

# Photochromism of nitrobenzospiropyran in phosphonium based ionic liquids†

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Received 23rd February 2009, Accepted 7th May 2009

First published as an Advance Article on the web

DOI: 10.1039/b903772a

The photo-, thermo- and solvatochromic properties of 2,3-dihydro-1',3',3'-trimethyl-6-nitrospiro[1-benzopyran-2,2'-1*H*-indole] (BSP) and its photo-induced merocyanine isomer (MC) were investigated in phosphonium based ILs by UV-vis absorption spectroscopy. It was found that the kinetics and thermodynamics of the BSP ↔ MC equilibrium were sensitive to the nature of the anion. The MC  $\lambda_{\text{max}}$  shifted from 560 nm to 578 nm when in solutions of [P<sub>1,4,4,4</sub>][tos] and [P<sub>6,6,6,14</sub>][dca], respectively. The BSP isomer was highly favoured at equilibrium in the ILs studied;  $K_{\text{c}}$  values observed were similar to non-polar solvents such as dichloromethane. The thermal relaxation of MC in all ILs is first order, and in comparison with aprotic polar solvents possessing comparable polarity (such as acetonitrile). Thermal relaxation rates of MC were monitored over a range of temperatures; at 293 K rates varied from 5.19 to 25.03 × 10<sup>-4</sup> s<sup>-1</sup>. A non-linear relationship between  $K_{\text{c}}$  and  $k$  was observed; this contradicts what is expected for BSP in molecular solvents and suggests the isomers exhibit different molecular/solvation environments. The energetics of the thermal relaxation of MC in ILs were observed; activation energies ranged from 71 to 90 kJ mol<sup>-1</sup> and all ILs exhibit negative activation entropies ranging between -72 and -8.2 J K<sup>-1</sup> mol<sup>-1</sup>. A linear relationship between activation energy and entropy was observed.

## Introduction

Ionic liquids (ILs) are a class of novel solvents with very interesting properties; they consist only of ions making them very different to conventional molecular solvents. ILs in some cases possess properties such as negligible vapour pressure, high thermal stabilities, tunable viscosities, and both hydrophobic and hydrophilic natures.<sup>1-3</sup> For these reasons, along with the fact that ILs can undergo multiple solvation interactions,<sup>4</sup> ILs are attracting the attention of a growing number of scientists and engineers for a range of applications.<sup>5-8</sup> However, the basic science involved with fully characterizing these ILs is still in its infancy, and this may be holding back the complete and most efficient utilization of these solvents.

Before the full potential of ILs as solvent systems can be explored, more information about their physicochemical properties needs to be gathered. Because chemical reactions are, in a sense, a relocation process of valence electrons, the charge distribution in the IL ions should profoundly affect the chemical reactions proceeding within them. It is therefore of considerable interest to examine the solute-solvent interaction and hence the molecular environments in ILs. It has been

argued that the solvent properties of ILs may not be well accounted for by conventional macroscopic parameters like polarity and dielectric constant, which have been extensively used for molecular solvents. Earlier approaches for classifying ILs involved the use of a polarity scale based on solvatochromic dyes such as Nile red and Reichardt's dye.<sup>9,10</sup> Unfortunately, all ILs studied appeared to have the same or similar properties, to that of short chain alcohols. It was postulated that these empirical results were not sufficiently sensitive as far as ILs were concerned since different ILs produced very different products (when used as reaction solvents), and different partitioning behaviour (when used as extraction solvents). Consequently, different approaches are needed to characterize the solvation properties of ILs that would account for the multiple solvent-solute interactions possible.

