Supporting Information

Physical Operation of Hydrodynamic Orientation of an Azobenzene Supramolecular Assembly with Light and Sound

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1. Materials

Unless otherwise noted, reagents and solvents were used as received from Kishida Chemical Co., Ltd. [$CHCl_3$ (>99%), CH_2Cl_2 (>99%), THF (>99%) and MeOH (>99%)], Nakarai Tesuque, Inc. [cyclohexane (>98%) and CuCl (>95%)], Wako Pure Chemical Industries, Ltd. [pyridine (>99%), conc. HCl (35wt%) and *N*,*N*-dimethylaminopyridine (>99%)], Sigma-Aldrich [diisopropylcarbodiimide (>99%)], Kanto Chemical Co., Inc. [THF dehydrated stabilizer free] and Tokyo Kasei Co., Ltd. (TCI) [4-aminophenylacid (>98%)]. Dry pyridine was prepared through dehydration with Type 3A molecular sieve. For column chromatography, Wakogel C-300HG (particle size 40–60 mm, silica) was used. The series of 3,4,5-[tris-alkyloxy]aniline were prepared by procedures analogous to those reported previously,[1] and unambiguously characterized by means of ^{1}H NMR spectroscopy.

2. Measurements.

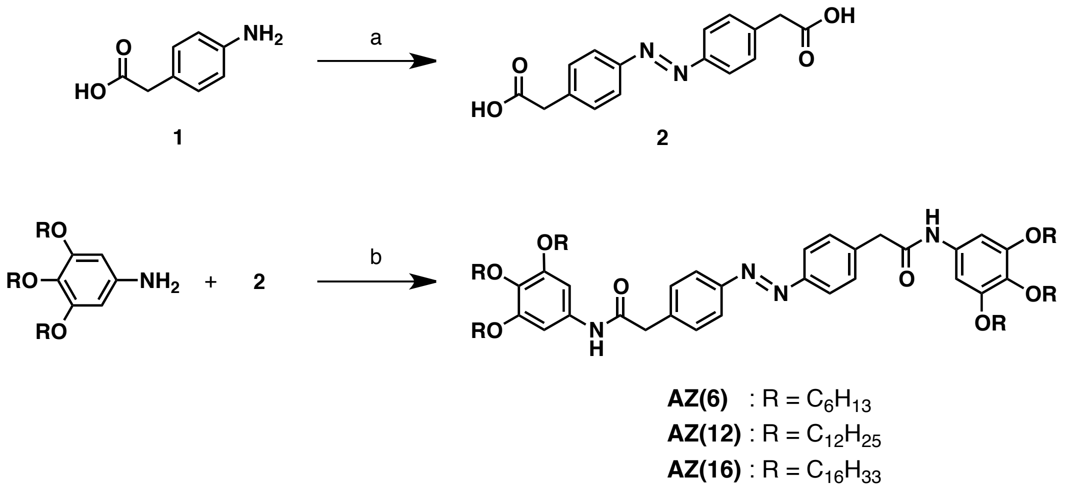
Characterizations. Absorption spectra were recorded on a JASCO V-670 UV/VIS/NIR spectrometer equipped with a JASCO ETC-717 temperature/stirring controller. ^{1}H and ^{13}C NMR spectra were recorded on a VARIAN model INOVA 400 spectrometer and Bruker AVANCE 500 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane as the internal standard. Infrared absorption spectra (IR) were recorded on a JASCO FT/IR-4200 fourier transform infrared spectrometer. MALDI-TOF mass spectrometry was performed on a Shimadzu model AXIMA-CFR plus spectrometer with *trans*-2-[3-(4-tetrabutylphenyl)-2-propenylidene]malonitrile as the matrix. Scanning electron microscopy (SEM) was performed using a JEOL JSM–7600F FE–SEM operating at 2.0 kV.

LD Spectroscopy. LD spectra were recorded on a JASCO J-820 spectropolarimeter equipped with a JASCO PTC-423L temperature controller and a custom made sound generator, composed of a function generator (NF model DF1906), an integral amplifier (DENON model PMA-390AE) and a sound speaker (AURA Sound model NS3-193-4A). The LD spectrometer was equipped with a 12 × 12 × 44 mm quartz optical cuvette, having a ϕ10 ×

10 mm cylindrical neck (outer diameter), composed of 1 mm-thick quartz glass, which was filled with a cyclohexane solution of **AZ**. LD intensity is defined as $\Delta_{\mathrm{LD}}A = A_{//} - A_{\perp}$ ($\Delta_{\mathrm{LD}}A$ represents magnitude of LD, while $A_{//}$ and $A_{\perp}$ denote horizontal and perpendicular absorbances, respectively). The cuvette, containing the sample solution, was fixed in the steel holder of the spectrometer. For the acoustic LD spectroscopy in this study, LD responses were monitored at a position 39 mm below the top of the optical cuvette using an 8 mm-diameter beam of linearly polarized light. Sound waves produced by a function generator from a speaker. A full range speaker, having a frequency response of ~15 kHz, was located 20 mm above the cuvette.

Atomic Force Microscopy (AFM). In the frequency-modulation AFM (FM-AFM), the resonant oscillation of a cantilever is mechanically excited. When a conservative force is applied to the tip, the resonant frequency shifts accordingly. The topography of a solid object is traced via controlling the tip–surface distance by keeping the frequency shift constant. The microscope used in this study was a commercially available AFM (Shimadzu, SPM9600) modified with the low-noise optical deflection scheme after Fukuma et al.[2] A cantilever (Nanosensors, NCH), which was backside-coated with gold, was used as a mechanical resonator in a self-oscillation circuit such that the cantilever vibrates at its resonance frequency with a constant oscillation amplitude.

