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Young Hoon Lee[a], Youssef Atoini[b], Sotaro Kusumoto[c], Shinya Hayami[d], Yang Kim[d,*], Jack Harrowfield[e,*], Pierre Thuéry[f,*]

[a] *Department of Chemistry, University of Ulsan, Tekeunosaneop-ro 55beon-gil, Nam-gu, Ulsan 44610, Republic of Korea*
[b] *Technical University of Munich, Campus Straubing, Schulgasse 22, 94315 Straubing, Germany*
[c] *Department of Material & Life Chemistry, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan*
[d] *Department of Chemistry, Graduate School of Science and Technology, Institute of Industrial Nanomaterials (IINa), Kumamoto University, 2-39-1 Kurokami, Chuo-ku, Kumamoto 860-8555, Japan*
[e] *Université de Strasbourg, ISIS, 8 allée Gaspard Monge, 67083 Strasbourg, France*
[f] *Université Paris-Saclay, CEA, CNRS, NIMBE, 91191 Gif-sur-Yvette, France*

* Corresponding authors.
E-mail addresses: ykim@kumamoto-u.ac.jp (Y. Kim), harrowfield@unistra.fr (J. Harrowfield), pierre.thuery@cea.fr (P. Thuéry)

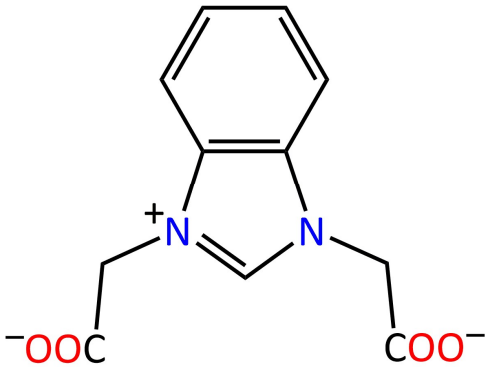
Abstract

$[UO_2(L)_2]$ (**1**) and $[(UO_2)_2(L)_2(C_2O_4)]$ (**2**), where L^- is 1,3-bis(carboxylatomethyl)-1H-benzimidazol-3-ium, are two uranyl ion complexes with a hemi-zwitterionic dicarboxylate ligand which have been synthesized under solvo-hydrothermal conditions and characterized by their crystal structure and luminescence properties. In both cases, the uranium atom is in a pentagonal-bipyramidal environment. Although diperiodic networks are formed in both cases, differences in the coordination mode of L^- and the presence of bis-chelating oxalate anions generated *in situ* in **2** result in distinct topologies, **hcb** (with double edges) in **1** and V_2O_5 in **2**. Parallel-displaced π–π interactions occur in both cases but are particularly prominent in **2**. While **2** is non-emissive under excitation at 420 nm, **1** gives a well-resolved spectrum with the maxima locations in agreement with those usual for O_5 equatorial uranyl environments. A photoluminescence quantum yield of ~43% has been measured for **1** in the solid state, this being among the highest values known for a uranyl carboxylate complex.

Keywords: Uranyl ion, Metal–organic networks, Photoluminescence, Structure elucidation, Zwitterionic ligand

1. Introduction

Among the huge variety of carboxylate ligands which have been used as ligands to generate uranyl ion coordination polymers or frameworks [1–7], those which can adopt a zwitterionic form are endowed with particular assembling abilities resulting from their neutrality and, particularly in the case where the positive charge is associated with the presence of protons, their ability to be involved in extended hydrogen bonding [8,9]. Particularly notable are the use of long-chain dizwitterionic dicarboxylates for the synthesis of polyrotaxanes and the ready synthesis of mixed-ligand complexes containing both classical (anionic) and zwitterionic carboxylates [9]. A subset of this group of ligands, more properly designated as pseudo-zwitterionic, is that in which only part of the molecule can adopt a zwitterionic form, for example, a dicarboxylate possessing only one positively charged centre and thus being mono-anionic and hemi-zwitterionic. The present work involves one such ligand, 1,3-bis(carboxylatomethyl)-1H-benzimidazol-3-ium (L^-, Scheme 1). This molecule was first synthesized and crystallographically characterized in its mono-deprotonated, neutral form HL



Scheme 1. The L^- ligand in its mono-anionic, hemi-zwitterionic form (note that the Valence Bond representation shown is one of two equivalent resonance forms which indicate that the positive charge is delocalized over both N atoms).

