

## Supporting Information for

# Thiazole as a weak electron-donor unit to lower the frontier orbital energy levels of donor-acceptor alternating conjugated materials.

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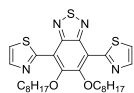
## I. Experimental

### General information

All reagents and chemicals were purchased from commercial sources (Aldrich, Across, Fluka) and used without further purification. 4,7-Dibromo-5,6-dioctyloxy-2,1,3-benzothiadiazole, 2,6-bis(trimethyltin)-4,8-dioctyloxy-benzo[1,2-b:3,4-b']dithiophene, and 4,7-di(thiophen-2-yl)-5,6-dioctyloxy-benzo[c][1,2,5]thiophene were synthesized by already described procedures.<sup>a, b, c</sup> All reactions were carried out in an argon atmosphere. All solvents were distilled over appropriate drying agent(s) prior to use and were purged with argon. Flash column chromatography was performed on silica gel 60 Å (230–400 mesh).

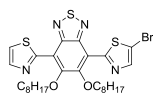
<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 400 NMR spectrometer, with <sup>1</sup>H and <sup>13</sup>C chemical shifts reported in ppm (δ) relative to CDCl<sub>3</sub> (7.26 and 77.16 respectively). UV-visible absorption spectroscopy measurements were performed using a Shimadzu UV-2101PC scanning spectrophotometer. Cyclic voltammetry analyses were carried out with a BioLogic VSP potentiostat using platinum electrodes at scan rates of 50 mV s<sup>-1</sup>. The measurements were performed in chloroform solutions (1.2×10<sup>-4</sup> M) containing 0.1 mol L<sup>-1</sup> of tetrabutylammonium tetrafluoroborate with a platinum working electrode or on thin films drop-casted from chloroform solutions onto a platinum working electrode in acetonitrile containing 0.1 mol L<sup>-1</sup> of tetrabutylammonium tetrafluoroborate. A Pt wire was used as a counter electrode and Ag/Ag<sup>+</sup> as a reference electrode. Ferrocene was used as internal standard to convert the values obtained in reference to Ag/Ag<sup>+</sup> to the saturated calomel electrode scale (SCE).

### 4,7-Di(thiazol-2-yl)-5,6-dioctyloxy-benzo[c][1,2,5]thiadiazole (TaBzTa)



To a degassed solution of 4,7-dibromo-5,6-dioctyloxy-2,1,3-benzothiadiazole (623 mg, 1.132 mmol)<sup>a</sup> and 2-tributylstannyl thiazole (1.76 mg, 2.830 mmol) in anhydrous toluene (35 mL), Pd(PPh<sub>3</sub>)<sub>4</sub> (118 mg, 0.102 mmol) was added. The mixture was heated at 115 °C during 48 h, the mixture was cooled at room temperature, filtered on celite®, the solution was washed with water and dried on sodium sulfate, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (dichloromethane/ethyl acetate : 8/2). Recrystallization from chloroform gave the title compound as a yellow powder (613 mg, 97 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.18 (d, 2H, *J*<sup>3,3</sup> 3.3 Hz), 7.59 (d, 2H, *J*<sup>3,3</sup> 3.3 Hz), 4.18 (t, 4H, *J*<sup>3</sup> 7.0 Hz), 1.92–1.82 (m, 4H), 1.41–1.32 (m, 4H), 1.32–1.22 (m, 16H), 0.98–0.82 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 158.8 (2C), 154.1 (2C), 150.3 (2C), 143.5 (2C), 121.2 (2C), 118.9 (2C), 75.5 (2C), 31.9 (2C), 30.3 (2C), 29.5 (2C), 29.3 (2C), 25.9 (2C), 22.7 (2C), 14.2 (2C).

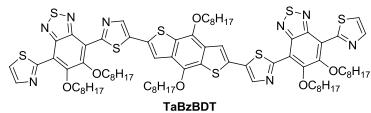
### 4-(5-bromothiazol-2-yl)-7-(thiazol-2-yl)-5,6-dioctyloxy-benzo[c][1,2,5]thiadiazole (1)



NBS (164 mg, 0.923 mmol) was added to a solution of 4,7-di(thiazol-2-yl)-5,6-dioctyloxy-benzo[c][1,2,5]thiadiazole **3a** (516 mg, 0.923 mmol) in chloroform (27 mL) and DMF (27 mL) and the reaction mixture was heated at 60 °C. After 24 h, the mixture was cooled at room temperature, extracted with chloroform, washed with water, and dried on sodium sulfate. The solvent was removed under reduced pressure and recrystallization from chloroform gave the title compound as a light red solid (275 mg, 47 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.21 (d, 1H, *J*<sup>3,3</sup> 3.1 Hz), 8.08 (s, 1H), 7.63 (d, 1H, *J*<sup>3,3</sup> 3.1 Hz), 4.25 (t, 2H, *J*<sup>3</sup> 7.1 Hz), 4.17 (t, 2H, *J*<sup>3</sup> 7.0 Hz), 1.99–1.82 (m, 4H), 1.51–1.16 (m, 20H), 0.96–0.78 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 154.2 (2C), 154.0 (2C), 144.6 (2C), 143.6 (1C), 121.5 (1C), 119.2 (1C), 118.3 (2C), 112.3 (1C), 75.7 (2C), 31.9 (2C),

30.43 (1C), 30.39 (1C), 29.5 (2C), 29.40 (1C), 29.37 (1C), 26.01 (1C), 25.99 (1C), 22.80 (1C), 22.79 (1C), 14.2 (2C).

