Supramolecular Chemistry

DOI: 10.1002/ange.200602286

Fluorescent H-Aggregates of Merocyanine Dyes**

Ulrich Rösch, Sheng Yao, Rüdiger Wortmann, and Frank Würthner**

Dedicated to Professor Hans-Georg Kuball
on the occasion of his 75th birthday

Traditionally, dye aggregates are classified as H- and J-type on the basis of the observed spectral shift of the absorption maximum relative to the respective monomer absorption band (hypsochromic for H-type and bathochromic for J-type).[1–3] Many J-aggregates exhibit fluorescence, and their fluorescence quantum yield quite often surpasses that of the monomeric dyes.[4] In contrast, it is well documented that the fluorescence of H-aggregates is strongly quenched. This behavior was already observed a long time ago for a large number of dimer aggregates of classical fluorophores, including fluorescein, eosin, thionine, methylene blue, and certain cyanine dyes, and the non-emissive character of the excited state became commonly accepted as a general feature of H-aggregates.[5,6]

Theoretical interpretation by Förster (coupled oscillator model) and Kasha (exciton theory) could plausibly explain the nonfluorescent nature of dimeric as well as extended H-type aggregates.[2,7] Two exciton states arise in the case of face-to-face-stacked dimer aggregates, but only the transition to the higher energy exciton state is allowed, and can be observed in the UV/Vis absorption spectrum as a blue-shifted band. Subsequent rapid internal conversion of this excited state into the lower energy exciton state quenches the fluorescence as a result of the decreasing transition probability for a radiative process from this state to the ground state. Only a few exceptions to this rule have been reported, mostly either under special conditions such as at low temperature in frozen solution[8] or for dye aggregates embedded in Langmuir–Blodgett layers.[9] Other more recent examples include tethered mero- and hemicyanine chromophores which can fold into fluorescent H-type aggregates.[10] In these cases, however, the UV/Vis absorption spectra are typically quite different from those of conventional cyanine dye sandwich dimers.

Herein, we report an example of a fluorescent H-aggregate composed of two face-to-face-stacked merocyanine dyes. The observation of fluorescence for this dye aggregate is particularly remarkable because its absorption properties match perfectly those of classical H-type dimer aggregates,[6,8] that is, they show a pronounced hypsochromic shift. According to our earlier studies, dimerization of such strongly dipolar merocyanine dyes is driven by electrostatic interactions that can be related to the magnitude of their dipole moments, that is, the Gibbs binding energy ΔG° is proportional to the square of the ground-state dipole moment μ_g of the dye.[11] As a consequence, these dimer aggregates exhibit a high thermodynamic stability in solvents of low polarity and a well-defined centrosymmetric geometry (Scheme 1).[11,12] These two aspects are advantageous attributes for the current study; ionic cyanine dyes, in contrast, exhibit less predictable aggregate structures and aggregation free enthalpies. Although several of our merocyanine dyes, for example, dyes **1**–**3** were found to form fluorescent dimers,[13] we will focus our attention on merocyanine dye **2**, whose high solubility enabled concentration-dependent investigations even in low-polarity solvents.[14] Furthermore, as a result of the very high dipole moment of this chromophore, significant amounts of dimer aggregates are already formed under the dilute conditions required for fluorescence spectroscopy.

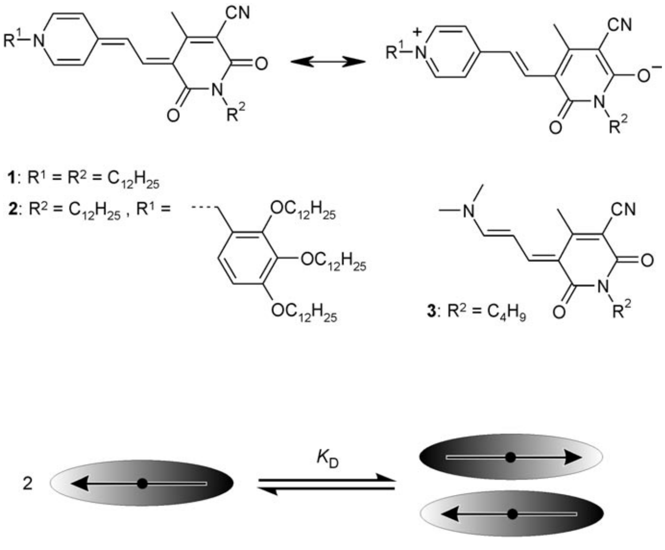
Figure 1 shows the concentration-dependent UV/Vis absorption spectra recorded in dioxane at concentrations between 0.8×10^{-6} and $5.5\times10^{-6}\,\mathrm{mol\,L^{-1}}$. The observed

