

Self-assembly of amphiphilic fluorescent dyes showing aggregate-induced enhanced emission: temperature dependence of molecular alignment and intermolecular interaction in aqueous environment†

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A 1-cyano-1,2-bis(biphenyl)ethene derivative having hexa(ethylene glycol) groups as amphiphilic side chains showed aggregate-induced enhanced emission in water; upon heating the intensity of the enhanced emission was attenuated in a lower temperature range than the temperature range where exciton interaction is still effective.

Recently, high-efficiency fluorescent materials in the condensed phase have attracted considerable interest among scientists because of their potential application for organic light-emitting diodes (OLEDs), optical sensors, biological probes,¹ and so on. In the case of most organic fluorescent dyes, however, the emission is strongly quenched when the dyes form aggregates in the condensed phase, mainly because intermolecular vibronic interactions induce nonradiative deactivation process.²

In order to overcome the problem of quenching in the condensed phase, several strategies have been proposed. The introduction of a bulky substituent can be a strategy for retaining highly fluorescent properties in the condensed phase by preventing unfavorable aggregation and decreasing intermolecular interaction.³ The second strategy is utilizing a unique luminescent property originating from an aggregated state. Some dyes show intense enhanced fluorescence in the aggregated state whereas they exhibit weak or almost no emission in dilute solution. This unique phenomenon is widely researched as aggregate induced enhanced emission (AIEE) or aggregate induced emission (AIE).⁴

Recently, Park and co-workers have reported interesting AIEE properties of cyano-bis(biphenyl)ethene (CNBE) derivatives, which involves not only fluorescence enhancement but also the significant red shift of emission along with the formation of nanoparticles.⁵ The specific emission from the aggregated state can be a suitable probe to evaluate the change of microscopic environment.

In this study, we synthesized 9,10-bis(phenylethynyl)anthracene (PEAnt) derivative **1** and CNBE derivative **2** having hexaethylene glycol (Hxg) groups as amphiphilic side chains⁶ (Fig. 1) and

investigated their self-assembling behavior and fluorescence enhancement properties in water. Compound **1** is simply an example of general fluorescent dyes that show quenching upon aggregation. Temperature dependent UV-Vis, induced CD, and fluorescence spectra, indicate a stepwise change of supramolecular environment of **2**.

PEAnt dyes possess quite high fluorescence quantum yield in dilute solution⁷ while CNBE dyes exhibit AIEE properties.⁵ Both dyes have similar molecular size and structural stiffness. Poly(ethylene glycol) (PEG) chains having appropriate length ($n = 6$) for surrounding the hydrophobic core moiety were introduced into both terminals of the dyes as hydrophilic side chains.⁸ In order to induce a chiral environment in the self-assembled structures and to probe the chiroptical properties, a methyl group was introduced nearby the aromatic core moiety as a chiral source.

Both amphiphilic compounds **1** and **2** were soluble in a wide range of solvents such as hexane, ethyl acetate, methanol, and even in water. The UV-Vis absorption spectrum was clearly different in water as compared with that in other organic solvents (Fig. 2(a) and (b)). The absorption maximum of **1** was red-shifted in water whereas that of **2** was oppositely blue-shifted by 10 nm from 365 nm in ethyl acetate to 355 nm in water. In both cases, the absorption bands are broadened and absorption edges are extended to longer wavelength in water than in the organic solvents. The distinctive spectral change in water suggests the operation of intermolecular electronic interaction or the formation of aggregates (such as H- or J-type aggregates⁹) in water.

The formation of self-assembled structures in water was strongly supported by CD spectrum measurements (Fig. 2(c) and (d)). Both **1** and **2** exhibited exciton-coupled CD signals in water whereas they were CD inactive in ethyl acetate. The result indicates that compounds **1** and **2** self-assemble into structures in water where exciton interaction occurs between transition dipole moments of adjacent molecules located on spatially twisted positions.¹⁰ In ethyl acetate, they are considered to be molecularly dispersed due to good solubility of the core moiety. The intensities of exciton-coupled CD signals are very different between compounds **1** and **2**. The CD

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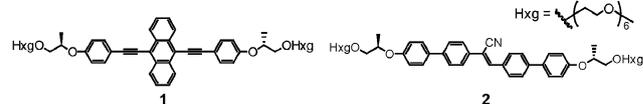


Fig. 1 Molecular structures of FL dye derivatives having Hxg side chains.

