Supplementary Information

Thiophene-fused dithiaoctaphyrins: π-system switching between cross-conjugated and macrocyclic π-networks

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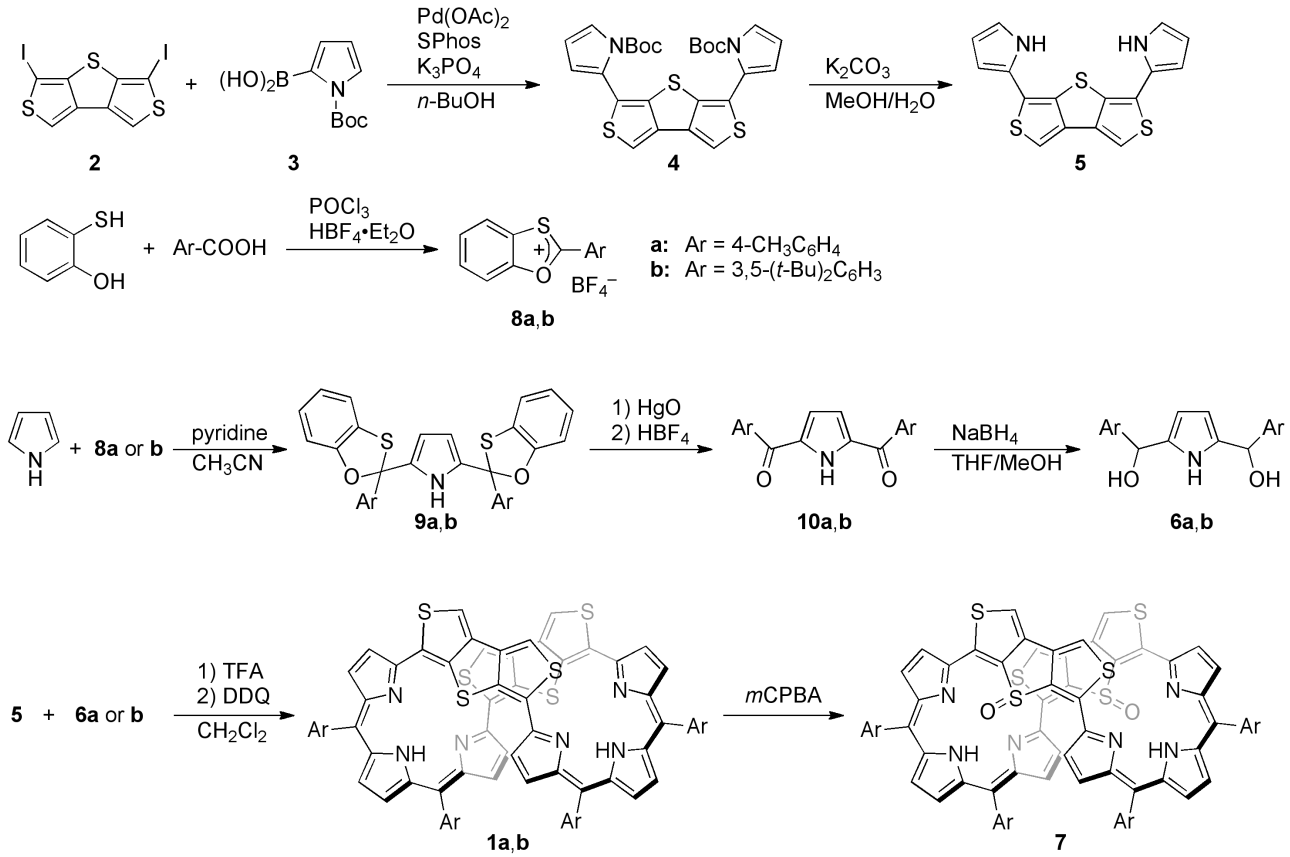
Contents

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 F_{254} (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 ($CDCl_3$: δ = 7.26 ppm) and ^{13}C ($CDCl_3$: δ = 77.16 ppm) or tetramethylsilane as the internal reference for ^{1}H and ^{13}C (δ = 0.00 ppm). High-resolution mass spectra (HRMS) were measured on a Thermo Fischer Scientific EXACTIVE spectrometer (APCI and ESI).

2. Synthesis



Scheme S1. Synthesis of thiophene-fused dithiaoctaphyrins.

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_3PO_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_2O (20 mL) and the product was extracted with EtOAc (20 mL×4). The combined organic layer was dried over Na_2SO_4. After the solvent was removed, the residue was purified by silica-gel column chromatography (*n*-hexane:CH_2Cl_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 $C_{26}H_{26}N_2O_4S_3Na$ $[M+Na]^+$ 549.0947; found 549.0942.

3,5-Di(pyrrol-2-yl)dithienothiophene (5):

Dithienothiophene **4** (215 mg, 0.41 mmol) and K_2CO_3 (170 mg, 1.23 mmol) were added to a 3:1 mixture of MeOH and H_2O (8.0 mL) under an argon atmosphere. The mixture was refluxed for 2 h. The mixture was cooled to room temperature and H_2O (10 mL) was added to the mixture. The product was extracted with CH_2Cl_2 (20 mL×4). The combined organic layer was dried over Na_2SO_4. After the solvent was removed, the residue was purified by silica-gel column chromatography (CH_2Cl_2) to give **5** (122.7 mg, 0.37 mmol, 92%) as a yellow solid.

5: ^{1}H NMR (399.65 MHz, $CDCl_3$, 25 °C): δ = 8.35 (s, 2H, NH), 7.29 (s, 2H, thienyl-H), 6.88 (d, J = 2.2 Hz, 2H, pyrrole-H), 6.49 (d, J = 2.2 Hz, 2H, pyrrole-H), and 6.35 (dd, J = 2.4 Hz, J = 2.9 Hz, 2H, pyrrole-H) ppm; ^{13}C NMR (100.40 MHz, $CDCl_3$, 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 $C_{16}H_{11}N_2S_3$ $[M+H]^+$ 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_2O (60 mL) were successively added and the tetrafluoroborate was precipitated. The product was collected by filtration, washed several times with dry Et_2O, and dried to give **8b** (2.03 g, 4.9 mmol, 70 %) as a yellow solid.

8b: ^{1}H NMR (399.65 MHz, TFA-d_1, 25 °C): δ = 8.83 (s, 1H, *para*-ArH), 8.29 (s, 2H, *ortho*-ArH), 8.22 (d, J = 7.8 Hz, 2H, benzoxathiolyl-H), 8.18 (d, J = 7.8 Hz, 1H, benzoxathiolyl-H), 7.98 (d, J = 7.7 Hz, 1H, benzoxathiolyl-H), 7.88 (d, J = 7.7 Hz, 1H, benzoxathiolyl-H), and 1.45 (s, 18H, *t*-Bu) ppm; ^{13}C NMR (100.40 MHz, TFA-d_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 $C_{21}H_{25}NOS$ $[M–BF_4]^+$ 325.1621; found 325.1611.

2,5-Bis[α-(3,5-di-*tert*-butylphenyl)-α-(1,3-benzoxathiolyl)]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 H_2O (140 mL) and the product was extracted with CH_2Cl_2 (300 mL×3). The combined organic layer was washed with aqueous sodium hydroxide solution (5%, 140 mL) and with water, and dried over Na_2SO_4. After the solvent was removed, the residue was purified by silica-gel column chromatography (*n*-hexane:CH_2Cl_2 = 2:1) to give **9b** (8.23 g, 11.5 mmol, 68%) as a white solid.

9b: ^{1}H NMR (399.65 MHz, $CDCl_3$, 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, 2 H, *para*-ArH), 7.04 (d, J = 7.8 Hz, 2H, benzoxathiolyl-H), 7.01 (d, J = 7.8 Hz, 2H, benzoxathiolyl-H), 6.94 (t, 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; ^{13}C NMR (100.40 MHz, $CDCl_3$, 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 $C_{46}H_{54}NO_2S_2$ $[M+H]^+$ 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 °C for 3 h. The reaction mixture was diluted with CH_2Cl_2 (500 mL), and then the reaction mixture was washed successively with 10% potassium iodide solution (50 mL×2), 5% sodium hydroxide solution (50 mL), and dried over Na_2SO_4. After the solvent was removed, pure **10b** was obtained (1.44 g, 2.9 mmol, 95%) as a white solid.

10b: ^{1}H NMR (399.65 MHz, $CDCl_3$, 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, 36H, *t*-Bu) ppm; ^{13}C NMR (100.40 MHz, $CDCl_3$, 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 $C_{34}H_{46}NO_2$ $[M+H]^+$ 500.3523; found 500.3511.

