Photoinduced Charge Transfer in Push/Pull Systems of Two-Photon Absorption

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ABSTRACT: A series of stilbene derivatives have been constructed by modifying the stilbene systems with different H, CN, NH2, NMe2, and NO2 groups. In a vacuum, it was found that a redshift in the ultraviolet–visible spectrum occurred because of the enhancement of the donor/acceptor capabilities of this group, with the order of redshift being NO2 > NMe2 > CN > NH2 > H. For stilbene molecular systems, the peak of two-photon absorption (TPA) observed in the simulated spectra should be attributed to two transitions that are contributed by two excited states with similar energy. In the case of derivatives, such a transition is separated by energy, and two TPA peaks can be clearly observed (derivatives containing NO2 and NMe2 groups have two TPA peaks), where the magnitude of the separation is directly related to the intensity of the peripheral group. In addition, the S1 state is the intermediate state in the TPA transitions to both of the final excited states.

1. INTRODUCTION

Two-photon absorption (TPA) is a nonlinear optical process that causes intramolecular or intermolecular electron excitation by absorbing two photons.1–3 The excitation wavelength of TPA is twice that of one-photon absorption (OPA), which indicates that the energy of the excitation light is reduced, which can effectively avoid light damage to the material by the excitation beam.4 Furthermore, TPA has been widely used in stereolithography,1–7 two-photon fluorescence microscopy,8–10 and photodynamic therapy.11,12 In addition, the excitation probability of TPA is directly proportional to the square of the intensity of the excitation light, which leads to good spatial selectivity in three-dimensional (3D) space,13 and can be used in many fields, such as 3D microfabrication,14–16 optical lithography,17,18 and optical information storage.19–21 By combination with organic light-emitting molecules, high-quality 3D images of TPA can be obtained, which are widely used in two-photon fluorescence imaging22–24 and molecular dye probes.25,26

A transition density matrix (TDM) can determine all of the single-electron properties for two states in the transition process, such as the atomic transition charge, transition electric/magnetic dipole moment, and other properties.27 By drawing a color-filling matrix diagram, the atomic number and fragment number of the molecular systems are displayed intuitively to assist with the understanding of the influence of electronic excitation via coupling between each site, which is beneficial for analyzing the intrinsic characteristics of the electronic excitation. The charge density difference (CDD) accurately reacts to changes in electrons and holes to describe the difference in electron density during the electron excitation process, where electrons are represented by an increase in electron density and holes are represented by a decrease in electron density.28 The type of excitation can be judged qualitatively by visually examining the transfer of electrons in the form of a 3D graph. In addition, the distance of electron transfer, the degree of separation between holes and electrons, and the contribution of atoms or fragments to the excitation of electrons can be quantitatively examined.29,30

We have constructed a series of donor-π-donor and acceptor-π-acceptor types of stilbene derivatives by modifying the stilbene systems with different groups, such as H, CN, NH2, NMe2, and NO2, which are referred to as molecules A–E, as shown in Figure 1. Among them NH2 and NMe2 are donor groups, and CN and NO2 are acceptor groups. The changes in OPA and TPA with respect to molecules A–E directly reflect the relationships between different groups and OPA and TPA. The methods of TDM and CDD can clearly and effectively analyze the intramolecular charge transfer (ICT). We constructed the transition density and density matrix for each process in the TPA process by TDM and CDD and then determined the 2D-TDM and 3D-CDD graphs of the two processes of TPA, which intuitively reflect the charge transfer of each atom or fragment in molecules A–E. It can be found that the TPA becomes greater with the
2. METHODS

In this article, quantum chemistry calculations were performed using Gaussian 16 software. The symmetrical styrene systems were optimized by density functional theory (DFT),32 a B3LYP functional and a 6-31G(d) basis set33 and time-dependent DFT.34 A CAM-B3LYP functional35 and a 6-31G(d) basis set were used for electronic excitation. After performing calculations related to OPA, the con

![Figure 1. Structural diagram of molecules (A–E) with different groups.](image)

the TDM into atoms involves removing the signs of the TDM matrix elements by squaring them and then adding them to form atoms.

\[ p_{\mu d} = \sum_{\nu \in c} \sum_{\epsilon \in d} (p_{\mu \nu})^2 \]

\[ c \text{ and } d \text{ are the sequence numbers of the atoms. Because } \]

hydrogen atoms typically contribute very little to the excitation of electrons of chemical interest, the matrix heatmap is, therefore, made compact by ignoring hydrogen atoms in general.

