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Structural and Electrochemical Properties of Yb^{III} in Various Ionic Liquids

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Solvation and ligand exchange reactions of ytterbium(III) as a model for the late trivalent f-elements have been studied in triflate and bistriflylamide ionic liquids (ILs) with the purpose of contributing to a wider understanding of f-element organometallic catalysis, as well as separation and nuclear fuel reprocessing, in ILs. Using the compounds $[C_4mpyr]_3[Yb(OTf)_6]$ and $[C_4mpyr][Yb(Tf_2N)_4]$ [C_4mpyr = *N*-methyl-*N*-propylpyrrolidinium; OTf = triflate, trifluoromethanesulfonate; Tf_2N = bistriflylamide, bis(trifluoromethanesulfonyl)amide] we were able to structurally characterize the local surroundings of Yb^{3+} in the ILs $[C_4mpyr][OTf]$ and $[C_4mpyr][Tf_2N]$ unequivocally. The formation of $[C_4mpyr]_3[Yb(OTf)_6]$-$[C_4mpyr][Tf_2N]$ from a solution of $Yb(Tf_2N)_3$ in $[C_4mpyr]$-$[OTf]$ shows that the stronger coordinating OTf^- anion completely replaces the less Lewis basic Tf_2N^- anion in the first coordination sphere of the lanthanide ion. As expected, such a ligand exchange could not be observed for $Yb(OTf)_3$ in $[C_4mpyr][Tf_2N]$. The ion exchange in the lanthanide coordination sphere can be efficiently monitored by means of cyclic voltammetry (CV). CV measurements also indicate that Yb^{3+} adopts a mixed OTf^-/Tf_2N^- coordination environment when $Yb(OTf)_3$ is dissolved in $[C_4mpyr][Tf_2N]$. The measured half-wave potentials of the studied systems can be linked to the electron-donor properties of the metal cation.

Introduction

Dissolution, solvation, as well as ligand exchange reactions, of f-element cations in conventional inorganic solvents, such as water or liquid ammonia, or classical organic solvents, like tetrahydrofuran or acetonitrile, are nowadays quite well understood, as extensive studies have been undertaken in the past.[1] In contrast, little is known about lanthanide ions in ionic liquids (ILs).[2] However, ILs are of immense interest with respect to liquid–liquid extraction for the separation and purification of lanthanides, as well as for the separation of fission materials from reusable fissile materials. Hydrophobic ILs have been discussed in this context as alternatives to the conventionally used volatile organic compounds/solvents.[3] The processing of nuclear fuel by high-temperature molten salt extraction has been extensively studied in the past.[4] ILs, especially room-temperature ionic liquids (RTILs), and hence room-temperature molten salts, offer the advantage that they work at much lower temperatures. In addition, lanthanide salts of weakly Lewis basic anions, like triflate or bistriflylamide, have shown to be efficient Lewis acid catalysts.[5] Although more and more reports on highly efficient lanthanide catalysis in ILs appear,[6] little is known about the local surroundings of the lanthanide ion in these comparatively new reaction media. So far only a few experimental[7] and theoretical[8] studies have appeared. However, catalytic properties are crucially determined by the surroundings of the metal cation. This finding is also observed in the areas of separation chemistry and fuel reprocessing. In order to gain a basic understanding of the processes in the ligand shell of cationic lanthanide ions in hydrophobic ILs, which are of interest for the above-mentioned applications, we investigated the solvation behavior of trivalent ytterbium in triflate and bistriflylamide-based ILs by means of structural analysis and electrochemistry.

Results and Discussion

Crystal Structures

Crystalline $[C_4mpyr][Yb(Tf_2N)_4]$ was obtained by carefully cooling a supersaturated solution of $Yb(Tf_2N)_3$ in $[C_4mpyr][Tf_2N]$ to room temperature. Structural analysis revealed that the asymmetric unit of $[C_4mpyr][Yb(Tf_2N)_4]$ contains two crystallographically independent lanthanide cations. Both exhibit Yb^{3+} in an oxygen atom surrounding that can be described as a trigonal dodecahedron (Figure 1a). This coordination polyhedron is mostly preferred over a cube when ligand–ligand repulsion, like in case of the Tf_2N^- anions, plays a role for coordination number eight. The mean Yb–O interatomic distance in $[C_4mpyr]$-$[Yb(Tf_2N)_4]$ is 229.3 pm, which is in the expected range for eightfold-coordinated Yb^{3+} and is slightly shorter than the mean distance in $[Yb(H_2O)_8][C(SO_2CF_3)_3]\cdot H_2O$ (232 pm).[9]

