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Fullerenes

Highly Curved Bowl-Shaped Fragments of Fullerenes: Synthesis, Structural Analysis, and Physical Properties**

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Dedicated to Professor Armin de Meijere on the occasion of his 75th birthday

Abstract: Highly curved buckybowls **3**, **4**, and **5** were synthesized from planar precursors, fluoranthenes **8**, benzo[*k*]fluoranthenes **10** and naphtho[1,2-*k*]-cyclopenta[*cd*]fluoranthenes **12**, respectively, using straightforward palladium-catalyzed cyclization reactions. These fluoranthene-based starting materials were easily prepared from 1,8-bis(arylethynyl)-naphthalenes **6**. Both buckybowls **3** and **4** are fragments of C_{60}, whereas **5** is a unique subunit of C_{70}. The curved structures were identified by X-ray crystallography, and they are deep bowls. The maximum π-orbital axis vector (POAV) pyramidalization angle in both **3** and **4** is 12.8°. Such a high curvature is very rarely obtained. Buckybowls **5** are less curved than the others because they have a lower density of five-membered rings, analogous to the tube portion of C_{70}. Cyclopentaannulation increases the bowl depths of **3** and **4**, but not the maximum POAV pyramidalization angle. Among the eight buckybowls studied herein, five form polar crystals. The bowl-to-bowl inversion dynamics of these buckybowls can be classified into two types; one has a planar transition structure, whereas the other has an S-shaped transition structure. A larger longitudinal length of these buckybowls corresponds to a stronger preference for the latter. The photophysical properties of these buckybowls were examined and compared with those of C_{60} and C_{70}. Buckybowls **5** have absorption bands at wavelengths greater than 450 nm, which are similar to those of C_{70}. The chiral resolution of the mono-substituted buckybowl **4ac** was also studied by using HPLC with a chiral column.

Introduction


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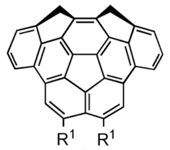

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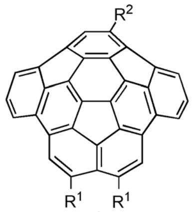

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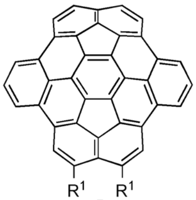

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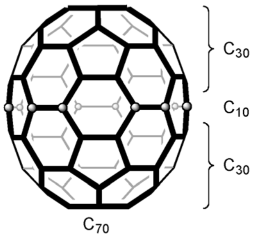

C_{70}

Introduction of five-membered rings into sp^2-carbon hexagonal π-networks enables the formation of aromatic bowls, consistent with Euler's rule.[1] Corannulene (**1**)[2] and sumanene (**2**)[3] are representative examples of such bowls. These bowl-shaped compounds (so-called buckybowls or π-bowls) can be extended to form fullerenes[4] or carbon nanotubes (CNTs).[5] Investigations of the bowl-shaped subunits of fullerenes may help to elucidate their chemistry. More importantly, buckybowls are known for their interesting physical properties, since they are remarkably effective in the stabilization of neutral radicals[6] and have (potential) applications as electro-optical organic materials, such as liquid crystals and organic semiconductors.[7] Buckybowls have the potential to be utilized as precursors in the formation of selected CNTs, some forms of which exhibit excellent electronic conductivity that greatly exceeds that of copper wire.[8] Owing to the low solubility in common organic solvents, their pure form cannot be obtained in useful amounts by either preparation or purification.[9] Hence, the synthesis of a single form of CNT from a buckybowl is sought.[10]

Highly curved buckybowls, which are defined herein as π-bowls being more curved than C_{60},[11] have a high inherent strain, so their synthesis is a challenge. They are most commonly prepared by a strategy that involves extension of the backbone of a smaller bowl and/or by the use of high-temper-

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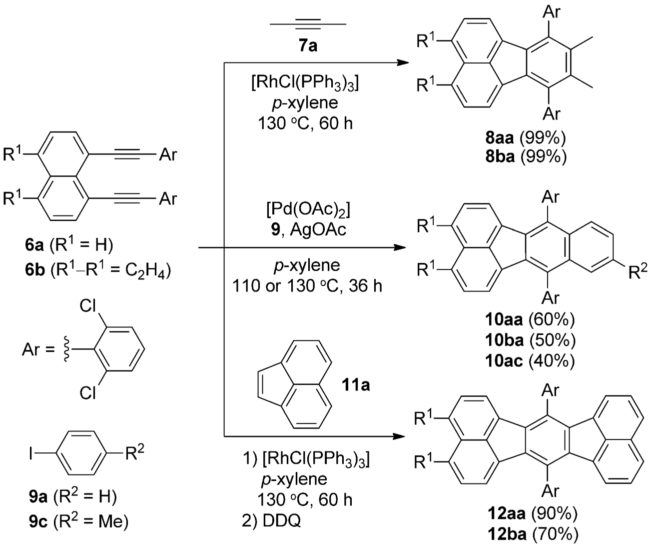
ature flash vacuum pyrolysis (FVP) as a synthetic tool.[2d,12] The conditions required for FVP considerably limit the range of functional groups and potentially cause thermal rearrangement of the molecular framework.[13] Although highly curved buckybowls have been generated efficiently from corannulene and sumanene with the help of metal-catalyzed reactions under mild conditions, the overall lengths of these syntheses can be quite long, when the many steps required to synthesize corannulene and sumanene are taken into account.[14] Examples of such approaches include the preparations of pentaindenocorannulene[15] and trinaphthosumanene ($C_{42}H_{18}$).[16] Unlike these synthetic methods, buckybowls **3 aa** ($R^1 = H$), **4 aa** ($R^1 = R^2 = H$),[17] and **5 aa** ($R^1 = H$)[18] can be directly formed from easily obtained planar precursors, as determined in our preliminary studies. Although similar protocols have been utilized to synthesize less-curved *as*-indaceno[3,2,1,8,7,6-*pqrstuv*]picenes[14f] and dibenzocorannulenes[13,14e] by Pd-catalyzed cyclizations, the reaction conditions for the preparation of highly curved bowls are yet to be systematically examined. Notably, both **3 aa** and **4 aa** are highly curved fragments of C_{60}, whereas **5 aa** is a distinctive subunit of C_{70}. Fullerene C_{70} can be considered to be two C_{60}-like hemispheres that are connected by a set of ten carbon atoms on the equatorial line. π-Bowl **5 aa** contains unique equatorial carbon atoms and maps onto the tube portion of C_{70}; furthermore, it is also a fragment of numerous higher fullerenes, such as C_{76}, C_{78},[19] C_{84},[20] and others.

