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Letter

Monitoring Hierarchical Assembly of Ring-in-Ring and Russian Doll Complexes Based on Carbon Nanoring by Förster Resonance Energy Transfer

Shengzhu Guo, Lin Liu, Feng Su, Huiji Yang, Guoqin Liu, Yanqing Fan, Jing He, Zhe Lian, Xiaonan Li, Weijie Guo, Xuebo Chen, and Hua Jiang*

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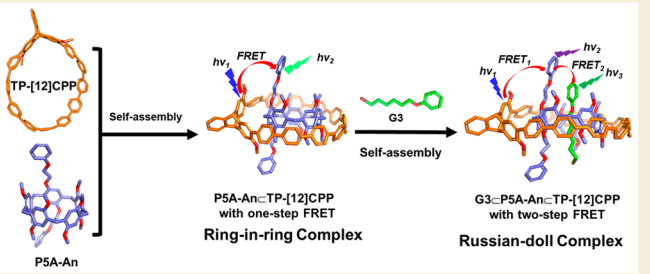
ABSTRACT: We presented the construction of the ring-in-ring and Russian doll complexes on the basis of triptycene-derived carbon nanoring (TP-[12]CPP), which not only acts as a host for pillar[5]arene (P5A) but also serves as an energy donor for building Förster resonance energy transfer (FRET) systems. We also demonstrated that their hierarchical assembly processes could be efficiently monitored in real time using FRET. NMR, UV−vis and fluorescence, and mass spectroscopy analyses confirmed the successful encapsulation of the guests P5A/P5A-An by TP-[12]CPP, facilitated by C−H···π and ···π interactions, resulting in the formation of a distinct ring-in-ring complex with a binding constant of $K_a = 2.23 \times 10^4$ M^{-1}. The encapsulated P5A/P5A-An can further reverse its role to be a host for binding energy acceptors to form Russian doll complexes, as evidenced by the occurrence of FRET and mass spectroscopy analyses. The apparent binding constant of the Russian doll complexes was up to 3.6×10^4 M^{-1}, thereby suggesting an enhanced synergistic effect. Importantly, the Russian doll complexes exhibited both intriguing one-step and sequential FRET dependent on the subcomponent P5A/P5A-An during hierarchical assembly, reminiscent of the structure and energy transfer of the light-harvesting system presented in purple bacteria.



KEYWORDS: *Triptycene, Carbon nanohoop, Host−guest interaction, Russian doll complexes, FRET*

INTRODUCTION

The construction of novel supramolecular complexes with unique structures remains an intriguing but challenging objective in supramolecular chemistry.[1,2] Over the past few decades, various macrocycles, including cucurbituril,[3−6] crown ethers,[7−9] and blue box,[10,11] have been extensively utilized to fabricate impressive hierarchical assembled structures. Among them, nonintertwined ring-in-ring or host-in-host assemblies through host−guest recognitions between two different macrocycles have garnered significant interest[12−21] and are promising for the development of new materials, including multicolor biological imaging reagents and information encryption.[6,22] In particular, some Russian doll (matryoshka) complexes[17,23,24] are able to mimic the structure of the natural photosynthetic antenna systems in purple bacteria in which the light-harvesting reaction center (LH1-RC) architecture absorbs sunlight and directs the excitation energy from LH2 to LH1 and subsequently transfers to the RC encapsulated within the LH1 ring.[25]

Recently, carbon nanohoops,[11,26−29] in particular, [n]-cycloparaphenylenes ([n]CPPs),[30−42] have attracted considerable research attention because of their ability to host π-conjugated molecules with a complementary convex surface, such as fullerene or metallofullerene. Both theoretical calculations and experimental investigations have demonstrated that larger CPPs could nest ever smaller ones to form a ring-in-ring complex when the ring size difference of CPPs reaches five phenylene units,[43−47] which further promotes the constructions of Russian doll complexes consisting of two differently sized carbon nanorings and (metallo)fullerenes.[44] However, there are limited examples of utilizing the carbon nanoring for encapsulating nonaromatic guests because of a lack of efficient concave−convex interactions between aromatic hosts and nonaromatic guests.[48,49] For instance, Dumele et al. developed a Russian doll complex by encapsulating a complex of crown ether−metal ions in the confined cavities of a carbon nanoring based on [5]cyclo-pyrenylene.[29] Recently, we[39] successfully constructed chiral Russian doll complexes on the basis of a planar chiral [2.2]paracyclophane-based CPP

