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A 2:1 Dicationic Complex of Tetraethyl Methylenebisphosphonate with Uranyl Ion in Acetonitrile and Ionic Liquids

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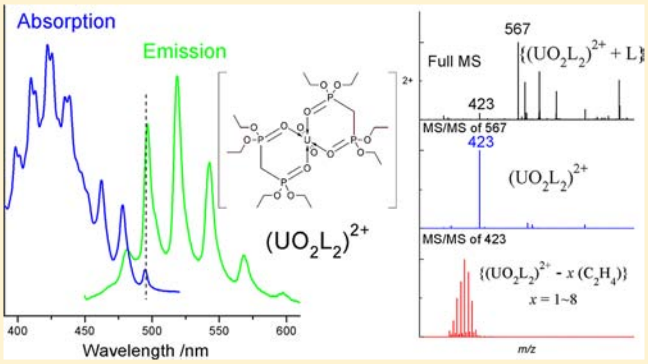
Ⓢ *Supporting Information*



ABSTRACT: A new 2:1 dicationic complex formed by TEMBP with uranyl ion in acetonitrile and two hydrophobic ILs, [BMIm][NTf$_2$] and [N$_{4111}$][NTf$_2$], has been identified with combination of optical spectroscopic and mass spectrometric studies. With excess of TEMBP ligand (L/U > 2.0), the uranyl is completely coordinated by two ligands to form a dicationic complex [UO$_2$(TEMBP)$_2$]$^{2+}$. The UV−vis spectra of [UO$_2$(TEMBP)$_2$]$^{2+}$ in acetonitrile and in the two ILs are similar. The vibronic fine structures in UV−vis spectrum of [UO$_2$(TEMBP)$_2$]$^{2+}$ show characters of tetragonal coordination in the uranyl equatorial plane. The symmetry of proposed structure of [UO$_2$(TEMBP)$_2$]$^{2+}$ is D_{2h}, and its UV−vis spectrum is tentatively interpreted based on the structural similarity to the well studied [UO$_2$Cl$_4$]$^{2-}$ complex. The luminescence emission spectrum of [UO$_2$(TEMBP)$_2$]$^{2+}$ shows typical vibronic bands, having a mirror relationship with the 455−500 nm region of the corresponding absorption spectrum. The stoichiometry of [UO$_2$(TEMBP)$_2$]$^{2+}$ is confirmed by electrospray ionization−ion trap mass spectrometry (ESI-ITMS) studies with acetonitrile as solvent. The "naked" dication (*m*/*z* 423) is characterized by the remarkable eight peaks with interval of 14 *m*/*z* units in its tandem mass spectra, representing the fragmentation of ligands by losing C$_2$H$_4$ units from their ethoxy groups. However, the dication tends to exist as a weak adduct with either an additional ligand or an anion in the ESI mass spectrum. The adducts {[UO$_2$(TEMBP)$_2$]$^{2+}$ + TEMBP} (*m*/*z* 567) and {[UO$_2$(TEMBP)$_2$]$^{2+}$ + [ClO$_4$]$^-$} (*m*/*z* 945) are favorable in pure acetonitrile, while only one adduct {[UO$_2$(TEMBP)$_2$]$^{2+}$ + [NTf$_2$]$^-$} (*m*/*z* 1126) is predominant in [BMIm][NTf$_2$] (diluted with acetonitrile). The results of ESI-ITMS study are consistent with those of optical spectroscopic studies.

■ INTRODUCTION

As a class of novel "green solvents", ionic liquids (ILs) have been widely applied in many fields such as separation, synthesis, catalysis, and electrochemistry.[1] The potentiality of ionic liquids in the nuclear industry has also been explored in recent years.[2] The bis(trifluoromethanesulfonyl)imide anion ([NTf$_2$]$^-$) based hydrophobic ionic liquids have been popular, especially in extraction studies,[2] for their superior chemical and thermal stability,[1,3] low viscosity,[1,3] and high stability to radiolysis.[4] Tri-*n*-butyl phosphate (TBP) is the extractant of the commercial PUREX (plutonium uranium reduction extraction) process for recovering uranium and plutonium from spent nuclear fuel,[5] and many studies involving extraction of uranium to ionic liquid phases also use TBP with ILs as alternatives for volatile and flammable solvents such as kerosene.[2] However, the extraction efficiencies of TBP−IL systems are not much better than those of the commercial system.[6] On the other hand, studies using multidentate extractants such as octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO)[7] and diglycolamides[8] have shown improved efficiencies in ILs versus molecular organic solvents. The tetraalkyl methylenebisphosphonates (TAMBPs) are also a class of bidentate extractants for lanthanides and actinides, and their 1:1 adducts with uranyl nitrate have been well studied.[9] The extraction of uranium to ILs by using TAMBPs, as well as the complexation of TAMBPs with uranyl in ILs, have not been reported yet.

Knowledge of the solvation and complexation of metal in ILs is of great importance to understand the extraction and other processes involving ILs. As for the chemistry of uranium in ILs, the study of structures of uranyl complexes formed in ILs is one of the key issues. Optical (UV−visible absorption and luminescence) spectroscopy is often used for study of coordination chemistry of uranyl in solution. The absorption spectra of uranyl complexes often show characteristic vibronic fine structures, representing certain symmetry (or geometry) of the first coordination sphere of uranyl, with the chemical nature of the ligands having a minor influence on the spectra.[10] Uranyl complexes formed with inorganic ligands such as Cl$^-$ and NO$_3$$^-$ in ILs are extensively studied with methods including optical spectroscopy.[11−13] The study by Nockemann et al.[13] on uranyl complexes in ILs with typical symmetries has demonstrated the

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power of optical spectroscopy for speciation of uranyl complexes. Nevertheless, spectroscopic studies on complexes of uranyl with organic ligands in ILs are rarely reported.

