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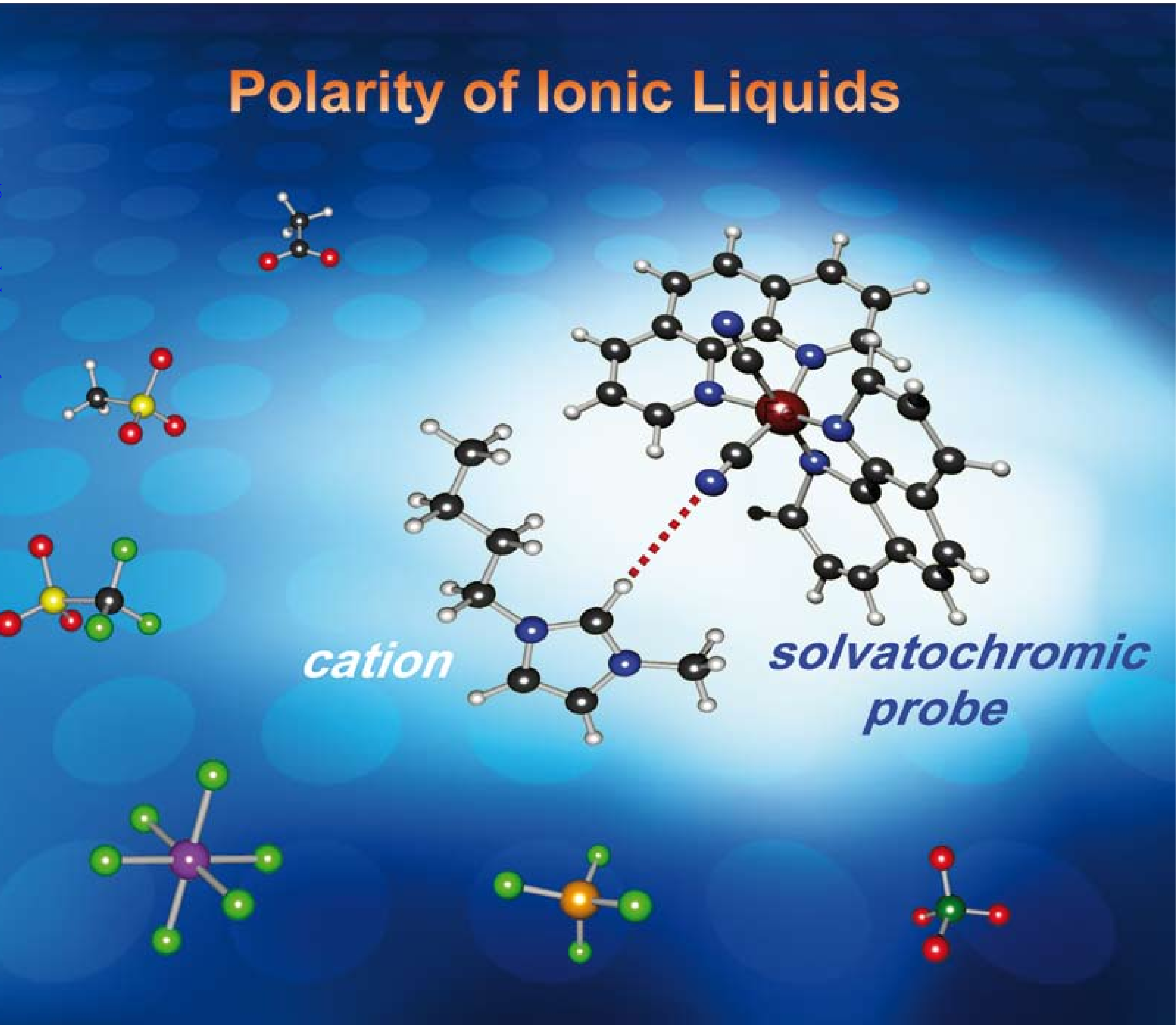

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PAPER
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New aspects on the hydrogen bond donor (HBD) strength of 1-butyl-3-methylimidazolium room temperature ionic liquids

New aspects on the hydrogen bond donor (HBD) strength of 1-butyl-3-methylimidazolium room temperature ionic liquids†

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Improved hydrogen bond donor (HBD) strength parameters of 1-butyl-3-methylimidazolium room temperature ionic liquids (RTILs), acceptor number (*AN*) of Gutmann and α of Kamlet–Taft, have been determined using $[Fe(phen)_2(CN)_2]ClO_4$ as an original solvatochromic probe. Each of the parameters shows an excellent correlation with the independently determined HBA strength β (Kamlet–Taft) of the anion which demonstrates that empirical polarity parameters of RTILs can be utilized independently of each other.

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Introduction

Room temperature ionic liquids (RTILs), although known for a long time, have awakened the interest of many scientists in recent years as reaction media for "green chemistry". The use of solvatochromic dyes for the determination of empirical polarity parameters for these liquids has attracted the attention of physical organic chemists. The state of the art regarding this problem has been presented by Reichardt in a very clear review article.[1] In further review articles, solvatochromic polarity parameters of ionic liquids were collected, more in order to compare them to the chemical reactivities and physical properties, respectively.[2,3]

What scientific importance do empirical polarity parameters have for ionic liquids? Thus, we want to go into the problems in a more detailed way as part of the state of the art for the hydrogen bond donor (HBD) ability of the 1-butyl-3-methylimidazolium cation ([Bmim]). The hydrogen bond donating ability of [Bmim] and related compounds is mainly attributed to three different kinds of hydrogen atoms as shown in Scheme 1.

The hydrogen bond donating ability of a solute or solvent can be determined by measuring the interaction strength with a reference base. If the reference base is a solvatochromic probe, then the UV/Vis absorption energy of the probe is the measure of the HBD strength. Suitable parameters for the hydrogen bond donor ability are in particular Gutmann's acceptor numbers (*AN*) and Kamlet–Taft's α-value.

