

Switchable Ternary Nanoporous Supramolecular Network on Photo-Regulation

Yong-Tao Shen,^{†,‡,§} Ke Deng,^{†,§} Xue-Mei Zhang,[†] Wei Feng,[‡] Qing-Dao Zeng,^{*,†} Chen Wang,^{*,†} and Jian Ru Gong^{*,†}

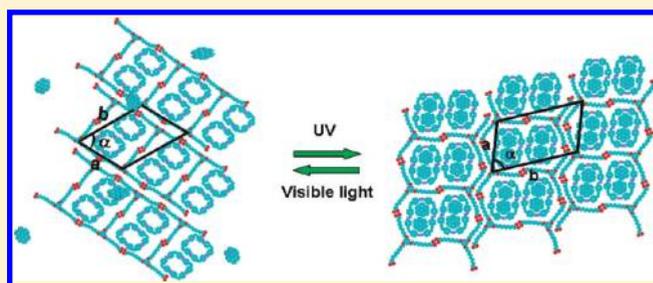
[†]National Center for Nanoscience and Technology, 11 Zhongguancun Beiyitiao, Beijing 100190, People's Republic of China

[‡]School of Materials Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300072, People's Republic of China

S Supporting Information

ABSTRACT: Controlled regulation of the switchable behavior of the supramolecular network is central to the potential application in the molecular scale nanodevices. In this work, it is reported that the reversible accommodation of the guest molecules in the nanoporous supramolecular network can be regulated by the UV/visible light. The nanoporous complex template of TCDB/4NN-Macrocycle (trans,trans,trans,trans) with photosensitive units is well-defined. After the UV irradiation, the template can be switched on to encapsulate coronene molecules due to the formation of a new photoisomer (trans,cis,trans,cis) and switched off to expel coronene from the inner cavities under the visible light. The photoregulated switchable multicomponent supramolecular guest–host network provides a novel strategy for fabricating the functional nanodevices at the molecular scale.

KEYWORDS: Photoregulation, macrocycle molecules, supramolecular network, azobenzene



With the development of science and technology, the scale of microelectronic devices by top-down approach continues to decrease and will come to the physical limit according to Moore's law. Therefore, the molecular self-assembly as one of the bottom-up techniques has been employed for exploring the fabrication of functional nanodevices.^{1–3} In particular, molecular-based optical devices with the merit of zero heat generation and high-speed and so on might be the next generation technology after microelectronics. Controlled regulation of the switchable and restorable behavior of the supramolecular network is central to the potential application in the molecular scale optical devices.⁴ The circle of restorable isomers changes of supramolecular network after irradiation by UV/visible light represents the conversion between on and off state. Many applications profiting from the conformational rearrangement of the molecule, such as optical data storage devices,^{5,6} switchable supramolecular cavities and sensors,⁷ and light-powered molecular machines,^{8,9} have been proposed.

Nanoporous supramolecular networks, which can immobilize guest molecules, could be constructed from interconnected molecular building blocks through various interactions such as hydrogen bond,^{10–12} van der Waals force,¹³ metal–organic coordination,¹⁴ and so forth. One of the reported approaches for fabricating such architectures is to use macrocyclic structures with the specific geometry and binding site to achieve high selectivity and adjustability.^{15–19} The macrocycles can form nanoporous networks when adsorbed onto the surface, which has been shown to be able to immobilize the guest molecules in the cavities.^{20–25} While a range of constructing strategies have

been demonstrated for nanoporous supramolecular networks, their responsiveness to the external stimuli has not been fully addressed, which could provide complementary venues for enriching the functionality of such networks.

Responsiveness of the molecular ordering to the external stimuli, such as photoirradiation,^{26–38} thermal-annealing,^{39–45} electric field^{46–48} and electrochemical potential, is an important aspect in constructing functional supramolecular architectures.^{49–52} The photoinduced molecular structural change is expected to be highly reversible. With the growing interest in constructing functional supramolecular networks, it would be of much interest to explore switchable nanoporous networks in response to the external stimuli, such as photoirradiation and thermal treatment. Herein, we report that the reversible switching behavior of the host–guest supermolecular complexes with coronene molecules as the guest species being either encapsulated in or excluded from the host networks on photoregulation due to the conformational change of the photosensitive isomers affected by the UV and visible light.

