

Theoretical study on counter anion- and solvent-dependent fluorescence quenching mechanism of 2-phenylbenzo[*b*]phospholium salts

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Abstract

Recently reported highly fluorescent 2-phenylbenzo[*b*]phospholium salt shows an interesting photochemical property. While the counter anion and solvent dependency indicate that the salt is mainly responsible for the absorption and fluorescence spectra, the fluorescence decay clearly depends on the counter anion. In the present study, the detailed mechanism is elucidated using quantum chemical computation and its hybrid with statistical mechanics called 3D-RISM-SCF. Based on the careful exploration of plausible structures of the ion pairs in the methanol and dichloromethane solution, we identify the structure of the charge transfer state, the key on the photoprocess.

Keywords: Solvation effect, absorption and fluorescence spectra, TDDFT, 3D-RISM-SCF

1. Introduction

In recent years, various organic compounds have been proposed with a wide range of applications in mind, including organic light-emitting diodes (LEDs), organic solar cells, biosensing and fluorescent imaging probes [1-3]. The organic molecules with π -extended phosphole are attractive as functional materials since their photophysical and electrochemical properties can be tuned by chemical modification. Among these, a group of molecules that change the wavelength of their fluorescence or quenching mechanism in response to the surrounding environment has attracted much attention. For example, the fluorescence of the molecules consisting of an electron-adapted benzophosphole oxide and an electron-donating group significantly depends on the polarity of the solvent [4,5]. Quantum chemical calculations such as density functional theory (DFT) and time-dependent DFT (TDDFT) have been widely used to investigate the photochemical properties of these compounds [5-10]. The substitution effect of 5-phenylbenzo[*b*]phosphindole 5-oxide (PhBPO) on photochemical properties have also been investigated with quantum chemical calculations based on molecular orbital, infrared and fluorescence spectra [5].

Recently, Koyanagi *et al.* reported the optical and photophysical properties of highly fluorescent 2-phenylbenzo[*b*]phospholium salts (**Scheme 1**), especially focusing on the effects

of counter anions, P-substituents, and solvents [11]. They found that the absorption and fluorescence spectra show little dependency: The positions of absorption and emission maxima are not largely different between the methanol and dichloromethane solvents, and the influence of the counter anions is negligible, implying that the cation is essentially responsible for the photophysical property. At the same time, however, the iodide and chloride salts exhibited clear concentration quenching of fluorescence. When the quenching occurs, short-lived species with lifetimes of ~ 1 ns appear in addition to fluorescence species with a lifetime of ~ 10 ns. The structural change of the ion pair and the heavy atom effect were considered to understand these puzzling observations. In general, the heavy atom effect often explains the fluorescence quenching, namely the intersystem crossing caused by the spin-orbit interaction. Still, many other possible mechanisms have been extensively discussed for such a quenching phenomenon, including a charge transfer (CT) between the fluorescent substance and the counter anion [12,13], random collision [14], hydrogen bonding [15], and so on. The quenching by photoinduced electron transfer through a dark (non-emissive) state is a plausible mechanism for benzazaborole-derivative systems [16]. Indeed, the anion- π CT mechanism is suggested to contribute to the quenching [17]. Further mechanisms have been considered, including thermal electron transfer (ET), and photoinduced electron transfer (PET) in the excited state [18-21]. This study aims to clarify the fluorescence quenching mechanism of 2-phenylbenzo[*b*]phospholium salts and their dependence on counter anions and solvents. The absorption and fluorescence energy of the compounds were studied based on the DFT and TDDFT computations changing the solvents and the counter anions. In particular, we focused on the electronic ground state (GS), low-lying excited states (ESs) including local excited (LE) state and charge transfer (CT) state. More precise energy level computations, considering solvation at the atomic level, were also performed with the 3D-RISM-SCF method.

2. Computational Method

The present study examined cation $\mathbf{P}^+$ (**Scheme 2**) and its complexes, *i.e.* ion pair, with counter anion $\mathbf{X}^-=\text{Cl}^-$, I^- in solvent dichloromethane (DCM) and methanol (MeOH). DFT and TDDFT calculations were performed with $\omega\text{B97X-D}$ functional to describe CT states appropriately [22]. After the optimisation using the def2-SVP basis set, the energy calculations were carried out with the def2-SVPD basis set [23] for Cl and I atoms, and def2-SVP basis set for the other atoms.