Following the successful synthesis of these buckybowls, the same method was extended to prepare more curved cyclopentaannulated derivatives and a chiral bowl. The results of studies of their synthesis, structures, stereochemistry, and physical properties are presented below.

Results and Discussion

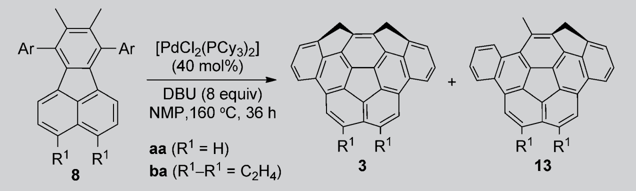
Synthesis

Fluoranthene derivatives are ideal precursors in the synthesis of buckybowls **3**, **4**, and **5** because they all contain a fluoranthene segment. Metal-catalyzed annulations of 1,8-bis(arylethynyl)naphthalenes **6** generate various fluoranthene-based arenes (Scheme 1).[21] Rh-catalyzed co-cyclotrimerization of diynes **6** with 2-butyne yielded fluoranthenes **8** in excellent yields.[14c] Pd-catalyzed annulation of **6** with iodoarenes **9** gave benzo[*k*]fluoranthene **10**.[22] The low yield of **10 ac** was unsurprising because our earlier studies revealed that substituted *o*-diiodoarene exhibits better annulation than substituted monoiodoarene. Naphtho[1,2-*k*]cyclopenta[*cd*]fluoranthenes **12** were efficiently prepared by the simple Rh-catalyzed [(2+2)+2] cycloaddition of diynes **6** with acenaphthylene (**11 a**),[14c] and were subsequently aromatized by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).



Scheme 1. Synthesis of precursors for buckybowls.

Table 1. Optimization of reaction condition for synthesis of buckybowls **3**.[a]



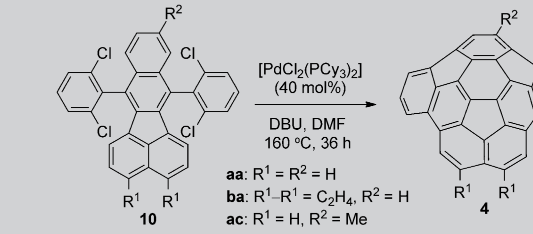
Entry	Fluoranthene	Condition change	Ratio **3**:**13**	Yield [%][b]
1	**8 aa**	DMF	54:46	26
2	**8 aa**	DMAc	78:22	23
3	**8 aa**	–	71:29	28[c]
4	**8 aa**	24 h	67:33	21
5	**8 aa**	48 h	71:29	24
6	**8 aa**	140 °C	74:26	23
7	**8 aa**	180 °C	79:21	19
8	**8 aa**	DBU (4 equiv)	67:33	12
9	**8 aa**	DBU (16 equiv)	62:38	24
10	**8 aa**	$[PdCl_2(PCy_3)_2]$ (20 mol %)	65:35	20
11	**8 ba**	–	36:64	11
12	**8 ba**	DMAc	40:60	5
13	**8 ba**	DMF	39:61	18

[a] The reaction was conducted with **8** (0.1 mmol) in NMP (5 mL). The **3**:**13** ratio was determined by ^1H NMR spectroscopy. [b] The yield for a mixture of isolated **3** and **13**. [c] Ref. [17].

Methylene-bridged buckybowls **3** were generated from fluoranthenes **8** through Pd-catalyzed benzylic and aryl C–H bond activations.[23] The cyclization of fluoranthenes **8** produced a mixture of **3** and **13**. The reaction conditions for the cyclization of fluoranthene **8 aa** using $[PdCl_2(PCy_3)_2]$ and 1,8-diazabicycloundec-7-ene (DBU) were systematically examined (Table 1). Although solvents dimethylformamide (DMF), *N*-methylpyrrolidone (NMP) and dimethylacetamide (DMAc) gave a mixture of **3 aa** and **13 aa** in similar yields, the amounts of the byproduct **13 aa** in the latter two solvents declined (entries 1–3 in Table 1). In general, the reaction temperature, reaction time, or amounts of DBU used did not significantly influence the **3 aa**/**13 aa** ratio, but some conditions drastically reduced their yields (entries 4–9 in Table 1), such as a temperature of 180 °C or the use of only four equivalents of DBU. Conducting the reaction at high temperature promoted the formation of dechlorinated intermediates. Insufficient DBU resulted in the incomplete conversion of **8aa**. Under the optimal conditions herein, a mixture of **3aa** and **13aa** (ratio 71:29) was obtained in 28% yield (entry 3 in Table 1). Cyclopentaannulated **3ba** was similarly prepared using DMF as a solvent (entry 13 in Table 1). The reaction was inefficient and **13ba** was observed as the major product, presumably because of the highly curved structure of **3ba**. Notably simple chromatography, eluting with a mixture CH_2Cl_2/hexane, did not completely separate the compounds **3** from compounds **13**. Only very small amounts of them were obtained in the pure form. Elution with cyclohexane without the application of external air pressure over several hours gradually eluted **3** from the column, leaving **13** behind.

Buckybowls **4** were prepared by the cyclization of **10** in the presence of a mixture of DBU and $[Pd(PCy_3)_2Cl_2]$ at 160 °C (Table 2). The concentration of **10** strongly affected the reaction efficiency. The reaction in either a concentrated (0.1 м) or a diluted (5×10^{-3} м) solution yielded only a trace of **4aa** (entries 1 and 5 in Table 2). At the former concentration, **10aa** did not completely undergo the fourfold cyclization reactions, and dechlorinated intermediates were formed, whereas a diluted solution of **10aa** caused many of the starting materials to be retained. Under the optimal conditions herein, compound **4aa** was generated in 31% yield (entry 3 in Table 2). It is noteworthy that **4aa** was first prepared in a 0.14% yield from 7,12-bis(2-bromophenyl)benzo[*k*]fluoranthene using FVP at 1100 °C.[24] Our protocol is superior to the conventional method. This synthetic approach was also applied in preparations of **4ac** and **4ba**, and they were obtained in 40 and 5% yields, respectively (entries 6 and 7 in Table 2). Presumably, the highly curved structure of **4ba** was the cause of the unsatisfactory result.

