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Molecular selectivity of indenopyridines for fullerenes: A comparative study

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ABSTRACT

Selectivity of [60]-Fullerene (C_{60}) over its [70]-analogue (C_{70}) is ably established for N-containing polynuclear aromatic planar indenopyridines (I) in organic media for the first time. The present work envisages the chemical physics behind non-covalent interaction between [70]-fullerene (C_{70}) and indenopyridines (I: I1, I3 and I4) in toluene alongwith a comparative analysis of previously studied interaction of C_{60} (Pal et al., 2019) via formation of multiple absorption isosbestic points and isoemissive point in UV–Vis and steady state fluorescence studies respectively, stable ground state equilibrium between C_{70} and I is recognized and is purely non-covalent in nature. All three indenopyridines showed high formation constant ($\sim 10^5$) with [70]-fullerene though the selectivity of binding favours [60]-fullerene. Experimental findings are well supported within *vacuo* DFT based computation. Loss of planarity of indenopyridines in the optimized adducts, FMO features, electrochemical indices and finally TD-DFT calculation validates the strong complexation. Taut wrapping of C_{70} by indenopyridines is most conspicuous for I4 among others as that of C_{60}.

1. Introduction

Huge studies has already been made in the field of charge transfer or electron donor-acceptor type weak interaction captivating Fullerenes viz. C_{60} and or C_{70} as electron acceptor [1–12]. The exploration of the emission and optical properties of fullerenes and their derivatives is a central topic among the dynamic research fields of fullerenes to study charge separation recombination phenomena in energy storage devices [12]. These studies are gently related to “donor-acceptor” molecular systems in polynuclear aromatic compounds [13–23]. Varieties of donors are available in literature for which comparative efficiency of charge transfer interaction reported in organic media for Fullerenes [1–6].

N-containing polynuclear aromatic donor indenopyridine [18–21] plays noteworthy chemical and biological consequence. The efficiency of indenopyridines to form a weak binding complex with C_{60} has already been reported by our group [9]. To the best of our knowledge, there is no report of its comparative interaction with other fullerenes as electron acceptors till date. So the purpose of this study is to investigate the mode and efficiency of interaction of indenopyridine donors with [70]-fullerene acceptor in comparison with its [60]-analogue.

In this study better selectivity of C_{60} for indenopyridine donors are established through the formation of reaction equilibrium between [70]-fullerene and three different indenopyridines viz., I1, I3 & I4 (Fig. 1). As that of C_{60}/I interactions reported earlier [9] all these are well established via the formation of both absorption isosbestic and isoemissive in toluene medium. Furthermore the interaction in the complex is modelled with density based change in global minimum geometry, Frontier orbital features, electrochemical indices and finally by TD-DFT transition estimation.

2. Experimental

2.1. Materials

Toluene HPLC (Merck India) grade is used as solvent. I1, I3 & I4, Indenopyridines are synthesized as reported [24], used in this study. Aldrich made [70]-fullerene (C_{70}) is used. The concentration range of 10^{-5} M -10^{-6} M of indenopyridines (I1, I3 & I4) is taken and the range of 10^{-6} M are taken for C_{70} in all the spectral measurements.

2.2. Instruments used

The UV–Vis spectral measurements are performed using Shimadzu UV 2400 series PC spectrophotometer fitted with an electronic