The solvent effect was considered by the integral equation formalism model of PCM (IEF-

PCM). To evaluate solvent effects with TDDFT, the corrected linear response (cLR) model was adopted [24]. The absorption and fluorescence properties of **P⁺**, **P-Cl** and **P-I** were calculated using the optimised structures for the GS and ES state, respectively. Further, the 3D-RISM-SCF computations [25,26] were employed to obtain the spatial distribution function (SDF) of solvent molecules at the optimised structure by the PCM-DFT/TDDFT calculations. The Kovalenko-Hirata closure is employed to solve the 3D-RISM equation. Lennard-Jones (LJ) parameters of solute were taken from General AMBER Force Field (GAFF) [27]. All the parameters of DCM and MeOH [28,29] solvents are listed in **Table 1**. The temperature was set to 300 K, and the densities at 1.33 g/cm³ for DCM and 0.79 g/cm³ for MeOH based on experimental data. The grid boxes for the 3D-RISM calculation consisted of 128×128×128 grid points at 0.5 Å intervals.

The 3D-RISM-SCF calculations were performed using the modified version of the GAMESS program [30]. Other calculations were carried out with the Gaussian 16 package [31].

3. Results and discussion

3.1 Ion pair structure and binding free energy in the GS

Several optimised structures were obtained from various initial geometries with different anion positions. To indicate them and classify the isomers, it is convenient to divide the space around **P⁺** into five parts called **a ~ e** as in **Figure 1**. The origin is fixed at the centre of the phosphole ring, and the cationic π -frame was placed on the *xy*-plane. The region close to the substituent on the benzophosphole side is designated as **a**, the region opposite across the substituent as **e**, and the region opposite the phosphorus atom as **b**. In all of them, the anion is almost located on the π -frame plane. Unlike these three, the anion is out of the plane in **c** and **d**. The combination of anions and these regions will be used to distinguish isomers of the ion pair. For example, when I⁻ locates in region **a**, the pair is denoted as **P-Ia**. It should be mentioned that the structure corresponding to the solvent-separated ion pair (SSIP) was searched by utilising molecular dynamics simulation and RISM-SCF-cSED computation [32-34] because a specific solute-solvent interaction may be crucial to form the SSIP [11]. In molecular dynamics simulation, the potential of mean force relative to the distance between the P and I atoms were analysed to search the minimum structures corresponding to SSIP. In RISM-SCF-cSED computation, the radial distribution function of solvent molecules around **P-I** and the distance between the P and I atom were compared. However, the corresponding structure could not be found in our exploration.

Figure 2 sketches the obtained structures of **P⁺** and **P-Ia** in DCM. Comparing them, the **P⁺** part of their structures is basically unchanged, indicating that the effect caused by the binding of I⁻ is very little. The selected structural parameters, the C-C and the C-P bond lengths and the torsion angle are almost the same as summarised in **Table 2**. These parameters are also consistent with the experimental data obtained by X-ray crystallography within the accuracy of 0.1 Å [11]. The same is true for the other pairs, **P-Ib** to **P-Ie** (**Figure S1**), as shown in **Table S1**. I⁻ in **P-Ia** is closest to the hydrogen atom in the P-methyl group at a distance of 2.90 Å. In the structure reported by X-ray crystallography and verified by ¹H NMR in CD₂Cl₂, the corresponding distance is 3.19 Å. These distances are shorter than the sum of the van der Waals radii of the hydrogen and iodine atoms (3.35 Å), implying a hydrogen bonding interaction. In the other pairs, **b-e**, the distances between I⁻ and the nearest hydrogen atom in **P⁺** are about 3.0 Å, still shorter than the van der Waals contact (**Figure S1**). The obtained structures of **P-Ia** to **P-Ie** in MeOH (**Figure S2**) are similar to those in DCM. In the case of the ion pair with Cl⁻, **P-Cl a** to **P-Cl e**, the distances between Cl⁻ and the nearest hydrogen atom are about 2.3 to 2.5 Å in DCM (**Figure S3**) and MeOH (**Figure S4**), which are also shorter than the sum of van der Waals radii of the hydrogen and chlorine atoms (2.95 Å).

Table 3 shows the binding free energy of the ion pairs in the solution phases. The minus value indicates that the complex is more stable than the separated ions. In the gas phase, *i.e.* an isolated state, the ion pair is formed as a stable complex due to strong Coulombic interaction between the different signs. Indeed, the binding free energy in an isolated state is typically minus several tens or hundreds of kcal/mol. On the contrary, the absolute value of the binding energy in the solution phase becomes much smaller as each of the cations and anions is solvated separately to provide a sufficiently large stabilisation. **P-Cl a** is the most stable for the chloride anion in DCM, with a binding free energy of -3.09 kcal/mol, and other isomers, **P-Cl b**, **P-Cl c** and **P-Cl e**, are also stable. In MeOH, **P-Cl b** is slightly more stable than **P-Cl a**, though all the binding free energies are positive for the complexes, implying that no complex is formed. Similarly, all the complexes are stable for the iodide complex in DCM, as indicated by negative binding energies. **P-Ia** is the most stable among them, with a strong binding energy of -3.81 kcal/mol. The trend in MeOH is similar to the chloride complex; all the binding energies are positive though the absolute values are relatively small. In other words, the less polar DCM solvent tends to promote the charge-neutral ion pairs formation, whereas the anion and cation prefer to dissociate in the polar MeOH solvent.

