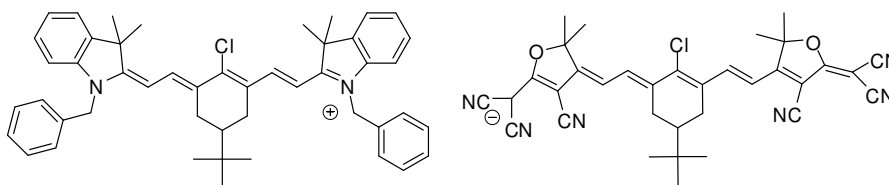


**“Cyanine – cyanine” salt exhibiting photovoltaic properties**

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**General.** All reactions were routinely performed under argon atmosphere. NMR spectra ( $^1\text{H}$ ) were recorded at room temperature on a BRUKER AC 200 operating at 200.13 MHz. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane ( $^1\text{H}$ ), residual solvent peaks being used as internal standard ( $\text{CHCl}_3$   $^1\text{H}$ : 7.26 ppm). UV-visible spectra were recorded on a Jasco V-550 spectrophotometer in diluted dichloromethane solution (*ca.*  $10^{-5}$  mol.L $^{-1}$ ). Elemental analysis were performed at the Service Central d'Analyse du CNRS (Vernaison, France). Column Chromatography was performed on Merck Gerdurant 60 (40-63  $\mu\text{m}$ ) silica. **1**[Br],<sup>i</sup> **[Na]2** and **[NBu<sub>4</sub>]2**<sup>ii</sup> were prepared according published procedures.

