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Photo/chemo dual-controlled reversible morphological conversion and chiral modulation of supramolecular nanohelixes with nanosquares and nanofibers†

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A photo/chemo dually interconvertible system was constructed through the supramolecular assembly of azobenzene-diphenylalanine (Azo-FF) with α-cyclodextrin. The resultant chiral nanohelix was able to interconvert into a nanosquare upon irradiation at different wavelengths, but into a nanofiber upon changing solvent polarity, which provides a feasible way to achieve highly ordered nanostructures with various morphologies, dimensions and chiralities.

Supramolecular assemblies with stimuli-responsivity have attracted considerable research interest because of their applications in various fields such as drug carriers, catalysts, sensors, protein probes, and optoelectronic materials.[1] Various external triggers, such as pH,[2] temperature,[3] solvent[4] photoirradiation,[5] enzyme,[6] and (electro)chemical redox,[7] have been used in these systems. Among them, light is widely regarded as a very important approach to achieve the smart control of supramolecular assembly because of its noninvasive, clean and remote-controlling properties. In the last decade, many photocontrolled supramolecular assemblies[8] based on azobenzene–cyclodextrin have been constructed taking advantage of the reversible photoisomerization of azobenzene and the different binding behaviors of *trans*- and *cis*-azobenzenes with cyclodextrin.[9] However, most of these studies were focused on the photocontrolled assembly/disassembly process, while the morphological conversion of supramolecular assembly switched by light irradiation was rarely reported. Kim *et al.* reported a chemocontrolled one-cycle nanotube–nanoparticle morphological conversion of pyrene-modified dendritic self-assembly induced by the sequential addition of cyclodextrin and poly(propylene glycol).[10] Stupp *et al.* reported a chemocontrolled reversible nanohelicoidal–nanocylinder conversion of a simultaneous covalent and noncovalent hybrid polymer though the addition/extraction of supramolecular compartments.[11] Recently, we reported a photocontrolled reversible nanotube–nanoparticle conversion mediated by β-cyclodextrin dimers.[8d] More recently, when we were preparing this manuscript, Chi, Tian and Zhu reported a photocontrolled reversible nanohelix-amorphous particle conversion accompanied by the dynamic amplification of chirality with photoreversibility.[12]

On the other hand, the diphenylalanine (L-Phe–L-Phe, FF) peptide, a core recognition motif of Alzheimer's β-amyloid polypeptide, was found to be able to self-assemble into stable nanotubes in 2003.[13] From then on, lots of effort was contributed to organize FF-based building blocks into various well-defined supramolecular nanostructures such as nanotubes, spherical vesicles, nanofibers, nanowires, macroporous honeycomb scaffolds and peony-flower-like hierarchical nanostructures through the self-assembly of diphenylalanine and its derivatives such as Ac-FF, Boc-FF, Z-FF, Cbz-FF, Nap-FF, Fc-FF and Cys-FF.[5a,6a,14,15] He *et al.* introduced a ferrocene group to diphenylalanine and made it capable of being reversibly controlled by altering its redox state.[16] They also created a range of rigid chiral nanostructures through the modulation of counterions, temperature, and solvent.[14c] Li and co-workers used the photoswitchable sulfonicazobenzene to co-assemble with diphenylalanine to achieve the photo-induced structural transition.[5a] Therefore, one can believe that the association of azobenzene–cyclodextrin with FF may become a significant approach to the construction of nano-scaled supramolecular assemblies with a smart stimuli-responsivity and structural diversity. In this work, we wish to report a photo/chemo dual-controlled nanotube based on azobenzene–diphenylalanine (Azo-FF) and α-cyclodextrin (Scheme 1), which can be reversibly converted into a nanosquare using a photocontrol but into a nanofiber using a chemocontrol.

