# Theoretical Designs of Molecular Photonics Materials

Yuanping Yi, Lingyun Zhu, Zhigang Shuai*

Different theoretical models for the computation of multiphoton absorption response are described and reviewed. The influences of intrinsic molecular structure parameters on the multiphoton absorption properties for organic conjugated molecules are discussed in terms of: i) the donor/acceptor substitutions; ii) the π conjugation length; iii) the ground-state polarization mimicking structural character such as bond-length alternation; iv) the molecular dimensionality; and, v) some other possible factors, such as vibronic coupling and the solvent, as well as aggregation effects. Some theoretical designing strategies for organic materials with large multiphoton cross-sections are then proposed.
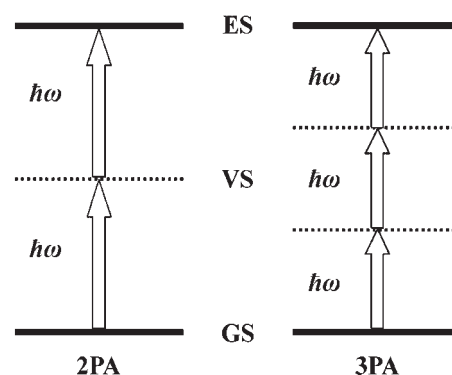
Introduction

Multi-photon absorption is a process in which an atom or molecule is excited from the ground state to an excited state by simultaneously absorbing two or three photons via one or two virtual states (see Figure 1). Early in 1931, the two-photon absorption (2PA) process was theoretically predicted by Göppert-Mayer,[1] and only after thirty years was the very first experimental observation, by Kaiser and Garrett,[2] realized, due to developments in high power-peak lasers. Shortly thereafter, in 1964, Singh and Bradley detected three-photon absorption (3PA) in naphthalene crystals by a ruby laser excitation.[3] Since then, and especially in recent years with the advent and development of high peak-power and tunable laser sources, numerous applications based on multi-photon absorption (MPA) (mainly on 2PA) have been demonstrated. These

applications include optical power limiting,[4–7] frequency up-converted lasing,[8–14] three-dimensional (3D) optical data storage,[15–22] 3D micro-fabrication,[23–27] 3D fluorescence imaging[28–31] and photodynamic therapy (PDT).[32–36] There are two key features in MPA resulting in such ubiquitous applications in photonics and biophotonics: i) a quadratic (even cubic) dependence of the 2PA (3PA) process on the input light intensity provides a spatially confined excitation; and, ii) a much longer excitation wavelength can be used which allows for a deeper penetration length.

To realize the full potentials of these applications, materials with large MPA cross-section are highly desirable. Owing to their flexibility for structure modification and molecular-level optimization for the nonlinear optical (NLO) response, a myriad of organic molecules have been designed, synthesized and characterized for MPA studies. At the same time, in order to find organic molecules with high MPA cross-sections, several theoretical methods have been developed to calculate the MPA response coefficients and to establish the relationship between the chemical structures of molecules and their MPA properties.

The widely employed theoretical method to calculate the MPA-related dynamic NLO coefficients is the

Y. Yi, L. Zhu, Z. Shuai
Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, 100080 Beijing, China
E-mail: zgshuai@iccas.ac.cn

Yuanping Yi was born in Jiangxi, China, in 1980. He studied polymer materials and engineering at University of Science and Technology of China, and received his BS degree in 2002. From then on, he has been a Ph.D. student at the Institute of Chemistry Chinese Academy of Sciences under the supervision of Prof. Zhigang Shuai. His current main research interest is the development and application of theoretical and computational methods for the excited-state electronic structures of organic conjugated molecules.

Lingyun Zhu was born in Shandong, China, in 1978. She received her MS degree in 2004 on ''theoretical study multi-photon absorption of organic molecules'' at Shandong Normal University and the Institute of Chemistry Chinese Academy of Sciences, under the supervision of Profs. Zhigang Shuai and Dezhan Chen. From 2005, she has become a PhD student at the Institute of Chemistry Chinese Academy of Sciences under the supervision of Prof. Zhigang Shuai. Her current domains of research interest are theoretical modeling of multi-photon absorption and other opto-electronic properties for organic materials.

Zhigang Shuai was born in Jiangxi, China, in 1962. He got his PhD (condensed matter theory) in 1989 from the department of physics, Fudan University, Shanghai. From 1990 to 2001, he worked as a research scientist at the University of Mons-Hainaut, Belgium. In 2002, he joined the Institute of Chemistry, the Chinese Academy of Sciences as a full research professor at the Key Laboratory of Organic Solids. He is the recipient of the prestigious "Outstanding Young Scientist Award" from the National Science Foundation of China in 2004. He was named as one of the chair scientists for the Ministry of Science and Technology of China's national key basic research program (alias "973 Program"). The major research interests in his group are theoretical modeling of organic functional opto-electronic materials and devices, including theory and computations on light-emitting materials, transport materials, organic photonics materials, organic photovoltaics, electronic devices at molecular scale, as well as nanostructure simulations. The fundamental problems his group is addressing include molecular excited state structure and dynamics; charge, spin and energy transports through organic materials and molecular devices; multiphoton absorption; and, organic device physics. He has authored or coauthored more than 170 research articles with more than 2 500 citations.
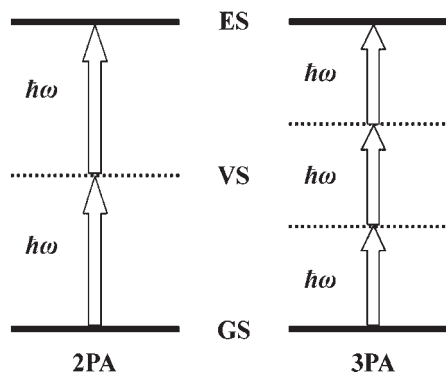
Figure 1. Scheme of multi-photon absorption processes (GS: ground state, ES: excited state, VS: virtual state).

