Cyanine-fullerene Dyad for Application in Broad Spectral Response Photovoltaic Devices

Fanshun Meng^a, Jianli Hua^a, Kongchang Chen^a, He Tian^{a,*}, Libero Zuppiroli^b, Frank Nüesch^{c,*}

^a Institute of Fine Chemicals, ECUST, Shanghai 200237, P. R. China

^b Institut des matériaux, EPFL, CH-1015 Lausanne, Switzerland

^c Laboratory for Functional Polymers, Empa, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

ABSTRACT

A novel cyanine-fullerene dyad is used as active layer in a heterostructure photovoltaic cell based on PEDOT and buckminsterfullerene C₆₀. The photocurrent spectrum of the device matches the absorption spectrum of the film and shows monochromatic quantum efficiencies of 5.5% and fill factors above 0.35 at white light irradiation intensities up to 310 mW/cm². By blending a long wavelength absorbing cyanine with the dyad, the photocurrent spectrum extends to 800 nm with appreciable monochromatic quantum efficiency. Sensitization by cyanine dyes demonstrates the possibility to achieve photovoltaic response in the near infrared.

1. INTRODUCTION

Organic photovoltaics can be dated back to 1960, when Meier et al. conceived a double layer device consisting of a merocyanine dye and crystal violet.¹ The photovoltaic effect observed in this heterojunction device was interpreted in terms of inorganic semiconductor p-n junctions. As a matter of fact the donor and acceptor like character of the dyes used in Meier's work are not doped materials in the sense of classical semiconductors. The ability of these materials to act as electron-donor or electron-acceptor in the photoinduced charge generation process is rather due to the position of the frontier molecular orbital energy levels of the dyes. In other words, it is the relative position of the reduction and oxidation potentials of the dyes that is relevant in this type of solar cell. Although the efficiency of these devices were fairly low, the concept of an organic heterointerface using molecules with different reduction and oxidation potentials, respectively, turned out to be extremely valuable. In 1986 Tang et al. reported on an organic heterojunction solar cell based on copper-phthalocyanine and a perylene derivative², which reached an efficiency of 1% at solar irradiation conditions of AM 1.5.

The heterojunction concept, however, bears an inherent weakness. When light is absorbed by the organic semiconductor, a tightly bound electron-hole pair (or exciton) is formed. This excited state is able to diffuse a distance of only a few nanometers up to 40 nm in the best cases.^{3,4} As a consequence, only those excitons that are generated close to the donor-acceptor interface can be dissociated and will be able to produce photocurrent. In order to absorb a major part of the solar irradiation, however, film thicknesses of about 100 nm are required. Among different approaches to solve this issue the "bulk heterojunction" concept was introduced.⁵ In a bulk heterojunction device, interpenetration of electron-donating and electron-accepting phases within the active film increases the charge-generating interface by several orders of magnitude leading to enhanced device performance. Ideally, the size of the nanostructure should be of the order of the exciton diffusion length, i.e. the distance an excited state is able to diffuse after having absorbed a photon. Efficiencies up to 3.85% were reported for solar cells based on P3HT, a polythiophene derivative and PCBM, a soluble C₆₀ derivative.⁶ More recent work even reached the 5% limit.⁷ At the same time, advances in bulk heterojunction devices made from small molecules such as copper phthalocyanine and C₆₀ reached an efficiency of 5.7%.⁸ In the search for materials with high exciton dissociation efficiency, molecules were developed, where donor and acceptor are covalently linked together. The active film is therefore not obtained by mixing two different components, but by using a

* Corresponding authors: tianhe@ecust.cn (He Tian); frank.nuesch@empa.ch (Frank Nüesch)

single donor-acceptor molecule. This concept may be termed as molecular heterojunction. Not only dyads but also polymers and oligomers were studied in this respect.⁹⁻¹⁴ Recent work by Imahori et al. shows that the efficiency based on optimized devices using porphyrin-fullerene dyads can reach 1%.¹⁵ It is clear that the performance of an organic solar cell not only relies on the exciton dissociation efficiency. The free positive and negative charges have to be transported through the thin film and collected at the electrodes. It has still to be shown, which of above strategies will prove most appropriate when considering charge transport and recombination issues.

