

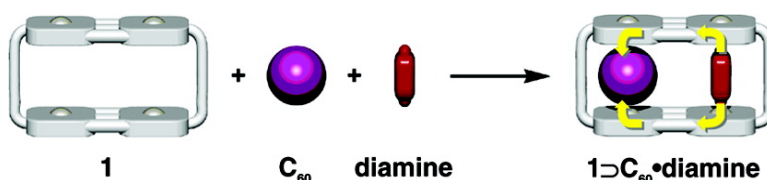
Communication

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Positive Heterotropic Cooperativity for Selective Guest Binding via Electronic Communications through a Fused Zinc Porphyrin Array

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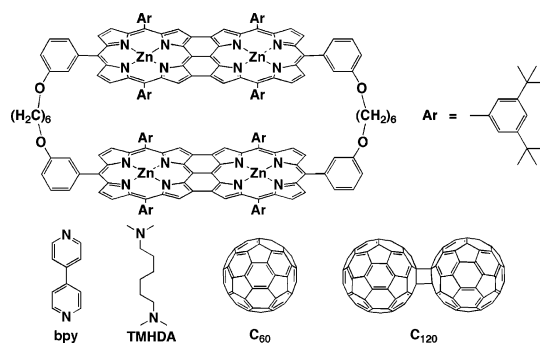
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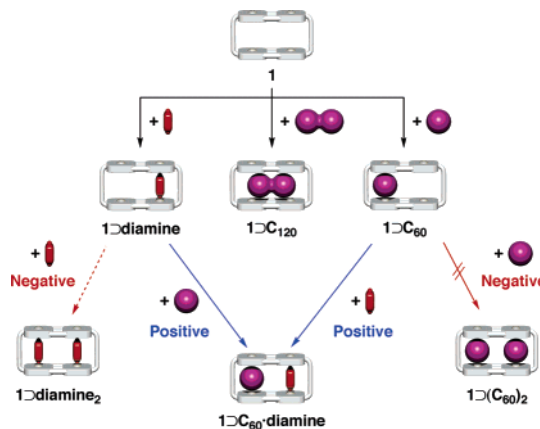
Molecular design of host molecules that can selectively trap a hetero-guest pair $A \cdot B$ has long been a challenging subject in supramolecular chemistry. Since the first success using cyclodextrins,¹ several examples have been reported,² most of which, however, make use of van der Waals fittings as the common strategy. Namely, a cavity that is too small for an $A \cdot A$ homo-guest pair but too large for a $B \cdot B$ homo-guest pair is expected to trap the $A \cdot B$ hetero-guest pair selectively, if the cavity is filled with A plus B . Here, we report a conceptually new strategy for the preferential trapping of hetero-guest pairs via an electronic communication between A and B through a π -conjugated host molecule. We have recently reported that cyclic host **1** (Chart 1)³ composed of two fused zinc porphyrin dimers⁴ displays strong negative cooperativity for the binding of bpy (4,4'-bipyridine; Chart 1),³ where a charge transfer (CT) interaction from the first-ligating bpy to **1** is transmitted through a π -electronic conjugation of the host to the second binding site and lowers the affinity toward bpy. This observation prompted us to investigate if the electronic effect of the first-bound bpy on **1** could be positively utilized for the selective inclusion of a different molecule as the second guest. To explore this interesting possibility, we chose C_{60} (Chart 1) as the second guest. As reported previously,⁵ cyclic dimers of metalloporphyrins can strongly interact with fullerenes to form highly stable inclusion complexes, in which a CT from the metalloporphyrin moieties to the included fullerenes plays a role.^{5c} Since the directions of the CT interactions of the metalloporphyrins with bpy and C_{60} are opposite to one another, we expected that positive heterotropic cooperativity might be realized for the simultaneous inclusion of these two guest molecules in the π -electronic cavity of **1** ($1 \supset C_{60} \cdot \text{bpy}$; Scheme 1).

We confirmed that **1** is capable of including C_{60} and C_{120} ⁶ (Chart 1) in its cavity. For example, mixing of **1** with C_{120} in toluene at 20 °C resulted in red-shifted absorption bands in the Soret (418 to 424 nm) and Q-band (1050 to 1080 nm) regions of **1** (Figure 1). Job's plots (inset), together with spectroscopic titration and mass spectrometry,⁷ demonstrated that **1** and C_{120} form a highly stable (association constant $K_{\text{assoc}} > 10^8 \text{ M}^{-1}$) 1:1 inclusion complex ($1 \supset C_{120}$; Scheme 1).⁸ Considering the size regime of **1**, the above results suggest that **1** is able to accommodate two molecules of C_{60} in its large π -electronic cavity. However, to our surprise, spectroscopic titration and Job's plots (Figure 1) indicated that **1** can include only one molecule of C_{60} even when it is present in large excess with respect to **1**. Here the K_{assoc} value for $1 \supset C_{60}$ (Scheme 1) was evaluated as $3.3 \times 10^4 \text{ M}^{-1}$.⁷ In conformity with this observation, ¹³C NMR spectroscopy of a 1:2 mixture of **1** and

