Self-assembly of $[\text{UO}_2\text{X}_4]^{2-}$ (X= Cl, Br) Dianions with γ Substituted Pyridinium Cations: Structural Systematics and Fluorescence Properties.

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Abstract

Room temperature self-assembly of $[\text{UO}_2\text{X}_4]^{2-}$ (X = Cl, Br) with γ substituted pyridinium cations has resulted in the formation of twelve compounds that were studied via single crystal X-ray diffraction and fluorescence spectroscopy. Systematic variation of electron donating groups on the pyridinium species is shown to influence the presence and/or strength of various supramolecular synthons, including hydrogen bonding and pi interactions. Combinations of such non-covalent interactions (NCIs) have given rise to a range of supramolecular assemblies, and are shown to influence uranyl emission by way of second sphere coordination to equatorial ligands.

Introduction

Sustained interest in uranium(VI) bearing hybrid materials has generated a rich portfolio of structure types and numerous compounds with intriguing (photo)physical properties.¹⁻⁴ Whereas much of the recent development of actinide bearing hybrid materials has been in the form of coordination polymers (e.g. structures comprised of covalent bonding extending in 1, 2 or 3 dimensions), supramolecular assembly has the potential to produce exotic structure types and unexpected properties that may be unobtainable through direct ligand-to-metal coordination. Vital to this approach is the formation of predictable building units (tectons) and assembly via synthons that are chemically robust and able to guide molecular arrangement. These motifs (synthons) consist of non-covalent interactions that stitch together discrete molecular units into an extended assembly.⁵ Interaction and acceptor-donor pairings are crucial, as these elements dictate the resulting topology and therefore influence both chemical and physical properties. The relationship between intermolecular interactions and the resulting structure must be fully understood in order to design a material with a desired set of properties.⁶ Thus, by pairing a fixed inorganic building block with a suite of carefully selected organic tectons, one can systematically probe, with some degree of control, a series of related molecular assemblies in order to establish trends that can

be applied to future design efforts.

In this respect, directed assembly utilizing U(VI), in the form of the uranyl cation $[\text{UO}_2]^{2+}$, is challenging as a diverse and variable suite of species convolute the ability to regulate the intermolecular interactions observed within crystal structures. The rather inert nature of the axial 'yl' oxygen atoms contributes to the unique crystal chemistry of the uranyl cation by (typically) restricting ligand coordination to the equatorial plane, forming a rather limited (square, pentagonal, and hexagonal bipyramidal) first coordination environment.⁷ These limited first coordination spheres are offset by a propensity for oligimerization, as a function of hydrolysis and reaction conditions, into an array of polynuclear species that tend to promote two dimensional assemblies. The cumulative effects of hydrolysis combined with a judicious choice of coordinating species, i.e. carboxylates, phosphonates, and N-donors, promotes a diverse building unit (BU) profile and consequently, a wide variety of topologies.^{3, 8-10} The proclivity of the uranyl cation to form a diverse array of structure types introduces a challenge, to directed assembly, as the ability to control both speciation and interactions thereof is diminished.

To circumvent this behavior, synthesis in acidic media containing high concentrations of anions (Cl^- , Br^- , SCN^-) promotes a more limited suite of reproducible uranyl tectons by restricting the speciation profile.¹¹⁻

¹⁷ In particular, acidic solutions containing high concentrations of halogens yield the square bipyramidal $[\text{UO}_2\text{X}_4]^{2-}$ tecton, almost exclusively (**Figure 1**). The uranyl tetrahalide dianion has demonstrated behavior similar to transition metal chlorides, which are capable of forming strong halogen and hydrogen bonds.¹⁸⁻

²⁰ The halogen atoms at the periphery of the metal centers, due to the largely dative bonding, are good hydrogen bond acceptors and can be used as a means to assembly. Pairing the $[\text{UO}_2\text{X}_4]^{2-}$ dianion with series of related cations (in this case, pyridinium ions) that are capable of forming supramolecular interactions allows one to investigate assembly as a function of interaction preference.

Figure 1: A schematic of the uranyl tetrahalide dianion $[\text{UO}_2\text{X}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) is provided on the left whereas a view down the uranyl axis is shown as a polyhedral representation on the right. The uranium center is drawn as a yellow polyhedron while the oxygen and chlorine atoms are depicted as red and green spheres, respectively.

The pyridinium cations featured in this study are substituted at the γ position with various electron donating groups that vary in hydrogen bond donor strength (Scheme 1). These groups, used in conjunction with the fixed pyridinium ion (N-H^+), allow one to probe relevant acceptor-donor pairings and in some cases interaction strengths. Moreover, exchange of the inorganic tecton ($[\text{UO}_2\text{Br}_4]^{2-}$ for $[\text{UO}_2\text{Cl}_4]^{2-}$) while holding the cation selection constant allows for exploring the role(s) of the halogen atoms in assembly.

Scheme 1: A representation of the various substituted pyridinium cations that were paired with the $[\text{UO}_2\text{X}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) dianions.

Subtle changes to molecular arrangement and constituent atoms can manifest as observable changes in the resulting photoluminescence properties of a material. UO_2^{2+} containing material typically exhibits a characteristic green (ca. 520 nm) emission profile that results from ligand-to-metal charge transfer transitions between the uranyl bonding ($3\sigma_u$, $3\sigma_g$, $2\pi_u$, and $1\pi_g$) and non-bonding $5f(\delta_u)$ and $5f(\phi_u)$ molecular orbitals.^{21, 22} Formally, the bonding molecular orbitals (HOMO) are attributed to a mixing of the oxygen 2p and uranium 5f electrons while the non-bonding molecular orbitals (LUMO) are comprised primarily of the U 5f non-bonding atomic orbitals, which differ in symmetry with respect to the orbitals of the O atoms.²² The composition and orbital contribution to the frontier orbitals are areas of interest and debate as both theoretical and experimental studies have suggested mixing of the equatorially bound Cl ligands (3p) atomic orbitals with the U 5f non-bonding orbitals in various U(VI) containing systems.²³⁻²⁶ This suggests the electronic structure and emissive properties of the UO_2^{2+} are sensitive to equatorial ligand coordination. In fact, this was shown experimentally by Natrajan et al. as a correlation between shifts in the uranyl emission and the electron donating capabilities of the equatorial ligands were established.²⁷ Utilizing a series of structurally related $[\text{UO}_2\text{X}_4]^{2-}$ dianion containing structures is advantageous as a relationship between structure and luminescence may be further explored. If the halogen atoms are oversimplified and thought of in purely electrostatics terms, then redistributions of their charge density due to hydrogen bonding interactions can affect the charge donation to the U(VI) center. The relative electron density contained within the U(VI) metal center has been suggested to influence the uranyl bond order, which directly impacts the UO_2^{2+} emission profile.²⁷ A logical extension of this rationale would lead one to expect strong hydrogen bonding interactions combined with halogen polarizability (size) to influence the electronic structure of the UO_2^{2+} by disrupting the relative electron distribution of the equatorial halide ligands.

Herein, we present our efforts to pair the $[\text{UO}_2\text{X}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) tecton with various substituted pyridinium cations that charge balance and facilitate assembly via hydrogen bonding. The pairing of various hydrogen bond donating groups with the fixed pyridinium ion allows one to scrutinize supramolecular interaction pairings and relative strengths. Utilizing two fixed uranyl tetrahalide tectons will augment these comments as the influence of the hydrogen bond acceptor can be explored. Furthermore, the subtle changes to the overall assembly will be analyzed in attempt to rationalize the differences between the corresponding emission spectra. As a result of these efforts, twelve new

compounds have been synthesized and characterized via single crystal X-ray diffraction and fluorescence spectroscopy.

Experimental

Synthesis. Caution! Whereas the uranium oxyacetate dihydrate ($\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) used in this investigation contains depleted uranium, standard precautions for handling radioactive and toxic substances should be followed.

The pyridinebased compounds were purchased and used without further purification.

Synthesis Compounds 1-12:

Uranyl acetate (0.295mmol) and 4-X-pyridine (0.590mmol), where X = H, CH₃, OH, SH, NH₂, N(CH₃)₂, were placed into a glass scintillation vial and dissolved in 5mL of 2M hydrochloric acid (**1-6**) or 2M hydrobromic acid (**7-12**). The resulting pale yellow or gold solution (pH ~ 0 – 0.5) was allowed to evaporate at ambient temperature to the open atmosphere. Over a period of weeks large yellow or green crystals formed and were harvested and weighed prior to the solutions reaching dryness to avoid the presence of impurities. As such the total yields are estimated to be >75% based upon product collection prior to dryness.

