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Nano-Supramolecular Assemblies Constructed from Water-Soluble Bis(calix[5]arenes) with Porphyrins and Their Photoinduced Electron Transfer Properties

Dong-Sheng Guo, Kun Chen, Hong-Qing Zhang, and Yu Liu*[a]

Abstract: Possessing 2D netlike and 1D linear morphologies, two nano-supramolecular architectures **A1** and **A2** are constructed by tetracationic porphyrin (**G1**) and dicationic porphyrin (**G2**), respectively, upon complexation with the novel water-soluble bis(*p*-sulfonatocalix[5]arenes) bridged at the lower rim (**H2**). Corresponding to the molecular design, the aggregation morphologies are well manipulated by the inherent binding sites of the building blocks through host–guest interactions as well as charge interactions. In comparison to the simple *p*-sulfonatocalix[5]arene **H1** which can only form particle-type complexes **C1** and **C2** with porphyrin guests, **H2** provides excellent pre-organized structure to construct highly complex nano-supramolecular assemblies. The exhibited electron-transfer process of the supramolecular systems is further investigated by steady-state and time-resolved fluorescence spectroscopy, electrochemical measurements, and transient absorption spectroscopy. The results obtained show that calixarenes are also effective electron donors in PET besides acting as significant building blocks, which gives them many advantages in constructing well-ordered nanomaterials with the capability of electron and energy transport.

Keywords: calixarenes · electron transfer · inclusion compounds · porphyrin · supramolecular chemistry

Introduction

Construction of nanoscopic architectures with well-defined shapes and dimensions from molecular components is attracting extensive interest because of their increasing significance in interdisciplinary research, including chemistry, life science, material science, and nanotechnology.[1] Porphyrins are demonstrated to be one of the most fascinating building blocks for constructing spectacular nanoarchitectures owing to their special electronic,[2] optical,[3] magnetic,[4] and biological properties.[5] To date, various multi-porphyrin arrays with definite morphologies have been reported, such as wire-shaped linear polymers,[6] nanotubes,[7] nanosheets,[8] nanoparticles,[9] nanorings,[10] hexagonal nanoprisms,[11] double-strand conjugated molecular ladders,[12] dendritic scaffolds,[13] and so forth, which further exhibit potential applications in simulating the electron and energy transfer processes, as well as in manufacturing artificial photoelectron devices.[14] For this purpose, covalent methods of linking porphyrins into well-ordered nanostructures have been augmented by the alternative noncovalent methodologies involving coordination,[10,12,15] H-bonding,[16] π-stacking,[17] ionic self-assembly,[7,18] and so forth.[14c] Such non-covalent assembling processes are of importance to obtain new types of nanoscale materials or devices with the desired properties and functions, resulting from their particular advantages of 'bottom-up' strategy, versatility, and simplicity that cannot be obtained by classical covalent chemistry.[19] Interestingly, one noticeable noncovalent interaction, the host-guest interaction based on the macrocyclic receptors, has essentially been ignored as a driving force to design and construct porphyrinic nanoarchitectures,[20] although several macrocyclic receptors, including cyclodextrins, calixarenes, and cucurbiturils, have been proven to be able to afford strong binding affinities to the specialized porphyrins.[21] Furthermore, the noncovalent interactions often employed (e.g., coordination, H-bonding, and π-stacking) are not very effective for designing water-soluble supramolecular architectures, and hence they lack the necessary biocompatibility for applica-

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[a] Dr. D.-S. Guo, K. Chen, H.-Q. Zhang, Prof. Dr. Y. Liu
Department of Chemistry
State Key Laboratory of Elemento-Organic Chemistry
Nankai University
Tianjin, 300071 (P.R. China)
Fax: (+86) 22-2350-3625
E-mail: yuliu@nankai.edu.cn

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tions in the fields of biotechnology. These macrocyclic receptors with certain water-solubilities can definitely overcome the problem.

Calixarenes,[22] composed of phenolic units linked by methylene groups, represent the third generation of supramolecular host molecules, next to the crown ethers and cyclodextrins, which are described as 'macrocycles with (almost) unlimited possibilities'.[23] In recent years, the combination of porphyrins and calixarenes has become an important topic for exploring novel functional supramolecular systems. Benefiting from the characteristics of calixarenes, intrinsic 3D platform and facile modification at both upper and lower rims, lots of covalently linked calixarene–porphyrin conjugates have been presented.[24] Furthermore, the noncovalent interactions between calixarenes and porphyrins were also investigated to a certain extent.[21b,25] All these investigations combining calixarenes and porphyrins show them to exhibit broad applications in molecular self-assembly, molecular machine, non-covalent synthesis, heme-protein active site models, light–energy conversion, and so forth. However, to the best of our knowledge, the construction of nanoscale ordered-supramolecular assemblies based on calixarenes and porphyrins has never been reported. In this paper, we wish to report the construction of a 2D net-like aggregate **A1** and a 1D linear aggregate **A2** by lower-rim bridged bis(*p*-sulfonatocalix[5]arenes) (**H2**) upon complexation with 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)porphyrin (**G1**) and 5,15-di(*N*-methyl-4-pyridyl)porphyrin **(G2)**, respectively. The aggregation morphologies are well manipulated by the inherent binding sites of the molecular building blocks through strong host–guest interactions. Moreover, porphyrins are famous antenna molecules possessing solar light-harvesting capability, whereas calixarenes are proven to be efficient electron donors on account of their intrinsic electron-rich cavities.[26] Therefore, the photoelectric properties of the obtained aggregates were further evaluated, revealing that a pronounced electron-transfer process occurs in the supramolecular systems. The transport of energy and electrons within well-ordered nanomaterials is significant to the realization of systems for artificial photosynthesis as well as engineering molecular electronics and optoelectronics.[27]

