Solution-Processable Multi-Substituted Buckybowls: Synthesis of Diindeno(1,2,3,4-*defg*:1',2',3',4'-*mnop*)chrysene Derivatives

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Dedicated to the memory of Prof. François Diederich.

Preparative synthesis of a new, soluble, and functionalized buckybowl is described. The precursor of dibenzo[*g,p*]chrysene having four bromine atoms at two *fjord* regions undertook palladium-catalyzed intramolecular cyclization to afford a skeletal buckybowl, namely, diindeno(1,2,3,4-*defg*:1',2',3',4'-*mnop*)chrysene. The resulting curved scaffold possesses two important substituents: four-fold alkyls increasing solubility and four-fold methoxy groups that could be further functionalized. These two features, coupled with the gently curved π-system, enable general access to solution-compatible and multi-functional buckybowl molecules.

Figure 1. Diindeno(1,2,3,4-*defg*:1',2',3',4'-*mnop*)chrysene (DIC), and C_{60} (buckminsterfullerene).

Diindeno(1,2,3,4-*defg*:1',2',3',4'-*mnop*)chrysene (DIC) is one of the buckminsterfullerene fragments commonly referred to as "buckybowls" (Figure 1).[1,2] DIC possesses a gently curved pi-surface like other buckybowls such as corannulene and sumanene. This entices us to explore DIC as a functional organic material that would be applicable to ongoing research and future technology.[3,4,5] Despite the potential of DIC, to the best of our knowledge, there are only three published approaches. First, Scott group reported a flash vacuum pyrolysis approach.[6] Second, Wu and co-workers performed palladium-mediated intra-molecular cyclization of tri-chloro-diarylphenanthrene and could construct five- and six-membered rings.[7] Third, Amsharov group reported that the alumina-mediated H–F elimination of fluoroarenes achieved double ring-closure making two pentagons.[8] While these three pioneering works gave the representative DIC skeleton, they lack a system for attaching functional groups to the periphery of the DIC core. If other chemical functionalities were possible, particularly at the rim,
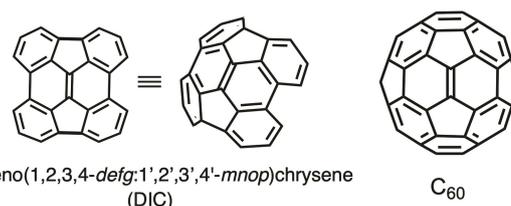
both solubility and functionalization would be tunable, giving broadened material capability and presumably application.

Recently, we have reported metal-free three-step-synthesis of dibenzo[*g,p*]chrysene framework (DBC) that is known as one of the non-planar polycyclic aromatic hydrocarbons.[9] Its scalable production led us to find the regio-specific reactivity of DBC cores along with varied new products having multiple substituents.[10] Of important note was that a solution-processable DBC undertook four-fold brominations at sterically demanding *fjord* regions to make the core twisted with the large torsion angle of 54°: the conspicuous non-planarity arouses our interest in activation of those four bromines.[11]

Herein we present a new approach with the definite attachment of functional groups onto the rim of DIC: four methoxy moieties and four alkyl groups (Figure 2). The key precursors include quadrant symmetric DBC bearing four
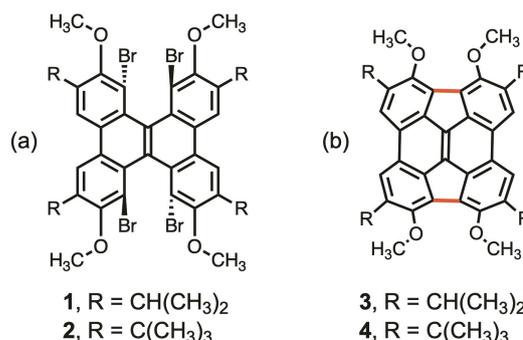
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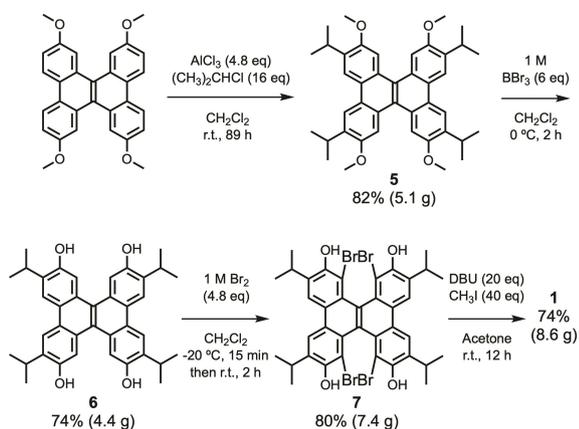   *Mizuho-ku, Nagoya, Aichi, 467-8501, Japan*

This article belongs to a Joint Special Collection dedicated to François Diederich.