2,5-Bis[α-hydroxy-α-(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 $NaBH_4$ (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 CH_2Cl_2. The combined organic layer was washed with water (30 mL ×3), and dried over Na_2SO_4. 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 CH_2Cl_2 (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 CH_2Cl_2 as eluent. After the solvent was removed, the residue was separated by silica-gel column chromatography (CH_2Cl_2) 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: ^{1}H NMR (399.65 MHz, $CDCl_3$, 25 °C): δ = 12.88 (s, 2H, NH), 7.58 (s, 2H, thienyl-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, thienyl-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, CH_3), and 2.47 (s, 6H, CH_3). UV/vis (CH_2Cl_2): 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 $C_{72}H_{47}N_6S_6$ $[M+H]^+$ 1187.2181; found 1187.2170. Due to the low solubility, we could not obtain a ^{13}C 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 CH_2Cl_2 (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 CH_2Cl_2 as eluent. After the solvent was removed, the residue was separated by silica-gel column chromatography (CH_2Cl_2) to give **1b** (6.0 mg, 3.7 mmol, 2.9%) as a dark green solid.

1b: ^{1}H NMR (399.65 MHz, $CDCl_3$, 25 °C): δ = 12.80 (s, 2H, NH), 7.57 (s, 2H, thienyl-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, thienyl-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; ^{13}C NMR (100.40 MHz, $CDCl_3$, 25 °C): δ = 162.6, 161.6, 153.6, 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, 123.5, 122.7, 122.3, 121.8, 114.5, 34.8, 34.7, 31.5, and 31.4 ppm. UV/vis (CH_2Cl_2): λ (ε, M^{-1} cm^{-1}) = 354 (40000), 414 (67000), 439 (75000), 563 (12000), 609 (15000), 653 (18000), 709

(10000) nm. HRMS (APCI) calcd. for $C_{100}H_{103}N_6S_6$ $[M+H]^+$ 1579.6563; found 1579.6570.

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 CH_2Cl_2 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 $NaHCO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layer was dried over $MgSO_4$. After the solvent was removed, the residue was purified by silica-gel column chromatography (CH_2Cl_2) to give **7** (19.4 mg, 12.0 μmol, 91%) as light green crystals.
7: ^{1}H NMR (399.65 MHz, $CDCl_3$, 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), 1.33 (s, 18H, *t*-Bu), 1.32 (s, 18H, *t*-Bu), 1.26 (s, 18H, *t*-Bu) ppm; ^{13}C NMR (100.40 MHz, $CDCl_3$, 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 (CH_2Cl_2): λ (ε, $M^{-1}cm^{-1}$) = 329 (49000), 411 (103000), 458 (63000), 589 (18000), 633 (30000), 682 (22000) nm. Fluorescence (CH_2Cl_2, λ_{ex} = 650 nm): λ_{max} = 754 nm. HRMS (APCI) calcd. for $C_{100}H_{103}N_6O_2S_6$ $[M+H]^+$ 1611.6461; found 1611.6433.

3. High-Resolution Mass Spectra

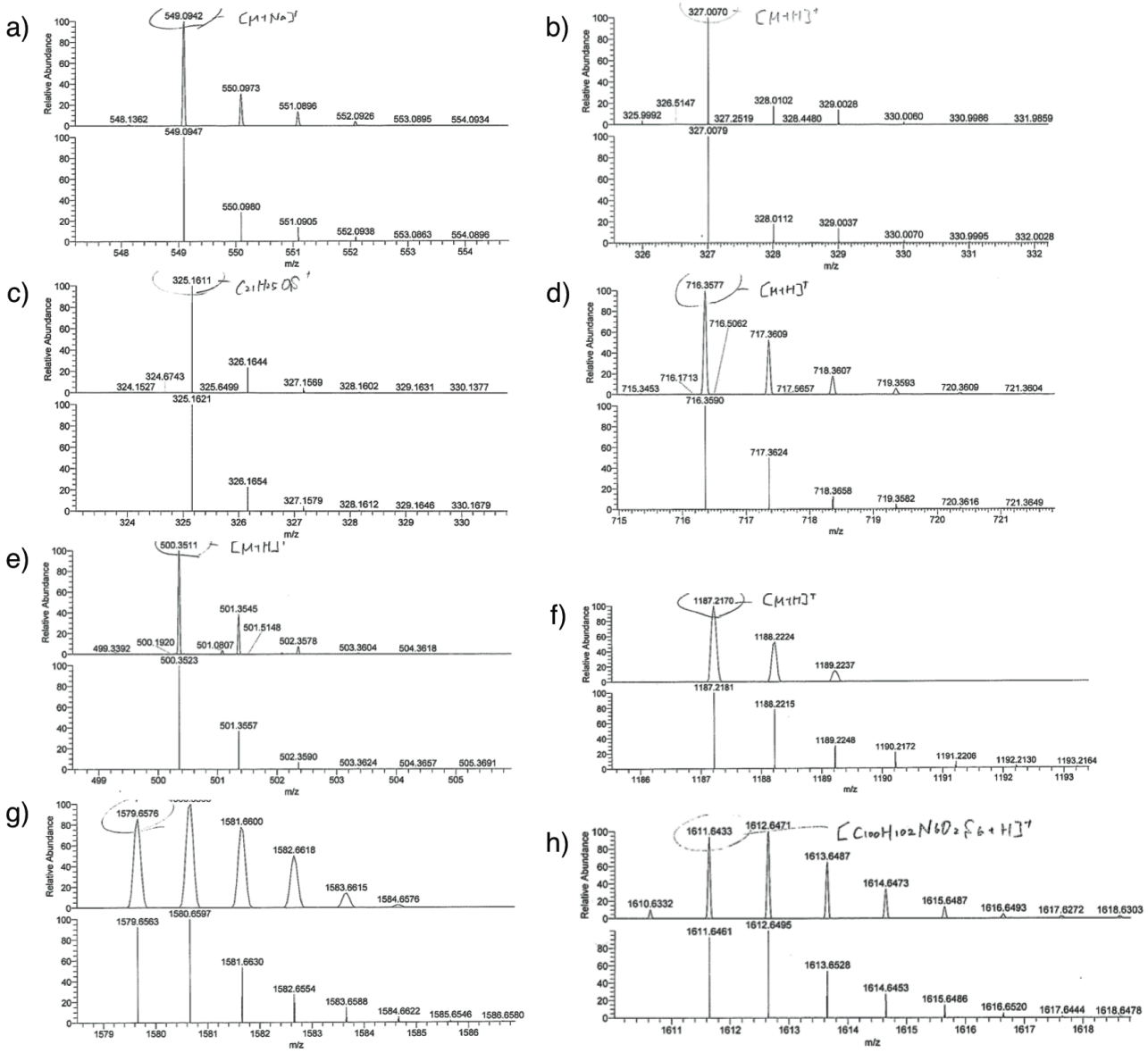


Figure S1. Observed (top) and simulated (bottom) high-resolution mass spectra of a) **4**, b) **5**, c) **8b**, d) **9b**, e) **10b**, f) **1a**, g) **1b**, and h) **7**.

