Supplementary Information

S-Pechmann Dye: A Thiolactone-Containing Organic Dye with Pronounced Electron-Accepting Character and Its Solid-State Photophysical Properties

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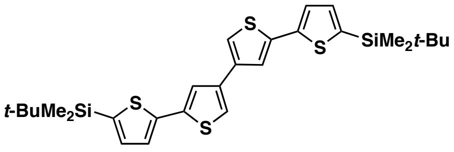
Contents

1. Experimental Detail

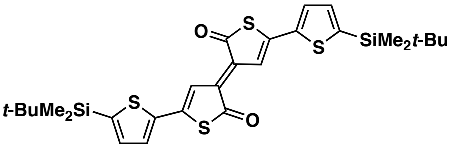
General. Melting points (mp) were determined with a Yanaco MP-S3 instrument (MP-S3) or a Stanford Research System OptiMelt MPA100 instrument (MPA100). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a JEOL AL-400 spectrometers (400 MHz for ^{1}H and 100 MHz for ^{13}C) in CD_2Cl_2 THF-d_8, or $CDCl_3$. The chemical shifts were reported in ppm using the signals of CH_2Cl_2, THF, and $CHCl_3$ as an internal standard (CH_2Cl_2: δ 5.32 and 53.84 in ^{1}H and ^{13}C NMR spectra, respectively; THF: δ 3.58 in ^{1}H NMR spectra; $CHCl_3$: δ 77.16 in ^{13}C NMR spectra). Mass spectra were measured with a Bruker micrOTOF Focus spectrometer with the APCI ionization method. Cyclic voltammetry (CV) was performed on an ALS/chi-617A electrochemical analyzer. The CV cell consisted of a glassy carbon electrode, a Pt wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurements were carried out under an argon atmosphere using a CH_2Cl_2 (for oxidation) or a THF solution (for reduction) of sample with a concentration of 1.0 mM and 0.10 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as a supporting electrolyte. The redox potentials were calibrated with a ferrocene/ferrocenium ion couple. UV/Vis absorption spectra were measured with a Shimadzu UV-3150 spectrometer with a resolution of 0.5 nm using dilute sample solutions in spectral grade solvents in a 1 cm square quartz cuvette. An emission spectrum was measured with Horiba SPEX Fluorolog 3 spectrofluorometer equipped with a Hamamatsu PMA R5509-73 and a cooling system C9940-01. The fluorescence quantum yield was determined using indocyanine green (IR-125) as an external standard (Φ_F = 0.132 in EtOH). A diffuse reflectance spectrum was measured with JASCO V-570 UV/VIS/NIR spectrophotometer equipped with a JASCO ISN-470 integrating sphere system. Thin layer chromatography was performed on plates coated with 0.25 mm thick silica gel $60F_{254}$ (Merck). Column chromatography was performed using PSQ 100B (Fuji Silysia). Recycling preparative gel permeation chromatography (GPC) was performed using LC-918 (Japan Analytical Industry) equipped with a polystyrene gel column (JAIGEL 1H and 2H, Japan Analytical Industry) and $CHCl_3$ as the eluent. Anhydrous THF was purchased from Kanto Chemicals and further purified by Glass Contour Solvent Systems. All reactions were carried out under a nitrogen atmosphere.



4

5,5'-Bis(*tert*-butyldimethylsilyl)-2,2';4',3'';5'',2'''-quaterthiophene (4). To a solution of 2-bromo-5-(*tert*-butyldimethylsilyl)thiophene (688 mg, 2.48 mmol) in anhydrous THF (5.0 mL) was added *n*-BuLi in hexane (1.62 M, 1.55 mL, 2.51 mmol) dropwise at –78 °C over 5 min. After stirring for 2 h, $ZnCl_2$(tmeda) (629 mg, 2.49 mmol) was added. The resulting mixture was allowed to warm to room temperature and stirred for 1.5 h. To a resulting solution of 5-(*tert*-butyldimethylsilyl)-2-thienylzinc chloride, was added a solution of 5,5'-dibromo-3,3'-bithiophene **3**[1] (302 mg, 0.932 mmol) in anhydrous THF (5.0 mL) and $PdCl_2$(dppf)•CH_2Cl_2 (83.2 mg, 0.102 mmol), and the resulting mixture was stirred for 14 h. As the starting materials **3** was found to remain by ^{1}H

NMR of the reaction mixture, another portion of a solution of 5-(*tert*-butyldimethylsilyl)-2-thienylzinc chloride in THF (prepared by the reaction of 5-bromo-2-silyl-thiophene (371 mg, 1.34 mmol) and *n*-BuLi in hexane (1.62 M, 0.83 mL, 1.34 mmol) in anhydrous THF (5.0 mL)) and $PdCl_2(dppf)•CH_2Cl_2$ (85.8 mg, 0.105 mmol) was added and stirred for 12 h. The mixture was quenched with 10% NH_4Cl aq. (18 mL), and the aqueous layer was extracted with Et_2O and $CHCl_3$. The combined organic layer was dried over anhydrous Na_2SO_4. After concentration of the organic layer under reduced pressure, the resulting crude product was subjected to silica gel column chromatography (hexane/EtOAc (100/1) as eluent) to afford 412 mg (R_f = 0.27, 0.737 mmol, 79% yield) of **4** as yellow solids. Mp (MPA100): 171.7–172.4 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ 0.33 (s, 12H), 0.96 (s, 18H), 7.19 (d, 2H, J = 3.4 Hz), 7.31 (d, 2H, J = 3.4 Hz), δ 7.32 (2H, J = 1.4 Hz), 7.45 (d, 2H, J = 1.4 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ –4.82, 17.21, 26.54, 119.40, 123.04, 125.54, 136.46, 137.86, 137.97, 138.47, 142.59. HRMS (APCI): *m/z* calcd. for $C_{28}H_{38}S_4Si_2$: 558.1389 ($[M]^+$). Obsd. 558.1406 ($[M]^+$).



