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Photoswitchable Helicity

Thermally Assisted Photonic Inversion of Supramolecular Handedness**

*Anesh Gopal, Mohamed Hifsudheen, Seiichi Furumi, Masayuki Takeuchi, and Ayyappanpillai Ajayaghosh**

Dedicated to Professor Samir K. Brahmachari on the occasion of his 60th birthday

Symmetry breaking, leading to a specific handedness (either right or left) of biological structures is one of the most fascinating phenomenon in nature.[1] Notably, nature is able to translate molecular chirality into supramolecular handedness, through genetic-information transfer, thereby creating functionally incredible helical structures of nanoscopic and macroscopic dimensions, including giant superstructures. While several factors such as vortex motion,[2] stirring,[3] magnetic field,[4] and redox forces[5] may be involved, natural light may have a key role in controlling the chirality and helical sense of biological helices.[6] Light is undoubtedly a versatile external stimulus to control the chemical and physical properties of molecules, both natural and synthetic.[7] Chirality is one of the chemical properties that can be manipulated using light. For example, photoisomerization of azobenzene[8] has been used as a trigger to induce point chirality on a molecular level,[9] whereas on a macromolecular level, light is known to influence the helicity of polymers[10] and self-assemblies.[11] While molecular chirality and single-chain polymer helicity are easy to manipulate with circularly polarized light, reversible control of supramolecular helicity in a macroscopic self-assembly using unpolarized light is challenging.

Chirality amplification and helicity induction are known to be predominant in π-systems.[12] The thermodynamic and kinetic complexities in supramolecular polymerization of π-systems have recently been revealed by Meijer and co-workers.[13] While co-assembly and guest binding have been shown to influence supramolecular helicity,[14] the use of light as a stimulus to control the macroscopic helical sense of self-assembled structures has rarely been used. Herein, we report that the helicity of supramolecular assemblies associated with a specific chirality can be reversibly switched to the opposite helical sense through a chiral-center-controlled photoisomerization of the attached azobenzene moieties. To understand the role of light and heat on helicity at a supramolecular level, we have synthesized the azobenzene linked phenyleneethynylene (PE) derivatives **1**–**3** (Scheme 1) using a Pd-catalyzed Sonogashira–Hagihara coupling method[15] and characterized them by FTIR, NMR spectroscopy, MALDI-TOF MS, and elemental analysis. The UV/Vis absorption spectra of **1**–**3** (1×10^{-5} M) in tetrahydrofuran (THF) showed two maxima at 324 and 419 nm.[16] In methyl cyclohexane (MCH), at a concentration of 1×10^{-5} M, the absorption band of (*S*)-**2** at 419 nm is red-shifted to 440 nm with a shoulder at 480 nm owing to aggregation, which was confirmed by temperature dependent UV/Vis absorption spectral changes (Figure S2).[16]

Upon UV irradiation of an MCH solution (1×10^{-5} M) at 323 K with a band-pass filter $\lambda = 350 \pm 30$ nm (intensity 0.1 W cm^{-2}), the *trans*-(*S*)-**2** (*E*,*E*) was isomerized to the corresponding *cis* form (*E*,*Z* or *Z*,*Z*) as indicated by the decrease in the absorption intensity at 330 nm, with a slight increase in the absorption intensity at 440 nm through two isosbestic points (298 and 396 nm) as shown in Figure S3.[16] A photostationary state (PSS) is attained within 15 minutes of irradiation. The reverse transition was attained by visible light irradiation using a band-pass filter $\lambda = 450 \pm 30$ nm (light intensity 0.3 W cm^{-2}) for 30 minutes or by keeping the solution at 343 K for 3–4 hours. The photoisomerization was monitored by ^{1}H NMR spectroscopy (Figure S4).[16] The percent conversion was calculated from the change in the integrated area of the signal at $\delta = 7.68$ ppm, with respect to a reference signal $\delta = 4.02$ ppm (m, 12 H), yielding nearly 53 % *cis*-isomers at the PSS. In principle, 50 % isomerization of (*S*)-**2** or (*R*)-**3** could lead to 100 % *E*,*Z* isomer. However, experimentally, the irradiated solution at the PSS contained a mixture of *cis*-isomers (*E*,*Z* and *Z*,*Z*) along with some remaining *E*,*E* isomers.[16] We were unable to find the exact percentage of each isomer in the mixture because these isomers were difficult to separate by HPLC.