3. Synthetic Scheme



Scheme S1. Syntheses of **AZ(n)** (n = 6, 12, and 16): Reagents and conditions: (a) CuCl, O_2 bubbling; (b) diisopropylcarbodiimide (DIC), *N*,*N*-dimethylaminopyridine (DMAP); pyridine

4. Synthesis

2,2′-(diazene-1,2-diylbis(4,1-phenylene))diacetic acid (2): To a pyridine solution (200 mL) 4-aminophenylacetic acid (**1**) (500 mg, 3.3 mmol) was added CuCl (396 mg, 4.0 mmol). The sample solution was stirred for 8 h with O_2 bubbling at r.t., and then washed with 1N aqueous HCl and extracted with THF. The combined organic extract was dried over Na_2SO_4, and the solvent was removed by evaporation. The residue was washed with ethyl acetate, and filtered to leave **2** as orange solid (445 mg, 2.97 mmol) in 90 % yield. ^{1}H NMR (500 MHz, DMSO-d_6, 20 °C): δ 12.47 (br., 2H, CO_2H), 7.85 (d, J = 8.0 Hz, 4H, phenyl), 7.48 (d, J = 8.0 Hz, 4H, phenyl), 3.71 (br., 4H, benzyl); ^{13}C NMR (125 MHz, DMSO-d_6, 20 °C): δ 172.24, 150.71, 138.79, 130.55, 122.43, 40.49; MALDI-TOF-MS: m/z calculated for M^+ ($C_{16}H_{14}N_2O_4$) 297.8, found 297.8; IR (ATR): 3031, 2956, 2906, 2731, 2646, 2561, 1692, 1424, 1410, 1338, 1245, 1197, 1173, 1155 cm^{-1}.

AZ(6): To a dry THF solution (5 mL) a mixture of 2,2′-(diazene-1,2-diylbis(4,1-phenylene))diacetic acid (**2**) (73 mg, 0.245 mmol), 3,4,5-tris(hexyloxyl)aniline (211 mg, 0.53 mmol), and *N*,*N*-dimethylaminopyridine (DMAP) (30 mg, 0.24 mmol) was added diisopropylcarbodiimide (DIC) (183 μL, 0.47 mmol) under Ar atmosphere. The sample solution was refluxed for 30 h, and washed with 1N aqueous HCl and extracted with CH_2Cl_2. The combined organic extract was dried over Na_2SO_4, and then evaporated to dryness. The residue was chromatographed on silica gel with CH_2Cl_2/MeOH (99:1) as an eluent, where the first red fraction was isolated and subjected to preparative size exclusion chromatography (SEC) with $CHCl_3$ as an eluent. The first orange fraction was corrected, and evaporated to dryness under reduced pressure to leave **AZ(6)** (33 mg, 0.031 mmol) as orange solid in 13% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.94 (d, J = 8.0 Hz, 4H, azobenzene), 7.49 (d, J = 8.0 Hz, 4H, azobenzene), 7.07 (s, 2H, amide), 6.72 (s, 4H, phenyl), 3.91 (t, J = 6.5 Hz, 8H), 3.89 (t, J = 6.0 Hz, 4H), 3.78 (s, 4H, benzyl), 1.79–1.68 (m, 12H), 1.48–1.40 (m, 12H), 1.31 (br., 24H), 1.26 (br., 12H), 0.84 (t, J = 7.0 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ 168.34, 153.33, 152.06, 137.71, 135.24, 133.24, 130.48, 123.76, 99.11, 73.63, 69.30, 44.79, 31.91, 31.69, 30.37, 29.85, 29.44, 25.91, 25.86, 22.82, 22.75, 14.22, 14.16; MALDI-TOF-MS m/z calculated for M$^+$ ($C_{64}H_{96}N_4O_8$) 1048.7 and [M+Na]$^+$ ($C_{64}H_{96}N_4O_8Na$) 1071.7, found 1049.2 and 1072.2; IR (ATR): 3262, 2947, 2922, 2856, 1650, 1600, 1533, 1506, 1465, 1426, 1388, 1340, 1232, 1127, 1115, 816 cm^{-1}.

AZ(12): To a dry pyridine solution (5 mL) a mixture of 2,2′-(diazene-1,2-diylbis(4,1-phenylene))diacetic acid (**2**) (70 mg, 0.235 mmol), 3,4,5-tris(dodecyloxyl)aniline (334 mg, 0.517 mmol) and *N*,*N*-dimethylaminopyridine (DMAP) (57 mg, 0.47 mmol) was added diisopropylcarbodiimide (DIC) (146 µL, 0.36 mmol) under Ar atmosphere. The sample solution was stirred for 12 h at 80 °C, and washed with 1N aqueous HCl and extracted with CH_2Cl_2. The combined organic extract was dried over Na_2SO_4, and then evaporated to dryness. The residue was chromatographed on silica gel with CH_2Cl_2/MeOH (99:1) as an eluent. The first orange fraction was corrected, and evaporated to dryness under reduced pressure to leave **AZ(12)** (101 mg, 0.065 mmol) as orange solid in 28% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.93 (d, J = 8.3 Hz, 4H, azobenzene), 7.48 (d, J = 8.3 Hz, 4H, azobenzene), 7.16 (s, 2H, amide), 6.72 (s, 4H, phenyl), 3.90 (t, J = 5.6 Hz, 8H), 3.88 (t, J = 5.6 Hz, 4H), 3.79 (s, 4H, benzyl), 1.76 (m, 12H), 1.25 (br., 96H), 0.87 (t, J = 5.0 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ 168.39, 153.29, 151.99, 137.70, 135.10, 133.26, 130.45, 123.72, 99.00, 73.63, 69.24, 44.74, 32.07, 29.84, 29.80–29.50 (m), 22.84, 14.27; MALDI-TOF-MS m/z calculated for M$^+$ ($C_{100}H_{168}N_4O_8$) 1554.3 and [M+Na]$^+$ ($C_{64}H_{96}N_4O_8Na$) 1577.3, found 1554.3 and 1577.4; IR (ATR): 3254, 2916, 2849, 1655, 1600, 1536, 1506, 1466, 1427, 1385, 1344, 1230, 1120 cm^{-1}.

