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Systems Chemistry Approach in Organic Photovoltaics

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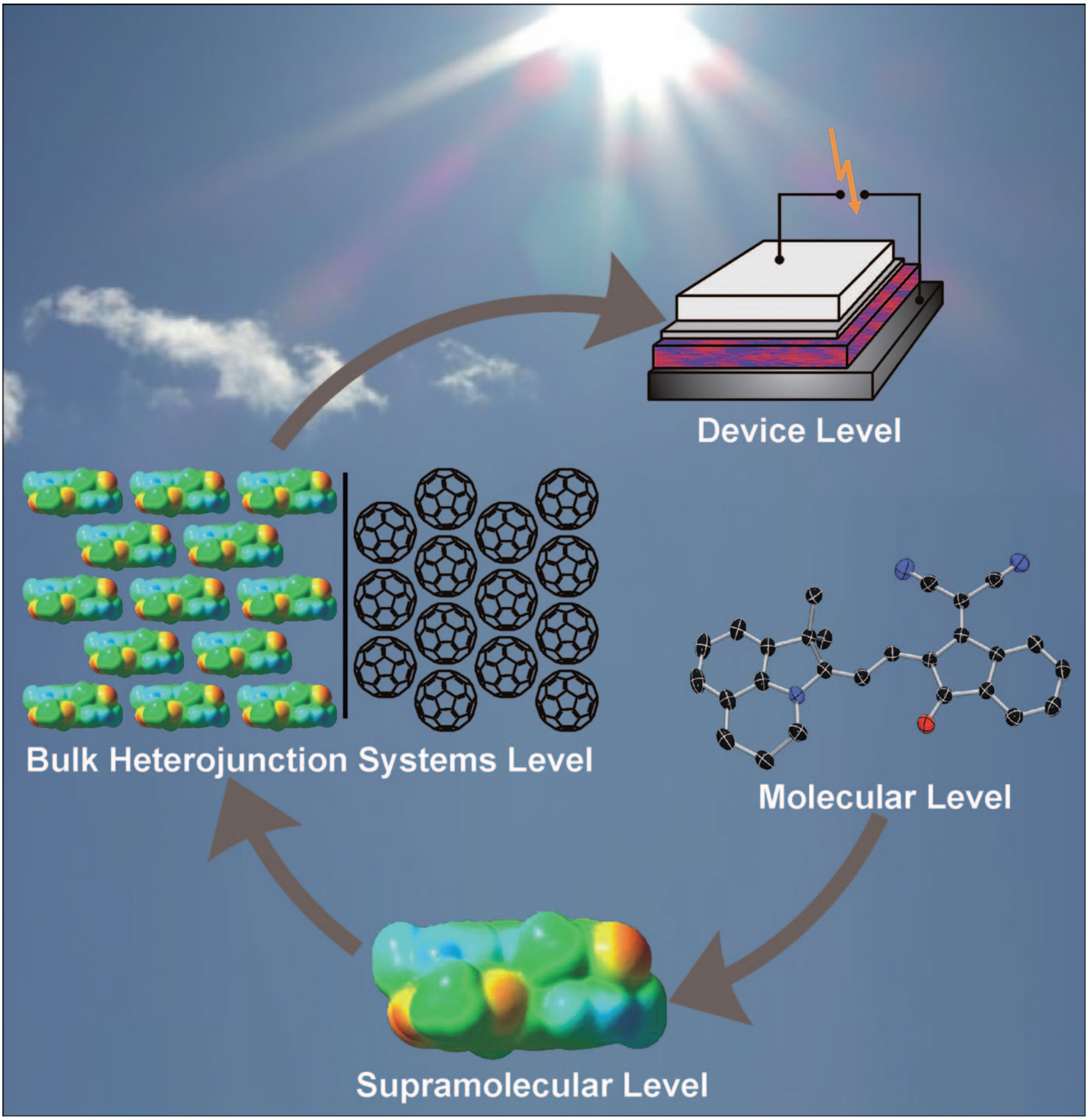

Abstract: The common approach in organic materials science is dominated by the perception that the properties of the bulk materials are virtually determined by the properties of the molecular building blocks. In this Concept Article, we advocate for taking into account supramolecular organization principles for all kinds of organic solid-state materials, irrespective of them being crystalline, liquid crystalline, or amorphous, and discuss a showcase example, that is, the utilization of merocyanine dyes as p-type organic semiconductors in bulk heterojunction (BHJ) solar cells. Despite their extraordinarily large dipole moments, which are considered to be detrimental for efficient charge carrier transport, BHJ organic photovoltaic materials of these dyes with fullerenes have reached remarkable power conversion efficiencies of meanwhile nearly 5%. These at the first glance contradictory properties are, however, well-understandable on the systems chemistry level.

