One- and two-photon absorption properties of two metalloporphyrin complexes*

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The linear and nonlinear optical properties of two metalloporphyrin complexes formed by the complementary coordination of central zinc or magnesium ions to the ligand 5, 10, 15-tri-(*p*-tolyl)-20-phenylethynylporphyrin are theoretically investigated by using the analytic response theory at the density functional theory level. The results indicate that the studied complexes present more symmetric geometry structures than the ligand. The charge-transfer states of the two complexes in the lower energy region are all almost degenerate but those of the ligand are well separated. The ratio of the two-photon absorption cross sections of the ligand, zinc-porphyrin and magnesium-porphyrin complexes is 1.0:1.5:1.8, demonstrating that the two-photon absorption capability can be greatly increased when the ligand is coordinated with a metal ion. Moreover, several physical micro-mechanisms including electron transitions and intramolecular charge-transfer processes are discussed to explore the differences in optical property between the ligand and two complexes.

Keywords: two-photon absorption, metalloporphyrin complexes, analytic response theory

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1. Introduction

Two-photon absorption (TPA) is an important nonlinear optical process related to the interaction of intense laser radiation with matter, where two photons with either the same or different energies can be absorbed simultaneously. The TPA process possesses the unique characteristics of long-wavelengh light absorption and short-wavelengh light emission, and the TPA probability is quadratically dependent on the incident light intensity. So, a material with a large TPA cross section has lots of applications in optical limiting,[1] three-dimensional optical data storage,[2,3] photodynamic therapy,[4] upconverted lasing,[5] and two-photon excited fluorescence microscopy.[6−8] In the recent decades, studies concerning TPA active materials have mainly focused on organic molecular materials with delocalized π-conjugation system, which show many advantages, such as large nonlinear optical coefficient, wide response wave-band, fast response speed, high optical damage threshold and easy combination. Lots of effort[9−19] both in theory and experiment have been made to establish the "structure-to-property" relation, as the strategy and the guideline for the design and the synthesis of the excellent TPA chromophores.

A metal complex comprised of a metal centre and a surrounding organic ligand not only has the advantages of an organic molecular material, but also has better thermal and chemical stabilities. Moreover, the charge transfer (CT) between the metal ion and the ligand can enhance the electronic delocalization of the system, and the nonlinear optical property of metal complex can be easily modified by changing the central metal ion. Therefore, metal complexes have been regarded as a promising nonlinear optical material. However, not much attention has been paid to the TPA properties of metal complexes. Recently, Seo *et al.*[20] reported the synthesis and the spectroscopic characterizations of a series of porphyrin and triporphyrin derivatives, they also measured the TPA cross-section values in tetrahydrofuran (THF) by using an open-aperture Z-scan method with ∼ 130 fs pulses and excitation at 800 nm. In the present work, considering the practical calculation difficulty, we choose only the monomeric

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porphyrin compounds namely 5, 10, 15-tri-(*p*-tolyl)-20-phenylethynylporphyrin (marked as H_2P), and [5, 10, 15-tri-(*p*-tolyl)-20-phenylethynylporphyrin]-zinc (ZnP) respectively as well as an analogous metalloporphyrin complex designed theoretically namely [5, 10, 15-tri-(*p*-tolyl)-20-phenylethynylporphyrin]-magnesium (MgP) as the study objects, then investigate the one-photon absorption (OPA) and TPA properties of three compounds. The theoretical results are compared with the available experimental results. Moreover, the CT processes for the excited states are illustrated in order to explore the origin of the molecular optical nature.

2. Computational details

The transition probability of OPA is given by oscillator strength

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

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

In terms of the sum-over-state formulae, the TPA transition matrix element of two-photon resonant absorption excited by a linearly polarized monochromatic beam is expressed as

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

Here $\alpha, \beta = \{x, y, z\}$ and $|j\rangle$ denote all the intermediate states, and ω_j is the excitation energy of the excited state. In principle, the calculation of $S_{\alpha\beta}$ requires information about all excited states, but it is extremely difficult to obtain a complete solution of all eigenstates, even for a single molecular system. Now, a reliable and rigorous theoretical method, the so-called analytic response theory, has been developed to overcome this difficulty, in which the TPA transition matrix element is described by the single residue of the quadratic response function. The TPA cross section is given as follows:[21]

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

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 TPA cross section directly comparable to experimental measurement is defined as

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

where a_0 is the Bohr radius, c_0 is the speed of light, α is the fine structure constant, $h\omega$ 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 and Γ_f is the level broadening of the final state, which is taken as a common value[22] 0.1 eV with a corresponding lifetime of a few femtoseconds.

