

## Solvent effects for fluorescence and absorption of tetra (fluoroalkyl) metallophthalocyanines: Fluorocarbon solvent cage

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### ABSTRACT

The UV–vis absorption and fluorescence spectra of a series of tetra (fluoroalkyl) metallophthalocyanines were measured in CH<sub>3</sub>OH, ethyl acetate, THF, CH<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>H<sub>6</sub>, perfluorooctane. Their absorption spectra and fluorescence spectra were related not only to the peripheral substitutes, but also to the solvent environment. In the strong polar solvents, their maximum absorption and emission wavelengths were blue-shifted. However, in perfluorooctane, the blue shift was found for the absorption, and the red shift for the emission. The fluorocarbon solvent cage concept was put forward to explain this special phenomenon.

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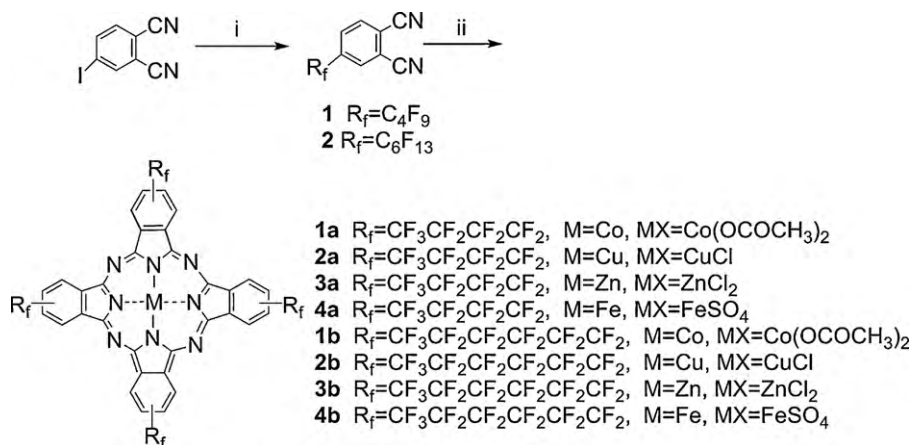
### 1. Introduction

Recently, fluorinated metallophthalocyanines (MPcs) have attracted more and more attention [1–3]. They have been proved to be advantageous over non-fluorinated derivatives as photosensitizers for the photodynamic therapy (PDT) treatment [4,5]. Generally, fluoroalkyl substituted compounds have high solubility in polar solvents due to the highest electronegativity of the fluorine atom in all elements [6]. The spectral characteristics of phthalocyanines and MPcs have been investigated in detail for many years because of their wide applications [7–9]. At present, more researchers focused on their study on the spectra of fluorinated MPcs. Sugimori reported the electronic absorption spectra of the tetrakis-octafluoropentoxo nickel phthalocyanine complexes [6]. Huang reported the characteristics of the UV–vis absorption spectra of the tetrakis (3-trifluoromethylphenoxy) phthalocyanine complexes with cobalt, nickel or zinc in THF [10].

Fluorocarbon solvents (perfluorocarbons) have been widely used as green solvents in Fluorous Biphasic Catalysis (FBC), artificial blood substitutes [11], new phase-screen medium [12]. They hold peculiar chemical and physical properties such as high-density, colorlessness, non-toxicity, chemical inertness, thermal stability, nonflammability, non-polarity, low intermolecular interaction, low surface energy, wide-range boiling point [13]. In general, fluorocarbons are immiscible with water and can be used as the nonaqueous phase [14–16]. Up to now, there is no report about the fluorocarbon solvents effects on metallophthalocyanines (MPcs) and even fluorinated MPcs.

The properties of phthalocyanines are decided not only by the nature of the substituent (electron-donating or withdrawing) of the ligand but also by the metal cation in the core of the ligand. In general, their solubility can be improved by the introduction of different kinds of substituent, such as alkyl, alkoxy, phenoxy and macrocyclic groups, into the peripheral of the Pc ring [17]. Nyokong et al. [18] reported the solvent effect for the absorption spectra of the zinc octaestrone phthalocyanine, and the largest red shift of the Q band observed in the aromatic solvents. Based on our knowledge, the study on the spectral characteristics of fluo-

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**Fig. 1.** Structures of tetra (fluoroalkyl) metallophthalocyanines: (i)  $CF_3CF_2CF_2CF_2I$  or  $CF_3CF_2CF_2CF_2CF_2CF_2I$ /Cu, DMF, 125 °C; (ii)  $H_2NCONH_2$ , MX,  $NH_4Cl$ ,  $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ , 200 °C.

roalkyl metallophthalocyanines (FMPcs) in the fluorous solvent will be significant.

