

Octapodal corannulene porphyrin-based assemblies: allosteric behavior in fullerene hosting

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ABSTRACT: An octapodal corannulene-based supramolecular system has been prepared by introducing eight corannulene moieties in a porphyrin scaffold. Despite the potential of this double picket fence porphyrin for double-tweezer behavior, NMR titrations show exclusive formation of 1:1 adducts. The system exhibits very strong affinity for C_{60} and C_{70} ($K_1 = (2.71 \pm 0.08) \times 10^4$ and $(2.13 \pm 0.1) \times 10^5 \text{ M}^{-1}$, respectively), presenting selectivity for the latter. DFT calculations indicate that, in addition to the four corannulene units, the relatively flexible porphyrin tether actively participates in the recognition process, resulting in a strong synergistic effect. This leads to a very strong interaction with C_{60} , which in turn also induces a large structural change on the other face (second potential binding site), leading to a negative allosteric effect. We also introduced Zn^{2+} in the porphyrin core in an attempt to modulate its flexibility. The resulting metalloporphyrin also displayed single-tweezer behavior, albeit with slightly smaller binding constants for C_{60} and C_{70} , suggesting that the effect of the coordination of fullerene to one face of our supramolecular platform was still transmitted to the other face, leading to the deactivation of the second potential binding site.

INTRODUCTION

Since its establishment, supramolecular chemistry¹ has been used to design and develop new entities with a wide range of applications in various areas of science. Inspired by nature, an interesting topic in supramolecular chemistry is the development of artificial receptors that echo the allosteric control of more complex biological systems.² The term allostereism describes structural changes that occur upon the coordination of a substrate to a binding site (allosteric site) of the host.³ The information associated with the first event is transmitted to a different binding site by a change in the conformation, which can lead to activation (positive cooperation) or deactivation (negative cooperation or inhibition) of the binding site. This represents a very useful tool to control the coordination of different sites, and not surprisingly, has attracted a great deal of attention in the supramolecular chemistry community.⁴

Additionally, carbon nanostructures, particularly fullerenes, have found a variety of applications in supramolecular chemistry due to their unique structures and electronic properties.⁵ Great efforts have been made to construct supramolecular assemblies that host fullerenes through weak intermolecular forces⁶ to develop high-performance devices, in particular, photoelectrochemical devices and solar cells.

Size and shape complementarity are crucial to achieving efficient supramolecular host-guest binding. In this regard, bowl-shaped aromatic hydrocarbons or buckybowl⁷ are attracting increasing attention and finding new applications in materials science.⁸ Corannulene,⁹ the

most-interesting buckybow, has unique properties not seen in planar π -conjugated compounds arising from its nonplanarity, which enables it to form supramolecular assemblies with fullerenes through non-covalent interactions. Its net dipolar moment,¹⁰ together with its exceptional concave-convex complementary for π - π stacking,¹¹ allows it to strongly interact with fullerenes via the well-known “ball-and-socket” interactions. Not surprisingly, corannulene has proven to be a very useful motif for the design of various materials and a very attractive building block in the construction of organic electronic devices, including solar cells and non-linear optical materials.^{8b,12} In particular, it has played a central role in the design of efficient receptors for fullerenes. The use of corannulene as a building block, however, has been limited by its tedious synthesis, which requires a large number of steps. Considerable efforts have been devoted to improve current synthetic methods as well as to its derivatization with suitable functional groups to enable its use in producing more complex architectures. Although a single pristine corannulene unit cannot bind fullerene strongly enough for the corannulene–fullerene inclusion complex to be observed in solution,¹³ the careful design of molecules incorporating two corannulene units has proven to be a very useful strategy to improve corannulene–fullerene interactions.

Researchers have long focused on improving the strength and selectivity of fullerene receptors. The historical evolution of multicorannulene ‘pincer’ systems is shown in **Figure 1**, which shows selected examples. The first and most obvious such pincer systems were based on two corannulene units and have had a great impact on supramolecular-fullerene interactions. In particular, Sygula’s buckycatcher I (**Figure 1, A**)¹⁴ represented a breakthrough as the first example of the formation of a stable inclusion complex with fullerene, and presented association constants of $2.78 \times 10^3 \text{ M}^{-1}$ (C_{60}) and $3.03 \times 10^3 \text{ M}^{-1}$ (C_{70}) in toluene at 298 K. Sygula subsequently engineered the tether between the two corannulene moieties to improve the preorganization of the host and the fullerene guest, expanding the buckycatcher family (buckycatchers II and III, not depicted in the figure)¹⁵ and improving the C_{60} binding constant by an order of magnitude. We developed a platinum-based system with two corannulene moieties, which was the first system capable of discriminating C_{60} over C_{70} (**B**); subsequently, Chen *et al.* achieved outstanding discrimination ($K_{\text{C}_{70}}/K_{\text{C}_{60}} = 230:1$) using the two corannulene moiety system **C**.¹⁶ In contrast, systems bearing tris-corannulene clips,¹⁷ such as **D** and **E**, have not had the same success as systems bearing two corannulene units due to their lower ability to associate fullerenes. The lower binding constants observed for these tripodal systems ($K_{\text{I}} = 1.50 \times 10^3 \text{ M}^{-1}$ (C_{60}) and $K_{\text{I}} = 2.19 \times 10^3 \text{ M}^{-1}$ (C_{60}) for **D** and **E** systems, respectively) seems to stem from their much greater flexibility, which favors self-interaction and consequently notably reduces their interaction with fullerenes. These examples highlight the importance of the preorganization and morphology of the supramolecular platform in fullerene association, which can be as important as the number of corannulene units attached. Therefore, to increase host-guest surface contact, careful design of fullerene receptors is required in addition to increasing the number of corannulene units.¹⁸