2b

5,5'-Di(5''-*tert*-butyldimethylsilyl-2''-thienyl)-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-dione (2b). To a solution of **4** (201 mg, 0.360 mmol) in anhydrous THF (4.0 mL) was added *t*-BuLi in pentane (1.65 M, 0.46 mL, 0.76 mmol) dropwise at –78 °C over 6 min. After stirring for 3 h, the resulting solution was cannulated into a solution of $B(OMe)_3$ (0.35 mL, 0.33 g, 3.15 mmol) in anhydrous THF (3.0 mL) over 14 min at the same temperature. The resulting mixture was allowed to warm to room temperature gradually, and stirred for 16 h. The mixture was treated with 1N HCl aq. (2.9 mL) and then 30% H_2O_2 aq. (1.0 mL), stirred for 5 h, and quenched with Na_2SO_3 aq. (10 mL) at 0 °C. The aqueous layer was extracted with $CHCl_3$ (4 times), and the combined organic layer was dried over anhydrous Na_2SO_4. After concentration of the organic layer under reduced pressure, the resulting crude product was dissolved in $CHCl_3$ and filtered through a plug of silica gel. The resulting crude mixture was subjected to silica gel column chromatography (hexane/$CHCl_3$ (6.7/1) as eluent), and the blue-colored eluate was collected to give 39.9 mg of blue solids containing **2b**. The crude product was further purified by preparative GPC followed by recrystallization from hexane/CH_2Cl_2 to give 30.4 mg of **2** (51.6 μmol, 14% yield) as black crystals with metallic luster. Mp (MP-S3): 291.4–292.2°C. ^1H NMR (400 MHz, THF-d_8): δ 0.37 (s, 12H), 0.97 (s, 18H), 7.37 (d, 2H, J = 3.6 Hz), 7.57 (d, 2H, J = 3.6 Hz), 8.17 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 50 ºC): δ –4.85, 17.15, 26.50, 117.72, 130.15, 135.28, 136.53, 142.51, 142.91, 145.20, 194.36. HRMS (APCI): *m/z* calcd. for $C_{28}H_{36}O_2S_4Si_2$: 588.1131 ($[M]^+$). Obsd. 588.1125 ($[M]^+$).

2. NMR Spectra

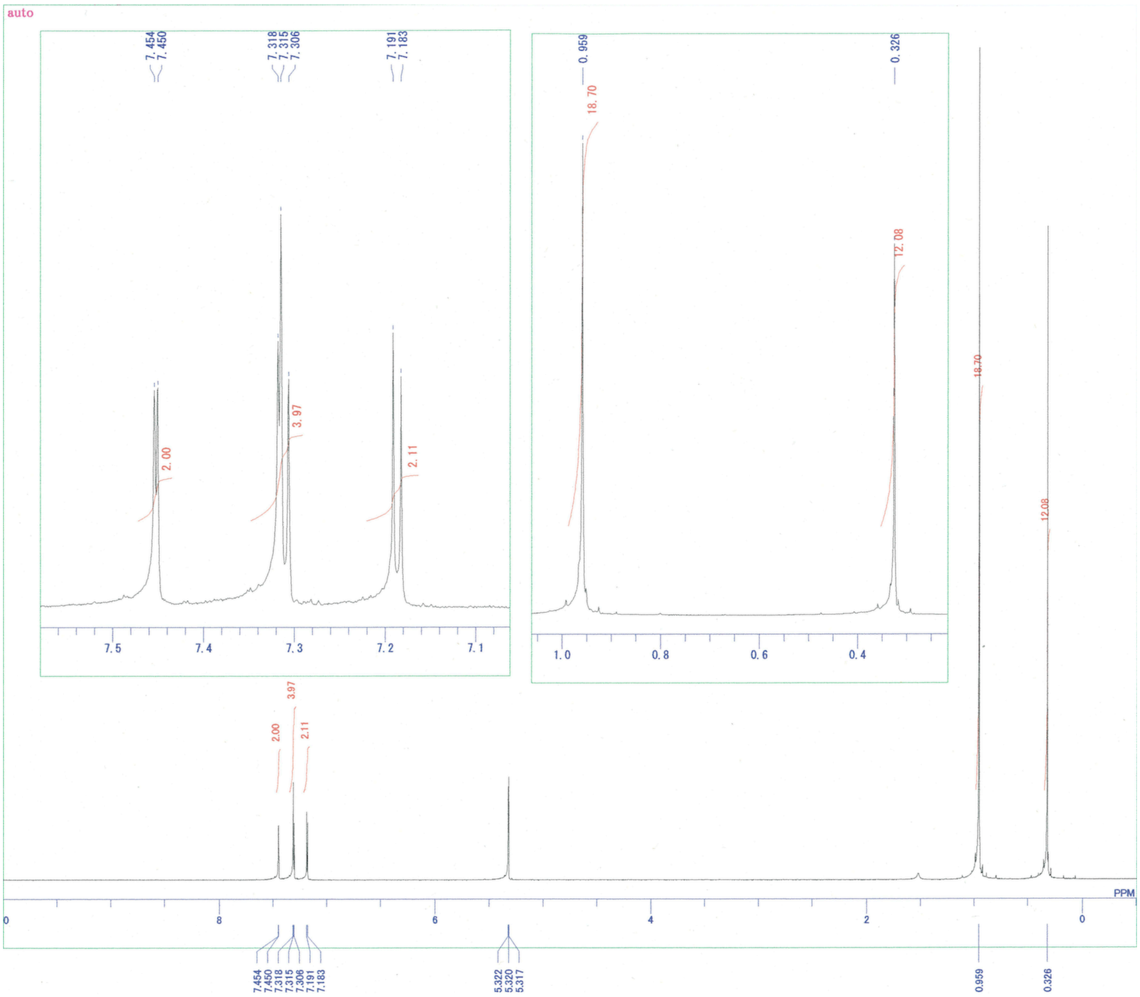


Figure S1. ^{1}H NMR spectrum of **4** (400 MHz, CD_2Cl_2).

