

## Foregoing Rigidity to Achieve Greater Intimacy\*\*

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Interactions between the surfaces of planar and nonplanar molecules have generated considerable interest in materials chemistry<sup>[1,2]</sup> as critical elements for understanding two-dimensional supramolecular assembly, molecular and chiral recognition, and heterogeneous catalysis. Carbon-rich ball- and bowl-shaped polyaromatic molecules, such as fullerenes and fullerene fragments or buckybowl, figure prominently in these studies. Fullerenes have been found to form solid constructs with planar metalloporphyrins with remarkably close contacts but without the need for matching their convex and concave faces.<sup>[3]</sup> Molecular self-organization of nonplanar polyaromatic bowls on a planar metal surface introduces the interesting additional factor of symmetry mismatch.<sup>[4]</sup> Studies of ordered structures formed by weakly bound corannulene, C<sub>20</sub>H<sub>10</sub>, on the Cu(110) surface examined by scanning tunneling microscopy (STM) have revealed interesting insights into their molecular interactions. However, the overall effect of these interactions on the geometry of the corannulene bowl could not be evaluated by the STM method.<sup>[4]</sup>

In this work, we selected a system that allowed us to investigate the mutual structural influences of bowl-shaped polyarenes and a planar polynuclear metal unit upon their attractive interaction (Figure 1). Curving of the planar

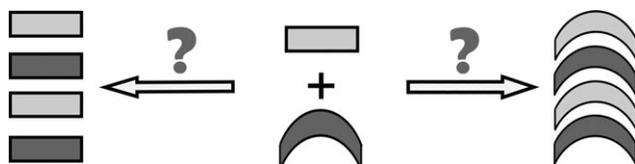


Figure 1. Matching planar and nonplanar molecules.

trimetal unit to match the convex surface of a  $\pi$  bowl may be required to form a stable metal–organic complex. Flattening of the bowl-shaped polyarene may also be anticipated, with both effects changing the strain energy of interacting partners and leading to “mutual curvature adaptations” at the

molecular level. By selecting the highly Lewis acidic perfluoro-*ortho*-phenylenemercury C<sub>18</sub>F<sub>12</sub>Hg<sub>3</sub> complex as a planar trimetal unit (Figure 2, [Hg<sub>3</sub>]), we have significantly

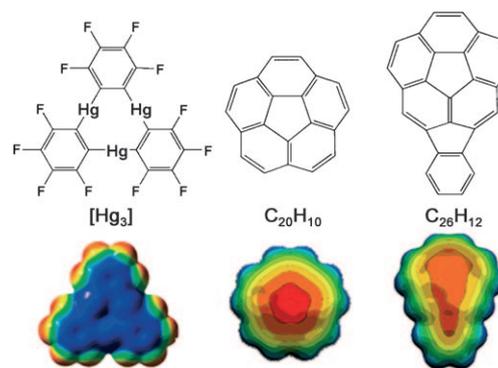


Figure 2. Perfluoro-*ortho*-phenylenemercury, corannulene, and monoindenocorannulene (top) along with their electrostatic potential (convex surfaces (bottom)).

enhanced molecular interactions with  $\pi$  bowls. Although [Hg<sub>3</sub>] is known to form stable complexes with a number of single-ring and planar polycyclic aromatic hydrocarbons,<sup>[5]</sup> its binding to curved polyarenes has never been examined. DFT calculations for [Hg<sub>3</sub>] show a positively charged electrostatic potential surface in the center of the trimercury complex,<sup>[6]</sup> thus making it an excellent electrophilic probe for solid-state interactions with the negatively charged surfaces of bowl-shaped polyarenes. As the latter, we chose corannulene, C<sub>20</sub>H<sub>10</sub>, and monoindenocorannulene, C<sub>26</sub>H<sub>12</sub> (Figure 2).

The former polyarene is the smallest subunit of the C<sub>60</sub> fullerene with a C<sub>5v</sub> symmetry,<sup>[7]</sup> whereas the latter has a larger surface area and deeper bowl depth than corannulene with a symmetry reduced to C<sub>v</sub>. Although the expected complex formation in the [Hg<sub>3</sub>·C<sub>20</sub>H<sub>10</sub>] and [Hg<sub>3</sub>·C<sub>26</sub>H<sub>12</sub>] systems should be favored by electrostatic interactions, the geometry and symmetry mismatch of building units ([Hg<sub>3</sub>] is planar with a D<sub>3h</sub> symmetry) makes both systems unique models to examine fine-structure deformation effects resulting from molecular interactions between planar and nonplanar molecules. Additionally, indenocorannulene has both planar (indeno group) and nonplanar (corannulene core) parts, which makes the C<sub>26</sub>H<sub>12</sub> bowl a distinctive object for further assessments of subtle interaction effects at the interface of planar and nonplanar surfaces.

