Fluorescence Enhancement from Self-Assembled Aggregates: Substituent Effects on Self-Assembly of Azobenzenes

Mina R. Han,* Yuuki Hirayama, and Masahiko Hara

Local Spatio-Temporal Functions Laboratory, Frontier Research System, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Fluorescent organic materials have attracted a great deal of attention because of their broad applicability in fluorescence biological labels, sensors, and light-emitting diodes.[1] From such a practical point of view, a high fluorescence quantum yield in the solid state is highly desirable. However, even though many organic chromophores and polymers are strongly fluorescent in dilute solutions, it has often been demonstrated that, in general, aggregate formation leads to a reduction in fluorescence efficiency in the solid state. A promising approach to overcoming this drawback is to develop new types of organic materials that exhibit intense fluorescence in their aggregated state.[2−4] For example, an asymmetric disulfide compound consisting of a photoisomerizable azobenzene unit coupled to a biphenyl fluorophore,[4] whose isolated species is weakly fluorescent in initial solution, spontaneously self-assembles into strongly fluorescent aggregates under UV light irradiation.

To extend the versatility of the system to general azobenzene derivatives and get insight into the determinants of spontaneous self-assembly, we prepared simple azobenzene derivatives para-substituted with electron-donating (EDGs) or electron-withdrawing groups (EWGs) (Figure 1a). During the course of our investigations, we discovered significant substituent effects on light-driven self-assembly and the resulting fluorescence enhancement of azobenzene molecules.

When initial azobenzene compounds (**1−7**, 6×10^{-5} M in dichloromethane) are excited at 365 nm at ambient temperature, no fluorescence is detected.[5−10] However, as the azobenzene solutions are continuously exposed to UV light at 365 nm (3 mW/cm^2), **1−5** begin to display blue fluorescence; the fluorescence intensity gradually increases with UV light irradiation time. The calculated fluorescence quantum yield (Φ_f)[11] increases up to approximately 1×10^{-3}
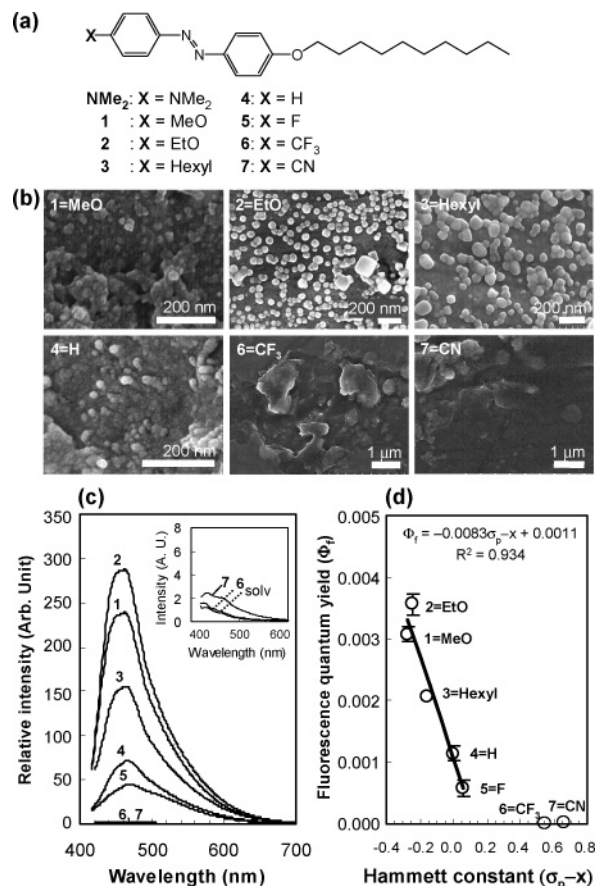

Figure 1. (a) Molecular structure. (b) SEM images of **1−7** after UV light irradiation for 300 min. (c) Fluorescence spectra of **1−7** after UV light irradiation for 300 min (365 nm excitation). Inset shows uncorrected fluorescence spectra of UV-exposed **6** and **7** and solvent itself. (d) Correlation of Hammett substituent constant ($\sigma_p−x$) and fluorescence quantum yield (Φ_f) of UV-exposed azobenzene molecules.

