A contorted nanographene shelter

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Nanographenes have kindled considerable interest in the fields of materials science and supramolecular chemistry as a result of their unique self-assembling and optoelectronic properties. Encapsulating the contorted nanographenes inside artificial receptors, however, remains challenging. Herein, we report the design and synthesis of a trigonal prismatic hexacationic cage, which has a large cavity and adopts a relatively flexible conformation. It serves as a receptor, not only for planar coronene, but also for contorted nanographene derivatives with diameters of approximately 15 Å and thicknesses of 7 Å. A comprehensive investigation of the host-guest interactions in the solid, solution and gaseous states by experimentation and theoretical calculations reveals collectively an induced-fit binding mechanism with high binding affinities between the cage and the nanographenes. Notably, the photostability of the nanographenes is improved significantly by the ultrafast deactivation of their excited states within the cage. Encapsulating the contorted nanographenes inside the cage provides a noncovalent strategy for regulating their photoreactivity.
Nanographenes (NGs), a class of large polycyclic aromatic hydrocarbons (PAHs) that extend over 1.0 nm², have attracted considerable attention both in the scientific community and in technological spheres on account of their unique self-assembling, redox, and optoelectronic properties. Of particular interest are the coronene (COR) homologous molecules (Fig. 1a), such as the bowl-like corannulene, planar hexa-peri-hexabenzocorone (p-HBC) and contorted hexa-cara-hexabenzocorone (c-HBC), which have been widely applied in field-effect transistors, light-emitting diodes, and nonlinear optical materials. Along with the advent of supramolecular chemistry, investigations on artificial receptors for PAHs, on the basis of noncovalent bonding interactions, have become an active research area in recent decades. To date, a series of receptors, including macrocycles, tweezer, covalent, and coordination cages, as well as carbon nanotubes, have been synthesized as hosts for COR. Several receptors are even able to bind bowl-like corannulene, despite the fact that they show lower binding affinities compared to that for COR. Well-rafted receptors for the larger and contorted c-HBC, however, are still few and far between, for the simple reason that their contorted conformations lead to (i) weaker interactions between the hosts and guests, and (ii) less shape complementarity in order to fit within the cavity of the host. In addition, large nanographenes often suffer from instability upon exposure to light, reducing considerably the stability and life of graphene-based materials. Typical examples are the acenes, larger than pentacene, an important class of one-dimensional nanographenes, which have been found to be unstable to light. This deficiency limits their utility severely. Hence, designing an artificial receptor, with the property of high binding affinities toward nanographenes and protecting them from photo-degradation, is a challenging, yet worthwhile, objective in noncovalent synthesis.

Macrocyclic arenes, such as calix[n]arenes, calixpyrroles, cyanostars, and pillar[n]arenes, represent a rapidly growing family of molecular receptors that play a crucial role in supramolecular chemistry by virtue of their properties of molecular recognition towards various guests. As a representative cationic cyclophane, CBPQT, which exhibits higher complexation strengths towards a series of neutral PAHs. Upon changing the central benzenoid rings within ExCage, into π-electron-deficient triazine rings, a more electron-poor cyclophane, so-called BlueCage, was obtained. Since it acts as a receptor for both planar aromatic guests and [PF₆]⁻ anions, binding affinities for the aromatic guests can be controlled by anion–π interactions. These two cage-like receptors, however, can only bind planar and relatively small aromatic guests because of their rigid conformations and the limited space within their cavities.

In this investigation, we introduced two triphenylamine units into a hexacationic cage, TPACage, (Fig. 1c). Its solid-state structure reveals that the cage adopts a relatively flexible conformation and has a large cavity with a diameter of 20.8 Å and a volume of 368 Å³. As a result, TPACage can form 1:1 complexes, not only with planar COR but also with large contorted c-HBC derivatives with diameters of 15.3 Å, as evidenced by single-crystal X-ray diffraction, NMR spectroscopy, and high-resolution mass spectrometry (HRMS). Benefiting from ideal size-matching, TPACage shows higher binding affinities towards c-HBC derivatives than that with COR in the solution state. Gradient tandem mass spectrometry revealed that as the electron density of guests increases, the stability of the host-guest complexes are enhanced in the gas phase. As a consequence of the ultrafast energy transfer between the host and guests, the photostability of c-HBC guests is significantly improved within the cavity of TPACage, as confirmed by femtosecond transient absorption spectroscopy.

Results

Synthesis and characterization of TPACage. The TPACage was synthesized (Fig. 1c and Supplementary Figs. 1–3) in three steps from commercially available starting materials. A coupling reaction between tris(4-bromophenyl)amine and 4-vinylpyridine in triethylamine was carried out under reflux for 6 h to obtain TPAP in a 58% yield. Thereafter, an SN2 reaction between an excess of p-xylene dibromide and TPAP in a MeCN/DMF solution for 2 days, led to TPAB in 80% yield.

Fig. 1 Structures and synthesis. a Structural formulas of corannulene, p-HBC and c-HBC. b Structural formulas of CBPQT, ExCage, and BlueCage. c Synthesis and labeling of protons on TPACage.
mixture under reflux for 2 days led to the formation of TPAB$_3$PF$_6$ after counterion exchange in a yield of 80%. Finally, equimolar amounts of TPAB$_3$PF$_6$ and TPAP in the presence of 0.2 equiv. of tetrabutylammonium iodide (TBAI) as a catalyst were heated under reflux in MeCN for 9 days, resulting in the isolation of the crude chloride salt as a red solid after precipitating with tetrabutylammonium chloride (TBACl). The desired product TPACage$_6$PF$_6$ was obtained in 30% yield after purification by reverse-phase column chromatography, followed by counterion exchange (NH$_4$PF$_6$/H$_2$O). Furthermore, another two salts—namely TPACage$_6$Cl and TPACage$_6$AsF$_6$—were obtained from TPACage$_6$PF$_6$ by counterion exchange in yields of 95% and 96%, respectively.

TPACage$_6^+$ was fully characterized by one-dimensional (1D, Supplementary Figs. 9–15) and two-dimensional (2D, Supplementary Figs. 22–26) $^1$H/$^1$C NMR spectroscopies, as well as by high-resolution mass spectrometry (HRMS). In the HRMS of TPACage$_6$PF$_6$, peaks with $m/z$ values of 313.1297 ([TPACage$_6$PF$_6$]$^{1+}$), 427.6539 ([TPACage$_2$2PF$_6$]$^{1+}$), and 618.5258 ([TPACage$_3$3PF$_6$]$^{1+}$) were observed (Supplementary Fig. 36), and were shown to be consistent with the calculated values. The UV-Vis absorption spectrum of TPACage$_6$PF$_6$ shows (Supplementary Fig. 46) a strong absorption at 487 nm, which originates from the 4-vinylpyridine-modified triphenylamine units in TPACage$_6^+$.

