

Electronic supplementary information

Solution-processed bulk heterojunction solar cells based on BF₂-hydroxychalcone complexes

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1- General procedures. All solvents for the syntheses were of analytic grade. Spectroscopic measurements were carried out with spectroscopic-grade solvents. NMR spectra (¹H, ¹³C, and ¹⁹F) were recorded at RT on a BRUKER AC 250 that operated at 250, 62.5, and 235MHz for ¹H-, ¹³C-, and ¹⁹F nuclei, respectively. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (¹H and ¹³C); residual solvent peaks of the deuterated solvents were used as an internal standard. MS and elemental analysis were performed at the Spectropole de Marseille (<http://www.spectropole.fr/>).

2- Syntheses. The chalcone derivatives and their difluoroboron complexes were synthesized according to the previously published procedures (A. D'Aléo, D. Gachet, V. Heresanu, M. Giorgi and F. Fages, *Chem.–Eur. J.*, 2012, 18, 12764)

1-H

¹H -NMR (250MHz, CDCl₃): 12.59 (s, 1H), 7.89 (d, ³J= 15.0Hz, 1H), 7.49 (m, 2H), 7.30 (m, 8H), 7.15 (m, 6H), 7.04 (d, ³J= 9.0Hz, 1H), 6.95 (d, ³J= 9.0Hz, 1H), 3.83 (s, 3H).

1-BF₂

¹H -NMR (250MHz, CDCl₃): 8.41 (d, ³J= 14.8Hz, 1H), 7.60 (d, ³J= 8.8Hz, 2H), 7.37 (m, 6H), 7.19 (m, 7H), 7.06 (d, ³J= 9.3Hz, 1H), 6.98 (d, ³J= 8.8Hz, 2H), 3.85 (s, 3H); ¹⁹F -NMR (235MHz, CDCl₃): -143.27 (¹⁰B-F, 0.2F), -143.34 (¹¹B-F, 0.8F). EI-MS: (positive mode): m/z: 492.2 [M+Na]⁺, [M+K]⁺ (negative mode): 508.2 [M-H]⁻. Anal. Calcd (Found) for C₂₈H₂₂BF₂NO₃: C: 71.66 (71.97), H: 4.73 (4.27), N: 2.98 (3.49).

2-H

¹H -NMR (250MHz, CDCl₃): 12.99 (s, 1H), 7.90 (dd, ³J= 8.3Hz, ⁴J= 1.5Hz, 1H), 7.89 (d, ³J= 15.3Hz, 1H), 7.50 (m, 4H), 7.32 (m, 4H), 7.14 (m, 6H), 7.04 (m, 3H), 6.93 7.90 (td, ³J= 8.3Hz, ⁴J= 1.3Hz, 1H).

2-BF₂

¹H -NMR (250MHz, CDCl₃): 8.44 7.90 (d, ³J= 14.5Hz, 1H), 7.88 7.90 (dd, ³J= 8.5Hz, ⁴J= 1.0Hz, 1H), 7.67 7.90 (td, ³J= 8.5Hz, ⁴J= 1.5Hz, 1H), 7.60 7.90 (d, ³J= 9.0Hz, 2H), 7.36 (m, 5H), 7.21 (m, 6H), 7.00 (m, 3H); ¹⁹F -NMR (235MHz, CDCl₃): -142.94 (¹⁰B-F, 0.2F), -143.00 (¹¹B-F, 0.8F). EI-MS: (positive mode): m/z: 462.2 [M+H]⁺, 478.1 [M+Na]⁺. Anal. Calcd (Found) for C₂₈H₂₀BF₂NO₂: C: 73.23 (73.83), H: 4.79 (4.59), N: 3.27 (3.19).

