



Photophysical properties of charge transfer pairs encapsulated inside macrocycle cage: A density functional theory study



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ABSTRACT

Density functional theory calculations have been performed on three charge transfer donor–acceptor (D–A) molecular pairs, i.e. naphthalene-diamine (Naph) and tetrathiafulvalene (TTF) molecules as electron donors and benzene-diimide (Diimide) and tetracyanoquinodimethane (TCNQ) as electron acceptors. Structural, charge transfer and optical properties of the systems have been studied. The D–A pairs then has been considered inside a macrocycle (cucurbit[8]uril) cavity and Naph–Diimide and TTF–Diimide pairs have been shown to exhibit changes in their structures and orientations, TTF–TCNQ pair does not show any significant structural change. Our work suggests that these changes in structures or orientations are result of electronic repulsion between the keto group oxygen atoms and it can lead to tuning of charge transfer and optical properties of the systems.

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1. Introduction

Recently, organic donor–acceptor molecules have received huge scientific interest because of their potential applications as organic semiconductors [1,2], organic field effect transistors [3,4], solar cell [5–9], development of supramolecular assemblies of different dimensionalities [10–15], organic room-temperature ferroelectrics [16] etc. π -Conjugated organic donor acceptor molecules form charge-transfer (CT) complexes by π stacking between the donor (D) and the acceptor (A) moiety. Though in some recent studies the term ‘ π stacking’ is referred as ‘misleading’ as it cannot define this type of interaction correctly and it is suggested that electrostatic contributions related to the polarized π systems can predict the stability of aromatic π systems correctly [17]. This so called π – π interaction and/or CT interaction can be tuned smartly in these complexes to obtain novel properties which are very useful for device fabrication. Because of the flexible nature (induced by the weak non-covalent interactions) of these complexes they can easily be used to form supramolecular network [10–15] or metal organic framework [18]. Properties of these CT complexes mainly depend on the orientation of the donor and acceptor molecule’s arrangements [15]. Change in the arrangement can lead to difference in the amount of charge-transfer, which consequently may change the properties of these complexes. Other non-covalent interactions,

like hydrogen-bonding, metal ion mediated co-ordination bonding etc. can in fact lead to the enhancement of these CT interactions [15,16]. Not only molecular systems, but these CT interactions are well known for tuning electronic and optical properties of 2-D materials, namely, graphene, BN or MoS₂ systems [19–22].

The molecular CT pairs can be stabilized in solvent by isolating them in some macrocycle molecule. Cucurbituril is one of such famous macrocycle molecule. Since it has ‘ n ’ glycoluril units and depending upon the ‘ n ’ value the name can be cucurbit[n]uril ($n = 6, 7, 8$ etc.). The cavity inside the macrocycle is suitable for capturing single or pair of organic molecules [23–26]. Even the functional keto groups in the periphery of the moiety can be used to capture organic cations [27] or anti-cancer drug molecules [28]. In recent past, cucurbit[8]uril molecule has been widely used to stabilize dimers of aromatic molecules or donor acceptor dimers in solvent [23,29,30]. Sometimes this macrocycle molecule along with the dimers present inside them can act as a motif for supramolecular polymer or even 2-D network [10,25,31–35]. Thus, one can use this macrocycle molecule to obtained CT complexes easily.

In this study, we have investigated three pairs of well-known electron donor–acceptor molecules and their electronic and optical properties without and in presence of cucurbit[8]uril macrocycle molecule. We have considered naphthalene-diamine (Naph) and tetrathiafulvalene (TTF) molecules as electron donors and benzene-diimide (Diimide) and tetracyanoquinodimethane (TCNQ) as electron acceptors. We have taken three pairs, namely, Naph–Diimide, TTF–Diimide and TTF–TCNQ into consideration. The first two pairs (modified) have been studied previously as room

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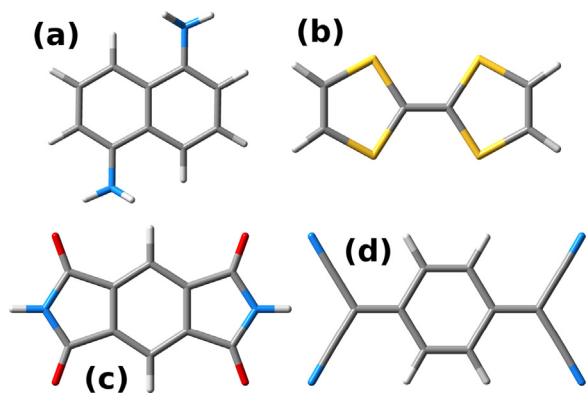


