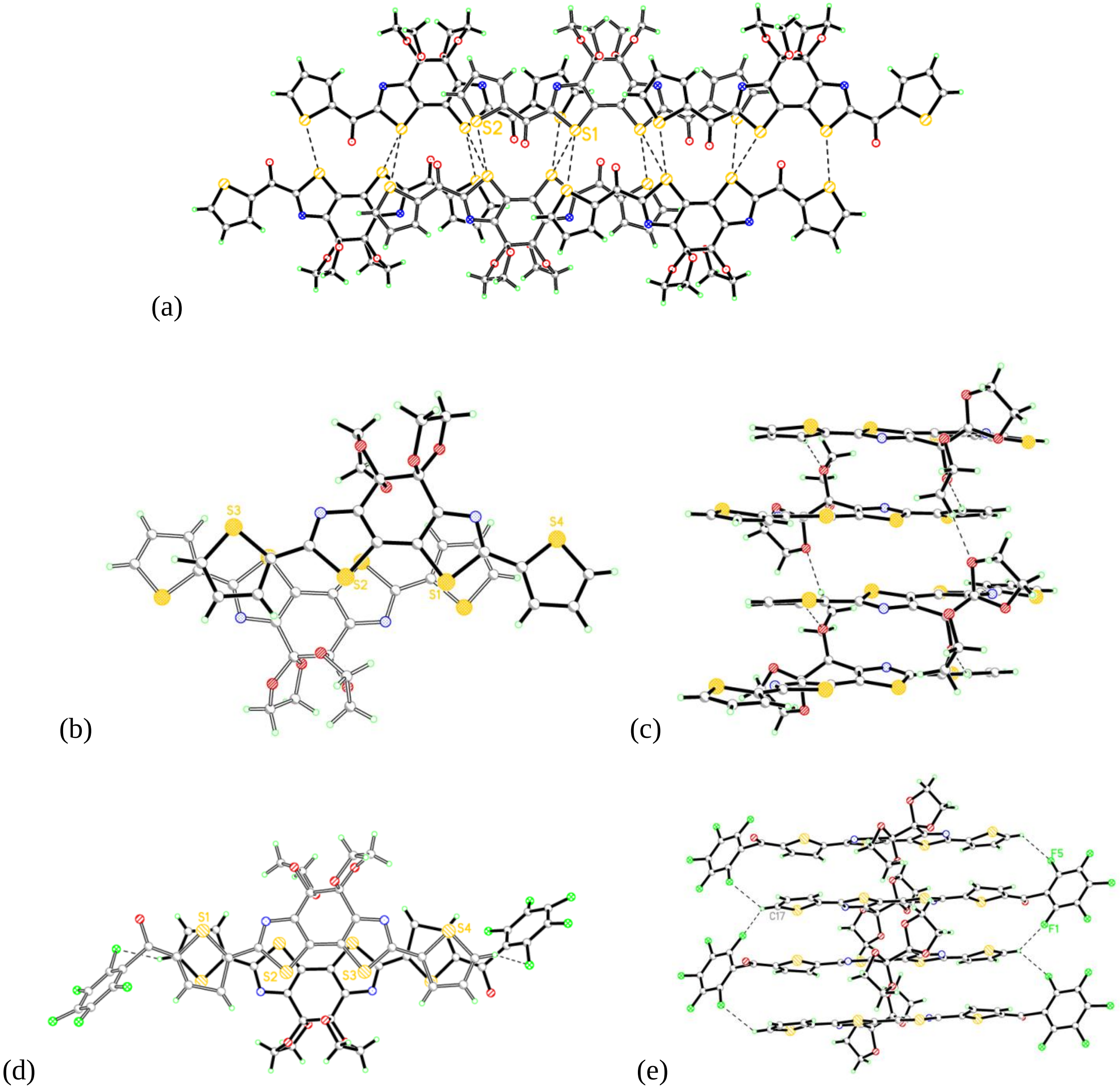


Figure S17. (a) ORTEP drawings for 16d (a), 19b (b) and 19d (c), 24 (d) and 26b (e) with numbering scheme (50% probability level, hydrogen atoms drawn arbitrary small).

The ketone-protected bis-thiophene derivatives **16d**, **24** and **26b** reveal the different modes of self-association. In **16d** molecules form the infinite chains along the *c* axis with an overlap of the terminal thiophene rings and central thiazole fragments with the distances between the centroids of the overlapping rings being 3.584 and 3.650 Ǻ. Two such chains related by inversion centers are coupled into ribbons through S···S short contacts, S(1)···S(2)(*x*, -*y*, *z*-0.5) 3.657 and S(1)···S(1)(-*x*, -*y*, -*z*) 3.446 Å (Figure S18 (a)). One short unit cell parameter close to 7 Ǻ (Table S2) in **24** and **26b** presuposes the similar mode of stacks organisation built of the anti-parallel molecules as it has been already observed in the ketone–protected materials **5-7, 9a** and **16c** and which is definitely observed in **24** and **26b**. In both structures the molecules form antiparralel stacks along the shortest directions differing by the overlapping areas. In **24** the distances between the centroids of the overlapping rings are quite long and equal to 3.711 Ǻ for thiazole/thiophene pair and 4.038 Å for thiazole/thiazole pair. In **26b** the distances between the centroids of the overlapping rings are equal to 3.783 Ǻ for thiophene/thiophene pair and 3.890 Ǻ for thiazole/thiazole pair. The stacks in **26b** are additionally supported by CH···F short contacts, C(17)···F(1) = 3.200 and C(17)···F(5)= 3.192 Ǻ (Figure S18 (e)).



(a)

(b)

(c)

(d)

(e)

Figure S18. Fragments of crystal packing in 16d, 24 and 26b: (a) the fragment of ribbon in 16d sustained by S···S contacts; (b), (c) overlapping pattern and fragment of stack in 24; (d), (e) overlapping pattern and fragment of stack in 26b.

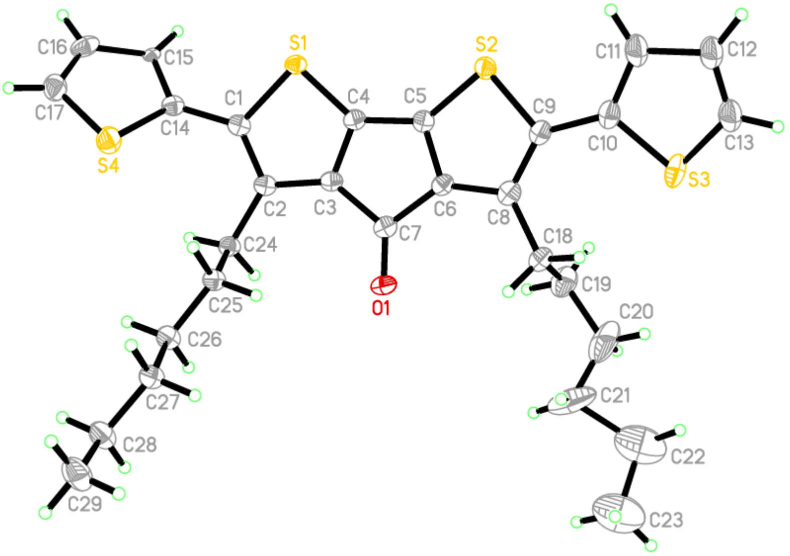
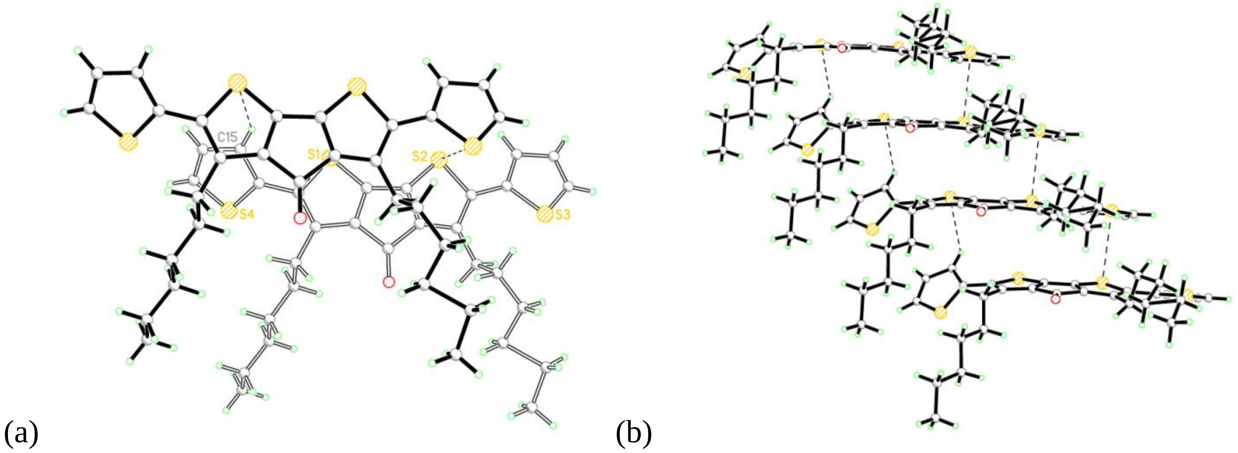


Figure S19. ORTEP drawing for 30a with numbering scheme (50% probability level, hydrogen atoms drawn arbitrary small). For the disordered fragments including terminal thiophene ring defined by S(3) atom and terminal C(22)-C(23) aliphatic group only major position is shown.

Compound **30a** crystallizes in the monoclinic $P2_1/c$ space group with one molecule per asymmetric unit. ORTEP drawing for **30a** (Figure S19). The molecule is characterised by the non-planar skeleton with significant deviation from planarity that reveals the terminal thiophene ring defined by S(4) atom (Table S1). Two aliphatic chains folded above and below the mid-plane of the molecule prevent the arrangement of the molecules in the ribbons sustained by short S···O contacts as found in **8b** and previously reported for 2,6-bis(triisopropylsilyl)cyclopenta[2,1-*b*;3,4-*b'*]dithiazole-4-one.[4] Molecules form co-facial stacks along the shortest crystallographic *a* axis with an interplanar distance between the tricyclic cores of 3.551 Ǻ and insignificant overlapping area. The stabilization of stacks is additionally provided by S(2)···S(3)(*x*-1, *y*, *z*) = 3.585 Ǻ and C(15)H···S(1)(*x*-1, *y*, *z*) = 3.595 Ǻ short contacts (Figure S20). The stacks pack in a herringbone mode with the carbonyl oxygen being involved in short CH···O contacts between the stacks.



(a) (b)

Figure S20. Fragments of crystal packing in 30a: (a) overlapping pattern; (b) fragment of stack.

Table S1. Dihedral angles (deg) between cyclic units in compounds studied by single crystal X-ray diffraction.

Compound	**1**[a]	**2**[b]	**3**[b]	**4**[c]
3a	2.9(1)	–	–	–
3b	1.8(3)	–	–	–
3c	3.0(1)	–	–	–
3d	3.5(8)	–	–	–
5	10.0(1)	–	–	–
6	9.9(1)	–	–	–
7	15.0(1)	–	–	–
8b (A)	1.9(7)	–	–	–
(B)	3.6(7)	–	–	–
(C)	0.5(7)	–	–	–
(D)	1.7(7)	–	–	–
9a	7.5(2)	49.4(1)	49.4(1)	87.4(1)
10a	3.7(1)	64.6(1)	60.6(1)	51.1(1)
10c	1.2(1)	8.6(2)	57.1(1)	53.7(1)

10d (A)	3.2(1)	38.3(2)	55.4(2)	90.0(2)
(B)	8.3(5)	24.3(4)	55.9(3)	40.9(3)
(C)	6.2(3)	36.9(2)	49.1(2)	14.6(4)
16a (A)	8.9(1)	57.4(1)	54.0(1)	83.9(1)
(B)	14.5(1)	60.8(1)	67.3(1)	78.8(1)
16c	10.3(1)	38.7(1)	37.7(1)	67.2(1)
16d	3.3(1)	14.6(1)	14.6(1)	23.5(1)
19b	2.3(2)	4.8(3)	7.1(2)	–
19d	2.4(1)	5.9(1)	5.9(1)	12.9(1)
24	13.0(1)	9.9(1)	19.1(1)	15.6(1)
26b	7.6(2)	12.4(2)	4.4(2)	5.3(3)
30a	7.4(2)	13.1(3)	43.6(1)	–

[a] Dihedral angle between the thiophene/thiophene rings (or thiazole/thiazole rings in the tricyclic core. [b] Dihedral angle between the thiophene/thiazole ring and the terminal ring attached to it. [c] Dihedral angle between the terminal rings.

Table S2. Crystallographic data for 3a-3d, 5a, 6, 7, 8b, 9a, 10a, 10c, 10d, 16a, 16c, 16d, 19b, 19d, 22, 24, 26b, 30a, and 4,4'-dibromo-2,2'-bis(4-*n*-hexyl-5-(trimethylsilyl)thiophen-2-yl)-5,5'-bithiazole S6.

	3a	**3b**	**3c**	**3d**	**5**	**6**
Empirical formula	$C_{10}H_2F_2O_2S_2$	$C_{10}H_2Cl_2O_2S_2$	$C_{10}H_2Br_2O_2S_2$	$C_{10}H_2I_2O_2S_2$	$C_{14}H_{10}Br_2O_4S_2$	$C_{14}H_{10}F_2O_4S_2$
FW	256.24	289.14	378.06	472.04	466.16	344.34
T, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal	triclinic
Space group	*P*2$_1$/*c*	*P*2$_1$/*c*	*C*2/*c*	*P*2$_1$/*c*	*P*4/*ncc*	*P*-1
a, Å	3.8903(7)	3.8509(11)	21.6810(17)	12.766(5)	20.229(5)	6.907(3)
b, Å	16.656(3)	19.822(5)	5.6778(5)	6.323(2)	20.229(5)	10.238(3)
c, Å	14.363(3)	13.742(4)	17.7679(14)	17.766(7)	7.688(3)	10.674(4)
α, deg.	90	90	90	90	90	100.888(6)
β, deg.	95.947(3)	92.669(6)	104.249(1)	92.054(5)	90°	103.524(6)
γ, deg.	90	90	90	90	90	99.264(4)
V, Å^3	925.7(3)	1047.9(5)	2119.9(3)	1433.2(9)	3146.0(16)	703.8(4)
Z	4	4	8	4	8	2
d_c, g × cm^{-3}	1.839	1.833	2.369	2.188	1.968	1.625
F(000)	512	576	1440	864	1824	352
μ, mm^{-1}	0.583	0.993	8.017	4.662	5.432	0.416
θ range for data collection, deg.	1.88 to 24.99	1.80 to 25.00	1.94 to 34.46	1.60 to 26.00	1.42 to 25.99	2.02 to 26.00
Index ranges	-4≤*h*≤4, -19≤*k*≤19, -16≤*l*≤16	-4≤*h*≤4, -23≤*k*≤23, -16≤*l*≤16	-34≤*h*≤34, -8≤*k*≤8, -27≤*l*≤28	-15≤*h*≤15, -7≤*k*≤7, -21≤*l*≤21	-24≤*h*≤24, -24≤*k*≤24, -9≤*l*≤9	-8≤*h*≤8, -12≤*k*≤12, -13≤*l*≤13

Reflections collected	10777	13327	22522	12838	36000	9144
Independent reflections	1633 [R(int)=0.0215]	2058 [R(int)=0.0336]	4430 [R(int)=0.0379]	2806 [R(int)=0.0541]	1554 [R(int) = 0.2325]	2764 [R(int) = 0.0203]
Data / restraints / parameters	1633 / 0 / 145	2058/ 0 / 145	4430 / 0 / 145	2806 / 0 / 91	1554 / 0 / 100	2764 / 0 / 199
GOF on F^2	1.065	1.225	1.006	1.157	1.064	1.036
R_1; wR_2 ($I > 2\sigma(I)$)	0.0257, 0.0681	0.0822, 0.2282	0.0221, 0.0537	0.0938, 0.2105	0.0468, 0.1073	0.0283, 0.0716
R_1; wR_2 (all data)	0.0281, 0.0706	0.0904, 0.2343	0.0272, 0.0559	0.0995, 0.2127	0.0885, 0.1347	0.0327, 0.0747
Largest diff. peak and hole e.Å^{-3}	0.263 and -0.139	1.527 and -0.378	0.850 and -0.539	4.221 and -2.522	0.840 and -0.537	0.293 and -0.192

Table S2. (Continuation).

	7	**8b**	**9a**	**10a**	**10c**	**10d**
Empirical formula	$C_{14}H_{10}Br_2O_4S_2$	$C_9H_2Br_2OS_2$	$C_{28}H_{10}F_{10}O_6S_2$	$C_{24}H_2F_{10}O_4S_2$	$C_{26}H_{10}F_6O_4S_2$	$C_{26}H_8F_{10}N_2O_6S_2$
FW	466.16	350.05	696.48	608.38	564.46	698.46
T, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2/c$	$P2_1/n$	$P2_1/n$	P-1
a, Å	14.021(4)	7.2936(10)	7.9083(8)	6.9519(12)	8.5420(9)	11.659(7)
b, Å	7.945(2)	20.532(3)	8.4393(8)	7.8710(13)	5.9376(6)	16.482(9)
c, Å	14.062(4)	26.509(4)	19.2066(19)	38.831(7)	44.370(5)	22.503(13)
α, deg.	90	90	90	90	90	75.532(11)

β, deg.	95.009(7)	90	92.076(2)	92.118(3)	93.560(2)	89.384(13)
γ, deg.	90	90	90	90	90	87.650(11)
V, Å^3	1560.4(7)	3969.7(9)	1281.0(2)	2123.3(6)	2246.0(4)	4184(4)
Z	4	16	2	4	4	6
d_c, g × cm^{-3}	1.984	2.343	1.806	1.903	1.669	1.668
$F(000)$	912	2656	696	1200	1136	2088
μ, mm^{-1}	5.476	8.545	0.328	0.374	0.322	0.307
θ range for data collection, deg.	1.97 to 25.00	1.25 to 24.99	2.12 to 26.00	1.05 to 27.49	1.84 to 25.00	1.38 to 25.00
Index ranges	$-12\leq h\leq 16$, $-9\leq k\leq 9$, $-16\leq l\leq 16$	$-8\leq h\leq 8$, $-24\leq k\leq 24$, $-31\leq l\leq 31$	$-8\leq h\leq 5$, $-10\leq k\leq 1$, $-23\leq l\leq 19$	$-9\leq h\leq 9$, $-9\leq k\leq 10$, $-50\leq l\leq 50$	$-10\leq h\leq 10$, $-7\leq k\leq 7$, $-52\leq l\leq 52$	$-13\leq h\leq 13$, $-19\leq k\leq 18$, $-26\leq l\leq 26$
Reflections collected	8860	44216	3274	22506	25278	22378
Independent reflections	2752 [R(int) = 0.0214]	6978 [R(int)=0.0464]	2228 [R(int) = 0.0558]	4861 [R(int) = 0.0624]	3960 [R(int) = 0.0573]	14504 [R(int) = 0.1203]
Data / restraints / parameters	2752 / 0 / 199	6978 / 0 / 296	2228 / 0 / 208	4861 / 0 / 361	3960 / 20 / 385	14504 / 0 / 1243
GOF on F^2	1.045	1.102	0.816	1.048	1.117	1.016
R_1; wR_2 ($I > 2\sigma(I)$)	0.0212, 0.0521	0.0450, 0.1054	0.0432, 0.0593	0.0429, 0.0909	0.0544, 0.1130	0.0974, 0.2338
R_1; wR_2 (all data)	0.0261, 0.0541	0.0523, 0.1090	0.1061, 0.0716	0.0693, 0.1060	0.0739, 0.1221	0.1776, 0.3094
Largest diff. peak and hole e.Å^{-3}	0.232 and -0.445	1.126 and -1.739	0.215 and -0.230	0.392 and -0.315	0.225 and -0.241	1.245 and -1.144

Table S2. Continuation.

	16a	**16c**	**16d**	**19b**	**19d**
Empirical formula	$C_{26}H_8F_{10}N_2O_6S_2$	$C_{28}H_{16}F_6N_2O_6S_2$	$C_{22}H_{14}N_2O_6S_4$	$C_{36}H_{44}O_2S_4$	$C_{28}H_{30}N_2O_2S_4$
FW	698.46	654.55	530.59	636.95	554.78
T, K	100(2)	100(2)	100(2)	100	100(2)
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	P-1	$Pccn$
a, Å	14.6242(10)	10.3282(9)	16.860(2)	7.349(3)	5.4624(10)
b, Å	17.9041(13)	7.4175(7)	15.304(2)	11.374(5)	34.996(6)
c, Å	21.1195(15)	34.636(3)	10.1282(14)	20.588(9)	14.787(3)
α, deg.	90	90	90	76.147(8)	90
β, deg.	109.0980(10)	94.423(2)	124.484(2)	82.786(8)	90
γ, deg.	90	90	90	75.325(7)	90
V, Å^3	5225.4(6)	2645.6(4)	2154.2(5)	1612.4(11)	2826.7(9)
Z	8	4	4	2	4
d_c, g × cm^{-3}	1.776	1.643	1.636	1.312	1.304
F(000)	2784	1328	1088	680	1168
μ, mm^{-1}	0.324	0.293	0.487	0.327	0.364
θ range for data collection, deg.	1.47 to 26.00	1.98 to 26.00	1.98 to 25.99	1.90 to 26.00	2.33 to 27.49
Index ranges	$-18\leq h\leq 18$, $-22\leq k\leq 22$, $-26\leq l\leq 26$	$-12\leq h\leq 12$, $-9\leq k\leq 9$, $-42\leq l\leq 42$	$-20\leq h\leq 20$, $-18\leq k\leq 18$, $-12\leq l\leq 12$	$-9 \leq h \leq 9$, $-14 \leq k \leq 14$, $-25 \leq l \leq 25$	$-7\leq h\leq 7$, $-45\leq k\leq 45$, $-19\leq l\leq 19$
Reflections collected	49699	24544	10066	15160	38099

Independent reflections	10272 [R(int) = 0.0401]	5206 [R(int) =0.0329]	2123 [R(int) =0.0282]	6315 [R(int) = 0.0936]	3242 [R(int) = 0.0625]
Data / restraints / parameters	10272 / 0 / 829	5206 / 0 / 429	2123 / 0 / 176	6315 / 0 / 381	3242 / 0 / 164
GOF on F^2	1.006	1.031	1.103	0.975	1.048
R_1; wR_2 ($I > 2\sigma(I)$)	0.0341, 0.0796	0.0308, 0.0790	0.0310, 0.0846	0.0690, 0.1520	0.0385, 0.0881
R_1; wR_2 (all data)	0.0463, 0.0875	0.0342, 0.0817	0.0318, 0.0855	0.1319, 0.1801	0.0621, 0.1019
Largest diff. peak and hole e.Å^{-3}	0.470 and -0.295	0.359 and -0.227	0.332 and -0.332	0.924 / -0.588	0.214 and -0.186

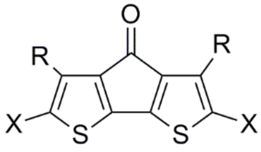
Table S2. Continuation.

	22	**24**	**26b**	**30a**	**S6**
Empirical formula	$C_{38}H_{54}N_2O_4S_4Si_2$	$C_{20}H_{14}N_2O_4S_4$	$C_{27}H_{13}F_5N_2O_5S_4$	$C_{29}H_3OS_4$	$C_{32}H_{46}Br_2N_2S_4Si_2$
FW	787.25	474.57	668.63	524.79	802.95
T, K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	$P2_1/c$	$C2/c$	$P2_1/c$	$C2/c$
a, Å	11.205(6)	7.4786(8)	40.227(8)	5.3435(4)	37.478(2)
b, Å	11.868(7)	21.309(2)	7.2753(15)	20.1523(15)	7.0932(4)
c, Å	16.094(9)	12.5339(13)	20.654(4)	24.6864(18)	14.7217(8)
α, deg.	103.904(11)	90	90	90	90
β, deg.	97.871(11)	94.645(2)	116.42(3)	92.0210(10)	108.2470(10)
γ, deg.	94.160(11)	90	90	90	90
V, Å^3	2045(2)	1990.9(4)	5413.6(19)	2656.7(3)	3716.8(4)
Z	2	4	8	4	4

d_c, g × cm^{-3}	1.278	1.583	1.641	1.312	1.435
F(000)	840	976	2704	0.379	2.495
μ, mm^{-1}	0.331	0.510	0.429	1112	1656
θ range for data collection, deg.	1.78 to 25.00	1.89 to 25.00	2.20 to 25.00	1.65 to 26	2.29 to 26.00°
Index ranges	$-13 \leq h \leq 11$, $-14 \leq k \leq 14$, $-19 \leq l \leq 18$	$-8 \leq h \leq 8$, $-25 \leq k \leq 25$, $-14 \leq l \leq 14$	$-47 \leq h \leq 47$, $-8 \leq k \leq 8$, $-24 \leq l \leq 24$	$-6 \leq h \leq 6$ $-24 \leq k \leq 24$ $-30 \leq l \leq 30$	$-46 \leq h \leq 46$ $-8 \leq k \leq 8$ $-18 \leq l \leq 18$
Reflections collected	12012	23402	22244	30649	20666
Independent reflections	7118 [R(int) = 0.0286]	3497 [R(int) = 0.0545]	4767 [R(int) = 0.1302]	5241 [R(int) = 0.0700]	3652 [R(int) = 0.0421]
Data / restraints / parameters	7118 / 0 / 459	3497 / 0 / 271	4767 / 0 / 322	5241 / 1 / 311	3652 / 0 / 194
GOF on F^2	1.037	1.043	1.401	1.028	1.051
R_1; wR_2 ($I > 2\sigma(I)$)	0.0442, 0.1113	0.0380, 0.0886	0.1661, 0.3989	0.0535, 0.1169	0.0356, 0.0920
R_1; wR_2 (all data)	0.0578, 0.1221	0.0539, 0.0976	0.2616, 0.4616	0.0775, 0.1300	0.0471, 0.0982
Largest diff. peak and hole e.Å^{-3}	0.547 and -0.490	0.361 and -0.511	1.434 and -0.889	0.845 and -0.505	1.435 and -0.533

3. Electrochemical data

Table S3. Summary of electrochemical properties of 2,6-dihalo-cyclopenta[2,1-*b*;3,4-*b*']dithiophen-4-ones 8.

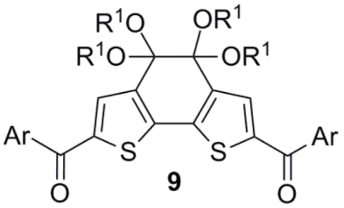


8

Compound	X	R	λ_{max}	$E_{1/2}^{0/1-}$, V vs Cp_2Fe (solvent)	$E_{1/2}^{1-/2-}$, V vs Cp_2Fe	$E_{1/2}^{0/1-}$, V vs SCE[1]	m.p. (°C)[2]
8a	I	H	283, 521	-1.49 (CH_2Cl_2)	-2.16	-0.93	
				-1.55 (THF)	n/a	-0.99	
8b	Br	H	281, 516	-1.48[3] (CH_2Cl_2)	n/a	-0.92	205.3[4]
8c	I	*n*-C_6H_{13}	288, 531	-1.61 (CH_2Cl_2)	n/a	-1.05	124.7
				-1.65 (THF)	n/a	-1.09	

[1] $E_{1/2}^{0/1-}$ (vs SCE) = $E_{1/2}^{0/1-}$ (vs Cp_2Fe) + 0.56 V (for THF); $E_{1/2}^{0/1-}$ = $E_{1/2}^{0/1-}$ (vs Cp_2Fe) + 0.46 (for dichloromethane)[2]; [2]determined by DSC analysis on the 1st heating-cooling cycle at 10 ºC/min rate; [3]for **8b** reversible oxidation peak at $E_{1/2}^{0/1+}$ = +1.05 V was observed. [4]Determined on the 1st heating cycle; melting with decomposition.

Table S4. Summary of electrochemical properties of 2,7-diacyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-diones 9 and 2,7-diacyl-benzo[1,2-*d*:4,3-*d*']bis(thiazole)-4,5-diones 16 with protected diketone bridges.



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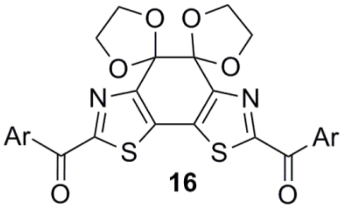
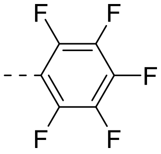
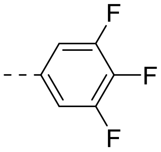
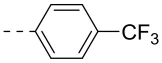
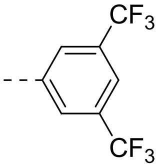
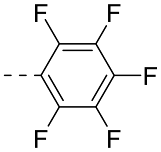
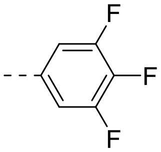
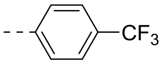
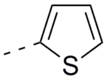
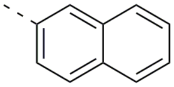


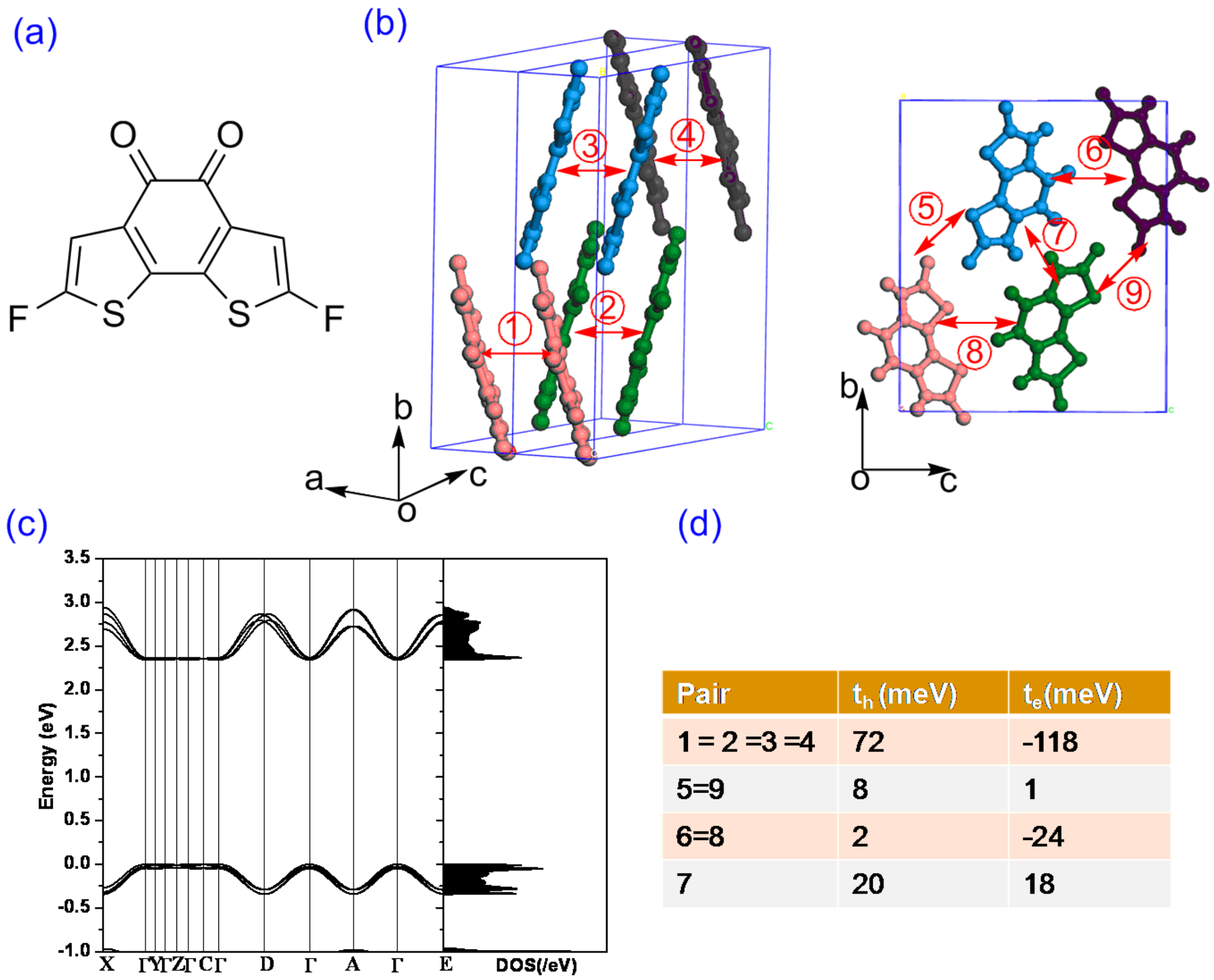
16

Compound	Protection group	Ar	$E_{1/2}^{0/1-}$, V vs Cp$_2$Fe[1]	$E_{1/2}^{1-/2-}$, V vs Cp$_2$Fe	$E_{1/2}^{0/1-}$, V vs SCE[2]
9a	propellane		-1.33	-1.65	-0.77
9b	ketal		-1.50	-1.72	-0.94
9c	propellane		-1.52	-1.76	-0.96
9d	ketal		-1.44	-1.64	-0.88
16a	ketal		-1.09	-1.43	-0.53
16b	ketal		-1.19	-1.31	-0.63

16c	ketal		-1.26	-1.50	-0.70
16d	ketal		-1.35	-1.59	-0.79
16e	ketal		-1.36	-1.60	-0.80

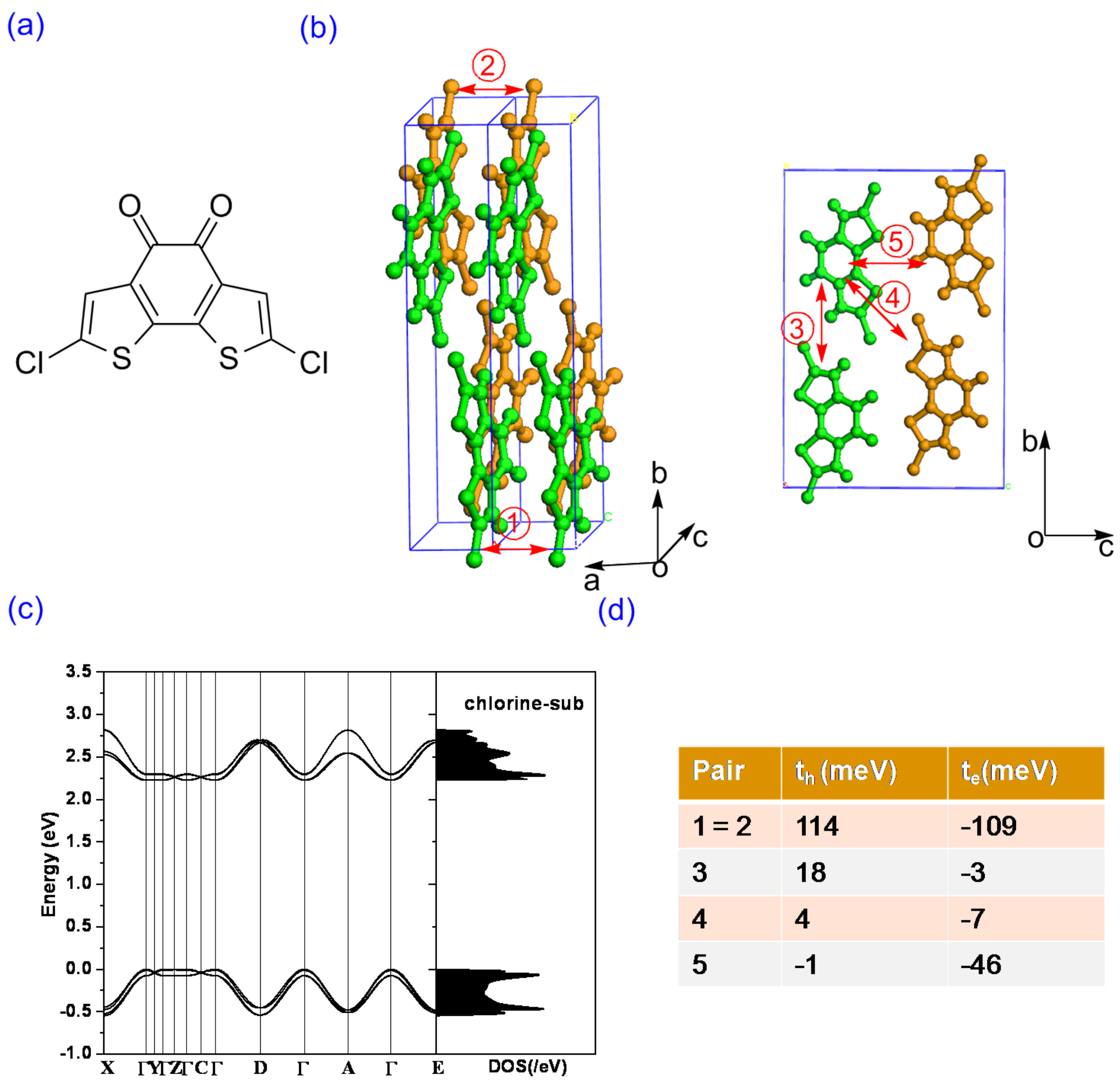
[1] CV analysis (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate); [2] $E_{1/2}^{0/1-}$ (vs SCE) = $E_{1/2}^{0/1-}$ (vs Cp_2Fe) + 0.56 V (for THF); $E_{1/2}^{0/1-}$ = $E_{1/2}^{0/1-}$ (vs Cp_2Fe) + 0.46 (for dichloromethane)

4. Computational Results



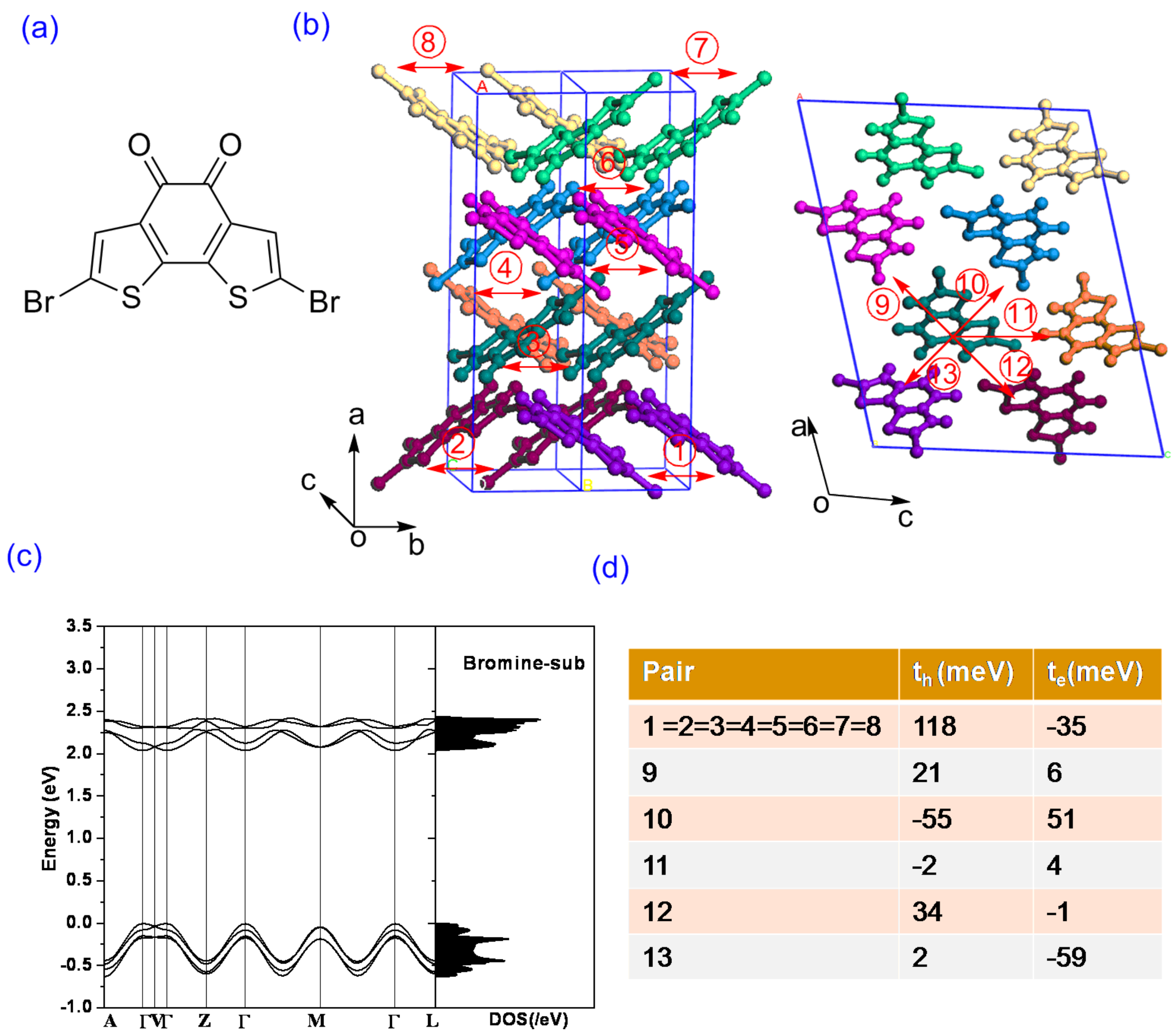
Pair	t_h (meV)	t_e(meV)
1 = 2 =3 =4	72	-118
5=9	8	1
6=8	2	-24
7	20	18

Figure S21. (a) Chemical structure of 3a. (b) Crystal structure and labeling of the charge-hopping pathways used in the calculations of the transfer integrals. (c) B3LYP/6-31G calculated band structure and density of states (DOS). Points of high symmetry in the first Brillouin zone are labeled as follows: Γ = (0,0,0), X = (0.5, 0, 0), Y= (0,0.5,0), Z= (0,0,0.5), C = (0, 0.5, 0.5), D = (0.5, 0, 0.5), A = (0.5, 0.5, 0) and E = (0.5, 0.5, 0.5), all in crystallographic coordinates. (d) Effective transfer integrals (t_h and t_e) calculated with the B3LYP/6-31G (d, p) method.



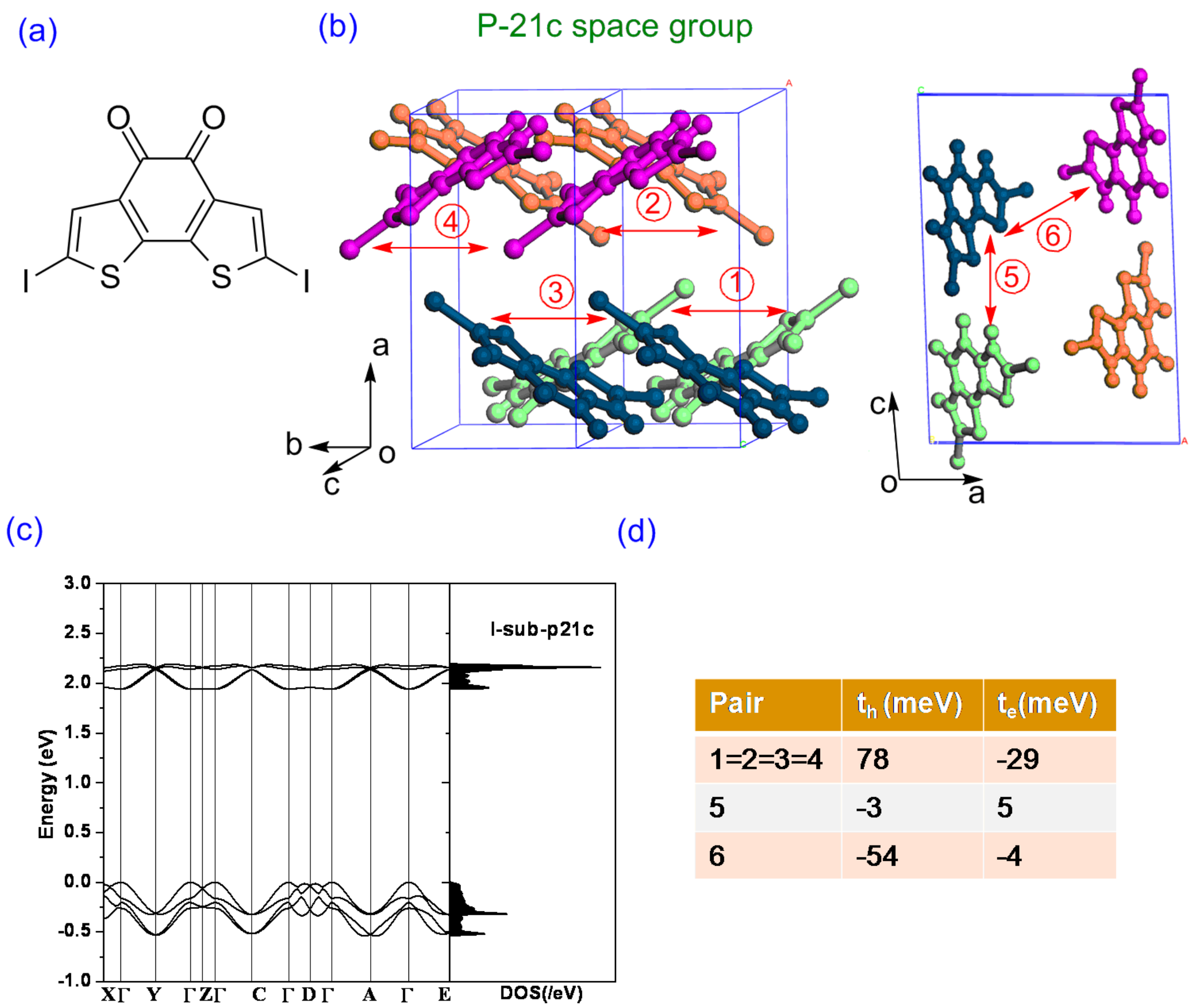
Pair	t_h (meV)	t_e(meV)
1 = 2	114	-109
3	18	-3
4	4	-7
5	-1	-46

Figure S22. (a) Chemical structure of 3b. (b) Crystal structure and labeling of the charge-hopping pathways used in the calculations of the transfer integrals. (c) B3LYP/6-31G calculated band structure and density of states (DOS). Points of high symmetry in the first Brillouin zone are labeled as follows: Γ = (0,0,0), X = (0.5, 0, 0), Y= (0,0.5,0), Z= (0,0,0.5), C = (0, 0.5, 0.5), D = (0.5, 0, 0.5), A = (0.5, 0.5, 0) and E = (0.5, 0.5, 0.5), all in crystallographic coordinates. (d) Effective transfer integrals (t_h and t_e) calculated with the B3LYP/6-31G (d, p) method.



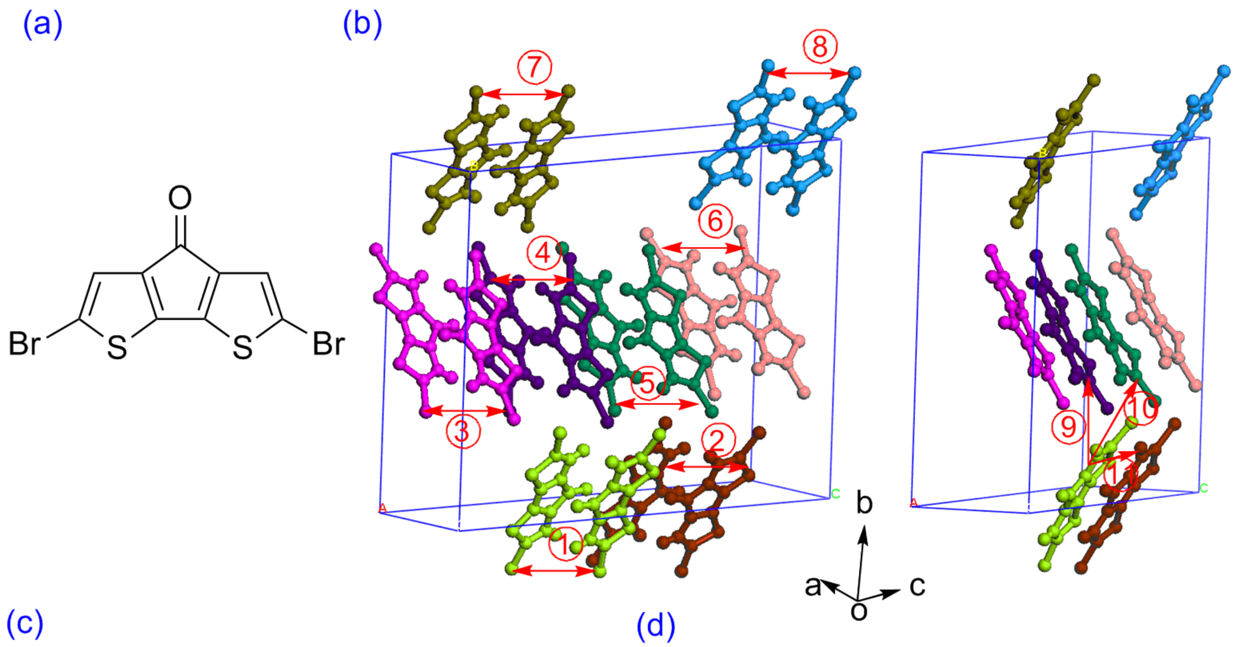
Pair	t_h (meV)	t_e(meV)
1 =2=3=4=5=6=7=8	118	-35
9	21	6
10	-55	51
11	-2	4
12	34	-1
13	2	-59

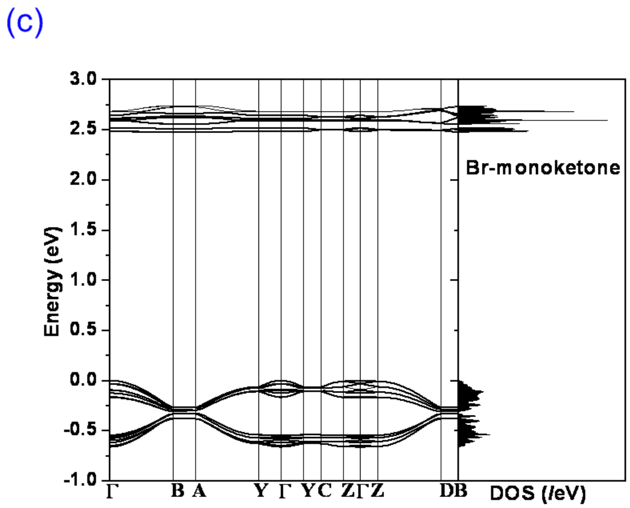
Figure S23. (a) Chemical structure of 3c. (b) Crystal structure and labeling of the charge-hopping pathways used in the calculations of the transfer integrals. (c) B3LYP/6-31G calculated band structure and density of states (DOS). Points of high symmetry in the first Brillouin zone are labeled as follows: Γ = (0,0,0), A = (0.5, 0, 0), V= (0,0,0.5), Z = (0, 0.5, 0.5), L = (0.5, 0, 0.5) and M = (0.5, 0.5, 0.5), all in crystallographic coordinates. (d) Effective transfer integrals (t_h and t_e) calculated with the B3LYP/6-31G (d, p) method.



Pair	t_h (meV)	t_e(meV)
1=2=3=4	78	-29
5	-3	5
6	-54	-4

Figure S24. (a) Chemical structure of 3d. (b) Crystal structure and labeling of the charge-hopping pathways used in the calculations of the transfer integrals. (c) B3LYP/6-31G calculated band structure and density of states (DOS). Points of high symmetry in the first Brillouin zone are labeled as follows: Γ = (0,0,0), X = (0.5, 0, 0), Y= (0,0.5,0), Z= (0,0,0.5), C = (0, 0.5, 0.5), D = (0.5, 0, 0.5), A = (0.5, 0.5, 0) and E = (0.5, 0.5, 0.5), all in crystallographic coordinates. (d) Effective transfer integrals (t_h and t_e) calculated with the B3LYP/6-31G (d, p) method.

