Chemistry–A European Journal
Full Paper
doi.org/10.1002/chem.202101925
Chemistry Europe
European Chemical Societies Publishing

Ionic Liquids $[M^{3+}][A^{-}]_3$ with Three-Valent Cations and Their Possible Use to Easily Separate Rare Earth Metals

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Abstract: We introduce a simple way to liquify rare earth metals (REM) by incorporating the corresponding cations, in particular Eu^{3+}, La^{3+}, and Y^{3+}, into polyvalent ionic liquids (ILs). In contrast to conventional methods, this is achieved not by transforming them into anionic complexes, but by keeping them as bare cations and combining them with convenient, cheap and commercially available anions (A) in the form $[REM^{3+}][A^{-}]_3$. To do so, we follow the COncept of Melting Point Lowering due to EThoxylation (COMPLET) with alkyl polyethylene oxide carboxylates as anions. We provide basic properties, such as glass transition temperatures, viscosities, electrical conductivities, as well as water-octanol partition constants *P* and show that these ILs have remarkably different properties, despite the similarity of their cations. In addition, we show that the ionic liquids possess interesting luminescent properties as non-conventional fluorophores.

Introduction

In the past decades, ionic liquids (ILs) have become a popular field of research. Their versatile physical and chemical properties, as well as their high customisability make them interesting for task-specific solvents in a wide variety of applications[1,2] (see also these special issues on the topic of 'ionic liquids'[3,4]). Ionic liquids are defined as salts with a melting point below 100 °C, with their most notable properties including high thermal and electrochemical stability, low flammability and negligible vapour pressure.[5,6] Most popular today are ILs with imidazolium, pyrrolidinium, pyridinium or phosphonium derivatives as cations.[7,8] However, not only are they toxic and poorly biodegradable, but also their synthesis and the subsequent purification is laborious and costly. Another notable characteristic of all these cations is their single positive charge, which is usually compensated by a monovalent anion. The nature of this anion can range from inorganic ions like PF^{-}_6 or BF^{-}_4 or simple halides to organic anions.[1,2,5]

In contrast to these common ILs, a new class of ILs based on oligoether carboxylates has been introduced by Kunz and coworkers: 2,5,8,11-Tetraoxatridecan-13-oic acid (TOTO) has been the archetypical compound that allowed the synthesis of a plethora of ionic liquids with highly tuneable properties.[9–12] Most conventional ionic liquids achieve their low melting point by low molecular symmetry, perturbing crystallisation due to unfavourable geometric parameters, and delocalised charges, weakening interionic interactions.[5,13] Alkyl PolyEthylene oxide Carboxylate Ionic Liquids (APECILs) rely on a different concept: the chain of ethylene oxide (EO) groups is highly flexible, and entropically favours the liquid phase. This effect has been termed the COncept of Melting Point Lowering due to EThoxylation (COMPLET).[9] ILs based on this concept can avoid the toxic cationic 'builder' ions in favour of readily biodegradable anionic 'builders' with low toxicity.[9,10,14] It should be noted that APECILs are very simple to synthesise and can be produced at low cost, because the anions are surfactants that are commercially available on a scale of thousands of tons. Due to their anionic nature, oligoether carboxylates allow for the combination with various cations. Previous experiments ranging from simple alkali metals to alkylammonium compounds yielded a multitude of ILs, their physical and chemical properties strongly depending on the choice of counterion.[9–11]

As mentioned above, ILs typically contain only monovalent ions. Ions of higher charge, for example rare earth metals, are usually incorporated into complexes with a single negative excess charge, which is in turn compensated by the common IL 'builder' cation, or by complexation by a functionalised ionic liquid following one of the common 'recipes'.[15–17]

The present study demonstrates that astonishingly, oligoether carboxylates, specifically 3,6,9,12,15,18-Hexaoxahexacosan-1-oic acid ([C8E5c]), conveniently form room temperature ionic liquids (RTILs) *even with 'naked' multivalent rare earth metal (REM) ions*. Both complex networks as well as crown-ether-like complexes have been found with alkali metal based APECILs (see Figure 1), resulting in vastly different glass transition temperatures.[10,12] It is evident that both the length of the EO chain and size of the metal ion play an important role on the strength of interaction, and the resulting geometry.

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202101925

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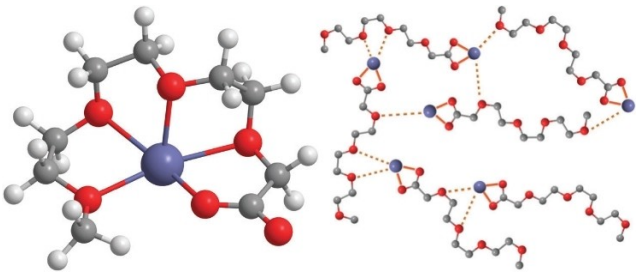

Figure 1. Crown ether-like structure of [Na][TOTO] obtained by ab initio quantum mechanical calculations (left, for computational details, see[12]) and sketch of a postulated cross-linked structure of the same IL (right). Reproduced from Ref. [12] with permission from the PCCP Owner Societies.

