Supporting Information for:

Dipolar Second-Order Nonlinear Optical Chromophores Containing Ferrocene, Octamethylferrocene, and Ruthenocene Donors and Strong π-Acceptors: Crystal Structures and Comparison of π-Donor Strengths

Tiffany Kinnibrugh, Seyhan Salman, Yulia A. Getmanenko, Veaceslav Coropceanu, William W. Porter III, Tatiana V. Timofeeva, Adam J. Matzger, Jean-Luc Brédas, Seth R. Marder, and Stephen Barlow*

I. Table of Crystal and Refinement Parameters

Table 1. Selected Crystal and Refinement Parameters for the Crystal Structure Determinations.

	1	**2**	**3**	**4**	**5**	**6**
Formula	$C_{23}H_{24}FeN_2O_2S$	$C_{31}H_{40}FeN_2O_2S$	$C_{23}H_{24}N_2O_2RuS$	$C_{26}H_{18}FeN_2O_2S$	$C_{34}H_{34}FeN_2O_2S$	$C_{26}H_{18}N_2O_2RuS$
M_r	448.35	560.56	493.57	478.33	590.54	523.55
crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a / Å	7.845(2)	13.203(3)	9.2218(10)	8.017(2)	8.772(4)	7.564(2)
b / Å	10.258(3)	14.472(4)	10.2988(11)	10.346(3)	10.597(5)	9.982(3)
c / Å	14.989(4)	14.620(4)	11.7624(13)	13.485(3)	16.285(8)	15.465(4)
α / °	74.724(5)	85.665(7)	91.517(2)	93.608(4)	94.158(8)	83.976(3)
β / °	85.733(5)	85.200(7)	96.695(2)	100.840(4)	95.374(7)	77.154(3)
γ / °	77.220(5)	82.663(6)	110.652(2)	106.161(4)	99.974(7)	74.250(3)
V / Å^3	1134.6(5)	2754.9(13)	1035.45(19)	1047.2(5)	1478.3(12)	1094.6(5)
Z	2	4	2	2	2	2
ρ_{calc} / gcm^{-3}	1.312	1.352	1.583	1.517	1.327	1.589

μ / mm^{-1}	0.777	0.654	0.880	0.847	0.614	0.838
F(000)	468	1192	504	492	620	528
Crystal size / mm^3	0.30×0.10×0.03	0.36×0.35×0.15	0.29×0.10×0.06	0.04×0.04×0.03	0.05×0.04×0.03	0.20×0.17×0.09
$2\theta_{\mathrm{max}}$ / $^{\mathrm{o}}$	59.0	52.0	59.0	60.0	59.0	59.0
reflections collected	19209	15852	12077	15996	16461	13254
unique reflections	6298	10828	5685	6044	8149	6027
R_{int}	0.0437	a	0.0431	0.0605	0.0874	0.0492
used reflections	6298	10828	5685	6044	8149	6027
reflns with $I > 2\sigma(I)$	4821	6786	4763	3624	3776	4403
no. of parameters	264	687	262	289	369	289
wR_2	0.0597	0.1041	0.0345	0.0580	0.1079	0.1081
R_1 [$I > 2\sigma(I)$]	0.0323	0.0594	0.0833	0.0448	0.0642	0.0480
S	1.007	0.998	1.002	1.000	1.003	1.023

[a] Reflections were merged in TWINABS.

II. Atom Numbering for Structures of 1-6

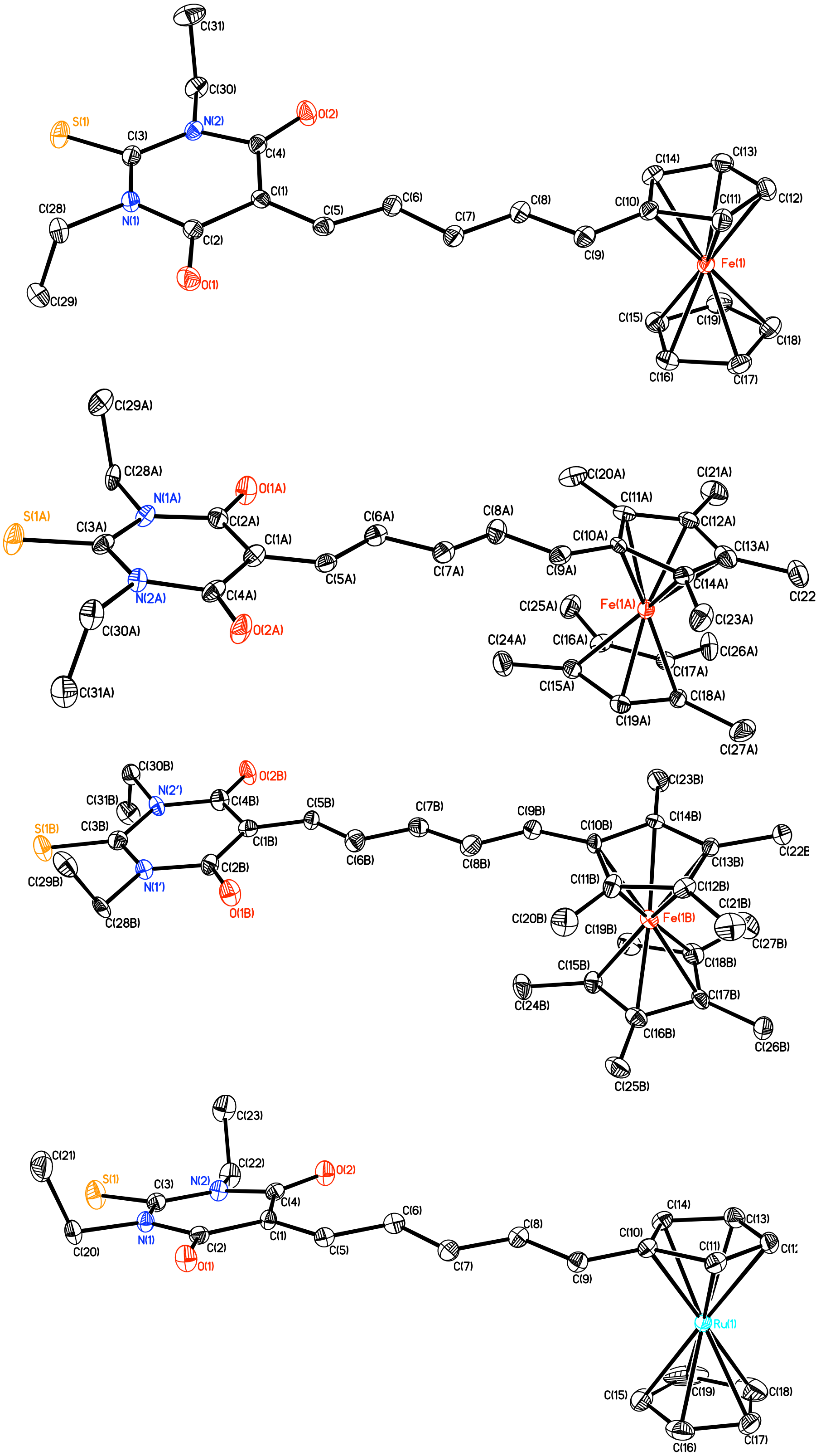


Figure S1. Atom labeling for TB chromophores; from top to bottom, **1**, **2A**, **2B**, **3**.