Results and Discussion

Synthesis of Building Blocks

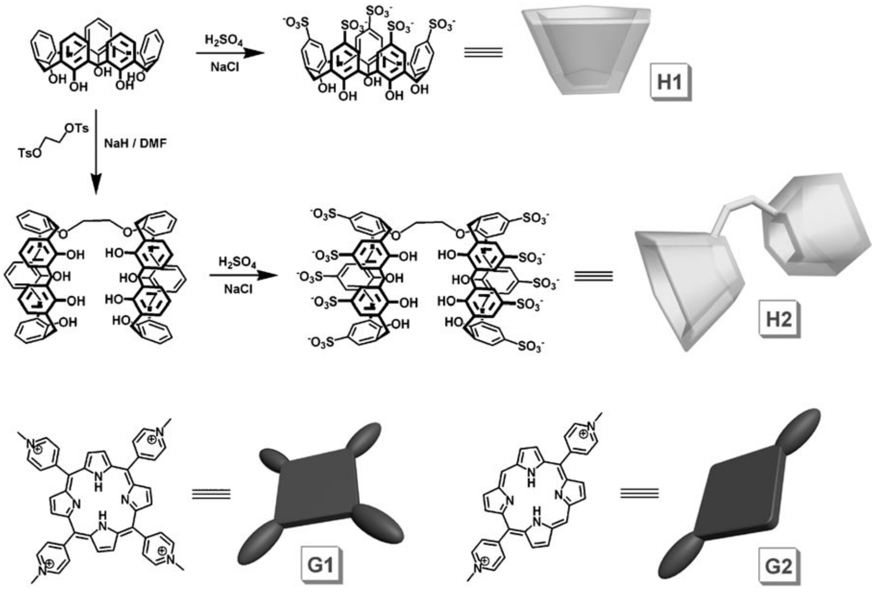
We selected *p*-sulfonatocalixarenes as building blocks for the following reasons: 1) they have benign water-solubility; 2) they possess three-dimensional, flexible, π-rich cavities that can strongly bind numerous guest molecules in aqueous solution, especially for organic cations;[28] 3) they are biocompatible, and have shown promising biological, pharmaceutical, and analytical applications.[29] In the past two decades, the water-soluble *p*-sulfonatocalixarenes and their derivatives have been widely investigated in various fields, including molecular recognition and sensing,[28,30] catalysis,[31] micro-reactor,[32] surfactants,[31a] enzyme-mimic/enzyme-assay,[33] crystal engineering,[34] biomedical applications,[29a] and so forth.[35]

In previous reports from other groups, *p*-sulfonatocalix[4]arene and its tetrakis(2-ethoxyethoxy) derivative formed highly stable 1:1 cage-like complexes with tetrakis-cationic porphyrins,[21b,25d,e] whereas the tetrakis(hydroxycarbonylmethoxy) derivative of *p*-sulfonatocalix[4]arene formed more complex species with programmable calixarene/porphyrin stoichiometry ranging from 4:1 to 4:7.[25a,b,c] In this work, we employed the larger analogue, *p*-sulfonatocalix[5]arenes, as building hosts. On the one hand, *p*-sulfonatocalix[5]arene possesses a cavity of larger size and one more electronegative sulfonate group than *p*-sulfonatocalix[4]arene, which may exclude the possibility of forming ion-pair complexes with cage-like structure because the 1:1 cage-like complexes mainly originate from the charge and size/shape considerations that the four positive charges of porphyrins are suitably matched to the four negative charges of calix[4]arenes owned by upper-rim sulfonate groups. On the other hand, differing from *p*-sulfonatocalix[6,8]arenes with more complicated conformations, the preferred stable cone conformation of *p*-sulfonatocalix[5]arene allows the basic precondition to construct supramolecular nanoarchitectures with well-defined geometries. *p*-Sulfonatocalix[5]arene (**H1**) was synthesized and purified according to the literature procedures.[36] Bis(*p*-sulfonatocalix[5]arenes) (**H2**) was prepared according to the synthetic route shown in Scheme 1. Although there are several *p*-sulfonatocalixarene derivatives reported,[31a,37] the bridged bis(*p*-sulfonatocalixarenes) has never been explored, and the present **H2** represents the first example of a building block with two equal binding sites of sulfonatocalixarenes, which offers us new opportunities leading to highly complex supramolecular nanoarchitectures rather than simple inclusion complexes. Moreover, two porphyrin guests **G1** and **G2** are employed in order to investigate how the disparity of the binding sites affects the resultant assembly morphologies.

Preparation and Characterization of Supramolecular Nanoarchitectures

UV/Vis Studies

The complex interactions between calixarene hosts (**H1** and **H2**) and porphyrin guests (**G1** and **G2**) were primarily investigated by UV/Vis spectroscopy. The absorbance of **G1** and **G2** is characterized by an intense absorption band at 422 nm and 406 nm, respectively, which belongs to the second excited state ($S_0 \rightarrow S_2$) of porphyrins (the Soret band). **H1** and **H2** do not exhibit any absorbance in this region, and thereby the Soret band can be used to monitor the absorption changes of **G1** and **G2** upon complexation with calixarenes. Interestingly, the absorbance titrations show that the absorbance of porphyrins undergoes a pronounced decrease and then an inverse increase upon gradual addition of calixarenes. As shown in Figure 1, the absorb-



Scheme 1. The synthetic routes and structural illustrations of **H1**, **H2**, **G1**, **G2**.

ance of **G1** was firstly quenched by **H1** to over 90%, followed by a visible recovery (about 70%) accompanied with the excess augmentation of **H1**. The absorption changes of **G1** induced by **H1** and **H2** are absolutely distinguishable from that of **G1** by *p*-sulfonatocalix[4]arene,[21b] which indicates that *p*-sulfonatocalix[5]arenes form higher-order complexes with **G1** rather than the 1:1 cage-like complexes.

