Supramolecular Chemistry

Synthesis and Photophysical Behavior of a Supramolecular Nanowire made from Dithienylethene-Bridged Bis(permethyl-β-cyclodextrin)s and Porphyrins

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Abstract: A photochromic dithienylethene-bridged bis(permethyl-β-cyclodextrin)s was successfully synthesized through an amide condensation reaction, and its photochromic properties were also investigated by ^{1}H NMR spectra and UV/vis spectroscopy. Moreover, taking advantage of the strong interaction between permethyl-β-cyclodextrin and water soluble porphyrins, a supramolecular nanowire was then successfully constructed and characterized by UV/vis spectroscopy, atomic force microscopy (AFM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Significantly, the fluorescence resonance energy transfer (FRET) process from the porphyrin to the dithienylethene core can be modulated by alternate irradiation with ultraviolet and visible light and, thus, light-controlled quenching and recovery of fluorescence of porphyrins was realized.

Introduction

The design and construction of organic nanomaterials with particular photophysical and photochemical properties, such as photochromic molecules that are used as photo memory media and molecular switches, are still the most challenge tasks in material chemistry.[1] Among the various types of photochromic components, it is realized that dithienylethene is one of the most attractive family because of its excellent properties, including fatigue resistance, thermally stability, high photocyclization/cycloreversion quantum yields, and rapid response time.[2] Through a controlled cyclization and cycloreversion reaction by alternate ultraviolet (UV) and visible (Vis) light irradiation, the input, rewrite and non-destructive read out of data information could be readily achieved by means of the spectral analysis of ring-open and ring-closed isomers of dithienylethene derivatives.[3] Consequently, dithienylethene was fully investigated and applied in the study of ion and molecular recognition,[4] logic gates,[5] liquid crystals,[6] gel and chiral amplification,[7] supramolecular polymers,[8] conductive materials,[9] and light storage.[10] For instance, Feringa and co-workers synthesized a series of dithienylethene molecules with different functional groups and investigated their photochromic and infrared properties under the UV/vis light irradiation, revealing that the synthesized dithienylethene compounds possess satisfactory thermal irreversible and fatigue resistant properties.[11] Branda et al. connected dithienylethene molecule with porphyrin and studied its photo-responsive fluorescence resonance energy transfer (FRET) process from porphyrin moiety as donor to dithienylethene moiety as acceptor.[12] Moreover, our group constructed a [2] pseudorotaxane through host-guest interactions between diarylethene and Eu^{3+}/terpyridinyldibenzo-24-crown-8 complex, and revealed excellent reversible lanthanide luminescence switching behavior.[13]

In the present work, we synthesized a novel photochromic dithienylethene-bridged bis(permethyl-β-CD)s **1** through the amide condensation reaction between 1,2-dithienylethene carboxylic acid **3** and mono-6-deoxyl-6-amino-permethyl-β-CD **4**, and then the photochromic properties of **1** was investigated by ^{1}H NMR spectra and UV/vis spectroscopy. Then, benefiting from the extremely strong association between permethyl-β-CD and water-soluble porphyrins **5** and **6**, a supramolecular nanowire was successfully constructed and adequately characterized by UV/vis spectroscopy and microscopic observations. Using dithienylethene linker as a photoswitching unit, the FRET process from the porphyrin to the dithienylethene core in the resultant nanowires could be conveniently controlled, leading to the photo-controlled quench and recovery cycles of porphyrin fluorescence.

Results and Discussion

Synthesis

Compound **3** was obtained by hydrolysis from compound **2**, according to the reported method with slight modification.[14]

