Supplementary Information

Shortcut to highly π-extended optoelectronic systems based on the dibenzothiophene core

Clara Fabregat,[a,b] Roger Bujaldón,*[a,b] Silvia Oliva,[a] Jaume Garcia-Amorós,[a,b] Dmytro Volyniuk,[c] Melika Ghasemi,[c] Juozas V. Grazulevicius,[c] Joaquim Puigdollers,[d] Dolores Velasco *[a,b]

[a] *Grup de Materials Orgànics, Departament de Química Inorgànica i Orgànica, Secció de Química Orgànica, Universitat de Barcelona, Martí i Franquès 1, E-08028, Barcelona, Spain.*

[b] *Institut de Nanociència i Nanotecnologia (IN^{2}UB), E-08028, Barcelona, Spain.*

[c] *Department of Polymer Chemistry and Technology, Kaunas University of Technology, Barsausko 59, Kaunas, Lithuania.*

[d] *Dept. Enginyeria Electrònica, Universitat Politècnica de Catalunya, Jordi Girona 1–3, E-08034, Barcelona, Spain.*

** Corresponding authors: E-mail: dvelasco@ub.edu: rr.bujaldon@ub.edu*

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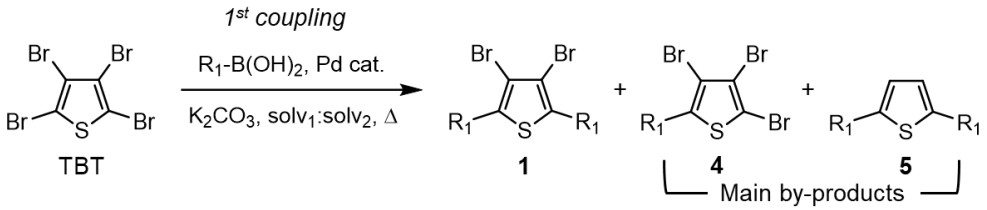
1. Experimental section

1.1. General remarks

All chemicals were of commercial grade and used as received. All solvents were dried and degassed by standard methods. Anhydrous CH_2Cl_2 was prepared by distillation over CaH_2 prior to use. Anhydrous nitromethane was obtained by distillation to remove the water/nitromethane azeotrope, and kept under nitrogen with molecular sieve (4 Å). Reactions were monitored by thin layer chromatography (TLC) using aluminum sheets coated with silica gel (Merck, 60 F_{254}). Flash chromatography was carried out over commercial silica gel (VWR, 40-63 µm).

1.2. Synthetic procedures

1.2.1. Synthesis of compounds 1a–d

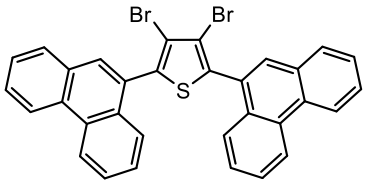


- General method A: TBT (0.400 g, 1.00 mmol), arylboronic acid (2.10 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 g, 0.050 mmol), PPh_3 (0.027 g, 0.10 mmol) and K_2CO_3 (1.38 g, 10.0 mmol) are dissolved in a mixture of DMF and H_2O (22.5 mL, 8:1 v/v) under nitrogen and stirred at 110 °C overnight. After cooling to room temperature, the reaction mixture is diluted with water and the resulting precipitate, filtered off and thoroughly washed with water. The crude is purified by flash column chromatography.
- General method B: TBT (0.400 g, 1.00 mmol), arylboronic acid (2.10 mmol), $Pd(PPh_3)_4$ (0.058 g, 0.050 mmol) and K_2CO_3 (1.38 g, 10.0 mmol) are dissolved in a mixture of THF and H_2O (35 mL, 6:1 v/v) under nitrogen and stirred under reflux overnight. After cooling to room temperature, the reaction mixture is diluted with water and the product, extracted with dichloromethane. The combined organic layers are dried over anhydrous $MgSO_4$, filtered and the solvent is removed under reduced pressure. The crude is purified by flash column chromatography.
- General method C: TBT (0.400 g, 1.00 mmol), arylboronic acid (2.10 mmol), $Pd(PPh_3)_2Cl_2$ (0.035 g, 0.050 mmol), PPh_3 (0.027 g, 0.10 mmol) and K_2CO_3 (1.39 g, 10.0 mmol) are dissolved in a mixture of toluene and H_2O (65 mL, 10:3 v/v) under nitrogen and stirred at 110 °C

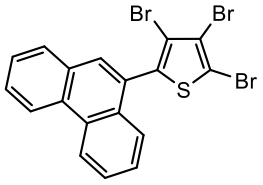
overnight. After cooling to room temperature, the reaction mixture is diluted with water and the product, extracted with dichloromethane. The combined organic layers are dried over anhydrous $MgSO_4$, filtered and the solvent is removed under reduced pressure. The crude is purified by flash column chromatography.

- General method D: TBT (0.400 g, 1.00 mmol), arylboronic acid (2.10 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.050 mmol), and K_2CO_3 (1.39 g, 10.0 mmol) are dissolved in a mixture of toluene and methanol (16 mL, 3:1 v/v) under nitrogen and stirred under reflux overnight. After cooling to room temperature, the reaction mixture is diluted with dichloromethane, filtered and the solvent, removed under reduced pressure. The crude is purified by flash column chromatography.

1.2.1.1. Synthesis of compound **1a**

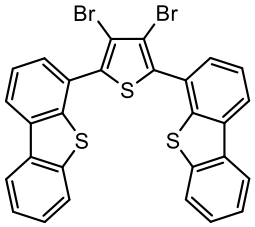


Compound **1a** was obtained as a pale yellow solid after purification with hexane as eluent, in a yield of: (A) 56% (0.335 g, 0.564 mmol); (B) 26% (0.157 g, 0.263 mmol); (C) 12% (0.074 g, 0.120 mmol) and (D) 51% (0.304 g, 0.512 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.81 (d, *J* = 8.1 Hz, 2H), 8.77 (d, *J* = 8.2 Hz, 2H), 7.98 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.97 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.96 (s, 2H), 7.78–7.65 (m, 8H).

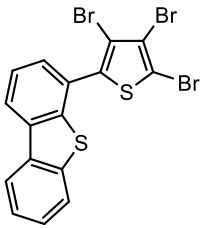


Compound **4a** was obtained as a pale yellow by-product in the synthesis of **1a**, in a yield of: (B) 23% (0.113 g, 0.227 mmol); (C) 6% (0.030 g, 0.060 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.83 (d, *J* = 8.0 Hz, 1H), 8.81 (d, *J* = 8.1 Hz, 1H), 7.93 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.86 (s, 1H), 7.77–7.71 (m, 1H), 7.69–7.62 (m, 2H), 7.51 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.41–7.35 (m, 1H).

1.2.1.2. Synthesis of compound **1b**

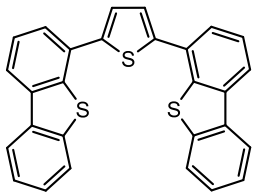


Compound **1b** was obtained as a pale yellow solid after purification with hexane as eluent, in a yield of: (A) not obtained; (B) 46% (0.279 g, 0.461 mmol); (C) 41% (0.248 g, 0.409 mmol) and (D) 70% (0.423 g, 0.698 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.26 (dd, *J* = 7.8, 1.2 Hz, 2H), 8.24–8.19 (m, 2H), 7.90–7.85 (m, 2H), 7.67 (dd, *J* = 7.4, 1.2 Hz, 2H), 7.61 (dd, *J* = 7.8, 7.4 Hz, 2H), 7.54–7.47 (m, 4H).



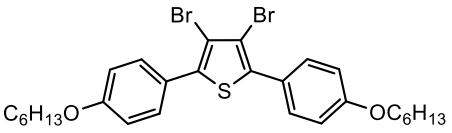
Compound **4b** was obtained as a pale yellow by-product in the synthesis of **1b**, in a yield of: (C) 26% (0.132 g, 0.263 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.24 (dd, *J* = 7.7, 1.3 Hz, 1H), 8.21–8.18 (m, 1H), 7.88–7.82 (m, 1H), 7.58–7.54 (m, 1H), 7.52–7.47 (m, 3H).

