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Synthetic, Structural, and Luminescent Study of Uranyl Coordination Polymers Containing Chelating Terpyridine and Trispyridyltriazine Ligands

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Abstract

Seven uranyl coordination polymers $[(UO_2)(BrC_8H_3O_4)(C_{15}H_{11}N_3)]$ (**1**), $[(UO_2)(ClC_8H_3O_4)(C_{15}H_{11}N_3)]$ (**2**), $[(UO_2)(BrC_8H_3O_4)(C_{18}H_{12}N_6)] \bullet H_2O$ (**3**), $[(UO_2)(ClC_8H_3O_4)(C_{18}H_{12}N_6)] \bullet 2H_2O$ (**4**), $[(UO_2)(C_8H_3IO_4)(C_{18}H_{12}N_6)] \bullet 2C_3H_7O$ (**5**), $[(UO_2)(C_9H_6O_4)(C_{18}H_{12}N_6)] \bullet H_2O$ (**6**), and $[(UO_2)(C_6H_2O_4S)(C_{18}H_{12}N_6)] \bullet 2H_2O$ (**7**) containing N-donor ligands 2,2':6',2"-terpyridine (TPY) and 2,4,6-tripyridyl s-triazine (TPTZ); and O-donor linkers thiophene 2,5-dicarboxylic acid (TDC) and X-1,4-benzene dicarboxylic acid (X-BDC, where X = Me, Cl, Br, I) were synthesized and characterized using single crystal X-ray diffraction (SC-XRD), powder X-ray diffraction (PXRD), and fluorescence spectroscopy. Each compound crystallizes as binuclear pseudo dimers containing an UO_2^{2+} pentagonal bipyramidal primary building unit. Fluorescence spectra of **1**-**4**, and **6**-**7** show characteristic UO_2^{2+} emission whereas its **5** is non-emissive. Red shifts within the emission of **1-4** are noted as a function of N-donor ligands TPY and TPTZ whereas emission shifts are not observed in TPTZ bearing compounds (**3**, **4**, **6**, **7**) containing different O-donor linkers. Luminescent lifetimes of **1-7** were obtained and fitted with either bi-exponential or tri-exponential components.

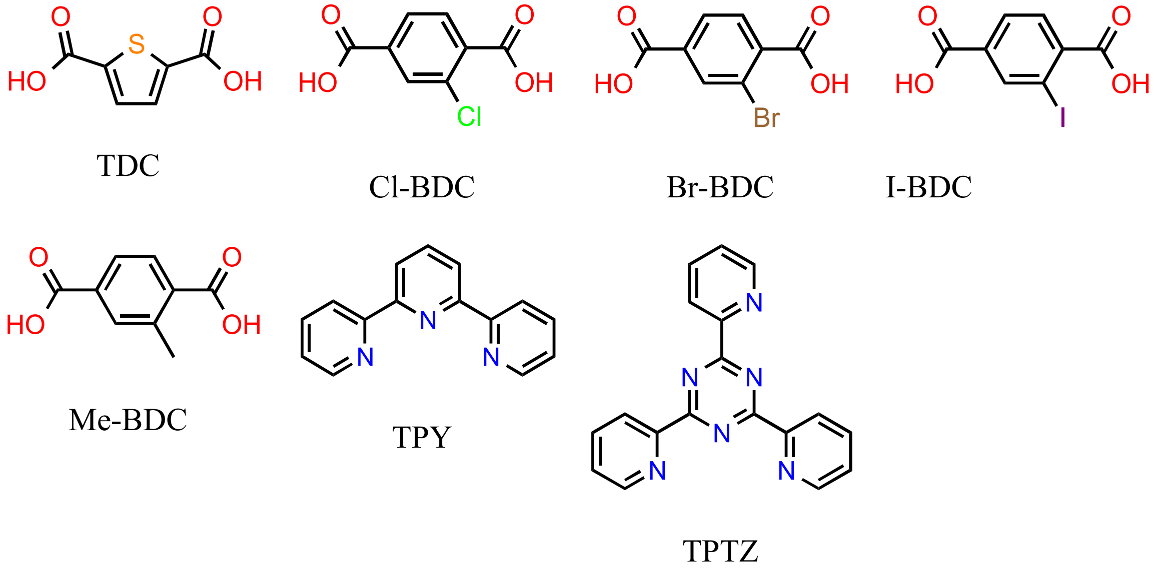
Introduction

A recurring structural theme in the syntheses and structures of uranyl coordination polymers (CPs) is the presence of oligomerized secondary building units (SBUs) resulting from hydrolysis during hydrothermal syntheses. The degree of oligomerization is generally influenced by pH, temperature, or concentration of uranyl species in aqueous preparations.[1-5] Consequently, the portfolio of uranyl bearing hybrid materials is indeed quite rich when one considers the diverse speciation profiles possible and subsequent pairing with organic ligands. Common ligands used in the construction of uranyl CPs include the hard O-donor dicarboxylates,[6-11] and phosphonates,[12-16] due to their affinity for uranyl centers. Moreover, metalloligands, may also promote additional structural diversity as a result of coordination preferences by secondary metals centers to form heterobimetallic CPs.[17-21] The incorporation of a secondary metal center often imparts additional properties to the overall material as well, including tuned uranyl emission using a transition metal (Fe^{2+}) [19] or sensitization of a lanthanide (Sm^{3+}) by uranyl via energy transfer.[22]

Whereas the diversity of uranyl SBUs has given rise to a rich family of materials, challenges remain in directing the syntheses of topologies of interest. For example, one may influence speciation during synthesis with a combination of temperature, concentration and/or pH, yet determining which BUs will ultimately manifest themselves in the solid state remains elusive. That said, we have had some recent success in preparing a family of materials containing a fixed (and reproducible) uranyl center via the combined use of both chelating and ditopic ligands. Our previous efforts have shown TPY to be an effective chelator that promotes formation of a non-hydrolyzed uranyl building unit which may be assembled through various bifunctional carboxylates. Examples include thiophene 2,5-dicarboxylic acid (TDC), benzene 1,4-dicarboxylic acid (BDC), and naphthalene 1,4-dicarboxylic acid (NDC), which allowed for a systematic exploration of the structural features and influence of ligands on uranyl emission.[23] Herein, we expand our family of uranyl CPs to include another N-donor chelating ligand, 2,4,6-tripyridyl-s-triazine (TPTZ), since together with TPY, has been shown to chelate to uranyl centers[24] and thus may be a good candidate to promote a specific BU. Moreover, these materials may also provide a platform for luminescent studies. In general, photoluminescence of uranyl CPs is of interest due to possible energy transfer between ligands and metals,[21,22,25,26] as well as photocatalysis.[27-30] The study of energy transfer between uranyl centers and/or ligands is complicated, however, by the spectral overlap of the UO_2^{2+} ligand-to-metal charge transfer (LMCT) band and the π-π^* transitions within the organics.[23] Despite this limitation, we have shown that energy transfer within TPY containing uranyl CPs may be explored by comparing appropriately situated triplet states of organic linkers to the energy level of the emissive UO_2^{2+} cation.[23]

