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Journal of Materials Chemistry C

Carboxyl-functionalized ionic liquids: synthesis, characterization and synergism with rare earth ions

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Experimental Procedure

Reagents: All chemicals were purchased from commercial sources. 1-Methyl imidazolium (Aldrich); Bromoethanol (Vetec); Ethyl acetate (Dinâmica); Anhydrides: Succinic, Phthalic, Phenyl succinic or 3,3-Dimethyl gutaric; Nitric acid (Dinâmica); NaOH (Dinâmica); Europium/Gadolinium oxides (Aldrich); Ultra pure water was obtained in a laboratory ultra-pure water purification unit Direct-Q 3,5,8.

Synthesis of Ionic Liquids: The four monocationic carboxylates (MC1-4) ionic liquids were prepared starting from 1-Methylimidazolium (10 mmol; 0,820 g) and 1-Bromoethanol (10 mmol; 1,248 g) added in a 100 mL round bottom flask. This mixture was kept at 70 °C, under magnetic stirring, for 24 hours. Translucent and colourless crystals of Bromide 2-(1-methylimidazolium-1-yl)-1-ethanol were obtained with yield up to 90%. In the synthesis of ionic liquids, the imidazol core (2-(1-ethylimidazoly)-1-ethanol bromide (4 mmol; 0,828 g) was added to acetonitrile (20 mL) and 4 mmol of the corresponding anhydride (succinic, phthalic, phenyl succinic or 3,3-dimethyl gutaric), in a 150 mL round bottom flask. The reactions were conditioned by a reflux system, with controlled temperature at 80°C and magnetic stirring, for 18 hours. The products were washed 3x with 20 mL of ethyl acetate and then the solvent was removed completely under vacuum. Ionic liquids obtained and yields: (2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide, (MC1); 80%. (2-(3-methylimidazolion-1-yl)-etoxy)-carboyl) benzoic-phthalic acid bromide (MC2); 78%. 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3); 75%. 3, 3-dimethyl-5-(2-(3methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4); 98%. The experimental procedure for obtaining ionic liquids is illustrated in Figure 1: SI. Ionic liquids were stored in a desiccator because of their high hydrophilicity.



Figure S1. Scheme for representation the synthesis route of ionic liquids: (2- (3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1), (2- (3-methylimidazolion-1-yl) etoxy) carboyl) benzoic-phthalic acid bromide (MC2), 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3), 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4).

Synthesis of Ln(MCx)₃(H2O)_y:Hydrated complexes were synthesized from Ionic liquids (MCx) and Ln(NO₃).6H₂O as reacted:

$Ln(NO_3).6H_2O + 3H(MCx) \rightarrow Ln(MCx)_3(H2O)_y + (3-y)H_2O$ (1)

Where: Ln= Eu or Gd; x=1, 2, 3, or 4; y= 0 or 1

Luminescent ionogels (shown in Figure S2) were obtained from the synthesized RTILs and lanthanide salts. The lanthanide salts used in this procedure were prepared by a well-established procedure available in the literature.¹ Luminescent ionogels were prepared in a proportion of 1 mmol lanthanide nitrate hexahydrate to 0.3 mmol of Carboxylate-ionic liquids. At first, we dissolved the NaOH and the IL, separately, in 0,2 mL of ultra pure water in the ratio 1:1. In a single beaker of 10 mL we added the NaOH and the dissolved ionic liquid (in 0,3 mL of ethanol). To this beaker we added the lanthanide salt. This mixture was maintained under magnetic stirring for 25 minutes and at ambient temperature. The synthesized ionogels were kept in a desiccator under vacuum.



Figure S2. Ionic Liquid (MC3) and ionogels photographs acquired under daylight and UV exposure.

Characterization

For the structural analysis of ionic liquids and ionogels, the following were used: Nuclear Magnetic Resonance (NMR), Infrared (FTIR) and Raman spectroscopies. NMR studies were performed on a Varian Spectrometer 400 MHz for ¹H and ¹³C. Chemical shift values are expressed in parts per million (ppm). NMR spectra recorded in D₂0 (99%, Aldrich). Microanalyses for C, N and H were carried using a Carlo Erba Instrument, model EA1110. Raman spectroscopy was carried out in Witec, model Alpha 300s (532 nm; 55 mw) with a resolution of 2 cm⁻¹ and range operation of 200-3800 cm⁻¹. The FTIR spectra were obtained using a Perkin Elmer Spetrum 400-4000 cm⁻¹. For each sample analyzed, 1 mg in all characterization procedures was used, except for the thermal analysis when samples weighed ~6 mg. Thermal gravimetric analysis were carried out using a DSC 2910 instrument (TA Instruments). The samples were heated in platinum crucibles, starting from room temperature up to 700° C with a heating rate of 5° C min⁻¹ using N₂ as a the purge gas. The melting temperatures were determined by a micro-binocularloupe melting point apparatus. Optical properties: Absorbance spectra were obtained using a UV-Vis-NIR Varian Cary 5000 spectrophotometer within the spectral range 200-1700 nm. Photoluminescence spectra and lifetime measurements were collected using a FLUOROLOG3 ISA/Jobin-Yvon Spectrofluorimeter, right-angle collection methods, equipped with Hamamatsu R928P photomultiplier a SPEX 1934 D phosphorimeter, a 450 W Xe arc lamp, and a pulsed 450W Xe-Hg lamp. All spectra were corrected for the spectral response of the monochromators and the detector corrected via correction spectra provided by the manufacturer. Additionally, the excitation spectra were corrected for the spectral distribution of the lamp intensity from 240-600 nm using a photodiode as reference. Photostability of Eu³⁺-complexes were evaluated by monitoring the emission/excitation spectra intermittently under continuous exposure to UV irradiation by different absolute doses (0, 0.5 and 1.0 J). Illumination performed by UVA (365 nm) and UVB (302 nm) lamps (8 watts each), and TL-200 Ultraviolet Translinker/Crosslinker UVP that provides exposure in absolute controlled doses.

NMR studies

In addition to the structural characterization, NMR studies were obtained to gain an understanding of any preferential interactions, such as H-bonding, between specific cation sites and the anions, as well as the magnitude of these associations. The ¹H and ¹³C NMR spectra are presented in Tables 1 and 2, respectively. Assignments of these spectra follow those found in the ionic liquids, and are in accord with those found in the literature. To facilitate interpretation, Figure 3 shows the structures listed.

¹*H NMR Spectra of lonic Liquids.* The ¹*H* NMR spectra of the carboxylate-ILs, reported in Figure S4, clearly demonstrate the presence of residual water at ~4.650 ppm. It is well known that the imidazolium ring is conventionally aromatic and, therefore, capable of sustaining a ring current.² It is the effects of this ring current that have been observed in the NMR chemical shift data of the analyzed samples.



Figure S3. Structures for ionic liquids with sites labelled as they will be referred to within this article. ILs: 2-(3-methylimidazolyl-1yl) etoxy-4-oxobutanoic acid bromide (MC1), 2- (3-methylimidazolion-1-yl)-etoxy-carboyl benzoic-phthalic acid bromide (MC2), 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3), 3,3-dimethyl-5-(2-(3-methylimidazolyl-1yl)-ethoxy)-5-oxopentanoic acid bromide (MC4).

The behaviour of the H(1) and H(C3) signals is best attributed to changes in electronic distribution in the cation.² The increase in the strength of the H-bonding interactions has been associated with a downfield shift of the H-bond donating resonance in the ¹H NMR, i.e. an increased chemical shift.³ The protons H(C1) and H(C3) are shifted less under the influence of only one neighbouring nitrogen atom. The spectrum of ¹H-ILs in D₂O shows a broad singlet for the H(C2) signal. In addition, irradiation of the H(C2) signal results in a simplified multiplet for the H(C1) signal, showing that H(C2) is coupled to H(C1) and H(C3), and that H(C1) and H(C3) are not equivalent, as has been previously observed by Avent et al.² The results indicate that H(C2) preferentially interacts with the stronger H-bond accepting anion, while H(C3) and H(C4) either exhibit no preference for either anion or a slight preference for the weaker H-bonding anion, as reported by Matthews et al.³ Preferential interactions of the imidazolium ring atoms with anions are identified, cation-anion interactions occur at the H(C1) and H(C3) ring protons, but are strongest for the proton H(C2). Thus, within a given solvation shell the cation is rotating so as to interact through H(C2) with the anion. Simple rotation of the cation within a diffuse solvation shell is in accordance with the low energy.³

Table S1. Chemical shifts reported by NMR for the ¹H spectrum obtained in deuterated water, were: 2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1), 2- (3-methylimidazolion-1-yl)-etoxy-carboyl

benzoic-phthalic acid bromide (MC2), 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide
(MC3), 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4).

Attribution	Multiplicity	Sample / Chemical Shift (ppm)						
		MC1	MC2	MC3	MC4			
H(C1) _{assym}	S	7.462	7.350	7.326	7.377			
H(C2) _{assym}	S	7.375	7.296	7.383	7.471			
H(C2) _{sym}	d	7.901	7.893	7.865	7.910			
		8.711	8.614	8.610	8.731			
H(C3) _{assym}	S	7.431	7.383	7.304	7.373			
H(C1,3) _{sym}	d	6.890	7.481	6.736	6.787			
Н(С4)	S	3.825	3.747	3.811	3.841			
H(C5) _{assym}	t	-	3.774	-	-			
H(C5) _{sym}		4.386	4.458	4.188	4.366			
H(C6) _{assym}	t	-	4.160	-	-			
H(C6) _{sym}		4.427	4.536	4.296	4.430			
H(C8)	t	2.527	-	2.860	2.309			
H(C9) _{assym}	t	2.435	-	2.631	-			
H(C9) _{sym}	t	4.236	-	3.968	-			
H(C11)	S	-	7.524	-	-			
H(C12)	d	-	7.603	7.196	0.925			
H(C13)	d	-	7.583	7.264	0.925			
H(C14)	d	-	7.505	7.239	-			
H(C15)	d	-	-	7.264	-			
H(C16)	d	-	-	7.196	-			
Residual water	S	4.650	4.600	4.650	4.650			

The change in chemical shift with concentration is indicative of the formation of a substantial hydrogen bond, since the formation of a hydrogen bond will cause a proton chemical shift to move to a lower field.⁴ This explains the symmetrical and asymmetric displacements for the protons that make up the imidazolium ring. The population of the more-shielded proton increases and the signal moves to upfield. This is the behaviour observed for the H(C2)that is lying within the shielding cone of a neighbouring imidazolium ring, and, to a lesser extent, for the H(C4) and H(C5) signals.⁵ The H(C1) and H(C3) signals typically shift downfield indicating they are outside the shielding cone. Taken together these results have been interpreted as the formation of rotated π stacked structures.² All other protons are sufficiently distant from the ring so that the ring-current effects are negligible. This suggests a model for the structure of Ils, in which the imidazolium rings are arranged in columns of stacked imidazolium rings, with any two adjacent

rings related by a centre of symmetry (staggered).^{2, 6} The term π - π stacking is taken here to include the π^+ - π^+ interactions between cationic aromatic imidazolium rings within an IL. For these interactions, the positive charge acts both to reduce dispersive interactions through the contraction of the π electron cloud, and to introduce a repulsive cation-cation Coulombic contribution.³ Several stacking conformations are possible, depending on the relative orientation of the two imidazolium rings. These may be stacked-parallel, stacked-rotated, stacked-antiparallel, stacked-displaced and T-shaped conformers.⁷ The stabilisation of the cationic π^+ - π^+ interactions occours through both Coulombic and H-bonding interactions between the IL cations and anions.³ Hence, the highest displacements observed in the spectrum are attributed to H(C1), H(C2) and H(C3), which reflects the acid character of these protons when compared to the others.

We noted that the NMR spectra represents a weighted average over all conformations present within the liquid phase. These results imply that rotated π -stacked structures are preferentially formed or are longer lived than other conformations within the liquid. As reported in previous studies, imidazole derivatives show a stacked cation conformer where the anions are located on the periphery but are positioned vertically (in the "middle") between the cations, and an alternating anion above or below the cation conformer, where the anions are located on the "diagonal" and the cation rings are displaced relative to each other.⁷ The displacements reported by the protons that make up the imidazolium ring, together with H(C5) and H(C6) for all samples (besides C(H9) to the MC1 and MC3 structures) corroborate the hypothesis of the formation of rotamers. The conformations enable an exhibition of possible internal atomic overlaps if built in ideal geometry with all hydrogen atoms. The possible formation of rotamers is currently being evaluated against a conformational analysis by Density Functional Theory (DFT) Calculation, applied to chemical species with imidazolium cations⁸ that behave similarly to those observed in this work.

¹³C NMR Spectra of Ionic Liquids. The impact of H-bonding on the ¹³C NMR signals is more complex as there is an interplay between electron density changes due to the formation of the H-bond, and variations in the energy of the molecular orbitals.³ The ¹³C signals of C2,C4 and C5 move downfield with increasing H-bond accepting ability of the anion,⁹ as can be observed in the spectra (Figure S5). This phenomenon has been attributed to the reduction in the natural bond order of the C-H bond dominating electron density effects.³ Correspondingly, the influence of stronger H-bonding on the chemical shift of ¹³C NMR signals would be expected to follow a similar trend to that of the ¹H NMR, i.e. a downfield (higher ppm) shift. The ¹³C NMR of the carboxylate-ILs are shown in Figure S5 and interpreted in Table S2.