Keywords: dyes/pigments • organic semiconductors • solar cells • supramolecular chemistry • systems chemistry

Introduction

Organic semiconductor research has experienced a growing popularity during the last three decades and heralded the revitalization of a classical field of organic chemistry, that is, the research on π-conjugated systems, in particular dye chemistry. At the time when this research field was almost expatriated from traditional organic chemistry courses the first technological applications of organic semiconductors in photocopiers and later on in laser printers emerged from industrial laboratories as key materials of a multi-billion dollar industry in the 1980s.[1] Subsequently, within one decade in the 1990s organic light-emitting diodes (OLEDs) have been developed from technological curiosity to commercial products by concerted research efforts of academic and industrial laboratories, which are now approaching the next major challenges of high relevance for modern society. These are the scientific understanding and technological realization of efficient and robust organic transistors[2] and solar cells.[3] For the latter, the bridge to traditional dye chemistry is obvious because in addition to typical specifications of an organic semiconductor, that is, good charge carrier mobilities, intense absorption bands in the visible and near infrared spectral range are essential criteria. In this Concept Article, we will particularly focus on solution-processed bulk heterojunction (BHJ) organic photovoltaic (OPV) materials based on small molecules and illustrate the recent achievements based on the class of merocyanine colorants as a model case for a systems chemistry approach in organic materials science. To start with, it appears appropriate to provide a lean overview on the current state-of-the-art materials applied in BHJ-OPVs.

A milestone for organic photovoltaics was laid in 1986 with vacuum-deposited bilayer solar cells (sometimes called as “Tang cells”)[4] with about 1% power conversion efficiency (PCE) containing a p–n heterojunction of a p-type copper phthalocyanine and an n-type perylenetetracarboxylic bisbenzimidazole dye. The limitation of this single heterojunction cell is due to the modest exciton diffusion length of the molecular materials that is around 20 nm. A device with such a thin active layer cannot absorb the solar irradiation efficiently, whereas for a thicker one the excitons cannot reach the donor–acceptor interface to generate the charge carriers. Nearly a decade later, BHJ solar cells containing a single active layer have been introduced.[5a] These BHJ materials consist of blends of a p-type semiconducting polymer and a n-type semiconducting C_{60}-fullerene derivative, usually [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM). The major advantage of these polymer/fullerene systems is a favorable phase separation of the semiconducting polymer and the fullerenes on an ideal length scale of about 20 nm accomplished by a facile solution-cast deposition.[6a] This nanophase separation can be further optimized by solvent variations and thermal annealing processes.[6b] The initial choices for the donor polymers were derivatives of poly(-phenylenevinylene) such as MEH-PPV (Figure 1). In combination with PCBM power conversion efficiencies up to 2.5% were reported.[5b] The second generation of materials was based on regioregular poly-(3-hexylthiophene) (P3HT), which achieved PCEs of up to 5% after optimization of the morphology by proper choice of solvent and thermal annealing procedures.[5c,d] While these materials were homopolymers, the third and most recent generation of materials introduced the concept of donor/acceptor co-polymers (so called low-bandgap polymers) to extend the absorption more into the NIR region of the solar spectrum. Most recently, PCEs $>7\%$ have been reported for these materials.[7]

However, the disadvantages of these polymer-based materials are the cumbersome purification and the difficult structural optimization of the polymers in terms of their molecular weight, polydispersity, and regioregularity, and the challenge involved in the formation of well-defined and long-term stable interpenetrating networks for such blend materials. Thus, several groups have started in the last few years to