Azo-FF was prepared *via* a four-stepped synthesis as described in Scheme S1 (ESI†). Firstly, diphenylalanine was esterified through a reaction with AcCl and CH_3OH, and the residue was cast to the next step directly. After the reaction with bromoacetyl bromide at a low temperature (−10 °C), N-terminus-modified bromide was obtained and then undertook a substitution

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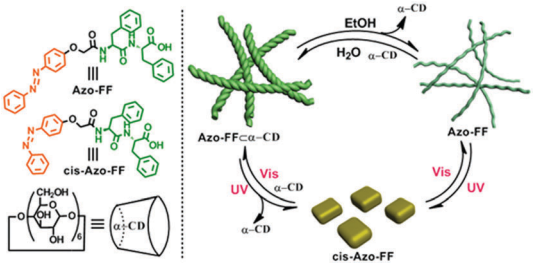
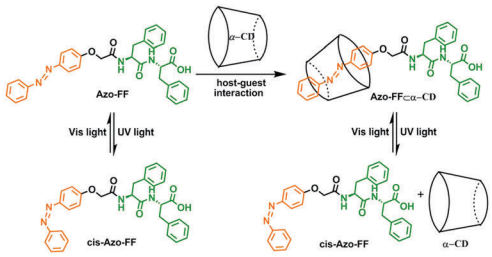
† Electronic supplementary information (ESI) available: Detailed synthesis, characterization data, Job's plot, 2D NMR spectra, DLS date, CD, and scanning electron micrograph. See DOI: 10.1039/c6cc07089b



Scheme 1 Structural illustration of the host and guest and the dual-controlled conversion of self-assembly.



Scheme 2 Self-assembly/disassembly based on the photo-responsive interconversion of Azo-FF and α-cyclodextrin.

reaction with hydroxyazobenzene to give compound **3**. Through a subsequent hydrolysis under basic conditions, Azo-FF was obtained as an orange solid in 44% yield.

Generally, upon irradiation with UV light, the *trans*-isomer of an azobenzene compound can transform to the *cis*-isomer, which can reverse back to the *trans*-isomer through either visible light irradiation or heating. Herein, ^{1}H NMR experiments were performed in D_2O : DMSO (v : v/9 : 1) to investigate the binding behavior of the *trans*- (*trans*-Azo-FF) or *cis*-isomer (*cis*-Azo-FF) of Azo-FF with α-cyclodextrin. With the addition of α-cyclodextrin to a solution of *trans*-Azo-FF, the ^{1}H NMR signals of azobenzene protons (marked by orange dots) of *trans*-Azo-FF shifted to the low field, while the ^{1}H NMR signals of aromatic protons of the diphenylalanine moiety (marked by green dots) showed no significant shifts (Fig. 1a and b). Moreover, the NOESY spectrum of an equimolar *trans*-Azo-FF + α-cyclodextrin mixture showed the clear NOE correlations between the inner protons of α-cyclodextrin and the azobenzene protons of Azo-FF (Fig. S4, ESI†). These jointly indicate that the azobenzene moiety of *trans*-Azo-FF was included in the α-cyclodextrin cavity to form the *trans*-Azo-FF/α-cyclodextrin complex.[17] On the other hand, after irradiating the *trans*-Azo-FF/α-cyclodextrin complex using UV light (365 nm) for 10 min, all of the aromatic protons in the Azo-FF/α-cyclodextrin complex gave ^{1}H NMR signals very similar to those of free *cis*-Azo-FF (Fig. 1c and d). Moreover, no NOE correlations between the inner protons of α-cyclodextrin and the protons of Azo-FF could be observed after expositing the *trans*-Azo-FF/α-cyclodextrin complex to UV light (Fig. S6, ESI†). A possible reason for these observations may be that the photo-induced conversion from *trans*-Azo-FF to *cis*-Azo-FF led to the dissociation of the Azo-FF/α-cyclodextrin complex (Scheme 2), because α-cyclodextrin was reported as unfavorable to bind the *cis*-isomer of azobenzene.[18] In addition, the mass spectrum also gave evidence for the photo-responsive host–guest association/dissociation (Fig. S5 and S7, ESI†). Through a comparison of the integral area in the ^{1}H NMR spectra, the conversion ratio of *cis–trans* isomerization was calculated to be 90%.