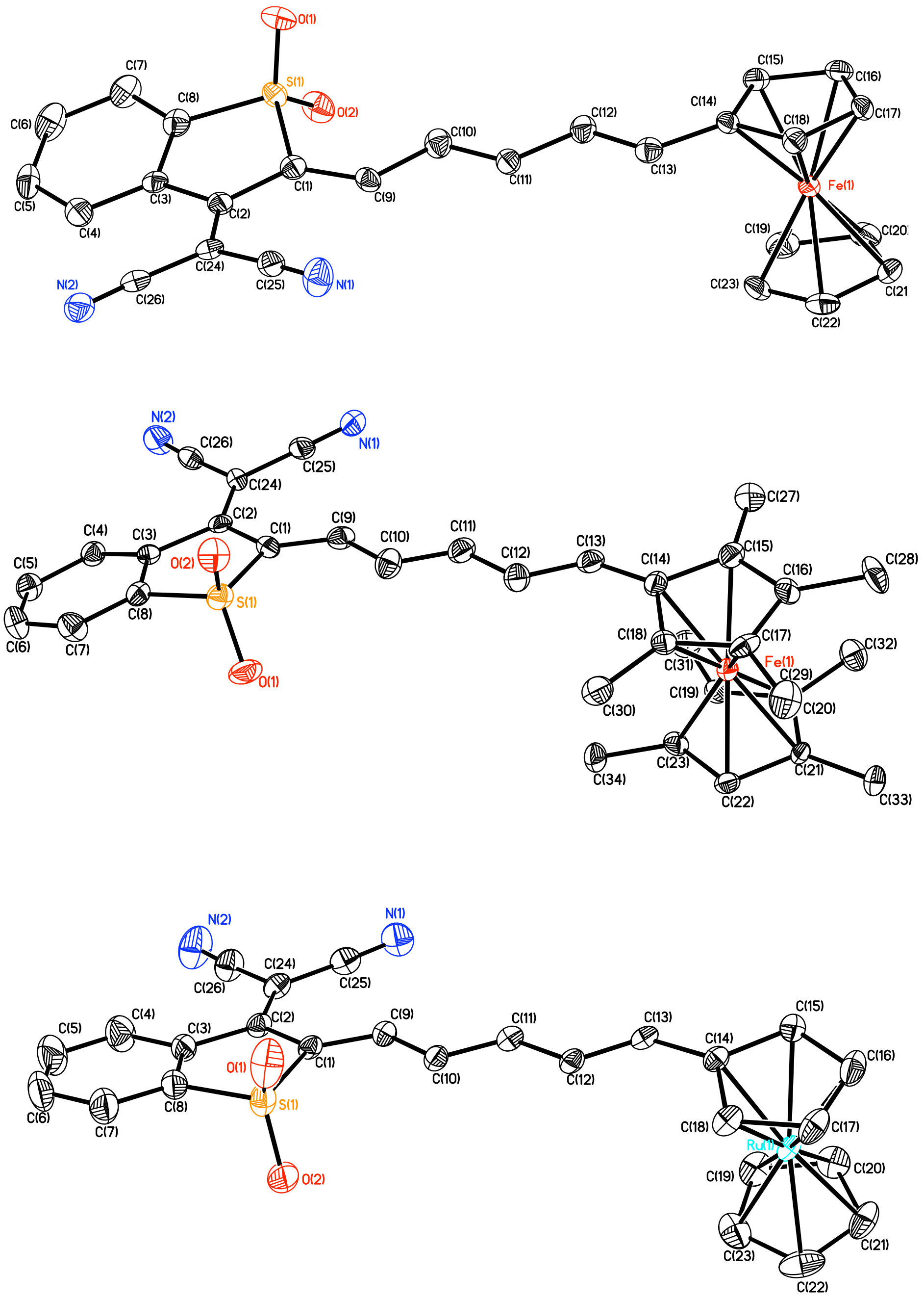


Figure S2. Atom labeling for SDS chromophores; from top to bottom, **4**, **5**, **6**.

II. Polymer-Induced Heteronucleation Studies of 3

As discussed in the main text, crystals obtained from **1-6** were all centrosymmetric. Nonetheless, many compounds are known to crystallize in multiple arrangements, that is, to exhibit polymorphism, leaving open the possibility that alternative NLO-active non-centrosymmetric polymorphs might be obtained under different conditions. We chose **3** as a system for further investigation due to the fact that the X-ray quality crystals of **3** used for structure determination (recrystallized from ethyl acetate) exhibit different morphologies from the microcrystalline material obtained from the synthesis (which crystallizes from the hot ethanolic reaction mixture). To further investigate the possibility of growing non-centric crystals, polymer-induced heteronucleation[1,2] (PIHn) was employed to screen for polymorphs of **3**. This method exploits the ability of the surface of an insoluble material to direct crystallizing phase formation through heteronucleation processes.

PIHn studies of **3** were carried out using three cross-linked polymer libraries – one containing polymers with non-polar and aromatic functional groups, one containing nitrogen-rich functional groups, and the final library containing acidic functional groups – the components of which were as follows. Non-polar/aromatic library: 4-acetoxystyrene (AOS), *n*-butyl methacrylate (*n*-BuMA), *tert*-butyl methacrylate (*t*-BuMA), benzyl methacrylate (BzMA), methyl methacrylate (MMA), and styrene (STY) with divinylbenzene (DVB). Polar/Nitrogen library: 2-dimethylaminoethyl methacrylate (DMAEMA), *N,N*-dimethylmethacrylamide (DMMAA), methacrylonitrile (MAN), 2-methyl-2-nitropropylmethacrylate (MNPMA)**,** 2-vinylpyridine (2VP), 4-vinylpyridine (4VP). Polar/Acidic library: acrylic acid (AA), 2-ethoxyethyl methacrylate (EEMA), ethylene glycol methacrylate phosphate (EGMAP), 2-hydroxyethyl methacrylate

---

1. Lang, M. D.; Grzesiak, A. L.; Matzger, A. J., *J. Am. Chem. Soc.* **2002**, *124*, 14834.
2. Price, C. P.; Grzesiak, A. L.; Matzger, A. J., *J. Am. Chem. Soc.* **2005**, *127*, 5512.

(HEMA), methacrylic acid (MAA), and methyl methacrylate (MMA) with DVB. Libraries were synthesized in 96-well plates by a previously published procedure.[2] Briefly, six 1:1 (v/v) monomer solutions in ethanol were dispensed as 90 pairwise combinations of varied ratios (43:7, 36:14, 29:21, 21:29, 14:36, and 7:43) and six pure monomer solutions by a Gilson 215 liquid handler to a volume of 100 μ L. To each of these 96 solutions was added 50 μL of a 1:1 (v/v) solution of DVB in ethanol containing 2 mol% 2,2′-azobisisobutyronitrile with respect to DVB. The solutions were photopolymerized in a nitrogen atmosphere and then annealed at 80 °C under vacuum to produce cross-linked polymer libraries.

Solutions of **3** in acetone (1.9 mM) were allowed to evaporate in the presence of the three polymer libraries described above. Optical microscopy and Raman spectroscopy were performed *in situ* and crystals were removed from the polymers with a cryoloop for powder X-ray diffraction. Raman spectra were obtained using a Renishaw inVia Raman Microscope equipped with a Leica microscope, RenCam CCD detector, 785 nm laser, 1200 lines/mm grating, and 50 μm slit. Spectra were collected in extended scan mode in the range of 1800-100 cm^{-1} at 0.5 % laser power and analyzed using the WiRE 2.0 software package. Calibration was performed using a silicon standard. Powder X-ray diffraction patterns were collected at ambient temperature using a Rigaku R-AXIS SPIDER diffractometer with an imaging plate detector using graphite monochromated Cu-Kα radiation (1.5406 Å). Samples were mounted on a cryoloop. To obtain powder patterns with minimized preferred orientation, images were collected for 5 minutes while rotating the sample about the ϕ-axis at $10°\cdot s^{-1}$ while oscillating ω between 120° and 180° at $1°\cdot s^{-1}$ with χ set at 45°. Images were integrated from 2.5° to 50° 2θ with a 0.05° step size with the AreaMax[3] software package. Powder patterns were processed in Jade Plus[4]

---

[3] *AreaMax, 2.0.0.4*, Rigaku: Tokyo, 2005.

to calculate peak positions and intensities. SHG measurements were conducted on each form with a 1064 nm laser.