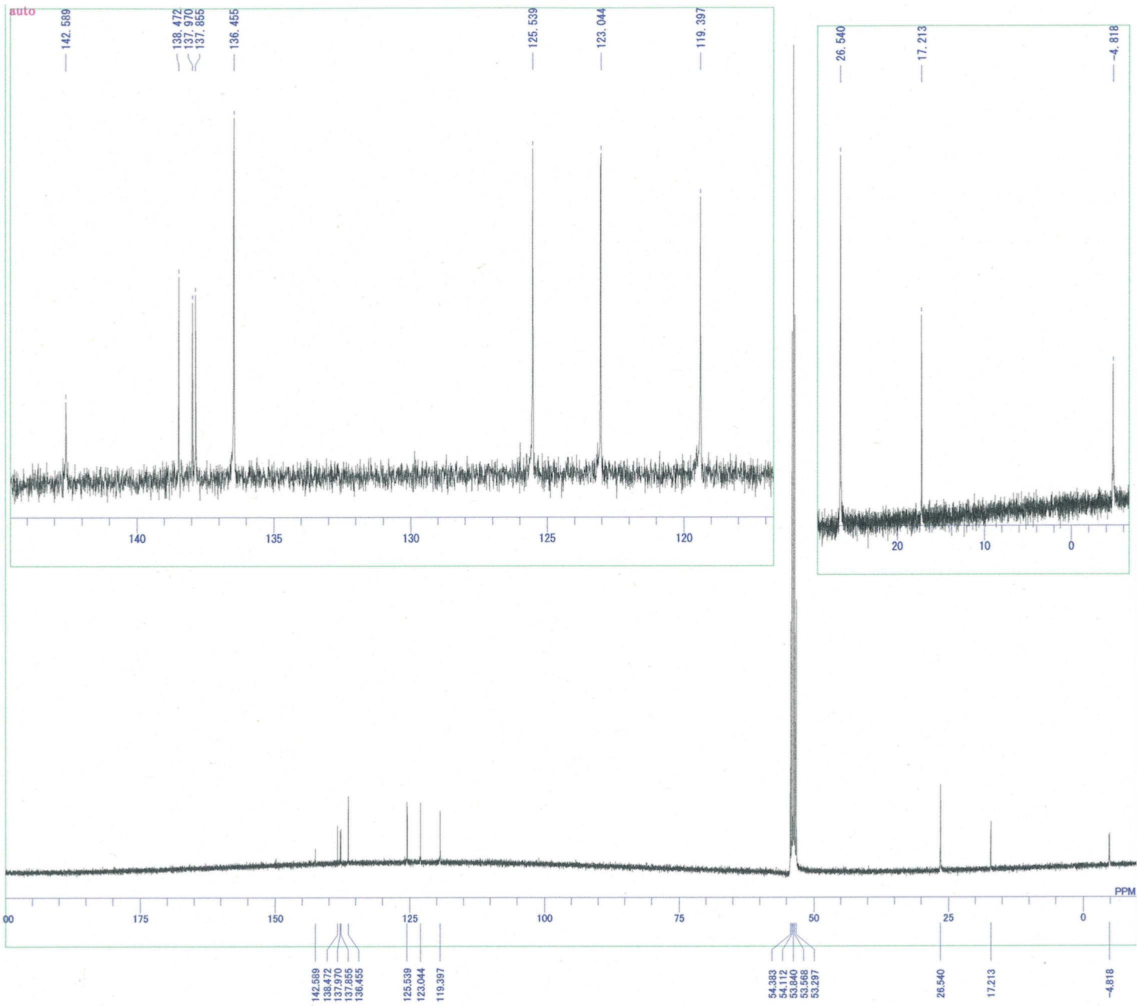


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **4** (100 MHz, CD_2Cl_2).

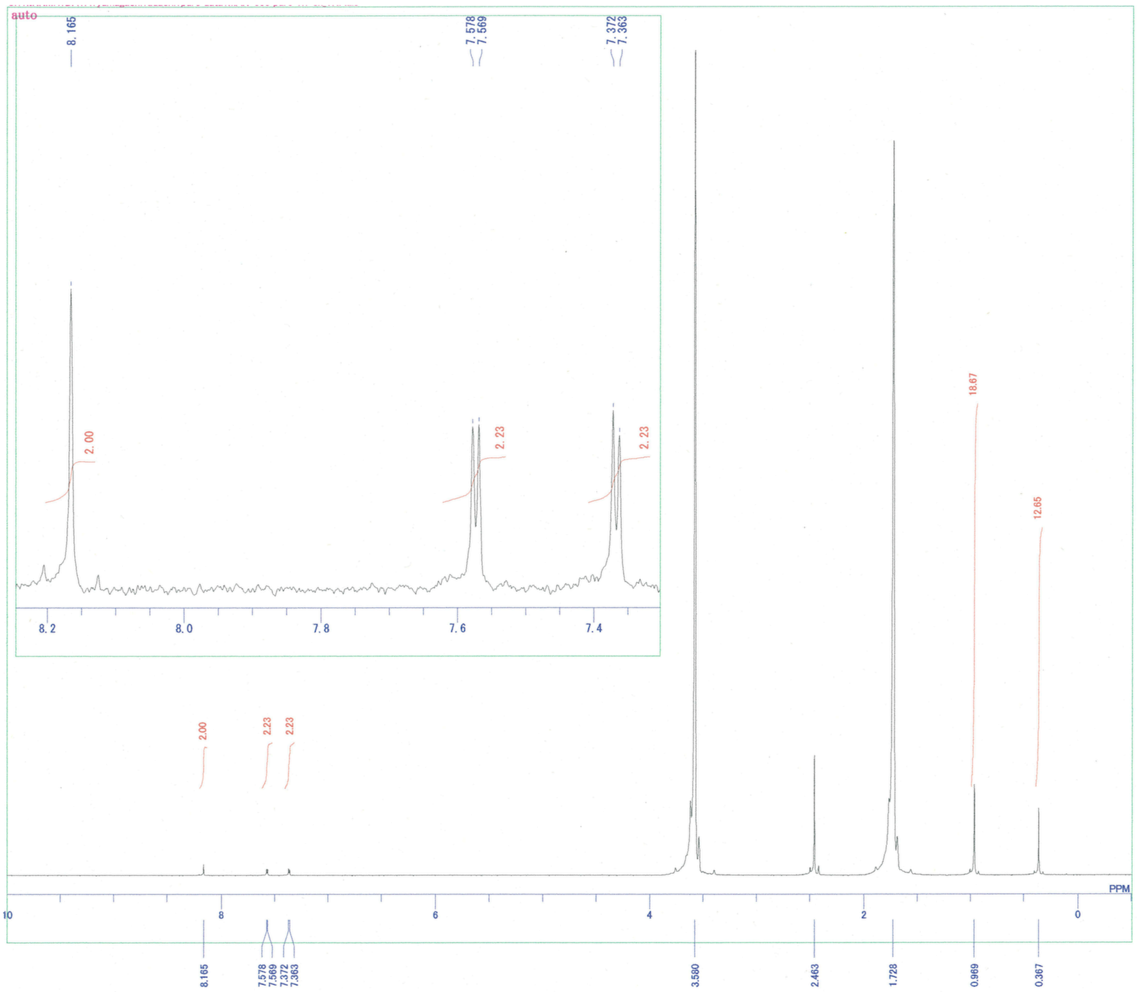


Figure S3. ^{1}H NMR spectrum of **2b** (400 MHz, THF-d_8).