Compound **5b** was obtained as a pale yellow by-product in the synthesis of **1b**, in a yield of: (A) 71% (0.317 g, 0.706 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.24–8.19 (m, 2H), 8.17 (dd, *J* = 7.9, 1.1 Hz, 2H), 7.96–7.90 (m, 2H), 7.78 (dd, *J* = 7.5, 1.1 Hz, 2H), 7.75 (s, 2H), 7.57 (dd, *J* = 7.9, 7.7 Hz, 2H), 7.54–7.48 (m, 4H).

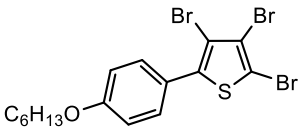


1.2.1.3. Synthesis of compound **1c**

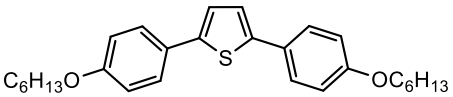
Compound **1c** was obtained as a pale brown solid after purification with a mixture of hexane and dichloromethane (20:1 v/v) as eluent, in a yield of: (A) not obtained; (B) 45% (0.269 g, 0.453 mmol); (C) 19% (0.114 g, 0.191 mmol) and (D) 38% (0.226 g, 0.381 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.56 (d, *J* = 8.8 Hz, 4H), 6.96 (d, *J* = 8.8 Hz, 4H), 4.00 (t, *J* = 6.5 Hz, 4H), 1.84−1.77 (m, 4H), 1.54−1.30 (m, 12H), 0.92 (t, *J* = 7.0 Hz, 6H).



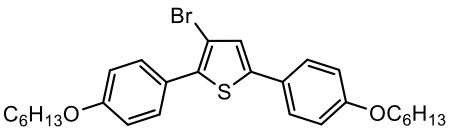
Compound **4c** was obtained as white by-product in the synthesis of **1c**, in a yield of: (C) 71% (0.352 g, 0.708 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.47 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.99 (t, *J* = 6.5 Hz, 2H), 1.83−1.76 (m, 2H), 1.52−1.30 (m, 6H), 0.91 (t, *J* = 7.0 Hz, 3H).



Compound **5c** was obtained as a pale brown by-product in the synthesis of **1c**, in a yield of: (A) 69% (0.301 g, 0.689 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.57–7.49 (m, 4H), 7.13 (s, 2H), 6.95–6.87 (m, 4H), 3.98 (t, *J* = 6.6 Hz, 4H), 1.85–1.74 (m, 4H), 1.53–1.41 (m, 4H), 1.41–1.27 (m, 8H), 0.96–0.84 (t, *J* = 7.1 Hz, 6H).

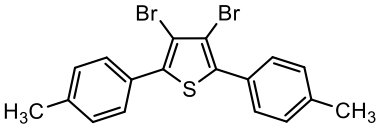


Compound **5c'** was obtained as a white by-product in the synthesis of **1c**, in a yield of: (D) 36% (0.186 g, 0.360 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.61–7.58 (m, 2H), 7.49–7.45 (m, 2H), 7.11 (s, 1H), 6.97–6.93 (m, 2H), 6.93–6.88 (m, 2H), 4.03–3.93 (m, 4H), 1.86–1.71 (m, 4H), 1.50–1.43 (m, 4H), 1.40–1.31 (m, 8H), 0.97–0.89 (m, 6H).

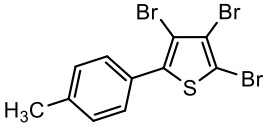


1.2.1.4. Synthesis of compound **1d**

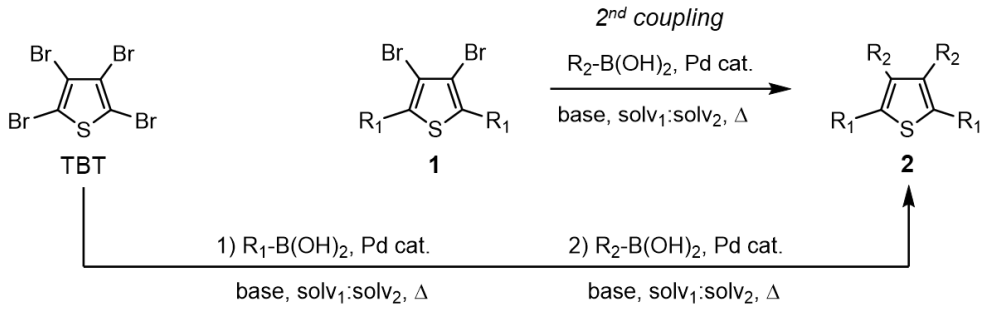
Compound **1d** was obtained as a white solid after purification with a mixture of hexane and dichloromethane (20:1 v/v) as eluent, in a yield of: (A) 42% (0.177 g, 0.419 mmol); (B) 58% (0.246 g, 0.582 mmol); (C) 3% (0.014 g, 0.033 mmol) and (D) 83% (0.352 g, 0.833 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.58–7.52 (m, 4H), 7.30–7.24 (m, 4H), 2.41 (s, 6H).



Compound **4d** was obtained as white by-product in the synthesis of **1d**, in a yield of: (C) 71% (0.291 g, 0.709 mmol). **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 7.50–7.46 (m, 2H), 7.25–7.21 (m, 2H), 2.38 (s, 3H).



1.2.2. Synthesis of compounds 2a–d

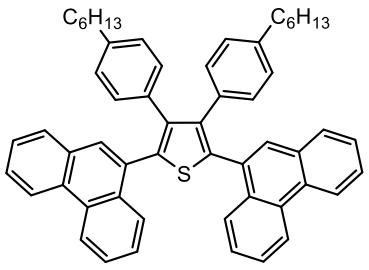


One-pot procedure

- General method A: **1**, arylboronic acid 2 (2.1 eq.), $Pd(PPh_3)_2Cl_2$ (5 mol%), PPh_3 (10 mol%) and K_2CO_3 (10 eq.) are dissolved in a mixture of DMF and H_2O (22.5 mL $mmol_1^{-1}$, 8:1 v/v) under nitrogen and stirred at 110 °C overnight. After cooling to room temperature, the reaction mixture is diluted with water and the resulting precipitate, filtered off and thoroughly washed with water. The crude is purified by flash column chromatography.
- General method B: **1**, arylboronic acid 2 (2.1 eq.), $Pd(PPh_3)_4$ (5 mol%) and K_2CO_3 (10 eq.) are dissolved in a mixture of THF and H_2O (35 mL $mmol_1^{-1}$, 6:1 v/v) under nitrogen and stirred under reflux overnight. After cooling to room temperature, the reaction mixture is diluted with water and the product, extracted with dichloromethane. The combined organic layers are dried over anhydrous $MgSO_4$, filtered and the solvent is removed under reduced pressure. The crude is purified by flash column chromatography.
- General method D: **1**, arylboronic acid 2 (2.1 eq.), $Pd(PPh_3)_4$ (5 mol%) and K_2CO_3 (10 eq.) are dissolved in a mixture of toluene and methanol (16 mL $mmol_1^{-1}$, 3:1 v/v) under nitrogen and stirred under reflux overnight. After cooling to room temperature, the reaction mixture is diluted with dichloromethane, filtered and the solvent is removed under reduced pressure. The crude is purified by flash column chromatography.
- General method E: **1**, arylboronic acid 2 (4.0 eq.), $Pd(AcO)_2$ (5 mol%), SPhos (20 eq.) and K_3PO_4 4.0 eq.) are dissolved in a mixture of toluene and methanol (16 mL $mmol_1^{-1}$, 3:1 v/v) under nitrogen and stirred under reflux overnight. After cooling to room temperature, the reaction mixture is diluted with dichloromethane, filtered and the solvent is removed under reduced pressure. The crude is purified by flash column chromatography.
- General one-pot procedures:
  - One-pot A: TBT (0.600 g, 1.50 mmol), arylboronic acid 1 (3.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.053 g, 0.075 mmol), PPh_3 (0.039 g, 0.15 mmol) and K_2CO_3 (2.07 g, 15.0 mmol) are dissolved in a mixture of DMF and H_2O (33.8 mL, 8:1 v/v) under nitrogen and stirred at 110 °C overnight. After cooling to room temperature, arylboronic acid 2 (3.6 mmol), $Pd(PPh_3)_2Cl_2$ (0.053 g, 0.075 mmol), PPh_3 (0.039 g, 0.15 mmol) and K_2CO_3 (2.07 g, 15.0 mmol) are added to the mixture, which is purged again with nitrogen and stirred at 110 °C overnight. Then, the mixture is diluted with water, and the resulting precipitate, filtered off and thoroughly washed with water. The crude is purified by flash column chromatography.

