

Ionic Liquids Formed with Polycyano 1,1,3,3-Tetracyanoallyl Anions: Substituent Effects of Anions on Liquid Properties

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A series of ionic liquids based on five kinds of polycyano 1,1,3,3-tetracyanoallyl anions with 2-substituents having different electron-withdrawing or -donating abilities were prepared. The influence of the chemical modification on their thermal properties, viscosity, ionic conductivity, ion association, and solvatochromic shifts was characterized and compared with the case of previously reported polycyano anions, $\text{N}(\text{CN})_2^-$ and $\text{C}(\text{CN})_3^-$. Among the 1-butyl-3-methylimidazolium (BMI) salts, cyano-substituted (i.e., 1,1,2,3,3-pentacyanoallyl anion) salt has the highest melting point (42 °C), possibly indicating the importance of high local symmetry over decreased interionic $\text{CN}\cdots\text{cation}$ interactions due to the limited electron densities on terminal nitrogens of the anions, predicted by *ab initio* calculations. In the liquid state, methoxy-substituted (i.e., 2-methoxy-1,1,3,3-tetracyanoallyl anion) salt has the highest fluidity and ionic conductivity, associated with the significant conformational degree of freedom in the methoxy group. Although the ion diffusivity has no definite correlation with the Hammett parameter of the substituents, the introduction of electron-withdrawing cyano or cyanomethyl (i.e., 2-cyanomethyl-1,1,3,3-tetracyanoallyl anion) groups leads to the decrease in the degree of ion association and solvent donor ability, which were manifested in the Walden rule deviation and solvatochromic shift, respectively.

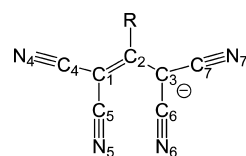
Introduction

Molecular design of ionic liquids, which are entirely composed of ions and melt below room temperature (RT) or 100 °C, appears to be one of the most grown areas in chemistry.¹ A special fascination of the ionic liquids is that the selection of component ions not only can tailor the liquid properties such as melting point, miscibility, solubility, polarity, electrochemical window, viscosity, and ionic conductivity^{1,2} but also can introduce new functionalities such as paramagnetic,³ luminescence,⁴ and redox properties.⁵ For these reasons, the ionic liquids increasingly came to be called the “designer solvents”.⁶ However, although it is known that this sort of anions exerts a drastic effect on various liquid properties,^{2,7} the main developments of the ionic liquids have tended to focus on the modification of the cationic structures while keeping the anion invariant. This is mainly caused by the inorganic nature of most anions such as BF_4^- , PF_6^- , AlCl_4^- , $\text{N}(\text{CN})_2^-$, and $\text{N}(\text{SO}_2\text{CF}_3)_2^-$. They are originally difficult chemically modify, with some exceptions such as BF_3X^- ($\text{X} = \text{C}_n\text{H}_{2n+1}$,⁸ $\text{C}_n\text{F}_{2n+1}$,⁹ or MeCH-CN^{10}), $\text{PF}_3(\text{C}_n\text{F}_{2n+1})_3^-$,¹¹ $\text{N}(\text{SO}_2\text{C}_m\text{F}_{2m+1})\text{X}^-$ ($\text{X} = \text{SO}_2\text{C}_m\text{F}_{2m+1}$ or COCF_3),^{7b,12} and $\text{C}(\text{CN})_2\text{X}^-$ ($\text{X} = \text{H}$, NO , NO_2 ,¹³ or $\text{CN}^{13,14}$) anions. It is thus obvious that combination with the chemically tunable organic anions would open up not only an ongoing exploration of new and more versatile ionic liquids but also an in-depth understanding of the relationship between the molecular structures of component ions and liquid properties. However, despite the presence of some ionic liquids formed with organic anions,^{1e,3de,7hj,15} there are no systematic studies on the influence

of the substituents of anions, especially in terms of the electron-withdrawing or -donating ability, on liquid properties.

In this work, we prepared a series of 1-ethyl-3-methylimidazolium (EMI) and 1-butyl-3-methylimidazolium (BMI) salts made by combining the 1,1,3,3-tetracyanoallyl (TCA) anion and its derivatives, replacing the 2-hydrogen with methyl (2-methyl-1,1,3,3-tetracyanoallyl; Me-TCA), methoxy (2-methoxy-1,1,3,3-tetracyanoallyl; MeO-TCA), cyano (1,1,2,3,3-pentacyanoallyl; PCA), and cyanomethyl (2-cyanomethyl-1,1,3,3-tetracyanoallyl; CM-TCA) groups (Scheme 1). Their liquid properties such as melting and decomposition temperatures, viscosity, ionic conductivity, ion association, and ion solvation (Gutmann’s acceptor (AN) and donor numbers (DN)¹⁶) were characterized. Comparable anion sizes, namely, van der Waals (vdW) radii (r_a) of 3.08 Å for TCA, 3.21 Å for Me-TCA, 3.28 Å for MeO-TCA, 3.22 Å for PCA, and 3.37 Å for CM-TCA anions (Table 1),¹⁷ with the same basic skeleton give us a good opportunity for studying the influence of the electron-withdrawing or -donating ability of the 2-substituents on liquid properties. Many anions including natural amino anions^{1e,7j} used so far are composed of a neutral moiety with attached acidic groups such as carboxylic

SCHEME 1: Molecular Structures of TCA-Type Anions



R = H: TCA
 Me: Me-TCA
 OMe: MeO-TCA
 CN: PCA
 CH₂CN: CM-TCA

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and sulfonic groups,^{3d,e,15d} which would result in the decrease of both fluidity and ionic conductivity due to the confined negative charge to the acidic group. On the other hand, the negative charge is well delocalized over the TCA-type anions (vide infra) as a consequence of the multiple cyano groups with high electron-withdrawing ability, and thus, the high fluidity and ionic conductivity are anticipated.

