Influence of rotational isomerism on two-photon absorption properties of FTC chromophores*

Han Guang-Chao(韩广超), Zhao Ke(赵 珂)†, Liu Peng-Wei(刘朋伟), and Zhang Li-Li(张立立)

College of Physics and Electronics, Shandong Normal University, Jinan 250014*, China*

(Received 18 March 2012; revised manuscript received 27 May 2012)

The influence of rotational isomerism on the two-photon absorption (TPA) of FTC chromophores has been investigated using the quadratic response theory with the B3LYP functional. Eight rotamers induced by three rotatable single bonds in the molecule are fully optimized, and it is found that their conformational energies are nearly degenerate. Our calculations demonstrate that rotational isomerism has an important effect on the TPA cross sections. For a certain rotamer, the maximum TPA cross section is enhanced significantly. In addition, in the longer wavelength region, the rotational isomerism could lead to a large shift of the TPA position.

Keywords: rotational isomerism, two-photon absorption, organic molecule

PACS: 82.30.Qt, 33.80.Wz, 42.65.–k **DOI:** 10.1088/1674-1056/21/11/118201

1. Introduction

Substantial research effort has been devoted to the design of organic molecules exhibiting desirable two-photon absorption (TPA) responses because of their applications.[1−6] The theoretical investigations of the so-called structure-to-property relationships could provide a useful guidance for molecular synthesis. It has been revealed that the linear and the nonlinear optical (NLO) properties of TPA active chromophores could be modified via controlling the molecular architecture and substituent groups.[7−11] Several structural factors, such as the electron richness and planarity of the π-conjugation center, the molecular symmetry, the conjugated length and dimensionality, as well as the strengths of donor and accepter substituents, play significant roles in enhancing the TPA activities of many organic molecules. In addition, the solvent environment[12−14] and the formation of aggregates[15,16] could also strongly influence the TPA properties.

Recently, the effect of isomerism on the NLO properties has been investigated,[17−21] and has drawn our attention.[20,21] Arnbjerg *et al.*[18] reported that the TPA cross section of porphycene is significantly larger than that of its isomer, porphyrin, due to the phenomenon of resonance enhancement. Guillaume *et al.*[19] studied the effects of conformational averaging on one- and two-photon absorptions and the circular dichroism of (L)-tryptophan. The comparison between the Maxwell–Boltzmann (MB) weighted spectra and the experimental linear spectroscopies turned out to be rather satisfactory. In our recent study,[21] the effects of isomerism on the TPA for several X-shaped molecules have been investigated, and our calculations exhibited that the geometrical isomers possess quite different TPA properties and the rotational isomerism has non-negligible effects on the absorption position and intensity.

Unlike geometrical isomerism that can be easily controlled by the synthetic chemist, rotational isomerism cannot be obtained with the same certainty. Many organic NLO materials can have thermal populations of rotational isomers (rotamers) with different optical properties in real applications. In the work of Kinnibrugh *et al.*,[17] the influence of rotational isomerism on the first-order hyperpolarizability of 2-dicyanomethylen-3-cyano-4-{2-[E-(4-N,N-di(2-acetoxyethyl)-amino)-phenylene-(3,4-dibutyl)-thien-5]-E-vinyl}-5,5-dimethyl-2,5-dihydrofuran (FTC) chromophores have been investigated, and their calculations indicated that the conformational averaging of flexible molecules should not be neglected. In order to further explore the effects of rotational isomerism on the TPA properties, in the present work, we also take the FTC as a model molecule. The TPA cross sections of the most probable rotamers are calculated using the quadratic response theory.

*Project supported by the Young Scientists Fund of the National Natural Science Foundation of China (Grant No. 10904085).

