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Clawlike Tripodal Porphyrin Trimer: Ion-Controlled On−Off Fullerene Binding

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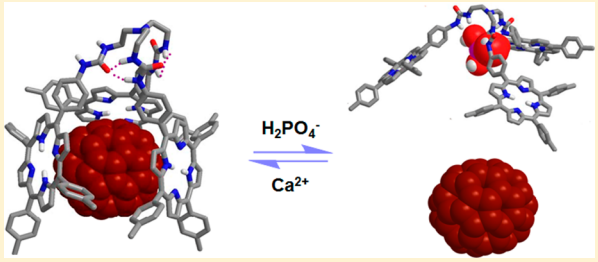
Supporting Information

ABSTRACT: A practical method for the preparation of novel tripodal tris(porphyrinato-urea) **TP$_3$ 1** was readily achieved. Because of its appreciable preorganized triangular cone-shaped cavity resulting from the intramolecular hydrogen bonds of the tripodal tris-urea backbone, this porphyrin trimer host was found to have a high affinity toward fullerenes to form stable inclusion complexes in solution. A 120-fold binding selectivity toward C_{70} (K_{assoc} = 1.81 × 10^7 M^{-1}) over C_{60} (K_{assoc} = 1.51 × 10^5 M^{-1}) was further achieved in toluene. Moreover, the dissociation of such inclusion complexes can be easily realized by introducing $H_2PO_4^-$, and recapturing of the fullerene can be achieved after withdrawing $H_2PO_4^-$ by Ca^{2+}. A recyclable process for the inclusion and release of fullerene was therefore built by alternately feeding $H_2PO_4^-$ and Ca^{2+}. Benefiting from this approach, **TP$_3$ 1** was sequentially applied to isolate C_{70} from the C_{60}-enriched fullerene mixture successfully.



INTRODUCTION

Porphyrins and fullerenes, owing to their characteristic structural features, have attracted great interest and have been widely applied in host−guest chemistry,[1] artificial photosynthesis,[2] and pharmaceutical and biological science.[3−7] Porphyrins, which possess a highly delocalized π-electron-rich system, have been extensively used as π hosts for electron-deficient molecules, especially for fullerenes, which have excellent electron-accepting characteristics.[1,8] Enormous functional porphyrin−fullerene assemblies have been constructed through covalent and noncovalent pathways.[9] Owing to its high efficiency in mimicking natural photosystems as well as its potential application in the separation and purification of fullerene, achieving assemblies of porphyrins and fullerenes by supramolecular organization has been actively studied during recent decades.[10,11]

Host molecules with a single porphyrin unit were first introduced to interact with fullerenes, but the donor−acceptor complexes can be obtained only in the solid state and quickly dissociate in solution.[12−14] Receptors consisting of two porphyrin subunits were subsequently explored and found to be more suitable to form stable complexes both in solution and in solid state. Many acyclic bisporphyrin hosts with a variety of scaffolds and linkers were prepared,[15−19] and the binding affinity was significantly enhanced. A more efficient binding interaction has been further observed in cyclic bisporphyrins by Aida[20,21] and Zhang.[22] The suitable preorganized cavity, which is hardly accomplished in the acyclic porphyrin system, was considered to be the most crucial reason for extremely high binding constant.

With the aim of obtaining higher affinity toward fullerenes and overcoming the structural constraints, receptors with three or more porphyrin subunits were also designed.[23−29] Anderson reported a rigid cyclic porphyrin trimer that showed a higher affinity toward fullerenes than a cyclic zinc porphyrin dimer, indicating a positive influence of the third porphyrin unit on binding fullerenes.[23] Other porphyrin-containing hosts have also been synthesized by means of tridentate[24] and four-coordinate[25] complexes, metal-coordinate self-assemblies,[26] complex of tripodal porphyrin trimer,[27] and porphyrin nanobarrel.[28] Although many excellent porphyrin-based hosts have been reported to encapsulate fullerene,[15−30] the syntheses of such receptors are usually low efficiency and time-consuming and thus inevitably face a lack of methods to realize their large-scale preparation. The design of novel porphyrin host to balance its high affinity and easy access is still a challenge.

Because of its commercial availability and excellent multi-hydrogen-bond self-assembly property, tripodal tris(2-aminoethyl) amine (TREN)-based tris-urea receptors with functional arms have been widely utilized as anion-selective sensors and coordinated ligands. Small molecules such as benzene,[31,32] pyridine,[33] naphthalene,[34] and ferrocene[35] have been involved in such arm design. However, a larger chromophore is seldom considered as a functional arm. As a continuous focus on the porphyrinoids,[36−38] herein, we combined a TREN-based tris-urea backbone and porphyrin arm as a new strategy for designing a fullerene receptor, which resulted in a stable and clawlike π-electron-rich cavity to capture an electron-deficient