The GAUSSIAN03 program is used to optimize the molecular geometry structures and compute the electronic structures. The DALTON2.0 quantum-chemical program based on the analytic response theory is employed to compute the TPA cross sections. Moreover, the CT processes on the excited states are depicted by making use of the MOLEKEL program. All calculations are carried out at the hybrid density functional theory (DFT/B3LYP) level with a 6-31G basis set.

3. Results and discussion

3.1. Molecular structure

The geometric structures of the studied molecules are shown in Fig. 1, where the sign M denotes the central hydrogen atom or metal ion. From Fig. 1, one can see that the porphyrin rings are comprised of four pyrrole rings and four methine bridges

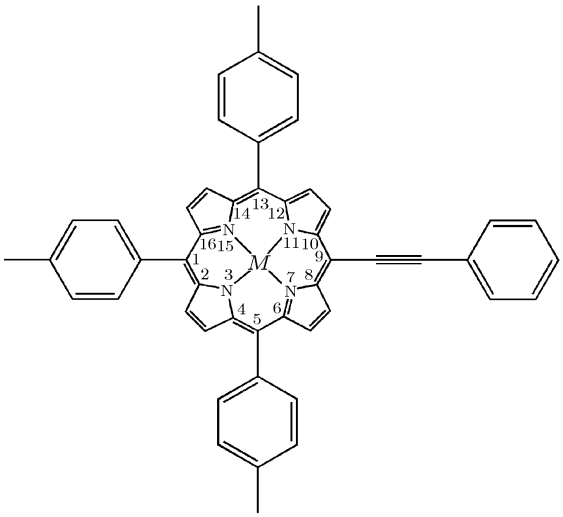


Fig. 1. Geometrical structures of the studied molecules (H_2P: M=2H; ZnP: M=Zn; MgP: M=Mg).

are a macrocyclic conjugated system facilitating the π-electron delocalization. The metalloporphyrin complexes ZnP and MgP are formed by replacing the hydrogen atoms of H_2P with zinc and magnesium ions, respectively.

The optimized results indicate that for each compound, the porphyrin ring and the phenyl ring linked by alkynyl bridge are coplanar while other three tolyl groups all deviate from the porphyrin centre with about 68° dihedral angle. Table 1 lists the calculated bond lengths of inner porphyrin rings and diagonal N–N distances for three compounds. In comparison with the case of H_2P, the C–N bonds of ZnP are stretched and the C–C bonds are compressed, while the C–N and C–C bonds of MgP are all slightly lengthened. The corresponding bond length alterations (BLA) are respectively 0.0298, 0.0174, and 0.0215 Å (1 Å=0.1 nm) for H_2P, ZnP, and MgP, which shows that ZnP and MgP have more delocalized electronic density distributions in porphyrin rings than H_2P. In addition, the same distance of N–N for each complex is observed, owing to the covalent-bond interactions between the metal centre and nitrogen atoms. So, ZnP and MgP exhibit more symmetrical porphyrin ring structures than H_2P. From the above analysis, one can conclude that the extended π-conjugations and symmetric porphyrin structures will be helpful for improving the OPA and TPA abilities of ZnP and MgP.

Table 1. Selected bond lenghs/Å of the studied molecules (1 Å=0.1 nm).