Electrospray ionization mass spectrometry (ESI-MS) allows acquisition of mass spectra directly from solutions with minimized fragmentation and thus has become a very useful method for the study of metal−ligand interactions in solution.[14] With an ion trap mass analyzer, ESI−ion trap mass spectrometry (ESI-ITMS) enables investigation of the multistage collision-induced dissociation (CID) of coordinated complexes and thus provides structural information of the complexes from the characteristic fragmentation patterns.[14a] A number of studies on the uranyl complexes in aqueous or organic solvents have been reported.[15]

In this paper, we have investigated the complexation of tetraethyl methylenebisphosphonate (TEMBP) with uranyl in acetonitrile and two ionic liquids, 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide ([BMIm][NTf$_2$]) and *N*-butyl-*N*,*N*,*N*-trimethylammonium bis(trifluoromethanesulfonyl)imide ([N$_{4111}$][NTf$_2$]). With combination of optical spectroscopic and mass spectrometric studies, a new dicationic $[UO_2(TEMBP)_2]^{2+}$ complex in solution has been identified.

■ EXPERIMENTAL SECTION

Materials. Tetraethyl methylenebisphosphate (TEMBP) (98%) was purchased from Alfa-Aesar (Tianjin, China). Except as otherwise noted, other reagents were of A.R. grade from Sinopharm Chemical Reagent Company of China.

The ionic liquid [BMIm][NTf$_2$] was prepared from [BMIm]Cl (99%, Lanzhou Institute of Chemical Physics, CAS, Lanzhou, China) and Li[NTf$_2$] (99%, TCI, Japan) with the procedure described in ref 3. [N$_{4111}$]Br was synthesized from *n*-butyl bromide (99%) and trimethylamine alcoholic solution (33%) according to ref 16. [N$_{4111}$][NTf$_2$] was then prepared from [N$_{4111}$]Br and Li[NTf$_2$] in the same manner as [BMIm][NTf$_2$]. The ILs were washed with deionized water several times until no Cl$^-$ or Br$^-$ was detected in the aqueous phase by AgNO$_3$. The detection limit of Cl$^-$ in aqueous solutions by AgNO$_3$ method is less than 10 ppm,[17] and the halogen ions remaining in the ILs could be much lower because these inorganic ions tend to gathering into the aqueous phase. After drying under vacuum at 70 °C for more than 12 h, the water amount was found below 100 ppm as measured by Karl Fischer titration.

$UO_2(ClO_4)_2{\cdot}xH_2O$ is used as the source of "free" uranyl ions, because $[ClO_4]^-$ is a well-known weakly coordinating anion.[13,18] $UO_2(ClO_4)_2{\cdot}xH_2O$ was prepared from UO$_3$ and perchloric acid according to literature.[13] The resulting yellow solid of $UO_2(ClO_4)_2{\cdot}xH_2O$ was dissolved in ILs and acetonitrile to prepare stock solutions with $c(UO_2^{2+}) \approx 0.2$ M. The uranyl stock solutions were stored in the dark at room temperature. The samples for spectroscopic studies were prepared by mixing the $UO_2(ClO_4)_2{\cdot}xH_2O$ stock solutions with an adequate amount of TEMBP and then diluting with the corresponding solvents.

Caution: Heating a mixture of perchloric acid or its salt solution with an organic material to dryness may cause explosion!

Spectroscopic Study. The UV−vis absorption spectra were recorded within the wavelength range of 340−520 nm with a Perkin-Elmer Lambda-35 spectrometer (PerkinElmer Inc., Santa Clara, CA, USA). The luminescence experiments were performed with a Hitachi F-4500 fluorescence spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan) with a 150 W xenon lamp. Emission spectra were recorded between 450 and 650 nm, with excitation at 330 or 423 nm. All of the spectra were recorded at room temperature using 1.00 cm quartz cells. The uranyl concentration was 10 mM with varied ligand-to-uranyl (L/U) ratios.

Mass Spectrometric Study. ESI-ITMS study was performed using a Finnigan LCQ Advantage MAX ion-trap mass spectrometer (ThermoFinnigan, San Jose, CA, USA), which was modified to accept a homemade versatile spray ionization source. The distance between spray emitter and MS inlet was 12 mm. The diluted uranium-containing solutions were infused into the ESI source at a flow rate of 0.2 μL/min with the incorporated Harvard Apparatus syringe pump (Harvard Apparatus, USA). The major experimental parameters used were as follows: spray voltage 5.5 kV, capillary voltage 3.0 V, tube lens offset −50.0 V, and heated capillary temperature 150 °C. No nebulizing gas was used. All data were processed using the instrument software (Xcalibur version 1.4 SR1). Acetonitrile was used as solvent for ESI-MS study, the uranyl concentrations were 0.7 mM (pure acetonitrile) and 1.0 mM (IL diluted in acetonitrile), and the L/U ratio was 4.0.

■ RESULTS AND DISCUSSION

UV−Vis Spectra. As shown in Figure 1, in acetonitrile and ionic liquids, the UV−vis spectra of uranyl ion with excess (3.0 equiv) of TEMBP show similar fine structures, suggesting that the uranyl complexes in those solvents may have the same structure. The spectra of $UO_2(ClO_4)_2{\cdot}xH_2O$ (10 mM) with varied L/U ratios from 0 to 3.0 in [BMIm][NTf$_2$] at room temperature are shown in Figure 2. Since no major changes in the spectra are observed when the L/U ratio exceeds 2.0, the L/U ratio of the complex will most likely be 2.0. Similar trends are found in the spectra of samples in acetonitrile and [N$_{4111}$][NTf$_2$] (See Figure S1 and Figure S2 in Supporting Information).

