

Two-Photon Absorption and Nonlinear Optical Properties of Octupolar Molecules

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Abstract: Two-photon absorption (TPA) cross sections of four representative series of octupolar molecules are theoretically investigated. The general structure–TPA-property relationship is described by using the effective four-state valence-bond three-charge-transfer model. As the charge-transfer character of the ground electronic state increases due to the strong donors or acceptors, (i) the transition dipole matrix elements between the ground and 2-fold degenerate excited states increase, (ii) the energy gap decreases, and consequently (iii) the TPA transition amplitude monotonically increases. Thus, the design strategy to maximize the TPA cross section of the octupolar molecule is established. On the basis of the four-state model, the first hyperpolarizability of the octupolar molecule is found to be linearly proportional to the TPA cross section. This theoretical relationship is confirmed by using the ab initio calculation results. The Hammett correlation analysis of the TPA cross section and first hyperpolarizability is also presented.

I. Introduction

The two-photon absorption (TPA) process of a conjugated polyene system has been paid much attention recently due to a variety of applications of TPA dyes to three-dimensional optical memory device,^{1–3} photodynamic therapy,⁴ and two-photon fluorescence microscopies.^{5–9} Despite the fact that there are many references in the literature on the TPA of a variety of dyes, the structure–TPA–cross-section relationship has not been studied much. Only recently, Albota et al. presented an interesting work on the TPA cross section of linear quadrupolar molecules.¹⁰ Varying the conjugation lengths and donor and acceptor strengths, they found that some of the quadrupolar dyes have exceptionally large TPA cross-section. Due to the molecular symmetry, that is, centrosymmetry, of those quadrupolar

molecules, the first excited electronic state is TP-forbidden, whereas there is a high-lying excited electronic state, which is one-photon-forbidden but two-photon-allowed. To systematically study the structure–TPA-property relationship of the linear quadrupolar molecules, we carried out quantum chemical calculations of TPA transition amplitude of a few series of quadrupolar molecules and found that the TPA transition amplitude is a monotonically increasing function of the donor and acceptor strengths.¹¹ Also, the conjugation-length dependencies of the TPA cross section were investigated and presented in ref 11. In relation to this work, Barzoukas and Blanchard-Desce¹² presented a theoretical description of the TPA properties of linear quadrupolar molecules based on the three-state model, which is a simplified version of VB-2CT model discussed in ref 13, and showed how one can enhance the TPA cross section of the quadrupolar molecules.

In contrast to the linear quadrupolar molecules, the push–pull (donor–bridge–acceptor) molecules have both one- and two-photon-allowed first excited electronic state. Kogej et al. performed a semiempirical calculation of the TPA cross section when the TP excited state is the first excited electronic state.¹⁴ They found that the TPA cross section changes nonmonotonically with respect to the bond-length alternation (BLA). In other words, as the donor and acceptor strengths increase for a given conjugated polyene bridge, the TPA cross section shows a very similar trend that was observed for the first hyperpolarizability of the push–pull polyene.^{15–21} Conclusively, if the TPA state is the first electronically excited state, there is an optimum pair

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of donor and acceptor maximizing the corresponding TPA cross section. They further showed, that if the TPA state is one of the high-lying excited electronic states and half of the energy gap between that excited state and the ground state happens to be close to the energy gap between the first excited state and the ground state, due to the resonance enhancement, the TPA cross section can be dramatically increased.¹⁴ The TPA of another series of two-dimensional cumulene-containing polyenes was also theoretically investigated by Norman, Luo, and Ågren.²² They showed that the donor–acceptor substituted cumulenes containing aromatic molecules have large TPA cross sections, which are quantitatively comparable to those TPA dyes studied by Kogej et al.¹⁴

Experimentally, Reinhardt et al.²³ synthesized a series of TPA dyes, both donor–bridge–acceptor and donor–acceptor–acceptor–donor types, and observed that some of the dyes they organically synthesized have TPA cross sections that are orders of magnitude higher than the commercially available organic dyes. Recently, Prasad and co-workers showed that the multi-branched structure significantly increases the TPA cross section in comparison to the one-branched counterparts.²⁴ The effect of the electronic coupling between different branches was studied by Macak et al. by using the ab initio response theory.²⁵

Nevertheless, there does not exist any systematic theoretical study on the TPA process of planar octupolar molecules, even though the nonlinear optical (NLO) properties of octupolar molecules have been studied extensively over the past decade due to their potential applications as NLO materials replacing the conventional push–pull polyene-type NLO organic molecules. Particularly, the NLO properties of octupolar molecules have been extensively studied by Zyss and co-workers,^{26–30} and they showed that due to the zero permanent dipole moment in the ground electronic state, a new crystal engineering principle can be applied to produce novel NLO materials with large first hyperpolarizability.³¹ Furthermore, they showed that the optimization of the octupolar field can also be a useful direction to maximally use the NLO properties of those octupolar molecules.³² Particularly, it is interesting that the second-harmonic

response of the ordered octupolar material does not depend on the polarization of the incident field. Recently, the structure–NLO-property relationship of a few series of octupolar molecules, for example, triphenylmethane dyes and so forth, were investigated by Lee et al.,³³ and there it was shown that the first hyperpolarizability of an octupolar molecule monotonically increases as the donor and acceptor strengths increase. This trend is in strong contrast with that of the push–pull type of NLO molecules. In this article, we apply the same valence-bond three-charge-transfer (VB-3CT) model,^{33,34} which was used to describe the NLO properties of octupolar molecules, to the description of the TPA of octupolar molecules. Also, for four distinctive series of octupolar molecules, the ab initio calculations of the TPA transition amplitude will be presented, and the quantitative relationship between the TPA cross section and the first hyperpolarizability of the octupolar molecule will be discussed. Thus, the main goals of this paper, in summary, are (1) to show that a novel class of dyes, having C_3 symmetry, can be an alternative candidate for large TPA molecules, (2) to establish the structure–TPA-property relationship of octupolar molecules, (3) to confirm the predicted linear relationship between TPA cross section and first hyperpolarizability of the octupolar molecules on the basis of the effective four-state model, and (4) to show that there are good correlations between the NLO and TPA properties of octupolar molecules and the Brown–Okamoto constants of donors.

In section 2, the VB-3CT model description of TPA cross section of octupolar molecule is presented. Ab initio calculation results of TPA and NLO properties of four representative series of octupolar molecules are presented in section 3. The correlation between the TPA cross section and first hyperpolarizability of the octupolar molecule is discussed in section 4. Hammett correlation analyses of the TPA and NLO properties are given in section 5, and finally the main results are summarized in section 6.

2. TPA Transition Amplitude Calculated by Using the VB-3CT Model

For a single-beam TPA cross section measurement, the second-order tensorial TPA transition matrix element, $\tilde{\Gamma}_{fg}$, between the ground and TPA states, denoted as $|g\rangle$ and $|f\rangle$, respectively, is given as^{35,36}

$$[\tilde{\Gamma}_{fg}]_{\alpha\beta} = 2\hbar \sum_i \left(\frac{M_{fi}^\alpha M_{ig}^\beta}{E_{fi} - E_{i,g}} + \frac{M_{fi}^\beta M_{ig}^\alpha}{E_{fi} - E_{i,g}} \right) \quad (1)$$

The transition dipole vector is denoted as $\mathbf{M}_{i,g} (= \langle i | \hat{\mu} | g \rangle)$, where $\hat{\mu}$ is the electric dipole operator. $E_{i,g} \equiv E_i - E_g$ and $E_{f,i} \equiv E_f - E_i$. The summation in eq 1 should be performed over all electronic states including the ground and TPA states. The TPA cross section is proportional to the absolute square of the TPA transition matrix element $\tilde{\Gamma}_{fg}$. For the sake of comparison with experiment, the orientationally averaged TPA probability will

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be used, which is defined as^{25,37}

$$\delta = \sum_{\alpha,\beta} \{F[\tilde{\Gamma}_{fg}]_{\alpha\alpha}[\tilde{\Gamma}_{fg}]_{\beta\beta}^* + G[\tilde{\Gamma}_{fg}]_{\alpha\beta}[\tilde{\Gamma}_{fg}]_{\alpha\beta}^* + H[\tilde{\Gamma}_{fg}]_{\alpha\beta}[\tilde{\Gamma}_{fg}]_{\beta\alpha}\} \quad (2)$$

For linearly polarized lights, the three coefficients, F , G , and H , are equal to 2. Throughout this paper, we shall use the notation, $\delta^{(n)}$, representing the δ -value calculated by considering only n electronically excited states in the summation of $[\tilde{\Gamma}_{fg}]_{\alpha\beta}$.

