Light-driven modulation of fluorescence color from azobenzene derivatives containing electron-donating and electron-withdrawing groups†

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We report a simple preparation and color-tunable fluorescence of a series of azobenzene derivatives. The introduction of an electron-withdrawing or electron-donating group at the X position of azobenzenes (**1–8**) containing a biphenyl unit makes it possible to modulate the fluorescence color of the UV-exposed azobenzene solutions from blue to yellow, which correlates with the electron-donating abilities of the respective substituents. Theoretical calculations suggest that changes in both the dihedral angles between two phenyl rings of the biphenyl unit and the dipole moments between the *trans* and *cis* forms depending on the substituents seem to be important factors in determining the photochemical properties of chromophores.

Introduction

Fluorescent organic materials have attracted considerable attention due to their potential uses in light-emitting diodes (LEDs), sensors, biological probes, and optoelectronics.[1–5] Due to such a broad range of applications, exploring organic fluorescent cores exhibiting the ability to tune fluorescence emission maxima in the visible region is desirable.[6] Chemical modification of the π conjugation or variations in substituents and substitution positions can influence the energy levels and/or dipole moments in the ground and excited states of the core fluorophores,[6–8] which gives rise to different optical and photochemical properties of such fluorescent materials.[7–9] Thus, to design an organic chromophore with desirable photochemical and photophysical properties, an understanding of the relationship between its molecular structure and its function is required.

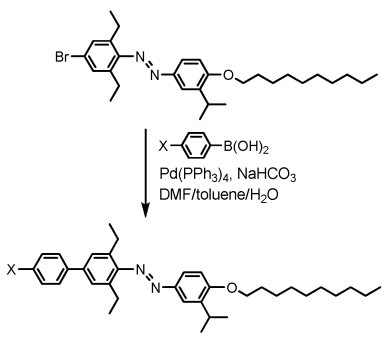
One of our research groups has reported that a photochromic azobenzene molecule with a long alkyl chain can show unusual fluorescence enhancement under continuous UV light irradiation and form self-assembled spherical aggregates.[10] Changes in fluorescence intensity have also been detected in a series of azobenzene-containing side-chain polymers having biphenyl and naphthalene fluorophores by Smitha and Asha.[11] However, modulating the fluorescence color over a wide wavelength range in the visible region has not been explored thus far. In this paper, we prepared a series of azobenzene derivatives (**1–8**, see Fig. 1) with substituents bearing various electronic properties, composed of a phenylazo core attached to biphenyl fluorophore as a head segment and a long decyloxy group as a tail segment. These compounds were found to exhibit tunable fluorescence from blue to yellow under UV light irradiation, which correlated with the values of the Hammett constant (σ_p-X) of the respective substituents.

Experimental

Synthesis

Compounds (**1–8**) were all synthesized by the same literature procedure – the well-known Williamson reaction and subsequent Suzuki coupling reaction.[12–14] Compound **1** is described as a representative example.

1 (X = CN). The compound (**1**) was prepared from the Suzuki coupling reaction of the precursor ((*E*)-1-{4-bromo-2,6-diethylphenyl}-2-{4-(decyloxy)-3-isopropylphenyl}diazene) in the presence of palladium(0) catalyst. A catalytic amount of



1: X = CN
2: X = COOMe
3: X = CF_3O
4: X = H
5: X = Me
6: X = MeO
7: X = BuO
8: X = NMe_2

Fig. 1 Synthesis of **1–8**.

