JOC The Journal of Organic Chemistry

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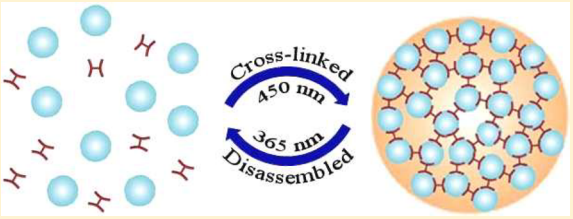
# Hierarchical Organization of Spherical Assembly with Reversibly Photocontrollable Cross-Links

Zhi-Qiang Li, Ying-Ming Zhang, Hong-Zhong Chen, Jin Zhao, and Yu Liu*

Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P.R. China

Supporting Information

**ABSTRACT:** A ternary photocontrollable assembly was hierarchically constructed by the "orthogonal" host–guest interaction of different types of cyclodextrins toward the porphyrin and azobenzene. Spectroscopic titrations and microscopic investigations demonstrate that the inclusion complex of azobenzene modified water-soluble porphyrin (**1**) with phthalocyanine-grafted permethyl $\beta$-cyclodextrins (**2**) could be reversibly cross-linked to relatively larger nanospheres with naphthyl bridged bis($\alpha$-cyclodextrin)s (**3**). Moreover, the large-sized spheres (**1**·**2**·**3**) could be disassembled and switched to small-sized complex (**1**·**2**) upon the photoinduced isomerization of an azophenyl group.






Recent advances in supramolecular nanotechnology at the interface of chemistry, biology, and medicine have focused on the investigation of hierarchical self-assembling systems consisting of stimulus-responsive blocks, in which the original state could be simply adjusted by reversing the relevant stimuli.[1,2] Among the numerous external signals including temperature, pressure, redox, pH, and ionic strength, light irradiation has emerged as an ideal candidate to reversibly and precisely control the physio-chemical properties of stimuli-responsive supramolecular systems.[3] In particular, considerable effort has been devoted to exploring the structure–activity relationship in light-switchable systems (e.g., nanovalves and supramolecular gels) using the photochromic azobenzene derivatives,[4] which is a well-established photochemical process because of their superior characteristics of reversible *E*(*trans*)/*Z*(*cis*) photoisomerization.

The controllable nanoarchitectures with three-dimensional periodicity and collective behaviors based on the cooperative noncovalent interactions are particularly useful, as they may show enhanced binding abilities toward target substrates arising from the effect of multivalency.[5] Adopting this strategy, we have previously demonstrated a supramolecular nanowire through the complexation of phthalocyanine-grafted cyclodextrins and sulfonated porphyrins, where the pristine fullerene could be efficiently captured by the preorganized $\pi$-electronic cage in water.[6] These findings encourage us to design a cyclodextrin-based stimuli-responsive supramolecular system, taking both the "orthogonal" host–guest interaction of different types of cyclodextrins toward the appropriate guest molecules[7] and photoinduced isomerization properties of azophenyl group into account.

Herein, we report a novel supramolecular spherical assembly upon complexation with a water-soluble porphyrin derivative (**1**) bearing azophenyl moiety (Figures S1–S5, Supporting Information) and phthalocyanine-grafted 8 permethyl $\beta$-cyclodextrins (PMCDs) units (**2**) through strong noncovalent interaction. The relatively small-sized spherical complex could be spontaneously formed with pendant azophenyl groups at the periphery of the porphyrin cores. Upon addition of naphthyl-bridged bis($\alpha$-CD)s (**3**), the small-sized spheres were further cross-linked to relatively larger spheres through the hierarchically intermolecular organization. Moreover, the large-sized particles could be disassembled and switched to small-sized ones with good reversibility as soon as the *trans*-azobenzene was transformed to *cis*-isomer upon UV irradiation. The structural illustration of compounds **1**–**3**, PMCD, and $\alpha$-CD is shown in Scheme 1.

