# New donor-π-acceptor sensitizers containing 5H-[1,2,5]thiadiazolo [3,4-f]isoindole-5,7(6H)dione and 6H-pyrrolo[3,4-g]quinoxaline-6,8(7H)-dione units

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#### **Experimental Details**

**Materials and Equipments.** Reactants and reagents appeared in this report, unless otherwise stated, were purchased either from Sigma-Aldrich or Alfa-Aesar, and used without further purification. Column chromatography was carried out with Merck silica (230 – 400 mesh) while thin layer chromatography (TLC) was performed on Merck silica 60 Al-backed plates (20 cm × 20 cm). <sup>1</sup>H and <sup>13</sup>C NMR data were obtained on a Bruker DPX 400 MHz spectrometer with chemical shifts referenced to CDCl<sub>3</sub>. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Shimadzu Biotech AXIMA-TOF<sup>2</sup>. Elemental analysis was obtained via a Thermo Scientific Flash 2000 Series CHNS/O Analyzer. UV-Vis absorption spectra were recorded on a Lambda 900 Spectrometer from Perkin Elmer. Cyclic voltammetry (CV) experiments were performed using a Multichannel Potentiostat (Model

1470E) from Solartron Analytical. All CV measurements were recorded in dichloromethane (DCM) with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte (scan rate of 100 mV  $\cdot$  s<sup>-1</sup>). The experiments were performed at room temperature with a conventional three electrode configuration consisting of a platinum wire working electrode, a gold counter electrode, and a Ag/AgCl in 3 M KCl reference electrode. The measured potentials were converted to orbital energies by using value of SCE (saturated calomel electrode) having potential of -4.4 eV relative to vacuum. For the photovoltaic measurements, the solar cells having 0.16 cm<sup>-2</sup> active area were measured with 0.25 cm<sup>-2</sup> metal mask using solar simulator (San-EI Electric, XEC-301S) under AM 1.5G standard. J-V characteristics were recorded by applying external potential bias while measuring the current response with a Keithley 2612A SourceMeter. For electrochemical impedance spectroscopy study, measurements were carried out using AutoLab PGSTAT302N under illumination condition and different bias potentials were applied ranging from 0.05 V to open-circuit voltage and frequencies between 1MHz and 0.1 Hz. Incident photon current efficiency studies was carried out using PVE300 from Bentham, with dual Xenon/quartz halogen light source, measured in DC mode.

**DSC Device Fabrication.** After being cleaned with soap solution, a fluorine-doped tin oxide (FTO) glass plate was immersed in aqueous 0.04 M TiCl<sub>4</sub> solution at 70 ° C for 30 min and washed with deionized water and ethanol. Nanocrystalline TiO<sub>2</sub> paste was coated on top of the

FTO glass by manual screen printing method. Two transmission layers (18 nm particle size and 3  $\mu$ m thickness per layer) and two reflection layers (150 nm particle size and 3  $\mu$ m thickness per layer) were printed in sequence with 6 min relaxation time in between. The 2+2 TiO<sub>2</sub> coated FTO glass was sintered following the programme shown in the table below:

	Step 1	Step 2	Step 3	Step 4	Step 5
Ramp time (mins)	15	15	5	10	10
Temp (degC)	125	325	375	450	500
Stabilize time (mins)	10	5	5	15	15

The sintered FTO glass plate was immersed in aqueous 0.04 M TiCl<sub>4</sub> solution at 70 ° C for 30 min and washed with deionized water and ethanol. The prepared TiO<sub>2</sub> electrodes were immersed into dye solutions (0.5 mM in a mixture of tetrahydrofuran (THF) and tert-butanol (v/v 8/2), and kept at room temperature for 12 hours. Counterelectrodes were prepared by drilling a hole on the FTP glass followed by coating a drop of H<sub>2</sub>PtCl<sub>6</sub> solution and heating at 400 °C for 15 min. The dye-adsorbed TiO<sub>2</sub> electrode and Pt counterelectrode were assembled and sealed with a Surlyn film under a hot-press. The cell was filled with a drop of the electrolyte comprising of 1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.05 M LiI, 0.03 M I<sub>2</sub>, 0.5 M 4-tert-butylpyridine (TBP), 0.1 M guanidiniumthiocyanate (GuSCN) in acetonitrile : valeronitrile (v/v 85/15) by means of

vacuum backfilling. The hole was quickly sealed with the a Surlyn film covered with glass. Finally, the contacts were soldered with Sn metal at 290 °C and 60 kHz.