The solid-state (super)structure of TPACage$_6^+$ was determined unambiguously by single-crystal X-ray diffraction analysis of a dark red crystal, which was obtained by slow vapor diffusion of iPr$_2$O into a MeOH solution of TPACage$_6$Cl after four days. The cage displays (Fig. 2a) $D_3h$ symmetry, and possesses (Fig. 2b) three identical large rectangular windows with average dimensions of 18.7 × 6.7 Å$^2$. These rectangular windows allow potential guests to undergo association/dissociation with the internal cavity of the cage. The distance between the two central nitrogen atoms in the two TPAP propellers is (Fig. 2b) 8.6 Å, which is larger than that (6.7 Å) between the two nitrogen atoms bridged by the p-xylylene linkers. The volume of the resulting slot-like cavity is estimated (Fig. 2a) to be 368 Å$^3$, indicating that TPACage$_6^+$ may serve as a receptor for some large PAHs. The solid-state superstructure of TPACage$_6$Cl reveals how TPACage$_6^+$ assembles into a 3D framework with relatively large 1D channels with diameter of 25.0 Å. Solvent molecules have been omitted for the sake of clarity. C skyblue and red, H white, N blue, Cl green.
sets of short contacts with its neighbors through [C−H···Cl] hydrogen bonding interactions with distances in the range of 2.6−2.9 Å. Combined with the intermolecular [π···π] stacking (Fig. 2d) between adjacent styrene-pyridinium arms with a plane-to-plane distance of 3.4 Å, two sets of three TPACage6+ are stacked with each other in a coaxial manner with a perpendicular rotation angle of 60°, forming (Fig. 2e) an infinite hexagonal channel. The third styrene-pyridinium arm within each cage is involved directly in the formation of adjacent channels. Consequently, a three-dimensional (3D) supramolecular organic framework with interconnected 1D channels along the c-axis is formed. This observation indicates that the TPACage6+ has the potential for constructing organic porous materials.

Solution-phase characterizations of the host-guest complexes.

Since the constitution of TPACage6+ is based on the well-known family61 of “extended viologen cyclophanes”, we can anticipate that TPACage6+ will be able to encapsulate PAHs as a result of primarily intermolecular [π···π] interactions. The planar COR (Figs. 3a–c), with a diameter of 7.3 Å and a thickness of 3.4 Å, was selected as a representative guest. In the 1H NMR spectrum of an equimolar mixture of TPACage6+ and COR, the chemical shifts of both the protons on COR (Δδ = −0.25 ppm for H-α) and on TPACage6+ (Δδ = −0.05, −0.14, −0.12, −0.17, and −0.17 ppm for H-4, H-5, H-6, H-7, and H-8, respectively) show (Fig. 4b) significant upfield shifts compared with the chemical shifts of the free COR and the free TPACage6+, indicating the presence of aromatic [π···π] stacking interactions between COR and the styrene-pyridinium units. A 2D 1H−1H ROESY spectrum confirmed (Supplementary Fig. 30) the binding mode with through-space correlations between H-α on COR and H-7 and H-8 on TPACage6+. A Job plot showed (Supplementary Fig. 29) a maximum at a mole fraction of 0.5, confirming the existence of a 1:1 stoichiometry between TPACage6+ and COR in solution. Upon adding dropwise 8 equiv. of TPACage6+ to a CD3CN / CDCl3 (4:1) solution of COR, the resonance for H-α on COR moved gradually upfield in the 1H NMR spectra (Supplementary Fig. 27), indicating that the association and disassociation of CORTPACage6+ are undergoing fast exchange on the 1H NMR timescale. The binding constant (Kb) was determined (Supplementary Fig. 28) to be 1.3 × 10^3 M^−1, according to the chemical shift changes undergone by H-α.

In order to explore the binding ability of TPACage6+ towards some larger and thicker PAHs, three C1-symmetrical contorted hexa-cata-hexabenzocoronene derivatives (Fig. 3d)—namely, 3H-HBC, 3Me-HBC, and 3F-HBC—were synthesized (Supplementary Fig. 4) according to previously reported protocols. The single-crystal structure of 3H-HBC reveals (Fig. 3e) that its diameter reaches 15.3 Å. To determine that it adopts a contorted conformation with a thickness of 6.9 Å. Upon adding an equimolar amount of TPACage6+ into a CD3CN / CDCl3 (4:1) solution of 3H-HBC, the chemical shifts for protons on TPACage6+ and 3H-HBC all show (Fig. 4d) marked changes with some of the peaks undergoing severe broadening in the 1H NMR spectrum, suggesting the formation of a host-guest complex. The peaks in the spectrum were assigned in so far as possible on the basis of in-depth analyses of their 2D 1H−1H COSY (Supplementary Fig. 31) and ROESY (Supplementary Fig. 32) spectra. The chemical shifts of protons on the 1,2-dimethoxybenzene rings (Δδ = −0.72 and −0.29 ppm for H-α and H-β, respectively) in 3H-HBC exhibited (Fig. 4d) larger upfield shifts than those of H-γ and H-δ (Δδ = −0.27 and −0.18 ppm for H-γ and H-δ, respectively). This observation may result

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**Fig. 3 Structure formulas and solid-state structures of guest molecules.** a Structural formula and labeling of the proton on the planar COR. b, c Capped-stick and space-filling representations of the solid-state structure (obtained from CCDC:1129883) and the electrostatic potential map of COR. d Structural formulas and labeling of protons on the contorted c-HBC guest molecules, namely, 3H-HBC, 3Me-HBC, and 3F-HBC. e, f Capped-stick and space-filling representations of the solid-state structure and electrostatic potential map of 3H-HBC, showing its characteristic dimensions, tilt angles, and electron density distribution.
from the fact that the 1,2-dimethoxybenzene rings are located in the cavity formed by pairs of styrene-pyridinium units. The resonances for protons (H-5, H-6, H-7, and H-8) on the styrene units in TPACage display (Fig. 4d) severe broadening, possibly on account of the free pedaling motion about the C=C double bonds within the 3H-HBCCTPACage complex. Protons H-1 and H-2, associated with the p-xylene linkers, exhibit (Fig. 4d) downfield shifts (Δδ = 0.18 and 0.14 ppm for H-1 and H-2, respectively). In the 1H NMR spectra (Supplementary Fig. 33) of 3Me-HBCCTPACage and 3F-HBCCTPACage, a new set of resonances also appears, accompanied by severe broadening. The resonances for protons H-1 and H-2 attached to the p-xylene linkers show (Supplementary Fig. 33) characteristic downfield shifts, confirming that 3Me-HBC and 3F-HBC are encapsulated by TPACage. Because of the contorted conformations of the c-HBC guests, the association and dissociation of their complexes with TPACage undergo (Supplementary Fig. 33) slow exchange on the 1H NMR timescale, in contrast to the fast exchange process observed for CORTPACage. The cage serves as a receptor for both planar COR and contorted c-HBC derivatives in the solution state, on account of the relatively flexible conformation and the extensive cavity present in TPACage.