1, R = CH(CH₃)₂
2, R = C(CH₃)₃

3, R = CH(CH₃)₂
4, R = C(CH₃)₃

Figure 2. (a) Dibenzo[*g,p*]chrysene (DBC) **1** and **2**; (b) Diindeno(1,2,3,4-*defg*:1',2',3',4'-*mnop*)chrysene (DIC) **3** and **4**.

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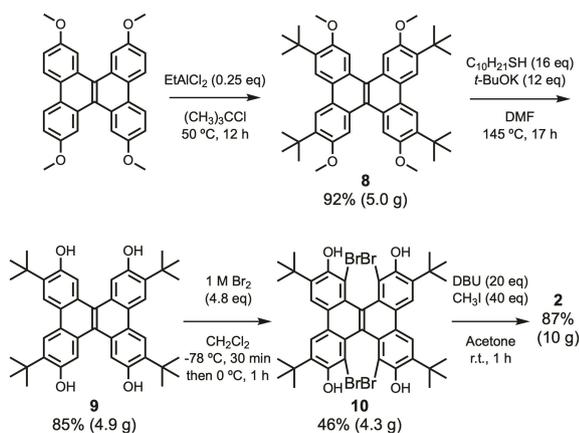**Europe**
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bromines, four methyl ethers, and four alkyl groups (**1** and **2**). We anticipated that the double ring-closure at the two *fjord* areas through activation of bromines gives novel DIC-typed buckybowls **3** and **4**.

Precursor **1** was prepared starting from commercially available 2,7-dihydroxy-9-fluorenone (Scheme 1),[12] according to our previous report.[9] For synthesis of **5** through Friedel-Crafts alkylation, AlCl$_3$ was effective for regio-specific four-fold alkylation at 2,7,10,15-positions although the reaction needed 4 days to provide appreciable yield of **5**. The conventional demethylation of **5** yielded **6** in 74%, followed by sterically demanding tetra-bromination at the two *fjord* regions to afford **7** in 80% yield. The final four-fold methylation occurred in the presence of DBU,[13] which gave **1** in 74% yield. Each derivative in the sequence was readily soluble and could be elaborated on multi-gram scale.

Following the route to **1**, **2** was synthesized. (Scheme 2). The weaker Lewis acid EtAlCl$_2$ than AlCl$_3$ turned out to be effective for introduction of *tert*-butyl groups in **8**. AlCl$_3$ was too reactive giving only 2% of **8** along with uncharacterized materials, while Et$_2$AlCl was too mild to activate *tert*-butyl chloride. Noteworthy is that EtAlCl$_2$ worked catalytically

(0.25 equiv) in 92%. Demethylation of **8** under basic condition in the presence of alkyl thiol gave **9** in 85% yield.[14] The following four-fold bromination by addition of Br$_2$ resulted in 46% yield of **10**, because the acidic condition removed the *tert*-butyl moieties from the core; hence, the bromination step was conducted at low −78 °C for 0.5 h. The final methylation to produce **2** was carried out in 87% yield. As with **1**, all intermediates to **2** were readily soluble and compatible with multigram techniques.

The molecular structures of **1** and **2** were determined by crystallographic analyses, which made apparent their greatly distorted pi-conjugations (Figure 3 and Figure 4).[15] The two bromine atoms at the narrow cove spaces rebel against each other, which twists the whole molecules in torsion angles of 56.1° for **1** and 46.2° for **2**. The torsion angle of **1** was significantly larger than that of **2**, which indicates that **2** is charged with more planar property than **1**. This structural
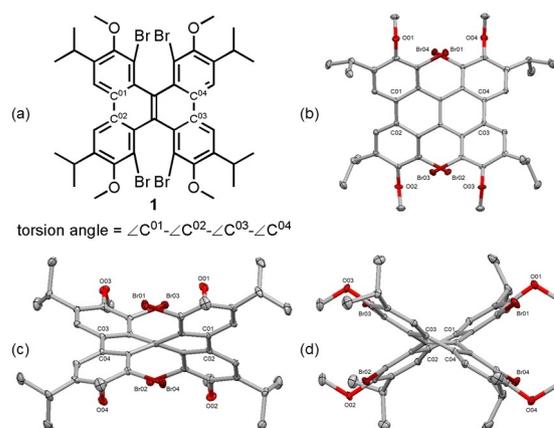