Another area of interest with respect to luminescence is lifetimes. Uranyl lifetimes have been well studied in aqueous solution to characterize uranyl hydrolysis products, in which multiple lifetimes are observed at different temperature and pH ranges.[31-34] Other interpretations for the observed lifetimes include reversible intersystem crossing between uranyl centers, presence of a UO_2^{+} species, or formation of a UO_2^{2+} exciplex.[35-39] In the context of coordination polymers, lifetimes within lanthanide(III) CPs are widely explored to elucidate different emissive species or radiative decay processes occurring within the metal center. The coordination of organic linkers to lanthanide (III) centers may extend or reduce the observed lifetimes depending on functional groups or “quenchers” present within the linker.[40-45] Similar studies in uranyl CPs on the other hand are more limited.[46] In uranyl complexes, however, Kumar et al. reports a comprehensive treatment on the influence that organic ligands may have on the emissive UO_2^{2+} ion.[47] Thus, the study of lifetimes in general is indeed warranted and may offer an opportunity to explore such properties in our family of uranyl-bearing materials.

In the current study, TPY and TPTZ ligands were systematically paired with five O-donor aromatic linkers: thiophene-2,5-dicarboxylic acid (TDC), 2-chloro-1,4-benzene dicarboxylic acid (Cl-BDC), 4-bromo-1,4-benzene dicarboxylic acid (Br-BDC), 4-iodo-1,4-benzene dicarboxylic acid (I-BDC), and 4-methyl-1,4-benzene dicarboxylic acid (Me-BDC) (Scheme 1) to result in a family of seven molecular pseudo dimers: $[(UO_2)(BrC_8H_3O_4)(C_{15}H_{11}N_3)]$ (**1**), $[(UO_2)(ClC_8H_3O_4)(C_{15}H_{11}N_3)]$ (**2**), $[(UO_2)(BrC_8H_3O_4)(C_{18}H_{12}N_6)] \cdot H_2O$ (**3**), $[(UO_2)(ClC_8H_3O_4)(C_{18}H_{12}N_6)] \cdot 2H_2O$ (**4**), $[(UO_2)(C_8H_3IO_4)(C_{18}H_{12}N_6)] \cdot 2C_3H_7O$ (**5**), $[(UO_2)(C_9H_6O_4)(C_{18}H_{12}N_6)] \cdot H_2O$ (**6**), and $[(UO_2)(C_6H_2O_4S)(C_{18}H_{12}N_6)] \cdot 2H_2O$ (**7**). We herein report the synthesis, structures, and luminescence properties of these materials.



Scheme 1. The O-donor dicarboxylates and N-donor ligands used in this study.

Experimental Section

General Synthesis of Compounds 1-7. Ligands 2-chloroterephthalic acid (Cl-BDC), 2-iodoterephthalic acid (I-BDC), and 2-methylterephthalic acid (Me-BDC) were synthesized and characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy as reported in the literature.[48,49] 2,2′:6,2″-terpyridine (TPY) and 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ) were purchased from VWR. The ligands thiophene 2,5-dicarboxylic acid (2,5-TDC) and 2-bromoterephthalic acid (Br-BDC) were purchased from Sigma Aldrich. All commercial sources were used as received.

Caution: $UO_2(CH_2COO)_2 \bullet 2H_2O$ *used in this study contains depleted uranium. Standard precautions for handling radioactive and toxic substances should be followed.*

Compounds **1** and **2** were synthesized as follows: in a 25 mL Teflon cup, the reagents $UO_2(CH_3COO)_2 \cdot 2H_2O$ (106 mg, 0.251 mmol, 1 equiv.), organic acid (64.8 to 110 mg, 0.377 mmol, 1.5 equiv.), TPY (87.9 mg, 0.377 mmol, 1.5 equiv.), and 25 µL 6 M NaOH were added to a solution of 2.5 mL H_2O-2-propanol mixture (1:1.5). The Teflon cup was then placed in a stainless steel Parr Bomb and heated statically at 150 °C for 5 days. The Parr bomb was then allowed to cool overnight on the bench top. Solids were isolated from the mother liquor, washed with H_2O and 2-propanol and allowed to air-dry. Single crystals were then isolated and characterized using single crystal XRD. Compounds **3-7** were synthesized following the same synthetic conditions except the temperature was changed to 120 °C and TPTZ (117 mg, 0.377 mmol, 1.5 equiv) was used. A summary of the synthetic conditions and molar ratios of **1-7** can be found in Table 1.

Table 1. Synthetic conditions and molar ratios for compounds **1-7**.

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$[(UO_2)(BrC_8H_3O_4)(C_{15}H_{11}N_3)]$	$[(UO_2)(ClC_8H_3O_4)(C_{15}H_{11}N_3)]$	$[(UO_2)(BrC_8H_3O_4)(C_{18}H_{12}N_6)] \bullet H_2O$	$[(UO_2)(ClC_8H_3O_4)(C_{18}H_{12}N_6)] \bullet 2H_2O$	$[(UO_2)(C_8H_3IO_4)(C_{18}H_{12}N_6)] \bullet 2C_3H_7O$	$[(UO_2)(C_9H_6O_4)(C_{18}H_{12}N_6)] \bullet H_2O$	$[(UO_2)(C_6H_2O_4S)(C_{18}H_{12}N_6)] \bullet 2H_2O$
O-donor (mg, mmol)	Br-BDC (92.3 mg, 0.377 mmol)	Cl-BDC (75.6 mg, 0.377 mmol)	Br-BDC (92.3 mg, 0.377 mmol)	Cl-BDC (75.6 mg, 0.377 mmol)	I-BDC (110 mg, 0.377 mmol)	Me-BDC (67.8 mg, 0.377 mmol)	TDC (64.8 mg, 0.377 mmol)
N-donor (mg, mmol)	TPY (87.9 mg, 0.377 mmol)	TPY (87.9 mg, 0.377 mmol)	TPTZ (117 mg, 0.377 mmol)	TPTZ (117 mg, 0.377 mmol)	TPTZ (117 mg, 0.377 mmol)	TPTZ (117 mg, 0.377 mmol)	TPTZ (117 mg, 0.377 mmol)
Temperature (°C)	150	150	120	120	120	120	120
pH initial	4.20	3.73	3.70	3.86	3.00	2.02	3.17
pH adjusted	5.02	4.82	5.40	5.35	4.41	3.36	6.92
pH final	5.19	5.69	5.04	5.15	5.43	4.92	5.12
Mass (% yield based on U)	160 mg (85% yield)	127 mg (70% yield)	161 mg (38% yield)	124 mg (63% yield)	141 mg (30% yield)	37 mg (19% yield)	154 mg (39% yield)
Crystals?	Yes, yellow block crystals	Yes, yellow block crystals	Yes, yellow block crystals	Yes, yellow block crystals	Yes, yellow block crystals	Yes, yellow block crystals	Yes, yellow block crystals
Pure?	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Crystal Structure Determination. Single crystals isolated from each bulk sample were mounted on MiTeGen micromounts. Reflections were collected using 0.5° φ and ω scans on a Bruker SMART diffractometer equipped with an APEX II CCD detector using Mo Kα radiation at 298 K. All data was integrated using *SAINT*[50] and an absorption correction was applied using *SADABS*.[50] Structures were solved using direct methods (*SIR-92*[51] and *SHELXS-2013*[52]) and then refined using *SHELXL-2013* within the WinGX software package,[53] in which all non-hydrogen atoms were refined anisotropically.