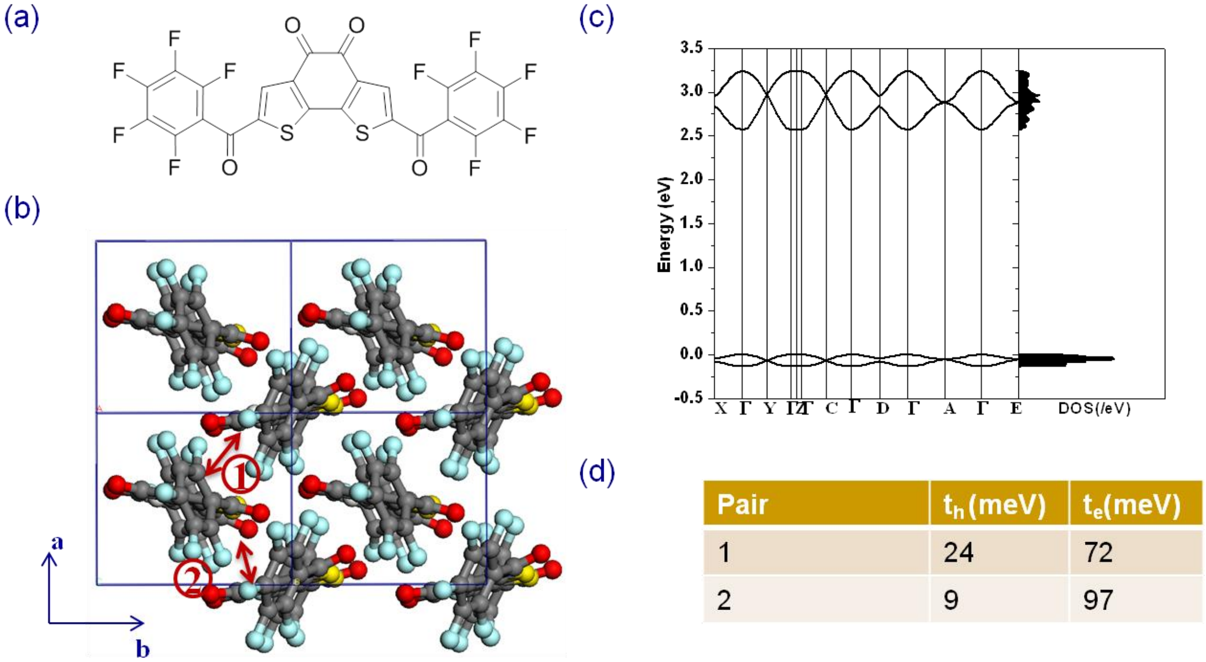




(d)

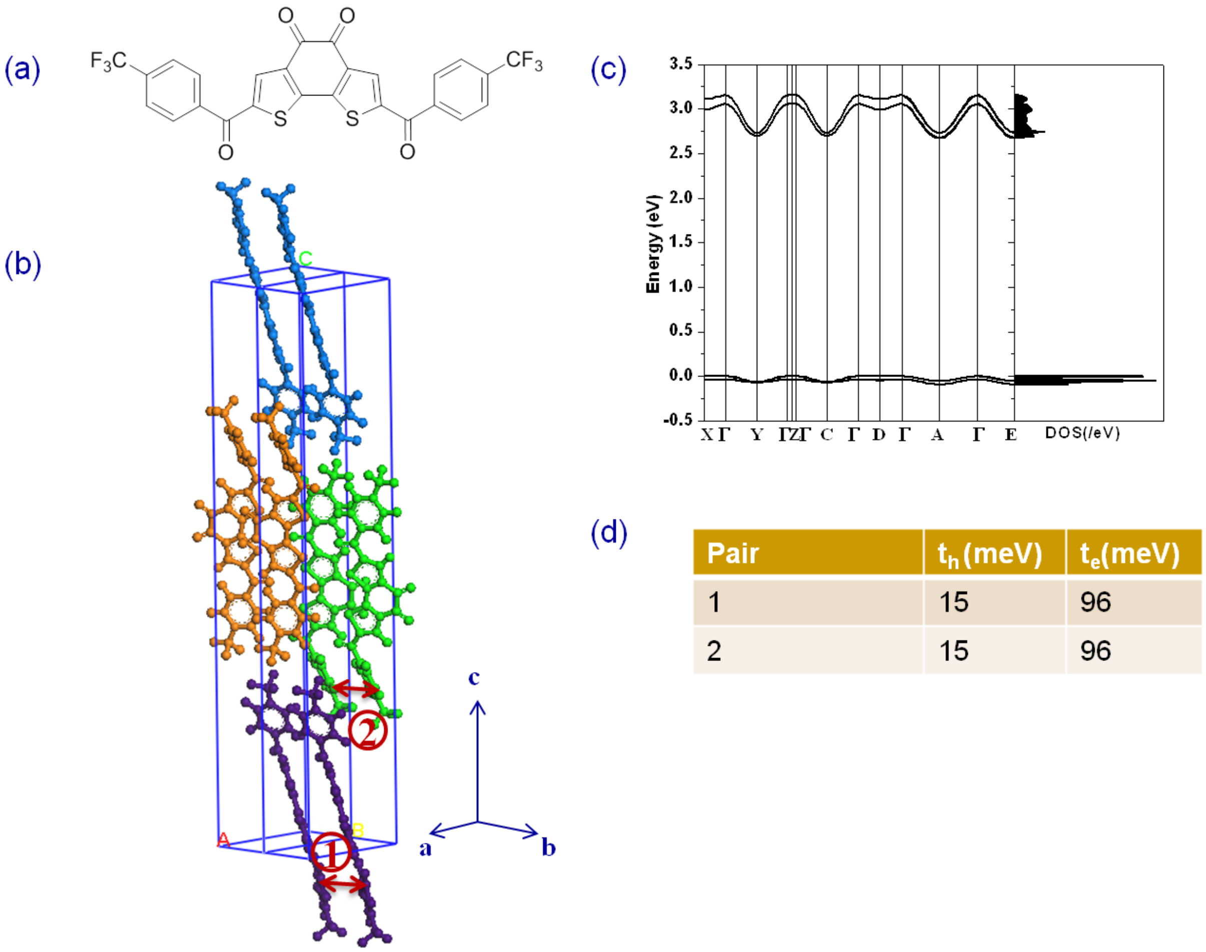
Pair	t_h (meV)	t_e(meV)
1 =3	-116	40
2=6	124	12
4=7	111	44
5=8	-120	29
9	1	1
10	1	1
11	0	40

Figure S25. (a) Chemical structure of 8b. (b) Crystal structure and labeling of the charge-hopping pathways used in the calculations of the transfer integrals. (c) B3LYP/6-31G calculated band structure and density of states (DOS). Points of high symmetry in the first Brillouin zone are labeled as follows: Γ = (0,0,0), B = (0.5, 0, 0), Y= (0,0.5,0), Z= (0,0,0.5), C = (0, 0.5, 0.5), D = (0.5, 0, 0.5) and A = (0.5, 0.5, 0), all in crystallographic coordinates. (d) Effective transfer integrals (t_h and t_e) calculated with the B3LYP/6-31G (d, p) method.



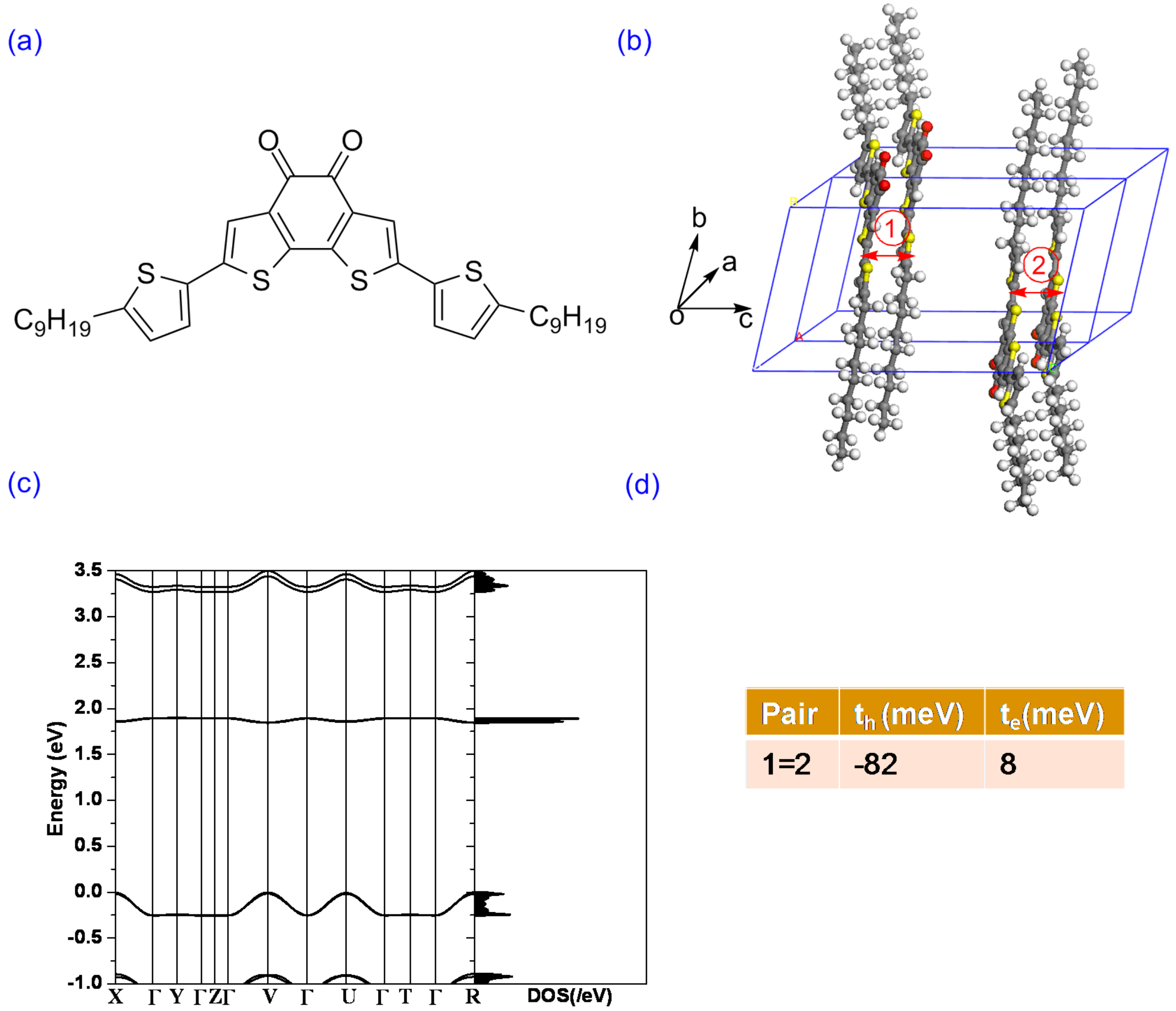
Pair	t_h(meV)	t_e(meV)
1	24	72
2	9	97

Figure S26. (a) Chemical structure of 10a. (b) Crystal structure and labeling of the charge-hopping pathways used in the calculations of the transfer integrals. (c) B3LYP/6-31G calculated band structure and density of states (DOS). Points of high symmetry in the first Brillouin zone are labeled as follows: Γ = (0,0,0), X = (0.5, 0, 0), Y= (0,0.5,0), Z= (0,0,0.5), C = (0, 0.5, 0.5), D = (0.5, 0, 0.5), A = (0.5, 0.5, 0) and E = (0.5, 0.5, 0.5), all in crystallographic coordinates. (d) Transfer integrals calculated with the B3LYP/6-31G (d, p) method.



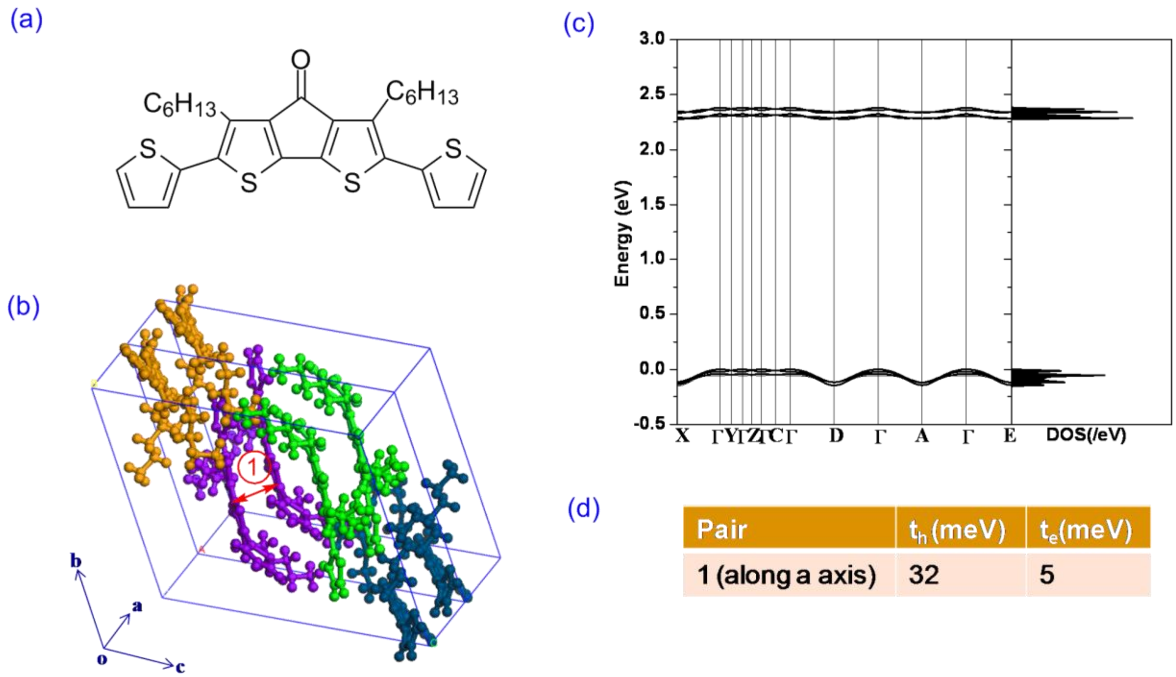
Pair	t_h(meV)	t_e(meV)
1	15	96
2	15	96

Figure S27. (a) Chemical structure of 10c. (b) Crystal structure and the labeling of charge hopping pathways as used in the calculations of the transfer integrals. (c) B3LYP/6-31G calculated band structure and density of states (DOS). Points of high symmetry in the first Brillouin zone are labeled as follows: Γ = (0,0,0), A = (0.5, 0, 0), V= (0,0,0.5), Z = (0, 0.5, 0.5), L = (0.5, 0, 0.5) and M = (0.5, 0.5, 0.5), all in crystallographic coordinates. (d) Transfer integrals calculated with the B3LYP/6-31G (d, p) method.



Pair	t_h (meV)	t_e(meV)
1=2	-82	8

Figure S28. (a) Chemical structure of 19b. (b) Crystal structure and the labeling of charge hopping pathways as used in the calculations of the transfer integrals. (c) B3LYP/6-31G calculated band structure and density of states (DOS). Points of high symmetry in the first Brillouin zone are labeled as follows: Γ = (0,0,0), X = (0.5, 0, 0), Y= (0,0.5,0), Z= (0,0,0.5), V = (0, 0.5, 0.5), U = (0.5, 0, 0.5), T = (0.5, 0.5, 0) and R = (0.5, 0.5, 0.5), all in crystallographic coordinates. (d) Effective transfer integrals (t_{eff}) calculated with the B3LYP/6-31G (d, p) method.



Pair	t_h(meV)	t_e(meV)
1 (along a axis)	32	5

Figure S29. (a) Chemical structure of 30a. (b) Crystal structure and the labeling of charge hopping pathways as used in the calculations of the transfer integrals. (c) B3LYP/6-31G calculated band structure and density of states (DOS). Points of high symmetry in the first Brillouin zone are labeled as follows: Γ = (0,0,0), X = (0.5, 0, 0), Y= (0,0.5,0), Z= (0,0,0.5), C = (0, 0.5, 0.5), D = (0.5, 0, 0.5), A = (0.5, 0.5, 0) and E = (0.5, 0.5, 0.5), all in crystallographic coordinates. (d) Transfer integrals calculated with the B3LYP/6-31G (d, p) method.

Table S5. Adiabatic ionization potential (AIP) and electron affinity (AEA)[a] as determined at the B3LYP/6-311G level of theory. The AEA was also determined at the B3LYP/6-311++G** level. All values are in eV.**

Compound	**B3LYP/6-311G****		**B3LYP/6-311++G****
	AIP	**AEA**	**AEA**
3a	7.97	-2.13	-2.40
3b	7.93	-2.27	-2.45
3c	7.84	-2.25	-2.46
3d	7.72	-2.27	-2.47
4a	7.58	-2.18	-2.35
4b	7.51	-2.20	-2.37
10a	8.45	-3.05	-3.32
10b	8.35	-2.92	–[b]
10c	8.27	-2.86	–[b]
10d	8.46	-3.04	-3.16
17a	8.78	-3.24	-3.51
17b	8.70	-3.17	-3.38
17c	8.70	-3.12	-3.30
17d	7.17	-2.25	-2.45
19a	6.80	-2.13	-2.32
19b	6.56	-2.06	-2.23
19c	6.68	-2.10	-2.28
19d	7.04	-2.22	-2.40
27a	7.30	-2.95	-3.17
28a	7.63	-3.03	-3.26
30a	6.33	-1.65	-1.78
30b	6.11	-1.58	-1.69
31a	6.86	-2.69	–[b]

[a] Adiabatic ionization energies determined as E(ion) - E(neutral). b) AEA results for **10b**, **10c**, and **31a** are not provided due to SCF convergence issues.

Table S6. Low-energy vertical transition energies (E_{opt}, eV), wavelengths (λ_{opt}, nm), oscillator strengths (*f*), and electronic configurations as determined with time-dependent DFT (TDDFT) at the B3LYP/6-311G level of theory.**

Compound	Transition	E_{opt}	λ_{opt}	*f*	Electronic configuration
3a	$S_0 \rightarrow S_2$[a]	2.27	547	0.068	HOMO→LUMO
3b	$S_0 \rightarrow S_2$	2.29	541	0.091	HOMO→LUMO
3c	$S_0 \rightarrow S_2$	2.27	546	0.097	HOMO→LUMO
3d	$S_0 \rightarrow S_2$	2.24	554	0.108	HOMO→LUMO
4a	$S_0 \rightarrow S_2$	2.22	558	0.118	HOMO→LUMO
4b	$S_0 \rightarrow S_2$	2.21	561	0.129	HOMO→LUMO
10a	$S_0 \rightarrow S_2$	2.61	475	0.236	HOMO→LUMO
10b	$S_0 \rightarrow S_2$	2.56	484	0.221	HOMO→LUMO
10c	$S_0 \rightarrow S_2$	2.57	482	0.225	HOMO→LUMO
10d	$S_0 \rightarrow S_2$	2.60	476	0.241	HOMO→LUMO
17a	$S_0 \rightarrow S_2$	2.81	441	0.261	HOMO-1→LUMO[b]
17b	$S_0 \rightarrow S_2$	2.74	452	0.268	HOMO→LUMO
17c	$S_0 \rightarrow S_2$	2.75	452	0.243	HOMO→LUMO
17d	$S_0 \rightarrow S_1$	2.07	600	0.169	HOMO→LUMO
19a	$S_0 \rightarrow S_1$	1.89	656	0.162	HOMO→LUMO
19b	$S_0 \rightarrow S_1$	1.80	689	0.177	HOMO→LUMO
19c	$S_0 \rightarrow S_1$	1.86	668	0.170	HOMO→LUMO
19d	$S_0 \rightarrow S_1$	2.03	612	0.179	HOMO→LUMO
27a	$S_0 \rightarrow S_1$	1.99	622	0.352	HOMO→LUMO
28a	$S_0 \rightarrow S_2$	2.19	566	0.405	HOMO→LUMO

[a] For molecules in which the first transition with significant oscillator strength is the $S_0 \rightarrow S_2$ transition, the $S_0 \rightarrow S_1$ transition has little-to-no oscillator strength and involves the excitation of an electron from the HOMO-1→LUMO. [b] For **17a**, the HOMO (-7.64 eV) and HOMO-1 (-7.72 eV) are nearly iso-energetic.

5. OFET Fabrication

OFET were fabricated on heavily doped n-type silicon substrate with 200 nm thermally grown SiO2 as dielectric. SiO_2 dielectric surface was then passivated with a thin buffer layer of BCB (Cyclotene^{TM}, Dow Chemicals), to provide a high-quality hydroxyl-free interface. The samples were annealed at 250°C for 1 hour inside N2 glove box for crosslinking. The total capacitance density (C_{OX}) measured from parallel-plate capacitors, and it was ~15 nF/cm^2. A thin organic layer (14-15 mg/ml) from chloroform, chlorobenzene, tetrahydrofuran or 1,4 dioxane was spin coated at 500 RPM for 10 seconds and 2000 RPM for 20 seconds. In case of **10a**, 45 nm of organic film was vacuum evaporated. Finally, 100 nm of Au, 40nm/100nm of Ca/Ag or 40nm/100nm of Ca/Au were evaporated as source/drain electrode mask.

OFETs with bottom contact and top gate structure were fabricated on glass substrates (Corning$^{®}$ Eagle^{2000TM}). Au (50 nm) bottom contact source/drain electrodes were deposited by thermal evaporation through a shadow mask. A thin (45 nm) organic layer of **10a** was vacuum evaporated. A CYTOP (45 nm)/Al_2O_3(50 nm) bi-layers was used as top gate dielectrics. CYTOP solution (CTL-809M) was purchased from Asahi Glass with a concentration of 9 wt%. To deposit the 45-nm-thick fluoropolymer layers, the original solution was diluted with their solvents (CT-solv.180) to have solution:solvent volume ratios of 1:3.5. CYTOP layers were deposited by spin coating at 3000 rpm for 60 sec. Al_2O_3 (50 nm) films were deposited on fluoropolymer layers by atomic layer deposition (ALD) at 110 °C using alternating exposures of trimethyl aluminum [$Al(CH_3)_3$] and H_2O vapor at a deposition rate of approximately 0.1 nm per cycle. All spin coating and annealing processes were carried out in a N_2-filled dry box. Finally, Al (150 nm) gate electrodes were deposited by thermal evaporation through a shadow mask.

All current-voltage (*I-V*) characteristics of OFETs were measured with an Agilent E5272A source/monitor unit in a N_2-filled glove box (O_2, H_2O < 0.1 ppm).

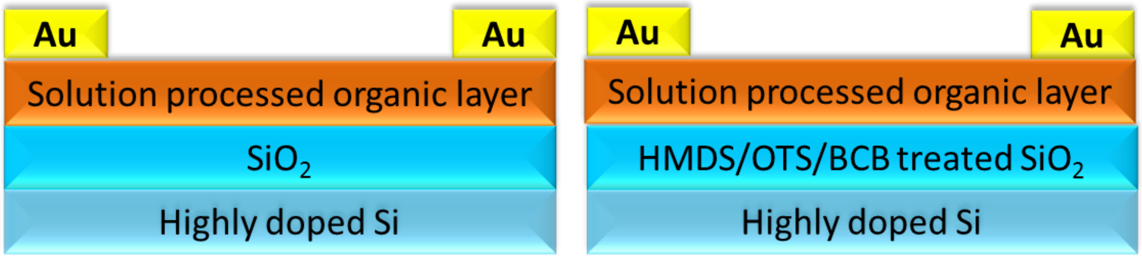


Figure S30. Device architecture used for the electrical characterisation of the solution-processed 10a.

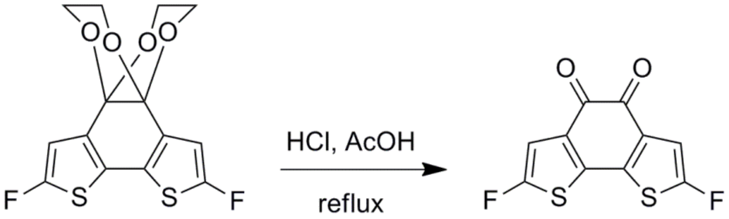
For the OFET with the solution-processed **10a** (Figure S30), 300 nm thermally grown silicon oxide on top of doped Si was utilized as the bottom gate dielectric (10.6 nF/cm^2). The substrate was cleaned by a sequential sonication in acetone and isopropyl alcohol for 10 min. Material **10a** was dissolved into chlorobenzene at the concentration of 8 mg/mL. After half an hour, the solution was spin coated on top of the substrate at 1000 rpm for 60 sec. Finally 60 nm Au was thermally evaporated on top as source and drain through a stencil mask with the channel width of 2000 µm and length of 100 µm. All the fabrication and testing process was carried out in the nitrogen filled glove box (<1ppm O_2 and H_2O). The average and standard deviation were extracted from five different devices on the same substrate.

6. Experimental Details

Solvents: tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl; anhydrous diethyl ether and dimethylformamide (DMF) were used as received. ^{1}H and ^{13}C{^{1}H} and DEPT-135 NMR spectra were acquired in $CDCl_3$ (peaks in ^{1}H NMR were referenced to residual $CHCl_3$ signal at δ 7.27 ppm or tetramethylsilane at δ 0.00 ppm), THF-*d8*, 1,2-dichloroethane-*d4*, 1,1,2,2-tetrachloroethane-*d2* (peaks in ^{1}H NMR were referenced to residual non-deuterated solvent signal. UV-vis absorption spectra were recorded in 1 cm cells using dichloromethane as solvent. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were carried out on dry deoxygenated dichloromethane or THF solutions *ca*. 10^{-4} M of analyte and 0.1 M solution of tetra-*n*-butylammonium hexafluorophosphate under nitrogen using a potentiostat, a glassy carbon working electrode, a platinum auxiliary electrode, and a silver wire anodized in 1 M aqueous potassium chloride (a pseudo-reference electrode). Potentials were referenced to ferrocenium/ferrocene ($Cp_2Fe^{0/1+}$) as an internal standard at 0 V. Cyclic voltammograms were recorded at scan rates of 50 $mV \cdot s^{-1}$. DSC analysis was carried out with 10 ºC/min heating/cooling rate. 2,6-Bis-trimethylsilyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one, 2,7-bis-trimethylsilyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**1**), 2,7-bis-trimethylsilyl-3,6-di-*n*-hexyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**2**) were prepared using the literature procedure.[1] 2,6-Di-iodo-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (**8a**) was prepared as described in the literature.[3] 2,2'-Bis(triisopropylsilyl)-4,4'-dibromo-5,5'-dithiazole was prepared as described in the literature.[4]

Deprotection reactions of materials **16** were attempted, and the presence of the desired products **17** (except **17d**) was confirmed by the mass spectrometry analysis, but materials were difficult to obtain in pure form, and only limited characterisation was acquired.

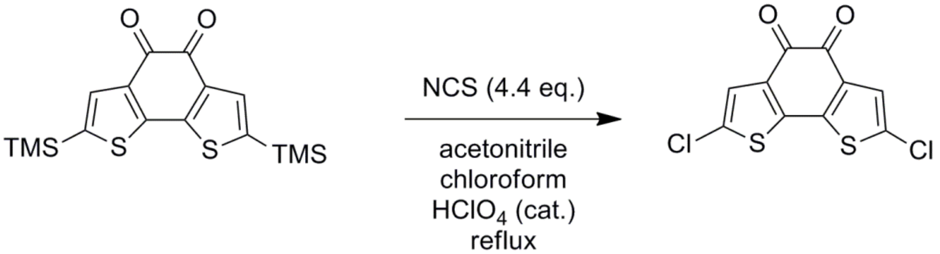
2,7-Difluoro-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione-4,5-dione (3a).



2,7-Difluoro-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(ethyloxolane) (**6**) (0.5 mmol, 0.172 g) was mixed with acetic acid (10 mL) and the resulting mixture was heated to reflux. HCl (1 mL) was added dropwise, and yellowish mixture became purple within a few minutes. The mixture was refluxed for ~10 minutes, analyzed by TLC (chloroform as eluant) and complete consumption of the starting material was confirmed (a new purple spot of the product was detected as well). The reaction mixture was cooled to room temperature, treated with water and dark precipitated was separated by vacuum filtration, washed with water, then ethanol and dried (0.144 g, 113% crude yield, probably still contained some solvents). This material was recrystallized from toluene-hexanes and very dark purple needles were obtained (0.123 g, 96% yield). This material was further purified by column chromatography twice (silica gel, dichloromethane as eluant), followed by recrystallization from toluene-hexanes mixture (0.102 g, 82.9% recovery). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.89 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 172.9 (quaternary C(O)), 165.4 (d, J = 300 Hz, quaternary C-F), 133.0 (quaternary C), 132.2 (quaternary C), 107.3 (d, J = 11 Hz, CH) (assignment of the CH and quaternary carbons was made based on DEPT-135 analysis). HRMS (EI) calculated for $C_{10}H_2F_2O_2S_2$ 255.9464; found 255.9476. Anal. Calcd. for $C_{10}H_2F_2O_2S_2$: C, 46.87; H, 0.79. Found: C, 46.94; H, 0.66.

T_d (5% weight loss): 196 ºC.

2,7-Dichloro-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (3b).



Conditions for conversion of the TMS group into chlorine were adapted from the literature.[5]

2,7-Bis-trimethylsilyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**1**) (4.0 mmol, 1.42 g) was mixed with *N*-chlorosuccinimide (2.2 eq., 8.8 mmol, 1.18 g) and acetonitrile (50 mL) was added. Dark red mixture was heated to reflux overnight and analyzed by TLC analysis. Only starting material was detected and $HClO_4$ (0.05 mL, 69-72%) was added followed by addition of *N*-chlorosuccinimide (2.2 eq., 8.8 mmol, 1.18 g) and chloroform (10 mL). Two new more polar red spots were detected by TLC analysis (possible products of protiodesilylation), and the resulting mixture was refluxed overnight. Reaction mixture was cooled to room temperature, treated with aqueous solution of $Na_2S_2O_3$ and organic solvents were removed by rotary evaporation. Organic matter was extracted with dichloromethane, purple organic phases were dried over anhydrous magnesium sulfate, and the solvent was removed by rotary evaporation. Almost black microcrystalline compound was obtained (1.24 g, 107% crude yield). This crude product was purified by column chromatography (silica gel, chloroform as eluant). Fractions containing pure product were combined, the solvent was removed by rotary evaporation and very dark crystalline compound was obtained (0.59 g, 45.6% yield). This material was dissolved in toluene (~40 mL) under reflux (purple solution) and allowed to cool to room temperature. Long very dark purple needles were obtained by vacuum filtration (0.39 g, 66.1% recovery). First two fractions containing the product with minor impurities were combined separately, the solvent was removed and the residue was dissolved in boiling 2-propanol with addition of dichloromethane and purple solution was allowed to cool to room temperature. Long needles/blades were separated by vacuum filtration (0.063 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 172.6 (quaternary C(O)), 141.0 (quaternary C), 134.5 (quaternary C), 132.2 (quaternary C), 126.2 (CH). HRMS (EI) calculated for $C_{10}H_2Cl_2O_2S_2$ 287.8873; found 287.8876. Anal. Calcd. for $C_{10}H_2Cl_2O_2S_2$: C, 41.54; H, 0.70. Found: C, 41.54; H, 0.67.

T_d (5% weight loss): 234 ºC.

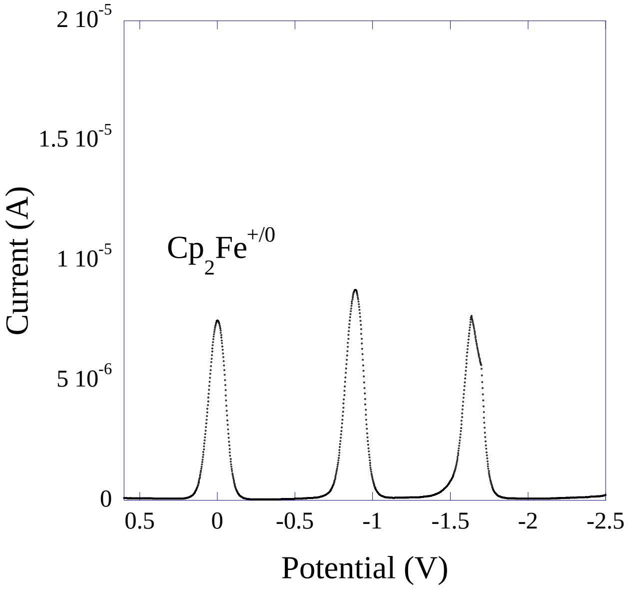
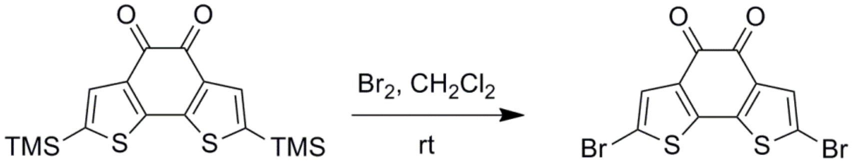


Figure S31. Differential pulse voltammetry (DPV) (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V) of 2,7-dichloro-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione: $E^{0/1-}$ = -0.89 V, $E^{1-/2-}$ = -1.64 V.

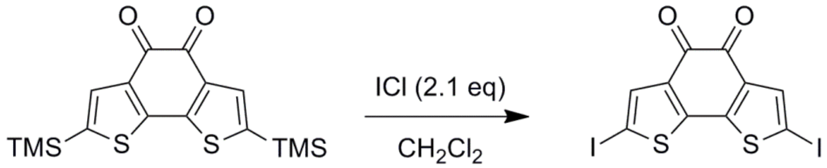
2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (3c)



2,7-Bis-trimethylsilyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**1**) (4.0 mmol, 1.459 g) was dissolved in dichloromethane (40 mL) and bromine (2.2 eq., 8.8 mmol, 1.41 g) was added dropwise to a red-black solution. The reaction mixture became purple-black. The reaction mixture was analyzed by TLC (dichloromethane as eluant), and a new product and a minor impurity was detected. Additional amount of bromine (0.33 g) was added, the mixture was stirred for 0.5 h and treated with 10 mL of aqueous $Na_2S_2O_3$. The organic solvent was removed by rotary evaporation and the crude product was separated by vacuum filtration (1.95 g, 128% crude yield, slightly wet). This crude material was purified by column chromatography (silica gel, CH_2Cl_2 as eluant). The solvent was removed from the combined fractions, and very dark shiny microcrystalline material was obtained (0.90 g, 59.5% yield). The heavily stained column was eluted with chloroform, the solvent was removed from the combined fractions and additional amount of product was obtained as very dark microcrystalline solid (0.52 g, 34.4% yield). HRMS (EI) calculated for $C_{10}H_2Br_2O_2S_2$ 375.7863; found 375.7869. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.47 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 172.51 (quaternary C), 143.59 (quaternary C), 135.38 (quaternary C), 130.07 (CH), 114.67 (quaternary C-Br) (assignment of the quaternary and CH signals was made based on the DEPT experiment). Anal. Calcd. for $C_{10}H_2Br_2O_2S_2$: C, 31.77; H, 0.53. Found: C, 32.06; H, 0.40.

T_d (5% weight loss): 275 ºC.

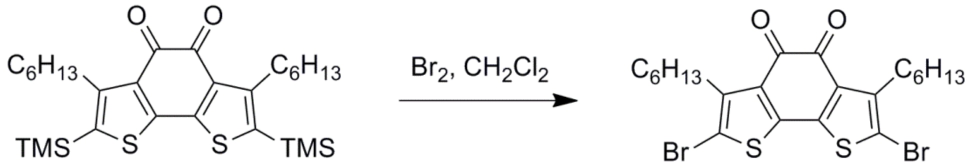
2,7-Diiodo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (3d)



2,7-Bis-trimethylsilyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**1**) (1.536 mmol, 0.56 g) was dissolved in dichloromethane (10 mL), cooled in ice-water bath, and a solution of iodine monochloride (2.1 eq., 3.255 mmol, 0.53 g) in dichloromethane (5 mL) was added dropwise to a red-purple solution. The mixture was warmed to room temperature, stirred for ~1 h, and treated with aqueous solution $Na_2S_2O_3$ (15 mL). The mixture was stirred for ~20 minutes and the dark solid was separated by vacuum filtration (0.71 g, 97.9% yield) (pure based on TLC analysis (dichloromethane as eluant). HRMS (EI) calculated for $C_{10}H_2I_2O_2S_2$ 471.7586; found 471.7608 (2.4 ppm). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (s, 2H); ^{1}H NMR (THF-*d8*, 400 MHz): δ 7.88 (s, 2H); ^{13}C{^{1}H} NMR (THF-*d8*, 100 MHz): δ 172.6 (quaternary C(O)), 147.0, 138.4 (quaternary C), 137.4 (CH), 77.13 (quaternary C-I). Anal. Calcd. for $C_{10}H_2I_2O_2S_2$: C, 25.44; H, 0.43. Found: C, 24.10; H, 0.47. This material was further purified by column chromatography (silica gel, chloroform as eluant) and elemental analysis was acquired. Found: C, 23.91; H: 0.43 (this analysis is in agreement with a structure that crystallizes with $CHCl_3$ (2:1 ratio)). The presence of chloroform was further confirmed by ^{1}H NMR in THF-*d8* and TGA analysis. Material was dried under vacuum with heating (<100 ºC), and elemental analysis was acquired. Found: C, 25.68; H, 0.29.

T_d (5% weight loss): 302 ºC (for material recrystallized from toluene: beginning of the solvent loss (0.5%) at 76 ºC, complete solvent loss at 163 ºC (3.8%), T_d (5% loss) at 302 ºC; for material recrystallized from chloroform: beginning of the solvent loss (0.5%) at 110.5 ºC, complete solvent loss at 151 ºC (11.7%), T_d (5% loss) at 323 ºC).

2,7-Dibromo-3,6-di-*n*-hexyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (4a)



2,7-Bis-trimethylsilyl-3,6-di-*n*-hexyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**2**) (0.70 mmol, 0.37 g) was dissolved in dichloromethane (20 mL), and bromine (2.2 eq., 1.54 mmol, 0.25 g) was added dropwise to a red-purple solution. The dark purple mixture was stirred for 0.5 h, and aqueous $Na_2S_2O_3$ was added. The organic phase was removed, dried over anhydrous magnesium sulfate, the drying agent was filtered off, and the solvent was partially removed by rotary evaporation. Purple solution was column chromatographed (silica gel, hexanes:dichloromethane (1:1) to pack the column, hexanes to elute the byproduct, then hexanes:dichloromethane (1:1) to elute the product). Material, which was obtained after evaporation of combined fractions containing slightly contaminated product (**4a**), was further purified by recrystallization from 2-propanol, and pure product was obtained as purple solid (0.163 g). Fractions with pure material were combined separately, the solvents were re moved by rotary evaporation, and the residue was recrystallized from 2-propanol to give purple solid (0.078 g). Total yield of the product is 63.2% (0.242 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.88 (t, J = 7.6 Hz, 4H), 1.51 (m, 4H), 1.38 (m, 4H), 1.32 (m, 8H), 0.91 (t, J = 6.9 Hz, 6H); ^{13}C{^{1}H} NMR

($CDCl_3$, 100 MHz): δ 173.5 (quaternary C), 145.5 (quaternary C), 144.1 (quaternary C), 131.8 (CH), 111.7 (quaternary C-Br), 31.5 (CH_2), 29.1 (CH_2), 28.7 (CH_2), 28.5 (CH_2), 22.6 (CH_2), 14.1 (CH_3) (assignment of the carbon signals was made based on the DEPT-135 experiment). HRMS (EI) calculated for $C_{22}H_{26}Br_2O_2S_2$ 543.9741; found 543.9722. Anal. Calcd. for $C_{22}H_{26}Br_2O_2S_2$: C, 48.36; H, 4.80. Found: C, 48.46; H, 4.81.

DSC analysis (10 ºC/min rate): 122.2 ºC (melting point observed on first heating), (peak with two maxima at 85.8 ºC and 87.0ºC was observed on cooling (crystallization); one endothermic peak at 120.8 ºC was observed on second heating (melting point).

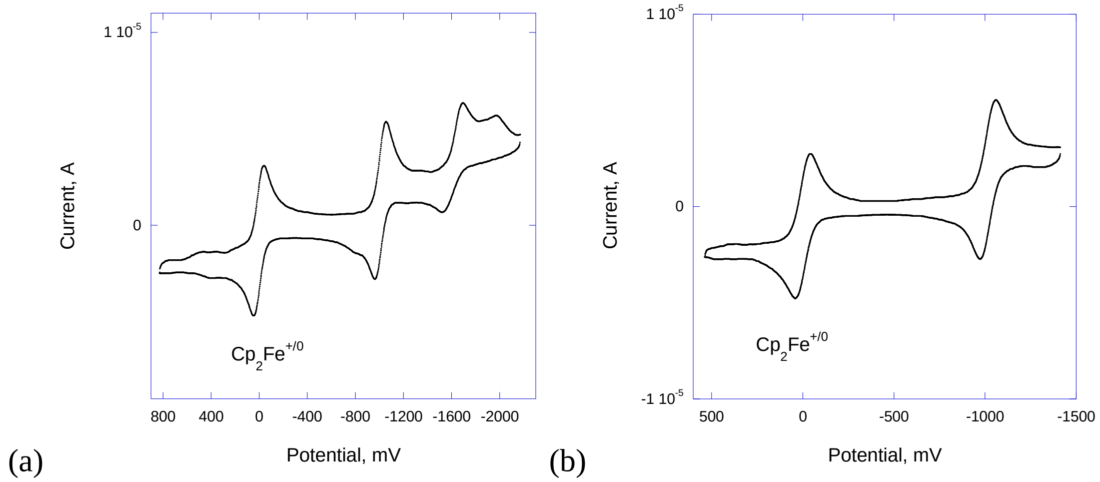


Figure S32. CV analysis of 2,7-dibromo-3,6-di-*n*-hexyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (4a) (0.1 M $^nBu_4NPF_6$ in CH_2Cl_2, Cp_2Fe internal standard at 0 V, 50 mV rate) (a) 1st and 2nd reductions at $E_{1/2}^{0/1-}$ = -1.01 V (reversible) and $E_{1/2}^{1-/2-}$ = -1.62 V (partially reversible) respectively; (b) only 1st reduction at $E_{1/2}^{0/1-}$ = -1.02 V (reversible).

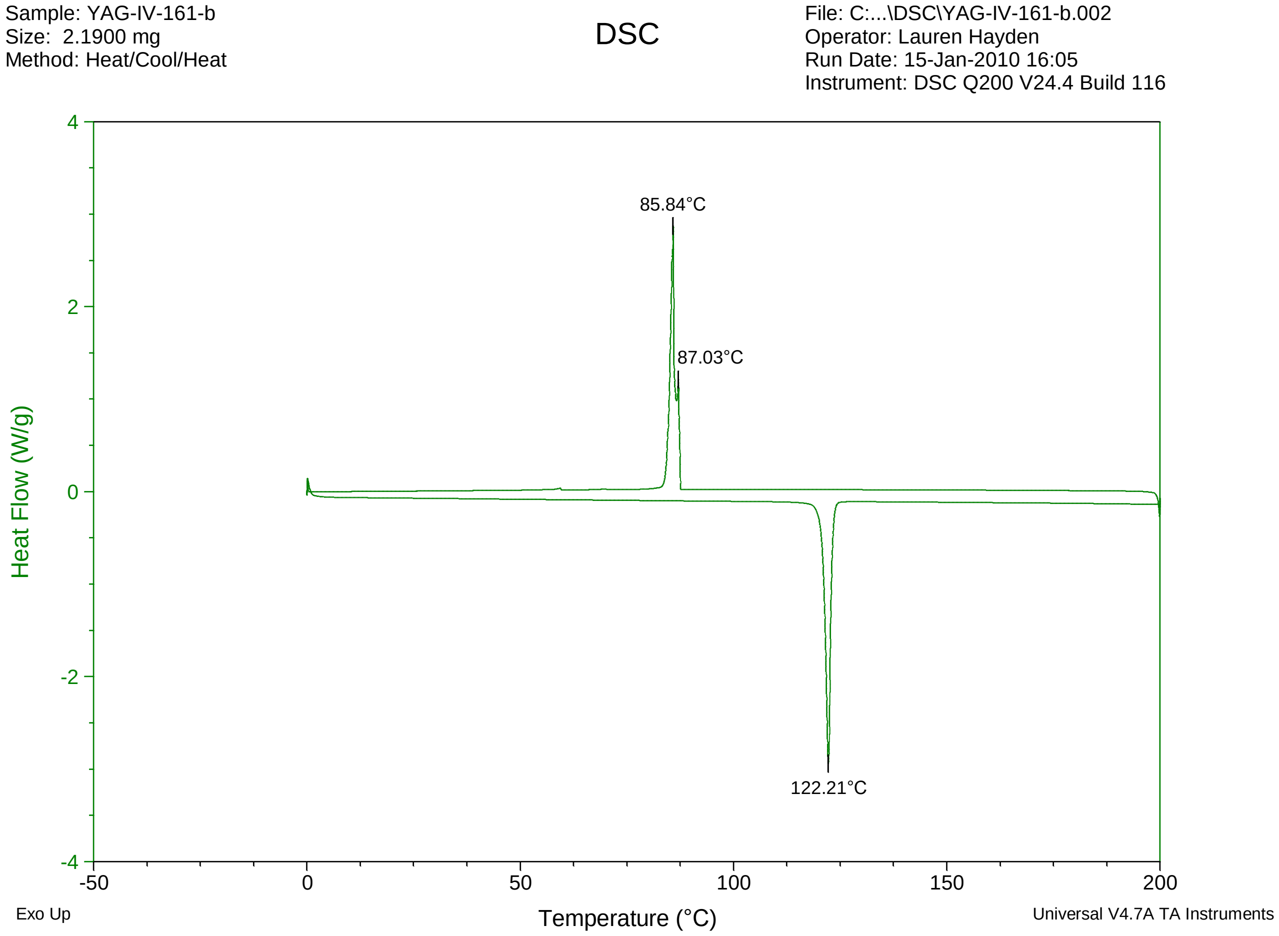
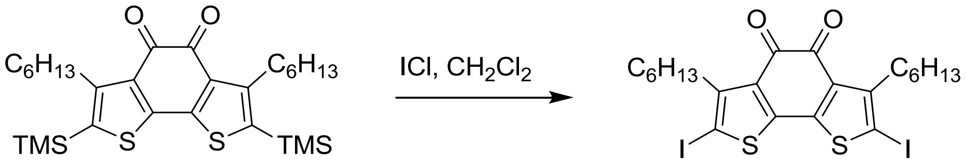


Figure S33. DSC analysis (10ºC/min rate) of 3,6-di-*n*-hexyl-2,7-dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (4a).

2,7-Diiodo-3,6-di-*n*-hexyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (4b)



2,7-Bis-trimethylsilyl-3,6-di-*n*-hexyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**2**) (0.20 mmol, 0.107 g) was dissolved in dichloromethane (10 mL) and iodine monochloride (2.1 eq., 0.42 mmol, 0.068 g) was added dropwise to a dark red-purple solution. The purple mixture was stirred for 20 minutes and aqueous $Na_2S_2O_3$ was added. The purple organic phase was removed, dried over anhydrous magnesium sulfate, and the solvent was removed by rotary evaporation. Crude product was purified by column chromatography (silica gel, hexanes:dichloromethane

(2:1) as eluant). The combined fractions were subjected to rotary evaporation and the residue was purified from 2-propanol (~10 mL). Material was obtained as purple solid in 55.9% yield (0.0716 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.86 (t, J = 7.4 Hz, 4H), 1.44 (m, 8H), 1.23 (m, 8H), 0.92 (t, J = 7.0 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 173.1 (quaternary C), 145.5 (quaternary C), 148.8 (quaternary C), 131.3 (CH), 78.02 (quaternary C-I), 31.5 (CH_2), 31.2 (CH_2), 29.2 (CH_2), 28.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3) (assignment of the carbon signals was made based on the DEPT experiment). HRMS (EI) calculated for $C_{22}H_{26}I_2O_2S_2$ 639.9464; found 639.9468. Anal. Calcd. for $C_{22}H_{26}I_2O_2S_2$: C, 41.26; H, 4.09. Found: C, 41.44; H, 4.06.

DSC analysis (10 ºC/min rate): 121.0 ºC (melting point observed on first heating), (somewhat broad peak at 70.8 ºC was observed on cooling (crystallization); two transitions were detected on second heating: exothermic at 96.7 ºC (completion of crystallization?) and endothermic at 120.0 (melting point).

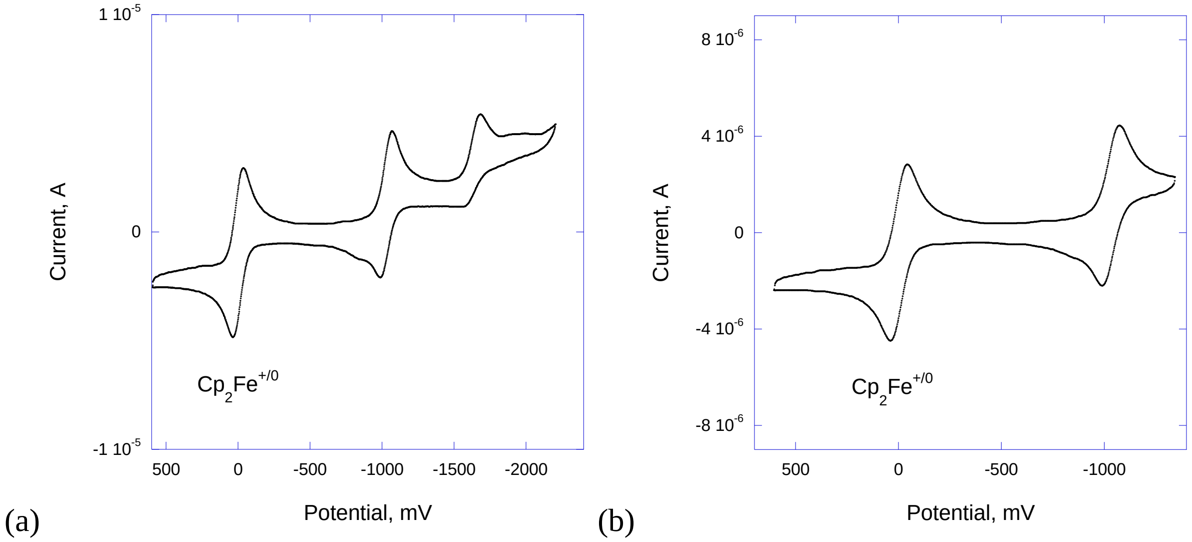


Figure S34. CV analysis of 2,7-diiodo-3,6-di-*n*-hexyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (4b) (0.1 M $^nBu_4NPF_6$ in CH_2Cl_2, Cp_2Fe internal standard at 0 V, 50 mV rate) (a) with 1st and 2nd reductions at $E_{1/2}^{0/1-}$ = -1.02 V (reversible) and $E_{1/2}^{1-/2-}$ = -1.62 V (partially reversible) respectively; (b) only 1st reduction at $E_{1/2}^{0/1-}$ = -1.03 V (reversible).

