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Twofold fused concave hosts containing two phosphorus atoms: modules for the sandwich-type encapsulation of fullerenes in variable cavities†

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The design and synthesis of extended concave host **P2** by fusion of two concave phosphorus-containing units is reported. Co-crystallization of **P2** and the fullerene guests C_{60} and C_{70} afforded the 2 : 1 host–guest complexes $(\mathbf{P2})_2 \supset C_{60}$ and $(\mathbf{P2})_2 \supset C_{70}$, in which the two concave surfaces of **P2** encapsulate the convex surface of the fullerenes in a sandwich fashion. Interestingly, the orientation of the two **P2** molecules with respect to each other was observed to be flexible, resulting in the formation of a variety of cavity shapes. MALDI-TOF mass, NMR, and UV-vis absorption spectra supported the formation of host–guest complexes between **P2** and the fullerenes in solution. The affinity of **P2**, containing two phosphorus atoms, towards fullerenes was significantly enhanced relative to **P1** with one phosphorus atom.

Introduction

The recognition of fullerenes is one of the most intensively pursued research subjects in contemporary supramolecular and host–guest chemistry.[1] The applications of fullerene recognition are manifold and reach from fullerene purification[2] and nanoscale organisation[3] to the formation of photovoltaic cells.[4] A central paradigm for the design of molecular hosts is the generation of well-defined three-dimensional architectures so that suitable arrangements of the binding sites are obtained.[5] For the recognition and capture of fullerenes, which usually do not contain any functional groups, only weak interactions such as π–π and CH–π interactions are available, and therefore aromatic compounds have often been used as binding sites. Even though benzene rings represent a relatively small binding site, recent studies have demonstrated a very high affinity for fullerene derivatives arising from the macrocyclic arrangement of benzene rings (carbon-nanorings),[6] and can therefore be considered as an analogy of crown ether chemistry. Coordinative self-assembly of small molecules is also effective to capture fullerenes.[7] Concave π-conjugated molecules[8,9] are also promising binding sites for fullerenes, as their concave surfaces resemble and match the convex π-surface of fullerenes.[10,11] Although individual concave molecules exhibit merely a weak affinity towards fullerenes, the fusion of multiple molecular units can substantially increase this affinity.[12,13] Recently, we reported phosphorus-containing concave molecule **P1** (Chart 1),[14,15] and although four host molecules perfectly wrapped around the convex surface of C_{60} in the crystalline state, the host–guest interaction between the host and the C_{60} guest was found to be negligible in organic solvents. Concave **P1** is considered to be a good molecular host fragment, but a carefully crafted arrangement of multiple such fragments is necessary for an efficient recognition of C_{60}.

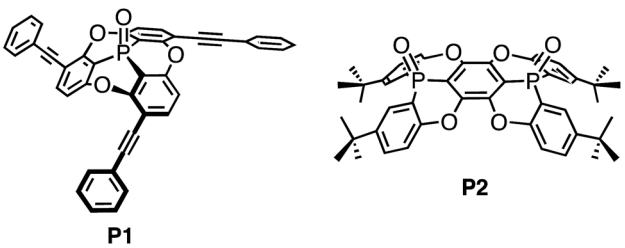

Chart 1 Concave host **P1** and twofold fused concave host **P2**.

Therefore, we have designed and synthesised the extended concave molecule **P2** by fusing two phosphorus-containing concave units similar to **P1**. The expanded concave surface of **P2** is expected to enhance the affinity of **P2** towards fullerene guests through increased concave–convex interactions.

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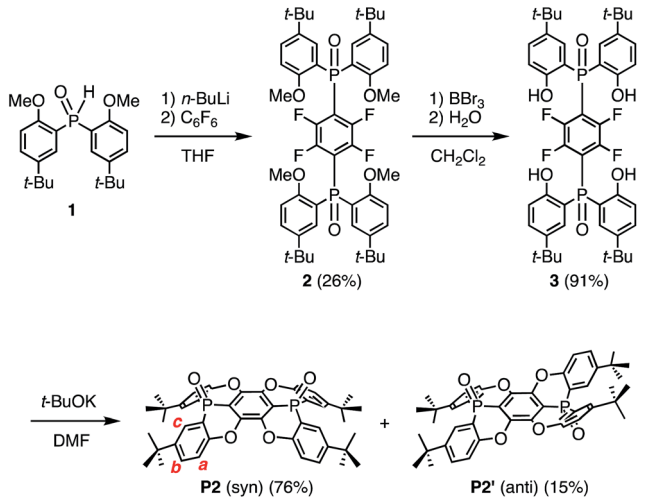
Results and discussion