†Corresponding author. E-mail: zhaoke@sdnu.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

2. Computational methods

The transition matrix element of the two-photon resonant absorption excited by a linearly polarized monochromatic beam is expressed as[22]

$$S_{\alpha\beta} = \sum_s \left(\frac{\langle i|\,\mu_\alpha\,|s\rangle\,\langle s|\,\mu_\beta\,|f\rangle}{\omega_{si} - \omega_1} + \frac{\langle i|\,\mu_\beta\,|s\rangle\,\langle s|\,\mu_\alpha\,|f\rangle}{\omega_{si} - \omega_2} \right), \tag{1}$$

where $\mu_{\alpha(\beta)}$ is the electric dipole moment operator, $|s\rangle$ denotes all the intermediate states including the ground state $|i\rangle$ and the final state $|f\rangle$, $\hbar\omega_{si}$ is the excitation energy from state $|i\rangle$ to state $|s\rangle$. Here, $\omega_1 = \omega_2 = \omega_f/2$, and $\hbar\omega_f$ is the excitation energy of the final state. The TPA cross section is then given by[22,23]

$$\begin{aligned}\delta_{\rm tpa} = & \sum_{\alpha\beta}[F \times S_{\alpha\alpha}S^*_{\beta\beta} + G \times S_{\alpha\beta}S^*_{\alpha\beta} \\ & + H \times S_{\alpha\beta}S^*_{\beta\alpha}],\end{aligned} \tag{2}$$

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

The TPA cross section directly comparable to the experimental measurements is defined as[23]

$$\sigma_{\rm tpa} = \frac{4\pi^2 a_0^5 \alpha_0}{15 c_0} \frac{\omega^2 g(\omega)}{\Gamma_f} \delta_{\rm tpa}, \tag{3}$$

where a_0 is the Bohr radius, c_0 is the speed of light, α_0 is the fine structure constant, $g(\omega)$ denotes the spectral line profile, which is assumed to be a δ function here, and Γ_f is the lifetime broadening of the final state, which is generally taken to be 0.1 eV.[24]

According to the Boltzmann distribution, the probability of each molecular conformation with energy E_α at temperature T can be calculated by the corresponding MB weight X, which is expressed as

$$X = \frac{\exp[-(E_\alpha/kT)]}{\sum\limits_\alpha \exp[-(E_\alpha/kT)]}, \tag{4}$$

where k is Boltzmann's constant, and the summation runs over all possible conformers.

The geometry optimizations of all conformers are performed at a hybrid density functional theory (B3LYP) level with the 6-31G(d,p) basis set[25] utilizing the Gaussian03 program.[26] The 6-31+G(d,p) basis set is used to obtain the single point energies on the optimized geometries. The TPA cross sections are calculated at the same level with the 6-31G(d) basis set through a residue of quadratic response function using the Dalton program.[27] Our previous works[13,28,29] have shown that this basis set is appropriate for molecules of large sizes. The use of larger basis sets could probably provide better numerical results, but we believe that the overall picture would not change.

3. Results and discussion

3.1. Molecular structures

The structural formula of the FTC molecule is depicted in Fig. 1. By inspecting the structure, one can realize that there are three rotatable single bonds along the conjugated backbone: two bonds connecting the thiophene and the vinyl units (indicated by A and B in Fig. 1.), and one joining the vinyl unit and the substituted furan ring (labeled as C). It is these rotatable single bonds that can give rise to a set of rotamers.

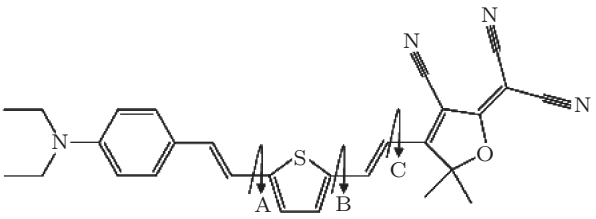


Fig. 1. Structural formula of the FTC chromophore. The rotatable single bonds are labeled as A, B, and C.

With different initial conformations, the most probable rotamers are fully optimized, and the convergent geometries are shown in Fig. 2. For each of the rotatable single bonds, two rotational states located near 0° and 180° are denoted by transoid (trans) and cisoid (cis) to distinguish the orientations of the hydrogen atoms adjacent to the rotatable bonds, as illustrated in Fig. 2. It should be mentioned that the geometrical cis–trans isomerism of the double bonds is not considered here. The optimizations show that eight low-energy conformers are obtained by various combinations of the hydrogen atom orientations. It is noticed that these rotamers have different structural characters. The angle between the branch with the benzene and the one with the furan ring is quite different among these structures. For example, it is obvious that conformer ttt has a considerable angle between those two branches, while conformers cct and ccc each have a nearly linear backbone. Such a different conjugation could lead to different absorption properties. In addition, the rotation about bond C at the furan ring could produce different strengths for the electron acceptor groups.

