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Solvent effect on excited states of merocyanines: A theoretical study using the RISM–SCF method

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ABSTRACT

The solvent effect on the excited states of streptopolymethinemerocyanine (SPMC) was investigated using the RISM–SCF method. The magnitudes of the shifts in both the π–π^* and n–π^* excitation energies caused by solvation were water > methanol > acetonitrile. The analysis of the solvation structure showed that the difference in the interactions between SPMC and solvent molecules produced this order. The correlation between the chain length and the solvent effect on the excitation energy was also investigated. The results showed the excitation energy shift caused by solvation to be nearly equal regardless of the chain length.

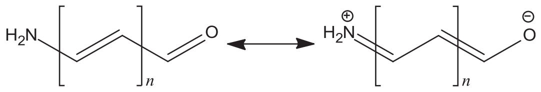
1. Introduction

Solvatochromism is a phenomenon in which the color of the solution depends on the solvent [1,2]. This phenomenon occurs because the electronic structures of solvated molecules are affected by the solvents, and the excitation energies of the molecules are shifted accordingly. A widely known example is 1-methyl-4-[(oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine, which is called Brooker's merocyanine [3,4]. This merocyanine shows different colors depending on the solvent species [4,5]. The magnitude of solvatochromic shift is roughly understood from the polarity of the solvents. However, the microscopic viewpoint is necessary as well as macroscopic properties such as polarity [6,7]. To understand and control the chromism from a microscopic viewpoint, studies on the solvent effect based on molecular theory are crucial.

Solvatochromism of merocyanines has been investigated using quantum chemical calculations coupled with solvent models [8–10]. The solvent models that have been mainly used so far are the polarizable continuum model (PCM) [11], the quantum mechanics/molecular mechanics (QM/MM) method [12], and the reference interaction site model self-consistent field (RISM–SCF) method [13–15]. Guillaume et al. [8] investigated the excitation energies of several merocyanines in methanol, acetonitrile, and dimethyl sulfoxide using the PCM, and they systematically reproduced the experimental results. Gao and Alhambra [9] calculated the excitation energy of 5-(dimethylamino)pentadienal in various solvents using the QM/MM method, and they pointed out that not only the polarity of the solvents but also the local solvation structure, such as hydrogen bonding, was important. Ishida and Rossky [10] examined the electronic structures of a betaine dye using the RISM–SCF method and reproduced the solvatochromic blue shift. They reported in detail the total free energy profiles as well as solvation structures in both the ground and excited states with respect to variation in the reaction coordinate.

The RISM–SCF method is an ab initio molecular orbital theory combined with the RISM integral equation theory [16–19]. In this method, the electronic structures of the solute and the distribution of the solvent are determined self-consistently. The RISM–SCF method allows us to investigate both the electronic structure of a solvated molecule with high-level quantum mechanics theory in the ground and excited states, and the solvation structure with a detailed solute–solvent interaction, such as hydrogen bonding, at the molecular level.

In this Letter, with the use of the RISM–SCF method, we examine the excitation energies of streptopolymethinemerocyanine (SPMC), $H_2N(C_2H_2)_nCHO$, a model merocyanine that has a conjugated chain, in various solvents by systematically changing the chain length. Because SPMC has conjugated chains with heteroatoms at their ends, it can be written as a superposition of neutral and zwitterionic resonance structures.



The ratios of the resonance structures in SPMC are affected by the molecular features of the solvent molecules, and cause the excitation energy shift.

In the present study, we focus on the solvent and chain length dependencies of the excitation energies. The correlation between the excitation energies and the chain length of the molecule, which

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has conjugated chains, has been investigated by several experiments and quantum chemical calculations [20–22]. However, the solvent effect on the correlation between the excitation energies and the chain length has not yet been examined from the microscopic viewpoint.