---

[*] Dr. U. Rösch, Prof. Dr. R. Wortmann[+]
Technische Universität Kaiserslautern
Physikalische Chemie
Erwin-Schrödinger-Strasse, 67663 Kaiserslautern (Germany)
Dr. S. Yao, Prof. Dr. F. Würthner
Universität Würzburg
Institut für Organische Chemie
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4756
E-mail: wuerthner@chemie.uni-wuerzburg.de

[+] deceased on March 13, 2005

[**] This work was supported by the Deutsche Forschungsgemeinschaft. We are grateful to Prof. Gereon Niedner-Schatteburg and Prof. Hans-Georg Kuball (both Physical Chemistry, Kaiserslautern) for helpful discussions and their ongoing support, and to the referees for valuable suggestions.



Scheme 1. Highly dipolar merocyanines **1**–**3** and formation of their dimer aggregates driven by dipole–dipole interactions.

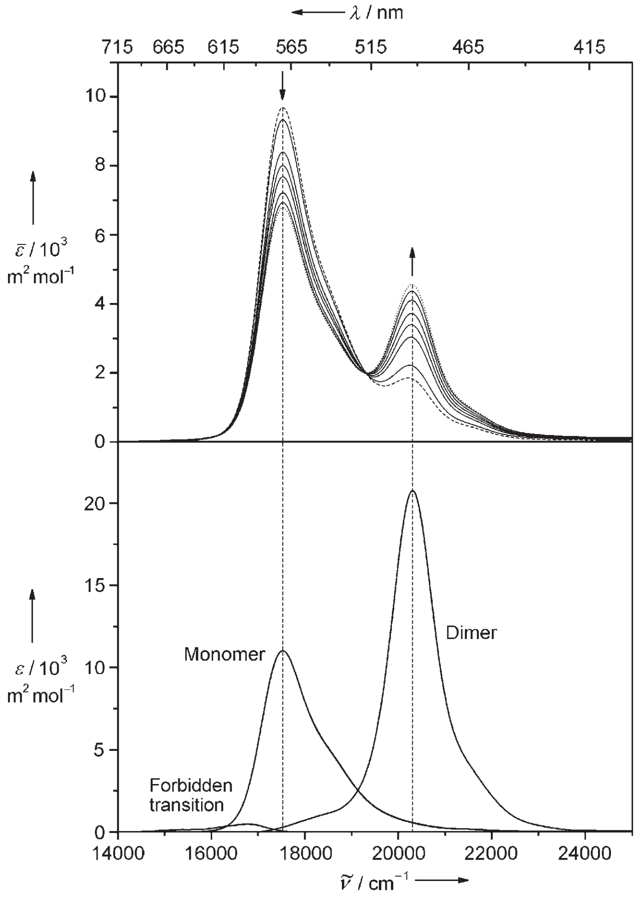


Figure 1. Top: UV/Vis absorption spectra of merocyanine **2** in dioxane at concentrations between 0.8×10^{-6} (dashed line) and 5.5×10^{-6} mol L^{-1} (dotted line) at 298 K. Arrows indicate the changes upon increasing the concentration. Bottom: UV/Vis absorption spectra for the monomer and dimer of merocyanine **2** calculated from the concentration-dependent spectra.

spectral changes and the well-defined isosbestic points at 19 300 cm^{-1} and 16 050 cm^{-1} provide good evidence for an equilibrium between monomeric and dimeric species (Scheme 1) and allow us to calculate the binding constant ($K_D^{298} = 108\,000$ L mol^{-1}) as well as the spectra for the pure monomer and dimer (Figure 1, bottom).[15] It is noteworthy that in addition to the very intense hypsochromically shifted absorption band ($\varepsilon_{max} = 20\,800$ m^2 mol^{-1}) for the dimer, a weak band ($\varepsilon_{max} = 480$ m^2 mol^{-1}) appears at longer wavelength which can be ascribed to the forbidden transition to the lower energy exciton state.