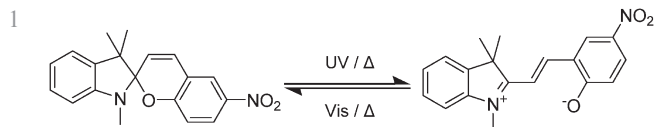
A number of fundamental physicochemical studies have already been reported for ILs<sup>11-14</sup> ranging from the photoisomerization kinetics of *trans*-stilbene,<sup>15</sup> 4',7-dihydroxyflavylium<sup>16</sup> and 3,3'-diethyloxadicarbocyanine iodide,<sup>17</sup> to picosecond time-resolved fluorescence of 6-propionyl-2-(*N,N*-dimethylamino)naphthalene<sup>18</sup> and 2-aminoquinoline.<sup>19</sup> Some of these physicochemical IL studies have reported unique observations, such as  $\pi$ - $\pi$  aromatic complexes in imidazolium based ILs and 'unusual charge-transfer networks' formed by coordinative anions and viologens.<sup>11,19,20</sup> Iwata *et al.* have proposed that ILs have specific local structures that cause many of their intriguing properties. ILs appear to be homogeneous macroscopically, but they are likely to be heterogeneous microscopically in the nanometre scale.<sup>19,21</sup> Molecular dynamics simulations have supported this view.<sup>22,23</sup>

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† Electronic supplementary information (ESI) available: [DETAILS]. See DOI: 10.1039/b903772a



**Fig. 1** Photo and thermochromism of BSP (left) to the merocyanine (right).

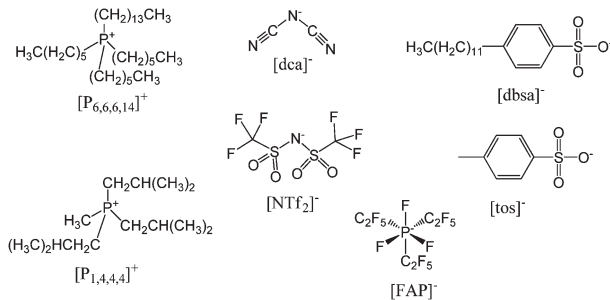
We recently reported the photo- and solvatochromic properties of nitrobenzospiropyran (BSP) in ionic liquids containing the anion  $[\text{NTf}_2]^-$ .<sup>24</sup> BSP when exposed to UV light undergoes an isomerization wherein the spiro linkage is severed, resulting in the merocyanine isomer, a highly polar zwitterion that is coloured. The merocyanine thermally reverts back to the BSP isomer following first order kinetics, Fig. 1. The  $\text{BSP} \leftrightarrow \text{MC}$  isomerization can reveal a significant amount of information about its surrounding molecular environment: (i) at equilibrium an estimate of polarity can be calculated from the value  $K_e$ , the population of non-polar BSP versus the highly polar MC,<sup>25</sup> (ii) the MC isomer exhibits a large negative solvatochromic shift with increasing polarity,<sup>26</sup> (iii) the MC isomer possesses a large polarizable  $\pi$ -electron system, suitable for the registration of dispersion interaction, (iv) the phenolate oxygen on the MC exhibits a highly basic, electron pair donor, suitable for interaction with hydrogen bond donors and Lewis acids, an example is the coordination with the metal ion  $\text{Co}^{2+}$ ,<sup>27</sup> also (v) the thermal isomerization of MC to BSP is dependent on all of the above, an example is the interaction of amino acids at the complementary binding sites on the MC retarding the thermal back reaction.<sup>28–30</sup>

It was found that the kinetics and thermodynamics of the BSP–MC equilibrium were sensitive to the nature of the cation; these ILs were then classed with respect to similar results obtained from molecular solvents. Yusong also reported similar interactions of imidazolium based ILs with BSP derivatives and in some cases negative photochromism was observed for BSP.<sup>31</sup>

At the outset, the goal was to use BSP, as a molecule probe, to learn more about the modes of interaction and polarity of a number of the anions used in common phosphonium based ILs and classify these ILs accordingly with common molecular solvents. In the process some unusual BSP spectroscopic effects have been observed that may relate to specific local molecular domains within the ILs.

