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Assembly of fullerenes using a highly preorganized janusarene

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ABSTRACT

Molecular recognition of fullerene using various host compounds is well-known in literature. But most studies focus on host-guest complexation in solution using host compounds with a single binding cavity. Herein, we report a series of highly preorganized janusarene derivatives with homoditopic binding sites. These novel janusarenes can bind and align various fullerenes such as C_{60}, C_{70}, C_{84}, and Gd@C_{82} in a highly efficient manner. Robust shape complementary association and assembly are observed in solution, in the bulk solid state, in the liquid crystalline state, or on surface, and the assembled structures are characterized by nuclear magnetic resonance (NMR) titration, X-ray diffraction, polarized optical microscopy, and scanning tunneling microscopy.

Concave-convex shape complementary interaction has been widely used for the construction of different molecular hosts of fullerenes [1-10]. However, most of these host compounds either form discrete complexes with fullerenes in solution, or cocrystallize with them under a defined condition. Except for a kind of judiciously designed conical fullerene derivative [11], extending the capability of using concave-convex interaction to direct supramolecular assembly of fullerenes [12-15], especially the unmodified ones, is still underdeveloped, which may result in highly ordered hierarchical supramolecular structures of broad interests in materials science and nanotechnology [16-18].

In 2017, we introduced a kind of hexaphenylbenzene (HPB) based homoditopic molecular host, named janusarene [19,20], which can bind and align fullerene C_{60} and some polycyclic aromatic hydrocarbons in the solid crystalline state. Although the binding interaction is only modest in solution, cocrystal structures of these janusarene complexes show a general alternate linear host-guest binding mode, which promises janusarene as a modular host compound to direct the assembly of unmodified fullerenes under various conditions.

Herein, we report a series of new janusarene derivatives (**1**, **2**, and **4**), which have highly preorganized bowl-shaped binding cavities, and the binding constant for fullerene C_{60} is 25-fold stronger than that of the previous one. Impressively, these new janusarenes can assemble with various fullerenes, such as C_{60}, C_{70}, C_{84}, and Gd@C_{82} *via* concave-convex shape complementary interaction. Molecular recognition and assembly in solution, in the bulk solid state, in the liquid crystalline state, or on surface highlight the generality and robustness of the current system, distinct from various supramolecular assembly of unmodified fullerenes [21-24], or fullerene derivatives [25-27].

To design a highly preorganized janusarene (Fig. 1), we use HPB and triphenylbenzene (TPB) as the basic polyphenyl structural subunits. Briefly, free rotation of the peripheral (p-) phenyl rings of HPB is limited with an energy barrier of 73.2 kJ/mol [28]. This unique structural feature of HPB allows us to prepare the homoditopic janusarene derivatives, *e.g.*, **3**, by twelve-fold attaching of the fencing (f-) phenyl rings to the *meta*-position (red star) of HPB's p-rings [19]. However, in the original design, free rotation of f-ring around the C–C bond to p-ring, like that in biphenyl (BP, $\Delta G^{\ddagger} = 7.2$ kJ/mol) [29], leads to an ill-defined binding cavity (Fig. 2B), which is deleterious on host-guest association. We now attach additional "back" (b-) phenyl ring between each two f-rings, resulting in a TPB subunit. This simple structural modulation will substantially increase the rotational barrier of f-rings ($\Delta G^{\ddagger} = 33.2$ kJ/mol), thereby favoring the formation of two highly preorganized bowl-shaped binding cavities. In addition, two flexible branched alkyl chains are appended on each b-ring, which enhance solubility and are essential for molecular assembly under different conditions.