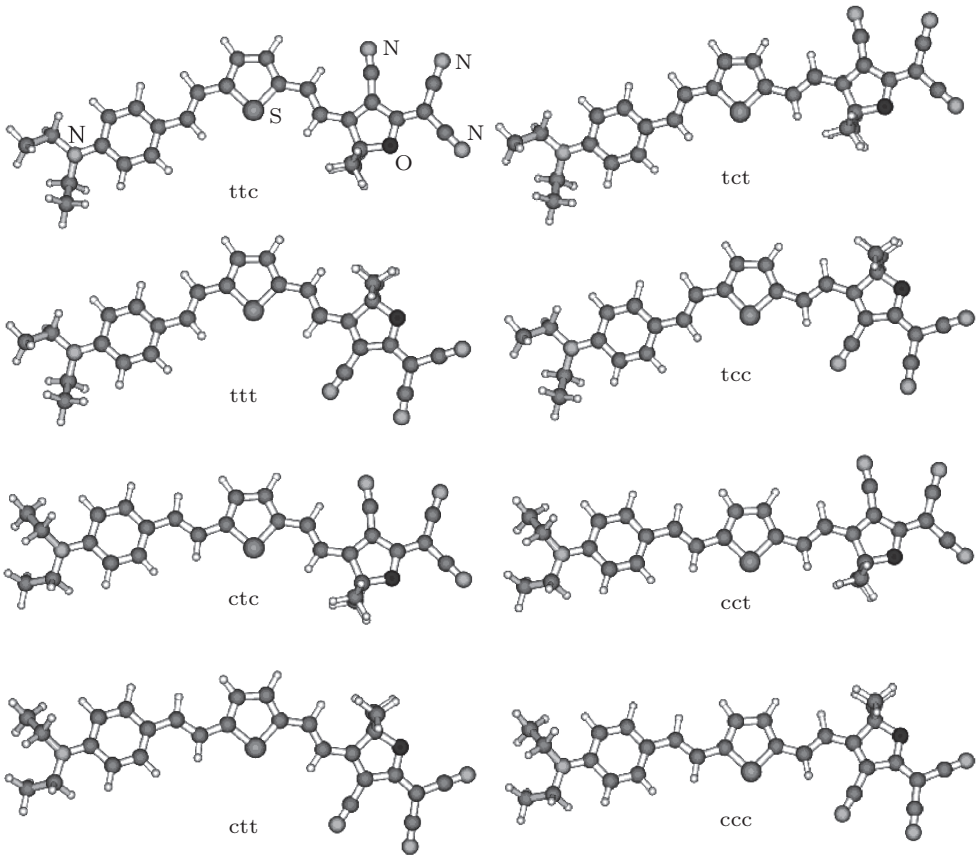


Fig. 2. Optimized structures of FTC rotamers.

The permanent dipole moments and the energies of the eight rotamers are examined, and the results are listed in Table 1. According to Eq. (1), it is known that the TPA transition matrix element is determined by the electronic structures including the dipole moments and the excitation energies. Table 1 reveals that the permanent dipole moments of the rotamers range from 20.31 D to 23.12 D. The conformer ctc has the largest dipole moment, and the conformer ttt has the smallest one due to the lack of linear backbone. By the calculation of single point energy on the optimized geometries using a bigger basis set 6-31+G(d,p), it is found that ttc has the lowest energy among these rotamers, and the energy differences between the other structures and ttc are very small in general. The two barriers for ttt and ctc are only 0.34 kcal/mol and 0.88 kcal/mol, respectively. Such small energy barriers indicate that these rotamers could be thermally populated. The corresponding MB weights are calculated at room temperature (T = 298.15 K), and the values are also given in Table 1. One can see that the conformers with small energy differences can be populated at certain percentages, such as 28.27% for ttt and 11.17% for ctc. The ttc, which has the lowest energy, only takes up 50.76%. By carefully analyzing the structures and the energies of the rotamers, it is interesting to find that the rotational potentials of bond B are higher than those of bond A and the rotations about bond C have the lowest barriers. The specific rotations about bonds A, B, and C are shown in Table 2, along with the corresponding rotational potentials.