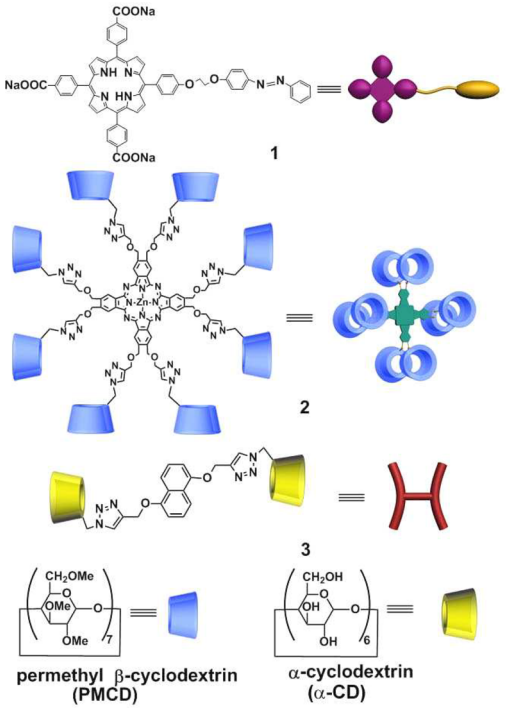
The molecular binding behaviors of complexation process of **1** with **2** were investigated by UV/vis spectroscopy. As shown in Figure 1, the Soret band of **1** became sharp and its intensity gradually increased upon addition of **2**, accompanied by a new absorption at 418 nm. These absorbance changes of **1** reached the plateau in the presence of 0.25 equiv of **2**. The 4:1 binding stoichiometry between guest **1** and host **2** was further identified by Job's plot, which was consistent with our previous results (Figure S6, Supporting Information).[6] These phenomena jointly indicate that the porphyrin backbone has been encapsulated in the cavity of PMCD.[8] Moreover, the fluorescence spectral changes of **1**·PMCD and complex **1**·**2** show that there was an excited energy transfer process from porphyrin **1** as donor to phthalocyanine **2** as acceptor (Figure S7, Supporting Information).

Subsequently, dynamic light scattering (DLS) results in Figure 2a gave an average hydrodynamic radius of 12.4 nm, which was in accordance with the optimized molecular modulation of inclusion complex **1**·**2** by the minimized energy method (Figure S8, Supporting Information). Moreover, the small nanospheres with an average height of 8.2 nm in atomic

**Received:** April 12, 2013
**Published:** April 30, 2013

   dx.doi.org/10.1021/jo400772j | *J. Org. Chem.* 2013, 78, 5110–5114

**Scheme 1. Structural Illustration of Compounds 1−3, Permethyl β-Cyclodextrin (PMCD), and α-Cyclodextrin (α-CD), Respectively**



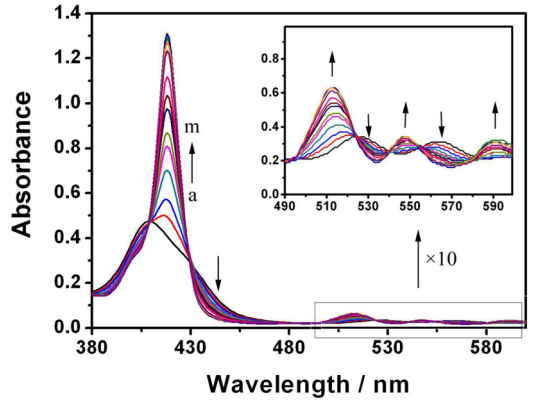




**Figure 1.** UV/vis spectral changes of **1** ($5.0 \times 10^{-6}$ M) upon addition of 0−0.275 equiv of **2** (from a to m) in pH 7.2 phosphate buffer solution at 25 °C. Inset: magnified area in the range of 490−600 nm.

