

Supporting information

Two New Two-dimensional Layered Uranyl-bearing Polycarboxylates From Semi-rigid Tetracarboxylic Acids

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Experimental Section

Materials and Instruments.

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Vario EL III elemental analyzer. Solution ^1H NMR spectra were recorded on a Bruker AVANCE-III NMR (600 MHz). Powder X-ray patterns were obtained on a Bruker D8 Advance diffractometer using $\text{CuK}\alpha$ radiation (see Figures S1 and S2). IR spectra were recorded on a Nicolet 6700 FTIR Spectrometer as KBr pellets in the range of $4000\text{--}400\text{ cm}^{-1}$ (see Figure S3 and S4). Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under a nitrogen atmosphere (see Figure S5). UV-vis absorption spectra were measured at room temperature on a HITACHI U-4100 spectrophotometer in the range of $200\text{--}600\text{ nm}$. To confirm the existence of fluoride anion in compound **1**, microprobe elemental analyses were performed on a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDS, Oxford INCA) (see Table S3 in the supporting information).

Single-Crystal Structure Determination.

Single crystal X-ray diffraction measurements of compounds **1** and **2** were carried out on a Bruker SMART APEX II CCD diffractometer ($\text{Mo K}\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$) at room temperature. SAINT was used for integration of intensity of reflections and scaling.¹ Absorption corrections were carried out with the program SADABS.² Crystal structures were solved by direct methods using SHELXS.³ Subsequent difference Fourier analyses and least squares refinement with SHELXL-97⁴ allowed for the location of the atom positions. In the final step of the crystal structure refinement, hydrogen atoms of $-\text{CH}_2$ and $-\text{CH}_3$ groups were modeled and treated while riding on the parent carbon atom. The isotropic displacement factor was chosen at 1.2 and 1.5 times the preceding carbon atom, respectively. The hydrogen atoms on the water molecule were located from the difference Fourier map. The high residue peaks in compound **1** around the uranium (VI) ion are meaningless. The data have been deposited in the Cambridge Crystallographic Data Centre (CCDC), deposition number CCDC 997026-997027 for **1** and **2**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing

data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Syntheses of 2,2',2'',2'''-(2,5-dimethyl-1,4-phenylene)bis(methylene)bis(azanetriyl)tetraacetic acid (H₄L¹) and 2,2',2'',2'''-(2,4,6-trimethyl-1,3-phenylene)bis(methylene) bis(azanetriyl)tetraacetic acid (H₄L²)

H₄L¹ and H₄L² were synthesized from the reaction of diethyl iminodiacetate with 1,4-dibromomethyl-2,5-dimethylbenzene and 1,4-dibromo-2,3,5,6-tetramethylbenzene,⁵ respectively, using a published procedure.⁶ ¹HNMR (D₂O, ppm) data for H₄L¹: δ 2.318 (s, 6H, -CH₃), 3.806 (s, 8H, N-CH₂-), 4.418 (s, 4H, Ar-CH₂-), 7.247 (s, 2H, Ar-H). ¹HNMR (*d*₆-DMSO, ppm) data for H₄L²: δ 2.27 (s, 6H, Ar-CH₃), 2.38 (s, 3H, Ar-CH₃), 3.37 (s, 8H, N-CH₂), 3.88 (s, 4H, Ar-CH₂), 6.82 (s, 1H, Ar-H).

Synthesis of compound [(UO₂)F(H₂L¹)_{0.5}][H₂O] (1)

A mixture of H₄L¹ (0.25 mmol, 0.0991 g), UO₂(Ac)₂·2H₂O (0.125 mmol, 0.053 g), two drops of HF solution (40 %) and 10 mL of water were placed and stirred in a Teflon-lined autoclave. Afterward, it was sealed and heated at 140 °C for 4 days and allowed to cool to room temperature in a time period of 24 hours. Yellow plate crystals (0.024 g) were collected and washed with deionized water in satisfying yield (38%, based on metal source). Elemental analysis (%) calcd for C₉H₁₄NO₈U (502.24): C 21.52, H 2.81, N 2.79; found: C 21.60, H 3.02, N 2.91. IR(KBr, cm⁻¹): 3642 (m), 3525 (m), 3083 (m), 2977 (w), 1655 (s), 1595 (s), 1433 (m), 1411 (m), 1366 (m), 1332 (s), 1267 (w), 1200 (vw), 1168 (vw), 1029 (w), 942 (s), 894 (w), 851 (w), 710 (w), 600 (w), 583 (w), 535 (w), 490 (w), 436 (w) (see Figure S3).

