

Electronic Supporting Information

The Uranyl Tetrachloride Anion as a Tecton in the Assembly of U(VI) Hybrid Materials

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Synthesis of 1-7

[UO₂Cl₄](C₁₀H₁₀N₂) (1)

Compound **1** was prepared by dissolving 1.023 g of UO₂(CH₃COO)₂·2H₂O in water (10 mL) and concentrated HCl (3 mL) in a 50 mL Erlenmeyer flask. To this yellow solution, a solution of 4,4'-dipyridyl (0.817 g) in water (10 mL) and concentrated HCl (2 mL) was added. The resulting mixture was evaporated using gentle heat to an approximate volume of 10 mL and allowed to cool. The flask was then covered with a piece of Parafilm into which several holes were punched. After two months, yellow-green, X-ray quality crystals were obtained.

[UO₂Cl₄](C₁₂H₁₄N₂) (2)

Compound **2** was prepared by dissolving 0.256 g of UO₂(CH₃COO)₂·2H₂O in water (2.5 mL) and concentrated HCl (0.75 mL) in a 50 mL Erlenmeyer flask. To this yellow solution, a solution of 1,2-bis(4-pyridyl)ethane (0.221 g) in water (2.5 mL) and concentrated HCl (0.5 mL) was added. The resulting mixture was evaporated using gentle heat to an approximate volume of 3 mL and allowed to cool. The flask was then covered with a piece of Parafilm into which several holes were punched. After 16 days, yellow-colored, X-ray quality crystals were obtained.

[UO₂Cl₄](C₁₂H₁₂N₂) (3)

Compound **3** was prepared by dissolving 0.249 g of UO₂(CH₃COO)₂·2H₂O in water (2.5 mL) and concentrated HCl (0.75 mL) in a 50 mL Erlenmeyer flask. To this yellow solution, a solution of trans-1,2-bis(4-pyridyl)ethylene (0.264 g) in water (2.5 mL) and concentrated HCl (0.5 mL) was added. The resulting mixture was evaporated using gentle heat to an approximate volume of 3 mL and allowed to cool. The flask was then covered with a piece of Parafilm into which several holes were punched. After 11 days, yellow-colored, X-ray quality crystals were obtained.

[UO₂Cl₄](C₇H₇NCOOH)₂ (4)

Compound **4** was prepared by dissolving 0.251 g of UO₂(CH₃COO)₂·2H₂O in water (2.5 mL) and concentrated HCl (0.75 mL) in a 50 mL Erlenmeyer flask. To this yellow solution, a solution of trans-3-(4-pyridyl)acrylic acid (0.188 g) in water (2.5 mL) and concentrated HCl (0.5 mL) was added. The resulting mixture was evaporated using gentle heat to an approximate volume of 3 mL and allowed to cool. The flask was then covered with a piece of Parafilm into which several holes were punched. After 2 months, pale yellow-brown, X-ray quality crystals were obtained in low yield.

[UO₂Cl₄](C₁₃H₁₆N₂) (5)

Compound **5** was prepared by dissolving 0.260 g of UO₂(CH₃COO)₂·2H₂O in water (2.5 mL) and concentrated HCl (0.75 mL) in a 50 mL Erlenmeyer flask. To this yellow solution, a solution of 4,4'-trimethylene dipyridine (0.248 g) in water (2.5 mL) and concentrated HCl (0.5 mL) was added. The resulting mixture was evaporated using gentle heat to an approximate volume of 3 mL and allowed to cool. The flask was then covered with a piece of Parafilm into which several holes were punched. After 3 months yellow-colored, X-ray quality crystals were obtained in low yield.

[UO₂Cl₄](C₁₀H₁₂N₃)₂·2Cl·2H₂O (6)

Compound **6** was prepared by dissolving 0.252 g of UO₂(CH₃COO)₂·2H₂O in water (2.5 mL) and concentrated HCl (0.75 mL) in a 50 mL Erlenmeyer flask. To this yellow solution, a solution of 4,4'-dipyridylamine (0.205 g) in water (2.5 mL) and concentrated HCl (0.5 mL) was added. The resulting mixture was evaporated using gentle heat to an approximate volume of 3 mL and allowed to cool. The flask was then covered with a piece of Parafilm into which several holes were punched. After 3 months yellow-colored, X-ray quality crystals were obtained.

