

Tetraalkylphosphonium-based ionic liquids

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Abstract

Ionic liquids are salts that are liquid at or near room temperature. Their wide liquid range, good thermal stability, and very low vapor pressure make them attractive for numerous applications. The general approach to creating ionic liquids is to employ a large, unreactive, low symmetry cation with and an anion that largely controls the physical and chemical properties. The most common cations used in ionic liquids are *N*-alkylpyridinium and *N,N'*-dialkylimidazolium. Another very effective cation for the creation of ionic liquids is tetraalkylphosphonium, $[\text{PR}_1\text{R}_2\text{R}_3\text{R}_4]^+$. The alkyl groups, R_n , generally are large and not all the same. The halide salts of several phosphonium cations are available as starting materials for metathesis reactions used to prepare ionic liquids. The large phosphonium cations can combine with relatively large anions to make viscous but free flowing liquids with formula mass greater than 1000 g mol^{-1} . Some other more massive salts are waxes and glasses. The synthesis and the physical, chemical, and optical properties of phosphonium-ionic liquids having anions with a wide range of masses were measured and are reported here.

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1. Introduction

The diverse nature of room temperature ionic liquids (RTILs) continues to expand significantly as more resources are dedicated to understanding these materials as solvents, electrolytes, thermal fluids, and much more [1–3]. RTILs have numerous advantages over molecular organic materials, particularly in their stability due to their negligible vapor pressure. Other advantages include easy functionalization, large liquid ranges, high effective concentrations as compared to solutions, and the ability to flow – an interesting and attractive quality from a materials perspective.

The structural tunability of both the cations and anions suggest great flexibility in the potential applications of ionic liquids. Our interests in optical and magnetic

materials have led us to RTILs with large phosphonium cations, $[\text{PR}_1\text{R}_2\text{R}_3\text{R}_4]^+$. The anions in the phosphonium salts contain structural features which have been predicted to display significant third order nonlinear optical properties, particularly nonlinear indices or refraction (often designated as n_2) and nonlinear absorptions (α_2), – such as multiphoton absorption – both of which are intensity dependent functions, and therefore useful for optical limiting applications. These include conjugated thiolate and dithioacetate compounds [4], Fig. 1, such as methylxanthate (xan), diethyldithiocarbamate (dtc), nitrodithioacetate – also known as the K-salt, and dithiomaleonitrile (dtmn). Other conjugated anions of interest for their physical properties are bistriflylamide (NTf_2), nonafluorobutylsulfonate ($\text{C}_4\text{F}_9\text{SO}_3$), tricyanomethanide ($\text{C}(\text{CN})_3$), and dicyanamide ($\text{N}(\text{CN})_2$). Some further potentially magnetically and/or optically interesting anions are those such as thiocyanate, cyanide, or dicyanamide complexes of Ni(II), Co(II), and Fe(II), bis-dicarbollylcobalt(III) (CoCB) – which is

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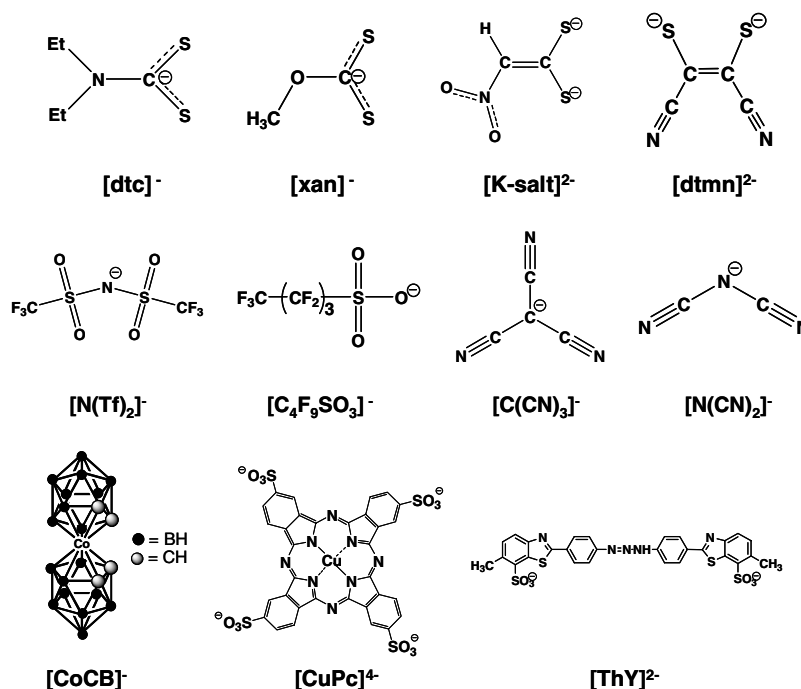