In this paper, UV–vis absorption and fluorescence properties of a series of tetra (fluoroalkyl) metallophthalocyanines (Fig. 1) in the organic solvents and perfluorooctane, which were synthesized in our previous research, were investigated [19]. The fluorocarbon solvent cage effect was introduced to elucidate the unusual correlation between their electronic spectra and the solvents.

## 2. Experimental

### 2.1. Materials and methods

Perfluorooctane used was purchased from Aldrich Chemicals Co., and the solvents were purified with standard methods and dried as needed. All reagents are off-the-shelf commercial products. Perfluoroalkyl phthalocyanine metal derivatives (**1a–4b**) (FMPcs) were synthesized according to the method reported in the previous paper [19]. The desired compounds were prepared according to the route shown in Fig. 1. Absorption spectra were determined on PGENRAL TU-1901 UV-vis Spectrophotometer. Fluorescence spectra were measured on a Perkin Elmer LS 50 spectrophotometer. The relative fluorescence quantum yield was estimated using the 0.1 M quinine sulfate with  $\Phi_F = 0.55$  in 0.1 N sulfuric acid solution as a standard sample [20,21]. Fluorescence lifetimes were measured on an Edinburgh Lifespec-Ps spectrofluorometer (FL920).

## 3. Results and discussion

### 3.1. UV–vis absorption spectra in the organic solvent

The UV–vis spectral data of tetra (fluoroalkyl) metallophthalocyanine derivatives (**1a–4b**) are shown in Table 1. The maximum absorption wavelengths and values of  $\log \epsilon$  in different solvents were listed. The intense Q absorption bands around 665 nm was observed and shown in Fig. 2.

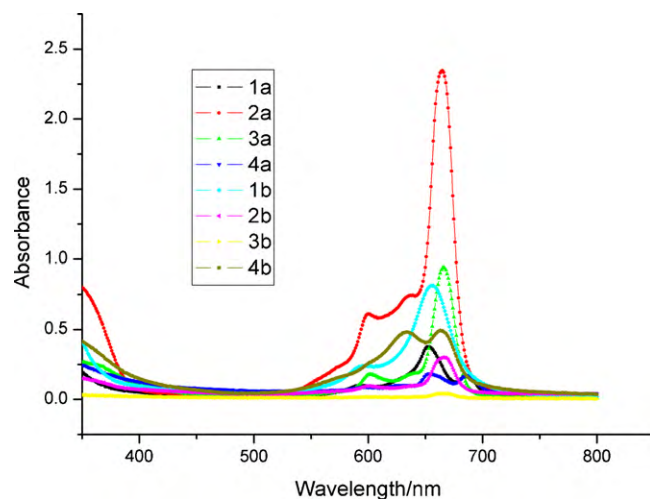
Aggregation is usually depicted as a coplanar association of rings progressing from monomer to dimer and higher order complexes [22,23]. Different solvents or various central metals also greatly influence the aggregation [24]. The aggregation behaviors of the FMPcs (**1a–4b**) with different central metal cations were investigated in ethyl acetate and THF (tetrahydrofuran), and it was found that a sharper and narrower absorption peak was observed at about 665 nm for cobalt (compound **1a**, **1b**), copper (compound **2a**, **2b**) and zinc (compound **3a**, **3b**) coordinated fluoroalkyl phthalocyanines, respectively, in THF at the concentration  $10^{-5}$  M. This means

that there was no aggregation in these systems. However, the spectrum of iron (compound **4a**, **4b**) was split into two distinct peaks in THF, which indicated an obvious aggregation tendency for iron (**4a**, **4b**) centered fluoroalkyl phthalocyanines. The same phenomenon was observed in ethyl acetate. The excitation spectra of **3a** was recorded and compared with its absorption, two spectra were similar which indicated the sample is pure. The spectra are shown in Fig. 3.

### 3.2. Fluorescence spectra in the organic solvent

The fluorescence spectral data are shown in Table 1. Their fluorescence and quantum yields ( $\Phi_F$ ) were determined in different solvents as shown in Table 1.

