# Tunable interchromophore electronic interaction of a merocyanine dye in hydrogen-bonded supramolecular assemblies scaffolded by bismelamine receptors†

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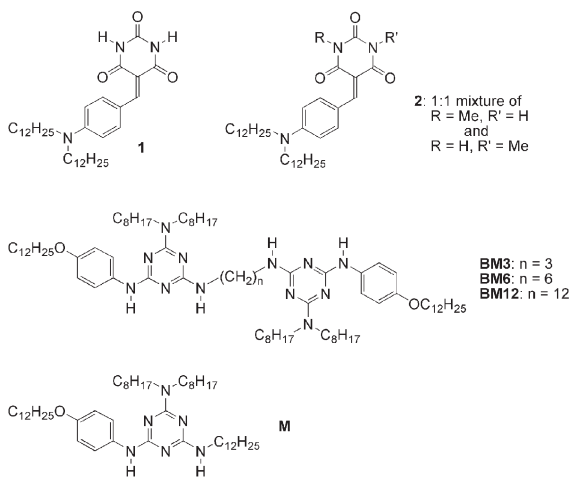
**The absorption and fluorescence properties of a barbiturate-type donor–π–acceptor (D–π–A) merocyanine dye are controlled by complexation with dimeric melamine receptors featuring different tether lengths.**

Control of interchromophore electronic interaction is a pivotal topic both in biological systems and in organic optoelectronics.[1] Light-harvesting/emitting and energy/electron transferring properties are all dramatically influenced by electronic interactions between dyes. In photosynthetic apparatus, the electronic interactions between chlorophyllous pigments are dexterously tuned by protein scaffolds *via* noncovalent interactions.[2] Thus, construction of well-defined chromophoric supramolecular assemblies featuring tunable interchromophore electronic interactions is a challenging topic for the exploitation of novel optoelectronic nanomaterials.[3] Here we report on novel chromophoric supramolecular assemblies where the interchromophore electronic interaction of a barbiturate-functionalized merocyanine dye (**1**) is dramatically tunable by complexation with bismelamine (**BM**) receptors. **BM**s are dimeric melamines where the triaminotriazine monotopic hydrogen-bonding sites are tethered through flexible alkyl chains with different carbon numbers ($n$ = 3, 6 and 12).[4]

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† Electronic supplementary information (ESI) available: Detailed description of the complexation between **1** and **M** and the dilution experiments for **1**–**BM6** and **1**–**BM12**, fluorescence spectrum of **1**–**M**, excitation spectra and $^1$H NMR spectra of the complexes, molecular modeled structure of **1**·**BM6** and experimental details. See DOI: 10.1039/b516698e

Though merocyanine **1** and its analogues are versatile supramolecular building blocks owing to their D–π–A dipolar character and hydrogen-bonding ability,[5] less attention has been devoted to their emission properties, because in solution their excited state nonradiatively decays *via* the twisting of the C=C bond connecting D and A groups.[5c] **1** is marginally soluble in aliphatic solvents such as methylcyclohexane (MCH) at ambient temperature. The absorption spectrum of the saturated solution (*ca.* $10^{-5}$ M) exhibits an intermolecular charge transfer (ICT) band at $\lambda_{max}$ = 456 nm. This band follows Lambert–Beer's law upon dilution, indicating the absence of intermolecular electronic interaction between dyes dissolved in MCH. Monomeric **1** exhibits very weak fluorescence at 528 nm with the fluorescence quantum yield ($\Phi_f$) of 0.0029.

Binding of diaminopyridine type receptors to the two imide functionalities of **1** *via* complementary DAD·ADA hydrogen-bonding interaction moderately affects its absorption spectrum. Concentration-dependent ($2 \times 10^{-6}$ M to $3 \times 10^{-4}$ M) absorption spectra of the 1 : 2 molar mixture of **1** and monotopic melamine **M** in MCH show a small red-shift of the ICT band of **1** from $\lambda_{max}$ = 456 to 465 nm upon increasing concentration, indicating the transition of the monomeric blend to the hydrogen-bonded 1 : 2 complex (**M**·**1**·**M**).[6] From the plot of the mole fraction of the complexed **1** *versus* the concentrations, the concentration threshold at which the dye starts to interact with **M** is estimated as *ca.* $2 \times 10^{-6}$ M.[7] Complexed **1** is weakly emissive at around 515 nm ($\Phi_f < 0.01$), indicating the hydrogen-bonding has a negligible influence on the emission properties of **1**.

