

A uranium–zinc–organic molecular compound containing planar tetranuclear uranyl units †

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A molecular uranium–zinc–organic complex has been prepared by hydrothermal reaction; this compound consists of tetranuclear uranium units, zinc–organic components and mixed bridging organic ligands and exhibits photoluminescent and photovoltaic properties.

It is of stimulating interest to explore polynuclear metal–cluster organic complex materials because these materials show interesting physical–chemical properties, and may find applications in the fields of magnetism, optics, electronics and catalysis.¹ The preparation of polynuclear clusters remains a challenge. However, through use of appropriate chelating ligands such as carboxylates, polyketonates and alkoxides to control the hydrolysis or alcoholysis of metal ions, the formation of polynuclear metal complexes seems to be easier.² Recently, a number of transition and/or 4fⁿ lanthanide metal polynuclear organic complexes have been reported. Among these compounds, polyoxovanadates, ferric wheels, and manganese clusters have been shown to exhibit rather fascinating magnetic properties or display unusual structural features.³ On the other hand, the family of uranium compounds with fascinating structural topologies are currently gaining considerable attention due to their physical–chemical properties and their behavior in the nuclear industry and natural environments.⁴ The uranyl ion gives rise to a series of positively charged linear dioxo cations (O=U=O)ⁿ⁺ (*n* = 1–3) coordinated by various ligands in the equatorial plane, whose structural and electronic properties are unique to the actinides. The uranyl ion forms inorganic polymeric U(VI) hydroxide or chlorohydroxooxo species at near-neutral pH values, in which monomeric, dimeric and trimeric ions are the most major examples.⁵ However, there are few solid-state polynuclear structures, except for mono- and dinuclear uranium–organic complexes, in the literature to date.^{4c,6} In this Communication, we describe the preparation, crystal structure, photoluminescent and photovoltaic properties of a new uranium–organic complex built up from O-bridged tetrauranium clusters, namely, [Zn₂(phen)₄U₄O₁₀(OAc)₂(NA)₂(QA)₂] **1** (phen = 1,10-phenanthroline; HOAc = acetic acid; HNA = nicotinic acid; H₂QA = quinolinic acid). The intermolecular packing in **1** is controlled by π – π interactions.

The yellow–green **1** was crystallized through the hydrothermal reaction of Zn(OAc)₂·4H₂O, UO₂(OAc)₂·2H₂O, phen, H₂QA and water in a molar ratio of 1 : 0.5 : 1 : 1 : 500 in a Teflon-lined autoclave at 160 °C for 3 days (80% yield based on U). In the reaction process a part of H₂QA was transformed into HNA *via* decarboxylation. The resulting product is stable to air and insoluble in water. It is phase-pure on the basis of the experimental X-ray diffraction pattern because the pattern corresponds well with that simulated from the single crystal structure (see ESI †). The elemental analysis shows that the contents of C, H, N, Zn and U are 35.08, 2.50, 6.47, 5.00 and 35.96 wt.% (calculated: 35.24, 2.00, 6.55, 4.92 and 35.84 wt.%),

respectively. Thermal analyses indicate that the weight loss is *ca.* 50% (calculated: 49%) from 350 to 620 °C with an exothermic effect at around 520 °C, suggesting that **1** is stable up to *ca.* 350 °C in air. If using the mixture of HNA and H₂QA instead of H₂QA alone to synthesize the complex, a powder form of **1** can also be obtained in 20% yield based on U. However, the crystals in this powder sample are not large enough for single crystal structure analysis.