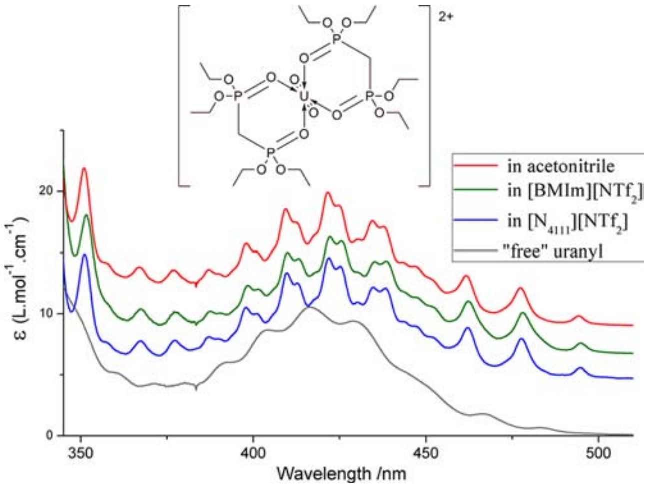

Figure 1. Proposed structure of the complex (upper) and UV−vis spectra of the "free" uranyl ion (gray) and $[UO_2(TEMBP)_2]^{2+}$ (red, in acetonitrile; green, in [BMIm][NTf$_2$]; blue, in [N$_{4111}$][NTf$_2$]) at room temperature (lower). Concentrations are $c(UO_2^{2+})$ = 10 mM and c(TEMBP) = 30 mM. The spectra are stacked up for clarity.

It is known that the characteristic vibronic fine structure represents the certain symmetry (and geometry) of the first coordination sphere of the uranyl complexes,[10,13] which enables structure elucidation by UV−vis spectra. The spectra in Figure 1 show typical band splitting in the 380−450 nm region, and this character is much different from the spectra of pentagonal coordinated species (e.g., $[UO_2(H_2O)_5]^{2+}$) and the hexagonal coordinated 1:1 complex of TAMBP with uranyl nitrate.[9] By means of spectral characters of this complex, it can be inferred that the real L/U ratio must be 2.0 (a tetragonal coordination to the uranyl with the four O-donors from the two bidentate ligands). The similarity between the spectra of this complex and the well studied $[UO_2Cl_4]^{2-}$[11,13,19] also suggests a tetragonal

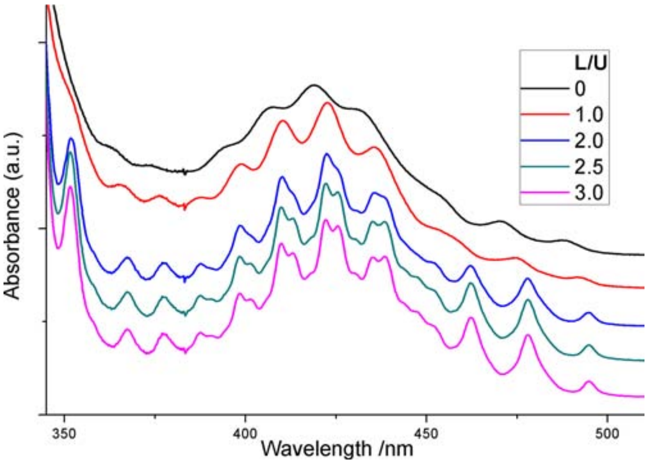

Figure 2. Absorption spectra of uranyl (10 mM) with various L/U ratios from 0 to 3.0 in [BMIm][NTf$_2$] at room temperature. The spectra are stacked up for clarity.

coordination in the uranyl equatorial plane, especially for their band splitting characters. Moreover, because of a tetragonal coordination to the uranyl in this 2:1 complex, there could not be available coordination sites for additional small ligands such as water molecules. Therefore, the composition of the complex is proposed as $[UO_2(TEMBP)_2]^{2+}$, and its structure, with a D_{2h} symmetry, is shown in Figure 1 (upper). The difference in spectra of L/U = 2.0 and 2.5 may be attributed to the following equilibrium shifting from the left to the right: $[UO_2(TEMBP)]^{2+}$ + TEMBP = $[UO_2(TEMBP)_2]^{2+}$. For example, assuming the equilibrium constant as high as 10^4 (though the actual value cannot be determined in the present work), in a total uranyl concentration of 10 mM, 5 mM excess of TEMBP ligand will be required to reach a 98% formation.

