Solvatochromism

Deutsche Ausgabe: DOI: 10.1002/ange.201510620
Internationale Ausgabe: DOI: 10.1002/anie.201510620

Conformational Switching of π-Conjugated Junctions from Merocyanine to Cyanine States by Solvent Polarity

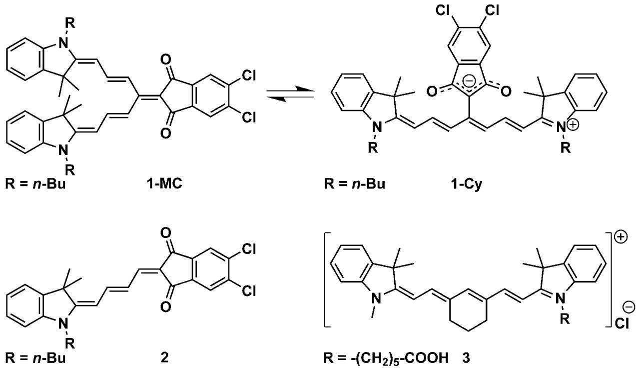
*Alhama Arjona-Esteban, Matthias Stolte, and Frank Würthner**

Dedicated to Professor Siegfried Hünig on the occasion of his 95th birthday

Abstract: *Directed by the solvent polarity, the prevalent conformation of a polymethine dye bearing a branched π-conjugated junction can be switched from a heptamethine donor–acceptor (DA) merocyanine-type π-conjugated system to a nonamethine DAD cyanine-type π-conjugated scaffold. Concomitantly the absorption maximum shifts from 585 nm in dichloromethane to 748 nm in methanol solution.*

Because of the exciting perspectives arising for sensing, actuation, or other functional properties, there is currently great interest in molecular scaffolds with properties that are strongly governed by conformational changes.[1] Among π-conjugated scaffolds, temperature-dependent topology changes between Hückel and Möbius conformations have received particular attention[2] as well as the planarization of V-shaped antiaromatic cyclooctatetraenes (COT) in the reduced or photoexcited state.[3] The latter effect has recently been exploited by Yamaguchi and co-workers to shift the emission wavelength bathochromically by about 100 nm with a concomitant color change from blue to green by embedding a COT unit between two anthraceneimides.[4] Accordingly, whilst the special resonance stabilizations of cyclic π-scaffolds has attracted much attention, another special resonance state given for conjugated chains, that is, the ideal polymethine state[5] (also called cyanine limit[6]), received little attention with regard to conformational switching phenomena. Herein, we report the synthesis of an unusual bifurcated π-scaffold that exhibits an unprecedented solvent polarity dependent conformational switching, leading to a shift of the absorption maximum by more than 160 nm.

The conformationally amphoteric dye **1** (Scheme 1) could be synthesized in 28% yield by double Knoevenagel condensation as described in detail in the Supporting Information. For comparison, reference merocyanine dye **2** was also synthesized by condensation of the corresponding indolenine salt. Both dyes were fully characterized by NMR spectroscopy, high resolution mass spectrometry, and elemental analysis. The second reference cyanine dye **3** was purchased from commercial sources.



Scheme 1. Conformational equilibrium for dye **1** between merocyanine- and cyanine-type structures as well as chemical structures of reference merocyanine dye **2** and cyanine dye **3**.

Figure 1 shows the UV/Vis absorption spectra of reference dyes **2** and **3** as well as the bifurcated dye **1** for selected solvents of varying polarity (for spectra in further solvents, see the Supporting Information, Figures S1–S3).