We first calculate $\tilde{\Gamma}_{fg}$ by using the VB-3CT model Hamiltonian and briefly summarize the key aspects of the VB-3CT model. Although in ref 33 the VB-3CT model including the three BLA coordinates was discussed, in the present paper we shall focus on the electronic part of the VB-3CT model Hamiltonian to provide a simple picture on the relationship between molecular structure and electronic TPA property. Assuming that the electronic wave functions of the octupolar molecules can be approximately represented by the linear combinations of the four basis functions, for example, a single valence-bond (VB) configuration, $|\phi_{VB}\rangle$ and three charge-transfer (CT) configurations, $|\phi_{CT,j}\rangle$ for $j = 1,2,3$, the VB-3CT model Hamiltonian is given as³³

$$\begin{aligned} H = & |\phi_{VB}\rangle E_{VB} \langle\phi_{VB}| + \sum_{j=1,2,3} |\phi_{CT,j}\rangle E_{CT} \langle\phi_{CT,j}| \\ & - \sum_{j=1,2,3} \{|\phi_{VB}\rangle t \langle\phi_{CT,j}| + |\phi_{CT,j}\rangle t \langle\phi_{VB}|\} \\ & - \sum_{j=1,2,3} \sum_{k>j} \{|\phi_{CT,j}\rangle T \langle\phi_{CT,k}| + |\phi_{CT,k}\rangle T \langle\phi_{CT,j}|\} \quad (3) \end{aligned}$$

where the diagonal elements are the Coulombic energy of each configuration. t and T denote the transfer integrals between VB and CT configurations and between any two CT configurations, respectively. As shown in ref 34, the Hamiltonian (eq 3) can be diagonalized to find the four eigenvalues,

$$\begin{aligned} E_g &= \frac{1}{2}(E_{VB} + E_{CT} - 2T) - \frac{1}{2}[(V - 2T)^2 + 12t^2]^{1/2} \\ E_{e1} &= E_{e2} = E_{CT} + T \\ E_{e'} &= \frac{1}{2}(E_{VB} + E_{CT} - 2T) + \frac{1}{2}[(V - 2T)^2 + 12t^2]^{1/2} \quad (4) \end{aligned}$$

where $V \equiv E_{CT} - E_{VB}$. Note that the first excited state is 2-fold degenerate, and those two states are denoted as $|e1\rangle$ and $|e2\rangle$. An additional excited-state denoted as $|e'\rangle$ does not contribute to the TPA process between $|g\rangle$ and 2-fold degenerate excited states, since one-photon dipole transition from $|g\rangle$ to $|e'\rangle$ is not allowed due to the assumed D_{3h} symmetry. The corresponding eigenfunctions were found to be

$$\begin{aligned} |g\rangle &= (1 - 3l)^{1/2} |\phi_{VB}\rangle + l^{1/2} \sum_{j=1}^3 |\phi_{CT,j}\rangle, \\ |e1\rangle &= -2^{-1/2} (|\phi_{CT,1}\rangle - |\phi_{CT,3}\rangle), \\ |e2\rangle &= -\frac{1}{\sqrt{6}} (|\phi_{CT,1}\rangle - 2|\phi_{CT,2}\rangle + |\phi_{CT,3}\rangle) \end{aligned}$$

and

$$|e'\rangle = (1 - 3m)^{1/2} |\phi_{VB}\rangle - m^{1/2} \sum_{j=1}^3 |\phi_{CT,j}\rangle$$

where

$$l \equiv \frac{1}{6} - \frac{V - 2T}{6\sqrt{(V - 2T)^2 + 12t^2}}$$

and $m \equiv (1/3) - l$. As emphasized in ref 33, the magnitude of l represents the CT character of the ground state, that is to say, as l increases, the electronic structure of the ground state becomes close to the linear combination of the three CT configurations. Typically, for a variety of octupolar molecules with relatively strong donors and acceptors it was found that the range of l is around 0.15.³³ By using the above results with the usual assumptions, $\langle\phi_{VB}|\hat{\mu}|\phi_{VB}\rangle = 0$, $\langle\phi_{VB}|\hat{\mu}|\phi_{CT,j}\rangle = 0$, and $\langle\phi_{CT,j}|\hat{\mu}|\phi_{CT,k}\rangle = 0$ (for $j \neq k$), the transition dipole matrix elements and permanent dipole moments were found to be $\mathbf{M}_{g,e1} = -l^{1/2}\mu(\sqrt{3}/2\sqrt{2}, 3/2\sqrt{2}, 0)$, $\mathbf{M}_{g,e2} = 3l^{1/2}\mu(1/2\sqrt{2}, -1/2\sqrt{6}, 0)$, $\mathbf{M}_{e1,e2} = \mu(1/4, \sqrt{3}/4, 0)$, $\mathbf{M}_{e1,e1} = -\mu(\sqrt{3}/4, -1/4, 0)$, and $\mathbf{M}_{e2,e2} = \mu(\sqrt{3}/4, -1/4, 0)$ in the molecular coordinate system. The remaining transition dipoles are not presented here because they will not be used. Here, $\mathbf{M}_{g,e1}$ is, for instance, the transition dipole matrix element between $|g\rangle$ and $|e1\rangle$ and $\mathbf{M}_{e1,e1}$ denotes the permanent dipole moment of $|e1\rangle$ state. To obtain the above dipole moments, it should be noted that the three dipole vectors for $|\phi_{CT,1}\rangle$, $|\phi_{CT,2}\rangle$, and $|\phi_{CT,3}\rangle$ are $(0, \mu, 0)$, $(\sqrt{3}\mu/2, -\mu/2, 0)$, and $(-\sqrt{3}\mu/2, -\mu/2, 0)$, respectively. Here μ is the absolute magnitude of the dipole moment of a fictitious CT configuration, and μ should not be confused with the electric dipole operator $\hat{\mu}$. It should also be emphasized that the VB-3CT model is based on the assumption that μ is a constant for a given series of octupolar molecules regardless of the substituted donors or acceptors as long as the conjugated skeleton is the same. Note that the VB-3CT model satisfies all of the symmetry-required properties, such as orthogonality condition between $\mathbf{M}_{g,e1}$ and $\mathbf{M}_{g,e2}$ and globally vanishing dipole moment for the degenerate level, that is, $\mathbf{M}_{e1,e1} = -\mathbf{M}_{e2,e2}$.

Hereafter, we shall consider the case when the TPA state is the two-fold degenerate excited state, which is the strong one-photon-allowed state. Therefore, the beam frequency for the TPA is half of the transition frequency from $|g\rangle$ to $|e1\rangle$ (or $|e2\rangle$). Then, by taking the low-lying three-state ($|g\rangle$, $|e1\rangle$, and $|e2\rangle$) contributions to $\tilde{\Gamma}$ defined in eq 1, we have

$$\begin{aligned} [\tilde{\Gamma}^{(2)}]_{\alpha\beta} = & -\frac{2\hbar}{\Delta} \{M_{e1,e1}^\alpha M_{e1,g}^\beta + M_{e2,e2}^\alpha M_{e2,g}^\beta + M_{e2,e1}^\alpha M_{e1,g}^\beta + \\ & M_{e1,e2}^\alpha M_{e2,g}^\beta \\ & + M_{e1,e1}^\beta M_{e1,g}^\alpha + M_{e2,e2}^\beta M_{e2,g}^\alpha + M_{e2,e1}^\beta M_{e1,g}^\alpha + \\ & M_{e1,e2}^\beta M_{e2,g}^\alpha\} \quad (5) \end{aligned}$$

where the energy gap, Δ , is defined as

$$\Delta \equiv E_{e1} - E_g = \frac{1}{2}(V + 4T) + \frac{1}{2}[(V - 2T)^2 + 12t^2]^{1/2} \quad (6)$$

The superscript (2) in $\tilde{\Gamma}^{(2)}$ emphasizes that the TPA matrix element was approximately calculated by only taking into account the two electronically excited states. The energy level diagrams associated with the first four terms in eq 5 are shown

in Figure 1. Then, inserting the corresponding dipole matrix elements given above, we find that

$$\begin{aligned} [\tilde{\Gamma}_{VB-3CT}^{(2)}]_{xx} &= -[\tilde{\Gamma}_{VB-3CT}^{(2)}]_{yy} = -\frac{\sqrt{l}\mu^2}{\Delta} \left\{ \frac{3 + \sqrt{3}}{\sqrt{2}} \right\} \\ [\tilde{\Gamma}_{VB-3CT}^{(2)}]_{xy} &= [\tilde{\Gamma}_{VB-3CT}^{(2)}]_{yx} = \frac{\sqrt{l}\mu^2}{\Delta} \left\{ \frac{3 - \sqrt{3}}{\sqrt{2}} \right\} \end{aligned} \quad (7)$$

and all other tensor elements vanish. From eq 2, we have $\delta_{VB-3CT}^{(2)} = 48l\mu^4/\Delta^2$. On the basis of this result, eq 7, it is found that, as the ground-state CT-character l is increased by substituting strong donors and acceptors, the products of transition dipole matrix elements *monotonically increase*. Note that, as the donor and acceptor strengths increase in a given series of octupolar molecules, the energy gap between the ground and first excited state decreases.³³ Consequently, combining these two effects, *the overall TPA transition matrix element of the octupolar molecule will exhibit a monotonically increasing pattern with respect to the donor and acceptor strengths*. This will be confirmed by using the ab initio calculations of the TPA matrix elements for four representative series of octupolar molecules.