The crystals obtained were analyzed by Raman spectroscopy (Figure S3, Table S2) which indicated the presence of three distinct forms; differences in the vibrational modes in the 1500–1600 cm^{-1} range and the 600–700 cm^{-1} range are particularly diagnostic. The forms identified by Raman spectroscopy were confirmed to be distinct forms via powder X-ray diffraction (Figure S4, Table S3). The diffraction patterns shown in Figure S4 indicate that Form I corresponds to the structurally characterized form, Form II corresponds to that obtained in the synthesis, and Form III is unique. However, none of the three forms produced a second harmonic generation signal (using incident light of wavelength 1064 nm) suggesting that none of these forms is non-centrosymmetric. Terpolymers made from the monomers DMAEMA, MNPMA, and DVB and EGMAP, HEMA, and DVB produced crystals of Form I. Terpolymers made from AOS, *n*-BuMA, and DVB produced crystals of Form II. Terpolymers made from HEMA, MAA, and DVB and MAN, 2VP, and DVB produced crystals of Form III.

---

4. *Jade Plus 8.0, 8.2*, Materials Data, Inc: Livermore, CA, 1995-2007.

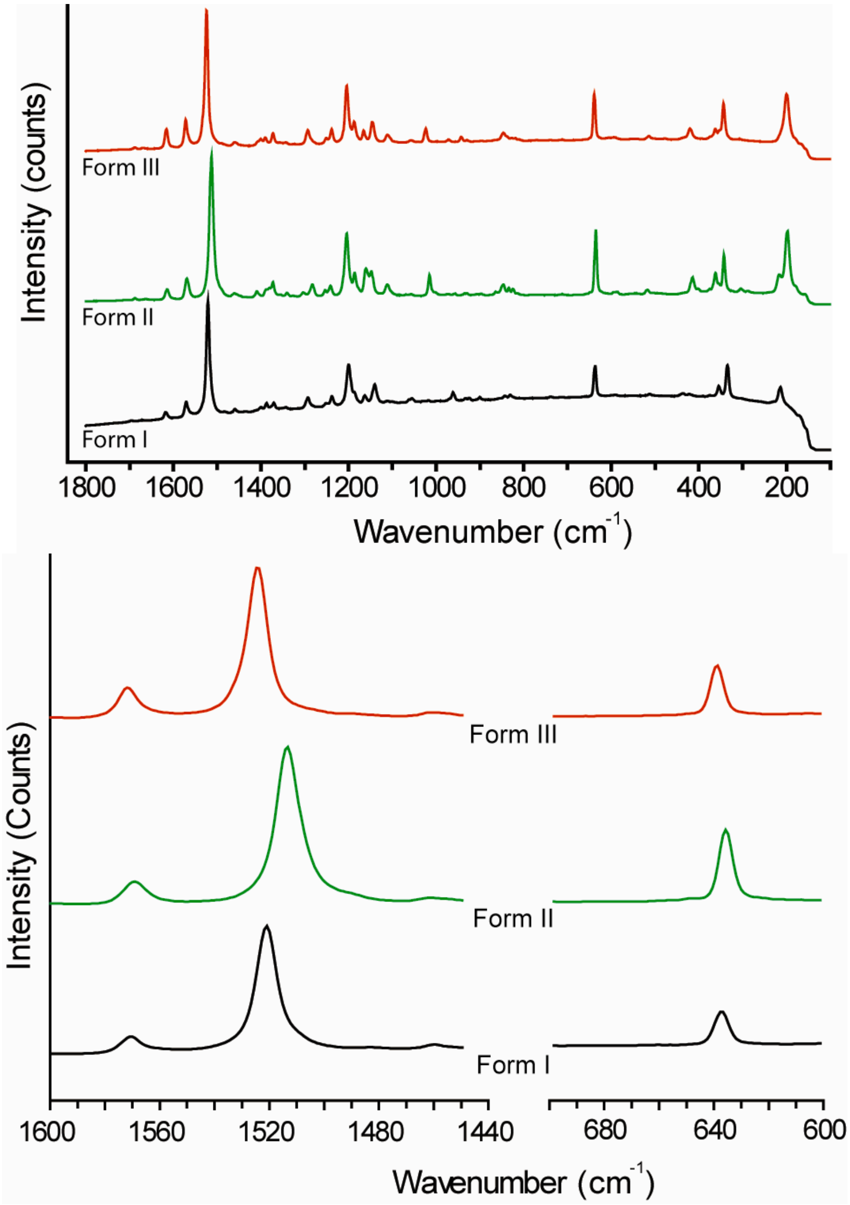


Figure S3. Raman spectra for the three forms of **3** showing (top) the full range examined and (below) the diagnostic regions.

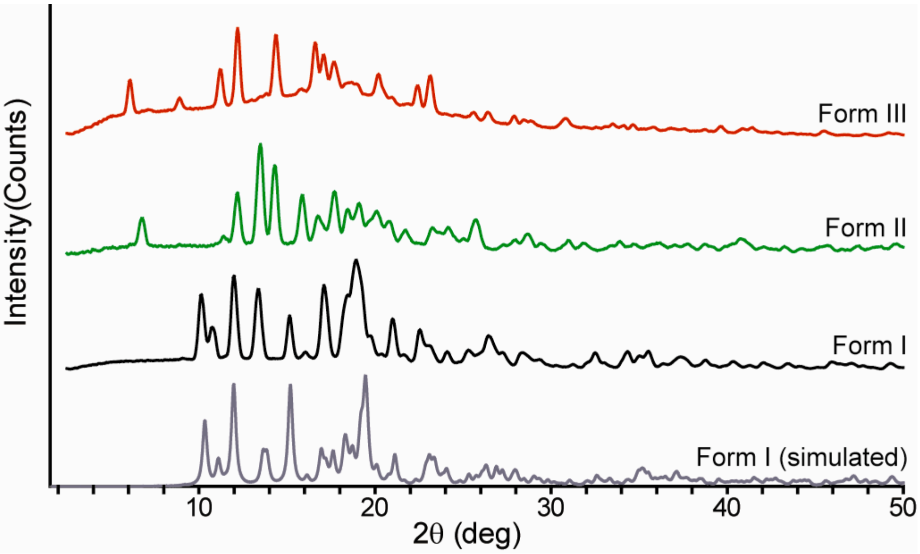


Figure S4. Powder X-ray diffraction pattern of **3** simulated from the single crystal structure and experimental patterns of the three forms obtained utilizing PIHn.

Table S2. Frequencies of Raman Vibrational Modes (cm^{-1}) of the Three Forms of 3.

Form I		Form II		Form III	
1696.2	1061.5	1687.5	1015.2	1687.5	1111.5
1670.2	1054.7	1664.4	1001.7	1668.3	1057.6
1617.2	961.3	1614.3	971.9	1616.3	1050.9
1571.0	933.4	1569.1	957.4	1571.9	1023.9
1520.9	924.7	1513.2	929.5	1524.7	971.9
1460.2	900.6	1461.2	864.0	1461.2	943.0
1400.5	842.8	1410.1	846.7	1454.4	929.5
1387.0	831.3	1387.0	834.1	1407.2	846.7
1370.6	738.8	1380.3	824.5	1400.5	828.4
1343.7	636.7	1372.6	635.7	1389.9	818.7
1292.6	591.4	1340.8	593.4	1372.6	810.1
1251.2	512.4	1303.2	586.6	1343.7	638.6
1237.7	436.4	1282.0	518.2	1293.6	593.4
1199.2	420.9	1253.1	414.2	1250.2	514.4
1187.6	375.7	1241.6	402.6	1238.7	420.0
1162.6	354.5	1204.0	362.2	1204.0	362.2
1140.4	334.3	1185.7	342.9	1187.6	343.9
1111.5	213.9	1160.7	303.4	1165.5	199.4
1101.9		1148.1	289.0	1145.3	
		1111.5	216.7		
			197.5		

Table S3. Experimental Powder X-ray Diffraction Peak Positions (°) and Relative Peak Intensities for the Three Forms of 3.

