# Electronic Supplementary Information

for

# Macroscopic Motion of Supramolecular Assemblies Actuated by Photoisomerization of Azobenzene Derivatives

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## General Information

All reagents and distilled water were purchased and used without purification. For NMR spectra, $CDCl_3$ and DMSO-$d_6$ were purchased from Euriso-top and $CD_3OD$ was purchased from Cambridge Isotope Laboratory Inc. For microscopic observation of photoinduced behavior, a differential interference contrast microscope (Nikon TE2000) equipped with a mercury lamp epi-fluorescent unit and UV-1A and BV-1A filter units was used. Movies were recorded using a USB-CCD camera (Sentech STC-TC152USB). The movie files were edited and compacted using a Sony Vegas Movie Studio Platinum 9.0 software. A Nikon ECLIPS TS100 microscope was used for recording phase contrast micrographs. Solution $^1$H NMR spectra were recorded on a JEOL JEX 270 spectrometer, and TMS was used as an internal reference. Solution $^{13}$C-NMR spectra were recorded on a JEOL JEX 270 spectrometer and the central peak of the solvents was used as reference. Photoisomerization of azobenzene derivatives in chloroform was monitored using a JASCO UV/VIS spectrophotometer V-650 and a xenon arc lamp (USHIO) equipped with photo fiber and band pass filters that are the same filters for micrographic experiments.

## Preparation of Materials

4-*n*-Butyl-4'-hydroxyazobenzene (**6**) was obtained from the azocoupling reaction between 4-*n*-butylaniline and phenol and was recrystallized from hexane. The amphiphilic azobenzenes (6-[4-(phenylazo)phenoxy]hexanoic acid, **2**)[lit1] was obtained by etherization of **6** with *n*-bromohexanoic acid ethyl ester to form 6-[4-(phenylazo)phenoxy]hexanoic acid ethyl ester (**2EE**[lit1]), de-esterification, and recrystallization from ethanol.

$^1$H-NMR of **2** δ(270 MHz, $CDCl_3$): 0.94 (t, 3H, $J$= 7.3 Hz, 1.31-1.45 (m, 2H), 1.51-1.91 (m, 8H), 2.42 (t, 2H, $J$= 7.3 Hz), 2.68 (t, 2H, $J$= 7.7 Hz), 4.05 (t, 2H, $J$= 6.3 Hz), 6.99 (d, 2H, $J$= 8.9 Hz), 7.31 (d, 2H, $J$= 8.4 Hz), 7.80 (d, 2H, $J$= 8.4 Hz), 7.89 (d, 2H, $J$= 8.9 Hz).

Compound **3**, **4**,[lit2] and **5**[lit3] were also obtained by hydrolysis of corresponding ethyl esters (**3EE**, **4EE**, **5EE**) prepared in a similar manner with preparing of ethyl ester of **2** using corresponding anilines and *n*-bromoalkylcarboxylic acid ethyl esters.

$^1$H-NMR of **3EE** δ(270 MHz, $CDCl_3$): 0.94 (t, 3H, *J* = 7.3 Hz), 1.27 (t, 3H, *J* = 7.3 Hz), 1.31－1.45 (m, 2H), 1.59－1.70 (m, 2H), 2.10－2.20 (m, 2H), 2.54 (t, 2H, *J* = 7.3 Hz), 2.68 (t, 2H, *J* = 7.7 Hz), 4.10 (t, 2H, *J* = 8.6 Hz), 4.16 (qurtet, 2H, *J* = 7.2 Hz), 6.99 (d ,2H, *J* = 9.2 Hz), 7.30 (d, 2H, *J* = 8.6 Hz), 7.79(d, 2H, *J* = 8.4 Hz), 7.89 (d, 2H, *J* = 8.9 Hz). $^{13}$C-NMR of **3EE** δ (67.8 MHz, $CDCl_3$): 13.8, 14.1, 22.2, 24.4, 30.6, 33.3, 35.4, 60.4, 67.0, 114.7, 122.6, 124.6, 129.1, 145.9, 147.2, 151.1, 161.2, 173.3. Anal. Calcd for $C_{22}H_{28}N_2O_3$: C, 71.71; H, 7.66; N, 7.60. Found: C, 71.80; H, 7.82; N, 7.69.