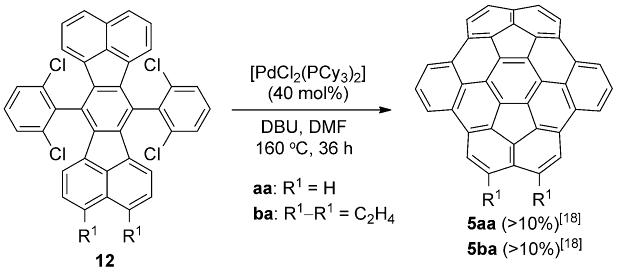
Table 2. Preparation of buckybowls **4**.[a]



Entry	Starting material	*C* [м]	Product	Yield [%]
1	**10aa**	0.10	**4aa**	trace
2	**10aa**	0.04	**4aa**	29
3	**10aa**	0.02	**4aa**	31[b]
4	**10aa**	0.01	**4aa**	14
5	**10aa**	5×10^{-3}	**4aa**	trace
6	**10ba**	0.02	**4ba**	5
7	**10ac**	0.02	**4ac**	40

[a] Reaction was conducted with **11** (0.1 mmol) in DMF (5 mL). [b] Ref. [17].

The reaction conditions that were used in the synthesis of **4** were applied in the preparation of **5**, but low yields were obtained (Scheme 2). Since bowls **5** were only weakly soluble in common organic solvents, some of the material was irreversibly lost during chromatography. The eluent cyclohexane was much more effective in purification than the mixture of CH_2Cl_2/hexane. Elution with cyclohexane without the application of external air pressure over several hours gave compounds **5** in around 10% yields. The soluble residues in the column were collected by flushing it with CH_2Cl_2. Small amounts of **5** were obtained from the collected residues by column chromatography and elution with cyclohexane.



Scheme 2. Synthesis of buckybowls **5**.

X-ray crystallographic structures

X-ray-quality crystals of new compounds **3ba**, **4ba**, and **13ba** were obtained by the slow evaporation of the mixed CH_2Cl_2/MeOH solvent (Table 3).[25] Single crystals of **3aa** were grown by the diffusion of MeOH into a solution in benzene. The curvature of buckybowls was determined by analyzing the bowl depth of the corannulene fragment. The bowl depths follow the order **4** > **3** > **5** > **13**, and all significantly exceed that of corannulene (0.87 Å; Table 4).[26] Bowls **5** are less curved than **3** and **4** owing to the lower density of five-membered rings, analogous to the tube portion of C_{70}. Cyclopentaannulated buckybowls **3ba**, **4ba**, and **5ba** have 0.10–0.14 Å larger bowl depths than their corresponding parent compounds **3aa**, **4aa**, and **5aa**, respectively. Compound **4ba** is the deepest bowl, with a depth of 1.34 Å. Compounds **4** contain both corannulene and sumanene segments. The bowl depths that were measured from the sumanene core in **4aa** (1.48 Å) and **4ba** (1.50 Å) also exceed that of sumanene (1.11 Å).[27] Cyclopentaannulation in **4** insignificantly affects the bowl depth of the sumanene core. Notably, the geometric calculations at the B3LYP/cc-pVDZ level are highly consistent with the X-ray structural data (Table 4 and Tables S3 and S4 in the Supporting Information).

The π-orbital axis vector (POAV) pyramidalization angle is another useful metric of the curvature of buckybowls. The values for planar benzene and C_{60} are determined to be 0 and 11.6°, respectively.[28] As presented in Figure 1, the POAV pyramidalization angle is highest at the hub carbon atoms of a corannulene core, and follows the order **3** ≈ **4** > **5**. All members of the first two classes of compounds have a maximum POAV pyra-

Table 3. Crystal structure data.

	3aa	**3ba**	**4aa**	**4ba**	**5aa**	**5ba**	**13aa**	**13ba**
formula	$C_{30}H_{14}$	$C_{32}H_{16}$	$C_{64}H_{24}$	$C_{34}H_{14}$	$C_{38}H_{14}$	$C_{40}H_{16}$	$C_{30}H_{16}$	$C_{32}H_{18}$
M_r	374.41	400.45	792.83	422.45	470.49	496.53	376.43	402.46
solvent	C_6H_6/MeOH	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH
T [K]	100(2)	100(2)	296(2)	100(2)	296(2)	100(2)	100(2)	100(2)
crystal system	monoclinic	trigonal	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	$C1c1$	$R\bar{3}$	$Cmc2_1$	$Cmc2_1$	$Cmc2_1$	$Pbca$	$Pna2_1$	$P12_1/n1$
Z	4	18	2	4	4	8	8	4
unit cell dimensions								
a [Å]	20.4913(14)	18.3650(5)	17.7727(8)	16.897(4)	18.1315(4)	14.975(3)	20.405(12)	13.2867(9)
b [Å]	10.0252(7)	18.3650(5)	12.6382(6)	13.523(4)	13.7073(3)	16.934(4)	23.455(14)	7.3257(4)
c [Å]	8.4972(5)	29.5206(11)	8.1349(4)	8.179(2)	8.37540(10)	17.587(4)	7.762(4)	19.8902(14)
α [°]	90	90	90	90	90	90	90	90
β [°]	103.5200(10)	90	90	90	90	90	90	104.199(2)
γ [°]	90	120	90	90	90	90	90	90
V [Å^3]	1697.20(19)	8622.6(5)	1827.22(15)	1868.9(8)	2081.57(7)	4459.8(17)	3715(4)	1876.9(2)
R factor [%]	2.84	4.54	3.28	3.65	3.74	4.70	6.43	4.30
ref.	this work	this work	[17]	this work	[18]	[18]	[17]	this work

Table 4. Bowl depth.[a]

	X-ray	calcd	Reference
1	0.87	0.88	[26]
3aa	1.19	1.19	[17]
3ba	1.32	1.31	this work
4aa	1.24 (1.48)	1.23 (1.49)	[17], [18]
4ba	1.34 (1.50)	1.34 (1.52)	this work
5aa	1.07	1.07	[18]
5ba	1.21, 1.07	1.21, 1.07	[18]
13aa	1.04[b]	–	[17]
13ba	1.19	–	this work
2	1.11	–	[27]

[a] Bowl depths determined from corannulene core. The bowl depths for the sumanene segment are shown in brackets. Theoretical studies were calculated at B3LYP/cc-pVDZ level. [b] There are two molecules in the asymmetric unit.

