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Investigation on solvation and protonation of meso-tetrakis(*p*-sulfonatophenyl)porphyrin in imidazolium-based ionic liquids by spectroscopic methods

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ABSTRACT

The solvation and protonation of the meso-tetrakis(*p*-sulfonatophenyl)porphyrin (TPPS) were investigated by spectroscopic methods in pure or mixed imidazolium-based ionic liquids: 1-butyl-3-methyl-imidazolium terafluoroborate ([MBIM]BF_4), 1-butylimidazolium terafluoroborate ([HBIM]BF_4), 1-butyl-imidazolium dodecylalkylbenzenesulfonate ([HBIM]DS), 1-butyl-imidazolium *p*-toluenesulfonate ([HBIM]TS) and 1-butyl-imidazolium methylsulfonate ([HBIM]MS). Compared with absorption properties of TPPS in aqueous solution, Soret band of TPPS monomer was obviously red-shifted in the ionic liquids, while special absorption of TPPS J-aggregates was located at higher energy level, 483 nm and 702 nm, in protonic ionic liquids (PILs) [HBIM]BF_4. Next, the protonation of TPPS in aprotonic ionic liquids (AILs, i.e., [MBIM]BF_4) is dependent not only on the concentration of protonic ionic liquids as proton sources, but also on the characteristic of anion and viscosity of PILs. The proton transfer constants between TPPS and four protonic ionic liquids are $(2.32 \pm 0.23) \times 10^2$ for [HBIM]BF_4, $(1.52 \pm 0.08) \times 10^2$ for [HBIM]MS, $(1.12 \pm 0.21) \times 10^2$ for [HBIM]DS and $(0.84 \pm 0.45) \times 10^2$ for [HBIM]TS, respectively.

1. Introduction

In recent years, considerable attention has been paid to the room temperature ionic liquids (RTILs) because of their novel applications in catalytic chemical industry, chemical separation and electrochemistry, etc. [1–5]. RTILs are suitable to reaction media in industrial processes because they can dissolve many polar or apolar organic and inorganic compounds and have negligible vapor pressures. Particularly, the imidazolium-based ILs are stable in water. They should have more extensive uses due to this property. Solvent properties can dramatically influence the rate of chemical reaction, even reaction direction. Therefore, the fundamental aspects, e.g., solvation dynamics, of interaction of solutes with ionic liquids appear to be important either in industry processes or theoretical chemistry. Up to now a lot of research work have been reported toward exploring the correlation of unique behaviors of solutes to physicochemical properties of ionic liquids, such as structures and components, dielectric constant, polarity and viscosity [6–10], etc. Many researches showed that the solvation dynamics is biphasic or more complex non-exponential form [11,12]. In biphasic dynamics, the faster and slower components arise from the diffusional motion of the anion and the collective motion of the anion and the cation, respectively [13–17]. The contrasted viewpoint exists, too, i.e., the faster component arises from the collective motion of the anion and the cation [18]. In fact, solvation in ionic liquids compared to dipolar solvents can be attributed to their much larger viscosities [12,15]. In few cases it is cation size dependent [12].

At present, imidazolium-based ionic liquids widely used in various fields can be classified aprotonic (AILs) and protonic ionic liquids (PILs). They show both the characters of an aromatic solvent and general ionic liquid [19,20]. They are not only dynamically homogeneous but also display locally heterogeneous environments [21–24]. Although the researches and applications on AILs have received far more attention than PILs, PILs also showed high potential due to their distinguishing features such as proton donation to the base associated with the application in advanced fuel-cell technologies or catalysis chemistry [25–32].

Proton transfer reactions are important in either industrial or biochemical system. Porphyrin diacids, typically meso-tetrakis(*p*-sulfonatophenyl)porphyrin (H_4TPPS^{2-}, TPPS), have been obtained persistent interest for decades because of biological importance

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Table 1
Name and abbreviations of the ionic liquids used in the present work.

Name	R_1	R_2	A^-	Abbreviation
1-Butyl-3-methyl-imidazolium terafluoroborate	Butyl	CH_3	BF_4^-	$[MBIM]^+BF_4^-$
1-Butyl-imidazolium terafluoroborate	Butyl	H	BF_4^-	$[HBIM]^+BF_4^-$
1-Butyl-imidazolium methylsulfonate	Butyl	H	$CH_3SO_3^-$	$[HBIM]^+MS^-$
1-Butyl-imidazolium *p*-toluenesulfonate	Butyl	H	$CH_3C_6H_4SO_3^-$	$[HBIM]^+TS^-$
1-Butyl-imidazolium dodecylalkylbenzenesulfonate	Butyl	H	$C_{12}H_{15}C_6H_4SO_3^-$	$[HBIM]^+DS^-$

[33–35] and the copious information can be obtained from their spectroscopic properties.

