Supplementary Information

Thiophene-fused dithiaoctaphyrins: $\pi$-system switching between cross-conjugated and macrocyclic $\pi$-networks
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1. Experimental Section

Instrumentation and Materials.

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Silica-gel column chromatography was performed with UltraPure Silica Gel (230-400 mesh, SiliCycle) unless otherwise noted. Thin-layer chromatography (TLC) was performed with Silica gel 60 F254 (Merck). UV/Vis/NIR absorption spectra were measured with a Perkin-Elmer Lambda 900 UV/vis/NIR spectrometer. Steady-state fluorescence spectra were obtained by a HORIBA Nanolog spectrometer. $^1$H and $^{13}$C NMR spectra were recorded with a JEOL EX-400 spectrometer (operating at 399.65 MHz for $^1$H and 100.40 MHz for $^{13}$C) by using the residual solvent as the internal reference for $^1$H (CDCl$_3$: $\delta = 7.26$ ppm) and $^{13}$C (CDCl$_3$: $\delta = 77.16$ ppm) or tetramethylsilane as the internal reference for $^1$H and $^{13}$C ($\delta = 0.00$ ppm). High-resolution mass spectra (HRMS) were measured on a Thermo Fischer Scientific EXACTIVE spectrometer (APCI and ESI).
2. Synthesis

3,5-Diiododithienothiophene (2),[S1] N-Boc-2-pyrrolylboronic acid (3),[S2] and 2,5-bis[α-hydroxy-α-(4-methylphenyl)]methylpyrrole (6a),[S3] were prepared according to literature.

3,5-Di(N-Boc-pyrrol-2-yl)dithienothiophene (4):
To a mixture of dithienothiophene 2 (30.0 mg, 70 µmol), N-Boc-pyrrolylboronic acid 3 (44.0 mg, 210 µmol), Pd(OAc)$_2$ (0.68 mg, 3.0 µmol), SPhos (2.18 mg, 5.3 µmol), and K$_3$PO$_4$ (57.3 mg, 270 µmol) was added n-BuOH (1.0 mL) under an argon atmosphere. The reaction mixture was stirred at 50 °C for 12 h and subsequently allowed to cool to room temperature. The mixture was poured into H$_2$O (20 mL) and the product was extracted with EtOAc (20 mL×4). The combined organic layer was dried over Na$_2$SO$_4$. After the solvent was removed, the residue was purified by silica-gel column chromatography (n-hexane:CH$_2$Cl$_2$ = 1:1) to give 4 (24.3 mg, 50 µmol, 69%) as a dark yellow solid.

4: $^1$H NMR (399.65 MHz, CDCl$_3$, 25 °C): δ = 7.45 (s, 2H, thienyl-H), 7.39 (dd, $J = 2.0$ Hz, $J = 1.5$ Hz, 2H, pyrrole-H), 6.42 (dd, $J = 2.0$ Hz, $J = 1.5$ Hz, 2H, pyrrole-H), 6.24 (t, $J = 3.4$ Hz, 2H, pyrrole-H), and 1.38 (s, 18H, t-Bu) ppm; $^{13}$C NMR (100.40 MHz, CDCl$_3$, 25 °C): δ = 148.8, 142.7, 135.3, 124.1,
123.5, 121.4, 117.1, 114.1, 110.8, 83.9, and 27.6 ppm. HRMS (ESI) calcd. for C\textsubscript{26}H\textsubscript{26}N\textsubscript{2}O\textsubscript{4}S\textsubscript{3}Na [M+Na]\textsuperscript{+} 549.0947; found 549.0942.

3,5-Di(pyrrol-2-yl)dithienothiophene (5):
Dithienothiophene 4 (215 mg, 0.41 mmol) and K\textsubscript{2}CO\textsubscript{3} (170 mg, 1.23 mmol) were added to a 3:1 mixture of MeOH and H\textsubscript{2}O (8.0 mL) under an argon atmosphere. The mixture was refluxed for 2 h. The mixture was cooled to room temperature and H\textsubscript{2}O (10 mL) was added to the mixture. The product was extracted with CH\textsubscript{2}Cl\textsubscript{2} (20 mL×4). The combined organic layer was dried over Na\textsubscript{2}SO\textsubscript{4}. After the solvent was removed, the residue was purified by silica-gel column chromatography (CH\textsubscript{2}Cl\textsubscript{2}) to give 5 (122.7 mg, 0.37 mmol, 92\%) as a yellow solid.

