

Bowl-Shaped Polyarenes as Concave–Convex Shape Complementary Hosts for C₆₀- and C₇₀-Fullerenes

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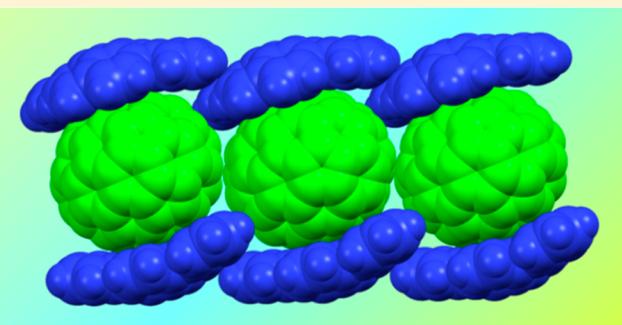
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S Supporting Information

ABSTRACT: The X-ray crystal structures of two new co-crystals comprised of C₆₀ and C₇₀ fullerenes and a dibenzofullerene bowl, namely, (C₂₈H₁₄)·(C₆₀) and (C₂₈H₁₄)₂·(C₇₀), are reported. A clear difference is observed between C₆₀ to C₇₀, with the latter fullerene molecule being fully ordered and lacking the orientational disorder found in many fullerene co-crystallized products. In the solid state structure of (C₂₈H₁₄)₂·(C₇₀), two bowl-shaped C₂₈H₁₄ molecules encapsulate the C₇₀-cage and exhibit a preferential spatial alignment parallel to the longer axis of the fullerene. In this case, dibenzofullerene utilizes only its concave surface for binding, showing a staggered conformation of carbon atoms over the convex surface of C₇₀-fullerene. In the solid-state structure of (C₂₈H₁₄)·(C₆₀), both convex–convex and convex–concave π···π interactions are observed between the curved surfaces of C₂₈H₁₄ and C₆₀. The C₆₀-core is disordered showing no preferential orientation. In both cases, the formation of π···π adducts was not observed in solutions of chlorinated benzene solvents from which the co-crystals were grown.



INTRODUCTION

Studies of π···π intermolecular interactions have gained considerable interest due to their fundamental role in a variety of biochemical^{1–3} and chemical crystallization processes.^{4–7} The stacking interactions of prototypical planar polyarenes, such as naphthalene, anthracene, and pyrene have been given special attention.^{8–10} The importance and strength of π···π stacking interactions were recently illustrated by calculations of large polyarene dimers such as graphene bilayers.¹¹ The study showed that a graphene bilayer doped with atoms ranging from Al to S with a short interlayer distance and without a covalent bond between heteroatoms is more energetically favorable than that having covalently bonded heteroatoms but a longer interstack distance. With the discovery of fullerenes, which are ball-shaped carbon molecules such as C₆₀ and C₇₀ (Scheme 1), the issue of the shape complementarity required to effectively promote dispersive interactions between flat-curved and curved–curved surfaces has arisen.¹² Different molecular systems, such as porphyrins,^{13–15} tribenzotriquinacenes,^{16–19} calixarenes,²⁰ or tetraazaannulene,²¹ that can accommodate fullerenes have been considered.

Bowl-shaped polyarenes, such as corannulene (C₂₀H₁₀) and dibenzofullerene (C₂₈H₁₄) (Scheme 1), are fragments of fullerenes (often called “buckybowls”) and thus naturally

offer good geometric compatibility with the convex surface of fullerenes (“ball-and-socket” or “ball-to-bowl” interactions). In addition to having a good shape match, buckybowls have a dipole moment due to their curvature and that should provide enhanced intermolecular electrostatic interactions for concave–convex host/guest interactions. The C₆₀-fullerene has an electron-deficient surface, which is illustrated by the coordination of electron-rich metal complexes.^{22–24} In turn, buckybowls have more negative surface potentials due to their curvature and additional supply of electron density from H-atoms capping the rim. For example, the corannulene interior face is known to react with electrophiles, such as alkyl⁺,^{25,26} and therefore it can be used as a ligand in coordination reactions with strong Lewis acidic complexes.^{27,28}