TableS2. Chemical shifts reported by NMR for the ¹³ C spectrum obtained in deuterated water, were: 2-(3-
methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1), 2- (3-methylimidazolion-1-yl)-etoxy-carboy
benzoic-phthalic acid bromide (MC2), 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide
(MC3), 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4).

Attribution	Sample / Chemical Shift (ppm)							
	MC1	MC2	MC3	MC4				
C1 _{assym}	123.632	123.594	123.586	123.594				
C1 _{sym}	123.753	123.814	123.685	123.799				
C2 _{assym}	136.361	136.323	136.004	136.346				
C2 _{sym}	136.475	136.490	136.285	136.467				
C3 _{assym}	122.607	122.440	122.425	122.433				
C3 _{sym}	122.478	122.524	122.501	122.600				
Attribution	Sample / Ch	emical Shi	ft (ppm)					

	MC1	MC2	MC3	MC4
C1,3 _{sym}	106,804	-	106.736	106.766
C4	35.903	35.857	39.599	35.789
C5	48.298	48.078	48.063	48.192
C6	31.227	35.766	35.721	27.197
C7	174.798	168.802	178.388	173.637
C8	59.797	59.767	59.752	59.752
С9	62.826	64.017	62.788	62.477
C10	179.459	171.717	179.656	176461
C11	-	128.945	127.708	138.114
C12	-	131.837	127.936	44.897
C13	-	131.837	128.831	44.897
C14	-	-	127.237	-
C15	-	-	128.831	-
C16	-	-	127.936	-

The ¹H NMR spectra (Figure S4) show qualitatively similar behaviour to the ¹³C NMR spectra (Figure S5), and both are consistent with those results from COSY/HSQC characterization (Figure S6-S9) suggesting the formation of the proposed structures for ILs (Figure S3).



Figure S4. ¹H NMR spectrum, obtained in deuterated water, for: 2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1; black line), 2- (3-methylimidazolion-1-yl)-etoxy-carboyl benzoic-phthalic acid bromide (MC2; blue line), 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3; green line), 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4; pink line).



Figure S5. ¹³C NMR spectrum, obtained in deuterated water, for: 2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1; black line), 2- (3-methylimidazolion-1-yl)-etoxy-carboyl benzoic-phthalic acid bromide (MC2; blue line), 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3; green line), 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4; pink line).



Figure S6. (A)COSY NMR spectra (B) HSQC spectra of 2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1).



Figure S7. (A)COSY NMR spectra (B) HSQC spectra of 2- (3-methylimidazolion-1-yl)-etoxy-carboyl benzoic-phthalic acid bromide (MC2).



Figure S8. (A)COSY NMR spectra (B) HSQC spectra of 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3).



Figure S9. (A)COSY NMR spectra (B) HSQC spectra of 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4).

Elemental Analysis

Elemental analysis calculated (%) for C₁₀H₁₅N₂O₄Br (MC1): C 39.10, H 4.92, N 9.12, O 20.83, Br 22.49. Found (%): C 36.37, H 5.22, N 11.40, O 26.18.

Elemental analysis calculated (%) for C₁₄H₁₅N₂O₄Br (MC2): C 47.34, H 4.25, N 7.88, O 18.01, Br 22.49. Found (%): C 36.65, H 4.97, N 11.28, O 24.51.

Elemental analysis calculated (%) for C₁₅H₁₇N₂O₄Br (MC3): C 44.70, H 6.06, N 8.02, O 18.32, Br 22.49. Found (%): C 41.64, H 6.39, N 10.08, O 18.40.

Elemental analysis calculated (%) for C₁₂H₁₉N₂O₄Br (MC4): C 44.70, H 6.07, N 8.02, O 18.32 Br 22.49. Found (%): C 38.29, H 9.94, N 7.16, O 22.12.

The above experimental results give an idea of the synthesis of the proposed structures for MC1, MC2, MC3 and MC4-lonic Liquids.

Infrared Spectroscopy (FTIR)

FT-IR spectra were first employed in order to understand at a molecular level the general interactions that exists in the 1-methylimizodalium carboxylate-ILs (Figure S10).



Figure S10. Infrared spectrum for ionic liquids: 2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1; black line), 2- (3-methylimidazolion-1-yl)-etoxy-carboyl benzoic-phthalic acid bromide (MC2; blue line), 4-(2- (3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3; green line), 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4; pink line).

Carboxyl-ILs are characterized by absorption bands around 3500 cm⁻¹ associated with the O-H stretch, usually coalesced with the N-H stretch.¹⁰ MC2 shows a smaller enlargement relative to the O-H oscillators, while it presents a relevant enlargement associated to the N-H bond identified in ~3200 cm⁻¹. This suggests that the H-bonds have a more pronounced character in this compound. Hydrogen bonding interactions were observed (in~3590cm⁻¹) between the anions.¹¹ The signals were identified at 3090 cm⁻¹ which is consistent with the deformation of the C-H bonds on the imidazolium ring, as previously published.¹² The stretches identified in range 2629 - 1700 cm⁻¹ refer to the C=C/C=N bonds in imidazolium ring, present in all structures (MC1-4).

The stretching in the 1800-1600 cm⁻¹ region which is assigned to the *v*C-O in COOH bonds of carboxyl-functionalized IL is quite pronounced for all samples. The flexibility of the carboxylic rings allows the adoption of a non-planar conformation and thus, the absorption frequencies approximate long acyclic chains for the ketones (~1715 cm⁻¹).¹³ The absorption band at 1730 cm⁻¹ is assigned to *v*C-O for COOH of carboxyl-functionalized IL. The signal identified at 1460 cm⁻¹ is assigned to CH₂, and that at 1650 cm⁻¹ refers to the C=C and/or C=N bonds.¹⁴ The water molecule has C₂v symmetry with three IR active vibrations modes. From the appearance of combination, vibrational and overtone bands we can, however, observe more than three bands in the IR spectrum of water.¹¹ However, In the elaborated structures (MC1-4) it was not possible to determine the state, and quantify it as has been previously reported¹¹, of water in each sample due to the overlap of bands in the region 1595±1650 cm⁻¹. The stretching observed at 1250 cm⁻¹ refers to the electrostatic interaction between the imidazolium cation and the bromide anions. This stretching is very common in ionic liquids having a torsion angle of 100.05 ° (C-N-C-C) from the imidazole group and allows the formation of hydrogen bonds.¹⁵ The intensity differences for this stretch may be related to the steric hindrance of the structures with phenols (MC2 and MC3), and is more pronounced for the open chains in MC1 and MC4.

Table S3. Key observed vibrational modes (cm⁻¹)and assignment associates of ionic liquids: 2- (3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1), 2- (3-methylimidazolion-1-yl)-etoxy)-carboyl) benzoic-phthalic acid bromide (MC2), 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3), 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4).

Assignment	Spectral Region	Ionic Liquid / Stretch Observed (cm ⁻¹)	References

	(cm ⁻¹)	MC1	MC2	MC3	MC4	
V _(N-H)	3300 - 3500	3345 (m)	3081 <i>(m)</i>	3340 <i>(m)</i>	3401 <i>(m)</i>	10, 13
V _(0-H)	3100 - 3650	3155 <i>(w)</i>	3171 <i>(w)</i>	3181 <i>(w)</i>	3148 <i>(w)</i>	11
asymmetric/symmetric						
V _{(=(C-H))}	3000 - 3100	3096 <i>(m)</i>	3087 (m)	3092 <i>(m)</i>	3085 (m)	17
V _{(C-H)asymmetric} /symmetric	2800 - 3200	2941 <i>(m)</i>	2876 (m)	2966 (m)	2943 (s)	12, 17
V _(BrH)	3590; ~2550	2543 <i>(w)</i>	2518 <i>(w)</i>	2582 <i>(w)</i>	2519 <i>(w)</i>	11
V _(C=N)	1610 - 1680	1727 (vs)	1680 <i>(vs)</i>	1699 (vs)	1727 (vs)	13, 14
V _(C=O)	1680 - 1820					
$V_{(C=C/C=N)imidazolium}$	1500 - 1900	1553 (s)	1570 (s)	1560 (s)	1563 (s)	14, 18
$\mathbf{V}_{ ext{(CC)}}$ aromatic ring chain vibrations	*1580; 1600	-	1581 <i>(m)</i>	1586 <i>(m)</i>	-	17
V _(С-H2)	1460	1386 (m)	1400 <i>(m)</i>	1384 <i>(m)</i>	1372 <i>(m)</i>	17
V _{(С—н} о)	~1250	1146 <i>(vs)</i>	1272 (s)	1274 (s)	1216 (s)	13
V (C-C) alicyclic, aliphatic chain vibrations	1300-600	747/617 <i>(w)</i>	747/635 (s)	759/620 (s)	751/621 <i>(w)</i>	14, 18
Y	1060 1150	1052 (m)	1074 (m)	1075 (m)	1088 <i>(m</i>)	10
V (C-O-C)asym	1060-1150	1053 (11)	1074 (<i>III</i>)	1075 (11)	1088(11)	10
	000.070	1174 (VS)	1146 (11)	1129 (2)	1100 (VS)	10
V (c-o-c)	800-970	819 (w)	824 (<i>w</i>)	830 (w)	826 (<i>w</i>)	42
* V _(C=O)	565	535 (s)	545 (s)	522 (<i>m</i>)	549 (<i>m</i>)	13
$\delta_{\text{(C-C)aliphatic chains}}$	250 - 400	437 (m)	465 <i>(m)</i>	495 (m)	407 <i>(m)</i>	10

The region known as fingerprint (1300-800 cm⁻¹) is consistent with the carbon-carbon, carbon-oxygen, carbonnitrogen stretch. The stretching observed at approximately 565 cm⁻¹ is due to the overtone of the carbonyl.¹³ The vibrational band in the IV-far spectra (<200 cm⁻¹) characterizes a cation-anion interaction between the imidazolium cation and the bromide ions.¹⁶

To achieve complementary information on the nature of intermolecular interactions, and investigate the coordination of LIs with lanthanides, established in the ionogels, we employed Raman spectroscopy that when compared to NMR/FTIR spectroscopy is less sensitive to the presence of water. Vibrational modes related to basic structures of the ionic liquids (stretches reported in Table 1) were observed, owing to the coordination of Eu³⁺ ions (Figures S11-14). A broad band at 3500 cm⁻¹ was also observed which corresponds to the O-H stretch, indicating greater hydrophilicity of the gels compared to ionic liquids. The formation of H-bonding between water and anions in RTILs may have several implications for the properties of RTILs as a solvent, or viscosity due the direct correlation to the strength of these H-bonding interactions.¹¹ The strong character of the bands identified helps to explain the viscosity of the elaborated ionogels. The driving force for the formation of supramolecular ionogels is attributed to the intermolecular hydrogen bonding of imidazolium cations (in 3300 – 3500 cm⁻¹)¹⁰ into networks based on the electrostatic interactions, due the vibrational modes in the region in the IV-far spectra (<200 cm⁻¹).¹⁶ The FTIR results (Figure S11-S14) reveals a typical trend in imidazolium-ionic liquids: in the solid state, they form an extended network

of cations and anions connected together by hydrogen bonds. The monomeric unit is always constituted of one imidazolium cation surrounded by at least three anions and in turn each anion is surrounded by at least three imidazolium cations, as reported previously by Dupont.¹⁹ The strong character of the identified bands helps to explain the viscosity of the elaborated ionogels.



Figure S11. Infrared spectrum for ionic liquid2- (3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1) represented by a black line, and ionogels: $Eu(MC1)_3(H_2O)_3$ by a red line; $Gd(MC1)_3(H_2O)_3$; by a blue line, MC1=2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide.



Figure S12. Infrared spectrum for ionic liquid 2- (3-methylimidazolion-1-yl) etoxy-carboyl benzoic-phthalic acid bromide (MC2) represented by a light blue, and ionogels: $Eu(MC2)_3(H_2O)_2$ by a red line; $Gd(MC2)_3(H_2O)_2$; by a blue line, were MC2= 2- (3-methylimidazolion-1-yl) etoxy) carboyl) benzoic-phthalic acid bromide.



Figure S13. Infrared spectrum for ionic liquid 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3) represented by a green line, and ionogels: $Eu(MC3)_3(H_2O)_2$ by a red line; $Gd(MC3)_3(H_2O)_2$ by a blue line, were MC3= 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide.



Figure S14.Infrared spectrum for ionic liquid 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4) represented by a pink line, and ionogels: and ionogels: $Eu(MC4)_3(H_2O)_3$ by a red line; $Gd(MC4)_3(H_2O)_3$; and by a blue line, were MC4= 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide.

Raman spectroscopy

The Raman spectrum covering the region 70-300 cm⁻¹, as shown in Figure 3, presents the lattice vibrations of structures 2-(3-methylimidazolyl-1-yl)etoxy-4-oxobutanoic acid bromide (MC1), 2-(3-methylimidazolion-1-yl)-etoxy-carboyl benzoic-phthalic acid bromide (MC2), 4-(2-(3-methylimidazolion-1-yl)-methyl-4-oxo-2-phenylbutanoic acid bromide (MC3), 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4). Figures S15-S22 presents the characterization of the active modes in the Raman spectroscopy for the ionogels $Eu/Gd(MC1)_3(H_2O)_3$, $Eu/Gd(MC2)_3(H_2O)_2$, $Eu/Gd(MC3)_3(H_2O)_2$, and $Eu/Gd(MC4)_3(H_2O)_3$.