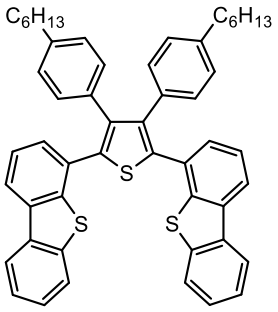
- One-pot B: TBT (0.600 g, 1.50 mmol), arylboronic acid 1 (3.2 mmol), $Pd(PPh_3)_4$ (0.087 g, 0.075 mmol) and K_2CO_3 (2.07 g, 15.0 mmol) are dissolved in a mixture of THF and H_2O (52.5 mL, 6:1 v/v) under nitrogen and stirred under reflux overnight. After cooling to room temperature, arylboronic acid 2 (3.6 mmol), $Pd(PPh_3)_4$ (0.087 g, 0.075 mmol) and K_2CO_3 (2.07 g, 15.0 mmol) are added to the mixture, which is purged again with nitrogen and stirred under reflux overnight. Then, the mixture is diluted with water and the product, extracted with dichloromethane. The combined organic layers are dried over anhydrous $MgSO_4$, filtered and the solvent is removed under reduced pressure. The crude is purified by flash column chromatography.
- One-pot D: TBT (0.600 g, 1.50 mmol), arylboronic acid 1 (3.2 mmol), $Pd(PPh_3)_4$ (0.087 g, 0.075 mmol) and K_2CO_3 (2.07 g, 15.0 mmol) are dissolved in a mixture of toluene and methanol (24 mL, 3:1 v/v) under nitrogen and stirred under reflux overnight. After cooling to room temperature, arylboronic acid 2 (3.6 mmol), $Pd(PPh_3)_4$ (0.087 g, 0.075 mmol) and K_2CO_3 (2.07 g, 15.0 mmol) are added to the mixture, which is purged again with nitrogen and stirred under reflux overnight. Then, the mixture is diluted with dichloromethane, filtered and the solvent is removed under reduced pressure. The crude is purified by flash column chromatography.
- One-pot E: TBT (0.600 g, 1.50 mmol), arylboronic acid 1 (3.6 mmol), $Pd(PPh_3)_4$ (0.087 g, 0.075 mmol) and K_2CO_3 (0.87 g, 6.3 mmol) are dissolved in a mixture of toluene and methanol (24 mL, 3:1 v/v) under nitrogen and stirred under reflux overnight. After cooling to room temperature, arylboronic acid/pinacol ester 2 (6.0 mmol), $Pd(AcO)_2$ (0.017 g, 0.075 mmol), SPhos (0.123 g, 0.300 mmol) and K_3PO_4 (1.28 g, 6.00 mmol) are added to the mixture, which is purged again with nitrogen and stirred under reflux overnight. Then, the mixture is diluted with dichloromethane, filtered and the solvent is removed under reduced pressure. The crude is purified by flash column chromatography.

1.2.2.1. Synthesis of compound **2a**



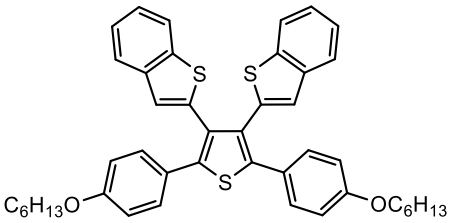
Compound **2a** was obtained as a pale yellow solid after purification with a mixture of hexane and dichloromethane (20:1 v/v) as eluent, in a yield of: (A) 55% (0.218 g, 0.288 mmol); (D) 86% (0.228 g, 0.301 mmol); (one-pot A) 70% (0.795 g, 1.05 mmol) and (one-pot D) 73% (0.829 g, 1.09 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.68 (d, *J* = 8.3 Hz, 4H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.90 (s, 2H), 7.85 (dd, *J* = 7.9, 1.1 Hz, 2H), 7.69–7.63 (m, 2H), 7.62–7.56 (m, 4H), 7.51–7.45 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 4H), 6.68 (d, *J* = 8.0 Hz, 4H), 2.33 (t, *J* = 7.6 Hz, 4H), 1.42–1.33 (m, 4H), 1.24–1.03 (m, 12H), 0.82 (t, *J* = 6.9 Hz, 6H).

1.2.2.2. Synthesis of compound **2b**



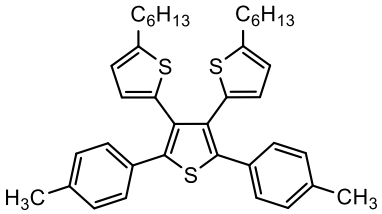
Compound **2b** was obtained as a white solid after purification with a mixture of hexane and dichloromethane (20:1 v/v) as eluent, in a yield of: (B) 76% (0.381 g, 0.495 mmol); (D) 86% (0.212 g, 0.276 mmol); (one-pot B) 53% (0.608 g, 0.790 mmol) and (one-pot D) 69% (0.796 g, 1.03 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.18–8.12 (m, 2H), 8.07 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.84–7.78 (m, 2H), 7.50–7.39 (m, 4H), 7.33 (dd, *J* = 7.7, 7.6 Hz, 2H), 7.27 (dd, *J* = 7.6, 1.2 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 4H), 6.80 (d, *J* = 8.0 Hz, 4H), 2.44 (t, *J* = 7.6 Hz, 4H), 1.48 (m, 4H), 1.34–1.12 (m, 12H), 0.85 (t, *J* = 6.8 Hz, 6H).

1.2.2.3. Synthesis of compound **2c**



Compound **2c** was obtained as a white solid after purification with a mixture of hexane and dichloromethane (20:1 v/v) as eluent, in a yield of: (B) 52% (0.221 g, 0.315 mmol); (D) not obtained; (E) 71% (0.299 g, 0.426 mmol); (one-pot B) 34% (0.353 g, 0.503 mmol) and (one-pot E) 46% (0.484 g, 0.691 mmol assegurar). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.64 (m, 2H), 7.58 (m, 2H), 7.28 (d, *J* = 8.5 Hz, 4H), 7.26–7.18 (m, 4H), 7.01 (s, 2H), 6.77 (d, *J* = 8.5 Hz, 4H), 3.90 (t, *J* = 6.5 Hz, 4H), 1.74 (m, 4H), 1.47–1.26 (m, 12H), 0.90 (t, *J* = 6.8 Hz, 6H).

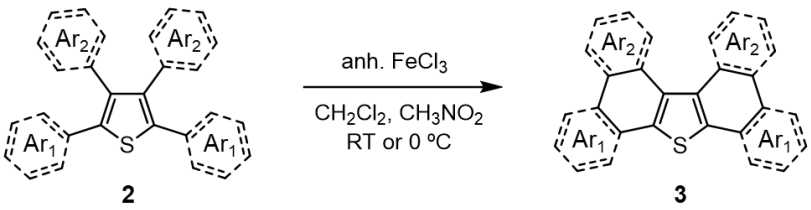
1.2.2.4. Synthesis of compound **2d**



For the synthesis of compound **2d**, 4,4,5,5-tetramethyl-2-(5-hexylthiophen-2-yl)-1,3,2-dioxaborolane was used instead of the corresponding boronic acid. It was synthesized following a reported methodology.[1] Compound **2d** was obtained as a white solid after purification using hexane as eluent, in a yield of: (B) not obtained; (D) not obtained; (E) 78% (0.795 g, 1.05 mmol) and (one-pot E) 76% (0.681 g, 1.14 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.25 (d, *J* = 8.1 Hz, 8H), 7.08 (d, *J* = 8.1 Hz, 4H), 6.55–6.49 (m, 3H), 2.69 (t, *J* = 7.5 Hz, 4H), 2.33 (s, 6H), 1.29–1.24 (m, 16H), 0.92–0.84 (m, 6H).

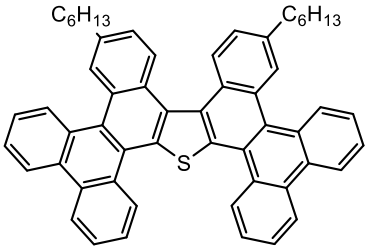
[1] C.-H. Lee and K. N. Plunkett, *Org. Lett.*, 2013, **15**, 1202–1205.