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One crystallographically independent ytterbium cation (Yb1) is coordinated to four chelating Tf_2N^- ligands with two of the ligands in s-*cis* and two in s-*trans* conformation. The s-*trans* Tf_2N^- ligands both have λ configuration. Similarly, the other crystallographically independent lanthanide cation in $[C_4mpyr][Yb(Tf_2N)_4]$ is coordinated to four chelating Tf_2N^- ligands, of which two adopt s-*cis* and two s-*trans* conformation. But here disorder between λ- and δ-configured s-*trans* ligands was observed (Figure 1a). In $[C_4mpyr][Yb(Tf_2N)_4]$, a mean S–O interatomic distance of 146.6 pm was found for the coordinating oxygen atoms, whereas the mean S–O interatomic distance for the "free" S–O bonds was 140.5 pm. This distance compares well to that of the free anion. A small but distinct change in the S–O interatomic distances within the Tf_2N ligand upon coordination was detected. A similar change has already been noted for the compounds $[C_4mpyr]_2[Ln(Tf_2N)_5]$ (Ln = Nd, Tb) and $[C_4mpyr][Ln(Tf_2N)_4]$ (Ln = Tm, Lu),[10] the latter two crystallizing isotypically with $[C_4mpyr][Yb(Tf_2N)_4]$, as well as $[C_4mpyr]_2[Eu(Tf_2N)_5]$, $[C_xmim][Eu(Tf_2N)_4]$ (x = 3, 4)[11] (mim = *N*-methylimidazole), and $[C_4mim][Y(Tf_2N)_4]$.[12] The change in the S–O bond length is far more pronounced in the trivalent complex compound $[C_4mpyr][Yb(Tf_2N)_4]$ than in the analogous divalent complex compound $[C_3mpyr]_2[Yb(Tf_2N)_4]$, where values of 144 pm for the S–O bond with the coordinating oxygen atom and 141 pm for the noncoordinating oxygen atom were observed.[13] This indicates, together with a shorter Yb–O interatomic distance (in $[C_3mpyr]_2[Yb(Tf_2N)_4]$, a Yb^{2+}–O interatomic distance of 250 pm was found), a stronger interaction of the Tf_2N oxygen atoms with the higher oxidized ytterbium. For tables compiling the interatomic distances for all the compounds see Supporting Information. In $[C_4mpyr][Yb(Tf_2N)_4]$ a mean N–S–N angle of 127° and a mean S–N distance of 155 pm was found. In all cases no significant changes in the mean N–S–N angle or in the S–N bonding distance relative to noncoordinated Tf_2N were observed.

In order to obtain structural data on the coordination sphere of the later trivalent lanthanides in triflate ILs, $Yb(OTf)_3$ was treated with $[C_4mpyr][OTf]$ to yield the compound $[C_4mpyr]_3[Yb(OTf)_6]$. To the best of our knowledge, this is the first structurally characterized homoleptic triflate complex. In this compound all OTf^- ligands coordinate in a monodentate, nonbridging fashion, which yields isolated octahedra embedded in a $[C_4mpyr]$ matrix (Figure 1b). The OTf anions are all *trans* and arranged in a way to minimize steric repulsion. In the equatorial positions the CF_3 groups are directed oppositely in such a way that the *trans* stereochemistry is also realized with the axial CF_3 groups. The Yb–O distances are in the range 216 to 220 pm. These are significantly shorter than those observed in $[C_4mpyr][Yb(Tf_2N)_4]$ with eightfold-coordinated trivalent Yb^{3+} but are similar to those found for sixfold-coordinated Yb^{3+}, as in hexakis(tetramethylurea-O-)ytterbium(III) perchlorate (218 pm).[14] The S–O bonds of the coordinating oxygen atoms are slightly elongated (145.2 pm on the average) in contrast to those of the "free" oxygen atoms (143.5 pm).