The interconversion between the *trans*-Azo-FF/α-cyclodextrin and *cis*-Azo-FF/α-cyclodextrin systems can also be tracked using UV-vis spectroscopy. As seen in Fig. 2a, the absorption band of the *trans*-Azo-FF/α-cyclodextrin complex around 344 nm dramatically decreased under the irradiation at 365 nm, accompanied by the obvious hypsochromic shift of the absorption maximum. In addition, the appearance of a new absorption band around 431 nm and a clear isosbestic point at 410 nm jointly indicated the one-step transformation of the *trans*-Azo-FF/α-cyclodextrin complex to the simple mixture of α-cyclodextrin with *cis*-Azo-FF, because the free *cis*-Azo-FF has a π–π* transition that is less intense and blue-shifted relative to its *trans* isomer as well as a weak n–π* transition that is more intense in the *cis* form than in the *trans* one in the visible region.[19] However, the decreased intensity at 344 nm was recovered to its original level upon the subsequent irradiation at 450 nm. A possible reason may be that, owing to the reverse photoisomerization from *cis* to *trans* form of Azo-FF, the simple mixture of *cis*-Azo-FF with α-cyclodextrin could revert to the *trans*-Azo-FF/α-cyclodextrin

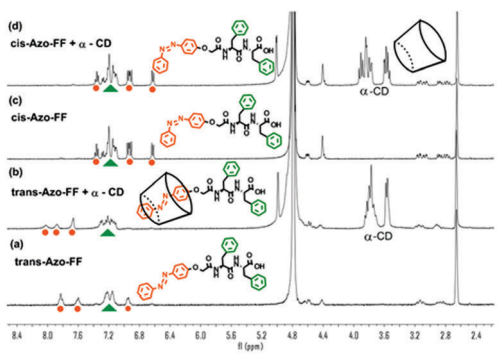


Fig. 1 Partial ^{1}H NMR spectra (400 MHz, D_2O : DMSO-d_6/(v/v) 9 : 1, 25 °C) of (a) *trans*-Azo-FF, (b) *trans*-Azo-FF + α-cyclodextrin (1 : 1), and (c) after 365 nm irradiation of (a) and (d) after 365 nm irradiation of (b), Azo-FF = [α-cyclodextrin] = 1 mM.

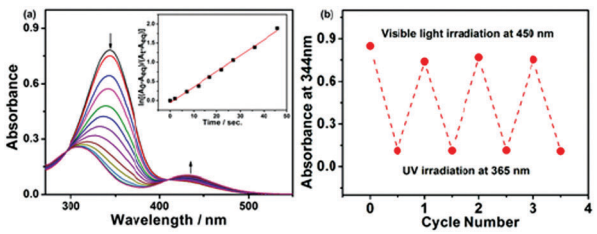


Fig. 2 (a) UV-vis spectra of Azo-FF/α-cyclodextrin (1 : 1) (0.03 mM in H_2O) to determine the photoisomerization rate constant (k_t) in water. The duration of UV light was set at 0 → 121 s at 365 nm. Inset: Determination of the k_t value of Azo-FF/α-cyclodextrin (1 : 1) upon exposure to UV light at 365 nm. (b) Cyclic responses of the absorbance values at 344 nm of *trans*-Azo-FF/α-cyclodextrin solution (0.03 mM) on alternating irradiation between UV and visible light.

system (Scheme 2). Significantly, this assembly/disassembly cycle could be repeated several times (Fig. 2b). In addition to the light irradiation, the continuous heating of a *cis*-Azo-FF/α-cyclodextrin mixture at 80 °C for 2 h could also result in the conversion of the *cis*-Azo-FF + α-cyclodextrin mixture to the *trans*-Azo-FF/α-cyclodextrin system (Fig. S8, ESI†). By utilizing first-order kinetics, the *trans* → *cis* photoisomerization rate constant (k_t) of *trans*-Azo-FF in solution was measured to be 0.03628 s^{-1} (Fig. S9, ESI†), but increased to 0.04096 s^{-1} in the presence of 1.0 equiv. of α-cyclodextrin (Fig. 2a, inset). This result suggested that the association of Azo-FF with α-cyclodextrin could accelerate the isomerization of Azo-FF.[20]