Fig. 1. Anion structures for new phosphonium RTILs.

interesting due to its σ -aromaticity, as well as copper phthalocyaninetetrasulfonate (CuPc) and thiazolium yellow G (ThY), both of which are common dyes.

The tetraalkylphosphonium salts, $[\text{PR}_1\text{R}_2\text{R}_3\text{R}_4]^+$, were chosen for a number of features which differentiate them from other common RTIL cations. The numerous possible permutations that can be synthesized using various alkyl and aryl side chains increases the fine tunability of the resulting properties, Table 1, such as their melting/glass transitions or viscosities. The phosphoniums lack the weakly acidic ring protons of the more common imidazolium cations – a limitation when strongly basic anions are used, such as the thiolates mentioned above. Also, the quaternary phosphonium salts have been reported to be more stable to increased temperatures for longer periods of time than nitrogen-based cations [5]. With materials aspects in mind, they are additionally attractive because the steric bulk of

the large side chains around the phosphonium cation interferes with electrostatic interactions between the anions and the cation – which is generally localized on the phosphorus – allowing for greater impact of the properties of the anion itself, as compared to salts with more strongly interacting smaller cations. Naturally, there are disadvantages as well, such as very high viscosities, poorly understood solubility properties, etc. – all of which may potentially be optimized through functionalization of the cations alkyl/aryl components.

Although the quaternary phosphonium ILs have not received the attention and extensive resources that the more common imidazolium and other nitrogen-containing ILs do, they have been used extensively in several areas of chemistry for many years, particularly catalysis and phase transfer reactions and extractions [6]. Additionally, they have been applied to materials as well, such as liquid crystals [7].

Table 1
Physical properties of $[\text{PR}_1\text{R}_2\text{R}_3\text{R}_4][\text{X}]$ salts

$\text{R}_1 = \text{R}_2 = \text{R}_3$	R_4	X^-	Solid/liquid ^a	Trade name ^b
Ethyl	Ethyl	Br	Solid ($T_{\text{mp}} > 300$ °C)	CYPHOS 422
<i>n</i> -Butyl	<i>n</i> -Butyl	Cl	Solid ($T_{\text{mp}} = 87$ °C)	CYPHOS IL 164
<i>n</i> -Butyl	<i>n</i> -Tetradecyl	Cl	Solid ($T_{\text{mp}} = 56$ °C)	CYPHOS IL 167
<i>n</i> -Pentyl	<i>n</i> -Tetradecyl	Cl	Liquid	CYPHOS IL 127
<i>n</i> -Hexyl	<i>n</i> -Tetradecyl	Cl	Liquid ($T_g = -56$ °C)	CYPHOS IL 101
<i>n</i> -Hexyl	<i>n</i> -Tetradecyl	Br	Liquid	CYPHOS IL 102
<i>n</i> -Octyl	<i>n</i> -Tetradecyl	Cl	Liquid	CYPHOS IL 128
Isobutyl	<i>n</i> -Octyl	I	Liquid	CYPHOS IL 205

^a State at room temperature.

^b Cytec specialty chemicals.

A number of these quaternary phosphonium salts with desired anions were synthesized, with nearly all being liquid at and well below room temperature, and stable up to 400 °C in some cases. Their chemical and physical properties were measured, and while the anions do dictate the major physical properties such as optical and magnetic features, there appears to be slight correlations between the cation size/structure with their viscosity and glass transition temperatures.

