

Two photon absorption of extended substituted phenylenevinylene oligomers: A TDDFT study

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Abstract

Time dependent density functional theory has been applied to analyze the effect of substituent groups on one-photon (OPA) and two-photon (TPA) absorption properties of extended amine-terminated phenylenevinylene oligomers. All investigated molecules are characterized by increased TPA activity. Calculated TPA cross-sections for these compounds do not show TPA enhancements observed in experimental measurements. Stabilization of the TPA active excited state in these chromophores leads to the small (~0.2 eV) energy separation between the OPA and TPA allowed excited states, which agrees well with experimental data and may lead to the enhancement of the TPA response due to the strong vibronic couplings.

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1. Introduction

The growing potential for utilizing two photon absorption (TPA) applications has initiated a wave of theoretical and experimental investigations towards the design of organic chromophores with large TPA cross-sections. Enhanced TPA optical response is seen in push–pull dipolar [1,2], quadrupolar [3,4] and octupolar molecular structures [5], multibranching compounds [6,7], porphyrines [8], functionalized conjugated polymers, and three-dimensional chromophores [9]. Recent studies have elucidated the ways of manipulating TPA cross-sections and energies by increasing effective conjugation length, and by modifying the charge transfer patterns through changing the molecular backbone and introducing different substituent groups [3,10–15]. It is advantageous for many TPA-based applications, such as nonlinear optical transmission, to have optical activity in a wide energy region. Recently, large (up to

fivefold) increase of the TPA cross-sections was reported for a series of extended amine terminated cyano-substituted phenylenevinylene oligomers due to the addition of extra donor and acceptor moieties to the conjugated backbone [16]. This enhancement was attributed to stabilization of the charge transfer in the TPA state and to possible increase of the transition dipole moment between the excited states. These compounds, however, were characterized by unusually small energy separation between the OPA and TPA active states. It is still unclear whether an enhanced TPA response originates purely from the electronic degrees of freedom or if there is another mechanism responsible for observed TPA activities [16].

In this Letter we report a computational study of one and two photon absorption of extended amine-terminated phenylenevinylene oligomers (Fig. 1) to investigate the effect of additional substituents in the π -bridge on the magnitude of optical response. Some of the chromophores having similar homology have been studied experimentally and theoretically [9,11,13,16]. We utilize time-dependent density functional theory (TD-DFT) in combination with quasi-particle formalism for nonlinear optical polarizabilities [17] aiming to obtain insights into the origins of