2. Computational details

SPMC with chain lengths $n = 1$–5 immersed in various solvents at infinite dilution was investigated using the RISM–SCF method. The details of the method can be found in Refs. [13–18]. In the present study, the solute SPMC was treated as a quantum molecule by Kohn–Sham DFT calculations. The long-range corrected Becke one-parameter progressive (LC-BOP) exchange-correlation functional [23] and the correlation-consistent polarized valence double-zeta (cc-pVDZ) basis set were used. The functional was compared with some other functionals and chosen as reproducing the experimental excitation energies of polyenes. The basis set was checked through the calculations in the gas phase using the augmented cc-pVDZ (aug-cc-pVDZ) basis set. The changes in the excitation energies with the extension of the chain length were qualitatively unaltered from those using the cc-pVDZ basis set. The molecular structures were optimized in the gas phase with C_s symmetry. The vertical excitation energies were calculated using time-dependent density functional theory (TD-DFT) in both the gas phase and the solution phase (in water, methanol, and acetonitrile). To extract the pure dependencies on the solvent and the chain length (namely, excluding the dependency on the structure change by solvation), the molecular structures in the gas phase were also used in the solution phase. The RISM equations were solved with the Kovalenko–Hirata (KH) closure [24]. The densities of the solvents are 0.9970 (water), 0.7867 (methanol), and 0.7762 (acetonitrile) g cm^{-3}, which correspond to 0.033316 (water), 0.014781 (methanol), and 0.011383 (acetonitrile) molecules Å^{-3}. The temperature was 298 K. The Lennard-Jones (LJ) parameters and point charges are listed in Table 1. Those of water were taken from the extended simple point charge model (SPC/E) [25]. The OPLS parameters were used for SPMC, methanol, and acetonitrile [26–28]. The LJ parameters of the hydrogen atoms of water, the hydroxyl group of methanol, and the amino group of SPMC were taken from Ref. [29]. The RISM calculations were carried out on a grid of 2048 points with a spacing of 0.01 Å. All of the calculations were performed with a modified version of the GAMESS program package [30,31].

Table 1
The solute and solvent parameters for the RISM–SCF calculations taken from Refs. [24–28].

	σ Å	ε kcal mol^{-1}	q e
SPMC			
H(CH)	2.420	0.030	
H(CHO)	2.420	0.015	
H(NH_2)	0.400	0.046	
C(CH)	3.550	0.076	
C(CHO)	3.750	0.105	
N	3.250	0.170	
O	2.960	0.210	
Water			
O	3.166	0.155	−0.8476
H	0.400	0.046	0.4238
Methanol			
CH_3	3.775	0.207	0.265
O	3.070	0.170	−0.700
H	0.400	0.046	0.435
Acetonitrile			
CH_3	3.775	0.207	0.150
C	3.650	0.150	0.280
N	3.200	0.170	−0.430

3. Results and discussion

3.1. Solvent dependency

Two types of dependency are considered in the present Letter: the solvent dependency and the chain length dependency. In the present subsection, we fix the chain length at $n = 2$ to focus the discussion on the solvent dependency. Figure 1 shows the π–π^* and n–π^* excitation energies of SPMC, and Figure 2 shows the molecular orbitals in the gas phase involved in the excitations. The n orbital is the second HOMO at this chain length. This orbital is well localized around the carbonyl group at the end and contains the lone-pair electrons. The π_1 and π_1^* orbitals are the HOMO and LUMO, respectively, and are delocalized over the whole molecule. As can be seen in Figure 1, the π–π^* excitation energy exhibits a red shift upon solvation, while the n–π^* excitation energy exhibits a blue shift. The red shifts in the π–π^* excitation energy caused by the solvation are 0.28 eV (in water), 0.21 eV (in methanol), and 0.16 eV (in acetonitrile). In contrast, the blue shifts in the n–π^* excitation energy caused by the solvation are 0.59 eV (in water), 0.35 eV (in methanol), and 0.18 eV (in acetonitrile). In other words, the shifts in the n–π^* excitation energy are larger than those in the π–π^* excitation energy. In addition, the largest solvatochromic shift is in water and the smallest is in acetonitrile. These differences in the excitation energy shift as a result of solvation suggest that the water may show larger solute–solvent interactions than those of the other solvents.

To clarify the nature of the solute–solvent interactions, we investigated the radial distribution functions (RDFs), namely the distribution or density of the solvent molecules around SPMC. Figure 3 shows the RDFs of the carbonyl oxygen, amino nitrogen, and amino hydrogen of SPMC. For the RDFs of the carbonyl oxygen atom (the first row of Figure 3), the conspicuous peaks of the hydrogen atom are located at around $r = 1.4$ Å in water and methanol, while those of the oxygen atom are at around $r = 3.0$ Å. These peaks indicate that the hydrogen atoms of the solvent molecules are oriented to the oxygen atom of SPMC, namely the formation of hydrogen bonds. In acetonitrile, the peak of the methyl group is located around $r = 3.3$–3.4 Å, and the distributions of cyanic carbon and nitrogen are found in the vicinity of the peak of the methyl group, but they do not form a single peak. This indicates that the methyl groups of the solvent acetonitrile are weakly oriented to the oxygen atom of SPMC.

