Reversible solvent-induced transformation of a one-dimensional uranyl coordination polymer Using 4,4'-oxybis(benzoate)

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Abstract

The solvothermal synthesis of uranyl nitrate with 4,4'-oxybis(benzoic acid) produces a coordination polymer $[(\text{UO}_2)(\text{C}_{15}\text{H}_8\text{O}_5)(\text{DMF})]_n$ with coordinated DMF residing in the void space. This compound consists of one-dimensional chains that extend down [010] from UO_7 pentagonal bipyramidal monomers. Thermogravimetric analysis indicates that the material loses the coordinated DMF ligand at 200 °C. No sensitized uranyl emission is seen within this system and the only other uranyl compound reported with the same target linker, but weak emission from the organic linker is observed and justified through molecular modeling studies. This system is able to convert between the DMF coordinated and previously reported water coordinated systems upon treatment with water or DMF, respectfully. The title compound showed marked resistance to transformation and/or degradation in a host of other organic solvents.

1. Introduction

The design and synthesis of coordination polymers (CPs) and metal-organic frameworks (MOFs) with uranium is an active field due to the unique nature of the uranyl ion (UO_2^{2+}) and its potential environmental implications [1-7]. This can be attributed to the structural diversity of these materials and the luminescent behavior the uranyl ion exhibits. The axial oxygen atoms of the uranyl cation directs coordination by organic species to the uranium ion through equatorial positions only, leading largely to one or two dimensional compounds [8-11]. This unique structural characteristic of the uranyl cation provides an advantage of a more predictable bonding than lanthanide CPs, but control over target architectures is not as refined as it is in transition metal systems [12-15].

Selection of the organic linker is critical in not only the self-assembly process, but it can also impart targeted functionality upon the material. Using rigid, aromatic linkers reduces the flexibility of the organic species, decreasing the likelihood of forming dense interpenetrated structures [16, 17]. Linkers with chelating functional groups such as carboxylic acid are commonly employed to coordinate to the metal ion, in an attempt to exclude coordinating solvent molecules which may hinder desired properties [18, 19]. Previously, we reported a U-based CP built from benzophenonedicarboxylic acid, and as a continuation of this work, a structurally similar organic linker was chosen for study. The linker selected, 4,4'-oxybis(benzoic acid) (OBA) is comprised of two benzoic acid groups bridged together at

the para positions by an sp^3 ether oxygen atom rather than a carbonyl group as in our earlier system [8]. This linker has been used in previous uranyl coordination polymers [20, 21] and has shown promise as a linker with indium(III) in MOF heterogeneous catalysis [22].

Only one other U-CP has been obtained from this linker obtained under hydrothermal treatment with the addition of base and also resulted in a one dimensional coordination polymer [20, 21]. This CP has one coordinated aqua ligand in the equatorial position and hydrogen bonding from this ligand links neighboring chains into a three dimensional motif. Herein, we report the synthesis, structure, solvent stability, thermal properties, and structural conversion of a one dimensional uranyl coordination polymer, $[(UO_2)(C_{15}H_8O_5)(DMF)]_n$, assembled from 4,4'-oxybis(benzoate) linkers. The photoluminescent behavior of this compound was studied and justified using structural and computational analyses.

2. Materials and methods

Caution! Uranyl nitrate hexahydrate $[UO_2(NO_3)_2] \cdot 6H_2O$ used in this study contains depleted uranium. Standard precautions for handling radioactive materials and toxic substances should be followed.

