Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Facile Synthesis of Oligo(3-hexylthiophene)s Conductive Wires with Charge-Transfer Functions

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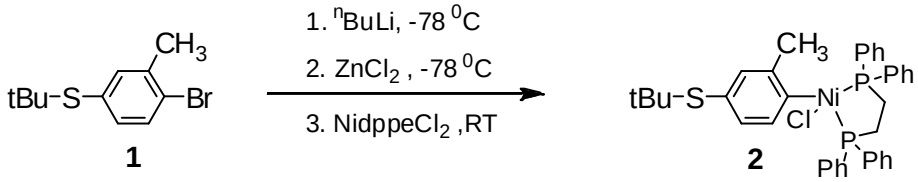
Precursor Synthesis

All reactions were carried out under argon atmosphere unless otherwise mentioned. All reagents and solvents were used without further purifications. 2.0 M *i*-PrMgCl solution in THF, 2.5 M ^{n}BuLi solution in hexane, $ZnCl_2$, and all catalysts ($Ni(dppe)Cl_2$ - $Pd(PPh_3)_2Cl_2$ - $Pd(PPh_3)_4$) were stored and used in glove box. *i*-PrMgCl and ^{n}BuLi, were purchased as solutions and used without further dilutions. (4-bromo-3-methylphenyl)(*tert*-butyl)sulfane (**1**),[1] (4-bromophenyl)(*tert*-butyl)sulfane (**4**),[2] 4-ethynyl-N,N-dimethylaniline (**5**),[3] ethynylferrocene (**6**),[4] 2-bromo-3-hexylthiophene and 2-bromo-3-hexyl-5-iodothiophene[5] were synthesized according to reported papers.

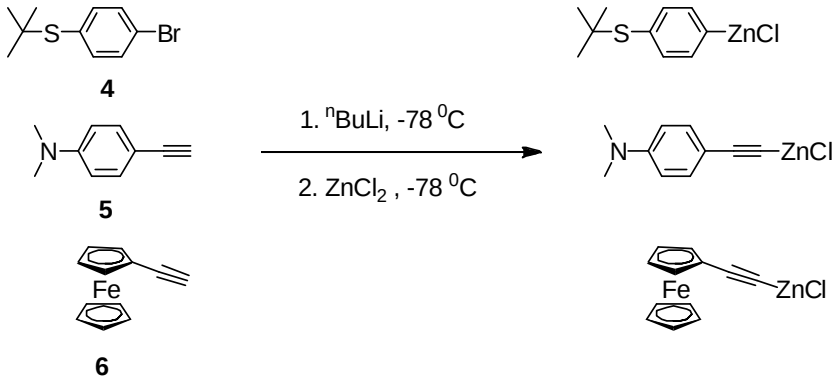
Polymerization Route

Preparation of initiator



Initiator, **2**, was prepared as follows: nBuLi (2.5 M in hexane, 2.51 mmol, 1.0 ml) was added dropwise to a solution of (4-bromo-3-methylphenyl)(*tert*-butyl)sulfane **[1]** (2.51 mmol, 0.65 g) in dry THF (10 ml) under argon atmosphere at -78 ^{0}C with a change in color from colorless to yellow. The reaction mixture was allowed to react for 1 hr at this temperature. Then previously prepared solution of $ZnCl_2$ (2.51 mmol, 342 mg) in dry THF (5 ml) was added to reaction mixture at -78 ^{0}C and immediate change in color to pink was seen. Reaction mixture was stirred to reach room temperature. Afterwards, 0.87 mg (1.65 mmol) of $Ni(dppe)Cl_2$ dissolved in dry THF (32 ml) was added to already warm reaction mixture, followed by a change in color from pink to red-brownish color. The initiator mixture was stirred for additional 1 hr before used for polymerization. After withdrawal of exact volumes from initiator mixture with respect to the desired initiator: monomer ratio in polymerization, the remaining solution was taken into glovebox. Excess amount of hexane was added to the remaining solution and the mixture was left in glovebox fridge (-20 ^{0}C) for overnight to settle initiator molecules. Thereafter, precipitated yellow-orange crystals **[2]** (0.921 g, 87 %) were separated from the solution via vacuum filtration in glovebox and used further polymerizations.

Preparation of reactive quenchers

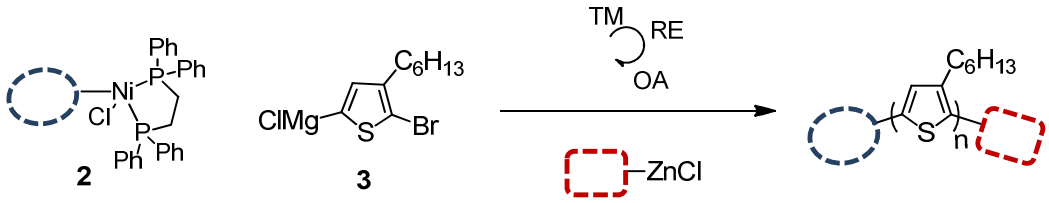


ZnCl-substituted quenchers were prepared in similar experimental conditions. (4-bromophenyl)(*tert*-butyl)sulfane **[4]** (2.13 mmol, 0.52 g) and 10 ml dry THF was stirred in a round-bottom flask under argon atmosphere and the flask was cooled down to -78 ^{0}C. nBuLi (2.5 M in hexane, 2.13 mmol, 0.85 ml) was added dropwise to the solution and the reaction was allowed to react for additional 1 hr at this temperature. Then previously prepared solution of $ZnCl_2$ (2.13 mmol, 290 mg) in dry THF (4 ml) was added to mixture at -78 ^{0}C. Reaction mixture was stirred to reach room temperature. Afterwards, quencher solutions in excess amount were withdrawn from the reaction mixtures and added to the polymerization media with respect to the desired initiator/monomer/quencher ratio in polymerization ([I]/[M]/[Q] for DP 1:10:5 and for DP 1:15:5). A small aliquot was taken to test the complete exchange of metal ions; 1 ml of the reaction mixture was added to methanol and extracted with $CHCl_3$ and water, and from ^{1}H-NMR spectra it was proved that all bromine was converted into ZnCl-substituent. ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.56-7.54 (m, 2H, Ar-H), 7.37-7.32 (m, 3H, Ar-H), 1.30 (s, 9H, -SC($C\underline{H}_3$)$_3$).

Preparation of reactive monomer [3]

2-Bromo-3-hexyl-5-iodothiophene (5.52 g, 14.8 mmol) was taken in a round-bottomed flask and the flask filled with argon. Dry THF (21.6 ml) was added and the flask was cooled down to 0 ^{0}C. Isopropyl magnesium chloride (2.0 M solution in THF, 7.4 ml, 14.8 mmol) was added via syringe and the reaction mixture was allowed to stir at 0 ^{0}C for 2 hrs.

Polymerization via externally-prepared initiator



Experimental details for polymers were given for only one batch of polymerization sets (DP 10) as an example. In order to obtain the desired degree of polymerization, the exact volumes of initiator and monomer solutions were withdrawn from the ongoing reactions (for DP 10; 1.48 mmol, 43 ml from initiator solution and 14.8 mmol, 29 ml from reactive monomer solution). Freshly-prepared initiator solution **[2]** was transferred to a clean round-bottom flask and a solution of reactive monomer **[3]** was added in one portion. Subsequently, the polymerization mixture was stirred at room temperature till the respective time for the monomer consumption. While a portion was quenched with MeOH to obtain mono-functionalized polymer segment (**P1**), the rest (60 ml) was divided into three portions and each portion was quenched by the freshly prepared quencher solutions to get bis-end functionalized polymer segments, **P2**, **P3**, and **P4**. Required quencher volumes were withdrawn from parent reactions in 1 to 5 ratio with respect to the initiator for DP 10 ([I]/[M]/[Q] 1:15:5 for DP 15) and were added to the already separated polymerization batches for termination. Those quenched parts, except the one quenched with methanol, were heated to 50 ^{0}C for 15 min, and then cooled to room temperature. The reaction mixture was poured into water and extracted with $CHCl_3$. Organic layers were combined, dried over $MgSO_4$, vacuum filtrated and concentrated under reduced pressure. Acetone was added to the flask and the insoluble material was collected on a filter paper and further purified from low DP products via Soxhlet extraction. After acetone; hexane and chloroform were used as solvents in Soxhlet extraction to separate polymer chains in different molecular weights, respectively. In some cases; in order to remove catalyst residues in polymers, which can be defined by additional peaks of catalyst in ^{1}H-NMR spectra, column chromatography (with Hexane:CH_2Cl_2 as eluent with a gradient change) was used as further purification method after Soxhlet extraction. (*percent yields for polymerizations were calculated using the weights after acetone soxhlet.)