The complexation reactions between equimolar quantities of [Hg<sub>3</sub>] and the selected bowls yield the desired products, [Hg<sub>3</sub>·C<sub>20</sub>H<sub>10</sub>] (**1**) and [Hg<sub>3</sub>·C<sub>26</sub>H<sub>12</sub>] (**2**), in excellent yields (see the Supporting Information). The elemental analyses of **1** and **2** indicate a 1:1 stoichiometry of [Hg<sub>3</sub>] to the polyarene. The

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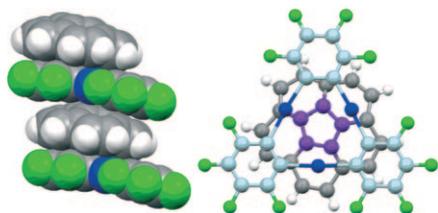
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IR data for both complexes clearly confirm the involvement of hydrocarbons in coordination. While the infrared spectra of **1** and **2** are mostly dominated by strong absorption bands of [Hg<sub>3</sub>] in the 1000–1600 cm<sup>-1</sup> region, the data permit the detection of intense symmetrical out-of-plane C–H deformation bands of coordinated C<sub>20</sub>H<sub>10</sub> and C<sub>26</sub>H<sub>12</sub>. These bands (843 and 823 cm<sup>-1</sup> in **1** and **2**, respectively) are shifted to higher energies by 10 and 7 cm<sup>-1</sup>, respectively, in comparison to free buckybowls (see the Supporting Information for details).

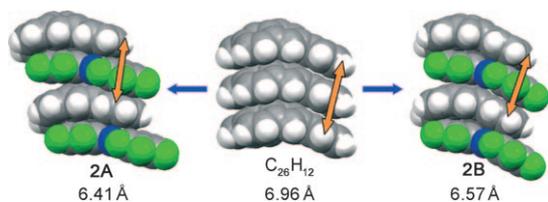
The single-crystal X-ray diffraction analysis of **1**<sup>[8]</sup> reveals the formation of extended binary stacks in which molecules of [Hg<sub>3</sub>] alternate with C<sub>20</sub>H<sub>10</sub>, thus rendering the first example of multiple metal binding to the interior buckybowl surface (Figure 3).



**Figure 3.** Space-filling view of the stack (left) and top view to the convex surface of C<sub>20</sub>H<sub>10</sub> (right) in the solid-state structure of [Hg<sub>3</sub>·C<sub>20</sub>H<sub>10</sub>] (**1**). F: green, C: violet/gray/light blue, Hg: dark blue, H: white.

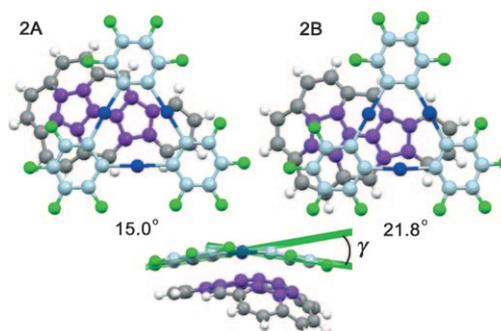
In **1**, the successive trimercury units adopt an eclipsed arrangement displaying short intermolecular Hg–C<sub>aromatic</sub> distances with the hub C atoms of convex (3.14–3.51 Å) surfaces and the flank C atoms of concave (3.17–3.40 Å) surfaces. These contacts are significantly shorter than the sum of the van der Waals radii of Hg ( $r_{vdw} = 2.0\text{--}2.2$  Å) and C ( $r_{vdw} = 1.7$  Å) and noticeably stronger than those previously reported for the [Hg<sub>3</sub>] complexes with planar aromatic hydrocarbons.<sup>[5]</sup> Additionally, although a number of metal complexes of corannulene are known to date,<sup>[9]</sup> none exhibits multiple metal binding to its central five-membered ring. In the case of indenocorannulene, no isolated metal complexes have ever been reported.