force microscopy (AFM) images (Figure 3a), as well as the uniform size with an average diameter of 12.0 nm in transmission electron microscope (TEM) images (Figure 3c), jointly confirm the formation of supramolecular complex **1**·**2**. As compared with the height of **2** alone (4.2 nm) in our previous results,[6] the one of complex **1**·**2** in AFM images seemed a little higher, mainly due to the introduction of four flexible azophenyl coils into one phthalocyanine core. Moreover, no linear aggregation could be observed even at high concentration of **1**·**2**. Therefore, we can reasonably infer that two PMCD cavities of **2** can concurrently encapsulate one porphyrin group of **1** with pendant azophenyl group at the periphery of the porphyrin cores to form small-sized spherical complex **1**·**2**. The molecular modeling studies have showed that 8 PMCD units in **2** isotropically spread around one phthalocyanine core originating from the steric hindrance of

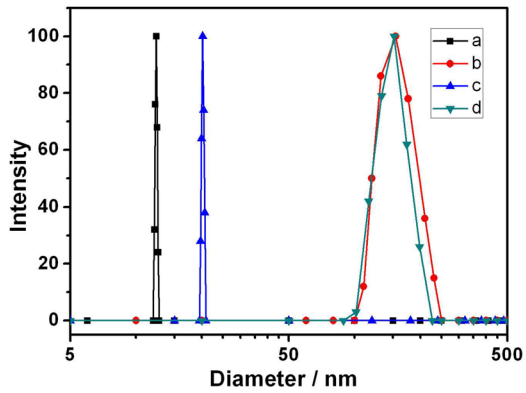



**Figure 2.** Diameter distributions of (a) the complex **1**·**2** and (b) assembly **1**·**2**·**3**, the assembly **1**·**2**·**3** after irradiation at (c) 365 nm and then (d) 450 nm in water at 25 °C.

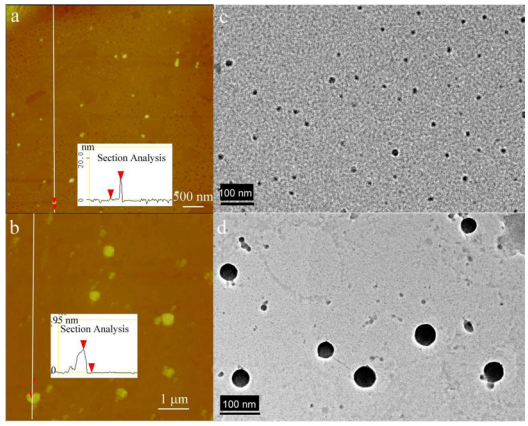



**Figure 3.** Typical AFM (a, b) and TEM (c, d) images of the complex **1**·**2** (a, c) and the assembly **1**·**2**·**3** (b, d), respectively.

adjacent PMCD units.[6] Therefore, it is very possible to form symmetrically spherical assembly upon addition of porphyrin derivative **1** bearing the flexible azophenyl moiety. As shown in Figure S9 (Supporting Information), only amorphous morphological structures could be observed in the presence of either individual compound **1** or **2**. DLS measurements also showed that no signal of large assembly could be observed in the presence of free **1** or **2**. These results indicate that the host−guest complexation between **1** and **2** is the decisive factor to form the small-sized spherical complex.

Furthermore, spectroscopic titrations were performed to check the orthogonality in this photoresponsive supramolecular system. The binding behaviors between **1** and α-CD in the presence of PMCDs were primarily measured, giving the stability constant of $2.3 \times 10^4$ $M^{-1}$ using a nonlinear least-squares curve-fitting method (Figure S10, Supporting Information).[9] Then, the results in rotating-frame Overhauser effect spectroscopy (ROESY) experiment demonstrate that the porphyrin moiety of **1** was accommodated in the cavity of the PMCD,[10] whereas the azophenyl group was located out of the cavity of PMCD (Figure S11, Supporting Information). These results imply that the existence of PMCDs could not affect the binding behaviors of α-CD with azophenyl moiety. In addition, UV/vis spectral titrations also reveal that the introduction of **3** and mixing order could not affect this orthogonal process (Figure S12, Supporting Information).