The RDFs of the amino hydrogen atom, in the third row of Figure 3, show the peaks of the oxygen atom at $r = 1.4$–1.5 Å in water and methanol. These peaks also suggest the formation of hydrogen bonds between the amino hydrogen atom of SPMC and

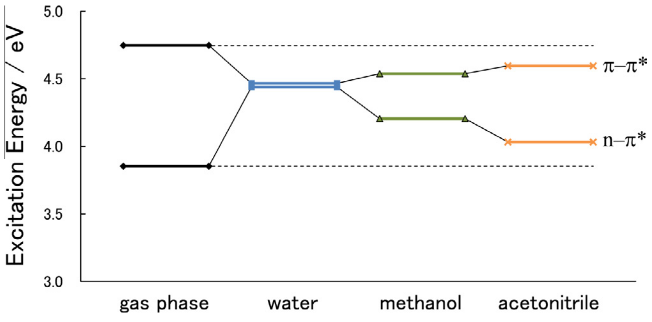

Figure 1. The π–π^* and n–π^* excitation energies of SPMC ($n = 2$) in the gas and solution (water, methanol, and acetonitrile) phases.

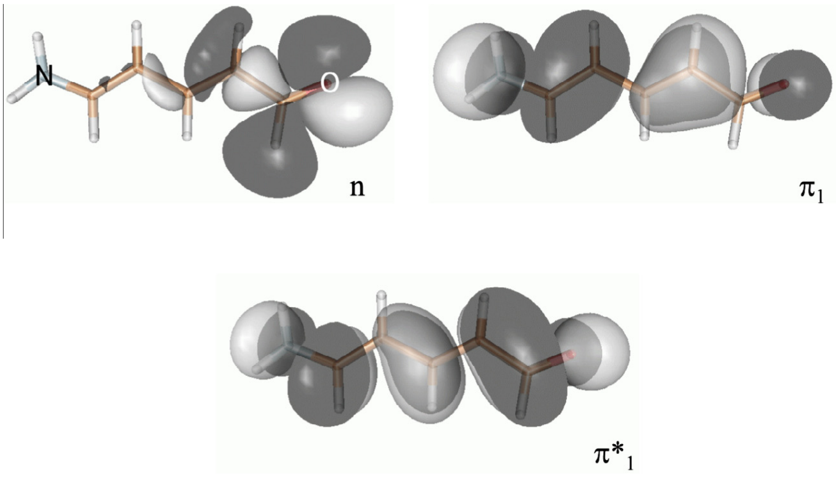

Figure 2. The n, π_1, and π_1^* orbitals of SPMC ($n = 2$) in the gas phase.

