The aggregation effects on the two-photon absorption properties of para-nitroaniline polymers by hydrogen-bond interactions*

Sun Yuan-Hong(孙元红)[a)†], Li Jing(李 晶)[b)], Zhao Ke(赵 珂)[b)], and Wang Chuan-Kui(王传奎)[b)]

[a)] *Fundamental Division of Shandong Police College, Jinan* 250014, *China*
[b)] *College of Physics and Electronics, Shandong Normal University, Jinan* 250014, *China*

(Received 18 April 2009; revised manuscript received 16 July 2009)

This paper has theoretically designed a series of aggregate polymers on the basis of several para-nitroaniline monomers by hydrogen-bond interactions. At the level of time-dependent hybrid density functional theory, it has optimized their geometrical structures and studied their two-photon absorption (TPA) properties by using analytical response theory. The calculated results exhibit that the aggregation effects not only bring out the considerable red shift of the excited energies but also greatly enhance the TPA intensities of the aggregate polymers in comparison with the para-nitroaniline monomer. The aggregate configurations also have an important influence on the TPA abilities of the polymers; the trimer has the largest TPA cross section. The electron transitions between the molecular orbits involving the strong TPA excitations of the trimer are depicted to illuminate the relationship between the intermolecular charge transfer and the TPA property.

Keywords: two-photon absorption, aggregation effect, analytical response theory

PACC: 4265, 3120A, 7855K

1. Introduction

Along with the development of significant two-photon technique applications in a wide range of fields, such as optical power limiting,[1] three dimensional (3D) optical data storage,[2,3] photodynamic therapy,[4] laser scanning fluorescence microscopy,[5] and so on, research on organic molecular materials with large two-photon absorption (TPA) cross sections has attracted growing attention from both theoretical and experimental aspects. Abundant efforts have been made to establish the structure-property relationship of chromophores; the available research results indicate that the TPA abilities of organic polymers are strongly related to a few factors, for example, the π conjugated centre length, the push (pull) election capacities of the substituting groups and whether they are symmetrically or asymmetrically attached to the π centre, and the dimensionalities of the organic molecules.[6−13] These studies are of benefit for designing and synthesizing efficient TPA molecular materials.

Because experimental measures of organic molecular TPA properties usually operate in solution, the solvent effects on TPA cross sections have been always a concern of theoretical workers. So far, theoretical simulations of solvent effects have mostly supposed an individual solute molecule resolved in a sea of solvent molecules; some work takes into account the long-range interactions of solute and solvent molecules by using the polarized continuum model or Onsager reaction field model,[14,15] and others consider the short-range interactions by hydrogen bonds formed between the solute and solvent molecules.[16,17] However,, in the practical experimental process with the organic crystals dissolved in solvents, the concentrations of solute molecules are generally higher, therefore hydrogen bonds between solute molecules, especially for asymmetric D–π–A molecules, are probably produced due to strong dipolar interactions. Recently, a popular research subject about aggregation effects on the TPA properties of polymers has aroused extensive interest in both theoretical and experimental fields.[18−21]

In this work, we have theoretically designed several aggregate polymers by making use of di-, tri- and

*Project supported by the State Key Development Program for Basic Research of China (Grant No. 2006CB806000), the Open Fund of the State Key Laboratory of High Field Laser Physics (Shanghai Institute of Optics and Fine Mechanics), Natural Science Foundation of Shandong Province of China (Grant No. Z2007A02).
†Corresponding author. E-mail: yhsunhill@126.com
© 2010 Chinese Physical Society and IOP Publishing Ltd

tetra-para-nitroaniline (PNA) monomers; each PNA monomer is a typical dipolar molecule and intermolecular hydrogen bonds are easily formed between them. Then we have studied the aggregation effects on the TPA cross sections of these polymers and made a comparison with individual PNA molecules.

2. Computational details

The transition probability of one-photon absorption is given by the oscillator strength

$$\delta_{\rm opa} = (2\omega_{\rm f}/3)\sum_{\alpha} |\langle 0|\,\mu_\alpha\,|f\rangle|^2, \qquad (1)$$

where μ_α is the electric dipole moment operator, $|0\rangle$ and $|f\rangle$ denote the ground and final states respectively, $\omega_{\rm f}$ means the excitation energy of the final state, the summation is performed over the molecular x, y and z axes.