The single-crystal X-ray diffraction analysis of **2**<sup>[10]</sup> reveals the existence of two crystallographically independent extended stacks (**2A** and **2B**) similar to that observed in **1** (Figure 4). The overall strength of interactions along the stacks is illustrated by shortening of the distance between



**Figure 4.** Space-filling views of the stacks in [Hg<sub>3</sub>·C<sub>26</sub>H<sub>12</sub>] and free C<sub>26</sub>H<sub>12</sub>.

indenocorannulene molecules in the binary complexes compared to that in the solid-state structure of free C<sub>26</sub>H<sub>12</sub>.<sup>[11]</sup> This difference in stacking distance between **2A** and **2B** correlates well with the variation in bowl depths of the corresponding C<sub>26</sub>H<sub>12</sub> molecules. Coordination slightly flattens the indenocorannulene surface compared to its free form with the bowl being less curved in **2A** (bowl depth is 1.008 vs. 1.047 Å in **2B** and 1.056 Å in free indenocorannulene), and that allows a closer packing of molecules along the stack in the former. For comparison, corannulene is significantly more affected by coordination, with its bowl depth being reduced to 0.754 Å in **1** compared to 0.870 Å in free C<sub>20</sub>H<sub>10</sub>.<sup>[12]</sup> The smaller bowl deformation in the indenocorannulene complex can be attributed to the shift of primary Hg–C interactions away from the corannulene core to the peripheral indeno group (Figure 5).



**Figure 5.** Views to the convex surface of C<sub>26</sub>H<sub>12</sub> in **2A** and **2B** in the solid-state structure of [Hg<sub>3</sub>·C<sub>26</sub>H<sub>12</sub>] (top). Bending the planar [Hg<sub>3</sub>] unit over the nonplanar surface of indenocorannulene (bottom).

The observed difference in curvature of the C<sub>26</sub>H<sub>12</sub> bowls in **2A** and **2B** is a result of strong bonding interaction of [Hg<sub>3</sub>] and the spoke bond connecting the two five-membered rings of indenocorannulene in **2A**. This Hg–C<sub>spoke</sub> contact (3.052 Å) is the shortest in the series of [Hg<sub>3</sub>·arene] complexes. The effect of this interaction shows up in significantly reduced  $\pi$ -orbital axis vector (POAV) angles of the C atoms forming the bond and can even be seen in the infrared spectrum of **2**, as discussed in the Supporting Information. Two other Hg atoms of the trimercury unit interact with the convex surface of C<sub>26</sub>H<sub>12</sub> through binding to the indeno group, with longer contacts ranging from 3.395 to 3.634 Å. In **2B**, the [Hg<sub>3</sub>] unit is side-shifted along the convex surface of C<sub>26</sub>H<sub>12</sub> and exhibits weaker interactions with the spoke carbon atoms of indenocorannulene, thus causing less deformation of the bowl. On the concave face of C<sub>26</sub>H<sub>12</sub> in both **2A** and **2B**, the Hg centers bind the peripheral carbon atoms with the average Hg–C contacts being noticeably longer than those to the convex side of indenocorannulene.

Importantly, in addition to Hg–C interactions, strong arene–fluoroarene interactions exist in both [Hg<sub>3</sub>·C<sub>20</sub>H<sub>10</sub>] and [Hg<sub>3</sub>·C<sub>26</sub>H<sub>12</sub>]. In **1**,  $\pi$ – $\pi_F$  interactions between one of the C<sub>6</sub>F<sub>4</sub> rings of the trimercury unit and the concave surface of corannulene are identified (3.64 and 3.78 Å, Figure S14 in the Supporting Information). In **2A** and **2B**, both convex and

concave surfaces are involved in arene–fluoroarene interactions because of the larger surface area availability of indenocorannulene compared to that of corannulene. The shortest distances between the centroids of the  $C_6F_4$  rings of  $[Hg_3]$  and the six-membered rings of indenocorannulene are 3.84 and 3.33 Å with the convex and 3.88 and 3.97 Å with the concave surfaces of  $C_{26}H_{12}$  in **2A** and **2B**, respectively (Figures S18 and S19 in the Supporting Information).