The spectrum of $[UO_2(TEMBP)_2]^{2+}$ can be tentatively interpreted by comparison with that of $[UO_2Cl_4]^{2-}$ from literature.[11,13,19] According to the assignments in literature for spectra of $[UO_2Cl_4]^{2-}$ in ILs[11b,c] and molecular organic solvent,[19b,c] the spectra in 380−500 nm can be roughly divided to two regions: I, 455−500 nm (22000−20000 cm^{-1}), and II, 380−455 nm (26000−22000 cm^{-1}). In region I, the most intense bands are at 492, 476, and 459 nm (20325, 21026, and 21758 cm^{-1})[11,13,19] for $[UO_2Cl_4]^{2-}$, and these bands belong to one vibronic progression with peak separation of ~720 cm^{-1} (representing the O=U=O symmetric stretching frequency (ν_s) of the first excited state). There are also three similar intense bands in region I of the $[UO_2(TEMBP)_2]^{2+}$ spectra at 495, 478, and 462 nm with peak separation of 718 ± 5 cm^{-1}. Besides the red shift of ~3 nm for those peaks, differences between the two spectra are mainly in intensity and shape of those bands in region I and can be interpreted as the results of their difference in distortion from a perfect D_{4h} symmetry. It is known that the 476 and 492 nm bands of $[UO_2Cl_4]^{2-}$ are very sensitive to solvent environment and their intensity can be enhanced greatly by distortion (e.g., hydrogen bonding from H−X).[11,13,19] In the $[UO_2(TEMBP)_2]^{2+}$ complex, the symmetry is D_{2h}, so the distortion from D_{4h} is much greater than that of $[UO_2Cl_4]^{2-}$ (which is in a slightly distorted D_{4h} symmetry). And moreover, this distortion is essentially governed by the combination of the bonding interactions between the metal atom (U) and the ligating atoms (O), the structure of the bidentate ligand, and the nonbonding interactions between the two coordinating ligand molecules; thus it is less sensitive to the solvent environment. As a result, the 495/478/462 bands in $[UO_2(TEMBP)_2]^{2+}$ spectra are more intense than their counterparts in $[UO_2Cl_4]^{2-}$ spectra, and the weaker satellite bands seen in $[UO_2Cl_4]^{2-}$ spectra are merged into the strong bands, so that only broad "single" bands are visible. In region II, both of the spectra of the two complexes show typical band splitting and in which three vibronic progressions with interval of ~700 cm^{-1} can be identified (Table S1 in Supporting Information). As shown in Figure 1, the spectra of $[UO_2(TEMBP)_2]^{2+}$ in acetonitrile and the two ILs have minor differences in their splitting features. Similar solvent or environment sensitive spectral changes of $[UO_2Cl_4]^{2-}$ had been reported,[11a,c,13,19a] and those were mainly explained as results of hydrogen bonding. However, the dicationic $[UO_2(TEMBP)_2]^{2+}$ is not likely to form hydrogen bonds, so the spectral changes may be caused by other intermolecular interactions. Due to the complexity of the spectra of uranyl compounds and the lack of reference data, those interpretations could be very preliminary.

Luminescence Spectra. In the luminescence studies with ILs as solvent, the quaternary ammonium based IL [N$_{4111}$][NTf$_2$] is used instead of [BMIm][NTf$_2$], since the latter emits fluorescence strongly in the 500−700 nm region.[20] Figure 3 shows the luminescence emission spectra of uranyl ion with varied L/U ratios in ionic liquid [N$_{4111}$][NTf$_2$] at room temperature. The excitation wavelength is chosen to be 330 nm, because the broad luminescence band centered at ~510 nm due to the IL is much lower than that excited at 423 nm. The luminescence of "free" uranyl in [N$_{4111}$][NTf$_2$] is very weak, whereas that of $[UO_2(TEMBP)_2]^{2+}$ (Figure 3e) is much stronger. The luminescence spectrum of $[UO_2(TEMBP)_2]^{2+}$ shows typical vibronic bands with peak separation of 854 ± 5 cm^{-1} (the spectra of L/U = 2.5 and 3.0 are almost the same with their difference in intensity less than 5%). Similar luminescence "enhancement" of uranyl complexes in ILs has been reported.[11c,13] The emission of sample with L/U = 1.0 (Figure 3b) is higher than that of "free" uranyl but still much lower than that of $[UO_2(TEMBP)_2]^{2+}$. It may be attributed to the contribution of a mixture of "free" uranyl, $UO_2(TEMBP)^{2+}$ intermediate (which may have a largest proportion), and a

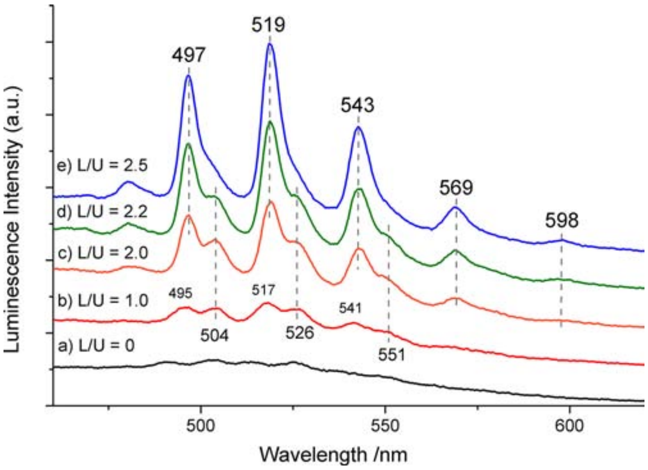

Figure 3. Luminescence emission spectra of uranyl ion with varied L/U ratios in ionic liquid [N$_{4111}$][NTf$_2$] at room temperature. The uranyl concentration is 10 mM, and the L/U ratio varies from 0 to 2.5. The excitation wavelength is 330 nm. The intensity is given in arbitrary units.