The TPA transition matrix element of two-photon resonant absorption excited by a linearly polarized monochromatic beam is expressed as

$$S_{\alpha\beta} = \sum_j [\langle 0|\mu_\alpha|j\rangle\langle j|\mu_\beta|f\rangle/(\omega_{\rm j} - \omega_{\rm f}/2) + \langle 0|\mu_\beta|j\rangle\langle j|\mu_\alpha|f\rangle/(\omega_{\rm j} - \omega_{\rm f}/2)]. \qquad (2)$$

Here $|j\rangle$ denotes all the intermediate states including the ground state $|0\rangle$, $\omega_{\rm j}$ is the excitation energy of the excited state. The TPA cross section is[22]

$$\delta_{\rm tpa} = \sum_{\alpha\beta} [F \times S_{\alpha\alpha}S^*_{\beta\beta} + G \times S_{\alpha\beta}S^*_{\alpha\beta} + H \times S_{\alpha\beta}S^*_{\beta\alpha}]. \qquad (3)$$

The coefficients F, G and H are related to the incident radiation. For linearly polarized light, F, G and H are 2, 2 and 2, but for the circular case, they are -2, 3, and 3, respectively. The summation goes over the molecular axes α, $\beta = \{x,\ y,\ z\}$.

The TPA cross section directly comparable with experimental measurements is defined as

$$\sigma_{\rm tpa} = (4\pi^2 a_0^5 \alpha/(15c_0))(\omega^2 g(\omega)/\Gamma_{\rm f})\delta_{\rm tpa}, \qquad (4)$$

where a_0 is the Bohr radius, c_0 is the speed of light, α is the fine structure constant, $\hbar\omega$ is the photon energy of the incident light, $g(\omega)$ denotes the spectral line profile that is assumed to be a δ function in the work, $\Gamma_{\rm f}$ is the level broadening of the final state, which is taken as a common value[23] 0.1 eV with the corresponding lifetime of a few femtoseconds.

The geometrical optimizations of all polymers are completed by utilizing the GAUSSIAN03 program package; the DALTON quantum chemistry program was employed to compute the TPA cross sections, and all calculations are carried out at the hybrid density functional theory (B3LYP) level and 6-31G basis set.

3. Results and discusssion

3.1. Molecular structures

The PNA monomer and our theoretically designed dimer, trimer and tetramer are labelled with numbers 1, 2, 3 and 4, respectively. Their optimized geometrical structures are shown in Fig. 1.

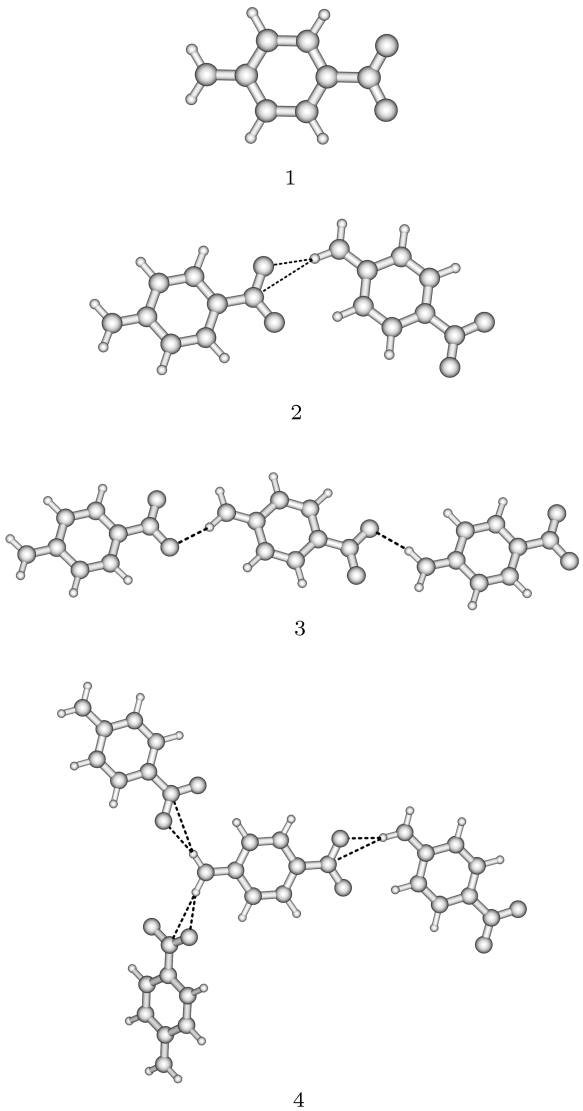


Fig. 1. Optimized structures of the studied polymers: 1 monomer; 2 dimer; 3 trimer; 4 tetramer.