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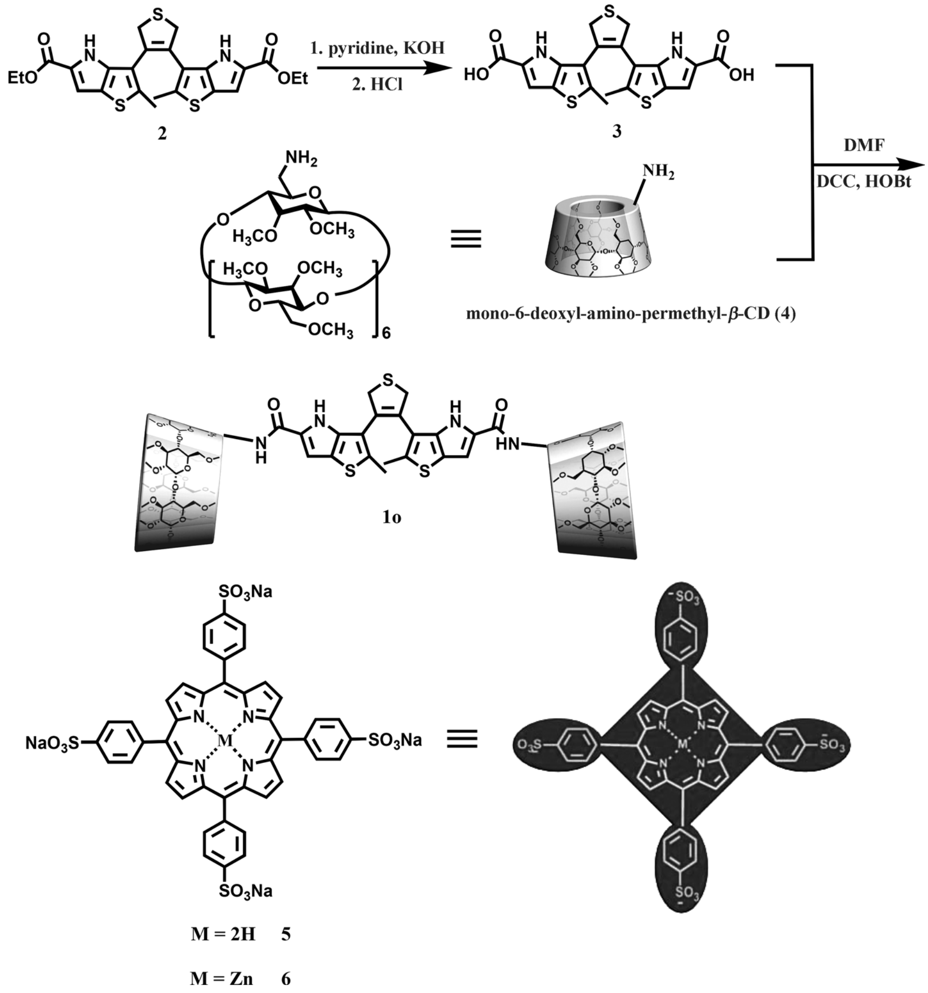


Scheme 1. Synthetic routes to compound **1 o** and the chemical structures of compounds **5** and **6**.

Then, the photochromic dithienylethene-bridged bis(permethyl-β-CD)s of ring-open isomer **1 o** was synthesized from 1,2-dithienylethene carboxylic acid **3** and mono-6-deoxyl-6-amino-permethyl-β-CD **4** through an amide condensation reaction in 26% yield (Scheme 1), which was completely characterized by ^{1}H and ^{13}C NMR spectroscopy, MALDI-MS, and elemental analysis (Figure S1–S5 in the Supporting Information). Benefiting from the permethyl-β-CD unit, the solubility of compound **1 o** in aqueous solution was good. Due to the strong binding complexation of permethyl-β-CD with 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin **5** and [5,10,15,20-tetrakis (4-sulfonatophenyl)porphinato] zinc(II) **6** in 2:1 complex stoichiometry,[15] it was expected that the simple mixture of compound **1 o** with **5** or **6** could construct a linear supramolecular nanowire in aqueous solution.

