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Pierre-Antoine Bouit, Daniel Rauh, Stefan Neugebauer, Juan Luis Delgado, Emmanuel Di Piazza, et al.. A “Cyanine–Cyanine” Salt Exhibiting Photovoltaic Properties. *Organic Letters*, 2009, 11 (21), pp.4806-4809. 10.1021/ol901764t . hal-01089801

HAL Id: hal-01089801

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Submitted on 16 Mar 2017

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A “Cyanine-Cyanine” salt exhibiting photovoltaic properties.

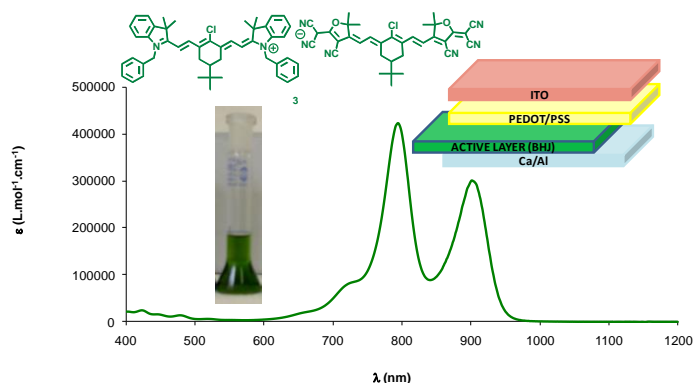
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Received Date (will be automatically inserted after manuscript is accepted)

ABSTRACT



Association between cationic and anionic heptamethine dyes led to the formation of a new organic salt (3) displaying exceptional light harvesting properties in the NIR spectral range and having amphoteric redox character. Preliminary results of molecular bulk heterojunction solar cells based on the title compound 3 and [60]PCBM as the only active layer reveal this new dye as a promising light harvesting material for photovoltaics.

Organic dyes displaying strong absorption/emission in the near-infrared (NIR) have received a great interest over the last decade. On the one hand, their fluorescence properties in the “biological window” allowed designing

efficient bioprobes.¹ On the other hand, their exceptional absorption properties have been used in the field of

¹ Ghorroghchian, P.P.; Frail, P.R.; Susumu, K.; Blessington, D.; Brannan, A.; Bates, F.S.; Chance, B.; Hammer, D.A.; Therien, M.J. *Proc. Nat. Ac. Sci.* **2005**, *102*, 2922-2927.

materials science (nonlinear absorbing materials², hybrid solar cells^{3...}). More recently, organic photovoltaic has appeared as a new field of application for these light harvesting molecules.⁴ After 16 years of intensive studies, bulk heterojunction (BHJ) organic solar cells based on poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) have reached around 5 % of power conversion efficiency (PCE).⁵ However, the low absorbing properties of most of conjugated polymers such as P3HT, especially in the NIR range - where almost 50 % of the sunlight intensity is displayed - remains the main drawback of these devices.^{5a} To overcome this trouble, a first strategy has been the use of low-band gap polymers.⁶ However, another appealing strategy is the replacement of the polymer by organic dyes. Hence, in addition to their good absorption properties, organic dyes are monodisperse and are easily and reproducibly synthesizable. In this context, PCE in the range of 1.5 % have been described in the last few months using squaraine dyes,⁷ push-pull chromophores⁸ or Bodipy.^{9,10}

At the same time we emphasize that the lowering of the band gap of the donor material well below 2 eV (as in P3HT) alone is not sufficient in case of single-junction solar cells, as other parameters, such as LUMO level of the donor should comply accordingly to keep the open circuit voltage maximum.¹¹ Very low band gap materials with the gap of 1.2 eV could however find potential in the low-band gap part of organic multi-junction cells. In this communication, we describe the properties of a new organic salt composed of two NIR absorbing cyanine dyes. In this salt, both the cationic and the anionic moiety are chromophoric units. The outstanding optical properties of this new dye are presented as well as its electrochemical properties. As an example of its

applications, preliminary report of photovoltaic performance displaying PCE of about 0.4 % are presented.

