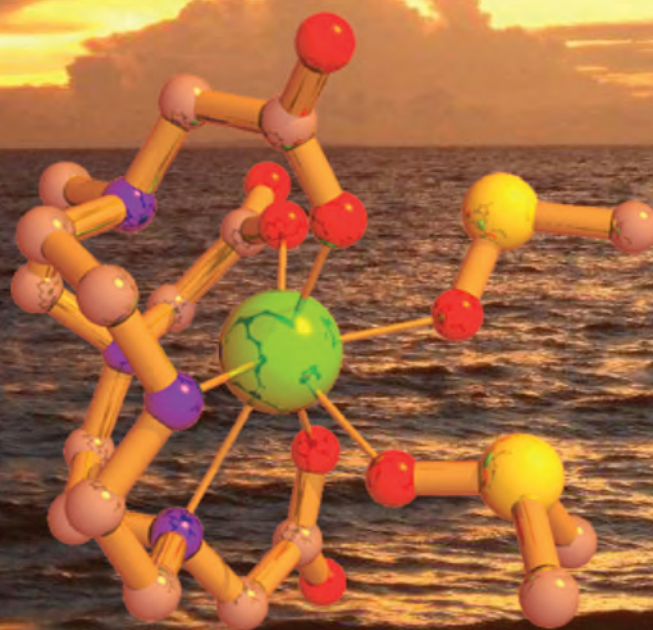


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PAPER

The first structural and spectroscopic study of a paramagnetic 5f DO3A complex†‡

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A $5f^2$ uranium(IV) complex of the macrocycle DO3A (DO3A = [4,7,10-tris-carboxymethyl-,1,4,7,10-tetraaza-cyclododec-1-yl]-acetic acid) has been prepared and characterised in the solid state and in solution. The DO3A scaffold containing no strongly absorbing chromophores enables the facile detection of relatively long-lived (8–13 ns) UV-visible emission that possesses significant charge transfer character tentatively assigned to deactivation of the excited $^3F_2\ 5f^1\ 6d^1$ electronic configuration. This study demonstrates, for the first time, that luminescence of simple U(IV) chelates is detectable in the absence of an antenna, potentially serving as a diagnostic tract for environmental U(IV) species.

Introduction

Uranium chemistry is currently receiving renewed interest, with the advent of synthetic routes to less well known oxidation states and the observation of unusual magnetic properties and reactivities.¹ This revitalisation has been motivated by the important technological attributes of uranium including nuclear power production and recent fundamental studies have provided the means to understand the electronic structures of open shell actinide ions in greater detail than previously.² Over the past few years, the importance of the identification of radiotoxic metal ions and their coordination complexes in the environment and in separation technologies based on liquid–liquid extraction has increased significantly.³ In this regard, emission spectroscopy of the trivalent actinides Am^{3+} and Cm^{3+} in particular,⁴ is a promising technique that is beginning to address these issues in addition to providing important information on chemical composition. In stark contrast to these and the wealth of studies detailing the photophysical properties of uranyl(VI), (UO_2^{2+}) compounds,⁵ the emissive properties of the U^{4+} ion has received little attention. This is perhaps surprising given that the +IV oxidation state plays an extremely important role regarding the bio-availability of uranium and that problems associated with environmental release have prompted a number of studies into the mobility of U^{4+} species in the environment.⁶