The title compound (**1**, $[(UO_2)(C_{15}H_8O_5)(DMF)]_n$) was synthesized through solvothermal methods. To a 23 mL Teflon-lined autoclave, 4,4'-oxybis(benzoic acid) (OBA) (0.25 mmol, 65 mg) and uranyl nitrate hexahydrate (0.25 mmol, 126 mg) were added and dissolved with dimethylformamide (DMF) (7 mL) to produce a clear pale yellow solution. The autoclave was sealed and placed in an oven at 120 °C for 3 days, and then slow cooled at 20 °C a day for 3 days. After the slow cooling process, a clear, bright yellow solution was decanted from yellow block-like crystals and washed twice with water and ethanol, after which the crystals were allowed to air dry. Yield: 13%. Reaction times of 5 and 7 days also produced the title compound, however, the 3 day reaction produced the highest quality crystals for single crystal X-ray diffraction studies (See SI for diffractograms of 3, 5, and 7 day reactions). The synthesis could also be performed with metal to linker ratios of 2:1 and 1:2 in otherwise identical conditions. Successful syntheses of this compound can also be accomplished using uranyl acetate at 1:1, 2:1, and 1:2 ratios. Elemental analyses were conducted by Galbraith Laboratories in Knoxville, TN, USA (theoretical/experimental): C (34.07%/33.91%), H (2.52%/2.53%), and N (2.34%/2.42%). FTIR: (cm^{-1}) 3072 (w), 2955 (w), 1651 (m), 1592 (s), 1541 (m), 1498 (m), 1427 (s), 1377 (s), 1306 (w), 1242 (s), 1162 (m), 1115 (w), 921 (s), 858 (s), 779 (s), 766 (s), 683 (s), 660 (s), 502 (s). Single crystal X-ray diffraction data were collected [23] and crystallographic details can be found in Table 1.

3. Results and discussion

3.1 Structural description

Table 1. Crystallographic details of $[(UO_2)(C_{15}H_8O_5)(DMF)]_n$

Formula Weight	599.33
Crystal Class	Triclinic
Space Group	$P\bar{1}$
a (Å)	8.5911(11)
b (Å)	10.2130(11)
c (Å)	10.9762(11)
α (°)	79.9770(10)

β (°)	84.6530(10)
γ (°)	84.8580(10)
V (Å ³)	941.40(18)
Z	2
T (K)	293(2)
μ (mm ⁻¹)	8.665
Reflections collected	11422
R_{int}	3.16%
R_1^a	4.01%
wR_2^a	6.98%
Goodness-of-fit	1.078
$^a R_1 = \sum \frac{\left F_o - F_c \right }{ F_o }; \quad wR_2 = \left(\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right)^{\frac{1}{2}}$	

The title compound, $[(\text{UO}_2)(\text{C}_{15}\text{H}_8\text{O}_5)(\text{DMF})]_n$, consists of UO_7 monomers exhibiting a pentagonal bipyramidal coordination geometry, which are joined together through the carboxylate group of the organic linker to form pseudo dimer units (Fig. 1). The uranium ion is coordinated by two axial oxygen atoms (O4, O8) at bond lengths of 1.753(3) and 1.757(3) Å, which is consistent for typical bond distances of the UO_2 cation [24]. The five equatorially bound oxygen atoms come from one bidentate attachment of an OBA linker (O3, O5), two monodentate linkages from two OBA linkers through carboxylate oxygen atoms (O2, O6), and one coordinated DMF ligand oxygen atom (O1) (Fig. 1). Selected bond lengths and angles can be found in Table 2.

The UO_7 monomers are bridged together by the monodentate carboxylate group (O2-C4-O6) to form a chain-like motif that runs down [101], and can be clearly seen when viewed down the [010] direction (Fig. 1). The bidentate carboxylate group on the OBA linkers (O3-C15-O5) coordinate to U atoms on neighboring monomers to afford the overall one dimensional chain.

Fig. 1. View of the title compound **1** down [100] (left, highlighting the linker binding) and [010] (right, highlighting the stacking of the one dimensional chains). Yellow polyhedra are UO_7 , red spheres are oxygen atoms, blue spheres are nitrogen atoms, and black lines are carbon atoms. Hydrogen atoms have been omitted for clarity.