4-Mercaptopyridine was used in the synthesis of both **4** and **9**, yet was incorporated in **9** only. The bis(4-Pyridinium)disulfide cation incorporated into **4** was formed via HCl catalyzed *in-situ* disulfide bond formation. The substitution of HBr for HCl in **9** retards this conversion as the bis(4-pyridinium)disulfide cation was not observed.

Room temperature self-assembly removes the influence of extrinsic factors (heat, pressure, etc.) and lends itself to the growth of large single crystals of sufficient quality for a wide range of analytical techniques that may be unobtainable via other synthetic routes (e.g. hydro/solvo thermal).²⁴ Subtle changes to the reaction conditions (concentration, solvent volume, evaporation rate, etc.) can affect crystal growth; e.g. size and quality. A sampling of the crystals obtained in this study is given in Figure 2.

Figure 2: A selection of the crystals of **1-12** that were grown via slow evaporation from aqueous solutions containing high concentrations of chloride and bromide ions.

X-Ray Crystal Determination

Single crystals of compounds **1-12** were isolated from aqueous evaporations and were cut to an appropriate size for single crystal X-ray diffraction. The single crystals were mounted on MicroMounts (Mitegen) and reflection data were collected using 0.5° ω scans at 100K on a Bruker SMART diffractometer equipped with an APEX II CCD detector and Mo K- α source. The APEX II software suite²⁸ was used to integrate the data and to apply an absorption correction.²⁹ All twelve structures were solved via direct methods using *SIR92*³⁰ and refined using *SHELXL-14*³¹ within the *WINGX* software suite³² (**Tables 1 and 2**). Publication materials were prepared using the WinGX software suite and figures of the compounds were made using CrystalMaker V9.1.4.³³ All non-hydrogen atoms were located using difference Fourier maps and were refined anisotropically. The hydrogen atoms of the carbon atoms that form the aromatic pyridinium rings in **1-12** were placed in idealized positions and allowed to ride on their parent atoms. All hydrogen atoms belonging to methyl substituents in compound **2**, **6**, **8** and **12** were found on the difference Fourier maps, yet modeled in idealized positions and allowed to ride on their parent atom(s). The hydrogen atom associated with the heteroatom (nitrogen) in each pyridinium cation in all twelve crystal structures was located in difference Fourier maps, modeled, distance restrained (DFIX) and allowed to refine isotropically. The hydrogen atoms of the hydroxyl (**3** and **9**), mercapto (**10**) and amino (**5** and **11**) substituents were located in difference Fourier maps and given similar treatment (DIFX and isotropic refinement) to the nitrogen heteroatoms.

The refinement of **1**, $(C_5H_6N)_2[UO_2Cl_4]$, was straightforward, but merits mention as an alert B (PLAT112) regarding the possibility of missed additional (pseudo) symmetry remains in the final refinement. An error in the assignment of the space group and/or unit cell dimensions were ruled out as manual trial-and-error assignments and figure of merit score analysis confirmed our selection. Further, the programs Cell_Now and ADDSYM failed to recommend any changes to the unit cell or space group assignment. We did not find any evidence that a twin component was responsible for the presence of this alert. Standard and calculated twin laws were used during stages of the refinement, yet they failed to improve the final R factors or to resolve the alert B.

We confirmed that each of the two unique uranyl tetrachloride dianions and four unique pyridinium cations in **1** were in fact crystallographically distinct from one another. The uranium atomic coordinates (x, y, z) are not within 0.5 of one another, which suggests they are not equivalent by means of a missed symmetry element. A plane was calculated and inserted coaxial to the linear uranyl cation (O=U=O) at each of the two unique uranyl sites, while a second set of planes were placed such that they were coplanar with the four bonds created by the U(VI) center and four equatorial chloro ligands. The angles between the respective planes (comparing dianion to dianion) were calculated to be non-zero numbers and hence the two $[UO_2Cl_4]^{2-}$ tectons were not coplanar and/or relatable via a symmetry element. A similar process was

followed to compare the four unique pyridinium cations, which were neither coplanar nor related by a missing symmetry element. As such we have concluded our space group assignment of $P\bar{1}$ is appropriate for compound **1**.

Luminescence

Compounds **1** – **12** were studied via single crystal solid state excitation and emission spectroscopy on a Horiba Jobin Yvon Fluorolog spectrophotometer at low temperature (~77K). Data analysis was performed using the FluorEssence software package. Single crystals (by visual inspection) of **1-12** were placed into a quartz NMR tube, immersed in liquid N₂, and allowed to equilibrate. Each sample was excited at 420nm and quickly scanned to determine the positions of each emission maxima. The most intense emission band was chosen and used to collect excitation spectra of compounds **1-12**. The excitation spectra of **1-12** were used to define an excitation value of 410nm that was suitable for obtaining emission spectra. The experimental parameters (slit widths, scan time, etc.) were adjusted sample-to-sample to obtain suitable data with a sufficiently high signal-to-noise ratio and can be found in the electronic supporting information (ESI Table 1).

Table 1: Selected crystallographic data of Compounds **1– 6**.

Compound	1	2	3	4	5	6
Empirical formula	C ₁₀ H ₁₂ Cl ₄ N ₂ O ₂ U	C ₁₂ H ₁₆ Cl ₄ N ₂ O ₂ U	C ₁₀ H ₁₂ Cl ₄ N ₂ O ₄ U	C ₁₀ H ₁₀ Cl ₄ N ₂ O ₂ SU	C ₁₀ H ₁₄ Cl ₄ N ₄ O ₂ U	C ₁₄ H ₂₂ Cl ₄ N ₄ O ₂ U
Formula mass	572.05	600.10	604.05	634.15	602.08	658.18
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
a/Å	11.132(2)	7.772(1)	7.028(2)	7.4032(9)	6.8528(9)	7.527(2)
b/Å	11.278(2)	11.549(2)	7.537(3)	8.939(1)	7.0665(9)	8.314(2)
c/Å	13.943(2)	9.882(2)	8.501(3)	13.348(2)	9.348(1)	9.084(2)
α/°	107.512(2)	90.00	87.714(5)	94.56(2)	89.304(2)	82.489(4)
β/°	107.962(2)	90.536(2)	66.262(4)	103.840(1)	72.424(2)	69.55(2)
γ/°	90.171(2)	90.00	84.952(5)	91.590(2)	81.136(2)	84.197(3)
Unit cell volume/Å³	1579.1(4)	887.0(2)	410.6(2)	854.0(2)	426.1(1)	527.1(2)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
D_{calc}/Mg cm⁻³	2.406	2.247	2.443	2.466	2.346	2.073
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
No. of formula units per unit cell, Z	4	2	1	2	1	1
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient, μ/mm⁻¹	10.952	9.756	10.547	10.375	10.157	8.220
No. of reflections measured	22906	12760	6112	12411	6296	7827
No. of independent reflections	8566	2528	2272	4706	2353	2927
R_{int}	0.0288	0.0444	0.0340	0.0389	0.0321	0.0204
Final R_I values(I > 2σ(I))	0.0229	0.0169	0.0200	0.0213	0.0167	0.0123
Final wR₂(F²) values(I > 2σ(I))	0.0558	0.0411	0.0422	0.0537	0.0416	0.0290

Final R_1 values (all data)	0.0339	0.0196	0.0200	0.0216	0.0167	0.0123
Final $wR_2(F^2)$ values (all data)	0.0624	0.0424	0.0422	0.0539	0.0416	0.0290
Goodness of fit on F^2	1.020	1.077	1.046	1.128	1.063	1.053
CCDC deposition number	1409802	1409803	1409804	1409805	1409806	1409807

Table 2: Selected crystallographic data of Compounds **7** – **12**.