3.2 The absorption and the fluorescence processes

TDDFT computations were performed for the cation $\mathbf{P}^+$, $\mathbf{P-Cl}$ and $\mathbf{P-I}$ to investigate the absorption properties, as shown in **Table 4** and **Table S2**. The energies are almost the same in all the computations, about 3.8 eV, regardless of the presence or absence or type of counter anions and solvent environment. The fact indicates that the benzophosphole moiety is solely responsible for the absorption property, and this is consistent with experimentally observed little dependence of the absorption spectra on the anions and solvents. The oscillator strength does not change significantly, although the presence of the anion and the DCM solvent slightly enhances the strengths. **Figure 3** shows the molecular orbitals of $\mathbf{P}^+$ and $\mathbf{P-Ia}$ contributing to the absorption processes. In cation $\mathbf{P}^+$, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are involved. In case of $\mathbf{P-Ia}$, the HOMO-3 and the LUMO are involved. All these orbitals are π -type orbitals spread over the cationic part $\mathbf{P}^+$. Therefore, typical $\pi\pi^*$ local excitation (LE) characterises all these absorption processes. Next, the optimisations were performed using the TDDFT to compute the fluorescence property. Similarly, the fluorescence energies depend very little on the anions and solvents (**Table 4** and **Table S3**). Both computed absorption and fluorescence energies are in good agreement with the experimental values.

3.3 The relaxation process from the LE state

As described in the introduction, the relaxation after the absorption significantly depends on the environment, and the detail of the process was unknown. To clarify the electronic excited states and their connections, we explored the energy surfaces and focused on the charge transfer (CT) state. **Figure 4** shows the optimised structure of $\mathbf{P-I}$ in DCM at the GS, LE, and CT states. In the GS and LE states, I⁻ is located at the site **a**, caused by the electrostatic interaction and the C-H...I hydrogen bonding. On the other hand, I⁻ is located at the site **c** in the CT state, characterised by the transition from the HOMO on I⁻ to the LUMO on $\mathbf{P}^+$ (**Figure 5**). The change of anion site may be explained by the charge reduction of I⁻. In the GS and LE state, negatively charged I⁻ can interact with acidic hydrogen atoms, while the overlap between the molecular orbitals of I⁻ and $\mathbf{P}^+$ is more significant as I⁻ reduces the negative charge in the CT state.

Figure 6 summarises the energy level of the GS, LE, and CT states. As described earlier, little dependence on the counter anions and the solvents is seen for the GS and LE states. On the other hand, the CT state shows remarkable dependence, especially on the anion. Notably, the

CT states with I⁻ are much lower in energy than the LE state. Therefore, a possible scenario is as follows: after being excited to the LE state, **P-I** are relaxed to the energetically favourable CT state and then return to the GS by non-radiative decay. **P-Cl** in MeOH is exceptional because the CT state is energetically unfavourable, while in DCM, it is slightly lower than the LE state. The difference in orbital energies can explain this counter anion dependence of the CT state. The orbital energies of the HOMO and the LUMO of **P-Cl** in the LE state are -7.96 and -1.58 eV, while these energies of **P-I** are -7.78 and -1.66 eV in DCM. The CT state is essentially the excitation from the HOMO of the anion to the LUMO in **P⁺**. Because the HOMO energy of I⁻ (-7.46 eV) is higher than that of Cl⁻ (-8.25 eV), less energy is needed to excite the CT state, resulting in more stable CT energy levels.

