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Influence of C2-Methylation of Imidazolium Based Ionic Liquids on Photoinduced Spin Dynamics of the Dissolved ZnTPP Studied by Time-Resolved EPR

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Abstract: Unusual physical properties of ionic liquids (ILs) can be implemented in many different applications and are very sensitive to the structure of IL. In this work we investigate the spin dynamics of probe molecule Zn tetraphenylporphyrin (ZnTPP) dissolved in a series of ILs using time-resolved electron paramagnetic resonance (TR EPR). We compare the TR EPR characteristics in C2-methylated imidazolium-based ILs [bmmim]BF₄ and [bmmim]PF₆ and in their C2-protonated analogs [bmim]BF₄ and [bmim]PF₆ to assess the influence of C2-methylation. The corresponding TR EPR signatures are drastically different in the two types of ILs. The analysis of experimental data allows assumptions that the ZnTPP molecule is distorted in C2-methylated ILs, contrary to other organic media and C2-protonated analogs. The mobility of ZnTPP in C2-methylated ILs is smaller compared to that in C2-protonated analogs, implying different microenvironment formed around dissolved ZnTPP.

Keywords: EPR; ionic liquids; photoexcited triplets; polarization; TR EPR.

Dedicated to: Kev Salikhov on the occasion of his 80th birthday.

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1 Introduction

Ionic liquids (ILs) consist of separated cations and anions, whose recombination into neutral molecules is sterically hindered. Such unusual structure of ILs leads to advanced properties making them perspective as energetic materials and green chemistry solvents [1–5]. In addition, ILs are interesting and promising media for photolysis, redox and polymerization reactions [6, 7]. The properties of ILs are mainly determined by interactions between cations and anions, and thus can be tuned by adjusting the chemical structure of each component.

Of particular recent interest, it was found that 1-alkyl-3-methylimidazolium based ILs have drastically different physicochemical properties compared to their dimethyl-substituted analogs, in which the C2 proton is replaced by a methyl group. Supposedly, such methyl group in C2 position of the imidazolium ring shifts the balance between Coulombic and hydrogen bonding interactions, and in this way strongly affects the properties of the IL. As is known from literature, the methylation at C2 position leads to a higher melting point and higher viscosity in comparison with C2-protonated ILs [8]. Such behavior was intensively researched, and some explanations were suggested [9–13].

Zhang and colls. applied molecular dynamics simulations to study the structure of 1-*n*-butyl-3-methylimidazolium and 1-ethyl-3-imidazolium ILs with hexafluorophosphate as anion [14]. It was found that C2-methylated ILs reveal more stable ion pair and ion cage structures in comparison with C2-protonated analogs. Qualitatively the same phenomena were studied in Ref. [15] in [bmim] N_3 and [bmmim] N_3 ILs, where C2-methylation led to a slower ion motion and significant structural changes, particularly to a shift of the preferred anion position relative to imidazolium ring. Despite of the great interest to the structural peculiarities of C2-methylated ILs, there are only a few studies where the direct influence of IL media on the dissolved molecule was investigated with respect to the specific role of the C2-group.

The rotational dynamics of neutral (2,5-dimethyl-1,4-dioxo-3,6-diphenylpyrrolo[3,4c]pyrrole) and charged (rhodamine 110) solutes was compared in C2-methylated and C2-protonated ILs [16]. It was demonstrated that nondipolar solute is not sensitive to the structure of cation, and the rotational diffusion obeys classical Stokes-Einstein-Debye theory, contrary to the charged solute where a dramatic influence of the imidazolium ring structure takes place and faster rotation in C2-methylated ILs was observed. The authors explained such result by increased Coulombic interaction between cation and anion of IL, which effectively eliminates the hydrogen-bonding interaction of the cation with the charged solute.