UV/vis spectroscopy

As shown in Figure 1, the UV/vis spectrum of **1 o** showed a strong absorption peak at 302 nm, which was attributed to the open form of the dithienylethene group.[4d] No overlapped absorption band with emission bands of porphyrin **5** and **6** was observed around 550–650 nm. When irradiation with 254 nm UV light, the absorption peak at 302 nm decreased and a new broad absorption band appeared around 400–600 nm, corresponding to the ring-closing reaction from **1 o** to **1 c** with an enlarged π-conjugation system in dithienylethene group (Scheme 2).[4d] No spectral change was observed in the UV/vis spectrum when the compound **1 o** reached its photostationary state after 14 min irradiation. Then under irradiation by visible light ($\lambda > 500$ nm), the photostationary state mixture proceeded with the ring-opening reaction from **1 c** to **1 o** completely in 4 min and the UV/vis spectrum almost recovered (Figure S6 in the Supporting Information). A weak absorption band around 420 nm indicates that only few **1 o** molecules were decomposed during the conversion process. Moreover, the photochromic process could also been distinguished by the naked eye; that is, the colorless aqueous solution of **1 o** turned pink upon irradiation with 254 nm UV light and then returned to colorless under visible light irradiation (Figure S7 in the Supporting Information). Meanwhile, this ring-closing and ring-opening cycle could be repeated several times without obvious light-fatigue phenomenon (Figure S8 in the Supporting Information), indi-

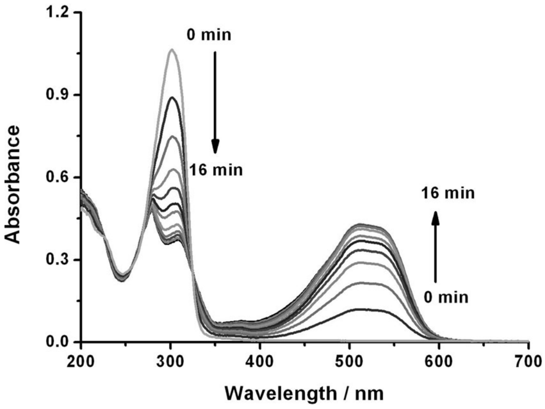
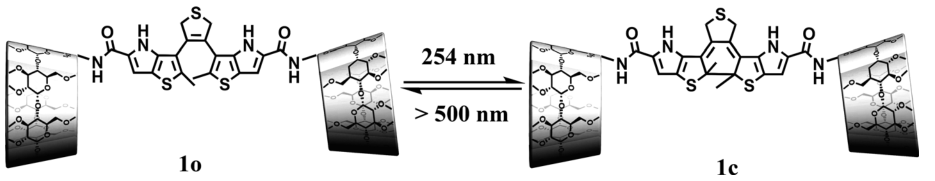


Figure 1. Changes in the UV/vis absorption spectra of an aqueous solution of **1 o** (2.0×10^{-5} M) upon irradiation with 254 nm light, which reached a photostationary state after irradiation for 14 min.



Scheme 2. Interconversion between **1 o** and **1 c** under UV/vis light irradiation.

cating that the introduction of the two large permethyl-β-CD groups could not disturb the photochromic properties and switching process of the dithienylethene unit.

The binding behaviors of an inclusion complex formed by **1 o** and **5** (or **6**) were investigated by means of UV/vis spectroscopy titration in phosphate buffer solution (PBS, 10 mM, pH 7.2). As shown in Figure 2, the Soret band of **5** showed an obvious red shift from 413.0 nm to 415.4 nm upon addition of **1 o**, (for **6**, from 421.0 nm to 424.1 nm in Figure S9 the in Supporting Information), accompanied by an isosbestic point at 414.5 nm (for **6**, 421.9 nm). These phenomena indicate that the porphyrin backbone in **5** and **6** was included in the cavities of permethyl-β-CD of **1 o**. The curve of ΔA_{1o-5} ($\Delta A_{1o-5} = A_{1o+5}$ - A_5, A_5 was defined as the absorption intensity of **5** at 413.0 nm and 415.4 nm, respectively) versus the molar ratio of **1 o**/**5** showed an inflection point at a molar ratio of one in Figure 3 (Figure S10 for **1 o**/**6** in the Supporting Information). Meanwhile, the binding stoichiometry was also confirmed by Job's plot, in which a maximum peak at a molar ratio of 0.5 (Figure S11–S12 in the Supporting Information) was clearly observed. After validating the 1:1 binding stoichiometry, the complex stability constants (K_S) of **1 o** with **5** and **6** were calculated as $3.80\times10^{8}\,\text{M}^{-1}$ and $7.15\times10^{7}\,\text{M}^{-1}$, respectively, according to the results of UV/vis spectroscopy titration by analyzing the sequential changes of the absorption intensity at varying the concentrations of **1 o** through a nonlinear least-squares fitting method using the following equation (Equation S1 in the Supporting Information):[16]

