

Self-Assembly-Triggered Cis-to-Trans Conversion of Azobenzene Compounds

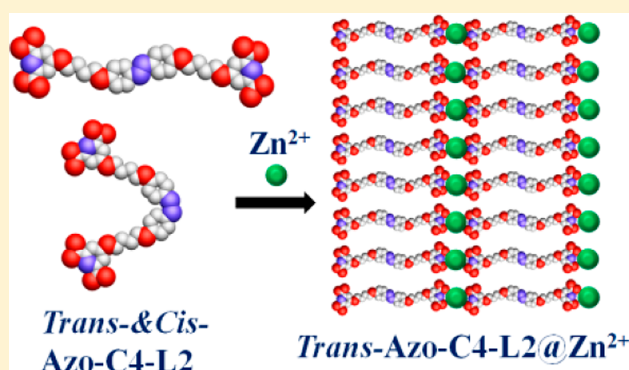
Zheng Wu,[†] Rongrong Xue,[†] Mengqi Xie,[†] Xuejiao Wang,[†] Zihao Liu,[†] Markus Drechsler,[‡] Jianbin Huang,[†] and Yun Yan^{*,†}

[†]Beijing National Laboratory for Molecular Sciences (BNLMS), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[‡]Bavarian Polymer Institute (BPI), Key Lab of Electron and Optical Microscopy, University of Bayreuth, Universitaetsstr. 30, D-95440 Bayreuth, Germany

S Supporting Information

ABSTRACT: Cis-to-trans transition of azobenzene compounds usually occurs under appropriate light irradiation or slow thermal relaxation, and one can hardly obtain complete cis-to-trans transition of azos due to the overlap of the $n-\pi^*$ transition of the trans and the cis isomers. We show that by viewing the photostationary state as a chemical equilibrium between the cis and trans isomers, triggered self-assembly of the trans isomers can promote the cis-to-trans transition, and trans azos with spectrum-grade purity can even be achieved using an elegantly designed coordinating azo. This work establishes a new paradigm for manipulating the cis-to-trans transition of azo compounds, which may inspire designs for various azo-based advanced materials.



Azobenzene compounds have been extensively employed in the construction of diversified photoresponsive materials in virtue of their trans–cis conversion triggered by photoirradiation.^{1–12} It is well-established that the azos undergo trans-to-cis conversion under UV irradiation, while the reverse process occurs under visible light or via thermal relaxation.^{13–17} In many cases, one can hardly get complete trans isomers in an azo system due to the overlap of the $n-\pi^*$ transition of the trans and the cis isomers.^{12,18,19} As a result, the azo compounds are always a mixture of the trans and cis isomers in a photostationary state (PSS).^{18,20–24} Because the cis isomers are nonplanar with larger dipole, they can hardly self-assemble into well-defined structures, which disfavors applications where planar geometry of azos are required.^{25–27} Although separation of the $n-\pi^*$ transition of the trans and the cis forms via synthetic approaches is possible,^{12,18,19,28} it does not ideally lead to entire trans-to-cis conversion either, which appeals reconsidering the physical insight that governs the photostationary state of azo systems. Herein we show that by viewing the PSS of azos as chemical equilibrium between the trans and the cis azos, the cis-to-trans transition was found to occur simply by inducing the self-assembly of the trans isomers. The key is that the process of self-assembly continuously removes the trans isomers, which are in equilibrium with the cis ones. As a result, the cis isomers have to transform into the trans form to establish new equilibrium. In this way, we are able to establish an azo-system composed of trans azo with a purity of spectrum grade, which

not only discloses a new approach toward high-efficiency photoreaction locking of azo compounds but also paves the way for the fabrication of high-quality azo-based optical materials.

The azo compound in this study is designed to have two coordinating heads attached to each end of the azo moiety, and it is referred to as Azo-C4-L2 (see Figure 1a and the SI for synthesis details). Azo-C4-L2 can form irregular colloidal suspension in water at pH above 11.0 (Figure S1). Qualitative ¹H NMR measurements^{29–32} suggest that the photostationary state (PSS) of Azo-C4-L2 system is composed of 75% trans isomer and 25% cis isomer (Figure 1b, line 2; Figure S2). Upon irradiation with 365 nm UV light, the system can be entirely transformed into the cis isomers (Figure 1b, line 1; Figure 1c; and TEM image in Figure S1), which can revert to the PSS state under daylight or thermal relaxation in the dark (Figure 1c and Figure S3). However, upon the addition of Zn²⁺ to the aqueous PSS system, the UV–vis spectrum blue-shifts immediately (Figure 1d), indicative of significant $\pi-\pi$ stacking of the azo moiety.³³ The spectrum keeps blue-shifting with increasing the amount of Zn²⁺, and the final absorption peak centers at 325 nm, which has been blue-shifted 35 nm from the initial PSS position of 360 nm (Figure 1d). Meanwhile, ¹H NMR measurements reveal vanishing of the

