

Electronic Supporting Information for:

Bent-core luminescent and electroactive bis(triazolyl)triazines with compact columnar mesomorphism

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General experimental details

^1H -NMR and ^{13}C -NMR experiments were performed on a Bruker ARX 300 or a Bruker AVANCE 400 spectrometer. Chemical shifts are given in ppm relative to TMS, and the solvent residual peak was used as internal standard (CDCl_3 $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.0$ ppm). Infrared spectra were obtained in a Nicolet Avatar 360 FTIR spectrophotometer in the $400\text{--}4000\text{ cm}^{-1}$ range. MS analyses were performed using a Bruker Microflex spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 microanalyzer. UV-vis and Fluorescence spectra were obtained using ATI-Unicam UV4-200 and Perkin-Elmer LS50B spectrophotometer respectively. Liquid crystal behaviour were studied using an Olympus BH-2 polarizing microscope equipped with a Linkam TMS91 hot-stage and a CS196 hot-stage central processor. DSC TA Instruments Q-20 and Q-2000 systems were used to carry out differential scanning calorimetry experiments. Samples were sealed in aluminum pans, and measured at a scanning rate of $10\text{ }^\circ\text{C min}^{-1}$ under a nitrogen flow. Temperatures were taken from the onset of the transition unless otherwise noted. Thermogravimetric analyses (TGA) were performed using a TA Instrument TGA Q5000 at a rate of $10\text{ }^\circ\text{C min}^{-1}$ under a nitrogen flow. Data was taken for a 4 % weight loss and the maximum rate of the weight loss (DTGA). X-ray diffraction experiments of the mesophases were performed in a pinhole camera (Anton-Paar) operating with a point focused Ni filtered Cu-K α beam. Lindemann glass capillaries with 0.9 mm inner diameter were used to contain the sample and heated, when necessary, with a high-temperature attachment. The capillary axis was held perpendicular to the X-ray beam and the pattern collected on flat photographic film. Bragg's law was used to calculate the d spacings. Cyclic voltammetry (CV) measurements were performed with a Metrohm μ -Autolab ECO-Chemie potentiostat, using a glassy carbon working electrode, a Pt counter electrode, and a Ag/AgCl reference electrode in a three-electrode cell. The experiments were carried out under argon, in CH_2Cl_2 , with Bu_4NPF_6 as supporting electrolyte (0.1 M). Scan rate was 100 mV s^{-1} . The potential was checked against ferrocene/ferrocenium (FOC) couple after each measurement. The dielectric permittivity for BT6 has been measured on Linkam cells, $5\text{ }\mu\text{m}$ thick, using a HP 4192A impedance analyzer on cooling and on heating at $1\text{ }^\circ\text{C min}^{-1}$.

Synthesis and characterisation

2-metoxi-4,6-bis(trimethylsilyl)-1,3,5-triazine (C). To a Schlenk flask containing trimethylsilylacetylene (34.6 mmol) and dry tetrahydrofuran (20 mL) at -78 °C was added butyllithium (34.6 mmol) and stirred for 40 minutes. Then, a solution of zinc chloride (34.6 mmol) in 30 mL of dry tetrahydrofuran was added dropwise to the reaction mixture at -78 °C, and then allowed to reach room temperature and stirred for 3 hours (NOTE: zinc chloride was previously dried under vacuum at 80 °C for 12 hours). The reaction mixture was filtered under an argon atmosphere and cannulated to another Schlenk flask containing a suspension of cyanuric chloride (17.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.89 mmol) in dry tetrahydrofuran (50 mL) at 20 °C. The reaction mixture was additionally stirred at 20 °C for 3 hours. After that, methanol (34.6 mmol) was added and the reaction mixture was refluxed for 8 hours. The solid was filtered out and washed with hexane, the filtrate was evaporated under vacuum and recrystallized in methanol to yield **C** as a white solid. Yield: 57 %.