Cyanine dyes are generally cationic organic colorant in which a positive charge is delocalized on an odd-number carbon skeleton (for example, **1[Br]**,^{2b} Figure 1). Some of us previously reported an unusual anionic heptamethine cyanine dye (**[Na]2**, Figure 1) in which the delocalized charge is negative.¹² This chromophore displayed the typical photophysical properties of heptamethine dyes.

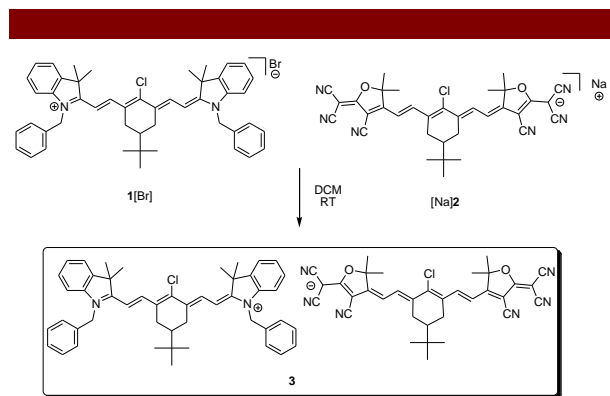


Figure 1. Synthesis and structure of the new dye **3**.

By mixing, the easily synthesizable **1[Br]** and **Na[2]** in dichloromethane at room temperature, spontaneous ion metathesis occurred between the two chromophores, as evidenced by thin-layer chromatography (TLC). Further washing with water and chromatography on silica gel allowed to remove the inorganic salt and to afford quantitatively the new organic salt **3**, composed by the two chromophores **1**⁺ and **2**⁻ (Figure 1). NMR analyses clearly showed the presence of both dyes in the complex **3** and elemental analysis confirmed the removal of the inorganic counter-ions. Interestingly, **3** presents good solubility in organic solvents, while **Na[2]** was only soluble in highly polar solvents. Zwitterionic cyanines composed by cationic dye with tethered sulfonate have already been described,¹³ but to our knowledge, this is the first example of such a compound in which both ions are cyanines.

Optical properties of **3** were studied by means of UV-vis spectroscopy. The absorption spectrum of **3** in dichloromethane consists of two absorption bands in the NIR with high extinction coefficients [$\lambda_1 = 795$ nm ($\epsilon = 420000$ L.mol⁻¹.cm⁻¹), $\lambda_2 = 902$ nm ($\epsilon = 300000$ L.mol⁻¹.cm⁻¹)] (Figure 2). Moreover, the compound displays an extinction coefficient superior to 50000 L.mol⁻¹.cm⁻¹ between 700 nm and 940 nm. The two transitions are assigned to the two chromophoric units of **3** (**1**⁺ and **2**⁻) and the obtained spectrum appears as a superposition of

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⁵ a) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58-77; b) Ma, W.; Yang, C.; Gong, X.; Lee, K. and Heeger, A. J., *Adv. Funct. Mater.* **2005**, *15*, 1617-1622; c) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K. and Yang, Y., *Nat. Mater.* **2005**, *4*, 864-865. For other fullerenes derivatives, see: d) Riedel, I.; Von Hauff, E.; Parigi, J.; Martin, N.; Giacalone, F.; Dyakonov, V. *Adv. Funct. Mat.* **2005**, *15*, 1979-1987; e) Backer, S. A.; Sivula, K.; Kavulak, D. F.; Fréchet, J. M. J. *Chem. Mater.* **2007**, *19*, 12, 2927-2929.

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⁸ a) Roquet, S.; Cravino, A.; Leriche, P.; Alévêque, O.; Frère, P.; Roncali, J. *J. Am. Chem. Soc.* **2006**, *128*, 3459-3466; b) Kronenber, N. M.; Deppish, M.; Würthner, F.; Ledemann, H. V. A.; Deing K. Meerholz, K. *Chem. Commun.* **2008**, 6489-6491.

