Chain length-dependent photoinduced formation of azobenzene aggregates

Mina R. Han* and Masahiko Hara

Received (in Montpellier, France) 11th August 2005, Accepted 9th December 2005
First published as an Advance Article on the web 22nd December 2005
DOI: 10.1039/b511462d

We describe photoinduced formation of blue fluorescent aggregates of azobenzene derivatives, whose isolated molecules in solution are not fluorescent at ambient temperature, with different alkyl chain lengths. In contrast to nonfluorescent C0 (4-hydroxyazobenzene), C10 and C24 with long alkyl chains started being blue fluorescent upon UV light irradiation for 60 min and the fluorescence intensities were more enhanced with increasing UV light irradiation time. Such a striking fluorescence enhancement by UV light irradiation is closely associated with the unique formation of self-assembled nanoaggregates (50–70 nm and 30–60 nm in diameter for C10 and C24, respectively) of *cis*-azobenzene derivatives with long alkyl chains as a result of intermolecular interaction of azobenzene moieties with long alkyl chains. Moreover, photoinduced blue fluorescence kept stable even after sufficient thermal *cis*-to-*trans* isomerization.

Introduction

Functionalization of self-assembling systems has been a challenging research topic in the field of chemical biology and materials science because it leads to significant supramolecular structures exhibiting selective binding affinity, synthetic bilayer membranes, photoluminescence, and optical data storage.[1–6] Incorporation of photochromic azobenzene compounds into such supramolecular structures can give rise to artificial photoresponsive systems. The photoisomerization of azobenzene and its derivatives influences versatile physical properties such as wettability, viscosity, and aggregation behaviors because of changes in molecular structure and dipole moment (from 0 of *trans* form to *ca.* 3 debye of *cis* form) between the rod-shaped *trans* form and the bent-shaped *cis* form.[7]

While it is well known that in general the azobenzene molecule in solution is not fluorescent with reasonable quantum yield, only a few exceptional azobenzenes incorporated into Nafion (Nafion-H^+) membrane[8] and into an aluminophosphate framework ($AlPO_4$-5)[9] were reported to be fluorescent at room temperature. However, the fluorescence was not due to azobenzene itself but due to the protonated azobenzenes. On the other hand, even though the uncomplexed azobenzene compound was nonfluorescent in solution, cyclopalladated azobenzene derivatives were weakly fluorescent ($\Phi \sim 10^{-4}$).[10] By cyclometallation, the photoisomerization of a *trans*-blocked azobenzene ligand was suppressed and the efficiency of emission could increase significantly.[11]

Here we describe significant photoinduced fluorescence enhancement of simple azobenzene derivatives with different alkyl chain lengths. Unlike nonfluorescent C0 without an alkyl chain length, upon UV light irradiation in organic solution C10 and C24, with long alkyl chains, spontaneously assembled into aggregates, which showed blue fluorescence.

Experimental

Materials and instrumentation

Dichloromethane was freshly distilled prior to use under a nitrogen atmosphere in order to remove extra oxygen and water. After a 30-sec nitrogen purge, a screw-cap quartz cuvette containing a dichloromethane solution of an azobenzene derivative was sealed with Parafilm.

Photoisomerization measurements were taken using a Mineralight® lamp (365 nm, Model UVGL-25, UVP, Upland, CA 91786, USA) as a light source. ^1H NMR spectra were recorded on JEOL JNM-EX270 (270 MHz) in $CDCl_3$ (Merck, 99.8%) and CD_2Cl_2 (Aldrich, 100 atom% D). Absorption and fluorescence spectra were obtained using a Shimadzu UV-3100PC UV-VIS-NIR scanning spectrophotometer and a JASCO FP-6500 spectrofluorometer, respectively. The SEM (scanning electron microscopy) was recorded on a Hitachi S-5200, after putting one drop of an azobenzene solution on a clean glass substrate and coating it with platinum about 2 nm thick using the Hitachi E-1030 ion-sputter.