Figure 3. Molecular structures with ORTEP drawing of **1** with thermal ellipsoids at the 50% probability level (the hydrogen atoms are omitted for clarity); (a) torsion angle determined by the four carbon atoms of C^{01}, C^{02}, C^{03}, and C^{04}; (b) top view; (c) side view from a *fjord* region with torsion angle 56.1°; (d) side view from a *bay* region.

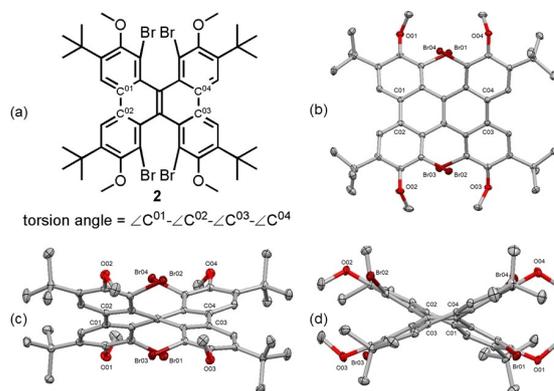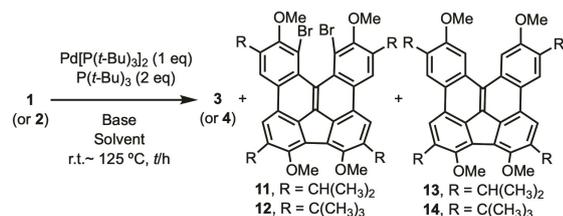**Scheme 1.** Synthesis of **1** through **5**, **6**, and **7**.

Figure 4. Molecular structures with ORTEP drawing of **2** with thermal ellipsoids at the 50% probability level (the hydrogen atoms are omitted for clarity); (a) torsion angle determined by the four carbon atoms of C^{01}, C^{02}, C^{03}, and C^{04}; (b) top view; (c) side view from a *fjord* region with torsion angle 46.2°; (d) side view from a *bay* region.

Scheme 2. Synthesis of **2** through **8**, **9**, and **10**.

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difference reflects the lower solubility of **2** than that of **1**: The 1 gram of **1** was readily dissolved into 10 mL of toluene, and the minimum amount of toluene for dissolving the 1 gram of **2** was 50 mL. On the other hand, geometrically optimized structures using DFT method (B3LYP/6-31G(d,p)) showed results that didn't fit the crystal structures: the torsion angles of **1** and **2** were calculated to be 50° and 49°, respectively (Figure S1 in the Supporting Information).[16] The twisted geometries of **1** and **2** in the ORTEP drawings may be due to the effect of crystal packing.

With large amounts of **1** and **2** in hand, the ring-closing reactions at the *fjord* regions were attempted through palladium-mediated activation of the bromines (Scheme 3). Preliminary experiments led to identification of a base set of starting conditions to develop upon (entry 1 in Table 1). A stoichiometric amount of Pd[P(*t*-Bu)₃]₂ with external P(*t*-Bu)₃ under gradual heating to 125 °C resulted in consumption of **1** and yielded 68% of **3** along with 25% of side-product **13**. For entry 2, K₃PO₄ instead of Hünig's base gave **3** in 62% yield with 16% of side-product **11**.[17] None of additional P(*t*-Bu)₃ decreased the productivity, and catalytic amount of the palladium was ineffective (entries 3 and 4). Changing the Pd ligand set to Pd(PPh₃)₄/PPh₃ combination in entry 5, failed. Alternate solvents in entries 6–9, such as NMP and DMSO proved to be workable, and non-polar solvents of toluene and xylene were useless. Our

work preparing **3** from **1** readily translated into good conditions for **4** starting from **2**. Yields from 18–25% were realized (entries 10–12). The markedly lower yields are not yet fully understood; perhaps the more congested *tert*-butyl groups prevent the cyclization from proceeding smoothly.