Much to our surprise, an increase in the fluorescence intensity could be observed for solutions of dye **2** upon increasing the concentration, thus suggesting the existence of fluorescent aggregates of the merocyanine dimer. Fluorescence spectra were recorded at excitation wavelengths between 400 and 650 nm in a matrix scan experiment. Figure 2 shows the recorded emission intensities which clearly confirm that the emission arises predominantly from the dimeric species. The strongest emission (black) is observed upon excitation of the dimer at about 480 nm. The pronounced hypsochromic shift of the UV/Vis absorption spectrum upon formation of the dimer aggregate enabled the monomeric and the dimeric species to be excited selectively and their fluorescence spectra to be recorded (Figure 3).

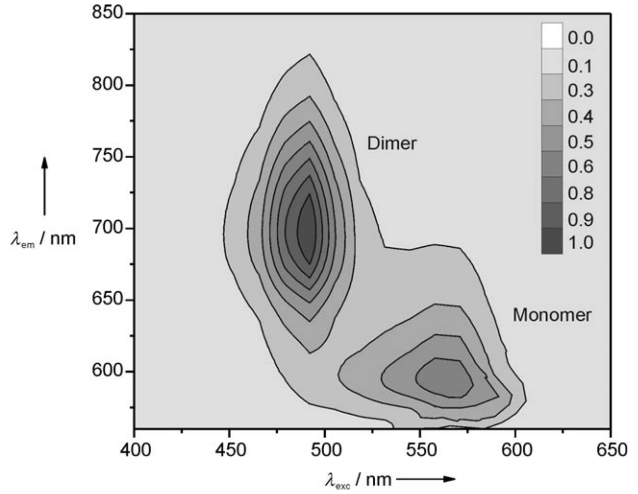


Figure 2. Contour map of the observed fluorescence intensity as a function of the fluorescence excitation λ_{exc} and emission wavelength λ_{em} ("matrix scan") for merocyanine **2** in dioxane at 298 K. Darker shades represent higher intensity.

The absorption and fluorescence spectra of the monomeric dye exhibit no special features. Thus, they are close to mirror images, with a Stokes shift of 780 cm^{-1} between the absorption maximum at $\tilde{\nu}_{max,abs} = 17\,520$ cm^{-1} and the fluorescence maximum at $\tilde{\nu}_{max,fl} = 16\,740$ cm^{-1}. The full width at half maxima (FWHM) values for the absorption band and the fluorescence band were 1360 cm^{-1} and 1810 cm^{-1}, respectively.[16] The broader fluorescence band can be attributed to solvent-dependent influences on the vibronic progression. We have observed such a behavior for many betain-type mero-