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[*] A. Gopal, M. Hifsudheen, Prof. A. Ajayaghosh
Photosciences and Photonics Group, Chemical Sciences and Technology Division
National Institute for Interdisciplinary Science and Technology (NIIST), CSIR
Trivandrum-695019 (India)
E-mail: ajayaghosh@niist.res.in
Homepage: http://www.niist.res.in/english/scientists/ajayaghosh-a-/personal.html
Prof. M. Takeuchi
Organic Materials Group, National Institute for Materials Science (Japan)
Dr. S. Furumi
Applied Photonic Materials Group, National Institute for Materials Science (Japan)
and
PRESTO Japan Science and Technology Agency (Japan)

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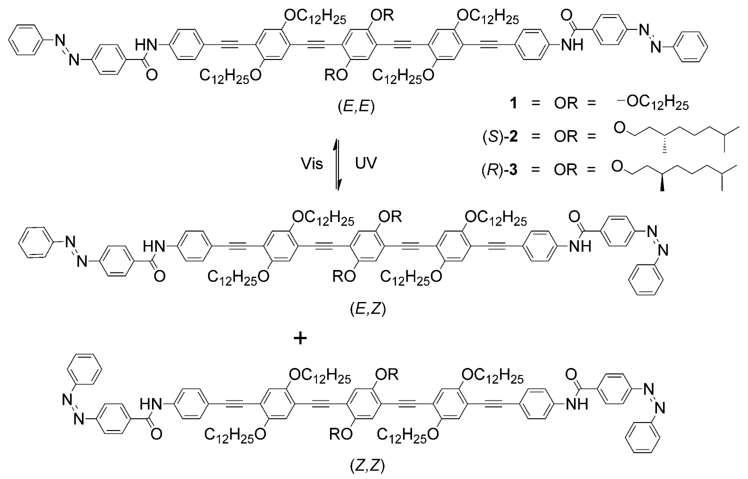

Scheme 1. Photoisomerization of the azobenzene-linked phenyleneethynylene derivatives **1**–**3**. A mixture of *E,E*; *E,Z* and *Z,Z* isomers are possible.

The molecule **1** was inherently achiral before and after irradiation, whereas the CD spectra of (*S*)-**2** and (*R*)-**3** showed they were chiral and had opposite Cotton effects. For example, the CD spectrum of (*S*)-**2** showed an intense positive signal at 464 nm with two negative signals at 407 nm and 322 nm with a zero crossing at 421 nm corresponding to the π–π^* transition of the PE moiety (Figure 1 a). Surprisingly, the CD spectrum after UV irradiation at 323 K, followed by cooling the solution to a lower temperature, showed a reversal of the CD spectrum, however with a lower intensity of the CD bands (Figure 1 a). On the other hand, the molecule (*R*)-**3** with opposite stereocenters exhibited an intense negative signal at 464 nm with two positive signals at 407 and 322 nm (Figure 1 b). In this case also, photoirradiation resulted in a reversal of the CD signal. The quantitative CD response from the chromophore excitonic coupling could be estimated from the dissymmetry factor ($g_{abs} = \Delta\varepsilon/\varepsilon$), which is the ratio of the circularly polarized absorption to the total absorption.[17] The values of $|g_{abs}|$ at 464 nm for (*S*)-**2**, before and after irradiation, are 0.0111 and 0.0092, respectively, with a difference of 0.0020. The corresponding values for (*R*)-**3** are 0.0115 and 0.0093, respectively, with a difference of 0.0022.