The molecular structures of **3** and **4** were determined by crystallographic analyses, which disclosed that two new pentagons shape the starting **1** and **2** into the gentle curvatures of buckybowls **3** and **4** (Figure 5 and Figure 6).[18,19] These two bowl-shaped molecules definitely resemble each other in structural characters of bond-lengths, bond-angles, and bowl-depths.[20] The bond lengths of the central 6:6-bond are 1.339 Å for **3** and 1.342 Å for **4**; thus, they are comparable to 1.334 Å for unsubstituted DIC. For bowl depth, unsubstituted DIC gives 1.44 Å,[6] and multiple substituents in **3** and **4** would affect an increase to 1.54 Å. Haddon's POAV analysis of the X-ray data
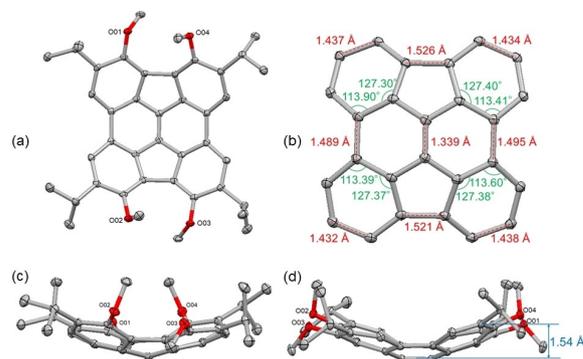

Figure 5. Molecular structures with ORTEP drawing of **3** with thermal ellipsoids at the 50% probability level (the hydrogen atoms are omitted for clarity); (a) top view from a concave face; (b) top view from a convex face with description of angles those are more than 120 ± 5° and selected bond lengths those are more than 1.43 Å and 1.339 Å of central 6:6-bond (*iso*-propyl groups and methoxy moieties are omitted for ease of viewing); (c) side view from a five-membered ring; (d) side view form a *bay* region with a description of bowl-depth (1.54 Å).

Scheme 3. Synthesis of buckybowls **3** and **4** with side-products **11–14**.

Table 1. Evaluation of reactivities of **1** and **2** conducted like given in Scheme 3.[a]

Entry	1/2	Solvent[b]	Base	t/h	[%]Yield[c]		
					3/4	11/12	13/14
1	1	DMF	EtN(*i*Pr)₂	1	68	0	25
2[d]	1	DMF	K₃PO₄[e]	4	62	16	0
3[f]	1	DMF	EtN(*i*Pr)₂	4	46	22	0
4[g]	1	DMF	EtN(*i*Pr)₂	4	49	11	0
5[h]	1	DMF	EtN(*i*Pr)₂	17	0	38	0
6	1	NMP	EtN(*i*Pr)₂	2	69	0	20
7	1	DMSO	EtN(*i*Pr)₂	2	55	0	19
8	1	Toluene	EtN(*i*Pr)₂	20	35	61	0
9[d]	1	Xylene	EtN(*i*Pr)₂	22	45	44	0
10	2	DMF	EtN(*i*Pr)₂	2	18	7	19
11[d]	2	DMF	K₃PO₄[e]	45	20	13	0
12	2	NMP	EtN(*i*Pr)₂	2	25	31	0

[a] Conditions, unless otherwise noted: **1** or **2** (0.15 mmol), solvent (3 mL), base (1.2 mmol), Pd[P(*t*-Bu)₃]₂ (0.15 mmol, 77 mg), P(*t*-Bu)₃ (0.30 mmol, 1 M in hexane). [b] NMP; *N*-methyl pyrrolidone. Xylene; mixtures of *o*-, *m*-, *p*-xylene. [c] Isolated yields. [d] Reaction temperature, 140 °C. [e] K₃PO₄ (0.3 mmol, 64 mg). [f] None of free P(*t*-Bu)₃ was loaded. [g] Usage amounts of Pd[P(*t*-Bu)₃]₂ and P(*t*-Bu)₃ was decreased to 0.5 eq and 1 eq, respectively. [h] Pd(PPh₃)₄ and PPh₃ were used instead of Pd[P(*t*-Bu)₃]₂ and P(*t*-Bu)₃.

