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COMMUNICATION

Non-Covalent Composites of Antiaromatic Isophlorin-Fullerene

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Cocrystallates of fullerene C_{60} with antiaromatic planar tetraoxaisophlorins have been characterized by single crystal X-ray diffraction analysis. The ring-juncture bonds of C_{60} are found to be at a very close approach to the plane of the antiaromatic isophlorins. NMR measurements, 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 π surface of fullerene has attracted significant attention in the synthesis of heterogeneous self-assembled architectures. Interaction of fullerenes with other molecules was initially discovered as its complex with calixarene.^{1, 2} 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 π plane could harbor the curved π surface of fullerene.³ This intermolecular interaction between two dissimilar π systems is largely attributed to the van Der Waal's dispersion forces. Similarly, other planar systems also have affinity for the formation of the non-covalent complex with the π surface of fullerene.⁴⁻⁸ Even though π - π interaction is common between fullerene and flat molecules, the shape of these assemblies can be either non-linear or in the form of columnar stacking. A variety of hosts have been designed, synthesized and explored to bind the C_{60} spheroid.⁹⁻¹⁶ In this context, the unique aromatic character of fullerene is a topic of intense discussion.^{17, 18} Small aromatic sub-units such as benzene, pyrrole, thiophene¹⁹ etc. are a common feature of all such hosts that favor close contacts with C_{60} . Therefore, is aromaticity the only driving force to attract fullerene towards a planar π surface? Unlike its interaction of with aromatic

molecules, it is uncommon to observe the binding of fullerene to antiaromatic hosts.

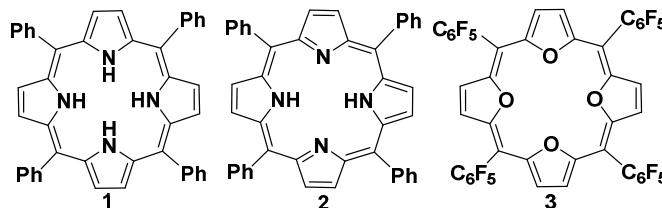
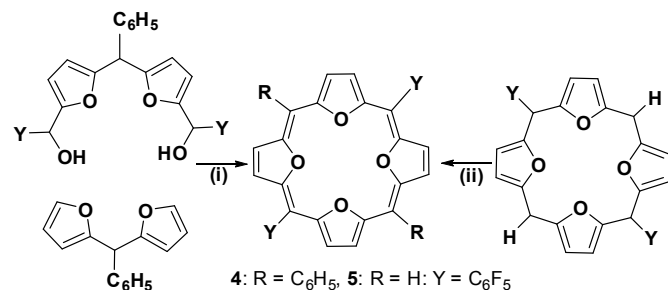


Chart: 20 π anti-aromatic isophlorins (1), 18 π aromatic porphyrin (2) and 20 π anti-aromatic tetraoxaisophlorin (3).

Isophlorin,²⁰ **1**, is an unstable 20 π antiaromatic tetrapyrrolic macrocycle with a structural resemblance to porphyrin, **2** (Chart). Nonetheless, its furan / thiophene derivatives are stable under ambient conditions and sustain a planar π surface.^{21, 22} They represent ideal examples to explore the interaction of fullerene with a 4n π macrocyclic host. In addition, isophlorins do not exhibit π stacking which can favour better interaction with guest molecules. In contrast to aromatic hosts, such studies are not well explored with anti-aromatic 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. The tetraoxaisophlorins **4** and **5** were synthesized by acid catalyzed reactions of suitable precursors, followed by oxidation (Scheme 1).