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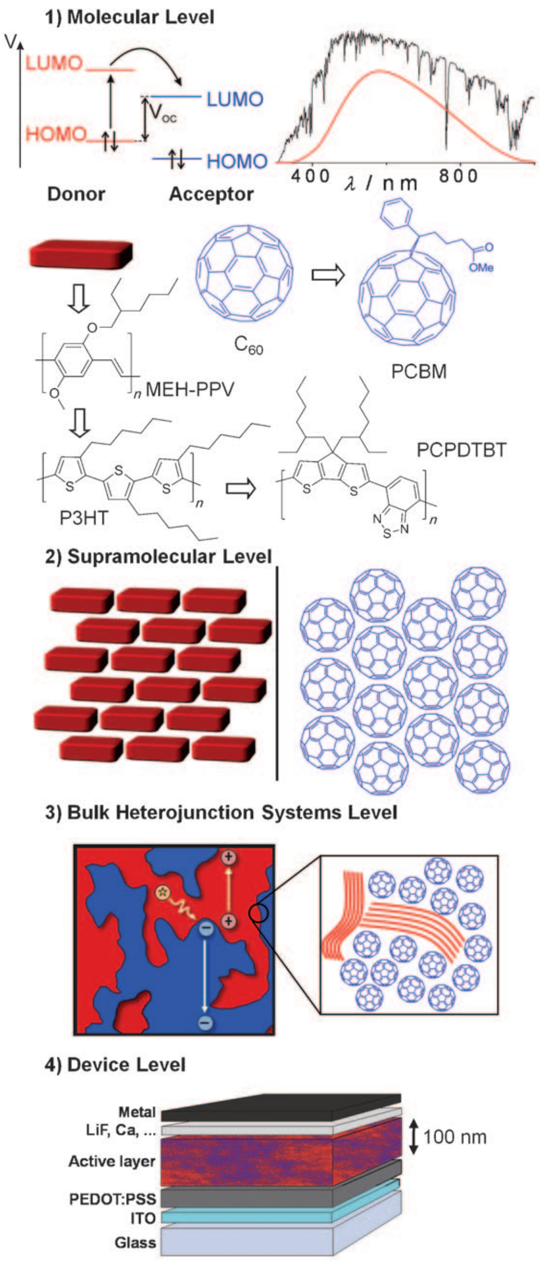


Figure 1. Four levels of structural hierarchy that need to be optimized to achieve an efficient BHJ solar cell. On the first level, optical and electrochemical properties are optimized on the molecular level. An ideal donor/acceptor dye combination provides a high open-circuit voltage V_{OC} (left) and a broad absorption band over the entire range of the solar spectrum (right). The displayed molecular structures show the structural improvements during the last fifteen years for p-type semiconducting polymers. The second and the third levels illustrate supramolecular and morphological aspects, and the fourth level the device architecture. See the text for details.

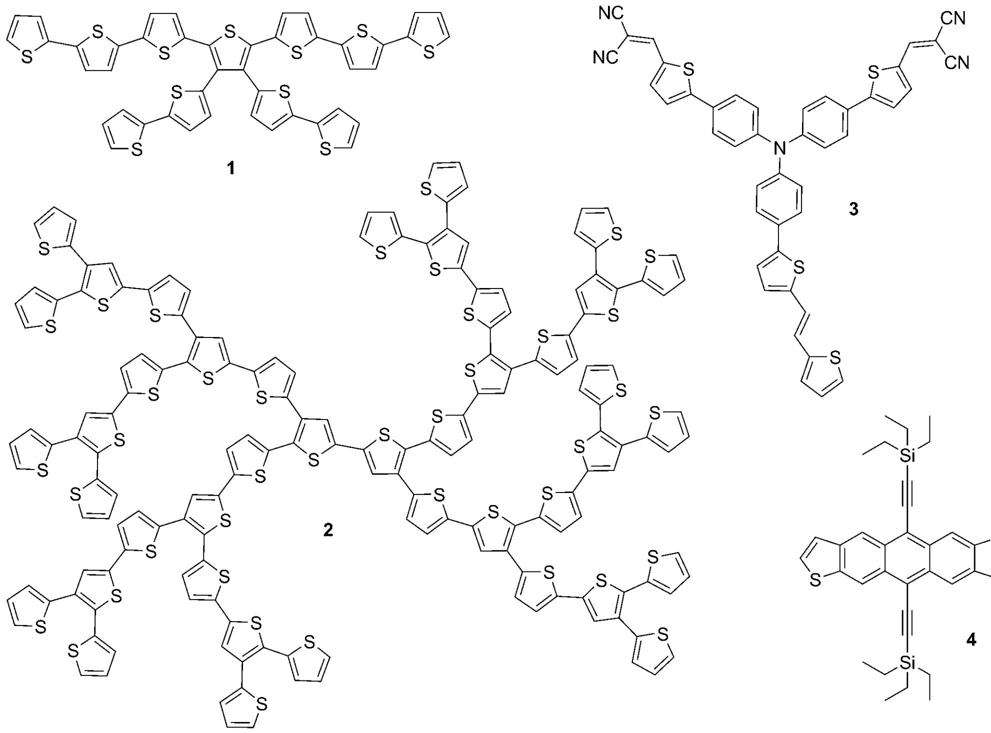
develop BHJ devices based on composites of electron-rich and electron-poor π-conjugated small molecules with good hole and electron transport characteristics, respectively, in their pristine states.[8] Scheme 1 shows a selection of the "first generation" solution-processable electron-rich small molecules that afforded reasonably good BHJ-OPV blends in combination with the electron-poor fullerene derivative PCBM. It is remarkable that the molecular design of all of these hole-transporting molecules is based on well-established classes of p-type organic semiconductors, such as, triarylamines,[9] oligothiophenes,[10] and acenes.[11] These three classes of compounds as well as fullerenes are outstanding with regard to their rather low reorganization energies upon photoexcitation, and formation of stable radical anion or cation, which is considered as a prerequisite for fast charge separation and transport.[12] So far power conversion efficiencies up to approximately 2% have been achieved for photovoltaic blends of these p-type molecular semiconductors in combination with PCBM.[8]