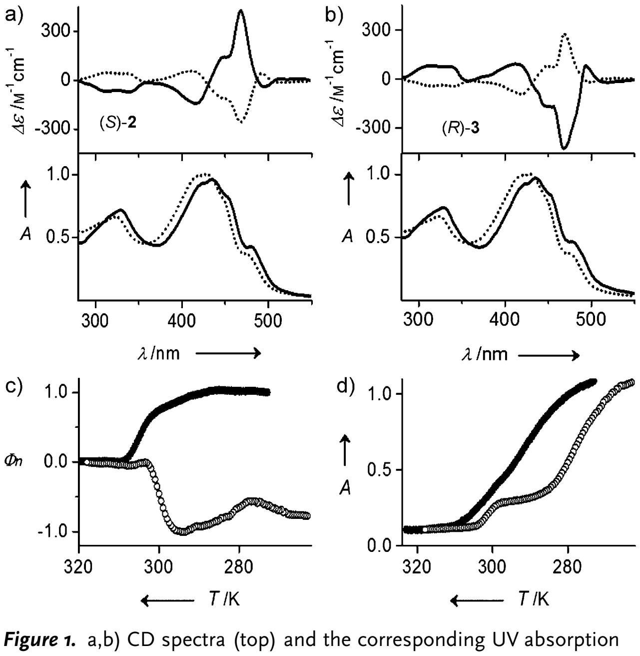

Figure 1. a,b) CD spectra (top) and the corresponding UV absorption spectra (bottom) for (*S*)-**2** and (*R*)-**3** before (——) and after (•••••) UV irradiation at 273 K. c) Normalized CD intensity (Φ_n) at $\lambda = 464$ nm upon cooling of (*S*)-**2** before (●) and after (○) UV irradiation. d) The corresponding normalized absorption spectral changes.

The temperature-dependent CD spectral-intensity variations (Φ_n) for (*S*)-**2** (1×10^{-5} M, in MCH) were monitored at 464 nm before and after photoisomerization and are shown in Figure 1 c. In a slow cooling experiment (2 K min^{-1}), before photoisomerization, the molecules follow a nucleation elongation pathway which is characteristic of a cooperative self-assembly[17] with an elongation temperature (T_e) of 310 K. Interestingly, after irradiation, the cooling curve of the mixture of isomers showed a decreased T_e of 303 K, with reversal in the sign of the CD signal. Upon cooling, the CD signal turned sharply negative, which upon further cooling reverted back towards zero. However, with continued cooling, the original trend towards the negative was regained, with overall reversal of the original helicity (Figure 1 c). This unusual variation of the cooling curve indicates that after UV irradiation the co-operative self-assembly involves more than one type of aggregate. The initial nucleation may occur with the partially isomerized species present in higher concentration, with an inverted helicity, followed by the elongation of the helical chain with aggregates of the non-isomerized molecules with the initial *P*-helicity. Upon further cooling, aggregates of the fully isomerized molecules with lower stability and inverted helicity may also join the growing helices, further accelerating the overall opposite handedness. The corresponding cooling curves obtained from the absorption spectra also support a multistep growth process after irradiation (Figure 1 d).

Circularly polarized luminescence (CPL) is characteristic of helical assembly of luminophores, which exist in a dissymmetric environment in the photoexcited state.[18] The degree of CPL is given by the luminescence dissymmetry ratio, which is defined as $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the luminescence intensities of left and right circularly polarized light. As expected, (*S*)-**2** before isomerization showed a positive CPL with a g_{lum} value of $+0.008$ at 503 nm (Figure 2 a). Interestingly, after photoisomerization, the sign of CPL was reversed with a decrease in the g_{lum} value ($g_{lum} = -0.002$ at 503 nm). In the case of (*R*)-**3**, a negative CPL emission with $g_{lum} = -0.01$ was obtained before photoisomerization (Figure 2 b).[19] After photoisomerization, the CPL sign was reversed with a g_{lum} value of $+0.002$ at 503 nm. The corresponding emission spectra are shown in Figure 2 c,d. Even though these g_{lum} values are relatively low when compared to other systems,[20] it is apparent that the CPL seen here is associated with the respective helicity of the

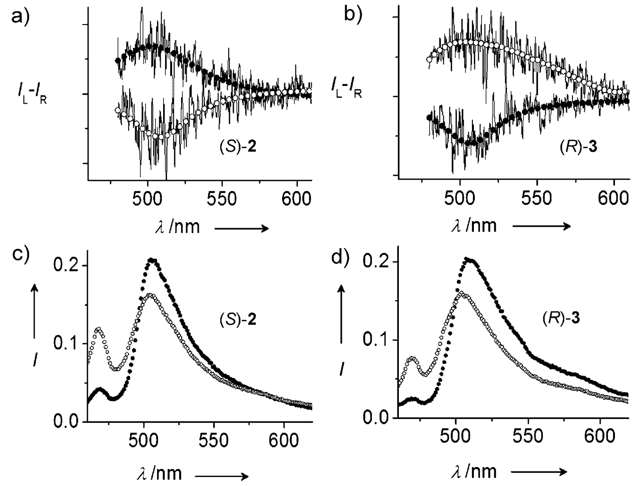

Figure 2. a) CPL spectra for (*S*)-**2** before (●) and after (○) UV irradiation; b) CPL spectra for (*R*)-**3** before (●) and after (○) UV irradiation. The corresponding fluorescence emission spectra are shown in (c) and (d), respectively. All spectra were obtained using 1×10^{-4} M (*S*)-**2** or (*R*)-**3** in MCH.