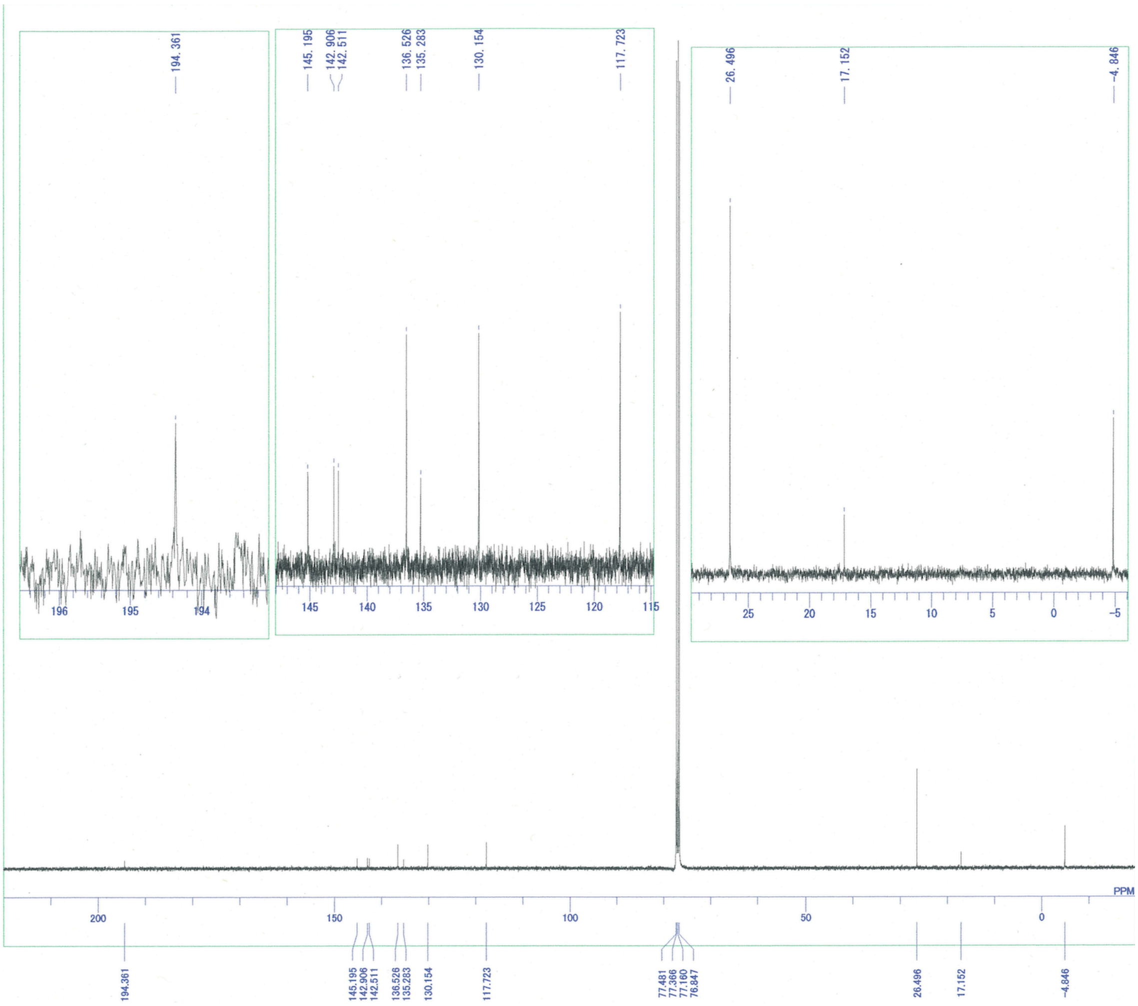


Figure S4. ^{13}C{^{1}H} NMR spectrum of **2b** (100 MHz, CDCl$_3$, VT 50 ºC).

3. X-ray Crystallographic Analysis of 2b

X-ray Data Collection of 2b. Needle-shaped dark blue single crystals were grown by recrystallization from hexane/$CHCl_3$. Intensity data were collected at 123 K on a Rigaku Single Crystal CCD X-ray diffractometer (Saturn 70 with MicroMax-007) with MoKα radiation ($\lambda = 0.71070$ Å) and graphite monochromator. A total of 5112 reflections were measured with the maximum 2θ angle of 50.0°, of which 2544 were independent reflections ($R_{\mathrm{int}} = 0.1162$). The structure was solved by direct methods (SHELXS-97) and refined by the full-matrix least-squares on F^2 (SHELXL-97).[2] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were placed using AFIX instructions. The crystal data are as follows: $C_{28}H_{36}S_4Si_2$; FW = 588.99, crystal size 0.20 × 0.02 × 0.01 mm^3, triclinic, P–1 (#2), $a = 6.472(6)$ Å, $b = 7.017(6)$ Å, $c = 16.835(16)$ Å, $\alpha = 82.70(4)°$, $\beta = 84.68(4)°$, $\gamma = 78.40(4)°$, $V = 741.0(11)$ Å^3, $Z = 1$, $D_c = 1.320$ g cm^{-3}, $\mu = 0.426$ mm^{-1}, $R_1 = 0.1126$ ($I > 2\sigma(I)$), $wR_2 = 0.3482$ (all data), GOF = 1.028. CCDC 923201.

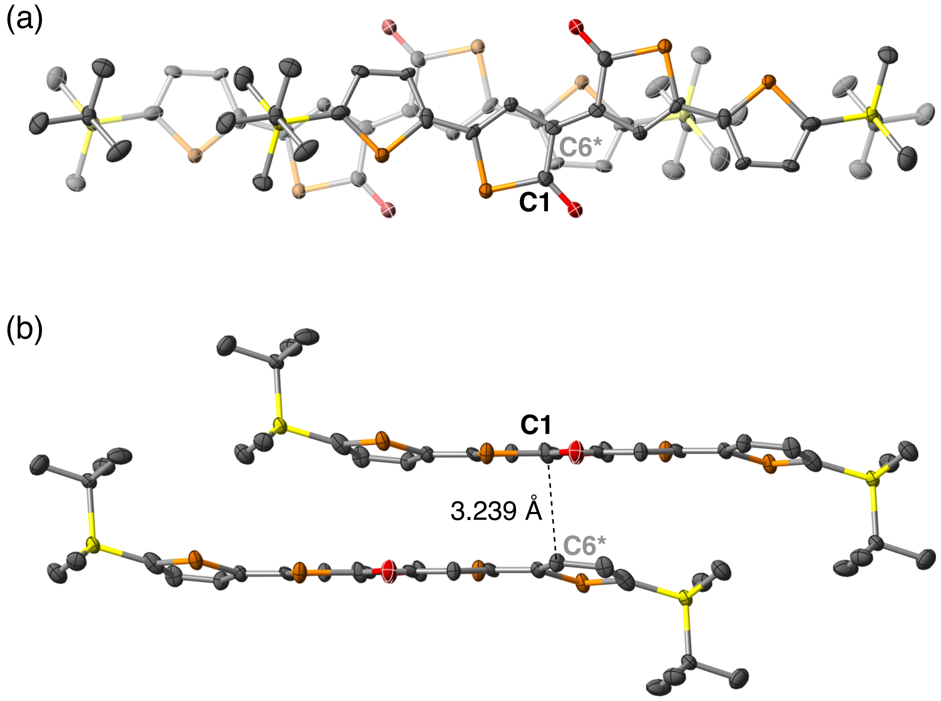


Figure S5. Stacked two molecules in the crystal packing of **2b**: (a) top view, (b) front view.