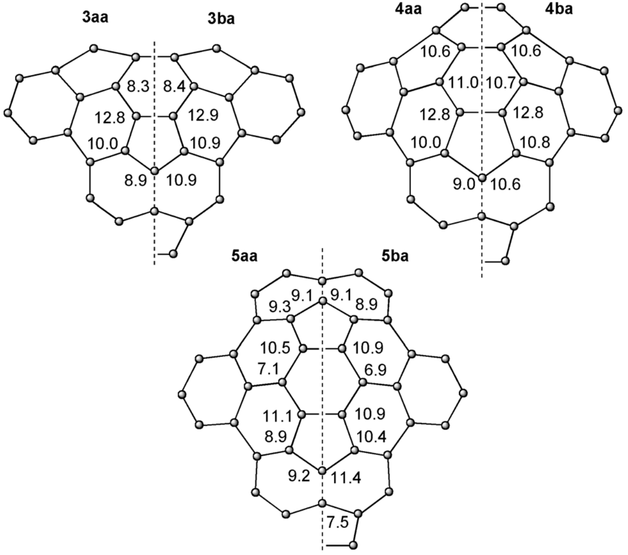


Figure 1. POAV pyramidalization angles of buckybowls based on X-ray crystallography. The values obtained by averaging the symmetry-related data.

midalization angle of approximately 12.8°, which exceeds that of C_{60}. Bowl-shaped molecules seldom have such high values. To the best of the our knowledge, compounds **3**, **4**, and pentaindenocorannulene (12.7°) are the most curved π-bowls that map onto fullerenes.[29] Cyclopentaannulation does not increase the maximum POAV pyramidalization angle in **3** or **4**, but it does do so in less curved **5** and acecorannulene.[30] This result may suggest that the maximum POAV pyramidalization angle reaches its highest value in **3** and **4**, and the change in curvature reflects only on an increase in the bowl depth. This phenomenon has also been observed in a series of symmetric corannulene-based molecules $(C_{10})_nH_{10}$ ($n=2$–5), whose structures change from a bowl ($n=2$, 3) to a tube ($n=4$, 5).[31] The corannulene core at the end cap in $C_{50}H_{10}$ has the largest bowl depth (calcd 12.2; exptl 12.3°, 1.539 Å[10]), but that in $C_{30}H_{10}$ (calcd 12.4°) has the highest POAV pyramidalization angle.

The curvature of buckybowls causes their solid-state packing to be highly interesting but complex. The stacking order of buckybowls provides useful information concerning their potential applications as organic materials with high electron mobility (organic semiconductors),[7c] piezoelectricity or pyroelectricity,[32] or the ability to generate second harmonics (nonlinear optoelectronics).[33] The factors that are required to make bowl-in-bowl stacks and control the orientations of neighboring columns are not yet well-known.[2e,34] The crystallographic data clearly reveal intermolecular interactions of buckybowls, and they are useful for testing theoretical predictions. The intermolecular interactions include π–π stacking and CH⋅⋅⋅π hydrogen bonding. In this context, the distance of the π–π stacking is determined by measuring the separation between the centroids of two aromatic five- or six-membered rings. The intermolecular π–π contact of arenes/fullerenes complexes are typically observed to be in the range 3.5–4.1 Å.[34,35] A theoretical study has demonstrated that the concave-to-convex stacked corannulene dimer has its highest binding energy when two corannulenyl five-membered rings are separated with an equilibrium distance of 3.64 Å,[36] which somewhat exceeds the sum of the van der Waals radii of two carbons (3.40 Å).[37] The strength of the interaction between a CH group and an aromatic π surface can be determined from the CH–π contact distance, which is measured as the separation from the concerned hydrogen atom to the centroid of the nearest aromatic ring. Alternatively, the extent of CH···π interaction (referred to as the CH–Cπ contact in context) can also be gauged by the distance between the hydrogen atom and a carbon atom in a large aromatic surface, such as the central carbon of acenaphthylene. The CH–Cπ data can be directly compared to the results that were obtained by analyzing the separation between the CH group with the fullerene convex surface. Suezawa et al. estimated a regular value of 2.85 ± 0.13 Å for both sp^3CH–Cπ and sp^2CH–Cπ contact distances based on a systematic analysis of Cambridge Structural Database.[38] This range of values is consistent with the sum of the van der Waals radii of the corresponding atoms (2.90 Å).[37]

The structure of **3aa** was determined to have the polar monoclinic space group *C*1*c*1. The translational element along the *a* axis is offset by two steps along the column of the stacked bowls, and a molecular pair **A** and **B** are therefore formed (Figure 2 and Table 5). Within a molecular pair, the shortest intermolecular carbon–carbon, π–π, and CH–Cπ distances are 3.36, 3.61, and 2.86 Å, respectively. The latter interaction is that of a hydrogen atom on a methylene group with a carbon atom in the corannulenyl hub ring. The bowl directions of the molecular pair up the stack are the same, but bowls slip from side to side with a slipping angle of 5°. The slipping angle is defined as that between the stacking axis and the normal to the molecule. The interstack π–π and CH–π interactions are insignificant. Neighboring columnar stacks are oriented with the same bowl direction, forming polar crystals.

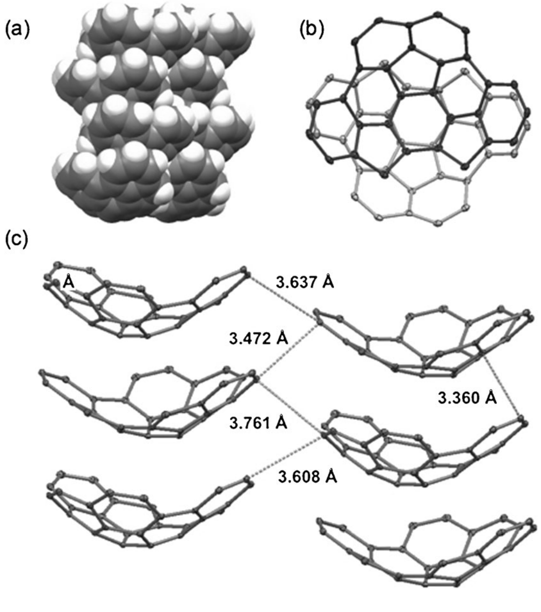
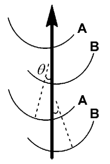


Figure 2. Crystal packing in **3aa** along: a) the *a* axis, and b) the *c* axis; only the carbon atoms are shown for clarity. c) Fragment of the extended 2D stack.

Table 5. The stacking order parameters of the columnar structures.

		Slipping angle θ [°][a]	**A···A** [Å]
	**3aa**	5.0	8.50
	4aa	31.8	8.14
	4ba	32.1	8.18
	5aa	20.0	8.38
	13aa	17.5	7.76
	13ba	29.2	7.33

[a] The slipping angle is defined as that between the stacking axis and the normal to the molecule.