Synthesis of compound [(UO₂)(H₂L²)][H₂O]_{0.5} (2)

A mixture of H₄L² (0.25 mmol, 0.1026 g), UO₂(Ac)₂·2H₂O (0.125 mmol, 0.053 g), and 10 mL of water were placed and stirred in a Teflon-lined autoclave. Afterward, it was sealed and heated at 140 °C for 4 days and allowed to cool to room temperature in a time period of 24 hours. Yellow prism crystals (0.052 g) were collected and washed with deionized water in satisfying yield (61%, based on metal source). Elemental analysis (%) calcd for C₁₉H₂₅N₂O_{10.5}U (687.44): C 33.20, H 3.67, N 4.08; found: C 33.26, H 3.89, N 4.16. IR(KBr, cm⁻¹): 3423 (b, m), 3100 (w), 2966 (w), 1669 (sh, s), 1637 (s), 1594 (m), 1454 (m), 1415 (s), 1401 (s), 1360 (s), 1334 (m), 1305 (s), 1274 (m), 1044 (w), 949 (w), 921 (s), 897 (w), 858 (vw), 720 (w), 706 (w), 618 (vw), 594 (vw), 541 (w), 496 (w), 448 (vw) (see Figure S4).

Crystal data for [(UO₂)F(H₂L¹)_{0.5}][H₂O] (1): C₉H₁₃FNO₇U, *M* = 504.23 g mol⁻¹, *T* = 296 (2) K, orthorhombic, *Pbca*, *Z* = 8, *a* = 12.1361(8), *b* = 8.5565(6), *c* = 23.3240(15), *V* = 2422.0(3) Å³, ρ_{calcd.} = 2.766 g cm⁻³, μ (Mo-Kα) = 13.447 mm⁻¹, 10278 measured reflections, 2120 independent reflections (*R*_{int} = 0.0459), for intensities with *I* > 3σ *R*₁ = 0.0362 and *wR*₂ = 0.0746, for all data *R*₁ = 0.0485, and *wR*₂ = 0.0796, GOF all data = 1.095.

Crystal data for [(UO₂)(H₂L²)][H₂O]_{0.5} (2): C₁₉H₂₅N₂O_{10.5}U, *M* = 687.44 g mol⁻¹, *T* = 296 (2) K, monoclinic, *C2/c*, *Z* = 8, *a* = 23.664(3), *b* = 14.077(2), *c* = 14.386(2), β = 106.281(5)°, *V* = 4599.9(9) Å³, ρ_{calcd.} = 1.985 g cm⁻³, μ (Mo-Kα) = 7.116 mm⁻¹, 17376 measured reflections, 4025 independent reflections (*R*_{int} = 0.0266), for

intensities with $I > 3\sigma$ $R1 = 0.0190$, and $wR2 = 0.0501$, for all data $R1 = 0.0218$, and $wR2 = 0.0512$, GOF all data = 1.060.

1. SAINT, Version 6.45; Bruker Analytical X-ray Systems Inc.: 2003.
2. G. M. Sheldrick, SADABS, Version 2.10; Bruker AXS Inc.: Madison, WI, 2003.
3. G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution and Refinement; University of Göttingen, 1997.
4. G. M. Sheldrick, SHELXTL, Crystallographic Software Package, SHELXTL, Version 5.1, Bruker-AXS, Madison, WI, 1998.
5. W. van der Made, R. H. van der Made, *J. Org. Chem.*, **1993**, *58*, 1262-1263.
6. a) M. A. Fazal, B. C. Roy, S. Sun, S. Mallik, K. R. Rodgers, *J. Am. Chem. Soc.* **2001**, *123*, 6283–6290; b) X. Lv, S.-F. Tang, L. Li, J. Cai, C. Wang, X. Xu, X. Zhao, *Eur. J. Inorg. Chem.*, **2013**, 5081–5085.

