Supplementary Information

Anionic Uranyl Oxyfluorides as a Bifunctional Platform for Highly Selective Ion-Exchange and Photocatalytic Degradation of Organic Dyes

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S1. EXPERIMENTAL SECTION

S1.1 Thermal Properties. TGA indicates that **MeUF** is stable up to 362 °C and starts to decompose between 362−514 °C due to the loss of the organic template (Fig. S3). The remaining residue can be attributed to UO_2F_2 and the total weight loss is 18.30% (*calcd*. 18.49%). For **EtUF-1**, the initial weight loss of 3.06% between 97−144 °C is due to the loss of coordinated water molecules (*calcd*. 3.41%). A sharp mass loss follows from 340–425 °C and the final weight loss (21.14%) equals the mass sum of one NEt_4 group and two moles of F (*calcd*. 22.25%). **EtUF-2** experiences a weight loss upon heating that is mainly due to the less robust nature of its 1D chained topology compared to the 3D or 2D structures of the other complexes. The sharp weight loss of 33.65% occurring between 327−421 °C could be originating from the loss of the template molecule and one mole of F (*calcd*. 32.64%). An additional mole of F is lost over the range of 421−900 °C with 3.80% weight loss (*calcd*. 4.16%). For **PrUF**, **BuUF-1,** and **BuUF-2**, TGA indicates an initial weight loss of 1.53% at 234 °C, 1.48% at 192 °C and 2.04% at 247 °C, respectively, which corresponds to the loss of coordinated water molecules (*calcd*. 1.57% for **PrUF**, 1.50% for **BuUF-1**, and 1.98% for **BuUF-2**). A rapid mass loss from 301−442 °C for **PrUF**, 325−390 °C for **BuUF-1**, and 289–385 °C for **BuUF-2** can be observed, owing to the loss of NPr_4^+ and one mole of F for **PrUF-1** (19.44%), one NBu_4^+ and two moles of F for **BuUF-1** (23.24%), or one NBu_4^+ and two moles of F for **BuUF-2** (22.19%) (*calcd*. 19.47% for **PrUF**, 23.22% for **BuUF-1**, and 21.11% for **BuUF-2**), respectively. Further heating resulted in more loss of F for all compounds.

S1.2 Geometrical optimization. Geometrical optimizations of the methylene blue (**MB**$^+$), ethyl violet (**EV**$^+$), rhodamine B (**RB**$^+$), Sudan III (**SD**^{0}), and charged acid orange 7 (**AO7**$^-$) in their ionized form, were performed by using the B3LYP16 exchange–correlation functional as incorporated in the Gaussian 09 computational program without any symmetry constraint.[1] Basis sets of 6-311G for S, O, N, C, and H atoms were applied. Harmonic vibrational frequency calculations were used to confirm that the vibrational frequencies of optimized structures were minimal. The dimensions of organic dye molecules in their ionized form from the calculation are shown in Table 1.

S1.3 Fourier Transform Infrared (FTIR) Spectra. The IR spectra of **MeUF**, **EtUF-1**, **EtUF-2**, **PrUF**, **BuUF-1**, and **BuUF-2** are shown in Fig. S10. The presence of water in **EtUF-1**, **PrUF-1**, **BuUF-1**, and **BuUF-2** was confirmed by the O−H stretching bands ranging from 3,000−3,600 cm^{-1} and the

H−O−H bending mode at approximately 1,600 cm^{-1}.[2] No water bands can be observed in the spectra of **MeUF** and **EtUF-2**. The U=O stretching bands are located at 850−970 cm^{-1}, 830−980 cm^{-1}, 820−930 cm^{-1}, 820−1,000 cm^{-1}, 830−990 cm^{-1}, and 850−1,000 cm^{-1} for **MeUF**, **EtUF-1**, **EtUF-2**, **PrUF**, **BuUF-1**, and **BuUF-2**, respectively. The peaks ranging from 440−500 cm^{-1} in each spectrum (excluding that for **EtUF-1**) can be attributed to the U−F stretching. The bands related to $-CH_3$ and $-CH_2-$ in NEt_4^+, NPr_4^+, and NBu_4^+ groups have been assigned decades ago and the stretching vibrations of $-CH_3$ and $-CH_2-$ are displayed in the range of 2,800−3,100 cm^{-1}. The bending vibrations of $-CH_3$ and $-CH_2-$ are found near 1,486−1,340 cm^{-1} and 740−780 cm^{-1}, respectively. The stretching vibration of C−C in **EtUF-1** and **EtUF-2** can be observed at approximately 1,170 cm^{-1}.

S1.4 Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS) Analysis. SEM images and EDS data were recorded on a Zeiss Merlin Compact LEO 1530 VP scanning electron microscope. The energy of the electron beam voltage was 10 keV for imaging and was 15 keV for quantitative identifications of elements. Samples were attached directly on the carbon conductive tape. The spectra acquisition time was 60 s and all EDS results are provided in Fig. S11.