The subtle balance between the interactions of the metal ions with the EO-groups and their different affinity towards the carboxylic acid group may lead to different interaction strengths between the anions and very similar cations. This has a direct impact on many properties, promoting strong ion-specific behaviour. In this first paper on $[M^{3+}][A^-]_3$ ILs, the most relevant physicochemical properties of three REM-based APECILs are presented (for details on preparation and experimental procedures, see Supporting Information), and an attempt is made to exploit these interactions in the context of rare earth metal extraction. We have chosen to focus on Y^{3+}, La^{3+} and Eu^{3+} as typical representations of rare earth metal ions.

Results and Discussion

Glass transition temperatures

Previous research on APECILs based on 2,5,8,11-Tetraoxatridecan-13-oic acid (TOTO) has yielded glass transition temperatures (T_g) or melting temperatures (T_m) in the vicinity of −60 °C for sodium and lithium, and up to 60 °C for potassium and alkylammonium based ionic liquids.[9,10] In addition, [Na][C8E5c], which slowly solidifies at room temperature in the span of several weeks, was examined as a reference point. Differential Scanning Calorimetry (DSC) scans of the $[REM][C8E5c]_3$ ILs, studied in this work, have not revealed any phase nor glass transitions within the measured range, down to −80 °C. However, the glass transition temperatures can still be estimated from viscosity measurements. For that, the viscosity data were fitted by Vogel-Fulcher-Tammann (VFT) equations (see Supporting Information), and T_g was taken as the temperature, at which the extrapolated viscosity reached a value of 10^{12} Pas, following a process suggested in the literature.[18–20] The resulting glass transition temperatures are similar for $[La][C8E5c]_3$ (224 K/−49 °C) and $[Eu][C8E5c]_3$ (232 K/−41 °C), but significantly lower for $[Y][C8E5c]_3$ (190 K/−83 °C) (see Table 1). These estimates are within the range that has been studied in the DSC scans. However, both ionic liquids and polyethylene glycol, as well as its derivatives, are well-known to experience supercooling. DSC scans of [Na][C8E5c] show a peak at 28 °C during the heating cycle, and another one at 9 °C during the cooling cycle, resulting in a supercooling of 19 °C (see Figure S3 in the Supporting Information). Assuming a similar supercooling effect of the REM-APECILs could shift the crystallisation peak out of the measured range. The measurement of the melting point is additionally made more difficult by the remarkably slow phase transition as demonstrated by [Na][C8E5c]. This effect can be explained by COMPLET, which would predict the crystallisation to be kinetically hindered, due to the high flexibility of the ethylene glycol chains.

Table 1. Glass transition temperatures (Tg) and water contents of [Y]-, [La]- and $[Eu][C8E5c]_3$ ionic liquids as well as their water to metal ratios n_{H2O}/n_M. T_g was estimated from VFT-fitting of viscosity data at $\eta = 10^{12}$ Pas. Water contents were determined by volumetric Karl-Fischer titration.

Cation	Tg [K]	H_2O [wt %]	n_{H2O}/n_M
Y	190	1.22	0.90
La	224	0.73	0.56
Eu	232	1.11	0.86

Another notable temperature boundary for ILs is their decomposition temperature, which for many ionic liquids is quite high. So far, we did not determine the thermal stability of the present ionic liquids as we worked within temperature ranges where thermal decomposition was not an issue. Previous experiments with TOTO-based APECILs have yielded good thermal stabilities (> 350 °C) with alkali metal ILs[10] and decent stabilities (> 240 °C) with alkyl ammonium cations.[9] As such, we would expect at least decent thermal stability in the present APECILs.

Viscosities and conductivities

In Figure 2, the viscosities (a) and specific conductivities (b) of the studied ILs are displayed. In both cases, the experimental data could be described by the empirical VFT equation. More details are provided in the Supporting Information, in Tables S1 and S2. This deviation from Arrhenius-like behaviour is typical of fragile glass-forming materials above their glass transition temperature (see Figures S1 and S2 in the Supporting Information).[19,21]

The viscosities of [La]- and $[Eu][C8E5c]_3$ are quite similar with 56.1 and 42.2 Pas at 25 °C, respectively, whereas $[Y][C8E5c]_3$ is significantly less viscous with only 1.67 Pas. Usually, the viscosity is expected to rise with increasing size of the counterion,[5] which holds true for organic cations,[9,11] but not so much for metal ions.[10] For metal ions, the respective complexation geometry must be taken into account, and even bridging modes have to be considered.

