Electronic supplementary materials *Mendeleev Commun*., 2013, **23**, 78−80

Synthesis of photochromic 6-aryl-substituted bis(benzothiophenyl)-perfluorocyclopentenes by the Suzuki−Miyaura cross-coupling

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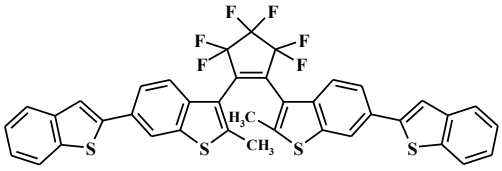
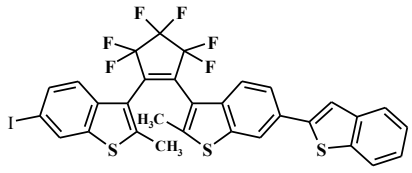
Experimental

All reagents and solvents were used as received. Column chromatography was performed on silica gel (Merck Kieselgel 60 H). Analytical thin-layer chromatography was carried out on aluminium-backed plates coated with Merck Kieselgel 60 F254 that were visualized under UV light (at 254 or 365 nm). ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 MHz), Bruker AM-300 (300 MHz) and Bruker Avance II 300 (75 MHz) spectrometers, respectively. Chemical shifts in $CDCl_3$ are reported downfield from TMS (= 0) as the internal reference. ESI spectra were measured on a Kratos MS-30 instrument. Absorption spectroscopy was performed on a CARY UV 50 (Varian) spectrophotometer. Absorption spectra were recorded in acetonitrile solution (4×10^{-5} M) in 1 cm-length quartz cuvettes. Acetonitrile used for spectroscopy was of spectrophotometric grade.

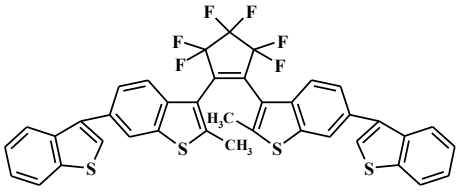


1,2-Bis[6-(benzo[*b*]thiophen-2-yl)-2-methylbenzo[*b*]-thiophen-3-yl]hexafluorocyclopentene (3a): $Pd(PPh_3)_4$ (11 mg, 0.01 mmol), Na_2CO_3 (110 mg), water (1 ml) and benzothiophen-2-ylboronic acid (37 mg, 0.021 mmol) were added to a solution of **2** (50 mg, 0.07 mmol) in THF (10 ml). The reaction mixture was heated under reflux for 24 h. The reaction mixture was poured into water, extracted with CH_2Cl_2, washed with water, dried. The solvent was distilled off, and the residue was purified on a chromatographic column (light petroleum). Yield 80%, mp 90−91 ^{o}C (EtOH). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.29 (s, 6H, CH_3); 7.23-7.45 (m, 6H, ArH); 7.56 (m, 2H, ArH); 7.72-8.04 (m, 8H, ArH). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm): 29.46 (CH_3); 119.98; 121.52; 122.28; 122.38; 122.53; 123.74; 123.83; 124.61; 124.76; 124.90; 125.03; 128.53;

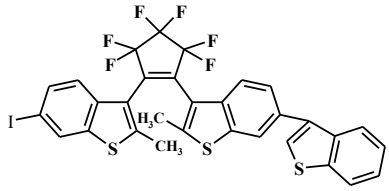
128.69. ^{19}F NMR (280 MHz, $CDCl_3$, *δ*, ppm): -109.31 – (-112.01) (m, 4F, CF_2); -133.31 – (-133.56) (m, 2F, CF_2). HRMS (ESI) (m/z) [MH+] calculated for $C_{39}H_{22}F_6S_4$: 732.0475; found 732.0503.



