

Supporting Information for:

**[N(CH<sub>3</sub>)<sub>4</sub>][(UO<sub>2</sub>)<sub>2</sub>F<sub>5</sub>]: A New Organically Templated Open-Framework Uranium Oxide Fluoride (MUF-2)**

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S1. Calculated and observed powder X-ray diffraction pattern for [N(CH<sub>3</sub>)<sub>4</sub>][(UO<sub>2</sub>)<sub>2</sub>F<sub>5</sub>]

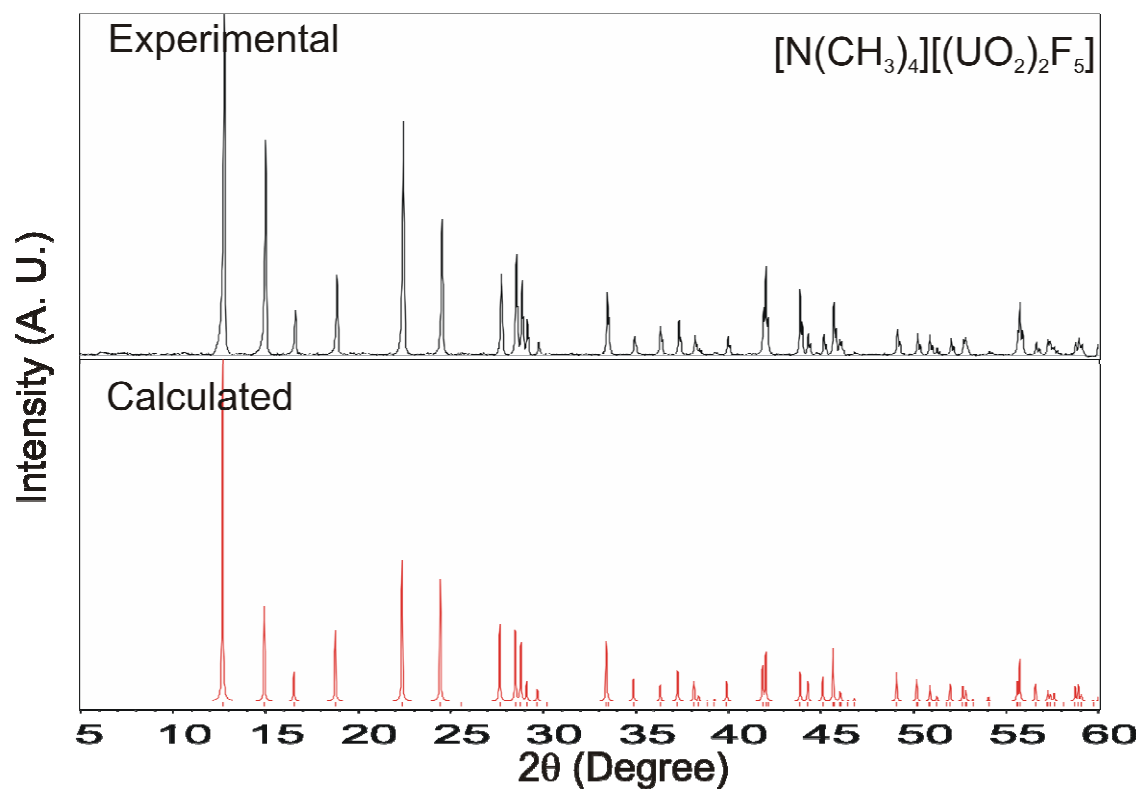
S2. Crystallographic data for [N(CH<sub>3</sub>)<sub>4</sub>][(UO<sub>2</sub>)<sub>2</sub>F<sub>5</sub>] and [N(CH<sub>3</sub>)<sub>4</sub>][(UO<sub>2</sub>)(NO<sub>3</sub>)<sub>3</sub>]

S3. Six-membered Ring (6-MR) Channels in [N(CH<sub>3</sub>)<sub>4</sub>][(UO<sub>2</sub>)<sub>2</sub>F<sub>5</sub>] along the (a) [100] and (b) [311] directions

S4. (a) Ball-and-stick representation in the bc-plane and (b) thermal ellipsoid view (50% probability) of zero-dimensional [N(CH<sub>3</sub>)<sub>4</sub>][(UO<sub>2</sub>)(NO<sub>3</sub>)<sub>3</sub>]

S5. Selected bond distances (Å) for [N(CH<sub>3</sub>)<sub>4</sub>][(UO<sub>2</sub>)<sub>2</sub>F<sub>5</sub>] and [N(CH<sub>3</sub>)<sub>4</sub>][(UO<sub>2</sub>)(NO<sub>3</sub>)<sub>3</sub>]

S1. Calculated and observed powder X-ray diffraction pattern for  $[\text{N}(\text{CH}_3)_4][(\text{UO}_2)_2\text{F}_5]$