by Cronstrand et al.,[38] it is formidable to calculate the 3PA-related fifth-order polarizability via the full SOS approach. The alternative choice is a tensor approach,[38–41] which also involves SOS, but with fewer folds of summation. To better understand the nature of MPA process, essential-state models have been developed to analyze the MPA response.[41–44]

To date, molecular systems investigated experimentally and/or theoretically include dipolar,[41,45–47] quadrupolar[41,48–56] and octupolar[57–60] molecules. More complex systems such as dendritic[61–65] and porphyrin-based[40,66–78] molecules have also been investigated. It has been shown that donor/acceptor substitutions[52,79–81] and/or extending conjugation length[51,82,83] of organic conjugated molecules can lead to tremendous increases in MPA cross-sections. Modulating ground-state polarization could greatly influence MPA response.[41,54,55] The increase of molecular dimensionality may also enlarge MPA cross-sections.[59,62–64]

This paper is organized as following. We first describe the theoretical methodologies for MPA response and then we give a detailed discussion about the influences of molecularly intrinsic structure parameters, such as donor/acceptor substitution, π-conjugation length, molecular polarization and dimensionalities on the MPA properties, as well as some other factors, such as vibronic coupling and intermolecular interaction effects. At the same time, we will propose some theoretical design strategies for organic molecules with large MPA cross-sections. The final section will present the concluding remarks.

Theoretical and Computational Methods for MPA

Sum-Over-States (SOS) Method

From perturbation theory, the MPA cross-section is related to the imaginary part of the molecular polarizability.[37]

sum-over-states (SOS) approach.[37] In this method, the NLO coefficients of a molecule can be expressed as summation over transition dipole moment products divided by transition energies. However, as pointed out

For linear absorption, the one-photon absorption (1PA) cross-section, $\sigma_1(\omega)$, can be derived from the first-order polarizability $\alpha(-\omega; \omega)$,[84] as:

$$\sigma_1(\omega) = \frac{4\pi L^2}{\hbar n c} \bullet (\hbar\omega) \bullet \mathrm{Im}[\alpha(-\omega; \omega)] \qquad (1)$$

In the above expression, $\hbar$ denotes Planck's constant, c is the speed of light in vacuum, n represents a refractive index (equal to 1 for a vacuum), L is a local-field correction [within the simple Lorentzian model, $L = (n^2 + 2)/3$], and ω denotes the frequency of the incident light. With the SOS method, the components of $\alpha(-\omega; \omega)$ are written as:[37]

$$\alpha_{ij}(-\omega; \omega) = \sum_m \left(\frac{\mu_{gm}^i \mu_{mg}^j}{\Omega_{gm} - \hbar\omega} + \frac{\mu_{gm}^j \mu_{mg}^i}{\Omega_{gm}^* + \hbar\omega} \right) \qquad (2)$$

where i, j denote the Cartesian coordinates; $\Omega_{gm} = E_{gm} - i\Gamma$, where E_{gm} is the excitation energy from the ground state g to the excited state m, Γ denotes a Lorentzian broadening factor; μ_{gm}^i is the ith Cartesian component ($i = x, y, z$) of the transition dipole moment between the eigenstates g and m.

For a general third-order nonlinear process, the SOS formula of the third-order molecular polarizability, $\gamma(-\omega_\sigma; \omega_1, \omega_2, \omega_3)$ can be expressed as:[37]

and, P_{ijk} is an operator that sums over the six terms generated by permutation over the index pairs (ω_1, i), (ω_2, j), (ω_3, k). The 2PA cross-section $\sigma_2(\omega)$ is related to the imaginary part of the tensor γ when $\omega_1 = \omega_3 = \omega$ and $\omega_2 = -\omega$:[84]

$$\sigma_2(\omega) = \frac{4\pi^2 L^4}{\hbar n^2 c^2} \bullet (\hbar\omega)^2 \bullet \mathrm{Im}[\gamma(-\omega; \omega, -\omega, \omega)] \qquad (4)$$

To allow a comparison between the calculated 2PA cross-section and the experimental value measured in solution, it is necessary to take into account spatial averaging over all possible molecular orientations; The orientationally averaged value of γ is defined as:[85,86]

$$\gamma_{av} = \frac{1}{15} \sum_{i,j=x,y,z} (\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji}) \qquad (5)$$