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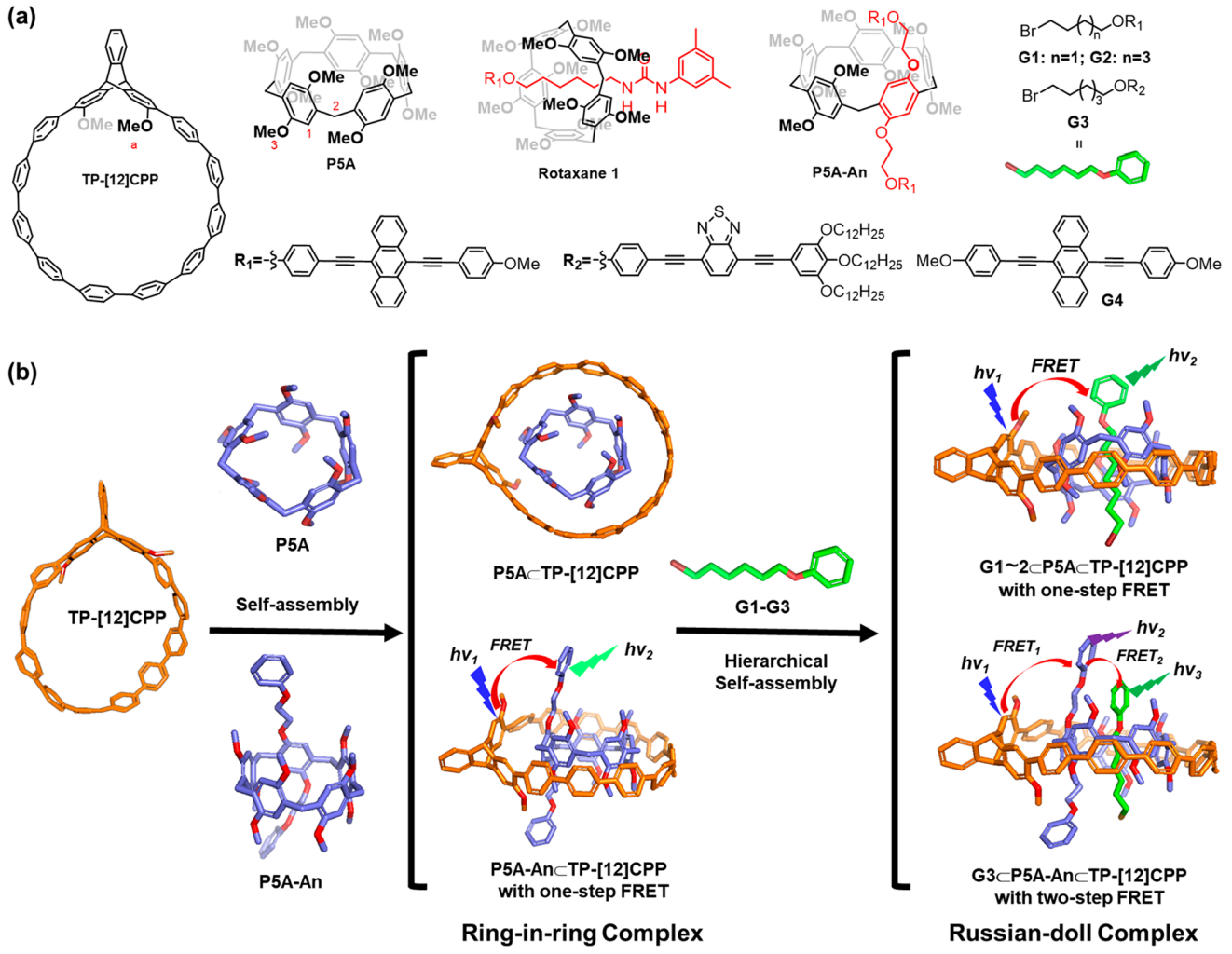

Figure 1. (a) The chemical structure of **TP-[12]CPP**, **P5A**, **P5A-An**, **Rotaxane 1**, and **G1−G3**. (b) The cartoon illustrations of FRET processes in the proposed ring-in-ring and Russian doll complexes in this work.

featuring highly selective chiral self-recognition for chiral amines. Nevertheless, Russian doll complexes based on carbon nanohoops are still very challenging to achieve.

The physicochemical methodologies, such as gel electrophoresis, atomic force microscopy, cryo-transmission electron microscopy, and X-ray analysis, are commonly employed for the characterization of supramolecular assemblies.[50−52] However, it is worth noting that these methodologies are often destructive and primarily allow for end-point analysis of the final product. This limitation hinders the ability to detect and optimize the assembly process through manipulation of the same sample.[53] Förster resonance energy transfer (FRET),[54,55] a nonradiative energy transfer process through dipole−dipole interaction between donor and acceptor, has been established as an ideal method for real-time monitoring of the processes and dynamics associated with supramolecular self-assembly,[56−62] which has widespread applications in fields like fluorescent probes,[63,64] chemosensors,[65,66] imaging agents,[67−69] photodynamic therapy,[70,71] and artificial light-harvesting systems (LHSs).[72−75] For instance, Rebek et al. successfully utilized FRET to characterize the dynamic features of supramolecular capsules on the basis of hydrogen bonds.[56−58] Yang presented the real-time monitoring of coordination-driven self-assembly dynamics through FRET.[59−62] Recently, we have constructed two efficient FRET systems on the basis of heterotopic bisnanohoops[41] and double helicates[74] for achieving multiple color-tunable emissions, including white light LED devices, respectively.