Synthesis of the fused concave host

Concave host **P2** was synthesised in three steps (Scheme 1), starting from the reaction between hexafluorobenzene and two equivalents of an anion, which was generated from the



Scheme 1 Synthesis of bowl-shaped phosphorus-containing host **P2**.

deprotonation of **1** with *n*-BuLi. Thus, 1,4-bis(phosphoryl)tetrafluorobenzene **2** was obtained in 26% yield.[16] Subsequent treatment of **2** with BBr_3 resulted in the removal of four methyl groups to afford **3** in 91% yield. Deprotonation of **3** with *t*-BuOK furnished concave **P2** (76%) and its *anti*-isomer **P2′** (15%) in excellent stereo-selectivity, whereby the intramolecular S_NAr reaction is the key step. The molecular structures of **P2** and **P2′** were determined unequivocally by single crystal X-ray diffraction analysis (Fig. S27†).

Single crystals of **P2**, suitable for X-ray crystallographic analysis, were obtained by recrystallization from $CHCl_3$/hexane, and the crystal structure clearly showed the concave shape of **P2** (Fig. 1). The two phosphorus atoms, P1 and P2, are positioned slightly above (0.167/0.269 Å) the plane of the central benzene ring **A**.[17] The P–O axes are aligned almost vertically with respect to **A**, comprising dihedral O–P–C–C angles of 82.0° (P1) and 88.2° (P2). Accordingly, no mirror planes pass through the two phosphorus atoms, resulting in a molecular structure of **P2** with low symmetry. One P–O bond is twisted in clockwise direction, while the other is twisted in the opposite direction. Torsion angles of 24.2° and 17.4° were observed between the central ring **A** and the terminal **B** and **C** rings, respectively. Much larger values were observed between **A** and **D** (32.2°) or **E** (38.4°). This distorted structure is probably caused by steric repulsion between the **B**/**D** or **C**/**E** benzene rings. In contrast to the molecular structure in the crystal, the ^{1}H NMR spectrum displayed four magnetically equivalent terminal benzene rings (**B**–**E**), most likely due to a fast interconversion of the twisting on the NMR timescale.

For extended concave hosts such as **P2**, two depth parameters can be defined in order to characterise the concave surface (Fig. S26†). The first (*d*) is defined as the distance between the centroids of **A** and the plane of the *t*-Bu-substituted carbon atoms in **B**–**E** (Fig. 1). The second (*D*) is defined as the distance

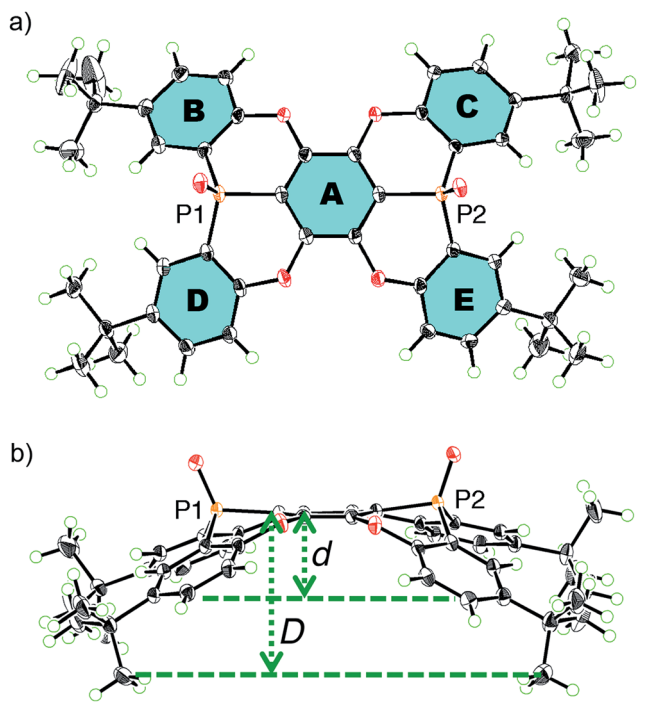


Fig. 1 (a) Top and (b) side views of an *ORTEP* drawing of **P2** with thermal ellipsoids set at 50% probability.