Buckybowl **3ba** crystallizes with the centrosymmetric trigonal $R\bar{3}$ space group. In the crystalline state, the **3ba** molecules do not form columnar stacks. Instead, every set of six molecules constitutes a propeller-like structure (Figure 3). Within this propeller structure, the acenaphthenyl moiety of **3ba** can be treated as a propeller blade and two neighboring propeller blades are arranged one behind the other. Along the resulting C_3 propeller axis, three of the six ethylene-bridged moieties are oriented toward the front, and the other three point toward the back. If the three ethylene-bridged groups on each side are regarded as the components of an "unconnected cyclohexane", then all of the "unconnected distances" are equal, with a value of 3.82 Å. The intermolecular interactions are complex. Each molecule is observed to exhibit the concave/convex (cc/cv) and the convex/convex (cv/cv) interactions with its nearest neighbors. In the cc/cv interaction, the effective π–π overlapping is small. The shortest CH–π contact distance is determined to be 2.65 Å. In the cv/cv interaction with neighboring molecules, the shortest π–π and CH–π contact distances are observed to be 3.70 and 2.78 Å, respectively.

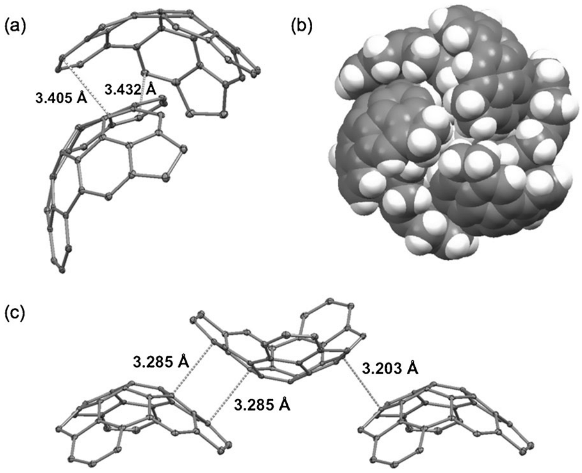


Figure 3. Crystal packing in **3ba**: a) concave/convex interaction, b) propeller-like stack, and c) concave/concave interaction. In (b) and (c), only carbon atoms are shown for clarity.

The structure of **4aa** was solved to have the polar orthorhombic space group $Cmc2_1$. All bowls form bowl-in-bowl stacks and all columnar stacks are arranged with a single bowl direction (Figure 4). The translational element along the *a* axis moves two steps along the column of stacked bowls. The bowls slip from side to side with a slipping angle of 31.8°, producing a small effective π–π overlap. The shortest carbon–carbon contact distance and CH–π separation within a molecular pair in a columnar stack are observed to be 3.35 and 3.06 Å, respectively. The interstack π–π interaction is insignificant; the shortest interstack CH–Cπ contact distance is determined to be 2.80 Å.

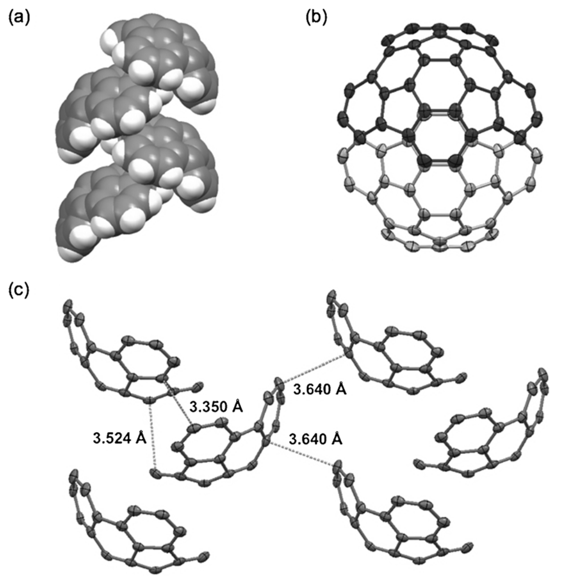


Figure 4. Crystal packing in **4aa** along: a) the *a* axis, and b) the *c* axis; only carbon atoms are shown for clarity. c) Fragment of the extended 2D stack.

Buckybowl **4ba** crystallizes in the polar orthorhombic space group $Cmc2_1$. The translational element along the *a* axis shifts two steps along the column of stacked bowls, forming a molecular pair **A** and **B** (Figure 5 and Table 5). The stacked molecular pair have the same bowl directions, but the bowls slip from side to side with a slipping angle of 32.1°. The shortest carbon–carbon contact distance within a molecular pair is 3.24 Å, but the π–π and the CH$\cdots\pi$ interactions are negligible. An observed significant CH–Cπ contact distance (2.85 Å) corresponds to a separation between a hydrogen atom on an ethylene group in a molecule **A** and a carbon atom of the corannulenyl hub ring in the closest molecule **A** within a columnar stack. The bowl directions are the same in all neighboring columnar stacks. The interstack π–π interaction is insignificant; the shortest interstack CH–Cπ contact distance is determined to be 2.81 Å.

The structure of **5aa** was determined to exhibit the polar orthorhombic space group $Cmc2_1$. The translational element along the *a* axis is offset by two steps up the column of stacked bowls (Figure 6). Within a molecular pair in a columnar stack, the shortest carbon–carbon and π–π contact distances are determined to be 3.20 and 3.82 Å, respectively. The bowl directions in a molecular pair up the stack are identical, but the bowls slip from side to side with a slipping angle of 20.0° (Table 5). Neighboring columnar stacks have the same bowl direction. The interstack π–π interaction is unimportant; the interstack CH–Cπ contact distances start from 2.91 Å.

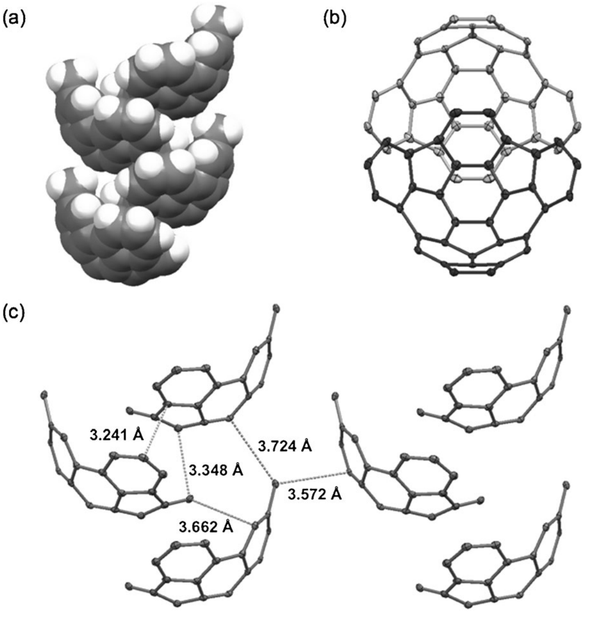


Figure 5. Crystal packing in **4ba** along: a) the *a* axis, and b) the *c* axis; only carbon atoms are shown for clarity. c) Fragment of the extended 2D stack.

