The theoretical studies on the two-photon absorption properties of symmetric 1,4-bis{2-[4-(2-aryl)phenyl]vinyl}-2,5-bisdialkoxybenzenes*

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On the level of the time-dependent hybrid density functional theory, the one- and two-photon absorption properties of a series of symmetric 4-bis{2-[4-(2-aryl) phenyl]vinyl}-2,5-bisdialkoxybenzenes are studied respectively utilizing the analytic response theory and the few-state model methods. The calculated results show that the planarity of the geometrical structure plays a great role in enhancing the linear and nonlinear optical abilities of the molecule. However the effect of the length of the chain linked to the π-centre on the optical property is very little. For the investigated compounds, the A–π–A type charge-transfer molecules display more superior one- and two-photon absorption characteristics than the D–π–D type ones. Furthermore, the two-photon absorption results by use of few-state model are generally consistent with those by analytic response theory, demonstrating the reliability of the few-state model for evaluating the two-photon absorption cross section. The numerical simulations are in good agreement in tendency with the available experimental measurements.

Keywords: two-photon absorption, analytic response theory, few-state model

PACC: 3120A, 3280K, 4265

1. Introduction

The concept related to the two-photon absorption (TPA) process by simultaneously absorbing two photons was first theoretically predicted by Göppert-Mayer in 1931.[1] Until 1961, one year after the advent of the intense coherent laser, the first experimental observation of TPA induced frequency-upconversion fluorescence was reported by Kaiser and Garrett.[2] Since then, abundant researches both in theory and in experiment have confirmed that the TPA active materials exhibit unique advantages in various new techniques, for example, two-photon excited fluorescence microscopy,[3−5] optical limiting,[6] upconverted lasing,[7] three-dimensional optical data storage,[8,9] and so on. Therefore, the design and synthesis of the chromophores possessing the large TPA cross sections has become the popular subject highly concerned by the theoretical and experimental workers. Up to now, great efforts have been paid to establish a so-called "structure-to-property" relationship, as the effective strategy and guideline of design and synthesis for excellent TPA chromophores. It is shown that the TPA abilities of organic compounds are strongly dependent on a few factors, such as the π centre property and conjugated length, the symmetrical or asymmetrical arrangement of the electron–donor (D) and electron–acceptor (A) attached to the π centre and their strengths of pushing and pulling electrons, and the dimensionality of the molecule.[10−19]

Recently, Yan *et al.*[20] have successfully synthesised a series of symmetrical compounds, namely 9-(4-{(1E,11E)-4-[(E)-4-(9H-carbazol-9-yl)styryl]-2,5-dimethoxystyryl}phenyl)-9H-carbazole (marked as M1), N-(4-{(1E,8E)-4-[(E)-4-(diphenylamino)styryl]-2,5-dimethoxystyryl}phenyl)-N-phenylbenzeneamine (M2), 1,4-bis{2-[4-(2-pyridin-4-ylvinyl)phenyl]vinyl}-2,5-bisdimethoxybenzene (M3) and 1,4-bis{2-[4-(2-pyridin-4-ylvinyl)phenyl]vinyl}-2,5-bisdodecyloxybenzene (M4). Experiments have measured the one-photon absorption (OPA), one-photon fluorescence and fluorescence quantum yields, as well as the two-photon fluorescence in various solvents. Moreover, the experimental observations have proved that all

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the compounds are very effective two-photon photon-polymerisation initiators.

In the present work, we investigate theoretically the OPA and TPA properties of the compounds by means of the analytic response theory on the density functional theory (DFT) level. Furthermore, a few-state model is also provided to calculate the TPA cross sections of M3 and M4 molecules in order to understand the TPA mechanism more clearly, meanwhile the reliability of the few-state model approach is discussed by comparing the TPA results of both theoretical methods. In addition, the intramolecular charge-transfer (CT) processes in the excited states of the compounds are illustrated for the purpose of exploring the intrinsic origin of the molecular optical nature.

