

# Bulk heterojunction organic solar cells based on merocyanine colorants†

Nils M. Kronenberg,<sup>a</sup> Manuela Deppisch,<sup>b</sup> Frank Würthner,<sup>\*b</sup> Hans W. A. Lademann,<sup>a</sup> Kaja Deing<sup>a</sup> and Klaus Meerholz<sup>\*a</sup>

Received (in Cambridge, UK) 1st August 2008, Accepted 11th September 2008

First published as an Advance Article on the web 6th November 2008

DOI: 10.1039/b813341g

**Traditional low-molecular weight colorants that are widely applied in textile coloration, for printing purposes and nonlinear optics, now afford bulk heterojunction solar cells in combination with soluble C<sub>60</sub> fullerene derivative PCBM with power conversion efficiencies up to 1.7% under standard solar radiation.**

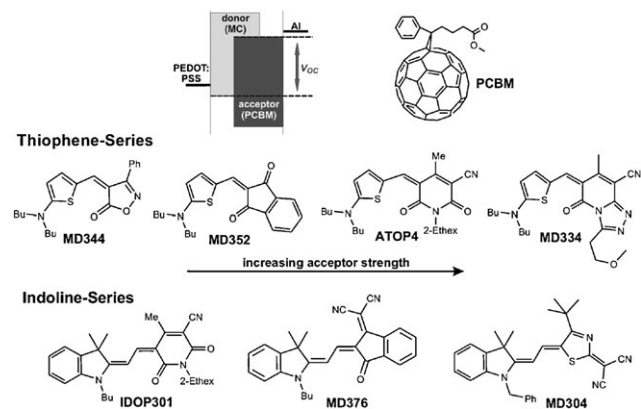
Bulk heterojunction (BHJ) organic solar cells have attracted a great deal of attention in view of their potential for the fabrication of low-cost and flexible photovoltaic devices.<sup>1</sup> BHJ solar cells can be deposited from solution, *e.g.* by a printing process, and are thus compatible with low-cost roll-to-roll fabrication technology, and they perform with a power conversion efficiency (*PCE*) from solar light into electrical energy of up to about 5%.<sup>2</sup> The active layer of BHJ solar cells is composed of interpenetrating networks of electron donor and acceptor domains, which are formed during the deposition/drying process. Currently, the favoured materials for BHJ solar cells are composites of *n*-type semiconducting fullerenes with *p*-type semiconducting polymers such as poly(3-hexylthiophene) (P3HT). These composites have the advantage of good charge carrier mobilities but suffer from relatively large band gaps and low absorption coefficients, hence they lack ideal absorption characteristics for solar radiation.

Merocyanine (MC) dyes are an important class of traditional colorants with widely tunable absorption properties that are manufactured on a technical scale for mass applications, *e.g.* textile coloration.<sup>3</sup> Owing to their high absorption coefficients, polarizabilities and dipole moments, merocyanine dyes are also a privileged class of functional dyes for nonlinear optics, photorefractive materials, and other high technology applications.<sup>4,5</sup> In recent years, merocyanine dyes have also been recognized as very promising substitutes for ruthenium complex dyes in Graetzel-type dye-sensitized solar cells.<sup>6</sup> As for the above-mentioned applications, also in the latter case the high tinctorial strength and the conveniently tunable absorption wavelength are the most appreciable advantages of merocyanine dyes. In the past, we developed MC dyes including ATOP and IDOP derivatives (Fig. 1) for photorefractive applications.<sup>7</sup> Here we report our recent discovery that simple solution-processed BHJ cells based on blends of

MC dyes with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) show remarkable *PCEs* of up to 1.7% under standard AM 1.5 solar radiation. To the best of our knowledge, this represents the highest value reported for a BHJ solar cell based on solution-processed small molecules.<sup>8</sup>

We have investigated here two series of MC dyes bearing either a 2-aminothiophene or an indoline electron donor group and various electron acceptor groups connected by a mono- or dimethine chain (chemical structures are depicted in Fig. 1). All these dyes exhibit intense absorption bands ( $\epsilon$  up to  $1.4 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>7</sup> at different wavelengths in the visible spectral region (see Fig. SI-1 in supplementary information†). Dye MD344 appears orange, ATOP4 and IDOP301 magenta, MD376 violet, and MD304 is deep blue. These MC dyes are applied in the present study as *p*-type semiconducting components in solution-processed BHJ solar cells in combination with the soluble fullerene derivative PCBM as *n*-type semiconductor (see Fig. 1).