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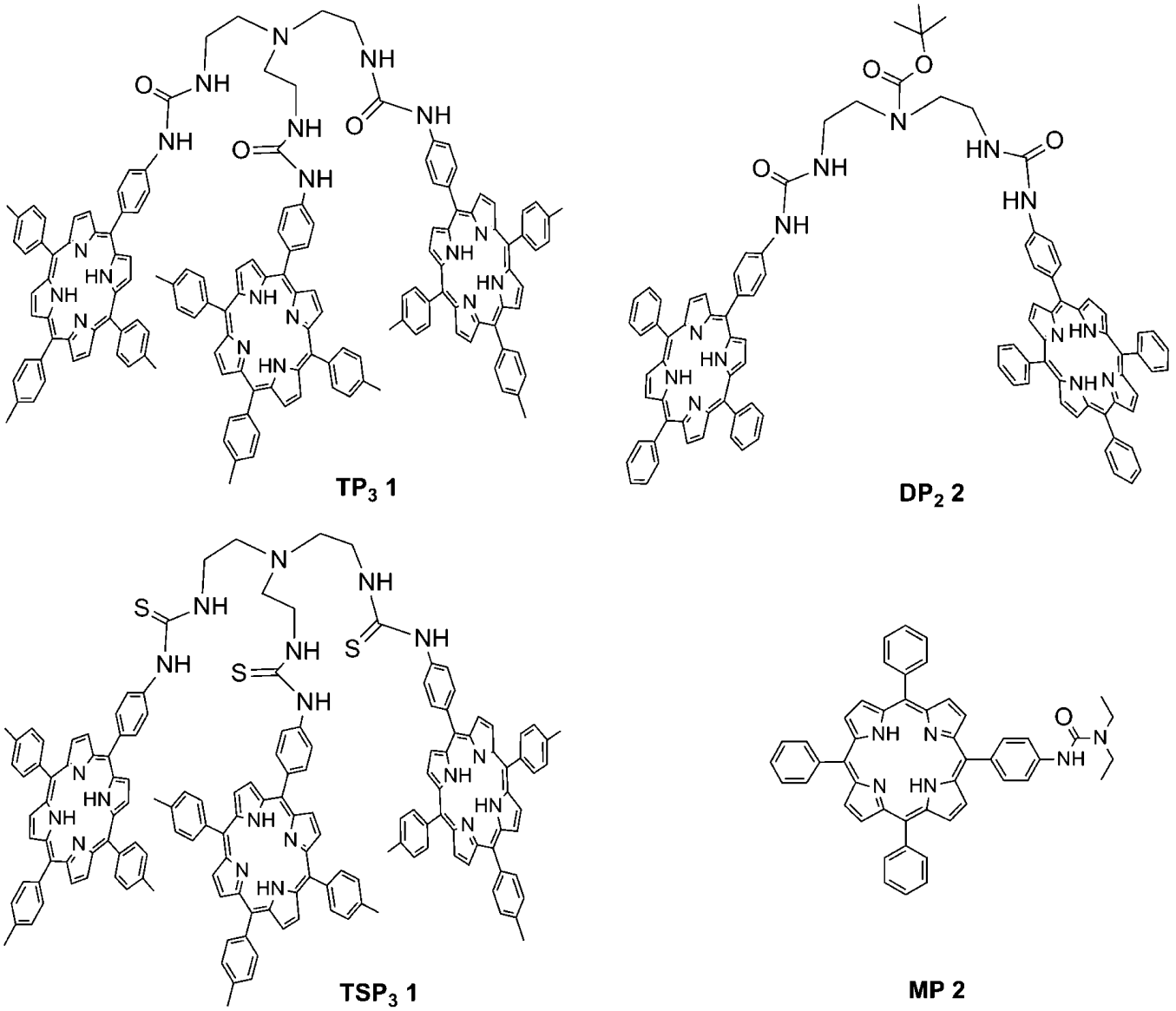
Scheme 1. Structures of TP_3 1, TSP_3 1, DP_2 2, and MP 2



Scheme 2. Synthesis of Porphyrin Host TP_3 1

guest. The tunable anion-binding cavity of TREN-based tris-urea will further benefit the host to realize ion-controlled guest binding.

In this article, simple porphyrin trimer **TP_3 1** (Scheme 1) was synthesized with readily accessible 5-(4-aminophenyl)-10,15,20-tris(4-methylphenyl)-porphyrin and commercial TREN in high yield (Scheme 2). The one-pot two-step procedure under mild conditions will facilitate its large-scale preparation. Two more obvious advantages make it a good candidate to interact with fullerene. The conformational

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preorganization through the intramolecular hydrogen bonds of the urea units will promote the interaction between porphyrin and fullerene via a 3D cooperative effect, further benefiting the stabilization of the complex. In addition, the cone cavity resulting from the hydrogen-bonding-driven preorganization of the tripodal tris-urea structure can be adjusted because of its reported strong oxoanion-binding preference,[31−35] which will provide an easy way to realize the controllability of the fullerene inclusion.

RESULTS AND DISCUSSION

Properties of UV−Vis and Fluorescence Titration. Compound **TP$_3$ 1** has been observed to show one typical Soret-band and four Q-bands, similar to the free-base porphyrin precursor (Figure 1). Accompanying the introduction of

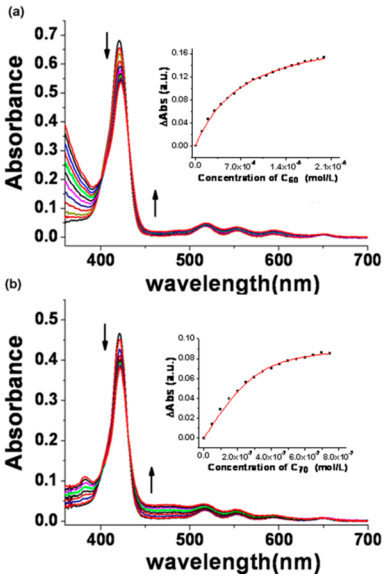

Figure 1. UV−vis titration spectra in toluene at 25 °C of (a) **TP$_3$ 1** (0.5 μM) with 0−20 equiv C_{60} (the inset shows the plot of $\Delta_{421\ nm}$ equiv of C_{60} added) and (b) **TP$_3$ 1** (0.3 μM) with 0−2.5 equiv C_{70} (the inset shows the plot of $\Delta_{421\ nm}$ equiv of C_{70} added).