The counter anion is thought to move from site **a** to **c** during the relaxation from the LE to CT as a plausible process. Note that isomers **P-Clc** in MeOH, **P-Cl a** in DCM and **P-Ic** in both solvents are the second stable species, as shown in **Table 3**, suggesting that these species could also be excited directly to the LE state in reality. Especially for **P-Clc** and **P-Ic**, whose structures are close to the CT structure, the LE state can be immediately relaxed to the CT state. As increasing the concentration, the populations of the ion pair should be increased. This is related to the marked difference between the two anions in fluorescence decay in MeOH (**Figure S5**). For iodide ions, increasing the concentration of anions in the **c** region should increase the total number of CT states produced. On the other hand, in a system of chloride ions, there is no relaxation pathway to the CT state, and the optical process should be unaffected by ion concentration. In DCM, both chloride salts and iodide salts show fluorescence quenching. The difference is that the relative ratio of the faster decay component to the slower component is greater for chloride salts than for iodide salts [11]. This difference could be due to the difference in the energies of CT states. In terms of perturbations, transitions may occur more readily in the chloride systems where the LE and CT states are energetically close.

3.4 The solvation structures

3D-RISM-SCF calculations [25,26] were performed for two purposes: One is to properly consider the contribution from the hydrogen bonding effect, especially to the energy level of low-lying excited states, which cannot be treated in PCM computations. The other is to obtain the details of the solvation structure around the compounds. The 3D-RISM-TDDFT calculations were performed for the optimised structures of **P-I** in MeOH with PCM. The LE and CT state energies are 3.34 and 2.78 eV, respectively; both are very close to the cLR-PCM

results (**Figure 6**) and the LE energy is similar to the experimental one (**Table 4**). **Figure 7** shows the spatial distribution function of the H atoms in MeOH solvents computed from the 3D-RISM-SCF method. As expected, the distribution is localised around I⁻ in the GS and LE states, indicating H...I⁻ hydrogen bonding formation. The distribution in the CT state is considerably different, spreading over the π -framework. This implies that a drastic change in solvation occurs during the transition from the LE to the CT state, while the change is small in the transition from the GS to the LE state. Compared with the GS and LE states, the CT state is more destabilised because of the loss of hydrogen bonding interactions, explaining the relatively high CT energy illustrated in **Figure 6**. A similar solvent structure change was found in DCM (**Figure S6**). However, the differences among the three states are relatively moderate due to the lack of specific interaction, unlike the MeOH solvent.

The dipole moment change explains the solvent dependence of the CT state, as shown in **Table 5** for **P-Cl** and **P-I** in DCM and in **Table S3** for those in MeOH. The dipole moments of the GS and LE states are about 20 Debye, independent of the geometrical structure. However, the dipole moment is much smaller for the CT state, 5.9 (7.1) and 7.0 (8.7) Debye, for **P-Cl** and **P-I** in DCM (MeOH), respectively, because of the charge transition from Cl⁻ or I⁻ to **P**⁺. Thus, the stabilisation effect of the polar MeOH solvent on the less polarised CT state is smaller than that of the less polar DCM solvent among the same counter anion species as in **Figure 6**. On the other hand, the CT state is less stable when X⁻=Cl⁻ than when X⁻=I⁻ at the same solvent condition although the dipole moment of **P-Cl** is smaller than that of **P-I**, indicating that the dominant contribution is the difference in orbital energy.

4. Conclusions

The present article studied a puzzling observation on the highly fluorescent 2-phenylbenzo[*b*]phospholium salts in the solution phases using quantum chemical computations with PCM and a hybrid method of quantum chemistry and statistical mechanics for molecular liquid, 3D-RISM-SCF. The exploration over a wide range of energy surfaces found several isomers stable in the solution phase. Whilst the relative stability of the isomers depends on the solvent environment, the cation is essentially responsible for the observed absorption and fluorescent spectra, attributed to the typical $\pi\pi^*$ local excitation in the cation. We found that the relaxation to the CT state can explain the solvent and anion dependence of the experimentally observed quenching. As elucidated by the 3D-RISM-SCF computations, solvation structures are remarkably different between the LE and CT states, showing that the relaxation process of the solvent could be a key to understanding the photophysical process. The collaborative work of

spectroscopic experiments and computational chemistry can reveal the nature of such complex processes in condensed chemical systems in greater detail.

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Table1. The LJ parameters and charges for DCM and MeOH solvents.

		$\sigma/\text{\AA}$	$\epsilon/\text{kcal mol}^{-1}$	Charge
MeOH [28, 29]	O	3.070	0.170	-0.700
	H	1.000	0.056	0.435
	Me	3.775	0.207	0.265
DCM ^a	Cl	3.400	0.300	-0.250
	CH ₂	3.800	0.118	0.500

^a OPLS-UA**Table 2.** Selected optimised structure parameters, the C-C and the C-P bond lengths and the torsion angle of **P⁺** and **P-Ia** in DCM.

