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ARTICLE

Twofold Fused Concave Hosts Containing Two Phosphorous 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 $(\mathbf{P2})_2=C_{60}$ and $(\mathbf{P2})_2=C_{70}$, 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 phosphorous atoms, towards fullerenes was significantly enhanced relative to **P1** with one phosphorous 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 purification² and nanoscale organisation³ 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} . 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.

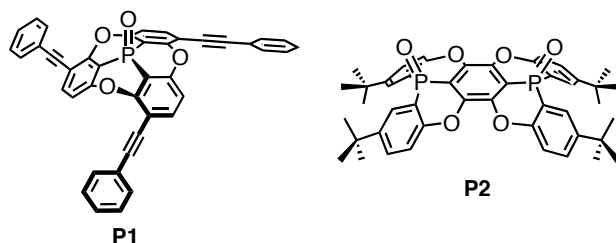
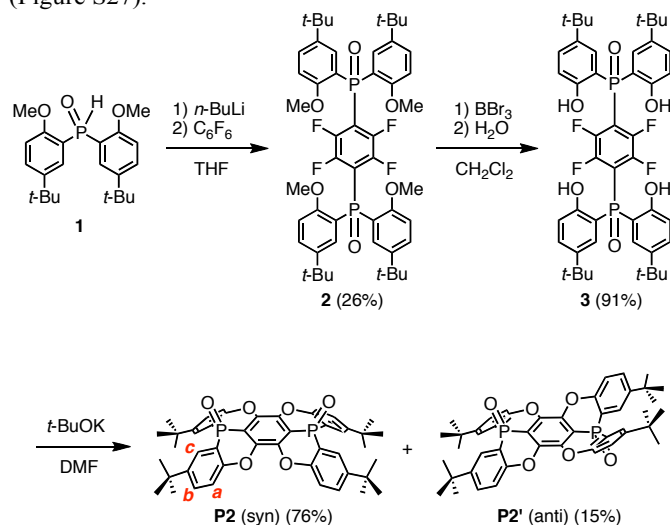


Chart 1. Concave host **P1** and twofold fused concave host **P2**.

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 deprotonation of **1** with *n*-BuLi. Thus, 1,4-bis(phosphoryl)tetrafluorobenzene **2** was obtained in 26% yield.¹⁶ Subsequent treatment of **2** with BBr₃ 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 (Figure S27).



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

Single crystals of **P2**, suitable for X-ray crystallographic analysis, were obtained by recrystallization from CHCl₃/hexane, and the crystal structure clearly showed the concave shape of **P2** (Figure 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 phosphorous 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. Dihedral 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 ¹H 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 (Figure 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 (Figure 1). The second (*D*) is defined as the distance 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.

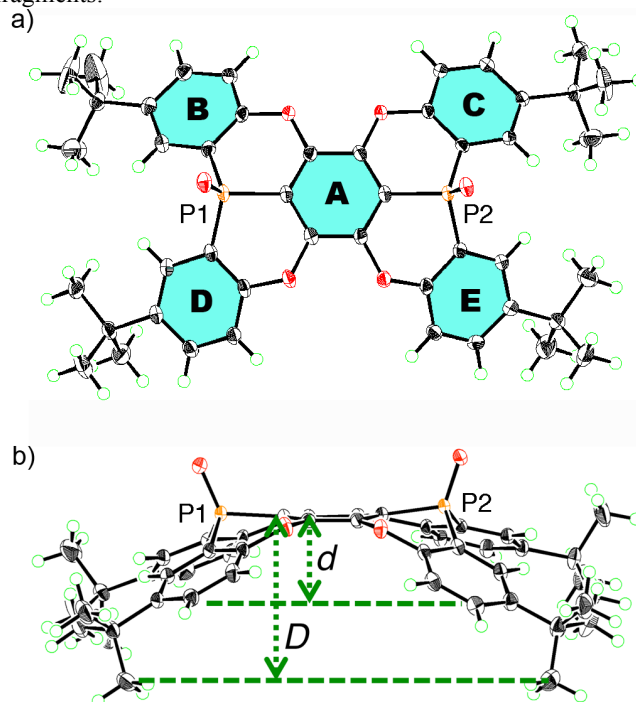


Figure 1. (a) top and (b) side views of an ORTEP drawing of **P2** with thermal ellipsoids set at 50% probability.