	H_2P	ZnP	MgP
C1–C2	1.4097	1.4064	1.4108
C2–N3	1.3842	1.3919	1.3910
N3–C4	1.3826	1.3907	1.3897
C4–C5	1.4120	1.4084	1.4129
C5–C6	1.4040	1.4038	1.4079
C6–N7	1.3886	1.3949	1.3941
N7–C8	1.3803	1.3845	1.3834
C8–C9	1.4125	1.4133	1.4178
C9–C10	1.4182	1.4133	1.4178
C10–N11	1.3747	1.3844	1.3834
N11-C12	1.3884	1.3949	1.3941
C12–C13	1.4064	1.4038	1.4079
C13–C14	1.4086	1.4084	1.4129
C14–N15	1.3853	1.3907	1.3897
N15–C16	1.3862	1.3919	1.3910
C16–C1	1.4066	1.4064	1.4108
N3–N11	4.0845	4.0948	4.1272
N7–N15	4.2234	4.0947	4.1272

3.2. One-photon absorption

The excited energies, wavelengths and oscillator strengths of the lowest ten excited states of all compounds are summarized in Table 2. The maximum OPA wavelengths of H_2P and ZnP measured in THF solvent are shown in parentheses.

Table 2. OPA properties of the studied molecules.

	ω/eV	λ_{opa}/nm	δ_{opa}/arb. units		ω/eV	λ_{opa}/nm	δ_{opa}/arb. units		ω/eV	λ_{opa}/nm	δ_{opa}/arb. units
H_2P	2.05	606	0.13	ZnP	2.20	563	0.24	MgP	2.15	576	0.25
	2.20	564	0.19		2.23	557	0.02		2.18	569	0.02
	3.04	408	0.94		3.00	413	0.01		3.09	401	1.05
	3.13	397(432)*	1.27		3.10	400	0.94		3.09	401	1.62
	3.19	389	0.11		3.11	399(439)*	1.60		3.37	368	0.10
	3.30	376	0.17		3.16	393	0.06		3.44	360	0.12
	3.37	368	0.27		3.39	366	0.10		3.48	356	0.03
	3.44	360	0.05		3.45	360	0.12		3.56	349	0.01
	3.50	354	0.02		3.52	353	0.00		3.58	346	0.08
	3.60	344	0.17		3.57	347	0.00		3.64	340	0.03

*Experimental results in THF solvent, cited from Ref. [20]

As shown in Table 2, each compound has two obvious CT states at about 400 nm due to the macrocyclic π-conjugated centre, namely, the third and fourth excited states for H_2P and MgP while the fourth and fifth excited states for ZnP. Among them, the strongest CT states of H_2P, ZnP, and MgP are, respectively, located at 397, 399, and 401 nm, and the corresponding oscillator strengths are, respectively, 1.27, 1.60, and 1.62. It is thus manifested that the metal-ligand interactions can greatly enhance the OPA intensities. In addition, experimental measurements show that the maximum OPA wavelengths of

H_2P and ZnP are, respectively, 432 and 439 nm, which are consistent with the corresponding theoretical results in the slight red-shift tendency. However, there is a difference of about 40 nm between the theoretical and the experimental data, which is possibly derived from the fact that in the numerical simulations only the single molecule in gas phase is considered, but the experimental measurements are implemented in THF solvent where the solvent effects cannot be neglected.

It is noteworthy that the CT states of ZnP and MgP are all degenerate, while those of H_2P are well separated. It can be well understood by the electron transition natures shown in Table 3. At the same time, the dominating molecular orbital energy-levels that involve the electronic transitions are schemed in Fig. 2, including HOMO-4, HOMO-3, HOMO-2, HOMO-1, HOMO (the highest occupied molecular orbital), and LUMO (the lowest unoccupied molecular orbital), LUMO+1 and LUMO+2. One can see that for each compound, the LUMO and the LUMO+1 are almost degenerate, obviously apart from the LUMO+2 level. Analogously, three contiguous energy levels HOMO-2, HOMO-3 and HOMO-4 are also degenerate, well-separated from HOMO-1 level. In addition, the energy gaps between the HOMO and HOMO-1 are slightly larger and may not be ignored. From Table 3, the OPA nature of the third excited state of H_2P is related to eight transition configurations while that of the fourth excited state is mainly dependent on five configurations, which will contribute to the bigger energy gap between the third and fourth states. With regard to ZnP, the transition natures of two CT states show a minor difference. Especially for MgP, the orbital-transition configurations of the third and fourth excited states are almost similar, respectively, from HOMO-9, HOMO-2, HOMO-1, HOMO to degenerate LUMO and LUMO+1, which is the reason why two CT states of MgP are completely degenerate.