Hierarchy Levels in BHJ Solar Cells

BHJ organic solar cells offer a most favorable example to illustrate the importance of materials optimization on various levels of structural hierarchy (Figure 1).

The first level is the *molecular level* (length scale of about 1 nm) at which the electron-donor and electron-acceptor molecules (or the conjugated segments of a polymer) have to be optimized with regard to their optical and redox properties. Concerning the optical properties, it is desirable that the two individual molecules complement each other in spectral absorption to ensure the highest possible utilization of the terrestrial solar irradiation. With regard to the redox properties, the HOMO and LUMO levels of the two molecules need to be adjusted in such a way that a rapid photoinduced electron transfer from the electron donor to the electron acceptor is ensured, while the highest possible open-circuit voltage V_{OC} is maintained which is dependent on the difference of the HOMO level of the donor and LUMO of the acceptor. Because of the still unmatched amenities of fullerenes, in particular [60]PCBM (and more recently also [70]PCBM owing to better absorption properties), most research work has been focussed on the search of electron-donating molecules with redox properties that properly match with those of fullerenes and whose absorption bands cover a large fraction of the solar light. The latter aspect is of particular importance because fullerenes are rather poor absorbers in the entire visible range. In general, suitable π-conjugated molecules can be explored in a rational way by making use of established structure–property relationships, performing quantum-chemical calculations,[12] and characterizing new molecules by UV/Vis absorption spectroscopy and cyclic voltammetry.

The second level is the *supramolecular level* (length scale of about 10 nm) where two issues need to be addressed. The first one is the necessity of proper phase separation of the two molecular building blocks which requires a distinct preference for the formation of homoaggregates instead of heteroaggregates for the two individual species. This is a delicate issue because self-aggregation is directed by weak intermolecular interactions.[13] On the one hand, dispersion interactions may help to trigger the formation of homoaggregates



Scheme 1. A selection of the first generation of small molecules for which appreciable photovoltaic efficiencies were demonstrated with fullerenes in solution-cast BHJ solar cells: Amorphous oligothiophenes **1** by Zhu and co-workers,[8a] oligothiophene dendrimers **2** by Bäuerle and co-workers,[8d] acceptor-functionalized triarylamines **3** by Roncali and co-workers,[8b] and acenes **4** by Anthony and co-workers.[8c]

because they are maximized by contacts between molecules of the same kind ("similia similibus solvuntur"). On the other hand, co-crystallization, that is, heteroaggregation, has been observed between electron-rich and electron-poor molecules if charge-transfer interactions prevail. The well-known fact that polymer mixtures are prone to phase separation, as widely utilized in block copolymers, is an important reason why the concept of BHJ-OPV worked out so favorably for a large number of polymer/fullerene blends. But also the globular shape of the fullerenes seems to play a role because their shape does not ideally match the shape of planar π-conjugated molecules, and thus facilitates phase separation and formation of microcrystalline fullerene domains.[6] Note that the magnitude of dispersion interactions strongly depends on the contact surface between the involved molecules, which is necessarily not ideal between molecules of such different shape. Besides the necessity of phase separation, a second issue needs to be considered on the supramolecular level and this is the homo-self-assembly of the respective building blocks. Well-ordered aggregates appear promising, in particular if the molecular packing is favorable for desired intermolecular couplings for exciton transport to the BHJ interface and charge transport to the electrodes. For this reason, regioregular poly-(3-hexylthiophene) (P3HT) exhibits better transport characteristics than the more amorphous irregular P3HT. For fullerenes it is assumed that they form nanocrystalline domains that ensure a rapid transport of the photogenerated charge carriers away from the BHJ interface, and thus decrease the probability for undesired charge carrier recombinations.[6a]

The third level of hierarchy (*systems level* in Figure 1), that is, the formation of optimal domains and percolation paths for charge carriers to the electrodes over macroscopic dimensions (length scale of 100 nm), is probably the level that is most difficult to address by rational means. Thus, even for optimally mastered functional properties of the molecules and most desirable supramolecular arrangements for the two constituent species their proper intermixing and macroscopic orientation is a big challenge, for which barely rational design concepts exist and accordingly time-consuming optimization by trial-and-error is warranted. In the area of printable electronics, variations of the solvent, the deposition technique and, in particular, thermal post-treatment ("annealing") of the cast photoactive layers are the most commonly applied strategies for successfully approaching this issue.[6b] Structure–property relationships are not easily accessible on this level because it is rather difficult to get insight into the organization of the constituent molecules in the interior of soft matter.