## Experimental

2,3-Dihydro-1',3',3'-trimethyl-6-nitrospiro[1-benzopyran-2,2'-1H-indole] (BSP) was purchased from Aldrich and used as received. Acetonitrile was HPLC grade and used without further purification. Tetradecyl(trihexyl)-phosphonium bis(trifluoromethylsulfonyl)imide ( $[\text{P}_{6,6,6,14}][\text{NTf}_2]$ ), tetradecyl(trihexyl)-phosphonium dicyanamide ( $[\text{P}_{6,6,6,14}][\text{dca}]$ ), tetradecyl(trihexyl)-phosphonium dodecylbenzenesulfonate ( $[\text{P}_{6,6,6,14}][\text{dbsa}]$ ), and triisobutyl(methyl)phosphonium tosylate ( $[\text{P}_{1,4,4,4}][\text{tos}]$ ) were supplied by Cytec industries. Tetradecyl(trihexyl)-phosphonium tris(pentafluoroethyl)trifluorophosphate ( $[\text{P}_{6,6,6,14}][\text{FAP}]$ ) was supplied by Merck. All ILs were purified by column chromatography as described pre-



**Fig. 2** Molecular structures of ILs studied. Tetradecyl(trihexyl)-phosphonium  $[\text{P}_{6,6,6,14}]^+$ , triisobutyl(methyl)phosphonium  $[\text{P}_{1,4,4,4}]^+$ , bis(trifluoromethylsulfonyl)imide  $[\text{NTf}_2]^-$ , dicyanamide  $[\text{dca}]^-$ , dodecylbenzenesulfonate  $[\text{dbsa}]^-$ , tosylate  $[\text{tos}]^-$ , and tris(pentafluoroethyl)trifluorophosphate  $[\text{FAP}]^-$ .

viously and stored under reduced pressure.<sup>24</sup> All spectra were recorded on a UV-Vis-NIR Perkin-Elmer Lambda 900 spectrometer. The ultraviolet irradiation source was a BONDwand UV-365 nm obtained from Electrolyte Corporation. The white light source was a Lumina obtained from Chiu Technical Corporation. Samples were irradiated at a distance of 5 cm for 60 s. Standard solutions of BSP were made up to  $1 \times 10^{-4}$  M in acetonitrile. 1 ml of this solution was placed in a vial and the solvent removed by  $\text{N}_2$  stream. To this 1 ml of the selected IL (Fig. 2) was added to the vial and placed in a sonicator for 10 min at 40 °C. Samples were stored under argon in the dark at 20 °C for 15 h before absorbance measurement was taken. The kinetic parameters of the MC thermal reversion to BSP were determined at each temperature by monitoring the disappearance of the MC at  $\lambda_{\text{max}}$  after having removed the irradiating source.

## Results and discussion

### Ground state equilibrium

The absorption spectrum of BSP in acetonitrile at room temperature has two major bands with maxima in the UV and the visible; UV irradiation of BSP results in an increase of absorbance in the visible region due to the formation of the merocyanine (MC). It is accepted that BSP in acetonitrile at room temperature has maxima at,  $\lambda_{\text{BSP}} = 336$  nm ( $\epsilon_{\text{BSP}} = 0.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and  $\lambda_{\text{MC}} = 555$  nm ( $\epsilon_{\text{MC}} = 3.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>25,32</sup> These data are well documented and for the results discussed herein, the properties of BSP in acetonitrile are used as the point of reference. To support and validate our experimental results, the solvatochromic probe Reichardt's dye 30 has been used as a solvent-dependent reference process to define empirically a solvent polarity scale, called  $E_{\text{T}}(30)$  scale.<sup>33</sup>

In determining the equilibrium constants  $K_e$  between BSP and MC in these ILs, it was required that the samples were kept in the dark at 20 °C for 15 hours to reach equilibrium. At equilibrium, from Beer's law, we have

$$K_e = \frac{[\text{MC}]}{[\text{BSP}]} = \frac{A}{3.5 \times 10^4 \times C - A} \quad (1)$$

where  $K_e$  is the equilibrium constant between BSP and MC,  $A$

**Table 1** Equilibrium and photo-physical constants of BSP and  $E_T(30)$  values of various molecular solvents and ionic liquids. (BSP and Reichardt's dye 30 concentration  $10^{-4}$  M). All measurements carried out at 20 °C