Herein our research using TPPS as probe in imidazolium-based ILs focus on (i) how and/or what differences in the spectroscopic features of TPPS dissolved ILs compared with that in conventional solution; (ii) how do the PILs affect the TPPS protonation in AILs medium; (iii) how do the specific local structure of ILs influence the solute–solvent interaction between TPPS.

2. Experiment

2.1. Reagents

RTILs used in this work (Scheme 1 and Table 1) were synthesized and purified according to Ref. [36]. Before experiment, all of the ionic liquids was dried for nearly 4 h by rotation evaporator under vacuum at 70–80 °C. Meso-tetrakis(*p*-sulfonatophenyl)porphyrin was obtained from Alfa Aesar Chemicals Company (U.S.A.) and used as received. The stock solution of 1.0×10^{-4} mol/L was prepared by dissolving appropriate amount of TPPS in $[MBIM]BF_4$. Because TPPS was dissolved much slowly in $[HBIM]BF_4$ under ambient conditions, the TPPS-$[HBIM]BF_4$ mixture was treated by sonication and then was separated by centrifugation. The supernatant was transferred into a dry test tube as stock solution to be used.

2.2. Apparatus

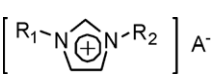
The UV–vis absorption spectra were taken on Hitachi U-3010 UV–vis spectrophotometer (Kyoto, Japan) and the fluorescence and resonance light scattering (RLS) spectra were recorded using LS-55 luminescence spectrometer (PerkinElmer Co. Ltd.) equipped with a pulse xenon lamp under the condition of 1% attenuator. The excitation and emission bandpasses were typically set at 10 nm and 15 nm, respectively. RLS spectra were obtained by simultaneous pattern by setting wavelength difference between the excitation and emission at $\Delta\lambda = 0$ nm and bandpass width 10 nm both for the excitation and emission. Fluorescence decay measurements were carried out on a FL920 Fluorescence Lifetime Spectrometer (Edinburgh Instruments Ltd.) with the pulse width of 1 ns. The fluorescence decay curves were fitted by reconvolution patterns.

All the experiments were performed at room temperature unless specially indicated.

2.3. Procedures

Initially, a certain amount of TPPS was directly dissolved in different ILs, and was then diluted by the same ILs to 10 mL in a dry comparison tube for the measuring absorption spectrum or fluorescence spectrum. TPPS concentration was controlled under 4 μM in both $[MBIM]BF_4$ and [HBIM]TS. The experiment on the solvation of TPPS in $[HBIM]BF_4$ was performed below the saturation concentration of TPPS.

In terms of the protonation of TPPS, a certain amount of TPPS-$[MBIM]BF_4$ stock solution was transferred into a comparison tube, and then diluted by $[MBIM]BF_4$ to the final 10 mL. The concentration of TPPS 4 μM in the working solution was kept during the experimental process. Then a very small amount of PILs was titrated into working solution, the sample solution was stirred thoroughly and allowed to equilibrate for sufficient time before each measurement.



Scheme 1. The structure of ionic liquids used here.

3. Results and discussion

3.1. Absorption spectra of TPPS in single ILs

The absorption spectra of TPPS were shown in Fig. 1 in three different ILs, namely, $[MBIM]BF_4$, $[HBIM]BF_4$ and [HBIM]TS. [HBIM]MS is solid at room temperature and TPPS does not completely dissolve in high viscosity [HBIM]DS, so they were not used here. The absorption spectra of TPPS display obvious differences in ionic liquids compared to that in aqueous solution, as summarized in Table 2.

TPPS as free base (H_2TPPS^{4-}) with D_{2h} symmetry exists usually in neutral aqueous solution, two nitrogen atoms of the macrocyclic core of H_2TPPS^{4-} remaining unprotonated form. Absorption of the free base was characterized by an intense Soret band at 413 nm and four weak Q bands at 515 nm, 550 nm, 589 nm and 645 nm, respectively. The intensity of four Q bands in turn decrease in the order 515 nm, 550 nm, 589 nm and 645 nm. However, at acidic medium (pH less than 4), the symmetry increases to D_{4h} featuring a red-shifted Soret band from 413 nm to 434 nm and a weak Q band at 645 nm. At even lower pH, some of diacid monomers of TPPS (H_4TPPS^{2-}) self-assemble to J-aggregates. Consequently, a new sharp band at 490 nm in Soret band region appeared in parallel with another new weaker and wider band at 705 nm in Q region

