

# Templated Synthesis of a Unique Type of Tetra-nuclear Uranyl-Mediated Two-fold Interpenetrating Uranyl-Organic Frameworks

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## S1. General Methods

**Caution!** Suitable measures for precautions and protection should be taken, and all operations should follow the criteria while handling such substances although natural uranium was used in the experiment. All the reagents including 4, 4'-dicarboxybiphenyl sulfone (**H<sub>2</sub>dbsf**) and 1,3-bi(4-pyridyl)propane (**bpp**) were obtained commercially and used as received.

Solid-state fluorescence spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer. Powder XRD measurements were recorded on a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.5406$  Å) in the range 5-50° (step size: 0.02°). Thermogravimetric analysis (TGA) was performed on a TA Q500 analyzer over the temperature range of 30-800 °C in air atmosphere with a heating rate of 5 °C/min. FTIR spectra were recorded by using BRUKER TENSOR27 FTIR spectrometer with KBr disk method.

### Synthesis of [U<sub>4</sub>O<sub>10</sub>(dbsf)<sub>3</sub>]<sub>2</sub>[H<sub>2</sub>bpp]<sub>2</sub> (**1**)

A mixture of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (200  $\mu$ L, 0.1 mmol), 4,4'-dicarboxybiphenyl sulfone (30.6 mg, 0.1 mmol), 1,3-bi(4-pyridyl)propane (19.8 mg, 0.1 mmol) and H<sub>2</sub>O (1.8 ml) was placed in a Teflon-lined stainless steel vessel. After treating with NaOH, the pH of the mixture was adjusted to 7.85, and then the mixture was sealed, kept at 180°C for 72 h and cooled to room temperature slowly. The pH of the final solution was 5.68. Red-brown block crystals were washed with water and ethanol and dried in air. The yield for compound **1** was 36% on the basis of uranium.

### Synthesis of [U<sub>4</sub>O<sub>10</sub>(dbsf)<sub>3</sub>][H<sub>2</sub>bpp] (**2**)

Compound **2** was obtained using the same procedure as that for **1**. Yellow platelike crystals were obtained with a very low yield.

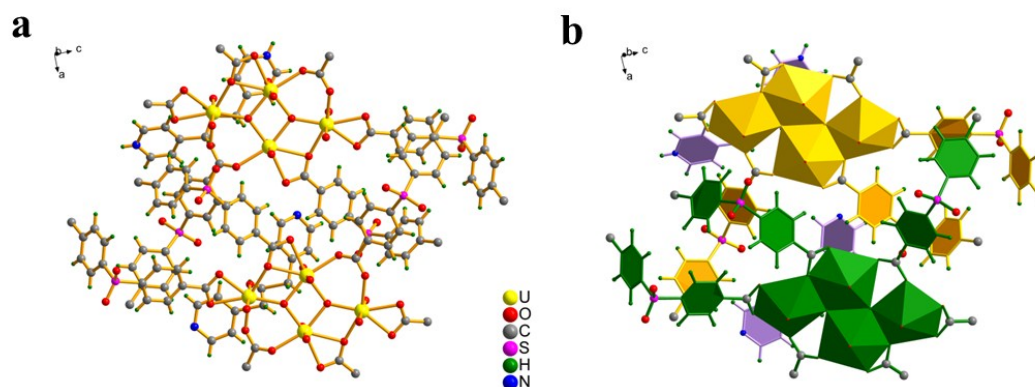
### X-ray Single Structural Determination

X-ray diffraction data collection of compounds **1** and **2** performed with synchrotron radiation facility at BSRF (beamline 3W1A of Beijing Synchrotron Radiation Facility,  $\lambda = 0.71073$  Å) using a MAR CCD detector. The crystal was mounted in nylon loops and cooled in a cold nitrogen-gas stream at 100 K. Data were indexed, integrated and scaled using DENZO and SCALEPACK from the HKL program suite (Otwinowski & Minor, 1997). The crystal structures were solved by means of direct methods and refined with full-matrix least squares on SHELXL-97.