1.2.3. Synthesis of compounds 3a–d



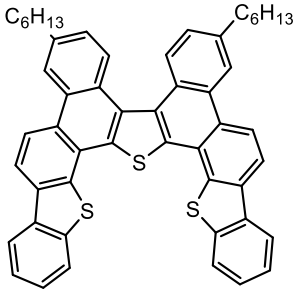
2 **3**

1.2.3.1. Synthesis of compound **3a**



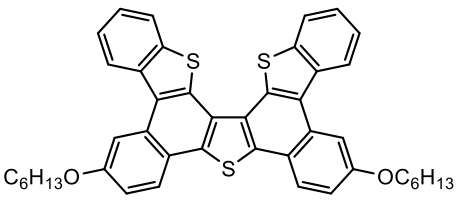
2a (218 mg, 0.288 mmol) was dissolved in anhydrous dichloromethane (8.6 mL) under nitrogen atmosphere. Then, a purged solution of anhydrous $FeCl_3$ (841 mg, 5.18 mmol) in nitromethane (2.9 mL) was added and stirred for 3.5 h. The reaction was then diluted with methanol. The resultant precipitate was filtered off and thoroughly washed with methanol and dried. The product was purified by flash column chromatography using hexane as eluent. Compound **3a** was obtained as a bright yellow solid in a yield of 81% (175 mg, 0.232 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 9.42 (d, *J* = 8.2 Hz, 2H), 8.97–8.90 (m, 2H), 8.87–8.76 (m, 6H), 8.63 (s, 2H), 7.89 (dd, *J* = 7.6, 7.5 Hz, 2H), 7.82 (dd, *J* = 7.6, 7.5 Hz, 2H), 7.78–7.71 (m, 4H), 7.41 (d, *J* = 8.5 Hz, 2H), 2.86 (t, *J* = 7.8 Hz, 4H), 1.82–1.71 (m, 4H), 1.49–1.39 (m, 4H), 1.38–1.27 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 140.3, 134.7, 130.6, 130.5 (2C), 129.9, 129.6, 129.1 (2C), 128.5, 127.6, 127.5, 127.1, 126.7, 126.3, 126.2, 126.0, 124.7, 123.6 (2C), 36.4, 31.8, 31.5, 29.1, 22.7, 14.1. **MS (**MALDI-TOF**)** (*m*/*z*): calculated for $C_{56}H_{48}S$: 752.3 $(M^{\cdot})^+$; found: 752.3.

1.2.3.2. Synthesis of compound **3b**



2b (351 mg, 0.456 mmol) was dissolved in anhydrous dichloromethane (13.7 mL) under nitrogen atmosphere at 0 °C. Then, a purged solution of anhydrous $FeCl_3$ (1.33 g, 8.21 mmol) in nitromethane (4.2 mL) was added and stirred for 20 min at 0 °C. The reaction was then diluted with methanol and dried. The resultant precipitate was filtered and thoroughly washed with methanol. The product was further purified by subsequent crystallizations from hexane/dichloromethane mixtures. Compound **3b** was obtained as a pale yellow solid in a yield of 93% (323 mg, 0.422 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.94 (d, J = 8.7 Hz, 2H), 8.80 (d, J = 8.5 Hz, 2H), 8.65 (s, 2H), 8.56–8.48 (d, J = 8.5 Hz, 2H), 8.43–8.36 (m, 2H), 8.26–8.19 (m, 2H), 7.65–7.59 (m, 4H), 7.43 (d, J = 8.4 Hz, 2H), 2.95 (t, J = 8.0 Hz, 4H), 1.91–1.81 (m, 4H), 1.54–1.32 (m, 12H), 0.94 (t, J = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 158.6, 138.6, 138.3, 137.6, 136.0, 134.9, 133.8, 130.1, 128.1 (2C), 126.8, 125.0, 123.8, 122.8 (2C), 122.1, 116.7, 106.0, 105.0 (2C), 68.5, 31.7, 29.4, 25.9, 22.7, 14.1. **MS (**MALDI-TOF**)** (*m*/*z*): calculated for $C_{52}H_{44}S_3$: 764.3 $(M^{\cdot})^+$; found: 764.0.

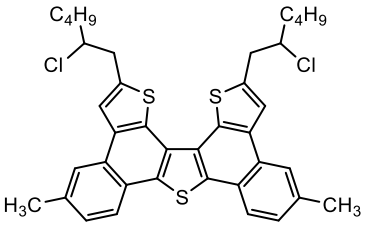
1.2.3.3. Synthesis of compound **3c**



2c (221 mg, 0.315 mmol) was dissolved in anhydrous dichloromethane (9.5 mL) under nitrogen atmosphere. Then, a purged solution of anhydrous $FeCl_3$ (1.06 g, 6.52 mmol) in nitromethane (3.2 mL) was added and stirred for 1 h. The reaction was then diluted with methanol. The resultant precipitate was filtered and thoroughly washed with methanol and dried. The product was further purified by subsequent crystallizations from hexane/dichloromethane mixtures. Compound **3c** was obtained as a pale yellow solid in a yield of 74% (163 mg, 0.234 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.84 (d, *J* = 8.2 Hz, 2H), 8.47 (s, 2H), 8.31 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 7.3 Hz, 2H), 7.67–7.62 (m, 2H), 7.59–7.53 (m, 2H), 7.35

(d, *J* = 8.4 Hz, 2H), 4.29 (t, *J* = 6.5 Hz, 4H), 2.02–1.93 (m, 4H), 1.67–1.57 (m, 4H), 1.48–1.38 (m, 8H), 0.97 (t, *J* = 6.8 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 135.5 (2C), 134.5, 129.6, 128.9, 128.3, 127.1 (2C), 126.6, 126.1, 124.7, 123.5, 122.9, 121.7, 120.4, 119.8. **MS (**MALDI-TOF**)** (*m*/*z*): calculated for $C_{44}H_{40}O_2S_3$: 696.2 $(M^{\cdot})^+$; found: 696.4.

1.2.3.4. Synthesis of compound **3d**



2d (250 mg, 0.419 mmol) was dissolved in anhydrous dichloromethane (12.6 mL) under nitrogen atmosphere at 0 °C. Then, a purged solution of anhydrous $FeCl_3$ (1.35 g, 8.32 mmol) in nitromethane (4.2 mL) was added and stirred for 2 h at 0 °C. The reaction was then diluted with methanol. The resultant precipitate was filtered and thoroughly washed with methanol and dried. The product was purified by flash column chromatography with a mixture of hexane and dichloromethane (10:1 v/v) as eluent. Compound **3d** was obtained as a pale yellow solid in a yield of 14% (37 mg, 0.057 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 8.23 (d, *J* = 8.3 Hz, 2H), 8.16 (s, 2H), 7.93 (s, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 3.60–3.53 (m, 4H), 2.64 (s, 6H), 1.45–1.12 (s, 16H), 0.97–0.87 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 136.5, 135.5, 134.4, 133.8, 130.4, 126.8, 126.4 (2C), 123.8, 123.4, 122.7, 120.2, 62.2, 38.6, 36.3, 27.6, 21.2, 20.9, 13.0. **MS (**MALDI-TOF**)** (*m*/*z*): calculated for $C_{38}H_{38}Cl_2S_3$: 660.2 $(M^{\cdot})^+$; found: 660.3.