For the ionogels obtained with MC1 liganting, low intensity peaks are observed, which are associated with the translational vibration of the water molecules at 169 cm⁻¹ for Gd(MC1)₃(H₂O)₃ (blue line in Figure S15), and 137 cm⁻¹ for Eu(MC1)₃(H₂O)₃(wine line in Figure S16).²⁰ For a sample Gd(MC1)₃(H₂O)₃ we see an intense signal at ~400 cm⁻¹ which is attributed to δ (C-C) for aliphatic chains derived from the structure of the ionic liquid.²¹ In the region of 1534-2646 cm⁻¹(for Eu(MC1)₃(H₂O)₃), we see common Raman lines for systems with europium ions.²², while for Gd(MC1)₃(H₂O)₃ typical ionic Raman lines start at 758 and range up to 2579 cm⁻¹.²² For Gd³⁺-ionogel (bue line in Figure S15) transitions are observed at 2948 cm⁻¹, corresponding to the imidazolium cations.²³ In both samples stretches are reported at ~3411 cm⁻¹ which are due to the hydrogen bonds from the imidazolium cation.²³ Comparing the results, we can see that in the ionic liquid we have a peak at 1743 cm⁻¹(medium intensity) associated to the C=O stretch.²¹ In ionogels, this peak is not identified due to the coordination of the lanthanide ion with this point on the ionic liquid structure.

For systems containing 2-(3-methylimidazolion-1-yl)-ethoxy-carboyl benzoic-phthalic acid bromide (MC2), signals are identified for IL structure at ~119 cm⁻¹ (lattice vibrations) and 774 cm⁻¹ (N-H/CH₃(N)CN; v(C-O)aliphatic; v(N-C)).^{24, 25}As previously described²² in the region of 1534 to 2646 cm⁻¹, for Eu(MC2)₃(H₂O)₂, the wine line in Figure S18, we see common Raman lines for systems with europium ions, while for Gd(MC2)₃(H₂O)₂, the blue line in Figure S17, shows typical ion Raman lines at at 758-2579 cm⁻¹. The absence of the signal at 1646 cm⁻¹ (to Eu³⁺/Gd³⁺-MC2) and the unfolding of the signals at 2986/2921 cm⁻¹ (Gd(MC2)₃(H₂O)₂) suggest the coordination of Eu³⁺/Gd³⁺ with the ionic liquid from the C=O terminal. Small signals at ~3464 cm⁻¹indicate the supramolecular interactions from the imidazolium ring.^{23, 26}



Figure S15. Raman spectrum for ionic liquid 2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1) represented by a black line, $Gd(NO_3)_3.6H_2O$ by light blue, and $Gd(MC1)_3(H_2O)_3$ by a blue line.



Figure S16. Raman spectrum for ionic liquid 2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1) represented by a black line, $Eu(NO_3)_3.6H_2O$ by a red line, and $Eu(MC1)_3(H_2O)_3$ by a wine line.



Figure S17. Raman spectrum for ionic liquid 2-(3-methylimidazolion-1-yl) etoxy) carboyl) benzoic-phthalic acid bromide (MC2) represented by a black line, $Gd(NO_3)_3.6H_2O$ by a light blue line, and $Gd(MC2)_3(H_2O)_2$ by a blue line.



Figure S18. Raman spectrum for ionic liquid 2-(3-methylimidazolion-1-yl)etoxy)-carboyl) benzoic-phthalic acid bromide (MC2) represented by a black line, $Eu(NO_3)_3.6H_2O$ by a red line, and $Eu(MC2)_3(H_2O)_2$ by a wine line.

Typical peaks are identified at lattice vibrations²⁷ (~ 130 cm⁻¹) and vCH₃(N) (~1039 cm⁻¹) in samples MC3, Eu/Gd(MC3)₃(H₂O)₂, as well as MC4, and Eu/Gd(MC4)₃(H₂O)₃. The peaks identified at 1596 cm⁻¹ for MC3 are shifted to ~1590 cm⁻¹ in the luminescent materials, as previously described,²⁸ are associated with stretching: v(C=C); v(N=N); and v(C-C) aromatic ring . Considering the Raman spectrum of MC3 (green line in Figure S3) and the spectrum obtained for structure MC4 (pink line in Figure 3) we see, at ~1730 cm⁻¹ the peak associated with C=O.²¹ The intensity of this peak is

greatly reduced in samples containing the lanthanide ions. This suggests the coordination of the lanthanide with the ionic liquids from C=O.



Figure S19. Raman spectrum for ionic liquid 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3) represented by a black line, $Gd(NO_3)_3.6H_2O$ by light blue line, and $Gd(MC3)_3(H_2O)_2$ by a blue line.



Figure S20. Raman spectrum for ionic liquid 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3) represented by a black line, $Eu(NO_3)_3.6H_2O$ by a red line, and $Eu(MC3)_3(H_2O)_2$ by a wine line.



Figure S21. Raman spectrum for ionic liquid 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4) represented by a black line, $Gd(NO_3)_3.6H_2O$ by a light blue, and $Gd(MC4)_3(H_2O)_3$ by a blue line.



Figure S22. Raman spectrum for ionic liquid 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4) represented by a black line, $Eu(NO_3)_3$.6H₂O by a red line, and $Eu(MC4)_3(H_2O)_3$ by a wine line.



SUPPORTING INFORMATION

Table S4. Raman vibrational modes for ionic liquids (MC1-4), gadolinium-complexes (Gd(MC1-4)₃(H₂O)_y) and their assignments. Where: vw= very weak; w= weak; m= medium, s= strong; sh= shoulder; b= band; v= Str= stretch; δ = deformation; bend= bending deformation; ω = wagging; ρ = rocking; v_t = translational vibration; s= symmetric; as= antisymmetric); * = rare earth luminescence.

Region	MC1	GdMC1	MC2	GdMC2	MC3	GdMC3	MC4	GdMC4	Gd(NO ₃) ₃ .6H ₂ O	Attribution	Ref
(cm ⁻¹)	(cm ⁻¹)	(cm-1)	(cm-1)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm-1)	(cm ⁻¹)		
10 - 200	111 (vs)	163 (m)	111 /125(vs)	115/145 (vs)	111 (vs)	120/160 vs	97 (m)	100/156 (vs)	103 <i>(vs)</i>	Lattice vibrations	21
~108									103 <i>(vs)</i>	Ag	22
169-181		169 <i>(m)</i>		170 (m)		170 <i>(m)</i>		179 <i>(w)</i>	181 <i>(vw)</i>	v _t (H ₂ O)	20
~171		142	-							ω(NC) <i>(vw)</i>	29
250 - 400	275 (vw)	309 <i>(vw)</i>	229 (vw)	225 <i>(vw)</i>	265 <i>(vw)</i>	-	279 <i>(vw)</i>	-		$\delta(C = C)$ aliphatic chains (s, 21
	405 <i>(w)</i>	386 (vs)	369 <i>(w)</i>	335 <i>(vw)</i>	375 (vw)	358 (vw)	398 <i>(w)</i>	-			
410 - 600	-	-	438 (m)	422 <i>(vw)</i>	416 <i>(m)</i>	418 <i>(vw)</i>	-	-		H ₂ C N <i>(m),</i>	21, 28
	490 <i>(w)</i>	484 <i>(vw)</i>	488 <i>(w)</i>	489 <i>(w)</i>	480 (vw)	477 <i>(w)</i>	498 <i>(w)</i>			H_3C_{1} N(CH) bond (w),	
	588 (m)	589 <i>(w)</i>	548 (m)	572 <i>(w)</i>	588 (m)	600 <i>(w)</i>	-	-		CH₃bend <i>(m),</i>	
	-	484 (vw)	-	489 <i>(w)</i>	-	477 <i>(w)</i>	-	408/ 491 <i>(w)</i>	398/486 (vw)	symmetric stretching	20, 22

										vibration for Gd ³⁺ ,Bg/ Ag	
Region	MC1	GdMC1	MC2	GdMC2	MC3	GdMC3	MC4	GdMC4	$Gd(NO_3)_3.6H_2O$	Attribution	Ref
(cm ⁻¹)	(cm-1)	(cm-1)	(cm ⁻¹)	(cm-1)	(cm ⁻¹)						
610 - 790	640(<i>w</i>)		638 <i>(w)</i>	638 <i>(w)</i>	624 <i>(m)</i>	657 <i>(w)</i>	598 (m)	-		ω(NH/CH ₃ (N)CN <i>(s)</i>	24, 25, 29
	699 <i>(w)</i>	690 <i>(vw)</i>	-	-	-	-	687 <i>(w)</i>	-		v (C-O) aliphatic (<i>w)</i>	
	749 <i>(w)</i>	754 <i>(vw)</i>	737 (w)	740 <i>(w)</i>	704 <i>(vw)</i>	706 <i>(vw)</i>	747 <i>(w)</i>	707/749 <i>(w)</i>		v (NC) <i>(vw)</i>	
	-	-	747 (m)	-	-	722 (w)	-	-			
	-	-	777 (m)	780 <i>(m)</i>	788 (m)	771 <i>(w)</i>	738 (w)	-			
710 - 730		726 (vw)		726 (vw)		709 (vw)		711 (vw)	711 (vw)	δ(NO3) / vs(NO3)	30
~732									751 <i>(m)</i>	A _g , B _g	22
800 -970	839 <i>(m)</i>	-	807 <i>(w)</i>	-	808 <i>(w)</i>	801 <i>(vw)</i>	798 <i>(w)</i>	-		v (C-O-C) <i>(m)</i>	24
	893 <i>(w)</i>	870 <i>(vw)</i>	887 <i>(vw)</i>	870 <i>(vw)</i>	893 (vw)	850 <i>(w)</i>	887 (vw)	-		$\rho(CH_2)$ rocking (w)	
	998 (vw)	947 <i>(vs)</i>	996 <i>(w)</i>	949 <i>(vw)</i>	973 (vw)		936 (vw)	940 <i>(vw)</i>			
1006 - 1170	1031 <i>(s)</i>	1054 <i>(m)</i>	1044 <i>(vs)</i>	1041 vs	1048 <i>(vs)</i>	1038 <i>(vs)</i>	1031 <i>(m)</i>	1032 <i>(m)</i>		υ(C-O-C) asym <i>(m)</i>	21, 29
	1113 (vw)	1112 <i>(vw)</i>	1180 <i>(w)</i>	1180 <i>(w)</i>	1172 <i>(vw)</i>	1167 <i>(vw)</i>	1108 (vw)	1107 <i>(vw)</i>		v(CC) (w)	
1004-1043									1023/1053 (vs)	A _g , B _g	22
600 - 1300	1250 <i>(bvw)</i>	1237 <i>(vw)</i>	1265 <i>(s)</i>	1260 <i>(s)</i>	1272 (m)	1266 <i>(s)</i>	1255 (bvw)	1254 <i>(vw)</i>		v (C-C) cyclic,	21
										aliphatic chain vibrations (I	m,
1030-1050	1031 <i>(s)</i>	-	1044 <i>(vs)</i>	-	1048 <i>(vs)</i>	-	1031 <i>(m)</i>	-	-	v (CH ₃ (N)) <i>(s)</i>	27
1335-1380	1332 (m)	1382 <i>(m)</i>	1350 <i>(vw)</i>	1328 <i>(w)</i>	1352 <i>(w)</i>	1349 <i>(w)</i>	1340 (msh)	1319 (msh)	1314 <i>(vw)</i>	δ(CH3) <i>(m)</i>	21, 28

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										CH ₃ NCN (<i>m</i>)	
Region	MC1	GdMC1	MC2	GdMC2	MC3	GdMC3	MC4	GdMC4	$Gd(NO_3)_3.6H_2O$	Attribution	Ref
(cm ⁻¹)	(cm-1)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm-1)	(cm-1)	(cm-1)	(cm-1)		
1400 – 1470	1421 <i>(s)</i>	1449 <i>(s)</i>	1425 <i>(vw)</i>	1422 (m)	1431 <i>(s)</i>	1421 <i>(s)</i>	1425 <i>(m)</i>	1409 <i>(m)</i>		$\delta(CH_2)$ (vw),	28
1410 - 1461										δ(CH₃) asym <i>(m);</i>	
										v (N=N) aromatic <i>(m);</i>	
										CH ₃ (N)HCH sym bending	
1500 – 1900;	1571 <i>(m)</i>	-	1578 /	1581 <i>(m)</i>	1591 <i>(s)</i>	1604 <i>(s)</i>	1574 <i>(m)</i>	1574 <i>(m)</i>		v (C=C) <i>(s)</i> ;	21, 28
1550 – 1580;			1604 <i>(s)</i>							v (N=N) aliphatic (m);	
1580, 1600;										v (CC) aromatic ring	
										chain vibrations (s);	
										CH ₂ N/CH ₃ NO	CN .
1526									1526/1626 (wb)	*	22
1610 - 1680	-		1674 <i>(w)</i>		1611		-			v (C=N) <i>(s)</i>	21
~1640	1646 <i>(vw)</i>	1662 <i>(m)</i>	1644 <i>(s)</i>	1634 <i>(m)</i>		1654 <i>(m)</i>	1634 <i>(vw)</i>			δ(H2O) <i>(wb)</i>	21
1500 – 1900;	1735 (m)	-	1795 (vw)	1720 <i>(w)</i>	1730 <i>(s)</i>	1911 wb	1734 (m)	1725 (m)		v (C=C) <i>(s)</i> ;	21
1680 - 1820										v (C=O) <i>(m)</i>	
	-	-	-	-	-	-	-	1911 (wb)	1918 (wb)	*	22
									2531/2602 (wb)	*	22
2550 - 2600	2548 <i>(w)</i>	2572 <i>(w)</i>	2481 <i>(vw)</i>	2580 (mb)	-		2511 <i>(w)</i>	2571 (mb)		v (-N-H) <i>(s)</i>	21