For compounds **1** and **2**, a PART command was used to model positional disorder of the bromine and chlorine atoms on the benzene dicarboxylate rings. For compound **5**, a DFIX command was used to restrain the sp^3-sp^2 bond distances (1.45 Å) on solvent 2-propanol. Hydrogen atoms residing on the carbon atoms of TPY, TPTZ, X-BDC, TDC, and 2-propanol solvent molecules were placed in calculated positions and allowed to ride on their parent atoms. Efforts to model the hydrogen atoms on the solvent waters Ow1 and Ow2 for compounds **3**, **4**, **6**, and **7** were unsuccessful and thus not included in the final refinement. Tests for additional symmetry in all compounds were done using *PLATON*.[54] A summary of the crystallographic data for **1-7** can be found in Table 2. Bond lengths and bond angle tables for **1-7** along with their ORTEP representations can be found in the Supporting Information (Tables S1-S7 and Figures S1-S7). Crystallographic Information Files (CIFs) of compounds **1-7** were deposited to the Cambridge Crystallographic Data Centre (CCDC) and can be obtained via http://www.ccdc.cam.ac.uk by citing deposition numbers 1400915 (**1**), 1400916 (**2**), 1400917 (**3**), 1400918 (**4**), 1400919 (**5**), 1400920 (**6**), 1400921 (**7**).

Table 2. Crystallographic data for compounds **1-7**.

Compound	**1**	**2**	**3**	**4**	**5**	**6**	7
Formula	$[(UO_2)(BrC_8H_2O_4)(C_{15}H_{11}N_3)]$.	$[(UO_2)(ClC_8H_2O_4)(C_{15}H_{11}N_3)]$	$[(UO_2)(BrC_8H_3O_4)(C_{18}H_{12}N_6)] \cdot H_2O$	$[(UO_2)(ClC_8H_3O_4)(C_{18}H_{12}N_6)] \cdot 2H_2O$	$[(UO_2)(C_8H_3IO_4)(C_{18}H_{12}N_6)] \cdot 2C_3H_7O$	$[(UO_2)(C_9H_6O_4)(C_{18}H_{12}N_6)] \cdot H_2O$	$[(UO_2)(C_6H_2O_4S)(C_{18}H_{12}N_6)] \cdot 2H_2O$
Formula weight	1490.61	1401.69	1682.76	1625.84	1864.93	1553.01	1569.00
Temperature	298 K	298 K	298 K	298 K	298 K	298 K	298 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1	P-1	P-1	P-1	P-1
Unit cell dimensions	a = 9.323(9) Å b = 12.510(1) Å c = 18.785 (1) Å β = 94.335(2)°	a = 9.292(3) Å b = 12.589(5) Å c = 18.697(7) Å β = 95.618(1)°	a = 8.074(9) Å b = 11.971(1) Å c = 15.041(1) Å α = 106.612(1)° β = 102.208(1)° γ = 100.750(1)°	a = 8.081(6) Å b = 12.673(1) Å c = 13.376(1) Å α = 100.472(1)° β = 91.219(1)° γ = 98.444(1)°	a = 10.534(8) Å b = 11.548(8) Å c = 13.410(1) Å α = 68.203(1)° β = 77.871(1)° γ = 87.132(1)°	a = 7.997(1) Å b = 12.061(1) Å c = 14.965(2) Å α = 106.548(2)° β = 101.601(2)° γ = 101.362(2)°	a = 9.314(4) Å b = 10.897(5) Å c = 14.017(6) Å α = 67.557(6)° β = 77.931(7)° γ = 85.379(7)°
Volume	2184.4(4) $Å^3$	2176.81(14) $Å^3$	1313.5(3) $Å^3$	1331.01(18) $Å^3$	1480.17(19) $Å^3$	1304.9(4) $Å^3$	1285.8(10) $Å^3$
Z	2	2	1	2	1	1	1
Density (calculated)	2.269 Mg/m^3	2.142 Mg/m^3	2.127 Mg/m^3	2.028 Mg/m^3	2.090 Mg/m^3	1.976 Mg/m^3	2.026 Mg/m^3
Absorption coefficient	9.307 mm^{-1}	7.627 mm^{-1}	7.758 mm^{-1}	6.260 mm^{-1}	6.583 mm^{-1}	6.279 mm^{-1}	6.454 mm^{-1}
Reflections collected	40659	39911	17950	19093	16574	18961	25026
Independent reflections	6157 [R(int) =0.0340]	6069 [R(int) =0.0300]	7209 [R(int) =0.0515]	7303 [R(int) =0.0521]	5442 [R(int) =0.0387]	6874 [R(int) =0.0512]	7028 [R(int) =0.0434]
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0195, wR_2 = 0.0406	R_1 = 0.0205, wR_2 = 0.0392	R_1 = 0.0460, wR_2 = 0.1062	R_1 = 0.0434, wR_2 = 0.0784	R_1 = 0.0420, wR_2 = 0.1038	R_1 = 0.0472, wR_2 = 0.1162	R_1 = 0.0333, wR_2 = 0.0623

Powder X-ray Diffraction (PXRD). Diffraction patterns of compounds **1-7** were obtained on a Rigaku MiniFlex II Desktop Powder X-ray Diffractometer (Cu Kα, 3-60°) and analyzed using the JADE software package. Purity of bulk samples for **1-7** was determined by comparing observed and calculated PXRD patterns. These patterns can be found in the Supporting Information (Figures S8-S14).

Fluorescence Measurements. Compounds **1-7** were crushed to fine powders and placed between two glass slides. Spectra were collected on a Horiba JobinYvon Fluorolog spectrophotometer (298 K, excitation: 365 nm, 420 nm, excitation/ emission slit widths: 1.5 nm) using the face forward (45°) setting. Fluorescence spectra of **1-7** collected at 365 nm can be found in the Supporting Information Figures S24-S25.

Lifetime Measurements. Compounds **1-7** were crushed to fine powders and placed between two glass slides. Fluorescence decays were collected on a Horiba JobinYvon Fluorolog spectrophotometer (298 K, excitation: 365 and 420 nm, emission: 513 nm, excitation/emission slit widths: 1 or 2 nm) using a xenon lamp as the pulse excitation source under the face forward (45°) setting. Data was acquired in the measurement range of 680 μs with the peak-preset set to 10,000 and the detector S1 HV set to 950 V.

