

## SUPPORTING INFORMATION

### Star-Shaped Diketopyrrolopyrrole–Zinc Porphyrin that Delivers 900 nm Emission in Light-Emitting Electrochemical Cells

Mariza Mone,<sup>†</sup> Shi Tang,<sup>‡,§</sup> Petri Murto,<sup>†</sup> Birhan A. Abdulahi,<sup>†,||</sup> Christian Larsen,<sup>‡,§</sup> Jia Wang,<sup>‡</sup> Wendimagegn Mammo,<sup>||</sup> Ludvig Edman,<sup>\*,‡,§</sup> and Ergang Wang<sup>\*,†,⊥</sup>

<sup>†</sup> Department of Chemistry and Chemical Engineering/Applied Chemistry, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden

<sup>‡</sup> The Organic Photonics and Electronics Group, Umeå University, SE-90187 Umeå, Sweden

<sup>§</sup> LunaLEC AB, Umeå University, SE-90187 Umeå, Sweden

<sup>||</sup> Department of Chemistry, Addis Ababa University, P.O. Box 33658, Addis Ababa, Ethiopia

<sup>⊥</sup> School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

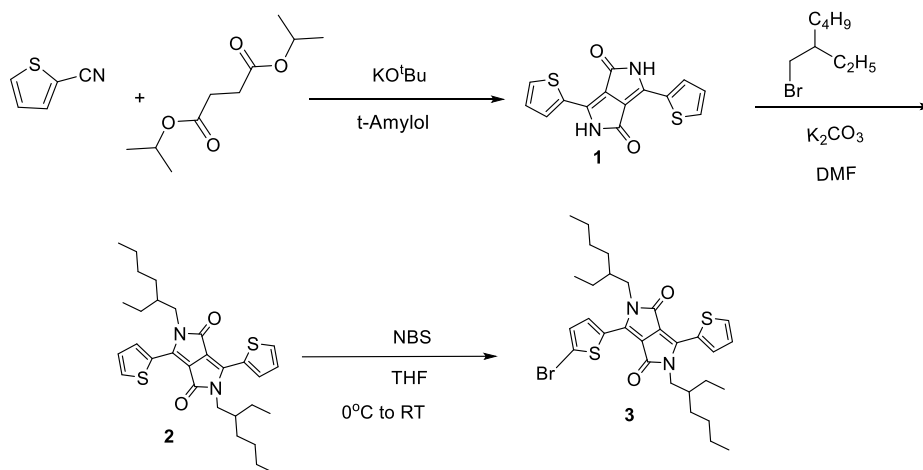
#### Table of Contents

<b>Synthesis</b> .....	S2
<b>DFT</b> .....	S11
<b>TGA</b> .....	S21
<b>Optical Characterization</b> .....	S22
<b>Device Stability</b> .....	S23
<b>References</b> .....	S24

## Synthesis

All starting materials, reagents and monomers such as 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (BDD) were purchased from commercial sources and used without further purification. Compound ZnP(TDPP)<sub>4</sub> and monomer ((2,6-bis(trimethylstannyl)benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-diyl)bis(thiophene-5,2-diyl))bis(tributylsilane) (BDTSi) were synthesized by modifying procedures reported in the literature.<sup>1-5</sup> All moisture and oxygen-sensitive reactions were carried out using Schlenk techniques in oven-dried glassware.

**Scheme S1.** Synthesis of 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (compound **3**).



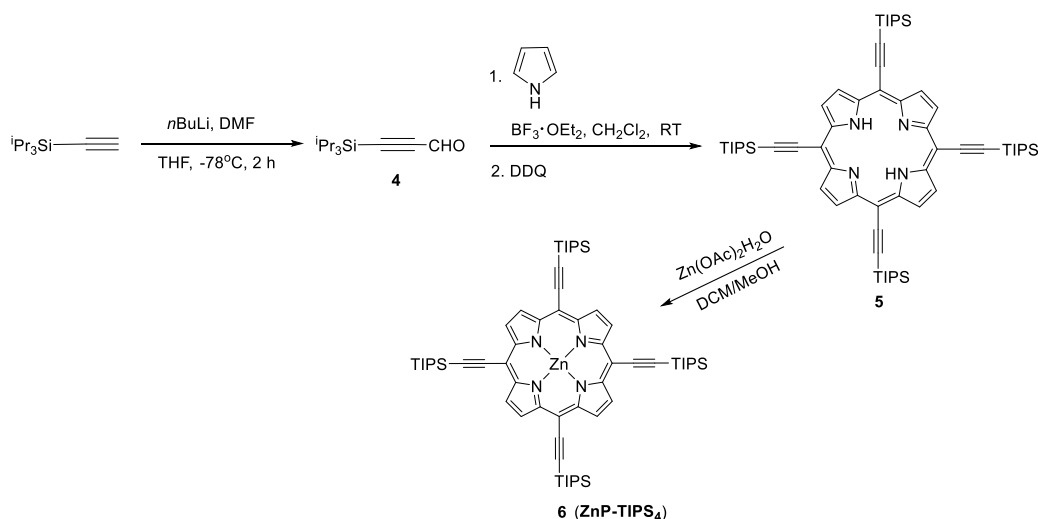
**Compound 1.** A three neck round bottom flask equipped with a condenser and a dropping funnel was charged with potassium *tert*-butoxide (33.2 g, 296.6 mmol) and *tert*-amyl alcohol (200 mL). The mixture was heated to 105 °C for 1.5 h. Then 2-thiophenenitrile (26.9 g, 247.2 mmol) was added and the stirring continued at 105 °C for further 30 min. At this point a mixture

of diisopropyl succinate (20.0 g, 98.8 mmol) in *tert*-amyl alcohol (30 mL) was added dropwise from a pressure-equalizing dropping funnel over a period of 2 h, then the mixture was stirred at 105 °C overnight. It was then cooled to 50 °C and a mixture of methanol (100 mL) and water (20 mL) was added. The mixture was heated to reflux for 45 min, allowed to cool to room temperature and was poured over ice water. Hydrochloric acid (35% aq) (50 mL) and methanol (300 mL) were added sequentially and the mixture was stirred for an additional 45 min, filtered and the solid was washed extensively with warm methanol and water until no more color was observed at the filtrate. Finally, the solid was oven-dried to give a dark red product (10.4 g, 35%). The compound was used without further purification.

**Compound 2.** A round bottom flask equipped with a condenser was charged with compound **1** (10.0 g, 33.2 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (18.4 g, 133.1 mmol). Anhydrous DMF (200 mL) was added under nitrogen atmosphere and the mixture was heated to 130 °C for 1 h. To this was added 2-ethylhexyl bromide (19.2 g, 99.8 mmol) and the mixture was refluxed overnight, cooled to room temperature, extracted with chloroform and washed with water (3x). After removing the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (dichloromethane: heptane = 2:1) and then recrystallized from isopropanol to yield a red solid (8.7 g, 50%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.82 (dd, *J* = 3.9, 1.2 Hz, 2H), 7.55 (dd, *J* = 5.0, 1.2 Hz, 2H), 7.19 (dd, *J* = 3.6, 1.4 Hz, 2H), 4.02 – 3.90 (m, 4H), 1.78 (q, *J* = 6.8 Hz, 2H), 1.38 – 1.06 (m, 16H), 0.86 – 0.73 (m, 12H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 161.7, 140.40, 135.2, 130.5, 129.8, 128.3, 107.8, 45.8, 39.0, 30.1, 28.3, 23.5, 23.0, 13.9, 10.5.