AZ(16): To a dry THF solution (20 mL) a mixture of 2,2′-(diazene-1,2-diylbis(4,1-phenylene))diacetic acid (**2**) (70 mg, 0.235 mmol), 3,4,5-tris(dodecyloxyl)aniline (334 mg, 0.517 mmol) and *N*,*N*-dimethylaminopyridine (DMAP) (57 mg, 0.47 mmol) was added diisopropylcarbodiimide (DIC) (146 µL, 0.36 mmol) under Ar atmosphere. The sample solution was stirred for 12 h at 80 °C, and washed with 1N aqueous HCl and extracted with CH_2Cl_2. The combined organic extract was dried over Na_2SO_4, and then evaporated to dryness. The residue was chromatographed on silica gel with

CH_2Cl_2/MeOH (99:1) as an eluent. The first orange fraction was corrected, and evaporated to dryness under reduced pressure to leave **AZ(16)** (58 mg, 0.031 mmol) as orange solid in 13% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.95 (d, J = 8.3 Hz, 4H, azobenzene), 7.49 (d, J = 8.3 Hz, 4H, azobenzene), 6.99 (s, 2H, aimde), 6.71 (s, 4H, phenyl), 3.91 (t, J = 6.5 Hz, 8H), 3.88 (t, J = 6.3 Hz, 4H), 3.79 (s, 4H, benzyl), 1.77–1.70 (m, 12H), 1.46–1.41 (m, 12H), 1.25 (br., 126H), 0.88 (t, J = 7.3 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ 168.23, 153.36, 152.14, 137.70, 135.34, 133.26, 130.50, 123.79, 99.15, 73.65, 69.34, 44.88, 32.09, 29.95–29.57 (m), 22.88, 14.29; MALDI-TOF-MS m/z calculated for M^+ ($C_{124}H_{216}N_4O_8$) 1890.7 and $[M+Na]^+$ ($C_{124}H_{216}N_4O_8Na$) 1913.7, found 1890.7 and 1913.7; IR (ATR): 3249, 2954, 2916, 2849, 1650, 1600, 1537, 1507, 1467, 1426, 1382, 1342, 1230, 1121 cm^{-1}.

5. AFM image of *trans*-AZ(12)

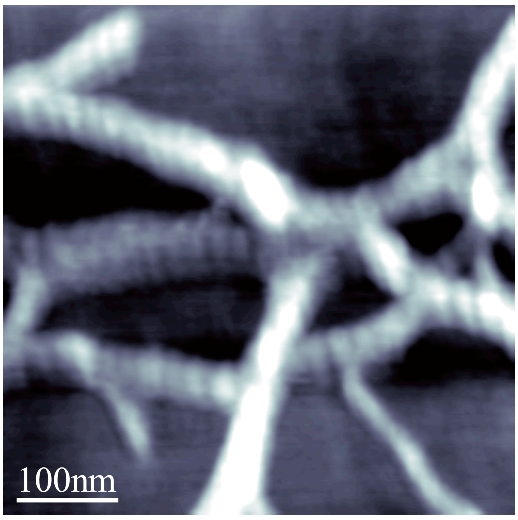


Fig. S1. FM-AFM image of self-assembled *trans*-**AZ(12),** prepared from a cyclohexane solution with the concentration of 4.0 × 10^{-5} M on a HOPG substrate immersed in pure water at room temperature. Cantilever oscillation amplitude: 0.3 nm. Frequency-shift setpoint: +170 Hz.

6. SEM images of *trans*-AZ(6) and *trans*-AZ(16)

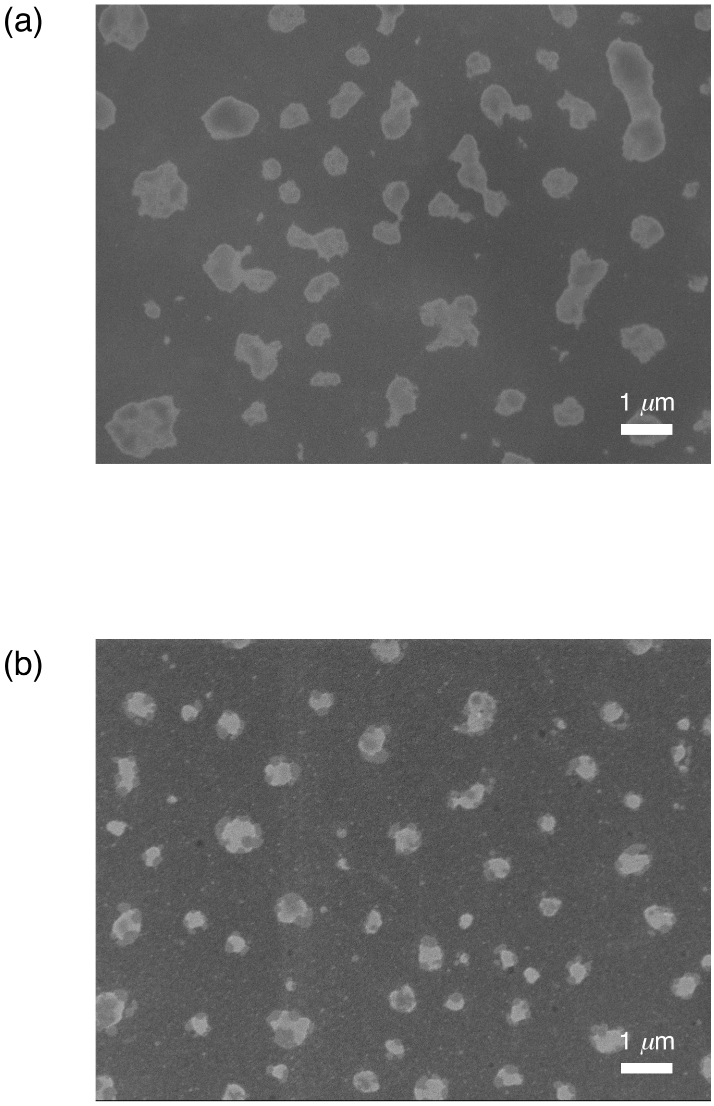


Fig. S2. SEM images of air dried samples of self-assembled (a) *trans*-**AZ(6)** and (b) *trans*-**AZ(16)** prepared from cyclohexane solutions with the concentration of 4.0 × 10^{-5} M deposited on a specimen grid covered with a thin carbon support film at room temperature.

