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AB-stacking pattern in natural graphite

### Journal Name

### COMMUNICATION

## Novel graphite-like stacking structure in a discrete molecule and its molecular recognition behavior

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2-laver stacking

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Graphite-like stacking structure was nicely reproduced in a discrete molecule that was prepared by 2+2 macrocyclic Schiff base formation. In the crystal structure, two hexabenzocoronene planes are closely stacked with displacement, yielding the intramolecular stacking structure similar to AB- or ABC-stacking pattern in natural graphite. This molecule showed recognition ability toward electron-deficient aromatic molecules in solution.

Graphite is one of the allotropes of carbon that has a layered structure of sp<sup>2</sup> carbon atoms. Each of the layers has a hexagonal honeycomb structure called a graphene sheet, which has recently attracted the increasing interests of researchers.<sup>1</sup> Along with the infinite graphene sheet, there is a class of nano-sized discrete analogues, e.g., polycyclic aromatic hydrocarbons (PAHs) with a finite  $\pi$ -surface, which can be synthesized as pure organic compounds.<sup>2</sup> Hexa-perihexabenzocoronene (HBC, hereafter) is one of the representative examples that has been well studied as a nanosized graphene. While the chemistry of nanographenes has been well established,<sup>2</sup> it has been difficult to reproduce the graphite-like stacking in a discrete nano-sized molecule. Nevertheless, it should be interesting to know how nano-sized graphene molecules are stacked and how the stacked sheets interact with each other, while it has been well understood that graphite has a layered structure with a 3.35 Å separation in a staggered (AB or ABC-stacking) pattern<sup>3</sup> rather than an eclipsed (AA-stacking) one.4

To obtain a layered nanographite structure, the bottom-up assembling of nanographene subunits would be effective. In general, nanographene molecules tend to form stacking structures due to  $\pi$ -stacking interactions,<sup>5–7</sup> but the number of stacks depends on the molecular structures. Parallel infinite



nanographene derivatives with peripheral bulky substituents.<sup>9</sup> However, it has been difficult to control the number of stacked molecules via self-assembly due to the formation of an infinite polymeric stack or dissociation equilibrium<sup>10</sup> with the monomer in solution, while some double-decker graphenes are reported to show unique physical and electrical properties.<sup>11</sup> In this context, it would be advantageous to covalently link a limited number of nanographene subunits<sup>12,13</sup> so that the number of stacks is controlled both in solution and in the crystalline state. In fact, a discrete dimeric sack was efficiently formed by using a macrocyclic bis(HBC) compound, although its stacking pattern was ambiguous.<sup>12</sup> We designed a macrocyclic HBC dimer 1 as a unimolecular nanographite, in which two nanographene moieties are connected with two diimine linkages (Figure 1). The two HBC planes, which are slightly curved and each facing its convex side, are stacked in a staggered fashion, which nicely reproduces the AB- or ABCstacking structures found in natural graphite. The

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intermolecular interaction between **1** and some electrondeficient planar molecules was also investigated.

For efficient synthesis of the macrocyclic molecular graphite, we used the Schiff base formation, because the reversible feature of the Schiff base formation is known to be effective for high-yield macrocyclization (Scheme 1).<sup>14</sup> Suzuki-coupling of diiodide  $2^{15}$  and 4-bromophenylboronic acid  $(3)^{16}$  using a palladium catalyst afforded dibromide **4** in 81% yield. The HBC derivative  $5^{17}$  was synthesized by the oxidation of **4** with iron(III) chloride in 97% yield. The precursor **7** having two 3-formylphenyl groups was synthesized by Suzuki coupling of the dibromo-HBC **5** with 3-formylphenylboronic acid (**6**) in 52% yield.

The reaction of the diformyl precursor **7** with an equimolar amount of the diamines with different chain lengths  $(8a-8c)^{18}$  was investigated in CDCl<sub>3</sub> by <sup>1</sup>H NMR spectroscopy. After mixing, the peak for the formyl group (10.3 ppm) completely disappeared and a new peak for the aldimine functionality was observed for each reaction mixture. This indicated that a single macrocyclic product was formed in each of the reaction mixtures. Mass spectrometric measurements (MALDI-TOF MS) clearly indicated the molecular ions at m/z 1957.0 (for 1a), 2044.8 (for 1b), and 2132.8 (for 1c) corresponding to the 2+2 macrocyclic products consisting of two HBC units.