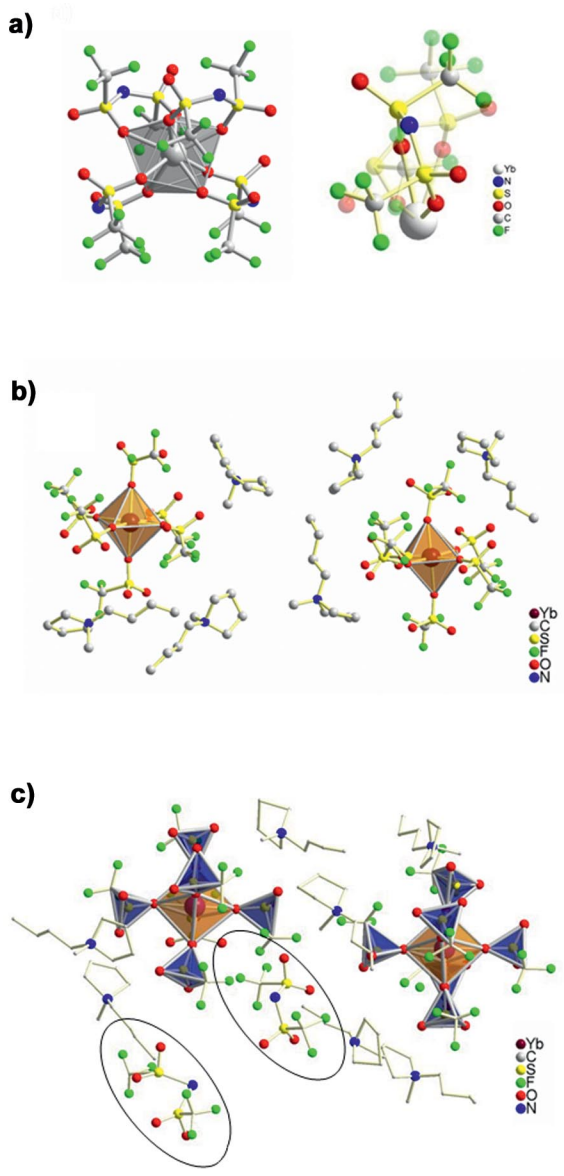

Figure 1. (a) Coordination of Yb(1) in $[C_4mpyr][Yb(Tf_2N)_4]$ (left), disorder of Tf_2N around Yb(2) (right); (b) the asymmetric unit of $[C_4mpyr]_3[Yb(OTf)_6]$; (c) part of the crystal structure of $[C_4mpyr]_4[Yb(OTf)_6][Tf_2N]$ where noncoordinating Tf_2N ligands are encircled and coordinating SO_3R-groups are shown as tetrahedra.

In order to investigate ligand exchange reactions, $Yb(Tf_2N)_3$ was dissolved in the IL $[C_4mpyr][OTf]$. Ligand exchange was evident in the crystalline compound $[C_4mpyr]_4[Yb(OTf)_6][Tf_2N]$ (Figure 1c), in which the Tf_2N^- anions are incorporated in the crystal structure only in a noncoordinating fashion. The ytterbium cation is surrounded solely by OTf^- anions in an octahedral fashion as in $[C_4mpyr]_3[Yb(OTf)_6]$.

Cyclic Voltammetry

Cyclic voltammetry is a well-suited tool used to monitor ligand displacement reactions in solution. The cyclic voltammograms of 0.025 M solutions of $Yb(Tf_2N)_3$ in