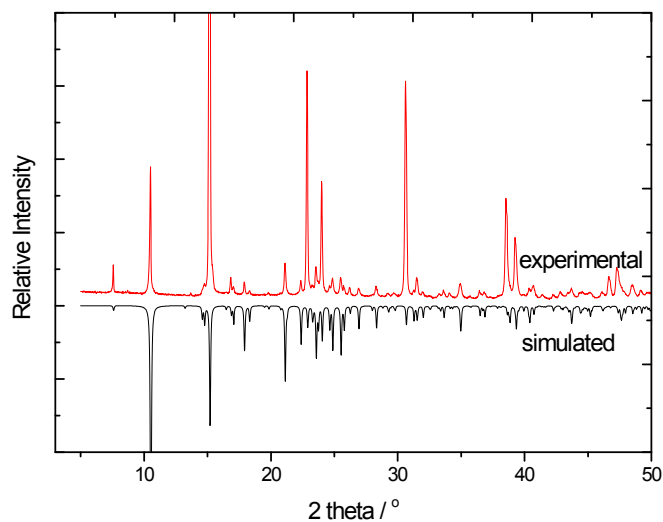


Figure S1. Comparison of the simulated and experimental XRD patterns of compound **1**.

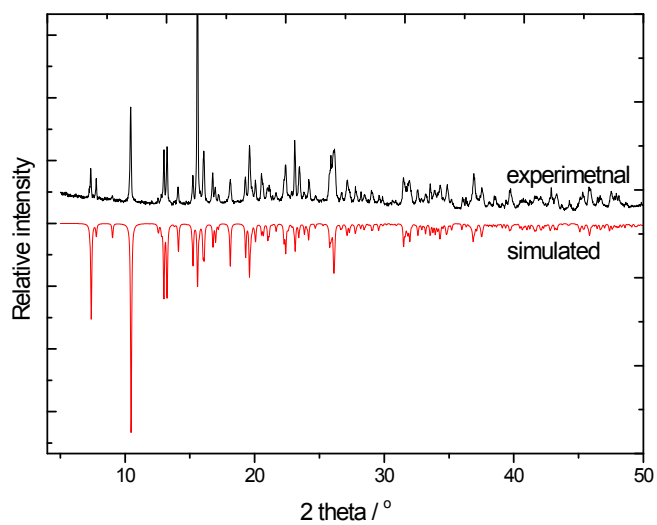


Figure S2. Comparison of the simulated and experimental XRD patterns of compound **2**.

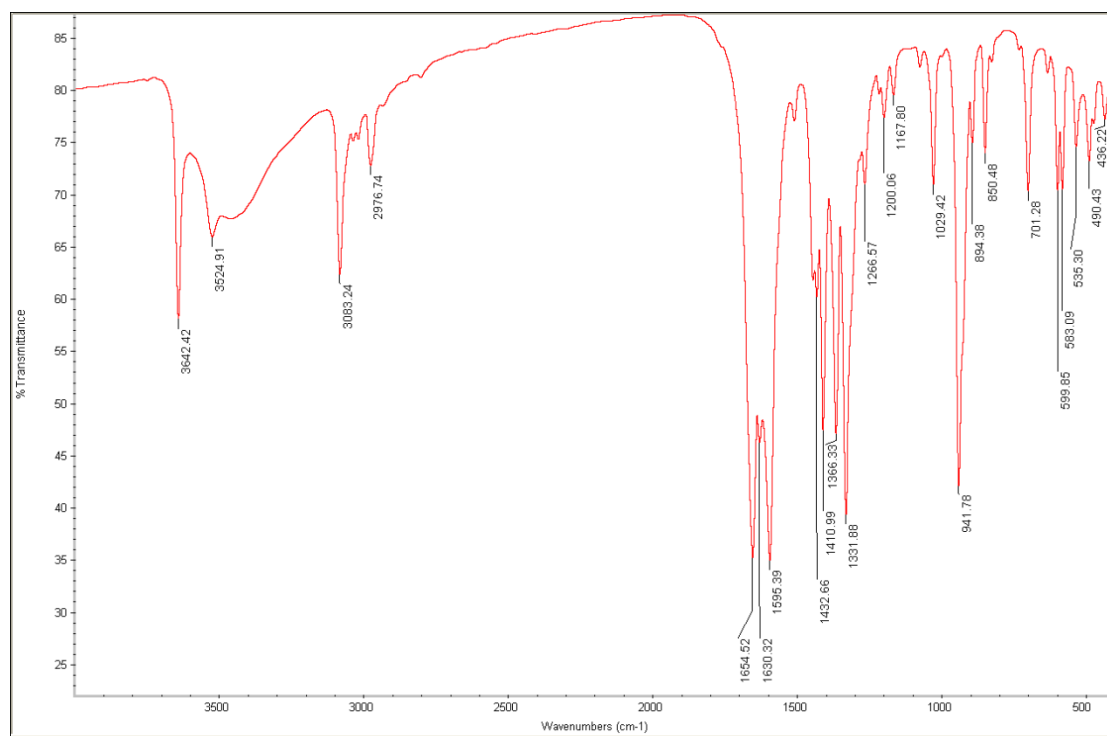


Figure S3. IR spectrum of compound **1**.