Addition of 1 equiv. of ditopic **BM**s increases the solubility of **1** in MCH (over $10^{-2}$ M) by the formation of stable assemblies *via* complementary hydrogen-bonding. The resulting homogeneous solutions showed remarkable changes in their absorption spectra, indicating that the ground-state interchromophore electronic interaction of **1** depends on the tether length of the bismelamines.

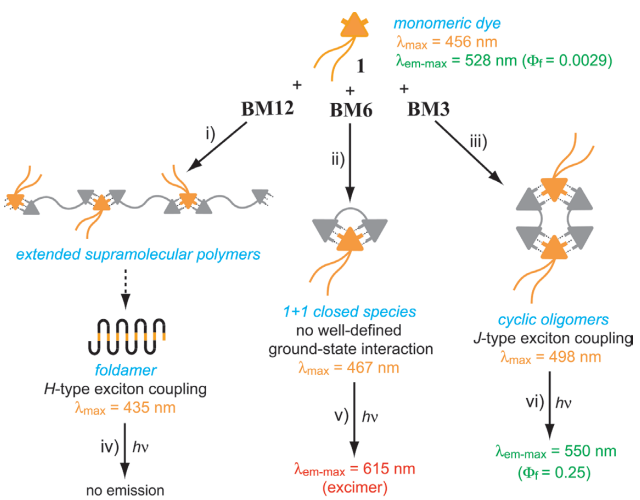
At low concentrations around $10^{-5}$ M, the mixtures of **1**–**BM12** and **1**–**BM6** showed analogous absorption spectra with $\lambda_{max} \approx$ 467 nm, indicating the fully complexed chromophores. Dilution experiments implied that these components form Hamilton-type 1 + 1 closed species at low concentrations.[4c,7,8] When these mixtures were condensed, a dramatic difference was found between **BM12** and **BM6**, depending on the stability of the 1 + 1 closed species. As reported previously,[4b] the 1 + 1 closed species **1**·**BM12** undergoes chain-opening supramolecular polymerization upon increasing concentration because of the conformational flexibility of the dodecamethylene tether. Dynamic light scattering (DLS) revealed that the average particle size reaches *ca.* 90 nm

even at 2.5 × $10^{-4}$ M at 25 °C, and gelation occurs at around $10^{-2}$ M. Moreover, it has been revealed that the supramolecular polymerization is accompanied by the intrachain *H*-type aggregation of **1** (Scheme 1, i), affording folded supramolecular polymers as judged from the UV–vis, rheological and microscopic investigations.[4b] Thus, the transition of the ICT band of **1** in the 1 + 1 closed species at $\lambda_{max}$ = 467 nm to the blue-shifted one at $\lambda_{max}$ = 435 nm (H-band) in the folded supramolecular polymers takes place upon increasing concentration (Fig. 1a).

In sharp contrast, condensation of **1**–**BM6** solution up to 5 × $10^{-4}$ M resulted in a very marginal shift of the ICT band of **1** from $\lambda_{max}$ = 467 to 465 nm (Fig. 1b). For this mixture, no supramolecular polymerization was observed in DLS analysis upon increasing concentration up to 7.5 × $10^{-3}$ M. Instead, a concentration-independent hydrodynamic diameter of 4.1 nm was observed, which matches well with the gyration diameter of the molecular modeled 1 + 1 closed species (*ca.* 4.0 nm).[7] Furthermore, the $^1$H NMR spectrum in cyclohexane-$d_{12}$ (5 × $10^{-3}$ M) showed well-resolved sharp signals of the hydrogen-bonded and the aromatic protons.[7] This is in clear contrast to that of the polymeric species formed between **1** and **BM12**, where those signals are too broad to be observed.[7] These results demonstrated that the 1 + 1 closed species **1**·**BM6** undergoes neither chain-opening supramolecular polymerization nor well-defined hierarchical association (Scheme 1, ii).