2. Computational details

The transition probability of the OPA is given by oscillator strength

$$\delta_{\rm op} = (2\omega_f/3)\sum_{\alpha} |\langle 0|\,\mu_\alpha\,|f\rangle|^2, \tag{1}$$

where μ_α is the electric dipole moment operator, $|0\rangle$ and $|f\rangle$ denote respectively the ground and final states, ω_f stands for the excitation energy of the final state, the summation is performed over the molecular x, y and z axes.

In terms of the sum-over-state formulae, the TPA transition matrix element of two-photon resonant absorption excited by linearly polarized monochromatic beam is expressed as

$$\begin{aligned} S_{\alpha\beta} = & \sum_j [\langle 0|\mu_\alpha|j\rangle\langle j|\mu_\beta|f\rangle(\omega_j - \omega_f/2) \\ & + \langle 0|\,\mu_\beta\,|j\rangle\,\langle j|\,\mu_\alpha\,|f\rangle/\,(\omega_j - \omega_f/2)]. \end{aligned} \tag{2}$$

Here α, $\beta = \{x, y, z\}$, and $|j\rangle$ denotes all the intermediate states, ω_j is the excitation energy of the excited state. The TPA cross section is given by orientational averaging over the TPA probability[21]

$$\begin{aligned} \delta_{\rm tp} = & \sum_{\alpha\beta} [F \times S_{\alpha\alpha} S^*_{\beta\beta} + G \times S_{\alpha\beta} S^*_{\alpha\beta} \\ & + H \times S_{\alpha\beta} S^*_{\beta\alpha}]. \end{aligned} \tag{3}$$

The coefficients F, G, and H are related to the incident radiation. For the linearly polarized light, F, G, and H are 2, 2, and 2, respectively. Then the TPA cross section is expressed as

$$\begin{aligned} \delta_{\rm tp} = & \, 6\,(S_{xx} + S_{yy} + S_{zz})^2 \\ & + 8(S^2_{xy} + S^2_{xz} + S^2_{yz} - S_{xx}S_{yy} \\ & - S_{xx}S_{zz} - S_{yy}S_{zz}). \end{aligned} \tag{4}$$

The TPA cross section, directly comparable with experimental measurements, is defined as

$$\sigma_{\rm tp} = \left(4\pi^2 a_0^5 \alpha/(15c_0)\right)\left(\omega^2 g\,(\omega)/\Gamma_f\right)\delta_{\rm tp}. \tag{5}$$

Among them a_0 is the Bohr radius, c_0 is the speed of light, α is the fine structure constant, $\hbar\omega$ is the photon energy of the incident light, $g(\omega)$ denotes the spectral line profile that is assumed to be a δ function in this work. Γ_f is the level broadening of the final state, which is taken as a common value[22] 0.1 eV with the corresponding lifetime of a few femtoseconds.

For a centrosymmetric molecule, the permanent electric dipole moment is very little, so its contribution to the TPA cross section can be neglected. Inserting Eq. (2) into Eq. (4), the total TPA cross section can be simplified as

$$\delta_{\rm tp} = \sum_i \delta^i_{\rm tp} + \sum_i \sum_{j>i} \delta^{ij}_{\rm tp}, \tag{6}$$

where

$$\begin{aligned} \delta^i_{\rm tp} &= 8(\mu^{0i})^2(\mu^{if})^2(2\cos^2\theta^{\mu^{0i}}_{\mu^{if}} + 1)/\Delta E_i^2, \\ \delta^{ij}_{\rm tp} &= 16(\mu^{0i}\mu^{if}\mu^{0j}\mu^{jf}) \\ &\quad \times (\cos\theta^{\mu^{0i}}_{\mu^{if}}\cos\theta^{\mu^{0j}}_{\mu^{jf}} + \cos\theta^{\mu^{0i}}_{\mu^{0j}}\cos\theta^{\mu^{if}}_{\mu^{jf}} \\ &\quad + \cos\theta^{\mu^{0i}}_{\mu^{jf}}\cos\theta^{\mu^{if}}_{\mu^{0j}})/(\Delta E_i \cdot \Delta E_j). \end{aligned}$$