**3**

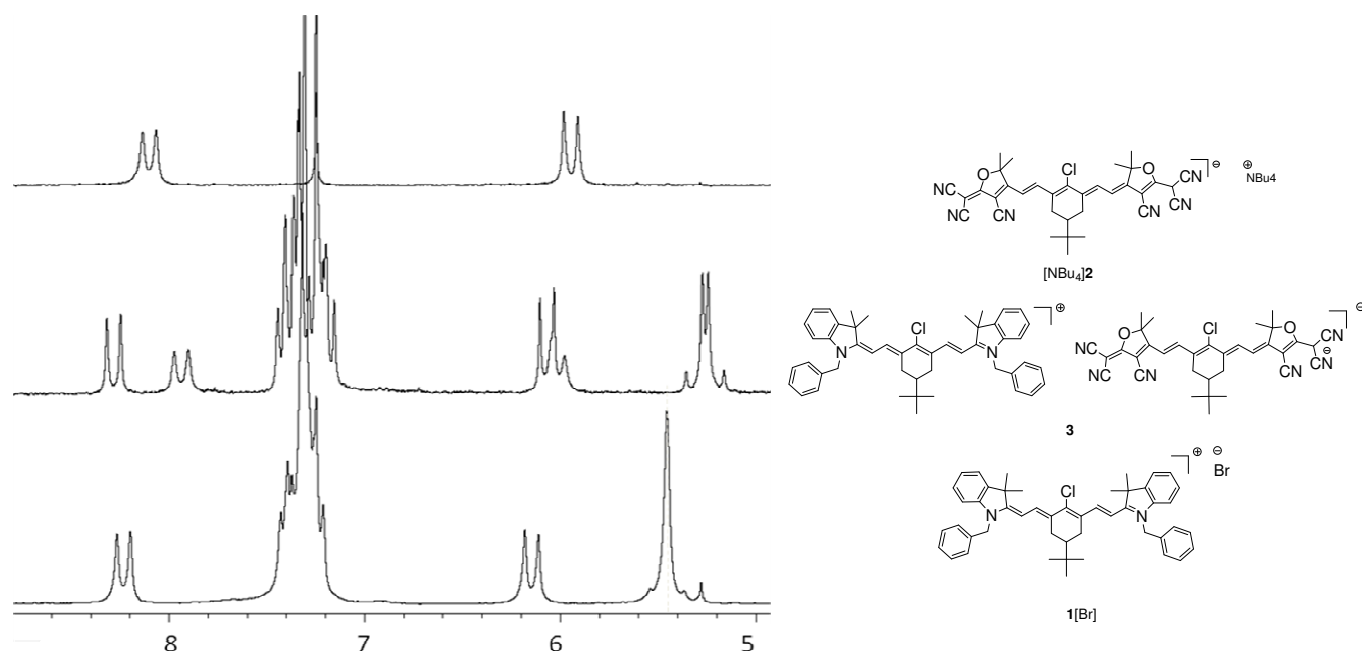


**1**[Br] (50 mg, 0.06 mmol, 1 eq.) and **[Na]2** (36 mg, 1 eq.) were dissolved in DCM (10 mL) and the solution was stirred 30 min at RT. The solution was washed with water (3 x 15 mL),

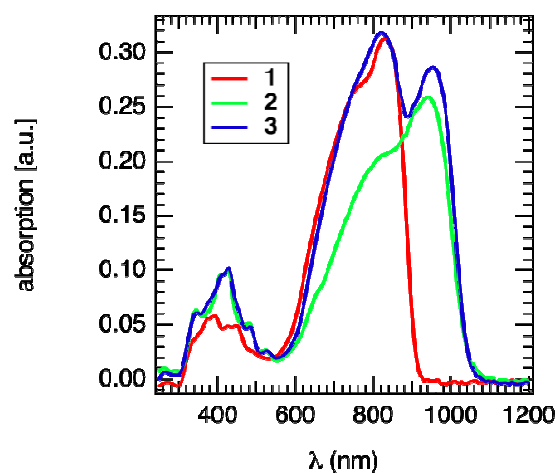
filtrated trough a silica plug (washed with DCM). Then the solvents were evaporated to afford a green solid (85 %).

$^1\text{H}$  NMR (200.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.98 (m, 18 H), 1.4 (m, 2H), 1.54 (s, 12H) 1.74 (s, 12H), 1.90-2.10 (m, 4H), 2.58 (dd,  $^3J = 2$  Hz,  $^2J = 13$  Hz, 2H), 2.72 (dd,  $^3J = 2$  Hz,  $^2J = 13$  Hz, 2H), 5.19 (d,  $^2J = 16$  Hz, 2H), 5.31 (d,  $^2J = 16$  Hz, 2H), 6.00 (d,  $^3J = 14$  Hz, 2H), 6.07 (d,  $^3J = 14$  Hz, 2H), 7.2-7.5 (m, 18H), 7.93 (d,  $^3J = 14$  Hz, 2H), 8.23 (d,  $^3J = 14$  Hz, 2H).

Anal. calculated for  $\text{C}_{82}\text{H}_{84}\text{N}_8\text{Cl}_2\text{O}_3$ : C, 75.73, H, 6.51, N, 8.62, Found C, 75.85, H, 6.54, N, 8.49.