Form I		Form II		Form III	
2θ	I / I_0	2θ	I / I_0	2θ	I / I_0
10.2	66.6	6.8	32.2	6.1	40.9
10.7	32.1	11.4	15.8	7.1	3.0
12.0	85.8	12.2	55.4	8.9	15.6
13.4	72.8	13.5	100.0	11.2	48.0
15.2	43.8	14.3	80.3	12.2	100.0
16.1	5.2	15.9	53.3	13.8	5.5
17.1	74.6	16.8	34.3	14.4	85.0
18.4	62.1	17.7	56.5	15.8	9.7
18.9	100.0	18.5	40.4	16.6	73.6
21.0	43.1	19.1	45.9	17.0	57.3
21.6	5.4	20.1	38.6	17.7	47.0
22.6	31.7	20.8	29.3	18.7	18.5
23.0	15.7	21.7	21.3	20.2	38.0
24.1	10.2	23.3	23.5	21.0	9.2
25.4	12.6	24.2	23.9	22.4	33.9
26.5	27.8	25.7	30.6	23.1	51.8
27.3	12.1	27.2	8.1	25.6	9.9
28.4	11.8	28.0	12.4	26.4	13.5
29.3	6.5	28.7	17.7	27.9	12.7
31.2	2.4	29.5	9.2	28.4	8.5
32.5	14.7	31.0	11.9	28.8	7.7
34.3	16.1	31.8	9.4	30.8	13.9
35.5	16.3	33.9	11.0	33.5	5.4
36.4	3.4	34.7	8.6	34.1	4.0
37.4	10.7	36.2	9.7	34.6	5.7
38.8	7.1	37.1	7.8	35.7	4.1
40.3	5.3	37.7	8.7	36.8	3.1
41.3	1.3	38.8	8.4	37.4	2.6
42.1	4.5	40.8	13.4	38.7	2.6
43.5	4.3	42.1	6.0	39.6	8.2
46.0	6.3	43.3	6.3	40.9	5.4
47.0	5.0	44.2	4.4	41.4	7.0
		45.7	7.4	42.8	2.3
		47.5	6.9	45.5	5.7
		48.7	6.3	49.2	4.2

IV. Crystal Packing for 1-6

All six crystal structures determined were found to belong to a centrosymmetric space group (in fact they all belong to the triclinic space group $P\bar{1}$), as is typical for chromophores with large dipole moments, ruling out bulk second-order nonlinear effects. Apart from **2**, all the chromophores presented in this paper have two molecules per unit cell, related by an inversion center. In all cases there are stacking interactions between the polyene-substituted cyclopentadienyl rings and the acceptor groups of adjacent molecules; for the SDS chromophores **4-6** it is the dicyanomethylidene portion of the acceptor that stacks with the donor. Depending on whether these stacked neighbors are those related by inversion or translation leads to the formation of either dimers (**4** and **6**) or chains (**1** and **5**), neighboring chains in the crystal showing antiparallel orientation. The dimer formed by **4** is shown in Figure S5; similar dimers in which the acceptor groups stack with the substituted cyclopentadienyl rings of adjacent molecules have previously been observed in other crystal structures of chromophores containing ferrocene donors linked to strong π-acceptors, including those of **IV**, **V** and **VII**.[5] Two antiparallel chains for chromophore **5** are shown in Figure S6. Crystals of **2** contain two crystallographically independent molecules (denoted **2A** and **2B**) in the asymmetric unit differing slightly in their conformations and consequently exhibits more complex packing (Figure S7). The conjugated polyene chains are coplanar and lie perpendicular to the *c* axis, with the polyene axes for **2A** molecules oriented at ca. 111 ° relative to those of the

---

[5] Liao, Y.; Eichinger, B. E.; Firestone, K. A.; Haller, M.; Luo, J.; Kaminsky, W.; Benedict, J. B.; Reid, P. J.; Jen, A. K.-Y.; Dalton, L. R.; Robinson, B. H., *J. Am. Chem. Soc.* **2005**, *127*, 2759.

2B molecules. Pairs of **2A** molecules form antiparallel units with an intermolecular distance of 4.122 Å between the centroid of the polyene-substituted cyclopentadienyl ring of the donor and centroid of the TB heterocycle. Pairs of **2B** molecules also form similar antiparallel dimers. **2A-2B** interactions appear to be stronger than **2A-2A** and **2B-2B** interactions, with distances of 3.746 Å between the C_5Me_4H centroid of **2A** and the TB centroid of **2B** and 3.712 Å between the C_5Me_4H centroid of **2B** and the TB centroid of **2A**. Short contacts are present between one of the TB methyl C–H moieties of **2A** and one of the oxygen atoms of neighboring (1+x, −1+y, 1+z) **2B** and vice versa (H···O distances of 2.408 and 2.408 Å respectively, C–H···O angles of 170.7 and 174.5 °, respectively).

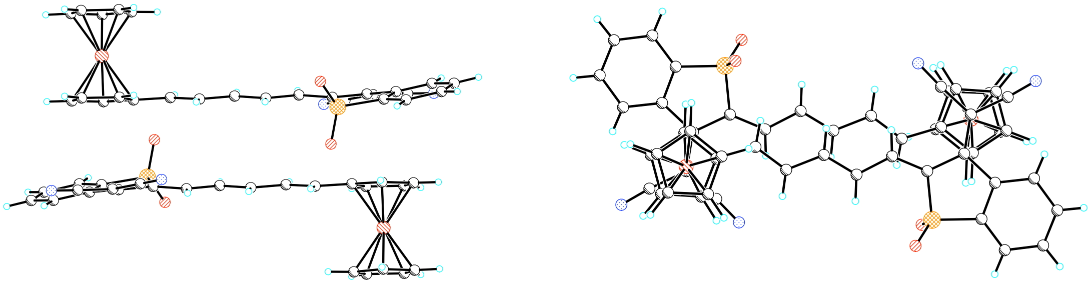
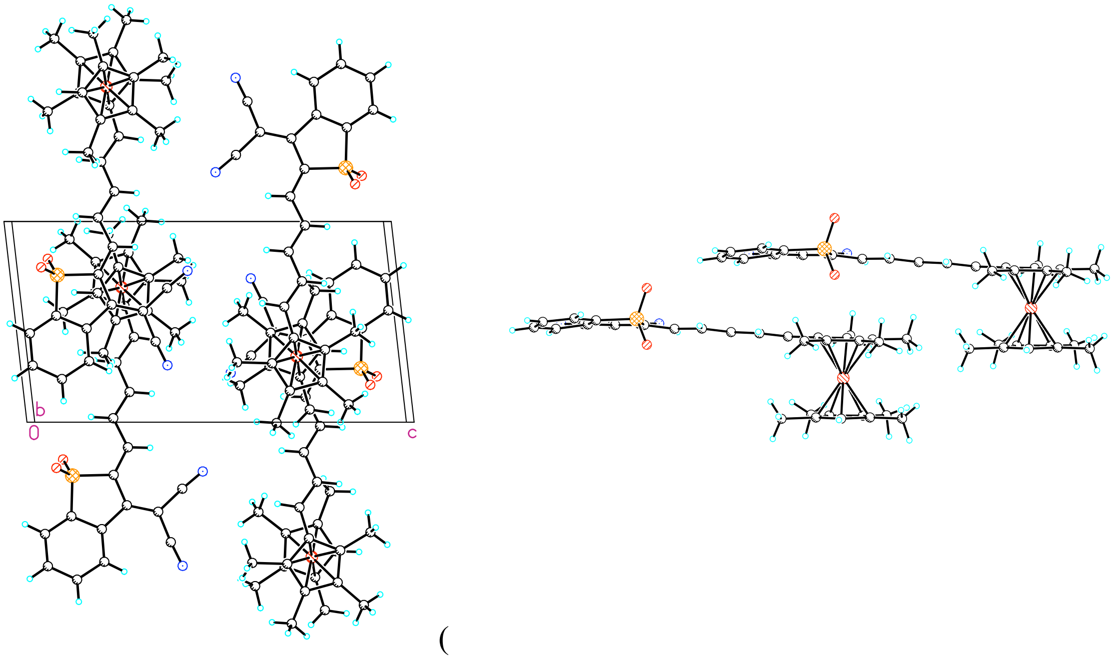

(a) (b)

Figure S5. Two views of the stacking between donor and acceptor found in the crystal structure of **4** resulting in the formation of centrosymmetric dimers.