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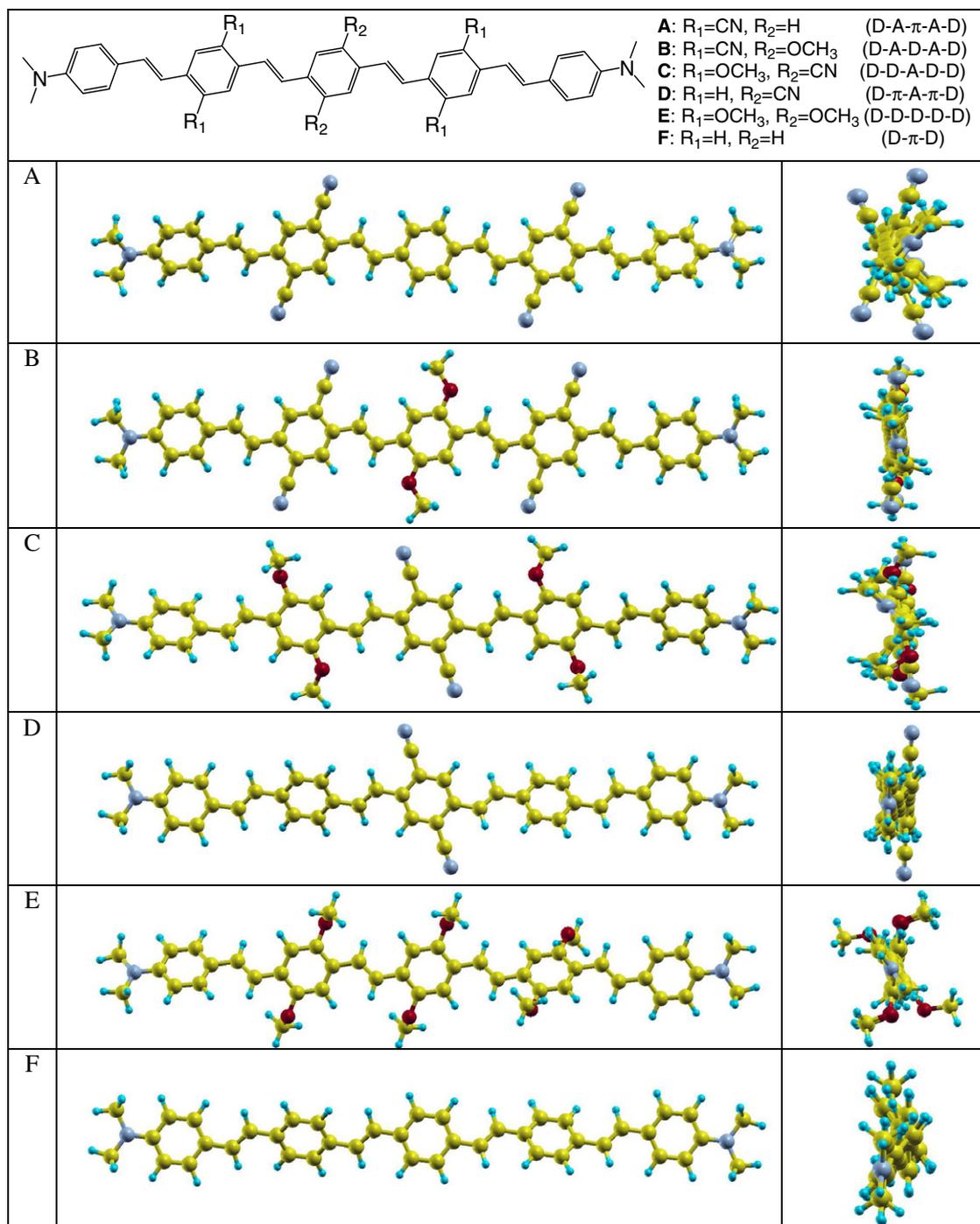


Fig. 1. General scheme (top) and optimized ground state geometries of molecules A–F.

strongly enhanced TPA cross-sections of substituted chromophores. We present a generalized picture describing the nature of the electronic excitations and general absorption parameters, such as transition dipole moments, transition orbitals and excitation energies. Details of the computational approach are presented in the next section. In Section 3 we analyze the computational results and compare them with the available experimental data. Finally, we discuss the emerging trends and summarize our findings in Section 4.

2. Theoretical methodology

Adiabatic TD-DFT [18] in the Kohn–Sham (KS) form is currently the method of choice for calculating excited-state structure of large organic molecules [19,20]. Recently, TD-DFT extensions for the calculations of molecular nonlinear optical properties have been suggested based on the residues of the quadratic response functions for TPA [21], and quasi-particle formalism of the TD-KS equations for arbitrary frequency-dependent nonlinear optical polariz-

abilities [22]. Subsequently, the latter approach was applied to calculate OPA and TPA properties of several families of donor/acceptor substituted conjugated organic dyes [9,13–15,23]. Excellent quantitative performance of TD-DFT based on hybrid functionals have been shown for both OPA and TPA responses.

In this study, we apply the approach described above [13,22] to model linear and two photon absorption spectra of chromophores **A–F**, shown in Fig. 1. Ground state geometry optimizations are performed at the Hartree–Fock (HF) level of theory with the 6-31G basis set. According to our previous studies, this level of theory is sufficient to describe the molecular geometries of similar compounds acceptably well [13,14]. Excited state electronic structure has been calculated with the TD-DFT formalism implemented in the GAUSSIAN 98 program suite [24]. The lowest excited-state geometries are obtained next using the Turbomole program [19]. OPA and TPA responses based on the GAUSSIAN 98 output have been calculated using computational technique described in detail elsewhere [13,22]. To understand the nature of the excited states involved in the linear and nonlinear absorption processes, a natural transition orbital analysis has been performed [25]. This approach provides the most compact representation of the electronic transitions in terms of single particle orbitals derived from the respective the transition density matrices associated with electronic excitations. Figures showing natural transition orbitals have been obtained using the XCrysDen package [26].