The application of high-level computational methods for the evaluation of π···π interactions in the C₆₀/C₂₀H₁₀ system is still problematic, and geometric constraints (like imposing C_{5v} symmetry on a particular geometry) were used for calculations.^{29,30} Such restrictions do not allow a detailed discussion of surface overlap but, nevertheless, predict that

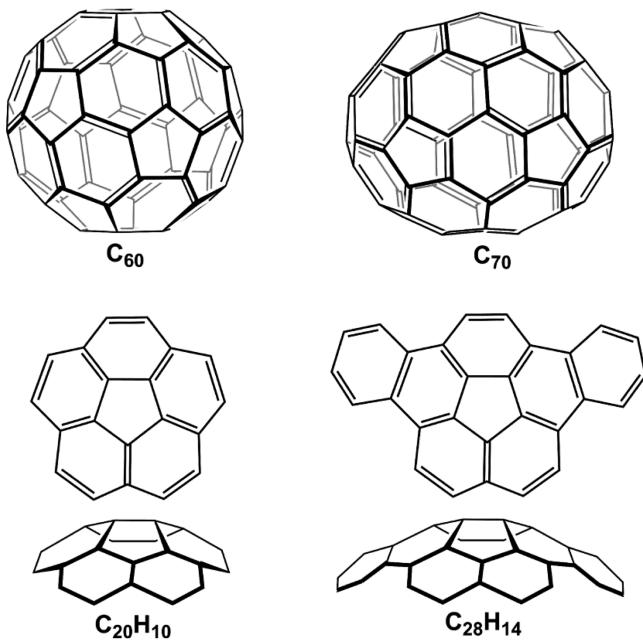
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Scheme 1. Chemical Drawing of the C₆₀ and C₇₀ Fullerenes and the C₂₀H₁₀ and C₂₈H₁₄ Bowls^a



^aChemical drawing and three-dimensional skeleton.

complexation of the concave face of C₂₀H₁₀ toward the C₆₀- or C₇₀-fullerenes is energetically similar to the $\pi\cdots\pi$ interactions between homodimers of corannulene.³⁰ This conclusion allows the more detailed computational studies of buckybowl–fullerene interactions to be transferred on somewhat simpler models, such as evaluation of C₂₀H₁₀/C₂₀H₁₀ stacking interactions.^{31,32} Computations showed that the eclipsed structure of corannulene dimers is only slightly more favorable than the staggered conformation (by ca. 1.3–1.4 kcal/mol).³³ The concave–convex interactions are about 15–16 kcal/mol with the equilibrium separation of the C₂₀H₁₀-monomers being 3.6–3.7 Å. It can be noted here that only a partial bowl-to-bowl overlap of corannulene cores is observed in the solid state.^{34,35} To provide a full overlap and aligned bowl-to-bowl column stacking of corannulene molecules, its core needs to be trifluoromethylated³⁶ or annulated with one additional five-membered ring to make cyclopentacorannulene.³⁷ The attachment of two corannulene moieties to ferrocene also leads to a desirable π -stacking motif.³⁸

With the better synthetic availability of bowl-shaped polyarenes,^{39–45} experimental studies of buckybowl as suitable fullerene hosts have been initiated. The gas phase reaction between neutral corannulene and fullerene cations produced by electron ionization showed the formation of ion/molecule dimerization products.⁴⁶ Despite the initial success, further attempts to find interactions between neutral C₂₀H₁₀ and C₆₀ molecules in solution were ineffective, and modulation of the electronic structure of the corannulene core was needed.^{47,48} It was demonstrated that craftily prepared organic receptors containing properly oriented corannulene bowls linked by predesigned linkers bind rather strongly the C₆₀-fullerene through complementary $\pi\cdots\pi$ interactions.^{49,50} It was also shown that $\pi\cdots\pi$ interactions between pristine C₂₀H₁₀ and C₆₀ can be promoted by the adsorption of the former on a Cu(110)-surface.²⁹ However, while no evidence of the complexation between corannulene and C₆₀-fullerene in

solution is documented, the solid-state co-crystallization of two molecules was recently reported.⁵¹ The C₆₀-fullerene cage was found to be severely disordered and that precluded any detailed geometrical evaluation of co-crystallized moieties.

