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Supporting Information

A dual redox-responsive supramolecular polymer driven by molecular recognition between bisporphyrin and trinitrofluorenone

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General: All reagents and solvents were commercial reagent grade and were used without further purification unless otherwise noted. Dry CH₂Cl₂ and dry diisopropylamine were obtained by distillation over P₂O₅ and KOH, respectively. ¹H and ¹³C NMR spectra were recorded on a Varian mercury-300 spectrometer and a JEOL ECA-500 spectrometer, and chemical shifts were reported on the delta scale in ppm relative to residual chloroform ($\delta = 7.26$ and 77.0 for ¹H and ¹³C, respectively). DOSY experiments were carried out using a JEOL JNM-ECA500 spectrometer. ESR spectra were recorded on a Bruker E500 spectrometer. UV-vis-NIR absorption spectra were recorded on a JASCO V-770 spectrophotometer. High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ Orbitrap XL hybrid FTMS by electron splay ionization (ESI) methods. Melting points (M.p.) were measured with a Yanagimoto micro melting point apparatus. Infrared (IR) spectra were recorded on a JASCO FT/IR-4600 spectrometer with ZeSe ATR accessory. Electrochemical mesurements were carried out in nitrogen-purged dry CH₂Cl₂ at room temperature using a BAS ALS Electrochemical Analyzer Model 1220A (BAS, Inc., Tokyo, Japan) and a BAS ALS Electrochemical Analyzer Model 600D (BAS, Inc., Tokyo, Japan). The working electrode was a glassy carbon electrode (Amel; 0.07 cm²), the counter electrode was a Pt wire, and an Ag wire separated from the solution by a frit was employed as a quasi-reference electrode. Ferrocene was used as an external standard. Tetrabutylammonium hexafluorophosphate (TBAPF₆) of 0.1 mol L^{-1} was added as a supporting electrolyte. Solution viscosity were recorded on an Anton Paar Microviscometer Lovis 2000ME. Preparative separations were performed by silica gel gravity column chromatography (Silica Gel 60 N (spherical, neutral)). Recycling preparative GPC-HPLC separations were carried out on a JAI LC-908s using preparative JAIGEL-2H, 2H, 1H columns in series. 5¹, 6¹, 7^1 , and 8^2 were synthesized according to reported methods.



Scheme S1. Synthesis of head-to-tail monomer 1a.



Synthesis of head-to-tail monomer 1a:

To a solution of **5** (266 mg, 0.155 mmol) in chloroform (78 mL), Zinc acetate (262 mg, 1.43 mmol) in ethanol (48 mL) was added. After being stirred for 1 h at room temperature, the reaction mixture was extracted with chloroform. The organic layer was washed with water and saturated aqueous NaCl, and dried over anhydrous Na₂SO₄. The chloroform was removed under reduced pressure to afford **1a** as a purple solid (285 mg, 0.117 mmol) in 75% yield.

M.p. > 300 °C; ¹H NMR (300 MHz, CDCl₃): δ 10.31 (br, 2H), 8.58 (m, 10H), 8.48 (d, J = 4.7 Hz, 4H), 8.40 (d, J = 4.7 Hz, 4H), 8.20 (d, J = 7.3 Hz, 2H), 8.07 (d, J = 7.2 Hz, 4H), 7.69–7.98 (m, 20H), 7.42–7.68 (m, 12H), 7.29 (m, 2H), 6.93 (d, J = 8.7 Hz, 2H), 6.85 (br, 1H), 6.51 (br, 1H), 6.26 (br, 1H), 5.32 (br, 1H), 4.22 (t, J = 7.0 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 1.84 (quin, J = 7.0 Hz, 2H), 1.61 (br, 2H), 1.50 (br, 2H), 1.27 (br, 54H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 177.8, 163.1, 161.3, 160.0, 149.8, 149.6, 149.0, 148.3, 144.3, 142.5, 142.3, 142.1, 141.9, 140.4, 135.3, 135.0, 134.6, 134.1, 133.4, 132.5, 132.0, 131.8, 131.7, 131.2, 130.9, 130.2, 128.0, 127.5, 127.4, 127.1, 126.7, 126.7, 126.5, 126.4, 125.2, 124.8, 120.9, 120.8, 119.6, 118.8, 117.6, 114.4, 112.6, 97.5, 84.8, 68.0, 66.9, 29.8, 29.8, 29.7, 29.7, 29.7, 29.7, 29.6, 29.6, 29.6, 29.6, 29.5, 29.5, 29.5, 29.3, 29.2, 29.0, 28.3, 25.9, 25.8 ppm; FTIR-ATR (neat): v 3307, 3056, 2919, 2848, 2203, 1734, 1685, 1594, 1539, 1481, 1338, 1172, 1068, 994 cm⁻¹; HRMS (ESI⁺) calcd. for C₁₄₉H₁₃₀O₁₂N₁₄Zn₂ *m/z* 1219.4289 M²⁺, found *m/z* 1219.4273.