5: \textsuperscript{1}H NMR (399.65 MHz, CDCl\textsubscript{3}, 25 °C): δ = 8.35 (s, 2H, NH), 7.29 (s, 2H, thienyl-H), 6.88 (d, \textit{J} = 2.2 Hz, 2H, pyrrole-H), 6.49 (d, \textit{J} = 2.2 Hz, 2H, pyrrole-H), and 6.35 (dd, \textit{J} = 2.4 Hz, \textit{J} = 2.9 Hz, 2H, pyrrole-H) ppm; \textsuperscript{13}C NMR (100.40 MHz, CDCl\textsubscript{3}, 25 °C): δ = 136.4, 136.0, 125.0, 122.4, 119.0, 110.7, 110.5, and 107.8 ppm. HRMS (APCI) calcd. for C\textsubscript{16}H\textsubscript{11}N\textsubscript{2}S\textsubscript{3} [M+H]\textsuperscript{+} 327.0079; found 327.0070.

2-(3,5-Di-tert-butylphenyl)-1,3-benzoxathiolium tetrafluoroborate (8b):
A mixture of o-mercaptophenol (878 mg, 7.00 mmol), 3,5-di-tert-butylbenzoic acid (1.64 g, 7.00 mmol) and phosphorus oxychloride (4.3 mL) was heated at 110 ºC for 15 min, and then allowed to cool to room temperature. Tetrafluoroboric acid-ether complex (50% in ether, 2.9 mL) and dry Et\textsubscript{2}O (60 mL) were successively added and the tetrafluoroborate was precipitated. The product was collected by filtration, washed several times with dry Et\textsubscript{2}O, and dried to give 8b (2.03 g, 4.9 mmol, 70 %) as a yellow solid.

8b: \textsuperscript{1}H NMR (399.65 MHz, TFA-d\textsubscript{1}, 25 °C): δ = 8.83 (s, 1H, para-ArH), 8.29 (s, 2H, ortho-ArH), 8.22 (d, \textit{J} = 7.8 Hz, 2H, benzoxathioliyl-H), 8.18 (d, \textit{J} = 7.8 Hz, 1H, benzoxathioliyl-H), 7.98 (d, \textit{J} = 7.7 Hz, 1H, benzoxathioliyl-H), 7.88 (d, \textit{J} = 7.7 Hz, 1H, benzoxathioliyl-H), and 1.45 (s, 18H, t-Bu) ppm; \textsuperscript{13}C NMR (100.40 MHz, TFA-d\textsubscript{1}, 25 °C): δ = 157.9, 140.1, 134.9, 132.4, 127.0, 126.4, 125.1, 120.9, 118.1, 115.3, 112.4, and 31.7 ppm. HRMS (APCI, positive) calcd. for C\textsubscript{21}H\textsubscript{25}NOS [M–BF\textsubscript{4}]\textsuperscript{+} 325.1621; found 325.1611.

2,5-Bis[α-(3,5-di-tert-butylphenyl)-α-(1,3-benzoxathioliyl)]pyrrole (9b):
Tetrafluoroborate 8b (14.8 g, 35.8 mmol) was added to a solution of pyrrole (1.13 g, 16.8 mmol), dry pyridine (2.9 mL) and dry acetonitrile (29.2 mL) in one portion with stirring. The reaction was exothermic and the salt dissolved at once. The mixture was stirred for 30 minute at room
temperature. The reaction was quenched with H2O (140 mL) and the product was extracted with CH2Cl2 (300 mL x 3). The combined organic layer was washed with aqueous sodium hydroxide solution (5%, 140 mL) and with water, and dried over Na2SO4. After the solvent was removed, the residue was purified by silica-gel column chromatography (n-hexane:CH2Cl2 = 2:1) to give 9b (8.23 g, 11.5 mmol, 68%) as a white solid.

9b: 1H NMR (399.65 MHz, CDCl3, 25 °C): δ = 9.04 (s, 1H, NH), 7.44 (d, J = 3.9 Hz, 4H, ortho-ArH), 7.35 (d, J = 3.9 Hz, 2H, para-ArH), 7.04 (d, J = 7.8 Hz, 2H, benzoxathiolyl-H), 7.01 (d, J = 7.8 Hz, 2H, benzoxathiolyl-H), 6.88 (t, J = 7.8 Hz, 2H, benzoxathiolyl-H), 5.81 (d, J = 2.4 Hz, 2H, pyrrole-H), and 1.28 (s, 36 H, t-Bu) ppm; 13C NMR (100.40 MHz, CDCl3, 25 °C): δ = 154.2, 150.1, 140.7, 133.5, 126.1, 122.7, 122.5, 121.8, 120.9, 111.5, 111.2, 110.8, 98.7, 34.9, and 31.4 ppm. HRMS (ESI) calcd. for C46H54NO2S2 [M+H]+ 716.3590; found 716.3577.