For each individual dye, a series of BHJ devices with the general structure ITO/PEDOT:PSS (40 nm)/MC:PCBM/Al (100 nm) were fabricated by varying the layer thickness, for which an optimum was found to be in the range of 50 nm, and the MC:PCBM content. We discuss in more detail the devices containing MC dye ATOP4, which has been the most successful photorefractive dye in our earlier work due to its outstanding glass formation properties.<sup>7c</sup> In Fig. 2 the open-circuit voltage ( $V_{OC}$ ), the short-current density ( $J_{SC}$ ), the fill factor (*FF*), and the *PCE*, the latter being the product of  $V_{OC}$ ,  $J_{SC}$  and *FF* divided by the power of the incident light, are plotted as a function of the PCBM content in the mixture of



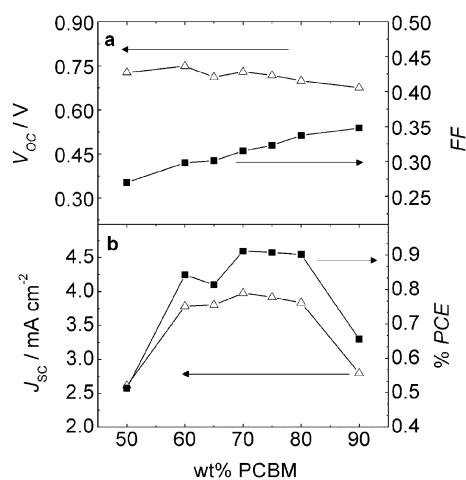
**Fig. 1** Top: Illustration of the energetic situation in BHJ solar cells and the chemical structure of the fullerene derivative PCBM. Bottom: Chemical structures of the investigated merocyanine dyes (2-Ethex = 2-ethylhexyl).

<sup>a</sup> Universität zu Köln, Department of Chemistry, Luxemburger Str. 116, D-50939 Köln, Germany. E-mail: klaus.meerholz@uni-koeln.de

<sup>b</sup> Universität Würzburg, Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Am Hubland D-97074 Würzburg, Germany.

E-mail: wuerthner@chemie.uni-wuerzburg.de

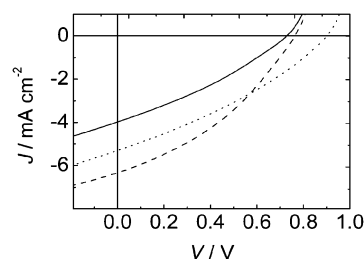
† Electronic supplementary information (ESI) available: Experimental details including synthesis, spectroscopy, device fabrication, Kelvin-probe measurements, IV and EQE curves. See DOI: 10.1039/b813341g



**Fig. 2** (a) Dependence of  $V_{OC}$  ( $\Delta$ ) and  $FF$  ( $\blacksquare$ ) and (b)  $J_{SC}$  ( $\Delta$ ) and  $PCE$  ( $\blacksquare$ ) on the PCBM content in ATOP4:PCBM solar cells.

the BHJ layer. Remarkably, the photovoltaic performance of these blends exhibits little change upon variation of the ATOP4 : PCBM ratio. Thus,  $V_{OC}$  remains almost unchanged and a broad maximum is observed for 60–80 wt% PCBM for the  $J_{SC}$  curve. The overall behaviour of the  $J_{SC}$ -characteristics can be attributed to two counteracting effects: On the one hand, an increase of the MC portion in the active layer enhances the numbers of absorbed photons since the absorption of the MC dye is much stronger than that of PCBM (see Fig. S1 in ESI†) and, on the other hand, the transport of photo-generated charges through the active layer seems to improve with the increasing PCBM content. The significant (20%) increase of the  $FF$  (from 0.27 to 0.35; Fig. 2) with increasing PCBM content (from 50 to 90 wt%) can be taken as an indication for this assumption. In BHJ solar cells, the  $FF$  is related to the series resistance of the active layer, which reduces as the charge mobility increases.<sup>9</sup>