The decay curves were analyzed using the Data Station fluorescence decay analysis (DAS6, version 6.6) software, in which lifetimes were determined by applying double exponential or tri exponential curve fits to the observed data using the equation $F(t) = \sum \alpha_i e^{\frac{-\tau}{\tau_i}}$. The α_i is the pre-exponential factor represents the contribution a component with lifetime τ_i has to the overall time-resolved decay and F(t) is the fluorescence intensities of excited fluorophores at time = t. The goodness of fits were assessed from its chi-squared (χ^2) value, in which values close to unity were deemed satisfactory.

Lifetimes of **5** could not be taken as uranyl emission was not observed. Lifetime measurements of previously reported pseudo dimer structures containing TPY $[(UO_2)(C_6H_2O_4S)(C_{15}H_{11}N_3)]$[23] (**8**) and Cl-TPY $[(UO_2)(C_6H_2O_4S)(ClC_{15}H_{10}N_3)]$[23] (**9**) were also taken. A description of their emission properties has been published elsewhere.[23] Spectroscopic data for **1-9** can be found in Table 4 and Supporting Information Table S10.

Results and Discussion

Structural Description.

Crystal Structures of $[(UO_2)(BrC_8H_3O_4)(C_{15}H_{11}N_3)]$ (1) and $[(UO_2)(ClC_8H_3O_4)(C_{15}H_{11}N_3)]$ (2). Single crystal X-ray diffraction analysis reveals that the structures of **1** and **2** are isomorphous and crystallize in the *P2₁/n* space group. As such, only compound **1** will be described in detail. The crystal structure and packing of **2** can be found in the Supporting Information (Figures S16 and S17).

Compound **1** contains one crystallographically unique uranyl cation (U1, O1, O2) as seen in Figure 1. U1 is bound by one tridentate TPY via N1, N2, N3 (U –N_{avg} 2.583 Å), and two monodentate Br-BDC linkers via O4 (2.269(4) Å) and O6 (2.276(4) Å) to result in a pentagonal bipyramidal building unit. These units are linked by bridging Br-

BDC linkers to result in a binuclear pseudo dimer (Figure 1). These dimers interact with each other via long π- π contacts within the Br-BDC linkers (ring Cg-Cg distance 3.926(3) Å, and via π- π contacts (4.221(4) Å) between TPY ligands to generate chains in [010] (see Supporting Information, Figure S15).

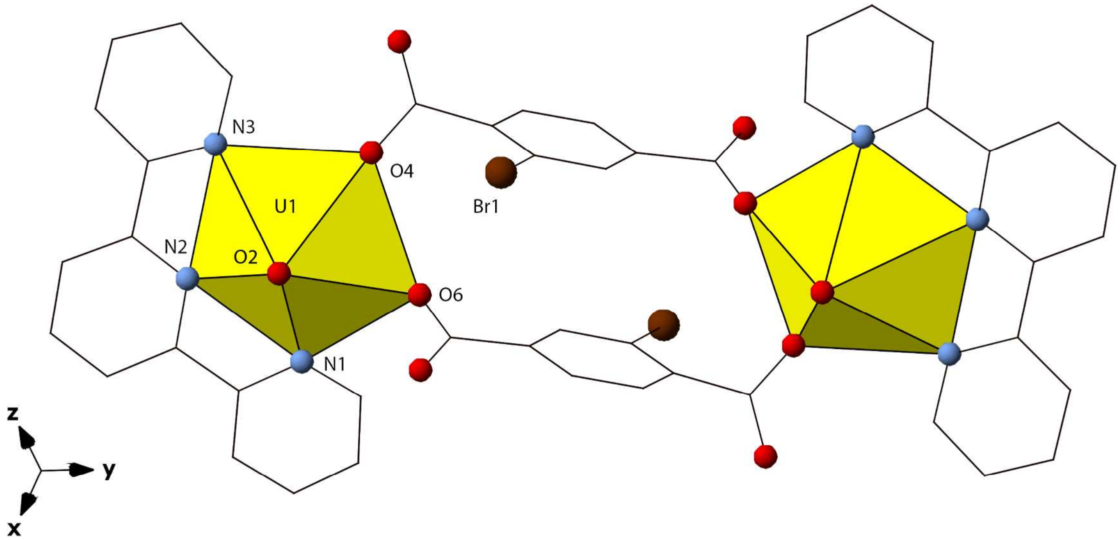


Figure 1. The binuclear pseudo dimer found in **1**. Yellow polyhedra are uranyl centers whereas spheres represent bromine (brown), nitrogen (blue), and oxygen (red).

Crystal Structures of $[(UO_2)(BrC_8H_3O_4)(C_{18}H_{12}N_6)]$ • H_2O (3) and $[(UO_2)(ClC_8H_3O_4)(C_{18}H_{12}N_6)]$ • $2H_2O$ (4). Single crystal X-ray diffraction reveals that the structures of **3** and **4** are isomorphous and crystallize in the P-1 space group. As such only compound **3** will be discussed in detail. The crystal structure and packing of **4** can be found in the Supporting Information Figures S19 and S20. It is also of note that the number of lattice solvent water molecules in **3** and **4** differ, in which two solvent water molecules are observed in **4**.

The structure of **3** (Figure 2) contains one crystallographically uranyl cation (U1, O1, O2). U1 is bound by one tridentate TPTZ via N1, N2, N3 (U –N_{avg} 2.591 Å), and two monodentate Br-BDC linkers via O3 (2.309(8) Å) and O6 (2.243(6) Å) to result in a pentagonal bipyramidal building unit. These units are linked by bridging Br-BDC dicarboxylates to result in a binuclear pseudo dimer (Figure 2). These dimers interact with each other via π- π interactions [55,56] within the Br-BDC linkers (ring Cg-Cg distance 3.926(2) Å) and via π- π interactions (3.621(8) Å) between TPTZ ligands to generate chains approximately in [010] (see Supporting Information, Figure S18).

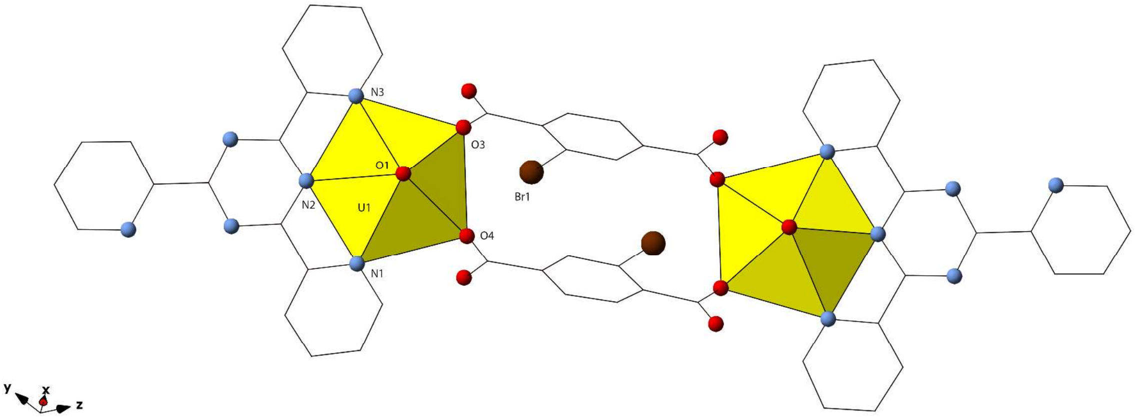


Figure 2. The binuclear pseudo dimer of **3**. Solvent water molecule is not shown for clarity.