Region	MC1	GdMC1	MC2	GdMC2	MC3	GdMC3	MC4	GdMC4	Gd(NO ₃) ₃ .6H ₂ O	Attribution	Ref
(cm ⁻¹)	(cm⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)						
	2680 <i>(vw)</i>	2677 (vw)	2601 (vw)		2608 (wb)	2588 (mb)	-			*	22
	-	-	2750 <i>(vw)</i>		2748 (vw)		2720 (vw)	2739 (vw)		*	22
2800 - 3000	2832 (vw)	2819 <i>(vw)</i>	2820 (vw)	2881 <i>(vw)</i>	2837 (vw)	2829 (vw)	2870 (vwb)			v (C–H) <i>(s)</i>	23, 26
	2963 (vs)	2897/2936/	2950 (m)	2963 (m)	2963 <i>(vs)</i>	2885 <i>(w)</i>	2963 <i>(vs)</i>	2959 <i>(vs)</i>		vimidazolium cations	
		2975 (s)				2966 <i>(s)</i>					
3000 - 3100	3070 <i>(w)</i>	3008 <i>(m)</i>	3080 <i>(m)</i>	3083 (m)	3067 <i>(s)</i>	3081 <i>(m)</i>	3097 <i>(w)</i>	3085 <i>(w)</i>		v (=(C-H)ring) <i>(s)</i>	23, 26
									3267/3347/	*	22
									3502 (wb)		
3100 - 3650	3165 <i>(wb)</i>	3118 (wb)	3159 (vwb)	3162 <i>(wb)</i>	3165 <i>(m)</i>	3163 <i>(w)</i>	3165 <i>(vw)</i>	3169 <i>(vw)</i>		v (O-H) <i>(w)</i>	21, 29
3300 - 3500	3421 <i>(wb)</i>	3411 (wb)	3428 (vwb)	3408 (wb)	3428 (vwb)	3415 (wb)	3400 <i>(wb)</i>	3425 (wb)		v (N-H) <i>(m)</i>	23, 26

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Table S5. Raman vibrational modes for ionic liquids (MC1-4), europium-complexes (Eu(MC1-4)₃(H₂O)_y), and their assignments. Where: *vw*= very weak; *w*= weak; *m*= medium, *s*= strong; *sh*= shoulder; *b*= band; *v*= Str= stretch; δ = deformation; *bend*= bending deformation; ω = wagging; ρ = rocking; *v_t*= translational vibration; *s*= symmetric; as= antisymmetric); *** = rare earth luminescence.

Region	MC1	EuMC1	MC2	EuMC2	МСЗ	EuMC3	MC4	EuMC4	EuCl ₃ .6H ₂ O	Attribution	Ref
(cm-1)	(cm-1)	(cm-1)	(cm ⁻¹)	(cm-1)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm-1)	(cm-1)		
10 - 200	111 (vs)	-	111 /	-	111 (vs)	125 <i>(vw)</i>	97 (m)	-		Lattice vibrations	21
			125(vs)								
130-181		137							177 <i>(vw)</i>	v _t (H ₂ O)	20
<171	111 (vs)	-	111/	-	111 (vs)	125 (vw)	97 (m)	-		ω(NC) <i>(vw)</i>	29
			125(vs)								
~175									193 <i>(vw)</i>	B _g , A _g	22
250 - 400	275 (vw)	-	229 (vw)	-	265 (vw)	-	279 (vw)	-	-	δ(CC) aliphatic chains (s)	21
	405 <i>(w)</i>	-	369 <i>(w)</i>	-	375 (vw)	-	398 <i>(w)</i>	-	-		
410-600	-	-	438 (m)	-	416 <i>(m)</i>	-	-	-	-	H ₂ CN <i>(m),</i>	21, 28
	490 <i>(w)</i>	-	488 (w)	-	480 (vw)	-	498 <i>(w)</i>	-	-	H_3C N(CH) bond (w),	
	588 (m)	-	548 (m)	-	588 (m)	-	-	-	-	CH_3 bend (m),	
~471		494 (vw)	-	494 (vw)		476 (m)		-	-	symmetric stretching	20, 22
										vibration for Eu^{3+} , A_g	
610 - 790	640 <i>(w)</i>	-	638 <i>(w)</i>	-	624 (m)	-	598 (m)	-	-	ω(NH/CH ₃ (N)CN <i>(s)</i>	24, 25, 29
	699 <i>(w)</i>		-	-	-	-	687 <i>(w)</i>	-	-	v (C-O) aliphatic (<i>w)</i>	
	749 <i>(w)</i>	-	737 <i>(w)</i>	-	704 <i>(vw)</i>	-	747 <i>(w)</i>	-	-	v (NC) <i>(vw)</i>	

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	-	-	747 (m)	-	-	-	-	-	-		
	-	-	777 (m)	-	788 (m)	-	738 (w)	-	-		
Region	MC1	EuMC1	MC2	EuMC2	MC3	EuMC3	MC4	EuMC4	EuCl ₃ .6H ₂ O	Attribution	Ref
(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)		
629-945		-	-	-		-		-	725/851 (vw)	A _g , B _g	22
800 -970	839 (m)	-	807 <i>(w)</i>	-	808 <i>(w)</i>	-	798 <i>(w)</i>	-	-	v (C-O-C) <i>(m)</i>	24
	893 <i>(w)</i>	-	887 <i>(vw)</i>	-	893 (vw)	-	887 <i>(vw)</i>	-	-	$\rho(CH_2)$ rocking (w)	
	998 (vw)	-	996 <i>(w)</i>	-	973 (vw)	-	936 <i>(vw)</i>	-	-		
1030-1050	1031 <i>(s)</i>	-	1044 <i>(vs)</i>	-	1048 <i>(vs)</i>	-	1031 <i>(m)</i>	-	-	ν (CH ₃ (N)) <i>(s)</i>	27
1006 - 1170	1113 (vw)	-	1180 <i>(w)</i>	-	1172 (vw)	-	1108 (vw)	-	-	v (C-O-C) asym <i>(m)</i>	21, 29
										v(CC) (w)	
~1069	-	-	-	-		-		-	1023/1053 (vs)	v(CC) (w) A _g	22
~1069 600 - 1300	- 1250 <i>(bvw)</i>	-	- 1263 <i>(s)</i>	-	1272 (m)	-	1255 (bvw)		1023/1053 (vs) -	v(CC) (w) A _g v (C-C) cyclic,	22 21
~1069 600 - 1300	- 1250 (bvw)	-	- 1263 <i>(s)</i>	-	1272 (m)	-	1255 (bvw)	-	1023/1053 (vs) -	v(CC) (w) A _g v (C-C) cyclic, aliphatic chain vibrations <i>(m)</i>	22 21
~1069 600 - 1300 1314-1380	- 1250 (bvw) 1335 (m)	-	- 1263 (s) 1350 (vw)	-	1272 (m) 1352 (w)	- -	1255 (bvw) 1340 (msh)	-	1023/1053 (vs) - 1314 (vw)	v(CC) (w) A _g v (C-C) cyclic, aliphatic chain vibrations (m) δ(CH3) (m)	22 21 21, 28
~1069 600 - 1300 1314-1380	- 1250 (bvw) 1335 (m)	-	- 1263 (s) 1350 (vw)	-	1272 (m) 1352 (w)	-	1255 (bvw) 1340 (msh)	-	1023/1053 (vs) - 1314 (vw)	v(CC) (w) A _g v (C-C) cyclic, aliphatic chain vibrations (m) δ(CH3) (m) CH ₃ NCN (m)	22 21 21, 28
~1069 600 - 1300 1314-1380 1400 - 1470	- 1250 (bvw) 1335 (m) 1421 (s)	-	- 1263 (s) 1350 (vw) 1425 (vw)	-	1272 (m) 1352 (w) 1412 (s)	-	1255 (bvw) 1340 (msh) 1419 (m)	-	1023/1053 (vs) - 1314 (vw) -	v(CC) (w) A _g v (C-C) cyclic, aliphatic chain vibrations (m) δ(CH3) (m) CH ₃ NCN (m) δ(CH ₂) (vw),	22 21 21, 28 21, 28, 31
~1069 600 - 1300 1314-1380 1400 - 1470 1410 - 1461	- 1250 (bvw) 1335 (m) 1421 (s)	-	- 1263 (s) 1350 (vw) 1425 (vw)	-	1272 (m) 1352 (w) 1412 (s)	-	1255 (bvw) 1340 (msh) 1419 (m)	-	1023/1053 (vs) - 1314 (vw) -	v(CC) (w) A _g v (C-C) cyclic, aliphatic chain vibrations (m) δ(CH3) (m) CH ₃ NCN (m) δ(CH ₂) (vw), δ(CH ₃) asym (m);	22 21 21, 28 21, 28, 31
~1069 600 - 1300 1314-1380 1400 - 1470 1410 - 1461	- 1250 (bvw) 1335 (m) 1421 (s)	-	- 1263 <i>(s)</i> 1350 <i>(vw)</i> 1425 <i>(vw)</i>	-	1272 (m) 1352 (w) 1412 (s)	-	1255 (bvw) 1340 (msh) 1419 (m)	-	1023/1053 (vs) - 1314 (vw) -	v(CC) (w) A _g v (C-C) cyclic, aliphatic chain vibrations (m) δ(CH3) (m) CH ₃ NCN (m) δ(CH ₂) (vw), δ(CH ₃) asym (m); v (N=N) aromatic (m);	22 21 21, 28 21, 28, 31
~1069 600 - 1300 1314-1380 1400 - 1470 1410 - 1461	- 1250 (bvw) 1335 (m) 1421 (s)	-	- 1263 <i>(s)</i> 1350 <i>(vw)</i> 1425 <i>(vw)</i>	-	1272 (m) 1352 (w) 1412 (s)	-	1255 (bvw) 1340 (msh) 1419 (m)	-	1023/1053 (vs) - 1314 (vw) -	v(CC) (w) A _g v (C-C) cyclic, aliphatic chain vibrations (m) δ(CH3) (m) CH ₃ NCN (m) δ(CH ₂) (vw), δ(CH ₃) asym (m); v (N=N) aromatic (m); CH ₃ (N)HCH sym bending	22 21 21, 28 21, 28, 31