Figure 6. Molecular structures with ORTEP drawing of **4** with thermal ellipsoids at the 50% probability level (the hydrogen atoms are omitted for clarity); (a) top view from a concave face; (b) top view from a convex face with description of angles those are more than 120 ± 5° and selected bond lengths those are more than 1.43 Å and 1.342 Å of central 6:6-bond (*tert*-butyl groups and methoxy moieties are omitted for ease of viewing); (c) side view from a five-membered ring; (d) side view form a *bay* region with a description of bowl-depth (1.54 Å).
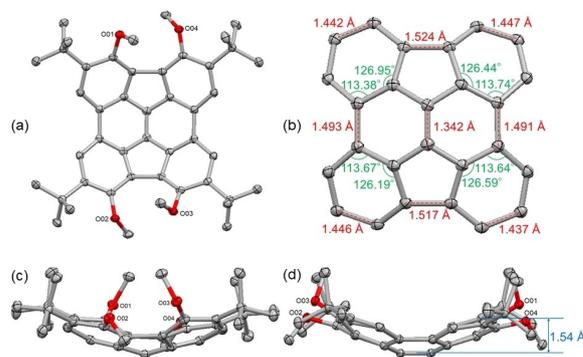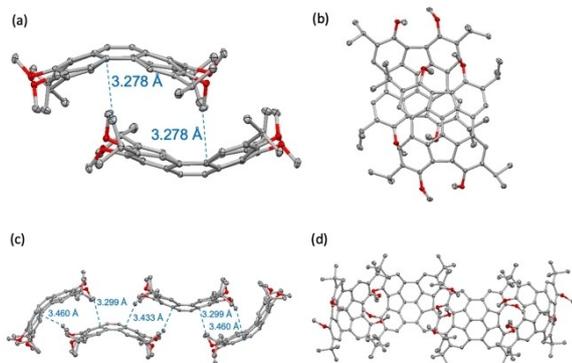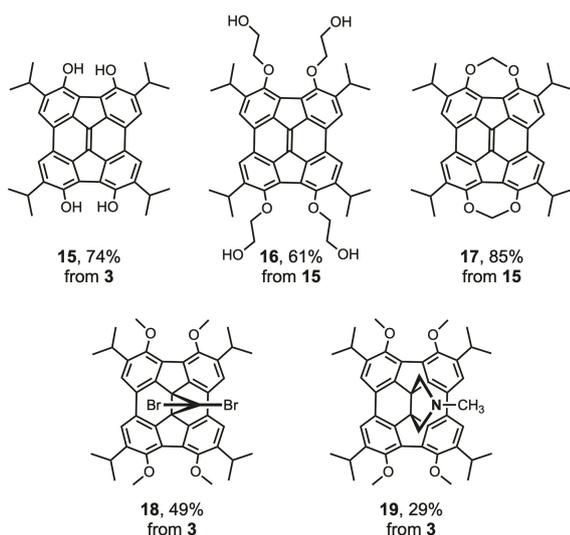
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revealed that the two carbons of the 6:6-bond are pyramidalized to 8.6° for **3** and 9.1° for **4**. POAV angles of unsubstituted DIC, corannulene, and sumanene are well-known as 9.0°,[6] 8.2°,[3c] and 9.0°,[4a,b] respectively (Table S1 in the Supporting Information). The substituents in **3** and **4** don't seem to influence the steepness of the curvature. Packing views of **3** and **4** were also obtained (Figure 7). Although the deep bowl-shaped pi-aromatics are known to favor a stacking architecture in a concave-convex fashion, such an arrangement was not observed in **3** and **4**, presumably due to the multiple substituents.[4b,6,21] Methyl groups in the methoxy moieties seem to interact with another concave surface with the stacking distance of approximately 3.3 Å.

Figure 7. Molecular packing structures with ORTEP drawing of **3** and **4**, with description of intramolecular distances: (a) side view of **3**, (b) top view of **3**, (c) side view of **4**, and (d) top view of **4**. The hydrogen atoms are omitted for clarity.

Table 2. Gram-scale synthesis of **3** conducted like given in entry 1 of Table 1.[a]

Entry	Scale of **1**		T [h]	[%] Yield[b]		
	mmol	gram		**3** (gram)	**11**	**13**
1	0.15	0.14	1	68 (0.063)	0	25
2	0.45	0.42	1	67 (0.18)	3	5
3	1.40	1.30	2	66 (0.60)	0	10
4	2.70	2.50	2	66 (1.10)	0	14
5	5.40	5.00	2	62 (2.10)	0	19

[a] Reactions were carried out in DMF at 125 °C. [b] Isolated yields.