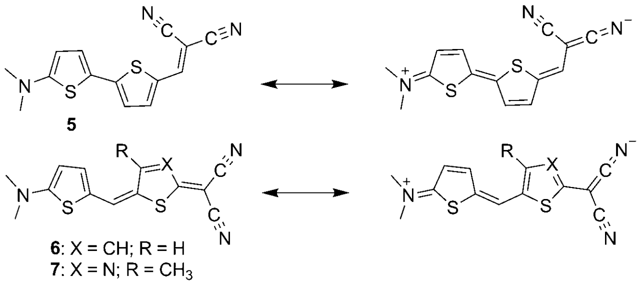
The fourth level of hierarchy (*device level* in Figure 1) involves the interfacing of the two-component BHJ material with the electrodes. This is primarily a research area of surface physics and a number of principles for the proper choice of the respective contact materials based on their work functions have been elaborated. In particular, for vapor-deposited organic solar cells additional hole and electron-blocking layers are typically introduced to improve the charge extraction from the active layer. But also in solution-based OPV cells additional layers like PEDOT-PSS (poly-(3,4-ethylenedioxythiophene) polystyrenesulfonate) are commonly applied.

From this discussion it becomes clear that the first and fourth level of hierarchy are scientifically the best understood ones. Chemists have a profound knowledge on semiconducting molecules whose optical and redox properties can be predicted based on structure–property relationship guidelines and theoretical calculations, and characterized by relatively simple experimental techniques. Likewise, in-depth knowledge in work functions of various metals and the organic material/metal contact has been acquired by surface and device physicists. Now, the most serious challenges remain on the supramolecular/systems levels if BHJ materials or other complex organic materials are to become accessible by rational design in the future.

Merocyanine Colorants

The utilization of p-type semiconducting polymers such as P3HT or related amorphous oligothiophenes in BHJ-OPV is very reasonable owing to their outstanding hole-transport properties. For a hopping-transport process, it is known from experimental and theoretical studies that small reorganization energies upon oxidation of the neutral molecules to their radical cations are advantageous[12] as well as the absence of dipolar groups in molecules.[14] According to Borsenberger and Bässler, dipolar groups generate a random electrostatic potential in amorphous solid-state materials leading to a larger energetic disorder that slows down the charge-carrier transport ("dispersive" transport).[14] Therefore, dipolar molecules and even dipolar functional groups should actually be avoided in organic photo- and semiconducting materials. Although, for a better adjustment of the p-semiconductors' frontier orbitals Roncali and Bäuerle have introduced dicyanovinyl substituents symmetrically to triarylamines, for example, compound **3** (Scheme 1), and to oligothiophenes.[8b,15]

On the basis of the above-mentioned considerations, the class of merocyanine dyes does not appear promising at all for application as semiconducting materials due to their large dipole moments. Indeed, the highest dipole moments among all known dye molecules have been reported for merocyanine dyes.[16] Nevertheless, merocyanine dyes are excellent colorants with tunable optical properties and intense absorption bands (i.e. large transition dipole moments) that could be beneficially utilized in thinner photoactive layers. From our earlier work in the field of nonlinear optics and photorefractive materials,[17] we realized that the reorganization energy of merocyanines upon oxidation should be rather small if they exhibit equal dipole moments in the ground and the excited state (so-called "cyanine limit"), which relates to equal contributions of the polyene-type and the zwitterionic resonance structures in the valence bond model (Scheme 2). Merocyanines in the cyanine limit are also dyes with most favorable absorption properties, that is, intense absorption bands at the longest possible wavelength for a given polymethine chain (Figure 2), and they possess enhanced thermal and photochemical stability owing to equalized bond orders.[17,18]



Scheme 2. Polyene-type and zwitterionic resonance structures for two different merocyanine dye scaffolds. Note that for **5** the zwitterionic structure is disfavored by the loss of aromaticity in both heterocyclic units. This is the reason why its constitutional isomer **6** as well as derivative **7** are significantly more dipolar in the ground state (Figure 2).

