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## Non-covalent composites of antiaromatic isophlorin–fullerene†

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**Cocrystallates of fullerene C<sub>60</sub> and antiaromatic planar tetraoxaisophlorins have been characterized by single crystal X-ray diffraction analysis. The ring-juncture bonds of C<sub>60</sub> are found to be at a very close distance to the plane of the antiaromatic isophlorins. NMR measurements and MALDI-TOF mass spectrometry show that this interaction can persist in both solution and gaseous states, which can be attributed to van der Waals dispersion forces.**

The curved  $\pi$  surface of fullerene has attracted significant attention in the synthesis of heterogeneous self-assembled architectures. It was discovered that fullerene and calixarene can form molecular complex through non-covalent interaction.<sup>1,2</sup> Their binding was found to be dependent on the size of the spheroids interacting with the macrocyclic hosts. Later, it was also observed that molecules with a flat surface such as porphyrin or its metal derivatives possessing a  $\pi$  plane could harbor the curved  $\pi$  surface of fullerene.<sup>3</sup> This intermolecular interaction between two dissimilar  $\pi$  systems is largely attributed to the van der Waals dispersion forces. Similarly, other planar systems also have the ability to form a non-covalent complex with the  $\pi$  surface of fullerene.<sup>4–8</sup> Even though  $\pi$ – $\pi$  interaction is common between fullerene and flat molecules, the shape of these assemblies can be either non-linear or in the form of columnar stacks. A variety of hosts have been designed, synthesized and explored to bind the C<sub>60</sub> spheroid.<sup>9–16</sup> In this context, the unique aromatic character of fullerene is a topic of intense discussion.<sup>17,18</sup> Small aromatic sub-units such as benzene, pyrrole, and thiophene<sup>19</sup> are a common feature of all such hosts that favor close contacts with C<sub>60</sub>. Therefore, is aromaticity the only driving force to attract fullerene towards a planar  $\pi$  surface? Unlike its interaction with aromatic molecules, it is uncommon to observe the binding of fullerene to antiaromatic hosts.

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† Electronic supplementary information (ESI) available: Experimental details, synthesis, characterization coordinates for the DFT optimized structures and the X-ray crystal data of complexes (CIF). CCDC 1043384 (3-C<sub>60</sub>), 1043385 (4), 1043386 (4-C<sub>60</sub>)<sub>2</sub>, 1043387 (4)<sub>2</sub>-C<sub>60</sub>, 1043388 (5) and 1043389 (5-C<sub>60</sub>). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc00771b

Isophlorin,<sup>20</sup> **1**, is an unstable 20 $\pi$  antiaromatic tetrapyrrolic macrocycle with a structural resemblance to porphyrin, **2** (Chart 1). Nonetheless, its furan/thiophene derivatives are stable under ambient conditions and sustain a planar  $\pi$  surface.<sup>21,22</sup> They represent ideal examples to explore the interaction of fullerene with a 4n $\pi$  macrocyclic host. In addition, isophlorins do not exhibit  $\pi$  stacking which can favour better interaction with guest molecules. In contrast to aromatic hosts, such studies are not well explored with antiaromatic hosts. Herein we describe the discrete nature of fullerene–isophlorin interaction along with the structural characterization of these non-covalent complexes.

It has been observed that the *meso* substituents on the porphyrin ring provide cooperative effects in the binding of fullerene. In this context we employed three different tetraoxaisophlorins, **3–5**, by varying the substituents on the *meso* carbon atoms. Tetraoxaisophlorins **4** and **5** were synthesized by acid catalyzed reactions of suitable precursors, followed by oxidation (Scheme 1).

Isophlorins **4** and **5** were characterized by mass spectrometry, <sup>1</sup>H NMR spectroscopy and single crystal X-ray diffraction analysis (ESI†). Their anti-aromatic character was confirmed by the upfield chemical shift values for the proton on the  $\beta$ -carbons of the furan in the <sup>1</sup>H NMR spectra (ESI†). The estimated NICS(0)<sup>24</sup> values of +38.13 and +39.64 for **4** and **5** are amongst the highest reported positive values for any anti-aromatic macrocycles.<sup>25–27</sup> The solutions of these three anti-aromatic macrocycles were individually treated with a toluene solution of C<sub>60</sub>. The colour of the solutions displayed a distinct change from green to brown, upon the addition of fullerene, suggesting the formation of the  $\pi$  complex. Co-crystals of isophlorins

