Electronic Supplementary Material (ESI) for ChemComm.

Supplementary information

Non-Covalent Composites of Antiaromatic Isophlorin and Fullerene

B. Kiran Reddy, Santosh C. Gadekar and Venkataramanarao G. Anand*

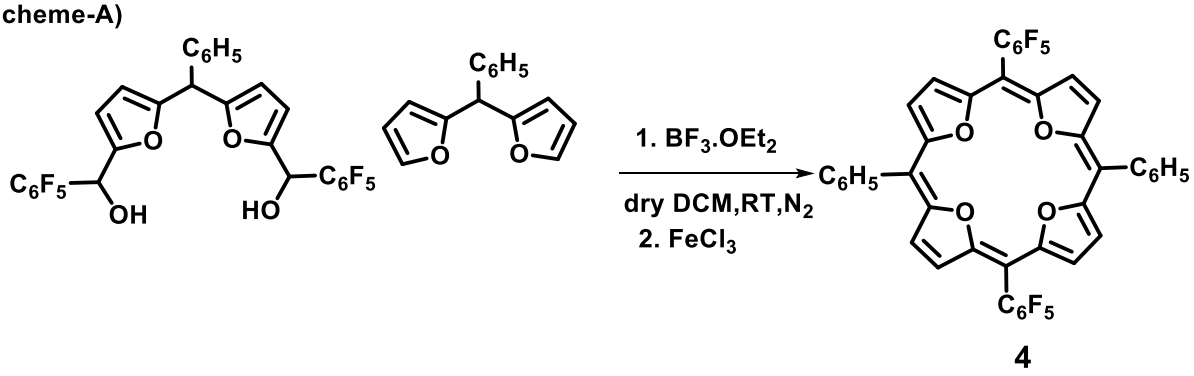
Indian Institute of Science Education and Research (IISER), Pune – 411008, Maharashtra, India

Email: vg.anand@iiserpune.ac.in

1. General Experimental Methods

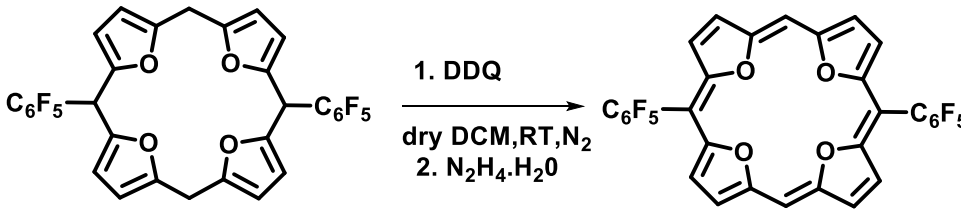
All reagents and solvents were of commercial reagent grade and were used without further purification except where noted. Dry CH_2Cl_2 was obtained by refluxing and distillation over P_2O_5. Column chromatography was performed on basic alumina and silica gel (230-400) in glass columns. ^1H NMR spectra were recorded on a JEOL 400 MHz spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.26 ppm) or $(CH3)_2CO$ (δ = 2.05 ppm) or Toluene-d_8 (δ = 7.09, 7.00, 6.98 and 2.09 ppm) as internal reference for ^1H. Electronic spectra were recorded on a Perkin-Elmer λ-950 ultraviolet–visible (UV–vis) spectrophotometer. High Resolution Mass spectra were obtained using WATERS G2 Synapt Mass Spectrometer. Single crystals were grown using suitable solvents and were diffracted on BRUKER KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).

(Scheme-A)



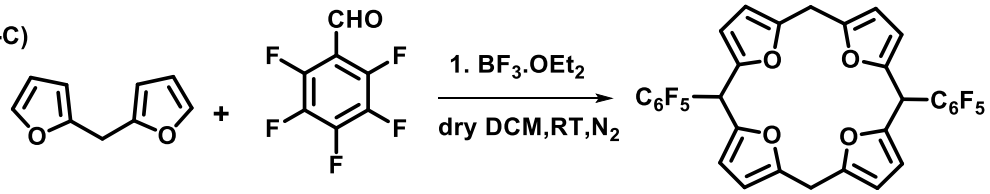
4

(Scheme-B)



5

(Scheme-C)



6

Synthetic procedure for 4 :

A mixture of mesophenyl difuromethane, (224 mg, 1 mmol) and the difuromethanediol, (616 mg, 1 mmol) were stirred in 100 ml dry dichloromethane. The solution was bubbled with argon for 10 min. $BF_3.OEt_2$ (0.12 ml, 1 mmol) was added under dark, and the resulting solution was stirred for 2h. After adding five equivalents of $FeCl_3$, solution was opened to air and stirred for additional two hours. The reaction mixture was passed through a short basic alumina column. This mixture was separated by repeated silica gel column chromatography by using CH_2Cl_2/n-hexane as eluent. A yellowish green color band obtained was identified as **4** (2.5mg) in 2.5% yield.

^{1}H NMR (400 MHz, Toluene-d_8) δ 6.67 – 6.53 (m, 6H), 6.09 – 5.96 (m, 4H), 2.53 (d, J = 4.8 Hz, 4H), 2.17 (d, J = 4.8 Hz, 4H). **^{19}F NMR** (376 MHz, Acetone-d_6) δ -143.64 (d, J = 19.9 Hz), -157.32 (t, J = 20.4 Hz), -163.07 (t, J = 20.8 Hz). **UV-vis** (CH_2Cl_2) : λ_{max}(ε): 368(102300), 328(83900); **HRMS** m/z: calcd.For $C_{44}H_{18}F_{10}O_4$: 800.1035; Observed: 800.1045(100.0% M+). **Crystal data** $C_{44}H_{18}F_{10}O_4$, 2(C H Cl_3) (Mr = 1039.32), monoclinic, space group $P2_1/c$ (no. 14) , a = 10.3234(9), b = 15.5838(14), c = 13.5017(12)Å, α = 90.00° β = 102.531(2)° γ = 90.00°, V = 2120.4(3)Å^3, Z = 2, T = 100(2) K , D_{calcd} = 1.628g cm^{-3}, R_1 = 0.0408 (I>2s(I)), R_w (all data) = 0.0475, GOF = 1.268.

Synthetic procedure for 5 :

To a solution of **6** (100 mg, 1.39 mmol) in 20 ml of dichloromethane was added a solution of DDQ (136 mg, 5.7 mmol) in 50 ml of dichloromethane. Upon mixing the two solutions, a black precipitate formed immediatelay. To this 10 ml of hydrazine (95%) was added. After boiling for 10 min, the reaction mixture was passed through a short basic alumina column and further purified by recrystalization in hexane-dichloromethane combination. A green color solid was identified as **5**(20mg) in 20% yield.

^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 2.16 (d, J = 4.8 Hz, 4H), 1.81 (d, J = 4.6 Hz, 4H), -0.38 (s, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -139.92 (d, J = 19.0 Hz), -153.37 (s), -159.91 (s). **UV-vis** (CH_2Cl_2): λ_{max}(ε): 348(112200), 318(97900). **HRMS** m/z: Calcd. for $C_{32}H_{10}F_{10}O_4$: 648.0419; observed: 648.0419 (100.0%, M+). **Crystal data** $C_{32}H_{10}F_{10}O_4$ (Mr = 648.40), monoclinic, space group $P2_1/c$, a = 14.649(4), b = 10.269(3), c = 8.425(2) Å, α = 90.00° β = 99.013(6)° γ = 90.00°, V = 1251.7(6)Å^3, Z = 2, T = 100(2) K , D_{calcd} = 1.720g cm^{-3}, R_1 = 0.0497 (I>2s(I)), R_w (all data) = 0.0380, GOF = 1.035.

Synthetic procedure for 6:

A mixture of mesofree difuromethane, (400 mg, 2.7 mmol) and the pentafluoro benzaldehyde, (0.32 ml, 2.7 mmol) were stirred in 500 ml dry dichloromethane. The solution was bubbled with argon for 10 min. $BF_3.OEt_2$ (0.33 ml, 2.7 mmol) was added under dark, and the resulting solution was stirred for 3h. A few drops of triethylamine were then added and the reaction mixture passed through a short basic alumina column. This mixture was further separated by silica gel column chromatography by using 1% ethylacetate/n-hexane as eluent. A white color solid obtained as **6**(160mg) in 2% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (d, J = 3.0 Hz, 4H), 5.98 (d, J = 2.8 Hz, 4H), 5.79 (s, 2H), 3.87 (s, 4H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -138.93 (dd, J = 43.3, 19.0 Hz),

-155.11 (d, *J* = 21.1 Hz), -161.40 (t, *J* = 20.4 Hz). **HRMS** m/z: calcd.For $C_{32}H_{14}F_{10}O_4Na^+$: 675.0625; Observed: 675.0625 (100.0% $(M+Na)^+$).

Table 1. Crystal data and structure refinement for **$(4)_3.C_{60}$**

Identification code	**$(4)_3.C_{60}$**	
Empirical formula	C78.25 H24 F10 O4.75	
Formula weight	1229.97	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 15.928(2) Å	α= 101.456(7)°.
	b = 19.014(2) Å	β= 110.099(7)°.
	c = 20.624(3) Å	γ = 108.543(7)°.
Volume	5218.1(12) Å3	
Z	4	
Density (calculated)	1.566 Mg/m3	
Absorption coefficient	1.033 mm-1	
F(000)	2486	
Crystal size	0.150 x 0.080 x 0.020 mm3	
Theta range for data collection	2.431 to 67.498°.	
Index ranges	-19<=h<=18, -22<=k<=22, -24<=l<=24	
Reflections collected	89924	
Independent reflections	18724 [R(int) = 0.0570]	
Completeness to theta = 67.679°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.980 and 0.906	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	18724 / 391 / 1722	
Goodness-of-fit on F2	1.197	
Final R indices [I>2sigma(I)]	R1 = 0.0992, wR2 = 0.3163	
R indices (all data)	R1 = 0.1277, wR2 = 0.3566	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.538 and -0.821 e.Å-3	

Table 2. Crystal data and structure refinement for **4.$(C_{60})_2$.**

Identification code	4.(C60).2	
Empirical formula	C82 H9 F5 O2	
Formula weight	1120.89	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.962(7) Å	α= 90°.
	b = 13.616(3) Å	β=97.746(8)°.
	c = 24.071(5) Å	γ = 90°.
Volume	8756(3) $Å^3$	
Z	8	
Density (calculated)	1.701 Mg/m^3	
Absorption coefficient	0.116 mm^{-1}	
F(000)	4496.0	
Crystal size	0.110 x 0.110 x 0.040 mm^3	
Theta range for data collection	1.524 to 28.450°.	
Index ranges	-33<=h<=36, -18<=k<=18, -32<=l<=21	
Reflections collected	77663	
Independent reflections	10939 [R(int) = 0.1153]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.995 and 0.987	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10939 / 0 / 802	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0610, wR2 = 0.1514	
R indices (all data)	R1 = 0.1431, wR2 = 0.1919	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.458 and -0.297 $e.Å^{-3}$	

Table 3. Crystal data and structure refinement for **5.C_{60}**.

Empirical formula	C106 H26 F10 O4
Formula weight	1553.27
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 27.439(4) Å α= 90°.
	b = 9.7293(13) Å β=97.272(3)°.
	c = 23.787(3) Å γ = 90°.
Volume	6299.1(14) $Å^3$
Z	4
Density (calculated)	1.638 Mg/m^3
Absorption coefficient	0.119 mm^{-1}
F(000)	3136
Crystal size	0.360 x 0.245 x 0.065 mm^3
Theta range for data collection	0.748 to 28.080°.
Index ranges	-36<=h<=36, -12<=k<=11, -31<=l<=31
Reflections collected	109735
Independent reflections	15286 [R(int) = 0.0854]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.992 and 0.966
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15286 / 0 / 1123
Goodness-of-fit on F^2	1.214
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1794
R indices (all data)	R1 = 0.0993, wR2 = 0.1995
Extinction coefficient	n/a
Largest diff. peak and hole	0.373 and -0.409 $e.Å^{-3}$

Table 4. Crystal data and structure refinement for **3.C_{60}.**

Identification code	3.C60
Empirical formula	C76 H28 F10 O2
Formula weight	1162.98
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal

Space group	I41/a	
Unit cell dimensions	a = 28.7283(16) Å	α= 90°.
	b = 28.7283(16) Å	β= 90°.
	c = 12.1809(9) Å	γ = 90°.
Volume	10053.1(13) Å3	
Z	8	
Density (calculated)	1.537 Mg/m3	
Absorption coefficient	0.117 mm-1	
F(000)	4720	
Crystal size	0.220 x 0.103 x 0.062 mm3	
Theta range for data collection	1.418 to 28.293°.	
Index ranges	-38<=h<=37, -33<=k<=38, -9<=l<=16	
Reflections collected	28361	
Independent reflections	6246 [R(int) = 0.0642]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.993 and 0.986	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	6229 / 96 / 412	
Goodness-of-fit on F2	1.234	
Final R indices [I>2sigma(I)]	R1 = 0.0648, wR2 = 0.1841	
R indices (all data)	R1 = 0.1071, wR2 = 0.2043	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.700 and -0.619 e.Å-3	

Table 5. Crystal data and structure refinement for **4**.

