Light-driven self-assembly of cyanostilbene derivative with reversible chirality in aqueous media

Xiaoxuan Zeng, Yue Wu*, Lin Zou, Xingwang Liu, Xin Qi and Zhen-Qiang Yu*

Chirality, which is one of the defining features of biological molecules, plays a critical role in many important life processes. Controlled supramolecular assembly of biomolecules into functional structures with low structural fluidity, e.g., cytoskeleton filaments [1], flagellar filaments of bacteria [2], and high structural fluidity (e.g., cell membranes [3]), serves key roles in the correct functioning of biological processes. Inspired by natural supramolecular assembly, a large number of discrete two- and three-dimensional chiral polygons with well-defined shapes have been successfully prepared through self-assembly [4–8]. In particular, chiral amplification by self-assembly of chiral building blocks into artificial nanostructures shows great promise in materials science [9–12]. There are, however, few examples that display chiral switching in response to external signals, in contrast to the well-controlled tunability of chirality in living systems [13,14]. Stimuli-responsive strategies to control the assembly system using switchable chiral signals, especially in aqueous media, would thus be very valuable.

Light is a perfect external trigger to stimulate self-assembly since photon input is not only clean and waste-free, but also offers precise spatiotemporal control [15–26]. Photon-triggered chiroptical switching in molecules and materials is attracting particular interest because the simultaneous realization of both optical and chiral signals can add extra information density [27–35]. With this in mind, we envisioned a new photochromism that combines chirality and amphiphilicity. Herein, we describe a rational molecular design strategy to prepare *trans*-CS by combining a photochromic unit (cyanostilbene), a hydrophilic unit (sulfonate), and a hydrophobic chiral moiety (cholesterol) through flexible spacers (Scheme S1, Figs S1–S8 and Fig. 1). The chiral and amphiphilic *trans*-CS showed photoswitchable chirality, which accompanied self-assembly or disassembly in aqueous media. This newly designed material showed the following extraordinary features: (i) self-assembly into spherical aggregates to create circular dichroism (CD) signals with good reversibility, (ii) 90% conversion yield from *trans*-CS to *cis*-CS upon irradiation at 365 nm, and (iii) excellent thermal stability in water. Importantly, this approach provides a general route to the self-assembly of water-soluble, chiral, and photoswitchable amphiphiles.

Because of the presence of the cyanostilbene moiety, *trans*-CS is expected to undergo *trans/cis* isomerization when irradiated with ultraviolet (UV) light. ¹H nuclear magnetic resonance (NMR) spectra recorded during the UV-light-induced transformation can be used to follow the *trans*-CS to *cis*-CS process

(Fig. S9). The ratio of *trans*-CS to *cis*-CS could be calculated using the integration ratio of the original and new signals. After irradiation with 365 nm light for 5 min, the *trans/cis* ratio in solution was 9:1. The amount of *trans*-CS gradually decreased with increasing irradiation time and the *trans/cis* ratio stabilized at 1:9 after irradiation for 40 min. The high photoconversion from *trans*-CS to *cis*-CS (90% after 40 min) indicates the high efficiency of the photoisomerization reaction.

When the concentration of *trans*-CS in aqueous solution was increased from 0.01 to 1 mmol L^{−1}, an absorption peak at 336 nm and a CD peak at 361 nm appeared synchronously (Fig. 2a, b). The inset in Fig. 2a shows the absorbance at 336 nm increased linearly with different slopes when the concentration was lower or higher than 0.1 mmol L^{−1}. The change in slope indicates the sample self-assembled at the appropriate concentration of 0.1 mmol L^{−1}. Meanwhile, the concentration dependence of CD intensity in the inset of Fig. 2b also shows the self-assembly concentration was 0.1 mmol L^{−1} in water. Thus, we selected 0.1 mmol L^{−1} *trans*-CS to investigate its self-assembly behavior. Meanwhile, the reference compound CS-OH without cholesterol group shows no CD signal, confirming that the chirality of *trans*-CS was originated from the cholesteric moiety (Fig. S10). *Trans*-CS, which absorbs strongly at 336 nm (Fig. 2c) in water, can be photoconverted to *cis*-CS upon irradiation at 365 nm (10 mW cm^{−2}). The resultant *cis*-isomer has an absorption band at 237 nm, and the appearance of this band is a characteristic indicator of transformation from a *trans*-isomer to a *cis*-isomer. The photostationary state (PSS) shows weak absorption at 336 nm, indicating majority of *trans*-isomer isomerized into *cis*-isomer (Fig. 2a). Conversely, irradiation of photochemically generated *cis*-CS with 254 nm light mostly converts it back to the *trans*-isomer (90%).