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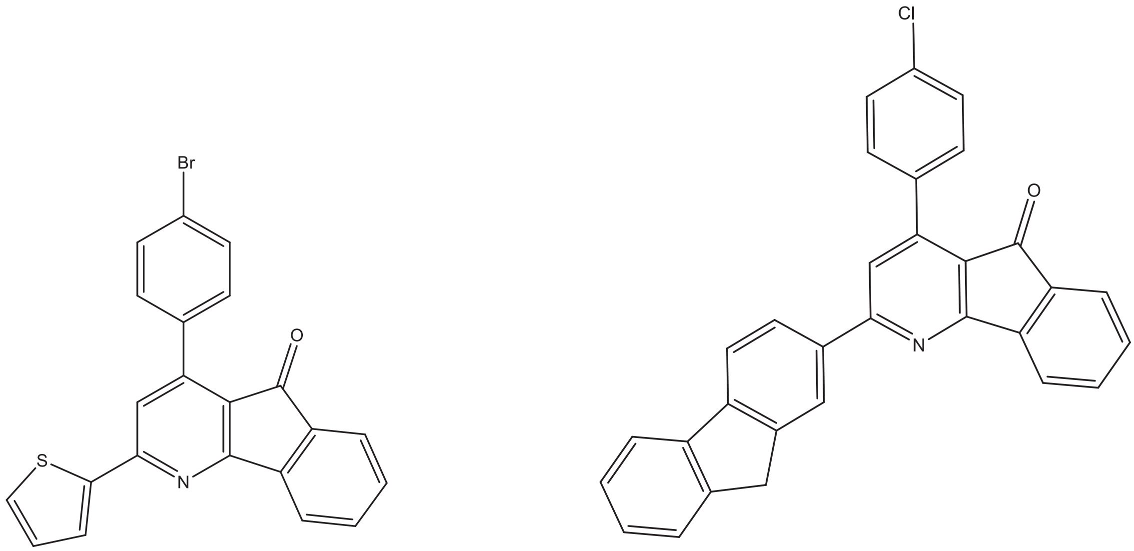
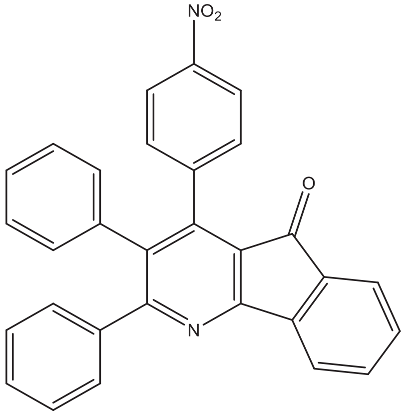


4-(4-Bromo-phenyl)-2-thiophen-2-yl-indeno[1,2-*b*]pyridin-5-one 4-(4-chlorophenyl)-2-(9*H*-fluoren-2-yl)-5*H*-indeno[1,2-*b*]pyridin-5-one

I1

I4



4-(4-Nitro-phenyl)-2,3-diphenyl-indeno[1,2-*b*]pyridin-5-one

I3

Fig. 1. Structures of the indenopyridines (I) used.

temperature controller unit (TCC –240 A). The emission and excitation spectra are recorded with a spectrofluorometer (Hitachi F-4500) equipped with a temperature controlled cell holder. Temperature is guarded to within ±0.1 K, by water circulation from a constant temperature bath (Heto Holten, Denmark).

Molecular simulations are performed using Spartan’14 molecular modelling software of Wavefunction Inc. (Irvine, CA, USA). The searches of global minima for all the three optimized complexes are done by the Monte Carlo simulation in vacuum using Merck molecular force-field calculations (MMFF). Gaussian 09 (Linux), Gaussian, Inc. (USA), software is used for DFT and TD-DFT theoretical calculations. For all the free systems and their complexes, MPW1PW91/6-31G functional is chosen for calculating single point geometries and frontier orbitals.

3. Results and discussion

3.1. Ground state interactions

The photon induced interaction processes of the electron deficient fullerene to indenopyridines (I1, I3 & I4) are scrutinized both by visible absorption and fluorescence spectroscopy. The three solutions of indenopyridines (I1, I3 & I4), are titrated separately with a stock C_{70} solution, in toluene. Titration process is as described earlier for C_{60} interaction [9]. Fig. 2 shows appearance of a set of three isosbestic points for all the three indenopyridine systems, for which intensity of maximum absorption of indenopyridine decreased by adding solutions of C_{70}. Table 1 listed the multiple isosbestic points in different regions of the spectra on interaction of I1, I3 and I4 with C_{70} in toluene. Thus all the three indenopyridine (I1, I3 & I4) systems form ground state steady equilibria with C_{70} in toluene medium.

Comparing with C_{60} isosbestic points, are red shifted for C_{70} interaction, irrespective of all three indenopyridines (shown in Table 1).