### Synthetic Details.

4,7-Dibromo-benzo[c][1,2,5]thiadiazole-N-2-ethylhexyl-5,6-imide (1). N-ethylhexyl-5,6diaminoisoindoline (1.2 g, 3.48 mmol), and bromine (0.45 ml, 8.7 mmol) were dissolved in chloroform (60 mL). The reaction solution was stirred for 1 h followed by adding thionylchloride dropwise (1.0 mL, 13.9 mmol) and then triethylamine dropwise (2.9 mL, 20.1 mmol). The reaction mixture was heated to 50 °C for 1 d, cooled down and poured into ice water, then extracted with dichloromethane (DCM). The organic layer was collected, washed with water, dried over anhydrous MgSO<sub>4</sub>, and concentrated. The residue was purified by chromatography, eluting with hexane/DCM (1/2) to obtain a white solid (1.17 g, 63%). <sup>1</sup>H NMR (CDCl<sub>3</sub>  $\delta$  ppm):  $3.64 (d, 2H, J = 7.2, NCH_2), 1.87 (quintet, 1H, J = 6.4 Hz, NCH_2CH), 1.27-1.37 (m, 8H, CH_2),$ 0.85-0.92 (m, 6H, J = 6.8 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>  $\delta$  ppm): 166.7, 157.2, 133.7, 130.8, 43.5, 38.7, 31.3, 29.2, 24.6, 23.7, 14.7, 11.1. MALDI-TOF-MS m/z: 474.93 (M<sup>+</sup>, 100 %); calcd. for C<sub>16</sub>H<sub>17</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>2</sub>S: 474.94. Anal.: calcd. for C<sub>16</sub>H<sub>17</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>2</sub>S: C, 40.44; H, 3.61; N, 8.84; S, 6.75; found: 40.27; H, 3.65; N, 9.10; S, 6.63.

#### 4,7-Dithien-2-yl-benzo[c][1,2,5]thiadiazole-N-2-ethylhexyl-5,6-imide (2). Compound 1

(1 g, 2.10 mmol), 2-(tributylstannyl)thiophene (1.54 mL, 4.84 mmol) and (PPh<sub>3</sub>)<sub>2</sub>Pd(II)Cl<sub>2</sub> (90 mg, 0.13 mmol) were dissolved in THF (25 mL) under an inert atmosphere. The reaction was stirred under reflux overnight, cooled down and poured into water, then extracted with DCM. The organic layer was collected, washed with water and dried over anhydrous MgSO<sub>4</sub> and concentrated. The residue was purified by chromatography, eluting with hexane/DCM (1/2) to obtain a yellow solid (0.92 g, 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>  $\delta$  ppm): 7.89 (dd, 2H, J = 4 Hz, ThH), 7.71 (dd, 2H, J = 4 H, ThH), 7.26-7.29 (m, 2H, ThH), 3.63 (d, 2H, J = 7.2, NCH<sub>2</sub>), 1.89 (quintet, 1 H, J = 6.4 Hz, NCH<sub>2</sub>CH), 1.27-1.36 (m, 8H, CH<sub>2</sub>), 0.85-0.92 (m, 6H, J = 6.8 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub> δ ppm): 166.6, 156.7, 134.7, 133.7, 130.5, 127.0, 126.6, 119.3, 43.6, 38.7, 31.3, 29.2, 24.6, 23.7, 14.7, 11.1. MALDI-TOF-MS m/z: 481.08 (M<sup>+</sup>, 100 %); calcd. for  $C_{24}H_{23}N_3O_2S_3$ : 481.10. Anal.: calcd. for  $C_{24}H_{23}N_3O_2S_3$ : C, 59.85; H, 4.81; N, 8.72; S, 19.97; found: 59.66; H, 4.97; N, 8.96; S, 19.74.