Encapsulation of fullerenes. Three different types of black single co-crystals of **P2** and C₆₀ (I–III), suitable for X-ray crystallographic analysis, were obtained by diffusing hexane vapour into solutions of **P2** and C₆₀ in toluene/CHCl₃, anisole, or CHCl₃, respectively. These crystals consist of 2:1 host-guest complexes (**P2**)₂⊃C₆₀ 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 C₆₀ in a sandwich fashion, and the differences between I–III is ascribed to different solvates.¹⁷ The orientation of the encapsulated C₆₀ 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 C₆₀ and **P1**, for which no disorder of C₆₀ within the tetrahedral cavity was observed.¹⁴ In I, two host molecules encapsulated C₆₀ in a sandwich fashion, *i.e.* the host molecules occupy opposing apex positions of the guest (Figure 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 C₆₀. In contrast, distances of 6.8–7.0 Å were observed between the centroids of B–E and C₆₀, which is longer than the sum of the van der Waals radii of C₆₀ 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 molecules are offset by 67° with respect to each other (Figure 2b), reflecting the twisted arrangement of the two **P2** molecules in **I**. In **II**, two comparable, yet crystallographically independent $(\text{P2})_2\text{C}_{60}$ complexes are contained within the asymmetric unit (Figure 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 (Figure 2c). In contrast to **I**, the P1-P2 axes of the two hosts are aligned in **II** (Figure 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 (Figure 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.¹⁸

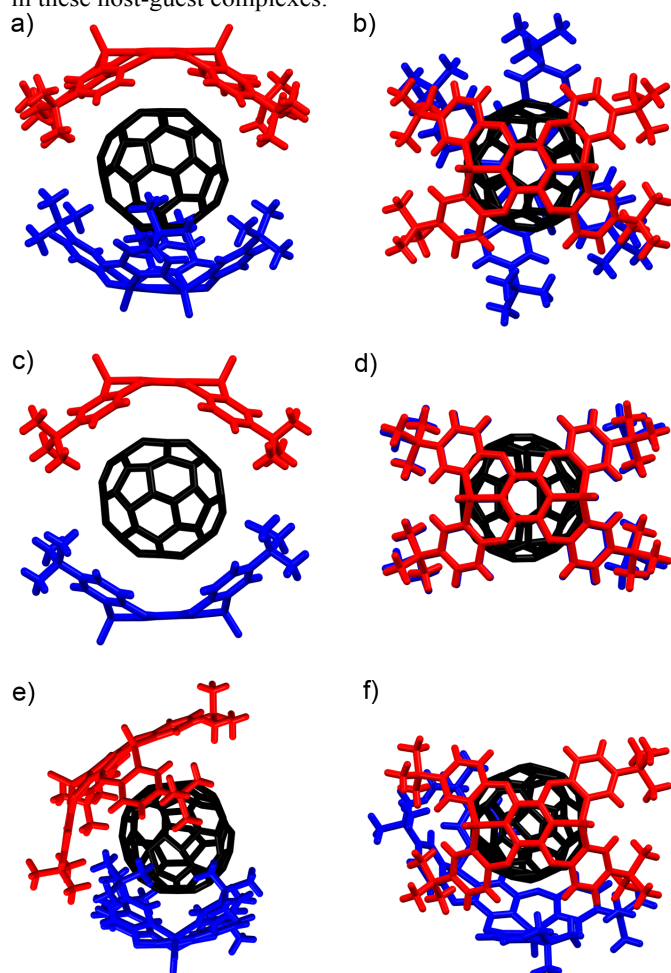


Figure 2. Molecular structures of the $(\text{P2})_2\text{C}_{60}$ forms **I-III**. (a) side and (b) top view of **I** (twisted); (c) side and (d) top view of **II** (horizontal); (e) side and (f) top view of **III** (misaligned).

The internal structure of the **P2** hosts was observed to vary in the different crystals (Figure 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 (34.5-36.2°), that in **III** is larger (17.3-41.5°), and hence, **P2** should be able to adapt its structure according to the specific architecture of the host-guest complex.

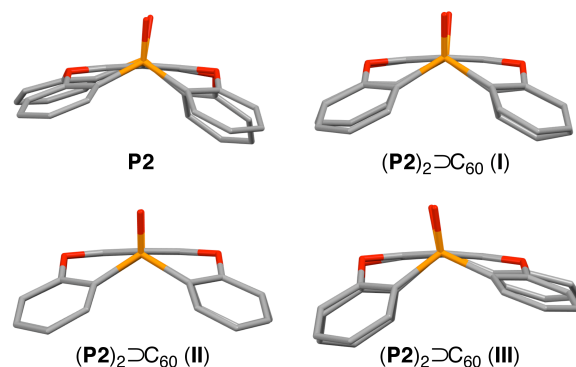


Figure 3. Comparison of the host **P2** moiety in uncomplexed **P2** and in **I-III**.

