Synthesis and characterization of luminescent room temperature ionic liquids based on Ru(bpy)(CN)$_4^{2-}$

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Novel ammonium and phosphonium room temperature ionic liquids based on Ru(bpy)(CN)$_4$ as a luminescent complex anion have been developed and characterized by comparative absorption, emission, NMR and electrochemical studies as well as the evaluation of their polarity behaviour.

Introduction

In the last 20 years the study of d^6 transition metal complexes with polypyridine ligands has been one of the most prominent areas of research for their useful applications in solar cells, luminescent sensors and organic light emitting diode (OLED) displays.[1] Among this family, particularly interesting is the luminescent metal complex Ru(bpy)(CN)$_4^{2-}$, first reported by Bignozzi *et al.* in 1986,[2] but that has received much less attention in the molecular and supramolecular photochemistry field compared with Ru(bpy)$_3^{2+}$, despite its peculiar properties. Like Ru(bpy)$_3^{2+}$ it has a luminescent ^{3}MLCT Ru → bpy excited state, but the great difference is that in the case of Ru(bpy)(CN)$_4^{2-}$ it is highly solvent dependent, which provides a simple means of tuning the redox and photophysical properties. The presence of cyanide ligands allows the formation of Ru–CN–M bridged coordination oligomers and polymers, by coordination of the lone pairs on the N atoms to other metal cations, or can act as hydrogen bond acceptors enabling the incorporation into polynuclear assemblies. Finally, the CN vibrations are highly sensitive to changes in electron distribution in the complex which provides the monitorization of the excited state by time-resolved infrared spectroscopy.[1,3] These features make polypyridyl tetracyanoruthenates suitable for several applications such as solid state humidity sensors,[4] due to their reversible colour change from purple (in anhydrous form) to yellow (when exposed to humidity), as optical water sensors of low water contents in organic solvents (below 50 ppm),[5] as photosensitisers for TiO$_2$ solar cells,[6,7] or as energy trap in a multicomponent assembly that resembles the natural photosynthetic systems.[8] Beyond the solvatochromism of Ru(bpy)(CN)$_4^{2-}$, its photophysical properties can also be tuned by the interaction of the anion with protonated polyaza

macrocycles, the formation of Ru–CN···HN$^+$ hydrogen bonds mimics an environment around the anion similar to that experienced in strongly hydrogen bonding solvents,[9–11] or by interaction with several metal cations[12] or *N*-methyl-halopyridinium in solid state or in solution.[13]

Ionic liquids (ILs)[14] have been largely studied in last two decades as an attractive class of ionic organic compounds. The simplest definition of ILs is a low temperature-melting organic salt (liquids at temperatures lower than 100 °C) composed by the combination of large organic cations with a variety of organic or inorganic anions. They present some peculiar and tunable properties,[15] such as almost negligible vapour pressure, high ionic conductivity, chemical and thermal stability as well as significant ability to solubilize organic, inorganic and polymeric materials. Applications of ILs include their use for extraction and dissolution of metals and metal complexes,[16] as alternative solvents for several metal catalytic and non-catalytic syntheses[17] including asymmetric transformations.[18] Recently, some examples of task-specific ILs such as magnetic ILs based on paramagnetic FeCl$_4$ anions,[19] luminescent ILs based on lanthanides[20] have been also developed. The use of ILs for the synthesis and stabilization of metal nanoparticles[21] as well as novel inorganic materials[22] is an emerging research topic.

In the course of our work in the IL research field the development of functionalised IL cations combined with several organic and inorganic anions, including chiral ones,[23] has been achieved. Our recent studies include photochromic, electrochromic and magnetic ILs as examples of smart materials.[24] In this line, intrinsically ionic liquids involving metal complexes of ethylenediaminotetraacetate (EDTA) coordinated with cobalt(III), chromium(III) and iron(III) as an example of magneto and electrochromic materials were prepared.[25]

Herein, novel room temperature ionic liquids (RTILs) based on luminescent metal complex [Ru(bpy)(CN)$_4$]$^{2-}$ as an anion combined with trihexyltetradecylphosphonium [P$_{6,6,6,14}$] and trioctylmethylammonium [N$_{1,8,8,8}$] cations have been developed (Fig. 1).