Crystal structure of $[(UO_2)(C_8H_3IO_4)(C_{18}H_{12}N_6)] \bullet 2C_3H_7O$ (5). The structure of **5** contains one crystallographically unique uranyl cation (U1, O1, O2) (Figure 3). U1 is bound by one tridentate TPTZ via N1, N2, N3 (U –N_{avg} 2.586 Å), and two monodentate I-BDC linkers via O3 (2.280(6) Å) and O5 (2.245(8) Å) to result in a pentagonal bipyramidal building unit. These units are linked by bridging I-BDC dicarboxylates to result in a binuclear pseudo molecular dimer as seen in Figure 3. These dimers interact with each other through O-H···N; 2.404 Å hydrogen bonds [57] via O7 of solvent 2-propanol and N4 of TPTZ to generate chains in [001] (see Supporting Information, Figure S21).

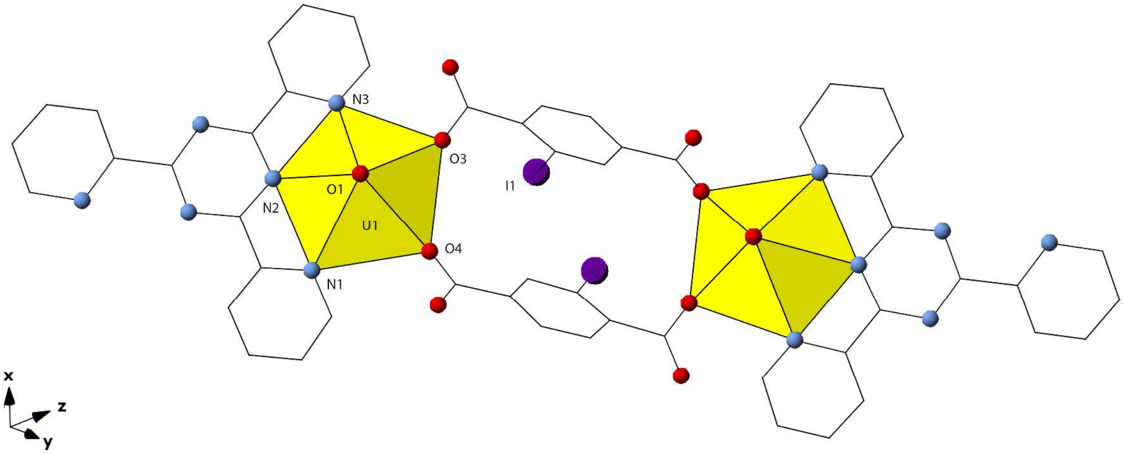


Figure 3. The crystal structure of **5**. The solvent 2-propanol is not shown for clarity. Purple spheres represent iodine.

Crystal Structure of [$(UO_2)(C_9H_6O_4)(C_{18}H_{12}N_6)$] • H_2O (6). The structure of **6** (Figure 4) consists of one crystallographically unique uranyl cation (U1, O1, O2). U1 is bound by one tridentate TPTZ via N1, N2, N3 (U –N_{avg} 2.601 Å), and two monodentate Me-BDC linkers via O4 (2.234(5) Å) and O5 (2.308(6) Å) to result in a pentagonal bipyramidal building unit. These units are linked by bridging Me-BDC dicarboxylates to result in a binuclear pseudo dimer as seen in Figure 4. These dimers interact with each other via π- π interactions within the Me-BDC linkers (ring Cg-Cg distance 3.893(2) Å) and via π- π interactions (3.740(3) Å) between TPTZ ligands to generate chains approximately in [001] (see Supporting Information, Figure S22).

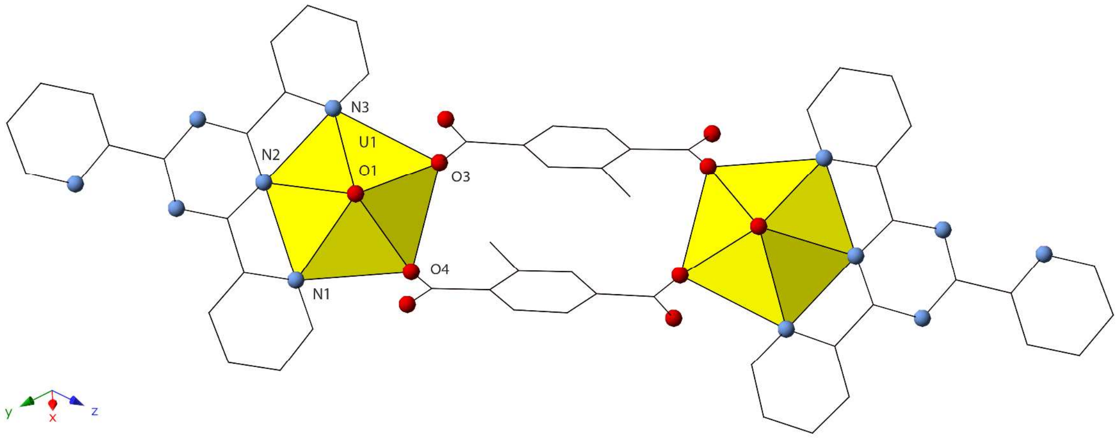


Figure 4. The crystal structure of **6**. The solvent water molecule has been omitted for clarity.

Crystal Structure of [$(UO_2)(C_6H_2O_4S)(C_{18}H_{12}N_6)$] • $2H_2O$ (7). The structure of **7** (Figure 5) consists of one uranyl cation (U1, O1, O2). U1 is bound by one tridentate TPTZ via N1, N2, N3 (U –N_{avg} 2.601 Å), and two monodentate TDC linkers via O3 (2.264(5) Å) and O6 (2.283(5) Å) to result in a pentagonal bipyramidal building unit. These units are linked by bridging TDC dicarboxylates to result in a binuclear pseudo dimer as seen in Figure 5. These dimers interact with each other via π- π interactions within the TDC (ring Cg-Cg distance 3.687(3) Å) and via π- π interactions (3.757(2) Å) between TPTZ ligands to generate chains approximately in the [010] (see Supporting Information, Figure S23).