JPPORTING INFORMATION							Journal of Materials Chemistry C				
MC1	EuMC1	MC2	EuMC2	MC3	EuMC3	MC4	EuMC4	EuCl ₃ .6H ₂ O	Attribution	Ref	
(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)			
1571 (m)	-	1578 /		1584 <i>(s)</i>	-	1574 (m)	1547 m		v (C=C) <i>(s)</i> ;	21, 28	
		1624 <i>(s)</i>							v (N=N) aliphatic <i>(m)</i> ;		
									v (CC) aromatic ring		
									chain vibrations (s);		
									CH ₂ N/CH ₃ NCN (s)		
	1535 <i>(w)</i>		1521 (m)		1517 <i>(m)</i>		1544 (w)	1551 <i>(w)</i>	*	22	
-	-	1674 <i>(w)</i>	-	1611	-	-	-	-	v (C=N) <i>(s)</i>	21	
1646 <i>(vw)</i>		1644 <i>(s)</i>	-		-	1634 <i>(vw)</i>	-	-	δ(H2O) <i>(wb)</i>	21	
1743 (m)	-	1795 <i>(vw)</i>	-	1726 <i>(s)</i>	-	1734 (m)	-	-	v (C=C) <i>(s)</i> ;	21	
									v (C=O) <i>(m)</i>		
-	1865/	-	1773 (s)	-	1895 <i>(sb)</i>	-	1842 <i>(m)</i>	1843 (m)	*	22	
	1895 <i>(s)</i>										
-	1962 (m)	-	1962 (m)	-	-	-	1908/	1943 (mb)	*	22	
							1990 (m)				
-	2487 (s)	-	2490 (vs)	-	-	-		2487 (vs)	*	22	
-	2557 (vs)	-	2557 <i>(vs)</i>		2570 <i>(vs)</i>	-	2570 (vs)	2629 (m)	*	22	
	INFORMATIO MC1 (cm ⁻¹) 1571 (m) - 1646 (vw) 1743 (m) -	MC1 EuMC1 (cm ⁻¹) (cm ⁻¹) 1571 (m) - 1535 (w) - 1535 (w) - 1646 (vw) - 1743 (m) - - 1865/ 1895 (s) - - 1962 (m) - 2487 (s) - - - -	MC1 EuMC1 MC2 (cm ⁻¹) (cm ⁻¹) (cm ⁻¹) 1571 (m) - 1578 / 1571 (m) - 1624 (s) 1571 1535 (w) 1624 (s) - 1535 (w) 1624 (s) - 1535 (w) 1644 (s) 1646 (vw) - 1644 (s) 1743 (m) - 1795 (vw) - 1865/ - - 1895 (s) - - 1962 (m) - - 2487 (s) - - 2557 (vs) -	MC1 EuMC1 MC2 EuMC2 (cm ⁻¹) (cm ⁻¹) (cm ⁻¹) (cm ⁻¹) 1571 (m) - 1578 / - 1571 (m) - 1624 (s) - 1624 (s) - 1521 (m) - - 1535 (w) - 1521 (m) - 1535 (w) - 1521 (m) - 1535 (w) - 1521 (m) - - 1644 (s) - 1646 (vw) - 1644 (s) - 1743 (m) - - 1795 (vw) - - 1865/ - 1962 (m) - - 1962 (m) - 1962 (m) - - 2487 (s) - 2490 (vs) - - 2557 (vs) - 2557 (vs) - -	INFORMATION MC1 EuMC1 MC2 EuMC2 MC3 (cm ⁻¹) 1571 (m) - 1578 / (cm ⁻¹) 1584 (s) 1571 (m) - 1578 / Issa 1584 (s) 1571 (m) - 1578 / Issa 1584 (s) 1521 (m) - 1521 (m) Issa 1584 (s) - 1535 (w) 1574 (w) - 1611 1646 (vw) - 1644 (s) - 1611 1743 (m) - 1795 (vw) - 1726 (s) - 1865/ - 1773 (s) - - 1962 (m) - 1962 (m) - - 2487 (s) - 2490 (vs) - - 2557 (vs) - 2557 (vs) -	INFORMATION MC1 EuMC1 MC2 EuMC2 MC3 EuMC3 (cm ⁻¹) 1571 (m) - 1578 / (cm ⁻¹) 1584 (s) - 1571 (m) - 1578 / IS84 (s) - - 1571 (m) - 1524 (s) IS84 (s) - - 1571 (m) - 1521 (m) IS84 (s) - - 1525 (w) IS21 (m) IS17 (m) - - - - 1535 (w) IS21 (m) IS11 - - - 1535 (w) IS21 (m) IS11 - - - 1644 (s) - - - - 1743 (m) - 1795 (w) - 1726 (s) - - 1885 (s) - - - - - 192 (m) - 192 (m) - - <	INFORMATION Journal MC1 EuMC1 MC2 EuMC2 MC3 EuMC3 MC4 (cm ⁻¹) 1571 (m) - 1578 / IS84 (s) - 1574 (m) 1571 (m) - 1578 / IS84 (s) - 1574 (m) 1521 (m) IS84 (s) - 1574 (m) - 1574 (m) - 1535 (w) IS21 (m) IS177 (m) - 1634 (w) - 1674 (w) - 1611 - - 1646 (vw) 1644 (s) - 1634 (w) 1734 (m) 1743 (m) - 1795 (w) - 1726 (s) - 1734 (m) - 1865/ - 1773 (s) - 1895 (sb) - - - 1962 (m) - 1962 (m) - - - - - 2487 (s) - 2490 (vs) <	INFORMATION LuMC1 MC2 EuMC2 MC3 EuMC3 MC4 EuMC4 (cm ⁻¹) (cm ⁻¹)	INFORMATION Journal of Materials Chemistry C MC1 EuMC1 MC2 EuMC2 MC3 EuMC3 MC4 EuMC4 EuCl3, 6H,O (cm ⁻¹) (cm ⁻¹) <td>INFORMATION MC1 MC2 EuMC2 MC3 EuMC3 MC4 EuMC4 EuG.6H₂O Attribution (cn^{-1}) (cn^{-1})</td>	INFORMATION MC1 MC2 EuMC2 MC3 EuMC3 MC4 EuMC4 EuG.6H ₂ O Attribution (cn^{-1})	

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Region	MC1	EuMC1	MC2	EuMC2	MC3	EuMC3	MC4	EuMC4	EuCl ₃ .6H ₂ O	Attribution	Ref
(cm ⁻¹)											
2550 - 2600	2548 <i>(w)</i>	-	2481 (vw)	-	2584	-	2511 (w)	-	-	υ(-N-H) <i>(s)</i>	21
	2680 <i>(vw)</i>	2610 (vs)	2601 <i>(vw)</i>	2605 <i>(s)</i>	2608 (wb)	-	-	2679 (m)	-	*	22
	-	-	2750 <i>(vw)</i>	-	2748 (vw)	-	2720 <i>(vw)</i>	-	-	vas (C-H) <i>(s)</i>	31
2800 - 2870	2832 (vw)	-	2820 <i>(vw)</i>	-	2837 <i>(vw)</i>	-	2870 (vwb)	-	-	vsym (C–H) <i>(s)</i>	31
2950-2963	2963 (vs)	-	2950 <i>(m)</i>	-	2963 <i>(vs)</i>	-	2963 <i>(vs)</i>	-	-	v sym (N)CH ₃	31, 32
										vimidazolium cations	
3000 - 3100	3070 <i>(w)</i>	-	3080 <i>(m)</i>	-	3067 <i>(s)</i>	-	3097 <i>(w)</i>	-	-	v (=(C-H)ring) <i>(s)</i>	23, 26
	-		-	-		-		-	-		
	-	3441 (wb)	-	3431 (wb)		3418 (wb)		3435 (wb)	3267/3347/	*	22
									3502(wb)		
3100 - 3650	3165 <i>(wb)</i>	-	3159 (vwb)	-	3165 <i>(m)</i>	-	3165 <i>(vw)</i>	-	-	v _{as} (O-H) <i>(w)</i>	21, 29
3300 - 3500	3421 (wb)	3444 (w)	3428 (vwb)	-	3428 (vwb)	-	3400 (wb)	-	-	v (N-H) <i>(m)</i>	23, 26

SUPPORTING INFORMATION

Physical-chemical properties

The more branched the chain of IL, less pronounced are the intermolecular interactions. Thus, there is a lower structural packaging and a lower melting point. The higher melting points are associated with the MC1 and MC4 structures (21° C and 20° C, respectively). The structures have aliphatic chains between the ester and the carboxylic acid terminus. In the MC2 and MC3 samples, which have a phenyl structure and which hinder structural packaging at lower melting points (19° C). These melting points are explained by the interactions between cation and anion, hydrogen bonding, van der Waals interactions and the distribution of charge. However, the melting point of the IL can be reduced at below-room temperature, e.g. the substitution of the methyl- by an ethyl-group in the 1-methylimidazolium cation, resulting in a melting point below 20° C.³³ The melting points of the ionic liquids are set out in Table 4. A wide variety of solvents were found to exhibit high solubilities.

Table S6. Physico-chemical properties and miscibility of the 1-methylimizodalium carboxylate-ILswith several solvents. Where: 1 = Water; 2 = Acetone; 3 = dichloromethane; 4 = dimethylformamide; 5 = dimethylsulfoxide; 6 = Ethanol; h = high; m = medium; and l = low.

						Misci	bility		
Name of structure	Molecular form	Molar Mass (gmol ^{.1})	Mp (°C)	1	2	3	4	5	6
1{2-[3-carboxypropanoyl)oxy]ethyl}-3- methyl-1H-imidazol-3-ium acid bromide (MC1)	$C_{10}H_{15}N_2O_4Br$	307.1385	21	h	1	I	m	т	h
1{2-[2-carboxybenzoyl)oxy]ethyl}-3- methyl-1H-imidazol-3-ium (MC2)	$C_{14}H_{15}N_2O_4Br$	355.1785	19	h	1	1	т	h	h
1{2-[2-carboxybenzene)oxy]ethyl}-3- methyl-1H-imidazol-3-ium acid bromide (MC3)	$C_{15}H_{17}N_2O_4Br$	383.2301	19	h	1	1	h	h	h
1{2-[3-carboxybutanoyl)oxy]ethyl}-3- methyl-1H-imidazol-3-ium acid bromide (MC4)	$C_{12}H_{19}N_2O_4Br$	349.2159	20	h	1	I	т	h	h

All of the 1-methylimizodalium carboxylate ILs prepared were miscible with water, and other polar solvents (for example, acetonitrile and ethanol). This is similar to other hydrophilic ILS.³⁵ The ILs were not miscible with dichloromethane, or acetone, at room temperature. Again, this behaviour closely resembles that of imidazolium chlorides.³⁵ We provide the evidence of chemical stability the four ionic liquids in water and common organic solvents by UV-vis and NMR measurements. The obtained results shows the peaks associated with the IL-carboxylate structures previously described. Its noteworthy, even in the low miscibility under some solvents, the MCx are stable in several solvents which increases the possibility of ILs applications. Experimental Studies on the physicochemical properties, such densities (ρ), viscosities (η), and refractive indices (n) have been conducted by our research group. An understanding of the safe operating temperatures of an ionic liquid is crucial. Because this,

we have provided a thermophysical characterization composed of Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and melting point.

Thermogravimetric analysis (TGA)

Thermogravimetric Analysis (TGA) was obtained on a PerkinElmer Thermogravimetric Analyzer, using platinum sample pans with a 6 mm diameter. Scanning TGA experiments were carried out for compounds the range of $30 - 700^{\circ}$ C. Between 4 - 8 mg of the ionic liquid was measured into the platinum pan. All samples were dried thoroughly under high vacuum prior to TGA measurement. However, during the transferal of the hygroscopic ionic liquids into the TGA pan, a small quantity of water (\leq 7 weight %) would have been absorbed from the atmosphere.

Thermogravimetric analysis was performed under a N_2 atmosphere, at a rate of 5 °C min⁻¹ and is shown in Figure S23. The decomposition of the carboxyl-functionalized IL occurs in two steps for MC4 and three weight losses to MC1/MC2/MC3. The first event is attributed to moisture loss up to 150°C (~7% to MC1 and MC4; 5% to MC2 and MC3). This moisture loss is most significant for samples with higher water uptake, as shown by the broadband at 3500 cm⁻¹ in the FTIR spectra, and must be associated with the structural availability for formation of hydrogen bonds in MC1 and MC4. MC4 degradation occurs in only one step (95%), while for the other samples the first event is followed by a loss of the methyl group, decomposition of the imidazolium structure, and exit of the bromide (~226°C). Finally, the alkyl structure (MC1 in 362 °C) decomposed, and structures with benzene –MC2 and MC3– the chain is collapsed at ~322°C.



Figure S23. Thermalgravimetric analysis for ionic liquids: 2- (3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1; black line); 2- (3-methylimidazolion-1-yl)-etoxy)-carboyl) benzoic-phthalic acid bromide (MC2; blue line); 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3; green line), and 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4; pink line).

The thermal stability of the soft materials was investigated by Thermogravimetric (TG) analysis. The slowly decomposition of the ILs after incorporation with lanthanides can improve the thermal stability of the organic compound as observed from the TG profiles (Fig. 3). Five decomposition stages can be observed in the TG curve. The first weight loss below 223 °C is attributed to the release of water molecules, which is determined to be 7% in $Eu(MC1)_3(H_2O)_y/Eu(MC3)_3(H_2O)_y/Eu(MC4)_3(H_2O)_y$ and 12% in $Eu(MC2)_3(H_2O)_y$. According to TGA, the system prepared contains 3 water molecules to $Eu(MC1)_3(H_2O)_3/Eu(MC4)_3(H_2O)_3$, and 2 to $Eu(MC2)_3(H_2O)_2/Eu(MC3)_3(H_2O)_2$. The

second event reported a collapse of the 1- methyl imidazolium structure added a to the degradation of the alkyl structure and release of bromide ions, in one step to $Eu(MC1)_3(H_2O)_3$ (55%), whereas two steps were needed for $Eu(MC2)_3(H_2O)_2$ (22% and 32%), $Eu(MC3)_3(H_2O)_2$ (14% and 35%), and $Eu(MC4)_3(H_2O)_3$ (11% and 34%). The last event reports exit of the nitrates (as first observed by Stern *et al.*⁴¹) as well as the degradation of the carboxylate terminal, and formation of europium oxide.



Figure S24. Thermalgravimetric analysis for ionogels based on ionic liquids. $Eu(MC1)_3(H_2O)_3$ represented by a black line, were MC1= 2- (3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide; $Eu(MC2)_3(H_2O)_2$ by a blue line, were: MC2=2- (3-methylimidazolion-1-yl)-etoxy)-carboyl) benzoic-phthalic acid bromide; $Eu(MC3)_3(H_2O)_2$ by a green line, were MC3= 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide; and $Eu(MC4)_3(H_2O)_3$ by a pink line, were MC4=3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide.

UV-vis Spectrophotometry

The carboxylate-ionic liquids were dissolved in cuvette of 1 cm pathlength with distilled water, enabling the measurement of the absorption spectra (Figure 4) at room temperature.



Figure S25. Absorption spectra of 1-Methylimidazole (Aldrich) represented by wine line, monocarboxylate ionic liquids 2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1; by black line), 2-(3-methylimidazolion-1-yl)-etoxy-carboyl benzoic-phthalic acid bromide (MC2; by blue line), 4-(2-(3-methylimidazolion-1-yl)-methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3; by green line), 3,3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4; by pink line). Measurements obtained with a cuvette of 1 cm pathlength and at ambient temperature.



Figure S26. Absorption spectra for Eu-complexes: $Eu(MC1)_3(H_2O)_3$ represented by a black line, $Eu(MC2)_3(H_2O)_2$ by a blue line, $Eu(MC3)_3(H_2O)_2$ by a green line, and $Eu(MC4)_3(H_2O)_3$ by a pink line. Measurements obtained with a cuvette of 1 cm pathlength and at ambient temperature.