High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) also provided strong evidence for the formation of these four host-guest complexes. The monoisotopic masses of the four complexes (Supplementary Figs. 42–45), after deconvolution, were calculated as 2590.56 Da (CORTPACage+6PF6), 3070.71 Da (3H-HBCCTPACage+6PF6), 3112.77 Da (3Me-HBCCTPACage+6PF6), and 3124.70 Da (3F-HBCCTPACage+6PF6), respectively. These values match well with the calculated ones.

UV-Vis absorption and fluorescence spectra of both the cage and guests exhibit marked changes in the formation of host-guest complexes. Upon addition of 1 equiv. of c-HBC guests to a MeCN/CHCl3 (4:1) solution of TPACage, the characteristic absorption peak (Fig. 5a) of TPACage centered on 487 nm decreases and is accompanied by a redshift. The bright green fluorescence of c-HBC guests is almost fully quenched (Fig. 5b), while the fluorescence quantum yields for 3H-HBC, 3Me-HBC, and 3F-HBC change (Supplementary Table 1) from 3.8% to 0.6%, 3.7% to 0.9%, and 3.7% to 0.3%, respectively. Meanwhile, the emission of c-HBC overlaps well (Fig. 5) with the absorption band of TPACage, enabling potential energy transfer from c-HBC to TPACage. In the UV-Vis absorption of CORTPACage, the absorbance at 487 nm does not change much (Fig. 5a) compared with that of the free TPACage, because of the low binding affinity (Kb = 1.3 × 10^3 M^-1) between COR and TPACage. By contrast, on adding 4 equiv. of TPACage to a solution of COR, the blue fluorescence of COR is almost completely quenched (Fig. 5b) with the fluorescence quantum yield decreasing (Supplementary Table 1) from 1.8 to 0.2%, an observation that can be attributed to (i) the formation of a host-guest complex, and (ii) the strong absorption of the excess of TPACage present in the solution.

The changes in the absorption spectra induced by the formation of the host-guest complexes afford us an easy way to track the molecular recognition processes. The Job plots for 3H-HBC (Supplementary Fig. 48), 3Me-HBC (Supplementary Fig. 51), and 3F-HBC (Supplementary Fig. 54) with TPACage all show maxima at mole fractions of 0.5, confirming a stoichiometric ratio of 1:1 for all three complexes. The binding affinities between TPACage and the different c-HBC guests were determined by...
Within TPACage$^{6+}$ was estimated (Supplementary Fig. 62) to be $-3.2$ kcal mol$^{-1}$ from an isotherm obtained from a single injection experiment$^{63}$. The value of $\Delta S$ was calculated (Table 1) to be $3.9$ kcal mol$^{-1}$, while the change in entropy ($\Delta S$) is $13.1$ kcal mol$^{-1}$ K$^{-1}$. The increase in the entropy upon forming the 3H-HBCTPACage$^{6+}$ complex can be attributed most likely to the desolvation of the guest and the expulsion of solvent molecules originally residing inside the cavity of the TPACage$^{6+}$, a phenomenon similar to that observed in previous reports$^{57,64}$. Using the same procedures, the $K_a$ values for the 3H-HBCTPACage$^{6+}$ (Supplementary Fig. 50) and the 3F-HBCTPACage$^{6+}$ (Supplementary Fig. 53) complexes were determined to be $2.4 \times 10^5$ and $8.0 \times 10^4$ M$^{-1}$, respectively. The $\Delta H$ values for the formation of 3Me-HBCTPACage$^{6+}$ (Supplementary Fig. 63) and 3F-HBCTPACage$^{6+}$ (Supplementary Fig. 64) were estimated to be $-3.5$ and $-2.4$ kcal mol$^{-1}$ by ITC, and the corresponding $\Delta S$ values were calculated to be $3.8$ and $4.3$ kcal mol$^{-1}$, respectively. It follows that the formation of the c-HBC guests and TPACage$^{6+}$ are arranged in the order 3Me-HBC > 3H-HBC > 3F-HBC, indicating that, as the electron density of the guests increases, the binding affinities between the host and guests become stronger in the solution state. The kinetics associated with the encapsulations of the c-HBC guests by the TPACage$^{6+}$ can be obtained$^{63}$ by following the change in absorbance with time. The association rate constants

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**Table 1 $K_a$ Values and thermodynamic parameters for the 1:1 complexes formed between TPACage$^{6+}$ and four corone-based guests in MeCN / CHCl$\text{$_3$}$ at 25°C.**

| Entry | Guest     | $K_a$ (M$^{-1}$) | $\Delta G$ (kcal mol$^{-1}$) | $\Delta H$ (kcal mol$^{-1}$) | $\Delta S$ (kcal mol$^{-1}$ K$^{-1}$) | $\Delta S$ (cal mol$^{-1}$) |
|-------|-----------|------------------|-------------------------------|-------------------------------|----------------------------------------|-----------------------------|
| 1     | COR       | $1.3 \times 10^3$ | $-4.2$                        | $-3.2$                        | $3.9$                                  | 13.17                       |
| 2     | 3H-HBC    | $1.7 \times 10^5$ | $-7.1$                        | $-3.5$                        | $3.8$                                  | 12.86                       |
| 3     | 3Me-HBC   | $2.4 \times 10^3$ | $-7.3$                        | $-3.5$                        | $3.8$                                  | 12.86                       |
| 4     | 3F-HBC    | $8.0 \times 10^4$ | $-6.7$                        | $-2.4$                        | $4.3$                                  | 14.40                       |

*Standard errors are presented in the Supplementary Information. $^a$Estimated from 1H NMR titrations. $^b$Estimated from UV-Vis titrations. $^c$Not determined. $^d$Directly determined by ITC.