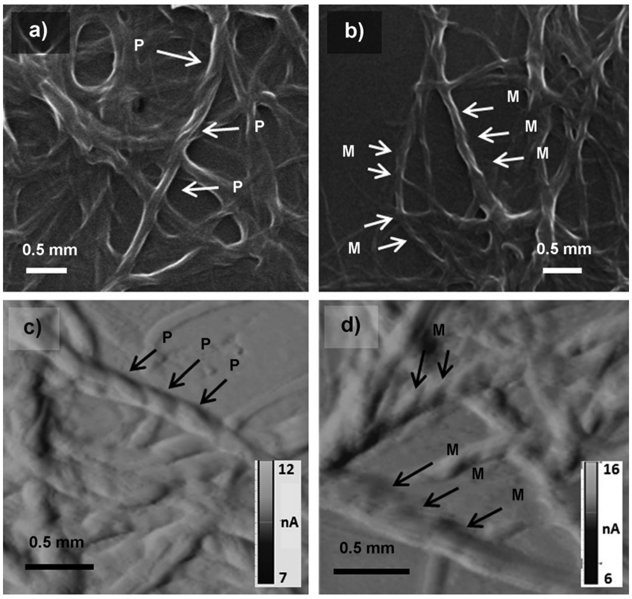

Figure 3. SEM images of (*S*)-**2** a) before and b) after photoisomerization. The SEM analysis was done on a silicon wafer substrate after evaporating a drop of 5×10^{-5} M (*S*)-**2** in MCH. AFM images for (*S*)-**2** c) before and d) after photoisomerization. The AFM analysis was done on a freshly cleaved mica surface drop cast with 1×10^{-5} M (*S*)-**2** in MCH. The arrows indicate the helical twist (*P* or *M*) of the fibers.

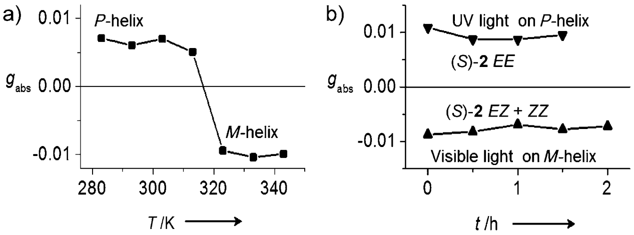

Figure 4. Evidence for the depolymerization pathway of the helicity inversion. a) Change in g_{abs} for (*S*)-**2** as a function of heating, UV irradiation, and cooling. Each point on the plot was obtained by irradiating at 350 nm at the specified temperature, followed by cooling. The reversal of the CD signal occurs above 313 K, indicating depolymerization of the aggregate. b) Plot of g_{abs} versus time for the *P*- and *M*-helices under UV and visible light irradiation, respectively, in the absence of heating.

complex and not related to selective absorption of the emission by the chiral compounds. This is clear from the fact that the achiral derivative did not exhibit any CPL.

SEM analysis of (*S*)-**2** before photoirradiation showed entangled right-handed (*P*) helical ropes of diameters ranging from 50 nm to 1 μm and lengths of several micrometers (Figure 3a). After irradiation at 323 K followed by cooling, the helicity of the fibers were found to be left-handed (*M*), as shown in Figure 3b. AFM analysis of (*S*)-**2** revealed reversal of their native helicity to the induced opposite screw sense after irradiation (Figure 3c,d). From CD, SEM, and AFM analyses, it is apparent that the helical ropes are formed by the coiling of the elementary fibrils, which are formed by the helical packing of the chiral aggregates in a preferred helical sense.

The relatively low CD intensity after photoirradiation indicates the possibility for the coexistence of fibers with both helicities. However, since the SEM and AFM images did not show the presence of fibers with opposite helicity, it can be inferred that the low intensity of the CD signal after photoisomerization could be associated with the relatively low stability of the *cis* isomer aggregates. This hypothesis is clear from the temperature-dependent plots of the CD and the absorption data of the aggregates before and after photoisomerization (Figure 1c,d).