P1: α-R_1/ω-H(Br) ; 295 mg, 72 % ; DP: 10, Mn= 3429 g/mol, Mw= 3818, Đ= 1.11; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.45 (bs, 1H, Ar-H), 7.40 (m, 2H, I/Ar-H), 6.99 (bs, 3HTh-H), 6.98 (s, Th-H), 6.95 (s, I-3HT-H), 6.91 (s, ω-H end Th-H), 6.84 (s, ω-Br end Th-

H), 2.82 (t, *J*=7.3x(2) Hz, ThC$\underline{H}_2(CH_2)_4CH_3$), 2.72 (t, *J*=7.9x(2) Hz, α-I-Th-α-C$\underline{H}_2$), 2.63 (t, *J*=7.3x(2) Hz, ω-H end Th-α-C$\underline{H}_2$), 2.58 (m, ω-Br end Th α-C$\underline{H}_2$), 2.51 (s, 3H, I-C$\underline{H}_3$), 1.72 (m, $ThCH_2C\underline{H}_2(CH_2)_3CH_3$), 1.45 (m, $ThCH_2CH_2C\underline{H}_2(CH_2)_2CH_3$), 1.37 (m, $ThCH_2CH_2CH_2(C\underline{H}_2)_2CH_3$), 1.35 (s, I-SC(C$\underline{H}_3)_3$), 0.93 (m, $Th(CH_2)_5C\underline{H}_3$)

P2: α-R_1/ω-R_2 ; 377 mg, 92 % ; DP:10, Mn= 3269 g/mol, Mw=3493 g/mol, Đ= 1.07 (for DP:15; 541 mg, 88 % ; Mn= 4188 g/mol, Mw= 4532 g/mol, Mn/Mw= 1.08); ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.58 (d, *J*=8.0 Hz, 2H, Q/Ar-H), 7.45 (bs, 1H, I/Ar-H), 7.44 (d, *J*=8.0 Hz, 2H, Q/Ar-H), 7.40 (m, 2H, I/Ar-H), 7.04 (s, ω-Q end Th-H), 6.99 (bs, 3HTh-H), 6.98 (s, Th-H), 6.96 (s, I-3HT-H), 6.91 (s, ω-H end Th-H), 6.84 (s, ω-Br end Th-H), 2.82 (t, *J*=7.9x(2) Hz, ThC$\underline{H}_2(CH_2)_4CH_3$), 2.77 (t, *J*=7.9x(2) Hz, α-I Th-α-C$\underline{H}_2$), 2.69 (t, *J*=7.6x(2) Hz, ω-Q end Th-α-C$\underline{H}_2$), 2.63 (t, *J*=7.9x(2) Hz, ω-H end Th-α-C$\underline{H}_2$), 2.57 (m, ω-Br end Th-α-C$\underline{H}_2$), 2.51 (s, 3H, I-C$\underline{H}_3$), 1.70 (m, $ThCH_2C\underline{H}_2(CH_2)_3CH_3$), 1.45 (m, $ThCH_2CH_2C\underline{H}_2(CH_2)_2CH_3$), 1.37 (m $ThCH_2CH_2CH_2(C\underline{H}_2)_2CH_3$), 1.35 (s, Q-SC(C$\underline{H}_3)_3$), 1.34 (s, I-SC(C$\underline{H}_3)_3$), 0.92 (m, $Th(CH_2)_5C\underline{H}_3$)**;** ^{13}C NMR (125.8 MHz; $CDCl_3$; Me_4Si) δ (ppm): 143.6 (ω-H end Th), 140.2 (I-3HTh), 139.9 (P3HT), 139.7 (I-Ar), 139.6 (ω-Br end Th), 139.5 (Q-3HTh), 137.5 (Q-Ar), 136.9 (Q-3HTh), 135.7 (I-Ar), 135.5 (ω-H end Th), 134.9 (Q-Ar), 134.8 (I-Ar), 134.4 (Q-3HTh), 134.2 (I-Ar), 133.8-133.6-133.5 (I-3HTh & ω-Br end Th), 133.7 (P3HT), 132.0 (I-Ar), 131.9 (Q-Ar), 130.5 (P3HT), 129.9 (I-Ar & I-3HTh), 129.0 (Q-Ar), 128.6 (P3HT), 128.4 (ω-Br end Th), 128.3 (Q-3HTh), 127.2 (ω-H end Th), 120.0 (ω-H end Th), 46.2 (Q-S$\underline{C}(CH_3)_3$), 46.0 (I-S$\underline{C}(CH_3)_3$), 31.7 (-Th$\underline{C}H_2CH_2CH_2(CH_2)_2CH_3$), 31.6 (ω-Br end Th), 31.1 (I-SC($\underline{C}H_3)_3$), 31.0 (Q-SC($\underline{C}H_3)_3$), 30.5 (-$ThCH_2\underline{C}H_2CH_2(CH_2)_2CH_3$), 30.4 (ω-H end Th), 29.5 (I-Th-$\underline{C}H_2$-), 29.2 (-$ThCH_2CH_2\underline{C}H_2(CH_2)_2CH_3$), 29.0 (Q-Th-$\underline{C}H_2$-), 22.6 (-$ThCH_2CH_2CH_2(\underline{C}H_2)_2CH_3$), 21.3 (I-Ar-$\underline{C}H_3$), 14.1 (-$ThCH_2CH_2CH_2(CH_2)_2\underline{C}H_3$)

P3: α-R_1/ω-R_3 ; 192 mg, 47 % ; DP:10, Mn= 3122 g/mol, Mw= 3278 g/mol, Đ= 1.05; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.46 (bs, 1H, I/Ar-H), 7.41 (m, 4H, I/Ar-H & Q/Ar-H), 7.00 (s, ω-Q end Th-H), 6.99 (bs, 3HTh-H), 6.96 (s, I-3HT-H), 6.93 (s, ω-H end Th-H), 6.84-6.83 (s, ω-Br end Th-H), 6.69 (d, *J*=8.5 Hz, Q/Ar-H), 3.02 (s, -N(C$\underline{H}_3)_2$), 2.83 (t, *J*=7.3x(2) Hz, ThC$\underline{H}_2(CH_2)_4CH_3$), 2.76 (t, *J*=7.9x(2) Hz, I-Th-α-C$\underline{H}_2$ & ω-Q end Th-α-C$\underline{H}_2$), 2.68, 2.63 (t, *J*=7.3x(2) Hz, ω-H end Th-α-C$\underline{H}_2$), 2.58 (m, ω-Br end Th-α-C$\underline{H}_2$), 2.51 (s, 3H, I-C$\underline{H}_3$), 1.72 (m, $ThCH_2C\underline{H}_2(CH_2)_3CH_3$), 1.45 (m, $ThCH_2CH_2C\underline{H}_2(CH_2)_2CH$), 1.36 (m, $ThCH_2CH_2CH_2(C\underline{H}_2)_2CH_3$), 1.35 (s, I-SC(C$\underline{H}_3)_3$), 0.91 (m, $Th(CH_2)_5C\underline{H}_3$)

P4: α-R_1/ω-R_4 ; 201 mg, 49 % ; DP:10, Mn= 3047 g/mol, Mw=3215, Đ= 1.06; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.46 (bs, 1H, I/Ar-H), 7.44 (d, *J*=8.0 Hz, 2H, Q/Ar-H), 7.41

(m, 2H, I/Ar-H), 6.99 (bs, 3HTh-H), 6.98 (s, ω-Q end Th-H), 6.96 (s, I-3HT-H), 6.93 (s, ω-H end Th-H), 6.84-6.83 (s, ω-Br end Th-H), 4.53 (t, *J*=1.9 x(2) Hz, 2H, Fc-H), 4.28 (m, 7H, Fc-H), 2.82 (t, *J*=7.9x(2) Hz, $ThCH_2(CH_2)_4CH_3$), 2.78 (m, I-Th-α-CH_2), 2.75 (t, *J*=7.9x(2) Hz, ω-Q end Th-α-CH_2), 2.69 ,2.63 (t, *J*=7.6x(2) Hz, ω-H end Th-α-CH_2), 2.58 (m, ω-Br end Th-α-CH_2), 2.51 (s, 3H, I-CH_3), 1.72 (m, $ThCH_2CH_2(CH_2)_3CH_3$), 1.45 (m, $ThCH_2CH_2CH_2(CH_2)_2CH_3$), 1.37 (m, $ThCH_2CH_2CH_2(CH_2)_2CH_3$), 1.35 (s, I-$SC(CH_3)_3$), 0.93 (m, $Th(CH_2)_5CH_3$)

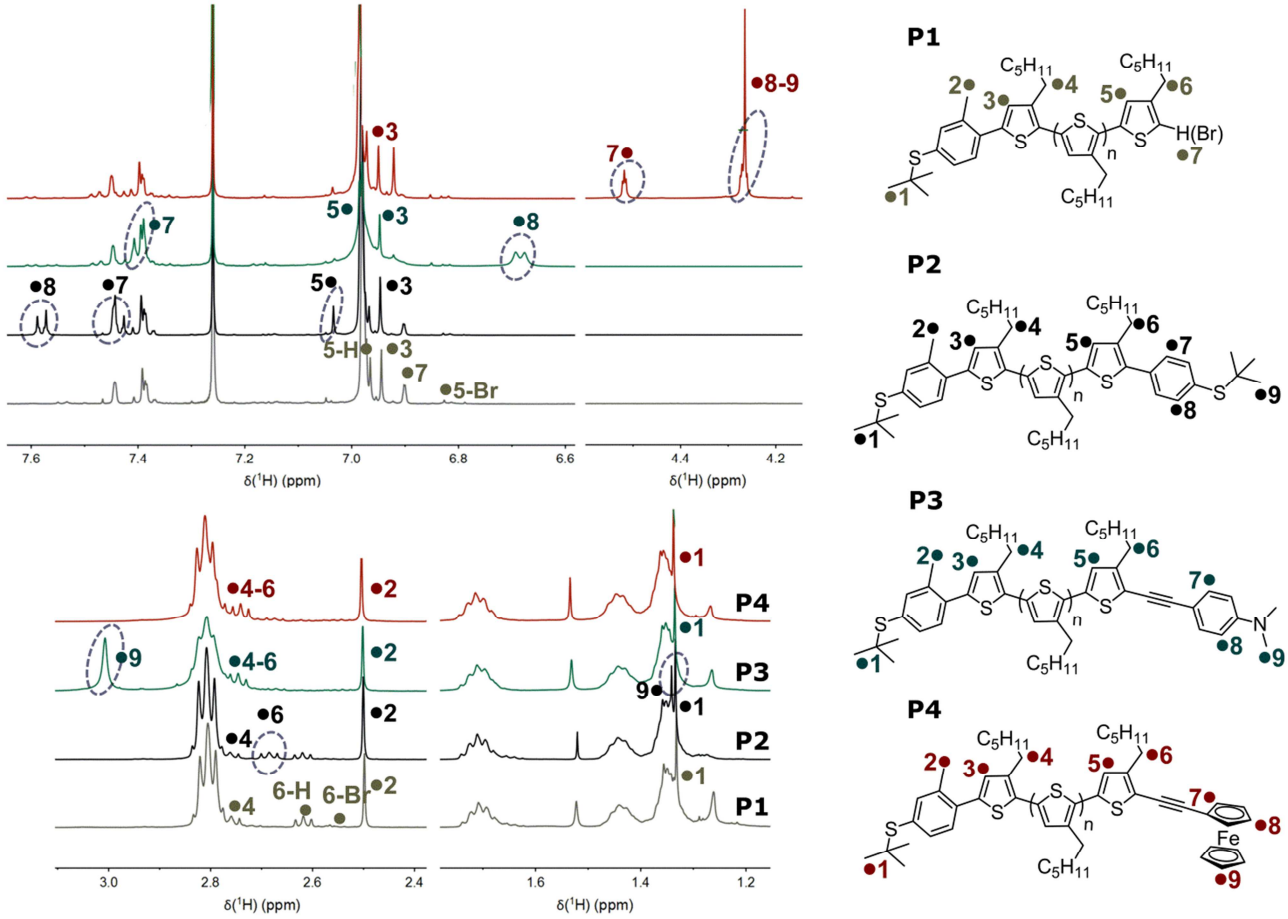


Figure S1. ^{1}H-NMR spectra of **P1**-**P4**; products from externally initiated KCTP