3.2. Excited state interaction

The excited state C_{70} – indenopyridine association has not yet been well established. The fluorescence maxima of indenopyridines systematically quenches without any remarkable shift. Still give rise to an iso-emissive point in lower wavelength region with the increasing concentration of C_{70} in the solution, as shown in Fig. 3.

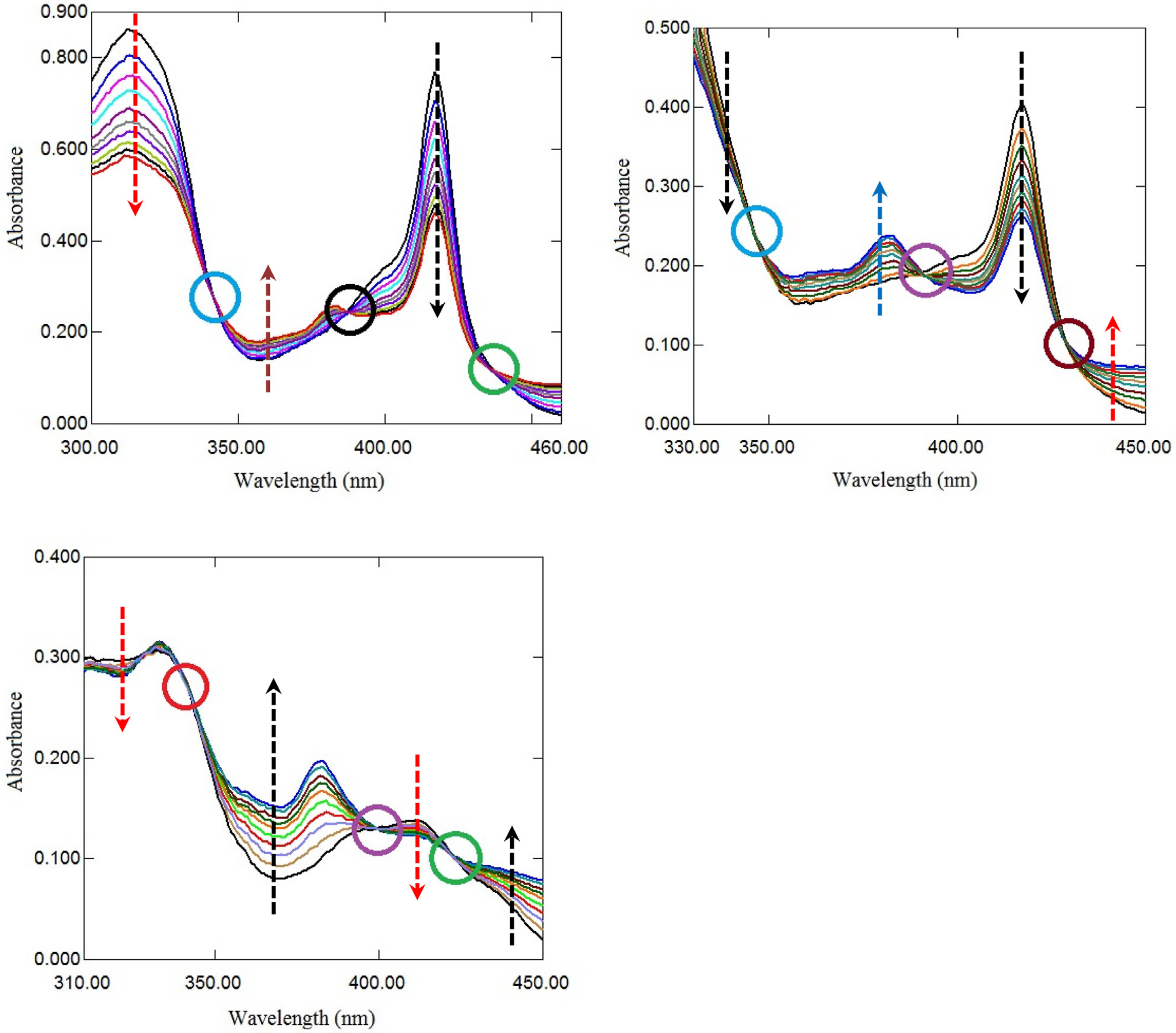


Fig. 2. Absorption isosbestic appearedin toluene medium due to interaction of (a) I1 (2.50×10^{-5} mol/dm^3) with [70]-fullerene, concentration of [70]-fullerene: 0.00, 6.88×10^{-7}, 1.26×10^{-6}, 1.75×10^{-6}, 2.16×10^{-6}, 2.52×10^{-6}, 2.84×10^{-6}, 3.12×10^{-6}, 3.36×10^{-6}, 3.58×10^{-6} mol/dm^3 (b) I3 (3.80×10^{-6} mol/dm^3), with [70]-fullerene, concentration of [70]-fullerene: 0.00, 6.88×10^{-7}, 1.26×10^{-6}, 1.75×10^{-6}, 2.16×10^{-6}, 2.52×10^{-6}, 2.84×10^{-6}, 3.12×10^{-6}, 3.36×10^{-6}, 3.58×10^{-6} mol/dm^3 (c) I4 (7.31×10^{-6} mol/dm^3), with [70]-fullerene, concentration of [70]-fullerene: 0.00, 6.88×10^{-7}, 1.26×10^{-6}, 1.75×10^{-6}, 2.16×10^{-6}, 2.52×10^{-6}, 2.84×10^{-6}, 3.12×10^{-6}, 3.36×10^{-6}, 3.58×10^{-6} mol/dm.^{3}.

Table 1
Isosbestic and isoemissive points appear upon interaction of indenopyridines (I1, I3 and I4) with two fullerenes in toluene. The excited state association constants for the corresponding three complexes.

