Dalton Transactions

Cite this: *Dalton Trans.*, 2012, **41**, 12156

www.rsc.org/dalton

PAPER

Cyclic metalloporphyrin dimers and tetramers: tunable shape-selective hosts for fullerenes†

Byungman Kang,‡ Ryan K. Totten,‡ Mitchell H. Weston, Joseph T. Hupp and SonBinh T. Nguyen*

Received 25th May 2012, Accepted 4th August 2012
DOI: 10.1039/c2dt31126g

Covalently linked cyclic metalloporphyrin dimers and tetramers have been demonstrated to be good shape-selective hosts for fullerene guests. The fullerene affinities of these hosts can readily be tuned by modulating the covalent linkage and the metal ions in the porphyrin subunits. A rigid Zn(porphyrin) dimer with conjugated bis(alkynyl) linkers exhibits a high selectivity towards C_{70} over C_{60} in toluene ($K_{a,C70}/K_{a,C60}$ = ~28). For the host structures examined, a synergistic combination of rigidity in the linker and electropositive Al ions gives rise to the strongest binding of C_{70}. In the case of a bisected Zn(porphyrin) tetramer, two well-defined cavities exist; however, due to their comparatively small size, only one C_{60} can be accommodated. Studies of fullerene binding as a function of metal ion in a porphyrin divider suggest that the right combination of shape and steric match is essential to exploit both van der Waals and local-charge/induced-dipole interactions.

Introduction

The tetrapyrrole unit in porphyrins is well-known to interact favorably with the curved surfaces of fullerenes, both in solution and in the solid state, *via* a combination of π–π and van der Waals interactions.[1–5] These interactions have been exploited in the design of a variety of porphyrin-based hosts for fullerenes,[3,6–9] among which covalently linked cyclic porphyrin dimers and trimers have been reported to give association constants as high as ~10^8 M^{-1} for C_{60} and C_{70}.[10–13] In these constructs, the electron-rich walls of multiporphyrin hosts and their close contacts with fullerenes were described as the key factors that drive strong intermolecular interactions. Furthermore, it was found that the metal center of a metalloporphyrin can also interact with the fullerene in an attractive fashion. For instance, varying the metal center in a series of cyclic metalloporphyrin dimers can modulate their association constants with fullerenes by more than two orders of magnitude.[10] While several studies have been carried out to elucidate the effect of the metal species in the porphyrin core toward fullerene binding,[10,14] the shape selectivity for fullerene isomers by multiporphyrin hosts has not been examined in a systematic fashion.[14–17] We hypothesized that the selective binding of fullerenes with different shapes and sizes can be achieved by modulating the cavity shape and rigidity of cyclic di- and tetrameric porphyrin hosts as well as their metal sites.

To evaluate the aforementioned hypothesis, we chose cofacial porphyrin dimers **A**, covalently connected *via* alkynyl, alkenyl, or alkyl groups, whose porphyrin cores can be easily modified with electropositive metal ions (Fig. 1a).[18] Such dimers have been shown by us to be capable of complexing a large *p*-nitrophenyl diphenyl phosphate (PNPDPP) (C_{60} (~10 Å) < PNPDPP (~12 Å) < C_{70} (~13 Å)). We were further intrigued by the possibility of achieving a 2 : 1 guest : host binding stoichiometry inside a bisected Zn(porphyrin) tetramer (**B**, Fig. 1b), especially because the large cavity of this host has recently been shown to

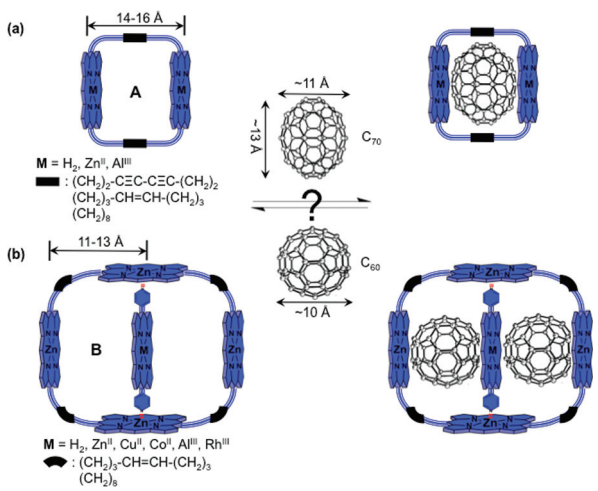


Fig. 1 Schematic representation of selective fullerene binding by cofacial porphyrin dimers possessing linkers with tunable rigidity and bisected Zn(porphyrin) tetramers.

Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA. E-mail: stn@northwestern.edu; Fax: +1 847 491-7713; Tel: +1 847-467-3347

†Electronic supplementary information (ESI) available: Complete experimental details of syntheses; compound characterization data and spectra; UV-vis/fluorescence titration experimental methods, spectra, and data analysis. See DOI: 10.1039/c2dt31126g

‡Authors contributed equally.

complex up to two PNPDPP guests.[19] By incorporating a *trans*-10,20-bis(4-pyridyl)porphyrin "divider", this large cavity can be partitioned into two "conjoined" cofacial porphyrin hosts potentially capable of encapsulating two C_{60} guests. We reasoned that such a bisected porphyrin tetramer, with smaller cavity sizes and more rigid "walls" than the aforementioned dimers, would have better interactions with C_{60}. Along with shape optimization for C_{60} binding, the metal site in the porphyrin divider can be readily tuned to allow us to determine the effect that different metalloporphyrins have on the affinity for C_{60} by the bisected tetramers.