Thus, the investigation of the influence of C2-methylation in imidazolium based ILs and understanding of the underlying mechanisms are of considerable

interest. A valuable approach to study the influence of IL structure on the dissolved molecule is provided by electron paramagnetic resonance (EPR) spectroscopy. In this technique the paramagnetic molecule is used as a probe reflecting its interaction with surrounding media via the EPR spectrum. A number of papers were focused on the research of ILs and their influence on spin probes recently, including high-field EPR spectroscopy on ILs and IL-water mixtures [8, 17–26]. In those works, as a rule, various nitroxide spin probes were used as molecular reporters dissolved in ILs, whose mobility was monitored by continuous wave (CW) EPR and analyzed theoretically. However, a few works were also concerned with application of time-resolved (TR) EPR to address the unusual properties of ILs [27, 28]. In such approach, it is most feasible to use photoexcited triplet states as paramagnetic probes, because the strong spin-polarized signals and reversibility of photoinduced reactions strongly simplify the experiments. There is also a long history of studying the photoexcited triplet states by EPR techniques, including naturally occurring and artificial systems relevant for photosynthesis, studies of molecular order and dynamics of triplets in liquid crystals, implication of triplet porphyrins as spin probes for distance measurements, etc. [29–40]. In particular, recently we demonstrated that the sensitivity of TR EPR operating on triplet Zn tetraphenylporphyrin (ZnTPP) to the effects of microstructuring in ILs is higher than that for CW EPR of nitroxide spin probes [28].

In this work we apply TR EPR with ZnTPP probe to investigate the C2-methylated imidazolium-based ILs and compare the observed trends with those found previously for their C2-protonated analogs [28]. We demonstrate high sensitivity of TR EPR to the interactions between spin probe and IL. The detailed analysis demonstrates possible distortion of ZnTPP molecule in C2-methylated IL. In addition, longer relaxation times of spin polarization are observed in C2-methylated ILs.

2 Experimental section

Ionic liquids 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([bmmim]BF₄), and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([bmmim]PF₆) were synthesized in the Boreskov Institute of Catalysis SB RAS. The procedure for obtaining selected C2-methylated ILs was the following. A 100 mL round-bottomed flask fitted with magnetic stirrer bar and reflux condenser was charged by 5.0 g (26.5 mmol) of 1,2-dimethyl-3-butylimidazolium chloride (obtained by analogy with the literature method [41] from 1,2-dimethyl imidazole and butyl chloride), 53 mmol of corresponding salt (NaBF₄ or NaPF₆) and 100 mL of acetone.

The mixture was stirred for 3 h at 50 °C. The solid was filtered and washed by 10 mL of acetone. The second portion of corresponding salt (20 mmol) was added to the filtrate and the resulting mixture was stirred for 3 h at 50 °C. The solid was filtered and washed by 10 mL of acetone. The filtrate was evaporated in vacuo. The residue was solved in 30 mL of dry dichloromethane (to remove NaCl and excess of starting salt) and filtered. The filtrate was evaporated and the product was dried in high vacuo (10^{-3} bar) at 80 °C for 6 h. Yields of products were 75 %–85 %. The reaction of an ionic liquid sample with AgNO₃ was negative, demonstrating the absence of Cl⁻ ions in the IL media.

Zn tetraphenylporphyrin (ZnTPP) was purchased from Sigma-Aldrich and used as received. The excess of ZnTPP powder was dissolved in the corresponding IL and then the solution was kept in an ultrasonic bath at 70 °C in the closed Eppendorf tube for 24 h. In this way the maximum possible amount of ZnTPP was dissolved and the rest was precipitated by centrifuging. The fraction with dissolved ZnTPP was then isolated and transferred into the EPR quartz tube. Then the solution in the quartz tube was evacuated $(10^{-2}$ Torr pressure) with simultaneous heating at 85 °C during 3 h to reduce the amount of remaining water in IL and to eliminate the remaining oxygen. Finally, the tube was sealed off under vacuum.

