Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Modulation of the charge transfer and photophysical properties in non-fused tetrathiafulvalene-benzothiadiazole derivatives

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SUPPORTING INFORMATION

Experimental

4-((trimethylsilyl)ethynyl)-benzo[c][2,1,3]thiadiazole 13

4-Bromo-benzo[c][2,1,3]thiadiazole **15** (500 mg, 2.32 mmol), CuI (44 mg, 10 %) and $Pd(PPh_3)_4$ (134 mg, 5 %) were mixed in 30 mL dry THF and then diisopropylamine (DIPA) (1.37 ml, 9.74 mmol) and $Si(CH_3)_3$-acetylene (0.66 mL, 4.64 mmol) were added under argon. The resulting brown solution was heated to 60 °C and stirred for 20 h. The solvent was concentrated under vacuum and the crude product was purified by chromatography on silica using as eluent petroleum spirit/dichloromethane 4/1 to afford a light brown solid. Yield: 530 mg (98 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, ^3J = 9.0 Hz, 1H, C*H*), 7.76 (d, ^3J = 6.9 Hz, 1H, C*H*), 7.54 (dd, ^3J = 8.7 Hz, ^{3}J = 6.9 Hz, 1H, C*H*), 0.33 (s, 9H, $Si(CH_3)_3$). MS (ESI): m/z = 232.8 (M+) (calc. 232.05).

4,7-bis((trimethylsilyl)ethynyl)-benzo[c][2,1,3]thiadiazole 14

4,7-Dibromo-benzo[c][2,1,3]thiadiazole **5** (500 mg, 1.7 mmol), CuI (32 mg, 10 %) and $Pd(PPh_3)_4$ (98 mg, 5 %) were mixed in 30 mL dry THF and then diisopropylamine (DIPA) (1.08 mL, 7.65 mmol) and $Si(CH_3)_3$-acetylene (0.26 mL, 1.87 mmol) were added under argon. The mixture was heated to 60 °C and stirred overnight. The solvent was concentrated under vacuum and the crude product was purified by chromatography on silica using as eluent petroleum spirit/dichloromethane 4/1 to afford a light yellow solid. Yield: 540 mg (97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (s, 2H, C*H*), 0.32 (s, 18H, $Si(CH_3)_3$). MS (MALDI-TOF): m/z = 329.1 (M+) (calc. 328.09).

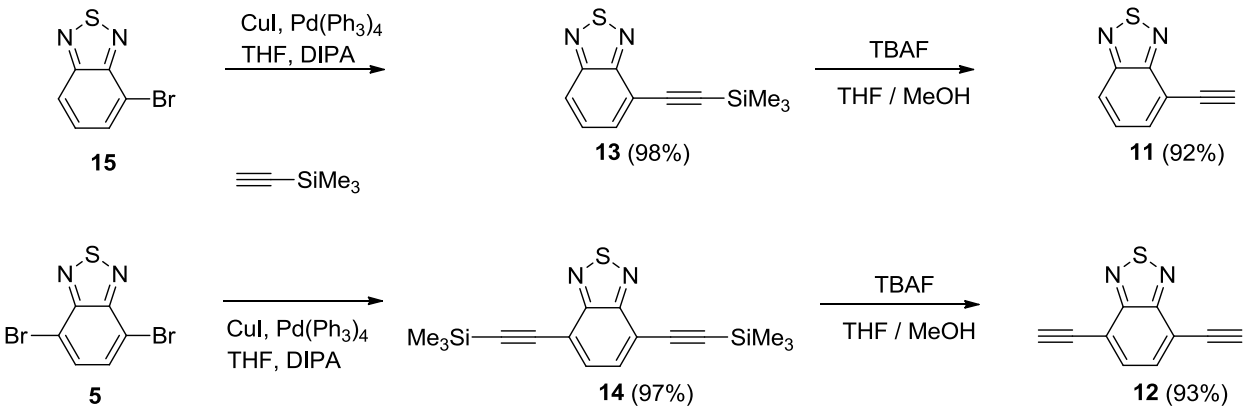
4-ethynyl-benzo[c][2,1,3]thiadiazole 11

To a degassed solution of **13** (250 mg, 1.08 mmol) in 30 mL of THF/methanol (1/1), 1 M TBAF solution in THF (1.3 mL, 1.3 mmol) was added under argon. The solution was stirred for 1 h at room temperature and then the solvent was concentrated. The crude product was purified by chromatography on neutral alumina using dichloromethane as eluent to afford a light brown solid. Yield: 160 mg (92 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (d, ^3J = 9.0 Hz, 1H, C*H*), 7.80 (d, ^3J = 6.9 Hz, 1H, C*H*), 7.58 (dd, ^3J = 8.7 Hz, ^3J = *6.9* Hz, 1H, C*H*), 3.59 (s, 1H, C*H*).

4,7-diethynyl-benzo[c][2,1,3]thiadiazole 12

To a degassed solution of **14** (250 mg, 0.76 mmol) in 20 mL of THF/methanol (1/1), 1 M TBAF solution in THF (1.82 mL, 1.82 mmol) was added under argon. The mixture was stirred at room temperature for 1.5 h and then the solvent was concentrated. The crude product was purified by chromatography on neutral alumina using dichloromethane as eluent

to afford a light brown solid. Yield: 130 mg (93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (s, 2H, CH), 3.68 (s, 2H, C*H*).



Electrochemical studies. Cyclic voltammetry measurements were performed in a glove box containing dry, oxygen-free (< 1 ppm) argon, using a three-electrode cell equipped with a platinum millielectrode of 0.126 cm^2 area, an Ag/Ag^+ pseudo-reference and a platinum wire counter-electrode. The potential values were then re-adjusted with respect to the saturated calomel electrode (SCE). The electrolytic media involved a 0.1 M solution of $[(n\text{-}Bu_4)N)PF_6$ in dichloromethane and tetrahydrofurane. All experiments have been performed at room temperature at 0.1 Vs^{-1}. Experiments have been carried out with an EGG PAR 273A potentiostat with positive feedback compensation.

Table S1. Redox potentials (V *vs* SCE) of compound **1a**, **1b**, **2a** and **3a** in CH_2Cl_2 and of compound **4a** in THF.

Compound	$E^1_{1/2ox}$	$E^2_{1/2ox}$	E_{red} (rev)
	(V *vs* SCE)	(V *vs* SCE)	(V *vs* SCE)
2a	0.40	0.87	-1.36
3a	0.42	0.88	-1.19
1a	0.42	0.83	-1.19
1b	0.45	0.82	-1.21
4a	0.47	0.89	-1.17

UV-Vis spectroscopy

Table S2. UV-Vis data for **1a**, **1b**, **2a**, **3a** (10^{-4} M in CH_2Cl_2), and **4a** (5×10^{-5} M in THF).

Compound	λ (nm)	ε (L/mol*cm)
2a	481	3300
3a	501	3500
1a	565	3530
1b	551	3900
4a	609	4360