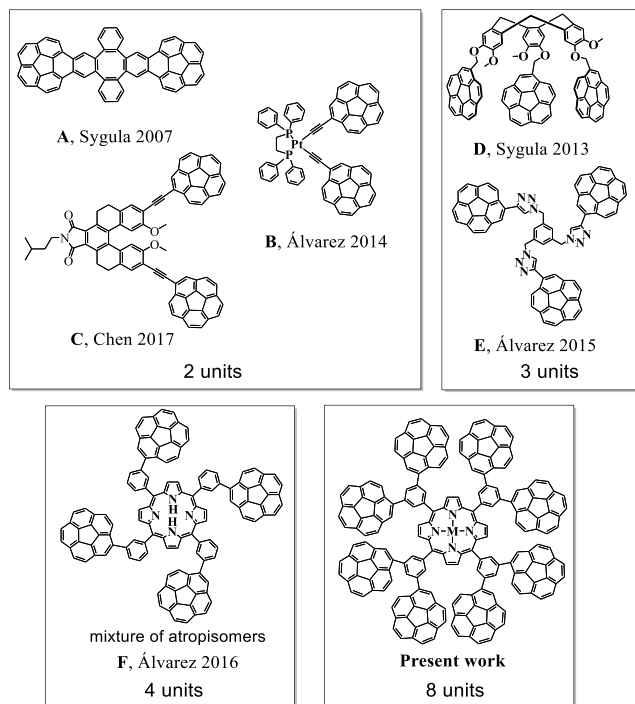


Figure 1. Development of systems bearing different numbers of corannulene units.

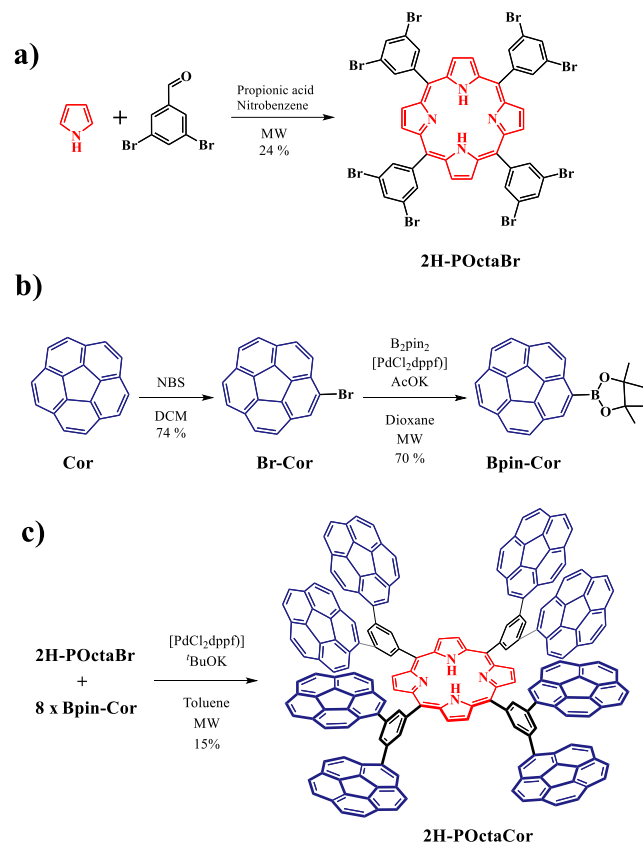
We have recently explored the use of porphyrin-based systems as molecular scaffolds for fullerene hosting. Although porphyrins and fullerenes can interact, the presence of only a single porphyrin core usually results in interactions with fullerenes that are too weak to be observed in solution.¹⁹ These systems are relatively rigid and allow for the active participation of the tether in the supramolecular interaction, and are therefore ideally suited to host fullerenes. We envisaged that a meso-substituted tetraaryl porphyrin core would be an ideal scaffold for supramolecular interactions, and prepared the *meta*-substituted porphyrin **F** with four corannulene units.^{18b} However, while this tetrakis-corannulene porphyrin clip was able to associate with C_{60} , **F** was present as a difficult-to-analyze mixture of four atropisomers resulting from the orientation of the four corannulene units above and below the porphyrin plane. These atropisomers could not be separated, resulting in a complex system and marked decrease in C_{60} binding ability. In a recent work, we subsequently circumvented the formation of atropisomers by introducing eight pyrene units at the *meta* positions of the tetraaryl porphyrin system.²⁰ This resulted in a double tweezer with a remarkably high association for fullerenes, despite the poor shape complementarity between pyrene and fullerenes, due to the synergistic effect between the porphyrin tether and the pyrene units. As the combination of well-organized corannulene fragments and a porphyrin tether resulted in synergistic effects and good fullerene hosting ability, in the present work, we explore the possibility of introducing eight corannulene units on a single porphyrin core (**Figure 1**, Present work) and their impact on the fullerene affinity and selectivity of the new octapodal corannulene supramolecular platform (which contains the most corannulene moieties on a single-molecule receptor to date). The effect of the association on the geometry of the double tweezer (allosteric effect) and its impact on a second association event, which determines whether the receptor will exhibit double or single tweezer behavior, is studied. This is an im-