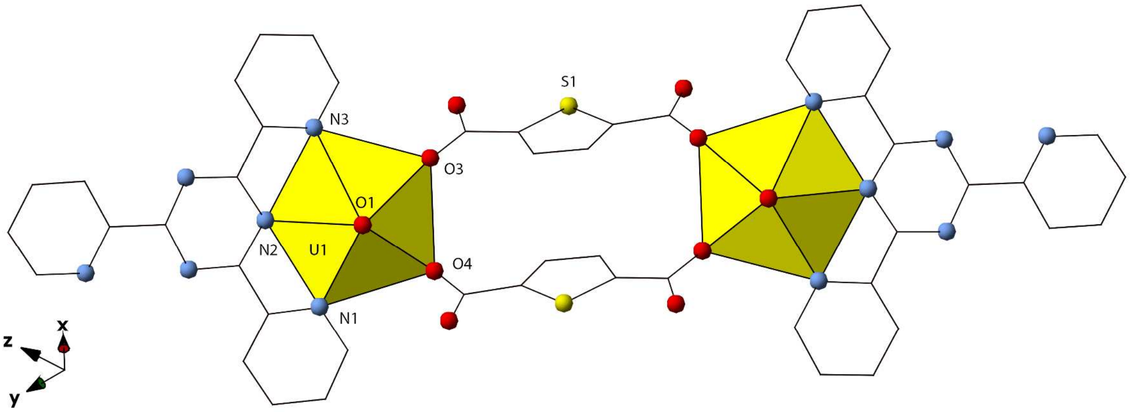


Figure 5. The crystal structure of **7**. Yellow spheres represent sulfur. The two lattice water molecules are not shown for clarity.

Synthesis and Structural Studies. The promotion of a fixed and consistent uranyl coordination geometry by chelating N-donor ligands was successful as observed in the crystal structures of **1-7**. Compounds **1-7** each contain uranyl monomers with pentagonal bipyramidal coordination geometries bridged by O-donor dicarboxylates to result in binuclear pseudo dimers. These dimers are then stabilized by supramolecular interactions to form chains (Table 4, see Supporting Information Figures S15, S17-S18, S20-S23). Moreover, we reintroduce our previously reported compounds $[(UO_2)(C_6H_2O_4S)(C_{15}H_{11}N_3)]$ and $[(UO_2)(C_6H_2O_4S)(ClC_{15}H_{10}N_3)]$ as **8** and **9** for structural comparison and ensuing lifetime measurements below. Briefly, these compounds are analogous to **7**, with the chelating ligands replaced with TPY and Cl-TPY respectively. Detailed descriptions of their crystal structures and packing can be found in our previous publication.[23]

Table 3. Summary of intermolecular distances present in compounds **1-9**.

Compound	O-donor linker	N-donor ligand	Cg-Cg distances (O-donor-O-donor)	Cg-Cg distances (TPY-TPY)	Cg-Cg distances (TPTZ-TPTZ)	Hydrogen bonding O-H···N
1	Br-BDC	TPY	3.926(3) Å	4.221(4) Å	-	-
2	Cl-BDC	TPY	4.270(3) Å	4.144(7) Å	-	-
3	Br-BDC	TPTZ	3.926(2) Å	-	3.621(8) Å	-
4	Cl-BDC	TPTZ	4.173(4) Å	-	3.522(4) Å	-
5	I-BDC	TPTZ	4.599(2) Å	-	4.453(2) Å	2.404(5) Å
6	Me-BDC	TPTZ	3.893(2) Å	-	3.740(3) Å	-
7	TDC	TPTZ	3.687(3) Å		3.757(2) Å	-
8	TDC	TPY	3.661(4) Å	3.919(3) Å	-	-
9	TDC	Cl-TPY	3.684(2) Å	-	-	-

The π-π distances between adjacent X-BDC linkers in **1-4** and **6**; and between adjacent TDC linkers in **7-9** differ. In **1-4**, and **6** the ring Cg-Cg distances are within the same range (3.9-4.2 Å), but the distances are smaller in **7-9** (3.6-3.8 Å). These differences seem to suggest that aromatic ring size (six-member benzene ring versus a five-member thiophene ring) may influence the π-π distance. The ring Cg-Cg distances are also affected between TPY or TPTZ ligands within neighboring pseudo dimers (see Supporting Information Figures S23 and S27). For example, the distances of 3.9-4.2 Å between adjacent TPY ligands in **1**, **2**, and **8** are longer compared to **3**, **4**, and **7** (3.5-3.7 Å) between adjacent TPTZ ligands. We believe that the extent of conjugation or perhaps the size of N-donor ligands may indirectly influence π-π distances within these materials. These observations are consistent to those reported by Janiak[55] and Martinez et al.[56]

In compound **5**, π-π interactions between I-BDC linkers (ring Cg-Cg distance: 4.599 Å) and between neighboring TPTZ ligands (ring Cg-Cg distance: 4.453 Å) are not within the acceptable π-stacking distances of 3.3-3.8 Å.[55] When compared to the ring Cg-Cg distances between neighboring TPTZ ligands within **3** and **4** using Cl-BDC (3.522(4) Å) and Br-BDC (3.621(8) Å), we observe the distances become larger as the size of the halogen atom becomes larger. Given the size of the iodine atom, this may be a possible reason why π-stacking was not observed in **5**. A similar trend is also observed between X-BDC (X = Cl, Br, I) linkers within **3-5** (Table 4). As such, the interaction observed between pseudo dimers in **5** are O-H···N hydrogen bonds between 2-propanol and TPTZ (2.404 Å, Table 4, see Supporting Information Figure S21).

Luminescence Studies. The UO_2^{2+} cation typically shows green emission with a spectral profile characterised by vibronically structured peaks between 450 nm and 650 nm. These peaks arise from electronic transitions between the LUMO 5*f* non-bonding uranyl orbitals and a HOMO U=O sigma orbital within UO_2^{2+} and are commonly referred to as ligand-to-metal charge transfer (LMCT) states.[31,58,59] Further, these electronic transitions are coupled with vibrational relaxation between $S_{11} \rightarrow S_{01}$ and $S_{10} \rightarrow S_{0v}$ (v = 0-4) states within the U=O axial bond.[10,18,60] While water is known to act as an efficient quencher of *f*-localised excited states (of both lanthanides and actinides) *via* coupling to the O-H vibrational manifold,[61] the emission from the uranyl LMCT excited state does not display such predictable sensitivity to water.[35]

Luminescence spectra of **1-7** were obtained using an excitation wavelength of 420 nm, which corresponds to the well-known axial LMCT band of the UO_2^{2+} cation.[58,62]

The spectra of **1-4** and **6-7** show characteristic uranyl emission containing vibronically structured peaks between 450 nm and 600 nm (Figures 6-8; see Supporting Information Figures S24-S25 for additional spectra wherein λex = 365 nm.). Compound **5** was found to be non-emissive using either excitation wavelength.