Huddlestone *et al.* discussed the fact that the α value of [Bmim] salts decreases as a function of the β values (hydrogen bond accepting ability) for 1,3-dialkylimidazolium ionic liquids.[4]

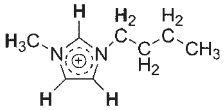
Fujisawa *et al.* determined acceptor numbers (*AN*) for RTILs using diphenylcyclopropenone as a Raman sensitive probe.[5]

As well as Reichardt's $E_T(30)$ solvent parameters,[6] Kamlet–Taft's solvent parameters have been established for liquids, which allow a differentiated polarity assignment to be made.[7–13] The Kamlet–Taft equation, in its simple form, is given in eqn (1).

$$(XYZ) = (XYZ)_0 + a\alpha + b\beta + s(\pi^* + d\delta) \qquad (1)$$

(XYZ) is the result of a solvent-dependent process; $(XYZ)_0$ is the value for the reference system, for example the gas phase or a nonpolar solvent. α describes the hydrogen bond acidity, β the hydrogen bond basicity and π* the dipolarity/polarisability of the solvent. δ is a polarisability correction term that is 1.0 for aromatic solvents, 0.5 for polyhalogenated solvents, and zero for aliphatic solvents. This is a problem, as it does not permit a differentiated separation of the polarisabilities of solvents. A very well defined parameter set has been developed in recent years by Catalàn, where together with the Kamlet–Taft parameters, a polarisability scale for solvents was also briefly presented for the first time.[14] The parameters *a*, *b*, *s* and *d* are the solvent-independent correlation coefficients, which reflect predictions of the influence of the respective parameters on the result (XYZ) of the chemical process.

The sets of polarity parameters for ionic liquids, which have been presented in the literature up to now,[1,2,4,15–25] show that singular linear relationships between different solvatochromic dyes (Reichardt's dye, 1-pyrene aldehyde, Nile red,



Scheme 1 Chemical structure of [Bmim] and the hydrogen atoms (bold) suitable to undergo hydrogen bonds with bases.

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dansyl amide) can deliver, according to eqn (2a) and (2b) (n = number of solvents, r = correlation coefficient, sd = standard deviation and F = significance),[26,27] different values for polarity parameters within the framework of the $E_T(30)$ scale for a defined ionic liquid, such as [Bmim]PF_6.[24]

$$E_T(30) = 30.2 + 14.45\alpha + 2.13\beta + 12.99(\pi^* - 0.21\delta)$$
$$n = 100,\ r = 0.98,\ sd = 1.25,\ F < 0.0001 \qquad (2a)$$

$$E_T(30) = 31.2 + 15.2\alpha + 11.5\pi^*(a/s = 1.32)$$
$$n = 155,\ r = 0.98,\ sd = 1.1,\ F < 0.0001 \qquad (2b)$$

The differences are explained using ''additional effects'' such as viscosity, polarisability or specific hydrogen bonds. The last of these should, however, actually be already integrated in singular linear solvation energy (LSE) determinations, as the $E_T(30)$ parameter is preferentially a function of α und π^*.[6] Therefore, $E_T(30)$ values of RTILs have been mostly used to calculate the α values reported until now.

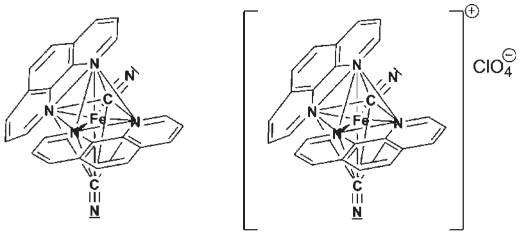
The decisive scientific question still remains, namely can the empirical polarity parameters of the Kamlet–Taft equation be determined for ionic liquids really independently of the probe molecule used? If not, then are the parameters a product of the complementary solvent and solute parameters? If yes, then which thermodynamic parameters are included?

In two recent articles we have shown that β and π^* can be determined when carefully selected solvatochromic probes have been employed. Unfortunately, the well established α indicator $Fe(phen)_2(CN)_2$ dye **1** (Scheme 2) is completely insoluble in dry RTILs.[28,29] Therefore, a specific solvatochromic probe is required which measures the α value as independent as possible of other influences of the solvent.

In this work we will introduce a related solvatochromic indicator for RTILs which measures as independently as possible the α value. For this purpose we have found that $[Fe(phen)_2(CN)_2]ClO_4$ **2** (Scheme 2) as a probe is well suited, because it is sufficiently soluble in RTILs.

The solvatochromism of **2** is briefly mentioned in the literature, but a detailed UV/Vis spectroscopic investigation taking into account a larger set of solvents is lacking.[30–33]

The objective of this work is to investigate the solvatochromism of **2** in detail and to show its application to RTIL. Furthermore, probe **1** has been used in mixtures of RTILs with dichloromethane to provide an independent support for the dimension of determined α values.



1 **2**

Scheme 2 Solvatochromic probes **1** and **2** used in this work.

Results and discussion

Solvatochromism of $[Fe(phen)_2(CN)_2]ClO_4$ in well behaved organic solvents

Acidochromism and solvatochromism of **2** have been sporadically reported in the literature.[30–33] It has been discussed that the solvatochromism of $[Fe(phen)_2(CN)_2]ClO_4$ is the reverse of $Fe(phen)_2(CN)_2$ due to the fact that hydrogen bond formation by hydrogen bond donor solvents lower the transition energy of the longest wavelength UV/Vis absorption band of $[Fe(phen)_2(CN)_2]ClO_4$.[33] Solvatochromism of **2** has been studied in several organic solvents, but a linear solvation energy correlation analyses taking into account a representative set of organic solvents has not been reported till now. Due to the fact that $[Fe(phen)_2(CN)_2]ClO_4$ is well soluble in pure RTILs, we were interested in the solvatochromism of **2** in detail.