[10], a structure later redetermined as part of a study of the use of the zwitterion as a coating on CuO for catalytic purposes [11]. L^- has been found as a ligand in several complexes with

alkaline-earth [12], d-block [13–20], and lanthanide [21–23] metal ions, but no complex with an actinide cation is reported in the Cambridge Structural Database (CSD, Version 5.45) [24]. We report here the synthesis, crystal structure, and luminescence properties of two uranyl ion complexes with L^-, either alone or with the oxalate coligand, obtained during the course of an investigation of the use of zwitterionic or pseudo-zwitterionic carboxylates in uranyl chemistry. Both complexes crystallize as diperiodic networks and one of them has a photoluminescence quantum yield (PLQY) among the highest measured for such a complex.

2. Experimental section

2.1. Synthesis

Caution! Uranium is a radioactive and chemically toxic element, and uranium-containing samples must be handled with suitable care and protection. Small quantities of reagents and solvents were employed to minimize any potential hazards arising both from the presence of uranium and the use of pressurized vessels for the syntheses.

Dioxouranium(VI) nitrate hexahydrate, $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (RP Normapur, 99%) was purchased from Prolabo. 1,3-Bis(carboxymethyl)-1H-benzimidazol-3-ium chloride (H_2LCl) was prepared by the previously reported method [10,23]. For the syntheses of complexes, the mixtures in demineralized water/acetonitrile were placed in 10 mL tightly closed glass vessels and heated at 140 °C in a sand bath, under autogenous pressure. The crystals characterized were those deposited under the reaction conditions and not from subsequent cooling and depressurization.

*2.1.1. $[UO_2(L)_2]$ (**1**)*

H_2LCl (14 mg, 0.05 mmol) and $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (25 mg, 0.05 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL). Yellow crystals of complex **1** were obtained within one month (15 mg, 41% yield based on L). *Anal.* Calc. for

$C_{22}H_{18}N_4O_{10}U$: C, 35.88; H, 2.46; N, 7.61. Found: C, 35.03; H, 2.58; N, 7.40%. The same complex was obtained in similar experiments involving additional dicarboxylic acids (*trans*- and *cis*-1,2-cyclohexanedicarboxylic, 1,3- and 1,4-phenylenediacetic, 1,3-adamantanediacetic, and pimelic acids) as potential coligands, as well as in an experiment with additional $KReO_4$.

*2.1.2. $[(UO_2)_2(L)_2(C_2O_4)]$ (**2**)*

H_2LCl (14 mg, 0.05 mmol), $[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O$ (35 mg, 0.07 mmol), and 1,2-phenylenedioxydiacetic acid (12 mg, 0.05 mmol) were dissolved in a mixture of water (0.6 mL) and acetonitrile (0.2 mL). Orange crystals of complex **2** were obtained within four days (9 mg, 33% yield based on L). *Anal.* Calc. for $C_{24}H_{18}N_4O_{16}U_2$: C, 26.34; H, 1.66; N, 5.12. Found: C, 26.62; H, 1.79; N, 5.01%.

2.2. Crystallography

The data were collected at 100(2) K on a Bruker D8 Quest diffractometer equipped with an Incoatec Microfocus Source (IμS 3.0 Mo) and a PHOTON III area detector, and operated through the APEX4 software [25]. The data were processed with SAINT [26], and absorption effects were corrected empirically with SADABS [27,28]. The structures were solved by intrinsic phasing with SHELXT [29] and refined by full-matrix least-squares on F^2 with SHELXL, using the ShelXle interface [30]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. A void in the structure of **1** is probably occupied by half a disordered and unresolved water molecule, whose contribution to the structure factors was subtracted with SQUEEZE [31] (6 electrons added per formula unit). Crystal data and structure refinement parameters are given in Table 1. Drawings were made with ORTEP-3 [32,33] and VESTA [34], and topological analyses were performed with ToposPro [35].

Table 1

Crystal data and structure refinement details.