$$\Delta A = 0.5 \times \{\Delta\varepsilon\ ([\text{H}] + [\text{G}_0] + 1/K_S) \pm [\Delta\varepsilon^2\ ([\text{H}] + [\text{G}]_0 + 1/K_S)^2 - 4\Delta\varepsilon\ [\text{H}] \times [\text{G}]_0]^{0.5}\}$$

where ΔA is the change of absorbance of the guest, $\Delta\varepsilon$ is the change of molar absorption coefficient, [H] is the different concentrations of the host, $[\text{G}]_0$ is the constant concentration of the guest.

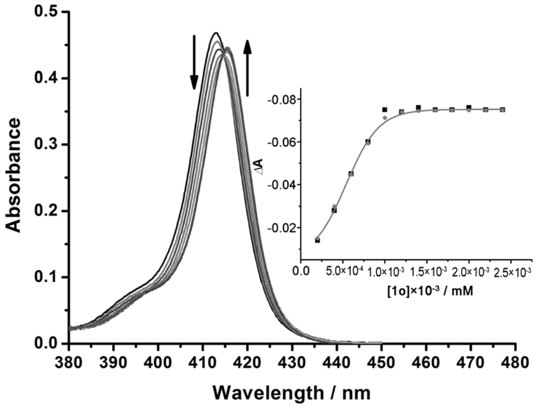


Figure 2. UV/vis titration spectra of **5** (1.0×10^{-6} M) upon addition of **1 o** (0–2.4×10^{-6} M) in PBS (pH 7.2). Insert: Nonlinear least-squares analysis of the differential absorbance (ΔA, $\lambda = 413.0$ nm) to calculate the complex binding constant (K_S). Note that **1 o** solutions at the same concentration (0–2.4×10^{-6} M) were used as references to avoid the absorption of **1 o** in the same wavelength region.

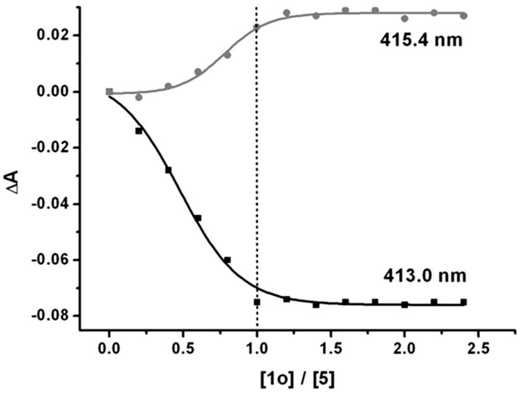


Figure 3. Absorption change (ΔA) versus **1 o**/**5** molar ratio recorded at 413.0 nm and 415.4 nm, respectively.

^{1}H NMR spectroscopy

^{1}H NMR spectroscopy was performed to investigate the photochromic properties of **1 o**. As shown in Figure 4a, **1 o** gave two single peaks at $\delta = 6.92$ ppm and 1.77 ppm, which were assigned to proton signals of aromatic and methyl groups of the dithienylethene core in **1 o**, respectively. After irradiation with 254 nm UV light for 14 min to reach photostationary equilibrium, two new peaks appeared at $\delta = 6.88$ ppm and 1.94 ppm, corresponding to the formation of ring-closed form **1 c** (Fig-

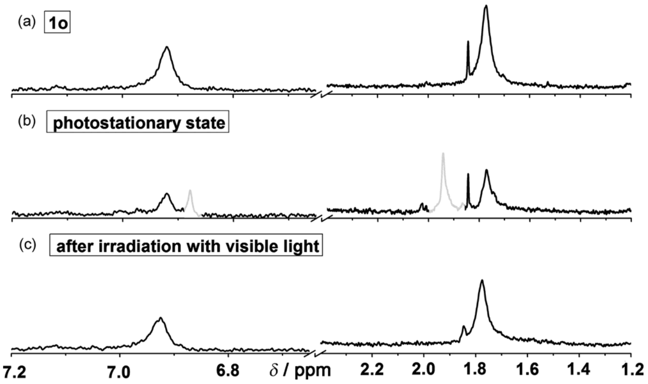


Figure 4. Partial ^{1}H NMR spectra of **1 o** assigned to (a) before and (b) after irradiation with 254 nm UV light until photostationary state, and (c) the sample in (b) after irradiation with visible light.

