

Supporting Information

Photoswitchable Fluorescence On/Off Behavior between Cis and

Trans-rich Azobenzenes

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Experimental

Materials and Instruments

Sodium nitrite (NaNO_2), hydrochloride acid (HCl), sodium hydroxide (NaOH), Sodium carbonate (Na_2CO_3), 4-bromo-2,6-dimethylaniline, phenol, iodomethane (CH_3I), n-butylmagnesium chloride (20 wt% solution) were all obtained as high-purity reagent-grade chemicals from Acros and used without further purification. [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II), complex with dichloromethane [$\text{Pd}(\text{dppf})\text{Cl}_2$] and 9,10-diphenylanthracene were purchased from Sigma-Aldrich. 4-butyl-4'-methoxyazobenzene (BMAB) was synthesized following the previous procedure.¹ All organic solvents were AR grade and purchased from either Mallinckrodt or Echo chemicals. Toluene was dried over calcium hydride under N_2 before used. HPLC grade tetrahydrofuran (THF) was distilled over sodium under N_2 in the presence of benzophenone as the indicator prior to use in the spectroscopic measurements. Water used in the materials synthesis was purified by a Milli-Q system to a resistivity of at least $18 \text{ M}\Omega\text{cm}^{-1}$. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer at room temperature using CDCl_3 as the solvent. Ultraviolet-Visible (UV-Vis) absorption spectra were performed on a Thermo Genesys 10S UV-vis spectrometer. Fluorescence spectroscopic analysis was carried out either on a Hitachi F-2500 spectrometer at ambient temperature. UV light illumination for generating light-driven fluorescence

was performed on high intensity UV lamp (UVP, model B-100AP, 100-watts). The photoswitchable trans \leftrightarrow cis isomerization was conducted using a handheld UV lamp (UVP, model UVGL-25, 4-watts) and CCFL white light bulb (Wellypower Optronics Corporation, AURORA series, 100-watts). Transmittance electron microscopy (TEM) images were taken by a Jeol JEM-1230 with Gatan dual vision CCD camera operated at an accelerating voltage of 120 kV. The samples in THF solutions were placed on 200-mesh copper grids for TEM observation.

Synthesis of 4-butyl-2,6-dimethyl-4'-methoxyazobenzene (BDMAB)

Synthesis of compound 1. An aqueous solution of NaNO₂ (1.56 g, 22.6 mmol) was slowly added into a solution of 4-bromo-2,6-dimethylaniline (2.04 g, 10.2 mmol) in 15 mL of 1.5 M HCl, and then the mixture was stirred under 0°C for 30 min, followed

by adding an aqueous buffer solution containing phenol (1.24 g, 13.2 mmol), NaOH (0.803 g, 20.1 mmol), and Na₂CO₃ (1.38 g, 13.0 mmol). After stirred at 0 °C for 2 h, the mixing solution was extracted by ether, dried over anhydrous magnesium sulfate, and rotary evaporation to dryness afforded the crude product. Further purification was performed on flash column chromatography (SiO₂, ethyl acetate/hexane = 2:8, *R_f* = 0.5) to yield the final product as orange solid (2.13 g, 68%).

Synthesis of compound 2. An aqueous solution of NaOH (0.596 g, 14.9 mmol) and compound **1** (2.10 g, 6.89 mmol) was added by iodomethane (2.17 mL, 34.9 mmol), and the mixture was stirred at 60 °C for 6 h, followed by adding another portion of iodomethane (2.17 mL, 34.9 mmol) and then continued stirring for another 12 h. The mixing solution was extracted with ether, dried over anhydrous magnesium sulfate, and rotary evaporation to dryness afforded the crude product. Further purification was performed on flash column chromatography (SiO₂, ethyl acetate/hexane = 1:19, *R_f* = 0.6) to give the final product as orange solid (0.958 g, 44%).