Solvent	MC $\lambda_{\max}$ <sup>a</sup> /nm	$A_e$ <sup>b</sup>	$K_e$ <sup>c</sup>	$k^d \times 10^{-4}/s^{-1}$	1/k/s	$E_T(30)^e$ /kcal mol <sup>-1</sup>
[P <sub>6,6,6,14</sub> ][dbsa]	574	0.05	$1.45 \times 10^{-2}$	8.12	1231	46.6
[P <sub>6,6,6,14</sub> ][dca]	578	0.02	$5.7 \times 10^{-3}$	25.03	399	46.1
[P <sub>6,6,6,14</sub> ][NTf <sub>2</sub> ]	570	0.04	$1.16 \times 10^{-2}$	6.51	1538	47.9 (47.97)
[P <sub>1,4,4,4</sub> ][tos]	560	0.06	$1.74 \times 10^{-2}$	5.19	1926	48.2
[P <sub>6,6,6,14</sub> ][FAP]	564	0.04	$1.16 \times 10^{-2}$	7.31	1367	48
Acetonitrile	554	0.13	$3.85 \times 10^{-2}$	8.40	1190	45.5 (45.6)
Ethanol	539	0.15	$4.57 \times 10^{-2}$	1.91	5235	51.8 (51.9)
Dichloromethane	578	0.01	$5.1 \times 10^{-3}$	70.04	142	40.6 (40.7)

<sup>a</sup> Merocyanine  $\lambda_{\max}$  measured after 1 min UV light. <sup>b</sup> Absorbance measured at  $\lambda_{\max}$  of MC after 15 h in dark. <sup>c</sup> Calculated from eqn (1). <sup>d</sup> Thermal relaxation rate constant calculated from plotting  $\ln(A_0/A_t)$  vs. time where  $k = \text{slope}$ . <sup>e</sup>  $E_T(30)$  values in parenthesis are from the literature.

is the equilibrium absorbance at the absorption maximum,  $C$  is the total concentration of BSP initially dissolved and  $\epsilon_{MC} = 3.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for the MC form of BSP according to Flannery;<sup>34</sup> though the extinction coefficient is known to be solvent dependent, the effect is relatively small compared to the effects seen in this work.

This thermal equilibrium between the BSP and MC is affected by the change in solvent polarity; polar solvents promote the formation of the coloured (MC) form and non-polar solvents promote the formation of the colourless (BSP) form. This relationship is reinforced by plotting the  $K_e$  value vs.  $E_T(30)$  values in the corresponding molecular solvents and achieving good linearity.<sup>32</sup> The correlation between the  $\pi-\pi^*$  transition energies of the MC isomer and  $E_T(30)$  implies the contributions of different solute-solvent interactions, as measured by Reichardt's dye 30, are nearly the same as for the  $\pi-\pi^*$  absorptions of MC. Therefore, transition energies of the MC isomer can be used to probe micro-polarity of a solvent at the molecular level.