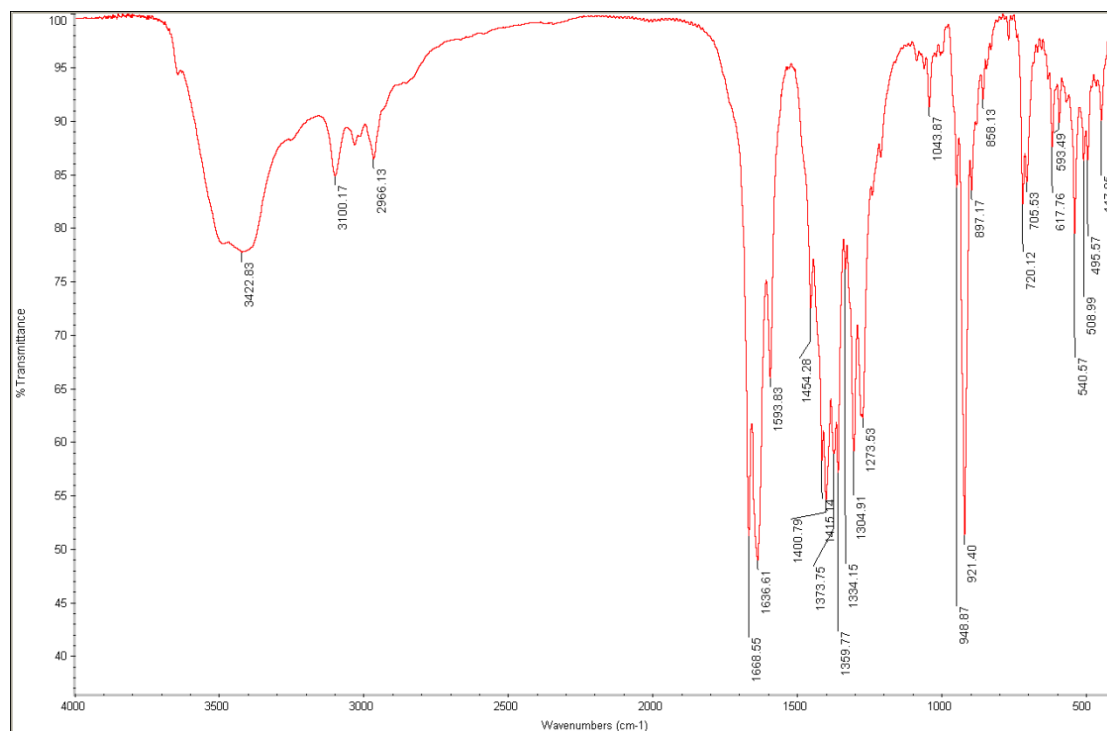


Figure S4. IR spectrum of compound **2**.

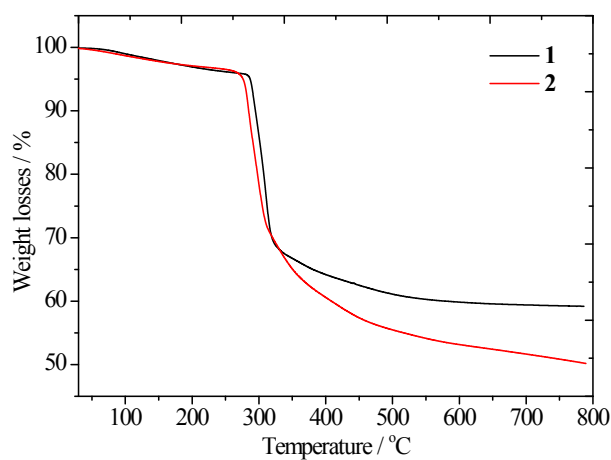


Figure S5. TGA curves of compounds **1** and **2**.

Table S1. Selected bond lengths and angles of compounds **1** and **2**.