Identification code	4	
Empirical formula	C46 H20 Cl6 F10 O4	
Formula weight	1039.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.3234(9) Å	α= 90°.
	b = 15.5838(14) Å	β= 102.531(2)°.
	c = 13.5017(12) Å	γ = 90°.
Volume	2120.4(3) $Å^3$	
Z	2	

Density (calculated)	1.628 Mg/m^3
Absorption coefficient	0.496 mm^{-1}
F(000)	1040.0
Crystal size	0.220 x 0.110 x 0.060 mm^3
Theta range for data collection	2.021 to 26.368°.
Index ranges	-12<=h<=12, -19<=k<=19, -14<=l<=16
Reflections collected	34313
Independent reflections	4335 [R(int) = 0.0560]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.971 and 0.937
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4335 / 84 / 298
Goodness-of-fit on F^2	1.268
Final R indices [I>2sigma(I)]	R1 = 0.0408, wR2 = 0.1460
R indices (all data)	R1 = 0.0475, wR2 = 0.1549
Extinction coefficient	n/a
Largest diff. peak and hole	0.686 and -0.668 $e.Å^{-3}$

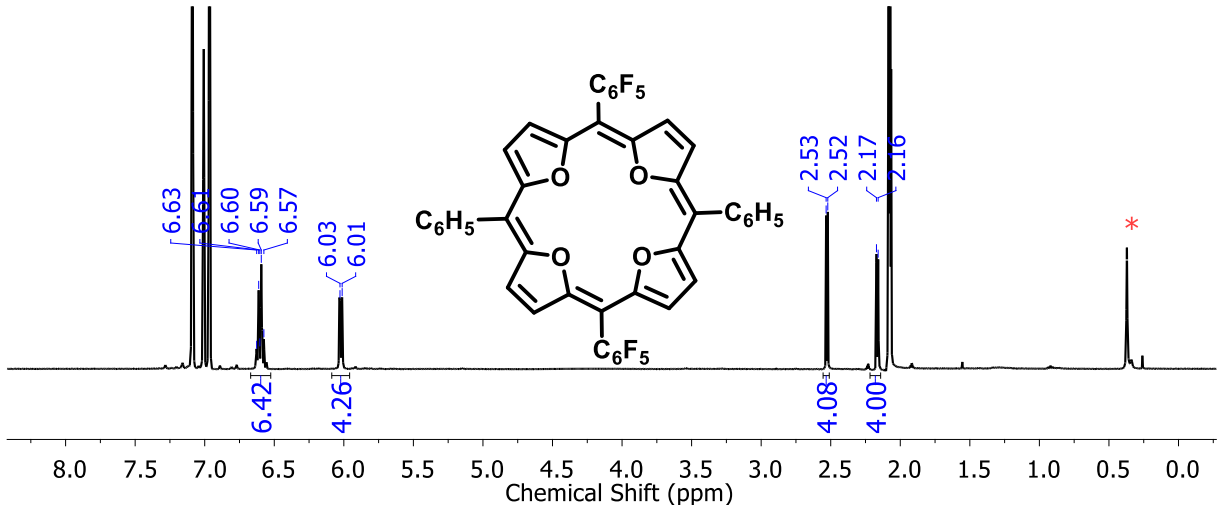
Table 6. Crystal data and structure refinement for **5**.

Identification code	5	
Empirical formula	C32 H10 F10 O4	
Formula weight	648.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.649(4) Å	α= 90°.
	b = 10.269(3) Å	β=99.012(6)°.
	c = 8.425(2) Å	γ = 90°.
Volume	1251.8(6) $Å^3$	
Z	2	
Density (calculated)	1.720 Mg/m^3	
Absorption coefficient	0.163 mm^{-1}	
F(000)	648	
Crystal size	0.220 x 0.100 x 0.080 mm^3	
Theta range for data collection	2.432 to 29.074°.	
Index ranges	-19<=h<=20, -11<=k<=14, -11<=l<=10	

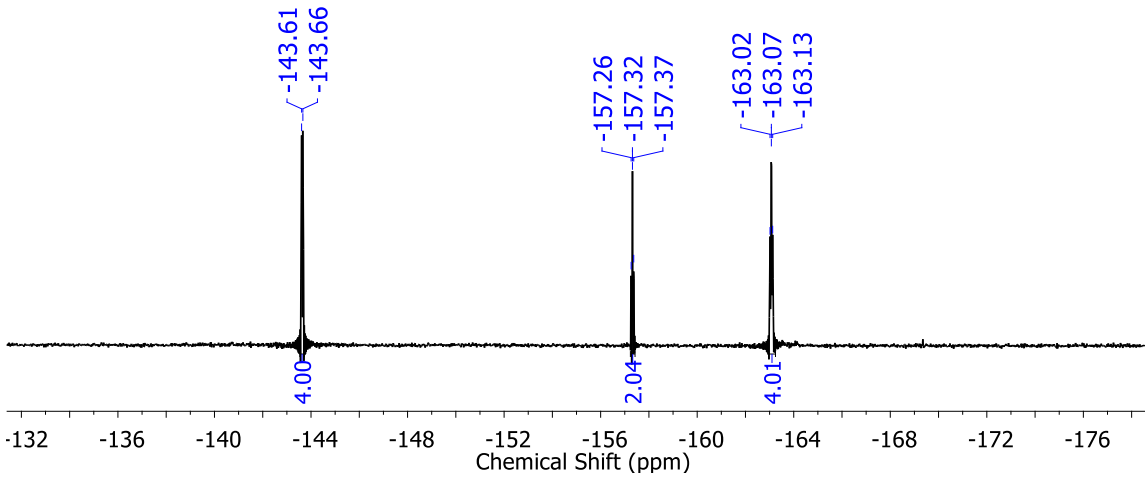
Reflections collected	15032
Independent reflections	3342 [R(int) = 0.0300]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.987 and 0.981
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3342 / 0 / 208
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.1021
R indices (all data)	R1 = 0.0500, wR2 = 0.1102
Extinction coefficient	n/a
Largest diff. peak and hole	0.440 and -0.223 e.$Å^{-3}$

Density Functional Theory (DFT) Calculations

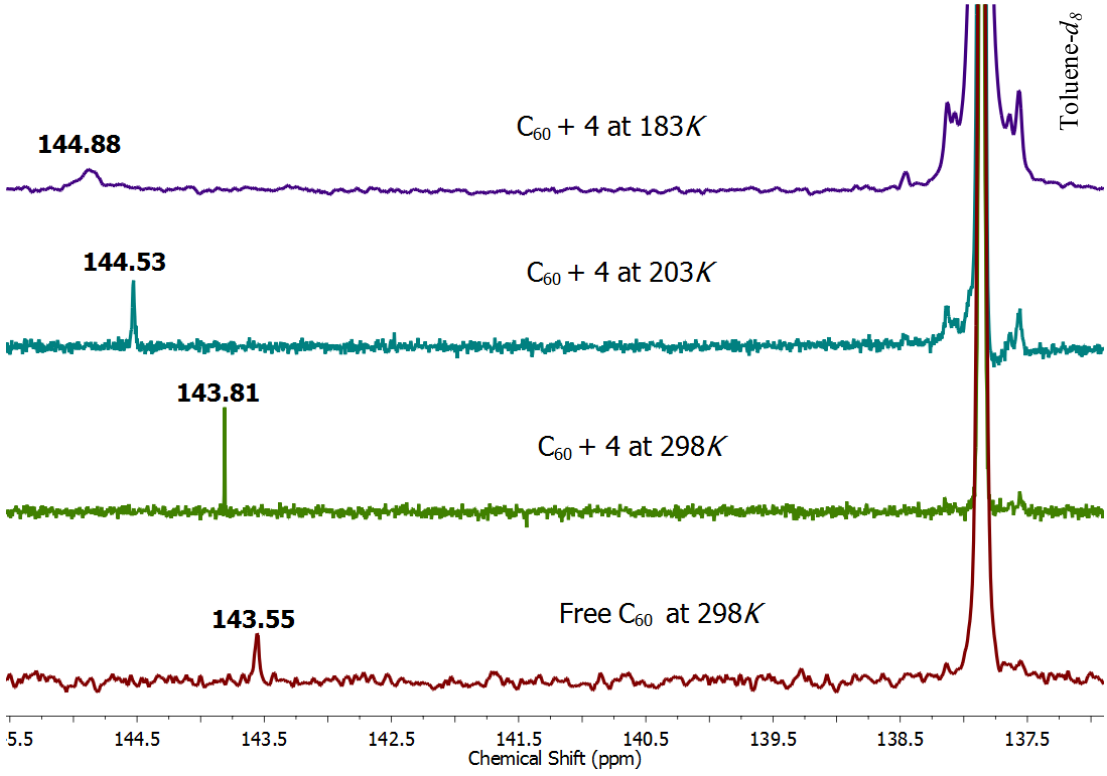
Quantum mechanical calculations were performed with the Gaussian09[1] program suite using a High Performance Computing Cluster facility of IISER PUNE. All calculations were carried out by Density functional theory (DFT) with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP) and 6-31G(d,p) basis set for all the atoms were employed in the calculations. The molecular structures obtained from single crystal analysis were used for geometry optimization. To verify the optimized structures frequency calculations were performed where no imaginary frequency was found. To simulate the steady-state absorption spectra, the time-dependent TD-DFT calculations were employed on the optimized structures. Molecular orbital contributions were determined using GaussSum 2.2.Program package. The global ring centres for the NICS (0) values were designated at the non weighted mean centres of the macrocycles. The NICS (0) value was obtained with gauge independent atomic orbital (GIAO) method based on the optimized geometries.



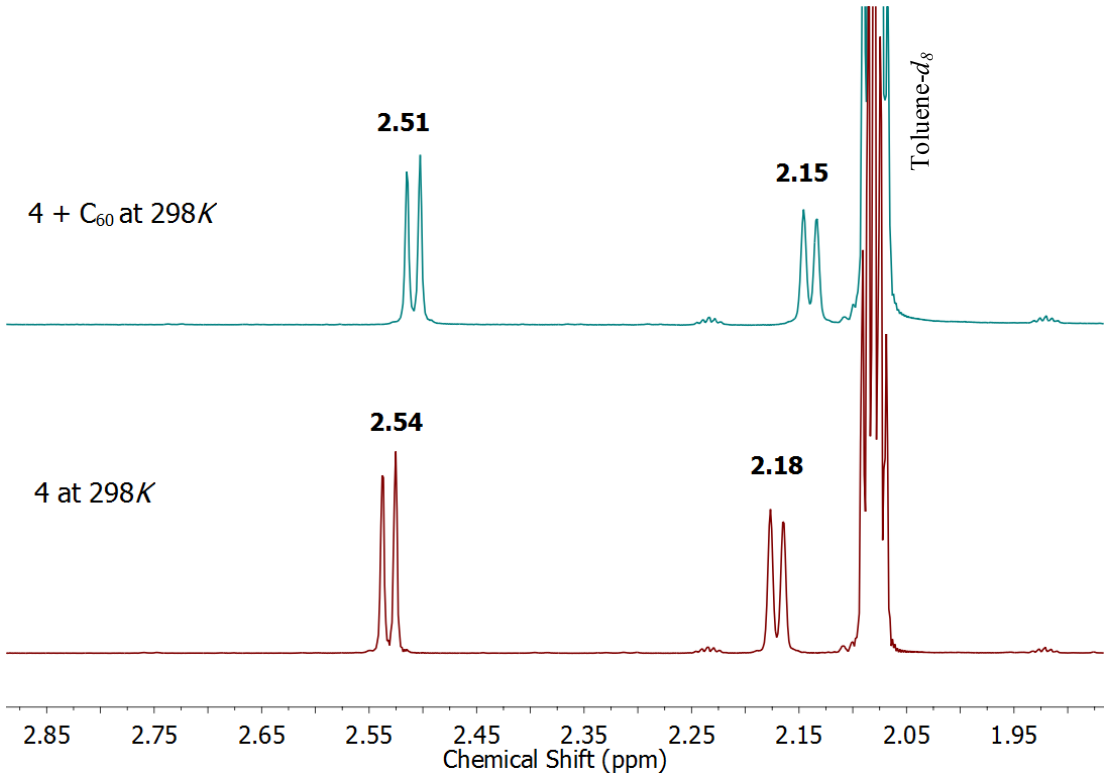
S1: ^{1}H NMR spectrum of **4** in Toluene-$d_{8.}$ at 298*K.* Water peak *