## N-(2-ethylhexyl)-2,3-diphenyl-5,9-di(thiophen-2-yl)-7H-pyrrolo[3,4-g]quinoxaline-6,8-

**dione (5).** Compound **2** (0.5 g, 1.04 mmol) dissolved in anhydrous THF (10 mL) was cooled down to 0 °C, NaBH<sub>4</sub> (156 mg, 4.16 mmol) dissolved in THF (5 mL) was added dropwise. The reaction was stirred at 0 °C for 6 h, poured into ice water and acidified with 1 M HCl to pH~4

and then filtered. The collected bright vellow solid was washed with water, then with MeOH, and dried without further purification. The as prepared solid together with benzil (0.22 g, 1.04 mmol) were dissolved in glacial acetic acid (20 mL). The suspension was heated up to 140 °C for 1 d, cooled down and poured into water, then extracted with DCM. The organic layer was collected, washed with water and dried over anhydrous MgSO<sub>4</sub> and concentrated. The residue was purified by chromatography, eluting with hexane/DCM (1/3) to obtain a yellow solid (0.45)g, overall yield 70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 7.97 (d, 2H, J = 4 Hz, ThH), 7.68 (m, 4H, PhH), 7.46 (m, 4H, PhH), 7.29-7.39 (m, 4H, PhH ThH), 7.28 (d, 2H, J = 4.4 Hz, ThH), 7.10 (m, 2H, ThH), 3.62 (d, 2H, J = 6.8 Hz, NCH<sub>2</sub>), 1.75 (t, 1H, J = 6.0 Hz, NCH<sub>2</sub>CH), 1.35-1.49 (m, 8H, CH<sub>2</sub>), 0.91-0.98 (m, 6H, J = 6.8 Hz, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 167.1, 153.7, 141.8, 138.4, 133.4, 133.2, 131.0, 130.9, 130.4, 129.2, 129.0, 127.8, 126.8, 43.4, 38.7, 31.3, 29.2, 24.6, 23.7, 14.7, 11.1. MALDI-TOF-MS m/z: 627.19 (M<sup>+</sup>, 100 %); calcd. for C<sub>38</sub>H<sub>33</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: 627.20. Anal.: calcd. for C<sub>38</sub>H<sub>33</sub>N<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: C, 72.70; H, 5.30; N, 6.69; S, 10.21; found: C, 72.42; H, 5.49; N, 6.83, S, 9.96.

**Compound 7.** Compound **2** (150 mg, 0.31 mmol) and N-bromosuccimide (NBS, 116 mg, 0.65 mmol) were dissolved in THF (12 mL) at 0 °C and stirred at r.t. The reaction was monitored by TLC until completion, then poured into water, neutralized with  $Na_2S_2O_3$  and

filtered. The solid (compound 3) was washed with water and vacuum dried, then redissolved in THF (15 mL) and transferred to a 50 mL two-neck round bottom flask, to which the 4-boronic acid-N,N-bis(4-hexyloxyphenyl)aniline (152 mg, 0.31 mmol), Pd(0)(PPh<sub>3</sub>)<sub>4</sub> (22 mg, 0.018 mmol) and K<sub>2</sub>CO<sub>3</sub> (2M aq, 5 ml) were added. The reaction solution was refluxed under an inert atmosphere for 3 h followed by addition of 5-carboxaldehyde-thiophene-2-boronic acid (58 mg, 3.74 mmol) in THF (5 mL) via syringe. The reaction was continued for 1 d, cooled down and cooled down and poured into water, then extracted with DCM. The organic layer was collected, washed with water and dried over anhydrous MgSO<sub>4</sub> and concentrated. The residue was purified by chromatography, eluting with DCM to obtain a purple red solid (190 mg, 58%). <sup>1</sup>H NMR  $(CDCl_3, \delta ppm)$ : 9.89 (s, 1H, CHO), 8.05 (d, 1H, J = 4 Hz, ThH), 7.89 (d, 1H, J = 4 Hz, ThH), 7.71 (d, 1H, J = 4 Hz, ThH), 7.50 (m, 3H, ThH PhH), 7.38 (d, 2H, J = 4 Hz, ThH), 7.34 (b, 1H, ThH), 7.08 (b, 4H, PhH), 6.92 (b, 2H, PhH), 6.84 (d, 4H, J = 8.0 Hz, PhH), 3.94 (b, 4H, OCH<sub>2</sub>), 3.66 (d, 2 H, J = 7.2 Hz, NCH<sub>2</sub>), 1.89 (t, 1 H, J = 6.0 Hz, NCH<sub>2</sub>CH), 1.78 (quintet, J = 6.8 Hz, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.43-1.50 (m, 4H, CH<sub>2</sub>), 1.28-1.36 (m, 16H, CH<sub>2</sub>), 0.86-0.93 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 183.2, 166.9, 166.8, 156.8, 156.5, 147.1, 143.0, 140.9, 137.9, 136.4, 135.1, 134.1, 130.1, 128.4, 128.0, 127.6, 126.4, 126.1, 125.6, 125.2, 122.4, 120.4, 116.0, 68.9, 43.6, 38.7, 32.3, 31.3, 30.0, 29.2, 26.4, 24.6, 23.7, 23.3, 14.78, 14.76, 11.1. MALDI-TOF-