No classic hydrogen bonding is observed in the title compound. Very weak hydrogen bonding interactions are present between the benzene moiety and the axial oxygen atoms (O4 and O8) coordinated to the uranium ion with donor acceptor distances of 3.242(8), 3.516(8), and 3.1036(5) Å. A summary of all hydrogen bonding interactions can be found in the SI. The closest centroid distance is 4.736 Å and is not within the acceptable range of 3.3 to 3.8 Å to be considered a significant π - π interaction (Table S2) [25].

Comparing **1** to the other U-OBA system [20, 21] (CSD code KUSDAE and KUSDAE01) shows similarities in overall topology. Both systems form one dimensional chains comprised from UO_7 pentagonal bipyramidal monomers that are linked into a pseudo-dimer motif by bridging monodentate binding from the OBA carboxylate group. The bond lengths of the axial uranyl oxygens are similar, 1.753(3) and 1.757(3) Å in **1** and 1.758(5) and 1.770(5) Å in KUSDAE.

The geometry and coordinating behavior of the linker is similar in both systems as well. The oxygen atom connecting phenyl rings together has an angle of 121.6(5)° in **1** and 120.8(5)° in KUSDAE. The torsion angles between phenyl rings in both **1** and KUSDAE are also very similar at 58.84° and 59.53°, respectively. The coordinating modes of the OBA linker are also identical in these systems. One carboxylate group chelates to the uranyl ion, where the second carboxylate group bridges two nearby U monomers. Neither systems have any significant π - π interactions. The KUSDAE system was synthesized hydrothermally unlike **1**, so it does have hydrogen bonding occurring with the coordinated aqua ligand, where in **1**, there is no coordinated water is present strengthen the hydrogen bonding network. Our previously reported compound from the structurally related benzophenonedicarboxylate linker is just a strikingly similar to **1** and KUSDAE.

3.3 Thermogravimetric analysis

TGA was performed on the title compound from 30 to 600 °C at 5 °C per minute under a nitrogen gas flow. Beginning around 200 °C, a loss of 12.0% is observed, which is attributed to the loss of one DMF molecule (calculated 12.0%). The mass loss of 42.6% starting at 370 °C is from the loss of the OBA linker (calculated 42.7%). The total mass loss is 54.7%, leaving UO_3 as the likely final degradation product (calculated 54.9%).

3.4 Luminescence

Upon excitation of the sample with a UV lamp, no discernable luminescence was observed. Photoluminescence spectroscopy of **1** confirmed that no uranyl emission upon OBA excitation occurs in **1**, unexpected in that many aromatic organic species have been observed to promote uranyl luminescence [26, 27]. This lack of sensitized emission has been observed in other systems with large conjugated linkers, and was attributed to the conjugation of the linker quenching uranyl emission [10, 28]. The KUSDAE compound was also synthesized to determine if sensitized uranyl emission could be observed with the OBA linker. The system showed no discernable uranyl emission either, strengthening the premise that the conjugation extended through the ether oxygen atom of the linker may quench

uranyl luminescence. Other groups have synthesized systems with tetracarboxylate OBA linkers and templating ligands, with observed uranyl emission occurred [7]. This was attributed to the polynuclear uranium environments (tetramers) and/or sensitization from the templating imidazole ligands [29, 30].

Fig. 2. Emission spectra of the title compound **1** and KUSDAE.

Previous work in the group with a similar linker, benzophenone-4,4'-dicarboxylic acid (BPDC), exhibited sensitized uranyl emission upon excitation of the BPDC linker at 371 nm. The structure of this compound is nearly identical to both **1** and KUSDAE, constructed from one dimensional chains built from a similar UO_7 pentagonal bipyramidal monomers that form a pseudo-dimer motif. The carbonyl moiety in the BPDC system may play a role in reducing the torsional strain in the system, allowing for better delocalization of electrons, where in **1** the sp^3 carbon may be detrimental. These systems have a slight difference in torsion angles between phenyl rings $\sim 36^\circ$ (58.84° between rings) in **1** and $\sim 30^\circ$ (53.09° between rings) in the BPDC system. The BPDC system has a closer π - π interaction distance of $4.492 \text{ \AA}$, but still not significant enough for traditional π - π interactions (3.3 - $3.8 \text{ \AA}$). From these two systems it is evident that even a small difference in linker may either promote or quench uranyl sensitized luminescence.