(Table 1), which is very high and unusual when considering that isolated initial azobenzene is not fluorescent at ambient temperature. More interestingly, the Φ_f of the UV-exposed azobenzene molecule correlates with the value of the known Hammett substituent constant ($\sigma_p−x$), indicating a relative electron-withdrawing (positive σ-value) or electron-donating (negative σ-value) effect of a particular substituent (X) when attached to a phenyl ring.[12] That is, the Φ_f increases linearly with increasing electron-donating abilities of the substituents

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Table 1. Hammett Substituent Constants ($\sigma_p - x$), Spectroscopic Data, Calculated Dipole Moments, and Fluorescence Quantum Yields (Φ_f) of NMe$_2$ and 1−7

	$\sigma_p - x^a$	λ_{max}^{abs} (nm)^b	$\mu_{trans}{}^c$	$\mu_{cis}{}^c$	$\Delta (= \mu_{cis} - \mu_{trans})$	$\bar{\Phi}_f{}^d$	λ_{max}^{em} (nm)
NMe$_2$	−0.83	409.5	2.2				510
1	−0.27	359	0.4	4.4	+4.0	0.0031	462
2	−0.24	359.5	0.1	4.6	+4.5	0.0036	462
3	−0.16	352	1.3	4.5	+3.2	0.0021	463
4	0	348	1.5	4.4	+2.9	0.0011	465
5	0.06	349.5	2.9	3.6	+0.7	0.0006	468
6	0.54	355	5.1	3.8	−1.3		
7	0.66	366	5.0	3.6	−1.4		

^{a} See ref 15. ^{b} As prepared (before UV light irradiation). ^{c} The dipole moment was calculated with the AM1 method as implemented in the HyperChem 7.5 program (Hypercube, Inc., Gainsville, FL). ^{d} The mean fluorescence quantum yield[11] after prolonged UV light irradiation.
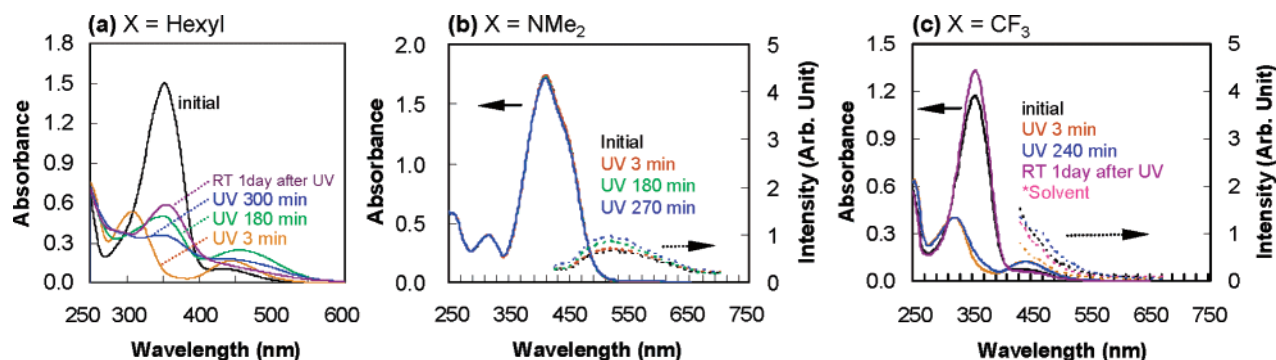

Figure 2. (a) Changes in UV−vis absorption spectra of X = hexyl (**3**) in dichloromethane. (b) Changes in UV−vis absorption and uncorrected fluorescence spectra of X = NMe$_2$ (**NMe$_2$**). (c) Changes in UV−vis absorption and uncorrected fluorescence spectra of X = CF$_3$ (**6**).

(i.e., as the substituent constant, $\sigma_p - x$, decreases), as shown in panels c and d of Figure 1 (correlation factor $R^2 = 0.934$). Although there are a few reports on the relationship between the σ_p and Φ_f of fluorescent organic materials[13] and Al (III) complexes,[14] to the best of our knowledge, the finding of the significant substituent effects on fluorescence enhancement of UV-exposed azobenzene molecules is unprecedented.

Moreover, as the substituents become more electron-donating (e.g., MeO, EtO, hexyl, and H), the azobenzenes seem to more efficiently assemble into spherical aggregates, with diameters ranging from approximately 10 to 200 nm, as confirmed by scanning electron microscopy (SEM) experiments (Figure 1b). The spontaneous formation of spherical aggregates is considered to be responsible for the unique enhancement of fluorescence intensity.[2−4]

To further corroborate that aggregation of UV-exposed azobenzenes in dilute solution induces fluorescence enhancement and that the fluorescence remains stable in the solid state, we performed fluorescence optical microscopy experiments. A fluorescence microscope image obtained after placing a few drops of the UV-exposed **2** solution on a quartz substrate and drying it for 2−3 h revealed a blue fluorescence (see the Supporting Information, Figure S1) that remained stable for months. Therefore, the preliminary investigation of the effect of substituents attached to azobenzenes is of significance for understanding important factors in determining the self-assembly of azobenzene derivatives under UV light irradiation.