4. NMR Spectra

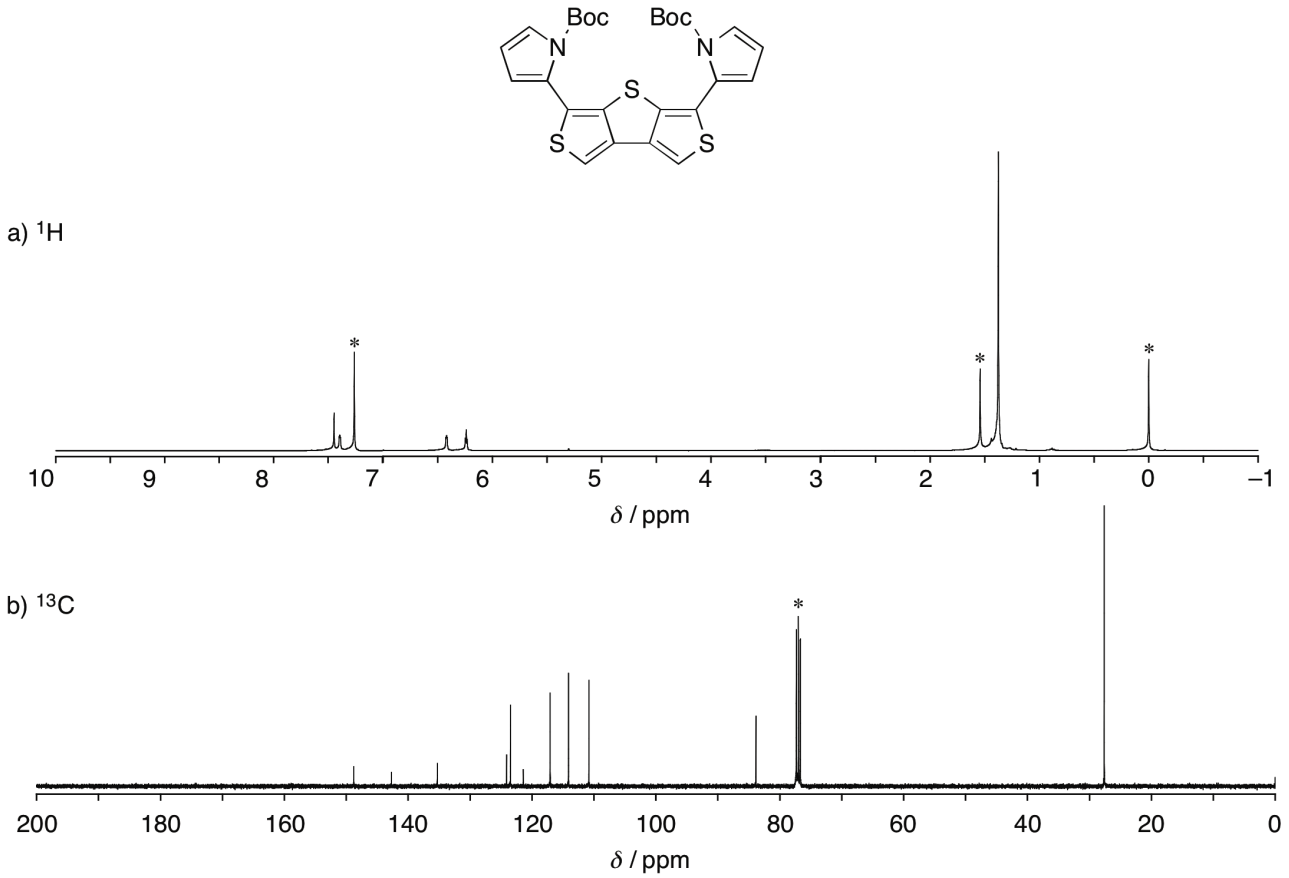


Figure S2. (a) ^{1}H and (b) ^{13}C NMR spectra of **4** at 25 °C in $CDCl_3$. Peaks marked with ∗ arise from residual solvents.

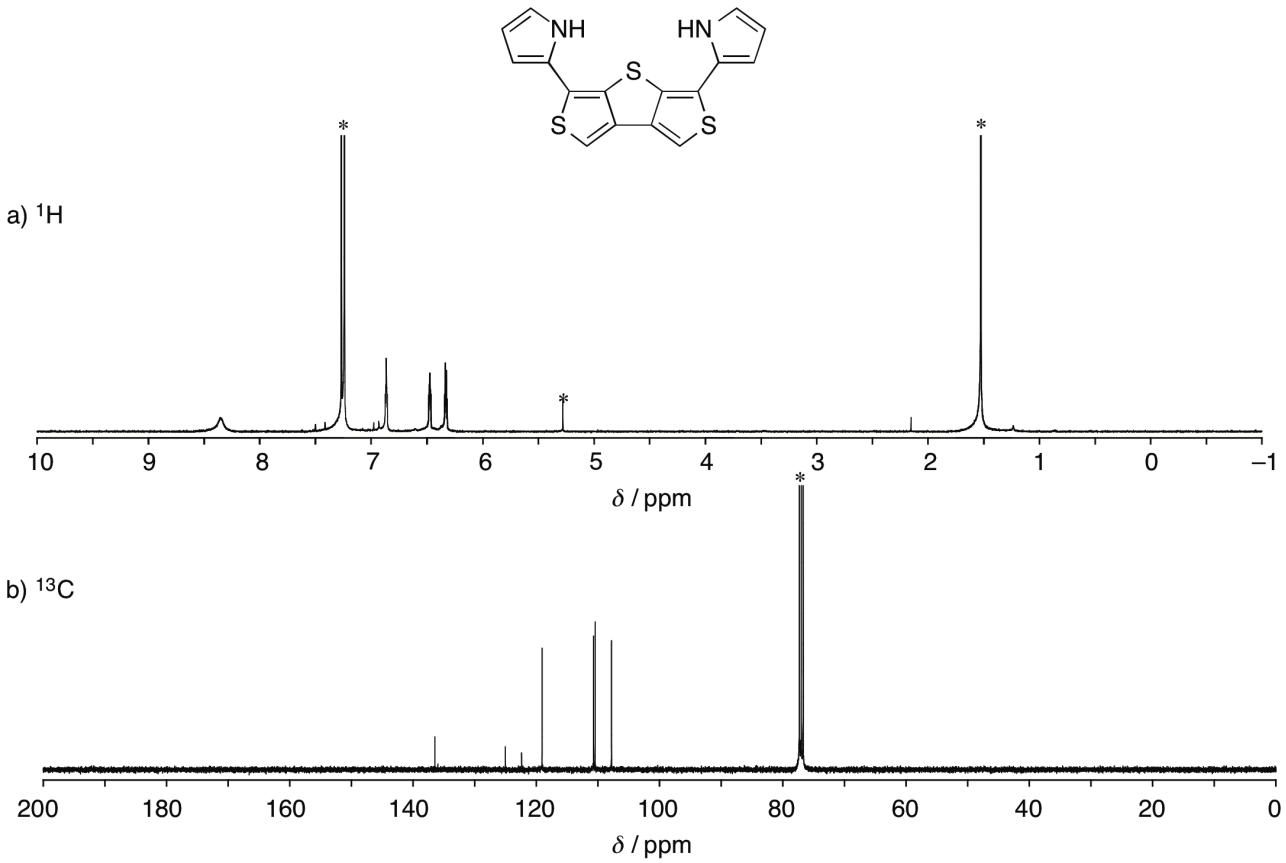


Figure S3. (a) ^{1}H and (b) ^{13}C NMR spectra of **5** at 25 °C in $CDCl_3$. Peaks marked with ∗ arise from residual solvents.

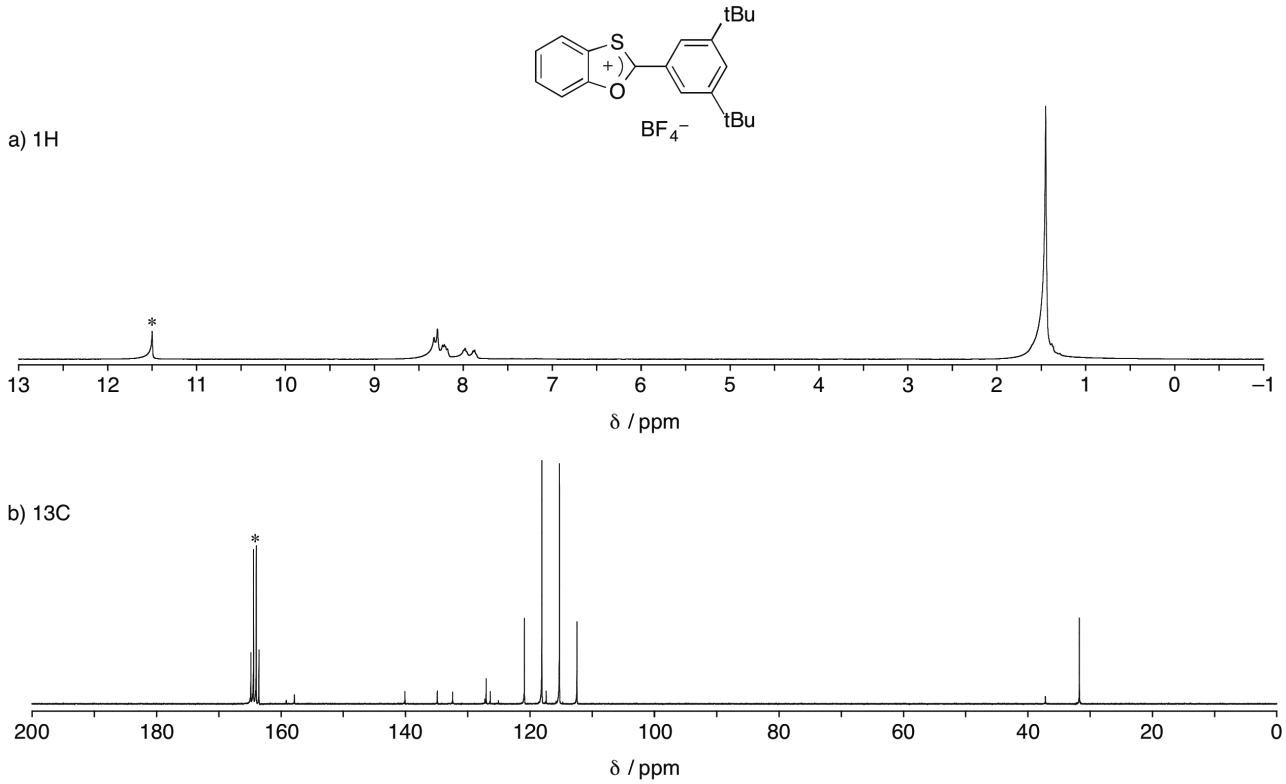


Figure S4. (a) ^{1}H and (b) ^{13}C NMR spectra of **8b** at 25 °C in TFA-d_1. Peaks marked with ∗ arise from residual solvents.

