

## Supporting Information

# Polyether-Bridged Sexithiophene as a Complexation-Gated Molecular Wire for Intramolecular Photoinduced Electron Transfer

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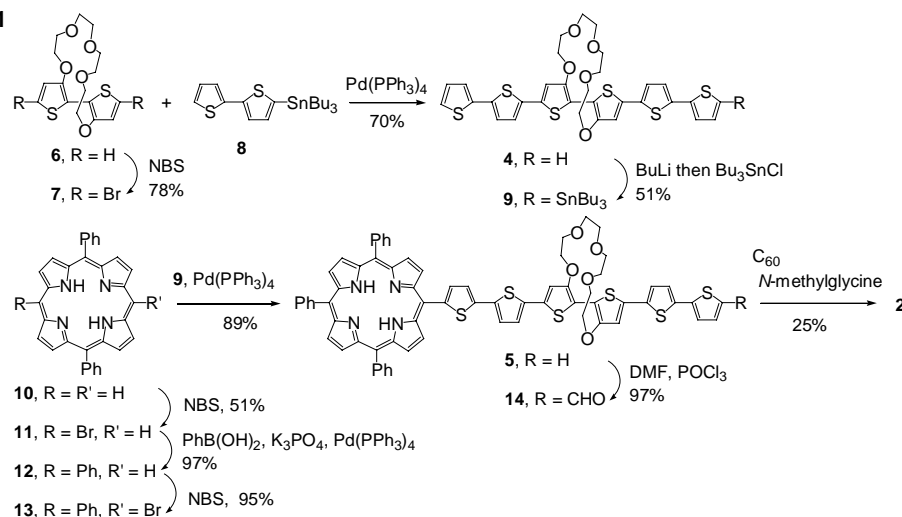
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**Synthetic outline.** The syntheses of new compounds **2**, **4**, and **5** were carried out via the route outlined in Scheme 1. First, polyether-bridged sexithiophene **4** was obtained by treatments of known 3,3'-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)-2,2'-bithiophene (**6**)<sup>1</sup> with NBS followed by the Stille coupling of the resulting dibromo derivative **7** with tributylstannylbithiophene **8**.<sup>2</sup> Next, 21*H*,23*H*-5,10,15-triphenylporphine (**12**) was obtained by bromination of known 21*H*,23*H*-5,15-diphenylporphine (**10**)<sup>3</sup> with NBS and the subsequent Suzuki coupling of the resulting **11** with benzenboronic acid. After the first component **4** was converted to the tributylstannyl derivative **9** by treatment with butyllithium followed by tributylstannyl chloride, and the second component **12** was converted to the bromo derivative **13** by bromination with NBS, a Stille coupling between **9** and **13** gave the porphyrin-sexithiophene dyad **5**. Finally, **5** was converted to the carboaldehyde **14** by the Vilsmeier reaction, which was subsequently coupled with [60]fullerene in the presence of *N*-methylglycine according to the Prato method<sup>4</sup> to give the target porphyrin-sexithiophene-fullerene triad **2**.

**Scheme 1**



## References

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- 2) Zhu, S. S.; Swager, T. M. *Adv. Mater.* **1996**, *8*, 497–500.
- 3) Manka, J. S.; Lawrence, D. S. *Tetrahedron Lett.* **1989**, *30*, 6989–6992.
- 4) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799.

**5,5'-Dibromo-3,3'-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)-2,2'-bithiophene (7).** Into a solution of 3,3'-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)-2,2'-bithiophene (**6**) (750 mg, 2.1 mmol) in DMF (40 ml) was added NBS (786 mg, 4.4 mmol), and the mixture was stirred at room temperature for 1 min. Water (20 ml) was added, and the stirring was continued for 15 min, and the mixture was extracted with dichloromethane. After evaporation of the solvent, the residue was purified by column chromatography (alumina, 1:1 hexane–dichloromethane, *R<sub>f</sub>* 0.2)

followed by recrystallization from 1:1 hexane–ethanol to give colorless needles of **7** (847 mg, 78% yield): mp 136–137 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.40 ( $\text{A}_2\text{B}_2$  t,  $J = 4.6$  Hz, 4H), 3.48 ( $\text{A}_2\text{B}_2$  t,  $J = 4.6$  Hz, 4H), 3.74 ( $\text{A}_2\text{B}_2$  t,  $J = 4.5$  Hz, 4H), 4.26 ( $\text{A}_2\text{B}_2$  t,  $J = 4.5$  Hz, 4H), 6.83 (s, 2H), 7.26 (s, 2H); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix)  $m/z$  512.0 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{Br}_2\text{O}_5\text{S}_2$ : C, 37.37; H, 3.53%. Found: C, 37.33; H, 3.45%.

