

## Supporting Information

### Experimental Part

#### 1. Measurements and methods

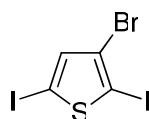
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 400 spectrometer and a Bruker Avance 250 spectrometer. Chemical shifts are denoted in  $\delta$  unit (ppm), and were referenced to residual solvent. Mass spectra were recorded with a Finnigan MAT and VG Instruments ZAB 2-SE-FPD. Maldi-TOF data was acquired from a Bruker FM Reflex-TOF 405. UV/Vis spectra were recorded at room temperature on a Perkin-Elmer Lambda 900 spectrometer with dichloromethane as solvent. Fluorescence emission spectra were recorded on a J&M Tidas spectrometer. Infrared spectra were recorded on a Nicolet 730 FT-IR spectrometer. Elemental analyses were performed on an Elementar Vario EL.

The oxidation potentials of the dyes were determined by cyclovoltammetry on a EG&G Princeton Applied Research potentiostat, model 273. The measurements were performed in a solution of  $\text{Bu}_4\text{NPF}_6$  (0.1 M) in dry dichloromethane: working electrode: inlaid platinum disk (1.5 diameter); counter electrode: platinum wire; reference electrode: silver wire. Internal calibration by ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) measurements.

#### 2. Synthesis

N,N'-bis(octyl)-1,7-dibromo-perylene-3,4:9,10-tetracarboxylic acid diimide (**4**)<sup>1</sup> and (5'-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-5,5''-trimethylsilyl)-2,2':3',2''-terthiophene (**5**)<sup>2,3</sup> were synthesized according to literature.

#### 3-Bromo-2,5-diiodothiophene



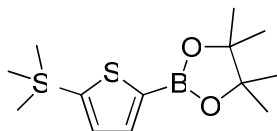
500 mg of 3-bromothiophene (3.07 mmol) were dissolved in 30 mL of  $\text{CHCl}_3$  under argon. After cooling the solution to 0 °C and addition of 2.07 g of fresh N-iodosuccinimide (9.20 mmol) and 10 mL of acetic acid the solution was stirred for one hour at this temperature in the dark. Then it was heated under reflux over night. The reaction was quenched with an aqueous solution of sodium thiosulfate and the water phase was extracted with  $\text{CH}_2\text{Cl}_2$ . The organic phase was washed with water and dried over  $\text{Na}_2\text{SO}_4$ . The solvent was evaporated under reduced pressure and the resulting oil was purified by column chromatography on silica gel (hexane) and was recrystallized from hexane to yield 1.06 g (2.54 mmol, 83%) of pale yellow needles.

M.p.: 55 – 56 °C (lit. 55 – 57 °C)<sup>4</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.02 ppm.

The analytical data correspond with the data given in literature.

### Trimethyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)silane<sup>5</sup>



To a solution of 1.0 mL of 2-(trimethylsilyl)thiophene (6.0 mmol) in 16 mL of dry THF 4.5 mL of *n*-butyl lithium (7.2 mmol, 1.6 M in hexane) were added dropwise at -78 °C and stirred for 30 minutes at this temperature. Subsequently 1.7 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8.4 mmol) were added dropwise at -78 °C. The reaction mixture was allowed to warm to room temperature and was stirred at this temperature for two hours. The reaction was quenched with a solution of ammonium chloride and the water phase was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The residue was recrystallized from methanol to yield 1.5 g (5.3 mmol, 89%) of a white solid.

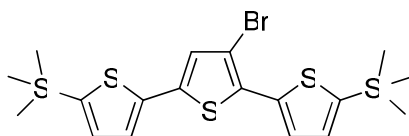
M.p.: 89-91 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ. 7.69 (d, *J* = 3.3 Hz, 1H, Ar), 7.33 (d, *J* = 3.3 Hz, 1H, Ar), 1.34 (s, 12H, CH<sub>2</sub>), 0.32 (s, 9H, TMS) ppm.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 148.5, 137.9, 135.0, 84.0, 24.7, -0.1 ppm.

MS (EI): *m/z* = 267 (100%) [M-CH<sub>3</sub>]<sup>+</sup>, 282 (21%) [M]<sup>+</sup>.