The optimization results show that the PNA monomer is completely planar, as a typical unsymmet-

rical molecule, which has a larger permanent dipole moment 8.3D. The dimer is created by two individual PNA molecules. It is interesting that one hydrogen atom of a PNA molecule forms two hydrogen bonds with the oxygen and nitrogen atoms of the other molecule. It can be seen that two PNA molecules lie on the same plane, but their dipolar orientations are not in the same direction, the angle of two molecular axes is about 50°. The calculations display that the intermolecular charge transfer between two PNA molecules augments the polarization of polymer 2 with 18.6D permanent dipole moment. Three identical PNA molecules make up the trimer by means of the conjunctions of two hydrogen–oxygen bonds. It is found that three PNA molecules are almost coplanar, and the angle between the central molecule and either molecule of both sides is approximately 27°. This combined structure is much more beneficial for the intermolecular charge transfer than the dimer, so polymer 3 possesses the largest permanent dipole moment 32.5D. With respect to the tetramer, in order to examine the influences of different aggregate configurations on TPA properties for polymers, we design four PNA molecules composing polymer 4 being arranged not along a line, with one PNA molecule as the central conjugation backbone; the donating and accepting groups connect two and one PNA molecules, respectively. The geometrical optimization indicates that the structure of polymer 4 is twisted; one PNA molecule deviates from the central backbone with a dihedral angle of about 60°. The permanent dipole moment of polymer 4 is 29.8D, slightly smaller than that of polymer 3. From the above observation, it can be anticipated that polymer 3 will have a large TPA cross section because of the more perfect conformation structure.

3.2. The TPA cross sections

The response theory at the B3LYP level with 6-31G basis set is used to discuss the TPA properties of the four polymers; considering the practical applications and our computing abilities, only the ten lowest excited states are investigated, and the corresponding energy range is from 400 nm to 1600 nm. The calculated TPA cross sections and wavelengths are listed in Table 1; by Lorentz broadening, we obtain the TPA spectra of all polymers (see Fig. 2).

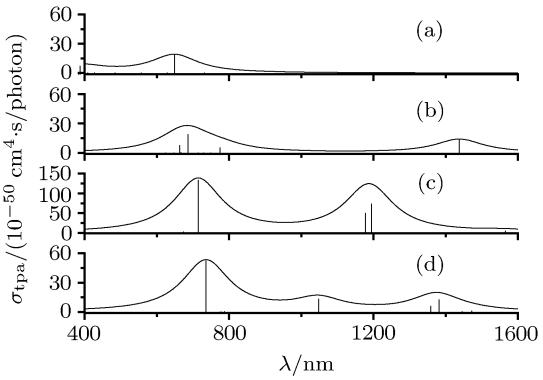


Fig. 2. Calculated TPA spectra of all polymers: (a) monomer; (b) dimer; (c) trimer; (d) tetramer.

Table 1. The TPA cross sections $\sigma_{\rm tpa}$ and wavelengths $\lambda_{\rm tpa}$ of the ten lowest excited states.

monomer		dimer		trimer		tetramer	
$\lambda_{\rm tpa}$ /nm	$\sigma_{\rm tpa}$ /(10^{-50} cm^{4}s/photon)	$\lambda_{\rm tpa}$ /nm	$\sigma_{\rm tpa}$ /(10^{-50} cm^{4}s/photon)	$\lambda_{\rm tpa}$ /nm	$\sigma_{\rm tpa}$ /(10^{-50} cm^{4}s/photon)	$\lambda_{\rm tpa}$ /nm	$\sigma_{\rm tpa}$ /(10^{-50} cm^{4}s/photon)
732	0.0	1438	13.7	1565	5.0	1472	0.8
649	18.6	775	5.0	1195	72.8	1446	0.3
629	0.0	749	0.0	1178	49.1	1382	12.5
557	0.0	730	0.0	814	0.0	1359	5.8
484	0.1	715	0.0	803	0.6	1050	12. 9
427	0.2	687	18.5	717	0.0	788	0.1
408	0.0	667	0.3	715	133.4	780	0.0
399	0.1	663	7.3	691	0.0	780	0.0
387	7.2	647	0.0	678	0.3	775	0.0
383	0.3	625	0.0	674	2.1	736	52.3