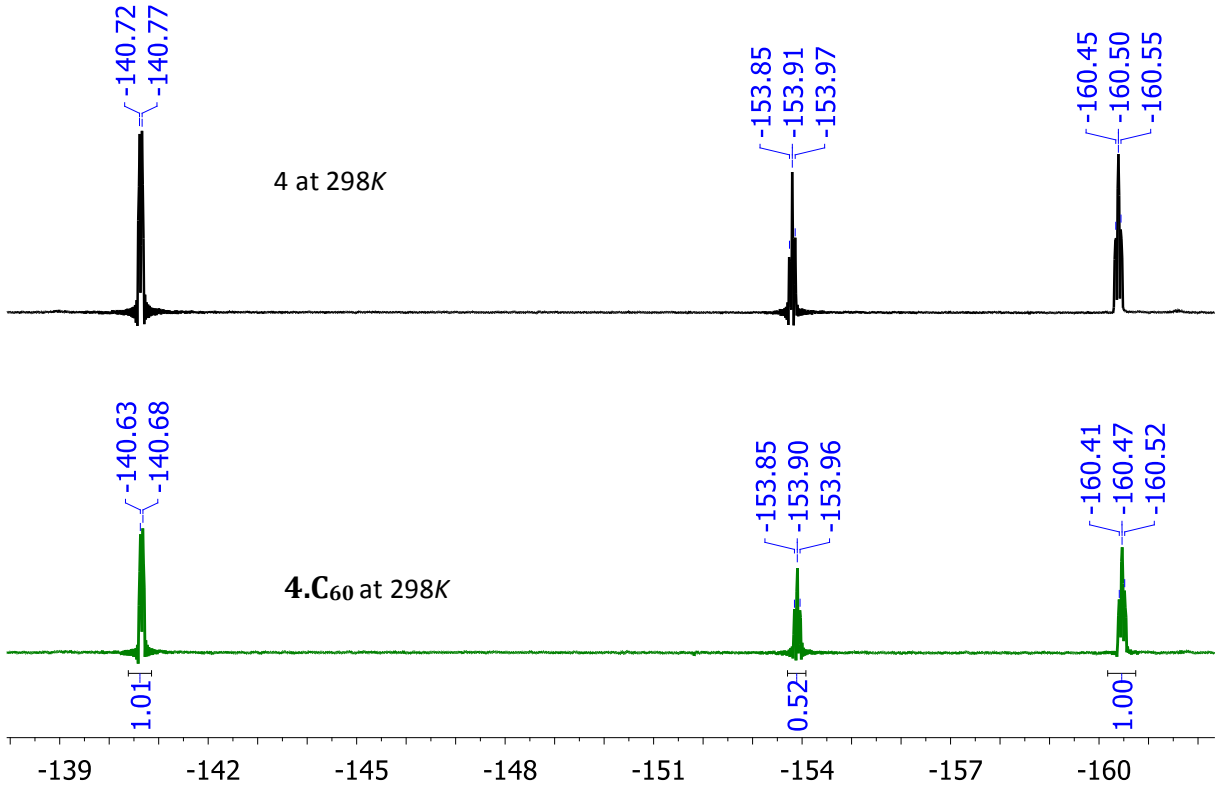
S2: ^{19}F NMR spectrum of **4** in Toluene-d_8 at 298*K.*



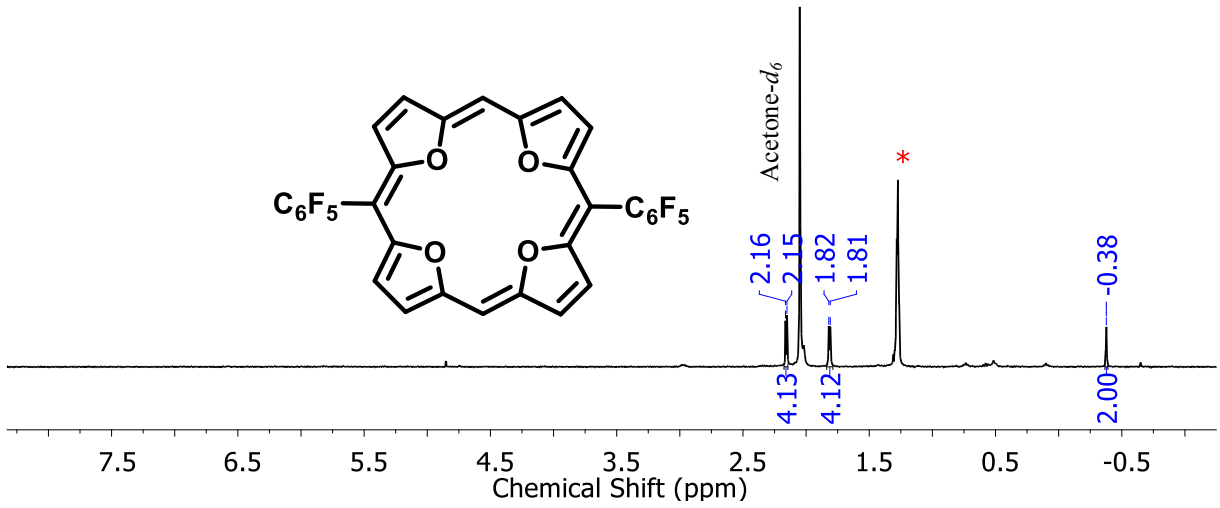
S3: Variable temperature ^{13}C NMR spectrum of **4**.C_{60} complex 1:1 ratio in Toluene-d_8.



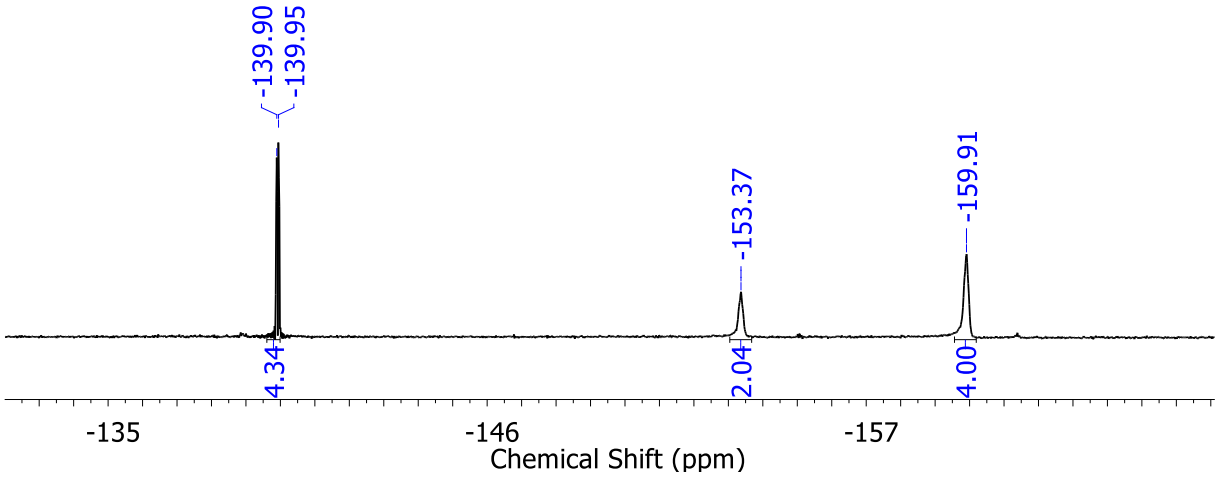
S4: ^{1}H NMR spectrum of **4**.C_{60} complex in Toluene-d_8 at 298K.



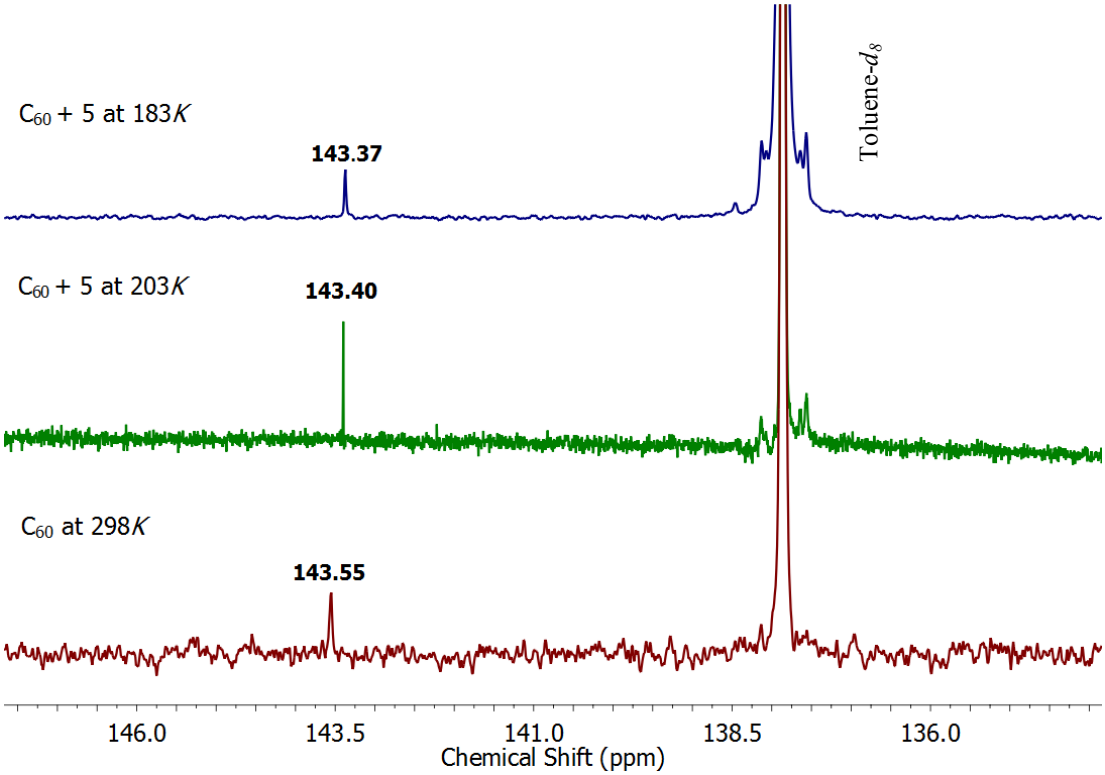
S5: ^{19}F NMR spectrum of **4**.C_{60} complex in Toluene-d_8 at 298*K*.



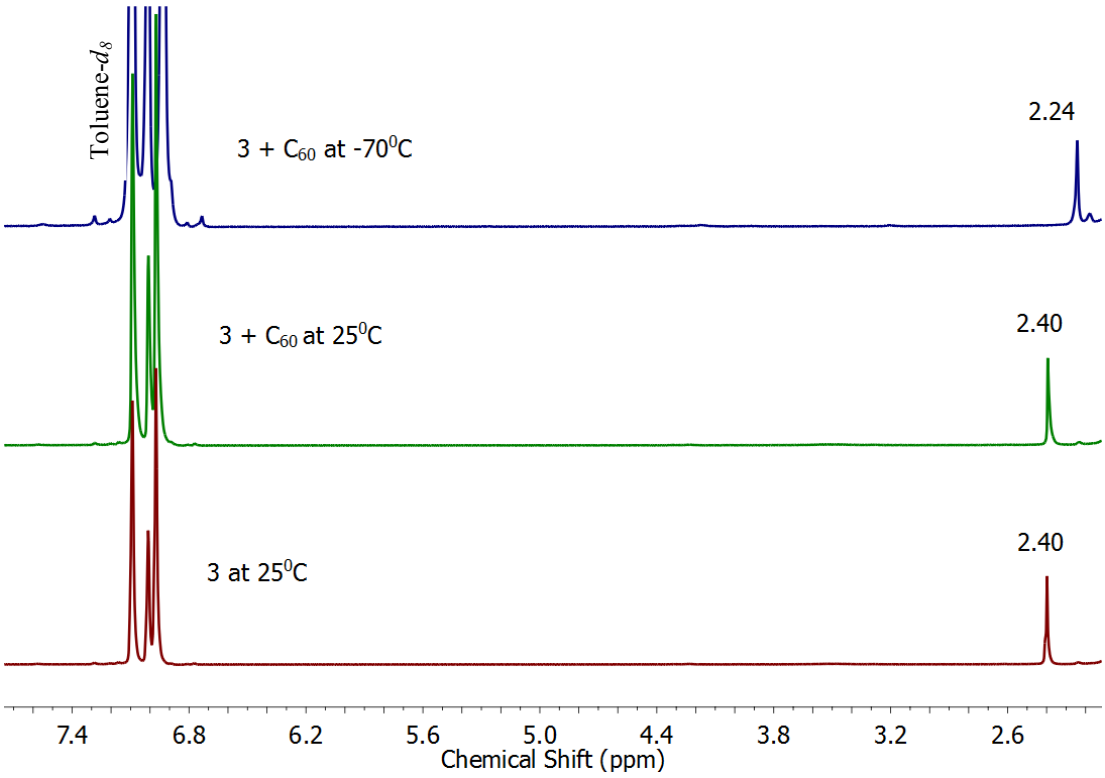
S6: ^{1}H NMR spectrum of **5** in Acetone-d_6 at 298*K*. residual solvent peak *



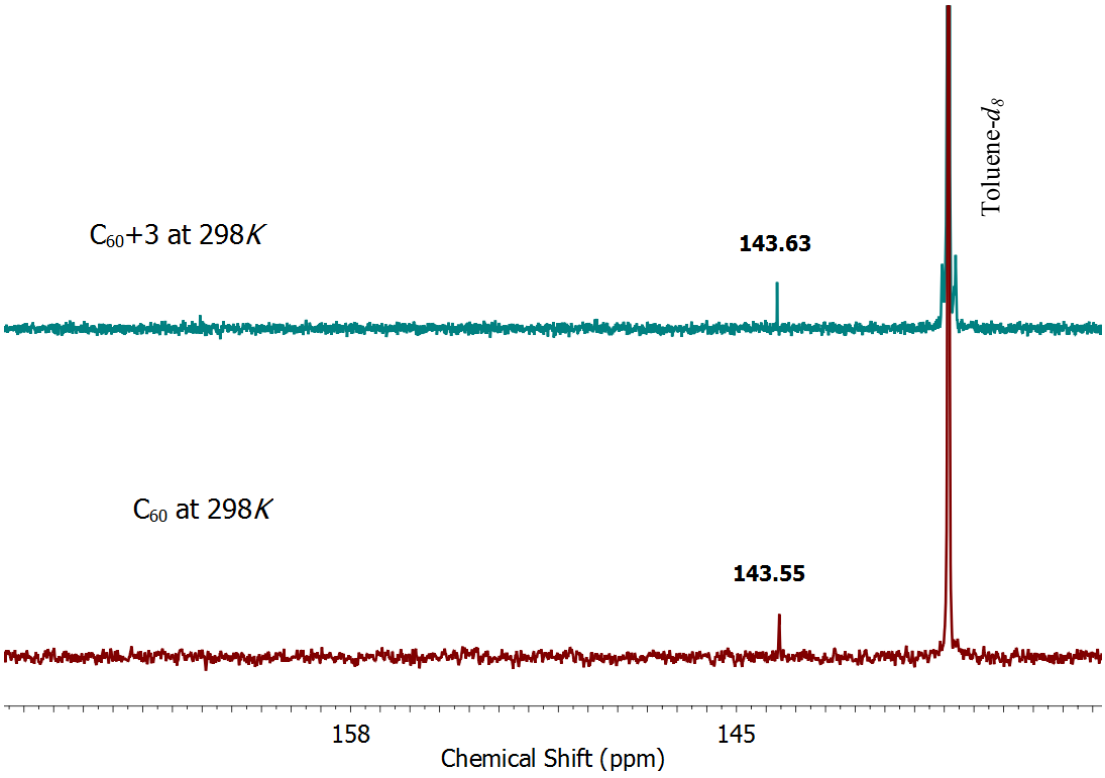
S7: ^{19}F NMR spectrum of **5** in Acetone-d_6 at 298*K*.