Photoluminescence Characterization





Figure S27. Excitation (dotted line) and emission (full line) spectra for ionic liquid 2-(3-methylimidazolyl-1-yl) etoxy-4-oxobutanoic acid bromide (MC1) in black line (λ_{em} = 440 nm and λ_{ex} = 361 nm) and, Gd(MC1)₃(H₂O)₃ in blue line (λ_{em} = 425 nm and λ_{ex} = 350 nm). Measures performed at steady state, and at room temperature. Stokes displacement identified: 79 nm. Ligand change caused by coordination: $\Delta\lambda$ Ex = 24 nm; $\Delta\lambda$ Em = 16 nm.



Figure S28. Excitation (dotted line) and emission (full line) spectra for ionic liquid 2-(3-methylimidazolyl-1-yl) etoxy)carboyl) benzoic-phthalic acid bromide (MC2) in black line (λ_{em} = 440 nm, λ_{ex} = 350 nm) and, Gd(MC2)₃(H₂O)₂ in blue line (λ_{em} = 400 nm; λ_{ex} = 330 nm).All measures were performed at steady state, and at room temperature. Stokes displacement identified: 104 nm. Ligand change caused by coordination: $\Delta\lambda$ Ex = 11 nm; $\Delta\lambda$ Em = 38 nm.



Figure S29.Excitation (dotted line) and emission (full line) spectra for for ionic liquid 4-(2-(3- methylimidazolyl-1-yl)methyl)-4-oxo-2-phenylbutanoic acid bromide (MC3) represented by a black line (λ_{em} = 396 nm, λ_{ex} = 327 nm), and Gd(MC3)₃(H₂O)₂ by a dark cyan line (λ_{em} = 390 nm; λ_{ex} = 320 nm). All measures were performed at steady state, and at room temperature. Stokes displacement identified: 96 nm. Ligand change caused by coordination: $\Delta\lambda$ Ex = 21 nm; $\Delta\lambda$ Em (nm) = 54 nm.



Figure S30.Excitation (dotted line) and emission (full line) spectra ionic liquid 3, 3-dimethyl-5-(2-(3-methylimidazolyl-1-yl)-ethoxy)-5-oxopentanoic acid bromide (MC4) in black line (λ_{em} = 410 nm, λ_{ex} = 360 nm) and, in blue line for Gd(MC4)₃(H₂O)₃ (λ_{em} = 388 nm; λ_{ex} = 326 nm). All measures were performed at steady state, and at room temperature. Stokes displacement identified: 86 nm. Ligand change caused by coordination: $\Delta\lambda$ Ex = 16 nm; $\Delta\lambda$ Em = 39 nm.

In Figures S31-34, it was noteworthy that the maximum excitation peaks were broadened and gradually red-shifted from 394 nm (in $Eu(MC1)_3(H_2O)_3$) to 395 nm (in $Eu(MC3)_3(H_2O)_2$) with the growth of the alkyl chain length, reflecting the reduction of covalence of Eu-O bonds in complexes, as has been previously reported. ³⁷

For all Eu³⁺-complexes, the emission spectrum obtained with an excitation wavelength of 395 nm contains sharp emission lines assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J= 0–4) transitions. Similar emission spectra (shown in Figure S35) are obtained upon excitation with a wavelength of 350 nm to Eu(MC1)₃(H₂O)₃; 350 nm to Eu(MC2)₃(H₂O)₂; 350 nm to Eu(MC3)₃(H₂O)₂; and 350 nm to Eu(MC4)₃(H₂O)₃. Five sharp emission lines at (approximately) 579, 593, 617, 650, and 696 nm arising from the transitions between ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ crystal-field components (J = 0, 1, 2, 3, 4) are clearly seen, which also indicates the energy transfer from ionic liquid (MC1-4) to Europium ion.



Figure S31. Excitation (black line; λ_{em} = 619 nm) and emission (red line; λ_{ex} = 394 nm) for Eu(MC1)₃(H₂O)₃;. All measures were performed at steady state, and at room temperature.

The excitation spectrum obtained by monitoring the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ line at 614 nm shows a broad band, which is overlapped with the absorption spectrum and can be ascribed to the absorption of the MC2 moieties. The relatively weak broadband at 333 nm, when compared to strong peaks at 450-550 nm (corresponding to intra-4*f* transitions of Eu³⁺), is due to the energy transfer from ligand (MC2) to central metal ions.

There are multiplicities of the transitions: 1 for ${}^5D_0 \rightarrow {}^5F_0$ transition; 3 for ${}^5D_0 \rightarrow {}^5F_1$ transition; 5 for ${}^5D_0 \rightarrow {}^5F_2$ transition; 7 for ${}^5D_0 \rightarrow {}^5F_3$ transition; 9 for ${}^5D_0 \rightarrow {}^5F_4$ transition. Thus, we can infer that the point group for the environment of symmetry around the europium ion is C_{2v} . This supports the hypothesis, represented by the transition ${}^5D_0 \rightarrow {}^5F_0$, that the chemical environment around Eu³⁺ must be of low symmetry. The transition ${}^5D_0 \rightarrow {}^5F_2$ (more intense for all systems) represents 64% for Eu(MC1)₃(H₂O)₃; 70% for Eu(MC2)₃(H₂O)₂; 70% Eu(MC2)₃(H₂O)₂ and 66% for Eu(MC4)₃(H₂O)₃ of the integrated emission spectrum. This transition is the main one responsible for the red colour observed in the photoluminescence of the ionogels.



Figure S32. Excitation (black line; $\lambda_{em} = 614$ nm) and emission (red line; $\lambda_{ex} = 394$ nm) for Eu(MC2)₃(H₂O)₂. All measures were performed at steady state, and at room temperature.



Figure S33. Excitation (black line; $\lambda_{em} = 614$ nm) and emission (red line; $\lambda_{ex} = 395$ nm) for Eu(MC3)₃(H₂O)₂. All measures were performed at steady state, and at room temperature.



Figure S34. Excitation (black line; λ_{em} = 617 nm) and emission (red line; λ_{ex} = 394 nm) for Eu(MC4)₃(H₂O)₃. All measures were performed at steady state, and at room temperature.



Figure S35. Emission spectra for Eu-complexes: Eu(MC1)₃(H₂O)₃ represented by a black line (obtained at λ_{ex} = 361 nm), Eu(MC2)₃(H₂O)₂ by a red line (obtained at λ_{ex} = 350 nm),Eu(MC3)₃(H₂O)₂ by a wine line (obtained at λ_{ex} = 327 nm), and Eu(MC4)₃(H₂O)₃ by a gray line (obtained at). All measures were performed at steady state, and at room temperature.

The lifetime of Eu³⁺-ionogels are determined from excitation in Eu³⁺ (${}^{7}F_{0} \rightarrow {}^{5}L_{6}$ transition). Decay curves (showed in Figure S36) can be wellfitted with monoexponential function.



Figure S36. In red circles: Exponential decay curves for: (A) $Eu(MC1)_3(H_2O)_3$; (B) $Eu(MC2)_3(H_2O)_2$; (C) $Eu(MC3)_3(H_2O)_2$; and (D) $Eu(MC4)_3(H_2O)_3$. Excitation and emission wavelength for each measure: (A) λ_{em} = 619 nm, λ_{ex} = 394 nm; (B) λ_{em} = 614 nm, λ_{ex} = 394 nm; (C) λ_{em} = 614 nm, λ_{ex} = 395 nm; and (D) λ_{em} = 617 nm, λ_{ex} = 394 nm. In black line: fit to monoexponential decay curve.

The lifetime of Eu³⁺-ionogels are determined from excitation in ionic liquid ($\pi \rightarrow \pi^*$ transition). Decay curves (shown in Figure S37) can be wellfitted to the monoexponential function.



Figure S37. In red circles: Exponential decay curves for: (A) $Eu(MC1)_3(H_2O)_3$; (B) $Eu(MC2)_3(H_2O)_2$; (C) $Eu(MC3)_3(H_2O)_2$; and (D) $Eu(MC4)_3(H_2O)_3$. Excitation and emission wavelenght for each measure: (A) λ_{em} = 619 nm, λ_{ex} = 361 nm; (B) λ_{em} = 614 nm, λ_{ex} = 350 nm; (C) λ_{em} = 614 nm, λ_{ex} = 327 nm; and (D) λ_{em} = 617 nm, λ_{ex} = 326 nm. In black line: fit to monoexponential decay curve.

Photostability of the Eu³⁺-complexes were evaluated by monitoring the emission/excitation spectra intermittently under continuous exposure to UV irradiation by different absolute doses (0, 0.5 and 1.0 J). Emission and excitation spectra are reported in figures Sx-Sy. For the expositions at UV radiation we used TL-200 Ultraviolet Translinker/Crosslinker UVP that provides exposure in absolute controlled doses. UVA (365 nm) and UVB (302 nm) lamps are used with 8 watts each. Under UV exposure (365 nm and 320 nm) the luminescence intensities of the intraconfigurational Eu³⁺ transitions suffer insignificant changes, as observed in Figures x.



Figure S38. Excitation (black line) and emission (red line) spectra for Eu(MCX)₃(H₂O)_y. All measures were performed at steady state, and at room temperature. Measurements performed with the same sample over different absolute doses of UVA radiation (365 nm): 0, 0.5 and 1.0 J. Eu(MC1)₃(H₂O)₃: λ_{em} = 619 nm and λ_{ex} = 394 nm. Eu(MC2)₃(H₂O)₂: λ_{em} = 614 nm and λ_{ex} = 394 nm. Eu(MC3)₃(H₂O)₂: λ_{em} = 614 nm and λ_{ex} = 395 nm. Eu(MC4)₃(H₂O)₃: λ_{em} = 617 nm and λ_{ex} = 394 nm.



Figure S39. Excitation (black line) and emission (red line) spectra for Eu(MCX)₃(H₂O)_y. All measures were performed at steady state, and at room temperature. Measurements performed with the same sample over different absolute doses of UVB radiation (320 nm): 0, 0.5 and 1.0 J. Eu(MC1)₃(H₂O)₃: $\lambda_{em} = 619$ nm and $\lambda_{ex} = 394$ nm. Eu(MC2)₃(H₂O)₂: $\lambda_{em} = 614$ nm and $\lambda_{ex} = 394$ nm. Eu(MC3)₃(H₂O)₂: $\lambda_{em} = 614$ nm and $\lambda_{ex} = 395$ nm. Eu(MC4)₃(H₂O)₃: $\lambda_{em} = 617$ nm and $\lambda_{ex} = 394$ nm.

We checked the photostability curves of these novel compounds. All elaborated complexes presented good photostability in comparison with the compounds with the several types of ligands. It is worth mentioning that the photostability of these compounds at different excitation wavelengths by using a TL-200 Ultraviolet Translinker/Crosslinker UVP (much more intense than the UV radiation from the Sun). We, therefore, conclude that under UV Sun exposure their stability should be even better. By the intensity of the ${}^{5}D_{0}{}^{-7}F_{2}$ transition we elaborated the graph that provide evidence of photostability to systems against UV radiation.



Figure S40 Photostability curves of Eu(MCx)₃(H2O)_y by monitoring the integrated area of to the ${}^{5}D_{0}{}^{-7}F_{2}$ transition of the Eu³⁺ ion. All curves were recorded at room temperature under irradiation with a 450W Xenon lamp. Emission spectra obtained at steady state, and at room temperature. Measurements performed with the same sample over different absolute doses (0, 0.5 and 1.0 J). of UVA (365 nm) and UVB radiations (320 nm). Complexes and wavelengths used in photoluminescence analysis: Eu(MC1)₃(H₂O)₃, $\lambda_{ex} = 394$ nm; Eu(MC2)₃(H₂O)₂, $\lambda_{ex} = 394$ nm; Eu(MC3)₃(H₂O)₂, $\lambda_{ex} = 395$ nm; Eu(MC4)₃(H₂O)₃, $\lambda_{ex} = 394$ nm.

We studied photostability by comparing the measurements performed in the same sample over three years (2016, 2017 and 2018). The emission and excitation spectra are reported in Figure S41 for all coordination systems. Eu–complexes showed great chemical and photostability to present exactly the same spectral emission/excitation even three year after the synthesis of the ionogels.



Figure S41. Excitation (black line) and emission (red line) spectra for Eu(MCX)₃(H₂O)_V. All measures were performed at steady state, and at room temperature. Measurements performed with the same sample over three years (2016, 2017 and 2018). Eu(MC1)₃(H₂O)₃: λ_{em} = 619 nm and λ_{ex} = 394 nm. Eu(MC2)₃(H₂O)₂: λ_{em} = 614 nm and λ_{ex} = 394 nm. Eu(MC3)₃(H₂O)₂: λ_{em} = 614 nm and λ_{ex} = 395 nm. Eu(MC4)₃(H₂O)₃: λ_{em} = 617 nm and λ_{ex} = 394 nm.