Recent computations revealed that the interaction energy of geodesic polyarenes and fullerenes is proportional to the surface contact area.³⁰ Thus, to enhance shape complementary ball-bowl interactions, larger systems than C₂₀H₁₀ and C₆₀ should be tested. In contrast to C₆₀, comprising of 20 hexagons and 12 pentagons, C₇₀ consists of the same number of pentagons but has more hexagons (25). In order to further investigate the effect of size and curvature on $\pi\cdots\pi$ interactions in curved carbon-based systems, we set out to use dibenzo-[*ag*]corannulene (C₂₈H₁₄, Scheme 1) for our studies. This curved polyarene has a larger surface area than C₂₀H₁₀ due to the attachment of two additional hexagons to the corannulene core.⁵² This bowl should provide a better geometrical match with C₇₀ that has a spheroid egg-shaped structure due to additional hexagons. We also investigated the C₂₈H₁₄–C₆₀ system for comparison and now report the first crystallographic studies of co-crystals of dibenzo[*ag*]corannulene with both C₆₀- and C₇₀-fullerenes.

EXPERIMENTAL SECTION

Materials and Methods. Synthesis of dibenzo[*ag*]corannulene was performed according to the established procedures.⁵³ The product

Table 1. Crystallographic Data and Structural Refinement Parameters of [(C₂₈H₁₄)·(C₆₀)]·0.5C₆H₅Cl (1) and [(C₂₈H₁₄)₂·(C₇₀)]·3C₆H₄Cl₂ (2)

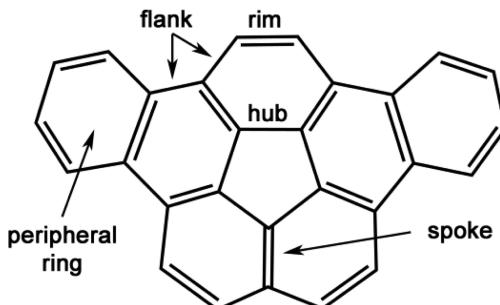
	1	2
empirical formula	C ₁₈₂ H ₃₃ Cl	C ₁₄₄ H ₄₀ Cl ₆
fw	2254.53	1982.46
cryst system	monoclinic	triclinic
space group	P2 ₁ /n	P\bar{1}
<i>a</i> (Å)	22.0143(18)	15.8747(6)
<i>b</i> (Å)	9.8317(9)	16.0091(6)
<i>c</i> (Å)	22.891(2)	18.2908(7)
α (°)	90	66.713(2)
β (°)	112.715(5)	71.600 (2)
γ (°)	90	80.733(3)
<i>V</i> (Å ³)	4570.2(7)	4047.9(3)
<i>Z</i>	2	2
<i>T</i> (K)	100(2)	100(2)
λ (Å)	1.54178	1.54178
<i>D</i> _{calc} (g·cm ⁻³)	1.638	1.626
no. of reflns collected	25358	55529
<i>R</i> (int)	0.0680	0.0897
data/restr/parameters	7637/2403/1406	13885/1493/1376
largest diff. peak/hole	0.266/−0.304	0.521/−0.402
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0561, 0.1187	0.0659, 0.1278
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0899, 0.1361	0.1231, 0.1511
quality-of-fit ^c on <i>F</i> ²	1.026	1.020

^a*R*₁ = $\Sigma |F_o| - |F_c| / \Sigma |F_o|$. ^b*wR*₂ = $[\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)]]^{1/2}$.

^cQuality-of-fit = $[\Sigma [w(F_o^2 - F_c^2)^2] / (N_{obs} - N_{params})]^{1/2}$.

was additionally purified by sublimation at 220 °C prior to use. C₆₀ was purchased from TCI, and C₇₀ was purchased from Sigma Aldrich; both were used as received. Anhydrous chlorobenzene and 1,2-dichlorobenzene were purchased from Sigma-Aldrich, dried over 4 Å molecular sieves, and degassed prior to use. All manipulations were carried out using Schlenk line and glovebox techniques under an

Table 2. Key Distances of 1 and 2 (Å)