More recently, we[76] reported the synthesis and properties of a novel series of nanometer-sized cavity triptycene (TP)-derived carbon nanohoops with highly fluorescence emission (the quantum yields achieved were up to 92.5%). Among these carbon nanohoops, **TP-[12]CPP** possesses a large cavity size (18.08 Å × 15.84 Å), as demonstrated in the solid phase, along with impressive (chir)optical properties. Encouraged by these observations, we anticipated that **TP-[12]CPP** would not only serve as a host for other macrocycles with corresponding dimensions so as to facilitate the formation of ring-in-ring complexes but could also act as an energy donor for FRET, which enables us to monitor the hierarchical assembly of supramolecular complexes via FRET. Notably, our theoretical calculations identified a striking similarity between the cavity of **TP-[12]CPP** and the contour of pillar[5]arene (**P5A**), which strongly suggests that **TP-[12]CPP** could potentially host **P5A** to form a ring-in-ring complex. Although it is well-known that **P5A** is mainly used as a host for encapsulating linear guests,[77−83] the utilization of **P5A** as a guest in the construction of nested supramolecular structures and, con-

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sequently, for building Russian doll complexes via hierarchical assembly has been rarely documented.[77−83]

In this contribution, **TP-[12]CPP**, **P5A**, or its derivative **P5A-An**, was initially designed to construct ring-in-ring complexes, respectively. Linear, fluorescent guests **G1−G3** were functionalized with different haloalkyl groups that are able to associate with **P5A**/**P5A-An** to form pseudo rotaxanes, which consequently form Russian doll complexes when encapsulated by **TP-[12]CPP**. The anthracene and benzothiadiazole derivatives were carefully chosen as fluorescent groups in **G1−G3** to construct a FRET, which requires the excitation spectrum of the energy acceptor to be well overlapped with the emission spectrum of the energy donor (*vide infra*), so that the formation of ring-in-ring and Russian doll complexes could be monitored by FRET in real time. We demonstrated that the encapsulated **P5A**/**P5A-An** in ring-in-ring complexes showed a role reversal and became a host to bind linear guests (Figure 1b). Also, **P5A**-based **Rotaxane 1** was prepared to form a Russian doll complex with **TP-[12]CPP**. As expected, a typical one-step FRET process was observed in the ring-in-ring complex of **P5A-An⊂TP-[12]CPP** and the Russian doll complexes of **G1−2⊂P5A⊂TP-[12]CPP** and **rotaxane 1⊂TP-[12]CPP**. Notably, the Russian doll complexes of **G3⊂P5A-An⊂TP-[12]CPP** displayed an intriguing sequential two-step FRET process reminiscent of the structure and energy transfer in typical purple bacteria.

RESULTS AND DISCUSSION

Construction of Ring-in-Ring Complex of P5A⊂TP-[12]CPP

We first constructed ring-in-ring or Russian doll supramolecular structures by assembling **TP-[12]CPP** with **P5A**. ^{1}H NMR spectra revealed that the chemical shifts of protons in P5A showed an upfield shift upon addition of **P5A** into a solution of **TP-[12]CPP** in $CDCl_3$ (Figure 2a−c and Figures S6 and S7). For instance, protons H_1 and H_3 display obvious upfield shifts up to $\Delta\delta$ = −0.04 and −0.03 ppm, respectively, which demonstrate that **P5A** experienced a shielded magnetic environment in the cavity of **TP-[12]CPP** and formed a ring-in-ring complex. Meanwhile, diffusion-ordered NMR spectroscopy (DOSY) experiments showed that the ring-in-ring complex **P5A⊂TP-[12]CPP** displays one set of the distinct signal band for all components with a diffusion coefficient 1.23 × 10^{-9} m^2/s [log(D) = −8.91, Figure 2e and Figure S1], which is similar to that of free **TP-[12]CPP** [D = 1.44 × 10^{-9} m^2/s, log(D) = −8.84, Figure 2d and Figure S2], thereby demonstrating a 1:1 stoichiometry of the nested complex **P5A⊂TP-[12]CPP** in solution. Moreover, the 2D NOESY NMR spectrum of the 1:1 mixtures of **P5A** and **TP-[12]CPP** presented several obvious cross-peaks between **TP-[12]CPP** and **P5A** (Figure S4), which clearly confirmed the proximity of each component in the ring-in-ring complex and further provided solid evidence for the formation of a ring-in-ring complex. Moreover, the mass spectrum of the ring-in-ring complex **P5A⊂TP-[12]CPP** was determined by ESI TOF-MS analysis, and the mass peak at m/z 1845.7942 found for [M + Na]$^+$ (Figure S49) further confirmed the formation of the ring-in-ring complex **P5A⊂TP-[12]CPP**.