Another issue to be solved regards light absorption in a broad spectral domain, particularly in the near infrared. A few works report on the sensitization of conjugated polymers by using small dye molecules.¹⁶⁻¹⁹ These works demonstrate the possibility to blend small molecules into a conjugated polymer in order to broaden the spectral photosensitivity of the devices. Still, efficient photocurrent generation in the near infrared domain is lacking. Cyanine dyes were developed at the beginning of the 20th century, mainly for the photographic industry. Numerous properties of cyanines make them most interesting for organic photovoltaic devices. In particular, cyanines owing a long polymethine chain are very efficient light absorbers in the near infrared. So far, there have been only few reports on photovoltaic properties of cyanine dyes as thin solid films^{13, 20-23} or dispersed in polymer matrices^{24, 25}.

Here the potential of cyanine-fullerene dyads used in thin film multilayer organic photovoltaic devices is presented. A carbocyanine dye with a long polymethine chain was taken to sensitize the dyad and thus broaden the photocurrent spectrum.

2. EXPERIMENTAL

The chemical structures of the materials used in this study are shown in Figure 1. Cyanine-fullerene dyad 1 and 3-butyl-2-[5-(3-butyl-1,3-dihydro-1,1-dimethyl-2H-benz[e]indol-2-ylidene)-1,3-pentadienyl]-1,1-dimethyl-1H-benz[e]indolium perchlorate (cyanine 2), were synthesized by us. PEDOT:PSS (Baytron) was supplied by H. C. Starck and was filtered using successive filter pore sizes of 5 μm , 1.2 μm and 0.8 μm . C₆₀ (purified) was supplied by SES Research Inc. and was used without further purification.

Figure 1. The chemical structures of the materials used in this study.

UV-Vis spectra were recorded on a Cary 50 Bio UV-Visible Spectrophotometer, while fluorescence spectra were measured using a FluoroMax-3. Cyclic voltammetry measurements were performed on an EG&G Instruments VersaStat II with a three-electrode cell in dichloromethane solution using tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. Glassy carbon and Pt were used as working electrode and counter electrode, respectively, while Ag/AgCl was taken as reference electrode. Typically, a scan rate of 100 mV/s was chosen for cyclic voltammetry measurements. The redox potentials E_{red} and E_{ox} related to the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), respectively, were determined by taking the middle value between the peaks of the oxidation and reduction wave. The energy level diagram in Figure 2 displays the energies of the frontier orbitals measured for the various compounds according to the physical scale. Here, the potential of our reference electrode was taken to be -4.71 eV vs. vacuum. The frontier orbital energy levels of C₆₀ and PEDOT:PSS were inferred from the literature.^{26, 27} Dashed lines for dyad 1 indicate the frontier orbital energy levels of the cyanine dye moiety, while the full line corresponds to the LUMO of the fulleropyrrolidine moiety of the dyad. Unfortunately, it was not possible to

determine the HOMO of the fulleropyrrolidine moiety under the conditions chosen for cyclic voltammetry. As we have shown, the energy levels of the dyad correspond precisely to the superposition of the free fulleropyrrolidine and cyanine dye, respectively.¹³

Figure 2. Frontier orbital energy levels of the different materials used in this work. For dyad 1 and cyanine 2 the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) were inferred from cyclic voltammetry measurements, while literature values^{26, 27} were taken for the levels of C₆₀ and PEDOT:PSS. In the case of dyad 1, the dashed lines indicate the frontier orbital levels of the cyanine moiety, while the full line corresponds to the LUMO of the fulleropyrrolidine moiety.¹³

Multilayer photovoltaic devices were fabricated by spin coating and thermal evaporation on indium tin oxide (ITO, AFC) glass substrates with a sheet resistance of 30 Ohm/square. The ITO substrates were first cleaned in ethanol, acetone and soap ultrasonic baths. The device architectures used to investigate the performance of the dyad as well as the sensitization of the latter are depicted in Figure 3. In the case of device I, the precleaned ITO glass was first coated with a layer of PEDOT:PSS and then dried for several hours at 80°C under vacuum. The cyanine-fullerene dyad (60 nm) was then spin-coated on top of PEDOT from chlorobenzene solution, heated to 35°C under high vacuum and cooled down to room temperature. To study the sensitization effect, a solution using a 50% molar ratio mixture of dyad 1 and cyanine 2 was used for spin-coating (device II). In the case of the blend, the film was considerably thicker than for the film made from the pure dyad. To provide a better device quality, a layer of C₆₀ (40 nm) was evaporated under high vacuum (<10⁻⁶ Torr). Finally, aluminium (75 nm) was evaporated under high vacuum to deposit the cathode. All film thicknesses were measured using a Tencor Alpha-Step 550 surface profilometer.