Compound	7	8	9	10	11	12
Empirical formula	C ₁₀ H ₁₂ Br ₄ N ₂ O ₂ U	C ₁₂ H ₁₆ Br ₄ N ₂ O ₂ U	C ₁₀ H ₁₂ Br ₄ N ₂ O ₄ U	C ₁₀ H ₁₂ Br ₄ N ₂ O ₂ S ₂ U	C ₁₀ H ₁₄ Br ₄ N ₄ O ₂ U	C ₁₄ H ₂₂ Br ₄ N ₄ O ₂ U
Formula mass	749.89	777.94	781.89	814.01	779.92	836.02
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
a/Å	7.4535(4)	7.816(2)	7.121(2)	6.946(2)	7.0033(8)	8.4077(7)
b/Å	7.9836(4)	11.832(3)	7.746(2)	7.625(2)	11.7114(14)	10.6372(8)
c/Å	8.3261(5)	10.381(3)	8.801(2)	9.142(2)	11.2148(13)	13.167(1)
α/°	78.2410(7)	90.00	88.745(3)	91.554(4)	90.00	90.00
β/°	73.1580(7)	90.784(4)	67.809(3)	105.14(1)	100.145(2)	107.513(1)
γ/°	67.4940(6)	90.00	84.412(4)	97.027(3)	90.00	90.00
Unit cell volume/Å³	435.66(6)	959.9(5)	447.3(2)	463.0(2)	905.44(18)	1123.0(2)
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
D_{calc}/Mg cm⁻³	2.858	2.691	2.903	2.920	2.861	2.472
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
No. of formula units per unit cell, Z	1	2	1	1	2	2
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
Absorption coefficient, μ/mm⁻¹	18.484	16.783	18.017	17.624	17.796	14.357

No. of reflections measured	6440	10373	6561	6757	12999	16139
No. of independent reflections	2396	2702	2443	2558	2580	3202
R_{int}	0.0178	0.0737	0.0268	0.0362	0.0457	0.0274
Final R_1 values($I > 2\sigma(I)$)	0.0142	0.0354	0.0201	0.0300	0.0225	0.0158
Final $wR_2(F^2)$ values($I > 2\sigma(I)$)	0.0326	0.0851	0.0483	0.0778	0.0546	0.0328
Final R_1 values (all data)	0.0148	0.0396	0.0209	0.0310	0.0245	0.0190
Final $wR_2(F^2)$ values (all data)	0.0328	0.0874	0.0487	0.0784	0.0555	0.0335
Goodness of fit on F^2	1.105	1.038	1.050	1.042	1.062	1.119
CCDC deposition number	1409808	1409809	1409810	1409811	1409812	1409813

Structure Descriptions

The inorganic tecton remains fixed in compounds **1-6** ($[\text{UO}_2\text{Cl}_4]^{2-}$) and **7-12** ($[\text{UO}_2\text{Br}_4]^{2-}$), respectively. The uranyl tetrahalide tecton $[\text{UO}_2\text{X}_4]^{2-}$ consists of a U(VI) center bound axially by twoterminal oxygen atoms and equatorially by four halide (Cl or Br) atoms. Typical bond lengths and angles associated with the local coordination geometry of the uranyl tetrahalide tectons are provided(**Table 3**). As such, we will not re-visit these parameters and instead focus on modes of assembly.

Table 3: Selected bond lengths and angles of the uranyl halide tectons found in **2** and **7** serve as a representative for all compounds.

	U=O	U –X ₁	U –X ₂	U –X ₁ '	U –X ₂ '
$[\text{UO}_2\text{Cl}_4]^{2-}$	1.7707(14) Å	2.6549(6) Å	2.6927(6) Å	2.6549(6) Å	2.6927(6) Å
$[\text{UO}_2\text{Br}_4]^{2-}$	1.769(2) Å	2.8372(3) Å	2.8186(3) Å	2.8372(3) Å	2.8186(3) Å
	$\angle \text{O}=\text{U}=\text{O}$	$\angle \text{X}_1-\text{U}-\text{X}_2$	$\angle \text{X}_1-\text{U}-\text{X}_2'$	$\angle \text{X}_1'-\text{U}-\text{X}_2'$	$\angle \text{X}_1' - \text{U} - \text{X}_2$
$[\text{UO}_2\text{Cl}_4]^{2-}$	180.0°	89.17(1) °	90.84(1)°	89.17(1)°	90.84(1)°
$[\text{UO}_2\text{Br}_4]^{2-}$	180.0°	90.70(1)°	89.30(1) °	90.70(1)°	89.30(1)

Compound 1: $(\text{C}_5\text{H}_6\text{N})_2[\text{UO}_2\text{Cl}_4]$, crystallizes in the space group $P\bar{1}$ and consists of $[\text{UO}_2\text{Cl}_4]^{2-}$ dianions charge balanced by pyridinium cations (**Figure 2**). The asymmetric unit consists of two unique $[\text{UO}_2\text{Cl}_4]^{2-}$ dianions and four unique pyridinium cations that form an infinite chain (along [011]). The overall chain is best illustrated by a repeating unit that consists of four (two unique) UO_2^{2+} containing metal centers: U1', U1, U2, U2' (**Figure 2**). The pyridinium cation forms a bifurcated bridging N-H...Cl hydrogen bond with Cl2' and Cl1, both of tectons U1' and U1 (**Table 4**). This interaction is repeated through symmetry such that it exists on either side of the uranyl tecton chain. The pyridinium cations containing atoms N2 and N3 flank and link uranyl tectons U1 and U2 together via bifurcated N-H...Cl hydrogen bonds to the chlorine atoms Cl4 and Cl5 and Cl1 and Cl5, respectively (**Figure 2** and **Table 4**). Tectons U2 and U2' are in turn stitched together via dual bifurcated bridging hydrogen bonds between pyridinium nitrogen atoms N4 and N4' and chlorine atoms Cl7 and Cl7' (**Table 4**). The dual hydrogen bonding pattern is propagated infinitely along the [011] direction.

Table 4: Selected interaction lengths and angles of **1**.

Interaction	Length (Å) (D···A)	Angle (°) (∠D-H···A)
N ₁ -H _{1n} ···Cl ₁	3.263(3)	103.8(2)
N ₁ -H _{1n} ···Cl ₂	3.456(4)	129(3)
N ₂ -H _{2n} ···Cl ₄	3.362(3)	128(3)
N ₂ -H _{2n} ···Cl ₅	3.300(4)	133(3)
N ₃ -H _{3n} ···Cl ₁	3.291(3)	118(3)
N ₃ -H _{3n} ···Cl ₅	3.270(3)	129(3)
N ₄ -H _{4n} ···Cl ₇	3.282(3)	128(3)
N ₄ -H _{4n} ···Cl _{7'}	3.271(4)	131(3)

The individual pyridinium-uranyl tetrachloride chains interlock with one another via offset π interactions to form 2D sheets in the (011) plane. The pyridinium cations associated with neighboring uranyl chains align anti-parallel (with respect to heteroatom orientation) to one another and are displaced to form offset π interactions. A majority of these interactions are long (4.3 – 5.5 Å) and are likely a consequence of crystal packing. The two most notable of these offset π interactions are between the pyridinium rings containing N1 and N2 and N3 and N4. Relevant distances and angles associated with these interactions were measured using calculated centers of gravity (Cg) of each ring associated with the interactions and are reported (Table 5).

Table 5: Select distances and angles relevant to the offset π interactions found in **1** – **6**.

Compound	Pyridinium Ring (Containing atom N _n)	Distance Cg···Cg (Å)	Perpendicular Displacement (Å)*	Angle β (°)**
1	N ₁ – N ₂	3.802(2)	3.374(2)	24.2
1	N ₃ – N ₄	3.536(2)	3.306(1)	19.1
2	N ₁ – N _{1'}	3.628(1)	3.363(1)	22.1
3	N ₁ – N _{1'}	3.948(2)	3.301(1)	33.3
4	N ₁ – N _{1'}	4.320(2)	3.336(1)	39.4
4	N ₂ – N _{2'}	3.957(2)	3.454(1)	29.2
6	N ₁ – N _{1'}	3.753(1)	3.5564(7)	18.6
6	N _{1'} – N ₁	3.817(1)	3.4146(7)	26.5

*The perpendicular distance between Cg_1 and the plane parallel to Cg_2 .

**The beta angle is formed between the vector $Cg_1 \cdots Cg_2$ and the perpendicular distance between Cg_1 and the plane parallel to Cg_2 .

Figure 2: A bifurcated N-H $\cdots$ Cl hydrogen bonding network forms fundamental repeat units in **1** that are related by crystallographic centers of inversion (one of which is depicted as a hollow circle). As in all subsequent figures the hydrogen atoms have been omitted for clarity and the nitrogen atoms are represented by blue spheres.