Here $\Delta E_{i(j)} = \omega_{i(j)} - \omega_f/2$, i and j respectively denote the intermediate states not including the ground and final states, μ^{0i} displays the magnitude of the vector $\boldsymbol{\mu}^{0i}$, and θ is defined as the angle between two transition dipole moment vectors.

In principle, the total TPA cross section requires the information of all excited states according to Eq. (2). Practically, it is extremely difficult to obtain a complete solution of all eigenstates even for a single molecular system. To overcome this difficulty, a reliable and rigorous theoretical method, so-called the analytic response theory,[23] was developed to compute the TPA cross sections of the chromophores, where the TPA transition matrix element can be described by the single residue of the quadratic response function. On the other hand, it is found that the maximal TPA cross sections in the visible region are mainly dominated by a few low-lying excited states. Therefore, a simplified few-state model only including several CT states can provide satisfactory results of the TPA response especially for the ones with one-dimensional CT geometrical configuration.

3. Results and discussion

3.1. Molecular structures

The geometrical structures of four newly synthesized molecules are shown in Fig. 1. From Fig. 1, one can see that the four compounds possess the identical π-conjugated backbone. In terms of the different intramolecular CT types, all the molecules may be divided into two essential classes, D–π–D type for M1 and M2 as well as A–π–A type for M3 and M4. Different donors distinguish M1 and M2 molecules, carbazole ring in M1 and diphenylamine in M2, while M3 and M4 have the same substituted pyridine rings; the remarkable distinctions between them are the lengths of the alkoxy chains linked to the π centres, methoxy for M3 and dodecyloxy for M4.

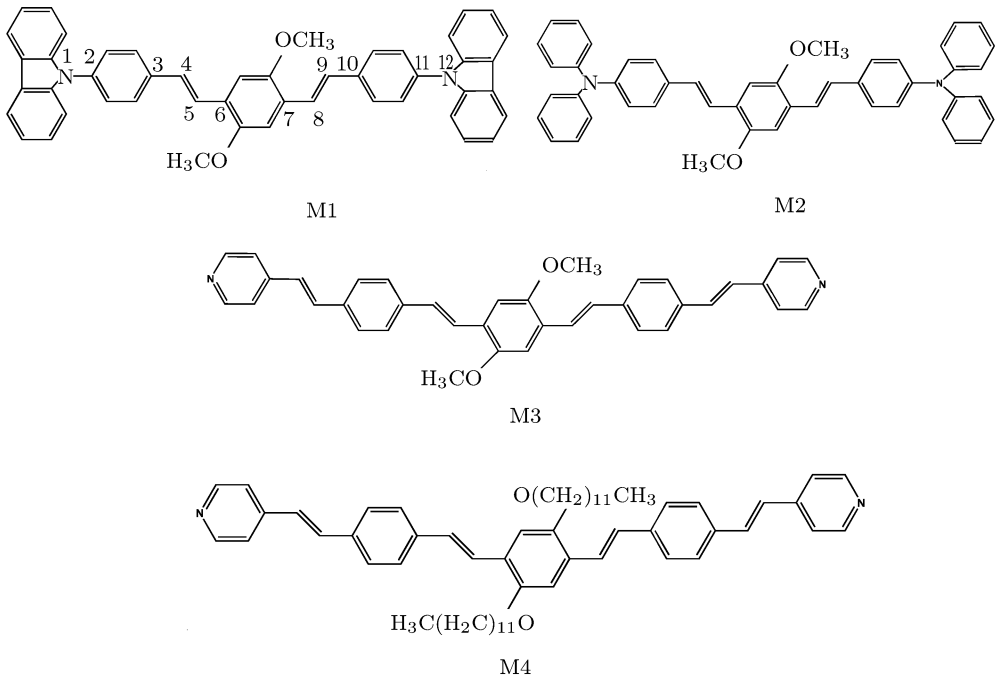


Fig. 1. The geometrical structures of the molecules studied.