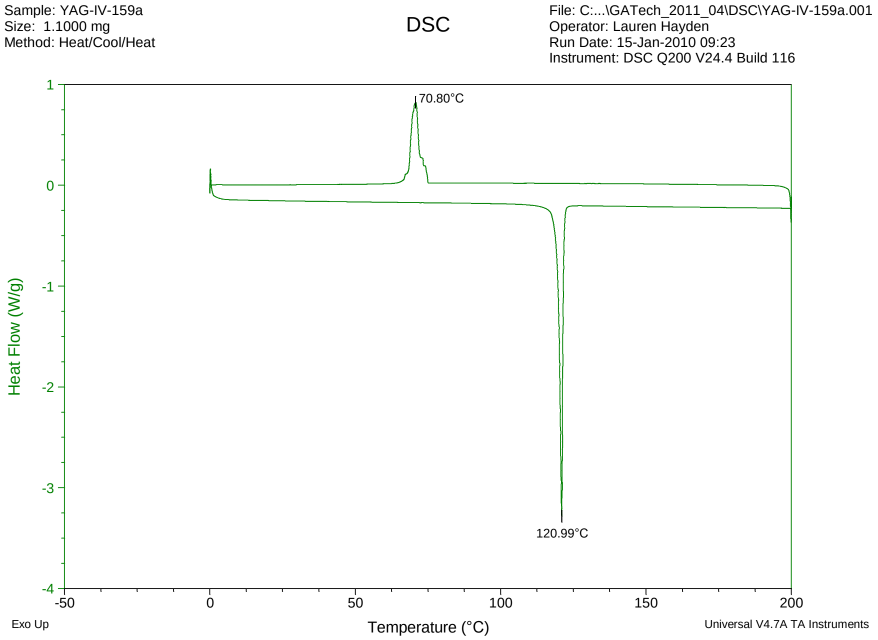


Figure S35. DSC analysis (10 0ºC/min rate) of 3,6-di-*n*-hexyl-2,7-diiodo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (4b):first cycle.

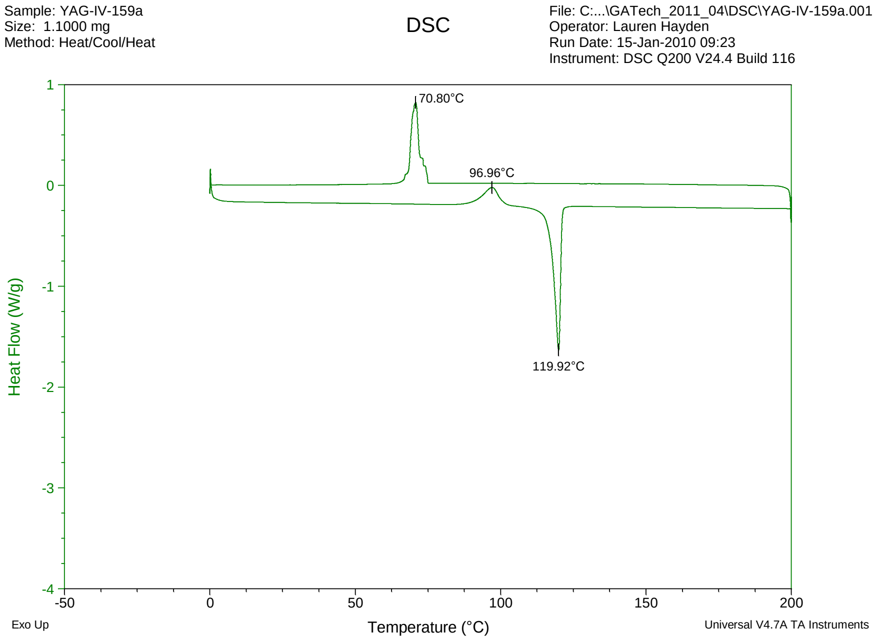
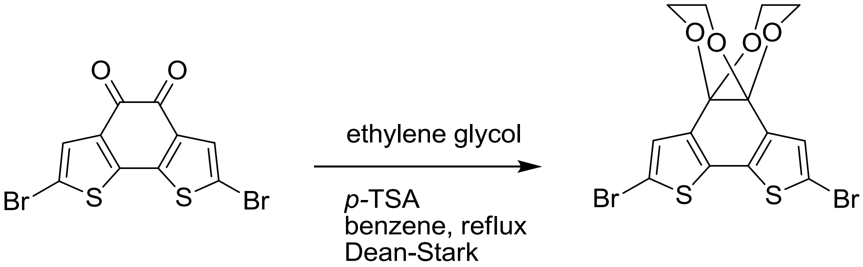


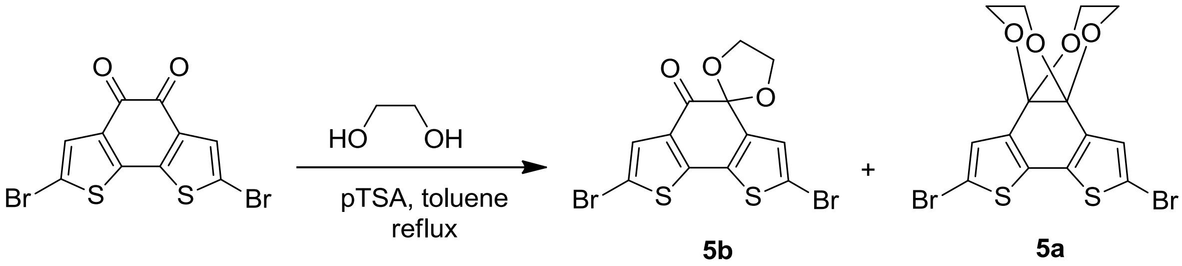
Figure S36. DSC analysis (10 0ºC/min rate) of 3,6-di-*n*-hexyl-2,7-diiodo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (4b): (top) first cycle; (bottom) second cycle.

2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis(ethyleneoxolane) (5a).



2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**3c**) (18.0 mmol, 6.81 g), ethylene glycol (20 mL) and benzene (100 mL) were mixed together in a round bottom flask equipped with a magnetic stir bar, Dean-Stark trap and a condenser. A catalytic amount (a few crystals) of *p*-toluenesulfonic acid (*p*-TSA) was added and the mixture was heated to reflux. Additional amount of ethylene glycol (40 mL) was added after a few hours, and mixture was refluxed for 4 days until complete consumption of the starting material. Reaction mixture with greenish precipitate was cooled to room temperature, subjected to rotary evaporation to remove volatile organic solvent, treated with water and greenish solid was separated by vacuum filtration (6.50 g, 77.5% crude yield). Organic matter in the filtrate was extracted with dichloromethane, combined with the greenish solid and purified by column chromatography (silica gel, dichloromethane:hexanes (2:1) as eluant). First fractions with product **5a** slightly contaminated with mono-protected byproduct **5b** were combined, the solvents were removed, the residue was heated with ~250 mL of 2-propanol, cooled to room temperature and vacuum filtered (4.40 g, barely yellowish solid). Later fractions were kept separately, the solvents were removed by rotary evaporation and the residue was heated with ~150 mL of 2-propanol to give off-white solid (1.21 g, combined yield of **5a** was 5.61 g, 66.9% purified yield, 85% recovery). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.15 (s, 2H), 4.16 (m, 4H), 3.70 (m, 4H); ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ 135.9 (quaternary C), 133.5 (quaternary C), 128.1 (CH), 111.5 (quaternary C), 92.8 (quaternary C), 61.6 (CH_2) (while ^{1}H NMR in CD_2Cl_2 reported in the literature[6] matches well with our data, in the literature ^{13}C NMR data[6] 7 resonances were reported, while we observed 6 resonances). HRMS calculated for $C_{14}H_{10}Br_2O_4S_2$ 463.8387; found 463.8388. Anal. Calcd. for $C_{14}H_{10}Br_2O_4S_2$ C, 36.07; H, 2.16. Found: C, 36.35; H, 2.02.

2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4-one-5-(1,3-dioxolane) (5b)



2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**3c**) (1.0 mmol, 0.376 g) was mixed with toluene (50 mL), ethylene glycole (10 eq., 10.0 mmol, 0.62 g) and catalytic amount of *p*-toluenesulfonic acid (polymer bound). The red-purple solution was heated to reflux and after 2 hours additional amount of ethylene glycol was added (0.3 mL). After reflux overnight additonal amount of *p*-toluenesulfonic acid (polymer bound) and ethylene glycol (2 mL) was added and the mixuter was refluxed for additional 8 h. The orange-reddish mixture was cooled to room temperature and applied to the column (150 mL of silica gel, dichloromethane as eluant). First bright yellow fractions were combined, the solvent was removed and the resilue was recrystallized from 2-propanol. Mono-protected product (**5b**) was obtained as bright yellow needles (0.16 g, 37.9 %). Later yellowish fractions with more polar product **5a** were comibned separately, the solvents were removed and the residue was recrystallized from 2-propanol. Pale yellowish needles of **5a** were isolated after vacuum filtration (0.078 g, 16.7 %).

(**5b**): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (s, 1H), 7.13 (s, 1H), 4.47 (m, 2H), 4.31 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 189.03 (quaternary C(O)), 144.91 (quaternary C), 139.47 (quaternary C), 132.44 (quaternary C), 131.7 (quaternary C), 130.3 (CH), 128.21 (CH), 114.3 (quaternary C-Br), 111.61 (quaternary C-Br), 98.7 (quaternary C), 66.2 (CH_2) (assignment of the quaternary, CH, CH_2 and CH_3 signals was made based on the DEPT-135 experiment). HRMS (EI) calculated for $C_{12}H_6Br_2O_3S_2$ 419.8125; found 419.8134. Anal. Calcd. for $C_{12}H_6Br_2O_3S_2$: C, 34.14, H, 1.43. Found: C, 34.38; H, 1.32.

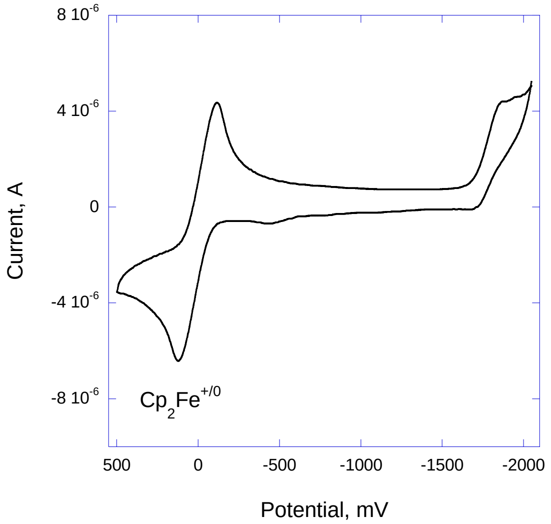
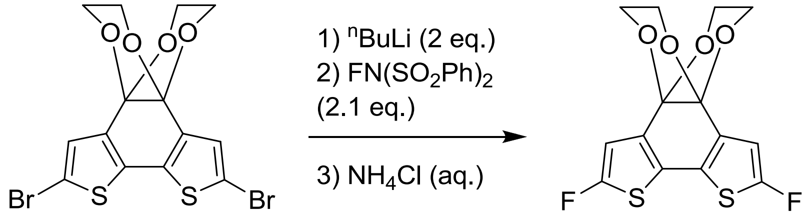


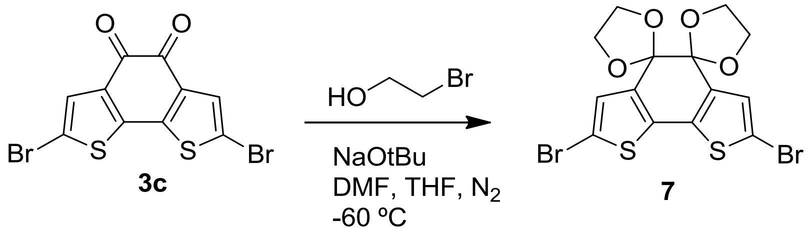
Figure S37. CV analysis of 2,7-dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4-one-5-(1,3-dioxolane) (0.1 M ^{n}Bu$_4$NPF$_6$ in THF, Cp$_2$Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1-}$ = -1.79 (irreversible).

2,7-Difluoro-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(ethyleneoxolane) (6).



2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(ethyleneoxolane) (**5a**) (2.5 mmol, 1.165 g) was dissolved in anhydrous THF (75 mL) (nitrogen atmosphere), and the resulting yellowish solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.87 M in hexanes, 5.0 mmol, 1.75 mL) was added dropwise, and yellowish solution became almost colorless suspension, which became light pink after stirring for a few minutes. The reaction mixture was stirred for 15 minutes, and a solution of *N*-fluorobenzenesulfonimide (2.1 eq., 5.25 mmol, 1.66 g) in anhydrous THF (25 mL) was added dropwise. Reaction mixture became orange solution. After stirring for 10 minutes additional amount of *N*-fluorobenzenesulfonimide (0.16 g) was added, the reaction mixture was allowed to warm to room temperature, and then treated with water. Organic phase was separated, the aqueous phase was extracted with dichloromethane, and combined organic phases (yellow-brownish) were subjected to rotary evaporation. The residue was mixed with chloroform, heated to reflux, and insoluble matter was separated by vacuum filtration. Filtrate was column chromatographed (silica gel, dichloromethane as eluant). Fractions containing the product (**6**) were combined, the solvent was removed by rotary evaporation and beige solid was obtained (microcrystalline compound, 0.46 g, 53.5% yield). Part of the solid (0.21 g) was recrystallized from 2-propanol, and purified product was obtained as yellowish large crystals (0.16 g, 76.2% recover). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.61 (s, 2H), 4.13 (m, 4H), 3.71 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 165.2 (d, J = 295 Hz, quaternary C-F), 131.7 (quaternary C), 120.8 (quaternary C), 105.8 (d, J = 11 Hz, CH), 92.7 (quaternary C), 61.6 (CH_2) (assignment of the quaternary, CH, CH_2 and CH_3 signals was made based on the DEPT-135 experiment). ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -129.9 (1,1,2-trichlorotrifluoroethane was used as internal reference with δ at -71.75 ppm (t)). HRMS (EI) calculated $C_{14}H_{10}F_2O_4S_2$ 343.9989; found 343.9982. Anal. Calcd. for $C_{14}H_{10}F_2O_4S_2$: C, 48.83; H, 2.93. Found: C, 48.73; H, 2.90.

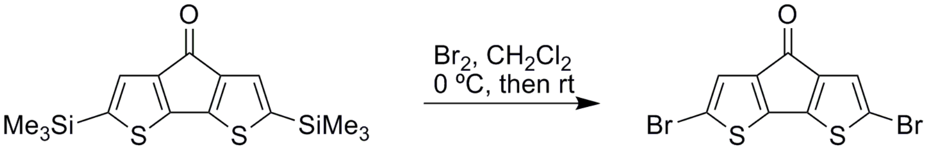
2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(1,3-dioxolane) (7)



Modified literature[7] conditions were used for the protection reaction.

2,7-Bis-trimethylsilyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (**3c**) (1.0 mmol, 0.378 g) was dissolved in anhydrous THF (30 mL) under nitrogen atmosphere, anhydrous DMF (30 mL) and 2-bromoethanol (3.0 eq., 0.37 g) were added, and dark red reaction mixture was cooled in chloroform/dry ice bath. A solution of ^{t}BuONa (3.0 eq., 3.0 mmol, 0.29 g) in anhydrous DMF (10 mL) was added dropwise. After addition of 4 mL of the base solution a thick suspension formed (dirty yellow-red-brown color). After addition of 6 mL of base (out of 10 mL), the reaction mixture became very difficult to stir, and anhydrous THF (10 mL) was added to a green suspension. After completion of addition of the base additional amount of THF (10 mL) was added, the mixture was stirred for 20 minutes, warmed to room temperature, and then treated with water. Organic phase was removed, the aqueous phase was extracted with hexanes, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, organic solvents were removed by rotary evaporation and the residue was purified by column chromatography (silica gel, dichloromethane:hexanes (2:1) as eluant). Fractions with mono-protected byproduct **5b** were combined, the solvent was removed, and a few mg of material **5b** was obtained. Fractions with the desired product (**7**) were combined, the solvent was removed, and the residue (0.23 g, 49.3% yield) was recrystallized from 2-propanol. Crystals suitable for the single crystal X-ray analysis were obtained after vacuum filtration. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.04 (s, 2H), 4.22 (m, 4H), 4.15 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 138.2, 132.6, 128.1 (CH), 111.0, 107.3, 66.6 (CH_2) (assignment of CH and CH_2 carbons was made based on DEPT-135 experiment; all other carbons are quaternary). HRMS (EI) calculated for $C_{14}H_{10}Br_2O_4S_2$ 463.8387; found 463.8387. Anal. Calcd. for $C_{14}H_{10}Br_2O_4S_2$: C, 36.07; H, 2.16. Found: C, 35.97; H, 2.09.

2,6-Dibromo-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (8b).



2,6-Bis-trimethylsilyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one[1] (3.0 mmol, 1.01 g) was dissolved in dichloromethane (20 mL), cooled in ice-water bath and a solution of bromine (2.1 eq., 6.3 mmol, 1.01 g) in dichloromethane (10 mL) was added to a dark red solution. The reaction mixture became purple in color, and after stirring for about 0.5 h it was allowed to warm to room temperature. Aqueous solution of $Na_2S_2O_3$ was added, and organic solvent was removed by rotary evaporation. The dark purple solid was filtered off, washed with ethanol and dried. Crude product was obtained in 91.5% yield (0.96 g). This material was purified by column chromatography (silica gel, dichloromethane as eluant; material was dissolved in boiling chloroform to apply to the column). Fractions with pure material were combined, the solvent was removed, and product **8b** was obtained as dark purple solid. This material forms plates on cooling from hot chloroform, which were suitable for the single crystal X-ray structural analysis. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.00 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 180.5 (quaternary C(O)), 148.7 (quaternary C), 139.5 (quaternary C), 124.4 (CH), 114.0 (quaternary C-Br) (assignment of CH signal was made based on the DEPT-135 experiment) (^{1}H NMR analysis is in agreement with the literature data,[8] while only four resonances at 180.45, 148.63, 139.49, and 113.95 were reported[8] for $^{13}C\{^1H\}$ NMR analysis (one resonance is missing)). Anal. Calcd. for $C_9H_2Br_2OS_2$: C, 30.88; H, 0.58. Found: C, 30.87; H, 0.47.

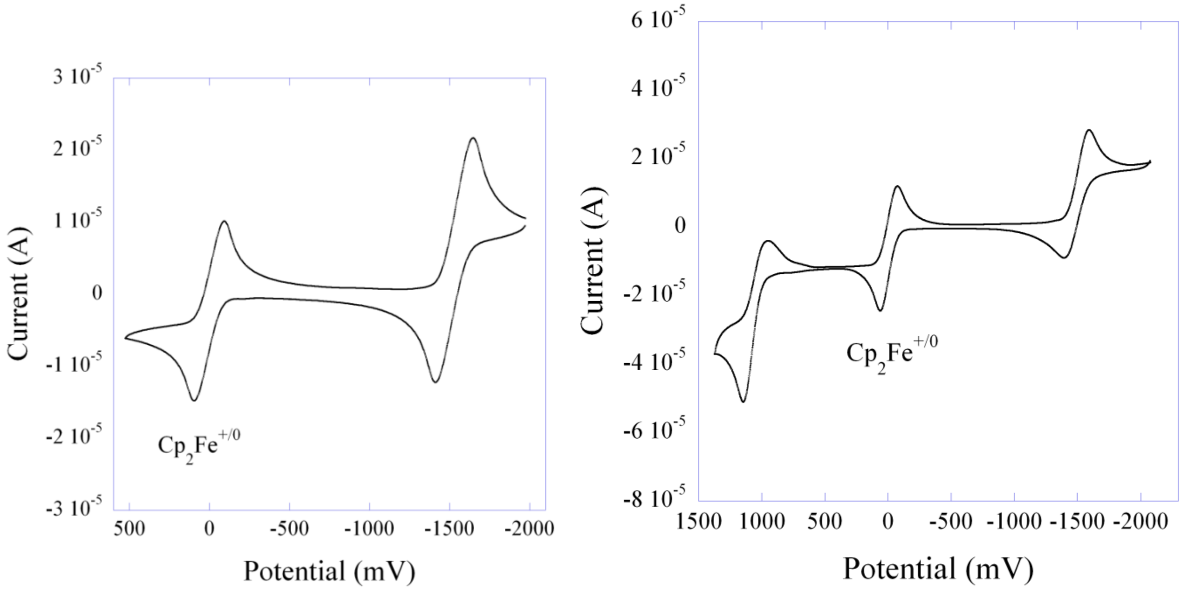
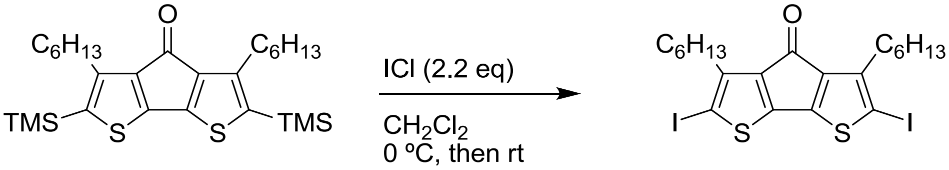


Figure S38. Cyclic voltammograms 2,6-dibromo-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (8b): (*left*) (0.1 M $^nBu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1-}$ = -1.52 V; (*right*) (0.1 M $^nBu_4NPF_6$ in CH_2Cl_2, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1+}$ = +1.05 V (partially reversible), $E_{1/2}^{0/1-}$ = -1.48 V.

2,6-Diiodo-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (8c).



2,6-Bis-trimethylsilyl-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one[1] (5.41 mmol, 2.73 g) was dissolved in dichloromethane (50 mL), and the dark red solution was cooled in ice-water bath). A solution of iodine monochloride (2.1 eq., 11.35 mmol, 1.84 g) in dichloromethane (20 mL) was added dropwise, and the dark purple mixture was warmed to room temperature. Aqueous $Na_2S_2O_3$ (40 mL) was added, and the organic solvents were removed by rotary evaporation. The mixture (aqueous layer with purple solid on the top) was treated with hexanes, the organic phase (red-purple) was removed, and the aqueous phase was extracted with hexanes (15 mL). The combined organic phases were concentrated, and the residue was purified by column chromatography (silica gel, hexanes as eluant). The solvent was removed from combined fractions, and the residue was recrystallized from 2-propanol (~30 mL) to give purple-black material (2.19 g, 66.2% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.61 (t, J = 7.7 Hz, 4H), 1.55 (m, 4H), 1.33 (m, 12H), 0.90 (t, J = 6.4 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 181.2 (C(O) carbon), 152.6 (quaternary C), 144.2 (quaternary C), 137.6 (quaternary C), 75.9 (C-I quaternary), 31.6 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 22.6 (CH_2), 14.1 (CH_3) (assignment of the carbons was made based on DEPT-135 experiment). HRMS (EI) calculated for $C_{21}H_{26}I_2OS_2$ 611.95146; found 611.95005. Anal. Calcd. for $C_{21}H_{26}I_2OS_2$: C, 41.19; H, 4.28. Found: C, 41.39; H, 4.31.

DSC analysis (10 ºC/min rate): 124.7 ºC (melting point observed on first heating) (sharp peak at 92.9 ºC was observed on cooling (crystallization); melting point on the second heating was observed at 122.5 ºC).

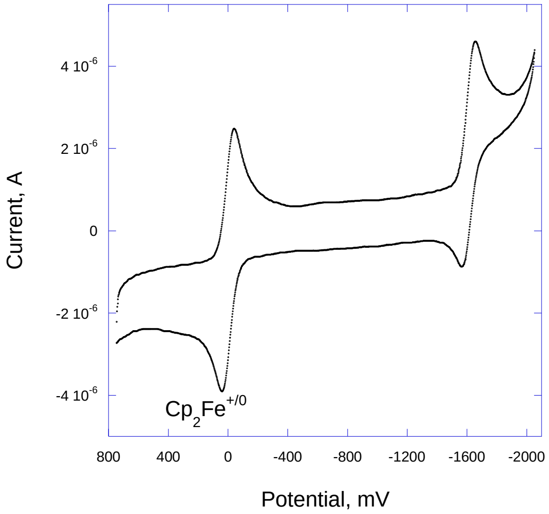


Figure S39. CV analysis (0.1 M $^nBu_4NPF_6$ in CH_2Cl_2, Cp_2Fe internal standard at 0 V, 50 mV rate) of 2,6-diiodo-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (8c): $E_{1/2}^{0/1-}$ = -1.61 V (reversible).

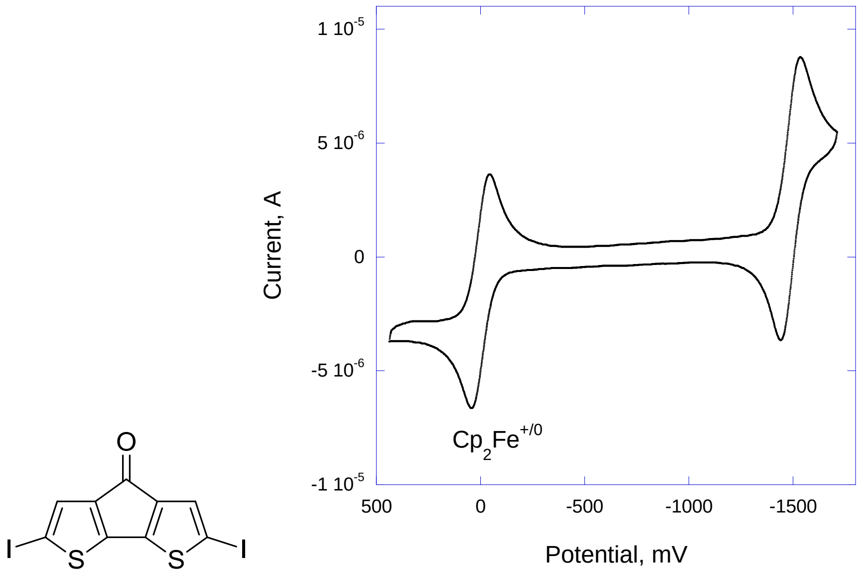


Figure S40. Structure (*left*) and CV analysis (*right*) (0.1 M ^{n}Bu$_4$NPF$_6$ in CH$_2$Cl$_2$, Cp$_2$Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2,6-diiodo-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one[3] (8a): $E_{1/2}^{0/1-}$ = -1.49 V (reversible.).

Both diodes also have 2nd irreversible reduction as shown on Figure S41.

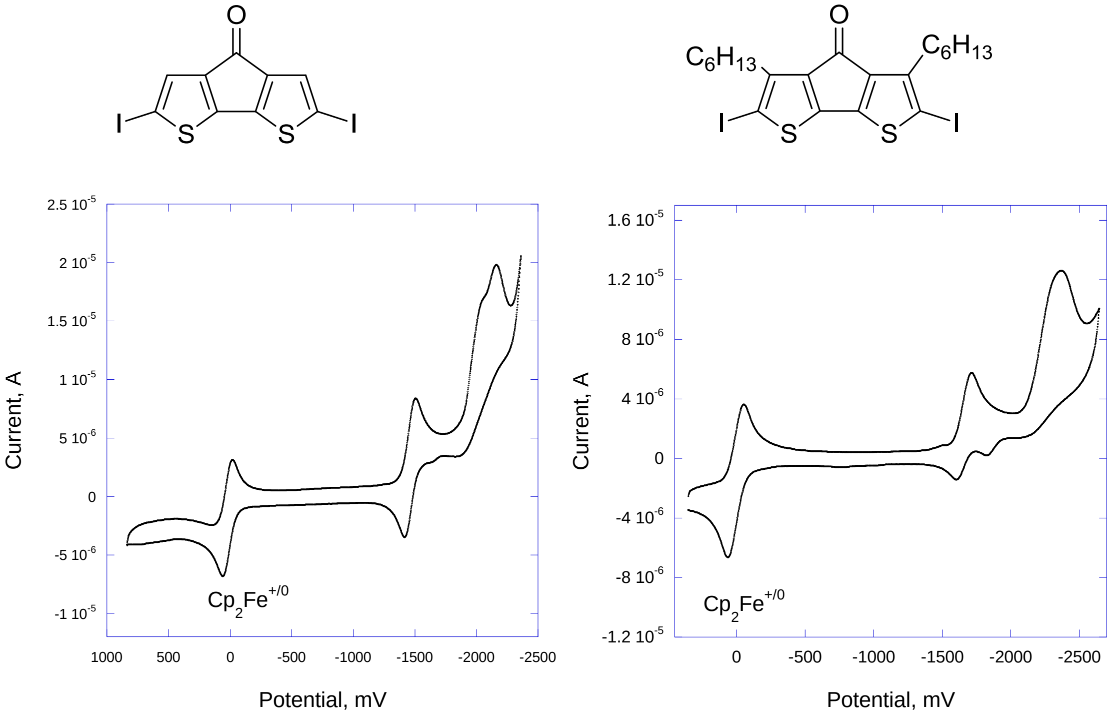


Figure S41. CV analyses of diodes with the second irreversible reduction shown.

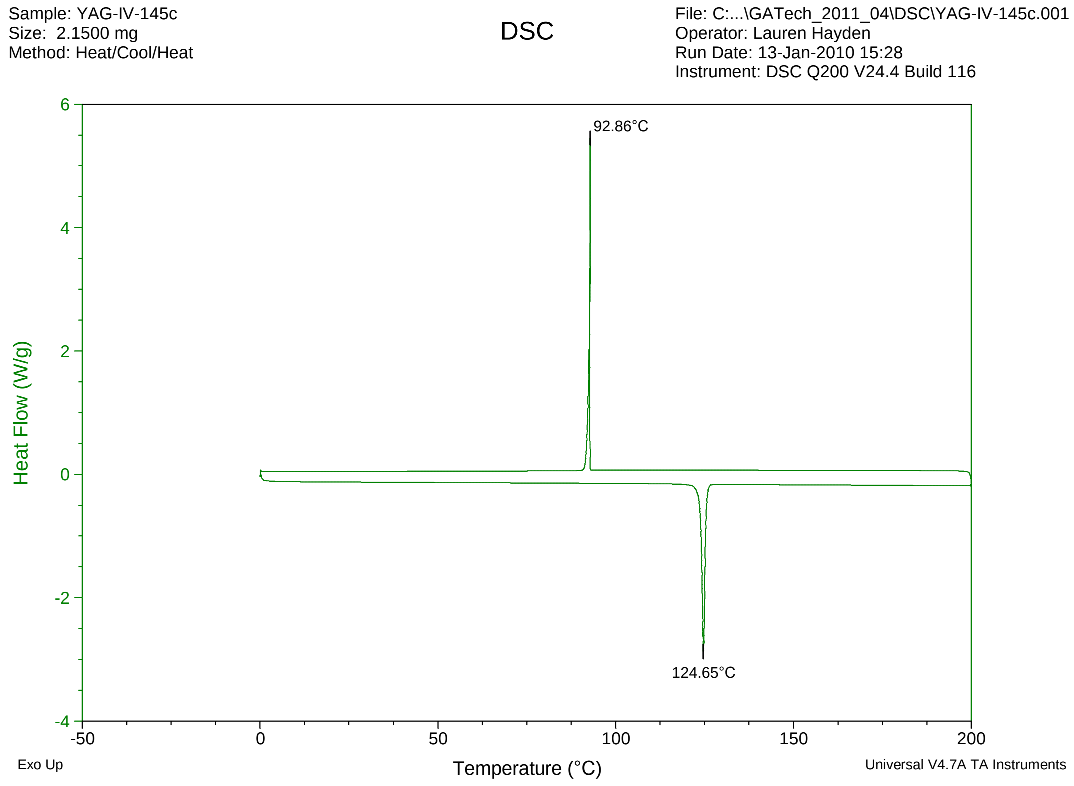
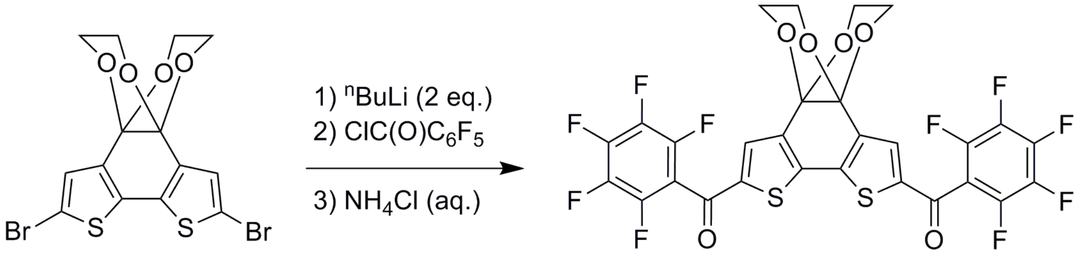


Figure S42. DSC analysis (10 ºC/min rate) of a2,6-di-iodo-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (8c).

2,7-Bis-(pentafluorobenzoyl)-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(ethyleneoxolane) (9a)



2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(ethyleneoxolane) (**5a**) (3.0 mmol, 1.40 g) was dissolved in anhydrous THF (75 mL), and resulting solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 6.0 mmol, 2.11 mL) was added dropwise, and a purple suspension formed. The reaction mixture was stirred for ~40 minutes, and transferred via cannula into a solution of pentrafluorobenzoyl chloride (9.0 mmol, 2.07 g) in anhydrous THF (75 mL) (acetone/dry ice bath), and yellow-brown solution formed. After stirring for ~2 h the cooling bath was removed, the mixture was treated with aqueous solution of NH_4Cl, and organic phase was removed. Aqueous phase was extracted with dichloromethane, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, and the solvents were removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, hexanes:dichloromethane as eluant). Fractions with pure product **9a** were combined, and the solvents were removed from yellow solution, and yellow solid was obtained (0.58 g). Later fractions with product slightly contaminated by **9a'** were combined separately, and yellow solid was obtained after solvent removal (0.76 g, 64% combined yield). Fractions with the second product, identified as 2-pentafluorobenzoyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(ethyleneoxolane) **9a'**, was obtained (~50-100 mg). Material **9a** crystallized with some dichloromethane based on ^{1}H NMR, and 100 mg was recrystallized from 2-propanol (~75 mL) to obtain analytically pure yellow solid (83 mg, 83% recovery).

9a: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (s, 2H), 4.17 (m, 4H), 3.70 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 176.0, 142.9, 141.7, 140.1, 133.6 (CH), 61.5 (CH_2) (multiplets for C-F carbons were observed as weak signals at 145.1, 142.6, 139.0, 136.5 and are not certain). ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ –139.4 (m, 4F), -148.9 (m, 2F), -159.0 (m, 4F) (1,1,2-trichlorotrifluoroethane was used as internal reference with δ at -71.75 ppm (t)). HRMS (EI) calculated for $C_{28}H_{10}F_{10}O_6S_2$ 695.9759; found 695.9733. Anal. Calcd. for $C_{28}H_{10}F_{10}O_6S_2$: C, 48.28; H, 1.45. Found: C, 48.14; H, 1.54.

9a': ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (s, 1H), 7.43 (m, 2H), 7.26 (m, 2H, *overlaps with residual $CHCl_3$*), 4.18 (m, 4H), 3.69 (m, 4H) (this materials contained ~10% of 2,7-bis-(pentafluorobenzoyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(ethyleneoxolane) **9a**).

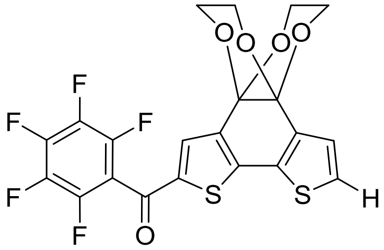
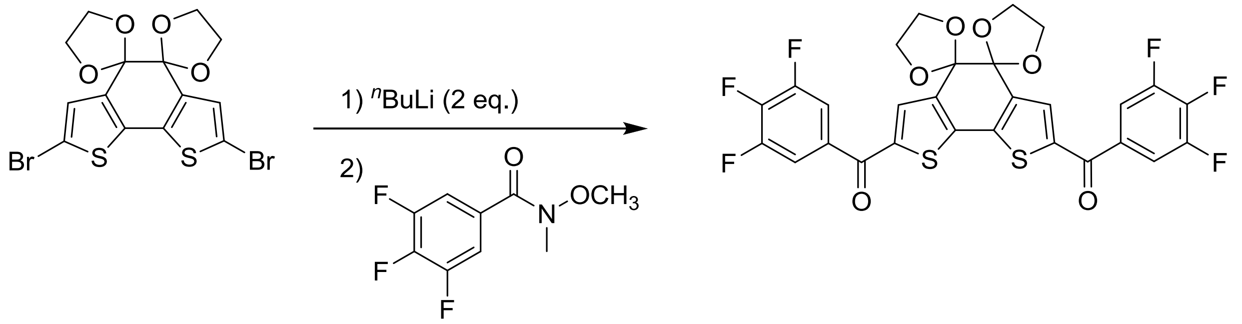


Figure S43. Structure of the byproduct 9a'.

2,7-Bis-(3,4,5-trifluorobenzoyl)-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(1,3-dioxolane) (9b)



2,7-Dibromo-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(1,3-dioxolane) (**7**) (2.0 mmol, 0.93 g) was dissolved in anhydrous THF (100 mL) under nitrogen atmosphere, and the colorless solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 4.0 mmol, 1.4 mL) was added dropwise, and greenish suspension formed. The reaction mixture was stirred for 15 minutes, and *N*-methoxy-*N*-methyl-3,4,5-trifluorobenzamide (**11b**) (4.4 mmol, 0.96 g) was added. After 10 minutes of stirring yellow mixture (solution) was warmed to room temperature, and aqueous NH_4Cl was added (purple-yellow mixture formed). Aqueous phase was removed, organic matter was extracted with dichloromethane-hexanes mixture, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filterred off, the solvents were removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, dichlromethane as eluant; chloroform to dissolve the material to apply to the column). Combined fractions were subjected to rotary evaporation, yellow solid was dissolved in 2-propanol-chloroform, and yellow solution was concentrated by reflux until saturation point was reached. Yellow-greenish tiny crystals were separated by vacuum filtration (0.52 g). Mother liquor with some precipitate was subjected to rotary evaporation, and additional amount of yellow solid was obtained (0.40 g; 0.92 g total yield, 73.6% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.58 (m, 6H), 4.29 (m, 4H), 4.20 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 183.6, 151.2 (dd, *J* = 252 Hz, 8.5 Hz), 147.7, 140.0, 132.1 (CH), 113.7 (dd, *J* = 16.1 Hz, 6.6 Hz, CH), 92.5, 66.8 (CH_2) (two quaternary CF signals are not certain; two weak multiplets at 143 and 133 ppm were observed). ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -131.5 (dd, *J* = 20.0 Hz, 7.3 Hz, 4F), -152.8 (m, 2F) (1,1,2-trichlorotrifluoroethane was used as internal reference with δ at -71.75 ppm (t)). HRMS (EI) calculated for $C_{28}H_{14}F_6O_6S_2$ 624.0136; found 624.0139. Anal. Calcd. for $C_{28}H_{14}F_6O_6S_2$: C, 53.85; H, 2.26. Found: C, 53.59; H, 2.44.

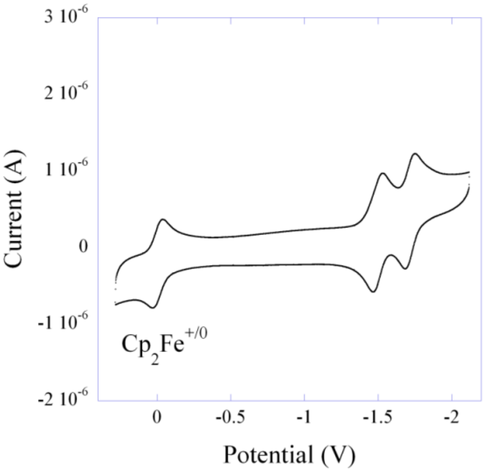
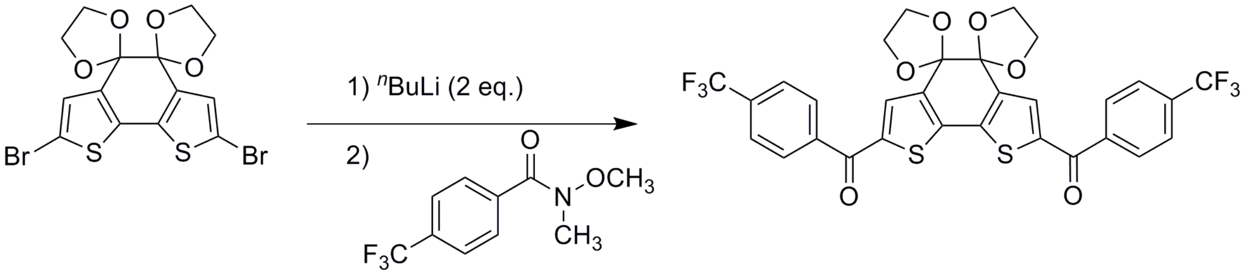


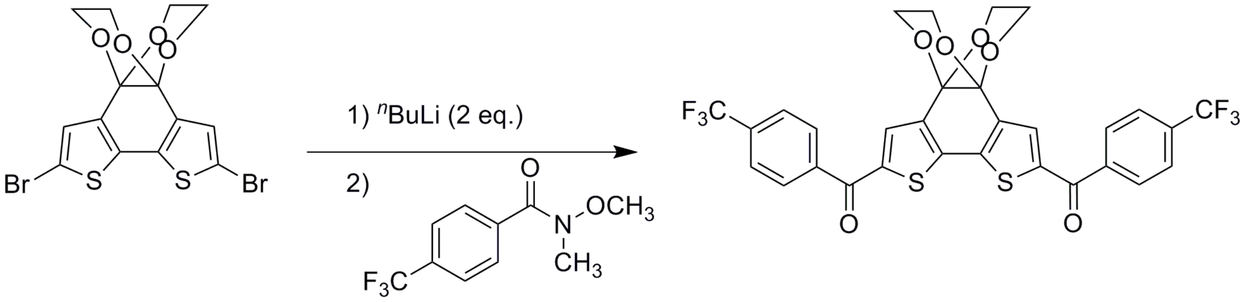
Figure S44. Cyclic voltammogram of 2,7-bis-(3,4,5-trifluorobenzoyl)-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(1,3-dioxolane) (9b) (0.1 M ^{n}Bu$_4$NPF$_6$ in THF, Cp$_2$Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1-}$ = -1.50 V, $E_{1/2}^{1-/2-}$ = -1.72 V.

2,7-Bis-(4-trifluoromethylbenzoyl)-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(1,3-dioxolane) (9c)



2,7-Dibromo-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(1,3-dioxolane) (**7**) (5.0 mmol, 2.33 g) was dissolved in anhydrous THF (200 mL) under nitrogen atmosphere, and the resulting solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 10.0 mmol, 0.4 mL) was added dropwise, the reaction mixture was stirred for 40 minutes ,and *N*-methoxy-*N*-methyl-4-(trifluoromethyl)benzamide (**11c**) (2.1 eq., 10.5 mmol, 2.45 g) was added. The reaction mixture was stirred for ~0.5 h, cooling bath was removed, and the mixture was allowed to warm to room temperature. Aqueous ammonium chloride was added, organic phase was removed, and aqueous phase was extracted with hexanes:dichloromethane. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and the solvents were removed by rotary evaporation to give crude product, which was purified by column chromatography (silica gel, chloroform as eluant). Fractions with almost pure compound were combined, the solvent was removed, and yellow solid was obtained (0.8 g). Fractions with contaminated product were combined separately, and the solvent was removed to give additional amount of product (2.02 g), which was further purified by column chromatography (silica gel, dichloromethane as eluant) (1.13 g, yellow solid; 59% combined yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 8.1 Hz, 4H), 7.81 (d, J = 8.2 Hz, 4H), 7.57 (s, 2H), 4.26 (m, 4H), 4.17 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 183.30, 142.53, 141.54, 140.57, 139.97, 133.9 (q, J = 48.8 Hz), 129.48, 129.21, 125.70 (m), 124.92, 119.50, 107.06, 66.79. ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -63.0 (s, 6F) (1,1,2-trichlorotrifluoroethane was used as a reference with δ at -71.75 ppm (t)). HRMS (EI) calculated for $C_{30}H_{18}F_6O_6S_2$ 652.0449; found 652.0449. Anal. Calcd. for $C_{30}H_{18}F_6O_6S_2$: C, 55.21; H, 2.78. Found: C, 54.95; H, 2.66.

2,7-Bis-(4-trifluoromethylbenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyleneoxolane) (9c')



2,7-Dibromo-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyleneoxolane) (**5a**) (0.3 mmol, 0.14 g) was dissolved in anhydrous THF (50 mL) under nitrogen atmosphere, and the resulting solution was cooled in acetone/dry ice bath. *n*-Butyllithium (1.6 M in hexanes, 0.6 mmol, 0.4 mL) was added dropwise, the reaction mixture was stirred for 10-15 minutes and *N*-methoxy-*N*-methyl-4-(trifluoromethyl)benzamide (2.2 eq., 0.66 mmol, 0.154 g) was added. The reaciton mixture was stirred for ~0.5 h, warmed to room temperature, and then treated with aqueous NH_4Cl. Yellow organic phase was separated, aqueous phase was extracted with hexanes, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, the solvent were removed by rotary evaporation and the residue (yellow solid) was purified by column chromatography (silica gel, dichloromethane as eluant). Combined fractions were subjected to rotary evaporation, and product was obtained as yellow solid (0.111 g, 56.6% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 8.1 Hz, 4H), 7.81 (d, J = 8.2 Hz, 4H), 7.70 (s, 2H), 4.19 (m, 4H), 3.70 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 186.3, 143.1, 140.4, 140.37, 139.2, 134.0 (q, J = 32 Hz), 132.9 (CH), 129.3 (CH), 125.7 (q, J = 4 Hz, CH), 124.9, 122.2, 92.5, 61.5 (CH_2) (assignment of CH and CH_3 carbons was made based on DEPT-135 experiment; all other carbons are quaternary). HRMS (EI) calculated for $C_{30}H_{18}F_6O_6S_2$ 652.0449; found 652.0453. Anal. Calcd. for $C_{30}H_{18}F_6O_6S_2$: C, 55.21; H, 2.78. Found: C, 54.92; H, 3.30.

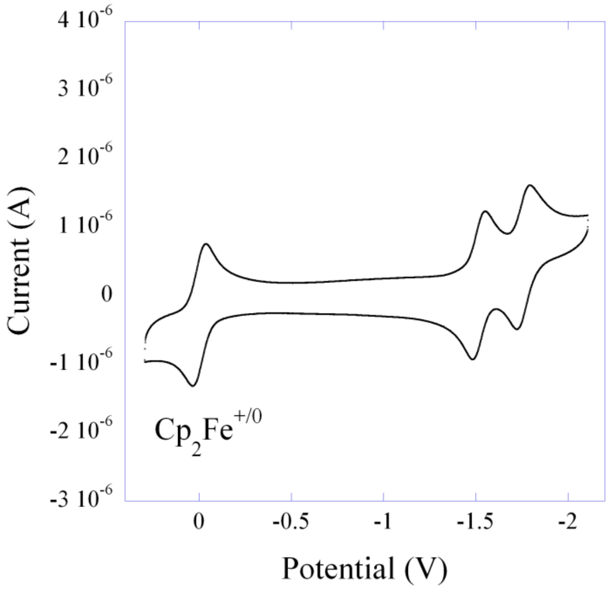
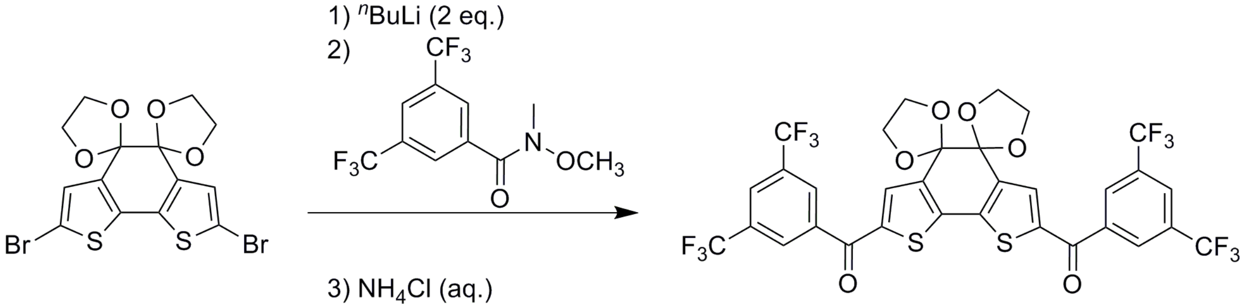


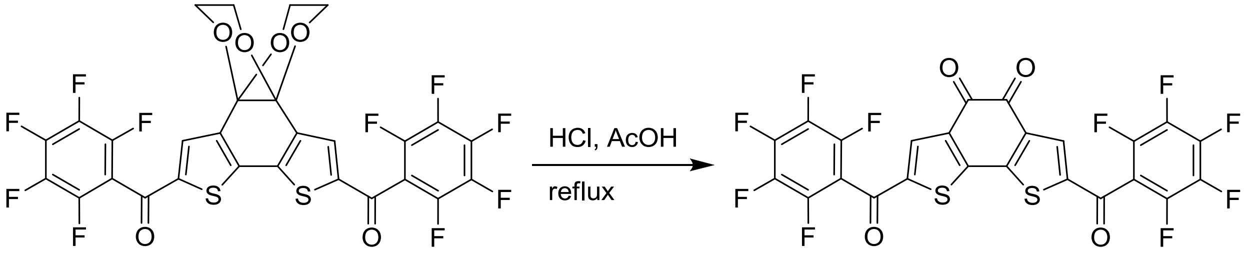
Figure S45. Cyclic voltammogram of 2,7-bis-(4-trifluoromethylbenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyleneoxolane) (9c') (0.1 M $^nBu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1-}$ = -1.52 V, $E_{1/2}^{1-/2-}$ = -1.76 V.

2,7-Bis-(3,5-bistrifluoromethyl-benzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(1,3-dioxolane) (9d)



2,7-Dibromo-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(1,3-dioxolane) (**7**) (5.0 mmol, 2.33 g) was dissolved in anhydrous THF (150 mL) under nitrogen atmosphere, and the resulting solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 10.0 mmol, 3.5 mL) was added dropwise, and the yellowish solution became colorless suspension. The reaction mixture was stirred for 20 minutes, and *N*-methoxy-*N*-methyl-3,5-bis(trifluoromethyl)benzamide (**11d**) (2.1 eq., 10.5 mmol, 3.16 g) was added. After 10 minutes of stirring clear yellow solution was allowed to warm to room temperature. The reaction mixture was treated with aqueous ammonium chloride, yellow organic phase was separated, and aqueous phase was extracted with hexanes:dichloromethane. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and the solvents were removed by rotary evaporation to give crude product, which was purified by column chromatography (silica gel, chloroform as eluant). Fractions with pure product were combined, the solvent was removed and yellow solid was obtained (1.90 g). Fractions with slightly contaminated product were kept separately (1.58 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.31 (s, 4H), 8.14 (s, 2H), 7.57 (s, 2H), 4.27 (m, 4H), 4.17 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 184.30, 142.20, 141.73, 140.39, 139.28, 132.65 (CH), 132.54, 132.20, 128.90 (m, CH), 125.76 (m, CH), 122.82 (q, J = 272 Hz, CF_3), 106.91, 66.87 (CH). ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -62.9 (s, 12F) (1,1,2-trichlorotrifluoroethane was used as internal reference with δ at -71.75 ppm (t)). HRMS (EI) calculated for $C_{32}H_{16}F_{12}O_6S_2$ 788.0197; found 788.0187. Anal. Cacld. for $C_{32}H_{16}F_{12}O_6S_2$: C, 48.74; H, 2.05. Found: C, 48.55; H, 1.96.

2,7-Bis-(pentafluorobenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (10a)



2,7-Bis-pentafluorobenzoyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyleneoxolane) (**9a**) (0.4 mmol, 0.279 g) was mixed with acetic acid (50 mL), and the mixture was heated to reflux. HCl (~5 mL) was added to a yellow solution, and the reaction mixture became orange and then red-orange. After reflux for 1 h the mixture was cooled to room temperature, and only small amount of precipitate formed. The mixture was heated to reflux, and water was added until precipitation was observed. The reaction mixture was cooled, and orange solid was separated, washed with water, ethanol and dried (0.190 g, 78.2%). This material was purified for mobility measurement by column chromatography (silica gel, CH_2Cl_2 as eluant). Middle fractions with the product were combined, the solvent was removed and orange-red powder was obtained (0.109 g, 77.9% recovery). A better purified yield of 94% (1.61 g) was obtained on larger reaction scale (2.80 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 176.5 (quaternary C(O)), 173.1 (quaternary C(O)), 148.7, 144.3, 137.3, 134.4 (weak C-F carbons were detected as multiplets at 145.2, 142.7, 139.2, 136.6). ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -139.1 (m, 4F), -147.1 (tt, J = 20.7 Hz, 3.3 Hz, 2F) -158.2 (m, 4F) (1,1,2-trichlorotrifluoroethane was used as internal reference with δ at -71.75 ppm (t)). HRMS (EI) calculated for $C_{24}H_2F_{10}O_4S_2$ 607.9235; found 607.9216 (M+2H at 609.9 was observed with ~80% intensity with respect to molecular ion). Anal. Calcd. for $C_{24}H_2F_{10}O_4S_2$: C, 47.38; H, 0.33. Found: C, 47.13; H, 0.34.

