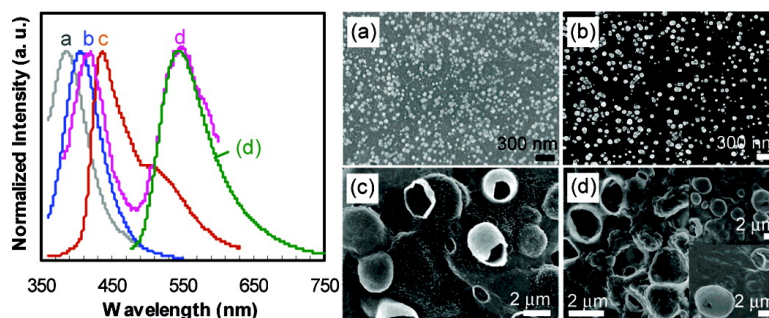


## Intense Fluorescence from Light-Driven Self-Assembled Aggregates of Nonionic Azobenzene Derivative

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## Intense Fluorescence from Light-Driven Self-Assembled Aggregates of Nonionic Azobenzene Derivative

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**Abstract:** We describe here the highly fluorescent self-assembled spherical aggregates of an azobenzene molecule without a specific ionic component in organic solution under UV light illumination. The first stage of *trans*-to-*cis* photoisomerization by UV light at 365 nm was followed by a significant enhancement, up to about 1000 times, of the emission from an azobenzene molecule (CN2Azo) with a long alkyl chain, which is due to the spontaneous formation of spherical organic aggregates. Fluorescence emission was further enhanced in the dark, and the quantum yield increased to about 0.3. We also report the significant size and structural changes of the aggregates, from nanometer-scale micelle-like aggregates to micrometer-scale vesicular aggregates, obtained only from the variation in the concentration of an azobenzene derivative. The light-driven azobenzene aggregates show the size and structure dependences of emission wavelength from violet-blue to green-yellow.

### Introduction

Photoresponsive azobenzene-containing amphiphiles have been extensively studied thus far for their interesting aggregation phenomena into assemblies such as bilayers (vesicles), micelles, and monolayers.<sup>1,2</sup> Although it has been known that generally the azobenzene molecule in solutions does not fluoresce with appreciable quantum yield (about  $10^{-7}$ – $10^{-5}$ ),<sup>3</sup> a few exceptional self-assembled bilayer aggregates of azobenzene-containing amphiphiles<sup>4</sup> and of azobenzene-functionalized dendrimers<sup>5</sup> in aqueous solutions exhibited fluorescence emission at  $\sim$ 600 nm. This emission is attributed to the densely packed arrangement of azobenzene chromophores in the bilayer structure. To form supramolecular aggregates such as vesicles and micelles, azobenzene-substituted amphiphiles containing ionic species as a hydrophilic component have been mainly employed.<sup>6</sup>

Recently, on the other hand, it has been reported that unique organic molecules such as silole derivatives and 1-cyano-*trans*-1,2-bis-(4'-methylbiphenyl)ethylene, whose isolated species are

virtually nonfluorescent in dilute solutions, assemble into nano-aggregates with extraordinarily high fluorescent quantum yields in water/organic solvent mixtures.<sup>7,8</sup> Such an unprecedented result of aggregation-induced emission enhancement has significant implications for the design of emissive organic materials.<sup>9</sup>

Unlike the attempts reported thus far, here we describe the highly fluorescent self-assembled spherical aggregates of azobenzene molecules without a specific ionic component under UV light illumination, even though azobenzene itself is negligibly fluorescent in nonirradiated initial solution. We also report the significant size and structural changes of aggregates, from nanometer-scale micelle-like aggregates to micrometer-scale vesicular aggregates, obtained only from the variation in the concentration of azobenzene derivatives. With a fluorescent azobenzene chromophore in mind, we prepared an azobenzene derivative, [12-{4-(4'-cyanobiphenylazo)phenoxy}dodecyl]dodecyl disulfide (CN2Azo), consisting of a photoisomerizable azobenzene core coupled directly to biphenyl fluorophore as a head segment and a long alkyl chain as a tail segment, that is weakly fluorescent at ambient temperature.