Indenopyridine	Interaction with [60]-fullerene [9]			Interaction with [70]-fullerene			K_{C60}/K_{C70}
	Absorption isosbestic point at wavelength (nm)	Isoemissive point at wavelength (nm)	Stern-Volmer constant (K_{SV}) × 10^{-5} (M^{-1})	Absorption isosbestic point at wavelength (nm)	Isoemissive point at wavelength (nm)	Stern-Volmer constant (K_{SV}) × 10^{-5} (M^{-1})	
I1	369.8, 330.7	450.8	9.5 ± 0.18	435.60, 387.52, 341.03	446.6	1.90 ± 0.11	5.0
I3	369.5, 329.3	471.6	10.7 ± 0.24	428.23, 391.50, 345.32	446.1	2.06 ± 0.15	5.19
I4	381.4, 318.3, 300.5	440.2, 627.8	11.0 ± 0.30	421.85, 399.41, 340.76	431.2	2.35 ± 0.13	4.68

Thus with the appearance of isoemissive point static interaction between the fluorophore indenopyridines (I1, I3 & I4) and the fluorescence quencher (C_{70}) is well established as earlier [9]. On contrary, isoemissive points are blue shifted (shown in Table 1) on switching from C_{60} to C_{70}.

3.3. *Determination of equilibrium constant*

Stern-Volmer equation [25] is used to determine the association constant values (Fig. 4) and is listed in Table 1. I4 binds most efficiently with C_{70} among the indenopyridines used; reflects massive charge

