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Prediction of charge transfer transition energies of the molecular complexes of PMDA with a series of methylbenzenes by TDDFT

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The functionals M06, M06-L, M06-2X and B3LYP were used to establish molecular complex formation and to calculate CT transition energies of the molecular complexes of PMDA with benzene, toluene, *p*-xylene, mesitylene and durene in CCl_4 medium by a TDDFT calculation under the PCM formalism. Using the ground state optimized geometries as starting points, attempts were made to calculate the CT transition energies of the molecular complexes by TDDFT/6-31++G(d,p). The calculated $h\nu_{CT}$ values obtained by the different functionals were compared among themselves and also with experimentally reported values. Agreement of the calculated CT transition energies with experimental values is reasonably good, M06 results being closest. The lowest energy CT absorption bands as calculated by TDDFT were found to abide by the theory of charge transfer complexes given by Mulliken (*J. Am. Chem. Soc.,* 1952, **74**, 811).

Keywords: TDDFT, charge transfer, PMDA complex, M06 functionals, Mulliken's theory.

Introduction

Transition energies and excited state properties of molecules are generally calculated by the time dependent density functional theory (TDDFT)[1–5]. It is well known that some inherent deficiencies[6–10] of the traditional functionals like B3LYP, MPW1PW91, PBE etc., make them unreliable for the prediction of electronic transition energies of charge transfer (CT) complexes (non-covalently bonded molecular adducts) by TDDFT. It has been found that the M06 family of functionals[11–14] developed by Truhlar *et al.* overcome these deficiencies to a great extent by reducing the self-interaction and self-correlation errors through inclusion of the kinetic energy density in the generalized gradient approximations (GGA) and also different percentages of Hartree-Fock exchange. Such functionals have been shown to work well in case of weak interactions[15–18]. Suitability of these functionals was tested for prediction of electronic excitation energies of some main group (benchmark) molecules and also of the $C_2H_4....C_2F_4$ CT complex. Performance of these functionals in predicting the CT transition energies of TCNE with two series of electron donor molecules have been tested fairly recently[19,20] and have been found to be reasonably suitable.

According to Mulliken's theory[21] the molecule of a charge transfer complex is a linear combination of a 'no-bond' and a 'dative' structure; the ground and excited states of such a complex formed between a donor (*D*) and an acceptor (*A*) is described by the wave functions

$$\psi_{\text{ground}} = a\psi(D\cdots A) + b\psi(D^+\cdots A^-),\ a>>b$$
$$\psi_{\text{excited}} = a^*\psi(D\cdots A) + b^*\psi(D^+\cdots A^-),\ b^*>>a^*$$

where $D\cdots A$ means a 'no-bond' structure in which the molecules *D* and *A* are held together by van der Waals type of interactions and $D^+\cdots A^-$ is a 'dative' structure formed by the transfer of an electron from *D* to *A*, the resulting ions being held by Coulombic interaction. The ground state is dominated by the 'no-bond' structure while in the excited state the 'dative' form predominates. The charge transfer transition energy corresponds to the transition

$$\psi_{\text{ground}} \xrightarrow{h\nu_{CT}} \psi_{\text{excited}}$$

Using this model Mulliken[21] arrived at the following expression for the charge transfer transition energy:

$$h\nu_{CT} = I_D^V - C_1 + \frac{C_2}{I_D^V - C_1} \qquad (1)$$

$$C_1 = E_A^V + G_1 + G_0 \qquad (2)$$

Here E_A^V = vertical electron affinity of the acceptor (PMDA),

G_0 = total 'no-bond' interaction energy (dipole-dipole, van der Waals interaction, etc.) in the state, G_1 = energy of electrostatic attraction between D^+ and A^- (the positively charged donor and the negatively charged acceptor) in the 'dative' state of the complex, C_2 = resonance energy of interaction between the 'no-bond' and 'dative' forms in the ground and excited states.