Alkyl oligoether carboxylates like [C8E5c] can interact via the carboxyl group and, in a crown-ether-like fashion, with its EO groups (see Figure 1). This has previously led to vast differences in the physicochemical properties of ILs containing alkali metals.[10,12] In contrast to these rather simple metal ions, rare earth metal ions are known to have widely varied complex geometries, and their carboxylates are no exception. REM(III) ions generally prefer high coordination numbers of eight and

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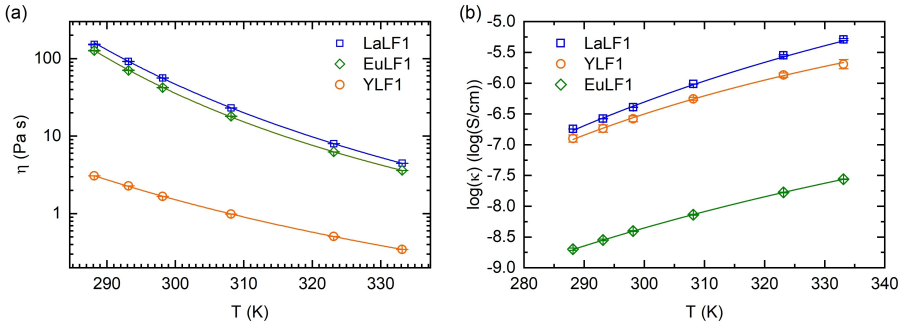

Figure 2. (a) Viscosities η and (b) specific conductivities κ of [REM][C8E5c]$_3$ ILs as a function of temperature ((□, blue) [La][C8E5c]$_3$, (◇, green) [Eu][C8E5c]$_3$, (○, orange) [Y][C8E5c]$_3$). The lines represent Vogel-Fulcher-Tammann-fits. The uncertainty of the individual fits was used to calculate the error bars in (a). The error bars in (b) represent the standard deviation of multiple conductivity measurements. The experimental uncertainty is smaller than the symbol size.

above. The carboxylate ions can bind to these metals in a variety of bridging and non-bridging modes.[22] Bridging modes aside, the three oligoether carboxylates in [REM][C8E5c]$_3$ ILs can at most occupy six binding sites at the metal as bidentate ligands. The remaining vacant sites can then bind to the EO groups or form polynuclear bridging complexes with the carboxylates. As a small amount of water is retained despite extensive drying, it is also highly plausible that the complex directly incorporates water as hydrate or hemihydrate (see Table 1). The same has been observed by Apblett et al., who synthesised short-chain oligoethylene glycol carboxylate salts of yttrium, which could only be isolated as trihydrates.[23]

The resulting coordination structure in REM-APECILs is quite complex, leading to flexible and ion-specific behaviour. The trend visible in Figure 2 (a) is not immediately transferable to the specific conductivity (see Figure 2 (b)). Here, the conductivity of [Eu][C8E5 C]$_3$ is lower (3.95 nS cm^{-1}) than those of [La][C8E5c]$_3$ and [Y][C8E5c]$_3$ (405 and 263 nS cm^{-1}, respectively). One would expect low conductivities for high viscosities and vice versa. Both [Y][C8E5c]$_3$ and [Eu][C8E5c]$_3$ behave this way, but [La][C8E5c] deviates from this expected behaviour and has both the highest viscosity *and* conductivity. Overall, the *specific* conductivities are markedly lower than initially expected for a liquid electrolyte. In contrast, the *molar* conductivities (see Table 2) lie in a range that even exceeds that of NaTOTO, an APECIL with smaller charge carriers.[10] The molar conductivities of [La][C8E5c]$_3$ and [Y][C8E5c]$_3$ are roughly three times that of NaTOTO, resulting in similar *equivalent* conductivity, which accounts for the different charges.

The reason for this behaviour may be the low density of charge carriers in the [REM][C8E5c]$_3$ ILs, stemming from the high molar masses of both the REM cations and especially from their large anions. Generally, the values of both viscosities and conductivities vary more strongly depending on the individual counter ions, and show much more specific behaviour than all other series of APECILs,[9–11] despite strong similarities between the rare earth elements. The small differences between REM cations leading to significant changes in physical-chemical properties of their respective APECILs is promising for future applications, especially in context of the separation and extraction of these metals.

Table 2. Viscosities (η), specific (κ), and molar (Λ) conductivities at 25 °C of [REM][C8E5c]$_3$ ILs in comparison with NaTOTO[10] and Choline-TOTO (ChTOTO).[11]

Ionic Liquid	η [Pa s]	κ [nS cm^{-1}]	Λ [Scm^2 mol^{-1}]
[La][C8E5c]$_3$	56.1	405	4.6×10^{-4}
[Y][C8E5c]$_3$	1.67	263	3.1×10^{-4}
[Eu][C8E5c]$_3$	42.2	3.95	4.5×10^{-6}
NaTOTO	164	0.5×10^{3}	9.1×10^{-5}
ChTOTO	0.665	10.8×10^{3}	0.031