Scheme S2. Synthesis of monomer 1b.



Synthesis of monomer 1b:

To a solution of **6** (36 mg, 18 μ mol) in chloroform (4.5 mL), zinc acetate (30 mg, 0.16 mmol) in ethanol (2.0 mL) was added. After being stirred for 1 h at room temperature, the reaction mixture was extracted with chloroform. The organic layer was washed with water and saturated aqueous NaCl, and dried over anhydrous Na₂SO₄. The chloroform was removed under reduced pressure to yeild **1b** as a purple solid (37 mg, 17 μ mol) in 94% yield.

M.p. > 300 °C; ¹H NMR (300 MHz, CDCl₃): δ ppm; 9.35 (br, 2H), 8.90 (m, 8H), 8.75 (br, 8H), 8.36 (br, 2H), 8.20 (m, 6H), 8.06 (br, 8H), 7.79 (br, 2H), 7.37–7.76 (m, 22H), 6.82 (br, 2H), 6.60 (br, 2H), 4.00 (t, *J* = 6.8 Hz, 2H), 3.87 (br, 2H), 1.99 (s, 3H), 1.77 (m, 2H), 1.58 (m, 2H), 1.19–1.56 (br, 56H) ¹³C NMR (75 MHz, CDCl₃): δ 171.2, 160.4, 159.6, 150.1, 149.9, 149.5, 146.6, 143.4, 142.9, 142.7, 134.8, 134.5, 134.2, 132.9, 132.0, 131.9, 131.4, 127.3, 127.2, 126.9, 126.5, 126.4, 125.4, 124.5, 121.1, 120.9, 119.4, 118.8, 113.8, 111.7, 96.5, 83.5, 67.9, 64.6, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.2, 29.1, 28.5, 26.1, 25.9, 20.9 ppm; FTIR-ATR (neat): *v* 3319, 3052, 2920, 2848, 2202, 1639, 1587, 1523, 1480, 1338, 1246, 1067, 994 cm⁻¹; HRMS (ESI⁺) calcd. for C₁₃₇H₁₂₉O₅N₁₁Zn₂*m/z* 1067.9375 M²⁺, found *m/z* 1067.9351.



Scheme S3. Synthesis of linker 4.



Synthesis of linker 4:

To a solution of 7 (100 mg, 0.15 mmol) and CuI (2.8 mg, 15 µmol) in THF (4 mL) was added diisopropylamine (100 µL, 0.71 mmol) under an argon atmosphere. After being stirred for 15 minutes at room temperature, **8** (39 mg, 0.18 mmol) and PdCl₂(PPh₃)₂ (5.2 mg, 7.4 µmol) were added to the resultant solution. After being stirred for 2 h at room temperature under an argon atmosphere in the dark, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with saturated aqueous NH₄Cl and saturated aqueous NaCl, and dried over anhydrous Na₂SO₄. The ethyl acetate was removed under reduced pressure. The residue was dissolved in dry CH₂Cl₂ (30 mL). To the resulting dry CH₂Cl₂ solution was added DMAP (230 mg, 1.9 mmol) and acetic anhydride (140 µL, 1.5 mmol) at 0 °C. After being stirred for 5 h at room temperature under an argon atmosphere, the reaction mixture was diluted with CH₂Cl₂. The organic layer was washed with 1.0 mol L⁻¹ aqueous hydrochloric acid, saturated aqueous NaHCO₃, and saturated aqueous NaCl. The organic layer was dried over Na₂SO₄ and concentrated *in vacuo*. The crude product was purified by column chromatography on silica-gel (CH₂Cl₂ : EtOAc = 19 : 1) to give desired product **4** as a white solid (100 mg, 0.12 mmol) in 83% yield for two steps.

M.p. 110-113 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.33 (s, 2H), 7.51 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.05 (t, J = 6.8 Hz, 2H), 4.03 (s, 6H), 3.99 (t, J = 6.6, 2H), 2.04 (s, 3H), 1.80 (quin, J = 6.8 Hz, 2H), 1.61 (m, 3H), 1.46 (m, 2H), 1.25 (br, 54H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ 171.3, 164.8, 160.5, 148.3, 135.0, 133.8, 129.4, 114.8, 113.0, 97.7, 84.5, 68.2, 64.7, 53.3, 29.7, 29.7, 29.6, 29.6, 29.6, 29.6, 29.5, 29.4, 29.2, 29.1, 28.6, 26.0, 25.9, 21.0 ppm; FTIR-ATR (neat): v 2915, 2848, 2215, 1731, 1715, 1595, 1513, 1473, 1444, 1372, 1289, 1248, 1106, 1039, 984 cm⁻¹; HRMS (ESI⁺) calcd. for C₅₁H₈₀O₇N *m/z* 818.5929 M⁺, found *m/z* 818.5939.