In unpolar solvents such as methylcyclohexane (MCH), dye **1** features the clear signature of a push–pull chromophore (conformation **1-MC** in Scheme 1) with an intense absorption band at 576 nm and vibronic progressions similar to merocyanine **2**. On the other hand, in polar protic solvents such as methanol the main absorption band of dye **1** is even more intense and located at 748 nm. This strongly red-shifted band of high intensity is typical for cyanine dyes with the same polymethine chain length as suggested by structure **1-Cy**,[7] as demonstrated in Figure 1a by comparison with reference cyanine **3**. In solvents of intermediate polarity, such as di- or trichloromethane, a broad and unstructured band is observed that is still centered at 585 nm (**1-MC**) but exhibits a shoulder above 700 nm.

It is well-known that solvent polarity has a profound impact on the absorption wavelengths of (dipolar) merocyanine dyes, which is explained by a different stabilization of ground- and excited states of molecules of different dipolarity by polar solvents (solvatochromism).[8] In the case of positive solvatochromism, as observed here, indeed red-shifts of up to 130 nm have been observed for DA dyes when going from *n*-hexane to DMF/water mixtures.[8b] However, in our case the even larger red-shift of 160 nm cannot be attributed to such a kind of solvatochromism because otherwise a continuous displacement of the absorption band with increasing solvent polarity should be observed instead of the bimodal distribution of absorption intensity at ca. 585 nm and ca. 750 nm, which is most striking in ethanol where both bands coexist in

---

[*] A. Arjona-Esteban, Dr. M. Stolte, Prof. Dr. F. Würthner
Universität Würzburg, Institut für Organische Chemie and
Center for Nanosystems Chemistry
Am Hubland, 97074 Würzburg (Germany)
E-mail: wuerthner@chemie.uni-wuerzburg.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201510620.

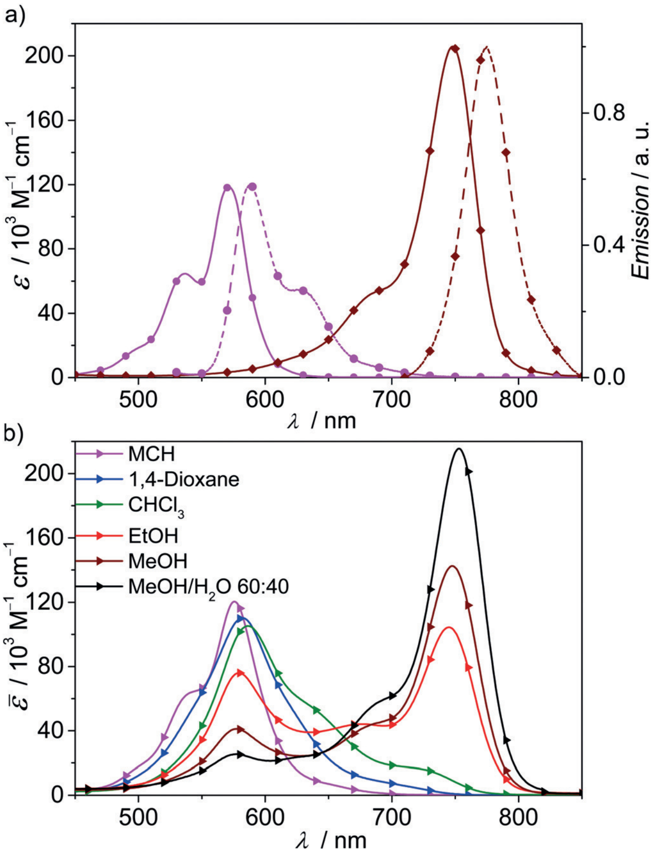


Figure 1. a) UV/Vis (——) and fluorescence (-----) spectra of reference dyes **2** (pink ●, $c \approx 10^{-6}$ M, 298 K) and **3** (brown ◆, $c \approx 10^{-6}$ M, 298 K) and b) of dye **1** ($c \approx 10^{-5}$ M, 298 K) in solvents of increasing polarity (pink methylcyclohexane, blue 1,4-dioxane, green trichloromethane, red ethanol, brown methanol, black methanol/water 60:40).