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tetrakis(triphenylphosphine)palladium(0) was added to a solution of the precursor (1.00 g, 1.94 mmol) in degassed DMF (30 mL). 4-Cyanophenylboronic acid (0.57 g, 3.87 mmol), a solution of $NaHCO_3$ (1.00 g) in 30 mL of distilled water, and toluene (15 mL) were added to the mixture solution. The reaction mixture was heated under reflux for 6 h with vigorous stirring. After the mixture was cooled down to room temperature, water and ethyl acetate were added to it. The organic layer was separated and purified by silica gel column chromatography (dichloromethane) and recrystallized from ethyl acetate twice to afford an orange solid (yield: 0.48 g, 46%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.81 (t, 3H, CH_3), 1.09–1.53 (m, 26H, CH_2 and CH_3), 1.78 (m, 2H, CH_2), 2.65 (q, 4H, ArCH_2CH$_3$), 3.31 (m, 1H, ArC*H*), 4.00 (t, 2H, ArOCH_2), 6.88 (d, J = 6.87 Hz, 1H, Ar-*H*), 7.18–7.77 (m, 8H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 14.1, 15.3, 22.4, 22.6, 25.2, 26.1, 27.2, (–CH_2–; 29.2, 29.3, 29.5, 29.5), 31.9, 68.3, 110.6, 110.8, 119.0, 120.4, 122.4, 126.2, 127.6, 132.5, 136.9, 137.9, 137.9, 145.6, 146.8, 151.9. Anal. Calcd: C, 80.40; H, 8.81; N, 7.81. Found: C, 80.20; H, 8.98; N, 7.72. FAB-HRMS (m/z): [M + H]$^+$: found 538.3821 (M + H), calcd for $C_{36}H_{48}N_3O$ 538.3797.

2 (X = COOMe). (yield: 39%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.87 (t, 3H, CH_3), 1.03–1.54 (m, 26H, CH_2 and CH_3), 1.84 (m, 2H, CH_2), 2.72 (q, 4H, ArCH_2CH$_3$), 3.37 (m, 1H, ArC*H*), 3.93 (s, 3H, CH_3OCO), 4.05 (t, 2H, ArOCH_2), 6.93 (d, J = 8.64 Hz, 1H, Ar-*H*), 7.29–8.10 (m, 8H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 14.1, 15.4, 22.4, 22.6, 25.2, 26.1, 27.2, (–CH_2–; 29.2, 29.3, 29.5, 29.5), 31.9, 52.0, 68.2, 110.8, 120.4, 122.3, 126.3, 126.9, 128.7, 130.0, 136.8, 137.8, 138.9, 145.5, 146.8, 151.5, 159.3, 167.0. Anal. Calcd: C, 77.85; H, 8.83; N, 4.91. Found: C, 77.82; H, 9.02; N, 4.89. FAB-HRMS (m/z): [M + H]$^+$: found 571.3906 (M + H), calcd for $C_{37}H_{51}N_2O_3$ 571.3900.

3 (X = CF_3O). (yield: 45%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.81 (t, 3H, CH_3), 1.08–1.48 (m, 26H, CH_2 and CH_3), 1.78 (m, 2H, CH_2), 2.65 (q, 4H, ArCH_2CH$_3$), 3.30 (m, 1H, ArOC*H*), 3.99 (t, 2H, ArOCH_2), 6.86 (d, J = 8.91 Hz, 1H, Ar-*H*), 7.17–7.76 (m, 8H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 14.1, 15.4, 22.4, 22.7, 25.2, 26.2, 27.2, (–CH_2–; 29.2, 29.3, 29.5, 29.6), 31.9, 68.3, 110.9, 120.4, 121.2, 122.3, 126.1, 128.4, 136.8, 137.9, 138.8, 139.9, 146.9, 148.6, 151.1. Anal. Calcd: C, 72.45; H, 7.94; N, 4.69; F, 9.55. Found: C, 72.55; H, 7.97; N, 9.53; F, 4.68. FAB-HRMS (m/z): [M + Na]$^+$: found 619.3473 (M + Na), calcd for $C_{36}H_{47}F_3N_2O_2Na$ 619.3487.