In the condensed phase (*e.g.* U^{4+} doped in LiYF_4 ,⁷ ThBr_4 , ThCl_4 , ThSiO_4 and Cs_2ZrBr_6 , Cs_2GeBr_6 and Cs_2UCl_6),⁸ both charge transfer emission bands in the UV and relatively broad, less intense emission bands in the visible region have been observed following photoexcitation and assigned to $5f^1\ 6d^1 \rightarrow 5f^2$ electronic transitions. In 2003, Kirishima *et al.*, reported the luminescence properties of tetravalent uranium in aqueous 0.1 M perchloric acid solution.⁹ Excitation at 245 nm with a nano-second pulsed dye laser, resulted in structured emission with ten relatively sharp bands centered between 289 and 525 nm. These emission bands were assigned as transitions from the 1S_0 highest lying electronic state to the lower lying levels of the f^2 LS coupled energy level scheme, 1I_6 , 1G_4 , 3P_0 , 1D_2 , 3F_3 , 3F_4 and 3H_5 (Fig. S8†).¹⁰ In a fluid solution, the observed luminescence lifetimes were shorter than the instrument response function (<20 ns in this case), but in a frozen solution appreciably long emissive lifetimes of 149 ns in H_2O and 198 ns in D_2O were determined.¹¹

By contrast, there are no reports of emissive U^{IV} coordination complexes which may serve as well defined models of complexed environmental species such as humics.¹² This is partly due to the fact that the U^{4+} ion is redox sensitive and the vast majority of work has been performed with organometallic complexes under strictly anaerobic conditions.¹³ In these cases, the ligands employed usually possess low energy broad charge transfer absorptions that conceal any weaker $f\text{--}f$ or charge transfer transitions. For example, in the metallocene ketimide system $(\text{Cp}^*)_2\text{U}[\text{NC}(\text{Ph})(\text{CH}_2\text{Ph})]_2$ (Cp^* = pentamethylcyclopentadienyl),¹⁴ no $5f$ -centered emission was observed following photoexcitation; decay from the ligand centered singlet state proceeds directly through the $5f$ -electron manifold resulting in efficient quenching of the emission. We therefore sought to investigate the coordination chemistry and luminescent properties of a U^{IV} DO3A complex, where the absorption profile of the ligand is limited to the ultraviolet and there are no strongly absorbing chromophores that could compete with the emission

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‡ Electronic supplementary information (ESI) available: Full experimental details, Crystallographic Information File (CIF) of $[\text{U}(\text{DO3A})(\text{dmsO})_2]\text{Br}$, UV-vis-nIR absorption spectrum, emission spectra following 250, 310 and 405 nm excitation, excitation spectra recorded at the emission maxima 300, 350 and 415 nm and LS coupled energy level diagram for the $5f^2$ electronic configuration. CCDC 871258. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30573a

from the excited 5f electronic configuration.¹⁵ Moreover, the low symmetry of the resultant complex means that any formally Laporte forbidden emission may be somewhat relaxed.

Results and discussion

Kinetically stable lanthanide complexes derived from DOTA and DO3A (DOTA = 1,4,7,10-tetraazacyclododecane-*N',N'',N''',N''''*-tetraacetic acid) currently find widespread use as imaging agents in magnetic resonance imaging (MRI) and luminescence microscopy.¹⁶ Since the 8-coordinate ionic radius of U⁴⁺ is almost identical to that of Tm³⁺,¹⁷ the DO3A ligand should provide an ideal scaffold to access kinetically inert U^{IV} complexes.

The synthetic route to the complex [U(DO3A)]⁺ is shown in Scheme 1. Reaction of the tris-ethyl ester of DO3A (Et₃DO3A·HBr)¹⁸ with potassium trimethylsilanolate (KOTMS) in CH₂Cl₂ yielded the tris-potassium salt K₃DO3A (K₃L¹) in moderate yield after work up re-crystallisation from methanol and diethyl ether. This method of ethyl ester cleavage was chosen rather than the more conventional base hydrolysis reaction in order to eliminate the use of water during the reaction and to limit the number of associated water molecules in the final product. In the subsequent step, treatment of K₃DO3A with UCl₄ in degassed methanol under argon resulted in the precipitation of potassium halide salts and the formation of a mint green solution containing the complex [U(DO3A)]Br ([U(L¹)]Br). Green needles of the bis DMSO adduct [U(DO3A)(DMSO)₂]Br suitable for a diffraction study were grown by slow diffusion of diethyl ether into a 1 : 1 v : v MeOH–DMSO solution of the complex at room temperature.