7. Absorption spectroscopy of *trans*-AZ(12) and *cis*-AZ(12) in $CHCl_3$

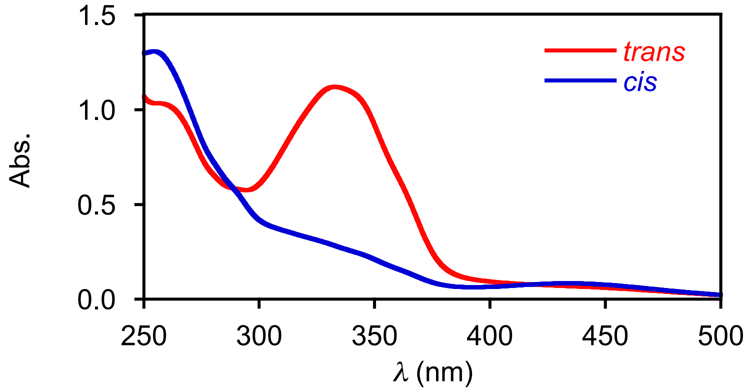


Fig. S3. Absorption spectra of a $CHCl_3$ solution of *trans*-**AZ(12)** (red line) and *cis*-**AZ(12)** (blue line) at 20 °C. [**AZ(12)**] = 4.0×10^{-5} M.

8. Dynamic light scattering analysis of *cis*-AZ(12) in cyclohexane

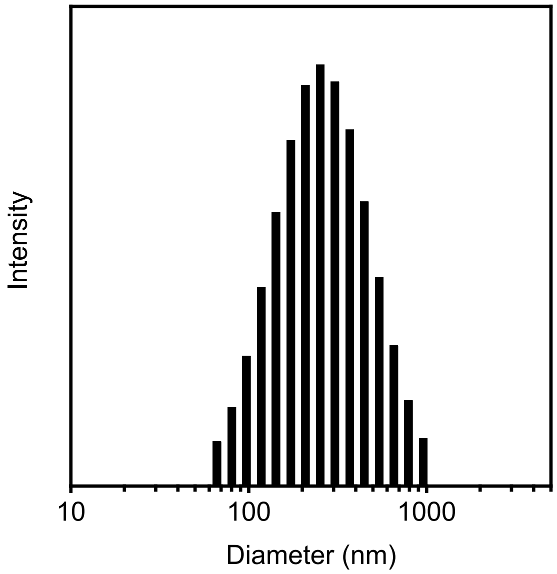


Fig. S4. A DLS histogram profile of a cyclohexane solution of *cis*-**AZ(12)** with the concentration of 2.0×10^{-4} M at 20 °C. Average diameter: 171.1 nm.

9. Thermal isomerization from *cis*- to *trans*-AZ(12)

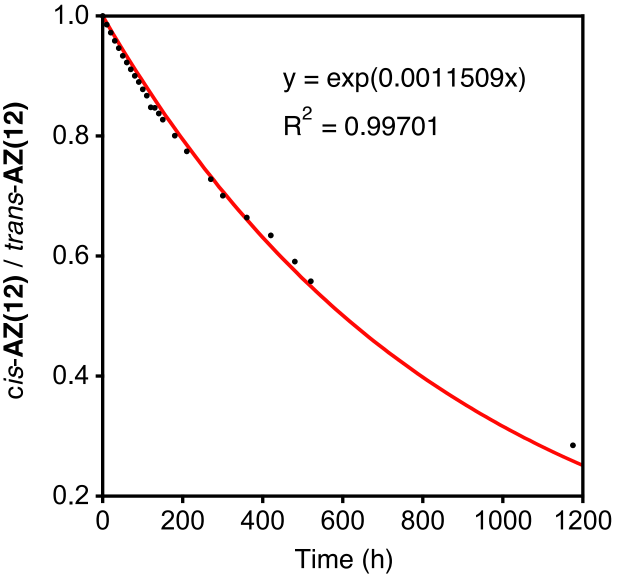


Fig. S5. Plot of molar ratio of *cis*-**AZ(12)** to *trans*-**AZ(12)** upon thermal isomerization in cyclohexane with the concentration of 4.0 × 10^{-5} M at 20 °C.

10. Arrhenius plot for thermal isomerization of *cis*- to *trans*-AZ(12)

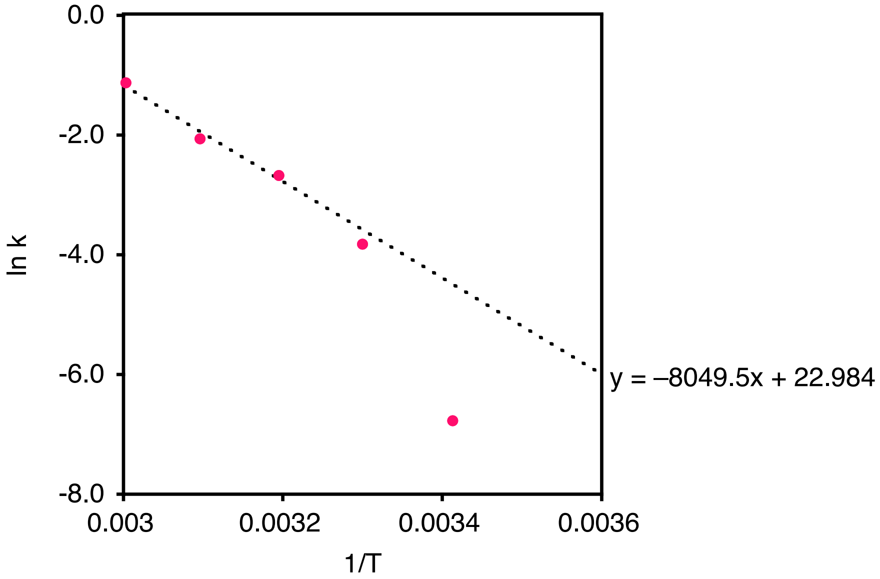
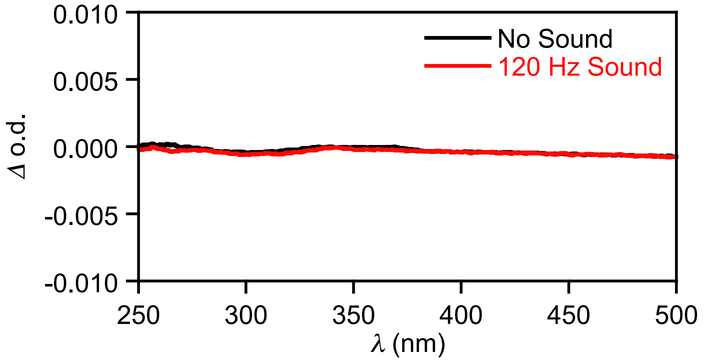


Fig. S6. Arrhenius plot for thermal isomerization of *cis*- to *trans*-**AZ(12)** in cyclohexane at 20–60 °C. [**AZ(12)**] = 4.0 × 10^{-5} M. Linear line with the equation of y = –8049.5x + 22.984 was obtained from the values at 60, 50 and 40 °C.