A series of UV/Vis absorption spectra of **2** dissolved in various organic solvents are shown in Fig. 1. UV/Vis absorption maxima of **1** and **2** dissolved in well behaved solvents as well as the corresponding Kamlet–Taft empirical polarity parameter and Gutmann's *AN* are given in Table 1. Both dyes show a pronounced negative solvatochromism, with an increasing solvent polarity.

There are two remarkable effects observed, which should be clearly mentioned from the beginning. First the shapes of the UV/Vis spectra of $[Fe(phen)_2(CN)_2]ClO_4$ are different for two sets of solvents. In nitromethane and acetonitrile the UV/Vis band shows a completely different profile than in all the other solvents (listed in Table 1) (see ESI†). This is in accord with the results from acidic aqueous solutions where a typical broad UV/Vis spectrum is measured.[31] Second the UV/Vis spectrum of dissolved $[Fe(phen)_2(CN)_2]ClO_4$ is identical to that of $Fe(phen)_2(CN)_2$ in other solvents such as alcohols, carbonic acid amides, and in the RTILs. This result suggests that **2** seems to be reduced to **1** during the dissolution process. It is known from the literature, that $[Fe(phen)_2(CN)_2]^+$ salts are susceptible to reduction when dissolved, according to Scheme 3 and are often used as oxidizing agents in organic reactions.[31,34–36] This consideration is supported by the linear correlation of the UV/Vis absorption maxima of **1** with **2** in various solvents as shown in Fig. 2 and by eqn (3).

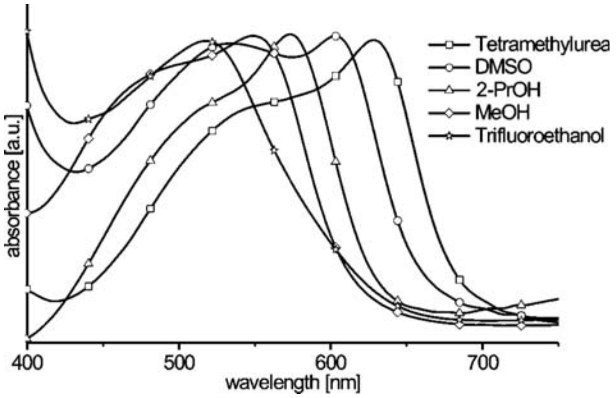


Fig. 1 UV/Vis absorption spectra of $[Fe(phen)_2(CN)_2]ClO_4$ **2** dissolved in various well behaved solvents.

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Table 1 UV/Vis absorption maxima of **1** and **2** in 19 'well behaved' solvents, Kamlet–Taft (α, β, π^*) empirical solvent polarity parameters and Gutmann's *AN*[8]

Solvent	$10^{-3}\tilde{\nu}_{\max(\mathbf{1})}/\text{cm}^{-1}$	$10^{-3}\tilde{\nu}_{\max(\mathbf{2})}/\text{cm}^{-1}$	α	β	π^*	*AN*
Tetramethylurea	15.92	15.90	0.00	0.80	0.83	9.2
Acetone	16.08	16.16	0.08	0.43	0.71	12.5
Pyridine	16.10	16.08	0.00	0.64	0.87	14.2
Dimethylacetamide	16.10	16.13	0.00	0.76	0.88	13.6
Benzonitrile	16.31	16.37	0.00	0.37	0.90	15.5
Dimethyl sulfoxide	16.50	16.58	0.00	0.76	1.00	19.3
Dichloromethane	16.61	16.72	0.13	0.10	0.82	20.4
Chloroform	16.67	16.72	0.20	0.10	0.58	23.1
2-Propanol	17.51	17.45	0.76	0.84	0.48	33.5
1-Butanol	17.67	17.57	0.84	0.84	0.47	36.8
1-Propanol	17.67	17.67	0.84	0.90	0.52	37.3
Methylformamide	17.73	17.76	0.62	0.80	0.90	32.1
Ethanol	17.82	17.82	0.86	0.75	0.54	37.1
Methanol	18.21	18.21	0.98	0.66	0.60	41.3
Formamide	18.28	18.32	0.71	0.48	0.97	39.8
Ethylene glycol	18.38	18.48	0.90	0.52	0.92	—
TFE[a]	19.27	19.30	1.51	0.00	0.73	53.8
Water	19.49	19.53	1.17	0.47	1.09	54.8
HFIP[b]	19.92	19.80	1.96	0.00	0.65	66.7

[a] 2,2,2-Trifluoroethanol. [b] 1,1,1,3,3,3-Hexafluoropropan-2-ol.

$$[\mathrm{Fe^{III}(phen)_2(CN)_2}]^{\oplus} + \mathrm{S} \longrightarrow \mathrm{Fe^{II}(phen)_2(CN)_2} + \mathrm{S}^{\bullet\oplus}$$

Scheme 3 Basic reaction scheme for the reduction of $[\mathrm{Fe(phen)_2(CN)_2}]^+$ to $\mathrm{Fe(phen)_2(CN)_2}$ by an electron donor solvent (S = solvent).[35]

$$\tilde{\nu}_{\max(\mathbf{1})}10^{-3}/\text{cm}^{-1} = -0.37 + 1.02\tilde{\nu}_{\max(\mathbf{2})}10^{-3}/\text{cm}^{-1}$$
$$n = 19,\ r = 0.998,\ sd = 0.06,\ F < 0.0001 \qquad (3)$$

The solvent serves obviously as the reducing agent. To prove this, EPR measurements of **2** were carried out in nitromethane, 2-propanol and acetonitrile and EPR spectra are given in ESI†. In acetonitrile and nitromethane the occurrence of $\mathrm{Fe^{III}}$ (signal of the low spin form $S = 1/2$) is clearly observed by the EPR experiment, whereas in 2-propanol only a very small EPR signal of $\mathrm{Fe^{III}}$ has been detected. Qualitative results are shown in Table 2.