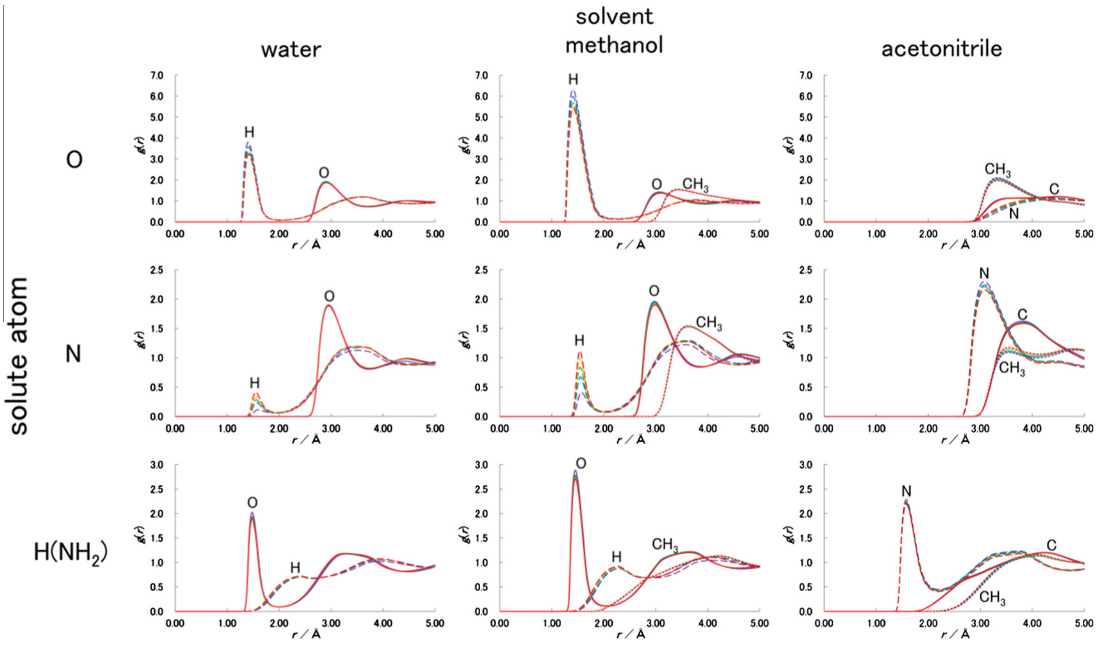

Figure 3. The radial distribution functions around solute SPMC for $n = 1$ (purple), 2 (blue), 3 (green), 4 (orange), and 5 (red). The symbol H(NH$_2$) denotes the amino hydrogen in the trans-position from the methine hydrogen adjacent to the amino group. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the oxygen atoms of the solvent molecules. In the case of acetonitrile, the peak of the nitrogen atom appears at around $r = 1.6$ Å, which indicates the formation of hydrogen bonds. In water and methanol, the RDFs of the nitrogen atom (the second row of Figure 3) have small peaks of the hydrogen atom at $r = 1.5$–1.6 Å. Therefore, the hydrogen atoms of the solvent molecules can come close to the nitrogen atom of SPMC. On the other hand, the RDF of the nitrogen atom has a peak of the cyanic nitrogen of acetonitrile at around $r = 3.1$ Å. This peak may correspond to the distribution of cyanic nitrogen that makes a hydrogen bond with the amino hydrogen of SPMC.

From the features of the RDFs mentioned above, the difference in solute–solvent interactions can be discussed. In water and methanol, namely in protic solvents, hydrogen bonds are formed around both the carbonyl oxygen atom and the amino hydrogen atom of SPMC; on the other hand, in acetonitrile, namely in an aprotic solvent, hydrogen bonds are formed only around the amino hydrogen atom. Consequently, the interactions between SPMC and the solvent molecules in acetonitrile are weaker than those in water and methanol, and accordingly the shift in excitation energy in acetonitrile is smaller than in the other two solvents.

In a comparison between water and methanol, the peaks of the solvent hydrogen in the RDFs of the oxygen and the nitrogen of SPMC in water are lower than those in methanol. Similarly, the peak of the solvent oxygen in the RDFs of the amino hydrogen of SPMC in water is lower than that in methanol. Apparently, the higher peaks in methanol seem to mean that the interaction in methanol is stronger than in water. However, the magnitudes of the solute–solvent interactions are affected by also the density of solvent and the pair interaction potential as well as the RDFs. The density of water is larger than that of methanol (0.033316 molecules Å^{-3} (water), 0.014781 molecules Å^{-3} (methanol)) and a water molecule has two hydrogen atoms. Considering these factors, we can conclude that the interactions between SPMC and the solvent molecules in water are actually stronger than those in methanol.

To understand the directions of the shift in the excitation energy caused by solvation, we consider the n, π_1, and π_1^* orbital energies. Because the π–π* and n–π* excited states of SPMC ($n = 2$) are well described by a single configuration (the weights of the main configuration in the π–π* and n–π* excited states were 97% and 81%, respectively), we can qualitatively discuss the excitations by the orbital energy difference. Figure 4 shows the orbital energies of SPMC ($n = 2$). The π_1 and π_1^* orbital energies in acetonitrile increase by solvation, while all of the other orbitals decrease. The lowering in the n orbital energies caused by solvation in water and methanol is larger than those in the π_1 and π_1^* orbital energies because the hydrogen atoms of the solvent molecules are oriented to the oxygen atom of SPMC and the hydrogen bonds are formed as shown in Figure 3. In addition, the lowering in the π_1 orbital energies caused by solvation in water and methanol is smaller than that in the π_1^* orbital energy, and the rise in the π_1 orbital energy in acetonitrile is larger than that in the π_1^* orbital energy. In other words, the energy gap between the π_1 and π_1^* orbitals becomes narrower and that between the n and π_1^* orbitals becomes wider. In addition, the change in orbital energy caused by solvation indicates that the mechanisms for the red shifts in the π–π* excitation energies are different and depend on the solvent.