Syntheses

4-(12-Bromododecyloxy)azobenzene (C12-Br). C12-Br was synthesized by reacting 4-(hydroxyl)azobenzene (C0, 2.50 g, 0.0126 mol) with 1,12-dibromododecane (12.4 g, 0.0379 mol) in 100 mL of acetone in the presence of excess anhydrous K_2CO_3 (3.48 g, 0.0250 mol) and a catalytic amount of potassium iodide. 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 three times with water, dried in vacuum and recrystallized from 2-propanol (3.1 g, yield: 55%). ^1H NMR

Local Spatio-Temporal Functions Laboratory, Frontier Research System, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan. E-mail: minahjp@riken.jp; Fax: (+81) 48 462 4695; Tel: (+81) 48 462 1111

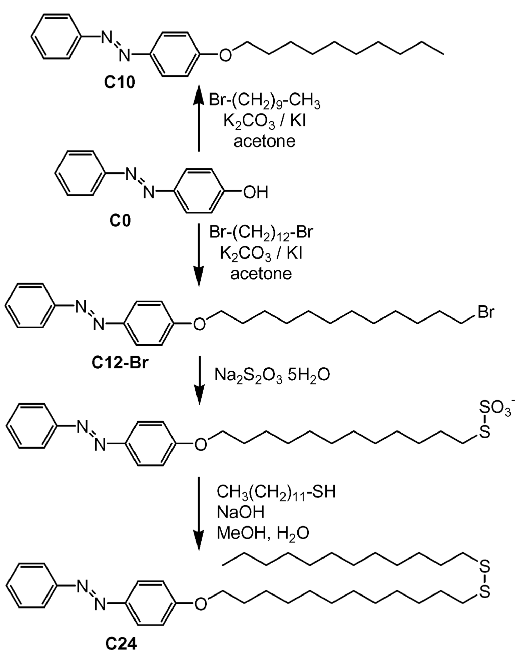
(270 MHz, $CDCl_3$) δ 1.2–1.6 (m, 16H, CH_2), 1.6–1.9 (m, 4H, $BrCH_2CH_2$, $ArOCH_2CH_2$), 3.40 (t, 2H, $BrCH_2$), 4.04 (t, 2H, $ArOCH_2$), 7.00 (d, 2H, Ar-H), 7.39–7.52 (m, 3H, Ar-H), 7.85–7.92 (dd, 4H, Ar-H).

4-[12-(Dodecyldithio)dodecyloxy]azobenzene (C24). Sodium thiosulfate pentahydrate (0.836 g, 0.0337 mol) in 6 mL of distilled water was added to C12-Br (1 g, 0.00225 mol) in 50 mL of DMF solution under a 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 (0.088 g). A solution of Bunte salt in 30 mL of DMF was added to a solution of dodecanethiol (0.499 g, 0.00247 mol), methanol (2 mL) and NaOH (0.109 g) in 1 mL of distilled water, and the reaction mixture was stirred for 3 h under a nitrogen atmosphere. Chloroform (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 (10 : 1) as eluent, to afford an orange crystal (0.25 g, yield: 18%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, 3H, CH_3), 1.2–1.6 (m, 34H, CH_2), 1.61–1.69 (m, 4H, $SSCH_2CH_2$), 1.76–1.87 (m, 2H, $ArOCH_2CH_2$), 2.68 (t, 4H, $SSCH_2$), 4.04 (t, 2H, $ArOCH_2$), 7.00 (d, 2H, Ar-H), 7.39–7.52 (m, 3H, Ar-H), 7.86–7.92 (dd, 4H, Ar-H). IR (ATR): 2918, 2849 (C–H stretching), 1604, 1587, 1500 (benzene ring), 1253 (Ph–O stretching) cm^{-1}. FAB-MS (*m*/*z*): $[M + H]^+$ found, 599.40 (=M + 1), calcd for $C_{36}H_{58}N_2OS_2$, 598.40. Anal. Calcd: C, 72.19; H, 9.76; N, 4.68; S, 10.71. Found: C, 71.84; H, 9.80; N, 4.69; S, 10.58%.