The objective of the present work is to verify this model in the light of density functional theory. The series of complexes under study have the common acceptor, pyromellitic dianhydride (PMDA) and the donors are benzene, toluene, *p*-xylene, mesitylene and durene. These complexes were experimentally studied in CCl_4 medium and their CT transition energies were reported long ago[22] by Rosenberg and Eimutis. In the present work each complex in the series has been considered as a single whole molecule and the CT transition energies have been estimated computationally by applying TDDFT using the Truhlar functionals M06, M06L and M06-2X and also the traditional B3LYP functional for a comparison. Effect of solvent has been taken into account by using the polarizable continuum model.

Before proceeding to the calculation of CT excitation energy, formation of the complexes in CCl_4 solvent in the ground state was established by theoretical computation of the ground state geometry. According to Mulliken's model practically very little charge transfer should occur in the ground state. In the first part of the present work attempt has been made to verify this by optimizing the ground state geometries of the complexes and calculating the electronic charge distributions by natural population analysis (NPA); for further substantiation of such charge distributions in the ground state, ^{13}C and ^1H NMR chemical shifts of the atoms in the PMDA moiety in the complexed and isolated states were calculated and the results were checked against the NPA charges. After thus characterizing the ground states TDDFT calculations in CCl_4 medium on the optimized geometries were performed to estimate the CT transition energies of the complexes. The calculated CT transition energies were compared with experimentally reported values[22] and finally, for the whole series of complexes, an attempt was made to see how far the calculated CT transition energies agree with eq. (1) i.e. with Mulliken's model of CT complexes.

Computational details:

The Gaussian 09 Revision A.02 suite of programmes[23] was used to perform DFT calculations. The Minesota functionals of Truhlar *et al.*[11–14], namely, M06L, M06 and M06-2X (which include respectively 0%, 27% and 54% HF exchange) were used for DFT calculations. The traditional B3LYP functional, which comprises a combination of Becke's three parameter hybrid[24] exchange potential with the correlation functional of Lee, Yang and Parr[25] was also used for a comparison of the results. The basis set 6-31++G** which is standard for elements up to the second row of the periodic table was used for all the complexes under study. Ground state geometry optimization of the molecules was carried out in CCl_4 solution. The polarizable continuum model (PCM) was utilized for consideration of solvation effects. This model was devised by Tomasi *et al.*[26,27]; it places the solute in the solvent reaction field created by a series of overlapping spheres. In the Gaussian the PCM was implemented by Barone *et al.*[28–30] and also by Tomasi and co-workers[31,32]. The PCM results are sensitive to the radius of the added spheres and the average area of the tesserae generated on each sphere; the area can be adjusted, with best compromise between accuracy and numerical stability, in the range 0.2–0.4 Å^2. For the whole series of complexes under study, the average tesserae area of 0.2 Å^2 was found to give satisfactory results. The first step of the computational work was ground state geometry optimization of all the complexes under study (and also of their component molecules). This was followed by calculation of vibrational frequencies, ^1H and ^{13}C NMR chemical shifts and electronic charge distribution on the atoms by natural population analysis (NPA). The optimized structures were subjected to TDDFT calculation for obtaining the electronic transition energies.

Results and discussion

Formation of molecular complex in the ground state: Computational evidence:

The individual molecules, PMDA, benzene, toluene, *p*-xylene, mesitylene and durene were subjected to geometry optimization in CCl_4 medium. Geometries of the molecular adducts benzene-PMDA, toluene-PMDA, *p*-xylene-PMDA, mesitylene-PMDA and duene-PMDA, considered as single supermolecules were first optimized in the gas phase. For taking into account solvation effects these optimized structures were then further optimized in CCl_4 medium using the PCM model with an average tesserae area of 0.2 Å^2. Frequency calculations were carried out on the optimized (energy minimized) structures to examine whether they correspond to real minima or not. All the functionals yielded optimized structures giving positive frequencies for each of the five complexes under study; this showed that the optimized geometries did correspond to real minima and not to saddle points. Geometry optimizations for the complexes were carried out by taking initial guess coordinates from the minima of the potential energy surface scans performed prior to optimization. Optimized structure of the toluene-PMDA complex obtained by using the M06-2X functional is given in Fig. 1 as a typical case. In the Supplementary information the ground state optimized structures (along with co-ordinates) obtained by using the M06 functional are given for all the five complexes under study. That some amount of the electronic charge has been transferred to the acceptor molecule (PMDA) from the donor molecules (the aromatic hydrocarbons) by complexation even in the ground state is indicated by the direction of the calculated dipole moment vector (Fig. 1). The distribution of the electronic charges on the atoms of isolated PMDA, calculated by natural population analysis, are in accordance with symmetry requirement (Tables S1 and S2 in Supplementary information). NPA calculation on the molecular adducts shows that this distribution of electronic charge becomes somewhat asymmetrical on complexation. Moreover, the natural charges on the atoms of the PMDA moiety in each complex add up to a negative value; this indicates the transfer of some electronic charge, although very little (about 1.0%), from the aromatic hydrocarbon to the PMDA moiety in the complex in its ground state. This is in compliance with Mulliken's theory of charge transfer complexes[21] which states that in the ground state the 'no-bond' structure predominates. The calculated NPA charges and ^{1}H NMR chemical shifts of the H-atoms of PMDA in the complexes are summarized in Table 1 with atom labels as shown in Fig. 2 (C-atom charges and ^{13}C NMR chemical shifts are given in Tables S1- S3 of the Supplementary information). It is found that the ^{1}H chemical shifts are approximately in accordance with the electronic charge distribution for the PMDA

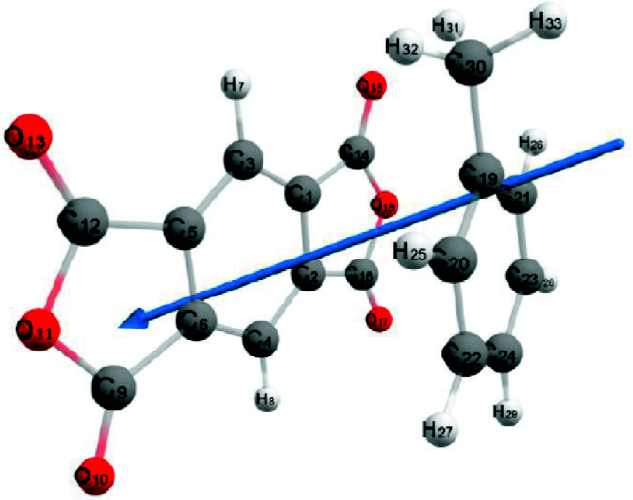

Fig. 1. Ground state optimized geometry of the toluene-PMDA complex calculated at DFT/M06/6-31++G(d,p). Arrow shows the direction of calculated dipole moment.

Table 1. Calculated ^{1}H NMR chemical shifts (δ) and electronic charges (*q*) of the H-atoms of PMDA in isolated molecule and in complexes with the aromatic hydrocarbons in CCl_4 medium [Ref = TMS B3LYP/ 6-311+G(2d,p) GIAO]

Functional	M06-2X		M06-L		M06		B3LYP	
	q_h	δ	q_h	δ	q_h	δ	q_h	δ
Isolated PMDA	$q_g = q_h =$ 0.299	9.6 (g,h)	$q_g = q_h =$ 0.283	8.5 (g,h)	$q_g = q_h =$ 0.293	8.9 (g,h)	$q_g = q_h =$ 0.291	9.0 (g,h)
Benzene-PMDA	$q_g = q_h =$ 0.296	8.9 (g,h)	$q_g = q_h =$ 0.280	8.5 (g,h)	$q_g = q_h =$ 0.291	8.5 (g), 8.6 (h)	$q_g = q_h =$ 0.290	8.6 (g,h)
Toluene-PMDA	$q_g = q_h =$ 0.296	9.0 (g,h)	$q_g = 0.279$, $q_h = 0.280$	8.1(h), 8.3 (g)	$q_g = q_h =$ 0.291	8.2 (g), 8.5 (h)	$q_g = q_h =$ 0.290	8.6 (g,h)
p-Xylene-PMDA	$q_h = q_h =$ 0.296	9.2 (g,h)	$q_g = 0.279$, $q_h = 0.280$	8.2 (g), 8.3 (h)	$q_g = q_h =$ 0.290	8.3 (g,h)	$q_g = 0.291$, $q_h = 0.290$	8.6 (g), 837 (h)
Mesitylene-PMDA	$q_g = 0.288$, $q_g = 0.291$	9.3 (h), 9.5 (g)	$q_g = 0.273$, $q_h = 0.195$	8.2 (h), 8.6 (g)	$q_g = 0.285$, $q_h = 0.154$	9.6 (g,h)	$q_g = q_h =$ 0.290	8.7 (g,h)
Durene-PMDA	$q_g = 0.042$, $q_h = 0.291$	9.1 (h), 9.5 (g)	$q_g = 0.121$, $q_h = 0.274$	8.0 (h), 8.2 (g)	$q_g = 0.145$, $q_h = 0.296$	8.2 (h), 8.4 (g)	$q_g = q_h =$ 0.290	8.6 (g,h)