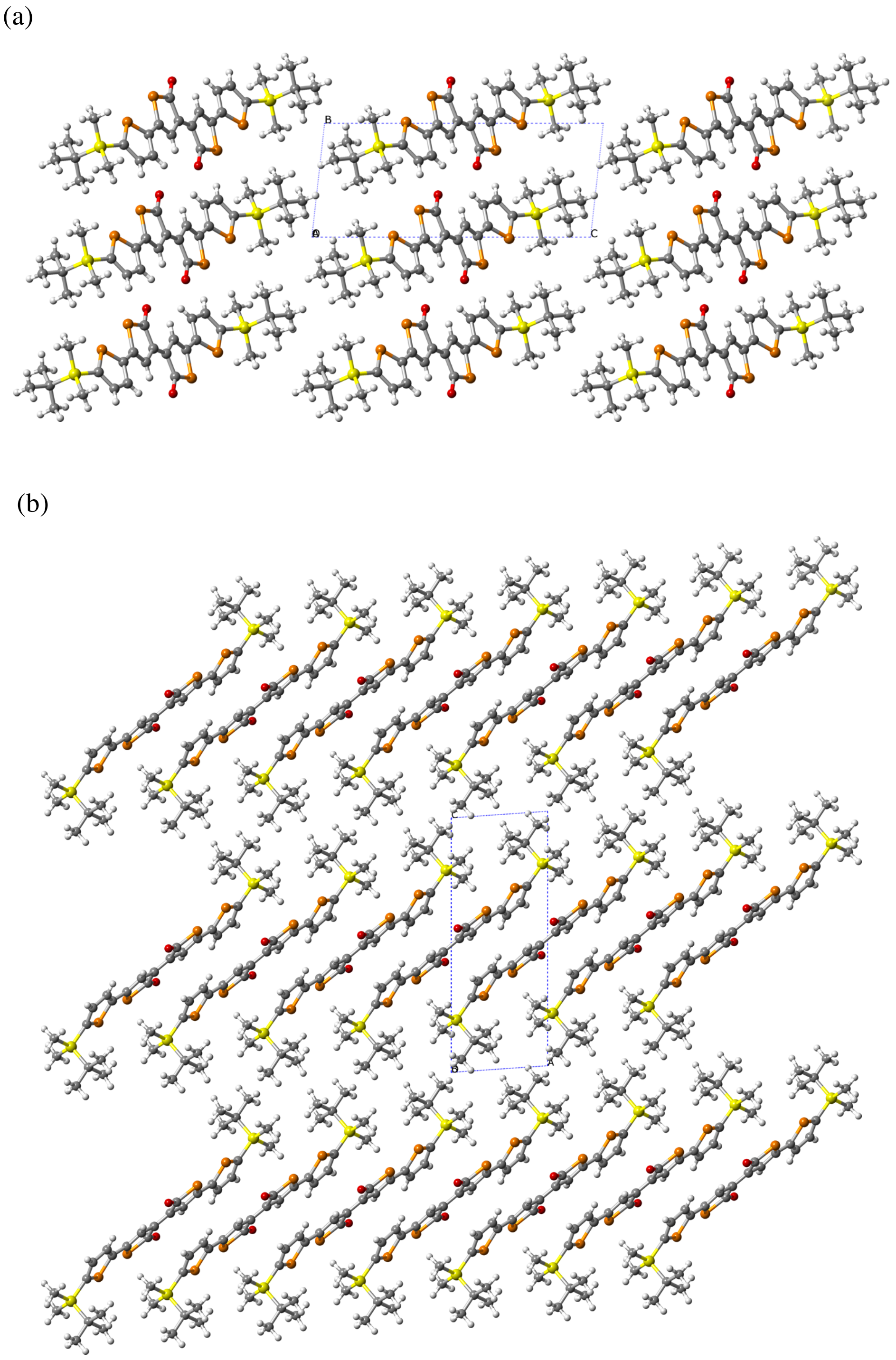


Figure S6. Crystal packing of **2b**: (a) view along *a* axis; (b) view along *b* axis.

4. DFT Calculations

Computational Method. The geometry optimizations of **1b**' and **2b',** and single-point calculations of $\mathbf{3}_\mathrm{O}$ and $\mathbf{3}_\mathrm{S}$ were performed using the B3LYP functional[3] with the 6-31G(d) basis set,[4] implemented in the Gaussian 09 program.[5] For the geometry optimizations, a stationary point was optimized without any symmetry assumptions and characterized by frequency analysis at the same level of theory (the number of imaginary frequencies, NIMAG, was 0.) The Cartesian coordinates for **1b**', **2b**', $\mathbf{3}_\mathrm{O}$, and $\mathbf{3}_\mathrm{S}$ are given in Tables S1–S4. Geometries of $\mathbf{3}_\mathrm{O}$ and $\mathbf{3}_\mathrm{S}$ are derived from the optimized structures of **1b**' and **2b**', respectively by just removing the endocyclic oxygen and sulfur atoms and adding hydrogen atoms. The Kohn-Sham molecular orbitals of **1b**', **2b**', $\mathbf{3}_\mathrm{O}$, and $\mathbf{3}_\mathrm{S}$ are illustrated in Figure S7. TD-DFT vertical excitation calculations[6] of **1b**' and **2b**' were performed using the optimized geometry at the B3LYP/6-31G(d) level, implemented in the Gaussian 09 program.[5] The excitation energies and the oscillator strengths are shown in Tables S5 and S6.

Evaluation of the Intermolecular Interactions for 2b in the Crystalline State. Single-point calculations for one molecule and two neighboring molecules in **2b** are performed using the B3LYP functional[3] with the 6-31G(d) basis set,[4] implemented in the Gaussian 09 program.[5] The geometries determined by X-ray crystallographic analysis of **2b** were used as the initial geometries. The Kohn-Sham molecular orbitals of **2b** are illustrated in Figure S8. Electronic coupling (*V*) calculations between neighboring molecules in the crystalline state were performed using PW91 functional with the DZP basis set implemented in the ADF2010 program,[7] and the results were summarized in Table S7.