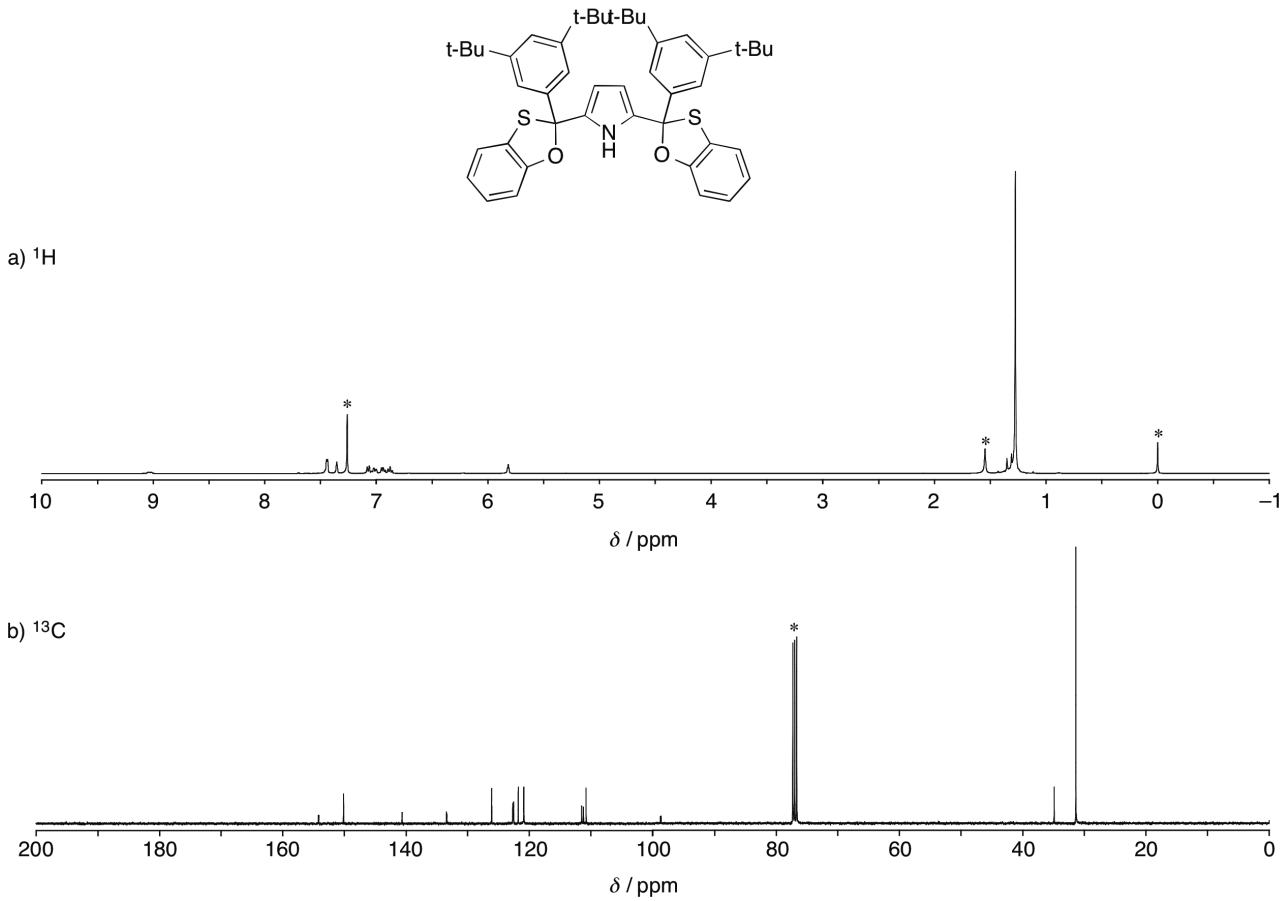


Figure S5. (a) ^{1}H and (b) ^{13}C NMR spectra of **9b** at 25 °C in $CDCl_3$. Peaks marked with ∗ arise from residual solvents.

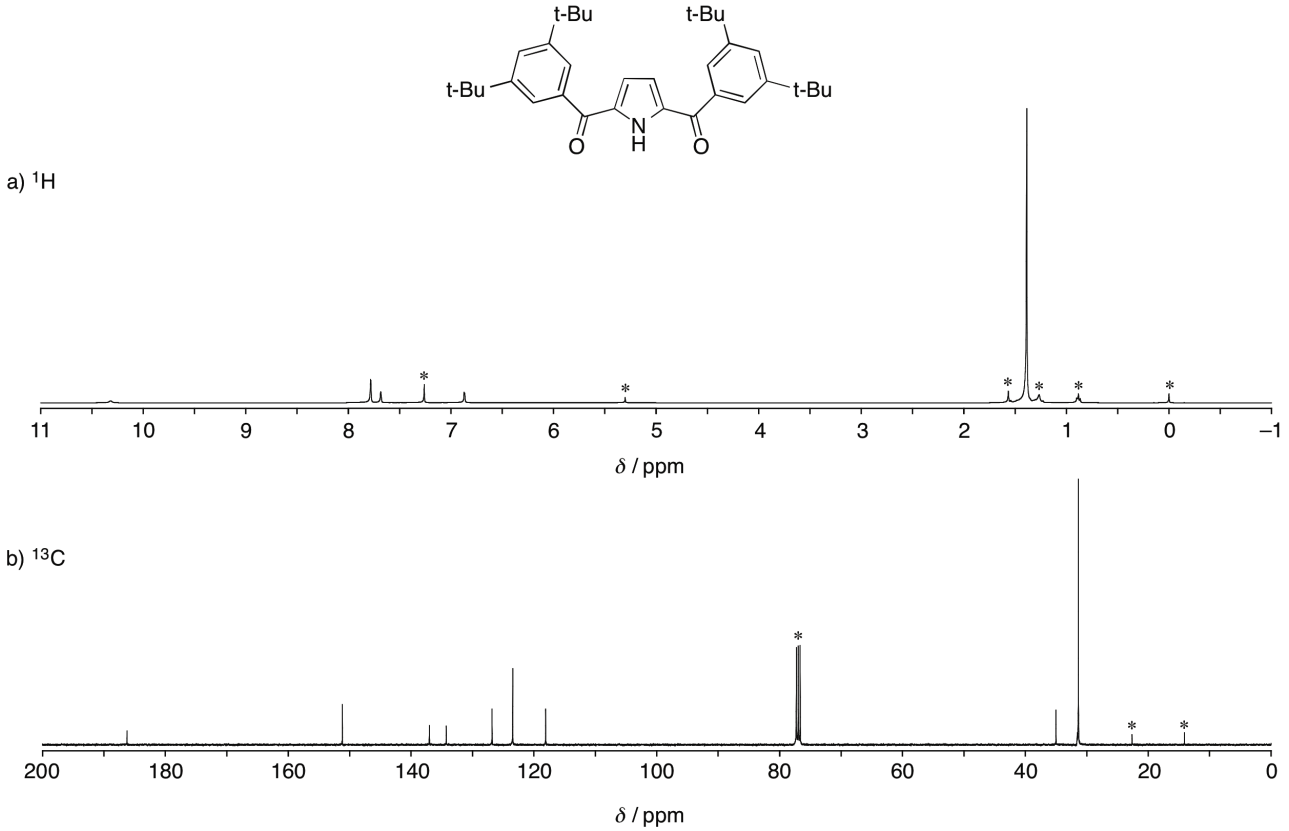


Figure S6. (a) ^{1}H and (b) ^{13}C NMR spectra of **10b** at 25 °C in $CDCl_3$. Peaks marked with ∗ arise from residual solvents.