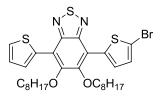
### Compound TaBzBDT



$\text{Pd}(\text{PPh}_3)_4$  (10 mg, 0.009 mmol) was added to a degassed solution of 4-(5-bromothiophen-2-yl)-7-(thiophen-2-yl)-5,6-dioctyloxy-benzo[*c*][1,2,5]-thiadiazole **4a** (275 mg, 0.433 mmol) and 2,6-bis(trimethyltin)-4,8-dioctyloxy-benzo[1,2-*b*:3,4-*b'*]dithiophene (139 mg, 0.180 mmol)<sup>b</sup> in

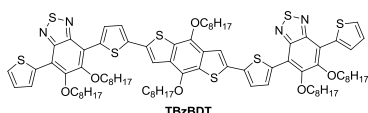
anhydrous toluene (8 mL). The mixture was heated at 115 °C during 24 h, cooled to room temperature, and filtered on celite®. The solution was washed with water, dried on sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (dichloromethane). Precipitation of the resulting product (saturated solution in chloroform) in methanol gave the title compound as an orange-red powder (208 mg, 74 %). <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400°MHz):  $\delta$  8.38 (s, 2H), 8.23 (d, 2H,  $J^3$  3.2 Hz), 7.68 (s, 2H), 7.64 (d, 2H,  $J^3$  3.2 Hz), 4.36 (t, 4H,  $J^3$  6.6°Hz), 4.30 (t, 4H,  $J^3$  7.0 Hz), 4.23 (t, 4H,  $J^3$  7.0 Hz), 2.03–1.87 (m, 12H), 1.67–1.58 (m, 4H), 1.53–1.22 (m, 56H), 0.94–0.82 (m, 18H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  158.8 (2C), 158.3 (2C), 154.4 (2C), 154.2 (2C), 150.4 (2C), 150.1 (2C), 144.4 (2C), 143.6 (2C), 140.9 (2C), 134.7 (2C), 133.2 (2C), 132.8 (2C), 129.9 (2C), 121.5 (2C), 119.2 (2C), 118.9 (2C), 118.6 (2C), 75.8 (2C), 75.6 (2C), 74.4 (2C), 32.0 (2C), 31.97 (2C), 31.96 (2C), 30.7 (2C), 30.5 (2C), 30.4 (2C), 29.64 (2C), 29.59 (4C), 29.47 (2C), 29.45 (2C), 29.40 (2C), 26.2 (2C), 26.1 (2C), 26.0 (2C), 22.8 (6C), 14.27 (2C), 14.25 (2C), 14.22 (2C); MALDI-MS: calcd. for  $[\text{C}_{82}\text{H}_{110}\text{N}_8\text{O}_6\text{S}_8+\text{H}^+]$  1559.64, found. 1559.62.

### 4-(5-bromothiophen-2-yl)-7-(thiophen-2-yl)-5,6-dioctyloxy-benzo[*c*][1,2,5]thiophene (2)



To a solution of 4,7-di(thiophen-2-yl)-5,6-dioctyloxy-benzo[*c*][1,2,5]thiophene **3b** (1.42 g, 2.54 mmol)<sup>c</sup> in chloroform (150 mL) and acetic acid (150 mL), NBS (431 mg, 2.42 mmol) was added and the reaction mixture was stirred at r.t. in the dark. After 16 h, the mixture was washed with water, extracted with chloroform, dried on sodium sulfate, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (petroleum ether/dichloromethane : 9/1) to give the product as a light red solid (1.02 g, 66 %). <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  8.46 (dd, 1H,  $J^3$  3.8 Hz,  $J^4$  1.1 Hz), 8.37 (d, 1H,  $J^3$  4.1 Hz), 7.51 (dd, 1H,  $J^3$  5.1 Hz,  $J^4$  1.1 Hz), 7.23 (dd, 1H,  $J^3$  3.8 Hz,  $J^3$  5.1 Hz), 7.17 (d, 1H,  $J^3$  4.1 Hz), 4.16 (t, 2H,  $J^3$  7.1 Hz), 4.08 (t, 2H,  $J^3$  7.1 Hz), 1.99–1.86 (m, 4H), 1.52–1.23 (m, 20H), 0.94–0.82 (m, 6H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  151.93 (1C), 151.87 (1C), 151.2 (1C), 150.6 (1C), 136.0 (1C), 134.1 (1C), 131.0 (1C), 130.8 (1C), 129.8 (1C), 127.7 (1C), 126.9 (1C), 118.1 (1C), 116.9 (1C), 115.4 (1C), 74.7 (1C), 74.6 (1C), 32.0 (2C), 30.5 (2C), 29.6 (2C), 29.4 (2C), 26.1 (2C), 22.8 (2C), 14.3 (2C).