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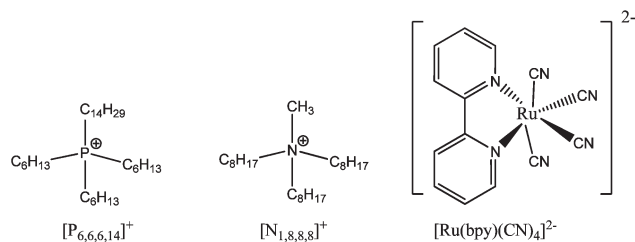
Fig. 1 Structures of novel RTILs based on $[Ru(bpy)(CN)_4]^{2-}$.

In order to illustrate the potential of these new ILs some absorption, emission, NMR and electrochemical studies were also performed.

Results and discussion

Synthesis

The novel RTILs $[P_{6,6,6,14}]_2[Ru(bpy)(CN)_4]$ and $[N_{1,8,8,8}]_2[Ru(bpy)(CN)_4]$ were obtained by an optimized metathesis exchange reaction using a mixture of potassium 2,2′-bipyridyl (tetracyano)ruthenate $K_2([Ru(bpy)(CN)_4]$ and trihexyltetradecylphosphonium chloride $[P_{6,6,6,14}]Cl$ or trioctylmethylammonium chloride $[N_{1,8,8,8}]Cl$ salts, respectively, in methanol solution (Scheme 1). After 24 h of reaction at room temperature, the final compounds were purified by addition of dichloromethane in order to precipitate the inorganic salts. The two RTILs were characterized by ^1H NMR and FTIR spectra. Both spectra contain the signals of the bipyridine moieties[26] and the signals attributed to the $[P_{6,6,6,14}]^+$ and $[N_{1,8,8,8}]^+$ cations. Concerning the infrared spectra, the potassium salt of $[Ru(bpy)(CN)_4]$ in solid state shows four strong CN vibrations between 2035 and 2090 cm^{-1} but the ionic liquids have only one band at 2076 cm^{-1} in the case of $[P_{6,6,6,14}]_2[Ru(bpy)(CN)_4]$ and at 2061 cm^{-1} in the case of $[N_{1,8,8,8}]_2[Ru(bpy)(CN)_4]$. This effect was observed previously with the $[Ru(bpy)(CN)_4]$ in aqueous solution[27] (with CN vibration at 2050–2060 cm^{-1}).

Physical and thermal properties

Both ruthenium based RTILs were obtained as viscous violet liquids at room temperature. In general, they are highly soluble in most common organic solvents such as alcohols (methanol, ethanol and isopropanol), acetone, dichloromethane, DMSO, acetonitrile and diethyl ether and completely insoluble in n-hexane and other alkanes.

Contrarily to starting salt $K_2[Ru(bpy)(CN)_4]$, these ionic liquids are water immiscible mainly due to the hydrophobicity of the phosphonium and ammonium cations.
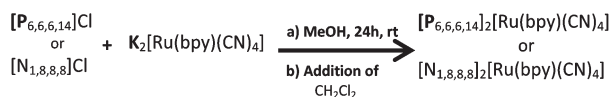
Scheme 1

Table 1 Some properties of RTILs based on the $[Ru(bpy)(CN)_4]$ anion compared with potassium salt

Compound	Physical state[a]	T_g[a] (mp)	Solubility[b]	
			Miscible	Immiscible
$[P_{6,6,6,14}]_2$ $[Ru(bpy)(CN)_4]$	Violet liquid	−69.9 °C	MeOH acetone, DCM, Et$_2$O, ACN	n-Hexane, H$_2$O
$[N_{1,8,8,8}]_2$ $[Ru(bpy)(CN)_4]$	Violet liquid	Not observed	MeOH acetone, DCM, Et$_2$O, ACN	n-Hexane, H$_2$O
$K_2[Ru(bpy)$- $(CN)_4]$	Yellow solid	(>300 °C)	H$_2$O, MeOH	n-Hexane, acetone, DCM, Et$_2$O, ACN