[UO₂Cl₄](C₁₀H₁₀N₂)₂·2Cl·H₂O (7)

Compound **7** was prepared by dissolving 0.268 g of UO₂(CH₃COO)₂·2H₂O in water (2.5 mL) and concentrated HCl (0.75 mL) in a 50 mL Erlenmeyer flask. To this yellow solution, a solution of 2,4'-dipyridyl (0.209 g) in water (2.5 mL) and concentrated HCl (0.5 mL) was added. The resulting mixture was evaporated using gentle heat to an approximate volume of 3 mL and allowed to cool. The flask was then covered with a piece of Parafilm into which several holes were punched. After 2 months yellow-colored, X-ray quality crystals were obtained.

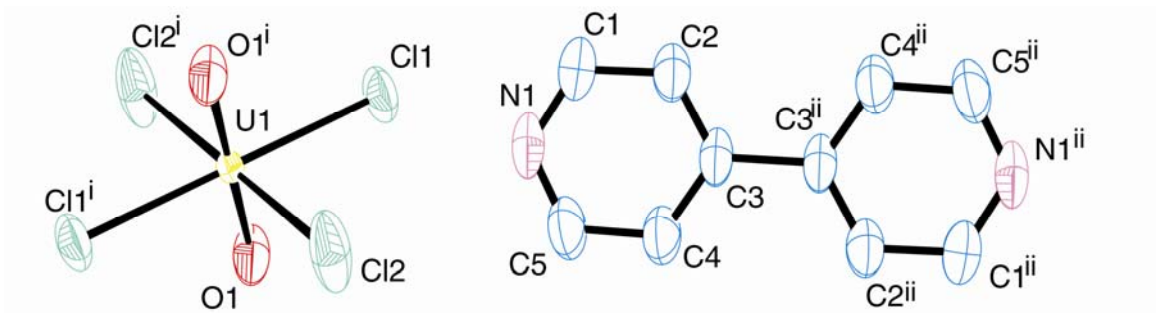


Fig S1. ORTEP illustration of **1**. Ellipsoids are shown at 50% probability level. Inter-layer organic molecules are omitted for clarity. Superscript denotes symmetry transformations $i = -x, -y, -z$; $ii = -x+1, -y+1, -z+1$.

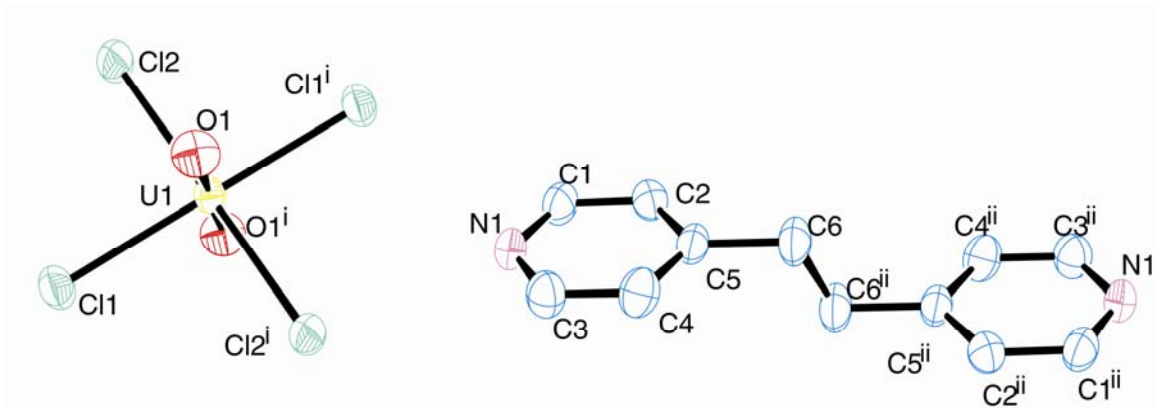


Fig S2. ORTEP illustration of **2**. Ellipsoids are shown at 50% probability level. Superscript denotes symmetry transformations $i = -x+1, -y, -z+1$; $ii = -x+3, -y+1, -z$.