Table 3. Electronic transition properties of CT states.

	CT states	Configuration coefficient
H_2P	S_3	–0.18(H-4,H-2→L) 0.12(H-4→L+1) 0.15(H-3→L) 0.32(H-1→L,L+1) –0.12(H→L) 0.19(H→L+1)
	S_4	0.21(H-2→L) 0.33(H-1→L) –0.32(H-2→L+1) 0.14(H→L) 0.20(H→L+1)
ZnP	S_4	0.19(H-3→L+1) –0.12(H-2→L+1) 0.43(H-1→L) 0.32(H→L+1)
	S_5	0.27(H-2→L) 0.47(H-1→L+1) –0.24(H→L)
MgP	S_3	0.10(H-9→L+1) –0.16(H-2→L+1) 0.45(H-1→L) 0.32(H→L+1)
	S_4	–0.11(H-9→L) 0.27(H-2→L) 0.48(H-1→L+1) –0.23(H→L)

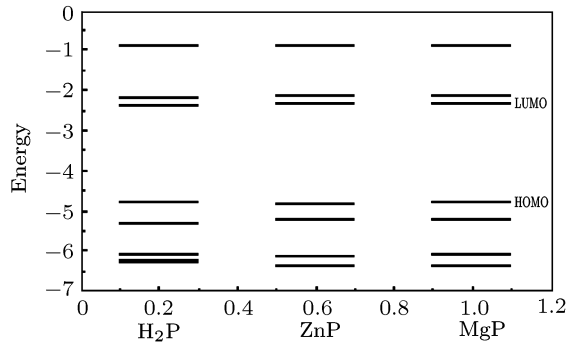


Fig. 2. Molecular orbital energy-levels of the studied molecules.

3.3. Two-photon absorption

Taking into account the difficulty in practical calculation, only the TPA properties of the lowest ten excited states are discussed, the calculated TPA cross sections and the corresponding wavelengths are listed in Table 4. By carrying out the Lorenz expands of the TPA cross sections, we obtain the TPA spectra illustrated in Fig. 3. It is shown that all investigated compounds display a relatively broad TPA spectra in the lower energy region because of several active TPA states. For example, the TPA spectrum of H_2P is formed by three consecutive two-photon excited states, and those of ZnP and MgP are mainly determined by two dominating TPA states. Among them, the highest TPA peaks of H_2P, ZnP, and MgP are respectively located at 749, 730, and 734 nm, with a slight blue-shift tendency, which is opposite to the OPA case. Moreover, the maximal TPA peak values are, respectively, 464.5, 688.1, and 840.7 GM (1 GM=10^{-50} cm^4·s), with a value ratio 1.0:1.5:1.8. So it can be concluded that the metal-ligand interactions by four coordination bands can greatly enhance the TPA cross sections of complexes.

Table 4. TPA properties of the studied molecules.

	λ_{TPA}/nm	$\sigma_{TPA}/10^{-50}$ cm^4·s		λ_{TPA}/nm	$\sigma_{TPA}/10^{-50}$ cm^4·s		λ_{TPA}/nm	$\sigma_{TPA}/10^{-50}$ cm^4·s
H_2P	1206	1.6	ZnP	1124	0.3	MgP	1150	0.3
	1124	1.7		1109	3.1		1134	3.0
	814	9.0		822	0.0		800	1.1
	790	11.1		798	0.9		800	29.3
	775	2.6		795	29.6		734	840.7
	749(800)*	464.5(540)*		783	0.1		719	0.7
	734	215.6		730(800)*	688.1(630)*		711	2.4
	719	452.7		717	0.2		695	344.6
	707	9.5		703	5.2		691	44.8
	687	13.0		693	580.1		679	14.7

*Experimental results in THF solvent, cited from Ref. [20]

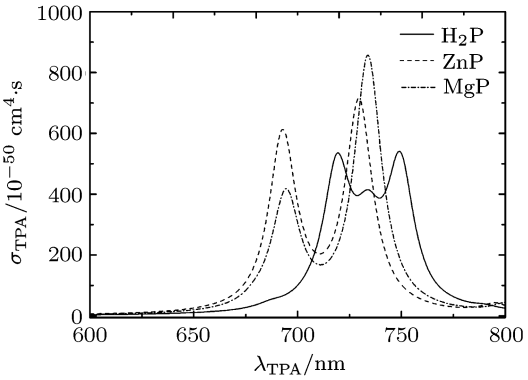


Fig. 3. TPA spectra of the studied compounds.