The method of interfragment charge transfer (IFCT) uses the following formula to calculate the amount of electron transfer from a snippet R to a snippet S during the electron excitation

\[ Q_{R,S} = \Theta_{R,\text{hole}} \Theta_{S,\text{ele}} \]

where \( \Theta_{R,\text{hole}} \) is the number of excited electrons in R and \( \Theta_{S,\text{ele}} \) is the number of electrons accepted in S. The net electron change of a segment can be defined by the sum of the net electron transfers between this segment and all other segments

\[ \Delta p_{R} = \sum_{S \neq R} p_{S \rightarrow R} = \sum_{S \neq R} (Q_{S,R} - Q_{R,S}) \]

where \( p_{S \rightarrow R} \) is the net electron transfer from snippets S to R and \( \Delta p_{R} \) is the variation of the electron population of snippet R.

We can construct the ground state and excited state from the density matrix4

\[ p_{\text{excited}} = p_{\text{ground}} + \sum_{a \rightarrow b} (w_a^b)^2 (p^b - p^a) \]

\[ + \sum_{a \rightarrow b} (w_a^b)^2 (p^b - p^a) \]

where \( p^a \) is the density matrix composed of only orbit a and \( p_{\text{excited}} \) is the density matrix of the excited state wave function.

The TPA cross-section refers to the ratio of the molecular transition probability to the square of the photon flux in unit time. The TPA cross-section can be calculated from the two-photon transition matrix elements of the initial, intermediate, and final states, and it can be expressed as follows5

\[ \delta_{tp} = 8 \sum_{j \neq g} \frac{|(f|\mu|l)^2|j|\mu|g|^2}{(\omega_l - \omega_f/2)^2 + \Gamma_l^2} (1 + 2 \cos^2 \theta_j) \]

\[ + 8 \frac{|\Delta \mu_{\text{pe}}| \delta_{tp}}{(\omega_f/2)^2 + \Gamma_l^2} (1 + 2 \cos^2 \phi) \]

where \( |g\rangle, |l\rangle, \) and \( |f\rangle \) represent the ground state, intermediate state, and final state, respectively; \( (j|\mu|g), (f|\mu|l), \) and \( (f|\mu|g) \) are the transition dipole moments from the ground state to the intermediate state, from the intermediate state to the final state, and from the ground state to the final state, respectively; and \( \Delta \mu_{\text{pe}} \) is the difference between the permanent dipole moment in the final state and the permanent dipole moment in the ground state. Furthermore, \( \theta_j \) is the angle between \( (j|\mu|g) \) and \( (f|\mu|l) \) and \( \phi \) is the angle between \( \Delta \mu_{\text{pe}} \) and \( (f|\mu|g) \). \( \omega_f \) and \( \omega_i \) are the excitation energies of the intermediate and final
states, respectively, and $\Gamma_f$ is the lifetime of the final state, which is calculated by the Einstein relationship formula.

**3. RESULTS AND DISCUSSION**

**3.1. UV−Visible and TPA Spectra.** We use different colored lines to represent the systems of diphenylmethane modified by different groups in the spectrum, as shown in Figure 2a, in which A, B, C, D, and E are represented by black lines, red lines, green lines, blue lines, and dark yellow lines, respectively. The spectrum redshifts with the enhancement of donor group capabilities, and molecules C and D are redshifted by 4.85 and 36.10 nm with respect to molecule A, as shown in Figure S1 in the Supporting Information. At the same time, as the acceptor capacity increases, molecules B and E also move 25.16 and 37.36 nm toward the infrared region, respectively, as shown in Figure S2 in the Supporting Information. The spectral redshift size caused by different groups is also significantly different on the whole, and the order of the spectral redshifts from the largest distance to the smallest distance is $E > D > B > C > A$.