small amount of $UO_2(TEMBP)_2^{2+}$. In the former two cases, water molecules or $[NTf_2]^-$ anions might enter the inner coordination sphere of UO_2^{2+}. The emission spectrum of L/U = 1.0 shows two groups of bands with interval of ~835 cm^{-1} in each group. The spectra of L/U 2.0 to 2.5 exhibit gradual increase in band intensities of $[UO_2(TEMBP)_2]^{2+}$ accompanied by the disappearance of bands at 504, 526, and 551 nm probably belonging to the $UO_2(TEMP)^{2+}$ intermediate. Unlike the absorption spectrum of the $UO_2(TEMBP)^{2+}$ intermediate (which bands overlap heavily with those of $UO_2(TEMBP)_2^{2+}$), the emission spectrum of the $UO_2(TEMBP)^{2+}$ has distinct bands, thus helping to observe the gradual decrease of $UO_2(TEMBP)^{2+}$ concentration in the evolution on the spectra with L/U from 2.0 to 2.5. As discussed above for the UV−vis absorption spectra in Figure 2, the spectral change from L/U 2.0 to 2.5 is caused by the equilibrium among $[UO_2(TEMBP)_2]^{2+}$, intermediate species, and free TEMBP ligand. The luminescence emission spectrum of $[UO_2(TEMBP)_2]^{2+}$ shows a mirror relationship with its UV−vis spectrum in region I (Figure 4). The common band at 495 nm (497 nm in emission spectrum) is identified as the first electronic transition (the 0−0 transition) of $[UO_2(TEMBP)_2]^{2+}$. In the absorption spectrum, this transition is predominantly coupled with the excited state ν_s (~720 cm^{-1}), whereas the ground state ν_s (~850 cm^{-1}) is involved in the emission spectrum. The small peak at 481 nm can be assigned as "hot band" (in this case, it is involving the transition from the first vibrational level of the first excited state to the lowest vibrational level of the ground state, thus having an energy of ~700 cm^{-1} higher than the 0−0 transition).

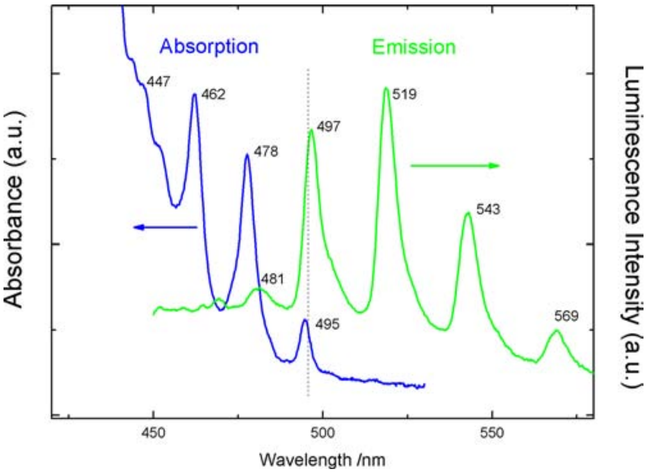

Figure 4. The mirror relationship for UV−vis absorption (blue) and luminescence emission (green) spectra of $[UO_2(TEMBP)_2]^{2+}$ in $[N_{4111}][NTf_2]$ at room temperature. The excitation wavelength of emission spectrum is 330 nm. Concentrations are $c(UO_2^{2+})$ = 10 mM and c(TEMBP) = 30 mM, and the y-axis is given in arbitrary units.

The emission spectra in acetonitrile are somehow more complex than those in $[N_{4111}][NTf_2]$. The emission of "free" uranyl in acetonitrile (Figure 5a) is much higher than that in $[N_{4111}][NTf_2]$, though still weaker than that of $[UO_2(TEMBP)_2]^{2+}$ (Figure 5d). The intensity of the spectrum with L/U = 1.0 (Figure 5b) is comparable to that of spectra with L/U = 2.0 and 3.0, with a minor blue shift (<1.5 nm) from the bands of $[UO_2(TEMBP)_2]^{2+}$. As shown in the inset graph of Figure 5, besides the minor blue shift (<1 nm) of the emission peaks in acetonitrile compared with those in $[N_{4111}][NTf_2]$, the intensity of the former is much higher (Figure 5e,f). And most surprisingly, the intensity of L/U =3.0 (Figure 5d) is lower than that of L/U = 2.0 (Figure 5c). Actually, the intensity decreases with L/U increasing from 2.0 to 4.0 (See Figure S3 in Supporting Information). The UV−vis spectra of L/U > 2.0 almost do not change with increasing L/U ratios, so the main species in samples with L/U 2.5−4.0 should be same (and no new complexes are further formed). On this basis, the decrease of luminescence intensity could only be the result of quenching, and the excess TEMBP ligand could be the only cause of quenching.

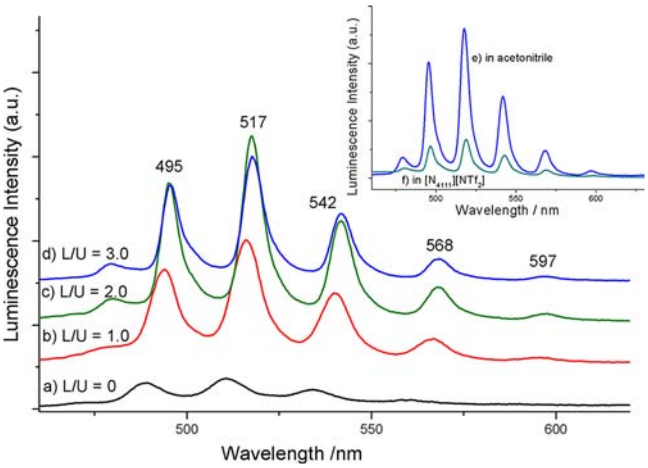

Figure 5. Luminescence emission spectra of uranyl ion with varied L/U ratios in acetonitrile at room temperature. The L/U ratios in spectra a−d vary from 0 to 3.0. The inset graph shows spectra of uranyl with L/U = 3.0 in different solvents: (e) pure acetonitrile; (f) pure $[N_{4111}][NTf_2]$. The uranyl concentration is 10 mM, and the excitation wavelength is 330 nm. The intensity is given in arbitrary units.