Walden plot

The Walden rule correlates the molar conductivity Λ, or, more specifically, the ionic mobility of a system, with its fluidity η^{-1} and provides a possibility to quantify and compare the association of the ions in an ionic liquid. If the ions can move freely, and the salt is fully dissociated, the corresponding Walden plot yields a line of unit slope. This line is commonly given by dilute aqueous KCl solutions, which show ideal behaviour. Hence, this line is often termed the 'ideal' KCl line. If ion-pairs are formed, the ionic mobility is reduced, which is expressed in a negative deviation ΔW from the ideal KCl-line. Those ionic liquids that possess small ΔW and consequently are close to the ideal KCl line are termed 'good' ILs. They combine high fluidities and high ionic mobilities, and are largely, if not fully, dissociated. Ionic liquids with large ΔW are in turn classified as 'poor' ILs. Here, ion-pairs are formed, and the liquid takes on more and more characteristics of molecular liquids instead of molten electrolytes.[18,24] The Walden plot of [Y]-, [La]-, and [Eu][C8E5c]$_3$ reveals a very significant difference between the three ILs (see Figure 3). Yttrium and europium form rather poor ionic liquids, with significant deviations from the ideal line of $\Delta W > 2$, whereas [La][C8E5c]$_3$ forms a good ionic liquid with $\Delta W = 0.6$, comparable to TOTO salts with small quaternary ammonium ions.[11] Consequently, it can be presumed that the yttrium and europium salts express significant ion-pairing with highly correlated movements of anions and cations, while the lanthanum salt is mostly dissociated, and the ions are able to move independently from one another. A possible explanation

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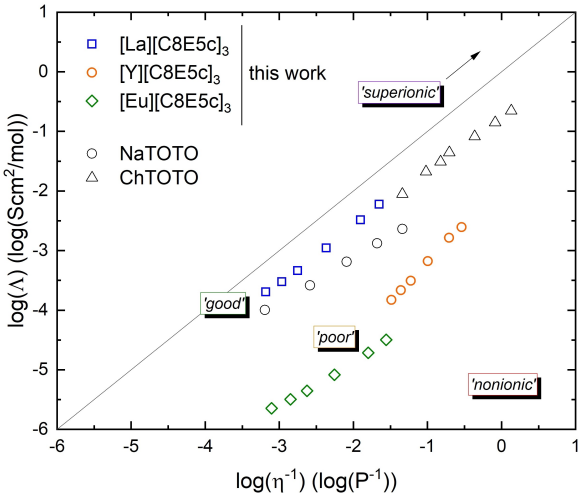

Figure 3. Walden plot of [REM][C8E5c]$_3$ ionic liquids for a temperature range of 15–60 °C in comparison to the ideal KCl line, as well as Na-[10] and Choline (Ch)-TOTO.[11] For a full overview of all properties associated with the Walden plot, see Tables S3 to S7 in the Supporting Information.

for this disparity could be the differing size and complexation behaviour of these rare earths. Yttrium is the smallest of the three ions and prefers lower coordination numbers than lanthanum and europium.[22,25,26] The reduced number of interactions with multiple anions leads to a less tightly interwoven network, allowing the molecules to move more freely throughout the liquid, resulting in a lower viscosity. It is more difficult to rationalise the unusually high conductivity of [La][C8E5c]$_3$. It is possible that lanthanum does not form these networks, or that the networks are structured differently. Another possibility is the existence of multiple charge carriers. If anions and cations are strongly bound and do not traverse the medium independently, as is evidently the case for yttrium and europium, they might travel predominantly as [Ln][C8E5c]$^{2+}$ and [Ln][C8E5c]$_2^+$ complexes. These ions are significantly larger than the independent ions, and they transport less charge. Both these effects contribute to a decrease of conductivity. The behaviour of the europium IL falls in line with the expected behaviour, as coordination strengths and complex stabilities generally increase from the light rare earths up to europium, after which it becomes more complex.[26] It is evident that alkyl polyethylene glycol carboxylates respond to even small differences between their respective counterions, yielding ionic liquids with finely tuneable properties. Although the high viscosities of some of these ILs might be less favourable for some applications, this issue can be resolved by altering the hydrophobic residue, or by varying the length of the EO-chain, as indicated in previous works.[23,27,28] By fine-tuning these parameters, we presume that 'good' ionic liquids can be produced independently of the choice of cation and its valency. Naturally, more detailed understanding of how the aforementioned parameters impact the internal structure and ion mobility will aid the focussed design of these novel ionic liquids.

Separation of rare earth metals

The separation of rare earth metals is a historically difficult process, as there are only small differences between the individual elements.[25,26] Most modern REM separation processes that rely on liquid/liquid extraction use toxic and hazardous extractants such as organophosphorus or quaternary ammonium compounds in combination with kerosene as organic phase.[25] Various attempts have been made to replace either extractant or solvent, or, in case of cation functionalisation, both, with ionic liquids.[15,29] These attempts, however, still use the toxic 'builder' molecules that were described above. Here, we attempted to exploit the direct interaction between the metal ions and the oligoethylene glycol carboxylate. As a proof of concept, the distribution coefficients *P* of the ionic liquids between water and 1-octanol have been determined (see Table 3).