3. Results and discussion

The general scheme and optimized ground state geometries of the molecules examined in this work are shown in Fig. 1. All chromophores are derivatives of symmetrically amine-substituted phenylenevinylenes with extended conjugated backbone and a D–A–D or D– π –D motif. Compounds **A–F** have the following donor (D) and acceptor (A) substitution pattern: **A** (D–A– π –A–D), **B** (D–A–D–A–D), **C** (D–D–A–D–D), **D** (D–A– π –A–D), **E** (D–D–D–D–D), and compared to the simpler structure, **F** (D– π –D). Overall, quantum-chemical geometry optimization with HF/6-31G level leads to some torsional disorder in the molecules, depending on the position of the donor and acceptor moieties and the degree of the charge transfer

between them. Compound **B** is almost perfectly flat, while the other chromophores are less planar with up to 30° torsions along the backbone.

The calculated absorption and emission maxima and transition dipole moments are summarized in Table 1 and compared to experimental data when possible [9,11,16]. The main features of the OPA predicted by theory are two strong bands in the visible (e) and near-UV (e') regions with the absorption maxima around ~ 3.0 – 3.5 eV and ~ 2.3 – 2.8 eV, respectively. The two-band OPA spectra agree well with previously reported experimental line shapes [9,11,16]. The calculated absorption maxima for the strongest low-energy peak are consistently red-shifted by ~ 0.1 eV compared to experiment. However, TD-DFT calculations accurately reproduce ~ 0.2 eV red shift of the absorption maxima of compounds **A–C** with respect to the chromophores **E–F**, in agreement with experimental measurements. This trend can be attributed to the increased polarity (charge transfer) of the chromophores **A–D** and, to a lesser extent, the reduced torsional disorder. Calculated transition dipole moments (μ_{ge}) are usually overestimated in respect to experimental data. Meanwhile, the trends are clearly seen from the calculations. As a rule, the lowest excited singlet state (S_1) has the largest transition dipole. The satellite peak in the higher energy region is much weaker for all compounds except **D** where it becomes much more pronounced due to substantial increase in the transition dipole moment ($\mu_{ge'}$). This is an expected trend for push–pull quadrupolar molecules with large donor–acceptor separation [3,10,11,14].

The lowest excited state geometry optimization provides essentially planar structures for all chromophores. The calculated Stokes shift ($\Omega_e - \Omega_e^f$) is about 0.3–0.4 eV while experiment gives 0.2–0.25 eV. Experimental fluorescence measurements were done in toluene, which may favor the planar ground state geometry and require smaller reorganization of the molecular structure upon excitation. Indeed, calculations in the presence of solvent (toluene) using the IFF-PCM model [27,28] (molecule **B**, parenthesis values in Tables 1 and 2) provide 50 meV solvatochromic stabilization. Similar solvent effects were observed in our previous studies [13–15].

In order to analyze the excited states contributing to the linear absorption, natural transition orbital (NTO) analysis [25] has been performed. NTOs of the brightest OPA active

Table 1
One-photon absorption properties: experimental (from Refs. [1,11,16]) and calculated vertical transition energies of the first Ω_e (eV) and second $\Omega_{e'}$ (eV) OPA allowed excited states; energy of the respective fluorescence maximum Ω_e^f (eV); transition dipole moments to the first excited state μ_{ge} (D) and to the second excited state $\mu_{ge'}$ (D). The values calculated in toluene are given in parenthesis

Compound	μ_{ge}^{exp}	μ_{ge}^{theor}	$\mu_{ge'}^{theor}$	Ω_e^{exp}	Ω_e^{theor}	$\Omega_{e'}^{theor}$	$(\Omega_e^f)^{theor}$	$(\Omega_e^f)^{exp}$
A		15.9	8.4	2.48	2.37	3.03	2.03	2.20
B		17.3 (17.0)	6.1 (5.7)	2.45	2.30 (2.26)	3.01 (2.92)	1.97	2.18
C		15.3	9.2	2.44	2.32	3.07	1.96	2.07
D		13.0	11.0		2.34	3.20	1.99	
E	14.2	15.4	8.1	2.65	2.68	3.44	2.28	
F	14.7	16.4	9.8	2.85	2.78	3.47	2.34	2.56

Table 2

Two-photon absorption properties: experimental (from Refs. [1,11,16]) and calculated transition energies of the first Ω_E (eV) and second $\Omega_{E'}$ (eV) TPA allowed excited states; transition excited state dipole moment μ_{eE} (D) and TPA cross-sections at the first and second absorption maxima, σ_E (GM) and $\sigma_{E'}$ (GM), respectively