It is also interesting to note that the general trend of the TPA cross section with respect to the structural change of octupolar molecules is similar to that of the static first hyperpolarizability (β) of the octupolar molecules. As discussed in ref 34, the β -tensor within the three-state approximation was found to be

$$\beta_{ijk}^{(2)} = \frac{1}{\Delta} \sum_P \{ M_{g,e1}^i M_{e1,e2}^j M_{e2,g}^k + M_{g,e2}^i M_{e2,e1}^j M_{e1,g}^k + M_{g,e1}^i M_{e1,e1}^j M_{e1,g}^k + M_{g,e2}^i M_{e2,e2}^j M_{e2,g}^k \} \quad (8)$$

where \sum_P represents a sum over the six permutations of M^i , M^j , and M^k . Note that the sum-over-state expressions of the three-state-approximated $\beta^{(2)}$ and $\tilde{\Gamma}^{(2)}$, given in eqs 5 and 8, appear to be different from each other. Particularly, the nonzero β -tensor elements are, within the VB-3CT model,

$$[\beta_{VB-3CT}^{(2)}]_{yyy} = -[\beta_{VB-3CT}^{(2)}]_{yxx} = \frac{4.5l\mu^3}{\Delta^2} \quad (9)$$

Also, the modulus of β -tensor is found to be $||\beta_{VB-3CT}^{(2)}|| \equiv (\sum_{i,j,k} [\beta_{VB-3CT}^{(2)}]_{ijk}^2)^{1/2} = 2[\beta_{VB-3CT}^{(2)}]_{yyy}$. Therefore, as the ground-state charge-transfer character l increases, Δ decreases, and $||\beta||$ increases. Comparing the two expressions, $[\tilde{\Gamma}_{VB-3CT}^{(2)}]_{yy}$ and $[\beta_{VB-3CT}^{(2)}]_{yyy}$, given in eqs 7 and 9, we find that the two quantities are related to each other as

$$\mu[\beta_{VB-3CT}^{(2)}]_{yyy} \propto [\tilde{\Gamma}_{VB-3CT}^{(2)}]_{xx}^2 = [\tilde{\Gamma}_{VB-3CT}^{(2)}]_{yy}^2 \quad \text{or} \quad \delta_{VB-3CT}^{(2)} \propto \mu ||\beta_{VB-3CT}^{(2)}|| \quad (10)$$

Again, by noting that μ is assumed to be a constant for a given series of octupolar molecules regardless of the substituted donors (or acceptors), eq 10 suggests that *the first hyperpolarizability of the octupolar molecule is linearly proportional to the TPA cross section*—a similar linear relationship between β and TPA cross section was found in refs 14 and 25b for push-pull polyenes. Nevertheless it should be emphasized that the linear proportionality relationship given in eq 10 should not be applied to all NLO molecules, and in fact it is valid only for those planar octupolar molecules that are merely different from one another by the substituted donors or acceptors. On the basis of this

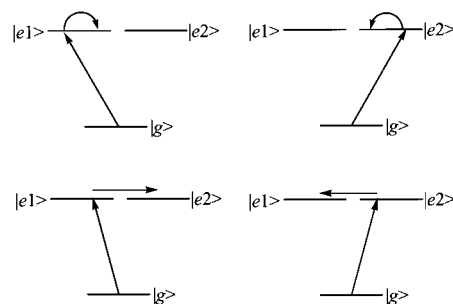


Figure 1. Energy-level diagrams associated with four optical transition pathways are shown. The doubly degenerate excited states are denoted as $|e1\rangle$ and $|e2\rangle$.

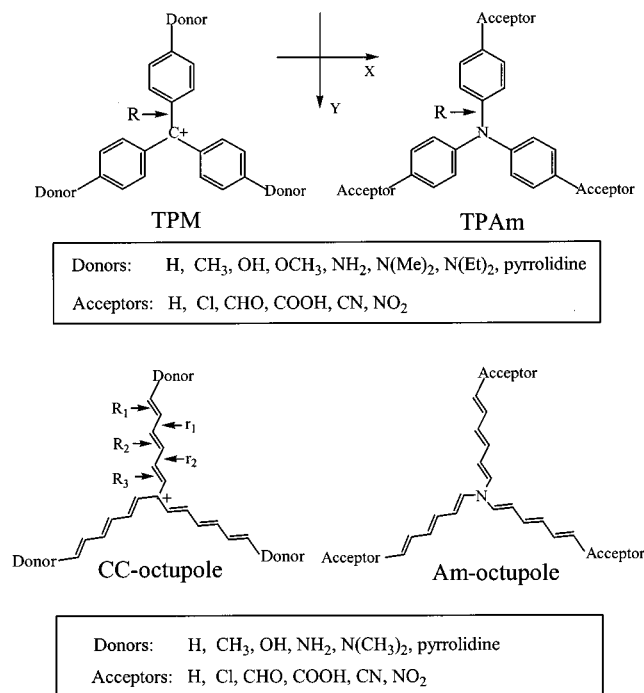


Figure 2. Four different octupolar molecules, TPM (triphenylmethane) dyes, TPAm (triphenylamine) derivatives, CC(carbocation)-octupolar molecules, and Am(amine)-octupolar molecules are shown.

relationship, once $||\beta||$ value are measured for a series of octupolar molecules, it is possible to predict which one of them should have the largest TPA cross section, when the TP absorption is achieved by the electromagnetic field of which frequency is half of the transition frequency between the ground and first excited electronic state. Thus, it is believed that the relationship, eq 10, can be a useful guideline for the development of a new strategy for organic synthesis of large NLO and TPA dyes. The linear relationship, eq 10, motivates us to carry out a series of ab initio calculations presented in the following section.

3. Calculation of the Two-photon Absorption Matrix Elements of Four Series of Prototype Octupolar Molecules

The molecular structures of the triphenylmethane (TPM) dyes and triphenylamine (TPAm) derivatives are shown in Figure 2. Also two other types of octupolar molecules having simple conjugated polyene bridges will be considered in detail. Note that the central carbocation in the TPM dyes and the nitrogen atom in the TPAm compounds act like the central acceptor and the central donor, respectively. Three peripheral donors (ac-

Table 1. Ab Initio (HF/SCI 6-31G) Calculation Results of the Four Types of Octupolar Molecules^a

TPM					TPAm				
donor	<i>R</i> (Å)	$\delta^{(2)}$	$\delta^{(10)}$	$ \beta ^*(10^{-29} \text{ esu})$	acceptor	<i>R</i> (Å)	$\delta^{(2)}$	$\delta^{(10)}$	$ \beta (10^{-29} \text{ esu})$
-H	1.44934	8500	8670	2.69 (1.88)	-H	1.42176	740	2540	0.53
-CH ₃	1.44720	17600	18000	4.47 (3.65)	-CN	1.41933	3190	4190	1.38
-OH	1.44504	23500	22900	4.89 (4.06)	-COOH	1.41883	6670	6970	1.99
-OCH ₃	1.44462	31500	31000	6.27 (4.37)	-COOCH ₃	1.41903	7890	8160	2.07
-NH ₂	1.44215	35500	35300	7.87 (8.16)	-NO ₂	1.41827	9050	9490	2.45
-N(Me) ₂	1.44161	59800	59200	12.49 (12.7)					
-N(Et) ₂	1.44097	69800	69400	15.05 (15.1)					
-pyrrolidine	1.44130	69000	68300	14.90 (11.5)					