### 3'-Bromo-5,5''-bistrimethylsilyl-2,2':5',2''-terthiophene



250 mg of 3-bromo-2,5-diiodothiophene (0.60 mmol), 347 mg of trimethyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)silane (1.33 mmol), 25.0 mg of tris-(dibenzylideneacetone)dipalladium(0) chloroform adduct (24.1 μmol) and 14.0 mg of tri-*tert*-butyl-phosphonium tetra-fluoroborate (48.2 μmol) were dissolved in 12 mL of well degassed THF. The mixture was cooled to 0 °C and 2.4 mL of a well degassed potassium phosphate solution (4.8 mmol, 2 M) were added. After stirring the mixture for 50 minutes at this temperature the reaction was quenched with an aqueous solution of ammonium chloride. The water phase was extracted with diethyl ether and the combined organic layers were washed with brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane) to give 225 mg (0.48 mmol, 79%) of a yellow oil.

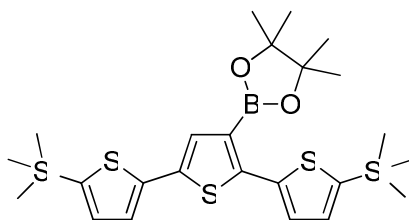
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.50 (d, *J* = 3.5 Hz, 1H, Ar), 7.23 (d, *J* = 3.5 Hz, 1H, Ar), 7.20 (d, *J* = 3.5 Hz, 1H, Ar), 7.15 (d, *J* = 3.5 Hz, 1H, Ar), 7.09 (s, 1H, Ar), 0.35 (s, 9H, TMS), 0.34 (s, 9H, TMS) ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  141.6, 141.1, 140.6, 139.2, 135.6, 134.8, 134.2, 130.8, 127.7, 127.7, 125.4, 107.8, -0.1, -0.2 ppm.

MS (CI):  $m/z$  = 472 (100%) [ $\text{M}^+$ ], 457 (59%) [ $\text{M}-\text{CH}_3$ ] $^+$ .

Elemental Analysis ( $\text{C}_{18}\text{H}_{23}\text{BrS}_3\text{Si}_2$ ): Calculated: (%) C 45.84, H 4.92, S 20.40, Found: (%) C 45.73, H 5.04, S 20.26.

### 3'-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-5,5''-bistrimethylsilyl-2,2':5',2''-terthiophene



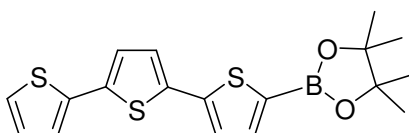
To a solution of 594 mg of 3'-bromo-5,5''-bistrimethylsilyl-2,2':5',2''-terthiophene (1.26 mmol) in 10 mL of dry THF 0.9 mL of *n*-butyl lithium (1.5 mmol, 1.6 M in hexane) were added dropwise at  $-78^\circ\text{C}$  and stirred for 30 minutes at this temperature. Subsequently 0.4 mL of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.8 mmol) were added dropwise at  $-78^\circ\text{C}$ . The reaction mixture was allowed to warm to room temperature and was stirred at this temperature for two hours. The reaction was quenched with a solution of ammonium chloride and the water phase was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated under reduced pressure. The residue was precipitated from methanol to give 544 mg (1.05 mmol, 83%) of a yellow solid that was pure enough for the next step.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.56 (d,  $J$  = 3.5 Hz, 1H, Ar), 7.39 (s, 1H, Ar), 7.20 (d,  $J$  = 3.5 Hz, 1H, Ar), 7.15 (d,  $J$  = 3.5 Hz, 1H, Ar), 7.12 (d,  $J$  = 3.5 Hz, 1H, Ar), 1.35 (s, 12H,  $\text{CH}_3$ ), 0.34 (s, 9H, TMS), 0.33 (s, 9H, TMS) ppm.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  141.9, 141.2, 139.7, 135.9, 134.7, 134.4, 131.3, 128.2, 125.0, 124.3, 123.8, 83.9, 24.8, -0.1, -0.1 ppm.

MS (CI):  $m/z$  = 519 (100%) [ $\text{M}+\text{H}$ ] $^+$ , 518 (93%) [ $\text{M}^+$ ], 503 (41%) [ $\text{M}-\text{CH}_3$ ] $^+$ , 547 (11%) [ $\text{M}+\text{C}_2\text{H}_5$ ] $^+$ .