UV/vis absorption titration experiments (Figure S5a) revealed an increasing absorption at 295 nm and a decreasing one at 334 nm upon adding **P5A** to the **TP-[12]CPP** solution. Job's plots based on UV/vis spectra validated a 1:1 host−guest binding model (Figure S5b) with the binding constant of 2.2 × 10^4 M^{-1} (Table 1), thereby suggesting a strong interaction between **TP-[12]CPP** and **P5A**. Moreover, an independent gradient model based on Hirshfeld partition (IGMH) analysis[84] (Figure 3a) revealed the presences of both C−H···π and π···π interactions in the **P5A⊂TP-[12]CPP** complex, which played the crucial roles in the formation of a stable ring-in-ring complex.

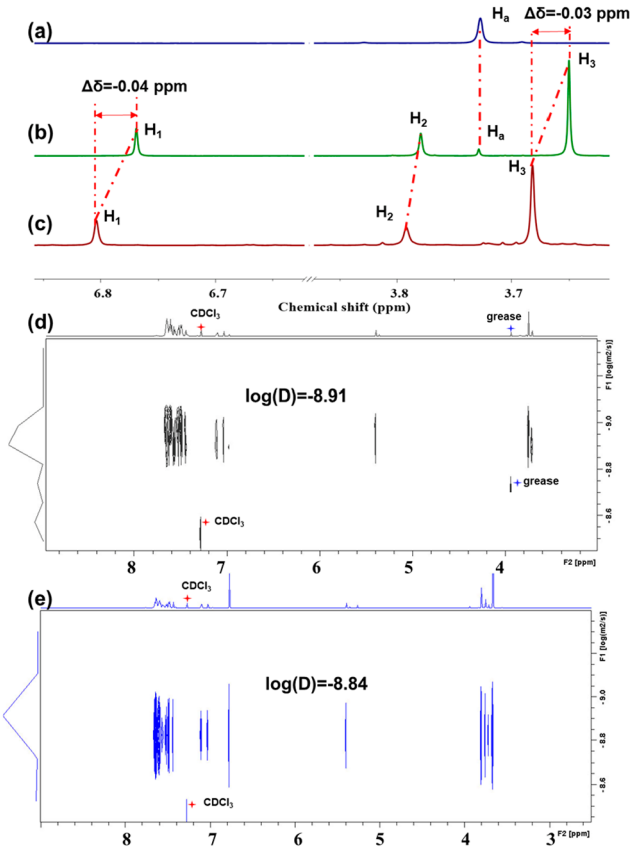

Figure 2. Partial ^{1}H NMR (600 MHz, 5 mM in $CDCl_3$, 298 K) of (a) **TP-[12]CPP**, (b) **P5A⊂TP-12CPP** (1:1), and (c) **P5A**. ^{1}H DOSY spectra (600 MHz, 5 mM in $CDCl_3$, 298 K) of (d) **TP-12CPP** and (e) **P5A⊂TP-12CPP** (1:1). The red plus sign is the signal of $CDCl_3$, and the blue plus sign is the signal of grease.

Table 1. Summary of Apparent Binding Constants K_a (M^{-1}) and Φ_{ET} Calculated of Different Complexes

complexes	K_a/M^{-1} (×10^4)[d]	Φ_{ET}
P5A⊂TP-[12]CPP	2.2 ± 0.1[a]	
G1⊂P5A	(2.9 ± 0.1)×10^2[b]	
G1⊂P5A⊂TP-[12]CPP	3.5 ± 0.1[c]	75%
G2⊂P5A⊂TP-[12]CPP	3.1 ± 0.2[c]	61%
Rotaxane 1⊂TP-[12]CPP	2.9 ± 0.1[c]	48%
P5A-An⊂TP-[12]CPP	2.2 ± 0.1[c]	80%
G3⊂P5A-An⊂TP-[12]CPP	3.3 ± 0.1[c]	95%
G3⊂P5A-An	1.2 ± 0.1[c]	43%

[a]The results were determined by UV−vis titration experiments. [b]The results were determined by NMR titration experiments. [c]The results were determined by FL titration experiments. [d]The results were according to triplicate experiments.

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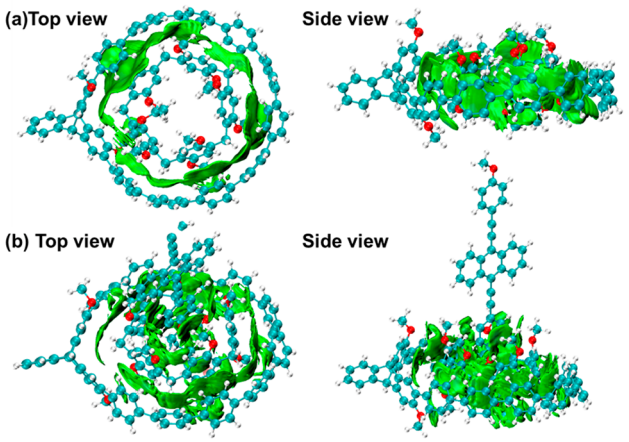

Figure 3. IGMH analyses of (a) the ring-in-ring complex of **P5A⊂TP-12CPP** and (b) the Russian doll complex of **G1⊂P5A⊂TP-12CPP** (δg_{inter} = 0.002).