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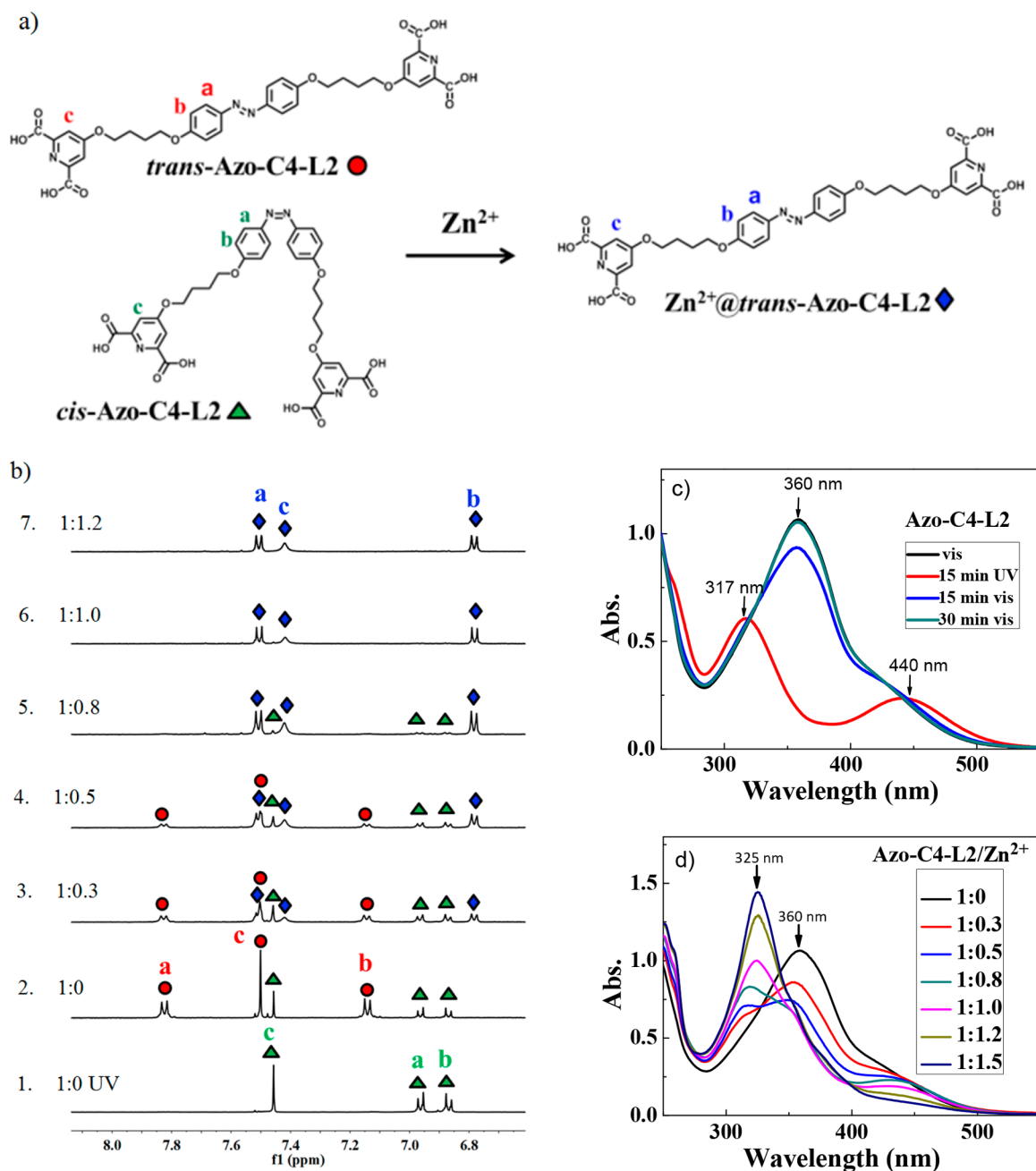