11. LD spectra of *trans*-AZ(6) and *trans*-AZ(16)

(a) *trans*-**AZ6**



(b) *trans*-**AZ16**

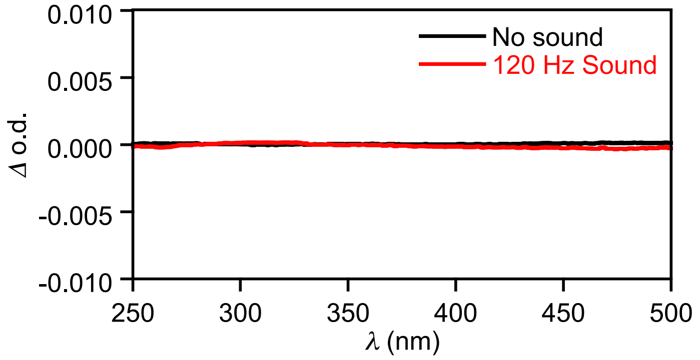
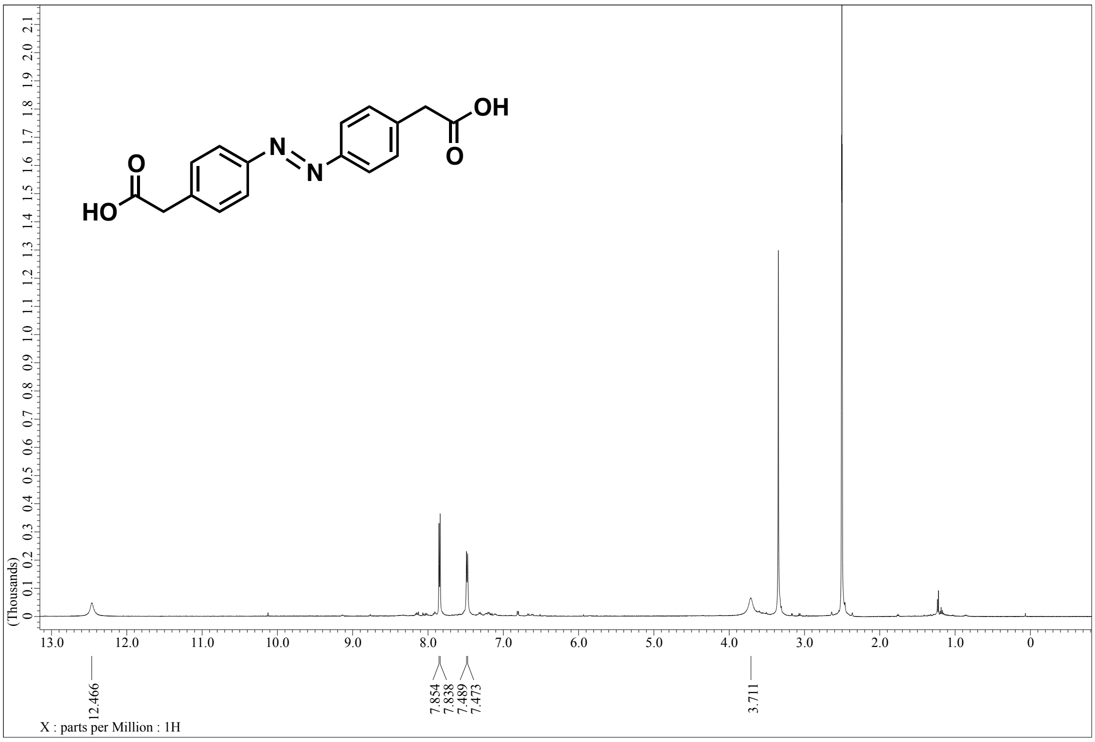
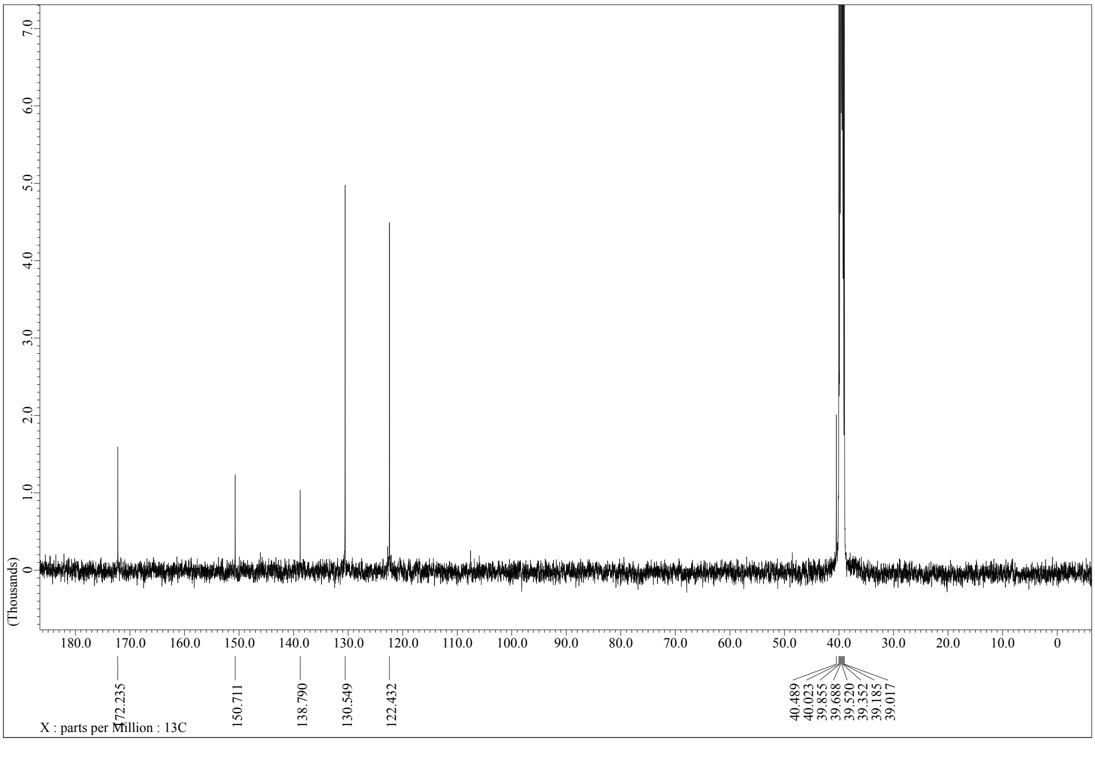