### Compound TBzBDT

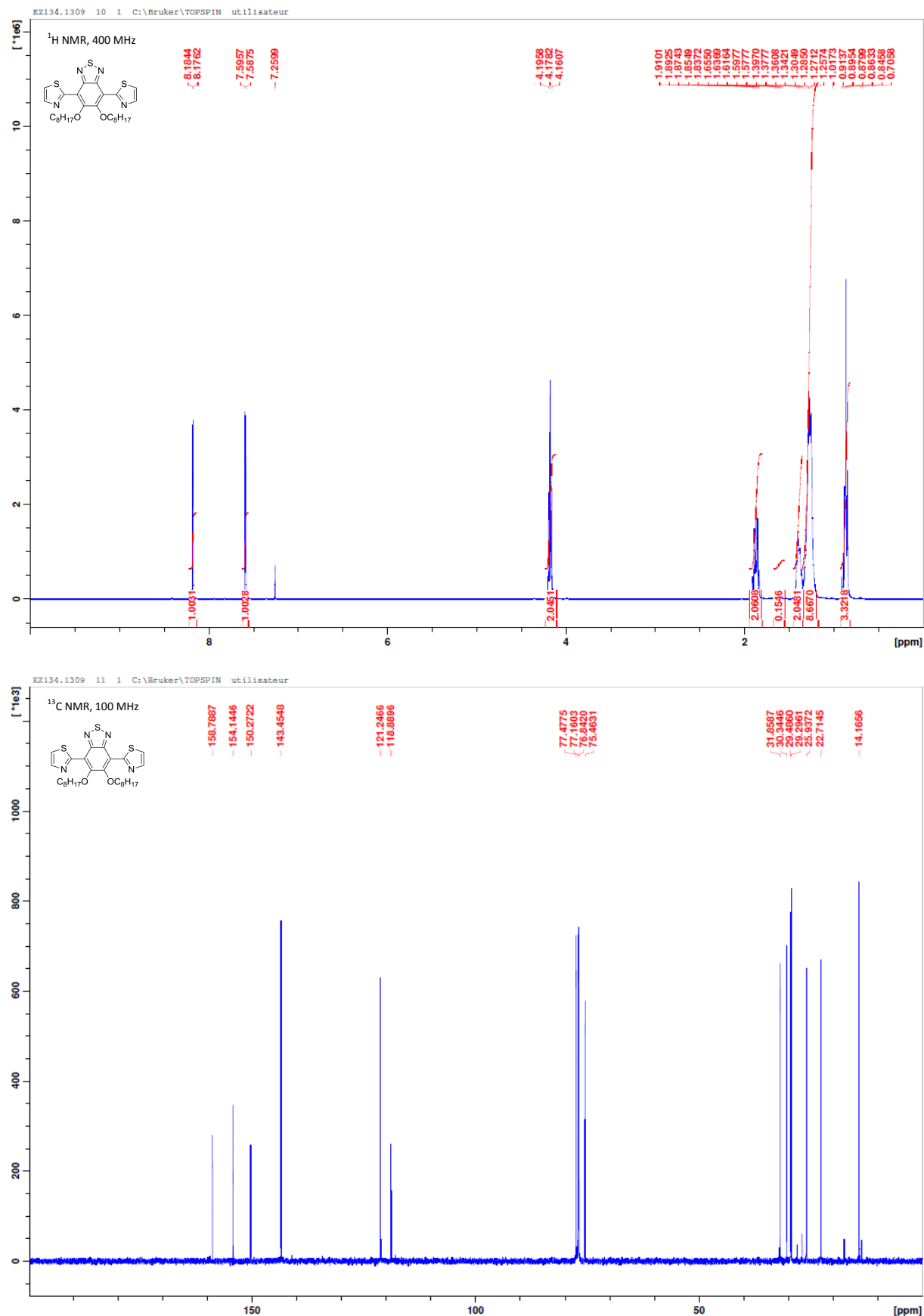


$\text{Pd}_2\text{dba}_3$  (30 mg, 0.033 mmol) and  $\text{P}(o\text{-tolyl})_3$  (40 mg, 0.131 mmol) were added to a degassed solution of 4-(5-bromothiophen-2-yl)-7-(thiophen-2-yl)-5,6-dioctyloxy-benzo[*c*][1,2,5]thiadiazole **4b** (500 mg, 0.786 mmol) and 2,6-bis(trimethyltin)-4,8-dioctyloxy-benzo[1,2-*b*:3,4-*b'*]dithiophene (253°mg, 0.327°mmol)<sup>b</sup> in anhydrous toluene (14 mL). The mixture was heated at 115 °C during 24 h, cooled to room temperature, and filtered on celite®. The solvent was removed under reduced pressure, and the solution was washed with water and dried on sodium sulfate. The