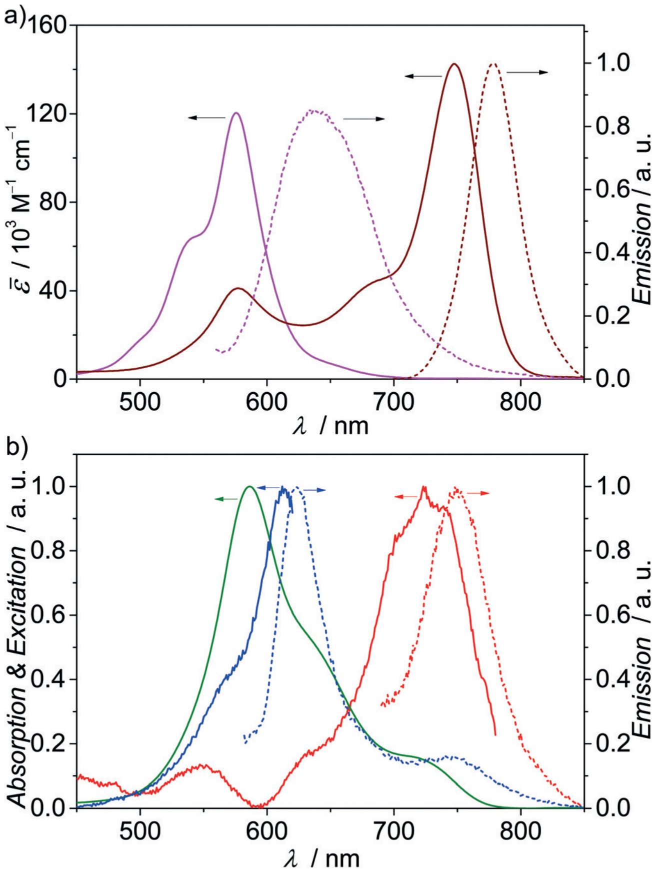


Figure 2. a) Absorption (——) and normalized emission (-----) of dye **1** in MCH (pink) and MeOH (brown) solutions. b) Normalized absorption (green), excitation (——, blue for $\lambda_{em} = 630$ nm and red for $\lambda_{em} = 790$ nm) and emission (-----, blue for $\lambda_{exc} = 550$ nm and red for $\lambda_{exc} = 680$ nm) spectra of dye **1** in trichloromethane solution ($c \approx 10^{-6}$ M, 298 K). The blue curves correspond to the merocyanine conformation **1-MC** and the red curves to the cyanine conformation **1-Cy**.

almost equal intensity. Thus, different molecular species have to be considered to explain the observed bands at 585 and 748 nm.

The nature of the two bands has been studied further by fluorescence spectroscopy. In Figure 2a the absorption and normalized emission spectra of dye **1** in MCH and methanol solutions are depicted. Again the fluorescence spectra are very similar to those of reference dyes **2** and **3** in the same solvents, depicted in Figure 1a. Moreover, the absorption, excitation and emission spectra of dye **1** in trichloromethane solutions are depicted in Figure 2b. Interestingly, for an excitation wavelength of 550 nm, the recorded emission is centered at 624 nm with a small shoulder at 750 nm. The main emission at 624 nm is accordingly very similar to the emission of reference merocyanine dye **2**. The corresponding excitation spectrum for an emission wavelength of 630 nm featured a maximum at 612 nm and a shape typical for merocyanine dyes. In contrast, when exciting at 680 nm, the small shoulder observed in the previous experiment evolved as the main emission band, with a maximum at 750 nm. This band correlates well with the emission in methanol attributed to the cyanine conformation. Likewise, the corresponding excitation spectrum for the emission maximum of 790 nm revealed a band centered at 725 nm. The fact that two different excitation spectra were found for the two emission bands supports the hypothesis of two independently absorbing species, that is, co-existence of conformational isomers **1-MC** and **1-Cy**. Owing to the similarity of the spectra with the corresponding reference dyes, we can assume that the short-wavelength absorption belongs to the merocyanine-type conformational isomer **1-MC** while the long-wavelength transition corresponds to the cyanine-type conformational isomer **1-Cy** (Scheme 1). Further corroboration for two distinct species is provided by the absorption spectra of solid state materials of **1** obtained from dichloromethane and methanol solutions by evaporation of the solvent (see Supporting Information, Figure S4), which exhibit similar features as in solution.