**Compound 3.** In a round bottom flask containing dry and degassed THF (100 mL), compound **2** (4.6 g, 8.7 mmol) was added and the mixture was cooled to 0 °C. Then *N*-bromosuccinimide (1.7 g, 9.6 mmol), dissolved in THF (40 mL), was added to the flask dropwise in the dark and the mixture was allowed to warm to room temperature and stirred for 5 h. At that point aqueous sodium thiosulfate solution was added to the mixture, extracted with dichloromethane and the combined organic phase was dried over MgSO<sub>4</sub>. The crude compound was purified by column chromatography over silica gel (dichloromethane:heptane = 2:1) and then recrystallized from isopropanol to yield a dark purple solid (2.8 g, 53.8%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.83 (dd, *J* = 3.9, 1.1 Hz, 1H), 8.56 (d, *J* = 4.2 Hz, 1H), 7.57 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.20 – 7.17 (m, 1H), 7.15 (d, *J* = 4.2 Hz, 1H), 4.01 – 3.79 (m, 4H), 1.77 (hept, *J* = 6.4 Hz, 2H), 1.35 – 1.11 (m, 16H), 0.87 – 0.71 (m, 12H). <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 161.6, 161.4, 140.8, 138.9, 135.5, 135.0, 131.3, 131.2, 130.7, 129.7, 128.4, 118.6, 108.1, 107.7, 45.9, 39.0, 30.1, 28.3, 23.5, 23.0, 14.0, 10.5. *m/z* (ESI<sup>+</sup>): 603.1713 (M+H)<sup>+</sup>.

**Scheme S2.** Synthesis of ZnP-TIPS<sub>4</sub> (compound **6**).

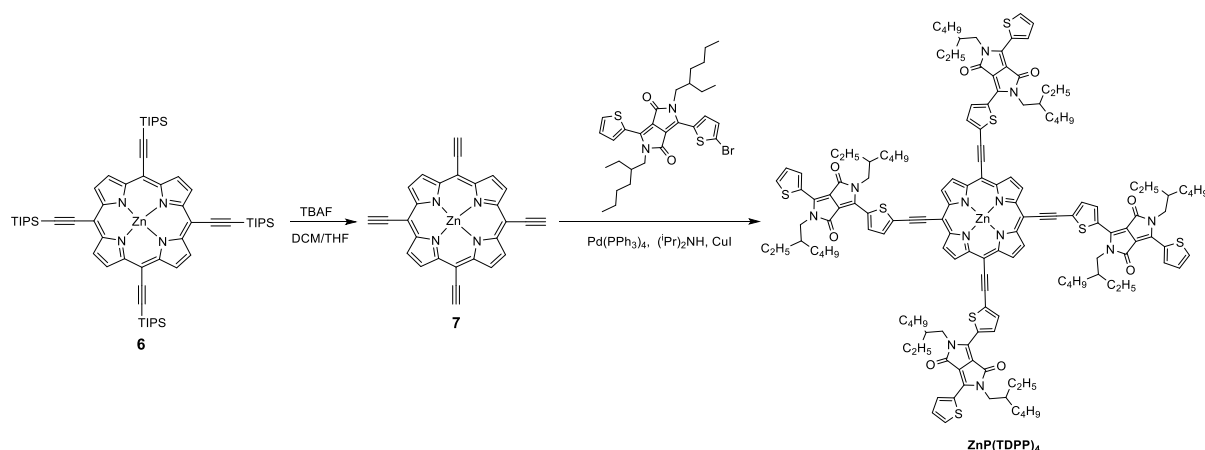


**Compound 4.** In a round bottom flask containing triisopropylsilyl acetylene (45 mL, 191.9 mmol), dry and degassed THF (300 mL) was added and the solution was cooled to  $-78^{\circ}\text{C}$  under inert atmosphere. To this solution, a 2.5 M *n*-BuLi (84.4 mL, 211.1 mmol) solution in hexane was added dropwise at  $-78^{\circ}\text{C}$  and the stirring continued for 1 h. Then the mixture was allowed to slowly warm to room temperature for 1 h, cooled again to  $-78^{\circ}\text{C}$  and DMF (16.3 mL, 211.1 mmol) was added slowly. After keeping the mixture at  $-78^{\circ}\text{C}$  for 1 h, it was allowed to slowly warm to room temperature overnight. After 20 h the mixture was poured into a stirred solution of 10% aqueous solution of  $\text{KH}_2\text{PO}_4$  and diethyl ether at  $0^{\circ}\text{C}$  and stirred for 5 min, at which point the layers were separated and the organic layer was washed with water (5x), dried over  $\text{MgSO}_4$ , filtered, and concentrated under vacuum. The compound was purified by column chromatography over silica gel (ethyl acetate:hexane (1:20) ) to yield a yellowish oil. (28.7 g, 71%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.20 (s, 1H), 1.12 – 1.09 (m, 21H).

**Compound 5.** To a solution of freshly distilled pyrrole (9.18 g, 136.84 mmol) and compound **4** (28.79 g, 136.84 mmol) in dichloromethane (3 L), boron trifluoride diethyl etherate (7.9 mL, 64.01 mmol) was added slowly under nitrogen at room temperature and was stirred for 1.30 h. Then, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (23.3 g, 102.6 mmol) was added and after 30 min of stirring at room temperature the reaction mixture was filtered through silica. The solvent was evaporated and the residue was crystallized from dichloromethane/methanol to yield a purple solid (7.8 g, 22%).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  9.48 (s, 8H), 1.60 – 1.00 (m, 96H), -1.89 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  107.7, 102.3, 100.1, 19.1, 11.8.  $m/z$  (ESI<sup>+</sup>): 1031.6627 ( $\text{M}+\text{NH}_4$ )<sup>+</sup>.

**Compound 6.** In a round bottom flask containing a solution of compound **5** (2 g, 1.94 mmol) in chloroform (80 mL), a solution of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (1.06 g, 4.85 mmol) in methanol (20 mL) was added. The reaction mixture was refluxed for 2 h and then washed with water and dried over anhydrous MgSO<sub>4</sub>. After the solvent was removed, the residue was recrystallized from chloroform/methanol to give compound **6** as a purple solid (2 g, 94%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.55 (s, 1H), 1.81 – 0.58 (m, 11H). <sup>13</sup>C NMR (100 MHz, Chloroform-*d*) δ 152.08, 131.87, 108.35, 103.02, 99.35, 19.18, 11.92. m/z (ESI<sup>+</sup>): 1093.577 (M+H)<sup>+</sup>.

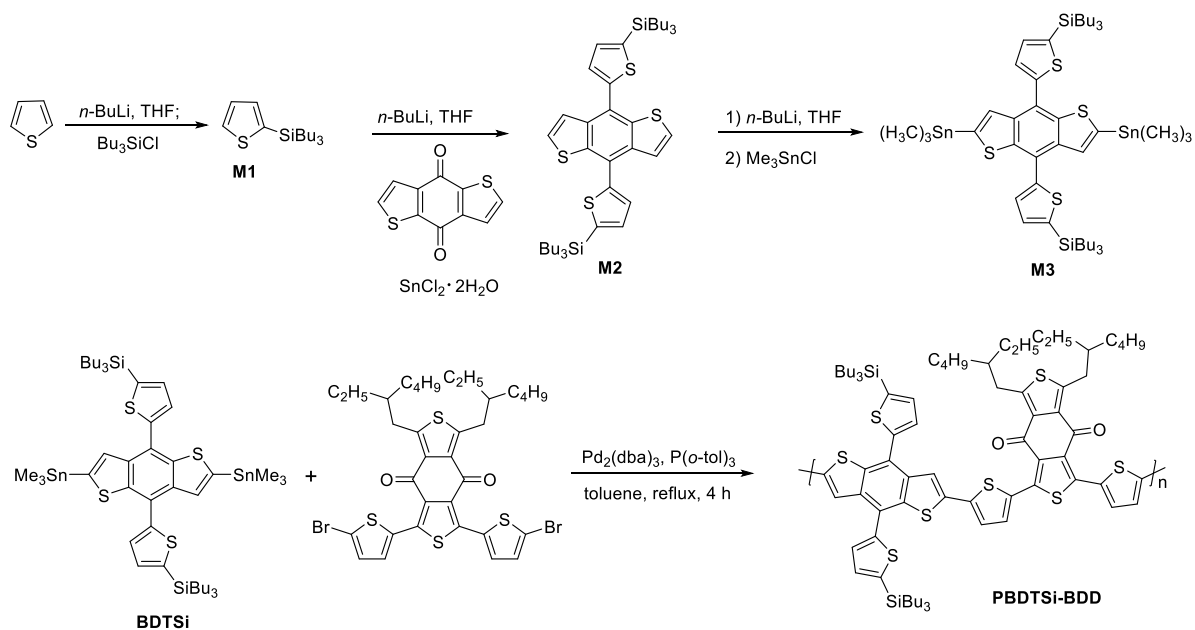
**Scheme S3.** Synthesis of ZnP(TDPP)<sub>4</sub>.



