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A physical operation of hydrodynamic orientation of an azobenzene supramolecular assembly with light and sound†

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Photoisomerizations of a newly designed azobenzene derivative reversibly change its self-assembly in a solution to form twisted supramolecular nanofibers and amorphous aggregates, respectively. When irradiating the sample solution with audible sound, the former assembly exhibits a LD response due to its hydrodynamic orientation, but the latter one is LD silent, in the sound-induced fluid flows.

Functional materials composed of macroscopic molecular assemblies that bring about reversible changes of their shape and/or physical properties upon external physical stimuli have attracted much attention in material sciences.[1] Light is used for bringing about photoreactions and structural isomerizations of molecules, leading to changes of matter. Sound is also available for controlling orientations of nanoscale objects, such as polymers and molecular assemblies in solutions.[2–4] However, no example has yet been reported of matter capable of reacting to both these physical stimuli. In the present study, we succeeded in synthesizing a novel photo- and/or sound-responsive supramolecular nanoarchitecture. Visible and UV light reversibly turn their capability for acoustic alignment in a solution on and off through photoconversions between fibrous and amorphous nanostructures. The sample solution exhibits a linear dichroism (LD) response with inputs of visible light and audible sound, which has potential as a molecular-based AND Boolean logic gate.[5]

We recently reported that supramolecular nanofibers, composed of a porphyrin or an anthracene derivative, hydrodynamically align in solutions under exposure to audible sound of 100–1000 Hz frequency.[4] When molecules or molecular assemblies are long enough to average local effects of the Brownian motions of the solvent molecules, they begin to react to weak sheared flows generated by sound vibration.[6] With the expectation that photoisomerization of the molecular components changes hydrodynamic interactions of their assemblies with the fluid flows, we designed azobenzene derivatives **AZ(*n*)** ($n = 6$, 12, and 16), bearing *N*-phenyl amide groups with long alkyl chains (Fig. 1a).[7]

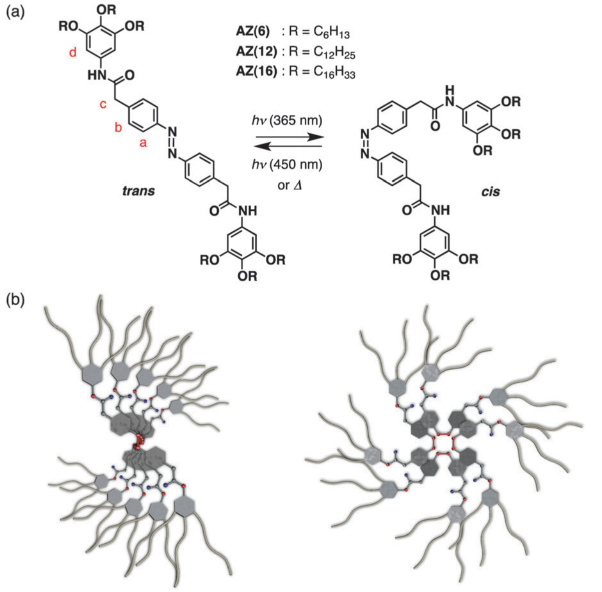

Fig. 1 (a) Chemical structures of *trans*-**AZ(*n*)** and *cis*-**AZ(*n*)** (n = 6, 12, and 16), and (b) their possible self-assemblies.

AZ(*n*) was synthesized starting from 4-aminophenylacetic acid, which was successfully converted to 4,4′-azobenzenediacetic acid, condensed with 3,4,5-(tris-alkoxy)benzenamine, and characterized by means of NMR, IR, and electronic absorption spectroscopies, together with MALDI-TOF mass spectrometry (see ESI†). A representative ^{1}H NMR spectrum of *trans*-**AZ(12)** dissolved in $CDCl_3$ at 20 °C showed characteristic peaks owing to its molecular structure (Fig. 2a). The spectrum obtained in low polar cyclohexane-d_{12} solvent showed notably broadened peaks, but they became sharper at an elevated temperature of 70 °C. Thus, *trans*-**AZ(12)** molecules