	1	**2**
Chemical formula	$C_{22}H_{18}N_4O_{10}U$	$C_{24}H_{18}N_4O_{16}U_2$
M_r	736.43	1094.48
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	13.9413(5)	6.7455(3)
b (Å)	9.6457(3)	9.8674(4)
c (Å)	18.6538(6)	10.9862(4)
α (°)	90	105.9699(17)
β (°)	110.4736(13)	95.9422(19)
γ (°)	90	98.549(2)
V (Å^3)	2349.99(14)	687.15(5)
Z	4	1
No. of reflections collected	107874	19716
No. of independent reflections	6062	2602
No. of observed reflections [$I > 2\sigma(I)$]	5807	2477
R_{int}	0.042	0.040
No. of parameters refined	334	208
R_1	0.020	0.026
wR_2	0.051	0.069
S	1.131	1.085
$\Delta\rho_{min}$ (e Å^{-3})	−1.08	−1.13
$\Delta\rho_{max}$ (e Å^{-3})	1.97	2.71

2.3. Luminescence measurements

Emission spectra were recorded on solid samples using an Edinburgh Instruments FS5 spectrofluorimeter equipped with a 150 W CW ozone-free xenon arc lamp, dual-grating excitation and emission monochromators (2.1 nm/mm dispersion; 1200 grooves/mm), and an R928P photomultiplier detector. The powdered compounds were pressed to the wall of a quartz tube, and the measurements were performed using the right-angle mode in the SC-05 cassette. An excitation wavelength of 420 nm was used in all cases and the emission was monitored between 450 and 600 nm. The quantum yield measurements were performed by using a Hamamatsu Quantaurus C11347 absolute photoluminescence quantum yield spectrometer and exciting the samples between 300 and 400 nm.

3. Results and discussion

3.1. Crystal structures

The complex $[UO_2(L)_2]$ (**1**) was obtained under solvo-hydrothermal conditions with acetonitrile as organic cosolvent, either with L^- as sole possible ligand or in the presence of various other anionic dicarboxylates (*trans*- and *cis*-1,2-cyclohexanedicarboxylates, 1,3- and 1,4-phenylenediacetates, 1,3-adamantanediacetate, and pimelate) which were added in attempts to form mixed-ligand complexes. It was also obtained in the presence of $KReO_4$, the formation of neutral uranyl ion complexes with zwitterionic carboxylates being of interest for sequestration of anions such as perrhenate [36], which was, however, not achieved here. Considering that associating anionic and zwitterionic carboxylates is an efficient way of generating true, heteroleptic mixed-ligand species [9], this result is somewhat disappointing. It may possibly be ascribed to the pseudo-zwitterionic nature of L^- since the previous examples of neutral mixed-ligand complexes involved true, neutral dizwitterionic dicarboxylates. This would confirm the hypothesis that the neutrality of zwitterionic carboxylates could be essential to the formation of such neutral complexes through a reduction of electrostatic repulsions in the uranium coordination sphere when compared with complexes with anionic carboxylates only. However, the preferential crystallization of **1** from the various mixtures employed could also be a simple consequence of its low solubility.

The uranium atom in **1** is bound to four L^- ligands, three of them monodentate and one κ^2O,O'-chelating [U–O(oxo), 1.7861(19) and 1.7889(18) Å; U–O(carboxylato), 2.4684(17) and 2.5946(19) Å for the chelating group, 2.2818(18)–2.3575(19) Å for the others], the uranium atom environment being pentagonal-bipyramidal (Fig. 1). Uranium is a 4-coordinated (4-c)

