Dye Assemblies

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Gelation-Assisted Control over Excitonic Interaction in Merocyanine Supramolecular Assemblies**

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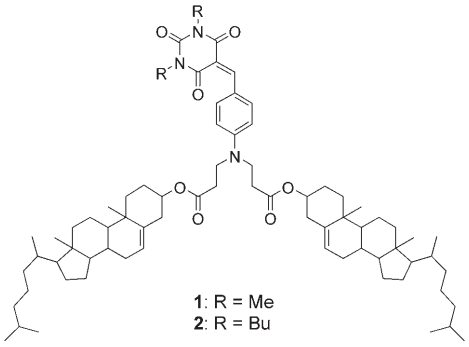
One of the most fascinating aspects of functional dye assemblies is their variable optical properties, which depend on the chromophore packing arrangements through excitonic interactions.[1] Archetypal examples might be chlorophyll arrays in light-harvesting complexes of photosynthetic bacteria, in which the chromophore packing can be rationally controlled by protein scaffolds, thereby diversifying their optical properties.[2] Thus, the exploitation of artificial dye assemblies in which the chromophore packing arrangements and the resulting optical properties can be controlled by some means is a fascinating avenue of research.[3] One possible approach might be the application of the "organogelation" phenomenology by which fibrous supramolecular assemblies can be obtained from low-molecular-weight compounds as solvent-incorporated soft materials, because a very subtle balance between the structures of gelators and the solvent characters can have a dramatic impact on local packing arrangements of the building blocks as well as self-assembled nanostructures.[4]

Merocyanines are an important class of dyes and represent promising nonlinear optical and photorefractive materials owing to their donor–π–acceptor (D–π–A) structures.[5] This structural character also makes these dyes attractive as supramolecular components because different chromophore packing or spatial arrangements result in prominent changes in their optical properties through excitonic interactions.[6–8] Covalently tethered merocyanine dimers are interesting examples in that their optical properties can be tuned through the control of the relative orientation of two merocyanine chromophores by selecting the media.[7] Other examples include merocyanine assemblies supported by specific noncovalent interactions such as multiple hydrogen bonds, which show drastic changes in their optical and electronic properties.[8] We report herein that the aggregation of cholesterol-appended merocyanines with minor structural differences in various organic solvents results in the formation of organogels with dramatically different chromophore packing, thus giving rise to distinct optical properties through excitonic interactions.

To endow merocyanines with definitive gelation ability in organic solvents,[9] we selected the cholesterol group as a gelation auxiliary. The cholesterol group has been effectively utilized to endow functional dyes with excellent gelation ability for various organic solvents.[10] Shinkai and co-workers conjugated cholesterol to azobenzene,[11] a porphyrin,[12] perylene bisimide,[13] and oligothiophene[14] to fabricate various functional organogels. Ajayaghosh et al. reported on cholesterol-appended oligo(*p*-phenylenevinylene) gelators for which the chromophore packing can be controlled by the substitution patterns of the cholesterol group.[15] These studies corroborate the versatility of the cholesterol group for organizing functional chromophores to gel-like materials. In this work we combine a barbituric acid type merocyanine dye with the cholesterol group as in compounds **1** and **2**[16] to address gelation-assisted control over the packing arrangements of merocyanine self-assemblies.



1: R = Me
2: R = Bu

While investigating proper substituents R on the barbituric acid moiety of merocyanines for gelating organic solvents, we found that the *N*,*N*′-dimethyl derivative **1** gelates cyclohexane whereas *N*,*N*′-dibutyl derivative **2** gelates acetone.[16] This result demonstrates that the substituents on the barbituric acid moiety have a great impact on their gelation properties. Polarized optical microscopy (POM) showed that the acetone gel of **2** is more birefringent than the cyclohexane gel of **1**, indicating a higher degree of molecular anisotropy in the former (insets in Figure 1 a,b). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) of the spin-coated gels reveal that the acetone gel of **2** consists of