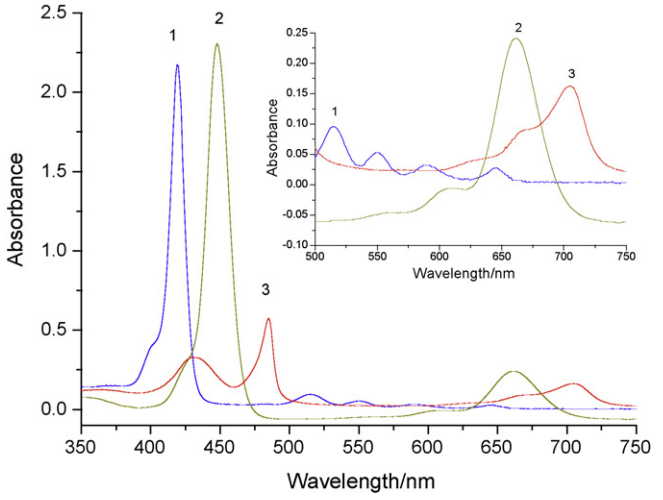


Fig. 1. Absorption spectra of TPPS dissolved in single $[MBIM]BF_4$ (1), [HBIM]TS (2) and $[HBIM]BF_4$ (3), respectively. The concentration of TPPS was 4 μM in both $[MBIM]BF_4$ and [HBIM]TS, and saturated in $[HBIM]BF_4$. The inset was the absorption in Q bands region of TPPS in the three ILs medium, respectively.

Table 2
The maximum absorption positions of TPPS in ILs and aqueous solution.

Medium	Species of TPPS	Soret bands (nm)	Q bands (nm)	Ref.
H_2O	H_2TPPS^{4-}	413	515, 550, 589, 645	[37,38,39]
H_2O	H_4TPPS^{2-} monomer	434	645	[37,38,39]
H_2O	H_4TPPS^{2-} J-aggregate	434, 490	702	[37,38,39]
$[MBIM]BF_4$	H_2TPPS^{4-}	420	515, 550, 589, 645	Here
[HBIM]TS	H_4TPPS^{2-} monomer	448	661	Here
$[HBIM]BF_4$	H_4TPPS^{2-} J-aggregate	437, 483	702	Here

[37–39]. While in aprotonic IL $[MBIM]BF_4$ medium, the spectral property of TPPS was closely similar to that in neutral aqueous solution except that Soret band changes from 423 nm to 420 nm. However, in the other two protonic ILs medium, i.e., $[HBIM]BF_4$ and [HBIM]TS, absorption of TPPS show obvious change. TPPS has D_{4h} symmetry in [HBIM]TS and the Soret band red-shifted from 420 nm to 448 nm, while Q bands was intense at 661 nm, very weak at 555 nm and 605 nm. It was suggested that TPPS existed in the protonated species (H_4TPPS^{2-}) in [HBIM]TS. Whereas in the $[HBIM]BF_4$, besides red-shifted band at 437 nm, a new band at 483 nm occurred in parallel with a red-shifted Q band at 702 nm, indicating that TPPS J-aggregates were formed in $[HBIM]BF_4$ medium. Although both $[HBIM]BF_4$ and [HBIM]TS are usually strong acid, TPPS J-aggregates can be induced in $[HBIM]BF_4$ medium, rather than in [HBIM]TS medium.

In addition, it was noteworthy that the splitting extent of characteristic absorption spectra of TPPS J-aggregates relative to their Soret band were smaller in single $[HBIM]BF_4$ compared to aqueous solution, that is, $\Delta\lambda = 46$ nm (from 437 nm to 483 nm) in $[HBIM]BF_4$ and $\Delta\lambda = 56$ nm (from 434 nm to 490 nm) in aqueous solution [37–39].

3.2. The effects of PILs on the absorption spectra of TPPS in AILs

PILs can act as proton-donors besides as solvents. This is important in acid–base catalytic reaction. Therefore, next attention was focused on the effect of PILs on the protonation of TPPS in $[MBIM]BF_4$ medium. Fig. 2 displayed typically the absorption spectral changes of TPPS upon the increase of [HBIM]MS in [MBIM] BF_4 medium.

Upon the addition of [HBIM]MS, the Soret band of TPPS produced the expected red-shift to 446 nm, going with the collapse of the four Q bands into one new band at 665 nm. No TPPS aggregation band appeared in the presence of [HBIM]MS, even the concentration of [HBIM]MS was increased to higher level. Moreover, an ill-isobestic point at *ca.* 430 nm revealed that the equilibrium between TPPS free base (H_2TPPS^{4-}) and the protonated TPPS (H_4TPPS^{2-}) existed under the experimental environment. In other words, the proton transfer from [HBIM]MS to TPPS (H_4TPPS^{2-}) occurred efficiently in AILs.