$[C_4mpyr][Tf_2N]$ (Figure 2a), $Yb(OTf)_3$ in $[C_4mpyr][Tf_2N]$ (Figure 2b), $Yb(OTf)_3$ in $[C_4mpyr][OTf]$ (Figure 2c), and $Yb(Tf_2N)_3$ in $[C_4mpyr][OTf]$ (Figure 2d) at a scan rate of 100 mV/s are shown in Figure 2 (for other scan rates see Supporting Information). The half-wave potentials (HWP) versus Fc/Fc^+ are found at –0.34 V, –0.79 V, –1.35 V, and –1.35 V, respectively. The large difference between the oxidation and the reduction peaks in the cyclic voltammograms indicate a nonreversible process. Lower scan rates led to a smaller separation of the two peaks (see Supporting Information). But even with a scan rate as low as 10 mV/s, the redox process is irreversible. It seems that the viscosity of the IL plays an important role. $[C_4mpyr][Tf_2N]$ has a lower viscosity (95 mPa s at 20 °C) than $[C_4mpyr][OTf]$ (158 mPa s at 20 °C)[15] and, indeed, lowering the scan rate does affect the separation of the reduction and the oxidation peaks more for $[C_4mpyr][Tf_2N]$ than for $[C_4mpyr][OTf]$. When comparing the HWP of a solution of $Yb(Tf_2N)_3$ in $[C_4mpyr][Tf_2N]$, where Yb^{III} is solely coordinated to Tf_2N^- (HWP = –0.34 V), with the HWP of a solution of $Yb(OTf)_3$ in $[C_4mpyr][OTf]$, where Yb^{III} is coordinated to OTf^- (HWP = –1.35 V), a distinct difference is observed. For the OTf solutions a substantially higher redox potential Yb^{III}/Yb^{II} was measured. This observation is in agreement with the stronger Lewis basicity of the OTf ligand compared to that of Tf_2N. Generally higher redox potentials are observed for metal cations if the ligand surroundings it is able to donate more electron density to the metal and hence has a higher donor number or stronger Lewis basicity. A comparison of the cyclic voltammograms of $Yb(Tf_2N)_3$ in $[C_4mpyr][OTf]$ and $Yb(OTf)_3$ in $[C_4mpyr][OTf]$ reveals the striking observation that the reduction peaks of the trivalent species are both located at –1.35 V. From this we conclude that the Tf_2N^- ligands in the coordination sphere of Yb^{III} get replaced by OTf^- upon dissolution of $Yb(Tf_2N)_3$. This is backed by the fact that $[C_4mpyr]_4[Yb(OTf)_6][Tf_2N]$ crystallizes from such a solution. For a solution of $Yb(OTf)_3$ in $[C_4mpyr][Tf_2N]$ such a complete ligand exchange obviously does not occur and the determined HWP of –0.79 V lies between those of $Yb(OTf)_3$ in $[C_4mpyr][OTf]$ and $Yb(Tf_2N)_3$ in $[C_4mpyr][Tf_2N]$, pointing to a mixed OTf^-/Tf_2N^- coordination.