22 S2. Crystallographic data for  $[\text{N}(\text{CH}_3)_4][(\text{UO}_2)_2\text{F}_5]$  and  $[\text{N}(\text{CH}_3)_4][(\text{UO}_2)(\text{NO}_3)_3]$

formula	$[\text{N}(\text{CH}_3)_4][(\text{UO}_2)_2\text{F}_5]$	$[\text{N}(\text{CH}_3)_4][(\text{UO}_2)(\text{NO}_3)_3]$
fw	710.21	530.21
crystal dimensions ( $\text{mm}^3$ )	$0.10 \times 0.10 \times 0.24$	$0.06 \times 0.08 \times 0.12$
color, habit	yellow, block	yellow, block
crystal system	tetragonal	monoclinic
space group	$I4_1/amd$ (No. 141)	$P2_1/c$ (No. 14)
$a$ (Å)	7.2721(10)	7.7670(16)
$b$	7.2721(10)	16.964(3)
$c$	23.632(5)	11.255(2)
$\beta$ (°)	90	105.98(3)
$V$ (Å <sup>3</sup> )	1249.7(4)	1425.7(5)
$Z$	4	4
$T$ (°C)	150.0(2)	150.0(2)
$\lambda$ (Å)	0.71073	0.71073
$\rho_{\text{calcd}}$ ( $\text{g cm}^{-3}$ )	3.770	2.470
$\mu$ ( $\text{mm}^{-1}$ )	25.945	11.444
$2\theta_{\text{max}}$ (deg)	54.94	54.96
no. of refln collected/unique	1259/418	5971/3221
absorption correction	multi-scan	multi-scan
GOF	1.007	0.89
$R(F)^a$	0.0209	0.0296
$R_w(F_o^2)^b$	0.0436	0.0585

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24  $^a R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$

25  $^b R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}.$

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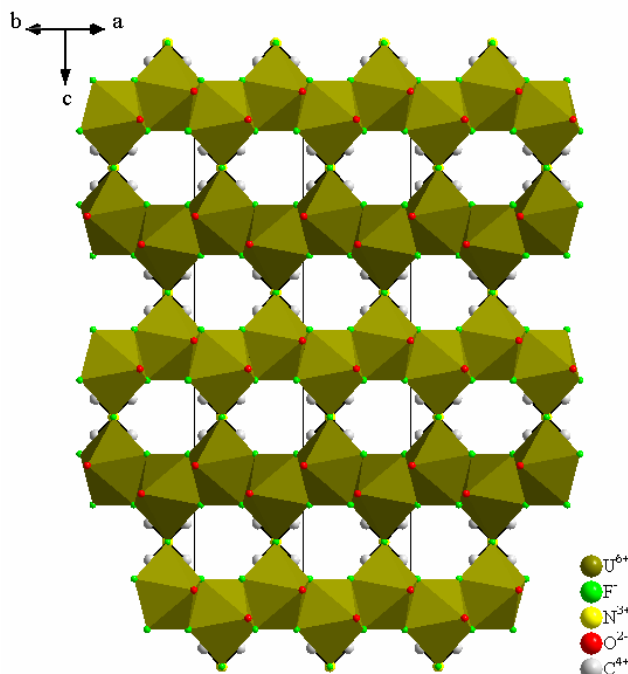
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S3. Six-membered Ring (6-MR) Channels in  $[\text{N}(\text{CH}_3)_4][(\text{UO}_2)_2\text{F}_5]$  along the (a)  $[100]$  and (b)  $[311]$  directions

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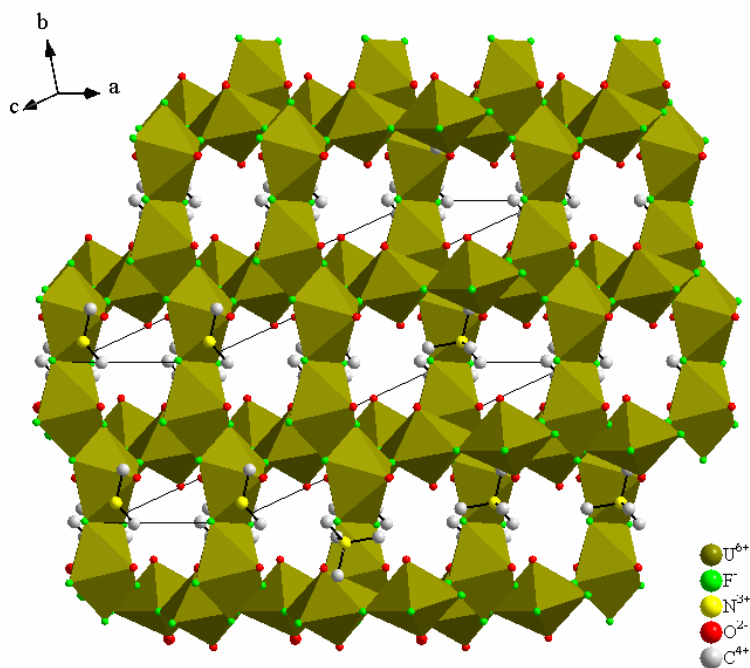
(a)