Solid state structure of [U(DO3A)(DMSO)₂]Br

To the best of my knowledge, there is only one previous structural report of a lanthanide DO3A complex for comparison and one description of a polyol N-functionalised DO3A ligand; these are the complexes gadolinium-(1*R*,4*R*,7*R*)-α,α',α''-trimethyl-1,4,7,10-tetraazacyclododecane-1,4,7-triacetate, [Gd(DO3MA)] where the three carboxylate arms have been functionalised with a methyl group¹⁹ and gadolinium-DO3A-butrol.²⁰ However, both of these examples are dimeric in the solid state. Generally, lanthanide DO3A complexes are in rapid conformational exchange in solution associated with a fast exchange of labile solvent molecules in the first coordination sphere and conformational isomerism of macrocyclic ring and arms. Analogous

isomerism processes occur in the lanthanide DOTA derivatives, but the rates of exchange tend to be significantly slower (~μs).²¹

The solid state structure of the cation [U(DO3A)(DMSO)₂]⁺ (Fig. 1) shows that the U⁴⁺ ion is 9 coordinate; the resultant coordination geometry is best described as a distorted mono capped square antiprism (SAP). The complex crystallises as a racemate and the Δ(λλλ) configuration is observed in the asymmetric unit cell. Average cyclen N–C–C–N and N–C–C–O torsion angles are respectively measured as –57.9° and 25.3° in accordance with previous reports.²² The basal plane is described by the four cyclen N atoms (N(1)–N(4)) and the orthogonal plane occupied by the three acetate O atoms (O(005), O(006) and O(011)) and an O atom of one of the DMSO solvent molecules (O(007)), whereas the approximate apical position is occupied by the second DMSO solvent molecule (O(010)). The dihedral angle between the cyclen N₄ donor set and that of the acetate/DMSO donor set is 40° (±1°) and is characteristic of distorted SAP coordination polyhedra observed in lanthanide DOTA and in mono, bis, tri and tetraamide DOTA derivatives.²³ These two planes lie almost parallel to one another; the angle between them being 0.5° and the U⁴⁺ cation lies 1.664 Å from the centre of the N₄ plane and 0.667 Å from the O₄ plane. These values are respectively, slightly longer and shorter than those measured for [Ln·DOTA][–] complexes in the latter half of the 4f series²⁴ reflecting the differences in charge density between the Ln³⁺ ions and the U⁴⁺ cation. For example, in the X-ray structure

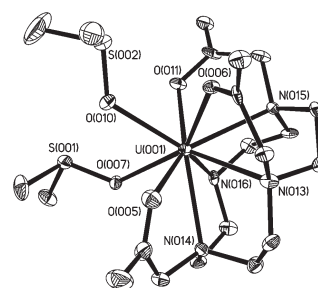
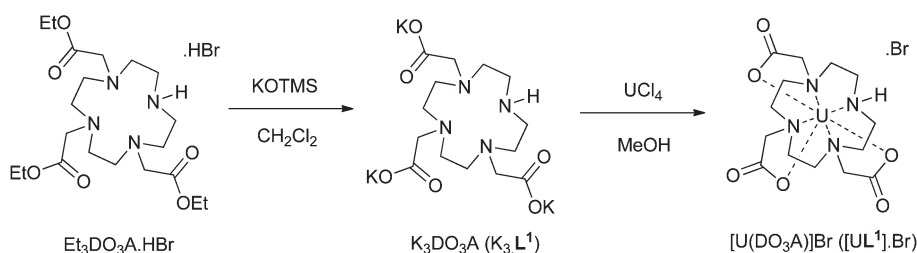