Figure 1. (a) Naphthalene-diamine (Naph), (b) tetrathiafulvalene (TTF), (c) benzene-diimide (Diimide) and (d) tetracyanoquinodimethane (TCNQ) molecules. Silver, grey, blue, red and yellow colours represent H, C, N, O and S atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

temperature organic ferroelectric material [16] and the TTF–TCNQ pair have been used as organic field effect transistor [36]. We have considered our systems in free phase as well as in captured phase (inside the macrocycle), and we have calculated the change in structure, orientation, amount of charge transfer, electronic and optical absorption properties of the D–A pairs in both the phases. Our calculations suggest that, two of the pairs, e.g., the Naph–Diimide and TTF–Diimide pairs show a considerable amount of changes in the structure when incorporated inside the macrocycle cage (i.e. in captured phase), but the TTF–TCNQ pair does not show appreciable change in the structure or orientation inside the cage. We have attributed this finding as the result of the electronic repulsion between the keto groups of the cage and the Diimide moiety. As a result of the structural change, amount of the charge transfer and adsorption energy of the molecules also change. This change leads to the modification in electronic property also, the HOMO–LUMO (H–L) gap of the systems change. Thus, we have found that the absorption spectra also shift to some extent for these two pairs, but for the other pair (i.e. TTF–TCNQ) the change in absorption profile is very less. We have verified our result using different functionals also for the robustness of our results.

2. Computational detail

The geometry of the molecules and pair of molecules are optimized using density functional theory (DFT) as implemented in the GAUSSIAN 09 program package [37]. All the calculations are performed using the wB97XD hybrid functional [38,39], as it considers dispersion interaction as well as long and short range interactions in order to take into account the weak non-covalent interactions like charge transfer interactions and van der Waals interactions. We have directly used the structure of crystal geometry of cucurbit[8]uril macromolecule, as it was found to be stable in presence of guest molecules [31]. Thus, we have relaxed the donor–acceptor pairs inside the cage again using wB97XD functional. We have used 6-31g(d) basis set for all the atoms. In order to calculate the amount of charge transfer between the pairs, we have performed natural population analysis (NPA) using wB97XD functional and 6-31g(d) basis set. As it is known that the charge transfer in the CT systems depends on the exact Hartree exchange (α) employed in hybrid functional [40–42], we have checked the amount of charge transfer by using M06-2X [43] which takes into account $\alpha=0.54$, as well as wB97XD which takes into account $\alpha=0.22$, and we find that the amount of CT is very similar by both. These values also are very small, thus CT is not possible in ground state, as found for TTF–TCNQ pair previously [41,42]. We have also calculated the

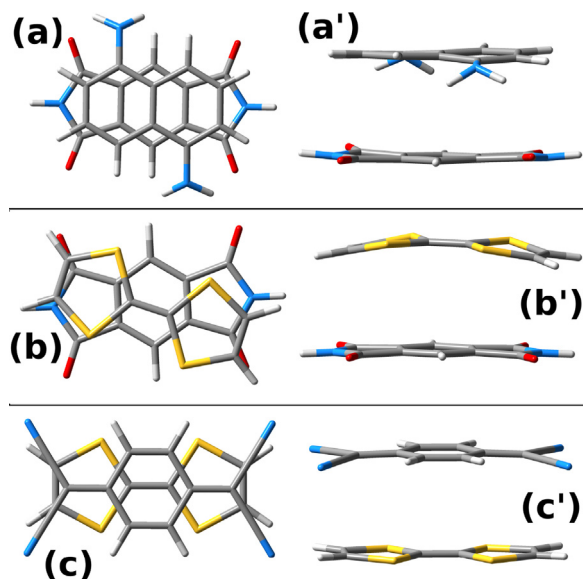


Figure 2. (a) Naph–Diimide, (b) TTF–Diimide, and (c) TTF–TCNQ pairs. Left and right column depicts the top and side views, respectively.

adsorption energy values for the donor–acceptor pairs corrected with basis set superposition error (BSSE). We have calculated the HOMO–LUMO (H–L) gaps of the systems using M06-2X. We have calculated the electronic absorption spectra using time-dependent density functional theory (TD-DFT) methods. For the TD-DFT calculations, we have used wB97XD along with 6-31g(d) basis set, as it was found to give good results for these types of systems [44]. We have also checked the optical adsorption spectra with B3LYP hybrid functional [45–47] and CAM-B3LYP functional [48] which is the long range corrected version of B3LYP and uses the Coulomb-attenuating method (results are given in supporting information).