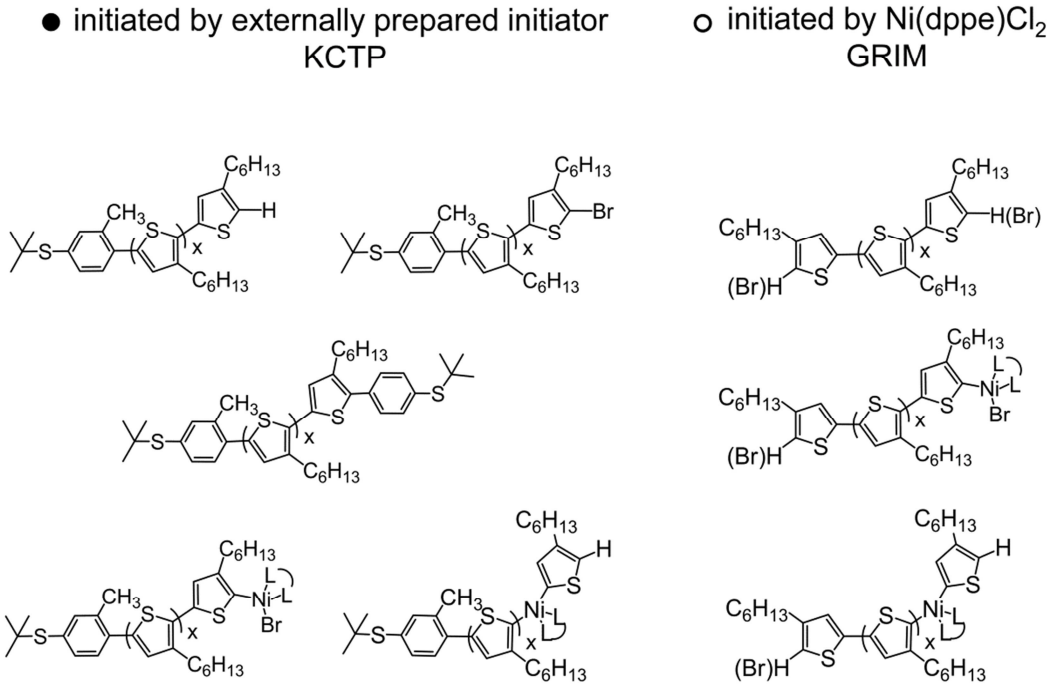
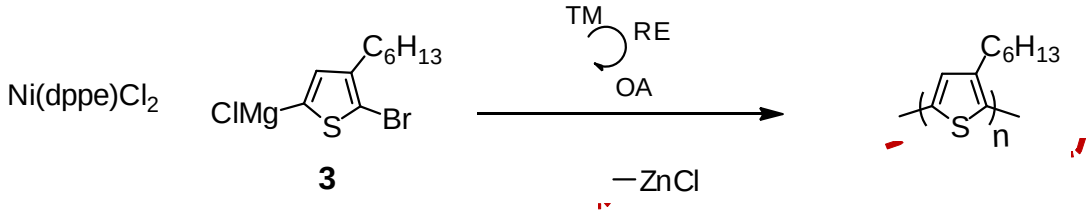


Figure S2. Chemical structures of the end group combinations for **P2**

Polymerization via classical Grignard metathesis synthesis [5b]



Experimental details for polymers were given for only one batch of polymerization sets as an example. $Ni(dppe)Cl_2$ (378 mg, 0.715 mmol) was transferred in a clean round-bottom flask and the flask was sealed carefully in glove box. Then for the polymerizations the flask was taken outside from glove box. Dry THF (15 ml) and reactive monomer **3** was added in a ratio for defined degree of polymerization (7.15 mmol for DP 1:10 and 10.725 mmol for DP 1:15). Subsequently, the polymerization mixture was stirred at room temperature till the respective time for the monomer consumption. While a portion quenched with MeOH to obtain polymer segments without specific anchoring groups **(P5)**, the rest was divided and quenched by the freshly prepared quencher solutions. Those quenched portions, except the one quenched with methanol, were heated to 50 ^{0}C for 15 min, and then cooled to room temperature. Obtained polymers were extracted and purified similarly with the polymers obtained via externally prepared initiator.

P5: α-H(Br)/ω-H(Br) ; 204 mg, 86 % ; DP:10, Mn= 3347 g/mol, Mw=3734 g/mol, Đ= 1.12 ; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.00 (m, *HH* ω-H end Th-2-H), 6.99 (bs, 3HTh-H), 6.96 (s, *HT* ω-H end Th-H), 6.93 (s, *HH* ω-H end Th-H), 6.91 (s, *HT* ω-H end Th-2-H), 6.86 (s, *HH* ω-Br end Th-α-H), 6.84 (s, *HT* ω-Br end Th-α-H), 2.81 (m, $ThCH_2(CH_2)_4CH_3$), 2.70 (m, *HH* ω-H end Th-α-CH_2), 2.63 (t, *J*=7.3x(2) Hz, *HT* ω-H end Th-α-CH_2), 2.58 (m, *HH* ω-Br end Th-α-CH_2), 2.55 (m, *HT* ω-Br end Th-α-CH_2), 1.71 (m, $ThCH_2CH_2(CH_2)_3CH_3$), 1.45 (m, $ThCH_2CH_2CH_2(CH_2)_2CH_3$), 1.35 (m, $ThCH_2CH_2CH_2(CH_2)_2CH_3$), 0.93 (m, $Th(CH_2)_5CH_3$).

P6: α-R_2/ω-R_2 ; 209 mg, 88 % ; DP:10 , Mn= 3087 g/mol, Mw= 3657 g/mol, Đ= 1.18; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.59 (d, *J*=8.2 Hz, 2H, I-Q/Ar-H), 7.44 (d, *J*=8.2 Hz, 2H, I-Q/Ar-H), 7.07 (s, ω-I/Q end Th-H), 7.05 (s, ω-I/Q end Th-H), 7.01 (s, *H-H* ω-H end Th-2-H), 7.00 (bs, 3HTh-H), 6.97 (s, ω-H end Th-H), 6.92 (s, ω-H end Th-H), 6.81 (s, ω-Br end Th-H), 2.82 (t, *J*=7.9x(2) Hz, $ThCH_2(CH_2)_4CH_3$), 2.78 (m, α-I-Th-α-CH_2), 2.70 (t, *J*=7.9x(2) Hz, I/Q end Th-α-CH_2), 2.63 (m, ω-H end Th-α-CH_2), 2.60 (m, ω-Br end Th-α-CH_2), 1.71 (m, $ThCH_2CH_2(CH_2)_3CH_3$), 1.45 (m, $ThCH_2CH_2CH_2(CH_2)_2CH_3$), 1.37 (m, $ThCH_2CH_2CH_2(CH_2)_2CH_3$), 1.35 (s, I/Q-$SC(CH_3)_3$), 0.92 (m, $Th(CH_2)_5CH_3$).

P7: α-R_3/ω-R_3 ; 164 mg, 69 % ; DP:10 , Mn= 3272 g/mol, Mw= 3573 g/mol, Đ= 1.09; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.42 (d, *J*=8.8 Hz, Ar-H), 7.02 (bs, 3HTh-H), 7.00 (s, bis-3HT-H), 6.96 (s, mono-ω-H end Th-H), 6.95-6.93 (s, HT-HH ω-H end Th-H), 6.88 (s, mono-ω-Br end Th-H), 6.86-6.85 (HH-HT ω-Br end Th-H), 6.71 (d, *J*=8.8 Hz, Ar-H), 3.02 (s, $-N(CH_3)_2$), 2.83 (m, $ThCH_2(CH_2)_4CH_3$), 2.78 (m, mono/bis-Th-α-CH_2), 2.70 (t, *J*=7.3x(2) Hz, *HH* ω-H end Th-α-CH_2), 2.65 (t, *J*=7.3x(2) Hz, HT ω-H end Th-α-CH_2), 2.61 (t, *J*=7.3x(2) Hz, HH ω-Br end Th-α-CH_2), 2.57 (t, *J*=7.6x(2) Hz, HT ω-Br end Th-α-CH_2), 1.71 (m, $ThCH_2CH_2(CH_2)_3CH_3$), 1.48 (m, $ThCH_2CH_2CH_2(CH_2)_2CH_3$), 1.39 (m, $ThCH_2CH_2CH_2(CH_2)_2CH_3$), 0.93 (m, $Th(CH_2)_5CH_3$).

P8: α-R_4/ω-R_4 ; 138 mg, 58 % ; DP:10, Mn= 3104 g/mol, Mw= 3401 g/mol, Đ= 1.09; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.02 (bs, 3HTh-H), 7.01 (s, bis-3HT-H), 6.96 (s, mono-ω-H end Th-H), 6.94-6.93 (s, HT-HH ω-H end Th-H), 6.88 (s, mono-ω-Br end Th-H), 6.86-6.85 (HH-HT ω-Br end Th-H), 4.55 (t, *J*=1.9 x(2) Hz, 2H, Fc-H), 4.29 (m, 7H, Fc-H), 2.85 (m, $ThCH_2(CH_2)_4CH_3$), 2.78 (m, mono/bis-Th-α-CH_2), 2.71 (t, *J*=7.9x(2) Hz, *HH* ω-H end Th-α-CH_2), 2.65 (t, *J*=7.6x(2) Hz, HT ω-H end Th-α-CH_2), 2.61 (m, HH ω-Br end Th-α-CH_2), 2.57 (t, *J*=7.3x(2) Hz, HT ω-Br end Th-α-CH_2), 1.74 (m, $ThCH_2CH_2(CH_2)_3CH_3$), 1.47

(m, $ThCH_2CH_2C\underline{H}_2(CH_2)_2CH_3$), 1.39 (m, $ThCH_2CH_2CH_2(C\underline{H}_2)_2CH_3$), 0.96 (m, $Th(CH_2)_5C\underline{H}_3$).