3-H

¹H -NMR (250MHz, CDCl₃): 14.00 (s, 1H), 8.20 (d, ⁴J= 1.8Hz, 1H), 8.13 (d, ⁴J= 2.0Hz, 1H), 7.94 (d, ³J= 15.0Hz, 1H), 7.52 (d, ³J= 8.5Hz, 2H), 7.36 (d, ³J= 14.8Hz, 1H), 7.31 (m, 4H), 7.15 (m, 6H), 7.02 (d, ³J= 8.8Hz, 2H).

3-BF₂

¹H -NMR (250MHz, CDCl₃): 8.48 (d, ³J= 14.5Hz, 1H), 8.35 (d, ⁴J= 2.0Hz, 1H), 8.10 (d, ⁴J= 2.0Hz, 1H), 7.63 (d, ³J= 8.8Hz, 2H), 7.40 (m, 4H), 7.23 (m, 7H), 6.97 (d, ³J= 8.8Hz, 2H); ¹⁹F -NMR (235MHz, CDCl₃): -143.58 (¹⁰B-F, 0.2F), -143.64 (¹¹B-F, 0.8F). EI-MS: (positive mode): 713.8 [M+Na]⁺, 729.7 [M+K]⁺. Anal. Calcd (Found) for C₂₇H₁₈BF₂I₂NO₂.1/3 (C₂H₅)₂O: C: 47.54 (47.52), H: 3.00 (2.83), N: 1.96 (2.08).

3 - Optical spectroscopy: UV/Vis-absorption spectra were measured on a Varian Cary 50[®]. Solid-state spectra were measured by drop-casting a solution of the compound in dry CH₂Cl₂ onto a quartz plate and correcting for a scattered-light background.

4 – Cyclic Voltammetry. Experiments were performed with an Autolab electrochemical analyzer (PGSTAT 12, EcoChemie). Cyclic voltammetry were recorded using a standard 3-electrode configuration. The working electrode was a glassy carbon disk (3 mm diameter) polished with alumina slurry (Buehler, 1µm) and sonicated thoroughly in distilled water. A platinum wire was used as a counter electrode, and a saturated calomel electrode (SCE) was used as reference electrode. This electrode was calibrated by recording ferrocene signal after each experiment. All potentials are reported relative to the Fc/Fc⁺ couple as reference. All cyclic voltammetry were recorded in dichloromethane (CH₂Cl₂) solution containing 0.1M tetrabutylammonium hexafluorophosphate (TBAPF₆). Before and during experiments, the electrochemical cell was flushed with argon. The scan rate was 200 mV/s and the concentration was 1 mM.

5 - Device fabrication. The bulk heterojunction used in this study is based on a chalcone dye used as a donor material and PC₆₁BM (supplied by *Solaris-Chem Inc.*) as the acceptor. Organic solar cells have been fabricated using conventional architectures Glass/ITO/PEDOT:PSS/Active Layer/Al and Glass/ITO/PEDOT:PSS/Active Layer/Ca/Al using standard procedures. 15 × 15 mm² ITO-coated glass sheets (10 Ohm square, *Kintec*) were successively washed in acetone, ethanol and isopropanol in an ultrasonic bath and exposed to UV-ozone for 20 min. PEDOT:PSS suspension (Aldrich, conductive grade) was filtered at 0.8 mm and spin-coated at 1000 rpm onto the cleaned substrate. Afterwards, the layer was dried at 110°C in an oven under a dynamic primary vacuum. The samples were then inserted in a glovebox with controlled atmosphere (O₂ and H₂O < 0.1 ppm) where the rest of the fabrication procedure will take place. Solutions of chalcone dyes and PC₆₁BM were prepared in chlorobenzene or o-dichlorobenzene, at a 1:4 weight ratio. Solutions were first stirred at 50 °C for 24 h. The active layer was formed by spin-coating the chalcone dye:PCBM solution onto the substrates at 1000 rpm during 80 s. Directly after spin-coating, the samples were introduced in the thermal evaporator. For completion of the conventional solar cell, a 80 nm-thick aluminum top electrode was thermally-evaporated (Al deposition