S2. FIG.S AND TABLES

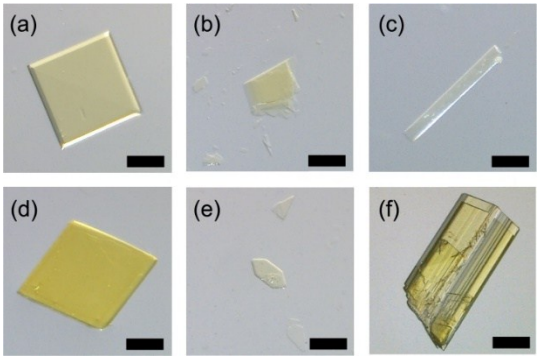

Fig. S1. Crystal images of (a) **MeUF**, (b) **EtUF-1**, (c) **EtUF-2**, (d) **PrUF**, (e) **BuUF-1**, and (f) **BuUF-2**. The black scale bars in the photographs represent 100 μm in length.

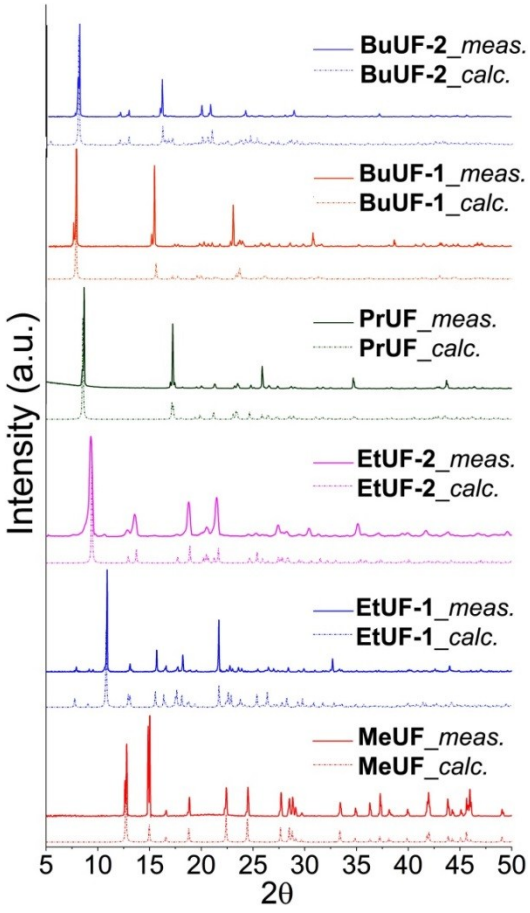

Fig. S2. PXRD patterns of **MeUF-1**, **EtUF-1**, **EtUF-2**, **PrUF**, and **BuUF-1**.

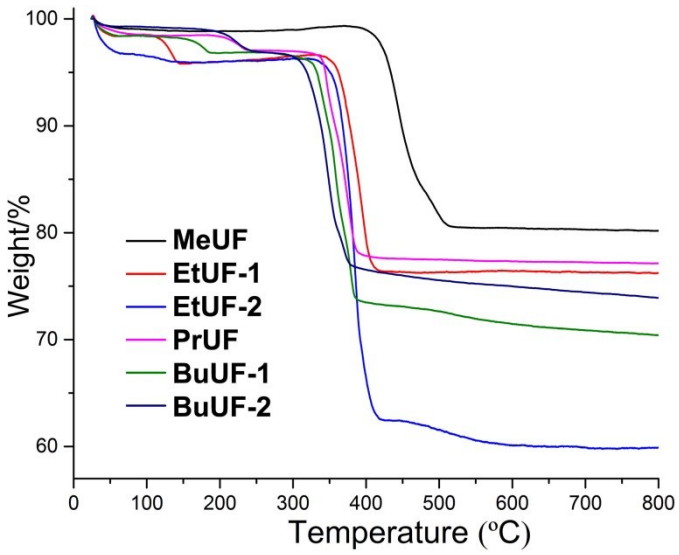

Fig. S3. Thermogravimetric curves of compounds **MeUF**, **EtUF-1**, **EtUF-2**, **PrUF**, **BuUF-1**, and **BuUF-2**.

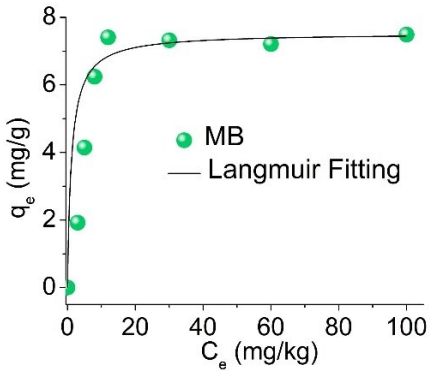

Fig. S4. The sorption isothermals of $\mathbf{MB}^{+}$ by **BuUF-2**.

