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Theoretical studies on nonlinear optical properties of two newly synthesized compounds: EPVPC and OPVPC*

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The nonlinear optical properties of two newly synthesized 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) have been studied with hybrid density functional theory (DFT/B3LYP). The generalized few-state model is employed to calculate the two-photon absorption cross sections of the compounds. The theoretical results are in good agreement with the available experimental measurements. It is found that the maximal two-photon absorption (TPA) cross sections of the compounds can be well described by a three-state model. The numerical simulation shows that both compounds have large two-photon absorption (TPA) cross sections and, furthermore, OPVPC displays a little stronger TPA activity than EPVPC in a lower frequency region.

Keywords: few-state model, two-photon absorption, density-functional theory
PACC: 3280K, 3120A, 4265

1. Introduction

Experimental and theoretical studies on the organic materials with strong two-photon absorption (TPA) cross sections have attracted considerable attention during the last decade. A variety of two-photon techniques, such as optical power limiting, 3D microfabrication and optical data storage, and photodynamic therapy,[1] have been expected in practical applications. Great efforts have then been made to establish the so-called structure-to-property relation of chromophores. The available research results indicate that the TPA activities of organic compounds are related to a few factors including the conjugated length, the π centre property, the symmetrical or asymmetrical arrangement of electron-donor (D) and electron-acceptor (A) attached to the π centre and their strength to push and pull electrons, the molecular dimensionality.[2−8] At present, these factors are seriously considered for the designation of molecular materials.

Recently, we have successfully synthesized two new two-photon photo-polymerization initiators (EPVPC and OPVPC) and measured their one-photon absorption (OPA) and fluorescence spectra. The experimental results reveal that both compounds are highly delocalized π-electron systems and can be operated as two-photon photo-polymerization initiators.[9]

The response theory approach in the random phase approximation, where the contributions from all intermediate states are taken into account explicitly, is often used for computing the TPA cross sections of chromophores. However, the available implementation is carried out at Hartree–Fock level in which the correlated energy is neglected. Thus the corresponding calculations cannot give an accurate description for excited energies and dipole moments of molecules:

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namely, the OPA and TPA properties of molecules are not well anticipated. It is known that time-dependent density functional theory is expected to provide good results for excited energy and dipole moment.[10] At the same time, the maximal TPA of charge-transfer system in the visible region is known to often be dominated by a few states, i.e. charge-transfer (CT) states.[2,11–14] We thus combine the few-state model with density functional theory to calculate the TPA cross sections of the studied compounds.

2. Computational details

2.1. One-photon absorption

The transition probability of the OPA is given by oscillator strength

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

where μ_α is the electric dipole moment operator, ω_f denotes the excitation energy of the excited state $|f\rangle$, $|0\rangle$ denotes the ground state, and the summation is performed over the x, y and z axes of the molecule.

2.2. Two-photon absorption

In terms of sum-over-state formulae, the two-photon matrix element for the two-photon resonant absorption of identical energy is written as[15]

$$S_{\alpha\beta}=\sum_j\left[\frac{\langle 0|\,\mu_\alpha\,|j\rangle\,\langle j|\,\mu_\beta\,|f\rangle}{\omega_j-\omega_f/2}+\frac{\langle 0|\,\mu_\beta\,|j\rangle\,\langle j|\,\mu_\alpha\,|f\rangle}{\omega_j-\omega_f/2}\right], \tag{2}$$

where $|0\rangle$ and $|f\rangle$ denote the ground state and the final state, respectively, $|j\rangle$ means all the intermediate states including the ground state, ω_j is the excitation energy of the excited states, and $\boldsymbol{\mu}$ electronic dipole moment.