Results and discussion

In designing a flexible, cofacial porphyrin dimer host (**A**) that can encapsulate fullerenes in a shape-selective fashion, we were interested in exploring secondary interactions between the linkers of **A** and the fullerene guest. In particular, tuning the structural rigidity of these linkers from purely alkyl to alkenyl, and then conjugated diynyl, may result in pre-organization of the host towards a specific fullerene shape, leading to optimal selectivity. Moreover, the inclusion of π electrons into the hydrocarbon linkers could potentially enhance the binding through additional π–π interactions between the host and the fullerene.

In addition to rigidifying the porphyrin cavity towards different fullerene guests, we are also interested in investigating the effect that electropositive metal ions in the core of the porphyrin may have towards fullerene binding. For instance, a cyclic Ir^{III}-(porphyrin) dimer has been shown to give the highest reported binding constant (>10^9 M^{-1} in C_6H_6) to C_{60} to date.[11] Such strong binding has been attributed to the formation of an η^2 complex between the 6 : 6 ring-juncture double bond of the fullerenes and the Ir^{III} metal center, which is strong enough to override the side-on mode normally associated with the van der Waals interactions between the host and C_{70} and "fix" the latter into an end-on mode *via* strong covalent bonds to the Ir^{III}-(porphyrin) panels.[11] As we are interested in obtaining porphyrin hosts that can strongly bind fullerenes through purely non-covalent interactions, we reasoned that local-charge/induced-dipole interactions between the highly polarizable fullerenes and electropositive metalloporphyrins would lead to large association constants without the need for covalent bond formation. In such cases, the strength of this interaction increases with the charge of the metal ion and polarizability of the guest molecule. Given the formal +3 charge of Al^{III}, and its inability to form η^2 complexes with olefins, porphyrin-embedded Al^{III} ions can be expected to induce significant dipoles with proximal C_{60} and C_{70}, which have average polarizabilities (α) of ~80 and ~100 Å^3, respectively (*cf.* $\alpha(C_6H_6)$ = ~10 Å^3).[20,21] For comparison, the analogous Zn(porphyrin) host is not expected to bind fullerene as strongly given its +2 charge (which will be partially screened by the anionic porphyrin) and its softer ionic character.

Cofacial porphyrin dimers **A** and bisected Zn(porphyrin) tetramers **B** (unsaturated or saturated (**Zn-PP**)$_4$·(**M-DPyDPP**)) used in the present work are shown in Fig. 2 (**M-DPyDPP** = 5,15-bis(4-pyridyl)-10,20-diphenylmetallo-porphyrin). Syntheses of these cyclic porphyrin assemblies have recently been reported by us.[18,19] The incorporation of 3,5-di-*tert*-butylphenyl or trihexylsilyl substituents in the *meso* positions of the porphyrin building block allows these dimers and tetramers to maintain solubility in common solvents such as methylene chloride, tetrahydrofuran, and toluene. An additional potential advantage of using these substituents is that they could further engage in CH–π interactions with bound fullerene to increase the van der Waals contacts in the inclusion complex.[22] Finally, the delocalization of the porphyrin electron density into a silyl-protected acetylene would increase the positive character of the metal center of the porphyrin, further strengthening any local-charge/induced-dipole interaction with fullerene species.[18]

The binding of C_{60} and C_{70} within the cavity of cyclic diporphyrin hosts

The binding stoichiometry of C_{60} within the cavity of a saturated Zn(porphyrin) dimer **A1** was evaluated using UV-vis spectroscopy and the continuous variation method.[23] As expected, a Job plot, obtained by monitoring the Soret absorption of **A1** (0.5×10^{-6} M) upon addition of C_{60} in toluene, indicated the formation of a 1 : 1 complex (Fig. 3). To corroborate the complexation between fullerene and **A1**, we also employed variable-temperature (VT) ^{13}C NMR spectroscopy.[8,10] A 3 : 1 mixture of ^{13}C-enriched C_{60} (2.4×10^{-3} M) and **A1** (0.8×10^{-3} M) in toluene-d_8 shows a single resonance (142.0 ppm) for C_{60} at 296 K due to the time averaging of the signals for bound and unbound C_{60} (Fig. 4b). Upon cooling, this peak broadens and splits into separate resonances for bound (139.8 ppm) and unbound (142.7 ppm) C_{60} in a ratio of 2 : 1 at 183 K (Fig. 4e). The observed upfield shift of C_{60} in the bound state is attributed to the shielding effect of the electron-rich π system of the porphyrin ring on the fullerene.[8]

Notably, the 1 : 1 adduct of fullerene (C_{60} or C_{70}) with **A1** was found to remain intact as the major molecular ion (Fig. 3) when the adduct was subjected to analysis by matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) mass spectrometry. Upon ionization, the MALDI-ToF spectrum of a 1 : 2 mixture of **A1** (0.5×10^{-3} M) and C_{60} (1.0×10^{-3} M) in toluene exhibited a single peak at *m*/*z* 2808.77 ([**A1**·C_{60}]$^+$), suggesting that the 1 : 1 inclusion complex is the only one present (Fig. 5a). Similarly, MALDI-ToF mass analysis of a mixture of **A1** and C_{70} revealed a strong molecular-ion peak at *m*/*z* 2927.99 for the 1 : 1 complexed material (Fig. 5b). Assuming that the ionization cross-sections of **A1**·C_{60} and **A1**·C_{70} are the same, **A1** appears to have a higher preference for C_{70}: the MALDI-ToF mass spectrum of a mixture of **A1** : C_{60} : C_{70} (1 : 2 : 2) only exhibits a signal for the inclusion complex **A1**·C_{70} (Fig. 5c). Along with UV-vis and VT ^{13}C NMR spectroscopies, this demonstrates the absence of concentration-dependent effects on the function of the multiporphyrin host.