### 5-(4,4,5,5-Tetramethyl-[1,3,2]dioxaborolan-2-yl)-2,2':5',2''-terthiophene (9)



To a solution of 4.5 g of 2,2':5',2''-terthiophene (18 mmol) in 70 mL dry THF *n*-butyl lithium (12 mL, 1.6 M in hexane, 19 mmol) was added dropwise at  $-78^\circ\text{C}$  and stirred for 30 minutes at this temperature. The reaction mixture was warmed to  $0^\circ\text{C}$  and stirred for another 30 min. Then it was cooled to  $-78^\circ\text{C}$  again, and subsequently 4.3 g of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (22 mmol) were added dropwise at  $-78^\circ\text{C}$ . The reaction

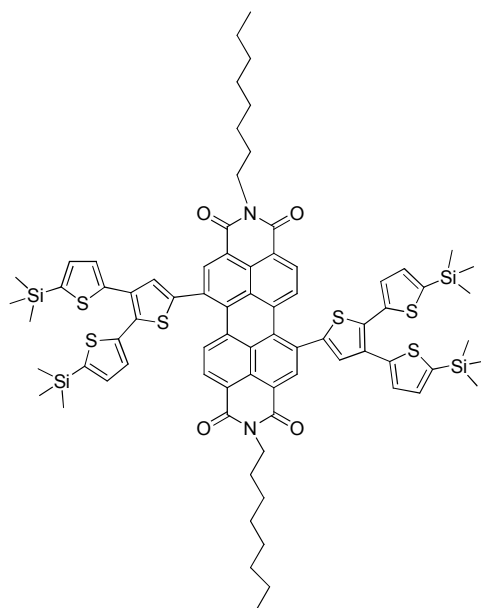
mixture was allowed to warm to 0 °C and was stirred at this temperature for one hour. The reaction was quenched with a solution of ammonium chloride and the water phase was extracted with diethyl ether. The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/hexane, 1:10) to give product 1.45 g (3.87 mmol, 21%) as solid.

<sup>1</sup>H NMR (in CDCl<sub>3</sub>, 298K): δ 7.54-7.53 (d, J = 3.6 Hz, 1H), 7.24-7.22 (m, 2H), 7.19-7.18 (d, J = 3.6 Hz, 1H), 7.15-7.14 (d, J = 4.0 Hz, 1H), 7.09-7.08 (d, J = 3.6 Hz, 1H), 7.03-7.01 (dd, J<sub>1</sub> = 3.6 Hz, J<sub>2</sub> = 4.8 Hz, 1H), 1.36 (s, 12H) ppm.

<sup>13</sup>C NMR (in CDCl<sub>3</sub>, 298K): δ 143.8, 138.0, 137.0, 136.9, 136.0, 127.9, 125.0, 124.8, 124.6, 124.4, 123.8, 84.2, 77.3, 77.0, 76.7, 24.8 ppm.

MS (CI): m/z = 375 (100%) [M+H]<sup>+</sup>, 360 (4%) [M-CH<sub>3</sub>+H]<sup>+</sup>, 332 (14%), 274 (33%).

### **N,N'-Bis(octyl-1,7-bis[(5,5''-bistrimethylsilyl)-2,2':3',2''-terthien-5'-yl]-perylene-3,4:9,10-tetracarboxylic acid diimide**



2

200 mg of N,N'-bis(octyl-1,7-dibromo-perylene-3,4:9,10-tetracarboxylic acid diimide (0.256 mmol), 300 mg of 5'-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-5,5''-bistrimethylsilyl-2,2':3',2''-terthiophene (0.578 mmol), and 1 g of potassium carbonate (7.246 mmol) were dissolved in 20 mL of toluene, 2 mL of water, and 0.2 mL of ethanol in a Schlenk tube. The solution was deoxygenated with argon, 90 mg of tetrakis(triphenylphosphine)palladium (0.081 mmol) were added and the solution was stirred under argon at 80 °C for three days.

The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over MgSO<sub>4</sub>. The solvent was evaporated under reduced pressure and the resulting solid was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/petrol ether, 3:2) to yield 170 mg (0.122 mmol, 47%) of a dark green solid.

<sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ 8.63 (s, 2H), 8.39 (m, 4H), 7.48 (s, 2H), 7.31 – 7.11 (m, 8H), 4.18 (m, 4H), 1.77-1.68 (m, 4H), 1.43-1.29 (m, 19H), 0.91-0.86 (m, 7H), 0.34-0.32 (m, 36H) ppm.

$^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K)  $\delta$  163.6, 163.4, 143.8, 142.8, 142.5, 142.0, 139.8, 135.6, 134.9, 134.9, 134.7, 134.6, 134.0, 133.3, 132.7, 130.9, 130.5, 130.00, 129.5, 128.8, 128.3, 123.0, 41.2, 32.4, 30.0, 29.8, 28.7, 27.8, 23.3, 14.5, 0.2, 0.1 ppm.