The optimized geometrical and electrical structures are acquired by use of the Gaussian package combined with the DFT/B3LYP theory and the 6-31G basis set. From the optimisation results, it is found that the four molecules are apparently centrosymmetric systems and their permanent dipole moments are almost negligible. Moreover, we find that M1, M3 and M4 display good planarity in favour of the π-electron delocalization over the whole molecular distance. But for M2, a nonplanar geometry is observed where both terminal diphenylamine donors are twisted in the opposite directions by a dihedral angle about 42° with respect to the π centre. So we can anticipate that the optical properties of M2 will be negatively affected.

It is worth while to point out that experiments have measured the molecular structure of M1 in crystal phase.[20] Table 1 lists some selected bond lengths of both theoretical and experimental results. One can see from Table 1 that the numerical simulations based on B3LYP indicate that the C–C single bonds are compressed while the C–C double bonds are stretched, namely, the bond length alternation (BLA) are relatively smaller than that of measurements. Early works[24,25] found that the DFT theory describes the electron density distribution more delocalized, on the contrary, the Hartree–Fock (HF) method generally yields quite larger BLA value and seems to be more realistic for describing the molecular geometry. Whereas the experimental measurements showed that the structure of M1 is nonplanar, where the dihedral angles between the central phenyl and two adjacent phenyls are 55.7° and 113.9° and the dihedral angles between the terminal carbazole rings and their respective adjacent phenyls are 51.8° and 126.3°, respectively. The great discrepancies between

the theoretical and experimental results are caused by the fact that our calculations only take into account the single molecule in gas phase, but the experimental measurements are implemented in crystal phase where the stronger intermolecular interactions cannot be neglected.

Table 1. The selected bond lengths/Å of M1 molecule in gas and crystal phase (1 Å=0.1 nm).

	N1–C2	C3–C4	C4–C5	C5–C6	C7–C8	C8–C9	C9–C10	C11–N12
B3LYP	1.435	1.463	1.357	1.459	1.459	1.355	1.462	1.434
crystal*	1.423	1.480	1.329	1.469	1.462	1.339	1.468	1.402

*Experimental results in the crystal structure taken from Ref. [20].

3.2. One-photon absorption

The calculated excited energies and oscillator strengths of the lowest six excited states for the compounds studied are listed in Table 2, and the asterisked values are the experimental values in DMF solvent.

From Table 2, it is found clearly that for all the compounds, the first excited states are the dominant OPA states, namely, the CT states. In respect of the D–π–D molecules M1 and M2, the calculated excited wavelengths of the CT states are respectively 449 nm and 473 nm, appearing 24-nm red-shift with the increase of the strengths of the terminal donors, which is in good agreement with the 25-nm red-shift observed by experimental measurements. Although the diphenylamine group in M2 is considered to have a stronger ability of donating electron than carbazole group in M1, the oscillator strength of M2 (2.34) is apparently smaller than that of M1 (2.68), mainly attributing to the inferior planarity of the geometry in M2. As for the A–π–A molecules M3 and M4, the remarkable thing is that these two molecules display almost identical OPA characteristics. Their excited wavelengths of the first excited states are 494 nm and 497 nm respectively, that is, the longer dodecyloxy chain only induces a slight red-shift of 3 nm, close to the corresponding experimental value 5 nm. Whereas the oscillator strengths of M3 and M4 are 2.81 and 2.68 respectively, thus we can see that the dodecyloxy chain in M4 does not produce a positive effect on the OPA intensities. This is probably because the dodecyl chain is composed of C–C single bonds, not effective π-conjugated branch, and is unfavourable to the electric delocalization.