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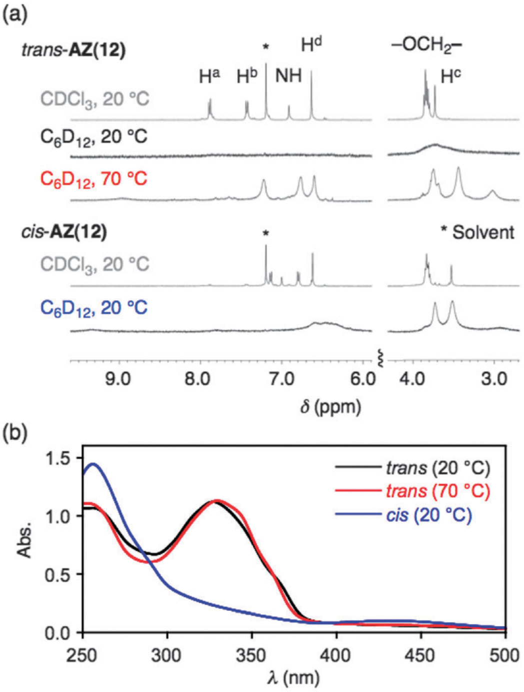


Fig. 2 (a) ^{1}H NMR spectra of *trans*-**AZ(12)** at 20 and 70 °C and *cis*-**AZ(12)** at 20 °C in $CDCl_3$ or cyclohexane-d_{12} with a concentration of 1.2×10^{-2} M. (b) Absorption spectra of *trans*-**AZ(12)** at 20 and 70 °C and *cis*-**AZ(12)** in cyclohexane with a concentration of 4.0×10^{-5} M.

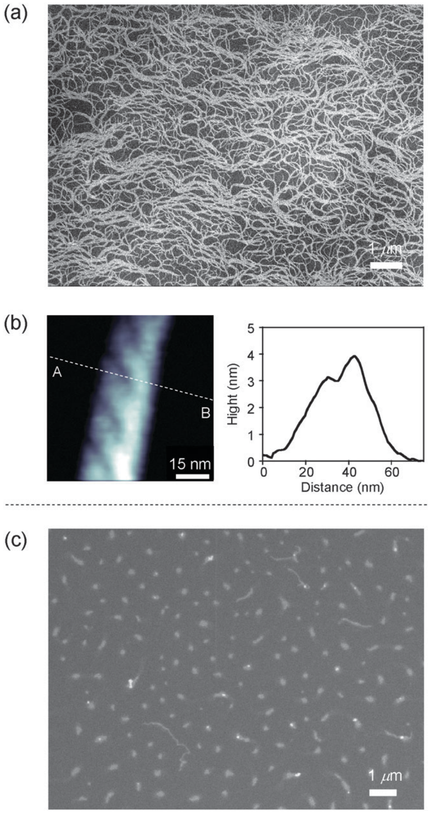


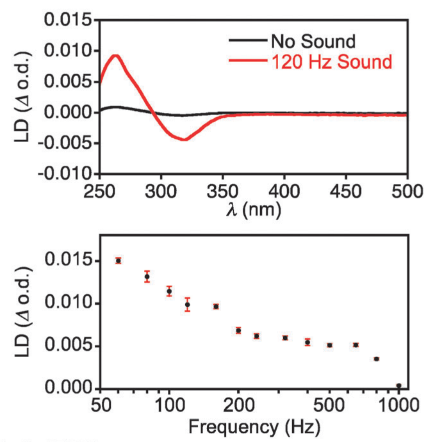
Fig. 3 Scanning electron micrographs of air-dried samples of (a) *trans*-**AZ(12)** and (c) *cis*-**AZ(12)** prepared from a cyclohexane solution with a concentration of 4.0×10^{-5} M deposited on a specimen grid covered with a thin carbon support film. (b) FM-AFM image and height profile (positions A to B) of a *trans*-**AZ(12)** fiber on the HOPG surface immersed in pure water. Cantilever oscillation amplitude: 0.2 nm. Frequency-shift setpoint: +80 Hz.