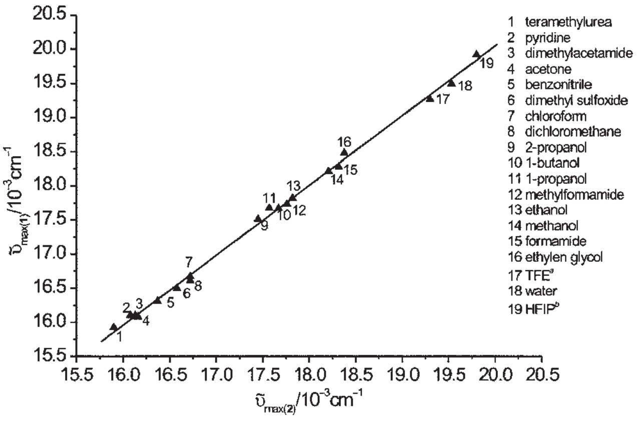

Fig. 2 Comparison of the UV/Vis absorption maxima of **1** and **2** in well behaved solvents. [a]2,2,2-Trifluorethanol. [b]1,1,1,3,3,3-Hexafluoropropan-2-ol.

The EPR results are in accordance to the UV/Vis spectra: the disappearance of the EPR signal of $\mathrm{Fe^{III}}$ agrees with observation of the UV/Vis spectrum of **2**.

To study the influence of the organic radical on the position and/or the form of the UV/Vis absorption band, concentration dependent measurements were performed. **2** was dissolved in three different concentrations in 1-butanol, ethanol and methylformamide (spectra and procedure are given in the ESI†). There was no change in the form and position of the UV/Vis absorption spectra observable in all three solvents. Hence, the formation of organic radicals derived from the solvent do not affect the UV/Vis absorption band, which is in addition based by the correlation shown in Fig. 2. The formed organic radicals probably will be quenched by molecular oxygen.

Thus, solid $\mathrm{Fe(phen)_2(CN)_2]ClO_4}$ can be used as a UV/Vis solvatochromic probe in many solvents, because it undergoes redox transformation to $\mathrm{Fe(phen)_2(CN)_2}$ by dissolution. The results of the multiple regression analysis are given in Table 3.

There is a significant dependence of the UV/Vis absorption maxima of **2** on both the α and the π^* terms, as expected from the solvatochromic behavior of **1**.[29] β plays no role upon the solvent induced hypsochromic UV/Vis shift. The single correlation of $\tilde{\nu}_{\max(\mathbf{2})}$ with α gives also highly significant, results, as shown by eqn (4) and Fig. 3. As expected there is a clear linear correlation between the determined UV/Vis absorption maxima of **2** and Gutmann's acceptor numbers *AN*, as shown by eqn (5).

Table 2 Qualitative results of the EPR measurements of **2** dissolved in three solvents

Solvent	Signal intensity of $\mathrm{Fe^{III}}$	Signal intensity of the organic radical
Acetonitrile	Large	Very small
Nitromethane	Large	Very small
2-Propanol	Small	Large

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Table 3 Results of the multiple regression analysis of the solvatochromism of **2**. Data are taken from Table 1

$(XYZ) = (XYZ)_0 + a\alpha + b\beta + s\pi^*$

$(XYZ)_0$	a	b	s	n	r	sd	F
15.019	2.162	−0.032	1.559	19	0.98	0.25	< 0.0001
14.991	2.168	—	1.569	19	0.98	0.24	< 0.0001
16.273	2.023	—	—	19	0.95	0.38	< 0.0001

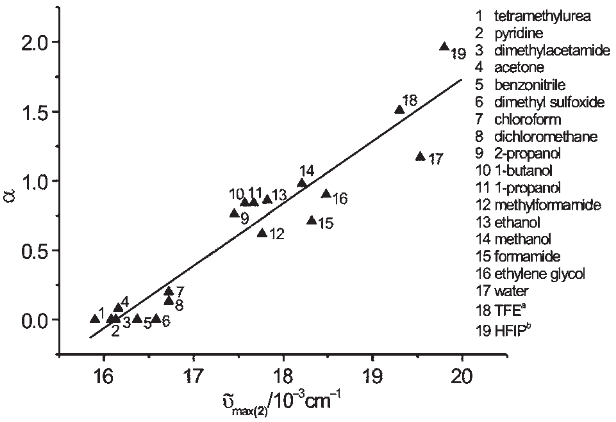

Fig. 3 Correlation of α with the measured UV/Vis absorption maxima of **2** dissolved in 19 well behaved solvents. Data are taken from Table 1. [a]2,2,2-Trifluorethanol. [b]1,1,1,3,3,3-Hexafluoropropan-2-ol.

$$\alpha = -7.263 + 0.450\tilde{\nu}_{\max(2)}10^{-3}/\mathrm{cm}^{-1}$$
$$n = 19,\ r = 0.95,\ sd = 0.18,\ F < 0.0001 \qquad (4)$$

$$AN = -200.66 + 13.29\tilde{\nu}_{\max(2)}10^{-3}/\mathrm{cm}^{-1}$$
$$n = 19,\ r = 0.99,\ sd = 2.52,\ F < 0.0001 \qquad (5)$$

The correlations clearly justify the use of **2** to determine hydrogen bond donor strength α and Gutmann's acceptor numbers *AN* of well behaved solvents.

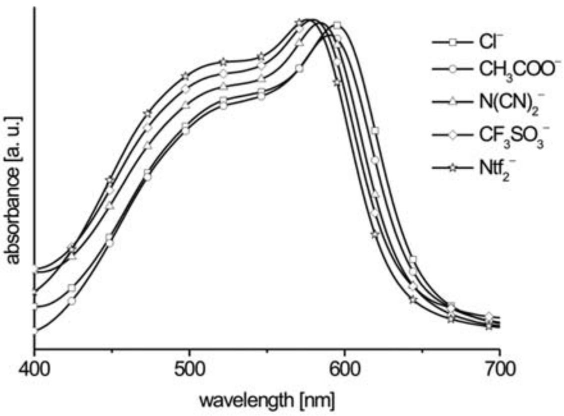

Fig. 4 UV/Vis absorption spectra of **2**, dissolved in 1-butyl-3-methylimidazolium ionic liquids with various anions (Ntf_2^- = bis(trifluoromethanesulfonyl)imide).