Ionic liquids have been considered as green solvents mainly associated with their negligible vapor pressure, and environmental and safety problems arising from the volatility of molecular solvents could be avoided by the use of such involatile liquids.¹⁸ Typical ionic liquids are composed of halogen-containing anions (e.g., BF₄⁻, PF₆⁻, AlCl₄⁻, and N(SO₂CF₃)₂⁻), and the presence of halogen may cause serious concerns when the hydrolysis stability of the anions is poor and/or when a thermal treatment of spent ionic liquids is required. Therefore, it appears that these situations empower the chemically tunable ionic liquids composed only of light elements (C, H, N, and O) as the present TCA-type salts to serve as solvents for many aspects of green chemistry.

Results and Discussion

Preparation. Silver salts of TCA-type anions were synthesized according to the literature procedures.¹⁹ The EMI or BMI salts were prepared by the metathesis of [EMI]I or [BMI]Br with a slight excess of the appropriate silver salts in distilled water at RT, filtered and washed by distilled water, and dried in vacuo at RT for 2 days. Some salts were decolorized by activated carbon treatment and/or by column chromatography on silica. Resulting salts were yellowish, reddish, or brown in color. It must be because of an absorption band centered at 330–410 nm, which could be assigned to the intramolecular transition between nonbonding HOMO ($n\pi$) and LUMO (π^*) orbitals.²⁰ We note that needle-shaped single crystals of [EMI][PCA] obtained by recrystallization are yellowish in color. For all of the salts, no impurity signal was observed in their ¹H NMR spectra, and no trace of halogen and silver was detected for energy-dispersive X-ray spectroscopy (EDS). The present salts are much less hygroscopic than EMI and BMI salts with other cyano-containing anions such as SCN⁻, N(CN)₂⁻, and C(CN)₃⁻.

Electron Density Distribution. The electron density distribution in TCA-type anions was calculated based on ab initio restricted Hartree–Fock (RHF) method with the 6-31G* basis set.¹⁷ The average electron density on N4–N7 is on the order Me-TCA (−0.523e) > MeO-TCA (−0.519e) > TCA (−0.516e) > CM-TCA (−0.508e) > PCA (−0.496e), which coincides with the reciprocal order of the electron-withdrawing ability, as quantified by the Hammett σ value,^{21,22} of the 2-substituents of the anions. It is possible that the limited electron density on N4–N7 for the PCA and CM-TCA anions could have a favorable effect on the decrease of interionic interactions, especially between 2-hydrogen of imidazolium cations and cyano groups of anions.

Thermal Behavior. Table 2 summarizes glass transition (T_g), crystallization (T_c), solid–solid transition (T_{s-s}), and melting (T_m) temperatures determined by the analysis of differential scanning calorimetry (DSC) traces, as well as decomposition temperatures (T_d) determined by thermogravimetric analysis (TGA). Among the EMI salts, only [EMI][MeO-TCA] and [EMI][CM-TCA] are in liquid form at RT, which derives from a significant orientational freedom in methoxy and cyanomethyl groups. The highest T_m of [EMI][PCA] (115 °C), although lower than those of PCA salts formed with several heterocyclic cations

TABLE 1: Some Parameters of TCA-Type Salts in This Text^a

cation	anion	Hammett σ^b	$r_c/\text{Å}^c$	$r_a/\text{Å}^c$	$r/\text{Å}^c$	$d/\text{g cm}^{-3}$	$C/\text{mol cm}^{-3}$
EMI	TCA	0	3.04	3.08	1.53	1.20 ^d	4.76×10^{-3} ^d
	Me-TCA	−0.12	3.04	3.21	1.56	1.16 ^d	4.36×10^{-3} ^d
	MeO-TCA	−0.07	3.04	3.28	1.58	1.14	4.04×10^{-3}
	PCA	0.61	3.04	3.22	1.56	1.20 ^d	4.34×10^{-3} ^d
	CM-TCA	0.17	3.04	3.37	1.60	1.14	3.91×10^{-3}
	N(CN) ₂		3.04	2.37	1.33	1.08 ^e	6.09×10^{-3} ^e
BMI	C(CN) ₃		3.04	2.65	1.42	1.11 ^e	5.52×10^{-3} ^e
	TCA	0	3.31	3.08	1.60	1.09	3.89×10^{-3}
	Me-TCA	−0.12	3.31	3.21	1.63	1.09	3.70×10^{-3}
	MeO-TCA	−0.07	3.31	3.28	1.65	1.10	3.54×10^{-3}
	PCA	0.61	3.31	3.22	1.63	1.18 ^d	3.86×10^{-3} ^e
	CM-TCA	0.17	3.31	3.37	1.67	1.10	3.44×10^{-3}
	N(CN) ₂		3.31	2.37	1.38	1.06 ^f	5.16×10^{-3} ^f
	C(CN) ₃		3.31	2.65	1.47	1.06	4.62×10^{-3}

^a r_c : cation radius; r_a : anion radius; $r = (r_c^{-1} + r_a^{-1})^{-1}$; d : density at 20 °C; C : molar concentration at 20 °C. ^b Average value of σ_m and σ_p of the substituent group at the 2-position of TCA-type anions. ^c Calculated using Hyperchem software 8.0.4 based on the geometries optimized at the RHF/6-31G* level.¹⁷ ^d In the solid state. ^e Reference 14. ^f Reference 27.