	$C_{28}H_{14}^{S2}$	1	2 ^a
hub	1.420(2)–1.428(2)	1.416(3)–1.427(3)	1.4130(13)–1.4289(16)
rim	1.385(2)–1.447(2)	1.380(4)–1.440(3)	1.4042(14)–1.4311(16)
spoke	1.367(2)–1.380(2)	1.367(4)–1.374(3)	1.3819(12)–1.4394(17)
flank	1.435(2)–1.472(2)	1.430(4)–1.484(3)	1.3775(13)–1.4479(16)
peripheral rings	1.382(2)–1.407(2)	1.367(4)–1.410(3)	1.3669(15)–1.3816(16)
bowl depth	0.830(2)	0.802(3)	1.3623(12)–1.3767(16)
			1.4262(15)–1.4756(12)
			1.4183(15)–1.4807(12)
			1.3730(15)–1.4128(12)
			1.3723(15)–1.4051(12)
			0.796(2)
			0.790(2)

^aIn 2, there are two independent $C_{28}H_{14}$ molecules.

atmosphere of argon. The UV-vis spectra were recorded on a Thermo Scientific Evolution 300BB spectrometer.

Synthesis of $[(C_{28}H_{14})\cdot(C_{60})]\cdot0.5C_6H_5Cl$ (1) and $[(C_{28}H_{14})_2\cdot(C_{70})]\cdot3C_6H_4Cl_2$ (2). To a mixture of dibenzocorannulene (3.0 mg, 0.009 mmol) and C_{60} (6.18 mg, 0.009 mmol) 2.2 mL of chlorobenzene was added. The resulting purple solution was filtered into an L-shaped ampule, which was then sealed under a vacuum. Slow evaporation of the solvent initiated by cooling one end of the sealed container afforded black block-shaped crystals of 1 formed in 5 days. Crystal growth of 2 followed the same procedure as for 1 by substituting C_{60} with C_{70} (7.2 mg, 0.009 mmol) and chlorobenzene with 1,2-dichlorobenzene. 1H NMR studies in deuterated benzene show no interactions between $C_{28}H_{14}$ and C_{60} or C_{70} in solution.

X-ray Data Collection and Structure Refinement. The X-ray intensity data sets for 1 were measured on a Bruker Kappa APEX DUO diffractometer equipped with a Cu INCOATEC μ s microfocus source ($\lambda = 1.54178 \text{ \AA}$). The X-ray intensity data for 2 were measured on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a Cu INCOATEC μ s microfocus source ($\lambda = 1.54178 \text{ \AA}$). The frames were integrated with the Bruker SAINT⁵⁴ software package using a narrow-frame algorithm, and data were corrected for absorption effects using the numerical method (SADABS).⁵⁴ The structures were solved by direct methods and refined against F^2 by the full-matrix least-squares technique as implemented in the Bruker SHELXTL software.^{55,56} All non-hydrogen atoms were refined anisotropically including the disordered C-atoms of the C_{60} -fullerene core in 1. This disorder was modeled over two rotational orientations with the final occupancy of two parts refined to a ratio of 0.564:0.436. The U^{ij} components of anisotropically refined C-atoms in both parts were restrained to behave approximately isotropic within a standard uncertainty of 0.01 \AA^2 and have the same U^{ij} components for bonded atoms within the 0.04 \AA^2 uncertainty value. Also, the pairs of carbon atoms of each part were further restrained to have equal anisotropic displacement parameters in the direction of the bond between them within the standard uncertainty of 0.01 \AA^2 . The monochlorobenzene solvent molecule is half-occupied and disordered over two rotational positions. The Cl-atom was modeled with two parts with the ratio of 0.4:0.1. Since the occupancy of the second part of monochlorobenzene is only 0.1 and C-atoms

essentially take the same positions, these atoms were not divided into two parts. Geometrical restraints and restraints of U^{ij} components were also used to model this disorder. The C_{70} -fullerene molecule in 2 was found to be essentially not disordered in contrast to many other reported fullerene structures.⁵⁷ The anisotropic components were still needed to be restrained for the C_{70} -core. One out of three 1,2-dichlorobenzene solvent molecules is positionally disordered and was modeled over two orientations with the 0.918:0.072 ratio. Both parts were restrained to be flat, and the anisotropic displacement parameters for the atoms in the minor part were constrained to be the same as those of the corresponding atoms in the major part. Hydrogen atoms in 1 and 2 were placed in geometric positions using a riding model. Crystallographic data and X-ray experimental conditions for 1 and 2 are listed in Table 1. Selected geometric parameters are given in Table 2. The CCDC reference numbers 964533 and 964532 contain the supplementary crystallographic data for 1 and 2.