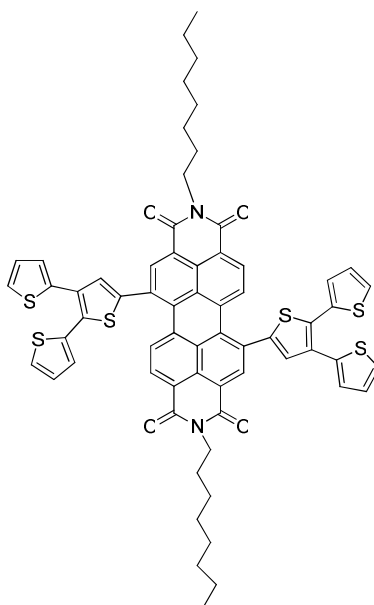
IR Spectrum:  $\nu_{\text{max}}$  = 2920, 2920, 2853, 1697, 1660, 1596, 1432, 1400, 1341, 1326, 1247, 1205, 1129, 1066, 1042, 984, 836, 811, 796, 754, 720, 696  $\text{cm}^{-1}$ .

UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ): 475 (17,631); 601(15,855).

FD Mass Spectrum (8kV):  $m/z$  = 1394.9 (100%) [ $\text{M}^+$ ], 2791.7 (35%) [ $2\text{M}^+$ ], 698.6 [ $1/2\text{M}^+$ ] (Calc. 1394.40).

Elemental Analysis ( $\text{C}_{76}\text{H}_{86}\text{N}_2\text{O}_4\text{S}_6\text{Si}_4$ ): Calculated: (%) C 65.38, H 6.21, N 2.01, S 13.78, Found: (%) C 65.62, H 5.87, N 2.00, S 14.02.

### **N,N'-Bis(octyl-1,7-bis(2,2':3',2''-terthien-5'-yl)-perylene-3,4:9,10-tetracarboxylic acid diimide**



140 mg of N,N'-Bis(octyl-1,7-bis[(5,5''-bistrimethylsilyl)-2,2':3',2''-terthien-5'-yl]-perylene-3,4:9,10-tetracarboxylic acid diimide (0.100 mmol) were dissolved in THF. A solution of 100 mg of tetra-*n*-butylammonium fluoride (0.402 mmol) in THF was added dropwise under stirring at room temperature. The mixture was stirred for 30 minutes at room temperature, concentrated, and precipitated in methanol. The precipitate was then filtered and washed with methanol. The yield of the dark green product was 86 mg (0.078 mmol, 78%).

$^1\text{H}$  NMR (250 MHz,  $\text{CD}_2\text{Cl}_2$ , 298K)  $\delta$  8.50 (s, 2H), 8.33 – 8.20 (m, 4H), 7.39 (s, 2H), 7.28 (ddd,  $J$  = 1.2, 5.1, 9.4, 4H), 7.15 – 7.07 (m, 4H), 6.97 (dt,  $J$  = 3.5, 5.1, 4H), 4.17 – 3.99 (m, 4H), 1.63 (m, 4H), 1.27 (m, 20H), 0.80 (m, 6H) ppm.

$^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 298.3 K)  $\delta$  163.6, 163.4, 142.9, 137.2, 135.6, 134.6, 134.2, 133.4, 132.6, 130.7, 130.5, 130.1, 129.5, 129.1, 128.3, 128.1, 128.0, 127.9, 127.7, 126.7, 123.0, 41.2, 32.4, 30.3, 30.2, 30.0, 29.8, 28.6, 27.7, 23.3, 23.2, 14.4 ppm.

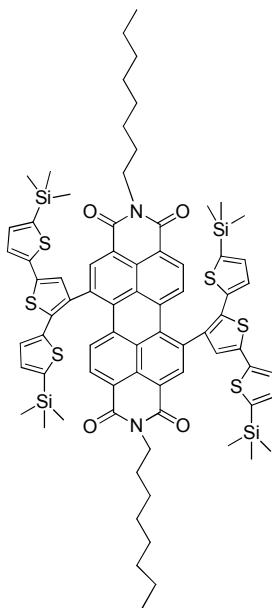
IR Spectrum:  $\nu_{\text{max}}$  = 2921, 2852, 1695, 1654, 1584, 1432, 1400, 1327, 1245, 1169, 1121, 1019, 845, 810, 756, 692  $\text{cm}^{-1}$ .

UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ): 461 (16,878); 591(16,671).

FD Mass Spectrum (8kV):  $m/z = 1106.7$  (100%) [ $M^+$ ] (Calc. 1106.24).

Elemental Analysis ( $C_{64}H_{54}N_2O_4S_6$ ): Calculated: (%) C 69.41, H 4.91, N 2.53, S 17.37, Found: (%) C 69.29, H 5.09, N 2.52, S 17.55.