Chart 1



Scheme 1. Inclusion of Fullerenes (C_{60} , C_{120}) and Diamines (bpy, TMHDA) within Cyclic Host **1**



¹³C-enriched C_{60} in toluene-*d*₈ showed two singlet signals at δ 141.7 and 143.0 ppm at -50 °C due to included and free C_{60} , respectively.⁷ The integral ratio of these two signals was close to unity. Considering that the π -electronic cavity of **1** is large enough to accommodate two molecules of C_{60} , this unexpected observation suggests that the first-bound C_{60} considerably reduces the affinity of **1** toward the second C_{60} and prevents the formation of 1:2 complex $1 \supset (C_{60})_2$ (Scheme 1). Thus, irrespective of whether the guest is a CT donor (bpy)³ or acceptor (C_{60}),^{5c} the cyclic host **1** consisting of π -conjugated fused zinc porphyrin dimers displays strong negative homotropic cooperativity for the guest binding (Scheme 1).

By means of NMR spectroscopy, we confirmed that cyclic host **1**, in the presence of an equimolar mixture of C_{60} and bpy, can selectively include a pair of these two guests in its cavity ($1 \supset C_{60} \cdot \text{bpy}$; Scheme 1). ¹³C NMR spectroscopy at -50 °C of a 1:1 mixture of **1** ($2.0 \times 10^{-4} \text{ M}$) and ¹³C-enriched C_{60} exhibited a singlet signal due to included C_{60} in $1 \supset C_{60}$ at δ 141.7 ppm (Figure 2a, left).

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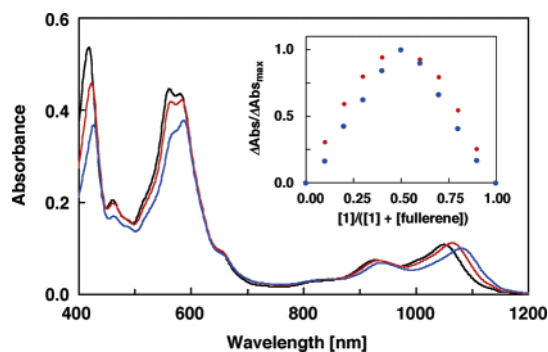


Figure 1. Absorption spectrum of **1** ($[1] = 1.7 \mu\text{M}$; black) and differential spectra of $1/\text{C}_{60}$ (1:22; $[1] = 17 \mu\text{M}$; red) and $1/\text{C}_{120}$ (1:1; $[1] = 1.7 \mu\text{M}$; blue) mixtures, obtained by subtracting the absorption spectra of C_{60} and C_{120} alone from those of equal concentrations of $1/\text{C}_{60}$ and $1/\text{C}_{120}$, respectively. Inset: Job's plots ($\Delta\text{Abs}/\Delta\text{Abs}_{\text{max}}$ at 418 nm) upon mixing **1** with C_{60} (red) or C_{120} (blue); $[1] + [\text{C}_{60}]$ and $[1] + [\text{C}_{120}] = 430$ and $2.0 \mu\text{M}$, respectively. Conditions: in toluene at 20°C .

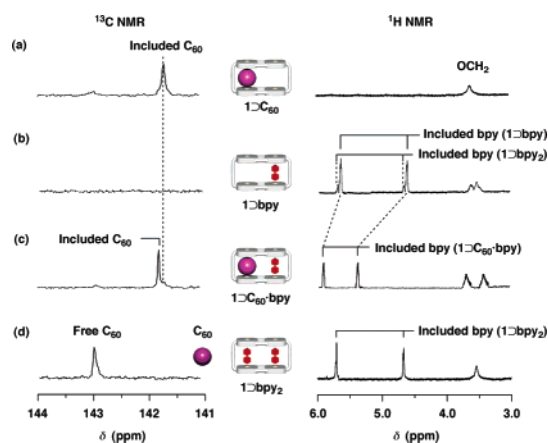


Figure 2. ^{13}C and ^1H NMR spectra of mixtures of **1**, C_{60} , and 4,4'-bipyridine (bpy) at the molar ratios of (a) 1:1:0, (b) 1:0:1, (c) 1:1:1, and (d) 1:1:2 in toluene- d_8 at -50°C .