A summary of all investigated cells at an optimized MC : PCBM ratio of 70–80 wt% of PCBM is given in Table 1 and the  $JV$ -characteristics of the three best cells are presented in Fig. 3. The largest open-circuit voltage  $V_{OC}$  (0.9 V) was measured for a cell containing the violet dye MD376. This is remarkable because the absorption maximum of this dye is located at rather long wavelengths. Thus, MCs can be easily tuned for absorption at longer wavelength and high  $V_{OC}$  values as well by simple attachment of strongly electron-withdrawing acceptor heterocycles that



**Fig. 3**  $JV$ -characteristics of ATOP4:PCBM (solid line), MD304:PCBM (dashed line) (both 70 wt% PCBM) and MD376:PCBM (dotted line) (75 wt% PCBM) solar cells measured under AM 1.5 illumination.

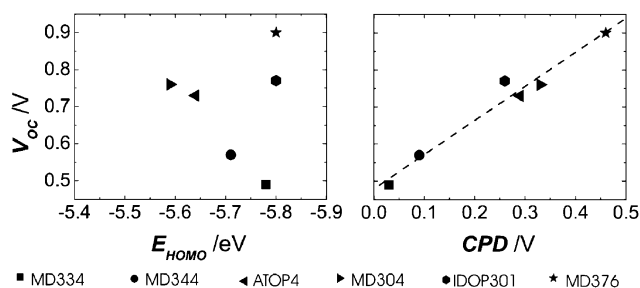
lower the dyes' HOMO energy. Although it has a slightly lower  $V_{OC}$  value (0.76 V), the highest  $PCE$  of 1.74% was achieved for the blue dye MD304 due to a higher  $J_{SC}$  value ( $6.3 \text{ mA cm}^{-2}$ ) enabled by a better absorption profile for solar radiation ( $\lambda_{max} = 649 \text{ nm}$ ). Notably, solar cells based on the  $p$ -type semiconducting polymers P3HT and OC<sub>1</sub>C<sub>10</sub>-PPV with comparable layer thicknesses exhibit almost the same  $PCEs$  (<2%).<sup>10</sup> The  $FF$  of all MC solar cells are rather small ( $\sim 0.3$ ). This, together with the fact that optimum devices are found for comparatively thin active layers, is an indication of only moderate charge transport inside the solar cells. No significant leakage currents were detected in the dark current of our devices (see ESI, Fig. S2†). It is also noteworthy that these MC:PCBM solar cells show decent external quantum efficiencies ( $EQE$ ) up to 50% at the peak absorption wavelengths of the respective MC dyes (see ESI, Fig. S3†).

The present dye series offers a unique opportunity for the elucidation of structure–property relationships. For organic BHJ materials, the general perception is that  $V_{OC}$  reflects the energy difference between the HOMO of the donor and the LUMO of the acceptor<sup>11</sup> (see Fig. 1). Thus, for one given acceptor (here PCBM) a linear relationship between  $V_{OC}$  and the HOMO energy ( $E_{HOMO}$ ) with a slope of unity is expected.<sup>12</sup> In Fig. 4,  $V_{OC}$  is plotted as a function of the  $E_{HOMO}$  of the MC dye as determined by cyclic voltammetry. As can be seen, no correlation is given for the data. The latter can be explained by the fact that electrochemical studies are carried out for dissolved molecules in solution, while tightly packed  $\pi$ - $\pi$ -aggregates are formed for these dyes in the solid state,<sup>13</sup> thus we assume that the redox potentials of individual molecules in solution do not properly reflect the energetic situation in a solid material and hence in the actual device. This leads to an alteration of the frontier orbital energies of

**Table 1** Electronic properties of the MC dyes and best performance of the investigated MC:PCBM BHJ solar cells with Al top electrode

MC dye	$E_{HOMO}^a/eV$	$\lambda_{max}^b/nm$	$E_{LUMO}^c/eV$	wt% PCBM	$V_{OC}/V$	$J_{SC}/\text{mA cm}^{-2}$	$FF$	% $PCE$
MD344	-5.71	515	-3.31	80	0.57	2.8	0.28	0.44
MD352	-5.58	530	-3.24	70	0.63	2.9	0.27	0.49
MD334	-5.78	563	-3.58	75	0.49	3.1	0.29	0.43
ATOP4	-5.64	554	-3.40	70	0.73	4.0	0.32	0.91
IDOP301	-5.80	544	-3.52	70	0.77	4.0	0.29	0.87
MD376	-5.80	607	-3.76	75	0.90	5.3	0.32	1.54
MD304	-5.59	649	-3.68	70	0.76	6.3	0.36	1.74

<sup>a</sup> Determined by cyclic voltammetry calibrated against the ferrocene/ferrocenium redox couple ( $-5.15 \text{ eV}$ ). <sup>b</sup> UV-Vis measurements of a thin film. <sup>c</sup>  $E_{LUMO} = E_{HOMO} - (hc/\lambda_{max})$ .