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

	P2	$(\text{P2})_2\text{C}_{60}$ (I)	$(\text{P2})_2\text{C}_{60}$ (II)	$(\text{P2})_2\text{C}_{60}$ (III)
bowl depth				
<i>d</i> (Å)	1.81	2.40	2.32	2.04
<i>D</i> (Å)	3.56	4.60	4.22	4.07
dihedral angles				
A-B (°)	24.2	36.0	33.9	23.2
A-C (°)	17.4	34.9	35.7	17.3
A-E (°)	32.2	36.0	33.9	41.5
A-F (°)	38.4	36.4	35.7	41.0

Using C_{70} as a guest molecule, two different 2:1 host-guest complexes $(\text{P2})_2\text{C}_{70}$ (**IV**, **V**) were obtained by crystallization from different solvents (Figure 4). Similar to $(\text{P2})_2\text{C}_{60}$, the two host molecules encapsulated C_{70} in a sandwich fashion. The $P2_12_12$ space group of **IV**, prepared from $\text{CHCl}_3/\text{toluene}$, 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} (Figure 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 $\text{CHCl}_3/\text{CS}_2$, crystallises in the centrosymmetric space group $C2/c$. 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} (Figure 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 $(\mathbf{P2})_2\supset\text{C}_{60}$ host-guest complexes, the torsion angles are flexible and are thus able to facilitate different host-guest architectures (Figure 5). To the best of our knowledge, no reports exist on concave hosts encapsulating fullerene guests in such a variable fashion.

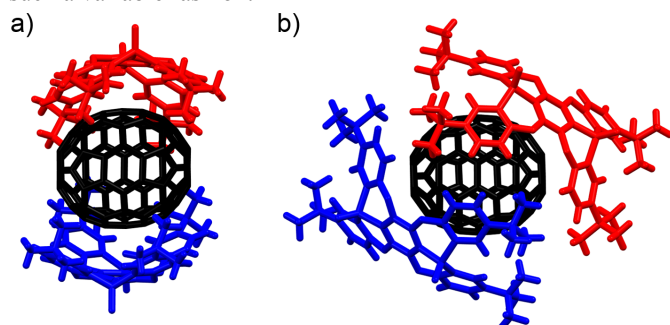


Figure 4. Side view of the molecular structures of the $(\mathbf{P2})_2\supset\text{C}_{70}$ forms (a) **IV** (faulting-like) and (b) **V** (misaligned).

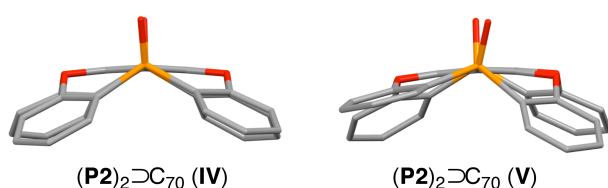


Figure 5. Comparison of the **P2** host moiety in **IV-V**.

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

	$(\mathbf{P2})_2\supset\text{C}_{70}$ (IV)	$(\mathbf{P2})_2\supset\text{C}_{70}$ (V)
bowl depth		
d (Å)	2.05	1.83
D (Å)	4.16	3.47
dihedral 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

Negative-mode MALDI-TOF mass spectra of $(\mathbf{P2})_2\supset\text{C}_{60}$ and $(\mathbf{P2})_2\supset\text{C}_{70}$ revealed prominent peaks at $m/z = 1478.3$ and 1597.3 , which were assigned to the corresponding 1:1 complexes (Figure 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 $(\mathbf{P2})_2\supset\text{C}_{60}$ and $(\mathbf{P2})_2\supset\text{C}_{70}$ 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 $\text{CDCl}_3/\text{CS}_2$ (1:3 v/v). In the ^{31}P NMR spectra, the signal for **P2** experienced a downfield shift ($\Delta\delta_{\text{P}}$: 0.20 ppm) upon addition of three equivalents of C_{60} (Figure 7a).

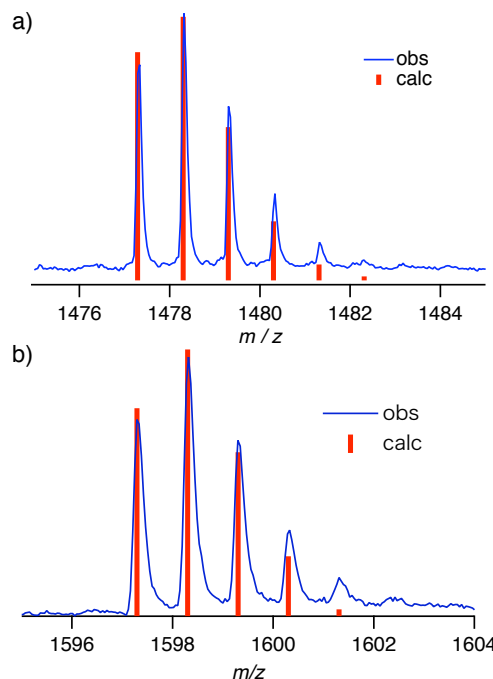


Figure 6. MALDI TOF MS of (a) $[\mathbf{P2}\supset\text{C}_{60}]^-$ and (b) $[\mathbf{P2}\supset\text{C}_{70}]^-$.