2,5-Bis(3,5-di-tert-butylbenzoyl)pyrrole (10b):

Pyrrole 9b (2.18 g, 3.0 mmol) was added to a mixture of mercury(II) oxide (1.32 g, 6.0 mmol) in THF (15 mL) and 42% aqueous tetrafluoroboric acid (2.3 mL). The reaction was exothermic, and mercury(II) oxide dissolved at once. The mixture was heated at 50 ºC for 3 h. The reaction mixture was diluted with CH2Cl2 (500 mL), and then the reaction mixture was washed successively with 10% potassium iodide solution (50 mL x 2), 5% sodium hydroxide solution (50 mL), and dried over Na2SO4. After the solvent was removed, pure 10b was obtained (1.44 g, 2.9 mmol, 95%) as a white solid.

10b: 1H NMR (399.65 MHz, CDCl3, 25 °C): δ = 10.32 (s, 1H, NH), 7.78 (s, 4H, ortho-ArH), 7.68 (s, 2H, para-ArH), 6.87 (d, J = 2.2 Hz, 2H, pyrrole-H), and 1.39 (s, 36 H, t-Bu) ppm; 13C NMR (100.40 MHz, CDCl3, 25 °C): δ = 186.3, 151.2, 137.0, 134.3, 126.8, 123.5, 118.1, 35.0, and 31.6 ppm. HRMS (ESI) calcd. for C34H46NO2 [M+H]+ 500.3523; found 500.3511.

2,5-Bis[a-hydroxy-a-(3,5-di-tert-butylphenyl)]methylpyrrole (6b):

To a stirred solution of pyrrole 10b (129 g, 0.26 mmol) in MeOH (15 ml) and THF (15 ml) was carefully added NaBH4 (490 mg, 13.0 mmol) and the mixture was stirred for 30 min. After the solvent was removed, water (30 mL) was added to the residue and the resulting suspension was extracted with CH2Cl2. The combined organic layer was washed with water (30 mL x 3), and dried over Na2SO4. The solvent was removed to afford pyrrole 6b (129.5 mg, 99%) as a white solid, which was used immediately in the next step without further purification.
Thiophene-fused meso-(4-methylphenyl)-41,45-dithiaoctaphyrin (1a):
Trifluoroacetic acid (1.1 µL, 14 µmol) was added to the mixture of 5 (15.3 mg, 46 µmol) and 6a (14.0 mg, 46 µmol) in dry CH₂Cl₂ (105 mL) and the reaction mixture was stirred for 4 h at room temperature under argon atmosphere. After addition of DDQ (21.0 mg, 92 µmol), the mixture was stirred for 1 h. The reaction mixture was passed through an alumina column using CH₂Cl₂ as eluent. After the solvent was removed, the residue was separated by silica-gel column chromatography (CH₂Cl₂) to give 1a (6.6 mg, 11.1 µmol, 24%) as a dark green solid. Single crystals suitable for X-ray crystallographic analysis were obtained by vapor diffusion of 2-propanol into a 1,2-dichloroethane solution of 1a.
1a: ¹H NMR (399.65 MHz, CDCl₃, 25 °C): δ = 12.88 (s, 2H, NH), 7.58 (s, 2H, thieryl-H), 7.42 (d, J = 7.8 Hz, 4H, Ar-H), 7.26 (br, 4H, Ar-H), 7.17 (br, 8H, Ar-H), 7.06 (d, J = 4.4 Hz, 2H, β-H), 7.01 (d, J = 4.9 Hz, 4H, β-H), 6.65 (s, 2H, thieryl-H), 6.59 (d, J = 4.9 Hz, 2H, β-H), 6.42 (d, J = 4.9 Hz, 2H, β-H), 6.38 (m, 2H, β-H), 6.36 (m, 2H, β-H), 2.50 (s, 6H, CH₃), and 2.47 (s, 6H, CH₃). UV/vis (CH₂Cl₂): λ (ε, M⁻¹ cm⁻¹) = 354 (37000), 414 (54000), 439 (56000), 555 (11000), 598 (12000), 649 (14000), and 709 (7000) nm. HRMS (ESI) calcd. for C₇₂H₄₂N₆S₆ [M+H⁺] 1187.2181; found 1187.2170. Due to the low solubility, we could not obtain a ¹³C NMR spectrum in a sufficient S/N ratio.