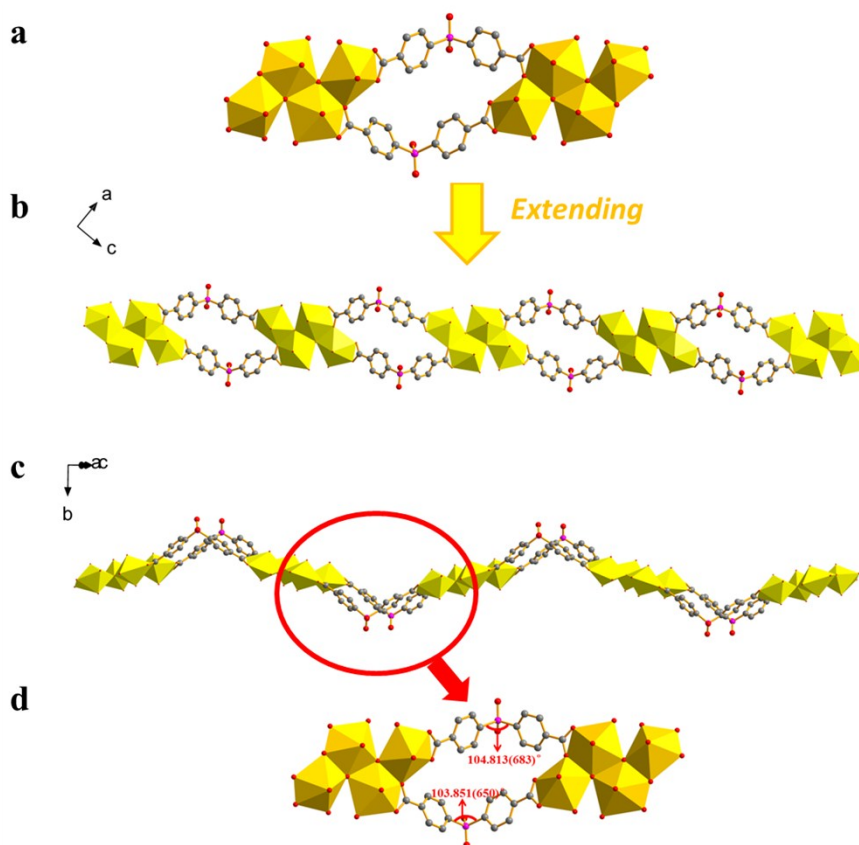
Crystal data for **1**:  $C_{110}H_{78}N_4O_{56}S_6U_8$ ,  $[U_4O_{10}(dbsf)_3]_2[H_2bpp]_2$ , Mr = 4448.36, Monoclinic,  $P2_1/c$ ,  $a = 23.831(5) \text{ \AA}$ ,  $b = 20.716(4) \text{ \AA}$ ,  $c = 29.555(6) \text{ \AA}$ ,  $\beta = 90.75(3)^\circ$ ,  $V = 14589.55(511) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd.}} = 2.025 \text{ g}\cdot\text{cm}^{-3}$ . The crystal structures were solved by means of direct methods and refined with full-matrix least squares on SHELXL-97 and converged to  $R_1 = 0.0367$  and  $wR_2 = 0.0919$ , and GOF = 1.047 ( $R_{\text{int}} = 0.0412$ ) for 4248 reflections [ $I > 2\sigma(I)$ ].

Crystal data for **2**:  $C_{55}H_{29}N_2O_{28}S_3U_4$ ,  $[U_4O_{10}(dbsf)_3][H_2bpp]$ , Mr = 2214.1, Triclinic,  $P-1$ ,  $a = 10.523(2) \text{ \AA}$ ,  $b = 11.866(2) \text{ \AA}$ ,  $c = 29.288(6) \text{ \AA}$ ,  $\alpha = 90.81(3)^\circ$ ,  $\beta = 92.91(3)^\circ$ ,  $\gamma = 92.71(3)^\circ$ ,  $V = 3647.77(120) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd.}} = 2.016 \text{ g}\cdot\text{cm}^{-3}$ . The crystal structures were solved by means of direct methods and refined with full-matrix least squares on SHELXL-97 and converged to  $R_1 = 0.0462$  and  $wR_2 = 0.1113$ , and GOF = 1.037. ( $R_{\text{int}} = 0.0307$ ) for 4469 reflections [ $I > 2\sigma(I)$ ].