**3'',3'''-(1,4,7,10,13-Pentaoxatridecane-1,13-diyl)-2,2':5',2'':5'',2''':5''',2''''':5''''',2''''''-sexithiophene (4).** A mixture of **7** (476 mg, 0.93 mmol), 2-tributylstannyl-2,2'-bithiophene (**8**) (844 mg, 1.85 mmol), and tetrakis(triphenylphosphine)palladium (210 mg) in toluene (60 ml) was refluxed for 15 h under an argon atmosphere under dark. The mixture was allowed to cool to room temperature and filtered through a celite. The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (alumina, 1:2 hexane-dichloromethane,  $R_f$  0.5) followed by recrystallization from 2:1 hexane–dichloromethane to give deep orange needles of **4** (450 mg, 70% yield): mp 171–172 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.41 ( $\text{A}_2\text{B}_2$  t,  $J = 4.8$  Hz, 4H), 3.52 ( $\text{A}_2\text{B}_2$  t,  $J = 4.2$  Hz, 4H), 3.83 ( $\text{A}_2\text{B}_2$  t,  $J = 4.2$  Hz, 4H), 4.39 ( $\text{A}_2\text{B}_2$  t,  $J = 4.2$  Hz, 4H), 6.96 (s, 2H), 7.03 (dd,  $J = 3.6, 5.2$  Hz, 2H), 7.07 (d,  $J = 3.6$  Hz, 2H), 7.09 (d,  $J = 3.6$  Hz, 2H), 7.18 (dd,  $J = 0.8, 3.6$  Hz, 2H), 7.23 (dd,  $J = 0.8, 5.2$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  70.34, 70.90, 71.35, 72.22, 114.34, 114.46, 123.40, 123.55, 124.33, 124.38, 127.84, 132.80, 135.91, 136.57, 137.08, 152.86; MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix)  $m/z$  683.5 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{32}\text{H}_{28}\text{O}_5\text{S}_6$ : C, 56.11; H, 4.12%. Found: C, 56.01; H, 4.15%.

**5-Tributylstanyl-3'',3'''-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)-2,2':5',2'':5'',2''':5''',2''''':5''''',2''''''-sexithiophene (9).** Into a solution of **4** (400 mg, 0.58 mmol) in dry THF (60 ml) cooled at  $-80$  °C was added a 1.6 *N* hexane solution of butyllithium (0.45 ml, 0.7 mmol) in a nitrogen atmosphere, and the mixture was stirred at  $-50$  °C for 45 min and again cooled to  $-80$  °C. Tributyltin chloride (0.19 ml, 0.7 mmol) was added into the mixture, which was then stirred at room temperature for 12 h. After water (30 ml) was added, the mixture was stirred another 30 min and extracted with dichloromethane. After evaporation of the solvent, the residue was purified by column chromatography (alumina, dichloromethane,  $R_f$  0.2) and then preparative gel permeation liquid chromatography (JAIGEL 1H/2H, chloroform) to give a reddish orange oil of **9** (654 mg, 51 %):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.91 (t,  $J = 7.2$  Hz, 9H), 1.12 (t,  $J = 8.2$  Hz, 6H), 1.35 (sex,  $J = 7.2$  Hz, 6H), 1.59 (quin,  $J = 7.6$  Hz, 6H), 3.40 ( $\text{A}_2\text{B}_2$  t,  $J = 4.5$  Hz, 4H), 3.51 ( $\text{A}_2\text{B}_2$  t,  $J = 4.5$  Hz, 4H), 3.82 ( $\text{A}_2\text{B}_2$  t,  $J = 3.9$  Hz, 4H), 4.37 ( $\text{A}_2\text{B}_2$  t,  $J = 3.9$  Hz, 4H), 6.94 (s, 1H), 6.95 (s, 1H), 7.03 (dd,  $J = 3.6, 5.0$  Hz, 1H), 7.07 (m, 5H), 7.17 (dd,  $J = 1.2, 3.6$  Hz, 1H), 7.22 (dd,  $J = 1.2, 5.0$  Hz, 1H), 7.29 (d,  $J = 3.4$  Hz, 1H); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix)  $m/z$  970.72 ( $\text{M}^+$ ); Anal. Calcd for  $\text{C}_{44}\text{H}_{54}\text{O}_5\text{S}_6\text{Sn}$ : C, 54.26; H, 5.59%. Found: C, 54.20; H, 5.58%.