	Bond length / $\text{\AA}$						Torsion angle / $^{\circ}$
	C1-C2	C2-C3	C3-C4	C4-C5	C5-C6	C6-C1	C2-C1-C6-C7
P⁺	1.352	1.473	1.409	1.794	1.813	1.473	27.0
P-Ia	1.353	1.471	1.409	1.795	1.815	1.473	15.6
Exp.	1.350	1.466	1.406	1.785	1.811	1.472	30.8

Table 3. Binding free energy of (a) **P-Cla** to **P-Cle** and (b) **P-Ia** to **P-Ie** in DCM and MeOH (in kcal mol⁻¹).**(a)**

	P-Cla	P-Clb	P-Clc	P-Cl d	P-Cle
DCM	-3.09	-1.38	-1.44	0.49	-1.74
MeOH	2.65	2.30	3.67	5.52	3.57

(b)

	P-Ia	P-Ib	P-Ic	P-Id	P-Ie
DCM	-3.81	-2.45	-3.61	-1.58	-2.54
MeOH	0.93	3.23	1.12	2.93	2.77

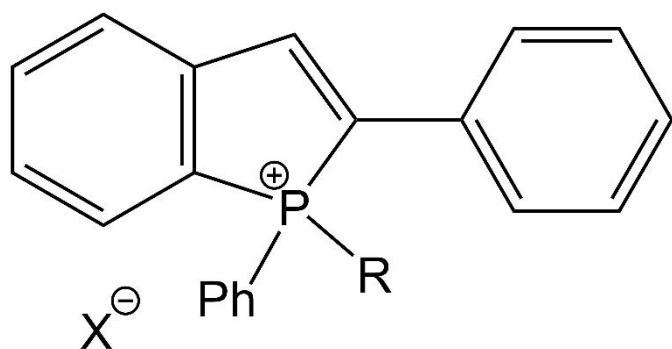
Table 4. The absorption and fluorescence energies of **P⁺**, **P-Cl_a** and **P-I_a** in DCM and MeOH (in eV). The values in parentheses describe the oscillator strength.

		Absorption		Fluorescence	
		calc.	exp.	calc.	exp.
DCM	P⁺	3.80 (0.401)		2.70 (0.392)	
	P-Cl_a	3.83 (0.450)		2.82 (0.541)	
	P-I_a	3.82 (0.427)	3.46 ^a	2.80 (0.521)	2.77 ^a
MeOH	P⁺	3.83 (0.386)		2.73 (0.383)	
	P-Cl_a	3.82 (0.427)		2.81 (0.580)	
	P-I_a	3.82 (0.405)	3.50 ^a	2.78 (0.359)	2.81 ^a

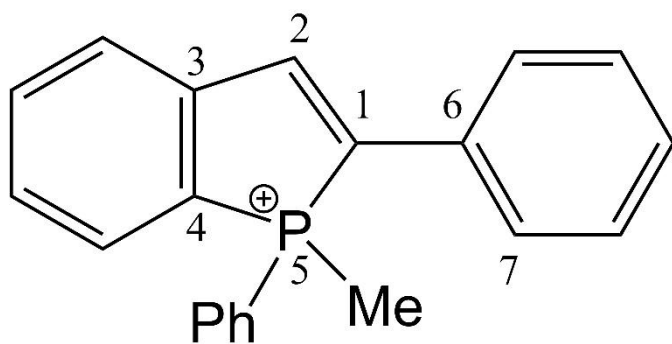
^a Experimental values are taken from ref [11].

Table 5. The dipole moment of **P-Cl** and **P-I** in the GS, LE and CT state in DCM for each optimised geometry (in Debye).

		Optimised structure		
		GS	LE	CT
P-Cl	GS		15.8	17.8
	LE		18.7	19.2
	CT		–	–
P-I	GS		21.2	21.7
	LE		22.7	23.3
	CT		–	–



Scheme 1. 2-Phenylbenzo[*b*]phospholium salts



Scheme 2. The cationic frame of 2-phenylbenzo[*b*]phospholium salt **P**⁺.