The maximum emission wavelengths of all the synthesized compounds were around 670–695 nm in THF as shown in Fig. 4, and the compound **3b** had higher  $\Phi_F$  value in THF and benzene, compared with that of the reported fluoroalkoxy MPcs [25]. For example, the  $\Phi_F$  value of tetra (trifluoroethoxy) zinc phthalocyanine was 0.058 (ethyl acetate, 25 °C), while the  $\Phi_F$  value of **3b** was up to 0.38 (ethyl acetate, 25 °C). However, the fluorescence intensities of compound **2a** and **2b** were too weak to be detected, which might be caused by the strong fluorescence-quenching effect due to their core-metal cation.



**Fig. 2.** UV–vis absorption spectra of tetra (fluoroalkyl) metallophthalocyanines (**1a–4b**) in THF. Concentration:  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>.

**Table 1**  
The spectral properties of fluoroalkyl metallophthalocyanines in different solvents.

Solvent Solvent polarity	Methanol 6.60	Ethyl acetate 4.30	THF 4.20	Dichloromethane 3.50	Benzene 3.00	Perfluorooctane
<b>1a</b>						
$\lambda_{\max}/\text{nm} (\log \epsilon)$	646(3.84)	662(4.47)	653(3.78)	662(3.16)	663(3.86)	610(2.40)
$\lambda_{\text{em}}/\text{nm} (\Phi_{\text{F}})$	– <sup>a</sup>	690(0.024)	694(0.032)	693(0.042)	697(0.016)	698(0.0073)
$(\nu_{\text{abs}} - \nu_{\text{em}})/\text{cm}^{-1}$	–	613	904	676	736	2067
<b>2a</b>						
$\lambda_{\max}/\text{nm} (\log \epsilon)$	607(3.17)	663(3.31)	665(5.22)	668(3.02)	673(3.60)	592(3.20)
$\lambda_{\text{em}}/\text{nm} (\Phi_{\text{F}})$	–	–	–	–	–	–
<b>3a</b>						
$\lambda_{\max}/\text{nm} (\log \epsilon)$	661(3.90)	667(4.28)	666(4.75)	672(3.94)	673(3.88)	617(3.77)
$\lambda_{\text{em}}/\text{nm} (\Phi_{\text{F}})$	673(0.19)	676(0.032)	677(0.024)	678(0.077)	688(0.079)	700(0.0037)
$(\nu_{\text{abs}} - \nu_{\text{em}})/\text{cm}^{-1}$	270	200	244	132	324	1922
<b>4a</b>						
$\lambda_{\max}/\text{nm} (\log \epsilon)$	–	684(3.24)	687(3.70)	692(3.21)	692(2.28)	598(3.12)
$\lambda_{\text{em}}/\text{nm} (\Phi_{\text{F}})$	–	692(0.17)	693(0.074)	694(0.16)	696(0.063)	701(0.07)
$(\nu_{\text{abs}} - \nu_{\text{em}})/\text{cm}^{-1}$	–	169	126	42	83	2457
<b>1b</b>						
$\lambda_{\max}/\text{nm} (\log \epsilon)$	645(3.41)	660(4.26)	656(4.70)	–	668(2.69)	598(3.17)
$\lambda_{\text{em}}/\text{nm} (\Phi_{\text{F}})$	–	–	676(0.01)	–	678(0.008)	701(0.065)
$(\nu_{\text{abs}} - \nu_{\text{em}})/\text{cm}^{-1}$	–	–	451	–	221	2457
<b>2b</b>						
$\lambda_{\max}/\text{nm} (\log \epsilon)$	609(3.10)	665(3.23)	666(4.27)	671(2.84)	673(3.40)	588(4.31)
$\lambda_{\text{em}}/\text{nm}$	–	–	–	–	–	–
<b>3b</b>						
$\lambda_{\max}/\text{nm} (\log \epsilon)$	657(3.38)	666(4.12)	668(3.29)	670(3.46)	672(3.40)	598(3.36)
$\lambda_{\text{em}}/\text{nm} (\Phi_{\text{F}})$	673(0.12)	674(0.38)	674(0.68)	677(0.09)	679(0.875)	700(0.04)
$(\nu_{\text{abs}} - \nu_{\text{em}})/\text{cm}^{-1}$	362	178	133	154	153	2437
<b>4b</b>						
$\lambda_{\max}/\text{nm} (\log \epsilon)$	–	685(3.13)	663(4.36)	670(3.47)	693(2.81)	598(3.35)
$\lambda_{\text{em}}/\text{nm} (\Phi_{\text{F}})$	–	691(0.09)	674(0.014)	694(0.014)	697(0.018)	700(0.02)
$(\nu_{\text{abs}} - \nu_{\text{em}})/\text{cm}^{-1}$	–	126	178	516	83	2437