dx.doi.org/10.1021/jo400772j | J. Org. Chem. 2013, 78, 5110−5114

As an intriguing class of building blocks in the photoresponsive supramolecular systems, azobenzene and its analogues are known to have excellent isomerization activities to induce the morphological transformation, especially under UV and visible lights.[11] Considering that there were 4 azobenzene groups extending out of the small-sized spheres and *trans*-azobenzene can form stable inclusion complex with $\alpha$-CD, we further cross-linked the small nanospheres to large-sized spheres by the hierarchical build-up method. When 2.0 equiv of bridged bis($\alpha$-CD)s **3** (relative to **2**) was added to complex **1·2**, a hydrodynamic diameter centered at 154 nm was contributed to the formation of assembly **1·2·3** (Figure 2b). Meanwhile, the height and diameter of large-scale spheres were 49 and 50 nm, respectively, as shown in AFM and TEM images of assembly **1·2·3** (Figure 3b,d). Viscosity measurements further gave the lower critical assembly concentration (CAC) at $8.9 \times 10^{-6}$ M, above which the large-scaled nanospheres **1·2·3** were exclusively formed in water (Figure S13, Supporting Information). Combining these aforementioned results, we can reasonably deduce the smaller nanospheres **1·2** could be orthogonally assembled into larger ones with cross-linker **3**.

Some controlling experiments were carried out to confirm the size control mechanism. As shown in Figures S14 and S15 (Supporting Information), DLS and TEM experiments confirm that the morphology of nanospheres **1·2·3** could be seriously destroyed in presence of excess amount of PMCD and $\alpha$-CD as competitive hosts. Moreover, the formation of larger complex **1·2·3** is critically ratio-dependent; that is, the ratio of 4:1:2 with compounds **1**, **2**, and **3** is the optimized condition for the stable formation of larger assembly, at which most of azophenyl and porphyrin units could be effectively converted to the azobenzene/$\alpha$-CD and porphyrin/PMCD inclusion complexes (Figure S16, Supporting Information).

Moreover, it have been proven that, once *trans*-azobenzene is transformed to *cis*-isomer, the bulky *cis* form cannot be encapsulated in the cavity of $\alpha$-CD anymore.[12] As seen in Figure S17 (Supporting Information), after irradiation at 365 nm for 5 min, $\pi-\pi^*$ absorption of *trans*-azobenzene at 351 nm decreased,[13] indicating the transformation of *trans*-isomer to *cis*-isomer of azobenzene group. As shown in Figure 2c, only a narrow diameter distribution at 20.2 nm was observed after UV irradiation. AFM and TEM images (Figure 4a,c) also showed the spherical morphology with an average size of 12.2 nm in the dried state. These phenomena clearly indicate that the azobenzene group was released from the cavity of $\alpha$-CD and the assembly **1·2·3** was accordingly disassembled to the inclusion complex **1·2** and free compound **3** upon irradiation at 365 nm.

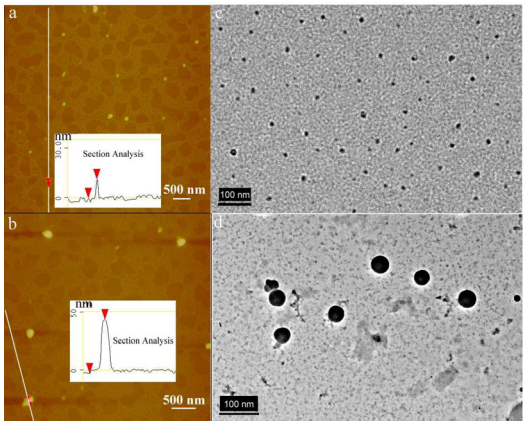



**Figure 4.** Typical AFM (a, b) and TEM (c, d) images of assembly **1·2·3** under irradiation at 365 nm (a, c) and 450 nm (b, d), respectively.