The shape-selective binding of C_{60} and C_{70} with cofacial porphyrin dimers

The ability of cofacial porphyrin dimers **A1–A6** to bind fullerenes was evaluated by measuring the respective association constants (K_a) using UV-vis absorption spectroscopy. In a typical

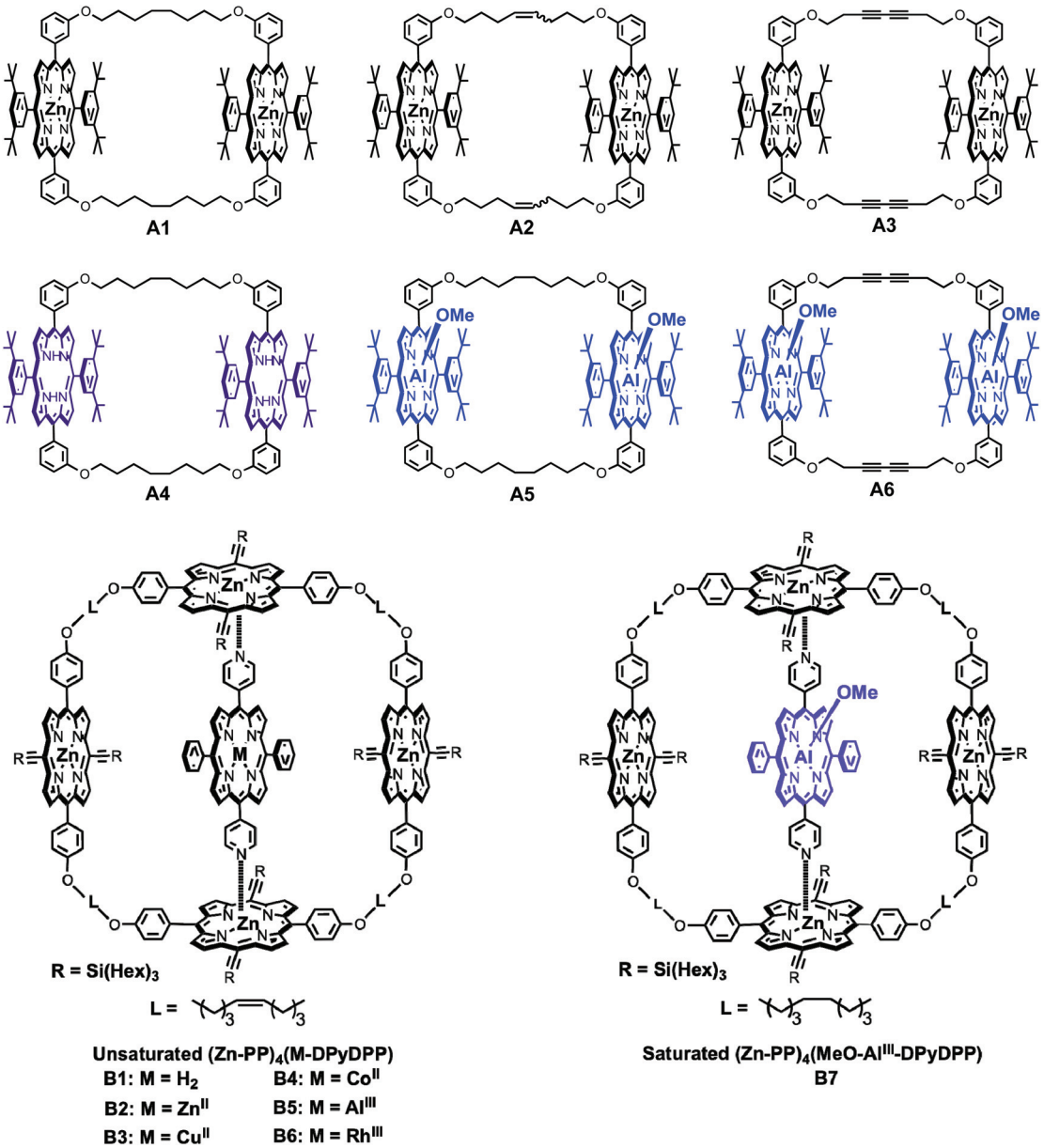


Fig. 2 Molecular structures of the cofacial porphyrin dimers **A1–A6** and the bisected porphyrin tetramers **B1–B7**.

experiment, a solution of **A1** (0.5×10^{-6} M in toluene) was titrated with small aliquots of a solution of C_{60} or C_{70} in toluene (to a total of 80 or 7 molar equiv, respectively; see section V in the ESI†). An increase in the concentration of C_{60} produces an appreciable decrease in absorption in the region of the Soret band, along with the appearance of two isosbestic points at 414 and 429 nm (Fig. 6a). A similar trend in the UV-vis titration curve was also observed when a solution of **A1** in toluene was titrated with C_{70} (Fig. 6b). Incremental addition of C_{70} caused a modest bathochromic shift with a concomitant decrease of the Soret band intensity. On the basis of the 1 : 1 binding mode and the nonlinear fit of the adsorption titration data,[23] K_a values of C_{60} and C_{70} with **A1** were estimated to be $\sim 3.3 \times 10^4$ M^{-1} and $\sim 7.0 \times 10^5$ M^{-1}, respectively.