Moreover, the circular dichroism spectrum of *trans*-Azo-FF showed a positive Cotton effect peak ($\Delta\varepsilon$ = 2.63 dm^3 mol^{-1} cm^{-1}) at 325 nm and a negative Cotton effect peak ($\Delta\varepsilon$ = −3.17 dm^3 mol^{-1} cm^{-1}) at 367 nm, but these peaks changed to $\Delta\varepsilon$ = 4.06 dm^3 mol^{-1} cm^{-1} at 329 nm and $\Delta\varepsilon$ = −1.39 dm^3 mol^{-1} cm^{-1} at 382 nm, respectively, in the circular dichroism spectrum of the *trans*-Azo-FF/α-cyclodextrin system, probably due to the chirality transfer of FF and α-cyclodextrin to the azobenzene moiety. With the gradual irradiation of UV light, the circular dichroism signal intensity of either the *trans*-Azo-FF/α-cyclodextrin system or free *trans*-Azo-FF gradually decreased and nearly vanished after 80–100 s (Fig. S10, ESI†). The circular dichroism experiment showed that the *trans*-Azo-FF/α-cyclodextrin or *trans*-Azo-FF system would lose most of its chirality when irradiated by UV light.

The photo-controlled morphological interconversion of the Azo-FF/α-cyclodextrin assembly was characterized using a scanning electron microscope (SEM). As shown in Fig. 3a, the free *trans*-Azo-FF exists as one-dimensional ambiguous spiral nanofibers with a uniform width of *ca.* 25 nm and a length of over 10 μm, although a very slight helix could not be rigorously ruled out. However, the SEM image of the *trans*-Azo-FF/α-cyclodextrin system showed a number of right-handed nanohelixes (Fig. 3b) with a length of over 10 μm, a width of *ca.* 40 nm and a helical pitch of *ca.* 100 nm, which were conformationally uniform in size and shape. Significantly, after the irradiation of the *trans*-Azo-FF/α-cyclodextrin solution at 365 nm for 3 min, the original nanohelixes turned to a number of nonhelical nanosquares with a side length of 100–500 nm (Fig. 3c). In the control experiment, similar nanosquares could also be obtained by irradiating the nanofibers of free *trans*-Azo-FF at 365 nm (Fig. S11, ESI†). Besides the SEM images, the morphological conversion of the assembly could also be distinguished by the naked eye through the turbidity experiments. As shown in Fig. 3d, the subtransparent *trans*-Azo-FF/α-cyclodextrin solution became completely transparent after the irradiation of UV light for 10 min due to the conversion of the nanohelix to the nanosquare, and the resultant transparent solution of the nanosquare would revert to being subtransparent after the irradiation of visible light owing to the photoreversible nanosquare → nanohelix transformation. DLS data (Fig. S12, ESI†) showed that the assembly of the *trans*-Azo-FF/α-cyclodextrin complex and the *trans*-Azo-FF monomer possess a hydrodynamic diameter of up to thousands of nanometers, which is dramatically larger than the diameter observed for their *cis*-Azo-FF system. Consequently, UV-vis, circular dichroism, turbidity, DLS and SEM experiments jointly confirmed the good reversibility and repetitiveness of the photocontrolled nanohelix–nanosquare morphological conversion as well as the chiroptical property change. A similar photo-switchable nanofiber–nanosquare morphological conversion was also observed in the case of free Azo-FF (Fig. S11, ESI†).