### Experimental Section

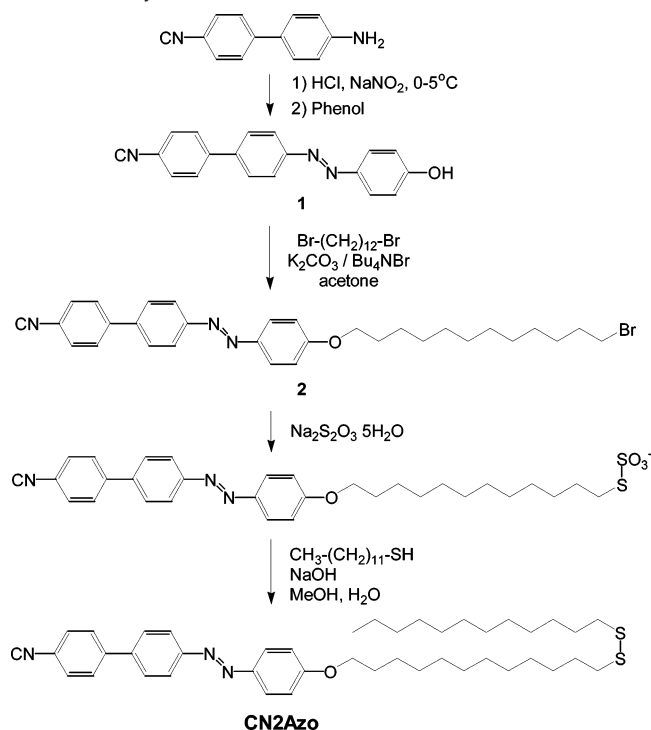
**Synthesis.** CN2Azo was synthesized according to the procedure in the literature via the corresponding Bunte salt (Scheme 1).<sup>10</sup>

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**Scheme 1.** Synthesis of CN2Azo

**4-(4'-Cyanobiphenylazo)phenol (1).** A solution of  $\text{NaNO}_2$  (1.24 g, 18.0 mmol) in 18 mL of distilled water was added to a solution of 4-amino-4'-cyanobiphenyl (3.00 g, 15.4 mmol) in 1.6 M HCl (36 mL) at 0–5 °C. A solution of phenol (1.69 g, 18.0 mmol), NaOH (0.78 g, 19.0 mmol), and  $\text{Na}_2\text{CO}_3$  (2.06 g, 19.0 mmol) in 60 mL of distilled water was added to the diazonium salt solution at 0–5 °C. The mixture was stirred for 4 h, and the precipitate was collected. The crude product was washed with water three times and recrystallized from acetone (3.7 g, yield: 80%).

$^1\text{H NMR}$  (270 MHz, acetone- $d_6$ )  $\delta$  7.0 (d, 2H, Ar–H), 7.7–8.0 (m, 10H, Ar–H).

**12-[4-(4'-Cyanobiphenylazo)phenoxy]dodecyl Bromide (2).** **2** was synthesized by reacting 4-(4'-cyanobiphenylazo)phenol (**1**, 2.50 g, 8.36 mmol) with 1,12-dibromododecane (13.7 g, 40.2 mmol) in 100 mL of acetone in the presence of excess anhydrous  $\text{K}_2\text{CO}_3$  (3.47 g, 25.1 mmol) and a catalytic amount of tetrabutylammonium bromide. The reaction mixture was stirred at 60 °C for 11 h. After cooling the mixture to room temperature, acetone was removed under reduced pressure. The residue was washed with water and *n*-hexane and recrystallized from ethyl acetate (2.0 g, yield: 44%).

$^1\text{H NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  1.2–1.6 (m, 16H,  $\text{CH}_2$ ), 1.80–1.88 (m, 4H,  $\text{BrCH}_2\text{CH}_2$ ,  $\text{ArOCH}_2\text{CH}_2$ ), 3.40 (t, 2H,  $\text{BrCH}_2$ ), 4.05 (t, 2H,  $\text{ArOCH}_2$ ), 7.00 (d, 2H,  $J = 8.91$  Hz, Ar–H), 7.7–8.0 (m, 10H, Ar–H).