The key step in the synthesis of **1** and **2** involves a $Co_2(CO)_8$ catalysed [2 + 2 + 2] cyclotrimerization reaction of a bis-TPB functionalized tolan precursor (Scheme S1 in Supporting information),

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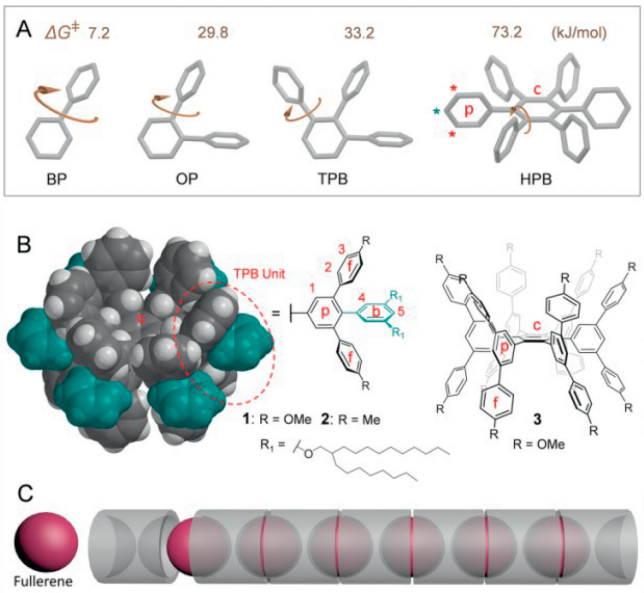

Fig. 1. Design and structure of new janusarenes. (A) Rotational barriers of various polyphenylene structural subunits of janusarene. (B) Molecular model of janusarene, optimized using molecular mechanics. One of the six TPB subunits (circled area) is shown with the ChemDraw structure. Note: In the molecular model, all the functional groups are substituted with hydrogens. (C) Cartoon representation of the alternate linear assembly of janusarene and fullerene.

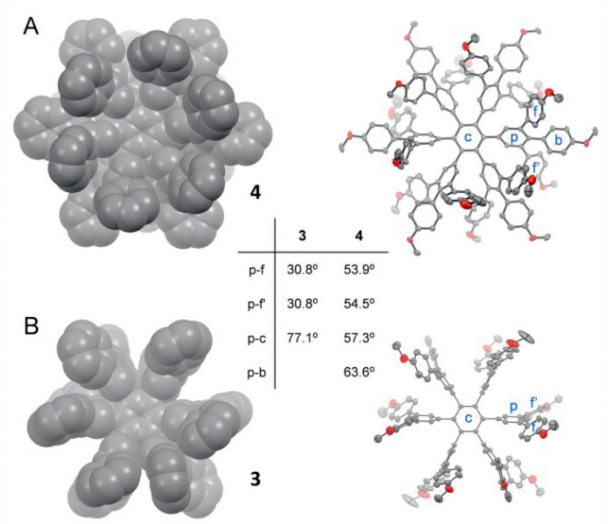

Fig. 2. Crystal structures of janusarene derivatives with (A, **4**) and without (B, **3**) the b-rings. All the f- and b-rings are 4-methoxyphenyls, whose methoxy groups are removed in the space-filling crystal structures for clarity. DA is reported as an average value, f and f' denote the f-rings around different binding cavities.

which incorporates 25 phenyl rings on a newly formed HPB platform and affords the desired product in excellent yield (>90%) [30,31]. We also prepared **4** (Fig. 2A and Scheme S2 in Supporting information), in which all the b- and f-rings are 4-methoxyphenyls, for crystallographic investigation. Compound **3** had been prepared previously [19].

Incorporation of b-rings has a significant effect on the conformation of janusarene. Single crystal X-ray structure of **4**, possessing the same polyphenyl skeleton as that of **1** and **2**, shows a perfect bowl-shaped conformation, which is better preorganized than **3** (Fig. 2, Tables S2 and S3 in Supporting information). The average dihedral angle (DA) between p-f rings are increased, from 30.8° to 53.9°, with the introduction of b-rings. This structural change