4 (X = H). (yield: 26%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.82 (t, 3H, CH_3), 1.02–1.48 (m, 26H, CH_2 and CH_3), 1.78 (m, 2H, CH_2), 2.65 (q, 4H, ArCH_2CH$_3$), 3.31 (m, 1H, ArOC*H*), 3.99 (t, 2H, ArOCH_2), 6.87 (d, J = 8.64 Hz, 1H, Ar-*H*)), 7.18–7.77 (m, 8H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 14.1, 15.5, 22.4, 22.6, 25.3, 26.1, 27.2, (−CH_2−; 29.2, 29.3, 29.5, 29.5), 30.9, 31.9, 68.2, 110.8, 120.4, 122.1, 126.2, 127.1, 127.2, 128.7, 136.6, 137.8, 140.3, 141.1, 146.9, 150.7, 159.1. Anal. Calcd: C, 81.98; H, 9.44; N, 5.46. Found: C, 81.96; H, 9.52; N, 5.46. FAB-HRMS (m/z): [M + Na]$^+$: found 535.3677 (M + Na), calcd for $C_{35}H_{48}N_2ONa$ 535.3664.

5 (X = Me). (yield: 40%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85 (t, 3H, CH_3), 1.07–1.54 (m, 26H, CH_2 and CH_3), 1.81 (m, 2H, CH_2), 2.38 (s, 3H, Ar–CH_3), 2.70 (q, 4H, ArCH_2CH$_3$), 3.36 (m, 1H, ArOC*H*), 4.05 (t, 2H, ArOCH_2), 6.92 (d, J = 8.64 Hz, 1H, Ar-*H*), 7.22–7.83 (m, 8H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 14.1, 15.5, 21.1, 22.4, 22.6, 25.3, 26.1, 27.2, (–CH_2–; 29.2, 29.3, 29.5, 29.6), 31.9, 68.2, 110.8, 120.3, 122.1, 126.0, 126.9, 129.4, 136.7, 136.9, 137.7, 138.2, 140.2, 146.9, 150.4, 159.1. Anal. Calcd: C, 82.08; H, 9.57; N, 5.32. Found: C, 81.90; H, 9.77; N, 5.29. FAB-HRMS (m/z): [M + Na]$^+$: found 549.3819 (M + Na), calcd for $C_{35}H_{50}N_2ONa$ 549.3821.

6 (X = MeO). (yield: 59%): ^{1}H NMR (270 MHz, $CDCl_2$) δ 0.87 (t, 3H, CH_3), 1.04–1.53 (m, 26H, CH_2 and CH_3), 1.81 (m, 4H, CH_2), 2.73 (q, 4H, ArCH_2CH$_3$), 3.36 (m, 1H, ArOC*H*), 3.84 (s, 3H, CH_3O–), 4.04 (m, 4H, ArOCH_2), 6.92–7.82 (m, 9H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 14.1, 15.5, 22.4, 22.7, 25.4, 26.1, 27.2, (–CH_2–; 29.2, 29.3, 29.5, 29.6), 31.9, 55.3, 68.2, 110.8, 114.1, 120.3, 122.1, 125.8, 128.1, 133.6, 136.8, 137.7, 139.9, 146.9, 150.1, 159.0, 159.1. Anal. Calcd: C, 79.66; H, 9.28; N, 5.16. Found: C, 79.48; H, 9.46; N, 5.13. FAB-HRMS (m/z): [M + Na]$^+$: found 565.3781 (M + Na), calcd for $C_{36}H_{50}N_2O_2Na$ 565.3770.