The macrocyclic building block used in our experiment is 4NN-Macrocycle (Figure 1a) containing photosensitive groups (1,2,17,18,33,34,48,49-octaaza-[2₈](4,4')cyclophane-1,17,33,48-tetraene⁵³) with four azobenzene groups that have rich variety of conformational and photoisomers. It was observed that

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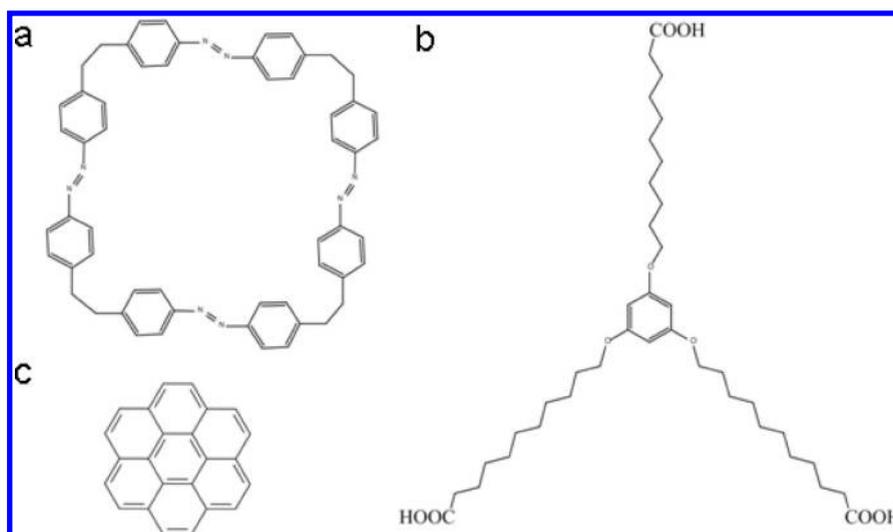


Figure 1. The chemical structures of (a) 4NN-Macrocycle, (b) TCDB, and (c) coronene.

4NN-Macrocycle could be immobilized in the molecular template formed by TCDB^{3,54} (Figure 1b) and the well-ordered self-assembled molecular structure of TCDB is shown in Figure S1 of Supporting Information.⁵⁵

The molecular structure of the TCDB₁/4NN-Macrocycle-(trans-trans-trans-trans, i.e., t,t,t,t) composite template is shown in the high-resolution scanning tunneling microscopy (STM) image (Figure 2a). It can be observed that four T-shaped TCDB₁ molecules self-assemble into one parallelogram cavity, in which two 4NN-Macrocycle(t,t,t,t) isomer molecules are entrapped, and the matching molecular model with a superimposed unit cell of $a = 3.7 \pm 0.2$ nm, $b = 5.2 \pm 0.2$ nm, and $\alpha = 61.1 \pm 2.1^\circ$ is shown in Figure 2b. After adding coronene molecules on the composite template, the self-assembled molecular adlayer in Figure 2c displays that the molecular structure and the structural parameters of the TCDB₁/4NN-Macrocycle(t,t,t,t) network are not changed compared to those in Figure 2a. Careful inspection shows that areas of some bright molecular fragments are coexisting with the ordered domains of TCDB₁/4NN-Macrocycle-(t,t,t,t). These bright molecular fragments can be associated with coronene molecules. However, the submolecular structure of coronene cannot be observed clearly, which indicates that these coronene molecules are not located inside the cavity of the macrocycles but rather randomly on top of the TCDB₁/4NN-Macrocycle(t,t,t,t) template. The corresponding molecular model of TCDB₁/4NN-Macrocycle(t,t,t,t)/coronene is illustrated in Figure 2d. In order to differentiate the TCDB configuration before irradiation from that after irradiation, the TCDB structure before irradiation is named as TCDB₁ and after irradiation as TCDB₂. The experimental process is described in Supporting Information.

