

Light-Triggered Reversible Supramolecular Transformations of Multi-Bisthiénylene Hexagons

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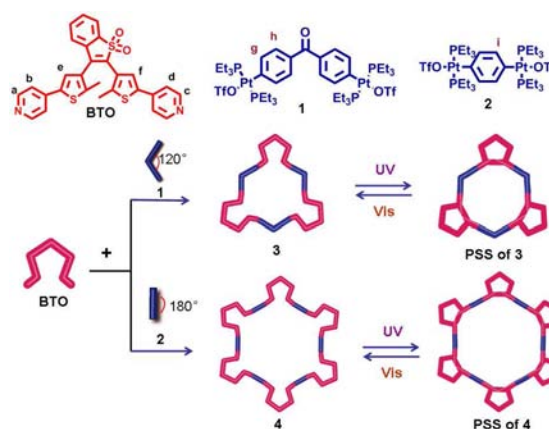
S Supporting Information

ABSTRACT: It is very challenging to realize well-controlled structural transformations in artificial supramolecules. Herein we report the construction of a novel family of multi-bisthiénylene hexagons with precise control of the shape and size as well as the specific number of photochromic units via coordination-driven self-assembly. These newly developed multi-bisthiénylene hexagons are highly sensitive and responsive to photo-stimuli, especially allowing for quantitative reversible supramolecular transformations triggered by light irradiation.

One of the growth areas at the forefront of modern chemistry is the preparation of discrete artificial architectures with desirable functionality via supramolecular self-assembly.¹ In nature, there are numerous examples of assembled biomolecules that are capable of achieving a variety of biological functions through conformational changes induced by external inputs such as coordinating metal ions, pH, redox potential, magnetic field, and light irradiation.² Therefore, the design and construction of supramolecular structures through supramolecule-to-supramolecule transformations triggered by external stimuli is of particular interest. However, well-controlled structural transformations of discrete self-assembled supramolecules have rarely been studied.³ In particular, quantitative reversible supramolecule-to-supramolecule conversions are still extremely challenging.

Bisthiénylene, which can undergo a reversible transformation between ring-open and ring-closed conformations that have markedly different optical and electronic properties, has been extensively explored in photochemistry and materials science.^{4,5} Recent efforts have been devoted to the construction of multiple bisthiénylene systems with potential applications nonlinear optical (NLO) materials, multifrequency optical memories, and data storage.⁶ Inspired by the successful examples of the nanoscale multifunctionalized supramolecular metallacycles,⁷ we envisioned that coordination-driven self-assembly could be used for the efficient preparation of a new family of multicomponent bisthiénylene macrocycles that may allow for reversible supramolecule-to-supramolecule conversions induced by light irradiation. Herein we present the first example of quantitative, reversible light-triggered transformations of supramolecular hexagons (Scheme 1), which

Scheme 1. Graphical Representation of Self-Assembled Multi-Bisthiénylene Hexagons and Their Structural Transformations



possess several merits: (i) precise control of shape and size as well as the specific number of photochromic units; (ii) the unprecedented achievement of quantitative ring closure for all photochromic units in the hexagons due to the coordination induction; and (iii) reversible interconversion between the ring-open and ring-closed conformations via alternate irradiation with the UV and visible light, respectively.

The photochromic dipyriddy compound 2,3-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)benzo[*b*]thiophene-1,1-dioxide (BTO), which exhibits a typical photoresponse in both solution and bulk crystals,⁸ was employed as a 120° bisthiénylene-based donor in this study. According to the “directional bonding” model and the “symmetry interaction” model,⁹ combining BTO with suitable 120° or 180° diplatino(II) acceptors generates a new family of photochromic hexagons (Scheme 1). Briefly, stirring mixtures of BTO with 120° acceptor 1 and 180° acceptor 2 in 1:1 molar ratios resulted in the formation of [3 + 3] hexagon 3 and [6 + 6] hexagon 4, respectively, containing different numbers of photochromic units [Scheme S1 in the Supporting Information (SI)].