4-(Decyloxy)azobenzene (C10). C10 was synthesized by a procedure analogous to that for C12-Br. ^{1}H NMR (270 MHz, CD_2Cl_2) δ 0.89 (t, 3H, CH_3), 1.2–1.6 (m, 14H, CH_2), 1.76–1.87 (m, 2H, $ArOCH_2CH_2$), 4.05 (t, 2H, $ArOCH_2$), 7.00 (d, 2H, Ar-H), 7.41–7.54 (m, 3H, Ar-H), 7.85–7.93 (dd, 4H, Ar-H). Anal. Calcd: C, 78.06; H, 8.93; N, 8.28. Found: C, 77.58; H, 8.94; N, 8.30%.

Results and discussion

The structures of azobenzene derivatives used in this investigation are shown in Scheme 1. All the azobenzene compounds exhibited good solubility in dichloromethane to give solutions characterized by the typical azobenzene monomer-like absorption spectra with an intense π–π* absorption band at 342 nm (for C0) and 348 nm (for C10 and C24) and a weak n–π* absorption band at about 400–500 nm (Fig. 1).[12] Exposure of azobenzene solutions to UV light at 365 nm for 3 min for inducing sufficient *trans*-to-*cis* photoisomerization led to a marked reduction in the *trans*-azobenzene π–π* absorption band and a concomitant increase in the n–π* absorption band at 440 nm. Dark incubation of the UV-exposed C10 and C24 solutions resulted in slow thermal *cis*-to-*trans* back isomerization, keeping two sharp isosbestic points at 304 and 408 nm (Fig. 1), indicating that conversion between only two species, *trans* and *cis* forms of C10 and C24, occurs in solution in the early stage of UV light irradiation. In contrast to sufficient *trans*-to-*cis* photoisomerization of C10 and C24 with long alkyl chains, as small as about 20% of the *cis* form of C0 was generated by UV light irradiation and underwent very fast thermal *cis*-to-*trans* isomerization (within ~5 min) at ambient temperature (inset of Fig. 1).



Scheme 1 Synthesis of C10 and C24.

When initial dilute solutions (6×10^{-5} M for C0 and C10, and 5×10^{-5} M for C24) were excited at 365 nm, no fluorescence was observed at ambient temperature, regardless of alkyl chain length. After 3-min UV irradiation for generating a *cis*-rich photostationary state, the solutions (C0, C10, and C24) did not fluoresce as well.

However, obviously different from nonfluorescent C0 even after prolonged UV light (365 nm light, 3 mW cm^{-2}) irradiation, C10 and C24 with long alkyl chains started being weakly

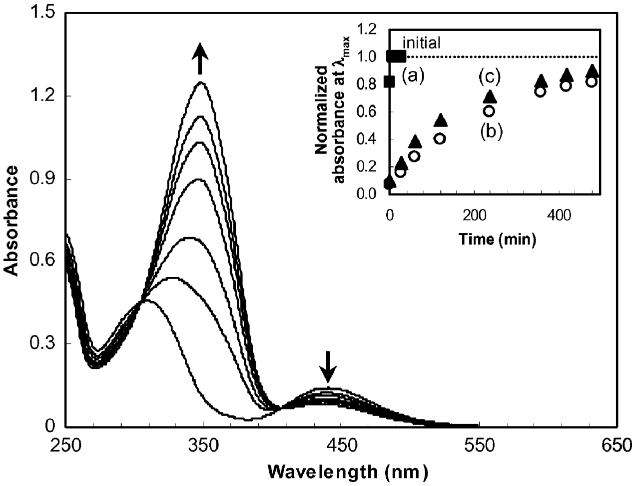


Fig. 1 Changes in UV-Vis absorption spectra of C24 in dichloromethane as a function of time for thermal *cis*-to-*trans* isomerization in the dark after 365 nm light irradiation for 3 min. Inset: Changes in normalized absorbance at λ_{max} of (a) C0, (b) C10 and (c) C24 as a function of time for thermal *cis*-to-*trans* back isomerization after 365 nm light irradiation for 3 min.

