Electronic Supplementary Material (ESI) for Chemical Communications

Pinning effect for photoisomerization of dicationic azobenzene derivative by anionic sites of clay surface

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Experimental and Computational Section

Figure S1. ^{1}H-NMR spectra of 100% *trans*-Azo^{2+}. NMR spectra were recorded on Bruker500 (500-MHz) and taken in D_2O.

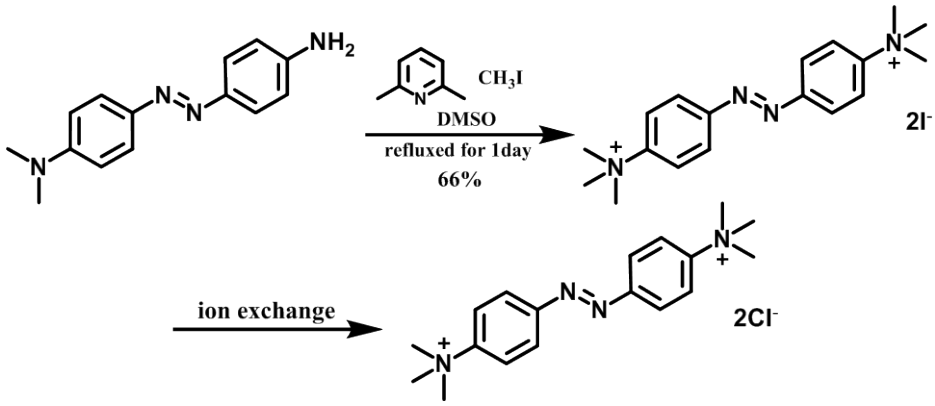
Figure S2. (a) Absorption spectra of Azo^{2+}/clay complexes at various dye loadings up to 100% vs. CEC in water. (b) Lambert-Beer plot for azo^{2+}/clay complexes at 340 nm.

Figure S3. Absorption spectral changes upon visible light irradiation (420 nm light, 6.9 mW) for (a) *cis*-rich Azo^{2+} in water ($[Azo^{2+}] = 2.0\times10^{-5}$ M) and (b) *cis*-rich Azo^{2+}/clay complex ($[Azo^{2+}] = 2.0\times10^{-5}$ M, $[SSA] = 2.0\times10^{-4}$ equiv. L^{-1}).

Figure S4. ^{1}H-NMR spectra of Azo^{2+} sample irradiated UV light a certain time. t and c means *trans* isomer and *cis* isomer respectively. NMR spectra were recorded on Bluker500 (500-MHz) and taken in D_2O.

Experimental and Computational Section

Azo^{2+} was synthesized as shown in Scheme 1. About 5 mL of iodomethane and 0.1 mL of 2,6-lutidine were added to a solution of 4-amino-4'-dimetylaminoazobenzene (100 mg, 0.42 mmol) in 4.0 mL of dimethyl sulfoxide. The mixture was refluxed for a day. After the solution was filtered and washed by dichloromethane, the orange powder was obtained (150.5 mg, 66%). Recrystallization from a mixture of ethanol (50 mL) and water (5 mL) afforded 55.6 mg (37%) of 4,4'-Bis(*N,N,N*-trimetylammonium)azobenzene. Finally the counterion (iodide anion) was exchanged with chloride by use of an ion exchange column (ORGANO AMBERLITE). Identity of the product was confirmed using ^{1}H-NMR and elemental analysis. ^{1}H-NMR (D_2O, 500 MHz) δ (ppm): 8.21 (d, 4H), 8.21 (d, 4H), 3.78 (s, 18H). Elemental analysis: Found: C, 58.2; H, 7.09; N, 14.9. Calculated: C, 58.5; H, 7.10; N, 15.1.



Scheme 1. The synthetic route of Azo^{2+}.

UV-visible absorption spectra were measured by Shimadzu UV-3150 and all experiments were conducted in an ambient atmosphere and under the red light.

Azo^{2+}/clay complex was prepared by mixing of the aqueous clay suspension and the respective aqueous Azo^{2+} solution under stirring. The concentration of clay for a Lambert-Beer plot was always kept 2.7×10^{-5} equiv. L^{-1} and the dye loading levels were changed by varying the concentration of Azo^{2+} (6.6×10^{-7}M~1.2×10^{-5}M).

The molar extinction coefficient of *trans* isomer ε_{trans} can be determined from absorption spectra of 100% *trans* isomer sample which was confirmed from ^{1}H-NMR spectra (Figure S1 in Supporting Information). That of *cis* isomer ε_{cis} was derived as follows. The ratio between *trans* and *cis* isomers can be obtained from ^{1}H-NMR spectra of the Azo^{2+} sample which was previously irradiated UV light a certain time (Figure S4 in Supporting Information). Then, the molar extinction coefficient of *cis* isomer is obtained from the ratio (18.0:25.4), the absorption of the irradiated sample and the molar extinction coefficient of *trans* isomer.[19] ε_{trans} in water at 309 nm and 440 nm is 2.50×10^4 $dm^3mol^{-1}cm^{-1}$ and 730 $dm^3mol^{-1}cm^{-1}$ respectively. ε_{cis} in water at 272 nm and 420 nm is 6.55×10^3 $dm^3mol^{-1}cm^{-1}$ and 1.59×10^3 $dm^3mol^{-1}cm^{-1}$ respectively.