3. Results and discussions

3.1. Structure and energetics of the donor–acceptor pairs

In this study, we have considered naphthalene-diamine (Naph) and tetrathiafulvalene (TTF) molecules as electron donors and benzene-diimide (Diimide) and tetracyanoquinodimethane (TCNQ) as electron acceptors (see Figure 1). We have performed all our calculations on three sets of electron donor–acceptor pairs, namely, Naph–Diimide, TTF–Diimide and TTF–TCNQ pairs.

After optimizing the structures, we have found that all the donor–acceptor systems are almost parallel to each other and remain face to face because of π stacking; only the TTF moiety bends in a slight amount towards the acceptor molecules. In Naph–Diimide pair, the molecules stay in a staggered geometry to minimize the steric repulsion (Figure 2a). In the other two pairs the C=C of the TTF moiety remains inside the benzene ring of the acceptor moiety [Figure 2b and c].

We have calculated the adsorption energy of the pairs using the following formula:

$$E_{\text{adsorption}} = E_{\text{total}} - E_{\text{donor}} - E_{\text{acceptor}} \quad (1)$$

We find that the BSSE corrected adsorption energy values are -0.70 eV, -0.33 eV and -0.68 eV for Naph–Diimide, TTF–Diimide and TTF–TCNQ, respectively. The negative adsorption energy values suggest that all the systems are thermodynamically stable (Table 1).

We have calculated the charge transfer from the donor to the acceptor moiety. We find that, in each case there is a finite amount of charge transfer present in the system. We have presented the

Table 1
Adsorption energy values and charge transfer values of all the systems are given.

System	BSSE corrected adsorption energy eV	HOMO–LUMO gap eV	Charge transfer by wB97-XD (e)			Charge transfer by M06-2X (e)		
			Macrocycle	Donor	Acceptor	Macrocycle	Donor	Acceptor
Naph–Diimide	–0.70	4.28	–	0.06	–0.06	–	0.06	–0.06
Naph–Diimide in framework	–2.36	3.97	0.03	–0.02	–0.013	0.028	–0.014	–0.0136
TTF–Diimide	–0.33	3.88	–	0.021	–0.021	–	0.023	–0.023
TTF–Diimide in framework	–2.25	3.85	0.03	–0.02	–0.01	0.03	–0.017	–0.014
TTF–TCNQ	–0.68	2.44	–	0.044	–0.044	–	0.024	–0.024
TTF–TCNQ in framework	–1.82	2.52	0.036	0.03	–0.066	0.033	0.036	–0.07

charge transfer values in Table 1. The positive (negative) values indicate that the molecule gives (accepts) electrons. Thus, it is evident that there is a charge transfer always from the donor to the acceptor moiety. We have also found that, the amount of charge transfer is highest for Naph + Diimide, followed by TTF–TCNQ and TTF–Diimide.

3.2. Structure and energetics of the donor–acceptor pairs inside the macrocycle molecule

We have considered the three donor–acceptor pairs inside the cucurbit[8]uril macromolecule and optimized our systems in the experimentally realized cage structure. We find that the structure and orientation of two pairs change significantly when captured inside the cage, the Naph–Diimide and TTF–Diimide pairs change their structure and orientation. In free state, the molecules are completely in parallel and exactly one on top of the other position, but inside the cage, the molecules are in a slipped-stack position and in the TTF–Diimide pair, the TTF moiety bends to a significant amount. Interestingly, the TTF–TCNQ pair does not show that much change in the structure or orientation. Only the TCNQ molecule bends to some extent, but they still remain parallel to each other (Figure 3). We attributed this finding to the fact that the electronic repulsion between the oxygen atoms of the cage and the Diimide moiety pushes the Diimide molecule little away from the cage, but TTF–TCNQ pair does not have any such effect, thus it remains as it is.