Scheme 1. Syntheses of 20 π tetraoxaisophlorins. (i) One equiv. of BF₃·OEt₂, five equiv. of FeCl₃, dry DCM (100 ml), rt, N₂, 2h. (ii) five equiv. of DDO, N₂H₄·H₂O, DCM, reflux.²³

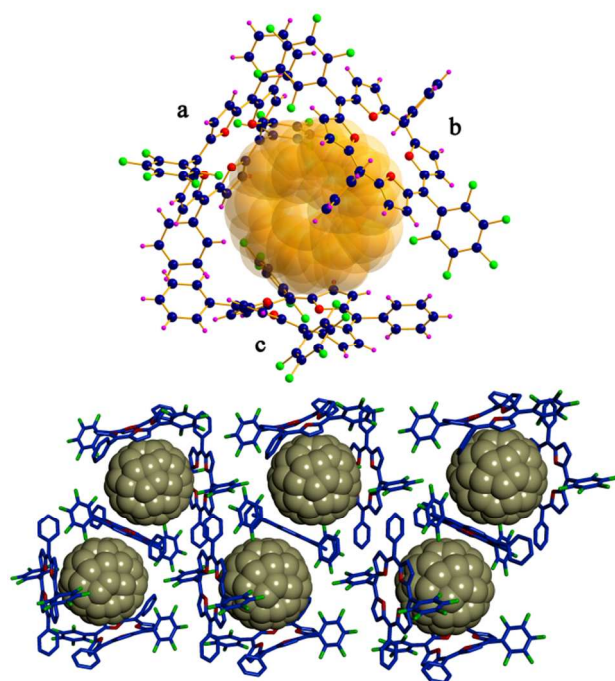


Figure 1. (Top) Molecular complex of (4)₃·C₆₀ displayed Prismatic arrangement of three isophlorin molecules around a C₆₀. (Below) Packing diagram of the prismatic arrangement. Color code: C₆₀ in space filled gray color and O (red), C (blue), and F (green).

The isophlorins, **4** and **5**, were characterized by mass spectrometry, ¹H NMR spectroscopy and single crystal X-ray diffraction analysis (Supporting Information, SI). Their anti-aromatic character was confirmed by the upfield chemical shift values for the proton on the β -carbons of the furan in the ¹H NMR spectra (SI). The estimated NICS(0)²⁴ values of +38.13 and +39.64 for **4** and **5** are amongst the highest reported positive values for any anti-aromatic macrocycles.²⁵⁻²⁷ The solutions of these three anti-aromatic macrocycles were individually treated with a toluene solution of C₆₀. The colour of the solutions displayed a distinct change from green to brown, upon the addition of fullerene, suggesting the formation of the π complex. Co-crystals of isophlorins (**4** and **5**) and fullerene were grown from a combination of toluene-acetone solvents by slow

evaporation method at room temperature, to yield black coloured crystals. The molecular complex of (4)₃·C₆₀ revealed a fullerene trigonally engulfed by three isophlorins (a, b and c in Figure-1).¹⁸ The isophlorin surface was found to be extremely close to the π surface of the fullerene, compared to standard values for π - π interactions. These values are comparable to that observed between C₆₀ and a free base porphyrin. The C₆₀ 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 2.61Å, 2.68Å, and 2.76Å 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 3.10Å respectively. Curiously, one of the 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,²⁸ **4**·(C₆₀)₂ (Figure-2). The close contacts observed between both the C₆₀ and the macrocycle are 2.64 and 2.66Å. These values are extremely short compared to conventional π - π stacking even in a homogeneous system.

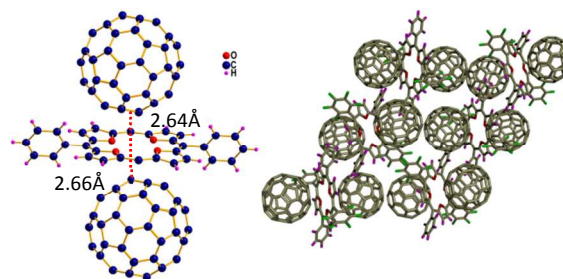


Figure-2. (a) 1:2 contact with a single isophlorin in **4**·(C₆₀)₂. Pentafluorophenyl rings are omitted for clarity. (b) Packing structure of **4**·(C₆₀)₂.