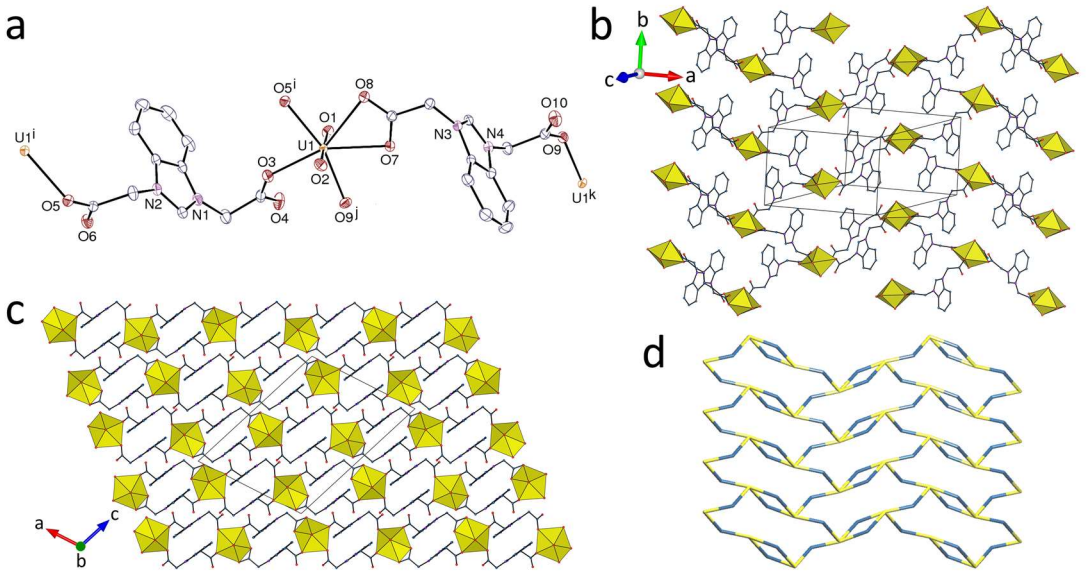


Fig. 1. (a) View of complex **1** with displacement ellipsoids shown at the 50% probability level and hydrogen atoms omitted. Symmetry codes: i = 1 – *x*, 1 – *y*, 1 – *z*; j = 2 – *x*, *y* – 1/2, 1/2 – *z*; k = 2 – *x*, *y* + 1/2, 1/2 – *z*. (b) View of the diperiodic coordination polymer with uranium coordination polyhedra colored yellow. (c) Packing with layers viewed edge-on. (d) Nodal representation of the network (U nodes, yellow; L edges, blue; same orientation as in (b)).

node, and the two inequivalent L^- ligands are simple edges in the diperiodic network formed, parallel to (102), which has the $\{6^3\}$ point symbol and the **hcb** topological type, with however some edges being double. These double edges involve what may be considered as stacked pairs of each ligand. Analysis of short contacts with PLATON [37] shows however that the only possibly significant parallel-displaced π-stacking interactions involve five- and six-membered aromatic rings from neighbouring layers [centroid···centroid distances, 3.8584(16)–4.1143(17) Å; dihedral angles, 3.95(15)–4.39(15)°; slippages, 1.70–2.23 Å]. Within the double edges, although the interplanar spacing is quite short, overlap in projection is very slight, and the ligands are only associated through CH···π interactions involving the two hydrogen atoms of one methylene group [C···centroid distances, 3.338(3) and 3.601(3) Å; C–H···centroid angles, 105 and 136°]. These interactions, as well as the ubiquitous CH···O hydrogen bonds, are well apparent on the Hirshfeld surface (HS) [38,39]. The Kitaigorodski packing index (KPI,

evaluated with PLATON) is 0.70, with a small void probably occupied by half a disordered and unresolved water molecule (see Experimental section).

The complex $[(UO_2)_2(L)_2(C_2O_4)]$ (**2**) incorporates an oxalate coligand, the generation of oxalate during solvothermal syntheses involving uranyl ion complexes being a not uncommon observation [40–46] attributed to oxidation of organic substrates (ligands, solvent) under the reaction conditions, which usually involve extended periods of heating under pressure at moderately elevated temperatures. While uranyl ion is an oxidant, both early [42] and recent [46] mechanistic studies have shown that the actual oxidant is nitrate ion, introduced through the use of uranyl nitrate as a reactant. Uranyl ion might have some role in activating nitrate ion, though this is yet to be established, and it is known [47] that similar oxidations occur in solvothermal reactions involving a non-oxidising lanthanide (Nd^{III}) when also used as its nitrate. In early studies [42,47], it was found that heterocyclic C–N bonds appeared to be particularly susceptible to oxidation. This may explain the present observation of oxalate as a ligand in complex **2**, though of course the 1,2-phenylenedioxydiacetic acid in the reaction mixture here may also have been the source.