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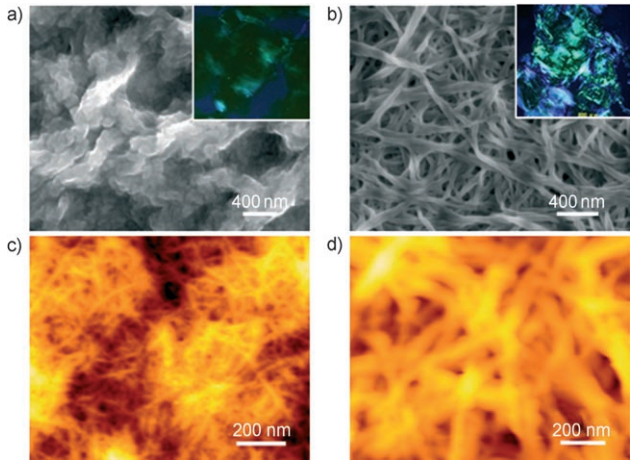

Figure 1. Microscopy images of the cyclohexane gel of **1** (a,c) and the acetone gel of **2** (b,d). a,b) FE-SEM images of the spin-coated gels; insets show the corresponding POM images of the pristine gels ($c = 2 \times 10^{-3}$ M), 600×600 μm^2; c,d) AFM height images of the spin-coated gels.

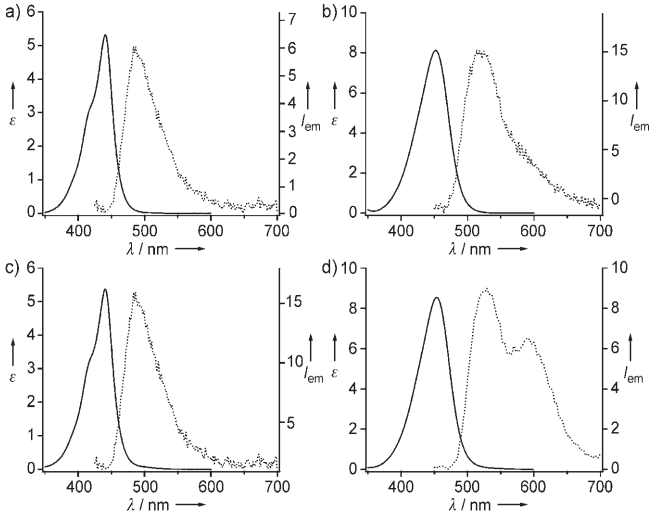

Figure 2. UV/Vis absorption (solid lines, left axes (ε in 10^4 M^{-1} cm^{-1})) and fluorescence spectra (dotted lines, right axes, $\lambda_{ex} = 400$ nm) of a) **1** in cyclohexane, b) **1** in acetone, c) **2** in cyclohexane, and d) **2** in acetone. Concentration $= 1.0 \times 10^{-5}$ M.

nanofibers with an average width of 100 nm (Figure 1 b,d).[16] In contrast, SEM images of the cyclohexane gel of **1** only shows fused, irregular structures (Figure 1 a). The fine structures could be visualized only with AFM, whereby thinner fibers of about 20 nm in width are entangled (Figure 1 c).[16] These observations at the microscopic level suggest that elemental aggregates of **2** in acetone have ordered structures capable of hierarchically organizing into larger nanoscopic fibers. In contrast, the elemental aggregates of **1** in cyclohexane are dispersed at a level closer to the molecular scale (the molecular width of **1** is 4 nm), and the gels are thereby supported by much finer fibrous networks. This interpretation is supported by the significantly higher gel-to-sol transition temperature (T_{gel}) and lower minimum gelation concentration (c_{min}) for the cyclohexane gel of **1** ($T_{gel} = 65\,^{\circ}$C at $c = 2 \times 10^{-3}$ M, $c_{min} = 1 \times 10^{-3}$ M) compared to the acetone gel of **2** ($T_{gel} = 40\,^{\circ}$C at $c = 2 \times 10^{-3}$ M, $c_{min} = 2 \times 10^{-3}$ M).[17]

UV/Vis absorption spectra of molecularly dissolved **1** and **2** in cyclohexane and acetone under diluted conditions (1×10^{-5} M) show intramolecular charge transfer (ICT) absorption bands of the merocyanine chromophore in the 350—500-nm wavelength region which are almost independent of the substituents on the barbituric acid moiety in the respective solvents (solid lines in Figure 2). The absorption maxima in cyclohexane are located at $\lambda = 440$ nm, whereas in acetone they move to $\lambda = 460$ nm because the excited state is more charge-separated than the ground state (positive solvatochromism).