7 (X = BuO). (yield: 55%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, 3H, CH_3), 0.99 (t, 3H, CH_3), 1.1–1.6 (m, 28H, CH_2 and CH_3), 1.82 (m, 4H, CH_2), 2.74 (q, 4H, ArCH_2CH_3), 3.37 (m, 1H, ArC*H*), 4.02 (tt, 4H, ArOCH_2), 6.94 (m, 3H, Ar-*H*), 7.31 (s, 2H, Ar-*H*), 7.53–7.83 (m, 4H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 13.9, 14.1, 15.6, 19.3, 22.4, 22.7, 25.4, 26.2, 27.2, (–CH_2–; 29.72, 29.31, 29.54, 29.57), 31.3, 31.9, 67.8, 68.3, 110.9, 114.7, 120.4, 122.1, 125.8, 128.1, 133.4, 136.8, 137.8, 140.0, 147.0, 150.1, 158.7, 159.1. Anal. Calcd: C, 80.09%; H, 9.65%; N, 4.79%. Found: C, 80.03%; H, 9.75%; N, 4.72%. FAB-MS (m/z): [M + H]$^+$: found 585 (M + H), calcd for $C_{39}H_{56}N_2O_2$ 584.43.

8 (X = NMe_2). (yield: 60%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.81 (t, 3H, CH_3), 1.1–1.5 (m, 26H, CH_2 and CH_3), 1.8 (m, 2H, CH_2), 2.69 (q, 4H, ArCH_2CH$_3$), 2.93 (s, 6H, N(CH_3)$_2$), 3.28 (m, 1H, ArOC*H*), 4.00 (t, 2H, ArOCH_2), 6.72–7.76 (m, 9H, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$) 14.1, 15.6, 22.4, 22.6, 25.5, 26.1, 27.2, (–CH_2–; 29.2, 29.3, 29.5, 29.6), 31.9, 40.6, 68.2, 110.8, 112.7, 120.3, 122.0, 125.4, 127.6, 129.1, 136.9, 137.7, 140.4, 147.0, 149.5, 150.0, 158.9. Anal. Calcd: C, 79.95; H, 9.61; N, 7.56. Found: C, 80.01; H, 9.74; N, 7.55. FAB-HRMS (m/z): [M]$^+$: found 555.4171 (M), calcd for $C_{37}H_{53}N_3O$ 555.4189.

Instrumentation

Dichloromethane of spectroscopic grade was used to dissolve azobenzene compounds. After a 30-s nitrogen purge, a screw-cap quartz cuvette containing azobenzene solution was sealed with Parafilm®. Azobenzene solutions were exposed to UV light (365 nm, Mineralight® lamp, Model UVGL-25) or visible light (436 nm, a high-pressure UV lamp, Ushio Inc., combination of Toshiba color filters, Y-43 + V-44). Absorption and fluorescence spectra were recorded on a Shimadzu UV-3100PC UV-VIS-NIR scanning spectrophotometer and a JASCO FP-6500 (RF-5300PC) spectrofluorometer, respectively. NMR spectra were obtained using JEOL JNM-EX270 (270 MHz)

and JEOL JNM-ECP300 (300 MHz) spectrometers. The TEM (transmission electron microscope) was performed at 120 kV using JEOL JEM-2100F/SP. The sample was prepared by placing a few drops of the UV-exposed solution onto carbon-coated grids as well as silica-coated grids, and by drying fully at ambient temperature.

The fluorescence lifetimes were measured with a picosecond light source and an ultrafast photodetector. The picosecond pulse light (3 ps, 800 nm, 1 kHz) was generated by a Ti:sapphire amplifier (Quantronix Titan-I-3p), and the second harmonics of the pulse (400 nm) were used for sample excitation. The fluorescence from the sample was collected and focused on a MSM (metal–semiconductor–metal) photodetector (Hamamatsu G4176) using condenser lenses (f = 23.5 mm). The response time of the photodetector was 50 ps. The output signal of the detector was monitored with a 50 GHz digitizing oscilloscope (Hewlett Packard 54750A). The FWHM (full width at half maximum) of the instrumental function was 500 ps.