2. Supplementary Figures and Tables

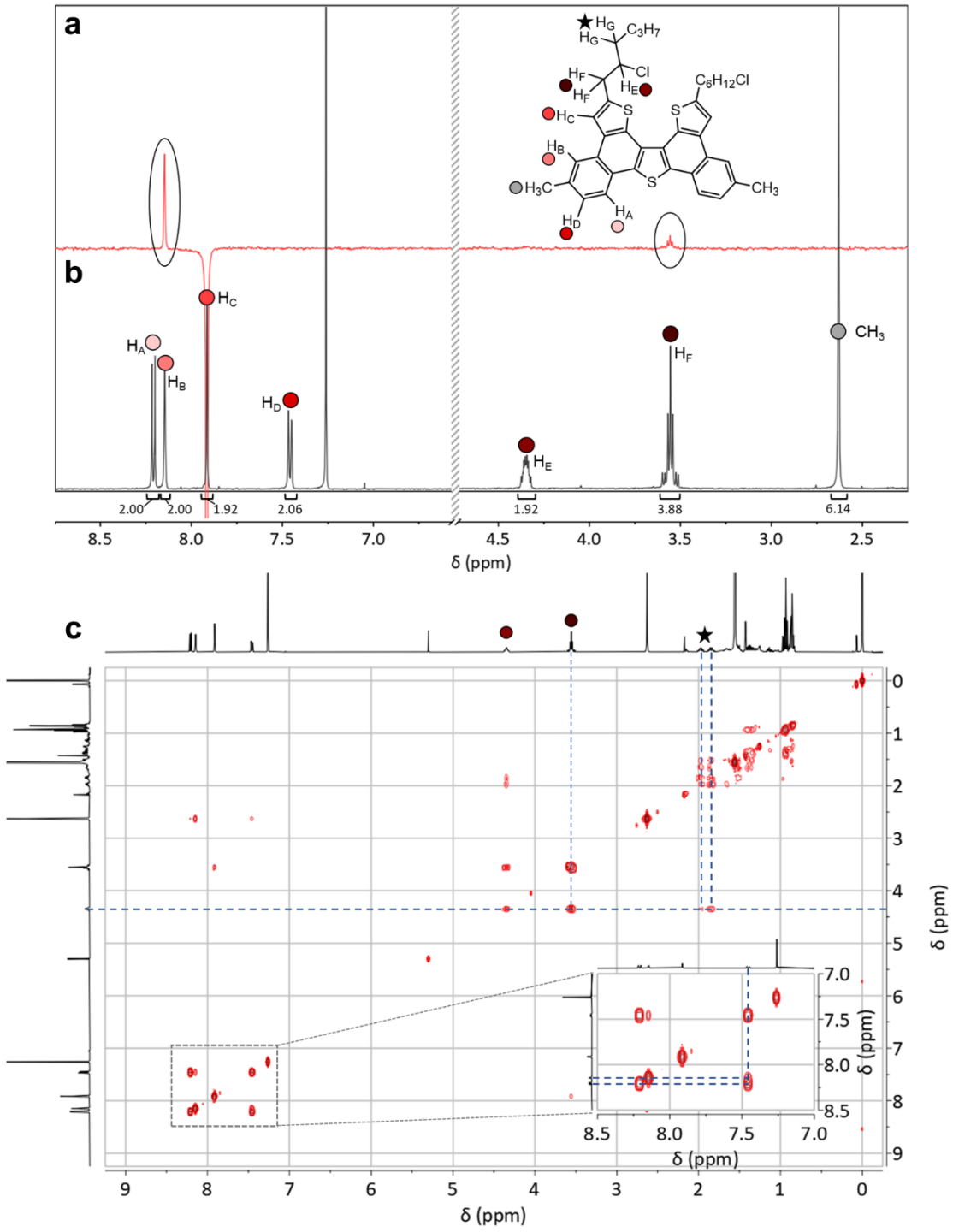


Figure S1. Structure elucidation of compound **3d** via NMR spectrometry: comparison between the 1D-NOESY spectrum irradiated at 7.94 ppm (a) and the ^{1}H NMR spectrum (b) that reveals NOE effect between proton C and protons B and F, implying that chlorine was not inserted at the benzylic position but at the second carbon of the hexyl chain; (c) COSY spectrum, which confirms that proton E, adjacent to the chlorine, is not benzylic because is directly coupled to protons F and G.

Table S1. Crystal data and structure refinement for **3a** crystallized from hexane/dichloromethane.

Identification code	Q38ACB034	
Deposition Number CCDC	2489352	
Empirical formula	$C_{62}H_{62}S$	
Formula weight	839.17 g mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P –1	
Unit cell dimensions	a = 10.7737(4) Å	α = 82.049(2)°
	b = 14.4183(7) Å	β = 81.140(2)°
	c = 15.0926(7) Å	γ = 79.941(2)°
Volume	2265.87(18) $Å^3$	
Z	2	
Density (calculated)	1.230 g/cm^3	
Absorption coefficient	0.113 mm^{-1}	
F(000)	900	
Crystal size	0.179 x 0.112 x 0.055 mm^3	
Theta range for data collection	1.88 to 30.60°	
Index ranges	–15<=h<=15, –20<=k<=20, –21<=l<=21	
Reflections collected	151320	
Independent reflections	13926 [R(int) = 0.1148]	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	13926 / 0 / 572	
Goodness-of-fit on F^2	1.052	
Final R indices	10563 data; I>2σ(I)	R1 = 0.0563, wR2 = 0.1269
	all data:	R1 = 0.0839, wR2 = 0.1409
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 1.4877P]$	
	where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.556 and –0.463 e $Å^{-3}$	
R.M.S. deviation from mean	0.067 e $Å^{-3}$	

Table S2. Crystal data and structure refinement for **3a** crystallized from dichloromethane/ethanol.

Identification code	Q38ABB142	
Deposition Number CCDC	2489351	
Empirical formula	$C_{114}H_{102}OS_2$	
Formula weight	1552.07 g mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P –1	
Unit cell dimensions	a = 10.6339(12) Å	α = 98.108(4)°
	b = 14.6568(19) Å	β = 98.948(4)°
	c = 28.381(4) Å	γ = 103.368(4)°
Volume	4178.5(9) $Å^3$	
Z	2	
Density (calculated)	1.234 g/cm^3	
Absorption coefficient	0.118 mm^{-1}	
F(000)	1652	
Crystal size	0.171 x 0.100 x 0.050 mm^3	
Theta range for data collection	1.75 to 26.14°	
Index ranges	–13<=h<=13, –18<=k<=18, –35<=l<=35	
Reflections collected	149319	
Independent reflections	16611 [R(int) = 0.2673]	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	16611 / 0 / 1060	
Goodness-of-fit on F^2	1.012	
Final R indices	8844 data; I>2σ(I)	R1 = 0.0879, wR2 = 0.1794
	all data:	R1 = 0.1746, wR2 = 0.2231
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0843P)^2 + 3.7185P]$	
	where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.764 and –0.413 e $Å^{-3}$	
R.M.S. deviation from mean	0.085 e $Å^{-3}$	

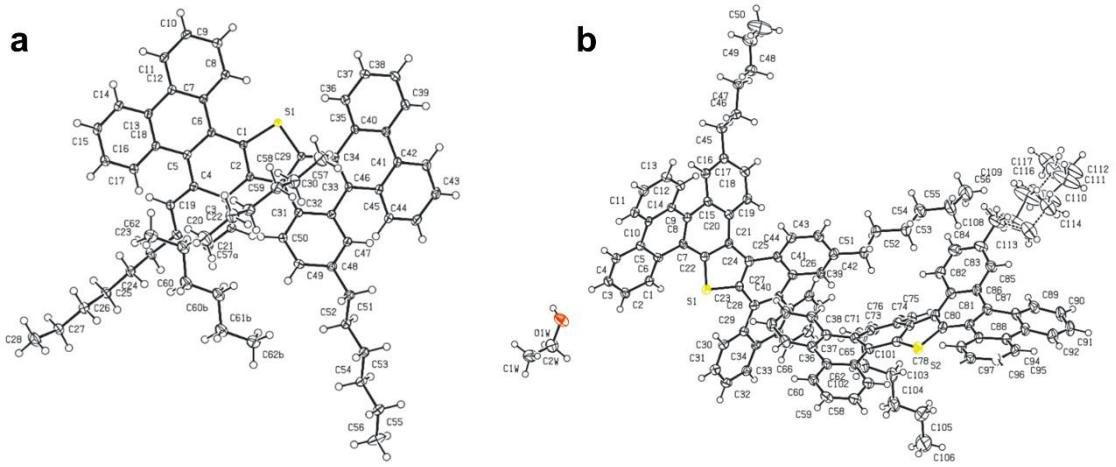


Figure S2. ORTEP projections corresponding to the single crystal of **3a** crystallized from a mixture of: (a) hexane and dichloromethane and (b) dichloromethane and ethanol.