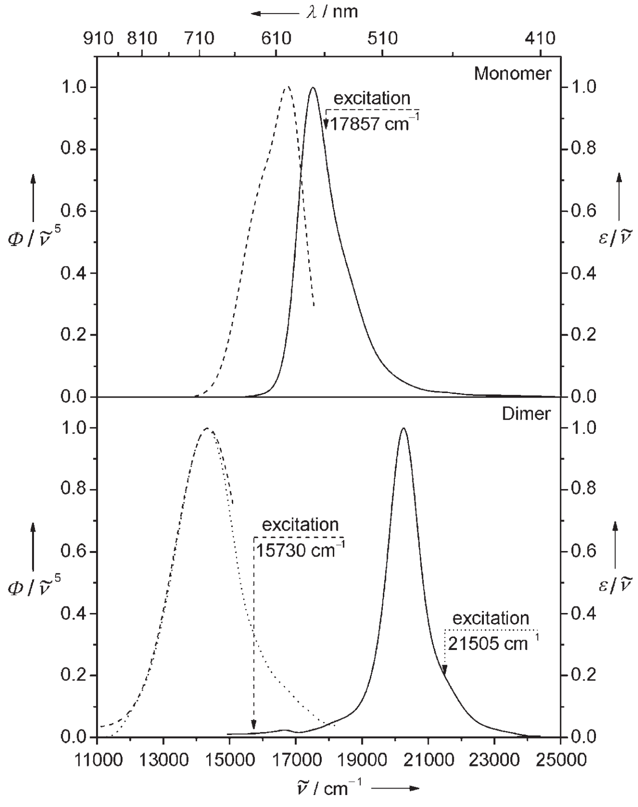


Figure 3. Top: Calculated UV/Vis absorption (solid line) and measured fluorescence (dashed line) spectra of monomeric dye **2** in dioxane at 298 K at a concentration of $c_0 = 8.32\times10^{-7}$ mol L^{-1} (leading to concentrations of the monomeric and dimeric species of $c_M = 7.20\times10^{-7}$ mol L^{-1} and $c_D = 5.59\times10^{-8}$ mol L^{-1}). Bottom: Calculated UV/Vis absorption spectrum (solid line) for dimer aggregates of **2** and the fluorescence spectra upon excitation at 21 505 cm^{-1} (dotted line) and 15 730 cm^{-1} (dashed line) in dioxane at 298 K at a concentration of $c_0 = 1.27\times10^{-6}$ mol L^{-1} (leading to $c_M = 5.70\times10^{-6}$ mol L^{-1} and $c_D = 3.50\times10^{-6}$ mol L^{-1}).

cyanine dyes such as **2** which exhibit a more polar ground state than excited state, as well as negative solvatochromism.

In contrast, the spectra of the dimer were more unusual. First, whilst the absorption spectra of dimer aggregates are typically much broader than those of their monomers, we note a narrowing of the dimer absorption band at $\tilde{\nu}_{\max,\mathrm{abs}} = 20330$ cm^{-1} for merocyanine dye **2** (FWHM = 1160 cm^{-1}). Second, the fluorescence band is observed at a rather long wavelength, that is, $\tilde{\nu}_{\max,\mathrm{fl}} = 14350$ cm^{-1} (FWHM = 2180 cm^{-1}). Most remarkably, the same fluorescence spectrum could be recorded upon excitation of the dimer aggregate at the tail of its weak low-energy absorption band (Figure 3). This observation provides unequivocal evidence that the dimer emission originates from the lower exciton state of the aggregated dimeric species. These observations by steady-state fluorescence spectroscopy were further substantiated by time-resolved fluorescence measurements, which showed two independent fluorescence lifetimes, a short one of 0.5 ns for the monomeric and a longer one of 4.4 ns for the dimeric species.[16]

These results confirm that a unique example of a fluorescent merocyanine H-type dimer aggregate is provided. Although our present observation seems to contradict the common perception that H-aggregates are not fluorescent, it complies with the exciton coupling theory.[2,3] Accordingly, the presence of the small but detectable absorption band at 16 780 cm^{-1} results in a nonvanishing transition probability between the ground and the lowest exciton state from which a weak fluorescence arises. This weak band may emanate from vibronic coupling or a small rotational twist between the two chromophores. Indeed, the latter interpretation is in accordance with our earlier electrooptical absorption (EOA) studies that revealed a small ground-state dipole moment for these dimer aggregates.[12,17] On the other hand, X-ray crystallographic data[11] as well as the optimized dimer geometry according to MP2/6-31G(d,p) calculations[18] show a perfectly centrosymmetric dimeric unit as the energetically preferred geometry (Figure 4).