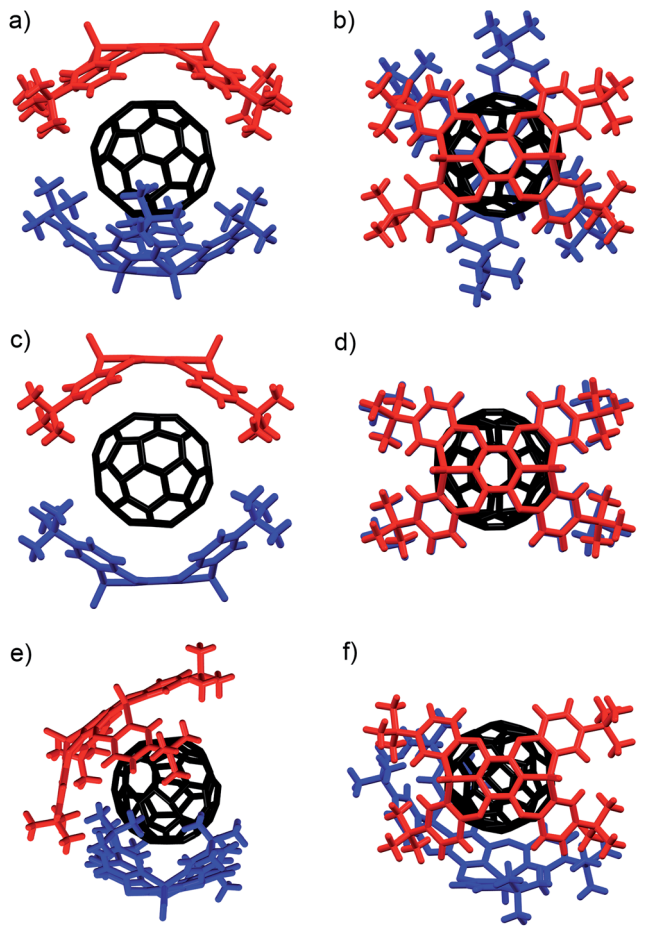


Fig. 2 Molecular structures of the $(P2)_2 \supset C_{60}$ forms **I**–**III**. (a) Side and (b) top view of **I** (twisted); (c) side and (d) top view of **II** (horizontal); (e) side and (f) top view of **III** (misaligned).

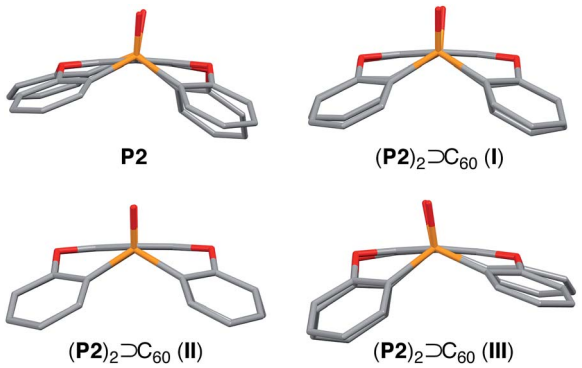


Fig. 3 Comparison of the host **P2** moiety in uncomplexed **P2** and in **I**–**III**.