We have calculated the adsorption energy of the pairs inside the cage using the following formula:

$$E_{\text{adsorption}} = E_{\text{total}} - E_{\text{cage}} - E_{\text{donor}} - E_{\text{acceptor}} \quad (2)$$

We find that again all the systems are thermodynamically stable and have negative adsorption energy values. When the systems are inside the cage, they are more stable compared to their

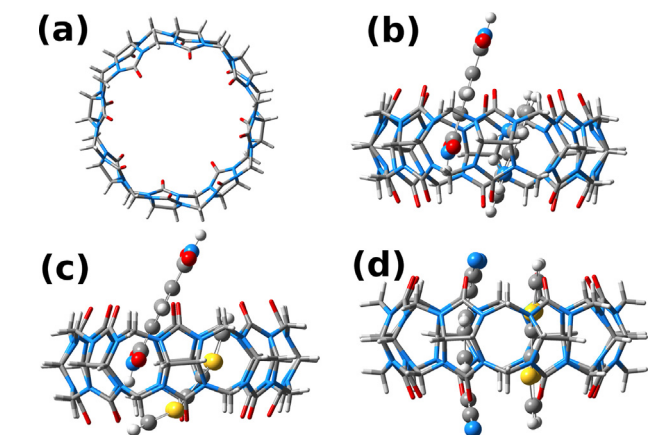


Figure 3. (a) Cucurbit[8]uril, (b) Naph–Diimide, (c) TTF–Diimide, and (d) TTF–TCNQ pairs inside the macrocycle.

free state, i.e. their absorption energy values are more negative (Table 1).

We have also calculated the amount of charge transfer in the systems (Table 1) and we find that always the cage gives ~0.03 e charge irrespective of the systems. In the Naph–Diimide and TTF–Diimide pairs, both the donor and acceptor molecules take some amount of charge from the cage. But, in the TTF–TCNQ pair, both the cage and the donor molecule transfer some amount of charge to the acceptor molecule. This change in the charge transfer nature of the pairs is due to their structural changes inside the macrocycle.

3.3. Optical absorption of the systems

We now present the electronic transitions for the donor–acceptor pairs in free state and inside the macrocycle in Figure 4 (for reference, we have also given absorption spectra of isolated molecules). We are presenting the data obtained by wB97XD functional here; the other results are given in supporting information. The results sometimes vary with functionals; we have discussed it in details in S.I.

We find that, the cage does not have any effect in the optical properties of the systems. It shows a very weak peak around ~182 nm ($f=0.0006$) and does not interfere with any optical absorption peaks of the D–A pairs, but it is the incorporation of the ring which changes the orientation of the D–A pairs. Thus, the changes in optical properties of the D–A pairs inside the cage is solely because of the changes in their geometries inside the cage.

We have calculated the HOMO–LUMO (H–L) gaps of the systems and found that for all the three systems, H–L gaps does not change very much when incorporated inside the cage.

The optical property mainly changes due to the change in the type of transition (from which orbital to which), We have discussed the type of the transitions in Table 2. So, in case of TTF–TCNQ, the type is same in both the free and encapsulated state (HOMO – 1 to LUMO), thus, the peak does not shift to a large extent. In the other cases, because of the change in structure, the transition type changes, which leads to shift in the peaks. Also, peaks are not created or destroyed in case of the macrocycle, they are either shifted from original position (free pairs), or have very low oscillation strength.

In case of the free Naph–Diimide, we got two high intensity peaks centred at 301.92 nm and 477.54 nm and when the pair is inside the cage, it shows an intense peak around 293.04 nm and a weak peak at 320.46 nm. We have plotted the wave-functions corresponding to those transitions to understand the nature of the spectra and we have found that both the peaks are of charge transfer in nature in the free pair. But, in the captured pair, the intense peak comes because of naphthalene $\pi-\pi^*$ transition and the small peak arises because of the D–A charge transfer (Figure 5a). Thus, it is very clear that the cavity binding of the D–A pair changes the nature of spectra from CT transition to naphthalene $\pi-\pi^*$ transition.