Preliminary measures of absolute emission quantum yields were performed at room temperature using a system (C9920-02, Hamamatsu) with a 150 W xenon lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as the sample chamber, and a multichannel analyzer for signal detection. The method is accurate to within 10%. The determined absolute quantum yield and wavelength used in excitation are shown in Table S8.The absolute quantum yield reported in this work for Eu(MC3)₃(H₂O)₂ was 83%,much higher than when compared to luminescent gels recognized as high emission performance reported in the literature.³⁸

Sample description	λ _{exc} (nm)	Φ (%)
MC1	348	1
MC2	340	1
Eu(MC2) ₃ (H ₂ O) ₂	394	27
	340	7
Eu(MC3) ₃ (H ₂ O) ₂	394	12
	380	10

Table S8. Preliminary measures of absolute emission quantum yields for Ionic Liquids (MC1 and MC2) and complexes $(Eu(MC2)_3(H_2O)_2 \text{ and } Eu(MC3)_3(H_2O)_2).$

Based on the methodology previously reported³⁹, we calculated the efficiency of sensitization for the liganting MC2 and MC3. The results were 26% and 83%, respectively. Thus, the high quantum yield observed for these complexes seems to be due to the calculated high yield energy transfer from these various ligand states to the quasi-resonant Eu(III) energy levels (Figure 6 shows ionic liquid energy levels when compared with europium ones).

Computational Modelling

Computational methodology employed in this work has already been well established in the literature and its main objective is to provide data for a detailed study of photoluminescence for the most diverse materials.⁴⁰⁻⁴³ Structures of the ionogels were optimized via a Sparkle/PM7 model. The theoretical structure of the Eu-complexes presents the metallic centre coordinated with nine oxygen atoms (to Eu(MC1)₃(H₂O)₃/Eu(MC4)₃(H₂O)₃ complexes) or eight oxygen atoms (to $Eu(MC2)_3(H_2O)_2$ and $Eu(MC3)_3(H_2O)_2$ complexes), where six oxygen are composed of three IL ligands in the form of a chelating coordination compound, and two coordinating water molecules in case of $Eu(MC2)_3(H_2O)_2/Eu(MC3)_3(H_2O)_2$ structures or three coordinating water molecules to EuMC1/EuMC4 complexes. These numbers of water molecules agree with those predicted by thermogravimeric analysis. Figures of coordination geometries of complexes Eu(MC1)₃(H₂O)₃, Eu(MC3)₃(H₂O)₂, and Eu(MC4)₃(H₂O)₃ are available in Figures S38, S39 and S41, respectively. The ligand coordination comes from its carboxylate group in chelating coordination, as predicted by FTIR analysis. The coordination polyhedron is organized in a distorted symmetry bicapped trigonal prism, which indicates that the arrangement in point group symmetry is to C_{2V}. This symmetry require sp³d³f hybrids and is a common coordination polyhedra for coordination with numbers eight or nine.⁴⁴ The proposed symmetry is consistent with the estimate by the emission spectra of all compounds. The distances between the metal center and the oxygen atoms from the ionic liquid and coordinated water are shown in TablesS9-S11. These distances are in agreement with values reported in the literature for hydrated complexes of lanthanides,45 coordination polymers based on carboxylate ligands and carboxylate complexes. 46, 47



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Figure S42. (A) Ground State solid geometry calculate by Sparkle/PM7 model for $Eu(MC1)_3(H_2O)_3$. (B) Individual coordination polyhedron is organized in a distorted symmetry bicapped trigonal prism, which indicates that the arrangement in point group symmetry is C_{2V} .



Figure S43. (A) Ground State solid geometry calculate by Sparkle/PM7 model for $Eu(MC2)_3(H_2O)_2$. (B) Individual coordination polyhedron is organized in a distorted symmetry bicapped trigonal prism, which indicates that the arrangement in point group symmetry is C_{2V} .



Figure S44. (A) Ground State solid geometry calculate by Sparkle/PM7 model forEu(MC3)₃(H₂O)₂. (B) Individual coordination polyhedron is organized in a distorted symmetry bicapped trigonal prism, which indicates that the arrangement in point group symmetry is C_{2v} .



Figure S45. (A) Ground State solid geometry calculate by Sparkle/PM7 model forEu(MC4)₃(H₂O)₃. (B) Individual coordination polyhedron is organized as a distorted symmetry bicapped trigonal prism, which indicates that the arrangement in point group symmetry is C_{2v} .

The distances between the metal center and the oxygen atoms from the coordinated water are in agreement with values reported in the literature for hydrated complexes of lanthanides.⁴⁵ The metal–ligand distance of O-donors

from the ionic liquids are reported in Table S9 for $Eu(MC1)_3(H_2O)_3$, Table S10 for $Eu(MC2)_3(H_2O)_2$, Table S11 for $Eu(MC3)_3(H_2O)_2$, and Table S12 for $Eu(MC4)_3(H_2O)_3$. It is possible to observe that the RL values, i.e., the distance from the donor state (from organic ligand) in relation to the nucleus formed by the Eu^{3+} ion, are somewhat higher for the triplet state than those determined for the singlet state.

Table S9. Selected RL distance, bond lengths (Å) and bond angles (°) for $Eu(MC1)_3(H_2O)_3$ (optimized geometry via PM7 Model).

RL distances (Å)	Atoms	R distances (Å)	theta	phi
			(°)	(°)
Singlet: 4.9438	Eu-010	2.4757	54.73	34.25
Triplet: 6.3029	Eu-016	2.5092	106.54	169.08
	Eu-017	2.4817	75.88	262.77
	Eu-012	1.3171	24.92	162.46
	Eu-O105	2.5362	133.56	324.57
	Eu-O11	2.5435	88.37	338.24
RL distances (Å)	Atoms	R distances (Å)	theta	phi
			(°)	(°)
	Eu-O2	2.5163	149.15	98.87
	Eu-O3	2.5623	104.55	80.23
	Eu-O4	2.4895	133.35	233.82

Figure S46. Chemical environment around the europium ion in $Eu(MC1)_3(H_2O)_3$.

Table S10. Selected RL distance, bond lengths (Å) and bond angles (°) for $Eu(MC2)_3(H_2O)_2$ (optimized geometry via PM7 Model).

RL distances (Å)	Atoms	R distances (Å)	theta	phi
			(°)	(°)
Singlet: 4.9438	Eu-012	2.4102	30.01	10.33
Triplet: 6.3029	Eu-O10	2.4808	153.14	289.63
	Eu-011	2.4815	75.35	294.81
	Eu-013	1.3033	78.28	205.67
	Eu-016	2.4809	83.71	49.33
	Eu-017	2.5055	107.86	5.45
	Eu-O2	2.5518	122.38	98.47
	Eu-O4	2.5555	76.48	107.98

Figure S47. Chemical environment around the europium ion in $Eu(MC2)_3(H_2O)_2$.

Table S11. Selected RL distance, bond lengths (Å) and bond angles (°) for $Eu(MC3)_3(H_2O)_2$ (optimized geometry via PM7 Model).

RL distances (Å)	Atoms	R distances (Å)	theta	phi	
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			(°)	(°)	
Singlet: 7.1881	Eu-010	2.4810	77.08	126.84	
Triplet: 2.0742	Eu-016	2.4909	103.42	184.29	
	Eu-012	1.3151	117.48	297.17	
	Eu-013	2.4665	51.16	227.81	
	Eu-O11	2.5197	22.78	74.85	
	Eu-017	2.5439	51.85	6.16	
	Eu-O2	2.5450	113.37	65.16	
	Eu-O4	2.5014	139.06	118.37	

Figure S48. Chemical environment around the europium ion in $Eu(MC3)_3(H_2O)_2.$

Table S11. Selected RL distance, bond lengths (Å) and bond angles (°) for $Eu(MC4)_3(H_2O)_3$ (optimized geometry via PM7 Model).

RL distances (Å)	Atoms	R distances (Å)	theta	phi
			(°)	(°)
Singlet: 7.2900	Eu-013	2.4994	77.43	64.36
Triplet: 9.8762	Eu-O10	2.4909	147.79	196.59

Eu-011	2.4822	110.95	266.53
Eu-016	1.2994	35.91	311.03
Eu-012	2.5231	149.19	24.61
Eu-O17	2.5398	106.08	354.08
Eu-O2	2.5419	123.54	110.31
Eu-O3	2.5374	83.18	135.79
Eu-O4	2.4967	83.57	198.13

Figure S49. Chemical environment around the europium ion in Eu(MC4)₃(H₂O)₃.

Intermolecular interactions involving the cationic species are responsible for the stability of the charge in the structure, as well as promotion of the formation of hydrogen bonds with the coordinated carboxylate-ILs groups. These C–H…O interactions play an important role in the packing of the complexes, as observed by the results of FTIR, Raman, UV-Vis, Photoluminescence, and explained by theoretical modelling.

Triplet energies are calculated by INDO/S (intermediate neglect of differential overlap/spectroscopy). The intramolecular energy transfer (ET) and back transfer (BT) for Eu^{3+} -complexes were calculated considering that the Eu^{3+} levels arise from the metal ion at an intermediate coupling. The energy of the ligand singlet state must be lower than 38 000 cm⁻¹, and the triplet level of the lowest energy must be related to the singlet state previously chosen. The values of energy transfer rates are exhibited in Table S12 for $Eu(MC1)_3(H_2O)_3$, Table S13 for $Eu(MC3)_3(H_2O)_2$, and Table S14 for $Eu(MC4)_3(H_2O)_3$.

Table S12. Calculated values of intramolecular energy transfer (W_{ET}) and back-transfer (W_{BT}) rates for Eu(MC1)₃(H₂O)₃.

Ligand state	4f state	Transfer rate - W _{ET}	Back-transfer rate - W_{BT}		
(cm ⁻¹)	(cm ⁻¹)	(s ⁻¹)	(s ⁻¹)		
Singlet (31632.60) \rightarrow	⁵ D ₄ (27700.83)	2.45x 10 ⁴	9.15x 10 ⁻⁵		

SUPPORTING INFORMAT	ION			Journal of Materials Chemistry C
Triplet (15952.20) \rightarrow	⁵ D ₁ (18691.59)	1.79x 10 ⁻²	4.54x 10 ⁴	
Triplet (15952.20) \rightarrow	⁵ D ₀ (17301.04)	5.68 x 10 ⁻²	3.53x 10	

The theoretical data indicate that the energy transfer occurs from the singlet state of the IL ligand to ${}^{5}D_{4}$ states of the Eu³⁺ ion, this suggests that, is observed the intramolecular energy transfer process by the multipolar mechanism.⁴⁸ Furthermore, it is possible to observe that the RL values, i.e., the distance from the donor state (from organic ligand) to the nucleus formed by the Eu³⁺ ion, are somewhat higher for the triplet state than those determined for the singlet state. The singlet state of the complex (~31633 cm⁻¹) is above the ${}^{5}D_{4}$ state (27701 cm⁻¹) so, the mechanism of energy transfer (WET₁) for S- ${}^{5}D_{4}$ is very favoured as shown by meaningful value of WET₁. The mechanism of energy back-transfer (WBT₁) for ${}^{5}D_{4}$ - S carries little in the depopulation of the ${}^{5}D_{4}$ level. Triplet state of the Eu(MC1)₃(H₂O)₃ (15952.20cm⁻¹) was below the ${}^{5}D_{1}$ state (18691.59 cm⁻¹) so, the mechanism of energy transfer (WBT₂) for ${}^{5}D_{1}$ - T₁ presents the energy transfer rate with two orders of magnitude greater than WET₁ and should act in the depopulation of the ${}^{5}D_{1}$ level. The mechanism of energy transfer rate with two orders of magnitude greater than WET₁ and should act in the depopulation of the ${}^{5}D_{1}$ level. The mechanism of energy transfer rate with two energy transfer rate (WET₃) in ${}^{5}D_{0}$ - T₁ shows no significant value. In Fig.S46 we present every possible energy transfer mechanism for the Eu(MC1)₃(H₂O)₃ complex and a diagram of energy levels.

For the $Eu(MC2)_3(H_2O)_2$ complex, the calculated values of intramolecular energy transfer (W_{ET}) indicate that the energy transfer mostly occurred from the singlet state of the IL ligand to 5D_4 state of the Eu³⁺ ion, as presented in Table 4.

Table S13. Calculated values of intramolecula	r energy transfer (W _{FT}) and l	back-transfer (W _{BT}) rates f	or Eu(MC2) ₃ (H ₂ O) ₂ .
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Ligand state	4f state	Transfer rate - W_{ET}	Back-transfer rate - W _{BT}			
(cm ⁻¹)	(cm ⁻¹)	(s ⁻¹)	(s ⁻¹)			
Singlet (29418.10) \rightarrow	⁵ D ₄ (27700.83)	6.83 x 10 ⁶	1.04 x 10 ³			
Triplet (17215.80) $ ightarrow$	⁵D ₁ (18691.59)	1.83 x 10 ²	1.08 x 10 ⁶			

SUPPORTING INFORMAT	ΓΙΟΝ			Journal of Materials Chemistry C
Triplet (17215.80) →	⁵ D ₀ (17301.04)	4.35 x 10 ²	6.30 x 10 ²	

It's noteworthy that the energy level of a singlet state for the complex (29418 cm⁻¹) is crucial to avoid deactivation mechanisms by vibration coupling of the O-H oscillators from the aqua ligands (3400 - 3500 cm⁻¹). This explains the high quantum efficiency identified for the compound, even with two water molecules coordinated with europium. The mechanism of energy transfer (WET₁) for S - ${}^{5}D_{4}$ is favoured because of energy position between the states and acts in the depopulation of the singlet level. Thus, in this system the intramolecular energy transfer process by the multipolar mechanism may be observed.² Due to proximity between S level (30752 cm⁻¹) and ⁵D₄ (27701 cm⁻¹) the mechanism of energy back-transfer rate (WBT₁) is favoured. On the other hand, the triplet state of the Eu(MC2)₃(H₂O)₂ (17216 cm^{-1}) shows a resonance effect in the ⁵D₁ state (18696 cm⁻¹) so, the second mechanism of energy transfer (T₁- ${}^{5}D_{1}$) is pronounced as shown for the value of WET₂. For the same reason, the mechanism of energy back-transfer (WBT₂) for ⁵D₁- T_1 is highly favoured and should act in the depopulation of the ⁵D₁ level. The WBT₂ is on the order of 10⁶ s⁻¹, which has the same magnitude non-radiative decay rates of ${}^{5}D_{1}$ - ${}^{5}D_{0}$ as found in coordination compounds⁵⁴ implying a simultaneous occurrence of the two deactivation mechanism. The mechanism of energy transfer rate (WET₃) for T_1 - ${}^{5}D_0$ was favoured because triplet energy (18696cm⁻¹) was below ${}^{5}D_0$ energy state (17301 cm⁻¹). For the same reason, a significant value for energy back-transfer (WBT₃) in ⁵D₀ - T₁mecanisms observed. Figure 9 shows a representative population transfer diagram profile for Eu(MC2)₃(H₂O)₂. From schematic energy level diagram shown in Fig. 8, the resonance conditions may be represented. For the four Eu-complexes studied, the singlet levels were below the ⁵D₄ europium excited state (Figures S46-S48 ESI).