portant issue since the development of artificial and well-defined systems in which allosteric effects can control the association behavior, echoing more complex biological systems, is a great challenge.

RESULTS AND DISCUSSION

To obtain the octapodal corannulene target compound, we employed a ‘corannulene LEGO brick’ approach using a divergent synthesis in which a suitable porphyrin-based scaffold is first prepared to further allow the introduction of eight corannulene units. The *meta*-substituted octabromo-porphyrin **2H-POctaBr** was selected as an ideal starting porphyrin core from which further elaboration of the porphyrin framework could be accomplished. **2H-POctaBr** presents eight bromine atoms in the *meta* positions of the tetraaryl *meso*-substituted porphyrin (**Scheme 1a**), and therefore could be used in the palladium-catalyzed Suzuki reaction with the appropriate boronic ester of corannulene. Synthesis of **2H-POctaBr** was accomplished using our previously reported microwave-assisted method.²⁰ We next prepared 1-pinacol corannuleneboronate (**Bpin-Cor**), which is the key ‘LEGO’ fragment for the introduction of corannulene to the system via Suzuki reactions at the eight bromines of **2H-POctaBr**. The borylation of corannulene to furnish **Bpin-Cor** was accomplished from 1-bromocorannulene (**Br-Cor**) via a microwave-assisted Miyaura reaction in just 80 min (**Scheme 1b**), which represented a significant improvement over the routine bench-top preparation (typically 24 h reflux in dioxane). Subsequently, the Suzuki reaction of **2HPOctaBr** and **Bpin-Cor** was accomplished via a MW-assisted octuple Suzuki reaction (150 °C, 135 min, toluene) (**Scheme 1c**). In this manner, compound **2H-POctaCor** was isolated in 15% total yield after optimization, which we considered quite satisfactory given the eight reactions involved. The use of a MW reactor has been reported to be crucial in multiple C–C coupling reactions in which the rapid buildup of byproducts might hinder product formation.²¹ Indeed, changing the cross-coupling partners in the Suzuki reaction (i.e. Br-corannulene and octaborylated porphyrin) led to a disappointing 3% yield. In this case, a range of impurities and incomplete reaction products (containing less than eight corannulene moieties) prevented us from obtaining **2H-POctaCor** in pure form.

Scheme 1. Synthesis of 2H-POctaCor^a



^a Yields of every step are included.

Despite its low solubility, the octapodal corannulene porphyrin **2H-POctaCor** was characterized by spectroscopic methods (see the Experimental Section). Further confirmation of the formation of **2H-POctaCor** was provided by high-resolution mass spectrometry, which showed the expected $[M + H]^+$ peak at m/z 2601.7586 (calcd 2601.7619, see the Supporting Information, Figure S24). The UV-Vis absorption spectra show the typical intense Soret band at 426 nm and the ^1H NMR spectrum of **2H-POctaCor** in chloroform-*d* was remarkably simple due to the highly symmetrical nature of the compound. A characteristic upfield signal for the porphyrin NH protons is observed at $\delta = -2.50$ ppm. Only one beta pyrrole proton resonance was observed, which along with the equivalence of the eight corannulene moieties, indicated an effective D_{4h} symmetry in solution. Notably, the ^1H NMR signals are markedly broad and do not change significantly upon dilution (see the Supporting Information, Figure. S2). Although a certain degree of intermolecular π - π stacking is likely, this suggests that intramolecular π - π interactions could also be occurring.^{17a,22}