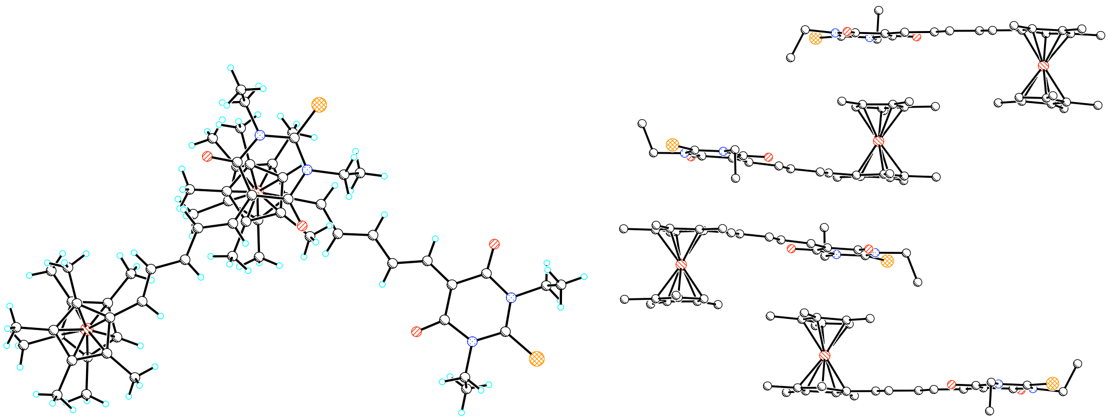


(

(b)

a)

Figure S6. Crystal packing in the structure of **5** showing (a) the presence of antiparallel chains and (b) two molecules in one of the chains.



(a) (b)

Figure S7. Crystal packing in the structure of **2** showing (a) a **2A** molecule (left) oriented at ca. 111° relative to a **2B** molecule (right) and (b) the stacking between a **2A** pair (center molecules) and two **2B** molecules (top and bottom molecules).

V. NMR Data for 1-6 and IX

The following data were all acquired in CD_2Cl_2 at 400.14 (^{1}H) or 100.62 (^{13}C) MHz.

1. ^{1}H NMR: δ 8.11 (d, J = 12.6 Hz, 1H, H_ε), 8.00 (distorted t, apparant J = ca. 13 Hz, 1H, H_δ), 7.26 (dd, J =14.0 Hz, 11.5 Hz, 1H, H_γ), 7.05 (d, J =15.1 Hz, 1H, H_α), 6.77 (dd, J = 15.0 Hz, 11.4 Hz, 1H, H_β), 4.60 (apparent s, 2H, C_5H_4), 4.58 (apparent s, 2H, C_5H_4), 4.50 (m, 4H, Et CH_2 groups), 4.20 (s, 5H, C_5H_5), 1.26 (m, 6H, Et CH_3 groups). $^{13}C\{^1H\}$ NMR: δ 179.42 (C=S), 161.11 (C=O), 160.17 (C=O), 158.38 (C_ε), 157.05 (C_γ), 148.10 (C_α), 127.40 (C_δ), 126.64 (C_β), 113.05 (C_A, i.e. $=C(CO)_2$), 81.22 (Fc quat.), 72.53 (C_5H_4 CH), 70.61 (C_5H_5), 69.25 (C_5H_4 CH), 43.81 (Et CH_2), 43.27 (Et CH_2), 12.56 (Et CH_3), 12.51 (Et CH_3).

2. ^{1}H NMR: δ 8.12 (d, J = 12.8 Hz, 1H, H_ε), 8.00 (distorted t, apparent J = ca. 13 Hz, 1H, H_δ), 7.27 (dd, J = 13.5 Hz, 10.9 Hz, 1H, H_γ), 6.86 (m, 2H, H_β and H_α), 4.51 (m, 4H, Et CH_2 groups), 3.58 (s, 1H, Fc" CH), 1.64 (s, 12H, overlapping Fc" CH_3 groups), 1.34 (s, 6H, Fc" CH_3), 1.32 (s, 6H, Fc" CH_3), 1.18 (m, 6H, Et CH_3 groups). $^{13}C\{^1H\}$ NMR: δ 179.19 (C=S), 161.41 (C=O), 160.43 (C=O), 159.61 (C_γ), 158.26 (C_ε), 152.67 (C_α), 125.64 (C_δ), 125.20 (C_β), 110.69 (C_A, i.e. $=C(CO)_2$), 89.50 (Fc" quat.), 84.60 (2 overlapping Fc" quat.), 83.71 (Fc" quat.), 78.70 (Fc" quat.), 74.19 (Fc" CH), 43.69 (Et CH_2), 43.15 (Et CH_2), 12.58 (Et CH_3), 12.52 (Et CH_3), 11.08 (Fc" CH_3), 10.88 (Fc" CH_3), 10.04 (Fc" CH_3), 9.04 (Fc" CH_3).

3. ^{1}H NMR: δ 8.06 (d, J = 12.7 Hz, 1H, H$_\varepsilon$), 7.93 (m, 1H, H$_\delta$), 7.20 (dd, J =14.0 Hz, 11.7 Hz, 1H, H$_\gamma$), 6.94 (d, J =15.1 Hz, 1H, H$_\alpha$), 6.71 (dd, J =15.1 Hz, 11.4 Hz, 1H, H$_\beta$), 4.93 (apparent s, 2H, C_5H_4), 4.78 (apparent s, 2H, C_5H_4), 4.55 (s, 5H, C_5H_5), 4.47 (m, 4H, Et CH_2 groups), 1.26 (m, 6H, Et CH_3). ^{13}C{^{1}H} NMR: δ 179.40 (C=S), 161.04 (C=O), 160.07 (C=O), 158.34 (C$_\varepsilon$), 157.77 (C$_\gamma$), 145.97 (C$_\alpha$), 127.45 (C$_\delta$), 125.94 (C$_\beta$), 113.17 (C$_A$, i.e. =*C*(CO)$_2$), 85.39 (Rc quat.), 73.24 (C_5H_4 CH), 72.29 (C_5H_5), 70.74 (C_5H_4 CH), 43.80 (Et CH_2), 43.26 (Et CH_2), 12.54 (Et CH_3), 12.49 (Et CH_3).

4. ^{1}H NMR: δ 8.84 (d, J = 7.43 Hz, 1H, A CH), 8.50 (d, J = 11.4 Hz, 1H, H$_\varepsilon$), 7.95 (m, 1H, A CH), 7.85 (m, 2H, A CH), 7.25 (m, 2H, H$_\delta$ and H$_\gamma$), 7.14 (d, J = 15.0 Hz, 1H, H$_\alpha$), 6.78 (dd, J = 14.9, 10.9 Hz, 1H, H$_\beta$), 4.66 (m, 2H, C_5H_4), 4.63 (m, 2H, C_5H_4), 4.22 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR: δ 154.76, 150.27, 149.85, 144.21, 139.02, 135.38, 134.88, 129.39, 127.96, 126.32, 126.23, 123.32, 122.18, 115.44 (CN), 115.33 (CN), 81.23 (Fc quat.), 73.34 (C_5H_4 CH), 70.91 (C_5H_5), 69.68 (C_5H_4 CH) (*C*(CN)$_2$ resonance not observed); a satisfactory HSQC spectrum was not obtained for this compound.