**21H,23H-10-Bromo-5,15-diphenylporphine (11).** Into an ice-cooled solution of 21H,23H-5,15-diphenylporphine (**10**) (250 mg, 0.54 mmol), in dichloromethane (250 ml) was added NBS (86 mg, 0.48 mmol). The mixture was then stirred at 0 °C for 17 h, and washed with water, and dried (MgSO<sub>4</sub>). After evaporation of the solvent, the residue was purified by column chromatography (silica gel, 2:1 hexane–dichloromethane, *R<sub>f</sub>* 0.3) to give purple powder of **11** (150 mg, 51% yield): mp >300 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ –2.99 (s, 2H), 7.80 (m, 6H), 8.22 (dd, *J* = 1.8, 7.4 Hz, 4H), 8.96 (d, *J* = 4.6 Hz, 2H), 8.97 (d, *J* = 4.6 Hz, 2H), 9.30 (d, *J* = 4.6 Hz, 2H), 9.75 (d, *J* = 4.6 Hz, 2H), 10.19 (s, 1H); MS (DI, 70 eV) *m/z* 540, 542 (M<sup>+</sup>); Anal. Calcd for C<sub>32</sub>H<sub>21</sub>BrN<sub>4</sub>: C, 70.99; H, 3.91; N, 10.35%. Found: C, 70.95; H, 3.75; N, 10.30%.

**21H,23H-5,10,15-Triphenylporphine (12).** A mixture of **11** (630 mg, 1.2 mmol), benzeneboronic acid (420 mg, 3.5 mmol), potassium phosphate hydrate (760 mg), and tetrakis(triphenylphosphine)palladium(0) (200 mg) in DMF (120 ml) was heated at 90 °C for 10 h under an argon atmosphere. After removal of insoluble materials by filtration through a celite, the filtrate was treated with methyl *t*-butyl ether (200 ml), and successively washed with aq. sat sodium carbonate solution, water, and brine. After dryness (MgSO<sub>4</sub>), the solvent was evaporated, and the residue was purified by column chromatography (silica gel, 1:2 hexane–dichloromethane, *R<sub>f</sub>* 0.6) to give a purple powder of **12** (610 mg, 97% yield): mp 277–278 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ –3.00 (s, 2H), 7.80 (m, 9H), 8.24 (m, 6H), 8.87 (d, *J* = 3.6 Hz, 2H), 8.90 (d, *J* = 3.6 Hz, 2H), 9.02 (d, *J* = 4.6 Hz, 2H), 9.34 (d, *J* = 4.6 Hz, 2H), 10.23 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 119.62, 126.53, 126.81, 127.70, 131.29, 131.34, 131.46, 131.49, 134.49, 134.68, 141.76; MS (DI, 70 eV) *m/z* 538 (M<sup>+</sup>); Anal. Calcd for C<sub>38</sub>H<sub>26</sub>N<sub>4</sub>: C, 84.73; H, 4.87, N, 10.40%. Found: C, 84.49; H, 4.67; N, 10.43%.

**21H,23H-5-Bromo-10,15,20-triphenylporphine (13).** Compound **13** was prepared in 95% yield from **12** in a similar manner as described for the synthesis of **11**: purple power; mp 297–298 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ –2.76 (s, 2H), 7.77 (m, 9H), 8.18 (m, 6H), 8.79 (s, 4H), 8.90 (d, *J* = 4.6 Hz, 4H), 9.67 (d, *J* = 4.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 120.76, 120.96, 126.76, 127.85, 134.35, 134.46, 134.58, 141.26, 141.81; MS (DI, 70 eV) *m/z* 616 (M<sup>+</sup>); Anal. Calcd for C<sub>38</sub>H<sub>25</sub>BrN<sub>4</sub>: C, 73.91; H, 4.08; N, 9.07%. Found: C, 73.75; H, 3.97; N, 9.12%.