ure 4b). It is known that the ring-open form of 1,2-dithienylethene possesses two conformations that can interconvert: parallel and antiparallel.[4a] The antiparallel form can proceed with the ring-closing reaction under irradiation of UV light but the parallel form cannot, and the content ratio of these two conformations is 50% in solution. After appending two permethyl-β-CD molecules, it is found that the interconversion of these two conformations was seriously blocked because of the steric hindrance of the CDs, only giving the maximum value of 50% conversion ratio of **1 o**. When the ring-open form **1 o** converted to ring-closed form **1 c**, the 1,2-dithienylethene part underwent a cyclization reaction to form a rigid π-conjugation system, and consequently, the emerging signals of protons at the aromatic nucleus and methyl groups in **1 c** exhibited upfield and downfield shifts, respectively. According to the integrals in the NMR spectrum, the light conversion ratio was calculated as 40% from **1 o** to **1 c**. After irradiation with visible light for 4 min, the peak pattern of **1 c** completely recovered to the one of **1 o**, indicating the regeneration of the ring-open form from the photostationary state (Figure 4c).

Fluorescence spectroscopy

As shown in Figure 5 and Figure S13 in the Supporting Information, fluorescence spectroscopy was carried out to investigate the FRET process between **1 o**/**1 c** and **5**/**6**. Since the UV spectrum of **1 o** showed no absorption band beyond 550 nm, no FRET process occurred between **1 o** and **5**. Comparatively, there was a new absorption band that gradually appeared around 400–600 nm originating from the cyclization reaction from **1 o** to **1 c** under irradiation at 254 nm, which can partly overlap with the emission band of **5** in the range of 550–650 nm. As a result, when the porphyrin **5** was excited at 422 nm, the excited **5** would transfer its energy to **1 c** bearing a ring-closed dithienylethene core, ultimately resulting in the fluorescence quenching of the porphyrin. As discerned from Figure 5, the fluorescence intensity of **5** gradually decreased upon exposure to UV light, and it approached equilibrium in 14 min, which is consistent with the time of which **1 o** reached a photostationary state under UV light irradiation. Moreover, the efficiency of energy transfer E can be calculated by the following equation:[17]

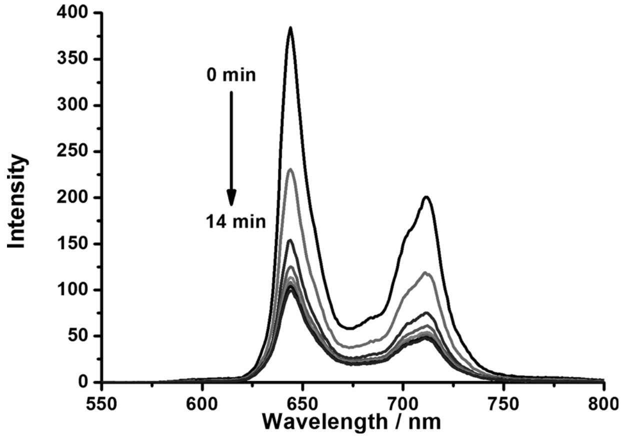


Figure 5. Fluorescence spectral change of **1 o**/**5** complex ([**1 o**] = [**5**] = 2.0×10^{-6} м, corresponding to 97% complexation) in PBS (pH 7.2) upon irradiation with 254 nm UV light for 14 min.

$$E = 1 - F_{PS}/F_0$$

where F_{PS} is the fluorescence intensity of the chromophore at photostationary equilibrium and F_0 is its original fluorescence intensity without light irradiation. In the case of the **1 o**/**5** complex, F_{PS} and F_0 were measured as 99.4 and 384.1 at 644 nm, respectively, and, therefore, E was calculated as 74.1% (E value for $\mathbf{1}_{PS}$/**6** complex was 73.7%). The relatively moderate energy transfer efficiency in our system may contribute to the incomplete light conversion from **1 o** to **1 c** and the partial spectral overlap between **1 c** and **5**/**6** (Figure S14 in the Supporting Information). In addition, as discerned from Equation S2 and Figure S15 in the Supporting Information, the Förster resonance energy transfer equation was employed to calculate the theoretical value of the energy transfer distance between **1 c** and **5** as 1.80 nm, which is consistent with the molecular simulation result (2.15 nm).