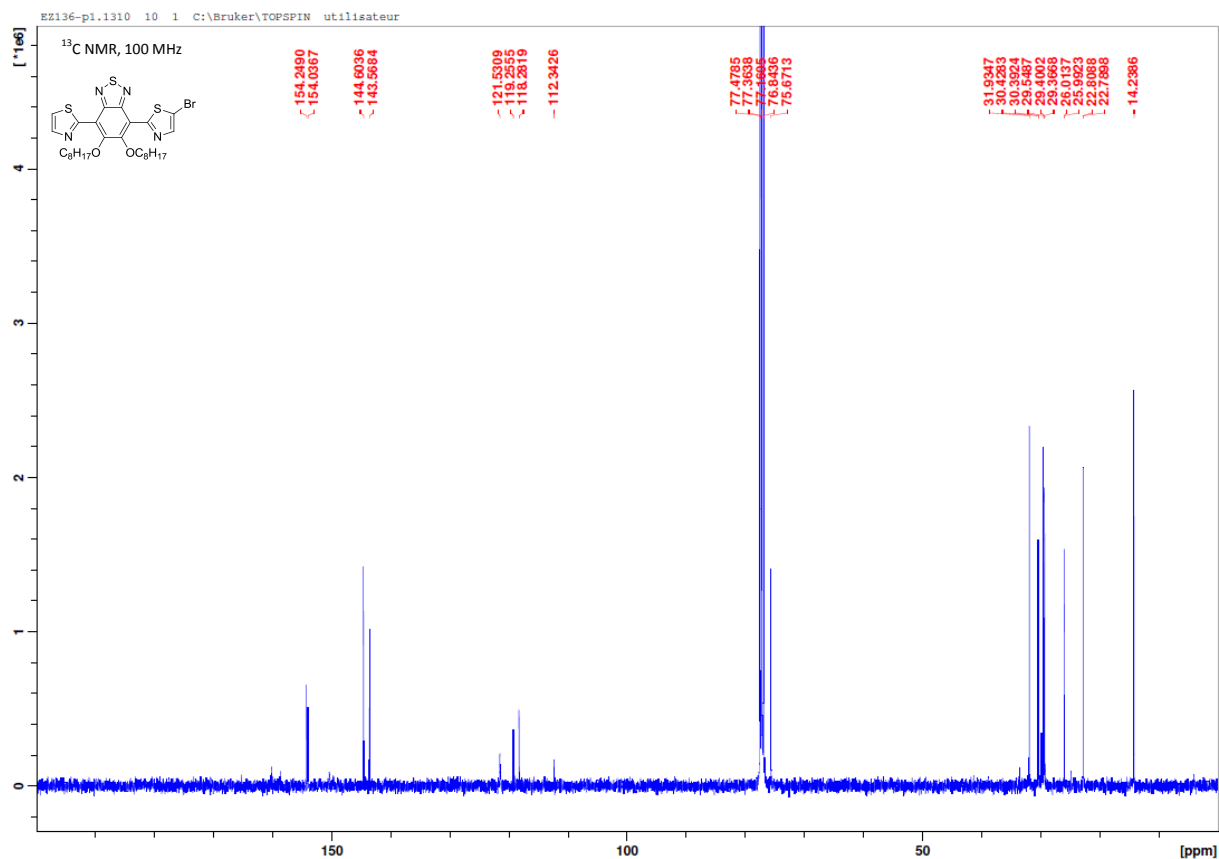
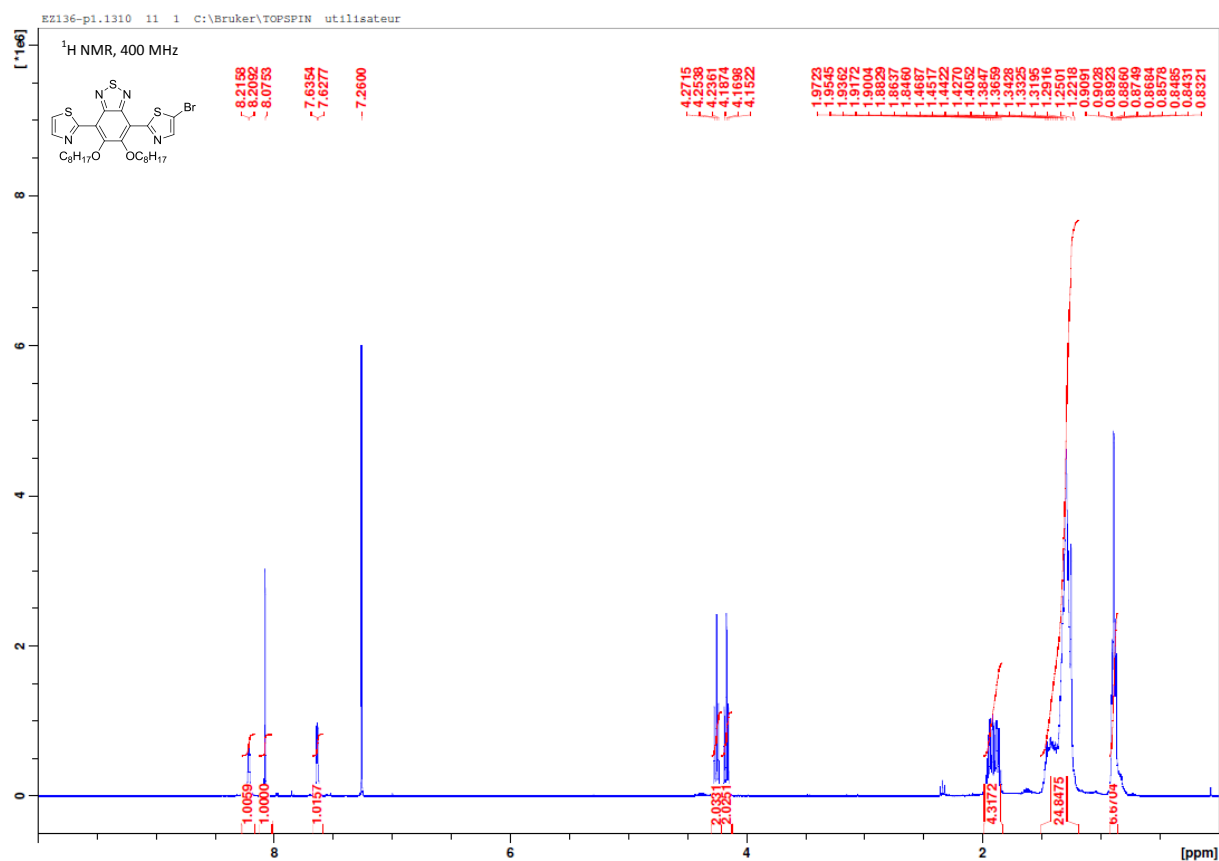
crude product was purified by column chromatography (petroleum ether/dichloromethane : 8/2). Precipitation of the resulting product (saturated solution in chloroform) in methanol gave the title compound as a red powder (283 mg, 56 %). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400°MHz):  $\delta$  8.55 (d, 2H,  $J^3$  3.9 Hz), 8.49 (d, 2H,  $J^3$  3.3 Hz), 7.61 (s, 2H), 7.51 (d, 2H,  $J^3$  4.9 Hz), 7.44 (bs, 2H), 7.24 (dd, 2H,  $J^3$  3.9 Hz,  $J^3$  4.9 Hz), 4.35 (bs, 4H), 4.21 (t, 4H,  $J^3$  7.0 Hz), 4.14 (t, 4H,  $J^3$  7.0 Hz), 2.11–1.85 (m, 12H), 1.66–1.58 (m, 4H), 1.58–1.21 (m, 56H), 0.98–0.81 (m, 18H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz):  $\delta$  152.1 (2C), 152.0 (2C), 151.2 (2C), 150.8 (2C), 144.1 (2C), 138.8 (2C), 136.9 (2C), 134.8 (2C), 134.2 (2C), 132.8 (2C), 131.8 (2C), 130.8 (2C), 129.7 (2C), 127.6 (2C), 126.9 (2C), 125.3 (2C), 118.0 (2C), 117.3 (2C), 116.3 (2C), 74.7 (2C), 74.6 (2C), 74.1 (2C), 32.05 (2C), 32.01 (2C), 31.99 (2C), 30.8 (2C), 30.6 (2C), 30.5 (2C), 29.8 (2C), 29.7 (2C), 29.6 (2C), 29.5 (4C), 29.4 (2C), 26.3 (2C), 26.2 (2C), 26.1 (2C), 22.9 (2C), 22.8 (4C), 14.29 (2C), 14.27 (2C), 14.24 (2C); **MALDI-MS**: calcd. for [C<sub>86</sub>H<sub>113</sub>N<sub>4</sub>O<sub>6</sub>S<sub>8</sub>] 1554.65, found. 1554.76.