**Compound 7.** To a round bottom flask charged with compound **6** (0.699 g, 0.63 mmol) dissolved in dry and degassed dichloromethane (50 mL) and THF (20 mL) under nitrogen atmosphere, a solution of tetrabutylammonium fluoride (1 M in THF, 3.83 mL, 3.83 mmol) was added dropwise and the mixture was stirred at room temperature for 30 min. Then a mixture of ethanol (250 mL) and water (250 mL) was added to the reaction flask and the reaction mixture was concentrated by evaporation of the solvent until the product precipitated. The precipitate was then collected by filtration and washed extensively with extra methanol and water under a blanket of nitrogen and the deprotected compound was used immediately in the next step without further purification.

**ZnP(TDPP)<sub>4</sub>**. In an oven-dried two-neck round bottom flask equipped with a condenser Compound **7** (directly from the previous step), compound **3** (1.49 g, 2.47 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (71.3 mg, 61.7 μmol), CuI (14.7 mg, 77.1 μmol), dry THF (14 mL) and *i*Pr<sub>2</sub>NH (3 mL) were added and the reaction mixture was heated to 50 °C overnight. It was then allowed to cool to room temperature, the solvent was removed under reduced pressure, and the crude compound was purified first by column chromatography over silica gel (dichloromethane:pyridine = 99:1) and then by size exclusion chromatography (toluene:pyridine = 99:1) to give a dark blue solid (0.2 g, 25% yield). <sup>1</sup>H NMR (500 MHz, Pyridine-*d*<sub>5</sub>) δ 9.87 (s, 4H), 9.67 (d, *J* = 3.5 Hz, 4H), 9.32 (s, 8H), 8.27 (d, *J* = 3.8 Hz, 4H), 7.94 (d, *J* = 4.8 Hz, 4H), 7.32 (t, *J* = 4.3 Hz, 4H), 4.92 – 4.49 (m, 8H), 4.48 – 4.17 (m, 8H), 2.50 (s, 4H), 2.20 (h, *J* = 6.6 Hz, 4H), 2.08 – 1.13 (m, 88H), 1.10 – 0.69 (m, 24H). <sup>13</sup>C NMR (200 MHz, Pyridine-*d*<sub>5</sub>) δ 161.56, 161.46, 151.80, 140.50, 138.81, 136.55, 133.42, 131.93, 131.68, 130.33, 129.43, 128.65, 108.96, 108.09, 102.69, 91.61, 84.16, 46.39, 46.11, 39.97, 39.43, 30.93, 30.43, 29.03, 28.39, 24.03, 23.67 (overlapping peaks), 23.25, 14.63, 14.10, 10.70, 10.51. (two signals are missing) MALDI-TOF: *m/z* 2559.51 [M]<sup>+</sup>.

**Scheme S4.** Synthesis of PBDTSi-BDD.



**Compound M1.** To a solution of thiophene (4.2 g, 50 mmol) in dry THF (60 mL) was added dropwise *n*-BuLi (2.5 M in hexanes) (20 mL, 50 mmol). The mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h and allowed to warm to room temperature and stirred for further 1 h and then cooled to  $-78\text{ }^{\circ}\text{C}$ . Chlorotributylsilane (11.7 g, 50 mmol) was added and the mixture was stirred overnight. It was then extracted with diethyl ether and washed with water and brine and dried over anhydrous  $\text{MgSO}_4$ . After the solvent was removed, the residue was passed through a column of silica gel using hexane as eluent to obtain **M1** (12 g, 85%) as a colorless liquid.  $^1\text{H-NMR}$  (400 MHz, Chloroform-*d*):  $\delta$  7.60 (dd,  $J = 4.4, 1.0$  Hz, 1H), 7.27 (dd,  $J = 3.6, 1.0$  Hz, 1H), 7.21 (dd,  $J = 4.4, 3.6$  Hz, 1H), 1.36 (m, 10H), 0.91 (m, 8H), 0.83 (m, 9H);  $^{13}\text{C-NMR}$  (100 MHz, Chloroform-*d*):  $\delta$  137.31, 134.40, 130.24, 127.89, 26.81, 26.03, 13.91, 13.48.

**Compound M2.** To a solution of **M2** (12.5 g, 44.3 mmol) in THF (60 mL) at  $-78\text{ }^{\circ}\text{C}$  under nitrogen atmosphere, *n*-BuLi (2.5 M in hexanes) (18 mL, 44.3 mmol) was added dropwise. The

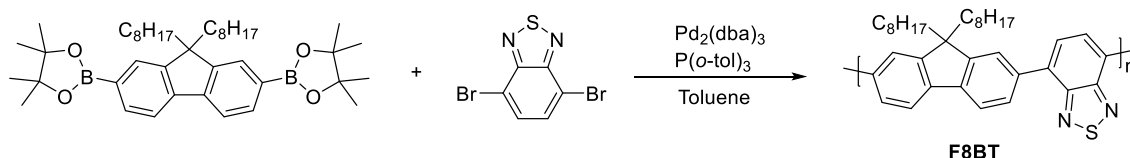


mixture was kept at  $-78\text{ }^{\circ}\text{C}$  for 1 h and stirred for 2 h at room temperature. Benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (3.3 g, 15 mmol) was added quickly and the mixture was stirred for 2 h at  $50\text{ }^{\circ}\text{C}$ . After cooling to room temperature,  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$  (26.6 g, 118 mmol) in 10% HCl (50 mL) was added and the mixture was stirred overnight. It was then extracted with diethyl ether, washed with water and brine, and the solvent was removed. The residue was passed through a column of silica gel using hexane as eluent to obtain compound **M2** (7.4 g, 65%) as a light yellow solid.  $^1\text{H}$ -NMR (400 MHz, Chloroform-*d*):  $\delta$  7.63 (d,  $J = 5.7\text{ Hz}$ , 2H), 7.55 (d,  $J = 3.4\text{ Hz}$ , 2H), 7.45 (d,  $J = 5.7\text{ Hz}$ , 2H), 7.34 (d,  $J = 3.4\text{ Hz}$ , 2H), 1.45 – 1.32 (m, 24H), 0.94 – 0.83 (m, 30H);  $^{13}\text{C}$ -NMR (100 MHz, Chloroform-*d*):  $\delta$  145.01, 139.42, 139.42, 136.58, 134.76, 129.06, 127.50, 124.29, 124.24, 26.64, 26.01, 13.77, 13.19.