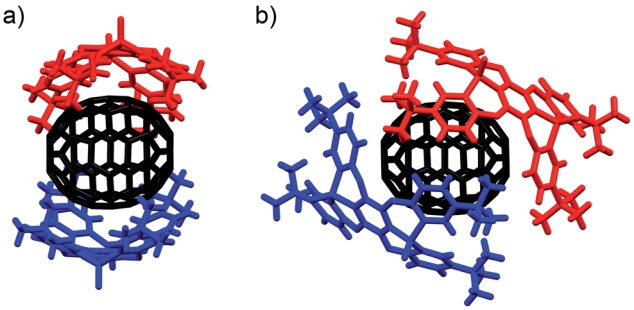


Fig. 4 Side view of the molecular structures of the $(P2)_2 \supset C_{70}$ forms (a) **IV** (faulting-like) and (b) **V** (misaligned).

between the centroids of **A** and the plane of the terminal methyl groups. For **P2**, depth values of 1.8 Å (*d*) and 3.6 Å (*D*) were observed, *i.e.* **P2** may be considered a deep concave host, if the methyl groups are included as host fragments.

Encapsulation of fullerenes

Three different types of black single co-crystals of **P2** and C_{60} (**I**–**III**), suitable for X-ray crystallographic analysis, were obtained by diffusing hexane vapour into solutions of **P2** and C_{60} in toluene/$CHCl_3$, anisole, or $CHCl_3$, respectively. These crystals consist of 2 : 1 host–guest complexes $(P2)_2 \supset C_{60}$ with centrosymmetric space groups $P2_1/c$ (**I**), $C2/m$ (**II**), and $C2/c$ (**III**). In **I**–**III**, the two concave surfaces of **P2** surround the convex surface of C_{60} in a sandwich fashion, and the differences between **I**–**III** is ascribed to different solvates.[18] The orientation of the encapsulated C_{60} guest molecule could not be determined accurately, due to the presence of disorder. This is contrary to the previously reported tetrahedral host–guest complex between C_{60} and **P1**, for which no disorder of C_{60} within the tetrahedral cavity was observed.[14]

In **I**, two host molecules encapsulated C_{60} in a sandwich fashion, *i.e.* the host molecules occupy opposing apex positions of the guest (Fig. 2a). The distance between the **A** centroids in the two hosts is 13.2 Å, which corresponds to the sum of a benzene ring and the diameter of C_{60}. In contrast, distances of 6.8–7.0 Å were observed between the centroids of **B**–**E** and C_{60}, which is longer than the sum of the van der Waals radii of C_{60} and a carbon atom (6.5 Å). The observed lengths thus suggested that the fullerene should be in direct contact with the two concave surfaces of both host molecules. The P1–P2 axes of the two host molecule are offset by 67.6° with respect to each other (Fig. 2b), reflecting the twisted arrangement of the two **P2** molecules in **I**. In **II**, two comparable, yet crystallographically independent $(P2)_2 \supset C_{60}$ complexes are contained within the asymmetric unit (Fig. S29 and S30†). The host molecules are arranged in a similar manner to **I**, and the distance between the **A** centroids of the two hosts is 13.2 Å (Fig. 2c). In contrast to **I**, the P1–P2 axes of the two hosts are aligned in **II** (Fig. 2d), reflecting a horizontal arrangement of the two **P2** molecules in **II**. In **III**, the two hosts do not occupy opposing apex positions of the C_{60} guest, as one host molecule is positioned at a latitudinal angle of 54.3° relative to the apex position (Fig. 2e), reflecting the misalignment of the two **P2** molecules in **III**. Based on these observations, it can be concluded that the surface of C_{60} is too large to be covered entirely by two **P2** host molecules, but simultaneously too small to be covered by three **P2** host molecules. This mismatch in size should be at least partially responsible for the formation of different crystal forms in these host–guest complexes.

The internal structure of the **P2** hosts was observed to vary in the different crystals (Fig. 3). In **I**, a significantly smaller deviation of the torsion angles (29.5–37.4°) between the central (**A**) and terminal benzene rings (**B**–**E**) in **P2** was observed (Table 1) relative to that in uncomplexed **P2** (17.4–38.4°). While the corresponding deviation in **II** was observed to be even smaller (33.9–35.7°), that in **III** is larger (17.3–41.5°), and hence, **P2**