**N,N'-Bis(octyl-1,7-bis[(5,5''-bis-trimethylsilyl)-2,2':5',2''-terthien-3'-yl]-perylene-3,4:9,10-tetracarboxylic acid diimide**



130 mg of N,N'-bis(octyl-1,7-dibromo-perylene-3,4:9,10-tetracarboxylic acid diimide) (0.168 mmol), 180 mg of 3'-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-(5,5''-bistrimethylsilyl)-2,2':5',2''-terthiophene (0.347 mmol) and 500 mg of potassium carbonate (3.623 mmol) were dissolved in 10 mL of toluene, 1 mL of water, and 0.1 mL of ethanol in a Schlenk tube. The solution was deoxygenated with argon, 60 mg of tetrakis(triphenylphosphine)palladium (0.054 mmol) were added and the solution was stirred under argon at 80 °C for three days.

The reaction mixture was extracted with  $CH_2Cl_2$  and dried over  $MgSO_4$ . The solvent was evaporated under reduced pressure and the resulting solid was purified by column chromatography on silica gel ( $CH_2Cl_2$ /petrol ether, 3:2) to yield 70 mg (0.050 mmol, 30%) of a dark purple solid.

$^1H$  NMR (250 MHz,  $CD_2Cl_2$ )  $\delta$  8.60 (d,  $J = 6.1$ , 1H), 8.54 (d,  $J = 2.4$ , 1H), 8.35 – 8.06 (m, 4H), 7.40 – 7.06 (m, 6H), 7.02 – 6.75 (m, 3H), 6.69 – 6.58 (m, 1H), 4.29 – 3.92 (m, 4H), 1.80 – 1.61 (m, 4H), 1.31 (m, 20H), 0.86 (t,  $J = 4.9$ , 6H), 0.39 – -0.10 (m, 36H) ppm.

$^{13}C$  NMR (126 MHz,  $CD_2Cl_2$ , 298.3 K)  $\delta$  163.8, 163.7, 163.6, 142.5, 142.3, 142.2, 141.8, 141.7, 141.6, 141.5, 140.6, 140.1, 140.0, 139.8, 139.4, 139.2, 139.1, 138.9, 138.8, 138.7, 136.3, 135.8, 135.7, 135.6, 135.5, 135.4, 135.3, 135.1, 134.8, 134.7, 134.6, 134.3, 133.0, 132.5, 132.3, 132.0, 130.7, 130.5, 129.6, 129.2, 128.9, 128.6, 128.3, 128.0, 127.9, 127.8, 127.7, 126.2, 125.9, 125.8, 125.6, 123.3, 123.0, 122.8, 41.1, 41.0, 40.9, 37.6, 33.3, 32.5, 32.4, 30.6, 30.3, 29.9, 29.8, 28.6, 27.9, 27.8, 27.7, 27.6, 23.3, 23.2, 20.0, 14.4, 0.1, 0.00 ppm.

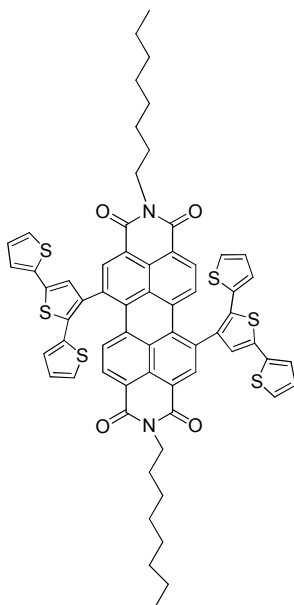
IR Spectrum:  $\nu_{max} = 2954, 2925, 2855, 1697, 1659, 1587, 1433, 1416, 1345, 1326, 1247, 1212, 1169, 1103, 1068, 986, 921, 834, 811, 798, 751, cm^{-1}$ .

FD Mass Spectrum (8kV):  $m/z = 1394.8$  (100%) [ $M^+$ ] (Calc. 1394.40).

UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  ( $\epsilon/M^{-1}cm^{-1}$ ): 368 (51,319); 515 (25,340).

Elemental Analysis ( $C_{76}H_{86}N_2O_4S_6Si_4$ ): Calculated: (%) C 65.38, H 6.21, N 2.01, S 13.78, Found: (%) C 65.29, H 6.63, N 1.97, S 13.51.

**N,N'-Bis(octyl-1,7-bis(2,2':5',2''-terthien-3'-yl)-perylene-3,4:9,10-tetracarboxylic acid diimide**



70 mg of N,N'-Bis(octyl-1,7-bis[(5,5''-bistrimethylsilyl)-2,2':5',2''-terthien-3'-yl]-perylene-3,4:9,10-tetracarboxylic acid diimide (0.050 mol) were dissolved in THF. A solution of 53 mg of tetra-*n*-butylammonium fluoride (0.200 mmol) in THF was added dropwise under stirring at room temperature. The mixture was stirred for 30 minutes at room temperature, concentrated and precipitated from THF in methanol. The precipitate was then filtered and washed with methanol to yield 45 mg (0.041 mmol, 81%) of the dark purple product.