For a planar molecule oriented in the x–y plane, the TPA cross section excited by a single linear polarized beam can be expressed as[16]

$$\delta_{\rm tp} = 6(S_{xx}+S_{yy})^2+8(S_{xy}S_{xy}-S_{xx}S_{yy}). \tag{3}$$

The TPA cross section directly comparable with experimental measurement is defined as[16]

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

where 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, and $g(\omega)$ denotes the spectral line profile; here it is assumed to be a δ-function. Γ_f is the lifetime broadening of the final state, which is assumed to be 0.1eV.[11]

In general, the total TPA probability requires the information of all the excited states that is not easy to obtain clearly. On the other hand, a few-state model often provides satisfying results for TPA cross section in the visible region.[11–13] If three states are taken into consideration, Eq.(2) can be simplified into

$$S_{\alpha\beta} = \frac{\mu_\alpha^{01}\Delta\mu_\beta+\mu_\beta^{01}\Delta\mu_\alpha}{\Delta E_1}+\frac{\mu_\alpha^{04}\mu_\beta^{41}+\mu_\beta^{04}\mu_\alpha^{41}}{\Delta E_4}, \tag{5}$$

where $\Delta E_i = \hbar\omega_i-\hbar\omega_1/2$ (i=1, 4), $\Delta\boldsymbol{\mu}$ denotes the difference of dipole moments between the lowest excited and the ground states, $\boldsymbol{\mu}^{ij}$means the transition dipole moment from the state $|i\rangle$ to $|j\rangle$, $\Delta\mu$ and μ^{ij} are the norms of their corresponding vectors, respectively. $\alpha,\beta\in\{x,y\}$.

Inserting Eq.(5) into Eq.(3), the total TPA probability can be obtained as follows:

$$\delta_{\rm tp} = \delta_{\rm tp}^1+\delta_{\rm tp}^2+\delta_{\rm tp}^{12}, \tag{6}$$

where

$$\delta_{\rm tp}^1 = \frac{8(\mu^{01}\Delta\mu)^2\left(2\cos^2\theta_{\Delta\mu}^{\mu^{01}}+1\right)}{(\Delta E_1)^2},$$

$$\delta_{\rm tp}^2 = \frac{8(\mu^{04}\mu^{41})^2\left(2\cos^2\theta_{\mu^{04}}^{\mu^{41}}+1\right)}{(\Delta E_4)^2},$$

$$\delta_{\rm tp}^{12} = \frac{16(\mu^{01}\Delta\mu\mu^{04}\mu^{41})\left(\cos\theta_{\Delta\mu}^{\mu^{01}}\cos\theta_{\mu^{04}}^{\mu^{41}}-\sin\theta_{\Delta\mu}^{\mu^{01}}\sin\theta_{\mu^{04}}^{\mu^{41}}+2\cos\theta_{\mu^{01}}^{\mu^{04}}\cos\theta_{\Delta\mu}^{\mu^{41}}\right)}{\Delta E_1\Delta E_4},$$

where $\theta_{\Delta\mu}^{\mu^{01}}$ and $\theta_{\mu^{04}}^{\mu^{41}}$ are defined as the angles included between two vectors $\Delta\boldsymbol{\mu}$ and $\boldsymbol{\mu}^{01}$ and two vectors $\boldsymbol{\mu}^{04}$ and $\boldsymbol{\mu}^{41}$, respectively.

From the above formula (6), one can see that the total TPA cross section $\delta_{\rm tp}$ comprises three parts: the contributions from each excitation channel ($\delta_{\rm tp}^1$ and $\delta_{\rm tp}^2$) and an interference term $\delta_{\rm tp}^{12}$. The contribution from each excitation channel is always positive, and the maximum value can be obtained when $\Delta\boldsymbol{\mu}$ and $\boldsymbol{\mu}^{01}$, $\boldsymbol{\mu}^{04}$ and $\boldsymbol{\mu}^{41}$ are parallel or antiparallel. The interference term can play a part in construction or destruction, resulting in increase or decrease of the

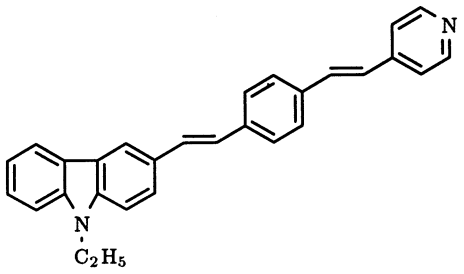
TPA cross section.