2. Results and discussion

2.1. Synthesis of RTILs

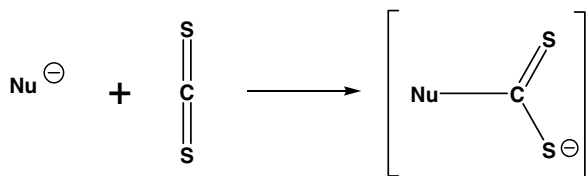
The sources of the anionic components of the RTILs were alkali metal salts, and those which are not commercially available could generally be made by known syntheses. The salts of dtmn and the K-salt, could be made via simple nucleophilic additions to CS₂, as seen in Scheme 1. The metal complexes are also easily produced from metal chloride salts reacted with an excess of the salts of the desired ligands. These syntheses are generally higher yield reactions and use fairly inexpensive starting materials – desirable qualities should a large scale-up process be considered.

Simple metathesis reactions of these alkali metal salts of the desired anions with the appropriate phosphonium halide, [PR₁R₂R₃R₄]X, in an organic solvent or organic/aqueous system, results in the alkali halide precipitating out or extracted into the aqueous layer, and the [PR₁R₂R₃R₄]_x[anion]^{x-} left in the organic layer, as with the [PR₁R₂R₃R₄]₂[dtmn] salt shown in Scheme 2. Washing the organic layer several times with water generally removes the alkali halide and excess starting materials. In most cases, the [PR₁R₂R₃R₄]X was dis-

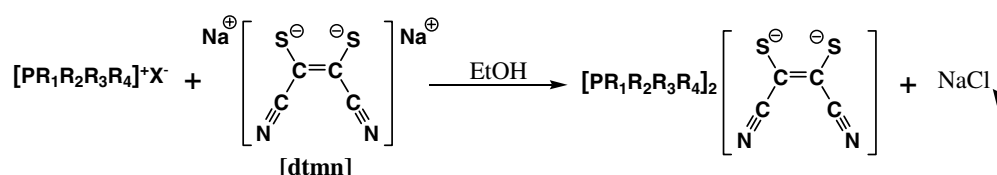
solved in chloroform, and added to an aqueous solution of the anion salt. In cases where the anion salt was not water-soluble, e.g., the Na₂(dtmn), the metathesis reaction was carried out in pure EtOH, the resulting solid byproducts (NaCl) filtered, the solvent evaporated, and then the product redissolved in chloroform for washing and purifying. Any remaining solvent and traces of water could be removed by heating the sample in vacuo to 90–120 °C. All of the anions discussed here were incorporated into salts with the trihexyltetradecylphosphonium cation, [PC₆C₆C₆C₁₄]⁺. The dtmn and NTf₂ anions were also made as salts with [PC₄C₄C₄C₁₄]⁺, [PC₄C₄C₄C₄]⁺, [PC₈C₈C₈C₈]⁺, and [PPh₄]⁺ cations.

The amount of residual alkali metal and chloride in the resulting liquids was determined through ICP–OES measurements. As most of the [PR₁R₂R₃R₄] RTILs are not water-soluble, they were dissolved in minimal amount of chloroform and extracted with 20 ml of 20% nitric acid to try to dissolve as much of the RTIL components in the aqueous layer as possible, and in doing so should extract any alkali or chloride salts present in the RTIL. In all cases, less than 100 ppm of either impurity was found. The minute chloride impurities are also confirmed through chloride elemental analyses on a few selected ILs, which included both the purely organic ILs and those with inorganic complexes. In all samples, the chloride levels were below the detection limits of the instrument – less than 0.2% by mass, which even for the lowest molecular weight IL calculates to be less than 5 mol% (5 mol Cl per 100 mol IL). This indicates that the samples are pure, and are not solutions or binary salts of the two starting materials.

Water content of the RTILs was determined using Karl–Fischer titrations. Not all of the salts could be tested, however, due to low solubilities in the methanol solvent used in the titrations. Most of the thiol-containing ILs were tested before and after drying, including the xan, dtc, dtmn, and K-salt salts. Before drying, these RTILs had water content ranging from 0.75 to 1.5 water molecules per formula unit – fairly high presumably due to strong [R–S⁻][H–OH] interactions. After drying at 90 °C under vacuum for several hours, these dropped to less than 0.05 waters per formula unit (less than 0.1% by mass).