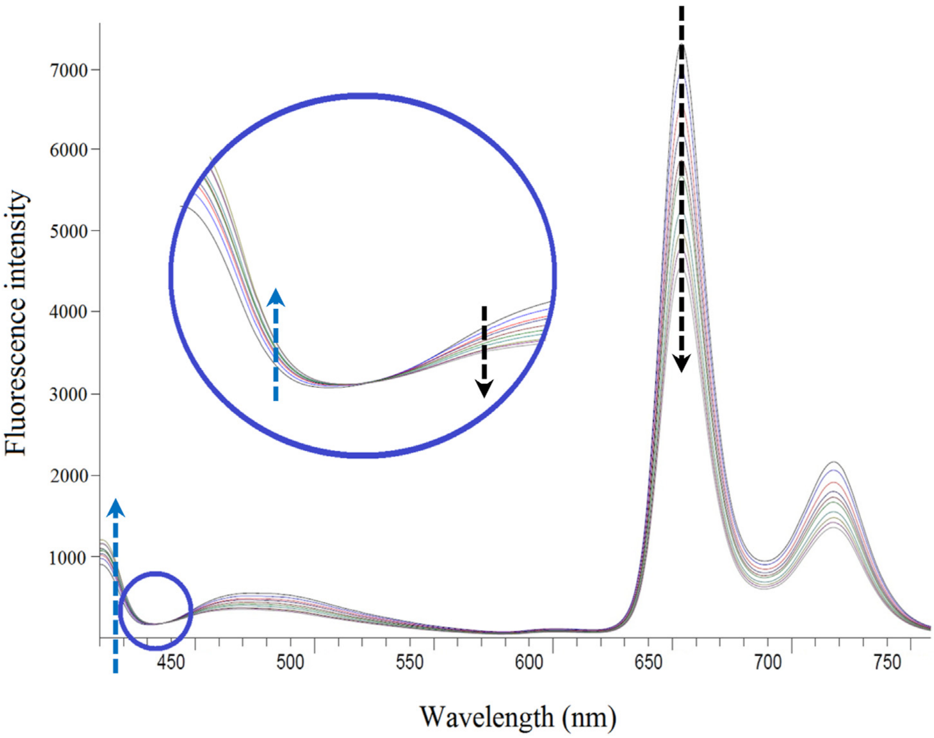


Fig. 3. Fluorescence spectra appeared on excitation at wavelength 436 nm in toluene medium due to interaction of I1 (2.50×10^{-5} mol/dm^3) with [70]-fullerene, concentration of [70]-fullerene: 0.00, 6.88×10^{-7}, 1.26×10^{-6}, 1.75×10^{-6}, 2.16×10^{-6}, 2.52×10^{-6}, 2.84×10^{-6}, 3.12×10^{-6}, 3.36×10^{-6}, 3.58×10^{-6} mol/dm.^{3}.

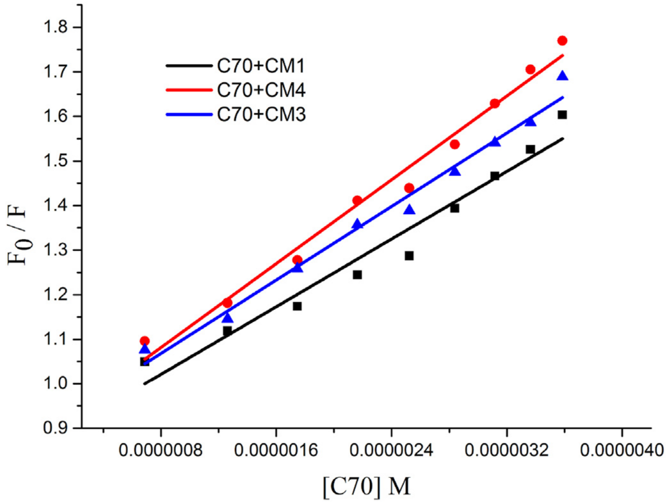


Fig. 4. Stern-Volmer plot of the three C_{70}/I interacting systems.

transfer of I4 with [70]-Fullerene amongst others. The order of excited state equilibrium constants follows $K_{C70/I4} > K_{C70/I3} > K_{C70/I1}$. Similar order of the binding is observed earlier in case of C_{60} also. However the association capability between fullerene and indenopyridines are 5 fold less in C_{70} in contrast to that of C_{60} might be due to lack of planarity [70]-analogue.

3.4. Theoretical analysis

A precise Monte Carlo (MC) conformational search protocol [25,26] is used for these associated complexes also. For studying weak intermolecular interactions such as CT, van der Waals, H-bonding, and hydrophobic [27–30], normally DFT optimization calculations of the adduct structures are employed. Fig. 5 presents best possible geometries of the three complexes. The donor (I) and the acceptor (C_{70}) intermolecular distances (shown in Table 2) are within 3.44 Å – 3.55 Å which is in the charge transfer range of interaction. This intermolecular distances are slightly higher compared to that of [60]-fullerene analogue (shown in Table 2) [9]. Between the interacting molecules strong π-π interaction originated due to π-parallel orientation as shown in Fig. 5. The angle between pyridine and indeno moiety of each indenopyridines in the fullerene adduct increases as reported earlier [9]. The interaction is more pronounced in case of C_{60} than C_{70} as evident from intermolecular distances and the angle between pyridine and fluorenyl moiety of I's, might be due to spherical symmetric structure of [60]-analogue. The aforesaid angle of I4 changes from 10.64° to 46.42° to create a suitable cavity for C_{70} and among the indenopyridines, I4 has the greatest binding constant with both the Fullerenes. The similar order as that of [60]-fullerene [9], the ability to wrap up [70]-fullerene in the opening of different indenopyridines and the distance between three sets of the interacting moieties, are followed.