Table S1. The Cartesian Coordinates (Å) of the Optimized Structure for **1b**'

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
C	-0.20023429	-0.24484723	-0.61237966	O	-1.82264383	-1.96470551	0.05626076
C	-1.20152629	-1.33237672	-0.76043512	Si	-0.42581193	-0.06211018	8.42534256
C	0.19026601	0.11566408	-1.93252213	Si	0.42540212	0.06257791	-8.42531129
H	0.90812624	0.87797019	-2.19638172	C	-0.06376990	-1.90360288	8.65566362
C	-0.51103818	-0.68133210	-2.79762725	H	-0.40238526	-2.24606490	9.64130663
O	-1.35224929	-1.55873446	-2.12978879	H	1.00934767	-2.11240114	8.57868384
C	0.20076294	0.24409971	0.61236680	H	-0.57493001	-2.51271613	7.90085319
C	1.20217498	1.33151950	0.76042487	C	0.52458805	0.96451876	9.69594048
C	-0.18979833	-0.11634801	1.93250913	H	0.22525178	0.68004217	10.71201948
H	-0.90769940	-0.87861425	2.19637579	H	0.32621953	2.03669905	9.58384719
C	0.51160373	0.68055300	2.79761733	H	1.60689272	0.81056044	9.61719181
O	1.35293598	1.55784709	2.12977600	C	-2.28406152	0.25249573	8.57992820
C	1.29373151	1.63020226	4.99754605	H	-2.65088913	-0.05786322	9.56614737
H	1.97747701	2.35034519	4.56409606	H	-2.85192152	-0.30457579	7.82548581

C	0.53344153	0.77050354	4.22451184
C	1.07492325	1.45812739	6.38567013
H	1.58647022	2.04779328	7.13938448
C	0.15494663	0.47644369	6.70795474
S	-0.45552813	-0.25449700	5.24250623
C	-1.29279596	-1.63125272	-4.99758562
H	-1.97616305	-2.35176780	-4.56415492
C	-0.53292385	-0.77121210	-4.22452136
C	-1.07410536	-1.45900290	-6.38570490
H	-1.58535515	-2.04890725	-7.13943513
C	-0.15463020	-0.47683567	-6.70795469
S	0.45548437	0.25435877	-5.24250132
O	1.82334300	1.96380258	-0.05627109
H	-2.51955629	1.31539332	8.45380198
C	-0.52545800	-0.96337737	-9.69610944
H	-1.60771904	-0.80927317	-9.61707296
H	-0.32725523	-2.03563897	-9.58448744
H	-0.22626136	-0.67854905	-10.71212875
C	0.06314442	1.90419465	-8.65437518
H	0.57581867	2.51300513	-7.90034666
H	-1.00979485	2.11311917	-8.57534018
H	0.39998914	2.24689782	-9.64054382
C	2.28361430	-0.25173058	-8.58096142
H	2.85176061	0.30497748	-7.82647108
H	2.64988208	0.05929534	-9.56718133
H	2.51934193	-1.31466818	-8.45561896

Table S2. The Cartesian Coordinates (Å) of the Optimized Structure for **2b'**

atom	*x*	*y*	*z*
C	2.80048240	-1.15035578	0.00136702
C	1.92581703	-0.09192448	0.01163227
H	2.25540899	0.93853223	0.01234616
C	0.54469899	-0.4338487	0.01508658
C	0.34732698	-1.91732176	0.01085730
C	-0.54469707	0.43391100	0.01507061
C	-1.92581076	0.09196990	0.01169534
H	-2.25538825	-0.93849210	0.01251273
C	-0.34734342	1.91738768	0.01070773
C	-2.80049122	1.15038856	0.00138096
C	-4.23541157	1.09544156	-0.00963725
C	-5.13380500	2.14894364	-0.05616119
H	-4.82205929	3.18748159	-0.08936799
C	-6.48621148	1.73271405	-0.06227308
H	-7.31662240	2.43017923	-0.10019251
C	-6.66570036	0.3618482	-0.01852125
C	4.23540305	-1.09542749	-0.00970749
C	5.13377889	-2.14893364	-0.05646279
H	4.82201702	-3.18746119	-0.08984437
C	6.48619148	-1.73272178	-0.06255141
H	7.31659208	-2.43019133	-0.10061456
C	6.66570126	-0.36186642	-0.01855745
O	0.68501080	2.54889454	0.01422875
Si	-8.29275127	-0.60201771	0.00269678
Si	8.29277006	0.60196737	0.00273769
C	-9.69400644	0.63863783	-0.26023843
H	-9.59973081	1.16016378	-1.21958084
H	-9.72548867	1.39396794	0.53359555
H	-10.66159344	0.12228902	-0.25910824
C	-8.26807061	-1.88309484	-1.38770730
H	-8.15378626	-1.40686875	-2.36814933
H	-9.20034931	-2.46106559	-1.40197825
H	-7.44165550	-2.59332678	-1.26628377
C	-8.48422840	-1.46909698	1.67241972
H	-9.42137474	-2.03822305	1.71081553
H	-8.49624707	-0.74792956	2.49761619
H	-7.66243359	-2.17073144	1.85725440
C	8.26849961	1.88255728	-1.38812415
H	8.15460902	1.40596959	-2.36843669
H	9.20074080	2.46059236	-1.40226362
H	7.44198312	2.59276579	-1.26725883
C	8.48383004	1.46961526	1.67221114
H	9.42104861	2.03861479	1.71071082
H	8.49546971	0.74874047	2.49766846

S	1.98372905	-2.73240769	-0.00131989	H	7.66208275	2.17144204	1.85652825
S	-1.98375806	2.73245050	-0.00141420	C	9.69405137	-0.63882147	-0.25942826
S	-5.10957259	-0.42799429	0.02885717	H	9.59986771	-1.16083741	-1.21851420
S	5.10958549	0.42799051	0.02899548	H	9.72545639	-1.39374614	0.53479391
O	-0.68503812	-2.54880982	0.01450892	H	10.66163826	-0.12247275	-0.25848134

Table S3. The Cartesian Coordinates (Å) of the Optimized Structure for **3**$_\text{O}$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
C	-0.20023429	-0.24484723	-0.61237966	C	0.52458805	0.96451876	9.69594048
C	0.19026601	0.11566408	-1.93252213	H	0.22525178	0.68004217	10.71201948
H	0.90812624	0.87797019	-2.19638172	H	0.32621953	2.03669905	9.58384719
C	0.20076294	0.24409971	0.61236680	H	1.60689272	0.81056044	9.61719181
C	-0.18979833	-0.11634801	1.93250913	C	-2.28406152	0.25249573	8.57992820
H	-0.90769940	-0.87861425	2.19637579	H	-2.65088913	-0.05786322	9.56614737
C	1.29373151	1.63020226	4.99754605	H	-2.85192152	-0.30457579	7.82548581
H	1.97747701	2.35034519	4.56409606	H	-2.51955629	1.31539332	8.45380198
C	0.53344153	0.77050354	4.22451184	C	-0.52545800	-0.96337737	-9.69610944
C	1.07492325	1.45812739	6.38567013	H	-1.60771904	-0.80927317	-9.61707296
H	1.58647022	2.04779328	7.13938448	H	-0.32725523	-2.03563897	-9.58448744
C	0.15494663	0.47644369	6.70795474	H	-0.22626136	-0.67854905	-10.71212875
S	-0.45552813	-0.25449700	5.24250623	C	0.06314442	1.90419465	-8.65437518
C	-1.29279596	-1.63125272	-4.99758562	H	0.57581867	2.51300513	-7.90034666
H	-1.97616305	-2.35176780	-4.56415492	H	-1.00979485	2.11311917	-8.57534018
C	-0.53292385	-0.77121210	-4.22452136	H	0.39998914	2.24689782	-9.64054382
C	-1.07410536	-1.45900290	-6.38570490	C	2.28361430	-0.25173058	-8.58096142
H	-1.58535515	-2.04890725	-7.13943513	H	2.85176061	0.30497748	-7.82647108
C	-0.15463020	-0.47683567	-6.70795469	H	2.64988208	0.05929534	-9.56718133
S	0.45548437	0.25435877	-5.24250132	H	2.51934193	-1.31466818	-8.45561896
O	1.82334300	1.96380258	-0.05627109	C	0.51160373	0.68055300	2.79761733
O	-1.82264383	-1.96470551	0.05626076	C	-1.20152629	-1.33237672	-0.76043512
Si	-0.42581193	-0.06211018	8.42534256	C	1.20217498	1.33151950	0.76042487
Si	0.42540212	0.06257791	-8.42531129	C	-0.51103818	-0.68133210	-2.79762725
C	-0.06376990	-1.90360288	8.65566362	H	1.11501524	1.31136165	2.36626284
H	-0.40238526	-2.24606490	9.64130663	H	1.56377707	1.75877940	1.55715858
H	1.00934767	-2.11240114	8.57868384	H	-1.56309496	-1.75966716	-1.55716761
H	-0.57493001	-2.51271613	7.90085319	H	-1.11433224	-1.31225734	-2.36627900