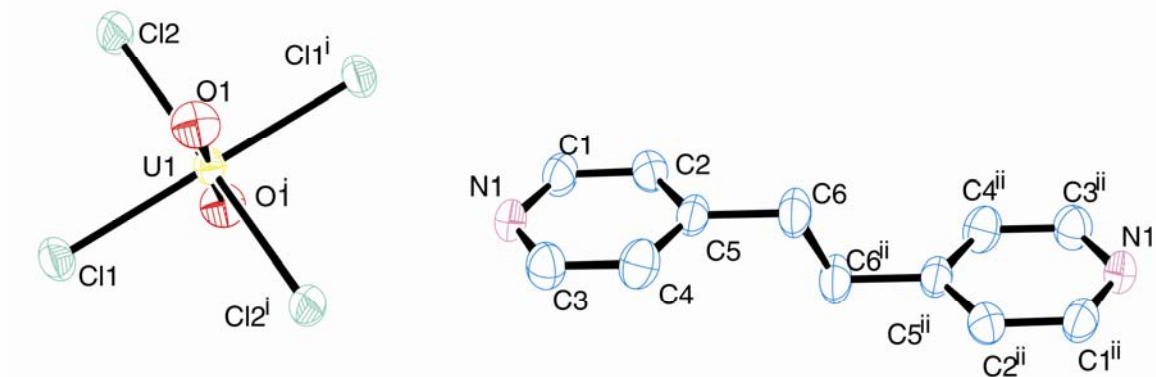


Fig S3. ORTEP illustration of **3**. Ellipsoids are shown at 50% probability level. Superscript denotes symmetry transformations $i = -x, -y, -z$; $ii = -x+2, -y+1, -z+1$.

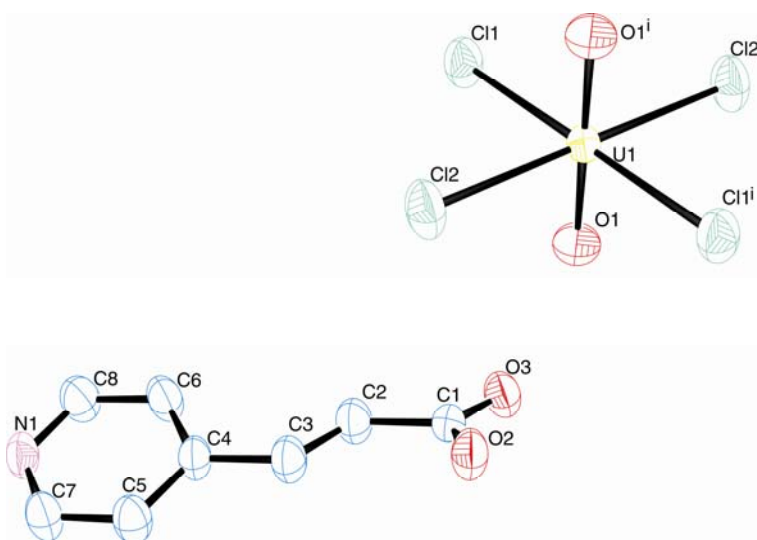


Fig S4. ORTEP illustration of **4**. Ellipsoids are shown at 50% probability level. Superscript denotes symmetry transformations $i = x, -y, -z$.