TABLE 2: Thermal Properties of TCA-Type Salts

cation	anion	$T_g/^\circ\text{C}^a$	$T_c/^\circ\text{C}^a$	$T_{s-s}/^\circ\text{C}^a$	$T_m/^\circ\text{C}^a$	$T_d/^\circ\text{C}^b$
EMI	TCA				42	341
	Me-TCA	−59	−20		42	254
	MeO-TCA	−65				254
	PCA			52	115	327
	CM-TCA	−53	−1		25	280
	N(CN) ₂ ^c	−90	−54		−12	240
BMI	C(CN) ₃ ^c	−95	−60	−31	−11	240
	TCA	−62	−7		20	295
	Me-TCA	−65				261
	MeO-TCA	−65				265
	PCA			35	42	302
	CM-TCA	−54				286
	N(CN) ₂ ^d	−94	−35		−10	220
	C(CN) ₃	−84				260

^a Onset temperatures of a heat capacity change (T_g), an exothermic peak (T_c), and an endothermic peak (T_{s-s} , T_m) determined by DSC upon the heating process. ^b Temperatures of 10% weight loss determined by TGA upon the heating process. ^c Reference 14. ^d Reference 27.

(>124.8 °C) reported by Shreeve et al.,²³ would arise from the increased number of cyano groups and high local symmetry of the PCA anions. The former effect reminds us of the higher melting point of the EMI salt formed by the PF₆ anion with six fluorides (58–62 °C^{7b,c,24}) than that formed by BF₄ anion with four fluorides (11–15 °C^{7b,c,9a,24b,25}).

By contrast, all of the BMI salts, with the exception of [BMI][PCA] having a T_m of 42 °C, are in the liquid form at RT. The low-temperature phase of the four BMI-based RT ionic liquids is in the glass state, and there is little anion effect on the T_g value. All of the salts prepared in this study decompose at fairly high temperatures (261–302 °C) and thus show a wide liquid range of more than 260 °C. The excellent thermal stability of [BMI][PCA] ($T_d = 302$ °C) would promote the works toward practical use in energetic liquids.^{23,26} We note that the heats of formation (ΔH_f) of the PCA (456.4 kJ mol^{−1}) and CM-TCA (429.6 kJ mol^{−1}) anions calculated by the AM1 method are much higher than those of the other three anions (179.3–316.6 kJ mol^{−1}), mainly due to a large number of cyano groups.

Viscosity. The viscosity (η) and ionic conductivity (σ) of all of the salts except for [EMI][PCA] were measured upon heating

TABLE 3: Physical Properties of TCA-Type Salts^a

cation	anion	$\eta(25\text{ }^\circ\text{C})/\text{cP}$	$\eta(50\text{ }^\circ\text{C})/\text{cP}$	$E_a(\eta)^b/\text{kcal mol}^{-1}$	$\sigma(25\text{ }^\circ\text{C})/\text{S cm}^{-1}$	$\sigma(50\text{ }^\circ\text{C})/\text{S cm}^{-1}$	$E_a(\sigma)^b/\text{kcal mol}^{-1}$
EMI	TCA		29	6.9		7.3×10^{-3}	6.1
	Me-TCA	127 ^c	34	7.6	2.0×10^{-3c}	6.3×10^{-3}	6.8
	MeO-TCA	105	27	7.4	2.4×10^{-3}	7.5×10^{-3}	6.8
	PCA						
	CM-TCA	480	95	10.9	8.2×10^{-4}	3.4×10^{-3}	8.0
	$\text{N}(\text{CN})_2^{d,e}$	16	8.2	4.8	2.8×10^{-2}	4.7×10^{-2}	3.3
	$\text{C}(\text{CN})_3^{d,e}$	18	8.6	4.6	2.2×10^{-2}	3.7×10^{-2}	4.1
BMI	TCA	194	44	8.9	1.4×10^{-3}	4.6×10^{-3}	7.1
	Me-TCA	239	52	9.4	1.0×10^{-3}	3.5×10^{-3}	7.7
	MeO-TCA	149	40	7.9	1.1×10^{-3}	4.0×10^{-3}	7.9
	PCA		65	9.6		3.9×10^{-3}	7.8
	CM-TCA	450	95	11.0	6.4×10^{-4}	2.6×10^{-3}	8.4
	$\text{N}(\text{CN})_2^e$	29	12	6.0	1.1×10^{-2}	2.0×10^{-2}	3.7
	$\text{C}(\text{CN})_3$	33	13	5.8	9.6×10^{-3}	1.9×10^{-2}	4.5

^a η : viscosity; σ : ionic conductivity; $E_a(\eta)$: activation energy for viscous flow; $E_a(\sigma)$: activation energy for ionic conduction. ^b Estimated in the temperature range of 50–70 °C. ^c In the supercooled liquid state. ^d Reference 14. ^e Reference 27.

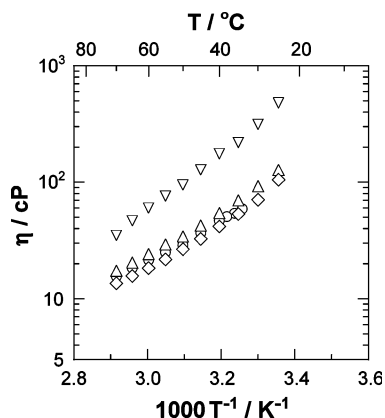


Figure 1. Temperature dependence of viscosity for EMI salts with TCA (○), Me-TCA (△), MeO-TCA (◇), and CM-TCA (▽) anions.