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UV-Vis titrations. The $K_a$ value for the 3H-HBCTPACage$^{6+}$ complex was determined (Supplementary Fig. 47) to be $1.7 \times 10^5$ M$^{-1}$ by following the change in absorbance at 487 nm. The Gibbs free energy ($\Delta G$) was calculated (Table 1) to be $-7.1$ kcal mol$^{-1}$, a value which is more negative than that ($-4.2$ kcal mol$^{-1}$) for CORcTPACage$^{6+}$ complex. It follows that the better the size matching between the host and guests, the stronger are the binding affinities. Because of the poor solubility of 3H-HBC in MeCN/CHCl$\text{$_3$}$(4:1), it is difficult to obtain the $K_a$ value for the 3H-HBCTPACage$^{6+}$ complex using isothermal titration calorimetry (ITC). The change in enthalpy ($\Delta H$) on complexing 3H-HBC with TPACage$^{6+}$ was estimated (Supplementary Fig. 62) to be $-3.2$ kcal mol$^{-1}$ from an isotherm obtained from a single injection experiment$^{63}$. The value of $\Delta S$ was calculated (Table 1) to be $3.9$ kcal mol$^{-1}$, while the change in entropy ($\Delta S$) is $13.1$ kcal mol$^{-1}$ K$^{-1}$. The increase in the entropy upon forming the 3H-HBCTPACage$^{6+}$ complex can be attributed most likely to the desolvation of the guest and the expulsion of solvent molecules originally residing inside the cavity of the TPACage$^{6+}$, a phenomenon similar to that observed in previous reports$^{57,64}$. Using the same procedures, the $K_a$ values for the 3H-HBCTPACage$^{6+}$ (Supplementary Fig. 50) and the 3F-HBCTPACage$^{6+}$ (Supplementary Fig. 53) complexes were determined to be $2.4 \times 10^5$ and $8.0 \times 10^4$ M$^{-1}$, respectively. The $\Delta H$ values for the formation of 3Me-HBCTPACage$^{6+}$ (Supplementary Fig. 63) and 3F-HBCTPACage$^{6+}$ (Supplementary Fig. 64) were estimated to be $-3.5$ and $-2.4$ kcal mol$^{-1}$ by ITC, and the corresponding $\Delta S$ values were calculated to be $3.8$ and $4.3$ kcal mol$^{-1}$, respectively. It follows that the formation of the c-HBC guests and TPACage$^{6+}$ are arranged in the order 3Me-HBC > 3H-HBC > 3F-HBC, indicating that, as the electron density of the guests increases, the binding affinities between the host and guests become stronger in the solution state. The kinetics associated with the encapsulations of the c-HBC guests by the TPACage$^{6+}$ can be obtained$^{63}$ by following the change in absorbance with time. The association rate constants
(k∞) for TPACage6+ with 3H-HBC, 3Me-HBC, and 3F-HBC were found (Supplementary Figs. 59–61) to be 7.2 \times 10^6, 2.6 \times 10^6, and 3.2 \times 10^6 M^{-1} s^{-1}, respectively. These k∞ values indicate that, as the size of the guests increases, the rates of association between the TPACage6+ and the c-HBC guests decrease.

**Solid-state superstructures of the host-guest complexes.** In order to elucidate the binding modes of TPACage6+ toward COR and c-HBC guests in the solid state, their complexes were analyzed by single-crystal X-ray diffraction. Dark red single crystals of the 1:1 complex between TPACage6+ and COR were obtained by slow vapor diffusion of iPr2O into MeNO2 / CHCl3 (4:1) solution containing equimolar amounts of TPACage6AsF6 and 3H-HBC over three days. In the solid-state superstructure of 3H-HBCcTPACage6+, 3H-HBC is located (Fig. 6e) in the center of the cavity inside TPACage6+, forming a C3-symmetrical host-guest complex. Three 1,2-dimethoxybenzene groups in 3H-HBC are located in the slots defined by three pairs of styrene-pyridinium units, which are stabilized by intermolecular [π···π] and [C−H···π] interactions with average distances of 3.7 Å and 3.2 Å, respectively. The outer benzenoid rings in 3H-HBC reside in the spaces between two

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**Fig. 6 Solid-state superstructures of the host-guest complexes.** a, b Capped-stick and space-filling representations of the solid-state superstructure and the intermolecular binding iso-surface of CORcTPACage6+. c, d Capped-stick and space-filling representations of the corresponding solid-state structures of individual TPACage6+ and COR molecules in their 1:1 complex. e, f Capped-stick and space-filling representations of the solid-state superstructure and intermolecular binding iso-surface of 3H-HBCcTPACage6+. g, h Capped-stick and space-filling representations of the corresponding solid-state structures of individual TPACage6+ and 3H-HBC molecules in their 1:1 complex, showing the characteristic parameters defining the changes in their geometries. i, j Capped-stick and space-filling representations of the solid-state superstructure and intermolecular binding iso-surface of 3Me-HBCcTPACage6+. k, l Capped-stick and space-filling representations of the corresponding solid-state structures of individual TPACage6+ and 3Me-HBC molecules in their 1:1 complex, showing the characteristic parameters defining the changes in their geometries. Solvent molecules and counterions have been omitted for the sake of clarity. C skyblue, pink and purple, H white, O red, N blue.
possess positively charged states of the host-guest complexes. The gas-phase stability of these four complexes in the gas phase was investigated in-depth by gradient tandem mass spectrometry (gMS²). The TPACage⁺⁻⁺ represents the three positively charged states of the free TPACage·6PF₆, while brown "HG 3⁺" represents the three positively charged states of the host-guest complexes.

![Figure 7](https://example.com/figure7.png)

**Figure 7** Gradient tandem mass spectra (gMS²) of four host-guest complexes. The gMS² of (a) [COR·TPACage·3PF₆]⁺⁺, (b) [3H-HBC·TPACage·3PF₆]⁺⁺, (c) [3Me-HBC·TPACage·3PF₆]⁺⁺, and (d) [3F-HBC·TPACage·3PF₆]⁺⁺, showing that the signal intensity for complexes gradually decreases as the voltage is increased. Blue "H 3⁺" represents the three positively charged states of the free TPACage·6PF₆ while brown "HG 3⁺" represents the three positively charged states of the host-guest complexes.

The reasons for this particular binding mode are (i) the [C−H−π] interaction (Fig. 6f) between the hydrogens attached to methoxy groups on the 1,2-dimethoxybenzene groups and the central benzene ring is 28°. These two tilt angles are different from those (26 and 24°) in the free 3H-HBC (Fig. 3e), on account of the tight encapsulation of 3H-HBC by TPACage⁺⁺. The additional strain energy for 3H-HBC in the host-guest complex is (Supplementary Table 4) 2.1 kcal mol⁻¹ according to DFT calculations. The TPACage⁺⁺ also becomes deformed in order to accommodate the twisted geometry of 3H-HBC. It changes (Fig. 6g) to a yurt-like shape, in which one of the TPAP units bulges outwards. These observations are reminiscent of the induced fit enzymes with respect to their substrates in biological systems.