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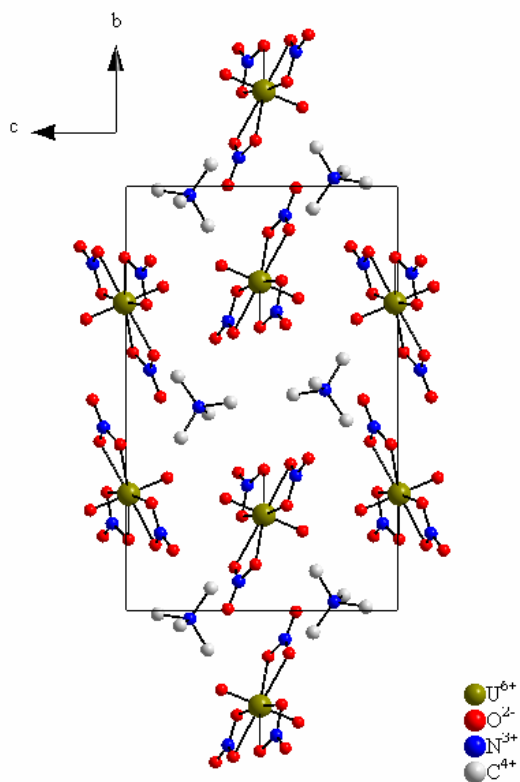
(b)



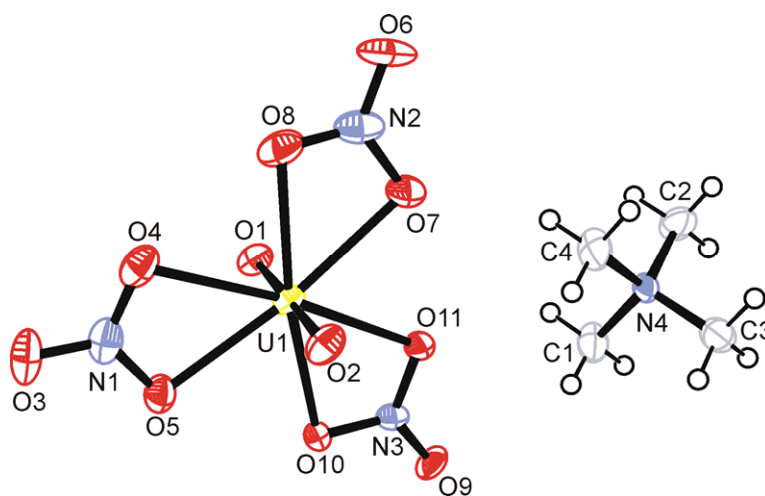
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S4. (a) Ball-and-stick representation in the *bc*-plane and (b) thermal ellipsoid view (50% probability) of zero-dimensional  $[\text{N}(\text{CH}_3)_4][(\text{UO}_2)(\text{NO}_3)_3]$

(a)



(b)



45 S5. Selected bond distances (Å) for  $[\text{N}(\text{CH}_3)_4][(\text{UO}_2)_2\text{F}_5]$  and  $[\text{N}(\text{CH}_3)_4][(\text{UO}_2)(\text{NO}_3)_3]$

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47  $[\text{N}(\text{CH}_3)_4][(\text{UO}_2)_2\text{F}_5]$

48 U(1)–O(1) × 2 1.769(5)

49 U(1)–F(1) × 2 2.323(4)

50 U(1)–F(1) × 2 2.327(4)

51 U(1)–F(2) 2.2803(6)

52 N(1)–C(1) × 4 1.491(9)

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54  $[\text{N}(\text{CH}_3)_4][(\text{UO}_2)(\text{NO}_3)_3]$

55 U(1)–O(1) 1.760(4)

56 U(1)–O(2) 1.758(4)

57 U(1)–O(4) 2.469(4)

58 U(1)–O(5) 2.460(4)

59 U(1)–O(7) 2.468(4)

60 U(1)–O(8) 2.448(4)

61 U(1)–O(10) 2.481(4)

62 U(1)–O(11) 2.475(3)

63 N(1)–O(3) 1.212(5)

64 N(1)–O(4) 1.291(6)

65 N(1)–O(5) 1.265(6)

66 N(2)–O(6) 1.204(6)

67 N(2)–O(7) 1.286(6)

68 N(2)–O(8) 1.289(6)

69 N(3)–O(9) 1.211(5)

70 N(3)–O(10) 1.298(5)

71 N(3)–O(11) 1.274(5)

72 N(4)–C(1) 1.495(7)

73 N(4)–C(2) 1.501(6)

74 N(4)–C(3) 1.491(7)

75 N(4)–C(4) 1.490(7)

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