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Interaction of Indenopyridines with [60]-fullerene: A spectroscopic and computational study

Chiranjit Pal[a], Tandrima Chaudhuri[b, *], Chhanda Mukhopadhyay[c] & Manas Banerjee[d]

[a]Department of Chemistry, Ramananda College, Bishnupur, Bankura 722 122, India
[b]Department of Chemistry, Dr. Bhupendranath Dutta Smriti Mahavidyalaya, Burdwan 713 407, India
[c]Department of Chemistry, University of Calcutta, 92 APC Road, Kolkata 700 009, India
[d]Department of Chemistry, University of Burdwan, Burdwan 713 104, India.
Email: tanchem_bu@yahoo.co.in

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Heterocyclic polynuclear planar indenopyridines (I1, I3 and I4) revealed superior wrapping of [60]-fullerene and formed stable ground state equilibrium defined via formation of absorption isosbestic and isoemissive as well. All three indenopyridines showed almost similar order of ground state formation constant both in Benesi-Hildebrand and in Stern-Volmer methods with [60]-fullerene in toluene medium. Density functional theory (DFT) based computation warranted the experimental finding in terms of loss of planarity of indenopyridines, FMO features to define electron donor and acceptor, electrochemical indices to affirm the direction of electron swing and finally time dependent density functional theory (TD-DFT) calculation showed that HOMO to (LUMO+2) has been found to be the most pronounced transition for the strongest binding with I4.

Keywords: Indenopyridines, Fullerene, Isosbestic formations, Density functional theory, Electrochemical indices

Different aspects of donor-acceptor interaction between fullerene and aromatic hydrocarbons have already been studied[1-5]. Ogilby *et al*., reported a very weakly bound ground-state CT complex with a small equilibrium constant of 0.08 M^{-1} for the [60]-fullerene-1-methyl naphthalene complex in toluene[1]. Sibley *et al*., reported formation constant (K) = 0.1 M^{-1} for the [60]-fullerene-naphthalene complex and increasing values slightly as the number of the aromatic rings of the donor is increased[2]. Bhattacharya *et al*., reported the interaction of both [60]- and [70]-fullerene-polycyclic aromatic hydrocarbons in carbon tetrachloride medium by ^1H NMR study[3,5].

Indenopyridine like planar N-containing polynuclear aromatic compounds exhibit significant chemical and biological importance and behave as good electron donors in the presence of an acceptor[6-9]. Our previous works show that Indenopyridines are as efficient as polynuclear aromatic hydrocarbons like naphthalene and anthracene, to donate electron and form a weak binding complex with (dibenzoylmethanato) borondifluoride[8,9]. To the best of our knowledge, there is no report of its interaction with any of the fullerene-like electron acceptors till date. So the purpose of this study is to investigate the mode and efficiency of interaction of indenopyridine donors with [60]-fullerene acceptor. To examine whether the weakly bound adduct of fullerene-indenopyridine system may be useful as electron or energy transfer device, both spectroscopic and DFT based computational study have been investigated and reported in detail. In this study the formation of reaction equilibrium between [60]-fullerene and three different indenopyridines viz., I1, I3 & I4 (Supplementary Data, Fig. S1) are well established via the formation of both absorption isosbestic and isoemissive in toluene medium. Furthermore the interaction in the complex was modelled with DFT based global minimum geometry change, FMO features, electrochemical indices and finally by TD-DFT calculations.

Materials and Methods

Toluene used as solvent was of HPLC (Merck India) grade. Indenopyridines (I1, I3 & I4)used were prepared according to the reported methods[10-11]. The [60]-fullerene was purchased from Sigma Aldrich. The concentration of Indenopyridines (I1, I3 & I4) was taken in the range of 10^{-5} M–10^{-6}M and [60]-fullerene was taken in micro molar range in all the spectral measurements.

Absorption and fluorescence spectroscopy

Using Shimadzu UV 2400 series, PC spectrophotometer fitted with an electronic temperature controller unit (TCC–240 A), the absorption (UV-vis) spectral measurements were performed. A Hitachi F-4500 spectrofluorometer equipped with a temperature controlled cell holder was used to record steady state fluorescence emission and excitation spectra. Temperature controlling unit is a constant temperature bath (Heto-Holten, Denmark), where temperature within ±0.1 K was maintained by circulating water.