$^1H$  NMR (250 MHz,  $CD_2Cl_2$ , 298 K)  $\delta$  8.57 (d, 2H), 8.42 – 8.14 (m, 4H), 7.38 – 7.25 (m, 4H), 7.16 – 6.68 (m, 10H), 4.27 – 3.94 (m, 4H), 1.78 – 1.64 (m, 4H), 1.46 – 1.20 (m, 20H), 0.93 – 0.82 (m, 6H) ppm.

$^{13}C$  NMR (126 MHz,  $CD_2Cl_2$ , 298.3 K)  $\delta$  163.8, 163.7, 139.4, 139.3, 138.8, 138.7, 136.7, 136.1, 136.0, 135.7, 135.6, 135.5, 135.4, 135.3, 135.1, 135.1, 135.0, 134.7, 134.6, 132.3, 132.2, 132.1, 130.9, 130.8, 130.6, 129.4, 129.2, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.8, 126.9, 126.8, 126.7, 126.6, 126.0, 125.8, 125.7, 125.6, 125.1, 125.0, 123.3, 123.2, 123.1, 123.0, 41.0, 40.1, 32.5, 32.4, 30.6, 30.3, 30.2, 30.0, 29.9, 29.8, 28.6, 27.7, 27.6, 24.5, 23.3, 23.2, 14.5, 14.4, 13.9 ppm.

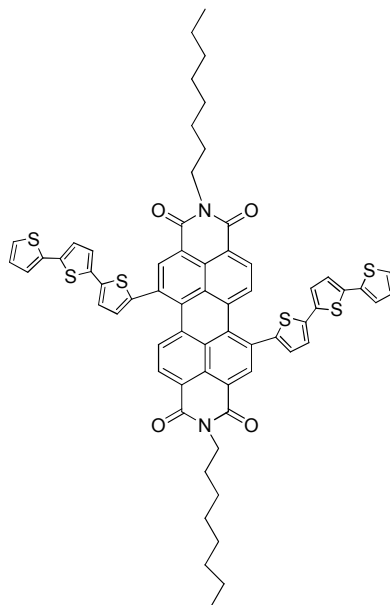
IR Spectrum:  $\nu_{max}$  = 2923, 2853, 1695, 1654, 1588, 1500, 1432, 1403, 1326, 1241, 1169, 1103, 1045, 931, 835, 812, 750, 690  $cm^{-1}$ .

FD Mass Spectrum (8kV):  $m/z$  = 1106.6 (100%) [ $M^+$ ], 553.7 (45%) [ $1/2 M^+$ ], (Calc. 1106.24).

UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  ( $\epsilon/M^{-1}cm^{-1}$ ): (27,869).

Elemental Analysis ( $C_{64}H_{54}N_2O_4S_6$ ): Calculated: (%) C 69.41, H 4.91, N 2.53, S 17.37, Found: (%) C 69.14, H 5.03, N 2.41, S 16.38.

**N,N'-Bis(octyl-1,7-bis(2,2':5',2''-terthien-5-yl)-perylene-3,4:9,10-tetracarboxylic diimide** acid



180 mg of N,N'-bis(octyl-1,7-dibromo-perylene-3,4:9,10-tetracarboxylic acid diimide) (0.233 mmol), 190 mg of 5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-2,2':5',2''-terthiophene (0.508 mmol), and 850 mg of potassium carbonate (6.159 mmol) were dissolved in 18 mL of toluene, 1.8 mL of water, and 0.18 mL of ethanol in a Schlenk tube. The solution was deoxygenated with argon, 100 mg of tetrakis(triphenylphosphine)palladium (0.090 mmol) were added and the solution was stirred under argon at 80 °C for three days.

The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried over MgSO<sub>4</sub>. The solvent was evaporated under reduced pressure and the resulting solid was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) to yield 120 mg (44%) of a dark green solid.

<sup>1</sup>H NMR (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ 8.58 (d, *J* = 2.7, 2H), 8.31 – 8.16 (m, *J* = 8.1, 4H), 7.26 – 6.94 (m, 16H), 4.17 – 3.96 (m, 4H), 1.77 – 1.53 (m, *J* = 6.5, 11.9, 4H), 1.36 – 1.09 (m, 20H), 0.85 – 0.74 (m, 6H) ppm.