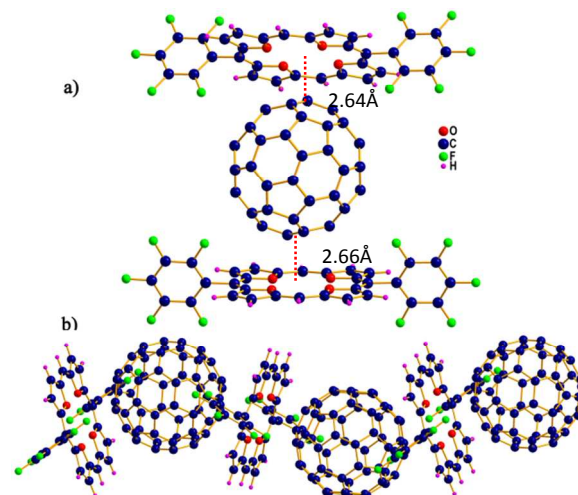


Figure 3. (a) Molecular structure of the **5** and C_{60} complex. (b) Packing diagram in the crystal lattice of **5**· C_{60} reveals a zigzag chain of alternating isophlorin and C_{60} .

In contrast to the above structures, the molecular complex of **5**· C_{60} revealed a zig-zag assembly of alternating isophlorin/ C_{60} interactions (Figure 3). The orientation of C_{60} is very similar to that found in **4**·(C_{60})₂ with the 5:6 ring junction carbon atoms lying over the centre of the isophlorin ring (Figure 3) at distances of 2.64 and 2.66 Å from 24 mean plane of the isophlorins (SI). The closest atom to atom contacts are from the two 5:6 fullerene carbon atoms to the isophlorin oxygen atoms, they range from 2.96 to 4.31 Å. The ortho-F atoms from 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 π - π interactions, weak C-F...H-C bonds²⁹ were also observed between the C_6F_5 groups and the furan β hydrogens of neighbouring macrocycles. Soft ionization MALDI mass spectrometry also confirmed the complex formation between **5** and C_{60} . Using dihydroxybenzoic acid as the matrix, an m/z value of 1366.96 was observed at, corresponding to 1:1 ratio of **5**· C_{60} complex (Figure 4).

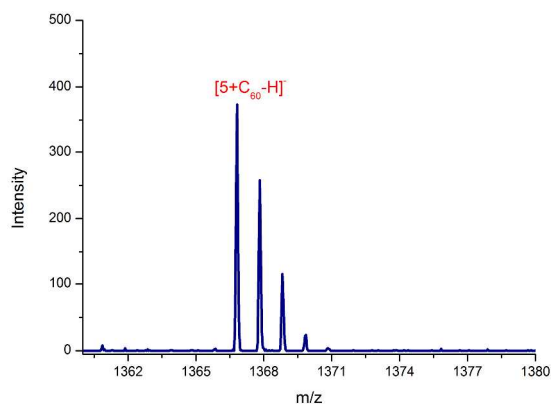


Figure 4. MALDI-TOF mass spectrum of molecular complex **5**· C_{60} .

The crystal-packing diagram of **3**· C_{60} , displayed a columnar stacking of 1:1 alternative C_{60} -isophlorin in benzene (Figure 5). However, the zig-zag assembly was not displayed and the isophlorin planes are parallel, leading to a linear chain kind of assembly. The C_{60} is centered over the porphyrin with electron-rich 6:6 ring-juncture C-C bonds in close approach to the plane of the porphyrin core (C to mean 24-atom plane distance) 2.62 Å. 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 of 3.16 and 3.18 Å, indicating that the ortho C-F bonds have relatively weak contribution to the association than in **5**· 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 also we found weak C-F...H-C type H-bonding interactions like **5**· C_{60} . Our attempts at co-crystallization with different composition of C_{60} /isophlorin in various solvents selectively yielded 1:1 ratio of **3**· C_{60} and **5**· 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. The solution shows remarkable shifts in both ¹³C as well as ¹H NMR spectrum. A 1:1 solution of **4** and C_{60} displayed 0.03 ppm upfield shift for the β 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 ¹⁹F NMR at room temperature. In the ¹³C NMR, C_{60} displayed a single resonance for **4**· C_{60} at 298K with a marginal downfield shift of 0.26 ppm relative to free C_{60} . Upon cooling to 203K, this signal was downfield shifted by 0.98 ppm. A large downfield shift of 1.33 ppm was observed upon cooling to 183K but with significant signal broadening. Similarly, a 1:1 solution of **5**· C_{60} complex exhibited a 0.18 ppm upfield shift for the C_{60} carbon in ¹³C NMR at 183K. In the case of 1:1 complex of **3**· C_{60} we observed a 0.16 ppm upfield shift in ¹H NMR at 183K. The larger shift suggests significant interaction between 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. Absence of any charge-transfer bands in the electronic absorption spectra further supported 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 π conjugated molecules (see SI).