The experimental  $K_e$  values obtained, Table 1, for the majority of the phosphonium based ILs are quite similar to aprotic molecular solvents, ranging from 1.16 to  $1.74 \times 10^{-2}$ . [P<sub>6,6,6,14</sub>][dca] on the other hand has a very small equilibrium constant ( $K_e = 5.7 \times 10^{-3}$ ) in comparison to the rest of the ILs; this value is similar to the  $K_e$  value for the non-polar solvent dichloromethane. As stated above when plotting  $K_e$  vs.  $E_T(30)$  values in the corresponding molecular solvents, good linearity is achieved.<sup>32</sup>  $E_T(30)$  values of the phosphonium based ILs studied appear to have similar values to acetonitrile (45.5 kcal mol<sup>-1</sup>), though these results deviate from the expected linear relationship between  $K_e$  vs.  $E_T(30)$ , see ESI†, Fig. S1. This can be clearly seen when comparing the  $K_e$  and  $E_T(30)$  values of [P<sub>6,6,6,14</sub>][dbsa] and [P<sub>6,6,6,14</sub>][FAP], [P<sub>6,6,6,14</sub>][dbsa] with a larger equilibrium constant but smaller  $E_T(30)$  value, although [P<sub>6,6,6,14</sub>][dca] has the smallest equilibrium constant coupled with the smallest  $E_T(30)$  value (46.1 kcal mol<sup>-1</sup>) of the ILs studied. This would suggest that the molecular probes (BSP and Reichardt's dye 30) exhibit different modes of interactions within the phosphonium ILs studied herein. In general, phosphonium ILs fit into the same category as aprotic molecular solvents, compared with the  $K_e$  values obtained for molecular solvents.

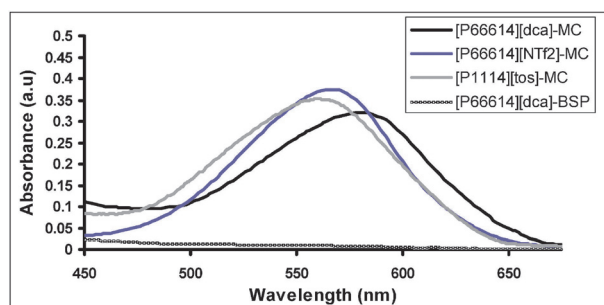
It has been previously reported that a direct relationship can be observed between the equilibrium constant  $K_e$  and the

solvatochromic absorption shift of MC; as  $K_e$  decreases the  $\lambda_{\max}$  shifts towards longer wavelengths. This trend is also seen in the ILs studied herein, for [P<sub>6,6,6,14</sub>][dca]-MC  $\lambda_{\max} = 578$  nm and  $K_e = 5.7 \times 10^{-3}$ , whereas, [P<sub>1,4,4,4</sub>][tos]-MC exhibits a  $\lambda_{\max} = 560$  nm and  $K_e = 1.74 \times 10^{-2}$ . Dichloromethane has a similar MC  $\lambda_{\max}$  to [P<sub>6,6,6,14</sub>][dca] but its  $E_T(30)$  value is significantly lower. Examples of the solvatochromic shifts of the MC isomer in ILs are listed in Table 1.

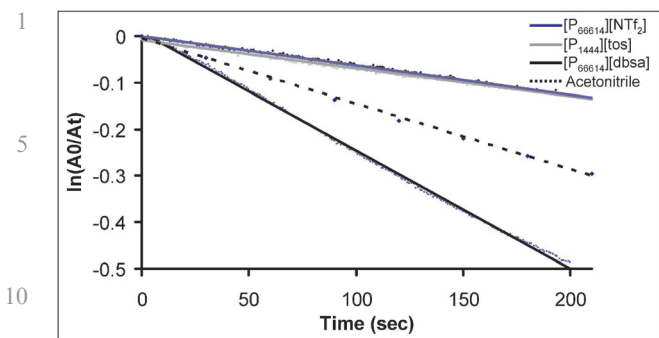
### Photochromic properties

The equilibrium between BSP and MC is strongly displaced upon irradiation with visible ( $\geq 450$  nm) light towards the BSP isomer and when irradiated with UV light (360 nm) towards the MC isomer. Fig. 3 displays the resulting spectra of selected ILs after 60 seconds of UV irradiation. A photochemical back-conversion into the BSP isomer is possible by irradiation of the MC at  $\geq 450$  nm;<sup>34,35</sup> this is shown for comparison in Fig. 3 (spectrum [P<sub>6,6,6,14</sub>][dca]-BSP) to show the significant difference between the MC and BSP spectra.