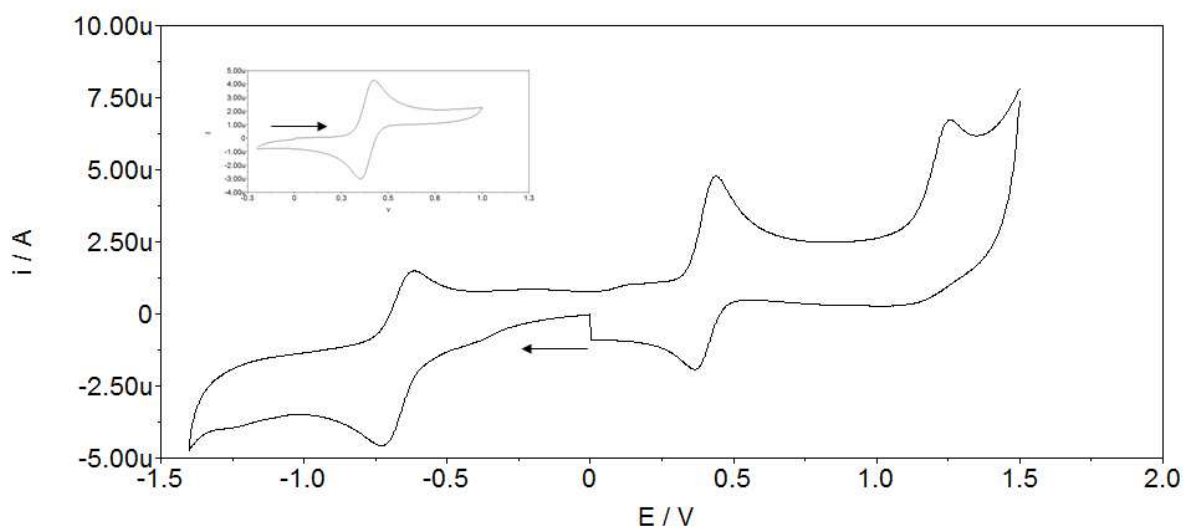


**Figure S1.**  $^1\text{H}$ -NMR (200 MHz,  $\text{CDCl}_3\text{-}d_6$ ) spectra of the aromatic part of **1[Br]** (bottom), **3** (middle) and **[NBu<sub>4</sub>]**2**** (top).

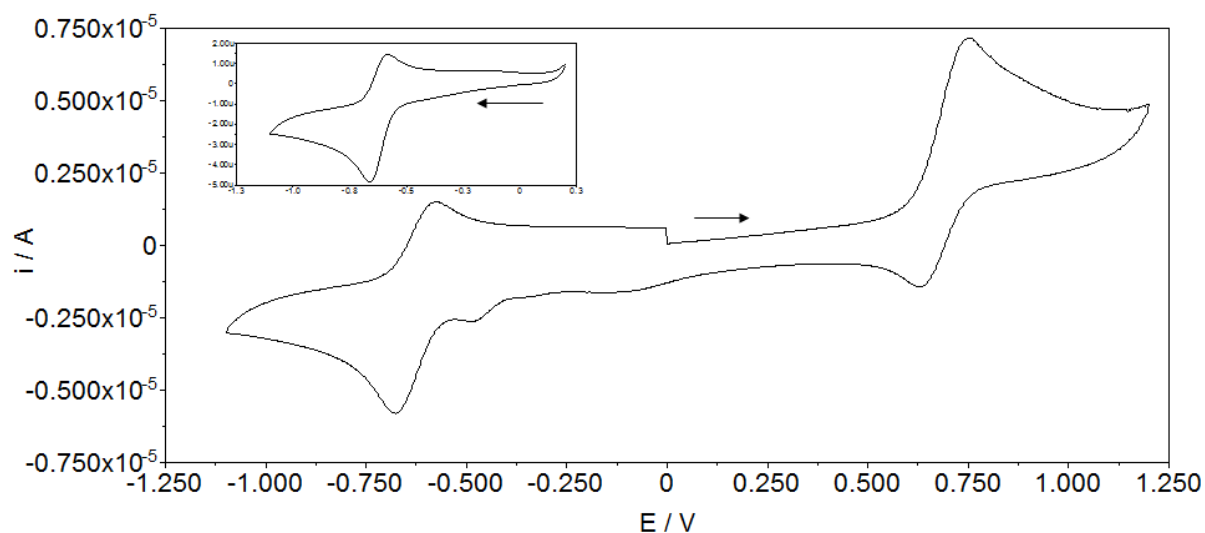


**Figure S2.** The absorption of solid state films of **1**[Br] (red), [NBu<sub>4</sub>]**2** (green) and **3** (blue) at room temperature. All films are spin casted from chloroform solution.