Theoretical calculation

Theoretical calculations were performed by the GAUSSIAN 03W program package[15] on a DELL Workstation T5400 (Xeon CPU 3.00 GHz × 2, 4.0 GB RAM). For each optimized geometry, frequency analyses were carried out and we found no imaginary frequency. Zero-point energy (ZPE) corrections were also calculated using computed harmonic frequencies. Time-dependent density functional theory (TD-DFT) calculations were performed on each optimized geometry using B3LYP/6-31G(d,p) to estimate the electronic absorption spectra (see ESI†).

Results and discussion

Azobenzenes (**1–7**) in dichloromethane solution showed strong π–π* absorption bands at around 344–352 nm and weak n–π* absorption bands near 450 nm in the initial state (Table 1 and Fig. S1†). When **1** solution was excited at 330 nm, negligible fluorescence ($\Phi_f < \sim 10^{-4}$)[10a,16] at around 410 nm was observed. Upon exposure to UV light for 2 min to reach a *cis*-rich state, the fluorescence intensity increased slightly,[17] along with a drastic reduction in the π–π* absorption band in the UV-vis absorption spectrum, as shown in Fig. 2 and Fig. S2†. Subsequent visible light irradiation of the UV-exposed solution for 3 min to induce *cis*-to-*trans* photoisomerization (approximately 30% of the *cis* form still existed at the photostationary state of visible light) did not weaken the fluorescence intensity to the original value, but rather somewhat raised it. Alternating UV and visible light irradiation brought about a gradual increase in its fluorescence intensity, accompanied by reversible *trans* ↔ *cis* photoisomerization. As the azobenzene **1** solution was continuously exposed to UV light for 1 h, the blue fluorescence intensity increased significantly ($\Phi_f \sim 10^{-3}$, Table 1, Fig. 3 and Fig. S2). NMR spectra revealed that the fluorescent solution of **1** mainly comprised *cis*-azobenzene, and that no additional photoreaction of the azobenzene unit (6.7–8.0 ppm) was found under prolonged UV light irradiation (Fig. S4†). Slow thermal *cis*-to-*trans* isomerization in the dark was observed at ambient temperature without a significant reduction of the fluorescence intensity.[10]

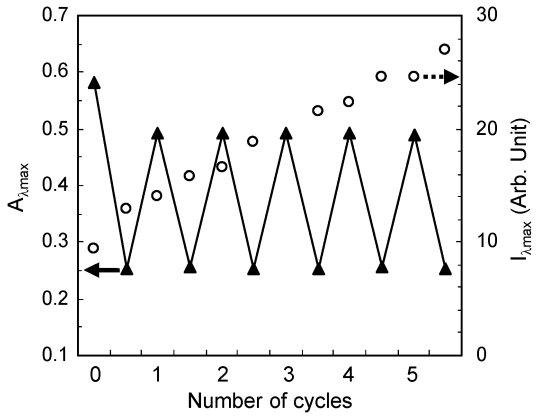

Fig. 2 Changes in absorbance at λ_{max} ($A_{\lambda_{max}}$, filled triangles) and fluorescence intensity at emission maximum ($I_{\lambda_{max}}$, open circles) of **1** in dichloromethane solution upon alternating UV and visible light irradiation.

Fig. 4 shows the fluorescence of the UV-exposed **1–7** solutions and the linear relationship between the value of the Hammett constant (σ_p-X)[18] of each substituent X and the fluorescence wavelength maximum of the UV-exposed azobenzene solution when the solution was excited at 365 nm (correlation coefficient r = 0.94). That is, the fluorescence color can be readily modulated from blue to yellow by increasing the electron-donating abilities of the substituents in the order of cyano (σ_p-**1** = 0.66), methyl (σ_p-**5** = −0.17), and butoxy (σ_p-**7** = −0.32). The fluorescence remained stable at ambient temperature for more than 1 month. Unlike previous reports,[8,10c,19] we have found little relationship between the Hammett substituent constant and either the fluorescence quantum yield or the lifetime (Table 1 shows the difference

Table 1 Hammett substituent constants, computed (Gaussian 03W) data, and absorption and fluorescence data of **1–8**