**[12-[4-(4'-Cyanobiphenylazo)phenoxy]dodecyl]dodecyl Disulfide (CN2Azo).** Sodium thiosulfate pentahydrate (0.65 g, 2.62 mmol) in 5 mL of distilled water was added to **2** (1.0 g, 1.83 mmol) in 50 mL of DMF solution under nitrogen atmosphere, and the reaction mixture was stirred at 60 °C for 6 h. After cooling to room temperature, 2 mL of water was added to the mixture, and the precipitate was filtered out to obtain Bunte salt. A solution of Bunte salt in 30 mL of DMF was added to a solution of dodecanethiol (0.41 g, 2.03 mmol), methanol (2 mL), and NaOH (0.088 g, 2.20 mmol) in 1 mL of distilled water, and the reaction mixture was stirred for 3 h under nitrogen atmosphere. Ethyl acetate (30 mL) and water (30 mL) were poured into the mixture, and the organic layer was collected and evaporated. The residue was purified

by silica gel column chromatography using hexane:chloroform (1:3) as eluent to afford an orange crystal (0.25 g, yield: 19%).

$^1\text{H NMR}$  (270 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t, 3H,  $\text{CH}_3$ ), 1.2–1.6 (m, 34H,  $\text{CH}_2$ ), 1.66 (m, 4H,  $\text{SSCH}_2\text{CH}_2$ ), 1.83 (m, 2H,  $\text{ArOCH}_2\text{CH}_2$ ), 2.68 (t, 4H,  $\text{SSCH}_2$ ), 4.05 (t, 2H,  $\text{ArOCH}_2$ ), 7.01 (d, 2H,  $J = 8.91$  Hz, Ar–H), 7.7–8.0 (m, 10H, Ar–H). FAB-MS ( $m/z$ ):  $[\text{M} + \text{H}]^+$  found, 700.3 (=  $\text{M} + 1$ ), calcd for  $\text{C}_{43}\text{H}_{61}\text{N}_3\text{OS}_2$ , 699.4. IR (ATR): 2920, 2850 (C–H stretching), 2240 (cyano group), 1603, 1584, 1499 (benzene ring), 1253 (Ph–O stretching), 1156 (=N–Ph stretching)  $\text{cm}^{-1}$ .

**Sample Preparation.** Freshly distilled dichloromethane under nitrogen atmosphere was used to dissolve CN2Azo so as to remove extra oxygen. After a 1-min nitrogen purge, a screw-cap quartz cuvette containing CN2Azo solution was sealed with Parafilm. Azobenzene solutions ( $2 \times 10^{-6}$ ,  $4 \times 10^{-5}$ ,  $8 \times 10^{-4}$ , and  $2 \times 10^{-3}$  M) were irradiated with UV light (365 nm, 2 mW/cm<sup>2</sup>, Mineralight lamp, model UVGL-25, UVP, Upland, CA 91786) at ambient temperature to generate spherical aggregates.

**Instrumentation.**  $^1\text{H NMR}$  and FT-IR spectra were recorded on a JEOL JNM-EX270 (270 MHz) and a Nicolet OMNI-Sampler (Avatar 320-FT-IR) spectrometer, respectively. Absorption and fluorescence spectra were obtained using a Shimadzu UV-3100PC UV–vis–NIR scanning spectrophotometer and a JASCO FP-6500 spectrofluorometer, respectively. The FE-SEM (field-emission scanning electron microscopy) was recorded on a Hitachi S-5200, after putting one drop of CN2Azo solution on a clean glass substrate and coating it with platinum about 2 nm thick using the Hitachi E-1030 ion-sputter. The TEM (transmission electron microscope) was performed at 120 kV using JEOL JEM-2000EX and JEOL JEM-2100F/SP. The sample was prepared by placing a drop of CN2Azo solution onto a carbon-coated copper grid and drying at room temperature. Fluorescence microscopic images were obtained using an Olympus BX51WI fluorescence microscope equipped with a Nikon Coolpix digital camera (MDC Lens 0.82–0.29 $\times$ , Nikon Japan), after putting a few drops of CN2Azo solution on a clean quartz substrate.