The spectral influence of the triimine terminal ligand (*i.e.* TPY *vs* TPTZ) was examined through a comparison of the emission spectra of compounds **1** and **3** (where the bridging ligand was Br-BDC) and revealed an average red shift of +80 cm^{-1}, as determined by measuring the energy difference between each vibronic peak of both **1** and **3** (Figure 6, see Supporting Information Table S8). Similarly, the emission spectra of **2** and **4** which incorporate the Cl-BDC linker, showed a +55 cm^{-1} red shift upon substituting TPY for TPTZ (Figure 6, see Supporting Information Table S9).

It is noteworthy that the emission spectra of **1-4** are consistent with our previous work, in which substitution between N-donor ligands TPY and Cl-TPY, within binuclear pseudo dimers containing TDC dicarboxylates (e.g. **8** and **9**), resulted in a red shift (+80 cm^{-1}) of the emission spectrum of **9** relative to **8**.[23] The origin of the shift may be rationalised by considering the π-stacking distances between neighboring TPY and TPTZ ligands within **1-4** (Table 3 and see Supporting Information Figure S26). That π-stacking may influence the emission spectra has been noted previously,[63] and may be a result of possible orbital mixing between uranyl and TPY molecular orbitals. This tentative interpretation is consistent with preliminary observations from our supporting computational studies.[64]

Within the complexes of the TPTZ series (**3**, **4**, **6**, and **7**), the emission wavelengths were closely comparable (Figure 7, Table 4, see Supporting Information

Table S10, Figure S24) and unperturbed by variations in the substitution of the aromatic bridging O-donor dicarboxylates. Uranyl emission in **5** was not observed (Figure 7) and quenching of the uranyl luminescence with iodo-substituted organic linkers can be attributed to enhanced non-radiative processes via the proximate heavy atom effect.[65-67]

The luminescence spectra of complexes **1-7** are clearly influenced by the choice of N-donor ligands (TPY, TPTZ) and O-donor dicarboxylates. These observations are consistent with our earlier work, in which systematic substitution between TPY (compare Cl-TPY) ligands and aromatic dicarboxylates in pseudo dimers resulted in tuned uranyl emission. Further, the choice of O-donor dicarboxylate can also quench uranyl emission.

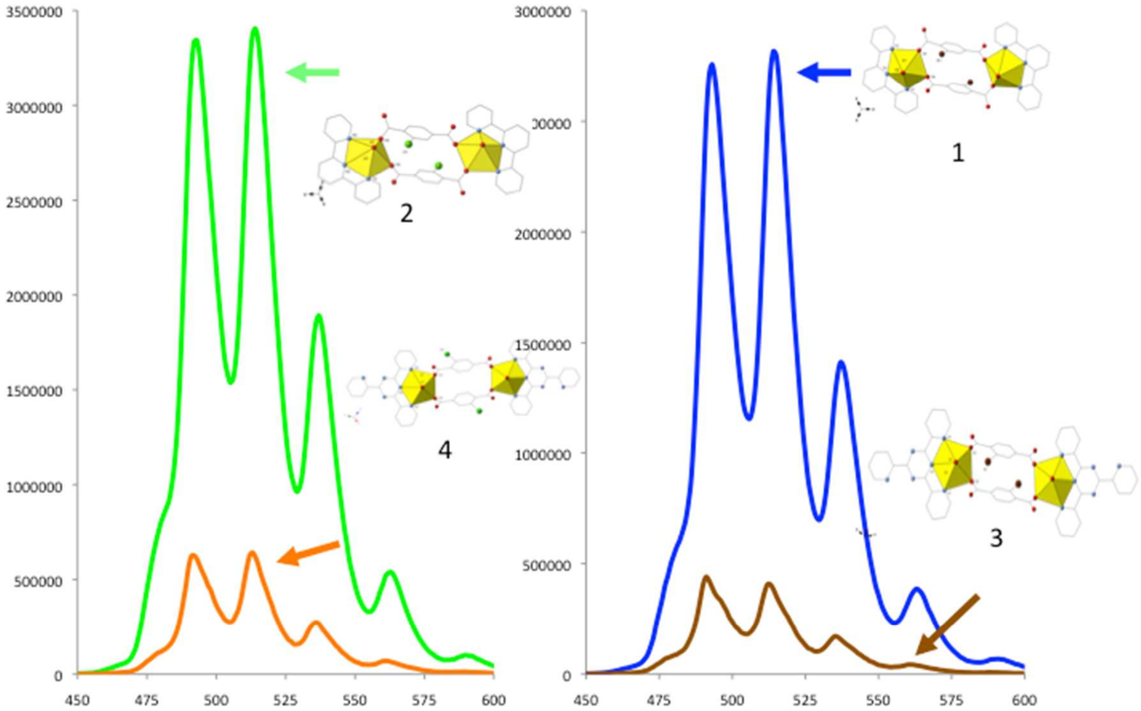


Figure 6. Solid-state emission spectra (excitation: 420 nm, 298 K) of **1-4**. A Bathochromic shifts were determined by comparing the emission spectrum of **2** relative to **4**; and the emission spectrum of **3** relative to **1**.

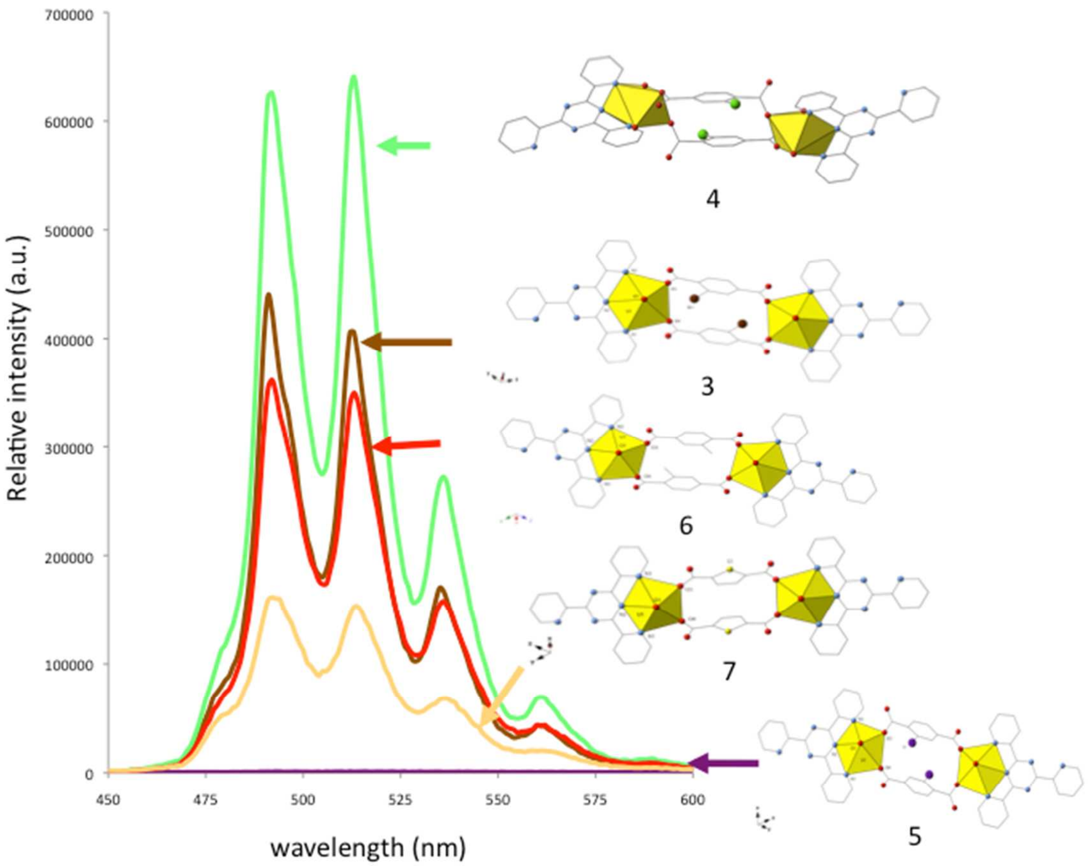


Figure 7. Solid-state emission spectra (excitation: 420 nm, 298 K) of the TPTZ series **3-7**.