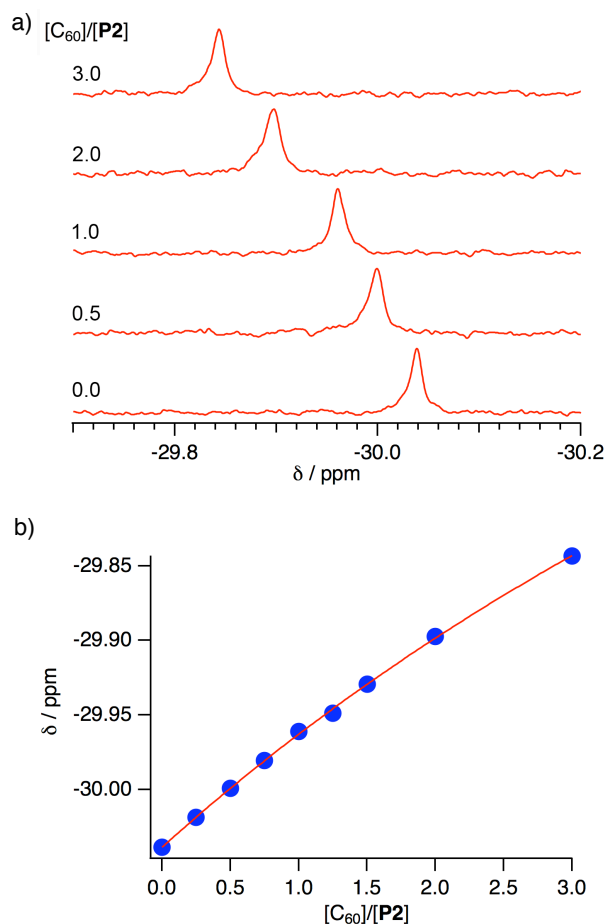


Figure 7. (a) Spectral changes in the ^{31}P NMR spectra (243 MHz) of **P2** in $\text{CDCl}_3/\text{CS}_2$ (1:3 v/v) upon addition of C_{60} , and (b) 1:1 binding isotherm.

In the ^1H NMR spectra, signals for the protons attached to the peripheral benzene rings were shifted slightly upfield ($\Delta\delta_{\text{H}}$ for H_a : -0.0049 ; H_b : -0.0038 ; H_c : 0.0028 ppm; see Scheme 1 and Figure S21). This result clearly demonstrated the interactions of **P2** with C_{60} in this solvent mixture, while the interaction 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} (Figure 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 $200 \pm 20 \text{ M}^{-1}$ (Figure 7b),¹⁹ while between **P2** and C_{70} a K_a value of $210 \pm 30 \text{ M}^{-1}$ was estimated (Figure S23). 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 toluene solution of C_{60} , the weak absorption at 450-600 nm, which is associated with the forbidden excitation of C_{60} , gradually increased (Figure 8), while **P2** is transparent in this region (Figure S18). In contrast, addition of **P2'** to a toluene solution of C_{60} did not change the UV-vis absorption spectrum (Figure 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.

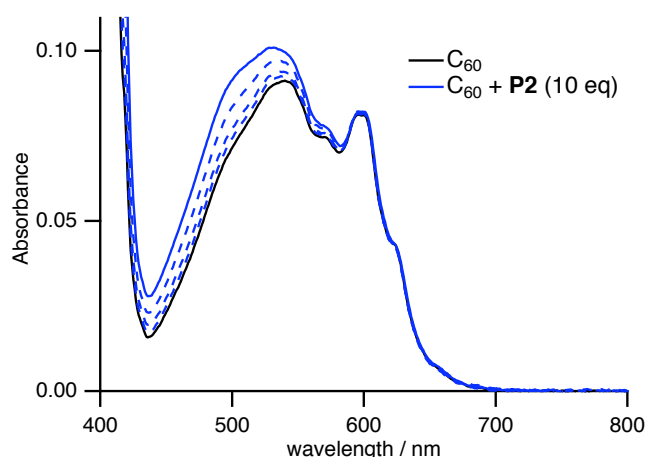


Figure 8. Change of the UV-vis absorption spectrum of C_{60} in $\text{CHCl}_3/\text{toluene}$ (1:4 v/v) upon addition of **P2** ($[\text{C}_{60}] = 0.10 \text{ mM}$, $0 \leq [\text{P2}]/[\text{C}_{60}] \leq 10$).

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 phosphorous atom, the affinity of **P2**, containing two phosphorous 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.

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