[a] Physical state of final compounds at room temperature. [b] Glass transition temperature (T_g) obtained by DSC studies. [c] Observed solubility behavior in the case of methanol (MeOH), dichloromethane (DCM), diethyl ether (Et$_2$O), acetonitrile (ACN), acetone, n-hexane and water.
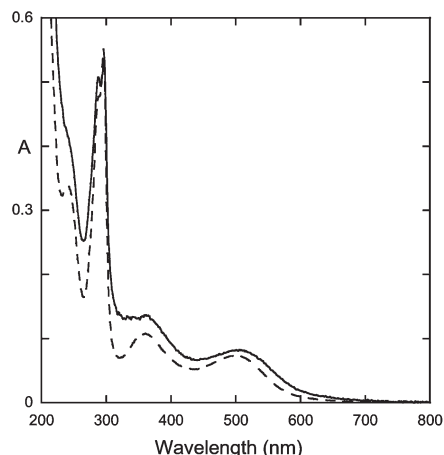

Fig. 2 Absorption spectra of the pure RTILs (---) $[N_{1,8,8,8}]_2[Ru(bpy)(CN)_4]$ and (—) $[P_{6,6,6,14}]_2[Ru(bpy)(CN)_4]$ (cell path length 0.1 cm).

In Table 1 are summarized their thermal properties (glass transition temperature, T_g or melting point, mp) and solubility behaviours in different organic solvents.

$[P_{6,6,6,14}]_2[Ru(bpy)(CN)_4]$ showed a characteristic glass transition temperature (T_g, −69.9 °C) while in the case of RTIL $[N_{1,8,8,8}]_2[Ru(bpy)(CN)_4]$ the T_g value was not detectable.

Spectroscopic properties

Absorption and emission studies. The absorption spectra are shown in Fig. 2. The spectra are typical of $[Ru(bpy)(CN)_4]^{2-}$ with three absorption bands: two metal to ligand charge transfer (^1MLCT) bands centered at 510 nm and 370 nm, and one intense band ligand centered (^1LC) at 295 nm.[2]

In order to clarify the interaction between the anion $[Ru(bpy)(CN)_4]^{2-}$ and the cations $[P_{6,6,6,14}]^+$ and $[N_{1,8,8,8}]^+$, the titrations of the anion, in acetonitrile, with the two cations were performed. In the case of addition of increasing amounts of $[P_{6,6,6,14}]^+$ the bands ^1MLCT are blue shifted (Fig. 3A), with a
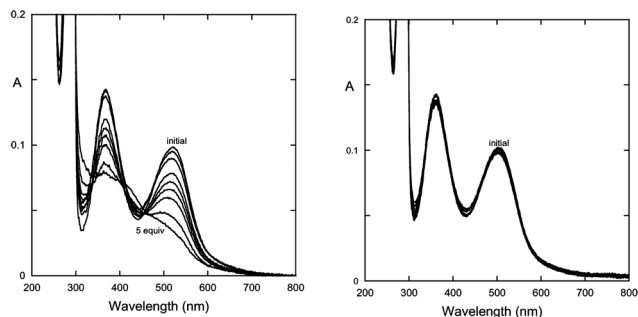
Fig. 3 (A) Absorption spectra obtained by titration of $[Ru(bpy)(CN)_4]^{2-}$ (3.06 × 10^{-5} M in acetonitrile) with $[P_{6,6,6,14}]^+$ (addition of 0, 0.5, 1, 1.5, 2, 2.5, 3, 4 and 5 equiv.). (B) The same for the titration with $[N_{1,8,8,8}]^+$.

decrease in intensity of both bands converging to one band after addition of 5 equiv. The color of the solution changes from deep violet to yellow. Curiously, the addition of $[N_{1,8,8,8}]^+$ to $[Ru(bpy)(CN)_4]^{2-}$ does not lead to significant changes in the absorption (Fig. 3B) or emission spectra and the color of the solution remains deep violet in acetonitrile.

The titrations were also followed by fluorescence. The emission spectra of titration with $[P_{6,6,6,14}]^+$ are shown in Fig. 4, the emission maximum is blue shifted and the intensity increases. In the case of titration with $[N_{1,8,8,8}]^+$ there are no changes in the emission spectra. Both alterations in absorption and emission spectra for the titration with $[P_{6,6,6,14}]^+$ are consistent with that observed for the addition of solvents with higher polarity and increasing H-bond donating ability[5,28] or with the interaction with a polyaza macrocycle cavity.[9] The explanation of this behavior can be related with the relative sizes of the P and N atoms as well as the possibility of P atoms to accommodate 5 or even 6 coordination whereas N atoms do not exceed 4. In this context, cyano groups can more easily electrostatically interact with $[P_{6,6,6,14}]^+$ cations than $[N_{1,8,8,8}]^+$ cations.