CC-Octupole					Am-Octupole				
donor	BLA (Å)	$\delta^{(2)}$	$\delta^{(20)}$	$ \beta (10^{-29} \text{ esu})$	acceptor	BLA (Å)	$\delta^{(2)}$	$\delta^{(20)}$	$ \beta (10^{-29} \text{ esu})$
-H	-0.09799	169000	132000	24.0	-H	-0.12421	21800	11200	3.38
-CH ₃	-0.09182	223000	178000	32.1	-CN	-0.11607	41100	24900	6.86
-NH ₂	-0.06859	347000	286000	47.0	-CHO	-0.11570	53000	46900	8.17
-N(Me) ₂	-0.06169	483000	408000	67.1	-COOH	-0.11586	62000	43900	7.97
-N(Et) ₂	-0.06169	535000	457000	75.0	-NO ₂	-0.11443	69900	49100	10.48
-pyrrolidine	-0.06027	512000	431000	76.5					

^a The dimension of δ is D^4/eV^2 . The values inside the parentheses are the three-state-approximated sum-over-state results calculated by using the permanent and transition dipole moments obtained with HF/SCI 6-31G method.

ceptors) are connected to the central acceptor (donor) by a phenyl bridge. In ref 33, the first hyperpolarizabilities of the series of TPM dyes were calculated by using the semiempirical AM1 Hamiltonian. It was found that β_{yyy} monotonically increases as the donor strength increases, which is in good agreement with the VB-3CT model prediction. In this contribution, all calculations will be performed by using the Gaussian 98 program³⁸ with 6-31G basis set at the HF/SCI level.³⁹

To calculate the TPA matrix element, one has to sum over all intermediate states (see eq 1). In this paper, we shall consider 10 or 20 excited electronic states to calculate the sum-over-state TPA matrix element. Also, we shall consider the three-state approximated TPA probability, $\delta^{(2)}$. Since the first excited electronic states are 2-fold degenerate in the case of octupolar molecules and typically the oscillator strengths of these states are much larger than those of any other states, the TPA probability, $\delta^{(2)}$, calculated by only considering the three states ($|g\rangle$, $|e1\rangle$, and $|e2\rangle$) can be a useful measure of the TPA matrix element.

The ab initio TPA probabilities, $\delta^{(n)}$, of the four series of octupolar molecules are listed in Table 1. Note that the three-state approximated $\delta^{(2)}$ -values quantitatively close to $\delta^{(20)}$ (or $\delta^{(10)}$), which means that the TPA cross sections of the octupolar molecules considered in this paper are mainly determined by the doubly degenerate first excited states. As was predicted by

the VB-3CT model, $\delta^{(n)}$ is a monotonically increasing function of the donor and acceptor strengths. Since the bond-length-alternation coordinate is not a suitable value representing the CT character of the TPM and TPAm molecules, the bond length *R* (see Figure 2) is chosen to approximately represent the CT character - note that, if the donor (or acceptor) strength of TPM (or TPAm) molecule increases, the bond length *R* decreases. For the two series of molecules, CC(carbocation)-octupoles and Am(amine)-octupoles in Figure 2, the BLA value is defined as $BLA = (1/3)\sum_{j=1}^3 R_j - (1/2)\sum_{j=1}^2 r_j$ (see definitions of R_j and r_j). In Figure 3, the $\delta^{(10)}$ values of the TPM and TPAm molecules and the $\delta^{(20)}$ values of the CC- and Am-octupolar molecules are plotted with respect to *R* and BLA, respectively. Indeed, the general increasing patterns with respect to the donor and acceptor strengths are manifest, even though there exist a few data points slightly deviated from a smooth curve. Also, we found that the partial Mulliken charge of the central carbon of TPM and CC-octupole (the central nitrogen atom of TPA or Am-octupole) is a measure of the charge transfer from (to) the peripheral donors (acceptors) to the central acceptor (donor). The correlation between the partial charge of the central acceptor (donor) and δ was found to be excellent (the corresponding figures are not shown in this paper).

Although, in this section, the electronic contribution to the TPA cross section was only considered, one should note that the vibronic contribution was shown to be sizable for the multibranch charge transfer systems as shown by Macak, Luo, Norman, and Agren in ref 25. They considered a series of the multibranch molecules that were experimentally studied by Prasad and co-workers.²⁴ As the number of branches increases, Chung et al. found that the TPA cross section is enhanced and they suggested that this enhancement is mainly due to the electronic coupling between different branches.²⁴ On the basis of the theoretical investigation by Macak et al.,²⁵ the vibronic contribution to the TPA cross section plays a crucial role in that respect. Thus, for the octupolar molecules considered in this paper, the vibronic contribution might not be negligibly small. In Appendix, we present a theoretical description of the vibronic contribution to the TPA transition amplitude by including three BLA coordinates into the VB-3CT model Hamiltonian discussed in ref 33c. It is hoped that this additional aspect will be clarified by using ab initio response theory in near future.

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(39) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135. Although the 6-31G basis set does not include diffuse functions so that the absolute values of the calculated excited state properties may not be quantitatively reliable than those with diffuse functions. However, based on the comparative studies on the TPA of relatively large linear quadrupolar molecules in ref 11 above, it was found that the HF/SCI/6-31G calculation is acceptable in studying the general trend. Furthermore, it is computationally expensive to carry out the calculation with 6-31+G(d) basis set for the series of molecules considered in the present article.

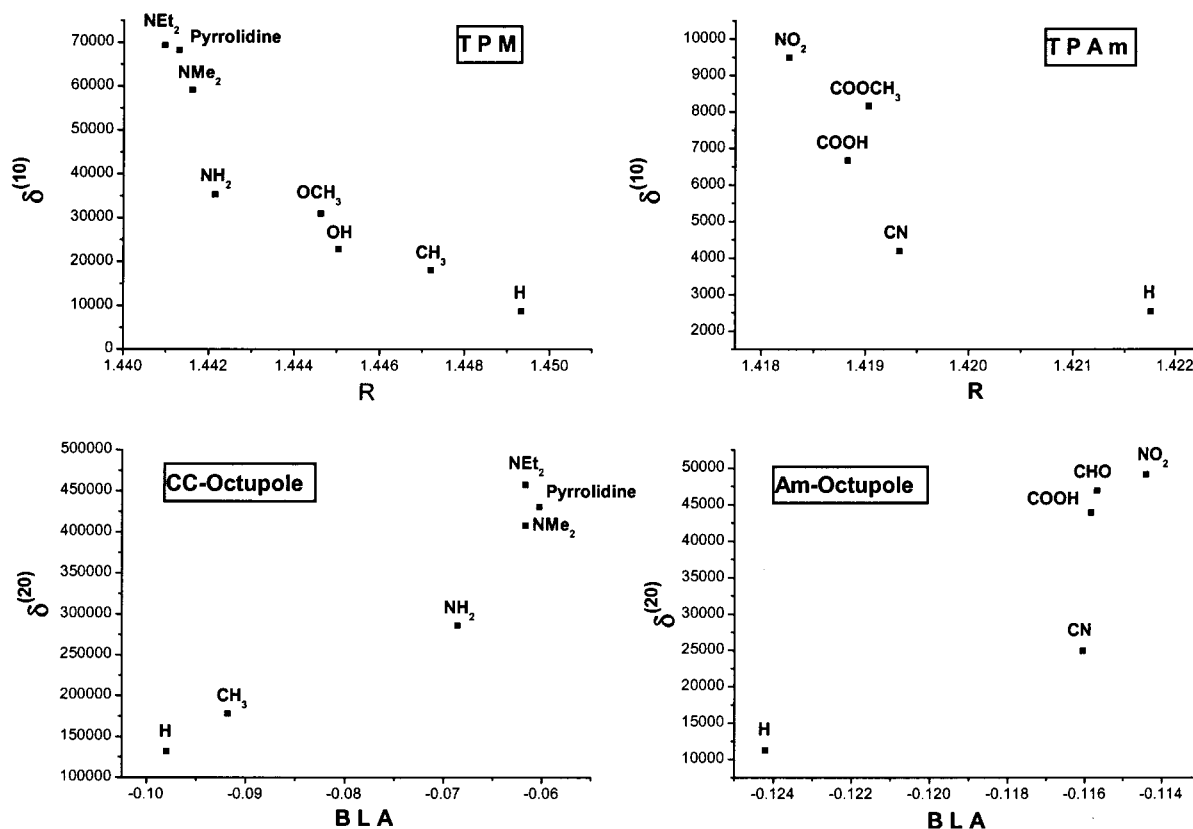


Figure 3. Ab initio calculated TPA probability, $\delta^{(n)}$, is plotted with respect to R (for TPM and TPAM derivatives) or to BLA (for CC- and Am-octupolar molecules).