Figure 3. Device architectures used for multilayer heterojunction devices based on cyanine-fullerene dyad 1 as well as the blend with long chain cyanine 2.

The photocurrent action spectra were measured using monochromatic light from a JY HR 460 monochromator with a tungsten halogen lamp source. The intensity of the monochromatic light beam was measured by a Grasby Optronics 247 calibrated radiometric photodiode. The incident photon-to-current conversion efficiency (IPCE) is defined as the

number of electrons collected in the external circuit divided by the number of incident photons per second and was calculated according to:

$$IPCE (\%) = \frac{1240 J_{sc} (\mu A/cm^2)}{\lambda (nm) P_{in} (W/m^2)}$$

where J_{sc} is the short-circuit photocurrent density generated by the incident monochromatic light with wavelength λ and P_{in} is the incident light intensity.

Current-voltage characteristics were measured in nitrogen atmosphere using a Keithley 236 source-measure unit. A tungsten halogen lamp was used for white light irradiation from the ITO side. To vary the irradiation intensity, neutral density filters (ND1, ND2) were taken. The power conversion efficiency, η was calculated as:

$$\eta(\%) = \frac{FF \cdot V_{oc} \cdot J_{sc}}{P_{in}} \times 100\% , \text{ with } FF = \frac{(J \cdot V)_{max}}{V_{oc} \cdot J_{sc}}$$

where P_{in} is the incident light intensity, $(J \cdot V)_{max}$ is the maximum electrical power output of the device and FF is the fill factor.

3. RESULTS AND DISCUSSION

The absorption spectra of dyad 1 in solution and film are shown in Figure 4. In dichloromethane solution, the dyad shows a maximum absorption peak and a vibronic shoulder at 580 nm and 547 nm, respectively. The dyad also shows a weak absorption at about 703 nm (see inset to Figure 4), which corresponds to the characteristic absorption of fulleropyrrolidine. The film made of dyad 1 shows two obvious absorption peaks at 558 nm and 600 nm when spin coated from solution. Compared to the absorption in solution, the absorption peaks of the film are red-shifted by 20 nm and 11 nm, respectively. The relative intensity of the peaks in the film is also different from that in solution. The red shifted absorption and the modified peak intensity are due to solid state effects such as aggregation and polarization.

Figure 4 also shows the incident photon-to-current conversion efficiency (IPCE) spectrum of the device made from dyad 1. The IPCE spectrum is consistent with the absorption spectrum of the cyanine (sympatric relationship), indicating that charge carriers are generated within the bulk of the film. The increased photocurrent yield in the blue spectral region can be attributed to photo-carriers generated by C_{60} .⁴ The intensity of this shoulder depends on the biasing conditions and is probably related to ion displacement in the device. Device I reaches a maximum IPCE value of 6%, which is higher than what we obtained for previous cyanine/ C_{60} two layer devices.²¹ The small IPCE feature at about 750 nm is due to the small absorption of fulleropyrrolidine, since the cyanine is not absorbing in this region.

The current-voltage characteristics in the dark and under irradiation at different irradiation intensities are shown in Figure 5. A tungsten lamp was used as white light source. Device I shows nice diode behavior with a rectification ratio taken between -1V and 1V of about 300. The open circuit voltages (V_{oc}) of the device reaches 0.33V at an irradiation intensity of 310 mW/cm². The fill factors increase with decreasing irradiation intensity reaching 0.40 at an irradiation intensity of 0.31 mW/cm². At an irradiation intensity of 31 mW/cm², the energy conversion efficiency reaches 0.062 % ($V_{oc} = 0.275V$, $J_{sc} = 0.19 \text{ mA/cm}^2$, $FF = 0.37$). Since we used a tungsten lamp for white light irradiation, the blue and ultra-violet spectral range are underweighted as compared to the solar irradiation spectrum. Furthermore, no filters were used to cut off part of the infrared irradiation. Therefore, the energy conversion efficiency has to be considered as a lower limit.