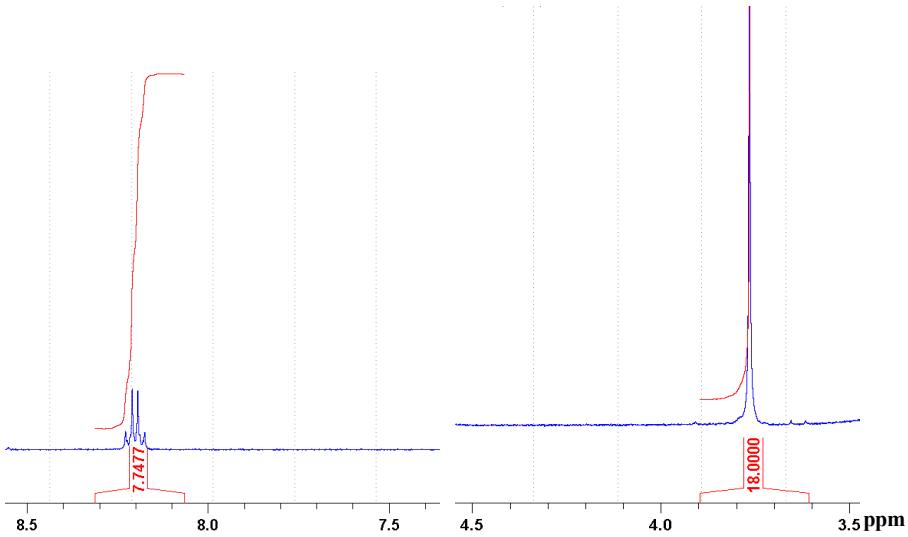
The molar extinction coefficient of *cis*-Azo^{2+}/clay complex was calculated from the absorption which was measured after the irradiated Azo^{2+} sample whose ratio between *trans* and *cis* isomers was known from ^{1}H-NMR spectra was adsorbed on the clay (loading level: 20%). ε_{trans} on the clay at 313 nm and 444 nm is 2.65×10^4 $dm^3mol^{-1}cm^{-1}$ and 490 $dm^3mol^{-1}cm^{-1}$ respectively. ε_{cis} on the clay at 277 nm and 425 nm is 8.02×10^3 $dm^3mol^{-1}cm^{-1}$ and 1.88×10^3 $dm^3mol^{-1}cm^{-1}$ respectively.

Concentration of Azo^{2+} for the photoisomerization reactions was 2×10^{-5} M. The loading level of Azo^{2+} is 20% vs. CEC of the clay ([SSA] = 2×10^{-4} equiv. L^{-1}). For the *trans*→*cis* photoisomerization reaction by irradiating with 323 nm light (Hg lamp, USHIO USH-500SC), a band pass filter (Hoya U-340), solution filter ([K_2CrO_4] = 0.28 g L^{-1}, [Na_2CO_3] = 1.0 g L^{-1}) and a glass filter were used. For the reaction *cis*→*trans* by irradiating with 420 nm light (Xe lamp, USHIO UXL-500SX), a interference filter (Edmund, Central Wavelength; 420 nm, FWHM; 10 nm) and IR cutoff filter (Edmund #54-516) were used.

The photoisomerization quantum yields can be calculated from the kinetic differential eq. 1 (the Zimmerman equation)[1-4] ,

$$\frac{dC_c}{dt} = \frac{1-10^{-A'}}{A'} \cdot \frac{I_0 \lambda l}{N_A V h c} (\varepsilon'_t \phi_{t\to c} C_t - \varepsilon'_c \phi_{c\to t} C_c) - k_\Delta C_c \qquad (1)$$

where A', I_0, λ, l, N_A, V, h, c, ε'_t, ε'_c, $\varphi_{t\rightarrow c}$, $\varphi_{c\rightarrow t}$, C_t, and C_c are the absorbance at the irradiation wavelength, the incident light intensity of the irradiation light (Js^{-1}), the irradiation wavelength (m), optical pass length (cm), Avogadro's constant (mol^{-1}), the volume of the solution (L), the Plank's constant (Js), the light speed (ms^{-1}), the molar extinction coefficients of the *trans* and *cis* isomers at the irradiation wavelength ($Lmol^{-1}cm^{-1}$), the photoisomerization quantum yields of *trans*→*cis* and *cis*→*trans* reactions, the concentration of *trans* and *cis* isomers in the solution ($molL^{-1}$) respectively. k_Δ is the thermal rate constant, which is negligible in these experiments. Thus, this term is safely treated as zero.