Table 2. Oscillator strengths $\delta_{\rm op}$, the excited energies ω, and corresponding wavelengths $\lambda_{\rm op}$ of the lowest six excited states for the four compounds.

M1			M2			M3			M4		
ω/eV	$\lambda_{\rm op}$/nm	$\delta_{\rm op}$/arb. units	ω/eV	$\lambda_{\rm op}$/nm	$\delta_{\rm op}$/arb. units	ω/eV	$\lambda_{\rm op}$/nm	$\delta_{\rm op}$/arb. units	ω/eV	$\lambda_{\rm op}$/nm	$\delta_{\rm op}$/arb. units
2.76	449	2.68	2.62	473	2.34	2.51	494	2.81	2.49	497	2.68
	401*			426*			423*			428*	
3.32	374	0.00	3.02	410	0.00	2.94	422	0.00	2.91	426	0.00
3.54	350	0.01	3.43	361	0.07	3.35	370	0.19	3.32	373	0.37
3.56	348	0.05	3.57	348	0.01	3.37	368	0.15	3.35	370	0.04
3.60	345	0.01	3.74	331	0.02	3.54	351	0.18	3.52	352	0.20
3.80	326	0.00	3.76	330	0.01	3.72	333	0.44	3.71	334	0.42

*Experimental results in DMF solvent taken from Ref. [20]

In comparison with M1 and M2, the molecules M3 and M4 generally display lower excited energies and greater oscillator strengths. Therefore, the A–π–A type geometrical conformations is superior to the D–π–D type structures for the investigated π-conjugated centre. It can be found that the general trend expected by calculations consists with the available results by measurements. However, the excited ener-

gies given by the theoretical studies are commonly smaller than what have been obtained from the experiments, similar to the observations in our previous works.[26−30] The discrepancy may be caused by the following two factors. The theoretical calculations are only related to the electron motions, that is, the vibronic and rotational motions are not taken into account here. Besides, the neglect of the solvent effects may have contribution to the discrepancy.

3.3. Two-photon absorption

The analytic response theory method implemented in DALTON package is applied to study the TPA properties of the compounds in combination with the DFT/B3LYP and 6-31G basis set. The TPA cross sections and the corresponding excited wavelengths of the lowest eight excited states are listed in Table 3. By carrying out the Lorenz expansion of the TPA cross sections, the TPA spectra of all compounds are obtained, as illustrated in Fig. 2. In general, for a centrosymmetrical molecule, the selection rules for one- and two-photon transitions are mutually exclusive. So the second excited states for the compounds studied are the maximal TPA states, rather than the first excited states in which the maximal OPA behaviours occur.

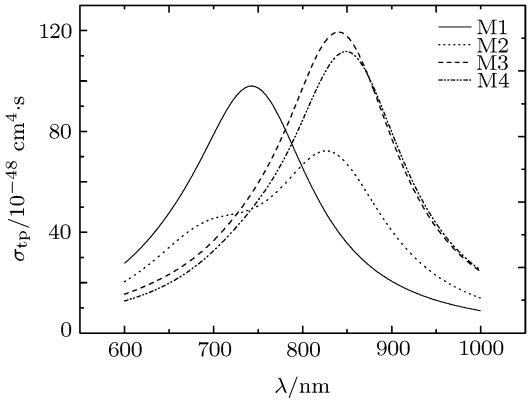


Fig. 2. The TPA spectra of the compounds.

Table 3. The TPA cross sections σ_{tp} and wavelengths λ_{tp} of the lowest eight excited states.