Next, the fluorescence intensity of porphyrin **5** was monitored under alternating irradiation with UV and visible light. After irradiation with 254 nm UV light, the fluorescence of **5** was quenched because of the FRET process from **5** to **1 c**, and comparatively, when the dithienylethene ring of **1 c** opened again to form **1 o** under irradiation with visible light, the FRET effect could be suppressed, then resulting in the fluorescence recovery of **5**. However, owing to the strong interaction between permethyl-β-CD and porphyrin derivatives, the tightly compact supramolecular **1**/**5** complex can greatly impede the dithienylethene core from the efficient ring-open reaction, and only a few ring-closed molecules could go back to the ring-open state. Under such circumstances, the ring-closing reaction of **1 o** to **1 c** was also deficient. Finally, as shown in Figure S16 in the Supporting Information, it can be seen that, after several cycles of light irradiation, the amplitudes of changes in fluorescence of **5** gradually decayed.

UV/vis spectroscopy was further carried out to confirm the inefficient transition from **1 c**/**5** to **1 o**/**5** under visible light irradiation. As shown in Figure S17 in the Supporting Information, after irradiation with 254 nm UV light, the absorbance at 302 nm decreased and the one around 400-600 nm inversely increased, indicating the formation of the **1 c**/**5** complex. Comparatively, after irradiation with visible light, the absorbance at 302 nm slightly changed, suggesting that only few **1 c** molecules in **1 c**/**5** were converted to the **1 o**/**5** complex, and the conversion ratio was calculated as 2.2%. The inefficient transition from **1 c**/**5** to **1 o**/**5** form may be responsible for the poor reversibility in the fluorescence emission of **1 o**/**5** under the alternating irradiation with UV and visible light (Figure S16 in the Supporting Information). Moreover, quantum chemical calculations have revealed that the conversion from **1 c** to **1 o** is driven in a thermodynamically favorable way, whereas this ring-opening reaction was severely inhibited after complexation with two porphyrins of **5**. These results can be attributed to the molecular restriction in the bulky **1c**/**5** complex, by which the photochromism of thienylethene moiety was blunted in light responsiveness (Figure S18 and S19 in the Supporting Information).

AFM, TEM, SEM, and DLS characterization

Benefiting from the highly affinitive complex between PMCD and porphyrin, the linear **1o**/**5** assembly was conveniently obtained and visual information on size and shape was provided by microscopic observation. As shown in Figure 6a, the AFM image showed that a fine linear nano-supramolecular assembly was formed in a single-lined way by mixing compound **1o** and **5**, and its length was longer than 400 nm. In addition, the measured average height of **1o**/**5** linear assembly was 1.2 nm, which is equal to the height of a single β-CD unit, further proving that the linear assembly was a single-lined assembly without any undesirable aggregation. In parallel, the TEM image (Figure 6b) displayed several linear structures whose lengths were more than 200 nm, and the observed lines had a tendency to aggregate from the single-lined array shown in AFM image. This phenomenon was further confirmed by SEM images, in which a number of square columns composed of parallel fiber-like nanowires were observed and their lengths ranged from hundreds of nanometers to several micrometers (Figure 6c). The assemblies in SEM image were the three-dimensional extension of single lines in AFM image. Furthermore, along with these microscopic results, a dynamic light scattering (DLS) experiment was performed to confirm the formation of **1o**/**5** assembly in aqueous solution. As shown in Figure 6d, the DLS signals showed large-sized particles after equimolar mixing of **1o** and **5**, and the obtained average hydrodynamic radius of them was around 200 nm. Therefore, we can reasonably infer that the complexation of **1o** and **5** leads to *n*:*n* supramolecular nanowires as illustrated in Figure 6e.