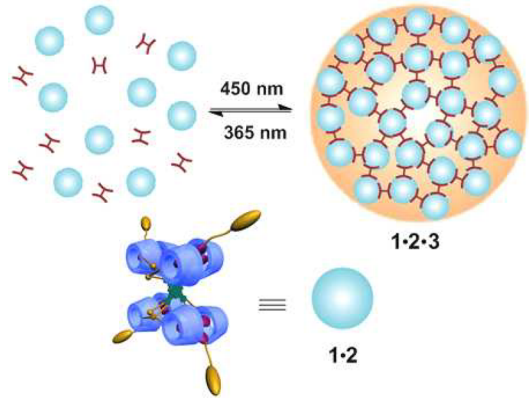
For the purpose of reversible controlling the nanoarchitecture morphology, visible light was employed to investigate the recuperability of assembly **1·2·3**. After irradiation at 450 nm for 15 min, the large-scale diameter distribution was reproduced at 152 nm (Figure 2d), which was in agreement with AFM and TEM images of larger nanospheres (Figure 4b,d). Thus, we achieved a complete circle in modulating the supramolecular morphology from the inclusion complex **1·2** to large-scaled nanoassembly **1·2·3** by external light stimulation. It is noteworthy that this optical switching process can be recycled for several times (Figure S18, Supporting Information).

Moreover, the optical switching process was confirmed by $^1$H NMR titration experiment. Since the serious overlap and broadened tendency of phthalocyanine and porphyrin in the aromatic areas, we took PMCD instead of **2** as a reference compound to investigate the inclusion binding mode of **1** with PMCD and $\alpha$-CD in $D_2O$. As seen in Figure S19a (Supporting Information), it was rather difficult to validate the proton assignments of free **1**, due to the concentration-dependent aggregation of anion porphyrin derivatives.[14] Comparatively, the signals were sharp and clear upon addition of PMCD, indicating the formation of inclusion complex of **1**·PMCD to prevent the intrachromophoric interactions of porphyrin from self-associated $\pi$-stacking oligomers (Figure S19b, Supporting Information). Moreover, when 0.5 equiv of cross-linker **3** was added to the complex of **1**·PMCD, it is found that the proton signals of azobenzene ($H_\alpha$) were drastically broadened, accompanied by an obvious upfield shift from 7.49 to 7.36 ppm (Figure S19c, Supporting Information). It is generally accepted that the proton signals of azobenzene moiety are accordingly shifted upon their isomerization from *trans*- to *cis*-configuration.[15] In our case, after irradiation at 365 nm for 5 min, the chemical shifts of $H_\alpha$ were restored, suggesting that azophenyl part was compelled out of the cavity of $\alpha$-CD as a result of photoinduced isomerization from *trans*- to *cis*-isomer (Figure S19d, Supporting Information). Moreover, as compared with the peak pattern of $H_\alpha$ in Figure S19b (Supporting Information), it was changed to multiple ones in Figure S19d (Supporting Information) after light irradiation, which is ascribable to the isomerization of azobenzene. In addition, the *trans*-isomer could be regenerated along with the reproduction of proton signals at 7.36 ppm upon irradiation at 450 nm, indicative of the recombination of azobenzene and $\alpha$-CD under visible light (Figure S19e, Supporting Information). On the basis of all of the spectroscopic and microscopic investigation results, we can deduce the intermolecular binding behaviors in complex **1·2** and assembly **1·2·3**, as illustrated in Scheme 2.

In conclusion, taking advantage of the strong affinity of porphyrin/PMCD and *trans*-azobenzene/$\alpha$-CD supramolecular couples, we have constructed an optical switching system through the orthogonal and hierarchical self-assembly under light irradiation, leading to a highly reversible morphological change in the transition of spherical nanoarchitectures with different sizes. As investigated by spectroscopic experiments, the introduction of a photocontrollable cross-linker could greatly affect the morphological size. We also envision that this


dx.doi.org/10.1021/jo400772j | J. Org. Chem. 2013, 78, 5110−5114

**Scheme 2. Binding Mode of Complex 1·2 and Assembly Behaviors of 1·2·3**




photoresponsive supramolecular assembly in a reversibly manipulated manner makes our system an appealing alternative for biological applications and construction of other smart functional materials.