fullerenes is a red shift of the electronic absorption band and an obvious isosbestic point, revealing a strong binding interaction between **TP$_3$ 1** with fullerenes. However, the reference compounds, dimeric host **DP$_2$ 2** and monomeric host **MP 2** (Scheme 1), show no obvious $\pi-\pi$ interaction with C_{60}/C_{70} under the same titration conditions (Figures S21 and S22 in the Supporting Information), which indicates that the TREN tris-urea linker is important to construct and stabilize the inclusion complexes (fullerene@**TP$_3$ 1**). Moreover, tris-(porphyrinato-thiourea) host **TSP$_3$ 1** (Scheme 1), which only replaced the carbon−oxygen double bonds of urea in **TP$_3$ 1** with carbon−sulfur double bonds, also displays no apparent $\pi-\pi$ interaction with C_{60}/C_{70} (Figures S23 and S24 in the Supporting Information). The weaker hydrogen-bonding tendency of the carbon−sulfur double bond makes it more difficult for **TSP$_3$ 1** to form an effective preorganization similar to **TP$_3$ 1**; thus, it takes on a relatively loose and random conformation. The aforementioned control experiments indicate that the preorganization resulting from the intramolecular hydrogen bonds of the tripodal tris-urea backbone in **TP$_3$ 1** is very critical for its binding ability toward fullerenes. This result is similar to that of the fullerene-directed supramolecular peapods consisting of six carboxylic acid functionalities.[39]

The detailed binding behaviors of **TP$_3$ 1** with C_{60} and C_{70} were characterized by UV−vis titration experiments in toluene (Figure 1). In the typical experiment, 0.5 μM solutions of **TP$_3$ 1** were titrated against a solution of C_{60} with progressive concentrations (0−20.0 equiv) at room temperature. A decrease of absorption at 421 nm and a slight bathochromic shift of the Soret band with a tight observable isosbestic point (431 nm) suggest a real $\pi-\pi$ interaction between **TP$_3$ 1** and C_{60}. The Job's plot analysis shows that a 1:1 complex has been constructed (Figure S18 in the Supporting Information). The association constant (K_{assoc}) of complex C_{60}@**TP$_3$ 1** was then estimated to be 1.51(0.03) × 10^5 M^{-1} (Table 1), which was subjected to standard nonlinear (1:1 mode) curve-fitting analysis (Figure 1a, inset).

Table 1. Association Constants for Fullerenes[a]

host	$K_{C_{60}}$ (M^{-1})	$K_{C_{70}}$ (M^{-1})	$K_{C_{70}}/K_{C_{60}}$
TP$_3$ 1	1.51(0.03) × 10^5	1.81(0.27) × 10^7	120
TSP$_3$ 1[b]			
DP$_2$ 2[b]			
MP 2[b]			

[a]Measured by UV−vis spectroscopy (see Supporting Information). [b]These demonstrated small spectral changes and were difficult to nonlinear fit from the collected data.

Similar spectroscopic changes were also observed in the titration with C_{70}. Owing to the greater variation than that of C_{60}, a lower feeding amount of C_{70} was added in each portion. Aliquots of C_{70} were added (up to 2.5 equiv) to a constant concentration of **TP$_3$ 1** (0.3 μM), and the association constant of complex C_{70}@**TP$_3$ 1** was evaluated to be 1.81(0.27) × 10^7 M^{-1}, which is approximately 120-fold higher than C_{60} (Table 1). Although the observed selectivity of C_{70}/C_{60} is not the best one compared to the reported cases,[19−23,40] the coexistence of high association constants and good selectivity will benefit its application in practical fullerene separation. UV−vis competition experiments were further carried out to understand the selectivity, and the results are shown in Figure 2. After a stable complex of C_{60}@**TP$_3$ 1** was shaped (Figure 2a), 0−1.6 equiv of C_{70} was added. The displacement of C_{60} by C_{70} was clearly observed, with an obvious decrease of the Soret band at 421 nm (Figure 2b). The specific isosbestic point at 429 nm indicated that the stable state of C_{60}@**TP$_3$ 1** was broken and another complex, C_{70}@**TP$_3$ 1**, was formed. In sharp contrast, the introduction of 0−10 equiv of C_{60} to the C_{70}@**TP$_3$ 1** solution resulted in no obvious change (Figure 2c,d). The fluorescence determinations (both excited at their isosbestic points) demonstrate a greater quenching of the excited state of porphyrin by C_{70} than C_{60} (Figure 3), which also verifies the binding selectivity.

Ion-Controlled Experiments. In view of the key role of the tripodal tris-urea backbone observed in the contrast experiments as well as its reported good potential application in ion binding, an attempt at the ion-controlled inclusion and release of fullerenes was carried out (Figure 4a−c). When 2 equiv of $H_2PO_4^-$ (as the tetrabutylammonium salt) was introduced into the mixture of **TP$_3$ 1** and C_{70}, the quenched emission of porphyrin by C_{70} (Figure 4a) was found to be significantly recovered (Figure 4b). In contrast, **TP$_3$ 1** without binding fullerene shows little fluorescence quenching even

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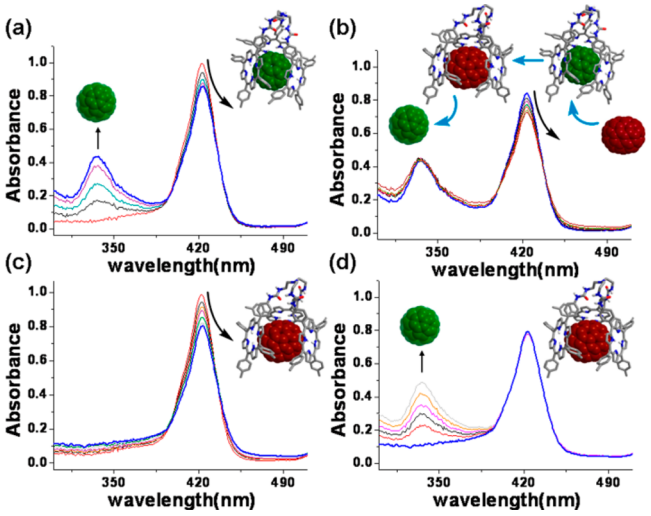

Figure 2. UV−vis titration spectra of competitive binding in toluene at 25 °C: (a) **TP$_3$ 1** (0.8 μM) + 0−10 equiv of C_{60}, (b) **TP$_3$ 1** (0.8 μM) + 10 equiv of C_{60} and then 0−1.6 equiv of C_{70}, (c) **TP$_3$ 1** (0.8 μM) + 0−1.6 equiv of C_{70}, and (d) **TP$_3$ 1** (0.8 μM) + 1.6 equiv of C_{70} and then 0−10 equiv of C_{60}.