Although the emission intensities of molecularly dissolved **1** and **2** are very weak ($\Phi_f < 0.01$) owing to the nonradiative decay associated with the twisting of the C=C bond between D and A groups in the excited state, an explicit difference was observed between the two. In cyclohexane the fluorescence maxima of the two compounds emerge at $\lambda = 486$ nm (dotted lines in Figure 2 a,c), and no difference is detected between the two. In acetone, however, an emission at $\lambda_{max} = 592$ nm contributes significantly only to the spectrum of **2** in addition to the emission from the monomer at $\lambda_{max} = 520$ nm (dotted lines in Figure 2 b,d). This new emission from **2** is attributable to an excimer fluorescence from its large Stokes shift (4847 cm^{-1}) and long lifetime ($\tau = 4.9$ ns) in comparison with that of the monomer ($\tau = 0.3$ ns).[7b] The formation of excimer species is rationalized in terms of the increased intermolecular charge-transfer interaction in the polar solvent. The absence of excimer species of **1** in acetone can be explained by the decreased solvophobicity on the barbituric acid moiety lacking butyl groups.

A significant consequence arising from the gelation by **1** and **2** is the quite distinct optical properties of the gels. The absorption spectrum of the cyclohexane gel of **1** is characterized by a new maximum at 460 nm, red-shifted by 20 nm from the molecularly dissolved state in the same solvent (red solid line in Figure 3 a). In sharp contrast, the maximum of the acetone gel of **2** is located at 425 nm (red solid line in Figure 3 b), blue-shifted by 35 nm from the molecularly dissolved state in the same solvent. In addition, significant absorption tailing is observed up to 600 nm, making this gel more of a red color (left insets in Figure 3 a,b). These spectral features are not observed for concentrated solutions ($c = 5 \times 10^{-3}$ M) of **1** in acetone and **2** in cyclohexane, indicating that they are characteristic for the aggregation of the respective dyes in specific solvents. Although the observed spectral changes are reminiscent of J- and H-type aggregation, they are considerably different from those reported for J- and H-aggregates of (mero)cyanines in view of their small absorption shifts. We rather ascribe these spectral changes to the formation of aggregates consisting of exciton-coupled antiparallel *dimeric units* in which the degrees of rotational displacements around the stacking axis are significantly different.[1,18] Judged from the shifted values, rotational displacement is more pronounced for **1**, leading to weaker exciton coupling. Such a difference in packing arrangements