The order of the equilibrium constant (K) depends directly on the amount of charge transfer taking place. Here the amount of charge transfer decreases with increase in distance between the interacting molecules. Consequently the K values follow the order.

The electronic chemical potential (μ) [31], the global electrophilicity index [32,33] (ω) and the global nucleophilicity N index [34] values are determined for donor-acceptor interaction as earlier [9]. Electronic chemical potential (μ) of Fullerenes (>-5.00eV) are found lower than that of indenopyridine derivatives (−4.39 to −4.70eV). Electrophilicity index (ω) of both [60]- and [70]-fullerene have higher values (4.06eV and 4.18eV) in compare to indenopyridine derivatives (2.77eV–2.95eV). Thus, in presence of Fullerene, indenopyridines act as donor and evidently fullerenes serves as acceptor during charge transfer process. The global nucleophilicity N index [34] value of indenopyridine derivatives are in the range (N > 3.0 eV) of a donor during charge transfer as shown earlier [9].

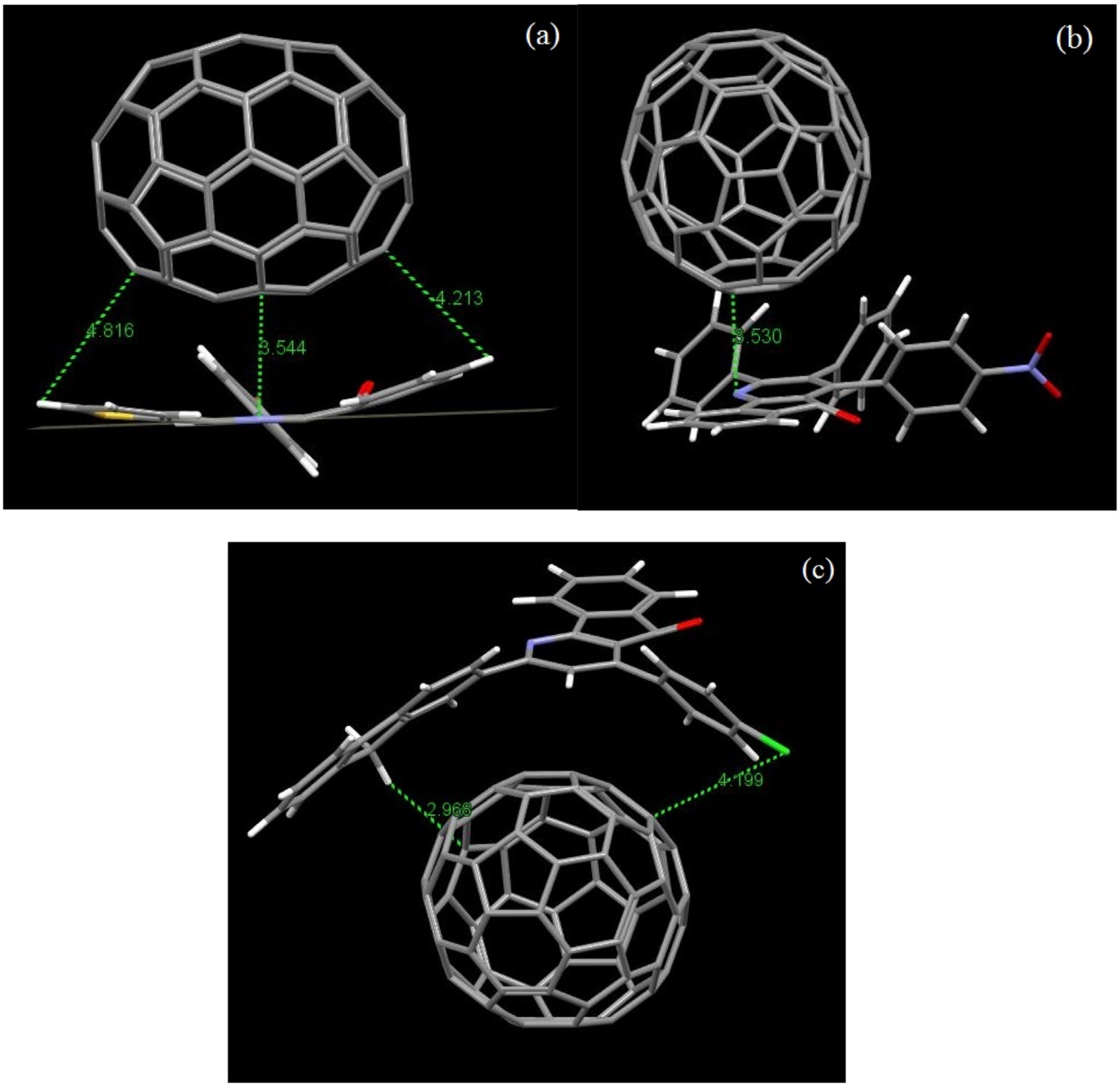