Using the same procedure, the crystal superstructure of 3Me-HBC·TPACage⁺⁺ was obtained. The binding mode (Fig. 6i−6l) of 3Me-HBC inside the cavity of TPACage⁺⁺ is almost the same as that of 3H-HBC, indicating that the yurt-like binding mode of complexes is thermodynamically stable in the solid state. The 3Me-HBC guest also undergoes distortion within the cavity of TPACage⁺⁺. Its strain energy is (Supplementary Table 4) 2.3 kcal mol⁻¹, a value which is close to that (2.1 kcal mol⁻¹) of 3H-HBC in its host-guest complex.

**Gas-phase stability of the host-guest complexes.** In addition, the stability of these four complexes in the gas phase was investigated in-depth by gradient tandem mass spectrometry (gMS²). The 3⁺ peaks for the complexes (Fig. 7), e.g., m/z = 718.56 for [COR·TPACage·3PF₆]⁺⁺, 878.61 for [3H-HBC·TPACage·3PF₆]⁺⁺, 892.62 for [3Me-HBC·TPACage·3PF₆]⁺⁺, and 896.60 for [3F-HBC·TPACage·3PF₆]⁺⁺, were selected as parent ions, which were isolated using a quadrupole, followed by disintegration in the trap cell through collision-induced dissociation (CID) while the trap voltage was gradually increased. As the voltages increase, the signal intensities for the complexes gradually decrease (Fig. 7), accompanied by the generation of a peak at m/z = 618.53, which can be assigned to the free [TPACage·3PF₆]⁺⁺. The [3Me-HBC·TPACage·3PF₆]⁺⁺ complex dissociates (Fig. 7c) fully at a trap voltage of 24 V, corresponding to a center-of-mass collision energy of 1.06 eV, which is the highest one among the four complexes. In sharp contrast, the [COR·TPACage·3PF₆]⁺⁺ complex dissociates (Fig. 7a) completely at a low trap voltage of 8 V, corresponding to a center-of-mass collision energy of 0.44 eV. The collision energies for dissociating the [3H-HBC·TPACage·3PF₆]⁺⁺ (Fig. 7b) and [3F-HBC·TPACage·3PF₆]⁺⁺ (Fig. 7d) complexes were calculated to
be 0.94 eV and 0.83 eV, respectively. The stability of the four complexes in the gas phase can be ranked 3Me-HBC > 3H-HBC > 3F-HBC ≫ COR according to the collision energies, a trend which is consistent with the order of binding constants (Table 1) obtained in solution.

DFT calculations. In order to probe the origins of the changes in photophysical properties and gain insights into the electronic properties of these four host-guest complexes, density functional theory (DFT) calculations were performed. The optimized superstructures (Supplementary Figs. 76–77) of COR⊂TPACage6+, 3H-HBC⊂TPACage6+, and 3Me-HBC⊂TPACage6+ are good matches with those obtained from single-crystal X-ray diffraction. Frontier molecular orbital (FMO) analyses show (Supplementary Fig. 76a) that both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of COR⊂TPACage6+ complex are localized on TPACage6+, a situation which is different from the FMOs (Supplementary Figs. 76–77) for the complexes between the TPACage6+ and c-HBC guests. The HOMOs for the c-HBC⊂TPACage6+ complexes are localized predominantly on the c-HBC guests, while the LUMOs are confined mainly to TPACage6+. The HOMO−LUMO energy gaps in MeCN (Supplementary Table 3) for the COR, 3H-HBC, 3Me-HBC and 3F-HBC guests, and TPACage6+ host are 4.07, 3.22, 3.20, 3.19, and 2.48 eV, respectively, while their corresponding host-guest complexes possess contracted energy gaps with the values of 2.44, 2.30, 2.24, and 2.32 eV, respectively. These narrowed energy gaps provide the internal reason for the red-shifted absorption spectra in the case of both the host and guests upon forming complexes. Electrostatic potential analyses revealed that the electron density in the original electron-rich guests decreases sharply (Supplementary Figs. 79–80) following complexation by TPACage6+, suggesting the presence of the intermolecular electron delocalization. The host-guest binding energies were also estimated by DFT calculations. The calculated binding energies in vacuum (Supplementary Table 5) between TPACage6+ and four different guests are arranged in the order of $|\Delta E_{3Me-HBC}| > |\Delta E_{3H-HBC}| > |\Delta E_{3F-HBC}| > |\Delta E_{COR}|$, a trend which is consistent with the sequence of Gibbs free energies in Table 1.
Guest protection within the cage. Upon exposing a 3H-HBC suspension to UV light (370 nm), we found, quite accidentally, that the suspension turned into a clear solution. In order to gain a better understanding of this phenomenon, UV-Vis absorption and fluorescence spectroscopic measurements were carried out. Upon irradiation of a 0.5 mM 3H-HBC solution with UV light (370 nm), the UV-Vis absorption spectra of its dilute solution revealed that the absorption peak centered on 384 nm decreases gradually (Fig. 8a). After irradiation for 120 min, the UV-Vis absorption spectrum no longer undergoes any change, and the absorbance at 384 nm is decreased by 9%. During the irradiation, no obvious new peak appears in the UV-Vis absorption spectra, indicating that the 3H-HBC may be undergoing degradation when exposed to UV light. The fluorescence of 3H-HBC also decreases dramatically (Fig. 8b), and its bright green fluorescence turns to a pale yellow when exposed to UV light for 120 min. These observations confirm the photo-degradation process of 3H-HBC. Upon adding 2 equiv. of TPACage$^{6+}$ to a MeCN/CHCl$_3$ (4:1) solution containing 0.5 mM 3H-HBC, we estimate that 99% of the 3H-HBC guest is encapsulated inside the cavity of the cage according to the association and dissociation equilibria. When this solution is irradiated with UV light (370 nm) for 120 min, the UV-Vis absorption spectra of its dilute solution show (Fig. 8c) slight changes. The characteristic absorption peak of 3H-HBC at 384 nm decreases (Fig. 8d) by only 4.7%. Similarly, when solutions of 3Me-HBC$^\subset$TPACage$^{6+}$ and 3F-HBC$^\subset$TPACage$^{6+}$ are irradiated with UV light (370 nm, 120 min), the characteristic absorption peak of the 3Me-HBC guest at 384 nm decreases (Supplementary Figs. 83–84) by 8.4%, while the absorbance of the 3F-HBC guest at 384 nm shows no appreciable decline (Supplementary Figs. 85–86). It follows that the TPACage$^{6+}$ acts as a protective shield, reducing the photo-degradation rates of the c-HBC guests to a considerable degree. When the irradiation times for the host-guest complexes were extended to 240 min, the characteristic absorption peaks of 3H-HBC and 3Me-HBC at 384 nm decreased (Supplementary Fig. 87) by 13.7 and 15.7%, respectively, while the absorbance of 3F-HBC at 384 nm exhibited very little change (Supplementary Fig. 87). The slow photo-degradation of the c-HBC guests after long periods of irradiation can be attributed to the dynamic and reversible nature of the host-guest complexes and the slight photodamage of the host. Possible reasons for the difference in the photo-degradation rate between the three c-HBC guests in the host-guest complexes could be the fact that (i) the different guests display different association/dissociation binding kinetics toward the TPACage$^{6+}$, and (ii) the intrinsic photostability of the three guests is different (Supplementary Figs. 88–89). The good photostability of the 3F-HBC$^\subset$TPACage$^{6+}$ complex may result from the relatively slow photo-degradation rate of the 3F-HBC, and ideal association/dissociation exchange kinetics of the 3F-HBC$^\subset$TPACage$^{6+}$ complex in solution.