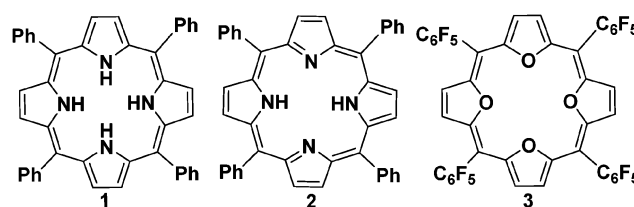
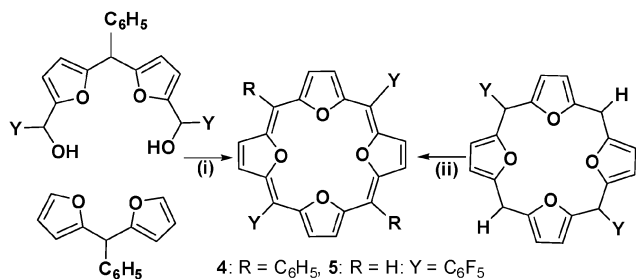


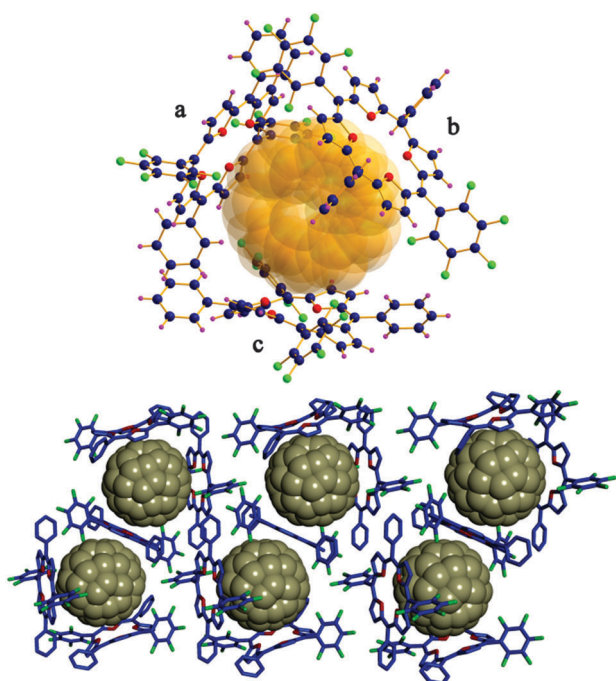
Chart 1 20 $\pi$  anti-aromatic isophlorins (**1**), 18 $\pi$  aromatic porphyrin (**2**) and 20 $\pi$  anti-aromatic tetraoxaisophlorin (**3**).



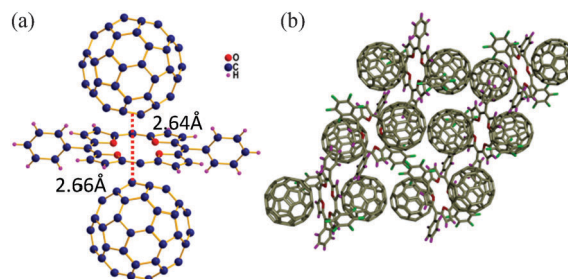


**Scheme 1** Syntheses of 20 $\pi$  tetraoxaisophlorins. (i) One equiv. of BF<sub>3</sub>·OEt<sub>2</sub>, five equiv. of FeCl<sub>3</sub>, dry DCM (100 ml), rt, N<sub>2</sub>, 2 h. (ii) Five equiv. of DDQ, N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, DCM, reflux.<sup>23</sup>

(4 and 5) and fullerene were grown from a combination of toluene–acetone solvents by a slow evaporation method at room temperature, to yield black coloured crystals. The molecular complex of (4)<sub>3</sub>·C<sub>60</sub> revealed a fullerene trigonally engulfed by three isophlorins (a, b and c in Fig. 1).<sup>18</sup> The isophlorin surface was found to be extremely close to the  $\pi$  surface of the fullerene, compared to standard values for  $\pi$ – $\pi$  interactions. These values are comparable to that observed between C<sub>60</sub> and a free base porphyrin. C<sub>60</sub> is centered over the isophlorin with electron-deficient 5:6 ring juncture C–C bonds at a close distance to the plane of the isophlorin core (C to mean 24-atom plane distances C with a, b and c are 2.61 Å, 2.68 Å, and 2.76 Å respectively). No close fullerene–fullerene contacts were observed in the packing diagram for this crystal. The short contacts of *ortho*-F atoms of the isophlorin “a” and “c” to the nearest carbon atom of fullerene were found to be 3.09 and 3.10 Å respectively.