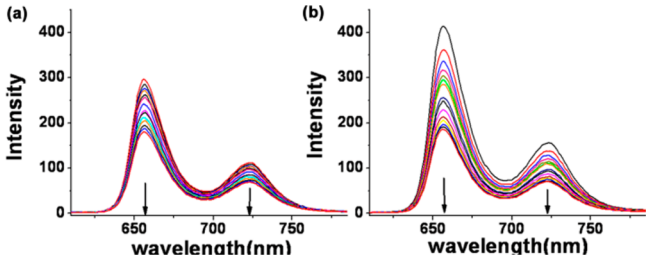

Figure 3. Fluorescence titration spectra in toluene at 25 °C: (a) **TP$_3$ 1** (0.4 μM, excited at 431 nm) with 0−60 equiv of C_{60} and (b) **TP$_3$ 1** (0.5 μM, excited at 429 nm) with 0−15 equiv of C_{70}.

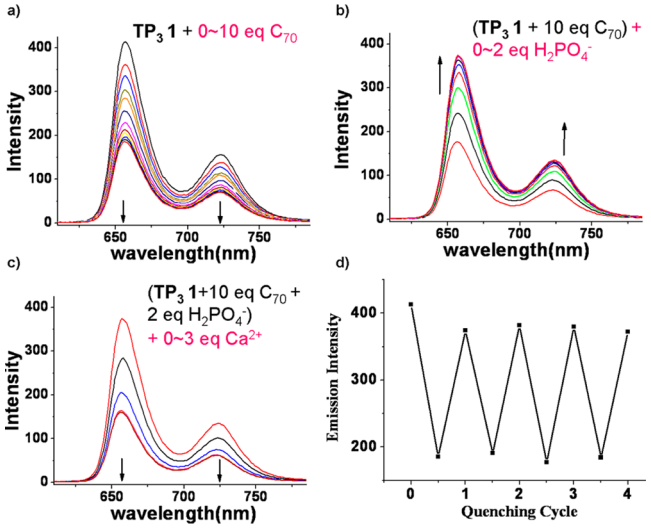

Figure 4. Fluorescence changes of **TP$_3$ 1** in toluene and ion-controlled on−off switch excited at 429 nm: (a) **TP$_3$ 1** (1.0 μM) + 0−10 equiv of C_{70}, (b) **TP$_3$ 1** (1.0 μM) + 10 equiv of C_{70} and then 0−2 equiv of $H_2PO_4^-$, and (c) **TP$_3$ 1** (1.0 μM) + 10 equiv of C_{70} + 2 equiv $H_2PO_4^-$ and then 0−3 equiv of Ca^{2+}. (d) Four continuous association−disassociation cycles were recorded at 657 nm (emission intensity).

when an excess amount of $H_2PO_4^-$ was added (Figure S25 in the Supporting Information). In consideration of the insolubility of $Ca(H_2PO_4)_2$, 3 equiv of Ca^{2+} (as perchlorate salt) was applied to withdraw $H_2PO_4^-$ and to regenerate the C_{70}@**TP$_3$ 1** complex (Figure 4c). A UV−vis titration experiment was also carried out to witness the on−off property (Figure S26a−c in the Supporting Information). Such spectroscopic distinction is most readily accounted for the formation of strong anion−urea intermolecular hydrogen bonds and the resulting expanded cavity of the host. The enlarged cavity leads to a complete dissociation of the porphyrin−fullerene complex and release of fullerene. To our delight, unlike the reported ion-assisted fullerene-encapsulation systems,[41] the association−dissociation process was found to be repeatable and can be realized in several cycles by alternately feeding $H_2PO_4^-$ and Ca^{2+} (Figure 4d). This reversible process is fast and highly efficient, which indicates an ion-controlled inclusion and release of fullerene was facilely achieved and could be potentially used as an ion-controlled on−off switch.

Properties of NMR Titration. The ^{1}H NMR spectrum of porphyrin trimer **TP$_3$ 1** shows several broad peaks at room temperature in non-hydrogen-bonding solvent such as toluene-d_8 (Figure 5a). These can be ascribed to the existence of many

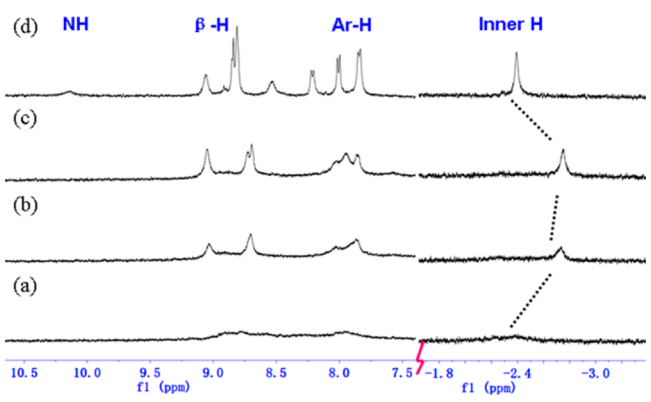

Figure 5. Partial ^{1}H NMR titration spectra (toluene-d_8, 298 K) of (a) **TP$_3$ 1** (1 mM), (b) **TP$_3$ 1** (1 mM) + 0.5 equiv of C_{60}, (c) **TP$_3$ 1** (1 mM) + 1.0 equiv of C_{60}, and (d) **TP$_3$ 1** (1 mM) + 1.0 equiv of C_{60} and then 1.0 equiv of $[H_2PO_4^-]\cdot[n\text{-}Bu_4N]^+$.