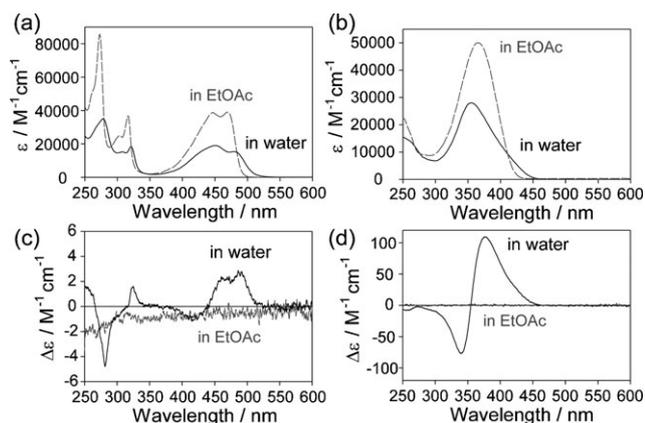


Fig. 2 UV-Vis absorption and CD spectra of **1** (a, c) and **2** (b, d) in ethyl acetate (gray dashed line) and in water (black solid line); $c = 3 \times 10^{-5}$ M (in water) and 1×10^{-5} M (in ethyl acetate) for **1**, and $c = 2 \times 10^{-5}$ M (in water) and 8×10^{-6} M (in ethyl acetate) for **2**.

signal of an aqueous solution of **2** was very strong relative to **1** and other similar derivatives reported previously.¹¹ The CD spectrum of **2** has a typical feature of an exciton-coupled CD signal separated by a Davydov splitting; the first positive Cotton effect was observed at 378 nm ($\Delta\epsilon = 109.5$, $g = 0.50\%$) and the second negative one at 339 nm ($\Delta\epsilon = -76.7$, $g = 0.37\%$).¹² Of note, the strength was comparable to the situation of the intramolecular exciton coupling of two dimethylamino-benzoate groups fixed in a cholesterol framework.¹⁰ The strong induced CD suggests the existence of suitable alignment of transition dipole moments and the strong exciton interaction in the supramolecular structure of compound **2** in water.

To obtain more information on the aggregated structure that shows a distinctively strong CD intensity, the supramolecular structure of **2** was evaluated by means of transmission electron microscopy (TEM), dynamic light scattering (DLS), and molecular modeling (Fig. 3). A TEM image of compound **2** showed hierarchical fiber-like structures. The size of one of the narrowest fibers was around 15 nm and other typical thicker fibers have diameters of 35 or 75 nm. The narrowest one was comparable with the molecular size of **2** that was calculated to be 7.1 nm by a semi-empirical MO method (AM1/MOPAC). The observation suggests that a few molecules aggregate with each other and construct a piece of the fundamental narrowest fibers. The size distribution of aggregates in an aqueous solution of **2** measured by DLS exhibited three peaks, whose maxima were observed at 5.9, 82.4 and 2.9 μm . The largest peak, assignable to micrometer-size structures, could be removed by filtration, however, a similar peak regenerated after standing for several minutes. These results support the existence of hierarchical structures and a large size distribution of self-assembled structures in aqueous solution.

In order to investigate fluorescence properties along with self-assembly, fluorescence spectra of **1** and **2** were evaluated in both solvents (Fig. 4). PEAnt derivative **1** showed a brilliant green emission in ethyl acetate ($\Phi_f = 0.77$), whereas the emission was strongly quenched in water ($\Phi_f = 0.0061$) probably due to self-quenching along with the formation of

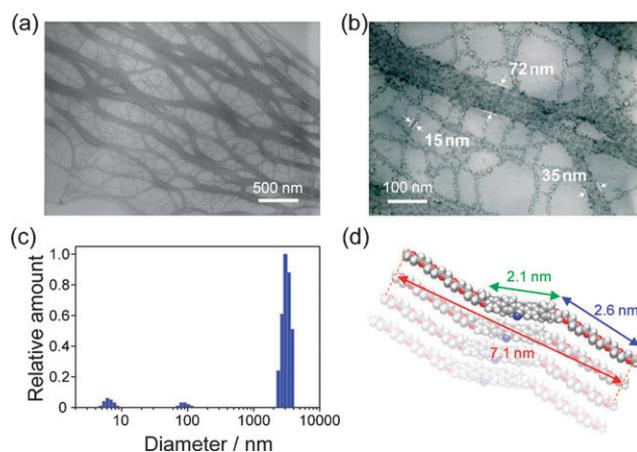


Fig. 3 (a) TEM image of **2**. (b) Small-area image of **2**. (c) DLS size distribution of **2** in water. (d) A calculated molecular model of compound **2** by semi-empirical MO method (AM1/MOPAC).

self-assembled structures (Fig. 4(a)). For CNBE derivative **2**, the fluorescence quantum yield was $\Phi_f = 0.0062$ in ethyl acetate and $\Phi_f = 0.021$ in water. Thus, about 3.4-fold enhancement of fluorescence efficiency was observed for **2** along with self-assembly in water (Fig. 4(b)). Furthermore, the maximum wavelength of fluorescence was red-shifted from 456 to 497 nm, and a bright green color was seen in water compared to dark blue in ethyl acetate. The behaviors of UV-Vis, induced CD, and fluorescence spectra were essentially the same in the range of concentrations measured (see ESI†).

Fluorescence lifetime experiments show that the lifetime of **2** in water was significantly longer than that in ethyl acetate (see ESI†). Considering that J-aggregates in which excitons are delocalized over a number of molecules have shorter fluorescence lifetime, the emission of **2** in water is not considered to originate from such ideal J-aggregates.^{9,13}

Poly(ethylene glycol) is a thermoresponsive polymers showing LCST (lower critical solution temperature) behavior.¹⁴ LCST is a type of phase transition phenomenon, which is usually explained on the basis of the thermal cleavage of hydrogen bonds between hydrophilic moieties and water molecules due to an entropic effect.