It is well known that, after removal of UV light, the predominant MC form generated will thermally isomerize back to its equilibrium state; this decay in absorbance should follow first order kinetics,<sup>25</sup> as it does in molecular solvents. The rate at which the thermal isomerization occurs is not sensitive to oxygen, yet is strongly medium dependent. First-order rate constants for the thermal isomerization of MC were determined by plotting  $\ln(A_0/A_t)$  vs. time. Examples are shown for [P<sub>6,6,6,14</sub>][NTf<sub>2</sub>], [P<sub>6,6,6,14</sub>][dca], [P<sub>1,4,4,4</sub>][tos] and acetonitrile in Fig. 4. The rate constants and relaxation times for MC



**Fig. 3** UV-vis spectra for solutions of  $10^{-4}$  M BSP in [P<sub>6,6,6,14</sub>][NTf<sub>2</sub>]-MC, [P<sub>6,6,6,14</sub>][dca]-MC and [P<sub>1,4,4,4</sub>][tos]-MC exposed to 60 s irradiation at 365 nm. [P<sub>6,6,6,14</sub>][NTf<sub>2</sub>]-BSP IL exposed to 60 s irradiation of visible light ( $< 450$  nm) for comparison.

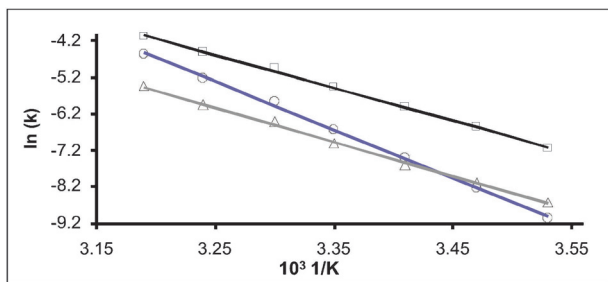


**Fig. 4** Thermal relaxation of MC in  $[P_{6,6,6,14}][NTf_2]$ ,  $[P_{6,6,6,14}][dca]$  and  $[P_{1,4,4,4}][tos]$  after 60 seconds irradiation of UV light (360 nm) at 293 K.

thermal isomerization in the selected ILs are tabulated in Table 1. It can be seen that all but one of the ILs studied exhibit similar rate constants to acetonitrile at their respective MC  $\lambda_{max}$ , whereas  $[P_{6,6,6,14}][dca]$  exhibits a much faster thermal reversion to BSP with a rate constant of  $25.03 \times 10^{-4} \text{ s}^{-1}$ . From the  $K_e$  values and  $\lambda_{max}$  positions in Table 1, it would be expected that the  $[P_{1,4,4,4}][tos]$  should exhibit the longest MC lifetime; this hypothesis proved to be correct, the rate constant and MC relaxation time being  $5.19 \times 10^{-4} \text{ s}^{-1}$  and 1926 seconds, respectively. The thermal relaxation of MC in  $[P_{6,6,6,14}][dca]$  is 5 times faster than that of  $[P_{1,4,4,4}][tos]$ . However, comparing  $[P_{6,6,6,14}][dca]$  with dichloromethane, whose  $\lambda_{max}$  position is identical, their rate constants differ by nearly a factor of three.

### Thermochromic properties

The results described for photochromic behaviour refer to room temperature (293 K), but the rate of thermal relaxation depends strongly on temperature. It has been reported in molecular solvents that changes of several orders of magnitude were observed from  $0^\circ$  to  $80^\circ\text{C}$ .<sup>25</sup> The linear temperature dependence of the rate of thermal relaxation of MC in the ILs studied were plotted using eqn (2). Plots of  $\ln k$  vs.  $1/T$  are shown in Fig. 5 for thermal relaxation of MC in  $[P_{6,6,6,14}][NTf_2]$ ,  $[P_{6,6,6,14}][dca]$  and  $[P_{1,4,4,4}][tos]$ . From the linear Arrhenius dependences in all cases, the values of activation energy ( $E_a$ ) and the pre-exponential factor are derived (Table 2). The activation thermodynamic parameters  $\Delta S^\ddagger$  (entropy of activation),  $\Delta H^\ddagger$  (enthalpy of activation) and



**Fig. 5** Arrhenius plot for the thermal relaxation of MC in  $[P_{6,6,6,14}][NTf_2]$  (O),  $[P_{6,6,6,14}][dca]$  (□) and  $[P_{1,4,4,4}][tos]$  (Δ) after 60 seconds UV irradiation. BSP concentration  $1 \times 10^{-4} \text{ M}$  (correlation coefficients  $> 0.99$ ).