NMR studies. The titrations with $[P_{6,6,6,14}]^+$ and $[N_{1,8,8,8}]^+$ were also followed by ^{1}H NMR in DMSO solution. The ^{1}H NMR spectra in the region 7–9.5 ppm are shown in Fig. 5. The initial spectrum of $Ru(bpy)(CN)_4^{2-}$ contains four signals attributed to bipyridine protons.[14] When 1.45 equiv. of $[P_{6,6,6,14}]^+$ are added (Fig. 5A) the protons 6 and 6′ shift upfield from 9.40 ppm to 9.23 ppm and the protons 3,3′, 4,4′ and 5,5′ shift downfield. The same tendency is observed as the number of $[P_{6,6,6,14}]^+$ equivalents is increased but with minor shifts. This NMR solution changed its colour from dark purple to yellowish. In the case of the titration with $[N_{1,8,8,8}]^+$ (Fig. 5B), the protons 6 and 6′ shift also upfield from 9.37 ppm to 9.35 ppm and the protons 3,3′, 4,4′ and 5,5′ shift downfield, however the changes are less pronounced than with $[P_{6,6,6,14}]^+$. With the increasing equivalents of $[N_{1,8,8,8}]^+$ cations the same trend is observed. Once again, the titration with $[P_{6,6,6,14}]^+$ resembles the titration with the polyaza macrocycle where the downshift of 3,3′, 4,4′ and 5,5′ protons is justified by the electron-withdrawing on the metal, which increases the σ-donation from bipyridine, decreasing its electron density and leading to a deshielding of its protons.[9] In the case of 6,6′ protons, their different
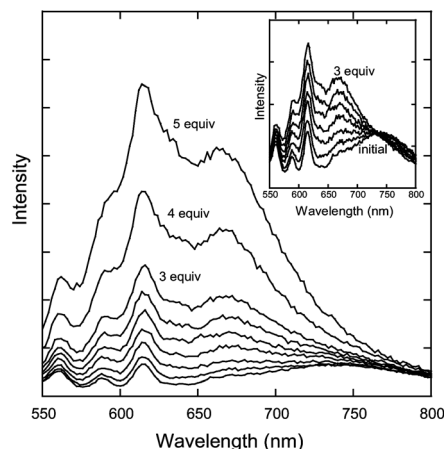

Fig. 4 Emission spectra obtained by titration of $[Ru(bpy)(CN)_4]^{2-}$ (3.06 × 10^{-5} M in acetonitrile) with $[P_{6,6,6,14}]^+$ (addition of 0, 0.5, 1, 1.5, 2, 2.5, 3, 4 and 5 equiv.), λ_{exc} = 520 nm, inset: expansion of the titration upon addition of 3 equiv. of $[P_{6,6,6,14}]^+$.
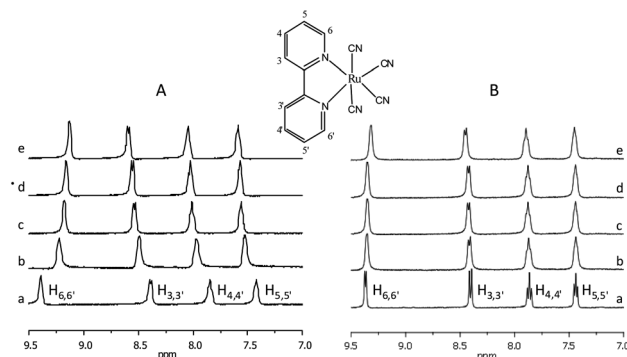

Fig. 5 (A) ^{1}H NMR spectra of $Ru(bpy)(CN)_4^{2-}$ in DMSO solution (a), with addition of 1.45 (b), 2.19 (c), 3.1 (d) and 4.7 (e) equiv. of the $[P_{6,6,6,14}]^+$ cation. (B) ^{1}H NMR spectra of $Ru(bpy)(CN)_4^{2-}$ in DMSO solution (a), with addition of 1.17 (b), 1.8 (c), 2.99 (d) and 4.8 (e) equiv. of the $[N_{1,8,8,8}]^+$ cation.