The formation of self-assembled aggregates resulted in significant changes in UV−vis absorption spectra before and after UV light irradiation (Figure 2a). When compared to a typical cis-rich state obtained by UV light irradiation for 3 min, prolonged UV light irradiation led to a deviation from two isosbestic points at 309 and 415 nm as well as dramatic changes in the $\pi - \pi^*$ and $n - \pi^*$ absorption bands near 350−360 nm and 430−470 nm, respectively. However, obviously different from azobenzenes (**1−5**) displaying blue fluorescence, compounds **NMe$_2$**, **6**, and **7** clearly show neither any critical absorption spectral changes nor fluorescence enhancement during UV light irradiation, as seen in panels b and c of Figure 2.

In the case of **NMe$_2$**, contrary to our expectation, no prominent increase in fluorescence intensity is observed under prolonged UV light irradiation (Figure 2b). Considering the fact that the dimethylamino group exhibits the highest electron-donating ability ($\sigma_p = -0.83$) in the present investigation, negligibly weak fluorescence might be unexpected. However, the reason **NMe$_2$** does not exhibit fluorescence enhancement under UV light irradiation can be clearly rationalized in terms of its peculiar photoisomerization behavior in solution. As seen in Figure 2b, because thermal cis-to-trans isomerization occurs too fast at ambient temperature,[5,16,17] only the trans form exists in the UV-exposed solution; this strongly indicates that the cis form, but not the trans form, possessing a sufficient lifetime is one of the key determinants for azobenzene molecules that self-assemble into aggregates under UV light irradiation.

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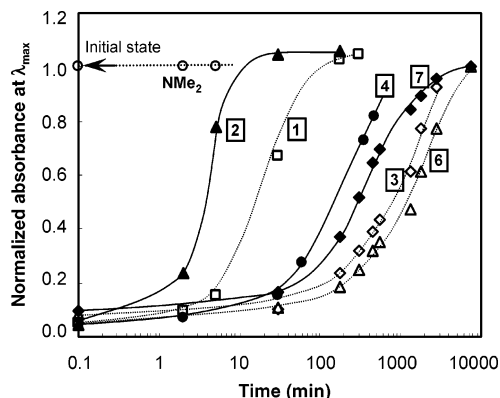(17) Ho, M.-S.; Natansohn, A.; Barrett, C.; Rochon, P. *Can. J. Chem.* **1995**, *73*, 1773.

Figure 3. Changes in normalized absorbance at λ_{max} of **NMe₂** and **1**−**7** as a function of thermal cis-to-trans isomerization time after UV light irradiation for 3 min.

Second, unlike **NMe₂**, the cis forms of **6** and **7** substituted with electron-withdrawing CF₃ and CN groups, respectively, have sufficient lifetimes (longer than 1000 min) (Figure 3). Nevertheless, both of them are nonfluorescent before and even after UV light irradiation (Figures 1c and 2c). Absorption spectral data in Figure 2c show that two sharp isosbestic points at 310 and 412 nm are kept even after prolonged UV light irradiation, confirming that no aggregated species and only two absorbing species, trans and cis isomers, exist in the UV-exposed solution. On the basis of the results of **6** and **7**, it is noted that the azobenzene molecules that cannot generate aggregates are nonfluorescent. This implies that another important factor (i.e., the larger dipole moment of *cis*-azobenzene compared with that of *trans*-azobenzene), along with the sufficient lifetime of the cis form, plays a key role in determining the light-driven self-assembly of azobenzene derivatives.

As summarized in Table 1, the dipole moments of **6** and **7** with the EWGs become smaller through trans-to-cis photoisomerization because the electron-withdrawing ability of the azo group is canceled out by CF₃ and CN groups, respectively.[18] In contrast, the dipole moments of the cis forms (**1**−**5**) are larger than those of the trans forms. The larger dipole moment of the cis form is attributed to the bent-shaped structure and electron-withdrawing property of the azo group. As a result, the cis azobenzene unit is more polar (hydrophilic) relative to the rod-shaped trans form,[19] whereas the long alkyl chain is hydrophobic. Such a cis azobenzene derivative with a long alkyl chain may function as an amphiphilic molecule and spontaneously assemble into aggregates under UV light irradiation.

In conclusion, we have demonstrated that, in general, the Φ_f of the UV-exposed azobenzene molecules increases with increasing electron-donating abilities of the substituents. The unusual fluorescence enhancement is attributed to the light-driven self-assembly of *cis*-azobenzenes showing (1) sufficient lifetime and (2) a larger dipole moment. This unprecedented result suggests the possibility of a powerful tool for the systematic preparation of fluorescent azobenzene aggregates with predictable photochemical properties.

Supporting Information Available: Detailed synthetic procedures, characterization, and fluorescence microscopic image. This material is available free of charge via the Internet at http://pubs.acs.org.

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