Two different approaches have been made here: first, the individual distributions of each element were examined separately, and secondly, their distributions in an equimolar mixture, to observe possible impacts of other ions. An important classification that should be kept in mind is the classification into light, medium and heavy rare earths. Lanthanum belongs to the light rare earths and europium to the medium rare earths. Yttrium, despite being the lightest element of the three, is usually counted towards the heavy rare earths due to chemical similarities.[25,26] The pure samples follow a clear trend: the lighter the rare earth metal salt, the more it prefers the aqueous phase. In fact, the lanthanum salt is the only one that is predominantly in the aqueous phase, while yttrium prefers the organic phase, and the europium salt distributes nearly equally between the phases. This behaviour is to be expected and reflects the lanthanide contraction.[25,30] The same trend cannot be observed in the mixed samples. Here, the preference of europium for the organic phase becomes more pronounced, and yttrium shows a slight preference for the aqueous phase, while lanthanum is only slightly affected. The separation factors, and consequently, the extractability of the rare earth metals for this 1:1:1 extraction follows a similar trend to other more common extractants such as naphthenic acids (La < Y < Eu).[25,31] While the extractability generally increases throughout the lanthanide series, yttrium often behaves differently depending on the steric hindrance of the extractant. For strongly sterically hindered carboxylic acid extractants such as Versatic™ acids, the yttrium is extracted with medium rare earth metals instead.[31,32] It is thus reasonable to assume low steric hindrance

Table 3. Distribution coefficients *P* of the [REM][C8E5c]$_3$ ionic liquids between water and 1-octanol from solutions of the neat ILs ($c = 1$ *mM*) and their equimolarly mixed solutions ($\Sigma c_i = 1$ *mM*) at room temperature. Separation Factors $SF_{A/B}$ are given for the equimolarly mixed solutions.

	[Y][C8E5c]$_3$	[La][C8E5c]$_3$	[Eu][C8E5c]$_3$
neat ILs	1.665 ± 0.095	0.572 ± 0.004	1.175 ± 0.027
1:1:1 mole ratio	0.821 ± 0.025	0.616 ± 0.020	1.529 ± 0.040
Separation factors (1:1:1 extraction)	$SF_{Y/La}$ 1.33	$SF_{La/Eu}$ 0.403	$SF_{Eu/Y}$ 1.86

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in the case of [C8E5c], possibly suggesting the existence of polynuclear ([REM][C8E5c]$_3$)$_n$ complexes.[22,31]

Nevertheless, in both cases, a separation of the individual elements is possible. This proof of concept already demonstrates the potential of this approach even without an optimisation of the partition coefficients. There are several factors to be considered for improving the extraction process ranging from the choice of solvents to a variety of additives. A change in temperature is expected to have an especially large impact. Alkyloligo- and polyethyleneglycol-based compounds are well-known for their weaker hydration and consequently lower water solubility at higher temperatures, and the competition between hydration and ion complexation should be particularly temperature-dependent. All in all, the presence of clear differences in phase distribution behaviour despite no optimisation being done is very promising. With the right choice of extraction conditions, full separation of these elements in only a handful of steps is well within reach.

Fluorescent properties

While ILs can have remarkable fluorescence properties,[33–35] rare earth metal ions exhibit interesting luminescent behaviour as well, also as part of ionic liquids.[15,36] Whereas yttrium and lanthanum three-valent cations are considered to be non-emitting[37,38] and usually are only present with photoluminescence in doped solid materials and some exceptional complexes, europium salts find widespread use due to their intense and characteristic fluorescence under UV illumination. The difference in luminescent behaviour can be easily attributed to the different occupancies of the f-orbitals, which are completely empty for Y^{3+} and La^{3+}, whereas Eu^{3+} possesses six electrons in its 4f shell. Both excitation and emission spectra were recorded for all [REM][C8E5c]$_3$ ILs, and significant fluorescence in the visual spectrum was seen for all compounds (see Figure 4).

There is a stark contrast between the individual spectra, [Y][C8E5c]$_3$ and [La][C8E5c]$_3$ both show singular, but very broad emission peaks with half widths of 112 and 114 nm respectively, whereas [Eu][C8E5c]$_3$ shows mainly the characteristic, narrow emission peaks of the various $^5D_0 \rightarrow {}^7F_J$ transitions and a broad, weak peak, which can be observed at higher excitation wavelengths. [Y][C8E5c]$_3$ has its emission maximum at 461 nm (excitation at 375 nm), and [La][C8E5c]$_3$ at 484 nm (excitation at 399 nm). [Eu][C8E5c]$_3$ has five distinct emission bands when excited at 394 nm. They can be directly attributed to the electronic transitions of the Eu^{3+} ion:[39] a very weak transition at 578 nm ($^5D_0 \rightarrow {}^7F_0$), a strong transition at 592 nm ($^5D_0 \rightarrow {}^7F_1$), a very strong transition at 615 nm ($^5D_0 \rightarrow {}^7F_2$), a very weak transition at 650 nm ($^5D_0 \rightarrow {}^7F_3$) and finally, a strong transition at 697 nm, with a shoulder at 690 nm ($^5D_0 \rightarrow {}^7F_4$). The spectrum is overlaid with a small but very broad peak centred around 610 nm.

The excitation spectrum of [Eu][C8E5c]$_3$ (Figure 4 (C0)) shows several narrow peaks, overlaid with two broader ones. The narrow peaks can be easily attributed to the respective transitions, while the broader ones are likely to result from the influence of the ligand. Usually, Eu^{3+} is excited between 390 and 405 nm, as the corresponding $^5L_6 \leftarrow {}^7F_0$ transition is the most intense in the absorption spectrum.[39] In the excitation spectrum of Figure 4(C0) however, the most intense band is the $^5D_1 \leftarrow {}^7F_1$ transition, which, similarly to the $^5D_2 \leftarrow {}^7F_0$ transition at 464 nm is a hypersensitive transition, and highly dependent on the local environment of the Eu^{3+} ion.[39] Excitation at these three wavelengths gives a distinct trend in the intensity and shape of the spectrum. When excited at 394 nm, only the narrow and defined transitions of the Eu^{3+} ion are visible, but moving to higher excitation wavelengths gradually introduces a broad, underlying peak with low intensity.