Each of the <sup>1</sup>H NMR spectra of the macrocyclic HBC dimers **1a–1c** showed three peaks assignable to the HBC skeletal protons at 8.7–8.9 ppm (Figure S3), which were significantly upfield shifted compared to the corresponding protons of the mono-HBC derivative **7** at around 9.3 ppm (Figure S2). Obviously, the upfield shifts are ascribed to the shielding effect of the counterpart HBC plane. This suggests that the dimers **1a–1c** are likely to adopt a structure in which the two HBC



planes are closely stacked on top of each other. In the UV-vis absorption spectra, **1b** and **1c** showed absorption maxima at 363 and 377 nm (Figure S8, S9), respectively, while mono-HBC derivative **7** showed the corresponding band at 366 nm (Figure S10). This suggests that the HBC planes in **1c** are more efficiently interacting with each other.

The X-ray crystallographic analysis of  $\mathbf{1b}^{*}$  confirmed the close stacking of the two HBC planes (Figure 2a,b) that are linked with two CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub> chains to afford the 2+2 macrocyclic structure. The molecule of **1b** has a crystallographically-imposed center of symmetry at the midpoint of the two HBC planes. Interestingly, the two HBC planes did not perfectly overlap, but are displaced from each other by 2.79 Å, which nearly corresponds to twice the average C–C bond lengths. For example, the centroid of the six-membered ring C1–C6, which is at the center of one of the HBC planes, is almost exactly above C19\* of the counterpart HBC plane (Figure 2c). Due to this displacement, the two HBC



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planes were stacked in a staggered fashion, which nicely reproduces the AB- or ABC-stacking pattern observed for natural graphite. This is the first crystallographic analysis of a macrocyclic HBC dimer that allows stacking of the two HBC planes. The arrangement of the two HBC planes is very similar to that observed in the crystal of hexa-*tert*-butyl derivative,<sup>9a</sup> while unsubstituted HBC forms an infinite column with a non-natural stacking pattern.<sup>8</sup>

The two HBC planes are slightly bent and each facing their convex side so that the atoms on lines 4 and 4\* (see Figure 2b,c) are close to each other. The interplane distances between lines 4 and 4\* were in the range of 3.30-3.38 Å, which were comparable to the interlayer distance of natural graphite (3.35 Å).<sup>3</sup> Since the two HBC planes are bent, the interplane distances at the periphery were longer (lines  $3-5^*$ , 3.40-3.44 Å; lines  $2-6^*$ , 3.49-3.61 Å; lines  $1-7^*$  3.73-3.80 Å), but still indicative of the  $\pi-\pi$  interaction. The steric demand of the *tert*-butyl groups at C16, C22, C34, and C40 should elongate the interplane distances at the periphery. As a result, the four outer six-membered rings (C13–C18, C19–C24, C31–C36, and C37–C42) attached to the *tert*-butyl groups were outwardly bent with the dihedral angles of 5.7–10.7 deg.

It is noteworthy that the molecules of **1b** did not form an intermolecular  $\pi$ -stacking structure in the crystal packing, leaving discrete dimeric structures isolated from other molecules (Figure S13). In general, extended  $\pi$ -aromatic molecules have a strong tendency to form intermolecular stacking structures such as an infinite assembly,<sup>8</sup> but in the case of **1b**, such an intermolecular stacking was not favored probably due to the *tert*-butyl groups at the periphery. However,  $\pi$ -aromatic molecules smaller than the HBC  $\pi$ -surface would efficiently interact with the dimeric compounds **1a–1c**. Thus, we investigated the interaction between **1c** and some electron-deficient planar compounds such as **A** and **B**.