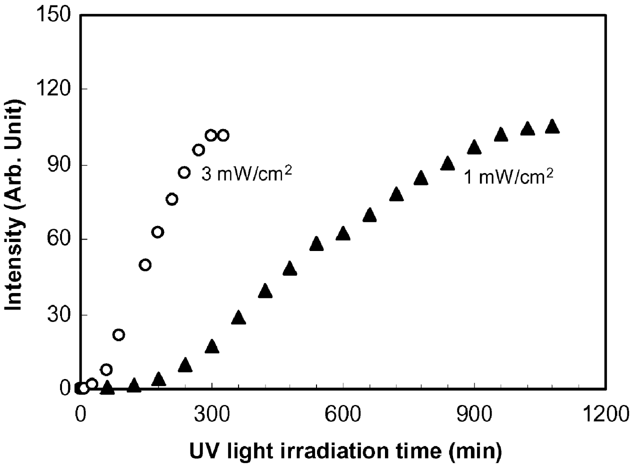


Fig. 2 Changes in fluorescence intensities of C24 (=5 × 10^{-5} M) as a function of 365 nm light irradiation time at different irradiation intensities of UV light.

fluorescent at about 440–470 nm upon UV light irradiation for 60 min. With increasing UV light irradiation time, the fluorescence intensities of C10 and C24 solutions were more enhanced and saturated within 180 min and 300 min, respectively. Their fluorescence maxima were red-shifted to 465 nm with increasing UV light irradiation time (Fig. 3e and 3f). Futhermore, with respect to a rate dependence on UV light intensity, it was observed that an induction period became shorter and an increasing rate of photoinduced fluorescence intensity was faster with increasing light intensity (Fig. 2). The finally saturated fluorescence intensity of the UV-exposed solution at a certain concentration was almost constant. The photographs in Fig. 4 display blue fluorescence from UV-exposed C10 and C24 solutions, compared with no emission from the C0 solution. The fluorescence quantum yields, estimated from 9,10-diphenyl anthracene in cyclohexane as the reference,[13] of UV-exposed C10 and C24 solutions were 1.1 × 10^{-3} and 2 × 10^{-3}, respectively. These quantum yields are very high when compared with those of earlier reports (∼10^{-7}–10^{-5}).[7] This unique fluorescence enhancement is not likely due to photodecomposition or further undesirable photoreaction of azobenzene units under UV light irradiation, but more likely due to the formation of self-assembled aggregates.

The formation of spherical aggregates of UV-exposed azobenzene derivatives with long alkyl chains in organic solution was confirmed by using scanning electron microscopy (SEM). The micrographs in Fig. 5 show spherical aggregates of approximately 50–70 nm and 30–60 nm in diameter for C10 and C24, respectively. However, no spherical aggregates were observed in the samples non-irradiated with UV light. This observation strongly suggests that the remarkable increases in fluorescence intensities are closely related to the photoinduced formation of aggregates, that is, aggregation-induced emission.[14,15]

To understand the reason for the formation of aggregates by UV light irradiation, additional UV-Vis absorption spectra were taken. In contrast to no apparent spectral change for nonfluorescent C0, upon prolonged UV light irradiation of both C10 and C24 solutions, an obvious deviation from two isosbestic points was observed (Fig. 3b and 3c), implying that other reactions such as photoinduced aggregation could follow the first stage of typical *trans*-to-*cis* isomerization. Further