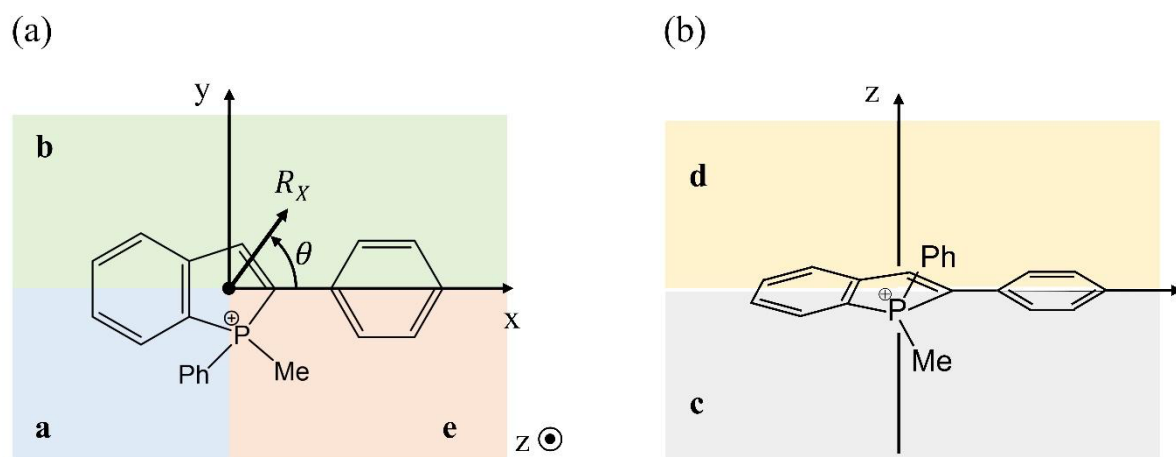


Figure 1. The definition of anion site around P^+ from (a) the top and (b) the side view. Note that the indene and phenyl moieties are not strictly planar in the optimised structure, but are briefly shown in this figure.

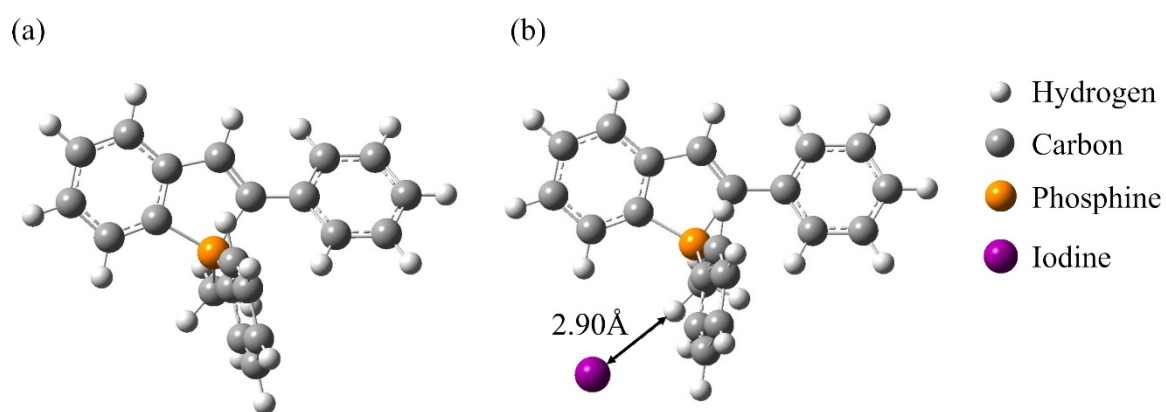
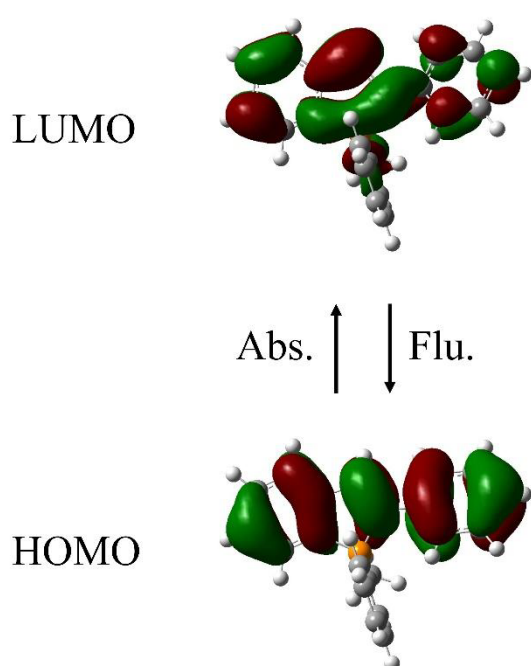


Figure 2. The GS optimised structures of (a) P^+ and (b) P-Ia in DCM.