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¹² 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.

¹³ Bouteiller, C.; Clave G.; Bernardin, A.; Chipon, B.; Massonneau, M.; Renard, P.-Y.; Romieu, A. *Bionconjugate Chem.* **2007**, *18*, 1303-1317.

the spectra of **1**[Br] and **[NBu₄]**2** measured under the same experimental conditions (Figure 2).^{2b, 12} From these observations, we may conclude that there is no electronic ground state interaction between the two chromophores. Nevertheless, it is important to point out that they both conserve their particular optical properties. The absorption spectra of solid films of **3**, **2**, and **1** made from chloroform solution (Figure S2) confirm that the spectrum of **3** is a superposition of those of **2** and **1**. It is evident that, in the solid state, absorption up to 1050 nm with the chromophore **3** is possible thus making it an excellent candidate for NIR absorption.**

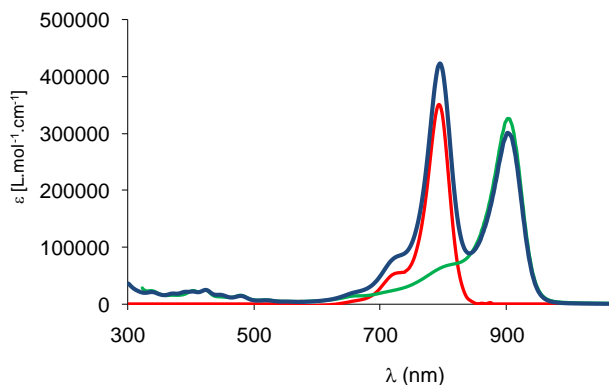


Figure 2. Absorption spectra in dichloromethane of **1**[Br] (red), **[NBu₄]**2** (green) and **3** (blue) at room temperature.**

Cyclic voltammetry (CV) was used to investigate the redox properties of complex **3**, as shown in Figure 3 (CH_2Cl_2 , 0.2 M Bu_4NPF_6 , $\nu = 100 \text{ mV}\cdot\text{s}^{-1}$). This compound undergoes two reversible mono-electronic oxidations at $E_{\text{ox}1}^{\circ} = 0.39 \text{ V vs. SCE}$ ($\Delta E_p = 60 \text{ mV}$, $I_{\text{pc}}/I_{\text{pa}} \approx 1$) and $E_{\text{ox}2}^{\circ} = 0.70 \text{ V vs. SCE}$ ($\Delta E_p = 60 \text{ mV}$, $I_{\text{pc}}/I_{\text{pa}} \approx 1$), followed by a third irreversible oxidation at $E_{\text{pa}} = 1.19 \text{ V}$. Comparison of the CV traces with those of **1**[Br] and **Na**[**2**] (Figure S2 and S3) suggests that the first and second oxidation processes correspond respectively to the oxidation of **2**⁻ ($E_{\text{ox}}^{\circ} = 0.39 \text{ V}$, $\Delta E_p = 60 \text{ mV}$, $I_{\text{pc}}/I_{\text{pa}} \approx 1$) and **1**⁺ ($E_{\text{ox}}^{\circ} = 0.69 \text{ V}$, $E_p = 90 \text{ mV}$, $I_{\text{pc}}/I_{\text{pa}} \approx 0.5$), while the irreversible oxidation has been assigned to the second oxidation of **2**⁻ ($E_{\text{ox}}^{\circ} = 1.22 \text{ V}$).¹⁰ On the other hand, the broad signal observed at negative potential for **3** ($E_{\text{pc}} = -0.69 \text{ V}$ and $E_{\text{pa}} = -0.58 \text{ V}$) is ascribed to the overlapping of their partially reversible reduction processes ($E_{\text{red}}^{\circ} = -0.62 \text{ V}$, $\Delta E_p = 70 \text{ mV}$, $I_{\text{pc}}/I_{\text{pa}} \approx 0.65$ for **1**⁺ and $E_{\text{red}}^{\circ} = -0.69 \text{ V}$, $\Delta E_p = 90 \text{ mV}$, $I_{\text{pc}}/I_{\text{pa}} \approx 0.85$ for **2**⁻). From these experiments, it appears that each chromophoric unit conserves its own redox properties in the complex **3** but with a notable increase in the reversibility of the second oxidation corresponding to oxidation of the **1**⁺ moiety.