$\Delta G^\ddagger$  (Gibbs energy of activation) of the thermal relaxation of MC are evaluated by using the Eyring equation (eqn (3)) and are shown in Table 2.

$$\ln k = E_a/RT + \ln A \quad (2)$$

$$\ln(k/T) = -\Delta H^\ddagger/RT + \ln(k_B/h) + \Delta S^\ddagger/R \quad (3)$$

where  $R$  = gas constant,  $h$  = Planck's constant, and  $k_B$  = Boltzmann constant.

Table 2 gives an overview of the parameters which govern the thermal relaxation of MC in ILs. It has been noted from the literature for molecular solvents that MC thermal relaxation  $E_a$  values range from 75 to 105  $\text{kJ mol}^{-1}$  with a tendency to be higher in polar solvents.<sup>25,36</sup> It can be seen that  $E_a$  values for phosphonium based ILs lie within the region of non-polar solvents such as benzene and chloroform, 70.6 and 95.9  $\text{kJ mol}^{-1}$ , respectively.<sup>36</sup> The activation energy of MC thermal relaxation in  $[P_{6,6,6,14}][NTf_2]$  and  $[P_{6,6,6,14}][dbsa]$  is quite high compared to the rest of the ILs studied and is very similar to the molecular solvent DMF literature value of 90  $\text{kJ mol}^{-1}$ .<sup>25</sup> This would indicate that the MC thermal relaxation process is strongly dependent on temperature. Albeit, it was observed that  $[P_{1,4,4,4}][tos]$  had the smallest thermal relaxation  $E_a$  and  $\Delta H^\ddagger$  values of 71  $\text{kJ mol}^{-1}$  and 69  $\text{kJ mol}^{-1}$ , respectively. For some applications, a photochrome such as MC with a low thermal relaxation  $E_a$  would be desirable in order to not have a large temperature dependence on colourability. Small frequency factors ( $10^9$ – $10^{10} \text{ s}^{-1}$ ) are associated with negative activation energies with respect to photochromic dyes.<sup>37</sup>

It has been suggested that the BSP–MC equilibrium is almost isoentropic, the consequence of balance between two opposite contributions to  $\Delta S^0$ : a positive contribution, which is related to the increased torsional freedom in the MC isomer, and a negative contribution, which is due to solvent reorientation around the more polar MC form. As reported previously for the thermal relaxation of photomerocyanines,  $\Delta S^\ddagger$  values for the ILs discussed herein show a strong linear correlation with  $E_a$ , see ESI†, Fig. S2.<sup>38,39</sup> As expected, the experimental activation entropies ( $\Delta S^\ddagger$ ) found for MC in the majority of ILs studied were significantly negative (e.g.  $[P_{1,4,4,4}][tos]$   $\Delta S^\ddagger = -72.8 \text{ J K}^{-1} \text{ mol}^{-1}$ ), indicating a more strongly solvated species, likely the result of electrostatic interactions with the charged groups, than the colourless BSP isomer. This result correlates well with the small MC thermal relaxation rate constants observed for ILs such as  $[P_{1,4,4,4}][tos]$ .  $[P_{6,6,6,14}][NTf_2]$  and  $[P_{6,6,6,14}][dbsa]$  have smaller negative values of  $\Delta S^\ddagger$  ( $-8.2$  and  $-12.3 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively) and larger rate constants for the MC thermal relaxation process indicating perhaps weaker interactions in these cases.