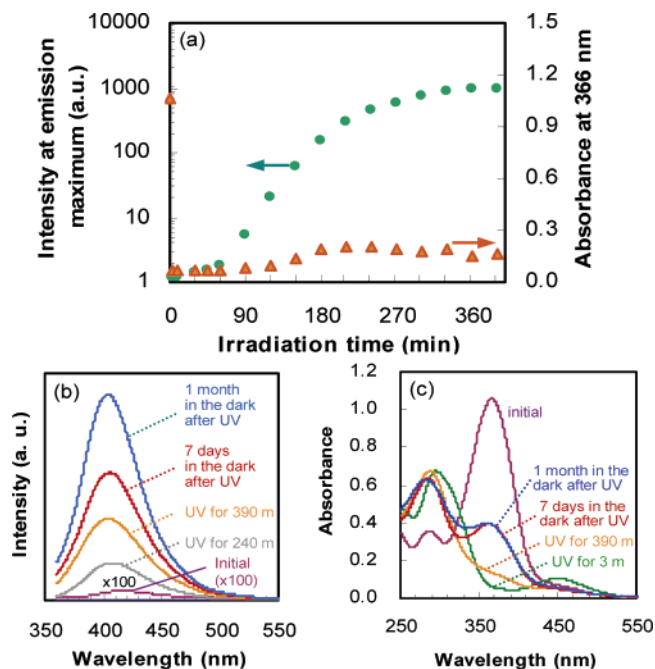
**Results and Discussion**

CN2Azo exhibited good solubility in organic solvents such as dichloromethane and chloroform to give transparent solutions before and after UV light irradiation and the typical monomer-like absorption spectrum containing an intense  $\pi$ – $\pi^*$  transition at 366 nm, a second  $\pi$ – $\pi^*$  transition at 287 nm, and a weak  $n$ – $\pi^*$  transition near 450 nm. Upon UV light irradiation at 365 nm for 3 min to sufficiently reach a *cis*-rich stationary state (about 95% of the *cis* form obtained from NMR and absorption spectra), a dramatic decrease at 366 nm and an increase in absorbance at 448 nm were observed (Figure 1c). Dark incubation of the UV-exposed solution resulted in maximizing the  $\pi$ – $\pi^*$  absorption band at 366 nm as a result of thermal *cis*-to-*trans* isomerization, keeping two isosbestic points at 325 and 430 nm.<sup>11</sup>

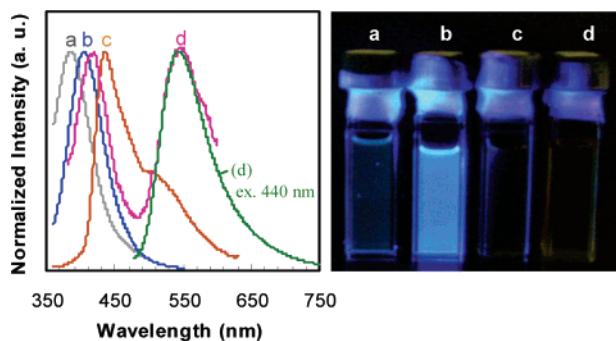
When a CN2Azo solution ( $4 \times 10^{-5}$  M) was excited at 325 nm, very weak fluorescence (with a fluorescence quantum yield,  $\Phi_f$ ,<sup>12</sup> of about 0.00013) centered at around 417 nm was observed. However, as the solution was continuously exposed to UV light (365 nm, 2 mW/cm<sup>2</sup>) for 90 min, the fluorescence intensity started increasing as shown in Figure 1a. Upon prolonged UV light irradiation for 390 min, the fluorescence intensity markedly increased by about 1000 times that of the

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 (13) CN2Azo solutions at concentrations ranging from  $2 \times 10^{-6}$  to  $4 \times 10^{-5}$  M, including nanometer-scale micelle-like aggregates, did not show apparent blue-shift or red-shift in the intense  $\pi$ – $\pi^*$  absorption.