(a)



(b)

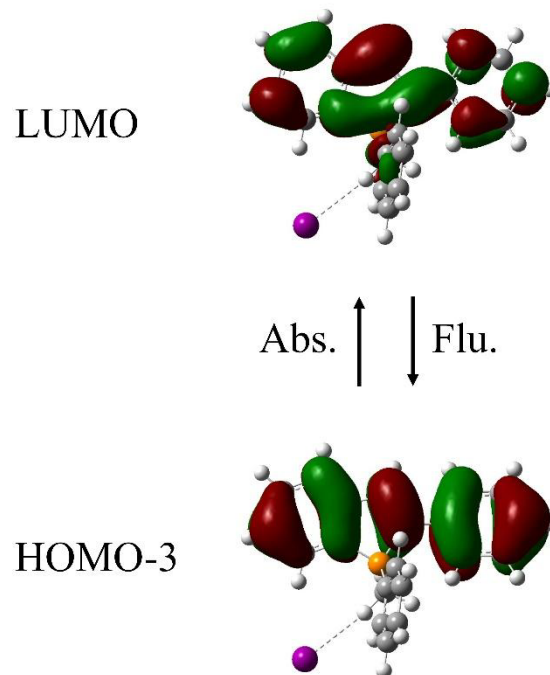


Figure 3. The molecular orbitals of (a) P^+ and (b) P-Ia , which contribute to the absorption and the fluorescence process in the GS optimised structure.

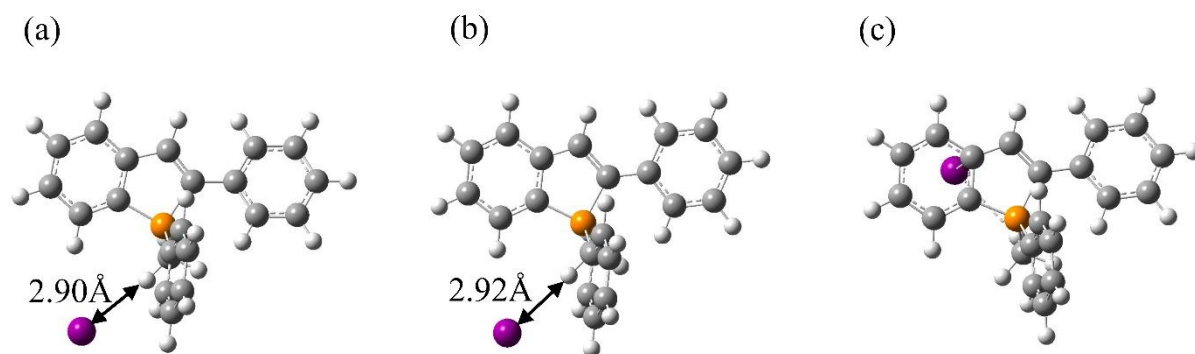


Figure 4. The structures of **P-I** in (a) the GS, (b) the LE, and (c) the CT state in DCM. The initial structure for the LE and the CT state optimization is **P-Ia**.

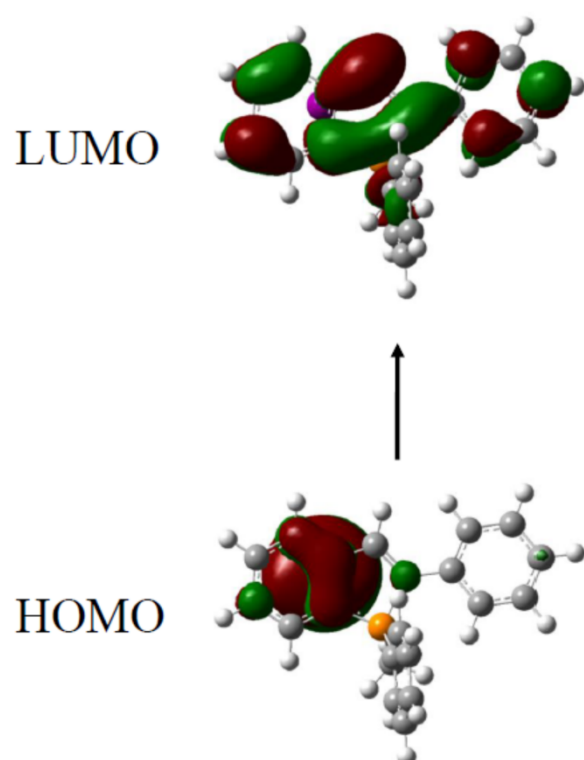


Figure 5. The molecular orbitals of **P-I** contributing to the CT process in the CT optimised structure.