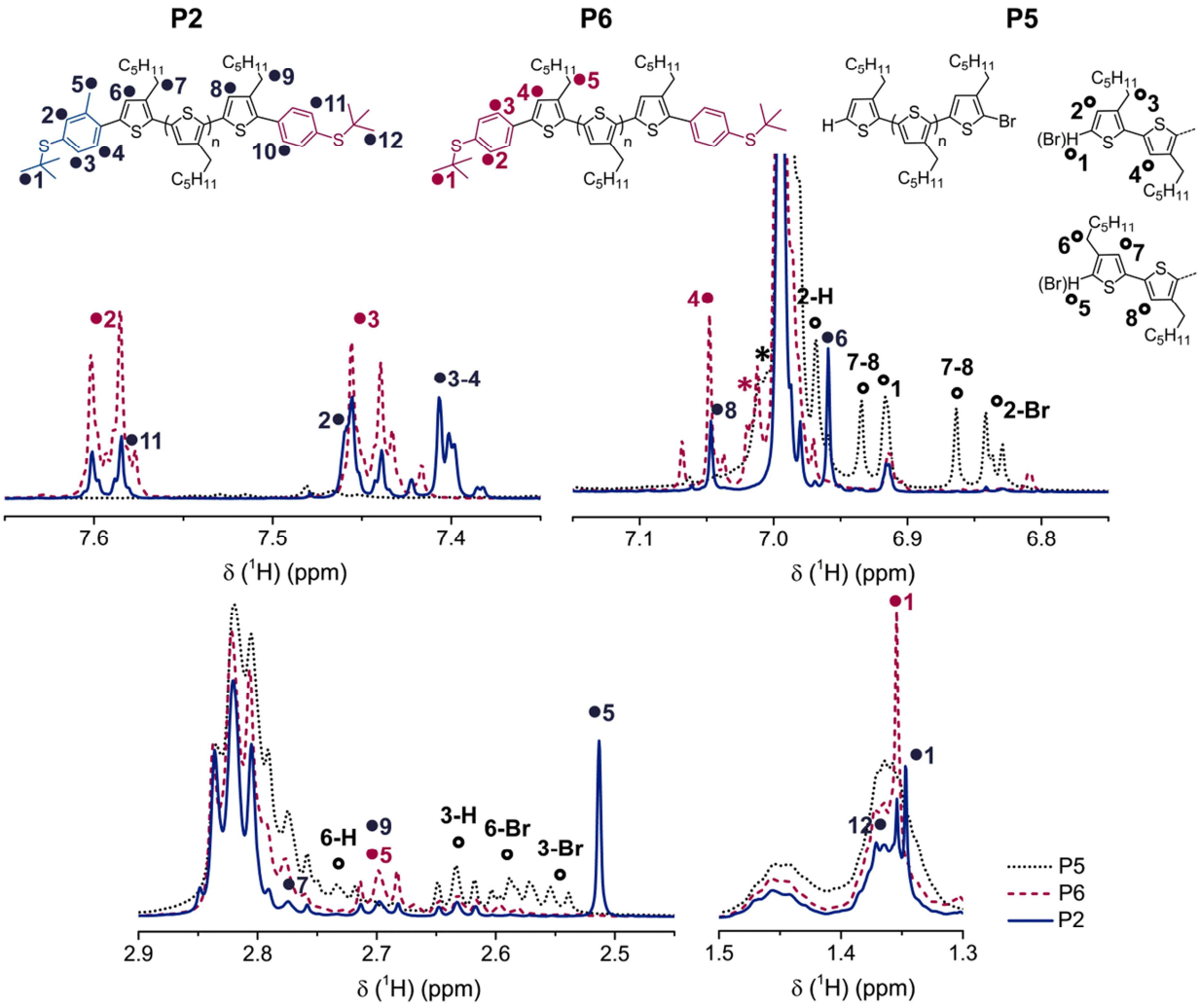


Figure S3. ^{1}H-NMR spectra of **P2**, **P5** and **P6** for an elaborative discussion of chain initiation with an external initiator (*broad shoulders indicating different chain lengths due to uncontrollable polymerization)

Table ESI- 1 Mn, Đ, DP and end-group compositions for oligomers P1-P8.

Oligomer	Mn(kg/mol)[a]	Đ[a]	DP[b]	Starting-	End-group composition[c]		
					bis-	H-	Br-
P1	3.4	1.11	14	R_1	-	76	24
P2	3.3	1.07	12	R_1	53 (R_2)	38	9
P3	3.1	1.05	10	R_1	70 (R_3)	14	16
P4	3.1	1.06	10	R_1	74 (R_4)	17	9
P5	3.3	1.12	12	H/Br	-	58[d]	42
P6	3.1	1.18	11-15	R_2	52 (R_2)	30	18
P7	3.3	1.09	10-13	R_3	52[e] (R_3)	29	19
P8	3.1	1.09	10-12	R_4	56[e] (R_4)	27	17

[a] Determined by SEC in chloroform; [b] Determined by ^{1}H-NMR spectra from the peak intensities for the region belongs to α-methylene protons of thiophenes as described in Fig. S4, by setting methyl of R_1 as reference point for P1-P4; setting α-methylene protons of repeating unit (2.81 ppm) as reference point for P5-P8;[c] Determined by ^{1}H-NMR spectra from the ratio of peak intensities of different end groups as described in Fig. 3; [d] The sum of peak integrals of HH and HT couplings is given, [e] Mono/bis-end functionalization with R_3 and R_4 is not distinguishable from ^{1}H-NMR spectra (peaks at 2.75 ppm & 2.74 ppm), therefore given percentage refers to the sum of functionalized compositions after the re-initiation product is excluded.

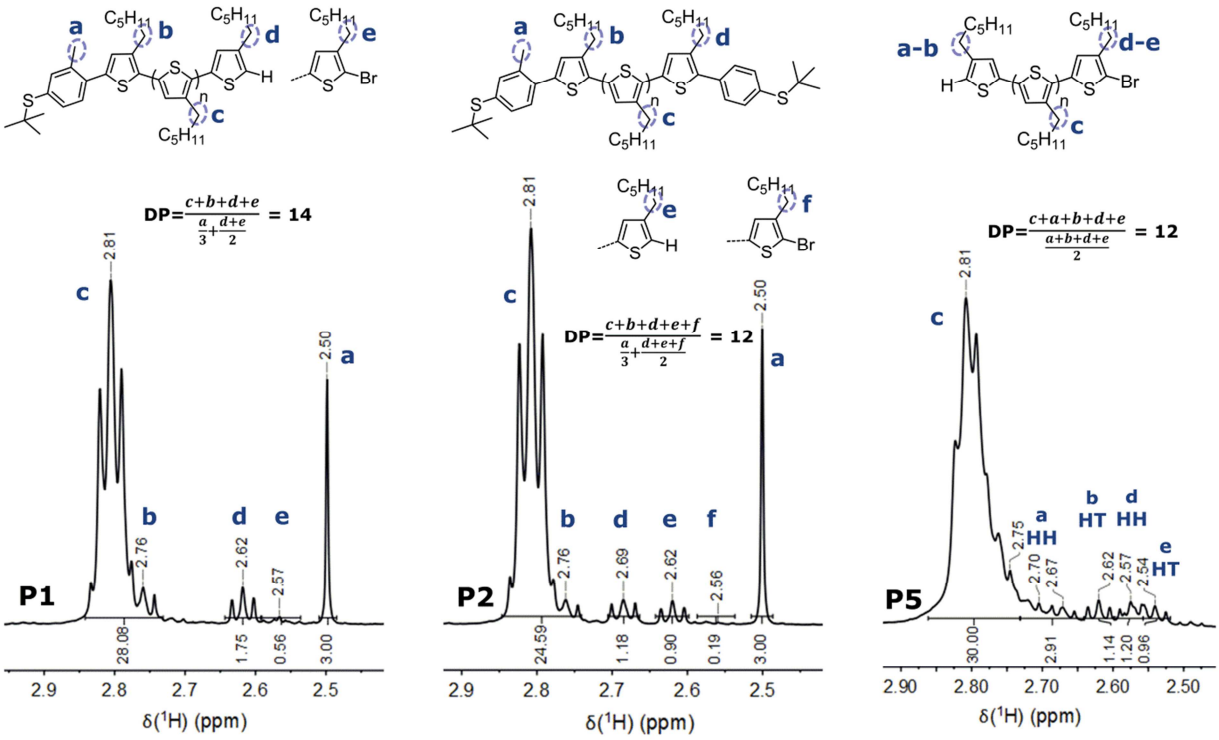


Figure S4. [1]H-NMR spectra of 2-3 ppm region for products **P1, P2** and **P5** and determination of degree of polymerization from assigned end group peaks

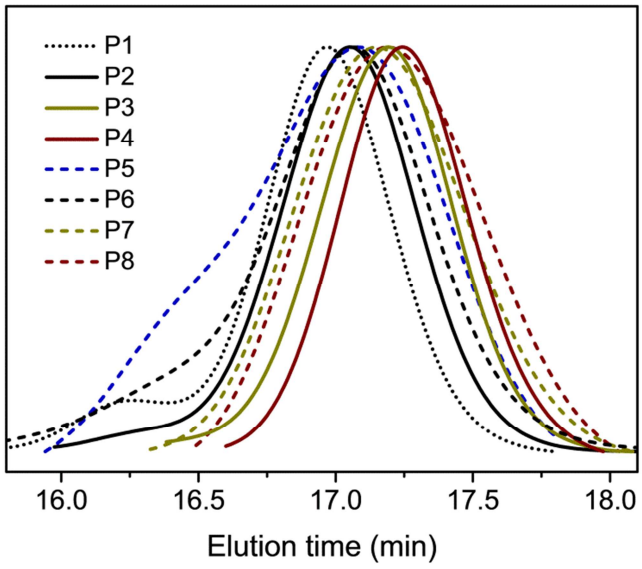


Figure S5. SEC profiles of oligomers obtained from both KCTP and GRIM

The components of P2 were aimed to be separated by column chromatography with a gradual change in polarity and [1]H-NMR spectra of fractions from each elution is given in Fig.SI-4. As seen from Figure, increasing polarity facilitates the elution of lower molecular weight fraction of bis-end and higher molecular weight fraction of mono-end functionalized structures.