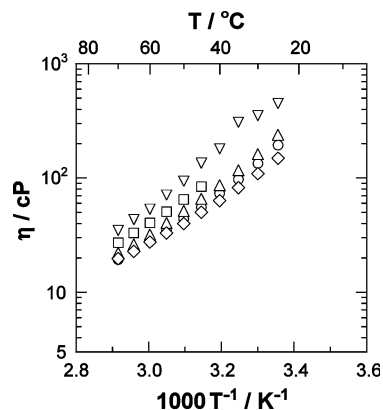


Figure 2. Temperature dependence of viscosity for BMI salts with TCA (○), Me-TCA (△), MeO-TCA (◇), PCA (□), and CM-TCA (▽) anions.

for six RT ionic liquids and upon cooling for the three crystalline salts. Figures 1 and 2 depict the temperature dependence of the viscosity of EMI and BMI salts, respectively, in their liquid region. At RT, all of the salts are much more viscous than the BMI salts formed with other polycyano anions, [BMI][N(CN)₂] (29 cP²⁷) and [BMI][C(CN)₃] (33 cP), mainly due to the larger ion size of the TCA-type anions (see Table 3). The EMI salts are less viscous than the corresponding BMI salts, and all of the viscosity data follow the Arrhenius equation $\eta = \eta_0 \exp(-E_a(\eta)/k_B T)$, where η_0 is a constant and $E_a(\eta)$ is the activation energy for viscous flow. The $E_a(\eta)$ values of the EMI salts (7.6–11.3 kcal mol⁻¹) are apparently low in comparison with

those of the corresponding BMI salts (9.5–12.2 kcal mol⁻¹), as seen previously in several ionic liquids with anions such as F(HF)_{2,3}⁻,²⁸ N(CN)₂⁻,²⁷ FeCl₄⁻,^{3c} and N(SO₂CF₃)₂⁻.²⁹ The viscosity at 50 °C follows the order of CM-TCA > PCA > Me-TCA > TCA > MeO-TCA for the BMI salts, which is consistent with that of the EMI salts (CM-TCA > Me-TCA > TCA > MeO-TCA). According to the Stokes–Einstein equation (eq 1), the self-diffusivity (D) of component ions with average ion radius r is correlated to the viscosity

$$D = RT/c\pi N_A \eta r \quad (1)$$

where c is a constant ($4 \leq c \leq 6$), R is the universal gas constant, and N_A is the Avogadro's number. The average ion radius r is given by $(r_c^{-1} + r_a^{-1})^{-1}$ (r_c : cation radius; r_a : anion radius) in an ionic liquid since the D value is the simple summation of cationic and anionic diffusivities. Provided the r_c and r_a values tabulated in Table 1¹⁷ and assuming the c value of 6, the ion diffusivity at 50 °C follows the order MeO-TCA (5.6×10^{-7} cm² s⁻¹) > TCA (5.3×10^{-7} cm² s⁻¹) > Me-TCA (4.5×10^{-7} cm² s⁻¹) > CM-TCA (1.6×10^{-7} cm² s⁻¹) for the EMI salts and MeO-TCA (3.6×10^{-7} cm² s⁻¹) > TCA (3.4×10^{-7} cm² s⁻¹) > Me-TCA (2.8×10^{-7} cm² s⁻¹) > PCA (2.2×10^{-7} cm² s⁻¹) > CM-TCA (1.5×10^{-7} cm² s⁻¹) for the BMI salts. It appears that the large D values of the MeO-TCA salts are related to the absence of crystallization event for [EMI][MeO-TCA].

Ionic Conductivity. A comparison of the temperature dependence of the ionic conductivity of the EMI and BMI salts is made in Figures 3 and 4, respectively. All of the salts have much lower σ values than those of [BMI][N(CN)₂] (1.1×10^{-2} S cm⁻¹²⁷) and [BMI][C(CN)₃] (9.6×10^{-3} S cm⁻¹), associated with their higher viscosities. The σ values of [EMI][TCA] and [BMI][PCA] steadily decrease down to around 40 and 30 °C, below which they show an abrupt drop by 2 orders of magnitude, presumably due to crystallization effects. The absence of such a conductivity drop for [EMI][Me-TCA], which is also in the crystalline form at RT, must be related to no freezing event during cooling in the measured temperature range. Ionic conductivities for the EMI salts at 50 °C lie in the range of 3.4 – 7.5×10^{-3} S cm⁻¹ and are higher than those for the corresponding BMI salts (2.6 – 4.6×10^{-3} S cm⁻¹). In the liquid region, all of the data can be fit well to the Arrhenius equation $\sigma = \sigma_0 \exp(-E_a(\sigma)/k_B T)$, where σ_0 is a constant and $E_a(\sigma)$ is the activation energy for ionic conduction. For six RT ionic liquids, each $E_a(\sigma)$ value is lower than the corresponding $E_a(\eta)$ value, as is the case in most ionic liquids.^{3c,7b,g,8,27–29}

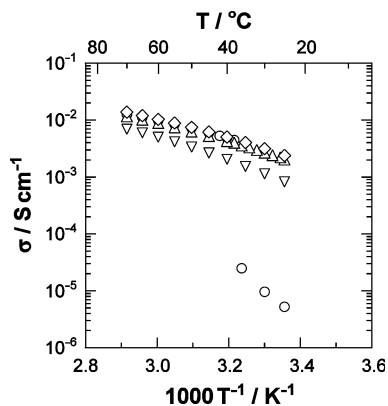


Figure 3. Temperature dependence of ionic conductivity for EMI salts with TCA (○), Me-TCA (△), MeO-TCA (◇), and CM-TCA (▽) anions.