The uranium atom in complex **2** is also in a pentagonal-bipyramidal environment, with three donors from three L^- ligands and a chelating oxalate anion, as shown in Fig. 2 [U–O(oxo), 1.772(4) and 1.786(4) Å; U–O(carboxylato), 2.305(4)–2.385(4) Å for L^-, 2.447(4) and 2.448(4) Å for oxalate]. One carboxylate group of L^- is monodentate and the other is *syn/anti* μ_2-κ^1O:κ^1O'-bridging. L^- is thus a 3-c node, while U is a 4-c node and oxalate is a simple edge. The coordination polymer present in **2** is diperiodic, as in **1**, and parallel to $(1\bar{1}1)$. It has the $\{4^2.6^3.8\}\{4^2.6\}$ point symbol and the V_2O_5 topological type, frequently found in uranyl-based

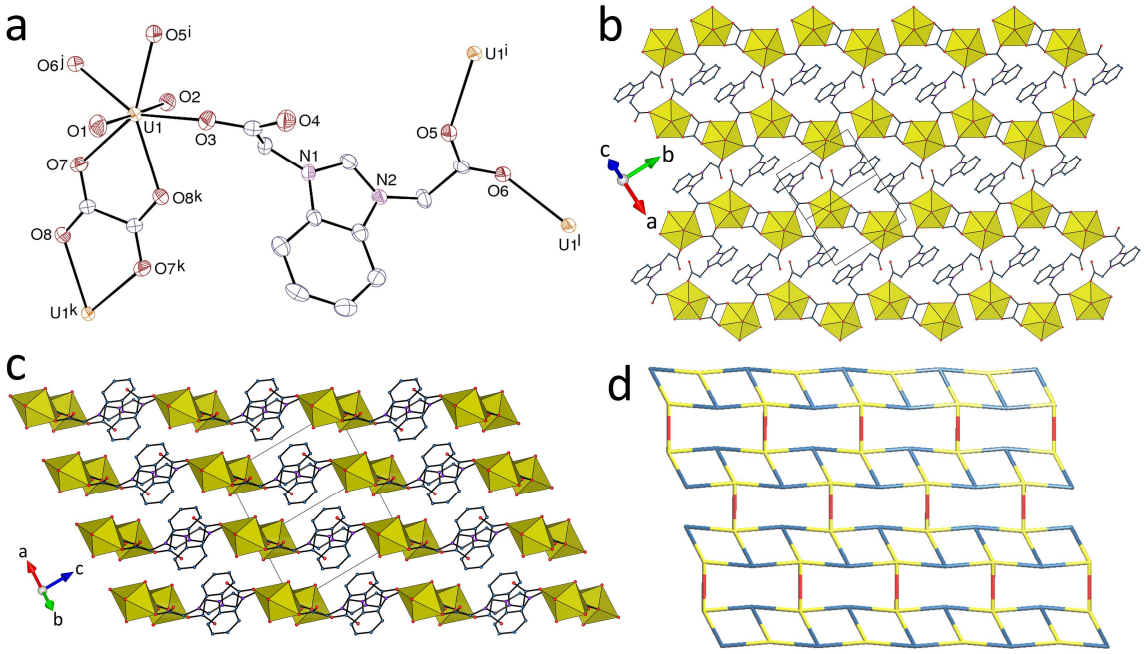


Fig. 2. (a) View of complex **2** with displacement ellipsoids shown at the 50% probability level and hydrogen atoms omitted. Symmetry codes: i = 2 – *x*, 1 – *y*, 1 – *z*; j = *x*, *y* + 1, *z* + 1; k = 1 – *x*, 1 – *y*, 2 – *z*; l = *x*, *y* – 1, *z* – 1. (b) View of the diperiodic coordination polymer with uranium coordination polyhedra colored yellow. (c) Packing with layers viewed edge-on. (d) Nodal representation of the network (U nodes, yellow; L nodes, blue; oxalate edges, red).

networks [45,48]. There are stacked pairs of strongly overlapped ligand units, with short contacts indicating significant parallel-displaced π–π interactions, both intra- and intersheet [centroid···centroid distances, 3.509(4)–3.523(3) Å; dihedral angles, 0–1.1(3)°; slippages, 1.08–1.27 Å]. The HS clearly shows these interactions to exceed dispersion. With a KPI of 0.73, the packing in **2** is very compact. The apparently quite strong tendency of the benzimidazolium units of ligand L^- to form parallel-displaced stacked associates seen in the structures of both **1** and **2** may be a factor engendering low solubility of the neutral aggregate UO_2L_2 seen as complex **1**.

