Making Azobenzene Fluorescent: Substituent Effects on Fluorescence Enhancement of Azobenzene Derivatives

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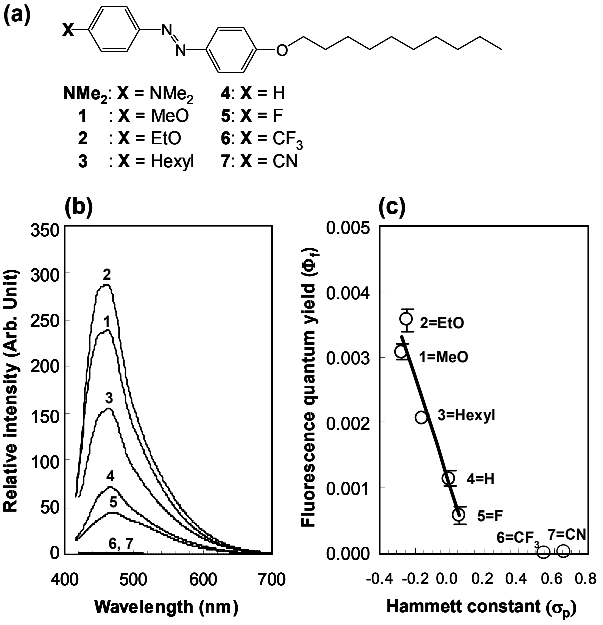
Azobenzene is a well known chromophore, which exhibits photoinduced and reversible trans/cis isomerization. The photoisomerization of azobenzene and its derivatives influences versatile physical properties such as wettability, viscosity, and aggregation behaviors because of changes in molecular structure 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. Owing to their ability to undergo trans/cis isomerization, generally azobenzene molecule does not fluoresce with appreciable quantum yield (about 10^{-7}~10^{-5}). However, a few exceptional self-assembled bilayer aggregates of azobenzene-containing amphiphiles and of azobenzene-functionalized dendrimers exhibited fluorescence emission at ~600 nm. This emission is attributed to the densely packed arrangement of azobenzene chromophores in the bilayer structure. It has also been reported that orthometallated azobenzene complexes were weakly fluorescent. By cyclometallation, the photoisomerization of *trans*-blocked azobenzene is suppressed and the efficiency of fluorescence increases significantly.

Unlike the attempts reported so far, here we describe that the first stage of *trans*-to-*cis* photoisomerization by UV light at 365 nm was slowly followed by a significant enhancement of the fluorescence from azobenzene molecule, which seems to be related to the spontaneous formation of spherical organic aggregates. In addition, to obtain an insight into significant substituent effect on the fluorescence enhancement of azobenzenes, we synthesized azobenzene derivatives *para*-substituted with electron-donating (EDGs) or electron-withdrawing groups (EWGs). The fluorescence enhancement is closely related to *cis*-azobenzene showing both sufficient lifetime and a larger dipole moment. The fluorescence quantum yield increased linearly with increasing electron-donating abilities of the substituents.



(a) Molecular structure. (b) Fluorescence spectra of 1–7 after UV light irradiation (365 nm excitation). (c) Correlation of Hammett substituent constant (σ_p) and fluorescence quantum yield (Φ_f) of UV-exposed azobenzene molecules (1–7).

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