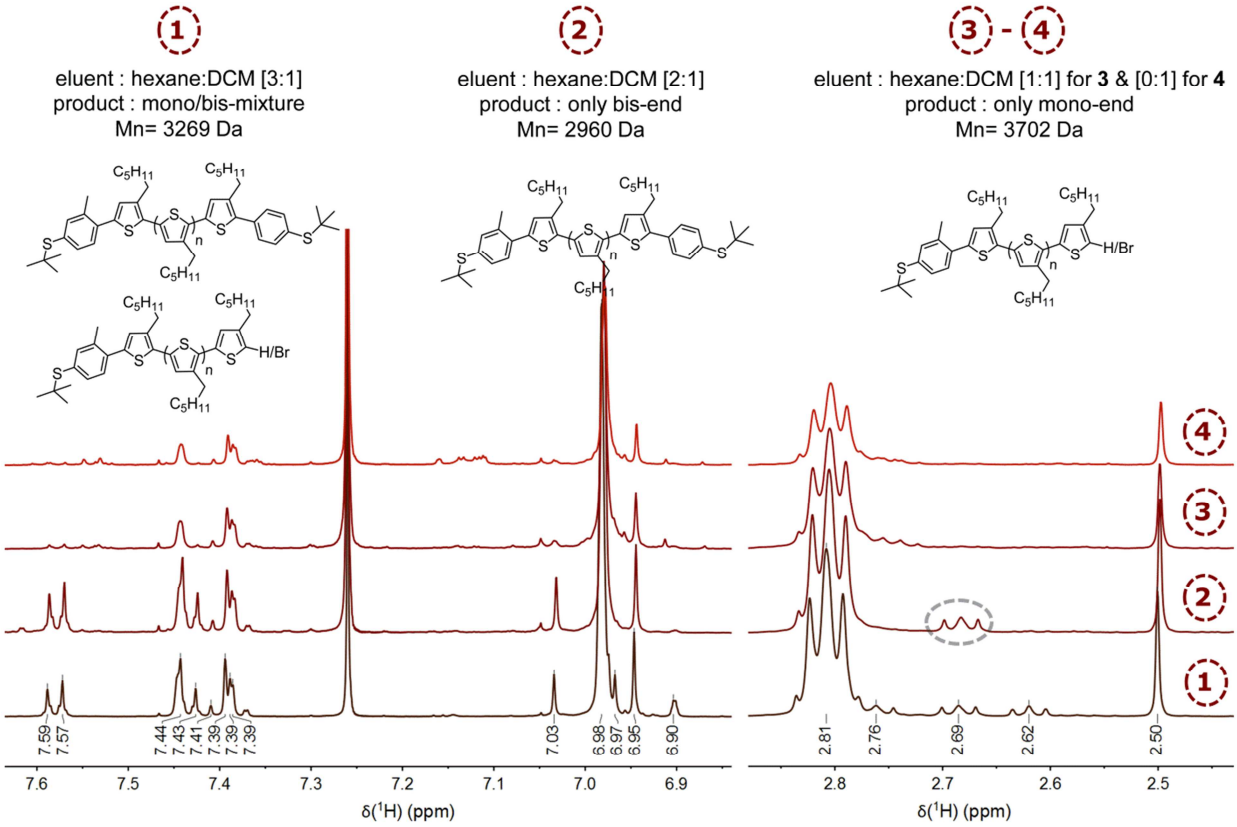
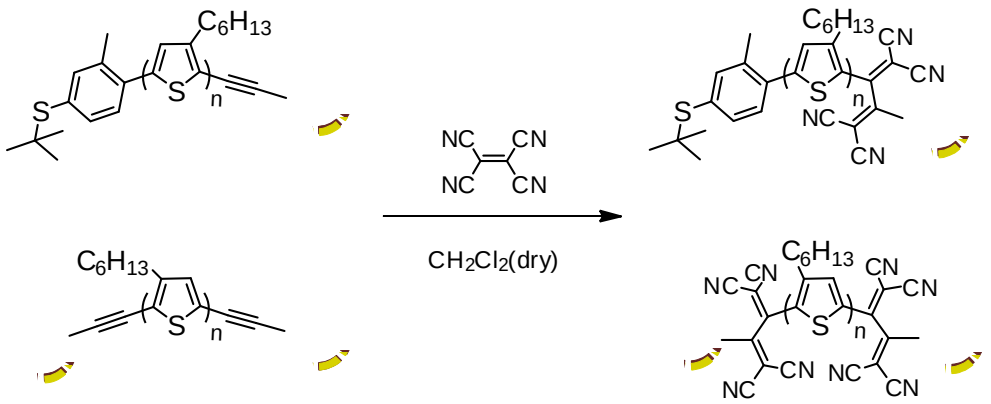


Figure S6. ^{1}H-NMR spectra of the column fractions of **P2** eluted from the successive solvent combinations in different polarity

Donor-Acceptor Chromophores as end groups



Polymers were dissolved in dry CH_2Cl_2 and excess amount of tetracyanoethylene (TCNE) (in 2:1 ratio (for mono-end donor), in 3:1 ratio (for bis-end donor) to the polymer/per donor-substituted end group) was added at room temperature with an immediate change in color to brownish from orange. The reaction mixtures were stirred for 2 more hrs at 50 ^{0}C and then the solvent was removed by evaporation. Methanol was added to the residue after evaporation and the precipitate was scratched via spatula to filter paper for Soxhlet extraction. After the

removal of light yellow methanol soluble part with soxhlet, the residual part dried under vacuum.

P3-TCBD: 94% ; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.84 (d, *J*=9.1 Hz, 2H, ω-DA end *dma*_Ar-H), 7.46 (bs, 1H, I/Ar-H), 7.40 (m, 2H, I/Ar-H), 7.17 (bs, ω-*DA*-end_3HT-H), 6.99 (bs, 3HTh-H), 6.96 (s, I-3HT-H), 6.94 (s, ω-H end Th-H), 6.77 (d, *J*=9.1 Hz, 2H, ω-DA end *dma*_Ar-H), 3.19 (s, -N(CH_3)$_2$), 2.80 (m, ThCH_2(CH_2)$_4$$CH_3$), 2.76 (m,α-I Th α-$CH_2$), 2.70 (t, *J*=7.3x(2) Hz, ω-DA-end Th α-CH_2), 2.52 (s, 3H, I-CH_3), 1.67 (m, ThCH_2CH_2(CH_2)$_3$$CH_3$), 1.45 (m, Th$CH_2CH_2CH_2$($CH_2$)$_2$$CH_3$), 1.36 (m, Th$CH_2CH_2CH_2$($CH_2$)$_2$$CH_3$), 1.34 (s, I-SC($CH_3$)$_3$), 0.92 (m, Th($CH_2$)$_5$$CH_3$)

P4-TCBD: 60% ; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.45 (bs, 1H, I/Ar-H), 7.40 (m, 2H, I/Ar-H), 7.14 (bs, ω-*DA*-end_3HT-H), 6.99 (bs, 3HTh-H), 6.96 (s, I-3HT-H), 6.93 (s, ω-H end Th-H), 6.84 (s, ω-Br end Th-H), 5.52 (bs, 1H, ω-*DA*-end_Fc-H), 5.05 (bs, 1H, ω-*DA*-end_Fc-H), 4.90 (bs, 1H, ω-*DA*-end_Fc-H), 4.60 (bs, 1H, ω-*DA*-end_Fc-H), 4.52 (bs, 5H, ω-*DA*-end_Fc-H), 2.81 (m, ThCH_2(CH_2)$_4$$CH_3$), 2.77 (m, α-I Th α-$CH_2$), 2.73 (t, *J*=7.6x(2) Hz, ω-DA-end Th α-CH_2), 2.69 - 2.67, 2.63 (m, ω-H end Th α-CH_2), 2.59 (m, ω-Br end Th α-CH_2), 2.51 (s, 3H, I-CH_3), 1.72 (m, ThCH_2CH_2(CH_2)$_3$$CH_3$), 1.45 (m, Th$CH_2CH_2CH_2$($CH_2$)$_2$$CH_3$), 1.36 (m, Th$CH_2CH_2CH_2$($CH_2$)$_2$$CH_3$), 1.34 (s, I-SC($CH_3$)$_3$), 0.90 (m, Th($CH_2$)$_5$$CH_3$)

P7-TCBD: 77% ; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.85 (d, *J*=9.1 Hz, 2H, ω-DA end *dma*_Ar-H), 7.19 & 7.17 (s, mono/bis-*DA*-end_3HT-H), 7.03-7.01-7.00 (bs, 3HTh-H), 6.96 (bs, mono-ω-H end Th-H), 6.93 (s, ω-H end Th-H), 6.84 (m, ω-Br end Th-H), 6.77 (d, *J*=9.1 Hz, 2H, ω-DA end *dma*_Ar-H), 3.19 (s, -N(CH_3)$_2$), 2.81 (m, ThCH_2(CH_2)$_4$$CH_3$), 2.71 (t, *J*=8.2x(2) Hz, mono/bis-DA-end Th α-CH_2 & HT ω-H end Th-α-CH_2), 2.63 (t, *J*=7.9x(2) Hz, HH ω-H end Th α-CH_2), 2.58 (m, *HH* ω-Br end Th-α-CH_2), 2.55 (m, HT ω-Br end Th-α-CH_2), 1.71 (m, Th$CH_2$$CH_2$($CH_2$)$_3$$CH_3$), 1.45 (m, Th$CH_2CH_2$$CH_2$($CH_2$)$_2$$CH_3$), 1.36 (m, Th$CH_2CH_2CH_2$($CH_2$)$_2$$CH_3$), 0.93 (m, Th($CH_2$)$_5$$CH_3$)