**Compound M3.** To a solution of compound **M2** (1.5 g, 2 mmol) in THF (30 mL) at  $-78\text{ }^{\circ}\text{C}$ , under nitrogen atmosphere, *n*-BuLi (2.5 M in hexanes) (2 mL, 5 mmol) was added dropwise and stirred for 1 h. The mixture was allowed to warm to room temperature and stirred for further 2 h. Then  $\text{Me}_3\text{SnCl}$  (1 M in hexane) (6 mL, 6 mmol) was added dropwise and the mixture was stirred at room temperature overnight. It was then poured into water, extracted with diethyl ether and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed, and the residue was recrystallized (twice) from isopropyl alcohol to yield compound **M3** (1.5 g, 70%) as yellow solid.  $^1\text{H}$ -NMR (400 MHz, Chloroform-*d*):  $\delta$  7.70 (s, 2H), 7.59 (d,  $J = 3.40\text{ Hz}$ , 2H), 7.35 (d,  $J = 3.40\text{ Hz}$ , 2H), 1.47 – 1.33 (m, 20H), 0.96 – 0.81 (m, 34H), 0.38 (s, 18H);  $^{13}\text{C}$ -NMR (100 MHz, Chloroform-*d*):  $\delta$  145.68, 143.11, 142.27, 138.68, 137.19, 134.71, 131.18, 128.83, 122.27, 26.76, 26.06, 13.80, 13.23,  $-8.40$ .

**PBDTSi-BDD.** In a 25 mL two-necked round-bottomed flask, 1,3-bis(5-bromothiophen-2-yl)-5,7-bis(2-ethylhexyl)-4*H*,8*H*-benzo[1,2-*c*:4,5-*c'*]dithiophene-4,8-dione (BDD) (153.4 mg, 0.2 mmol), **M4** (215.4 mg, 0.2 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (3.7 mg, 0.004 mmol), P(*o*-Tol)<sub>3</sub> (4.9 mg, 0.016 mmol) were dissolved in dry toluene (8 mL), purged with nitrogen for 10 min, and heated under reflux for 4 h. The polymer was then end-capped by adding 2-bromothiophene followed by 2-tributyl(thiophen-2-yl)stannane in 1 h interval. The mixture was cooled to room temperature and poured into acetone. The polymer was filtered through a Soxhlet thimble and was subjected to Soxhlet extraction with methanol, diethyl ether and chloroform. The chloroform fraction was passed through a column of silica gel, precipitated from acetone and dried in an oven at 40 °C overnight to yield PBDTSi-BDD. (250 mg, 92%; *M*<sub>n</sub> = 60 kDa, *M*<sub>w</sub>/*M*<sub>n</sub> = 2.4).

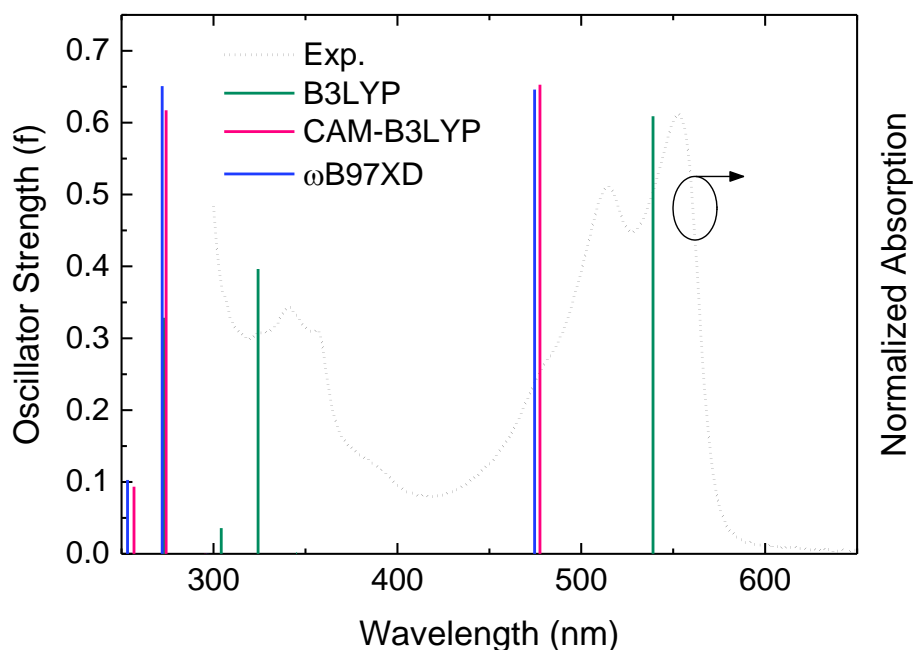
**Scheme S5.** Synthesis of 4-methyl-7-(7-methyl-9,9-dioctyl-9*H*-fluoren-2-yl)benzo[*c*][1,2,5]thiadiazole (**F8BT**).



**F8BT.** To a 50 mL two-neck round bottom flask 2,2'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (500 mg, 0.78 mmol), 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (228.74 mg, 0.78 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (14.25 mg, 0.015 mmol) and P(*o*-Tol)<sub>3</sub> (18.95 mg, 0.062 mmol) were added. The flask was subjected to five vacuum/nitrogen backfill cycles. Then 16 mL of degassed toluene was added, and the mixture was bubbled with nitrogen for 30 min and heated under reflux overnight. After 20 h the polymer was end-capped by 2-bromothiophene and allowed to react for further 1 h. After cooling to

room temperature, the mixture was precipitated into 300 mL of acetone and the polymer was collected by filtration. Then the polymer was washed by Soxhlet extraction using acetone, hexane and chloroform (overnight, ~20–24 h). The chloroform fraction was further purified by passing through a short silica gel column. Then the chloroform solution was concentrated and precipitated into 300 mL of acetone. The yellow polymer was collected by filtration through 0.45  $\mu\text{m}$  Teflon filter and dried under vacuum (170 mg, 39%;  $M_n = 10.3$  kDa,  $M_w/M_n = 1.7$ ).