The equilibrium geometries of the two molecules are optimized by use of the Gaussian package[17] with the hybrid density functional theory (DFT/B3LYP). Time-dependent density functional theory (TD-DFT) is applied to calculate the electronic structures and the few-state model is used to obtain the TPA cross section of the compounds. 6-31G basis set is used throughout all calculations. The dipole moments of the excited states are calculated using the finite field approach.

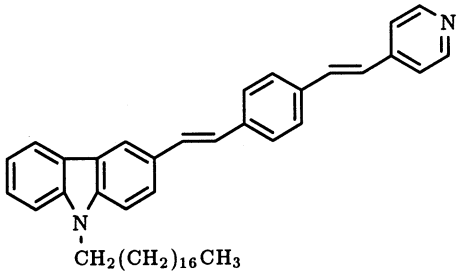
3. Results and discussion

3.1. Molecular structure

Molecular structures studied in the present work are shown in Fig.1. The two molecules have different donors, namely, the lengths of the chain linked with carbazole ring are different, Ethyl for EPVPC and Octadecyl for OPVPC.



EPVPC



OPVPC

Fig.1. Molecular structures.

We optimized the geometry structures of the two molecules at the level of density functional theory (DFT). The results indicate that the two molecular structures have little difference: for example, the maximum difference of the corresponding bond length in the π conjugated centres is just 9×10^{-6}nm. Therefore, the two different donors have little influence on molecular structures.

3.2. One-photon absorption

On the basis of optimized molecular structures, the calculated OPA properties of the two compounds for the six lowest excited states given by use of TD-DFT are listed in Table 1. Figure 2 is the measured linear absorption spectra in the visible region. The comparison between the theoretical and experimental results indicates that the theoretical simulation is in good agreement with the measurements.

Table 1. Oscillator strength δ_{op} (a.u.), the excitation energy ω (eV) and the corresponding wavelength λ (nm) of the six lowest excited states for EPVPC and OPVPC.

EPVPC			OPVPC		
ω	λ_{op}	δ_{op}	ω	λ_{op}	δ_{op}
2.91	426	1.49	2.90	428	1.51
	(387*)			(388*)	
3.54	351	0.19	3.53	352	0.20
3.73	332	0.23	3.72	333	0.23
3.78	328	0.38	3.77	329	0.40
3.88	320	0.00	3.88	320	0.00
4.03	308	0.01	4.02	309	0.01

Reproduced from Ref.[9]

It should be noted that the first excited states for the two compounds are CT states both from the theoretical study and from the experimental measurement. The first OPA peaks of EPVPC and OPVPC are located at 426nm and 428nm, respectively; it is clearly shown that the excitation wavelength of OPVPC appears to be slightly red-shifted compared to that of EPVPC due to the stronger donor in OPVPC. Furthermore, the OPA intensity of OPVPC for the first charge-transfer state is 1.51 that is larger than 1.49 of EPVPC. It is clearly demonstrated that the general trend expected by the theoretical simulation is in perfectly consistent with that measured by experiment.

From the linear absorption spectra, it is also noted that there is another weak OPA peak besides the first OPA peak for each compound in the visible region. We obtain a similar conclusion from the calculations, as shown in Table 1, and one can see that the second, third, and fourth excited states are very weak CT states. The energy gaps are relatively small for the three excited states, so we consider the weak peak comes from the cooperating contribution of the three excited states. The two compounds are thus anticipated to have strong TPA absorption in the visible region due to more charge-transfer states.