T_d (5% weight loss): 324 ºC. UV-vis: λ_{max} (CH_2Cl_2) ($\varepsilon \times 10^{-4}$, $cm^{-1}M^{-1}$): 280 (1.5), 330 (3.2), 370 (1.5), 460 (0.80).

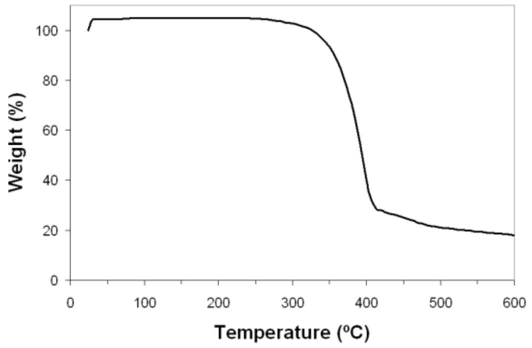


Figure S46. TGA analysis (5 ºC/min rate) of 2,7-bis-pentafluorobenzoyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione.

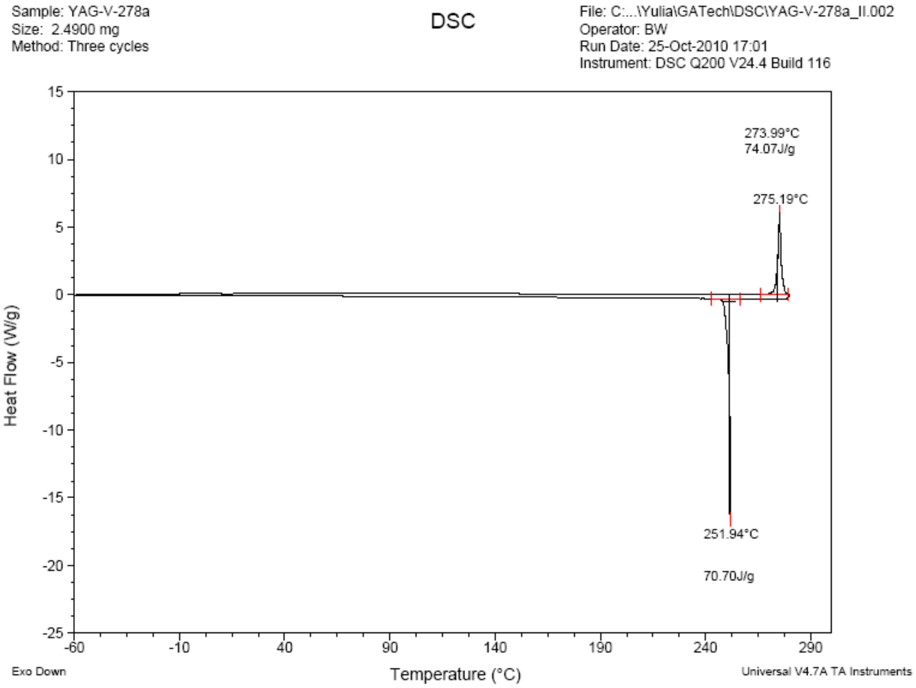
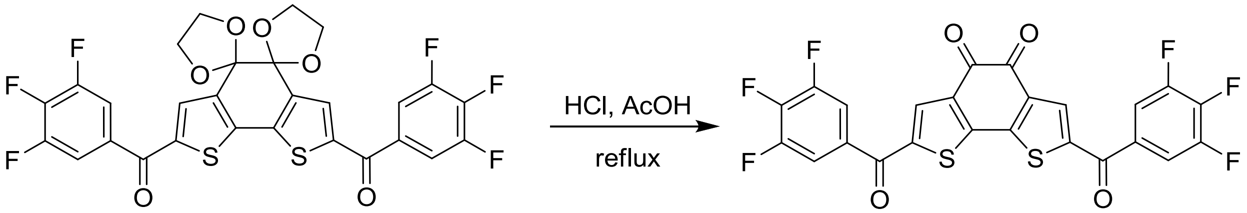


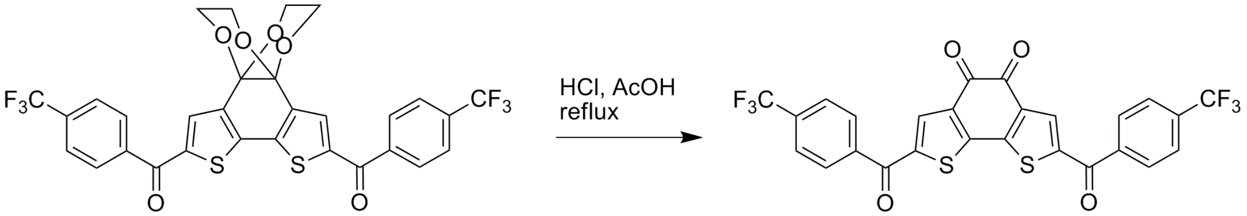
Figure S47. DSC analysis (10 ºC/min heating-cooling rate) of 2,7-bis-pentafluorobenzoyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione: m.p. 275.2 ºC.

2,7-Bis-(3,4,5-trifluorobenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (10b)



2,7-Bis-(3,4,5-trifluorobenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-(1,3-dioxolane) (**9b**) (0.7 mmol, 0.437 g) was heated to reflux with acetic acid (50 mL), and HCl (~5 mL) was added to a bright yellow solution. The reaction mixture became orange, then red-orange with precipitate. After reflux for ~1 h the mixture was cooled to room temperature, the precipitate was separated by vacuum filtration, washed with water and ethanol, and dried. Crude product was obtained as orange-red solid (0.33 g, 87.8% crude yield). This materials was recrystallized from 1,4-dioxane (~75 mL to dissolve it under reflux and then concentrated down to ~30 mL when the solution became cloudy). Product was obtained as red solid (0.25 g, 75.8% recovery). ^{1}H NMR (1,2-dichloroethane-*d4*, 400 MHz, 370 K): δ 8.02 (s, 2H), 7.64 (t, J = 6.8 Hz, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) was not recorded due to low solubility of this material at room or elevated temperature in $CDCl_3$ or 1,2-dichloroethane-*d4*). ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -130.4 (m, 4F), -150.8 (m, 2F) (1,1,2-trichlorotrifluoroethane was used as internal reference with δ at -71.75 ppm (t)). HRMS (EI) calculated for $C_{24}H_6F_6O_4S_2$ 535.9612; found 535.9616. Anal. Calcd. for $C_{24}H_6F_6O_4S_2$ C, 53.74; H, 1.13. Found: 53.57, H, 1.05.

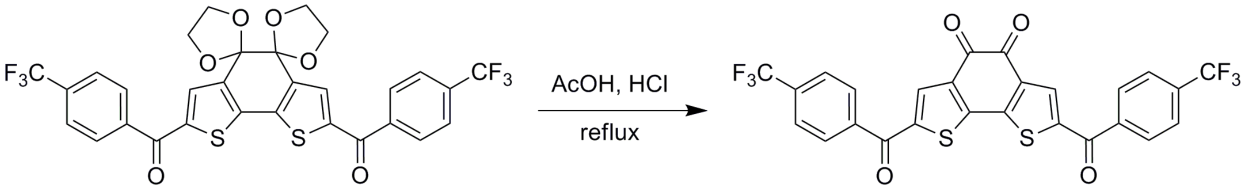
2,7-Bis-(4-trifluoromethylbenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (10c) from 9c'



2,7-Bis-(4-trifluoromethylbenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyleneoxolane) (**9c'**) (0.8 mmol, 0.522 g) was mixed with acetic acid (40 mL), and the resulting mixture was heated to reflux. HCl (~5 mL) was added to a bright yellow solution, and it became orange and then red. After reflux for ~1.5 h the reaciton mixture was cooled to room temperature, water was added and precipitate was separated by vacuum filtration (0.42 g, 93.3% crude yield, red-orange solid). This material was purified by column chromatography (~100 mL of silica gel, chloroform as eluant; hot chloroform to dissovle the material and apply to the column). Fraction with slighlty contaminated product was kept separately; fraction with pure product (by TLC) was subjected to rotary evaporation, and product was obtained as red shiny solid (0.196 g, 43.6% purified yield).

^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.00 (m, 6H), 7.86 (m, 4H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ (material is not sufficiently soluble in CDCl$_3$ or 1,2-dichloroethane at room temperature or elevated temperature). HRMS (EI) calculated for $C_{26}H_{10}F_6O_4S_2$ 563.9925; found 563.9921.

2,7-Bis-(4-trifluoromethylbenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (10c) from 9c.



2,7-Bis-(4-trifluromethylbenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis(1,3-dioxolane) (**9c**) (1.23 mmol, 0.80 g) was mixed with acetic acid (100 mL), and the resulting mixture was heated to reflux. HCl (~5 mL) was added to a bright yellow solution, and it became darker in color, and then precipitate formed. After reflux for ~5 h, reaction mixture was cooled to room temperature, and red solid was separated by vacuum filtration (0.42 g, 60.9% crude yield).

Material **10c** (500 mg) obtained from the deprotection reactions was purified by sublimation (6.5×10^{-7} torr, 250-285 ºC; 0.238 g, 47.6% recovery). Anal. Calcd. for $C_{26}H_{10}F_6O_4S_2$: C, 55.32; H, 1.79. Found: C, 55.51; H, 1.73.

T_d (5% weight loss): 344 ºC.

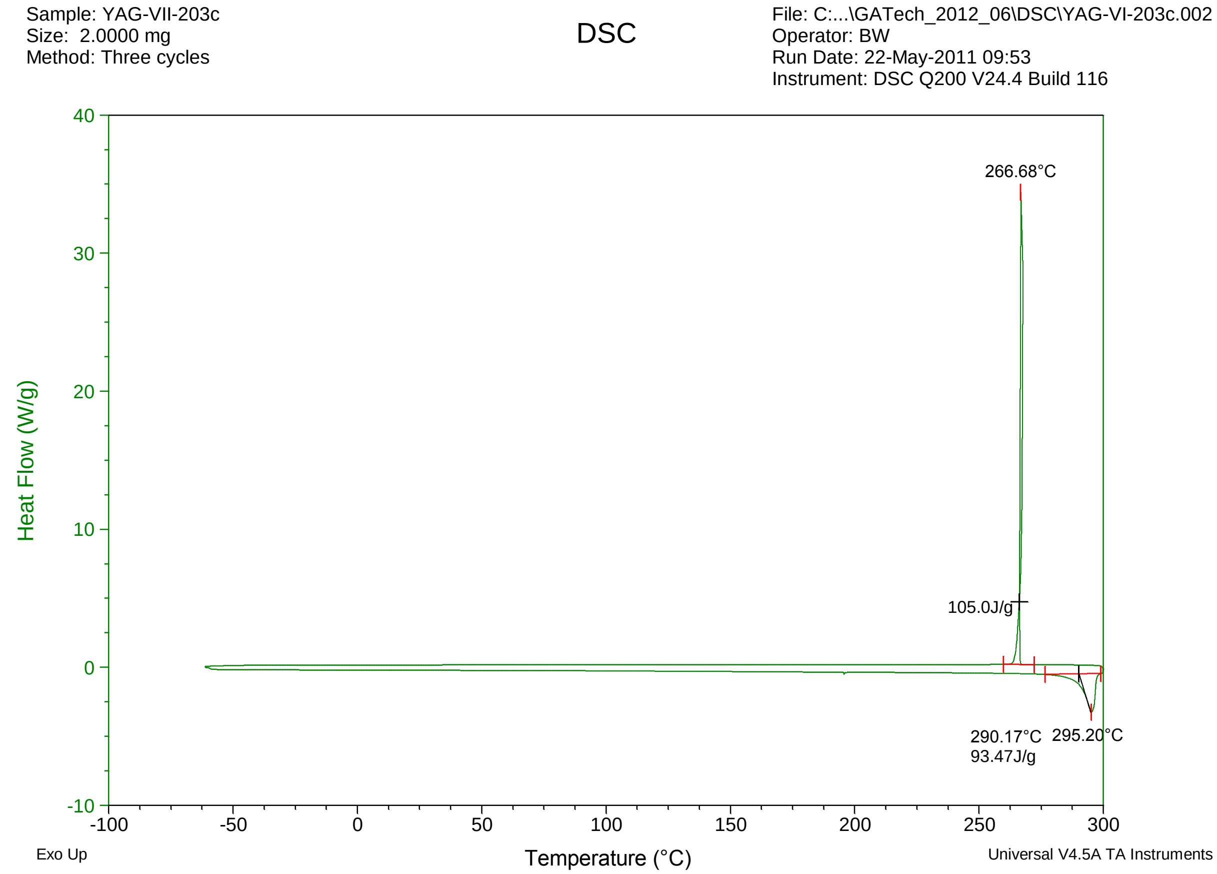
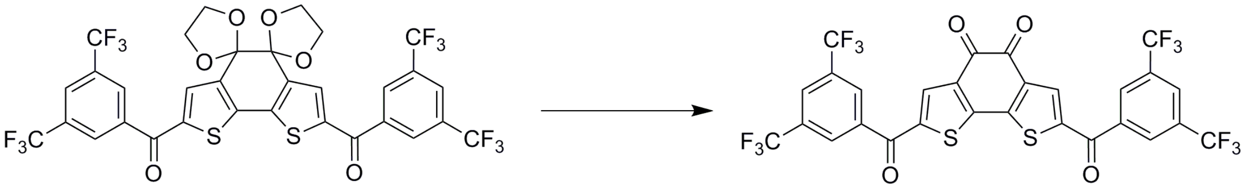


Figure S48. DSC analysis for material 2,7-bis-(4-trifluoromethylbenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (10c).

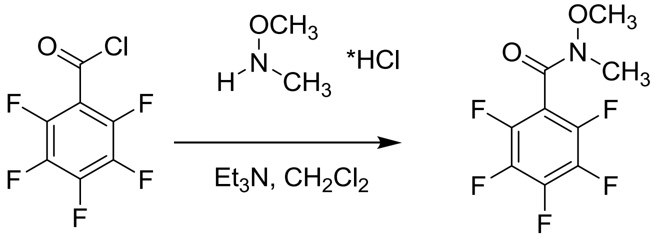
2,7-Bis-(3,5-di-trifluromethylbenzo-1-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (10d)



2,7-Bis-(3,5-ditrifluoromethylbenzoyl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-(1,3-dioxolane) (2.0 mmol, 1.58 g) (**9d**) was dissolved in boiling acetic acid (200 mL), and to a bright yellow solution HCl (5-10 mL) was added. The reaction mixture became organge, then orange-red. After refluxing for ~4 h dark red reaction mixture was cooled to room temperature, and shiny orange-red plates were separated by vacuum filtration (1.20 g, 85.7% crude yield). This crude product (~1.1 g) was purified by column chromatography (silica gel, dichloromethane as eluant). Combined fractions were subjected to rotary evaporation, the residue was heated with 2-propanol and some dichloromethane, and cooled to room temperature. Shiny red solid was separated by vacuum filtration (0.88 g). Mother liquor was subjected to rotary evaporation, the residue was dissolved in dichloromethane, and solution was left for slow concentration to grow single crystals (0.146 g). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.32 (s, 4H), 8.20 (s, 2H), 7.98 (s, 2H) (CH$_2$Cl$_2$ at 5.31 ppm was detected, indicating that the material traps dichloromethane (~2.8 to 1 ratio); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 184.3, 173.3, 148.0, 144.0, 137.9, 137.1, 133.4, 132.9 (q, J = 34 Hz), 128.9 (d), 126.7 (m), 124.0. ^{19}F NMR (CDCl$_3$, 376.3 MHz): δ -62.9 (12F). HRMS (EI) calculated for $C_{28}H_8F_{12}O_4S_2$ 699.9672; found 699.9688. Anal. Calcd. for $C_{28}H_8F_{12}O_4S_2$: C, 48.01; H, 1.15. Found: C, 48.10; H, 1.01 (for the sublimed material).

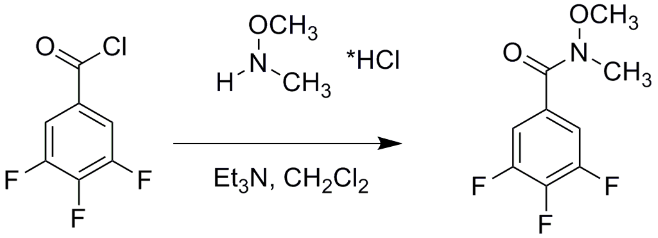
T_d (5% weight loss): ~320 ºC.

2,3,4,5,6-Pentafluoro-*N*-methoxy-*N*-methylbenzamide (11a)



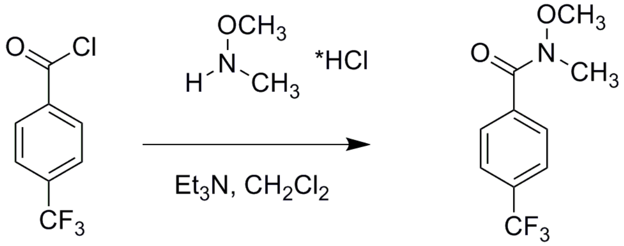
N,*O*-Dimethylhydroxylamine hydrochloride (24.0 mmol, 2.34 g) was mixed with dichloromethane (50 mL), and triethylamine (80.0 mmol, 8.1 g) was added. Colorless suspension formed, and pentafluorobenzoyl chloride was added dropwise (exotherm, water bath was used to keep the reaction at room temperature). The reaction mixture was stirred for ~0.5 h, analyzed by GC/MS analysis, and clean formation of the product was confirmed. The reaction mixture was treated with water, the organic phase was removed, the aqueous phase was extracted with dichloromethane and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, the solvents were removed by rotary evaporation and the residue was purified by column chromatography (~30 mL of silica gel, hexanes:ethyl acetate (3:1) as eluant). The solvents were removed from combined fractions and product was obtained as white crystalline solid (4.51 g, 88.4% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.56 (s, 3H), 3.37 (s, 3H). HRMS (EI) calculated for $C_9H_6F_5NO_2$ 255.0319; found 255.0324. Anal. Calcd. for $C_9H_6F_5NO_2$: C, 42.37; H, 2.37; N, 5.49. Found: C, 42.15; H, 2.17; N, 5.48.

N-methoxy-*N*-methyl-3,4,5-trifluorobenzamide (11b)



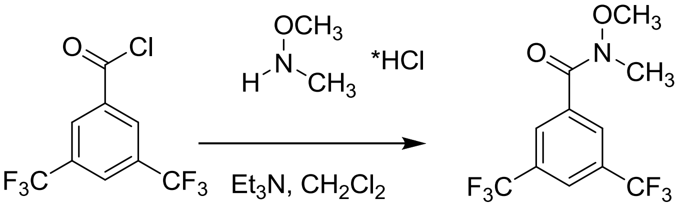
N,*O*-Dimethylhydroxylamine hydrochloride (12.0 mmol, 1.17 g) was added to dichloromethane (20 mL), and triethylamine (40.0 mmol, 4.1 g) was added. Colorless suspension formed, and 3,4,5-trifluorobenzoyl chloride (10.0 mmol, 1.94 g) was added. Reaction mixture was stirred for ~0.5 h, and analyzed by GC/MS analysis. Clean formation of the product was confirmed, and the reaction mixture was treated with water. Organic phase was removed, diluted with hexanes and washed with brine. Aqueous phase was extracted with diethyl ether, combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and organic solvents were removed by rotary evaporation. The residue (2.66 g) was purified by column chromatography (silica gel, hexanes:ethyl acetate (4:1) as eluant). Combined fractions were subjected to rotary evaporation, and material was obtained as almost colorless oil (1.37 g, 62.6%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.44 (m, 2H), 3.57 (s, 3H), 3.37 (s, 3H) (this analysis is in agreement with the literature data[9]); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 165.90, 150.59 (ddd, J = 250.4 Hz, 9.7 Hz, 3.8 Hz), 141.34 (dt, J = 256.6 Hz, 15.4 Hz), 129.3 (m), 113.5 (m, CH), 61.32 (CH), 33.37 (CH).

N-methoxy-*N*-methyl-4-(trifluoromethyl)benzamide (11c)



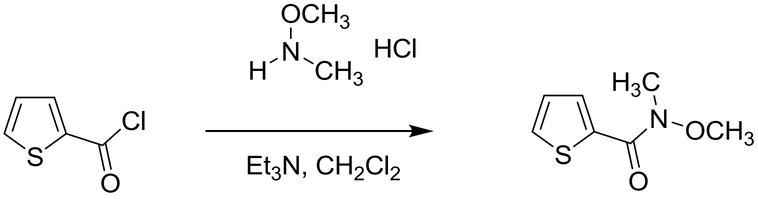
N,*O*-Dimethylhydroxylamine hydrochloride (30.0 mmol, 2.92 g) was mixed dichloromethane, and triethylamine (100 mmol, 10.12 g) was added. Colorless suspension formed, and 4-trifluoromethylbenzoyl chloride (25.0 mmol, 5.21 g) was added (ice-water bath). Suspension became thicker, and after stirring for 20 minutes, the cooling bath was removed. Reaction mixture was analyzed by GC/MS analysis, and clean formation of the product was confirmed. Reaction mixture was treated with water, organic phase was removed, dried over anhydrous magnesium sulfate, and the drying agent was filtered off. Organic solvent was removed by rotary evaporation and the residue was purified by column chromatography (silica gel, hexanes:ethyl acetate (~5:1) as eluant). Combined fractions were subjected to rotary evaporation and product was obtained as yellowish oil (3.97 g, 68% yield). Last fractions with the product were combined separately and the solvents were removed by rotary evaporation to give additional amount of product. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 3.52 (s, 3H), 3.40 (s, 3H) (this analysis is in agreement with the literature data[9]); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 168.5, 137.5, 132.2 (q, J = 33 Hz), 128.5 (CH), 124.9 (q, J = 4 Hz, CH), 122.3, 61.2 (CH_3), 33.3 (CH_3) (assignment of CH and CH_3 carbons was made based on DEPT-135 experiment; all other carbons are quaternary).

N-methoxy-*N*-methyl-3,5-bis(trifluoromethyl)benzamide (11d)



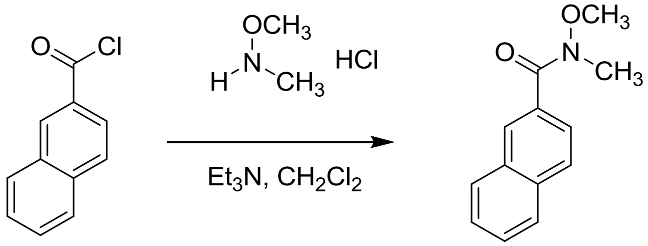
3,5-Bis(trifluoromethyl)benzoyl chloride (18.08 mmol, 5.0 g) was added to a suspension of *N,O*-dimethylhydroxylamine hydrochloride (21.69 mmol, 2.12 g) mixed with triethylamine (80.0 mmol, 8.1 g) in anhydrous dichloromethane (50 mL). The reaction mixture was stirred for 40 minutes, analyzed by GC/MS analysis, and clean formation of the product was confirmed. The reaction mixture was treated with water, organic phase was separated, and aqueous phase was extracted with dichloromethane. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was removed, and organic solvents were removed by rotary evaporation. Crude product, obtained as yellowish oil, was purified by column chromatography (silica gel, hexanes:ethyl acetate (3:1) as eluant). Combined fractions were subjected to rotary evaporation, and the product was obtained as yellowish oil (4.95 g, 90.8% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (s, 2H), 7.96 (s, 1H), 3.55 (s, 3H), 3.40 (s, 3H) (this analysis is in agreement with the literature data[9]); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 166.5, 131.4 (q, J = 33 Hz), 128.7 (m, CH), 124.3 (CH), 124.1 (m), 123.0 (q, J = 273 Hz), 61.3 (CH_3), 33.0 (CH_3) (assignment of CH and CH_3 carbon signals was made based on DEPT-135 experiment).

N-methoxy-*N*-methylthiophene-2-carboxamide (11e)



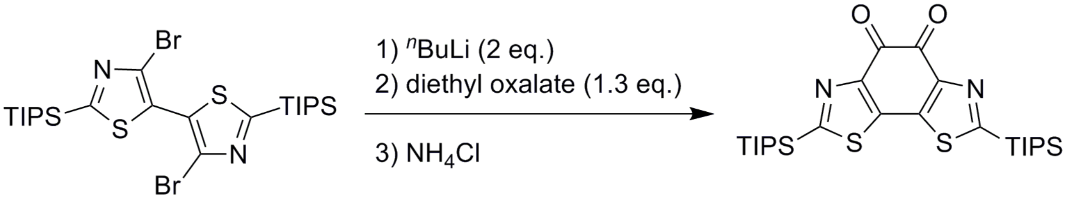
Thiophene-2-carbonyl chloride (20.0 mmol, 2.93 g) was added to a suspension of *N,O*-dimethylhydroxylamine hydrochloride (24.0 mmol, 2.34 g) and triethylamine (80.0 mmol, 8.1 g) in anhydrous dichloromethane (50 mL). Reaction mixture was stirred overnight at room temperature, treated with water, and yellowish organic phase was separated, dried over anhydrous magnesium sulfate, and the drying agent was filtered off. The solvent was removed by rotary evaporation, and the crude product was obtained as yellow oil, which was purified by column chromatography (silica gel, hexanes:EtOAc (3:1) as eluant). Combined fractions were subjected to rotary evaporation, the residual solvent was removed under vacuum, and the product was obtained as yellowish oil (3.2 g, 93.6% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95 (dd, J = 3.9 Hz, 1.3 Hz, 1H), 7.54 (dd, J = 5.1 Hz, 1.3 Hz, 1H), 7.09 (dd, J = 5.0 Hz, 3.9 Hz, 1H), 3.76 (s, 3H), 3.36 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 162.2 (quaternary C), 134.3 (CH), 133.1, 132.2 (CH), 126.7 (CH), 61.5 (CH_3), 32.9 (CH_3) (assignment of CH and CH_3 carbons was made based on DEPT-135 experiment) (NMR data is in agreement with the literature data[10]).

***N*-methoxy-*N*-methyl-2-naphthamide (11f)**



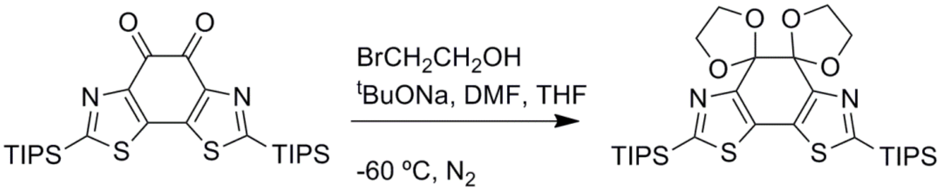
N,*O*-Dimethylhydroxylamine hydrochloride (24.0 mmol, 2.34 g) was added to dichloromethane (50 mL), and triethylamine (80.0 mmol, 8.1 g) was added. Colorless suspension formed, and 2-naphthaloyl chloride (0.0 mmol, 3.81 g) was added in ~1 g portions. The reaction mixture was stirred overnight, analyzed by GC/MS analysis, and clean formation of the desired product was confirmed. The reaction mixture was treated with water, organic phase was separated, and aqueous phase was extracted with dichloromethane. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and organic solvent was removed by rotary evaporation. Crude product obtained as oil was purified by column chromatography (silica gel, hexanes:ethyl acetate (4:1) as eluant). Combined fractions were subjected to rotary evaporation and product was obtained as very thick colorless oil (3.67 g, 85.3% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (s, 1H), 7.86 (m, 1H), 7.82 (m, 2H), 7.23 (m, 1H), 7.49 (m, 2H), 3.50 (s, 3H), 3.37 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 169.6, 133.9, 132.2, 131.1, 128.5 (CH), 128.3 (CH), 127.4 (CH), 127.3 (CH), 127.1 (CH), 126.2 (CH), 124.7 (CH), 60.8 (CH_3), 33.5 (CH_3) (assignment of CH and CH_3 carbons was made based on DEPT-135 experiment; all other carbons are quaternary).

2,7-Bis-triisopropylsilyl-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (13)



2,2'-Bis(triisopropylsilyl)-4,4'-dibromo-5,5'-dithiazole (20.0 mmol, 12.77 g) was dissolved in anhydrous THF (200 mL) under nitrogen atmosphere, and the resulting solution was cooled in pyridine/dry ace bath (~ -40 to -45 ºC bath). *n*-Butyllithium (2.85 M in hexanes, 40.0 mmol, 14 mL) was added dropwise, stirred for 15 minutes, and then the suspension was transferred via cannula to a solution of diethyl oxalate (1.3 eq., 26.0 mmol, 3.80 g) in anhydrous THF(150 mL) (acetone/dry ice bath). The reaction mixture was stirred for ~1 h, and then transferred via cannula to an aqueous solution of NH_4Cl. The resulting mixture with some insoluble white matter was vacuum filtered, orange-red organic phase was removed, and aqueous phase was extracted with hexanes:diethyl ether. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, the solvents were removed by rotary evaporation, and the crude product was purified by column chromatography (silica gel, dichloromethane to pack the column, dichloromethane:ethyl acetate (100:1) as eluant). First few fractions containing contaminated product were kept separately; later fractions with the pure product were combined, and the solvents was removed by rotary evaporation to give **13** as red-orange solid (6.74 g, 63% yield). ^{1}H NMR analysis was in agreement with the literature data.[1]

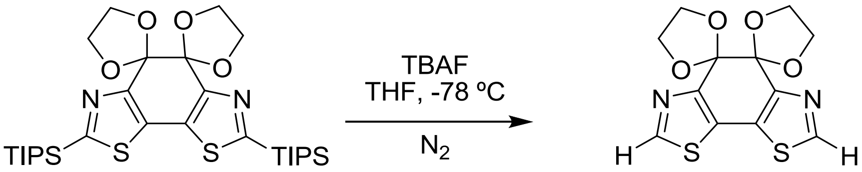
2,7-Bis-triisopropylsilyl-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (14)



Modified literature conditions[7] for the protection of the carbonyl group were used for bithiazole derivative **13**.

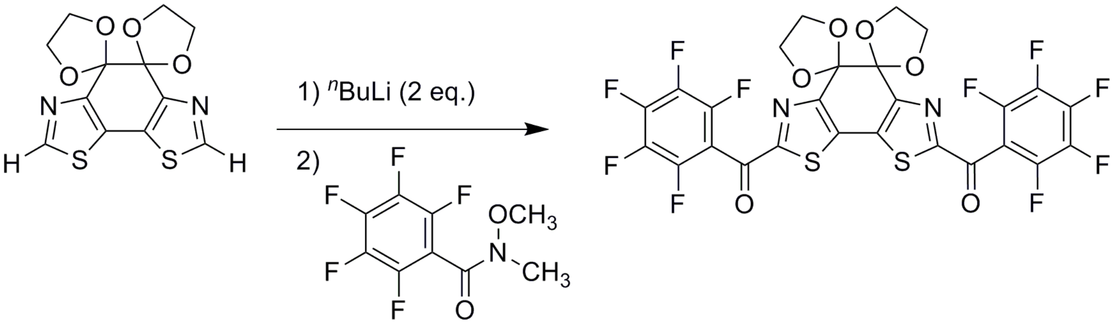
2,7-Bis-triisopropylsilyl-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (**13**) (6.92 mmol, 3.70 g) was dissolved in a mixture of anhydrous THF (70 mL) and anhydrous DMF (30 mL) under nitrogen atmosphere, and the orange-red solution was cooled in acetone/dry ice bath. 2-Bromoethanol (3.0 eq., 20.75 mmol, 2.59 g) was added followed by dropwise addition of a solution of ^{t}BuONa (3.0 eq., 20.75 mmol, 1.99 g) in anhydrous DMF (30 mL). After addition of 5 mL of the base solution thick precipitate formed, and the mixture from orange-red became yellow-brown, then brown-greenish. The rest of the base solution was added over 0.5 h, and the reaction mixture was allowed to warm to room temperature. After stirring for ~2 h aqueous solution of NH_4Cl was added to the dark green-brown suspension, and the mixture became orange. Organic phase was removed, aqueous phase was extracted with diethyl ether, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, the solvents were removed by rotary evaporation, and crude product (contains residual amount of DMF) was purified by column chromatography (silica gel, dichloromethane as eluant). Fractions with slightly contaminated product were combined, the solvents were removed and the residue was further purified by column chromatography (silica gel, dichloromethane as eluant). Fractions with the product were combined, subjected to rotary evaporation, and the residual solvent was removed under vacuum. Light-orange oil solidified to give yellowish solid (3.31 g, 76.8%). The material can be recrystallized from 2-propanol to give white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.32-4.39 (m, 4H), 4.25-4.32 (m, 4H), 1.38 (septet, J = 7.4 Hz, 6H), 1.13 (d, J = 7.4 Hz , 36H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 169.1, 154.0, 126.9, 106.4, 66.8, 18.4 (CH), 11.6 (CH_3). HRMS (EI) calculated for $C_{30}H_{50}N_2O_4S_2Si_2$ 622.2751; found 622.2754. Anal. Calcd. for $C_{30}H_{50}N_2O_4S_2Si_2$: C, 57.83; H, 8.09; N, 4.50. Found: C, 57.89; H, 8.02; N, 4.52.

Benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (15)



2,7-Bis-triisopropylsilyl-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**14**) (3.37 mmol, 2.10 g) was dissolved THF (50 mL), and the resulting yellowish solution was cooled in acetone/dry ice bath (nitrogen atmosphere). Tetra-*n*-butylammonium fluoride (1.0 M in THF, 2.2 equiv., 7.4 mL) was added dropwise, and the reaction mixture became darker in color (brown-green). After a few minutes no starting material was detected by TLC analysis (chloroform:ethyl acetate (4:1) as eluant), and a new more polar spot was detected. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (100 mL of silica gel, $CHCl_3$:EtOAc (~4:1) as eluant). Combined fractions were subjected to rotary evaporation, and the residue was recrystallized from ~50 mL of 2-propanol. Product was obtained as colorless plates (0.50 g, 47.6% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (m, 2H), 4.30-4.35 (m, 8H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 152.7, 151.2 (CH), 124.4, 106.9, 67.1. HRMS (EI) calculated for $C_{12}H_{10}N_2O_4S_2$ 310.0082; found 310.0082. Anal. Calcd. for $C_{12}H_{10}N_2O_4S_2$: C, 46.44; H, 3.25; N, 9.03. Found: C, 46.57; H, 3.25; N, 9.06.

2,7-Bis-(pentafluorobenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (16a)



Benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**15**) (0.7 mmol, 0.217 g) was dissolved in anhydrous THF (100 mL) under nitrogen atmosphere, and the reaction mixture was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 1.4 mmol, 0.5 mL) was added dropwise, and the reaction mixture became bright yellow, and then cloudy yellow-orange. After stirring for 15 minutes 2,3,4,5,6-pentafluoro-*N*-methoxy-*N*-methylbenzamide (**11a**) (2.2 eq., 1.54 mmol, 0.39 g) in anhydous THF (10 mL) was added. Still cloudy orange-yellow mixture was stirred for 40 minutes, and the cooling bath was removed. The mixture was allowed to warm to room temperature, and aqueous NH_4Cl was added followed by brine. Bright yellow organic phase was removed, aqueous phase was extracted with dichloromethane:hexanes mixture, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, and the solvent were removed by rotary evaporation. The residue was purified by column chromatography (silica gel, dichloromethane as eluant). Fractions with almost pure compound (by TLC analysis) were combined, solvents were removed by rotary evaporaiton, and product was obtained as yellow oil. This mateial was heated to reflux with 2-propanol, cooled (no precipitate formed), heated to reflux again, water was added, and yellow crystals formed on cooling (55 mg, 11.2%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.24 (m, 8H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 177.08, 163.8, 157.1, 144.6 (doublet (at 145.8 and 143.3, J = 252 Hz) of multiplet), 143.3 (doublet (at 144.6 and 142.1, J = 259 Hz) of multiplet), 137.6 (doublet (at 138.9 and 136.3, J = 256 Hz) of multiplet), 132.4, 112.1 (dt, J = 19 Hz, 4 Hz), 105.6, 67.3. HRMS (EI) calculated for $C_{26}H_8F_{10}N_2O_6S_2$ 697.9664; found 697.9656. Anal. Calcd. for $C_{26}H_8F_{10}N_2O_6S_2$: C, 44.71; H, 1.15; F, 27.20; N, 4.01. Found: C, 44.52; H, 1.02; N, 3.97.

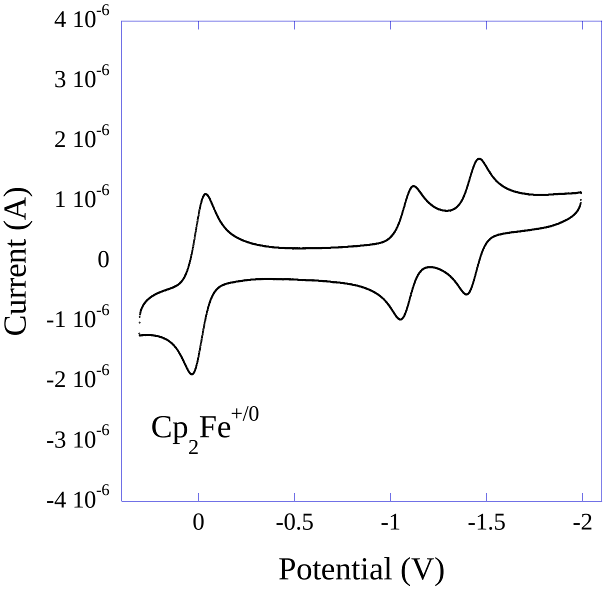
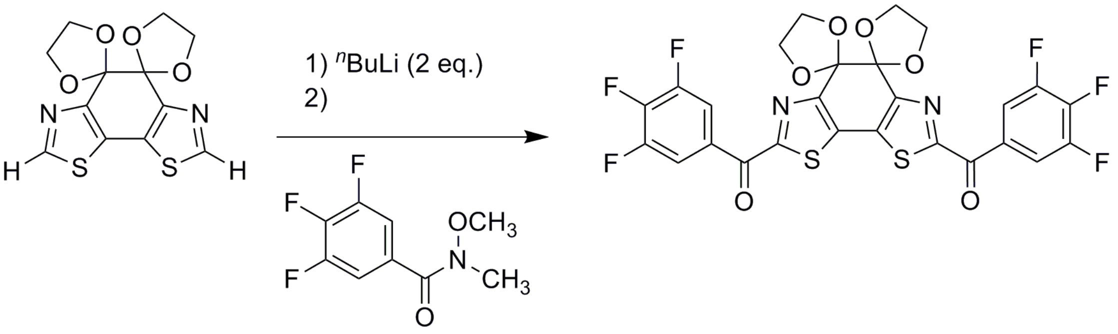


Figure S49. Cyclic voltammogram of 2,7-bis-(pentafluorobenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione-bis-(1,3-dioxolane) (16a) (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1-}$ = -1.09 V, $E_{1/2}^{1-/2-}$ = -1.43 V.

2,7-Bis-(3,4,5-trifluorobenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (16b)



Benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**15**) (0.17 mmol, 0.054 g) was dissolved in anhydrous THF (50 mL) under nitrogen atmosphere, and colorless solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 0.34 mmol, 0.12 mL) was added dropwise, and the reaction mixture became bright yellow, and then beige with precipitate. After stirring for 10 minutes *N*-methoxy-*N*-methyl-3,4,5-trifluorobenzamide (**11b**) (2.2 eq., 0.38 mmol, 0.083 g) was added, and the mixture became yellow in color. After 0.5 h of stirring the cooling bath was removed, the reaction mixture was warmed to room temparature, and treated with aqueous NH_4Cl. Organic phase was removed, dried over anhydrous magnesium sulfate, and the drying agent was filtered off. The solvents were removed by rotary evaporation, and the residue (tiny yellow needles) was recrystallized from 2-propanol. The product was separated by vacuum filtration (bright yellow long neeldes, 0.090 g, 82.6% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.39 (m, 4H), 4.41 (m, 8H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 178.8, 166.1, 155.9, 151.0 (two dd at 152.2 and 149.7 (ddd, J = 250 Hz, 10 Hz, 3 Hz)), 143.8 (triplets at 145.1 and 142.5 (dt, J = 260 Hz, 16 Hz)), 131.6, 129.7, 116.0 (m) (CH), 105.9, 67.5 (CH$_2$) (assignment of CH and CH$_2$ carbons was made based on DEPT-135 experiment; all other carbons are quaternary). HRMS (EI) calculated for $C_{26}H_{12}F_6N_2O_6S_2$ 626.0041; found 626.0141. Anal. Calcd. for $C_{26}H_{12}F_6N_2O_6S_2$: C, 49.84; H, 1.93; N, 4.47. Found: C, 49.63; H, 1.79; N, 4.41.

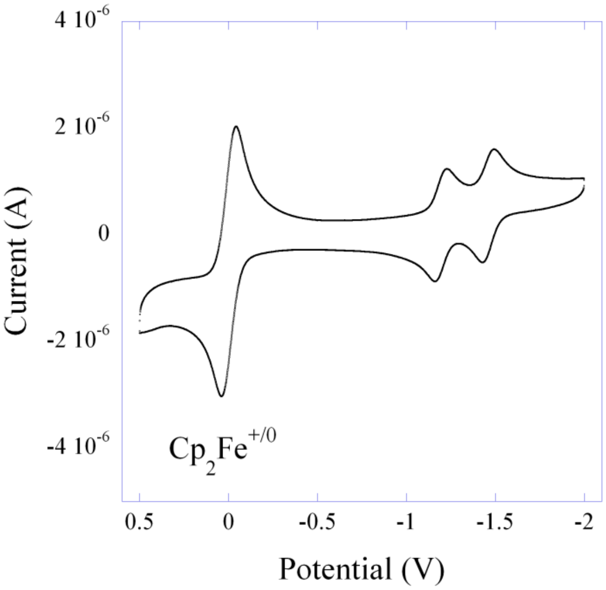
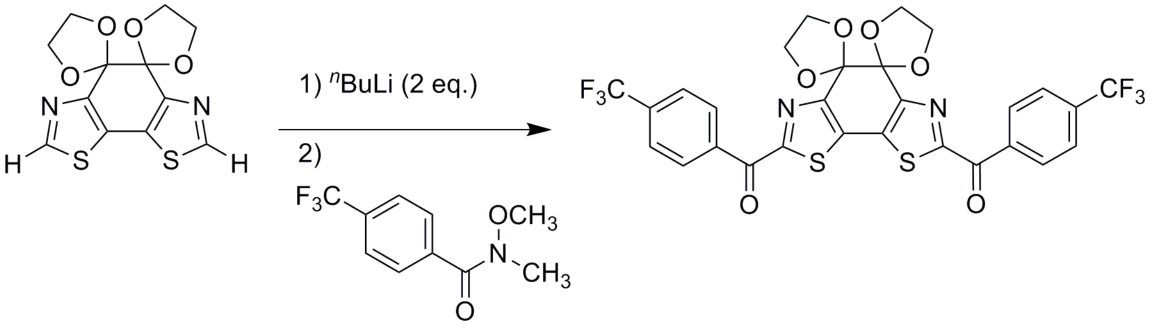


Figure S50. Cyclic voltammogram of 2,7-bis-(3,4,5-trifluorobenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (16b) (0.1 M ^{n}Bu$_4$NPF$_6$ in THF, Cp$_2$Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1-}$ = -1.19 V, $E_{1/2}^{1-/2-}$ = -1.46 V.

2,7-Bis-(4-trifluoromethylbenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (16c)



Benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**15**) (0.70 mmol, 0.217 g) was dissolved in anhydrous THF (70 mL) under nitrogen atmosphere, and colorless solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 1.4 mmol, 0.5 mL) was added dropwise, and the reaction mixture became bright yellow, and then precipitate formed. After stirring for 15 minutes *N*-methoxy-*N*-methyl-4-(trifluoromethyl)benzamide (**11c**) (2.2 eq., 1.54 mmol, 0.36 g) was added. After stirring for 10 minutes the cooling bath was removed, the reaction mixture was warmed to room temparature, and then treated with aqueous NH_4Cl. Organic phase was removed, aqueous phase was extracted with hexanes:dichloromethane, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, the solvents were removed by rotary evaporation, and the residue was recrystallized from ethanol. Product was obtained as bright yelllow needles (0.312 g, 68.1% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (d, J = 8.1 Hz, 4H), 7.80 (d, J = 8.3 Hz, 4H), 4.39 (s, 8H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 182.0, 176.1, 166.5, 155.8, 137.3, 134.9 (q, J =32.6 Hz), 131.5, 131.4(6) (CH), 125.4 (m, CH), 123.6 (d, J = 272 Hz), 106.0, 67.4 (CH_2) (assignment of CH and CH_2 carbons was made based on DEPT-135 experiment; all other carbons are quaternary). HRMS (EI) calculated for $C_{28}H_{16}F_6N_2O_6S_2$ 654.0354; found 654.0356. Anal. Calcd. for $C_{28}H_{16}F_6N_2O_6S_2$: C, 51.38; H, 2.46; N, 4.28. Found: C, 51.34; H, 2.31; N, 4.29.

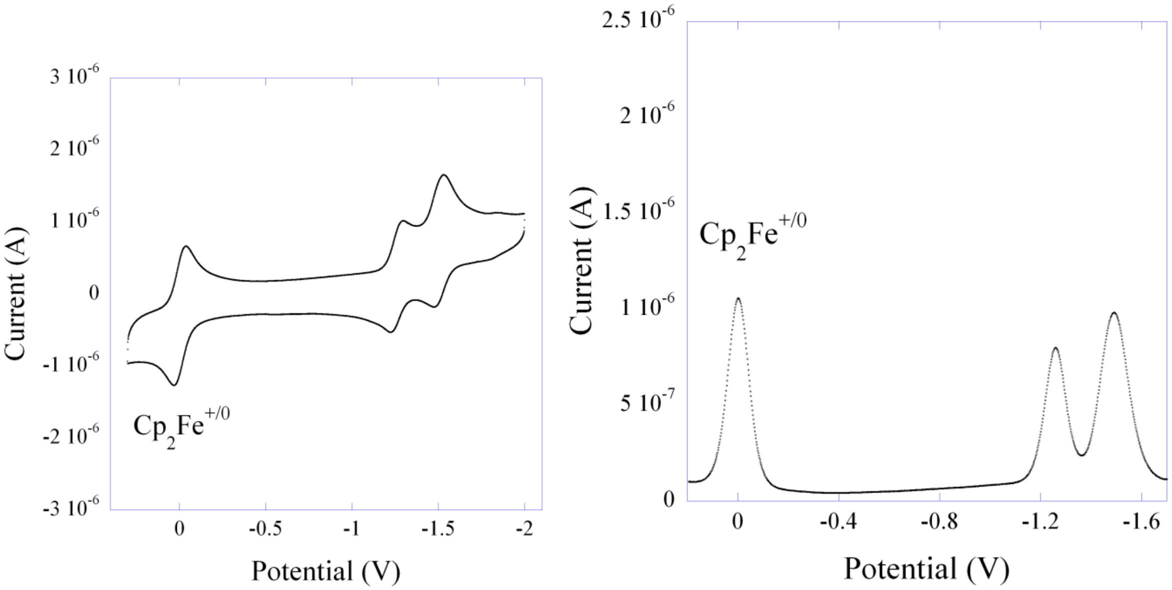
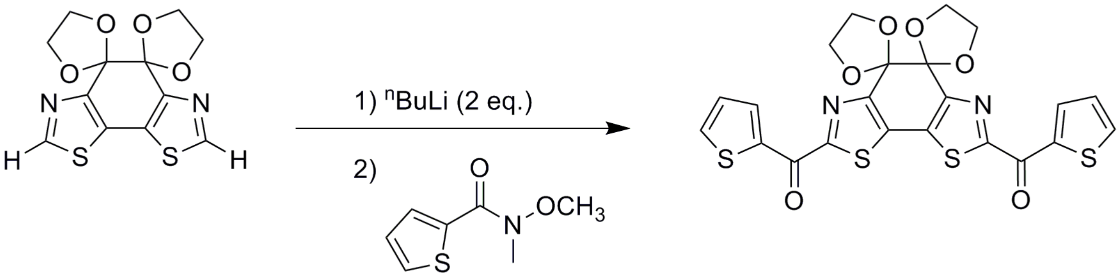


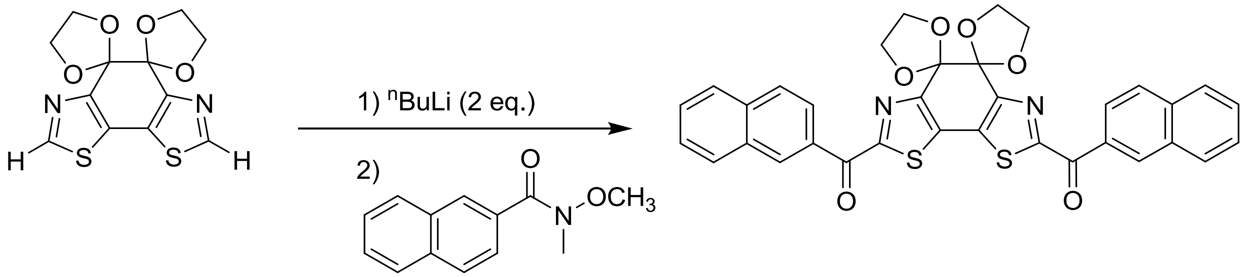
Figure S51. (*left*) Cyclic voltammogram of 2,7-bis-(4-trifluoromethylbenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (16c) (0.1 M ^{n}Bu$_4$NPF$_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1-}$ = -1.26 V, $E_{1/2}^{1-/2-}$ = -1.50 V; (*right*) Differential pulse voltammetry: $E_{1/2}^{0/1-}$ = -1.26 V (1 e$^-$), $E_{1/2}^{1-/2-}$ = -1.49 V (1.3 e$^-$).

2,7-Bis-(thiophen-2-oyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (16d)



Benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**15**) (1.0 mmol, 0.31 g) was dissolved in anhydrous THF (100 mL) under nitrogen atmosphere, and the solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 2.0 mmol, 0.7 mL) was added dropwise, and the reaction mixture became yellow, then peach-yellow with precipitate. Reaction mixture was stirred for 20 minutes, and *N*-methoxy-*N*-methylthiophene-2-carboxamide (**11e**) (2.1 eq., 2.1 mmol, 0.36 g) was added. The reaction mixture was stirred for 10 minutes, the cooling bath was removed, and the mixture was allowed to warm to room temperature. Aqueous NH_4Cl was added, brigh yellow organic phase was removed, and aqueous phase was extracted with hexanes:dichloromethane mixture. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and the solvents were removed by rotary evaporation. Crude product was purified by column chromatography (~150 mL of silica gel, dichloromethane as eluant). Fractions with pure product were combined, the solvents were removed by rotary evaporation and the residue was heated to reflux with 2-propanol with addition of dichloromethane, and cooled. Bright yellow solid was separated by vacuum filtration (0.236 g, 44.5% yield). Fractions with contaminated product were kept separately, and additional amount of product can be obtained after further purification. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.63 (s, 2H), 7.83 (d, J = 4.04 Hz, 2H), 7.24 (s, 2H), 4.60-4.40 (m, 8H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 174.8, 166.3, 155.2, 139.0, 137.0 (CH), 136.9 (CH), 130.9, 128.3 (CH), 105.9, 67.4 (CH_2). HRMS (EI) calculated for $C_{22}H_{14}N_2O_6S_4$ 529.9735; found 529.9723. Anal. Calcd. for $C_{22}H_{14}N_2O_6S_4$: C, 49.80; H, 2.66; N, 5.28. Found: C, 50.10; H, 2.51; N, 5.28.

