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 pi 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 MoS_2 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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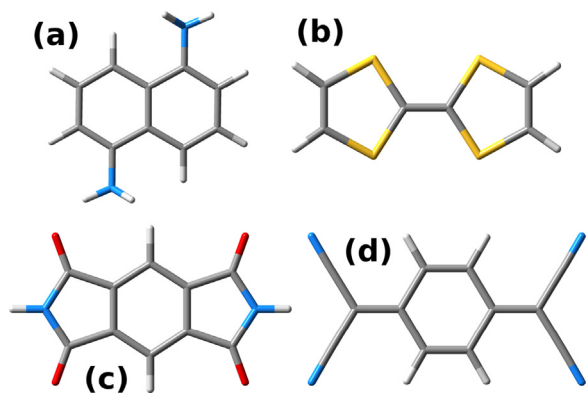 *E-mail address:* pati@jncasr.ac.in (S.K. Pati).

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
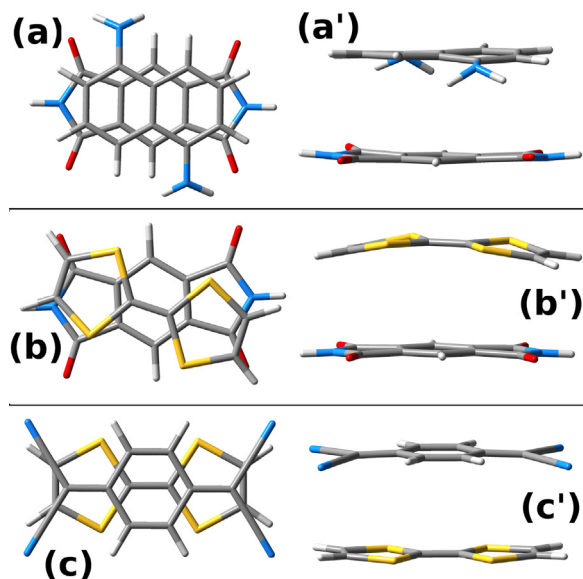

Figure 2. (a) Naph–Diimide, (b) TTF–Diimide, and (c) TTF–TCNQ pairs. Left and right column depicts the top and side views, respectively.

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:

$$E_{\text{adsorption}} = E_{\text{total}} - E_{\text{donor}} - E_{\text{acceptor}} \tag{1}$$

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