¹H NMR (400 MHz, CDCl₃) δ, ppm 0.28 (s, 18H, Csp³-Si), 4.07 (s, 3H, Csp³-O); ¹³C NMR APT (100 MHz, CDCl₃) δ, ppm -0.78, 55.7, 100.2, 100.2, 161.0, 170.6; IR (NaCl) ν, cm⁻¹ 2959 (C-C), 2899 (C-C), 2175 (Csp), 1524 (arC), 1243 (Si-C) 855 (Si-C); MS (ESI+): 304.1 [M+1]⁺ (Calcd for C₁₄H₂₁N₃OSi₂ 303.1); Rf = 0.3 (ethyl acetate/hexane 1/10).

General procedure for the synthesis of azides A/AB

Aromatic azides A/AB have been prepared by diazotization of alkoxyated anilines followed by addition of sodium azide according to the procedure reported by Gallardo *et al.* in *Liquid Crystals*, **2008**, 6, 719-725. Polyalkoxyated anilines were obtained by reduction of a nitrocompound with a Pd catalyst. **Nitro compounds** (3,4-di-*n*-decyloxynitrobenzene and 3,4,5-tri-*n*-decyloxynitrobenzene) and their corresponding **anilines** (3,4-di-*n*-decyloxyaniline and 3,4,5-tri-*n*-decyloxyaniline) were prepared as reported by Serrano *et al.* in *Chem. Mater.* **2004**, 16, 3308-3317 and *Liquid Crystals*, **2003**, 30, 651-661 and showed identical spectroscopic properties to those reported therein. 4-*n*-decyloxyaniline is commercially available.

Experimental details and characterization data can be found in Giménez *et al.* *Org. Lett.*, **2010**, 12 (7), 1404-1407 and *J. Mater. Chem.*, **2012**, 22, 7797-7805.

General procedure for the synthesis of BT/BTB compounds

0.77 mmol of compound **C** and 2.39 mmol of azides **A/AB** were dissolved in THF / H₂O (5 mL/5 mL). The solution was stirred for 3 minutes. Then, 0.23 mmol of sodium ascorbate, 0.11 mmol of copper(II) sulphate and 2.3 mmol of TBAF 1 M in THF were added. The flask was kept in dark for 12 hours. The reaction mixture was extracted with dichloromethane/water 2/1 (3x15 mL) and the combined organic layers were dried over MgSO₄. The solvent was evaporated, and the residue was purified by column chromatography with silica gel as the stationary phase and the suitable eluent.

BT2 was purified by column chromatography with ethyl acetate/dichloromethane 1/10 as eluent to give a white solid. Yield: 84%. ¹H NMR (400 MHz, CDCl₃) δ, ppm 0.88 (t, *J* = 7.0 Hz, 6H, CH₃), 1.21-1.39 (m, 31H, CH₂), 1.62-1.70 (m, 6H, CH₂), 4.06 (t, *J* = 7.5 Hz, 2H, OCH₂), 4.29 (s, 3H, OCH₃), 7.32-7.41 (m, AA'XX', 4H, ArH), 7.68-7.78 (m, AA'XX', 4H, ArH), 8.95 (s, 2H, triazole); ¹³C NMR APT (100 MHz, CDCl₃) δ, ppm 14.3,

22.8, 29.5, 29.6, 29.7, 31.5, 32.03, 55.9, 68.7, 120.8, 125.5, 130.0, 135.5, 144.8, 145.9, 168.3, 171.8; IR (NaCl) ν , cm^{-1} 2924 (C-C), 2846 (C-C), 1516 (triazole); Anal. Calcd for $\text{C}_{40}\text{H}_{55}\text{N}_9\text{O}_3$: C, 67.87; H, 7.91; N, 17.70 Found: C, 67.67; H, 7.81; N, 17.76; MS (MALDI+, dithranol): 732.7 $[\text{M}+\text{Na}]^+$ (Calcd for $\text{C}_{40}\text{H}_{55}\text{N}_9\text{NaO}_3$: 732.4); TGA 4%: 237 °C; DTGA: 293 °C; Rf = 0.3 (ethyl acetate/hexane 1/10).