**Fig. 1** (top) Molecular complex of (4)<sub>3</sub>·C<sub>60</sub> displayed prismatic arrangement of three isophlorin molecules around a C<sub>60</sub>. (below) The packing diagram of the prismatic arrangement. Color code: C<sub>60</sub> in space filled gray color and O (red), C (blue), and F (green).

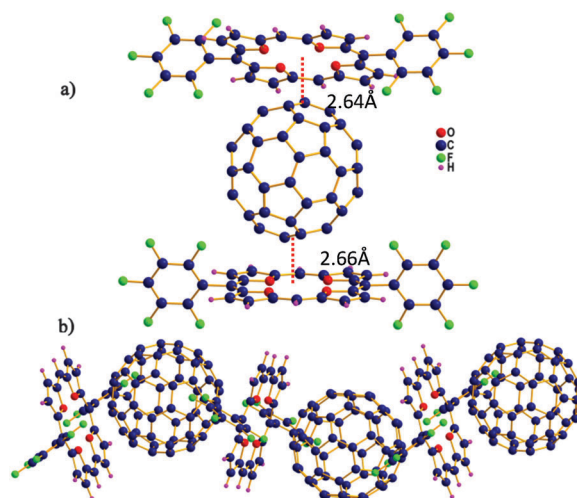


**Fig. 2** (a) 1:2 contact with a single isophlorin in 4·(C<sub>60</sub>)<sub>2</sub>. Pentafluorophenyl rings are omitted for clarity. (b) Packing structure of 4·(C<sub>60</sub>)<sub>2</sub>.

Curiously, isophlorin “c” was distorted from a regular planar structure in this non-covalent complex.

When crystals were grown upon addition of excess fullerene to a solution of 4, it was observed that the macrocycle was sandwiched by two fullerene units,<sup>28</sup> 4·(C<sub>60</sub>)<sub>2</sub> (Fig. 2). The close contacts observed between both C<sub>60</sub> and the macrocycle are 2.64 and 2.66 Å. These values are extremely short compared to conventional  $\pi$ – $\pi$  stacking even in a homogeneous system.

In contrast to the above structures, the molecular complex of 5·C<sub>60</sub> revealed a zig-zag assembly of alternating isophlorin–C<sub>60</sub> interactions (Fig. 3). The orientation of C<sub>60</sub> is very similar to that found in 4·(C<sub>60</sub>)<sub>2</sub> with the 5:6 ring junction carbon atoms lying over the centre of the isophlorin ring (Fig. 3) at distances of 2.64 and 2.66 Å from the mean 24-atom plane of isophlorins (ESI<sup>†</sup>). The closest atom to atom contacts are from the two 5:6 fullerene carbon atoms to the isophlorin oxygen atoms, and they range from 2.96 to 4.31 Å. The *ortho*-F atoms of the *meso* pentafluorophenyl ring were found to be at a distance of 2.98, 3.12 and 3.13 Å to the nearest carbon atom of fullerene suggesting their significant contribution in the complexation. The angle between the isophlorin planes was found to be 32.7°. The closest carbon-to-carbon atom distance between fullerenes in adjacent chains is 3.16–3.26 Å. In addition to close fullerene–isophlorin



**Fig. 3** (a) Molecular structure of the 5 and C<sub>60</sub> complex. (b) The packing diagram in the crystal lattice of 5·C<sub>60</sub> reveals a zigzag chain of alternating isophlorin and C<sub>60</sub>.