EPR measurements were performed using a homemade TR EPR setup based on an X-band Bruker EMX spectrometer. The temperature was controlled with an N₂-cooling system and a Lakeshore temperature controller. In all mentioned experiments the sample was first melted in hot water (~ 80 °C), shock-frozen in liquid nitrogen and then directly transferred into the cryostat. The final temperature was equilibrated within following 20 min. A Nd : YaG laser LOTIS-TII with the excitation wavelength of 532 nm was used. We used the unpolarized laser beam in all experiments. The computer simulations of all spectra were performed using EasySpin software [42]; the analysis of polarization kinetics was done using the numerical solution of Bloch equations similar to [26].

3 Results and discussion

Time-resolved EPR is a more specific technique compared to common CW EPR. TR EPR experiment employs laser excitation to create paramagnetic intermediates in the sample and continuous microwave irradiation to detect the subsequent evolution of these transient signals in time [43]. To achieve better time resolution, no phase-sensitive detection is used and zero harmonic signal is experimentally observed (so-called direct detection). Depending on the spin polarization



Scheme 1: Chemical structures of studied ILs and ZnTPP.

mechanism, the absorptive or/and emissive signals can be detected. ZnTPP is a well-known molecule that converts into a triplet state upon photoexcitation (λ =532 nm) with the lifetime on the order of milliseconds depending on temperature and microenvironment [29, 30, 44–47].

In this work we aim at investigation of interactions between the photoexcited ZnTPP molecule and ionic liquids, in particular on studying the effect of C2-methylation in anions (Scheme 1). For this sake we perform TR EPR studies in two C2-methylated ILs [bmmim]PF₆ and [bmmim]BF₄ and compare the results with previously obtained ones for their C2-protonated analogs [bmim]PF₆ and [bmim]BF₄ [28]. The glass transition/melting temperatures (T_g/T_m) of these four ILs are known to be approximately 180/190 K for [bmim]BF₄, 200/280 K for [bmim] PF₆, 205/310 K for [bmmim]BF₄ and 215/313 K for [bmmim]PF₆ [48–50]. Thus, in case of C2-methylated ILs all TR EPR data in the 100–295 K temperature range were recorded in the solid state of IL.

3.1 General comparison of TR EPR data in selected ILs

Figure 1 shows TR EPR spectra of ZnTPP in four selected ILs at 100 and 200 K. It is evident that the presence of the methyl group in C2 position crucially affects



Fig. 1: TR EPR spectra of ZnTPP in selected ILs at 100 and 200 K (as indicated). All spectra were obtained by integration of TR EPR data within 1 μ s after the laser flash. The spectra of C2-protonated ILs were measured by us in Ref. [28].

the shape of the triplet spectrum. The spectra in C2-methylated ILs are narrower and the canonical triplet peaks are sharper compared to C2-protonated ILs. The zero-field splitting (ZFS) parameters of the presented spectra were determined by simulations (more details in the next section) and are summarized in Table 1, which also reports typical ZFS parameters of ZnTPP in various media available from literature.

The data in Table 1 clearly show that the ZFS parameters of ZnTPP in C2-protonated ILs are close to those in other media found previously. Contrary, in case of C2-methylated ILs one systematically observes noticeably smaller D-values compared to other media, including C2-protonated analogs, and in general larger E-values (especially in case of [bmmim]PF₆). Since E relates to the rhombicity of the ZFS tensor and reflects the changes of molecular structure, we suggest that such trend arises from the distortion of originally closely planar ZnTPP, supposedly due to the displacement of Zn atom out of the TPP plane and concomitant bending of the molecule. For instance, a similar trend was found previously in bis(o-semiquinonato)copper(II) complexes exhibiting ligand-driven out-of-plane displacement of central copper atom [54].

Table 1: The parameters obtained from spectral simulations of TR EPR spectra of ZnTPP obtained at $\tau_{DAF} = 0$ ns delay after the laser flash at different temperatures. The available literature data are also given for comparison. The relative populations used in our simulations were $(P_z - P_x) : (P_z - P_y) = 1$. ZLI-1167 and E-7 exemplify trends in liquid crystals. The accuracy of D and E values obtained here and in [26] is ± 10 MHz.