We were able to confirm the merocyanine conformation **1-MC** by single crystal analysis of crystals grown from dichloromethane solutions where **1-MC** is the dominating species (Figure 3a,b).[9] Indeed, a flat and almost planar DA scaffold is found for the polymethine chain between one of the donor units and the acceptor heterocycle, whilst the polymethine chain connected to the second donor subunit is twisted out of planarity by an angle of almost 60° with respect to the acceptor unit. The symmetry-broken situation for the

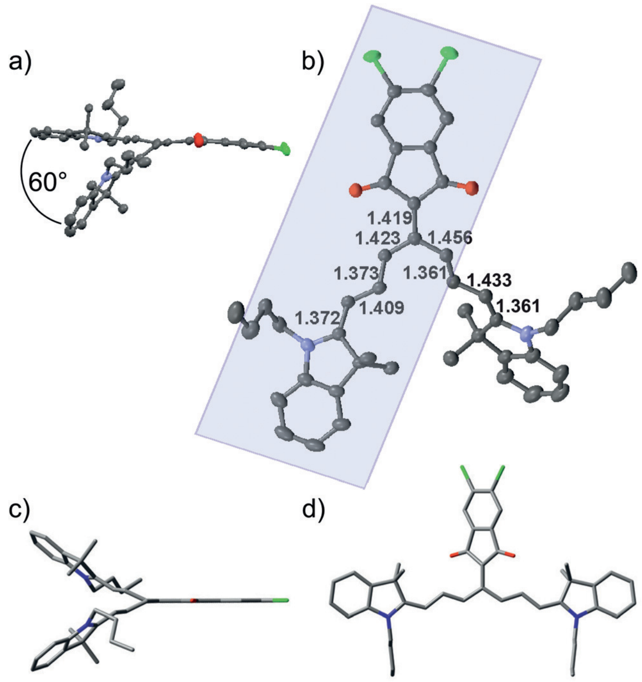


Figure 3. a) Side-view of the molecular structure of dye **1** in the crystal, where the angle between both donor units is noted.[9] b) Top-view of the molecular structure of dye **1** in the crystal with the corresponding bond lengths of the polymethine chains. The planar DA scaffold is highlighted in the blue rectangle. Optimized geometry of dye **1** in the gas phase for the c) merocyanine-like conformation **1-MC** as well as d) the cyanine-like conformation **1-Cy**, calculated with the software Gaussian 09[10] at the B3-LYP/6-31G(d)[10] level of theory.

two polymethine chains from the π-junction to the corresponding donor units is as well reflected in the bond lengths of the polymethine chain. Thus, the bond length alternation (BLA) is significantly smaller for the polymethine chain of the planar DA system than for the out-of-plane twisted polymethine chain to the second donor unit (Figure 3b). It is accordingly reasonable to conclude that the π-electronic system is delocalized within one D-π-A merocyanine scaffold and that the second donor unit of the second polymethine chain is disconnected, leading to a more polyene-like BLA behavior of this chain.