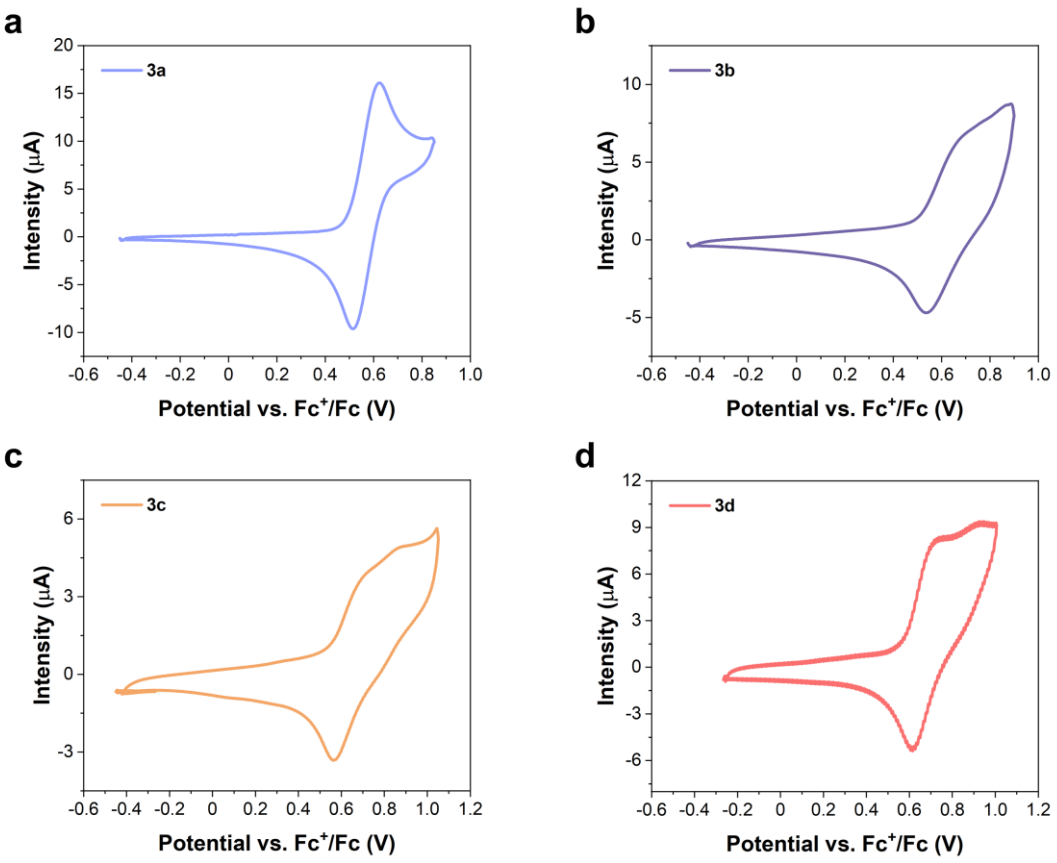


Figure S3. Cyclic voltammograms of compounds **3a–d** recorded at 100 mV s^{-1} in dichloromethane solutions (1 mM) referred to Fc^+/Fc.

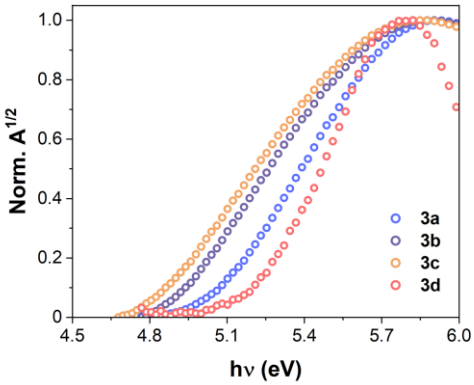


Figure S4. Photoemission spectra of vacuum-evaporated thin-films of **3a**–**d** in air at room temperature.

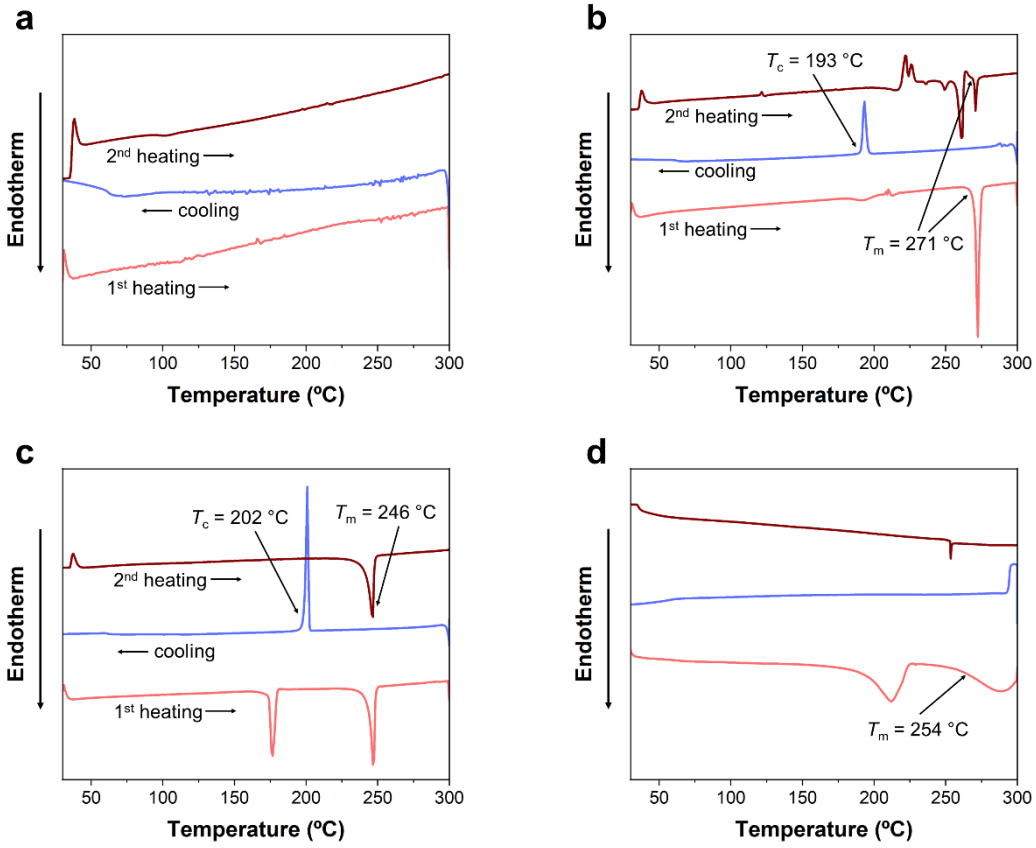


Figure S5. Differential scanning calorimetry (DSC) curves of the cyclized compounds recorded at a scan rate of 10 °C min^{-1}: (a) **3a**, (b) **3b**, (c) **3c** and (d) **3d**. The melting points (T_m) and crystallization temperatures (T_c) are also indicated.

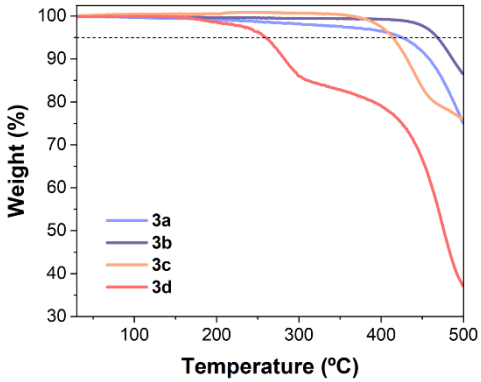


Figure S6. Thermogravimetric analysis (TGA) curves of compounds **3a**–**d** recorded at a scan rate of 10 °C min^{-1}.