Benesi-Hildebrand equation was used to determine association constant as follows:

$$\frac{1}{d}=\frac{1}{\varepsilon[Ii]_0}+\frac{1}{K_1\varepsilon[I_i]_0[\mathrm{C}_{60}]} \qquad \dots (1)$$

where $[\mathrm{I_i}]_0$ is the initial concentration of the Indenopyridine, and d is the absorbance of the complex at 512 nm against the solvent as reference i.e., $d = [d_{\mathrm{mix}} - d^0_{\mathrm{Ii}}]$ where d_{mix} and d^0_{Ii} are the absorbances of the donor-acceptor mixture and I solutions at the same molar concentration present in the mixture, at the same wavelength against solvent as reference. K_1 is the formation constant of the complex. Eqn 1 is valid[13] under the condition $[\mathrm{C}_{60}]>>[\mathrm{I_i}]_0$ for 1:1 EDA complexes. The linearity of the BH plot (Fig. S2) in all cases ensures 1:1 molecular complex formation between I and the [60]-fullerene.

The Stern-Volmer relationship[14] for a system with static components of interaction can be expressed as:

$$F_0/F= 1 + K_2\,[\mathrm{Q}] \qquad \dots (2)$$

In the above eqn 2, F_0 and F are the fluorescence intensities of the respective I's without and with the quencher (Q) [60]-fullerene. Here K_2 is the binding constant between I and the quencher.

Computational methods

Using molecular modelling software Spartan'14 from Wavefunction Inc. (Irvine, CA, USA) simulations were performed. A global minima search for all the three optimized complexes were performed by using the Monte Carlo simulation neglecting the solvent using Merck molecular force-field calculations (MMFF). DFT and TD-DFT theoretical calculations were carried out using Gaussian 09 (Linux), Gaussian, Inc. (USA), software. MPW1PW91/6-31G functional was used for calculating single point geometries and frontier orbitals for all the free systems and their complexes.

Results and Discussion

Ground state interactions

The photophysical binding processes of the electron deficient [60]-fullerene to indenopyridines (I1, I3 & I4) were monitored by visible absorption spectroscopy. A stock solution of [60]-fullerene was used to titrate separately the three solutions of indenopyridines (I1, I3 & I4)in toluene. For all the three indenopyridine systems, absorption of indenopyridine decreased monotonically except I4 (where intensity increased) by adding [60]-fullerene, each giving a set of isosbestic points, as shown in Fig. 1 and in Supplementary Data, Fig. S2. The multiple isosbestic points in different regions of the spectra on interaction of I1, I3 and I4 with [60]-fullerene in toluene are given in Table 1. Thus all the three interacting indenopyridine (I1, I3 & I4) systems