$\Phi_{\text{F}}$ : fluorescence quantum yield (in general the standard used for determination of  $\Phi_{\text{F}}$  is 0.1 M quinine sulfate in sulfuric acid ( $\Phi_{\text{F}} = 0.55$ )).

<sup>a</sup> Spectrum of the compound in these solvents were not detected.

It is well known that the absorption and emission wavelengths are sensitive to the environmental factors [26,27]. As indicated in Table 1, the absorption of FMPc was very sensitive to the solvent. For example, with the increase of solvent polarity, the maximum absorption wavelength of the compound **2a** was blue-shifted about 65 nm (from 673 nm in benzene to 607 nm in methanol).

Additionally, it was observed that the fluorescence of FMPc also depended on the “polarity” of the environment, which was consistent with their absorption spectra. As shown in Table 1, the maximum emission wavelength of compound **3b** was blue-shifted about 6 nm (from 679 nm in benzene to 673 nm in methanol). Similar blue shifts were also observed in other compounds.

It showed that the maximum absorption ( $\lambda_{\max}$ ) and emission wavelengths ( $\lambda_{\text{em}}$ ) of FMPcs were blue-shifted with the increase of the solvent polarity in Table 1. This indicated the energy gap ( $\Delta E$ ) between the ground state and the excited state gradually became large with the increase of the solvent polarity. Such increase of energy level indicated its instability in the excited state in strongly polar solvent.

The polarity of FMPcs molecule after the excitation in strongly polar solvents became weak as compared with its polarity in the ground state. This led to the rising of the energy level in the excited state in polar solvents and the decrease of the energy level of the ground state. Accordingly, the gap of the energy became larger and the maximum absorption wavelength was blue-shifted. This phenomenon was consistent with the result in our previous report [25].

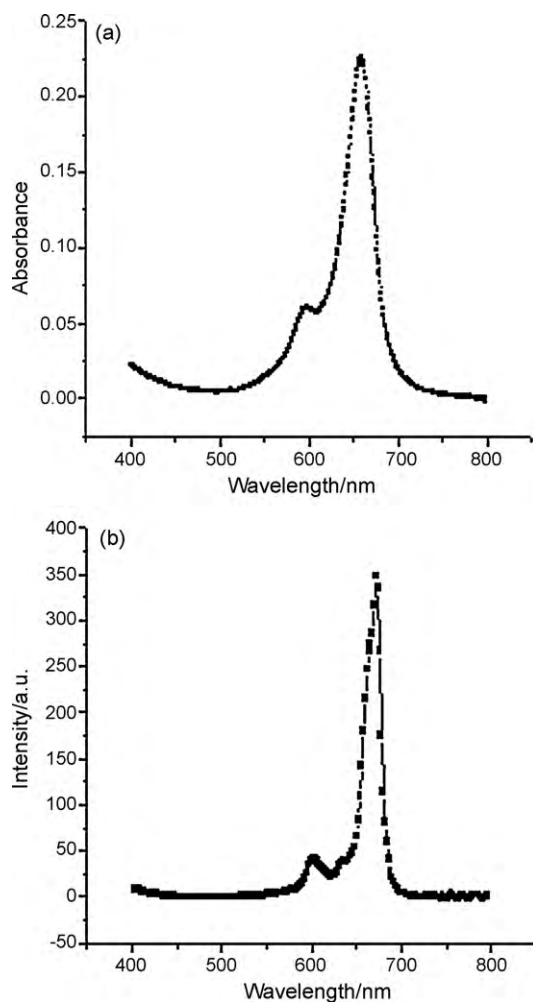
### 3.3. The solvent effects of the perfluorooctane

The UV–vis absorption spectra and fluorescence emission spectra of eight FMPcs in perfluorooctane were measured and listed in Table 1. The maximum absorption ( $\lambda_{\max}$ ) wavelengths of FMPcs

are at 590–610 nm, even much shorter than those in the strongly polar organic solvents (as shown in Fig. 5), leading to the blue shift. Accordingly, perfluorooctane has the typical characteristics of the strongly polar solvents. However, the fluorescence maximum emission wavelength ( $\lambda_{\text{em}}$ ) of FMPcs is near 700 nm, even longer than that in the weakly polar organic solvents, leading to the red shift. Perfluorooctane also has typical characteristics of the non-polar solvents.