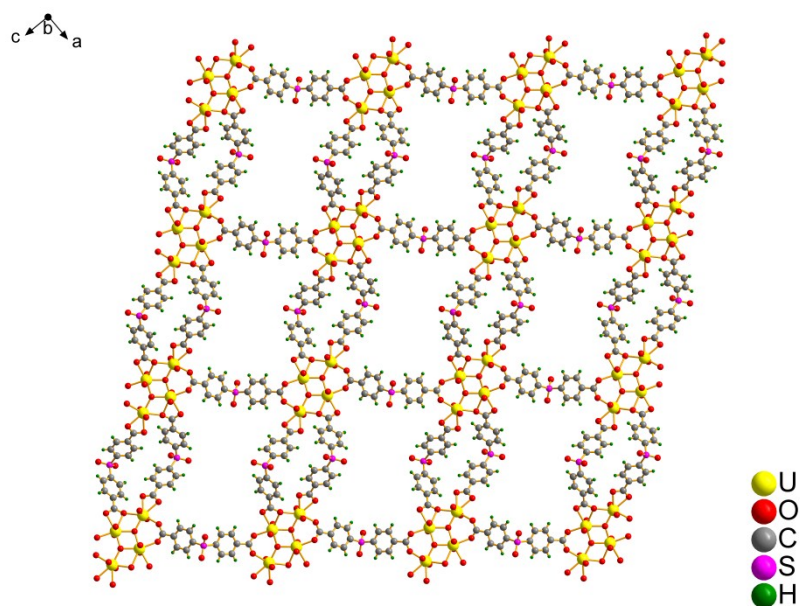
## S2. Typical figures and tables



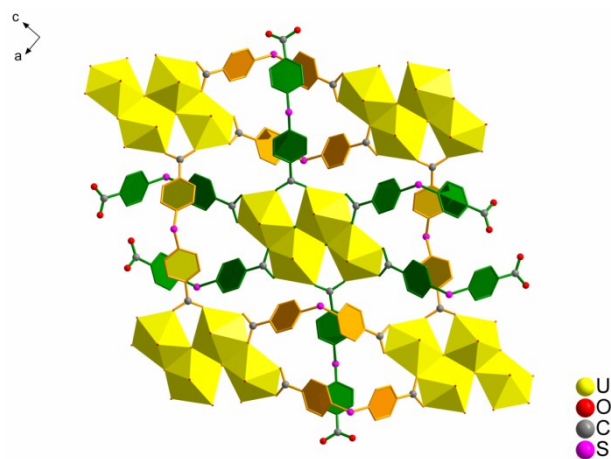
**Figure S1.** (a) Coordination environments of uranyl center in compound **1**; (b) two sets of tetranuclear uranium units: yellow and green; H<sub>2</sub>bpp<sup>2+</sup> ligand: lavender.



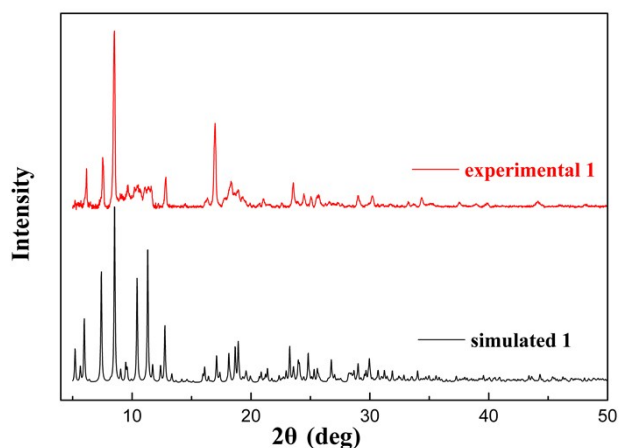
**Figure S2.** (a) U<sub>8</sub>(dbsf)<sub>2</sub> loop of compound **1**; (b) small loops extended to 1D tapes in compound **1**; (c) sideview of the 1D wave-like tapes; (d) the C-S-C angle of wave-like tapes was between 102.578(628)° and 104.813(683)°. Uranyl bipyramids are shown in yellow, carbon, sulfur, oxygen atoms are shown in gray, pink and red, respectively. Hydrogen atoms are omitted for clarity.