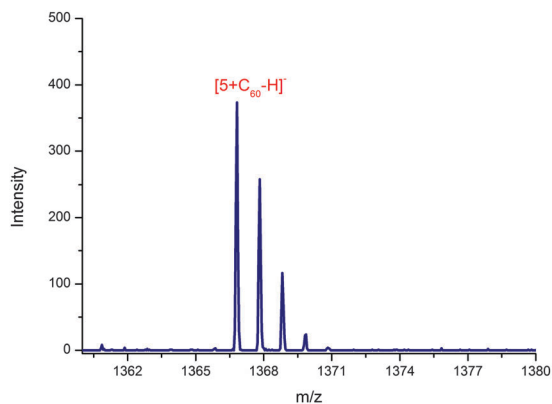


Fig. 4 MALDI-TOF mass spectrum of molecular complex  $5\text{-C}_{60}$ .

$\pi$ - $\pi$  interactions, weak  $\text{C-F}\cdots\text{H-C}$  bonds<sup>29</sup> were also observed between the  $\text{C}_6\text{F}_5$  groups and the furan  $\beta$  hydrogens of neighbouring macrocycles. Soft ionization MALDI mass spectrometry also confirmed the complex formation between **5** and  $\text{C}_{60}$ . Using dihydroxybenzoic acid as the matrix, an  $m/z$  value of 1366.96 was observed, corresponding to a 1 : 1 ratio of the  $5\text{-C}_{60}$  complex (Fig. 4).

The crystal-packing diagram of  $3\text{-C}_{60}$  displayed a columnar stacking of 1 : 1 alternative  $\text{C}_{60}$ -isophlorin in benzene (Fig. 5). However, the zig-zag assembly was not displayed and the isophlorin planes are parallel, leading to a linear chain kind of assembly. The  $\text{C}_{60}$  is centered over the porphyrin with electron-rich 6 : 6 ring-juncture C-C bonds at a close distance to the plane of the porphyrin core (C to mean 24-atom plane distance), 2.62 Å.

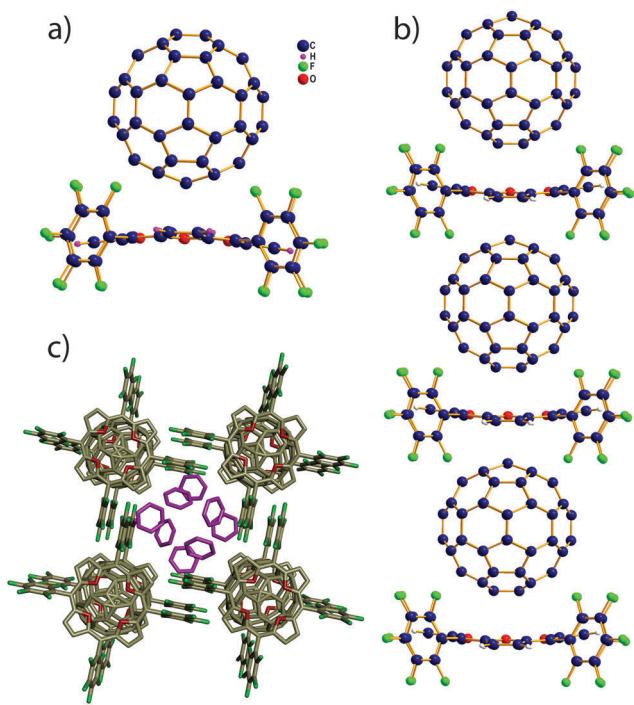


Fig. 5 (a) Molecular structure of the complex formed by **3** and  $\text{C}_{60}$ . (b) Columnar stacking of alternating isophlorin- $\text{C}_{60}$  in the  $3\text{-C}_{60}$  complex. (c) The solvent molecules are trapped in the voids.