Figure 1. (a) Structure of *trans*- and *cis*-Azo-C4-L2 and the isomerization triggered by the addition of Zn^{2+} . (b) 1H NMR spectra of Azo-C4-L2/ Zn^{2+} coordinating system in D_2O at different molar ratios. Red circle, green triangle, and blue diamond represent protons in the *trans*-, *cis*-, and zinc-coordinated Azo-C4-L2, respectively. The position of the protons is labeled in panel a in the molecular structure. [Azo-C4-L2] = 0.5 mM in all of the spectra, but the concentration of Zn^{2+} varies. (c) UV-vis spectra of Azo-C4-L2 before and after 365 nm UV irradiation. To avoid the generation of heat, a UV lamp of 6 W was used. Daylight was the source of visible light. (d) UV-vis spectra of Azo-C4-L2/ Zn^{2+} at different molar ratios. [Azo-C4-L2] = 0.5 mM.

chemical shifts for both the *trans*- and *cis*-Azo-C4-L2 with the addition of Zn^{2+} , which is accompanied by the occurrence of the signals of the coordination product of Zn^{2+} and *trans*-Azo-C4-L2 (Figure 1b, lines 3–7). This 1H NMR spectra change clearly indicates that both the *cis*- and *trans*-Azo-C4-L2 have transformed into the coordination complex of $Zn^{2+}@trans$ -Azo-C4-L2.

The coordination of *trans*-Azo-C4-L2 with Zn^{2+} simultaneously triggers the formation of nanoribbons (Figure 2a). The details of the ribbons can be clearly visualized in cryo-TEM images (Figure 2b,c). The ribbons are ~ 30 nm wide (Figure

2c), which can run up to several micrometers in length. Their thickness is only 2 to 3 nm estimated from the edge-on section, where the contrast becomes extremely high, as indicated by the red arrows in Figure 2c. AFM measurements also confirm this ultrathin nature of the nanoribbons (Figure S4). Regularly separated dark and light lines parallel to the long axis of the nanoribbons are observed. The dark/light periodicity determined from the Fourier analysis (FFT) is ~ 3.4 nm (inset in Figure 2c), which agrees well with the fully extended length of the *trans*-Azo-C4-L2. Metal ions are electron-dense, which show up dark compared with the hydrocarbon domain under