Figure S51. Schematic energy level diagram for the $Eu(MC2)_3(H_2O)_2$ showing the most probable channels for the intramolecular energy transfer process.

For Eu(MC3)₃(H₂O)₂ the calculated values of intramolecular energy transfer (W_{ET}) indicate that the energy transfer mostly occurs from the triplet state of the IL ligand to ${}^{5}D_{1}$ and ${}^{5}D_{0}$ states of the Eu³⁺ ion, as presented in Table S13. This profile suggests that the mechanism of energy transfer is the exchange mechanism.⁴⁵

Table S13. Calculated values of intramolecular energy transfe	er (W_{ET}) and back-transfer (W_{BT}) rates for Eu(MC3) ₃ (H ₂ O) ₂ .
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Ligand state	4f state	Transfer rate - W _{ET}	Back-transfer rate - W _{BT}			
(cm ⁻¹)	(cm ⁻¹)	(s ⁻¹)	(s ⁻¹)			
Singlet (30752.50) \rightarrow	⁵ D ₄ (27700.83)	7.38x 10 ²	1.87x 10 ⁻⁴			
Triplet (18193.40) \rightarrow	⁵D₁ (18691.59)	1.52x 10 ⁷	8.28x 10 ⁸			
Triplet (18193.40) \rightarrow	⁵ D ₀ (17301.04)	2.90x 10 ⁷	3.86x 10 ⁵			

The energy level of the singlet state for complex (30752 cm⁻¹) is crucial to avoid deactivation mechanisms by vibration coupling of the O–H oscillators from the aqua ligands (3400-3500 cm⁻¹). This explains the high quantum efficiency identified for the compound, even with two water molecules coordinated with europium. The mechanism of energy transfer (WET₁) for S-⁵D₄ is favoured because of energy position between the states and acts in the depopulation of the Singlet level. Because the S level is higher than ⁵D₄ (Singlet: 30752 cm⁻¹ and ⁵D₄: 27701 cm⁻¹) the mechanism of energy back-transfer rate (WBT₁) is not favoured. On the other hand, the triplet state of the Eu(MC3)₃(H₂O)₂ (18193cm⁻¹) shows a resonance effect with ⁵D₁ state (18691.59 cm⁻¹) so, the mechanism of energy transfer (WET₁) for T₁ - ⁵D₁ is very pronounced as by the higher value for WET₂. By the same reasoning, the mechanism of energy transfer rate (WBT₂) for ⁵D₁ - T₁ is favoured because the triplet energy (18193cm⁻¹) was below ⁵D₀ energy state (17301 cm⁻¹), as registered through the energy back-transfer (WBT₃) inthe⁵D₀ - T₁ mechanism. FigureS47 presents every possible energy transfer mechanism for the Eu(MC3)₃(H₂O)₂ complex and a diagram of energy levels. The WET₂ is on the order of 10⁶ s⁻¹, which has the same magnitude non-radiative decay rates as the ⁵D₁-⁵D₀ found in coordination compounds⁴⁹, implying the simultaneous occurrence of the two deactivation mechanisms.

Figure S52. Schematic energy diagram for the $Eu(MC3)_3(H_2O)_2$ showing the most probable channels for the intramolecular energy transfer process.

To $Eu(MC4)_3(H_2O)_3$ complex the theoretical values of intramolecular energy transfer reports that the energy transfer mostly occurs from the singlet state of the IL ligand to 5D_4 state of the Eu^{3+} ion, this indicates that the mechanism of energy transfer is the multipolar mechanism.⁴⁸ Theoretical results to intramolecular energy transfer are shown in Table S14.

Table S14. Calculated values of intramolecular energy to	ransfer (W_{ET}) and back-transfer (W_{BT}) rates for Eu(MC4) ₃ (H_2O) ₃
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Ligand state	4f state	Transfer rate - W _{ET}	Back-transfer rate - W_{BT}			
(cm ⁻¹)	(cm ⁻¹)	(s ⁻¹)	(s ⁻¹)			
Singlet (31326.80) \rightarrow	⁵ D ₄ (27700.83)	3.93 x 10 ²	6.36 x 10 ⁻⁶			
Triplet (6041.30) \rightarrow	⁵ D ₁ (18691.59)	1.33 x 10 ⁻¹⁰	1.48 x 10 ¹⁷			
Triplet (6041.30) \rightarrow	⁵ D ₀ (17301.04)	4.02 x 10 ⁻⁹	1.10 x 10 ¹⁵			

Singlet state of the complex (~ 31327 cm⁻¹) is above the ${}^{5}D_{4}$ state (27701 cm⁻¹), so the mechanism of energy transfer (assigned as S - ${}^{5}D_{4}$) is favoured as shown by value of WET₁. The mechanism of energy back-transfer (${}^{5}D_{4}$ -S) is not very active in the depopulation of the ${}^{5}D_{4}$ level. Triplet state of the Eu(MC4)₃(H₂O)₃ (6041cm⁻¹) was far below the ${}^{5}D_{1}$ state (18691.59 cm⁻¹) so, the mechanism of energy transfer (WET₁) for T₁- ${}^{5}D_{1}$ was not favoured, as shown for the very small value of WET₂ (1.33 x 10⁻¹⁰ s⁻¹). Due the level disposition (${}^{5}D_{1}$ >>T₁) the mechanism of energy back-transfer (WBT₂) for ${}^{5}D_{1}$ - T₁ was highly favoured. This mechanism of back-transfer acteds deactivates the emitter state non-radiatively, as shown by the low quantum efficiency of the system. FigureS48 presents every possible energy transfer mechanism for the Eu(MC4)₃(H₂O)₃ complex and a diagram of energy levels.

Figure S53. Schematic energy diagram for the $Eu(MC4)_3(H_2O)_3$ showing the most probable channels for the intramolecular energy transfer process.

Table S15 presents the results of the experimental and theoretical approach for all computational methods to optimize the geometry of the proposed structures. Percentage errors were calculated considering the experimental values found. We can explain the percentage errors due to the coordination network effect, since the systems were modelled as discrete complexes. Whereas for ionic liquids, a more realistic approach was through a three-dimensional arrangement of the imidazolium cations formed through chains of the imidazolium rings with weak π - π stacking interactions. This molecular arrangement generates channels in which the bromides anions and water molecules are accommodated as chains. ⁵⁰Due to the greater steric hindrance of the MC2 and MC3 structures, there was a less water concentration in the complexes Eu(MC2)₃(H₂O)₂ and Eu(MC3)₃(H₂O)₂, when compared to the other ligands. It has been confirmed that the hydrogen bond (H-bond) formed between imidazolium ions played a key role in the stability of europium complex, as reported previously.⁵¹ Obviously, the increase in the alkyl chain length would weaken the electron-withdrawing ability of imidazolium ions, and therefore the H-bonds between imidazolium rings. Because of this, the complexes with steric effects show fewer water molecules, as predicted by NMR, TGA, UV-vis and Photoluminescence analyses. Beyond H-bond, all structures showed strong supramolecular interactions, such as hydrogen bonds, anion-pi or cation-pi interactions. The errors reported, however, were the lowest for the computational modelling adopted^{41, 49} and are in agreement with the experimental results.

Table S15. Experimental and theoretical parameters of intensities: Ω_2 and Ω_4 , Einstein spontaneous emission coefficient (Arad) and the non-spontaneous emission coefficient (Anrad), quantum emission efficiency (η), $R_{0.2/0.1}$ and lifetime (τ) to complexes elaborated.

Complex	Ω2	Ω_2 Error	Ω_4	Ω_4 Error	Arad	Arad Error	Anrad	Anrad Error (%)	η	η Error
	(10 ⁻²⁰ cm ²)	(%)	(10 ⁻²⁰ cm ²)	(%)	(s-1)	(%)	(s-1)		(%)	(%)
$Eu(MC1)_3(H_2O)_3$ (experimental)	6.06		0.18		241.9		1296.9		15.7	
Eu(MC1) ₃ (H ₂ O) ₃ (modeling by AM1)	0.021	99.7	0.048	73.3	236.3	2.3	1302.6	0.43	15.4	1.9
$Eu(MC1)_3(H_2O)_3$ (modeling by RM1)	0.039	99.4	0.047	73.9	238.7	1.3	1300.2	0.25	15.5	1.2
Eu(MC1) ₃ (H ₂ O) ₃ (modeling by PM3)	0.021	99.7	0.018	90.0	236.4	2.2	1302.5	0.43	15.4	1.9
Eu(MC1) ₃ (H ₂ O) ₃ (modeling by PM6)	5.97	1.48	0.85	372.2	241.5	0.16	1297.5	0.04	15.7	0
Eu(MC1) ₃ (H ₂ O) ₃ (modeling by PM7)	6.06	0	0.37	105.6	236.7	2.1	1302.2	0.40	15.4	1.9
Eu(MC2) ₃ (H ₂ O) ₂ (experimental)	10.59		6.10		473.9		518.8		47.7	
$Eu(MC2)_{3}(H_{2}O)_{2}$ (modeling by AM1)	11.40	7.65	3.42	43.9	443.4	6.4	549.5	5.9	44.7	6.2
$Eu(MC2)_{3}(H_{2}O)_{2}$ (modeling by RM1)	11.14	5.19	1.33	78.2	403.8	6.4	1071.6	106.5	27.4	42.5
$Eu(MC2)_{3}(H_{2}O)_{2}$ (modeling by PM3)	11.26	6.32	2.03	66.7	417.9	11.8	574.9	10.8	42.1	11.7
$Eu(MC2)_3(H_2O)_2$ (modeling by PM6)	10.92	3.11	0.93	84.7	391.7	17.3	601.1	15.8	39.5	17.2
$Eu(MC2)_{3}(H_{2}O)_{2}$ (modeling by PM7)	10.70	1.03	5.98	1.96	461.2	2.6	531.6	2.4	46.4	2.7
Eu(MC3) ₃ (H ₂ O) ₂ (experimental)	8.46		9.07		452.9		522.9		46.4	
$Eu(MC3)_3(H_2O)_2$ (modeling by AM1)	10.22	20.8	2.90	68,0	399.9	11.7	575.8	10.1	40.9	11.8
Eu(MC3) ₃ (H ₂ O) ₂ (modeling by RM1)	9.05	6.97	0.51	94,4	328.6	27.4	647.3	23.8	33.7	27.4

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Complex	Ω2	Ω_2 Error	Ω_4	Ω_4 Error	Arad	Arad Error	Anrad	Anrad Error (%)	η	η Error
	(10 ⁻²⁰ cm ²)	(%)	(10 ⁻²⁰ cm ²)	(%)	(s-1)	(%)	(s-1)		(%)	(%)
$Eu(MC3)_3(H_2O)_2$ (modeling by PM3)	9.91	17.13	1.87	79,4	375.2	17.1	546.8	4.6	40.7	12.2
Eu(MC3) ₃ (H ₂ O) ₂ (modeling by PM6)	9.20	8.74	0.84	90,7	338.1	25.3	637.7	21.9	34.6	25.4
Eu(MC3) ₃ (H ₂ O) ₂ (modeling by PM7)	10.46	23.6	5.36	40,9	445.2	1.7	530.6	1.4	45.6	1.7
$Eu(MC4)_3(H_2O)_3$ (experimental)	4.33		7.11		295.7		1179.7		20.0	
$Eu(MC4)_3(H_2O)_3$ (modeling by AM1)	6.39	47.6	3.46	51,3	324.3	9.6	1151.0	2.4	21.9	9.5
$Eu(MC4)_{3}(H_{2}O)_{3}(modeling by RM1)$	6.38	47.3	3.77	46.9	323.8	9.5	1436.4	21.7	18.4	8.0
Eu(MC4) ₃ (H ₂ O) ₃ (modeling by PM3)	5.63	30.0	1.33	81.2	238.4	14.4	1236.9	4.8	16.2	19.0
Eu(MC4) ₃ (H ₂ O) ₃ (modeling by PM6)	5.48	26.6	1.03	85.5	229.4	16.7	1245.9	5.6	15.6	22.0
$Eu(MC4)_3(H_2O)_3$ (modeling by PM7)	6.30	45.5	4.05	43,0	300.3	1.1	1175.1	0.3	20.4	2.0

SUPPORTING INFORMATION

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