To further explore this possibility, compound **2H-POctaCor** was first optimized using a conformational screening by molecular mechanics and subsequently, full DFT optimization of the best candidates at the B97D3/6-31G(d,p) level of theory²³ (see the Supporting Information for details). Interestingly, the lowest energy minimum corresponds to a conformer whose porphyrin core has been substantially distorted, giving rise to a saddle-like geometry (**Figure 2**). This situation stems from the highly attractive concave-convex stacking interac-

tions between pairs of corannulene groups. The potential formation of conformers resulting from these interactions likely contributes to the broadening of the signals observed in the $^1\text{H-NMR}$ spectrum. **Figure 2a**, shows that $\pi\text{-}\pi$ interactions are established between pairs of corannulenes, leading to a 4+4 arrangement of the corannulene units below and above the distorted porphyrin plane in a “double picket fence” arrangement. This type of arrangement could potentially lead to the binding of two fullerenes. However, such corannulene $\pi\text{-}\pi$ interactions could conceivably produce a potential energy penalty for the adoption of an optimal structure for fullerene hosting by the molecule, as all the corannulene interactions must be overcome beforehand.

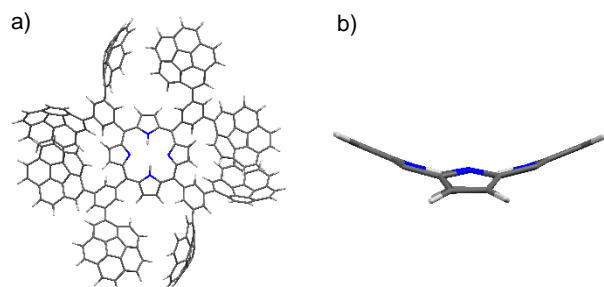


Figure 2. (a) Top view of the lowest energy minimum optimized structure of compound **2H-POctaCor** and (b) side view of the porphyrin core.

To investigate these potential issues and study the supramolecular behavior and fullerene hosting ability of **2H-POctaCor**, we carried out titration experiments with C_{60} and C_{70} in toluene- d_8 . One particular facet we were interested in exploring was whether our octapodal corannulene-based system could allow the binding of two fullerenes (see idealized **Scheme 1c**). Due to the low solubility of **2H-POctaCor**, a host concentration of $[\text{H}]_0 = 10^{-5} \text{ M}$ was selected. Upon the addition of 0.17 eq of C_{60} , a shift in the $^1\text{H NMR}$ signals was observed, indicating supramolecular association between **2H-POctaCor** and C_{60} . This shift was initially accompanied by further broadening of the signals (**Figure 3** above). This was attributed to an intermediate-exchange regime²⁴ between the free and bound guest on the NMR time scale, which is supported by the fact that towards the end of the titration (in the presence of an excess of C_{60}) the signals again became sharper, since the equilibrium was then completely shifted towards the formation of the $\text{C}_{60}@\text{2H-POctaCor}$ complex. The beta pyrrole proton resonance, which remained relatively sharp and well-defined throughout the process, was found to be a convenient signal to follow the titration (**Figure 3** above).

Similar behavior was observed in the titration of **2H-POctaCor** and C_{70} (**Figure 3** below). Upon the addition of C_{70} , a shift in the signals indicative of host-guest formation was observed, although in this case, much greater concomitant broadening of the signals was produced. Despite this, the beta pyrrole proton resonance could still be used as a good probe to follow the process (**Figure 3** below). For both titration experiments, the nonlinear binding isotherms obtained could be fitted to a 1:1 model (**Figure 3**, insets). The calculated binding constant for C_{70} ($K_1 = 2.13 \pm 0.10 \times 10^5 \text{ M}^{-1}$) was one order of magnitude larger than that of C_{60} ($K_1 = 2.71 \pm 0.08 \times 10^4 \text{ M}^{-1}$). This shows that our supramolecular platform exhibits a certain degree of selectivity for C_{70} and that the interactions among the corannulene moieties in the absence of fullerene (**Figure 2**) do not apparently diminish its fullerene hosting ability. This is in contrast to the more flexible tris-corannulene systems **D** or **E** in **Figure 1**, for which these interactions resulted

in very low affinities for C_{60} . Importantly, despite the obvious potential of our octapodal corannulene system to act as a double tweezer (**Scheme 1c**), no evidence for a 1:2 model was observed. As noted in the introduction, cooperative effects are a key aspect for understanding recognition processes in supramolecular chemistry and play a central role in complex biological systems (i.e. in the recognition processes of proteins such as allosteric control). Both positive and negative cooperation (inhibition) effects play very important roles in biological systems. A well-known example of the latter is the coordination of cytidine triphosphate to the enzyme aspartate-transcarbamoylase, which induces a conformational change that produces an inactive conformation.²⁵ Another iconic example is the coordination of O_2 to hemoglobin. The coordination of the first molecule of O_2 induces conformational changes that result in a larger binding affinity for the coordination of O_2 to the remaining binding sites.²⁶