RESULTS AND DISCUSSION

Crystal Structure of $[(C_{28}H_{14})\cdot(C_{60})]$. Single crystals of the π -adduct of $C_{28}H_{14}$ and C_{60} -fullerene were obtained by a slow evaporation of the monochlorobenzene solution containing C_{60} and $C_{28}H_{14}$ in a 1:1 ratio. The X-ray crystallographic study confirmed the formation of the product with a 1:1 composition, $[(C_{28}H_{14})\cdot(C_{60})]\cdot0.5C_6H_5Cl$ (1). Analysis of the structure shows the ball-and-socket inclusion of the convex surface of the C_{60} -fullerene into the concave cavity of the host $C_{28}H_{14}$ molecule (Figure 1).

The shortest distance measured from the concave surface of $C_{28}H_{14}$ to the C_{60} surface is 3.137(3) \AA . For comparison, the same distance in the $[(C_{20}H_{10})\cdot(C_{60})]$ adduct is 3.06 \AA . The distance between the centroids of the C_{60} -ball and of the five-membered ring in $C_{28}H_{14}$ is 6.71 \AA (6.94 \AA in the $[(C_{20}H_{10})\cdot(C_{60})]$). The geometric parameters of $C_{28}H_{14}$ in 1 are similar to those in pristine $C_{28}H_{14}^{S2}$ with the bowl depth of dibenzocorannulene being slightly reduced upon co-crystallization (Table 2). In the co-crystal of $C_{20}H_{10}$ with C_{60} , the bowl depth of corannulene is also essentially the same as in the

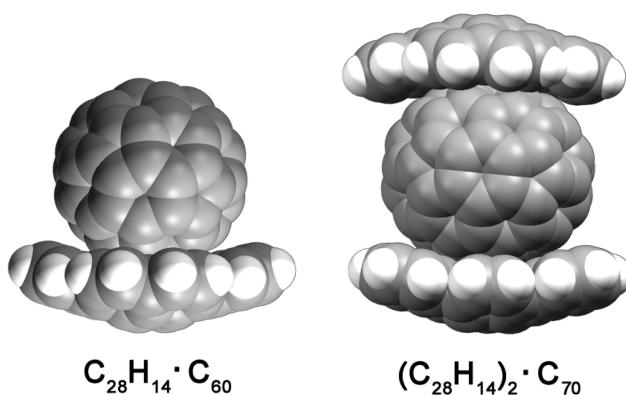


Figure 1. Space-filling views of ball-and-socket type inclusion complexes in **1** and **2**.

parent ligand (0.89 Å compared to 0.88 Å).³⁴ Despite the fact that dibenzocorannulene has additional peripheral six-membered rings increasing its surface, the C₆₀-molecule is found to be sitting over the central hub ring of C₂₈H₁₄. Such an arrangement can be related to the enhanced dipole–induced dipole interactions and to the maximized number of van der Waals contacts between the interacting molecules. As a result, C₆₀ and C₂₈H₁₄ interact clearly in a ball-to-bowl fashion without any shift of the C₆₀-sphere toward the less curved part of a buckybowl (peripheral triphenylene moiety).

In the solid-state structure of **1**, no selectivity in binding is observed. The C₆₀-fullerene shows no preferential orientation in the crystal and found to be disordered over two orientations. Notably, the fullerene molecule was even more strongly disordered in the corannulene analogue, $[(\text{C}_{20}\text{H}_{10}) \cdot (\text{C}_{60})]$.⁵¹ The authors even proposed that the C₆₀-molecule could be better described as a spherical shell of electron density. In that case, the C₆₀-core was modeled with four orientations with the final refinement cycles providing R_1 and wR_2 values for all data of 0.190 and 0.486. The disorder of the C₆₀-core shows that, while there is a shape complementarity between both buckybowl and C₆₀, there is no favored stereochemical

arrangement of these moieties. This disorder also prevents elucidation of a preferred ball-and-socket orientation: staggered vs eclipsed. It can be noted that calculations of C₂₀H₁₀/C₂₀H₁₀ dimer showed the slight preference for the eclipsed geometry.^{31,33}