Table 1 Structural parameters for the concave moiety in **P2** and **I**–**III**

	P2	$(P2)_2 \supset C_{60}$ (**I**)	$(P2)_2 \supset C_{60}$ (**II**)	$(P2)_2 \supset C_{60}$ (**III**)
Bowl depth				
d (Å)	1.81	2.40	2.32	2.04
D (Å)	3.56	4.60	4.22	4.07
Torsion angles				
A–**B** (°)	24.2	29.5	33.9	23.2
A–**C** (°)	17.4	33.8	35.7	17.3
A–**E** (°)	32.2	37.4	33.9	41.5
A–**F** (°)	38.4	34.4	35.7	41.0

Table 2 Structural parameters of the concave moiety in **IV**–**V**

	$(P2)_2 \supset C_{70}$ (**IV**)	$(P2)_2 \supset C_{70}$ (**V**)
Bowl depth		
d (Å)	2.05	1.83
D (Å)	4.16	3.47
Torsion angles		
A–**B** (°)	31.9	13.2
A–**C** (°)	29.1	30.3
A–**E** (°)	29.6	37.3
A–**F** (°)	33.8	30.5

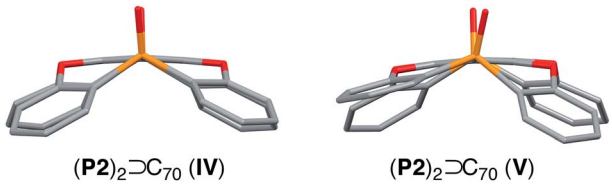


Fig. 5 Comparison of the P2 host moiety in IV–V.

should be able to adapt its structure according to the specific architecture of the host–guest complex.

Using C_{70} as a guest molecule, two different 2 : 1 host–guest complexes $(\mathbf{P2})_2 \supset C_{70}$ (**IV**, **V**) were obtained by crystallization from different solvents (Fig. 4). Similar to $(\mathbf{P2})_2 \supset C_{60}$, the two host molecules encapsulated C_{70} in a sandwich fashion. The $P2_12_12$ space group of **IV**, prepared from $CHCl_3$/toluene, is non-centrosymmetric with a Flack χ value of $-0.03(3)$. In **IV**, the P1–P2 axes of the two host molecules are almost perfectly aligned vertically with respect to the long axis of C_{70} (Fig. 4a), but the centroids of the **A** rings of the two **P2** molecules are slightly misaligned, resulting in a faulting-like chiral architecture of **IV**. Conversely, crystal **V**, obtained from $CHCl_3/CS_2$, crystallises in the centrosymmetric space group *C*2/*c*. In **V**, the two host molecules encapsulated C_{70} with their P1–P2 axes offset by 37.1° with respect to the long axis of C_{70} (Fig. 4b), and the two **P2** molecules are also misaligned. In **IV**, the torsion angle range between the central (**A**) and peripheral benzene rings (**B–E**) of **P2** (29.1–33.8°) was significantly narrower than that in **V** (13.2–37.3°) (Table 2). Similarly to the $(\mathbf{P2})_2 \supset C_{60}$ host–guest complexes, the torsion angles are flexible and are thus able to facilitate different host–guest architectures (Fig. 5).

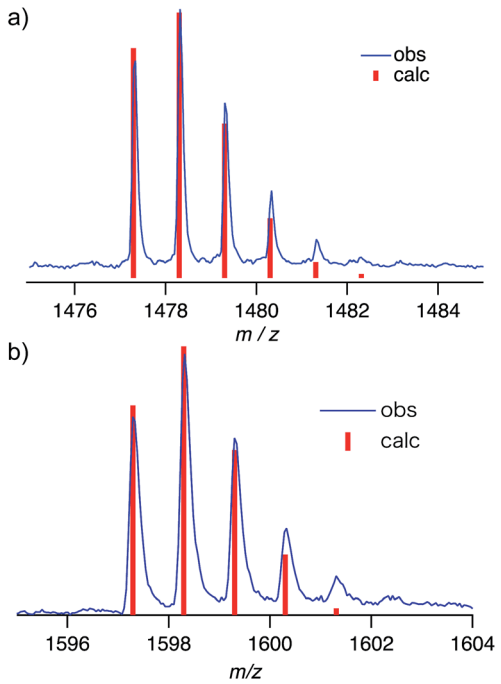


Fig. 6 MALDI TOF MS of (a) $[\mathbf{P2} \supset C_{60}\text{–H}]^-$ and (b) $[\mathbf{P2} \supset C_{70}\text{–H}]^-$.