Synthesis of BDMAB. The catalyst PdCl₂(dppf) (29.8 mg, 1.2 mol%) was added into a dry toluene solution containing compound **2** (0.958 g, 3.00 mmol) and n-butyilmagnesium chloride (3.00 mL, 6.00 mmol) at -80 °C under N₂ atmosphere. The mixture was allowed to warm to room temperature, stirred for 30 min, and then refluxed at 100 °C overnight. After quenched by water, the mixing solution was

extracted with ether, dried over anhydrous magnesium sulfate, and rotary evaporation to dryness afforded the crude product. Further purification was performed on flash column chromatography (SiO₂, CH₂Cl₂/hexane = 4:6, R_f = 0.5) to give the **BDMAD** as orange oil (0.475 g, 53%). ¹H NMR (400 MHz, CDCl₃): δ = 7.88 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 6.92 (s, 2H), 3.89 (s, 3H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.34 (s, 6H), 1.68-1.53 (m, 2H), 1.37 (sex, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ = 161.8, 149.7, 147.6, 142.8, 130.8, 129.2, 124.6, 114.1, 55.6, 35.3, 33.6, 22.4, 19.0, 14.0.

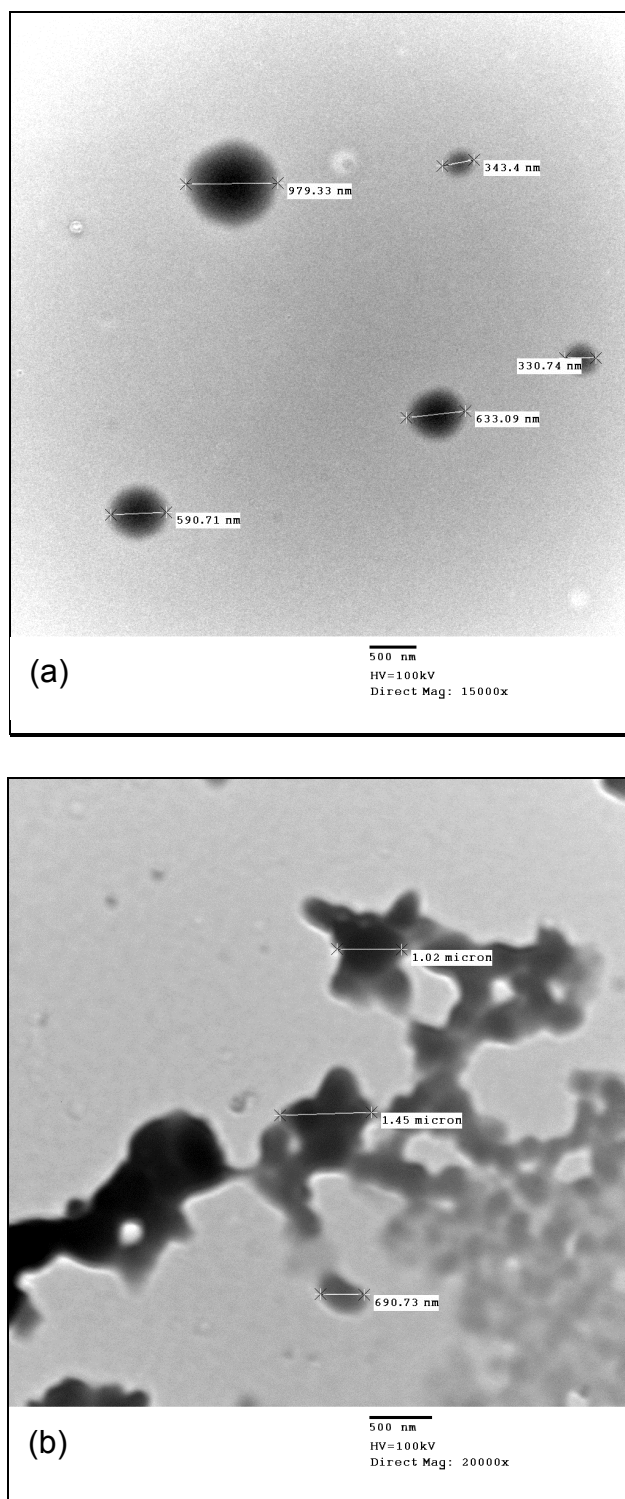


Figure S1. TEM micrographs of BMAB before (a) and after (b) UV light irradiation indicate the light-driven assembly of the particles in submicron dimension.