Solvent	T/K	D/MHz	E/MHz	g-Value	Reference
[bmmim]PF ₆	100	685	350	1.999	This work
-	200	671	311	1.998	This work
[bmmim]BF4	100	812	275	1.997	This work
	200	762	254	1.996	This work
[bmim]PF ₆	100	895	248	1.998	[28]
-	200	906	290	1.998	[28]
[bmim]BF ₄	100	910	257	1.996	[28]
	200	893	188	1.996	[28]
Toluene : chloroform (1 : 1)	10-20	920	292	2.0020	[37]
Toluene	40	906	284	[2.0020 2.0024 1.9968]	[51]
Toluene : ethanol (1 : 1)	100	894	294	-	[30]
Toluene	110	919	291	-	[52]
ZLI-1167	135	918	306	-	[53]
E-7	100	894	294	-	[30]
NR ₄ TFSI	298	924	0	-	[27]

In general, the TR EPR kinetics might reflect the spin relaxation of triplet sublevel populations or the lifetime of paramagnetic species formed upon laser excitation. Figure 2 shows the kinetic curves of ZnTPP for various ILs and temperatures. Since the lifetime of the triplet state of ZnTPP is known to be much longer than the kinetics shown in Figure 2 (25 ms [45] in rigid glass and possibly even higher in ILs [5]), the observed TR EPR decays should be mainly determined by spin relaxation. A significant lengthening of the TR EPR decay in C2-methylated ILs compared to C2-protonated ones is observed (more details in the next section), which can be ascribed to two factors. First, the suppressed hydrogen-bonding interactions in C2-methylated ILs lead to an essential increase of Coulombic interactions between anions and cations. Second, as was mentioned in the Introduction, the C2-methylated ILs have quite a pronounced tendency to form ordered microenvironments of cations and anions, so that the dissolved spin probe becomes effectively caged and shielded from efficient solid-state relaxation mechanisms.

3.2 Microenvironments of ZnTPP in selected ILs

In our previous study [28] we developed an approach to probe heterogeneities in frozen C2-protonated imidazolium-based ILs using TR EPR of photoexcited



Fig. 2: TR EPR kinetics of ZnTPP in selected ILs at 100 and 200 K. All curves are obtained by integration of TR EPR data in the region of maximum absorption signal within 317–333 mT range. The data on C2-protonated ILs are taken from Ref. [28]. Note that the similarity of the kinetics in [bmim]PF₆ and [bmmim]PF₆ at 200 K is well reproducible, but purely accidental at this particular temperature.

ZnTPP. The effects of microstructuring were identified by strongly time-dependent shapes of TR EPR spectra and, as a counterpart, TR EPR kinetics noticeably depending on spectral position. The observed dependences were explained by co-existence of two ZnTPP fractions with different relaxation times and therefore different corresponding microenvironments. In this work, we applied the same strategy to C2-methylated imadazolium-based ILs.

Figure 3 shows the spectra of ZnTPP in selected ILs at 100, 200 and 240 K. Each plot summarizes the spectra for certain IL and temperature at different delays after the laser flash (τ_{DAF}). In all cases we assumed the polarization being due to the triplet mechanism with the pattern described by relative populations ($P_z - P_x$): ($P_z - P_y$)=1. The variations of P_x , P_y , P_z did not lead to any significant improvement of the fit, and therefore these values were kept fixed. The ZFS parameters D, E and the g-factor (assumed to be isotropic) were varied, resulting in the best fits summarized in Table 1.

The spectra obtained in [bmmim]BF₄ are weakly-dependent on τ_{DAF} at all temperatures, whereas its C2-protonated analog [bmim]BF₄ shows a clearly visible dependence of the spectral shape on τ_{DAF} , especially at 200 K. Thus, contrary to [bmim]BF₄, the TR EPR spectra do not indicate an occurrence of different microenvironments of ZnTPP in frozen [bmmim]BF₄.