Compound 2: $(C_6H_8N)_2[UO_2Cl_4]$, crystallizes in the space group $P2_1/n$ and is composed of uranyl tetrachloride dianions charged balanced by 4-methylpyridinium (4-MP) cations (**Figure 3**). The 4-MP cations form N-H $\cdots$ Cl hydrogen bonds with the chlorine atoms Cl2 and Cl2' of the uranyl tecton to form cation-dianion-cation groups ($N_1 \cdots Cl_2$ 3.182(2) Å and $\angle N_1-H_7 \cdots Cl$ 167(2)°). Neighboring groups arrange such that offset π interactions are formed between the 4-MP cations (**Table 5**). These non-covalently linked groups give rise to a chain that propagates along the [101] direction (**Figure 3**). The methyl groups in the γ position of the cations form weak C-H $\cdots$ Cl hydrogen bonds to uranyl tectons in parallel chains ($C_6 \cdots Cl_1$ 3.829 Å and $\angle C_6-H_{6a} \cdots Cl_1$ 173°).

Figure 3: Hydrogen bonding and offset π interaction in **2** promotes the formation of chains. The methyl groups are represented by black spheres.

Compound 3: $(C_5H_5NOH)_2[UO_2Cl_4]$, crystallizes in the space group $P\bar{1}$ and consists of uranyl tetrachloride dianions charge balanced by 4-hydroxypyridinium (4-HP) cations (**Figure 4**). The 4-HP cation forms bifurcated bridging N-H $\cdots$ Cl and N-H $\cdots$ O hydrogen bonds to a chlorine, Cl1, and axial oxygen, O1, atom of two adjacent uranyl tectons (**Figure 4**). The interaction distances and angles associated with this bifurcated bridging interaction are: $N_1 \cdots Cl_1$ 3.266(3) Å ; $\angle N_1-H_6 \cdots Cl_1$ 142(4)° and $N_1 \cdots O_1$ 3.187(4) Å ; $\angle N_1-H_6 \cdots O_1$ 113(3)°. The hydroxyl group of the 4-HP cation in turn forms a hydrogen bond to a chlorine atom of third uranyl tecton ($O_2-H_7 \cdots Cl_2$ 3.062(3) Å and $\angle O_2-H_7 \cdots Cl_2$ 172(4)°). The dual hydrogen bond donor ability of the 4-HP cation promotes the formation of infinite chains, as the (pyridinium) N-H $\cdots$ Cl and (hydroxyl) O-H $\cdots$ Cl interactions function cooperatively to tie the uranyl and 4-HP BUs together (**Figure 4**). These chains propagate in a parallel fashion along the [1-1-1] direction and are stitched together via the bifurcated interaction (N-H $\cdots$ O) of the pyridinium ion to form a sheet (that spans the (0-11) plane) (**Figure 4**). The 4-HP cations align anti-parallel and form long offset π

interactions (Table 5 and Figure 4). We acknowledge the distance between the centers of gravity (3.948(2) Å) of the pyridinium rings are beyond the typical maximum (3.8 Å) for quantifying offset π interactions, but they are reported and illustrated for completeness.

Figure 4: Hydrogen bonds link parallel chains (outlined) in **3** to form sheets.

Compound 4: ($\text{C}_{10}\text{H}_{10}\text{N}_2\text{S}_2$)[UO_2Cl_4], crystallizes in the space group $P\bar{1}$ and consists of uranyl tetrachloride dianions charge balanced by bis(4-Pyridinium)disulfide (4-PDS) cations (Figure 5). The 4-PDS (dual donors) and uranyl tetrachloride tectons (acceptors) alternate and are stitched together via hydrogen bonds to form a chain that propagates in a zigzag fashion along the [001] direction (Figure 5). The pyridinium ion, $\text{N}_1\text{-H}_{1a}$, forms a bifurcated hydrogen bond to two chlorine atoms, Cl_1 and Cl_2 , of a [UO_2Cl_4] $^{2-}$ dianion, while the second pyridinium ion, $\text{N}_2\text{-H}_{2a}$, forms an interaction with the uranyl oxygen, O_1 , of a second [UO_2Cl_4] $^{2-}$ tecton (Figure 5 and Table 6). The corrugated supramolecular chains of alternating 4-BPS/[UO_2Cl_4] $^{2-}$ tectons stack to form layers that span the (110) plane. Inter-chain sulfur-chloro interactions are formed between the sulfur atoms, S_1 and S_2 , of the 4-PDS cations and the chloroligands, Cl_2 and Cl_3 , (of tectons in the adjacent chain) (Table 6). Although multiple short contacts resembling offset π interactions are present, such as those between the aromatic rings that contain ($\text{N}1$, $\text{N}1'$) and ($\text{N}2$, $\text{N}2'$), they are long (~ 4.0 Å) and may simply be a consequence of packing (Figure 5 and Table 5).

Figure 5: Chains of non-covalently linked uranyl and 4-PDS tectons (outlined) in **4** propagate along the [001] direction and pack to form supramolecular sheets in the (110) plane.

Table 6: Selected interaction lengths and angles of **4-6**.

Compound	Interaction	Length (Å) (D...A)	Angle (°) ($\angle \text{D-H}\cdots\text{A}$)
4	$\text{N}_1\text{-H}_{11}\cdots\text{Cl}_1$	3.126(3)	139(3)
	$\text{N}_1\text{-H}_{11}\cdots\text{Cl}_2$	3.390(3)	119(3)
	$\text{N}_2\text{-H}_{12}\cdots\text{O}_1$	2.826(3)	169(2)
	$\text{C}_3\text{-S}_1\cdots\text{Cl}_2$	3.451(1)	161.6(1)
	$\text{C}_8\text{-S}_2\cdots\text{Cl}_3$	3.520(1)	97.4(1)
5	$\text{N}_1\text{-H}_6\cdots\text{Cl}_2$	3.277(3)	164(3)
	$\text{N}_2\text{-H}_8\cdots\text{Cl}_2$	3.357(2)	176(3)

6	N ₂ -H ₇ ...Cl ₁	3.365(2)	164(3)
	N ₂ -H ₇ ...O ₁	3.208(3)	120(3)
	N ₁ -H ₆ ...Cl ₁	3.287(2)	136.2(2)
	N ₁ -H ₆ ...Cl ₂	3.340(20)	135.9(2)
	C ₆ -H _{6b} ...O ₁	3.319(2)	128
	C ₇ -H _{7b} ...O ₁	3.396(2)	138

Compound 5: (C₅H₇N₂)₂[UO₂Cl₄] crystallizes in the space group $P\bar{1}$ and consists of uranyl tetrachloride dianions charge balanced by 4-aminopyridinium (4-AP) cations (**Figure 6**). Two separate hydrogen bonding interactions, one originating from the pyridinium ion (N₁-H₆...Cl₂) and the second from the amino group (N₂-H₈...Cl₂), link the 4-AP cations and the uranyl tetrachloride tectons into parallel chains (**Figure 6** and **Table 6**). The 4-AP cations align anti-parallel and are slightly displaced, such that they stack (along the [100] direction) and form infinite pillars via hydrogen – π interactions (**Figure 6**). The relevant N-H... π interaction distances and angles are: N₂...Cg₁ 3.761 Å and $\angle$ C₃-N₂...Cg₁ 78.44° ; N₂...Cg₁ 3.279 Å and $\angle$ C₃-N₂...Cg₁ 88.65° (**Figure 6**). The pillars stitch the parallel chains together (down the *a* axis) to result in the formation of sheets. The amino groups (dual donors) form a second interaction, a bifurcated N-H...Cl and N-H...O hydrogen bond that stitches the sheets together to form an overall 3D supramolecular network (**ESI Figure 10** and **Table 6**).

Figure 6: A series of hydrogen bonding interaction in **5** give rise to sheets. The fundamental structural unit is outlined.

Compound 6: (C₇H₁₁N₂)₂[UO₂Cl₄], crystallizes in the space group $P\bar{1}$ and consists of uranyl tetrachloride dianions charge balanced by 4-dimethyl(amino)pyridinium (DMAP) cations (**Figure 7**). The DMAP cations form bifurcated planar N-H...Cl hydrogen bonds to chlorine atoms Cl1 and Cl2 of the uranyl tectons to form three-membered groups (two cations and one dianion). The three-membered building blocks are stitched to one another via offset π interactions that form between the cations of neighboring groups (**Table 5** and **Figure 7**). The DMAP cations form infinite pillars through these offset π interactions and ultimately facilitate the formation of sheets that span the (01-1) plane. A supramolecular motif is noted, although not significantly robust, as the methyl hydrogen atoms (on C6 and C7) form two C-H...O interactions with uranyl oxygen atoms O1 and O1'.