most likely self-assemble at the lower temperature. The broadened peaks observed in both aromatic and aliphatic regions at 20 °C indicate that *trans*-**AZ(12)** molecules are tightly held in the self-assembled structure. In the electronic absorption spectrum, the cyclohexane solution of *trans*-**AZ(12)** provided the lowest energy absorption band with λ_{max} at 326 nm (Fig. 2b, black curve), originating from the π–π* transition of the azobenzene group.[8] Since the spectrum is blue-shifted in comparison with that measured at 70 °C (Fig. 2b, red curve), *trans*-**AZ(12)** likely forms an H-aggregate.[9]

SEM of the sample, prepared from a cyclohexane solution with a concentration of [*trans*-**AZ(12)**] = 4.0×10^{-5} M, shows that nanofibers formed under those conditions have fibrous structures with diameters of 20–60 nm. The nanofibers may be formed through the bundling of the *trans*-**AZ(12)** supramolecular polymers (Fig. 3a). Frequency-modulation atomic force microscopy (FM-AFM) was then performed on a HOPG substrate with a solution of the self-assembled *trans*-**AZ(12)** in cyclohexane (4.0×10^{-5} M), after drying under flowing N_2. Topographic images observed in pure water (Fig. 3b and Fig. S1, ESI†) revealed that the formed nanofibers are actually bundles of supramolecular polymers. The height profile (~4 nm) in the cross section image and the calculated size of the *trans*-**AZ(12)** molecule (2–3 nm) indicate that the nanofiber observed in Fig. 3b is a double-stranded supramolecular polymer.[10] These micrograph images and the obtained spectral features described above indicate that the *trans*-**AZ(12)** molecules self-assemble to form the supramolecular polymer through possible intermolecular multiple hydrogen bonding interactions of amide groups and π–π interactions of the aromatic components (Fig. 1b, left). Both *trans*-**AZ(6)** and *trans*-**AZ(16)**, having shorter and longer alkyl chains, respectively, showed dominant formations of amorphous aggregates under the same conditions in SEM (Fig. S2, ESI†). Van der Waals interactions of the attached alkyl chains may also play an important role in bundling the single supramolecular polymers.

Photoisomerization of *trans*-**AZ(12)** to *cis*-**AZ(12)** in chloroform at 20 °C occurred upon photoirradiation by 365 nm light using a 150 W xenon lamp for 20 min. The absorption spectrum showed that the lowest energy absorption band of *trans*-azobenzene with λ_{max} at 332 nm decreased while that of *cis*-azobenzene at 256 and 433 nm increased (Fig. S3, ESI†). The ^{1}H NMR spectrum in $CDCl_3$ also showed characteristic peak shifts, and the resulting *trans*/*cis* ratio was estimated to be 92 : 8 in the photostationary state (Fig. 2a).[11] In the cyclohexane solution, where *trans*-**AZ(12)** formed supramolecular nanofibers, the photoisomerization slowly proceeded at 20 °C, but was accelerated upon increasing the temperature to 40 °C due to thermal dissociation of the molecular assembly.[12] The resulting cyclohexane solution containing *cis*-**AZ(12)** also provided the characteristic absorption spectrum of *cis*-azobenzene with λ_{max} at 256 and 431 nm (Fig. 2b, blue curve). However, the peaks observed in the ^{1}H NMR spectrum, obtained in cyclohexane-d_{12} solution at 20 °C, are broad as observed in the case of *trans*-**AZ(12)**. The broadened peaks and the relatively sharp peaks, corresponding to the aromatic and alkoxy groups, respectively, are observed in lower and higher magnetic field regions, respectively. These results indicate that *cis*-**AZ(12)** also self-assembles in cyclohexane solution. Here, it assembles through possible intermolecular dipole–dipole interactions of *cis*-azobenzene groups, having the polar structure compared with that of the *trans*-isomer, and hydrogen bonding interactions of the amide groups, with weak interactions of the alkyl chains (Fig. 1b, right). In fact, a SEM image obtained from the cyclohexane solution of *cis*-**AZ(12)** ([**AZ(12)**] = 4.0×10^{-5} M) shows the presence of amorphous aggregates with particle sizes of 250–300 nm (Fig. 3c), whose shapes are entirely different from those obtained from *trans*-**AZ(12)** (Fig. 3a). Dynamic light scattering (DLS) measurements of the sample with [**AZ(12)**] = 2.0×10^{-4} M also showed the presence of aggregates with an average radius of 171 nm with a size distribution in the range of 70–960 nm (Fig. S4, ESI†).[13] The observed conversions of the shapes of self-assembled *trans*- and *cis*-**AZ(12)** reversibly occurred through photoirradiation with UV or visible light. Thermal isomerization from *cis*-**AZ(12)** to *trans*-**AZ(12)** in the dark occurred very slowly at 20 °C with a half-life of 25 days (Fig. S5, ESI†). Since the Arrhenius plot for the thermal isomerization in the range of 20–60 °C provided a non-linear profile (Fig. S6, ESI†), it is also decelerated by the aggregation of *cis*-**AZ(12)** molecules at the lower temperature.[12]