3.A. Calculation of the TPA Spectrum of Crystal Violet.

Although the TPA transition matrix element between the ground and doubly degenerate excited state was calculated by using HF/SCI method, it is necessary to quantitatively determine the TPA cross section in the conventional unit, that is, $\text{cm}^4/\text{s/photon}$. Then, one can make a direct quantitative comparison between the TPA cross sections of the octupolar molecules considered in this paper with those of previously reported TPA chromophores. We shall consider the crystal violet in detail in this subsection.

The TPA spectrum can be calculated by using the following equation,²⁵

$$\sigma(\omega) = \frac{4\pi^3 a_0^5 \alpha \omega^2 L^4 \hbar^2}{15c_0 \eta^2} \sum_f \delta_{fg}(\omega) \frac{\gamma_{fg}/\pi}{(2\omega - \omega_{fg})^2 + \gamma_{fg}^2} \quad (11)$$

where a_0 , α , c_0 , and η are the Bohr's radius, fine structure constant, speed of light, and refractive index of the solvent, respectively. The solvent is chosen to be CH_2Cl_2 and η of liquid CH_2Cl_2 is 1.424. The local field correction factor, L , is given as $L = 3\eta^2/(2\eta^2 + 1)$. In eq 11 the general frequency-dependent TP transition probability from $|g\rangle$ to $|f\rangle$ was denoted as $\delta_{fg}(\omega)$,

$$\delta_{fg}(\omega) = 2 \sum_{\alpha\beta} \{ \Gamma_{\alpha\alpha}(\omega) \Gamma_{\beta\beta}^*(\omega) + 2\Gamma_{\alpha\beta}(\omega) \Gamma_{\alpha\beta}^*(\omega) \} \quad (12)$$

where the frequency-dependent TP transition amplitude tensor, Γ , is given as

$$\Gamma_{\alpha\beta}(\omega) = \sum_i \left\{ \frac{\mu_{fi}^\alpha \mu_{ig}^\beta}{\hbar\omega - (E_i - E_g)} + \frac{\mu_{fi}^\beta \mu_{ig}^\alpha}{\hbar\omega - (E_i - E_g)} \right\} \quad (13)$$

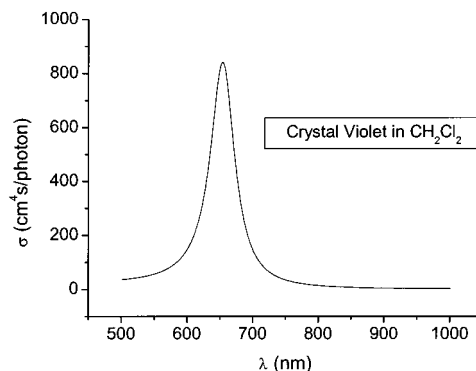


Figure 4. Calculated TPA spectrum of crystal violet in liquid CH_2Cl_2 . The TPA state is assumed to be the two-fold degenerate excited state, and the contributions from the other excited states are not included. The electronic energies and transition dipole moments are all calculated for an isolated crystal violet molecule in gas phase. Only the refractive index of liquid CH_2Cl_2 is used to simulate the crystal violet solution.

Note that eq 1 is a special case of eq 13, when $\omega = \{(E_f - E_g)\}/\{2\hbar\}$. The electronic dephasing constant of the $|f\rangle$ -state is γ_{fg} , and its magnitude is assumed to be 0.1 eV. Then, the unit of $\sigma(\omega)$ will become $10^{-50} \text{cm}^4 \text{s photon}^{-1}$, if cgs units are used for a_0 and c_0 and atomic units are used for $\sigma_{fg}(\omega)$, ω , \hbar , and γ_{fg} .

For the crystal violet molecule, TPM derivative with donor of $\text{N}(\text{Me})_2$, the TPA spectrum is calculated by considering two-fold degenerate excited state as the final state with 10 excited states as intermediate states and shown in Figure 4. The peak TPA cross section is at 654 nm, which is the half of the energy gap between the TPA and ground states, and the maximum value of the TPA cross section is $840 \times 10^{-50} \text{cm}^4 \text{s/photon}$. This value is quantitatively comparable with those linear quadrupolar

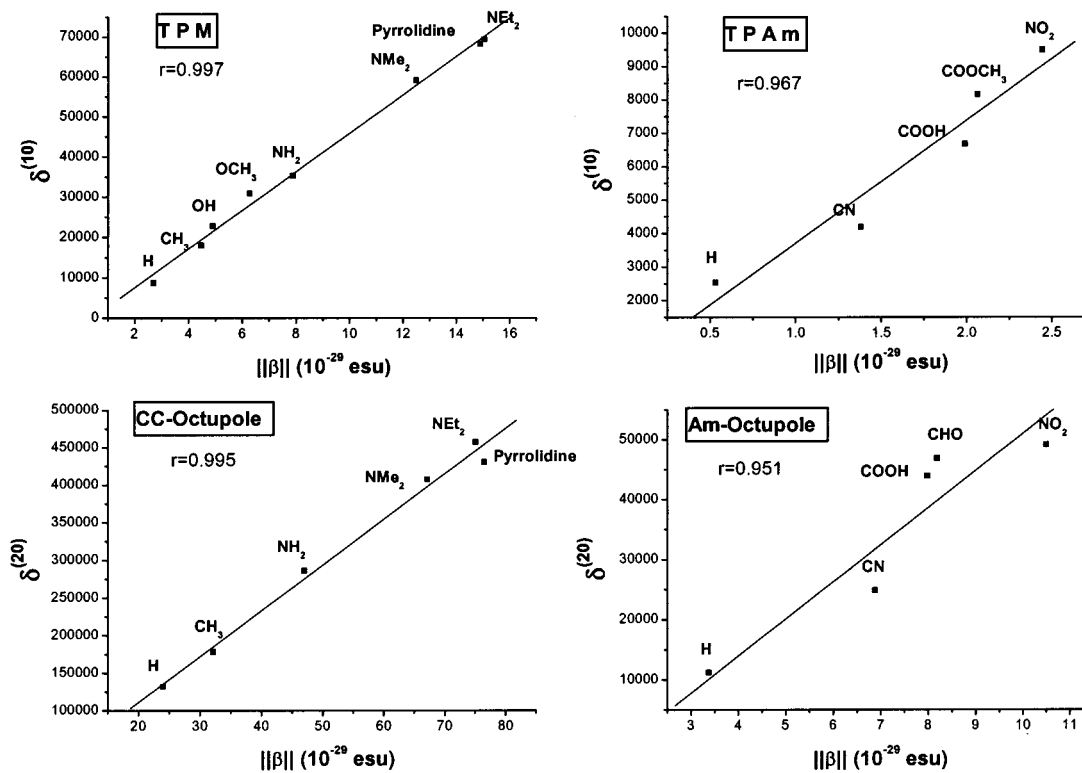


Figure 5. $\delta^{(n)}$ -values of the four series of octupolar molecules in Figure 2 are plotted with respect to $||\beta||$ values.

molecules considered in ref 10. Thus, the octupolar TPM molecules can be considered as possible TPA dyes with large TPA cross section. Currently, we have synthesized a number of extended octupolar molecules, measured TPA cross sections, and found that their cross sections are sizable. These experimental results will be presented elsewhere.

4. Comparison of the TPA Cross Section and First Hyperpolarizability

As discussed in section 2, the VB-3CT model predicted that the TPA probability is linearly proportional to the first hyperpolarizability (compare eqs 7 with 9). To confirm this relationship, we calculated the $||\beta||$ tensor elements of the four octupoles in Figure 2 by using the finite-field method and the results are presented in Table 1. To quantitatively test whether the HF/SCI calculation results of the transition and permanent dipole moments are acceptable, we carried out the three-state sum-over-state calculation of $||\beta||$ values for the TPM series (see Table 1). The agreement between the finite-field and three-state-approximated SOS calculation is acceptable. In Figure 5, δ vs $||\beta||$ is plotted. It is indeed found that these two quantities are linearly related to each other.

In this regard, it should be mentioned that the TPA cross section is related to the imaginary part of the molecular third-order susceptibility at finite frequency.^{14,40} On the other hand, the static first hyperpolarizability is the molecular second-order susceptibility at the zero frequency limit. Therefore, there is no obvious reason these two properties, the static *second-order* susceptibility and imaginary part of the finite-frequency *third-order* susceptibility, are linearly related to each other. However, note that δ and $||\beta||$ both are strongly dependent on the charge transfer extent of a given octupolar molecule. Furthermore, the dependencies of the transition dipole moments on the charge-

transfer character in the ground electronic state are, within the VB-3CT model, commonly found in the expressions of δ and β (compare eq 7 with 9). Combining these observations with the VB-3CT model, the linear relationship between δ and β could be qualitatively understood.