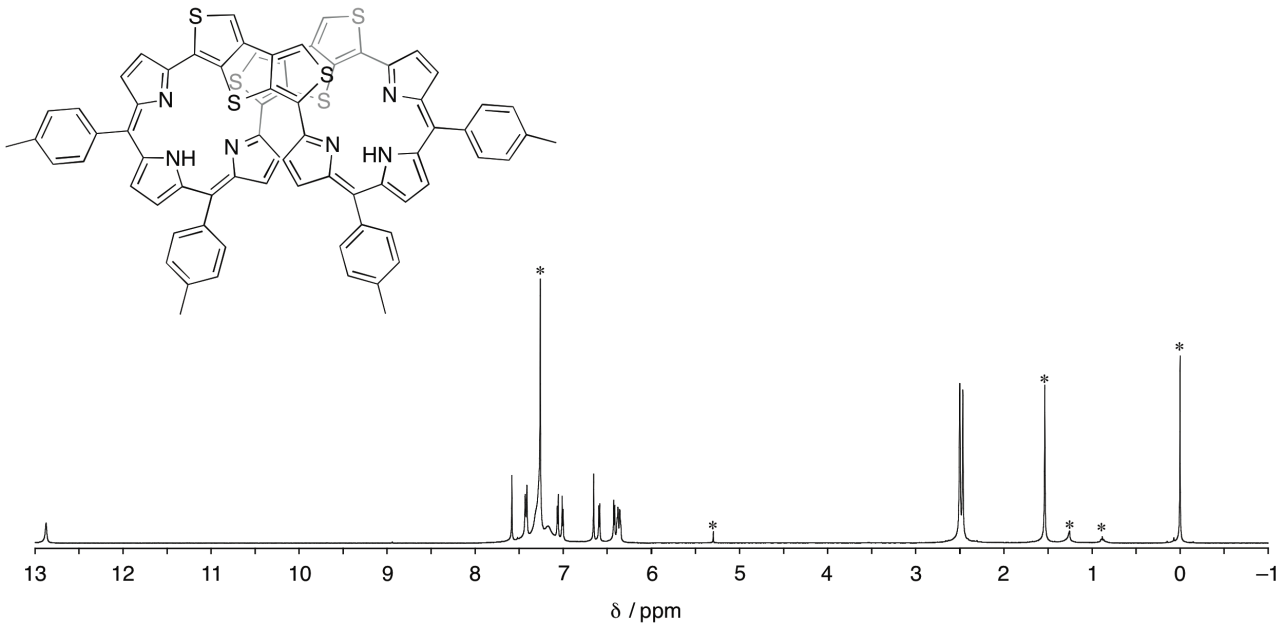


Figure S7. ^{1}H NMR spectrum of **1a** at 25 °C in $CDCl_3$. Peaks marked with ∗ arise from residual solvents.

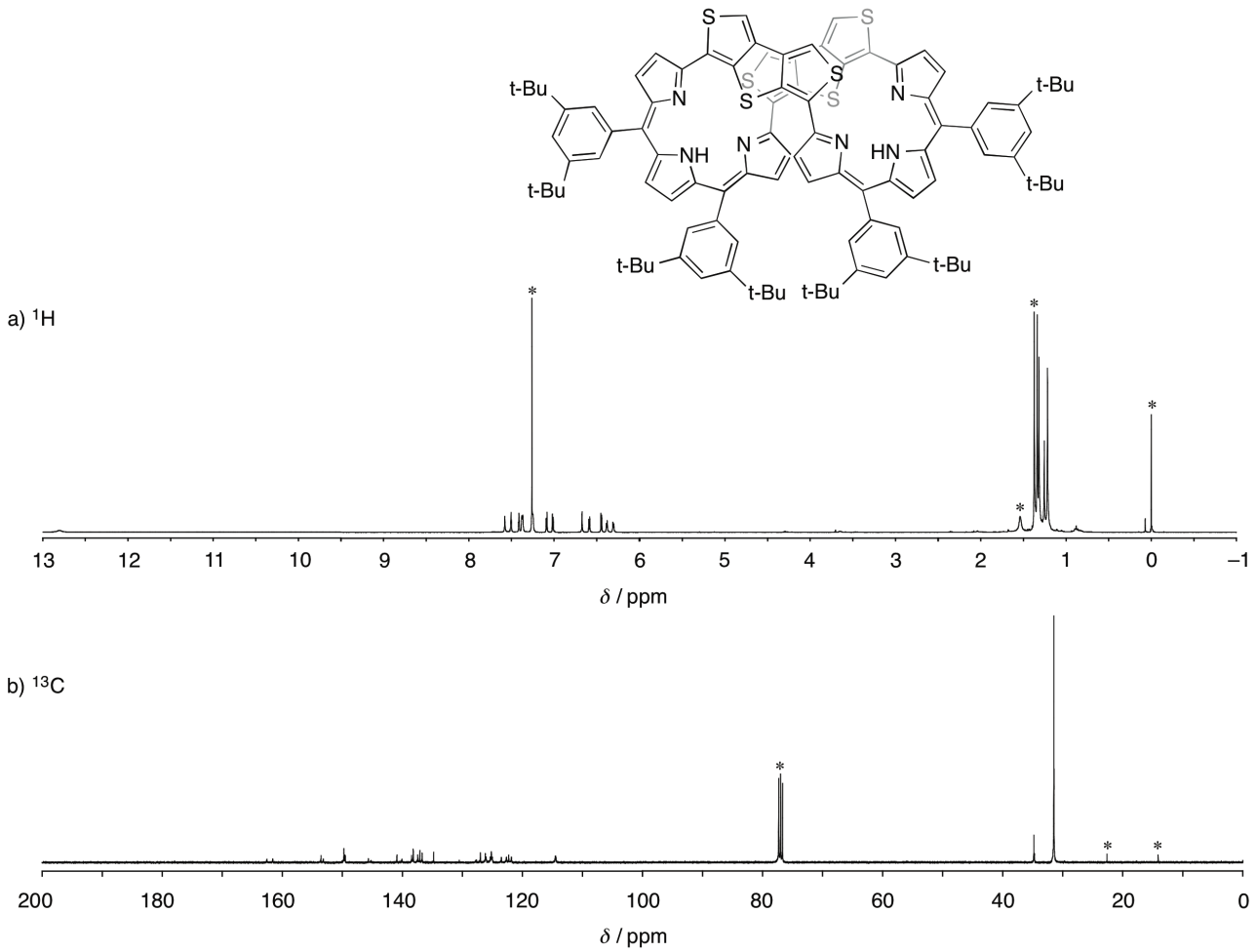


Figure S8. (a) ^{1}H and (b) ^{13}C NMR spectra of **1b** at 25 °C in $CDCl_3$. Peaks marked with ∗ arise from residual solvents.

