Supplementary information

A tailored hybrid BODIPY-oligothiophene donor for molecular bulk heterojunction solar cells with improved performances

Theodulf Rousseau,[a] Antonio Cravino,[a] Emilie Ripaud,[a] Philippe Leriche,[a] Sandra Rihn,[b] Antoinette De Nicola,[b] Raymond Ziessel [b] and Jean Roncali[a]*

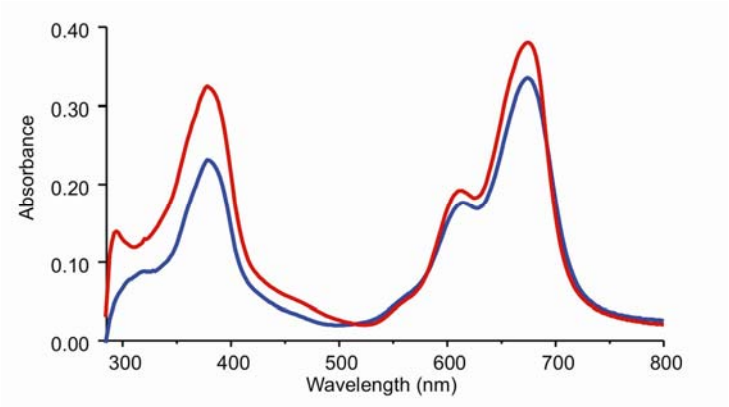
Devices preparation and characterization

PCBM was purchased from NanoC and used as received. The PEDOT:PSS Baytron® PH500 suspension used to apply smoothing and hole conducting layers was received from HC Stark. As electrodes, indium-tin-oxide (ITO) coated glasses (Merck, sheet resistance ≤ 20 Ω/□) 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.

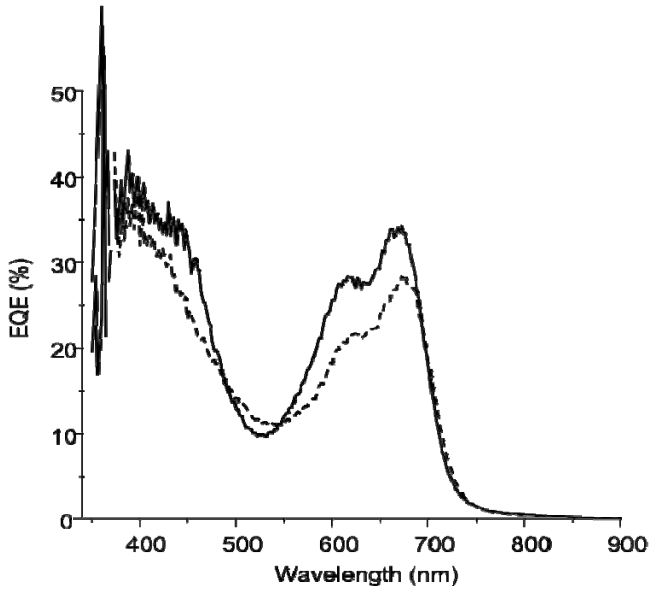
Devices with ITO/Baytron/**2**:$PC_{61}BM$/Al structure were realized from chloroform solutions containing the dye and PCBM. Spin-casting was done distributing the solutions drop by drop (5×) onto an already rotating stage (800-2000 rpm). The cell were completed by evaporation of Al through a round shadow mask (devices area of 0.28 cm^2) After preparation, the solar cells were stored and characterized in a glove-box under an argon atmosphere. 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. IPCE spectra were recorded with a Perkin Elmer 7225 lock-in amplifier under monochromatic illumination at a chopping frequency of 210 Hz. The light from a W lamp was dispersed by an Acton SpectraPro150. Electronic absorption spectra were recorded with a Perkin Elmer Lambda 19 spectrophotometer.