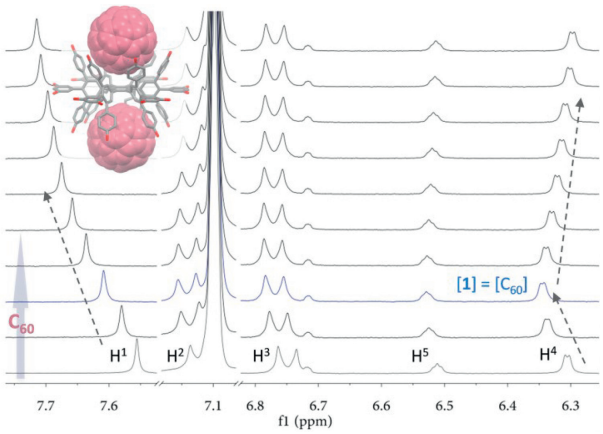

Fig. 3. Partial ^{1}H NMR spectral changes of **1** (in ^{8}D-toluene, 0.4 mmol/L) upon addition of up to 3.1 equiv. of C_{60}. Inset, molecular model of the **1**-C_{60} 1:2 complex, generated using molecular mechanics. In this model, the methoxy groups on f-rings and the branched alkoxy groups on b-rings are simplified for clarity.

preorganizes the π-surfaces of f-rings to form a conical cavity, which is expected to be in favor of concave-convex interaction with fullerenes. Moreover, the HPB subunit in **4** displays a regular propeller conformation with an average DA of 57.3° between p-c rings. In contrast to **4**, the polyphenyl skeleton of **3** is more disordered (Fig. 2B). The X-ray structure of **4** is highly promising for a strong shape complementary complexation with fullerenes.

When **4** and C_{60} (1:1, mole ratio) are mixed in a toluene solution, insoluble **4**-C_{60} complex is formed promptly, indicating a host-guest association. To characterize the host-guest interaction in solution, we performed ^{1}H-nuclear magnetic resonance (NMR) titration using janusarene **1** which has improved solubility. The result indicates that addition of b-rings results in a significantly enhanced binding capability (Fig. 3). The inner proton H^1, at the bottom of the binding cavity on p-ring, shifts from 7.55 ppm to 7.71 ppm in the presence of 3.1 equiv. of C_{60}. Job plot analysis gives a 1:2 binding stoichiometry (Fig. S4 in Supporting information), indicating that each binding cavity associates with one C_{60}. The first and second association constant K_1 and K_2 are determined to be 26,200 ± 340 and 2950 ± 6 L/mol, respectively (Fig. S6 in Supporting information). K_1 is more than 25-fold stronger than that of **3** without b-rings (1020 L/mol, determined previously using a monotopic analogue of **3**). Because K_2, 2950 L/mol, is less than 1/4 of K_1, ~6550 L/mol, a negative cooperativity is present.

In contrast to proton H^1, which shifts to the down-field monotonically upon addition of C_{60}, a turning point, from down- to up-field shift, at ~1.0 equiv. of C_{60} appears on the titration curves for all the other protons H^2-H^5 (Fig. 3, Figs. S5 and S6 in Supporting information). We reason that, (i) binding with the first C_{60} decreases the electron density of f-rings due to a charge transfer interaction between the electron-rich anisole groups (f-rings) and the electron-deficient C_{60}, as is supported by the ultraviolet–visible (UV–vis) absorption spectral changes (Fig. S7 in Supporting information), thereby leading to a deshielding effect which accounts for the initial down-field shift of protons H^1–H^5. However, (ii) complexation with the second C_{60} might result in a more rigidified conformation, in which the f- and b-rings, are sandwiched between two fullerenes (Fig. 3, inset), and adopt a near "cofacial" arrangement. In this way, f- and b-rings of the **1**-C_{60} 1:2 complex are expected to experience a stronger shielding effect than the 1:1 complex, dominating the changes in chemical shift of protons H^2–H^5 to high field. Due to fast exchange of free and bound host on the NMR timescale, only one set of resonance signals is observed.