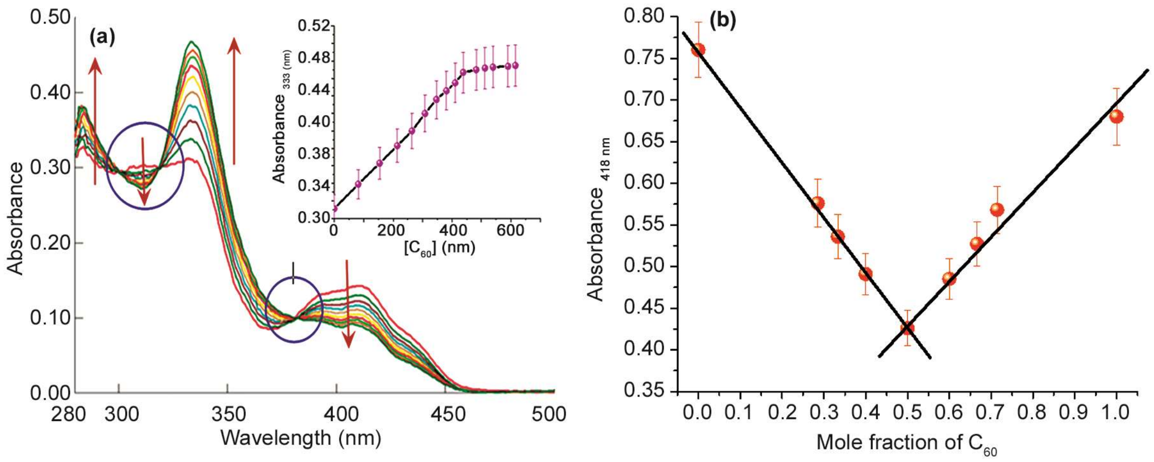

Fig. 1 — Fluorescence spectra in toluene medium due to interaction of I4 (7.31 µM) with [60]-fullerene, concentration of [60]-fullerene solution varied from 0.00 to 0.44 µM, λ_{ex} = 380 nm.

form stable equilibria with [60]-fullerene in toluene medium in the ground state.

All the above is endorsed to a ground state interaction between the [60]-fullerene and indenopyridine systems**.** The interaction is a collective phenomenon between the moiety incorporating electron donor-acceptor and π-stacking. [60]-fullerene is a well-accepted acceptor moiety and indenopyridines can act as both acceptors[12] and donors[8,9]. In the presence of [60]-fullerene, indenopyridines act as donors as is evident from the electrochemical index value in theoretical analysis.

Excited state interaction

To the best of our knowledge, the excited state [60]-fullerene-indenopyridine association has not been well recognized. The fluorescence maxima of indenopyridines did not suffer any shift with the escalating concentration of [60]-fullerene in the solution, as shown in Fig. 2. With the facade of isoemissive point(s) for each of the three indenopyridines (I1, I3 & I4) the fluorescence intensity of indenopyridines diminished monotonically with increasing concentration of [60]-fullerene. The effect was due to quenching of indenopyridines by [60]-fullerene in which case the emission frequency has not shifted. It appeared that the emission process suffers an interaction between the fluorophore (I1, I3 & I4) and the quencher ([60]-fullerene) which was adequately reflected in the emergence of isoemissive point (Fig. S3). It was observed that emission increases at 650 nm and decreases at 475 nm with the formation of iso-emissive at 627.8 nm. Fluorescence increase at 650 nm might be due to the emission of the newly formed complex. Absorption spectral study showed that at 650 nm, the absorption remains constant with increasing concentration of C_{60}. And quenching at 475 nm was also due to the new complex between C_{60} and I4. The complex probably had emission at 650 nm instead of 475 nm, which was the emission maxima of free Indenopyridine.

Thus, Fig. 2 reflects that the emission was due to both complexed and free species of the fluorophore which emit at different wavelengths giving rise to isoemissive point. For the appearance of isoemissive, we conjecture the existence of ground state equilibrium. Isoemissives have also been listed in Table 1.

Determination of formation constant

Ground state formation constants were determined using Benesi-Hildebrand equation[13] in absorption study and Stern-Volmer equation[14] in fluorescence study. The formation constant values are presented in Fig. 3

Table 1 — Isosbestic and isoemissive points appear upon interaction of [60]-fullerene (C_{60}) with Indenopyridines (I1, I3 and I4) in toluene. The excited state association constants for the corresponding three complexes

System	Absorption isosbestic point at wavelength (nm)	Isoemissive point at wavelength (nm)	Benesi-Hildebrand constant $(K_{BH})\times10^{-5}$ (M^{-1})	Stern-Volmer constant $(K_{SV})\times10^{-5}$ (M^{-1})
C_{60}/I1	369.8, 330.7	450.8	11.40 ± 0.12	9.5 ± 0.18
C_{60}/I3	369.5, 329.3	471.6	14.75 ± 0.45	10.7 ± 0.24
C_{60}/I4	381.4, 318.3, 300.48	440.2, 627.8	17.93 ± 0.32	11.0 ± 0.30