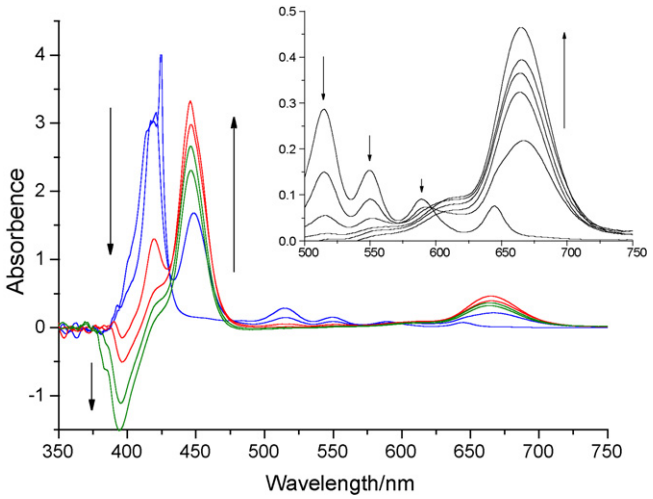


Fig. 2. Absorption spectra of TPPS in $[MBIM]BF_4$ upon the titration of [HBIM]MS. The concentration of TPPS in $[MBIM]BF_4$ was kept constantly at 4 μM. The inset was the amplified absorption spectrum of TPPS in $[MBIM]BF_4$ upon the titration of [HBIM]MS in the Q band region of 500–750 nm. The concentration of [HBIM]MS used here were 0.0 mol/L, 0.30 mol/L, 0.60 mol/L, 0.90 mol/L, 1.2 mol/L and 1.8 mol/L, respectively.

Just as expected, the absorption features of TPPS changed in very similar trend upon the titration of $[HBIM]BF_4$, [HBIM]TS and [HBIM]DS into $[MBIM]BF_4$ (the absorption spectra were not showed here). A well-isobestic point at *ca.* 430 nm was observed upon the addition of three PILs aforementioned, respectively, also showing that the equilibrium between the free H_2TPPS^{4-} and the protonated H_4TPPS^{2-} species was established. The absorbance of TPPS at 446 nm experienced a substantial increase to a platform with increase in PILs concentration to a certain degree, namely, 0.30 mol/L for $[HBIM]BF_4$, 0.60 mol/L for [HBIM]TS and [HBIM]DS, 0.80 mol/L for [HBIM]MS. More importantly, the change degree of the absorbance of protonated TPPS was slightly dependent on the properties of PILs under same concentration. Based on these observations, the ability of PILs transfer proton to TPPS seemly obey the following order: $[HBIM]BF_4$ > [HBIM]DS > [HBIM]TS > [HBIM]MS.

3.3. The effects of PILs on the fluorescence spectra of TPPS in AILs

In general, the fluorescence spectra of porphyrin free base and its derivatives exhibited a dual emission band in aqueous solution which appeared at *ca.* 645 nm and *ca.* 702 nm, respectively. The two emission bands merged to one centered at near 665 nm upon the formation of the protonated H_4TPPS^{2-} species.

Fig. 3 illustrated that the fluorescent properties of H_2TPPS^{4-} were sensitive to the presence of the four PILs in $[HBIM]BF_4$ medium. It can be seen that TPPS free base also exhibited the distinct dual emission patterns located at 649 nm and 710 nm in $[MBIM]BF_4$. When PILs was progressively added into the TPPS-$[MBIM]BF_4$ system, initially, the fluorescence intensity of TPPS decreased at both 649 nm and 710 nm. Whereas further addition of PILs, apparently, the broad band at 710 blue-shifted and gradually increased accompanying continuous decrease blue-shift of 5 nm of the band at 648 nm until ultimately disappearance. The enhancement degree of TPPS emission at longer wavelength was greatest in the titration of [HBIM]TS and smallest in the titration of $[HBIM]BF_4$, as shown in Fig. 3. Besides, an isoemission point at *ca.* 670 nm was observed for [HBIM]TS titration. These suggest that TPPS free base in neutral $[MBIM]BF_4$ has been converted to its protonated form upon the addition of the four PILs herein, respectively. Another property was that the fluorescence intensities of TPPS were much lower than that observed in conventional solvents either in the absence or presence of PILs in AILs medium.