IR Spectrum:  $\nu_{\text{max}}$  = 2919, 2852, 1695, 1657, 1592, 1465, 1435, 1403, 1324, 1245, 1172, 1128, 1034, 863, 835, 822, 812, 794, 757, 715, 701 cm<sup>-1</sup>.

UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\text{max}}$  ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ): 376 (61,861); 488 (22,205), 610 (15,426).

FD Mass Spectrum (8kV): *m/z* = 1107.3 (100%) [*M*<sup>+</sup>], 553.7 (70%) [*1/2 M*<sup>+</sup>] (Calc. 1106.24).

Elemental Analysis (C<sub>64</sub>H<sub>54</sub>N<sub>2</sub>O<sub>4</sub>S<sub>6</sub>): Calculated: (%) C 69.41, H 4.91, N 2.53, S 17.37, Found: (%) C 69.24, H 4.91, N 2.49, S 17.07.



### 3. Molecular Geometries:

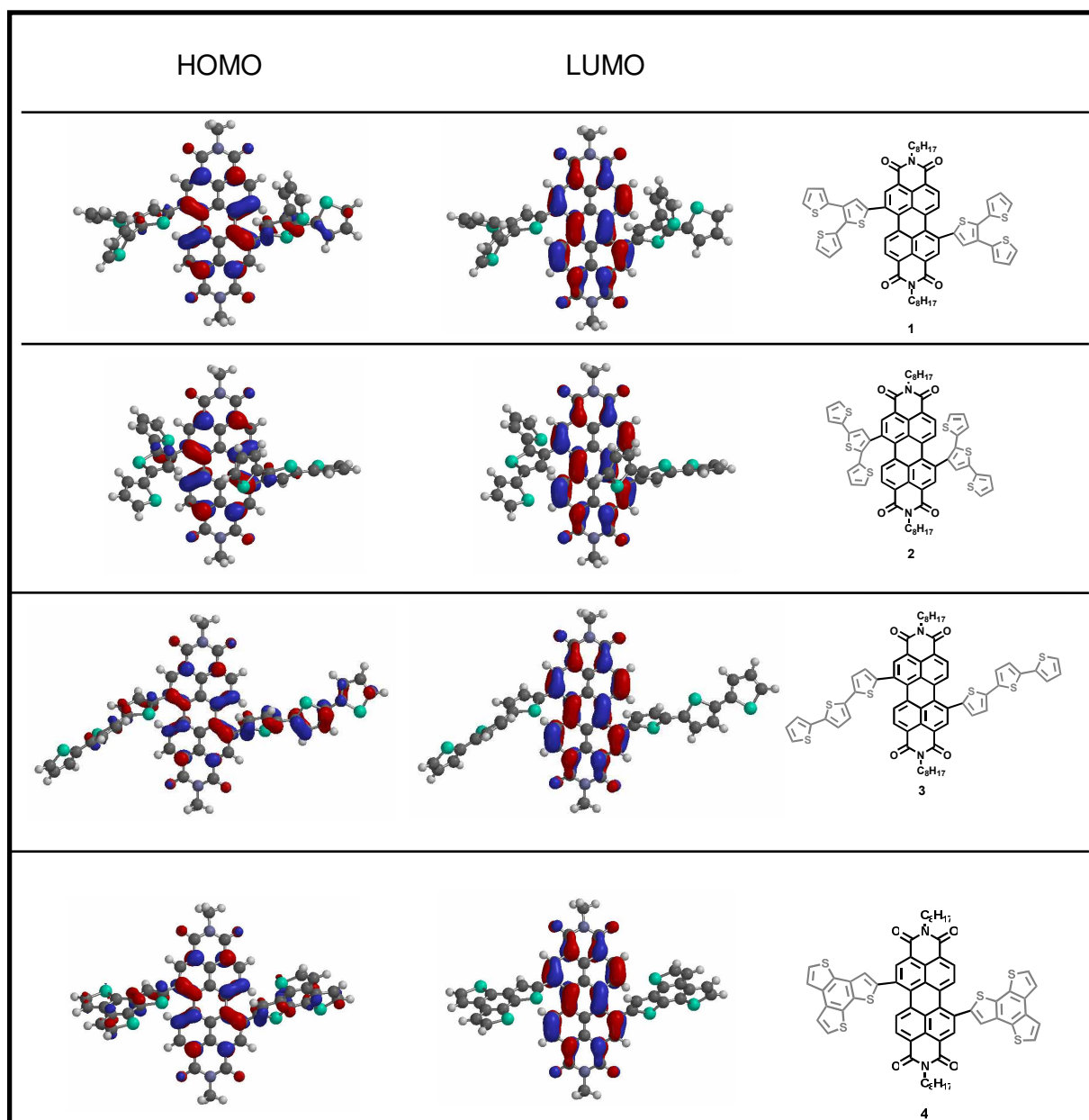


Figure 1: Molecular geometries of compound 1-3 (Spartan, Hatree-Fock, 3-21G(\*)).