To the best of our knowledge, no reports exist on concave hosts encapsulating fullerene guests in such a variable fashion.

Negative-mode MALDI-TOF mass spectra of $(\mathbf{P2})_2 \supset C_{60}$ and $(\mathbf{P2})_2 \supset C_{70}$ revealed prominent peaks at m/z = 1478.3 and 1598.3, which were assigned to the corresponding 1 : 1 complexes (Fig. 6). This result suggested that the concave–convex interactions between hosts and guests should be strong enough to preserve the host–guest complex at least partially even during ionization. However, no peaks corresponding to the 2 : 1 complexes $(\mathbf{P2})_2 \supset C_{60}$ and $(\mathbf{P2})_2 \supset C_{70}$ were observed, even though this stoichiometry was found in the crystal structure. This result indicated that the interactions with the second host molecules in the 2 : 1 complexes might be too weak in order to be observed. Therefore, NMR titration experiments were carried out in order to evaluate the concave–convex interactions in the binary organic solvent mixture $CDCl_3/CS_2$ (1 : 3 v/v). In the ^{31}P NMR spectra, the signal for **P2** experienced a downfield shift ($\Delta\delta_P$: 0.20 ppm) upon addition of three equivalents of C_{60} (Fig. 7a).

In the ^{1}H NMR spectra, signals for the protons attached to the peripheral benzene rings were shifted slightly upfield ($\Delta\delta_H$ for H_a: −0.0049; H_b: −0.0038; H_c: 0.0028 ppm; see Scheme 1 and Fig. S21†). This result clearly demonstrated the interactions of **P2** with C_{60} in this solvent mixture, while the interaction

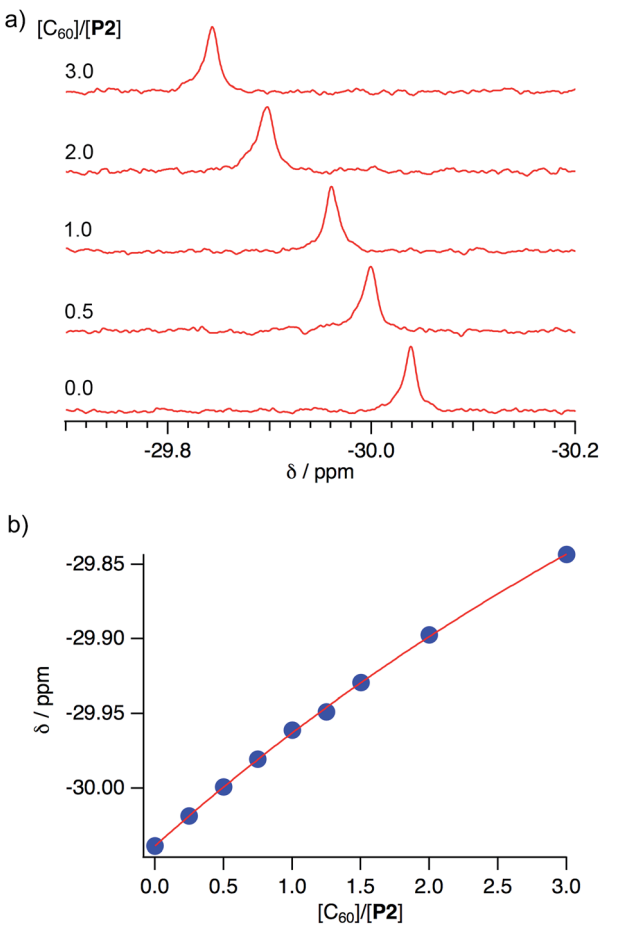


Fig. 7 (a) Spectral changes in the ^{31}P NMR spectra (243 MHz) of **P2** in $CDCl_3/CS_2$ (1 : 3 v/v) upon addition of C_{60}, and (b) 1 : 1 binding isotherm.