Table S4. The Cartesian Coordinates (Å) of the Optimized Structure for **3**$_S$

atom	*x*	*y*	*z*
C	1.92581703	-0.09192448	0.01163227
H	2.25540899	0.93853223	0.01234616
C	0.54469899	-0.43384870	0.01508658
C	-0.54469707	0.43391100	0.01507061
C	-1.92581076	0.09196990	0.01169534
H	-2.25538825	-0.93849210	0.01251273
C	-4.23541157	1.09544156	-0.00963725
C	-5.13380500	2.14894364	-0.05616119
H	-4.82205929	3.18748159	-0.08936799
C	-6.48621148	1.73271405	-0.06227308
H	-7.31662240	2.43017923	-0.10019251
C	-6.66570036	0.36184820	-0.01852125
C	4.23540305	-1.09542749	-0.00970749
C	5.13377889	-2.14893364	-0.05646279
H	4.82201702	-3.18746119	-0.08984437
C	6.48619148	-1.73272178	-0.06255141
H	7.31659208	-2.43019133	-0.10061456
C	6.66570126	-0.36186642	-0.01855745
S	-5.10957259	-0.42799429	0.02885717
S	5.10958549	0.42799051	0.02899548
O	-0.68503812	-2.54880982	0.01450892
O	0.68501080	2.54889454	0.01422875
Si	-8.29275127	-0.60201771	0.00269678
Si	8.29277006	0.60196737	0.00273769
C	-9.69400644	0.63863783	-0.26023843
H	-9.59973081	1.16016378	-1.21958084
H	-9.72548867	1.39396794	0.53359555
H	-10.66159344	0.12228902	-0.25910824
C	-8.26807061	-1.88309484	-1.38770730
H	-8.15378626	-1.40686875	-2.36814933
H	-9.20034931	-2.46106559	-1.40197825
H	-7.44165550	-2.59332678	-1.26628377
C	-8.48422840	-1.46909698	1.67241972
H	-9.42137474	-2.03822305	1.71081553
H	-8.49624707	-0.74792956	2.49761619
H	-7.66243359	-2.17073144	1.85725440
C	8.26849961	1.88255728	-1.38812415
H	8.15460902	1.40596959	-2.36843669
H	9.20074080	2.46059236	-1.40226362
H	7.44198312	2.59276579	-1.26725883
C	8.48383004	1.46961526	1.67221114
H	9.42104861	2.03861479	1.71071082
H	8.49546971	0.74874047	2.49766846
H	7.66208275	2.17144204	1.85652825
C	9.69405137	-0.63882147	-0.25942826
H	9.59986771	-1.16083741	-1.21851420
H	9.72545639	-1.39374614	0.53479391
H	10.66163826	-0.12247275	-0.25848134
C	-2.80049122	1.15038856	0.00138096
H	-2.37650524	2.13280165	0.00201739
C	2.80048240	-1.15035578	0.00136702
H	2.37648346	-2.13276322	0.00209252
C	-0.34734342	1.91738768	0.01070773
H	-1.05010434	2.72422163	0.00391949
C	0.34732698	-1.91732176	0.01085730
H	1.05007716	-2.72416514	0.00407901

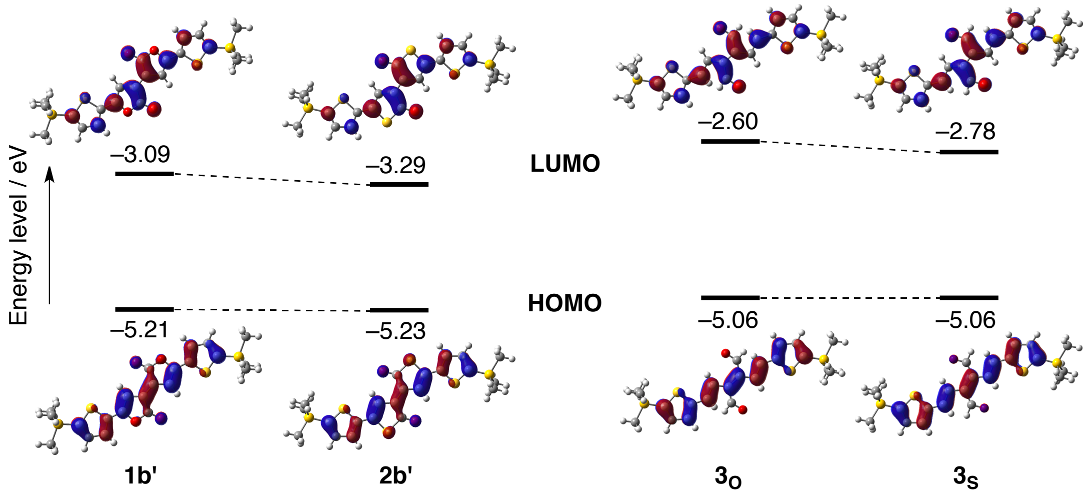


Figure S7. Kohn-Sham molecular orbitals of **1b'**, **2b'**, **3**$_{\mathrm{O}}$, and **3**$_{\mathrm{S}}$ calculated at the B3LYP/6-31G(d) level (isovalue = 0.03).