$^1$H-NMR of **3** δ(270 MHz, DMSO-$d_6$): 0.91 (t, 3H, *J* = 7.2 Hz), 1.26–1.40 (m, 2H), 1.54–1.65 (m, 2H), 1.89–1.99 (m, 2H), 2.27 (t, 2H, *J* = 7.3 Hz), 2.66 (t, 2H, *J* = 7.6 Hz), 4.08 (t, 2H, *J* = 6.6 Hz), 7.11 (d, 2H, *J* = 9.2 Hz), 7.38 (d, 2H, *J* = 8.6 Hz), 7.76 (d, 2H, *J* = 8.4 Hz), 7.85 (d, 2H, *J* = 8.6 Hz). $^{13}$C-NMR of **3** δ(67.8 MHz, $CD_3OD$): 14.4, 23.5, 26.1, 32.1, 34.9, 36.6, 68.7, 116.1, 123.8, 125.9, 130.5, 147.6, 148.6, 152.7, 163.3 (COOH signal was not detected.). Anal. Calcd. for $C_{20}H_{24}N_2O_3$: C, 70.56, H, 7.11; N, 8.23. Found: C, 70.59, H, 7.17; N, 8.20.

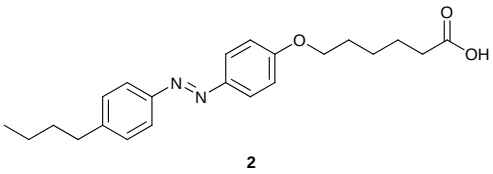
$^1$H-NMR of **4EE** δ(270 MHz, $CDCl_3$): 1.26 (t, 3H, *J* = 7.3 Hz), 1.50－1.59 (m, 2H), 1.67－1.78 (m, 2H), 1.80－1.90 (m, 2H), 2.35 (t, 2H, *J* = 7.4 Hz), 4.05 (t, 2H, *J* = 6.3 Hz), 4.14 (quartet, 2H, *J* = 7.2 Hz), 6.99 (d, 2H, *J* = 8.9 Hz), 7.43－7.53 (m, 3H), 7.87 (d, 2H, *J* = 7.0 Hz) 7.93 (d, 2H, *J* = 8.9 Hz). $^{13}$C-NMR of **4EE** δ (67.8 MHz, $CDCl_3$): 14.1, 24.6, 25.5, 28.8, 34.1, 60.2, 68.0, 114.7, 122.6, 124.8, 129.1, 130.4, 147.0, 152.9, 161.7, 173.8. Anal. Calc. for $C_{20}H_{24}N_2O_3$: C, 70.56; H, 7.11; N, 8.23. Found: C, 70.58; H, 7.22; N, 8.32.

$^1$H-NMR of **4** δ(270 MHz, DMSO-$d_6$): 1.40–1.48 (m, 2H), 1.51–1.59 (m, 2H), 1.68–1.80 (m, 2H), 2.18 (t, 2H, *J* = 7.3 Hz), 4.07 (t, 2H, *J* = 6.3 Hz), 7.12 (d, 2H, *J* = 8.9 Hz), 7.52–7.61 (m, 3H), 7.84 (d, 2H, *J* = 6.8 Hz), 7.88 (d, 2H, *J* = 9.5 Hz).

$^1$H-NMR of **5EE** δ(270 MHz, $CDCl_3$): 1.23–1.31 (m, 13H), 1.45–1.50 (m, 2H), 1.56–1.65 (m, 2H), 1.77–1.87(m, 2H), 2.29 (t, 2H, *J* = 7.6 Hz), 4.04 (t, 2H, *J* = 6.5 Hz), 4.13 (q, 2H, *J* = 7.0 Hz), 7.00 (d, 2H, *J* = 8.9 Hz), 7.43–7.54 (m, 3H), 7.87 (d, 2H, *J* = 7.0 Hz), 7.91 (d, 2H, *J* = 8.9 Hz). $^{13}$C-NMR of **5EE** δ(67.8 MHz, $CDCl_3$):14.1, 24.9, 25.9, 29.0, 29.1, 29.1, 29.2, 29.3, 29.4, 34.4, 60.1, 68.3, 114.7, 122.6, 124.8, 129.1, 130.4, 147.0, 152.9, 161.9, 174.1. Anal. Calcd. for $C_{25}H_{34}N_2O_3$: C, 73.14, H, 8.35; N, 6.82. Found: C, 73.03; H, 8.55; N, 6.61.