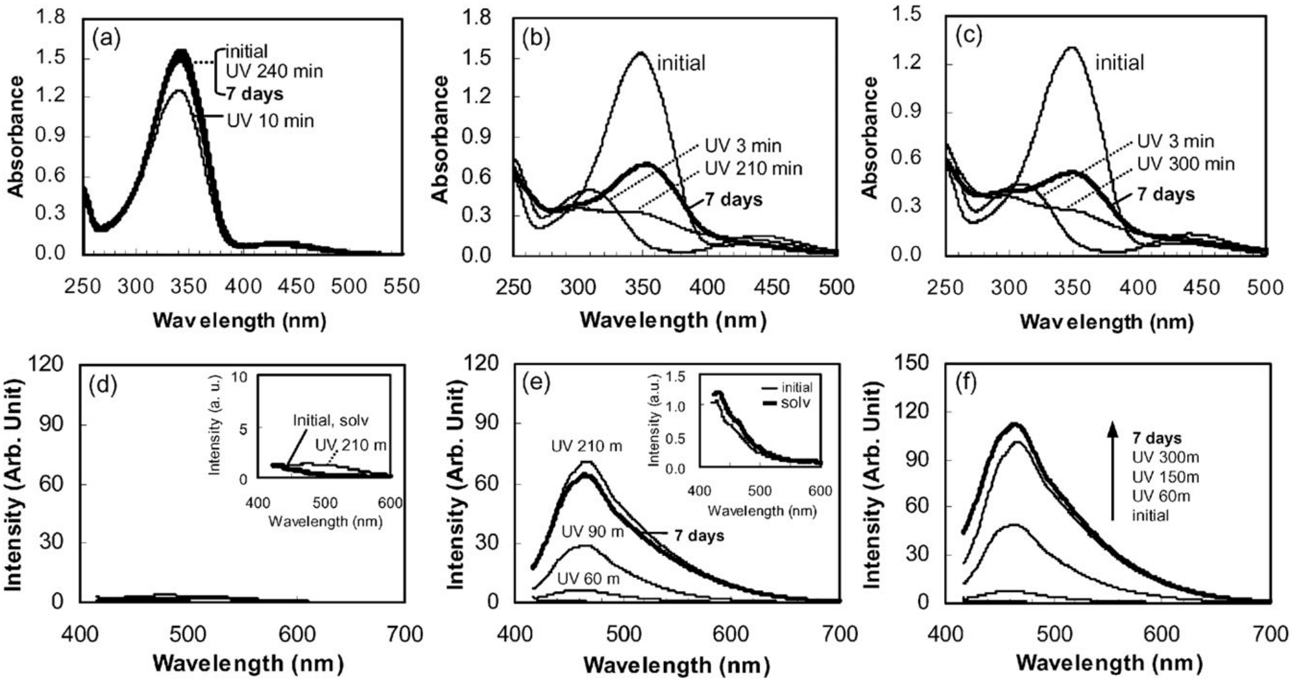


Fig. 3 Upper panel: changes in UV-Vis absorption spectra of (a) C0, (b) C10, and (c) C24 in dichloromethane. (*7 days*: dark incubation for 7 days after UV light irradiation, 3 mW cm^{-2}). Lower panel: fluorescence spectra of (d) C0, (e) C10, and (f) C24 at ambient temperature (365 nm excitation). Insets show uncorrected fluorescence spectra of the initial azobenzene solution and solvent (dichloromethane) itself.

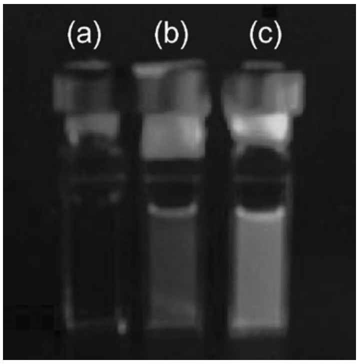


Fig. 4 Fluorescence from the UV-exposed azobenzene solutions under 365 nm irradiation. (a) C0, (b) C10, and (c) C24.

evidence for unexpected photoinduced reaction in a UV-exposed solution can be provided by an NMR study. The NMR spectra indicate that the *cis* form of C0 does not exist even after UV light irradiation for 300 min, as seen in Fig. 6A. This NMR result is in good agreement with the absorption spectral data of C0, as shown in Fig. 3a. On the other hand, upon UV light irradiation of C10 and C24 with long alkyl chains, ^{1}H NMR signals of the aromatic ring protons of the azobenzene molecules were significantly shifted upfield, not due to any decomposition of the azobenzene moieties or disulfide group but rather due to *trans*-to-*cis* isomerization (Fig. 6B and 6C). About 85% and 76% of *cis*-azobenzenes[16] of C10 and C24, respectively, were present in UV-exposed solutions (Fig. 6b) and the *cis*-azobenzenes were fully recovered to the *trans*-azobenzenes within 7 days in the dark (Fig. 6c).