The very weak $^5D_0 \rightarrow {}^7F_0$ transition is strictly forbidden by standard selection rules, but can be observed in C_n, C_{nv}, and C_s symmetry.[39] It is just barely visible in the present spectrum, suggesting that only a small part of Eu^{3+} ions sit at sites with

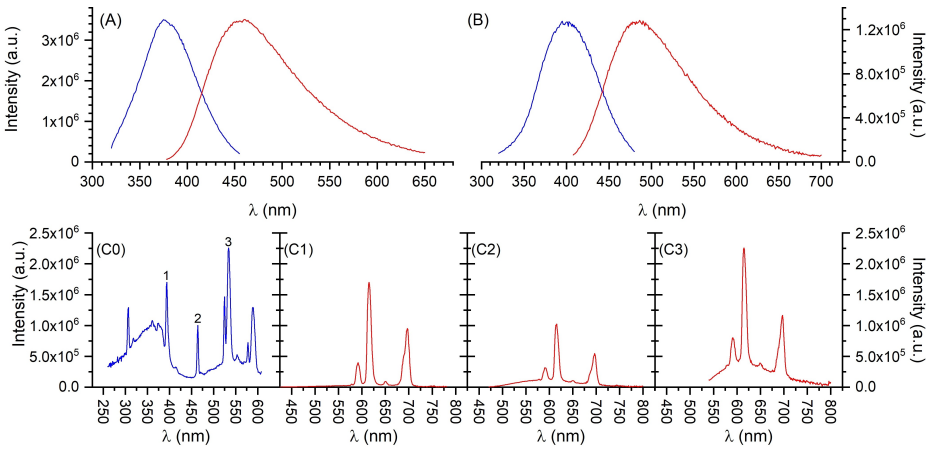

Figure 4. Excitation (blue) and emission (red) spectra of (A) pure [Y][C8E5c]$_3$, (B) [La][C8E5c]$_3$ and (C0-3) [Eu][C8E5c]$_3$ ionic liquids. Excitation wavelengths were (A) 375 nm, (B) 399 nm, (C1) 394 nm ($^5L_6 \leftarrow {}^7F_0$), (C2) 464 nm ($^5D_2 \leftarrow {}^7F_0$) and (C3) 534 nm ($^5D_1 \leftarrow {}^7F_1$). The fixed emission wavelengths for the measurement of the excitation spectra were (A) 461 nm, (B) 484 nm and (C0) 615 nm.

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these symmetries. The $^5D_0 \rightarrow {}^7F_0$ transition is usually very narrow, and broadening or splitting of this peak can indicate multiple different environments for the Eu^{3+} ion which exhibit the aforementioned symmetries. Due to the low intensity and the underlying broad peak however, it is difficult to determine precise peak widths for this transition.

The strong $^5D_0 \rightarrow {}^7F_1$ transition is a magnetic dipole transition, and is generally independent of the environment of the Eu^{3+} ion.[39] It can however still be used to detect multiple non-equivalent sites, as those can split the peaks differently, depending on the site symmetry. Measurements at lower temperatures would be necessary to allow further analysis.

The hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition is typically the most intense emission band, as is the case in the present spectrum. The intensity ratio $R = I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is often used to describe asymmetry of the Eu^{3+} site, since the $^5D_0 \rightarrow {}^7F_2$ transition is forbidden at a site with a centre of inversion. In the present spectra, this ratio varies with the excitation wavelength: $R_{394} = 4.32$, $R_{464} = 3.28$ and $R_{534} = 2.81$, diminishing with increasing excitation wavelength. A small R is often equated to a high symmetry of the Eu^{3+} site, but this usually is an oversimplification. There are multiple factors that impact R, including the dipolar polarizability of the ligands.[39,40] While it is certainly a possibility that different non-equivalent sites could be specifically excited at different wavelengths, it is more likely that ligand effects play a stronger role at higher wavelengths instead.

The $^5D_0 \rightarrow {}^7F_3$ transition is another forbidden transition, and its presence suggests strong crystal-field perturbation and significant J-mixing.[39] Finally, the $^5D_0 \rightarrow {}^7F_4$ transition presents itself as the second most intense peak in the emission spectrum at 697 nm with a shoulder at 690 nm. The splitting of this transition may help clarify the symmetry at the Eu^{3+} site, however lower temperature measurements would once again be beneficial to reduce line broadening and the resulting overlap of these peaks.

Generally, all present emission peaks possess relatively high line widths, likely due to inhomogeneous line broadening. This does indeed suggest non-equivalent environments for the Eu^{3+} ions in the ionic liquid.