M1		M2		M3		M4	
λ_{tp}/nm	$\sigma_{tp}/10^{-48}$ cm^4·s	λ_{tp}/nm	$\sigma_{tp}/10^{-48}$ cm^4·s	λ_{tp}/nm	$\sigma_{tp}/10^{-48}$ cm^4·s	λ_{tp}/nm	$\sigma_{tp}/10^{-48}$ cm^4·s
896	0.0	948	0.4	985	0.1	993	0.1
745	92.1	830	65.1	841	115.9	850	108.0
699	3.9	703	0.3	738	3.3	745	0.7
695	0.3	691	25.9	733	5.31	738	9.9
689	0.0	656	0.0	698	0.2	703	0.2
651	6.4	654	1.2	664	0.1	667	0.1
634	0.0	634	0.0	652	0.0	651	0.0
633	0.0	633	1.2	635	1.9	649	0.0

The maximal TPA cross sections of M1, M2, M3 and M4 are 92.1, 65.1, 115.9 and 108.0×10^{-48} cm^4·s, located at 745, 830, 841 and 850 nm, respectively. The first interesting observation regarding the TPA results is that the TPA intensity is extremely sensitive to the planarity of the geometrical structure. Although having a stronger electron donor, the M2 molecule displays the smallest TPA cross section, demonstrating once more the importance of the geometrical planarity for enhancing the molecular TPA ability. In early works, some theoretical studies related to the dependence of TPA on the planarity of the geometry have been carried out by Zhao *et al.*[24] and Li *et al.*[31], and they all verified that the TPA cross sections were dramatically reduced by the conformational distortion. In addition, we also find that for the linear and planar molecules M1, M3 and M4, there are only one exclusive TPA state to form the TPA spectra. Only the spectrum of M2 is dominated by two TPA states, namely, the second excited state with stronger TPA and the fourth excited state with relatively weaker TPA. Taking into account the TPA behaviour of M3 and M4, we find that the numerical simulations give the nearly same TPA cross sections and excited energies, and the similar trend is also obtained in OPA results. Previously, we have discussed the TPA properties[26] of the two asymmetrical molecules 9-Ethyl-3-{2-[4-(2-Pyridin-4-yl-vinyl)-phenyl]-vinyl}-9H-carbazole (EPVPC) and 9-Octadecyl-3-{2-[4-(2-Pyridin-4-yl-

vinyl)-phenyl]-vinyl}-9H-carbazole (OPVPC), with the different lengths of the alkyl chains linked to the substituted carbazole groups ethyl for EPVPC and octadecyl for OPVPC, the theoretical results showed that the maximal TPA cross sections are 33.3 (EPVPC) and 35.5×10^{-48} cm^4·s (OPVPC) respectively. From the above investigations, it can be found that the effects of the length of the side-chain on the TPA probability is very little, which may be a negligible factor for the design and synthesis of TPA molecule. Finally, it is noted that M3 and M4 molecules show relatively stronger TPA performances than M1 and M2 molecules, so the A–π–A type CT conformation is more effective for improving the TPA capability.

In the theoretical study of Zhao *et al.*,[24] a symmetrical diamino-substituted distyrylbenzene chromophore has been calculated, with the π-conjugated bridge similar that of the present work only without the methoxy groups, as well as the different terminal substituents with dimethylaminos. The calculated TPA cross sections on DFT level in gas phase are 45.3 and 34.1×10^{-48} cm^4·s corresponding to the B3LYP and HF optimized geometries, respectively. Compared to the available results, the compounds we investigated have relatively larger TPA cross sections and seem to be good candidates for the TPA materials.

In the preceding analysis, it is definitely indicated that a simplified few-state model will express the TPA micromechanism more clearly and straight forwardly. In order to prove the dependability of the few-state model, the TPA cross sections of the second excited states for M3 and M4 are calculated over again by use of this simple method. In terms of the transition property calculations, the transition dipole moments from the first, fifth, sixth to the second excited states are relatively larger, so a five-state model described by Eqs. (6) is employed. In other words, the ground and the second excited states are considered as the initial and final states, respectively, and the first, fifth and sixth excited states act as the interference states. Therefore, there are three scattering processes, that is, $S_g \rightarrow S_1 \rightarrow S_2$, $S_g \rightarrow S_5 \rightarrow S_2$ and $S_g \rightarrow S_6 \rightarrow S_2$, for the two-photon excitation from the ground state to the second excited state. Then the maximal TPA cross sections of the two compounds are composed of three scattering channel terms $\delta^i_{\rm tp}$ (i = 1, 5, 6) and three interference terms $\delta^{ij}_{\rm tp}$ (i = 1, 5, j = 5, 6, $i \neq j$) in between, and the corresponding results are shown in Table 4.