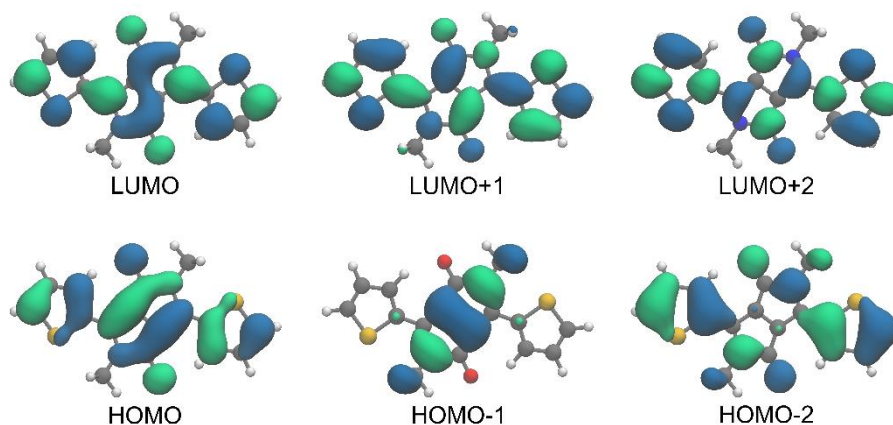
## DFT



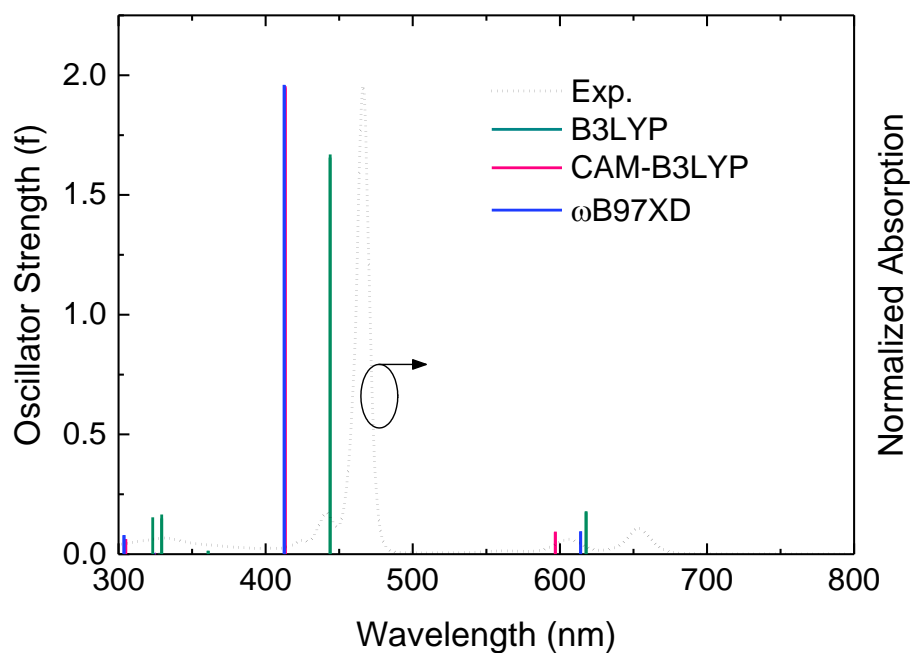
**Figure S1.** TD-DFT electronic transitions and oscillator strengths of TDPP, as calculated using B3LYP (green), CAM-B3LYP (pink), and  $\omega$ B97XD (blue) functionals and PCM with toluene as solvent. The normalized experimental absorption spectrum of TDPP in  $10^{-6}$  M toluene solution is shown for comparison (black dashed line).

**Table S1.** TD-DFT-calculated energies (eV), wavelengths (nm), and oscillator strengths (f) of the electronic transitions of TDPP shown in Figure S1. Only the main transitions ( $f > 0.05$  are listed). The percentage stands for the contribution of such orbitals to the transition.

Functional	Transition	eV	nm	f
B3LYP	100% HOMO $\rightarrow$ LUMO	2.300	539	0.609
	89% HOMO-2 $\rightarrow$ LUMO	3.824	324	0.397
	9% HOMO $\rightarrow$ LUMO+2			
	85% HOMO $\rightarrow$ LUMO+2	4.537	273	0.329
	7% HOMO-1 $\rightarrow$ LUMO+1			
	7% HOMO-2 $\rightarrow$ LUMO			
CAM-B3LYP	99% HOMO $\rightarrow$ LUMO	2.596	478	0.653
	91% HOMO-2 $\rightarrow$ LUMO	4.522	274	0.617
	3% HOMO-3 $\rightarrow$ LUMO+1			
	86% HOMO-4 $\rightarrow$ LUMO	4.828	257	0.094
	9% HOMO-5 $\rightarrow$ LUMO+1			
	2% HOMO-2 $\rightarrow$ LUMO			
$\omega$ B97XD	99% HOMO $\rightarrow$ LUMO	2.612	475	0.646
	90% HOMO-2 $\rightarrow$ LUMO	4.557	272	0.651
	5% HOMO-3 $\rightarrow$ LUMO+1			
	82% HOMO-4 $\rightarrow$ LUMO	4.895	253	0.103
	12% HOMO-5 $\rightarrow$ LUMO+1			



**Figure S2.** DFT-calculated frontier orbitals describing the electronic ground state of TDPP, as obtained using B3LYP functional and PCM with toluene as solvent.

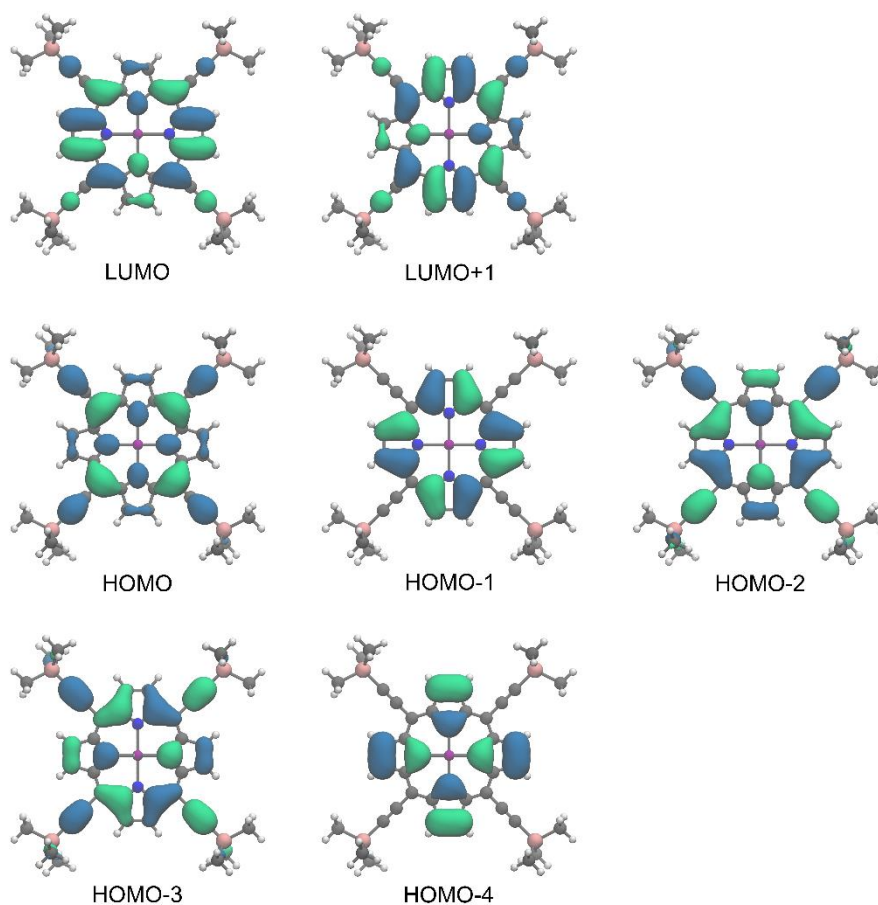


**Figure S3.** TD-DFT electronic transitions and oscillator strengths of ZnP-TIPS<sub>4</sub>, as calculated using B3LYP (green), CAM-B3LYP (pink), and  $\omega$ B97XD (blue) functionals and PCM with toluene as solvent. The normalized experimental absorption spectrum of ZnP-TIPS<sub>4</sub> in 10<sup>-6</sup> M toluene solution is shown for comparison (black dashed line).

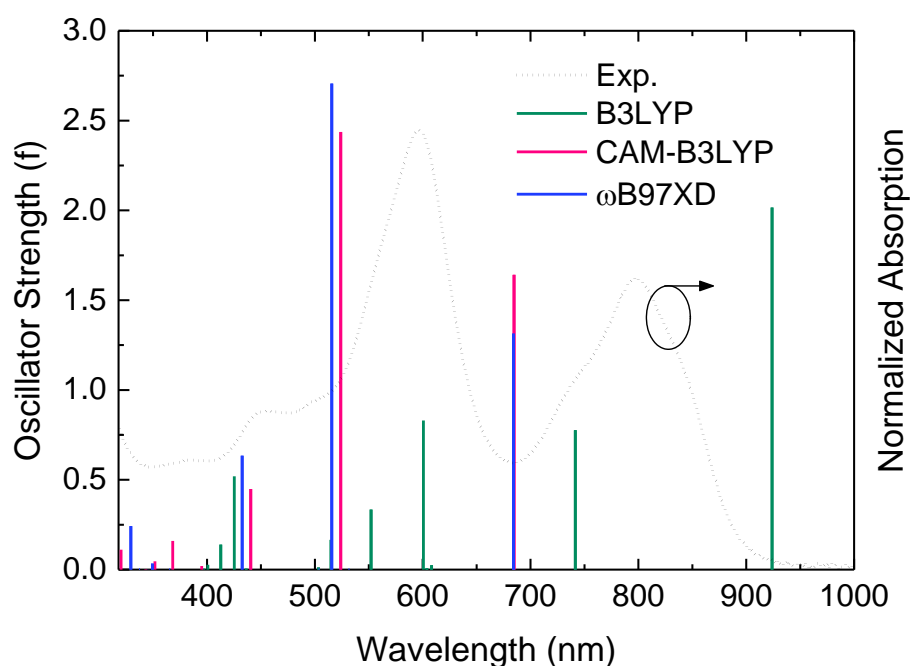
**Table S2.** TD-DFT-calculated energies (eV), wavelengths (nm), and oscillator strengths (f) of the electronic transitions of ZnP-TIPS<sub>4</sub> shown in Figure S3. Only the main transitions ( $f > 0.05$  are listed). The percentage stands for the contribution of such orbitals to the transition.