MS m/z: 1034.43 (M<sup>+</sup>, 100 %); calcd. for  $C_{59}H_{62}N_4O_5S_4$ : 1034.36. Anal.: calcd. for  $C_{59}H_{62}N_4O_5S_4$ : C, 68.44; H, 6.04; N, 5.41; S, 12.39; found: C, 68.21; H, 6.10; N, 5.57, S, 12.30.

Compound 8. Compound 8 was prepared from compound 5 by the same procedure used for making compound 7, as a bright yellow solid in an overall yield of 60%.<sup>1</sup>H NMR (CDCl<sub>3</sub>  $\delta$ ppm): 9.85 (s, 1H, CHO), 7.89 (d, 2H, J = 4 Hz, ThH), 7.82 (d, 4H, J = 8.4 Hz, PhH), 7.72 (m, 2H, PhH), 7.67 (m, 4H, PhH), 7.39-7.48 (m, 3H, ThH), 7.24-7.29 (m, 4H, PhH ThH), 7.08 (d, 4H, J = 8.8 Hz, PhH), 6.92 (d, 2H, J = 8.4 Hz, PhH), 6.83 (d, 4H, J = 8.8 Hz, PhH), 3.94 (t, 4H,  $J = 6.4 \text{ Hz}, \text{ OCH}_2$ , 3.63 (d, 2H,  $J = 6.8 \text{ Hz}, \text{ NCH}_2$ ), 1.79 (b, 1H, NCH<sub>2</sub>CH), 1.74-1.78 (m, 4H, CH<sub>2</sub>), 1.25-1.46 (m, 20H, CH<sub>2</sub>), 0.85-0.93 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub> δ ppm): 183.0, 166.7, 157.1, 156.5, 148.3, 142.0, 141.7, 140.7, 138.7, 138.1, 136.5, 133.7, 133.1, 132.9, 132.2, 132.1, 131.9, 131.4, 130.8, 129.2, 129.1, 127.65, 127.61, 127.5, 127.2, 127.1, 124.5, 120.4, 119.1, 115.9, 114.1, 68.9, 43.5, 38.6, 32.2, 31.2, 30.3, 29.9, 29.1, 26.4, 24.6, 23.7, 23.3, 14.7, 11.1. MALDI-TOF-MS m/z: 1180.38 ( $M^+$ , 100 %); calcd. for  $C_{73}H_{72}N_4O_5S_3$ : 1180.46. Anal.: calcd. for C<sub>73</sub>H<sub>72</sub>N<sub>4</sub>O<sub>5</sub>S<sub>3</sub>: C, 74.20; H, 6.14; N, 4.74; S, 8.14; found: C, 73.96; H, 6.23; N, 4.59; S, 7.97.