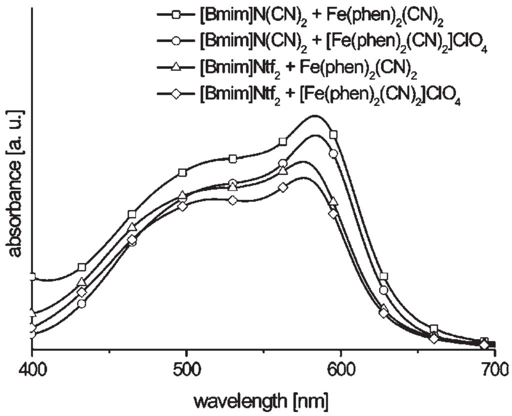

Fig. 5 UV/Vis spectra of **1** (solubility prior mediated by CH_2Cl_2) and **2**, respectively, dissolved in $[Bmim]N(CN)_2$ and $[Bmim]Ntf_2$.

Solvatochromism of $[Fe(phen)_2(CN)_2]ClO_4$ in RTILs

$[Fe(phen)_2(CN)_2]ClO_4$ when dissolved in RTILs relates completely to that of $Fe(phen)_2(CN)_2$ as seen definitively by the shape of the UV/Vis absorption bands. A series of UV/Vis absorption spectra of **2** dissolved in various 1-butyl-3-methylimidazolium RTILs are shown in Fig. 4. Accordingly, the reduction of $[Fe(phen)_2(CN)_2]ClO_4$ to $Fe(phen)_2(CN)_2$ also takes place in ionic liquids. This consideration is supported by the results of the EPR measurements of **2** dissolved in $[Bmim]N(CN)_2$ (spectrum is given in ESI†). The signal intensity of Fe^{III} is small and that of the organic radical appears large. However, the reduction process produces radicals from the RTIL which can have a disturbing effect on the UV/Vis absorption band. Therefore, **2** was measured in three different concentrations dissolved in $[Bmim]N(CN)_2$ and $[Bmim]Ntf_2$ to show whether an effect of radicals has a significant or negligible influence on the UV/Vis absorption band for polarity measurements (spectra and procedure are given in ESI†). There was no change observed in the form and position of the UV/Vis absorption spectra in all ionic liquids investigated. Hence, the formation of organic radicals derived from the solvent does not affect the UV/Vis absorption band. This result is also an evidence that aggregation of dye **2** does not occur in the RTILs. In a recent publication we have also found that *e.g.* 4-nitroaniline substituted solvatochromic probes and related dyes show no tendency of aggregation in RTILs.[37]

To show independently the compatibility of UV/Vis spectra of dissolved **1** compared to that of dissolved **2** in RTILs, we performed the following experiment. **1** was dissolved in dried dichloromethane and a portion of the ionic liquid was added. Then, dichloromethane was removed under reduced pressure. We observed that $Fe(phen)_2(CN)_2$ does not precipitate after completely removing the dichloromethane phase. The UV/Vis spectra of **1** were compared to that of **2** dissolved in the ionic liquid. This experiment was performed for $[Bmim]N(CN)_2$ and $[Bmim]Ntf_2$ and UV/Vis spectra are shown in Fig. 5.

Identical UV/Vis spectra were measured for **1** and **2** dissolved in the respective ionic liquid. This result is also an additional evidence that $[Fe(phen)_2(CN)_2]ClO_4$ undergoes reduction to $Fe(phen)_2(CN)_2$ when dissolved in ionic liquids. The approach of using a solution of **1** in dichloromethane, adding the ionic liquid and evaporating the solvent can also be

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Table 4 UV/Vis absorption maxima of **2** dissolved in 1-butyl-3-methylimidazolium ionic liquids: α values calculated from eqn (5), *AN* calculated from eqn (6), β value and ^{1}H NMR chemical shift of the proton in 2-position (from ref. 38)

Anion	$10^{-3}\tilde{\nu}_{max(\mathbf{2})}$/ cm^{-1}	α	β	*AN*	δ(H2)/ ppm
Cl^-	16.86^a	0.32	0.95	23.41	10.31
Br^-	16.95^a	0.36	0.87	24.61	9.94
CH_3COO^-	16.95	0.36	0.85	24.61	10.27
$CH_3SO_3{}^-$	16.95^a	0.36	0.85	24.61	9.64
$NO_2{}^-$	16.98	0.38	0.81	25.00	9.68
$CH_3OSO_3{}^-$	17.01	0.39	0.75	25.40	9.21
$NO_3{}^-$	17.04	0.40	0.74	25.80	9.75
$OctOSO_3{}^-$	17.06	0.41	0.77	26.07	9.32
I^-	17.06	0.41	0.75	26.07	9.68
CF_3COO^-	17.09	0.43	0.74	26.47	9.74
SCN^-	17.09	0.43	0.71	26.47	9.15
$N(CN)_2{}^-$	17.12	0.44	0.64	26.86	8.96
$CF_3SO_3{}^-$	17.24	0.50	0.57	28.46	8.91
$BF_4{}^-$	17.30	0.52	0.55	29.26	8.64
$PF_6{}^-$	17.33	0.54	0.44	29.66	8.38
$Ntf_2{}^-$	17.36	0.55	0.42	30.05	8.56

[a] Measured in the melt.