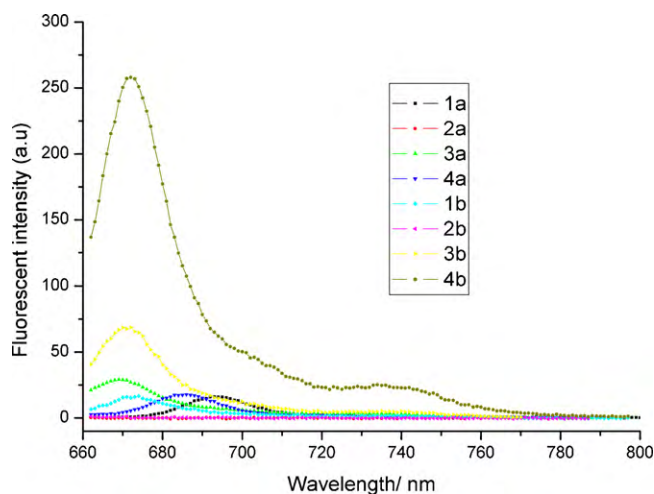
In order to investigate the effect of perfluorooctane, the fluorescence lifetime of one of compound **3b** was obtained by time resolved fluorescence measurement. The fluorescence lifetime of **3b** is 1.24  $\mu\text{s}$  (43.75%) and 9.60  $\mu\text{s}$  (56.25%), fitted with double exponential decaying with  $\chi^2 = 1.271$  in THF at the concentration  $10^{-5}$  M, while in perfluorooctane, the value changes to 1.15  $\mu\text{s}$  (49.02%) and 9.89  $\mu\text{s}$  (50.98%) with  $\chi^2 = 1.272$ . In addition, the range of Stokes shift of **3b** is 130–360  $\text{cm}^{-1}$  in common solvents, however, the Stokes shift of **3b** is 2437  $\text{cm}^{-1}$  in perfluorooctane solvent. These values mean that the spectral characteristics of FMPcs in perfluorooctane are quite different from that in the normal organic solvents. Therefore, in this paper we introduce the fluorocarbon solvent cage concept to explain this special phenomenon.

According to the Franck–Condon Principle [28] and the solvent cage molecular spectroscopy [29,30], both intermolecular interaction (solute–solute interactions, solute–solvent interactions) and the multiplexed excited states interactions of the composite molecule have to be taken into consideration when investigating the spectral characteristics of the molecular system. The target molecular system should be regarded as the molecule of an aggregation one. The study should not be focusing just on the electronic configuration of a single molecule in excited states, and it is also important to study the influence of the interaction between the host molecule and the surrounding solvent molecules in the excited state.

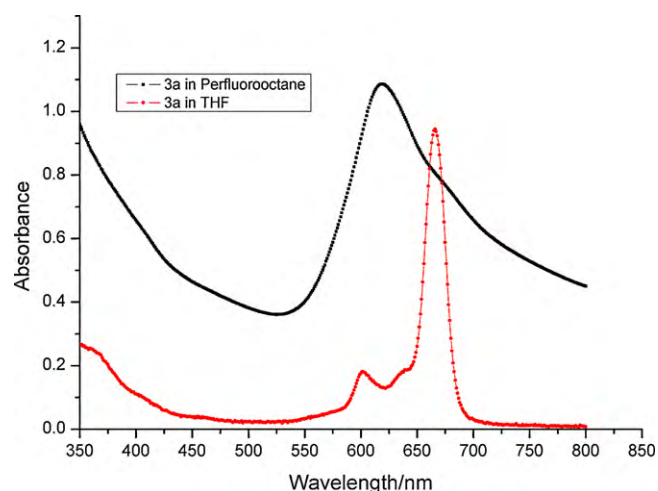


**Fig. 3.** (a) UV-vis absorption spectrum of **3a** in THF. Concentration:  $2.0 \times 10^{-5} \text{ mol L}^{-1}$ . (b) Fluorescence excitation spectrum of **3a** in THF. Concentration:  $2.0 \times 10^{-5} \text{ mol L}^{-1}$ .