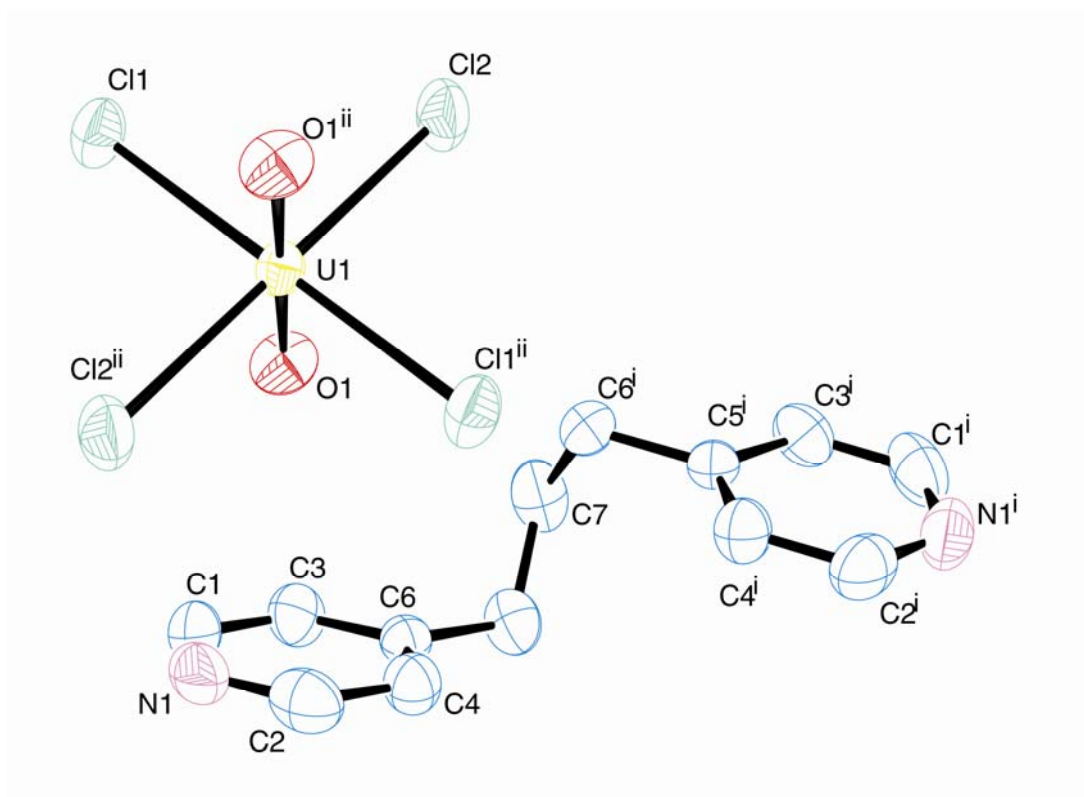


Fig S5. ORTEP illustration of **5**. Ellipsoids are shown at 50% probability level. Superscript denotes symmetry transformations $i = -x+1/2, -y+1/2, -z+1$; $ii = -x+1, y, -z+1/2$.

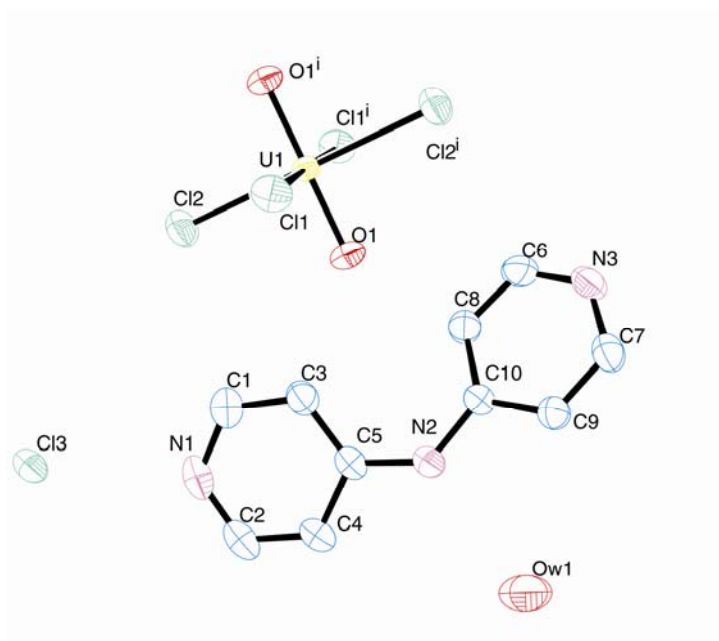


Fig S6. ORTEP illustration of **6**. Ellipsoids are shown at 50% probability level. Superscript denotes symmetry transformations $i = -x+2, -y, -z$.

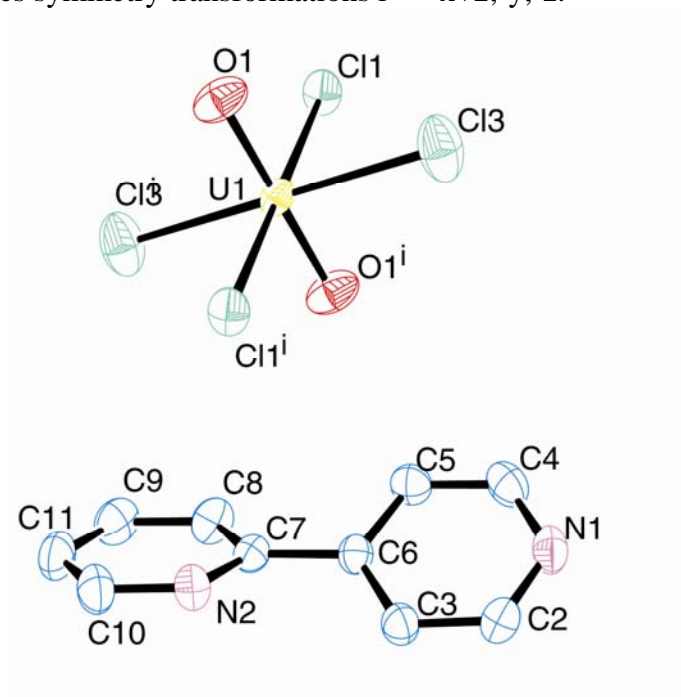


Fig S7. ORTEP illustration of **7**. Ellipsoids are shown at 50% probability level. An H_3O^+ and free Cl^- are omitted for clarity. Superscript denotes symmetry transformations $i = -x, -y, -z$.