types of hydrogen bonds, for instance, intramolecular and intermolecular hydrogen bonds.[42] In DMSO-d_6, the broad peaks become distinctively sharp because the porphyrin trimer becomes more symmetrical and conformationally stable via strong hydrogen-bond interactions with DMSO molecules. To gain insight into the structures of the complexes and the control action, we performed ^{1}H NMR titrations in toluene-d_8. Indeed, the broad NMR pattern of **TP$_3$ 1** in toluene-d_8 became sharper when 0.5−1.0 equiv of C_{60} was added, indicating that a more symmetrical complex conformation was formed after the binding of C_{60} (Figure 5b,c). The inner proton signal of free-base porphyrin also became sharp and was accompanied by a significant upfield shift from −2.383 to −2.755 ppm ($\Delta\delta$ = −0.372 ppm) because of the influence of the fullerene ring current. Such an obvious upfield shift reveals the existence of strong $\pi-\pi$ interactions between C_{60} and the porphyrin panels of **TP$_3$ 1**. Subsequently, a more clear splitting and sharpening of the signals was observed upon adding 1.0 equiv of $H_2PO_4^-$ (as the tetrabutylammonium salt). The chemical shift of porphyrin

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inner protons reshifted from −2.755 to −2.392 ppm ($\Delta\delta$ = 0.363 ppm), providing additional strong evidence in support of the dissociation of the complex (Figure 5d). The association and dissociation of complex C_{60}@**TP_3 1** was also supported by ^{13}C NMR spectroscopy in toluene-d_8 (Figure 6). The spectrum

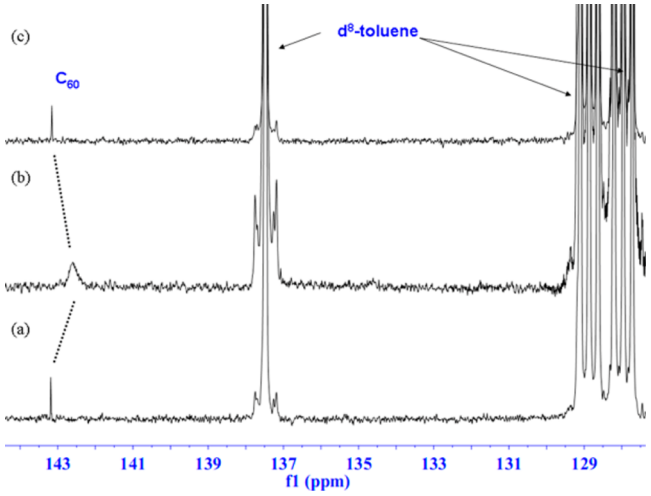

Figure 6. Partial ^{13}C NMR titration spectra (toluene-d_8, 298 K) of (a) C_{60} (1 mM), (b) **TP_3 1** (1 mM) + 1.0 equiv of C_{60}, and (c) **TP_3 1** (1 mM) + 1.0 equiv of C_{60} and then 1.0 equiv of $[H_2PO_4^-]\cdot[n\text{-}Bu_4N]^+$.

of the 1:1 solution of C_{60} and **TP_3 1** gave rise to a significant upfield shift from 143.185 (free C_{60}, Figure 6a) to 142.585 ppm (Figure 6b, $\Delta\delta$ = −0.600 ppm), which is attributed to the shielding effect of the porphyrin units. In addition, the broad signal of C_{60} reveals a highly constrained motion of C_{60} in the triangular cone cavity.[30] It is less surprising that the chemical shift of C_{60} was downfield shifted back to 143.158 ppm ($\Delta\delta$ = 0.573 ppm) when $H_2PO_4^-$ was further introduced into the solution (Figure 6c), which is consistent with the results of the ^1H NMR, UV−vis, and fluorescence spectra.

The competitive binding experiments were also recorded through ^{13}C NMR titration ($CDCl_3/CS_2$, v/v 1:1). The sharp signals of uncomplexed C_{60} and C_{70} (Figure 7a,e) were found to be broadened with an obvious upshift when the equivalent host was added (Figure 7b,d). One equiv of C_{70} was further fed into the mixture of **TP_3 1** and C_{60} to determine the competitive binding (Figure 7c). Broad signals of C_{70}, similar to that of the mixture of **TP_3 1** and C_{70}, were observed. Meanwhile, the signal of C_{60} became sharp again. This indicates that **TP_3 1** prefers binding C_{70} through a 1:1 mixture of C_{60} and C_{70}.