L101. Compound 7 (150 mg, 0.145 mmol), cyanoacetic aicd (37 mg, 0.43 mmol) and piperidine (0.1 mL, 1.0 mmol) were dissolved in chloroform (10mL). The solution was refluxed

overnight, cooled down, acidified with 1 M HCl, poured into water then extracted with DCM. The organic layer was collected, washed with water, dried over anhydrous MgSO<sub>4</sub>, and concentrated. The residue was purified by chromatography, eluting with DCM/MeOH (9/1) to obtain L101 as a black solid (138 mg, 87%). <sup>1</sup>H NMR (CDCl<sub>3</sub> δ ppm): 7.95 (b, 1H, ThH), 7.40 (d, 2H, J = 8.4 Hz, PhH), 7.19 (b, 1H, ThH), 7.18 (b, 1H, ThH), 7.06 (b, 3H, PhH, ThH), 7.01 (m, 2H, ThH), 6.92 (b, 2H, PhH), 6.83 (b, 5H, PhH ThH), 4.25 (d, 2H, J = 5.6 Hz, NCH<sub>2</sub>), 3.93  $(t, 4H, J = 6.4 Hz, OCH_2), 1.75-1.80 (m, 3H, OCH_2CH_2 NCH_2CH), 1.26-1.49 (m, 22H, CH_2),$ 0.87-0.99 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub> δ ppm): 166.4, 162.9, 156.4, 156.3, 151.4, 149.4, 145.7, 145.4, 141.0, 140.3, 138.6, 136.3, 136.1, 135.2, 133.6, 129.8, 127.6, 127.3, 127.1, 125.8, 125.6, 125.5, 125.3, 124.9, 121.9, 120.0, 115.7, 71.0, 39.8, 36.9, 31.8, 30.9, 29.4, 28.8, 24.2, 23.45, 23.44, 14.54, 14.52, 11.5, 10.9. MALDI-TOF-MS m/z: 1101.39 (M<sup>+</sup>, 100 %); calcd. for C<sub>62</sub>H<sub>63</sub>N<sub>5</sub>O<sub>6</sub>S<sub>4</sub>: 1101.36. Anal.: calcd for C<sub>62</sub>H<sub>63</sub>N<sub>5</sub>O<sub>6</sub>S<sub>4</sub>: C, 67.55; H, 5.76; N, 6.35; S, 11.63; found: 67.46; H, 5.82; N, 6.59; S, 11.44.

**L102. L102** was prepared from compound **8** by the same procedure used for making **L101** as a dark red solid in a yield of 85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 7.93-8.04 (b, m, 16H, Ph**H**, Th**H**), 7.83 (d, 4H, J = 8.4 Hz, Ph**H**), 7.77 (d, 2H, J = 4 Hz, Th**H**), 7.67 (d, 4H, J = 8.4 Hz, Ph**H**), 7.63 (m, 1H, Th**H**), 7.52-7.55 (m, 2H), 7.30 (b, 1H, Th**H**), 7.28 (m, 1H, Th**H**), 7.12 (b, 1H, Th**H**),

6.76 (b, 12H, ThH, PhH), 4.03 (b, 4H, OCH<sub>2</sub>), 3.64 (d, J = 7.2 Hz, 2H, NCH<sub>2</sub>), 1.84 (b, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.68-1.74 (m, 1H, NCH<sub>2</sub>CH), 1.25-1.46 (m, 21H, CH<sub>2</sub>), 0.87-0.90 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 168.3, 166.7, 156.4, 148.3, 148.1, 147.4, 146.0, 143.8, 142.8, 142.3, 140.7, 137.2, 133.6, 133.4, 130.4, 129.9, 129.3, 128.8, 128.0, 127.7, 127.5, 127.4, 126.7, 126.2, 125.6, 125.1, 123.8, 123.6, 120.4, 115.9, 68.9, 38.7, 35.2, 32.2, 31.2, 30.9, 30.3, 30.0, 29.9, 29.1, 26.4, 23.3, 14.7, 11.1. MALDI-TOF-MS m/z: 1247.55 (M<sup>+</sup>, 100 %); calcd. for C<sub>76</sub>H<sub>73</sub>N<sub>5</sub>O<sub>6</sub>S<sub>3</sub>: 1247.47. Anal.: Calcd. for C<sub>76</sub>H<sub>73</sub>N<sub>5</sub>O<sub>6</sub>S<sub>3</sub>: C, 73.11; H, 5.89; N, 5.61; S, 7.70; found: 72.95; H, 5.93; N, 5.72; S, 7.88.



Figure S1. Cyclic voltammetry spectra of L101 and L102.



