Theoretical calculations were performed for a better understanding of the electronic properties of dye **1**. On the one hand, a single point energy optimization was performed using the geometry of the molecule in the crystal structure to calculate the frontier molecular orbitals for this conformational isomer. For this purpose, the Gaussian 09[10] software was used, with the functional B3-LYP[10] and the basis set 6-31G(d). On the other hand, a geometry optimization of the merocyanine conformation **1-MC**, the cyanine conformation **1-Cy**, as well as the reference molecule **2** was performed using the same level of theory. In Figure 3, the optimized geometries of both conformations of dye **1** (c,d) are depicted. The FMO levels of dye **1-MC** in the crystal geometry, the FMOs of the optimized **1-Cy** geometry as well as the optimized geometry and FMOs of reference merocyanine dye **2** can be found in the Supporting Information (Figure S6). Interestingly, while the LUMO of dye **1-MC** in the crystal geometry is distributed all over the molecule, this is not the case for the HOMO and HOMO−1 orbitals. The HOMO−1 orbital is localized along the DA planar scaffold, in analogy to the HOMO of reference merocyanine dye **2**. Thus, we can assume that the main merocyanine-like absorption band displayed by dye **1-MC** in unpolar solvents corresponds to a transition from the HOMO−1 to the LUMO orbitals. This transition is of high intensity since both HOMO−1 and LUMO orbitals overlap well within the planar DA system, leading to a large oscillator strength. In contrast, the HOMO orbital of dye **1-MC** in the crystal geometry is localized on the distorted donor subunit and features almost no overlap with the LUMO orbital. Thus, the low intensity absorption from 650 to 700 nm is attributable to the HOMO–LUMO transition. For the by two methine units longer cyanine conformation **1-Cy**, the calculated FMOs are equally distributed along the cyanine π-scaffold, indicative of a fully conjugated polymethine chain which is responsible for the intense long-wavelength absorption at 748 nm.

The possibility of conformational switching between the merocyanine form **1-MC** and the cyanine form **1-Cy** by the solvent polarity is illustrated in Figure 4. Here, solutions with different CH_2Cl_2/MeOH and MeOH/H_2O ratios have been prepared and their absorption spectra were recorded. For the MeOH/H_2O 60:40 mixture the cyanine band shifts slightly from 748 nm to 753 nm, reaching an absorption of $200\times10^3\,\text{M}^{-1}\,\text{cm}^{-1}$, which is in the range of reference cyanine **3**. As shown in the inset of Figure 4, upon increasing the methanol content the short-wavelength absorption band decreases, while the long-wavelength absorption rapidly rises. Since a quasi-isosbestic point (ca. 660 nm) can be observed for the transition between the merocyanine-like **1-MC** and the cyanine-like **1-Cy** conformations, a two-state equilibrium for the process is confirmed. To determine the thermodynamic data of the conformational equilibrium the absorption maximum at 753 nm was chosen since this band is the most sharp and defined, and features no overlap with the **1-MC** absorbance. For this analysis two assumptions have

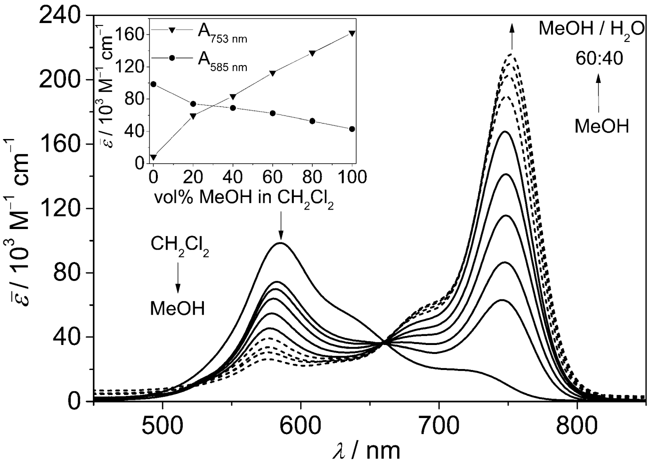


Figure 4. Solvent-dependent UV/Vis absorption spectra of dye **1** ($c\approx4\times10^{-6}$ M, 298 K) in CH_2Cl_2/MeOH mixtures starting in pure CH_2Cl_2 changing to pure MeOH by increasing the MeOH content (——, 20 vol% steps) as well as MeOH/H_2O mixtures up to 40% H_2O (-----, 10 vol% steps). Inset: Plot of the absorption maxima at 585 nm and 753 nm against the content of MeOH in CH_2Cl_2.