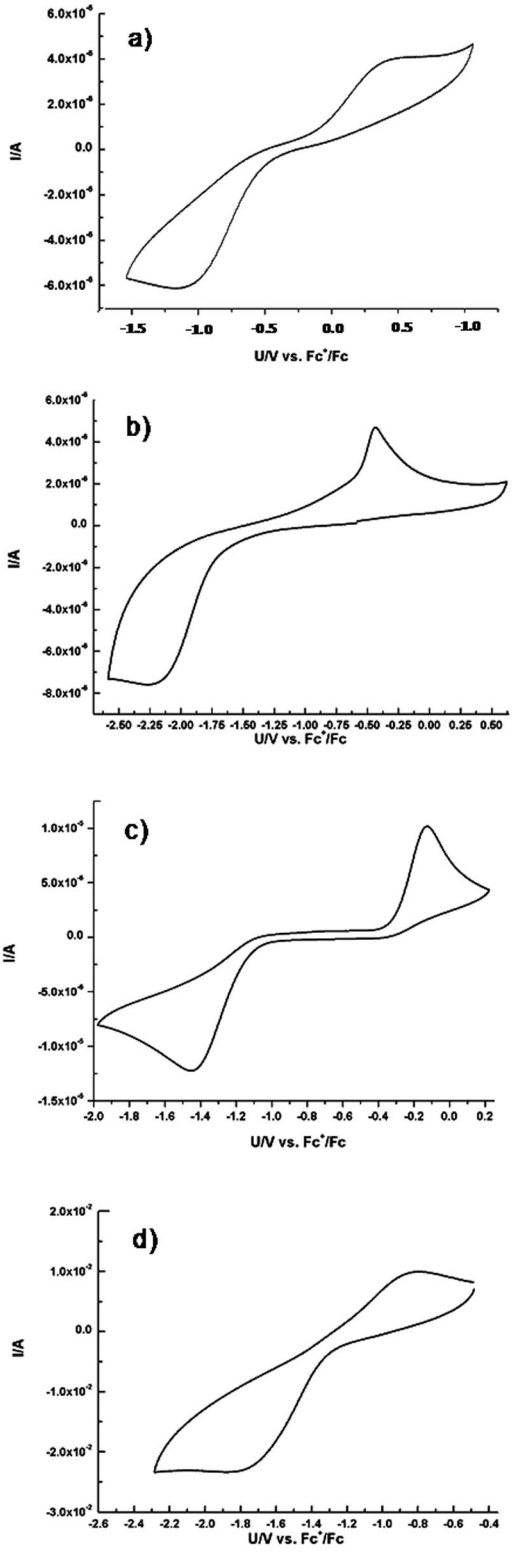

Figure 2. Cyclic voltammograms of (a) $Yb(Tf_2N)_3$ in $[C_4mpyr][Tf_2N]$; (b) $Yb(OTf)_3$ in $[C_4mpyr][Tf_2N]$; (c) $Yb(OTf)_3$ in $[C_4mpyr][OTf]$; (d) $Yb(Tf_2N)_3$ in $[C_4mpyr][OTf]$.

Conclusions

Combining all the gathered information, the following reaction paths can be presented for dissolving Yb^{III} in Tf_2N- and OTf-based ILs [Equations (1), (2), and (3)]:

$$Yb(Tf_2N)_3 + [C_4mpyr][Tf_2N] \rightarrow [C_4mpyr][Yb(Tf_2N)_4] \quad (1)$$

$$Yb(Tf_2N)_3 + 6[C_4mpyr][OTf] \rightarrow [C_4mpyr]_4[Yb(OTf)_6][Tf_2N] + 2[C_4mpyr][Tf_2N] \quad (2)$$

$$Yb(OTf)_3 + 3[C_4mpyr][OTf] \rightarrow [C_4mpyr]_3[Yb(OTf)_6] \quad (3)$$

$Yb(Tf_2N)_3$ dissolves upon complex formation in Tf_2N ILs. As a comparatively small trivalent lanthanide ion, Yb^{III} is surrounded by four Tf_2N ligands coordinating bidentately through their oxygen atoms. Similarly, $Yb(OTf)_3$ dissolves in the OTf IL, $[C_4mpyr][OTf]$, upon forming the

complex anion $[Yb(OTf)_6]^{3-}$. Dissolution of $Yb(Tf_2N)_3$ in $[C_4mpyr][OTf]$ yields $[C_4mpyr]_4[Yb(OTf)_6][Tf_2N]$, in which the Tf_2N^- ligand has been replaced by the stronger Lewis base OTf^- in the coordination sphere of Yb^{3+}. In contrast, we have no evidence for such a complete ligand exchange when $Yb(OTf)_3$ is dissolved in $[C_4mpyr][Tf_2N]$. Cyclic voltammetry proved to be a powerful tool to monitor the ligand exchange in solution.

Experimental Section

The compounds synthesized in this work, as well as the starting materials, are air- and moisture-sensitive. Therefore, the materials were prepared and stored under inert gas. The reactions were carried out by using either the standard "Schlenk technique" with a vacuum/argon line or by using glass ampoules in an argon glovebox (MBraun, Garching). The reaction ampoules were sealed under dynamic vacuum outside the glovebox while connected to a vacuum line. All the reaction vessels were carefully dried for several hours in a drying oven before use. All the starting materials were sublimed prior to use. The ILs were synthesized according to the given procedures, purified until they exhibited CV-grade purity, and dried for at least 24 h at 120 °C under reduced pressure (10^{-3} mbar).

$[C_4mpyr][Tf_2N]$: The IL $[C_4mpyr][Tf_2N]$ was synthesized following a modified literature procedure.[16] First, *N*-butyl-*N*-methylpyrrolidinium bromide was obtained by solvent-free alkylation of *N*-methylpyrrolidine with 1-bromobutane at 80 °C. The crude product was recrystallized from acetonitrile/toluene, dried in vacuo to remove the solvent mixture, and subsequently dissolved in water. One equivalent of $Li(Tf_2N)$ in water was added, and the mixture was stirred for 24 h at room temperature. The product that formed a second phase to water was separated, purified by addition of activated charcoal, and filtered through aluminum oxide. It was dissolved in dichloromethane and washed with small aliquots of water until no bromide residues could be detected in the extract ($AgNO_3$ test). The resulting IL was dried for 48 h in a Schlenk tube at 150 °C under reduced pressure and rigorous stirring. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 0.985 (t, J = 7.29 Hz, 3 H), 1.365 (sext, J = 7.25, 7.43 Hz, 2 H), 1.748 (m, J = 7.80, 7.47 Hz, 2 H), 2.156 (m, 4 H), 3.037 (s, 3 H), 3.349 (m, 2 H), 3.503 (m, 4 H) ppm. ^{19}F NMR (300 MHz, $CDCl_3$): δ = –79.43 (s, 6 H) ppm.