3.2. Luminescence

Complex **2** is non-emissive, possibly as a consequence of the presence of oxalate ligands, since it has been long-known that oxalate coordination leads to quenching of uranyl luminescence in solution [49] although, in the solid state, any such effect seems to be strongly dependent on the particular structure [50–53]. In contrast, complex **1** in the solid state displays the usual emission spectrum under excitation at 420 nm, with the typical vibronic progression due to the $S_{10} \rightarrow S_{0\nu}$ (ν = 0–4) transitions of the uranyl ion [54,55] (Fig. 3). The peaks are

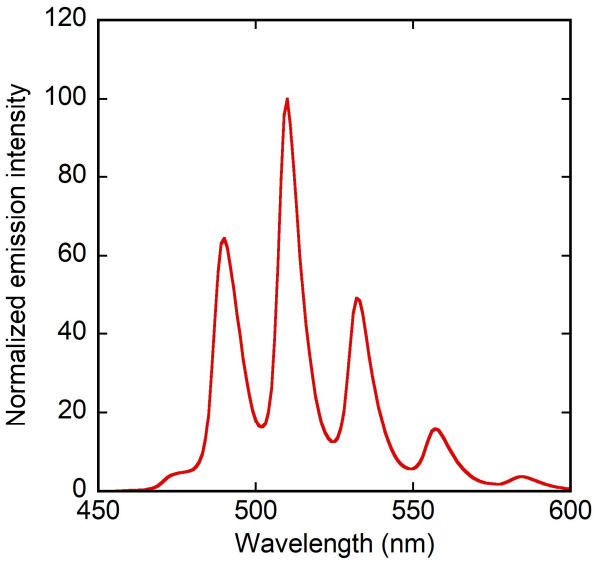


Fig. 3 Emission spectrum of complex **1** in the solid state, under excitation at 420 nm.

located at 490, 510, 532, 557, and 584 nm, i.e. in the range usually observed for uranium centres in a pentagonal-bipyramidal environment with five equatorial carboxylate oxygen donors [56]. The low intensity "hot-band" ($S_{11} \rightarrow S_{00}$) due to electron-phonon coupling [57] is observed at ~470 nm.

PLQY values of 41 and 44% have been measured for two different samples of **1**, these values being among the highest for a uranyl complex. Similar PLQYs of 42, 44 and 36% have been found for $[UO_2Rb_2(2,6\text{-pydc})_2]$, $[NH_4]_2[UO_2(2,6\text{-pydc})_2]\cdot 3H_2O$ and $[PPh_4][UO_2(OH)(2,3\text{-pyzdc})]$, respectively, and the higher value of 71% for $[PPh_3Me][UO_2(OH)(2,5\text{-pydc})]\cdot H_2O$

(pydc^{2-} = pyridinedicarboxylate, pyzdc^{2-} = pyrazinedicarboxylate) [58,59]. High values have also been reported for carboxylate ligands which do not contain heterocycles, for example, 58% for $[UO_2(btcH)]$ [60], and 49% for $[NMe_4]_2[(UO_2)_4(C_2O_4)_4(succ)]$ [61] (btc^{3-} = benzenetricarboxylate, succ^{2-} = succinate). A still higher PLQY, close to 100%, was measured in $[(UO_2)B_6O_{10}(OH)]\cdot 2H_2O$, a very different compound devoid of carboxylate donors [62]. Uranyl nitrate hexahydrate, taken as a reference, has a PLQY of 24% [59].

Various factors possibly operating to determine solid-state uranyl complex PLQY values have been discussed in numerous publications [63–68], not solely concerning uranyl carboxylates, but no one factor has provided a rationalization of all observations. The conventional view of the luminescence of uranyl ion [69–71] is that it originates from a charge-transfer transition from the uranyl oxo groups to U^{VI} that creates an excited state where (formally) O^+ has the capacity to act as a powerful oxidant capable, for example, of abstracting hydrogen atoms from organic substrates, and (formally) U^V has the capacity to act as a mild reductant. Where electron-hole recombination to give the vibronically structured green emission considered typical of uranyl centres [71] is not dominant, these excited state properties can give rise to the chemistry long known as photo-oxidation catalysis by uranyl complexes [2,51,72], more recently extended to applications in environmental remediation [7] and novel syntheses [73–77]. The implication of high PLQY values is that non-radiative deactivation processes inherent to a given complex are of limited importance and that with an appropriate substrate, efficient use of the bulk of the excited state species should be possible. In our experience [58,63], high solid-state PLQY values have been largely associated with uranyl ion complexes of aza-aromatic carboxylates, hence our interest in the present ligand.