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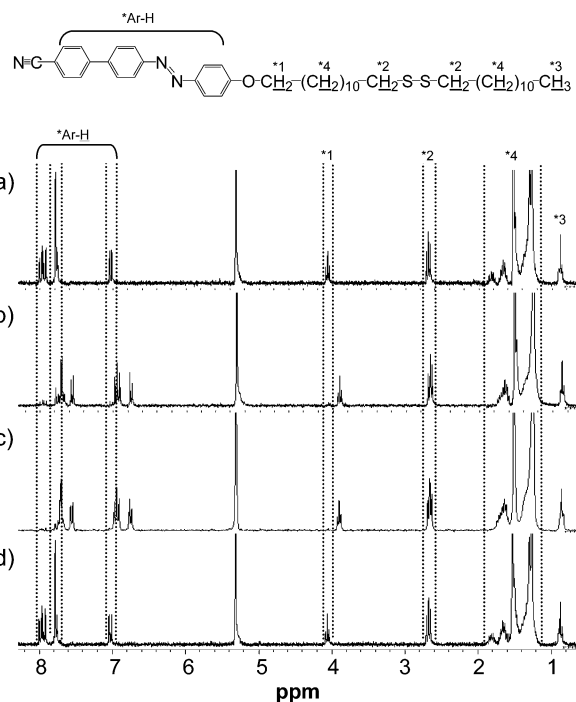
**Figure 1.** (a) Changes in emission intensity at emission maximum (green circle) and absorbance at 366 nm (orange triangle) as a function of 365 nm light irradiation time. (b) Emission spectra of CN2Azo ( $4 \times 10^{-5}$  M) in dichloromethane at ambient temperature (325 nm excitation). (c) Changes in UV-vis absorption spectra of CN2Azo ( $4 \times 10^{-5}$  M) in dichloromethane.<sup>13</sup>



**Figure 2.** Emission spectra (left panel, excitation at 325 nm) and emission (right panel, under 365 nm irradiation) of (a)  $2 \times 10^{-6}$  M, (b)  $4 \times 10^{-5}$  M, (c)  $8 \times 10^{-4}$  M, and (d)  $2 \times 10^{-3}$  M after UV light irradiation for 390 min. Green solid line (d) corresponds to emission of  $2 \times 10^{-3}$  M solution upon excitation at 440 nm. Upon irradiation with UV light, the emission intensities considerably increased, depending on the concentrations, which were 96 times, 1000 times, and 47 times higher than the initial solutions of  $2 \times 10^{-6}$ ,  $4 \times 10^{-5}$ , and  $8 \times 10^{-4}$  M, respectively.

nonirradiated initial solution (Figure 1a). Fluorescence emission was further enhanced at ambient temperature in the dark, and the quantum yield improved to about 0.3 (Figure 1b). The photograph in Figure 2 displays bright blue emission from UV-light-irradiated solution ( $4 \times 10^{-5}$  M).

Significantly, prolonged UV light irradiation led to a prominent deviation from two isosbestic points at 325 and 430 nm, compared with that of the solution irradiated with UV light for 3 min (Figure 1c). This implies that other reactions such as photoreaction or aggregation could occur together with *trans*-to-*cis* isomerization. NMR data indicate that no decomposition of the azobenzene molecule (7–8 ppm) and disulfide group occurs upon UV light irradiation, although a significant change in spectral signals at around 1–2 ppm, which is assigned to the protons from long alkyl chains, was observed (Figure 3).



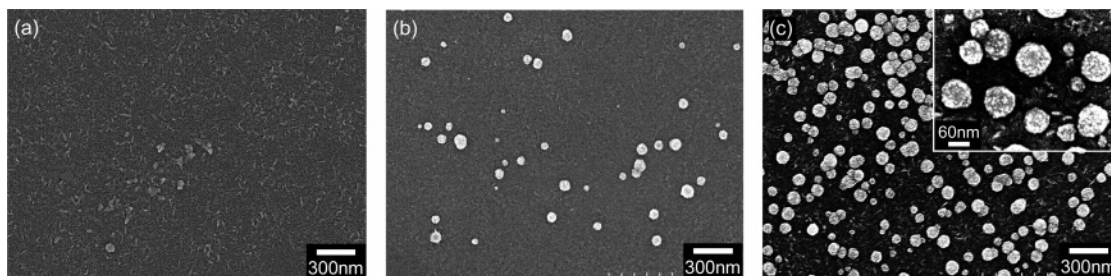
**Figure 3.** <sup>1</sup>H NMR spectra of CN2Azo in CD<sub>2</sub>Cl<sub>2</sub>. (a) Initial. (b) After exposure to UV light for 10 min. (c) After exposure to UV light for 390 min. (d) After thermal *cis*-to-*trans* isomerization for 7 days at ambient temperature in the dark.