BT4 was purified by column chromatography with ethyl acetate/dichloromethane 1/10 as eluent to give a yellowish paste. Yield: 80%. ^1H NMR (400 MHz, CDCl_3) δ , ppm 0.83-0.90 (m, 12H, CH_3), 1.22-1.39 (m, 48H, CH_2), 1.41-1.52 (m, 8H, CH_2), 1.79-1.88 (m, 8H, CH_3), 4.01-4.08 (m, 8H, OCH_2), 4.24 (s, 3H, OCH_3), 6.29 (d, J = 8.6 Hz, 2H, ArH), 7.25 (dd, J = 2.7 Hz, J = 8.6 Hz, 2H, ArH), 7.34 (d, J = 2.7 Hz, 2H, ArH), 8.90 (s, 2H, triazole); ^{13}C NMR APT (100 MHz, CDCl_3) δ , ppm 14.0, 22.6, 26.0, 29.0, 29.1, 29.3, 29.5, 31.8, 55.6, 69.4, 106.4, 112.6, 113.4, 125.3, 129.8, 145.5, 149.8, 149.9, 168.0, 171.5; IR (NaCl) ν , cm^{-1} 2922 (C-C), 2845 (C-C), 1519 (triazole); Anal. Calcd for $\text{C}_{60}\text{H}_{95}\text{N}_9\text{O}_5$: C, 71.98; H, 10.19; N, 9.44 Found: C, 72.10; H, 10.11; N, 9.37; MS (MALDI+, dithranol): 1044.9 $[\text{M}+\text{Na}]^+$ (Calcd for $\text{C}_{60}\text{H}_{95}\text{N}_9\text{NaO}_5$: 1044.7); TGA 4%: 250 °C; DTGA: 407 °C; Rf = 0.3 (ethyl acetate/dichloromethane 1/10).

BT6 was purified by column chromatography with ethyl acetate/dichloromethane 0.5/10 as eluent to give an yellowish paste. Yield: 76%. ^1H NMR (400 MHz, CDCl_3) δ , ppm 0.82-0.93 (m, 18H, CH_3), 1.20-1.42 (m, 72H, CH_2), 1.42-1.55 (m, 12H, CH_2), 1.72-1.92 (m, 14H, CH_3), 3.97-4.11 (m, 12H, OCH_2), 4.30 (s, 3H, OCH_3), 7.01 (s, 4H, ArH), 8.93 (s, 2H, triazole); ^{13}C NMR APT (100 MHz, CDCl_3) δ , ppm 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 29.8, 30.3, 31.9, 32.0, 55.8, 69.5, 73.7, 99.4, 125.6, 131.9, 138.8, 145.7, 153.9, 168.2, 171.7; IR (NaCl) ν , cm^{-1} 2921 (C-C), 2849 (C-C), 1512 (triazole); Anal. Calcd for $\text{C}_{80}\text{H}_{135}\text{N}_9\text{O}_7$: C, 71.98; H, 10.19; N, 9.44 Found: C, 72.10; H, 10.11; N, 9.37; MS (MALDI+, dithranol): 1357.5 $[\text{M}+\text{Na}]^+$ (Calcd for $\text{C}_{80}\text{H}_{135}\text{N}_9\text{NaO}_7$: 1357.05); TGA 4%: 240 °C; DTGA: 383 °C; Rf = 0.4 (ethyl acetate/dichloromethane 0.5/10).

BTB2 was purified by column chromatography with ethyl acetate/dichloromethane 1/10 as eluent to give a white solid. Yield: 67%. ^1H NMR (400 MHz, CDCl_3) δ , ppm 0.89 (t, J = 6.4 Hz, 6H, CH_3), 1.22-1.40 (m, 20H, CH_2), 1.43-1.52 (m, 6H, CH_2), 1.76-1.88 (m, 6H, CH_2), 4.06 (t, J = 6.4 Hz, 4H, OCH_2), 4.31 (s, 3H, OCH_3), 6.88-7.04 (m, AA'XX', 4H, ArH), 7.35-7.52 (m, AA'XX', 4H, ArH), 7.84-7.92 (m, AA'XX', 4H, ArH), 8.05-8.21 (m, AA'XX', 4H, ArH), 8.99 (s, 2H, triazole); ^{13}C NMR APT (100 MHz, CDCl_3) δ , ppm 14.1, 22.7, 26.0, 29.1, 29.3, 29.6, 31.9, 55.8, 68.4, 114.4, 120.8, 121.9, 123.5, 125.4, 132.4, 133.9, 150.0, 151.6, 163.8, 164.6, 168.1, 171.7; IR (NaCl) ν , cm^{-1} 2924 (C-C), 2854 (C-C), 1727 (C=O), 1513 (triazole), 1251 (C-O); Anal. Calcd for $\text{C}_{54}\text{H}_{63}\text{N}_9\text{O}_7$: C, 68.26; H, 6.68; N, 13.27 Found: C, 68.10; H, 6.77; N, 12.95; MS (MALDI+, dithranol): 972.9 $[\text{M}+\text{Na}]^+$ (Calcd for $\text{C}_{54}\text{H}_{63}\text{N}_9\text{NaO}_7$: 972.5); TGA 4%: 248 °C; DTGA: 400 °C; Rf = 0.1 (ethyl acetate/dichloromethane 1/10).