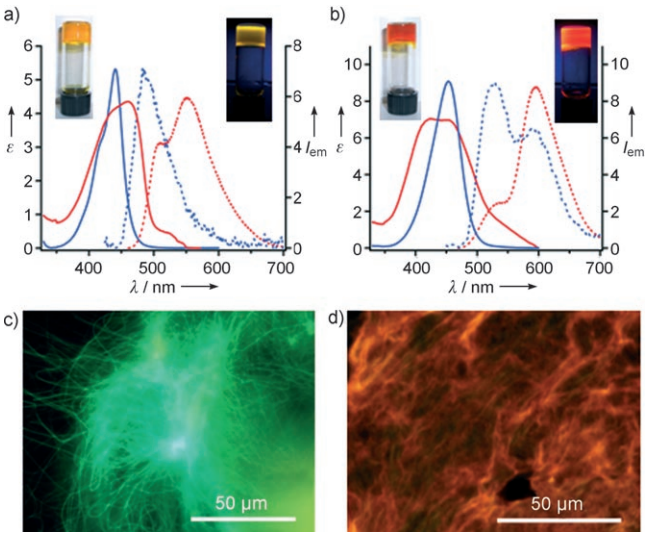

Figure 3. a,b) UV/Vis (red solid lines) and fluorescence spectra (red dotted lines) of a) the cyclohexane gel of **1** and b) the acetone gel of **2** ($c = 2 \times 10^{-3}$ M, $l = 0.1$ mm, $\lambda_{ex} = 430$ nm). The spectra of corresponding diluted solutions ($c = 1.0 \times 10^{-5}$ M) are also shown by blue lines for comparison. Insets: photographs of the gels under daylight (left) and under UV light (right). c,d) Fluorescence microscopy images ($\lambda_{ex} = 365$ nm, $\lambda_{em} > 450$ nm) of c) the cyclohexane gel of **1** and d) the acetone gel of **2**.

alters the emission properties of the merocyanine skeleton as described below.

When the above gels were illuminated with UV light, the cyclohexane gel of **1** exhibited a yellow emission whereas the acetone gel of **2** exhibited a red emission despite the fact that the emissions come from the same merocyanine skeleton (right insets in Figure 3 a,b). The fluorescence spectra of the gels measured with a front-face illumination setup display maxima at 550 nm for **1** and at 592 nm for **2** (red dotted lines in Figure 3 a,b). The 550-nm emission of **1** was shifted by 64 nm from the molecularly dissolved state in diluted cyclohexane solutions (Figure 2 a), indicating that the emission is derived from exciton-coupled chromophores, which was further supported by the fluorescence excitation spectra. On the contrary, the 592-nm emission of **2** was already observed for the corresponding diluted acetone solutions as excimer fluorescence (Figure 2 d), suggesting that the excimer formation is promoted by aggregation. Aggregation-induced excimer formation[19] has been reported for several dyes such as perylene bisimides[20] and a triphenylene derivative[21] as well as covalently tethered merocyanines.[7b]

Fluorescence microscopy of the pristine (nondried) gels provides further direct evidence for the occurrence of different exciton coupling in **1** and **2**. As shown in Figure 3 c,d, fibrous entities emanating green and red fluorescence could be visually observed for the cyclohexane gel of **1** and the acetone gel of **2**, respectively, the colors of which are consistent with the emission maxima of the respective gels. Above the gel-to-sol transition temperatures, these fluorescent fibers become invisible. Notably, **1** shows uniformly dispersed fluorescent fibers, which are in clear contrast to agglomerated fibrous networks of **2**. These highly contrasting images are consistent with the morphological insights given by SEM and AFM.

Thus, aggregation of **1** and **2** occurs in different solvents, affording fibrous nanostructures consisting of antiparallel dimeric units with different degrees of rotational displacement. Although such a difference in the degree of rotational displacement between **1** and **2** can partly be attributed to the steric effect of the substituents on the barbituric acid moiety, we believe that the degree of charge localization in the merocyanine D–π–A system may have some contribution: The charge-localized character of the present merocyanine skeleton is more pronounced in polar acetone (permittivity $\varepsilon = 2.0$) than in cyclohexane ($\varepsilon = 20.7$), thus reducing the rotational displacement by stronger intermolecular D–A interaction.

Finally, we present the unique morphological transformation observed for the nanofibers of **2** in acetone. While the cyclohexane gel of **1** is thermodynamically stable, the acetone gel of **2** proved to be a kinetic product that changes into thermodynamically more stable materials upon aging for a few days after gelation. This result was recognized by the increase of turbidity, indicating the formation of macroscopic aggregates. Surprisingly, SEM revealed that the turbid gels consist of globular objects with diameters at around 10 μm (Figure 4 a).[22] The globular objects are abirefringent, indicating a lack of long-range molecular anisotropy. Magnified imaging allowed visual observation of their grainy surface (inset in Figure 4 a), suggesting that they are constructed through the hierarchical association of smaller objects. Of particular interest is their emission behavior: They no longer emanate the original red fluorescence but emit in green (inset in Figure 4 b). The fluorescence spectra of the thermodynamic gels are dominated by the emission with a maximum at 518 nm (Figure 4 b), which corresponds to the fluorescence of