5. ^{1}H NMR: δ 8.85 (d, J = 7.6 Hz, 1H, A CH), 8.64 (d, J = 12.7 Hz, 1H, H$_\varepsilon$), 7.91 (d, J = ca. 7.7 Hz, 1H, A CH), 7.81 (m, 2H, A CH), 7.37 (t, J =12.4 Hz, 1H, H$_\gamma$), 7.17 (m, 2H, H$_\delta$ and H$_\alpha$), 6.87 (dd, J = 14.5, 11.8 Hz, 1H, H$_\beta$), 3.45 (s, 1H, $C_5Me_4\mathit{H}$), 1.81 (s, 6H, Fc" CH_3), 1.78 (s, 6H, Fc" CH_3), 1.47 (s, 12H, overlapping Fc" CH_3 groups). ^{13}C{^{1}H} NMR: δ 155.98 (C$_\gamma$), 154.90 (C$_\alpha$), 148.25 (A quat.), 142.74 (C$_\varepsilon$), 138.71 (A quat.), 134.69 (A CH), 134.39 (A CH), 130.07 (A quat.), 126.02 (C$_\beta$), 125.85 (A CH), 124.55 (A quat.), 122.44 (C$_\delta$), 121.92 (A CH), 116.93 (CN), 116.80 (CN), 90.84 (Fc" quat.), 84.79 (2 overlapping Fc" quat.), 83.88 (Fc" quat.), 79.78 (Fc" quat.), 74.25 (Fc" CH), 64.69 (*C*(CN)$_2$), 11.21 (Fc" CH_3), 11.04 (Fc" CH_3), 10.30 (Fc" CH_3), 9.23 (Fc" CH_3).

6. ^{1}H NMR: δ 8.83 (d, J =7.4 Hz, 1H, A CH), 8.44 (d, J =11.6 Hz, 1H, H$_\varepsilon$), 7.94 (m, 1H, A CH), 7.85 (m, 2H, A CH), 7.20 (m, 2H, H$_\delta$ and H$_\gamma$), 7.02 (d, J = 15.0 Hz, 1H, H$_\alpha$), 6.75 (dd, J = 15.0 Hz, 10.8 Hz, 1H, H$_\beta$), 4.97 (apparent t, J = 1.7 Hz, 2H, C_5H_4), 4.83 (apparent t, 2H, C_5H_4), 4.59 (s, 5H, C_5H_5). ^{13}C{^{1}H} NMR: δ 155.14 (C$_\gamma$), 149.94 (A quat.), 147.94 (C$_\alpha$), 144.25 (C$_\varepsilon$), 139.03 (A quat.), 135.45 (A CH), 134.87 (A CH), 129.32 (A quat.), 128.16 (A quat.), 126.24 (A CH), 125.54 (C$_\beta$), 123.34 (C$_\delta$), 122.18 (A CH), 115.27 (CN), 115.15 (CN), 85.38 (Rc quat.), 73.79 (C_5H_4 CH), 72.57 (C_5H_5), 71.03 (C_5H_4 CH) (*C*(CN)$_2$ resonance not observed).

IX. ^{1}H NMR: δ 8.81 (d, J = 7.2 Hz, 1H, A CH), 8.49 (d, J = 12.5 Hz, 1H, H$_\varepsilon$), 7.93 (poorly resolved dd, J = 8.6, 1.8 Hz, 1H, A CH), 7.81 (m, 2H, A CH), 7.45 (d, J = 8.9 Hz, 2H, D CH), 7.36 (dd, J = 13.4, 11.2 Hz, 1H, H$_\gamma$), 7.24 (t, apparent J = 13.0 Hz, 1H, H$_\delta$), 7.15 (d, J =14.7 Hz, 1H, H$_\alpha$), 7.05 (dd, J = 14.7, 11.1 Hz, 1H, H$_\beta$), 6.65 (d, J = 9.0 Hz, 2H, D CH), 3.37 (t, J = 7.8 Hz, 4H, NC*H*$_2$), 1.61 (m, 4H, NCH$_2$C*H*$_2$), 1.39 (m, 4H, C*H*$_2$CH$_3$), 0.97 (t, J = 7.3 Hz, CH$_3$). ^{13}C{^{1}H} NMR: δ 157.11 (C$_\gamma$), 151.61 (quat.), 149.98 (C$_\alpha$), 148.97 (quat.), 143.91 (C$_\varepsilon$), 138.96 (quat.), 134.82 (A CH), 134.61 (A CH), 132.02 (D CH), 129.71 (quat.), 126.07 (A CH), 125.68 (quat.), 123.63 (C$_\beta$), 123.18 (C$_\delta$), 121.90 (A CH), 115.99 (CN), 115.91 (CN), 112.38 (D CH), 67.21 (*C*(CN)$_2$), 51.31 (N*C*H$_2$), 29.80 (N*C*H$_2$CH$_2$), 20.58 (*C*H$_2$CH$_3$), 14.04 (CH$_3$) (1 quat. resonance not observed).

Ferrocene. ^{1}H NMR: δ 4.18. ^{13}C{^{1}H} NMR: δ 68.41.

Ruthenocene. ^{1}H NMR: δ 4.54. ^{13}C{^{1}H} NMR: δ 70.26.