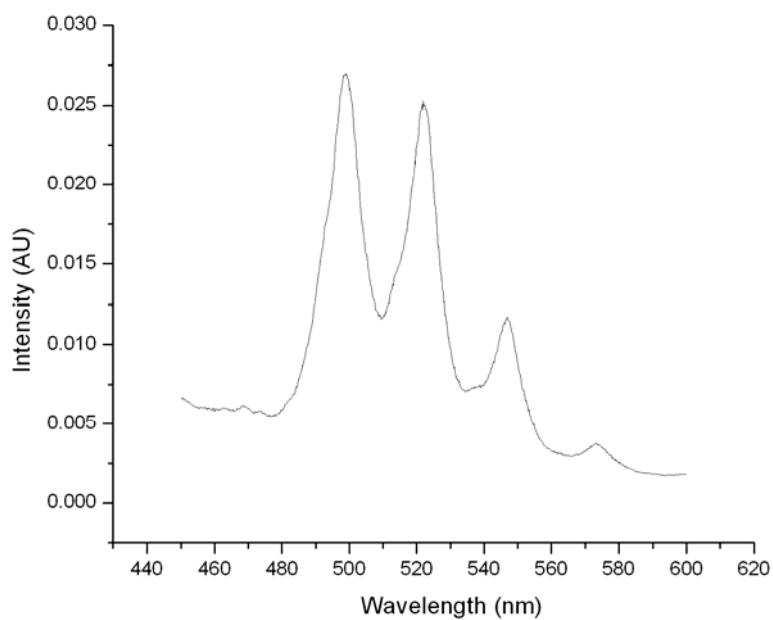


Fig S8. Emission spectra for compound **1** via uranyl excitation at 365 nm.

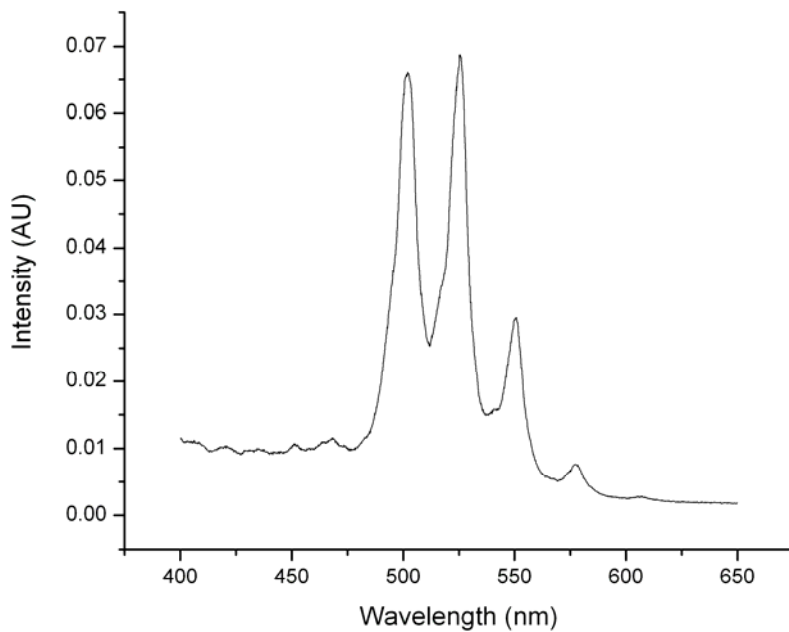


Fig S9. Emission spectra for compound **2** via uranyl excitation at 365 nm.

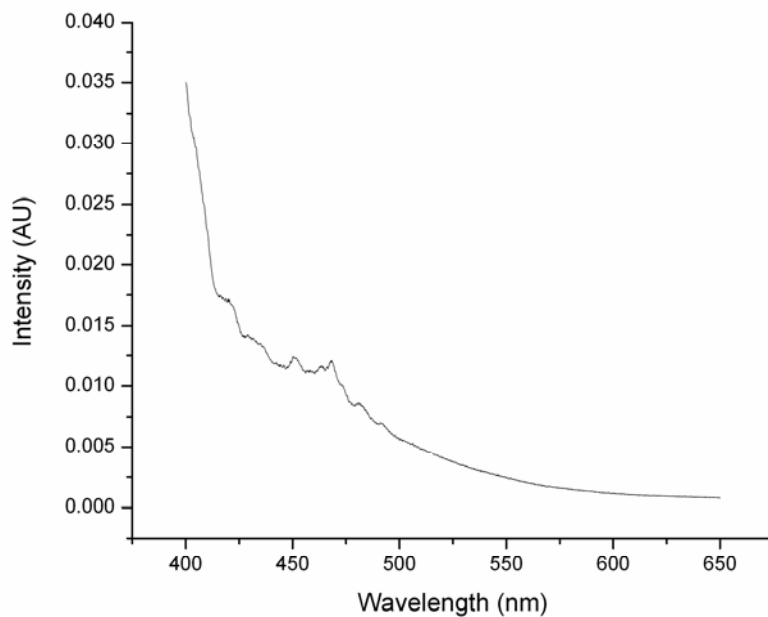


Fig S10. Emission spectra for compound **3** via uranyl excitation at 365 nm.