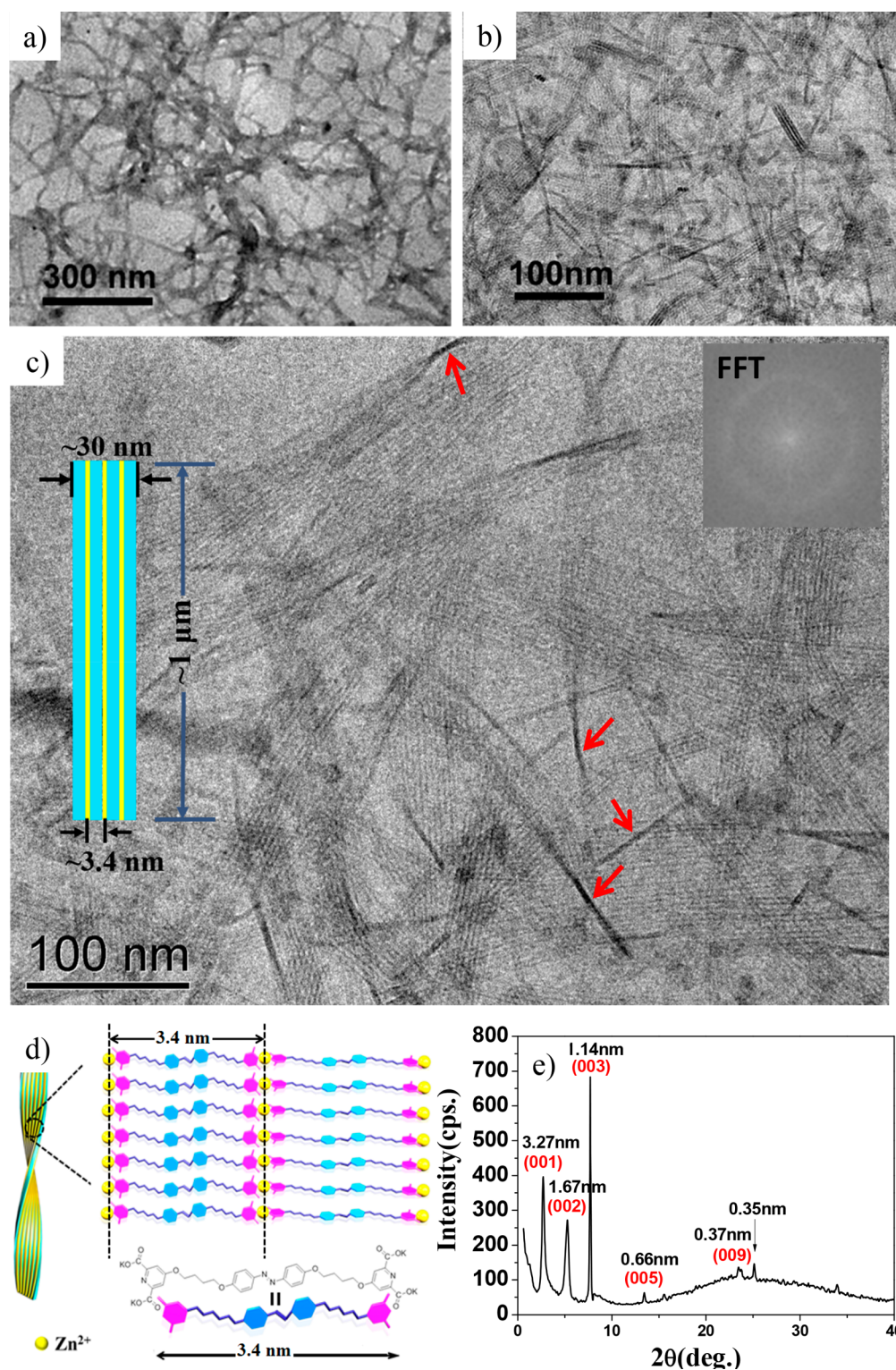


Figure 2. (a) TEM image of the aggregates formed in Azo-C4-L2/ Zn^{2+} = 1:1 system. (b,c) Cryo-TEM images of the aggregates formed in Azo-C4-L2/ Zn^{2+} = 1:1 system; [Azo-C4-L2] = 0.5 mM, the insets are the illustration of the ribbons (left) and the FFT analysis (right) of them, respectively. The red arrows indicate the edge-on sections displaying the thickness of the ribbons. (d) Schematic representation of the structures formed in the coordination system. (e) XRD result of Azo-C4-L2/ Zn^{2+} = 1:1.

TEM observation.³⁴ Therefore, the dark and light lines are the alternatively arranged *trans*-Azo-C4-L2 and Zn^{2+} , respectively, as illustrated in Figure 2c,d. These arrays signify the parallel self-assembly of the linear coordination supramolecule of $(\text{Zn}^{2+}@trans\text{-Azo-C4-L2})_n$, as demonstrated in Figure 2d. From the width of the ribbons or by counting the number

of the dark lines, we can estimate that $n = 7-9$ under the experimental conditions.

The parallel self-assembly of $(\text{Zn}^{2+}@trans\text{-Azo-C4-L2})_n$ was further verified with XRD measurements. Figure 2e shows a set of distances corresponding to the 001 (3.27 nm), 002 (1.67 nm), 003 (1.14 nm), 005 (0.66 nm), and 009 (0.37 nm)