From Table 1 and Fig. 2, the excited energies of aggregate polymers are greatly reduced due to the intermolecular charge-transfer by the hydrogen-bond interaction, for example, the energies of the first excited states for polymers 2, 3 and 4 are respectively 1.72, 1.58 and 1.68 eV, much smaller than that of monomer 3.38 eV, and therefore the TPA behaviours of these aggregate polymers are found at lower energies. In our studied energy region, the PNA monomer exhibits only one TPA excited state located at 649 nm, with a 18.6 GM (1 GM=10^{-50} cm^4·s/photon) TPA cross section. In comparison with the PNA monomer, polymers 2, 3 and 4 have more TPA excited states which bring out several TPA spectral peaks at a broad energy range, owing to the hydrogen-bond effect. For the dimer, there are two dominating TPA peaks relatively located at 684 nm and 1438 nm, the weaker peak only contains the first excited state with a TPA value of 13.7 GM, another intensive peak is from the corporate contributions of three TPA excited states with 7.3, 18.5, 5.0 GM TPA cross sections respectively. In regard to the trimer, because of possessing the more perfect structure and the largest permanent electronic dipole moment among all the polymers, it displays excellent TPA behaviour as in our previous anticipation. It is found that the TPA spectrum of polymer 3 exhibits two very strong peaks derived from three intense TPA excited states. The first peak is dominated by the strongest TPA excited state with 715-nm wavelength, the peak value is 133.4 GM, about 7.2 times of that of the PNA monomer. Another two TPA excited states form the second peak at lower energy, with considerable TPA cross sections 49.1 and 72.8 GM, respectively. The last, with respect to the tetramer, four positive TPA states come into being with three obvious spectral peaks. The first peak located at 736 nm is comparatively intense, the peak value is 52.3 GM, around 2.8 times of that of the monomer. The other two TPA peaks are weaker, similar to that of the PNA monomer. It is interesting that the strongest TPA peaks of the aggregate polymers lie near the unique peak of the monomer, displaying a slight red shift, and the corresponding peak values have become larger with the increment of PNA molecules composing aggregates, although not with a monotonic relationship.

To sum up, the aggregation effects have a significant impact on the TPA abilities of polymers. By analysing the molecular microscopic mechanism, we can see that the TPA aggregation-induced enhancements are mostly from several factors. First, the excited energies of aggregate polymers have been reduced greatly. Second, the molecular permanent dipole moments have been increased obviously. Third, there are more active TPA states to provide the effective two-photon excited access. The collective contributions of these factors enhance the TPA cross sections of polymers.

3.3. Charge transfer

It is well known that the electron transition between the molecular orbits involving the TPA excitation decides the TPA property of a molecule.[19,24] For the trimer, we analyse the charge distribution of the molecular orbits which take part in the strong TPA excitations, as illustrated in Fig. 3.

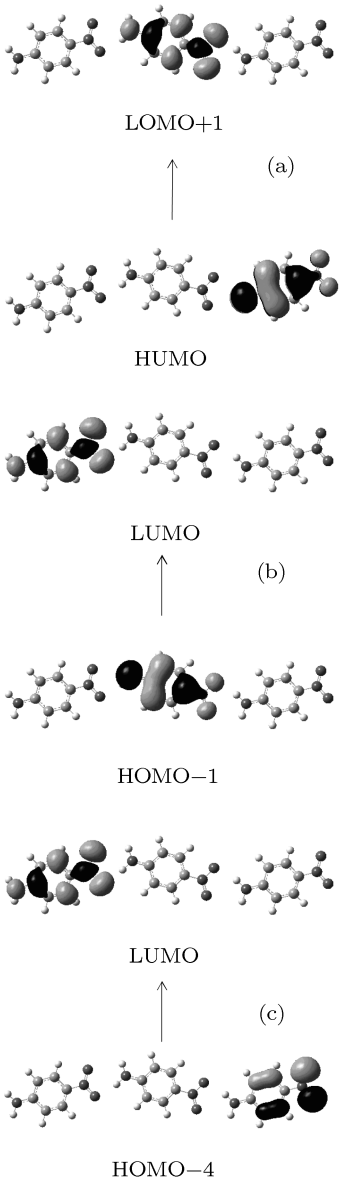


Fig. 3. Molecular orbits involving the strong TPA excitations of the trimer (a) the second excited state; (b) the third excited state; (c) the seventh excited state.

There are three strong TPA states for the trimer, namely the second, third and seventh excited states, which are generated from different origins. The TPA excitation of the second excited state comes from the transition from the highest occupied molecular orbital (HOMO) to the lower unoccupied molecular orbital (LUMO+1), corresponding to the charge transfer from the right to the central molecules. The transition from HOMO–1 to LUMO dominates the TPA excitation of the third excited state, equalling the charge transfer from the central to the left molecules. For the seventh excited state which possesses the largest TPA cross section, the transition is from HOMO–4 to LUMO, with considerable charge transfer from the right to the left molecules. From the above analysis, it is demonstrated that strong electron transition between molecular orbits resembling extensive intermolecular charge transfer will result in a large TPA cross section of the aggregate polymer.