Thiophene-fused meso-(3,5-di-tert-butylphenyl)-41,45-dithiaoctaphyrin (1b):
Trifluoroacetic acid (5.9 µL, 77 µmol) was added to a mixture of 5 (84.6 mg, 0.26 mmol) and 6b (129.5 mg, 0.26 mmol) in dry CH₂Cl₂ (60 mL) and the reaction mixture was stirred for 5 h at room temperature under argon atmosphere. After addition of DDQ (117.9 mg, 0.52 mmol), the mixture was stirred for 1 h. The reaction mixture was passed through an alumina column using CH₂Cl₂ as eluent. After the solvent was removed, the residue was separated by silica-gel column chromatography (CH₂Cl₂) to give 1b (6.0 mg, 3.7 mmol, 2.9%) as a dark green solid.
1b: ¹H NMR (399.65 MHz, CDCl₃, 25 °C): δ = 12.80 (s, 2H, NH), 7.57 (s, 2H, thieryl-H), 7.50 (t, J = 1.9 Hz, 2H, para-ArH), 7.41 (t, J = 1.9 Hz, 2H, para-ArH), 7.37 (dd, 4H, J = 1.4 Hz, J = 1.9 Hz ortho-ArH), 7.25 (m, 4H, ortho-ArH), 7.09 (d, J = 4.4 Hz, 2H, β-H), 7.01 (d, J = 4.4 Hz, 2H, β-H), 6.67 (s, 2H, thieryl-H), 6.59 (d, J = 4.4 Hz, 2H, β-H), 6.45 (d, J = 4.4 Hz, 2H, β-H), 6.38 (d, J = 4.4 Hz, 2H, β-H), 6.30 (d, J = 4.4 Hz, 2H, β-H), 1.34 (s, 18H, t-Bu), 1.32 (s, 18H, t-Bu), 1.26 (s, 18H, t-Bu), and 1.22 (s, 18H, t-Bu) ppm; ¹³C NMR (100.40 MHz, CDCl₃, 25 °C): δ = 162.6, 161.6, 156.3, 153.2, 149.8, 149.6, 149.5, 145.7, 140.9, 140.1, 138.5, 138.2, 137.5, 137.1, 136.7, 134.8, 130.5, 127.8, 127.7, 127.0, 126.2, 126.1, 125.4, 125.2, 125.0, 122.7, 122.3, 121.8, 114.5, 34.8, 34.7, 31.5, and 31.4 ppm. UV/vis (CH₂Cl₂): λ (ε, M⁻¹ cm⁻¹) = 354 (40000), 414 (67000), 439 (75000), 563 (12000), 609 (15000), 653 (18000), 709
Thiophene-fused meso-(3,5-di-tert-butylphenyl)-41,45-dithiaoctaphyrin 41,45-dioxide(7):
m-Chloroperbenzoic acid (m-CPBA) (5.1 mg of 75% pure reagent, 6.8 mg, 29.0 µmol) was added to a stirred solution of 1b (20.8 mg, 13.2 µmol) in 15 mL of CH₂Cl₂ at 0 °C in one portion. The reaction mixture was stirred for 30 min at 0 °C and at room temperature for 30 min. The reaction was quenched with saturated aqueous NaHCO₃ solution. The organic layer was separated, and the aqueous layer was extracted with Et₂O. The combined organic layer was dried over MgSO₄. After the solvent was removed, the residue was purified by silica-gel column chromatography (CH₂Cl₂) to give 7 (19.4 mg, 12.0 µmol, 91%) as light green crystals.

7: H NMR (399.65 MHz, CDCl₃, 25 °C): δ = 12.36 (s, 2H, NH), 7.53 (d, J = 1.8 Hz, 4H, ortho-ArH), 7.48 (s, 2H, thienyl-H), 7.47 (m, 2H, para-ArH), 7.38 (d, J = 1.8 Hz, 4H, ortho-ArH), 7.33 (m, 2H, para-ArH), 7.08 (dd, J = 4.9 Hz, J = 3.1 Hz, 4H, β-H), 6.96 (d, J = 4.3 Hz, 2H, β-H), 6.62 (d, J = 4.3 Hz, 2H, β-H), 6.53 (s, 2H, thienyl-H), 6.49 (m, 4H, β-H), 1.38 (s, 18H, t-Bu), 1.38 (s, 18H, t-Bu), 1.32 (s, 18H, t-Bu) ppm; C NMR (100.40 MHz, CDCl₃, 25 °C): δ = 160.4, 159.5, 153.7, 152.7, 150.7, 149.9, 149.8, 149.7, 149.6, 141.7, 141.5, 140.8, 140.6, 140.3, 139.9, 138.7, 138.6, 137.8, 137.6, 136.7, 136.3, 126.9, 126.6, 126.1, 125.7, 125.1, 124.4, 122.7, 122.4, 115.3, 34.9, 34.8, 31.5, and 31.4 ppm.