$[C_4mpyr][OTf]$: The IL $[C_4mpyr][OTf]$ was prepared following a literature procedure.[17] $[C_4mpyr]Cl$ (44.4 g, 0.25 mol) was dissolved in dichloromethane (50 mL), and Li(OTf) (39.0 g, 0.25 mol) was added. The suspension was stirred overnight and filtered. The decanted solution was washed with several aliquots of water until no chloride residues could be detected ($AgNO_3$ test). The solvent was removed, and the IL was dried in vacuo at 120 °C overnight. ^{1}H NMR (300 MHz, D_2O): δ = 0.98 (t, J = 7.42 Hz, 3 H, 9-H), 1.41 (sext., J = 7.42 Hz, 2 H, 8-H), 1.79 (quint., J = 8.43 Hz, 2 H, 7-H), 2.23 (br. s, 4 H, 3-H, 4-H), 3.04 (s, 3 H, 10-H), 3.29–3.38 (m, 2 H, 6-H), 3.42–3.59 (m, 4 H, 2-H, 5-H) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 12.8 (s, C-9), 19.2 (s, C-8), 21.3 (s, C-3, C-4), 25.1 (s, C-7), 48.0 (s, C-10), 64.2 (m, C-2, C-5, C-6) ppm.

$Yb(Tf_2N)_3$: $Yb(Tf_2N)_3$ was synthesized by dissolving ytterbium metal in aqueous HTf_2N and subsequent removal of the liquid phase.[18] The crude product was sublimed at 280 °C under reduced pressure (10^{-3} mbar) to give $Yb(Tf_2N)_3$.

$Yb(OTf)_3$: $Yb(OTf)_3$ was synthesized in a procedure similar to that used for $Yb(Tf_2N)_3$ by dissolving Yb metal in aqueous HOTf. The metal dissolves readily to give a colorless solution. The water from the acidic solution was removed, and the resulting colorless solid was dried for 24 h at 200 °C under reduced pressure (10^{-3} mbar).

$[C_4mpyr][Yb(Tf_2N)_4]$ (1) and $[C_4mpyr]_3[Yb(OTf)_6]$ (2): Compounds **1** and **2** were synthesized from equimolar amounts of $[C_4mpyr][Tf_2N]$ and $Yb(Tf_2N)_3$, and $[C_4mpyr][OTf]$ and $Yb(OTf)_3$, respectively. The starting materials were placed in a Schlenk tube and stirred for 2 h at 120 °C until a homogeneous compound was obtained. By cooling to room temperature colorless solids were obtained. Single crystals of compounds **1** and **2** formed as insoluble products after cooling the reaction mixture to room temperature (5 °C/min).

$[C_4mpyr]_4[Yb(OTf)_6][Tf_2N]$ (3): Single crystals of **3** formed from a solution of $Yb(Tf_2N)_3$ in $[C_4mpyr][OTf]$. $Yb(Tf_2N)_3$ was dissolved at 120 °C in $[C_4mpyr][OTf]$ until a homogeneous solution was obtained. As the solution was cooled to room temperature, colorless single crystals of **3** precipitated out.