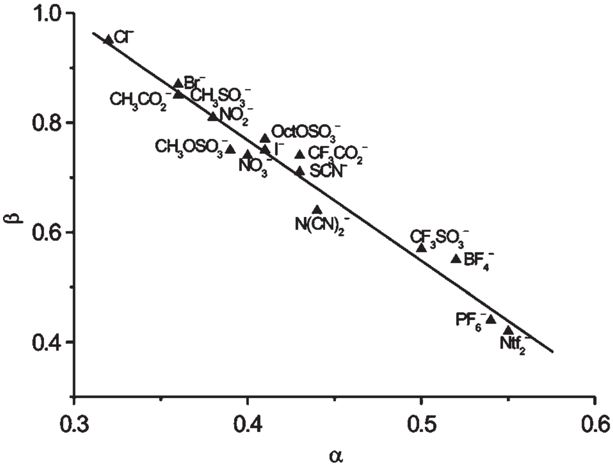

Fig. 6 Correlation of β with α values of 1-butyl-3-methylimidazolium ionic liquids with different anions.

applied to determine α values and *AN* of RTILs. However, the alternative procedure to use **1** for pure RTILs is much more time-consuming because the complete removal of the organic solvent must be secured.

The UV/Vis absorption maxima of **2**, dissolved in 16 1-butyl-methylimidazolium ionic liquids with different anions, the determined α value and *AN*, as well as the β value and ^{1}H NMR chemical shift of the proton in 2-position (from ref. 38) are given in Table 4.

Generally, the α values determined in this work are lower than those reported in the literature up to now for RTILs which are based on Reichardt's dye as the solvatochromic probe. The magnitude of α values from this work agrees with *AN* from the Raman sensitive probe diphenylcyclopropenone reported by Fujisawa *et al.*[5] The authors have found that *AN* is in the order of about 27 ± 1 for several 1-butyl-3-methylimidazolium ionic liquids. The independent determination of *AN* is of importance, because of the established relationship of *AN* with α and π* shown in eqn (6).[39]

$$AN = -0.1 + 33.73\alpha + 17.05\pi^*$$
$$n = 14, r = 0.99, sd = 1.83, F < 0.0001 \qquad (6)$$

Importantly, the *AN* determined by Fujisawa *et al.* would correspond to α values of about 0.3 (assuming $\pi^* = 1$) to 0.4 (assuming $\pi^* = 0.85$), calculated from eqn (6). Hence, this independent deliberation demonstrates that α values reported as determined by the use of Reichardt's dye seem really too large, because effects of the anion on the UV/Vis shift of Reichardt's dye may be involved which are not considered in the LSE correlations.

How far the influence of the β term on the $E_T(30)$ parameter must be taken into account is discussed in our preliminary work and is demonstrated for the LiCl–*N*,*N*-dimethylacetamide solvent system in detail.[40] Strong coordinating anions such as the chloride ion cause a significant increase of the $E_T(30)$ value although the α and π* value are hardly changed. A strong coordination of an anion at the pyridinium ring of the phenolate betaine dye (Reichardt's dye) causes a decrease of the electron affinity of the pyridinium cation site and thus, the intramolecular CT transition energy of Reichardt's dye increases. As a consequence, anion coordination can result in an increase of the $E_T(30)$ value which is not due to HBD effects. It raises the question whether the established equations for determination of α using the $E_T(30)$ value is justified to apply to RTILs? Those α values reported for [Bmim] ionic liquids are in the range from 0.41 to 0.73.

An effect of the nature of the anion on *AN* for [Bmim] RTILs was not discussed by Fujisawa *et al.* The independence of *AN* from the anion is in contrast to Huddlestone's results according to the expected anion effect. It is either possible that the dipolarity/polarisability effect deriving from the influence of the anion modifies the *AN* or the Raman spectroscopic method is not sensitive enough to observe gradually such differences.

The proton in the 2-position of the 1,3-dialkylimidazolium ring in RTILs undergoes an evident interaction with the anion as shown by ^{1}H NMR investigations by several authors.[38,41–43] There is an excellent correlation of α measured in this work with the independently determined β values, shown in Fig. 6 and by eqn (7).

$$\beta = 1.636 - 2.171\alpha$$
$$n = 16, r = 0.99, sd = 0.027, F < 0.0001 \qquad (7)$$

The value of α decreases significantly with increasing the hydrogen bond accepting strength β of the anion. This result is a convincing demonstration for the reliability of the α values determined by means of the solvatochromic probe **2** in this work. This relationship was already discovered by Huddlestone *et al.* for a fewer set of anions, but with lower significance of the correlation.[4] The correlation developed in this work provides a precise background for structure reactivity relationship.

The correlation of α with the ^{1}H chemical shift of the proton in the 2-position of the imidazolium ring, shown in

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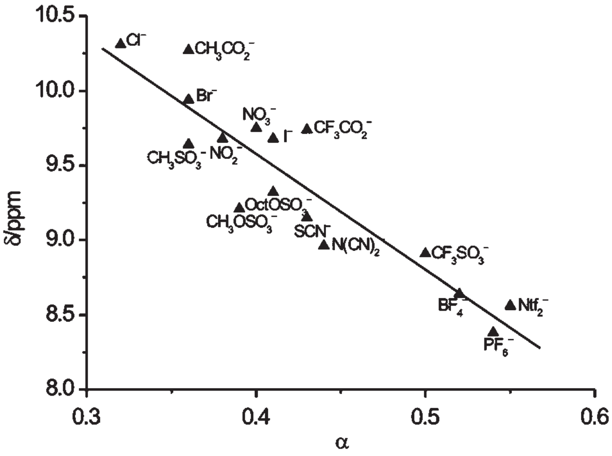

Fig. 7 Correlation of the ^{1}H chemical shift of the proton in 2-position of the imidazolium ring with the α value.