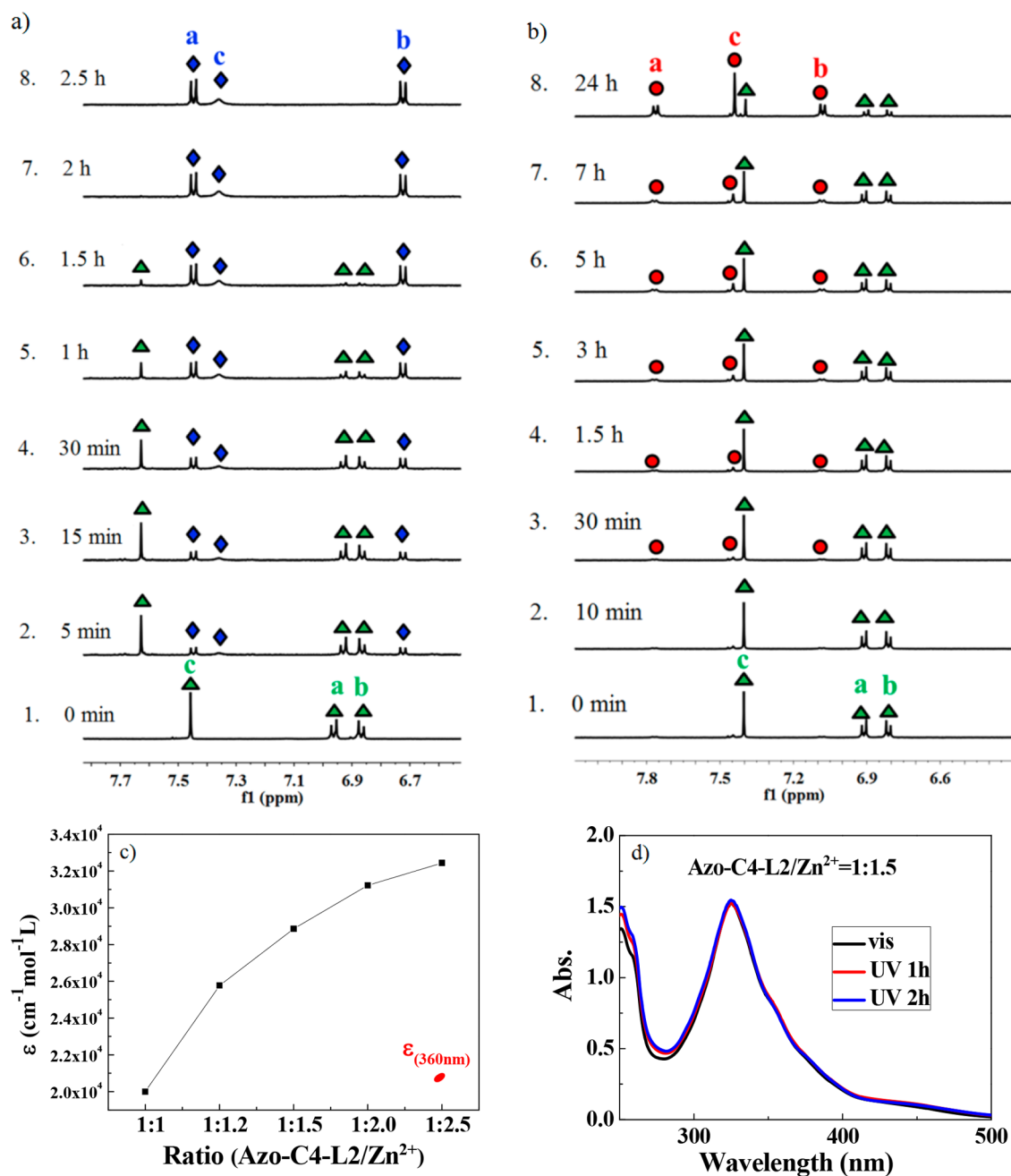


Figure 3. (a) ^1H NMR spectrum of Zn^{2+} added in the dark to the solution of *cis*-Azo-C4-L2. The molar ratio of Azo-C4-L2/ Zn^{2+} = 1:1.5. [Azo-C4-L2] = 0.5 mM, D_2O solution. (b) ^1H NMR spectrum of *cis*-Azo-C4-L2 solution in the dark over time. [Azo-C4-L2] = 0.5 mM, D_2O solution. (c) Molar extinction constant at 325 nm in different Azo-C4-L2/ Zn^{2+} systems. The red dot indicates the molar extinction of the *trans*-Azo-C4-L2 without Zn^{2+} . (d) UV-vis spectrum of Azo-C4-L2/ Zn^{2+} = 1:1.5 before and after UV irradiation.

diffractions, suggesting a perfect lamellar stacking of molecules.^{35,36} The 001 diffraction of 3.27 nm corresponds well with the extending length of the *trans* isomer of Azo-C4-L2, indicating that the lamellae is formed by the stretched *trans*-Azo-C4-L2. Specially, a distance of 3.5 Å featuring the π - π stacking³⁷ is also observed, confirming that π - π stacking of *trans*-Azo-C4-L2 have indeed happened.