UV/vis (CH₂Cl₂): λ (ε, M⁻¹cm⁻¹) = 329 (49000), 411 (103000), 458 (63000), 589 (18000), 633 (30000), 682 (22000) nm. Fluorescence (CH₂Cl₂, λₑx = 650 nm): λₑmax = 754 nm. HRMS (APCI) calcd. for C₁₀₀H₁₀₀N₆O₂S₆ [M+H]^+ 1611.6461; found 1611.6433.
3. High-Resolution Mass Spectra

Figure S1. Observed (top) and simulated (bottom) high-resolution mass spectra of a) 4, b) 5, c) 8b, d) 9b, e) 10b, f) 1a, g) 1b, and h) 7.
4. NMR Spectra

Figure S2. (a) $^1$H and (b) $^{13}$C NMR spectra of 4 at 25 °C in CDCl$_3$. Peaks marked with * arise from residual solvents.
Figure S3. (a) $^1$H and (b) $^{13}$C NMR spectra of 5 at 25 °C in CDCl$_3$. Peaks marked with * arise from residual solvents.
Figure S4. (a) $^1$H and (b) $^{13}$C NMR spectra of 8b at 25 °C in TFA-$d_1$. Peaks marked with * arise from residual solvents.
Figure S5. (a) $^1$H and (b) $^{13}$C NMR spectra of 9b at 25 °C in CDCl$_3$. Peaks marked with * arise from residual solvents.
Figure S6. (a) $^1$H and (b) $^{13}$C NMR spectra of 10b at 25 °C in CDCl$_3$. Peaks marked with * arise from residual solvents.
Figure S7. $^1$H NMR spectrum of 1a at 25 °C in CDCl$_3$. Peaks marked with * arise from residual solvents.
Figure S8. (a) $^1$H and (b) $^{13}$C NMR spectra of 1b at 25 °C in CDCl$_3$. Peaks marked with * arise from residual solvents.
Figure S9. (a) $^1$H and (b) $^{13}$C NMR spectra of 7 at 25 °C in CDCl$_3$. Peaks marked with * arise from residual solvents.
5. X-Ray Crystallographic Details

Figure S10. X-Ray crystal structure of 1a: (a) top view and (b) side view. Thermal ellipsoids represent 50% probability. Minor disorder component and solvent molecules are omitted for clarity. (c) Detailed structural data of 1a. Selected bond lengths in Å (numbers in green) and bond angles in deg (numbers in blue) are indicated.
6. Optical Properties

*Figure S11.* UV/Vis absorption spectra of 1a (black), 1b (red), and 7 (blue) in CH$_2$Cl$_2$.

*Figure S12.* Fluorescence spectra of 1b (red) and 7 (blue) in CH$_2$Cl$_2$. $\lambda_{ex} = 650$ nm.
7. Electrochemical Properties

Figure S13. Cyclic voltammograms (black) and differential pulse voltammetry (DPV) curves (red) of octaphyrins a) 1b and b) 7. Redox potentials were determined by DPV. Solvent: CH$_2$Cl$_2$; scan rate: 0.05 V s$^{-1}$; working electrode: glassy carbon; reference electrode: Ag/Ag$^+$ (0.01 M AgNO$_3$); electrolyte: 0.1 M $n$-Bu$_4$NPF$_6$. Peaks marked with * arise from oxygen. Ar = 3,5-(t-Bu)$_2$C$_6$H$_3$. 
8. DFT Calculations

All calculations were carried out using the Gaussian 09 program.\textsuperscript{[54]} The calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke’s three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional) level,\textsuperscript{[55,56]} employing a basis set 6-31G(d,p) for C, H, N, O, and S. Excitation energies and oscillator strengths for the optimized structures were calculated with the TD-SCF method at the B3LYP/6-31G(d,p) level.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_s14.png}
\caption{Selected Kohn-Sham orbitals of 1b and 7 on the optimized structures.}
\end{figure}
**Figure S15.** Optimized structural data of (a) 1b and (b) 7. The conjugated 36$\pi$-electron network (green) and selected bond lengths in Å are indicated. Averaged C–C bond lengths are calculated from red numbers for single bonds and blue numbers for double bonds. C–C bond length alternations (BLAs) are calculated by the following equation: BLA = $r_1 - r_2$. 
**Table S1.** Selected excitation energies and oscillator strengths of 1b and 7 calculated by the TD-DFT method.

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9. References