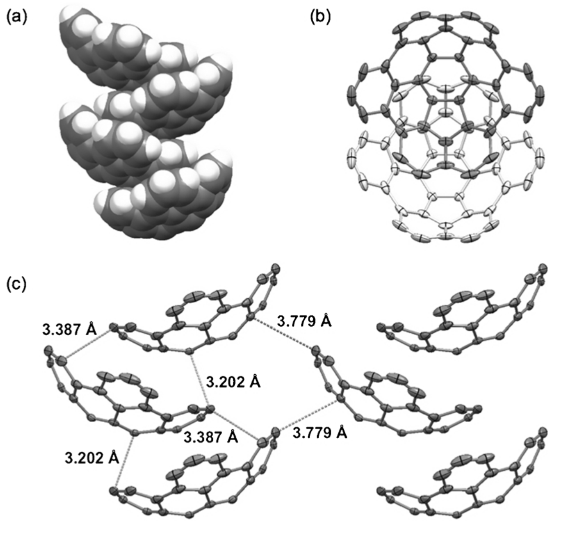


Figure 6. Crystal packing in **5aa** along: a) the *a* axis, and b) the *c* axis; only carbon atoms are shown for clarity. c) Fragment of the extended 2D stack.

Molecules of **5ba** pack in a centrosymmetric crystal form with the orthorhombic space group *Pbca*. Buckybowl **5ba** has a complex molecular packing. All eight of the molecules in a unit cell orient differently (Figure 7). All molecules form "dimer" pairs through the interactions of the protons on the ethylene bridge with the π surface, forming the CH–Cπ contact distance of 2.62 Å. No significant π–π interaction occurs within the "dimer". In addition, each molecule has strong intermolec-

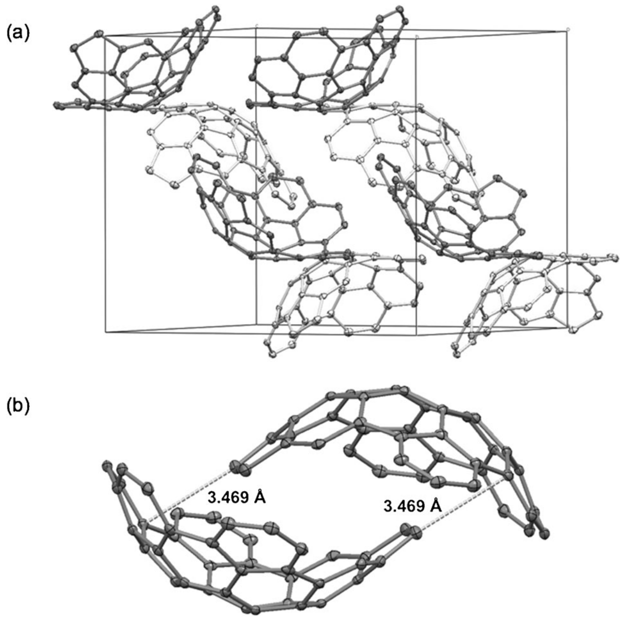


Figure 7. Crystal packing in **5 ba**: a) the unit cell, and b) the "dimer" structure. Only the carbon atoms are shown for clarity.

ular interactions with other nearest neighbors. The shortest π–π and CH–Cπ contact distances are measured to be 3.52 and 2.67 Å, respectively.

The structure of **13 aa** was determined to exhibit the polar orthorhombic space group $Pna2_1$, with half of the molecules in the asymmetric unit. The two kinds of molecules have very similar structural data, including bond lengths, bond angles, bowl depths and POAV angles (see the Supporting Information). The translational element along the *a* axis moves two steps up the column of the stacked bowls (Figure 8). The shortest carbon–carbon contact distance and π–π separation in a molecular pair in a columnar stack are determined to be 3.45 and 3.86 Å, respectively. The CH···π interaction between a methylene proton and a carbon atom in the corannulenyl hub ring is the strongest, with a value of 2.80 Å. The bowl directions of each molecular pair up the stack are the same, but the bowls slip from side to side with a slipping angle of 17.5° (Table 5). Neighboring columnar stacks have the same bowl direction. The interstack π–π interaction is insignificant; the shortest interstack CH–Cπ contact distance is found to be 2.70 Å.

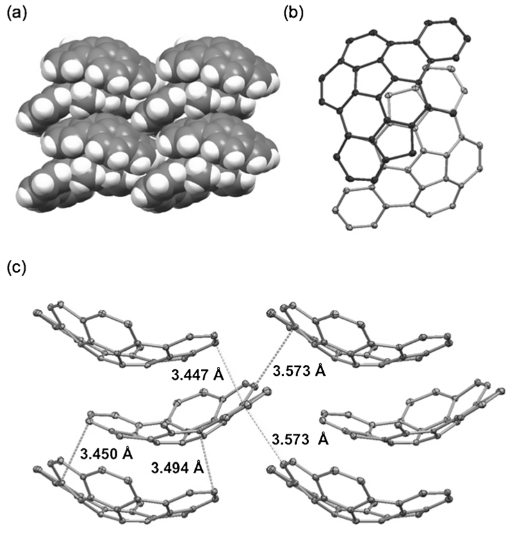


Figure 8. Crystal packing in **13 aa** along: a) the *a* axis, and b) the *c* axis; only carbon atoms are shown for clarity. c) Fragment of the extended 2D stack.

The structure of **13 ba** was determined to exhibit the centrosymmetric monoclinic space group $P12_1/n1$. All molecules form bowl-in-bowl stacks, but each columnar stack has one neighbor with the same bowl direction and one with the opposite bowl direction (Figure 9). Within a columnar stack, the bowls slip from side to side with a slipping angle of 29.2° (Table 5), and the π–π interaction is negligible. The shortest CH–π contact distance within a packed column is determined to be 2.72 Å. The interstack π–π interaction is unimportant. A significant interstack CH–Cπ contact separation is observed to be 2.81 Å, which is the distance between a methylene proton and a carbon atom of the corannulenyl hub ring.