BTB4 was purified by column chromatography with ethyl acetate/dichloromethane 1/10 as eluent to give a white solid. Yield: 68%. ^1H NMR (400 MHz, CDCl_3) δ , ppm 0.86-0.90 (m, 12H, CH_3), 1.24-1.43 (m, 48H, CH_2), 1.46-1.53 (m, 8H, CH_2), 1.82-1.91 (m, 8H, CH_2), 4.06-4.11 (m, 8H, OCH_2), 4.30 (s, 3H, OCH_3), 6.95 (d, J = 8.6 Hz, 2H, ArH), 7.35-7.50 (m, AA'XX', 4H, ArH), 7.67 (d, J = 2.0 Hz, 2H, ArH), 7.87 (dd, J = 2.0 Hz, J = 8.6 Hz, 2H, ArH), 7.89-7.94 (m, AA'XX', 4H, ArH), 8.99 (s, 2H, triazole); ^{13}C NMR APT (100 MHz, CDCl_3) δ , ppm 14.1, 22.6, 23.3, 25.9, 26.0, 29.0, 29.1, 29.3, 29.4, 29.5, 29.6, 31.9, 55.8, 69.1, 69.4, 111.9, 114.6, 120.8, 121.8, 124.5, 125.4, 133.9, 145.9, 148.7, 151.7, 154.1, 164.6, 168.1, 171.7; IR (NaCl) ν , cm^{-1} 2921

(C-C), 2851 (C-C), 1729 (C=O), 1515 (triazole); Anal. Calcd for $C_{74}H_{103}N_9O_9$: C, 70.39; H, 8.82; N, 9.98 Found: C, 70.00; H, 8.42; N, 9.83; MS (MALDI+, dithranol): 1285.0 $[M+Na]^+$ (Calcd for $C_{74}H_{103}N_9NaO_9$: 1284.8); TGA 4%: 304 °C; DTGA: 412 °C; Rf = 0.1 (ethyl acetate/dichloromethane 1/10).

BTB6 was purified by column chromatography with ethyl acetate/dichloromethane 1/10 as eluent to give a yellowish paste. Yield: 80%. 1H NMR (400 MHz, $CDCl_3$) δ , ppm 0.86-0.90 (m, 18H, CH_3), 1.22-1.40 (m, 72H, CH_2), 1.46-1.53 (m, 12H, CH_2), 1.74-1.79 (m, 4H, CH_3), 1.81-1.88 (m, 8H, CH_2), 4.05-4.10 (m, 12H, OCH_2), 4.31 (s, 3H, OCH_3), 7.42 (s, 4H, ArH), 7.42-7.48 (m, AA'XX', 4H, ArH), 7.88-7.96 (m, AA'XX', 4H, ArH), 9.00 (s, 2H, triazole); ^{13}C NMR APT (100 MHz, $CDCl_3$) δ , ppm, 14.1, 22.7, 26.1, 29.3, 29.4, 29.6, 29.7, 29.8, 30.4, 55.8, 69.3, 73.6, 108.0, 108.7, 121.9, 123.2, 123.5, 125.0, 134.1, 139.4, 143.4, 146.0, 151.6, 153.1, 164.7, 168.1, 171.7; IR (NaCl) ν , cm^{-1} 2923 (C-C), 2853 (C-C), 1734 (C=O), 1514 (triazole); Anal. Calcd for $C_{94}H_{143}N_9O_{11}$: C, 71.67; H, 9.15; N, 8.00 Found: C, 72.20; H, 9.32; N, 7.75; MS (MALDI+, dithranol): 1575.9 $[M]^+$, 1598.8 $[M+Na]^+$ (Calcd for $C_{94}H_{143}N_9O_{11}$: 1574.09); TGA 4%: 276 °C; DTGA: 414 °C; Rf = 0.4 (ethyl acetate/dichloromethane 1/10).