Table S1. Electrical characteristics of bulk heterojunction solar cells based on compounds **2** and $PC_{61}BM$ under AM 1.5 simulated solar irradiation at 90 mW cm^{-2}

D/A Ratio	A, λ=370 nm	A, λ =665 nm	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF* (%)	η (%)
1:3	0.42	0.18	2.51	0.80	35	0.80
1:3	0.45	0.22	6.51	0.79	35	1.98
1:3	0.96	0.38	5.75	0.80	35	1.80
1:2	0.33	0.18	4.16	0.75	39	1.35
1:2	0.50	0.32	7.09	0.76	34	2.06
1:2	0.47	0.28	6.93	0.74	38	2.17
1:1	0.32	0.24	3.24	0.75	32	0.86
1:1	0.36	0.28	4.40	0.74	36	1.28
1:1	0.41	0.33	3.93	0.69	34	1.02



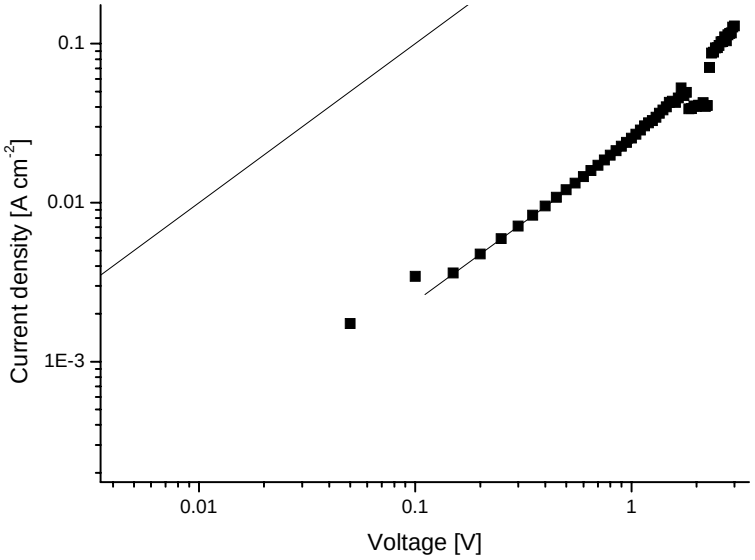
UV-Vis absorption spectra of ~60 nm films of compound **1** (blue) and **2** (red) spin-cast on glass from chloroform solutions

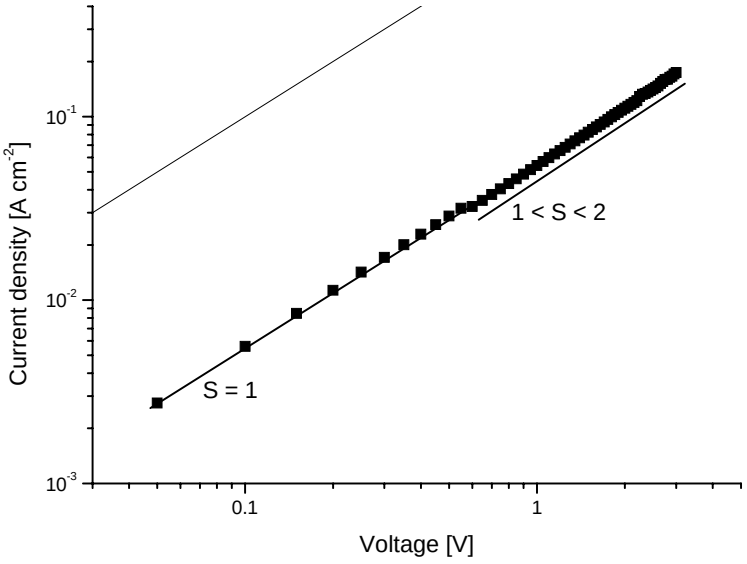


Comparison of the IPCE spectra of BHJ cells based on compound **1** (dashed line) and **2** (solid line)