The *trans*-CS/*cis*-CS system also exhibits good fatigue resistance. This is exemplified in Fig. 2d, which shows five rounds of back-and-forth shuttling between *trans*-CS and *cis*-CS, brought about by alternating irradiation with 365 or 254 nm light. The absorbance repeatedly oscillates between the minimum and maximum values, which correspond to the absorption values of *trans*-CS and *cis*-CS, respectively. Synchronously, the CD signals of the *trans/cis*-CS system also display oscillations (Fig. 2e), indicating that the optical chirality is strongly correlated with the isomeric structure, although the chiral moiety (cholesterol) is unchanged. Furthermore, the photoisomerization of *trans*-CS can be shown in the characterization of fluorescence performance (Fig. S11). Unlike many known photochromisms [36,37],

College of Chemistry and Environmental Engineering, Institute of Low-dimensional Materials Genome Initiative, Shenzhen University, Shenzhen 518071, China

* Corresponding authors (emails: wuyue@szu.edu.cn (Wu Y); zqyu@szu.edu.cn (Yu ZQ))

Figure 1 Reversible dual UV light shuttle of cyanostilbene between its two stable states, *trans*-CS and *cis*-CS. When self-assembled into spherical aggregates, *trans*-CS produces a strong CD signal, which disappears upon conversion to *cis*-CS by irradiation with 365 nm light.

Figure 2 Absorption (a) and CD (b) showing dynamic variations in self-assembly with increasing concentration of *trans*-CS. Insets in (a): absorbance changes at 336 nm, (b): CD changes at 361 nm. (c) High conversion photoswitching between *trans*-CS and *cis*-CS upon dual UV light shuttle (0.1 mmol L⁻¹, H₂O). Alternation between 365 nm light (140 mW cm⁻²) for 40 min and 254 nm light (10 mW cm⁻²) for 6 h reversibly photoswitches between *trans*- and *cis*-isomers in water, demonstrating good fatigue resistance and reversibility of absorption (d) and optical chirality (e) in aqueous media. (f) Absorbance of *trans*-CS and *cis*-CS in water monitored at 25°C for 500 min, followed by heating at 50°C for 500 min. No change in absorbance was observed at 336 nm, indicating that *cis*-CS and *trans*-CS are thermally stable (bistable states).

trans-CS and *cis*-CS both have excellent thermal stability and do not thermally interconvert. The two isomers showed no inter-conversion after 500 min at room temperature and no change in

absorption at 336 nm was observed after heating to 50°C for 500 min (Fig. 2f). Together, these data reveal that both *trans*-CS and *cis*-CS have excellent thermal stability (bistable states) and

good photoswitchable properties.

We next investigated the morphologies of the self-assemblies of *trans*-CS and *cis*-CS that give rise to the different optical properties of the two isomers. Chiral *trans*-CS and *cis*-CS contain a hydrophilic sulfonate unit and a hydrophobic cholesterol moiety and are thus amphiphilic. As above mentioned, *trans*-CS can self-assemble to form nanoparticles. Microscopic experiments were carried out to probe the morphology and size of the resulting aggregates. Transmission electron microscopy (TEM), using an aqueous solution of *trans*-CS, revealed the presence of spherical micelles, with an average diameter of 140 nm (Fig. 3a). This size estimation was also supported by dynamic light scattering measurements, which showed a hydrodynamic diameter of around 150 nm (Fig. 3c). We hypothesize that, to minimize contact between hydrophobic segments and water, the cholesterol units aggregate in the interior of the aggregate and are surrounded by hydrophilic SO_3^- units, leading to the formation of micelle structures. Upon irradiation with 365 nm UV light and conversion of *trans*-CS to *cis*-CS, these self-assemblies are transformed into irregular nanoparticles, with a small hydrodynamic diameter of around 18 nm (Fig. 3b, d). Upon light-driven *trans*-*cis* isomerization, the newly generated *cis*-isomers disrupt the equilibrium of the self-assembled system and thus contribute to the disassembly of the original nanospheres, as well as to the formation of smaller irregular nanoparticles. These results support the notion that *trans*-CS self-assembles into spherical aggregates, which then disassemble into irregular fragments on the photoisomerization of *trans*-CS to *cis*-CS, indicating that the different molecular structures and packing result in different morphologies of self-assembled particles and different hydrophilicities.