From the fifth-order polarizability $\varepsilon(-\omega; \omega, -\omega, \omega, \omega, -\omega)$, the 3PA cross-section, $\sigma_3(\omega)$, can be derived,[37] which is expressed as:

$$\sigma_3(\omega) = \frac{4\pi^3 L^6}{3\hbar n^3 c^3} \bullet (\hbar\omega)^3 \bullet \mathrm{Im}[\varepsilon(-\omega; \omega, -\omega, \omega, \omega, -\omega)] \qquad (6)$$

$$\gamma_{hijk}(-\omega_\sigma; \omega_1, \omega_2, \omega_3)$$

$$= P_{ijk} \left\{ \sum_{lmn} \left[\frac{\mu_{gl}^k \overline{\mu}_{lm}^j \overline{\mu}_{mn}^i \mu_{ng}^h}{(\Omega_{gl} - \hbar\omega_\sigma)(\Omega_{gm} - \hbar\omega_1 - \hbar\omega_2)(\Omega_{gn} - \hbar\omega_1)} + \frac{\mu_{gl}^j \overline{\mu}_{lm}^k \overline{\mu}_{mn}^i \mu_{ng}^h}{(\Omega_{gl}^* + \hbar\omega_3)(\Omega_{gm} - \hbar\omega_1 - \hbar\omega_2)(\Omega_{gn} - \hbar\omega_1)} \right. \right.$$

$$\left. + \frac{\mu_{gl}^h \overline{\mu}_{lm}^i \overline{\mu}_{mn}^k \mu_{ng}^j}{(\Omega_{gl}^* + \hbar\omega_1)(\Omega_{gm}^* + \hbar\omega_1 + \hbar\omega_2)(\Omega_{gn} - \hbar\omega_3)} + \frac{\mu_{gl}^h \overline{\mu}_{lm}^i \overline{\mu}_{mn}^j \mu_{ng}^k}{(\Omega_{gl}^* + \hbar\omega_1)(\Omega_{gm}^* + \hbar\omega_1 + \hbar\omega_2)(\Omega_{gn}^* + \hbar\omega_\sigma)} \right]$$

$$- \sum_{mn} \left[\frac{\mu_{gm}^k \mu_{mg}^j \mu_{gn}^i \mu_{ng}^h}{(\Omega_{gm} - \hbar\omega_\sigma)(\Omega_{gm} - \hbar\omega_3)(\Omega_{gn} - \hbar\omega_1)} + \frac{\mu_{gm}^j \mu_{mg}^k \mu_{gn}^i \mu_{ng}^h}{(\Omega_{gm} - \hbar\omega_3)(\Omega_{gn}^* + \hbar\omega_2)(\Omega_{gn} - \hbar\omega_1)} \right.$$

$$\left. \left. + \frac{\mu_{gm}^h \mu_{mg}^i \mu_{gn}^k \mu_{ng}^j}{(\Omega_{gm}^* + \hbar\omega_\sigma)(\Omega_{gm}^* + \hbar\omega_3)(\Omega_{gn}^* + \hbar\omega_1)} + \frac{\mu_{gm}^h \mu_{mg}^i \mu_{gn}^j \mu_{ng}^k}{(\Omega_{gm}^* + \hbar\omega_3)(\Omega_{gn} - \hbar\omega_2)(\Omega_{gn}^* + \hbar\omega_1)} \right] \right\} \qquad (3)$$

In this formula, h, i, j, k refer to the Cartesian coordinates; l, m, n represent the excited state index; the operator $\overline{\mu}_{mn}^i$ denotes the difference of state dipole moment between the excited and ground state if the two excited states are identical, otherwise it is the transition dipole moment between two different excited states; ω_1, ω_2, ω_3 denote the frequencies of incident light beams and $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$ is the polarization response frequency;

However, it is impossible to calculate ε via the full SOS approach under present computational conditions. An alternative and more simplified method for the computation of 3PA cross-section is the tensor approach.

Tensor Approach

Under resonant conditions,[87] the MPA cross-section is related to the MPA transition amplitudes from the ground

state to a final excited state $|f\rangle$, with $S_{g\to f}$ for 2PA and $T_{g\to f}$ for 3PA:

$$\sigma_2(\omega) = \frac{4\pi^2 L^4}{\hbar n^2 c^2} \bullet (\hbar\omega)^2 \bullet \sum_f |S_{g\to f}|^2 \bullet \frac{\Gamma}{\left(E_{gf} - 2\hbar\omega\right)^2 + \Gamma^2} \quad (7)$$

$$\sigma_3(\omega) = \frac{4\pi^3 L^6}{3\hbar n^3 c^3} \bullet (\hbar\omega)^3 \bullet \sum_f |T_{g\to f}|^2 \bullet \frac{\Gamma}{\left(E_{gf} - 3\hbar\omega\right)^2 + \Gamma^2} \quad (8)$$