Figure 7:(Top) The structure of **6** highlighting symmetric bifurcated N-H...Cl and weak C-H...O hydrogen bonds.(Bottom) Offset π -interactions stitch the fundamental cation-dianion-cation groups (outlined) together along the *a* axis to form sheets.

Compound 7: (C₅H₆N)₂[UO₂Br₄], crystallizes in the space group $P\bar{1}$ and consists of uranyl tetrabromide dianions charge balanced by pyridinium cations (**Figure 8**). Although supramolecular chains are present in both **1** and **7**, the crystal packing of **1** and **7** contrast as the overall construction and orientation of the chains differ. The pyridinium cations in **7** form planar bifurcated N-H...Br hydrogen bonds to the bromo ligands of the uranyl tetrabromide tectons; relevant interaction distances and angles are: N₁-H_{1a}...Br₁ 3.4131(19) Å ; $\angle$ N₁-H_{1a}...Br₁ 142.1(2)° and N₁-H_{1a}...Br₂ 3.400(2) Å ; $\angle$ N₁-H_{1a}...Br₂ 118.3(2)°. These bifurcated interactions give rise to three-membered building units, consisting of two cations and one dianion, which are in turn linked together to form chains that propagate along the [-1-10] direction (**Figure 8**). The pyridinium cations of each group overlap with those within neighboring groups to form offset π interactions that facilitate the formation of the chain motif (**Table 7**). The chains pack parallel to one another such that oxygen- π contacts form between the uranyl oxygen atoms, O1, of one chain and the pyridinium cations of an adjacent chain (U=O...Cg₁ 2.983(2) Å and $\angle$ U=O...Cg₁ 140.13(8)°).

Figure 8: Bifurcated N-H...Br hydrogen bonds and offset π interactions in **7** give rise to the chains (outlined). The bromine atoms are represented as brown spheres.

Table 7: Selected distances and angles relevant to the offset π interactions found in **7-12**.

Compound	Pyridinium Ring	Distance Cg...Cg (Å)	Perpendicular Displacement (Å)*	Angle β (°)**
7	N ₁ – N ₁ '	3.607(1)	3.468(1)	16.0
8	N ₁ – N ₁ '	3.664(3)	3.437(2)	20.3
9	N ₁ – N ₁ '	3.984(2)	3.326(2)	33.5
10	N ₁ – N ₁ '	4.323(3)	3.5267(2)	35.3
12	N ₁ – N ₁ '	4.041(2)	3.469(1)	30.9
	N ₁ ' – N ₁	4.468(2)	3.589(1)	36.6

*The perpendicular distance between Cg₁ and the plane parallel to Cg₂.

**The beta angle is formed between the vector Cg₁...Cg₂ and the perpendicular distance between Cg₁ and the plane parallel to Cg₂.

Compound 8: $(\text{C}_6\text{H}_8\text{N})_2[\text{UO}_2\text{Br}_4]$, crystallizes in the space group $P2_1/n$ and consists of uranyl tetrabromide tectons charged balanced by 4-MP cations (**Figure 9**). Compound 8 is isomorphous with **2** as non-covalent interactions link the 4-MP and uranyl tetrabromide building units into chains (in this case propagating along the [10-1] direction). The interaction types and pairings are identical to those in **2** and have been previously described. As such, only the relevant interaction distances and angles are provided (**Tables 7 and 8**).

Figure 9: Hydrogen bonding and offset π interactions in **8** give rise to supramolecular chains, one of which is outlined in black.

Compound 9: $(\text{C}_5\text{H}_6\text{NO})_2[\text{UO}_2\text{Br}_4]$, crystallizes in the space group $P\bar{1}$ and consists of uranyl tetrabromide dianions charge balanced by 4-hydroxypyridine (4-HP) cations (**Figure 10**). Compound 9 is isomorphous with **3** as non-covalently linked BUs give rise to a 2D assembly (supramolecular sheets). As the interaction pairing and crystal packing have previously been discussed in **3**, only the hydrogen bonding and offset π interaction distances and angles of **9** are provided (**Tables 7 and 8**).

Table 8: Selected interaction lengths and angles present in **9-11**.

Compound	Interaction	Length (Å) (D...A)	Angle (°) ($\angle \text{D-H}\cdots\text{A}$)
8	$\text{N}_1\text{-H}_7\cdots\text{Br}_2$	3.343(5)	160(4)
8	$\text{C}_6\text{-H}_{6a}\cdots\text{Br}_1$	3.897	169
9	$\text{N}_1\text{-H}_6\cdots\text{Br}_2$	3.421(3)	135(4)
9	$\text{N}_1\text{-H}_6\cdots\text{O}_1$	3.188(4)	126(4)
9	$\text{O}_2\text{-H}_7\cdots\text{Br}_1$	3.220(3)	174(3)
10	$\text{N}_1\text{-H}_6\cdots\text{Br}_1$	3.385(4)	140(4)
10	$\text{N}_1\text{-H}_6\cdots\text{O}_1$	3.032(5)	122(4)
10	$\text{S}_1\text{-H}_7\cdots\text{Br}_2$	3.794(1)	176(3)
11	$\text{N}_1\text{-H}_{1a}\cdots\text{Br}_2$	3.462(3)	142
11	$\text{N}_1\text{-H}_{1a}\cdots\text{Br}_2'$	3.560(3)	132
11	$\text{N}_2\text{-H}_{2a}\cdots\text{Br}_1$	3.453(3)	136
11	$\text{N}_2\text{-H}_{2B}\cdots\text{Br}_1'$	3.508(3)	173
11	$\text{N-H}_2\cdots\pi$	3.519	96.89*
11	$\text{N-H}_2\cdots\pi$	3.883	77.30*

*Represents the angle formed by $\angle C-N \cdots Cg$.

Figure 10: A supramolecular chain (outlined) is constructed in **9** via hydrogen bonding interaction.

Compound 10: $(C_5H_6NS)_2[UO_2Br_4]$, crystallizes in the space group $P\bar{1}$ and consists of uranyl tetrabromide dianions charge balanced by 4-mercaptopyridinium cations (4-MCP) (**Figure 11**). The crystal structure of **10** contains identical supramolecular interaction pairings as those in **9**, yet the distances of the interactions differ. The pyridinium ion forms a bifurcated bridging $N-H \cdots Br$ and $N-H \cdots O$ hydrogen bond to a bromo ligand (Br_1) and uranyl oxygen (O_1) of two neighboring $[UO_2Br_4]^{2-}$ tectons (**Table 8** and **Figure 11**). The mercapto group in turn forms an $S-H \cdots Br$ hydrogen bond to an adjoining $[UO_2Br_4]^{2-}$ tecton. The $N-H \cdots Br$ (pyridinium ion) and $S-H \cdots Br$ (mercapto) hydrogen bonds facilitate the formation of parallel chains (along $[-1-1-1]$), whereas the $N-H \cdots O$ (pyridinium ion) hydrogen bond stitches the chains into sheets that span the $(0-11)$ plane. The 4-MCP cations are aligned anti-parallel, yet do not form meaningful offset π interactions as the observed $Cg \cdots Cg$ distance of $4.8 \text{ \AA}$ is considered long (**Table 7**).

Figure 11: Hydrogen bonds in **10** connect parallel arranged supramolecular chains (outlined) to form sheets.

Compound 11: $(C_5H_7N_2)[UO_2Br_4]$, crystallizes in the space group $P2_1/n$ and consists of $[UO_2Br_4]^{2-}$ tectons charge balanced by 4-aminopyridinium (4-AP) cations (**Figure 12**). The 4-AP cations form two separate $N-H \cdots Br$ hydrogen bonds to the uranyl tetrabromide tectons, the first stems from the pyridinium ion whereas the second from the amino group (**Table 8**). These dual interactions link the 4-AP cations and uranyl tetrabromide dianions into chains, which pack in a parallel fashion along the $[001]$ direction (**Figure 12**). These chains are in turn stitched together (along the a axis) to form sheets in the (101) plane. The chains are tied together via infinite pillars of 4-AP cations (that propagate along the $[100]$ direction) (**Figure 12**). The pillars are formed by $N-H \cdots \pi$ interactions that stem from the overlap of the amino group and aromatic ring of neighboring cations (**Table 8** and **Figure 12**).