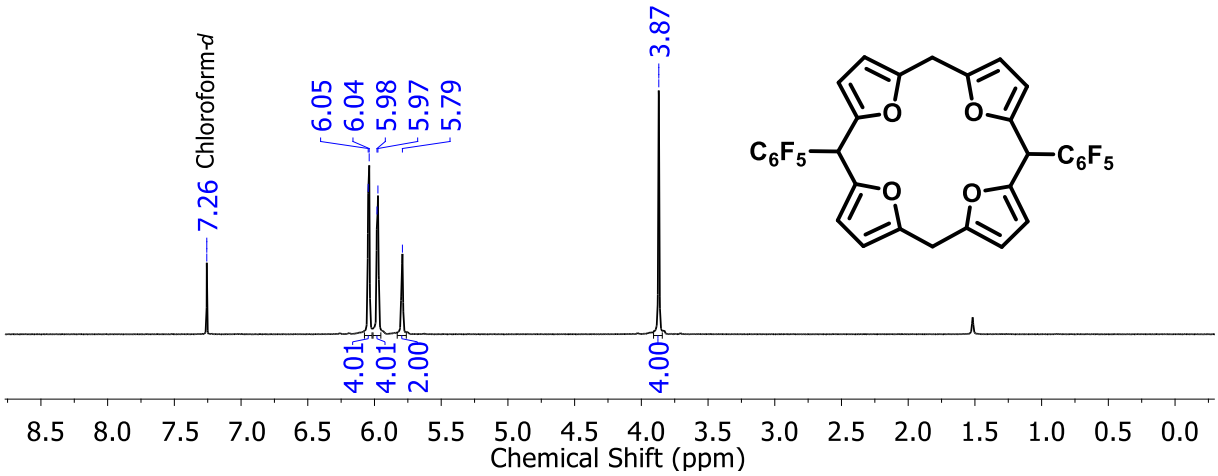
S8: Variable temperature ^{13}C NMR spectrum of **5**.C_{60} complex in Toluene-d_8.



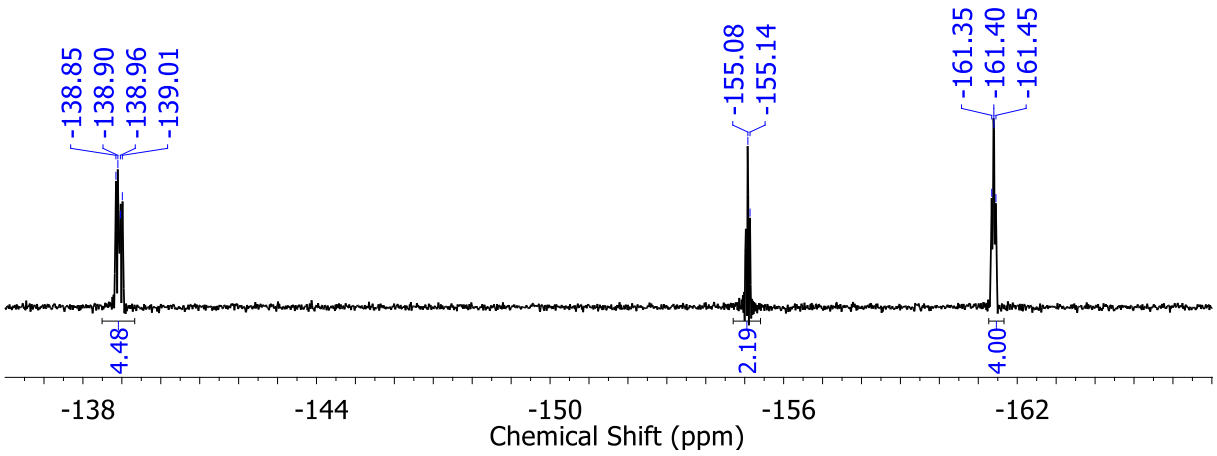
S9: Variable temperature ^{1}H NMR spectrum of **3**.C_{60} complex in Toluene-d_8.



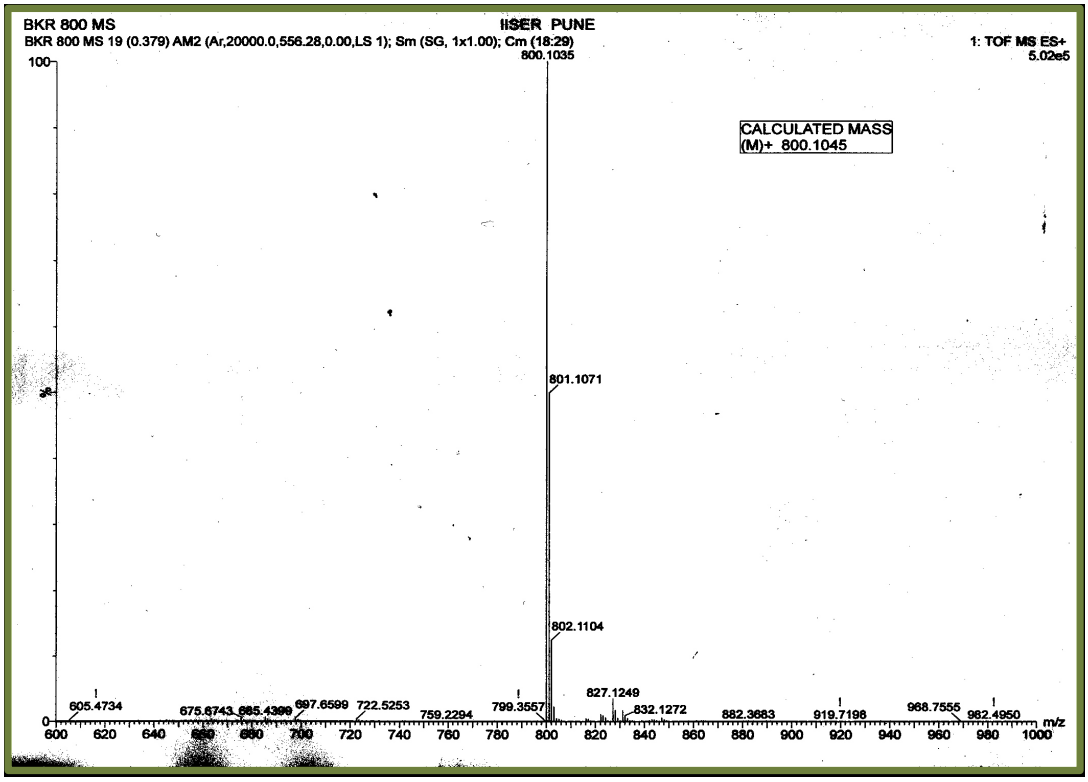
S10: ^{13}C NMR spectrum of **3**.C_{60} complex in Toluene-d_8 at 298K.



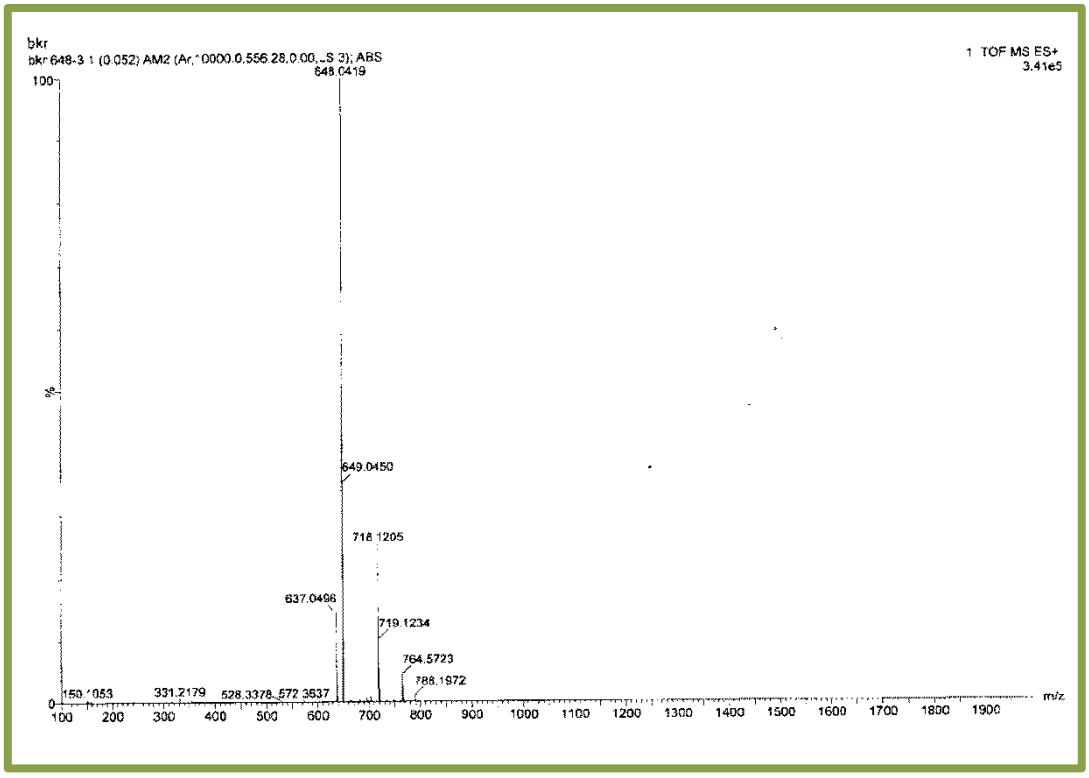
S11: ^{1}H NMR spectrum of **6** in $CDCl_3$ at 298*K*.



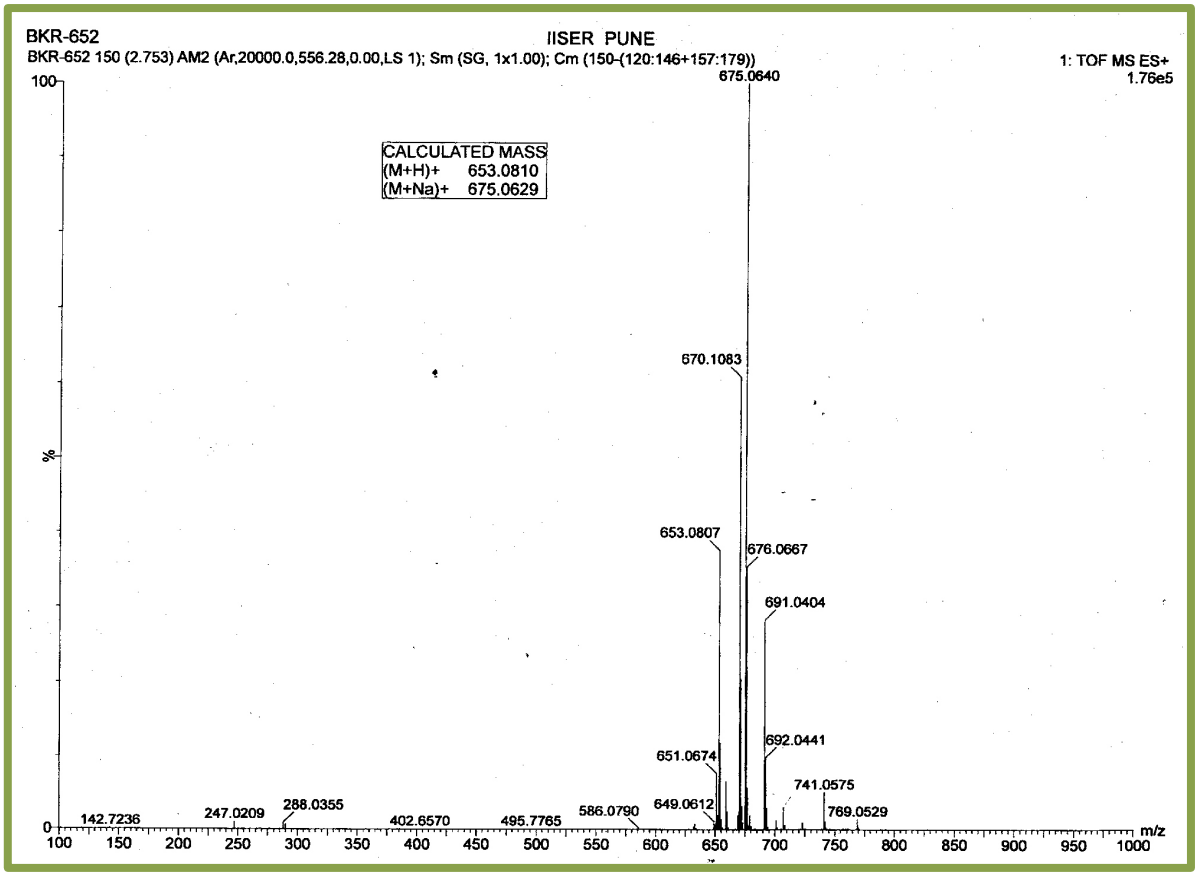
S12: ^{19}F NMR spectrum of **6** in $CDCl_3$ at 298*K*.