3.4. Resonance light scattering spectra

Fig. 4 displayed typically the RLS spectra of TPPS in the presence of various concentrations of [HBIM]TS in $[MBIM]BF_4$. When [HBIM]TS was added into the TPPS/AILs system, initially, the RLS

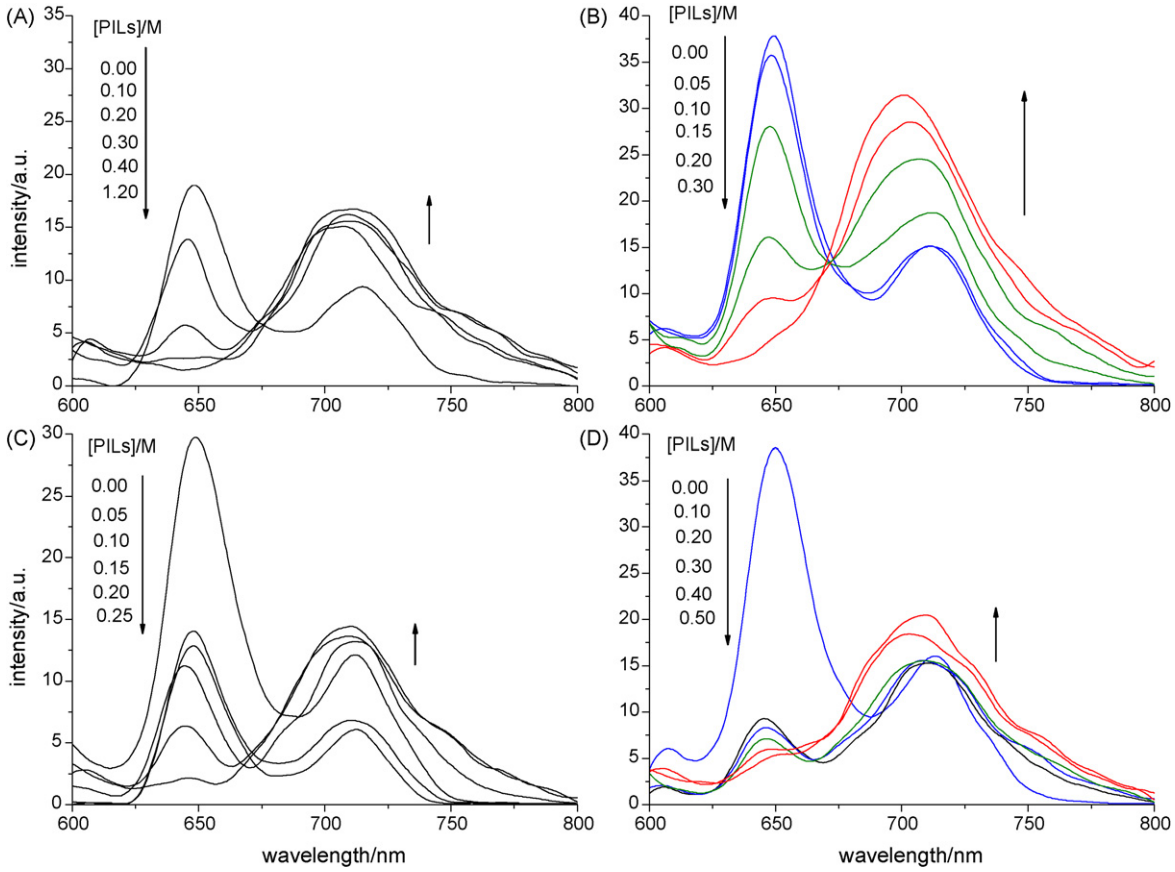


Fig. 3. Fluorescence spectra for TPPS in $[MBIM]BF_4$ upon the titration of $[HBIM]BF_4$ (A), [HBIM]TS (B), [HBIM]DS (C), and [HBIM]MS (D), respectively. The concentration of TPPS during the titration proceeding was kept constantly at 4 μM. λ_{ex} was set at 430 nm.

intensity at 651 nm reduced and disappeared immediately, and a new RLS signal appeared simultaneously at 689 nm and continuously enhanced. These RLS features can be rationally assigned to a fully protonated TPPS. The results were analogous to the other three PILs.

All of the experimental evidences above revealed that TPPS was fully protonated in $[MBIM]BF_4$ medium by PILs. Table 3 collected the main spectroscopic features of various TPPS species in the absence and presence of PILs in AILs medium.