Construction of Russian Doll Complexes on the Basis of P5A⊂TP-[12]CPP and G1−G2 with One-Step FRET

The encapsulation of **P5A** by **TP-[12]CPP** renders the central cavity of **P5A** available for binding a guest, which provides an appealing opportunity to construct Russian doll complexes. Therefore, two haloalkyl derivatives of 9,10-bis-(phenylethynyl)-anthracene, **G1** and **G2**, whose excitation spectra (Figures S17, S18) overlap well with the emission of **TP-[12]CPP**, were selected as linear guests and energy acceptors for the construction of Russian doll complexes, which was monitored through FRET. The complexation of **P5A** with **G1−G2** was confirmed through ^{1}H NMR experiments (Figures S8−S10). For instance, the proton peaks of **P5A** exhibited downshifts upon addition of **G1**, presumably due to multiple C−H···π interactions between the curved surface of **P5A** and **G1**, which indicated the complexation between **P5A** and **G1**. Meanwhile, the binding constant K_a between **P5A** and **G1** was estimated to be 2.9 × 10^2 M^{-1} (Figure S9b). To further validate the hierarchical assembly of the ternary complex, we also carried out ^{1}H NMR experiments (Figure 4b) by adding the complex of 1:1 **G1⊂P5A** into a solution of **TP-[12]CPP**. The results revealed the proton of **P5A** in the **G1⊂P5A⊂TP-[12]CPP** region exhibited upfield shifts with $\Delta\delta$ = −0.07 and −0.04 ppm for H_1 and H_3, respectively, which were attributed to the multiple C−H···π and π···π interactions between **P5A** and **TP-[12]CPP**, as well as **G1**, thereby suggesting the successful formation of Russian doll complexes. Furthermore, the DOSY spectrum (Figure 4d) of the Russian doll complex **G1⊂P5A⊂TP-[12]CPP** also displayed a single-set signal band with a diffusion coefficient of 3.47 × 10^{-9} m^2/s [log(D) = −8.46), which provided additional evidence for the formation of the Russian doll complexes. Independent gradient model based on Hirshfeld partition (IGMH) analysis (Figure 3b) unveiled that the long-chain alkane of **G1** was effectively accommodated within the inner cavity of **P5A⊂TP-[12]CPP**, accompanied by multiple C−H···π and ···π interactions in stabilizing the Russian doll complexes.

Fluorescence titration experiments provided obvious evidence for the formation of the Russian doll complexes. When the **G1⊂P5A** complex (1:1) was titrated into **TP-[12]CPP** solution in chloroform (Figure 5a), an increase in the emission

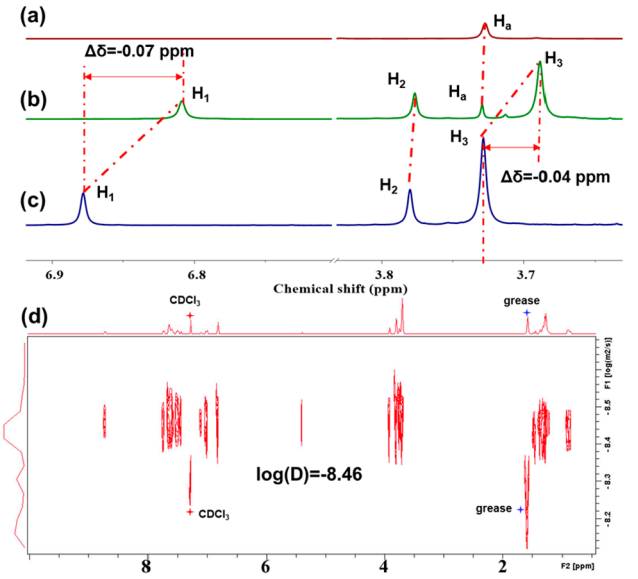

Figure 4. Partial ^{1}H NMR (600 MHz, 5 mM in $CDCl_3$, 298 K) of (a) **TP-[12]CPP**, (b) **G1⊂P5A⊂TP-12CPP** (1:1:1), and (c) **G1⊂P5A** (1:1). (d) ^{1}H DOSY spectra (600 MHz, 5 mM in $CDCl_3$, 298 K) of **G1⊂P5A⊂TP-12CPP** (1:1:1). The red plus sign is the signal of $CDCl_3$, and the blue plus sign is the signal of grease.