S13: HR-ESI-TOF mass spectrum of **4**.



S14: HR-ESI-TOF mass spectrum of **5**.



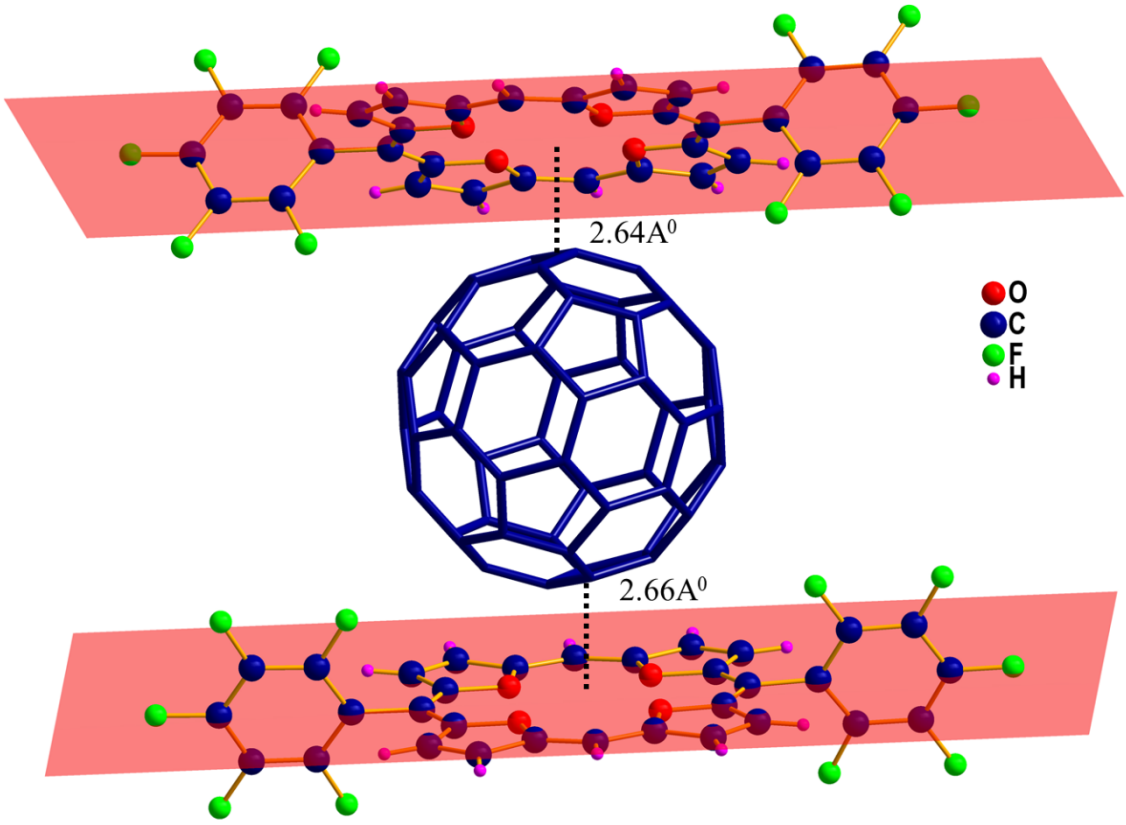
S15: HR-ESI-TOF mass spectrum of **6**.

Cocrystallization method :

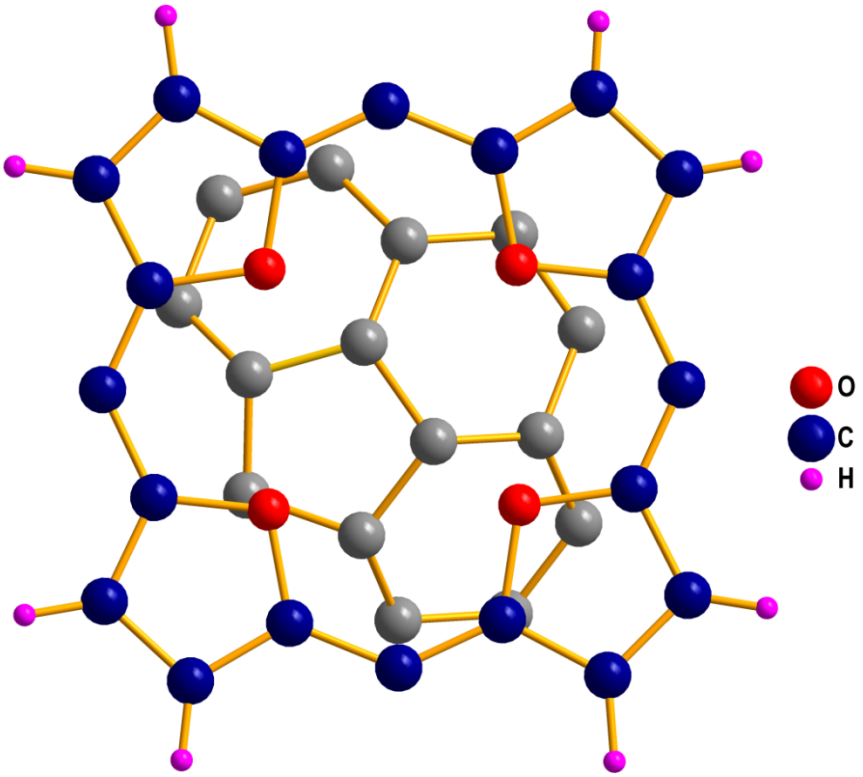
The cocrystals were prepared by slow evaporation of isophlorin-fullerene **(4)**$_3$**.C$_{60}$**, **4.(C$_{60}$)$_2$** and **5.C$_{60}$** in acetone and toluene combination. Complex **3.C$_{60}$** crystalized in benzene. We attempted different ratios of C_{60}/isophlorin, but complex **3.C$_{60}$** and **5.C$_{60}$** selectively cocrystallized in 1:1 fashion. In case of isophlorin **4**, it has been cocrystallized with C_{60} in 1:2 and 2:1 ratio displayed in its asymmetric unit of **4.(C$_{60}$)$_2$** and **(4)$_3$.C$_{60}$** respectively.

Isophlorin **5** | **C$_{60}$** | **5.C$_{60}$** complex

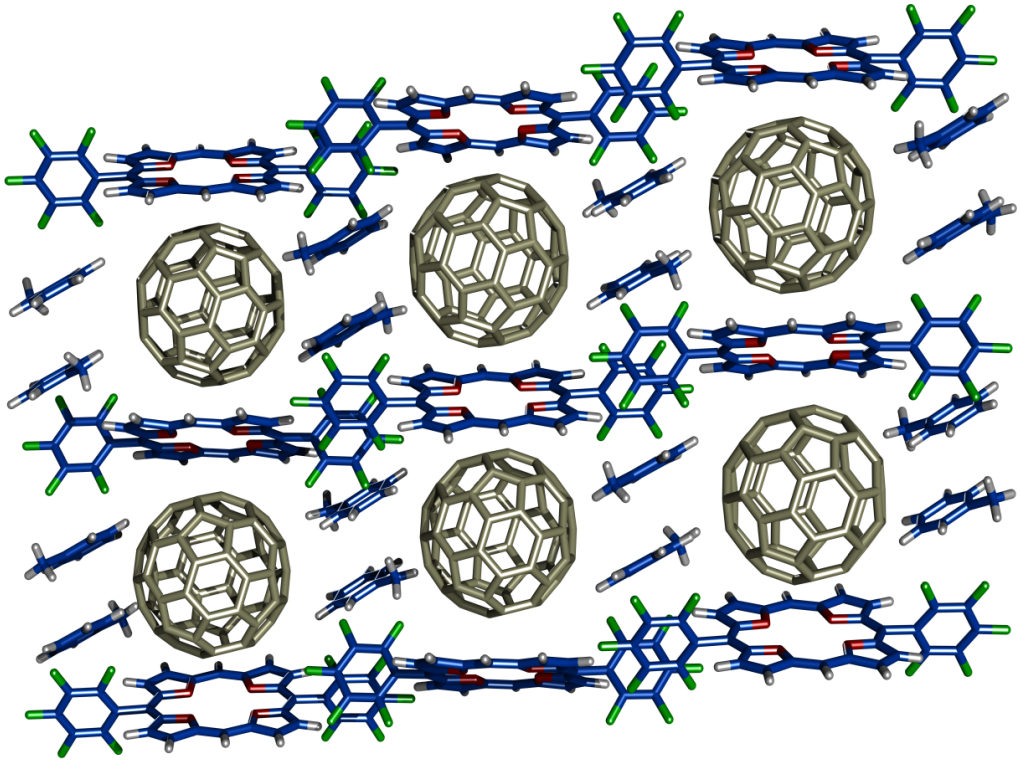
S16: Cocrystallization of isophlorin and C_{60}. The color of the complex solution **5.C_{60}** different from that of the individuvals.



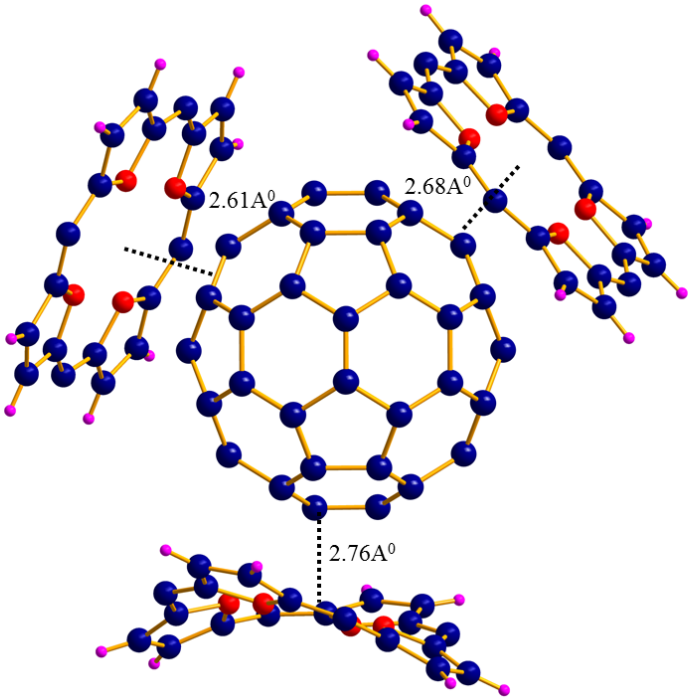
S17: Close approach of C_{60} to the molecular plane of the isophlorin in **5.C_{60}** complex.



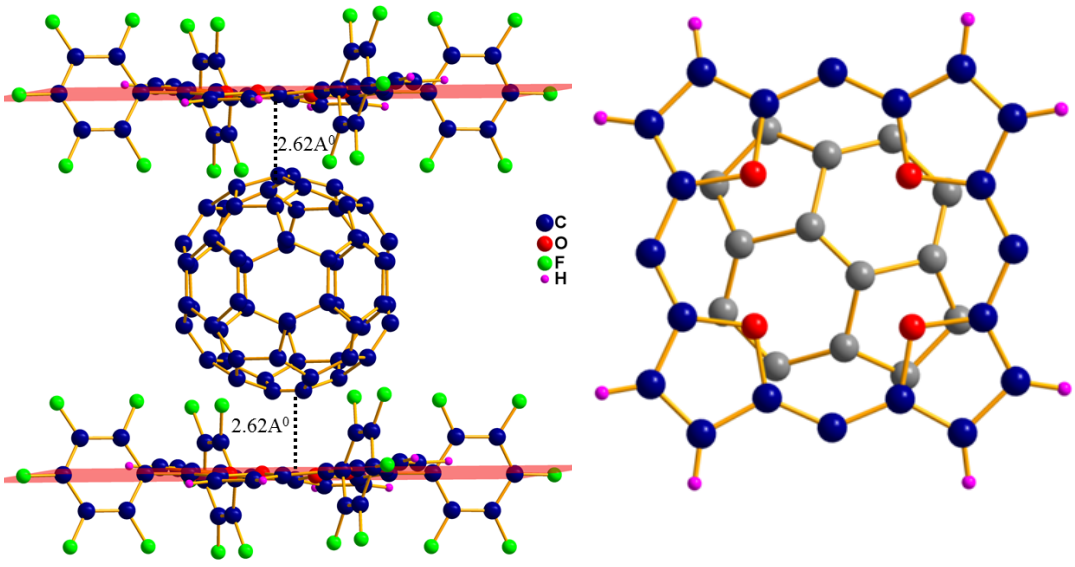
S18: The electron-deficient 5:6 ring juncture, C-C bond of fullerene lies over the centre of the isophlorin in **4.(C60)$_2$** and **5.C$_{60}$** For clarity, the partial fullerene is in gray color.