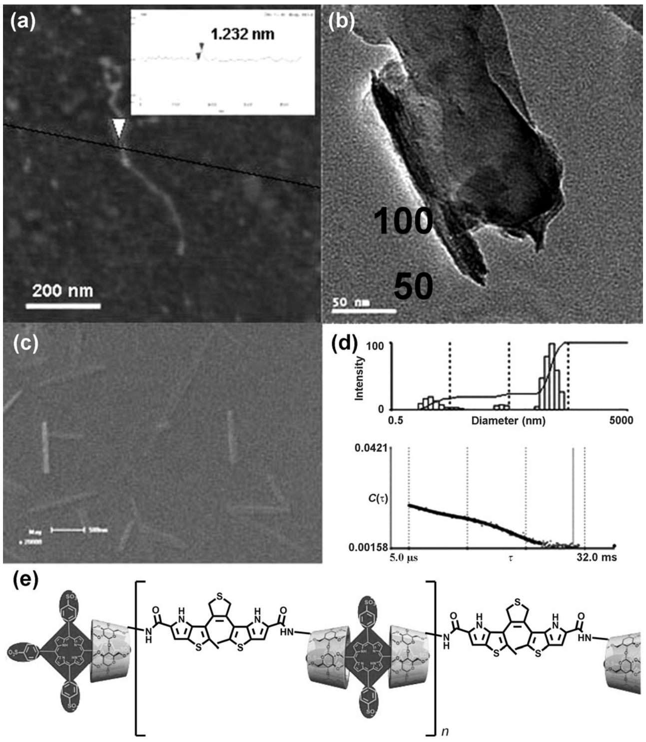


Figure 6. Typical (a) AFM, (b) TEM, and (c) SEM images, and the (d) DLS result, and (e) schematic of the **1o**/**5** assembly.

Conclusions

In conclusion, a photochromic dithienylethene-bridged bis(permethyl-β-CD)s **1o** was synthesized through an amide condensation reaction and was fully characterized in this work,. The introduction of permethyl-β-CD can effectively increase the aqueous solubility of **1o**. Under alternating irradiation with UV and visible light, **1o** exhibited fine photochromic properties without obvious optical fatigue and loss. After irradiation with UV light, the ring-open form of **1o** could convert into the ring-closed form of **1c**, and the fluorescence of **5**/**6** was dramatically quenched as a result of the FRET process between **1c** and porphyrin. Moreover, taking advantage of strong affinity between permethyl-β-CD and water-soluble porphyrin (**5** and **6**), we have successfully constructed a photochromic supramolecular nanowire. It is believed that this supramolecular nano-architecture can offer a new perspective for designing desirable photomemory devices and non-destructive readout systems. The optimization and improvement of this supramolecular assembly are currently in process.

Experimental Section

Materials

All chemicals were obtained from commercial sources and used as reagent grade. β-CD was recrystallized from water twice and dried in vacuo at 90 °C for 24 h before use. Phosphate buffer solution (pH 7.2) was used as solvent in all spectral measurements and is not specially mentioned in the data. Photochromic 1,2-dithienylethene (**2**),[14] mono-6-deoxyl-6-amino-permethyl-β-CD (**4**)[18] and compound **6**[19] were prepared according to the modified reported methods. Crude *N,N'*-dimethylformamide (DMF) was stirred in CaH_2 for three days and then distilled under reduced pressure prior to use. Column chromatography was performed on 200–300 mesh silica gels.