behaviour can be due to their proximity to the equatorial cyanides and to the $[P_{6,6,6,14}]^+$ or $[N_{1,8,8,8}]^+$ cations leading to additional shielding effects.[9]

Polarity studies. The polarities of the two ionic liquids were measured based on the solvatochromism of betaine dye no. 30 (commonly known as Reichardt's dye). This solvatochromic probe has been largely used to define empirically a solvent polarity scale called $E_T(30)$. The empirical $E_T(30)$ values are simply defined as the molar transition energies (in kcal mol^{-1}) of the standard betaine dye no. 30, measured in solvents of different polarity, at room temperature and normal pressure, according to eqn (1):[29,30]

$$E_T(30)/(\text{kcal mol}^{-1}) = hc\bar{\nu}_{max}N_A$$
$$= (28\,591 \times 10^{-3})\,\bar{\nu}_{max}/\text{cm}^{-1}$$
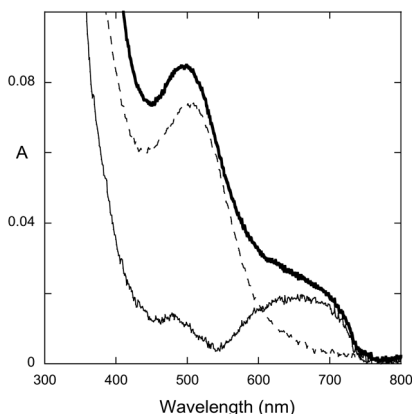$$= 28\,591/(\lambda_{max}/\text{nm}) \tag{1}$$

Fig. 6 Absorption spectra of the pure ionic liquid $[P_{6,6,6,14}]_2[Ru(bpy)(CN)_4]$ with betaine dye no. 30 (▬), $[P_{6,6,6,14}]_2[Ru(bpy)(CN)_4]$ (---) and the subtraction of the two spectra (—).

where $\bar{\nu}_{max}$ is the wavenumber, λ_{max} is the maximum wavelength and h, c, and N_A are the Planck's constant, the speed of light, and Avogadro's constant, respectively.

A high $E_T(30)$ value corresponds to high solvent polarity, the scale ranges from 30.7 kcal mol^{-1} for tetramethylsilane (TMS) to 63.1 kcal mol^{-1} for water. In order to avoid the dimension kcal mol^{-1}, normalized E_T^N values can be defined according to eqn (2):

$$E_T^N = [E_T(\text{solvent}) - E_T(\text{TMS})]/[E_T(\text{water}) - E_T(\text{TMS})]$$
$$= [E_T(\text{solvent}) - 30.7]/32.4 \tag{2}$$

Recently, the solvatochromic parameters of several solvents with interest in green chemistry, including 185 ionic liquids, have been collected from the literature or newly determined.[31] In our work, the λ_{max} of Reichardt's dye in $[P_{6,6,6,14}]_2[Ru(bpy)(CN)_4]$ was found at 655 nm (Fig. 6) and at 664 nm in $[N_{1,8,8,8}]_2[Ru(bpy)(CN)_4]$ giving a E_T^N value of 0.40 and 0.38, respectively.

Electrochemical properties

The electrochemical behaviour of the RTILs based on the [Ru(bpy)(CN)$_4$] anion was observed and compared with the corresponding tetrabutylammonium or potassium salts.

Cyclic voltammetry and differential pulsed voltammetry in dry ACN (0.1 M of TBAP as a supporting electrolyte) of the ruthenium(II) compounds using a platinum electrode vs. SCE were performed to elucidate redox potentials and assess reaction reversibility.

Oxidation peaks related with the metal-centered Ru(II)/Ru(III) couple are influenced by the type of selected cation. A considerable shift in the reversible oxidation potential of Ru(II)/Ru(III) between $[NBu_4]_2[Ru(bpy)(CN)_4]$ (+0.29 V) and the corresponding RTILs $[P_{6,6,6,14}]_2[Ru(bpy)(CN)_4]$ (+0.98 V) and $[N_{1,8,8,8}]_2[Ru(bpy)(CN)_4]$ (+1.03 V) was observed.