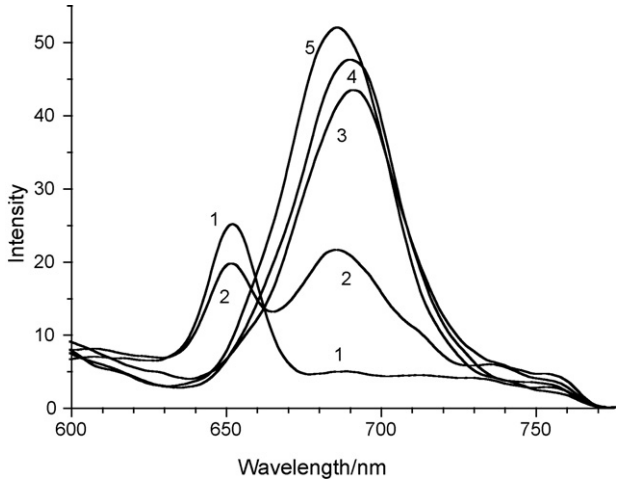


Fig. 4. Changes of TPPS RLS spectra upon the titration of [HBIM]TS in $[MBIM]BF_4$ medium. The concentrations of [HBIM]TS were 0.00 mol/L, 0.10 mol/L, 0.20 mol/L, 0.30 mol/L, and 0.40 mol/L, respectively. And the concentration of TPPS during the titration was kept 4 μM constantly.

3.5. Fluorescent decay of TPPS in RTILs

We typically measured the lifetimes of TPPS in three ILs, as listed in Table 4. In neutral $[MBIM]BF_4$ the fluorescence decay of TPPS is monoexponetial with lifetime 12.4 ns. While in acidic $[HBIM]BF_4$ and [HBIM]TS the fluorescence decay of TPPS is diexponetial. The lifetimes of long- and short-lived components are 12.8 ns and 2.89 ns, in $[HBIM]BF_4$ and 21.0 ns and 3.99 ns, respectively in [HBIM]TS. In both acidic ILs, the fractional contribution of short-lived components is dominant, corresponding to almost fully protonated TPPS. Compared to $[MBIM]BF_4$, long-lived component in $[HBIM]BF_4$ has almost same lifetime. However, lifetimes of both long- and short-lived components in [HBIM]TS are longer than in $[HBIM]BF_4$. This result represents the role of anion TS^-, which will be discussed, *vide post*.

3.6. Discussions

3.6.1. General solute–solvent interactions between TPPS and ILs

The effect of the solvent polarity. The Soret band of TPPS exhibited, respectively a bathochromic shift in $[MBIM]BF_4$, $[HBIM]BF_4$ and [HBIM]TS media with respected to those obtained in conventional aqueous solution (Fig. 2 and Table 2). It was well-defined that the spectrum positions were strongly dependent on the polarity of the medium. Therefore, these ILs should have high polarity comparable to water [40,41]. The polarity of $[HBIM]BF_4$ and water is 74.35 and 63.1, respectively, on the $E_T(30)$ polarity scale [42]. The polarity of [BMIM][BF4] is 48.9 and more polar than acetonitrile (45.6) but less polar than methanol (55.4) on the $E_T(30)$ polarity scale [16]. The solvent cage model was frequently used to explain the interaction between solvent and solute [8,20,43–45].

Table 3
UV–vis Absorption, fluorescence, and RLS features of TPPS derived species in the absence and presence of various PILs in [MBIM]BF_4 medium.

PILs	Species	UV–vis absorption		Fluorescence	RLS (nm)
		B-band (nm)	Q-band (nm)	Emission (nm)	
[MBIM]BF_4	H_2TPPS^{4-}	420	515, 550, 589, 645	649, 710	651
[HBIM]BF_4	H_4TPPS^{2-}	446	668[a]	703	698
[HBIM]TS	H_4TPPS^{2-}	446	662[a]	698	689
[HBIM]DS	H_4TPPS^{2-}	446	663[a]	702	697
[HBIM]MS	H_4TPPS^{2-}	446	665[a]	704	694

The concentration of TPPS was constantly controlled at 4 μM in AILs medium during the spectroscopic measurement aforementioned.
[a] Also 2–3 very weak peaks in Q band region are resoluble.

Table 4
Lifetimes of 2.9 μM TPPS in ILs.