Next, evaluation of the double ring-closure protocol was performed on gram-scale preparation of **3** (Table 2): the conversion of **1** to **3** was conducted at 125 °C in DMF, which was confirmed in entry 1 of Table 1. The scale-up went well without serious loss of chemical yields through entries 1–3, although the side-product **13** was persistently accompanied. Further scale production was achieved in up to 2.1 g of 62% yield (entries 4 and 5).

Lastly, to demonstrate rapid derivatization of these scaffolds we applied conventional transformations towards the synthesis of **15**–**19** (Scheme 4). For **15**, four-fold demethylation of **3** by BBr$_3$ reagent yielded 74% of the tetrol that was purified by silica-gel column chromatography. The following hydroxy alkylations proceeded to give 61% yield of **16**, in which usage amounts of methanol influenced the chemical yield importantly. **15** was bridged by bis-methylene moieties, producing **17** in 85% yield. The synthesis of **18** was executed by the *in situ* generated carbene from bromoform with strong base. The expected cyclopropane group was installed at center olefinic position in 49% yield.[22,23] The [3+2] cycloaddition with azomethine ylide (generated *in situ* by the reaction of sarcosine with paraformaldehyde) formed the corresponding cycloadduct **19**.[22] This transformation generally needed long periods of time and high temperatures as reported.[24] 29% yields was obtained with the added condition in which sarcosine and paraformaldehyde were added at regular 15-min intervals. We calculated the mappings and energies for frontier orbitals of **4** and unsubstituted DIC, using DFT method (B3LYP/6-31G(d,p); Figure S2 and Table S2 in the Supporting Information).[16] While substituents of **4** provide no coefficient of HOMO orbitals for its 6:6-bond, large coefficients of LUMO orbitals in the 6:6-bond of **4** were observed. This result means both production of **18** and **19** are consequences of reactions between LUMO of **3** and HOMO of reactants.[25]

In conclusion, the straightforward synthesis and crystallographic characterization of four-fold methoxy- and alkyl-anchored buckybowls were achieved. These multi-functional and solvent compatible DIC-typed buckybowls have relatively few counterparts in the organic synthetic realm. Our results suggest the following three salient features: One, DBC precursors **1** and **2** having bulky alkyl groups as solubilizing agents persist through the synthesis, were amenable to multi-gram scale technique, and were crystallographically analyzed revealing large torsion angles. Two, the precursors underwent Pd-mediated double ring-closure reactions to achieve gram-scale construction of multi-substituted DIC-buckybowls **3** and **4**. Three, buckybowl **3** was amenable to chemical transformations of the methoxy groups as well as the central 6:6-bond despite

15, 74%
from **3**

16, 61%
from **15**

17, 85%
from **15**

18, 49%
from **3**

19, 29%
from **3**

Scheme 4. Synthesis of **15**–**19**. Conditions for **15**, 1 M BBr$_3$ (4.8 eq), CH$_2$Cl$_2$, r.t., 4 h; for **16**, 2-chloroethanol (36 eq), K$_2$CO$_3$ (12 eq), CH$_3$OH, 50 °C, 46 h; for **17**, CH$_2$BrCl (20 eq), K$_2$CO$_3$ (4 eq), DMSO/toluene (4/1), 55 °C, 2 h; for **18**, CHBr$_3$ (30 eq), Et$_3$(PhCH$_2$)N$^+$Cl$^-$ (0.5 eq), 50% aq. NaOH, benzene, r.t., 4 h; for **19**, sarcosine (2 eq × 23), (HCHO)$_n$ (5 eq × 23), toluene, reflux, 24 h.

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the unusual steric hindrance at the periphery and uncommon geodesic bend in the bottom. Although yields and conditions in the final ring-closure step await improvement, these combined features serve as a practical synthetic basis for future buckybowl exploration.

Deposition Numbers 2067964 (for **1**), 2067960 (for **2**), 2067887 (for **3**), and 2067888 (for **4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Conflict of Interest

The authors declare no conflict of interest.