Functional	Transition	eV	nm	f
B3LYP	73% HOMO $\rightarrow$ LUMO	2.007	618	0.179

	26% HOMO-1 $\rightarrow$ LUMO+1 73% HOMO $\rightarrow$ LUMO+1 26% HOMO-1 $\rightarrow$ LUMO 68% HOMO-1 $\rightarrow$ LUMO+1 25% HOMO $\rightarrow$ LUMO 68% HOMO-1 $\rightarrow$ LUMO 25% HOMO $\rightarrow$ LUMO+1 96% HOMO-4 $\rightarrow$ LUMO 96% HOMO-4 $\rightarrow$ LUMO+1 99% HOMO-5 $\rightarrow$ LUMO 99% HOMO-5 $\rightarrow$ LUMO+1	2.007 2.794 2.794 3.435 3.436 3.765 3.765	618 444 444 361 361 329 329	0.175 1.669 1.656 0.014 0.014 0.149 0.166
CAM-B3LYP	62% HOMO $\rightarrow$ LUMO 36% HOMO-1 $\rightarrow$ LUMO+1 62% HOMO $\rightarrow$ LUMO+1 36% HOMO-1 $\rightarrow$ LUMO 62% HOMO-1 $\rightarrow$ LUMO+1 36% HOMO $\rightarrow$ LUMO 62% HOMO-1 $\rightarrow$ LUMO 36% HOMO $\rightarrow$ LUMO+1 77% HOMO-4 $\rightarrow$ LUMO 77% HOMO-4 $\rightarrow$ LUMO+1	2.077 2.077 2.999 3.000 4.066 4.067	597 597 413 413 305 305	0.094 0.092 1.954 1.946 0.063 0.062
$\omega$ B97XD	62% HOMO $\rightarrow$ LUMO 37% HOMO-1 $\rightarrow$ LUMO+1 62% HOMO $\rightarrow$ LUMO+1 37% HOMO-1 $\rightarrow$ LUMO 63% HOMO-1 $\rightarrow$ LUMO+1 37% HOMO $\rightarrow$ LUMO 63% HOMO-1 $\rightarrow$ LUMO 37% HOMO $\rightarrow$ LUMO+1 74% HOMO-4 $\rightarrow$ LUMO 74% HOMO-4 $\rightarrow$ LUMO+1	2.019 2.019 3.004 3.006 4.082 4.083	614 614 413 413 304 304	0.096 0.095 1.958 1.960 0.080 0.079



**Figure S4.** DFT-calculated frontier orbitals describing the electronic ground state of ZnP-TIPS<sub>4</sub>, as obtained using CAM-B3LYP functional and PCM with toluene as solvent.



**Figure S5.** TD-DFT electronic transitions and oscillator strengths of  $\text{ZnP(TDPP)}_4$ , as calculated using B3LYP (green), CAM-B3LYP (pink), and  $\omega\text{B97XD}$  (blue) functionals and PCM with toluene as solvent. The normalized experimental absorption spectrum of  $\text{ZnP(TDPP)}_4$  in  $10^{-7}$  M toluene + 1% pyridine solution is shown for comparison (black dashed line).

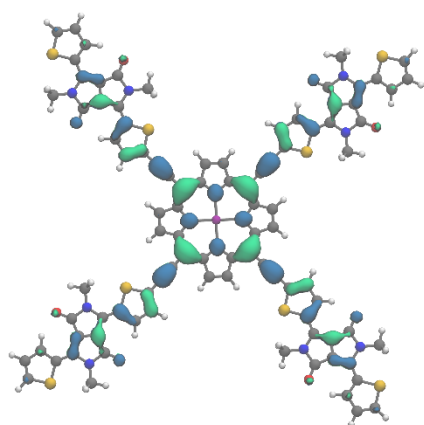
**Table S3.** TD-DFT-calculated energies (eV), wavelengths (nm), and oscillator strengths (f) of the electronic transitions of  $\text{ZnP(TDPP)}_4$  shown in Figure S5. Only the main transitions ( $f > 0.05$  are listed). The percentage stands for the contribution of such orbitals to the transition.

Functional	Transition	eV	nm	f
B3LYP	97% HOMO $\rightarrow$ LUMO	1.342	924	2.015
	97% HOMO $\rightarrow$ LUMO+1	1.342	924	2.017
	98% HOMO-1 $\rightarrow$ LUMO	1.672	742	0.777
	98% HOMO-1 $\rightarrow$ LUMO+1	1.672	742	0.775
	30% HOMO-2 $\rightarrow$ LUMO+2	2.064	601	0.831

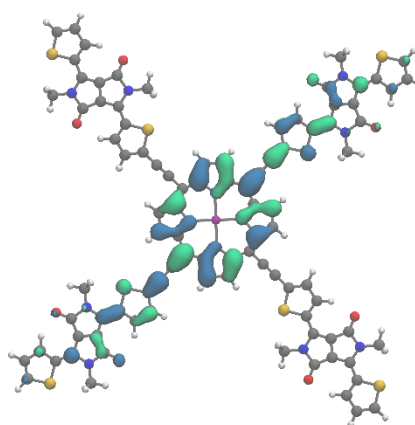


	31% HOMO → LUMO+5 16% HOMO-5 → LUMO 13% HOMO → LUMO+4 30% HOMO-3 → LUMO+2 30% HOMO → LUMO+4 16% HOMO-5 → LUMO+1 14% HOMO → LUMO+5 89% HOMO-2 → LUMO+3 89% HOMO-3 → LUMO+3 37% HOMO-5 → LUMO+1 31% HOMO-1 → LUMO+4 38% HOMO-5 → LUMO 31% HOMO-1 → LUMO+5 73% HOMO-8 → LUMO 15% HOMO-5 → LUMO+5 73% HOMO-8 → LUMO+1 15% HOMO-5 → LUMO+4 47% HOMO-5 → LUMO+4 22% HOMO-2 → LUMO+6 47% HOMO-5 → LUMO+5 22% HOMO-3 → LUMO+6	2.064       2.246 2.246 2.408  2.408  2.915  2.915 3.004 3.004	601       552 552 515  515  425  425 413 413	0.830       0.335 0.334 0.166  0.166  0.519  0.520 0.139 0.140
CAM-B3LYP	70% HOMO → LUMO 11% HOMO-4 → LUMO+1 70% HOMO → LUMO+1 11% HOMO-4 → LUMO 21% HOMO-4 → LUMO+1 14% HOMO-1 → LUMO 12% HOMO-2 → LUMO+2 11% HOMO-2 → LUMO+3 10% HOMO → LUMO+5 21% HOMO-4 → LUMO 14% HOMO-1 → LUMO+1 13% HOMO-3 → LUMO+2	1.811  1.811  2.366  2.366 2.366	685  685  524  524 524	1.642  1.640  2.436  2.437