Solutions	τ_1/ns	τ_2/ns	Fractional contribution	
			f_1	f_2
[MBIM]BF_4	12.4	/	100	/
[HBIM]BF_4	12.8	2.89	6.60	93.4
[HBIM]TS	21.0	3.99	4.74	95.3

The π–π complex of the solute–solvent between TPPS and ILs. The π–π interaction can be taken into account of the absorption profiles of TPPS dissolved in the three ILs medium, respectively. Significant red-shifts in Soret band region and Q band region were happened in [HBIM]BF_4 and [HBIM]TS medium, respectively. It indicated a complicated interaction between TPPS and the two PILs besides the general dipolar effect. The imidazolium cation is an aromatic π system. It is highly possible that the solute–solvent complex was stabilized by the π–π interaction between the TPPS macrocycle and the aromatic imidazolium cation [19,46]. Moreover, the repulsive force between the positive charges or the negative charges, the π–π interaction between TPPS and imidazolium cation counteracted the π–π stacking of the porphyrin itself, which favored the stability and dispersion of TPPS in ILs [44]. Besides that, in the case of the TPPS solvation in pure ILs, the anions might exist in the plane of the porphine ring and interact slightly with the positively charged ring-hydrogens, whereas the cations should exist in two sides of the porphyrin ring interacting with the electron-rich π-system [8]. Particularly, TS anions also exist in two sides of the porphyrin ring by π–π interaction to creative a located more hydrophobic environment to lead to longer excited longer lifetime of TPPS and to inhibit the aggregation of TPPS.

3.6.2. Protonation and J-aggregation of TPPS

Proton transfer. PILs are the proton carriers and can act as the Brønsted acids for conducting proton. An important aspect of protic ionic liquids is their ability of transfer proton to an acceptor in acid–base catalytic reaction. When PILs contacted with TPPS in AILs medium, the proton transfer should be generated between PILs and TPPS as described as the following equilibrium.

$$2L\text{–}H + H_2TPPS = H_4TPPS\text{–}L_2 \quad (1)$$

$$K_{PT} = \frac{[H_4TPPS\text{–}L_2]}{[L\text{–}H]^2[H_2TPPS]} \quad (2)$$

Where K_{PT} is the intermolecular proton transfer constant from PILs to H_2TPPS, L–H is PIL monocation, H_2TPPS is the porphyrin free base, and the H_4TPPS is the protonated TPPS. According to the analogous form reported previously in literature [47], the proton transfer constant (K_{PT}) of PILs to TPPS can be expressed as:

$$K_{PT} = \frac{1}{C_{PILs}^2}\frac{F_0 - F}{F - F_{max}} \quad (3)$$

Where F, F_0 and F_{max} correspond the fluorescence intensity of the porphyrin measured at 648 nm in the AILs medium in the presence of and absence of certain PIL concentration C_{PILs} and completely protonation, respectively. The results were listed in Table 5.

The pK_b of TPPS free base is 9.1 (or K_b *ca.* 8×10^{-10}) in aqueous solution and the titration constant of TPPS strong acid is *ca.* 4×10^4. However, the K_{PT} value in Table 4 is *ca.* two orders of magnitude smaller. It might be closely related to the ionic conductivity of PILs, which was mainly governed by the viscosity and the number of charge carriers. The viscosity of ILs was a consequence of the electrostatic interactions that were intrinsic to their ionic nature [5]. According to the Walden plot used by Angell and co-workers [41], PILs were generally regarded as "poor" media in protonic conduction with an exception for tetrafluoroborate anion, BF_4^- [42]. On the other hand, the solvent reorganization was slow so that the geminate ion pair was virtually confined to a viscous solvent cage in which the residency period of the radical ions in close proximity will be so long that scarcely any radical ion can escape from the cage before being annihilated by the geminate recombination [48]. The anions TS^-, DS^-, and MS^- had the comparable structural character. The π-stacking of benzene ring in both TS^- and DS^- anion leads to the stronger ion–ion interactions. Moreover, as the alkyl chain length of the organic anion increased, the steric hindrance of the chains became stronger. For the BF_4^- anion, it was considered as the "good" ionicity, due to the low polarizability of the fluorine atom [41,49], decreasing the electrostatic interaction between the cation and the anion, besides that, the delocalization of the charge on the anion, through the fluorination, decreased the viscosity by weakening hydrogen bonding [50].

TPPS J-aggregates can be generated in [HBIM]BF_4 medium, rather than in [HBIM]TS medium. Despite being the proton donator, as well as so-called "*strong acid*", TS^- anion in [HBIM]TS actually prevented TPPS from J-aggregates by steric hindrance or possible N–H···A^-···H–N hydrogen binding between pyrrole N–H groups in porphine core and oxygen-containing anion through the charge-transfer interaction [51]. In addition, the splitting extent of the Soret band of TPPS J-aggregates were smaller in [HBIM]BF_4 medium compared to aqueous solution. In the case of TPPS J-aggregates, the dipole–dipole interaction between porphyrins was usually performed on the $S_0 \rightarrow S_2$ transition (B- or Soret-band) [52]. With the increasing in the polarity of solvent, the stability of the higher exci-

Table 5
The proton transfer constant of TPPS with various PILs in [MBIM]BF_4 medium.