Compound	Ω_E^{theor}	Ω_E^{exp}	μ_{eE}^{theor}	μ_{eE}^{exp}	σ_E^{theor}	σ_E^{exp}	$\Omega_{E'}^{\text{theor}}$	$\Omega_{E'}^{\text{exp}}$	$\sigma_{E'}^{\text{theor}}$	$\sigma_{E'}^{\text{exp}}$
A	2.54	2.54	20.1		2400	3600	3.52	3.02	890	1600
B	2.53 (2.44)	2.56	18.3 (19.1)		2860 (3080)	4400	3.27 (3.19)	3.02	900 (990)	2700
C	2.50	2.56	19.8		2420	5300	3.23	2.99	650	1300
D	2.48		21.2		1980		3.22	3.0	456	
E	2.98	2.95	18.0		1630	1420	3.43	3.2	400	800
F	3.0	3.07	18.2	14.2	1990	1450	3.46	3.45	530	1230

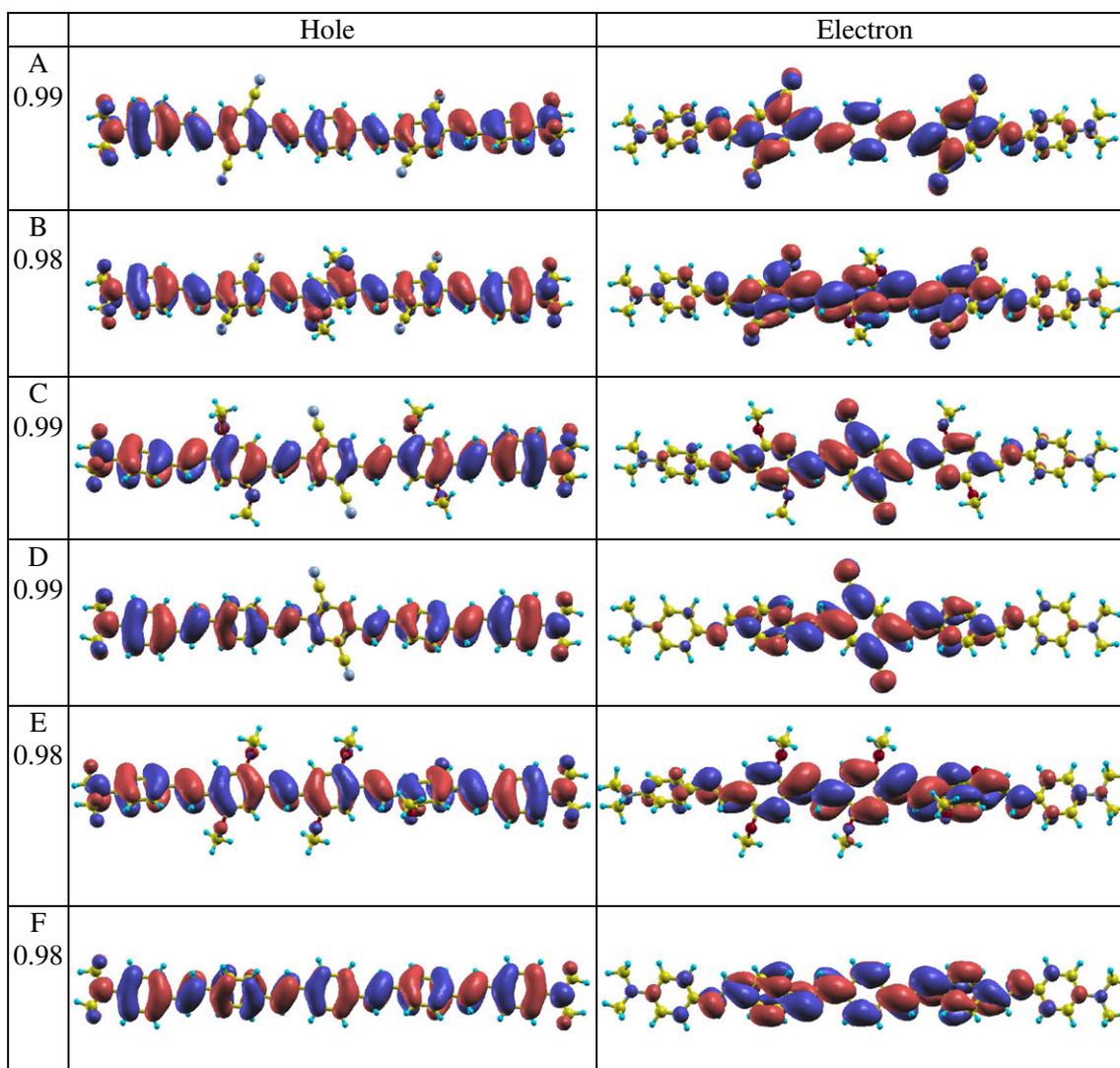


Fig. 2. Natural transition orbitals describing OPA state e for compounds A–F. The numbers indicate the fraction of the NTO pair contribution into the given electronic excitation.

excited state are shown in Fig. 2. For all chromophores, the electronic states contributing to the OPA response have a delocalized $\pi-\pi^*$ character. Wavefunctions of the electron and hole have approximately even and odd symmetries, respectively, and can be denoted as $A_g \rightarrow B_u$ -like transition. The electron density of the hole is delocalized over the

donor methylamino groups and conjugated π -bridge of the molecule. Upon excitation, the charge is shifted to the acceptor(s) and/or the conjugated center. It is important to note that the OPA states for the considered molecules possess only a partial charge transfer character, i.e. electrons and holes are not separated spatially. Notably, despite