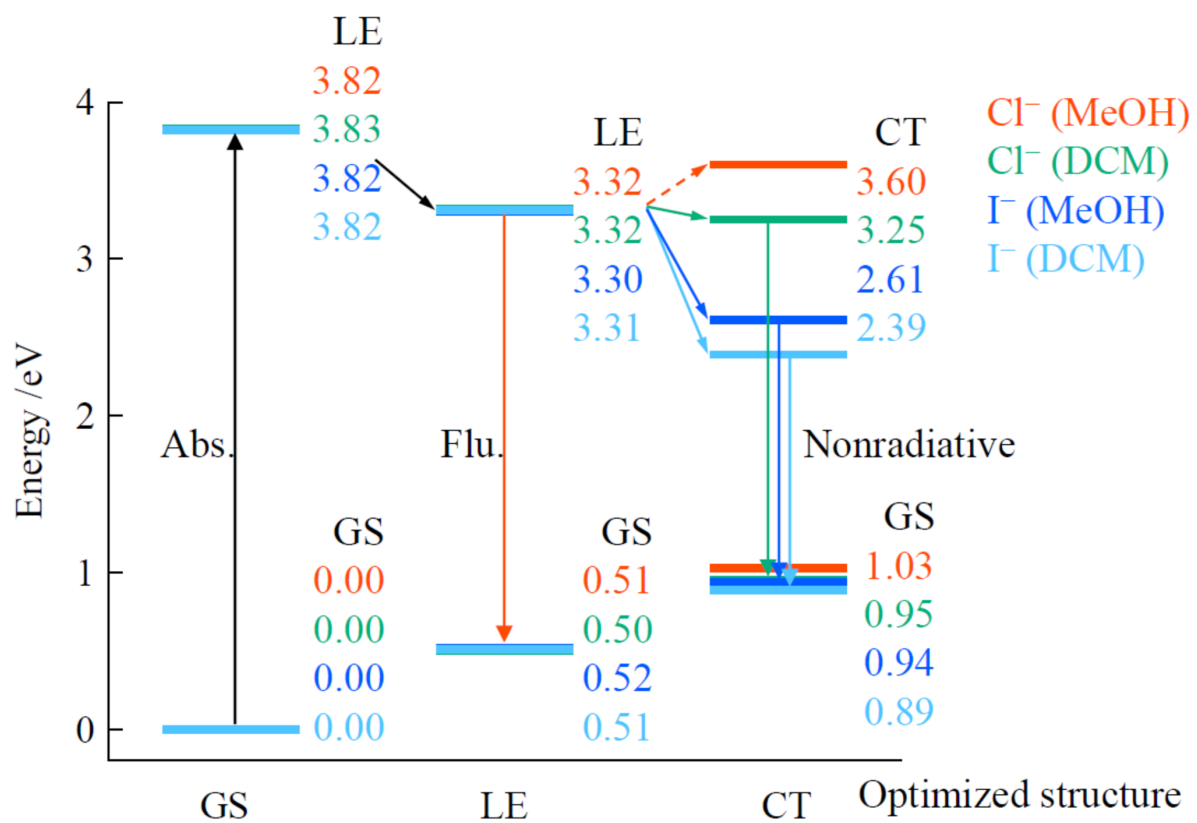


Figure 6. The energy diagram of **P-Cl** and **P-I** in the GS, LE, and CT states in DCM and MeOH.

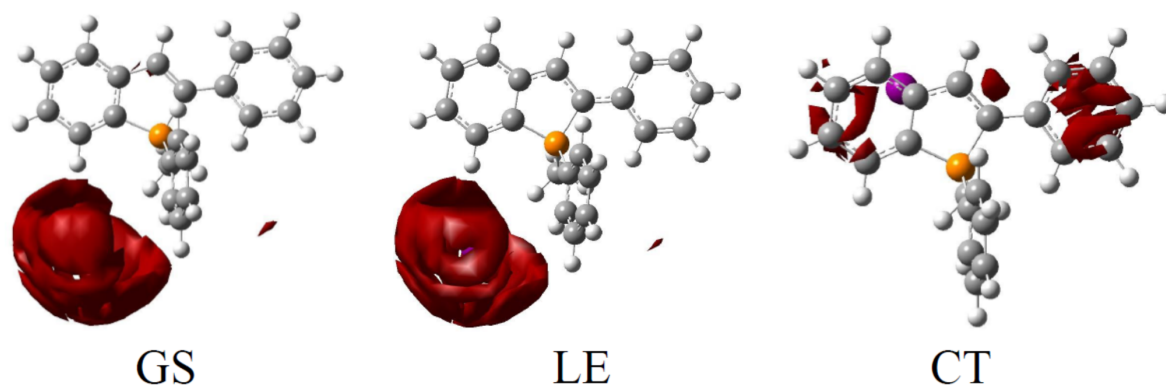


Figure 7. The spatial distribution function of H atoms in MeOH solvents around **P-I** in the GS, LE, and CT state (isosurface value= $2.0 \text{ \AA}^{-3}$).