Table 2 shows the weight in the π–π* and n–π* excited states in the gas phase. From Table 2, the main configurations in all of the excited states are of the same type for any chain length. Therefore, the discussions are applicable to the other SPMCs of different chain lengths.

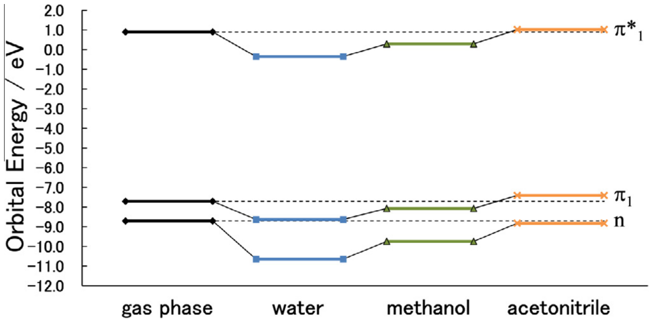

Figure 4. The energies of the n, π_1, and π_1^* orbitals of SPMC ($n = 2$) in the gas and solution (water, methanol, and acetonitrile) phases.

Table 2
The weights of some configurations in the π–π* and n–π* excited states of SPMC in the gas phase[a].

n	π–π*			
	$\pi_1 \rightarrow \pi_1^*$	$\pi_2 \rightarrow \pi_1^*$	$\pi_1 \rightarrow \pi_2^*$	$\pi_1 \rightarrow \pi_2^*$
1	0.96	–	–	0.00
2	0.97	–	–	0.01
3	0.96	0.00	0.00	0.02
4	0.94	0.01	0.01	0.03
5	0.90	0.02	0.03	0.04
n	n–π*			
	$n \rightarrow \pi_1^*$	$n \rightarrow \pi_2^*$	$n \rightarrow \pi_3^*$	$n \rightarrow \pi_4^*$
1	0.89	0.10	–	–
2	0.81	0.16	0.03	–
3	0.73	0.22	0.04	0.01
4	0.65	0.26	0.07	0.02
5	0.58	0.29	0.10	0.03

[a] Symbols π_x and π_y^* denote the x-th highest occupied π orbital and the y-th lowest unoccupied π* orbital, respectively.

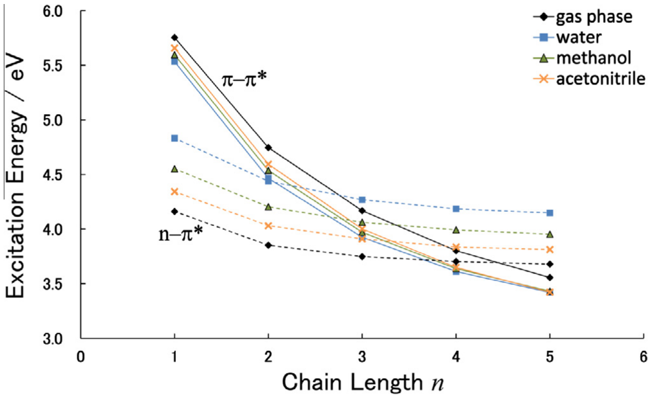

Figure 5. The π–π* (solid lines) and n–π* (dashed lines) excitation energies of SPMC for $n = 1$–5 in the gas (diamonds) and solution [water (squares), methanol (triangles), and acetonitrile (crosses)] phases.