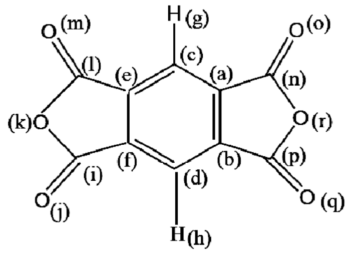

Fig. 2. Labels for atoms in the PMDA moiety of the complexes and also in isolated PMDA molecule.

moiety in the complexes and also in isolated PMDA molecule.

Calculation of CT transition energies of the molecular complexes by TDDFT:

Using the ground state optimized geometries of the complexes TDDFT/PCM calculations were performed on the five complexes under study. Results are summarized in Table 2 along with the experimentally reported[22] CT transition energies of the complexes. Electronic transition energies of the individual molecules (the aromatic hydrocarbons and PMDA) in CCl_4 medium were also calculated by TDDFT. Isolated PMDA was found to have electronic absorption bands above 35000 cm^{-1} and those of the aromatic hydrocarbons were above 40000 cm^{-1}. The calculated CT absorption bands of the complexes were all found to appear below 35000 cm^{-1}. The calculated TD spectra of isolated toluene, isolated PMDA and their CT complex are shown in Fig. 3 as a typical case. The CT absorption bands of the complexes in the calculated TD spectra were identified by excluding the calculated spectra of the individual components from those of complexes. Experimentally, two electronic charge transfer absorption bands were found for all the complexes in the series (excepting the durene complex which showed three bands). The present TDDFT calculations gave two to three CT absorption bands depending on the functional used. The transitions were assigned on the basis of the largest molecular orbital coefficients in the CI expansion as obtained in the output of the TDDFT calculations performed with 10 singlet excitations. With all the functionals, the lowest energy CT band for each complex corresponded to the HOMO-LUMO transition in the molecular adduct; the other two bands were of mixed type in which the major contribution came from (HOMO-1)-LUMO and (HOMO-1)-(LUMO+1).

Verification of eq. (1) using the calculated lowest energy CT transition energies:

In eq. (1) C_1 and C_2 are constants for a series of CT complexes of a particular acceptor and a number of structurally similar donors in a given solvent, and most often G_0 is small. Hence eq. (1) can be rearranged as

$$2I_D^V - h\nu_{CT} = \frac{I_D^V\left(I_D^V - h\nu_{CT}\right)}{C_1} + C_1 + \left(\frac{C_2}{C_1}\right) \qquad (3)$$

The longest wavelength CT transition energies and the ionization potentials (= negative of the highest occupied orbital energies) computed using the M06 functional give an excellent linear plot (Fig. 4) as expected from eq. (3) and the following linear regression equation is obtained:

$$2I_D^V - h\nu_{CT} = (0.152\pm0.009)\, I_D^V\left(I_D^V - h\nu_{CT}\right) + (6.915\pm0.339)$$

Correlation coeffient = 0.994 (4)