2,7-Bis-(napthal-2-oyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (16e)



Benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-(1,3-dioxolane) (**15**) (1.0 mmol, 0.31 g) was dissolved anhydrous THF (100 mL) under nitrogen atmosphere, and colorless solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 2.0 mmol, 0.7 mL) was added dropwise. After stirring for 15 minutes *N*-methoxy-*N*-methyl-2-naphthamide (**11f**) (2.2 eq., 1.54 mmol, 0.36 g) was added. After stirring 15 minutes the cooling bath was removed, the reaction mixture was warmed to room temperature, and treated with aqueous NH$_4$Cl. Yellow solid was separated by vacuum filtration (0.45 g, 72.8% yield). Organic phase was removed, dried over anhydrous magnesium sulfate, and the solvent was removed to give additional amount of yellow solid. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 9.53 (s, 2H), 8.54 (d, J = 8.2 Hz, 2H), 8.08 (d, J = 8.1 Hz, 2H), 7.99 (d, J = 8.5 Hz, 2H), 7.96 (d, J = 8.50 Hz, 2H), 7.65 (m, 4H) (this material had limited solubility in CDCl$_3$, and ^{13}C{^{1}H} NMR was not recorded).

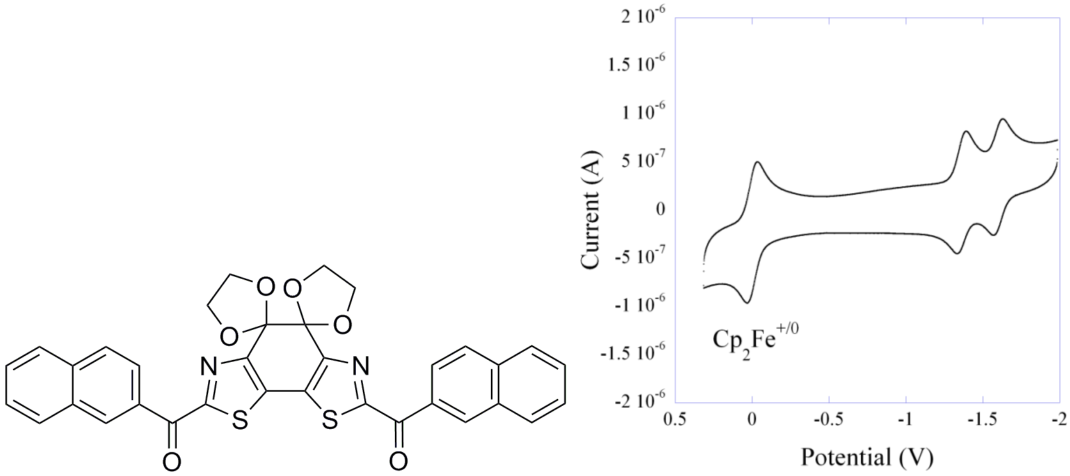
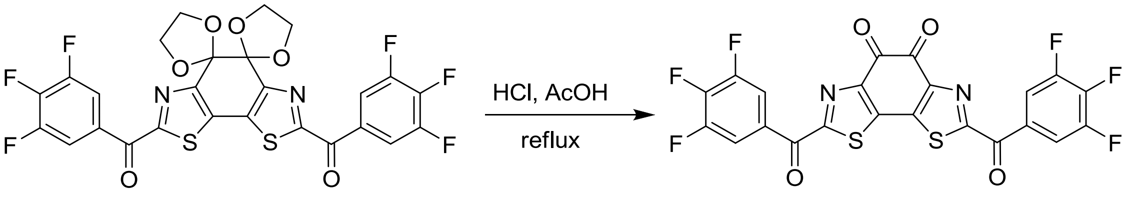


Figure S52. (*right*) Cyclic voltammogram of 2,7-bis-(naphthal-2-oyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (16e) (0.1 M ^{n}Bu$_4$NPF$_6$ in THF, Cp$_2$Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1-}$ = -1.36 V, $E_{1/2}^{1-/2-}$ = -1.60 V.

2,7-Bis-(3,4,5-trifluorobenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (17b).



2,7-Bis-(3,4,5-trifluorobenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**16b**) (0.07 mmol, 43.9 mg) was dissolved in hot acetic acid (10 mL) and HCl (~1 mL) was added dropwise. The reaction mixture remained bright yellow until it started to boil when the color changed to darker yellow, then orange-yellow. After a few minutes of reflux precipitate was observed. The reaction mixture was refluxed for ~10 minutes, cooled to room temperature, and solid was separated by vacuum filtration (25 mg, 66.3% crude yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.41 (m, 4H) (material has very limited solubility in CDCl$_3$, and ^{13}C{^{1}H} NMR was not recorded). HRMS (EI) calculated for $C_{22}H_4F_6N_2O_4S_2$: 537.9517, found 537.9535.

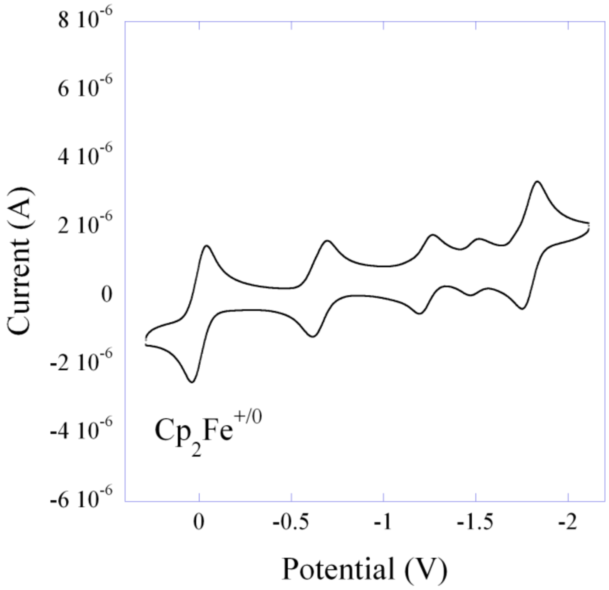
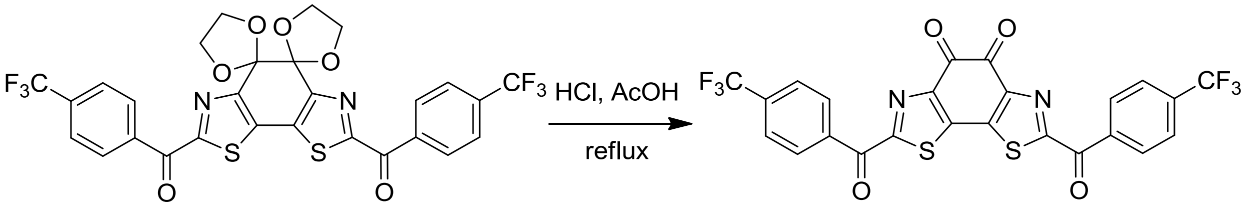


Figure S53. Cyclic voltammogram of 2,7-bis-(3,4,5-trifluorobenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (17b) (0.1 M ^{n}Bu$_4$NPF$_6$ in THF, Cp$_2$Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1-}$ = -0.65 V, $E_{1/2}^{1-/2-}$ = -1.23 V, $E_{1/2}^{2-/3-}$ = -1.49 V, $E_{1/2}^{3-/5-}$ = -1.79 V (preliminary data).

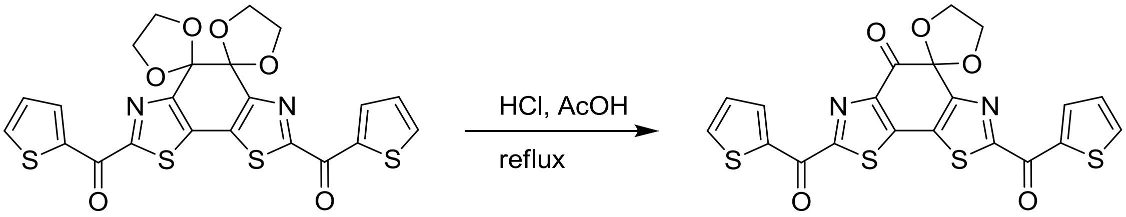
2,7-Bis-(4-trifluomethylbenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (17c).



2,7-Bis-(4-trifluoromethylbenzoyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**16c**) (0.023 mmol, 15 mg) was mixed with acetic acid (~15 mL), heated to reflux, and HCl (~5 mL) was added. The bright yellow reaction mixture became orange, and them precipitate formed. The reaction mixture was cooled to room temperature, orange solid was separated by vacuum filtration, washed with water, ethanol, and then dried. The crude product was obtained as orange solid (10.7 mg, 82.3% yield). A few mg of the crude product was dissolved in dichloromethane, filtered through a silica gel plug, the solvent was removed by rotary evaporation, and the residue was analyzed by ^{1}H NMR. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.73 (d, J = 8.3 Hz, 2H), 7.88 (d, J =

8.3 Hz, 2H) (the material has limited solubility in $CDCl_3$, and $^{13}C\{^1H\}$ NMR was not recorded). HRMS (EI) calculated for $C_{24}H_8F_6N_2O_4S_2$ 565.9830; found 565.9820.

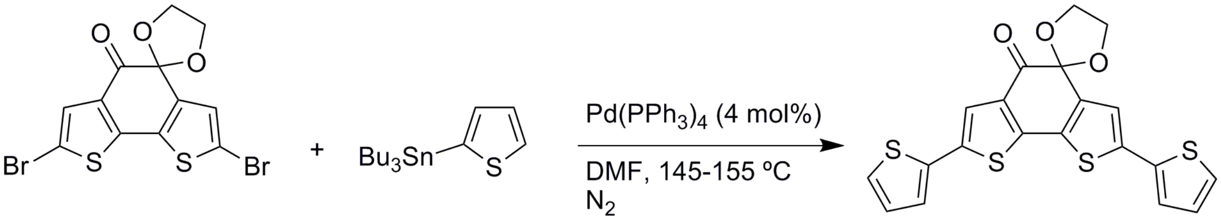
Attempt to prepare 2,7-bis-(thiophen-2-oyl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (17d).



Benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) derivative (**16d**) (0.358 mmol, 0.19 g) was dissolved in boiling acetic acid (~100 mL), and HCl (5-10 mL) was added. The bright yellow reaction mixture became orangish-yellow, and then after ~0.5 h of reflux precipitate formed. Reaction mixture was refluxed for additional 40 minutes, cooled to room temperature, and orange precipitate was separated by vacuum filtration (0.155 g, 89% crude yield). This material is not sufficiently soluble in $CHCl_3$, THF, or chlorobenzene at room temperature or on heating. ^{1}H NMR (1,1,2,2-tetrachloroethane-*d2*, 400 MHz): δ 8.65 (d, J = 3.7 Hz, 1H), 8.49 (d, J = 3.7 Hz, 1H), 7.85 (m, 2H), 2.20 (m, 2H), 4.47 (m, 4H). HRMS calculated for $C_{20}H_{10}N_2O_5S_4$ 485.9473, found 485.9492. Anal. Calcd. for $C_{20}H_{10}N_2O_5S_4$: C, 49.37; H, 2.07; N, 5.76. Found: C, 49.05; H, 1.79; N, 5.88.

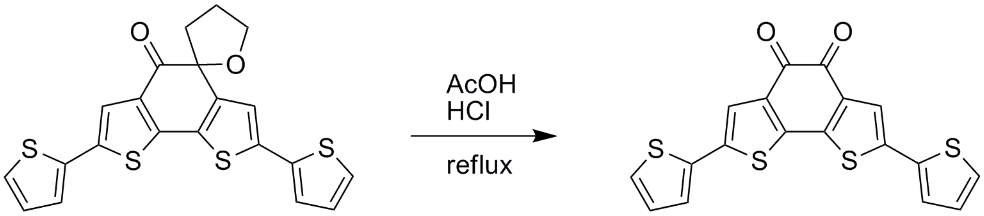
Preparation of 19a starting from mono-protected precursor 5b

Step 1. Preparation of S3



2,7-Dibromo-benzo[1,2-*b*:6,5-*b'*]dithiophene-4-one-5-(1,3-dioxolane) (**5b**) (1.42 mmol, 0.60 g), 2-tri-*n*-butylstannyl-thiophene (2.2 eq., 3.13 mmol, 1.17 g) and $Pd(PPh_3)_4$ (0.02 eq., 0.028 mmol, 0.033 g) were mixed under nitrogen atmosphere, and anhydrous DMF (20 mL) was added. The resulting yellow suspension was heated up to 145 ºC for several minutes, and yellow solution was becoming deeper in color (yellow, then orange, red-orange, red). After half an hour of stirring the bright red mixture was cooled to room temperature, treated with water, and the organic matter was extracted with diethyl ether several times. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and the solvent was removed by rotary evaporation to give the crude product as dark red matter. This material was purified by column chromatography (100 mL of silica gel, CH_2Cl_2 as eluant). After the first column chromatography purification material came out impure, the fractions containing the product were combined, the solvents were removed by rotary evaporation, and the residue was purified by column chromatography on silica gel using hexanes:CH_2Cl_2 (2:1, then 1:1) as eluant. Fractions with pure material were combined, the solvent was removed, and bright red solid was washed with hexanes and vacuum filtered. The product was obtained as bright red solid in 90.1% yield (0.55 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (s, 1H), 7.28 (m, 2H), 7.21 (m, 2H), 7.05 (dd, J = 5.04 Hz, 3.68 Hz, 2H), 4.53 (m, 2H), 4.38 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 190.47 (quaternary C(O)), 143.34 (quaternary C), 140.02 (quaternary C), 138.26 (quaternary C), 136.09 (quaternary C), 135.67 (quaternary C), 135.55 (quaternary C), 132.13 (quaternary C), 130.17 (quaternary C), 128.07 (CH) , 128.02 (CH), 125.66 (CH), 124.74 (CH), 124.67 (CH), 123.62 (CH), 121.29 (CH), 99.2, 66.15 (CH_2) (assignment of the quaternary C, CH andCH_2 a signals was made based on the DEPT experiment). HRMS (EI) calculated for $C_{20}H_{12}O_3S_4$: 427.9669; found 427.9678. Anal. Calcd. for $C_{20}H_{12}O_3S_4$: C, 56.05; H, 2.82. Found: C, 55.87; H, 2.71.

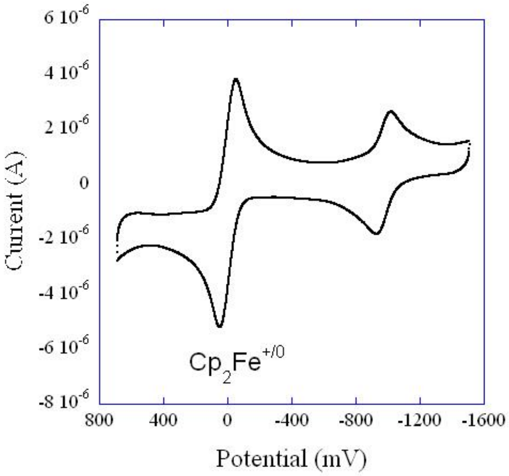
Step 2.



Starting 2,7-bis-(thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4-one-5-(1,3-dioxolane) (**S3**) (0.5 mmol, 0.214 g) was mixed with acetic acid (20 mL) and hydrochloric acid (2 mL), and the resulting mixture was heated to reflux. The reaction mixture became brownish, and then dark blue within a few minutes. The mixture was cooled to room temperature (precipitate formed), treated with water (~10 mL), and dark-blue solid was filtered off, washed with water and dried (0.186 g, 97% yield). This product was purified by column chromatography (silica gel, dichloromethane as eluant; hot chloroform was used to dissolve the material to apply to the column). Small amount (a few mg) of unreacted starting material came out first. The fractions with the product (blue solutions) were combined, the solvents were removed, and dark blue microcrystalline solid was obtained (0.191 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (s, 2H), 7.35 (d, J = 4.8 Hz, 2H), 7.09 (appears as t, J = 4.3 Hz, 2H) (one aromatic signal (2H) is missing probably due to overlap with residual $CHCl_3$ peak; a peak at 5.31 ppm corresponding to dichloromethane was observed, which indicates that the product crystallized with the solvent during the removal of dichloromethane after column chromatography) (^{1}H NMR and ^{13}C NMR data of this compound in THF-*d8* was reported in the literature[6]). HRMS (EI) calculated for

$C_{18}H_8O_2S_4$ 383.9407; found 383.9405 (M+2 was also observed (385.9553)). Anal. Calcd. for $C_{18}H_8O_2S_4$: C, 56.22; H, 2.10. Found: C, 55.57; H, 2.01 (0.65% difference on C). Material (100 mg) was recrystallized from toluene (41 mg, 41% recovery). Found: C, 55.99; H, 2.07.

TGA analysis showed the solvent loss (7.9%) with decomposition >250 ºC. DSC analysis showed the solvent loss during the first heating-cooling cycle with no melting point observed below 280 ºC. The melting transition was observed at 285.3 ºC on heating, and crystallization was observed on cooling (broad peak with maximum at 195.8 ºC) during the second heating-cooling cycle.



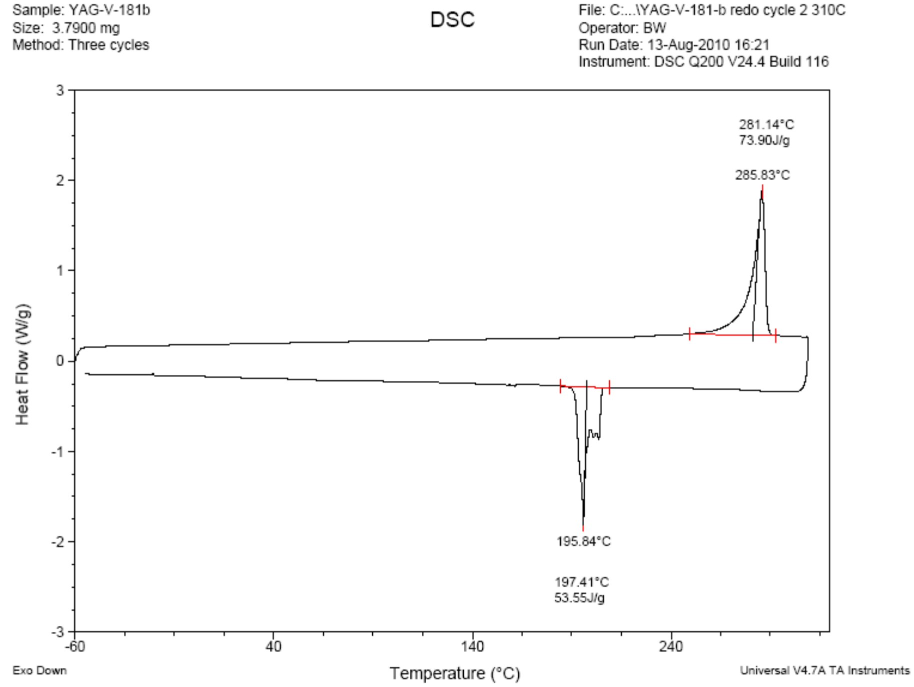
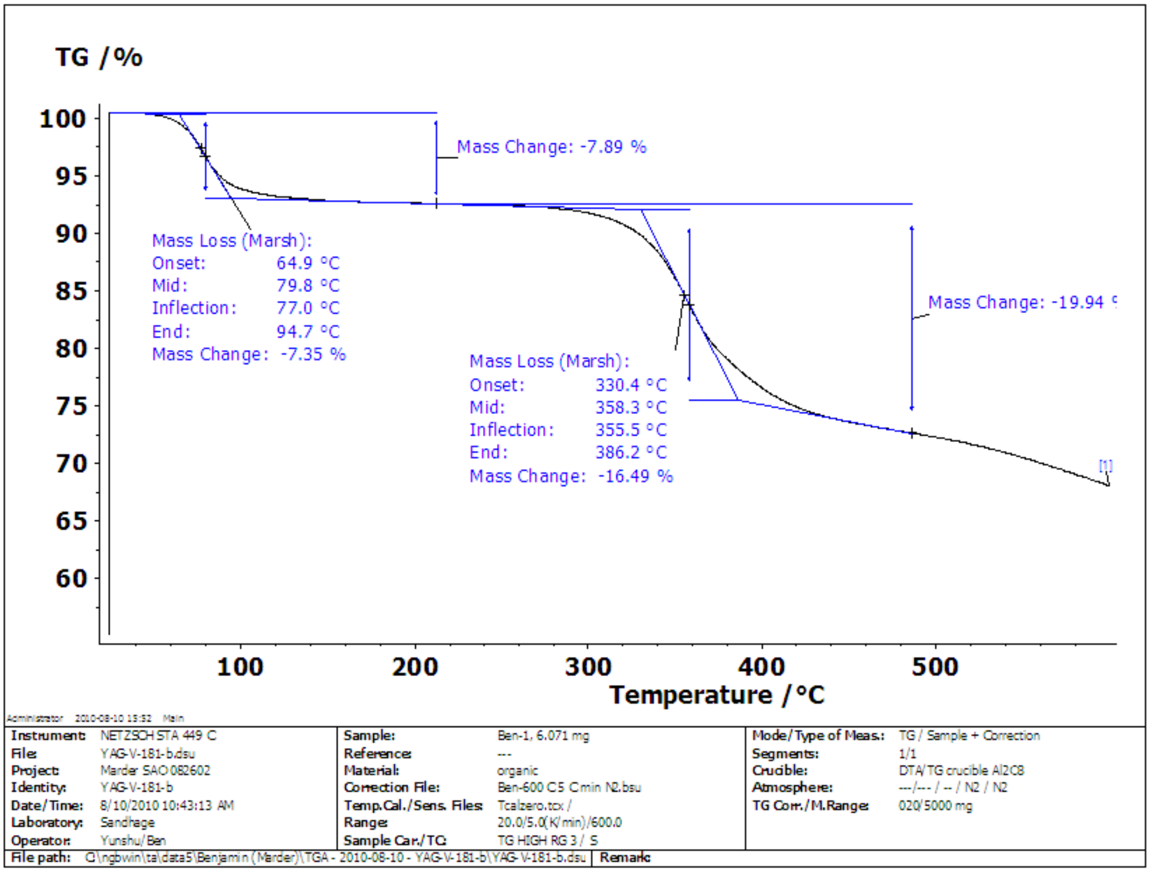


Figure S54. (*top*) Cyclic voltammogram (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2,7-bis-(thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19a): $E_{1/2}^{0/1-}$ = -0.97 V (rev.) and (*bottom*) DSC analysis 2,7-bis-(thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-diones: m.p. 285.8 C.

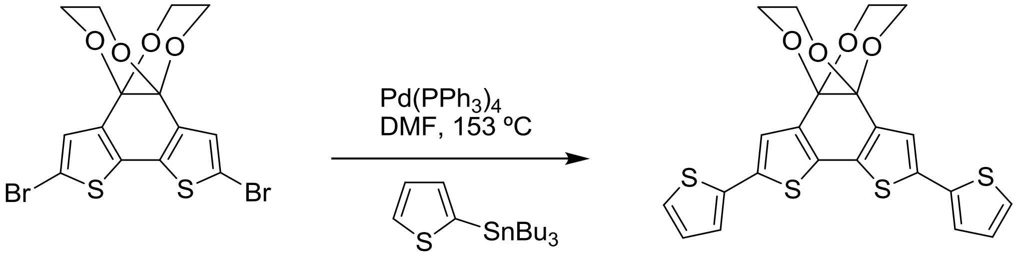


Instrument:	NETZSCH STA 449 C	**Sample:**	Ben-1, 6.071 mg	**Mode/Type of Meas.:**	TG / Sample + Correction
File:	YAG-V-181-b.dsu	**Reference:**	---	**Segments:**	1/1
Project:	Marder SAO 082602	**Material:**	organic	**Crucible:**	DTA/TG crucible Al2O3
Identity:	YAG-V-181-b	**Correction File:**	Ben-600 C5 Cmin N2.bsu	**Atmosphere:**	---/--- / -- / N2 / N2
Date/Time:	8/10/2010 10:43:13 AM	**Temp.Cal./Sens. Files:**	Tcalzero.tcx /	**TG Corr./M.Range:**	020/5000 mg
Laboratory:	Sandhage	**Range:**	20.0/5.0(K/min)/600.0		
Operator:	Yunshu/Ben	**Sample Car./TC:**	TG HIGH RG 3 / S		

File path: C:\ngbwin\ta\data5\Benjamin (Marder)\TGA - 2010-08-10 - YAG-V-181-b\YAG-V-181-b.dsu **Remark:**

Figure S55. TGA analysis of 2,7-bis-(thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19a).

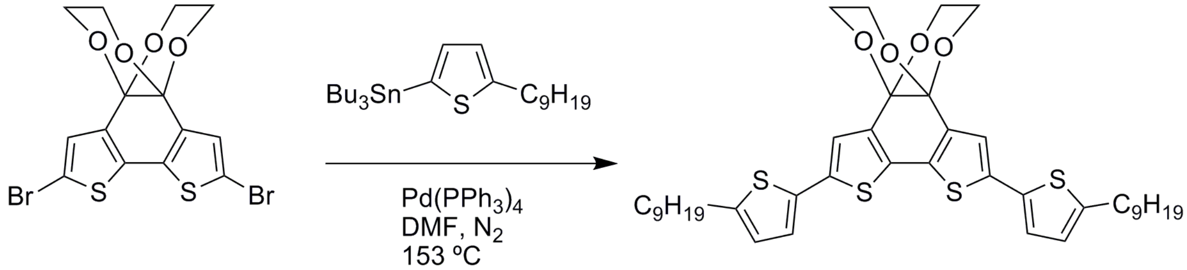
2,7-Bis-(thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (18a)



2,7-Dibromo-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (3.0 mmol, 1.40 g), 2-tri-*n*-butylstannyl-thiophene (2.1 eq., 6.3 mmol, 2.35 g) and $Pd(PPh_3)_4$ (2.5 mol%, 0.075 mmol, 0.087 g) were mixed in an oven-dried flask under nitrogen atmosphere. Anhydrous DMF (30 mL) was added and the suspension was heated to 153 ºC. Yellow solution formed during heating, and the color changed to orange, then orange-red, and within a few minutes very dark yellowish-brown. The reaction mixture was cooled to room temperature, treated with water and organic matter was extracted with dichloromethane several times. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and the organic solvents were removed by rotary evaporation. Crude product obtained as orange solid with some oil was purified by column chromatography twice (silica gel, dichloromethane as eluant). Fractions with pure product (by TLC analysis) were combined, the solvent was removed, and orange solid was obtained (1.34 g, 94.6% yield). Last fractions with product were combined separately, the solvent was removed, and the residue was dissolved in 2-propanol-dichloromethane mixture under reflux. No solid precipitated on cooling, and dichloromethane was removed by rotary evaporation. Shiny little orange crystals were collected by vacuum filtration (0.111 g). Material was recrystallized from toluene with addition of hexanes, and yellow-orange crystals were obtained (1.08 g, 80.6% recovery). Mother liquors from the recrystallizations were combined, the sides of the flasks were rinsed with dichloromethane and volatile solvent was removed by rotary evaporation, and orange crystals were obtained by vacuum filtration (0.118 g).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28 (s, 2H), 7.25 (dd, *J* = 5.1 Hz, 1.1 Hz, 2H), 7.20 (dd, *J* = 3.6 Hz, 1.1 Hz, 2H), 7.04 (dd, *J* = 5.1 Hz, 3.6 Hz, 2H), 4.21 (m, 4H), 3.80 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 136.7 (quaternary C), 136.5 (quaternary C), 136.3 (quaternary C), 131.5 (quaternary C), 127.9 (CH), 124.9 (CH), 124.0 (CH), 121.7 (CH), 93.3 (CH_2), 61.7 (quaternary C) (this analysis in good agreement with the literature data[6]). HRMS (EI) calculated for $C_{22}H_{16}O_4S_4$ 471.9931; found 471.9934. Anal. Calcd. for $C_{22}H_{16}O_4S_4$: C, 55.91; H, 3.41. Found: C, 56.38; H, 3.48.

2,7-Bis-(5-*n*-nonyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (18b)



2,7-Dibromo-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (**5a**) (1.5 mmol, 0.70 g), 5-*n*-nonly-2-tri-*n*-butylstannylthiophene (2.1 eq., 3.15 mmol, 1.57 g) and $Pd(PPh_3)_4$ (5 mol%, 0.075 mmol, 0.087 g) were mixed under nitrogen in an oven-dried flask. Anhydrous DMF (20 mL) was added, the resulting yellowish suspension was heated to reflux, and the mixture became yellow, then orange-red, and then dark brown within a few minutes. Reaction mixture was cooled to room temperature, treated with water and hexanes. Organic phase was removed, the aqueous phase was extracted with hexanes, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, the solvents were removed by rotary evaporation and the residue was purified by column chromatography (silica gel, hexanes:dichloromethane (1:1), then dichloromethane as eluants). Combined fractions were subjected to rotary evaporation, and orange shiny solid was heated to reflux with ~40 mL of EtOH (material did not dissolve completely). The mixture was cooled (some needles formed on cooling), and the product was separated by vacuum filtration (0.93 g, shiny orange solid, 85.3% yield). Part of this material (0.42 g) was recrystallized from 2-propanol, and bright orange needles were separated by filtration (0.37 g, 88.1% recovery). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 (s, 2H), 6.99 (d, J = 3.5 Hz, 2H) 6.69 (d, J = 3.6 Hz, 2H), 4.19 (m, 4H), 3.77 (m, 4H), 2.80 (t, J = 7.6 Hz, 4H), 1.67 (m, 4H), 1.50-1.20 (m, 24H), 0.91 (t, J = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 146.1 (quaternary C), 136.8 (quaternary C), 136.2 (quaternary C), 134.2 (quaternary C), 131.0 (quaternary C), 124.9 (CH), 123.7 (CH), 120.8 (CH), 93.4, 61.7 (CH_2), 31.9 (CH_2), 31.6 (CH_2), 30.2 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3). HRMS (EI) analysis calculated for $C_{40}H_{52}O_4S_4$ 724.2748; found 724.2734. Anal. Calcd. for $C_{40}H_{52}O_4S_4$: C, 66.26; H, 7.23. Found: C, 66.37; H, 7.23.

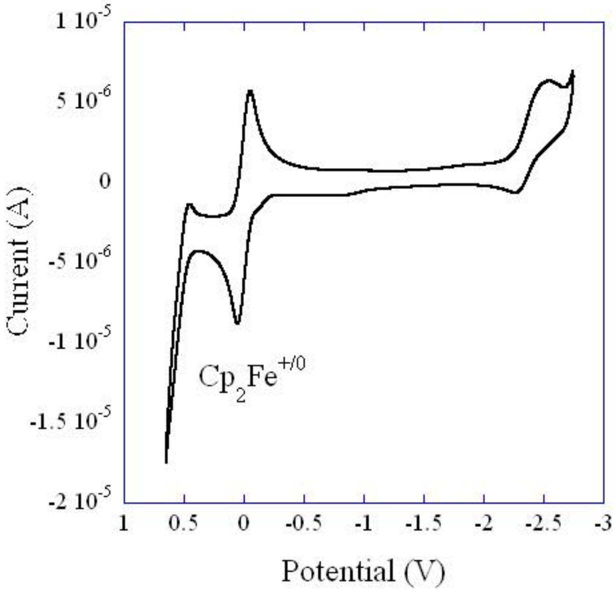
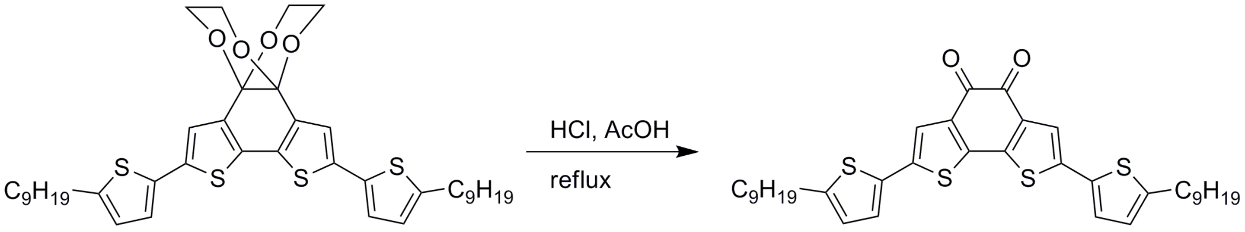


Figure S56. Cyclic voltammogram (0.1 M $^nBu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2,7-bis-(5-*n*-nonyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-di-(1,3-dioxolane) (18b): $E_{1/2}^{0/1-}$ = -2.42 V (partially reversible).

2,7-Bis-(5-*n*-nonyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19b)



2,7-Bis-(5-*n*-nonyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-di-(ethyleneoxolane) (0.7 mmol, 0.508 g) was mixed with acetic acid (50 mL) and THF (50 mL), and the resulting mixture was heated to reflux. HCl (10 mL) was added to a bright orange solution, and it became brown-yellow, then dark-green-brown, then very dark blue-green, and then dark blue. After 10 minutes after addition of HCl reaction mixture was analyzed by TLC, and complete consumption of the starting material was confirmed. The reaction mixture was cooled to room temperature, THF was removed by rotary evaporation, and the residue was treated with water (~50-70 mL). Green solid was separated by vacuum filtration, washed with water, ethanol and dried (0.39 g, 87.4% crude yield). This crude product was purified by column chromatography (silica gel, dichloromethane as eluant). Fractions (blue) with the product were combined, the solvent was removed by rotary evaporation, the residue was dissolved in dichloromethane, and the solution was left for slow evaporation to grow single crystals. Several very dark-blue crystals were separated for the single crystal X-ray analysis, and the rest of the material was further purified by column chromatography (silica gel, dichloromethane as eluant) for mobility measurements. Combined fractions were treated with ~30 mL of distilled 2-propanol, and dichloromethane was removed by rotary evaporation. Additional amount of 2-propanol (~20 mL) was added; mixture was heated to reflux, and then cooled to room temperature. Green shiny solid was separated by vacuum filtration (0.36 g, 92.3% recovery, 80.7% purified yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.34 (s, 2H), 7.00 (d, J = 3.5 Hz, 2H), 6.69 (d, J = 3.5 Hz, 2H), 2.79 (t, J = 7.5 Hz, 4H), 1.66 (m, 4H), 1.50-1.20 (m,24H), 0.89 (t, J = 6.6 Hz, 6H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 174.2 (quaternary C(O)), 147.9 (quaternary C), 141.1 (quaternary C), 138.4 (quaternary C), 135.5 (quaternary C), 132.2 (quaternary C), 125.2 (CH), 125.1 (CH), 121.8 (CH), 31.9 (CH$_2$), 31.5 (CH$_2$), 30.2 (CH$_2$), 29.5 (CH$_2$), 29.3 (CH$_2$), 29.2(9) (CH$_2$), 29.1 (CH$_2$), 22.7 (CH$_2$), 14.1 (CH$_3$). HRMS (EI) calculated for $C_{36}H_{44}O_2S_4$ 636.2224; found 636.2225 (M+2 (638.1) was observed as a major ion). Anal. Calcd. for $C_{36}H_{44}O_2S_4$: C, 67.88; H, 6.96. Found: C, 67.93; H, 6.87.

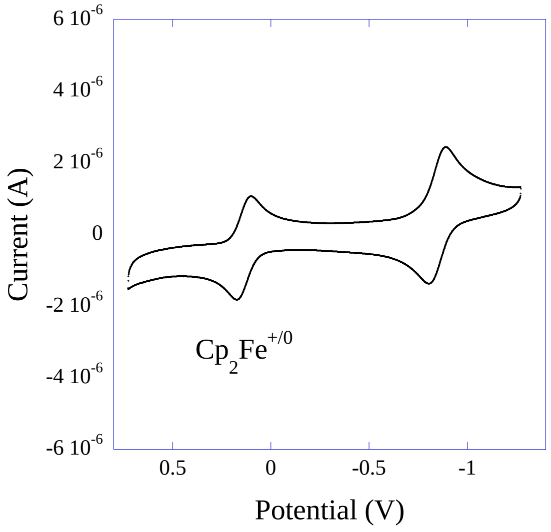


Figure S57. Cyclic voltammogram (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2,7-bis-(5-*n*-nonyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19b): $E_{1/2}^{0/1-}$ = -0.98 V (rev.).

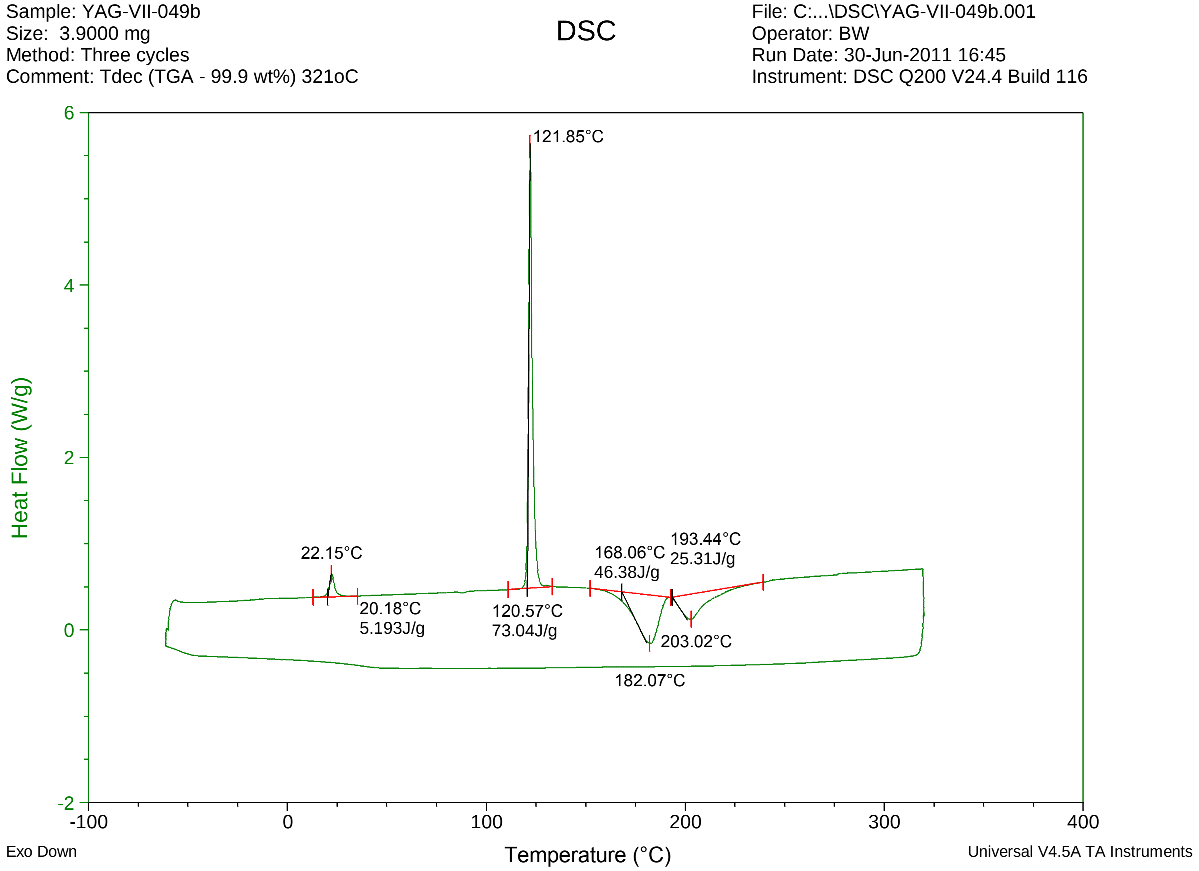


Figure S58. DSC analysis of 2,7-bis-(5-*n*-nonyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19b): on 1st heating two endothermic transitions (10 °C/min) at 22.2 °C and 121.9 °C, and two exothermic transitions (most probably decomposition) were observed.

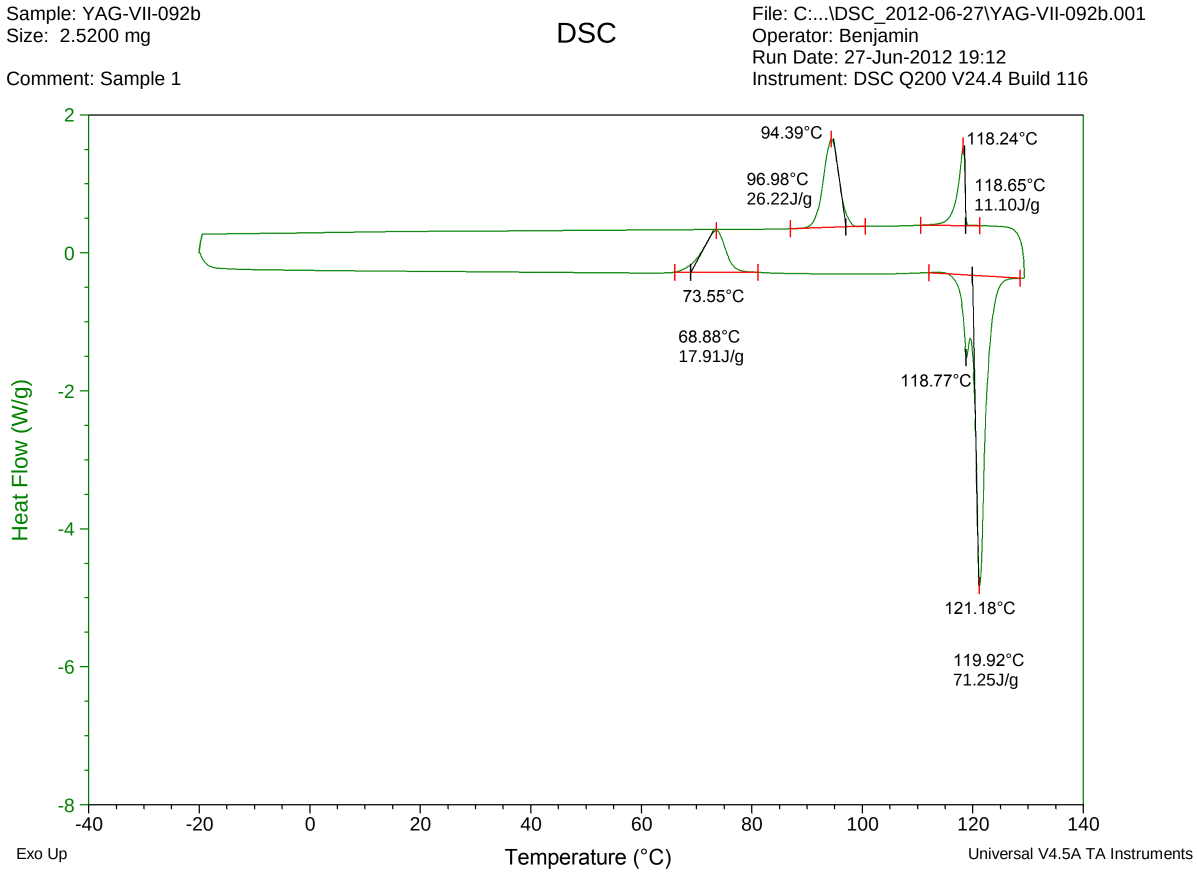


Figure S59. DSC analysis of 2,7-bis-(5-*n*-nonyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19b): 2nd heating-cooling cycle. On heating three transitions were observed: at 73.6 °C (exotherm, possibly crystallization), 118.8 and 119.9 (endotherm, Cr to LC, LC to Iso). On cooling two exothermal transitions at 118.2 (Iso to possibly LC phase) and at 94.4 (possibly LC to LC transition) were observed.

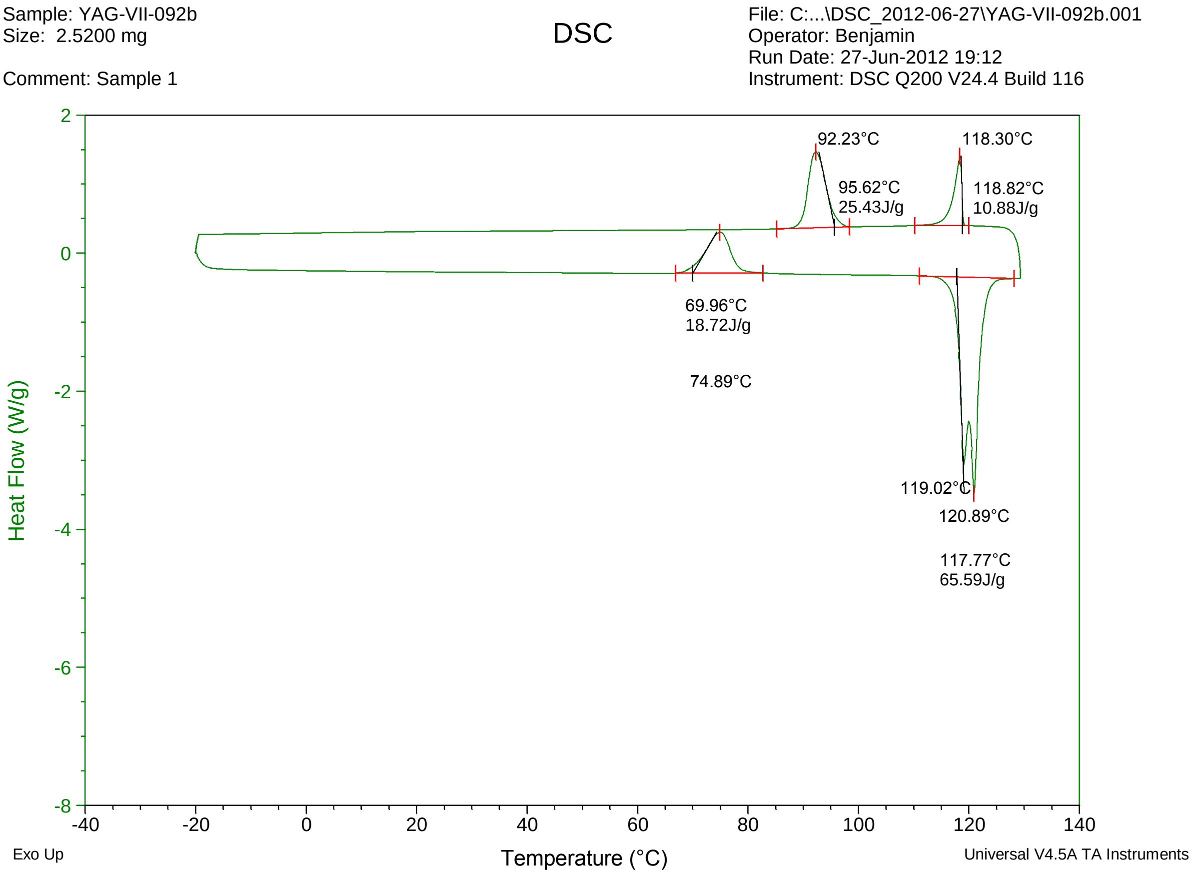
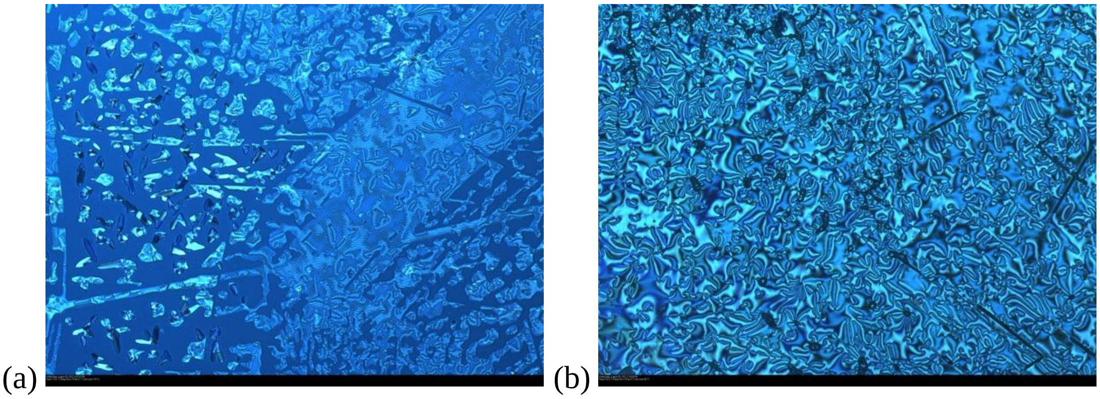


Figure S60. DSC analysis of 2,7-bis-(5-*n*-nonyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19b): 3rd heating-cooling cycle. On heating three transitions were observed: at 70.0 °C (exotherm, possibly crystallization), 119.0 and 120.9 (endotherm, Cr to LC, LC to Iso). On cooling two exothermal transitions at 118.3 (Iso to LC) and at 92.2 (LC to LC or Cr) were observed.


(a) (b)

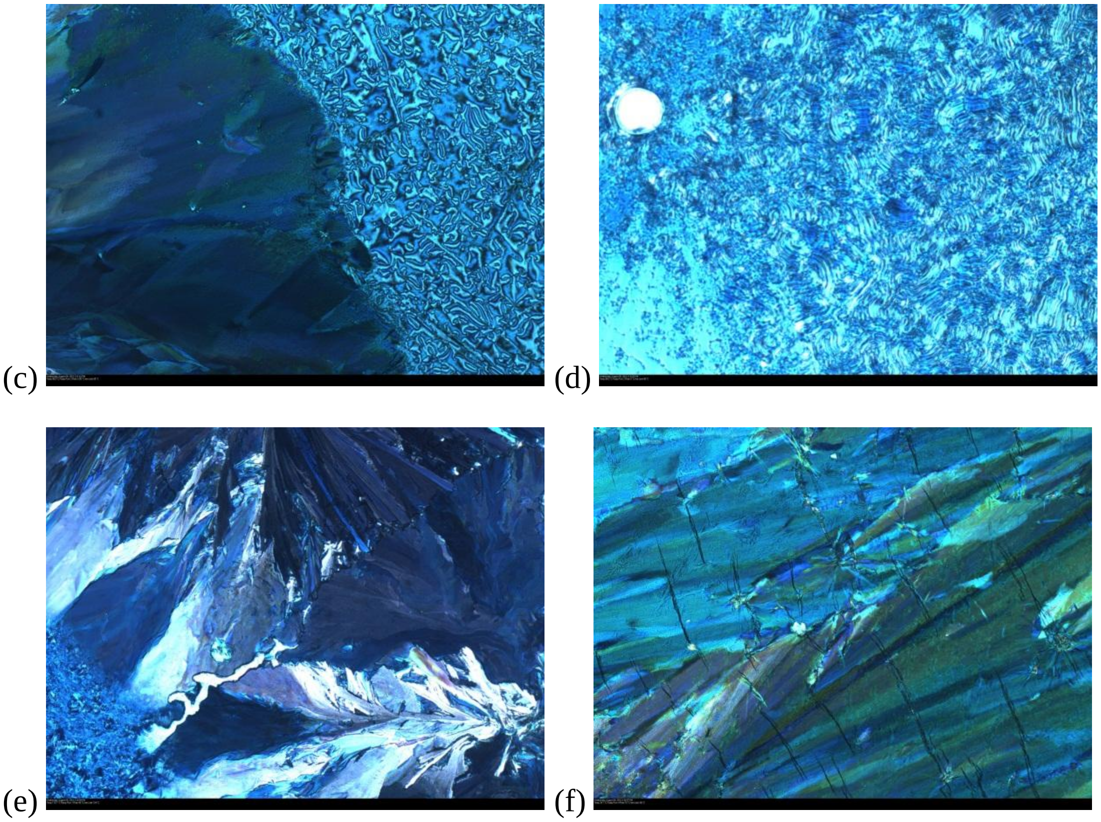


Figure S61. POM micrograph of 19b: (a) 119.2 °C, formation of the fan texture of SmC phase from isotropic liquid; (b) 103.0 °C, *schlieren* texture of SmC; (c) 98.5 °C, transition from SmC phase to Cr or higher order LC phase; (d) 95.0 °C, textures of Cr or higher order LC phase; (e) 115.7 °C, textures of Cr or higher order LC phase; (f) 34.1 °C, development of the cracks on cooling of Cr or higher order LC phase.