of **G1** (λ_{em} = 493 nm) and a decrease in that of **TP-[12]CPP** (λ_{em} = 450 nm) were observed when excited at λ = 330 nm. This behavior is indicative of the typical FRET process, which suggests that energy transfer occurs from **TP-[12]CPP** to **G1** due to the formation of the Russian doll complexes. The apparent binding constant[11,39] of **TP-[12]CPP** for **G1⊂P5A** was estimated to be 3.5 × 10^4 M^{-1} (Table 1 and Figure S22), which is obviously higher than that of **TP-[12]CPP** for **P5A**, thereby indicating that the presence of **G1** enhances the binding affinity between **TP-[12]CPP** and **P5A**. This finding is consistent with that of the Russian dolls reported by Stoddart et al.[11] The efficiency of energy transfer (Φ_{ET}) was calculated to be 78% according to the previous reports (Table 1 and the Supporting Information).[72,73] Similar observations were found for the Russian doll complex of **G2⊂P5A⊂TP-[12]CPP** (Figure 5d−f and Table 1), which further confirmed the hierarchical self-assembly of Russian doll complexes that can be monitored through FRET. The mass peak at m/z 2432.1001 was found for **G2⊂P5A⊂TP-[12]CPP** (Figure S50), which corresponded to the charge states of $[M + Na]^+$. In parallel, we synthesized a **P5A**-based **Rotaxane 1** to create a Russian doll complex with **TP-[12]CPP** for comparing the binding abilities of **TP-[12]CPP** toward **Rotaxane 1** and the pseudorotaxane **G2⊂P5A**. Fluorescence titration experiments (Figure S27) between **TP-[12]CPP** and **Rotaxane 1** were conducted to confirm energy transfer taking place from **TP-[12]CPP** to **Rotaxane 1** due to the formation of the Russian doll complexes. The binding constant of **TP-[12]CPP** for **Rotaxane 1** was determined to be 2.9 × 10^4 M^{-1}, which is comparable with that of **TP-[12]CPP** for pseudorotaxane **G2⊂P5A**, thereby suggesting that **TP-[12]CPP** possesses a comparable capacity for encapsulating both rotaxane and pseudo-one. The formation of Russian doll **Rotaxane 1⊂TP-[12]CPP** was further confirmed by HRMS with the mass peaks at m/z 2494.3232 and 2517.2683 for $[M + H]^+$ and $[M + Na]^+$, respectively (Figure S51). Additionally, the average

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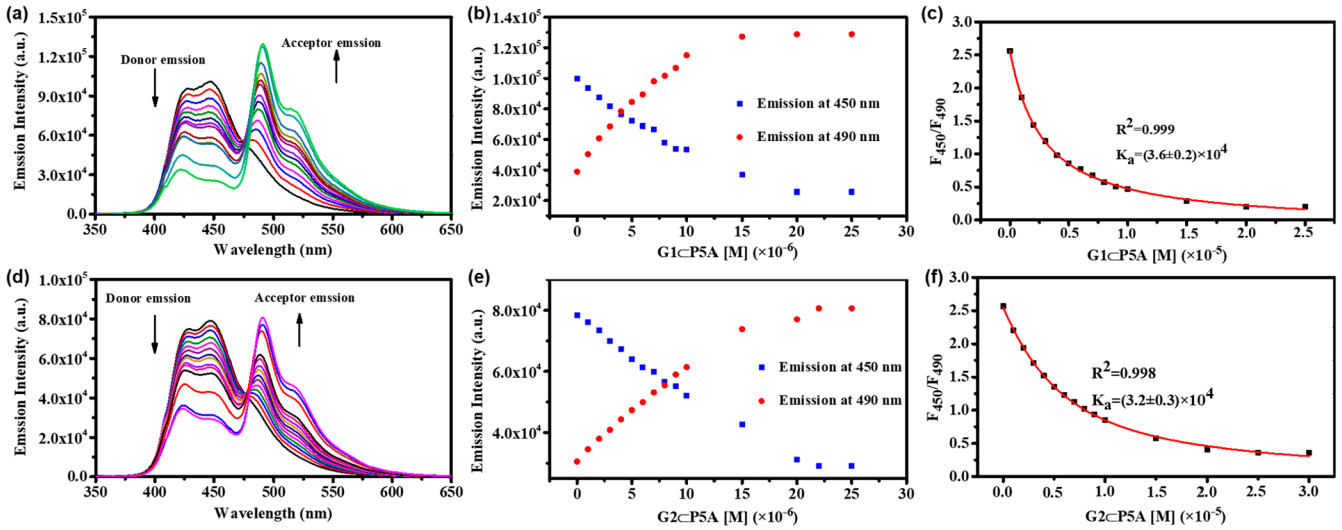

Figure 5. Fluorescence emission spectra of **TP-[12]CPP** (1×10^{-5} M, λ_{ex}= 330 nm) titrated with (a) **G1⊂P5A** (1×10^{-3} M/1×10^{-3} M) and (d) **G2⊂P5A** (1×10^{-3} M/1×10^{-3} M). Fluorescent intensity changes at 450 and 490 nm when titrated with (b) **G1⊂P5A** and (e) **G2⊂P5A**. Fluorescence emission titration plot for determination of the binding constant of **TP-[12]CPP** in the presence of (c) **G1⊂P5A** and (f) **G2⊂P5A**.