Figure 12: (Left) Bifurcated hydrogen bonding and $N-H \cdots \pi$ interactions in **11** increase the dimensionality of the chain motif (outlined) to form sheets. (Right) The amino functional groups link adjacent and out-of-plane chains.

Compound 12: $(C_7H_{11}N_2)_2[UO_2Br_4]$, crystallizes in the space group $P2_1/c$ and consists of uranyl tetrabromide dianions charge balanced by 4-dimethyl(amino)pyridinium (DMAP) cations (**Figure**

13). The DMAP cations form bifurcated N-H...Br/O hydrogen bonds with bromo (Br₁) and axial oxygen (O₁) atoms of the [UO₂Br₄]²⁻ tectons; relevant interaction distances and angles are: N₁-H₈...Br₁ 3.421(2) Å ; ∠N₁-H₇...Br₁ 148(2)° and N₁-H₇...O₁ 3.155(3) Å ; ∠N₁-H₇...O₁ 129(2)°. These bifurcated interactions produce three-membered BUs that are in turn loosely stitched together via offset π interactions as the cations of neighboring groups overlap (**Table 7** and **Figure 13**). These offset π interactions are rather long (4.0 – 4.4 Å) and one may consider their distances too long to be considered meaningful, yet the anti-parallel and stacked arrangements (aligning the dipoles of the cations) are unmistakable. Although we report these offset π interactions with caution, we feel they are relevant to assembly. The dimethylamino group in the γ position of the cation does not participate in any relevant interactions. The overall assembly can be described as two dimensional.

Figure 13: Hydrogen bonds form three-membered fundamental building units (outlined) in **12** that are stitched into sheets via offset π interactions.

Discussion

A qualitative survey of the predominant non-covalent interactions that govern the self-assembly of compounds **1-12** was performed in order to identify regularly occurring structural trends and similarities. Attempting to *rank* the relative strengths of the pertinent supramolecular interactions by crystallographic analysis is nearly impossible due to the emergence or disappearance of interaction motifs within a series featuring fixed inorganic building units (**1 - 6** or **7 - 12**). One could argue that the changes in interaction pairings (with a fixed inorganic tecton) occur as a function of the electron donating and hydrogen bonding ability of the pyridinium γ substituent. Thus, the presence of various synthons (π interactions and hydrogen bonding) and structural motifs (chains vs. sheets) is assessed and presented as a function of the γ substituent.

Compounds 1 – 6: Influence of the γ Substituent

The pyridinium cation in **1** contains no influence of a γ substituent. As a result, a series of bifurcated bridging N-H...Cl hydrogen bonds (3.26 - 3.36 Å) link the pyridinium cations and uranyl tetrachloride dianions together to form chains that propagate in the [011] direction (**Figure 2**). The chains run parallel to one another and are linked together by a number of offset π interactions (between cations of adjacent chains) that ultimately give rise to a sheet.

In **2**, each 4-methylpyridinium cation forms a monofurcated N-H...Cl hydrogen bond to a [UO₂Cl₄]²⁻ tecton to yield a number of distinct, non-covalently linked three-membered building units.

These molecular BUs are then stitched together via offset π interactions, as the 4-MP cations of neighboring groups overlap, to form a chain (**Figure 3**). The difference in supramolecular dimensionality between structures **1** and **2** (sheets in **1** vs chains in **2**) is likely a consequence of the presence of a terminating methyl substituent that prohibits additional connectivity.

The pyridinium ion of the 4-HP cation in **3** still forms an N-H $\cdots$ Cl hydrogen bond (similar to **2**), yet the interaction is bifurcated and bridging as a second N-H $\cdots$ O interaction is formed, linking the 4-HP cation to two distinct uranyl tetrahalide tectons (**Figure 4**). The hydroxyl group in turn forms a *new* O-H $\cdots$ Cl (O $\cdots$ Cl 3.063(3) Å) hydrogen bond, that when coupled with the N-H $\cdots$ Cl interaction, gives rise to a 1D chain consisting of non-covalently linked inorganic and organic BUs. The chain is similar to that as observed in **2**, yet does not form as a result of offset π interactions as these are rather insignificant in **3**. The bifurcated interaction of the pyridinium ion (N-H $\cdots$ O) further links the adjacent and parallel packed chains into a sheet.

One can argue that the electron donating ability and hydrogen bond donating ability of the hydroxyl group influences the manner in which assembly occurs. First, the electron donating ability of the R-OH group increases the amount of charge density that resides in the π system of the pyridinium rings (relative to those in **1** and **2**). This increases the repulsion between the rings and weakens the resulting offset π interactions; the weakening manifests as an observable increase to the (cation – to – cation) ring distances. This is supported as an increase in the Cg $\cdots$ Cg distances occurs from **1** $\rightarrow$ **3** and follows the trend of electron donating strength from the γ substituent (-H < -CH₃ < -OH). Second, the presence of a hydrogen bond donor in the γ position, as opposed to a terminating methyl group, allows for an increase to the dimensionality as the pyridinium ion and hydroxyl group can cooperatively direct assembly.

The electron donating ability of the amino substituent in **5** has a clear impact upon the participation of π type interactions in the assembly process. The 4-AP cations stack in an anti-parallel fashion to form infinite pillars along the [100] direction, yet interestingly, feature the longest distance between centers of gravity (average 4.270 Å) when compared to **1-3**. This elongation is consistent with electron donating ability: -H < -CH₃ < -OH < -NH₂. Thus, these cationic pillars are formed not of offset π interactions, but through hydrogen – π interactions (N-H $\cdots\pi$ 3.729 Å) as the amino group is positioned directly over the centers of (neighboring) pyridinium ring (**Figure 6**). Moreover, the pillars are a major structural motif as they join parallel H-bonded sheets into a three dimensional supramolecular assembly.

The dimethyl(amino)pyridinium cations in **6** (featuring a bulky electron donating substituent) is only capable of forming one planar-bifurcated N-H $\cdots$ Cl hydrogen bond, and gives rise to three-membered molecular groups (similar to those in **2**) (**Figure 7**). The difference in N-H $\cdots$ A pairing (monofurcated in **2** vs. bifurcated in **6**) is likely due to the steric bulk of the dimethyl(amino) substituent. No significant interactions stem from the substituent, thus offset π interactions (akin to **1** and **2**) once again stitch

together these molecular groups into sheets that span the (01-1) plane. The distances between the centers of gravity of the pyridinium ring in **6** (Avg. 3.78Å) are the longest, compared to **1**, **2**, **6**, and agree with the trend of increasing Cg – Cg distance as a function of electron donation ($-H < CH_3 < -NR_2$).

A collective look at compounds **1-3** and **5,6** allows for the delineation of the relationship between the electron donating ability of the γ substituent and the resulting supramolecular interactions. A clear influence over interaction participation (i.e. synthon appearance or disappearance) is observable, especially with respect to NCIs stemming from the pyridinium π – system. The more electron donating substituents cause apparent increases to Cg – Cg distances as a function of increased electron density in the π system, which leads to a subsequent increase to inter-ring π – π repulsion.³⁴⁻³⁷ Furthermore, the electron donation of the γ substituent, coupled with its hydrogen bond donating ability, can further cloud the role of the offset π interactions in assembly. Strong hydrogen bond donors ($-OH$ (**3**) and $-NH_2$ (**4**)) give way to hydrogen bonding as the primary means to assembly, whereas those containing weaker donors ($-H$ (**1**), $-CH_3$ (**2**), $-N(CH_3)_2$ (**6**)) display the offset π -interactions to promote structures of higher supramolecular dimensionality.

Comparison of Isomorphous Structures

A similar analysis of the compounds containing the $[UO_2Br_4]^{2-}$ tecton yields the same observations with respect to electron donation, synthon pairing and resulting structural dimensionality. As such we will instead focus on a few examples where isomorphous structures allow for direct comparisons of interaction pairings and overall strengths. First, we examine the case where the uranyl tetrabromide dianion is fixed and the cation is changed (4-hydroxypyridine (**9**) vs. 4-mercaptopyridine (**10**)).