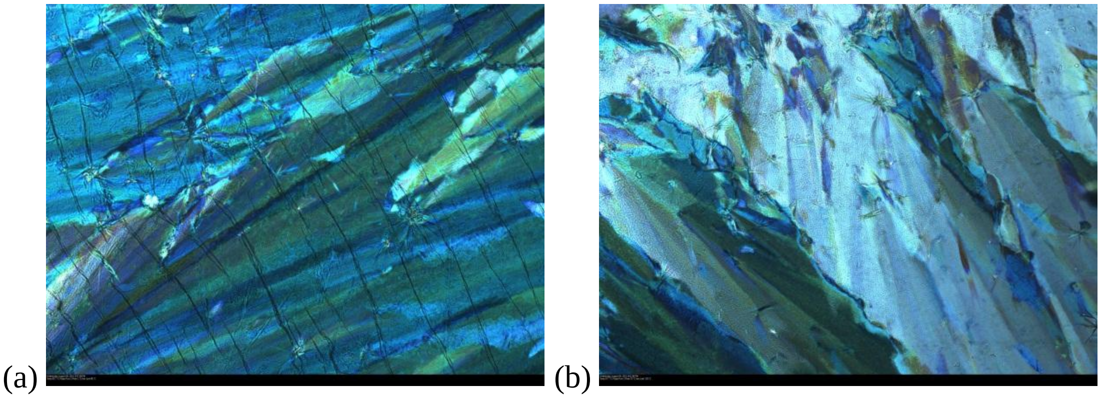
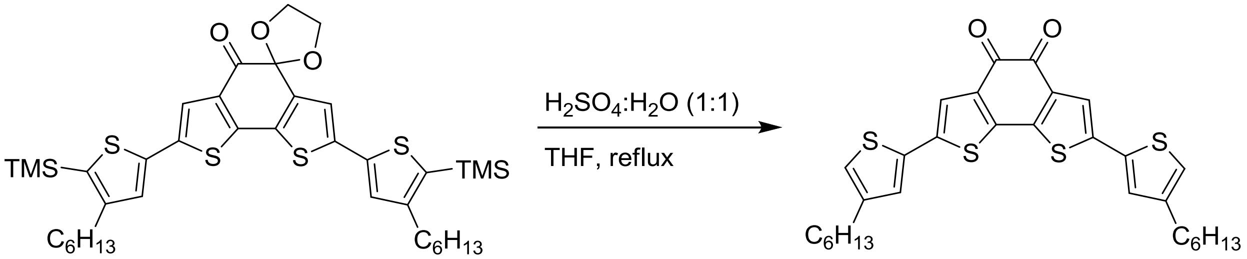


Figure S62. (a) 65.7 °C, before exothermic transition (detected by DSC on 2nd heating-cooling cycle at 74.9 °C); (b) 87.7 °C, on heating after the exothermic transition.

2,7-Bis-(4-*n*-hexylthiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19c)



Protected derivative (**20**) (1.09 mmol, 0.807 g) was dissolved in THF (30 mL), and aqueous H_2SO_4 (2 mL, 1:1 volume ratio) was added. The orange fluorescent reaction mixture was heated to reflux, and it became dark orange-brown. After reflux for 1.5 h the starting material was still detectable by TLC, and additional amount of aqueous H_2SO_4 (2 mL, 1:1 volume ratio) was added. The mixture was refluxed for additional 7 hours, and the dark blue solution was cooled to room temperature. TLC analysis (hexanes:chloroform (1:1) as eluant) showed complete consumption of the starting material. The mixture was treated with water (product precipitated out), and organic matter was extracted with diethyl ether several times. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and the solvent was removed by rotary evaporation. The crude product obtained as dark blue solid (0.5 g) was purified by column chromatography (silica gel, hexanes:dichloromethane (1:1) as eluant). Trace amount of unreacted starting material (less polar) was removed, blue fractions with desired product were subjected to rotary evaporation, and the residue was recrystallized from ~150 mL of 2-propanol. Purified material was obtained as black-blue solid (0.44 g, 73.1% yield). This material (100 mg) was further purified by three successive column chromatography purifications (silica gel, dichloromethane as eluant) for mobility measurements. The combined fractions were subjected to rotary evaporation, the residue was recrystallized twice from distilled 2-propanol, and dark blue material with grey shine was obtained after vacuum filtration. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (s, 2H), 7.05 (s, 2H), 6.91 (s, 2H), 2.59 (t, J = 7.7 Hz, 4H), 1.61 (m, 4H), 1.40-1.23 (m, 12H), 0.91 (t, J = 6.5 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 174.18 (quaternary C(O)), 144.65 (quaternary C), 141.40 (quaternary C), 138.38 (quaternary C), 135.66 (quaternary C), 134.49 (quaternary C), 126.66 (CH), 122.41 (CH), 121.22 (CH), 31.66 (CH_2), 30.41 (CH_2), 30.33 (CH_2), 28.97 (CH_2), 22.62 (CH_2), 14.12 (CH_3) (assignment of the carbon signals was made based on the DEPT experiment). HRMS (EI) calculated for $C_{30}H_{32}O_2S_4$ 552.1285; found 552.1263. Anal. Calcd. for $C_{30}H_{32}O_2S_4$: C, 65.18; H, 5.83. Found: C, 65.38; H, 5.80.

DSC analysis (10 ºC/min rate): 140.2 ºC (melting point observed on first heating), two small enthalpy transitions at 55.5 and 85.0 ºC were also observed on first heating; no crystallization peak was detected on cooling, and a small enthalpy peak was observed at 67.0 ºC (similar material[6] with different position of *n*-hexyl chains showed m.p. at 150 ºC).

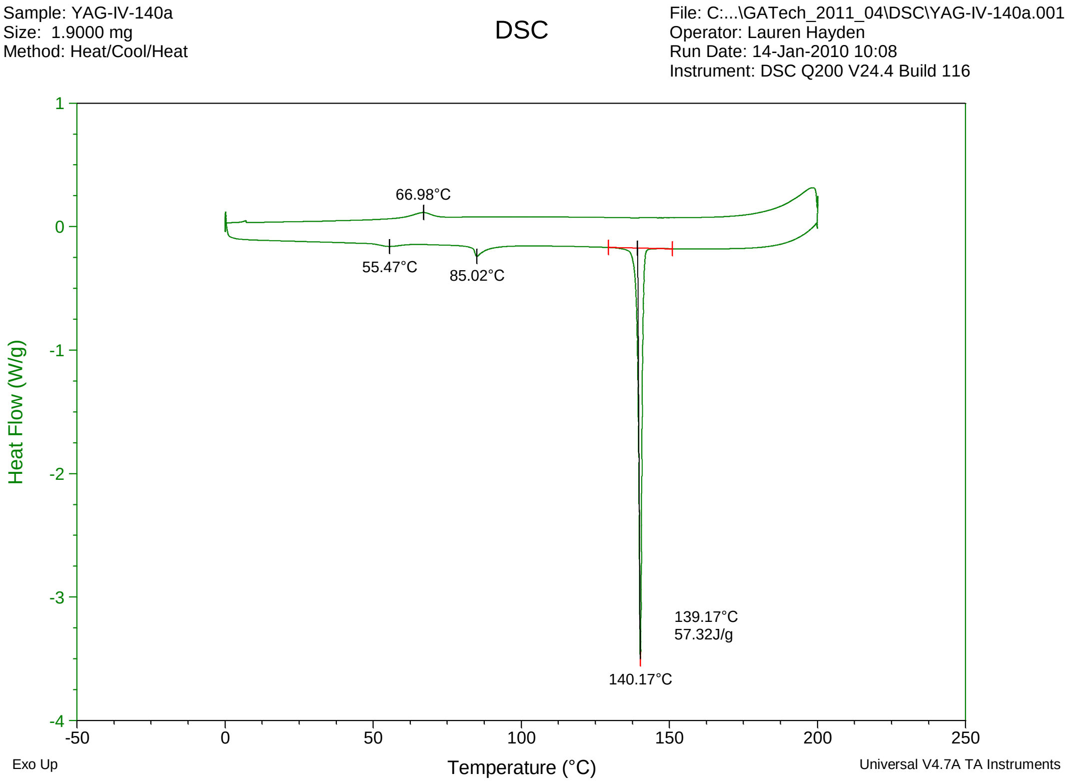


Figure S63. DSC analysis of 2,7-bis-(4-*n*-hexylthiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19c).

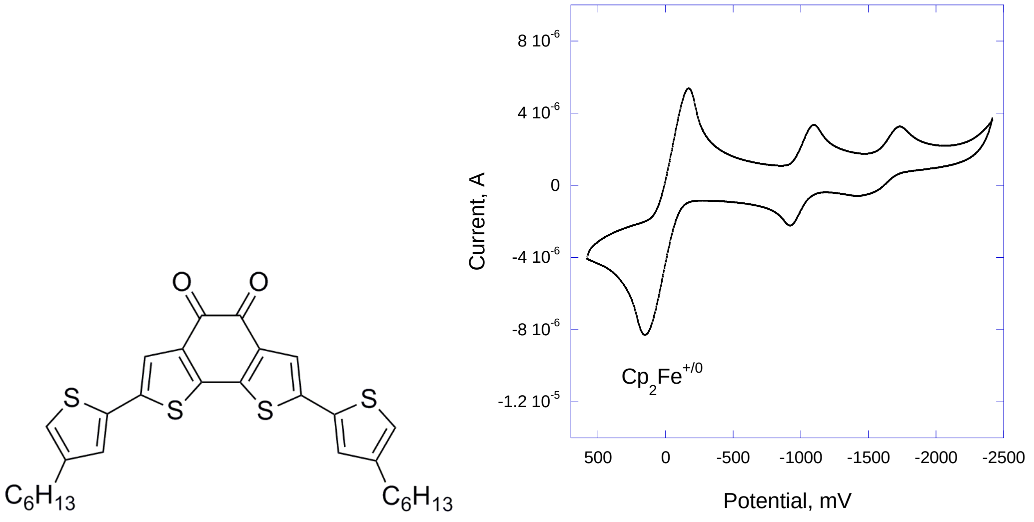
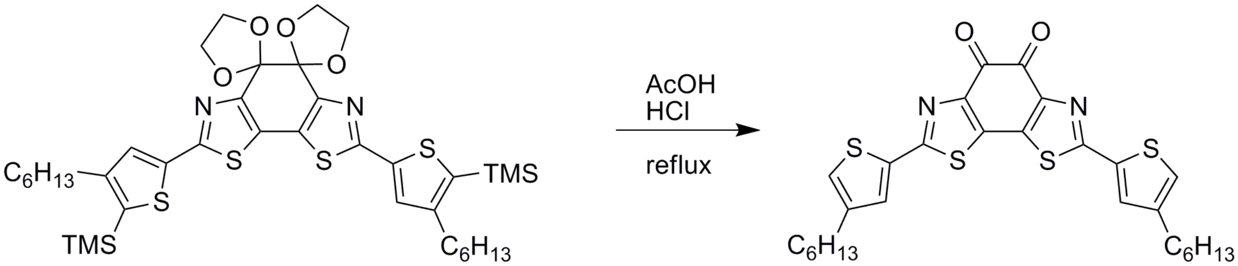


Figure S64. Structure and CV analysis (0.1 M $^nBu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV rate) of 2,7-bis-(4-*n*-hexylthiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (19c): $E_{1/2}^{0/1-}$ = -1.00 V (reversible), $E_{1/2}^{1-/2-}$ = -1.60 V (partially reversible).

2,7-Bis-(4-*n*-hexyl-thiophene-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (19d)



2,7-Bis-(5-trimethylsilyl-4-*n*-hexyl-thiophene-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**22**) (0.13 mmol, 0.102 g) was mixed with acetic acid (10 mL), and the suspension was heated to reflux. HCl (1 mL) was added to a bright yellow mixture, and it quickly became brown, and then precipitate formed. Reaction mixture was cooled to room temperature, and precipitate was separated by vacuum filtration (0.057 g, 79.2% crude yield). This material was purified by column chromatography (silica gel, dichloromethane, then dichloromethane:ethyl acetate (50:1) as eluants). Middle fractions with the product were combined, the solvents were removed by rotary evaporation, and the residue was heated to reflux with 2-propanol, and then cooled. Very dark tiny crystals (solution was purple) were filtered off and dried (28.4 mg). Several first and last fractions were combined with mother liquor, dichloromethane was removed by rotary evaporation, and little purple crystals were filtered off and dried (20.4 mg) (85.6% combined recovery; 67.8% purified yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (s, 2H), 7.12 (s, 2H), 2.62 (t, J = 7.7 Hz, 4H), 1.64 (m, 4H), 1.33 (m, 12H), 0.90 (t, J = 6.2 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 171.4 (C(O), 162.3 (quaternary C), 147.7 (quaternary C), 145.0 (quaternary C), 136.6 (quaternary C), 134.4 (quaternary C), 130.5 (CH), 125.8 (CH), 31.6 (CH_2), 30.3 (two CH_2), 28.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3). HRMS (EI) calculated for $C_{28}H_{30}N_2O_2S_4$ 554.1190. Found: 554.1182 (M+2 was observed as a major ion: calculated for ($C_{28}H_{30}N_2O_2S_4$ + 2H) 556.1347; found 556.1299). Anal. Calcd. for $C_{28}H_{30}N_2O_2S_4$: C, 60.62; H, 5.45; N, 5.05. Found: C, 60.62; H, 5.47; N, 5.03.

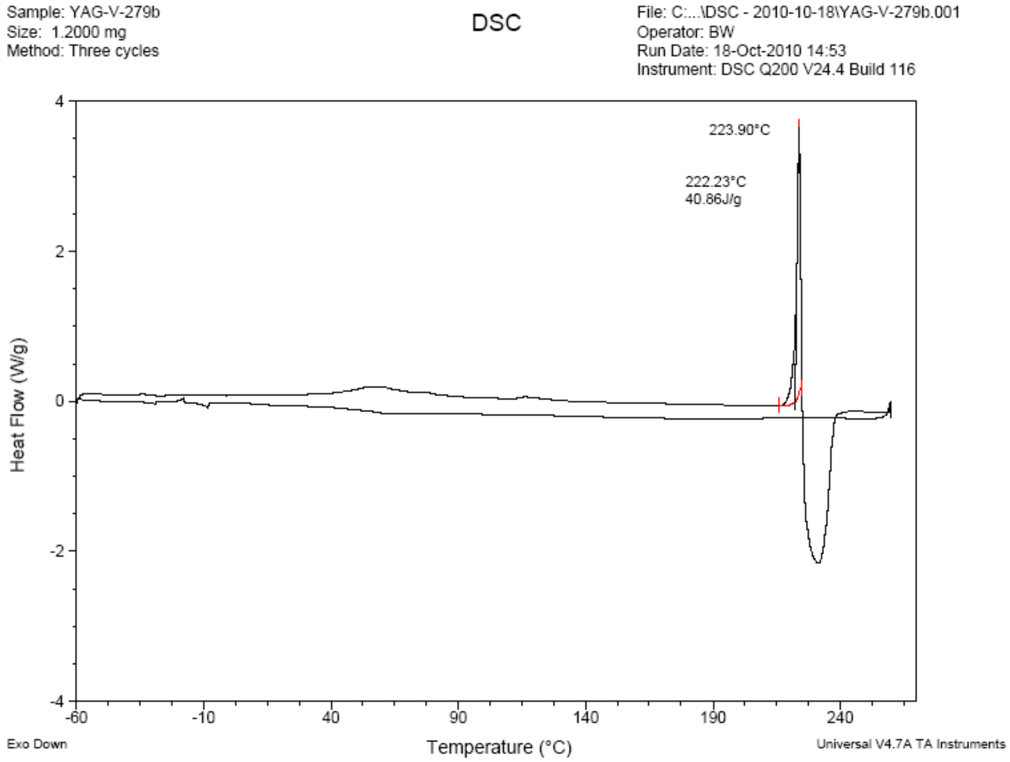


Figure S65. DSC analysis of 2,7-bis-(4-*n*-hexyl-thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione: m.p. 223.9 °C (decomposition).

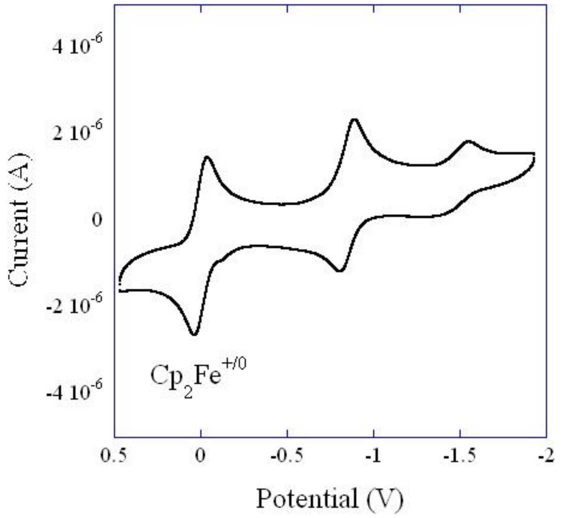
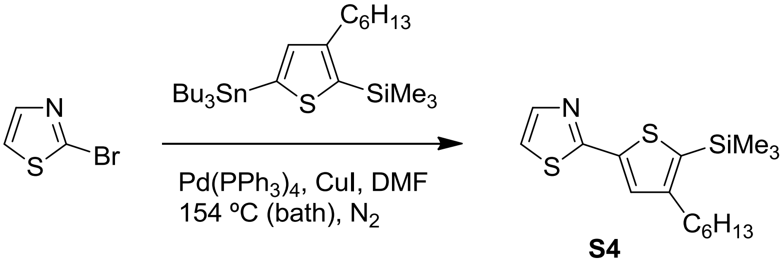


Figure S66. Cyclic voltammogram (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2,7-bis-(4-*n*-hexyl-thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (19d): $E_{1/2}^{0/1-}$ = -0.85 V (rev.), $E_{1/2}^{1-/2-}$ = -1.49 V (partially reversible)

2,7-Bis-(4-*n*-hexyl-5-trimethylsilyl-thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (19e)

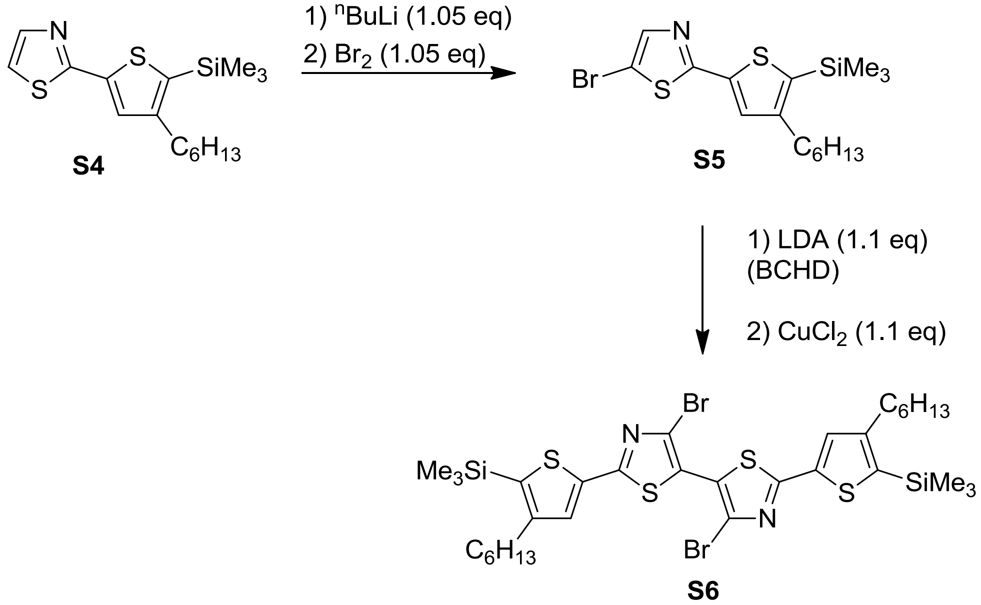
Step 1. 2-(4-*n*-Hexyl-5-(trimethylsilyl)thiophen-2-yl)-thiazole (S4).



S4

2-Bromothiazole (1.05 eq., 21.0 mmol, 3.44 g) was mixed with 2-trimethylsilyl-3-*n*-hexyl-5-tri-*n*-butylstannylthiophene (1.00 eq., 20.0 mmol, 10.60 g) in an oven-dried Schenk flask equipped with magnetic stirbar. Catalyst $Pd(PPh_3)_4$ (0.01 mol%, 0.2 mmol, 0.23 g), CuI (0.003 mmol, 0.06 mmol, 11.0 mg), and anhydrous DMF (40 mL) were added under nitrogen atmosphere, and the yellowish suspension was heated up to 155 ºC (bath temperature). The mixture became dark orange, and after heating for 0.5 h it became grey-black. The TLC analysis (dichloromethane as eluant) confirmed the complete consumption of stannane, and the mixture was cooled to room temperature. The reaction mixture was treated with water (~50 mL), and organic phase was extracted with hexanes several times. The combined organic phases were dried over anhydrous magnesium sulfate, and the solvents were removed by rotary evaporation to give crude product as yellow-orange oil. This crude material was purified by column chromatography (silica gel, hexanes:dichloromethane (2:1) as eluant). Fractions with the pure product were combined, the solvents were removed and the product was obtained as yellowish oil (3.50 g). Two first fractions with trace amount of impurities were combined separately and additional amount of product was obtained (0.75 g). Total yield of the product was 65.7% (4.25 g). GC/MS: 323 (exact mass calculated for $C_{16}H_{25}NS_2Si$ 323.1198). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74 (d, J = 3.28 Hz, 1H), 7.45 (s, 1H), 7.21 (d, J = 3.28 Hz, 1H), 2.65 (m, 2H), 1.65 (m, 2H), 1.45-1.25 (m, 6H), 1.38 (m, 3H), 0.37 (s, 18H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 161.92 (quaternary C), 151.05 (quaternary C), 143.20 (CH), 140.32 (quaternary C), 136.29 (quaternary C), 129.48 (CH), 117.84 (CH), 31.65 (CH_2), 31.79 (CH_2), 31.57 (CH_2), 31.33 (CH_2), 29.28 (CH_2), 22.54 (CH_2), 14.02 (CH_3), 0.14 (CH_3 of $SiMe_3$) (assignment of the quaternary, CH, CH_2 and CH_3 signals was made based on the DEPT experiment). Anal. Calcd. for $C_{16}H_{25}NS_2Si$: C, 59.39; H, 7.79; N, 4.33. Found: C, 59.24; H, 7.99, N, 4.28.

Step 2. 4,4'-Dibromo-2,2'-bis(4-hexyl-5-(trimethylsilyl)thiophen-2-yl)-5,5'-bithiazole (S6)



2-(4-*n*-Hexyl-5-(trimethylsilyl)thiophen-2-yl)-thiazole (**S4**) (3.0 mmol, 0.97 g) was dissolved in anhydrous THF (30 mL) under nitrogen atmosphere, and the yellowish solution was cooled in acetone/dry ice bath. *n*-Butyllithium (1 eq., 1.6 M in hexanes, 3.0 mmol, 1.88 mL) was added dropwise, and the yellowish solution became darker yellow in color. The reaction mixture was stirred for 20 minutes, and bromine (1.05 eq., 3.15 mmol, 0.50 g) was added dropwise. The reaction mixture was analyzed by GC/MS analysis, and clean formation of 2-(4-*n*-hexyl-5-(trimethylsilyl)thiophen-2-yl)-5-bromo-thiazole (**S5**) (401 and 403 molecular ion, 19.03 minutes) was confirmed. LDA (1.1 eq., 1.2 M in hexanes-THF, 2.75 mL) was added dropwise, and the reaction mixture became purple in color. The reaction mixture was analyzed by GC/MS, and completion of the BCHD reaction was confirmed (401 and 403 molecular ion, 19.24 min). Anhydrous $CuCl_2$ (1.1 eq., 3.3 mmol, 0.44 g) was added in one portion, and the purple mixture became brown-yellow. The reaction mixture was stirred for ~2 h, warmed to room temperature and treated with hexanes (some copper salts partially precipitated out). The organic solvents were removed by rotary evaporation, and the crude product was obtained as brown-yellow matter. This crude material was purified by column chromatography (silica gel, hexanes:dichloromethane (35:15) as eluant). Fractions with the product (**S6**) were combined, the solvents were removed by rotary evaporation, and the residue (very thick yellow-orange oil) was treated with ~20 mL of 2-propanol. Material solidified on scratching, and was recrystallized from 2-propanol. Bright yellow solution produced yellow-orange crystals on cooling (0.89 g, 74% yield).

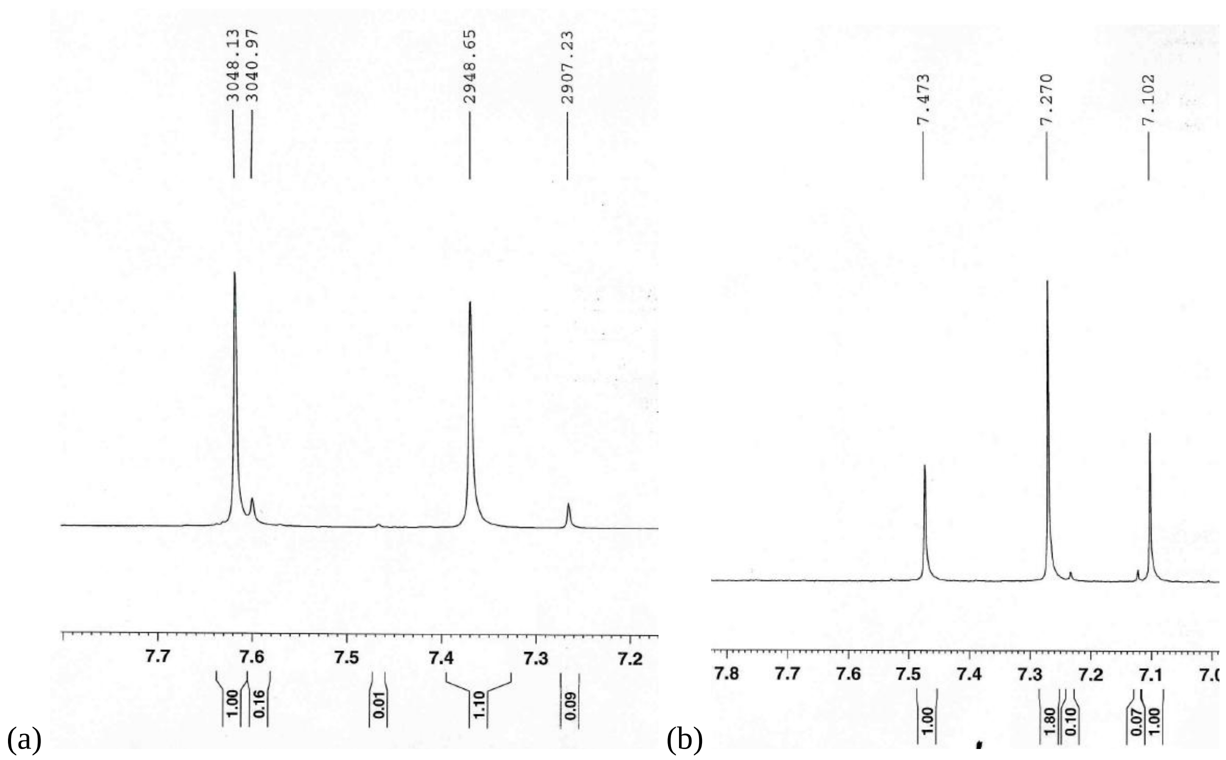
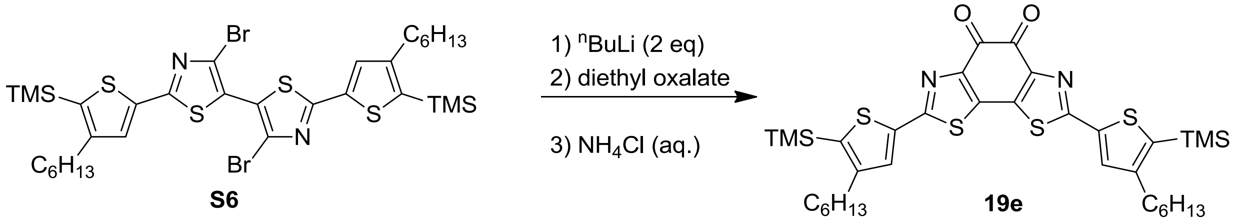


Figure S67. Aromatic region of ^{1}H NMR spectra (400 MHz, CDCl$_3$) of (a) starting 2-(5-trimethylsilyl-3-*n*-hexyl-thiophen-2-yl)-5-bromothiazole and (b) its BCHD reaction product, 2-(5-trimethylsilyl-3-*n*-hexyl-thiophen-2-yl)-4-bromothiazole.

2-(4-*n*-Hexyl-5-trimethylsilylthiophen-2-yl)-5-bromo-thiazole (S5): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.62 (s, 1H), 7.37 (s, 1H), 2.64 (t, *J* = 8.0 Hz, 2H), 1.61 (m, 2H), 1.42-1.28 (m, 6H), 0.91 (t, *J* = 6.7 Hz, 3H), 0.36 (s, 9H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 163.14 (quaternary C), 151.13 (quaternary C), 144.35 (CH), 139.65 (quaternary C), 137.12 (quaternary C), 129.63 (CH), 107.33 (quaternary C-Br), 31.66 (CH$_2$), 31.57 (CH$_2$), 31.29 (CH$_2$), 29.28 (CH$_2$), 22.56 (CH$_2$), 14.03 (CH$_3$), 0.12 (CH$_3$ of SiMe$_3$) (this material contained ~8% of impurity based on NMR analysis).

4,4'-Dibromo-2,2'-bis(4-hexyl-5-(trimethylsilyl)thiophen-2-yl)-5,5'-bithiazole (S6): ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.53 (s, 2H), 2.66 (t, *J* = 8.0Hz, 4H), 1.62 (m, 4H), 1.45-1.30 (m, 12H) 0.98 (t, *J* = 6.9 Hz, 6H), 0.38 (s, 18H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 162.14 (quaternary C), 151.42 (quaternary C), 138.95 (quaternary C), 138.54 (quaternary C), 130.51 (CH), 127.57 (quaternary C), 120.98 (quaternary C), 31.68 (CH$_2$), 31.59 (CH$_2$), 31.32 (CH$_2$), 29.32 (CH$_2$), 22.58 (CH$_2$), 14.06 (CH$_3$), 0.14 (CH$_3$) (assignment of CH, CH$_2$ and CH$_3$ signals was made based on the DEPT-135 experiment). HRMS (EI) calculated for $C_{32}H_{46}Br_2N_2S_4Si_2$ 800.0449; found 800.0420. Anal. Calcd. for $C_{32}H_{46}Br_2N_2S_4Si_2$: C, 47.87; H, 5.77; N, 3.49. Found: C, 47.72; H, 5.77; N, 3.47.

Step 3.



4,4'-Dibromo-2,2'-bis(4-hexyl-5-(trimethylsilyl)thiophen-2-yl)-5,5'-bithiazole (**S6**) (0.5 mmol, 0.40 g) was dissolved in anhydrous THF (50 mL) under nitrogen atmosphere and the resulting bright yellow solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2 eq., 1.6 M in hexanes, 1.0 mmol, 0.63 mL) was added dropwise, and bright orange solution was stirred for 10 minutes. This mixture was transferred via cannula into a solution of diethyl oxalate (0.55 mmol, 0.08 g) in anhydrous THF. The flask with greenish-yellow reaction mixture was partially removed from the cooling bath, and after stirring for ~ 15 minutes the reaction mixture was transferred via cannula into aqueous solution of NH_4Cl. Initially green organic phase quickly became dark red-grey-greenish. The organic phase was removed, the aqueous phase was extracted with hexanes, and combined organic phases were dried over $MgSO_4$. The solvents were removed, and the residue was purified by column chromatography (silica gel, hexanes:dichloromethane(4:1, 2:1) then dichloromethane:ethyl acetate (30:1) as eluants). Fractions with green product (still impure) were combined, the solvents were removed to give greenish-brownish residue, which was further purified by column chromatography (silica gel, dichloromethane as eluant). Combined fractions were subjected to rotary evaporation, and blue-green very dark residue was isolated (0.025 g, 7.1% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (s, 2H), 2.65 (t, J = 7.96 Hz, 4H), 1.61 (m, 4H), 1.45-1.30 (m, 12H), 0.91 (t, J = 6.60 Hz, 6H), 0.38 (s, 18H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 171.52, 162.00, 151.63, 147.85, 140.92, 137.83, 136.76, 131.95, 31.70, 31.56, 31.28, 22.61, 14.09, 0.09. HRMS (EI) calculated for $C_{34}H_{46}N_2O_2S_4Si_2$ 698.1981; found 698.1970. Anal. Calcd. for $C_{34}H_{46}N_2O_2S_4Si_2$: C, 58.41; H, 6.63; N, 4.01. Found: 58.50; H, 6.64, N, 4.11

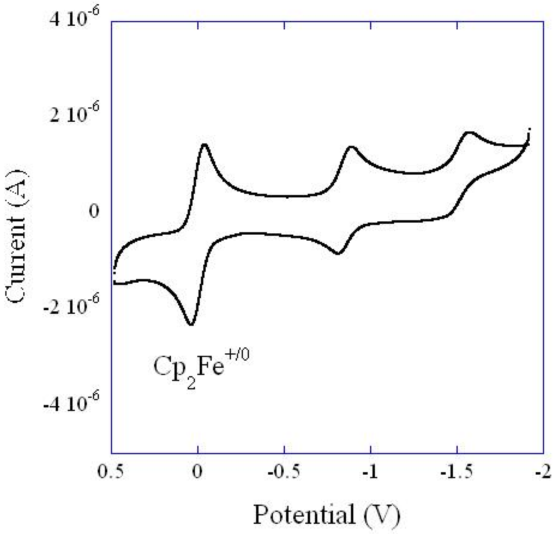
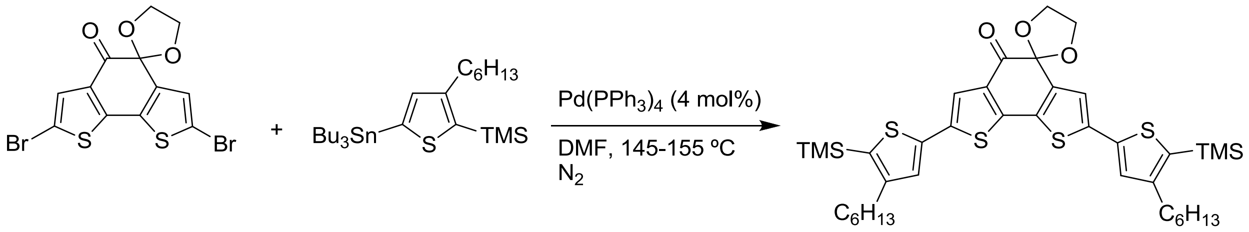


Figure S68. Cyclic voltammogram (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2,7-bis-(4-*n*-hexyl-5-trimethylsilyl-thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (19e): $E_{1/2}^{0/1-}$ = -0.85 V (reversible), $E_{1/2}^{1-/2-}$ = -1.51 V (partially reversible).

2,7-Bis-(4-*n*-hexylthiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4-one-5-(1,3-dioxolane) (20)



Aryl dibromide (**5b**) (3.0 mmol, 1.266 g) was mixed with 5-trimethylsilyl-3-*n*-hexyl-2-tri-*n*-butylstannylthiophene (2.1 eq., 6.3 mmol, 3.34 g) in the oven-dried two-neck flask equipped with magnetic stirbar, nitrogen inlet and septum. Catalyst $Pd(PPh_3)_4$ (0.02 mol%, 0.06 mmol, 0.069 g) and anhydrous *N*,*N*-dimethylformamide (40 mL) were added, and the bright yellow suspension was heated up to 145-155 ºC (bath temperature). After 15 minutes of stirring a very dark red mixture was cooled to room temperature, treated with water and organic matter was extracted with diethyl ether. The organic phase was separated, the aqueous phase was extracted with diethyl ether several times, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, the solvents were removed by rotary evaporation, and orange-red oil was purified by column chromatography (silica gel, hexanes:dichloromethane (2:1) as eluant). Combined fractions were subjected to rotary evaporation, and product was obtained as red oil, which solidified on standing (2.15 g, 96.4%). Part of this material (0.54 g) was further purified by column chromatography (silica gel, hexanes to pack the column, dichloromethane:hexanes (1:1) to elute the product), and pure material was obtained after solvent removal (red solid, 0.54 g, ~100% recovery). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (s, 1H), 7.21 (s, 1H), 7.16 (s, 1H), 7.14 (s, 1H), 4.52 (m, 2H), 4.36 (m, 2H), 2.63 (t, J = 7.94 Hz, 4H), 1.45-1.25 (m, 12H), 0.95-0.80 (m, 6H), 0.36 (s, 18H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 190.67 (quaternary C(O)), 151.42 (quaternary C), 151.39 (quaternary C), 143.39 (quaternary C), 140.05 (quaternary C), 139.56 (quaternary C), 139.13 (quaternary C), 138.43 (quaternary C), 135.70 (quaternary C), 134.20 (quaternary C), 132.09 (quaternary C), 130.06 (quaternary C), 127.95 (CH), 127.86 (CH), 123.43 (CH), 120.99 (CH), 99.37 (quaternary C), 66.14 (CH_2), 31.72 (CH_2), 31.65 (CH_2), 31.41 (CH_2), 29.37 (CH_2), 22.60 (CH_2), 14.08 (CH_3), 0.28 (CH_3) (one quaternary C is missing presumable due to overlap; assignment of CH, CH_2 and CH_3 signals was made based on the DEPT-135 experiment). HRMS (EI) calculated for $C_{38}H_{52}O_3S_4Si_2$ 740.2338; found740.2336. Anal. Calcd. for $C_{38}H_{52}O_3S_4Si_2$: C, 61.57; H, 7.07. Found: C, 61.41; H, 7.20.

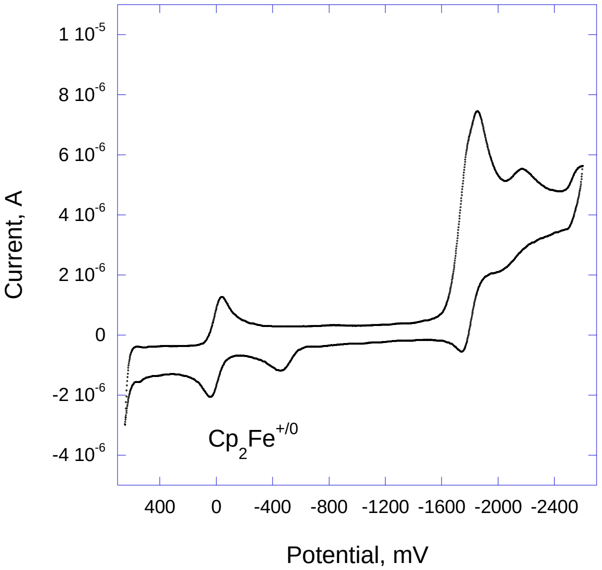
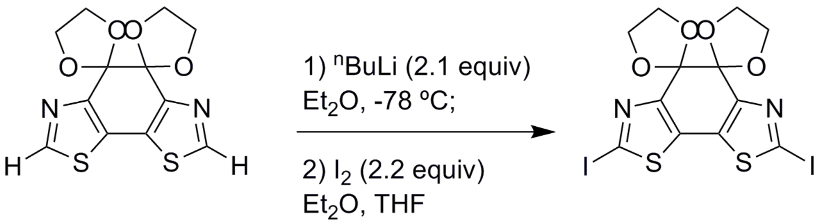


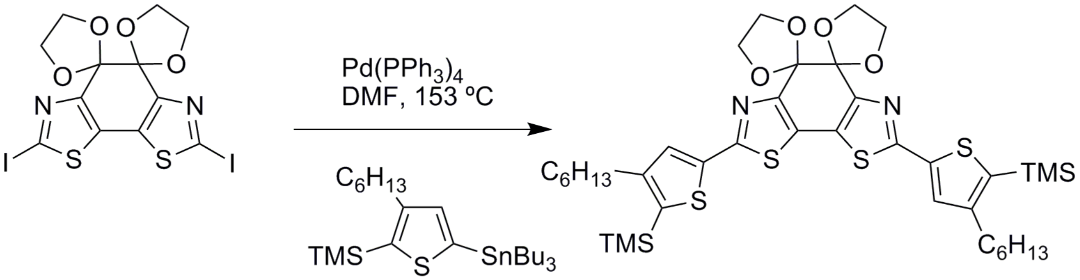
Figure S69. CV analysis of 2,7-bis-(4-*n*-hexylthiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4-one-5-(1,3-dioxolane) (20) (0.1 M $^nBu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV rate): $E_{1/2}^{0/1-}$ = -1.80 V (partially reversible), $E_{1/2}^{1-/2-}$ = -2.11 V (partially reversible).

2,7-Diiodo-benzo[2,1-*b*:3,4-*b'*]thiazole-4,5-bis-(1,3-dioxolane) (21)



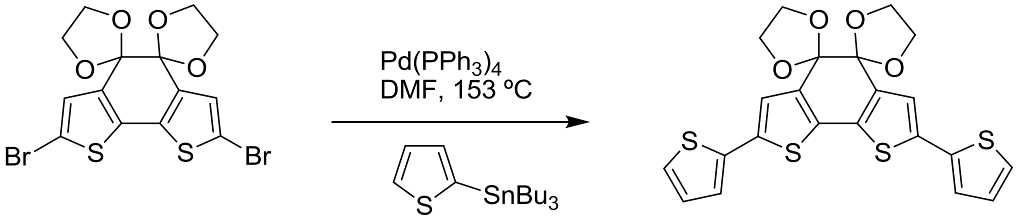
Benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**15**) (2.0 mmol, 0.62 g) was dissolved in a mixture of anhydrous THF (100 mL) and anhydrous diethyl ether (50 mL) under nitrogen atmosphere, and the solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 2.1 eq., 4.2 mmol, 1.5 mL) was added dropwise to a colorless solution, and it became yellow-orange in color with precipitate. The mixture was stirred for 20 minutes and a solution of iodine (2.2 eq., 4.4 mmol, 1.12 g) in anhydrous THF (20 mL) was added dropwise. The reaction mixture (suspension) became red, then orange, and then orange-red solution. After stirring for 10 minutes the reaction mixture was allowed to warm to room temperature, and then treated with aqueous $Na_2S_2O_3$. The mixture was transferred to a round bottom flask, and the organic solvents were removed by rotary evaporation. The off-white solid with some dark matter of the sides of the flask was separated by vacuum filtration, and the filtrate was extracted with dichloromethane. This organic phase was combined with the solid, and brown solution was column chromatographed (silica gel, dichloromethane:ethyl acetate (10:1) as eluant). Combined fractions were subjected to rotary evaporation, and the product was obtained as white solid (0.35 g, 31.1% yield). The material became yellowish after a few hours of exposure to ambient conditions. The residue on the sides of the flask was dissolved in boiling 2-propanol, and yellow tiny crystals formed on cooling (~50 mg). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.30 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 153.78, 129.35, 106.21, 98.83, 67.16. HRMS (EI) calculated for $C_{12}H_8I_2N_2O_4S_2$ 561.8015; found 561.8019. Anal. Calcd. for $C_{12}H_8I_2N_2O_4S_2$: C, 25.64; H, 1.43; N, 4.98. Found: C, 25.80; H, 1.34; N, 4.94.

2,7-Bis-(4-*n*-hexyl-5-trimethylsilylthiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (22)



2,7-Diiodo-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**21**) (0.35 mmol, 0.197 g), 2-tri-*n*-butylstannyl-4-*n*-hexyl-5-trimethylsilyl-thiophene (2.1 eq., 0.735 mmol, 0.39 g) and $Pd(PPh_3)_4$ (5 mol%, 0.0175 mmol, 0.02 g) were mixed in an oven-dried flask under nitrogen atmosphere. Anhydrous DMF (10 mL) was added, and the reaction mixture (yellowish suspension) was heated to reflux. A yellow solution became yellow-orange, then orange-reddish, and within a few minutes dark yellow-brown. The reaction mixture was cooled to room temperature, treated with water, and organic matter was extracted with hexanes:dichloromethane. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and organic solvents were removed by rotary evaporation to give crude product as orange-reddish oil. This crude material was purified by column chromatography (silica gel, dichloromethane to pack the column, then ~200 mL of hexanes, and then dichloromethane as eluants). Fractions with a product slightly contaminated product were combined, the solvents were removed, and material was purified by column chromatography (silica gel, hexanes:dichloromethane (1:3), then dichloromethane as eluants). Combined fractions were subjected to rotary evaporation, and yellow solid was obtained (0.201 g, 72.8% yield). Last fractions with product were combined separately, the solvents were removed by rotary evaporation and the residue (~50 mL) was dissolved in ethanol under heating. Long yellow needles grew on cooling (potentially suitable for single crystal X-ray structural analysis). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45 (s, 2H), 4.41-4.30 (two overlapping m, 8H), 2.64 (t, J = 7.8 Hz), 1.70-1.58 (m, 4H, overlap with water signal, observed integration 8H), 1.50-1.30 (m, 12H), 0.90 (t, 6H), 0.40-0.30 (s, 18H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 160.0 (quaternary C), 152.6 (quaternary C), 151.1 (quaternary C), 139.8 (quaternary C), 137.3 (quaternary C), 129.9 (CH), 123.7, 106.8, 67.2 (CH_2), 31.7 (CH_2), 31.6 (CH_2), 31.4 (CH_2), 29.3 (CH_2), 22.6 (CH_2), 14.1 (CH_3), 0.2 (CH_3). HRMS (EI) calculated for $C_{38}H_{54}N_2O_4S_4Si_2$ 786.2505; found 786.2525. Anal. Calcd. for $C_{38}H_{54}N_2O_4S_4Si_2$: C, 57.96; H, 6.91; N, 3.56. Found: C, 58.01; H, 6.89; N, 3.59.

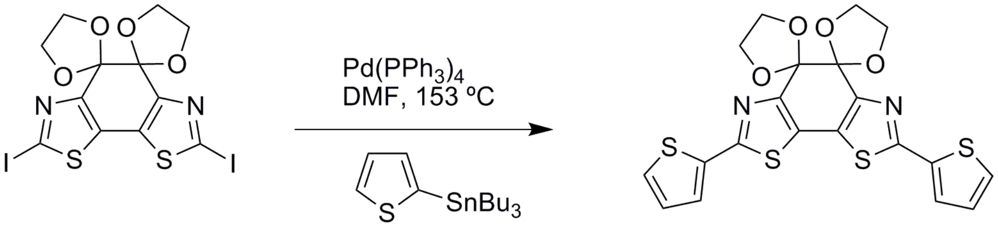
2,7-Bis-(thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(1,3-dioxolane) (23)



2,7-Dibromo-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(1,3-dioxolane) (**7**) (4.5 mmol, 2.10 g), 2-tri-*n*-butylstannyl-thiophene (2.1 eq., 9.45 mmol, 3.53 g) and $Pd(PPh_3)_4$ (2 mol%, 0.09 mmol, 0.10 g) were mixed in an oven-dried flask under nitrogen atmosphere. Anhydrous DMF (30 mL) was added, and the yellowish suspension was heated to 153 ºC. The reaction mixture became bright yellow, then yellow-orange, orange-red, and then brown within a few minutes. The reaction mixture was cooled to room temperature, water, hexanes and diethyl ether were added, and orange precipitate was separated by vacuum filtration (2.1 g). This material was purified by column chromatography (silica gel, dichloromethane as eluant). Bright yellow fluorescent fractions with the product were combined, the solvent was removed by rotary evaporation, and bright yellow solid was obtained (1.90 g, 89.2% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23 (dd, J = 5.1 Hz, 1.1 Hz, 2H), 7.16 (s overlapping with dd, J = 3.6 Hz, 1.1 Hz, 4H), 7.02 (dd, J = 5.1 Hz, 3.6 Hz, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 138.79, 136.84, 135.76, 130.81, 127.87 (CH), 124.71 (CH), 123.85 (CH), 121.76 (CH), 107.80, 66.65 (CH_2). HRMS (EI) calculated for

$C_{22}H_{16}O_4S_4$ 471.9931; found 471.9928. Anal. Calcd. for $C_{38}H_{54}N_2O_4S_4Si_2$: C, 55.91; H, 3.41. Found: C, 55.87; H, 3.57.

2,7-Bis-(thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (24)



2,7-Diiodo-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**21**) (0.20 mmol, 0.11 g) was mixed with 2-tri-*n*-butylstannyl-thiophene (2.1 eq., 0.42 mmol, 0.157 g) and $Pd(PPh_3)_4$ (0.05 eq., 0.01 mmol, 11.6 mg) in the oven-dried flask under nitrogen atmosphere. Anhydrous DMF (15 mL) was added, and the mixture was heated up to 153 ºC. The reaction mixture became orange, and then brown-yellow when it was reaching the boiling point. TLC analysis showed the presence of a new yellow spot, the mixture was cooled to room temperature, and treated with water. The organic matter was extracted with dichloromethane:diethyl ether mixture, combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and the solvents were removed by rotary evaporation to give crude product as bright yellow-orange solid with some oil. This crude product was purified by column chromatography (silica gel, dichloromethane, then dichloromethane:ethyl acetate (100:1, 25:1). Fractions with slightly contaminated product were combined, subjected to rotary evaporation, and the residue was recrystallized from 2-propanol:dichloromethane. Material was obtained as yellow-orange plates in 76.3% yield (72.5 mg). A slightly better yield (80%) was obtained on larger scale (0.35 mmol of diiodide **21**). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (dd, *J* = 3.7 Hz, 1.02 Hz, 2H), 7.41 (dd, *J* = 5.0 Hz, 1.0 Hz, 2H), 7.07 (dd, *J* = 5.0 Hz, 3.8 Hz, 2H), 4.45-4.30 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 160.06, 152.59, 136.80, 128.26, 127.85, 126.85, 123.57, 106.67, 67.21. HRMS (EI) calculated for $C_{20}H_{14}N_2O_4S_4$: 473.9836; found 473.9832. Anal. Calcd. for $C_{20}H_{14}N_2O_4S_4$: C, 50.61; H, 2.97; N, 5.90. Found: C, 50.41; H, 2.83; N, 5.88.