Multinuclear NMR (¹H and ³¹P) analysis of the reaction products revealed the formation of multi-bisthiénylene

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hexagons. For example, in the ^1H NMR spectra of **3**, the pyridine protons exhibited downfield shifts (H_a and H_c , ca. 0.04 ppm; H_b and H_d , ca. 0.42 ppm) resulting from the loss of electron density upon coordination of the pyridine N atom with the Pt(II) metal center. Meanwhile, the singlet peaks at 7.76 and 7.43 ppm for free BTO, corresponding to protons H_f and H_e on the thiophene ring, shifted downfield to 8.04 and 7.78

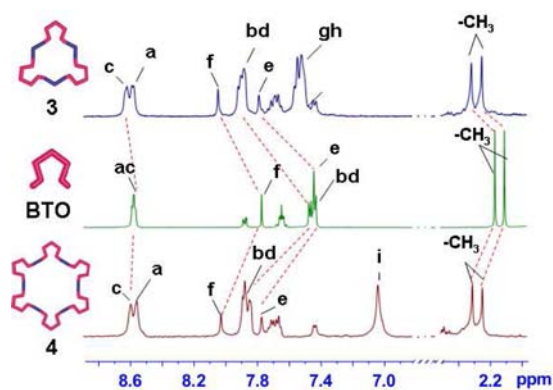


Figure 1. Partial ^1H NMR spectra (400 MHz, 298 K) of [3 + 3] hexagon **3**, 120° donor ligand BTO, and [6 + 6] hexagon **4** in CD_2Cl_2 .

ppm, respectively, upon Pt(II) coordination (Figure 1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3** and **4** showed two very close single peaks (ca. 13.14 and 13.08 ppm for **3**; ca. 12.94 and 12.90 ppm for **4**) that were shifted upfield by ca. 6.5 and 6.6 ppm, respectively, relative to those for the starting platinum acceptors **1** and **2** (Figure S1 in the SI). This change, as well as the decrease in the coupling of the flanking ^{195}Pt satellites ($\Delta J \approx -134.4$ Hz for **3** and -150.6 Hz for **4**), is consistent with electron back-donation from the Pt atoms. Electrospray ionization time of flight mass spectrometry (ESI-TOF-MS) analysis provided further support for the existence of multi-bisthiethylene hexagons **3** and **4**. The ESI-TOF-MS spectrum of **3** revealed two peaks at m/z 1241.17 and 963.14, corresponding to $[\mathbf{3} - 4\text{OTf}]^{4+}$ and $[\mathbf{3} - 5\text{OTf}]^{5+}$ species, respectively. In the ESI-TOF-MS spectrum of **4**, the peak at m/z 1950.80 is attributable to $[\mathbf{4} - 5\text{OTf}]^{5+}$. All of the peaks were isotopically resolved and in good agreement with the theoretical distributions (Figure S2).

The transformation behavior induced by light irradiation of these hexagons was investigated in CH_2Cl_2 at 298 K. The absorption spectrum of hexagon **3** exhibited an intense band at ca. 340 nm (Figure 2A). Upon irradiation at 365 nm, the colorless solution of hexagon **3** quickly turned to dark cyan. Notably, two new absorption bands at ca. 420 and 622 nm were observed in the visible region, along with two well-defined isosbestic points at 315 and 374 nm, arising from the corresponding ring-closed photostationary state (PSS) of **3** (Scheme 1) produced via the typical photocyclization^{4,10} (stereospecific electrocyclic mechanism; see the SI). Similarly, UV irradiation of hexagon **4** at 365 nm in CH_2Cl_2 resulted in the ring-closed PSS of **4** (Scheme 1), accompanied by a color change from colorless to cyan along with the formation of two intense absorption bands at 420 and 628 nm (Figure S3A). Furthermore, the fluorescence of the assembled hexagons **3** and **4** could be specifically modulated. As illustrated in Figure 2B, upon excitation at the isosbestic point of 315 nm, hexagon **3** displayed intense fluorescence at ca. 462 nm that was very