PLQY values for emissive solids are important in defining the potential utility of such materials, though their determination [78,79] and interpretation [71,80,81] can often be complicated. A relatively simple objective pertains to materials where any intended use depends

solely upon their emissive capacity, so that the ideal PLQY value is 100%, where no pathway to excited state deactivation other than photonic emission is available. In general, however, PLQY values rarely approach this limit [62] and there are indices of how various processes of excited state deactivation (intersystem crossing, vibrational cascade, energy transfer, chemical reaction) may compete with the direct excited state to ground state transition. In the case of uranyl ion complexes, solution PLQY values, although somewhat dependent on the solvent [82–84], are generally considerably less than those for solids such as carboxylate-based coordination polymers and frameworks [45,48,50,58,59,68,85], our particular interest, though both ranges are considerable. Recently, it has been found that, for at least some crystalline uranyl ion complexes, the emission intensity can vary with the time of irradiation [61,86]. Since the explanation offered for this effect concerns radical generation and possibly associated conformational changes which could well occur quite generally, we have used this opportunity to see if it is present in aza-aromatic carboxylate species, but no emission intensity decrease was observed after irradiation for 1 hour.

4. Conclusions

We have reported the synthesis and crystal structure of two uranyl ion complexes with a hemi-zwitterionic dicarboxylate ligand (L^-), one of them involving additional bridging oxalate anions. Although L^- is a quite flexible species, its connectivity is moderate since it is bound to either two or three metal ions only, and the oxalate coligand is a planar species, so that, as a consequence, the coordination polymers formed are only diperiodic. Intra- or interlayer parallel-displaced π-stacking of the central benzimidazole aromatic core appears to play a part as a structure-directing motif. The two complexes have quite distinct luminescence properties since that involving oxalate coligands is non-emissive while the other gives a well-resolved emission spectrum and has a PLQY exceeding 40%, one of the highest values reported for a

uranyl carboxylate complex. This confirms the interest of heterocyclic ligands in the design of highly emissive uranyl ion complexes.

Appendix A. Supplementary data

CCDC 2360060 and 2360061 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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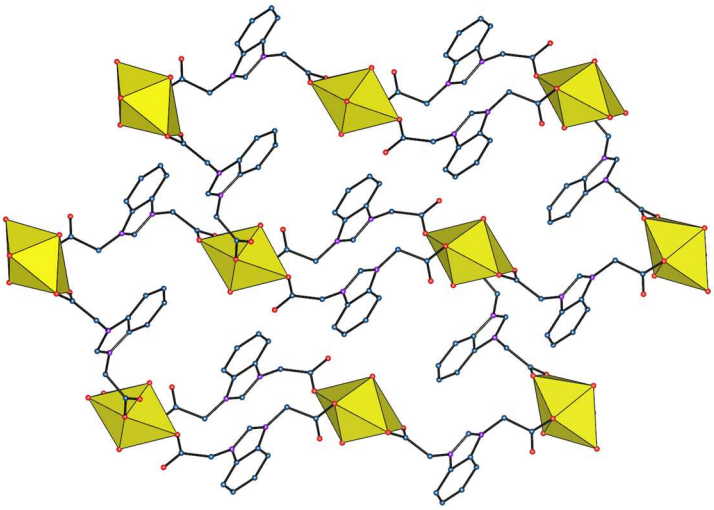
Table of Contents Entry

High photoluminescence quantum yield of a uranyl ion complex with the hemi-zwitterion 1,3-bis(carboxylatomethyl)-1H-benzimidazol-3-ium

Young Hoon Lee, Youssef Atoini, Shinya Hayami,
Yang Kim, Jack Harrowfield, Pierre Thuéry



Two uranyl ion complexes with a hemi-zwitterionic dicarboxylate ligand were synthesized, both crystallizing as diperiodic networks. One of them is luminescent and has one of the highest photoluminescence quantum yields among uranyl carboxylate complexes.