Fig. S7. LD spectra of (a) *trans*-**AZ(6)** and (b) *trans*-**AZ(16)** in cyclohexane (4.0×10^{-5} M) at 20 °C with and without 120 Hz sound irradiation (red and black curve, respectively).

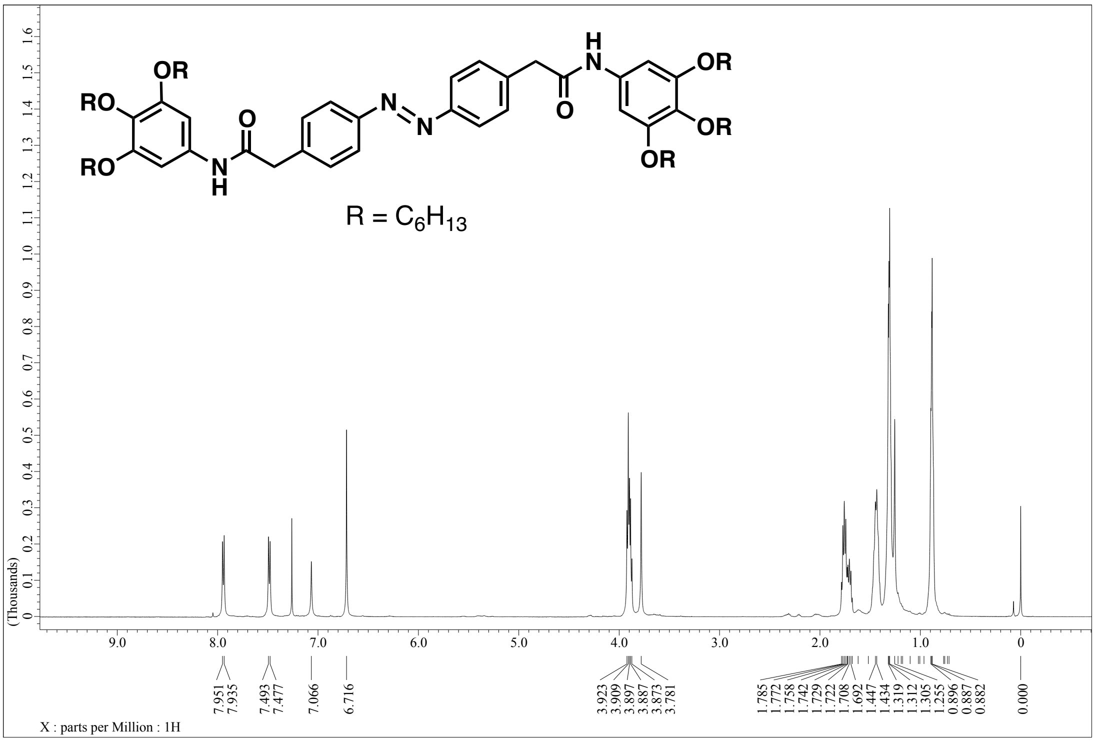
12. ^{1}H and ^{13}C NMR spectra

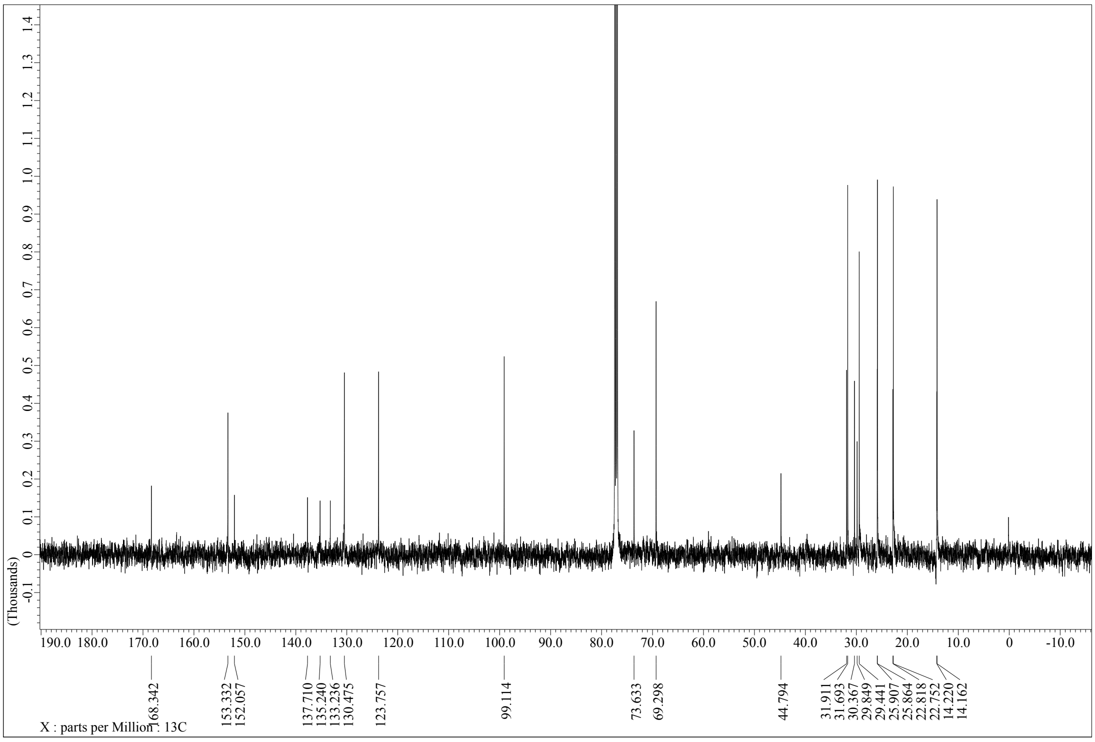
(a) ^{1}H and ^{13}C NMR spectra of **2**