Dark incubation of the UV-exposed C24 for sufficient thermal *cis*-to-*trans* isomerization resulted in the weak π–π* absorption band at about 347–351 nm. On the other hand, after sufficient thermal *cis*-to-*trans* isomerization, the π–π* absorption band (λ_{max}) of C10 was weak and more or less red-shifted to 354 nm (Fig. 3b). This red-shift of the absorption band can be explained in terms of the change in the intermolecular interactions of the azobenzene chromophores with long alkyl chains from the initial isolated species to self-assembled aggregates. Such a spectral change arising from intermolecular stacking between aromatic units to form aggregates has been seen from azobenzene chromophores, silole derivatives, and biphenylethylene derivatives.[14,15,17,18] In addition, the bent-shaped *cis* form is more polar and hydrophilic relative to the rod-shaped *trans* form, while long alkyl chains are hydrophobic.[19] When such a polar *cis*-azobenzene

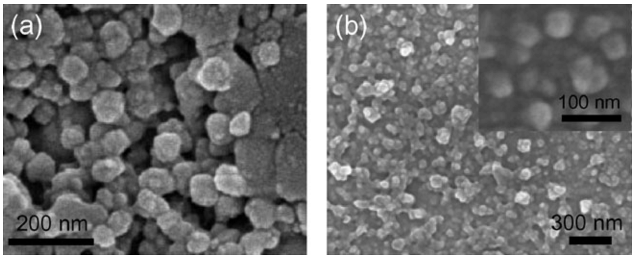


Fig. 5 SEM images of (a) C10 and (b) C24 after UV light irradiation for 240 min and 300 min, respectively.

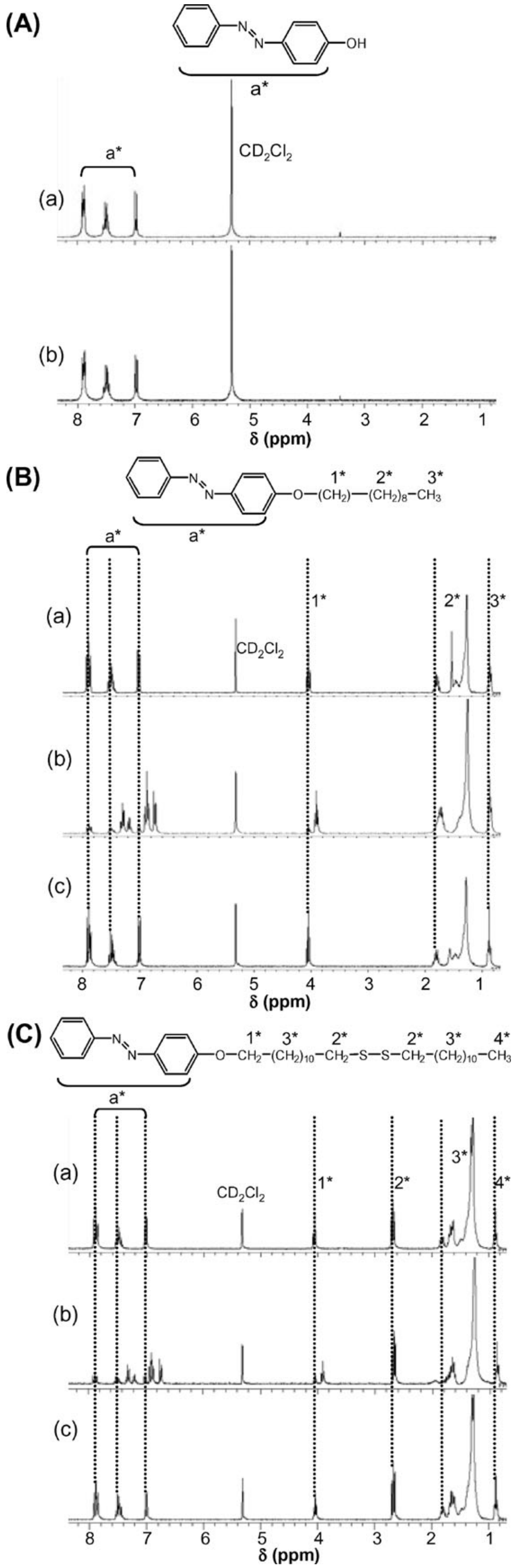


Fig. 6 ^{1}H NMR spectral changes of (A) C0, (B) C10 and (C) C24 in CD$_2$Cl$_2$. (a) Initial, (b) after UV light irradiation for 300 min, (c) after dark incubation for 7 days after UV light irradiation for 300 min.