The IFT method is used to calculate the net amount of electron transfer between different segments during the electronic excitation process as the difference between the electron-donating amount and the electron-withdrawing amount of the same segment. In Table 1, we can see the net amount of electron transfer of each molecule at the R group, benzene, and ethylene, where a positive value indicates that electrons are emitted and a negative value indicates the absorption of electrons. The net amounts of electron transfer of the R group and ethylene are $E > D > B > C > A$ in order from large to small, and because the net amount of electron transfer is positively correlated with the electron transition, the order of the redshifts from maximum to minimum in the spectrum is $E > D > B > C > A$. In addition, we compared the main contribution orbits of the holes and electrons of the molecular AE (the contribution rate exceeds 94.6%). It was found that as the donor/acceptor capacity of this group increased, the orbit of the main contribution changed, thereby reducing the energy gap and causing the spectral redshift.

The UV−vis spectrum can be obtained by Gaussian linear broadening of the oscillator strength, where the oscillator strength is positively correlated with the TDM. When the transition dipole moment is large, the oscillator strength is large, and the corresponding absorption is relatively strong. From Table 2, we can see that the TDM of molecules A−E is

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**Figure 2.** The UV−visible spectra (a) and TPA spectra (b) of molecules A−E with different groups.

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**Table 1.** Net Charge Transfer Amount, Contribution Orbits and Wavelengths of Molecules A−E at $S_1$

| molecule | R group | benzene | ethylene | hole     | electron | wavelength (nm) |
|----------|---------|---------|----------|----------|----------|-----------------|
| A        | 0.000   | 0.016   | 0.016    | MO 48    | MO 49    | 288.49          |
| B        | −0.018  | −0.020  | 0.038    | MO 60    | MO 61    | 313.64          |
| C        | 0.004   | 0.022   | −0.026   | MO 56    | MO 57    | 293.34          |
| D        | 0.118   | −0.002  | −0.116   | MO 72    | MO 73    | 324.59          |
| E        | −0.214  | 0.100   | 0.114    | MO 70    | MO 71    | 325.84          |

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**Table 2.** Fragment figures of the TDM and Components of the TDM in the X/Y/Z Directions for Molecules A−E at $S_1$

| Molecule | TDM fragment figure | X    | Y    | Z    |
|----------|---------------------|------|------|------|
| A        |                     | 3.1×10^4 | 1.2×10^6 | 5.0×10^7 |
| B        |                     | 3.9×10^4 | 8.1×10^6 | 1.0×10^7 |
| C        |                     | 3.3×10^4 | −7.4×10^6 | −1.4×10^6 |
| D        |                     | 4.0×10^4 | −4.2×10^6 | 8.9×10^5 |
| E        |                     | −3.7×10^4 | 9.5×10^5 | −4.1×10^4 |

*The green and red arrows in the figure depict the total TDM of the molecule and the TDM of the corresponding fragment, respectively.*
Figure 3. TDM and CDD of $S_1$ of molecules A–E in OPA.
mainly concentrated in the $x$ direction, and the order of the values of the transition dipole moment is $D > B > E > C > A$ from large to small, which is consistent with the magnitude of the spectral peak of molecular A.

In the TPA spectra in Figure 2b, the TPA increases significantly as the donor/acceptor ability of the group increases, resulting in an increase in the TPA cross-section, and the order of the TPA cross-sections of different molecules is $D > E > B > C > A$ from large to small. The TPA peak of molecule C is slightly larger compared with that of molecule A, which is mainly because $S_5$ forms the TPA peak of molecule C, whereas the TPA peak of molecule A is composed of the two excited states of $S_8$ and $S_7$. The two excitations greatly increase the TPA peak of molecule A, but their contribution still less than that of the introduction of the amino group to the TPA peak of molecule C. The TPA of molecules B, D, and E changed significantly; molecule B showed a strong peak, and molecules D and E appeared as strong double peaks. The two peaks of molecule D are both larger than the two peaks of molecule E because the introduction of the methyl group increases the molecular dimension and enhances the electron-donating ability of the dimethylamine group, resulting in a stronger TPA peak.