X-ray Crystallography

To obtain structural information on the respective lanthanide complex compounds, single crystals for X-ray analysis were grown out of the respective ILs by supersaturating the IL with the respective salt while hot. Subsequent careful cooling of the solution yielded crystals of sufficient quality for structural analysis. However, crystals of comparatively poor quality are a commonly encountered problem when crystals are grown from ILs because the synthesis of ILs generally employ ions that have a poor tendency to crystallize but rather show packing frustration and disorder.[19] It took huge effort to get the presented single-crystal X-ray diffraction data shown here. For most of the checked specimens we were just able to determine the cell parameters but the collected data were of too poor quality to allow for a full structure refinement. Single-crystal X-ray diffraction data were obtained with the aid of an image plate diffraction system with graphite monochromated Mo-K_α radiation (IPDS, Stoe&Cie, Darmstadt, Germany). Crystal structure solutions were accomplished by direct methods using the SHELXS-97 software package.[20] The remaining atomic positions were localized by subsequent difference Fourier analyses and least-squares refinements with the SHELXL-97 software package.[21] For $[C_4mpyr]_3[Yb(OTf)_6]$, hydrogen atoms were placed in idealized positions and constrained to reside on their respective parent atom. Because of the lower data quality for $[C_4mpyr][Yb(Tf_2N)_4]$ and $[C_4mpyr]_4[Yb(OTf)_6][Tf_2N]$, treatment of hydrogen atoms were omitted. Data reduction was carried out with the program package X-Red,[22] and numerical absorption corrections were performed with the program X-Shape.[23] For crystal structure drawings, the program Diamond was employed.[24]

Crystal Data for $[C_4mpyr][Yb(Tf_2N)_4]$ (1): $C_{17}H_{20}F_{24}N_5O_{16}S_8Yb$, M_r = 1435.90 g/mol, monoclinic, $P2/c$ (no. 13), a = 2013.33(15) pm, b = 14.8617(9) pm, c = 1620.65(11) pm, β = 113.182(5)°, V = $4457.7(5) \times 10^6$ pm^3, Z = 4, ρ = 2.140 g/cm^3, μ = 2.649 mm^{-1}. 68174 reflections were collected, of which 9973 were unique (R_{int} = 0.0743). GOF = 1.048. R_1/R_2 = 0.0913/0.2412 [$I > 2\sigma(I)$].

Crystal Data for $[C_4mpyr]_3[Yb(OTf)_6]$ (2): $C_{66}H_{120}F_{36}N_6O_{36}S_{12}Yb_2$, M_r = 2988.49 g/mol, monoclinic, $P2_1/c$ (no. 14), a = 2539.07(13) pm, b = 2027.26(6) pm, c = 2472.95(13) pm, β = 119.493(4)°, V = $11489.8(9) \times 10^6$ pm^3, Z = 4, ρ = 1.728 g/cm^3, μ = 1.969 mm^{-1}. 61158 reflections were collected, of which 15020 were unique (R_{int} = 0.0424). GOF = 1.052. R_1/R_2 = 0.0540/0.1318 [$I > 2\sigma(I)$].

Crystal Data for $[C_4mpyr]_4[Yb(OTf)_6][Tf_2N]$ (3): $C_{77}H_{140}F_{42}N_8O_{40}S_{14}Yb_2$, M_r = 3410.90 g/mol, monoclinic, $P2_1/c$ (no. 14), a =

2542.0(3) pm, b = 2056.78(12) pm, c = 2967.3(3) pm, β = 91.990(8)°, $V = 15504(2) \times 10^6$ pm^3, Z = 4, ρ = 1.573 g/cm^3, μ = 1.543 mm^{-1}. 81633 reflections were collected, of which 14473 were unique (R_{int} = 0.1484). GOF = 0.926. R_1/R_2 = 0.0826/0.2037 [$I > 2\sigma(I)$].

CCDC -769747 (for **1**), -769748 (for **2**), and -769749 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Cyclic Voltammetry: Cyclic voltammograms were measured with an Autolab PGStat-12 instrument (Metrohm, Filderstadt, Germany). A platinum working disc electrode, a glassy carbon counter electrode and a silver-rod quasi reference electrode were used. All measurements were carried out under an argon atmosphere with scan rates of 10, 50, 100, and 200 mV/s. The electrodes were polished after each measurement with CeO_2, washed with deionized water and acetone, and dried prior to use. The cyclic voltammograms and half-wave potentials are given with respect to the Fc/Fc^+ redox couple. In order to do so, the Fc/Fc^+ redox potential was measured in the corresponding ILs first and a numerical correction was applied to the measured data afterwards.

Supporting Information (see footnote on the first page of this article): Tables with selected interatomic distances and further information on cyclic voltammetry measurements at different scan rates.

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