**Fig. 4** Dependence of the open-circuit voltage  $V_{OC}$  of the different MC:PCBM solar cells (see Table 1) on the electronic properties of the MC dyes: (left) dependence on HOMO energy determined from cyclic voltammetry in solution (see Table 1); (right) dependence on  $CPD$  determined from thin film by Kelvin probe. The dashed line shows the linear fit of the data.

dyes in composite compared to those of isolated molecular species, specifically to an increase of  $E_{HOMO}$ .

To determine this solid-state property experimentally, we have measured the contact potential difference ( $CPD$ ) between thin films of the various MC dyes and a vibrating gold grid by Kelvin probe. By plotting  $V_{OC}$  as a function of  $CPD$  (Fig. 4, right panel), we obtained a linear curve with a slope of near unity, in agreement with theoretical expectations. Thus, the difference between the HOMO energy determined for single molecules in solution and the  $CPD$  determined for a solid film containing aggregated dye molecules can be considered as a qualitative measure for the dye–dye interactions in the solid state. A more detailed investigation on this subject is currently under way.

By considering the present two series of MC dyes, the favourable trend can be recognised that an increase of the acceptor strength shifts the absorption towards the NIR, and concurrently  $V_{OC}$  increases (Table 1). Thus, MC dyes absorbing at rather long wavelengths can provide exceptionally large  $V_{OC}$  values because they exhibit a low HOMO energy. In addition, the chemical stability of such MC dyes towards oxidation is enhanced. For the dyes with the longest absorption wavelengths,  $J_{SC}$  takes on the largest values which can be attributed to the best overlap with the solar spectrum.

In conclusion, we have introduced traditional low-molecular weight merocyanine colorants as  $p$ -type semiconducting components for solution-processible BHJ solar cells with the fullerene-based acceptor PCBM. For several merocyanine dyes, power conversion efficiencies in excess of 1% were achieved. The highest efficiency of 1.74% under standard AM 1.5 conditions was obtained for the indoline-based dye MD304. Our best solar cells show performances similar to those of P3HT solar cells for films of similar thickness. Because the absorption, redox, packing and film forming properties of MC dyes can be easily tuned, we anticipate significant advancement in the near future for this new class of BHJ cells. The tunability of the optical and redox properties of MC dyes will also be very beneficial for the fabrication of tandem devices.

We gratefully acknowledge financial support by DFG (priority programme “Elementary Processes of Organic Photovoltaics”), Fonds der Chemischen Industrie, and BASF SE.