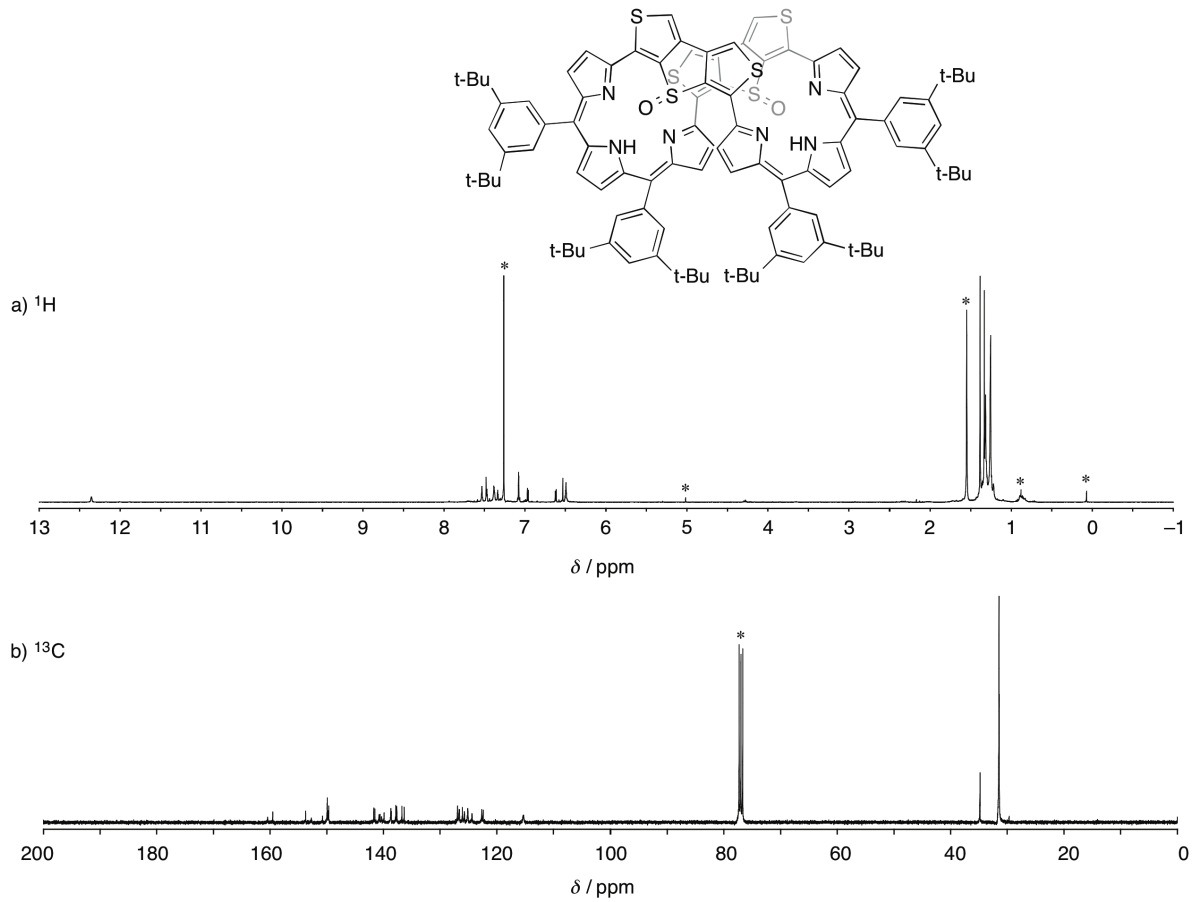


Figure S9. (a) ^{1}H and (b) ^{13}C NMR spectra of **7** at 25 °C in $CDCl_3$. Peaks marked with ∗ arise from residual solvents.

5. X-Ray Crystallographic Details

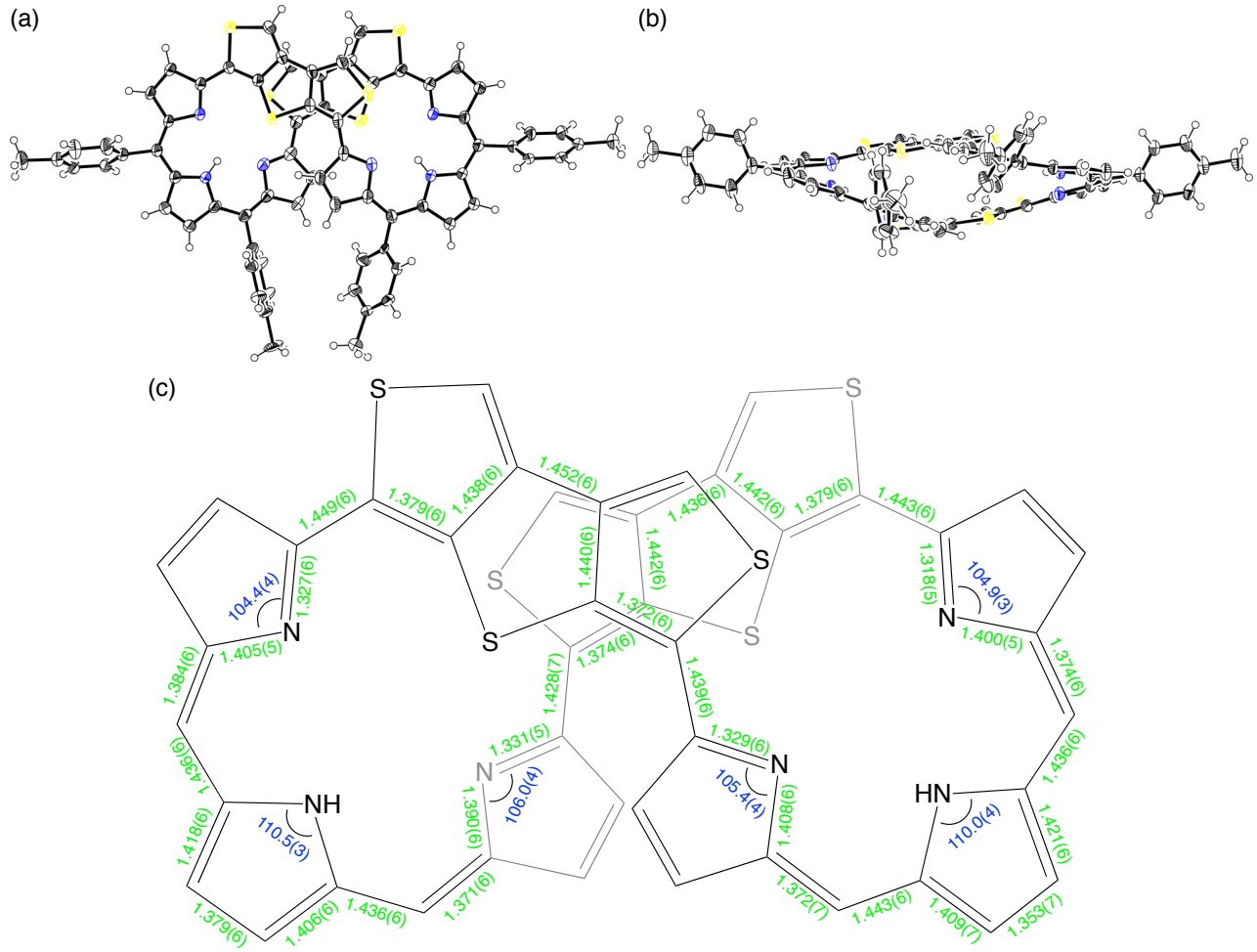


Figure S10. X-Ray crystal structure of **1a**: (a) top view and (b) side view. Thermal ellipsoids represent 50% probability. Minor disorder component and solvent molecules are omitted for clarity. (c) Detailed structural data of **1a**. Selected bond lengths in Å (numbers in green) and bond angles in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

6. Optical Properties

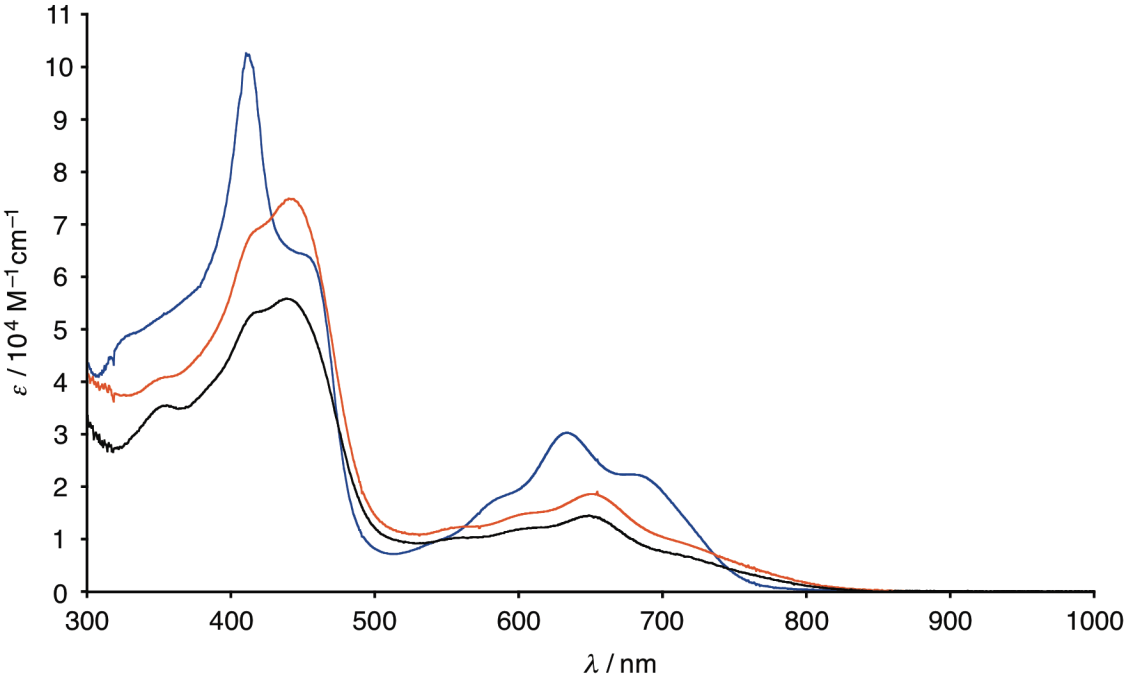


Figure S11. UV/Vis absorption spectra of **1a** (black), **1b** (red), and **7** (blue) in CH_2Cl_2.