5. Hammett Correlation Analyses of the TPA Cross Section and First Hyperpolarizability of Octupolar Molecule

Although, for various conjugated polyene compounds, the bond-length-alternation (or bond-order-alternation) concept has been found to be quite useful in describing the equilibrium structure of the ground electronic state, it may not be a useful parameter representing the CT character of the TPM derivatives having a common bridge, that is, benzene ring. Therefore, an alternative quantity representing the electron-donating ability of a given chemical group is required, and in this regard the Hammett constant should be the candidate. Depending on the chemical or physical processes, various sets of constants for electron donors and acceptors were presented and used to test the validity of the linear free energy approximation originally proposed by Hammett.⁴¹ Although there already exist several works on the Hammett analysis of the NLO properties of *linear push-pull polyenes*,⁴²⁻⁴⁵ the same analysis for a series of octupolar molecules was not discussed before. Furthermore, the Hammett correlation analysis of the TPA cross section was never been discussed before. In this section, we shall use the Brown-Okamoto (σ^+) constant⁴⁶ for the analysis of the TPA cross

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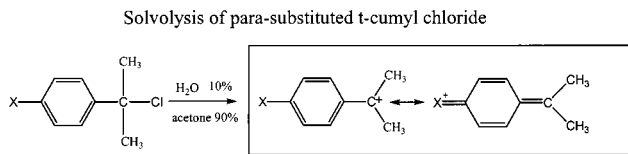


Figure 6. Solvolysis of para-substituted *tert*-cumyl chlorides was used to determine the Brown–Okamoto constant σ^+ of the substituent.

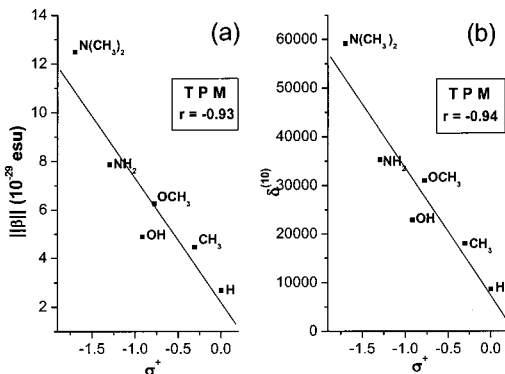


Figure 7. (a) $\|\beta\|$ and (b) $\delta^{(10)}$ values of the TPM derivatives are plotted with respect to the Brown–Okamoto constant, σ^+ .

section and the first hyperpolarizability of octupolar molecules with respect to the electron-donors. As well-known σ^+ -values were obtained by applying the linear-free-energy approximation to the solvolysis of para-substituted *t*-cumyl chlorides as shown in Figure 6.⁴⁶ Here it should be noted that the solvolysis of the *tert*-cumyl chloride involves a carbocation resonantly stabilized by the para-substituted benzene. Similarly, the σ^+ is likely to be a suitable choice for the Hammett correlation analysis for the TPM molecules having a central carbocation.

In Figure 7, a and b, the plots of $\|\beta\|$ vs σ^+ and $\delta^{(10)}$ vs σ^+ for the TPM dyes are shown. The correlation is found to be excellent. Therefore, the statement that the TPA cross section and the first hyperpolarizability are increasing functions of the electron-donating abilities of the substituted group is again proven to be valid.

6. Summary

In this paper, the TPA and NLO properties of octupolar molecules were investigated by using the VB-3CT model and ab initio calculation methods. On the basis of the VB-3CT model calculation of TPA cross section, we found that (1) the TPA cross section increases as the strength of the donor or acceptor increases and (2) the TPA cross section is linearly proportional to the first hyperpolarizability. These predictions were confirmed by carrying out the HF/SCI ab initio calculation. Also, the Hammett correlation analyses for the TPM molecules were performed and it was found that the Brown–Okamoto constants are linearly proportional to the TPA cross sections as well as the first hyperpolarizabilities, respectively. Currently, for a number of extended octupolar molecules, various experimental measurements of TPA cross section and NLO properties are under investigation to test the theoretical results discussed in this paper.

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Appendix

In this appendix, we present a theoretical description of the vibronic contribution to the TPA transition amplitude by using the generalized VB-3CT model including three BLA coordinates. As discussed in ref 33c, the vibrational properties and vibrational hyperpolarizability of a C_3 -symmetric octupolar molecule can be effectively described by considering three BLA coordinates that are associated with each branch of a given octupolar molecule similar to those in Figure 2. First, we briefly summarize the theoretical model in ref 33(c) for the sake of completeness. The generalized Hamiltonian with three BLA coordinates, Q_j , is assumed to be given as

$$H = \begin{pmatrix} H_{VB} & -t & -t & -t \\ -t & H_{CT1} & -T & -T \\ -t & -T & H_{CT2} & -T \\ -t & -T & -T & H_{CT3} \end{pmatrix} \quad (\text{A1})$$

where

$$\begin{aligned} H_{VB} &= E_{VB} + \sum_{i=1}^3 \frac{1}{2} k_0 (Q_i - Q_{i,VB}^0)^2 - \sum_{i=1}^3 \sum_{j=i+1}^3 k' Q_i Q_j \\ H_{CT1} &= E_{CT} + \sum_{i=1}^3 \frac{1}{2} k_0 (Q_i - Q_{i,CT1}^0)^2 - \sum_{i=1}^3 \sum_{j=i+1}^3 k' Q_i Q_j \\ H_{CT2} &= E_{CT} + \sum_{i=1}^3 \frac{1}{2} k_0 (Q_i - Q_{i,CT2}^0)^2 - \sum_{i=1}^3 \sum_{j=i+1}^3 k' Q_i Q_j \\ H_{CT3} &= E_{CT} + \sum_{i=1}^3 \frac{1}{2} k_0 (Q_i - Q_{i,CT3}^0)^2 - \sum_{i=1}^3 \sum_{j=i+1}^3 k' Q_i Q_j \end{aligned} \quad (\text{A2})$$

k_0 is the force constant of the bond-length-alternation vibration of an isolated polyene, and it was estimated to be 33.55 eV/Å². The electronic part of the Hamiltonian was only considered in the main text (see eq 3). The mode-coupling force constant is denoted as k' . The equilibrium BLA coordinates for the VB configuration are $Q_{1,VB}^0 = Q_{2,VB}^0 = Q_{3,VB}^0 = -0.12$ Å. Those of the CT configurations are $Q_{1,CT1}^0 = 0.12$ Å, $Q_{2,CT1}^0 = Q_{3,CT1}^0 = -0.12$ Å, $Q_{2,CT2}^0 = 0.12$ Å, $Q_{1,CT2}^0 = Q_{3,CT2}^0 = -0.12$ Å, $Q_{3,CT3}^0 = 0.12$ Å, and $Q_{1,CT3}^0 = Q_{2,CT3}^0 = -0.12$ Å, respectively. Note that these equilibrium BLA values are associated with those of the isolated chain.

Then, after carrying out the normal-mode analysis, the diagonal elements in eq A1 can be rewritten as

$$\begin{aligned} H_{VB} &= E_{VB} + \frac{1}{2} k_s (q_s - q_{s,VB}^0)^2 + \frac{1}{2} k_A (q_{A1} - q_{A1,VB}^0)^2 + \\ &\quad \frac{1}{2} k_A (q_{A2} - q_{A2,VB}^0)^2 \\ H_{CT1} &= E_{CT} + \frac{1}{2} k_s (q_s - q_{s,CT}^0)^2 + \frac{1}{2} k_A (q_{A1} - q_{A1,CT1}^0)^2 + \\ &\quad \frac{1}{2} k_A (q_{A2} - q_{A2,CT1}^0)^2 \\ H_{CT2} &= E_{CT} + \frac{1}{2} k_s (q_s - q_{s,CT}^0)^2 + \frac{1}{2} k_A (q_{A1} - q_{A1,CT2}^0)^2 + \\ &\quad \frac{1}{2} k_A (q_{A2} - q_{A2,CT2}^0)^2 \end{aligned}$$

$$H_{CT3} = E_{CT} + \frac{1}{2}k_S(q_S - q_{S,CT}^0)^2 + \frac{1}{2}k_A(q_{A1} - q_{A1,CT3}^0)^2 + \frac{1}{2}k_A(q_{A2} - q_{A2,CT3}^0)^2 \quad (\text{A3})$$