Compounds **9** and **10** are isomorphous and allow for a direct comparison of interaction strengths (as acceptor donor pairings are identical) as a function of electron donating ability of the γ substituent. Bridging bifurcated N-H $\cdots$ Br/O interactions, stemming from the pyridinium ions in **9** and **10**, work cooperatively with monofurcated D-H $\cdots$ Br (D = O, S) hydrogen bonds to form sheets (Figures **10** and **11**). The interactions in **9** and **10**, while identical, differ in their relative strengths as those in **9** are stronger as suggested by their shorter distances. The mercapto group is larger in size and less electronegative than the hydroxyl group. The mercapto group likely donates more electron density, as its lone pairs are more available, causing the pyridinium ion to become more acidic and consequently a better hydrogen bond donor. This is consistent with the decrease in N-H $\cdots$ A (A = Br, O) hydrogen bond lengths observed in **10** relative to **9** (Table 9). Second, the mercapto group, being less electronegative and perhaps more importantly, *larger* than the hydroxyl group, forms a longer and weaker S-H $\cdots$ Br hydrogen bond (3.794Å 104% vdW) than the corresponding O-H $\cdots$ Br interaction (3.220Å 97% vdW) in **9**. This result is

consistent with more electronegative donor atoms forming stronger hydrogen bonds. In this example, interaction distances (and likely strengths) are able to be tuned by the electron donating ability of the γ substituent. It is also worth noting that the role of offset π interaction between the pyridinium cations is minimal in **9** and **10**, as the distances between the centers of gravity of the cations increase **9** to **10**: ~ 3.98 vs. ~ 4.8 Å, respectively. This result supports our conclusion that the R-SH substituent is more electron donating, causing larger increases to the electron density in the π system, than that of the R-OH groups.

Table 9: Selected interaction distances of **9** and **10**.

Compound	Interaction and Distance (Å)		
9	N-H...Br ; 3.421(3)	N-H...O ; 3.188(4)	O-H...Br ; 3.220(3) 97% vdW (O and Br)
10	N-H...Br ; 3.385(4)	N-H...O ; 3.032(5)	S-H...Br ; 3.794(1) 104% vdW (S and Br)

In our second case, we examine structures **2** and **8** where the pyridinium cations (4-methylpyridinium) are kept constant while the uranyl tetrahalide tectons are swapped ($[\text{UO}_2\text{Cl}_4]^{2-}$ and $[\text{UO}_2\text{Br}_4]^{2-}$). Both N-H...Cl and N-H...Br hydrogen bonds in **2** and **8** form between the 4-MP cations and respective uranyl tetrahalide dianion, giving way to three-membered molecular groups. The groups are in turn stitched together via offset π interactions, similar in Cg...Cg distance (3.6285(13) (**2**) vs. 3.664(3) Å (**8**)), to give rise to chains. The N-H...Cl interaction is shorter than the corresponding N-H...Br distance, which is consistent with what is expected due to the size difference in the acceptor sites (Cl vs. Br). When the two interaction distances are compared on a relative scale (sum of the van der Waals radii) we find that the N-H...Cl hydrogen bond corresponds to 96.4% overlap in the vdW radii (Cl and N), while the N-H...Br interaction is 98.3% of the vdW radii (Br and N) (**Table 10**). This indicates that the interaction strength is greater when the chloro ligands of the $[\text{UO}_2\text{Cl}_4]^{2-}$ tectons serve as the acceptor sites (compared to the bromo ligands). This observation is supported by comparing the isomorphous structures of **3** and **9**, as similar contractions to the vdW overlap of the acceptor and donor atom are observed (**Table 10**). The acceptor site comparison clearly indicates that acceptor strength increases with a decrease in size and increase in electronegativity $\text{Br} < \text{Cl}$; this trend has been observed in similar studies of assembly pairing metal-bound halogens with hydrogen and halogen bond donors.³⁸⁻⁴¹

Table 10: Selected hydrogen bonding lengths and geometries of **2-3** and **8-9**.

Compound	2	8	3	9
Interaction(s)	N-H...Cl	N-H...Br	N-H...Cl / O	N-H...Br / O
			O-H...Cl	O-H...Br
Length (Å)	3.182(2)	3.343(5)	3.266(3) / 3.187(4)	3.421(3) / 3.188(4)
			3.062(3)	3.220(3)
vdW radii (%)	96.4	98.3	98.9 / 103.9	100.6 / 103.9
			93.4	95.5
H- Bond Type	Monofurcated	Monofurcated	Bridging Bifurcated	Bridging Bifurcated
	-	-	Monofurcated	Monofurcated
Angle (°)	167(2)	160(4)	142(4) / 113(3)	135(4) / 126(4)
	-	-	172(4)	174(3)

The overall structural trends elucidated from compounds **1** – **12** can be summarized into three main facets. First, the uranyl tetrahalide tectons (when paired with γ substituted pyridinium cations) are viable building units that can be exploited in the solid state to circumvent uranyl oligimerization and assemble extended supramolecular structures. Second, the electron donating ability of the γ substituent can be manipulated via substitution such that some control can be exhibited over the pairing and strengths of the resulting non-covalent interactions (hydrogen bonding and π – type interactions). Finally, one can also influence the relative strengths and, perhaps, pairings of the pertinent interaction by means of substitution at the acceptor sites (Cl vs. Br). Our attention will turn from ascertaining the structural influence of the γ substituent and the uranyl tectons to their relative contributions to the photo(physical) properties of these extended structures.

Emissive Properties

The compounds containing the uranyl tetrachloride tecton (**1-6**) are highly emissive and emit green light at room temperature upon excitation at 410nm. Although highly luminescent at room temperature, compounds **1-6** were cooled to ~77K for data collection for increased resolution and consistency with compounds **7-12**, which are not emissive at room temperature.

The emission profiles of **1- 12** exhibit vibronically resolved green emission; the coupling of the $^3\Pi_u$ excited triplet state with the Raman active ν_1 U-O_{axial} symmetric vibrational mode ($\sim 850\text{cm}^{-1}$) is characteristic of most uranyl containing salts.^{21, 42} The luminescence profiles of compounds **1- 12** feature three to five major vibronic peaks (e.g. in **1**: 505, 527, 551, 578 and 609nm) that proceed harmonically and have an average spacing (energy) between them of $\sim 830\text{cm}^{-1}$. The presence of these

major vibronic bands is common (**1-12**) and will not be discussed further. The presence of secondary vibronic peaks, that appear to split the major peaks, does require additional mention, yet their discussion will be limited to **1** as a common mechanism is expected to be responsible for their appearance.

In **1**, the first three vibronic peaks are clearly split into two apices 505/508nm, 527/529nm and 551/554nm; the energy differences between the apices are 116, 71, and 98cm⁻¹, respectively, while those in **2-6** range 71-190cm⁻¹. Minor vibronic peaks, similar to these, have been observed elsewhere in uranyl-containing salts, and have been attributed to additional coupling of the uranyl bending mode and/or the equatorial ligand vibrational modes with the uranyl excited state.^{21, 43} In our system it seems likely that the minor vibronic peaks are best explained by coupling with the U-Cl bending modes, as eleven total orthogonal modes have been observed in salts of the [UO₂Cl₄²⁻] dianion, all of which range between 90-130cm⁻¹ and 200-260cm⁻¹;⁴³ the ν_3 uranyl bending mode generally is measured between 200-250cm⁻¹.²¹ In the series containing the [UO₂Br₄]²⁻ tecton similar vibronic structure is observed and is also likely explained by coupling of the equatorial U-Br vibrational modes.⁴⁴

Figure 15: The emission spectra of compound **1** upon excitation at $\lambda = 410$ nm.

Effects of NCIs upon Luminescence: **1-6**

Some of the luminescence profiles of compounds **1-6** exhibit shifts as a function of second sphere interactions. Compounds **1** and **2** are ideal to compare as the axial uranyl oxygen atoms do not participate in hydrogen bonding, thus the equatorial plane (Cl ligands) is the only site on the uranyl tectons that participate in non-covalent interactions. The spectrum of **2** is blue shifted with respect to **1**; the energy difference of these shifts are provided in Table 10 (**Figure 16**). This result suggests that the interactions in **2** are slightly stronger than those in **1**. The rationale for this is the following: a stronger interaction by the pyridinium cation with the equatorial chloro ligand should result in less charge density being directed

towards the UO_2^{2+} center. Whereas this is speculative in the absence of a rigorous theoretical treatment, one may infer that a decrease in electron density at the uranyl would result produce a blue shift of the emission spectra as shown in analogous systems.^{27, 45}

Figure 16: The luminescence profiles of **1**(black – thin) and **2**(black – bold).