Still, device I is not photosensitive to a broad domain of the solar irradiation spectrum, ranging from 650 nm to the near infrared. Therefore, we explored the possibility to introduce the long wavelength absorbing cyanine 2 as sensitizer for dyad 1. For this purpose we used an active film consisting of a blend of dyad 1 and cyanine 2 with a molar ratio of 50 %. The absorption spectrum of the blend is the combination of the separate dyes and is broadened as compared to the spectra in solution (see Figure 6). The spectrum of the blended film is clearly different from the one of the pure film based on dyad 1. This underlines the significant impact of molecular packing on the optical properties of cyanine dye films.

Figure 4. The IPCE spectra of device I, ITO/PEDOT/1/C₆₀/Al (full line), and the absorbance spectra of dyad 1 in dichloromethane (5 × 10⁻⁶ M, dotted line) and in the film (dashed line). The inset shows the enlarged absorbance spectrum of 1 in CH₂Cl₂ in the range of 600-800 nm.

Figure 5. Current-voltage characteristics under different white light irradiation intensities for device I. The inset to the figure shows the current-voltage characteristics in the dark.

To investigate the photovoltaic properties of the blend, the device architecture ITO/PEDOT/1:2/C₆₀/Al was chosen. Indeed, the broad IPCE spectrum extending from 350 nm to 800 nm demonstrates unambiguously that dyad 1 is sensitized by the long chain cyanine 2 (Figure 6). The IPCE values are rather high and exceed 4% over a large spectral domain. The photocurrent efficiency is more intense for the spectral domain corresponding to dyad 1 as compared to the domain corresponding to sensitizer 2. There are several reasons, which can account for this behavior. Different absorption, an additional IPCE contribution in the blue to green domain due to C₆₀ and a more efficient intramolecular photoinduced charge transfer in the case of dyad 1 as compared to intermolecular transfer from cyanine 2 to dyad 1 may be invoked.

Figure 6. The IPCE spectra of device II (ITO/PEDOT/1:2/C₆₀/Al, dot-dashed line) and the absorption spectra of dyad 1 (5×10^{-6} M, dashed line) and cyanine 2 (2×10^{-6} M, dotted line) in CH₂Cl₂ and in the spin-coated film (solid line).

The current-voltage characteristics of device II in the dark and under different white light irradiation intensities are shown in Figure 7. The open circuit voltage of device II increases with irradiation intensity from 0.33 V at 0.31 mW/cm² to 0.47 V at 310 mW/cm². The V_{oc} values are 0.15 V larger than for device I, independently of the light intensities. Additionally, the short circuit current of device II is larger than for device I, which is due to the much broader spectral sensitivity. However, the fill factor of device II is lower than the one of device I. We have ascribed this behavior to the dilution of cyanine 2 in dyad 1, which could have an effect on charge transport in these layers in a twofold manner. First, the main distance between fullerenes increases, which lowers the hopping mobility of electrons in the blend. Second, the difference between the HOMO energy levels of dyad 1 and cyanine 2 forces the holes to hop between cyanine 2 molecules that are blended in dyad 1 molecules. Finally, the film in device II is thicker than in device I. Under an irradiation intensity of 31 mW/cm², we obtain an energy conversion efficiency for device II of 0.13% (V_{oc} = 0.425 V, J_{sc} = 0.39 mA/cm², FF = 0.24), which is twice the efficiency of device I. At low irradiation intensity, the energy conversion efficiency exceeds 0.2 %.

Figure 7. Current-voltage characteristics under different white light irradiation intensities for Device II. The inset to the figure shows the current-voltage characteristics in the dark.

4. CONCLUSIONS

In conclusion, we have investigated a novel cyanine-fullerene dyad in a double layer heterojunction device structure and studied its photovoltaic properties. We have demonstrated that longer cyanines can be used to sensitize the dyad. This allows obtaining high photocurrent quantum efficiency throughout the whole visible domain and part of the near infrared. This possibility opens the avenue toward photovoltaic materials with tailored absorption properties and demonstrates the potential of cheap cyanine dyes for organic photovoltaics.

5. ACKNOWLEDGEMENT

We thank the NSFC (China) and Education Committee of Shanghai for financial support.