Luminescence spectra of samples with $[BMIm][NTf_2]$-containing acetonitrile as solvent were also studied. The emission spectra of samples containing 0.15 M of $[BMIm][NTf_2]$ is shown in Figure S4 in Supporting Information. The $[BMIm][NTf_2]$ dissolved in acetonitrile seems to be a strong quencher of luminescence of uranyl complexes, especially for the "free" uranyl and the intermediate 1:1 complex. On the other hand, the coordination-saturated $[UO_2(TEMBP)_2]^{2+}$ complex is more resistant to quenching from $[BMIm][NTf_2]$. Contrary to the samples in pure acetonitrile, the emission intensities of samples in $[BMIm][NTf_2]$-containing acetonitrile increase with the growth of L/U ratio, while the UV−vis spectra of the two series are almost the same (Figures S1 and S5 in Supporting Information). Though the luminescence intensities of samples with L/U 2.5−4.0 in different solvents (pure acetonitrile, acetonitrile with $[BMIm][NTf_2]$, and pure $[N_{4111}][NTf_2]$) are different, their spectra are similar.

ESI-ITMS. The stoichiometry of $[UO_2(TEMBP)_2]^{2+}$ is further confirmed by ESI-ITMS studies with acetonitrile as a solvent. The solutions diluted to 1 mM with L/U < 3.0 are not stable because their UV−vis spectra cannot retain the spectral character in 10 mM concentration (Figure S6 in Supporting Information). But the solution with an L/U ratio of 4.0 remains stable at a concentration of 1 mM as evidenced by its UV−vis spectrum. The sample of $[UO_2(TEMBP)_2]^{2+}$ in $[BMIm][NTf_2]$ is also diluted with acetonitrile because undiluted ILs could cause serious contamination of the instrument.[14a]

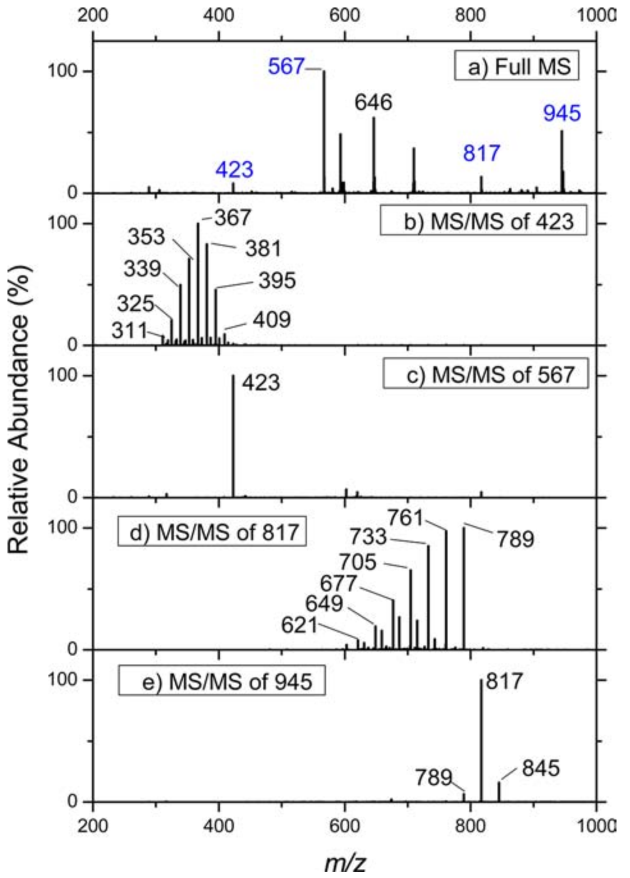

Figure 6. Positive ESI-ITMS spectra of the $[UO_2(TEMBP)_2]^{2+}$ complex in acetonitrile. The spectra are referred to (a) full ESI mass spectrum (full MS)and (b, c, d, e), MS/MS for ions of m/z = 423, 567, 817, and 945 in spectrum a. The uranyl concentration is 0.7 mM, and the L/U ratio is 4.0. The uranium-containing ions in spectrum a are colored in blue.

Figure 6 shows the positive ESI-ITMS spectra of $[UO_2(TEMBP)_2]^{2+}$ in acetonitrile. By multistage CID study, four peaks (m/z = 423, 567, 817, and 945) in the full mass spectrum (Figure 6a) are identified arising from species related to $[UO_2(TEMBP)_2]^{2+}$, and no other uranium-containing species are found. The compositions of those uranium-containing ions are listed in Table 1. The ion having m/z 423 is referred to the dicationic "naked" ion of $[UO_2(TEMBP)_2]^{2+}$ (846/2), as evidenced by the remarkable eight peaks (m/z 409−311) in its CID MS/MS spectrum (Figure 6b). That set of peaks with interval of 14 m/z units represents the fragmentation of the TEMBP ligand by losing of C_2H_4 units from the ethoxy groups in a dication, and there are eight peaks because the two ligands in a complex have eight ethoxy groups in total. Similar fragmentation behavior of the free ligand has been found in the MS^n spectra of TEMBP dimers with m/z 593 and 646 (Figure S7 in Supporting Information). The MS/MS of ion with m/z 567 produces only one peak at m/z 423 (Figure 6c), and its MS^3 has the same pattern as the MS/MS of the m/z 423 ion (Figure S8 in Supporting Information). Thus, the peak at m/z 567 must arise from an adduct of $[UO_2(TEMBP)_2]^{2+}$ with an additional ligand. The case is somehow similar for peaks at m/z 817 and 945: the m/z 945 ion produces ions with m/z 845 $\{[UO_2(TEMBP)_2]^{2+} - H^+\}$, 817, and 789 (Figure 6e), and the MS/MS spectrum of the m/z 817 ion (Figure 6d) also has the same pattern (peak separation of 28, losing a C_2H_4 unit from the ethoxy group of the ligand in a single charged cation) as the MS^3 spectrum of the m/z 945 ion (Figure S8 in Supporting Information). Then the m/z 817 ion can be identified as a fragment ion with a composition of $\{[UO_2(TEMBP)_2]^{2+} - (C_2H_5)^+\}$, and the m/z 945 peak arises from an adduct of $[UO_2(TEMBP)_2]^{2+}$ with a ClO_4^- anion (characterized by its M + 2 peak abundance of about 1/3).