In order to explore the origin of the TPA properties, we analyse the charge density distributions of studied molecules on the ground states. Table 5 lists the Mulliken charges of the nitrogen atoms, central hydrogen atoms and metal ions. The results by the quantum chemistry calculations indicate that charges mainly float from the porphyrin rings to the terminal phenylacetylene groups, while three tolyl groups almost do not involve the charge moving. Furthermore, it is found that the bonds of metal ions to ligand H_2P greatly change the charge distributions of nitrogen atoms but have little influence on those of carbon atoms of porphyrin rings. For example, N7 and N15 atoms of H_2P have more negative charges than N3 and N11 atoms because of being attached to hydrogen atoms, which results in the unsymmetric porphyrin-ring configuration. However, for each metalloporphyrin complex, the Mulliken charges of nitrogen atoms are almost equal due to the covalent-band interactions between the metal ions and nitrogen atoms, so a more symmetric porphyrin-ring structure than that of H_2P is observed. On average, the whole porphyrin rings act as the main electron-donating regions for all compounds and the capabilities of losing electrons are in the order of H_2P<ZnP<MgP. In conclusion, the metal-ligand interactions influence the molecular structures and the intensities of intramolecular CT in the ground states, which plays an important role in enhancing the TPA cross sections.

Table 5. Mulliken charges (in atomic unit a.u.) of selected atoms and porphyrin rings of studied molecules.

	N3	N7	N11	N15	H (-N7)	H (-N15)	Zn	Mg	Porphyrin ring
H_2P	–0.5660	–0.7922	–0.5717	–0.7879	0.4037	0.4027			0.3693
ZnP	–0.7037	–0.7096	–0.7096	–0.7037			0.9626		0.3702
MgP	–0.7579	–0.7634	–0.7634	–0.7579				1.1741	0.3792

In addition, the values of the experimental measurement implemented in THF at 800 nm are shown in parentheses. One can see that the measured TPA cross sections of H_2P and ZnP are, respectively, 540 GM and 630 GM, which are in good agreement with the corresponding theoretical results both from the values and the tendency. It is effectively demonstrated that the response theory method adopted in this work is very reliable for the numerical simulations of molecular TPA feature.

3.4. Charge-transfer process

It is well known that charge will be redistributed when a molecule is excited from the ground to the CT states. For a better understanding of the CT process, the charge density differences between the ground and the strongest one-photon excited states of the studied molecules are calculated and graphically described by use of the MOLEKEL program, as illustrated in Fig. 4. The black and grey areas, respectively, indicate the electron gain and loss. One can see that upon excitations, charges are mainly transferred from the phenylacetylene groups to the central porphyrin rings. It is also noted that carbon atoms rather than nitrogen atoms or central metal ions of porphyrin rings take part in the dominating CT processes. These observations are different from the cases of the ground states.

In addition, the calculations indicate that the charge density differences between the ground and CT states of phenylacetylene groups are 0.0844, 0.1345, and 0.1338 a.u. (in atomic unit), respectively for H_2P, ZnP, and MgP, namely, the donors of ZnP and MgP have more powerful capabilities of pushing electrons than donor of H_2P. Then the stronger CT intensities upon excitations improve the TPA properties of ZnP and MgP.