Of great interest is the complexation of **1** with **BM3** which possesses a trimethylene tether that is too short to adopt 1 + 1 closed species. In this case, the ICT band corresponding to the hydrogen-bonded **1** ($\lambda_{max}$ at around 467 nm) was not observed at any concentration. Instead, direct transition of the ICT band of the unbound **1** at $\lambda_{max}$ = 456 nm to the unprecedented red-shifted absorption band at $\lambda_{max}$ = 498 nm was observed upon increasing concentration (Fig. 1c). The large red-shift (42 nm) is indicative of strong *J*-type exciton coupling between the merocyanine dyes. Intuitively, binding with **BM3**, the two melamine hydrogen bonding sites of which are in close proximity,[9] seems to afford the dye a chance to achieve such a *J*-type exciton coupling. However, the following observations provide strong evidence for




**Scheme 1** Complexation of **1** with bismelamines **BM3**, **BM6** and **BM12** and the optical properties of the assemblies. For cyclic assemblies between **1** and **BM3**, a 2 + 2 species is illustrated as a candidate.

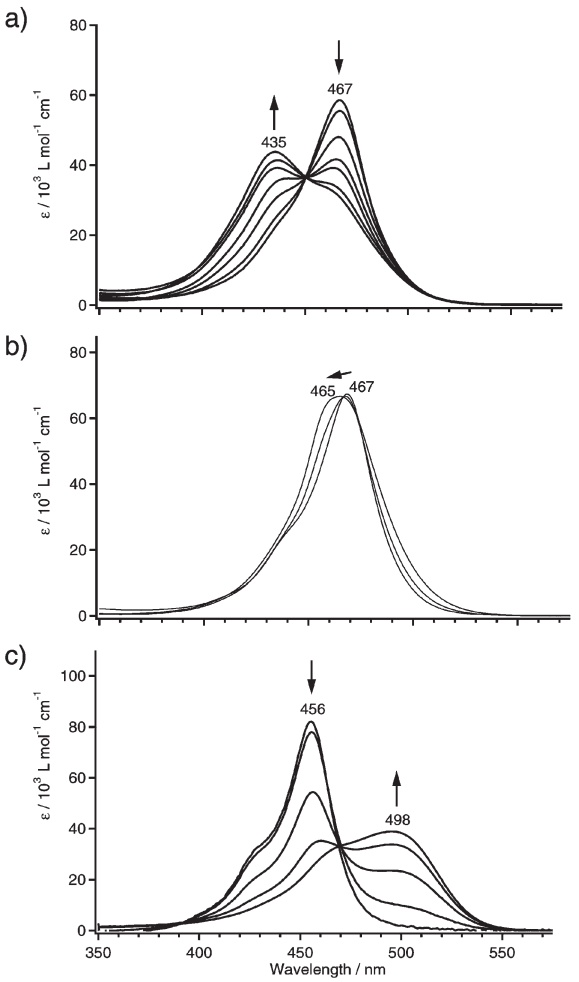



**Fig. 1** Concentration-dependent UV–vis spectra of the 1 : 1 molar mixtures of dye **1** and bismelamines in methylcyclohexane. a) [**1**] = [**BM12**] = 5 × $10^{-6}$ to 5 × $10^{-4}$ M, b) [**1**] = [**BM6**] = $10^{-5}$ to 5 × $10^{-4}$ M and c) [**1**] = [**BM3**] = 5 × $10^{-7}$ to 2 × $10^{-5}$ M. Arrows indicate the changes upon increasing concentrations.

the formation of cyclic oligomers between **1** and **BM3**. Firstly, 27% of the red-shifted species already emerge even at $10^{-6}$ M, the concentration is over one-order of magnitude lower than the complexation between **1** and monotopic **M** (see Fig. S3b). This is a clear sign of the formation of cyclic assemblies where the cooperative association of the components takes place. Secondary, *N*-monomethylated barbiturate **2** did not show such a red-shifted absorption band upon binding with **BM3** at any molar ratio. Therefore, simple binding of merocyanine dyes to the two proximal recognition sites of **BM3** does not induce *J*-type exciton coupling between the dyes. This finding confirms that the spatial fixation of the dye molecules in rigid oligomeric species is a prerequisite for the *J*-type exciton coupling. Thirdly, DLS analysis showed that no extended polymerization proceeds between **1** and **BM3** up to 7.5 × $10^{-3}$ M. Instead, small particles with hydrodynamic diameters of *ca.* 4.0 nm were constantly observed. Finally, the $^1$H NMR spectrum of cyclohexane-$d_{12}$ solution (5 × $10^{-3}$ M) showed several sets of the hydrogen-bonded proton signals of **1** at low magnetic field, indicating the formation of several oligomeric species with slow exchange on the NMR time

