Electronic Supplementary Information for

Azobenzene-based photochromic liquid crystalline amphiphile for the remote-controllable light shutter

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1. Materials

Octyl bromide (99%), 4-nitrophenol (99%), phenol (99%), hydrazine monohydrate (98%), Raney-Nickel catalyst (Ni ≥90%, Al ≥6%), triethylene glycol monochlorohydrin (96%), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, 93%), sodium nitrite (NaNO₂, 97%), potassium carbonate (K₂CO₃, 99%), magnesium sulphate (MgSO₄, 99.5%) and sodium chloride (NaCl, 99%) were used as received.

2. Synthesis

1-nitro-4-(octyloxy)benzene (1): To a suspension of K₂CO₃ (6.87 g) in 100 mL of anhydrous dimethylformamide was added 4-nitrophenol (6.92 g) and the mixture heated to 80 °C after which was added 1-bromoctane (8.0 g) and the reaction allowed to stir for 6h. After completion of the reaction, the solvent was removed. The crude product was dissolved in chloroform and washed with distilled water several times. After the organic layer was dried over MgSO₄, then, further purified by column chromatography with silica gel using CHCl₃:n-
hexanes = 1:2 to yield a viscous yellow liquid. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 0.89$ (t: 3H), 1.23-1.51 (m: 10H), 1.80 (m: 2H), 4.02 (t: 2H), 6.93 (d: 2H), 8.18 ppm (d: 2H).

4-(octyloxy)benzenamine (2): A solution of hydrazine monohydrate (1.10 g) was added slowly to a solution of 1 (2.82 g) in 40 mL of ethanol. After the solution was heated to 45 °C, the activated Raney-Nickel catalyst was carefully added in portions until no further reaction was observed. Reaction product was filtered and rinsed generously with ethanol. The filtrate was dried under reduced pressure. The crude was dissolved in diethyl ether and washed with water and brine. The organic layer was dried over MgSO$_4$ and concentrated to give the product as viscous brown liquid which was used without further purification. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 0.89$ (t: 3H), 1.23-1.51 (m: 10H), 1.80 (m: 2H), 3.2-3.7 (broad singlet: 2H), 3.85 (t: 2H), 6.63 (d: 2H), 6.75 ppm (d: 2H).

4-(4'-octyloxy)hydroxyazobenzene (3): A solution of 2.5 M NaNO$_2$ (1.35 mL) was slowly added at a temperature below 5 °C to a heterogeneous mixture of 7.2 g of 2 in 17.6 mL of 5 M HCl. The mixture held at near 5 °C was added carefully to a solution of 3.1 g of phenol in 27 mL of 2 M NaOH. The product was precipitated by the addition of NaCl. By the recrystallization of the product in $n$-hexanes, the purified reddish crystal was collected. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 0.89$ (t: 3H), 1.23-1.51 (m: 10H), 1.79 (m: 2H), 4.03 (t: 2H), 6.96 (q: 4H), 7.85 ppm (q: 4H).

2-(2-{2-(4-((4-(octyloxy(phenyl)diazenyl)phenoxy)ethoxy)ethoxy)ethoxy)ethanol (CAz-OH): A solution of compound 3 (4.0 g), triethylene glycol monochlorohydrin (8.26 g), and K$_2$CO$_3$ (6.77 g) in 100 mL of anhydrous dimethylformamide was refluxed for 24 h. After the reaction, solvent was removed in vacuum and remaining residue was dissolved in ethyl acetate and extracted with distilled water several times. The organic layer was dried over MgSO$_4$. The product is purified by recrystallization with methanol and a yellowish powder is obtained. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 0.89$ (t: 3H), 1.23-1.51 (m: 10H), 1.80 (m: 2H),
3.64 (t: 4H), 3.74 (m: 4H), 3.89 (t: 2H), 4.02 (t: 2H), 4.21 (t: 2H), 7.01 (q: 4H), 7.86 ppm (d: 4H).

3. Experiments

$^1$H NMR spectra were recorded on a JNM-EX400 spectrometer in deuterated chloroform ($\text{CDCl}_3$). Elemental analysis (Vario EL) experiments were conducted to identify the chemical structure. UV-Vis absorption spectra were obtained with a SCINCO S-3100 spectrometer. Additionally, the Cerius$^2$ simulation software from Accelrys (Version 4.6) was also used to calculate the minimal energy geometry in the isolated gas-phase utilizing the COMPASS force field. The macroscopic photographic images were taken by using the digital camera (EOS 5D, Canon).

Phase transition behaviours of CAz-OH were examined using a Perkin-Elmer PYRIS Diamond DSC with an Intracooler 2P apparatus. Heating experiments always preceded the cooling experiments at the same scanning rate of 2.5 °C min$^{-1}$ in order to eliminate previous thermal histories. The transition temperatures were determined by measuring the onset temperatures from both the cooling and heating scans at different rates. Optical textures of the ordered phases were observed with a POM (Nikon ECLIPSE E600POL) coupled with a heating stage (LINKAM LTS 350) in order to investigate morphology on the micrometer scale.