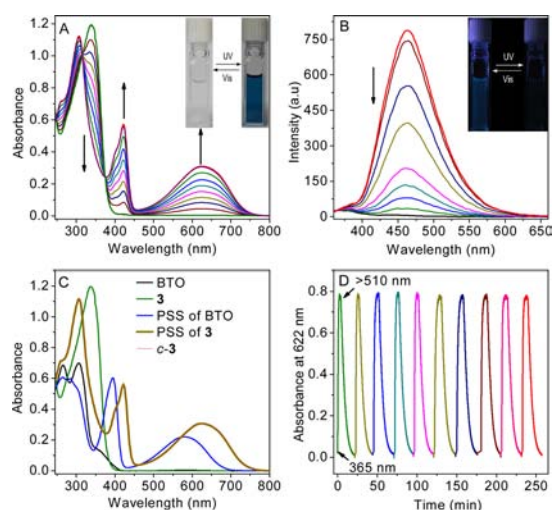


Figure 2. (A) Absorption spectral changes of hexagon **3** (6.7×10^{-6} M in CH_2Cl_2) upon UV irradiation at 365 nm. (B) Emission spectral changes of hexagon **3** (6.7×10^{-6} M in CH_2Cl_2 ; $\lambda_{\text{ex}} = 315$ nm) upon UV irradiation at 365 nm. (C) Absorption spectra of BTO (2.0×10^{-5} M), hexagon **3** (6.7×10^{-6} M), the corresponding photostationary states (PSSs) of BTO and hexagon **3** upon irradiation at 365 nm, and hexagon **c-3** (6.7×10^{-6} M). (D) Fatigue resistance of hexagon **3** (1.7×10^{-5} M in CH_2Cl_2) upon alternating UV (365 nm) and visible-light (>510 nm) irradiation. The inset photographic images in (A) and (B) show the absorption and fluorescence behavior of hexagon **3** (6.7×10^{-6} M in CH_2Cl_2) upon alternating UV and visible-light irradiation.

similar in energy and band shape to that of the corresponding free ligand BTO (467 nm; Figure S4B). In contrast, upon UV irradiation of **3**, the fluorescence was completely quenched (Figure 2B). Similar results for **4** are shown in Figure S3B.

The structural transformation processes of hexagons **3** and **4** were also monitored by ^1H and ^{31}P NMR spectroscopy. For example, in the ^1H NMR spectrum of **3** (Figure 3B), two sets of signals due to protons H_f and H_e on the thiophene rings were located at 8.04 and 7.78 ppm, respectively. Upon UV irradiation at 365 nm, these peaks gradually disappeared, and

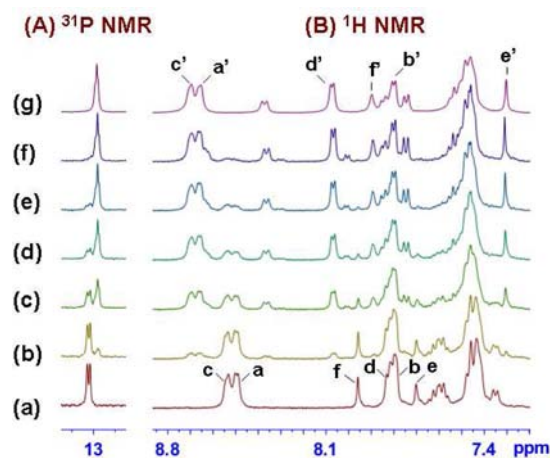


Figure 3. Partial (A) ^{31}P and (B) ^1H NMR spectra showing the structural transformation of hexagon **3** from the ring-open to the ring-closed form (CD_2Cl_2 , 298 K): (a) before irradiation; (b–f) after irradiation at 365 nm for (b) 5, (c) 30, (d) 90, (e) 180, and (f) 240 min; (g) hexagon **c-3**. A long irradiation time was necessary to reach the PSS because of the high concentration of the sample (ca. 2.2×10^{-3} M) during NMR monitoring of the spectral changes.

two new peaks appeared at 7.97 and 7.38 ppm, which can be attributed to the resulting ring-closed PSS of **3**. The characteristic upfield shift is due to the loss of aromaticity of the thiophene heterocycles as a result of the photocyclization reaction. Interestingly, in contrast to the two single peaks in the ^{31}P NMR spectrum of hexagon **3**, only one peak with a small upfield shift of 0.19 ppm was found in the ^{31}P NMR spectrum of the corresponding ring-closed species (Figure 3A). Here the difference between the two pyridine binding sites in **BTO** becomes very small upon the formation of the ring-closed species, resulting in almost identical chemical environments for the phosphorus atoms in the PET_3 groups in the PSS of **3**. Similar characteristics in the ^1H and ^{31}P NMR spectra resulted from the structural transformation process were also found for hexagon **4** (Figure S5). On the basis of the gradually changed ^1H and ^{31}P NMR spectra along with the absorption spectra, a stepwise conversion may take place during the structural transformation. However, the actual photoconversion pathway of these processes is still not well understood.