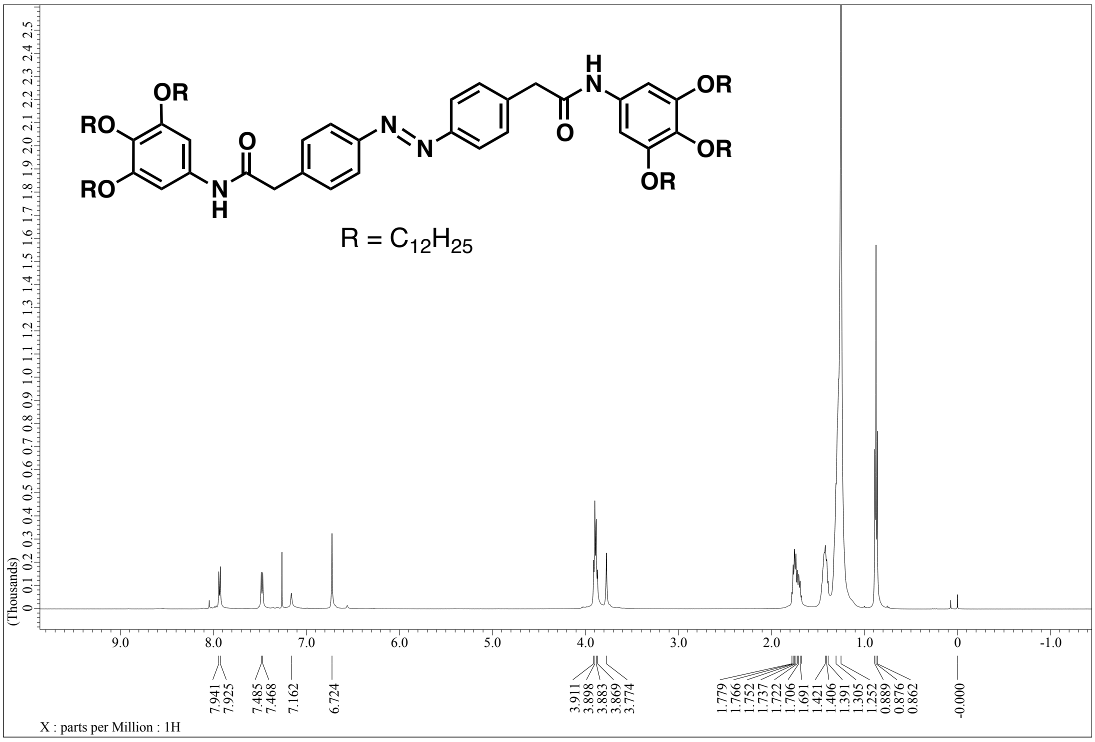


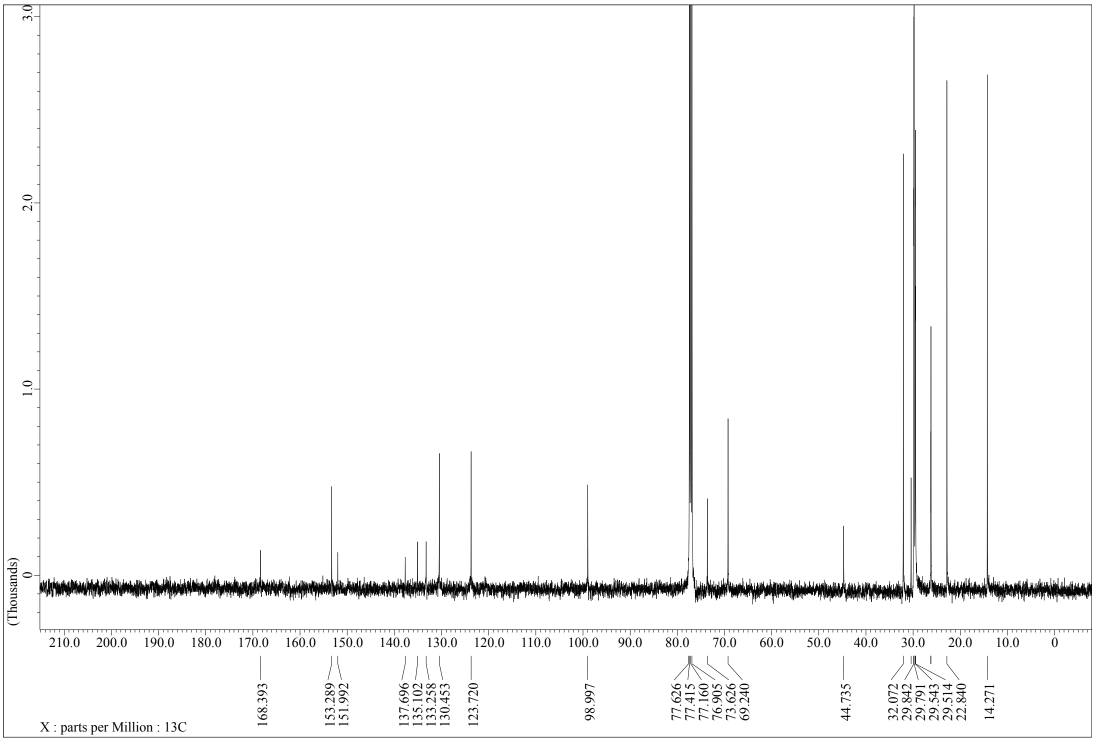
(b) ^{1}H and ^{13}C NMR spectra of **AZ(6)**