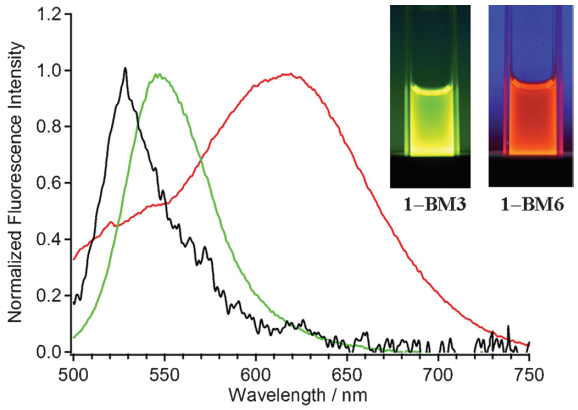



**Fig. 2** Fluorescence spectra of **1** in MCH in the absence (black, [**1**] = 5 × $10^{-6}$ M, $\lambda_{ex}$ = 456 nm), and in the presence of **BM3** (green: [**1**] = [**BM3**] = 5 × $10^{-6}$ M, $\lambda_{ex}$ = 490 nm) and **BM6** (red, [**1**] = [**BM6**] = 2 × $10^{-5}$ M, $\lambda_{ex}$ = 460 nm). Inset: fluorescence images of **1**–**BM3** solution ($c$ = 2 × $10^{-5}$ M, $\lambda_{ex}$ = 254 nm) and **1**–**BM6** solution ($c$ = 2 × $10^{-3}$ M, $\lambda_{ex}$ = 365 nm).

scale.[7] This is a typical behavior of cyclic assemblies. Though the precise assignment of the supramolecular species formed between **1** and **BM3** cannot be made at present, these observations strongly suggest that the *J*-type exciton coupling is a result of the formation of multichromophoric cyclic oligomers (for example, 2 + 2 species in Scheme 1-iii), where the spatial orientation of **1** is fixed in such a way that the *J*-type exciton coupling is allowed.

As a consequence of the tunable electronic interaction, the emission properties of **1** are dramatically diversified in the presence of **BM**s (Scheme 1, iv–vi). The normalized fluorescence spectra of **1** in the absence and the presence of 1 equiv. of **BM3** or **BM6** are shown in Fig. 2. Notably, the polymeric species formed between **1** and **BM12** is almost non-emissive as a result of the *H*-type exciton coupling (data not shown), which is consistent with the exciton theory.[10] In marked contrast, assemblies composed of **1** and **BM3** exhibit pronounced green emission at $\lambda_{em\text{-}max}$ = 550 nm (green line and left inset in Fig. 2). The excitation spectra revealed that the emission indeed originates from the red-shifted absorption species.[7] The relatively small Stokes shift (1899 $cm^{-1}$) is typical of *J*-type excitonic coupling. The fluorescence quantum yield is dramatically increased to 0.25, which is two orders of magnitude greater than that for the monomeric **1** in MCH.

On the other hand, **1**–**BM6** solution showed broadened and largely red-shifted fluorescence at $\lambda_{em\text{-}max}$ = 615 nm (red line and right inset in Fig. 2). The large Stokes shift (5107 $cm^{-1}$) is characteristic of excimer fluorescence. Indeed, excitation spectra unambiguously showed that the 615-nm fluorescence is derived from the absorption band at around 467 nm, which corresponds to the hydrogen-bonded **1** without ground state interchromophoric interaction.[7] The excimer formation is rationalized by the intramolecular charge transfer that takes place in the D–π–A dye moiety of the geometrically well-defined 1 + 1 closed species, reinforcing the stacking interaction of the assemblies in a highly aliphatic environment. This is not the case for the aforementioned complex **M**·**1**·**M** which shows almost no excimer fluorescence even at $10^{-4}$ M.[7] Since this complex is a mixture of four geometrical isomers rapidly exchanging with each other (see Fig. S2), the situation might be unfavorable for inter-complex interaction even in the excited state.

In summary, the excitonic interaction (*J*- or *H*-type) and the excimer formation of a barbiturate-functionalized merocyanine dye could be controlled in hydrogen-bonded supramolecular assemblies scaffolded by bismelamine receptors. Though several covalently-tethered bichromophoric cyanines have been shown to form controlled excitonic interactions based on the structural variety of the tether moieties,[11] to the best of our knowledge, this is the first example of a noncovalent alternative that can induce a variety of electronic interactions from a single merocyanine dye. The specific electronic interactions stem from the self-assembled architectures of the dye–bismelamine complexes, which originate from a marginal structural difference in the bismelamine components.

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7 See Supplementary Information.

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