Fig. 7 and by eqn (8), is consequently in the same order as that for β as discussed in our previous paper.[38]

$$\begin{aligned}&\delta(\text{ppm}) = 12.686 - 7.770\alpha\\&n = 16, r = 0.91, sd = 0.248, F < 0.0001\end{aligned} \qquad (8)$$

What is the reason for the result that the correlation of α with β is excellent, but each of them with the ^{1}H NMR chemical shift is only quite "good"? Both α and β values have been determined by those solvatochromic probes whose UV/Vis absorption bands show significant correlation with solely one solvent parameter. In spite of the established fact that the dipolarity/polarisability has also an effect on the position of the UV/Vis absorption band of the solvatochromic probe,[44] its contribution is not considered by the LSE equations used. The significant correlation of α with β for the RTILs studied demonstrates that the effect of dipolarity/polarisability on $\tilde{\nu}_{\max}$(probe) is obviously compensated because each of the probes reflects its contribution in the same closeness of agreement. This consideration is an independent support of the influence of π^* on $\tilde{\nu}_{\max}$ which is really not of importance for the determination of α or β when using solely $\tilde{\nu}_{\max(\mathbf{2})}$ or $\tilde{\nu}_{\max(\text{probe})}$ (for β).[38] Therefore, we conclude that the "only good" correlation of α with $\delta(^1\text{H})$ is due to dipolarity/polarisability effects of the ion pairing on the chemical shift which is not considered in this approach.

The density of ion pairing and its dielectric force can have an effect on the ^{1}H NMR chemical shift which is not reflected by the UV/Vis probe. The examination whether and how structural features of RTILs have an effect on π^* is an objective of further studies.

Conclusions

The results of this work have shown that $[Fe(phen)_2(CN)_2]ClO_4$ undergoes reduction to $Fe(phen)_2(CN)_2$ when dissolved in several well behaved solvents and ionic liquids. The generated $Fe(phen)_2(CN)_2$ serves as a suitable solvatochromic probe for measuring the hydrogen bond donor (HBD) strength α and Gutmann's acceptor numbers *AN*. Therefore, **2** can be recommended as a solvatochromic probe to measure HBD ability α and *AN* of ionic liquids.

The determined α parameter shows an excellent correlation with the independently determined hydrogen bond accepting (HBA) strength β of the anion which demonstrate that the empirical polarity parameters of RTILs can be utilized independently of each other.

Experimental

General

Solvents obtained from Merck, Fluka and Sigma Aldrich were dried and distilled prior use. 1-Butyl-3-methyl ([Bmim]), nitrite, iodide, trifluoroacetate, nitrate and bis(trifluoromethanesulfonyl)imide were synthesized according to established literature procedures.[41,45–49] All other chemicals were purchased in the highest available grade from commercial sources. $Fe(phen)_2(CN)_2$ and $[Fe(phen)_2(CN)_2]ClO_4$ was synthesized and purified according to Schilt.[35] 1-Butyl-3-methylimidazolium acetate was washed five times with ethyl acetate (distilled over P_2O_5) because of the lack of purity of the commercial available substance. All [Bmim] salts were dried by dissolving in dichloromethane (dried and distilled over CaH_2), adding molecular sieve 4 Å, stirring overnight, and evaporation of the solvent. Basic alumina from ICN Biomedicals GmbH was added to the dichloromethane solution of the bromide, methanesulfonate, and tetrafluoroborate, respectively, to remove acid traces. All ionic liquids were colorless or at most slightly yellow except for the iodide, nitride and thiocyanate salts, where the color is due to the anion. To reduce residual trace water, the ionic liquids were evaporated for 8 h at 60 °C and 24 h at room temperature with a pressure of 3 mbar.

UV/Vis measurements

A few crystals of **1** and **2** were completely dissolved in the respective solvent or ionic liquid. UV/Vis absorption spectra were recorded using precision quartz cells with a light path of 2 mm under exclusion of moisture by means of a MCS 400 diode-array spectrometer from Carl Zeiss (Jena) with a resolution of 1 nm. The longest wavelength absorption maximum was used for the calculation of the α values and *AN*. The analyses of the spectra were performed with Aspect Plus (Version 1.31, Carl Zeiss Jena GmbH). Multiple regression analysis were performed with the Origin Pro G8 SR1 statistic program from OriginLab Corporation.

EPR measurements

A few crystals of **2** were completely dissolved in the respective solvent or ionic liquid. EPR measurements were performed at 77 K with a Bruker ESP 300 E spectrometer (X band, ν = 9.470 GHz). The modulation frequency and amplitude were 100 kHz and 5.230 G, respectively.