rate 0.5 nm.s^{-1}) under a secondary vacuum (10^{-6} mbar) onto the active layer through a shadow mask to define a 8.6 mm^2 active area. In the case of devices fabricated with calcium/aluminum top electrode, a 20 nm-thick calcium layer was evaporated under the same conditions (Ca deposition rate 0.2 nm.s^{-1}) before the evaporation of the 80 nm-thick aluminum. Experiments were repeated on eight individual cells to evaluate the standard deviation. The devices were characterized using a *K.H.S. SolarCelltest-575* solar simulator with AM1.5G filters set at 100 mW/cm^2 with a calibrated radiometer (IL 1400BL). External Quantum Efficiency (EQE) (or Incident Photon to Converted Electron) measurements were performed outside the glovebox. Before exiting the glove box, the devices were encapsulated using Norland Optical Adhesive 61 (NOA 61) and glass cover. The EQE spectra were determined by measuring the current in short-circuit conditions from 300 to 1000 nm (1 nm step) using three different filters to get rid of the contributions of harmonics. Four to six thickness measurements were performed for the different active layer resulting from the 3 concentrations of dye **1**:PC₆₁BM (1:4) in *o*-DCB. Active layer thicknesses were determined using a *KLA Tencor – Alpha-Step IQ* stylus profilometer. Standard deviation was determined for each concentration: $187 \pm 4 \text{ nm}$ ($C_{\text{Dye1}}=10 \text{ mg.ml}^{-1}$); 92 ± 6 ($C_{\text{Dye1}}=5 \text{ mg.ml}^{-1}$) and 43 ± 4 ($C_{\text{Dye1}}=2.5 \text{ mg.ml}^{-1}$).

6 –Tables

Table S1 Photovoltaic characteristics of devices based on dyes **1-3** : PC₆₁BM (1:4 weight ratio) as active layer and different metal top electrodes Solvent used for deposition: CB for **1** and **3**, chloroform/CB (50/50 v:v) for **2** (Al top electrode)

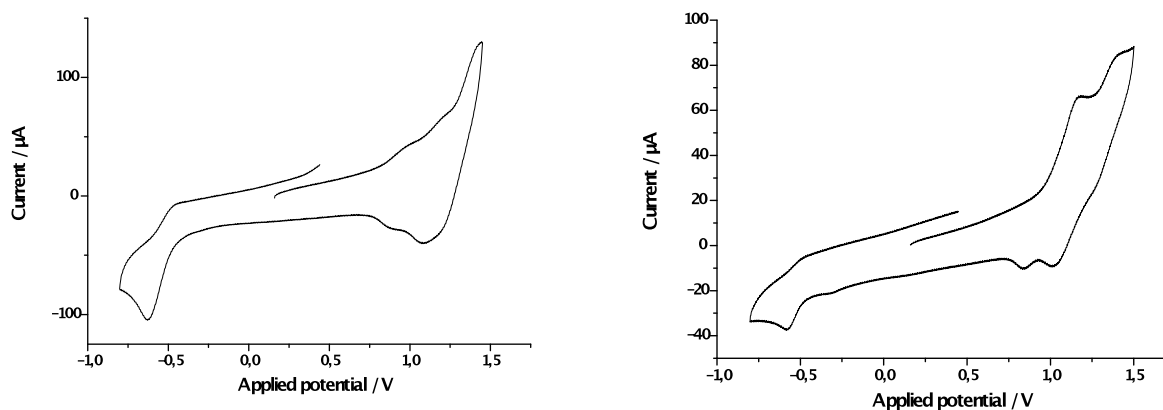
Dye	thickness (nm)	J_{sc} (mA.cm^{-2})	V_{oc} (V)	FF	PCE (%)
1	155	2.50 ± 0.15	0.57 ± 0.04	0.33 ± 0.01	0.47 ± 0.05
2	215	1.62 ± 0.06	0.57 ± 0.08	0.29 ± 0.01	0.26 ± 0.05
3	140	2.02 ± 0.09	0.52 ± 0.01	0.33 ± 0.01	0.34 ± 0.01

Table S2. Photovoltaic characteristics of devices fabricated with dye **1** :PC₆₁BM (1:4 weight ratio) as active layer. Influence of the active layer thickness and of top electrode. Solvent used for deposition: *o*-DCB.

