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Near-Infrared Absorbing Merocyanine Dyes for Bulk Heterojunction Solar Cells[†]

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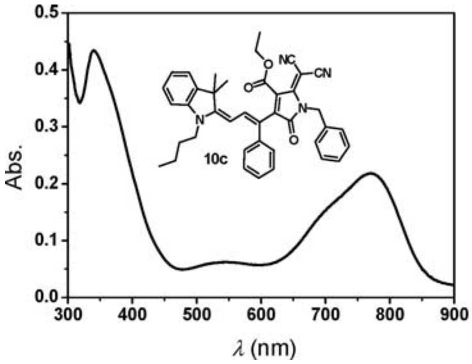
ABSTRACT



A series of near-infrared absorbing merocyanine dyes bearing the strong electron-accepting 2-oxo-5-dicyanomethylene-pyrrolidine unit was synthesized and applied in combination with $PC_{61}BM$ and $PC_{71}BM$ in solution-processed photoactive layers of bulk heterojunction solar cells, exhibiting a remarkable performance range with power conversion efficiencies from 0.01% to 1.00%.

Merocyanine dyes represent a traditional class of chromophores with a general structural feature consisting of an electron-donating and an electron-accepting moiety that are connected by a polymethine chain. Their unique dipolar and polarizability properties enable applications in nonlinear optics and as photorefractive materials.[1] The absorption wavelengths as well as band gaps of these chromophores are easily tunable by variation of the chain length and the donor and acceptor groups.[1] These features in combination with their high tinctorial strengths add up to materials well-suited for implementation in organic photovoltaics. Recently, we have shown the application of merocyanine dyes as electron donors in solution-processed and vapor-deposited bulk heterojunction (BHJ) organic solar cells in combination with a fullerene as an acceptor.[2] Moreover, merocyanine dyes have been used in dye-sensitized solar cells (also called Graetzel cells).[3]

In the field of solution-processed BHJ organic solar cells, great attention has been paid particularly to the combination of the polymeric donor poly(3-hexylthiophene) (P3HT) and the electron-accepting fullerene derivative $PC_{61}BM$, with enormous research efforts on the optimization of structural features such as regioregularity of the P3HT polymer and the morphology of the active BHJ layer by post-treatment of the devices.[4]

More recently, in order to improve the absorption properties and harvest more photons, low-bandgap polymers have been developed, and very high power conversion efficiencies (PCEs) exceeding 7% have been achieved.[5] Another recent strategy toward BHJ solar cells is based on substitution of the polymeric donor by small molecules whose monodispersity enables facile synthesis and convenient optimization of the absorption and redox properties. In the past years,

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[†] Dedicated to Prof. Karlheinz Drauz on the occasion of his 60th birthday.

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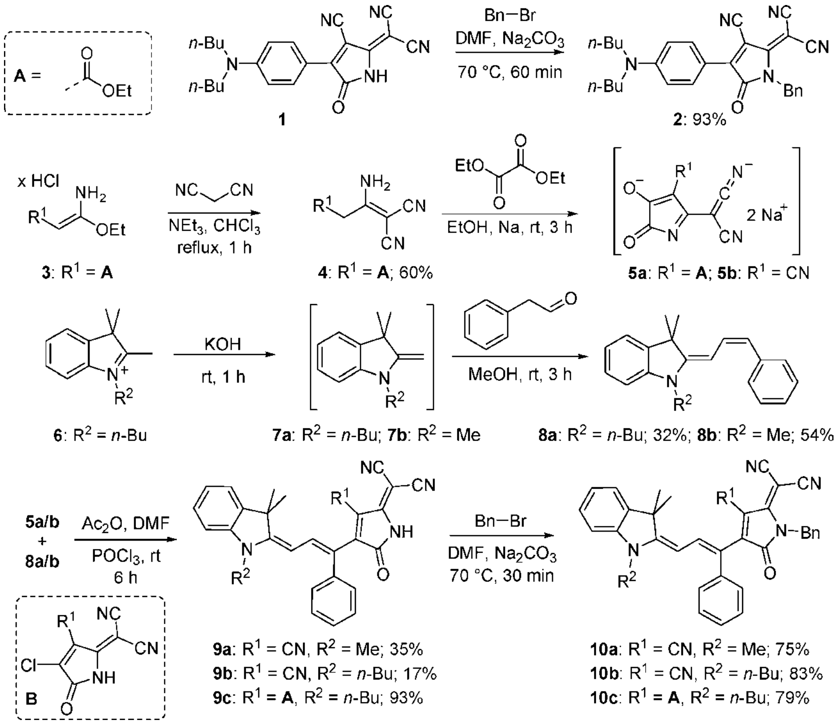
Scheme 1. Syntheses of Merocyanine Dyes **2** and **10a−c**