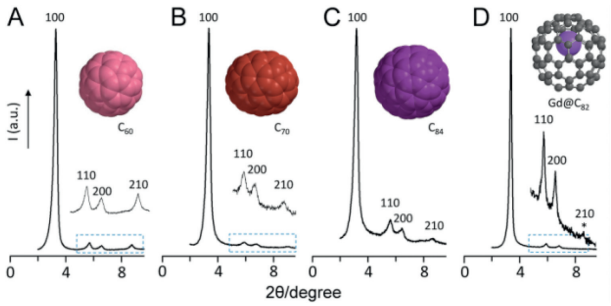

Fig. 4. XRD patterns of the **1**-C_{60} (A), **1**-C_{70} (B), **1**-C_{84} (C), and **1**-Gd@C_{82} (D) 1:1 complex at 25 °C. Inset, enlarged partial XRD signals. Evaporation of the fullerene complexes in toluene, under reduced pressure at 50 °C, resulted in the assembled materials within minutes.

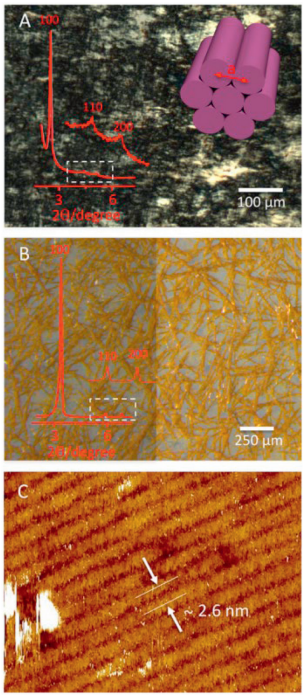

Fig. 5. Molecular assembly of janusarene and C_{60} under different conditions. (A) POM image of the lyotropic LC mesophase formed by mixing **1**-C_{60} complex and tetradecane (5/3, w/w) at 25 °C. Inset, XRD pattern of the material at 25 °C and the schematic representation of the hexagonal columnar structure. (B) Optical micrograph of the assembled **1**-C_{60} complex in a mixed solvent of dichloromethane and ethanol (6/5, v/v). Inset, XRD pattern of the fibers at 25 °C. (C) STM image of the columnar assembly of the **2**-C_{60} complex on a HOPG surface.

Well-defined bowl-shaped conformation and strong host-guest complexation prompt us to investigate molecular assembly of the newly designed janusarene with various fullerenes, such as C_{60}, C_{70}, C_{84}, and Gd@C_{82} (Fig. 4). Evaporation of the solvent from a solution of the **1**-C_{60} complex (1:1, mole ratio) in toluene generates a brown colored, clay-like material. X-ray diffraction (XRD) measurement shows a series of distinct diffraction signals with d-spacing of 26.9 (100), 15.4 (110), 13.5 (200), and 10.1 Å (210), respectively. In addition, a broad halo at ~4.5 Å can be attributed to the molten alkyl chains (Fig. S8 in Supporting information). The XRD pattern indicates an alternate linear assembly of janusarene and fullerene (Fig. 1C), which further organizes into a hexagonal columnar structure (d_{100}:d_{110}:d_{200} = 1:1/$\sqrt{3}$:1/2, Fig. 5A, inset), a result in agreement with the X-ray crystal structure of the **3**-C_{60} complex reported previously [19]. An intercolumnar distance of 30.6 Å, deduced from the XRD data (Table S4 in Supporting information), is reasonable considering the dimension of the polyphenylene core of janusarene (diam. ~20 Å) plus the periphery alkyl chains (~13.8 Å in an all-*trans* conformation).