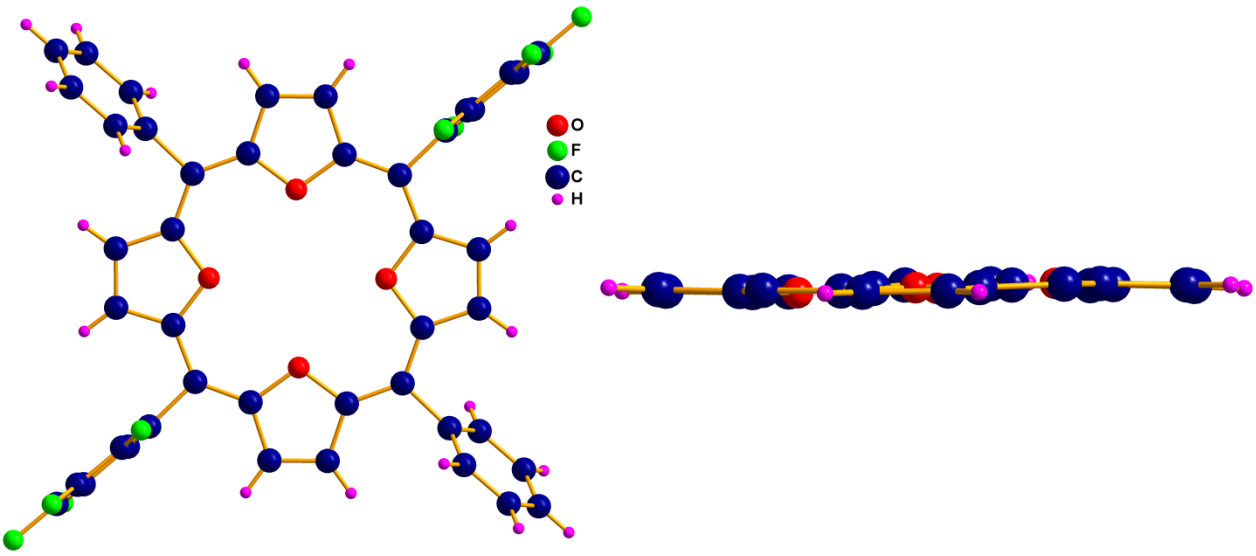
S19: Alternating layered isophlorin sheets (stick model) separated by C_{60} molecules (gray color) in **5.C$_{60}$** complex. channels between columns occupied by Toluene molecules.



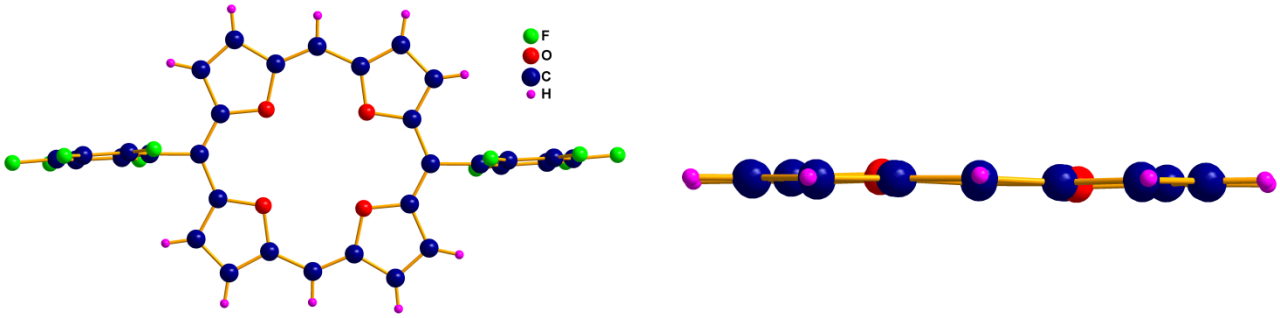
S20: Close approach of C_{60} to the molecular plane of the isophlorin in **(4)$_3$.C$_{60}$** complex.



S21: Close approach of C_{60} to the molecular plane of the isophlorin in **3.C$_{60}$** complex (left). The electron-rich 6:6 ring juncture, C-C bond of fullerene lies over the centre of the isophlorin ring **3** (right). For clarity, the partial fullerene is in gray color and meso substituents of macrocycle are omitted.



S22: Top view (left) Side view (right) Molecular structure of **4**. Meso-substituents are omitted for clarity.

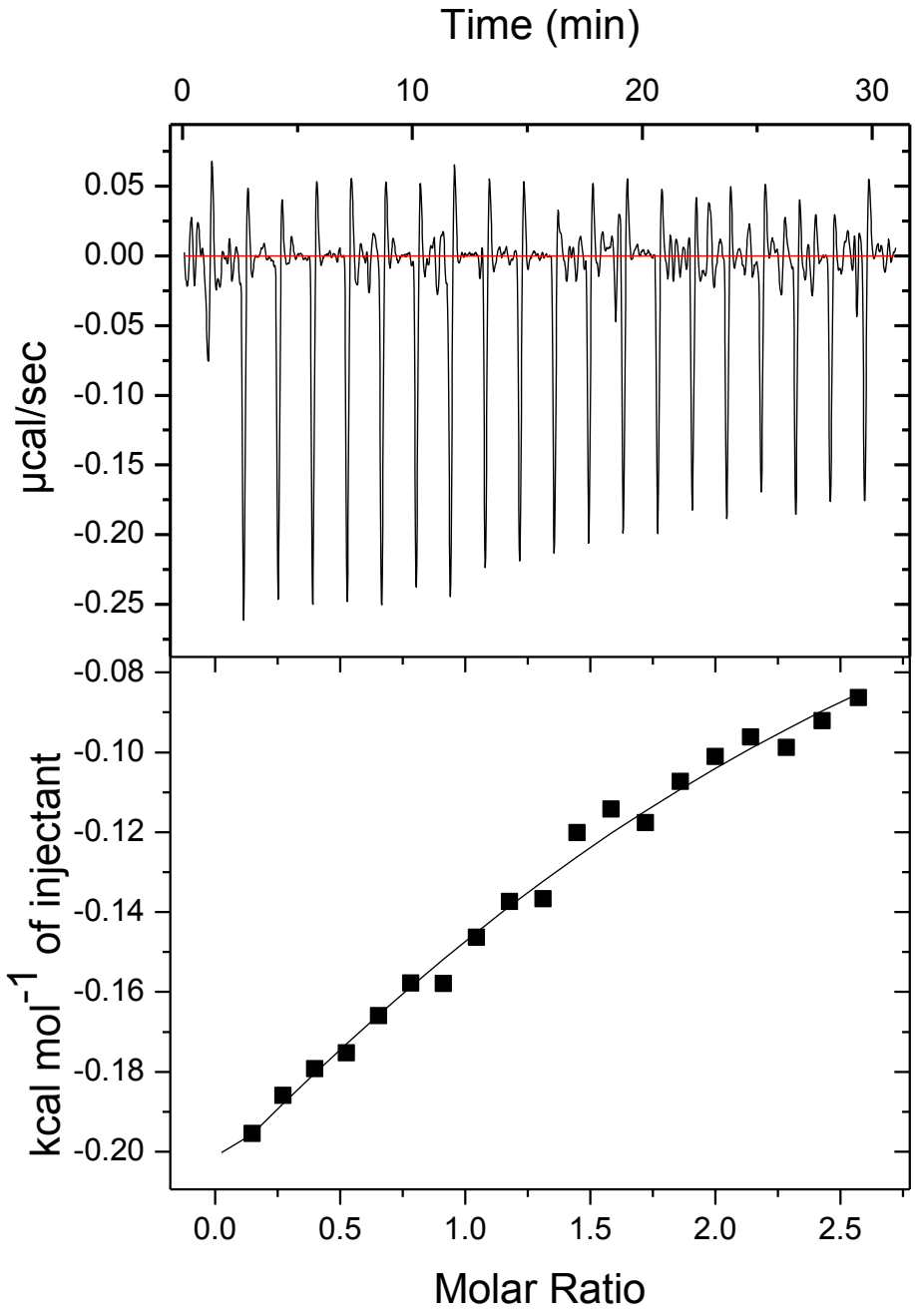


S23: Top view (left) Side view (right) Molecular structure of **5**. Meso-substituents are omitted for clarity.

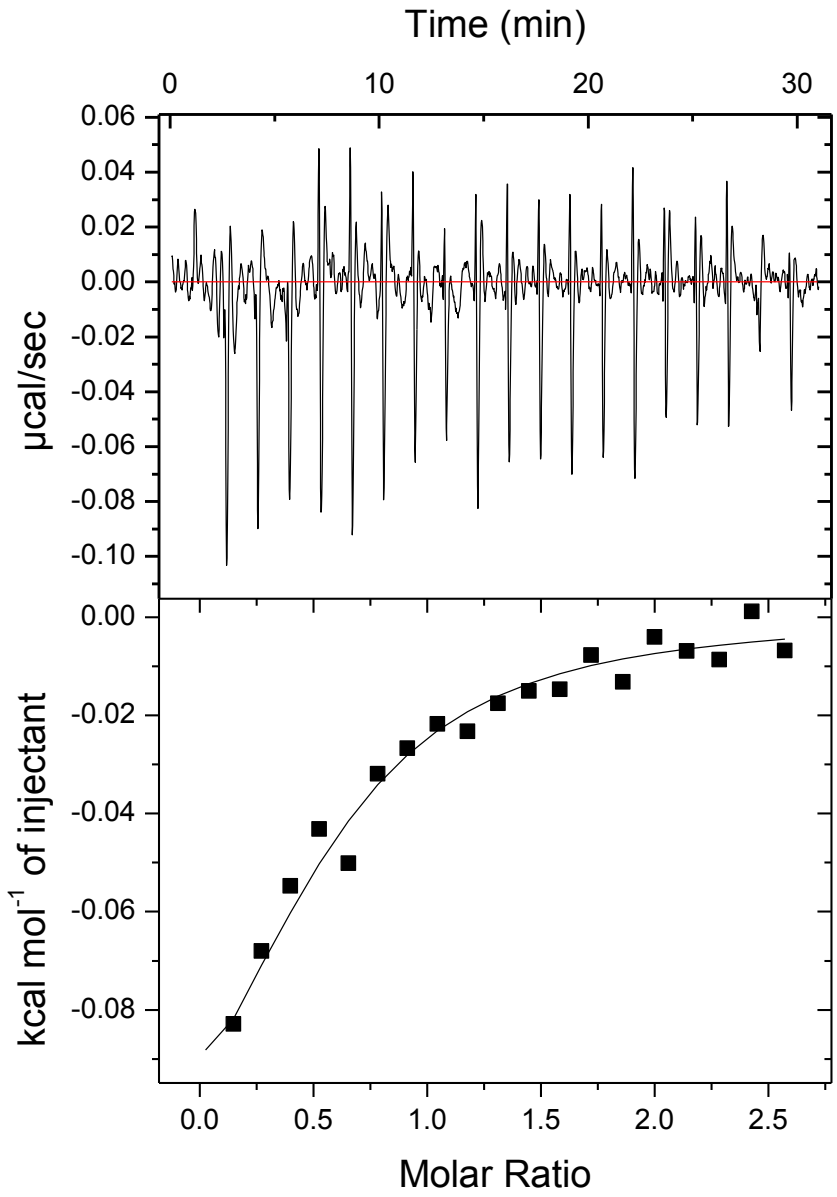
Determination of Binding constant:

Isothermal titration calorimetry (ITC) was used to quantify the complexations of the host (Isophlorin **4** or **5**) and guest (C_{60}) molecules in solution. The titration was carried out in chloroform:toluene (1:1 v/v) medium for host **5** and only toluene for host **4** at 25 ^{0}C using an isothermal titration calorimeter (Microcal iTC-200) with stirring at 1000 rpm. About 200 µl of host (**4** or **5**) solution was titrated with the guest (C_{60}) solution. A typical titration experiment consisted of 20 consecutive injections of 2 µl volume and 9 s duration each, with a 90 s interval between injections. Heat of dilution of the guest (C_{60}) were determined by injecting the guest solution into the solvent alone and the total observed heats of binding were corrected for the heat of dilution. A single set binding model fitted the binding isotherm, from where binding constant (K), binding stoichiometry (N), change of enthalpy (ΔH) and the change of entropy

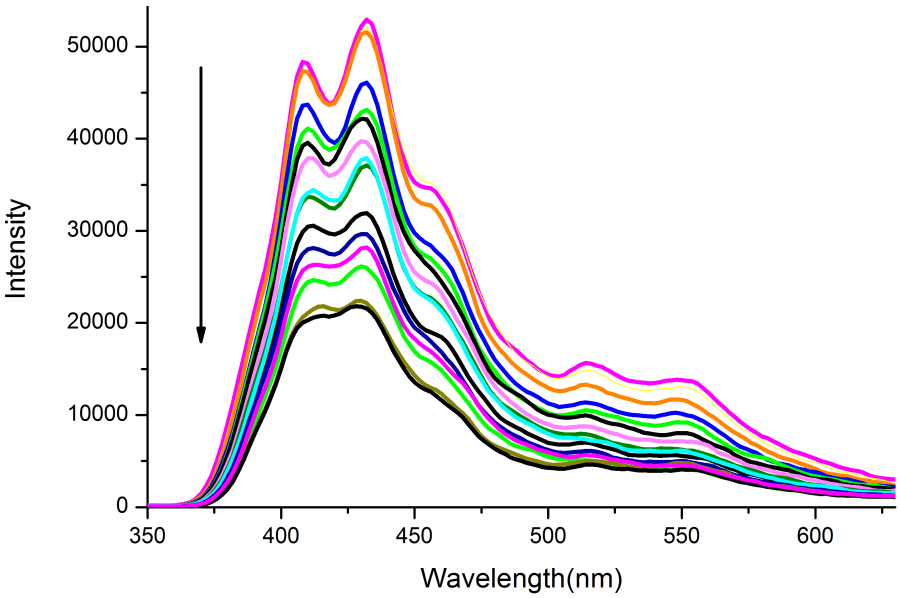
for the binding (ΔS) were obtained. For both the samples we have done solvent correction.