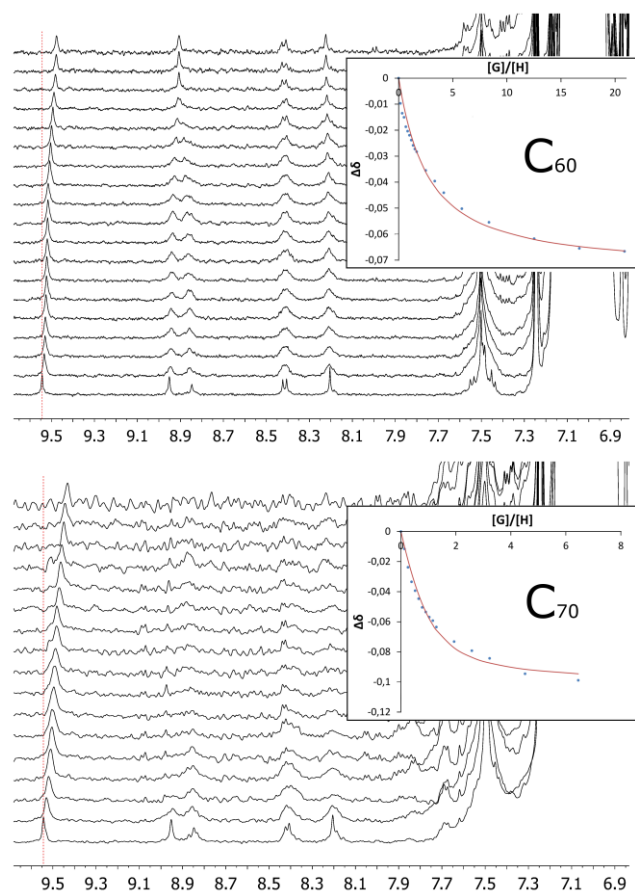


Figure 3. ^1H NMR spectra (500 MHz, toluene- d_8) showing the chemical shift of the H_2 proton of **2H-PoctaCor** upon the addition of aliquots of C_{60} (above) or C_{70} (below). Insets: Plots of the changes in the chemical shift against $[\text{G}]/[\text{H}]$, where G is C_{60} or C_{70} and H is **2H-PoctaCor**. The red line corresponds to the nonlinear fitting of $\Delta\delta$ for H_2 to a 1:1 binding isotherm. Note: The dotted red line over the spectrum is a guide for the eye.

In order to obtain further insight into this interesting phenomenon, DFT calculations were performed to determine the mechanism by which 1:1 rather than 1:2 binding stoichiometry was observed, and whether all the corannulene units are involved in the recognition process. Indeed, our octapodal corannulene system is ideally suited to study the possibility of cooperative effects in the fullerene recognition

process. The structure of the inclusion complex $C_{60}@2H-POctaCor$ obtained by DFT is shown in **Figure 4**, (see the Supporting Information for details). As can be seen, the porphyrin core has a degree of flexibility; this flexibility not only allows the approach of the four corannulene moieties to C_{60} for an optimal interaction, but also allows the core itself to actively participate in the recognition process (see later). The ortho hydrogens of the phenylene substituents tend to point away from the fullerene molecule, maximizing the interaction of the corannulene units with the outer surface of C_{60} . Thus, the structural arrangement is the result of the maximization of supramolecular binding, allowing better complementarity between both surfaces. This can be observed by the fact that all corannulene units on the same face of the porphyrin are arranged for an optimal interaction with the outer surface of the fullerene. Additionally, the contribution of the porphyrin core itself to this interaction is not negligible, as the distance between the core and the fullerene falls within the range of attractive dispersion contacts. These strong interactions lead to the compression of the corannulene arms of the active face of the porphyrin to effectively wrap the C_{60} surface.

The supramolecular bonding interactions between the host and C_{60} are most clearly illustrated on the basis of critical points.²⁷ **Figures 4c** and **4d** show five bowl-shaped attractive interactions between the fullerene and the molecular clip **2H-POctaCor**. In addition to the four interactions from the four corannulene arms, an additional interaction with the porphyrin core is clearly observed. This demonstrates the excellent complementarity between C_{60} and our molecular platform, as revealed by the fact that the isosurface almost totally covers the fullerene surface. Additional interactions between the remaining corannulenes on the other face of the molecule are also observed, indicating that the intramolecular interactions among the four remaining corannulenes also contribute to the stabilization of this structural arrangement.