To provide further support for the existence of the transformation processes, the ring-closed 120° donor *c*-**BTO** was prepared and used to synthesize the ring-closed $[3 + 3]$ hexagon *c*-**3** and $[6 + 6]$ hexagon *c*-**4** via platinum coordination-driven self-assembly (Scheme S2). Multinuclear NMR (^1H and ^{31}P) analysis of these hexagons revealed the same characteristics as those observed in the spectra of the PSSs of **3** and **4** upon UV irradiation (Figures S6–S8), confirming that the ring-closed PSSs are the same as hexagons *c*-**3** and *c*-**4** obtained using the alternative procedure. Moreover, the absorption bands of hexagons *c*-**3** and *c*-**4** were exactly identical to those of the PSSs of hexagons **3** and **4** obtained by UV irradiation (Figure 2C and Figure S3C). Meanwhile, no fluorescence signal was recorded from the pure ring-closed hexagons *c*-**3** and *c*-**4**, consistent with the observations during the light-driven structural transformation processes of hexagons **3** and **4**. Interestingly, upon self-assembly, ring-closed hexagons *c*-**3** and *c*-**4** exhibited large red shifts of 47 and 53 nm, respectively, in the visible absorption band (Figure 2C and Figure S3C) relative to the free *c*-**BTO** ligand (575 nm), which is indicative of an increase in the extension of the π conjugation upon coordination of Pt with the pyridine unit of *c*-**BTO**.¹⁰

Notably, the above-mentioned photocyclization processes for these multi-bisthienylethene hexagons are totally reversible. Upon visible-light irradiation (>510 nm), the cyan solutions of hexagons **3** and **4** turned colorless, regenerating the original ring-open conformations. In particular, hexagons **3** and **4** could be repeatedly transformed between the ring-open and ring-closed forms by alternate UV (365 nm) and visible-light (>510 nm) irradiation in degassed CH_2Cl_2 while remaining intact without any apparent degradation (Figure 2D and Figure S3D, respectively). After 10 cycles, no obvious degradation was observed in solution. These results demonstrate that quantitative reversible supramolecule-to-supramolecule transformations can be realized in these multi-bisthienylethene hexagons.

In the majority of photochromic cases reported to date, very few multi-bisthienylethene systems can be fully converted into the ring-closed form upon UV irradiation.¹¹ However, for the $[3 + 3]$ hexagon **3** and $[6 + 6]$ hexagon **4**, which contain three and six photochromic bisthienylethene units, respectively, the conversions from the ring-open forms to the ring-closed forms were achieved almost quantitatively (yields as high as 99%).

Obviously, these conversion yields are much better than that of free **BTO** (88%; Figure S4D). This unusual result may be caused by the preferable conformational transition during the thermodynamically controlled coordination-driven self-assembly process.¹² Generally, in photochromic bisthienylethene systems, only the antiparallel configuration is photoactive.^{4a} In fact, free **BTO** possesses parallel and antiparallel configurations with equal ratios in solution. Simulated molecular models obtained by the PM6 semiempirical molecular orbital method (Figures S9–S11) revealed that the angle between the two pyridyl rings is closer to 120° when **BTO** adopts the antiparallel configuration, which is more preferable for the formation of the molecular hexagons according to the directional bonding model and the symmetry interaction model.⁹ Moreover, the simulation disclosed that multi-bisthienylethene hexagons **3** and **4** with antiparallel configurations are somewhat more stable than their analogues with parallel conformations (e.g., in the case of **3**, $E_{\text{parallel}} - E_{\text{antiparallel}} = 7.67$ kcal/mol). Accordingly, during the self-assembly of hexagons **3** and **4**, **BTO** is more likely to have the antiparallel configuration rather than the parallel one because of the steric interactions, leading to a high conversion yield from the ring-open form to the ring-closed form for the established multi-bisthienylethene hexagons.

In summary, we have presented a convenient and effective approach for the construction of photochromic multi-bisthienylethene-based metallacycles with predetermined sizes and shapes via platinum coordination-driven self-assembly. More importantly, taking advantage of the photoinduced switchable property and good fatigue resistance of the photochromic bisthienylethene system, quantitative reversible supramolecule-to-supramolecule conversions have been successfully realized. To the best of our knowledge, these are the first examples of well-controlled reversible structural transformations of discrete self-assembled metallacycles triggered by light irradiation. This finding may provide a novel approach for the realization of the highly efficient supramolecule-to-supramolecule conversions. Efforts to extend this strategy to other polygons and polyhedra to build novel supramolecular structures are underway.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details and more data on the photochromic properties of the hexagons and free **BTO**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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