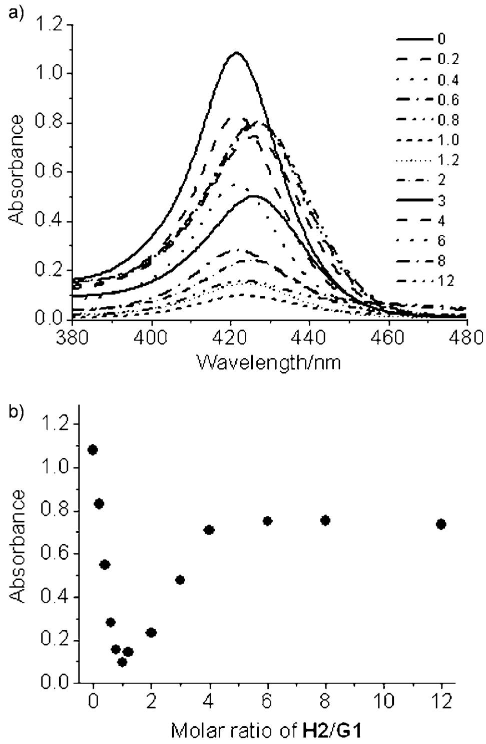


Figure 1. a) UV/Vis titration of **G1** with **H1** in phosphate buffer solution (pH 7.2, 0.1 M), [**G1**] = 5×10^{-6} M, [**H1**] from 0 to 6×10^{-5} M (12 equiv); b) Absorption changes of **G1** recorded at 422 nm upon gradual addition of **H1**.

We further determined the binding stoichiometries between calixarenes and porphyrins by the Job method. As can be seen in Figure 2a, the Job plot performed for **G1** with **H1** shows the maximum value of Δ*A* (complex-induced changes of absorbance) at a porphyrin molar fraction of about 0.56, and the Job plot performed for **G1** with **H2** shows the maximum value of Δ*A* at a porphyrin molar fraction of about 0.72, which indicate that the binding stoichiometries of **H1** and **H2** with **G1** are 4:5 and 2:5, respectively. Similarly, the binding stoichiometries of **H1** and **H2** with **G2** are inferred to be 2:5 and 1:5, respectively, from Figure 2b. The binding stoichiometries of **H1** are exactly two times those of **H2**, which is in accordance with the number of the calixarene cavities, one cavity in **H1** and two cavities in **H2**. Therefore, taking the structures of **H1** and

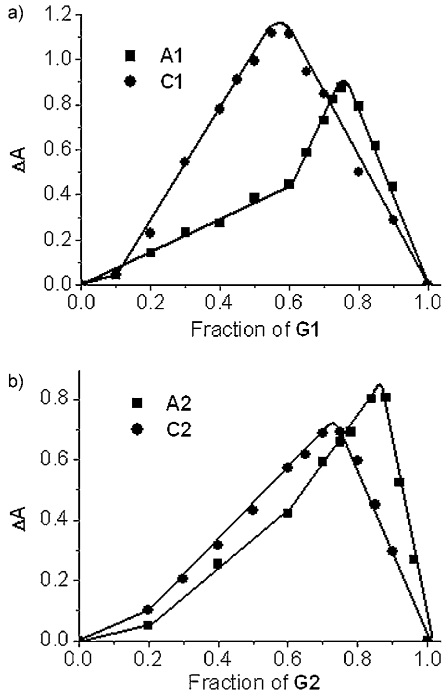
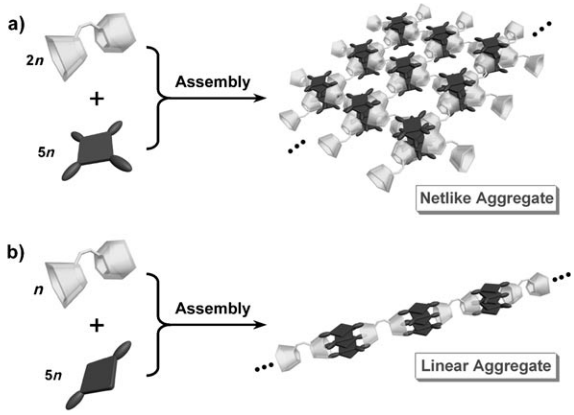
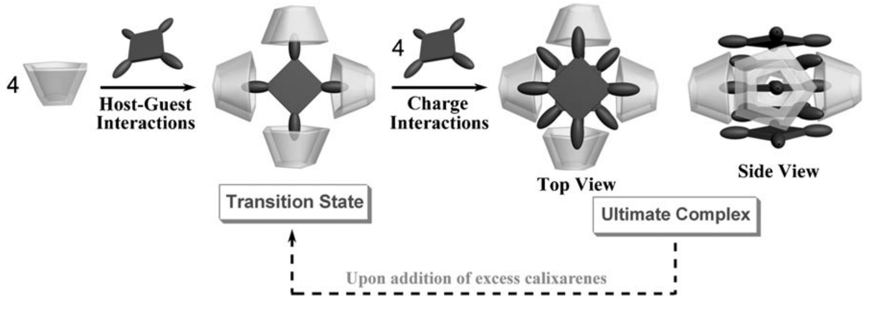


Figure 2. Job plots for **H1** and **H2** upon complexation with **G1** (a) and **G2** (b) in phosphate buffer solution (pH 7.2, 0.1 M). Absorption changes recorded at 422 nm for **G1** and 406 nm for **G2**. The sum of the total concentrations of hosts and guests is constant (1×10^{-5} M).