After the UV irradiation on the TCDB₁/4NN-Macrocycle(t,t,t,t)/coronene adlayer, the disk-like bright dots are observed to be completely encapsulated in the cavity of the nanoporous network as shown in Figure 2e. The previous studies indicate that coronene molecules can be immobilized inside the cavities of host networks,^{3,56,57} in which the detailed molecular structure of coronene can be observed very clearly by STM. Therefore, it can be deferred that the two coronene molecules are within each cavity of 4NN-Macrocycle. The ternary molecular model structure of TCDB₂/4NN-Macrocycle(t,c,t,c)/coronene from the

density functional theory (DFT) simulation is displayed in Figure 2f, on which a superimposed unit cell with $a = 3.2 \pm 0.2$ nm, $b = 5.0 \pm 0.2$ nm, and $\alpha = 73.1 \pm 2.1^\circ$ is overlapped. The shape of the macrocycle transfers from the parallelogram to the ellipse after irradiation, and such dramatic change in the capability for encapsulating guest species is attributed to the conformational change of 4NN-Macrocycle from (t,t,t,t) to trans-cis-trans-cis (t,c,t,c) induced by the UV light.

The contrast in the STM image shows the difference of the molecular electronic density, and it is also related to the height of the molecule. Therefore, the corresponding data acquired from the cross-sectional profile in the STM image can also prove that the coronene molecules are not located in the cavity before irradiation whereas entrapped in the cavity when the sample is irradiated by the UV light. The STM image and the corresponding cross-sectional profile of the TCDB₁/4NN-Macrocycle(t,t,t,t)/coronene adlayer are shown in Figures 3a and 3b. The part marked by A is attributed to an individual macrocycle without the overlaying coronene molecules. The coronene molecules marked by B are located on top of the cavity of the macrocycle. It can be clearly recognized that the height of the electronic density of the coronene on the macrocycle is about 0.19 nm higher than that of the empty macrocycles in the cross-sectional profile. In Figure 3c, d, the part marked by A is attributed to one side of the 4NN-Macrocycle(t,c,t,c) molecule. The coronene molecule marked by B is encapsulated in the macrocycle. The height of the electronic density of the coronene is only 0.044 nm higher than that of the 4NN-Macrocycle molecule, which is much lower than that in Figure 3b. The successive excluded/encapsulated cycles from the empty to entrapped architectures as shown in Figure S2 of Supporting Information, demonstrating that the photoregulation on the switchable behavior of the nanoporous supramolecular network is reversible.

Azobenzene is a typical photoactive isomer and has been widely studied because of its simple structure and reversible cis-trans isomerization under photo irradiation. Irradiation with UV and visible lights induces isomerization to metastable "cis" (c) and stable "trans" (t) conformations, respectively.⁵⁸⁻⁶⁴ According to the STM results of the macrocycles irradiated by the UV and visible light, it can be concluded that the conversion of photoisomer is a key factor for encapsulating or excluding the