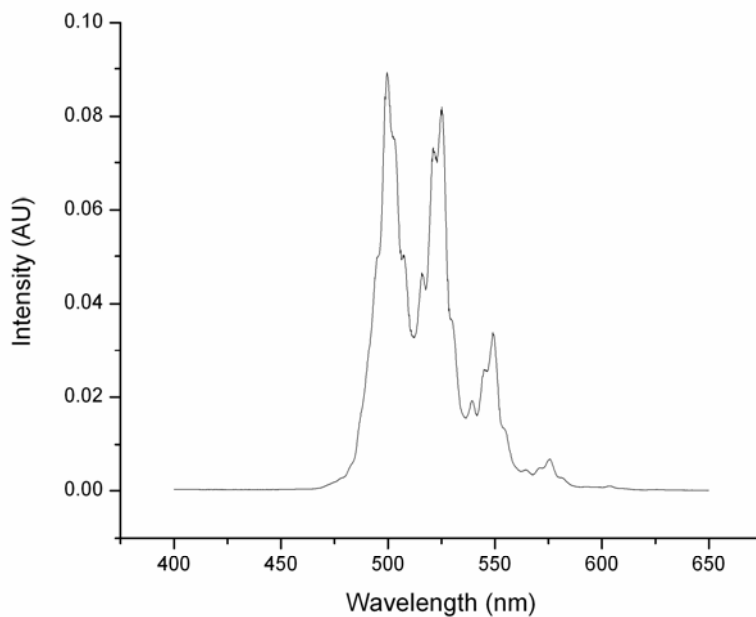


Fig S11. Emission spectra for compound **6** via uranyl excitation at 365 nm.

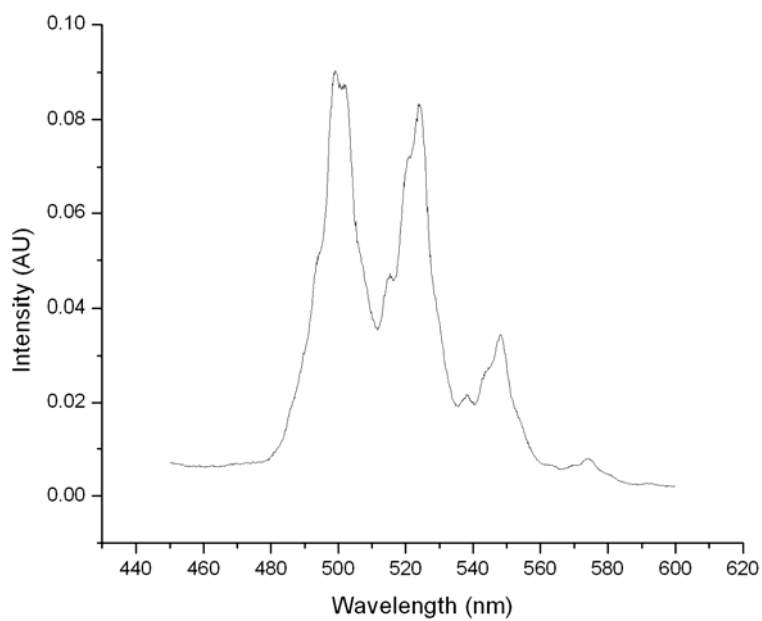


Fig S12. Emission spectra for compound **7** via uranyl excitation at 365 nm.

Table S1. Hydrogen bonds for **1** [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|--------------------|--------|----------|----------|--------|
| N(1)-H(1)...Cl(2) | 0.86 | 2.57 | 3.249(6) | 136.7 |
| N(1)-H(1)...O(1)#3 | 0.86 | 2.57 | 3.099(8) | 120.4 |
| N(1)-H(1)...Cl(1) | 0.86 | 2.98 | 3.531(6) | 123.9 |

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x+1,-y+1,-z+1 #3 x+1,y,z

Table S2. Hydrogen bonds for **2** [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------|--------|----------|----------|--------|
| N(1)-H(1)...Cl(2)#1 | 0.86 | 2.50 | 3.259(3) | 148.1 |
| N(1)-H(1)...Cl(1)#1 | 0.86 | 2.83 | 3.367(3) | 122.6 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1 #2 -x+3,-y+1,-z

Table S3. Hydrogen bonds for **3** [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---------------------|--------|----------|----------|--------|
| N(1)-H(1)...Cl(2)#3 | 0.86 | 2.64 | 3.318(2) | 136.3 |
| N(1)-H(1)...Cl(1)#4 | 0.86 | 2.65 | 3.286(2) | 132.3 |