6. REFERENCES

1. Meier, H.; Haus, A., *Angewandte Chemie* **1960**, 72, (17), 631.
2. Tang, C. W., *Applied Physics Letters* **1986**, 48, (2), 183.
3. Alam, M. M.; Jenekhe, S. A., *Chemistry of Materials* **2004**, 16, (23), 4647.
4. Peumans, P.; Yakimov, A.; Forrest, S. R., *Journal of Applied Physics* **2003**, 93, (7), 3693.
5. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J., *Science* **1995**, 270, (5243), 1789.
6. Brabec, C. J., *Solar Energy Materials and Solar Cells* **2004**, 83, (2-3), 273.
7. Brabec, C. J.; Hauch, J. A.; Schilinsky, P.; Waldauf, C., *MRS Bulletin* **2005**, 30, (1), 50.
8. Xue, J. G.; Uchida, S.; Rand, B. P.; Forrest, S. R., *Applied Physics Letters* **2004**, 84, (16), 3013.

9. Eckert, J. F.; Nicoud, J. F.; Nierengarten, J. F.; Liu, S. G.; Echegoyen, L.; Barigelletti, F.; Armaroli, N.; Ouali, L.; Krasnikov, V.; Hadziioannou, G., *Journal of the American Chemical Society* **2000**, 122, (31), 7467.
10. Peeters, E.; van Hal, P. A.; Knol, J.; Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. J., *Journal of Physical Chemistry B* **2000**, 104, (44), 10174.
11. Ramos, A. M.; Rispens, M. T.; van Duren, J. K. J.; Hummelen, J. C.; Janssen, R. A. J., *Journal of the American Chemical Society* **2001**, 123, (27), 6714.
12. Zhang, F. L.; Svensson, M.; Andersson, M. R.; Maggini, M.; Bucella, S.; Menna, E.; Inganas, O., *Advanced Materials* **2001**, 13, (24), 1871.
13. Meng, F. S.; Hua, J. L.; Chen, K. C.; Tian, H.; Zuppiroli, L.; Nuesch, F., *Journal of Materials Chemistry* **2005**, 15, (9), 979.
14. Cravino, A.; Zerza, G.; Maggini, M.; Bucella, S.; Svensson, M.; Andersson, M. R.; Neugebauer, H.; Brabec, C. J.; Sariciftci, N. S., *Monatshefte für Chemie* **2003**, 134, (4), 519.
15. Imahori, H.; Fukuzumi, S., *Advanced Functional Materials* **2004**, 14, (6), 525.
16. Mühlbacher, D.; Brabec, C. J.; Sariciftci, N. S.; Kotov, B. V.; Berendyaev, V. I.; Rumyantsev, B. M.; Hummelen, J. C., *Synthetic Metals* **2001**, 121, (1-3), 1609.
17. Sharma, G. D.; Sharma, S. K.; Roy, M. S., *Thin Solid Films* **2004**, 468, (1-2), 208.
18. Feng, W.; Fujii, A.; Lee, S.; Wu, H.; Yoshino, K., *Journal of Applied Physics* **2000**, 88, (12), 7120.
19. Winder, C.; Matt, G.; Hummelen, J. C.; Janssen, R. A. J.; Sariciftci, N. S.; Brabec, C. J., *Thin Solid Films* **2002**, 403, 373.
20. Nuesch, F.; Faes, A.; Zuppiroli, L.; Meng, F. S.; Chen, K. C.; Tian, H., *Journal of Materials Science* **2005**, 40, (6), 1353.
21. Meng, F. S.; Chen, K. C.; Tian, H.; Zuppiroli, L.; Nuesch, F., *Applied Physics Letters* **2003**, 82, (21), 3788.
22. Tameev, A. R.; Vannikov, A. V.; Schoo, H. F. M., *Thin Solid Films* **2004**, 451-52, 109.
23. Ishchenko, A.; Derevyanko, N.; Piryatinskii, Y. P.; Verbitsky, A.; Filonenko, D.; Studzinskiy, S., *Materials Science* **2002**, 20, (4), 5.
24. Kohn, F.; Hofkens, J.; Wiesler, U. M.; Cotlet, M.; van der Auweraer, M.; Mullen, K.; De Schryver, F. C., *Chemistry-a European Journal* **2001**, 7, (19), 4126.
25. Tan, C. Y.; Alas, E.; Muller, J. G.; Pinto, M. R.; Kleiman, V. D.; Schanze, K. S., *Journal of the American Chemical Society* **2004**, 126, (42), 13685.
26. Rogero, C.; Pascual, J. I.; Gomez-Herrero, J.; Baro, A. M., *Journal of Chemical Physics* **2002**, 116, (2), 832.
27. Petr, A.; Zhang, F.; Peisert, H.; Knupfer, M.; Dunsch, L., *Chemical Physics Letters* **2004**, 385, (1-2), 140.