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References

1 C. Reichardt, *Green Chem.*, 2005, **7**, 339.
2 C. Chiappe and D. Pieraccini, *J. Phys. Org. Chem.*, 2005, **18**, 275.
3 H. Weingärtner, *Angew. Chem.*, 2008, **120**, 664.
4 J. G. Huddlestone, G. A. Broker, H. D. Willauer and R. D. Rogers, Ionic Liquids: Industrial Applications to Green Chemistry, *ACS Symp. Ser.*, 2002, **818**, 270.
5 T. Fujisawa, M. Fukuda and M. Terazima, *J. Phys. Chem. A*, 2006, **110**, 6164.
6 (*a*) K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Justus Liebigs Ann. Chem.*, 1963, **661**, 1; (*b*) C. Reichardt and E. Harbusch-Görnert, *Justus Liebigs Ann. Chem.*, 1983, 721; (*c*) C. Reichardt, S. Asharin-Fard, A. Blum, M. Eschner, A.-M. Mehranpour, P. Milart, T. Niem, G. Schäfer and M. Wilk, *Pure Appl. Chem.*, 1993, **65**, 2593; (*d*) C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319.
7 M. J. Kamlet, J.-S. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.
8 Y. Marcus, *Chem. Soc. Rev.*, 1993, **22**, 409.
9 N. Palm and V. Palm, *Org. React. (Tartu)*, 1997, **104**, 141.
10 (*a*) J. H. Park and P. W. Carr, *J. Chromatogr.*, 1989, **456**, 123; (*b*) M. F. Vitha and P. W. Carr, *J. Phys. Chem. B*, 1998, **102**, 1888.
11 R. S. Helburn, S. C. Rutan, J. Pompano, D. Mitchem and W. T. Patterson, *Anal. Chem.*, 1994, **66**, 610.
12 F. Lagalante, A. M. Clarke and T. J. Bruno, *J. Phys. Chem. B*, 1999, **103**, 7319.
13 Y. K. Ryu, J. K. Park, H. J. Lim and J. H. Park, *Chromatographia*, 2000, **51**, 567.
14 (*a*) J. Catalàn, V. López and P. Pèrez, *Justus Liebigs Ann. Chem.*, 1995, 793; (*b*) J. Catalàn, V. López, P. Pèrez, R. Martín-Villamil and J.-G. Rodríguez, *Justus Liebigs Ann. Chem.*, 1995, 241; (*c*) J. Catalàn, C. Díaz, V. López, P. Pèrez, J.-L. G. de Paz and J.-G. Rodríguez, *Justus Liebigs Ann. Chem.*, 1996, 1785; (*d*) J. Catalàn and C. Díaz, *Liebigs Ann. Chem./Recueil*, 1997, 1941; (*e*) J. Catalàn and C. Díaz, *Eur. J. Org. Chem.*, 1999, 885; (*f*) J. Catalàn and H. Hopf, *Eur. J. Org. Chem.*, 2004, 4694.
15 A. J. Carmichael and K. R. Seddon, *J. Phys. Org. Chem.*, 2000, **13**, 591.
16 (*a*) K. A. Fletcher, I. A. Storey, A. E. Hendricks and S. Pandey, *Green Chem.*, 2001, **3**, 210; (*b*) K. A. Fletcher, S. N. Baker, G. A. Baker and S. Pandey, *New J. Chem.*, 2003, **12**, 1706.
17 L. Crowhurst, P. R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2790.
18 S. Carda-Brocj, A. Bertod and D. W. Armstrong, *Anal. Bioanal. Chem.*, 2003, **375**, 191.
19 J. Lu, C. L. Liotta and C. A. Eckert, *J. Phys. Chem. A*, 2003, **107**, 3995.
20 P. M. Mancini, G. G. Fortunato and L. R. Vottero, *Phys. Chem. Liq.*, 2004, **42**, 625.
21 M. Koel, *Proc. Estonian Acad. Sci. Chem.*, 2005, **54**, 3.
22 G. Angelini, C. Chiappe, P. De Maria, A. Fontana, F. Gasparrini, D. Pieraccini, M. Pierini and G. Siani, *J. Org. Chem.*, 2005, **70**, 8193.
23 S. N. V. K. Aki, J. F. Brennecke and A. Samanta, *Chem. Commun.*, 2001, 413.
24 M. J. Muldoon, C. M. Gordon and I. R. Dunkin, *J. Chem. Soc., Perkin Trans. 2*, 2001, 433.
25 S. Ishizaka, H.-B. Kim and N. Kitamura, *Anal. Chem.*, 2001, **73**, 2421.
26 Y. Marcus, *J. Solution Chem.*, 1991, **20**, 929.
27 Y. Marcus, *Chem. Soc. Rev.*, 1993, **22**, 409.
28 S. Spange, K. Fischer, S. Prause and T. Heinze, *Cellulose*, 2003, **10**, 201.
29 S. Prause and S. Spange, *J. Phys. Chem. B*, 2004, **108**, 5734.
30 (*a*) J. Burgess, *Spectrochim. Acta, Part A*, 1970, **26**, 1957; (*b*) J. Burgess, J. G. Chambers and R. I. Haines, *Transition Met. Chem.*, 1981, **6**, 145.
31 A. A. Schilt, *J. Am. Chem. Soc.*, 1960, **82**, 3000.
32 W. Linert, Y. Fukuda and A. Camard, *Coord. Chem. Rev.*, 2001, **218**, 113.
33 R. W. Soukup and R. Schmid, *J. Chem. Educ.*, 1985, **62**, 459.
34 A. A. Schilt, *J. Am. Chem. Soc.*, 1963, **85**, 904.
35 M. Matasumoto, T. Tarumi, K. Sugimoto, N. Kagayama, S. Funahashi and H. D. Takagi, *Inorg. Chim. Acta*, 1997, **255** 81.
36 E. Pelizzetti, E. Mentasti and E. Pramauro, *Inorg. Chem.*, 1978, **17**, 1181.
37 K. Schreiter and S. Spange, *J. Phys. Org. Chem.*, 2008, **21** 242.
38 R. Lungwitz and S. Spange, *New J. Chem.*, 2008, **32**, 392.
39 R. W. Taft and M. J. Kamlet, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1723.
40 S. Spange, A. Reuter, E. Vilsmeier, T. Heinze, D. Keutel and W. Linert, *J. Polym. Sci.*, 1998, **36**, 1945.
41 P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168.
42 J. Palomar, V. R. Ferro, M. A. Gilarranz and J. J. Rodriguez, *J. Phys. Chem. B*, 2007, **111**, 168.
43 A. G. Avent, P. A. Chalconer, M. P. Day, K. R. Seddon and T. Welton, *J. Chem. Soc., Dalton Trans.*, 1994, 3405.
44 S. Spange, S. Prause, E. Vilsmeier and W. Thiel, *J. Phys. Chem. B*, 2005, **109**, 7280.
45 J. Dupont, P. A. Z. Suarez, R. F. De Souza, R. A. Burrow and J.-P. Kintzinger, *Chem. Eur. J.*, 2006, **6**, 2377.
46 P. Wasserscheid, M. Sesing and W. Karth, *Green Chem.*, 2002, **4**, 134.
47 S. Rivera-Rubero and S. Baldelli, *J. Phys. Chem. B*, 2006, **110**, 4756.
48 L. Cammarata, S. G. Kazarian, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5192.
49 A. J. Carmichael and K. R. Seddon, *J. Phys. Org. Chem.*, 2000, **13**, 591.