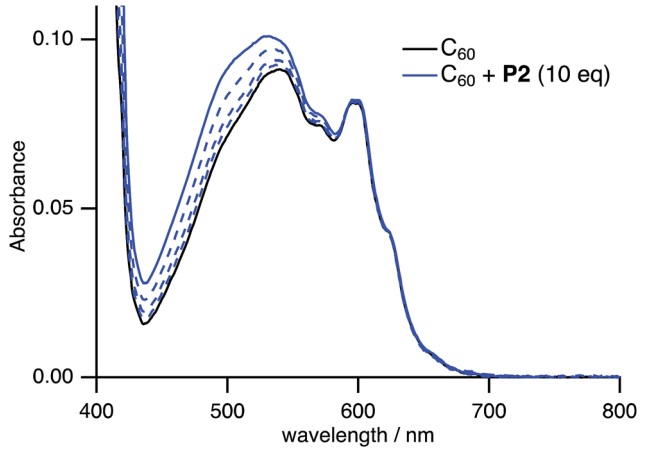


Fig. 8 Change of the UV-vis absorption spectrum of C_{60} in $CHCl_3$/toluene (1 : 4 v/v) upon addition of **P2** ($[C_{60}]$ = 0.10 mM, $0 \leq [\mathbf{P2}]/[C_{60}] \leq 10$).

between the *anti*-isomer **P2′** or previously reported **P1** and C_{60} was observed to be negligible. A Job plot analysis confirmed the formation of 1 : 1 complexes between **P2** and C_{60} (Fig. S19†), and the absence of any indications for the formation of a 2 : 1 complex is consistent with the results obtained from mass spectrometry measurements. Non-linear least-squares analysis for the change of the chemical shift afforded association constants (K_a) between **P2** and C_{60} of 210 ± 20 M^{-1} (Fig. 7b),[19] while between **P2** and C_{70} a K_a value of 200 ± 30 M^{-1} was estimated (Fig. S22†). Accordingly, **P2** exhibited an enhanced affinity for fullerenes relative to **P1**, containing one phosphorus atom, even though no selectivity for either C_{60} or C_{70} was observed. This result is consistent with the observation of multiple host–guest architectures in host–guest complexes between **P2** and fullerenes, which may reflect that **P2** is unable to selectively recognize the convex surface of specific fullerenes, due to its ability to accommodate various structures in accordance with the guest shape. A comparison of the observed K_a values with those of previously reported concave hosts, such as calixarenes and their analogues confirmed that **P2** exhibits a moderate affinity towards C_{60}.[20]

Spectral titration experiments based on the UV-vis absorption also confirmed the formation of host–guest complexes in solution. Upon addition of **P2** to a $CHCl_3$/toluene solution of C_{60}, the weak absorption at 450–600 nm, which is associated with the forbidden excitation of C_{60}, gradually increased (Fig. 8), while **P2** is transparent in this region (Fig. S18†). In contrast, addition of **P2′** to a $CHCl_3$/toluene solution of C_{60} did not change the UV-vis absorption spectrum (Fig. S25†). This result suggested that the stronger host–guest interaction between **P2** and C_{60} relative to **P2′** and C_{60} is responsible for the spectral change.

Conclusions

In this study, we have disclosed the synthesis of the extended concave host **P2**, containing two phosphorus atoms. Moreover, we have demonstrated that **P2** may serve as a suitable host for fullerenes. In co-crystals with C_{60} and C_{70}, two molecules of **P2** bind to the convex surface of the fullerenes in a sandwich fashion. Interestingly, the orientation of the two **P2** molecules with respect to each other is flexible, resulting in the formation of a variety of cavity shapes. MALDI-TOF mass, NMR, and UV-vis absorption spectra supported the formation of 1 : 1 host–guest complexes between **P2** and the fullerenes in solution. Relative to **P1** with one phosphorus atom, the affinity of **P2**, containing two phosphorus atoms, towards fullerenes was significantly enhanced. Accordingly, the expansion of the concave surface by fusing two phosphorus-containing concave units should result in an effective recognition of fullerenes. Considering that two molecules of **P2** are necessary for the encapsulation of fullerene, fusion of two **P2** molecules should enhance the affinity even further. Control over the cavity shape should be possible *via* a judicious choice of the connecting moiety between these two **P2** units. Studies in this direction are currently in progress in our laboratory.

Acknowledgements

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