Fig. 5. The orientation of the adduct of (a) C_{70}/I1 (b) C_{70}/I3 and (c) C_{70}/I4 interacting systems in optimized groundstate geometry showing the intermolecular distances in Å.

Table 2

Parameters of the optimized ground state geometry of adducts.

Indenopyridines	Interaction with [60]-fullerene [9]			Interaction with [70]-fullerene		
	Minimum distance between the Fullerene-60 (C_{60}) and indenopyridine moieties (in Å)	Number of conformers	Dipole moment (D)	Minimum distance between the Fullerene-70 (C_{70}) and indenopyridine moieties (in Å)	Number of conformers	Dipole moment (D)
I1	3.109	2	4.6029	3.54443	2	4.2342
I3	3.424	1	7.7364	3.52999	1	8.7120
I4	3.417	2	4.7734	3.46302	2	4.7159

3.4.1. *TD-DFT calculation*

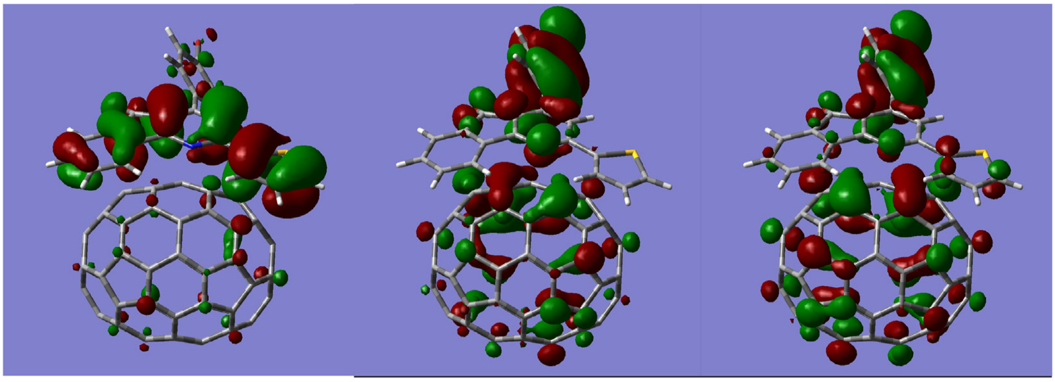
TD-DFT/MPW1PW91/6-31G calculation are done and reported in Table 3. Few of the possible transitions listed in Table 3 are there having little contribution in compare to others. The HOMO to (LUMO+1), HOMO to LUMO and (HOMO-1) to LUMO are the most prominent transitions in case of I/C_{70}.