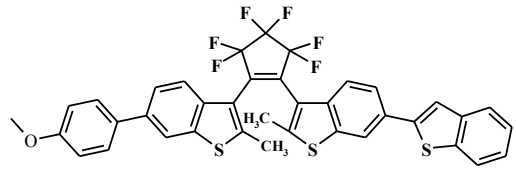
1-[6-(Benzo[*b*]thiophen-2-yl)-2-methylbenzo[*b*]thiophen-3-yl]-2-(6-iodo-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (4a): $Pd(PPh_3)_4$ (5.5 mg, 0.005 mmol), Na_2CO_3 (55 mg), water (1 ml) and benzothiophen-2-ylboronic acid (19 mg, 0.011 mmol) were added to a solution of **2** (50 mg, 0.07 mmol) in THF (10 ml). The reaction mixture was heated under reflux for 24 h. The reaction mixture was poured into water, extracted with CH_2Cl_2, washed with water, dried. The solvent was distilled off, and the residue was purified on a chromatographic column (light petroleum). Yield 60%, mp 100−105 °C (EtOH). ^{1}H NMR (300 MHz, $CDCl_3$, *δ*, ppm): 2.27 (s, 3H, CH_3); 2.53 (s, 3H, CH_3); 7.28-7.41 (m, 4H, ArH); 7.45 (m, 1H, ArH); 7.51-8.03 (m, 6H, ArH). ^{13}C NMR (50 MHz, $CDCl_3$, *δ*, ppm): 29.80 (CH_3); 119.94; 121.51; 122.28; 122.36; 123.70; 123.82; 124.56; 124.74; 124.89; 125.02. ^{19}F NMR (280 MHz, $CDCl_3$, *δ*, ppm): -109.43 – (-112.02) (m, 4F, CF_2); -133.39 – (-133.60) (m, 2F, CF_2). HRMS (ESI) (m/z) [MH+] calculated for $C_{31}H_{17}F_6IS_3$: 732.0475; found 732.0503.



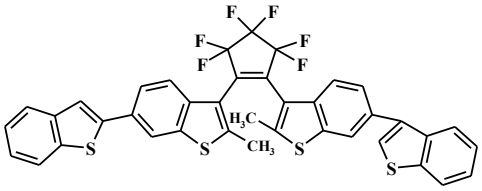
1,2-Bis[6-(benzo[*b*]thiophen-3-yl)-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene (3b): $Pd(PPh_3)_4$ (11 mg, 0.01 mmol), Na_2CO_3 (110 mg), water (1 ml) and benzothiophen-3-ylboronic acid (37 mg, 0.021 mmol) were added to a solution of **2** (50 mg, 0.07 mmol) in THF (10 ml). The reaction mixture was heated under reflux for 24 h. The reaction mixture was poured into water, extracted with CH_2Cl_2, washed with water, dried. The solvent was distilled off, and the residue was purified on a chromatographic column (light petroleum). Yield 70%, mp 90−91 °C (EtOH). ^{1}H NMR (300 MHz, $CDCl_3$, *δ*, ppm): 2.29 (s, 6H, CH_3); 7.33-7.59 (m, 6H, ArH); 7.61 (m, 2H, ArH); 7.74-8.04 (m, 8H, ArH). ^{13}C NMR (50 MHz, $CDCl_3$, *δ*, ppm): 29.29 (CH_3); 119.87; 122.26; 122.41; 123.43; 123.59; 123.69; 124.41; 124.48; 124.57; 124.64; 124.79; 124.53; 128.69. ^{19}F NMR (280 MHz, $CDCl_3$, *δ*, ppm): -109.40 – (-112.25) (m, 4F, CF_2); -133.29 – (-133.56) (m, 2F, CF_2). HRMS (ESI) (m/z) [MH+] calculated for $C_{39}H_{22}F_6S_4$: 732.0477; found 732.0500.