3.2. Electron–Hole Coherence of OPA. We performed TDM and CDD analysis on the excited states of different molecules in the UV–vis spectrum in the range of 185–375 nm, as shown in Figures 3 and 4. The red and green isosurfaces in the figures represent electrons and holes in the CDD diagram. We performed TDM and CDD analysis on the $S_1$ corresponding to the highest peak, as shown in Figure 3. The isosurfaces of the electrons and holes show alternating distributions on the conjugated stilbene of the molecules A–E and are ellipsoidal and strip-type on the ethylene and the benzene ring, respectively. Therefore, the conjugated chain of stilbene has an overall excitation of $\sigma_- > \pi^*$. The main difference is that molecule B also contains $\sigma_- > \pi^*$ excitation between the cyano group and the benzene ring, wherein the hole electrons are alternately distributed in a spherical shape between the two sites. There is a green isosurface on the N atom in molecules C–E and the $n_- > \pi^*$ excitation from the lone pair of electrons on the N atom and the $\pi$-bond of the benzene ring. The $\pi$-bond on the nitro group in molecule E and the $\pi$-bond of the ring and ethylene are...
excited by $\pi > \pi^*$, which is characterized by a red isosurface on the nitro group. We also found that the electron transfer direction of molecules $A$–$D$ also changed significantly with the modification of the group. In molecules $A$, $C$, and $D$, the holes are concentrated on the outer side, and the electrons converge on the inner side, so the electrons are transferred from both sides to the center; the green isosurface at the center is gradually enhanced as the electron-donating ability increases, and the electron transfer is more intense. However, the electron transfer directions of molecules $B$ and $E$ are from the center to both sides, and as the electron-withdrawing ability rises, the red isosurface on both sides is gradually enhanced, and the electrons shift more from the center to the sides.

$S_5$ of molecule $A$ has a spherical and alternating distribution of holes and electrons on the ethylene, and the holes on the benzene are distributed in a ring shape, so it is $\sigma_\pi > \pi^*$, in which electrons are transferred from both sides to the middle. In $S_6$ of molecule $B$, the number of electrons gradually increases from the center to the sides, and the isosurfaces are distributed on $N$ atoms, the $\pi$-bonds of ethylene and benzene. Therefore, $S_6$ is the $\sigma_\pi > \pi^*$ between the ethylene and the benzene ring and the $n_\pi > \pi^*$ excitation of the $N$ atom and the benzene ring, and the electrons transition from the center to both sides. $S_9$ of molecule $C$ shows an overall excitation of $\sigma_\pi > \pi^*$, the holes and electrons are mainly distributed on the benzene and ethylene, and the electrons converge from both sides toward the center. $S_{10}$ of molecule $C$ is mainly excited by the $\pi$-bond in the benzene, and the holes and electrons are mainly distributed on the two benzenes. The electrons in $S_5$, $S_{10}$ of molecule $D$ are mainly distributed in the benzene, and the

Figure 5. Physical mechanism of the TPA peak in molecule $A$. 

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holes are distributed on the π-bond of the benzene and ethylene and the N atom of the dimethylamine group. Therefore, S3 shows π > π* excitation between benzene and ethylene and n > π* excitation between a lone pair of electrons on the N atom and the large π-bond of benzene, and electrons are transferred from the dimethylamine group and ethylene to benzene. The electron isosurface in S8 of molecule D gradually increases from both sides to the middle, the holes are mainly concentrated on the dimethylamine groups on both sides of the molecule, and S8 of molecule D shows an overall excitation of n > π* and σ > π*.

The hole in S16 of molecule E is distributed on the O atom of the nitro group on both sides, and the electrons are distributed on the stilbene, indicating that S16 shows n > π* excitation of the π-bond of the stilbene and the lone pair of electrons on the O atom, and the electrons are transferred from both sides to the middle.

3.3. Electron–Hole Coherence of TPA. The TPA peak of molecule A is composed of the two excited states S6 and S7, as shown in Figure 5, wherein the intermediate states of S6 and S7 are both S1. We can see that electrons transfer from the benzene on both sides to the two C atoms on the central ethylene in the S0 → S1 process. The electrons in the S1 → S6 process are further transferred to the center, where electrons are transferred from the two C atoms on the ethylene to the C–C π-bond. The S1 → S7 process transfers charges from the ethylene to the benzene ring, and finally, a large electron isosurface appears at the outermost C atom of benzene. In addition, only one peak can be observed in the experiment, which is contributed by two excited states, so it is necessary to analyze the sum of the two excited states. We can find that the TDM map is similar to the TDM map of the S1 → S7 process, and the electrons are transferred from the center to the benzene on both sides during S1 to the final-state process, which indicates that the formation of the TPA peak of molecule A is mainly composed by S7.