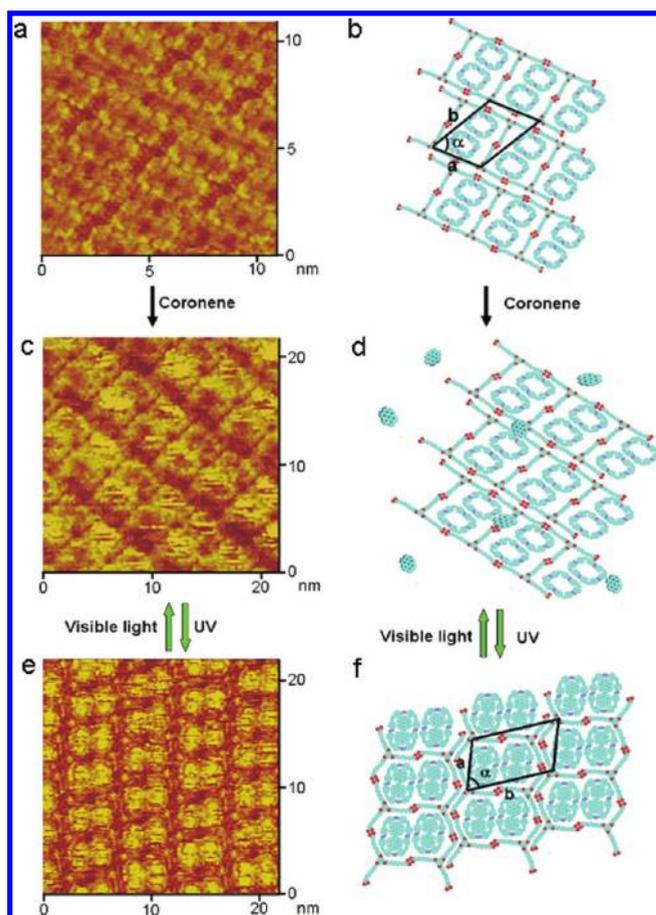


Figure 2. (a) High-resolution STM image ($I = 483$ pA, $V = 1021$ mV) of the TCDB₁/4NN-Macrocycle(*t,t,t,t*) network structure. (b) The molecular model for TCDB₁/4NN-Macrocycle(*t,t,t,t*) structure. (c) STM image ($I = 269$ pA, $V = 641$ mV) of the ternary adlayer of TCDB₁/4NN-Macrocycle(*t,t,t,t*)/coronene before the UV irradiation. (d) The molecular model for the TCDB₁/4NN-Macrocycle(*t,t,t,t*)/coronene adlayer. (e) STM image ($I = 269$ pA, $V = 641$ mV) of the TCDB₂/4NN-Macrocycle(*t,c,t,c*)/coronene architecture after the UV irradiation. (f) The molecular model for the ternary TCDB₂/4NN-Macrocycle(*t,c,t,c*)/coronene network. In all the molecular models, the red ball represents oxygen atom, the blue for carbon, and the purple for nitrogen. The hydrogen atoms are omitted for clarity.

guest species. Before irradiation, the macrocycle adopts the (*t,t,t,t*) photoisomer and the coronene is absorbed on top of the macrocycle. After TCDB₁/4NN-Macrocycle(*t,t,t,t*)/coronene adlayers is irradiated by the UV light, the macrocycle takes the (*t,c,t,c*) photoisomer and the coronene is entrapped inside the ellipse-shaped cavity of the 4NN-Macrocycle photoisomer. The azobenzene groups could also affect the $-\text{CH}_2-\text{CH}_2-$ groups, which could facilitate the conformational change of the macrocycle compared to that of the macrocycle without the UV irradiation. So the coadsorption of ellipse-shaped (*t,c,t,c*) isomer and TCDB can be achieved and the inner cavity of the (*t,c,t,c*) isomer can accommodate two coronene molecules. The accommodated coronene molecules can be stably immobilized on the highly oriented pyrolytic graphite (HOPG) surface because of the $\pi-\pi$ stacking interaction and diffusion limit by the inner boundary of the macrocycles. The schematic illustration of the switchable nanoporous supramolecular networks with light responsiveness is shown in Figure 4a,b, that is, from the TCDB₁

to TCDB₂ template. The inner cavity of 4NN-Macrocycle is deformed by the irradiation of UV light, and the coronene molecules can subsequently be encapsulated in the inner cavity of the (*t,c,t,c*) isomer. Reversely, when the nanoporous network is irradiated by the visible light, the (*t,c,t,c*) isomer can be switched to (*t,t,t,t*) isomer and the encapsulated coronenes will be expelled from the inner cavity of the 4NN-Macrocycle.

The host networks are able to selectively accommodate guest species in their cavities mainly depending on their suitable size and shape. The size of the macrocycle can also be obtained from simulations. The length and width of the parallelogram-shaped (*t,t,t,t*) isomer are 15.36 and 7.82 Å, respectively. The diameter of coronene molecule is 9.21 Å. Obviously, the coronene cannot be entrapped in the cavity of the (*t,t,t,t*) isomer. When the macrocycle is irradiated by the UV light, the shape of the isomer transfers from the parallelogram to the ellipse. Also, the major axis and semiminor axis of the ellipse-shaped (*t,c,t,c*) isomer are 21.75 and 10.08 Å, respectively. Surely the coronene molecule can be entrapped in the cavity of the new isomer. The above results clearly suggest that the coronene molecules can be entrapped in the (*t,c,t,c*) isomer but not in the (*t,t,t,t*) isomer.

Theoretical calculations were performed to evaluate the change of the system energy before and after the encapsulation of the guest molecule using density functional theory (DFT) (see Supporting Information for the computational details). During the calculations, we consider both the substrate effect and the interactions between the adlayer molecules. Before UV irradiation, the system energy of TCDB₁/4NN-Macrocycle(*t,t,t,t*)/coronene adlayer (Figure 4e) on HOPG is about -1118.59 kJ/mol. After the UV irradiation, the 4NN-Macrocycle(*t,t,t,t*) can form the (*t,c,t,c*) isomer. The system energy of TCDB₂/4NN-Macrocycle(*t,c,t,c*)/coronene adlayer (Figure 4f) on HOPG is about -1239.27 kJ/mol. The approximate system energy shows that the transformation can easily take place between the two forms when the sample is irradiated by the UV light and visible light.