1-[6-(Benzo[*b*]thiophen-3-yl)-2-methylbenzo[*b*]thiophen-3-yl]-2-(6-iodo-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (4b): $Pd(PPh_3)_4$ (5.5 mg, 0.005 mmol), Na_2CO_3 (55 mg), water (1 ml) and benzothiophen-3-ylboronic acid (19 mg, 0.011 mmol) were added to a solution of **2** (50 mg, 0.07 mmol) in THF (10 ml). The reaction mixture was heated under reflux for 24 h. The reaction mixture was poured into water, extracted with CH_2Cl_2, washed with water, dried. The solvent was distilled off, and the residue was purified on a chromatographic column (light petroleum). Yield 55%, mp 100−105 ^oC (EtOH). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.26 (s, 3H, CH_3); 2.50 (s, 3H, CH_3); 7.28-7.41 (m, 4H, ArH); 7.50(m, 1H, ArH); 7.56-8.03 (m, 6H, ArH). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm): 29.71 (CH_3); 119.84; 121.42; 122.28; 122.36; 123.70; 123.82; 124.56; 124.74; 124.89; 125.03. ^{19}F NMR (280 MHz, $CDCl_3$, δ, ppm): -109.46 – (-112.03) (m, 4F, CF_2); -133.40 – (-133.77) (m, 2F, CF_2). HRMS (ESI) (m/z) [MH+] calculated for $C_{31}H_{17}F_6IS_3$: 732.0475; found 732.0503.



1-[6-(Benzo[*b*]thiophen-2-yl)-2-methylbenzo[*b*]thiophen-3-yl]-2-[6-(4-methoxyphenyl)-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene (5a): $Pd(PPh_3)_4$ (5.5 mg, 0.005 mmol), Na_2CO_3 (55 mg), water (1 ml) and methoxyphenyl boronic acid (16 mg, 0.011 mmol) were added to a solution of **4a** (50 mg, 0.07 mmol) in THF (10 ml). The reaction mixture was heated under reflux for 24 h. The reaction mixture was poured into water, extracted with CH_2Cl_2, washed with water, dried. The solvent was distilled off, and the residue was purified on a chromatographic column (light petroleum). Yield 45%, mp 105 ^oC (EtOH). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.29 (s, 3H, CH_3); 2.55 (s, 3H, CH_3); 3.88 (s, 3H, OCH_3); 6.88-7.59 (m, 2H, ArH); 7.30-8.15 (m, 13H, ArH). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm): 29.73 (CH_3); 55.38 (OCH_3); 114.22; 114.33; 114.35; 114.36; 114.42; 119.71; 119.87; 122.31; 123.55; 123.61; 123.65; 124.06; 124.52; 124.69; 127.77; 128.31; 130.93; 133.08; 133.55; 136.98; 137.54; 138.19; 139.08; 140.74; 143.63; 158.76; 159.38. ^{19}F NMR (280 MHz, $CDCl_3$, δ, ppm): -109.86 – (-112.13) (m, 4F, CF_2); -133.39 – (-133.64) (m, 2F, CF_2). HRMS (ESI) (m/z) [MH+] calculated for $C_{38}H_{24}F_6OS_3$: 706.0888; found 706.0886.



1-[6-(Benzo[*b*]thiophen-2-yl)-2-methylbenzo[*b*]thiophen-3-yl]-2-[6-(benzo[*b*]thiophen-3-yl)-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene (5b): $Pd(PPh_3)_4$ (5.5 mg, 0.005 mmol), Na_2CO_3 (55 mg), water (1 ml) and benzothiophen-3-ylboronic acid (19 mg, 0.011 mmol) were added to a solution of **4a** (50 mg, 0.07 mmol) in THF (10 ml). The reaction mixture was heated under reflux for 24 h. The reaction mixture was poured into water, extracted with CH_2Cl_2, washed with water, dried. The solvent was distilled off, and the residue was purified on a chromatographic column (light petroleum). Yield 40%, mp 90−91 ^oC (EtOH). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.30 (s, 6H, CH_3); 7.33-7.59 (m, 6H, ArH); 7.61 (m, 2H, ArH); 7.74-8.04 (m, 8H, ArH). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm): 29.30 (CH_3); 119.87; 122.27; 122.41; 123.43; 123.60; 123.69; 124.41; 124.48; 124.57; 124.64; 124.79; 124.53; 128.70. ^{19}F NMR (280 MHz, $CDCl_3$, δ, ppm): -109.40 – (-112.25) (m, 4F, CF_2); -133.29 – (-133.56) (m, 2F, CF_2). HRMS (ESI) (m/z) [MH+] calculated for $C_{39}H_{22}F_6S_4$: 732.0478; found 732.0502.