Our data indicate that in the presence of fullerene, an equilibrium is reached between free C_{60} and 1:1 $C_{60}@2H-POctaCor$ adducts (K_1). This association deforms the geometry of **2H-POctaCor** in such a way that the second face of the porphyrin cannot effectively bind a second C_{60} fullerene. **Figure 4a** shows that concomitant to the organization of the active face of the porphyrin around C_{60} (compression), the arms of the other face expand significantly, leading to poor preorganization of the host for interaction with a second fullerene, as the four corannulene units of the inactive face are now too far away from each other to effectively interact with a second C_{60} .

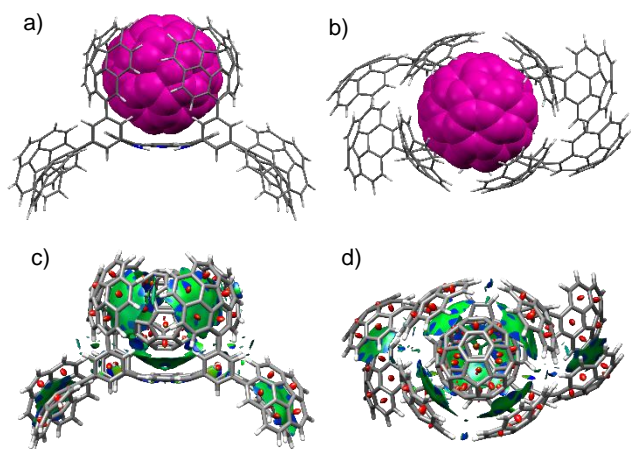


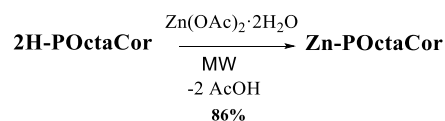
Figure 4. DFT-optimized structure of $C_{60}@2H\text{-POctaCor}$. Side (a) and top (b) views of the optimized structure. Side (c) and top (d) views of NCI plots for the optimized structure of $C_{60}@2H\text{-POctaCor}$.

We also explored the effect of a second binding event. The structure of the inclusion complex $(C_{60})_2@2H\text{-POctaCor}$ was optimized by DFT calculations (see the Supporting Information). The data reveals that, as expected, the hosting of one C_{60} in $(C_{60})@2H\text{-POctaCor}$ hampers the efficient association of a second C_{60} . Indeed, this results in a sub-optimal conformation of the receptor, in which the interaction between the first C_{60} and the porphyrin core is greatly reduced in order to partially cover the second C_{60} (see the Supporting Information for details). The acceptance of the first fullerene, therefore, leads to negative allosteric induction, preventing the binding of a second C_{60} . This effect can be ascribed to the change in the conformation of the second binding face of the receptor upon the coordination of the first fullerene.

Metal coordination is known to lead to changes in the geometry of the porphyrin ring. In order to study whether the inhibitory conformational change of the current system upon association with a first C_{60} moiety could be prevented, we introduced Zn^{2+} in the porphyrin. The resulting metalloporphyrin, **Zn-POctaCor**, was expected to exhibit a reduced degree of flexibility compared to that of the porphyrin **2H-POctaCor** as a result of metal coordination.

The introduction of a Zn^{2+} in the porphyrin was easily accomplished in a quantitative manner using a microwave-assisted method (see **Scheme 2** and the Experimental Section). The 1H NMR spectrum shows the disappearance of the inner 2H porphyrin protons, and the UV-Vis spectrum exhibited a small red-shift in the Soret band (431 nm) compared to that of **2H-POctaCor** (426 nm), suggesting that metal coordination slightly distorts the planarity of the porphyrin core.²⁸

Scheme 2. Synthesis of **Zn-POctaCor**^a



^aReagents and conditions: Zn(OAc)₂·2H₂O, CHCl₃/toluene, MW. Yield included.

Titration of **Zn-POctaCor** with C₆₀ and C₇₀ revealed a shift in the signals accompanied with a very large broadening. Although the peak broadening made the analysis challenging, a 1:1 model could be observed in both cases (see the Supporting Information). The calculated binding constants, K₁ = 2.19 ± 0.05 × 10⁴ M⁻¹ and K₁ = 1.16 ± 0.40 × 10⁵ M⁻¹ for C₆₀ and C₇₀, respectively, are slightly smaller than those obtained for **2H-POctaCor**, and also indicate selectivity for C₇₀ over C₆₀ (see **Table 1**).