The MPA transition amplitudes $S_{g\to f}$ and $T_{g\to f}$ are given with the ij and ijk tensor components by:[38–40,84]

$$S_{g\to f}^{ij} = P_{ij} \sum_m \frac{\overline{\mu}_{gm}^i \overline{\mu}_{mf}^j}{\Omega_{gm} - \hbar\omega} \quad (9)$$

$$T_{g\to f}^{ijk} = P_{ijk} \sum_{m,n} \frac{\overline{\mu}_{gm}^i \overline{\mu}_{mn}^j \overline{\mu}_{nf}^k}{\left(\Omega_{gm} - \hbar\omega\right)\left(\Omega_{gn} - 2\hbar\omega\right)} \quad (10)$$

where P_{ij} and P_{ijk} denote a complete permutation of the indices i, j and i, j, k; the intermediate states m, n involved in the summation include the ground state. From Equation (9) and (10), we know that these four resonant terms for 2PA and 36 resonant terms for 3PA in the general SOS expressions are accounted for in Equation (7) and (8), respectively. Compared with the SOS formula, though the tensor approach also involves summation over excited states, many fewer folds of summation make the tensor approach more applicable for the calculation of the MPA cross-section, especially for the 3PA cross-section. When averaged over molecular orientations assuming an isotropic medium, the 2PA and 3PA cross-section can be expressed as (assuming linearly polarized light):[38,85,86,88]

$$\sigma_2(\omega) = \frac{4\pi^2 L^4}{\hbar n^2 c^2}$$

$$\bullet (\hbar\omega)^2 \bullet \sum_f \frac{1}{15} \left| \sum_{i,j} \left(S_{g\to f}^{ii} S_{g\to f}^{jj*} + 2 S_{g\to f}^{ij} S_{g\to f}^{ij*} \right) \right|$$

$$\times \frac{\Gamma}{\left(E_{gf} - 2\hbar\omega\right)^2 + \Gamma^2} \quad (11)$$

$$\sigma_3(\omega) = \frac{4\pi^3 L^6}{3\hbar n^3 c^3}$$

$$\bullet (\hbar\omega)^3 \bullet \sum_f \frac{1}{35} \left| \sum_{i,j,k} \left(2 T_{g\to f}^{ijk} T_{g\to f}^{ijk*} + 3 T_{g\to f}^{iij} T_{g\to f}^{kkj*} \right) \right|$$

$$\times \frac{\Gamma}{\left(E_{gf} - 3\hbar\omega\right)^2 + \Gamma^2} \quad (12)$$

It is worth noting that the correction vector (CV)[89–92] technique has been successfully applied to calculate the NLO coefficients, which requires only the ground-state knowledge and gives results equal to the converged values obtained by the SOS or tensor approaches. Since the CV method gives only values of MPA cross-sections at fixed frequency without the knowledge of transition dipole moments or the excitation energies, it does not provide detailed insights into the MPA transition processes between the intermediate states. A detailed description of our implementations of the CV method for calculating MPA properties can be found in ref.[81,83,93].

Essential-State Models

Essential-state models have proved very useful in obtaining structure-property relationships. For quasi-one-dimensional noncentrosymmetric molecules, the longitudinal components of the 2PA S-tensor and 3PA T-tensor into the dominant one-photon-allowed state can be approximately obtained using the two-state model:[41,43,44]

$$S_{g\to e} = 2\left(\frac{\mu_{ge}\overline{\mu}_{ee}}{E_{ge}/2}\right) \quad (13)$$

$$T_{g\to e} = 6\left(\frac{9\mu_{ge}\overline{\mu}_{ee}^2}{2E_{ge}^2} - \frac{9\mu_{ge}^3}{4E_{ge}^2}\right) \quad (14)$$

where μ_{ge} is the transition dipole moment between the ground state and the one-photon state, $|e\rangle$, and $\overline{\mu}_{ee}$ is the change in state dipole moment up excitation along the molecular longitudinal axis. Combining Equation (11) and (13), and Equation (12) and (14), we can calculate the 2PA and 3PA cross-sections, respectively via the following expressions:

$$\sigma_2 = \frac{4\pi^2 L^4}{\hbar n^2 c^2} \bullet \frac{4}{5\Gamma} \mu_{ge}^2 \overline{\mu}_{ee}^2 \quad (15)$$

$$\sigma_3 = \frac{4\pi^3 L^6}{3\hbar n^3 c^3} \bullet \frac{27}{28\Gamma} \frac{\mu_{ge}^2 \left(2\overline{\mu}_{ee}^2 - \mu_{ge}^2\right)^2}{E_{ge}} \quad (16)$$

For quasi-one-dimensional centrosymmetric molecular systems, $\overline{\mu}_{ee}$ is equal to zero, one another strongly two-photon-allowed state, $|e'\rangle$, should be considered to calculate the 2PA cross-section into that state with the 2PA transition amplitude which reads:[42,44]

$$S_{g\to e} = 2\left(\frac{\mu_{ge}\mu_{ee'}}{E_{ge} - E_{ge'}/2}\right) \quad (17)$$

By substituting Equation (17) into (11), we will obtain the 2PA cross-section as:

$$\sigma_2 = \frac{4\pi^2 L^4}{\hbar n^2 c^2} \bullet \frac{1}{5\Gamma} \frac{E_{ge'}^2 \mu_{ge}^2 \mu_{ee'}^2}{\left(E_{ge} - E_{ge'}/2\right)^2} \tag{18}$$

where $\mu_{ee'}$ is the transition dipole moment between the 1PA and 2PA excited states and $E_{ge} - E_{ge'}/2$ is the so-called detuning energy. When taking the two-photon state (even parity state) $|e'\rangle$ into account, the 3PA transition amplitude into the one-photon state $|e\rangle$ is expressed as:[41]

$$T_{g \to e} = 6 \left[\frac{3}{2} \frac{\mu_{ge} \mu_{ee'}^2}{E_{ge} \left(E_{ge'} - 2E_{ge}/3\right)} - \frac{9}{4} \frac{\mu_{ge}^3}{E_{ge}^2} \right] \tag{19}$$