Scheme 1.



Scheme 2.

2.2. Thermal properties

All of the materials presented exhibit glass transitions occurring well below room temperature as seen in DSC measurements, Table 2, with the exception of the ThY salt, which is a glass at room temperature with its transition at +65 °C. Some do show significant transition enthalpies as seen in a true freezing/melting point, e.g. the $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{xan}]$, but most only show changes in their enthalpy at their transitions, Fig. 2. Correlations of the T_g 's amongst the $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]$ salts with varying anions is difficult to establish due to the charges of the anions, and thus different number of cations necessary for charge balance. Other factors that most likely contribute to the T_g 's and physical properties are morphology (planar versus nonplanar) and electrostatic distributions of the anions, which also contribute to packing efficiency of the salts.

In a series of common anions with the different phosphonium cations, a slight trend can be observed in the T_g versus size of the cation, Table 3. This trend is more easily seen in the $[\text{PR}_1\text{R}_2\text{R}_3\text{R}_4]_2[\text{dtmn}]$ salts, where cation size is $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}] = [\text{PC}_8\text{C}_8\text{C}_8\text{C}_8] > [\text{PC}_4\text{C}_4\text{C}_4\text{C}_4] > [\text{PC}_4\text{C}_4\text{C}_4\text{C}_4]$. This trend is not necessarily linear, again due to the morphology of the cation, as well as the symmetry and packing efficiency. The cation $[\text{PC}_4\text{C}_4\text{C}_4\text{C}_4]$ approaches the limit for creating RTILs due to its much smaller size and higher symmetry than the other cations. Introducing larger cations, such as

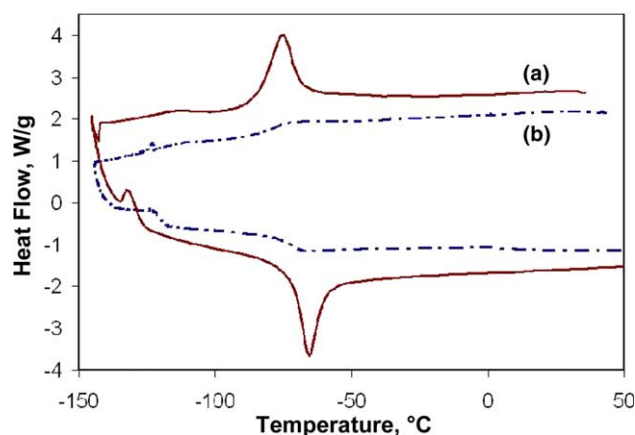


Fig. 2. DSC for: (a) $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{xan}]$, and (b) $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{CoCB}]$ RTILs.

the $[\text{PC}_8\text{C}_8\text{C}_8\text{C}_8]$, and less symmetry, such as $[\text{PC}_4\text{C}_4\text{C}_4\text{C}_4]$, results in RTILs with much lower T_g 's.

As salts, they have no readily apparent vapor pressure, thus their upper temperature limit is typically determined by their thermal decomposition temperatures, which generally occurs well below boiling. The carbamate and xanthate materials, $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{dtc}]$ and $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{xan}]$, tend to decompose at lower temperatures – around 250 °C – whereas most others are stable up to 400–450 °C based on TGA experiments, Table 2 (decomposition in these cases are the onset tem-

Table 2
Physical properties of $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{anion}]^{x-}$ RTILs