Table 1. Values of permanent dipole moments μ, energy differences ΔE, and Maxwell–Boltzmann weights X for the FTC rotamers.

Conformer	μ/D	ΔE/kcal·mol^{-1}	$X/10^{-2}$
ttc	22.76	0.00	50.76
ttt	20.31	0.34	28.27
ctc	23.12	0.88	11.17
ctt	21.65	1.43	4.37
tct	22.88	1.72	2.64
tcc	20.72	1.98	1.68
cct	23.04	2.47	0.71
ccc	21.84	2.83	0.40

Table 2. Rotations about bonds A, B, and C and the corresponding rotational potentials ΔE.

	Rotation	ΔE/kcal·mol^{-1}
A	ttc→ctc	0.88
	ttt→ctt	1.09
	tct→cct	0.75
	tcc→ccc	0.85
B	ttc→tct	1.72
	ttt→tcc	1.64
	ctc→cct	1.59
	ctt→ccc	1.40
C	ttc→ttt	0.34
	ctc→ctt	0.55
	tct→tcc	0.26
	cct→ccc	0.36

3.2. Two-photon absorption

The TPA cross sections of the five lowest excited states of all rotamers are calculated, and the results are presented in Table 3. For all rotamers, the first, second, and the fourth excited states have considerable TPA intensities, and the largest cross sections appear at the fourth excited states. The second and the fourth excited states have drawn our attention, because they are located in the experimentally measurable wavelength region.

For the second excited states, the TPA intensities are in the order cct>ctc>ccc>tct>ctt>ttc>tcc>ttt. The difference between the maximum and the minimum cross sections is large, which is 569.2 GM (1 GM=10^{-50} cm^4·s·photon^{-1}), about 35% of the maximum. An inspection of the structures of the rotamers quickly reveals the reason for the trend. The cct, ctc, ccc, and tct have superior linear structures in comparison with ctt, ttc, tcc, and ttt. The calculations also show that the rotations about bond C at the furan ring, which are specified in Table 2, always bring about the decreases of the cross sections. That is, the TPA cross sections of the second excited states are characterized by ttc>ttt, ctc>ctt, tct>tcc, and cct>ccc. This result indicates that the furan ring with the orientation in ttc is more advantageous to the charge transfer than that in ttt. From the viewpoint of absorption wavelength $\lambda_{\rm tpa}$, we find that the absorption positions of the rotamers range from 909 nm to 940 nm, which means that the absorption bands have large shifts between each other. Both ctt and cct have an intensive TPA at 909 nm, while the absorption wavelength of tcc is 940 nm, which has a red-shift of 31 nm with respect to ctt or cct.

Table 3. Values of the TPA cross section $\sigma_{\rm tpa}$ (GM) and the TPA wavelength $\lambda_{\rm tpa}$ (nm) of the five lowest excited states for the FTC rotamers.

ttc		ttt		ctc		ctt		tct		tcc		cct		ccc	
$\lambda_{\rm tpa}$	$\sigma_{\rm tpa}$	$\lambda_{\rm tpa}$	$\sigma_{\rm tpa}$	$\lambda_{\rm tpa}$	$\sigma_{\rm tpa}$	$\lambda_{\rm tpa}$	$\sigma_{\rm tpa}$	$\lambda_{\rm tpa}$	$\sigma_{\rm tpa}$	$\lambda_{\rm tpa}$	$\sigma_{\rm tpa}$	$\lambda_{\rm tpa}$	$\sigma_{\rm tpa}$	$\lambda_{\rm tpa}$	$\sigma_{\rm tpa}$
1212	600.8	1230	657.3	1183	653.1	1195	788.2	1237	870.7	1243	667.5	1206	917.8	1206	745.4
937	1353.6	916	1079.2	930	1638.7	909	1415.2	916	1463.9	940	1226.8	909	1648.4	933	1513.1
788	59.4	783	120.8	783	42.7	778	76.3	785	42.0	793	87.0	778	37.5	785	69.7
713	5771.3	717	4597.1	715	2763.8	717	2276.8	717	9333.8	715	12020.2	719	3876.7	717	4344.2
658	15.6	667	16.0	649	133.0	654	51.0	663	57.3	667	60.0	654	157.1	654	168.6