The molecular structure of **1**, as determined by X-ray analysis, is shown in Fig. 1. ‡ In this molecule all available donor sites of the ligands except for the O(4) atom of QA are involved in coordination with the metals. One interesting feature of **1** is the planar U₄(μ_3 -OH)₂ core sitting on a crystallographic two-fold axis, which is similar to the previously reported examples of inorganic [(UO₂)₄Cl₂O₂(OH)₂(H₂O)₆]·4H₂O containing a dinuclear aquachlorohydroxooxo uranyl complex^{5d} and a geometrically planar tetracopper–organic compound.⁷ The asymmetric unit of **1** consists of one ZnO₆ octahedron, and a (U₂O₁₁)¹⁰⁻ species built up from two different UO₇ pentagonal bipyramids which join together through a common edge. The two bridging O atoms between U(1)O₇ and U(2)O₇ are the μ_3 -O(9) and the O(3) of the 3-carboxyl group in the QA ligand. The zinc atom in **1** resides in a six-coordinate octahedral environment with two rigid phen fragments chelating to it *via* both N atoms with a distance varying from 2.128(5) to 2.196(5) Å. O(2) and N(2) from the QA ligand coordinate to Zn to complete its coordination sphere. The two O atoms from the OAc anion is bonded with U(1) and U(2), respectively. U(1) is also coordinated by a chelating QA ligand, with the remaining positions occupied by the two axial O(10) and O(11) atoms, and the bridging O(9) which is also linked with U(2). Besides the common O atoms and the axial O atoms, there is a chelating NA ligand in the coordination environment of U(2). The bond lengths in the equatorial plane of U(1)O₇ range from 1.775(4)–1.780(4) Å for the axial U=O bonds to 2.253(4)–2.507(4) Å for the U–O bonds, whereas in the U(2)O₇ units the double bond lengths vary from 1.760(4) to 1.765(4) Å and the single bond lengths change from 2.193(4) to 2.511(4) Å. The U–O distances

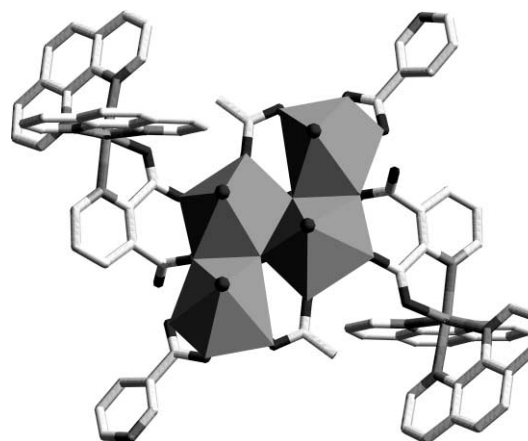


Fig. 1 View of the molecular structure of **1**.

† Electronic supplementary information (ESI) available: Additional figures and tables of crystallographic data for **1**. See <http://www.rsc.org/suppdata/dt/b3/b309634c/>

in the two UO_7 units are within the range observed in the previously reported uranyl-containing compounds.⁸ A pair of dinuclear cores is bridged to form a centrosymmetric tetranuclear uranium neutral molecular **1** through symmetry transformation. In **1**, the four U atoms are nearly located in a plane. The distance between U(1) and U(2) is 3.901(4) Å, whereas the distance between U(1) and U(2A) is 4.016(3) Å.

Using N-donor 1,10-phenanthroline as a chelating ligand, it is possible that the formed complex will adopt such a geometry that π - π aromatic stacking interactions exist.⁹ On the basis of the X-ray structure analysis, there is no hydrogen bonding in **1** and two types of supramolecular π - π interactions between the aromatic groups are evident. One π - π arrangement in **1** arises from the slipped stacking between adjacent phen ligands with the shortest C...C distance being 3.536 Å of C(31)...C(35). The other π - π interaction is between phen and NA ligands, the shortest C...C distance being 3.358 Å of C(12)...C(23). Because of the π - π interactions,¹⁰ the molecules in **1** are held together tightly and the crystals are insoluble in water and only slightly soluble in common organic solvents such as chloroform and acetone.