In order to ascertain the underlying mechanism giving rise to the additional photostability of c-HBC provided by encapsulation within TPACage$^{6+}$, femtosecond transient absorption (fsTA) measurements were carried out to probe the photo-induced dynamics of 3H-HBC and 3H-HBC$^\subset$TPACage$^{6+}$ complex. The fsTA spectra of 3H-HBC exhibit (Fig. 8e) a broad excited-state absorption feature at 525 nm when excited with a 350-nm pump pulse. Global analysis reveals (Supplementary Fig. 91) that the singlet excited-state ($S_1$) lifetime of 3H-HBC is $\sim$100 ps, preceded by a 6.2-ps relaxation attributed to vibrational relaxation within the initial $S_0$ excited state. The fsTA spectra of TPACage$^{6+}$ show (Supplementary Fig. 90a) a strong excited-state absorption transition centered at 560 nm upon excitation of its main absorption peak at 500 nm. When exciting the 3H-HBC$^\subset$TPACage$^{6+}$ at 350 nm, its fsTA spectra (Fig. 8f) do not show the $S_1$ excited-state signature of 3H-HBC, while only the spectral features of the TPACage$^{6+}$ are immediately observed. The excited-state dynamics of 3H-HBC$^\subset$TPACage$^{6+}$ (Fig. 8f and Supplementary Fig. 92) are analogous to those of the free TPACage$^{6+}$ (Supplementary Fig. 90) excited at 500 nm, and lacking the 6.2-ps relaxation of 3H-HBC. These observations suggest the presence of ultrafast energy transfer from 3H-HBC to TPACage$^{6+}$ upon excitation of the 3H-HBC$^\subset$TPACage$^{6+}$ complex, and the cage acts to quench the excited state of 3H-HBC in this process. The corresponding timescale of the energy transfer is estimated to be <0.3 ps (the fsTA instrument time resolution), a value which is much less than the excited-state lifetime (100 ps) of the free 3H-HBC. This ultrafast deactivation pathway (Supplementary Fig. 93) of the 3H-HBC $S_1$ excited state can suppress significantly the photo-induced degradation of 3H-HBC in the excited state. Consequently, the photostability of the c-HBC guest is enhanced on complexation inside the cavity of the TPACage$^{6+}$.

Discussion

A trigonal prismatic hexacationic cage, TPACage$^{6+}$, with a well-defined cavity and a relatively flexible conformation, has been designed and synthesized. The cage is able to encapsulate both planar coronene and contorted hexabenzocoronene guests with favorable changes in both enthalpy and entropy. As a result of the ideal dimensional matching, the binding affinities between the TPACage$^{6+}$ and the contorted hexabenzocoronene guests are larger than that in the case of coronene. To the best of our knowledge, the contorted hexabenzocoronene is the largest nanographene guest which has been investigated in the context of host-guest chemistry. Encapsulating the contorted hexabenzocoronene inside the cage, not only enriches host-guest chemistry but also extends the potential applications of synthetic receptors when it comes to the separation and stabilization of nanographenes. It is worthy of note that, benefiting from the ultrafast deactivation of the excited state of the hexabenzocoronene by transferring energy to the TPACage$^{6+}$, the photostability of the hexabenzocoronene guests is improved significantly. Enhancing the photostability of the c-HBC$^\subset$TPACage$^{6+}$ complexes constitutes a good example of regulating the photo-reaction pathway in nanographenes by a non-covalent strategy. We anticipate these complexes will serve as promising building blocks for the construction of nanographene-based mechanically interlocked molecules and new kinds of photo-stable synthetic materials that combine the properties of graphene derivatives and wholly synthetic receptors.

Methods

Materials. All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. The synthesis of TPACage$^{6+}$ is shown in Supplementary Figs. 1–3. Coronene, defined as COR, was purchased from Sigma-Aldrich. The hexa-cata-hexabenzocoronene guests, defined as c-HBC, were prepared according to the literature procedure with some modifications as shown in Supplementary Fig. 4.

NMR measurements. NMR spectra were recorded on a Bruker Avance III 600 MHz, Agilent 500 MHz, and Bruker Avance III 400 MHz spectrometers in CD$_{3}$CN, CDCl$_3$, CD$_3$OD or their mixed solvents, with working frequencies of 600, 500, and 400 MHz for recording $^1$H NMR spectra, and 150, 125 and 100 MHz for recording $^{13}$C NMR spectra, respectively. Chemical shifts (δ) are given in ppm with residual solvent signals as references.

Photophysical characterization. Both UV-Vis absorption and fluorescence spectroscopic experiments were performed at 298 K in MeCN / CHCl$_3$ (4:1). UV-Vis absorption spectra were recorded on a UV-3600 Shimadzu spectrophotometer in three types of rectangular quartz cells with the light paths of 10 mm, 4 mm, and 2 mm, respectively. Fluorescence spectra were measured in two types of rectangular
quartz cells, with the light paths of 10 mm and 2 mm, respectively, on a JASCO FP-2750 spectrometer or HORIBA FluoroMax-4 spectrometer, which were equipped with an integrating sphere for absolute fluorescence quantum yields determination.

High-resolution and gradient tandem mass spectrometry. High-resolution mass spectra (HRMS) for the precursors were recorded on an Agilent 6120 Time-of-Flight (TOF) LC-MS with an ESI source. HRMS and gradient tandem mass spectra for cage and host-guest complexes were recorded on a Waters Synapt G2-Si mass spectrometer equipped with ion-mobility under the following conditions: ESI Capillary voltage, 1.0 kV; sample cone voltage, 0 V; source offset, 1 V; source temperature, 90 °C; desolation temperature, 170 °C; cone gas flow, 10 L/h; desolation gas flow, 200 L/h (N2).