H2 into account, we primarily infer that **H1** forms 4:5 and 2:5 inclusion complexes (**C1** and **C2**) with **G1** and **G2**, while **H2** forms 2:5 and 1:5 nanoscale supramolecular aggregates (**A1** and **A2**) with **G1** and **G2** as illustrated in Scheme 2. Moreover, it is noticed that the host–guest stoichiometries in these complexes/aggregates are significantly satisfied to charge matching. That is, in all these complex species (**C1**, **C2**, **A1**, **A2**), the number of the positive charge on the porphyrins is equal to the number of negative sulfonate groups in the calixarenes. As a result, the charge interactions also play a crucial role in the formation of supramolecular complexes/aggregates besides the host–guest interactions between calixarenes and porphyrins. Inspired by the model reported by Sciotto and co-workers,[25a,b,c] we postulate the formation process of these supramolecular species as two steps such that the interacting components first undergo an instantaneous intermediate state with host–guest interactions as driving forces, and then fulfil the ultimate complexes/aggregates through charge interactions. As shown in Scheme 3, four cavities of **H1** include the four pyridinium portions of one **G1**, first forming the 4:1 central core, and then the other four **G1** molecules stack stepwise above and below the plane of the central unit, leading to the final 4:5 complex **C1**.



Scheme 2. Schematic representation of the construction of supramolecular nanoarchitectures: a) 2D network aggregate **A1**, b) 1D linear aggregate **A2**.



Scheme 3. The schematic illustration of the forming process of **C1** from **H1** and **G1**.

The deduced binding model can elucidate the dramatic absorbance changes of porphyrins in the UV/Vis titrations (Figure 1, and Figures S4 and S5 of the Supporting Information). In the present cases, there are two key factors of weakening the absorbance of porphyrins: one is the host–guest interactions between calixarenes and porphyrins; the other is the aggregation of porphyrins.[38] As shown in Figure 1b, in the left-hand portion of inflexion, **H1** and **G1** form the inclusion complex with the aggregation of **G1**, which results in the decrease of the absorbance of **G1** to a great extent; whereas in the right-hand portion of inflexion, the further addition of excess **H1** is prone to separate the aggregation of **G1** (Scheme 2) because the host–guest interactions between calixarenes and porphyrins are more dominant than the charge interactions, and thereby leads to the partial recovery of the absorbance of **G1**. The ultimate absorbance of **G1** in the presence of excess **H1** is still weaker than that of solely **G1**, mainly arising from the host–guest interactions.

According to the previous report,[39] free porphyrin **G1** molecules do not self-aggregate at the experimental concentrations investigated here. The aggregated porphyrin pentamers in these complex species of **C1**, **C2**, **A1**, and **A2** should originate from the ionic self-assembly of two oppositely charged tectons,[7,40] which is mainly contributed by the electrostatic forces between the negative sulfonate groups of calixarenes and the positive pyridinium groups of porphyrins. In addition, the aggregation of porphyrins is temperature-dependent.[41] The UV/Vis spectra of the complexes/aggregates with thermoregulation showed that the Soret bands of porphyrins present pronounced enhancement accompanied with the increase of the measuring temperature from 15 °C to 55 °C (Figure 3 and Figure S6 of the Supporting Information). The control experiments of single **G1** and **G2** with the same concentration of porphyrin units showed no appreciable changes in the absorption spectra in the 350–475 nm region. These results indicate that the aggregation of porphyrins can be destroyed by increasing temperature, which not only provides further evidence for the structural model of the complexes/aggregates, but also illuminates the fact that the present supramolecular species are able to be tuned by temperature, affording a potential approach to manipulate the compositions and structures of the supramolecular nanoarchitectures.

AFM and SEM Images

To further give the intuitionistic insight into the shape, size, and size distribution of the supramolecular nanoarchitectures **A1** and **A2**, atomic force microscopy (AFM) and scanning electron microscopy (SEM) measurements were performed. Representative AFM images of **A1** and **A2** are shown in Figure 4 as well as the AFM image of

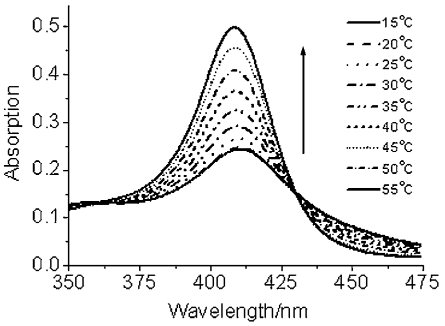


Figure 3. Absorption spectral changes of **C2** ([**G2**] = 5×10^{-6} M) in phosphate buffer solution (pH 7.2, 0.1 M) as a function of temperature. The measurements were carried out in 5 °C steps from 15 to 55 °C.

C1. Employing **H1** and **G1** as building blocks, the resultant **C1** presents many equally distributed nanoparticles, whereas employing **H2** and **G1** as building blocks, the resultant **A1** presents the 2D planar netlike morphology with a size in the micron range. Moreover, **A2** fabricated from **H2** and **G2** tectons shows the morphology of a 1D linear array with a length over 10 μm. All these three nanostructures have average heights of 1.5–1.7 nm, which is identical to the vertical height of the pentamer of five aggregated porphyrins[25a] and the size of *p*-sulfonatocalix[5]arenes.[42] The topological configurations of **A1** and **A2** are also validated by SEM measurements, further indicating the flakelike and fiberlike aggregations of **A1** and **A2** (Figure 5).