It was found that FMPcs dissolved easily in the perfluorooctane, which suggested that perfluorooctane might form a directional particular solvent cage around the FMPcs molecule, that is, fluorocarbon solvent cage. The fluorocarbon solvent cage would affect the energy variation between the ground state and the excited state

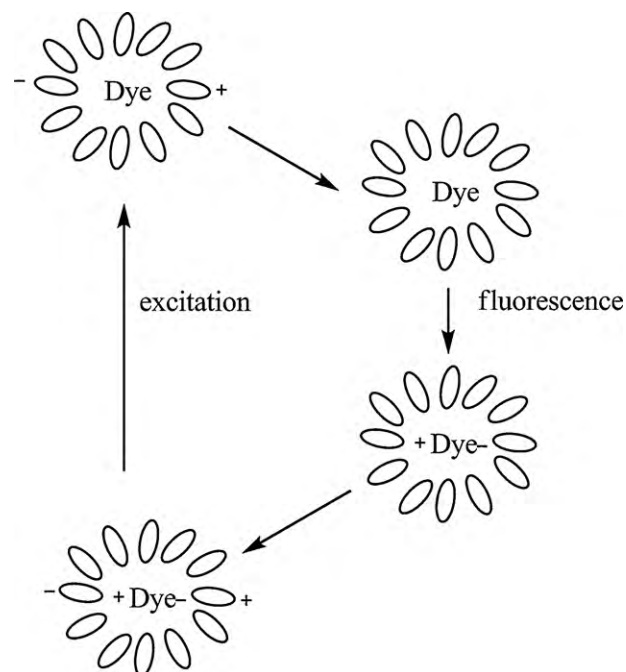


**Fig. 4.** Fluorescence emission spectrum of tetra (fluoroalkyl) metallophthalocyanines (**1a–4b**) in THF.



**Fig. 5.** UV-vis absorption spectrum of **3a** in THF and perfluorooctane. Concentration:  $1.0 \times 10^{-5} \text{ mol L}^{-1}$ .

of solute molecule of the FMPcs, leading to the special change of the spectral characteristics. In the ground state  $S_{00}$ , a directional fluorocarbon solvent cage was induced around the FMPcs molecule, having a static stability effect in the solute's ground state and accordingly, a lower energy at the ground state  $S_{00}$  in the perfluorooctane than that in the common organic solvents. When the FMPc molecule was excited by light, its electronic configuration instantly reached to a higher energy level  $S_1$ , an unstable excited state  $S_{1n}$ , whereas the molecular conformation could not catch up with the change immediately. From the spectral characteristics of FMPcs in polar and non-polar organic solvents described above, it was known that the polarity of the FMPc in the unstable excited state usually became weak after the excitation. Meanwhile, the perfluorooctane could not immediately re-orient through conformation changes during the light-irradiation and still kept the original fluorocarbon solvent cage and showed an induced lagging effect, that is, the fluorocarbon solvent cage corresponding to  $S_{1n}$  still stayed as the solvent cage to  $S_{00}$  at the ground state.



**Fig. 6.** The explanation of fluoro solvent cage on electronic transition of fluoroalkyl metallophthalocyanines in perfluorooctane.