The transformation between (*t,t,t,t*) and (*t,c,t,c*) isomers is related to the kinetics of azobenzene in 4NN-Macrocycle. Some previous studies discussed the kinetics of the photoexcited state of azobenzene on Au surface.^{65–67} The compounds in these studies had only one azobenzene group and were covalently immobilized on surface. It is concluded that the value of the kinetic constant calculated for the thermal back *cis*–*trans* reaction on metal surface is more than seven times lower than that in solution.⁶⁷ The rigidity of the aromatic backbone is responsible for the cooperative transformation and the interchain interactions are fundamental for the long lifetime of the *cis* isomers on Au surfaces. Therefore, we can conclude that the photosensitive macrocycles have different kinetic process in solution, TCDB and TCDB/coronene network as shown in Figure 5. In solution, the four azobenzene groups of 4NN-Macrocycle can photoisomerize randomly, so five 4NN-Macrocycle photoisomers, i.e., (*t,t,t,c*), (*t,t,c,c*), (*t,c,t,c*), (*t,c,c,c*) and (*c,c,c,c*), are formed.⁶⁸ While in TCDB network, some azobenzene groups of 4NN-Macrocycle are hindered by the frame, and only two kinds of photoisomers were observed in the TCDB networks on the surface in the previous report.⁵⁴ In the TCDB/coronene network, the coronene molecules fully occupy the cavity of 4NN-Macrocycle, thus only the (*t,c,t,c*) isomer can form on the HOPG surface, which indicates that the selection of isomers exists in

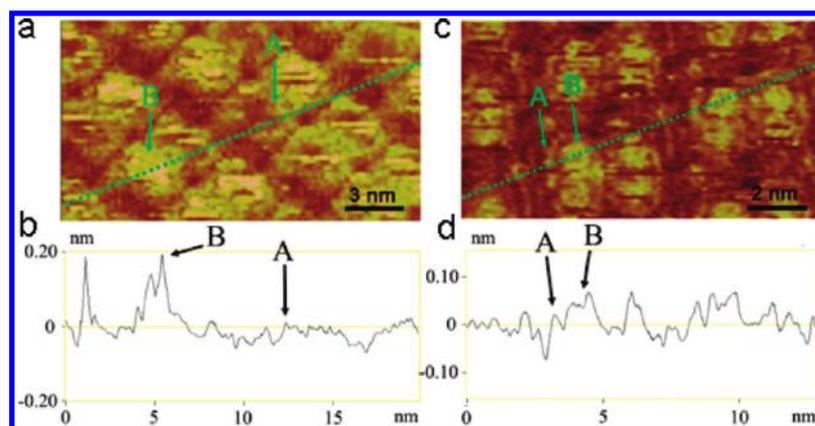


Figure 3. (a) STM image ($I = 269$ pA, $V = 640$ mV) of the TCDB₁/4NN-Macrocycle(t,t,t)/coronene adlayer. (b) A cross-sectional profile is shown for the indicated green line in (a). The peak marked by B corresponds to the height of the electronic density of the coronene molecule marked in (a). The peak marked by A corresponds to the longer side of the 4NN-Macrocycle with the (t,t,t) conformation. (c) High-resolution STM image ($I = 269$ pA, $V = 640$ mV) of the ternary TCDB₂/4NN-Macrocycle(t,c,t,c)/coronene network after the UV irradiation. (d) A cross-sectional profile is shown for the indicated line in (c). The peak marked by B corresponds to the height of the electronic density of the coronene molecule marked in (c). The peak marked by A corresponds to the side of the 4NN-Macrocycle with the (t,c,t,c) conformation.