Cpd	σ_p-X [a]	Δμ ($\mu_{trans} - \mu_{cis}$) [b]	Ph–Ph dihedral angle (°) [b]	π–π*, n–π* (nm) [c]	λ_{max} (nm) [c]	Φ_f [16]	τ (ns) [c]
1	0.66	2.46 (8.19 − 5.73)	36.39	344, 448	418	0.0012	4.4
2	0.45	−0.31 (4.61 − 4.92)	35.81	344, 447	427	0.0012	4.6
3	0.35	0.74 (4.75 − 4.01)	36.46	345, 447.5	479	0.0008	4.7
4	0	−2.00 (2.29 − 4.29)	37.03	345.5, 448	482	0.0023	5.3
5	−0.17	−2.69 (1.81 − 4.50)	36.40	347, 448.5	492	0.0023	5.2
6	−0.27	−4.46 (0.77 − 5.23)	35.16	352, 449	521	0.0013	5.6
7	−0.32	−5.05 (0.37 − 5.42)	34.61	352.5, 449	531	0.0027	5.2
8	−0.83	−3.71 (2.03 − 5.74)	33.71	377	—	—	—

[a] See ref. 17. [b] See ESI†. All decyloxy groups were replaced with methoxy groups to minimize calculation time and should have little influence on overall molecular geometry and spectroscopic features. [c] In dichloromethane.

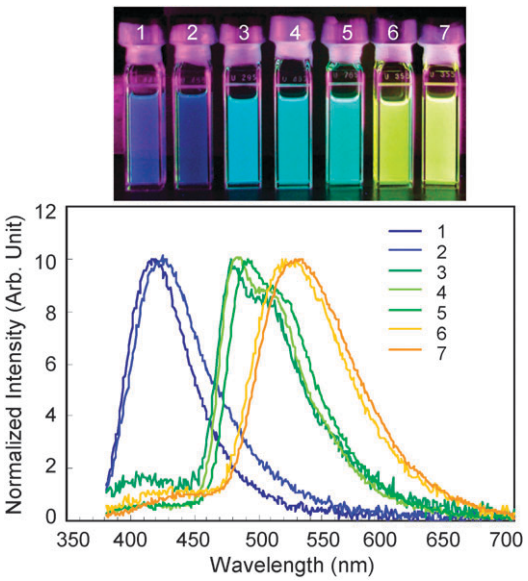

Fig. 3 Fluorescence emission spectra of UV-exposed **1–7** solutions upon excitation at 365 nm.

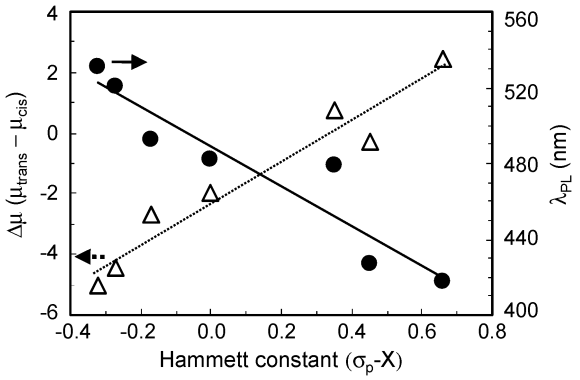

Fig. 4 Correlation plots of $\Delta\mu$ ($\mu_{trans} - \mu_{cis}$) and fluorescence maximum wavelengths (λ_{PL}) of **1–7** *versus* Hammett substituent constants (σ_p-X).

in the calculated dipole). Furthermore, transmission electron microscopy (TEM) studies indicated the existence of small aggregates approximately 10–50 nm in diameter for the UV-exposed solutions (Fig. 5), suggesting that light-driven fluorescence enhancement is more-or-less correlated with the formation of aggregates in solution.[10,20,21]