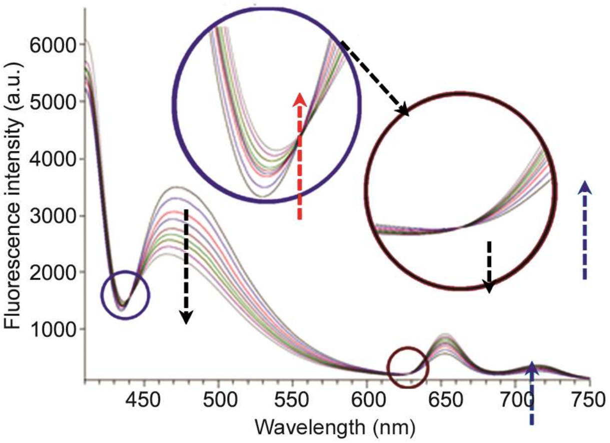

Fig. 2 — Fluorescence spectra in toluene medium due to interaction of I4 (7.31 μM) with [60]-fullerene, concentration of [60]-fullerene solution varied from 0.00 to 0.44 μM, λ_{ex} = 380 nm.

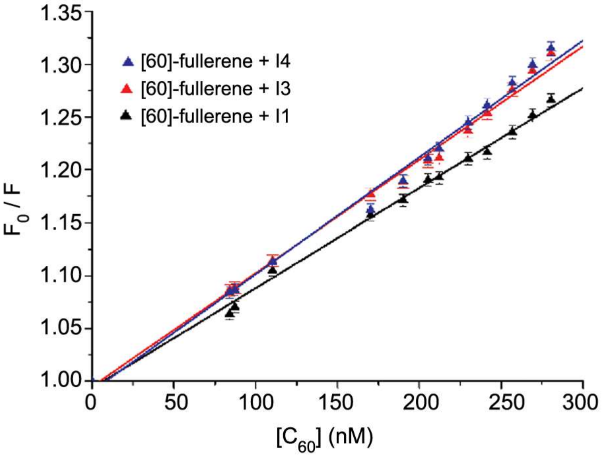

Fig. 3 — Stern-Volmer plot of the three [60]-fullerene-indenopyridine interacting systems at λ_{em} = 475 nm.

and Table 1. Table 1 indicated that I4 binds with [60]-fullerene most efficiently among all the three indenopyridine systems. The equilibrium constants follow the order $K_{[60]\text{-fullerene/I4}} > K_{[60]\text{-fullerene/I3}} > K_{[60]\text{-fullerene/I1}}$.This may be due to better charge transfer mechanism between I4 and [60]-fullerene in comparison to others. Alongside as Stern-Volmer plot shows linearity, and as ground state complex was formed, is concluded to be undoubtedly static quenching for all the three interacting systems.

Theoretical analysis

A meticulous conformational search protocol[15,16] was employed for these associated complexes. Density based geometry optimization calculations of the adduct structures are mostly used for studying weak intermolecular interactions such as CT, van der Waals, H-bonding and hydrophobic[17-20]. The conformational analysis of the weakly bonded adducts were proficient by means of a Monte Carlo protocol[15] based on force-field molecular mechanics[16] available in the Spartan-14 suite of programs. Structural optimization of all the three interacting systems were done by molecular mechanics and the single point energy calculation of all the three interacting systems were done at the MPW1PW91/6-31G level of DFT. The optimised geometries of the three complexes are presented in Fig. 4.

In all the cases, the intermolecular distances between the donor (I1-I4) and the acceptor ([60]-fullerene) moieties (Table 2) were within 3.41 Å–3.43 Å that is in the assortment of charge transfer interaction to crop up. The π-parallel orientation of the interacting molecules is given in Fig. 4. Thus, strong π-π interaction is taking place between [60]-fullerene and indenopyridines. The angle between pyridine and indeno moiety of indenopyridines in the adduct increases drastically due to strong charge transfer interaction between the moieties. Also, among the indenopyridines, I4 creates a suitable cavity for the [60]-fullerene to fit and has the greatest binding constant. The ability to wrap up [60]-fullerene in the cavity of indenopyridine increases upon going from I1 to I4 and also the distance between the interacting moieties decreases. With increasing distance between the interacting molecules, the amount of charge transfer decreases which is the determining factor for the order of the equilibrium constant (K). The direction of the electronic flux during the charge transfer within the system in its ground state is determined by the electrochemical potential index (μ)[21].