## II. Spectral Images

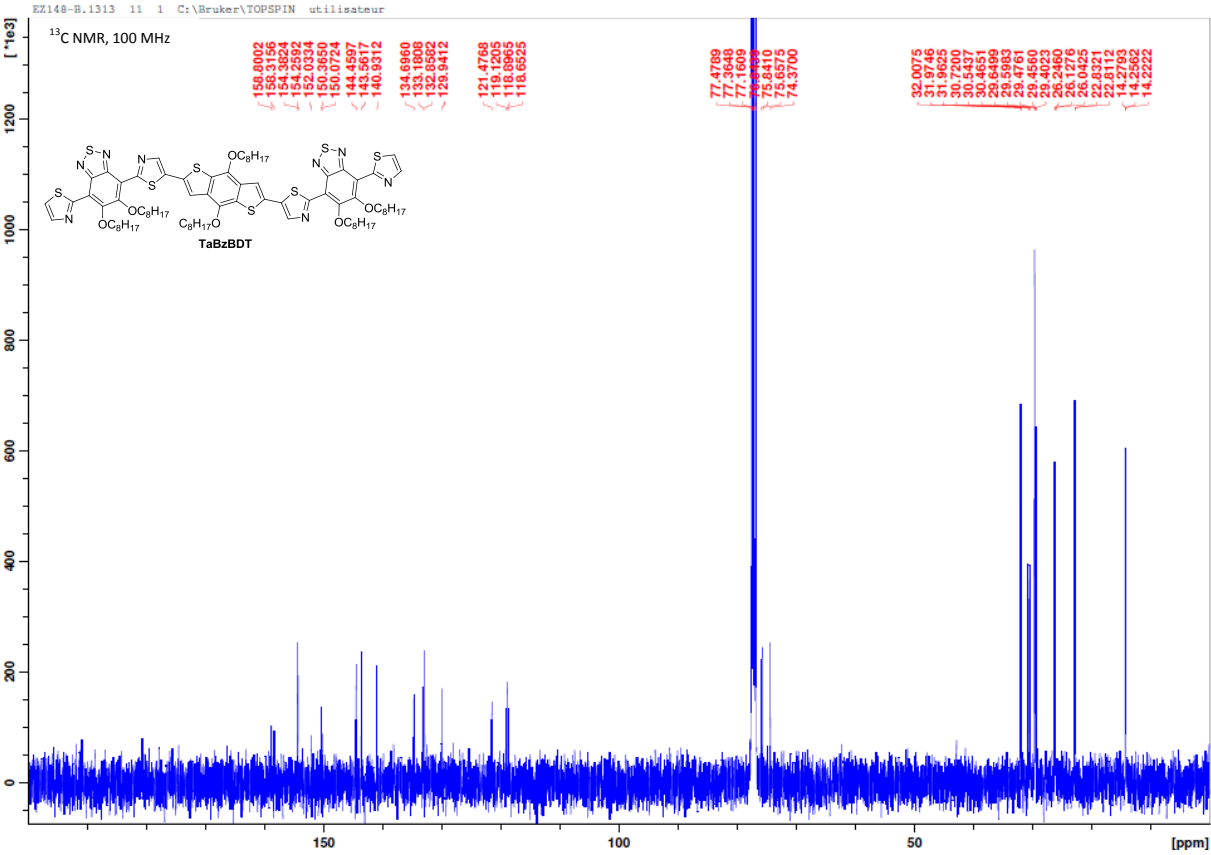
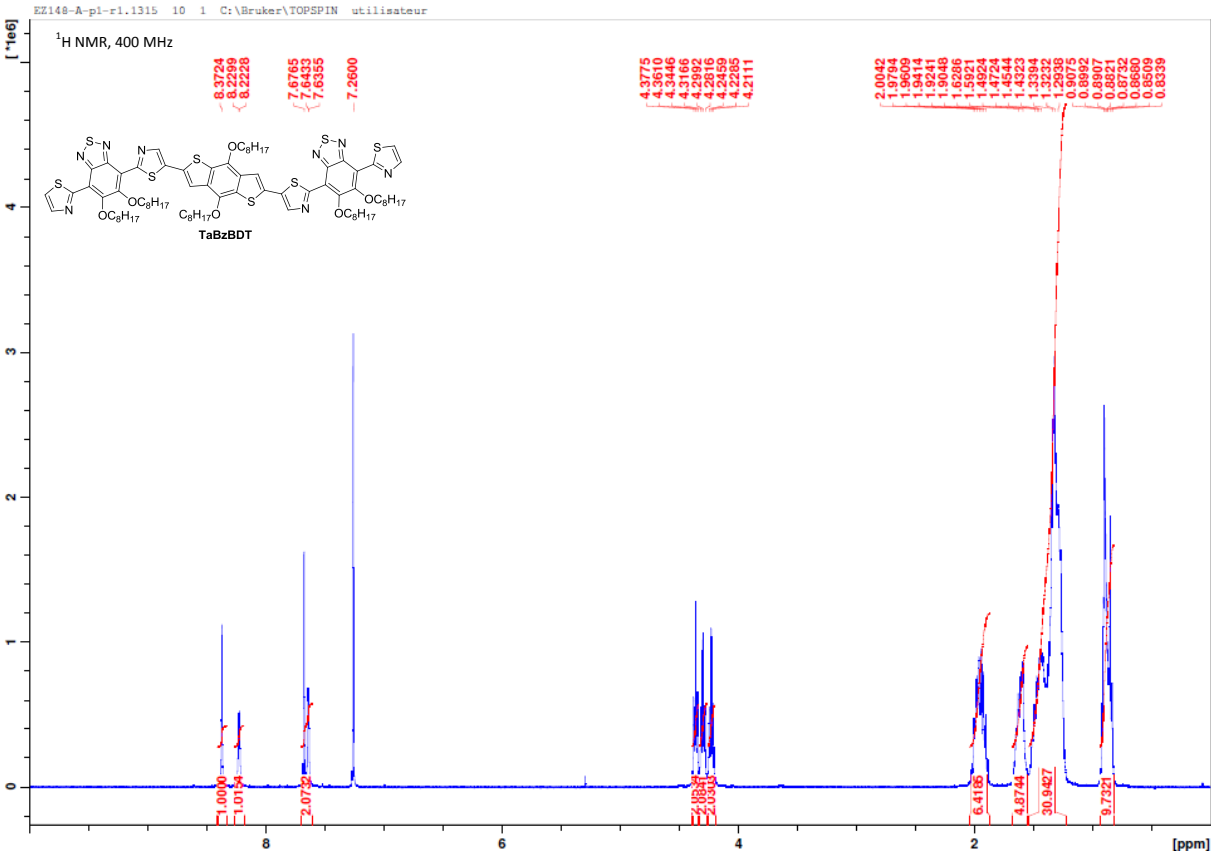
### 4,7-Di(thiazol-2-yl)-5,6-dioctyloxy-benzo[c][1,2,5]thiadiazole (TaBzTa)