As shown in Table 1, Zn(porphyrin) dimers **A1**, **A2**, and **A3** all have greater affinities for C_{70} than C_{60}. The differences can be attributed to a combination of larger size, elongated shape, and "flat" surface, that allow for better overall van der Waals contact with the porphyrin units.[1,10] This stronger binding of C_{70} was further evidenced by the aforementioned MALDI-ToF MS experiment where a 1 : 2 : 2 mixture of **A1** : C_{60} : C_{70} only shows a signal for **A1**·C_{70} (Fig. 5c). Notably, the preferential binding of C_{70} is greater in **A3**, which has rigid 3,5-octadiyn-1,8-diyl linkers, than in **A1**, which has flexible 1,8-octadiyl ones ($K_{a,C70}/K_{a,C60}$ = ~28 for **A3** and $K_{a,C70}/K_{a,C60}$ = ~21 for **A1**, respectively). We note that such selectivity for C_{70} over C_{60} are among the highest reported for Zn(porphyrin) dimer hosts ($K_{a,C70}/K_{a,C60}$ = 2–25).[7,15,22,24] The conformational rigidity in **A3**, together with the good shape-complementarity between the porphyrin host and the oval-shaped C_{70} guest, leads to a maximization of van der Waals contacts as indicated by a ~1.7-fold increase in $K_{a,C70}$ for **A3** over **A1** (Table 1, *cf.* entries 1 and 3).

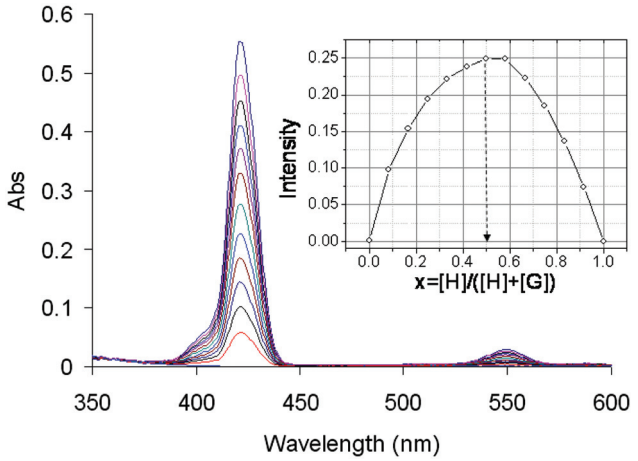


Fig. 3 UV-vis absorption spectra of **A1** at different mole fraction of C_{60}. Inset: Job plot for the determination of the binding stoichiometry between **A1** and C_{60} in toluene.

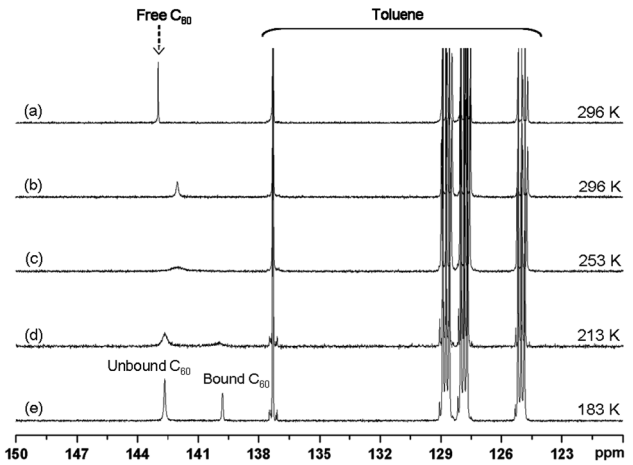


Fig. 4 Variable-temperature ^{13}C NMR spectra of ^{13}C-enriched C_{60} in the (a) absence or (b–e) presence of **A1** (0.33 equiv) in toluene-d_8.

Given the known attractive π–π interactions between fullerenes and porphyrins,[3,25] we reasoned that dimer **A5**, with its electropositive Al^{III} centers, would have additional and stronger localized-charge/induced-dipole interactions with fullerenes compared to the analogous Zn(porphyrin) dimer **A1** and free-base dimer **A4**. Indeed, the binding affinity of **A5** for C_{60} (Fig. 7a) was roughly two orders of magnitude stronger than those observed for **A1** and **A4** ($K_{a,C60}$ for **A5**/$K_{a,C60}$ for **A1** = 112 and $K_{a,C60}$ for **A5**/$K_{a,C60}$ for **A4** = 86, Table 1). For C_{70} (Fig. 7b), **A5** again exhibited a high affinity in toluene (~8.1 × 10^6 M^{-1}), albeit only a ~12-fold increase from the $K_{a,C70}$ observed for **A1**. Further supporting the existence of local-charge/induced-dipole interactions between the electropositive Al^{III} ions and fullerenes is the similarity in the binding affinities of **A5** for C_{70} over C_{60}: that the $K_{a,C70}/K_{a,C60}$ ratio for **A5** is only ~2 compared to ~20 for that of **A1** suggests that these interactions are strong enough to override the shape preference of this dimer host for C_{70}.

Since the conformational rigidity imparted by the 3,5-octadiyn-1,8-diyl linkers renders **A3** to bind C_{70} more favorably, we

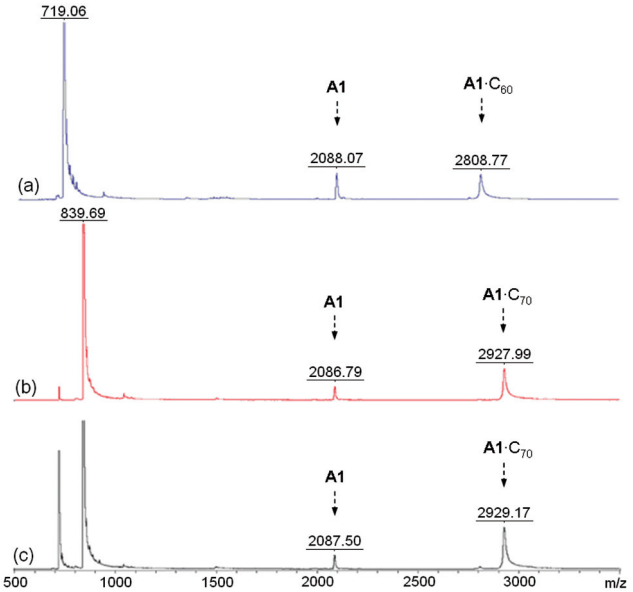


Fig. 5 MALDI-ToF mass spectra for the mixtures containing: (a) **A1** and C_{60} (2 equiv) in toluene, (b) **A1** and C_{70} (2 equiv) in toluene, (c) **A1** in the presence of C_{60} and C_{70} (2 equiv each) in toluene.