Contrary to one's expectation in this study of a significant bathochromic shift in the fluorescence wavelength for **8** with strong electron-donating ability ($\sigma_p = -0.83$), neither fluorescence enhancement nor absorption spectral changes under UV light irradiation were recorded (Fig. S5†). This result can be interpreted in terms of the isomerization characteristics in solution. Although *cis*-azobenzene, with a sufficient lifetime, plays an important role in light-driven fluorescence enhancement,[10c] as the lifetime of *cis*-**8** generated by UV light is too short and the *cis* form readily reverts to the *trans* form even in the dark, only the *trans* form is present in solution.[22,23]

While an unsubstituted biphenyl unit in vacuum has a dihedral angle of approximately 42–54°,[11,19a,24] the calculated dihedral angles between two phenyl rings for azobenzenes **1–8**

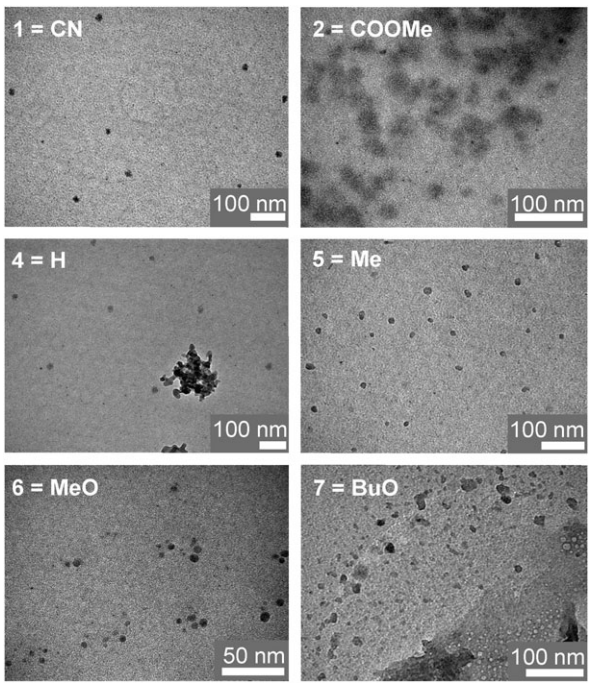

Fig. 5 TEM images of azobenzenes (8×10^{-5} M) after UV light irradiation.

were 37–33° (Table 1 and ESI†). These values are close to the dihedral angle of 32° obtained from the X-ray crystal structure analysis of an azobenzene derivative,[25] reflecting the fact that the two phenyl rings of the biphenyl unit have a more planar structure despite steric hindrance due to diethyl groups at the *ortho* positions with respect to the azo group. Moreover, the dihedral angles show a slight tendency to decrease from 37.0° for **4** to 33.7° for **8** with increasing electron-donating ability of the substituents. Hence, azobenzene becomes more planar, which might induce changes in the fluorescence properties of organic chromophores.[26]

In addition, the dipole moments are greatly influenced by the conformation change in the rod-shaped *trans* and the bent *cis* forms as well as by the electronic nature of the substituent. As shown in Fig. 4 and Table 1, the difference in the calculated dipole moments between the *trans* and *cis* forms of respective azobenzene compounds increased linearly with increasing electron-donating ability of the substituents. Although it remains difficult to elucidate the electronic effects on light-driven fluorescence enhancement and fluorescence properties, changes in the molecular geometry and the dipole moment (which depend on the substituents) seem to be important factors responsible for the photochemical and photophysical properties of chromophores.

Conclusions

We have shown that the fluorescence wavelength of the UV-exposed azobenzene solution can be modulated by simply changing the substituents with different electronic properties. Our theoretical calculations indicate that the substituents attached to the biphenyl unit affect not only the coplanarity of the chromophores but also the difference in the dipole moments between the *trans* and *cis* forms. The linear

relationship between the fluorescence wavelength maxima and the Hammett substituent constants allows one to predict and design fluorescence properties of azobenzene chromophores under UV light irradiation.

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