1D WAXD experiments were conducted in the reflection mode of a Rigaku 12 kW rotating-anode X-ray (Cu Kα radiation) generator coupled with a diffractometer. The position and width of diffraction peaks were calibrated with silicon crystals in the high 2θ-angle region (>15°) and silver behenate in the low 2θ-angle region. To monitor the structural evolutions with temperature changes, a hot stage calibrated to be within ±1 °C error was coupled to the diffractometer. Samples were scanned across a 2θ-angle range of 1.5° to 35° at
a scanning rate of 10° min⁻¹.

The oriented 2D WAXD patterns were obtained using a Rigaku X-ray imaging system with an 18 kW rotating anode X-ray generator. The diffraction peak positions and widths were also calibrated with silicon crystals and silver behenate. In 2D WAXD experiments, background scattering was subtracted from the sample scans. Basic unit cell parameters determined by crystallographic experimental data from WAXD of the macroscopically oriented CAz-OH film were used to build the crystal unit cell. The molecular packing symmetry in this unit cell was judged by comparing the calculated minimized geometry with those of experiments.

In order to fabricate the optical cell, glass substrates were washed with distilled water, acetone, and isopropyl alcohol several times and then dried in an oven (JEIO TECH, NO-600M, Korea) maintained at 80 °C. The CAz-OH powders were placed to the glass cells and test optical cells were made by sandwiching the CAz-OH between two glass substrates. The cell gap was controlled to be 50 μm by applying spacer. The UV exposure experiments of the CAz-OH film were performed to fabricate the remote-controllable light shutter. Here, the distance between the UV source and the sample was kept at 5 cm. In addition, to eliminate the possibility of the thermal effect which can be generated by the UV lamp, an infrared filter was located between the UV source and the CAz-OH film.

4. Characterization

All the chemical compounds synthesized in this research were purified by column chromatography and recrystallization. Chemical shifts were quoted in part per million (ppm) with a reference of tetramethylsilane (TMS). As shown in Fig. S2, chemical structure of compound 1 was confirmed by indentifying the disappearance of -C-OH proton peak from the nitrophenol and appearance of -CH₂-CH₃ at the end of the terminal aliphatic chains (0.89
ppm, 3H). Chemical structure of compound 2 (Fig. S3) was confirmed from the new broad peak at 3.2-3.7 ppm (-C-NH₂, 2H), and proton chemical shift (8.18 ppm → 6.63 ppm) of the phenyl group (C-CH₂-CH, 2H). Chemical structure of compound 3 (Fig. S4) was identified by increased integration of protons at azobenzene group (6.96-7.85 nm, 4H). As shown in Fig. S5, The protons from the ether group (-O-CH₂-) in compound CAz-OH at the range of 3.64 to 4.21 ppm correspond to the triethylene oxide tails.

As shown in Fig. S9, upon irradiating the UV light at 365 nm (0.1 mW cm⁻²), the thermodynamically stable trans (π-π*) conformer of azobenzene reaches into its metastable cis (n-π*) conformer in 25 s. Absorption bands recover the initial state after 15 min with visible light irradiation at 450 nm. Photo-isomerization rate constant of π-π* and n-π* transitions are $K_t = 1.87 \times 10^{-2} \text{ s}^{-1}$ and $K_c = 1.31 \times 10^{-2} \text{ min}^{-1}$, respectively (Fig. S10).

![Fig. S1 Synthetic procedures of CAz-OH compound: (i) 1-bromooctane, K₂CO₃, DMF, 80 °C, 6 h; (ii) Raney-Nickel catalyst, EtOH, 45 °C, 1 h; (iii) HCl, NaNO₂, NaOH, phenol, 0 °C, 1h; (iv) triethylene glycol monochlorohydrin, K₂CO₃, DMF, 80 °C, 24 h.](image)
Fig. S2 $^1$H NMR spectrum of compound 1.

Fig. S3 $^1$H NMR spectrum of compound 2.
Fig. S4 $^1$H NMR spectrum of compound 3.

Fig. S5 $^1$H NMR spectrum of compound CAz-OH.
Fig. S6 Elemental analysis of CAz-OH.

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Fig. S7 DSC thermograms of CAz-OH during heating and cooling at 2.5 °C min⁻¹.
Fig. S8 2D WAXD pattern of the macroscopically aligned CAz-OH liquid crystalline phase and its corresponding schematic illustration of molecular arrangement.

Fig. S9 UV-Vis absorption spectra of trans to cis (a) and cis to trans (b) photo-isomerization process for CAz-OH in chloroform solution.
Fig. S10 The *trans* to *cis* (a) and *cis* to *trans* (b) photo-isomerization rate constant of CAz-OH in chloroform solution.

Fig. S11. Absorption changes of CAz-OH film upon light irradiation.
Fig. S12 Photo-induced solidus ↔ liquidus states of CAz-OH observed by POM at room temperature.

Fig. S13. 1D WAXD patterns of CAz-OH compound upon light irradiation.