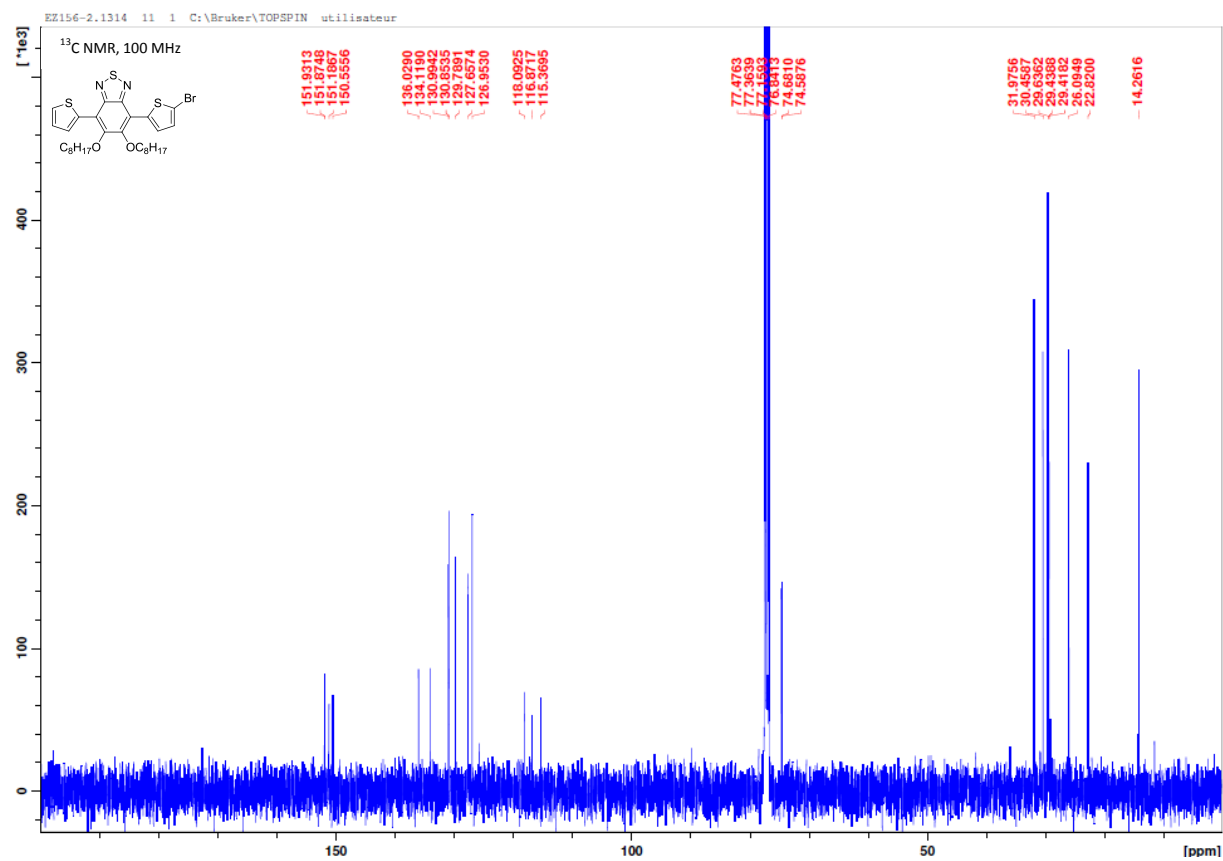
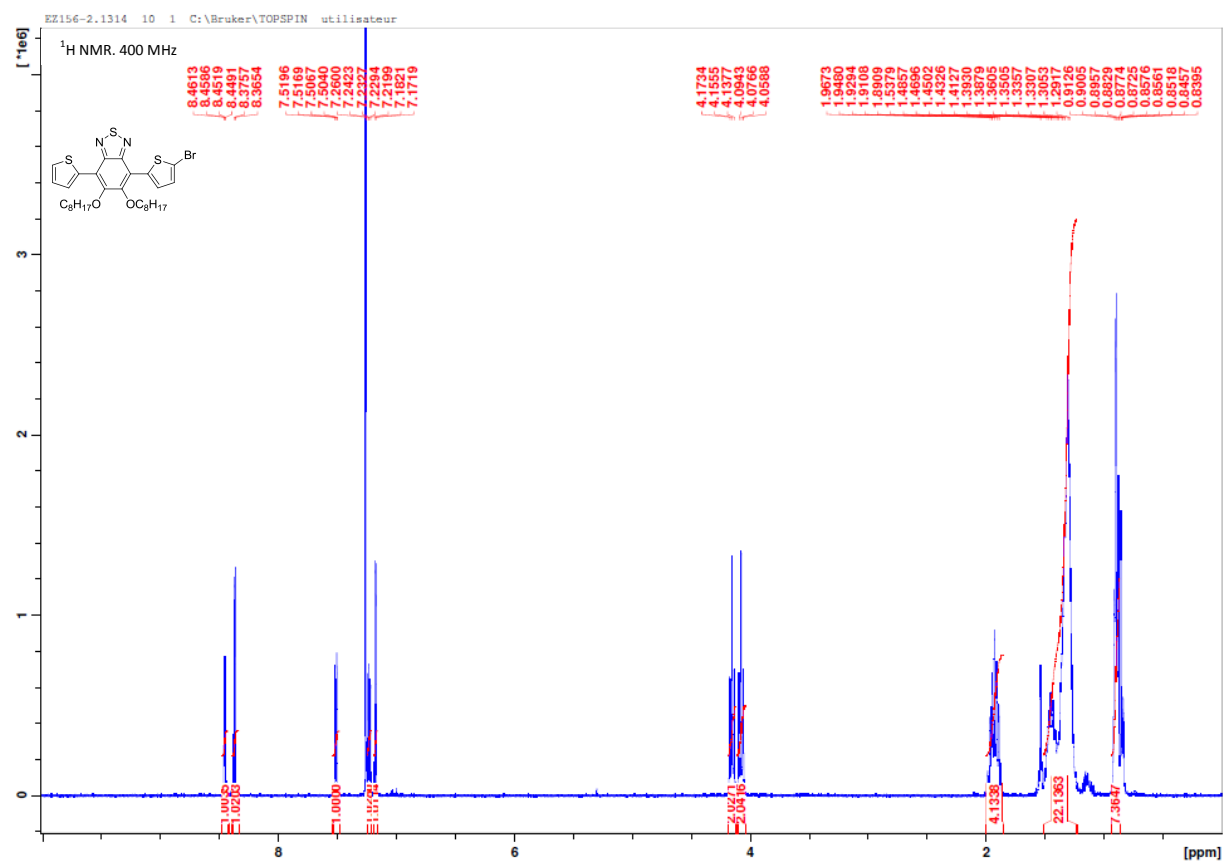
**4-(5-bromothiazol-2-yl)-7-(thiazol-2-yl)-5,6-dioctyloxy-benzo[c][1,2,5]thiadiazole (1)**