The three normal modes, one totally symmetric stretching mode (q_S) and two-fold degenerate asymmetric stretching modes (q_{A1} and q_{A2}), are $q_S = (Q_1 + Q_2 + Q_3)/\sqrt{3}$, $q_{A1} = (-Q_1 + Q_3)/\sqrt{2}$, and $q_{A2} = (-Q_1 + 2Q_2 - Q_3)/\sqrt{6}$. The corresponding force constants are $k_S = k_0 - 2k'$ and $k_A = k_{A1} = k_{A2} = k_0 + k'$, respectively. Due to the symmetry, we define $q_{S,CT}^0 \equiv q_{S,CT1}^0 = q_{S,CT2}^0 = q_{S,CT3}^0$, and the equilibrium values of $q_{S,m}^0$, $q_{A1,m}^0$, and $q_{A2,m}^0$, are, for $m = VB, CT1, CT2$, and $CT3$,

$$\begin{aligned} q_{S,m}^0 &= \frac{k_0}{\sqrt{3}k_S} (Q_{1,m}^0 + Q_{2,m}^0 + Q_{3,m}^0) \\ q_{A1,m}^0 &= \frac{k_0}{\sqrt{2}k_A} (-Q_{1,m}^0 + Q_{3,m}^0) \\ q_{A2,m}^0 &= \frac{k_0}{\sqrt{6}k_A} (-Q_{1,m}^0 + 2Q_{2,m}^0 - Q_{3,m}^0) \end{aligned} \quad (\text{A4})$$

Then, to calculate various quantities using the model Hamiltonian (eq A3) with eq A1, it is convenient to divide eq 1 into two parts as

$$H = H_0 + H' \quad (\text{A5})$$

where

$$H' = \begin{pmatrix} 0 & 0 & 0 & 0 \\ -k_A & q_{A1,CT1}^0 q_{A1} + q_{A2,CT1}^0 q_{A2} & 0 & 0 \\ 0 & 0 & q_{A1,CT2}^0 q_{A1} + q_{A2,CT2}^0 q_{A2} & 0 \\ 0 & 0 & 0 & q_{A1,CT3}^0 q_{A1} + q_{A2,CT3}^0 q_{A2} \end{pmatrix} \quad (\text{A6})$$

The zero-order Hamiltonian, H_0 , is the remaining part of eq A1 with A3. The eigenstates of H_0 are found to be

$$\begin{aligned} |g\rangle &= (1 - 3l)^{1/2} |\phi_{VB}\rangle + l^{1/2} \sum_{j=1}^3 |\phi_{CT,j}\rangle \\ |e1\rangle &= -2^{-1/2} (|\phi_{CT,1}\rangle - |\phi_{CT,3}\rangle) \\ |e2\rangle &= -\frac{1}{\sqrt{6}} (|\phi_{CT,1}\rangle - 2|\phi_{CT,2}\rangle + |\phi_{CT,3}\rangle) \end{aligned} \quad (\text{A7})$$

Although the results given above are identical to the case when only the electronic part of the Hamiltonian (eq A1) was considered, the CT character, l , is now dependent on the totally symmetric normal coordinate q_S as

$$l(q_S) \equiv \frac{1}{6} - \frac{V(q_S) - 2T}{6\sqrt{(V(q_S) - 2T)^2 + 12t^2}} \quad (\text{A8})$$

where

$$V(q_S) = E_{CT} - E_{VB} - k_S(q_{S,CT}^0 - q_{S,VB}^0)q_S + C \quad (\text{A9})$$

with

$$\begin{aligned} C &\equiv \frac{1}{2}k_A(q_{A1,CT1}^0)^2 + \frac{1}{2}k_A(q_{A2,CT1}^0)^2 = \\ &\quad \frac{1}{2}k_A(q_{A1,CT2}^0)^2 + \frac{1}{2}k_A(q_{A2,CT2}^0)^2 \\ &= \frac{1}{2}k_A(q_{A1,CT3}^0)^2 + \frac{1}{2}k_A(q_{A2,CT3}^0)^2 \end{aligned}$$

The eigenvalues of the zero-order Hamiltonian, H_0 , are

$$\begin{aligned} E_g &= \frac{1}{2}(U - 2T) - \frac{1}{2}[(V - 2T)^2 + 12t^2]^{1/2} \\ E_{e1} = E_{e2} &= E_{CT} + \frac{1}{2}k_S(q_S - q_{S,CT}^0)^2 + \frac{1}{2}k_A(q_{A1}^2 + q_{A2}^2) + C + T \\ E_f &= \frac{1}{2}(U - 2T) + \frac{1}{2}[(V - 2T)^2 + 12t^2]^{1/2} \end{aligned} \quad (\text{A10})$$

where

$$\begin{aligned} U(q_S) &= E_{CT} + E_{VB} + \frac{1}{2}k_S[(q_S - q_{S,VB}^0)^2 + (q_S - q_{S,CT}^0)^2] + \\ &\quad k_A(q_{A1}^2 + q_{A2}^2) + C \end{aligned} \quad (\text{A11})$$

The transition and permanent dipole moments can be calculated by using the zero-order eigenstates, $\mathbf{M}_{g,e1} = -l^{1/2}\mu(\sqrt{3}/2\sqrt{2}, 3/2\sqrt{2}, 0)$, $\mathbf{M}_{g,e2} = 3l^{1/2}\mu(1/2\sqrt{2}, -1/2\sqrt{6}, 0)$, $\mathbf{M}_{e1,e2} = \mu(1/4, \sqrt{3}/4, 0)$, $\mathbf{M}_{e1,e1} = -\mu(\sqrt{3}/4, -1/4, 0)$, and $\mathbf{M}_{e2,e2} = \mu(\sqrt{3}/4, -1/4, 0)$. Here, it should be emphasized that the transition dipole moments, $\mathbf{M}_{g,e1}$ and $\mathbf{M}_{g,e2}$, are functions of the symmetric normal coordinate, since l depends on q_S (see eq A8).

Now, let us consider the vibronic contributions to the TPA transition amplitude. In section 2, we assumed that, since the electronic contribution was only considered, the TP-absorbing transition does not involve any vibrational transition. However, as emphasized by Macak et al. in ref 25, the vibronic contribution to the TPA transition amplitude is sizable for the octupolar molecules. Thus, by Taylor expanding the TPA transition matrix element given in eq 1 and by assuming that only the three normal coordinates are strongly vibronically coupled to the TPA process, we have

$$\begin{aligned} \tilde{\Gamma}_{fg} &\cong \tilde{\Gamma}_{fg}^0 \delta_{v_S,0} \delta_{v_{A1},0} \delta_{v_{A2},0} + \tilde{\Gamma}_{fg}^{vib,S} \delta_{v_S,1} \delta_{v_{A1},0} \delta_{v_{A2},0} \\ &+ \tilde{\Gamma}_{fg}^{vib,A1} \delta_{v_S,0} \delta_{v_{A1},1} \delta_{v_{A2},0} + \tilde{\Gamma}_{fg}^{vib,A2} \delta_{v_S,0} \delta_{v_{A1},0} \delta_{v_{A2},1} \end{aligned} \quad (\text{A12})$$

where

$$\begin{aligned} \tilde{\Gamma}_{fg}^{vib,S} &\equiv \left(\frac{\partial \tilde{\Gamma}_{fg}}{\partial q_S} \right)_0 \sqrt{\frac{\hbar}{2m_S \omega_S}} \\ \tilde{\Gamma}_{fg}^{vib,A1} &\equiv \left(\frac{\partial \tilde{\Gamma}_{fg}}{\partial q_{A1}} \right)_0 \sqrt{\frac{\hbar}{2m_{A1} \omega_{A1}}} \\ \tilde{\Gamma}_{fg}^{vib,A2} &\equiv \left(\frac{\partial \tilde{\Gamma}_{fg}}{\partial q_{A2}} \right)_0 \sqrt{\frac{\hbar}{2m_{A2} \omega_{A2}}} \end{aligned} \quad (\text{A13})$$

In eq A12, v_j is the vibrational quantum number of the TPA final state, and the reduced mass and frequency of each oscillator are denoted as m_j and ω_j , respectively. For the actual calculation

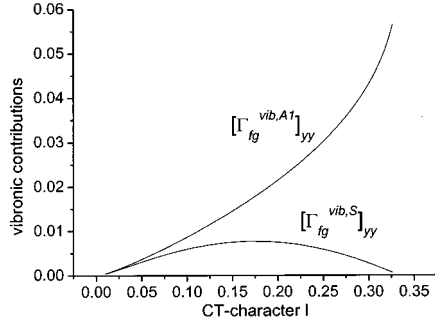


Figure 8. $[y,y]$ -tensor elements of the vibronic contributions to the TPA transition amplitude, $[\tilde{\Gamma}_{fg}^{vib,S}]_{yy}$ and $[\tilde{\Gamma}_{fg}^{vib,A1}]_{yy}$, are plotted.

of the TPA spectrum by using eq 15, the summation in eq 15 should also involve the vibrational quantum states on the TPA excited-state manifold.