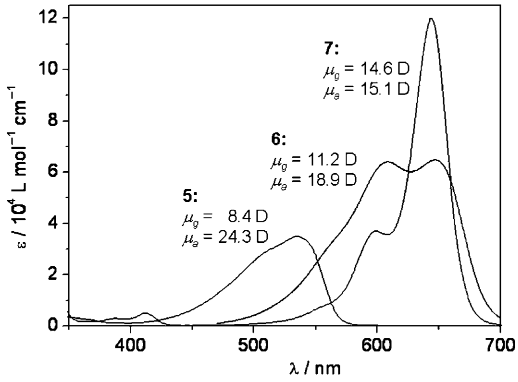


Figure 2. UV/Vis absorption spectra of three merocyanine dyes **5**–**7** and their dipole moments in the ground (μ_g) and the excited state (μ_a) in dioxane.[17c] Note that the characteristic sharp and intense absorption band of a cyanine has been realized for merocyanine **7** with almost equal dipole moments in the ground and the excited state.

Moreover, in our earlier work we discovered that such highly dipolar merocyanine dyes self-assemble into strongly bound centrosymmetric dimer aggregates with vanishing dipole moments already in dilute solutions as well as in polymeric matrices.[19] Figure 3 shows the calculated electrostatic potential map for centrosymmetric dimers of the dipolar merocyanine dye **8** ($\mu_g = 17$ D) at a larger and a closer distance.[13] From this presentation it becomes not only clear that the overall dipolarity has vanished in a dimer aggregate but that even an amalgamation of the electrostatic charge density has occurred. Accordingly, we envisioned that the unfavorable dipolar molecular properties of merocyanines might be healed on the supramolecular level and that exper-

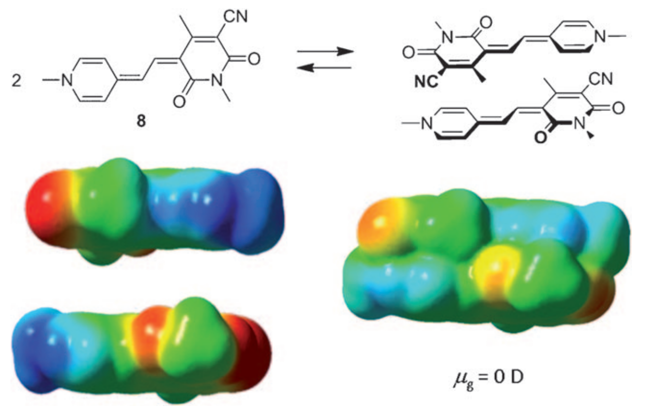
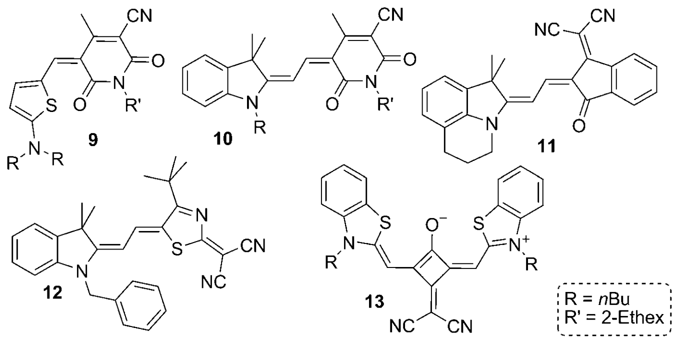


Figure 3. Formation of dimer aggregates of merocyanine dye **8** and electrostatic potential energy maps for two centrosymmetrically arranged highly dipolar monomers at a distance of 6.5 Å (left) and for a π-stacked dimer at the experimentally observed distance of 3.25 Å in single crystals.[19b]

imental investigations on their utilization in BHJ solar cells are warranted.

Pleasingly, already the first photovoltaic blends composed of available photorefractive ATOP (aminothienyl-oxopyridine compound **9**, Scheme 3) dyes and PCBM afforded power conversion efficiencies close to 1 % (Table 1).[20] Structural variations revealed that electronically and optically related dyes with an indolenine ("Fischer base") electron-donating group provided even better performance.[21] The exceptional behavior of this electron-donor group is attributed to its sterically demanding 3,3′-dimethyl subunit that affords much better soluble dyes and slipped packing arrangements in the solid state (Figure 4d,e). By simple condensation reactions with CH-acidic heterocyclic acceptor units a broad variety of merocyanines became accessible whose absorption bands cover the whole visible range (Figure 5). Note that these absorption spectra have been recorded in dilute solution, whilst upon aggregation in concentrated solution and in thin films a significant broadening of the absorption bands is observed. Owing to this band broadening, a combination of three of these dyes already ensures