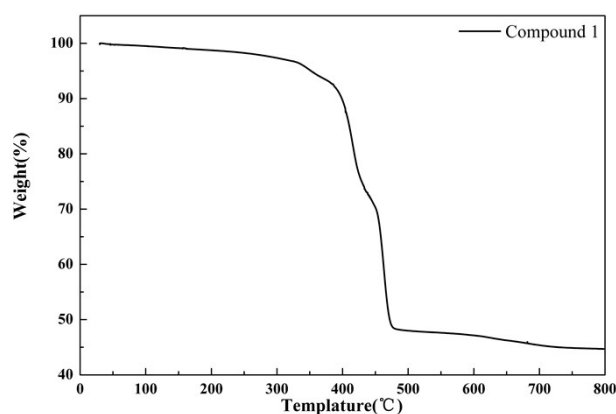
**Figure S3.** 2D network of compound **1** from b axis.



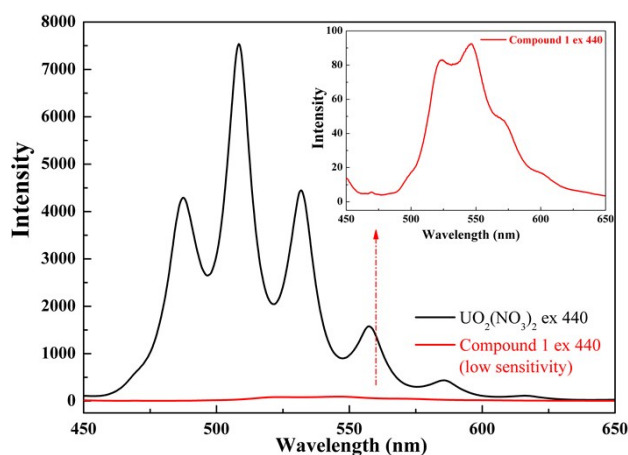
**Figure S4.** The bigger loops in the network were constructed by four tetranuclear uranium unit and four dbsf ligands, the tetranuclear uranium unit of another network located in the center of the bigger loops.



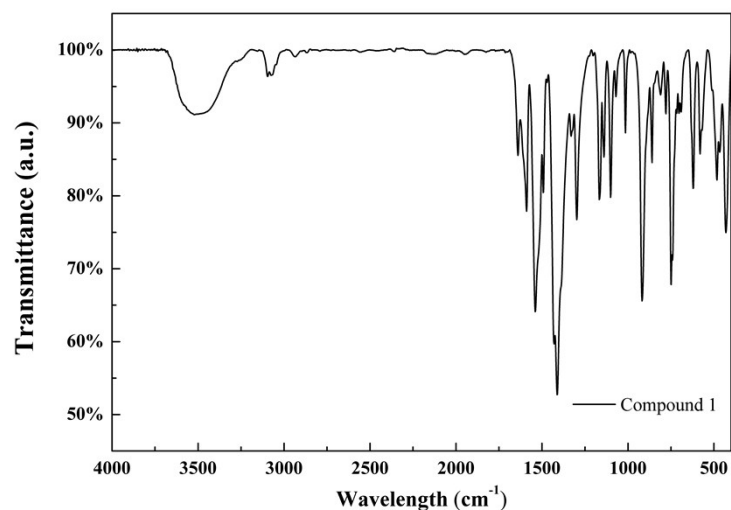
**Figure S5.** Powder X-Ray Diffraction of compound **1**. The upper and lower parts for each diagram are experimental spectra and simulated spectra from single crystal data.