Table 4. The excited energies ω, the TPA cross sections $\delta_{\rm tp}$ (in atomic unit) and $\sigma_{\rm tp}$ of the second excited states for M3 and M4.

	ω/eV	$\delta^1_{\rm tp}$ /10^7a.u.	$\delta^5_{\rm tp}$ /10^7a.u.	$\delta^6_{\rm tp}$ /10^7a.u.	$\delta^{15}_{\rm tp}$ /10^7a.u.	$\delta^{16}_{\rm tp}$ /10^7a.u.	$\delta^{56}_{\rm tp}$ /10^7a.u.	$\delta_{\rm tp}$ /10^7a.u.	$\sigma_{\rm tp}$ /10^{-48} cm^4·s
M3	2.94	15.08	0.15	0.19	–3.03	–3.38	0.34	9.35	197.4
M4	2.91	14.59	0.17	0.17	–3.11	–3.13	0.33	9.02	187.2

From Table 4, the values of three individual channel terms are positive, which display constructive effects on the TPA cross sections. Among them, $\delta^1_{\rm tp}$ are much larger than $\delta^5_{\rm tp}$ and $\delta^6_{\rm tp}$, playing the most important role in enhancing the TPA cross sections of the two compounds. However, because the calculated results show that the angles between different transition dipole moments have their sides nearly parallel or antiparallel, the interference terms may have constructive or destructive effects on the TPA cross sections according to Eq. (6). Since $\delta^{15}_{\rm tp}$ and $\delta^{16}_{\rm tp}$ listed in Table 4 are negative and relatively larger, they have stronger impact on the reduction of the TPA cross sections. Next, the values of $\delta^{56}_{\rm tp}$ are positive but small, displaying very little influence on the total TPA intensities. The maximal TPA cross sections of M3 and M4 are 197.4 and 187.2×10^{-48} cm^4·s respectively, which are relatively larger than what have been gained using the response theory. The values of the transition dipole moments between the excited states produced via the configuration interaction (CI) one-particle wavefunction in Gaussian program are greatly overestimated, which will be mainly responsible for the variations of TPA cross sections between the few-state model and response theory. Nevertheless, the agreeable trend of the two theoretical results verifies that the few-state model is reliable.

3.4. Charge-transfer process

It is well known that the charge will be redistributed when the molecule is excited from the ground state to the CT state. For a better understanding of the CT process, we calculated the charge density differences of the four compounds between the ground and the first excited states, which are visualized in Fig. 3 by making use

of the MOLEKEL program. The high peaks and low valleys represent the degrees of the electron gain and loss respectively. It can be clearly seen from Fig. 3 that upon excitation, the charges are mainly transferred from the terminal donors to the π centres for M1 and M2, and *vice versa* for M3 and M4. A noticeable thing is that the nitrogen atoms of the carbazole and diphenylamine groups for D–π–D molecules have more rich electrons and act as the major origins of reloasing electrons, and the centric phenyl rings and the adjacent oxygen atoms of A–π–A molecules are the dominating electron-donating region.

Another thing worthy of remarking is that the degrees of CT upon excitations determine the optical properties of molecules. For example, the molecules M1, M3, and M4 have the good planarity, so they display the relatively stronger CT, which induces the larger OPA and TPA intensities. Oppositely, the structure of M2 is nonplanar, where both terminal diphenylamine groups deviate from the plane of the π-conjugated bridge, then the distorted donors will block the electrons moving over the whole conjugated network. Thus the relatively weaker CT yields and accordingly results in the minimum OPA and TPA probabilities.