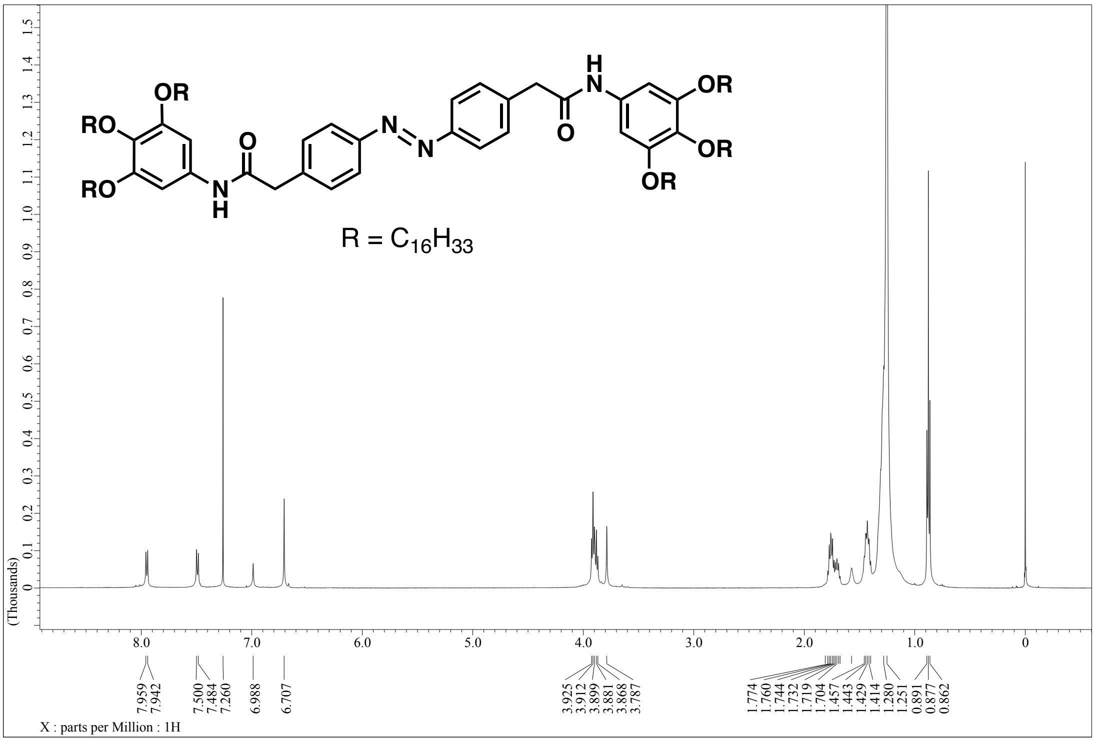


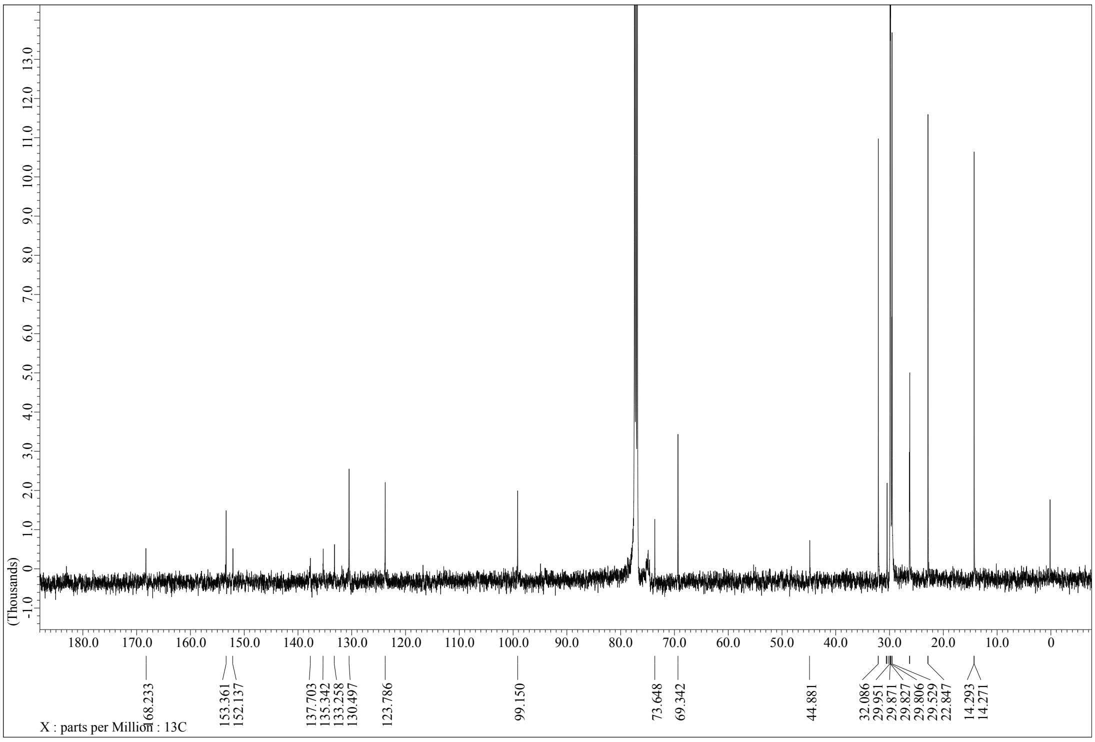
(c) ^{1}H and ^{13}C NMR spectra of **AZ(12)**





(d) ^{1}H and ^{13}C NMR spectra of **AZ(16)**





13. References

1. C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao and S. K. Prasad, *J. Org. Chem.*, **2007**, *72*, 8308-8318
2. T. Fukuma, M. Kimura, K. Kobayashi, K. Matsushige and H. Yamada, *Rev. Sci. Instrum.,* 2005, **76**, 053704.