## Notes and references

- (a) G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789–1791; (b) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature*, 1995, **376**, 498–500.
- (a) W. Ma, C. Yang, X. Gong, K. Lee and A. J. Heeger, *Adv. Funct. Mater.*, 2005, **15**, 1617–1622; (b) G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 864–868; (c) M. Reyes-Reyes, K. Kim and D. L. Carroll, *Appl. Phys. Lett.*, 2005, **87**, 083506-1–083506-3; (d) J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moes, A. J. Heeger and G. C. Bazan, *Nat. Mater.*, 2007, **6**, 497–500.
- H. Zollinger, *Color Chemistry*, Wiley-Vch., Weinheim, 3rd edn, 2003.
- (a) M. Blanchard-Desce, *C. R. Phys.*, 2002, **3**, 439–448; (b) F. Würthner, R. Wortmann and K. Meerholz, *ChemPhysChem*, 2002, **3**, 17–31; (c) T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays and A. Persoons, *J. Mater. Chem.*, 1997, **7**, 2175–2189; (d) S. R. Marder and J. W. Perry, *Adv. Mater. (Weinheim, Ger.)*, 1993, **5**, 804–815.
- P. Gregory, *High Technology Application of Organic Colorants*, Plenum, New York, 1991.
- (a) R. Chen, X. Yang, H. Tian, X. Wang, A. Hagfeldt and L. Sun, *Chem. Mater.*, 2007, **19**, 4007–4015; (b) D. P. Hagberg, T. Edvinsson, T. Mariando, G. Boschloo, A. Hagfeldt and L. Sun, *Chem. Commun.*, 2006, 2245–2247; (c) T. Horiuchi, H. Miura and S. Uchida, *Chem. Commun.*, 2003, 3036–3037; (d) S. Li, K. Jiang, K. Shao and L. Yang, *Chem. Commun.*, 2006, 2792–2794; (e) S. Ito, S. M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M. K. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida and M. Grätzel, *Adv. Mater. (Weinheim, Ger.)*, 2006, **18**, 1202–1205; (f) K. Sayama, K. Hara, N. Mori, M. Satsuki, S. Suga, S. Tsukagoshi, Y. Abe, H. Sugihara and H. Arakawa, *Chem. Commun.*, 2000, 1173–1174.
- (a) F. Würthner, C. Thalacker, R. Matschiner, K. Lukaszuk and R. Wortmann, *Chem. Commun.*, 1998, 1739–1740; (b) S. Beckmann, K.-H. Eitzbach, P. Krämer, K. Lukaszuk, R. Matschiner, A. J. Schmidt, P. Schuhmacher, R. Sens, G. Seybold, R. Wortmann and F. Würthner, *Adv. Mater. (Weinheim, Ger.)*, 1999, **11**, 536–541; (c) F. Würthner, S. Yao, J. Schilling, R. Wortmann, M. Redi-Abshiro, E. Mecher, F. Gallego-Gomez and K. Meerholz, *J. Am. Chem. Soc.*, 2001, **123**, 2810–2824.
- Whilst our approach starts from classical colorants with outstanding absorption but probably limited charge transport properties, previous work on small molecule based BHJ cells by others has focused on blends of PCBM and  $p$ -type organic semiconductors that exhibit good charge carrier transport but less favourable absorption properties: (a) M. T. Lloyd, A. C. Mayer, S. Subramanian, D. A. Mourey, D. J. Herman, A. V. Bapat, J. E. Anthony and G. G. Malliaras, *J. Am. Chem. Soc.*, 2007, **129**, 9144–9149; (b) J. Roncali, P. Frère, P. Blanchard, R. de Bettignies, M. Turbiez, S. Roquet, P. Leriche and Y. Nicolas, *Thin Solid Films*, 2006, **511**, 567–575; (c) X. Sun, Y. Zhou, W. Wu, Y. Liu, W. Tian, G. Yu, W. Qiu, S. Chen and D. Zhu, *J. Phys. Chem. B*, 2006, **110**, 7702–7707; (d) S. Roquet, A. Cravino, P. Leriche, O. Alévêque, P. Frère and J. Roncali, *J. Am. Chem. Soc.*, 2006, **128**, 3459–3466; (e) L. Schmidt-Mende, A. Fichtenkötter, K. Müllen, E. Moons, R. H. Friend and J. D. MacKenzie, *Science*, 2001, **293**, 1119–1122; (f) L. Valentini, D. Bagnis, A. Marrocchi, M. Seri, A. Taticchi and J. M. Kenny, *Chem. Mater.*, 2008, **20**, 32–34.
- P. Schilinsky, C. Waldauf, J. Hauch and C. J. Brabec, *J. Appl. Phys.*, 2004, **95**, 2816–2819.
- A. J. Moule, J. B. Bonekamp and K. Meerholz, *J. Appl. Phys.*, 2006, **100**, 094503-1–094503-7.
- (a) M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. L. Brabec, *Adv. Mater. (Weinheim, Ger.)*, 2006, **18**, 789–794; (b) V. D. Mihailetschi, P. W. M. Blom, J. C. Hummelen and M. T. Rispens, *J. Appl. Phys.*, 2003, **94**, 6849–6854.
- For a similar analysis with a series of fullerene derivatives, see: C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 374–380.
- F. Würthner, S. Yao, T. Debaerdemaeker and R. Wortmann, *J. Am. Chem. Soc.*, 2002, **124**, 9431–9447.