We postulate that shift of the *cis*-*trans* equilibrium should be responsible for the coordination triggered *cis*-to-*trans* transition. Compared with the native *trans*-Azo-C4-L2 molecule, the $(\text{Zn}^{2+}@trans\text{-Azo-C4-L2})_n$ supramolecule is much larger. Therefore, cooperative π - π interaction within the supramolecule of $(\text{Zn}^{2+}@trans\text{-Azo-C4-L2})_n$ is able to

bring the potential energy of the system to a much lower state.³⁸ As a result, the population of the free *trans*-Azo-C4-L2 in equilibrium with the *cis* form drastically reduced, and the *cis* azos have to continuously transform into the *trans* form. This mechanism can be further confirmed by the Zn^{2+} -triggered *cis*-to-*trans* transition that occurred in a system composed of entirely *cis*-Azo-C4-L2 (Figure 3, line 1). The system of *cis*-Azo-C4-L2 was obtained by irradiating the Azo-C4-L2 suspension under 365 nm UV light. To avoid the generation of heat, a 6 W UV lamp was used. However, we should bear in mind that there should be trace amount of *trans* isomers below the detection limit of ^1H NMR in the "entire" *cis* system due to the presence of "equilibrium" between the *cis* and the *trans*

isomers. Figure 3a shows that the ^1H NMR signals that belong to $(\text{Zn}^{2+}@trans\text{-Azo-C4-L2})_n$ already occur within 5 min (Figure 3a, line 2, and Figure S5 for UV-vis spectra), while control experiments suggest that thermal relaxation of the *cis*-Azo-C4-L2 to *trans*-Azo-C4-L2 in a system without Zn^{2+} did not occur until 30 min (Figure 3b and Figure S3). It was noticed that the *cis*-Azo-C4-L2 also coordinated with Zn^{2+} , but the signal for the $\text{Zn}^{2+}@cis\text{-Azo-C4-L2}$ reduced with time (Figure 3a, line 2–6), while that for the $\text{Zn}^{2+}@trans\text{-Azo-C4-L2}$ kept increasing, suggesting the $\text{Zn}^{2+}@cis\text{-Azo-C4-L2}$ had gradually transformed into $\text{Zn}^{2+}@trans\text{-Azo-C4-L2}$. This experiment clearly manifests even if there are only trace amount of *trans*-Azo-C4-L2, the enhanced self-assembling ability triggered by the formation of $(\text{Zn}^{2+}@trans\text{-Azo-C4-L2})_n$ supramolecule may finally bring the system into a state prominently dominated by the *trans* isomers. In principle, as long as the amount of Zn^{2+} is enough, the fraction of the *cis* content can be reduced to negligible level. As a fact, we indeed observed that at the amount of Zn^{2+} beyond 1:1, the UV absorption peak signifying the *trans* isomers kept increasing (Figure 1d), indicating the amount of *trans*-Azo-C4-L2 was increasing. Meanwhile, the broad peak at 440 nm became flattened (Figure S6), suggesting the *cis* isomers had been transformed into the *trans* form.

The coordination triggered promotion of *cis*-to-*trans* conversion allows enhancement of the molar extinction coefficient. Before the addition of Zn^{2+} , the molar extinction constant at the peak absorbance for *trans*-Azo-C4-L2 is $21\,260\text{ cm}^{-1}\text{ mol}^{-1}\text{ L}$ (indicated by the red dot in Figure 3c), while it was enhanced to $32\,440\text{ cm}^{-1}\text{ mol}^{-1}$ after the formation of $(\text{Zn}^{2+}@trans\text{-Azo-C4-L2})_n$ supramolecule (Figure 3c). To exclude the impact of Zn^{2+} on the molar extinction coefficient, a control experiment was made for the coordinating system of Zn^{2+} and a ligand without the Azo group but with the same coordinating head, L_2EO_4 (Figure S7). This compound was reported in our previous work, which forms reversible coordination polymers with Zn^{2+} .^{34,39–41} The UV-vis spectrum for the $\text{Zn-L}_2\text{EO}_4$ system has no absorbance in the region above 300 nm (Figure S7). Therefore, we can conclude that the current 1.5-fold enhancement of the peak absorption is mainly caused by the enhanced purity of *trans* isomers. The blue shift of the peak is originated from the strong π - π stacking between the $(\text{Zn}^{2+}@trans\text{-Azo-C4-L2})_n$ supramolecules. Obviously, the formation of coordinating self-assembly allows the azo moiety absorbs light of shorter wavelength with 1.5-fold enhanced ability.