of the overall similar nature of the first excited state for all molecules, there is a considerable difference in the transition dipole moments (μ_{ge}). Introduction of the additional substituents in **C** provides effective charge transfer over longer

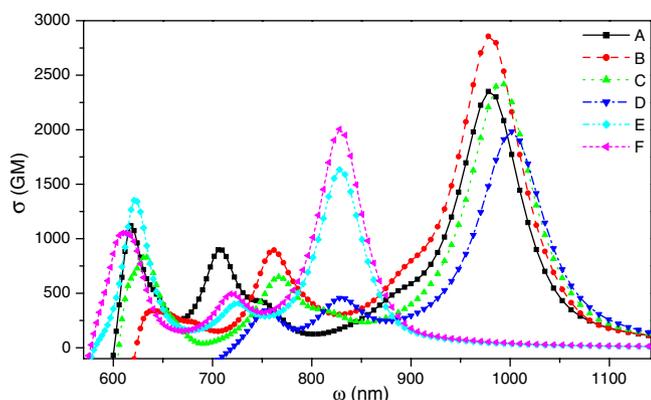


Fig. 3. Calculated two photon absorption spectra for chromophores A–F.

distances and enhances the transition dipole of the first excited state. The longer range charge transfer in **D** stabilizes the second OPA transition, therefore, causing oscillator strength redistribution to the high-energy peak. Interestingly, μ_{ge} of compound **D** is significantly smaller than that of its analogue with no acceptor in the middle, **F**. While the central unsubstituted benzene ring in **F** plays the role of a weak acceptor, CN is a much stronger acceptor, so charge transfer should be more pronounced in **D**.

Calculated TPA properties of chromophores A–F are summarized in Table 2 and compared with available experimental data [9,11,16]. A uniform empirical broadening parameter $\Gamma = 0.1$ eV was taken for all calculations, which is not the case in the real molecular systems [7,9]. However, the trends in the TPA parameters can be used as guidelines to understanding the nature of the TPA process. In agreement with experiment, all TPA spectra are characterized by two distinct bands in the energy region between 650 and 1100 nm (~ 1.1 – 1.9 eV). There is a third bright peak at