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x+2,-y+1,-z+1 #3 x,y,z+1 #4 -x,-y,-z+1

Table S4. Hydrogen bonds for **4** [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | $\angle(\text{DHA})$ |
|---------------------|--------|----------|----------|----------------------|
| N(1)-H(1)...Cl(2)#2 | 0.86 | 2.59 | 3.259(3) | 135.1 |
| N(1)-H(1)...Cl(1)#2 | 0.86 | 2.66 | 3.337(3) | 136.3 |
| O(2)-H(2)...O(3)#3 | 0.82 | 1.85 | 2.656(3) | 168.2 |

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 -x+1,-y,-z+1 #3 -x,-y+1,-z

Table S5. Hydrogen bonds for **5** [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | $\angle(\text{DHA})$ |
|---------------------|--------|----------|----------|----------------------|
| N(1)-H(1)...Cl(2)#3 | 0.86 | 2.37 | 3.209(3) | 165.4 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,-z+1 #2 -x+1,y,-z+1/2 #3 x+1/2,-y+1/2,z+1/2

Table S6. Hydrogen bonds for **6** [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | $\angle(\text{DHA})$ |
|---------------------|---------|----------|----------|----------------------|
| N(1)-H(1)...Cl(3) | 0.86 | 2.19 | 3.036(2) | 166.8 |
| N(2)-H(2)...OW1 | 0.84(3) | 1.99(3) | 2.802(3) | 162(3) |
| N(3)-H(3)...Cl(3)#2 | 0.86 | 2.30 | 3.061(2) | 147.0 |

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z #2 x,y+1,z-1

Table S7. Hydrogen bonds for **7** [\AA and $^\circ$].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|--------------------|--------|----------|------------|--------|
| N(2)-HN2...Cl(2)#2 | 0.86 | 2.20 | 2.9880(19) | 152.4 |
| N(1)-HN1...OW1#3 | 0.86 | 1.90 | 2.718(3) | 157.9 |

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z #2 x,y,z-1 #3 -x+1/2,y-1/2,-z+1/2

Fig S13. Image of crystal of compound **1**.