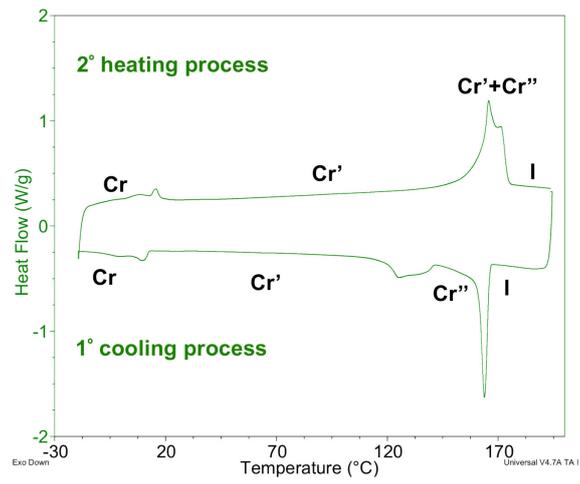


Figure S1. DSC trace for **BT2**

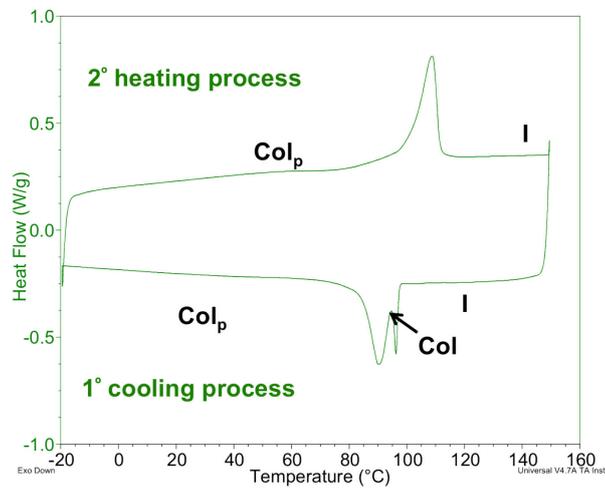


Figure S2. DSC trace for **BT4**

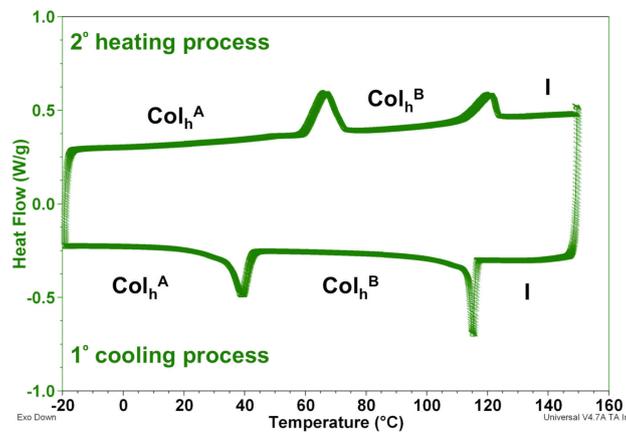


Figure S3. DSC trace for **BT6**

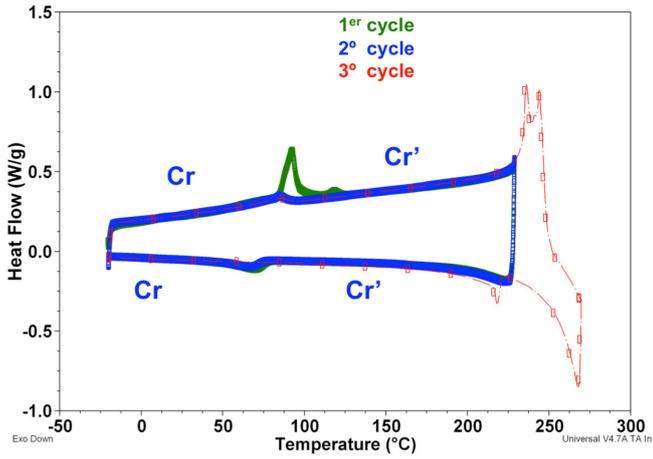


Figure S4. The DSC trace for **BTB2**

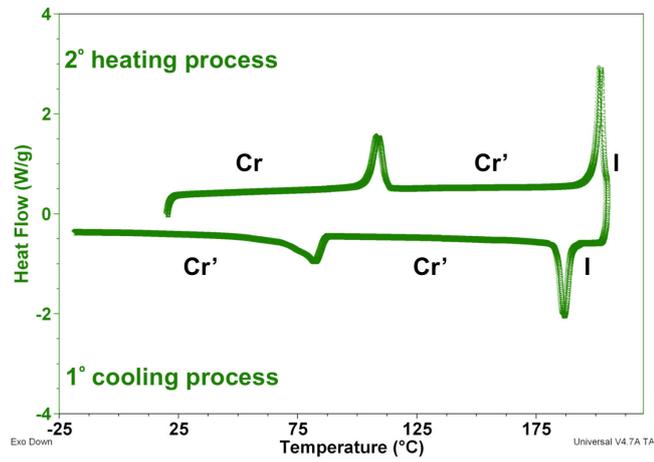


Figure S5. DSC trace for **BTB4**

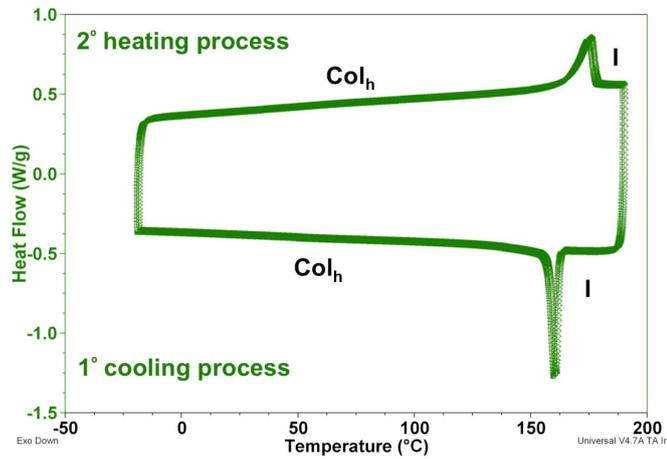


Figure S6. DSC trace for **BTB6**.

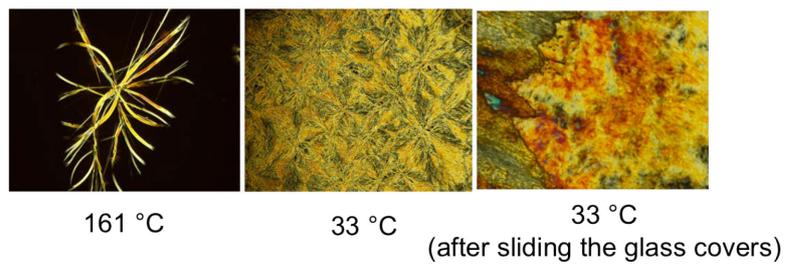


Figure S7. Fluidity test for **BTB6**. Along the three pictures (POM microphotographs between crossed polarisers) we can observe the growth of the texture from the isotropic liquid at 161 °C and the full developed texture at 33 °C. The last picture corresponds to the same area as the microphotograph at 33 °C after shearing.