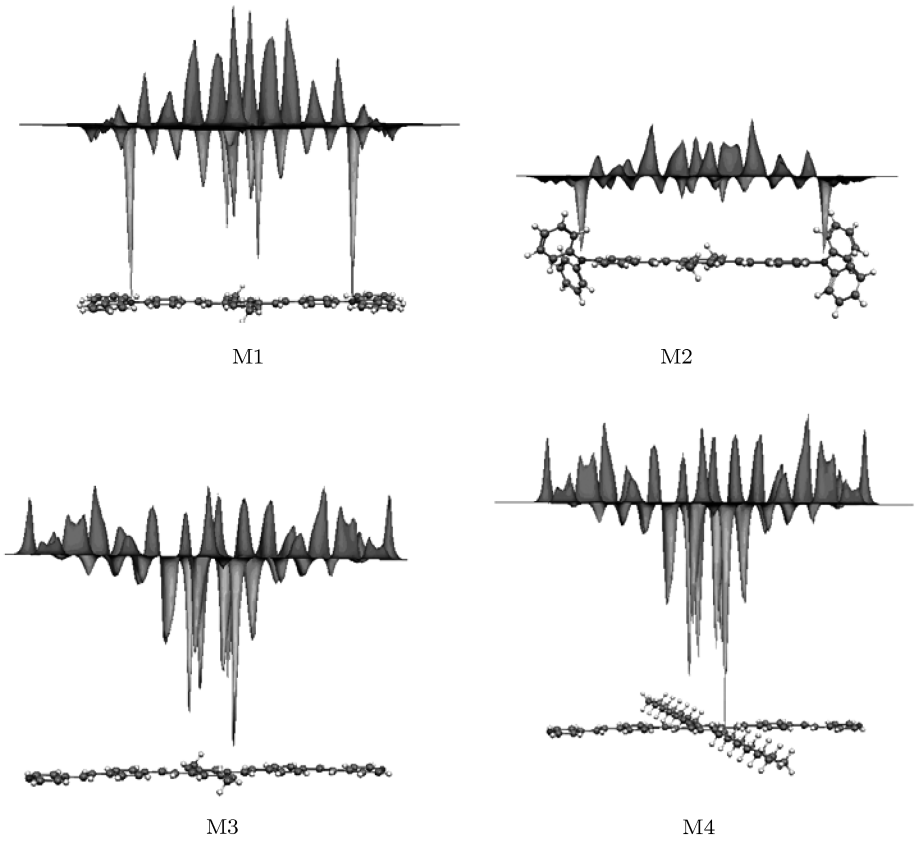


Fig. 3. The charge density differences between the first excited and the ground states of the four compounds.

4. Conclusion

We have studied the linear and nonlinear optical properties of the four symmetric compounds utilizing the response theory on the DFT/B3LYP level. The numerical results indicate that for all the compounds, the first excited states possess the largest oscillator strengths, and the maximal TPA cross sections occur in the second excited states because of the different transition selection rules.

Although the diphenylamine group has the stronger ability of donating electron compared to the carbazole ring, the molecule M2 displays relatively weaker OPA and TPA intensities than that of M1, effectively demonstrating that the molecular planarity is an important factor in determining the molecular optical characteristics. The similar OPA and TPA behaviours of M3 and M4 confirm that the effect of length of side-chain linked to the π centre on the optical property is nearly negligible. For the π-conjugated compounds investigated, the A–π–A geometrical conformations represent larger TPA cross sections in comparison with the D–π–D conformations.

Furthermore, we also computed the TPA cross sections of M3 and M4 by making use of the few-state model method. The computed results are generally in agreement with those of response theory, showing that the simplified few-state model can be trusted in evaluating the TPA cross section for some one-dimensional molecules.

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