Table 4. Spectroscopic data (fluorescence and lifetimes) for **1-9** using λ_{exc} = 420 nm (298 K).

Compound	O/N donor	λ_{em} / cm^{-1}	τ / μs
1	Br-BDC/ TPY	20283, 19455, 18622, 17825	55.05, 120.84 (84%)
2	Cl-BDC/ TPY	20325, 19493, 18657, 17857	34.77, 85.77 (79%)
3	Br-BDC/ TPTZ	20367, 19531, 18657, 17857	46.34, 97.94 (77%)
4	Cl-BDC/ TPTZ	20367, 19531, 18692, 17857	53.77, 104.02 (74%)
5	I-BDC/ TPTZ	-	-
6	Me-BDC/ TPTZ	20325, 19493, 18692, 17857	32.98 (75%), 65.71
7	TDC/ TPTZ	20367, 19493, 18692, 17794	3.88 (32%), 11.09 (59%), 35.52 (10%)
8	TDC/ TPY	20242, 19342, 18518, 17667	36.40 (16%), 119.23 (82%), 7.24 (2%)

9	TDC/ Cl-TPY	20283, 19455, 18621, 17793	44.18 (36%), 88.04 (52%), 1.49 (12%)

Lifetime Studies.

The lifetimes of solid state samples of **1-4** and **6-9** were collected using time-correlated single photon counting fluorescence spectroscopy (TCSPC) and reported using an excitation wavelength of 420 nm (Table 4). It should be noted that in all cases additional decay profiles were obtained using 365 nm excitation and these were all found to be within error of the companion 420 nm excitation measurements (see Supporting Information Table S10). The decay profiles of compounds **1-4** and **6,** which incorporate the X-BDC linkers, were best fitted with bi-exponential components yielding two distinct lifetimes, τ_1 and τ_2. The relative weightings of these components to the decay profile showed that the long-lived component dominated in each case. The UO_2^{2+} cation is well known to display bi-exponential decay lifetimes consisting of a long-lived (τ_1) and short-lived (τ_2) component.[60] Interpretation of these components has been attributed to many variables including uranyl speciation and the presence of different emissive species in solution. More recently, bi-exponential decay lifetimes of UO_2^{2+} have been measured in organic solutions.[62,68] These lifetimes have been attributed to radiative processes occurring in the equatorial and axial LMCT components within the U-O bonds. The case of lifetime analyses of solid state samples is also often complicated by emissive center differences due to packing and surface effects. Also, the varying extent of lattice solvent should not be ignored since it is possible that this could also provide a non-radiative quenching pathway.

For compounds **7-9** containing the TDC linkers, satisfactory data fits could only be obtained through three exponential components thus yielding three distinct lifetimes, τ_1, τ_2, and τ_3; the statistical significance of the relative weightings should be treated with caution. In all cases (**1-9**) the lifetimes are in the microsecond domain and again consistent with an emitting state that is phosphorescent in nature (*i.e.* ^{3}LMCT).

For the TPTZ-containing compounds **3-6** when the substituent of the bridging ligand is altered (Me-BDC *vs.* Br-BDC *vs.* Cl-BDC), the data show an increase in the ^{3}LMCT lifetime. The increase in the ^{3}LMCT from **6** (Me-BDC) to **3** (Br-BDC) to **4** (Cl-BDC), and the non-emissive nature of **5** (I-BDC) appears to be influenced by the presence of C-H quenchers and the presence of heavy atoms (Br, I), which may enhance non-radiative pathways. Given that **6** showed the shortest lifetime in the TPTZ complexes (**3-6**), a possible explanation could invoke discussion of proximate quenchers to the uranyl center. As noted above, quenching *via* C-H and O-H vibrational manifolds is well established for lanthanide excited states, but far less predictable for uranyl.[35,61,69,70] The X-ray structure of **6** shows that methyl groups are positioned close to the uranyl center (U-C$_{\text{methyl}}$ distance: 5.13(3) Å) and could therefore provide a non-radiative pathway.

Comparison of the data for the TPY-containing complexes **1** and **2** indicates a longer ^{3}LMCT lifetime for the Br-BDC compound. At present, it is unclear why this is the case and efforts to synthesize related CH$_3$-BDC and I-BDC compounds with TPY ligands have not yet been successful. In contrast to **1-6**, complexes **7-9**, which incorporate the TDC bridging group, show a marked dependence upon the specific nature of the terminating triimine ligand. Upon switching from TPY (**8**) to TPY-Cl (**9**) to TPTZ (**7**) the lifetimes are dramatically reduced from >100 μs (**8**, TPY) to <15 μs (**7**, TPTZ). Given our earlier discussion of **1-6**, it is possible that this dramatic variance has roots in the specific nature of the solid state molecular packing of each complex.

Conclusion

In summary, seven uranyl CPs (**1-7**) were synthesized under hydro(solvo)thermal conditions. The N-donor ligands TPY and TPTZ were used to select specific uranyl monomers, which were then subsequently assembled by O-donor dicarboxylates to result in binuclear pseudo dimers. A systematic study on the role organic ligands may have on the structures and luminescence within **1-7** was investigated. Substitution between N-donor ligands resulted in tuned emission (**1-4**). In TPTZ derivatives (**3-7**), emission shifts were not observed upon substitution of different O-donor aromatic dicarboxylates. Further, uranyl lifetimes were measured to probe the influence organic ligands may have on uranyl excited states. Different combinations of N-donor and O-donor ligands resulted in lifetimes that are affected by the choice of ligands and quite possibly by crystal packing effects in **1-9**.

Acknowledgements

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Supporting Information Available:

CIFs of **1-7** at 298 K (CCDC 1400915-1400921), Bond Tables and Angles, ORTEPs, PXRD patterns, luminescence spectra, and lifetime measurements. This material is available free of charge via the Internet at http://pubs.rsc.org.

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A series of uranyl complexes containing various O-donor aromatic dicarboxylates and N-donor chelating ligands TPY and TPTZ has been synthesized and characterized.