Furthermore, the self-assembly-triggered *cis*-to-*trans* conversion of Azo-C4-L2 allows a more stable PSS state than that composed of almost entire *trans*-Azo-C4-L2 isomers. The UV-vis spectra remained nearly stationary (Figure 3d) upon 2 h of UV irradiation, suggesting the possibility to generate a stably locked photostate of azo compound. However, the photostability can be tailored by EDTA, which is an excellent chelating agent for most metal ions. Upon the addition of EDTA to the supramolecular system of $\text{Zn}^{2+}@trans\text{-Azo-C4-L2}$, the system lost its photostability so that light-triggered reversible *cis* \leftrightarrow *trans* transition occurred immediately (Figure S8).

The self-assembly-triggered *cis*-to-*trans* transition can be a general rule in the azo systems. For instance, the *cis*-to-*trans* transition of Azo-C4-L2 can also be induced by electrostatic interactions. Because the *cis* isomer of azobenzene compounds has better solubility in water, it interacts much weaker with the

oppositely charged species.²⁰ When Azo-C4-L2 was mixed with an oppositely charged surfactant in water, such as DEAB (dodecyl triethylammonium bromide) or CTAB (cetyltrimethylammonium bromide), enhanced *cis*-to-*trans* conversion rate occurred as well. Figure S9 shows that the fraction of the *trans* isomers can be enhanced from 75 to 85% under visible light. The incomplete transition induced by surfactant is probably caused by the entrapment of the *cis* conformation due to the electrostatic interaction. Although the *cis* isomers interact with surfactants more weakly than the *trans* isomers do, there could be still some *cis* isomers interacting with oppositely charged surfactants, which entraps the conformation of the *cis* isomer. Furthermore, an ordinary ionic Azo compound azobenzene sodium acetate (AzoNa) also displays similar *cis*-to-*trans* transition behavior (Figure S10). The PSS state of AzoNa is composed of 75% *trans* and 25% *cis* isomer. Upon the addition of surfactant CTAB, the fraction of *trans* isomer is immediately enhanced to 84%.

The self-assembly-triggered *cis*-to-*trans* conversion strongly depends on the structure of the azo compounds and the way of triggered self-assembly. Actually, even for the Azo-C4-L2 molecule, only limited metal ions, such as Zn^{2+} and Mg^{2+} , are able to induce complete *cis*-to-*trans* conversion. Other metal ions, such as Ni^{2+} , Cu^{2+} , or Cd^{2+} (Figure S11–S13), can only induce partial conversion, so that the PSS state cannot be locked under UV light. We expect that upon rational molecular design, self-assembly can be a general strategy to enhance the *cis*-*trans* transition rate, which will greatly facilitate the efficiency of photoreaction based on azos.

In summary, we figured out that the *cis*-to-*trans* transition of azo compounds can be triggered by self-assembly of the *trans* isomers, which continuously removes the *trans* isomer from the equilibrium system composed of the mixture of the *trans* and *cis* azos, thus leading to the transition from *cis* to *trans* isomers. This is the first example that achieves *trans* azo compound of spectrum-grade purity, which establishes a new paradigm for manipulating the isomers of azobenzene compounds. We hope this work opens a new vista in the design of functional materials based on azo compounds and inspires further design of azo-based optical materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.7b03060.

Materials, methods, and experimental details; TEM image of the self-assembly of Azo-C4-L2 in water before and after UV irradiation; the ^1H NMR spectra of the Azo-C4-L2 before and after UV irradiation; UV-vis spectra of $\text{Zn/Azo-C4-L2} = 1:1$ under UV irradiation; UV-vis spectra of *cis*-Azo-C4-L2 in dark changes with time; UV-vis spectra of Azo-C4-L2/ Zn^{2+} at different molar ratios; UV-vis spectra of $\text{Zn-L}_2\text{EO}_4$; UV-vis spectra of Azo-C4-L2/ Zn^{2+} /EDTA; ^1H NMR and UV-vis spectra of Azo-C4-L2/DEAB at different molar ratios; ^1H NMR and UV-vis spectra of AzoNa/CTAB at different molar ratios; UV-vis spectra of Ni^{2+} , Cu^{2+} , and Cd^{2+} ions with Azo-C4-L2. (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: yunyan@pku.edu.cn.

ORCID

Yun Yan: 0000-0001-8759-3918

Notes

The authors declare no competing financial interest.

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