Table 1. Compositions of the Uranium-Containing Ions Identified by ESI-ITMS Study

solvent	m/z	composition[a]	MS/MS product(s)
acetonitrile	423	$[UO_2L_2]^{2+}$	409, 395, 381, 367, 353, 339, 325, 311
	567	$\{[UO_2L_2]^{2+} + L\}$	423
	817	$\{[UO_2L_2]^{2+} - C_2H_5^+\}$	789, 761, 733, 705, 677, 649, 621
	945	$\{[UO_2L_2]^{2+} + ClO_4^-\}$	845, 817, 789
IL[b]	1126	$\{[UO_2L_2]^{2+} + NTf_2^-\}$	817

[a] L = TEMBP. [b] [BMIm][NTf$_2$] diluted with acetonitrile.

The mass spectrum of the sample containing [BMIm][NTf$_2$] (by diluting the complex containing IL with acetonitrile) is less complicated (Figure 7a), because there is predominately one uranium-containing ion with m/z 1126 $\{[UO_2(TEMBP)_2]^{2+} + [NTf_2]^-\}$. The multistage CID behavior (Figure 7c,d) of this ion is similar to that of the m/z 945 ion in acetonitrile. Assignments for other major peaks in the full MS are listed in Table 2.

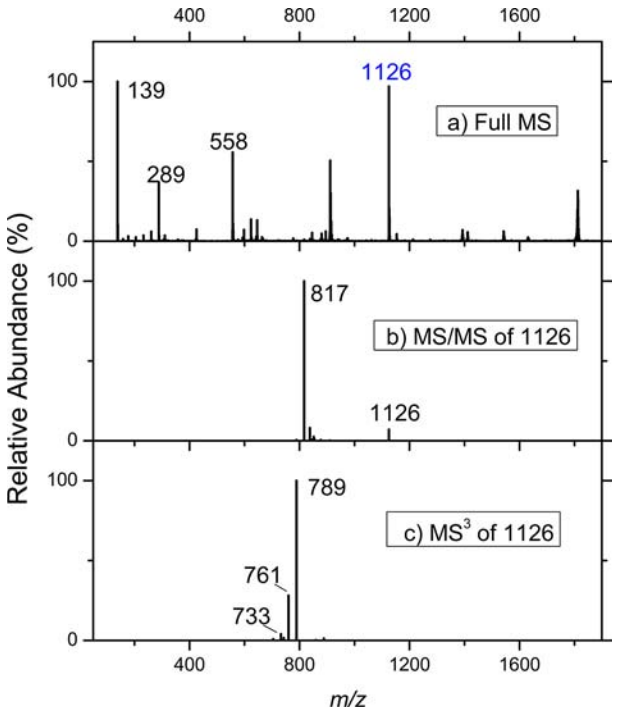

Figure 7. Positive ESI-ITMS spectra of the $[UO_2(TEMBP)_2]^{2+}$ complex in [BMIm][NTf$_2$] diluted by acetonitrile. The spectra are referred to (a) full ESI mass spectrum (full MS), (b) MS/MS of m/z = 1126 in spectrum a, and (c) MS^3 of 1126. The uranyl concentration is 1.0 mM, and the L/U ratio is 4.0.

Table 2. Compositions and Isotope Abundance (%) of the Identified Ions from the ESI Full Mass Spectra

			M + 1 abundance		M + 2 abundance		
m/*z*	composition[a]	formula	calcd	exptl	calcd	exptl	source
139	$[\mathrm{BMIm}]^+$	$C_8H_{15}N_2$	9.6	10.5			Figure 7a
289	$\{L + H^+\}$	$C_9H_{23}O_6P_2$	10.2	9.7	1.7	1.9	Figure 7a
558	$\{2[\mathrm{BMIm}]^+ + [\mathrm{NTf_2}]^-\}$	$C_{18}H_{30}F_6N_5O_4S_2$	23.4	20.2	12.5	12.0	Figure 7a
817	$\{[UO_2L_2]^{2+} - (C_2H_5)^+\}$	$C_{16}H_{39}O_{14}P_4U$	18.3	18.6	4.5	2.5	Figure 6a
945	$\{[UO_2L_2]^{2+} + [ClO_4]^-\}$	$C_{18}H_{44}ClO_{18}P_4U$	20.7	21.5	37.7	34.9	Figure 6a
1126	$\{[UO_2L_2]^{2+} + [\mathrm{NTf_2}]^-\}$	$C_{20}H_{44}F_6NO_{18}P_4S_2U$	24.8	21.3	15.7	15.6	Figure 7a

[a] L = TEMBP.