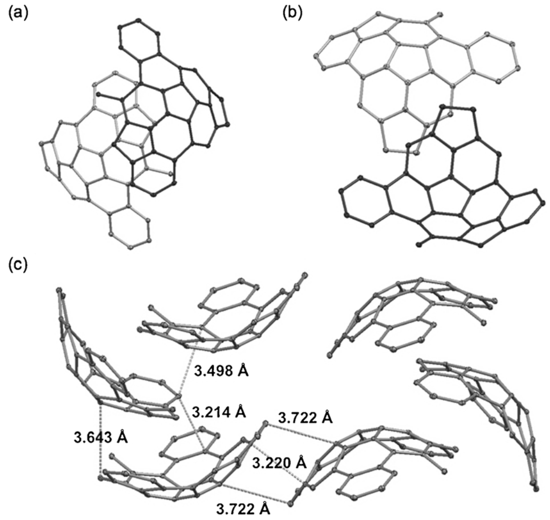
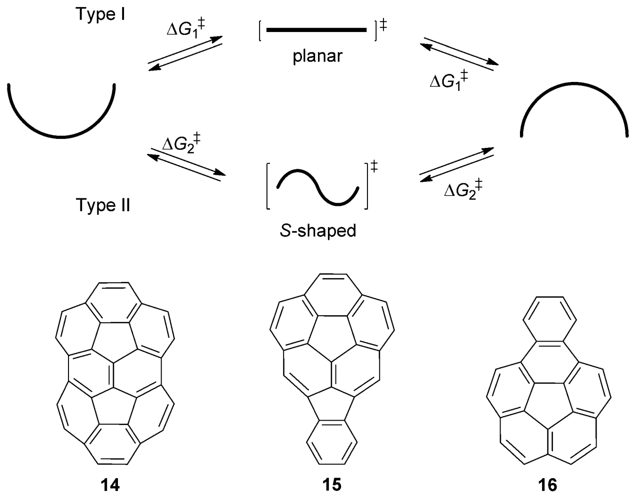


Figure 9. Crystal packing in **13 ba**: a) along the *b* axis, b) interstack convex/convex interaction, and c) fragment of the extended 2D stack. Only the carbon atoms are shown for clarity.

Among the eight buckybowls investigated herein, **3 aa**, **4 aa**, **4 ba**, **5 aa**, and **13 aa** all form polar crystals, as verified by their space groups (Table 3). Interestingly, **4 aa**, **4 ba**, and **5 aa** all crystallize with the orthorhombic space group $Cmc2_1$, and they have similar packing patterns. Buckybowl **5 aa** is less curved than **4 aa** and **4 ba**, and has a larger π-surface. The structural characteristics may cause **5 aa** to have greater π–π surface overlaps than the other two bowls and a smaller slipping angle with the respect to the bowl-stacking axis. Both **3 aa** and **13 aa** are methylene-bridged bowls, and the methylene proton provides strong intermolecular CH···π interactions within a columnar stack. Unlike the polar columnar packing in **4 aa**/**4 ba**, the additional ethylene bridge in **3 ba**, **5 ba**, and **13 ba** critically affects molecular packing, such that it differs from that of the parent compounds **3aa**, **5aa**, and **13aa**, respectively. The former three bowls crystallize with centrosymmetric space groups as apolar crystals, but in different molecular stacks. Bowl **13ba** exhibits apolar columnar packing, whereas **5ba** and **3ba** form dimers and cyclic hexamers, respectively. Although nearest neighbors are known critically to influence the packing, further investigations must be performed to identify the factors that govern this effect.

Inversion dynamics

Based on our preliminary investigations, the inversion dynamics of buckybowls **3**–**5** can be classified to two types: Type **I** involves a planar transition structure, and **II** involves an S-shaped (nonplanar) transition structure (Scheme 3).[18] These transition states were verified to exhibit only one imaginary frequency. The longitudinal length of these buckybowls critically influences their inversion dynamics: a larger length corresponds to a greater preference for route **II**. For example, bowl-to-bowl inversions of corannulene (**1**),[2e,39] sumanene (**2**),[3] and **3** proceed via a planar transition state (route **I** in Scheme 3). The inversion of semibuckminsterfullerene (**14**),[40] **4**, and **5** through inversion route **II** is suggested to have a lower inversion barrier than that through route **I** (Table 6). The inversion mechanisms of "softer" **5aa**[18] and "harder" **4aa** (see the Supporting Information) were confirmed using the pseudo-intrinsic reaction coordinate (pseudo-IRC), and the results thus obtained support their bowl-to-bowl inversion via a nonplanar transition structure. Importantly, the large longitudinal length of a buckybowl is not the only cause of inversion through route **II**. Compounds **15**[14c] and **16**[41] have longer longitudinal lengths than those of **14** and **4aa**, respectively. However, the former two buckybowls are less "condensed" and their inversions proceed through route **I**. Only a "condensed" buckybowl with a large longitudinal length undergoes inversion through route **II**.



Scheme 3. Inversion dynamics of buckybowls.

Table 6. Inversion dynamics.[a]

	Inversion barrier [kcal mol^{-1}] $\Delta G_1^{\ddagger}$	$\Delta G_2^{\ddagger}$	Inversion type	Reference
1	ca. 10	–	**I**	[39], [42]
3aa	56.2	–	**I**	[17]
3ba	84.4	–	**I**	this work
4aa	134.3	124.3	**II**	[18]
4ba	169.8	135.1	**II**	this work
5aa	116.3	79.8	**II**	[18]
5ba	148.4	84.3	**II**	[18]
14	73.8[b]	47.7[b]	**II**	[40]
15	26.4	–	**I**	[14c]
16	6.96[c]	–	**I**	[41]
2	ca. 20	–	**I**	[3a], [43]

[a] Theoretical studies of were calculated at B3LYP/cc-pVDZ level, unless otherwise mentioned. [b] Calculated at the B3LYP/6-311G** level. [c] Calculated at the B3LYP/6-31G* level.

Measurements of the inversion barrier of dideutero-substituted **3aa** reveal that it exceeds 40 kcal mol^{-1}.[17] Accordingly, the inversion barrier of buckybowls **3**–**5** was analyzed theoretically using DFT calculations at the B3LYP/cc-pVDZ level (Table 6). Unlike corannulene with an inversion barrier of approximately 10 kcal mol^{-1}[39,42] and sumanene with a barrier of around 20 kcal mol^{-1},[3,43] these buckybowls have very high inversion barriers (>50 kcal mol^{-1}), and so they can be regarded as static bowls at room temperature. A previous study of the relationship between the structure and energy of corannulene-based buckybowls has demonstrated that a deeper bowl corresponds to a higher inversion barrier.[39] However, the order of inversion barriers, **4**$>$**5**$>$**3**, is inconsistent with the order of bowl depths (Table 4). Importantly, the relationship between bowl depth and inversion barrier described above, is based on simple corannulene derivatives that undergo inversion process via a planar transition structure. Although the studied molecules herein are grouped into two types, depending by their inversion route, the obtained relationship between bowl depth and inversion barrier is reasonable. Within a compound class, *peri*-annelation increases the inversion barrier (Table 6).