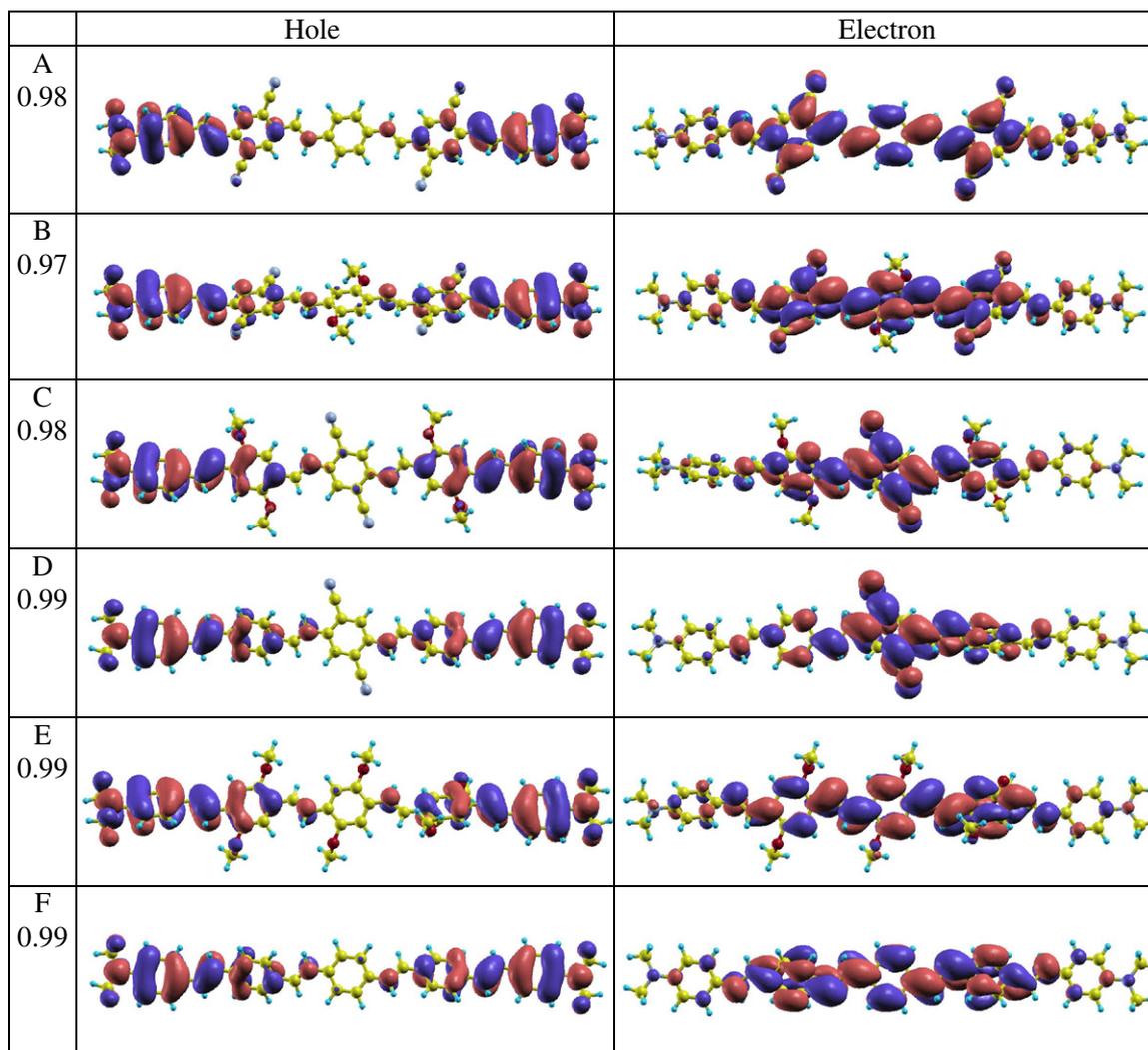


Fig. 4. Natural transition orbitals describing TPA state E for compounds A–F. The numbers indicate the fraction of the NTO pair contribution into the given electronic excitation.

higher energy (around 600 nm) for all compounds (not shown) except **A**. We focus on two excited states, E and E', contributing to TPA in the lower energy region. The low energy state E, has the largest TPA cross-sections. Calculated excited state energies (Ω_E) are within 50 meV of experimental values. Similar to the linear absorption, the TPA absorption maxima of compounds **A–D** are red shifted by 0.4–0.5 eV with respect to the chromophores **E–F**. However, the Ω_E red shifts are much larger than that of the OPA maxima (Ω_c). The TPA allowed excited state involves a more pronounced charge transfer from methylamino groups to the acceptors. Consequently, it is greatly stabilized by additional substituents. This makes the energies of the first OPA (e) and the first TPA (E) states much closer in **A–D** (~ 0.2 eV) than in **E–F** (~ 0.3 – 0.4 eV), which agrees well with experiment [16]. The small separation between the first (e) and second (E) excited states is rather unusual for the quadrupolar distyrylbenzenes of similar homology [9,11], and may lead to the increase of the experimentally measured TPA intensity caused by vibronic coupling to the lower lying OPA state, as was reported for branched compounds [29]. Indeed, the calculated TPA cross sections of the chromophores **A–C** do not reproduce trends observed in the experimental values [16].