Now, the remaining calculation is to obtain the first-order expansion coefficients in eq A13. By following the same procedure discussed in ref 33c, the three expansion coefficients are found to be

$$\begin{aligned} \left(\frac{\partial \tilde{\Gamma}_{fg}}{\partial q_S}\right)_0 &= (a_1 + a_2)(\mathbf{M}_{e1,e2} \otimes \mathbf{M}_{e2,g} + \mathbf{M}_{e1,e1} \otimes \mathbf{M}_{e1,g}) \\ \left(\frac{\partial \tilde{\Gamma}_{fg}}{\partial q_{A1}}\right)_0 &= b_1(\mathbf{M}_{e1,e2} \otimes \mathbf{M}_{e2,e1} + \mathbf{M}_{e1,e1} \otimes \mathbf{M}_{e1,e1}) \\ &\quad + b_2(\mathbf{M}_{e1,e2} \otimes \mathbf{M}_{e2,e2} + \mathbf{M}_{e1,e1} \otimes \mathbf{M}_{e1,e2}) \\ &\quad + b_3(\mathbf{M}_{e1,e2} \otimes \mathbf{M}_{e1,g} + 3\mathbf{M}_{e1,e1} \otimes \mathbf{M}_{e2,g}) \\ \left(\frac{\partial \tilde{\Gamma}_{fg}}{\partial q_{A2}}\right)_0 &= c_1(\mathbf{M}_{e1,e2} \otimes \mathbf{M}_{e2,e1} + \mathbf{M}_{e1,e1} \otimes \mathbf{M}_{e1,e1}) \\ &\quad + c_2(\mathbf{M}_{e1,e2} \otimes \mathbf{M}_{e2,e2} + \mathbf{M}_{e1,e1} \otimes \mathbf{M}_{e1,e2}) \\ &\quad + c_3(\mathbf{M}_{e1,e2} \otimes \mathbf{M}_{e1,g} + 3\mathbf{M}_{e1,e1} \otimes \mathbf{M}_{e2,g}) \end{aligned} \quad (\text{A14})$$

where the auxiliary functions are defined as

$$\begin{aligned} a_1 &\equiv \frac{2\sqrt{2}\hbar k_S(q_{S,VB}^0 - q_{S,CT}^0)t^2}{t^{eq}[(V^{eq} - 2T)^2 + 12t^2]^{3/2}(E_{e1}^{eq} - E_g^{eq})} \\ a_2 &\equiv \frac{\sqrt{2}\hbar k_S(q_{S,VB}^0 - q_{S,CT}^0)}{(E_{e1}^{eq} - E_g^{eq})^2} \left\{ 1 + \frac{V^{eq} - 2T}{[(V^{eq} - 2T)^2 + 12t^2]^{1/2}} \right\} \\ b_1 &\equiv -\frac{4\hbar k_A \sqrt{t^{eq}}(q_{A1,CT1}^0 - q_{A1,CT3}^0)}{\sqrt{2}(E_{e1}^{eq} - E_g^{eq})^2} \\ b_2 &\equiv -\frac{4\hbar k_A \sqrt{t^{eq}}(q_{A1,CT1}^0 - 2q_{A1,CT2}^0 + q_{A1,CT3}^0)}{\sqrt{6}(E_{e1}^{eq} - E_g^{eq})^2} \end{aligned}$$

$$\begin{aligned} b_3 &\equiv \frac{2\hbar k_A(q_{A1,CT1}^0 - q_{A1,CT3}^0)}{\sqrt{6}(E_{e1}^{eq} - E_g^{eq})^2} \\ c_1 &\equiv -\frac{4\hbar k_A \sqrt{t^{eq}}(q_{A2,CT1}^0 - q_{A2,CT3}^0)}{\sqrt{2}(E_{e1}^{eq} - E_g^{eq})^2} \\ c_2 &\equiv -\frac{4\hbar k_A \sqrt{t^{eq}}(q_{A2,CT1}^0 - 2q_{A2,CT2}^0 + q_{A2,CT3}^0)}{\sqrt{6}(E_{e1}^{eq} - E_g^{eq})^2} \\ c_3 &\equiv \frac{2\hbar k_A(q_{A2,CT1}^0 - q_{A2,CT3}^0)}{\sqrt{6}(E_{e1}^{eq} - E_g^{eq})^2} \end{aligned} \quad (\text{A15})$$

In eqs A15, the superscript eq means that the quantity is evaluated at the equilibrium geometry on the electronic ground potential energy surface. To carry out this calculation, one should use an iterative method to obtain the equilibrium BLA coordinate value (see ref 33c). Combining eqs A12–A15, one can calculate the vibronic contribution to the TPA spectrum. To show the BLA-dependence of the vibronic TPA transition amplitude, we will numerically calculate $\tilde{\Gamma}_{fg}^0$, $\tilde{\Gamma}_{fg}^{vib,S}$, $\tilde{\Gamma}_{fg}^{vib,A1}$, and $\tilde{\Gamma}_{fg}^{vib,A2}$, where the latter three functions were defined in eq A13 and the tensor elements of $\tilde{\Gamma}_{fg}^0$, within the VB-3CT model, were given in eq 7. The parameters required for the numerical calculation are given as; $k_0 = 33.55 \text{ eV/\AA}^2$, $k' = -1.0 \text{ eV/\AA}^2$, $\omega_0 = 1550 \text{ cm}^{-1}$, reduced mass $m = 2.486 \times 10^{-25} \text{ kg}$, two transfer integrals, $t = 1.0 \text{ eV}$ and $T = 0.8 \text{ eV}$, the dipole moment of the charge-transfer state, $\mu = 1$, and $\hbar = 1$. Here, we assume that (1) the three reduced masses, m_S , m_{A1} , and m_{A2} are identical since the coupling force constant is small in comparison to k_0 . Then, the expectation values, $\langle \nu_S = 1, \{0\} | q_S | \nu_S = 0, \{0\} \rangle = \sqrt{\hbar/2m_S\omega_S}$, $\langle \nu_{A1} = 1, \{0\} | q_{A1} | \nu_{A1} = 0, \{0\} \rangle = \sqrt{\hbar/2m_{A1}\omega_{A1}}$, $\langle \nu_{A2} = 1, \{0\} | q_{A2} | \nu_{A2} = 0, \{0\} \rangle = \sqrt{\hbar/2m_{A2}\omega_{A2}}$ are about 0.021 \AA . With parameters given above, we calculate the $[y,y]$ -tensor elements of $\tilde{\Gamma}_{fg}^{vib,S}$ and $\tilde{\Gamma}_{fg}^{vib,A1}$, and plot them in Figure 8. It is found that (1) $[\tilde{\Gamma}_{fg}^{vib,A2}]_{yy} = 0$, (2) the vibronic contribution, $[\tilde{\Gamma}_{fg}^{vib,A1}]_{yy}$ associated with the asymmetric vibration, q_{A1} -mode, is crucial, and (3) $[\tilde{\Gamma}_{fg}^{vib,A1}]_{yy}$ increases monotonically as the donor and acceptor strengths increase. This observation is in good agreement with the ab initio calculation results by Macak et al.²⁵ We also found that, with the parameter set specified above, the overall magnitudes of the vibronic contributions, $\tilde{\Gamma}_{fg}^{vib,S}$, $\tilde{\Gamma}_{fg}^{vib,A1}$, and $\tilde{\Gamma}_{fg}^{vib,A2}$, are less than 10% of the pure electronic contribution, $\tilde{\Gamma}_{fg}^0$. However, it is necessary to explore the entire range of parameter values to make a conclusive statement. Furthermore, the assumption that only three BLA coordinates are enough to describe the vibronic contribution to the TPA cross section may not be quantitatively acceptable, even though the characteristic vibrational motions of a given polyene are associated with the BLA vibrations. In other words, the density of vibrational states is very high as the chain-length of each conjugated polyene branch increases, and this aspect could not be taken into account in our theoretical model discussed in this appendix. Nevertheless, the vibronic contribution to the TPA spectrum is likely to be sizable or even comparable as the length of conjugated polyene bridge increases.