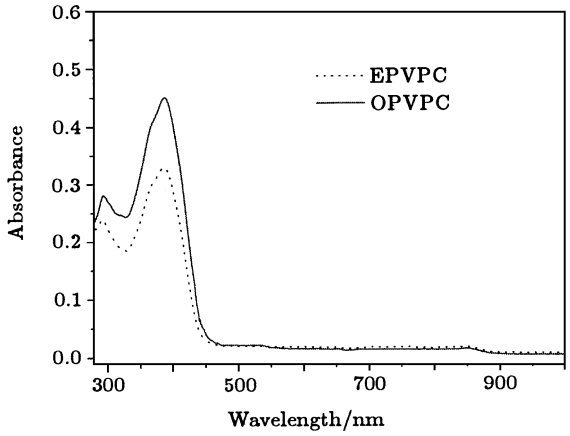


Fig.2. Linear absorption spectra of two compounds in chloroform with concentration of 1×10^{-5}mol·L^{-1}, reproduced from Ref.[9].

Note that the excited energies given by calculations are smaller than those corresponding values from the measurements. It should be pointed out that the OPA spectra of the two compounds are measured in chloroform, while the solvent effect is not considered in theoretical works. Moreover, the calculation is only related to the electronic motion, in other words, the vibronic and rotational motions are not taken into account here.

3.3. Two-photon absorption

It is known that the lowest excited state often has a maximum TPA cross section for one-dimensional organic molecule with an asymmetric D-π-A structure for the visible region. We thus choose the lowest excited state as the final state in order to obtain the maximum TPA cross section in the present work. According to Eqs.(2) and (3), the transition dipole moment between excited states is another important factor for enhancing the TPA cross section. Due to the large transition dipole moment between the fourth and first excited states, we just need to consider the fourth excited state when calculating the TPA cross sections besides the first excited state. Therefore, we employ a three-state model to calculate the maximum TPA cross sections of EPVPC and OPVPC as described by Eq.(6). Table 2 shows the corresponding results. It can be observed that both EPVPC and OPVPC display strong TPA properties, 3.33×10^{-47}cm^4·s·photon^{-1} and 3.55×10^{-47}cm^4·s·photon^{-1}, respectively.

Table 2. The TPA cross section $\delta_{\rm tp}$ (10^7 a.u.) and $\sigma_{\rm tp}$ (10^{-47}cm^4·s·photon^{-1}), the excitation energy ω (eV) and the corresponding wavelength λ (nm) of the lowest excited state for EPVPC and OPVPC.

Molecule	ω	$\lambda_{\rm tp}$	$\delta^1_{\rm tp}$	$\delta^2_{\rm tp}$	$\delta^{12}_{\rm tp}$	$\delta_{\rm tp}$	$\sigma_{\rm tp}$
EPVPC	2.91	852	1.010	0.069	0.530	1.610	3.33
OPVPC	2.90	856	1.086	0.075	0.571	1.732	3.55

In the previous work, we have synthesized one asymmetrical charge-transfer TPA organic molecule, 4-trans-[*p*- (N, N-Di-*n*-butylamino) -*p*-stilbenylvinyl] pyridine (DBASVP) only with the substituted donor different from those of EPVPC and OPVPC having a TPA cross section of 3.93×10^{-48}cm^4·s·photon^{-1}.[14] It is clearly shown that the two newly synthesized compounds have better behaviours of TPA than the DBASVP. Comparing with the available one-dimensional organic compounds, we should note that our two compounds are candidates for the best two-photon performing molecules up to now.[2,18]

Because of the existence of two charge-transfer states, there are two scattering processes, i.e. $S_g\rightarrow S_1\rightarrow S_1$ and $S_g\rightarrow S_4\rightarrow S_1$ (see Fig.3), for the excitation from the ground state to the first excited state by absorbing two photons simultaneously. The maximal TPA of the two compounds is thus mainly dominated by the two scattering channels and the interference in between. For individual channel terms, one can see from Table 2 that $\delta^1_{\rm tp}$ are 1.010a.u. and 1.086a.u. for EPVPC and OPVPC, respectively, which are about 14.5 times 0.069 and 0.075 of $\delta^2_{\rm tp}$. This shows that the first scattering channel plays an important role in the enhancement of the TPA cross section. Besides this, the interference term $\delta^{12}_{\rm tp}$ between the two