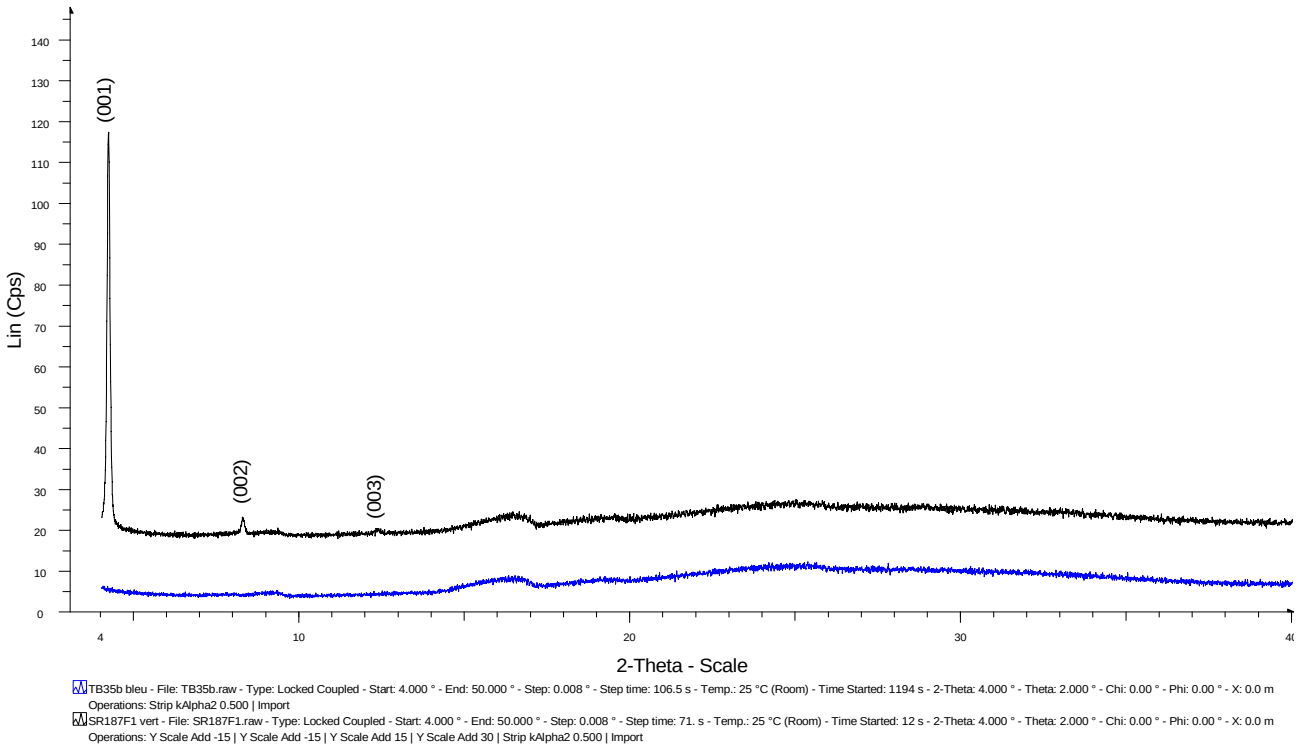
Estimation of the hole mobility of compounds 1 and 2

To compare the hole mobility of the two compounds hole-only devices with the structure ITO/Baytron/donor/Au have been fabricated. Both compounds form ohmic contacts at low voltage, as seen by a linear current-voltage relationship with slope of unity in the log-log plots. Considering the structural similarity between the two molecules, the same density of charge carriers is assumed. Since this quantity is not known, based on mass considerations, we have arbitrarily taken a value corresponding to the half of that generally admitted for poly(3-hexylthiophene) namely $N = 10^{15}$ cm^{-3} (*D. Chirvase, Z. Chiguvare, M. Knipper, J. Parisi, V. Dyakonov, J. C. Hummelen, J. Appl. Phys., 2003, 93, 3376*). For film thicknesses of *ca* 60 nm, measured by profilometry we obtained a hole mobility of 4.7×10^{-4} V cm^{-2} s^{-1} for compound **1** and a twice larger value of 9.0×10^{-4} V cm^{-2} s^{-1} for compound **2**. Due to the uncertainty on N, the absolute value of the hole mobility cannot be obtained in this way but nevertheless these results clearly show that whatever the value of N the hole mobility of donor **2** is twice larger than that of **1**.