VI. Calculated Atomic Charge Density Data

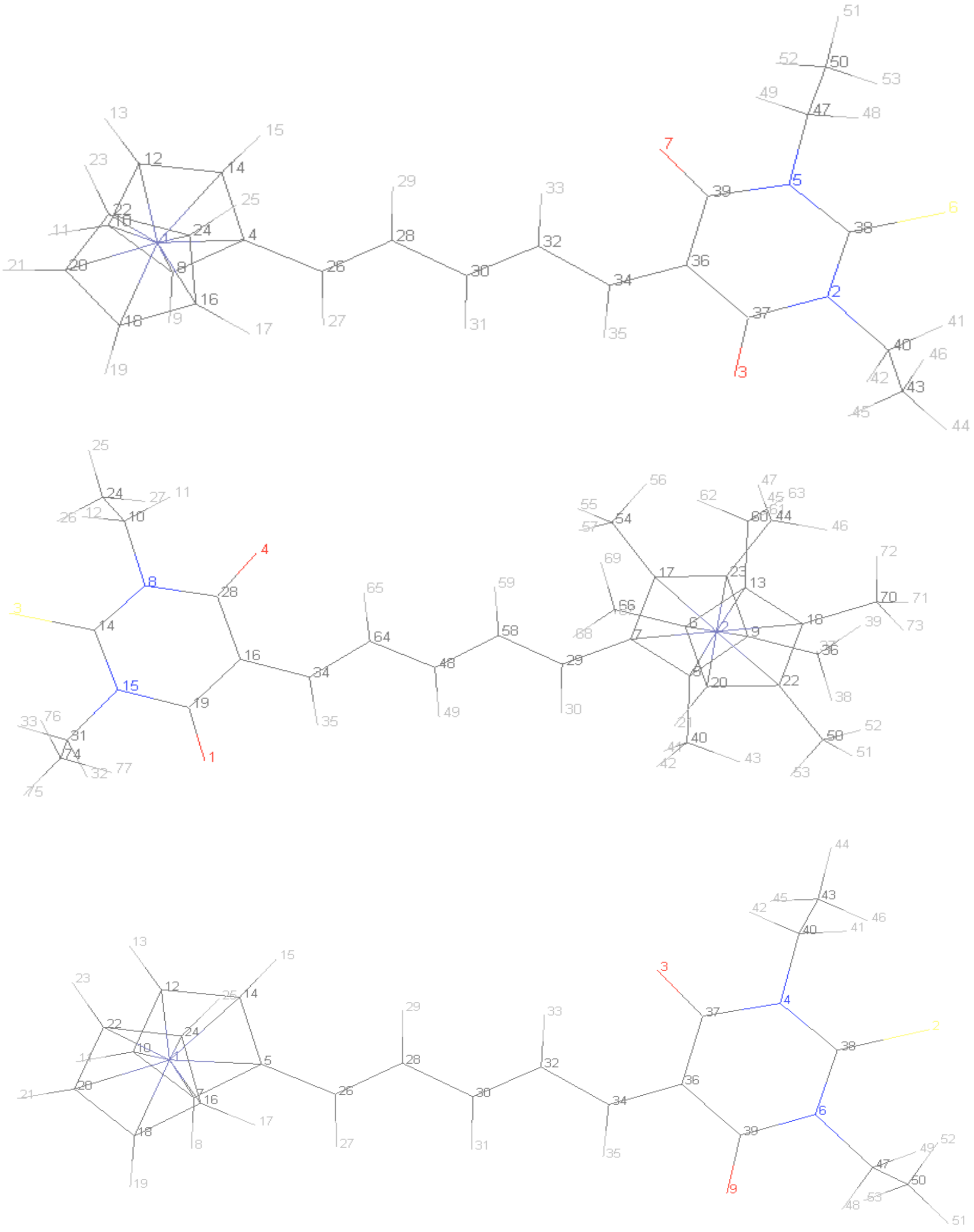


Figure S8. Atom Labels used for TB Chromophores, **1** (top), **2** (center) and **3** (bottom).

Table S4. Charge Density Data for TB Chromophores.

1			2			3		
Atom		Charge	Atom		Charge	Atom		Charge
1	Fe	0.576955	1	O	-0.520887	1	Ru	0.054916
2	N	-0.528196	2	Fe	0.624175	2	S	-0.246683
3	O	-0.516079	3	S	-0.242029	3	O	-0.48808
4	C	-0.013906	4	O	-0.526904	4	N	-0.461639
5	N	-0.519864	5	C	-0.020676	5	C	0.046408
6	S	-0.240324	6	C	0.03496	6	N	-0.460068
7	O	-0.516494	7	C	-0.018797	7	C	-0.189793
8	C	-0.216854	8	N	-0.509618	8	H	0.157499
9	H	0.138016	9	C	0.013008	9	O	-0.481992
10	C	-0.18191	10	C	-0.142706	10	C	-0.143619
11	H	0.140898	11	H	0.178846	11	H	0.161037
12	C	-0.183219	12	H	0.189708	12	C	-0.146446
13	H	0.141484	13	C	0.005421	13	H	0.162136
14	C	-0.221543	14	C	0.337677	14	C	-0.183405
15	H	0.140999	15	N	-0.509985	15	H	0.158725
16	C	-0.184643	16	C	-0.025805	16	C	-0.154122
17	H	0.14022	17	C	-0.016326	17	H	0.165505
18	C	-0.18666	18	C	-0.004548	18	C	-0.156282
19	H	0.14062	19	C	0.595508	19	H	0.160468
20	C	-0.187973	20	C	-0.270877	20	C	-0.148235
21	H	0.141239	21	H	0.140478	21	H	0.161603
22	C	-0.187689	22	C	0.042389	22	C	-0.150028
23	H	0.141372	23	C	0.007683	23	H	0.161697
24	C	-0.19064	24	C	-0.448806	24	C	-0.153315
25	H	0.143163	25	H	0.14747	25	H	0.163227
26	C	-0.089858	26	H	0.171734	26	C	-0.134272
27	H	0.118312	27	H	0.163242	27	H	0.145673
28	C	-0.102795	28	C	0.606473	28	C	-0.118886
29	H	0.117799	29	C	-0.155346	29	H	0.143652
30	C	-0.064854	30	H	0.133609	30	C	-0.09525
31	H	0.11691	31	C	-0.143548	31	H	0.142688
32	C	-0.098498	32	H	0.180509	32	C	-0.129893
33	H	0.150864	33	H	0.189431	33	H	0.189398
34	C	-0.128348	34	C	-0.177463	34	C	-0.172668
35	H	0.139791	35	H	0.175472	35	H	0.177977
36	C	-0.031618	36	C	-0.534259	36	C	-0.02428
37	C	0.598022	37	H	0.167106	37	C	0.539124
38	C	0.339806	38	H	0.159947	38	C	0.29177
39	C	0.595961	39	H	0.160412	39	C	0.523888
40	C	-0.140517	40	C	-0.530793	40	C	-0.141416
41	H	0.192095	41	H	0.168431	41	H	0.190937
42	H	0.181033	42	H	0.162703	42	H	0.181497
43	C	-0.460716	43	H	0.161569	43	C	-0.450469
44	H	0.158186	44	C	-0.532992	44	H	0.149225
45	H	0.172396	45	H	0.166768	45	H	0.162664
46	H	0.183171	46	H	0.159527	46	H	0.173054
47	C	-0.139106	47	H	0.16165	47	C	-0.142255

48	H	0.192949	48	C	-0.095365	48	H	0.182854
49	H	0.177121	49	H	0.139105	49	H	0.190468
50	C	-0.460018	50	C	-0.528763	50	C	-0.450798
51	H	0.157643	51	H	0.166413	51	H	0.149655
52	H	0.174829	52	H	0.15809	52	H	0.172483
53	H	0.180469	53	H	0.161695	53	H	0.163663
			54	C	-0.541864			
			55	H	0.168563			
			56	H	0.157806			
			57	H	0.171743			
			58	C	-0.130034			
			59	H	0.143637			
			60	C	-0.529785			
			61	H	0.165806			
			62	H	0.160385			
			63	H	0.157449			
			64	C	-0.134346			
			65	H	0.185993			
			66	C	-0.530274			
			67	H	0.165567			
			68	H	0.172874			
			69	H	0.156782			
			70	C	-0.529041			
			71	H	0.164835			
			72	H	0.158154			
			73	H	0.15723			
			74	C	-0.449061			
			75	H	0.148011			
			76	H	0.17105			
			77	H	0.163804			