An effortless operational formulation in terms of the one-electron orbital energies (ε) of Frontier Molecular orbital (FMO), viz., the HOMO and LUMO, may be represente as:

$$\mu \approx (\varepsilon_{\mathrm{HOMO}} - \varepsilon_{\mathrm{LUMO}})/2 \quad \ldots (3)$$

When the system acquires an additional electronic charge (ΔN) from the environment, the global electrophilicity index (ω) measures the stabilization in energy[21,22]. It can be basically expressed in terms of electrochemical potential and chemical hardness as:

$$\omega = \mu^2/2\eta \quad \ldots (4)$$

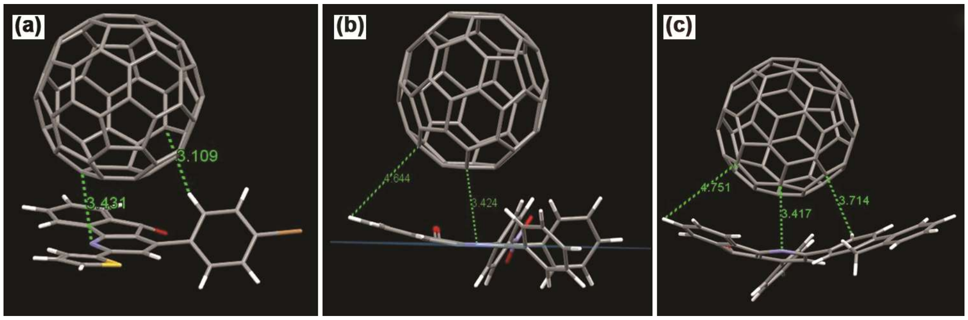

Fig. 4 — Orientation of the adduct of (a) [60]-fullerene/I1, (b) [60]-fullerene/I3, and, (c) [60]-fullerene/I4 interacting systems in optimized ground state geometry showing the intermolecular distances in Å.

Table 2 — Parameters of the optimized ground state geometry of adducts

System	Minimum distance between the fullerene-60 (C_{60}) and indenopyridine moieties (in Å)	Number of conformers	Dipole moment (D)	Angle between pyridine and indeno moiety of indenopyridines in adduct and in free state
C_{60}/I1	3.109	2	4.6029	2.92° and 2.18°
C_{60}/I3	3.424	1	7.7364	10.80° and 1.96°
C_{60}/I4	3.417	2	4.7734	13.03° and 2°

Higher electrochemical potential (μ) of indenopyridine derivatives (–4.39 to –4.70 eV) than [60]-fullerene (–5.05 eV) indicates that charge transfer occurs from indenopyridines to [60]-fullerene. Those with, ω > 1.5 eV are said to be the strong electrophiles. Electrophilicity index (ω) of indenopyridine derivatives are in the range of 2.77 eV to 2.95 eV but fullerene-60 has higher value (4.06 eV) of electrophilicity index (ω) in comparison to indenopyridine derivatives. Thus, in presence of [60]-fullerene indenopyridines act as donor and evidently [60]-fullerene serves as a better acceptor during charge transfer process. The global nucleophilicity index (N) value of indenopyridine derivatives are in the range of 2.91 eV to 3.01 eV[23]. Strong nucleophiles are those molecules with N > 3.0 eV and thus indenopyridines act as donor during charge transfer in this case.

TD-DFT calculation

D-DFT calculations were done at MPW1PW91/6-31G level (Table 3), the most effective transitions are the HOMO to (LUMO+1), HOMO to (LUMO+2) and HOMO to LUMO as predicted from TD-DFT calculation (Table 3). Other possible transitions present little contribution in comparison to these. But the HOMO to (LUMO+2) transition is the most pronounced as it has the highest oscillator strength.