(a) *trans*-**AZ(12)**



(b) *cis*-**AZ(12)**

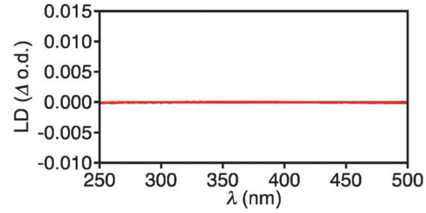


Fig. 4 LD spectra of (a) *trans*-**AZ(12)** and (b) *cis*-**AZ(12)** in cyclohexane (4.0×10^{-5} M) at 20 °C with and without 120 Hz sound irradiation (red and black curves, respectively). Changes in LD intensity of (a) at 261 nm by varying sound frequencies with the amplitude of 13.5 Pa. The obtained LD intensities were averaged for 50 s.

Hydrodynamic orientations of polymers and molecular assemblies having anisotropic structures give an LD response.[4–6] We conducted LD spectral measurements for the cyclohexane solution of *trans*- and *cis*-**AZ(*n*)** upon exposure to a sinusoidal audible sound, which generates fluid flows including a primary oscillatory flow and a secondary steady flow in the solution.[14] The LD spectrometer in this study was equipped with a 12 × 12 × 44 mm quartz optical cuvette, having a ∅10 × 10 mm cylindrical neck (outer diameter), composed of 1 mm-thick quartz glass, which was filled with the solution of **AZ(*n*)**. The cyclohexane solutions containing the self-assembled **AZ(*n*)** (*n* = 6, 12, and 16) at 20 °C showed no LD responses in the absence of irradiation by the audible sound (Fig. 4a, black curve and Fig. S7, ESI†). When the samples were irradiated with 120 Hz sound, interestingly, a bisignate LD spectrum was observed only with *trans*-**AZ(12)** that formed the supramolecular nanofiber (Fig. 4a, red curve). The mechanism of the alignment is such that the nanofiber reacts to velocity gradients of the media occurring in crossing areas of the downward and upward flows, and by the laminar flows generated around the glass surfaces of the vessel due to the sound-induced fluid flows.[4b] The observed LD intensity is, thus, highly dependent on the frequency and amplitude of the sound (Fig. 4a) and the shape of the optical cuvette used.[4b] A sound wave with low frequency, which causes larger vibrations of the fluid media, allows efficient alignment of the nanofibers in the solution to give an intense LD response. However, the sample becomes LD silent after photoisomerization from *trans*-**AZ(12)** to *cis*-**AZ(12)** (Fig. 4b). This result is reasonably explained in that the *cis*-**AZ(12)** aggregates without the anisotropic fibrous structure cannot orient in response to the shared flows.

In conclusion, self-assembled **AZ(12)** reversibly changes its capability to align acoustically through *trans*- and *cis*-photoisomerizations with visible and UV light. The alignment occurs only with *trans*-**AZ(12)**, forming supramolecular nanofibers, under sound-irradiation to give the LD response. This system has the potential to function as a molecular AND logic gate operated by both light and sound.

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