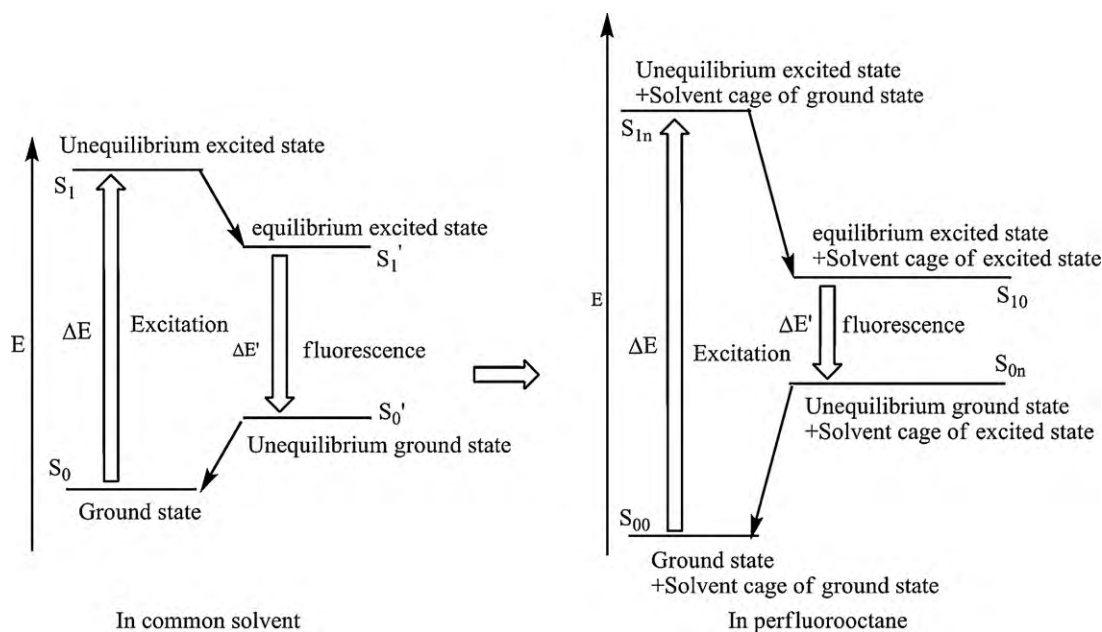


Fig. 7. The explanation of electronic transition of fluoroalkyl metallophthalocyanines in perfluorooctane and common solvent.

In this case, the weak polarity of the FMPc molecule in the unstable excited state  $S_{1n}$  was not compatible to the strong polarity of the original solvent cage, leading to the instability of the FMPc and the energy increase of the unstable excited state, subsequently, the energy gap  $\Delta E$  between  $S_{1n}$  and  $S_{00}$  increased and blue shift of  $\lambda_{\max}$  occurred, as shown in Figs. 6 and 7.

After FMPc reached to its unstable excited state ( $S_{1n}$ ), its energy was quickly released by the heat loss and the conformation slowly fell to the equilibrium excited state  $S_{10}$ , which induced the original solvent cage to form the second compatible fluorocarbon solvent cage with weak polarity. In this process, the FMPc's conformation changed and the fluorocarbon solvent cage around the FMPc was re-oriented, causing a static stability of the equilibrium excited state. The energy of FMPc at state  $S_{10}$  was very low. Furthermore, the FMPc returned from the equilibrium excited state to the unstable ground state  $S_{0n}$  and led to an emission of fluorescence. Similarly, due to the induced lagging effect of the fluorocarbon solvent cage, the solvent cage corresponding to  $S_{0n}$  remained as the second fluorocarbon solvent cage with weak polarity. The mismatch between the FMPc at unstable ground state with strong polarity and the second fluorocarbon solvent cage with low polarity caused the unstable FMPc and its energy increase. Thus, the energy gap  $\Delta E$  between  $S_{10}$  and  $S_{0n}$  decreased and the red shift of  $\lambda_{\text{em}}$  occurred, as shown in Figs. 6 and 7.

Although the spectral characteristics of the fluorobutyl metallophthalocyanine (FBMPc) were slightly different from that of the fluorohexyl metallophthalocyanine (FHMPc) in the perfluorooctane owing to the chain length difference of the substituent, the blue shift of  $\lambda_{\max}$  of the FHMPc was larger than that of the FBMPc and the red shift of  $\lambda_{\text{em}}$  of FHMPc was larger than that of FBMPc in perfluorooctane. The special phenomenon was investigated underway.

#### 4. Conclusion

The UV–vis absorption and fluorescence spectral properties of eight novel fluoroalkyl metallophthalocyanines were investigated in this paper. All the maximum wavelengths of the absorption and emission were blue-shifted with the increase of the solvent polarity.

As compared in the common organic solvents, the blue shift value of the maximum absorption wavelength was larger in perfluorooctane. In the fluorocarbon solvent perfluorooctane, FMPc solute molecules were enclosed by perfluorooctane solvent molecules that formed the fluorocarbon solvent cage. The fluorocarbon solvent cage and its lagging effect influenced the energy variation between the ground state and the excited state of the solute molecule of FMPc and further resulted in the special change of the spectral characteristics. The measurement of fluorescence lifetime also confirmed the solvent effect of fluorocarbon solvent perfluorooctane. Using the fluorocarbon solvent cage concept, this particular change of absorption and emission spectra in perfluorooctane was easily and clearly explained.

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