[Anion]	FW (g mol ⁻¹)	T_g (°C)	$T_{\text{dec}}^{\text{a}}$ (°C)	Density ^b (g cm ⁻³)	Viscosity ^b (η , cP)	$\lambda_{\text{max}}^{\text{c}}$ (nm)
[dtc] ⁻	631	-77	255	0.942	1470	305
[xan] ⁻	590	-70 ^d	290	0.920	1480	345
[K-salt] ²⁻	1101	-79	350	0.960	560	396
[dtmn] ²⁻	1106	-71	360	0.942	4780	394
[Co(dtmn) ₂] ²⁻	1198	-65	370	^e	^e	460
[Ni(dtmn) ₂] ²⁻	1198	-70	380	0.994	6480	475
[NTf ₂] ⁻	782	-76	400	1.080	450	NA
[C ₄ F ₉ SO ₃] ⁻	763	-68	390	1.079	805	NA
[C(CN) ₃] ⁻	585	-65	415	0.901	320	NA
[N(CN) ₂] ⁻	549	-67	395	0.904	490	NA
[Co(N(CN) ₂) ₄] ²⁻	1289	-70	375	0.907	310	618
[Co(NCS) ₄] ²⁻	1257	-72	405	0.963	2436	626
[Co(NCSe) ₄] ²⁻	1447	-70	^f	1.02	660	628
[Ni(NCS) ₆] ²⁻	2228	-60	380	0.902	760	346
[Fe(CN) ₆] ⁴⁻	2144	-70	^f	0.942	5790	355/410
[CoCB] ⁻	806	-71	420	1.00	3702	450
[CuPc(SO ₃) ₄] ⁴⁻	2816	-45	400	^e	^e	598/698
[ThY] ²⁻	1615	+65	395	^e	^e	405

^a T_{dec} is decomposition onset temperature.

^b Density and viscosity reported for room temperature (20 °C).

^c UV/Vis from neat samples with pathlength ~ 10 μm .

^d T_{mp} , not T_g .

^e Viscosity too large to measure at RT.

^f Not measured due to toxicity.

Table 3
Physical properties of $[\text{PR}_1\text{R}_2\text{R}_3\text{R}_4][\text{NTf}_2]$ and $[\text{PR}_1\text{R}_2\text{R}_3\text{R}_4]_2[\text{dtmn}]$ RTILs

	Cation	T_g (°C)	Density ^a (g cm ⁻³)	Viscosity ^a (η , cP)
NTf ₂	[PC ₆ C ₆ C ₆ C ₁₄]	-76	1.080	450
	[PC ₈ C ₈ C ₈ C ₈]	-60	1.071	418
	[PC ₄ C ₄ C ₄ C ₁₄]	-60	1.112	464
	[PC ₄ C ₄ C ₄ C ₄]	+65	^b	^b
	[PPh ₄]	+160	^b	^b
dtmn	[PC ₆ C ₆ C ₆ C ₁₄]	-71	0.942	4780
	[PC ₈ C ₈ C ₈ C ₈]	-69	0.946	5590
	[PC ₄ C ₄ C ₄ C ₁₄]	-46	0.950	7480
	[PC ₄ C ₄ C ₄ C ₄]	-35	^b	16,150 ^c
	[PPh ₄]	+154	^b	^b

^a Density and viscosity reported for room temperature (20 °C).

^b Not measured.

^c Measured at 30 °C.

peratures, which is the intersection of the baseline below their decomposition temperature with the tangent to the mass loss versus temperature plots in the TGA experiment).

Thermal stability for some of the RTILs was determined through isothermal TGA experiments. An example of the thiolates is the $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{xan}]$ salt, which shows moderate stability below 200 °C, but decomposes fairly rapidly at higher temperatures, Fig. 3(a). The $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{CoCB}]$ on the other hand, is fairly stable up to 375 °C, showing only 0.1%/min mass loss, Fig. 3(b). This sample rapidly decomposes and outgases around 400 °C. The lack of stability of the thiolate based salts seems to be due to decomposition of the anion, most likely though facile loss of CS₂. The salts with

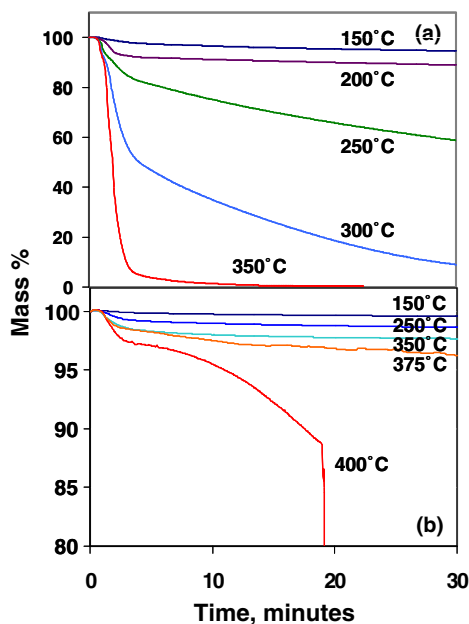


Fig. 3. Isothermal TGA for: (a) $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{xan}]$, and (b) $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{CoCB}]$ RTILs.

more robust anions tend to decompose at much higher temperatures, at which it appears the cation stability becomes an issue near 400 °C.