4. Conclusion

We have theoretically designed a series of aggregate polymers based on several PNA monomers by hydrogen-bond interactions. Utilizing the B3LYP theory and 6-31G basis set, we discuss the geometrical structures and TPA abilities of these aggregate polymers, and make a comparison with that of the PNA monomer. The numerical results show that the aggregation effects greatly increase the TPA cross sections of polymers. It is found that aggregate polymers exhibit strong TPA intensities in a broad energy region. It can be seen that the TPA properties of aggregate polymers are also sensitive to the aggregate configurations, for instance, the trimer rather than the tetramer has the largest TPA cross section.

References

[1] Tutt L W and Kost A 1992 *Nature* **356** 225

[2] Cumpston B H, Ananthavel S P, Barlow S, Dyer D L, Ehrlich J E, Erskine L L, Heikal A A, Kuebler S M, Lee I Y, McCord-Maughon D, Qin J Q, Röckel H, Rumi M, Wu X L, Marder S R and Perry J W 1999 *Nature* **398** 51

[3] Parthenopoulos D A and Rentzepis P M 1989 *Science* **245** 843

[4] Bhawalkar J D, Kumar N D, Zhao C and Prasad P N 1997 *J. Clin. Laser Med. Surg.* **15** 201

[5] Denk W, Strickler J H and Webb W W 1990 *Science* **248** 73

[6] Zhou W H, Kuebler S M, Braun K L, Yu T Y, Cammack J K, Ober C K, Perry J W and Marder S R 2002 *Science* **296** 1106

[7] Yan Y X, Tao X T, Sun Y H, Xu G B, Wang C K, Yang J X, Zhao X, Wu Y Z, Ren Y and Jiang M H 2005 *Mater. Chem. Phys.* **90** 139

[8] Norman P, Cronstrand P and Ericsson 2002 *J. Chem. Phys.* **285** 207

[9] Sun Y H, Zhao K, Wang C K, Luo Y, Yan Y X, Tao X T and Jiang M H 2005 *Chin. Phys.* **14** 115

[10] Zhao K, Sun Y H, Wang C K, Luo Y, Zhang X, Yu X Q and Jiang M H 2005 *Acta Phys. Sin.* **54** 2662 (in Chinese)

[11] Fisher J A N, Susumu F K, Therien M J and Yodh A G 2009 *J. Chem. Phys.* **130** 134506

[12] Zhao Y, Ren A M, Feng J K and Sun C C 2008 *J. Chem. Phys.* **129** 014301

[13] Huang X M, Tao L M, Guo Y H, Gao Y and Wang C K 2007 *Acta Phys. Sin.* **56** 2570 (in Chinese)

[14] Zhao K, Ferrighi L, Frediani L, Wang C K and Luo Y 2007 *J. Chem. Phys.* **126** 204509

[15] Munn R W, Luo Y and Macák P and Ågren H 2001 *J. Chem. Phys.* **114** 3105

[16] Guo Y H, Sun Y H, Tao L M, Zhao K and Wang C K 2005 *Chin. Phys.* **14** 2202

[17] Sun Y H, Zhao K and Wang C K 2005 *Acta Chim. Sin.* **63** 1116 (in Chinese)

[18] Liu K, Wang Y H, Tu Y Q, Ågren H and Luo Y 2007 *J. Chem. Phys.* **127** 026101

[19] Liu K, Wang Y H, Tu Y Q, Ågren H and Luo Y 2008 *J. Phys. Chem.* B **112** 4387

[20] Liu Z J, Shao P, Huang Z L, Liu B, Chen T and Qin J G 2008 *Chem. Commun.* 2260

[21] Tu Y Q, Luo Y and Ågren H 2005 *J. Phys. Chem.* B **109** 16730

[22] Monson P R and McClain W M 1970 *J. Chem. Phys.* **53** 29

[23] Albota M, Beljonne D, Brédas J L, Ehrlich J E, Fu J Y, Heikal A A, Hess S E, Kogej T, Levin M D, Marder S R, McCord-Maughon D, Perry J W, Röckel H, Rumi M, Subramaniam G, Webb W W, Wu X L and Xu C 1998 *Science* **281** 1653

[24] Lin N, Zhao X, Yang J X, Jiang M H, Liu J C, Wang C K, Shi W, Meng J and Weng J 2006 *J. Chem. Phys.* **124** 024704