In **1**, the C₆₀ molecules pack in a zigzag manner similar to the packing observed in $[(\text{C}_{20}\text{H}_{10}) \cdot (\text{C}_{60})]$ (Figure 2).⁵¹ The distance between the consecutive C₆₀ balls is 13.13 Å, and the angle between three successive molecules is 142.81°. The C₂₈H₁₄ bowls are involved in convex–convex $\pi \cdots \pi$ interactions with the C₆₀-surface with the shortest distance being ca. 3.23 Å. Such one-dimensional strands are further involved in $\pi \cdots \pi$ interactions between neighboring C₆₀ molecules with the shortest distance of 3.07 Å. An extended structure is formed by the translation of these strands forming a two-dimensional sheet through $\pi \cdots \pi$ interactions between the *exo* faces of adjacent C₂₈H₁₄ molecules at 3.25 Å and C–H \cdots π contacts between the peripheral ring of C₂₈H₁₄ and C₆₀ at 2.57 Å. Additional interactions also exist in the third dimension. The sheets appear to have intermolecular $\pi \cdots \pi$ interactions between neighboring C₆₀ molecules with the shortest distance observed at 3.28 Å and additional C–H \cdots π interaction between C₂₈H₁₄ and C₆₀. The C₆H₅Cl molecules exhibit severe rotational disorder and are not involved in $\pi \cdots \pi$ interactions with either C₂₈H₁₄ or C₇₀ moieties.

Similar to the previous studies of corannulene and C₆₀ that showed no complexation in solution,⁵¹ our UV–vis data also present no evidence of interactions between the fullerenes and C₂₈H₁₄ molecules in solution (Figure 3).

Crystal Structure of $[(\text{C}_{28}\text{H}_{14})_2 \cdot (\text{C}_{70})]$. The X-ray crystallographic study of crystals obtained by slow evaporation of a 1,2-dichlorobenzene solution containing C₇₀ and C₂₈H₁₄ revealed the formation of the product with the $[(\text{C}_{28}\text{H}_{14})_2 \cdot (\text{C}_{70})] \cdot 3\text{C}_6\text{H}_4\text{Cl}_2$ (**2**) composition. Analysis of the structure confirms the formation of a unique self-assembly in which the *endo* face of two C₂₈H₁₄ bowls embraces the C₇₀ spheroid parallel to the elongated major axis (Figure 1). The selective complexation of fullerenes and π-bowls showing such stereochemical recognition is observed for the first time. Two additional peripheral

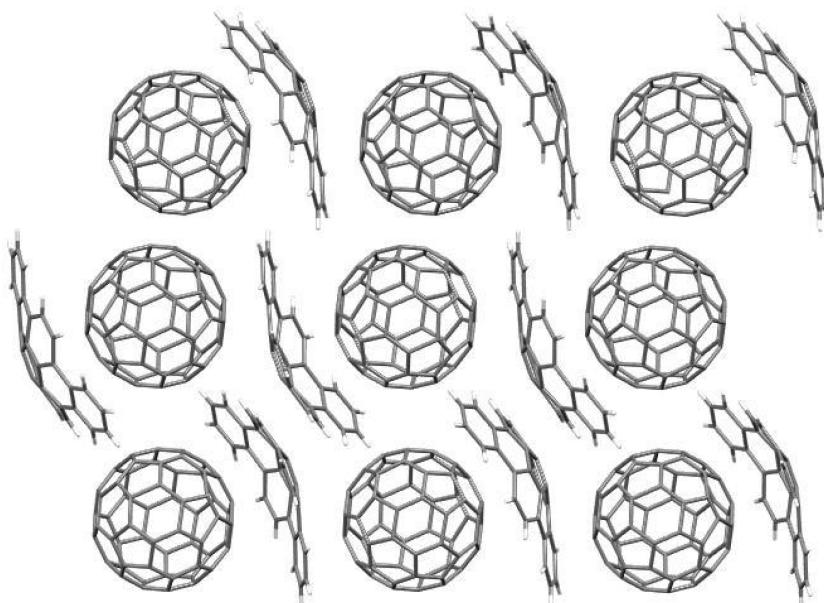


Figure 2. A 2D-sheet representation in **1** with C₆H₅Cl omitted for clarity.