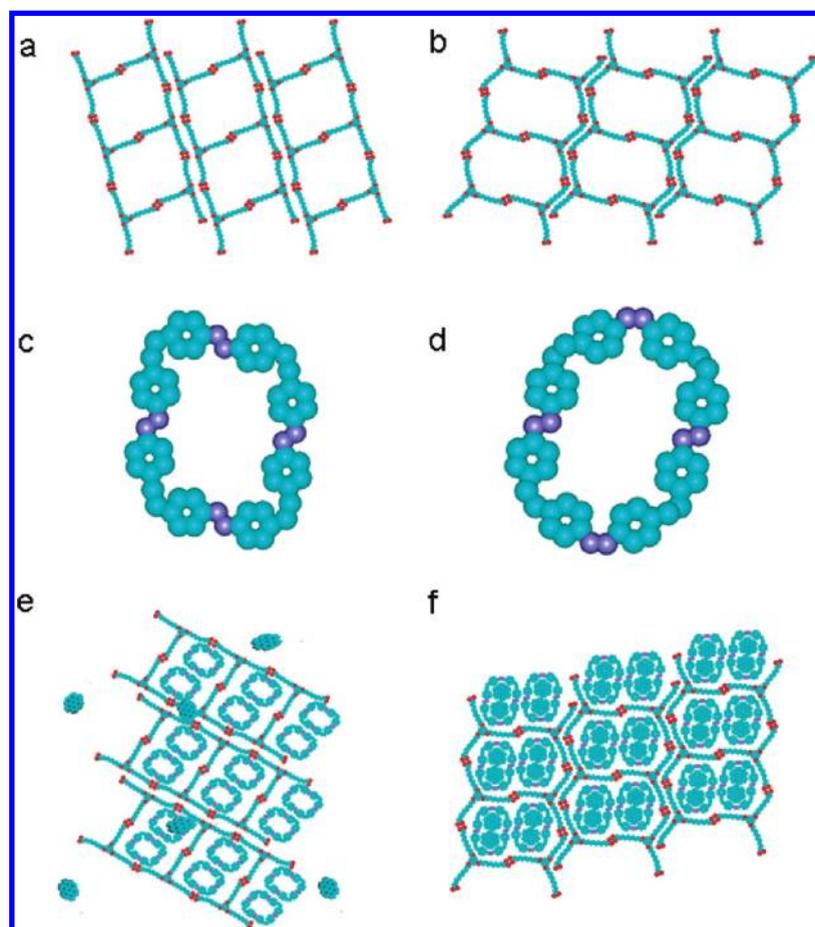


Figure 4. The molecular simulation models of (a) TCDB₁ and (b) TCDB₂ networks, (c) (t,t,t) isomer and (d) (t,c,t,c) isomer of 4NN-Macrocycle. (e) The molecular model for the TCDB₁/4NN-Macrocycle(t,t,t)/coronene adlayer. (f) The molecular model for the TCDB₂/4NN-Macrocycle(t,c,t,c)/coronene adlayer.

the self-assembled process and the network on the surface will influence the kinetic process of the photoisomerization of 4NN-Macrocycle.

In summary, the switchable responsiveness of the host–guest supramolecular network of TCDB/4NN-Macrocycle/coronene on photoregulation was investigated in this work. In the well-defined

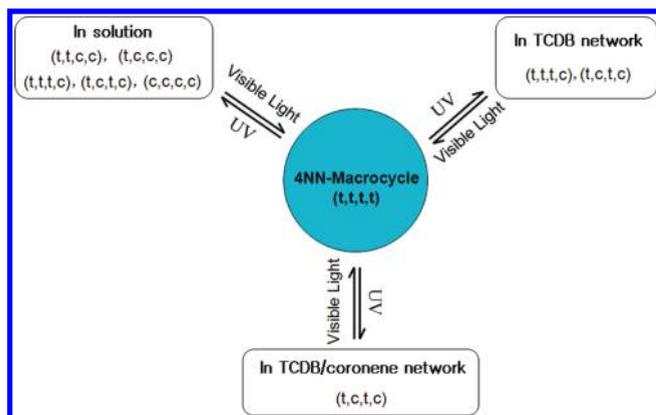


Figure 5. Photoisomerization of 4NN-Macrocycle in solution, TCDB and TCDB/coronene network.

host TCDB/4NN-Macrocycle template, a photosensitive macrocycle can encapsulate or expel guest coronene molecules under the UV or visible irradiation. The switchable bistability of nanoporous networks presented in this study could be beneficial for developing a general strategy for constructing photoregulated guest–host molecular architectures in molecular-based nanodevices.

■ ASSOCIATED CONTENT

S Supporting Information. Additional information and figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gongjr@nanoctr.cn (J.R.G.); zengqd@nanoctr.cn (Q.-D.Z.); wangch@nanoctr.cn (C.W.). Tel: 86-10-82545649. Fax: 86-10-62656765.

Author Contributions

[§]These authors contributed to the paper equally.

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