Theoretical Calculation. To gain deeper insight into the preorganized cone cavity of host **TP_3 1** and its binding selectivity for fullerenes, the optimized structures are calculated with Gaussian03 at the B3LYP/3-21G* level.[43,44] Host **TP_3 1** shows a cone cavity (Figure 8a,b), which is constructed and stabilized by three obvious intramolecular hydrogen bonds between the C═O and NH functions of the urea units. The hydrogen-bond distances were estimated to be 1.83, 2.07, and 1.93 Å. Meanwhile, the existence of another hydrogen bond (3.28 Å, 120°) indicates that one porphyrin moiety adopts a distortion model to ease the steric burden and resulted in a preorganized cone cavity. In spite the existence of a well-ordered C_{3v} symmetrical structure in both supramolecular complexes toward C_{60} and C_{70}, C_{70}@**TP_3 1** (Figure 8c) adopts a more rigid tripodal conformation compared to C_{60}@**TP_3 1** (Figure 8d). Similar to the free **TP_3 1**, three typical intramolecular hydrogen bonds (1.83, 2.07, and 1.93 Å) and a more loose one (3.30 Å) were observed in C_{70}@**TP_3 1**, in contrast to two hydrogen bonds with 1.91 and 2.21 Å in C_{60}@**TP_3 1**. Moreover, the minimum distances between the three porphyrin planes and C_{70} (3.03, 3.16, and 3.22 Å) are obviously shorter than those in C_{60}@**TP_3 1** (3.06, 3.33, and 3.40 Å). The closer distance reveals a stronger $\pi-\pi$ interaction between

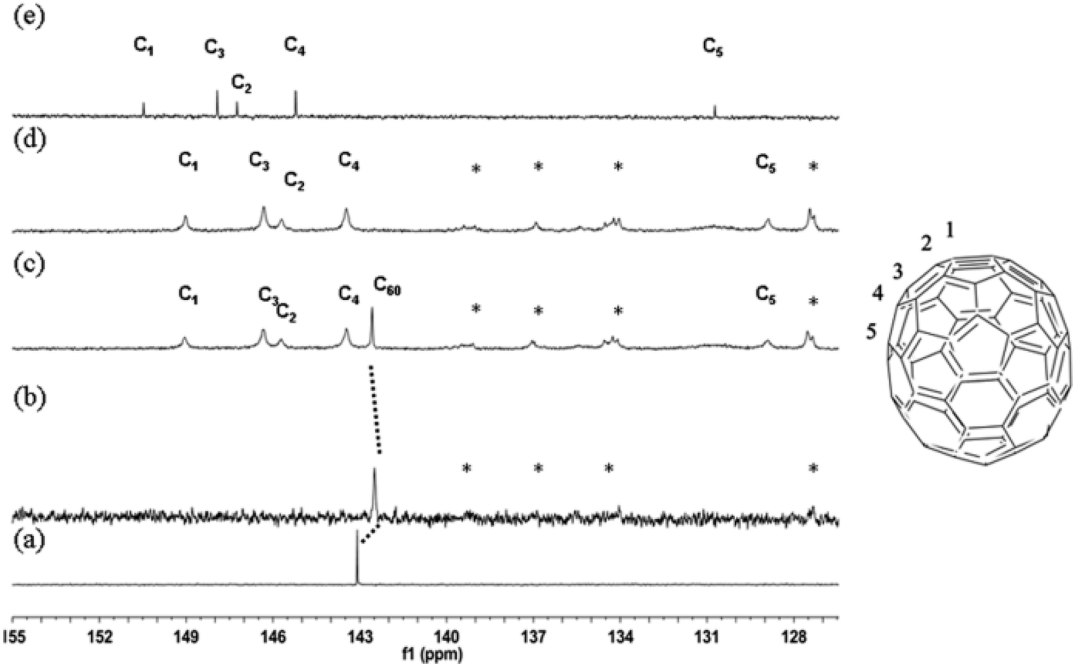

Figure 7. Partial ^{13}C NMR titration spectra ($CDCl_3/CS_2$, v/v 1:1, 298 K) of (a) C_{60} (1 mM), (b) **TP_3 1** (1 mM) + 1.0 equiv of C_{60}, (c) **TP_3 1** (1 mM) + 1.0 equiv of C_{60}, then 1.0 equiv of C_{70}, (d) **TP_3 1** (1 mM) + 1.0 equiv of C_{70}, and (e) C_{70} (1 mM). (The asterisks represent partial ^{13}C NMR signals of **TP_3 1**.)

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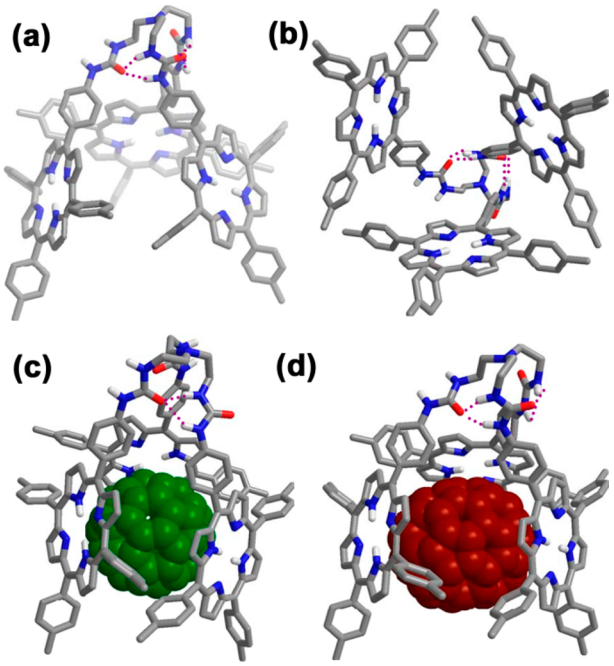

Figure 8. Optimized structure of TP_3 **1**: (a) side view, (b) bottom view, (c) C_{60}@TP_3 **1**, and (d) C_{70}@TP_3 **1**.

porphyrin and fullerene in the C_{70}@TP_3 **1** complex. These values are in good agreement with the experimental results of binding selectivity.