## EXPERIMENTAL SECTION

**Preparation of Compound 1.** Compound **6**[16] (183 mg, 0.6 mmol), 5,10,15-tris(4-methoxycarbonylphenyl)-20-(4-hydroxyphenyl)porphyrin[17] (**5**, 242 mg, 0.3 mmol), and $K_2CO_3$ (83 mg, 0.6 mmol) were added into 30 mL of anhydrous DMF with stirring. The mixture was heated at 80 °C for 24 h under $N_2$ atmosphere. After being cooled , the reaction mixture was filtered and the residue was washed with $CH_2Cl_2$. Then the filtrate was concentrated under the reduced pressure. The residue was dissolved by $CHCl_3$ (100 mL) and then washed twice with saturated NaCl solution. Then the organic phase was dried over anhydrous $Na_2SO_4$ and concentrated. The crude product was purified by column chromatography over silica gel (eluent: 500:1 $CHCl_3$/MeOH) was obtained as purple powder. Then an aqueous solution of 40% KOH (4 mL) was added to this purple powder dissolved in 60 mL of a 2:1 THF/$CH_3OH$ mixture. The reaction mixture was stirred at 40 °C for 1 h, acidified with concentrated HCl to pH 5, and extracted with THF/$CH_2Cl_2$ 1:2 (4 × 20 mL). The organic phase was evaporated under reduced pressure and washed with water and $CH_2Cl_2$ to afford 216 mg of the desired product **4** in 72% yield: $^1$H NMR (400 MHz, DMSO-$d_6$, ppm) $\delta$ 13.31 (s, 3H), 8.92 (m, 2H), 8.85 (s, 6H), 8.37 (dd, $J$ = 16.9, 8.1 Hz, 12H), 8.16 (d, $J$ = 8.4 Hz, 2H), 7.98 (d, $J$ = 8.8 Hz, 2H), 7.88 (d, $J$ = 7.4 Hz, 2H), 7.60 (t, $J$ = 7.4 Hz, 2H), 7.54 (m, 1H), 7.47 (d, $J$ = 8.5 Hz, 2H), 7.33 (d, $J$ = 8.9 Hz, 2H), 4.68 (m, 2H), 4.66 (m, 2H), −2.92 (s, 2H); $^{13}$C NMR (100 MHz, DMSO-$d_6$, ppm), $\delta$ 66.4 and 66.9 (−$CH_2CH_2$−), 113.0 (C8, C8′), 115.1 (C2′, C6′), 118.8 and 119.0 (C*meso*), 120.5 (C12 and C12′), 122.2 (C9 and C9′), 124.6 (C2 and C6), 127.8 (C13 and C13′), 129.3 (C1), 130.4 (C14), 130.8 (C4), 133.4 (C$\beta$-pyrrole), 134.4 (C3 and C5), 135.4 (C3′ and C5′), 145.5 (C4′), 146.2 (C$\alpha$-pyrrole), 152.0 (C10 and C11), 158.2 (C1′), 161.1 (C7), 167.4 (COO); HRMS $[M + H]^+$ calcd for $C_{61}H_{43}N_6O_8^+$ 987.3142, found 987.3130; UV/vis $\lambda_{max}$ = 409 nm. Anal. Calcd for $C_{61}H_{42}N_6O_8$: C, 74.23; H, 4.29; N, 8.51. Found: C, 74.18; H, 4.24; N, 8.47. Compound **4** in the protonated form was dissolved in water and neutralized with NaOH[8b] to directly afford the water-soluble anionic porphyrin tris(*p*-carboxyphenyl)porphyrin−azobenzene dyad **1**. The water solubility of compound **1** was up to 0.052 M (i.e., 54.8 mg/mL).

## ASSOCIATED CONTENT

### Supporting Information

Characterization data for new compounds, Job's plots and $^1$H ROESY spectrum of complex **1·2**, and computational modeling studies, DLS curves and TEM images in the presence of competitive hosts, viscosity measurements, as well as UV/vis and fluorescence spectra in the controlling experiments. These materials are available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: yuliu@nankai.edu.cn.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We thank the 973 Program (2011CB932502) and NNSFC (Nos. 20932004, 91227107, and 21102075) for financial support.

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