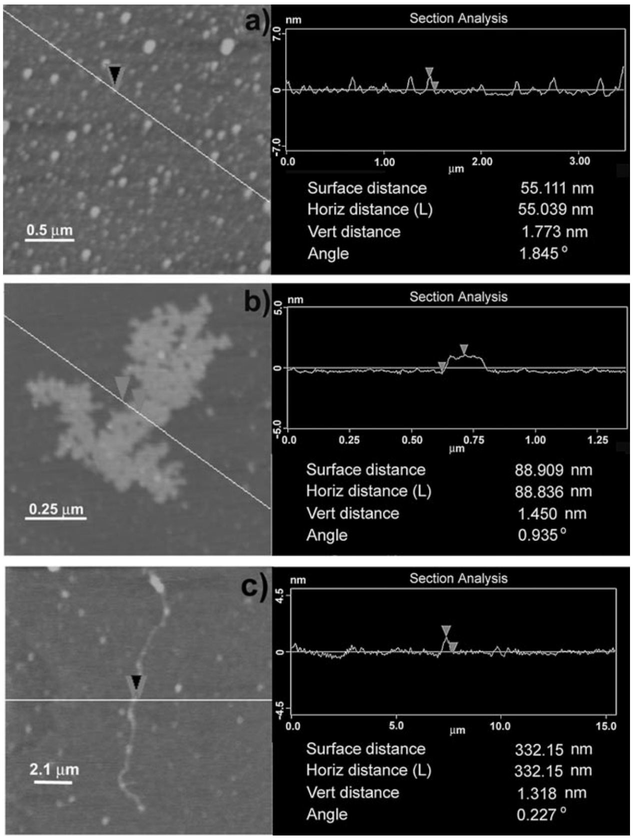


Figure 4. AFM images of **C1** (a), **A1** (b) and **A2** (c).

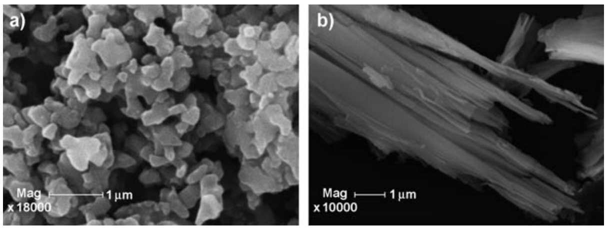


Figure 5. SEM images of **A1** (a) and **A2** (b).

Combining the AFM and SEM results together with the aforementioned UV/Vis results, we reasonably proved the self-assembly models between calixarenes and porphyrins (Scheme 2). These results undoubtedly demonstrate that the lower-rim bridged **H2** provides an excellent pre-organized structure to construct highly complex supramolecular nanoarchitectures rather than simple inclusion complexes of **H1** upon complexation with porphyrin guests. The design of a bis-calixarene building block **H2** with two cavities bridged at the lower-rim leads to the formation of nanoscale assemblies with higher dimensions, whereas **H1** forms exclusively complexed particles and no larger structures are observed. Moreover, the porphyrin guests with two or four pyridinium groups can precisely control the topologies of the supramolecular nanoarchitectures corresponding to the molecular design. Upon complexation with **H2**, **G1** with four pyridinium sites at all orientations enables the construction of 2D networks, while **G2** with two pyridinium sites of *trans* geometry adapts to construct long, linear chains.

Elemental and TG Analyses

The solid-state supramolecular complexes/aggregates are easily synthesized by neat addition and cooperative stoichiometric precipitation with high purity. Both calixarenes **H1**, **H2**, and porphyrins **G1** and **G2** are highly water-soluble. However, when the aqueous solutions of calixarene and porphyrin were mixed together, the complex species (**C1**, **C2**, **A1**, **A2**) can be obtained by collecting the precipitations because all of them are only slightly soluble in water. The identification results by elemental and thermogravimetric (TG) analysis are in good accordance with the Job plots obtained by UV/Vis spectroscopy. The results of element analysis also identified the binding stoichiometries between calixarenes and porphyrins in the solid-state complex species. All four complex species are water-rich (weight percentage 13–21 %), which corresponds to the single-crystal complexes of tetrakis(hydroxycarbonylmethoxy) derivative of *p*-sulfonatocalix[4]arene with **G1**.[25a] TG measurements (Figure S7 of the Supporting Information) also prove the high water percentages of the obtained complexes/aggregates by analyzing their weight loss from 25 °C to 350 °C, a region in which neither calixarenes nor porphyrins decompose. It is noticed that most of the water molecules are lost after heating samples up to 300 °C, which indicates that the complex species show strong adsorbability to water molecules although their water-solubility is poor.

Electron Transfer Properties of the Supramolecular Nanoarchitectures

Fluorescence Studies

The fluorescence titrations of porphyrins with calixarenes were first performed in phosphate buffer solution (pH 7.2, 0.1 M), and the representative fluorescence changes of **G2** with **H2** are shown in Figure 6. Differing from the UV/Vis titrations, the fluorescence of porphyrins is quenched continuously upon gradual addition of calixarenes. An excess of calixarenes did not give rise to a recovered fluorescence of porphyrins but further quenched it almost to completion, which indicates that the quenching of fluorescence is mainly ascribed to the host–guest interactions between calixarenes and porphyrins besides the aggregation of porphyrins. Moreover, there is no appreciable bathochromic/hypsochromic shift on the fluorescent emission wavelengths of the porphyrins. The suggestion that fluorescence quenching of porphyrins arises from energy transfer can be disregarded because the emission bands of porphyrins (ca. 600–800 nm) do not overlap with the absorption bands of calixarenes (280 and 288 nm). The fluorescence quenching is then ascribed to two possible reasons: one is the electron transfer from the calixarene moieties to the excited porphyrins;[21b] the other is the hydrogen-atom abstraction from the phenolic hydroxyl groups of calixarenes to the nitrogen atoms on the porphyrin ring.[43] The possibility of the latter was rationally excluded by the control experiment of zinc porphyrin (**G1**·Zn) with calixarene host **H2** (Figure S 9 of the Supporting Information). Upon addition of **H2**, the fluorescence of **G1**·Zn was also extensively quenched although there has been no protonation site available in **G1**·Zn. In this regard, the photoinduced electron transfer (PET) in the complex species can be therefore postulated.