From the above equation and Equation (12), the 3PA cross-section into the one-photon state $|e\rangle$ would be written as:

$$\sigma_3 = \frac{4\pi^3 L^6}{3\hbar n^3 c^3} \bullet \frac{3E_{ge}}{7\Gamma} \left[\frac{\mu_{ge} \mu_{ee'}^2}{E_{ge'} - 2E_{ge}/3} - \frac{3\mu_{ge}^3}{2E_{ge}} \right]^2 \tag{20}$$

It should be noted that the above essential-state models are not necessarily applicable to more complicated systems, since in these many more states could be "essential".[44,94] To properly link the structure to the MPA response, more excited states and transition channels should be taken into account; However, it does provide such simple guidelines for molecular design.

Excited-State Electronic Structures

The MPA process is strongly correlated to the excited states in nature. A proper description of excited states is essential to simulate the NLO properties of chromophores quantitatively, especially at higher orders. Usually a single configuration interaction (SCI) formalism is in most cases reliable to describe the first- or even the second-order polarizability.[95] For the third-order NLO response, a minimal description should include two-electron excitation contribution.[96,97] The multi-reference determinant single and double configuration interaction (MRDCI) formalism should be adopted for a better account of electron correlation effects.[98,99] The coupled-cluster equation of motion method with single and double excitations (CCSD-EOM)[100–102] has been shown to be efficient, size consistent, and highly accurate to describe the electron excitations for the many-body systems.[103–105] It has been successfully implemented to calculate MPA response.[40,81,106] At present, time-dependent density functional theory (TDDFT) implemented in the response

theory is available for describing MPA response.[46,47,107–112] However, as far as the nonlinear response is concerned, the nature of exchange-correlation functional is strongly influential.[113] Although an ab initio calculation of the Hamiltonian is highly desirable, the semi-empirical intermediate neglect of differential overlap (INDO) Hamiltonian[114] allows the study of larger molecular systems. It is especially suitable for the conjugated organic dyes.

Molecular Parameters for Multiphoton Absorption Properties

Donor/Acceptor Substitution

The donor/acceptor substitutions have great effects on the MPA properties of p-conjugated systems. With increased strength of donor/acceptor groups, the intensity of charge transfer will increase. This will lead to large transition dipole moments and low excitation energies, translating altogether into large MPA cross-sections. Recently, Zheng et al. reported experimental and theoretical studies on the 2PA properties of acceptor substituted electron-rich bis(heterocycle)vinylene (the so-called A-D-A molecules, see Figure 2)[52] The electron-withdrawing strength of the acceptor group 4,5-dimethyl-5-trifluoromethyl-3-cyano-2(5H)-furanylidenepropanedinitrile (CF$_3$-TCF) used in **3** and **4** is stronger than that of 4,5,5-trimethyl-3-cyano-2(5H)-furanylidenepropanedinitrile (TCF) used in **1** and **2**. From Table 1, we find that the INDO/MRDCI method calculated 2PA cross-sections of molecules **3** and **4** are larger than those of **1** and **2,** respectively, which is in line with experimental results. The calculations with three-state model [Equation (18)] reasonably reproduced the converged results (see Table 1), so we can analyze the origin of 2PA cross-sections using the quantities involved in the three-state model. From Table 1, we can find that the enhancement of 2PA cross-sections in **3** and **4** is due to the somewhat smaller detuning energies and increased transition dipole moments, especially the transition dipole moments from the intermediate 1PA-allowed states to the final 2PA-allowed states.

Increasing the strength of donor/acceptor groups also enhances the 3PA cross-section. Recently, we performed calculations on the symmetrically donor/acceptor substituted trans-stilbene molecules for their MPA cross-sections with CCSD-EOM/CV method at both ab initio and semiempirical INDO levels.[81] Figure 3 shows the correlation of between the MPA cross-sections and the donor/acceptor substituents. We can find that the 3PA cross-section, as well as the 2PA cross-section, increases with the strength of the donor/acceptor group and that the enhancement of 2PA cross-section is more pronounced than that of 3PA cross-section.
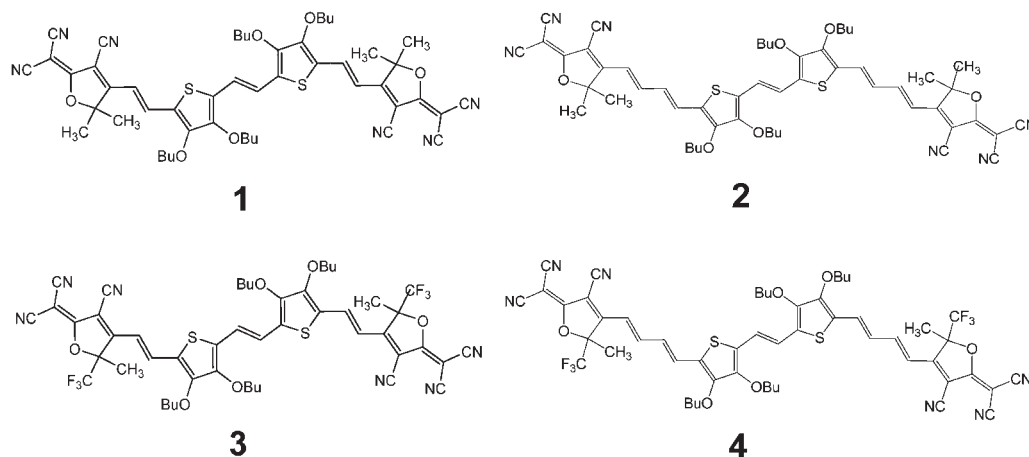
Figure 2. Structures of acceptor substituted electron-rich bis(heterocycle)vinylene.