**Electrochemistry.** Electrochemical studies were carried out under argon atmosphere using an Eco Chemie Autolab PGSTAT 30 potentiostat (CH<sub>2</sub>Cl<sub>2</sub>, 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>), the working electrode was a Pt disk. Ferrocene was used as an internal reference to calibrate the SCE electrode ( $E^\circ$  = at 0.460 V in CH<sub>2</sub>Cl<sub>2</sub>/[NBu<sub>4</sub>][PF<sub>6</sub>]).<sup>iii</sup>



**Figure S3.** CV trace obtained for [2]<sup>−</sup> (CH<sub>2</sub>Cl<sub>2</sub>, 0.2 M Bu<sub>4</sub>NPF<sub>6</sub>,  $\nu$  = 100 mV.s<sup>−1</sup>). Inset shows the reversibility of the first oxidation process.



**Figure S4.** CV trace obtained for  $[1]^+$  ( $\text{CH}_2\text{Cl}_2$ , 0.2 M  $\text{Bu}_4\text{NPF}_6$ ,  $v = 100 \text{ mV.s}^{-1}$ ). Inset shows the reduction only.

**Photophysical data.** UV-Vis absorption in dichloromethane.

**Table S5**

compound	$\lambda_{\text{max}}$ (nm)	$\epsilon$ ( $\text{L/mol}^{-1}\text{cm}^{-1}$ )
<b>1</b> [Br]	794	350 000
[NBu <sub>4</sub> ] <b>2</b>	900	325 000
<b>3</b>	795	400 000
“	900	300 000

**Preparation of Photovoltaic Devices.** BHJ solar cells were processed by spin-coating a mixture of dyes and [60]PCBM on cleaned patterned indium tin oxide (ITO) coated glass substrate. The cleaning procedure comprised the following steps: soap water, acetone and isopropanol (all 10 min in an ultrasonic bath). The ITO was then coated with a 40 nm poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layer. The PEDOT:PSS coated substrates were transferred to a nitrogen glove box to avoid the influence of oxygen and moisture and treated at 130°C for 10 min. In a next step, the

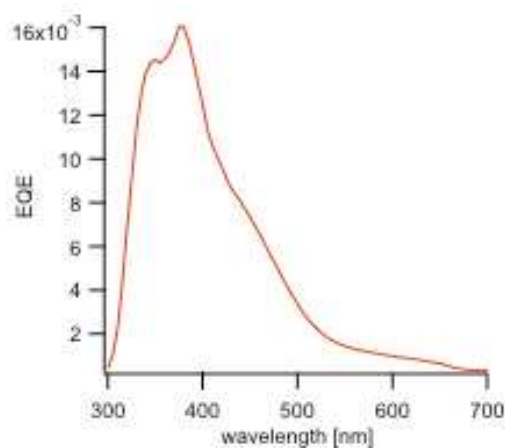
chromophore:[60]PCBM blend (active layer) was spin-coated on the top at 800 rpm for 60 sec with further annealing at 130°C for another 10 min. Chromophores as well as PCBM were dissolved in *chloroform* (20 mg/ml). The weight ratio was 1:2 (chromophores : [60]PCBM). Finally, the metal contact (Ca/Al) was thermally evaporated.

The device active layer thickness without a PEDOT:PSS layer (being in the range of 40-50 nm) is as follows:

□ Compound 3: d~160nm (JV-Measurements), d~160nm (EQE Measurement);

□Compound 2: d~230nm (JV), d~180nm (EQE)

The light intensity of the simulator was adjusted by using the EQE values prior the JV measurements. We used the xenon arc lamp with neutral density filters as light source.



**Figure S6:** EQE spectrum measured on pristine PCBM devices

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<sup>i</sup> Bouit, P.-A.; Wetzel, G.; Berginc, G.; Toupet, L.; Feneyrou, P.; Bretonnière, Y.; Maury, O.; Andraud, C. *Chem. Mater.* **2007**, *19*, 5325-5335.

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- <sup>ii</sup> Bouit, P.-A.; Di Piazza, E.; Rigaut, S.; Toupet, L.; Aronica, C.; Le Guennic, B.; Andraud, C.; Maury, O. *Org. Lett.* **2008**, 10, 19, 4159-4162.
- <sup>iii</sup> Connelly, N. G.; Geiger, W. E. *Chem.Rev.* **1996**, 96, 877-910.