### 3. Fluorescence Quenching in DMSO:

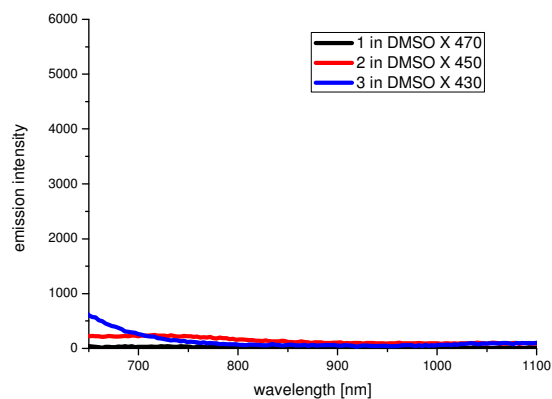


Figure 2: Fluorescence emission spectra of compound **1-3** in DMSO (Dimethylsulfoxide), excitation wavelengths according to the legend ( $x = \lambda_{\text{ex}}$ ,  $c = 2 \times 10^{-5}$  mol/L).

### 4. Absorption: no strong solvent sensitivity (example for compound 1)

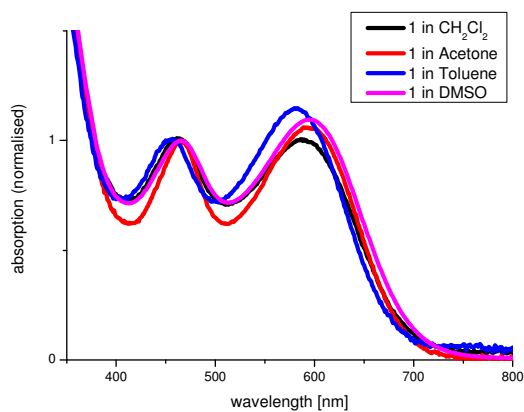


Figure 3: Absorption (normalised) of compound **1** in CH<sub>2</sub>Cl<sub>2</sub>, acetone, toluene, and DMSO

## 5. Maldi of branched terthiophene PDI 1 before and after sunlight irradiation (crude mixture)

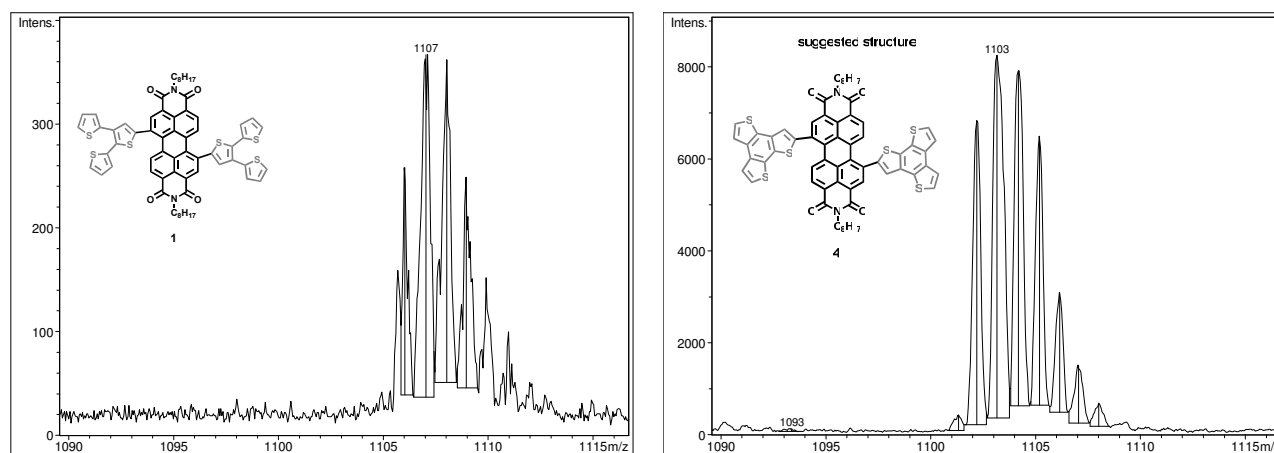


Figure 4: Maldi-TOF spectrum of compound 1 before (left) and compound 4 (suggested structure) after (right) sunlight irradiation.

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