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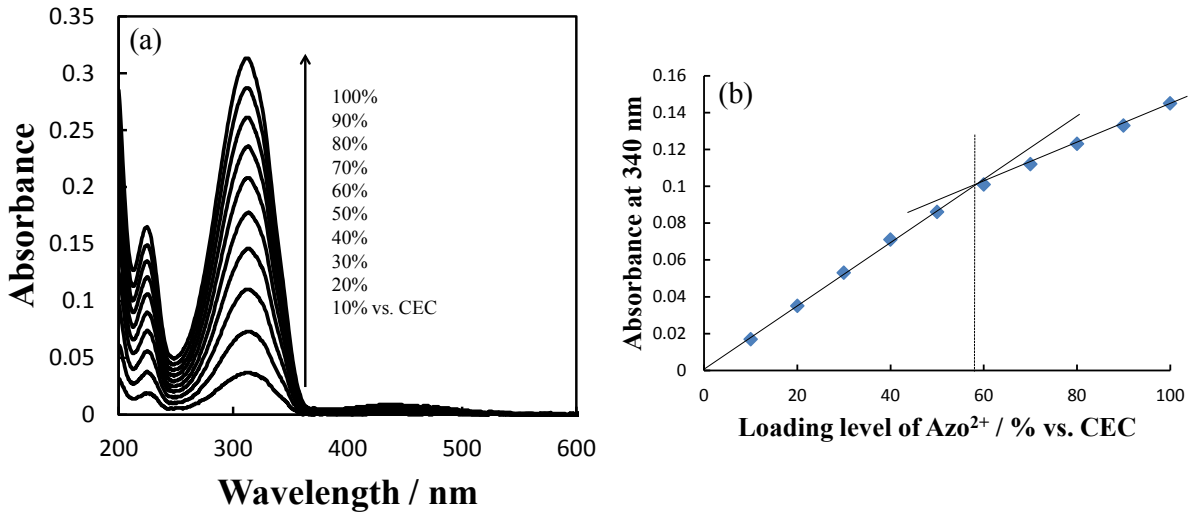

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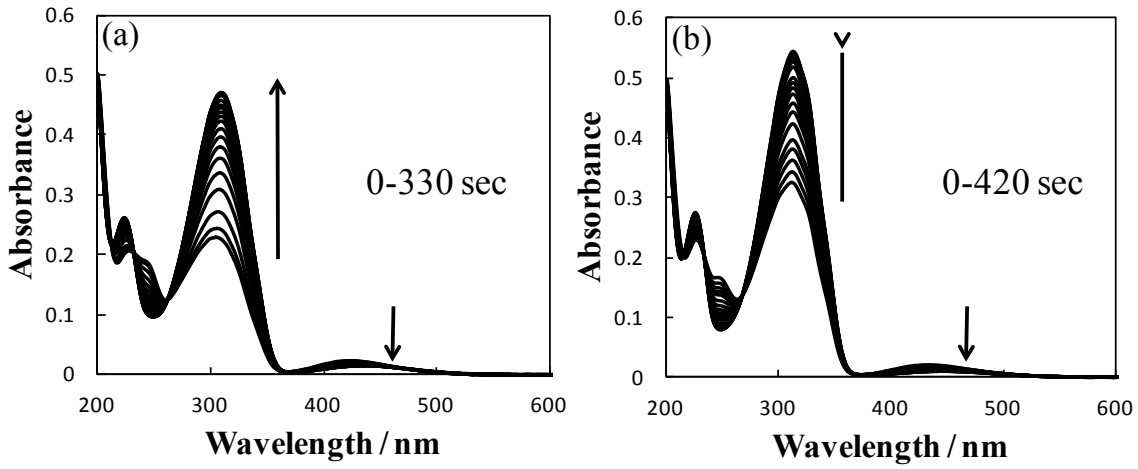

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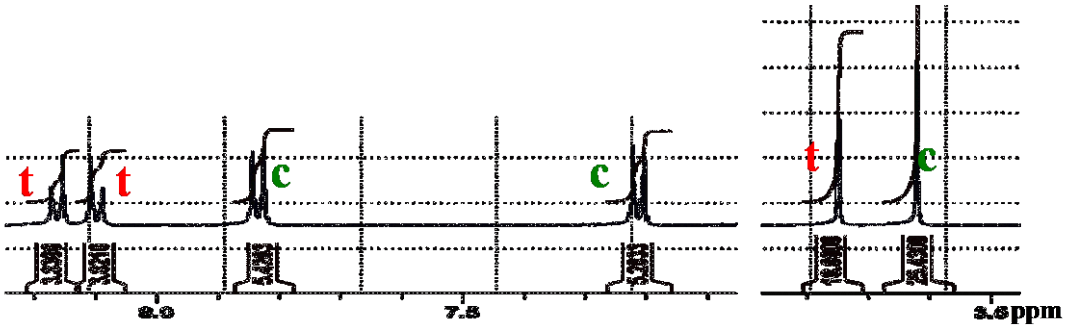

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References

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