For the fourth excited states, it is noticed that the TPA cross sections of the rotamers have significantly different values. The largest cross section of tcc comes to 12020.2 GM, while that of ctt is only 2276.8 GM, which is decreased by about 81% with respect to tcc. In comparison with the cross section of ttc, which has the lowest energy, the values of tct and tcc are enhanced significantly. In addition, it is interesting to see that the excitation energies of the fourth excited states of the rotamers are almost the same and the absorption positions are all located in the vicinity of 715 nm. Since the excitation energies of the state are nearly equal, according to Eq. (1), the great variations of TPA intensity might be attributed to the different electronic structures, such as the permanent and the transition dipole moments relating to this state.

To illustrate the influence of the ratational isomerism clearly, the simulated TPA spectra with Lorentz broadenings are given in Fig. 3. The absorption peaks in the wavelength regions of 650–850 nm and 850–1100 nm are included in Figs. 3(a) and 3(b) respectively because of the different intensity scales. It is obvious that the absorption peaks have quite different intensities in Fig. 3(a), but the absorption positions are at almost the same wavelength. Figure 3(b) shows that rotational isomerism plays an important role in absorption intensities and positions. It is expected that the total TPA spectrum of the FTC chromophore could be broadened in the longer wavelength region if all the possible rotamers are taken into account together.

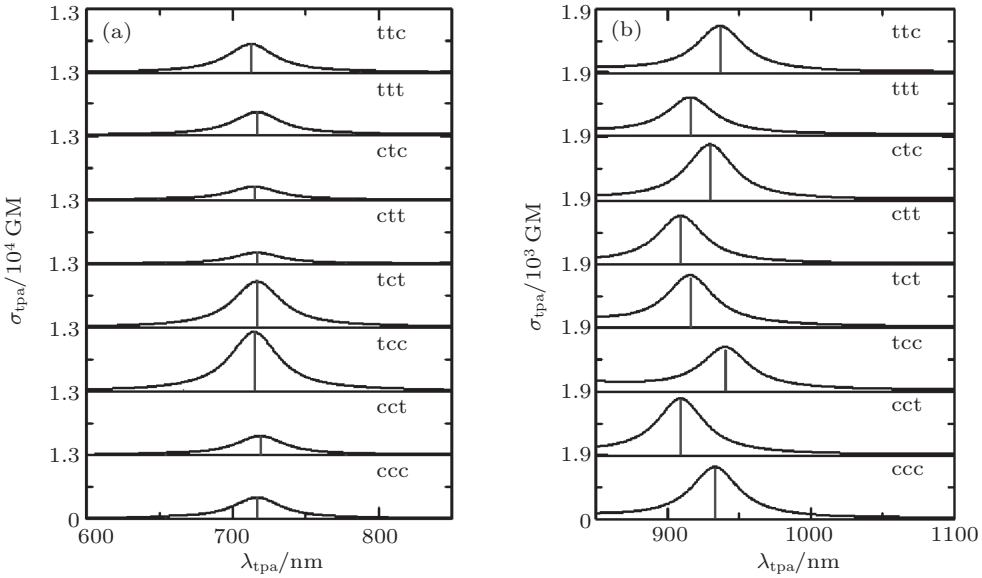


Fig. 3. Simulated TPA spectra of the FTC rotamers in the regions of (a) 600–850 nm and (b) 850–1100 nm.

4. Conclusion

The rotational isomerism effects on the TPA properties of FTC chromophores are examined carefully by employing the quadratic response theory at the B3LYP level. Eight low-energy rotamers are obtained by rotating three rotatable single bonds. It is found that the energy differences between these rotamers are very small above the minimum, which indicates that these rotamers could be thermally populated with considerable MB distributions. Our TPA calculations show that the rotational isomerism has a strong influence on the TPA intensity. At about 715 nm of the TPA wavelength, for a certain rotamer, a large enhancement of the TPA cross section is observed. In the longer wavelength region, the rotational isomerism not only affects the TPA intensity, but also induces the spectral peak position to shift a lot, and thereby broadens the peak width of the averaged spectrum. To the best of our knowledge, the influence of isomerism on the TPA properties has not been investigated extensively at present. Our study could be helpful to understand the NLO properties of many flexible molecules.