1			
U(1)-O(6)	1.770(6)	U(1)-F(1)	2.347(4)
U(1)-O(5)	1.787(6)	U(1)-O(1)	2.383(6)
U(1)-F(1)#1	2.326(4)	U(1)-O(2)#2	2.405(6)
U(1)-O(4)#1	2.346(6)	O(6)-U(1)-O(5)	179.2(3)
O(6)-U(1)-F(1)#1	92.6(2)	O(5)-U(1)-O(1)	90.0(3)
O(5)-U(1)-F(1)#1	88.1(2)	O(6)-U(1)-F(1)	89.2(2)
O(6)-U(1)-O(4)#1	87.4(3)	O(5)-U(1)-F(1)	90.0(2)
O(5)-U(1)-O(4)#1	93.2(3)	O(6)-U(1)-O(2)#2	94.2(3)


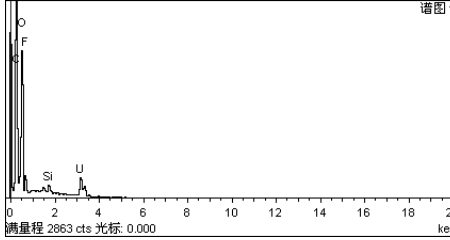
O(5)-U(1)-O(2)#2	85.5(3)	O(6)-U(1)-O(1)	89.8(3)
F(1)-U(1)-O(1)	68.49(18)	O(4)#1-U(1)-O(2)#2	75.1(2)
F(1)#1-U(1)-O(4)#1	74.09(19)	F(1)-U(1)-O(2)#2	72.8(2)
F(1)#1-U(1)-O(1)	70.04(18)	F(1)#1-U(1)-F(1)	138.49(5)
O(4)#1-U(1)-O(1)	143.9(2)	O(4)#1-U(1)-F(1)	147.39(19)
F(1)#1-U(1)-O(2)#2	148.1(2)	O(1)-U(1)-O(2)#2	141.0(2)
2			
U(1)-O(10)	1.765(3)	U(1)-O(1)	2.363(3)
U(1)-O(9)	1.769(3)	U(1)-O(4)#3	2.490(3)
U(1)-O(7)#1	2.324(3)	U(1)-O(3)#3	2.506(3)
U(1)-O(5)#2	2.357(3)	O(10)-U(1)-O(9)	178.69(12)
O(10)-U(1)-O(7)#1	93.18(11)	O(9)-U(1)-O(4)#3	89.03(12)
O(9)-U(1)-O(7)#1	87.83(11)	O(7)#1-U(1)-O(4)#3	74.80(9)
O(10)-U(1)-O(5)#2	90.59(11)	O(5)#2-U(1)-O(4)#3	152.36(9)
O(9)-U(1)-O(5)#2	90.44(11)	O(1)-U(1)-O(4)#3	124.95(9)
O(7)#1-U(1)-O(5)#2	77.56(9)	O(10)-U(1)-O(3)#3	88.26(11)
O(10)-U(1)-O(1)	89.78(11)	O(9)-U(1)-O(3)#3	90.47(12)
O(9)-U(1)-O(1)	89.55(11)	O(7)#1-U(1)-O(3)#3	127.17(9)
O(7)#1-U(1)-O(1)	160.04(10)	O(5)#2-U(1)-O(3)#3	155.26(9)
O(5)#2-U(1)-O(1)	82.68(9)	O(1)-U(1)-O(3)#3	72.61(9)
O(10)-U(1)-O(4)#3	90.43(12)	O(4)#3-U(1)-O(3)#3	52.38(9)

Table S2. Specified hydrogen bonds (with esds except fixed and riding H) for compounds **1** and **2**.

D-H	H···A	D···A	<(DHA)	
1				
0.85	2.24	3.024(13)	154.0	O1W-H2W···O3_\$1
0.85	2.46	2.956(12)	118.0	O1W-H1W···O2_\$2
0.98	2.87	3.222(12)	104.3	N1-H0A···O1W
0.98	2.11	2.619(8)	114.2	N1-H0A···O1
0.98	2.22	2.679(9)	110.5	N1-H0A···O4
2				
0.85	1.99	2.725(4)	144.2	O1W-H1W···O2_\$1
0.98	2.33	2.695(3)	101.2	N1-H1N···O1
0.98	2.03	2.633(4)	117.6	N1-H1N···O3
0.98	2.05	2.653(4)	117.4	N2-H2N···O6

Operators for generating equivalent atoms: For **1**: \$1 1-x, 0.5+y, 0.5-z; \$2 1-x, -0.5+y, 0.5-z. For **2**: \$1 -x+1, y, -z+3/2.

Table S3. EDS measurement results of compound 1.

Element	weight (%)	atom (%)		
C K	32.62	50.47		
O K	34.11	39.63		
F K	7.32	7.17		
Si K	1.21	0.80		
U M	24.74	1.93		
Total	100.00			