Fig. 1 Thermal ellipsoid drawing of the cation [U(DO3A)(DMSO)₂]⁺ at the 50% probability level, H atoms and Br[–] counterion removed for clarity. Selected distances (Å) and angles (°): U(001)–O(005) 2.302(6), U(001)–O(011) 2.304(6), U(001)–O(006) 2.311(6), U(001)–O(007) 2.365(6), U(001)–O(010) 2.402(6), U(001)–N(016) 2.619(6), U(001)–N(014) 2.653(7), U(001)–N(015) 2.680(7), U(001)–N(013) 2.683(7); O(005)–U(001)–O(011) 149.6(2), O(005)–U(001)–O(006) 84.7(2), O(005)–U(001)–O(007) 83.6(2), O(006)–U(001)–N(016) 138.2(2), O(005)–U(001)–N(014) 65.2(2), N(016)–U(001)–N(014) 66.4(2), N(016)–U(001)–N(015) 67.0(2), N(014)–U(001)–N(015) 104.2(2).



Scheme 1 Synthetic route to [U(DO3A)]Br ([U(L¹)]Br).

of [Ho-DOTA][−], which also crystallises as the mono-capped square antiprismatic diastereomer, the N₄ centroid Ho³⁺ distance is 1.608 Å and that measured for the O₄ plane is 0.728 Å. The relative positioning of the uranium cation in the macrocyclic cavity is by contrast, not reflected in the average bond distances, which are statistically equivalent to those measured in the [Ln-DOTA][−] series and in the Tb(DO3A)mono-amide complex bearing an isophthalate arm recently reported by us,²⁵ (av. *d*(U–N) = 2.658(7) Å and av. *d*(U–O) = 2.305(6) Å).

The DMSO oxygen–uranium distances of 2.365(6) and 2.402(6) Å are neither statistically different from one another nor from equivalent solvent and coordinated anion donors measured crystallographically in lanthanide DOTA, tetrapicolyl cyclen and DOTA-amide systems.²⁴

Solution properties of [U(DO3A)(DMSO)₂]Br

¹H NMR spectroscopy was used to investigate the solution structure of the complex. The ¹H NMR spectrum of [U(DO3A)]Br in a 1 : 1 v : v mixture of d₆-DMSO and d₄-MeOH is displayed in Fig. 2. Compared to the C₄ symmetric analogues of DOTA,²⁶ the broken symmetry in DO3A *f*-element complexes renders each individual CH proton inequivalent, giving rise to a total of 22 proton resonances. Notably, the chemical shift range of the paramagnetically shifted protons spans +80 ppm to −70 ppm. In the ¹H NMR spectrum of the related U^{IV} complex [U(HEHA)]^{2−} (HEHA = 1,4,7,10,13,16-hexaazacycloocta-decane-*N',N'',N''',N''',N''''*-hexaacetic acid) the chemical shift range of the minor asymmetric geometric isomer is similar.²⁷ Upon comparison with the isoelectronic 4f² ion in complexes [Pr(DOTA)][−] and [Pr(DTPA)]^{2−} the chemical shift range observed in [U(DO3A)]⁺ is significantly larger (for both these complexes proton resonances range +40 to −40 ppm).²⁸ However, in the less symmetric Pr³⁺ derivatives of DO3A in the complex [Pr(MOE-DO3A)] (MOE-DO3A = 10-(2-methoxyethyl)-1,4,7,10-tetraazacyclododecane-1,4,7-triacetate)²⁹ the induced dipolar shift range of the protons are larger ~+60 to −60 ppm yet still smaller than in the ¹H NMR spectrum of [U(DO3A)]⁺.

These differences may reflect the relative positioning of the U⁴⁺ cation in the macrocycle as identified by X-ray diffraction. In *pseudo*-axially symmetric complexes such as [Ln(DO3A)], the dipolar contribution to the lanthanide induced shift is

described by the Bleaney equation and in the 4f series the contact (through bond) contribution is usually considered negligible. The increased magnitude of the paramagnetic induced shift in [U(DO3A)]⁺ is likely to be due to a difference in the magnetic susceptibility tensor for U⁴⁺ compared to Pr³⁺ assuming the dipolar term dominates.³⁰ Since the chemical shifts of the resonances in [U(DO3A)]Br are well represented by the dipolar term (geometric factor) it is unlikely that there is a significant contact contribution to the overall shift.