In summary, we presented a design strategy for a chiral, amphiphilic, and photoswitchable molecule, using cholesterol, sulfonate, and cyanostilbene. The molecule could self-assemble to the *trans*-isomer in aqueous solution, which is accompanied by strong CD signals. Both *trans*- and *cis*-isomers are thermally stable, and the high conversion photoswitching between the *trans*- and *cis*-isomers with good fatigue resistance and reversibility, can be achieved using different wavelengths of UV irradiation.

Figure 3 Self-assembly properties of *trans*-CS and *cis*-CS. (a) TEM images of spherical nanoparticles formed by *trans*-CS in aqueous media. (b) TEM images of irregular fragments with significantly smaller size formed by *cis*-CS after 365 nm UV irradiation of *trans*-CS. Dynamic light scattering of nanoparticles formed by *trans*-CS before (c) and after (d) 365 nm UV irradiation in H_2O .

Furthermore, the optical chirality-CD was also modulated by UV irradiation. According to the TEM images and dynamic light scattering data, the photoswitching process involves self-assembly/disassembly from approximately 150 nm spherical particles to 18 nm irregular particles. We proposed a rational strategy using light-driven self-assembly for a molecular photoswitch in which optical chirality can be modulated by light irradiation in aqueous media.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

Xiaoxuan Zeng received her BSc degree from Huizhou University (2019). She is now an MSc student at the College of Chemistry and Environmental Engineering, Shenzhen University, under Prof. Zhen-Qiang Yu's supervision. Her research topic is chiral luminescent materials.

Yue Wu received his BSc degree from Jiangnan University and PhD degree from East China University of Science and Technology in 2014. Then he worked for Wilmar-Arowana as a senior R&D engineer for four years. In 2019, he joined Shenzhen University. Currently, his research interests focus on chiral luminescence and photoswitch.

Zhen-Qiang Yu received his BSc and PhD degrees from the Department of Chemistry, Beijing Normal University in 1997 and the College of Chemistry, Peking University in 2007, respectively. He joined the College of Chemistry and Environmental Engineering, Shenzhen University in 2007, where he is currently an associate professor. His research interests are focused on the synthesis, structures, properties and applications of functional materials.

水溶液介质中氰基苯乙烯衍生物的可逆手性光驱动自组装

曾晓璇*, 吴玥*, 邹林, 刘兴旺, 祁鑫, 余振强*

摘要 人工手性自组装一直是分子化学与材料化学的前沿挑战性课题。但由于缺少合适的手性光响应结构单元, 构造具有光控、可逆、手性专一性响应的分子体系具有很大的挑战性。本工作通过合理的分子设计: 以氰基二苯乙烯作为光致异构基团, 磺酸基作为亲水基团, 胆固醇作为疏水手性基团, 构造了独特的光响应组装体系。当氰基二苯乙烯处于反式构型时, 在水相中组装形成规则的球状组装体且具有较强的手性信号。通过365 nm光照后, 反式构型转变为顺式构型, 球状组装体解组装, 同时手性信号消失; 当采用254 nm光照后, 重新形成具有手性信号的球状组装体。核磁共振和吸收光谱结果表明光致异构转化率达到90%, 并且具有良好的光致异构重复性(抗疲劳性)及热稳定性。本研究成功实现了水相介质中光控、手性专一性响应的可逆光调控, 在构建双稳态光控手性开关方面表现出潜在的应用前景。