The photoluminescent spectra for **1** are shown in Fig. 2. **1** exhibits intense yellow-green photoluminescence in the solid state upon excitation at 438 nm, and the emission spectrum shows a main broad peak at 535 nm without fine structure, which is attributable to the charge transfer of uranyl ion from a triplet state to a singlet state.¹¹ The excitation spectrum of **1** has the same shape as that of $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ below 310 nm. However, the two spectra differ at above 310 nm, and the maxima are red-shifted from 330 and 395 nm of the latter to 340 and 438 nm of the former, respectively. The diffuse reflectance spectrum of **1** shows a broad band from 330 to 520 nm ($\lambda_{\text{max}} = 418$ nm) with two shoulders at 250 and 280 nm. The electronic absorptions for the compound are attributable to charge transfer transitions from the bonding orbitals on O to the non- or anti-bonding orbitals on U within the intrinsic uranyl group,¹² and the absorption band at 418 nm is responsible for the color of compound **1**.^{12b}

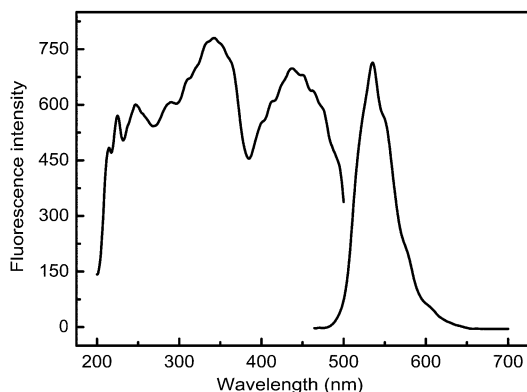


Fig. 2 Excitation spectrum (left) and solid state emission spectrum (right) for **1** at room temperature.

Photoelectrical property of **1** was investigated by recording surface photovoltage spectra (SPS) and field-induced surface photovoltage spectra (FISPS) on ITO-glass front and back electrodes. The SPS and FISPS shown in Fig. 3 indicate that compound **1** has photoelectric transformation ability.^{4a,13} The response signals of SPS lie at 339 and 440 nm, in good accordance with the excitation spectrum. Under a positive field of 0.5 V (the illuminated surface is regarded as positive), the photovoltaic response is considerably enhanced, indicating that the photogenerated charge carriers pass from molecule to molecule due to π - π overlap between the orbitals of neighboring molecules. Further detailed investigation is needed to elucidate the exact mechanism of the photovoltaic effects.

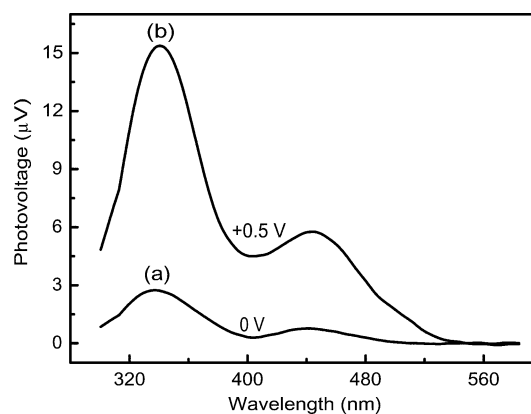


Fig. 3 SPS and FISPS of **1** under the biases of 0 V (a) and +0.5 V (b).

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Notes and references

‡ Crystal data for **1**: $\text{C}_{39}\text{H}_{26}\text{N}_6\text{O}_{13}\text{U}_2\text{Zn}$, $M = 1328.09$, monoclinic, space group $P2_1/C$, $a = 12.9751(6)$, $b = 20.3412(8)$, $c = 14.6543(6)$ Å, $\beta = 92.2870(10)^\circ$, $V = 3864.6(3)$ Å³, $T = 293(2)$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 0.71073$ Å, 18371 reflections measured of which 5563 were unique and 550 were observed ($R_{\text{int}} = 0.0444$) [$I > 2\sigma(I)$]. The final anisotropic values $R_1 = 0.0247$ and wR_2 (all data) = 0.0577, and the goodness-of-fit on F^2 is 1.002. CCDC reference number 213349. See <http://www.rsc.org/suppdata/dt/b3/b309634c/> for crystallographic data in CIF or other electronic format.

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