Of particular note, are the relative linewidths of the proton resonances in [U(DO3A)]⁺; these range from 220 Hz to 65 Hz. However, the fact that the fwhm of the proton resonances in the related complexes [U(HEHA)]^{2−} and [U(DOTA)]³¹ that are in slow chemical exchange on the NMR timescale are much smaller (average of approximately 65 Hz in [U(DOTA)]) suggests that the broadening of the resonances is largely due to exchange processes between bound and unbound solvent molecules occurring faster than the experimental timescale (as seen with [Ln(DO3A)] complexes).

Moreover, the complex [U(DO3A)]⁺ appears to exist in one major isomeric form at room temperature, with only small resonances for a minor species just above baseline intensity. The fact that the most upfield shifted proton in the major isomer corresponding to a *pseudo*-axial C–H proton of the DO3A framework resonates at a lower frequency than the corresponding most upfield shifted peak for the minor isomer suggests that the major solution isomer is the solvated square antiprismatic form. This is in agreement with ¹H NMR data and the solution structures of lanthanide DOTA and DOTA-amide derivatives.^{23,24}

Emission spectroscopy was used to probe the solution form of the complex in more detail and to establish the spectral fingerprint of the U⁴⁺ ion encapsulated in the DO3A macrocycle. In principle, many of the intra-configurational intra 5f transitions are formally Laporte forbidden by the electric dipole operator. However, lowering of the symmetry of the coordinated U⁴⁺ ion from cubic or octahedral (in the aforementioned doped crystal-line systems) to approximate C_s symmetry in [U(DO3A)]⁺ may be expected to increase the transition probabilities of the symmetry forbidden *f*–*f* absorptions.

The ground state electronic UV-vis-nIR absorption spectra of the complex were recorded in MeOH solutions; the UV-vis spectrum is shown in Fig. 3 and the vis-nIR spectrum is displayed in the ESI (Fig. S1†). The UV-vis spectrum of the complex displays three main intense broad transitions in the UV region,

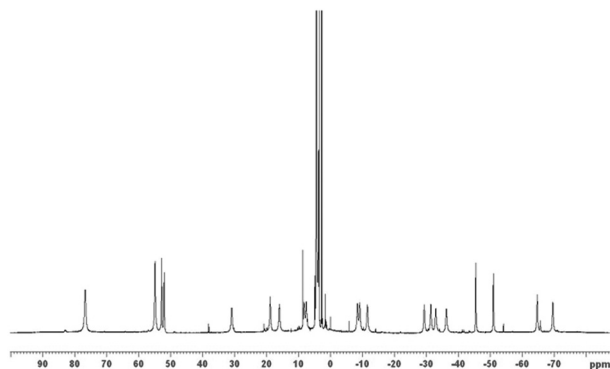


Fig. 2 ¹H NMR spectrum of [U(DO3A)]Br, 300 K, d₆-DMSO : d₄-MeOH.

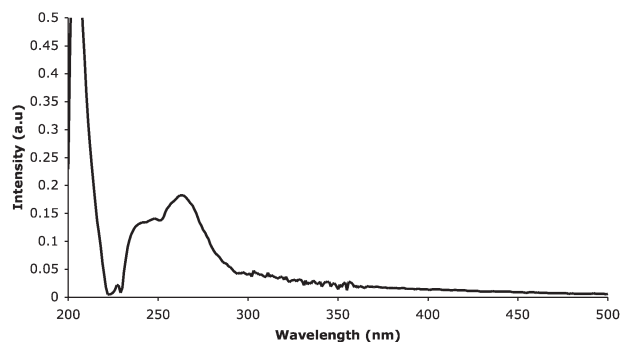


Fig. 3 UV-vis spectrum of [U(DO3A)]Br in MeOH, 298 K.