Compound TaBzBDT

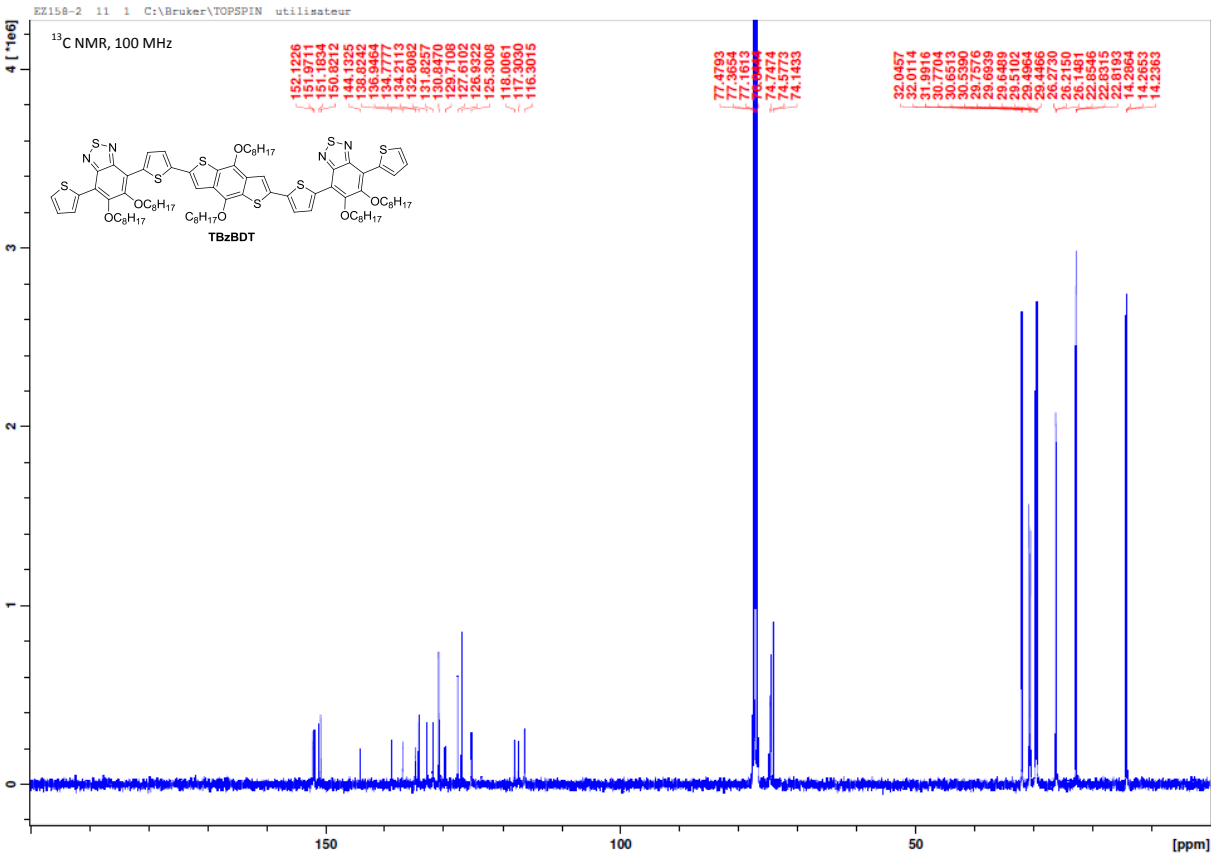
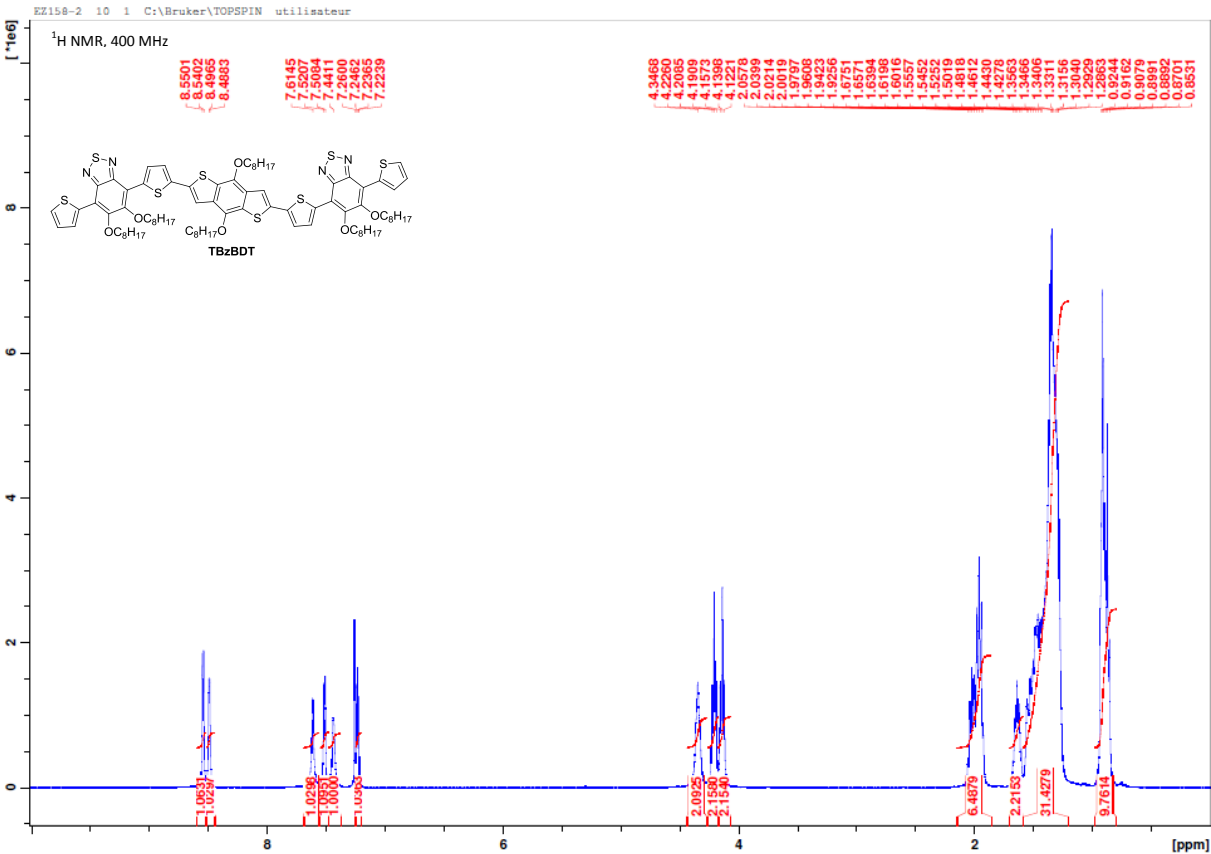