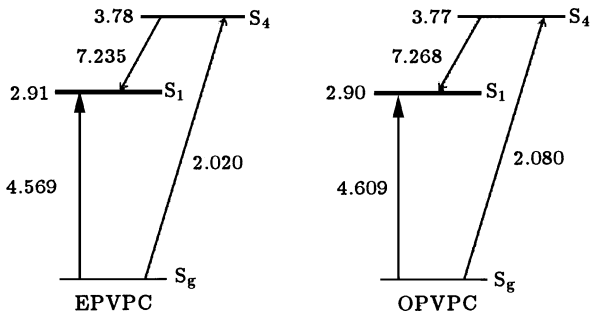


Fig.3. The excitation energies (boldface, eV), transition moments(a.u.) of EPVPC and OPVPC. The final states are marked with a bold line.

scattering channels displays a very strong constructive effect. $\delta_{\rm tp}^{12}$ of EPVPC and OPVPC are respectively 0.530au and 0.571au, which are about half of the corresponding values of $\delta_{\rm tp}^{1}$. It is clearly shown that the interference effect gives a great increase of the TPA cross section.

Table 3 lists the dipole moments and angles included between them for the two compounds. One can see that $\Delta\boldsymbol{\mu}$ and $\boldsymbol{\mu}^{01}$, $\Delta\boldsymbol{\mu}$ and $\boldsymbol{\mu}^{41}$, $\boldsymbol{\mu}^{01}$ and $\boldsymbol{\mu}^{04}$, $\boldsymbol{\mu}^{04}$ and $\boldsymbol{\mu}^{41}$ are nearly parallel or antiparallel to give maximal benefit for the increase of the TPA, demonstrating the good designation for the two compounds. Compared to EPVPC, the enhancement of the TPA cross section of OPVPC comes from the increase of the dipole moment difference between the first excited and the ground states $\Delta\mu$ and the transition dipole moments μ^{04} and μ^{41}.

Table 3. The energy difference $\Delta E_i = \omega_i - \omega_1/2$ (in eV, i=1, 4), the transition dipole moment μ^{ij} (a.u.), the dipole moment difference $\Delta\mu$ (a.u.) between the lowest excited and the ground states, and the angles θ (deg.) included between the dipole moments.

Molecule	ΔE_1	μ^{01}	$\Delta\mu$	ΔE_4	μ^{04}	μ^{41}	$\theta_{\Delta\mu}^{\mu^{01}}$	$\theta_{\mu^{04}}^{\mu^{41}}$	$\theta_{\mu^{01}}^{\mu^{04}}$	$\theta_{\Delta\mu}^{\mu^{41}}$
EPVPC	1.45	4.569	7.594	2.32	2.020	7.235	180.0	172.4	5.43	2.20
OPVPC	1.45	4.609	7.770	2.32	2.080	7.268	179.6	175.3	4.24	0.02

4. Summary

We have used the hybrid density functional theory (DFT/B3LYP) and the generalized three-state model to investigate the one/two-photon absorption properties of two newly synthesized compounds, EPVPC and OPVPC. The excited energies of the charge-transfer states for OPVPC have a slight red-shift compared to those for EPVPC because of the strong donor in OPVPC. The theoretical simulation for one-photon absorption is consistent with experimental measurements. The results for the TPA cross section show that the two compounds have strong TPA properties, which can be used as best candidates for the two-photon photopolymerization initiators.

The response theory method in the random phase approximation coded as DALTON[19] is also applied to study the OP and TPA properties of the molecules.[9] The electronic structures of the molecules are roughly described, however, the general trend for the optical properties of molecules is predicted correctly. The fully analytic solution is further used to prove the validity of the few-state model for calculating the TPA cross sections.

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