centred at 245 and 261 nm, with a weaker tail at 322 nm. By comparison with U^{4+} doped in $LiYF_4$,⁷ these transitions are tentatively assigned to the carboxylate $n \rightarrow \pi^*$ absorption and Laporte allowed charge transfer type (CT) $5f^2 \rightarrow 5f^1 6d^1$ ($^3H_4 \rightarrow ^3F_2$) transitions from the ground state and those derived from the higher energy terms of the $5f^2$ electronic configuration (e.g. 3H_6 , 3F_4 , 1D_2 , 1G_4 and 3P_2 terms, $J = 1-6$). In addition to these charge transfer transitions, the weaker intra $5f$ absorptions in the visible and near infra-red centred at 643, 1042 and 1103 nm are observed in concentrated solutions; these are characteristic of U^{4+} ions and remain unshifted with respect to the parent UCl_4 in donating solvents.^{31,32}

In fluid solution at room temperature, excitation into each of the absorption bands (220–380 nm) affords luminescence spectra that comprise three broad featureless transitions centred at 415, 430 and 520 nm (Fig. 4). The emission spectra are independent of excitation wavelength (see ESI†) which indicates that the emission originates from the same excited state. The excitation spectra recorded at the respective emission maxima exhibit two bands that correspond to those observed in the absorption spectrum and indicate that the absorption bands at 240 and 320 nm are responsible for the emission and that the same excited states are involved.

The emission and excitation spectra bear striking resemblance to those observed in the doped system $U:LiYF_4$,⁷ but the emission bands exhibit less structure in $[U(DO3A)]^+$. This is unsurprising given the increased vibrational broadening that occurs in solution. Interestingly, no visible or near infra-red emission was observed upon visible or near infra-red excitation (e.g. 640 and 980 nm) even at high concentration that may be expected if the lower energy excited $f-f$ states were being populated.

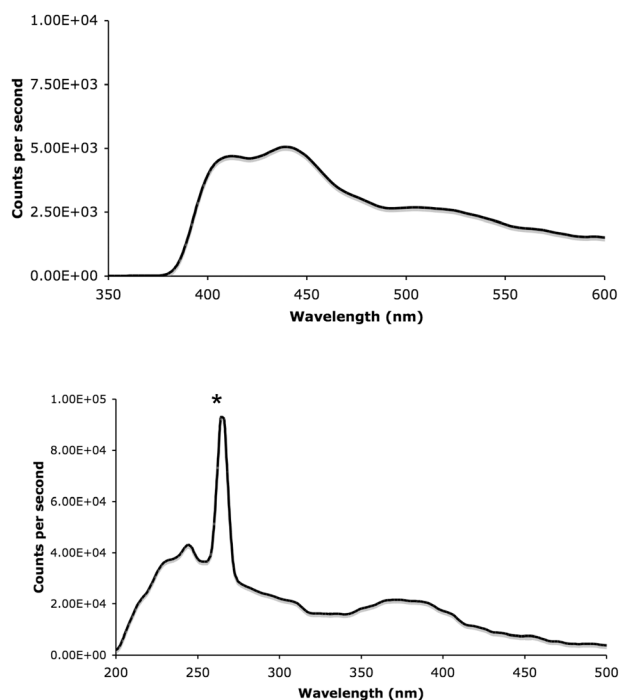


Fig. 4 Above, steady state emission spectrum of $[U(DO3A)]Br$ in MeOH at room temperature following excitation at 330 nm (with a 340 nm band pass filter). Below, excitation spectrum recorded at 520 nm, asterisk denotes scattered light at double the frequency of the emission.