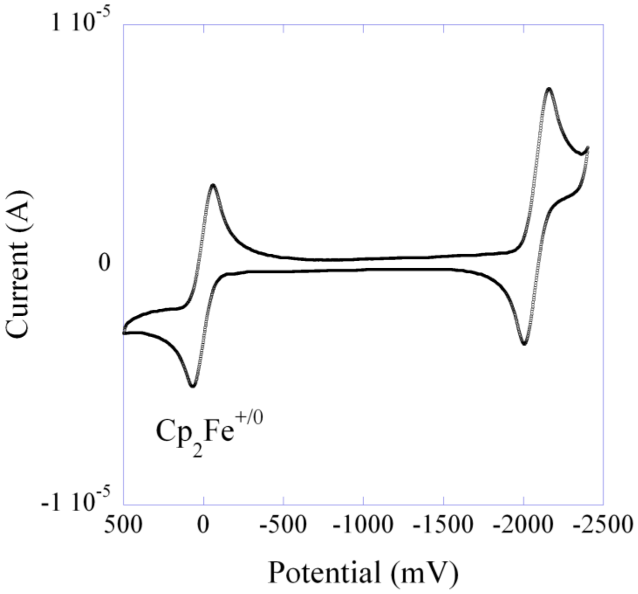
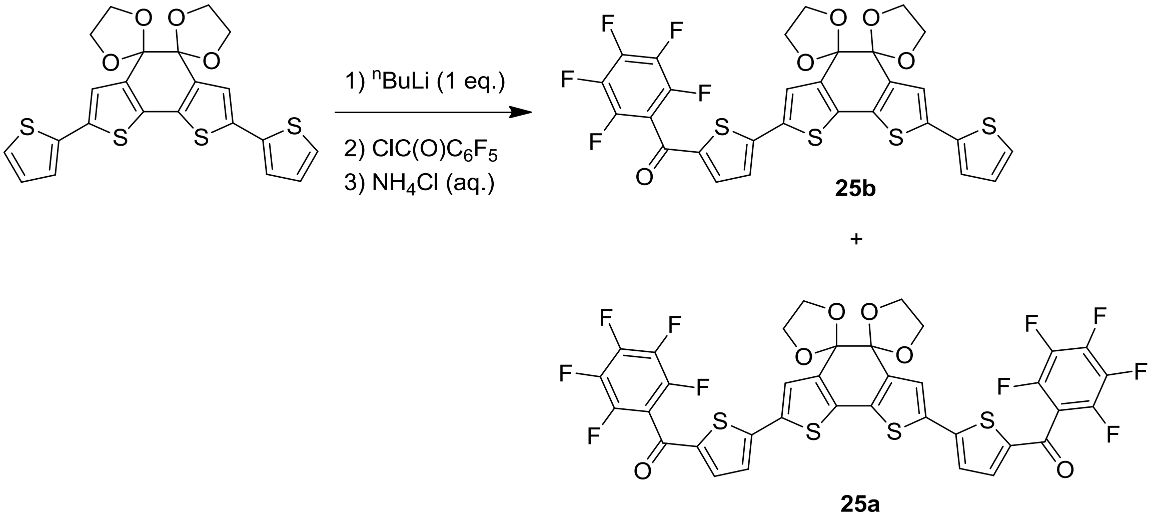


Figure S70. Cyclic voltammograms of 2,7-bis-(thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (24) (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate): $E_{1/2}^{0/1-}$ = -2.09 V.

2,7-Bis-(5-pentafluorobenzoyl-thiophene-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(1,3-dioxolane) (25a) and 2-(5-pentafluorobenzoyl-thiophene-2-yl)-7-(thiophene-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(1,3-dioxolane) (25b)



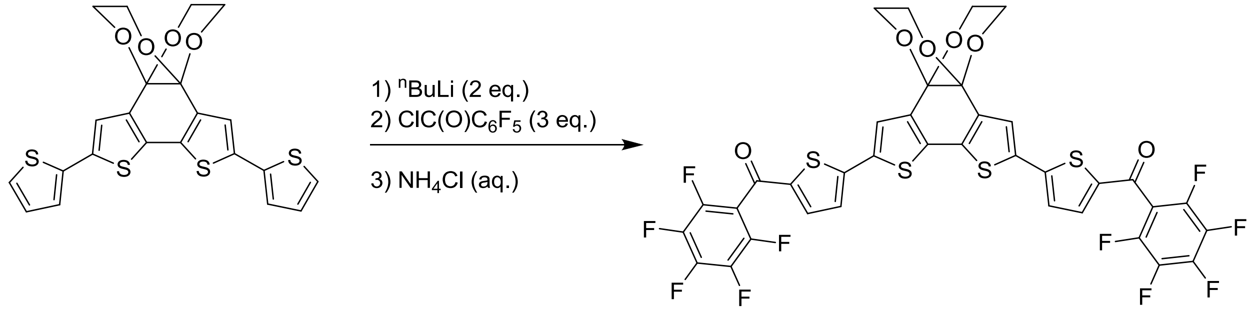
2,7-Bis-(thiophen-2-y)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(1,3-dioxolane) (**23**) (2.5 mmol, 1.18 g) was dissolved in anhydrous THF (50 mL) under nitrogen atmosphere, and yellow solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 1.0 eq., 1.0 mmol, 0.9 mL) was added dropwise, and reaction mixture became orange-red, and then orange.

After stirring for ~45 minutes pentafluorobenzoyl chloride (2.0 eq., 5.0 mmol, 1.15 g) was added, the mixture was stirred for ~15 minutes, and the cooling bath was removed. The reaction mixture was treated with aqueous NH_4Cl, organic phase was removed, dried over anhydrous magnesium sulfate, and the drying agent was filtered off. The solvents were removed by rotary evaporation, and crude product was purified by column chromatography (silica gel, hexanes:dichloromethane, then dichloromethane as eluants). First few fractions containing unreacted starting material were combined, and the solvents were removed a few mg of the starting material (**23**) was recovered. Fractions containing slightly impure desired product were combined, the solvent was removed, and the residue (0.84 g), was further purified by column chromatography (silica gel, dichloromethane as eluant). Combined fractions containing pure product were subjected to rotary evaporation, the residue was mixed with ethanol:dichloromethane, the mixture was heated at reflux for a few minutes to remove dichloromethane, cooled and the solid was separated by vacuum filtration (0.62 g, 37.3% yield), and then dried under vacuum. Di-substituted product **25a** was also obtained (0.16 g).

25b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (d, *J* = 4.0 Hz, 1H), 7.37 (s, 1H), 7.26 (d, *J* = 5.2 Hz, 1H; *overlaps with residual $CHCl_3$*), 7.21-7.14 (m, 4H), 7.03 (dd, *J* = 4.8 Hz, 3.8 Hz, 1H), 4.40-4.20 (m, 8H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 175.5, 148.9, 143.7 (doublet of multiplet, J = 251.2 Hz),140.3, 140.27, 139.5, 137.6 (doublet of multiplet, *J* = 260 Hz), 137.3, 137.1 (CH), 136.5, 134.5, 133.3, 129.9, 128.0 (CH), 125.2 (CH), 124.8 (CH), 124.3 (CH), 124.3 (CH), 124.3 (CH), 121.9 (CH), 113.8, 107.6, 107.56, 66.8 (CH_2), 66.7 (CH_2) (one carbon signal of pentafluorophenyl group was not clearly observed due to C-F coupling). ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -139.7 (d, *J* = 18.5 Hz, 2F), -150.2 (appears as t, *J* = 20.4 Hz, 1F), -151.5 (m, 2F) (1,1,2-trichlorotrifluoroethane was used as a reference with δ at -71.75 ppm (t)). HRMS (EI) calculated for $C_{29}H_{15}F_5O_5S_4$ 665.9722, found 665.9713. Anal. Calcd. for $C_{29}H_{15}F_5O_5S_4$ C, 52.25; H, 2.27. Found: C, 51.98; H, 2.27.

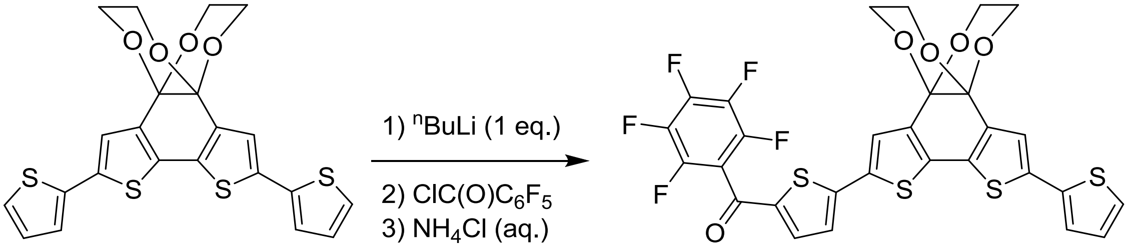
25a: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (d, *J* = 4.1 Hz, 2H), 7.38 (s, 2H), 7.20 (d, *J* = 4.1 Hz, 2H), 4.35-4.20 (m, 8H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 175.63, 148.33, 143.69 (appears as doublet of multiplet, *J* = 257 Hz), 140.80, 137.62 (appears as doublet of multiplets, *J* = 257 Hz), 136.96 (CH), 134.67, 133.36, 124.76 (CH), 124.74 (CH), 133.36, 113.66 (m), 107.37, 66.83 (CH_2).

2,7-Bis-(5-pentafluorobenzoyl-thiophene-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (25a')



2,7-Bis-(thiophene-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (**23**) (1.5 mmol, 0.709 g) was dissolved in anhydrous THF under nitrogen atmosphere, and yellow solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 3.0 mmol, 1.05 mL) was added dropwise, and yellow solution became lighter in color, and then precipitate formed. The reaction mixture was stirred for 1 h, and pentafluorobenzoyl chloride (3 eq., 4.5 mmol, 1.04 g) was added quickly to the suspension. Yellow mixture became orange-reddish, and after stirring for 40 minutes bright orange-red solution was allowed to warm to room temperature. After 10 minutes of stirring precipitate was observed. Mixture was treated with aqueous NH_4Cl, and dichloromethane was added. Organic phase was removed, dried over anhydrous magnesium sulfate, the drying agent was filtered off, and the organic solvents were removed by rotary evaporation. Crude product was purified by column chromatography (silica gel, dichloromethane as eluant). First fractions with a product slightly contaminated by mono-substituted material were combined separately, the solvent was removed by rotary evaporation, and red solid was obtained (0.45 g, ~35% yield). Fractions with pure product were combined separately, the solvent was removed by rotary evaporation, and dark red solid was obtained (0.67 g, 51.9% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50 (s, 2H), 7.42 (d, J = 4.1 Hz, 2H), 7.24 (d, J = 4.1 Hz, 2H), 4.23 (m, 4H), 3.76 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 175.70, 148.08, 141.04, 138.48, 136.93 (CH), 135.18, 133.93, 124.92 (CH), 124.82 (CH), 92.91, 61.69 (CH_2) (4 carbon signals of pentafluorophenyl groups appear as weak multiplets and are not certain). HRMS (EI) calculated for $C_{36}H_{14}F_{10}O_6S_4$ 859.9514; found 859.9509. Anal. Calcd. for $C_{36}H_{14}F_{10}O_6S_4$: C, 50.23; H, 1.64. Found: C, 50.14; H, 1.46.

2-(5-Pentafluorobenzoyl-thiophen-2-yl)-7-(thiophen-2-y)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (25b')



2,7-Bis-(thiophen-2-y)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (**18a**) (1.0 mmol, 0.473 g) was dissolved in anhydrous THF (50 mL) under nitrogen atmosphere, and yellow solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 1.0 eq., 1.0 mmol, 0.35 mL) was added dropwise, and reaction mixture became dark orange. After stirring for 25 minutes pentafluorobenzoyl chloride (1.5 eq., 1.5 mmol, 0.35 g) was added, the mixture was stirred for about 1 h and allowed to warm to room temperature. Dark orange cloudy mixture was treated with aqueous NH_4Cl and bright orange-red organic phase was separated. Aqueous phase was extracted with dichloromethane, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, the solvents were removed by rotary evaporation and the residue (dark red-orange solid) was purified by column chromatography (silica gel, dichloromethane: hexanes (3:1) to elute unreacted starting material, dichloromethane to elute the product and di-substituted byproduct **25b'**). Unreacted starting material **18a** was recovered (0.062 g, 13.1% recovery). Desired product, 2-(5-pentafluorobenzoyl-thiophen-2-yl)-7-(thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-4,5-bis-(ethyloxolane) (**25b'**), was obtained as red solid (0.237 g, 35.5%). Di-substituted material, 2,7-bis-(5-pentafluorobenzoyl-thiophen-2-y)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) **25a'** was also isolated (0.195 g, 25.2% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49 (s, 1H), 7.41 (d, J = 3.6 Hz, 1H), 7.32-7.25 (m, 2H; *overlaps with residual CHCl*$_3$), 7.21 (m, 2H), 7.05 (m, 1H), 4.22 (m, 4H), 3.78 (m, 4H) (based on ^{1}H NMR material contains dichloromethane (s, 5.31 ppm, 0.51 H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 175.57, 148.65, 140.54, 137,96, 137.79, 137.15, 137.01 (CH), 136.41, 135.00, 133.80, 130.57, 128.06 (CH), 125.42 (CH), 124.81 (CH), 124.51 (CH), 124.44 (CH), 121.81 (CH), 93.12, 98.08, 61.74 (CH_2), 61.64 (CH_2). HRMS (EI) calculated for $C_{29}H_{15}F_5O_5S_4$ 665.9722; found 665.9727. Anal. Calcd. for $C_{29}H_{15}F_5O_5S_4$: C, 52.25; H, 2.27. Found: C, 50.47; H, 2.46. This material was dried under vacuum (heating), and then submitted for the elemental analysis. Found: C, 50.72; H, 2.24. The material was further purified by column chromatography (silica gel, dichloromethane as eluant), the solvents were removed by rotary evaporation, and the residue was dried under vacuum with heating. Found: C, 51.48; H, 2.27. Found: C, 51.59; H, 2.30.

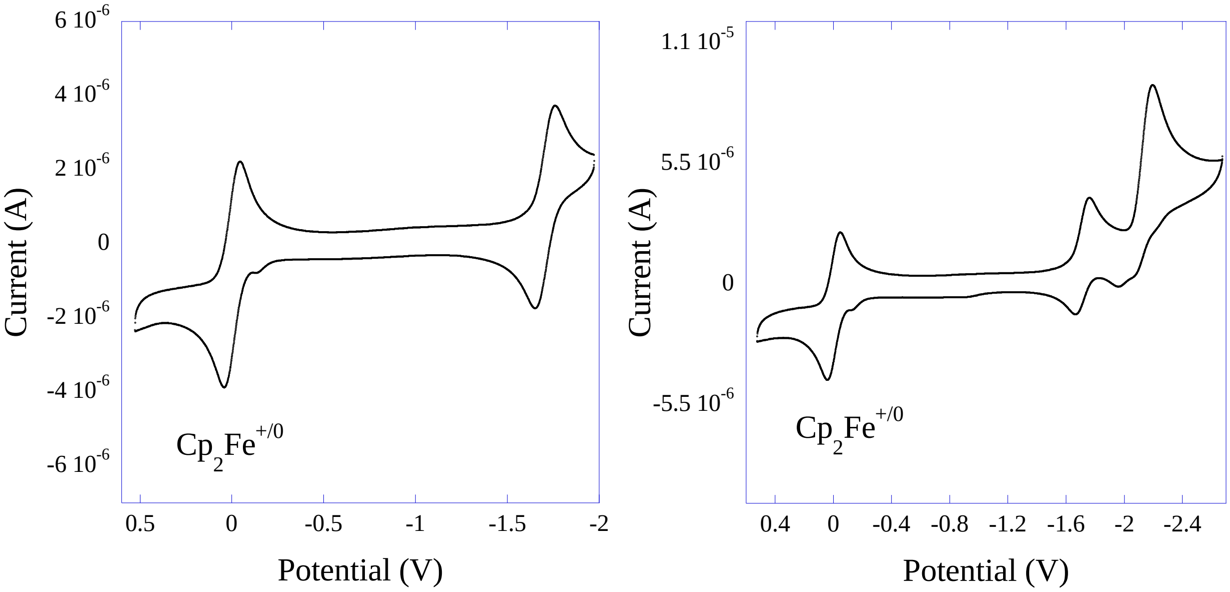
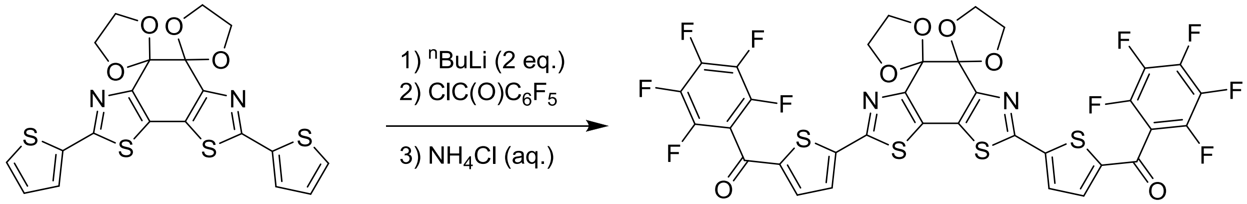


Figure S71. Cyclic voltammogram (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2-(5-pentafluorobenzoyl-thiophen-2-yl)-7-(thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane): $E_{1/2}^{0/1-}$ = -1.71 V, $E_{1/2}^{1-/2-}$ = -2.14 V (partially reversible).

2,7-Bis-(2-pentafluorobenzoyl-thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (26a)



2,7-Bis-(thiophene-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**24**) (0.455 mmol, 0.216 g) was dissolved in anhydrous THF (75 mL) under nitrogen atmosphere, and bright yellow solution was cooled in acetone/dry ice bath. *n*-Butyllithium (2.85 M in hexanes, 2 eq., 0.91 mmol, 0.32 mL) was added dropwise and the mixture became green-yellow. The reaction mixture was stirred for 45 minutes, and transferred via cannula into a solution of pentafluorobenzoyl chloride (4.0 eq., 1.82 mmol, 0.42 g) in anhydrous THF (50 mL) (acetone/dry ice bath). The reaction mixture was stirred for ~0.5 h, the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. Aqueous NH_4Cl was added, the organic phase was removed, and the aqueous phase was extracted with hexanes:dichloromethane mixture. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and the solvents were removed by rotary evaporation. The residue was purified by column chromatography (silica gel, dichloromethane:ethyl acetate (50:1)). Fractions with the desired material were combined, the solvents were removed, and product was obtained as orange-red solid (0.217 g, 47.7%). Fractions with mono-substituted product **26b** were combined separately, the solvents were removed, and the product **26b** was obtained (34 mg).

26a: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.54 (d, J = 4.1 Hz, 2H), 7.50 (d, J = 4.1 Hz, 2H), 4.38 (m, 8H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 158.4, 154.7, 146.7, 143.6, 136.1(CH), 127.3 (CH), 125.8, 106.3, 67.6 (CH$_2$) (quaternary C(O) and C-F signals were not detected due to not sufficient concentration). HRMS (EI) calculated for $C_{34}H_{12}N_2O_6S_4F_{10}$ 861.9419; found 861.9404. Anal. Calcd. For $C_{34}H_{12}N_2O_6S_4F_{10}$: C, 47.33; H, 1.40; N, 3.25. Found: C, 47.30; H, 1.46; N, 3.22.

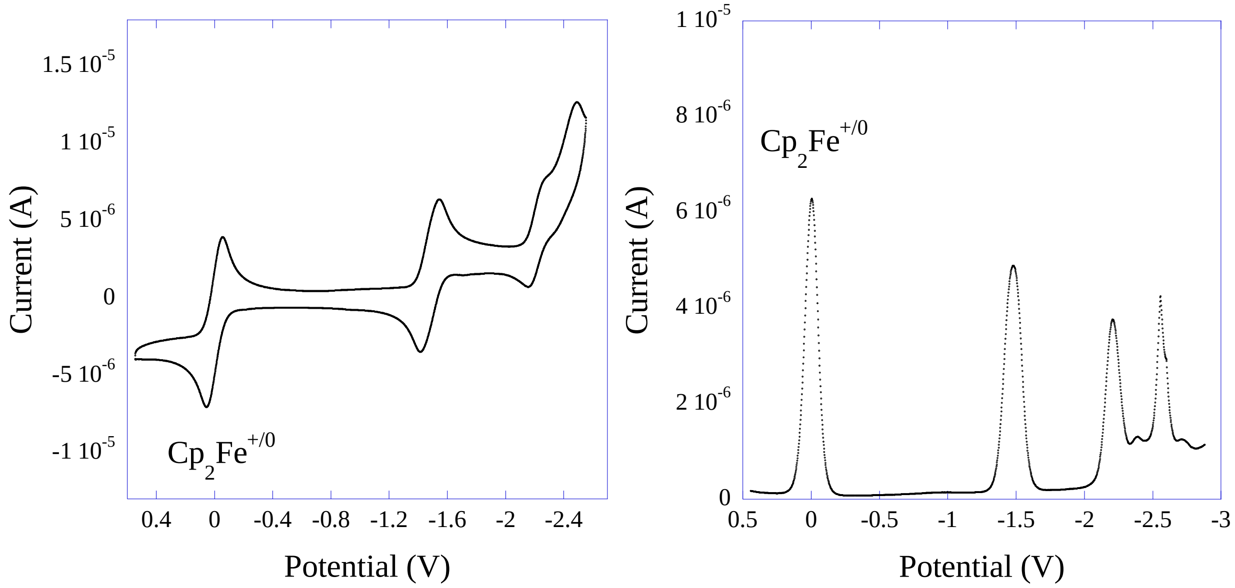
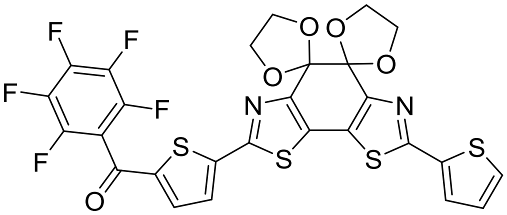


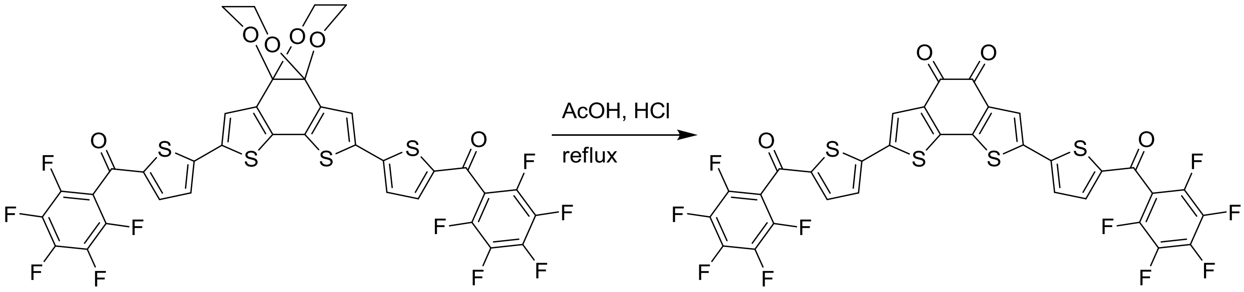
Figure S72. (*left*) Cyclic voltammogram (0.1 M ^{n}Bu$_4$NPF$_6$ in THF, Cp$_2$Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2,7-bis-(5-pentafluorobenzoyl-thiophene-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (26a): $E_{1/2}^{0/-1}$ = -1.48 V, $E_{1/2}^{-1/-2}$ = -2.21 V; (*right*) DPV (0.1 M ^{n}Bu$_4$NPF$_6$ in THF, Cp$_2$Fe internal standard at 0 V) of 2,7-bis-(5-pentafluorobenzoyl-thiophene-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (26a): $E^{0/1-}$ = -1.48 V, $E^{1-/2-}$ = -2.21 V, $E^{2-/3-}$ = -2.56 V.

2-(5-Pentafluorobenzoyl-thiophen-2-yl)-7-(thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (26b)



^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.54 (d, *J* = 3.4 Hz, 1H), 7.50 (m, 2H), 7.44 (d, *J* = 4.9 Hz, 1H), 7.09 (t, *J* = 4.2 Hz), 4.38 (m, 8H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 176.2, 161.1., 157.2, 153.7, 1153.6, 147.0, 143.1, 136.5, 136.1 (CH), 128.8 (CH), 128.0 (CH), 127.3 (CH), 126.8 (CH), 126.7, 122.8, 122.8, 106.4, 67.3 (CH$_2$) (C-F signals of pentafluorophenyl group were observed as weak multiplets and are not certain). HRMS (EI) calculated for $C_{27}H_{13}F_5N_2O_5S_4$ 667.9627, found 667.9631. Anal. Calcd. For $C_{27}H_{13}F_5N_2O_5S_4$: C, 48.50; H, 1.96; N, 4.19. Found: C, 48.75; H, 2.17; N, 4.03.

2,7-Bis-(5-pentafluorobenzoyl-thiophene-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (27a)



2,7-Bis-(5-pentafluorobenzoyl-thiophene-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (**25a'**) (0.5 mmol, 0.43 g) was mixed with acetic acid (75 mL), and the resulting mixture was heated to reflux. HCl (5 mL) was added to the orange-red solution, and the reaction mixture became dark immediately, and then precipitate formed. Reaction mixture was refluxed for 2 hours, cooled to room temperature, and precipitate was separated by vacuum filtration, washed with water, ethanol and dried (0.412 g, 107% crude yield, green-grey solid). This material was refluxed in ~120 mL 1,1,2,2-tetrachloroethane, filtered while hot (some material didn't dissolve) and cooled. Dark solid was separated by vacuum filtration (0.13 g). Material on the filter was combined with mother liquor, heated to reflux (~75 mL of 1,1,2,2-tetrachloroethane was added), gravity filtered while hot and cooled to room temperature. Dark solid was separated by vacuum filtration (0.22 g). Total yield was 90.7% (0.35 g). ^{1}H NMR (1,1,2,2-tetrachloroethane-*d2*, 380 K, 400 MHz): δ 7.78 (s, 2H), 7.55 (d, *J* = 3.9 Hz, 2H), 7.37 (d, *J* = 4.0 Hz, 2H). ^{19}F NMR (CDCl$_3$, 376.3 MHz): δ -140.5 (m, 4F), -150.5 (m, 2F), -160.2 (m, 4F) (1,1,2-trichlorotrifluoroethane was used as a reference with δ at -71.75 ppm (t)). HRMS (EI) calculated for $C_{32}H_6F_{10}O_4S_4$ 771.8989; found 771.8978. Anal. Calcd. for $C_{32}H_6F_{10}O_4S_4$: C, 49.74; H, 0.78. Found: C, 49.47; H, 0.77.

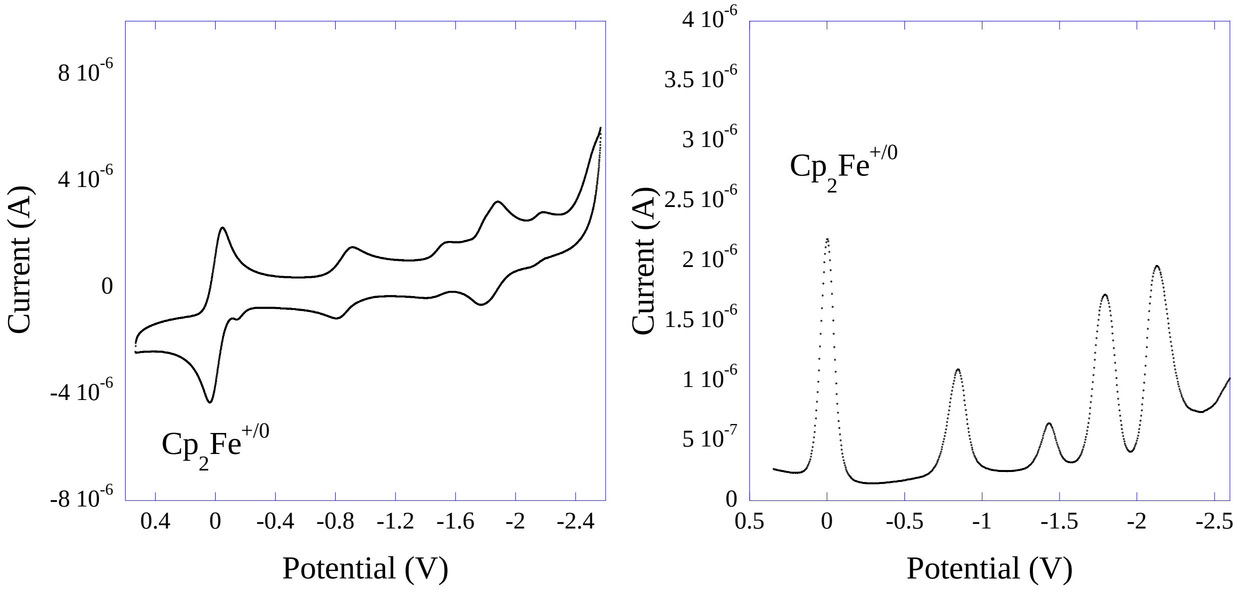
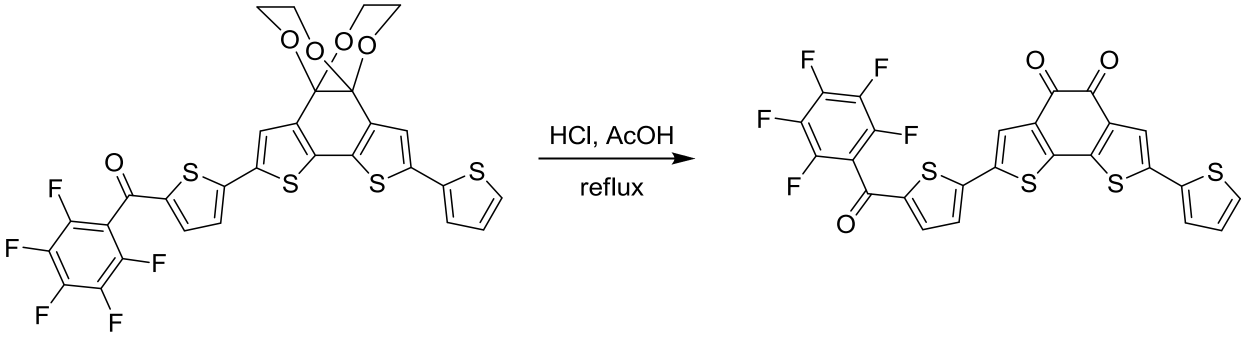


Figure S73. (*left*) Cyclic voltammogram (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2,7-bis-(5-pentafluorobenzoyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione : $E_{1/2}^{0/1-}$ = -0.86 V (rev.); $E_{1/2}^{1-/2-}$ = -1.49 V (partially rev.); $E_{1/2}^{2-/3-}$ = -1.82 V (rev.); $E_{1/2}^{3-/4-}$ = -2.15 V (partially rev); (*right*) differential pulse voltammetry (DPV) (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V) of 2,7-bis-(5-pentafluorobenzoyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione: E^{red1} = -0.85 V (1 e$^-$); E^{red2} = -1.42 V (0.8 e$^-$); E^{red3} = -1.79 V (1.6 e$^-$); E^{red4}= -2.13 V (2.4 e$^-$).

2,7-Bis-(2-pentafluorobenzoyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (27b)



2-(5-Pentafluorobenzoyl-thiophen-2-y)-7-(thiophen-2-y)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (**26b'**) (0.15 mmol, 0.100 g) was mixed with acetic acid (40 mL), and the resulting mixture was heated to reflux. HCl (3 mL) was added, and the red solution became dark in color. The reaction mixture was refluxed for ~1 h, cooled to room temperature, and treated with water. Dark solid was separated by vacuum filtration, washed with water and ethanol and dried (0.126 g). This crude material was purified by column chromatography (silica gel, dichloromethane, then dichloromethane:ethyl acetate (50:1) as eluants). Fractions with the product were combined, the solvents were removed by rotary evaporation, and the residue was heated to reflux with 2-propanol, cooled to room temperature, the solid was separated by vacuum filtration (81 mg, 93% yield), and dried under vacuum at 70-90 ºC.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 (s, 1H), 7.57 (s, 1H), 7.47 (m, 1H), 7.38 (m, 1H), 7.33-7.25 (m, 2H; *overlaps with residual* $CHCl_3$), 7.10 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) was not recorded due to poor solubility of the material in $CDCl_3$. HRMS (EI) calculated for $C_{25}H_7F_5O_3S_4$ 577.9198; found 577.9217 (M+2 ion was also observed in almost 1:1 intensity ratio with respect to molecular ion). Anal. Calcd. for $C_{25}H_7F_5O_3S_4$: C, 51.90; H, 1.22. Found: C, 52.11; H, 1.13.

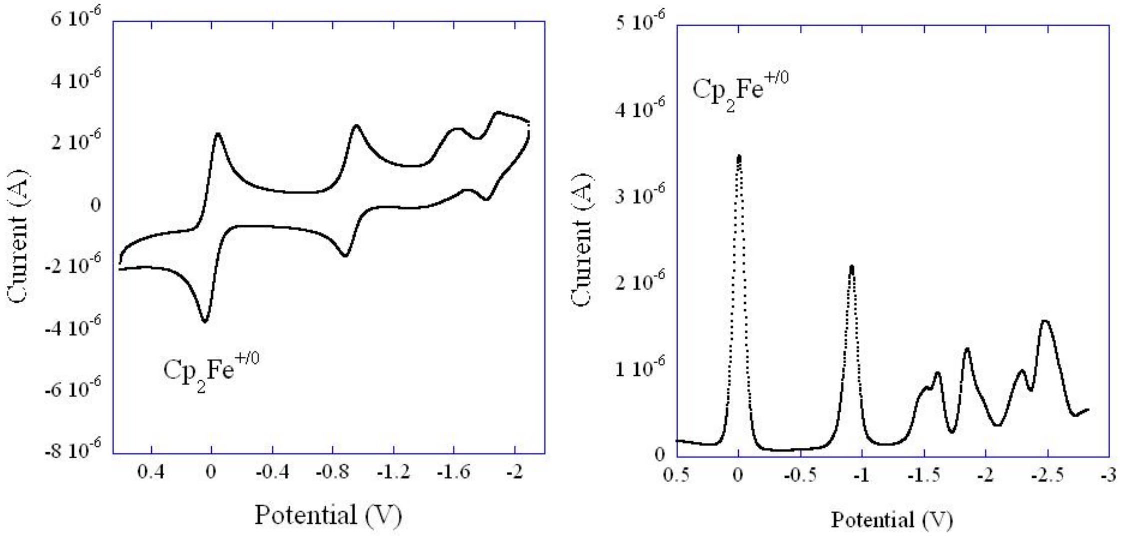
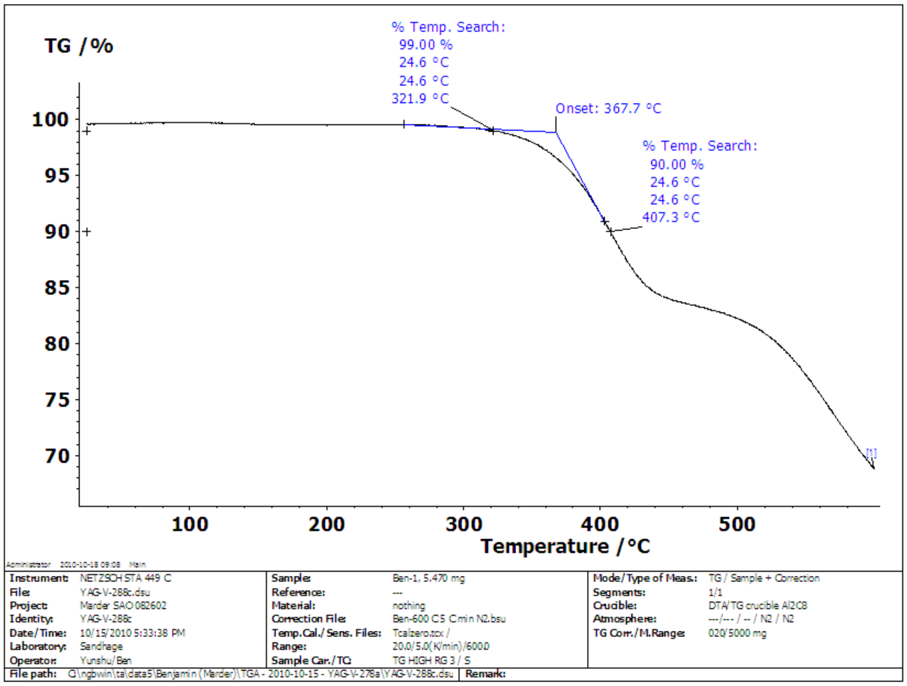


Figure S74. (*left*) Cyclic voltammogram (0.1 M $^nBu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2-(5-pentafluorobenzoyl-thiophen-2-yl)-7-(thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione: $E_{1/2}^{0/1-}$ = -0.92 V (rev.); $E_{1/2}^{1-/2-}$ = -1.63 V (partially rev.); $E_{1/2}^{2-/3-}$ = -1.86 V (rev.); $E_{1/2}^{3-/4-}$ = -2.15 V (partially rev); (*right*) differential pulse voltammetry (DPV) (0.1 M $^nBu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V) of 2,7-bis-(5-pentafluorobenzoyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione: $E^{0/1-}$ = -0.92 V (1 e$^-$); $E^{1-/2-}$ = -1.62 V (0.8 e$^-$); $E^{2-/3-}$ = -1.85 V (0.8 e$^-$); $E^{3-/4-}$ = -2.30 V (0.6 e$^-$); $E^{4-/5-}$ = -2.48 V (1.2 e$^-$)



Instrument:	NETZSCH STA 449 C	**Sample:**	Ben-1, 5.470 mg	**Mode/Type of Meas.:**	TG / Sample + Correction
File:	YAG-V-288c.dsu	**Reference:**	---	**Segments:**	1/1
Project:	Marder SAO 082602	**Material:**	nothing	**Crucible:**	DTA/TG crucible Al2O3
Identity:	YAG-V-288c	**Correction File:**	Ben-600 C5 Cmin N2.bsu	**Atmosphere:**	---/--- / -- / N2 / N2
Date/Time:	10/15/2010 5:33:38 PM	**Temp.Cal./Sens. Files:**	Tcalzero.tcx /	**TG Corr./M.Range:**	020/5000 mg
Laboratory:	Sandhage	**Range:**	20.0/5.0(K/min)/600.0		
Operator:	Yunshu/Ben	**Sample Car./TC:**	TG HIGH RG 3 / S		

File path: C:\ngbwin\ta\data5\Benjamin (Marder)\TGA - 2010-10-15 - YAG-V-278a\YAG-V-288c.dsu **Remark:**

Figure S75. TGA analysis (5 ºC/min heating rate) of 2-(5-pentafluorobenzoyl-thiophen-2-yl)-7-(thiophene-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione: T$_d$ = 379 ºC (5% mass loss).

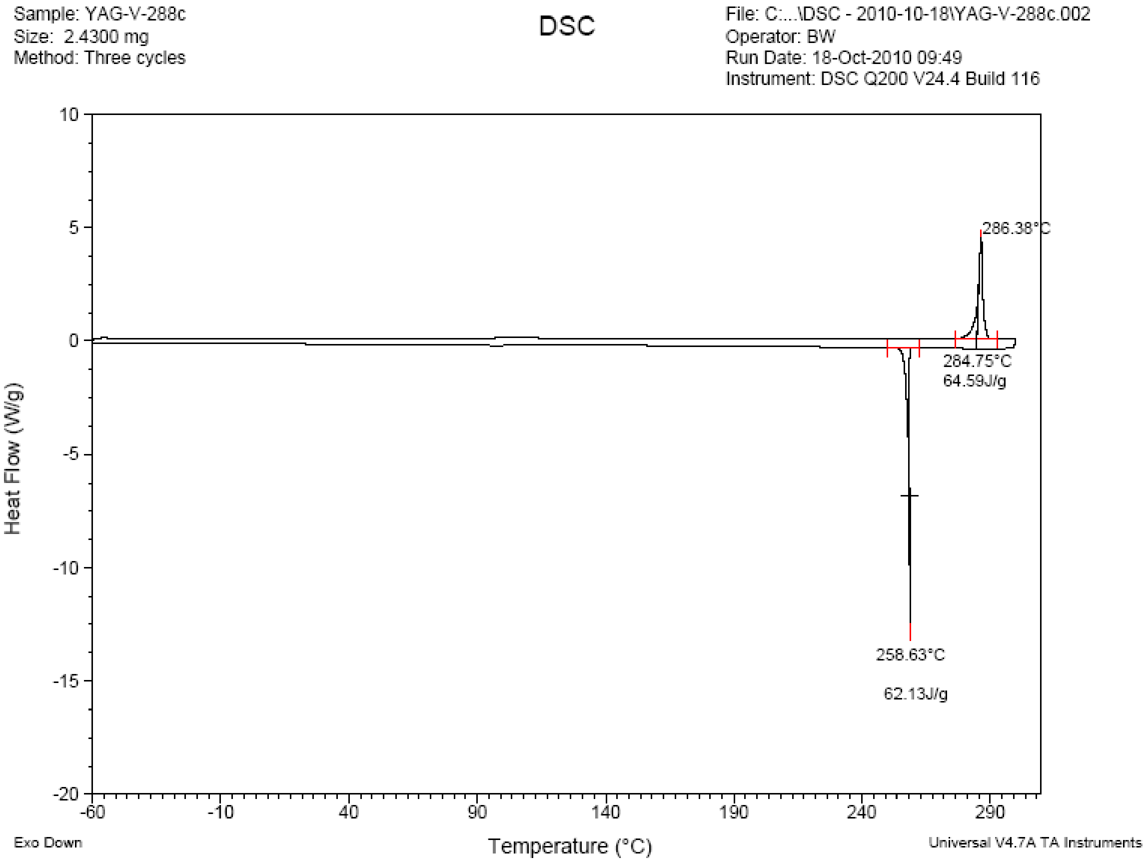
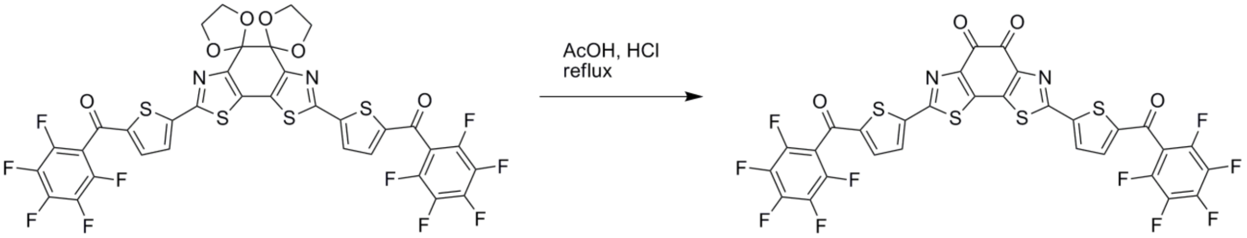


Figure S76. DSC analysis (10 ºC/min heating-cooling rate) of 2-(5-pentafluorobenzoyl-thiophen-2-yl)-7-(thiophene-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione: m.p. 286.4 ºC.

2,7-Bis-(2-pentafluorobenzoyl-thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (28a)



2,7-Bis-(5-pentafluorobenzoyl-thiophene-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**26a**) (0.087 mmol, 0.075 g) was mixed with acetic acid (20 mL), and the resulting mixture was heated to reflux. HCl (3 mL) was added dropwise to a bright orange solution, and the mixture became dark brown, and then within a few minutes precipitate formed. Additional amount of HCl (2 mL) was added, and the mixture was refluxed for ~1 h, cooled to room temperature, and treated with water. Green-grey shiny solid was separated by vacuum filtration, washed with water, ethanol and then dried (0.068 g, ~100% crude yield). This material was purified by column chromatography (silica gel, $CHCl_3$ and $CHCl_3$:EtOAc (50:1) as eluants, hot chloroform to dissolve material and load to the column). Middle fractions with pure material were combined, subjected to rotary evaporation and the residue (green solid) was heated to reflux with 2-propanol, cooled and green-grey solid was separated by vacuum filtration (17.4 mg). First few and last fractions with the product were combined with mother liquor, the volatile solvents were removed by rotary evaporation, THF was added until clear solution formed and then concentrated until precipitation took place. Green solid was separated by filtration (5 mg). Filter papers of were washed with THF, the solvent was removed and additional amount of product was obtained (13 mg, brown film on the sides).

^{1}H NMR (THF-*d8*, 400 MHz): δ 7.91 (d, J = 4.3 Hz, 2H), 7.78 (d, J = 4.1 Hz, 2H); ^{13}C{^{1}H} NMR (THF-*d8*, 100 MHz): 177.0, 171.2, 160.3, 151.1, 146.1, 145.7, 143.6 (m), 140.1 (m), 137.9 (CH), 137.6-136.9 (m), 130.4 (CH), 114.4 (m). ^{19}F NMR ($CDCl_3$, 376.3 MHz): δ -141.0 (4F), -151.7 (2F), -160.9 (m, 4F) (1,1,2-trichlorotrifluoroethane was used as a reference with δ at -71.75 ppm (t)). DEPT-135 ($CDCl_3$, 100 MHz): δ 137.8 (CH), 130.3 (CH). HRMS (EI) analysis calculated for $C_{30}H_4F_{10}N_2O_4S_4$ 773.8894; found 773.8885 (M+2 (776.1) was observed as a major ion). Anal. Calcd. for $C_{30}H_4F_{10}N_2O_4S_4$: C, 46.52; H, 0.52; N, 3.62. Found: C, 46.34; H, 0.57; N, 3.91.

DSC analysis: no melting event was observed below 350 ºC.

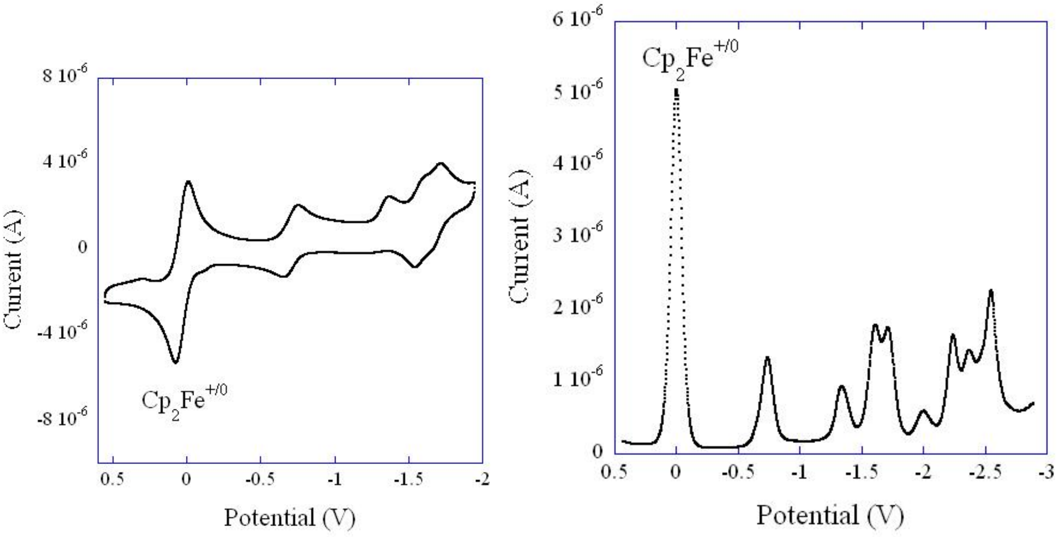
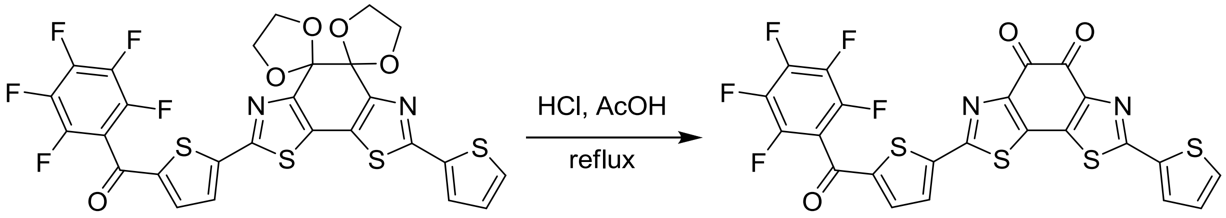


Figure S77. (*left*) Cyclic voltammogram (0.1 M $^nBu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 50 mV·s^{-1} rate) of 2,7-bis-(5-pentafluorobenzoyl-thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione: $E_{1/2}^{0/1-}$ = -0.74 V (rev.); (*right*) differential pulse voltammetry (DPV) (0.1 M $^nBu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V) of 2,7-bis-(5-

pentafluorobenzoyl-thiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione: $E^{0/1-}$ = -0.74 V (1 e^-); $E^{1-/2-}$ = -1.34 V (0.7 e^-); $E^{2-/4-}$ = -1.61 V and E^{red3} = -2.13 V.

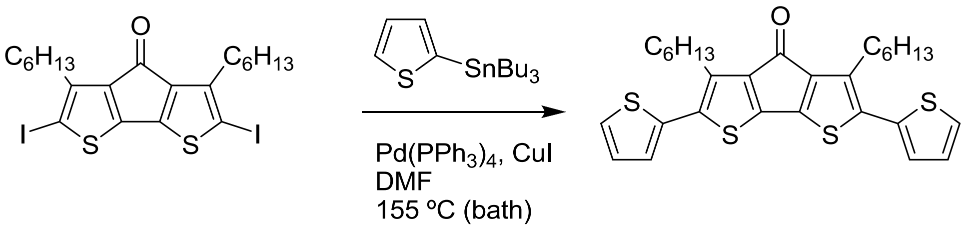
2,7-Bis-(pentafluorobenzoyl-thiophen-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-dione (28b)



2-(5-Pentafluorobenzoyl-thiophene-2-yl)-benzo[1,2-*d*:4,3-*d'*]bis(thiazole)-4,5-bis-(1,3-dioxolane) (**26b**) (0.135 mmol, 0.091 g) was mixed with acetic acid (25 mL), and the resulting mixture was heated to reflux. HCl (~5 mL) was added dropwise to a bright orange solution, and the mixture became brown, and then precipitate formed. After reflux for about 0.5 h the reaction mixture was cooled to room temperature, treated with water, brown solid was separated by vacuum filtration, washed with water, ethanol, and then dried (0.061 g, 77.2% yield, sample was pure based on ^{1}H NMR analysis). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, J = 4.1 Hz, 1H), 7.70 (dd, J = 3.8 Hz, 1.0 Hz, 1H), 7.61 (dd, J = 5.0 Hz, 1.0 Hz, 1H), 7.18 (dd, J = 5.0 Hz, 3.8 Hz, 1H); DEPT-135 ($CDCl_3$): δ 135.67 (CH), 131.38 (CH), 129.70 (CH), 129.19 (CH), 128.53 (CH) (the material was not sufficiently soluble in $CDCl_3$ to record $^{13}C\{^1H\}$ NMR spectrum). HRMS (EI) calculated for $C_{23}H_5F_5N_2O_3S_4$ 579.9103, found 579.9119 (M+2H (581.9253) was also detected). Anal. Calcd. for $C_{23}H_5F_5N_2O_3S_4$: C, 47.58; H, 0.87; N, 4.83. Found: C, 47.31; H, 0.68; N, 4.71.

DSC analysis (10 ºC/min): m.p. 292.7 ºC (decomposition).

2,6-Bis-(thiophen-2-yl)-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (30a)



2,6-Diiodo-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (**8c**) (3.0 mmol, 1.837 g) and 2-tri-*n*-butylstannylthiophene (2.2 eq., 6.6 mmol, 2.46 g) were mixed in an oven-dried flask. Catalyst $Pd(PPh_3)_4$ (0.05 mol%, 0.15 mmol, 0.173 g), CuI (0.015 mol%, 0.045 mmol, 8.6 mg) and anhydrous DMF (30 mL) were added, and the mixture was heated up to reflux (155 ºC bath temperature). The mixture changed color from purple to bluish-black. TLC analysis (hexanes:dichloromethane (1:1)) showed the complete consumption of the starting diiodide **8c**, and clean formation of the desired product. The mixture was cooled to room temperature, treated with water, and organic phase was extracted with hexanes. Dark blue-purple organic phase was dried over anhydrous magnesium sulfate and KF, and the solvent was removed by rotary evaporation to give product as dark blue-black soft matter. This crude product was purified by column chromatography (hexanes as eluant). Fractions containing the desired product were combined, the solvent was removed, and product was obtained as very dark solid (1.45 g, 92.4% yield). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.32 (dd, *J* = 5.0 Hz, 0.54 Hz, 2H), 7.11 (poorly resolved dd, 2H), 7.06 (dd, *J* = 5.0 Hz, 4.05 Hz, 2H), 2.18 (t, *J* = 7.9 Hz, 4H), 1.65 (m, 4H), 1.39 (m, 4H), 1.31 (m, 8H), 0.90 (t, *J* = 6.2 Hz, 6H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 184.39, 146.67, 140.84, 137.10, 135.12, 133.96, 127.49, 126.10, 125.83, 31.55, 30.11, 29.31, 26.76, 22.64, 14.07. HRMS (EI) calculated for $C_{29}H_{32}OS_4$ 524.1236; found 524.1329. Anal. Calcd. for $C_{29}H_{32}OS_4$: C, 66.37; H, 6.15. Found: C, 66.45; H, 6.31.