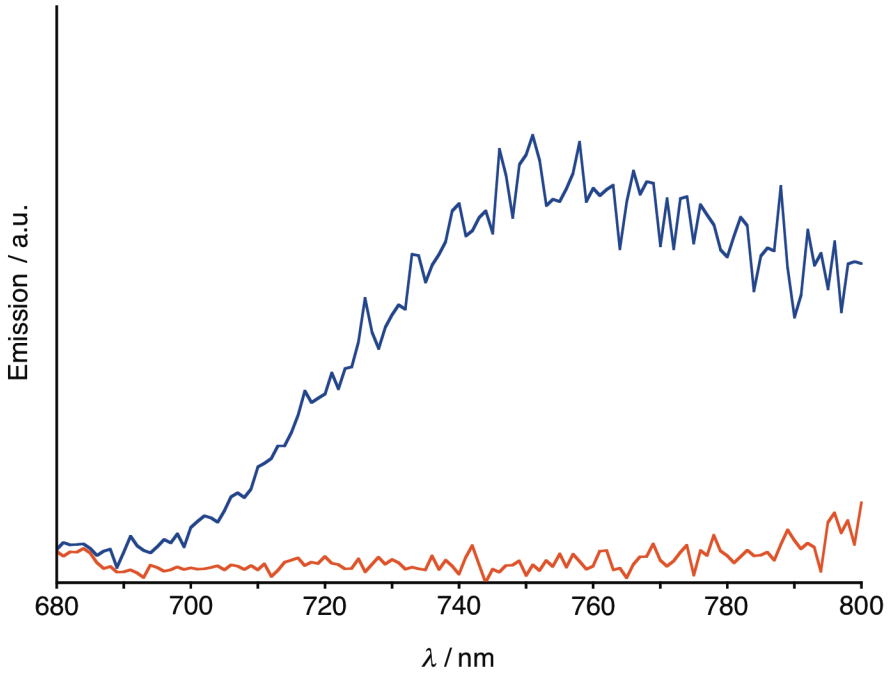


Figure S12. Fluorescence spectra of **1b** (red) and **7** (blue) in CH_2Cl_2. λ_{ex} = 650 nm.

7. Electrochemical Properties

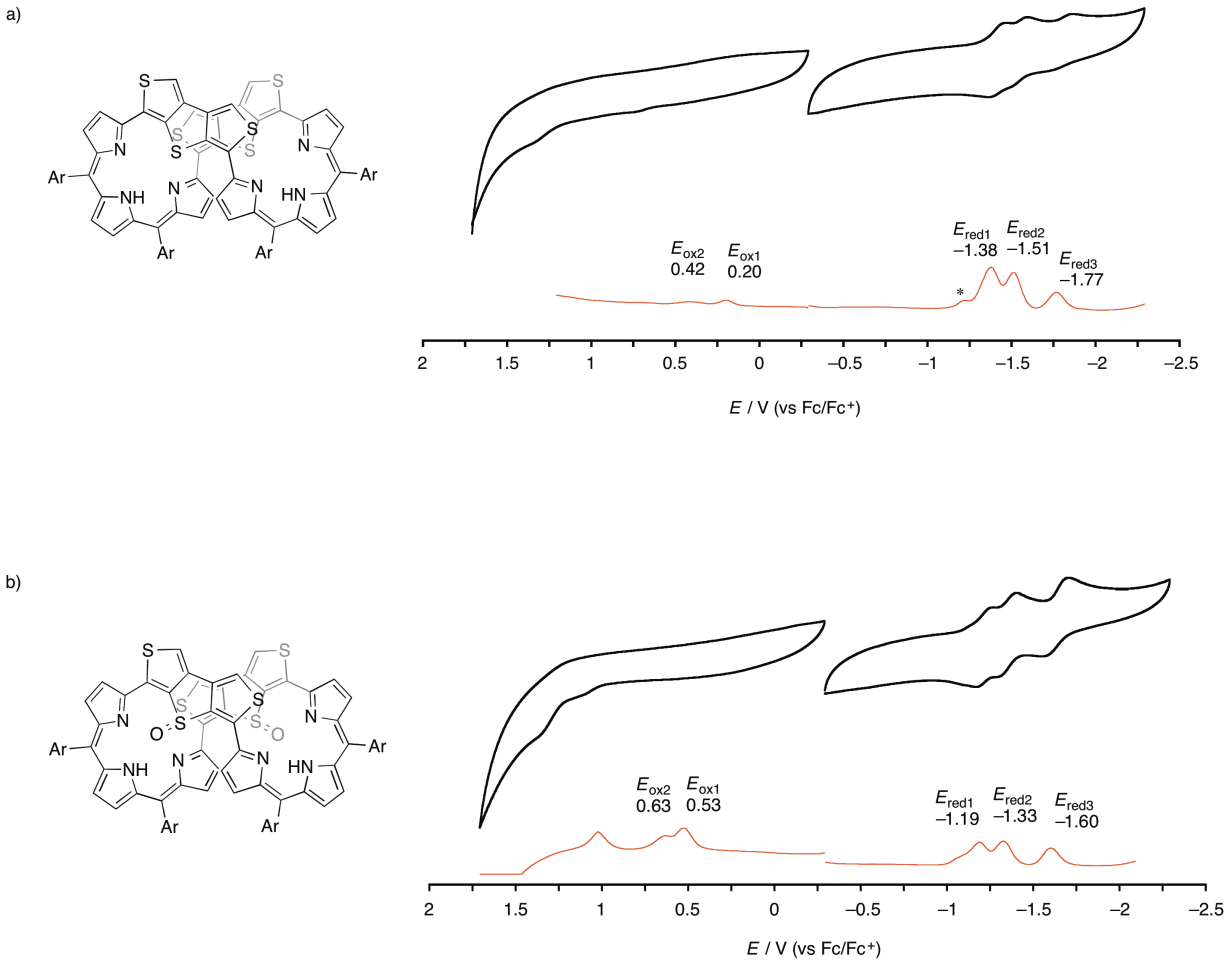


Figure S13. Cyclic voltammograms (black) and differential pulse voltammetry (DPV) curves (red) of octaphyrins a) **1b** and b) **7**. Redox potentials were determined by DPV. Solvent: CH_2Cl_2; scan rate: 0.05 V s^{-1}; working electrode: glassy carbon; reference electrode: Ag/Ag^+ (0.01 M $AgNO_3$); electrolyte: 0.1 M *n*-Bu_4NPF_6. Peaks marked with ∗ arise from oxygen. Ar = 3,5-(*t*-Bu)$_2C_6H_3$.

8. DFT Calculations

All calculations were carried out using the *Gaussian 09* program.[S4] 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,[S5,S6] 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.