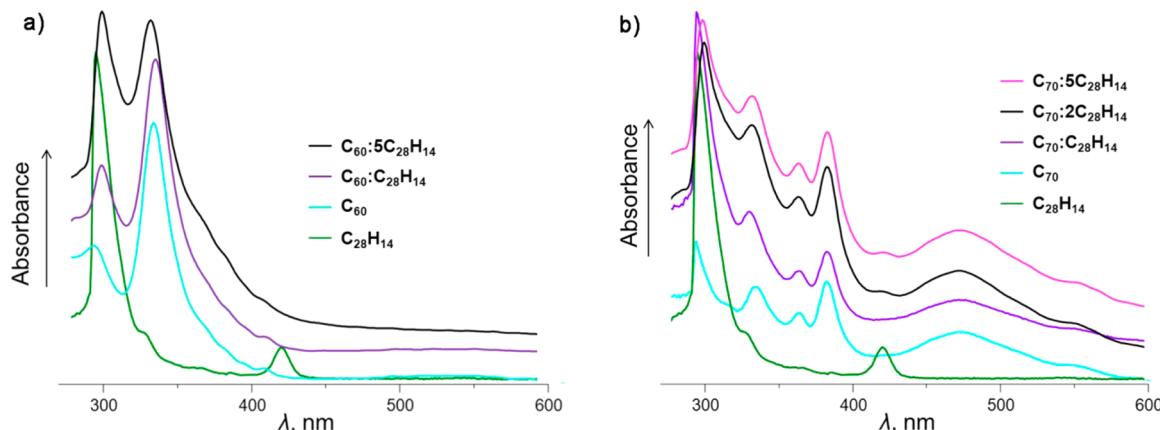


Figure 3. UV–vis absorption spectra of dibenzo[*a,g*]corannulene and C₆₀ (a) or C₇₀ (b) in 1,2-dichlorobenzene with different compositions.

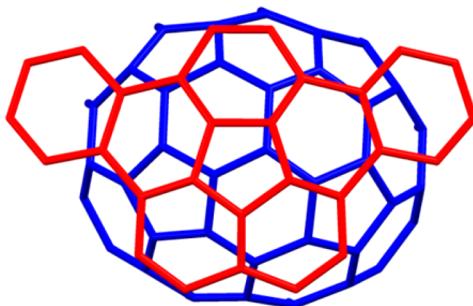


Figure 4. Overlay of the dibenzocorannulene and C₇₀-fullerene cores.

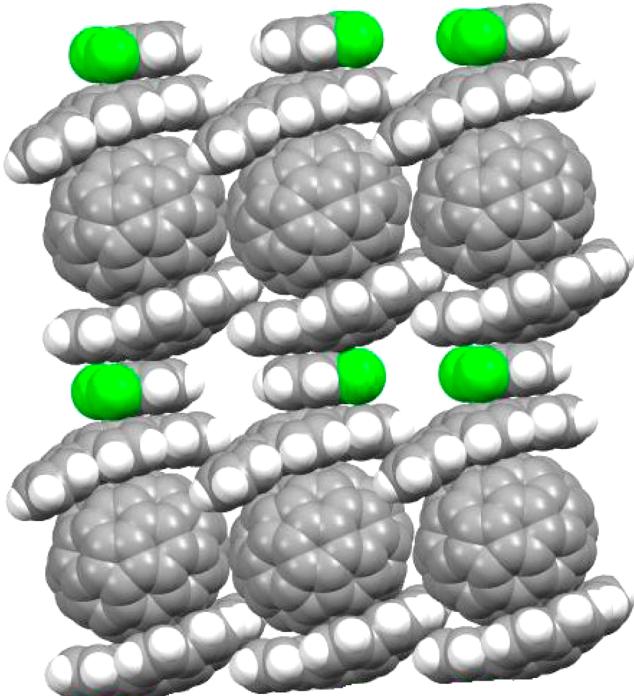


Figure 5. 2D stacking in 2.