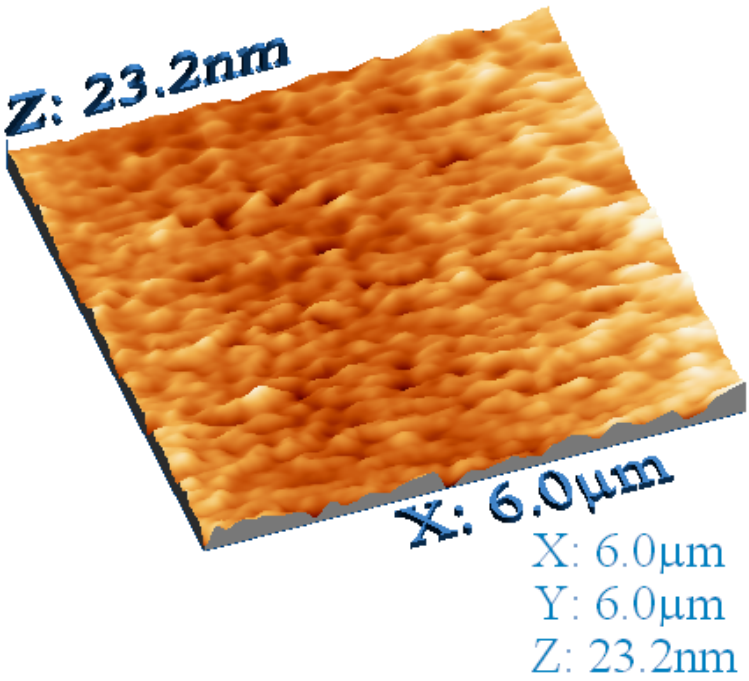
J-V plot for hole-only devices. Top: **1**. Bottom: **2**.



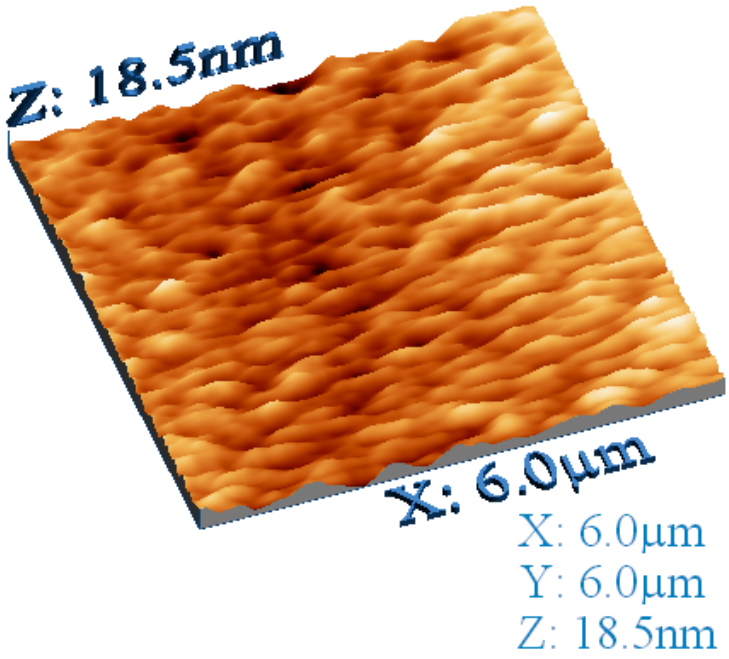
Caption	Angle 2-Theta °	d value Angstrom	Intensity Cps	h	k	l
d=20.98563	4.207	20.98563	120	0	0	1
d=10.66533	8.284	10.66533	23.8	0	0	2
d=7.15256	12.365	7.15256	22.6	0	0	3

Films of **1** and **2** cast on glass have been analyzed by X-ray diffraction in reflection mode on a Bruker D8 Advance diffractometer, equipped with a speed detector Vantec and utilizing CuKα radiation (λ = 1.5406 Å).
For **1**(blue) the XRD diagram shows no diffraction peak indicating an amorphous character while for **2 (**black) , thin diffraction peaks reveal a crystalline organisation on the substrate. The XRD diagram shows an intense diffraction peak (*001*) at $2\theta = 4.207°$ and two weak peaks respectively at $2\theta = 8.284°$ and $2\theta = 12.365°$ which should correspond to a distance between two molecular layers of approximatively 21 Å.