π Conjugation Length

It is known that the large optical nonlinearities in conjugated organic systems arise from the presence of a highly delocalized π-electron cloud. Extending the molecular conjugation length will make the π-electron more delocalized. This leads to lower excitation energies and larger dipole matrix elements, which result in larger MPA cross-section. Zheng et al. observed those phenomena in recent 2PA studies.[51] Figure 4 shows the model molecules for the theoretical calculations. Molecules **6** and **8** are extended from **5** and **7**, respectively, with an additional heterocycle-vinylene unit. From Table 2, we find that the INDO/MRDCI-calculated 2PA cross-sections of **6** and **8** for the most strongly allowed 2PA states are larger than those of **5** and **7**, respectively. According to Equation (18), the enhancement of the 2PA cross-sections is due to the smaller detuning energies and larger transition dipole moments from the dominant 2PA channel (see Table 2).

Similar to 2PA cross-section, the 3PA cross-section is also increased through extending the π conjugation length, and the increase is even faster. We have studied the MPA properties in the extended rylenebis(dicarboximide)s by the INDO/MRDCI/CV method.[83] It is found that the MPA cross-sections show a power law dependence on the π conjugation length, with exponents of 2.6 for 2PA and 5.6 for 3PA, respectively.

Ground-State Polarization

Zhu et al. studied the evolution of the 3PA cross-section as a function of the degree of ground-state polarization for the model dipolar and quadrupolar systems.[41] Figure 5 shows the chemical structures of prototypical dipolar and quadrupolar molecules (**9** and **10**) and an illustration of the system of point charges used to change the ground-state
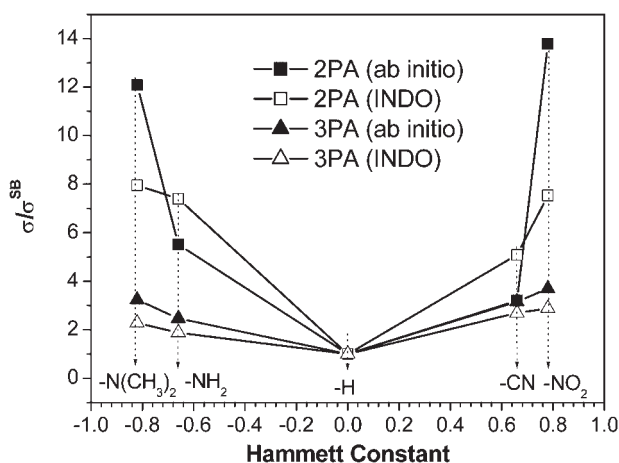
Table 1. INDO/MRDCI-calculated excitation energies and transition dipole moments of molecules **1–4**, along with calculated detuning energies and 2PA cross-sections obtained by the three-state model. The converged and experimental values of the 2PA cross-sections are also shown.

Molecule	1	2	3	4
E_{ge} (eV)	2.64	2.58	2.55	2.49
$E_{ge'}$ (eV)	3.11	3.02	3.01	2.90
$(E_{ge} - E_{ge})/2$ (eV)	1.09	1.07	1.05	1.04
μ_{ge} (D)	13.5	15.3	13.9	15.7
$\mu_{ee'}$ (D)	10.1	12.2	12.9	14.1
$^{3\text{-State}}\sigma_2$ (GM)	793	1 454	1 384	1 996
$^{\text{Converged}}\sigma_2$ (GM)	773	1 334	1 310	1 881
$^{\text{exptl}}\sigma_2$ (GM)	2 400	4 200	3 600	5 000

Figure 3. The enhancements of the CCSD-EOM/CV method calculated two- and three-photon absorption cross-sections at the first peak of the symmetrically substituted *trans*-stilbene molecules versus the strength (represented by the Hammett constant) of the substituent donor/acceptor groups.
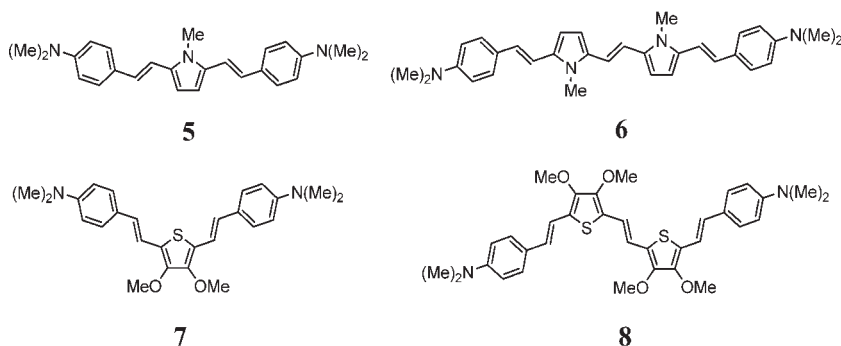
Figure 4. Structures of bis(aminostyryl) chromophores with electron-rich heterocycle (5, 7) and bis(heterocycle)vinylene (6, 8) bridges.

