Supplementary Material (ESI) for Chemical Communications
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**Bodipy Derivatives as Donor Materials for Bulk Heterojunction Solar Cells**

**Supplementary information**

**Compound 1 : 3-(4-(4,7-dioxahaeryl-1-oxy)styryl)-1,7-trimethyl-4,4-bis(2,5-dioxaoct-7-ynyl)-4-bora-3a,4a-diaza-s-indacene**

To a solution of 2,5-dioxaoct-7-yne (0.25 mL, 2.1 mmol) in anhydrous THF (5mL), at room temperature, was added ethylmagnesium bromide (1.0 M dans le THF, 1.90 ml). This mixture was stirred 2 h à 60°C, then this solution was transferred in a Schlenk tube containing 3-(4-(4,7-dioxahaeryl-1-oxy)styryl)-1,7-trimethyl-4-bora-3a,4a-diaza-s-indacene (273 mg, 0.418 mmol) in anhydrous THF (5mL). The mixture was then stirred at 60°C during 12h. After addition of water, the organic fraction was extracted with dichloromethane. After removal of the organic solvent, a chromatography (silicagel, ethylacetate/petroleum ether, gradient from 20 :80 to 40 :60), afforded compound 1 as purple-greenish powder (300 mg, 85%).

$^1$H NMR (CDCl$_3$ 300 MHz): $\delta = 1.40$ (s, 3H), 1.44 (s, 3H), 2.73 (s, 3H), 3.25 (s, 6H), 3.30 (m, 4H), 3.39 (s, 3H), 3.54 (m, 4H), 3.59 (m, 2H), 3.72 (m, 2H), 3.87 (m, 2H), 4.17 (s, 4H), 6.02 (s, 1H), 6.59 (s, 1H), 7.22 (AB sys, 4H, $J_{AB} = 8.7$ Hz, $\nu_0\delta = 180.0$ Hz); 7.48 (AB sys, 4H, $J_{AB} = 8.3$ Hz, $\nu_0\delta = 223.7$ Hz), 7.57 (AB sys, 2H, $J_{AB} = 16.2$ Hz, $\nu_0\delta = 296.87$ Hz)

$^{13}$C NMR (CDCl$_3$, 300 MHz): $\delta = 14.31$, 14.99, 15.20, 16.36, 58.94, 59.20, 59.58, 67.63, 68.41, 69.79, 70.91, 71.69, 72.06, 91.40, 94.64, 115.13, 118.01, 119.16, 121.84, 128.72, 129.94, 130.17, 130.52, 130.68, 133.94, 135.27, 138.28, 138.61, 140.44, 140.66, 152.45, 155.40, 159.58.

UV-Vis (CH$_2$Cl$_2$) $\lambda$ nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$) = 572 (93500), 533 (27600), 328 (47800).

EI-MS : 844.1 (100), 717. 2 (35).

**Compound 2 : 3,5-bis(4-(4,7-dioxahaeryl-1-oxy)styryl)-1,7-dimethyl-4,4-bis(2,5-dioxaoct-7-ynyl)-4-bora-3a,4a-diaza-s-indacene.**

To a solution of 2,5-dioxaoct-7-yne (0.49 mL, 0.41 mmol) in anhydrous THF (5mL), at room temperature, was added ethylmagnesium bromide (1.0 M dans le THF, 3.7 ml). This mixture was stirred 2 h à 60°C, then this solution was transferred in a Schlenk tube containing 3,5-bis(4-(4,7-dioxahaeryl-1-oxy)styryl)-1,7-dimethyl-4-bora-3a,4a-diaza-s-indacene (670 mg, 0.816 mmol) in anhydrous THF (10mL). The mixture was then stirred at 60°C during
12h. After addition of water, the organic fraction was extracted with dichloromethane. After removal of the organic solvent, a chromatography (silicagel, ethylacetate/petroleum ether, gradient from 80 :20 to 100 :00), afforded compound 2 as blue powder (780 mg, 91%).

$^1$H NMR (CDCl$_3$ 300 MHz) : $\delta$ = 1.46 (s, 6H), 3.15 (m, 4H), 3.19 (s, 6H), 3.40 (s, 6H), 3.50 (m, 4H), 3.59 (m, 4H), 3.74 (m, 4H), 3.88 (m, 4H), 4.15 (s, 4H), 4.18 (m, 4H), 6.62 (s, 2H), 7.26 (AB sys, 8H, $J_{AB} = 8.7$ Hz, $n_d = 180.6$ Hz), 7.11 (m, 4H), 7.82 (d, 2H), 8.05 (d, 2H).

$^{13}$C NMR (CDCl$_3$, 300 MHz): $\delta$ = 15.21, 27.01, 58.86, 59.19, 59.50, 67.64, 68.26, 69.80, 70.91, 71.61, 72.07, 91.64, 94.62, 115.20, 118.15, 119.15, 128.89, 130.24, 130.80, 131.33, 134.16, 135.37, 136.82, 138.23, 140.04, 152.26, 159.62.

UV-Vis (CH$_2$Cl$_2$) $\lambda$ nm (\(\epsilon\), M$^{-1}$ cm$^{-1}$) = 646 (126600), 600 (43000), 371 (76500), 266 (8080).

EI-MS : 1050.2 (100), 923. 3 (15).
Devices preparation and characterization

PCBM was purchased from NanoC and used as received. The Baytron® PH500 suspension used to apply smoothing and hole conducting layers was received from HC Stark. As electrodes, indium-tin-oxide (ITO) coated glasses (sheet resistance $\leq 20 \ \Omega/\square$) and evaporated Al films (ca. 100 nm thick) were used. The ITO electrodes were cleaned in ultrasonic baths then modified by a spin-cast layer of Baytron (filtered through a 0.45 µm membrane just prior of casting at 5000 rpm), which was then dried at 130 °C for 15 min.

Devices with ITO/Baytron/Bodipy:PCBM/Al structure were realized from solutions with a concentration of 4.9 and 4.1 mg.ml$^{-1}$ for molecules 1 and 2, respectively. The spin-casting was done distributing the solutions drop by drop ($5\times$) onto an already rotating stage. After preparation, the solar cells were stored and characterised in an argon glove-box. The $J-V$ curves were recorded in dark and under illumination using a Keithley 236 source-measure unit and a homemade acquisition program. The light source was an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttecknik, equipped with a metal halogenide lamp) and its intensity was measured by a broad-band power meter (13PEM001, Melles Griot). The devices were illuminated through the ITO electrode side. The efficiency values reported in this work are not corrected, neither for the possible solar simulator spectral mismatch nor for the reflection/absorbance of the glass/ITO/Baytron coated electrodes. The device area was defined using round shadow masks ($28 \text{ mm}^2$) plus 1 mm$^2$ contacting pad. Note that this layout should prevent edge-effects and a severe overestimation of the devices performance.$^{a,b}$ The IPCE spectra were recorded using the round portion of the devices with a Perkin Elmer 7225 lock-in amplifier under monochromatic illumination at variable at a chopping frequency of 210 Hz. The light source was a tungsten lamp which was dispersed by an Acton SpectraPro150. Electronic absorption spectra were recorded with a Perkin Elmer Lambda 19 spectrophotometer.
Figures S1. Absorption, emission, excitation spectra in dichloromethane at rt for 1 (upper) and for 2 (lower).

TB35a in dichloromethane
$\Phi = 75\%$

TB35b in dichloromethane
$\Phi = 46\%$