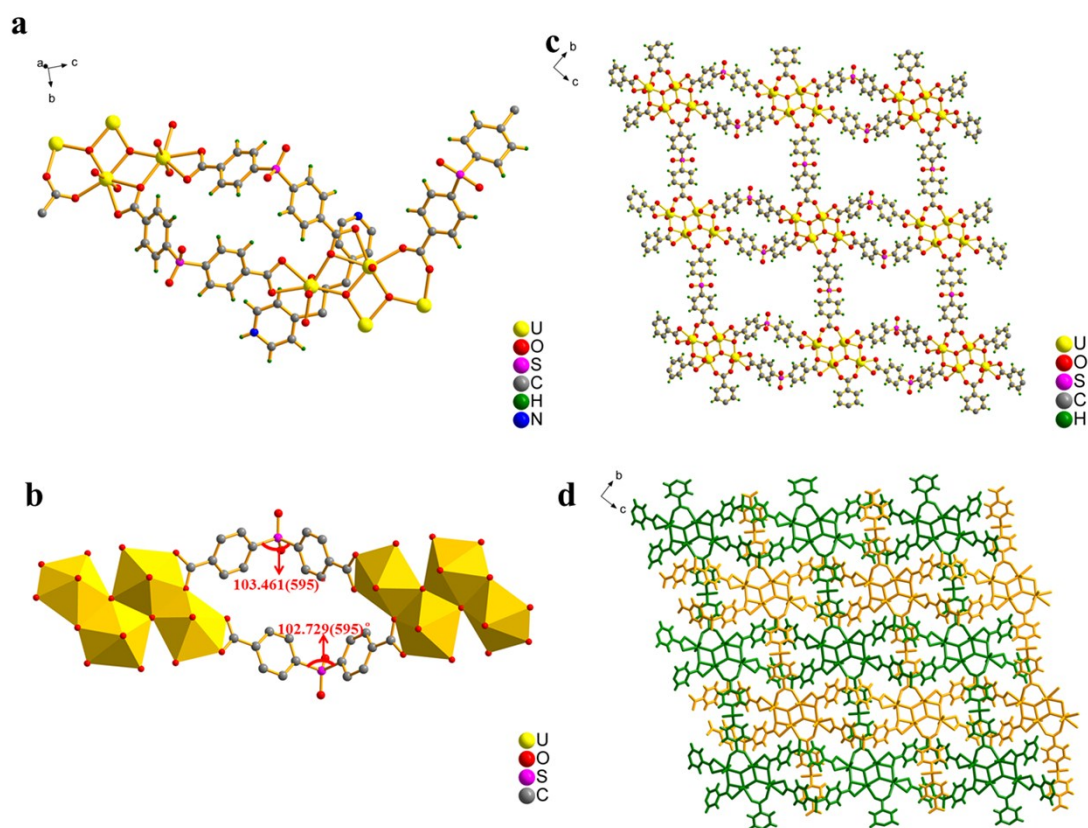
**Figure S6.** Thermogravimetric analysis for compound **1**.



**Figure S7.** (Left) Fluorescence spectra of  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (black line) and compound **1** (red line, low sensitivity) excited at 440 nm with excitation and emission slit width 3.0 nm. (Right) Fluorescence spectra of compound **1** illustrating the red shift when compared to  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .



**Figure S8.** Infrared spectra of compound **1**.



**Figure S9.** (a) Coordination environments of uranyl center in compound **2**; (b) the small  $U_8(dbsf)_2$  loop of compound **2** got smaller C-S-C angles than **1**, uranyl bipyramids are shown in yellow, hydrogen atoms are omitted for clarity; (c) 2D network of compound **2** from a axis; (d) the two-fold interpenetrating frameworks of compound **2** viewed down the a axis.

**Table S1.** Selected bond distances (Å) related to uranyl centers and distances (Å) for hydrogen bonds and C-H... $\pi$  bonds observed in uranyl compounds **1**.