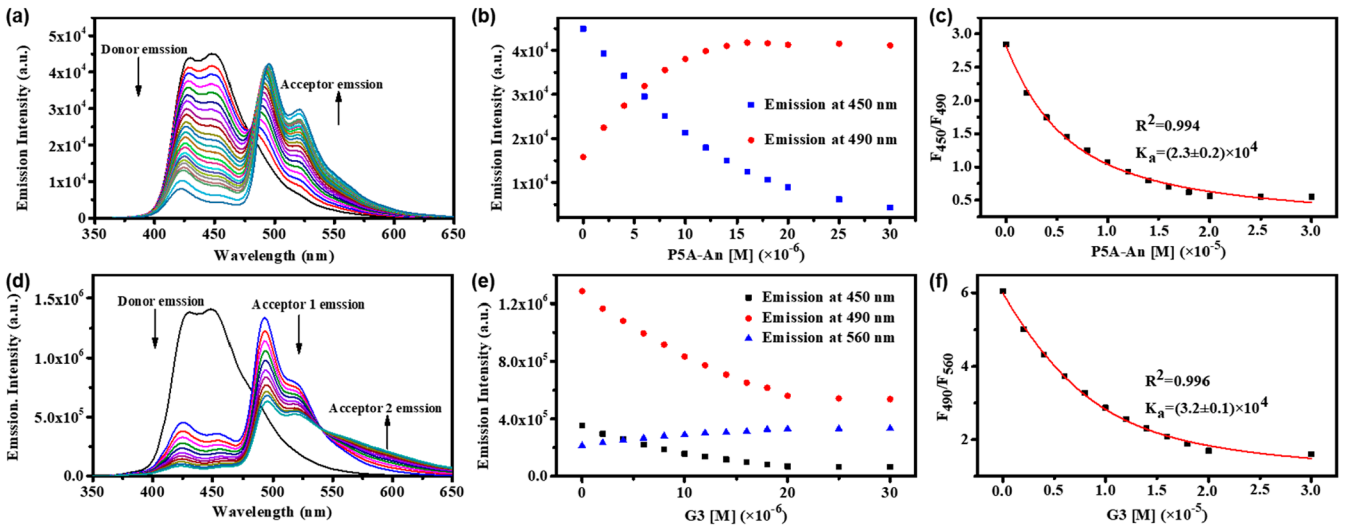

Figure 6. Fluorescence emission spectra of (a) **TP-[12]CPP** (1×10^{-5} M, λ_{ex}= 330 nm) titrated with **P5A-An** (1×10^{-3} M) and (d) **P5A-An⊂TP-[12]CPP** (2×10^{-5} M/1×10^{-5} M) titrated with **G3** (1×10^{-3} M). Fluorescent intensity changes of (b) **TP-[12]CPP** titrated with **P5A-An** and (e) **P5A-An⊂TP-[12]CPP** (2×10^{-5}/1×10^{-5} M, λ_{ex}= 330 nm) titrated with **G3**. Fluorescence emission titration plot for determination of the binding constant of (c) **TP-[12]CPP** in the presence of **P5A-An** and (f) **P5A-An⊂TP-[12]CPP** in the presence of **G3**..

lifetime of **TP-[12]CPP** was measured to be 0.98 ns, which increased to 1.55 ns upon the addition of **P5A** to **TP-[12]CPP** (Figures S34–S36 and Table S1). However, the addition of **G1** and **G2** into **P5A⊂TP-[12]CPP** resulted in a decrease in the average lifetime to 1.47 ns, which further supported the occurrence of FRET energy transfer from **TP-[12]CPP** to **G1** and **G2**. Furthermore, a control experiment carried out by gradual addition of the mixture of P5A and **G4** (1:1) into a solution of **TP-[12]CPP** (Figure S26) revealed no FRET takes place. This phenomenon strongly implies that the haloalkyl chains are indispensable for host–guest interactions between **P5A**/**P5A-An** and **G1**–**G3**.

Construction of Russian Doll Complexes on the Basis of P5A-An⊂TP-[12]CPP and G3 with Sequential FRET

Finally, we attempted to fabricate a two-step energy transfer system, which is widely found in LHSs responsible for capturing solar energy vital to living organisms.[25,67−69] To construct a Russian doll complex with a two-step FRET process, we rationally introduced 9,10-bis(phenylethynyl)-anthracene to **P5A** to create **P5A-An** as an energy acceptor whose excitation spectrum overlapped with the emission spectrum of **TP-[12]CPP** (Figure S20). ^{1}H NMR experiments demonstrated that **TP-[12]CPP** is able to bind **P5A-An**, thus forming a ring-in-ring complex (Figures S14 and S15). Also, the formation of **P5A-An⊂TP-[12]CPP** was been confirmed by HRMS measurement (Figure S52), which shows the mass peak at m/z = 2718.2947 for $[M + Na]^+$. Furthermore, fluorescence titration experiments demonstrated that the emission intensity of **TP-[12]CPP** decreased at 450 nm, while the emission intensity of **P5A-An** increased at 493 nm upon titration of 0–2 equiv of **P5A-An** (Figure 6a). The binding constant of **TP-[12]CPP** for **P5A-An** was estimated to

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be 2.2 × 10^4 M^{-1} (Table 1), which is consistent with that of **TP-[12]CPP** for the pristine **P5A**, and the Φ_{ET} was calculated to be 80% (Table 1).