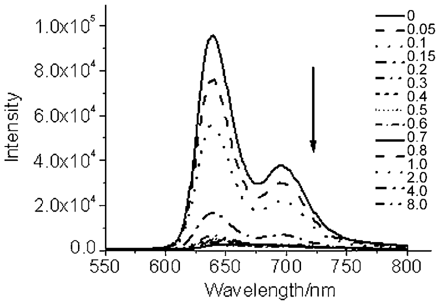


Figure 6. Fluorescence titration of **G2** with **H2** in phosphate buffer solution (pH 7.2, 0.1 M), [**G2**] = 5×10^{-6} M, [**H2**] from 0 to 4×10^{-5} M (8 equiv), $\lambda_{ex}=406$ nm.

To further demonstrate the electron-transfer process existing in the supramolecular complexes/aggregates, time-resolved fluorescence measurements were adopted to inspect the changes of the fluorescence lifetimes of porphyrins before and after complexation with calixarenes. The fluorescence emissions of **C2** and **A2** are so weak that their fluorescence lifetimes can hardly be obtained. Taking the **C1** and **A1** cases as examples, **G1** gives a single lifetime of 4.89 ns ($\chi^2=1.2$), while **C1** and **A1** give two lifetimes (Figure S 10 of the Supporting Information), 5.98 ns and 2.60 ns ($\chi^2=1.0$) for **C1**, and 5.84 ns and 2.17 ns ($\chi^2=1.2$) for **A1**. The presence of the short lifetimes of about 2 ns adequately proved that the electron-transfer process from calixarenes to porphyrin occurred in the **C1** and **A1** systems upon light excitation.

Electrochemical Measurements

The electrochemistry experiments were performed to obtain the oxidation potentials (E_{ox}) of electron donors (**H1** and **H2**) and reduction potentials (E_{red}) of electron acceptors (**G1** and **G2**), which can be used to assess the probability of an electron-transfer reaction. In the phosphate buffer solution (pH 7.2, $I=0.1$ M), **H1** and **H2** present the oxidation processes with half-wave potentials of 0.75 V and 0.98 V (vs Ag/AgCl), and **G1** and **G2** present the reduction processes with half-wave potentials of −0.50 V and −0.67 V, respectively, as shown in Figure S 11 of the Supporting Information.

The Gibbs free energy ΔG_{PET} of an electron-transfer reaction can be estimated according to the Rehm–Weller equation [Eq. (1)],

$$\Delta G_{\mathrm{PET}} = e(E_{\mathrm{ox}} - E_{\mathrm{red}}) - E_{00} - \frac{e^2}{\varepsilon d} \tag{1}$$

in which E_{00} is the excited singlet energies of porphyrins, e is the electron charge in Coulomb, d is the distance between the electron donor and acceptor, and ε is the dielectric constant of the phosphate buffer solutions (close to that of water). Considering that ε of water is a large value and that e^2 itself is small, the last term in Equation (1) can be neglected in the estimation. The E_{ox} and E_{red} values are the oxidation potentials of calixarenes and the reduction potentials of porphyrins, respectively. E_{00} values can be calculated from the maximum emission wavelengths of porphyrins, 712 nm for **G1** and 639 nm for **G2**. Therefore, with these known parameters E_{ox}, E_{red}, and E_{00}, ΔG_{PET} can be calculated according to the Rehm–Weller equation, and the corresponding data for each electron-transfer system are listed in Table 1.

The negative ΔG_{PET} values in the supramolecular calixarene–porphyrin systems account for the theoretical basis of the PET process. Taking the **G1** cases as examples, the electron-transfer processes in **C1** and **A1** can be illustrated in the energy level diagram based on the calculated results as shown in Figure 7.

Upon irradiation with light, one electron of the porphyrins is excited from the ground state to a singlet excited state, and usually, in the absence of calixarenes, it would relax back to the ground state accompanied with fluorescence emission. However, in the supramolecular calixarene–porphyrin systems, a much more energetically favorable pathway exists involving the electron of the calixarenes transferring to the empty ground-state orbital of the por-

Table 1. Gibbs Free Energy changes ΔG_{PET} of Photoinduced Electron Transfer in the supramolecular complexes/aggregates and related parameters (E_{ox} and E_{red} are measured versus Ag/AgCl in V, and E_{00} and ΔG_{PET} are expressed in eV).

	E_{ox}	E_{red}	E_{00}	ΔG_{PET}
C1	0.75	−0.50	1.75	−0.50
A1	0.98	−0.50	1.75	−0.27
C2	0.75	−0.67	1.95	−0.53
A2	0.98	−0.67	1.95	−0.30

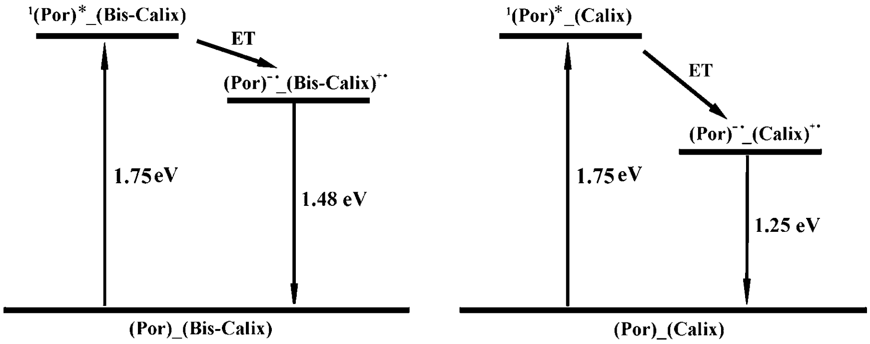


Figure 7. Energy level diagram of the PET processes in **C1** and **A1**, in which ET represents the electron transfer.

phyrins rather than radiation relaxation of porphyrins. The electron-transfer process gives rise to the charge-separated state of the complexes/aggregates, and the metastable species will subsequently disappear by undergoing a charge-recombination process, in which the electron of the porphyrin in the excited state transfers in turn to the ground state orbital of the calixarene. Moreover, the electron-transfer process as the dominant relaxation pathway proceeds quicker than the corresponding photon-emission process, and thereby the fluorescence of porphyrins is quenched to a great extent in the supramolecular complexes/aggregates.