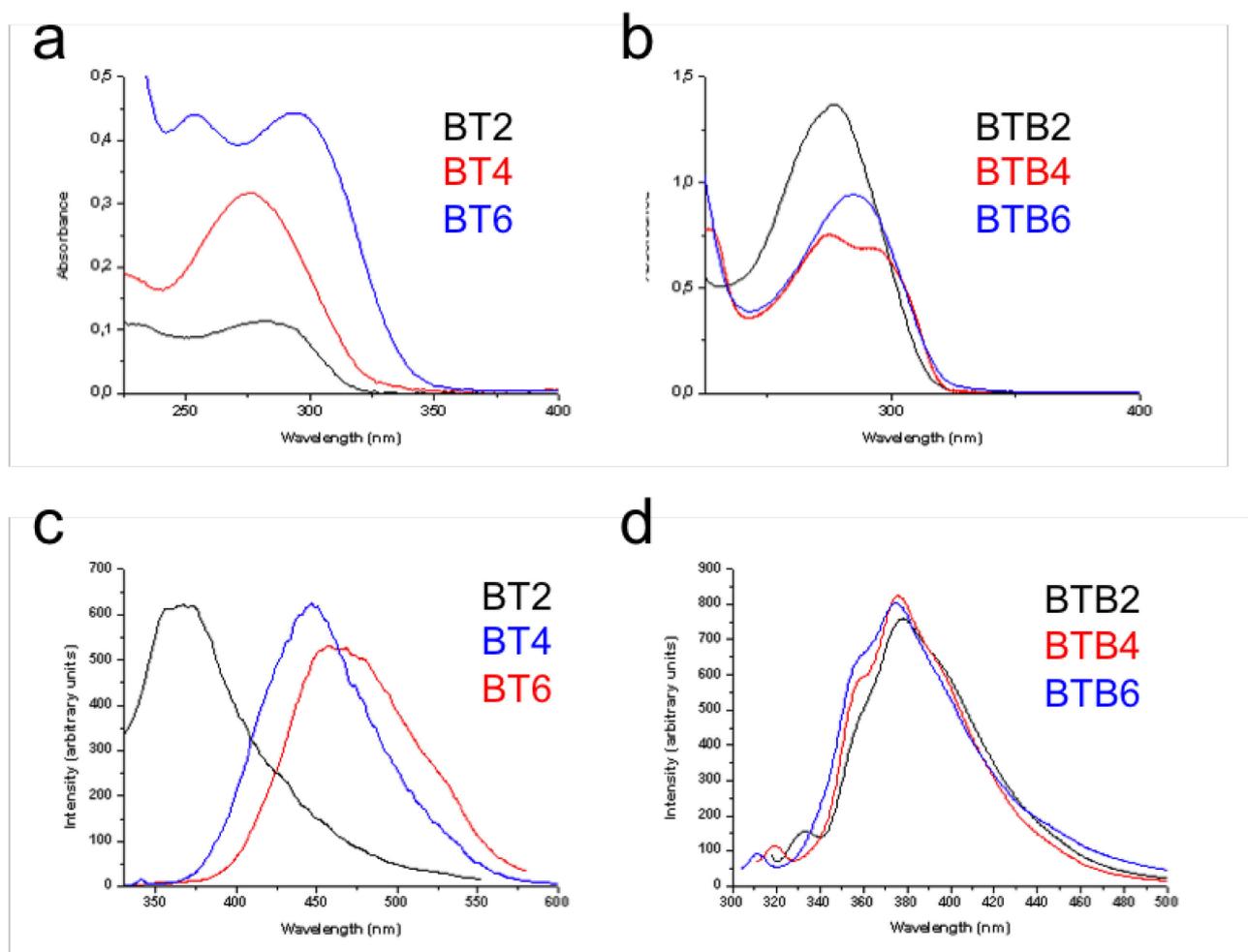


Figure S8. Absorption spectra in THF solution for BTs (a), and BTBs (b). Emission spectra in THF solution for BTs (c), and BTBs (d).

Table S1. Cyclic voltammetry data for BTs and BTBs.

Table S1 Cyclic voltammetry data for BTs and BTBs.

Compound	$E_{1/2}^{\text{red}}$ vs Ag/AgCl / V	$E_{1/2}^{\text{ox}}$ vs Ag/AgCl / V	$E_{1/2}^{\text{red}}$ vs FOC / V ^a	LUMO / eV ^b
BT2	-0.93, -1.79	–	-1.41, -2.27	-3.39
BT4	-0.92, -1.80	–	-1.40, -2.28	-3.40
BT6	-0.92, -1.78	1.49	-1.40, -2.26	-3.40
BTB2	-1.79	–	-2.27	-2.53
BTB4	-1.78	–	-2.26	-2.54
BTB6	-1.77	–	-2.25	-2.55

^a $E_{1/2} = 0.48 \text{ V vs Ag/AgCl}$. ^b $E_{\text{LUMO}} = -e [E_{1/2}^{\text{red1}} \text{ vs FOC} + 4.8 \text{ V}]$