Interestingly, the inversion of helicity occurs through a depolymerization pathway, which is clear from the plots of the g_{abs} obtained after irradiation at different temperatures and the subsequent reassembly of the helix by cooling of the solution (Figure 4a). For 1×10^{-5} M (*S*)-**2** in MCH, the helicity inversion occurs around 313 K or above. In the absence of heating, the helicity did not change even after irradiation for several hours, as shown in the plots of the g_{abs} against the irradiation time (Figure 4b). Even if there could be slow isomerization of the molecules within the helical fibers, the helical twist does not change significantly. However, reversible switching of helicity is possible for several cycles, as shown by the sign inversion of the g_{abs} values after heating the initial helices above room temperature, followed by UV irradiation and cooling (Figure S12).[16]

Based on the experimental data, a plausible mechanism for the observed photoinduced helicity inversion is proposed in Figure 5. After photoirradiation, a mixture of molecules with partially isomerized (Y), fully isomerized (Z), and the non-isomerized (X) azo groups may exist. The spectral and microscopic changes after UV irradiation, suggest that the major component at the PSS is the partially isomerized *E*,*Z* isomer (Y), in which only one of the two azobenzene moieties is isomerized. This argument is evident from the fact that the inversion of helicity occurs only through the aggregate

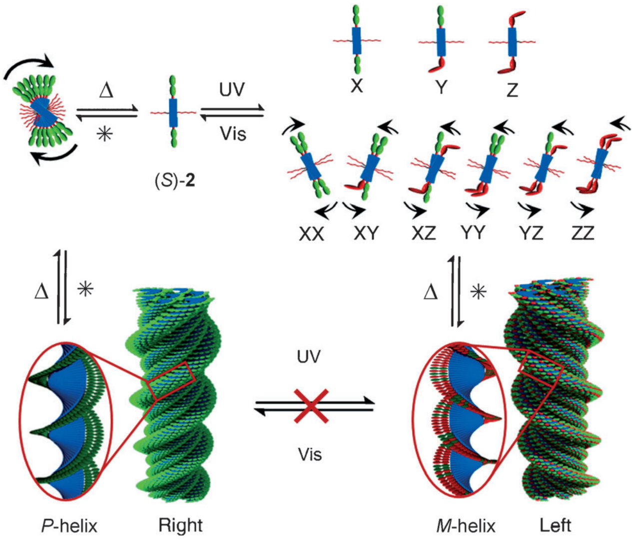

Figure 5. A schematic representation of the helicity inversion. As shown, the direct light-induced conversion of the helix handedness is not possible in the absence of heat. Δ = heating; ✳ = cooling.

depolymerization step for which a high concentration of the *cis*-isomer is required. Since the overall isomerization yield is only 53% at the PSS, to have a high concentration of the *E*,*Z* isomer (Y), the photoisomerization should restrict itself to the monoisomerized form Y. In the case of (*S*)**-2,** the flip of the azo moiety during the *trans* to *cis* isomerization process could be the cause of the right-handed helicity, which is dictated by the stereo center in the molecule. Therefore, the *S*-chiral center of (*S*)**-2** may facilitate a right-handed flip of the *trans* azo moiety to form the *cis* isomer, which may force the incoming molecules to follow the packing direction imposed by the *cis* forms (Y or Z). This situation could lead to the formation of six different non-isoenergetic aggregates which are XX, with inherent *P*-helicity, or XY, XZ, YZ, YY, and ZZ, all with the opposite *M*-helicity (Figure 5). Of these, XX, YY, and ZZ are homonuclear aggregates, whereas XY, XZ, and YZ are heteronuclear aggregates. Since the concentration of X at the PSS is expected to be low, the fraction of XX, XY and XZ may also be low. Similarly, if the relative fraction of Z with respect to Y is low (the Z isomer being the less stable *cis* form) the fractions of ZZ and YZ may also be low. Therefore, the self-assembly after photoisomerization will be mainly nucleated and controlled by the excess amount of the homonuclear *M*-helical YY aggregates, which will direct further assembly of the other aggregates leading to helix elongation with a left-handed screw sense as shown in Figure 5.

In conclusion, it has become apparent that the handedness of a photoresponsive supramolecular object can be biased with the action of light and heat, without changing the inherent molecular chirality of the individual building blocks. Thus, our study strengthens the general perception that in combination with other forces, light may help determine the parity violation in the symmetry of natural objects. Temperature-controlled photonic switching of macroscopic handedness of π-systems could be further used for the design of smart materials with switchable electronic properties, such as conductivity and charge carrier mobility.

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