Fullerene Separation. As mentioned earlier, the preorganized cone cavity of TP_3 **1** had proven to be more suitable to restrain C_{70} than C_{60} by UV−vis, NMR titration, theoretical calculation, and competitive binding experiments. Moreover, the solubility of TP_3 **1** in toluene was largely decreased when encapsulating fullerene. On the basis of the facile synthesis, good selectivity of binding C_{70} over C_{60}, and significant differentiation of solubility when forming the fullerene inclusion complex of TP_3 **1**, we directed our efforts to achieve a simple, rapid, low-cost, and highly efficient way to separate C_{70} from C_{60}/C_{70} mixtures. Fullerene separation has been actively studied for pursuing a highly efficient and low-cost process since the 1990s.[21,45−47] It is, however, still a challenge to realize an easy and highly efficient pathway for such purification. In the present work, a saturated toluene solution of a C_{60}/C_{70} mixture was initially treated with 1 equiv of TP_3 **1** (or slightly less than the stoichiometric amount of C_{70}) at room temperature. The resulting solution was then sonicated for 1 min, and the precipitate was collected by filtration. The mother solution was evaporated to dryness. The separated solids were further dispersed in chloroform and treated with 3 equiv of $H_2PO_4^-$ to release fullerenes as a black precipitate. The TP_3 **1** host was then regenerated with 3 equiv of Ca^{2+} for the next round of separation. The C_{70}-rich and C_{60}-rich products were evaluated by UV−vis absorption[22,48] (Table 2 and Figures S30−36 in the Supporting Information). As an example, with respect to 2:1:0.98 mixture of $C_{60}/C_{70}/TP_3$ **1**, the C_{70} abundance can be increased from 33 to 87% after a single extraction (Table 2, entry 1), and the C_{60} abundance increased from 67 to 96% simultaneously. Even the molar content of C_{70} was decreased to less 10% in the mixture; there is no obvious drop observed in the C_{70} abundance after a single extraction. Furthermore, a C_{70} abundance up to 95% can be obtained when the C_{70}-rich product from entry 1 (87%) was used as the raw mixture for the second cycle (Table 2, entry 4). A commercially available fullerene extract was further treated under this method, and C_{70} with a purity of 94% can be obtained after two cycles (Table 2, entry 6). It is noteworthy that only 30 min was needed for one cycle, and this approach should be a fast and cost-efficient way to purify C_{70} and C_{60} from fullerite (fullerene mixtures) without chromatography.

Table 2. Fullerene Extraction Selectivities[a,b]

entry	$C_{60}/C_{70}/TP_3$ **1**	C_{70}-rich (%)	C_{60}-rich (%)
1	2:1:0.98	87	80
2	4:1:0.98	86	89
3	10:1:0.98	84	95
4[c]	1:6.7:6.6	95	78
5[d]	4:1:0.98	88	84
6[e]	1:7.3:7.2	94	76

[a]Measured by UV−vis spectroscopy according to the reported work.[22] [b]All data was calculated using molarity. [c]The initial fullerene mixture of entry 4 was the C_{70}-rich product of entry 1. [d]The initial fullerene mixture of entry 5 was purchased commercially. [e]The initial fullerene mixture of entry 6 was the C_{70}-rich product of entry 5.

CONCLUSIONS

A novel porphyrin trimer, TP_3 **1**, has been readily synthesized via a one-pot two-step reaction with accessible amino porphyrin and commercial tris(2-aminoethyl)amine under mild conditions. Benefiting from the existence of intramolecular hydrogen bonds of tripodal tris-ureas, TP_3 **1** displays a good binding ability toward fullerenes. An ion-controlled and reversible association and dissociation of fullerene was further realized with a $H_2PO_4^-$−Ca^{2+} system. Meanwhile, highly selective binding C_{70} over C_{60} (120-fold) was found, thus facilitating a fast and efficient separation of C_{70} from a fullerene mixture.

EXPERIMENTAL SECTION

All solvents were purified according to standard methods. All other chemicals (AR) were obtained from commercial sources and used without further purification. All NMR solvents were used as received. *N*′-Boc-2,2′-diaminodiethylamine was synthesized according to the reported work.[49] The isocyanation of amino porphyrin was carried out using triphosgene.[50]

General Synthesis Procedure of the Hosts. Amino porphyrin and 4 equiv of Et_3N were dissolved in dry dichloromethane (DCM). Then, 1.2 mol equiv of triphosgene was added, and the mixture was stirred for 0.5 h at room temperature. After the amino porphyrin was completely consumed, a solution of the corresponding amine and Et_3N (2.0 equiv) in dry DCM was dropped slowly into the reaction mixture. The mixture was stirred vigorously for 5 h at room temperature. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography with DCM/methanol (20:1) as eluent. The porphyrin host was obtained as a purple solid by recrystallization from chloroform/methanol.

Synthesis of TP_3 1. TP_3 **1** was prepared according to the general synthesis procedure. Step 1: 5-(4-aminophenyl)-10,15,20-tris(4-methyl-phenyl)-porphyrin (1.019 g, 1.52 mmol), Et_3N (856 μL, 6.11 mmol), and triphosgene (544.1 mg, 1.83 mmol); step 2: tris(2-aminoethyl)amine (74.4 mg, 0.51 mmol) and Et_3N (428 μL, 3.06 mmol). Column chromatography separation and recrystallization afford a purple solid TP_3 **1**: 1.03 g, yield 91%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.30 (s, 3H), 8.75 (d, J = 16.6 Hz, 12H), 8.65−8.50 (m, 6H), 8.45−8.31 (m, 6H), 8.09 (d, J = 8.2 Hz, 6H), 8.03 (d, J = 7.8 Hz, 12H), 7.59 (t, J = 16.9 Hz, 6H), 7.54−7.37 (m, 12H), 7.12−6.87 (m, 12H), 6.79 (s, 3H), 3.60−3.45 (m, 6H), 2.94−2.75 (m, 6H), 2.64 (s, 9H), 2.30 (s, 18H), −2.99 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$/

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DMSO-d_6, v/v 1:1): δ 155.9, 146.2, 143.1, 140.3, 138.3, 138.0, 137.0, 136.9, 136.4, 134.7, 134.0, 133.9, 133.5, 130.5, 127.3, 127.2, 126.9, 119.9, 119.3, 116.4, 116.3, 109.5, 54.2, 37.7, 21.0, 20.7. HR-MS (ESI): m/z $[M + 2H]^{2+}$ calcd for $C_{150}H_{125}N_{19}O_3$, 1120.5117; found, 1120.5107.