SR187F1 : PCBM- 1:2 weight ratio

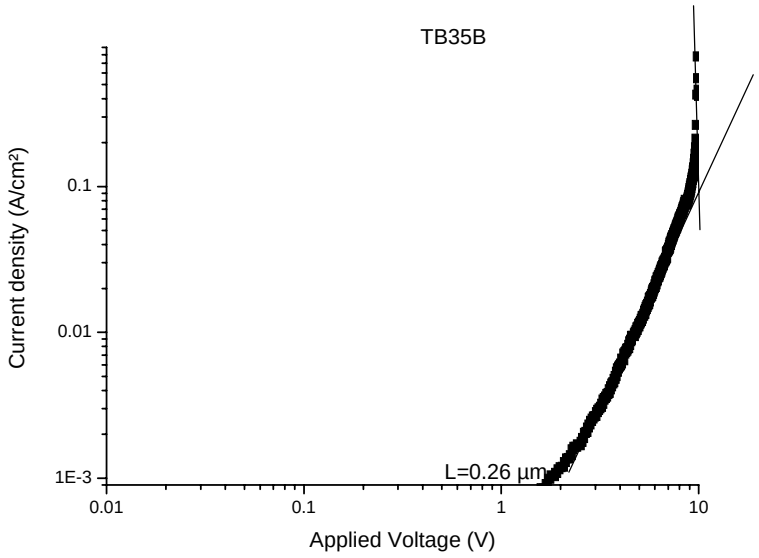


TB35B : PCBM- 1:2 weight ratio

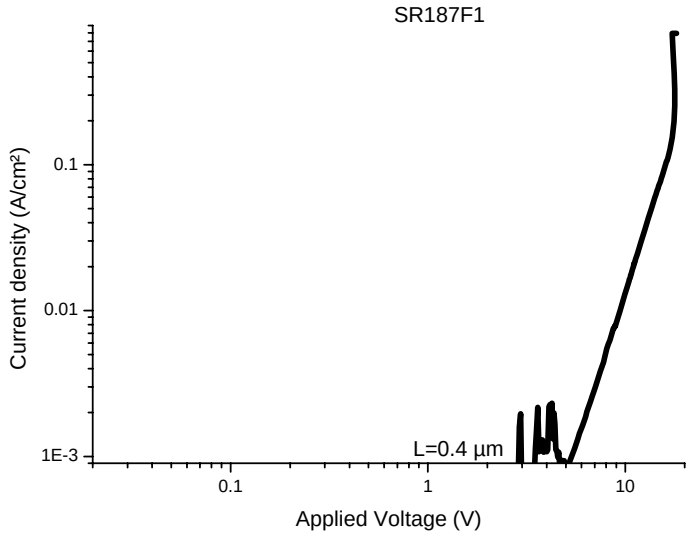


Contact mode AFM images of the blend **2**:PCBM (top) & **1**:PCBM (bottom) (1:2 ratio by weight) films spin cast from chloroform solution were obtained and compared. Images were collected in air using a silicon cantilevel. For each sample, images were collected on multiple locations to examine the film uniformity. We notice that the **2**:PCBM films appear slightly smoother (RMS of 3 nm) than the **1**:PCBM-films (RMS= 3.5 nm).

SCLC mobility measurements



$$\mu_h^{SCL}\ (1) = 5.10\ 10^{-5}\ cm^2V^{-1}s^{-1}$$



$$\mu_h^{SCL}\ (2) = 9.70\ 10^{-5}\ cm^2V^{-1}s^{-1}$$