been made. First, for methanol/water mixtures with 40% water dye **1** is supposed to be exclusively in the cyanine conformation **1-Cy** which is reasonable because of the similarity of the extinction coefficient value with the one of the reference cyanine **3**. Second, the spectrum of dye **1** in MCH (Figure 1) was taken as reference for the pure merocyanine-like conformation **1-MC**. Thus, the fraction of cyanine conformation α_{Cy} was calculated for every solvent mixture using Equation (1), which has been proposed for the study of foldamers:[11]

$$\alpha_{\mathrm{Cy}} = \frac{\varepsilon(\lambda)_{\mathrm{MC}} - \varepsilon(\lambda)}{\varepsilon(\lambda)_{\mathrm{MC}} - \varepsilon(\lambda)_{\mathrm{Cy}}} \qquad (1)$$

where $\varepsilon(\lambda)$ is the extinction coefficient at a particular wavelength for an intermediate solvent composition and $\varepsilon(\lambda)_{\mathrm{MC}}$ and $\varepsilon(\lambda)_{\mathrm{Cy}}$ are the extinction coefficients for the pure merocyanine and cyanine conformations, respectively, at the particular wavelength. Moreover, the values of the equilibrium constant and the free Gibbs energy for the equilibrium at each solvent composition can be derived from Equations (2)

$$K_{\mathrm{eq}} = \frac{c_{\mathrm{MC}}}{c_{\mathrm{Cy}}} = \frac{1-\alpha_{\mathrm{Cy}}}{\alpha_{\mathrm{Cy}}} \qquad (2)$$

and (3):

$$\Delta G^0 = -RT \ln K_{\mathrm{eq}} \qquad (3)$$

where c_{MC} and c_{Cy} represent the concentration of the merocyanine and cyanine species, respectively. From this analysis the free energy change between both states was found to depend linearly on the solvent composition. The fitted data can be found in the Supporting Information (Table S1 and Figure S7). For a solvent mixture with 57% MeOH and 43% dichloromethane the free Gibbs energy is zero, that is, both species are isoenergetic. For higher dichloromethane contents the **1-MC** isomer is energetically more favored ($\Delta G^0 < 0$) whilst for higher MeOH contents (as well as MeOH/water mixtures) the **1-Cy** isomer is energetically favored. The result in the lower polarity environment is in accordance with the theoretical calculations on the optimized geometries in the gas phase of merocyanine **1-MC** and cyanine **1-Cy** conformations (Figure 3c,d), which revealed a 10 kJ mol^{-1} lower energy for the **1-MC** conformation.

In conclusion, a new bifurcated π-scaffold has been synthesized that exhibits a conformational switching between a merocyanine-like **1-MC** donor-π-acceptor and a cyanine-like **1-Cy** zwitterionic (D-π-D)$^+$ A$^-$ structure upon increasing solvent polarity. This conformational switching is accompanied by a shift of the absorption band by more than 160 nm from the visible (ca. 585 nm) to the near infrared region (ca. 750 nm) when changing the solvent from dichloromethane to methanol. Both conformations **1-MC** and **1-Cy** have been characterized by means of UV/Vis and fluorescence spectroscopy. Additionally, the structure of **1-MC** has been confirmed by single-crystal analysis. The equilibrium between both conformations can be controlled by variation of the solvent polarity, as illustrated for CH_2Cl_2/MeOH mixtures. In MCH solutions of dye **1**, the merocyanine conformation **1-MC** was present exclusively, while in methanol/water mixtures with 40% water dye **1** featured almost exclusively the cyanine conformation **1-Cy**. Further studies on the spectroscopic features of this and related molecules as well as those towards interconversion of the two conformations by external stimuli are planned.