benzene rings of C₂₈H₁₄ provide extra surface for $\pi\cdots\pi$ interactions and offer a perfect complementary shape and curvature match for the elongated side of C₇₀. The distances measured from the centroids of the five-membered ring of two bowls to the centroid of the C₇₀ molecule are 6.95 and 7.00 Å, with the shortest distances between the concave surfaces of

C₂₈H₁₄ and C₇₀ being 3.258(2) and 3.267(2) Å. The geometric parameters of dibenzo[*a,g*]corannulene in **2** are similar to those in **1** and in pristine C₂₈H₁₄ (Table 2).⁵² The bowl depth of dibenzo[*a,g*]corannulene in **2** is only slightly smaller than that observed in C₂₈H₁₄. The geometric parameters of C₇₀ are also not affected by its encapsulation with two π -bowls and essentially the same as previously reported in some other host/guest complexes.^{58,59}

Notably, the C₇₀-molecules were found to be fully ordered in the solid state avoiding orientational disorder observed in many fullerene and fullerene co-crystal structures.^{13,57} This allowed us for the first time to reveal the preferential staggered conformation of the buckybowl core and that of fullerene (Figure 4). This experimental evidence of a preferred spatial arrangement should lay a foundation for further theoretical studies of $\pi\cdots\pi$ interactions in curved carbon-rich systems.

The [(C₂₈H₁₄)₂·(C₇₀)] moieties further interact with the adjacent C₂₈H₁₄ bowls and C₇₀ balls through C–H··· π interactions with the distances starting at ca. 2.83 Å (Figure S). Interestingly, the C₇₀-molecules are linearly arranged. The interlayer voids are filled by dichlorobenzene solvent molecules that interact with the convex side of each C₂₈H₁₄ bowl through $\pi\cdots\pi$ interactions with the shortest distance measured at 3.268(2) Å. Two types of interactions between the solvent molecule and the bowls are present. On one side of the adduct, the C₆H₄Cl₂ molecules interact with the central five-membered ring of C₂₈H₁₄, while on the opposite side these interactions are shifted to the peripheral six-membered ring. These interactions with solvents lead to the formation of an extended 2D network in the solid state. Unlike the above $\pi\cdots\pi$ adduct with C₆₀, there are no convex-to-convex interactions between the surfaces of C₂₈H₁₄-bowls and C₇₀-balls. In contrast to the insignificant role of C₆H₅Cl solvent in **1**, the C₆H₄Cl₂ solvent molecules play an important part in the formation of the extended solid state structure of **2**.

CONCLUSIONS

With the co-crystallization of [(C₂₈H₁₄)₂·(C₆₀)] (**1**) and [(C₂₈H₁₄)₂·(C₇₀)] (**2**) in this work we report the first two examples of π -adducts of dibenzo[*a,g*]corannulene with fullerenes. Upon analysis of their crystal structures, a remarkable difference between the two packing patterns is revealed. Adduct **1** exhibits a solid state packing similar to that of the previously reported [C₂₀H₁₀·C₆₀] system, in which a 1:1 ratio of fullerene:buckybowl was observed without differ-

entiation between the concave–convex and convex–convex binding. The structure of **2** exhibits a different and unique packing motif. In this assembly, two C₂₈H₁₄ molecules interact with C₇₀ only through the concave-convex interactions, essentially encapsulating each C₇₀ cage by two bowls in the crystal. Notably, the C₂₈H₁₄ bowl exclusively interacts with the elongated side of C₇₀, showing a preferential orientation of these two carbon-rich molecules in the solid state. The absence of the disorder in this case allowed us to reveal for the first time the preferred staggered stereochemical arrangement of the π-bowl and the fullerene surfaces. We should mention here that the observed supramolecular arrangements in the crystals of **1** and **2** may be mostly due to the crystal packing effects and may not necessarily reflect the lowest energy structures of calculated discrete ball-bowl dimers. We can also predict that future applications of π···π interactions between curved polyaromatic systems may include the use of dibenzo[*a,g*]corannulene as the target receptor in a pair of “molecular tweezers” for a selective capture of the C₇₀ guest molecules in the presence of C₆₀.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic information files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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