The characteristic change in proton signals is attributable to the strong hydrophobic interaction between long alkyl chains as a result of *trans*-to-*cis* photoisomerization as well as other reactions such as the formation of aggregates.

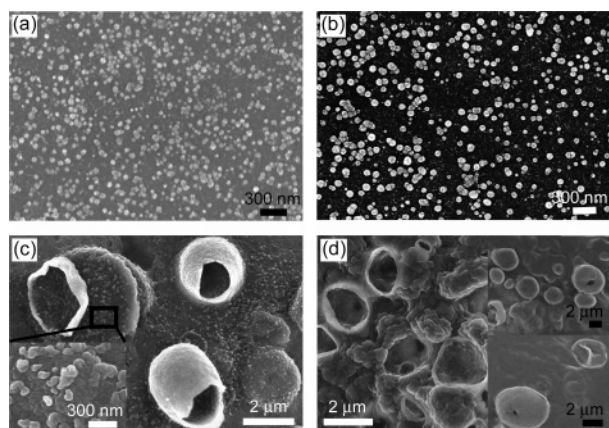
All of our results allowed us to take scanning electron microscope (SEM) images to confirm that the observed spectral features were indeed due to aggregates during prolonged UV light irradiation. Spherical aggregates of approximately 10–120 nm in diameter appeared in the samples exposed to UV light for 180 min, and many more aggregates were observed after 390 min (Figure 4). In contrast, such spherical aggregates were rarely observed in the samples exposed to UV light for less than 120 min. The SEM results are thus consistent with the dramatic changes in fluorescence intensity in Figure 1, strongly suggesting that the striking fluorescence enhancement by UV light irradiation originates from the formation of aggregates.

To obtain an insight into the concentration dependence of fluorescence enhancement, azobenzene solutions at concentrations ranging from  $2 \times 10^{-6}$  to  $2 \times 10^{-3}$  M were prepared. Surprisingly, unlike the single-emission peaks at 385 and 405 nm from dilute  $2 \times 10^{-6}$  and  $4 \times 10^{-5}$  M solutions upon excitation at 325 nm, respectively, the emission spectrum of UV-exposed  $8 \times 10^{-4}$  M solution showed a shoulder in the range of 490–630 nm along with blue emission at 436 nm (Figure 2c). The most concentrated solution ( $2 \times 10^{-3}$  M), which was not fluorescent before UV light irradiation because of concentration quenching,<sup>14</sup> exhibited two discrete emission peaks centered at 420 and 546 nm after UV light irradiation (Figure 2d; pink solid line). Moreover, when both UV-exposed transparent  $8 \times 10^{-4}$  and  $2 \times 10^{-3}$  M solutions were excited at

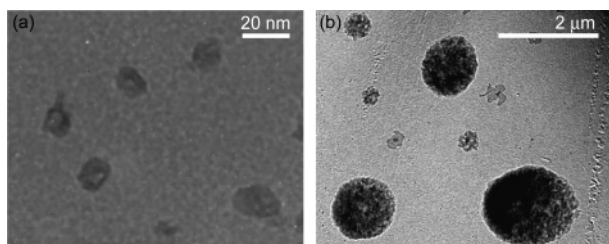
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**Figure 4.** SEM images of CN2Azo ( $4 \times 10^{-5}$  M) after exposure to UV light (a) for 120 min, (b) 180 min, and (c) for 390 min. (Inset) Magnified SEM image.



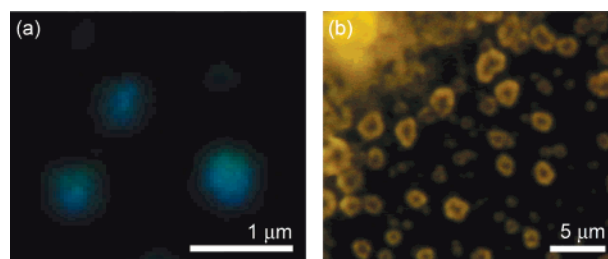
**Figure 5.** SEM images of (a)  $2 \times 10^{-6}$  M, (b)  $4 \times 10^{-5}$  M, (c)  $8 \times 10^{-4}$  M, and (d)  $2 \times 10^{-3}$  M after exposure to UV light for 390 min.