3.4.2. *HOMO-LUMO interactions*

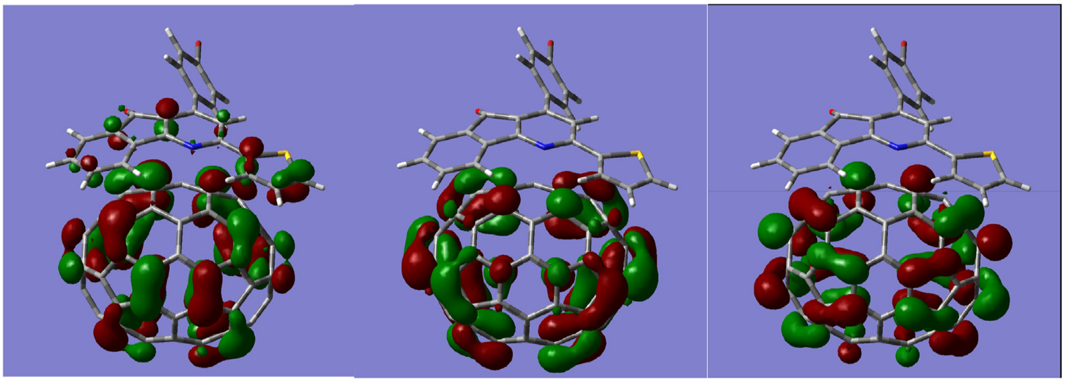
Investigating the interaction between the frontier HOMO/LUMO orbitals of the donor-acceptor adducts, the intermolecular type of interaction is conveniently interpreted. The FMO interactions between C_{70} and indenopyridines are studied through DFT/MPW1PW91/6-31G level calculation. Fig. 6 depicted that the HOMO, (HOMO-1) and (HOMO-2) orbitals of the complexes reside mainly on indenopyridine moiety and LUMO and (LUMO+1) mostly dwell on acceptor [70]-fullerene as that reported in case of C_{60} [9]. However, the direction of charge transfer from TD-DFT data in the CT transition is better explained. Thus the clear corroboration of charge transfer interaction between fullerene and indenopyridines are granted by frontier molecular orbital pictures.

Table 3
TD-DFT calculated percentage contribution of transitions of C_{70}/I1 adduct.

Excited state 1 Oscillator strength (f) = 0.0039		Excited state 2 Oscillator strength (f) = 0.0006		Excited state 3 Oscillator strength (f) = 0.0093	
Possible Transition	Percentage contribution	Possible Transition	Percentage contribution	Possible Transition	Percentage contribution
HOMO to LUMO	27.03%	HOMO to LUMO	54.87%	HOMO to LUMO	5.05%
HOMO to (LUMO+1)	15.92%	HOMO to (LUMO+1)	13.66%	HOMO to (LUMO+1)	25.12%
(HOMO-1) to LUMO	12.69%	(HOMO-2) to (LUMO+1)	2.11%	(HOMO-1) to LUMO	21.78%
(HOMO-2) to LUMO	16.80%	(HOMO-3) to LUMO	14.35%	(HOMO-2) to LUMO	31.05%
(HOMO-3) to (LUMO+1)	19.93%	(HOMO-3) to (LUMO+1)	6.92%	(HOMO-2) to (LUMO+1)	6.089%
–	–	(HOMO-1) to (LUMO+1)	2.24%	(HOMO-1) to (LUMO+1)	3.57%



HOMO HOMO-1 HOMO-2



HOMO-3 LUMO LUMO+1

Fig. 6. Frontier Molecular orbital pictures of C_{70}/I1 interacting system.

4. Conclusion

However the electrophilicity index (ω) suggest C_{70} as better acceptor in comparison with C_{60}, still better spherical symmetry of C_{60} confirmed higher binding complexes with all three Indenopyridines used in this study. Not only both [60]- and [70]-Fullerenes form stable ground state equilibrium but also both distorted the planarity of N-based heterocyclic aromatic donor indenopyridines. Though angle of distortion of planarity is higher to accommodate coconut shaped C_{70}, still Stern-Volmer association constant ratio shows 5 fold higher selectivity of spherical C_{60} on interacting with Indenopyridines in Toluene.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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