In case of free TTF–Diimide, we find three low intensity peaks (Figure 4 and Table 2) but when the pair is inside the cage, it shows a single intense peak around 278.04 nm and we have found that all

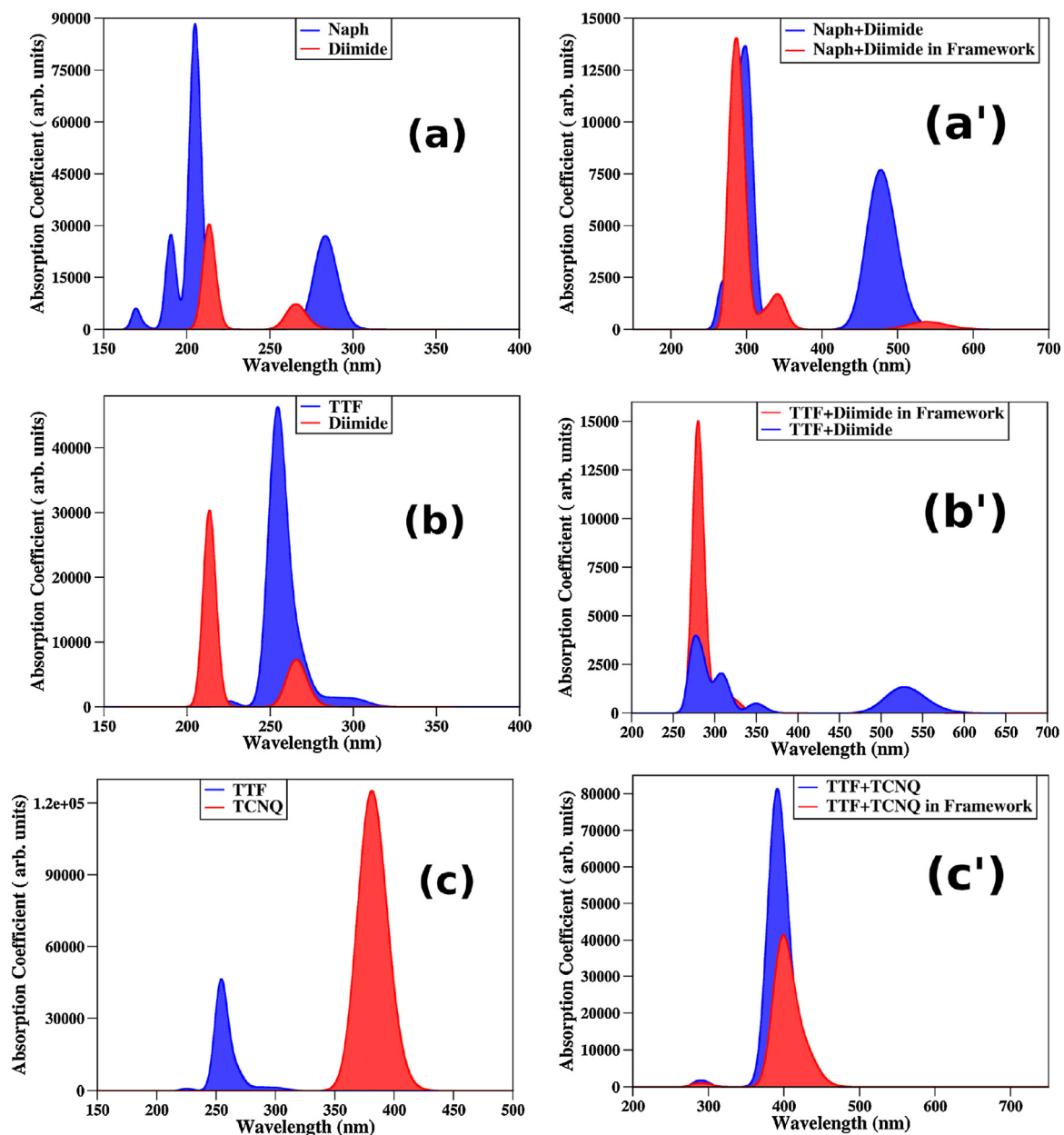


Figure 4. Optical absorption spectra of (a) Naph–Diimide, (b) TTF–Diimide, and (c) TTF–TCNQ. The left column (a)–(c) indicates the optical absorption spectra of separated molecules and the right column (a')–(c') indicates the optical absorption spectra of the D–A pairs in free and captured state.