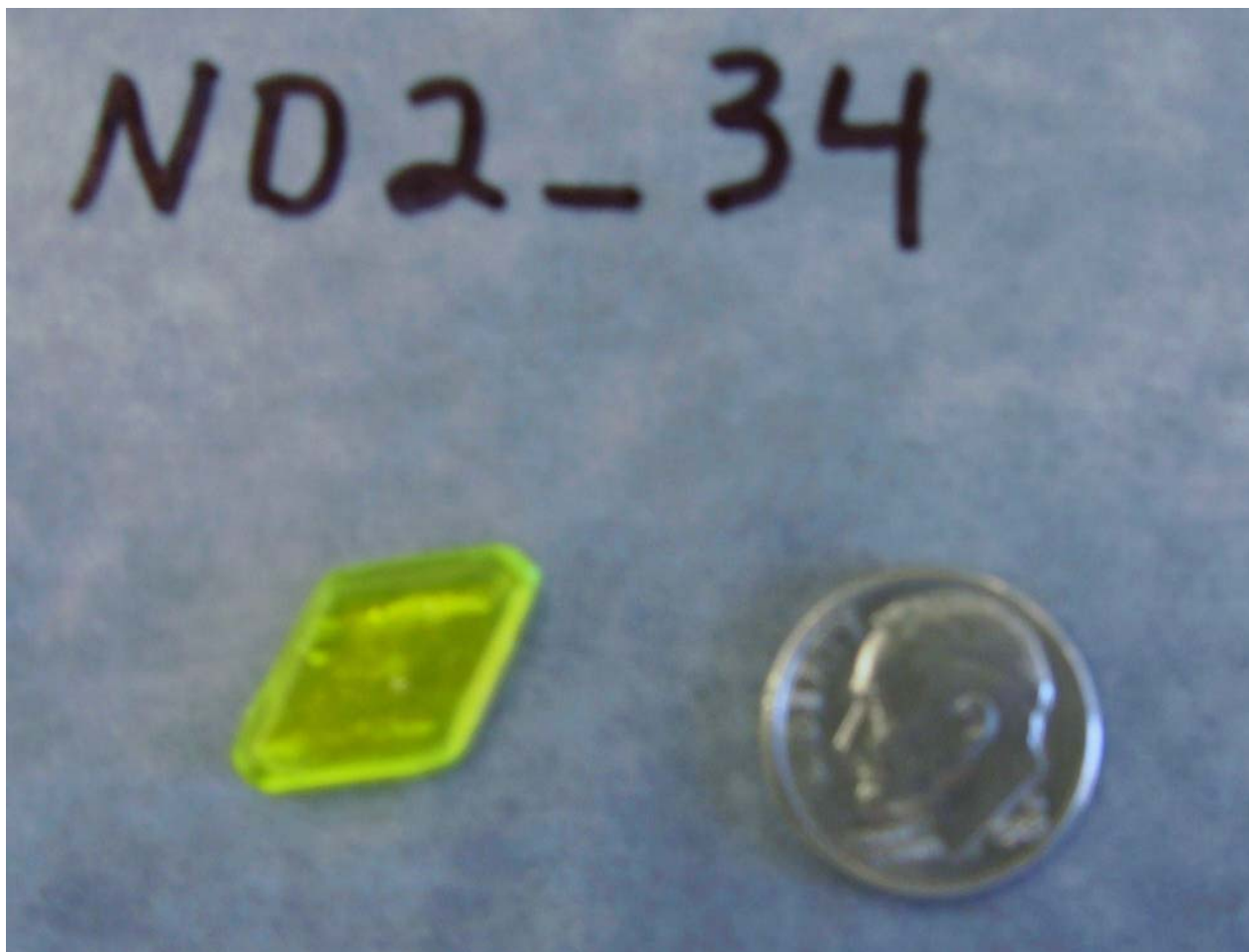


Fig S14. Image of crystals of compound 2.

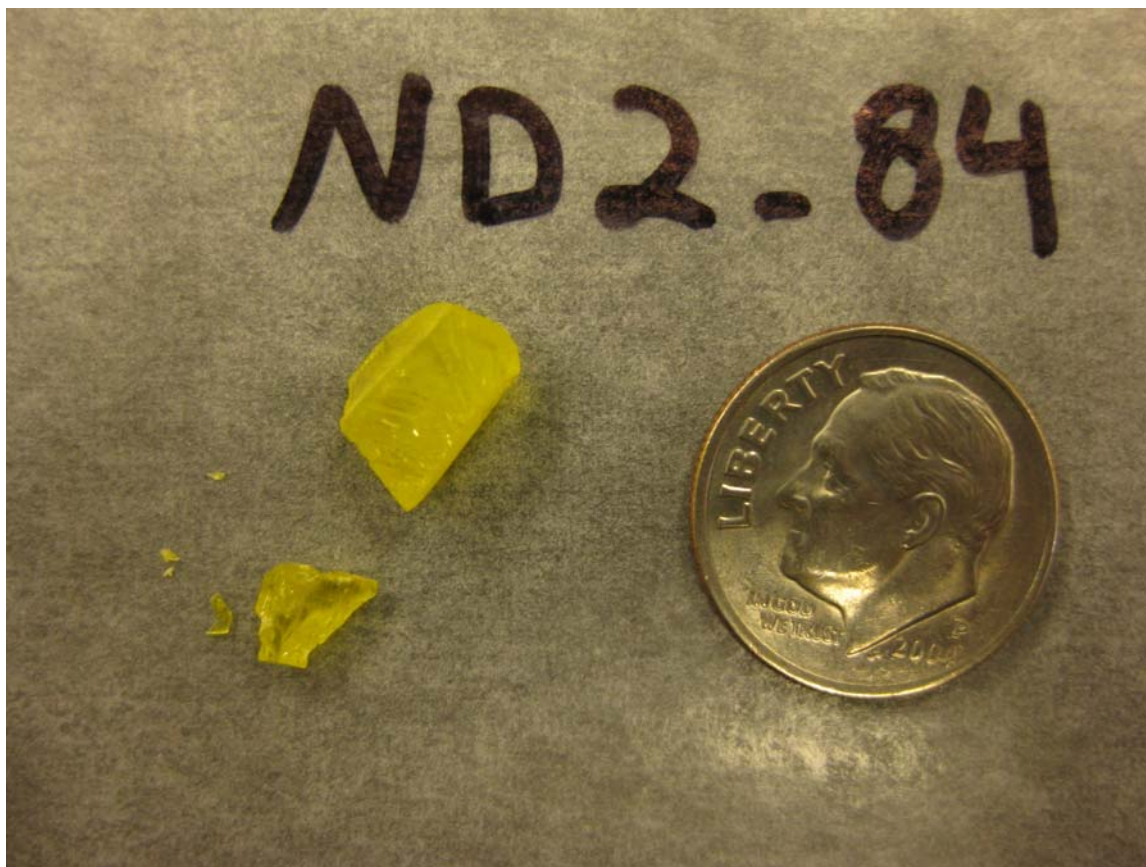


Fig S15. Image of crystals of compound **3**.



Fig S16. Image of crystal of compound **6**.