**Figure 6.** TEM image of (a) nanometer-scale aggregates from  $4 \times 10^{-5}$  M solution and (b) micrometer-scale aggregates from  $8 \times 10^{-4}$  M solution.

440 nm, strong emission at 546 nm was observed (Figure 2d, green solid line). This striking concentration dependence of emission wavelength seems to be closely associated with the size and structural changes of the aggregates generated by UV light irradiation. Obviously, SEM and transmission electron microscope (TEM) images showed nanometer-scale aggregates of approximately 10–60 nm and 10–120 nm in diameter for dilute  $2 \times 10^{-6}$  and  $4 \times 10^{-5}$  M solutions, respectively (Figure 5). As shown in Figure 6a, the smaller size of the aggregates corresponded to roughly twice the molecular length (approximately 4–5 nm), implying that the aggregates possess micelle-like structures.<sup>15</sup>

On the other hand, in concentrated solutions ( $8 \times 10^{-4}$  and  $2 \times 10^{-3}$  M), large aggregates of approximately 0.3–10  $\mu\text{m}$  in diameter existed together with nanometer-scale aggregates of approximately 50–150 nm in size (Figure 5). The measured diameters of large aggregates exceeded the molecular length by a factor of about 70–2000, suggesting that the aggregates have vesicle structures. We found wall collapse as well as



**Figure 7.** Fluorescence microscopic images of (a) nanometer-scale aggregates from  $4 \times 10^{-5}$  M solution (excitation at 365 nm) and (b) micrometer-scale aggregates from  $8 \times 10^{-4}$  M solution (excitation at 435 nm).

indentations on their surface (Figure 5 c and d), which is likely due to the high vacuum required for SEM sample preparation. In particular, the SEM image showed that large aggregate walls were thin on the order of about 10–30 nm. From the fact that the wall thickness was about twice or more the molecular length, the antiparallel arrangement of cyano-containing azobenzene aromatic units would occur in the bilayer structure.<sup>4,16</sup> Further evidence for the size and structure dependences of emission wavelength was provided by fluorescence optical microscopy. Fluorescence microscopic images displayed small aggregates showing blue emission, whereas large micrometer-scale aggregates were responsible for yellow emission (Figure 7).

On the basis of the results, even though the definitive mechanism of the spontaneous formation of aggregates upon UV light irradiation still remains to be solved, the following can be considered. First, while a long alkyl chain is hydrophobic, the nonplanar bent-shaped *cis* form of CN2Azo is more or less hydrophilic relative to the planar rod-shaped *trans* form.<sup>17</sup> When such a *cis* azobenzene molecule with a dual hydrophobic–hydrophilic character exists in solutions, the molecule can spontaneously self-assemble into spherical aggregates, particularly in the present case, due to the hydrophobic interaction between long alkyl chains. Second, the bulky and polar cyano group could play an important role in the head-to-tail intermolecular interactions of azobenzene aromatic units forming J-aggregates.<sup>8,18</sup> The head-to-tail stacking model for the enhanced emission mechanism has already been suggested in azobenzene-containing amphiphiles<sup>4,19</sup> and cyanine dyes having two twisted aromatic rings.<sup>20</sup> Thus, the resulting spherical

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aggregates are considered responsible for the unusual enhancement in fluorescence intensity. This is quite extraordinary that the *cis* azobenzene, which has been generally known to destroy molecular ordering and aggregation,<sup>21</sup> forms strongly fluorescent aggregates.

### Conclusion

We have demonstrated that the azobenzene molecule with a long alkyl chain can self-assemble into stable and tunable spherical aggregates, from nanometer-scale to micrometer-scale aggregates, with increasing azobenzene concentration. The light-

driven azobenzene aggregates show significant fluorescence enhancement and the size and structure dependences of emission wavelength from violet-blue to green-yellow. Further work will include studies of the physical origin and the detailed mechanism.

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