The CT nature of the TDDFT-calculated lowest energy absorption band (resulting from the HOMO-LUMO transition in the molecular adducts) is thus established in the light of Mulliken's theory[21]. This is further revealed by the electron density distribution of these two molecular orbitals, Gaussview picture of one typical case being shown in Fig. 5. In the HOMO

Table 2. CT transition energies (eV) of the five complexes of PMDA with the aromatic hydrocarbons in CCl_4 medium calculated by TDDFT method using B3LYP and three M06 functionals; experimentally reported values[22] are given in the last row

Functional	Benzene-PMDA	Toluene-PMDA	*p*-Xylene-PMDA	Mesitylene-PMDA	Durene-PMDA
M06-2X	3.884, 3.963	3.635, 3.840, 4.534	3.378, 3.769, 4.231	3.401, 4.256, 4.311	3.080, 3.498, 3.982
M06-L	2.386, 3.333, 3.842	3.290, 3.544, 3.923	3.194, 3.301, 3.746	2.822, 3.369, 3.935	3.309, 3.461, 3.936
M06	2.957, 3.903	3.563, 3.863, 4.312	3.310, 3.756, 4.070	3.407, 4.144	3.065, 3.805, 3.964
B3LYP	2.614, 3.575	2.299, 3.509	2.955, 3.412, 3.660	3.018, 3.703	3.060, 3.354, 3.766
Experimental	3.025, 3.596	3.757, 4.215	3.484, 4.029	3.385, 4.079	3.174, 3.546, 3.992