References

[1] Starkey J R, Rebane A K, Drobizhev M A, Meng F, Gong A, Elliott A, McInnemey K and Spangler C W 2008 *Clin. Cancer. Res.* **14** 6546

[2] Kim H M and Cho B R 2009 *Acc. Chem. Res.* **42** 863

[3] Dvornikov A S, Walker E P and Rentzepis P M 2009 *J. Phys. Chem.* A **113** 13633

[4] Beverina L, Crippa M, Landenna M, Ruffo R, Salice P, Silvestri F, Versari S, Villa A, Ciaffoni L, Collini E, Ferrante C, Bradamante S, Mari C M, Bozio R and Pagani G A 2008 *J. Am. Chem. Soc.* **130** 1894

[5] Brown S B, Brown E A and Walker I 2004 *Lancet Oncol* **5** 417

[6] He G S, Tan L S, Zheng Q D and Prasad P N 2008 *Chem. Rev.* **108** 1245

[7] Davies J A, Elangovan A, Sullivan P A, Olbricht B C, Bale D H, Ewy T R, Isborn C M, Eichinger B E, Robinson B H, Reid P J, Li X and Dalton L R 2008 *J. Am. Chem. Soc.* **130** 10565

[8] Wang C K, Macak P, Luo Y and Ågren H 2001 *J. Chem. Phys.* **114** 9813

[9] Macak P, Luo Y, Norman P and Ågren H 2000 *J. Chem. Phys.* **113** 7055

[10] Nguyen K A, Day P N and Pachter R 2009 *J. Phys. Chem.* A **113** 13943

[11] Sun Y H and Wang C K 2011 *Chin. Phys.* B **10** 104204

[12] Wang C K, Zhao K, Su Y, Yan R, Zhao X and Luo Y 2003 *J. Chem. Phys.* **119** 1208

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

[14] Wang C K, Xing X J, Huang X M and Gao Y 2007 *Chin. Phys.* **16** 3323

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

[16] Sun Y H, Li J, Zhao K and Wang C K 2010 *Chin. Phys.* B **19** 044207

[17] Kinnibrugh T, Bhattacharjee S, Sullivan P, Isborn C, Robinson B H and Eichinger B E 2006 *J. Phys. Chem.* B **110** 13512

[18] Arnbjerg J, Jiménez-Banzo A, Paterson M J, Nonell S, Borrell J I, Christiansen O and Ogilby P R 2007 *J. Am. Chem. Soc.* **129** 5188

[19] Guillaume M, Ruud K, Rizzo A, Monti S, Lin Z J and Xu X 2010 *J. Phys. Chem.* B **114** 6500

[20] Zhao K and Luo Y 2010 *J. Phys. Chem.* B **114** 13167

[21] Liu P W, Zhao K and Han G C 2011 *Chem. Phys. Lett.* **514** 226

[22] Luo Y, Norman P, Macak P and Ågren H 2000 *J. Chem. Phys.* **104** 4718

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

[24] 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, Maughon D M, Perry J W, Röckel H, Rumi M, Subramaniam G, Webb W W, Wu X L and Xu C 1998 *Science* **281** 1653

[25] Andzelm J, Rinderspacher B C, Rawlett A, Dougherty J, Baer R and Govind N 2009 *J. Chem. Theory Comput.* **5** 2835

[26] Frisch M J, Trucks G W, Schlegel H B, *et al.* 2004 *Gaussian 03* (Revision D.02) (Wallingford: Gaussian Inc.)

[27] Angeli C, Bak K L, Bakken V, *et al.* 2005 *Dalton2.0* (Release 2.0)

[28] Zhao K, Tu Y Q and Luo Y 2009 *J. Phys. Chem.* B **113** 10271

[29] Zhao K, Liu P W, Wang C K and Luo Y 2010 *J. Phys. Chem.* B **114** 10814