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Fig. 3: Normalized TR EPR spectra of ZnTPP in C2-methylated and C2-protonated ILs measured at different τ_{DAF} values (each color corresponds to a particular τ_{DAF}). Corresponding ILs and temperatures are indicated at the plot. All spectra were obtained directly at the indicated τ_{DAF} without integration over the time. All data on C2-protonated ILs were measured in [28] and reprocessed here at other τ_{DAF} values for convenient comparison with C2-methylated analogs. Simulations were performed for $\tau_{\text{nAF}} = 0$ µs and are shown by dashed black lines.

At the same time, the TR EPR spectra of ZnTPP in [bmmim]PF₆ are notably dependent on τ_{DAF} at 200 and 240 K. But, in comparison with [bmim]PF₆, the observed tendency is just the opposite. In C2-protonated IL sharp peaks at canonical orientations are observed at short τ_{DAF} , and the spectrum transforms

into the more isotropic-like shape at longer τ_{DAF} . In contrast, in the C2-methylated analog the canonical peaks get sharper at longer τ_{DAF} . Such a behavior in C2-protonated [bmim]PF₆ has been explained by some fraction of ZnTPP molecules exhibiting pronounced mobility (rotational motion) and supposedly localized in micelle-like cavities formed by frozen IL. At the same time, the opposite trend observed in C2-methylated [bmmim]PF₆ can more likely be explained by librational motions exhibited by ZnTPP. Such librations, as a rule, lead to anisotropic relaxation resulting in sharpening of the canonical peaks at long time delays.

Therefore, contrary to C2-protonated ILs, TR EPR spectra in their C2-methylated analogs do not indicate formation of cavities around ZnTPP, which would likely enhance its rotational mobility. Whether different microenvironments of ZnTPP coexist in C2-methylated ILs or not should be further investigated by analyzing the TR EPR kinetic curves.

To quantitatively analyze the TR EPR kinetics of ZnTPP in ILs we used the numerical solution of Bloch equations to fit the experimental data, yielding the TR EPR decays and relaxation times T_1 and T_2 at the output. Our previous study [28], as well as earlier work [55], have demonstrated that the TR EPR kinetics of TPPs is always biexponential in frozen solutions, even in common organic solvents. Therefore, such kinetics should be simulated assuming two contributions of species having different T_1 and T_2 (T_{11} and T_{21} , T_{12} and T_{22}) and weighted with the coefficients (1-k) and k, where k refers to the slower relaxing ("long-lived") fraction (the second subscript 2). We assumed the transverse relaxation times (T_{2}) to be equal for simplicity, and the most informative parameter obtained from this analysis is the relative contribution of each subsystem k. For common organic solvents k is universally found to be $\sim 1/3$ [28], whereas for frozen ILs it might strongly deviate from this value, to be assigned to the effects of microstructuring. The initial polarization patterns were assumed to be the same for the two components in all cases, $(P_z - P_y) : (P_z - P_y) = 1$, stemming from the triplet intersystem crossing mechanism. In case of C2-methylated ILs the ZFS parameters were assumed equal for both components, because the shape of the TR EPR spectrum showed similar trend vs. time delay as that in common organic solvents (compare with Figure 1 of Ref. [28]), likely to be attributed to librational motions of ZnTPP. However, in case of C2-protonated ILs the two components have different ZFS, therefore decomposition of the TR EPR spectra/kinetics is more complicated; it was described in detail in our previous work [28] (here we only use these previously obtained values). Note that the coexistence of several triplet species with different properties was found previously in other systems as well [56].

Figure 4 shows the temperature dependence of the longitudinal relaxation times T_{11} and T_{12} and the relative amount of the slow relaxing fraction of ZnTPP



Fig. 4: (a, b) $T_{1,1}$ and $T_{1,2}$ times obtained by simulation of TR EPR decays, and (c) the slow-relaxing fraction *k*. The data on C2-protonated ILs is taken from Ref. [28].