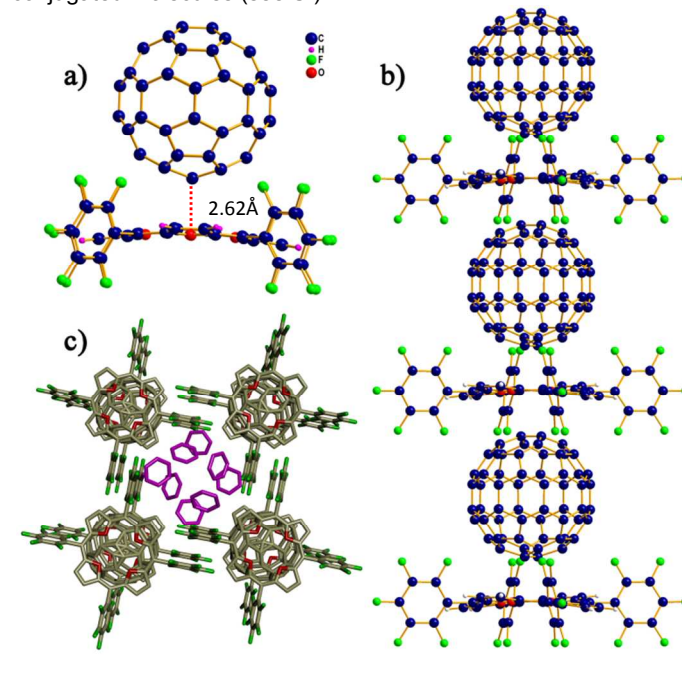


Figure 5.(a) Molecular structure of the complex formed by **3** and C₆₀. b) Columnar stacking of alternating isophlorin/C₆₀ in **3**.C₆₀ complex. c) The solvent molecules are trapped in the voids.

The complex formation in solution state between **4** or **5** and C₆₀ were studied using isothermal titration calorimetric (ITC) experiments³⁰ and fluorescence (see SI). The estimated association constant (K_a) was found to be 9.91 X 10² M⁻¹ and 7.16 X 10³ M⁻¹ for **4**.C₆₀ and **5**.C₆₀ respectively. The thermodynamic parameters, ΔG (-5.24 kcal mol⁻¹), ΔH (-0.146 kcal mol⁻¹), and TΔS (-5.24 kcal mol⁻¹), for **4**.C₆₀ and ΔG (-4.09 kcal mol⁻¹), ΔH (-0.434 kcal mol⁻¹), and TΔS (-3.66 kcal mol⁻¹), for **5**.C₆₀ further confirmed the binding between isophlorins and C₆₀. The value of binding constant estimated from fluorescence spectroscopy was also found to be of the same order (see SI).

Conclusions

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 π surface of a fullerene to the anti-aromatic π surface of isophlorin. These studies suggest that, anti-aromatic characteristics of a π surface to be as good as aromatic surfaces for binding fullerenes. The estimated binding constants also confirmed interaction between the isophlorins and C₆₀ in the solution state.

Notes and references

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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**.C₆₀), CCDC 1043385 (**4**), CCDC 1043386 **4**.(C₆₀)₂, CCDC 1043387 (**4**)₃.C₆₀ CCDC 1043388 (**5**) and CCDC 1043389 (**5**.C₆₀) is available For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/c000000x/

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