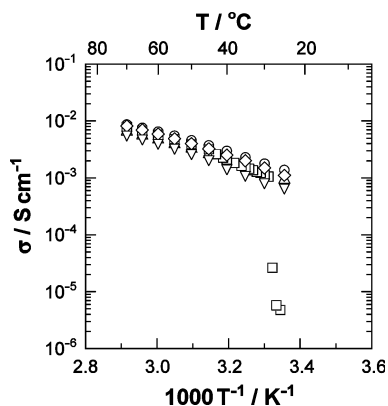


Figure 4. Temperature dependence of ionic conductivity for BMI salts with TCA (○), Me-TCA (△), MeO-TCA (◇), PCA (□), and CM-TCA (▽) anions.

Keeping the cation invariant (BMI), the order of both σ and molar conductivity ($\Lambda = \sigma/C$) (TCA > MeO-TCA > PCA > Me-TCA > CM-TCA) has no simple correlation with that of the Hammett σ value of the 2-substituents and does not coincide with that of ion diffusivity evaluated on the basis of the viscosity data (MeO-TCA > TCA > Me-TCA > PCA > CM-TCA), even though the molar conductivity is proportional to the ion diffusivity based on the Nernst–Einstein equation (eq 2)

$$D = RT\Lambda/z^2F^2 \quad (2)$$

where z is the charge of ions and F is the Faraday constant. It thus seems that this discrepancy arises from the difference in the degree of association of oppositely charged ions, which could result in the significant decrease in ionic conductivity for a given viscosity.

Ion Association. It has been found that the empirical Walden rule, namely, that molar conductivity is inversely proportional to the viscosity of the medium,³⁰ based on a wide range of aqueous solution systems can apply to the ionic liquid system.^{3c,7g,h,9a,c,27,28} According to the rule, the discrepancy from the Walden product $\Lambda\eta$ of KCl aqueous solution ($100 \text{ S cm}^2 \text{ cP mol}^{-1}$), in which the ions are completely dissociated, is strongly indicative of the significant degree of ion association,^{7g,h} which leads to the diminished ionic conductivity at a given viscosity. Here, we compare the Walden products for the five BMI salts at 50°C . Strictly, the molar conductivity used for this purpose must be evaluated at 50°C , whereas the density data are only available near RT for technical reason. However,

TABLE 4: Walden Products and Solvatochromic Parameters of TCA-Type BMI Salts^a

anion	$\Lambda'\eta/\text{S cm}^2 \text{ cP mol}^{-1}$	$E_T(30)/\text{kcal mol}^{-1}$	E_T^N	$\lambda_{\text{Cu}}/\text{nm}^b$	DN^b
TCA	52	50.3 ^b	0.601 ^b	589	29.3
Me-TCA	49	50.3 ^b	0.601 ^b	589	29.3
MeO-TCA	45	50.5 ^b	0.606 ^b	578	26.2
PCA	66	49.5 ^b	0.574 ^b	551	17.7
CM-TCA	72			540	14.4
N(CN) ₂	46	51.4 ^c	0.639 ^c	637	41.8
C(CN) ₃	56	51.1 ^c	0.630 ^c	603	33.2

^a For Λ' , $E_T(30)$, E_T^N , λ_{Cu} , and DN, see the text. ^b Data at $\sim 50^\circ\text{C}$. ^c Data at RT.

the effect of temperature on the volume between RT and 50°C is very small ($<3\%$ in most cases³¹), and thereby, we evaluated the molar conductivity using the density at RT and will denote the effective molar conductivity as Λ' in the following. For the same BMI cation, the $\Lambda'\eta$ values ($45\text{--}72 \text{ S cm}^2 \text{ cP mol}^{-1}$; see Table 4) are apparently less than the $\Lambda\eta$ of KCl aqueous solution, strongly indicating a significant fraction of ion association in the liquids. Although the $\Lambda'\eta$ value was originally anticipated to vary as the inverse first power of r according to eqs 1 and 2, the difference in r , being 1.60 \AA for [BMI][TCA], 1.63 \AA for [BMI][Me-TCA], 1.65 \AA for [BMI][MeO-TCA], 1.63 \AA for [BMI][PCA], and 1.67 \AA for [BMI][CM-TCA],¹⁷ is not large enough to account for the loss of more than 35% of $\Lambda'\eta$ in going from [BMI][CM-TCA] ($72 \text{ S cm}^2 \text{ cP mol}^{-1}$) to [BMI][MeO-TCA] ($45 \text{ S cm}^2 \text{ cP mol}^{-1}$). The high $\Lambda'\eta$ values, which indicate the low degree of ion association, for the PCA and CM-TCA salts are presumably associated with the weak interionic CN \cdots cation interactions due to the limited electron densities on N4–N7 for such anions, as mentioned above. The smallest $\Lambda'\eta$ value for [BMI][MeO-TCA] indicates that the effect of the conformational degree of freedom in the methoxy group is not large enough to intercept the formation of ion association.