When excited at longer wavelengths, the $[Eu][C8E5c]_3$ emission spectrum is overlaid with a broad, low-intensity peak centred at 610 nm. This peak cannot be easily attributed to any Eu^{3+} transition, but in turn, likely originates from the ligands. It is likely the result of charge or energy transfer mechanisms, and only the lower lying ^5D_J levels appear to participate effectively. These processes could also explain the diminishing asymmetry factor R at higher wavelengths.

The emission spectra of both $[La][C8E5c]_3$ and $[Y][C8E5c]_3$ also show this broad peak, albeit at different intensities, and centred around slightly different wavelengths. Neither La^{3+} nor Y^{3+} are commonly known as fluorophores, and in contrast to an aqueous $EuCl_3$ solution, the respective $LaCl_3$ and YCl_3 solutions show no luminescence in the observed spectral range. Hence, in the case of these two ILs, the rare earth metals cannot be responsible for the observed fluorescence. In the excitation spectra of Figure 4(A) and (B), the absence of characteristic peaks attributable to the rare earth metals rather suggest that the observed emission originates solely from the ligand.

In fact, polyethylene glycol units may fluoresce,[41,42] and also the ligand utilized here shows weak fluorescence (see Figure S4 in the Supporting Information), albeit at shorter wavelengths than observed in the fluorescence spectra of Figure 4. The fluorescence of [H][C8E5c] is quite surprising, as it does not fulfil the typical criteria of organic fluorophores, such as extended π-systems, and warrants further research. It is to be noted that [H][C8E5c] has two distinct emission maxima at 310 nm and 400 nm. We presume that the lower-wavelength emission belongs to fully protonated [H][C8E5c], and the higher-wavelength emission to partially deprotonated $[C8E5c]^-$ ions, as the ethylene oxide groups may act as weak proton acceptors. The emission of the deprotonated $[C8E5c]^-$ anion in combination with rare earth metals is however significantly shifted to longer wavelengths, from the UV into the visible spectrum. In addition, the intensity is noticeably increased. Further research into this topic is needed, and lifetime measurements as well as determination of quantum yields would give important insight into the processes at hand. Additionally, the ILs are likely to express strong red-edge effects due to their high viscosity, where the emission maximum is shifted towards higher wavelengths upon excitation with light of wavelengths above the excitation maximum.[43,44]

The luminescent properties of APECILs provide a wide field of possible applications as flexible liquid phosphors. Using various central metal ions and via variation of the chain lengths in the anions, customisable fluorescent liquids can be produced. They can be excited at, and likewise emit a wide range of wavelengths.

Previous studies have shown the formation of liquid crystals using low-molecular weight APECILs,[9] and liquid crystal formation may be possible with rare earth metal based APECILs as well, resulting in luminescent liquid crystals.

Conclusion

By using alkyl polyethylene oxide carboxylates as a novel class of anionic 'builder' molecules, triply charged rare earth metals cations could be easily and directly incorporated into a room-temperature ionic liquid, without requiring their complexation and transformation to an anionic species. Viscosity and conductivity measurements revealed strong ion-specific effects that led to different classifications in the Walden plot. $[La][C8E5c]_3$ was determined to be a 'good' IL, while $[Y][C8E5c]_3$ and $[Eu][C8E5c]_3$ were classified as 'poor' ILs. Proof-of-concept partition experiments with the mentioned three different ions showed that rare earths can be separated via liquid/liquid extraction without the use of toxic extractants. All $[REM][C8E5c]_3$ ILs fluoresce with differing luminescent properties, which might make them appropriate for spectroscopic applications as well.

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Acknowledgements

We kindly acknowledge the help of Thomas Rittner during the recording of fluorescence spectra. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: ionic liquids · lanthanides · rare earths · surfactants