This effect can be well-illustrated by titration experiments of the $[NBu_4]_2[Ru(bpy)(CN)_4]$ with the $[P_{6,6,6,14}]$ cation (1, 2 and 8 equiv.) as described in Fig. 7.
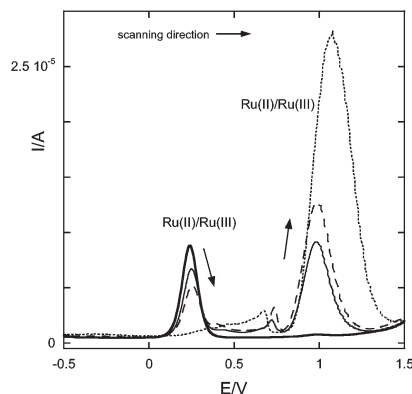

Fig. 7 Differential pulsed voltammetry of (▬) $[NBu_4]_2[Ru(bpy)(CN)_4]$ (1 mM in ACN containing 0.1 M TBAP) followed by sequential addition of $[P_{6,6,6,14}]Cl$ in (—) 1 : 1, (---) 1 : 2 and (....) 1 : 8 molar ratios.

Notably, when titrating $[NBu_4]_2[Ru(bpy)(CN)_4]$ with the $[P_{6,6,6,14}]^+$ cation the complete depletion of the initial oxidation wave at +0.29 V was observed, in contrast with the case of titration with the $[N_{1,8,8,8}]^+$ cation. In both cases, a small oxidation wave appeared at +0.62 V and +0.72 V, respectively. Electrochemical data also indicate that the interaction of this Ru based complex is stronger with the $[P_{6,6,6,14}]^+$ cation than with the $[N_{1,8,8,8}]^+$ cation.

Conclusions

Two novel room temperature ionic liquids based on Ru(bpy)-CN$_4$ as a luminescent anion combined with phosphonium ($[P_{6,6,6,14}]^+$) and ammonium ($[N_{1,8,8,8}]^+$) cations were synthesised.

The selected counter-ion (organic cation) modified significantly some physical, chemical and thermal properties of RTILs based on Ru(bpy)CN$_4$ complexes compared with the initial tetrabutylammonium or potassium salts.

In the case of $[P_{6,6,6,14}]_2[Ru(bpy)CN_4]$, second sphere donor–acceptor interaction between the nitrogen end of cyanides and the $[P_{6,6,6,14}]^+$ cations was observed. In particular, the cation can act as Lewis acid interacting with the lone pairs of cyanides and removing electronic charge from the metal. Contrarily, in the case of $[N_{1,8,8,8}]_2[Ru(bpy)(CN)_4]$ a weak interaction was detected due to the absence of a LUMO with accessible energy to accept the lone pairs from the cyanides. Absorption and emission spectra as well as NMR, polarity and electrochemical studies are in agreement with these observations.

Experimental section

Materials and methods

K$_2$[Ru(bpy)(CN)$_4$] was prepared following a literature procedure.[32] The ionic liquids trihexyltetradecylphosphonium chloride $[P_{6,6,6,14}]Cl$ and trioctylmethylammonium chloride $[N_{1,8,8,8}]Cl$ were purchased from Cytec and Sigma-Aldrich respectively. For solubility reasons the salt $[NBu_4]_2[Ru(bpy)-(CN)_4]$ was used for the studies performed in acetonitrile.

Acetonitrile (J.T. Baker) and methanol (Carlo Erba) were of gradient-HPLC grade. Acetonitrile was dried over CaH_2 and distilled under argon. Tetrabutylammonium perchlorate (TBAP) puriss electrochemical grade was purchased from Fluka, and was dried overnight at 80 °C before use. Type I water was obtained from a Watermax purification station (Diwer Technologies). Other organic solvents used were of analytical grade.