Equation (14)] dominates the evolution and is responsible for the peak of 3PA cross-section, while the N' term $(9/4)(\mu_{ge}^3/E_{ge}^2)$ [see Equation (14)] has a negative and much smaller contribution to the observed trend. This clearly shows that for the dipolar systems, by tuning the BLA, an optimal 3PA cross-section can be achieved by maximizing $\overline{\mu}_{ee}$.

Figure 7 shows the evolutions of the 3PA cross-section for the quadrupolar molecule 10 with ground-state polarization. Similar to the dipolar molecule 9, the 3PA cross-section of molecule 10 first increases and then drops with decreasing BLA, but there is another increase of 3PA cross-section at smaller BLA values. The three-state model reproduces only to a limited extent the trend seen in the converged calculations (see Figure 7). Moreover, the more complex behavior of 3PA cross-section varying with BLA should be explained by the complete terms in Equation (19), not by only one single term.

The calculated 2PA cross-sections in both dipolar and quadrupolar molecules strongly increase with increasing BLA, reach a maximum and then drop sharply (see Figure 6 and 7). That fully agrees with the results obtained by Zojer et al.[55] In one word, a maximum value in both 2PA and 3PA cross-sections can be obtained through tuning the ground-state polarization, but the optimal degree of ground-state polarization varies significantly.

polarization. Approaching the point charges toward the molecular plane allows a systematical tuning of the degree of ground-state polarization. The bond length alternation (BLA) is used as a measure for the induced ground-state polarization. The molecular geometries are optimized with the semi-empirical Austin model 1 (AM1) method and the electronic structures of the ground and excited states are calculated with INDO/MRDCI scheme. The converged MPA cross-sections are calculated by the T-tensor approach. The essential models described by Equation (16) and (20) are used to analyze the origin of the 3PA cross-section for the dipolar and quadrupolar molecule, respectively.

The evolutions of the 3PA cross-section into the lowest excited state as a function of BLA for the dipolar molecule 9 are shown at the bottom part of Figure 6. The BLA dependence of the 3PA cross-section derived from the two-state model well agrees with the trends obtained by the T-tensor approach: with increasing ground-state polarization (decreasing BLA), the 3PA cross-section firstly strongly increases, reaches a maximum, and then collapses. It is shown that the so-called D' term $(9/2)(\mu_{ge}\overline{\mu}_{ee}^2/E_{ge}^2)$ in the 3PA transition amplitude [see

Molecular Dimensionality

Recently, multi-branched octupolar and dendritic molecules have attracted much attention as potential multi-photon absorbing materials. It has been found that there would be additional cooperative enhancement of MPA cross-section in the branched molecules when compared with their constituent subunits.[59,62,63,115,116] Due to

Table 2. INDO/MRDCI method calculated 2PA cross-sections into the largest 2PA peak of molecules 5–8 (obtained including the 50 lowest singlet excited states) and the excitation energies and transition dipole moments along with calculated detuning energies for the dominant channel.

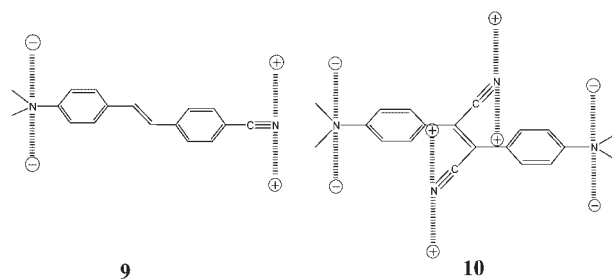| Molecule	5	6	7	8
E_{ge} (eV)	3.41	3.08	3.37	3.04
$E_{ge'}$ (eV)	5.20	4.73	4.94	4.42
$(E_{ge} - E_{ge})/2$ (eV)	0.81	0.71	0.90	0.83
μ_{ge} (D)	11.3	13.6	10.2	12.1
$\mu_{ee'}$ (D)	19.1	23.6	20.2	22.8
σ_2 (GM)	9 471	22 453	6 104	10 031