Table 1. Summary of binding constants K₁ (M⁻¹) for **2H-POctaCor** and **Zn-POctaCor** for different fullerenes in toluene-d₈

	C ₆₀	C ₇₀ []]
2H-POctaCor	2.71 ± 0.08 × 10 ⁴	2.13 ± 0.10 × 10 ⁵
Zn-POctaCor	2.19 ± 0.05 × 10 ⁴	1.16 ± 0.40 × 10 ⁵

These results suggest that although coordination to Zn²⁺ reduced the flexibility of the system somewhat, which in turn led to smaller binding constants, it did not completely prevent the expansion of the other porphyrin face upon the coordination of the fullerene. This structural arrangement would disfavor the coordination of a second fullerene, leading to the formation of the experimentally observed 1:1 fullerene adduct.

CONCLUSIONS

An octapodal corannulene porphyrin-based molecular clip and its Zn-complexed metalloporphyrin analogue have been prepared. This new molecular platform contains the largest number of corannulene units reported for a single molecule and show very strong associations as C₆₀ and C₇₀ hosts, with larger affinities for the latter, indicating selectivity for C₇₀ over C₆₀. Despite the presence of two potential binding sites, the system behaves as a single rather than a double tweezer, leading to the formation of 1:1 adducts with fullerene. DFT calculations indicate that the four corannulene moieties and the porphyrin core participate in the recognition process, resulting in very strong binding of C₆₀ and a large conformational change in the molecular clip. This conformational change is transmitted to the second binding site, resulting in the expansion of its cavity and consequently, its deactivation. The allosteric effects observed in the novel octacorannulene “double picket fence” porphyrin could enable the accommodation of a larger host (such as a higher-order fullerene) in the expanded second binding site, resulting in a modular supramolecular platform that echoes allosteric regulation in biological systems. Work in our group is underway to study the interplay (compression/expansion) of the two faces to tailor the system for specific host/guest interactions.

EXPERIMENTAL SECTION

General Methods

All reagents were purchased from commercial sources and used without further purification. Solvents were either used as purchased or dried according to procedures described elsewhere.²⁹ Microwave reactions were carried out on sealed vessels using an Anton Paar Monowave 300 Reactor. Column chromatography was carried out using silica gel 60 (particle size 0.040–0.063 mm; 230–400 mesh) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F254) and visualized under UV light and/or by immersion in anisaldehyde. NMR spectra and NMR titrations were recorded on 500 MHz Agilent DD2 instruments equipped with a cold probe in the Laboratory of Instrumental Techniques (LTI) Research Facilities, University of Valladolid. ¹H and ¹³C NMR chemical shifts (δ) are reported in parts per million (ppm) and are referenced to tetramethylsilane (TMS), using the residual solvent peak as an internal reference. Coupling constants (J) are reported in Hz. Standard abbreviations are used to indicate multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet. ¹H and ¹³C peak assignments were performed using 2D NMR methods (DQF-COSY, band selective ¹H-¹H-ROESY, band selective ¹H-¹³C HSQC, band selective ¹H-¹³C HMBC). Due to low solubility, some carbon signals were detected indirectly via ¹H-¹³C-HSQC/HMBC experiments. High resolution mass spectra were recorded at the mass spectrometry service of the Laboratory of Instrumental Techniques of the (LTI) University of Valladolid. A MALDI-TOF system (MALDI-TOF), the Bruker Autoflex Speed (N₂ laser: 337 nm, pulse energy 100 μ J, 1 ns; acceleration voltage: 19 kV, reflector positive mode) was used. Trans 2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) and 1,8,9-anthracenetriol, 1,8-dihydroxy-9(10H)-anthracenone (dithranol) were used as matrices. UV/Vis spectra were recorded using a Shimadzu UV-1603 with spectrophotometric grade solvents. UV/vis absorption spectral wavelengths (λ) are reported in nanometers (nm), and molar absorption coefficients (ϵ) are reported in M⁻¹·cm⁻¹. Corannulene was obtained following the literature procedures.^{9c} Synthesis and characterization of the compound **2HPOctaBr** was previously reported by our group.²⁰

Br-Cor: Corannulene (50 mg, 0.199 mmol) and freshly recrystallized *N*-bromosuccinimide (37.3 mg, 0.209 mmol) were placed into a 5 ml round-bottom flask and dissolved in 690 μ l of dry DCM. The reaction was monitored using ¹H-NMR spectroscopy until the corannulene signal disappeared. After stirring the mixture at RT for 21 h, 10 ml of saturated NH₄Cl was added to quench the reaction. The crude was treated with 10 ml of DCM and placed into a separatory funnel. The organic phase was washed with 15 ml of warm H₂O twice, and the aqueous phase was extracted with 10 ml of DCM. The solvent of the organic phase was removed under vacuum, and the crude was purified by column chromatography on silica gel (hexane) to obtain **Br-Cor** (48.4 mg, 74%) as a fluffy yellow solid. The spectroscopic data were in agreement with the data reported in literature.^{9c}