$^1$H-NMR of **5** δ(270 MHz, $CDCl_3$): 1.25–1.31 (m, 10H), 1.42–1.50 (m, 2H), 1.58–1.69 (m, 2H),

1.77–1.87 (m, 2H), 2.35 (t, 2H, *J* = 7.4 Hz), 4.04 (t, 2H, *J* = 6.6 Hz), 7.00 (d, 2H, *J* = 9.5 Hz), 7.43–7.53 (m, 3H), 7.87 (d, 2H, *J* = 7.0 Hz), 7.91 (d, 2H, *J* = 9.5 Hz). $^{13}$C-NMR of **5** δ(67.8 MHz, $CDCl_3$): 24.6, 25.9, 28.9, 29.1, 29.1, 29.2, 29.2, 29.4, 33.7, 68.3, 114.8, 122.6, 124.8, 129.1, 130.4, 147.0, 152.9, 161.9, 163.7. Anal. Calcd. for $C_{23}H_{30}N_2O_3$: C, 72.22, H, 7.91; N, 7.32. Found: C, 71.84; H, 8.19; N, 7.13.

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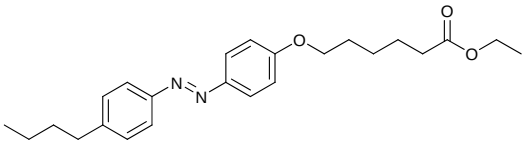


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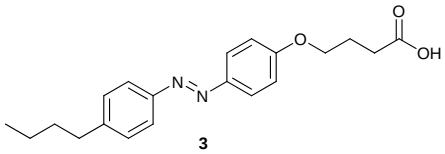


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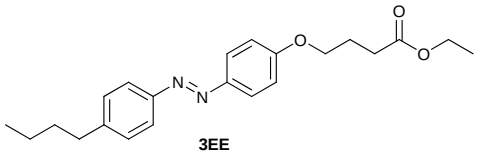


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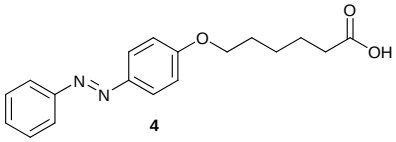


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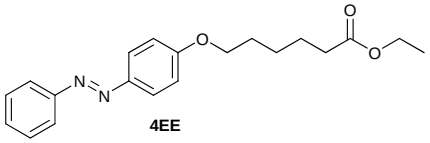


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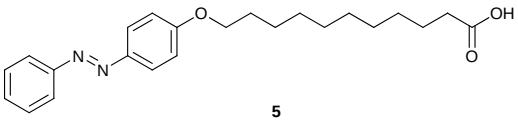


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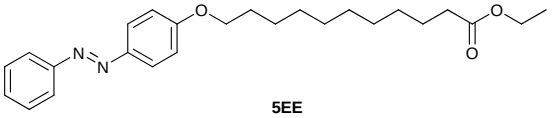


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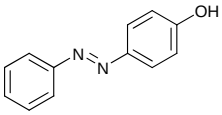


**6**

lit 1. Stewart, D.; Imrie, C. T., *J. Mat. Chem.* **1995**, *5*, 223–228.

lit. 2 Shimogaki, T.; Oshita, S.; Matsumoto, A., *Macromol. Chem. Phys.* **2011**, *212*, 1767–1777.

lit. 3 (a) Xu, X.; Era, M.; Tsutsui, T.; Saito, S., Thin Solid Films, 1989, 178, 541–547. (b) Shembekar, V. R.; Contractor, A. Q.; Major, S. S.; Talwar, S. S., *Thin Solid Films*, **2006**, *510*, 297–304.