Combining the results described above, we propose a possible mechanism for the assembly and transformation process. As illustrated in Fig. 4, mainly through the π–π stacking among aromatic units, the free *trans*-Azo-FF, which adopted a linear conformation, tended to self-assemble along the one-dimensional direction to form nanofibers. In contrast, the *cis*-Azo-FF, which adopted an L-type conformation, firstly formed a quadrate dimer through hydrogen bonding between the carboxylic groups of FF fragments, and then the resultant dimers further self-assembled along the two-dimensional direction mainly though π–π stacking among aromatic units to form nanosquares. With the addition of α-cyclodextrin, the azobenzene moiety of *trans*-Azo-FF would be included into the cavity of α-cyclodextrin. Therefore, the large steric hindrance between the adjacent α-cyclodextrin cavities would lead to twisting of the *trans*-Azo-FF units in the nanofiber and consequently the conversion of the nanofiber into a nanohelix. Therein, the D-configuration of glucose moieties in α-cyclodextrin was deduced to play an important role in the formation of a right-hand twist, although there was no direct evidence. On the other hand, once the *trans*-Azo-FF/α-cyclodextrin nanohelix was exposed to UV light, *trans*-Azo-FF photo-isomerized

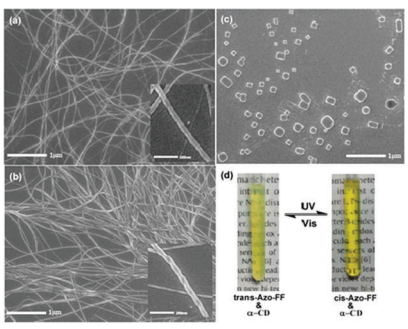


Fig. 3 SEM images of (a) nanofibers formed by *trans*-Azo-FF and (b) nanohelixes formed by *trans*-Azo-FF/α-cyclodextrin. (c) *trans*-Azo-FF/α-cyclodextrin after being irradiated by UV light (365 nm) for 3 min. (d) Photograph of Azo-FF/α-cyclodextrin solution under UV and visible light.

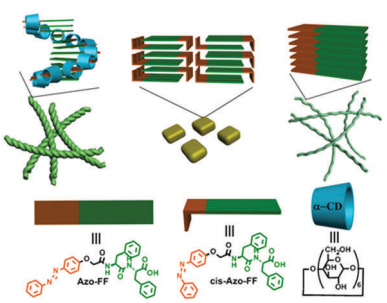


Fig. 4 Possible assembly mode of Azo-FF and *trans*-Azo-FF/α-cyclodextrin.

into *cis*-Azo-FF. Because the α-cyclodextrin cavity was unfavorable to include *cis*-Azo-FF,[20] the *trans*-Azo-FF/α-cyclodextrin nanohelix was disrupted. As a result, the dissociated *cis*-Azo-FF self-assembled into a nanosquare like in the case of free *cis*-Azo-FF (Fig. S11, ESI†).

In addition to the light irradiation, the change in polarity could also adjust the morphology of assembly owing to the non-covalent nature of the supramolecular interactions working between α-cyclodextrin and *trans*-Azo-FF. For example, the addition of ethanol to the aqueous solution of *trans*-Azo-FF/α-cyclodextrin would lead to the conversion of a nanohelix into a nanofiber (Fig. S13a and b, ESI†). A possible reason for this may be that the addition of ethanol weakened the hydrophobic interactions between α-cyclodextrin and *trans*-Azo-FF, which consequently resulted in the dissociation of the *trans*-Azo-FF/α-cyclodextrin complex. Then, the dissociated *trans*-Azo-FF self-assembled into a nanofiber (Fig. S13b, ESI†), like in the case of free *trans*-Azo-FF. However, when further adding water to the above described H_2O/EtOH solution, the nanofiber reversibly converted into a nanohelix (Fig. S13b and c, ESI†).

In conclusion, taking advantage of the photoisomerization properties of azobenzene derivatives, the distinct binding affinity of α-cyclodextrin with *trans*- and *cis*-conformers of azobenzene, as well as the non-covalent nature of supramolecular interactions, a photo/chemo dual-controlled supramolecular assembly was successfully constructed. Crucially, the morphology of the assembly could be switched between the nanohelix and nanosquare under light irradiation, and could be switched between the nanohelix and nanofiber by changing the polarity of the solvent; both of these morphological conversions were reversible and repeatable, accompanied by a controlled chiral amplification or attenuation. The photoswitchable and/or chemoswitchable morphological conversion and chiral modulation properties, along with the facile preparation and good water solubility, may make this supramolecular assembly approach well-suited for the design and smart control of new functional materials.

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