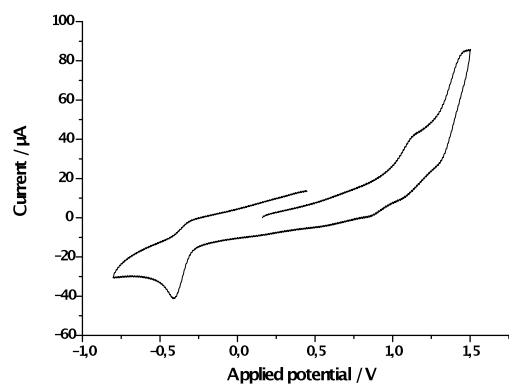
Top electrode	Device	thickness (nm)	J_{sc} (mA.cm^{-2})	V_{oc} (V)	FF	PCE (%)	R_s (Ω)	R_{sh} (Ω)
Al	1a	187	2.33 ± 0.20	0.55 ± 0.03	0.31 ± 0.01	0.39 ± 0.05	1230 ± 190	4030 ± 630
	1b	92	3.68 ± 0.20	0.49 ± 0.02	0.29 ± 0.01	0.52 ± 0.05	535 ± 50	2070 ± 150
	1c	43	2.77 ± 0.10	0.23 ± 0.02	0.31 ± 0.01	0.19 ± 0.02	105 ± 11	400 ± 64
Ca/Al	1d	187	3.26 ± 0.17	0.63 ± 0.01	0.34 ± 0.01	0.69 ± 0.04	192 ± 6	3990 ± 280
	1e	92	4.26 ± 0.14	0.55 ± 0.03	0.29 ± 0.01	0.67 ± 0.06	46 ± 2	2040 ± 120
	1f	43	4.80 ± 0.20	0.57 ± 0.02	0.35 ± 0.02	0.96 ± 0.10	35 ± 4	1860 ± 245

7 – Figures

Fig. S1. Cyclic voltammograms of compounds **1-3** in DCM containing 0.1M tetrabutylammonium hexafluorophosphate (TBAPF₆) under argon atmosphere (scan rate 200 mV/s; dye concentration: 1 mM).



Compound 1



Compound 2

Compound 3

Fig. S2. Schematic energy diagram for a ITO /PEDOT:PSS/dyes **1-3**:PC₆₁BM/Al solar cell.

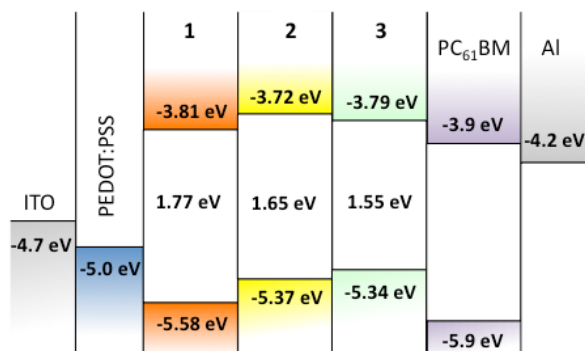


Fig S3. *I-V* characteristics (a) in the dark and (b) under illumination of direct organic solar cells fabricated with dye **1**: PC₆₁BM (purple triangles), dye **2**: PC₆₁BM (black squares) and dye **3**: PC₆₁BM (green circles) as active layers (1:4 dye/PC₆₁BM weight ratio). Solvent used for deposition: CB for **1** and **3**, chloroform/CB (50/50 v:v) for **2** (thickness: 155 nm (dye **1**), 215 nm (dye **2**) and 140 nm (dye **3**); Al top electrode).