increasingly promising results were reported with various types of dyes such as oligothiophene,[6] squaraine,[7] cyanine,[8] BODIPY,[9] diketopyrrolopyrrole (DPP),[10] indigoid,[11] acene,[12] and dibenzo[*b*,*def*]chrysene,[13] leading to PCEs up to 4.4%.[10a]

The photon flux of sunlight displays a maximum at ~690 nm (1.8 eV).[14] Thus, to achieve an ideal spectral overlap of the absorption of solar cells with the solar irradiation, materials with absorption reaching in the near-infrared (NIR) region are required.[15] Moreover, photovoltaics with NIR absorption render transparent solar cells for sun shading and solar power window applications possible.[16] Here, we report the synthesis and characterization of the optical, electrochemical, and photovoltaic properties of a series of new merocyanine (MC) dyes containing the strong electron-acceptor moiety 2-oxo-5-dicyanomethylene-pyrrolidine **5** (Scheme 1), which imparts absorption of the MC dyes in the NIR.[17] Application of the present merocyanine chromophores in solution-processed solar cells based on blends with PC$_{71}$BM yielded devices with PCEs of up to 1%.

The reference chromophore **2** consisting of an aniline donor and the heterocyclic acceptor that are directly connected was synthesized by the alkylation of **1**[18] with benzyl bromide in a high yield of 93% (Scheme 1). The synthesis of more extended merocyanine dyes **10a−c** involves three major sequences: the syntheses of the acceptor and the donor moieties and the condensation of these two moieties into the desired chromophores. The synthesis of the acceptor **5a** starts with the reaction of enolate **3** with malononitrile in the presence of triethylamine as a base to afford the intermediate **4** in 60% yield.[19] The subsequent condensation reaction of **4** with diethyl oxalate under basic condition results in the acceptor **5a**,[20] which exhibits poor solubility and thus was used in the further reaction as obtained. The donor component **8a** was built up by deprotonation of indolenine **6** ("Fischer base")[21] followed by condensation with phenylacetaldehyde in methanol.[22] The two-step reaction afforded **8a** in a moderate yield of 32%. A higher yield of 54% was obtained for the methyl derivative **8b** by condensation of the commercially available indolenine **7b** with phenylacetaldehyde.[22] The coupling of the donor and acceptor moieties comprises the in situ generation of component **B** by chlorination and protonation of dianionic acceptor **5**, followed by addition of component **8** to **B** leading to elimination of 1 equiv HCl to result in chromophores **9a−c**. A high yield of 93% was obtained in the case of **9c**, whereas the dyes **9a**,**b** resulting from acceptor **5b**[20] were obtained in significantly lower yields of

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17−35%. The final step involving the alkylation of the secondary amine **9** with benzyl bromide afforded the dyes **10a**−**c** in 79−83% yield.

Figure 1 displays the UV−vis spectra and the cyclic voltammograms of reference **2** and merocyanine dye **10a** in CH_2Cl_2. Further data along with those of dyes **10b**,**c** are listed in Table 1. The HOMO levels were derived from the half-wave oxidation potentials determined by cyclic voltammetry (CV), whereas the LUMO energies are calculated by the equation $E_{LUMO} = E_{HOMO} - (hc/\lambda_{max})$.

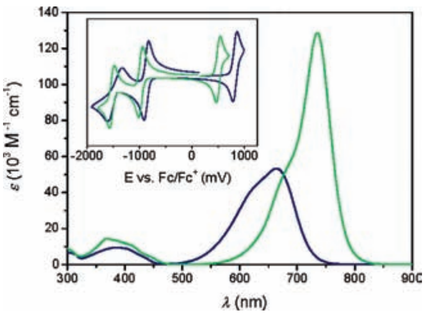

Figure 1. UV−vis absorption spectra (2×10^{-5} M, CH_2Cl_2) and cyclic voltammograms (inset, CH_2Cl_2, calibrated against Fc/Fc$^+$ couple) of **2** (blue line) and **10a** (green line).