Triplet Transient Absorption Spectra

The deactivation of the excited triplet state is also one important route to dissipate the energy of the singlet excited porphyrins, and therefore the triplet transient absorption spectra were measured to investigate the quenching process of porphyrin fluorescence. The obtained spectra of **G1**, **C1**, and **A1** are shown in Figure 8. **G1** exhibit a broad absorption band in the 450–800 nm with the maximum at 470 nm, and concurrently, a negative band (420 nm) caused by bleaching the ground-state absorption of porphyrin. However, in the complex species **C1** and **A1**, the triplet state absorption of **G1** was pronouncedly quenched, which indicates that the supramolecular **C1** and **A1** are much less likely to be excited to the triplet excited state, and it also confirms the existence of PET in the supramolecular calixarene–porphyrin systems as a preferable process.

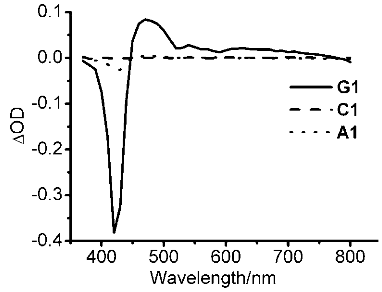


Figure 8. The triplet transient absorption spectra of **G1**, **C1** and **A1** obtained upon nanosecond flash photolysis (355 nm) in nitrogen saturated solutions.

Conclusions

In summary, we successfully construct two highly complex supramolecular nanoarchitectures with 2D netlike and 1D linear topological structures, by combining water-soluble bis(*p*-sulfonatocalix[5]arenes) and cationic porphyrins, respectively. Besides the precursory host–guest interactions, charge interactions also play a pivotal role in self-assembly, which make the supramolecular aggregates easily synthesized by neat addition and cooperative stoichiometric precipitation in high purity. The resultant nanostructures are well-ordered with definite size, shape, and dimensions, and can be precisely tuned by the design of complexation sites of hosts and guests. Furthermore, in these supramolecular systems, calixarenes and porphyrins act not only as the interacting tectons but also as the effective electron donor–acceptor pairs, and an unambiguous PET process is observed. As a consequence, the constructed supramolecular aggregates possess, in principle, benign photoelectric properties with transport of electrons between the building blocks in the nanoscale region. These results pave the way for ‘bottom-up’ assembly of supramolecular nanoarchitectures with potential future applications in artificial photosynthesis as well as engineering molecular electronics and optoelectronics.

Experimental Section

Materials

5,10,15,20-tetrakis (N-methyl-4-pyridyl) porphyrin (**G1**) was purchased from Sigma–Aldrich. 5, 15-di(N-methyl-4-pyridyl) porphyrin (**G2**)[44] and *p*-sulfonatocalix[5]arene (**H1**) were synthesized and purified according to the literature procedures.[36] Other chemicals and solvents were commercially available. Column chromatography was performed on silica gel (200–300 mesh). The phosphate buffer solution (pH 7.2, 0.1 M) was prepared by dissolving disodium hydrogen phosphate ($Na_2HPO_4{\cdot}12H_2O$, 25.79 g) and sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}2H_2O$, 4.37 g) in distilled, deionized water (1000 mL). The pH value of the buffer solution was verified on a Sartorius pp-20 pH meter calibrated with two standard buffer solutions.

Measurements

UV/Vis spectra were recorded in a conventional quartz cell (light path 10 mm) on a Shimadzu UV-2401PC spectrophotometer equipped with a PTC-348WI temperature controller to keep the temperature at 25 °C. Atomic force microscopy (AFM) was performed using a multi-mode IIIa AFM (Veeco Metrology, USA) in tapping mode in air at room temperature, and samples were prepared by dropping an aqueous solution on mica. SEM images were recorded on a HITACHI S-3500N scanning electron microscope. The thermogravimetric analysis was recorded with a RIGAKU Standard type TG analyzer with a heating rate of $10\,°\mathrm{C\,min^{-1}}$ from room temperature to 800 °C. The steady-state fluorescence spectra were recorded on an Edinburgh Analytical Instruments FLS920 (Edinburgh Instruments) spectrometer, equipped with a Xe900 450W steady-state xenon arc lamp and Red PMT with cooled housing, in a 10 mm quartz cell at 25 °C. The fluorescence lifetime measurements were performed on the same instrument equipped with an NF900 nanosecond flash lamp, using the time correlated single-photon-counting (TCSPC) method. Typically, 5000 or 10000 counts were collected at the peak channel, and the decay curves were fitted by least-squares deconvolution with original Edinburgh Instrument software; the quality of the parameters were judged by the reduced χ^2 values and the randomness of the weighted residuals. The cyclic voltammetry (CV) measurements were carried out on a BAS Epsilon electrochemical analyzer with C3-cell stand. All solutions were prepared in phosphate buffer (pH 7.2, 0.1 M) at 25 °C, and deoxygenated by purging with dry nitrogen for at least 15 min before each experiment. The glassy carbon working electrode was polished to a mirror with 0.05 μm BAS alumina suspension on a brown texmet polishing pad, sonicated in distilled water for a few minutes to remove any residual alumina particles and then rinsed with ethanol before usage. A platinum wire was used as the counter electrode. The measured potentials were recorded with respect to an Ag/AgCl (immersed in a solution containing 3 M sodium chloride) reference electrode. Nanosecond transient absorption spectra were performed on an LP-920 pump–probe spectroscopic setup. The excitation source was the unfocused third harmonic 355 nm output of a Nd:YAG laser (10 Hz, 8 ns) (Continuum surelite II); the probe light source was a pulse-xenon lamp. The signals were detected by Edinburgh analytical instruments (LP900) and recorded on a Tektronix TDS 3012B oscilloscope and a computer.