It must be noted that, in this study, we have primarily focused on the photomerocyanine due to the wealth of information that its molecular system can transduce about its immediate environment, and it can be seen from the results above that distinct spectroscopic effects can be associated with the molecular structure of the anion of the IL studied. However, on analysis of the equilibrium constant ( $K_e$ ), it must be noted that the non-polar BSP isomer is heavily favoured over the polar MC isomer in all cases, and slightly more so in the case of the ILs studied herein. This result is somewhat

1 **Table 2** Thermodynamic parameters for thermal relaxation of MC to BSP

IL	$E_a/\text{kJ mol}^{-1}$	$A/\text{s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$
[P <sub>6,6,6,14</sub> ][dbsa]	88	$3.97 \times 10^{12}$	85	89	-12.3
[P <sub>6,6,6,14</sub> ][dca]	75	$6.58 \times 10^{10}$	73	87	-46.1
[P <sub>6,6,6,14</sub> ][NTf <sub>2</sub> ]	90	$6.48 \times 10^{12}$	87	90	-8.2
[P <sub>1,4,4,4</sub> ][tos]	71	$2.74 \times 10^9$	69	90	-72.8
[P <sub>6,6,6,14</sub> ][FAP]	76	$2.41 \times 10^{10}$	74	89	-54.6

10 counterintuitive as ILs might be expected to solvate the MC form more strongly. The equilibrium constant in the ILs studied, ranging from  $5.7 \times 10^{-3}$  to  $1.74 \times 10^{-2}$ , might be expected to be somewhat higher, similar to ethanol ( $4.57 \times 10^{-2}$ ). If we consider the photoisomerization process, the non-polar BSP molecule when irradiated with UV light isomerizes into a highly polar zwitterionic system MC, and it is known that this system can be used to transport metal ions across organic-aqueous barriers with UV light.<sup>40-42</sup> However, it has recently been proposed that ILs are structured at the micro- and nanoscopic levels, containing polar and non-polar domains.<sup>22,23,43</sup> This hypothesis could explain the reason we observe such low values of  $K_e$ ; potentially at equilibrium the BSP isomer resides in the non-polar domain of the IL. The  $K_e$  difference between [P<sub>6,6,6,14</sub>][dca] ( $5.7 \times 10^{-3}$ ) and [P<sub>1,4,4,4</sub>][tos] ( $1.74 \times 10^{-2}$ ) supports this hypothesis since it would indicate that the BSP isomer is preferentially solvated by the cations' long alkyl chains [P<sub>6,6,6,14</sub>]<sup>+</sup>, as compared to [P<sub>1,4,4,4</sub>]<sup>+</sup>.

## 30 Conclusion

As compared to conventional organic solvents, ILs are much more complex solvent systems capable of undergoing many types of interactions. Characterizing them with a single 'polarity' term fails to describe the type and magnitude of individual interactions that make each IL unique. This work studies the interactions between the IL and the MC isomer and their consequences on the photo- and thermochromic properties of the MC system. It was found that the MC isomer's spectroscopic properties could be significantly altered by varying the anion of the phosphonium IL. There were some direct correlations observed between spectroscopic data found in ILs and molecular solvents with respect to the MC isomer. The activation parameters of the thermal relaxation process of MC to BSP can also be altered by varying the anion, to such an extent that for very low thermal relaxation activation energy  $E_a$  of [P<sub>1,4,4,4</sub>][tos] would be desirable for some applications, as it does not have a large temperature dependence of colourability compared to [P<sub>6,6,6,14</sub>][NTf<sub>2</sub>]. We also report some preliminary empirical results indicating possible polar and non-polar domains within the phosphonium based ILs, supporting the nanostructured hypothesis of ILs recently published by Lopes *et al.*<sup>44</sup> We plan to further investigate this hypothesis by synthesizing derivatives of BSP to locate themselves in specific areas of the IL; a similar molecular probe study in micelles was recently reported with moderate success. We regard these preliminary results as pointing the way towards more sophisticated materials capable of switching reversibly between two distinct forms, and simultaneously

providing a number of transduction modes for gathering information about its molecular environment.

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