The frontier orbitals of the OBA and BPDC linkers with the same torsion angles observed in the reported crystal structure are shown in Figure 3. What can be seen is that the electron density is delocalized across the OBA ring systems, but more broken up and localized in BPDC. The more delocalized the molecular orbitals and electron density could be a determining factor in transferring energy to the uranyl ion. The delocalization of the orbitals in OBA may explain the inability to transfer energy to the uranyl ion as electrons may be too mobile to sensitize emission, quickly returning to the

ground state before energy transfer can occur, resulting in a nonluminescent compound. In BPDC, however, the lack of full-molecule delocalization may result in a longer lived excited state, permitting energy transfer and subsequent sensitization of uranyl emission.

Fig. 3. Contour plots of the frontier orbitals of the OBA (left) and BPDC (right) molecules at torsion angles identical to what is observed in the crystal structures. Studies were conducted using the Gaussian [31] program with TD-DFT (B3YLP level of theory using the 6-31G basis set).

Stability studies

The title compound was exposed for three days to various solvents under solvothermal conditions to test its resistance to degradation. Powder X-ray diffractograms indicate that crystallinity was maintained in solvents with varying polarities at 120 °C for three days (Fig. 4). Solvents with polarity indices from 0 (heptane) to 5.8 (ACN) do not seem to disrupt the overall crystal structure. However, after seven days, there was significant material degradation and loss of crystallinity as evidenced by PXRD. Using a solvent with higher polarity than DMF (in this case, water, 9.0), a reversible structure transformation between **1** and KUSDAE was noted.

Fig. 4. Powder patterns obtained of **1** (bottom pattern) after exposure to solvents at 120 °C for 3 days.

DMF/H₂O exchange experiments

Experiments were performed to determine if the conversion of **1** to KUSDAE was reversible. Compound **1** was heated at 120 °C for 3 days in water. Recovered solids were analyzed with PXRD and the coordinated DMF in **1** can be exchanged with water to form the KUSDAE structure (Fig. 5). The PXRD patterns indicate the removal of the peak at 9 2θ from **1** and the presence of peaks at 17 and 19 2θ from the KUSDAE structure. The hydrothermally obtained structure was likewise treated with DMF in otherwise identical conditions. The resulting PXRD shows the conversion from the KUSDAE structure back to **1** after three days in DMF at 120 °C (Fig. 6). These results indicate the ability of the framework to change the overall structure upon exposure to these two coordinating solvent molecules. This interchange was reversible over at least four transformations (**1** → KUSDAE → **1** → KUSDAE, Fig. 7).

Fig. 5. Solvothermally synthesized title compound **1** (bottom, black) and after exposure to water for three days (middle, red), which resembles the hydrothermally synthesized KUSDAE pattern (top, blue).

Fig. 6. Hydrothermally synthesized KUSDAE PXRD pattern (top, blue) after exposure to DMF for three days (middle, red) conversion to **1** (bottom, black).

Fig. 7. Stability studies of conversion of **1** to KUSDAE after two full rounds of conversion between systems.

4. Conclusions

A one dimensional uranyl coordination polymer, $[(\text{UO}_2)(\text{C}_{15}\text{H}_8\text{O}_5)(\text{DMF})]_n$, comprised of 4,4'-oxybis(benzoate) linkers, was solvothermally synthesized and characterized with single crystal X-ray diffraction, thermogravimetric analysis, and luminescence. It was found that this compound is very similar structurally to other U-compounds based on OBA and BPDC linkers and can be converted between the DMF-coordinated and water-coordinated OBA structures. While the structurally related BPDC is an effective sensitizer of uranyl emission, no discernable uranyl luminescence was observed in this or any reported OBA compounds.

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Supplementary material

Supplementary data associated with this article can be found, in the online version, at xxxxx. CCDC 1496884 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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