As expected, when we mixed a yellow solution of **1c** with an orange solution of perylenebisimide derivative **A**, the color of the solution changed to red. In the UV-vis absorption spectra, a broad band was observed at 600–750 nm (Figure 3a, S11). The absorption band can be ascribed to the chargetransfer interaction between **1c** and **A**. The association constant was determined to be log  $K_a = 4.59 \pm 0.10$  ( $K_a$  in M<sup>-1</sup>) by nonlinear least-squares analysis of the titration curve. Similarly, a dark green solution was obtained upon the mixing of the yellow solution of **1c** with a red solution of isoviolanthrone (**B**). In the UV-vis absorption spectra, a structured CT band centered at 510, 546, 591, and 650 nm was observed (Figure 3b, S12). The association constant was determined to be log  $K_a = 2.64 \pm 0.10$ .

It is known that  $\pi$ -aromatic molecules often form D–A–D–A alternate stacking structures due to donor (D) acceptor (A) interactions. However, repeating patterns other than D–A–D– A structures have been generally difficult to be obtained when we use simple monomeric  $\pi$ -aromatic molecules. As demonstrated in this study, the dimeric HBC molecule **1c** showed a high affinity toward some electron-deficient  $\pi$ aromatic molecules. Although the structure of the chargetransfer complexes **1c**•A and **1c**•B were not elucidated, dimeric HBC derivatives, such as **1c**, would be useful to construct stacking structures having various kinds of stacking patterns such as D–D–A–D–D–A, some of which are known to show unique semiconducting properties.<sup>19</sup>

In conclusion, we have synthesized a new series of HBC dimers **1a–1c** using the macrocyclic Schiff base formation. In the crystalline state, the molecule of **1b** showed a unique intramolecular stacking structure with the shortest interplane distance of about 3.30 Å. The two HBC planes are stacked in a staggered fashion as observed in natural graphite with the AB-or ABC-stacking pattern. In addition, **1c** was found to form donor-acceptor complexes with some electron-deficient planar molecules. The intermolecular interaction of the dimeric unit of **1c** with aromatic molecules would enable the formation of various stacking patterns. Further investigation of the structures of donor-acceptor complexes and their electronic properties is now in progress.

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### **Conflicts of interest**

There are no conflicts to declare.

### Notes and references

<sup>‡</sup> Single crystal of **1b** (0.25 × 0.15 × 0.10 mm<sup>3</sup>, C<sub>156</sub>H<sub>140</sub>Cl<sub>12</sub>N<sub>4</sub>O<sub>4</sub> = C<sub>152</sub>H<sub>132</sub>N<sub>4</sub>O<sub>2</sub>•2H<sub>2</sub>O•4CHCl<sub>3</sub> (2560.11) was obtained by slow evaporation of the solution in chloroform/hexane. The intensity data were collected on a Bruker Smart APEX II Ultra at 120 K using Mo Kα radiation ( $\lambda$  = 0.71073 Å). The data were corrected for Lorentz and polarization factors, and for absorption based on symmetry equivalent and repeated reflections. The structure was solved by direct methods (SHELXD<sup>20</sup>) and refined by full-matrix least-squares on *F*<sup>2</sup> using SHELXL 2014.<sup>21</sup>

Crystallographic data: crystal system, monoclinic, space group,  $P2_1/n$ , a = 16.0494(3), b = 19.0406(3), c = 21.7646(4) Å, a = 90.00, b = 105.1990(10),  $\gamma = 90.00$  deg, V = 6418.4(2) Å<sup>3</sup>, Z = 2,  $D_{calcd} = 1.325$  g/cm<sup>3</sup>, Collected reflections, 68324, unique, 14013,  $R_{int} = 0.0384$ ,  $2\vartheta_{max} = 54.00$  deg,  $F_{000} = 2680$ ,  $\mu$ (Mo K $\alpha$ ) = 0.319, Limiting indices,  $-20 \le h \le 20$ ,  $-24 \le k \le 24$ ,  $-27 \le l \le 27$ , Parameters/restraints, 1091/365, Goodness of fit ( $F_2$ ) = 1.119, R1 Published on 25 April 2018. Downloaded by Gazi Universitesi on 02/05/2018 15:48:51

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 $(l > 2\sigma(l)) = 0.0903$ , wR2  $(l > 2\sigma(l)) = 0.2059$ , R1 (all data) = 0.1332, wR2 (all data) 0.2388. CCDC-1818716 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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Macrocyclic imines containing two hexabenzocoronene planes adopted a unique intramolecular stacking structure, similar to the stacking pattern in natural graphite.

### TOC graphic