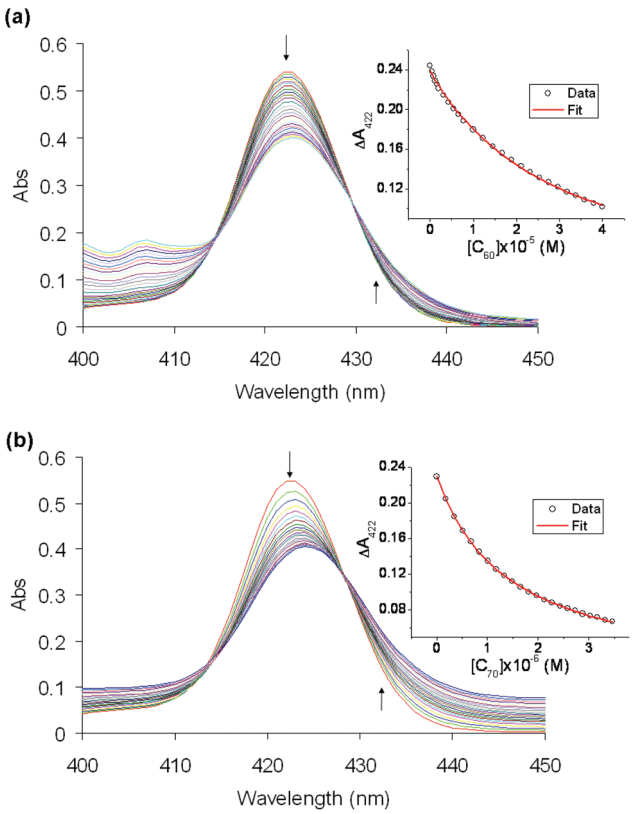


Fig. 6 Absorption spectra of **A1** (0.5 × 10^{-6} M) in toluene at 296 K upon titration with (a) C_{60} and (b) C_{70}. Insets: the absorption changes at 422 nm and the result of fitting the experimental data.

hypothesized that this rigidity may influence and/or enhance both the selectivity and binding affinity of **A5** towards C_{70}. Indeed, Al(porphyrin) dimer **A6**, with 3,5-octadiyn-1,8-diyl

Table 1 Association constants of cofacial porphyrin dimers with C_{60} and C_{70} in toluene[a]

Cyclic porphyrin dimer	Association constant (K_a, M^{-1})	
	C_{60}	C_{70}
A1	$(3.3 \pm 0.4) \times 10^4$	$(7.0 \pm 0.2) \times 10^5$
A2	$(5.0 \pm 0.9) \times 10^4$	$(6.9 \pm 0.1) \times 10^5$
A3	$(4.3 \pm 0.3) \times 10^4$	$(1.2 \pm 0.5) \times 10^6$
A4	$(4.5 \pm 0.3) \times 10^4$	$(6.3 \pm 0.1) \times 10^5$
A5	$(3.7 \pm 0.6) \times 10^6$	$(8.1 \pm 1.9) \times 10^6$
A6	$(2.8 \pm 0.1) \times 10^6$	$(1.4 \pm 0.7) \times 10^7$

[a] All association constants were measured by UV-vis titration at 296 K.

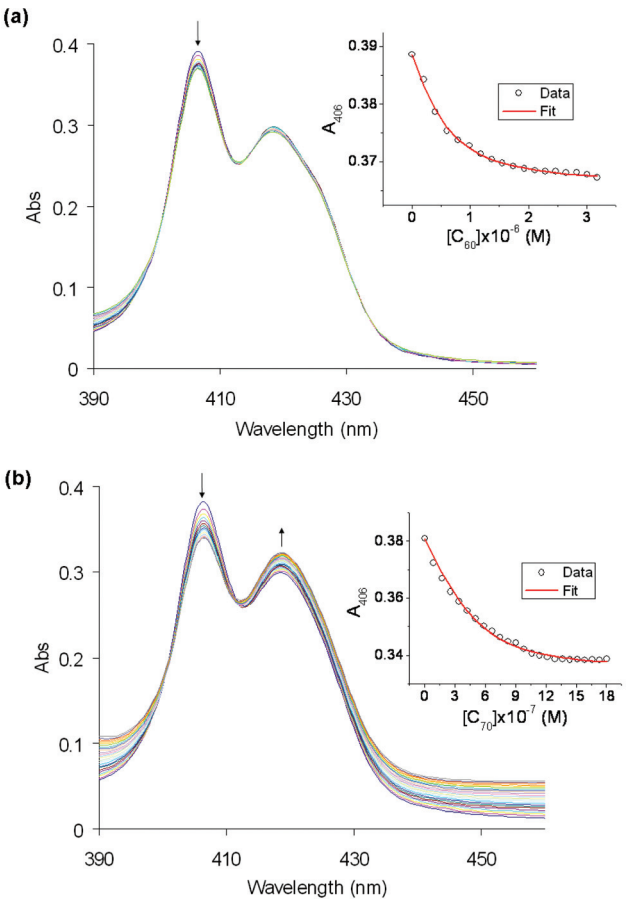


Fig. 7 Absorption spectra of **A5** (0.5×10^{-6} M) in toluene at 296 K upon titration with (a) C_{60} and (b) C_{70}. Insets: the absorption changes at 406 nm and the result of fitting the experimental data.

linkers, afforded the highest K_a for C_{70} (1.4×10^7 M^{-1}) as compared to the aforementioned dimers (Table 1). The C_{70}/C_{60} selectivity factor was also increased from ~2 to ~5 following this modification, supporting our claim that a synergistic effect results from the combination of Al^{III} ion and rigid hydrocarbon linkers in **A6**.