Table 10: The major vibronic bands in the emission spectra of **1– 2** are listed and their energy differences are provided.

Compound	Major Vibronic Peak Pairs (nm)				
1	505/508	527/529	551/554	578/580	609
2	502/506	525/528	548/553	574	603
Difference in cm^{-1}	118/78	72/36	99/33	120/ N/A	163

A second example of a similar blue shift (relative to **1**) is observed in the emission spectrum of **6**(**Figure 17**). Here, bifurcated $\text{N-H}\cdots\text{Cl}$ interactions flank the uranyl tetrachloride tectons (**Figure 7**) and potentially draw electron density away from the chloro ligands, and consequently the uranyl center as in **2**. The resulting blue shift is rather pronounced as each major peak is shifted by nearly 200cm^{-1} (**Table 11**). Finally, a similar shift to the uranyl emission in **5** (relative to **1**) is observed and is on the same order of magnitude as the shift in **2** (**ESI Figure 10**). Although blue shifting is also observed in the luminescence profiles of **3** and **4**, they are omitted from this discussion as each display NCIs at the uranyl oxygen atoms. As such, we make no attempt to delineate the influence of each NCI individually is problematic.

Figure 17: The luminescence profile of **1** (light) and **6** (bold).

Table 11: The major vibronic bands in the emission spectra of **1** and **6** are listed and their energy differences are provided

Compound	Major Vibronic Peak Pairs (nm)				
1	505/508	527/529	551/554	578/580	609
6	500/504	522/526	545/551	571	600
Difference between 1 and 6 in cm⁻¹	198/156	181/108	199/98	212/NA	191

Preliminarily, these results show a correlation between the supramolecular interactions and the observed photophysical properties that manifest as shifts to the uranyl emission spectra. At the very least, these results merit further experimental and theoretical investigation utilizing stronger hydrogen donor groups that can perhaps produce similar, if not more pronounced effects.

Effects of NCIs on Luminescence: 7-12

Compounds **8** and **11** are the only two structures containing the $[\text{UO}_2\text{Br}_4]^{2-}$ dianion that will be discussed, as the NCI pairing is limited to the equatorial plane. Compound **8** features 4-MP cations that form monofurcated $\text{N-H}\cdots\text{Br}$ hydrogen bonds whereas the 4-AP cations in **11** form two sets (pyridinium ion and amino group) of bridging bifurcated $\text{N-H}\cdots\text{Br}$ hydrogen bonds. In a uranyl tecton centric discussion, the first obvious difference between the structures of these compounds are the number of NCIs in which the bromo ligands participate: two in **8** vs. four in **11**. Thus, one may speculate that a greater portion of the electron density of the bromo ligands is distributed towards the hydrogen bonding

interactions in **11** vs. **8**. Second, one may also argue that the electron donating ability of the γ substituent ($R-CH_3 < R-NH_2$) in **11** renders the hydrogen atom of the pyridinium ion more available for hydrogen bonding interactions. The combined structural and electronic impact of these two phenomena would manifest as a greater shift of electron density from the bromo ligands in **11**, relative to **8**, which would in turn produce a blue shift in the uranyl emission spectra. Indeed, such a blue shift is observed when comparing the spectrum of **11** and **8** (Figure 18). The energy difference of the peaks (**11** vs. **8**) are provided in Table 12. These observations are consistent with those stated above for the uranyl tetrachloride system.

Figure 18: The luminescence profiles of **8** (light grey) and **11** (black).

Table 12: The major vibronic bands in the emission spectra of **8** and **11** are listed and their energy differences are provided.

Compound	Major Vibronic Peak Pairs (nm)				
8	505/509	527/532	551/557	578/583	607
11	502.5/507.5	525.5/530	549.5/555.5	576.5/583	606
Energy Difference (cm⁻¹)	98.5/58.0	54.2/70.1	49.5/48.5	45/0	27

Effect of the Uranyl Tecton on Emission

The luminescence profiles of this series (1-12) all contain similar vibronic structure, yet clear variation occurs as a function of second sphere interactions and inorganic tecton. The former was described above, yet when comparing profiles across tectons, as in the emission spectra of **2** and **8**, a clear red shift is observed for the $[UO_2Br_4]^{2-}$ compound (Figure 19). Similar red shifts are also observed when

comparing compounds **3** to **9**, **4** to **10** and **5** to **11**. This shift is likely the result of increased electron donation to the UO_2^{2+} center as the bromo ligands are larger and more polarizable. However, there are two inconsistencies in this trend as blue shifts are observed when comparing compounds **1** and **7** and **6** and **12**. The results, when viewed in their entirety, are intriguing as they suggest, even preliminarily, an observable link between the crystal packing and supramolecular interactions and the resulting luminescence properties. As such, these results call for further investigation and highlight the need for theoretical studies to proceed in parallel.

Figure 19: The luminescence profiles of **2** (light grey) and **8** (black).

Conclusions

Room temperature self-assembly of in high anion media has provided a forum for the formation of a family of related and systematically varied compounds containing tunable non-covalent interactions between uranyl tetrahalides and substituted pyridinium species. Beyond being a sound route to large single crystals bearing monomeric uranyl tetrahalides, these materials have highlighted the role of substituents on the presence/absence of specific synthons, and consequently, on supramolecular structure. Specifically, we have demonstrated the ability to tune pi- and hydrogen bonding interactions as a means to controlling dimensionality. Moreover, analogous influences of the NCIs on the emissive properties of the uranyl are apparent and are qualitatively a result of electronic perturbations to equatorial ligands.

Electronic Supporting Information (ESI)

Experimental details, fluorescence spectra and thermal ellipsoidal (ORTEP) representations of compounds 1-12 are provided. Crystallographic data for 1-12 can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Figure 1: A schematic of the uranyl tetrahalidedianion $[\text{UO}_2\text{X}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) is provided on the left whereas a view down the uranyl axis is shown as a polyhedral representation on the right. The uranium center is drawn as a yellow polyhedron while the oxygen and chlorine atoms are depicted as red and green spheres, respectively.

Scheme 1: A representation of the various substituted pyridinium cations that were paired with the $[\text{UO}_2\text{X}_4]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) dianions.

Figure 2: A selection of the crystals of **1-12** that were grown via slow evaporation from aqueous solutions containing high concentrations of chloride and bromide ions.

Figure 2: A bifurcated N-H...Cl hydrogen bonding network forms fundamental repeat units in **1** that are related by crystallographic centers of inversion (one of which is depicted as a hollow circle). As in all subsequent figures the hydrogen atoms have been omitted for clarity and the nitrogen atoms are represented by blue spheres.

Figure 3: Hydrogen bonding and offset π interaction in **2** promotes the formation of chains. The methyl groups are represented by black spheres.

Figure 4: Hydrogen bonds link parallel chains (outlined) in **3** to form sheets.

Figure 5: Chains of non-covalently linked uranyl and 4-PDS tectons (outlined) in **4** propagate along the [001] direction and pack to form supramolecular sheets in the (110) plane.

Figure 6: A series of hydrogen bonding interaction in **5** give rise to sheets. The fundamental structural unit is outlined.

Figure 7: (Top) The structure of **6** highlighting symmetric bifurcated N-H...Cl and weak C-H...O hydrogen bonds. (Bottom) Offset π -interactions stitch the fundamental cation-dianion-cation groups (outlined) together along the a axis to form sheets.

Figure 8: Bifurcated N-H...Br hydrogen bonds and offset π interactions in **7** give rise to the chains (outlined). The bromine atoms are represented as brown spheres.

Figure 9: Hydrogen bonding and offset π interactions in **8** give rise to supramolecular chains, one of which is outlined in black.

Figure 10: A supramolecular chain (outlined) is constructed in **9** via hydrogen bonding interaction.

Figure 11: Hydrogen bonds in **10** connect parallel arranged supramolecular chains (outlined) to form sheets.

Figure 12: (Left) Bifurcated hydrogen bonding and N-H $\cdots$ π interactions in **11** increase the dimensionality of the chain motif (outlined) to form sheets. (Right) The amino functional groups link adjacent and out-of-plane chains.

Figure 13: Hydrogen bonds form three-membered fundamental building units (outlined) in **12** that are stitched into sheets via offset π interactions.