Table S5. Excitation Energies of Pechmann Dye **1b'**[a]

excited state	transition energy [eV] (wavelength [nm])	main CI coefficient	oscillator strength *f*
1	2.20(564)	0.71785 (HOMO→LUMO)	1.3054
2	3.06 (405)	0.62611 (HOMO–1→LUMO)	0.0000
		–0.30154 (HOMO→LUMO+1)	
3	3.47 (358)	0.69843 (HOMO–5→LUMO)	0.0000
4	3.57 (347)	0.68787 (HOMO–3→LUMO)	0.0000
5	3.58 (347)	0.69141 (HOMO–2→LUMO)	0.0119
6	3.65 (341)	0.49837 (HOMO–4→LUMO)	0.0210
		–0.48860 (HOMO→LUMO+2)	
7	3.80 (326)	0.57310 (HOMO→LUMO+1)	0.0000
8	3.83 (324)	0.69552 (HOMO–7→LUMO)	0.0000
9	4.00 (310)	0.48915 (HOMO–4→LUMO)	0.5556
		0.48168 (HOMO→LUMO+2)	

[a] Calculated at the B3LYP/6-31G(d) level using TD-DFT method.

Table S6. Excitation Energies of S-Pechmann Dye **2b'**[a]

excited state	transition energy [eV] (wavelength [nm])	main CI coefficient	oscillator strength *f*
1	1.95 (635)	0.71412 (HOMO→LUMO)	0.8682
2	2.59 (479)	0.31568 (HOMO–2→LUMO) 0.61968 (HOMO–1→LUMO)	0.0000
3	2.79 (444)	0.69634 (HOMO–4→LUMO)	0.0001
4	3.06 (405)	0.68155 (HOMO–3→LUMO)	0.3231
5	3.09 (401)	0.58863 (HOMO–2→LUMO) 0.27458 (HOMO→LUMO+1)	0.0000
6	3.27 (379)	0.69491 (HOMO–7→LUMO)	0.0000
7	3.36 (369)	0.69865 (HOMO–5→LUMO)	0.0157
8	3.36 (369)	0.69870 (HOMO–6→LUMO)	0.0000
9	3.63 (342)	0.67717 (HOMO→LUMO+2)	0.5971

[a] Calculated at the B3LYP/6-31G(d) level using TD-DFT method.

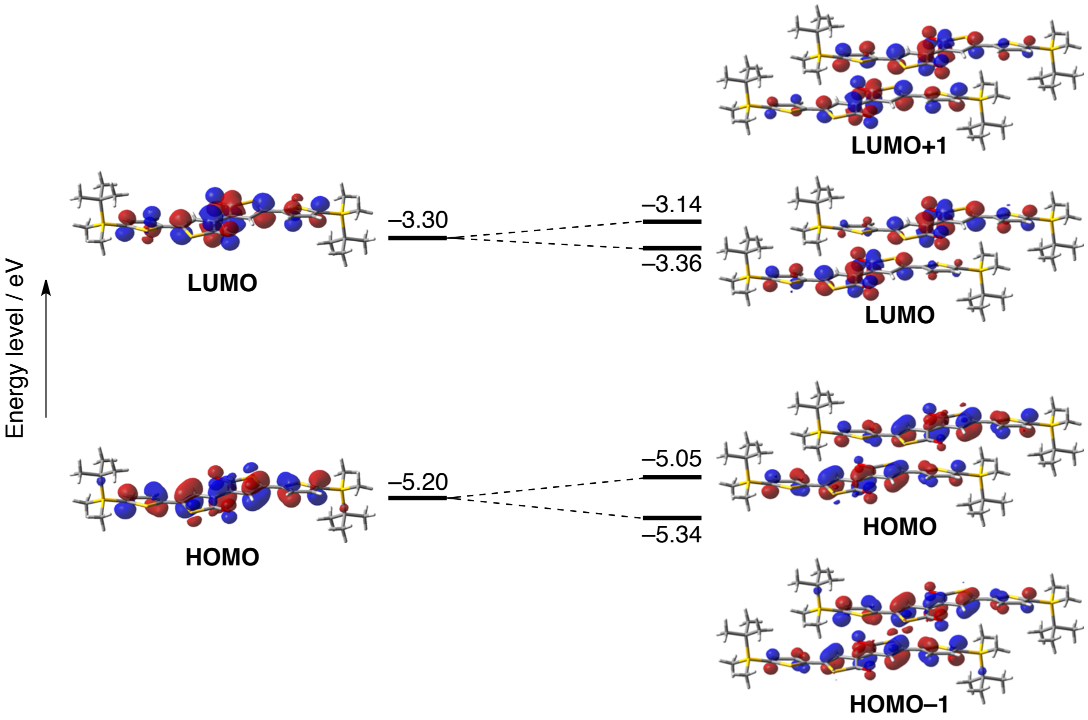
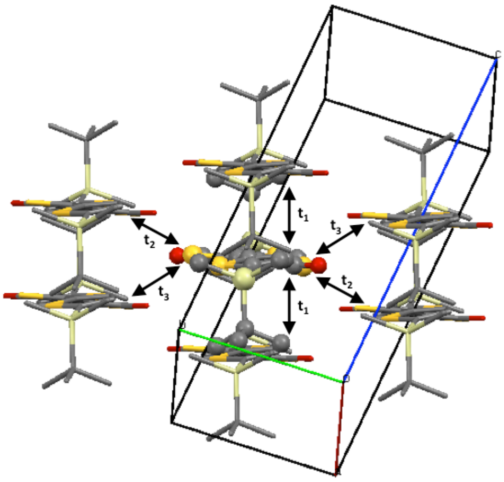


Figure S8. Kohn-Sham molecular orbitals of one molecule and two neighboring molecules of **2b** calculated at the B3LYP/6-31G(d) level.

Table S7. The Electronic Coupling (*V*) between Neighboring Molecules in **1b**'



The electronic coupling *V* (meV) between neighboring molecules (HOMO)

	|V| (meV)	V (eV)	H1 (eV)	H2 (eV)	J (eV)	S
t_1	116.5	0.116517528912	−0.005440122403	−0.005440134161	0.000245719892	−0.000646601159
t_2	8.8	0.008805198924	−0.005470202942	−0.005470203716	0.000016938297	−0.000040458303
t_3	2.4	−0.002438106729	−0.005542125541	−0.005542137918	−0.000006654973	0.000020704617

The electronic coupling *V* (meV) between neighboring molecules (LUMO)

	|V| (meV)	V (eV)	H1 (eV)	H2 (eV)	J (eV)	S
t_1	80.6	−0.080604623950	−0.004459078203	−0.004459069959	−0.000143221692	0.000382219115
t_2	6.9	−0.006919800777	−0.004497496741	−0.004497505142	−0.000012048301	0.000031029444
t_3	1.3	0.001371853578	−0.004580002502	−0.000014087953	0.000003743007	−0.000014087953

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