Upon addition of 1 equiv of bpy with respect to **1** to the mixture, the signal due to included C_{60} displayed a small downfield shift by 0.1 ppm (Figure 2c, left). Addition of 1 more equiv of bpy resulted in liberation of included C_{60} (δ 143.0 ppm) to give $1\text{C}_{60}\text{bpy}_2$ (Figure 2d, left). ^1H NMR spectroscopy of the above ternary mixture at -50°C showed signals due to included bpy at δ 5.92 and 5.38 ppm (Figure 2c, right), which are shifted by 0.26 and 0.78 ppm downfield from those of $1\text{C}_{60}\text{bpy}$ (Figure 2b, right). On the other hand, when included C_{60} was liberated from $1\text{C}_{60}\text{bpy}$ by 1 equiv of bpy, the resulting $1\text{C}_{60}\text{bpy}_2$ complex showed bpy signals at δ 5.70 and 4.66 ppm (Figure 2d, right), which are close to those of $1\text{C}_{60}\text{bpy}$. As expected, the ternary mixture also displayed two OCH_2 signals at δ 3.68 and 3.41 ppm with an integral ratio being unity (Figure 2c, right), reflecting that the two linkers of $1\text{C}_{60}\text{bpy}$ are not identical to one another. For reference, $1\text{C}_{60}\text{bpy}_2$ displayed a spectral pattern (Figure 2b, right) similar to that of $1\text{C}_{60}\text{bpy}$ due to its unsymmetrical structure, while symmetric $1\text{C}_{60}\text{bpy}_2$ with two identical bpy ligands exhibited a single OCH_2 signal (Figure 2d, right). 1C_{60} is an exception, as it showed a single OCH_2 signal despite the presence of only one guest molecule in the cavity (Figure 2a, right). This is most likely due to the relatively small K_{assoc} value of 1C_{60} that may allow a rapid oscillation of C_{60} between the two binding sites of **1**.

For obtaining the accurate K_{assoc} value of $1\text{C}_{60}\text{bpy}$ with C_{60} , contamination of $1\text{C}_{60}\text{bpy}$ with guest-free **1** has to be avoided. Since a separate experiment indicated that $1\text{C}_{60}\text{bpy}_2$ is inactive for the

inclusion of C_{60} , $1\text{C}_{60}\text{bpy}$, free from **1**, was prepared as a 1:1 mixture with $1\text{C}_{60}\text{bpy}_2$ by adding 1.5 equiv³ of bpy to **1** and was used for the titration with C_{60} . Addition of C_{60} to the above mixture in toluene at 20°C resulted in the formation of $1\text{C}_{60}\text{bpy}$ at the expense of $1\text{C}_{60}\text{bpy}_2$, while $1\text{C}_{60}\text{bpy}_2$ remained intact. From the spectroscopic titration profile, K_{assoc} of $1\text{C}_{60}\text{bpy}$ with C_{60} was evaluated as $2.8 \times 10^5 \text{ M}^{-1}$,⁷ that is 8.5 times greater than K_{assoc} of **1** with C_{60} ($3.3 \times 10^4 \text{ M}^{-1}$). Thus, it is obvious that C_{60} included in **1** is stabilized by the simultaneous inclusion of bpy.

Aliphatic diamine TMHDA (*N,N,N',N'*-tetramethylhexane-1,6-diamine; Chart 1) behaves similarly to bpy. Titrations using **1**, C_{60} , and TMHDA⁷ showed that K_{assoc} of $1\text{C}_{60}\text{TMHDA}$ with TMHDA is 16 times as small as that of guest-free **1** with TMHDA (negative homotropic cooperativity), while K_{assoc} of $1\text{C}_{60}\text{TMHDA}$ with C_{60} is 4.5 times greater than that of **1** with C_{60} (positive heterotropic cooperativity). Furthermore, by virtue of a moderate affinity of TMHDA toward **1**, we could also demonstrate that the precoordination of **1** with C_{60} (1C_{60}) enhances the affinity of the host toward TMHDA by a factor of 6.1.⁷ Such positive heterotropic cooperativity observed for the formation of $1\text{C}_{60}\text{bpy}$ and $1\text{C}_{60}\text{TMHDA}$ is most likely due to an electronic communication between C_{60} and the diamines through the π -conjugated fused metalloporphyrin arrays. No spectral change of C_{60} upon mixing with the diamines⁷ can exclude a possibility that the heterotropic guest binding is promoted by their direct CT interaction. Furthermore, although an entropic gain by inclusion of the first guest for the second guest binding might be expected for flexible hosts, it hardly explains the large negative cooperativity observed for **1** in the homotropic guest binding.

In conclusion, we have shown that an equimolar mixture of C_{60} , a diamine (bpy or TMHDA), and π -conjugated host **1** preferentially forms their ternary complex (positive heterotropic cooperativity), where the guests with complementary electronic effects on the binding properties of **1** are allowed to communicate with one another through the π -electronic conjugation of **1**. This approach is essentially different from those based on van der Waals fittings² and indicates a new potential of extra large π -conjugated molecules for supramolecular chemistry. Design of cyclic hosts with higher oligomers of fused metalloporphyrins is one of the challenging subjects worthy of further investigation.

Supporting Information Available: Electronic absorption, ^1H and ^{13}C NMR, and MALDI-TOF-MS spectral data of mixtures of **1**, fullerenes (C_{60} , C_{120}), and diamines (bpy, TMHDA). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (7) See Supporting Information.
- (8) Occupation of the two binding sites of **1** with C_{120} in 1C_{120} (Scheme 1) was supported by ^1H NMR titration of 1C_{120} with bpy. See Supporting Information.

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