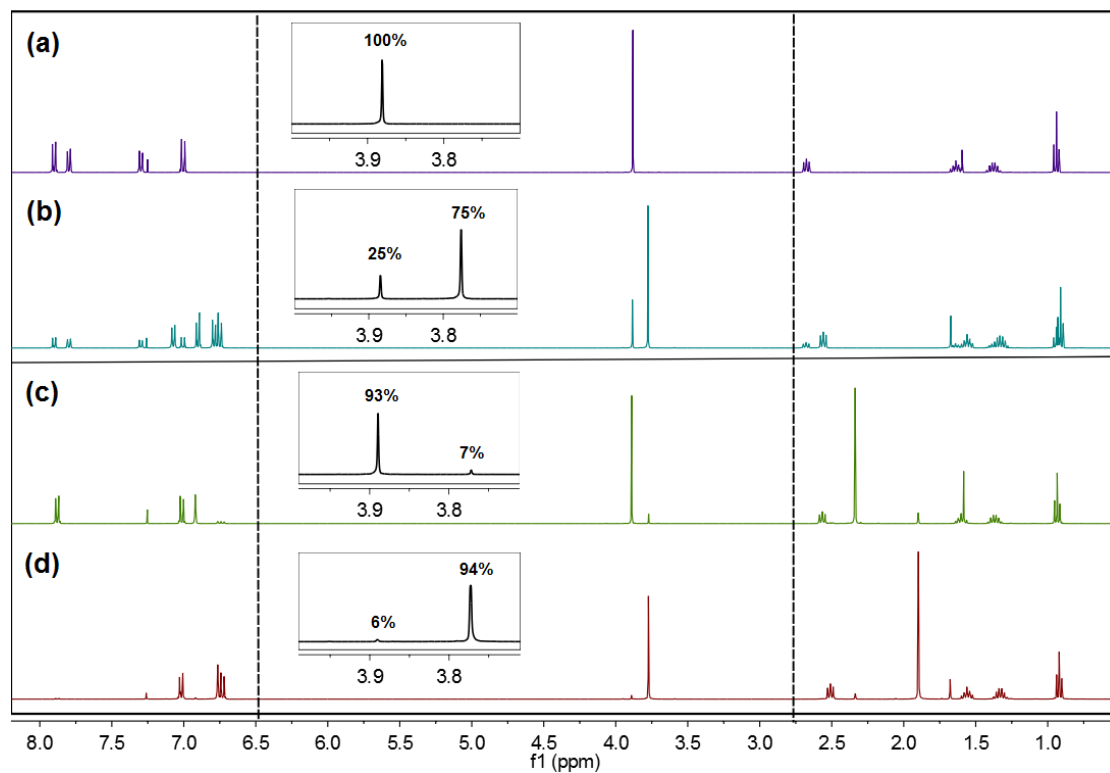


Figure S2. ^1H NMR spectra of (a) trans-BMAB, (b) cis-rich BMAB, (c) trans-rich BDMAB, and (d) cis-rich BDMAB. The trans and cis states were switched by UV and white light irradiation.