Table 1 Photophysical properties of $[U(DO3A)]Br$ at 298 K

λ_{em}	τ_{MeOH} (ns)	τ_{MeOD} (ns)	τ_{DMF} (ns)
415	2.6 (39%) 7.8 (61%)	2.6 (41%) 8.8 (59%)	1.6 (41%) 12.3 (59%)
440	2.8 (33%) 7.5 (67%)	2.5 (36%) 8.8 (54%)	1.6 (41%) 12.3 (59%)
520	2.8 (25%) 8.8 (75%)	2.7 (30%) 8.8 (70%)	1.9 (37%) 13.1 (63%)

All lifetimes recorded by TCSPC at 405 nm excitation using a pulsed picosecond diode laser and are subject to a $\pm 10\%$ error. Identical lifetimes were observed following 375 nm excitation.

The radiative lifetimes in degassed MeOH, MeOD and dry, degassed DMF were recorded following 375 and 405 nm excitation with a picosecond pulsed diode laser; the results are collated in Table 1.³³ In a methanolic solution, the lifetimes are of nanosecond order and were fitted to a bi-exponential decay, indicating the presence of two emissive components. For all three emission bands, the lifetimes are the same within error, being approximately 3 and 8 nanoseconds and the relative contribution to the total emission intensity is on average 40 and 60% respectively.

The origin of this bi-exponential behaviour is unclear, but it is reasonable to suggest that the two emissive species are due to the presence of coordination isomers in slow exchange on the nanosecond timescale or the existence of different solvates.³⁴ However, the fact that the emissive lifetimes are similar in deuterated methanol suggests that competitive vibrational quenching by O–H oscillators has only a small effect on the radiative lifetime. This indicates that other deactivation mechanisms operate on a faster timescale than coupling to energy matched harmonics of proximate O–H bonds. Compared to the condensed phase $U^{4+}:LiYF_4$ system, which possesses radiative lifetimes of *ca.* 17 ns for all emission bands at both 300 and 77 K,⁷ the radiative lifetimes of $[U(DO3A)]^+$ are of a similar magnitude, indicating the DO3A ligand has little effect on the intrinsic emissive properties of the U^{4+} ion. Additionally, the luminescence lifetimes in dry, degassed DMF bear this conclusion out to some degree; the minor component has a similar lifetime whereas the radiative lifetime of the major component increases to 12 nanoseconds. This observation may suggest that the emissive minor component originates from fluorescence from the DO3A chromophore or from an allowed ligand-to-metal charge transfer from the carboxylate oxygens to the uranium metal centre ($2p \rightarrow 6d$) (short lifetime < 3 ns). By contrast, the major component is metal based in origin and the lifetime is affected by the nature of the solvent, rate of solvent exchange and therefore the relative degree of bimolecular quenching.

Together, these data suggest that the emission from $[U(DO3A)]Br$ possesses considerable charge transfer character and are tentatively assigned to $^3F_2 \rightarrow ^3H_J$ transitions ($J = 4, 5, 6$) and radiative transitions to successively higher spin-orbit coupled states derived from the terms 3F , 1D , 1G and 3P . Rapid phonon-mediated non-radiative transitions through the $5f$ manifold considerably reduces the luminescence lifetime of the emissive state compared to the isoelectronic Pr^{3+} ion precluding observation of lower energy intra $5f-f$ transitions. This is in contrast to the data reported by Kirishima, where they observed that the emission arises solely from de-excitation of the intra f^1S_0

state (see Fig. S8† in ESI).⁹ It is plausible that the relative energies of the charge transfer and 1S_0 states may be similar and are particularly sensitive to changes in the local coordination environment since the energies of the emissive transitions in [U(DO3A)]Br are similar to those reported by Kirishima for U^{4+} in aqueous solution.

Conclusions

In conclusion, use of a chelating macrocycle devoid of strongly absorbing chromophores in the UV-vis serves as an ideal scaffold to encapsulate the U^{4+} cation in a low symmetry coordination environment and enables the detection of long-lived charge transfer emission most likely attributable to transitions arising from deactivation of the $5f^4 6d^1$ excited electronic state. This study demonstrates, for the first time, that luminescence of simple U(IV) chelates is detectable and characteristic for the $5f^2$ configuration in the absence of an antenna group, potentially serving as a diagnostic tract for environmental U(IV) species.

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