Scheme 3. A selection of merocyanine dyes that have been applied in solution-processed BHJ solar cells.[21]

Table 1. Photovoltaic characteristics of solution-processed BHJ solar cells composed of merocyanines **9**–**13** and PCBM under AM 1.5 illumination.[a]

Dye	V_{OC} [V]	J_{SC} [mA cm^{-2}]	FF	η [%]
9 (ATOP)	0.73	4.0	0.32	0.91
10 (IDOP)	0.77	4.0	0.29	0.87
11 (HB 194)	0.94	8.24	0.34	2.59
12 (MD 304)	0.76	6.3	0.36	1.74
13	0.31	12.6	0.47	1.79

[a] Typical device architecture: ITO/PEDOT:PSS layer, MC:PCBM layer, Al layer; V_{OC}: open circuit voltage; J_{SC}: short circuit current; FF: fill factor; η: power conversion efficiency.

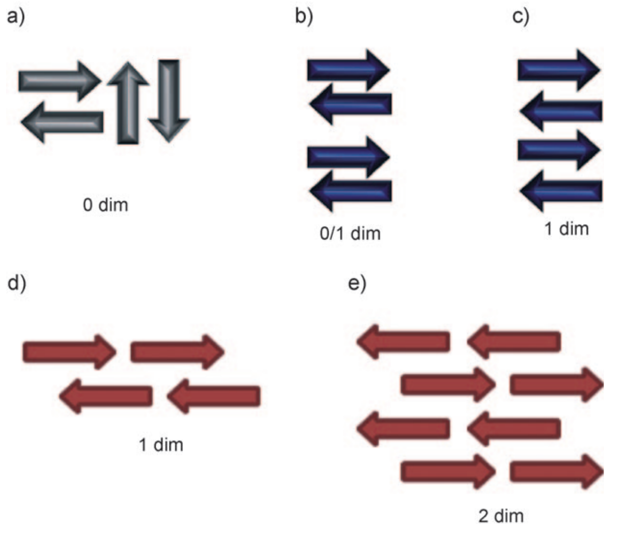


Figure 4. Schematic representation of molecular arrangements of dipolar merocyanine dyes (simplified representation by the direction of their dipole moments) as observed by X-ray diffraction in single crystals. The arrow color denotes isolated dimers (grey), one-dimensional stacks with H-coupling (blue), and one- and two-dimensional slipped arrangements with J-coupling (red).

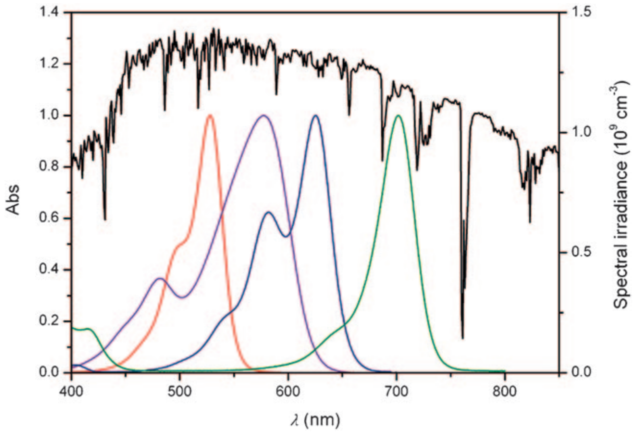


Figure 5. Terrestrial solar spectrum (black) and UV/Vis absorption spectra of merocyanine dyes **10** (red), **11** (violet), **12** (blue), and **13** (green) in dilute dichloromethane solution.

absorption of the entire visible and part of the near infrared spectral range,[21] which might offer interesting perspectives for multi-junction devices based on a single class of dyes.

The arrangement of the dipolar dyes in the solid state deserves some further discussion as it has an impact on solar cell efficiency. In more than twenty single-crystal analyses of merocyanine dyes we found centrosymmetric arrangements with almost perfect antiparallel orientations of the dipole moments of adjacent molecules in most cases. Schematic representations of the observed arrangements are depicted in Figure 4 in a simplified way based on the dyes' dipole moments. A common motif in the molecular arrangements are sandwich-type dimeric units (Figure 4a–c). Even for one-dimensional π-stacks with alternating dipole orientation (Figure 4b, c) often a difference in the distances of a molecule to its upper and the lower adjacent one (Figure 4b) was found, thus confirming the presence of centrosymmetric dimeric supramolecular synthons[22] (see Figure 3) in the crystalline state. Remarkably, the bulkiness of the 3,3′-dimethyl groups of the indolenine dyes induces different packing patterns like the one shown in Figure 4d, e which suggest favorable exciton and charge percolation pathways in one (Figure 4d) or two (Figure 4e) dimensions. Further studies will be necessary to reveal the influence of the packing motifs on the optical and reorganization energies that are decisive for the exciton and charge transport properties in these materials.