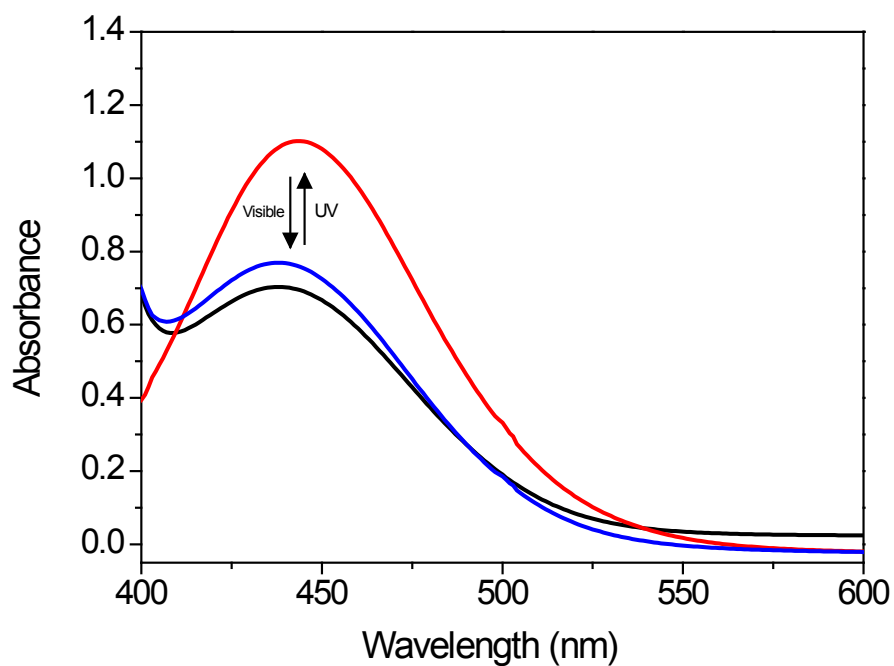


Figure S3. UV-Vis absorption spectra of initial all trans-BMAB solution (5×10^{-4} M in THF, black line), and a reversible photoisomerization between cis-rich (red line) and trans-rich (blue line) states.

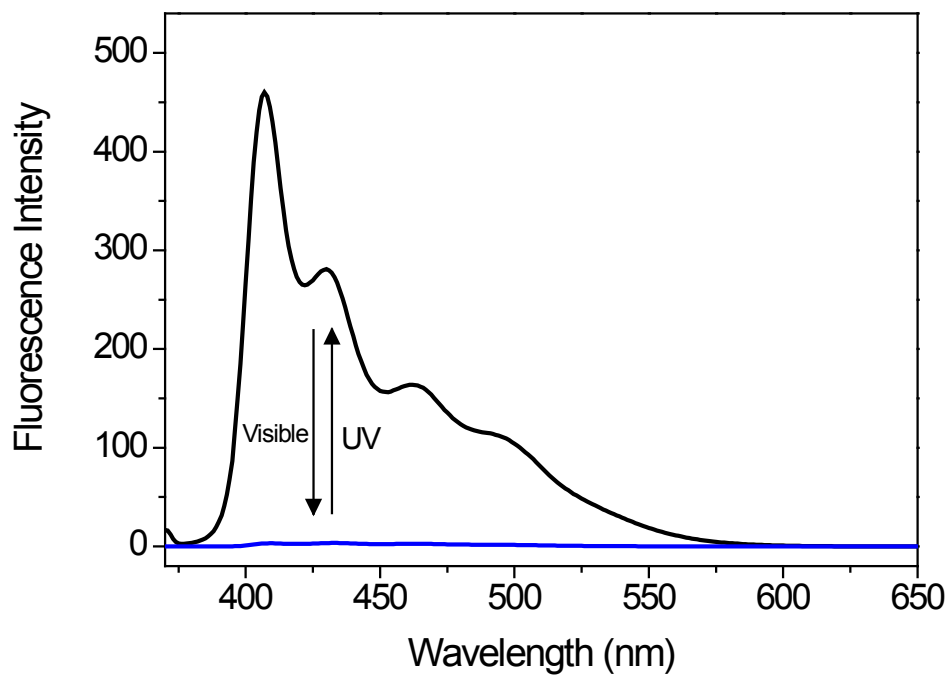


Figure S4. Fluorescence spectra of cis-rich (black line) and trans-rich (blue line) BMAB solution, and a reversible fluorescence “on/off” behavior accompanied by trans↔cis photoisomerization. $\lambda_{\text{ex}} = 375$ nm.

References:

1. Wu, M. H.; Chu, C. C.; Cheng, M. C.; Hsiao, V. K. S. *Mol. Cryst. Liq. Cryst.* **2012**, *557*, 176–189.