Acknowledgements

We thank Christian Simon for the synthesis of reference dye **2**, Dr. David Schmidt for the single-crystal X-ray analysis, and the BMBF for financial support of our research on merocyanine dyes within the LOTsE (FKZ: 03K3503C) program.

Keywords: conformation analysis · cyanines · dyes/pigments · solvatochromism

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 2470–2473
Angew. Chem. **2016**, *128*, 2516–2519

[1] a) H. John, C. Briehn, J. Schmidt, S. Hünig, J. Heinze, *Angew. Chem. Int. Ed.* **2007**, *46*, 449–453; *Angew. Chem.* **2007**, *119*, 453–457; b) C. Song, T. M. Swager, *Org. Lett.* **2008**, *10*, 3575–3578; c) R. M. Meudtner, S. Hecht, *Angew. Chem. Int. Ed.* **2008**, *47*, 4926–4930; *Angew. Chem.* **2008**, *120*, 5004–5008; d) M. Wolffs, N. Delsuc, D. Veldman, N. V. Anh, R. M. Williams, S. C. J. Meskers, R. A. J. Janssen, I. Huc, A. P. H. J. Schenning, *J. Am. Chem. Soc.* **2009**, *131*, 4819–4829; e) K. Miwa, Y. Furusho, E. Yashima, *Nat. Chem.* **2010**, *2*, 444–449; f) F. Schlosser, M. Moos, C. Lambert, F. Würthner, *Adv. Mater.* **2013**, *25*, 410–414; g) I. Pochorovski, F. Diederich, *Acc. Chem. Res.* **2014**, *47*, 2096–2105.

[2] S. Saito, J.-Y. Shin, J. M. Lim, K. S. Kim, D. Kim, A. Osuka, *Angew. Chem. Int. Ed.* **2008**, *47*, 9657–9660; *Angew. Chem.* **2008**, *120*, 9803–9806.

[3] M. J. Marsella, R. J. Reid, S. Estassi, L.-S. Wang, *J. Am. Chem. Soc.* **2002**, *124*, 12507–12510.

[4] a) C. Yuan, S. Saito, C. Camacho, S. Irle, I. Hisaki, S. Yamaguchi, *J. Am. Chem. Soc.* **2013**, *135*, 8842–8845; b) C. Yuan, S. Saito, C. Camacho, T. Kowalczyk, S. Irle, S. Yamaguchi, *Chem. Eur. J.* **2014**, *20*, 2193–2200.

[5] S. Dähne, *Chimia* **1991**, *45*, 288–296.

[6] a) S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J.-L. Brédas, B. M. Pierce, *Science* **1994**, *265*, 632–635; b) F. Würthner, R. Wortmann, R. Matschiner, K. Lukaszuk, K. Meerholz, Y. De Nardin, R. Bittner, C. Bräuchle, R. Sens, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2765–2768; *Angew. Chem.* **1997**, *109*, 2933–2936.

[7] S. Pascal, A. Haefele, C. Monnereau, A. Charaf-Eddin, D. Jacquemin, B. Le Guennic, C. Andraud, O. Maury, *J. Phys. Chem. A* **2014**, *118*, 4038–4047.

[8] a) V. G. Machado, R. I. Stock, C. Reichardt, *Chem. Rev.* **2014**, *114*, 10429–10475; b) F. Effenberger, F. Würthner, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 719–721; *Angew. Chem.* **1993**, *105*, 742–744; c) F. Würthner, G. Archetti, R. Schmidt, H.-G. Kuball, *Angew. Chem. Int. Ed.* **2008**, *47*, 4529–4532; *Angew. Chem.* **2008**, *120*, 4605–4608.

[9] CCDC 1436889 (**1**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[10] For details, see the Supporting Information.

[11] C. R. Ray, J. S. Moore, *Adv. Polym. Sci.* **2005**, *177*, 91–149.

Received: November 16, 2015