(*k*) in all selected ILs. One observes that, in general, the magnitudes of all parameters and all trends are similar in the two types of ILs. At the same time, in most cases $T_{1,1}$ and $T_{1,2}$ values are higher in C2-methylated ILs, resulting in longer TR EPR decays observed, being most obvious at 100 K (see also Figure 2).

Special attention should be given to the temperature dependence of the parameter *k*. This parameter in C2-protonated ILs could have been reliably measured only at T < 200 K due to the melting/softening of such ILs at T > 200 K [28]. In C2-methylated ILs, however, *k* can be followed up to nearly room temperature, and demonstrates monotonic decrease (Figure 4c). Assuming that two microenvironments of ZnTPP coexist at low temperatures in C2-methylated ILs similar to C2-protonated analogs, this means that the "slow-relaxing" phase gradually disappears with temperature, and close to the melting point all C2-methylated IL represents homogeneous ordering.

Thus, we observe qualitatively different manifestations of two microenvironments of ZnTPP in C2-protonated and C2-methylated imidazolium-based ILs. In case of C2-protonated [bmim] BF_4 and [bmim] PF_6 we observed manifestations of two microenvironments simultaneously in spectra and kinetics of TR EPR. The spectra changed their shape vs. time becoming more isotropic-like at long time delays; at the same time, the kinetics were biexponential, with contributions from ZnTPP in each environment. In case of C2-methylated [bmmim]BF₄ and [bmmim] PF₆ we did not observe any characteristic changes in the TR EPR spectra assignable to the two microenvironments; however, the TR EPR kinetics did demonstrate biexponential behavior characteristic of two microenvironments. In addition, the results of Section 3.1 show that ZnTPP is likely to be distorted in C2-methylated ILs, implying that interaction between ZnTPP and cations/anions of IL is strong (the latter potentially can be verified by optical spectroscopy methods in the future).

All these trends can be explained by different timescales and amplitudes of ZnTPP motion in these two types of ILs. In C2-protonated ILs, evidently, noticeable rotation of ZnTPP on the microsecond scale is observed, resulting in isotropic-like shapes developed at long time delays. In C2-methylated ILs, most likely the motion of ZnTPP is characterized by small-angle librations. In case of [bmmim]PF₆ the amplitude of librations is higher, because the spectral shapes do depend on τ_{DAF} . In case of [bmmim]BF₄ such librations should have smaller amplitude, so that the dependence of the spectrum on τ_{DAF} is negligible. Note that the latter conclusion is additionally supported by the temperature dependence of longitudinal relaxation times in both ILs (Figures 2 and 4). If at 100 K TR EPR decays are comparable for both ILs, at 200 K the kinetics in [bmmim]PF₆ decays much faster compared to that in [bmmim]BF₄ implying more efficient relaxation mechamisms, plausibly due to stronger librations of ZnTPP in [bmmim]PF₆.

4 Conclusions

In this work we applied TR EPR to investigate experimentally the influence of C2-methylation in methyl-imidazolium ILs on the spin dynamics of the dissolved photoexcited triplet ZnTPP. Physical properties of ILs are known to be dramatically dependent on the chemical structure of cationic and anionic components. In accordance with that, we have observed noticeably different TR EPR manifestations in C2-protonated and C2-methylated analogs. We preliminary assign these differences to different mobility of ZnTPP in the two types of ILs. On the one hand, unlike in C2-protonated ILs, no definite conclusions on types of microenvironments formed around ZnTPP in C2-methylated ILs can now be done. On the other, the shapes of the TR EPR spectra observed in C2-methylated ILs indicate possible distortion of the ZnTPP molecule compared to that in other media, including C2-protonated analogs of the same ILs. These observations need further investi-

gation and systematization, especially via increasing the number of studied ILs in order to derive more general trends, and will be the topic of our future studies.

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