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[12] Large quantities of 2,7-dihydroxy-9-fluorenone were purchased from BLD Pharmatech Ltd., which enabled us to readily prepare more than 300 grams of the 3,6,11,14-tetramethoxydibenzo[*g,p*]chrysene.

[13] DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene.

[14] Use of sodium ethane thiolate instead of decane thiolate was also effective. The smell of decane thiol is less disgusting than ethane thiol.

[15] a) The single crystal of **1** was prepared by slow evaporation of CH_3CN (1.0 mL) solution of the sample (10 mg), CCDC-2067964 (for **1**) Orthorhombic, space group F d d 2, colorless, $a = 34.5720(2)$ Å, $b = 21.3853(2)$ Å, $c = 11.9852(1)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 8861.05(12)$ Å^3, $Z = 12$, $T = 93$ K, $d_{calcd} = 1.521$ g cm^{-3}, $\mu(Mo\text{-}K\alpha) = 4.779$ mm^{-1}, $R_1 = 0.0270$, $wR_2 = 0.0701$, GOF = 1.090; b) The single crystal of **2** was prepared by slow evaporation of CH_2Cl_2/CH_3CN (2.0 mL/ 1.0 mL) solution of the sample (5 mg), CCDC-2067960 (for **2**). Monoclinic, space group p 1 21/c 1, colorless, $a = 20.4863(2)$ Å, $b = 21.2162(2)$ Å, $c = 11.3210(1)$ Å, $\alpha = 90°$, $\beta = 100.632°$, $\gamma = 90°$, $V = 4836.10(8)$ Å^3, $Z = 4$, $T = 293$ K, $d_{calcd} = 1.591$ g cm^{-3}, $\mu(Mo\text{-}K\alpha) = 6.429$ mm^{-1}, $R_1 = 0.0351$, $wR_2 = 0.0931$, GOF = 1.041.

[16] Density functional theory (DFT) calculations were performed at B3LYP/ 6-31G(d,p) using the Gaussian 16 suite program (G16RevC.01); see, M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al.*, Gaussian, Inc., Wallingford CT, 2019.

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[18] The single crystal of **3** was prepared by slow evaporation of EtCN (1.0 mL) solution of the sample (4 mg), CCDC-2067887 (for **3**). Triclinic, space group p −1, colorless, $a = 10.8115(2)$ Å, $b = 11.6744(2)$ Å, $c = 13.4845(2)$ Å, $\alpha = 80.500°$, $\beta = 82.686°$, $\gamma = 75.037°$, $V = 1615.31(5)$ Å^3, $Z = 2$, $T = 293$ K, $d_{calcd} = 1.260$ g cm^{-3}, $\mu(Mo\text{-}K\alpha) = 0.622$ mm^{-1}, $R_1 = 0.0401$, $wR_2 = 0.1055$, GOF = 1.31.

[19] The single crystal of **4** was prepared by slow evaporation of CH_2Cl_2/CH_3CN (4.0 mL/1.5 mL) solution of the sample (3 mg), CCDC-2067888 (for **4**). Monoclinic, space group p 1 21/c 1, colorless, $a = 135554(2)$ Å, $b = 9.8768(1)$ Å, $c = 27.5688(3)$ Å, $\alpha = 90°$, $\beta = 97.055°$, $\gamma = 90°$, $V = 3663.07(8)$ Å^3, $Z = 4$, $T = 293$ K, $d_{calcd} = 1.213$ g cm^{-3}, $\mu(Mo\text{-}K\alpha) = 0.588$ mm^{-1}, $R_1 = 0.0425$, $wR_2 = 0.1207$, GOF = 1.083.

[20] The bowl-depths of sumanene and corannulene are 1.11 Å and 0.87 Å, respectively (ref. 4b and ref. 3c). For POAV (pi-orbital axis vector) analysis, see: a) R. C. Haddon, L. T. Scott, *Pure Appl. Chem.* **1986**, *58*, 137–142; b) R. C. Haddon, *J. Am. Chem. Soc.* **1987**, *109*, 1676–1685.

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[25] Large coefficients of HOMO/LUMO orbitals in the 6:6-bond of unsubstituted DIC were observed (Figure S2). As depicted in Table S2, HOMO-LUMO energy gap of **4** (3.50 eV) was smaller than that of the unsubstituted DIC (3.82 eV).