PIL	[HBIM]BF_4	[HBIM]TS	[HBIM]DS	[HBIM]MS
K_{PT} (M^{-2})	$(2.32 \pm 0.23) \times 10^2$	$(0.84 \pm 0.45) \times 10^2$	$(1.12 \pm 0.21) \times 10^2$	$(1.52 \pm 0.08) \times 10^2$

The proton transfer constants were obtained according to TPPS fluorescence decreases at 648 nm.

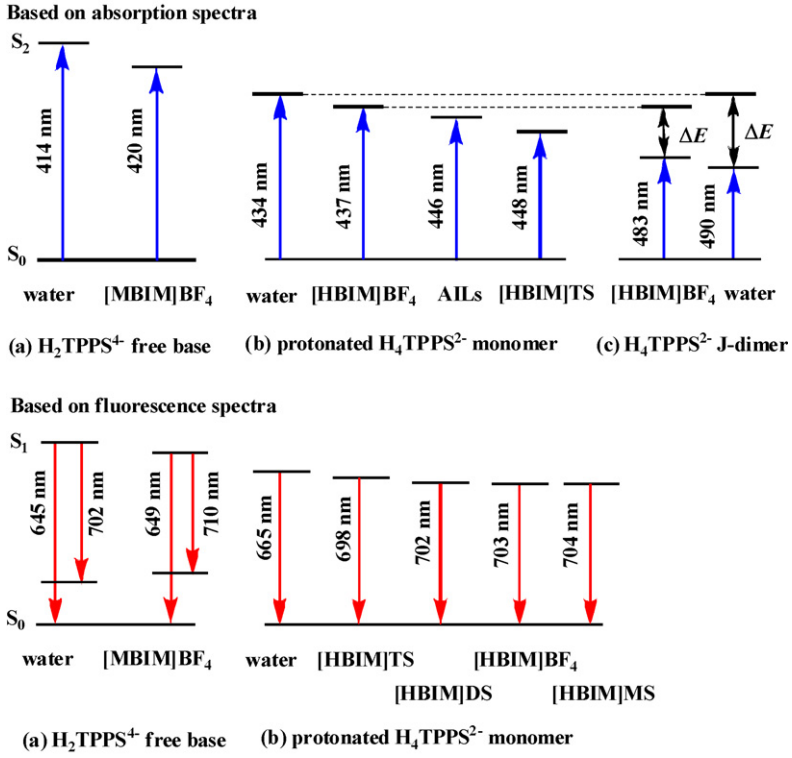


Fig. 5. Schematic energy diagram of various TPPS species in pure ILs and aqueous solution (upper) and fluorescence upon the addition of PILs in AIL (lower).

tonic state of the absorption related to TPPS J-aggregates in Soret band became higher. The transition dipole moments of the Soret band of TPPS J-aggregates were transferred to the lower energy level. Hence, the different polarity between $[HBIM]BF_4$ and water can account for the typical variation of excitonic splitting characteristics corresponding to TPPS J-aggregates.

3.6.3. Summary of energy levels of TPPS in ILs and in aqueous solution

Based on Section 3 above, the energy diagram of various TPPS species was summarized in Fig. 5.

ΔE means the energy slitting between the protonated monomer and corresponding J-aggregate; 446 nm (in absorption spectra (b)) means the wavelength position of the protonated TPPS by PILs in AIL ($[MBIM]BF_4$) medium.

Briefly, the energy change of TPPS in ILs should be attributed to complex interaction with ILs, including the solvent polarity (dielectric constant (ε) maybe being more important than refractive index (n)), π–π interaction, electrostatic interaction and also proton transfer, etc. But at present we could not resolve the contribution of each interaction yet.

4. Conclusions

The absorption and fluorescence spectra of TPPS in ILs displayed significant difference compared to aqueous solution. This should be attributed to the complicated interaction including π–π interaction and hydrophobility, electrostatic interaction, dipole–dipole and also proton transfer, etc. The $[HBIM]BF_4$, [HBIM]TS, [HBIM]DS, and [HBIM]MS as the proton conductors can effectively promote TPPS protonation. The lower proton transfer constant of PILs to TPPS should be relative to high viscosity of anion of PILs. The J-aggregation of TPPS is regulated by both cation and anion of ILs. Anion BF_4^- does not affect J-aggregation of TPPS, while TS^- inhibits the J-aggregation. Both cation and anion should be simultaneously considered in investigation of solute–solvent interaction [13–17]. This might be the largest difference from general dipolar organic solvents. Detail solvation dynamics of TPPS in ILs is currently under study in our group.

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