Solvatochromism. So far, a wide range of solvatochromic probes have been used to assess the solvent polarity scales by comparison to well-established empirical solvent scales based on molecular liquids.^{2e,7a,32} Among them, the $E_T(30)$ value of Dimroth and Reichardt^{32f,33} is a good general scale of the AN (Lewis acidity or electrophilicity) of a liquid³⁴ and is defined as $E_T(30)$ (in kcal mol^{-1}) = $28592/\lambda_{\text{Reichardt}}$ (in nm), where $\lambda_{\text{Reichardt}}$ is the wavelength maximum of the lowest-energy absorption band of a Reichardt's betaine dye, 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate. Table 4 also presents the $E_T(30)$ values of the four BMI salts measured at $\sim 50^\circ\text{C}$, together with dimensionless normalized scales of $E_T(30)$, E_T^N , by making use of water ($E_T^N = 1.00$) and TMS ($E_T^N = 0.00$) as reference solvents. Contrary to molecular solvents such as 2-cyanoethanol ($E_T^N = 0.892$) and ethanol ($E_T^N = 0.654$),³³ there is little substituent effect of replacing the 2-hydrogen (TCA, $E_T^N = 0.601$) with a cyano group (PCA, $E_T^N = 0.574$) while keeping the cation invariant because the acceptor ability of ionic liquids depends mainly on the cation species.^{2e,32f} Since the E_T^N value should relate not only to cation \cdots dye interactions but also to the ion association propensity, the comparable E_T^N values for the present BMI salts indicate that the difference in the degree of ion association is too little to influence the solvatochromic properties.

An alternative probe molecule is required to verify the anion effect on ion solvation. It is well-known that a four-coordinated copper complex [Cu(acac)(tmen)][BPh₄] (acac: acetylacacetate;

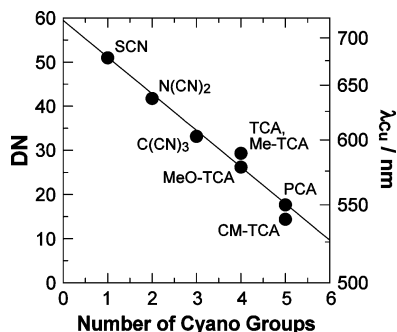


Figure 5. Plot of Gutmann's donor number (DN) against the number of cyano groups in anions for BMI salts. The solid line through the points is a guide to the eye.

tmen: *N,N,N',N'*-tetramethylethylenediamine) is diagnostic for the DN (Lewis basicity or nucleophilicity) of a liquid, and the wavelength maximum (λ_{Cu}) of the lowest d-d transition band depends on the splitting of d-orbitals of Cu^{2+} ions due to the solvent coordination at the axial sites on the metal center.³⁵ Using an empirical relationship, $10^4[\lambda_{Cu} \text{ (in nm)}]^{-1} = 20 - 0.103 \text{ DN}$, based on a wide range of molecular solvents,^{35b,c} the DN values of the [BMI][PCA] (17.7) and [BMI][CM-TCA] (14.4) are significantly lower in comparison with those of the other three BMI salts (26.2–29.3), as seen in Table 4. The lower donor ability of the PCA and CM-TCA salts could be a consequence of the lower electron density on N4–N7, as discussed in the previous section. This trend seems to be the same as the lower DN value for [BMI][PF₆] (6.4–8.9) than that of [BMI][BF₄] (14.4–22.3),^{32b,36} in which the limited electron density on each fluoride in the PF₆ anion gives rise to the depressed anionic donor ability. Figure 5 illustrates the DN value as a function of the number of cyano groups in anions for the BMI salts, including [BMI][SCN] (51.0), [BMI][N(CN)₂] (41.8), and [BMI][C(CN)₃] (33.2) salts. The linear variation clearly indicates that the donor ability of the ionic liquids is under the control of the number of cyano groups in anions, irrespective of the basic skeleton. We note that the DN values for the ionic liquids with cyano-containing anions plotted in Figure 5 lie in the wide range between 14.4 (CM-TCA salt) and 51.0 (SCN salt), which includes many conventional molecular solvents such as dioxane (14.8), acetone (17.0), diethylether (19.2), tetrahydrofuran (20.0), *N,N*-dimethylformamide (26.6), dimethyl sulfoxide (29.8), water (~33), and hydrazine (44).¹⁶ It thus appears that, by selecting the cyano-containing anions keeping the cation invariant, one can easily control the donor ability (Lewis basicity or nucleophilicity) of ionic liquids over such a wide range.

Concluding Remarks

In this study, our research interest is centered on the effects of the chemical modification of TCA-type organic anions on liquid properties of the resulting salts. [BMI][PCA] is the first PCA salt with T_m less than 100 °C and exhibits excellent thermal stability, which makes it an attractive material for energetic salts. Among the present BMI salts, [BMI][MeO-TCA] has the highest fluidity and ion conductivity, associated with the significant conformational degree of freedom in the methoxy group. Although ion diffusivity has no simple correlation with the Hammett σ value of the 2-substituents of the TCA-type anions, the introduction of electron-withdrawing groups exerts a drastic effect on the ion association propensity and solvent donor ability. One can therefore envisage the opening of many opportunities

for designing an ionic liquid with desired properties by chemically modifying the anion species.

Experimental Section

Synthesis. Solvents (acetonitrile, ethyl acetate, acetone, and water) were distilled prior to use. Crystalline [EMI]I and [BMI]Br were prepared by Menschkin reaction of distilled *N*-methylimidazole with corresponding distilled alkyl halides and purified by reprecipitation from acetonitrile/ethyl acetate. Silver salts of TCA-type anions were prepared by the metathesis of corresponding precursor salts, K[TCA],^{19a} [Py][Me-TCA] (Py: pyridinium),^{19b} [TBA][MeO-TCA] (TBA: tetrabutylammonium),^{19c} [Py][PCA],^{19d} and Na[CM-TCA]^{19e} with AgNO₃ in the dark in either water or water/acetone. 2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (Reichardt's betaine dye) was obtained from Fluka (99.0%) and used without purification. [Cu(acac)(tmen)][BPh₄] was synthesized and recrystallized according to the literature.^{35a,37}