All of these dyes possess one oxidation and two reduction waves, both processes being fully reversible (Figure 1).

Table 1. Optical and Electrochemical Properties of **2** and **10a**−**c** and Photovoltaic Characteristics of BHJ Solar Cell Devices Containing a MC Dye:$PC_{61}BM$ Blend

MC dye	λ_{max} (nm)[a]	ε (M^{-1} cm^{-1})[a]	λ_{max} (nm)[b]	E_{HOMO} (eV)[c]	E_{LUMO} (eV)[d]	wt % PCBM	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
2	664	53300	640	−5.98	−4.11	70	0.55	0.05	0.31	0.01
10a	735	128600	783	−5.65	−3.96	70	0.71	2.28	0.28	0.46
10b	738	121800	783	−5.66	−3.98	75	0.74	2.00	0.29	0.43
10c	736	87400	771	−5.48	−3.80	75	0.64	3.33	0.31	0.66
10c[e]	736	87400	771	−5.48	−3.80	75	0.66	4.83	0.31	1.00

[a] UV−vis measurements in CH_2Cl_2. [b] UV−vis measurements of a thin film of the blend. [c] From CV measurements ($E_{1/2}^{ox}$) in CH_2Cl_2 calibrated against ferrocene/ferrocenium couple (Fc/Fc$^+$, −5.15 eV) as internal standard. [d] $E_{LUMO} = E_{HOMO} - (hc/\lambda_{max})$. [e] Solar cell with $PC_{71}BM$ as acceptor.

Chromophore **2** exhibits an absorption maximum at 664 nm with a molar extinction coefficient of 53 300 M^{-1} cm^{-1}. The rather low tinctorial strength and the broad absorption band indicate a more polyene-like character of this dye.[23] Notably, **2** shows very low-lying HOMO and LUMO levels at −5.98 and −4.11 eV, respectively. Dyes **10a** and **10b** with extended π-systems differ only by the alkyl substituent (Me vs *n*-Bu) at the donor unit and show a bathochromic shift of the absorption maxima of 70 nm compared with that of **2** and sharp cyanine-like absorption bands with high extinction coefficients of 121 800−128 600 M^{-1} cm^{-1}. Their HOMO levels range at −5.65 eV, and their LUMOs are situated at energies around −3.96 eV. Replacement of the cyano substituent R^1 at the oxo-pyrrolidino acceptor unit by an ethyl ester group in compound **10c** results in a shift of both HOMO and LUMO levels by 0.18 eV to higher energies compared to those of **10a**,**b**, but without any alteration of the absorption features.

The presented dyes were characterized in solution-processed BHJ solar cell devices with the general structure ITO/PEDOT:PSS (∼40 nm)/dye:$PC_{61}BM$ (25/75% by weight; ∼ 50 nm)/Al (120 nm). The details for device fabrication are given in Supporting Information. The photovoltaic characteristics of the solar cells are presented in Table 1.

For the device of reference **2**, a very low PCE of 0.01% was observed. This low efficiency arises from the small short-circuit photocurrent (J_{SC}) of 50 μA cm^{-2}, which is very likely caused by a lack of driving force for charge-carrier separation owing to the low LUMO level of −4.11 eV. The latter energy level is not sufficiently high for electron injection into the LUMO level of the PCBM acceptor (−4.08 eV, Figure 2).

The introduction of the indolenine donor group in merocyanine dyes leads to the extension of the π-system and entailed better matched HOMO levels for the dyes **10a**−**c**. Moreover, these dyes

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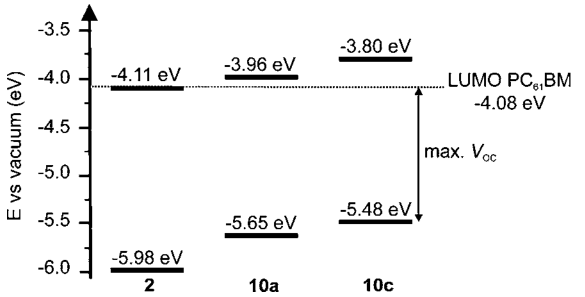

Figure 2. Illustration of the HOMO and LUMO energies of dyes **2**, **10a**, and **10c** in comparison with the LUMO energy of PC$_{61}$BM.

afforded solar cells with absorption in the NIR region (Figure S2 in Supporting Information), thus enabling the production of devices that are transparent in the visible range (Figure 3).