P8-TCBD: 74% ; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.15 (bs, mono/bis-*DA*-end_3HT-H), 7.11 (s), 7.02-7.00 (bs, 3HTh-H), 6.96 (bs, mono-ω-H end Th-H), 6.94 (s, ω-H end Th-H), 6.85 (s, ω-Br end Th-H), 5.53 (bs, 1H, ω-*DA*-end_Fc-H), 5.06 (bs, 1H, ω-*DA*-end_Fc-H), 4.90 (bs, 1H, ω-*DA*-end_Fc-H), 4.61 (bs, 1H, ω-*DA*-end_Fc-H), 4.53 (bs, 5H, ω-*DA*-end_Fc-H), 2.81 (m, ThCH_2(CH_2)$_4$$CH_3$), 2.74 (t, *J*=7.9x(2) Hz, mono/bis-DA-end Th α-CH_2 & HH ω-H end Th-α-CH_2), 2.69-2.67 (m, HH ω-H end Th-α-CH_2), 2.63 (m, HT ω-H end

Th α-C$\underline{H}_2$), 2.60 (m, HH ω-Br end Th α-C$\underline{H}_2$), 2.55 (m, HT ω-Br end Th-α-C$\underline{H}_2$), 1.70 (m, ThCH$_2$C$\underline{H}_2$(CH$_2$)$_3$CH$_3$), 1.45 (m, ThCH$_2$CH$_2$C$\underline{H}_2$(CH$_2$)$_2$CH$_3$), 1.37 (m, ThCH$_2$CH$_2$CH$_2$(C$\underline{H}_2$)$_2$CH$_3$), 0.93 (m, Th(CH$_2$)$_5$C$\underline{H}_3$)

Synthesis of Model Compounds

N,N-dimethyl-4-(thiophen-3-ylethynyl)aniline [7] To a round bottom flask under argon, 4-ethynyl-N,N-dimethylaniline (2.32 g, 16.0 mmol), 3-bromothiophene (1.5 ml, 16.0 mmol), CuI (152 mg, 0.8 mmol) were added and dissolved in degassed mixture of THF (20 ml) and diisopropylamine (10 ml). Pd(PPh$_3$)$_2$Cl$_2$ (281 mg, 0.4 mmol) was added and the reaction mixture was heated to 60 ^{0}C for overnight. After cooling to room temperature, mixture was poured into NH$_4$Cl solution, extracted with CH$_2$Cl$_2$, water, brine, respectively. After then, that dark red colored organic layer was dried over MgSO$_4$ and concentrated by evaporation. Purification with column chromatography (silica; eluent= Hexane: CH$_2$Cl$_2$ (4:1)) gave the desired product N,N-dimethyl-4-(thiophen-3-ylethynyl)aniline [**7**] as white powder in 65 % yield (2.4 g); ^{1}H NMR (500 MHz; CDCl$_3$; Me$_4$Si) δ (ppm): 7.45 (dd, J=3.1,1.0 Hz, 1H, Th-H), 7.40 (d, J=9.1 Hz, 2H, Ar-H), 7.29 (dd, J=3.1, 2.1 Hz, 1H, Th-H), 7.18 (dd, J=4.9,1.0 Hz, 1H, Th-H), 6.67 (d, J=9.1 Hz, 2H, Ar-H), 3.00 (s, 6H,-N(CH$_3$)$_2$); ^{13}C NMR (125.8 MHz; CDCl$_3$; Me$_4$Si) δ (ppm): 150.10 (Cq, Ar-N(CH$_3$)$_2$), 132.62 (Ct, Ar), 129.91 (Ct, Th$^{5'}$), 127.30 (Ct, Th$^{2'}$), 125.01 (Ct, Th$^{4'}$), 123.14 (Cq, Th$^{3'}$), 111.85 (Ct, Ar), 110.01 (Cq, Th-C≡C-Ar), 89.91 (Th-C≡C-Ar), 82.31 (Th-C≡C-Ar), 40.19 (-N(CH$_3$)$_2$); UV-Vis (in CH$_2$Cl$_2$): λ_{max} = 323 nm

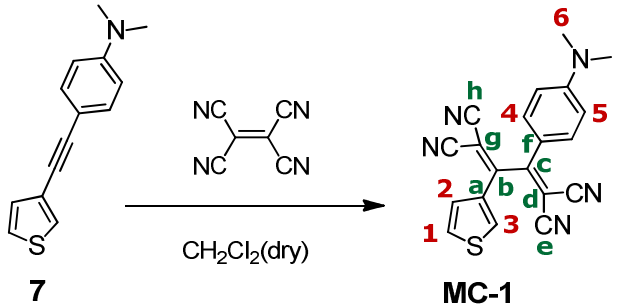
Thiophen-3-ylethynylferrocene [8] To a 50 ml flask under argon, ethynylferrocene (1.0 g, 4.76 mmol), 3-iodothiophene (1.0 g, 4.76 mmol), CuI (45 mg, 0.24 mmol) were added and dissolved in degassed mixture of THF (10 ml) and diisopropylamine (5 ml). Pd(PPh$_3$)$_4$ (137.5 mg, 0.12 mmol) was added and the reaction mixture was heated to 50 ^{0}C for overnight. After cooling to room temperature, mixture was poured into NH$_4$Cl solution, extracted with CH$_2$Cl$_2$, water, brine, respectively. After then, that orange organic layer was dried over MgSO$_4$ and concentrated by evaporation. Purification with column chromatography (silica; eluent= Hexane:CH$_2$Cl$_2$ (4:1)) gave the desired product **8** as orange powder in 85 % yield (1.18 g); ^{1}H NMR (500 MHz; CDCl$_3$; Me$_4$Si) δ (ppm): 7.46 (dd, *J*=2.8, 1.3 Hz, 1H, Th-H), 7.28 (dd, *J*=5.0, 2.8 Hz, 1H, Th-H), 7.17 (dd, *J*=4.9, 1.1 Hz, 1H, Th-H), 4.50 (t, *J*=1.9 x(2) Hz, 2H, Fc-H), 4.26 (s, 5H, Fc-H), 4.24 (t, *J*=1.9 x(2) Hz, 2H, Fc-H); ^{13}C NMR (125.8 MHz; CDCl$_3$; Me$_4$Si) δ (ppm): 129.92 (C^t, Th$^{5'}$), 127.66 (C^t, Th$^{2'}$), 125.11 (C^t, Th$^{4'}$), 122.96 (C^q, Th$^{3'}$),

87.65 (Th-C≡C-Fc), 80.74 (Th-C≡C-Fc), 71.34 (Cp-H), 69.94 (Cp-H), 68.74 (Cp-H), 65.24 (Cp-C-EtTh); UV-Vis (in CH_2Cl_2): λ_{max} = 298 nm

General reaction conditions for D-A model compounds

Donor molecule (1.0 eq.) was dissolved in anhydrous CH_2Cl_2 and TCNE (1.0-2.0 eq.) was added at room temperature with an immediate change in color. The reaction mixture was stirred for 2 more hrs and then the solvent was removed by evaporation. Afterwards, the crude product was filtered through a plug of silica with CH_2Cl_2 as eluent to obtain desired product with both donor-acceptor moieties.

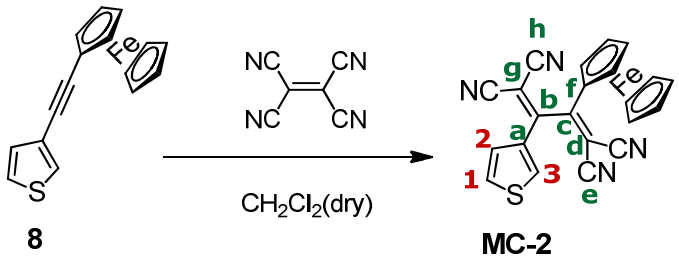
2-(4-(dimethylamino)phenyl)-3-(thiophen-3-yl)buta-1,3-diene-1,1,4,4-tetracarbonitrile [MC-1]



7 MC-1

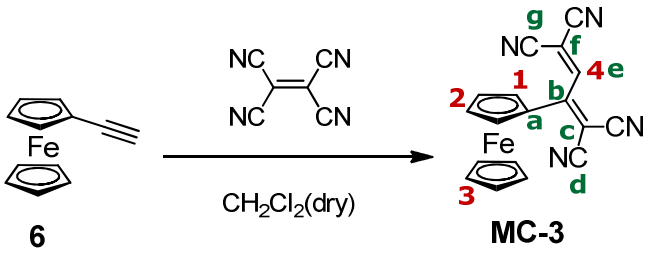
N,N-dimethyl-4-(thiophen-3-ylethynyl)aniline (**9**) (100 mg, 0.44 mmol), TCNE (75 mg, 0.585 mmol), 10 ml anhydrous CH_2Cl_2; an immediate change in color to dark red from colorless, **MC-1** as pink solid (142 mg, 91%); ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 8.16 (dd, *J*=2.9,1.6 Hz, 1H, Th-H; **3**), 7.78 (d, *J*=9.3 Hz, 2H, Ar-H; **4**), 7.70 (dd, *J*=5.3, 1.4 Hz, 1H, Th-H; **1**), 7.53 (dd, *J*=5.3, 3.0 Hz, 1H, Th-H; **2**), 6.73 (d, *J*=9.3 Hz, 2H, Ar-H; **5**), 3.17 (s, 6H,-N($C\underline{H}_3$)$_2$; **6**); ^{13}C NMR (125.8 MHz; $CDCl_3$; Me_4Si) δ (ppm): 162.93 (Th-$(CN)_2$C=C-$\underline{C}$=C$(CN)_2$-Ar; **c**), 161.41 (Th-$(CN)_2$C=$\underline{C}$-C=C$(CN)_2$-Ar; **b**), 154.46 (C^q, Ar-N($\underline{C}H_3$)$_2$), 135.86 (C^t, $Th^{2'}$), 133.59 (C^q, $Th^{3'}$; **a**), 132.40 (C^t, Ar), 128.65 (C^t, $Th^{4'}$), 126.97 (C^t, $Th^{5'}$), 117.55 (C^q, Th-$(CN)_2$C=C-C=C$(CN)_2$-$\underline{Ar}$; **f**), 114.26 - 113.28 -112.68 - 111.49 (Th-($\underline{C}$N)$_2$C=C-C=C($\underline{C}$N)$_2$-Ar; **e-h**), 112,19 (C^t, Ar), 83.10 - 73.94 (Th-$(CN)_2\underline{C}$=C-C=$\underline{C}$$(CN)_2$-Ar; **d-g**), 40.09 (-N($\underline{C}H_3$)$_2$); UV-Vis (in CH_2Cl_2): λ_{max} = 469 nm