[1] N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123–150.
[2] T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206–237.
[3] *Chem. Rev.* **2017**, *117*, 6633–7240.
[4] *ChemPhysChem* **2012**, *13*, 1601–1963.
[5] P. Wasserscheid, T. Welton, Eds., *Ionic Liquids in Synthesis*, Wiley-VCH Verlag GmbH & Co. KGaA, **2002**.
[6] H. Weingärtner, *Angew. Chem. Int. Ed.* **2008**, *47*, 654–670.
[7] M. Petkovic, K. R. Seddon, L. P. N. Rebelo, C. S. Pereira, *Chem. Soc. Rev.* **2011**, *40*, 1383–1403.
[8] M. Sivapragasam, M. Moniruzzaman, M. Goto, *Biotechnol. J.* **2020**, *15*, 1–9.
[9] E. Müller, L. Zahnweh, B. Estrine, O. Zech, C. Allolio, J. Heilmann, W. Kunz, *J. Mol. Liq.* **2018**, *251*, 61–69.
[10] O. Zech, M. Kellermeier, S. Thomaier, E. Maurer, R. Klein, C. Schreiner, W. Kunz, *Chem. A Eur. J.* **2009**, *15*, 1341–1345.
[11] R. Klein, O. Zech, E. Maurer, M. Kellermeier, W. Kunz, *J. Phys. Chem. B* **2011**, *115*, 8961–8969.
[12] O. Zech, J. Hunger, J. R. Sangoro, C. Iacob, F. Kremer, W. Kunz, R. Buchner, *Phys. Chem. Chem. Phys.* **2010**, *12*, 14341–14350.
[13] I. Krossing, J. M. Slattery, C. Daguenet, P. J. Dyson, A. Oleinikova, H. Weingärtner, *J. Am. Chem. Soc.* **2006**, *128*, 13427–13434.
[14] E. Jurado, M. Fernández-Serrano, J. Núñez-Olea, M. Lechuga, F. Ríos, *WIT Trans. Ecol. Environ.* **2011**, *144*, 497–505.
[15] K. Binnemans, *Chem. Rev.* **2007**, *107*, 2592–2614.
[16] A. G. Zazybin, K. Rafikova, V. Yu, D. Zolotareva, V. M. Dembitsky, T. Sasaki, *Russ. Chem. Rev.* **2017**, *86*, 1254–1270.
[17] D. Prodius, A. V. Mudring, *Coord. Chem. Rev.* **2018**, *363*, 1–16.
[18] C. Austen Angell, Y. Ansari, Z. Zhao, *Faraday Discuss.* **2012**, *154*, 9–27.
[19] P. G. Debenedetti, F. H. Stillinger, *Nature* **2001**, *410*, 259.
[20] IUPAC, *Compendium of Chemical Terminology*, Blackwell Scientific Publications, Oxford, **2019**.
[21] A. Grandjean, M. Malki, C. Simonnet, D. Manara, B. Penelon, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2007**, *75*, 1–7.
[22] J. Lu, R. Wang, *Encycl. Inorg. Bioinorg. Chem.* **2012**, 1–12.
[23] A. W. Apblett, J. C. Long, E. H. Walker, M. D. Johnston, K. J. Schmidt, L. N. Yarwood, *Phosphorus Sulfur Silicon Relat. Elem.* **1994**, *93*, 481–482.
[24] W. Xu, E. I. Cooper, C. A. Angell, *J. Phys. Chem. B* **2003**, *107*, 6170–6178.
[25] C. K. Gupta, N. Krishnamurthy, *Extractive Metallurgy of Rare Earths*, CRC PRess, **2016**.
[26] V. R. Sastri, J.-C. G. Bünzli, V. R. Rao, G. V. S. Rayudu, J. R. Perumareddi, *Modern Aspects of Rare Earths and Their Complexes*, Elsevier Science, **2003**.
[27] H. Shobukawa, H. Tokuda, S.-I. Tabata, M. Watanabe, *Electrochim. Acta* **2004**, *50*, 305–309.
[28] H. Shobukawa, H. Tokuda, M. A. B. H. Susan, M. Watanabe, *Electrochim. Acta* **2005**, *50*, 3872–3877.
[29] M. Iqbal, K. Waheed, S. B. Rahat, T. Mehmood, M. S. Lee, *J. Radioanal. Nucl. Chem.* **2020**, *325*, DOI 10.1007/s10967-020-07199–1.
[30] Z. Li, K. Binnemans, *AIChE J.* **2020**, *66*, 1–4.
[31] A. C. du Preez, J. S. Preston, *Solvent Extr. Ion Exch.* **1992**, *10*, 207–230.
[32] J. S. Preston, *Hydrometallurgy* **1985**, *14*, 171–188.
[33] S. Cha, T. Shim, Y. Ouchi, D. Kim, *J. Phys. Chem. B* **2013**, *117*, 10818–10825.
[34] S. Schmode, A. Petrosyan, F. Fennel, A. Villinger, S. Lochbrunner, R. Ludwig, *Angew. Chem. Int. Ed.* **2017**, *56*, 8564–8567.
[35] A. Paul, P. K. Mandal, A. Samanta, *J. Phys. Chem. B* **2005**, *109*, 9148–9153.
[36] B. Fan, J. Wei, X. Ma, X. Bu, N. Xing, Y. Pan, L. Zheng, W. Guan, *Ind. Eng. Chem. Res.* **2016**, *55*, 2267–2271.
[37] Y. Y. Xu, I. A. Hemmilä, *Anal. Chim. Acta* **1992**, *256*, 9–16.
[38] R. C. Leif, L. M. Vallarino, M. C. Becker, S. Yang, *Cytom. Part A* **2006**, *69*, 767–778.
[39] K. Binnemans, *Coord. Chem. Rev.* **2015**, *295*, 1–45.
[40] P. A. Tanner, *Chem. Soc. Rev.* **2013**, *42*, 5090–5101.
[41] Y. C. Chiu, E. M. Brey, V. H. Pérez-Luna, *J. Fluoresc.* **2012**, *22*, 907–913.
[42] C. Sun, X. Jiang, B. Li, S. Li, X. Z. Kong, *ACS Sustainable Chem. Eng.* **2021**, *9*, 5166–5178.
[43] Z. Hu, C. J. Margulis, *Acc. Chem. Res.* **2007**, *40*, 1097–1105.
[44] A. P. Demchenko, *Luminescence* **2002**, *17*, 19–42.

Manuscript received: June 1, 2021
Accepted manuscript online: July 1, 2021
Version of record online: August 3, 2021

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