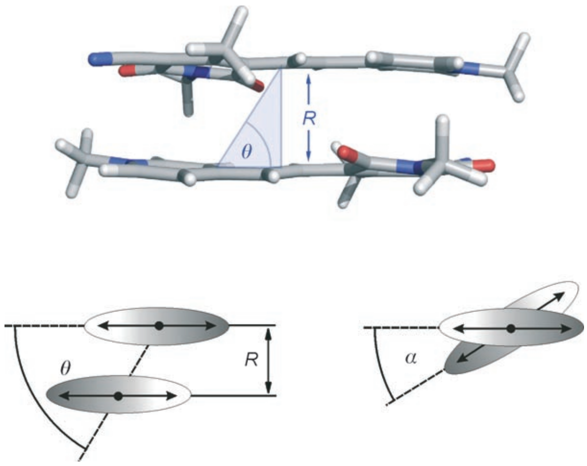


Figure 4. Top: MP2/6-31G(d,p)-optimized structure of the dimer aggregate of **2** with $\theta = 58.2°$ and $R = 3.25$ Å (all alkyl substituents have been replaced by methyl groups in the calculation). Bottom: Structural model (left: side view, right: top view) for the calculation of the exciton coupling between the transition dipole moments indicated as double arrows in the dimer aggregates arising from the distance R, the slipping angle θ, and the rotational angle α.

From the spectral deconvolution provided in Figure 3 we can calculate the transition dipole moments between the ground state and the allowed and forbidden exciton states $\mu_{\mathrm{ag}}^{\mathrm{D}} = 59.4\times10^{-30}$ C m and $\mu_{\mathrm{ag}}^{\mathrm{D2}} = 5.2\times10^{-30}$ C m. From these transition dipole moments, the transition dipole moment of the monomer $\mu_{\mathrm{M}}^{\mathrm{ag}} = 43.6\times10^{-30}$ C m, and the energy difference $V_{\mathrm{AB}} = hc(\tilde{\nu}_{\mathrm{D}}^{\mathrm{ag}} - \tilde{\nu}_{\mathrm{D2}}^{\mathrm{ag}}) = hc\Delta\tilde{\nu}_{\mathrm{D-D2}}^{\mathrm{ag}}$ between the two exciton states we can now obtain the angles $\theta = 59.9°$ and $\alpha = 10.0°$ from Equations (1) and (2).[2,19]

$$\frac{\mu_{\mathrm{ag}}^{\mathrm{D2}}}{\mu_{\mathrm{ag}}^{\mathrm{D}}} = \frac{(1-\cos\alpha)}{(1+\cos\alpha)} = \tan^2\left(\frac{\alpha}{2}\right) \tag{1}$$

$$V_{\mathrm{AB}} = \frac{2}{4\pi\varepsilon_0}\frac{(\mu_{\mathrm{ag}}^{\mathrm{M}})^2}{R^3}(\cos\alpha - 3\cos^2\theta)(\sin^3\theta) \tag{2}$$

If we consider the well-known deficiencies of the point dipole approximation,[3] the excellent agreement of these results with the geometry derived by XRD, NMR spectroscopy, and electrooptical absorption spectroscopy is remarkable.[11,12,17] The very small rotational twist of 10° is energetically only slightly disfavored according to our calculations[18] and is thus easily accessible in solution, either by a solvent effect or by the thermal energy provided at room temperature.

The fluorescence intensity of such a dimer should, however, be much weaker than the emission of the monomeric dye, which exhibits a strongly allowed $S_1 \leftarrow S_0$ transition. As a consequence, similar to other dimer aggregates, we might have expected that the fluorescence band corresponding to the dimer should be hidden beneath a more intense monomer band. The fact that nicely resolved fluorescence spectra of the dimer could be observed without any overlapping emission from the monomer in the given example can be attributed to the very weak fluorescence intensity (quantum yield $\Phi_f \approx 0.1\,\%$) of the monomeric dyes. The latter is a result of a rapid nonradiative deactivation pathway through a bond-twisting mechanism, as observed for most cyanine and merocyanine dyes,[20] which leads to fast rates of fluorescence decay. In accordance with this mechanistic picture, many polymethine dyes show increased fluorescence intensities after they have been rigidified by chemical or physical measures.[21] Thus, it is reasonable to assume that the major nonradiative decay channel for the excited monomeric dye **2** which causes the fast decay (0.5 ns) is suppressed upon formation of a tightly bound dimer aggregate that remains stable at least on the time scale of the observed fluorescence decay time of 4.4 ns.