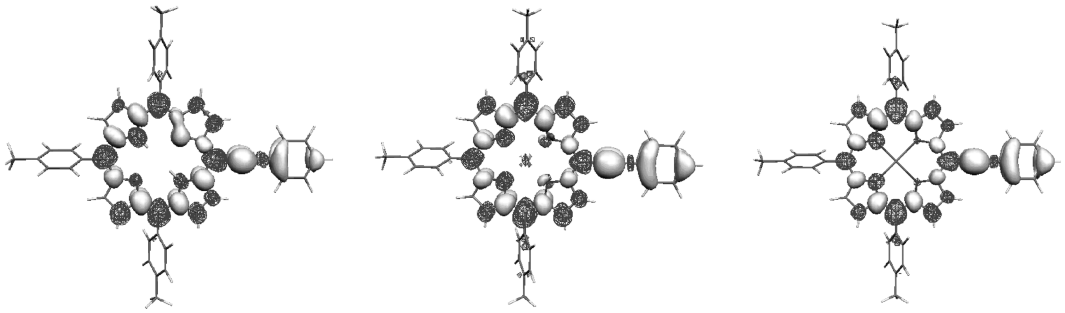


Fig. 4. Charge density differences between the ground and the strongest CT states of studied molecules.

4. Conclusion

In the present work, we theoretically investigate the linear and the nonlinear optical properties of two metalloporphyrin complexes ZnP and MgP by utilizing the analytic response theory at the DFT/B3LYP level, and compared them with those of the ligand H_2P. The results indicate that all molecules have strong OPA and TPA capabilities in broad energy regions. In comparison with H_2P, ZnP, and MgP display very symmetrical porphyrin ring structures because of the metal-ligand interactions by the covalent bonds between the nitrogen atoms and metal ions, which benefits the extended π-conjugated delocalization. Furthermore, the metal-ligand interactions also greatly increase the intensities of intramolecular CT both in the ground state and in the excited state, which plays a key role in the enhancement of TPA cross sections. The theoretical results are in good agreement with the available experimental results.

References

[1] Tutt L W and Kost A 1992 *Nature* **356** 225
[2] Belfield K D, Ren X B, van Stryland E W, Hagan D J, Dubikovsky V and Miesak E J J 2000 *J. Am. Chem. Soc.* **122** 1217
[3] He G S, Markowicz P P, Lin T C and Prasad P N 2002 *Nature* **415** 767
[4] Bhawalkar J D, Kumar N D, Zhao C F and Prasad P N 1997 *J. Clin. Laser Med. Surg.* **15** 201
[5] Tian Y P, Hao F Y, Wu J Y, Fang Q and Jiang M H 2001 *Chin. Chem. Lett.* **12** 631
[6] He G S, Tan L S, Zheng Q D and Prasad P N 2008 *Chem. Rev.* **108** 1245
[7] Denk W, Strickler J H and Webb W W 1990 *Science* **248** 73
[8] Lin Z Y, Fu Z, Liu L X, Hu T, Qu J L, Guo B P and Niu H B 2006 *Acta Phys. Sin.* **55** 6701 (in Chinese)
[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] Fisher J A N, Susumu K, Therien M J and Yodh A G 2009 *J. Chem. Phys.* **130** 134506
[11] Huang X M, Tao L M, Guo Y H, Gao Y and Wang C K 2007 *Acta Phys. Sin.* **56** 2570 (in Chinese)
[12] Wang C K, Zhang Z, Ding M C, Li X J, Sun Y H and Zhao K 2010 *Chin. Phys.* B **19** 103304

[13] Zheng Q D, Gupta S K, He G S, Tan L S and Prasad P N 2008 *Adv. Funct. Mater.* **18** 2770

[14] Li W C, Feng J K, Ren A M, Zhang X B and Sun C C 2009 *Chin. Phys.* B **18** 2271

[15] Kim H M, Lee Y O, Lim C S, Kim J S and Cho B R 2008 *J. Org. Chem.* **73** 5127

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

[17] Sun Y H and Wang C K 2009 *Acta Phys. Sin.* **58** 5304 (in Chinese)

[18] Collings J C, Poon S Y, Droumaguet C L, Charlot M, Katan C, Pålsson L O, Beeby A, Mosely J A, Kaiser H M, Kaufmann D, Wong W Y, Blanchard-Desce M and Marder T B 2008 *Chem. Eur. J.* **15** 198

[19] Sun Y H, Li L H, Li J and Wang C K 2010 *Chin. Phys.* B **19** 083102

[20] Seo J W, Jang S Y, Kim D and Kim H J 2008 *Tetrahedron* **64** 2733

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

[22] 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