All glassware was cleaned with a mixture of concentrated $H_2SO_4 : H_2O_2$ (1 : 1), thoroughly rinsed, oven dried and cooled in a dessicator prior to use. ^{1}H NMR spectra were recorded at 400.13 MHz with a Bruker AMX400. UV/Vis absorption spectra were recorded with a Varian-Cary 100 Bio spectrophotometer or in a Shimadzu VC2501-PC. Emission spectra were obtained on a Jobin Yvon Spex, Fluorolog FL3-22. For electrochemical studies 1 mM solutions of $[cation]_2[Ru(bpy)(CN)_4]$ complexes were prepared in 10 ml acetonitrile containing 0.1 M TBAP as a supporting electrolyte, de-aerated with argon, and were immediately analyzed. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using an Autolab PGSTAT12 potentiostat/galvanostat, controlled with GPES software version 4.9 (Eco-Chemie), using a cylindrical three-electrode cell of 10 ml. A platinum electrode (MF-2013, f = 1.6 mm, BAS) was used as a working electrode and a Pt wire as an auxiliary electrode. All potentials refer to an SCE reference electrode (Metrohm). EI spectra (positive or negative mode) were obtained by Mass Spectrometry Laboratory, Analytical Services Unit, ITQB-UNL.

Synthesis of ionic liquids $[P_{6,6,6,14}]_2[Ru(bpy)(CN)_4]$

To a suspension of $K_2[Ru(bpy)(CN)_4]$ (0.3 g, 0.68 mmol) in methanol (30 ml) $[P_{6,6,6,14}][Cl]$ (0.6 g, 1.14 mmol) was added. The resultant mixture was stirred at room temperature for 24 h. The methanol was removed under vacuum and the residue was redissolved in dichloromethane to precipitate the inorganic salt. The solution was filtered and the solvent removed under vacuum. A violet viscous liquid was obtained as a final product (η = 60%).

^{1}H-NMR (DMSO, 400.13 MHz, 298 K) δ (ppm): 9.23 (bpy-H6,6′, m), 8.49 (bpy-H3,3′, m), 7.97 (bpy-H4,4′, m), 7.53 (bpy-H5,5′, m), 2.17 (8H, m, $-CH_2(CH_2)_nCH_3$), 1.34 (48H, m, $-CH_2(CH_2)_nCH_3$), 0.86 (12H, m, $-CH_2(CH_2)_nCH_3$). IR (NaCl cell, ν/cm^{-1}): 3678 (m), 3390 (br), 2924 (vs), 2855 (vs), 2076 (m), 1626 (s), 1464 (s), 1416 (m), 1378 (m), 1300 (w), 1267 (w), 1215 (m), 1112 (m), 1043 (m), 988 (m), 812 (m), 720 (s). EI$^+$ (m/z): Calcd for $[C_{32}H_{68}P]^+$: 483.51 found 483.50; EI$^-$ (m/z): Calcd for $[C_{26.8}H_{33.2}N_6P_{0.4}Ru]^-$: 554.40 found 554.39 (related with the formation of [Anion–Cation$_{0.4}$]$^-$ cluster).

Synthesis of ionic liquids $[N_{1,8,8,8}]_2[Ru(bpy)(CN)_4]$

The same experimental procedure was followed to prepare $[N_{1,8,8,8}]_2[Ru(bpy)(CN)_4]$, using $[N_{1,8,8,8}][Cl]$ as starting material. A violet very viscous liquid was obtained as a final product (η = 65%).

^{1}H-NMR (DMSO, 400.13 MHz, 298 K) δ (ppm): 9.37 (bpy-H6,6′, d, J = 5.20 Hz), 8.37 (bpy-H3,3′, d, J = 8.00 Hz), 7.83 (bpy-H4,4′, t, J = 7.60 Hz), 7.40 (bpy-H5,5′, t, J = 6.00 Hz), 3.16 (6H, m, $-CH_2(CH_2)_5CH_2CH_3$), 2.92 (3H, s, $-NCH_3$), 1.58 (6H, m, $-CH_2(CH_2)_5CH_2CH_3$), 1.24 (30H, m, $-CH_2(CH_2)_5CH_2CH_3$), 0.85 (9H, m, $-CH_2(CH_2)_5CH_2CH_3$).

IR (NaCl cell, ν/cm^{-1}): 3390 (br), 2925 (vs), 2856 (vs), 2061 (m), 1634 (m), 1469 (s), 1378 (m), 1060 (w), 723 (m). EI$^+$ (m/z): Calcd for $[C_{25}H_{54}N]^+$: 368.43 found 368.40; EI$^-$ (m/z): Calcd for $[C_{19}H_{20.8}N_{6.2}Ru]^-$: 437.67 found 438.40 (related with the formation of [Anion–Cation$_{0.2}$]$^-$ cluster).

Acknowledgements

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