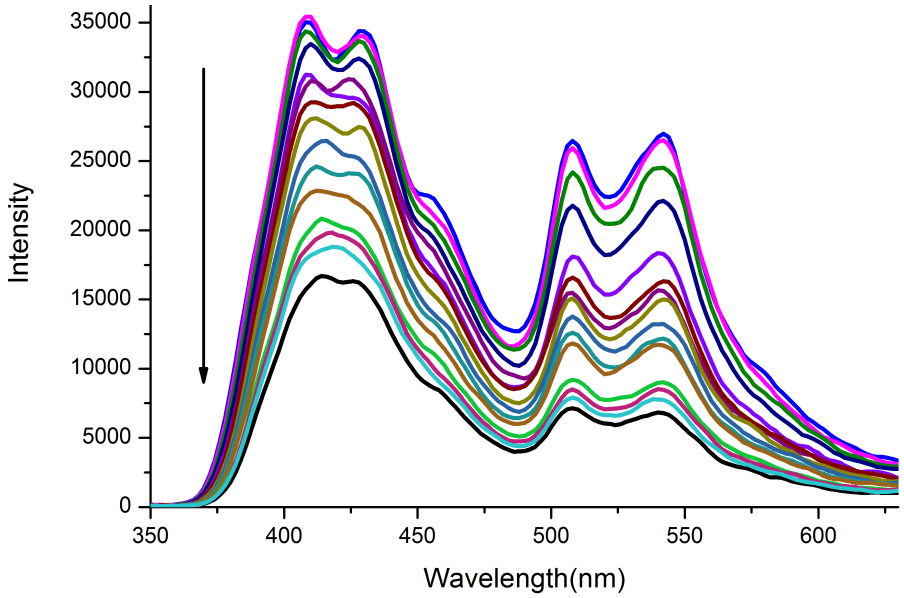
S24: ITC profiles for the binding of guest (C_{60}) to host (**4**) at 25 ^{0}C in toluene. Top: raw data for the sequential 2 µl injection of $\mathbf{C_{60}}$ (0.4 mM) into **4** (5 mM). Bottom: plot of the heat evolved (kcal) per mole of $\mathbf{C_{60}}$ added, corrected for the heat of $\mathbf{C_{60}}$ dilution, against the molar ratio of $\mathbf{C_{60}}$ to **4**. The data (filled squares) were fitted to a single set binding model and the solid line represents the best fit.



S25: ITC profiles for the binding of guest (C_{60}) to host (**5**) at 25 ^{0}C in chloroform :toluene (1 : 1 v/v). Top: raw data for the sequential 2 µl injection of C_{60} (0.4 mM) into **5** (5 mM). Bottom: plot of the heat evolved (kcal) per mole of C_{60} added, corrected for the heat of C_{60} dilution, against the molar ratio of C_{60} to **5**. The data (filled squares) were fitted to a single set binding model and the solid line represents the best fit.



S26: Fluorescence titration spectra in toluene at 25 °C: Isophlorin **4** (1 µM, excited at 326 nm; slit = 2/3 nm) with 0–30 µM of $\mathbf{C_{60}}$.



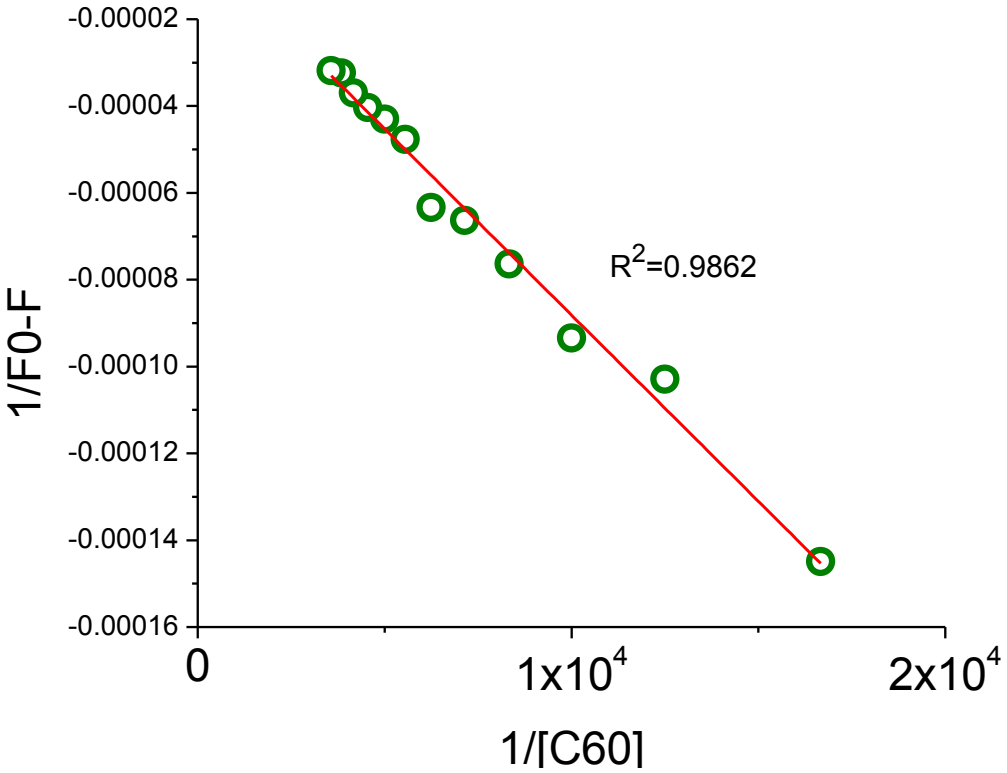
S27: Fluorescence titration spectra in toluene at 25 °C: Isophlorin **5** (1 µM, excited at 326 nm; slit = 2/3 nm) with 0–30 µM of $\mathbf{C_{60}}$.

Benesi-Hildebrand plot for binding studies of [C_{60}] towards Isophlorin (4 and 5).

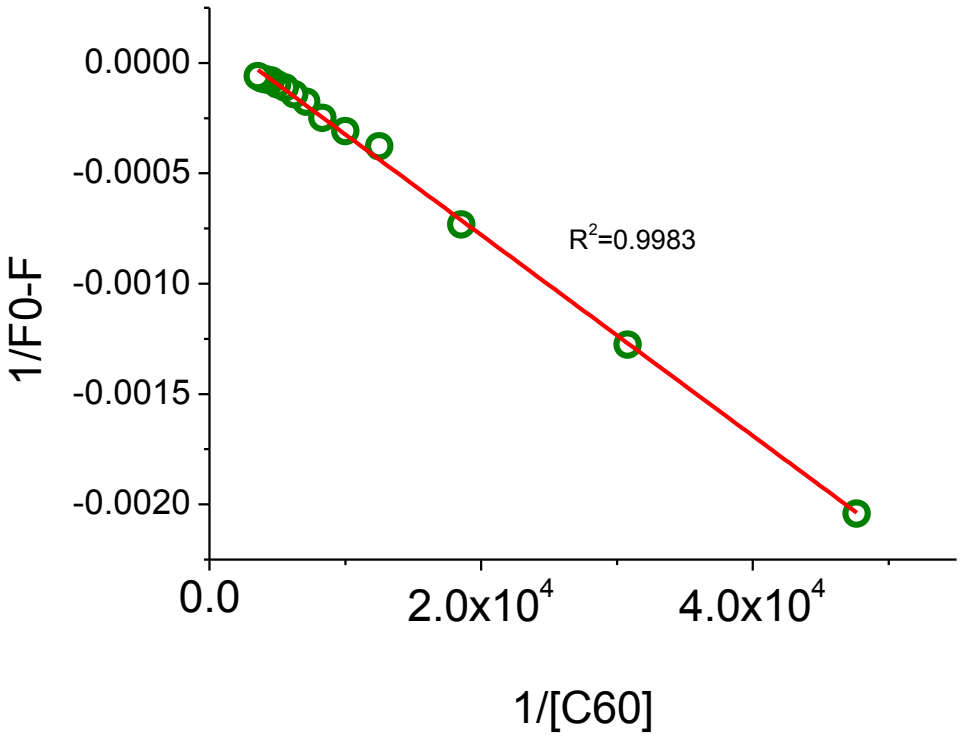
In order to determine the stoichiometry as well as binding constants of the inclusion complexes, the fluorescence intensity was analyzed using Benesi-Hildebrand (BH) plot[2] using the following equation (1);

$$\frac{1}{F-F_0} = \frac{1}{K(F_1-F_0)[host]} + \frac{1}{F_1-F_0} \qquad (1)$$

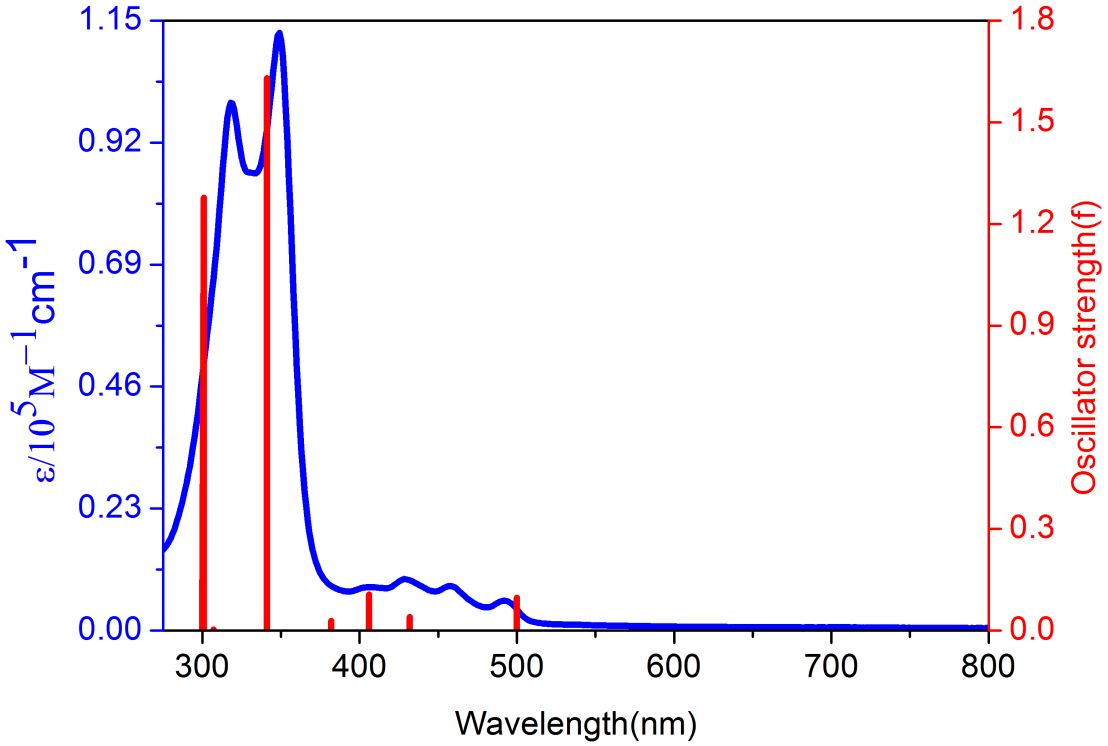
where F_0, F and F_1 are the fluorescence intensities of Isophlorin in absence, presence of host, and in the inclusion complex, respectively.