3.2. Chain length dependency

In the previous subsection, we discussed the solvent dependency of the excitation energies. Here, we consider their chain length dependency in Figure 5, where the π–π* and n–π* excitation energies of SPMC are displayed. The π–π* and n–π* excitation energies both decrease monotonically with the extension of the chain length, which is commonly observed in linear conjugated compounds. The decrease rate of the π–π* excitation energy with the extension is larger than that of the n–π* excitation energy. For instance, the decrease in the π–π* excitation energy between $n = 1$ and $n = 5$ is 2.19 eV in the gas phase, whereas that of the n–π* excitation energy is 0.48 eV. Because of the difference in the rate, the order of the π–π* and n–π* excitation energies changes at $n = 5$. In solution, the π–π* and n–π* excitation energies also decrease monotonically with the extension of the chain length. We can see that the shifts in excitation energies caused by solvation are almost the same regardless of the chain length and that the magnitudes of the shifts themselves depend on the solvent species. As a result, the length where the orders of the π–π* and n–π* excitation energies change moves from $n = 5$ to $n = 3$ in water and methanol, and to $n = 4$ in acetonitrile.

The RDFs for all chain lengths are also shown in Figure 3 to understand why the chain length dependency of the solvation shift in the excitation energy is small. The peaks have nearly equal heights at all chain lengths except for those of the hydrogen atom of water and methanol to the nitrogen atom of the SPMC amino

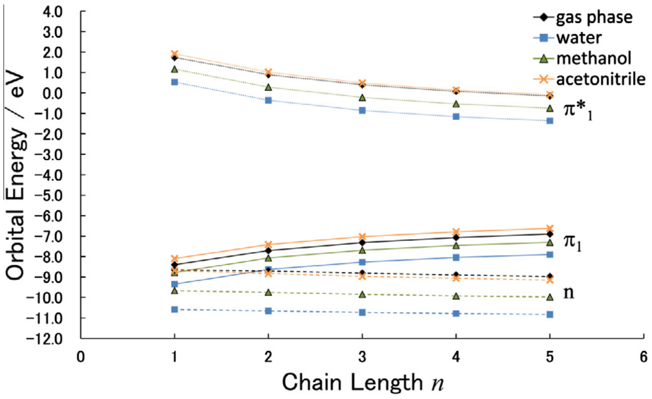

Figure 6. The n (dashed lines), π_1 (solid lines), and π_1^* (dotted lines) orbital energies of SPMC for $n = 1$–5 in the gas (diamonds) and solution [water (squares), methanol (triangles), and acetonitrile (crosses)] phases.

group. This indicates that the interactions between the solute and the solvent molecules are almost unchanged regardless of the chain length, which is the reason why the chain length dependency is so small.

This trend can also be interpreted by the dependency of the orbital energy. Figure 6 shows the orbital energies of SPMC. The n and π_1^* orbital energies decrease, while the π_1 orbital energy increases with the extension of the chain length, as is often the case in linear conjugated compounds. From these changes in the orbital energies, the changes in the excitation energies with the extension of the chain length mentioned above are explained. In addition, we can observe that the orbital energy changes caused by solvation are very close for all chain lengths. This also accounts for the smallness of the chain length dependency of the shift caused by solvation.

4. Conclusions

We used the RISM–SCF method to investigate the solvent effects on the excitation energies of SPMC from two aspects: the solvent dependency and the chain length dependency.

First, we focused on the solvent dependency. In all the solutions studied (water, methanol, and acetonitrile), the π–π^* excitation energy shows a red shift, whereas the n–π^* excitation energy shows a blue shift. We clarified the origin of the blue or red shift in the excitation energy from the change in orbital energy. In addition, the shift in the n–π^* excitation energy is found to exceed that in the π–π^* excitation energy, and the magnitudes of solvation shifts are water > methanol > acetonitrile. This order is ascribed to the difference in the interactions between SPMC and the solvent molecules and is explained by means of the RDFs. That is, in protic solvents, water and methanol, hydrogen bonds are formed around both ends of SPMC, while they are only formed around the amino group of SPMC in the aprotic solvent, acetonitrile.

Then, we examined the chain length dependency. Both the π–π^* and n–π^* excitation energies decrease monotonically with the extension of the chain length, and the decrease in the π–π^* excitation energy is more significant than that of the n–π^* excitation energy. RDFs also show that the solvent effects for all of the chain lengths are similar. In addition, we can explain the behavior of the excitation energy with the extension of the chain length, and the similarity in the behavior of the excitation energy between the gas phase and the solution phase by the orbital energies. The crossing point of the interchange of the excitation energy level between the π–π^* and n–π^* depends on the solvation. Therefore, the crossing occurs at a short chain length in the solvent that interacts strongly with SPMC.

Acknowledgements

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