Synthesis of DP_2 2. DP_2 **2** was prepared according to the general synthesis procedure. Step 1: 5-(4-aminophenyl)-10,15,20-trisphenylporphyrin (30 mg, 0.048 mmol), Et_3N (28 μL, 0.20 mmol), and triphosgene (17.8 mg, 0.06 mmol); step 2: *N*′-Boc-2,2′-diaminodiethylamine (5.1 mg, 0.025 mmol) and Et_3N (14 μL, 0.10 mmol). Column chromatography separation and recrystallization afford a purple solid DP_2 **2**: 35 mg, yield 88%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.07−9.08 (m, 2H), 8.93−8.86 (m, 4H), 8.85−8.74 (m, 12H), 8.25−8.16 (m, 8H), 8.14 (d, J = 6.6 Hz, 4H), 8.07 (t, J = 7.7 Hz, 4H), 7.90 (d, J = 8.3 Hz, 2H), 7.84−7.72 (m, 18H), 6.58−6.41 (m, 4H), 3.50−3.41 (m, 4H), 1.52 (s, 3H), 1.45 (s, 6H), −2.93 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.3, 142.1, 135.4, 134.7, 134.5, 131.3, 127.8, 127.6, 126.8, 126.6, 120.2, 117.9, 46.0, 29.9, 28.6, 28.2, 8.7. HR-MS (ESI): m/z $[M + H]^+$ calcd for $C_{99}H_{80}N_{13}O_4$, 1515.6482; found, 1515.6459.

Synthesis of MP 2. **MP 2** was prepared according to the general synthesis procedure. Step 1: 5-(4-aminophenyl)-10,15,20-trisphenylporphyrin (30 mg, 0.048 mmol), Et_3N (28 μL, 0.20 mmol), and triphosgene (17.8 mg, 0.06 mmol); step 2: diethylamine (3.7 mg, 0.05 mmol) and Et_3N (14 μL, 0.10 mmol). Column chromatography separation and recrystallization afford a purple solid **MP 2**: 32 mg, yield 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (d, J = 4.7 Hz, 2H), 8.87−8.81 (m, 6H), 8.26−8.16 (m, 6H), 8.14 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.79−7.70 (m, 9H), 6.64 (s, 1H), 3.54 (q, J = 7.2 Hz, 4H), 1.37 (t, J = 7.1 Hz, 6H), −2.78 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.9, 142.4, 139.2, 136.7, 135.2, 134.7, 131.2, 127.8, 126.8, 120.2, 120.1, 118.1, 42.0, 14.2. HR-MS (ESI): m/z $[M + H]^+$ calcd for $C_{49}H_{41}N_6O$, 729.3336; found, 729.3339; m/z $[M + Na]^+$ calcd for $C_{49}H_{40}N_6ONa$, 751.3156; found, 751.3158.

Synthesis of TSP_3 1. 5-(4-Aminophenyl)-10,15,20-tris(4-methylphenyl)-porphyrin (30 mg, 0.045 mmol) and Et_3N (25 μL, 0.18 mmol) were dissolved in dry THF (10 mL). Then, 5 mL of CS_2 (excess) was added, and the mixture was stirred for 5 h at room temperature. After the amino porphyrin was completely consumed, the solvent and CS_2 were removed under vacuum. A solution of tris(2-aminoethyl)amine (2.2 mg, 0.015 mmol) and Et_3N (13 μL, 0.09 mmol) in dry DCM (5 mL) was dropped slowly into the reaction mixture. The mixture was stirred vigorously for 5 h at room temperature. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography with DCM/methanol (10:1) as eluent. Column chromatography separation and recrystallization afford a purple solid TSP_3 **1**: 28 mg, yield 82%. HR-MS (MALDI): m/z $[M + Na + NH_4 + H]^{3+}$ calcd for $C_{150}H_{128}N_{20}S_3Na$, 776.3241; found, 776.3251. N−H signals of thioureas in TSP_3 **1** were difficult to observe in its ^{1}H NMR spectrum (Figure S8 in the Supporting Information), whereas the ^{1}H and ^{13}C NMR spectra of the zinc complex of TSP_3 **1** showed good one-to-one correspondence between structure and signal (Figure S9 and S10 in the Supporting Information). ^{1}H NMR (TSP_3 **1**-Zn, 400 MHz, DMSO-d_6): δ 9.28 (s, 3H), 8.80 (d, J = 6.6 Hz, 6H), 8.80 (s, 3H), 8.77−8.73 (m, 18H), 8.10 (d, J = 8.1 Hz, 6H), 8.06 (d, J = 7.0 Hz, 18H), 7.74 (d, J = 8.3 Hz, 6H), 7.60 (d, J = 7.5 Hz, 18H), 3.96−3.88 (m, 6H), 3.55−3.47 (m, 6H), 2.67 (s, 27H). ^{13}C NMR (TSP_3 **1**-Zn, 101 MHz, DMSO-d_6): δ 179.6, 149.4, 140.4, 139.9, 138.9, 136.6, 134.1, 133.7, 131.6, 131.4, 127.2, 124.5, 120.3, 120.0, 45.0, 29.0, 21.1.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and characteristic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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