Instruments

NMR spectra were recorded on a Bruker AV400 instrument. UV/vis spectra were recorded in a conventional quartz cell (light path 10 mm) on a Shimadzu UV-2401PC spectrophotometer equipped with a Thermo HAAKE-SC100 temperature controller to keep the temperature at 25 °C. Fluorescence spectra were recorded in a conventional quartz cell (10×10×45 mm) at 25 °C on a VARIAN CARY Eclipse spectrometer with the excitation and emission slits of 5 nm widths. In AFM measurements, a drop of sample solution (1.0×10^{-6} M) was dropped onto newly clipped mica and then air-dried, which was then examined using an AFM (Veeco Company, Multimode, Nano IIIa) in tapping mode in the air under ambient conditions. TEM experiments were performed using a JEOL JEM-2100F microscope operating at 200 kV. TEM samples (1.0×10^{-6} M) were prepared by placing a drop of solution onto a carbon-coated copper grid. SEM images were recorded on a HITACHI S-3500N scanning electron microscope. Geometry optimization for **1 o**, **1 c**, **1 o**/**5** and **1 c**/**5** were performed using the semi-empirical method AM1.[20] Single-point energies were calculated using the B3LYP functional[21] and the double-zeta basis set 6–31G(d) on AM1-optimized geometries. Since dispersion interactions were expected to be essential in the relative energies of these systems involving hydrogen bonding and π–π interactions, Grimme's DFT-D3(BJ)[22] dispersion corrections were calculated using the DFTD3 program.[23] All calculations were carried out with Gaussian 09.[24] The figures of three-dimensional molecular structures were prepared using CYLView.[25]

Synthesis of Dithienylethene-Bridged Bis(permethyl-β-CD)s in Ring-Open Conformation (1 o)

Photochromic 1,2-dithienylethene (**2**, 200 mg, 0.4 mmol) was dissolved in 60 mL pyridine, and then 25 mL 10% potassium hydroxide was added. The mixture was refluxed in the dark under an atmosphere of N_2 for 24 h. After cooling to room temperature, the mixture was evaporated under reduced pressure to remove the solvent. The residue was re-dissolved in 100 mL water and the pH of the solution was adjusted to <1 by adding 1 M HCl. The precipitate was filtered and washed with water three times. Photochromic 1,2-dithienylethene carboxylic acid **3** was obtained as pale white solid quantitatively without further purification. ESI-MS: *m/z*: 443.06 [*M*-H]$^-$. Then compound **3** (100 mg, 0.225 mmol) and 1-hydroxybenzotrizole (HOBt, 73.0 mg, 0.54 mmol) were dissolved in 20 mL of anhydrous DMF and stirred in an ice-bath for 0.5 h. A solution of mono-6-deoxyl-6-amino-permethyl-β-CD (**4**, 3.19 g, 2.25 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (DCC, 111.2 mg, 0.54 mmol) in 50 mL anhydrous DMF was then dropwise added. The reaction mixture was stirred in the dark at 0 °C under an atmosphere of N_2 overnight and then stirred at room temperature for another 48 h. The mixture was filtered and the filtrate was evaporated under reduced pressure to remove the solvent. The residue was dissolved in 100 mL chloroform and washed with water (3×100 mL), then the organic phase was dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (silica gel) using chloroform/methanol (20:1, v:v) as eluent to obtain **1 o** as white solid in 26% yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 1.79$ (s, 6H, H of CH_3 of dithienylethene), 3.15–3.97 (m, 204H, H of -OCH_3, C-3, C-5, C-6, C-2, C-4 of permethyl-β-CD), 4.20 (s, 4H, H of dithienylethene), 5.07–5.25 (m, 14H, H of C-1 of permethyl-β-CD), 6.72 (s, 2H, H of dithienylethene), 6.77 (t, $J = 6.1$ Hz, 2H, H of –C=O-NH-), 9.26 ppm (s, 2H, H of dithienylethene); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 15.7$, 40.1, 41.3, 58.3, 58.4, 58.5, 58.6, 58.8, 59.0,59.1, 59.3, 61.3, 61.4, 61.5, 61.6, 70.3, 71.0, 71.2, 71.5, 71.7, 79.9, 80.2, 80.5, 80.6, 81.2, 81.5, 81.6, 81.8, 81.9, 82.1, 82.2, 82.4, 98.9, 99.0, 99.1, 99.7, 102.0, 117.9, 121.2, 129.3, 132.7, 138.8, 139.2, 161.6 ppm; elemental analysis calcd (%) for $C_{144}H_{234}N_4O_{70}S_3\cdot 10H_2O$: C 50.61, H 7.49, N 1.64; found: C 50.63, H 7.52, N 1.62; MALDI-MS: *m/z*: 3259.43 [*M*+Na]$^+$.

Acknowledgements

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Keywords: cyclodextrins · fluorescence resonance energy transfer · organic electronics · porphyrins · supramolecular assembly

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