The binding of C_{60} with bisected Zn(porphyrin) tetramers

As reported previously, 5,15-bis(4-pyridyl)-10,20-diphenylporphine (**H_2-DPyDPP**) can be completely complexed by **(Zn-PP)$_4$** tetramer assembly and could be used to partition the latter into two conjoined cavities.[19] The ^{1}H NMR spectrum of assembly **B1** (**(Zn-PP)$_4$·(H_2-DPyDPP)**) differs significantly from those for unsaturated **(Zn-PP)$_4$** and **H_2-DPyDPP** divider (Fig. 8): the pyridyl α- and β-protons of the encapsulated **H_2-DPyDPP** displayed substantial upfield shifts (3.16 and 5.36 ppm) from those observed for free **H_2-DPyDPP** (8.88 and 8.09 ppm) (*cf.* Fig. 5b and c), indicative of the strongly shielded environment due to the coordination of the pyridyl group to Zn(porphyrin) centers.[26,27]

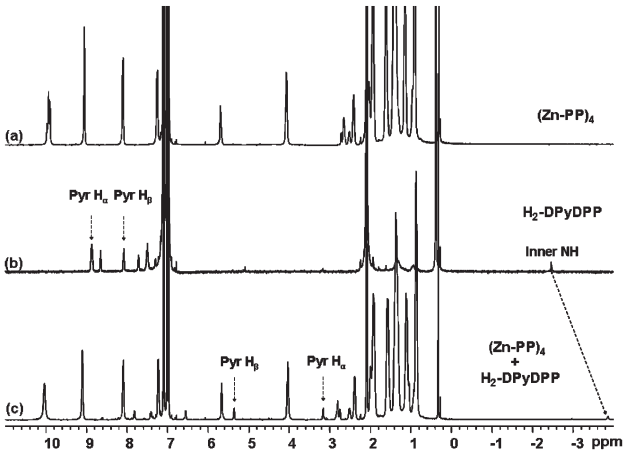


Fig. 8 ^{1}H NMR spectra of (a) unsaturated **(Zn-PP)$_4$** (1.3 mM), (b) **H_2-DPyDPP** divider (1.3 mM), and (c) a 1 : 1 mixture of unsaturated **(Zn-PP)$_4$** (1.3 mM) and **H_2-DPyDPP** (1.3 mM). Spectra a–c were obtained in toluene-d_8 at 296 K.

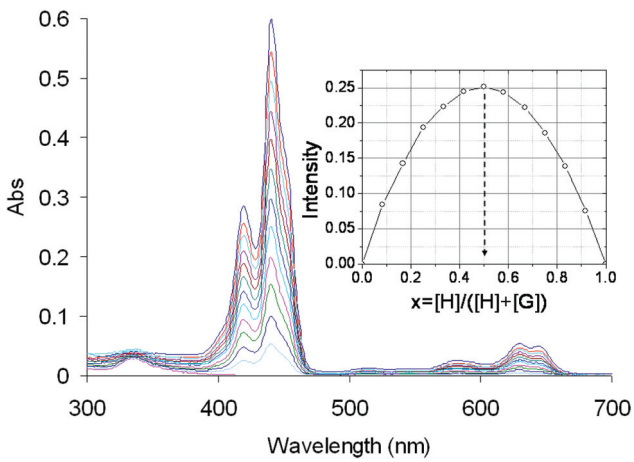
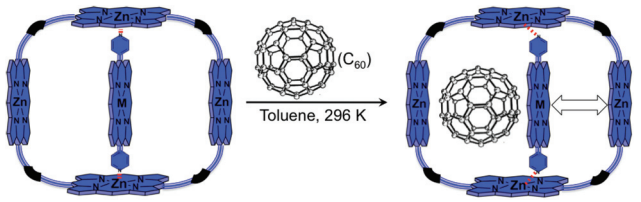


Fig. 9 UV-vis absorption spectra of **B1** at different mole fraction of C_{60}. Inset: Job plot for the determination of the binding stoichiometry between **B1** and C_{60} in toluene.

To determine the stoichiometry for encapsulation of C_{60} by the bisected cavity of **B**, a Job plot was constructed from the UV-vis absorption data of a mixture of **B1** and C_{60} at constant total concentration (0.5×10^{-6} M in toluene).[23] Unexpectedly, as can be seen in the inset of Fig. 9, a maximum is observed at a mole fraction value of only 0.5, indicating a 1 : 1 stoichiometry for the tetramer : fullerene complex. This 1 : 1 binding mode



Scheme 1 Schematic description of the 1 : 1 binding mode between the bisected Zn(porphyrin) tetramer and C_{60}.

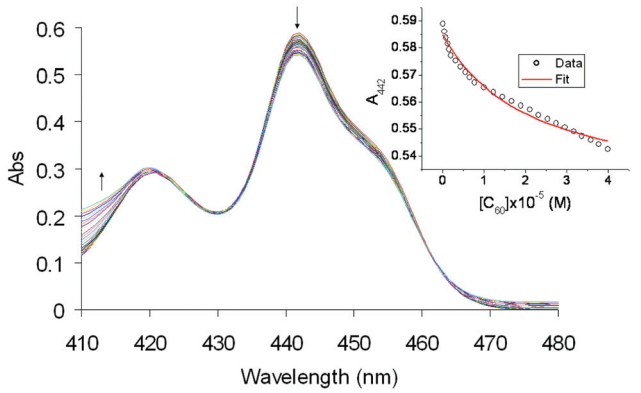


Fig. 10 Absorption spectra of **B1** (0.5×10^{-6} M) in toluene at 296 K upon titration with C_{60}. Inset: the absorption changes at 442 nm and the result of fitting the experimental data.

suggests that the binding of a second C_{60} to the remaining vacant conjoined cavity is severely inhibited by the tight fitting of one C_{60} into the first cavity. Presumably, complexation leads to a slight expansion of the C_{60}-encapsulated site, making the second cavity smaller and unable to accommodate another C_{60} (Scheme 1).