Figure S1. ¹H and ¹³C NMR spectra of **1a** in chloroform- d_1 .



Figure S2. ¹H and ¹³C NMR spectra of **1b** in chloroform- d_1 .



Figure S3. ¹H and ¹³C NMR spectra of **4** in chloroform- d_1 .



Figure S4. Cyclic voltammograms of (a) **2** (0.21 mmol L^{-1}) and (b) **4** (0.30 mmol L^{-1}) at 298 K in dichloromethane TBAPF₆ solution (0.10 mol L^{-1}). Potential vs. Fc/Fc⁺. Scan rate: 0.1 V s⁻¹.



Figure S5. Differential pulse voltammograms of **1a** (0.23 mmol L^{-1}) (solid line) and **2** (0.32 mmol L^{-1}) (dashed line) at 298 K in dichloromethane TBAPF₆ solution (0.10 mol L^{-1}). Potential vs. Fc/Fc⁺.



Figure S6. Cyclic voltammograms of **1c** (0.29 mmol L^{-1}) at 298 K in dichloromethane TBAPF₆ solution (0.10 mol L^{-1}). Potential vs. Fc/Fc⁺. Scan rate: 0.1 V s⁻¹.



Figure S7. ESR spectra of (a) a mixture of **2** (0.20 mmol L⁻¹) and BAHA (0.20 mmol L⁻¹) at 298 K in 1,2-dichloroethane, (b) a mixture of **3** (0.75 mmol L⁻¹) and CC (0.75 mmol L⁻¹) at 80 K in 1,2-dichloroethane. The g_{iso} values calculated are (a) 2.0030 and (b) 2.0042.



Figure S8. UV-vis-NIR absorption spectra of (a) **2** ($4.0 \times 10^{-5} \text{ mmol } \text{L}^{-1}$) (black trace) and a mixture of **2** ($4.0 \times 10^{-5} \text{ mmol}$ L⁻¹) and BAHA ($8.0 \times 10^{-5} \text{ mmol } \text{L}^{-1}$) (blue trace), and (b) **3** ($1.0 \times 10^{-4} \text{ mmol } \text{L}^{-1}$) (black trace) and a mixture of **3** $1.0 \times 10^{-4} \text{ mmol } \text{L}^{-1}$) and CC ($1.0 \times 10^{-4} \text{ mmol } \text{L}^{-1}$) (red trace) at 298 K in 1,2-dichloroethane.



Figure S9. ¹H NMR spectra of (a) **1a** (1.0 mmol L⁻¹), (b) a mixture of **1a** (1.0 mmol L⁻¹) and BAHA (4.0 mmol L⁻¹), and (c) a mixture of **1a** (1.0 mmol L⁻¹) and CC (2.0 mmol L⁻¹) in chloroform- d_1 .



Figure S10. The ¹H NMR signal decay, showing aliphatic peaks of **1a** (5.0 mmol L^{-1} in 1,2-dichloroethane-*d*₄) as a representative example, as a function of *G* (a-n: 3, 67, 131, 195, 259, 323, 387, 451, 515, 563, 611, 675, 739, 803 mT) for the determination of the diffusion coefficient shown in Fig. 4a.

Table S1. Summary of Ds (10⁻¹⁰ m² s⁻¹) of **1a** in chloroform- d_1 and 1,2-dichloroethane- d_4 in various concentrations. The plot is shown in Fig. 4b.

(mmol L ⁻¹)	1	3	5	7	10	15	20	25	31
1a in chloroform- <i>d</i> ₁	3.9(1)	3.52(5)	3.14(5)	2.92(6)	2.53(3)	2.21(1)	1.83(2)	1.56(2)	1.29(1)
1a in 1,2-dichloroethane-d ₄	2.70(2)	2.30(1)	1.93(2)	1.70(1)	1.51(1)	1.34(1)	-	-	-



Figure S11. Plots of diffusion coefficients in chloroform- d_1 of 1a versus concentration.

Table S2. Summary of Ds (10⁻¹⁰ m² s⁻¹) of **1a** in the absence and presence of redox reagents and **1b** in 1,2-dichloroethaned₄ at 5.0 mmol L⁻¹. The plot is shown in Fig. 4c.

Entry	Porphyrin	Reagent	Equivalent of reagent	D	
1				1.93(2)	
2		ВАНА	1	2.29(3)	
3	1a	БАПА	2	2.59(1)	
4		<u> </u>	0.5	2.46(1)	
5		00	1	2.67(3)	
6	1b			2.68(2)	



Figure S12. AFM image of spin-coated thin film of (a) **1a**, (b) a 1:2 mixture of **1a** and BAHA, and (c) a 1:1 mixture of **1a** and CC prepared from their 1,2-dichloroethane solution on HOPG. The scale bars denote 100 nm.

References

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