The closest atom-to-atom contacts are from the two 6 : 6 fullerene carbon atoms to the isophlorin oxygen atoms, which are in the range 2.94 to 3.76 Å. Short contacts of *ortho*-F atoms of the isophlorin to the nearest carbon atom of fullerene are found at 3.16 and 3.18 Å, indicating that the *ortho* C-F bonds have a relatively weak contribution to the association compared to that in  $5\text{-C}_{60}$ . Interestingly, there are no close fullerene-fullerene contacts. Benzene molecules occupied channels between columns, which suggest that aromatic solvents stabilize the assembly. Here we also found weak  $\text{C-F}\cdots\text{H-C}$  type H-bonding interactions like  $5\text{-C}_{60}$ . Our attempts at co-crystallization with different compositions of  $\text{C}_{60}$ -isophlorin in various solvents selectively yielded a 1 : 1 ratio of  $3\text{-C}_{60}$  and  $5\text{-C}_{60}$  complexes. These results are consistent with NMR results in solution. We also investigated the attraction of fullerene towards the isophlorin in solution by using variable-temperature NMR experiments. Toluene- $d_8$  was chosen as solvent because of good solubility for both the molecules. This solution shows remarkable shifts in both  $^{13}\text{C}$  as well as  $^1\text{H}$  NMR spectra. A 1 : 1 solution of **4** and  $\text{C}_{60}$  displayed 0.03 ppm upfield shift for the  $\beta$  hydrogens of furan and 0.03 ppm downfield shift for the *meso* phenyl hydrogens. Simultaneously, a 0.10 ppm shift was observed for the *ortho* fluorine atoms in  $^{19}\text{F}$  NMR at room temperature. In the  $^{13}\text{C}$  NMR,  $\text{C}_{60}$  displayed a single resonance for  $4\text{-C}_{60}$  at 298 K with a marginal downfield shift of 0.26 ppm relative to free  $\text{C}_{60}$ . Upon cooling to 203 K, this signal was downfield shifted by 0.98 ppm. A large downfield shift of 1.33 ppm was observed upon cooling to 183 K but with significant signal broadening. Similarly, a 1 : 1 solution of the  $5\text{-C}_{60}$  complex exhibited a 0.18 ppm upfield shift for the  $\text{C}_{60}$  carbon in  $^{13}\text{C}$  NMR at 183 K. In the case of a 1 : 1 complex of  $3\text{-C}_{60}$  we observed a 0.16 ppm upfield shift in  $^1\text{H}$  NMR at 183 K. The larger shift suggests significant interaction between  $\text{C}_{60}$  and isophlorin. However, UV-Visible experiments did not display any salient changes for all the complexes in solution. This can be attributed to the purely non-covalent interaction. The absence of any charge-transfer bands in the electronic absorption spectra further supported the lack of donor-acceptor complexes. The isophlorins are poor emitters compared to porphyrin. However, it was observed that even the negligible fluorescence intensity reduced upon the addition of fullerene, which can be attributed to cluster formation between the two  $\pi$  conjugated molecules (see ESI<sup>†</sup>).

The complex formation in the solution state between **4** or **5** and  $\text{C}_{60}$  was studied using isothermal titration calorimetric (ITC) experiments<sup>30</sup> and fluorescence (see ESI<sup>†</sup>). The estimated association constant ( $K_a$ ) was found to be  $9.91 \times 10^2 \text{ M}^{-1}$  and  $7.16 \times 10^3 \text{ M}^{-1}$  for  $4\text{-C}_{60}$  and  $5\text{-C}_{60}$  respectively. The thermodynamic parameters,  $\Delta G$  ( $-5.24 \text{ kcal mol}^{-1}$ ),  $\Delta H$  ( $-0.146 \text{ kcal mol}^{-1}$ ), and  $T\Delta S$  ( $-5.24 \text{ kcal mol}^{-1}$ ), for  $4\text{-C}_{60}$  and  $\Delta G$  ( $-4.09 \text{ kcal mol}^{-1}$ ),  $\Delta H$  ( $-0.434 \text{ kcal mol}^{-1}$ ), and  $T\Delta S$  ( $-3.66 \text{ kcal mol}^{-1}$ ), for  $5\text{-C}_{60}$  further confirmed the binding between isophlorins and  $\text{C}_{60}$ . The value of the binding constant estimated from fluorescence spectroscopy was also found to be of the same order (see ESI<sup>†</sup>).

In conclusion, the first molecular complexes of fullerene with antiaromatic isophlorin were obtained and successfully characterized by single-crystal X-ray diffraction studies. The close contacts between fullerenes and isophlorin arise from a



favourable van der Waals attraction of the curved  $\pi$  surface of a fullerene to the anti-aromatic  $\pi$  surface of isophlorin. These studies suggest that anti-aromatic  $\pi$  surfaces are as good as aromatic surfaces for binding fullerenes. The estimated binding constants also confirmed the interaction between the isophlorins and C<sub>60</sub> in the solution state.

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