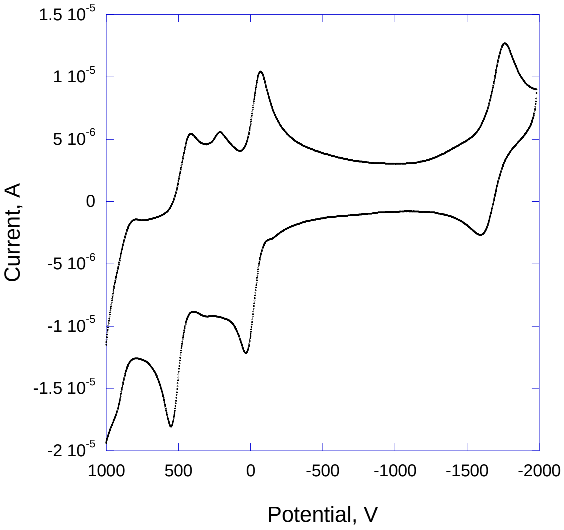


Figure S78. CV (0.1 M ^{n}Bu$_4$NPF$_6$ in CH$_2$Cl$_2$, Cp$_2$Fe internal standard at 0 V) of starting material 2,5-bis-(thiophen-2-yl)-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (8c).

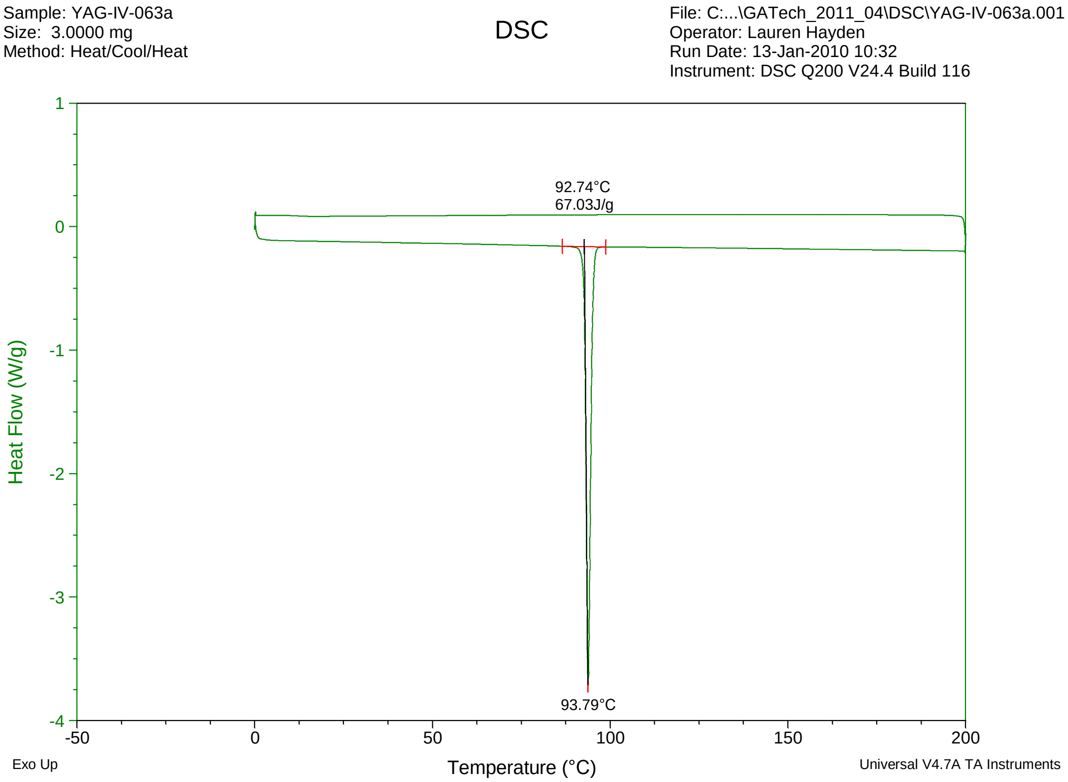
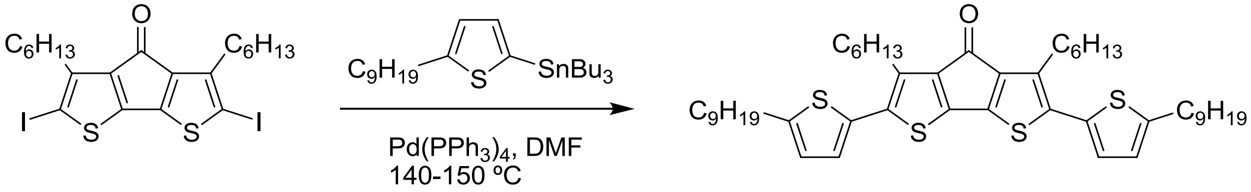


Figure S79. DSC analysis of 30a (10 ºC/min rate): 93.8 ºC (melting point observed on the first heating; crystallization was not observed on cooling).

2,5-Bis-(5-*n*-nonylthiophen-2-yl)-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (30b)



2,6-Diiodo-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (**8c**) (0.144 mmol, 0.088 g) was mixed with 2-*n*-nonyl-5-tri-*n*-butylstannylthiophene (2.1 eq., 0.302 mmol, 0.15 g) and $Pd(PPh_3)_4$ (5 mol% based on aryl diiodide **8c**, 7.19×10^{-3} mmol, 0.008 g). Anhydrous DMF (5 mL) was added under nitrogen atmosphere, and the resulting mixture was heated up to ~140-150 ºC for several minutes. The dark purple mixture became dark blue in color. TLC analysis (hexanes:ethyl acetate (a drop) as eluant) showed complete consumption of the starting aryl diiodide **8c**, and the mixture was cooled to room temperature, and treated with water (10 mL).

The organic matter was extracted with hexanes several times, the dark blue combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off and the solvents were removed by rotary evaporation to give dark blue product as a film on the sides of the flask. This material was purified by column chromatography (silica gel, hexanes, then hexanes:ethyl acetate (300:1, 30:1) as eluants). Solvents were removed from combined organic phases, and the product was isolated as dark blue matter (0.073 g, 65.8% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.88 (d, *J* = 3.5 Hz, 2H), 6.69 (d, *J* = 3.6 Hz, 2H), 2.79 (m, 8H), 1.70-1.55 (m, 8H), 1.45-1.20 (m, 36H), , 0.87 (m, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$ 100 MHz): δ□ 184.52, 146.63, 146.12, 140.59, 136.29, 134.37, 132.35, 125.56, 124.27, 31.74, 31.45, 31.43, 30.00, 29.97, 29.38, 29.22, 29.17, 28.99, 26.60, 22.54, 22.53, 13.98 (two alkyl carbon signals are missing due to overlap). HRMS (EI) calculated for $C_{47}H_{68}OS_4$ 776.4153, found 776.4153. Anal. Calcd. for $C_{47}H_{68}OS_4$: C, 72.62; H, 8.82; S, 16.50. Found: C, 72.66; H, 8.97.

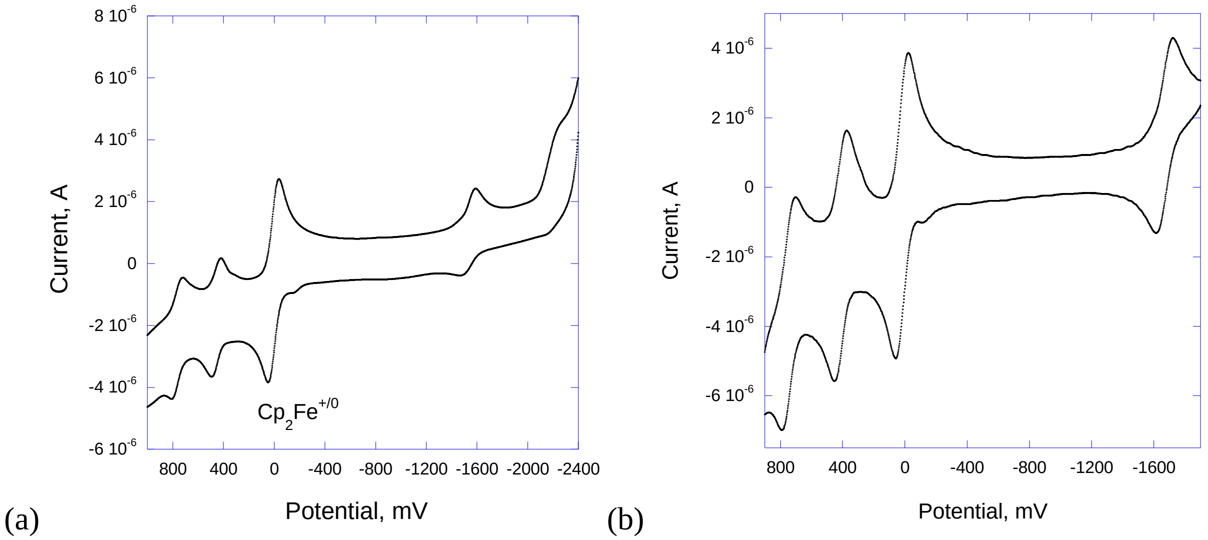
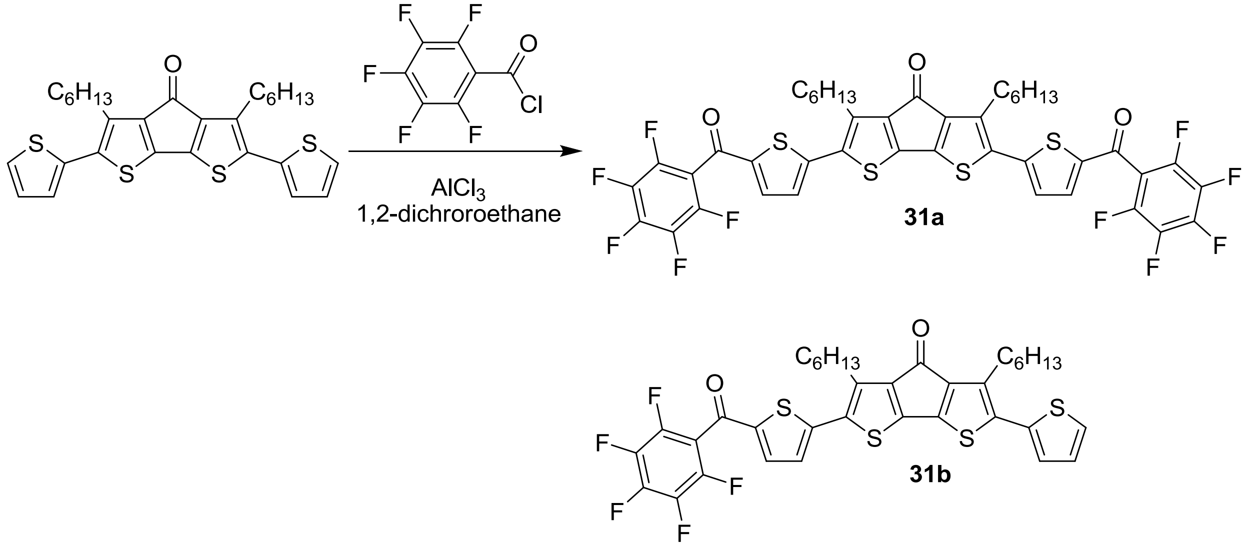


Figure S80. CV (0.1 M Bu_4NPF_6 in CH_2Cl_2, Cp_2Fe internal standard at 0 V) of *(a)* 2,6-bis-(5-*n*-nonyl-thiophen-2-yl)- 4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one $E_{1/2}^{1+/2+}$= +0.76 V, $E_{1/2}^{0/1+}$ = +0.46 V, $E_{1/2}^{0/1-}$ = -1.53 V, $E_{1/2}^{0/1-}$ = -2.28 V (large error, irreversible); *(b)* 2,6-bis-(5-*n*-nonylthiophene-2-yl)-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one $E_{1/2}^{+/2+}$ = +0.73 V, $E_{1/2}^{+/0}$ = +0.39 V, $E_{1/2}^{0/1-}$ = -1.69 V.

2,6-Bis-(5-perfluorobenzoyl-thiophen-2-yl)-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (31a) and 2-(5-perfluorobenzoyl-thiophen-2-yl)-3,5-di-*n*-hexyl-6-(thiophen-2-yl)-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (31b)



In a round bottom flask $AlCl_3$ (4 eq., 8.0 mmol, 1.07 g) was mixed with anhydrous 1,2-dichloroethane (20 mL), 2,3,4,5,6-pentafluorobenzoyl chloride (3 eq., 6 mmol, 1.38 g) was added under nitrogen atmosphere, and yellow suspension was stirred for a few minutes (ice-water bath). Dark blue solution of 2,6-bis-(thiophen-2-yl)-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophen-4-one (**30a**) (2.0 mmol, 1.050 g) in anhydrous 1,2-dichloroethane (10 mL) was added dropwise, and the reaction mixture became dark brown. After stirring for 15 minutes three materials were detected by TLC (chloroform as eluant): starting material, mono- and disubstituted products. The cooling bath was removed, the mixture was stirred for 2.5 h, analyzed by TLC (hexanes:chloroform as eluant), and starting material was detected. The reaction mixture was stirred overnight, analyzed by TLC (starting material was still present), and additional amount of $AlCl_3$ (~2 g) was added followed by the addition of 2,3,4,5,6-pentafluorobenzoyl chloride (~0.6 g). After stirring for 2.5 h only trace amount of the starting material was detected, and the mixture was stirred for additional 4 h. TLC analysis showed the complete consumption of the starting material, and two new byproducts. The reaction mixture was treated with water (exotherm), the organic matter was extracted with diethyl ether, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, the solvents were removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, hexanes:chloroform (350:150 mL) to remove traces amounts of starting material (0.032 g, 3% recovery), and then chloroform to elute two products. Fractions contacting mono-substituted product **31b** were combined, subjected to rotary evaporation and mono-substituted product was obtained as dark brown film on the sides of the vial (0.36 g, 25.0%). Fractions with the disubstituted product **31a** were subjected to rotary evaporation, and the product was obtained as dark brown matter (0.31 g, 16.9%). Both materials **31a** and **31b** were further purified by column chromatography (silica gel, chloroform as eluant).

31a: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.45 (d, J = 4.1 Hz, 2H), 7.19 (d, J = 4.1 Hz, 2H), 2.97 (t, J = 7.9 Hz, 4H), 1.68 (m, 4H), 1.45 (m, 4H), 1.34 (m, 8H), 0.90 (t, J = 6.9 Hz, 6H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 182.92, 175.77, 147.98, 147.13, 142.07, 141.49, 139.86, 136.40 (CH), 133.82, 126.24 (CH), 31.50 (CH$_2$), 29.90 (CH$_2$), 29.31 (CH$_2$), 27.09 (CH$_2$), 22.60 (CH$_2$), 14.03 (CH$_3$) (4 carbon singals of pentafluorophenyl group are missing due to coupling to fluorine). HRMS (EI) calculated for $C_{43}H_{30}F_{10}O_3S_4$ 912.0918, found 912.0854. Anal. Calcd. for $C_{43}H_{30}F_{10}O_3S_4$: C, 56.57; H, 3.31; Found: C, 56.83; H, 3.49.

31b: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.43 (d, J = 4.1 Hz, 1H), 7.37 (dd, J = 5.1 Hz, 1.1 Hz, 1H), 7.16 (d, J = 4.2 Hz, 1H), 7.14 (dd, J = 3.6 Hz, 1.10 Hz, 1H), 7.09 (dd, J = 5.1 Hz, 3.7 Hz, 1H), 2.96 (t, J = 7.9 Hz, 2H), 2.84 (t, J = 7.9 Hz, 2H), 1.70-1.60 (m, 4H), 1.50-1.35 (m, 4H), 1.35-1.25 (m, 8H), 0.95-0.80 (m, 6H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 183.63, 175.64, 149.18, 147.76, 145.56, 141.80, 141.28, 140.94, 139.80, 137.30, 136.47 (CH), 135.72, 134.75, 132.38, 127.62 (CH), 126.45 (CH), 126.29 (CH), 125.78 (CH), 31.53 (CH$_2$), 30.10 (CH$_2$), 29.87 (CH$_2$), 29.33 (CH$_2$), 29.30 (CH$_2$), 27.11 (CH$_2$), 26.76 (CH$_2$), 22.63 (CH$_2$), 22.62 (CH$_2$), 14.06 (CH$_3$), 14.04 (CH$_3$) (4 carbon singals of pentafluorophenyl group are missing due to coupling to fluorine). HRMS (EI) calculated for $C_{36}H_{31}F_5O_2S_4$ 718.1127, found 718.1130. Anal. Calcd. for $C_{36}H_{31}F_5O_2S_4$: C, 60.15; H, 4.35. Found: C, 60.34; H, 4.51.

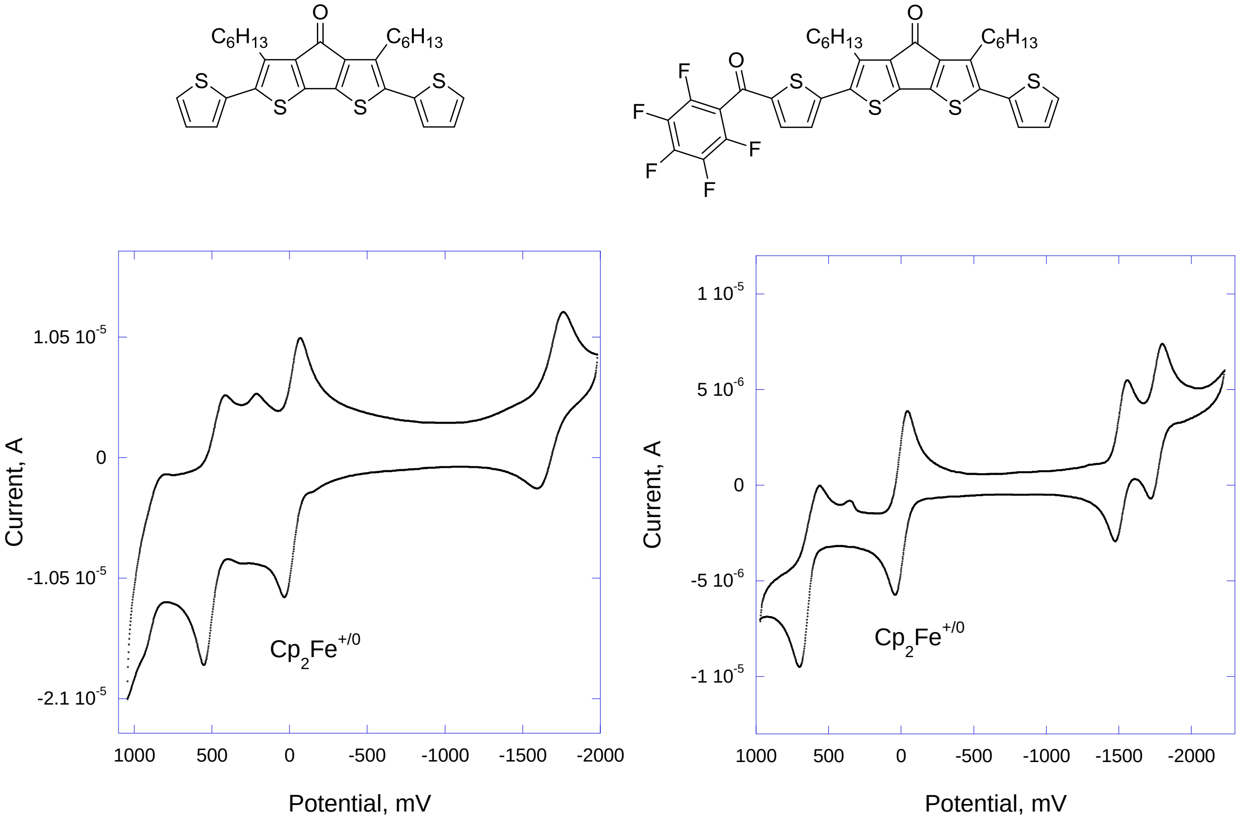
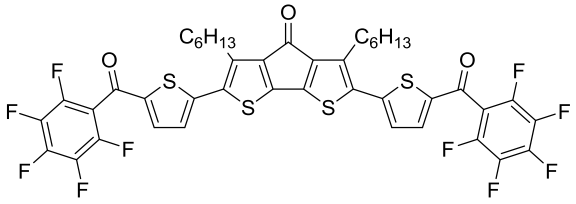


Figure S81. CV analyses of (0.1 M ^{n}Bu$_4$NPF$_6$ in CH$_2$Cl$_2$, Cp$_2$Fe internal standard at 0 V, 50 mV rate) (*left*) 2,6-bis-(thiophene-2-yl)-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-

b′]dithiophen-4-one (30a): $E_{1/2}^{+/0}$ = +0.50 V (partially reversible), $E_{1/2}^{0/1-}$ = -1.66 V (rev.); (*right*) 2-(5-perfluorobenzoyl-thiophen-2-yl)-6-(thiophen-2-yl)-3,5-di-*n*-hexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b′*]dithiophen-4-one (31b): $E_{1/2}^{+/0}$ = +0.63 V (partially reversible), $E_{1/2}^{0/1-}$ = -1.52 V (rev.), $E_{1/2}^{1-/2-}$ = -1.76 V (rev).



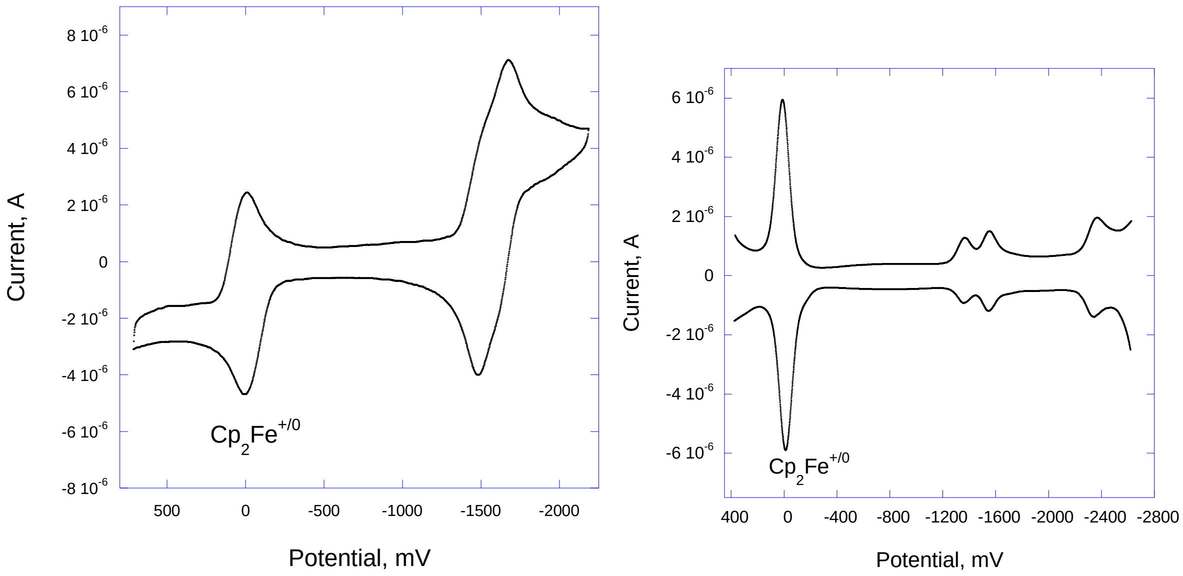
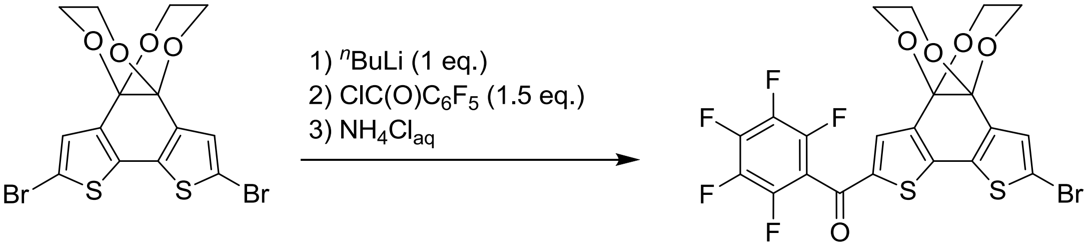


Figure S82. (*left*) CV analysis (0.1 M $^{n}Bu_4NPF_6$ in CH_2Cl_2, Cp_2Fe internal standard at 0 V, 50 mV rate) of 31a: $E_{1/2}^{0/2-}$ = -1.58 V; (*right*) DPV analysis of 31a (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V, 10 mV/sec rate), $E_{1/2}^{0/1-}$ = -1.37 V (rev.), $E_{1/2}^{1-/2-}$ = -1.56 V (rev.), $E_{1/2}^{2-/3-}$ = -2.36 V (rev.).

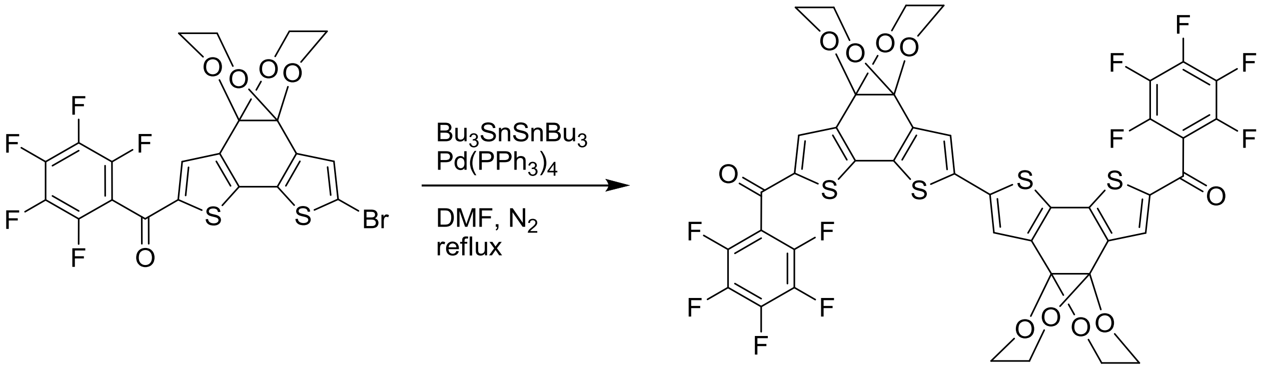
Synthesis of 7,7'-bis-pentafluorobenzoyl-2,2'-bis-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (34)

Step 1. 2-Bromo-7-pentafluorobenzoyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (32)



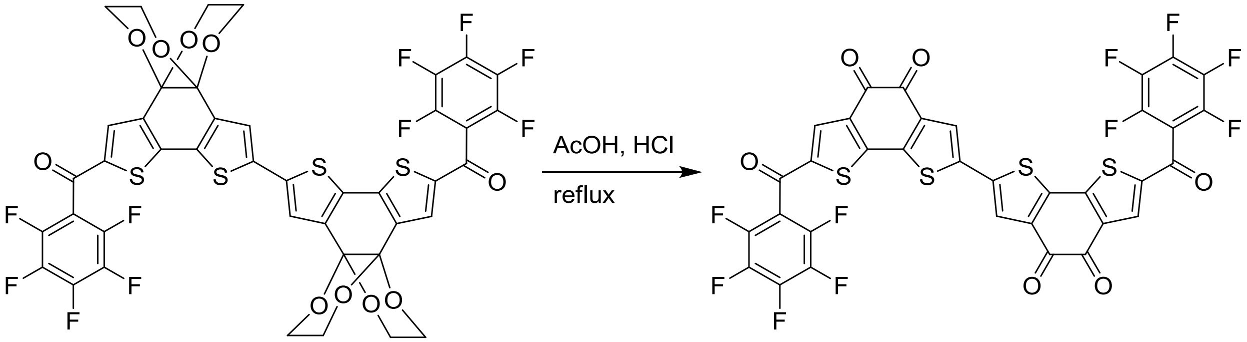
2,7-Dibromo-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (3.0 mmol, 1.40 g) was dissolved in anhydrous THF (75 mL), and yellowish solution was cooled in acetone/dry ice bath under nitrogen atmosphere. *n*-Butyllithium (2.85 M in hexanes, 1.0 eq., 3.0 mmol, 1.05 mL) was added dropwise, and the reaction mixture became purple in color. After stirring for 15 minutes pentafluorobenzoyl chloride (1.5 eq., 4.5 mmol, 1.04 g) was added quickly to the purple suspension, and the reaction mixture was allowed to warm to room temperature, and then treated with aqueous NH$_4$Cl. Organic matter was extracted with dichloromethane several times, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, and the residue was purified by column chromatography (silica gel, dichloromethane:hexanes (2:1) as eluant). Combined fractions were subjected to rotary evaporation, and purified product was obtained as yellow solid (1.53 g). ^{1}H NMR analysis showed the presence of the starting material and 2,7-bis-pentafluorobenzoyl-benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-bis-(ethyloxolane), and it was further purified by column chromatography (silica gel, dichloromethane:hexanes (35:15, then 2:1). Combined fractions were subjected to rotary evaporation, and the residue was recrystallized from 2-propanol. A yellow crystalline material was separated by vacuum filtration (0.93 g). Last fractions with material were combined separately, the solvents were removed by rotary evaporation and the residue was recrystallized from 2-propanol to give additional amount of yellow solid (0.24 g). ^{1}H NMR analysis showed the presence of the same impurities in a very similar ratio, which indicated that the purity of the material did not improve after column chromatography and recrystallization, and material was used in the next step without further attempts of purification. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.50 (s, 1H), 7.23 (s, 1H), 4.16 (m, 4H), 3.67 (m, 4H); ^{13}C{^{1}H} NMR (CDCl$_3$, 100 MHz): δ 175.7 (quaternary C(O), 143.3 (quaternary C), 140.3 (quaternary C), 139.8 (quaternary C), 136.9 (quaternary C), 134.0 (CH), 132.9, 128.8 (CH), 115.8 (quaternary C-Br), 92.5, 92.4, 61.6 (CH$_2$), 61.4 (CH$_2$) (C-F signals were observed as weak multiplets and not certain). DEPT-135 (CDCl$_3$, 100 MHz): δ 134.0 (CH), 128.8 (CH), 61.7 (CH$_2$), 61.5 (CH$_2$). HRMS (EI) calculated for C$_{21}$H$_{10}$BrF$_5$O$_5$S$_2$ 579.9073; found 579.9074.

Step 2. 7,7'-Bis-(pentafluorobenzoyl-2,2'-bis-benzo[2,1-*b*:3,4-*b'*]dithiophenyl-4,5-bis-(ethyloxolane) (33)



2-Bromo-7-pentafluorobenzoyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (**32**) (0.5 mmol, 0.29 g; ~70-80% purity), hexa-*n*-butylditin (0.55 mmol, 0.16 g) and $Pd(PPh_3)_4$ (2 mol%, 0.01 mmol, 0.012 g) were mixed under nitrogen atmosphere, and anhydrous DMF (15 mL) was added. The yellow reaction mixture was heated to reflux, and it became orange, and then red-orange. After 40 minutes the reaction mixture was cooled to room temperature, treated with water, and organic matter was extracted with dichloromethane. Combined organic phases were dried over anhydrous magnesium sulfate, the drying agent was filtered off, and solvents were removed to give crude product as dark red matter. This crude material was purified by column chromatography (dichloromethane, then dichloromethane:ethyl acetate (50:1, 30:1) as eluants). Fractions containing product were combined, the solvents were removed and bright orange solid was obtained (0.10 g). Last fractions with product were combined separately, the solvents were removed, and the residue was heated to reflux with 2-propanol (not soluble), and orange-red solid was removed by vacuum filtration (23 mg). Total yield of the product was 49%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (s, 2H), 7.40 (s, 2H), 4.20 (m, 8H), 3.72 (m, 8H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 175.7 (quaternary C(O)), 143.6 (quaternary C), 140.9 (quaternary C), 140.5 (quaternary C), 138.5 (quaternary C), 137.5 (quaternary C), 134.0 (CH), 131.4, 123.3 (CH), 92.7, 92.5, 61.7 (CH_2), 61.5 (CH_2) (C-F signals were detected as very weak multiplets at δ 145, 143, 139, 136 and are not certain). HRMS (EI) analysis calculated for $C_{42}H_{20}F_{10}O_{10}S_4$ 1001.9780; found 1001.9772. Anal. Calcd. for $C_{42}H_{20}F_{10}O_{10}S_4$: C, 50.30; H, 2.01. Found: C, 50.58; H, 2.21.

Step 3. 7,7'-Bis-(pentafluorobenzoyl-2,2'-bis-benzo[2,1-*b*:3,4-*b'*]dithiophenyl-4,5-dione (34)



7,7'-Bis-pentafluorobenzoyl-2,2'-bis-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (**33**) (0.083 mmol, 0.083 mg) was mixed with acetic acid (~40 mL), and the mixture was heated to reflux. HCl (~3 mL) was added to an orange-red solution, and the mixture became dark brown in color within a few minutes. The reaction mixture was refluxed for ~1 h, cooled to room temperature, and a very dark solid was separated by vacuum filtration, washed with water, ethanol, and then dried (0.043 g, 63.2% crude yield). This material is not soluble in chloroform, dichloromethane, acetonitrile; 1,4-dioxane and THF become purple-pink; material can be recrystallized from 1,1,2,2-tetrachloroethane. Recording of ^{1}H NMR (THF-*d8*, 400 MHz) was attempted, but the sample is not sufficiently soluble even under heating. HRMS (EI) calculated for $C_{34}H_4F_{10}O_6S_4$ 825.8731; found 825.8736 (M+2 (828) was observed as a minor ion). Anal. Calcd. for $C_{34}H_4F_{10}O_6S_4$: C, 49.13; H, 0.49. Found: C, 49.13; H, 0.38.

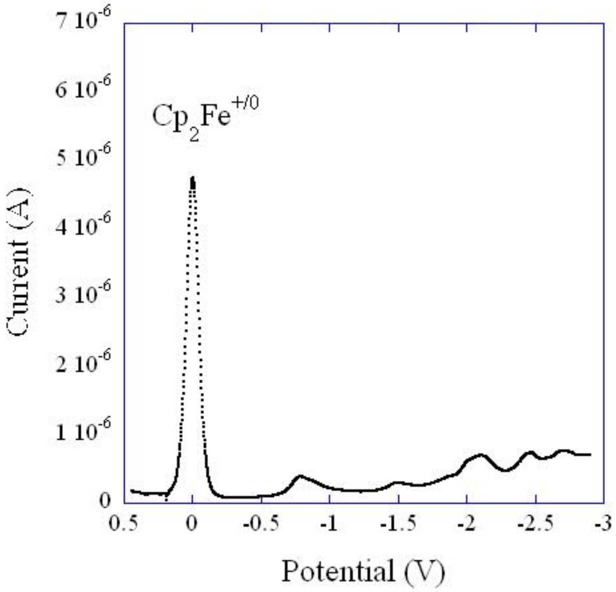
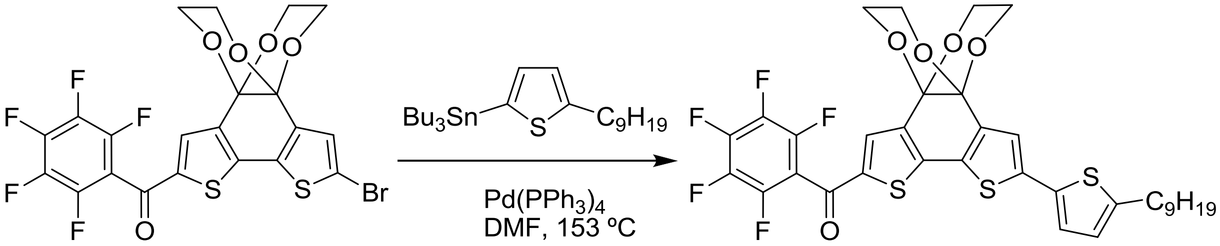


Figure S83. Differential pulse voltammetry (DPV) (0.1 M $^{n}Bu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V) of 7,7'-bis-pentafluorobenzoyl-2,2'-bis-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-

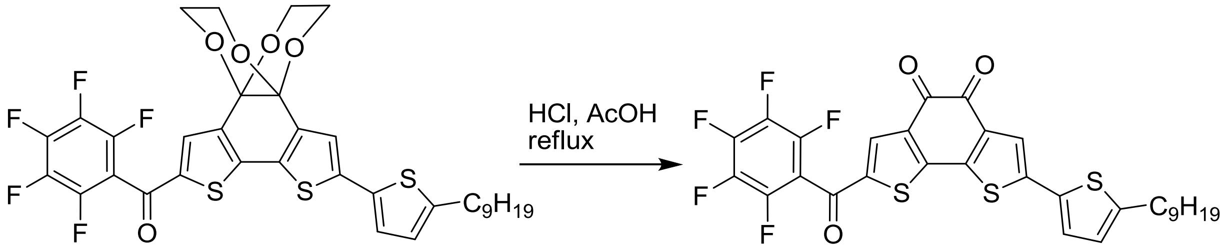
dione (34): $E^{0/2-}$ = -0.79 V (2 e$^-$), $E^{2-/3-}$ = -1.50 V (1.3 e$^-$), $E^{3-/5-(?)}$ = -2.10 V (4.8 e$^-$), $E^{5-/7-(?)}$ = -2.47 V (2.6 e$^-$).

2-Pentafluorobenzoyl-7-(2-*n*-nonylthiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (35)



2-Bromo-7-pentafluorobenzoyl-bis-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (**32**) (1.0 mmol, 0.58 g; ~80% purity) and 2-tri-*n*-butylstannyl-5-*n*-nonylthiophene (1.05 eq., 1.05 mmol, 0.52 g) were mixed in the oven-dried flask under nitrogen atmosphere. Catalyst $Pd(PPh_3)_4$ (0.05 mol%, 0.05 mmol, 0.06 g) was added followed by addition of anhydrous N,N-dimethylformamide (10 mL), and the reaction mixture was heated at reflux for a few minutes. Yellow mixture became orange, then orange-red, and then dark brown within a few minutes. Dark reaction mixture was allowed to cool to room temperature, treated with water and organic matter was extracted with dichloromethane. Combined organic phases were dried over anhydrous magnesium sulfate, and volatile organic solvent were removed by rotary evaporation. The residue was purified by column chromatography (silica gel, hexanes:dichloromethane (1:1) to pack the column, then hexanes:dichloromethane mixtures (2:1, 1:1, 1:2) as eluants). Yellow fractions containing the product were combined, the solvents were removed and orange solid was obtained (0.51 g, 71.8%, ~80% purity). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (s, 1H), 7.23 (s, 1H), 7.10 (d, *J* = 3.6 Hz, 1H), 6.73 (d, *J* = 3.6 Hz, 1H), 4.18 (m, 4H), 3.72 (m, 4H), 2.82 (t, *J* = 7.6 Hz, 2H), 1.80-1.50 (overlapping multiplets, 4H), 1.45-1.20 (m, 10H), 0.93 (t, *J* = 7.3 Hz, 3H) (dichloromethane with δ 5.31 ppm was detected even after drying with heating under vacuum). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 175.49, 147.71, 144.75, 141.30, 140.63, 139.59, 136.57, 134.12 (CH), 133.37, 129.12, 125.30 (CH), 125.00 (CH), 121.09 (CH), 92.88, 92.67, 61.76 (CH_2), 61.50 (CH_2), 31.88 (CH_2), 31.54 (CH_2), 30.25 (CH_2), 29.50 (CH_2), 29.34 (CH_2), 29.30 (CH_2), 29.05 (CH_2), 22.68 (CH_2), 14.12 (CH_3). HRMS calculated for $C_{34}H_{31}F_5O_5S_3$ 710.1254; found 710.1243. Anal. Calcd. for $C_{34}H_{31}F_5O_5S_3$: C, 57.45; H, 4.40. Found: C, 56.46; H, 4.19.

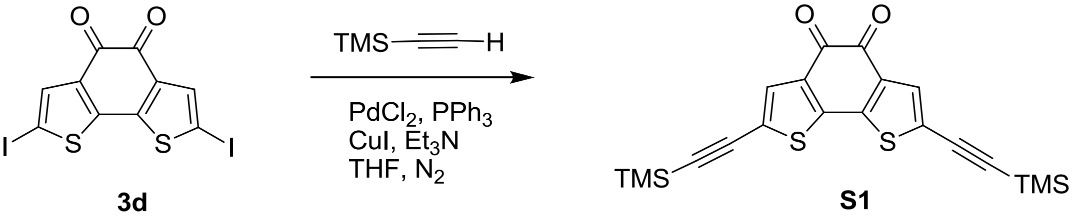
2-Pentafluorobenzoyl-7-(5-*n*-nonylthiophen-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (36)



2-Pentafluorobenzoyl-7-(5-*n*-nonyl-thiophene-2-yl)-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-bis-(ethyloxolane) (**35**) (~0.6 mmol, 0.42 g, ~80% purity) was heated to reflux with acetic acid (40 mL). HCl was added dropwise, and the reaction mixture became dark brown. After reflux for ~0.5 h the reaction mixture was cooled to room temperature, treated with water, and dark solid was separated by vacuum filtration, washed with water and ethanol (some precipitate started to form in the filtrate). Crude product was obtained as dark solid (0.22 g, 60% yield). Solid that formed in the filtrate was separated by vacuum filtration, combined with the crude product, and purified by column chromatography (silica gel, dichloromethane as eluant). Fractions with material (almost pure, trace amount of impurity was detected by TLC) were combined, the solvent was removed by rotary evaporation, and the residue was further purified by column chromatography (silica gel, chloroform as eluant). Less polar yellow impurity and more polar orange impurity were separated, and fractions with the product (blue-green, pure by TLC analysis) were combined, the solvents were removed, and the residue was purified by another column chromatography (silica gel, chloroform as eluant). Green-blue fractions were combined, the solvent was removed, and the residue was heated with ~100 mL of distilled 2-propanol (partially dissolved), cooled and blue-dark solid was separated by vacuum filtration (0.197 g, 53.5%). ^{1}H NMR analysis showed the presence of impurity (not detected by TLC), even after purification by successive chromatographic columns, and material was further purified by two successive silica gel columns (chloroform as eluant for the first column and dichloromethane as eluant for the second column). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (s, 1H), 7.52 (s, 1H), 7.16 (d, J = 3.6 Hz, 1H), 6.77 (d, J = 3.6 Hz, 1H), 2.84 (t, J =7.6 Hz, 2H), 1.70 (m, 2H), 1.50-1.20 (m, 12H), 0.90 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 176.3, 173.9, 173.6, 151.8, 149.6, 142.6, 141.2, 138.3, 138.2, 134.9 (CH), 134.7, 131.6, 126.4 (CH), 125.6 (CH), 122.3 (CH), 31.9 (CH_2), 31.5 (CH_2), 30.3 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.27 (CH_2), 29.02 (CH_2), 22.7 (CH_2), 14.1 (CH_3). HRMS (EI) calculated for $C_{30}H_{23}F_5O_3S_3$ 622.0729, found 622.0742. Anal. Calcd. for $C_{30}H_{23}F_5O_3S_3$: C, 57.87; H, 3.72. Found: C, 58.13; H, 3.67.

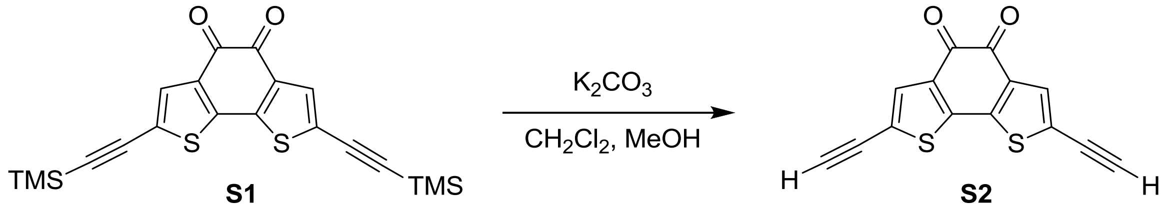
DSC analysis (10 ºC/min): m.p. 187.8 ºC (decomposition). UV-vis (CH_2Cl_2): λ_{max} 295, 343, 396, 586. CV analysis (0.1 M $^nBu_4NPF_6$ in THF, Cp_2Fe internal standard at 0 V): $E_{1/2}^{0/1-}$ = 0.85 V; $E_{1/2}^{1-/2-}$ = -1.45 V; $E_{1/2}^{2-/3-}$ = -2.07 V.

2,7-Bis-trimethylsilylethynyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (S1)



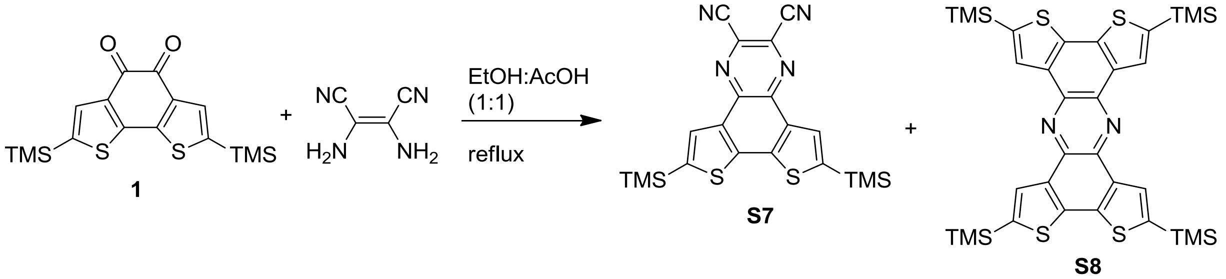
2,7-Diiodo-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (**3d**) (1.0 mmol, 0.472 g), $PdCl_2$ (0.04 eq., 0.04 mmol, 0.007 g), PPh_3 (0.1 equiv., 0.1 mmol, 0.026 g) and Et_3N (2.2 equiv., 2.2 mmol, 0.22 g) were mixed in an oven-dried Schlenk flask under nitrogen atmosphere. Anhydrous THF (30 ml) was added followed by addition of trimethylsilylacetylene (2.2 eq., 2.2 mmol, 0.22 g) and CuI (0.012 equiv., 0.012 mmol, 2.3 mg). The mixture was heated (58 ºC bath temperature initially, then 40-45 ºC), but no reaction was observed by TLC analysis (CH_2Cl_2 as eluant) after ~1.5 h of heating. Additional amount of Et_3N (0.3 ml) was added, followed by addition of trimethylsilylacetylene (2.4 mmol, 0.24 g). After stirring at heating (47-49 ºC bath temperature) for 4 hours no reaction was observed based on TLC analysis and additional amount of CuI (6.5 mg) was added. After ~20 minutes of stirring dark red-purple mixture became yellowish-greenish and the mixture was left to stir overnight (40 ºC, nitrogen atmosphere). The yellow-greenish mixture was cooled to room temperature and treated with water. Organic phase became dark purple-brown, brine was added and organic phase was separated. The aqueous phase was extracted with diethyl ether several times and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, the solvents were removed by rotary evaporation and the residue was purified by column chromatography (silica gel, dichloromethane as eluant). Material came out contaminated (dichloromethane is too polar solvent for this material), and the fractions with the product were combined, subjected to rotary evaporation, and the residue was recrystallized from 2-propanol. Product was obtained as very dark needles (0.058 g, 14%). The stained column was eluted with chloroform:ethyl acetate, and purple solution was collected, subjected to rotary evaporation, and the residue was purified by column chromatography (silica gel, chloroform as eluant). Combined fractions were subjected to rotary evaporation, and the residue was recrystallized from ~15 mL of ethanol. Very dark crystals were separated by vacuum filtration, and additional amount of product was obtained (0.029 g, 7.0%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53 (s, 2H), 0.27 (s, 18H) ; ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 173.62 (quaternary C(O)), 142.85 (quaternary C), 135.02 (quaternary C), 132.07 (CH), 124.51 (quaternary C), 104.48 (quaternary C), 95.01 (quaternary C) (assignment of CH, CH_2 and CH_3 signals was made based on the DEPT-135 experiment). HRMS (EI) calculated for $C_{20}H_{20}O_2S_2Si_2$: 412.0443; found 412.0449. Anal. Calcd. for $C_{20}H_{20}O_2S_2Si_2$: C, 58.21; H, 4.88. Found: C, 57.36; H, 4.87.

2,7-Bis-ethynyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (S2)



2,7-Bis-trimethylsilylethynyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (**S1**) (0.07 mmol, 0.029 g) was dissolved in a mixture of dichloromethane-methanol (10:10 mL), and K_2CO_3 (3.0 eq., 0.12 mmol, 0.029 g) was added to a dark blue-purple solution at room temperature. The reaction mixture was stirred for about 1 h, and treated with water. Organic phase was removed, aqueous phase was extracted with dichloromethane, and combined organic phases were dried over anhydrous magnesium sulfate. The drying agent was filtered off, the solvent was removed, and the crude product was purified by column chromatography (silica gel, dichloromethane as eluant). Solvent was removed from the combined fractions, and product was obtained as dark microcrystalline solid (100% yield, 0.019 g). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.61 (s, 2H), 3.56 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 173.50 (quaternary C(O)), 143.03 (quaternary C), 132.72 (CH), 123.41 (quaternary C), 85.69 (CH), 74.70 (quaternary C) (assignment of the CH signals was made based on the DEPT-135 experiment).

Condensation of 2,7-bis-trimethylsilyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (1) with diamine: Isolation of S7 and S8.



2,6-Bis-trimethylsilyl-benzo[1,2-*b*:6,5-*b'*]dithiophene-4,5-dione (**1**) (0.50 mmol, 0.182 g) was mixed with diaminomaleonitrile (0.50 mmol, 0.054 g) in a 100 mL-round bottom flask. Ethanol (20 mL) and acetic acid (2 mL) were added, and the dark red solution was heated to reflux. After 1.5 h of reflux 18 mL of acetic acid was added, and the mixture was refluxed overnight. TLC analysis (hexanes:dichloromethane (4:1) showed the presence of two new materials and a small amount of starting material, and additional amount of diaminomaleonitrile (0.08 mmol, 0.009 g) was added. The mixture was heated for additional 0.5 h, cooled to room temperature, and ethanol was removed by the rotary evaporation. The residue was treated with water, the organic matter was extracted with diethyl ether several times, and the combined organic phases were dried over anhydrous magnesium sulfate. The residue was purified by the column chromatography (silica gel, dichloromethane as eluant). First three fractions (bright yellow spot on TLC under visible light) were combined, the solvents were removed by rotary evaporation, and the yellow solid was obtained (**S8**, 0.044 g, 25% yield). The solvents were removed from combined fractions, brownish-yellow solid **S7** was obtained (0.051 g), and was further purified by column chromatography (silica gel, dichloromethane as eluant; then silica gel, chloroform:hexanes (1:1) as eluant). The solvents were removed from combined fractions, and the residue (yellow solid with a small amount of brownish impurities) was recrystallized from 2-propanol:chloroform, and bright yellow-orange material **S7** was obtained after vacuum filtration (0.024 g, 11.0% yield).

S7: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (s, 2H), 0.50 (s, 18H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 144.90 (quaternary C), 144.08 (quaternary C), 138.35 (quaternary C), 134.26 (quaternary C), 131.15 (CH), 128.69 (quaternary C), 114.28 (quaternary C), -0.23 (CH_3) (assignment of CH and CH_3 signals was made based on the DEPT-135 experiment). HRMS (EI) calculated for $C_{20}H_{20}N_4S_2Si_2$ 436.0668; found 436.0682. Anal. Calcd. for $C_{20}H_{20}N_4S_2Si_2$: C, 55.01; H, 4.62; N, 12.83. Found: C, 54.95; H, 4.62; N, 12.58.

S8: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (s, 2H), 0.54 (s, 18H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 140.82 (quaternary C), 139.56 (quaternary C), 137.83 (quaternary C), 136.21 (quaternary C), 131.33 (CH), 0.01 (CH_3 of TMS group) (assignment of the CH and CH_3 signals was made based on the DEPT-135 experiment). MS (EI) calculated for $C_{32}H_{40}N_2S_4Si_4$ 692.1151; found 692.1.

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