The "naked" dication $[UO_2(\mathrm{TEMBP})_2]^{2+}$ may not be favorable in gas phase (due to its higher inherent charge) after the ionization by electrospray, as indicated by the low abundance of the *m*/*z* 423 ion. The complex tends to exist as a weak adduct with either an additional ligand or a $[ClO_4]^-$ anion in pure acetonitrile, while the adduct of the dication with $[\mathrm{NTf_2}]^-$ is predominant in presence of $[\mathrm{BMIm}][\mathrm{NTf_2}]$. It is known that solvent molecules and anions may add to the cationic complexes in the ionization process of ESI-MS study,[14a,b] and the *m*/*z* 558 ion (two $[\mathrm{BMIm}]^+$ with one $[\mathrm{NTf_2}]^-$) (Figure 7a) is an example for such adducts. Since the perchlorate and $[\mathrm{NTf_2}]^-$ anions are well-known "non-coordinating" anions, they will not likely coordinate to the $[UO_2(\mathrm{TEMBP})_2]^{2+}$ complex. The case for the *m*/*z* 567 ($[UO_2(\mathrm{TEMBP})_2]^{2+}$ + TEMBP) ion is similar, because the third ligand can be easily stripped. Hence, the formation of adducts (from $[UO_2(\mathrm{TEMBP})_2]^{2+}$ with additional ligands) must be driven by Coloumbic attraction between the diaction and the anions (or dipolar neutral ligands). On the other hand, none of the identified uranium-containing ions have small ligands such as H_2O or CH_3CN in their compositions. Thus, the uranyl complex in the diluted solution has been identified as a composition of $[UO_2(\mathrm{TEMBP})_2]^{2+}$ by ESI-ITMS study, and that is consistent with the results of optical spectra study.

The compositions of the identified cations are also supported by the abundance of their M + 1 and M + 2 peaks (Table 2). Unfortunately, distributions of isotope peaks of the dicationic species (*m*/*z* 423 and 567) fit poorly with the calculated values (data not shown), which may be due to the low resolution (0.1 Da) of the instrument.

■ CONCLUSIONS

A new 2:1 complex formed by TEMBP with uranyl ion in acetonitrile and two hydrophobic ILs, $[\mathrm{BMIm}][\mathrm{NTf_2}]$ and $[\mathrm{N_{4111}}][\mathrm{NTf_2}]$, has been studied with combination of UV−vis absorption and luminescence emission spectroscopies and tandem ESI-ion trap mass spectrometry.

With excess of TEMBP ligand (L/U > 2.0), the uranyl is completely coordinated by two ligands to form a dicationic $[UO_2(\mathrm{TEMBP})_2]^{2+}$ complex. The UV−vis spectra of $[UO_2(\mathrm{TEMBP})_2]^{2+}$ in acetonitrile and in the two ILs are similar. The vibronic fine structures in UV−vis spectrum of $[UO_2(\mathrm{TEMBP})_2]^{2+}$ show characters of tetragonal coordination in the uranyl equatorial plane, similar to the well-studied $[UO_2Cl_4]^{2-}$. The symmetry of proposed structure of $[UO_2(\mathrm{TEMBP})_2]^{2+}$ is D_{2h}, and its UV−vis spectrum is tentatively interpreted based on the structural similarity to $[UO_2Cl_4]^{2-}$. The stronger absorption compared with $[UO_2Cl_4]^{2-}$ in the 455−500 nm region (region I) is interpreted as a result of lower symmetry.

The luminescence emission spectrum of $[UO_2(\mathrm{TEMBP})_2]^{2+}$ shows a mirror relationship with absorption spectrum in region I with the common band at 495 (497) nm. The interval between emission bands is about 850 cm^{-1}, representing the symmetric O═U═O stretching frequency in the ground state.

The stoichiometry of $[UO_2(\mathrm{TEMBP})_2]^{2+}$ is confirmed by ESI-ITMS studies with acetonitrile as solvent. The "naked" dication (*m*/*z* 423) is characterized by the remarkable eight peaks with interval of 14 *m*/*z* units in its CID MS/MS spectrum, representing the fragmentation of ligands by losing C_2H_4 units from their ethoxy groups. However, the dication tends to exist as a weak adduct with either an additional ligand or an anion in the ESI full mass spectrum. The adducts $\{[UO_2(\mathrm{TEMBP})_2]^{2+}$ + TEMBP} (*m*/*z* 567) and $\{[UO_2(\mathrm{TEMBP})_2]^{2+} + [ClO_4]^-\}$ (*m*/*z* 945) are favorable in pure acetonitrile, while only one adduct, $\{[UO_2(\mathrm{TEMBP})_2]^{2+} + [\mathrm{NTf_2}]^-\}$ (*m*/*z* 1126), is predominant in $[\mathrm{BMIm}][\mathrm{NTf_2}]$ (diluted with acetonitrile). Moreover, none of the identified uranium-containing ions have small ligands such as H_2O or CH_3CN in their compositions.

In conclusion, we first report the formation of a 2:1 dicationic complex of TEMBP and uranyl ion, $[UO_2(\mathrm{TEMBP})_2]^{2+}$, in hydrophobic ILs or acetonitrile solution under mild conditions in the present study. With excess of ligand (L/U > 2.0), the uranyl is completely coordinated with two TEMBP ligands. The structure of the complex is identified by using spectroscopic and mass spectrometric methods. $[UO_2(\mathrm{TEMBP})_2]^{2+}$, with a D_{2h} symmetry, shows characteristic fine structures in its optical spectra and remarkable CID fragmentation behavior in its multistage tandem mass spectra.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

UV−vis spectra of $UO_2(ClO_4)_2{\cdot}xH_2O$ with varied L/U ratios in acetonitrile and in $[\mathrm{N_{4111}}][\mathrm{NTf_2}]$, luminescence spectra of $[UO_2(\mathrm{TEMBP})_2]^{2+}$ with L/U 2.0−4.0 in acetonitrile, luminescence and UV−vis spectra of sample with varied L/U ratios in $[\mathrm{BMIm}][\mathrm{NTf_2}]$-containing acetonitrile, UV−vis spectra of $[UO_2(\mathrm{TEMBP})_2]^{2+}$ in diluted solution, ESI-ITMS multistage CID of ions *m*/*z* 593 and 646 and *m*/*z* 567 and 945, and UV−vis absorption and luminescence emission data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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