Calculated TPA spectral line shapes are shown in Fig. 3. All studied compounds have an enhanced TPA response: TPA cross-sections are ranging between 1600–3000 GM for the low-energy peak and 400–1300 GM for the higher energy bands. Large TPA cross-sections in dimethylamino substituted extended phenylenevinylenes are correlated with the strong excited state transition dipole moments (up to 20 D), although TD-DFT calculated transition dipoles are usually overestimated. Interestingly, compound **B** has the largest TPA cross-section, while its excited state transition dipole moment ($\mu_{eE} = 18.3$ D) is notably smaller than that of **A** (20.1 D) and **C** (19.8 D). Therefore, the TPA intensity in **B** is raised by an increase in the ground to excited state transition dipole, μ_{ge} . Calculations of the TPA properties in toluene lead to a 0.1 eV red shift in the TPA maxima and a decrease in μ_{ge} of compound **B**. However, stabilization of the μ_{eE} and the TPA allowed excited state E is much larger than the destabilizing effect of the solvent on the μ_{ge} (0.3 D decrease in μ_{ge} and ~ 1 D increase in μ_{eE} due to the solvent interactions). This is attributed to a larger charge redistribution upon excitation in the TPA process compared to OPA.

NTO plots of the first TPA transitions for the compounds **A–F** (Fig. 4) illustrate the charge transfer character and larger separation of the hole and electron. All the chromophores have similar charge transfer features. As expected, the TPA transition occurs between the excited states of the same parity. The electron density is shifted from the terminal methylamino donor to the central acceptor moiety. Interestingly, methoxy groups are not involved in the charge transfer pattern, but rather provide stabilization of the electron resonance along the conjugated core, when alternating with acceptor substituents. Such stabiliza-

tion enforces more planar geometry of compounds **B** and **C** (**D–A–D–A–D** and **D–D–A–D–D**, respectively), and is the cause of the increased transition dipole μ_{ge} of **B** compared to **A**. However, in the case when all three substituents have donating methoxy groups (compound **E**), conjugation is reduced due to the increased torsional disorder. Consequently, the transition dipole and TPA cross-sections of compound **E** are smaller than those of the compound **F**, which has no additional substituents. The short range charge transfer from the donors to cyano groups in compounds **A** and **B** stabilizes the high energy ($e \rightarrow E'$) transition, so the calculated cross sections for the second TPA peak are almost twice as large as for compounds **C–D**.

4. Conclusion

We have investigated in detail one and two photon absorption properties of extended amine-terminated phenylenevinylene oligomers with the motif **D– π –A– π –D** and have elucidated the effect of substituents in the conjugated core. Theoretical results illustrate that compounds **A–F** possess strong linear and non-linear responses in a wide energy spectrum. OPA and TPA transitions are dominated by two pairs of excited states. The OPA maxima are lying in the visible (3.0–3.5 eV) and near UV (2.3–2.8 eV) spectral windows. The absorption maxima for compound **F** with no substituents are the most blue shifted compared to other molecules. The TPA cross-sections up to 3000 GM at approximately twice the wavelength of the OPA maxima are observed. The chromophores **A–C**, which have two and three additional alternating donor and acceptor substituents, exhibit the largest TPA cross-sections. Introduction of additional methoxy groups with central cyano substituent (compounds **C** vs. **D**) leads to the enhanced TPA cross-sections due to charge delocalization in the first excited state, and, therefore, increased ground to excited state transition dipole moment. Our calculations show that small variations in the chemical structure strongly modify the charge transfer patterns, and, therefore, cause noticeable effects on the optical properties. We notice that introduction of extra substituents in the backbone stabilizes the TPA active excited state, which is found about 0.2 eV above the OPA active excited state. This supports the experimental studies of Chung et al. [16]. However, the enhancements in TPA cross-sections, which we observe from the electronic structure calculations, are much less pronounced compared to experiment [16]. This supports our conclusion that other mechanisms, e.g. vibronic coupling to the lower lying OPA active excited state [29], may come into play to give rise to the measured TPA responses. Future theoretical investigations of such processes would be helpful in elucidating observed increases of the TPA cross-sections.

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