UV-Vis titration. A 1 mM solution of c-HBC guest molecules in CH3CN, as the titrating solution was added dropwise to a micromolar solution of TPACage6PF6 in MeCN / CH3CN, (4:1). Spectra were recorded from 700 to 400 nm in 10 × 10 × 45 mm rectangular quartz cells. Binding constants were obtained by fitting a 1:1 isotherm according to the programs available at http://app.supramolecular.org/bindfit/.

ITC titration. All microcalorimetric titrations were performed using a thermostated TA Nano Isothermal Titration Calorimeter at atmospheric pressure and 298 K. The samples were dissolved in a solution of MeCN / CH3CN, (4:1) and allowed to equilibrate overnight before use. A solution of TPACage6PF6 (3 × 10−3 M) in a syringe was injected with stirring at 75 rpm into a solution of c-HBC (3 × 10−4 M) guests in the sample cell with an active volume of 185 μL. Hindered by (i) the relatively low solubility of c-HBC guests in MeCN/CH3CN (4:1) and (ii) the small enthalpy changes upon forming the complexes, we found it difficult to obtain accurate binding constants using a continuous calorimetric titration protocol with multiple attempts. We explored the independent single-injection experiments to estimate the binding enthalpies for the formation of host-guest complexes. The net reaction heat was obtained by subtracting the dilution heat from the apparent reaction heat.

Crystallographic data. Crystal structures of 3H-HBC complexes: Dark red single crystals were obtained by slow vapor diffusion of the PhMe / CHCl3 (4:1) solution of 0.5 mM, 1 mM, respectively, were exposed simultaneously to UV light of 365 nm at 10 μM in a 10 × 10 × 45 mm quartz cell every 12 min. All the UV-light treated samples were generated by focusing a portion of the 800-nm laser output into a 3-mm thick sapphire plate. For the experiments, the energy of the actinic pump pulse was 0.15–0.25 μJ. The 800-nm output was directed into a commercial optical focusing equipment.

ESI-MS. ESI-MS spectra were recorded on an Agilent 6210 Time-of-Flight (TOF) LC-MS with an ESI source. HRMS and gradient tandem mass spectra for c-HBC guests in MeCN/CH3CN (4:1) were recorded with a mass spectrometer equipped with ion-mobility under the following conditions: ESI Capillary voltage, 1.0 kV; sample cone voltage, 0 V; source offset, 1 V; source temperature, 90 °C; desolation temperature, 170 °C; cone gas flow, 10 L/h; desolation gas flow, 200 L/h (N2).