## Observation Methods

*General procedure for preparation of azobenzene derivative-oleate mixed assemblies*

Solution of sodium oleate in MeOH-$CHCl_3$ mixed solvent and chloroformic solution of azobenzene derivatives (**2**–**5**) were placed in a glass tube and the solvent was removed *in vacuo* to form films of mixture of sodium oleate (4.5 mg, 15 μmol) and azobenzene derivatives (0.45 mg, 1.2–1.4 μmol). To the glass tube, 75 mM phosphate buffered solution (1.0 mL) was added, and the films were dispersed under ultrasonication for 20 min in 25-30°C. The dispersed solution was placed on a thin slide glass (Matsunami NEO cover glass, No.1) and sealed using a Frame-Seal™ Slide Chamber (Bio-Rad) and another cover glass, and incubated for one day at 25°C. The assemblies were formed spontaneously in the sealed pool. To form vesicular structure, we used phosphate buffered solution of pH around 7.6 (the pH of dispersion after incubation was approximately 7.8). To form helical tube, we used phosphate buffered solutions of pH around 7.3 (the pH of dispersion after incubation was approximately 7.5).

*Procedure for preparation of azobenzene derivative-oleate mixed assemblies to obtain the result shown in **Fig.3** and **Movie 3***

Solution of sodium oleate in MeOH-$CHCl_3$ mixed solvent and chloroformic solution of **3** were placed in a glass tube and the solvent was removed *in vacuo* to form films of mixture of sodium oleate (1.2 mg, 3.9 μmol) and **3** (0.12 mg, 0.35 μmol). To the glass tube, 75 mM phosphate buffered solution (pH 7.4, 0.6 mL) was added, and the films were dispersed under ultrasonication for 10 min in 25-30°C. The dispersed solution was placed in sealed microscope slide to form helical tube in a manner similar to the general procedure written above.

*General method for observation of photoinduced macroscopic dynamics*

Assemblies in the slide glass chamber was observed using a differential interference contrast microscope (Nikon TE2000). To irradiate the assemblies by 365 nm light, a mercury lamp in the epi-fluorescent unit of the microscope and a UV-1A filter unit (the transmission window of excitation band-pass filter is 360–370 nm; the wavelength of the bright line spectrum is 366 nm) were used. To irradiate by 435 nm light, the same lamp and a BV-1A filter unit (the transmission window of excitation band-pass filter is 430–440 nm; the wavelength of the bright line spectrum is 435 nm) were used. The strength of the light was controlled manually using shutter unit of microscope.