molecule with a hydrophobic alkyl chain exists in solutions for a long time, the molecule seems to spontaneously self-assemble into aggregates. That is, the first stage of a *cis*-rich photostationary state induced by UV light can be slowly followed by the spontaneous formation of blue fluorescent aggregates of *cis*-azobenzenes with long alkyl chains. Furthermore, photoinduced blue fluorescence remained stable even after sufficient *cis*-to-*trans* thermal isomerization at ambient temperature. Nevertheless, it is still unusual that *cis*-azobenzenes with long alkyl chains self-assemble into aggregates exhibiting blue fluorescence in organic solution.

In conclusion, on the basis of the results of three azobenzene derivatives with different alkyl chain lengths, we note that long alkyl chains play an important role in causing the sufficient lifetime of *cis*-azobenzene for assembling into blue fluorescent aggregates as well as in facilitating intermolecular stacking between azobenzene moieties and hydrophobic interactions between long alkyl chains.

Acknowledgements

This work was supported by the postdoctoral fellowship of Japan Society for the Promotion of Science (JSPS).

References

1 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood Series in Physical Chemistry, Ellis Horwood Limited, New York, 1991.
2 (*a*) K. Ichimura, *Chem. Rev.*, 2000, **100**, 1847; (*b*) K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki and K. Aoki, *Langmuir*, 1988, **4**, 1214.
3 J. H. Jung, Y. Ono, K. Sakurai, M. Sano and S. Shinkai, *J. Am. Chem. Soc.*, 2000, **122**, 8648.
4 D. K. Hore, A. L. Natansohn and P. L. Rochon, *J. Phys. Chem. B*, 2003, **107**, 2197.
5 M. Han and M. Hara, *J. Am. Chem. Soc.*, 2005, **127**, 10951.
6 P. H. Rasmussen, P. S. Ramanujam, S. Hvilsted and R. H. Berg, *J. Am. Chem. Soc.*, 1999, **121**, 4738.
7 *Photoreactive Organic Thin Films*, ed. Z. Sekkat and W. Knoll, Academic Press, Elsevier Science, USA, 2002.
8 C.-H. Tung and J.-Q. Guan, *J. Org. Chem.*, 1996, **61**, 9417.
9 Z. Lei, A. Vaidyalingam and P. K. Dutta, *J. Phys. Chem. B*, 1998, **102**, 8557.
10 M. Ghedini, D. Pucci, G. Calogero and F. Barigelletti, *Chem. Phys. Lett.*, 1997, **267**, 341.
11 Y. Wakatsuki, H. Yamazaki, P. A. Grutsch, M. Santhanam and C. Kutal, *J. Am. Chem. Soc.*, 1985, **107**, 8183.
12 M. Han and K. Ichimura, *Macromolecules*, 2001, **34**, 82.
13 S. Hamai and F. Hirayama, *J. Phys. Chem.*, 1983, **87**, 83.
14 J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740.
15 B.-K. An, S.-K. Kwon, S.-D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410.
16 Because NMR measurement of a sample took 10–20 min, the presence of about 15% and 24% of *trans*-azobenzenes of C10 and C24, respectively, is closely related to the extent of thermal *cis*-to-*trans* isomerization for 10–20 min.
17 M. Shimomura and T. Kunitake, *J. Am. Chem. Soc.*, 1987, **109**, 5175.
18 R. Davis, N. P. Rath and S. Das, *Chem. Commun.*, 2004, 74.
19 (*a*) C. T. Lee Jr., K. A. Smith and T. A. Hatton, *Macromolecules*, 2004, **37**, 5397; (*b*) K. Aoki, Y. Kawanishi, T. Seki, M. Sakuragi and K. Ichimura, *Liq. Cryst.*, 1995, **19**, 119.