Electronic Supplementary Information

Uranyl-Halide Complexation in N,N-Dimethylformamide: Halide Coordination Trend Manifests Hardness of UO$_2^{2+}$

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Fig. S1. ORTEP drawing of [UO$_2$(DMF)$_3$](ClO$_4$)$_2$ showing 50% probability displacement ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: U(1)-O(1) 1.79(2), U(1)-O(2) 1.76(2), U(1)-O(3) 2.414(11), U(1)-O(4) 2.338(7), U(1)-O(5) 2.377(12), U(1)-O(6) 2.332(11), U(1)-O(7) 2.465(14), O(1)-U(1)-O(2) 177.8(7), O(1)-U(1)-O(3) 89.4(6), O(1)-U(1)-O(4) 90.3(8), O(1)-U(1)-O(5) 90.4(6), O(1)-U(1)-O(6) 90.6(6), O(1)-U(1)-O(7) 89.8(6), O(3)-U(1)-O(4) 69.3(6), O(4)-U(1)-O(5) 75.6(6), O(5)-U(1)-O(6) 71.0(4), O(6)-U(1)-O(7) 73.1(4), O(3)-U(1)-O(7) 70.9(5).
Fig. S2. Normalized X-ray absorption spectra of DMF solution dissolving [UO$_2$(DMF)$_3$(ClO$_4$)$_2$ (4.0 × 10$^{-2}$ M) and [TBA]Cl (0-2.0 × 10$^{-1}$ M) at 295 K. Panels b and c are magnified pictures of the regions surrounded by dashed rectangles in red and blue, respectively.
Fig. S3. Normalized X-ray absorption spectra of DMF solution dissolving [UO$_2$(DMF)$_3$](ClO$_4$)$_2$ (4.0 × 10$^{-2}$ M) and [TBA]Br (0-2.0 × 10$^{-1}$ M) at 295 K. Panels b and c are magnified pictures of the regions surrounded by dashed rectangles in red and blue, respectively. Inset in panel b is a further magnification of 17.20-17.22 keV region.
Fig. S4. $k^2$-weighted U L_{III}-edge EXAFS spectra of DMF solution dissolving [UO$_2$(DMF)$_5$(ClO$_4$)$_2$ (4.0 × 10^{-2} M) and [TBA]I (0-2.0 × 10^{-1} M) at 295 K.

Fig. S5. U L_{III}-edge XANES spectra of DMF solution dissolving [UO$_2$(DMF)$_5$(ClO$_4$)$_2$ (4.0 × 10^{-2} M) and [TBA]I (0-2.0 × 10^{-1} M) at 295 K.
**Fig. S6.** UV-vis absorption spectra of the photo-irradiated DMF solution dissolving [UO₂(DMF)₃](ClO₄)₂ (6.64 × 10⁻³ M) at different total I⁻ concentrations ([I⁻]ₜₒₜ) and 295 K.
Table S1. Cone Angles ($\theta$) of Coordinating Cl$^-$ and Br$^-$

<table>
<thead>
<tr>
<th>ion</th>
<th>$r_{\text{vdw}}$ /Å$^a$</th>
<th>$R(\text{U-X})$ /Å$^b$</th>
<th>$\theta$ /°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>2.252</td>
<td>2.68-2.71</td>
<td>112-114</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>2.298</td>
<td>2.88-2.89</td>
<td>105-106</td>
</tr>
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$^a$Van der Waals radius brought from J. Am. Chem. Soc. 1964, 86, 979-982. $^b$Interatomic distance from U to X (= Cl$^-$, Br$^-$) determined from EXAFS (Tables 3, 4).