The TPA peak of molecule B is formed by the contribution of S5, as shown in Figure 6, wherein the middle state is S1. From the process of S0 → S1, the electronegativity of nitrogen is larger than that of carbon, which leads to the electron cloud of C≡N being biased toward nitrogen, and the cyan group absorbs electrons, inducing electrons to shift to both sides. Therefore, electrons are transferred from the sides to the central ethylene in the S1 → S5 process. In the TPA process of molecule B, the transition of electrons is first from the center to the two sides and then from the two sides to the center. The electron transitions of the two processes are reversed, and the electron transfer is more intense, resulting in a larger TPA peak.

In Figure 7, the TPA peak of molecule C is composed of two excited states S7 and S9, wherein the intermediate state is S1. In the S0 → S1 process, the conjugation effect of the amino group as an electron-donating group and stilbene causes the transition of electrons from both sides to the center, and electrons are concentrated on the two C atoms of ethylene. During the S1 → S7 process, the electrons are further transferred to the center, and the electrons are finally concentrated on the C=C double bond of ethylene. Therefore, the charge in the TPA process of S7 of molecule C is from both sides to the middle. During the process of S1 → S9, the red isosurface of the central ethylene was significantly reduced, and the benzene on both sides increased significantly, indicating that the electron transition is from the center to the
sides. By adding the two excited states, we can see that $S_9$ shows a major contribution under the TPA peak, which is mainly because of the change in the electron transfer direction during two-photon excitation, which leads to more intense charge transfer.

Molecule D has two peaks in the TPA spectrum, which are respectively contributed by different excited states, as shown in Figure 8. The intermediate states of the two excited states are the same, and both are $S_1$, which results in the same charge transfer process for the two excited states from $S_0$ to $S_1$. In the process of $S_0 \rightarrow S_1$, dimethylamine as a strong electron-donating group produces a stronger conjugation effect with stilbene, which promotes the transition of electrons from the dimethylamine to the center of the molecule. The strong TPA peak of molecule D is formed by the contribution of $S_5$, where in the $S_1 \rightarrow S_5$ process, the holes are concentrated at the ethylene of the molecule center, and the electrons are distributed on the outer atom of benzene, indicating that electrons are transferred from the center to the benzene on both sides. The second TPA peak of molecule D is formed by the contribution of $S_4$. During the process of $S_1 \rightarrow S_4$, the electron isosurface gradually increases from the two sides to the center, indicating that the electrons move toward the center. According to eq 8, the TPA cross-section is proportional to $|\langle j | \mu | g \rangle|^2 |\langle f | \mu | j \rangle|^2$ and inversely proportional to $(W_j - W_f/2)$. We know that the intermediate states of the two TPAs of molecule D are the same, so $|\langle j | \mu | g \rangle|^2$ is the same as 16.1974. In addition, the values of $|\langle f | \mu | j \rangle|^2$ in $S_1 \rightarrow S_4$ and $S_1 \rightarrow S_5$ are similar at 21.5963 and 22.0119, respectively. However, $W_j - W_f/2$ of $S_1 \rightarrow S_4$ is 3.8197 eV $- 5.0974/2 = 1.271$ eV, a larger value. In contrast, if the fifth excited state is the final excited state, then, $(W_j - W_f/2) = 3.8197$ eV.
− 5.7853/2 eV = 0.9271 eV; this value is much smaller than 0.3449 eV, and we can find that the value of $S_1 \rightarrow S_5$ is smaller by calculation, so the TPA cross-section of $S_1 \rightarrow S_5$ is very strong.