2.3. Physical properties

The density of all of the materials show linear behavior over changing temperature as expected, Fig. 4. All of the RTILs, with the exception of $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2[\text{Co}(\text{NCS})_4]$, $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}][\text{C}_4\text{F}_9\text{SO}_3]$, and the NTf₂ salts, show densities below 1.0, Table 2, presumably due to a significant contribution from large alkyl chains on the cation.

All RTILs presented show very high viscosities at room temperature, ranging from 310 cP for $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2[\text{Co}(\text{N}(\text{CN})_2)_4]$ to >7000 cP $[\text{PC}_4\text{C}_4\text{C}_4\text{C}_{14}]_2[\text{dtmn}]$, Tables 2 and 3. The CuPc, ThY, and some dtmn salts could not be measured due to their extremely viscous and waxy/glassy state at room temperature and up to near 90 °C – the temperature limit for the viscometer. As with the glass transitions, varying cation size with common anions also correlates with the viscosity of the RTILs. This effect is shown for the dtmn and NTf₂ salts in Table 3. Arrhenius plots of the viscosities versus temperature of the RTILs show some deviation from two-parameter exponential behavior, Fig. 5. Therefore the viscosities were modeled with the Vogel–Tammann–Fulcher (VTF) formula, Eq. (1)

$$\ln \eta = \ln A + \left(\frac{B}{T - T_g} \right), \quad (1)$$

where A is the frequency factor, B is the activation energy, and T_g is the thermodynamic glass transition temperature. The three-parameter fits to this model are in Table 4 [8].

No trend is seen with viscosity or T_g with varying the anions with common cations, as expected due to various

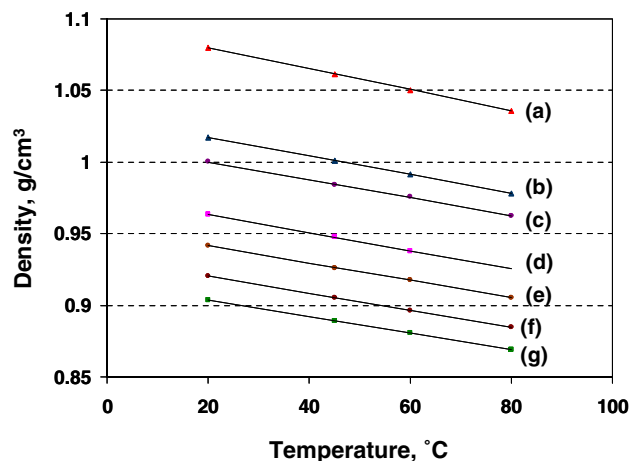


Fig. 4. Densities of $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]$ RTILs with anions: (a) NTf₂, (b) $[\text{Co}(\text{NCS})_4]$, (c) CoCB, (d) $[\text{Co}(\text{NCS})_4]$, (e) dtmn, (f) xan, and (g) $[\text{N}(\text{CN})_2]$.

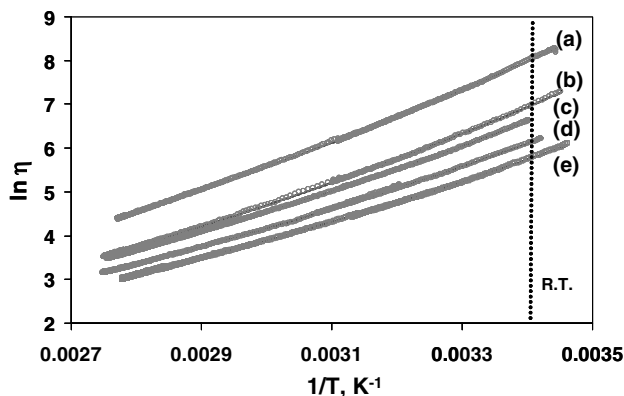


Fig. 5. Viscosities of $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]$ RTILs with anions: (a) dtmn, (b) dtc, (c) $[\text{Ni}(\text{NCS})_6]$, (d) $[\text{N}(\text{CN})_2]$, and (e) NTf_2 , with VTF model fit (solid lines mostly obscured by the data points).