Photophysical properties

The photophysical properties of buckybowls **3**–**5** in CH_2Cl_2 (10 μM) at room temperature were investigated and compared with those of fullerenes C_{60} and C_{70} (Table 7 and the Supporting Information). Within compound classes **3** and **5**, the effect of the ethylene bridge on the photophysical properties seems relatively unimportant because they have very similar spectra. Both the photoabsorption and photoluminescence of cyclopentaannulated **4ba**, unlike those of **4aa**, are significantly redshifted. Absorption bands of bowls **3** and **4** are below 450 nm, whereas **5** have absorption bands at greater than 450 nm. Notably, an absorption band in the region of 450–500 nm is important to distinguish C_{70} from C_{60}.[44] Based on this finding, the photoabsorption properties of **3**/**4** and **5** are similar to those of C_{60} and C_{70}, respectively. The photoluminescence of

Table 7. Photophysical properties of buckybowls.[a]

Compound	λ_{abs}[b] [nm]	λ_{em} [nm]
3aa	287, *337*, 374 (sh), 405 (sh)	416, 436, 463 (sh)
3ba	228, 268, 293, *336*, 378 (sh), 400 (sh)	414, 437, 462 (sh)
4aa	238, 288, 297, *308*, 354 (sh)	438, 466, 493 (sh)
4ba	252 (sh), 274, 300, *314*, 370 (sh)	467, 550 (sh)
5aa	*362*, 421, 436 (sh), 461 (sh), 502 (sh)	528, 560 (sh)
5ba	345, *362*, 416, 439, 466, 502 (sh)	528, 560 (sh)
C_{60}	*336*, 407	
C_{70}	336, 366, *383*, 470, 551 (sh)	

[a] Samples (concentration $\approx 10^{-5}$ M) measured in CH_2Cl_2; sh = shoulder. Wavelengths shown in italics represent excitation wavelengths.

C_{60} and C_{70} is known to be very weak because of the highly efficient intersystem crossing,[45] whereas **3** and **5** both exhibit strong fluorescence at approximately 416/436 and 528 nm, respectively. The photoluminescence of **4** is very weak.

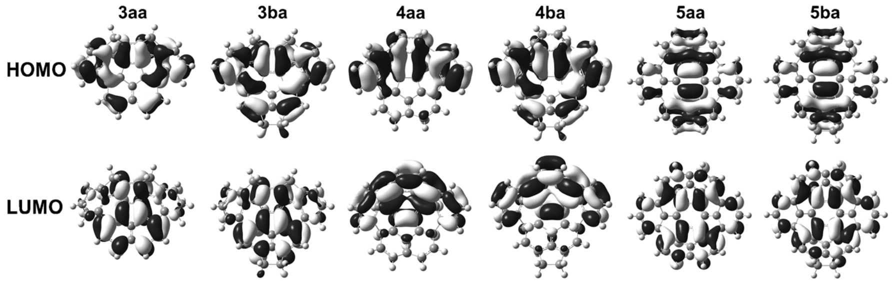


Figure 10. HOMO and LUMO distributions of compounds **3**–**5**.

Figure 10 demonstrates that ethylene bridges of **3ba** and **5ba** participate similarly in establishing their HOMOs and LUMOs, explaining why the photophysical properties of **3ba** and **5ba** are similar to those of their parent compounds. However, the ethylene bridge in **4ba** influences the HOMO more strongly than it does the LUMO, increasing the potential of the HOMO more than it does that of the LUMO (Table S1 in the Supporting Information). The consequently reduced band gap is responsible for the redshifting of the UV and PL spectra of **4ba** relative to those of **4aa**. Like C_{70}, bowls **5** have longer-wavelength absorptions than **3** and **4**, although **3**, **4** and **5** can all map onto C_{70}. The extent of π-conjugation of both HOMOs and LUMOs of the three compound classes follows the order **5** > **3**/**4** (Figure 10). Accordingly, bowls **5** have the smaller band gap. Time-dependent density functional theory (TD-DFT) calculations demonstrate that the strongest vertical excitation wavelengths for **3aa**, **4aa**, and **5aa** are 306, 345, and 439 nm, respectively (Table S2 in the Supporting Information).

The high inversion barriers of **3**–**5** cannot be measured using common NMR techniques, such as variable-temperature and 2D EXSY methods, owing to instrumental limitations. Since bowl inversion of an enantiopure bowl corresponds to the racemization process, the racemization at high temperature may help to confirm experimentally the value of the inversion barrier. Numerous chiral buckybowls have been synthesized and examined.[46] Mono-substituted **4ac** is a chiral buckybowl, which exhibits "bowl chirality", arising from the three-dimensional geometry. Attempts were made herein to produce enantiopure forms from the racemates of **4ac** by chiral resolution. The chiral resolution of **4ac** was performed with HPLC by using a DAICEL CHIRALPAK IA chiral column. A mixed eluent system composed of methanol and 2-propanol (1:1) gave the best results, clearly yielding two well-resolved peaks (see the Supporting Information). Owing to its very low solubility in the eluent system, the chiral resolution of **4ac** in useful amounts is impractical.

Conclusion

A simple method for synthesizing highly curved buckybowls was developed. These products can be directly generated from easily obtained planar precursors under mild reaction conditions. The bowl-shaped molecules thus formed exhibit a large bowl depth and a high bowl-to-bowl inversion barrier. These π-bowls can be used to study bowl-to-bowl inversion dynamics because they have planar or S-shaped transition structures. It is noteworthy that compounds **4** should be suitable starting materials for constructing the smallest corannulene-based carbon nanotube ($C_{40}H_{10}$).[31] The electron mobility of polar buckybowl crystals and the chiral auxiliary-assisted resolution of buckybowls are currently being examined.

Experimental Section

General procedures

^{1}H and ^{13}C NMR: Bruker 300 (300 and 75 MHz), 400 (400 and 100 MHz) and 500 (500 and 125 MHz). MS: High-resolution mass spectra (HRMS) were obtained on Finnigan MAT-95XL high-resolution mass spectrometer. X-ray crystal structure determination: Single-crystal X-ray diffraction was performed on a Bruker APEX DUO at 100(2) K. Data were collected and processed by using APEX II 4 K CCD detector. Melting points were determined with a Büchi melting point apparatus B545 and are uncorrected. UV spectra were recorded with VARIAN CARY 50 Probe. Photoluminescence experiments were accomplished with Jasco FP-6300.

Procedure for the preparation of buckybowls

The procedures for preparing buckybowls **3**/**4**[17] and **5**[18] have been described previously. The Supporting Information provides analytic data concerning new compounds generated herein.

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260-007-MY3). We also thank Prof. S.-L. Wang and Ms. P.-L. Chen (National Tsing Hua University, Taiwan) for the X-ray structure analyses, and the National Center for High-performance Computing for providing computational resources.

Keywords: fluoranthene · fullerene · palladium · rhodium · X-ray diffraction

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