[EMI][TCA]. A slight excess of Ag[TCA] (6.32 g, 25.4 mmol) and [EMI]I (5.74 g, 24.1 mmol) was dissolved in distilled water (30 cm³). The resulting suspension was stirred for 3 days in the dark at RT and filtered to remove any trace of AgI and unreacted Ag[TCA]. Evaporation of the filtrate under vacuum followed by activated carbon treatment gives a yellowish crystalline solid (4.76 g, 18.9 mmol, 78% yield). IR (KBr) ν_{CN} : 2194 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ : 1.59 (t, 3H, $J = 7.2$ Hz, CH₂CH₃), 4.00 (s, 3H, CH₃), 4.31 (q, 2H, $J = 7.2$ Hz, CH₂CH₃), 6.93 (s, 1H, CH), 7.27 (s, 1H, CH), 7.28 (s, 1H, CH), 8.91 (s, 1H, NCHN) ppm. Anal. Calcd for C₁₃H₁₂N₆: C, 61.89; H, 4.79; N, 33.31; I, 0.00%. Found: C, 61.73; H, 4.86; N, 33.54; I, 0.00%.

[BMI][TCA]. A yellowish liquid was prepared by the procedure described above for [EMI][TCA], except that [BMI]Br was used instead of [EMI]I. Yield: 78%. IR (KBr) ν_{CN} : 2196 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ : 1.00 (t, $J = 7.2$ Hz, 3H, CH₂CH₂CH₂CH₃), 1.40 (m, 2H, CH₂CH₂CH₂CH₃), 1.89 (m, 2H, CH₂CH₂CH₂CH₃), 3.98 (s, 3H, CH₃), 4.21 (t, 2H, $J = 8.0$ Hz, CH₂CH₂CH₂CH₃), 6.89 (s, 1H, CH), 7.34 (s, 2H, CH), 8.77 (s, 1H, NCHN) ppm. Anal. Calcd for C₁₅H₁₆N₆: C, 64.27; H, 5.75; N, 29.98; Br, 0.00%. Found: C, 64.25; H, 5.94; N, 29.96; Br, 0.00%.

[EMI][Me-TCA]. A pale pink crystalline solid was prepared by the procedure described above for [EMI][TCA], except that Ag[Me-TCA] was used instead of Ag[TCA]. Yield: 77%. IR (KBr) ν_{CN} : 2189 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ : 1.60 (t, 3H, $J = 7.2$ Hz, CH₂CH₃), 2.19 (s, 3H, CH₃), 3.99 (s, 3H, CH₃), 4.30 (q, 2H, $J = 7.6$ Hz, CH₂CH₃), 7.30 (s, 1H, CH), 7.32 (s, 1H, CH), 8.99 (s, 1H, NCHN) ppm. Anal. Calcd for C₁₄H₁₄N₆: C, 63.04; H, 5.30; N, 31.39; I, 0.00%. Found: C, 63.14; H, 5.11; N, 31.56; I, 0.00%.

[BMI][Me-TCA]. An orange liquid was prepared by the procedure described above for [BMI][TCA], except that Ag[Me-TCA] was used instead of Ag[TCA]. Yield: 88%. IR (KBr) ν_{CN} : 2196 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ : 0.99 (t, $J = 7.6$ Hz, 3H, CH₂CH₂CH₂CH₃), 1.40 (m, 2H, CH₂CH₂CH₂CH₃), 1.89 (m, 2H, CH₂CH₂CH₂CH₃), 2.18 (s, 3H, CH₃), 3.99 (s, 3H, CH₃), 4.22 (t, 2H, $J = 8.0$ Hz, CH₂CH₂CH₂CH₃), 7.30 (s, 1H, CH), 7.32 (s, 1H, CH), 8.88 (s, 1H, NCHN) ppm. Anal. Calcd for C₁₆H₁₈N₆: C, 65.29; H, 6.16; N, 28.55; Br, 0.00%. Found: C, 65.01; H, 6.06; N, 28.49; Br, 0.00%.

[EMI][MeO-TCA]. A reddish liquid was prepared by the procedure described above for [EMI][TCA], except that Ag[MeO-TCA] was used instead of Ag[TCA]. Yield: 86%. IR (KBr) ν_{CN} : 2197 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ : 1.60 (t,

3H, $J = 7.2$ Hz, CH_2CH_3), 4.00 (s, 3H, CH_3), 4.05 (s, 3H, CH_3), 4.30 (q, 2H, $J = 7.2$ Hz, CH_2CH_3), 7.32 (s, 1H, CH), 7.35 (s, 1H, CH), 8.92 (s, 1H, NCHN) ppm. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{N}_6\text{O}_1$: C, 59.56; H, 5.00; N, 29.77; I, 0.00%. Found: C, 58.99; H, 5.25; N, 29.49; I, 0.00%.

[BMI][MeO-TCA]. A reddish liquid was prepared by the procedure described above for [BMI][TCA], except that Ag[MeO-TCA] was used instead of Ag[TCA]. Yield: 75%. IR (KBr) ν_{CN} : 2189 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ : 1.00 (t, $J = 7.2$ Hz, 3H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.41 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.89 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.01 (s, 3H, CH_3), 4.07 (s, 3H, CH_3), 4.24 (t, 2H, $J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 7.26 (s, 2H, CH), 9.04 (s, 1H, NCHN) ppm. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{N}_6\text{O}_1$: C, 61.92; H, 5.85; N, 27.08; Br, 0.00%. Found: C, 61.65; H, 6.02; N, 27.01; Br, 0.00%.