References

1. Wu, J., Pisula, W. & Müllen, K. Graphenes as potential material for electronics. Chem. Rev. 107, 718–747 (2007).
2. Otsuki, K., Kawasaki, K., Shibata, M., Ito, H. & Itami, K. One-shot k-region-selective annulative π-extension for nanographene synthesis and functionalization. Nat. Commun. 6, 6251 (2015).
3. Boguslawski, E., Hansen, S. & Hild, J. P. Self-assembled hexa-peri-hexabenzocoronene photonic nanotubes. Science 359, 435–439 (2018).
4. Castro-Fernández, S. et al. Two-photon absorption enhancement by the inclusion of a tropone ring in distorted nanographene ribbons. Angew. Chem., Int. Ed. 59, 7139–7145 (2020).
5. Naito, A., Wang, Y. Y., Feng, X. & Müllen, K. New advances in nanographene chemistry. Chem. Soc. Rev. 44, 6616–6645 (2015).
6. Hill, J. P. et al. Self-assembled hexa-peri-hexabenzocoronene graphic nanotube. Science 304, 1481–1483 (2004).
7. Kang, J. et al. A rational strategy for the realization of chain-growth supramolecular polymerization. Science 347, 646–651 (2015).
8. Li, G. et al. Dearomatization toward a superbenzoquinone-based diradicaloid, tetraradicaloid, and hexaradicaloid. Angew. Chem., Int. Ed. 58, 14319–14326 (2019).
9. Yamamoto, Y. et al. Photoconductive coaxial nanotubes of molecularly connected electron donor and acceptor layers. Science 314, 1761–1764 (2006).
10. Kang, S. J. et al. Using self-organization to control morphology in molecular photovoltaics. J. Am. Chem. Soc. 135, 2207–2212 (2013).
11. Huang, Q. et al. Photoconductive curved-nanographene/fullerene supramolecular heterojunctions. Angew. Chem., Int. Ed. 58, 6244–6249 (2019).
12. Wu, Y. T. & Siegel, J. S. Aromatic molecular-bowl hydrocarbons: Synthetic derivatives, their structures, and physical properties. Chem. Rev. 106, 4843–4867 (2006).
13. Stabel, A., Herwiger, P., Müllen, K. & Rabe, J. P. Diiodelike current–voltage curves for a single molecule–tunneling spectroscopy with submolecular resolution of an alkylated, peri-condensed hexabenzozenocorone. Angew. Chem., Int. Ed. Engl. 34, 1609–1611 (1995).
14. Müllen, K. & Rabe, J. P. Nanographenes as active components of single-molecule electronics and how a scanning tunneling microscope puts them to work. Acc. Chem. Res. 41, 512–520 (2008).
15. Jiménez, V. G., David, A. H. G., Cuerva, J. M., Blanco, V. & Campaña, A. G. A macrocycle based on a heptagon-containing hexa-peri-hexabenzocorone. Angew. Chem., Int. Ed. 59, 15124–15128 (2020).
16. Claro, E. & Stephen, J. F. The synthesis of 1,2,3,4,5,6,7,8,9,10,11,12-hexaradicaloid, a diradicaloid, and a hexaradicaloid. Tetrahedron 21, 467–470 (1965).
17. Xiao, S. et al. Controlled doping in thin-film transistors of large contorted aromatic compounds. Angew. Chem., Int. Ed. 52, 4558–4562 (2013).
18. Pisula, W. et al. A zone-casting technique for device fabrication of field-effect transistors based on discotic hexa-peri-hexabenzocorone. Adv. Mater. 17, 468–470 (2005).
19. Zopp, L., Martin-Samors, L. & Baldridge, K. K. Effect of molecular packing on carboneulene-based materials electroluminescence. J. Am. Chem. Soc. 133, 14002–14009 (2011).
20. Wang, Y. et al. Two-photon excited deep-red and near-infrared emissive organic co-crystals. Nat. Commun. 11, 4633 (2020).
21. Pedersen, C. J. The discovery of crown ethers (Noble lecture). Angew. Chem., Int. Ed. Engl. 27, 1021–1027 (1988).
22. Lata, J.-M. Supramolecular chemistry—scope and perspectives molecules, supramolecules, and molecular devices (Nobel lecture). Angew. Chem., Int. Ed. Engl. 27, 89–112 (1988).
23. Cram, D. J. The design of molecular hosts, guests, and their complexes (Nobel lecture). Angew. Chem., Int. Ed. Engl. 27, 1009–1020 (1988).
24. Kim, K.-J. Functionalized cucurbiturils and their applications. Chem. Soc. Rev. 36, 267–279 (2007).
25. Harada, A., Takashima, Y. & Nakahata, M. Supramolecular polymeric materials via cycloextrin-guest interactions. Acc. Chem. Res. 47, 2128–2140 (2014).
26. Liu, C., Ni, Y., Lu, X., Li, G. & Wu, J. Global aromaticity in macrocyclic polycyclicarenes: Hückel’s rule or Baird’s rule? Acc. Chem. Res. 52, 2309–2321 (2019).
27. Ronson, T. K., Meng, W. & Nitschke, J. R. Design principles for the optimization of guest binding in aromatic-paneled Fe(II)La cages. J. Am. Chem. Soc. 139, 9698–9707 (2017).
28. Yazzaki, K. et al. Polyamorphous molecular peanuts. Nat. Commun. 8, 15914 (2017).
29. Wu, G. et al. Controllable self-assembly of macrocycles in water for isolating aromatic hydrocarbon isomers. J. Am. Chem. Soc. 140, 5955–5961 (2018).
30. Lozano, D., Alvarez-Yebra, R., Lopez-Coll, R. & Lledo, A. A flexible self-folding receptor for coronene. Chem. Sci. 10, 10351–10355 (2019).
31. Sintanta, S. K. & Schmittel, M. Guest encapsulation and coronene-C60 exchange in supramolecular zinc porphyrin tweezer, grids and prisms. Org. Biomol. Chem. 11, 3108–3115 (2013).
32. Duan, H. et al. Host-guest recognition and fluorescence of a tetraphenylethenyl-based octacationic cage. Angew. Chem., Int. Ed. 59, 10101–10110 (2020).
33. Ibáñez, S. & Peris, E. A rigid trigonal-prismatic hexagold metallocage that behaves as a coronene trap. Angew. Chem., Int. Ed. 58, 6693–6697 (2019).
34. Zhang, D., Ronson, T. K., Lavendornme, R. & Nitschke, J. R. Selective separation of polycyclic aromatic hydrocarbons by phase transfer of coordination cages. J. Am. Chem. Soc. 141, 18949–18953 (2019).
35. Okazaki, T. et al. Coaxially stacked coronene columns inside single-walled carbon nanotubes. Angew. Chem., Int. Ed. 50, 4853–4857 (2011).
36. Jurićek, M. et al. Induced-fit catalysis of coronallene bowl-to-bowl inversion. Nat. Chem. 6, 222–228 (2014).
37. Schmidt, B. M., Osuga, T., Sawada, T., Hoshino, M. & Fujita, M. Compressed coronallene in a molecular cage. Angew. Chem., Int. Ed. 55, 1561–1564 (2016).
38. Matsuno, T. et al. n arrays for single-axis rotations of a bowl in a tube. Nat. Commun. 9, 3779 (2018).
39. Kishida, N. et al. Anisotropic contraction of a polycyclic capsule and its cavity-induced compression effect. J. Am. Chem. Soc. 142, 9599–9603 (2020).
40. Ibáñez, S. & Peris, E. Dimensional matching versus induced-fit distortions: Bifunctional structure, planar and curved polyanionic hydrocarbons with tetragold metallorectangle. Angew. Chem. Int. Ed. 59, 6860–6865 (2020).
41. Hayashi, H., Aratani, N. & Yamada, H. Semiconducting self-assembled nanofibers prepared from photostable octafluorinated bisanthenyl derivatives. Chem. Eur. J. 23, 7000–7008 (2017).
42. Yang, W., Monteiro, J., de Bettencourt-Dias, A., Catalano, V. J. & Chalifoux, M. H. The key-lock theory and the induced fit theory. Angew. Chem., Int. Ed. Engl. 33, 2375–2378 (1994).
43. Wu, H. et al. Ring-in-ring(s) complexes exhibiting tunable multicolor photoluminescence. J. Am. Chem. Soc. 142, 16849–16860 (2020).
44. Hua, Y. & Flood, A. H. Click chemistry generates privileged CH hydrogen-bonding triazoles: The latest addition to anion supramolecular chemistry. Chem. Soc. Rev. 49, 1262–1271 (2010).
45. Xia, D. et al. Functional supramolecular polymeric networks: The marriage of covalent polymers and macrocycle-based host-guest interactions. Chem. Rev. 120, 6070–6123 (2020).
46. Raymo, F. M. & Stoddart, J. F. Interlocked macromolecules. Chem. Rev. 99, 1643–1664 (1999).
47. Blanco, M. et al. Positive and negative regulation of carbon nanotube catalysts through encapsulation within macrocycles. Nat. Commun. 9, 2671 (2018).

Acknowledgements
The authors thank Northwestern University (NU) for its support of this research. This research made use of the IMSEC X-ray crystallography facility at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS–1542205), and Northwestern University. The authors would like to thank Professor Bradley D. Smith for technical support relating to the stopped-flow experiments. H.W., J.Z., L.O.J., W.L., J.M.A., G.C.S., and J.F.S. are grateful for support from the Center for Sustainable Separations of Metals (CSSM), a National Science Foundation (NSF) Center for Chemical Innovation (CCI), grant number CHE-1925708. O.K.F. acknowledges the support from the Defense Threat Reduction Agency under award number HDTRA1-19-1-0101. Theoretical investigations were supported by the Department of Energy, as part of the Center for Molecular Quantum Transmission (CMQT) under grant DE-SC0013134. Theoretical investigations were also supported in part by the computational resources and staff contributions provided by the Quest High-Performance Computing Facility at NU, which is jointly supported by the Office of the Provost, the Office for Research, and Northwestern University Information Technology.

Author contributions
H.W. and Y.W. conceived the research, carried out the major experiments and analyses. B.S. did the MS analysis. H.J.W. and Y.L. carried out the part of photophysical measurements. J.Z. and J.M.A. performed the transient absorption measurements. Y.S. and J.W. prepared one of the guests. L.O.J., W.L., and G.C.S. conducted theoretical calculations. C.L.S., X.Z., L.Z., and O.K.F. carried out the X-ray crystallographic analyses. H.W., J.Z., L.O.J., W.L., J.M.A., G.C.S., and J.F.S. directed and supervised the research. All authors discussed the experimental results and contributed to the preparation of the manuscript.
Competing interests
The authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-021-25255-6.

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Peer review information Nature Communications thanks Susana Ibáñez and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

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