Synthesis

Bis(*p*-H-calix[5]arenes): *p*-H-calix[5]arene (530 mg, 1.0 mmol) and K_2CO_3 (138 mg, 1.0 mmol) were added to anhydrous acetonitrile to reflux for 0.5 hr. Subsequently, $TsOCH_2CH_2OTs$ (160 mg, 0.43 mmol) was added and the solution was refluxed for another 48 hrs. After being cooled and filtered, the solution was dried under reduced pressure. The solid obtained was subjected to a column spectrum (CH_2Cl_2). The white powder of pure bis(*p*-H-calix[5]arenes) (216 mg, 40 %) was obtained. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.80$ (s, 4H, ArOH), 7.60 (s, 4H, ArOH), 7.22–7.02 (m, 20H, ArH), 6.93–6.73 (m, 10H, ArH), 4.61–4.48 (m, 8H, $ArCH_2Ar$ and OCH_2CH_2O), 3.82–3.34 ppm (m, 16H, $ArCH_2Ar$); elemental analysis: calcd (%) for $(C_{72}H_{62}O_{10})\cdot(CH_2Cl_2)$: C 74.80, H 5.50; found: C 75.20, H 5.70.

Bis(*p*-sulfonatocalix[5]arenes) (H2): **H2** was obtained according to the procedure similar to literature process.[37e] Bis(*p*-H-calix[5]arenes) (542 mg, 0.5 mmol) conc. H_2SO_4 (3 mL, 98 %) was stirred at 50 °C for 24 hrs. After being cooled to room temperature, the solution was added to diethyl ether dropwise, and the resulting solid was obtained by filtration and washed twice with diethyl ether. The crude product in sulfonic acid form was dissolved in a little water (10 mL), and the solution was adjusted to pH 5 by titration with sodium hydroxide (1 M). Treatment of the crude solution with ethanol precipitated the sodium sulfonate of bis(calix[5]arenes), followed by recrystallization with water/ethanol and dried under vacuum overnight, giving the pure product of **H2** (932 mg, 75 %). ^{1}H NMR (D_2O, 400 MHz): $\delta = 7.58$–7.30 (m, 20H, ArH), 4.53–4.47 (m, 8H, $ArCH_2Ar$ and OCH_2CH_2O), 3.80–3.37 ppm (m, 16H, $ArCH_2Ar$). Elemental analysis: calcd (%) for $(C_{72}H_{52}O_{40}S_{10}Na_{10})\cdot(H_2O)_{21}\cdot(H_2SO_4)_2$: C 32.24, H 3.68; found: C 31.93, H 3.52; Atomic Absorption Spectrophotometer (AAS): calcd (%) for $(C_{72}H_{52}O_{40}S_{10}Na_{10})\cdot(H_2O)_{21}\cdot(H_2SO_4)_2$: Na 8.57; found: 8.85.

Supramolecular Complex C1: **H1** (10.4 mg, 0.01 mmol) and **G1** (13.6 mg, 0.01 mmol) was each dissolved in distilled, deionized water (3 mL). The two solutions were mixed and stirred for 2 hrs, giving a brown precipitate of complex **C1**. The precipitate was separated by centrifugation, washed with water twice and dried under vacuum at 60 °C, and was further characterized by AFM, TG, and elemental analysis. Elemental analysis: calcd (%) for $(C_{35}H_{25}O_{20}S_5)_4\cdot(C_{44}H_{38}N_8)_5\cdot(H_2O)_{87}$: C 49.90, H 5.40, N 6.47; found: C 50.46, H 5.93, N 6.15.

Supramolecular Aggregate A1: **H2** (13.4 mg, 0.005 mmol) and **G1** (13.6 mg, 0.01 mmol) were each dissolved in distilled, deionized water (3 mL). The two solutions were mixed and stirred for 2 hrs, giving a brown precipitate of aggregate **A1**. The precipitate was separated by centrifugation, washed with water twice and dried under vacuum at 60 °C, and was further characterized by AFM, SEM, TG, and elemental analysis. Elemental analysis: calcd (%) for $(C_{72}H_{52}O_{40}S_{10})_2\cdot(C_{44}H_{38}N_8)_5\cdot(H_2O)_{105}$: C 48.36, H 5.62, N 6.20; found: C 48.65, H 5.58, N 6.69.

Supramolecular Complex C2: **H1** (10.4 mg, 0.01 mmol) and **G2** (16.9 mg, 0.02 mmol) were each dissolved in distilled, deionized water (3 mL). The two solutions were mixed and stirred for 2 hrs, giving a brown precipitate of complex **C2**. The precipitate was separated by centrifugation, washed with water twice and dried under vacuum at 60 °C, and was further characterized by TG and elemental analysis. Elemental analysis: calcd (%) for $(C_{35}H_{25}O_{20}S_5)_2\cdot(C_{32}H_{26}N_6)_5\cdot(H_2O)_{35}$: C 55.75, H 5.09, N 8.48; found: C 55.13, H 5.73, N 8.63.

Supramolecular Aggregate A2: **H2** (13.4 mg, 0.005 mmol) and **G2** (21.1 mg, 0.025 mmol) was each dissolved in distilled, deionized water (3 mL). The two solutions were mixed and stirred for 2 hrs, giving a brown precipitate of aggregate **A2**. The precipitate was separated by centrifugation, washed with water twice and dried under vacuum at 60 °C, and was further characterized by AFM, SEM, TG, and elemental analysis. Elemental analysis: calcd (%) for $(C_{72}H_{52}O_{40}S_{10})\cdot(C_{32}H_{26}N_6)_5\cdot(H_2O)_{42}$: C 54.56, H 5.25, N 8.23; found: C 54.58, H 5.71, N 8.69.

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