When other fullerenes, such as C_{70}, C_{84}, and Gd@C_{82}, are applied (Figs. 4B–D, Fig. S8 in Supporting information), evaporation of a mixed solution of **1**-fullerene complex (1/1, mole ratio) in toluene delivers a hexagonal columnar structure consistent with that obtained with C_{60}. Although different isomers of the high fullerene C_{84}, and metallofullerene Gd@C_{82} are present, the XRD patterns are not affected significantly. Molecular modelling study suggests that janusarene **1** can adjust its conformation to accommodate different fullerenes by a slight change on the DAs between p-c and p-f rings (Fig. S10 in Supporting information). Furthermore, we observe an extremely high thermostability for the assembled columnar structure. For instance, XRD pattern of the assembled **1**-C_{60} complex is maintained even after being heated at 270 °C for 1 h (Fig. S11 in Supporting information). And the XRD signals get sharper after heating due to a thermal annealing effect.

To further demonstrate the generality and robustness of the current system, we systematically investigate the molecular assembly of **1** and C_{60} (or **1** and C_{70}, see Supporting information), under different conditions. A lyotropic liquid crystalline (LLC) mesophase [11] is formed, when *n*-tetradecane and **1**-C_{60} (or **1**-C_{70}) complex are mixed (w/w = 3/5) (Figs. S10–S13 in Supporting information). Polarized optical microscopy (POM) reveals a fluid and birefringent texture at 25 °C (Fig. 5A, Figs. S13 and S15 in Supporting information). The XRD pattern (Fig. 5A, inset) is similar to that recorded with the bulk **1**-C_{60} complex alone (Fig. 4A), indicating that the hexagonal columnar structure is maintained.

We find that the intercolumnar distance (a) increases linearly with the amount of intercalated alkane added (a = 39.8 Å, when alkane/C_{60}-complex = 3/5, w/w, Figs. S12 and S14 in Supporting information). The hexagonal columnar LLC mesophase is maintained until the mass ratio of *n*-tetradecane to **1** reaches 4/5, after that, only diffuse XRD signals are observed, indicating a less ordered structure. It is noteworthy that using host-guest chemistry to produce liquid-crystalline (LC) materials of pristine fullerene has rare precedents [32,33], and most LC fullerenes are obtained by covalent attaching of mesogenic pendants [34].

Assembly of janusarene and fullerene is robust and general. When a transparent solution of the **1**-C_{60} complex (10 mg) in a mixture of dichloromethane/ethanol (1.1 mL, 6/5, v/v, in a sealed vial) is cooled from 65 °C to 20 °C, a dark-yellow precipitate is formed quantitatively. Microscopic optical imaging shows a fiber-shaped structure of millimeter in length (Fig. 5B). XRD pattern of the precipitate obtained thereby reveals a columnar assembly structure comparable to the bulk, or LC state as discussed above (Fig. S16 in Supporting information). Furthermore, when a droplet of the **2**-C_{60} complex (5 μmol/L, in hexane) is dried on the highly oriented pyrolytic graphite (HOPG) surface, and examined using scanning tunneling microscopy (STM), uniform columnar structures aligned in parallel are observed (Fig. 5C). The intercolumnar distance on surface, *ca.* 2.6 nm (Fig. S17 in Supporting information), is shorter than the corresponding value in the bulk state, *ca.* 3.1 nm. This discrepancy is reasonable for STM imaging of assembled three-dimensional nano-objects, whose surfaces are coated with alkyl chains [35].

In conclusion, we present a series of highly preorganized janusarenes with perfect bowl-shaped binding cavities. Taking advantage of the shape complementary interactions, these biconcave molecular hosts exhibit remarkable capability to assemble various unmodified fullerenes, including C_{60}, C_{70}, C_{84}, and Gd@C_{82}. This system performs well in solution, in the bulk state, in the LC state, or on surface. We expect that a general and reliable method to assemble different fullerenes, especially the less accessible and highly precious high fullerenes and endohedral

fullerenes, may open new opportunity for exploring their potentials in interdisciplinary fields of chemistry, physics, and materials science.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Nianqiang Jiang: Writing – original draft, Investigation. **Yiqiang Ou:** Software, Formal analysis. **Yanpeng Zhu:** Project administration, Funding acquisition. **Dingyong Zhong:** Resources, Project administration, Methodology. **Jiaobing Wang:** Supervision, Conceptualization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.110004.

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