The observed  $\pi$ – $\pi_F$  interactions have a pronounced effect on the planar trimetal unit in the solid state. In **1** and **2**, the trimercury unit bends over the nonplanar polyarenes to embrace the convex faces of the  $\pi$  bowls. The best surface match of interacting units, and thus the strongest arene–fluoroarene interactions with the *convex* surface of  $C_{26}H_{12}$  in **2B**, lead to an unprecedented distortion of  $[Hg_3]$  upon coordination ( $\gamma = 21.8^\circ$ , Figure 5). This value exceeds those found in **2A** ( $15.0^\circ$ ) and the corannulene complex **1** ( $11.2^\circ$ ). The smaller surface area of  $C_{20}H_{10}$  leads to the absence of arene–fluoroarene interactions on the convex surface of the bowl, and only those on the concave side are observed in **1**. This results in the significantly reduced deformation of the planar  $[Hg_3]$  unit in **1** compared to that in **2**. It is worth stressing here that in **2A**, where the directional Hg– $C_{spoke}$  interaction takes place, the corannulene core of  $C_{26}H_{12}$  is affected substantially more strongly, whereas the  $[Hg_3]$  unit is less affected than **2B**, where the above Hg–C interactions could not be clearly identified. This fact corroborates the importance of  $\pi$ – $\pi_F$  interactions for matching the surfaces of the planar trimercury unit and the  $\pi$  bowls.

Although arene–fluoroarene interactions are widely used in crystal engineering with flat molecules,<sup>[13]</sup> herein they are utilized for the first time for bending a planar complex over nonplanar templates. The ability to manipulate and control attractive interactions between planar and curved surfaces that we have demonstrated here should further advance the fields of supramolecular assembly and molecular recognition, as well as generally expand the synthetic chemist's toolbox.

Nonplanar polyaromatic hydrocarbons exhibit interesting luminescent properties.<sup>[14]</sup> The emission of indenocorannulene in the solid state is substantially red-shifted ( $\lambda_{max} = 537$  nm,  $\lambda_{exc} = 400$  nm) in comparison with that of corannulene ( $\lambda_{max} = 454$  nm,  $\lambda_{exc} = 350$  nm) and other smaller bowls. In the solid state, both adducts **1** and **2** show bright photoluminescence at room temperature (Figures S10 and S11 in the Supporting Information). The energy for the emission of the crystalline solid **1** corresponds to that observed for the phosphorescence of free corannulene in a glass matrix at 77 K (lifetime 1.9 s).<sup>[14a]</sup> Similar observations have been made for the  $[Hg_3]$  complexes with planar polyaromatic hydrocarbons, which display phosphorescence of arenes and, importantly, the emission lifetimes are always shorter than those of the free arenes by 3–5 orders of magnitude.<sup>[5]</sup> Thus, adduct formation affords room-temperature-phosphorescent materials with excited-state lifetimes on the order of 100  $\mu$ s, which makes them great candidates for light-emitting applications. For comparison, the lifetime of the phosphorescence of tetrabromocorannulene in a glass matrix at 77 K is about 50 ms<sup>[14a]</sup> and, in contrast to complexes **1** and **2**, the shortening of the value is derived from an internal heavy atom effect. It is

also worth mentioning here that these room-temperature-phosphorescent materials with short lifetimes can be easily accessed without recourse to the challenging synthesis of heavy-atom-substituted buckybowls. Another possible advantage of using the  $[Hg_3]$  complexes of  $\pi$  bowls over those with planar arenes is the potential for substantial cost savings as a result of the longer excitation wavelengths (for example,  $\lambda_{exc} = 400$  nm for **2**, and excitation will be further red-shifted for more curved bowls).

In summary, matching the planar  $[Hg_3]$  unit with nonplanar surfaces of corannulene and indenocorannulene resulted in significant geometry adjustments of both interacting partners in the resulting solid-state complexes. This is manifested in such a way that  $[Hg_3]$  adopts highly bent configurations, which are deviating from planarity by up to  $21.8^\circ$ . The adducts display intermolecular Hg–C distances starting at 3.0 Å, which rank among the shortest contacts observed in organomercurial complexes. However, multiple arene–fluoroarene interactions seem to be responsible for a tight match of the interacting units during complexation. Utilization of these rather weak individual forces for large-surface molecules reinforces mutual attractive interactions of the symmetrically and geometrically mismatched partners and results in an unprecedented increase in strain energy at the molecular level. The observed curvature tradeoffs phenomenon should be further harnessed for enhancement of the chemical reactivity of the interacting units in subsequent chemical transformations, and tested for storage/release of strain energy in the solid state.

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