Figure 5. Structures of the model systems for a dipolar chromophore (4-dimethylamino-4′-cyano-E-stilbene), 9, and a quadrupolar chromophore (4,4′-bis(dimethyl)amino-α,β-dicyano-E-stilbene), 10, together with an illustration of the system of point charges used to continuously vary the ground-state polarization.
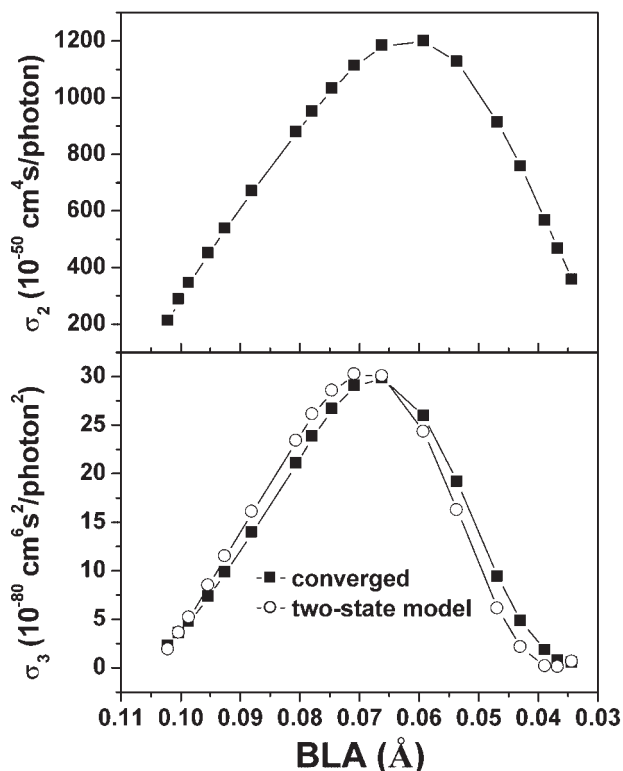
Figure 6. Evolution of the 2PA (top) and 3PA (bottom) cross-sections as a function of BLA for molecule 9. The 3PA cross-sections are obtained from the T-tensor approach and the two-state model [Equation (16)], respectively.
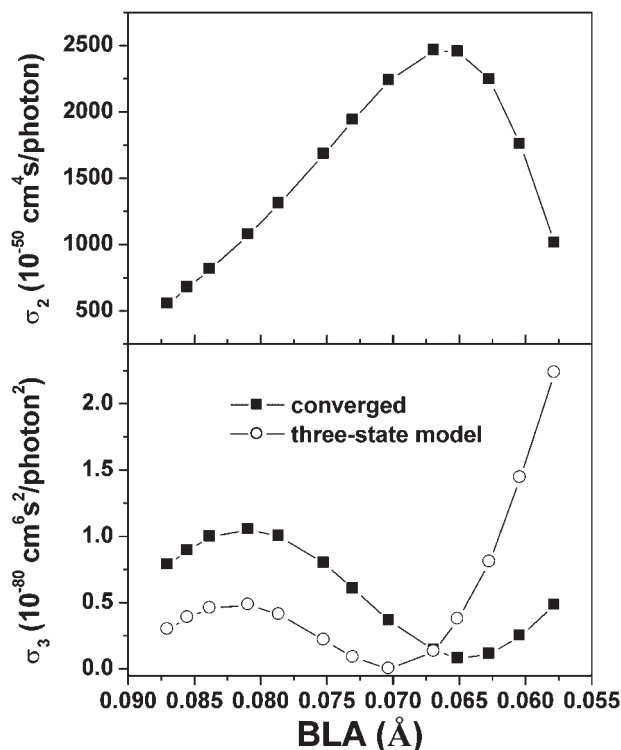

Figure 7. Evolution of the 2PA (top) and 3PA (bottom) cross-sections of molecule 10 as a function of BLA. For 3PA, the converged results obtained from the T-tensor approach are compared with those calculated using the three-state model [Equation (20)].

computational limitations, very few calculations have been carried out on the MPA properties of dendritic molecules. However, the calculations for octupolar compounds indicated that the enhancement could result from the electronic coupling between the branching subunits.[59] This significant coupling leads to essential changes in the excitation energies and transition dipole moments, which are responsible for the magnitude of MPA cross-sections.

Other Possible Factors

In some cases, the vibronic coupling effects on MPA must be taken into account for correct comparisons between theoretical and experimental results. It was found that the Herzberg-Teller coupling could greatly change the appearance of 2PA spectrum.[117–119] Furthermore, new vibrational 2PA channels would make strong (positive or negative) contributions to the size of 2PA cross-sections.[120–123]

Besides the intramolecular factors discussed above, intermolecular interaction may play an important role on the MPA properties in organic conjugated molecules. For examples, the 2PA cross-sections and peak photon energies of molecules in solutions can be very different from those of molecules in gas due to the significant change of molecular geometries, such as BLA and molecular planarity, induced by the interaction between the molecule and solvents.[92,124–126] As a result of the interaction between the molecules themselves, aggregation effects are also important to the MPA response.[77,117–129]

Conclusion

Different theoretical and computational methods proposed and extensively used in recent for calculating and analyzing the MPA properties in organic conjugated molecules have been presented. The molecular parameters influencing the MPA response were discussed and theoretical design strategies for large MPA cross-sections were summarized. The MPA cross-sections increase with the strength of donor and/or acceptor group and π conjugation length. Through modulating ground-state polarization, optimal MPA cross-sections could also be obtained. Increasing the molecular dimensionality could be another route to improve MPA response. Some other

possible factors, such as vibronic coupling, solvent and aggregation effects should be taken into account when they influence MPA response greatly.

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