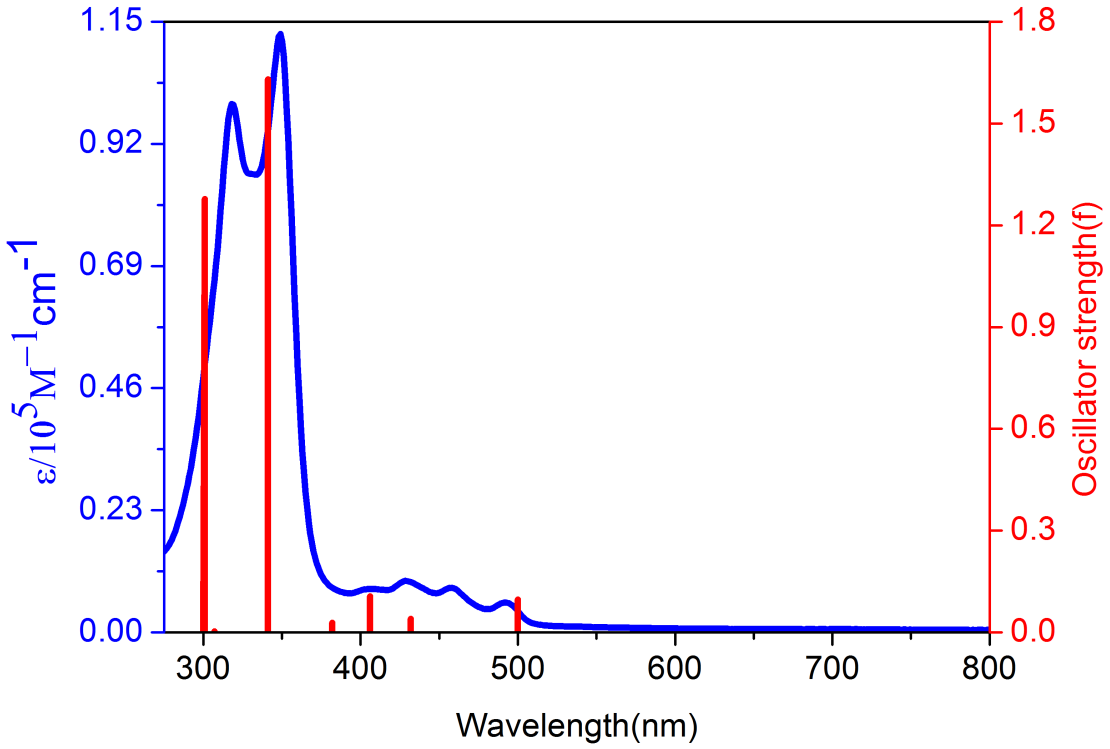
S28: Benesi-Hildebrand plot of **4** (1 μM) for varying [C_{60}] (0 to 30 μM) Fluorescence titration by using λ_{Ext} = 326. Good linear fit confirms the 1: 1 binding stoichiometry. The association constants (K) is estimated to be $3.712 \times 10^3\ M^{-1}$.



S29: Benesi-Hildebrand plot of **5** (1 μM) for varying [C_{60}] (0 to 30 μM) Fluorescence titration by using λ_{Ext} = 326. Good linear fit confirms the 1: 1 binding stoichiometry. The association constants (K) is estimated to be 1.328 × 10^3 M^{-1}.



S30: The steady state absorption spectra (blue line) of **4** recorded in CH_2Cl_2 along with the theoretical vertical excitation energies (red bar) obtained from TD-DFT calculations carried out at the B3LYP/6-31G(d,p) level.



S31: The steady state absorption spectra (blue line) of **5** recorded in CH_2Cl_2 along with the theoretical vertical excitation energies (red bar) obtained from TD-DFT calculations carried out at the B3LYP/6-31G(d,p) level.

No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength	Major contributions
1	6471.83744	1545.156239	0	HOMO→LUMO (101%)
2	19934.1304	501.6521814	0.0791	H-1→LUMO (29%), HOMO→L+1 (70%)
3	22780.48064	438.9723008	0.0242	HOMO→L+3 (94%)
4	24325.04304	411.0989643	0.1275	H-2→LUMO (72%), HOMO→L+10 (15%)
5	26013.97968	384.4086957	0.0289	HOMO→L+4 (91%)
6	26018.01248	384.3491123	0.0001	HOMO→L+5 (96%)
7	26188.19664	381.8514172	0.0408	HOMO→L+6 (95%)
8	27488.37136	363.7901958	0.0898	HOMO→L+8 (81%), HOMO→L+10 (12%)
9	28339.29216	352.8669645	1.6066	H-1→LUMO (57%), HOMO→L+1 (25%)
10	30631.53568	326.4609422	0.0087	H-4→LUMO (98%)
11	30786.3952	324.8188018	0.2017	H-6→LUMO (83%)
12	31157.4128	320.9509103	0.1771	H-8→LUMO (78%)
13	32350.31504	309.1160005	0.0011	HOMO→L+12 (99%)
14	32867.32	304.2535868	1.3052	H-8→LUMO (13%), H-2→LUMO (20%), HOMO→L+10 (58%)
15	33157.6816	301.5892402	0.1051	H-10→LUMO (94%)
16	36476.676	274.1477869	0.0087	H-12→LUMO (97%)

17	37571.17792	266.1614715	0.0016	H-1→L+2 (97%)

S32: Selected TD-DFT (B3LYP/6-31G (d, p)) calculated energies, oscillator strengths and compositions of the major electronic transitions of **4**.

No.	Energy (cm-1)	Wavelength (nm)	Osc. Strength(f)	Major contributions
1	6433.92912	1554.260206	0	HOMO→LUMO (101%)
2	32497.91552	307.7120437	0.0031	HOMO→L+8 (99%)
3	38363.21984	260.6663372	0.0032	H-1→L+2 (95%)
4	30504.90576	327.816125	0.007	H-4→LUMO (98%)
5	40865.97552	244.702344	0.0084	H-3→L+1 (41%), H-1→L+5 (33%)
6	36566.20416	273.4765675	0.0118	H-8→LUMO (96%)
7	38771.3392	257.922481	0.0138	H-2→L+2 (97%)
8	26175.29168	382.0396778	0.0288	HOMO→L+4 (93%)
9	39618.2272	252.409073	0.0331	H-10→LUMO (97%)
10	23106.33088	432.781823	0.0404	HOMO→L+3 (91%)
11	19984.13712	500.3968868	0.0972	H-1→LUMO (25%), HOMO→L+1 (73%)
12	24587.9816	406.7027608	0.1063	H-2→LUMO (69%), HOMO→L+6 (23%)
13	33291.57056	300.3763365	0.1509	H-6→LUMO (93%)
14	33129.452	301.8462243	1.2777	H-2→LUMO (26%), HOMO→L+6 (72%)
15	29245.8656	341.9286725	1.6306	H-1→LUMO (62%), HOMO→L+1 (26%)

S32: Selected TD-DFT (B3LYP/6-31G (d, p)) calculated energies, oscillator strengths and compositions of the major electronic transitions of **5**.

Macrocycle	**NICS(0) ppm[a]**	**Huckel 4nπ rule**
4	38.13	Antiaromatic
5	39.64	Antiaromatic

S33: Computational parameters to classify ring current effects in 20π core modified porphyrins. [a]Determined from quantum chemical calculations.

S34: Coordinates for optimized structure **4**

S.No	Atom	X	Y	Z
1	O	1.38359100	-1.56719100	-0.14078700
2	O	1.54972100	1.41043600	-0.12385600
3	F	5.18241800	-1.88083200	-1.59306700
4	F	4.76593600	1.45693800	1.75919800
5	F	9.01148500	-0.11505400	0.48685200
6	F	7.85490800	-1.82053800	-1.30683800
7	F	7.44798200	1.52467800	2.00854400
8	C	3.38520600	-0.21836100	-0.08316200
9	C	1.35591900	2.70661900	-0.53958200
10	C	2.81292200	1.04556100	-0.50376500
11	C	1.06970100	-2.90136000	0.08065300
12	C	4.86461200	-0.21637200	0.07726300
13	C	-0.16000300	-3.43791500	-0.18552900
14	C	2.71978600	-1.39276600	0.14001000
15	C	-0.30412300	-4.92334800	-0.13004900
16	C	5.70381900	-1.03792700	-0.68937800
17	C	3.41058700	2.08322500	-1.18590000
18	H	4.40196900	2.07139500	-1.61325200
19	C	2.47995400	3.14687500	-1.20547500
20	H	2.60588600	4.12285000	-1.64862800
21	C	5.49885200	0.64687100	0.98451000
22	C	3.24511900	-2.64049400	0.63766800
23	H	4.25463500	-2.78493200	0.99111700
24	C	2.24567300	-3.55308200	0.59663600
25	H	2.28231300	-4.58609000	0.90709200
26	C	7.68265500	-0.14596500	0.35273600
27	C	7.09045300	-1.01822300	-0.55563600
28	C	-1.30102100	-5.51825100	0.66372100
29	H	-1.96698800	-4.88508200	1.24109900
30	C	6.88199300	0.69337500	1.12518500
31	C	-1.42996900	-6.90379800	0.72436600
32	H	-2.19814700	-7.34484700	1.35286700
33	C	0.54329600	-5.75965900	-0.87625600
34	H	1.29535500	-5.31277000	-1.51893500
35	C	-0.57334300	-7.72411900	-0.01438900

36	H	-0.67793200	-8.80410000	0.03098900
37	C	0.41177000	-7.14742600	-0.81616300
38	H	1.07295500	-7.77605300	-1.40552900
39	O	-1.38360200	1.56716600	-0.14076200
40	O	-1.54972500	-1.41045400	-0.12387300
41	F	-4.76608700	-1.45677400	1.75937700
42	F	-5.18232000	1.88071500	-1.59320300
43	F	-9.01152900	0.11523200	0.48669300
44	F	-7.44815200	-1.52441000	2.00860700
45	F	-7.85483100	1.82052100	-1.30708800
46	C	-3.38521700	0.21832400	-0.08309400
47	C	-1.35599300	-2.70669500	-0.53944900
48	C	-2.81299800	-1.04563500	-0.50362300
49	C	-1.06971000	2.90133100	0.08070200
50	C	-4.86464000	0.21639700	0.07729500
51	C	0.15997600	3.43788700	-0.18556600
52	C	-2.71978700	1.39273100	0.14007000
53	C	0.30417200	4.92330800	-0.13005000
54	C	-5.49894300	-0.64675500	0.98458300
55	C	-3.41076400	-2.08340200	-1.18552100
56	H	-4.40220600	-2.07164100	-1.61273500
57	C	-2.48011300	-3.14702700	-1.20515800
58	H	-2.60611500	-4.12305100	-1.64817800
59	C	-5.70378500	1.03791900	-0.68945300
60	C	-3.24510700	2.64044300	0.63778000
61	H	-4.25460200	2.78486500	0.99129700
62	C	-2.24566100	3.55303400	0.59674600
63	H	-2.28228600	4.58602000	0.90727900
64	C	-7.68269000	0.14609700	0.35264400
65	C	-6.88209100	-0.69319900	1.12520300
66	C	-0.54325600	5.75970100	-0.87615800
67	H	-1.29538800	5.31288400	-1.51880000
68	C	-7.09042500	1.01826400	-0.55577400
69	C	-0.41163300	7.14745700	-0.81602800
70	H	-1.07282400	7.77614800	-1.40532100
71	C	1.30119300	5.51812200	0.66363000
72	H	1.96717800	4.88489300	1.24092200
73	C	0.57358800	7.72406100	-0.01432300
74	H	0.67825200	8.80403400	0.03108200
75	C	1.43023500	6.90366000	0.72431500
76	H	2.19850300	7.34463200	1.35276000

S35: Coordinates for optimized structure **5**

S.No	Atom	X	Y	Z
1	O	-1.534721	-1.380746	-0.251796
2	O	1.557765	-1.408472	-0.269085
3	C	7.134039	-0.628253	1.043796
4	C	7.157785	0.613012	-1.021728
5	C	5.019207	0.027926	0.007998
6	C	3.525954	0.0298	-0.0008
7	C	5.742018	-0.595772	1.032697
8	C	5.764446	0.623191	-1.016473
9	C	7.844205	-0.018906	0.011674
10	C	3.523781	-2.45088	-0.594719
11	H	4.584752	-2.622963	-0.687053
12	C	-0.025215	-3.248212	-0.666846
13	H	-0.035241	-4.308315	-0.901878
14	C	-1.262741	-2.707319	-0.54236
15	C	2.918061	-1.249216	-0.283326
16	C	1.298163	-2.720656	-0.573681
17	C	-2.904636	-1.222868	-0.240875
18	C	2.486036	-3.391634	-0.777258
19	H	2.582586	-4.437015	-1.032888
20	C	-3.513594	-2.50229	-0.531286
21	H	-4.576772	-2.675328	-0.59835
22	C	-2.516355	-3.398392	-0.708043
23	H	-2.602289	-4.450501	-0.942521
24	F	5.141135	1.237968	-2.030706
25	F	7.792503	-1.22874	2.041936
26	F	5.093287	-1.184581	2.04511
27	F	7.837803	1.197478	-2.015083
28	F	9.179564	-0.037764	0.015901
29	O	1.534722	1.380748	0.251791
30	O	-1.557765	1.408474	0.26908
31	C	-7.134042	0.628249	-1.043792
32	C	-7.157783	-0.613012	1.021735
33	C	-5.019208	-0.027926	-0.007997
34	C	-3.525954	-0.029799	0.000797
35	C	-5.742022	0.595769	-1.032696
36	C	-5.764443	-0.62319	1.016477
37	C	-7.844205	0.018903	-0.011667

38	C	-3.523781	2.450883	0.594713
39	H	-4.584752	2.622966	0.687047
40	C	0.025215	3.248214	0.66684
41	H	0.035242	4.308317	0.901871
42	C	1.262742	2.70732	0.542354
43	C	-2.918061	1.249218	0.283322
44	C	-1.298162	2.720658	0.573674
45	C	2.904637	1.222869	0.240872
46	C	-2.486036	3.391637	0.77725
47	H	-2.582586	4.437019	1.032879
48	C	3.513594	2.502291	0.531283
49	H	4.576772	2.675329	0.598349
50	C	2.516356	3.398394	0.708038
51	H	2.60229	4.450503	0.942514
52	F	-5.14113	-1.237964	2.03071
53	F	-7.79251	1.228733	-2.041931
54	F	-5.093292	1.184577	-2.045112
55	F	-7.837798	-1.197477	2.015093
56	F	-9.179565	0.037761	-0.015891

References:

1) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

2) Benesi, H. A.; Hildebrand, J. H. A Spectrophotometric Investigation of the Interaction of Iodine with Aromatic Hydrocarbons. *J. Am. Chem. Soc.* 1949, **71**, 2703-2707