2-(4-ferrocenyl)-3-(thiophen-3-yl)buta-1,3-diene-1,1,4,4-tetracarbonitrile [MC-2]



Thiophen-3-ylethynylferrocene (**10**) (250 mg, 0.86 mmol),TCNE (220 mg, 1.7 mmol), 10 ml anhydrous CH_2Cl_2; an immediate change in color to dark blue from orange, **MC-2** as dark blue solid (390 mg, 79%) ; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 8.03 (dd, *J*=2.8,1.6 Hz, 1H, Th-H; **3**), 7.50 (dd, *J*=1.6, 1.3 Hz, 1H, Th-H; **2**), 7.48 (dd, *J*=2.8x(2) Hz, 1H, Th-H; **1**), 5.49 (dt, *J*=2.8, 1.3 x(2) Hz, 1H, Fc-H), 5.04 (td, *J*=2.7x(2), 1.3 Hz, 1H, Fc-H), 4.86 (td, *J*=2.7x(2), 0.9 Hz, 1H, Fc-H), 4.48 (s, 6H, Fc-H); ^{13}C NMR (125.8 MHz; $CDCl_3$; Me_4Si) δ (ppm): 172.54 (Th-$(CN)_2$C=C-<u>C</u>=C$(CN)_2$-Fc; **c**), 158.55 (Th-$(CN)_2$C=<u>C</u>-C=C$(CN)_2$-Fc; **b**), 135.04 (C^t, $Th^{2'}$), 132.54 (C^q, $Th^{3'}$; **a**), 128.60 (C^t, $Th^{4'}$), 126.80 (C^t, $Th^{5'}$), 113.57 - 112.62 - 112.40 - 111.96 (Th-(<u>C</u>N)$_2$C=C-C=C(<u>C</u>N)$_2$-Fc; **e-h**), 107.85 (Cp-<u>C</u>-; **f**), 82.08 - 78.66 (Th-$(CN)_2$<u>C</u>=C-C=<u>C</u>$(CN)_2$-Fc; **d-g**) , 75.87 - 75.27 - 74.91 - 72.64 - 72.20 - 71.43 (Cp); UV-Vis (in CH_2Cl_2): λ_{max1} = 342 nm, λ_{max2} = 621 nm

2-(4-ferrocenyl)buta-1,3-diene-1,1,4,4-tetracarbonitrile [MC-3]



Ethynylferrocene (25 mg, 0.12 mmol), TCNE (15 mg, 0.12 mmol), 10 ml anhydrous CH_2Cl_2; an immediate change in color to blue from yellow, **MC-3** as dark blue solid; UV-Vis (in CH_2Cl_2): λ_{max1} = 353 nm, λ_{max2} = 639 nm; ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ (ppm): 7.70 (s, 1H, Fc-TCBD-<u>H</u>; **4**), 5.06 (bs, 4H, Fc-H; **1-2**), 4.45 (s, 5H, Fc-H; **3**); ^{13}C NMR (125.8 MHz; $CDCl_3$; Me_4Si) δ (ppm): 165.02 ($(CN)_2$C=CH-<u>C</u>=C$(CN)_2$-Fc; **b**), 154.16 ($(CN)_2$C=<u>C</u>H-C=C$(CN)_2$-Fc; **e**), 113.75 – 113.14 – 110.76 – 109.53 ((<u>C</u>N)$_2$C=CH-C=C(<u>C</u>N)$_2$-Fc; **d-g**), 95.06 ($(CN)_2$<u>C</u>=CH-C=<u>C</u>$(CN)_2$-Fc; **c-f**) , 76.32 - 73.74 - 73.27 - 72.34 - 71.22 (Cp); UV-Vis (in CH_2Cl_2): λ_{max1} = 350 nm, λ_{max2} = 636 nm

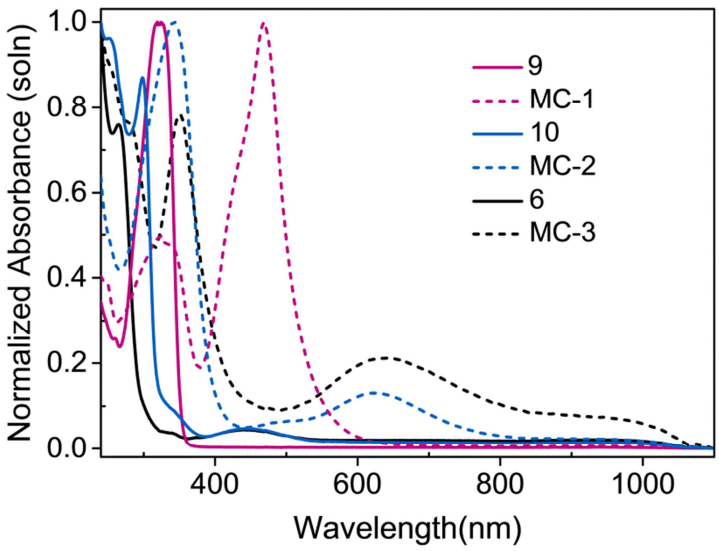


Figure S7. Normalized solution absorbance of model compounds and their precursors donor compounds

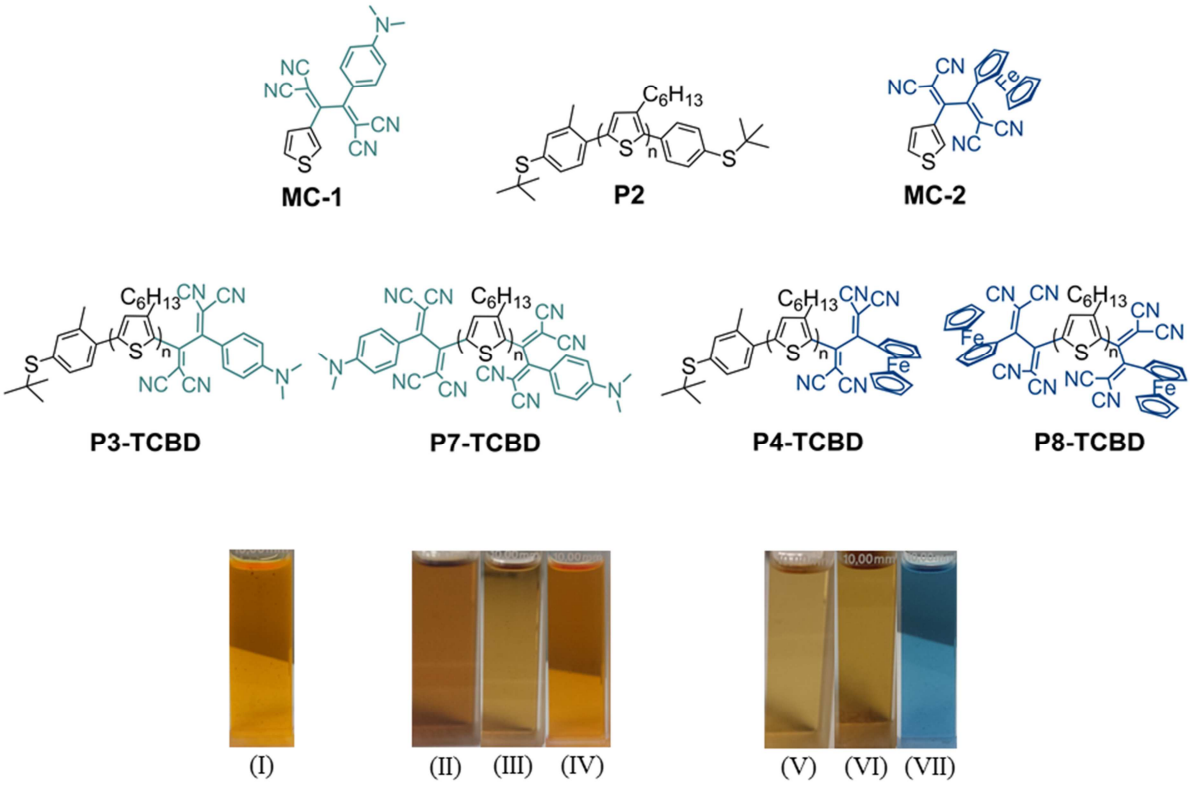


Figure S8. Chemical structures and solution colors of D-A substituted oligomers (0.03 mg/ml) in dry CH_2Cl_2; (I) P2, (II) P3-TCBD, (III) P7-TCBD, (IV) MC-1, (V) P4-TCBD, (VI) P8-TCBD, (VII) MC-2

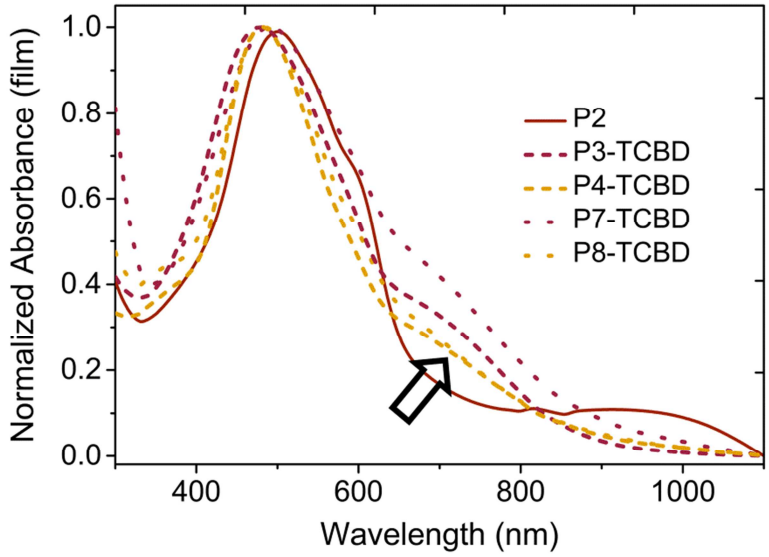


Figure S9. Thin film absorption spectra of D-A functionalized oligo(3-hexylthiophene)s.