HOMO-LUMO interactions

The intermolecular interaction of a donor-acceptor adduct is expediently interpreted by investigating the frontier molecular orbital of individuals and adduct. The HOMO-LUMO interactions between [60]-fullerene and indenopyridines were studied through density functional calculations at the DFT/MPW1PW91/6-31G level. The HOMO orbital of the complexes slouch mainly on indenopyridine moiety and (LUMO+2) mostly dwell on acceptor [60]-fullerene (Fig. 5). In fact, from TD-DFT data this is the most prominent CT transition. The (LUMO+1) and LUMO orbitals of the complexes predominantly lie on the acceptor [60]-fullerene moiety and the HOMO to (LUMO+2) and HOMO to LUMO transition also has a significant contribution in TD-DFT. Thus frontier molecular orbital pictures give the clear

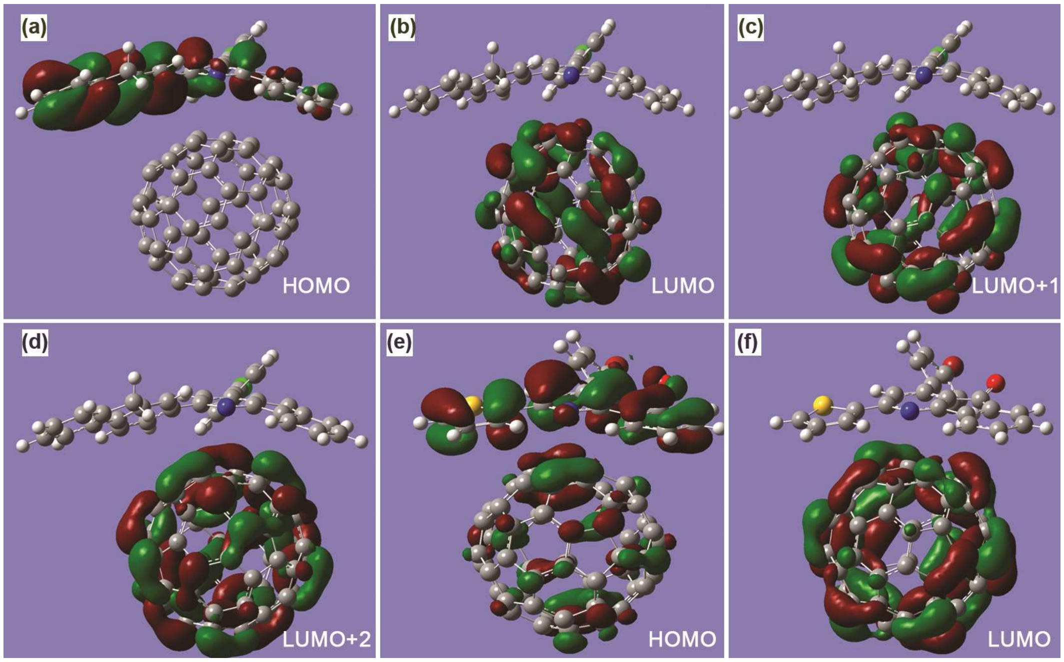

Fig. 5 — Frontier Molecular Orbital pictures of [60]-fullerene/I4 (a-d) and [60]-fullerene/I1 (e, f) interacting systems

Table 3 — TD-DFT calculated percentage contribution of transitions of [60]-fullerene/I4 adduct

Excited state 1 Oscillator strength (f) = 0.0014		Excited state 2 Oscillator strength (f) = 0.0080		Excited state 3 Oscillator strength (f) = 0.0004	
Possible Transition	Percentage contribution	Possible Transition	Percentage contribution	Possible Transition	Percentage contribution
HOMO to LUMO	87.43%	HOMO to (LUMO+1)	23.02%	HOMO to LUMO	7.01%
HOMO to (LUMO+1)	8.36%	HOMO to (LUMO+2)	69.52%	HOMO to (LUMO+1)	62.63%
-	-	-	-	HOMO to (LUMO+2)	24.59%

evidence of charge transfer interaction between [60]-fullerene and indenopyridines.

Conclusions

All three indenopyridines form stable absorption isosbestic as well as isoemissive on titrating with fullerene. Indenopyridines used in this study demonstrate similar order of both BH and SV formation constants with the fullerene. Experimental finding of formation of ground state equilibrium were well justified by DFT based geometry optimization, FMO calculation, electrochemical indices determination and by TD-DFT transitions. Thus Indenopyridines were found to be as good wrapping agents as polyaromatic hydrocarbons for [60]-fullerene in nonpolar toluene medium.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_58A(05)561-655_SupplData.pdf.

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