Bpin-Cor: Br-Cor (66 mg, 0.200 mmol), bis(pinacolato)diboron (76.18 mg, 0.300 mmol), [PdCl₂(dppf)] (7.31 mg, 0.01 mmol), AcOK (58.57 mg, 0.6 mmol) were mixed into a sealed vessel specifically designed for microwave irradiation, and placed into the microwave reactor inside a two-necked round-bottom flask in order to maintain the system under an inert atmosphere. Dry dioxane (1.2 ml) was added to the microwave vessel. The mixture was stirred inside the microwave reactor at 165 °C for 80 min; the pressure reached 5.8 bar. Subsequently, the solvent was removed under low pres-

sure and the crude was purified using column chromatography on silica gel; hexane/AcOEt gradient elution (20:1 – 15:1 – 10:1 – 5:1 – 3:1 -1:1 – AcOEt) yielded **Bpin-Cor** (52.5 mg, 70%) as a yellow oil. The spectroscopic data were in agreement with the data reported in literature.³⁰

2H-POctaCor: 2HPOctaBr (10 mg, 0.0080 mmol), Bpin-Cor (26.7 mg, 0.071 mmol), [PdCl₂(dppf)] (9.3 mg, 0.0128 mmol) and ^tBuONa (18.5 mg, 0.192 mmol) were mixed in a sealed vessel specifically designed for microwave irradiation and put the microwave reactor inside a two-necked round-bottom flask in order to keep the system under an inert atmosphere. 1.4 ml of dry toluene was added. The mixture was stirred inside the microwave reactor at 150 °C for 135 min; the pressure reached 3.8 bar. After cooling, the solvent was removed under vacuum, and the crude was purified by column chromatography on silica gel using hexane/AcOEt gradient elution (3:1– 2:1 – 1:1) and CHCl₃ to finally give a purple solid corresponding to **2H-POctaCor** (3.1 mg, 15%). ¹H NMR (500 MHz, chloroform-*d*) δ: 9.31 (s, 8H, H₂), 8.85 (s, 8H, H₆), 8.69 (s, 4H, H₈), 8.35–8.26 (m, 16H, H₁₀+H₁₁), 7.93–7.70 (m, 56H, H₁₂+H₁₃+H₁₄+H₁₅+H₁₆+H₁₇+H₁₈), -2.50 (br, 2H, H₁). ¹³C{¹H} NMR (126 MHz, chloroform-*d*) δ: 136.4, 136.2, 135.8, 135.6 (C₆), 135.3, 130.9, 130.8 (C₈), 129.5, 128.1–126.3 (C₁₀+C₁₁+C₁₂+C₁₃+C₁₄+C₁₅+C₁₆+C₁₇+C₁₈). HRMS (MALDI-TOF) *m/z*: [M+H]⁺ Calcd for C₂₀₄H₉₄N₄ 2601.7619; Found 2601.7586 (3.3 ppm error). UV/vis (toluene): λ 426 (ε = 279556), 520 (ε = 12969), 544 (ε = 7205).

Zn-POctaCor: 2H-POctaCor (2.1 mg, 0.00080 mmol) and Zn(AcO)₂·2H₂O (2.6 mg, 0.012 mmol) were mixed in a sealed vessel specifically designed for microwave irradiation, followed by 1.5 ml CHCl₃ and 1.5 ml toluene. The mixture was stirred inside a microwave reactor at 120 °C for 90 min; the pressure reached 4.7 bar. After cooling, the solvent was removed under vacuum, and the obtained solid was dissolved in 10 ml of CHCl₃, placed into a separatory funnel, and washed with 5 ml of H₂O. The organic layer was removed under low pressure to give a purple solid corresponding to **Zn-POctaCor** (1.8 mg, 86%). ¹H NMR (500 MHz, chloroform-*d*) δ: 9.41 (s, 8H, H₂), 8.84 (s, 8H, H₆), 8.66 (s, 4H, H₈), 8.34–8.19 (m, 16H, H₁₀+H₁₁), 7.91–7.65 (m, 56H, H₁₂+H₁₃+H₁₄+H₁₅+H₁₆+H₁₇+H₁₈). Due to the low solubility, carbon signals (CH) were detected indirectly via an ¹H-¹³C-HSQC experiment. ¹³C{¹H} NMR (126 MHz, chloroform-*d*) δ: 135.5 (C₆), 132.4 (C₂), 130.4 (C₈), 128.5–125.4 (C₁₀+C₁₁+C₁₂+C₁₃+C₁₄+C₁₅+C₁₆+C₁₇+C₁₈). HRMS (MALDI-TOF) *m/z*: [M]⁺ Calcd for C₂₀₄H₉₂N₄Zn 2663.6665; Found 2663.6528 (13.7 ppm error). UV/vis (toluene): λ 431 (ε = 202833), 552 (ε = 17205).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Methods and details, synthetic procedures and spectra of compounds are provided in PDF format.

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Notes

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