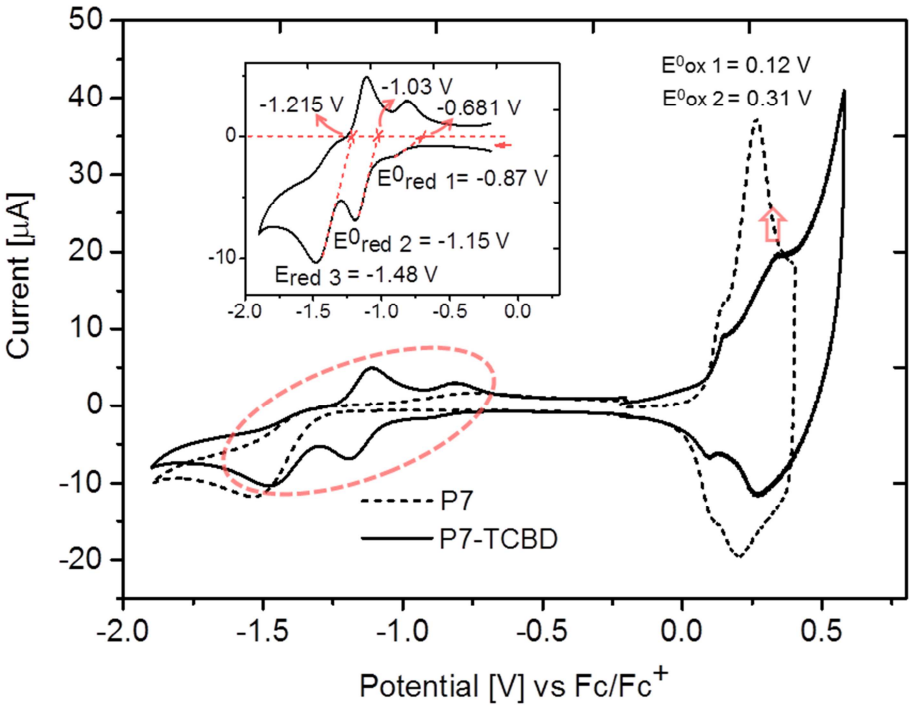


Figure S10. Cyclic voltammograms of DMA-end group functionalized P7 (GRIM product) and D-A-end group functionalized P7-TCBD with oxidation profiles and maxima potentials; enlarged reduction profile of P7-TCBD with well-defined reduction peaks, broader than P3-TCBD and onset potentials (inset graph)

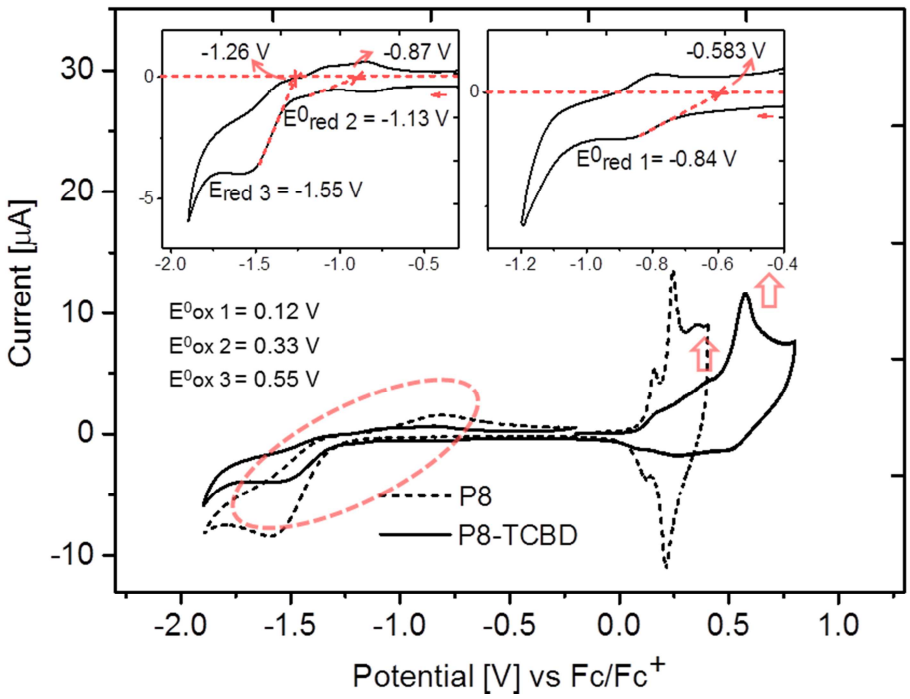


Figure S11. Cyclic voltammograms of Fc-end group functionalized P8 (GRIM product) and D-A-end group functionalized P8-TCBD with oxidation peak maxima; enlarged reduction profiles of P8-TCBD with reduction peak maxima and onset potentials (inset graphs)

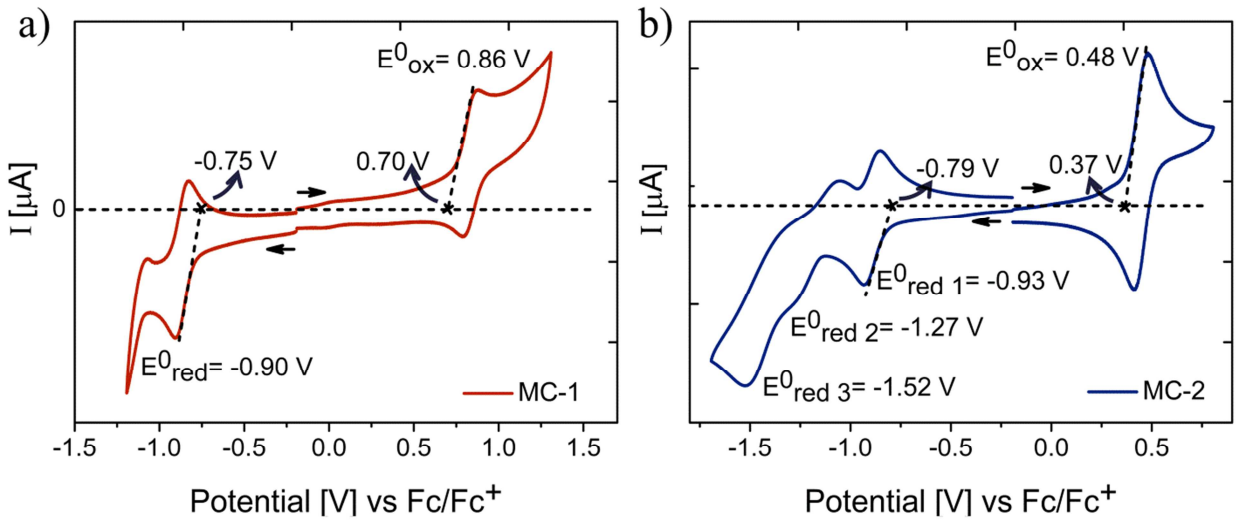


Figure S12. Cyclic voltammograms of model compounds (2mg/ml) measured by a Pt disc working electrode, a Pt wire counter electrode and an $Ag/Ag^{+}/CH_3CN_{(dry)}/(0.1M)$ Bu_4NPF_6 reference electrode under nitrogen atmosphere, at a speed of 100 mVs^{-1}; MC-1 (a) and MC-2 (b) with oxidation/reduction peaks and onset values.

Table ESI- 2. Optical and electrochemical data for oligomers and model compounds

Material	$\lambda_{max\ (soln)}$ (nm)[a]	$\lambda_{max\ (film)}$ (nm)[b]	$\Delta E_{opt\ (film)}$ (eV)[c]	Cyclic Voltammetry[d] E^0_{ox} (V)	E^0_{red} (V)	ΔE_{elec} (eV)[e]
P2	442	498	1.81	0.16,0.41	-1.74	1.53
P3	-	474	1.85	0.14,0.27	-1.73	1.45
P3-TCBD	439, 570[f]	480	1.69	0.13,0.34 ,0.45	-0.86, -1.13,-1.80	0.83
P4	-	465	1.85	0.15,0.23	-1.73	1.46
P4-TCBD	438, 571[f]	480	1.69	0.13,0.32 ,0.54	-0.86, -1.16,-1.71	0.75
P7	-	447	1.82	0.13,0.23	-1.53	1.38
P7-TCBD	445, 570[f]	490	1.55	0.12,0.31	-0.87, -1.15,-1.48	0.74
P8	-	496	1.66	0.15,0.23	-1.59	1.43
P8-TCBD	445, 571[f]	482	1.65	0.13,0.34 ,0.55	-0.84, -1.13,-1.55	0.66
7	303	316	1.53	0.43	-1.46	1.46
MC-1	323,469	367,551	1.37	0.86	-0.90	1.48
8	257, 298	270, 524	1.13	0.16	-1.50	1.23
MC-2	343,625	371,486, 637	1.34	0.48	-0.93, -1.27,-1.52	1.14

[a] Measured in dry CH_2Cl_2

[b] Thin films were prepared via drop-casting from CH_2Cl_2 solution on glass substrate

[c] Film-absorption onsets were taken from the broad shoulders of spectra in Fig.SI-9

[d] Cyclic voltammograms were measured preparing the films of oligomers on Pt electrode in ACN/$TBAPF_6$ (0.1 M) and oxidation/reduction potentials were referenced against Fc/Fc^+ redox couple

[e] HOMO-LUMO energy levels were calculated by setting Fc/Fc^+_{vac} at -5.1 eV *vs*. vacuum, then the electrochemical band gap is estimated from ΔE_{elec} [eV] = |HOMO-LUMO|

[f] Absorbance values belong to the small shoulders formed due to D-A structures

References

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