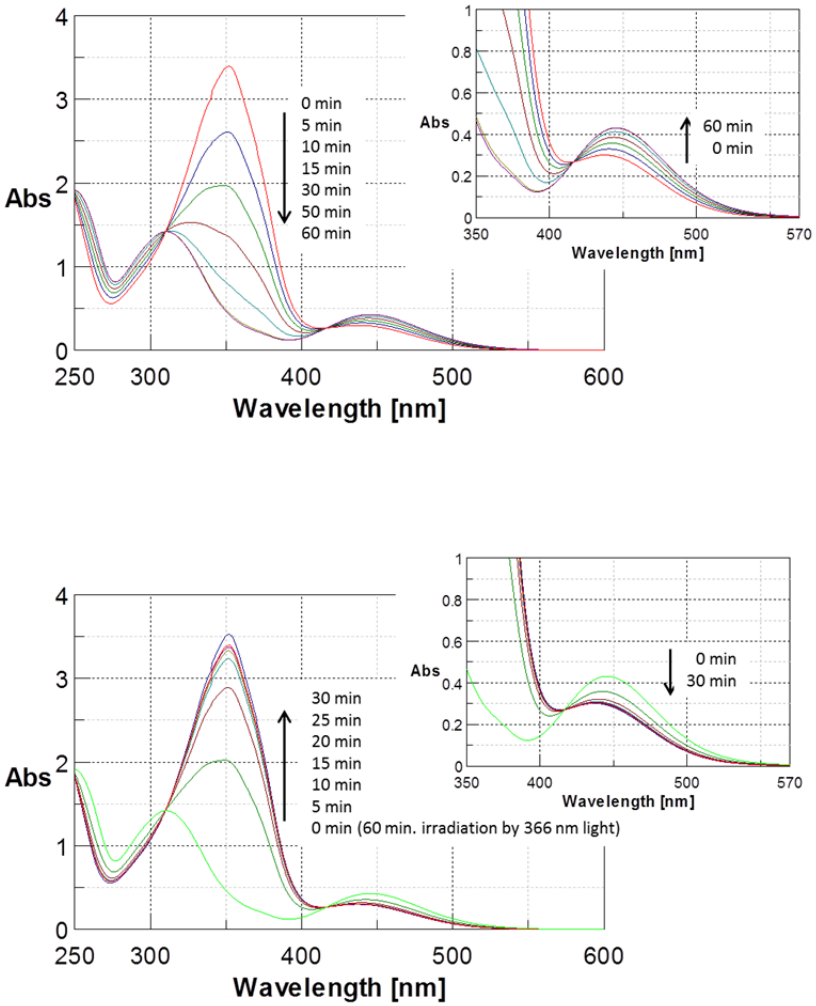


**Figure S1.** Photochromic behavior of **2** in chloroform. (top) Changes in UV-Vis absorption spectra by irradiation of 366 nm light (bottom) Change in UV-Vis absorption spectra by irradiation of 435 nm light.

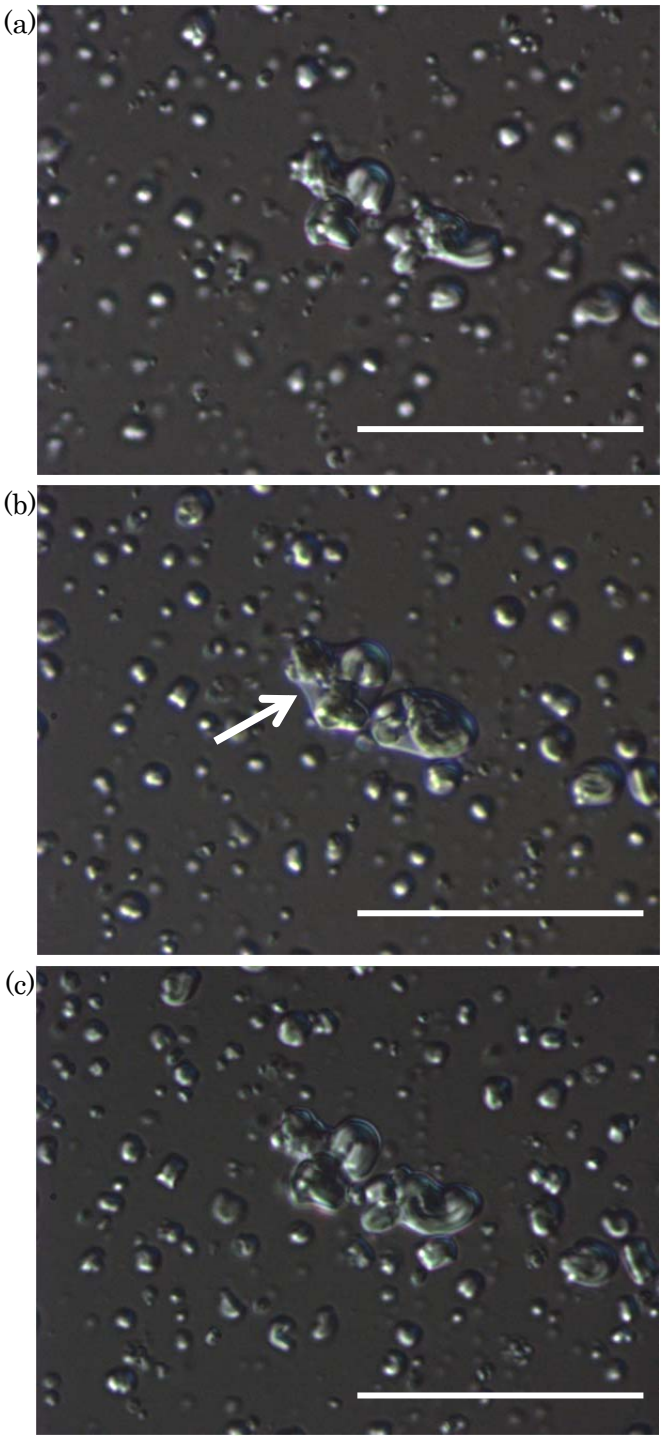


**Figure S2.** Photoreversible change of assemblies composed of oleate and 1wt% of **2**: (a) before irradiation, (b) irradiation with 366 nm light for 40 min, and (c) irradiation with 435 nm light for 30 min (bar : 50 μm). Membrane structure was formed from multilamelalr assemblies by 366 nm light irradiation and turned to multilamellar assemblies by 435 nm light irradiation with long-term induction period.