$S_8$ and $S_9$ of molecule E form the second strongest peak and the strongest peak of the TPA, respectively, where the intermediate state is $S_1$, as shown in Figure 9. The large delocalized π-bond in the nitro group induces the electrons on the π-bond of benzene and the ethylene to jump from the center to the nitro group on both sides during the $S_0 \rightarrow S_1$ process. During the $S_1 \rightarrow S_8$ process, the electrons are mainly distributed on the nitro group, only trace amounts of electrons...
are present on the C atom of benzene and the π-bond of ethylene, and the holes are all concentrated on the stilbene, indicating that the electrons in the S₁ → S₉ process transition from the center to both sides. In the process of S₁ → S₉, electrons are mainly distributed on the π-bond of ethylene, and electrons are also present on the C atom of benzene closed to ethylene but almost no electrons exist on the nitro group of both sides. It is shown that the electron transition that occurs is from both sides to the center in the process of S₁ → S₉. We can see that the |⟨ψ₁|ψ⟩|^2 of the two TPA sections are the same, and the |⟨ψ₁|ψ⟩|^2 values are similar, where |⟨ψ₁|ψ⟩|^2 is 14.0961, |⟨ψ₁|ψ⟩|^2 of S₁ → S₉ is 24.4131, and |⟨ψ₁|ψ⟩|^2 of S₁ → S₉ is 24.3218. When the eighth excited state is the final excited state, then, (W₁ − W₁/2) = 3.805 eV − 4.8115/2 eV = 1.3993 eV. In contrast, if the final excited state is the ninth excited state, then, (W₁ − W₁/2) = 3.805 eV − 5.5905/2 eV = 1.0098 eV. Because this value is small, the value of δₛ₂ is large.

3.4. Physical Mechanism. In the TPA spectrum, as the donor/acceptor ability of the group increases, the number of TPA peaks is increased from one to two. We found that the TPA peak of the stilbene systems is contributed by the two excited states, according to the analysis in the Section 3.3. The donor ability of the groups in molecules A, C, and D is gradually raised such that the wavelength interval between the two excited states is gradually enhanced, and the TPA cross-section is also enhanced, which shows that the number of peaks in the TPA spectrum changes from one to two. Molecules A and C appear as one peak, molecule D appears as two peaks, and the two excited states of molecules A, C, and D have wavelength intervals of 6.76, 12.54, and 57.91 nm, respectively. Molecule E containing a nitro group also exhibits two peaks, and the wavelength interval of the two excited states is 71.90 nm. In addition, the intermediate states of the two excited states in the TPA are all S₉, but the charge transfer directions from the intermediate state to the final state are opposite. There is a TPA peak in molecules A–C, which is mainly contributed by the excited state of the opposite direction of the electron transition in the two-photon excitation processes, whereas molecules D and E appear as a strong peak and a secondary peak. The eigenvalue of the orbital wave function determines the magnitude of the excitation energy of the excited state. The orbital wave function itself determines whether there is charge transfer. However, the spatial distribution of the orbital wave function will vary with different substituents. Exicted state transition is a configuration change process that occurs with multiple orbital wave functions. In summary, because of the different bonding form of different substituents, the linear combination of the wave function of the substituent and the molecular wave function changes the spatial distribution of the total wave function of the systems, resulting in different charge transfer phenomena. Moreover, as the spatial distribution of the total wave function of the systems changes, its eigenvalues also change to a certain degree, so the absorption spectrum shifts. This change is reflected in the OPA and TPA spectra.

4. CONCLUSIONS

It can be found that the UV–visible spectrum was redshifted as the donor/acceptor ability of the group was enhanced when the stilbene systems were modified with different H, CN, NH₂, NMe₂, and NO₂ groups. The order of the spectrum redshifts from large to small is NO₂ > NMe₂ > CN > NH₂ > H. We also found that the TPA peak of the stilbene systems shows the contribution of two excited states. As the donor/acceptor ability of the group improves, the wavelength interval between the two excited states is gradually enhanced, and the TPA cross-section also increases, which is manifested by the number of TPA peaks changing from one to two in the TPA spectrum. Among them, molecule D with a strong donor group and molecule E with a strong acceptor group each have two TPA peaks. In addition, the introduction of a methyl group can effectively increase the electron-donating ability and promote a stronger TPA cross-section compared with that in molecule D and molecule E. Our results can reasonably explain the mechanism of enhancement of the TPA cross-section by introduction of the donor/acceptor group and provide a basis for designing materials with larger TPA cross-sections.

ASSOCIATED CONTENT

Supporting Information

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The UV–visible and TPA spectra of molecules with different donor and acceptor groups (PDF)

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The authors declare no competing financial interest.
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