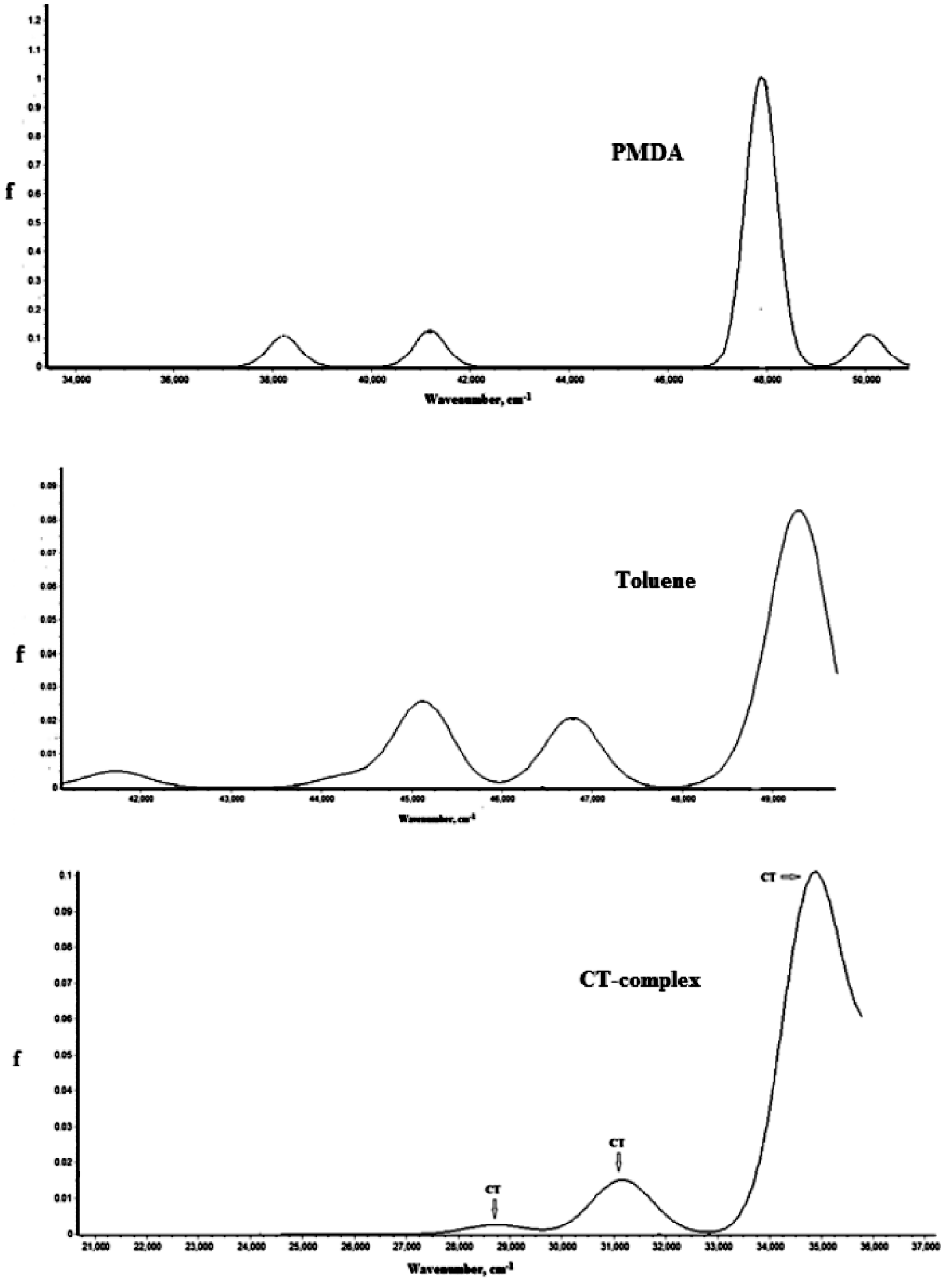

Fig. 3. Calculated TD spectra of isolated PMDA, isolated toluene and toluene-PMDA complex in CCl_4 medium calculated at TDDFT/M06/6-31++G(d,p) level of theory.

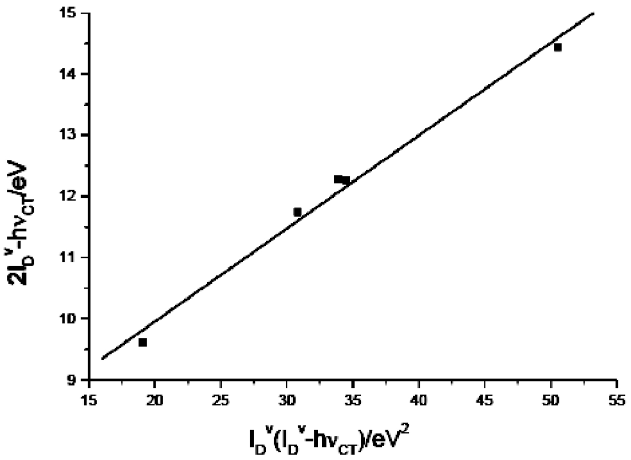

Fig. 4. Correlation between the vertical ionization potentials of the donors and calculated CT transition energies of the complexes of PMDA with benzene and four methyl-benzenes according to Mulliken's theory[21]. Level of calculation: TDDFT/M06/6-31++G(d,p).

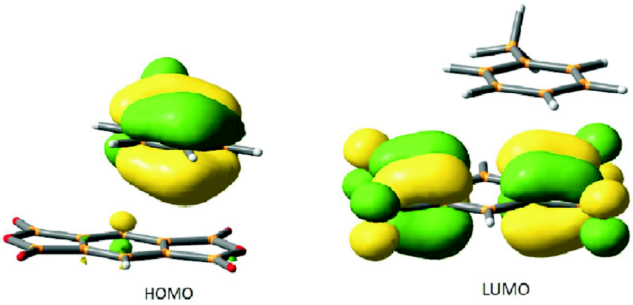

Fig. 5. Electron density distribution in the HOMO and LUMO of the toluene-PMDA complex in its ground state. Level of calculation: DFT/M06/6-31++G(d,p).

the electron density is mostly concentrated on the donor moiety while the LUMO is mostly concentrated on the acceptor moiety (PMDA).

Concluding remarks

Compared to experimental values, the B3LYP functional underestimates the CT transition energies throughout the series. With the other three functionals, agreement with experimental values is fairly good, the results found with M06 being closest to the experimental values. Moreover, the trend of the calculated CT bands in the series with variation in the number of methyl groups in the donor moiety is in accordance with Mulliken's theory of charge transfer complexes.

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