In conclusion, we have presented a unique example of a merocyanine H-aggregate which exhibits a well-resolved fluorescence spectrum and a significantly longer fluorescence lifetime relative to its monomer.[22] These unexpected findings could be rationalized within the concept of exciton theory by taking into account the small transition probability caused by a slight rotation of the two coupled dyes in the excited state as well as the rigidification of the polymethine chain in the closely π-π-stacked sandwich aggregate.

Received: June 7, 2006
Revised: August 11, 2006

Keywords: chromophores · dye aggregates · dyes/pigments · fluorescence · supramolecular chemistry

---

[1] a) A. H. Herz, *Adv. Colloid Interface Sci.* **1977**, *8*, 237 – 298; b) F. Dietz, *J. Signalaufzeichnungsmater.* **1973**, *3*, 157 – 180 (Part 1) and F. Dietz, *J. Signalaufzeichnungsmater.* **1973**, *4*, 237 – 252 (Part 2).

[2] M. Kasha, H. R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371 – 392. For good reasons, the expressions H- and J-aggregate have been avoided in this seminal paper on the theoretical description of dimer aggregate spectra by exciton theory. According to this theory as well as more elaborate ones (see Ref. [3]), for the majority of possible dimer geometries two absorption bands arise, one at higher ("H-band") and one at lower ("J-band") energy relative to the monomer band. Thus, spectra of perfect H- and J-aggregates (where the transition to one of the two exciton states is fully forbidden) will only occur for the special situation of a perfect parallel or antiparallel orientation of the two dyes in the dimer aggregate. Despite these facts, dye aggregates are most commonly classified as H- and J-type on the basis of their most intense absorption band. Accordingly, we regard aggregates of merocyanines **1**–**3** as typical representatives of H-type dimer aggregates.

[3] a) V. Czikklely, H. D. Försterling, H. Kuhn, *Chem. Phys. Lett.* **1970**, *6*, 207 – 210; b) H. Kuhn, C. Kuhn in *J-Aggregates* (Ed.: T. Kobayashi), World Scientific, Singapore **1996**, pp. 1 – 40; for a recent study by time-dependent quantum methodology with special emphasis on rotational displacements in perylenebisimide aggregates, see: c) J. Seibt, P. Marquetand, V. Engel, Z. Chen, V. Dehm, F. Würthner, *J. Chem. Phys.*, DOI:10.1016/j.chemphys.2006.07.023.

[4] a) G. Scheibe, *Z. Elektrochem.* **1948**, *52*, 283 – 292; b) D. Möbius, *Adv. Mater.* **1995**, *7*, 437 – 444; c) *J-Aggregates* (Ed.: T. Kobayashi), World Scientific, Singapore, **1996**.

[5] a) W. L. Lewschin, *Z. Phys.* **1927**, *43*, 230; b) E. Rabinowitch, L. Epstein, *J. Am. Chem. Soc.* **1941**, *63*, 69.

[6] a) T. Förster, E. König, *Z. Elektrochem.* **1957**, *61*, 344 – 348; b) K. Bergmann, C. T. O'Konski, *Z. Phys. Chem.* **1963**, *67*, 2169 – 2177; c) W. West, S. Pearce, *J. Phys. Chem.* **1965**, *69*, 1894 – 1903.

[7] T. Förster, *Naturwissenschaften* **1946**, *33*, 166 – 175.

[8] a) N. Cooper, N. B. Liebert, *Photogr. Sci. Eng.* **1972**, *16*, 25; b) R. W. Chambers, T. Kajiwara, D. R. Kearns, *J. Phys. Chem.* **1974**, *78*, 380 – 387; c) K. Teuchner, B. Bornowski, W. Becker, S. Dähne, *Z. Chem.* **1976**, *16*, 449 – 450; d) S. K. Rentsch, D. Fassler, P. Hampe, R. Danielius, R. Gadonas, *Chem. Phys. Lett.* **1982**, *89*, 249 – 253; e) V. Sundstöm, T. Gillbro, *J. Chem. Phys.* **1985**, *83*, 2733 – 2743; f) M. van der Auweraer, G. Biesmans, F. C. De Schryver, *Chem. Phys.* **1988**, *119*, 355 – 375.