Table 4
VTF parameters for viscosities of $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_x[\text{anion}]^{x-}$ RTILs using Eq. (1)

[Anion]	<i>A</i>	<i>B</i> (K)	<i>T_g</i> (K)	<i>R</i> ²
[dtc] [−]	0.0271	1531.1	149.0	0.99992
[xan] [−]	0.0227	1646.9	143.6	0.99931
[K-salt] ^{2−}	0.0477	1294.8	154.5	0.99988
[dtmn] ^{2−}	0.0210	1815.8	140.8	0.99985
[Co(dtmn) ₂] ^{2−}	^a			
[Ni(dtmn) ₂] ^{2−}	^a			
[NTf ₂] [−]	0.0427	1327.1	144.9	0.99981
[C ₄ F ₉ SO ₃] [−]	^a			
[C(CN) ₃] [−]	0.0741	1108.0	161.5	0.99985
[N(CN) ₂] [−]	0.0423	1374.4	145.8	0.99992
[Co(N(CN) ₂) ₄] ^{2−}	0.0734	1132.7	158.5	0.99992
[Co(NCS) ₄] ^{2−}	0.0156	1983.8	127.3	0.99994
[Co(NCSe) ₄] ^{2−}	0.0627	1311.3	152.3	0.99995
[Ni(NCS) ₆] ^{2−}	0.0347	1467.5	145.8	0.99993
[Fe(CN) ₆] ^{4−}	0.0024	2704.4	110.9	0.99932
[CoCB] [−]	0.0308	1600.6	155.8	0.99961
[CuPc(SO ₃) ₄] ^{4−}	^b			
[ThY] ^{2−}	^b			

^a Could not fit data with VTF or other models.

^b Wax/solid – did not obtain viscosity data.

other influences involved. However, the anions do dictate other properties of the salts, particularly the color. While some are colorless, such as the NTf_2 and $\text{C}_4\text{F}_9\text{SO}_3$, the conjugated thiolates are deep orange or red in color, Table 2. The colors of the metal complexes are determined by the spectrochemical series, which is a result of the metals and ligands used. It is therefore possible to develop these RTILs to absorb in any region of the UV, Visible and NIR region based on the anions utilized.

The magnetic properties of several of the Co(II) containing ILs were measured with an Evans balance. All of the Co(II) salts were paramagnetic, with room temperature (293 K) magnetic moments ranging from 3.3. to 3.7 μ_{B} – typical of high-spin ($S = 3/2$) Co(II) ions. Preliminary nonlinear optical measurements were done using

a Z-scan setup to determine nonlinear index of refraction, n_2 , and nonlinear absorptivity, α_2 , with a laser wavelength of 910 nm. Most of the samples did show nonlinear behavior, with the largest nonlinear refraction seen in the $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]_2[\text{dtmn}]$ salt, $n_2 = -6.1 \times 10^{-14} \text{ m}^2 \text{ W}^{-1}$. This value is slightly less than values observed for common NLO polymers and semiconductors ($\sim 10^{-12} \text{ m}^2 \text{ W}^{-1}$) [9], but greater than previously reported metal cluster compounds [10] and molecular organic compounds ($< 10^{-16} \text{ m}^2 \text{ W}^{-1}$) [11]. The dtmn salt is approximately 20,000 times greater than the typical carbon disulfide standard (CS_2), which has an $n_2 \sim 3 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}$. These results are only preliminary, as there appears to be a thermal contribution to the nonlinear behavior at the 910 nm wavelength. Nonlinear absorptions were also observed with several of the samples, but again linear absorptions – and therefore thermal effects – appear to contribute to the behavior.