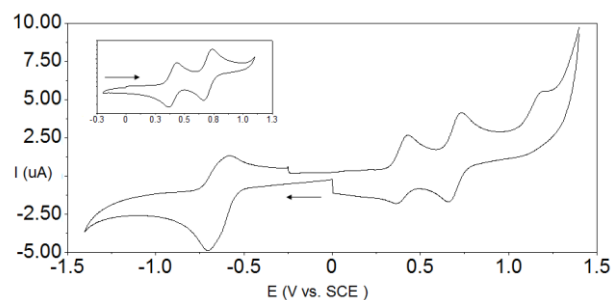


Figure 3. CV trace obtained for **3** (CH_2Cl_2 , 0.2 M Bu_4NPF_6 , $\nu = 100 \text{ mV}\cdot\text{s}^{-1}$). Inset shows the reversibility of the first two oxidation processes.

To justify our assumption on the applicability of the chromophores **1-3** for photovoltaic energy conversion, we fabricated solar cells in a configuration Glass/ITO/PEDOT:PSS/chromophore:[60]PCBM/Ca/Al. The details on device fabrication are available from the SI. The external quantum efficiency (EQE) and the current-voltage (J-V) characteristics were measured for chromophores **3** and **2** based devices (no operating devices with **1** could be made so far). The EQE determines the number of generated charge carriers extracted into the outer circuit relative to the number of incident photons. Additionally, the short circuit current density of the solar cell can be calculated for any illumination spectrum at given intensity; in our case for the AM1.5G solar spectrum at $100 \text{ mW}/\text{cm}^2$. The J-V measurements, and hence the PCE determination were performed with a solar simulator. Generally, the spectrum of the latter differs from the AM 1.5G; therefore, a so called *mismatch* factor should be calculated by using a reference cell with the known spectral response.¹⁴ In a next step, the light intensity of the solar simulator should be adjusted to yield the expected short circuit current of the reference cell, i.e., the short-circuit current of the reference cell under AM 1.5G divided by the mismatch factor. By using this intensity, the organic solar cell can finally be measured. This procedure is a common way for an accurate PCE determination. This is an indirect method to accurately determine the main solar cell parameters, such as the short circuit current density (J_{SC}), open-circuit voltage (V_{OC}) and fill factor (FF) of the solar cell. In Figure 4, the EQE spectra of BHJ solar cells with **3** and **2**, as electron donor, and [60]PCBM, as acceptor, are shown. The best EQE values of 11 % were obtained at the wavelength of 785 nm for the chromophore **3**. At a closer look at the EQE, one can see that there are two regions, where light is absorbed and charge carriers are generated: the first one around 400 nm (related to the absorption of PCBM, see Figure S6) and the second one between 700 to 1000 nm (related to the NIR absorption of the dye).

¹⁴ Shrotriya, V.; Li, G.; Yao, Y.; Moriarty, T.; Emery, K.; and Yang Y., *Adv. Funct. Mater.* **2006**, 16, 2016–2023

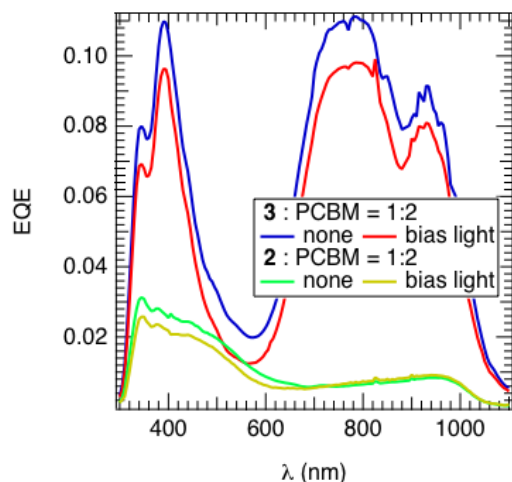


Figure 4. External quantum efficiency of BJJ solar cells fabricated with chromophore **3** (blue, red) and **2** (green, yellow) blended with [60]PCBM in 2:1 weight ratio. For comparison, the EQE spectra measured with and without white light bias are shown.