**Porphyrin-sexithiophene dyad (5).** A mixture of **9** (200 mg, 0.21 mmol), **13** (136 mg, 0.22 mmol), and tetrakis(triphenylphosphine)palladium(0) (200 mg) in toluene (50 ml) was refluxed for 15 h under a nitrogen atmosphere. After the insoluble material was removed by filtration, the filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography

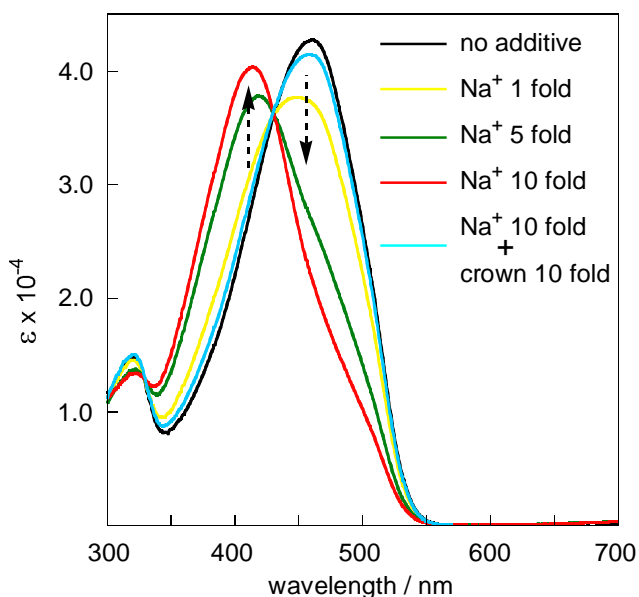
(alumina, 1:1 hexane–dichloromethane, *R<sub>f</sub>* 0.5) followed by recrystallization from 1:1 dichloromethane–methanol to give purple powder of **5** (230 mg, 89% yield): mp 222–223 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ –2.70 (s, 2H), 3.45 (A<sub>2</sub>B<sub>2</sub> m, 4H), 3.55 (A<sub>2</sub>B<sub>2</sub> m, 4H), 3.85 (A<sub>2</sub>B<sub>2</sub> m, 4H), 4.42 (A<sub>2</sub>B<sub>2</sub> m, 4H), 6.98 (s, 1H), 7.04 (dd, *J* = 3.6, 5.2 Hz, 1H), 7.05 (s, 1H), 7.09 (s, 2H), 7.18 (m, 2H), 7.22 (dd, *J* = 0.8, 5.2 Hz, 1H), 7.32 (d, *J* = 4.0 Hz, 1H), 7.58 (d, *J* = 3.6 Hz, 1H), 7.77 (m, 9H), 7.82 (d, *J* = 3.6 Hz, 1H), 8.21 (m, 6H), 8.83 (s, 4H), 8.88 (d, *J* = 4.6 Hz, 2H), 9.20 (d, *J* = 4.6 Hz, 2H); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 1221.0 (M<sup>+</sup>); Anal. Calcd for C<sub>70</sub>H<sub>52</sub>N<sub>4</sub>O<sub>5</sub>S<sub>6</sub>: C, 68.82; H, 4.18; N, 4.59%. Found: C, 68.94; H, 4.18; N, 4.75%.

**Porphyrin-sexithiophenecarbaldehyde (14).** Into an ice-cooled solution of **5** (100 mg, 0.082 mmol) in DMF (10 ml) was added phosphorus oxychloride (0.076 ml, 0.82 mmol) under a nitrogen atmosphere, and the mixture was stirred at 60 °C for 13 h. Water (20 ml) was added into the mixture, which was then stirred at room temperature for 1 h, and extracted with dichloromethane. The extract was concentrated *in vacuo*, and the residue was purified by column chromatography (silica gel, 1:2 hexane–ethyl acetate, *R<sub>f</sub>* 0.3) followed by recrystallization from 3:1 hexane–dichloromethane to give **14** as purple powder (99 mg, 97%): mp 231–232 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ –2.70 (s, 2H), 3.42 (A<sub>2</sub>B<sub>2</sub> m, 4H), 3.54 (A<sub>2</sub>B<sub>2</sub> m, 4H), 3.85 (A<sub>2</sub>B<sub>2</sub> m, 4H), 4.44 (A<sub>2</sub>B<sub>2</sub> m, 4H), 7.03 (s, 1H), 7.05 (s, 1H), 7.13 (d, *J* = 3.6 Hz, 1H), 7.20 (d, *J* = 3.6 Hz, 1H), 7.22 (d, *J* = 4.0 Hz, 1H), 7.27 (d, *J* = 3.6 Hz, 1H), 7.32 (d, *J* = 4.0 Hz, 1H), 7.58 (d, *J* = 3.6 Hz, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.77 (m, 9H), 7.82 (d, *J* = 3.6 Hz, 1H), 8.21 (m, 6H), 8.83 (s, 4H), 8.88 (d, *J* = 4.8 Hz, 2H), 9.20 (d, *J* = 4.8 Hz, 2H), 9.85 (s, 1H); MS (MALDI-TOF, 1,8,9-trihydroxyanthracene matrix) *m/z* 1248.1 (M<sup>+</sup>); Anal. Calcd for C<sub>71</sub>H<sub>52</sub>N<sub>4</sub>O<sub>6</sub>S<sub>6</sub>: C, 68.24; H, 4.19; N, 4.48%. Found: C, 68.11; H, 4.09; N, 4.48%.