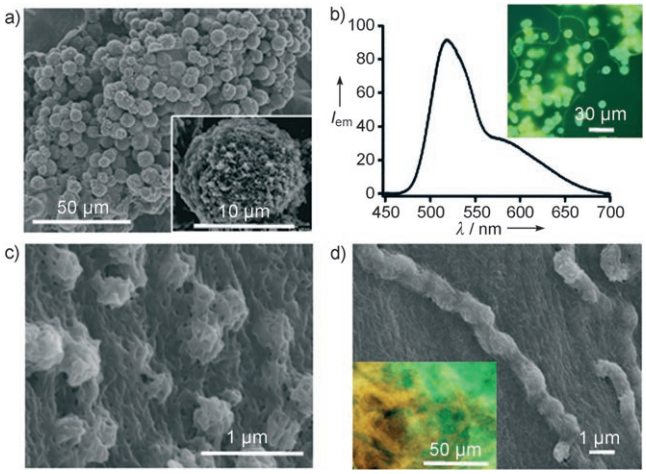

Figure 4. a) SEM image and b) fluorescence spectrum ($\lambda_{ex} = 430$ nm) of the thermodynamically stable acetone gel of **2**. The SEM image was taken after vacuum drying. Inset in (a) is a magnified image of a globule. Inset in (b) is the corresponding fluorescence microscopy image ($\lambda_{ex} = 365$ nm, $\lambda_{em} > 450$ nm). c,d) SEM images of transient gels. Inset in (d) is the fluorescence microscopy image in the corresponding state.

the monomer in acetone. Although we could not obtain reliable UV/Vis data of these globular micro-objects, the observed fluorescence property verifies that the fiber-to-globule transition is not a simple morphological transformation of nanoscopic objects, but is a result of the transition from kinetically formed exciton-coupled aggregates to thermodynamically stable non-exciton-coupled aggregates.[23]

To get some mechanistic insight into the above fiber-to-globule transition, *transient gels* obtained by different aging periods were spin-coated and observed by SEM.[16] The collected images clearly showed that the fiber-to-globule transition progresses in a manner reminiscent of fluff balls appearing on a sweater. Initially, the elemental fibers with 100-nm width start to entangle into globular clumps with diameters less than 1 μm (Figure 4c). These globular clumps subsequently fuse quasi-one-dimensionally, affording fibrous clumps composed of entangled elemental fibers (Figure 4d, and Figure S3c in the Supporting Information). Finally, these fibrous clumps further cohere and entangle to give the final products (Figure S3d in the Supporting Information). Fluorescence microscopic observation of a transient stage impressively showed the coexistence of fibrous networks exhibiting either red or green emissions, respectively (inset in Figure 4d, and Figure S4 in the Supporting Information). Thus, the kinetic assembly of merocyanine **2** into gel-forming nanofibers in acetone is presumably driven by the equal contribution of the dipole–dipole interaction between the merocyanine parts and the solvophobic interactions between the cholesterol groups. Molecular packing of the cholesterol moieties in such nanofibers is, however, considered not optimal, so that once a thermodynamic process toward optimal packing of cholesterol moieties starts, as demonstrated by the fibers–globule transition, exciton-coupled aggregates might be broken, thereby showing monomeric fluorescence.

In summary, the results described here demonstrate that a minor structural alteration of the cholesterol-appended merocyanine dyes results in the formation of organogels in organic solvents with different polarities, affording nanoscopic fibers with pronouncedly distinct absorption and fluorescence properties. This gelation-assisted control over the optical properties of the merocyanine chromophores is a consequence of different chromophore packing arrangements within the nanofibers through excitonic interactions. We have also presented an interesting example of the morphological transition from kinetically formed nanofibers to thermodynamically stable globules with the disappearance of excitonic interactions between the chromophoric building blocks. Thus, this study can expand the potential applicability of organogelation for fabricating functional dye assemblies featuring unique chromophore packing arrangements and optical properties which cannot be achieved by solution and solid-state chemistries.

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