The titration experiment of **B1** (0.5×10^{-6} M in toluene) against C_{60} revealed that the Soret band of the metalloporphyrin became hypochromic with two isosbestic points appearing at 425 and 460 nm (Fig. 10). These spectral characteristics coincide with our aforementioned findings for cofacial porphyrin dimer–fullerene complexation, indicating a close contact between the porphyrin moieties in **B1** and C_{60}. Assuming a 1 : 1 stoichiometry, the nonlinear least-square fitting of the titration data afforded a K_a value of 4.6×10^4 M^{-1} for C_{60} in toluene. In contrast, the UV-vis titration of C_{70} into **B1** showed no absorption changes in its Soret and Q bands, suggesting that the partitioned cavity in **B1** is too small and rigid to associate with C_{70}. Compared to the larger cavity of **A1** (up to 15.6 Å, see section VII in the ESI†), which is able to accommodate both C_{60} and C_{70}, the smaller dimensions of the bisected cavity **B1** (~11.1 to 13.2 Å) provide a tight fit only for C_{60}.

To assess the effect of a metalloporphyrin divider on the C_{60} binding affinity of bisected tetramer **B**, we synthesized several **M-DPyDPP** dividers and inserted them into hollow **(Zn-PP)$_4$** to generate new bisected cavities **B2–B6**. From the observed UV-vis absorption spectral profiles of these assemblies upon titration with C_{60}, $K_{a,C60}$ values were obtained. As shown in Table 2, the fullerene affinities of **B2–B6**, possessing **M-DPyDPP** complexes of first-row transition metals (Zn^{II}, Cu^{II}, and Co^{II}), are slightly

Table 2 Association constants of bisected Zn(porphyrin) tetramers **B1–B6** with C_{60} in toluene[a]

Bisected Zn(porphyrin) tetramer	Divider	Association constant (K_a, M^{-1})
B1	H_2-DPyDPP	$(4.6 \pm 1.7) \times 10^4$
B2	Zn^{II}-DPyDPP	$(7.5 \pm 2.0) \times 10^4$
B3	Cu^{II}-DPyDPP	$(7.0 \pm 1.9) \times 10^4$
B4	Co^{II}-DPyDPP	$(6.7 \pm 1.9) \times 10^4$
B5	MeO-Al^{III}-DPyDPP	$(6.3 \pm 2.2) \times 10^4$
B6	Me-Rh^{III}-DPyDPP	$(4.4 \pm 1.5) \times 10^4$

[a] All association constants were measured by UV-vis titration at 296 K.

enhanced relative to that of **B1**, which features a free-base **H_2-DPyDPP** divider. Interestingly, **B5** and **B6**, which contain Al^{III} and Rh^{III} ions, respectively, do not show any increase in $K_{a,C60}$ in comparison to that of **B1**. This insensivity to the metalloporphyrin divider confirms our early suspicion about the highly restrictive steric environment of the cavity, which eliminates any potential metal-dependent effects. That is, when the cavity is so restricted such that van der Waals interactions become the primary factor dictating fullerene binding, the tight fit of the guest inside the host would render impotent any possible attractive local-charge/induced-dipole interactions between the fullerene and the metalloporphyrin walls.

To confirm the aforementioned suspicion that **(Zn-PP)$_4$·(M-DPyDPP)** is too restrictive, we synthesized a saturated **(Zn-PP)$_4$** tetramer in which the unsaturated 4-octen-1,8-diyl linkers in the unsaturated **(Zn-PP)$_4$** were reduced to flexible 1,8-octadiyl linkers of approximately equal length (see section IV in the ESI†). As expected, based on the UV-vis titration of saturated **(Zn-PP)$_4$·(MeO-Al^{III}-DPyDPP)** (**B7**) with C_{60} in toluene (see Fig. S20 in the ESI†), the affinity of **B7** for C_{60} is ~2.4-fold greater than that of the unsaturated **B5** ($K_{a,C60}$ = ~1.5×10^5 M^{-1} for **B7** and ~6.3×10^4 M^{-1} for **B5**). This encouraging result indicates the important contribution of a flexible cavity such as **B7** in stabilizing C_{60}: C_{60} is better bound when the cavity between the **MeO-Al^{III}-DPyDPP** divider and the Zn(porphyrin) wall is not as conformationally restricted. Unfortunately, no association of **B7** with the larger fullerene was detected, suggesting that the partitioned cavity in **B7** is still too small.

Conclusions

In summary, we have demonstrated that matching the cavity of a porphyrin host to the shape of a fullerene guest, such as the case of our "rectangular" dimer to the ovoid C_{70}, can notably enhance the selective binding of the fullerene. Increasing the rigidity of the linkages in the host by replacing flexible octyl chains with more rigid 4-ethenyl and 3,5-octadiynyl ones can further enhance the interaction between the cavity and the guest. When the match is most optimal, further metal interactions can be beneficial: the high association constant of Al(porphyrin) dimers **A5** and **A6** with fullerenes indicates a strong interaction between the electropositive Al^{III} centers in the porphyrin walls and the highly polarizable fullerenes.