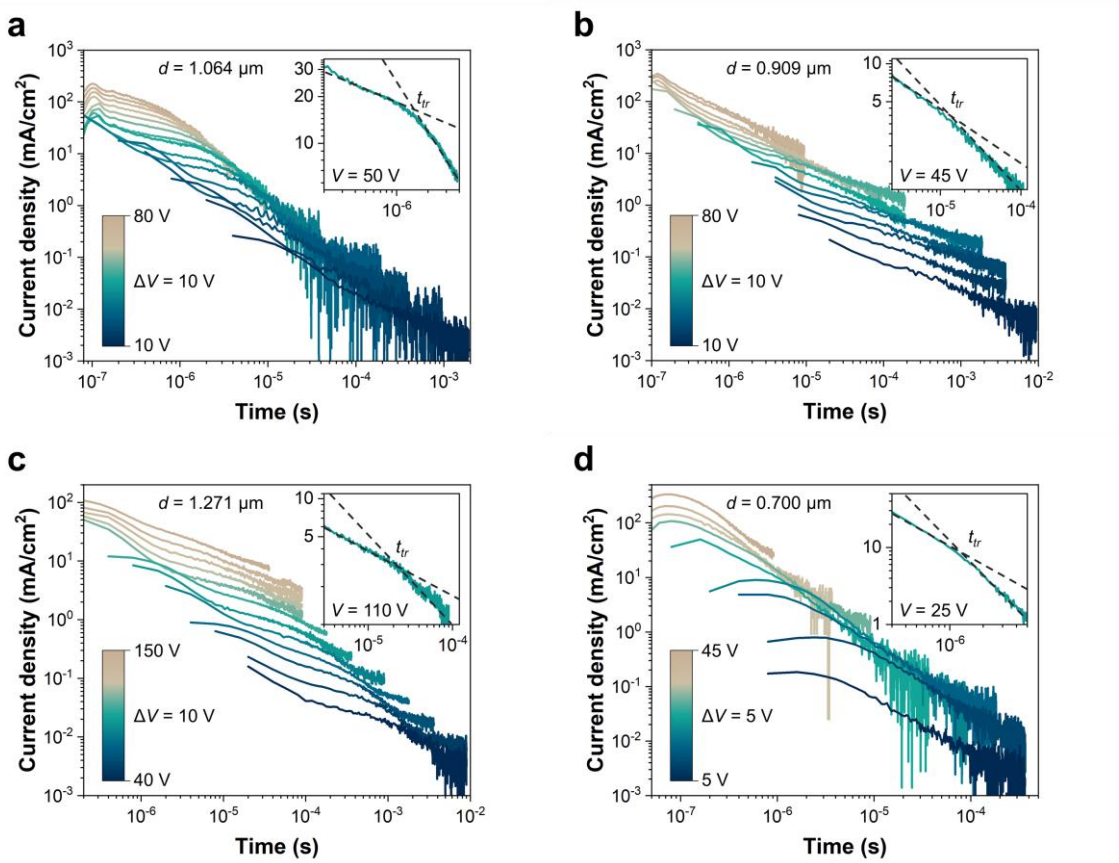


Figure S7. TOF transients in the log-log scale for hole transport of vacuum-evaporated thin-films containing compounds: (a) **3a**, (b) **3b**, (c) **3c** and (d) **3d**. The inset graphs present a zoomed transient example with the extraction of the transit time (t_{tr}). The thicknesses of the corresponding layers (*d*) are also indicated.

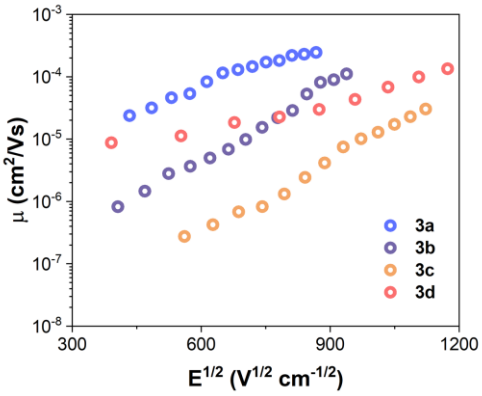


Figure S8. Electric field dependences of hole mobilities corresponding to vacuum-evaporated films of compounds **3a**–**d**.

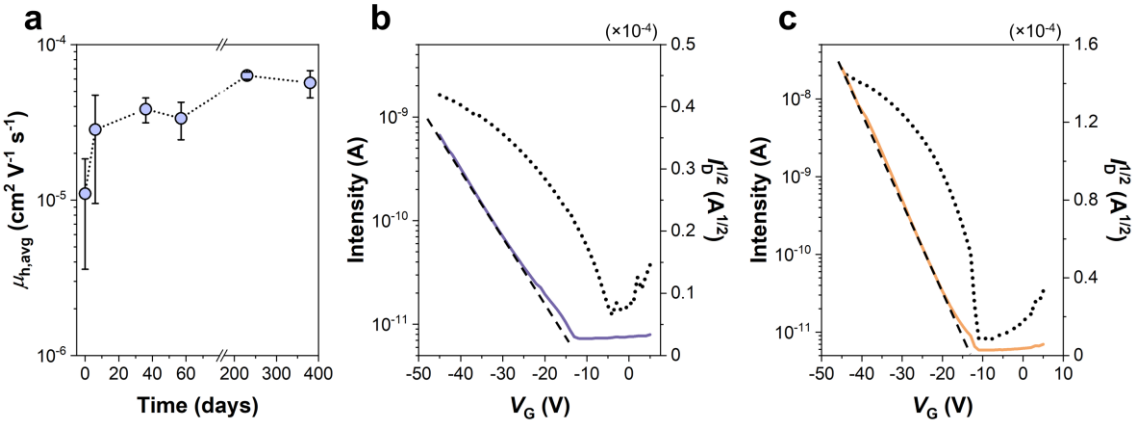


Figure S9. Characterisation of OTFT devices: (a) evolution of the $\mu_{h,avg}$ of a set of devices based on derivative **3a** over one year; transfer (V_D = –40 V) and saturation characteristics of PS-coated OTFTs based on derivatives **3b** (b) and **3c** (c).

Table S3. Photophysical characterization of the open intermediates **2a**–**d** in different media. Data corresponding to tetraphenylthiophene (TPT) is also added for comparison.

	Toluene		Solid state	
	$\lambda_{em,max}$ (nm)	Φ_f (%)	$\lambda_{em,max}$ (nm)	Φ_f (%)
TPT	400	2.0	398	1.0
2a	418	1.8	415	1.0
2b	412	1.4	406	0.6
2c	420	1.6	443	0.4
2d	438	1.4	443	0.5

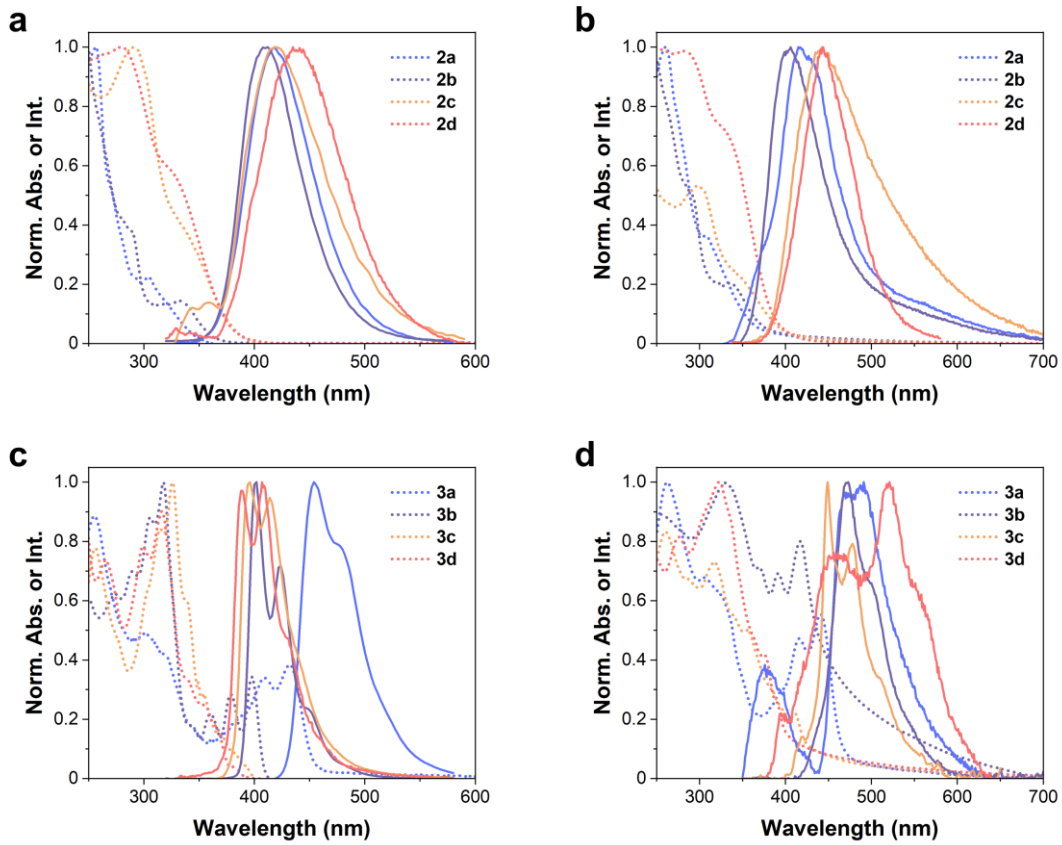


Figure S10. Absorption and emission spectra of compounds: **2a**–**d** in (a) dichloromethane and (b) drop-casted films over quartz; **3a**–**d** in (c) dichloromethane and (d) drop-casted films over quartz.