By applying the optical bias we are able to assess the role of traps as limiting factors. It can also be seen that steady-state white light bias affects the photocurrent measurement of a solar cell. It should be mentioned that this white light does not contribute to the photocurrent directly, as the lock-in technique was used. Therefore we concluded that the effect of the light bias is directly related to the trap filling and therefore hindering the transport of charge carriers.

The corresponding J-V curves are shown in Figure 5. As can be seen, the highest short circuit current density of 3.78 mA/cm^2 was achieved with **3**:[60]PCBM blends. For the **3**:[60]PCBM blend system we found the optimal blend ratio of 1:2. For this device, the PCE was found to be 0.4 %, which is, to our knowledge, one of the best results obtained for a cyanine based photovoltaic device.⁴

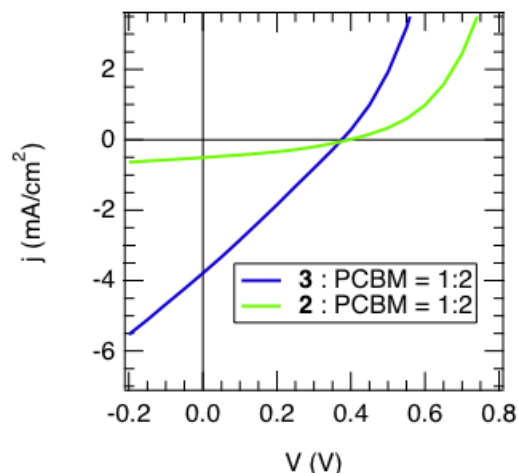


Figure 5. Current-voltage characteristics of BJJ solar cells fabricated with chromophores **3** (blue) and **2** (green) blended with [60]PCBM in 2:1 weight ratio under illumination. PEC (**3**) = 0.37 %; PCE (**2**) = 0.07 %.

In summary, a readily available new dye has been prepared by association of two NIR absorbing cyanine dyes, which exhibits a good solubility in organic solvents and outstanding light harvesting properties in the NIR region with giant extinction coefficients. The cyclic voltammetry measurements of **3** reveal an amphoteric redox character, preserving the typical features of their components (**1** and **2**). Furthermore, in preliminary experiments, we were able to demonstrate photovoltaic activity for chromophores **3** and **2** on BJJ solar cells using [60]PCBM as acceptor. The sun to power conversion efficiency (0.4 %) obtained for **3**:[60]PCBM reveals that the new dye is an appealing system for further studies as NIR light harvester for photovoltaics, for example in conjunctions with other materials or in tandem solar cells.

Acknowledgments. Authors thank the Délégation Generale des Armées (DGA) and IMDEA-Nanociencia for grants to PAB. D.R.'s work is funded by the DEPHOTEX project within the 7th framework programme of the EU. V.D.'s work at the ZAE Bayern is financed by the Bavarian Ministry of Economic Affairs, Infrastructure, Transport and Technology. This work has been supported by the European Science Foundation (05-SONS-FP-021 SOHYD), the MEC of Spain (CT2008-00795/BQU, and Consolider-Ingenio 2010C-07-25200, Nanociencia Molecular) and Comunidad de Madrid (P-PPQ-000225-0505). JLD thanks the MICINN for a Ramón y Cajal Fellowship, co-financed by the EU Social Funds.

Supporting Information Available Synthetic procedure, complete characterisations, device preparation. This material is available free of charge via the Internet at <http://pubs.acs.org>.