<b>1</b>			
<b>U1-O38</b>	1.733(12)	<b>U5-O40</b>	1.752(11)
<b>U1-O10</b>	1.761(10)	<b>U5-O42</b>	1.756(11)
<b>U1-O4</b>	2.221(9)	<b>U5-O1</b>	2.241(10)
<b>U1-O20</b>	2.390(11)	<b>U5-O12</b>	2.396(11)
<b>U1-O3</b>	2.450(9)	<b>U5-O22</b>	2.445(9)
<b>U1-O36</b>	2.465(10)	<b>U5-O21</b>	2.466(10)
<b>U1-O19</b>	2.507(10)	<b>U5-O13</b>	2.498(10)
<b>U2-O8</b>	1.752(10)	<b>U6-O41</b>	1.749(12)
<b>U2-O37</b>	1.766(12)	<b>U6-O30</b>	1.817(12)
<b>U2-O16</b>	2.239(10)	<b>U6-O28</b>	2.243(10)
<b>U2-O15</b>	2.405(10)	<b>U6-O1</b>	2.308(9)
<b>U2-O31</b>	2.451(9)	<b>U6-O34</b>	2.405(12)
<b>U2-O44</b>	2.470(11)	<b>U6-O23</b>	2.545(10)
<b>U2-O17</b>	2.525(10)	<b>U6-O22</b>	2.584(10)
<b>U3-O7</b>	1.733(11)	<b>U7-O29</b>	1.772(11)
<b>U3-O5</b>	1.814(10)	<b>U7-O43</b>	1.773(14)
<b>U3-O16</b>	2.247(10)	<b>U7-O28</b>	2.233(11)
<b>U3-O4</b>	2.295(9)	<b>U7-O35</b>	2.412(12)
<b>U3-O11</b>	2.40(1)	<b>U7-O2</b>	2.427(9)
<b>U3-O14</b>	2.521(9)	<b>U7-O25</b>	2.479(11)
<b>U3-O3</b>	2.627(10)	<b>U7-O24</b>	2.491(11)
<b>U4-O39</b>	1.731(11)	<b>U8-O26</b>	1.730(13)
<b>U4-O6</b>	1.778(12)	<b>U8-O27</b>	1.794(13)
<b>U4-O4</b>	2.269(10)	<b>U8-O1</b>	2.247(10)
<b>U4-O16</b>	2.309(9)	<b>U8-O28</b>	2.31(1)
<b>U4-O53</b>	2.435(10)	<b>U8-O58</b>	2.386(11)
<b>U4-O9</b>	2.532(9)	<b>U8-O33</b>	2.554(9)
<b>U4-O31</b>	2.607(10)	<b>U8-O2</b>	2.599(10)
<b>C20-H20...O24</b>	2.6119(120)	<b>C33-H146...O14</b>	2.5728(113)
<b>C54-H32...O21</b>	2.6097(105)	<b>C25-H25...O7</b>	2.6591(94)
<b>C26-H26...O26</b>	2.390(12)	<b>C38-H38...O8</b>	2.5772(94)
<b>C145-H145...O36</b>	2.5316(117)	<b>C1B-H1B...O17</b>	2.4926(97)
<b>C173-H173...O173</b>	2.4354(123)	<b>C56-H56...O13</b>	2.5187(96)
<b>C176-H176...O39</b>	2.4167(102)	<b>C40-H40...O40</b>	2.5453(95)
<b>C135-H135...O26</b>	2.6166(120)	<b>C82-H146...O33</b>	2.5575(114)



**Table S2.** Selected bond distances (Å) related to uranyl centers in uranyl compounds **2**.

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<b>2</b>			
<b>U1-O3</b>	1.756(10)	<b>U3-O2</b>	1.755(10)
<b>U1-O4</b>	1.778(10)	<b>U3-O1</b>	1.761(10)
<b>U1-O5</b>	2.252(9)	<b>U3-O5</b>	2.236(9)
<b>U1O5</b>	2.285(8)	<b>U3-O13</b>	2.38(1)
<b>U1-O12</b>	2.372(9)	<b>U3-O6</b>	2.437(8)
<b>U1-O7</b>	2.541(9)	<b>U3-O11</b>	2.472(10)
<b>U1-O6</b>	2.584(9)	<b>U3-O10</b>	2.477(9)
<b>U2-O18</b>	1.771(13)	<b>U4-O20</b>	1.732(19)
<b>U2-O19</b>	1.790(12)	<b>U4-O21</b>	1.790(12)
<b>U2-O29</b>	2.253(9)	<b>U4-O29</b>	2.229(9)
<b>U2-O29</b>	2.270(9)	<b>U4-O23</b>	2.389(12)
<b>U2-O22</b>	2.349(8)	<b>U4-O17</b>	2.436(10)
<b>U2-O16</b>	2.527(9)	<b>U4-O24</b>	2.451(11)
<b>U2-O17</b>	2.592(9)	<b>U4-O25</b>	2.470(9)
<b>C1J-H1J...O24</b>	2.6180(139)	<b>C42-H42...O25</b>	2.5212(114)
<b>C23-H23...O11</b>	2.5176(105)	<b>C41-H41...O10</b>	2.5132(96)
<b>C27-H27...O16</b>	2.7638(108)	<b>C37-H37...O2</b>	2.4954(85)
<b>C31-H31...O18</b>	2.7234(97)	<b>C34-H34...O4</b>	2.6121(93)
<b>C31-H31...O22</b>	2.6980(115)	<b>C29-H29...O7</b>	2.6778(100)
<b>C26-H26...O21</b>	2.4065(105)		

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