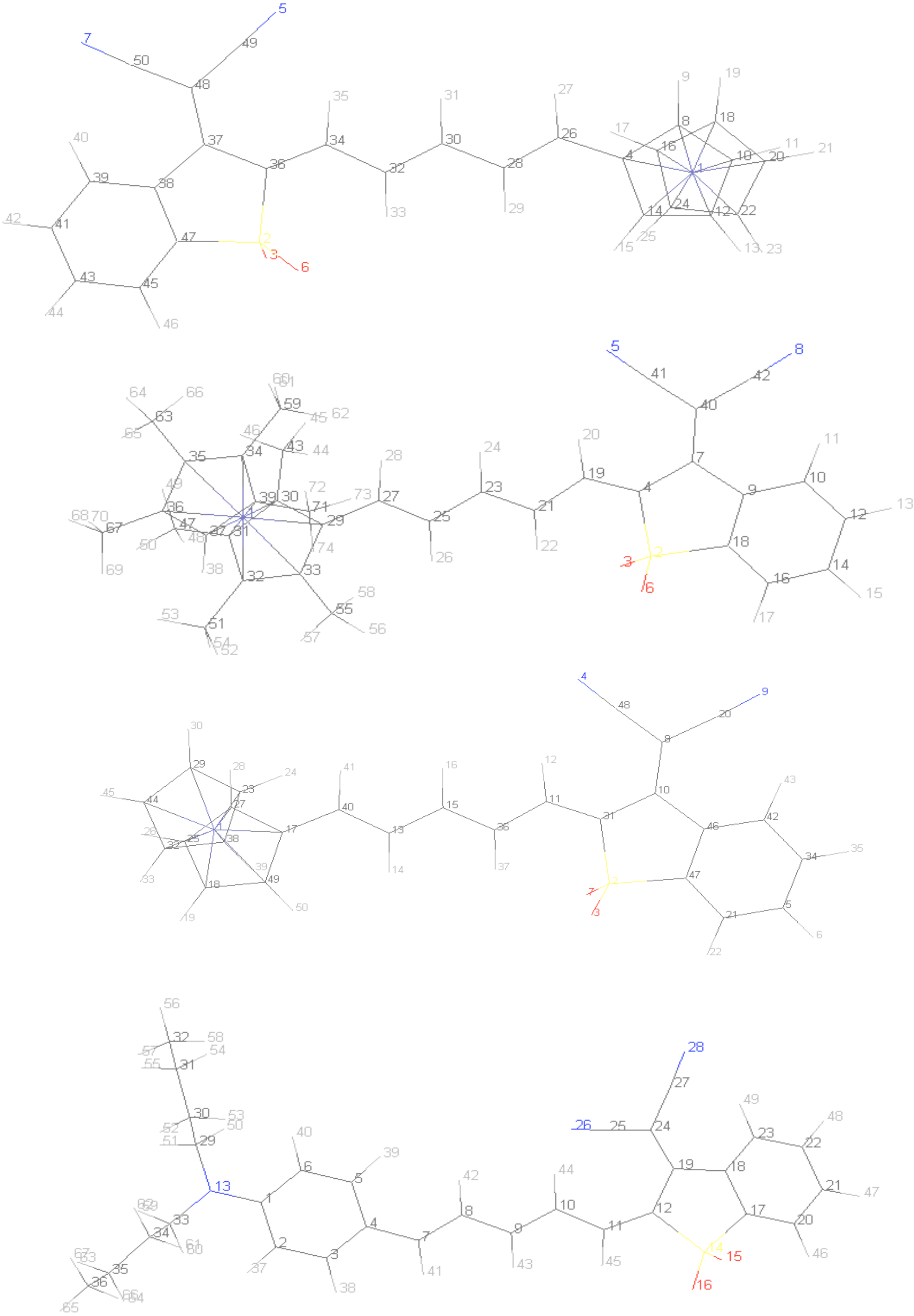


Figure S9. Atom Labels used for SDS Chromophores: from top-to-bottom, **4**, **5**, **6**, and **IX**.

Table S5. Charge Density Data for SDS Chromophores.

4		**5**		**6**		**6**	
Atom	Charge	Atom	Charge	Atom	Charge	Atom	Charge
1 Fe	0.572429	1 Fe	0.643693	1 Ru	0.055587	1 C	0.518537
2 S	1.141851	2 S	1.132365	2 S	1.138099	2 C	-0.225286
3 O	-0.496236	3 O	-0.563559	3 O	-0.564287	3 C	-0.214213
4 C	-0.001162	4 C	-0.309827	4 N	-0.338369	4 C	0.25906
5 N	-0.499434	5 N	-0.5143	5 C	-0.112041	5 C	-0.323579
6 O	-0.51658	6 O	-0.541002	6 H	0.158185	6 C	-0.212152
7 N	-0.489439	7 C	0.200472	7 O	-0.535316	7 C	-0.233989
8 C	-0.23052	8 N	-0.512244	8 C	0.028964	8 C	-0.12373
9 H	0.146209	9 C	0.104373	9 N	-0.33497	9 C	-0.16003
10 C	-0.180879	10 C	-0.176591	10 C	0.197179	10 C	-0.137399
11 H	0.148669	11 H	0.194354	11 C	-0.118045	11 C	-0.174329
12 C	-0.186208	12 C	-0.133764	12 H	0.195397	12 C	-0.183933
13 H	0.148844	13 H	0.158224	13 C	-0.119578	13 N	-0.554041
14 C	-0.229574	14 C	-0.114084	14 H	0.150732	14 S	1.042773
15 H	0.146351	15 H	0.157578	15 C	-0.103676	15 O	-0.498831
16 C	-0.180695	16 C	-0.161915	16 H	0.152977	16 O	-0.489679
17 H	0.149147	17 H	0.185894	17 C	0.042975	17 C	-0.166651
18 C	-0.195216	18 C	-0.190291	18 C	-0.144807	18 C	0.183305
19 H	0.146567	19 C	-0.123455	19 H	0.163925	19 C	-0.031466
20 C	-0.188755	20 H	0.197956	20 C	0.149455	20 C	-0.209124
21 H	0.146835	21 C	-0.152465	21 C	-0.154072	21 C	-0.083392
22 C	-0.189797	22 H	0.198606	22 H	0.185809	22 C	-0.186673
23 H	0.146858	23 C	-0.105488	23 C	-0.153064	23 C	-0.114954
24 C	-0.192336	24 H	0.151003	24 H	0.169065	24 C	0.252834
25 H	0.149219	25 C	-0.132167	25 C	-0.141883	25 C	0.149025
26 C	-0.096941	26 H	0.152184	26 H	0.162518	26 N	-0.451338
27 H	0.12953	27 C	-0.160752	27 C	-0.190011	27 C	0.197624
28 C	-0.095187	28 H	0.138855	28 H	0.159532	28 N	-0.530068
29 H	0.123743	29 C	-0.013528	29 C	-0.15552	29 C	-0.115745
30 C	-0.090816	30 C	-0.031534	30 H	0.162309	30 C	-0.307774
31 H	0.134434	31 C	0.017804	31 C	-0.305727	31 C	-0.26318
32 C	-0.111641	32 C	0.010611	32 C	-0.149216	32 C	-0.439096
33 H	0.1598	33 C	-0.018439	33 H	0.163154	33 C	-0.127103
34 C	-0.110285	34 C	-0.00412	34 C	-0.131359	34 C	-0.279332
35 H	0.160965	35 C	0.010196	35 H	0.158626	35 C	-0.252461
36 C	-0.295979	36 C	0.024635	36 C	-0.150048	36 C	-0.431561
37 C	0.166489	37 C	-0.26327	37 H	0.197791	37 H	0.126697
38 C	0.09054	38 H	0.142162	38 C	-0.152384	38 H	0.122082
39 C	-0.127108	39 C	0.035173	39 H	0.166883	39 H	0.126199
40 H	0.150611	40 C	0.050384	40 C	-0.130991	40 H	0.156932
41 C	-0.110948	41 C	0.310958	41 H	0.150332	41 H	0.122604
42 H	0.133638	42 C	0.307862	42 C	-0.173486	42 H	0.223518
43 C	-0.076072	43 C	-0.534305	43 H	0.191416	43 H	0.095379
44 H	0.131586	44 H	0.171797	44 C	-0.147474	44 H	0.305756
45 C	-0.133095	45 H	0.163042	45 H	0.162787	45 H	0.16717
46 H	0.149466	46 H	0.161992	46 C	0.109324	46 H	0.174589
47 C	-0.198403	47 C	-0.535277	47 C	-0.19806	47 H	0.148363
48 C	0.038407	48 H	0.16987	48 C	0.152145	48 H	0.148858
49 C	0.306919	49 H	0.161796	49 C	-0.183012	49 H	0.228932

50	C	0.304198	50	H	0.161284	50	H	0.162229	50	H	0.158239
			51	C	-0.532119				51	H	0.15829
			52	H	0.168948				52	H	0.224251
			53	H	0.161445				53	H	0.224277
			54	H	0.165631				54	H	0.130515
			55	C	-0.541766				55	H	0.130556
			56	H	0.172665				56	H	0.153718
			57	H	0.159582				57	H	0.14445
			58	H	0.177167				58	H	0.14441
			59	C	-0.529554				59	H	0.155239
			60	H	0.167934				60	H	0.155287
			61	H	0.157707				61	H	0.142893
			62	H	0.164027				62	H	0.142909
			63	C	-0.53				63	H	0.137622
			64	H	0.167704				64	H	0.137655
			65	H	0.158622				65	H	0.146968
			66	H	0.160153				66	H	0.141793
			67	C	-0.529145				67	H	0.1418
			68	H	0.167592						
			69	H	0.162069						
			70	H	0.157878						
			71	C	-0.53188						
			72	H	0.167022						
			73	H	0.172634						
			74	H	0.162935						