Figure 3. Picture of a transparent device containing a blend of **10c**:PC$_{61}$BM (25/75 wt %) lying on the seal of the Universität Würzburg.

The devices built with **10a**−**c** exhibit appreciable open-circuit voltage (V_{OC}) values of 0.64−0.74 V, in particular, if we consider their low bandgap. The observed fill factors (FF) of 0.3 are typical for solution-processed MC-based solar cells.[2] Devices containing **10a** and **10b**, whose chromophores solely differ by the side chains, displayed similar J_{SC} values of 2.28 and 2.00 mA cm^{-2}, respectively, and PCEs of 0.43−0.46%, though their LUMO energies are still quite similar to the LUMO of PCBM, imparting a driving force of only ~0.1 eV for electron transfer according to the solution data (which may, however, shift in the solid state).[2a] In the literature, an offset of 0.3−0.4 eV is proposed as trade-off between sufficient driving force and minimized energy loss upon charge injection.[24]

To increase the LUMO energy level, we have synthesized dye **10c**, which bears a slightly weaker acceptor moiety owing to the replacement of one cyano group by an ester group. Actually, both frontier molecular orbitals of **10c** are shifted to higher energies by 0.18 eV compared to those of dyes **10a**,**b** (Table 1).

While the higher-lying HOMO of dye **10c** leads to a lowering of V_{OC} of the respective solar cell (0.64 V) relative to the cells fabricated with **10a** (0.71 V), the increased LUMO confers a stronger driving force for electron transfer from the MC to the fullerene and, thus, enhances the J_{SC} values by 46%, resulting in an overall performance of 0.7% for **10c**.

The high symmetry of PC$_{61}$BM renders forbidden low-energy optical transitions and results in only weak absorption in the visible spectral region. For this reason PC$_{71}$BM has been applied in BHJ solar cells as its lower degree of symmetry affords an improved absorbance in the visible range.[25]

Thus, we have built devices containing a spin-coated **10c**: PC$_{71}$BM (25/75% by weight) blend. Upon changing the acceptor material, the fill factor and the V_{OC} were not altered but the photocurrent is increased by 45%, reaching a value of 4.83 mA cm^{-2} and a PCE of 1% (Table 1). The EQE characteristics emphasize that the enhanced absorption of PC$_{71}$BM especially in the range of 400−600 nm is the origin of this significant improvement (Figure 4).

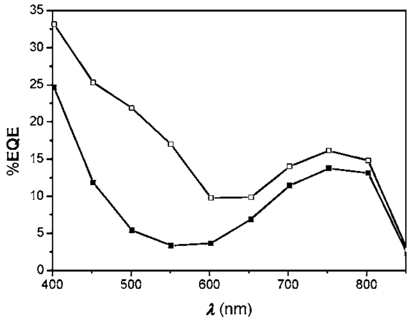

Figure 4. EQE characteristics of devices containing blends of **10c** with PC$_{61}$BM (filled squares) and PC$_{71}$BM (empty squares) (each 75 wt % PCBM).

In summary, we have presented here a series of novel functional merocyanine chromophores that feature NIR absorption for bulk heterojunction solar cells. Upon optimizing the electronic properties, we obtained dye **10c** whose HOMO and LUMO levels are well-suited for application in organic solar cells with PCBM fullerenes as electron-accepting materials. Solar cells fabricated with the newly synthesized merocyanine dyes afford appreciably high open-circuit voltages of up to 0.74 V despite the low bandgap and maximum power conversion efficiency of 1.0%. As a result of their absorption in the NIR region, these merocyanine dyes are promising materials for solar power windows or sun shading technologies as well as for tandem cell devices.

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Supporting Information Available: Synthetic procedures, complete characterizations (NMR, UV−vis, CV), device processing, absorption spectra, and *JV*-response of the solar cells. This material is available free of charge via the Internet at http://pubs.acs.org.

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