[EMI][PCA]. A yellowish crystalline solid was prepared by the procedure described above for [EMI][TCA], except that Ag[PCA] was used instead of Ag[TCA]. Yield: 41%. IR (KBr) ν_{CN} : 2200 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ : 1.60 (t, 3H, $J = 7.2$ Hz, CH_2CH_3), 4.00 (s, 3H, CH_3), 4.30 (q, 2H, $J = 7.2$ Hz, CH_2CH_3), 7.23 (s, 1H, CH), 7.28 (s, 1H, CH), 8.72 (s, 1H, NCHN) ppm. Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{N}_7$: C, 60.64; H, 4.00; N, 35.36; I, 0.00%. Found: C, 60.89; H, 4.24; N, 35.51; I, 0.00%.

[BMI][PCA]. A yellowish crystalline solid was prepared by the procedure described above for [BMI][TCA], except that Ag[PCA] was used instead of Ag[TCA]. Yield: 84%. IR (KBr) ν_{CN} : 2201 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ : 1.00 (t, $J = 7.6$ Hz, 3H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.40 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.88 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.97 (s, 3H, CH_3), 4.20 (t, 2H, $J = 7.6$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 7.26 (s, 1H, CH), 7.29 (s, 1H, CH), 8.62 (s, 1H, NCHN) ppm. Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{N}_7$: C, 62.94; H, 4.95; N, 32.11; Br, 0.00%. Found: C, 63.01; H, 4.91; N, 32.35; Br, 0.00%.

[EMI][CM-TCA]. A pale brown liquid was prepared by the procedure described above for [EMI][TCA], except that Ag[CM-TCA] was used instead of Ag[TCA], and the purification by column chromatography on silica (eluent solvent: ethyl acetate) was performed after activated carbon treatment. Yield: 62%. IR (KBr) ν_{CN} : 2193 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ : 1.62 (t, 3H, $J = 7.2$ Hz, CH_2CH_3), 3.50 (s, 2H, CH_2CN), 4.01 (s, 3H, CH_3), 4.31 (q, 2H, $J = 7.6$ Hz, CH_2CH_3), 7.29 (s, 1H, CH), 7.31 (s, 1H, CH), 8.81 (s, 1H, NCHN) ppm. Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_7$: C, 61.85; H, 4.50; N, 33.66; I, 0.00%. Found: C, 61.55; H, 4.27; N, 33.50; I, 0.00%.

[BMI][CM-TCA]. A brown liquid was prepared by the procedure described above for [BMI][TCA], except that Ag[CM-TCA] was used instead of Ag[TCA], and the purification by column chromatography on silica (eluent solvent: acetonitrile/ethyl acetate (1:1)) was performed after activated carbon treatment. Yield: 22%. IR (KBr) ν_{CN} : 2193 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) δ : 1.02 (t, $J = 7.2$ Hz, 3H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.42 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.90 (m, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.52 (s, 2H, CH_2CN), 4.02 (s, 3H, CH_3), 4.24 (t, 2H, $J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 7.36 (s, 2H, CH), 8.84 (s, 1H, NCHN) ppm. Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_7$: C, 63.93; H, 5.37; N, 30.70; Br, 0.00%. Found: C, 63.49; H, 5.39; N, 30.08; Br, 0.00%.

Measurements. ^1H NMR measurements were conducted on a JEOL JNM-FX400 spectrometer operating at 400 MHz, and CDCl_3 was used as the solvent. FT-IR spectra were taken in dispersed KBr pellets on a Perkin-Elmer 1000 Series spectrophotometer (400–4000 cm^{-1}). DSC thermograms were measured on a Shimadzu DSC-60 instrument equipped with nitrogen cryostatic cooling. The samples were sealed in aluminum pans under open air, and the temperature was calibrated by water

and indium. The glass transition (T_g), crystallization (T_c), solid–solid transition (T_{s-s}), and melting (T_m) temperatures were determined from the DSC traces during the heating scans (10 $^\circ\text{C min}^{-1}$). Thermogravimetric measurements were conducted on a Shimadzu DTG-60 M at a heating rate of 5 $^\circ\text{C min}^{-1}$ under nitrogen atmosphere with open aluminum pans. Density values of RT ionic liquids were obtained by measuring the weight of the sample in a 1 cm^3 pycnometer, whereas those of crystalline salts were obtained using a floatation method in a mixed solution of tetrachloromethane and cyclohexane. Viscosities were measured using a cone-type Tokyo Keiki RE-80 L rotational viscometer. Conductance measurements were performed in a two platinum electrode conductivity cell (cell constant of 38.3 cm^{-1}). The conductance of the samples was determined from the first real axis touchdown point in the Cole–Cole plot of the impedance data using an Agilent Technologies impedance analyzer 4294A over a frequency range of 40 Hz to 110 MHz. UV–vis absorption spectra of Reichardt's betaine dye and $[\text{Cu}(\text{acac})(\text{tmen})]\text{BPh}_4$ dissolved in ionic liquids were taken in a quartz cell with a light path length of 1 mm on a Shimadzu UV-3100 spectrophotometer (240–800 nm). The concentration was on the order of 10^{-3} M. The λ_{Cu} value of [BMI][PCA] (552 nm) was determined by fitting to the Gaussian function because the solvatochromic band appears as a shoulder of the dominant band of PCA anions centered at 413 nm. Elemental analyses (C, H, N, and halogen) were carried out by the Center for Organic Elemental Microanalysis of Kyoto University. Geometry optimizations of TCA-type anions were performed either by RHF/6-31G* calculations using HyperChem 8.0.4 or by AM1 calculations using MOPAC 97. Their vdW volumes, electron density distributions, and ΔH_f were calculated based on the optimized geometry.

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