Amphiphilic compounds **1** and **2** possessing Hxg side chains exhibited a LCST transition in water. An aqueous solution of **2** turned turbid upon heating and the absorption spectra dramatically changed along with the transition (Fig. 5(a)). By monitoring the change of absorbance at 600 nm, where the

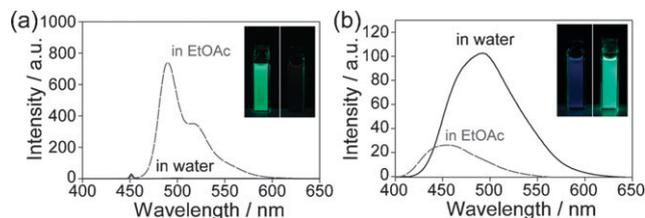


Fig. 4 Fluorescence spectra of (a) **1** ($\lambda_{\text{ex}} = 450$ nm) and (b) **2** ($\lambda_{\text{ex}} = 354$ nm) in ethyl acetate (gray dashed line) and in water (black solid line). The absorbance at the excitation wavelength was set to 0.09 for all samples. Photographs of solutions of **1** and **2** in ethyl acetate (left) and in water (right) upon irradiation with 365 nm light are shown as insets.

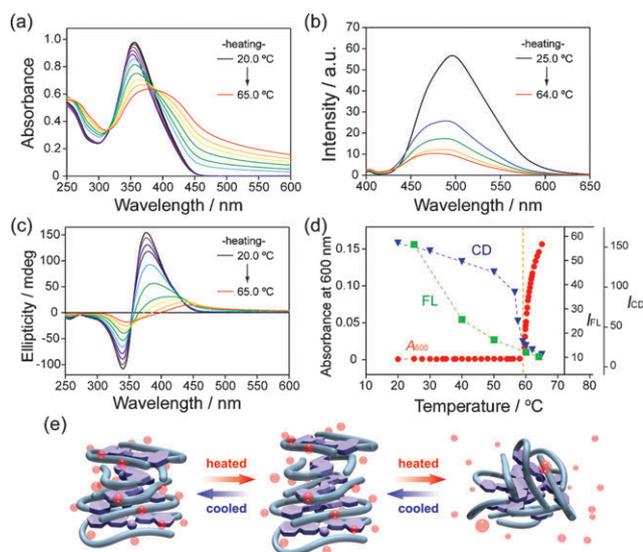


Fig. 5 Temperature dependence of (a) UV-Vis (3×10^{-5} M), (b) fluorescence (3×10^{-6} M) and (c) CD (3×10^{-5} M) spectra of compound **2** in water upon heating. (d) The plot of absorbance at 600 nm (red circle plots), fluorescent intensity (green square plots), and CD intensity (blue triangle plots) at its maximum wavelength against temperature. (e) An illustration of microscopic structural change and successive LCST transitions of **2** upon temperature change. Red spheres denote water molecules.

compound has no absorption, the LCST of an aqueous solution of **2** was determined to be 60 °C (Fig. 5(d), red plot).

Fluorescence and CD spectra of aqueous solutions of **2** were also affected by the temperature. As shown in Fig. 5(b), the intensity of fluorescence decreased with a blue shift of the maximum wavelength from 497 to 477 nm upon heating. Considering the fact that the shape of fluorescence spectra more closely resembled that in ethyl acetate with rising temperature, the aggregated state of compound **2** at low temperature turned more monomer-like state at high temperature. Interestingly, the changes of fluorescence spectra occurred in the temperature range from 20 to 60 °C rather than at 60 °C where the LCST transition was observed (Fig. 5(d), green plot). The AIEE effect was almost completely diminished just below the LCST.

The intensity of CD spectra also decreased upon heating (Fig. 5(c)). The temperature dependence of the CD spectra shows interesting behavior. The decrease of CD signal clearly proceeded in two stages; the first gradual decrease was observed in the temperature range from 20 to 60 °C and subsequent rapid decrease occurred around 60 °C (Fig. 5(d), blue plot). Although the absorbance of **2** did not change so much when the temperature is raised from 20 to 60 °C, the intensity of CD signal decreased by a factor of half and the fluorescence spectra showed a significant decrease. The decrease of the exciton-coupled CD signal shows that the spatial alignment of the transition dipole moments changed and the exciton interaction between moments significantly decreased. Thus, the CD signal seems sensitive both to

the microscopic change of molecular location and to the successive large structural change in the LCST transition. Furthermore, the enhanced emission originating from the aggregated state of **2** decreased faster than the CD signal. The result indicates that the AIEE behavior is more sensitive to the molecular environmental change than the exciton interaction, suggesting that the AIEE behavior can be used as a sensitive probe for the microscopic environmental change.

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