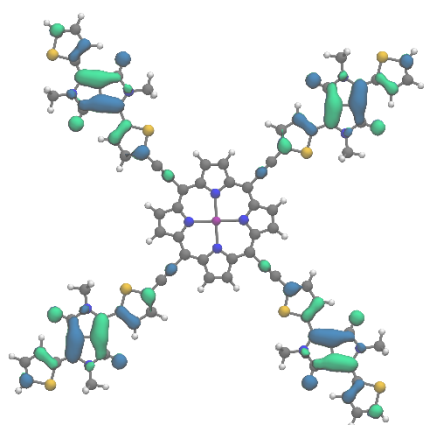
	11% HOMO-3 → LUMO+3 10% HOMO → LUMO+4 45% HOMO-4 → LUMO 14% HOMO → LUMO+1 45% HOMO-4 → LUMO+1 14% HOMO → LUMO 55% HOMO-5 → LUMO 24% HOMO → LUMO+5 55% HOMO-5 → LUMO+1 24% HOMO → LUMO+4 46% HOMO-2 → LUMO+2 46% HOMO-3 → LUMO+2	2.814  2.814  3.367  3.367  3.870 3.870	441  441  368  368  320 320	0.448  0.449  0.160  0.160  0.111 0.111
$\omega$ B97XD	65% HOMO → LUMO 15% HOMO-4 → LUMO+1 65% HOMO → LUMO+1 15% HOMO-4 → LUMO 23% HOMO-4 → LUMO+1 23% HOMO-4 → LUMO 35% HOMO-4 → LUMO+1 13% HOMO-4 → LUMO 11% HOMO → LUMO 35% HOMO-4 → LUMO 13% HOMO-4 → LUMO+1 11% HOMO → LUMO+1 39% HOMO → LUMO+4 11% HOMO-5 → LUMO+1 39% HOMO → LUMO+5 11% HOMO-5 → LUMO	1.812  1.812  2.404 2.404 2.866  2.866  3.764 3.764	684  684  516 516 433  433  329 329	1.315  1.313  2.706 2.707 0.635  0.634  0.242 0.242