[9] M. van der Auweraer, B. Verschuere, F. C. De Schryver, *Langmuir* **1988**, *4*, 583 – 588.

[10] a) L. Lu, R. J. Lachicotte, T. L. Penner, J. Perlstein, D. G. Whitten, *J. Am. Chem. Soc.* **1999**, *121*, 8146 – 8156; b) S. Zeena, K. G. Thomas, *J. Am. Chem. Soc.* **2001**, *123*, 7859 – 7865.

[11] F. Würthner, S. Yao, T. Debaerdemaeker, R. Wortmann, *J. Am. Chem. Soc.* **2002**, *124*, 9431 – 9447.

[12] R. Wortmann, U. Rösch, M. Redi-Abshiro, F. Würthner, *Angew. Chem.* **2003**, *115*, 2126 – 2129; *Angew. Chem. Int. Ed.* **2003**, *42*, 2080 – 2083.

[13] U. Rösch, PhD thesis, Technische Universität Kaiserslautern, **2006**.

[14] S. Yao, U. Beginn, T. Greß, M. Lysetska, F. Würthner, *J. Am. Chem. Soc.* **2004**, *126*, 8336 – 8348.

[15] In contrast to our earlier work,[11] in this study the nonlinear regression analysis was performed by taking into account the complete set of spectral data.

[16] The FWHM values have been calculated from Figure 3. If we plot the absorption data on a ε scale we obtain slightly different FWHM values of 1410 cm^{-1} for the monomer and 1160 cm^{-1} for the dimer band. If the fluorescence spectra are scaled against the measured intensity we obtain FWHM values of 1550 cm^{-1} for the monomer and 2260 cm^{-1} for the dimer band. All fluorescence measurements have been performed on a Jobin–Yvon Fluorolog 3–22 Tau instrument. The decay times were evaluated by applying single exponentials to the time-resolved measurements in the frequency domain.

[17] In our earlier study electooptical absorption (EOA) spectroscopy provided evidence for a non-disappearing ground-state dipole moment for the dimeric species and a value of 22×10^{-30} C m could be estimated (see Ref. [12], Table 1). If we now include the rotational angle of 10° obtained from this study into the formula for the evaluation of the EOA data, a more reliable value of 16×10^{-30} C m can be obtained for the dipole moment of the dimer aggregate. This value is in excellent agreement with the dipole

moment of 14 × 10^{-30} C m at a torsion angle of $\alpha = 10°$ calculated at the MP2/6-31G(d,p) level of theory. However, we would like to point out that we are not yet sure if the small transition dipole moment for the lower energy excitonic transition that arises from such a small torsional twist of 10° is sufficient to explain the observed intensity of the dimer fluorescence. Alternatively, a relaxation of the Franck–Condon excited state could be taking place that affords an even more twisted excited state geometry which exhibits an increased radiative transition probability.

[18] All ab initio calculations were done with *Gaussian 03*, Revision C.02, Gaussian, Inc., Wallingford CT **2004**.

[19] K. K. Rohatgi-Muskerjee, *Indian J. Chem. Sect. A* **1992**, *31*, 500–511.

[20] a) H. Ephardt, P. Fromherz, *J. Phys. Chem.* **1989**, *93*, 7717; b) R. F. Khairutdinov, N. Serpone, *J. Phys. Chem. B* **1997**, *101*, 2602–2610; c) V. Karunakaran, J. L. P. Lustres, L. Zhao, N. Ernsting, O. Seitz, *J. Am. Chem. Soc.* **2006**, *128*, 2954–2962.

[21] Intense fluorescence has been reported for several merocyanine dyes upon rigidification in frozen solution, the solid state, or in an organogel; see, for example, a) F. Würthner, R. Sens, K.-H. Etzbach, G. Seybold, *Angew. Chem.* **1999**, *111*, 1753–1757; *Angew. Chem. Int. Ed.* **1999**, *38*, 1649–1652; b) S. Yagai, M. Higashi, T. Karatsu, A. Kitamura, *Chem. Commun.* **2006**, 1500–1502.

[22] An even longer fluorescence lifetime of 11.2 ns has been observed for dimers of dye **3**, see Ref. [13].