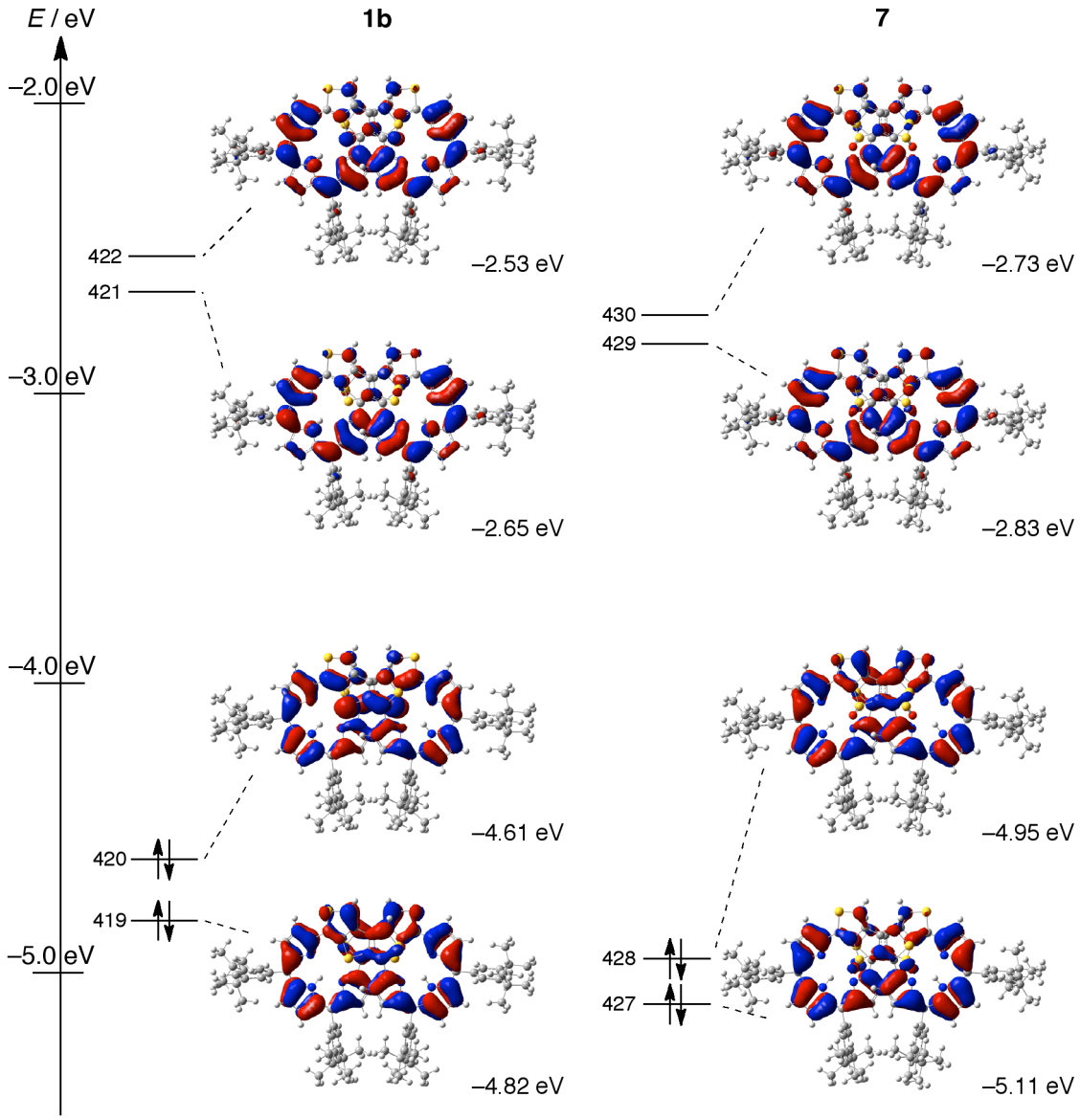


Figure S14. Selected Kohn-Sham orbitals of **1b** and **7** on the optimized structures.

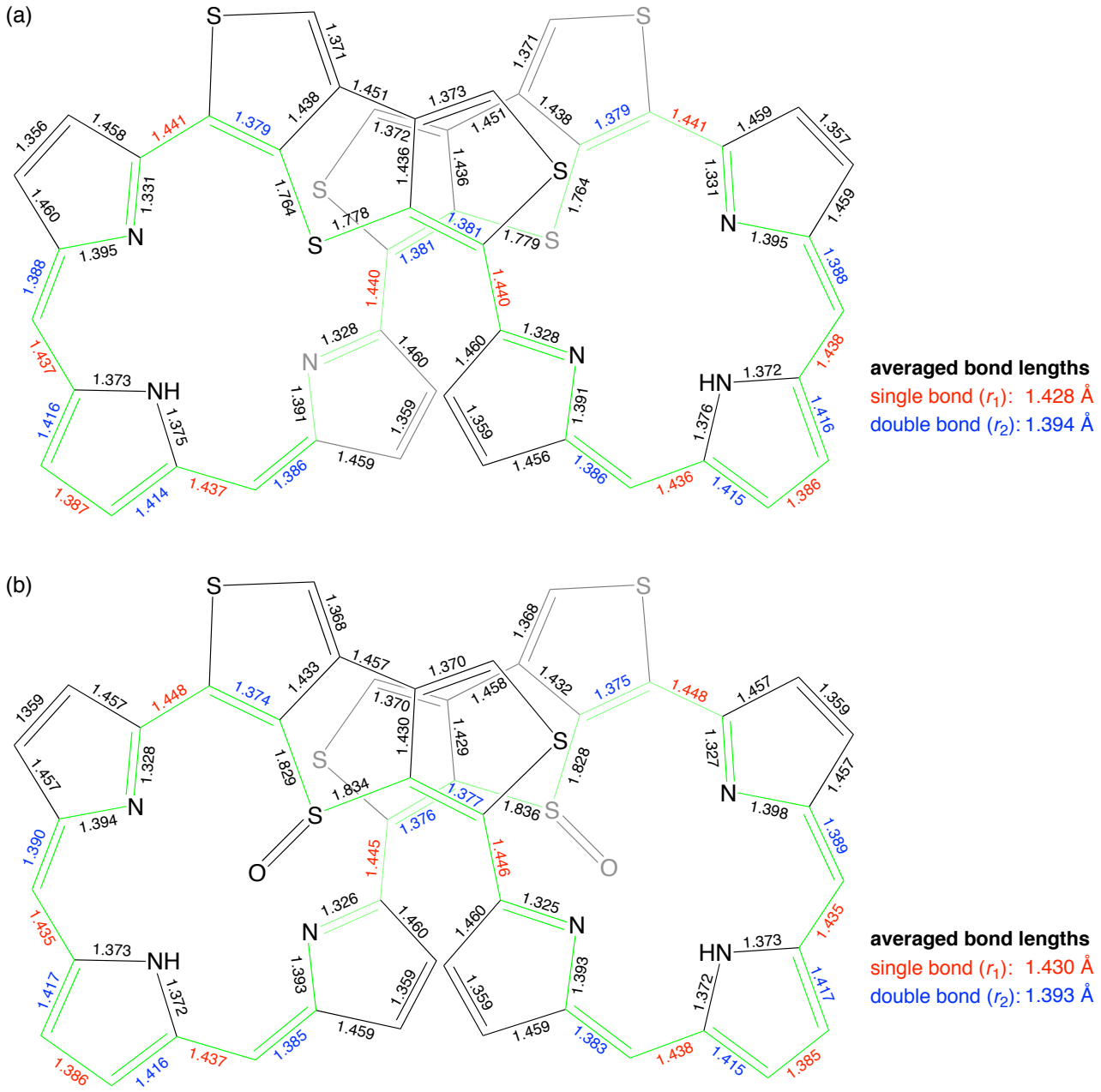


Figure S15. Optimized structural data of (a) **1b** and (b) **7**. The conjugated 36π-electron network (green) and selected bond lengths in Å are indicated. Averaged C–C bond lengths are calculated from red numbers for single bonds and blue numbers for double bonds. C–C bond length alternations (BLAs) 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.

	state	excitation energy		oscillator	excitation			weight [%]
		[eV]	[nm]	strength				
1b	1	1.51	823	0.0089	HOMO	→	LUMO	98.4
	2	1.73	716	0.0124	HOMO–1	→	LUMO	21.0
					HOMO	→	LUMO+1	78.0
	3	1.93	643	0.2508	HOMO–1	→	LUMO	78.4
					HOMO	→	LUMO+1	20.7
	4	1.95	636	0.0312	HOMO–1	→	LUMO+1	97.3
	5	2.09	592	0.2292	HOMO–2	→	LUMO	94.4
	6	2.22	557	0.0203	HOMO–2	→	LUMO+1	89.8
	7	2.38	521	0.0327	HOMO–3	→	LUMO	84.9
	8	2.46	503	0.0052	HOMO–3	→	LUMO+1	82.4
					HOMO	→	LUMO+2	12.3
	9	2.64	469	0.3319	HOMO	→	LUMO+2	76.5
	10	2.67	464	0.1040	HOMO–4	→	LUMO	25.2
					HOMO–1	→	LUMO+2	12.8
					HOMO	→	LUMO+3	50.4
7	1	1.74	713	0.0238	HOMO	→	LUMO	99.1
	2	1.89	657	0.0131	HOMO–1	→	LUMO	32.3
					HOMO	→	LUMO+1	67.0
	3	2.04	606	0.0438	HOMO–1	→	LUMO+1	96.0
	4	2.05	604	0.3361	HOMO–1	→	LUMO	66.1
					HOMO	→	LUMO+1	32.6
	5	2.33	531	0.0023	HOMO–3	→	LUMO	83.6
	6	2.35	528	0.0748	HOMO–2	→	LUMO	86.0
	7	2.37	523	0.0453	HOMO–4	→	LUMO	63.5
					HOMO–3	→	LUMO+1	30.9
	8	2.46	504	0.0429	HOMO–2	→	LUMO+1	82.2
	9	2.49	497	0.0029	HOMO–4	→	LUMO	31.3
					HOMO–3	→	LUMO+1	61.8
	10	2.55	487	0.0064	HOMO–4	→	LUMO+1	88.3

9. References

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