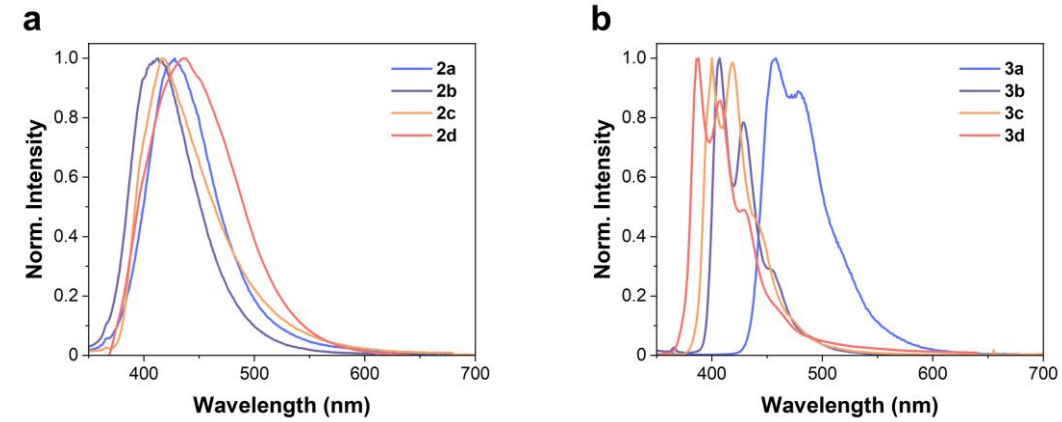


Figure S11. Emission spectra in toluene of: (a) the open intermediates **2a**–**d** and (b) the cyclized compounds **3a**–**d**.

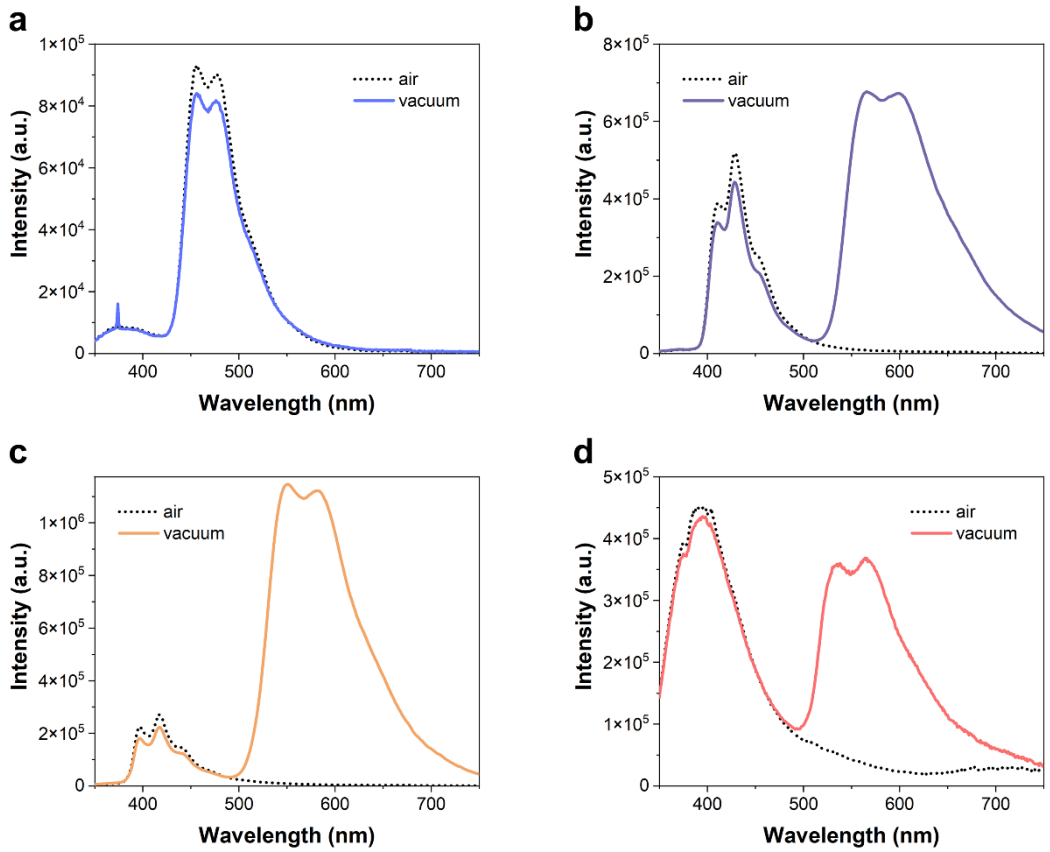


Figure S12. Photoluminescence spectra of Zeonex films containing compounds **3a**–**d** as dopants (1% wt) under air-equilibrated conditions and vacuum.

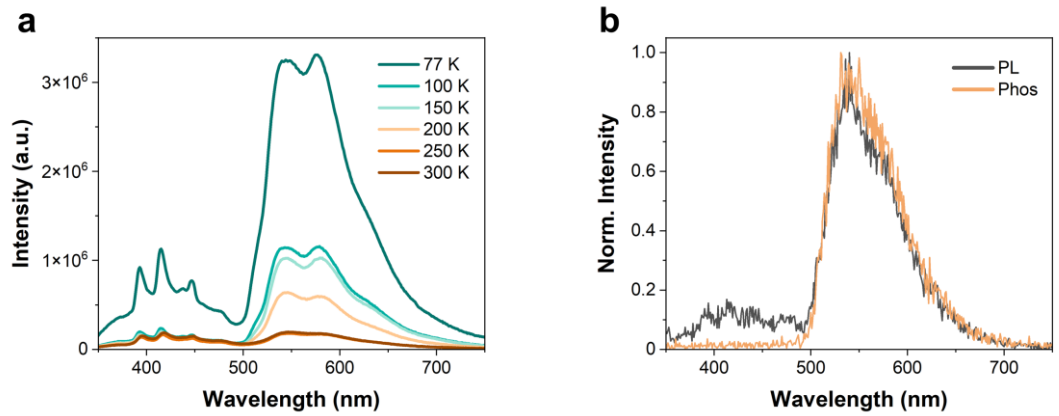


Figure S13. Insight into the photoluminescence of **3c** embedded as dopant (1% wt) within a Zeonex matrix: (a) temperature-dependent study; (b) superposed photoluminescence and phosphorescence spectra.

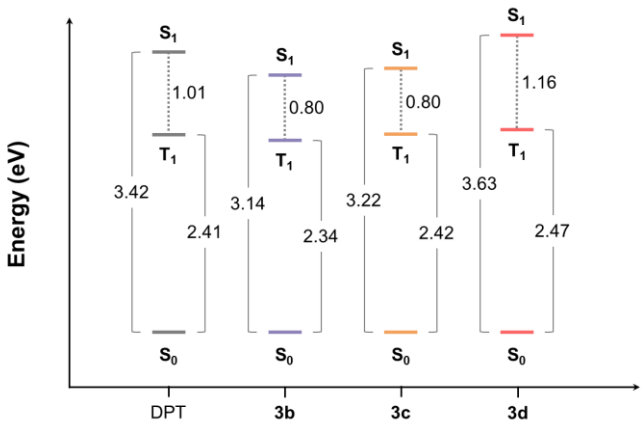


Figure S14. Diagram displaying the first singlet (S_1) and triplet (T_1) energy levels and the splitting energy ΔE_{ST} (in dotted lines) of compounds **3b–d**, estimated from the corresponding photoluminescence spectra in Zeonex-based films under air and vacuum. The values of the parent DPT are also included for comparison.