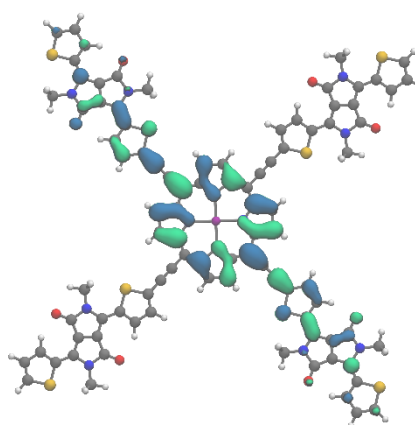
HOMO



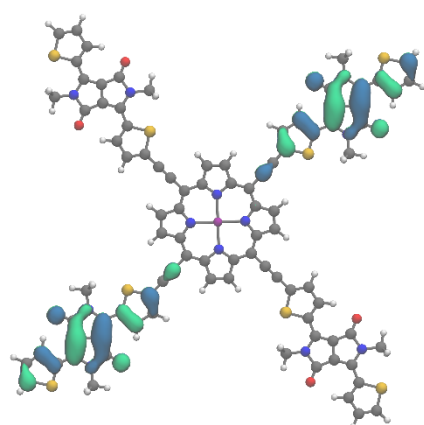
LUMO



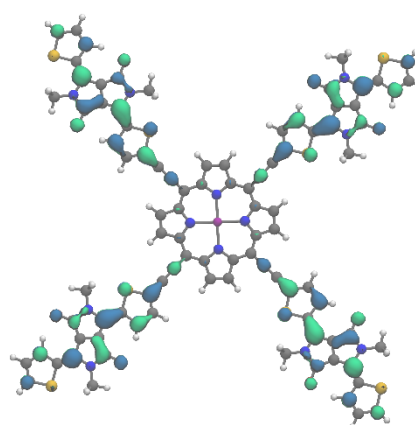
HOMO-1



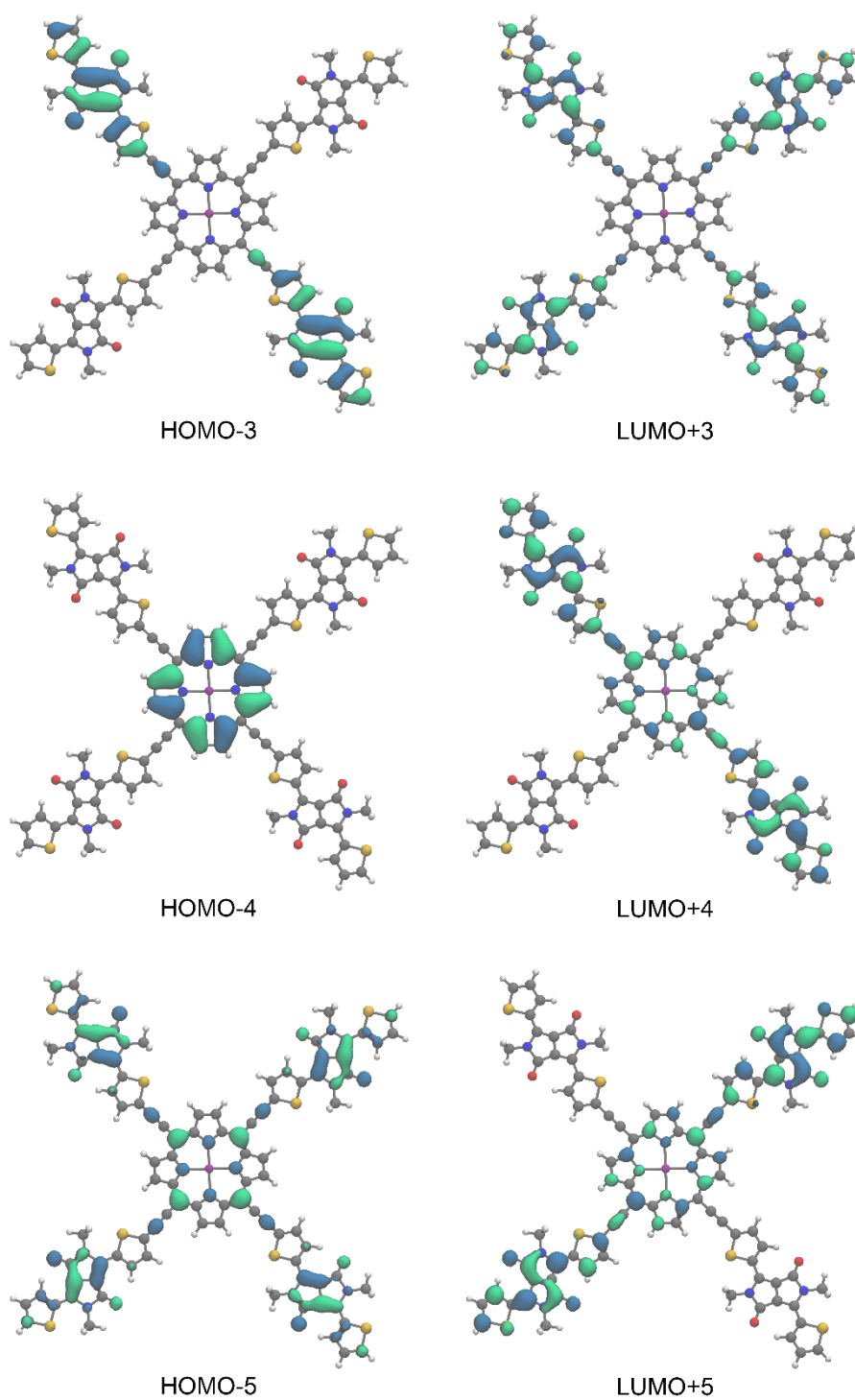
LUMO+1



HOMO-2



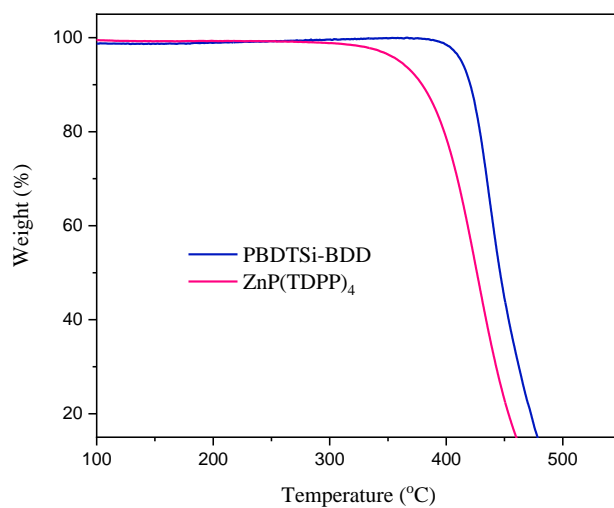
LUMO+2



**Figure S6.** DFT-calculated frontier orbitals describing the electronic ground state of  $\text{ZnP(TDPP)}_4$ , as obtained using CAM-B3LYP functional and PCM with toluene as solvent.

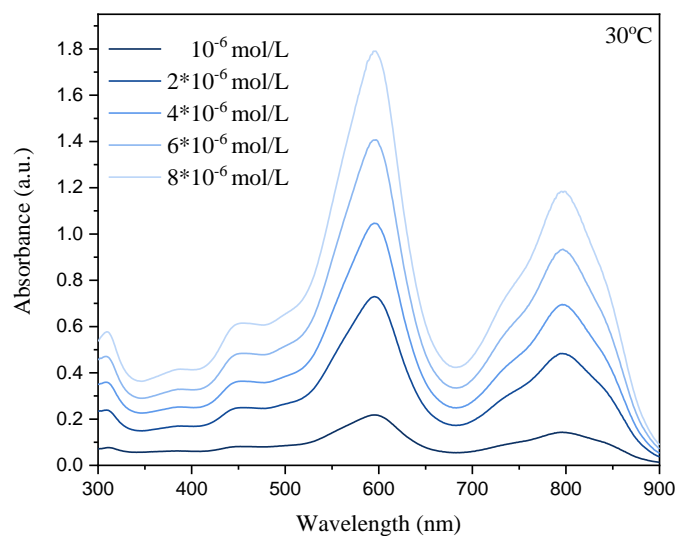
## TGA

Thermogravimetric analysis (TGA) was carried out on a METTLER TOLEDO thermogravimetric analyzer TGA/DSC 3+, from 50 °C to 500 °C at a heating rate of 10 °C/min under N<sub>2</sub> flow.

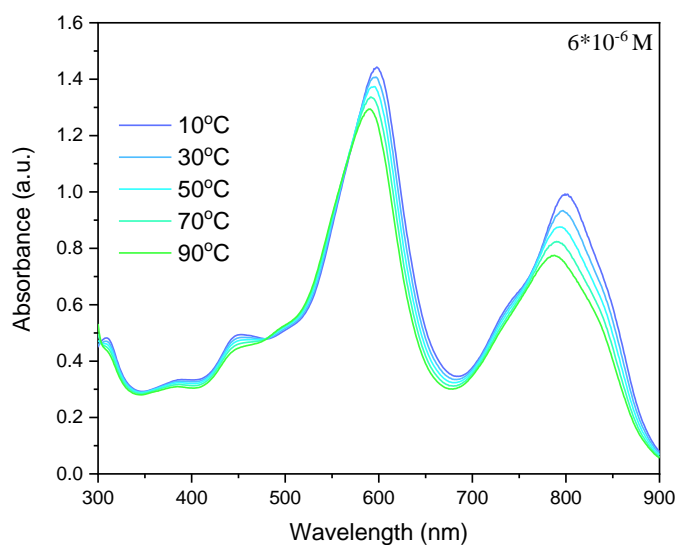


**Figure S7.** TGA plot of ZnP(TDPP)<sub>4</sub> and PBDTSi-BDD.

## Optical Characterization

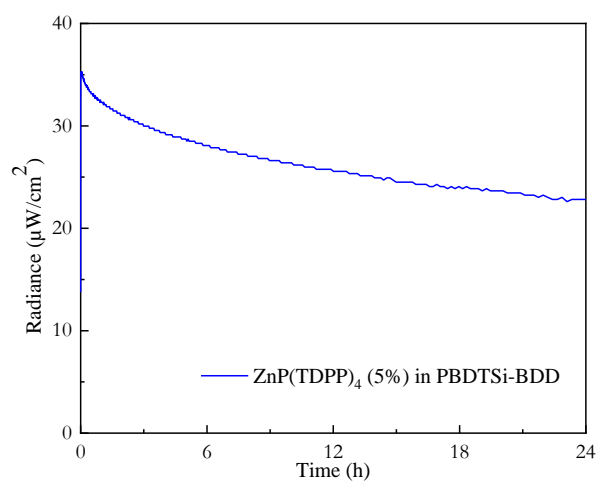


**Figure S8.** Absorption spectra of  $\text{ZnP(TDPP)}_4$  in toluene + 1% pyridine solution at concentration ranging from  $10^{-6}$  to  $8 \times 10^{-6}$  M, as identified in the legend.



**Figure S9.** Temperature dependent absorption spectra of  $\text{ZnP(TDPP)}_4$  in toluene + 1% pyridine solution at concentration  $6 \times 10^{-6}$  M.

## Device Stability



**Figure S10.** The temporal evolution of the radiance in a 24 h period. The host concentration is identified in the legend.

## References

- (1) John Plater, M.; Aiken, S.; Bourhill, G., Metallated porphyrins containing lead(II), copper(II) or zinc(II). *Tetrahedron* **2002**, 58 (12), 2415-2422.
- (2) Matthews, J. R.; Niu, W.; Tandia, A.; Wallace, A. L.; Hu, J.; Lee, W.-Y.; Giri, G.; Mannsfeld, S. C. B.; Xie, Y.; Cai, S.; Fong, H. H.; Bao, Z.; He, M., Scalable Synthesis of Fused Thiophene-Diketopyrrolopyrrole Semiconducting Polymers Processed from Nonchlorinated Solvents into High Performance Thin Film Transistors. *Chemistry of Materials* **2013**, 25 (5), 782-789.
- (3) Paioti, P. H. S.; Abboud, K. A.; Aponick, A., Catalytic Enantioselective Synthesis of Amino Skipped Dienes. *Journal of the American Chemical Society* **2016**, 138 (7), 2150-2153.
- (4) Gao, K.; Li, L.; Lai, T.; Xiao, L.; Huang, Y.; Huang, F.; Peng, J.; Cao, Y.; Liu, F.; Russell, T. P.; Janssen, R. A. J.; Peng, X., Deep Absorbing Porphyrin Small Molecule for High-Performance Organic Solar Cells with Very Low Energy Losses. *Journal of the American Chemical Society* **2015**, 137 (23), 7282-7285.
- (5) Abdulahi, B. A.; Xu, X.; Murto, P.; Inganäs, O.; Mammo, W.; Wang, E., Open-Circuit Voltage Modulations on All-Polymer Solar Cells by Side Chain Engineering on 4,8-Di(thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-Based Donor Polymers. *ACS Applied Energy Materials* **2018**, 1 (6), 2918-2926.