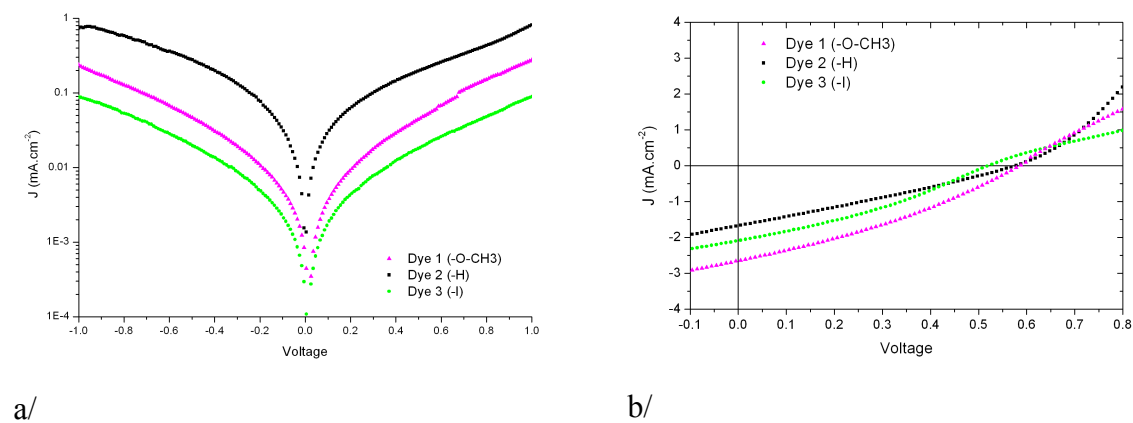


Fig. S4. *I-V* characteristics (a) in the dark and (b) under illumination of devices made with dye **1**:PC₆₁BM (1:4 weight ratio) active layers processed with *o*-DCB (black squares), CB (purple triangles) and *o*-DCB:CHCl₃ (green circles). Top electrode Al. Film Active layers thicknesses: 187 nm (*o*-DCB), 155 nm (CB) and 213 nm (*o*-DCB:CHCl₃).

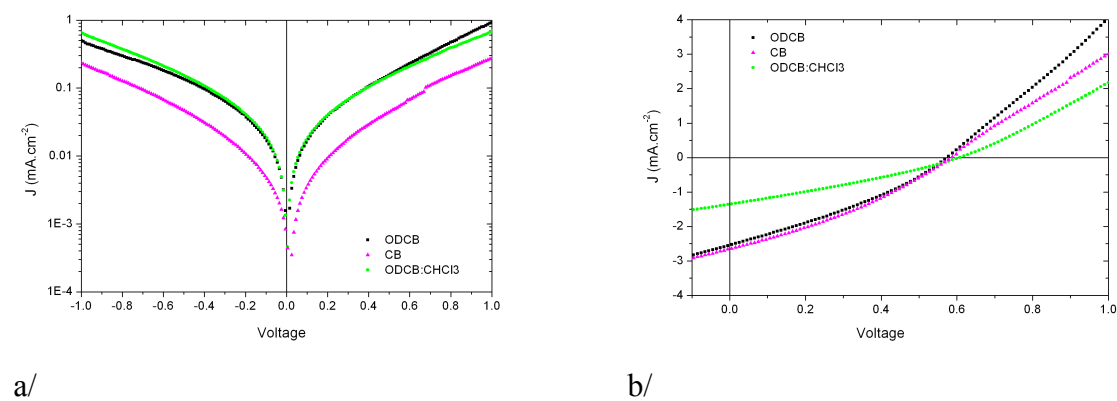


Fig. S5. *I-V* characteristic in the dark of devices made with 43 nm-thick (purple – triangle), 92 nm-thick (green – circle) and 187 nm-thick (black – square) dye 1:PC₆₁BM (1:4 weight ratio) active layers using Ca/Al top electrodes. Solvent used for deposition: *o*-DCB.