3. Conclusion

A number of phosphonium based RTILs have been synthesized, with optical and magnetic applications of these materials being the focus. The larger anions utilized along with their greater charges allow for development of massive ionic liquids which can exceed 2000 g mol^{-1} formula weight. Most of the materials are liquid well below room temperature and stable up to 400 °C, and those which are glass at RT are still potentially interesting due to their glassy state. In fact, the phosphonium cation $[\text{PC}_6\text{C}_6\text{C}_6\text{C}_{14}]^+$ actually results in an RTIL in conjunction with every anion attempted, with the exception of the ThY salt. Although viscosities are rather high compared to the more common RTILs, they still have flow, and the viscosities can be tuned through modification of the cation size and symmetry. Other properties such as their color (absorption) can be adjusted through the use of the various conjugated organic anions as well as the inorganic metal–ligand complex anions. Additionally, preliminary experiments do show nonlinear refractive indices in most of the samples, and nonlinear absorption processes in several samples, suggesting these new ILs as potential novel optical materials.

4. Experimental

4.1. General techniques and reagents

The alkali metal salts Na(dtc) (Fluka), Li(NTf₂) (Aldrich), K(C₄F₉SO₃) (Aldrich), Na[N(CN)₂] (Fluka), K[C(CN)₃] (Strem), K₄[Fe(CN)₆] (Strem), Na₄(CuPc) (Aldrich), and Na₂(ThY) (ACROS) are all commercially available, and were used as received. The

[PC₆C₆C₆C₁₄]Cl, [PC₄C₄C₄C₁₄]Cl, [PC₄C₄C₄C₄]Cl, and [PC₈C₈C₈C₈]Br salts were prepared by Cytec Specialty Chemicals, and dried under vacuum at 90 °C before being used.

For those that were not available, the K-salt [12], Na(xan) [13], Na₂(dtmn) and Na₂[M(dtmn)₂] [14] were synthesized by known methods. The Cs(CoCB) salt was provided by Los Alamos National Laboratory.

The metal complexes K₂[Co(NCS/Se)₄], K₄[Ni(NCS)₆], and Na₂[Co(N(CN)₂)₄] were made by simple substitution by reacting the MCl₂ salt with excess sodium or potassium salts of the desired ligands in water. The aqueous solutions were used without isolation of the salt.

Viscosities of the samples were measured on a Cambridge Applied Systems ViscoLab 4000 Viscometer and measured over the range of 20–90 °C. The densities were determined by a Mettler–Toledo DE40 Density Meter at 20, 45, 60 and 80 °C. Absorptions were measured on an HP 8452A diode array spectrophotometer, using neat samples in a 0.01 mm (10 μm) etched quartz cuvette. Thermal characterization was carried out using a TA Instruments Q100 DSC and SDT 2960 SDT-TGA. Alkali metal and halide impurities were determined using a Varian VistaPro ICP–OES with CCD detector. Water content of the RTILs was measured with a Mettler Toledo DL38 Karl–Fischer titrator.

4.2. Metathesis reactions to synthesize RTILs

To make the [PR₁R₂R₃R₄] phosphonium RTILs from the above alkali metal salts (all except the dtc, dtmn, [C₄F₉SO₃], and CoCB RTILs), metathesis reactions were carried out in which the [PR₁R₂R₃R₄]Cl (except in the case of the [PC₈C₈C₈C₈], which is only available as the Br salt) was dissolved in excess CHCl₃ and added to an aqueous solution of the above salts. The solution was rapidly stirred for 24 h, and the organic layer containing the RTIL product was separated and washed several times with water. The solvent was removed under vacuum, and the resulting RTIL dried at 90–120 °C, typically for 12 h.

The dtc and dtmn RTILs were synthesized by mixing the [PR₁R₂R₃R₄]Cl and respective alkali metal salt in ethanol. The NaCl precipitate was filtered, the ethanol evaporated, and the resulting crude RTIL purified by redissolving in CHCl₃ and washing with water as above. The [C₄F₉SO₃] and CoCB RTILs were made in a similar fashion except CHCl₃ and THF were the reaction solvents, respectively.

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