**4-(5-bromothiophen-2-yl)-7-(thiophen-2-yl)-5,6-dioctyloxy-benzo[c][1,2,5]thiophene (2)**





Compound TBzBDT



### III. Solid state characterizations

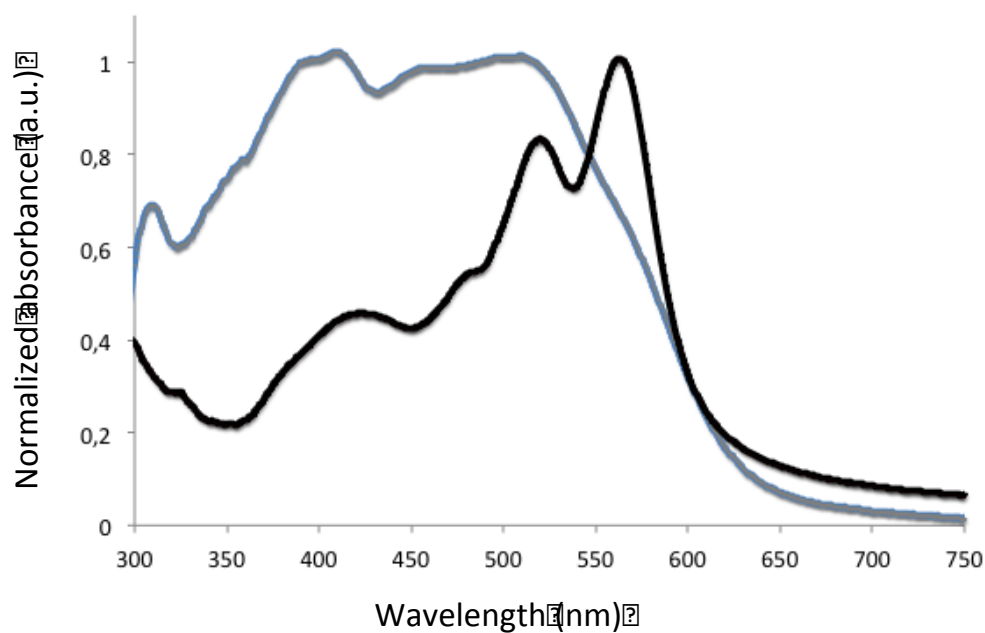


Figure S1: Absorption spectra of molecule TaBzBDT (grey line) and molecule TBzBDT (black line) in solid state in chloroform.

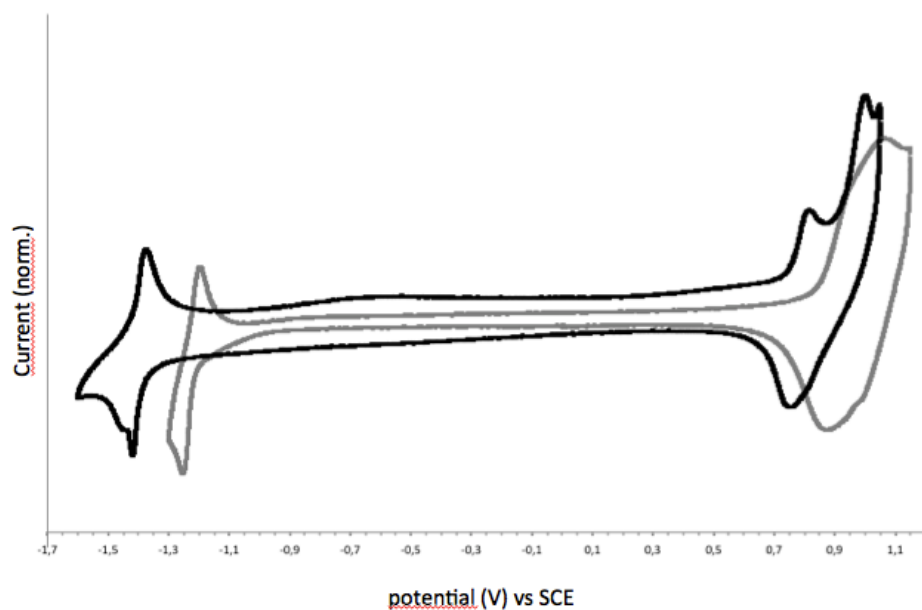


Figure S2: cyclic voltammograms in solid state of compound TaBzBDT (grey line) and compound TBzBDT (black line) in acetonitrile.

## IV. DFT calculations

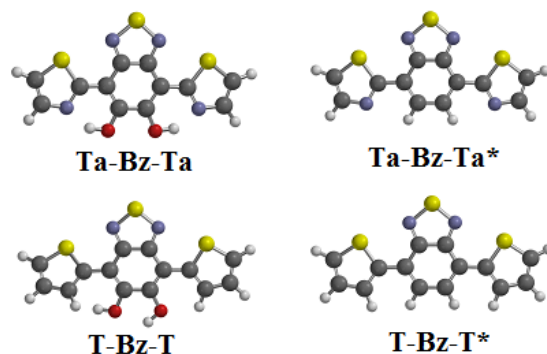


Figure S3 : ICT molecular trimers investigated by DFT calculations. The molecules are made of thiazole (Ta) or thiophene (T) heterocycles and with or without (\*) alkoxy side chains on the central benzothiadiazole (Bz) unit.

## V. References

- a) Y. Li, Y. Chen, X. Liu, Z. Wang, X. Yang, Y. Tu and X. Zhu, *Macromolecules*, 2011, **44**, 6370.
- b) M. Leclerc, A. Najari and Y. Zou, *PCT Int. Appl.*, 2011063534, 2011.
- c) J.-J. Kim, H. Choi, J.-W. Lee, M.-S. Kang, K. Song, S. O. Kang and J. Ko, *J. Mater. Chem.*, 2008, **18**, 5223.