In the case of the bisected Zn(porphyrin) tetramer **B1–B6** with 4-octen-1,8-diyl linkages, only one of the two well-defined

conjoined cavities is able to accommodate C_{60} due to the overall small size of the parent cavity. Together with the lack of binding by C_{70}, the negligible effects that different metalloporphyrin dividers have on the binding affinity for C_{60} clearly point to the importance of having the right combination of shape and steric match if one is to take advantage of both van der Waals and local-charge/induced-dipole interactions. In such cases, making the cavity flexible enough so that both effects can be utilized should result in the best binding constant possible.

Acknowledgements

This material is based upon research sponsored by the AFOSR under agreement FA-9550-07-1-0534. We acknowledge DTRA (grant HDTRA1-10-1-0023) and the DoE (grant DE-FG02-03ER15457) for additional financial support. We thank Professor George C. Schatz for his insightful discussions.

Notes and references

1 P. D. W. Boyd, M. C. Hodgson, C. E. F. Rickard, A. G. Oliver, L. Chaker, P. J. Brothers, R. D. Bolskar, F. S. Tham and C. A. Reed, *J. Am. Chem. Soc.*, 1999, **121**, 10487–10495.
2 E. M. Pérez and N. Martín, *Chem. Soc. Rev.*, 2008, **37**, 1512–1519.
3 P. D. W. Boyd and C. A. Reed, *Acc. Chem. Res.*, 2005, **38**, 235–242.
4 C. M. Drain, A. Varotto and I. Radivojevic, *Chem. Rev.*, 2009, **109**, 1630–1658.
5 L. P. Hernández-Eguía, E. C. Escudero-Adán, J. R. Pinzón, L. Echegoyen and P. Ballester, *J. Org. Chem.*, 2011, **76**, 3258–3265.
6 K. Tashiro and T. Aida, *Chem. Soc. Rev.*, 2007, **36**, 189–197.
7 M. Dudič, P. Lhoták, I. Stibor, H. Petříčkova and K. Lang, *New J. Chem.*, 2004, **28**, 85–90.
8 D. Sun, F. S. Tham, C. A. Reed, L. Chaker, M. Burgess and P. D. W. Boyd, *J. Am. Chem. Soc.*, 2000, **122**, 10704–10705.
9 K. Tashiro, T. Aida, J. Y. Zheng, K. Kinbara, K. Saigo, S. Sakamoto and K. Yamaguchi, *J. Am. Chem. Soc.*, 1999, **121**, 9477–9478.
10 J.-Y. Zheng, K. Tashiro, Y. Hirabayashi, K. Kinbara, K. Saigo, T. Aida, S. Sakamoto and K. Yamaguchi, *Angew. Chem., Int. Ed.*, 2001, **40**, 1858–1861.
11 M. Yanagisawa, K. Tashiro, M. Yamasaki and T. Aida, *J. Am. Chem. Soc.*, 2007, **129**, 11912–11913.
12 G. Gil-Ramírez, S. D. Karlen, A. Shundo, K. Porfyrakis, Y. Ito, G. A. D. Briggs, J. J. L. Morton and H. L. Anderson, *Org. Lett.*, 2010, **12**, 3544–3547.
13 A. R. Mulholland, C. P. Woodward and S. J. Langford, *Chem. Commun.*, 2011, **47**, 1494–1496.
14 D. Sun, F. S. Tham, C. A. Reed, L. Chaker and P. D. W. Boyd, *J. Am. Chem. Soc.*, 2002, **124**, 6604–6612.
15 L. P. Hernández-Eguía, E. C. Escudero-Adán, I. C. Pintre, B. Ventura, L. Flamigni and P. Ballester, *Chem.–Eur. J.*, 2011, **17**, 14564–14577.
16 Y. Shoji, K. Tashiro and T. Aida, *J. Am. Chem. Soc.*, 2010, **132**, 5928–5929.
17 Y. Shoji, K. Tashiro and T. Aida, *J. Am. Chem. Soc.*, 2006, **128**, 10690–10691.
18 R. K. Totten, P. Ryan, B. Kang, S. J. Lee, L. J. Broadbelt, R. Q. Snurr, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2012, **48**, 4178–4180.
19 B. Kang, J. W. Kurutz, K.-T. Youm, R. K. Totten, J. T. Hupp and S. T. Nguyen, *Chem. Sci.*, 2012, **3**, 1938–1944.
20 I. Compagnon, R. Antoine, M. Broyer, P. Dugourd, J. Lermé and D. Rayane, *Phys. Rev. A: At., Mol., Opt. Phys.*, 2001, **64**, No. 025201.
21 K. J. Miller and J. A. Savchik, *J. Am. Chem. Soc.*, 1979, **101**, 7206–7213.
22 A. Hosseini, S. Taylor, G. Accorsi, N. Armaroli, C. A. Reed and P. D. W. Boyd, *J. Am. Chem. Soc.*, 2006, **128**, 15903–15913.
23 K. Hirose, *J. Inclusion Phenom. Macrocyclic Chem.*, 2001, **39**, 193–209.
24 Y. Shoji, K. Tashiro and T. Aida, *J. Am. Chem. Soc.*, 2004, **126**, 6570–6571.
25 Y. Sun, T. Drovetskaya, R. D. Bolskar, R. Bau, P. D. W. Boyd and C. A. Reed, *J. Org. Chem.*, 1997, **62**, 3642–3649.
26 S. Anderson, H. L. Anderson, A. Bashall, M. McPartlin and J. K. M. Sanders, *Angew. Chem., Int. Ed.*, 1995, **34**, 1096–1099.
27 E. B. Fleischer and A. M. Shachter, *Inorg. Chem.*, 1991, **30**, 3763–3769.