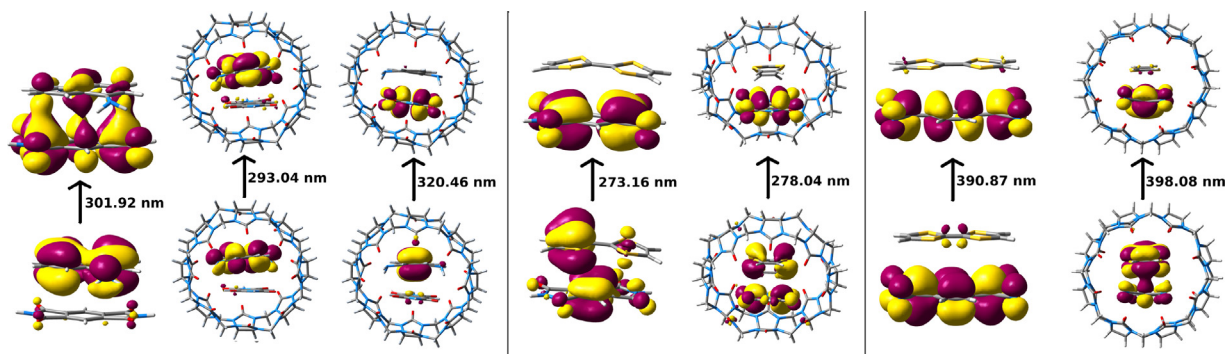


Figure 5. The wave-function plots corresponding to the electronic transitions of (a) Naph–Diimide, (b) TTF–Diimide, and (c) TTF–TCNQ pairs in free state and inside the cage.

Table 2
Optical absorption peaks and oscillator strengths of the systems.

System	Absorption peak	Type of transition (max. contribution)	Oscillator strength
	nm		f
Naph–Diimide	301.92	H→L+2	0.1031
	477.54	H→L	0.0707
Naph–Diimide in framework	293.04	H→L+3	0.0623
	320.46	H–2→L	0.0042
TTF–Diimide	273.16	H–2→L	0.0281
	311.83	H–1→L	0.0119
TTF–Diimide in framework	527.88	H→L	0.0123
	278.04	H–3→L	0.0774
TTF–TCNQ	390.87	H–1→L	0.7366
TTF–TCNQ in framework	398.08	H–1→L	0.3575
		H–2→L	

the peaks of the free D–A pair and the pair inside the cage are of charge transfer in nature (Figure 5) (in the captured phase, due to confinement the charge transfer is diminished).

Finally, for the TTF–TCNQ pair, there is only a red shift of ~7 nm when the D–A pair goes inside the cage from the free state (Table 2). But, the nature of the peaks changes. Free TTF–TCNQ pair shows the peak mainly because of π – π^* transition in the TCNQ moiety, but, inside the cage the peak is a charge transfer type.

Thus, to tune the charge transfer and optical properties of a D–A pair, a macrocycle cage can be selected in such a manner that there will be an interaction between the donor and/or acceptor molecule and as a result the structure or orientation of the molecule can change inside the cavity which, in term, will lead to the change in photophysical properties of the systems.

4. Conclusions

In conclusion, we have performed a detailed investigation on three organic D–A pairs, namely, Naph–Diimide, TTF–Diimide and TTF–TCNQ pairs. Our study suggests that these pairs form stable CT complexes via charge transfer from the donor to the acceptor moiety. These D–A molecules are almost parallel to each other in free state. These complexes show prominent optical absorption peaks because of charge transfer between the D–A pair or π – π^* transition in the donor or acceptor. Interestingly, when the D–A pairs were incorporated inside the cucurbit[8]uril cavity, Naph–Diimide, TTF–Diimide pairs show significant change in the structure. The benzene–diimide molecule tries to escape the cavity because of Coulombic repulsion between the keto groups. As a result, we have found the molecules to be stable in a slipped stack fashion and in TTF–Diimide pair, the TTF molecule gets puckered. But, the TTF–TCNQ pair does not show significant change in the structure or orientation of the D–A pair. These changes in structure manifests in the optical absorption profile of the D–A pairs. Thus, a macrocycle molecule and D–A pair can be designed in such a manner that they will be stable, interact and leading to the change in their photophysical properties.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2015.02.012.

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