In parallel to our work, other groups have also searched for new solution-processable p-type molecular semiconductor materials for OPVs based on typical colorants such as merocyanines, for example, squaraines,[21b,23] bodipy dyes,[24] diketopyrrolopyrroles,[25] indigoids,[26] and phthalocyanines.[27] Like merocyanines, these compounds possess high tinctorial strength and often contain polar functional groups. However, these polar groups are invariably arranged symmetrically leading to quadrupolar instead of dipolar molecules. This implies that the rationale behind the chromophore design for organic electronic materials is still dominated by the paradigm that dipolar molecules should be avoided due to their severe limitations in charge carrier transport.[14] In this regard, our concept is unique because it is clearly not based on a material design with focus on molecular properties (level 1 in Figure 1) but on supramolecular level 2 and systems level 3. Thus, we anticipated that strongly dipolar merocyanines should be treated as centrosymmetric dimer aggregates, which are quadrupolar and not dipolar functional entities on the supramolecular level (Figure 1, level 2) and that their polar character should favor homoaggregation by pronounced electrostatic interactions between these molecules, leading to phase-separated morphologies with nonpolar fullerene derivatives on the systems level (Figure 1, level 3). It is likely that the latter arguments hold also true for the successful utilization of other quadrupolar compounds mentioned here[23–26] that gain additional intermolecular interaction energies by electrostatic forces compared to pure polycyclic aromatic hydrocarbons.[13]

Summary and Outlook

In this article, we have disclosed the concepts behind our recent work on new materials for bulk heterojunction solar cells. Based on three concepts, that is, small reorganization energies for merocyanines in the cyanine limit (molecular level), preferential and strong dimerization of these dipolar dyes into antiparallel dimer units (supramolecular level), and pronounced phase separation from fullerenes (systems level), we have achieved BHJ organic photovoltaic materials with a class of colorants that initially appeared to be not at all suitable for this purpose on the basis of solely molecular considerations.

Currently, it is not possible to reliably predict the perspectives of these novel photovoltaic materials compared to those achieved by more traditional organic semiconductor designs. The tunability of the absorption properties and the simplicity of adjustment of the HOMO levels are clearly advantageous properties of merocyanine dyes. Thus, rather high open-circuit voltages could be achieved even for dyes like **11** and **12** (Scheme 3) whose absorption bands already reach the NIR region in thin films. The higher permittivity (dielectric constant) of dipolar and quadrupolar molecules might be advantageous for charge carrier separation at the p–n interface, but appears disadvantageous for the transport of these charge carriers to the electrodes. A critical issue will remain the optimization of the fill factors (Table 1), which seem to depend on problems of charge extraction due to the limited hole carrier mobility. Nevertheless, for merocyanine **11** an acceptable hole mobility of $>10^{-5}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ has been obtained,[21c] which was even surpassed by squarain-type merocyanine **13**.[21b] Apparently, the "right" balance between (micro)crystalline and amorphous domains will be of crucial importance for the further development of these materials. Here we are currently pursuing different strategies, including the deposition of merocyanine/fullerene BHJ layers under high-vacuum conditions by thermal evaporation where our initial attempts afforded right away power conversion efficiencies close to 5% for the combination of merocyanine **11** (HB 194) and C_{60}-fullerene in a very simple device architecture.[28] It is noteworthy that this value already reaches the performance level of the currently most efficient vacuum-processed BHJ devices based on single photoactive layers[29] (not tandem cells), which substantiates the arguments outlined in this article for the applicability of this unconventional class of semiconductor chromophores for organic photovoltaics owing to their advantageous self-organization properties.

Irrespective of the future developments and the most obvious question, which organic semiconductor materials will ultimately enter into the photovoltaic market (if at all), we hope that this striking example of a function-enabling supramolecular arrangement will influence the further thinking of chemists for the development of new organic materials. The lesson to be learned is that new properties can emerge in a complex molecular solid that are quite distinct from those expected from a pure molecular point of view. Due to the formation of centrosymmetric aggregates, strongly dipolar merocyanines have been rather disappointing in the field of nonlinear optics,[17a] but have now been surprisingly well-suited for organic photovoltaics.

Acknowledgements

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