**Porphyrin-sexithiophene-fullerene Triad (2).** A mixture of **14** (99 mg, 0.079 mmol), *N*-methylglycine (52 mg, 0.79 mmol), and [60]fullerene (115 mg, 0.159 mmol) in toluene (30 ml) was refluxed for 36 h in a nitrogen atmosphere. After filtration, the filtrate was concentrated *in vacuo*, and the residue was purified successively by column chromatography (alumina, carbon disulfide then chloroform, *R<sub>f</sub>* 0.8), preparative gel permeation liquid chromatography (JAIGEL 1H/2H, chloroform), and finally recrystallization from 3:1 hexane–carbon disulfide to give black powder of **2** (39 mg, 25%): mp >300 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ –2.71 (s, 2H), 2.94 (s, 3H), 3.43 (A<sub>2</sub>B<sub>2</sub> m, 4H), 3.53 (A<sub>2</sub>B<sub>2</sub> m, 4H), 3.83 (A<sub>2</sub>B<sub>2</sub> m, 4H), 4.22 (d, *J* = 10.0 Hz, 1H), 4.40 (A<sub>2</sub>B<sub>2</sub> m, 4H), 4.97 (d, *J* = 10.0 Hz, 1H), 5.20 (s, 1H), 6.96 (s, 1H), 7.04 (s, 1H), 7.08 (d, *J* = 3.6 Hz, 1H), 7.10 (d, *J* = 3.6 Hz, 1H), 7.11 (d, *J* = 4.0 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.31 (d, *J* = 4.0 Hz, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.59 (d, *J* = 3.6 Hz, 1H), 7.74 (m, 9H), 7.82 (d, *J* = 3.6 Hz, 1H), 8.22 (m, 6H), 8.83 (s, 4H), 8.88 (d, *J* = 5.2 Hz, 2H), 9.19 (d, *J* = 5.2 Hz, 2H); MS (MALDI-TOF,

1,8,9-trihydroxyanthracene matrix)  $m/z$  1995.3 ( $M^+$ ); Anal. Calcd for  $C_{153}H_{57}N_5O_5S_6$ : C, 79.98; H, 2.88; N, 3.51%. Found: C, 79.80; H, 2.89; N, 3.43%.

**Spectroscopic measurements.** The electronic absorption and emission spectra were measured in benzonitrile (concentration *ca.*  $10^{-6}$  M) on a Shimadzu UV-3100 spectrophotometer and a Perkin-Elmer LS 45 luminescence spectrometer, respectively, at ambient temperature. The time profiles of fluorescence decays were recorded by a single-photon counting method with a streak scope (Hamamatsu Photonics, C4334-01) using the second harmonic generation (SHG, 410 nm) of a Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, fwhm 1.5 ps) as an excitation source. The nanosecond transient absorption spectra were measured in benzonitrile (concentration *ca.*  $10^{-4}$  M) using the pulsed laser light (532 nm) from a SHG (Continuum, Surelite II-10). For the measurements in the 600 – 1600 nm region, probe light from a pulsed Xe lamp was detected with a Ge-avalanche photodiode equipped with a monochromator after passing through the sample in quartz cell (1 cm  $\times$  1 cm). All the samples were deaerated by bubbling Ar through the solution for 15 min.



**Figure S1.** Electronic absorption spectrum of **4** in benzonitrile and its spectral changes with addition of increasing amounts of sodium perchlorate and 15-crown-5.