In order to construct a Russian doll complex with two-step energy transfer processes, benzothiadiazole derivative **G3**, whose excitation spectrum overlaps well with the emission of **P5A-An** (Figure S20), was selected as a guest and energy acceptor for the **P5A-An⊂TP-[12]CPP** complex. We initially validated the host−guest complexation between **P5A-An** and **G3** through fluorescence titrations (Figure S18). The results revealed that **P5A-An** effectively served as a host for **G3** with a binding constant of 1.1 × 10^4 M^{-1}. Therefore, **G3** was titrated into the above **P5A-An⊂TP-[12]CPP** binary complex for constructing **G3⊂P5A-An⊂TP-[12]CPP**. Intriguingly, the fluorescence emission of **TP-[12]CPP** and **P5A-An** decreases significantly, while that of **G3** increases around 550−650 nm upon titration of **G3** (Figure 6d). The Φ_{ET} was calculated to be 95% (Table 1). Meanwhile the average lifetimes of the ring-in-ring complex **P5A-An⊂TP-[12]CPP** and the Russian doll complex **G3⊂P5A-An⊂TP-[12]CPP** were measured to be 1.96 and 1.94 ns, respectively (Figures S37 and S38). These results clearly demonstrated that Russian doll complex **G3⊂P5A-An⊂TP-[12]CPP** with two-step sequential energy transfer was effectively constructed.[73,74] The apparent binding constant of **P5A-An⊂TP-[12]CPP** for binding **G3** was determined to be 3.1 × 10^4 M^{-1} (Table 1 and Figure S33), which is larger than that of **P5A-An** for binding **G3**, as well as that of **TP-[12]CPP** for **P5A-An**, thereby indicating a strong synergistic effect in the Russian doll complex. To shed light on the host−guest interactions between the complexes, the energies of the binary and ternary complexes were calculated and are presented in Table S2. The results indicated that the energies of Russian dolls are much lower than those of binary complexes, thereby suggesting that Russian dolls are more stable than binary complexes, which is indicative of the synergistic effect.[85] These observations suggest that our Russian doll could mimic the structure of the natural photosynthetic antenna systems and transfer energy, as observed in typical purple bacteria.[17] Specifically, the Russian doll complexes absorb sunlight and direct the excitation energy from **TP-[12]CPP** to **P5A-An**, which subsequently funnels to **G3** encapsulated within **P5A-An** (Figure 2b).

CONCLUSION

In summary, we demonstrated that **TP-[12]CPP** not only accommodates **P5A** or its derivatives **P5A-An** but also effectively encapsulate their complexes with linear guests in their open concave cavity to form a novel ring-in-ring complex and Russian doll complexes, respectively. We further presented that **TP-[12]CPP** can be used as an energy donor for constructing one-step and sequential FRET systems. The fluorescence titration experiments confirmed the occurrences of FRET during the formation of these ring-in-ring and Russian doll complexes, thereby indicating that the assembly process could be monitored using FRET. Notably, the Russian doll complex of **G3⊂P5A-An⊂TP-[12]CPP** displayed a sequential energy transfer process that could mimic the structure and energy transfer in typical purple bacteria. These results not only emphasize the effectiveness of matching the dimensions of two distinct macrocycles for the development of hybrid supramolecular assemblies involving ring-in-ring complexes and smaller neutral guest molecules but also illustrate the value of FRET as a powerful tool for monitoring the formation of binary or Russian doll complexes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.3c00720.

Experimental details, additional NMR, mass spectroscopy, and fluorescence titration experiments (PDF)

AUTHOR INFORMATION

Corresponding Author

Hua Jiang − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*; orcid.org/0000-0002-9917-2683; Email: jiangh@bnu.edu.cn

Authors

Shengzhu Guo − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*

Lin Liu − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*

Feng Su − *College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, Guangdong 518060, P.R. China*

Huiji Yang − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*

Guoqin Liu − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*

Yanqing Fan − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*

Jing He − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*

Zhe Lian − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*

Xiaonan Li − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*

Weijie Guo − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*

Xuebo Chen − *College of Chemistry, Beijing Normal University, Beijing 100875, P.R. China*; orcid.org/0000-0002-9814-9908

Complete contact information is available at: https://pubs.acs.org/10.1021/jacsau.3c00720

Author Contributions

CRediT: **Shengzhu Guo** conceptualization, data curation, formal analysis, investigation, methodology, software, writing-original draft, writing-review & editing; **Lin Liu** methodology, software; **Huiji Yang** investigation, methodology; **Guoqin Liu** methodology, software; **Yanqing Fan** data curation, software; **Jing He** data curation, formal analysis; **Zhe Lian** formal analysis, software; **Xiaonan Li** software; **Weijie Guo** investigation, methodology; **Xuebo Chen** methodology, software; **Hua Jiang** conceptualization, methodology, project administration, resources, supervision, writing-original draft, writing-review & editing.

Notes

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