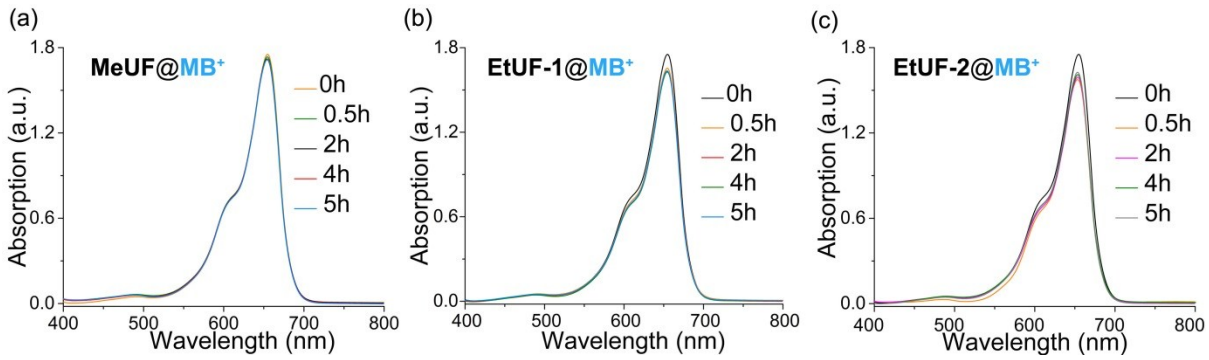

Fig. S5. UV-vis spectra of **MB**$^{+}$ solutions in the presence of (a) **MeUF**, (b) **EtUF-1**, (c) and **EtUF-2** monitored against time.

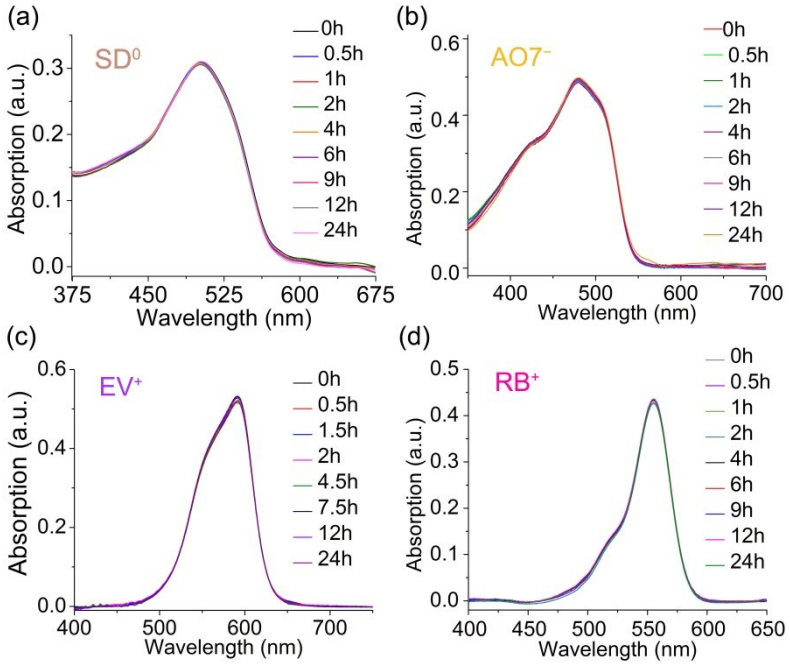

Fig. S6. UV-vis spectra of **SD**^{0}, **AO7**$^{-}$, **EV**$^{+}$, and **RB**$^{+}$ solutions in the presence of **BuUF-2** monitored against time.

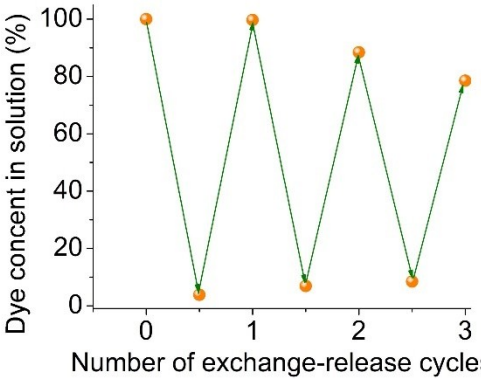

Fig. S7. The **MB**$^{+}$ concentration monitored for three adsorption-desorption cycles.

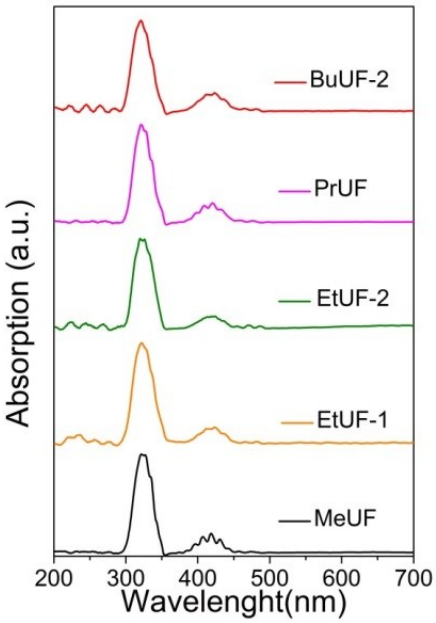

Fig. S8. UV-vis spectra of **MeUF**, **EtUF-1**, **EtUF-2**, **PrUF**, and **BuUF-2** crystals.

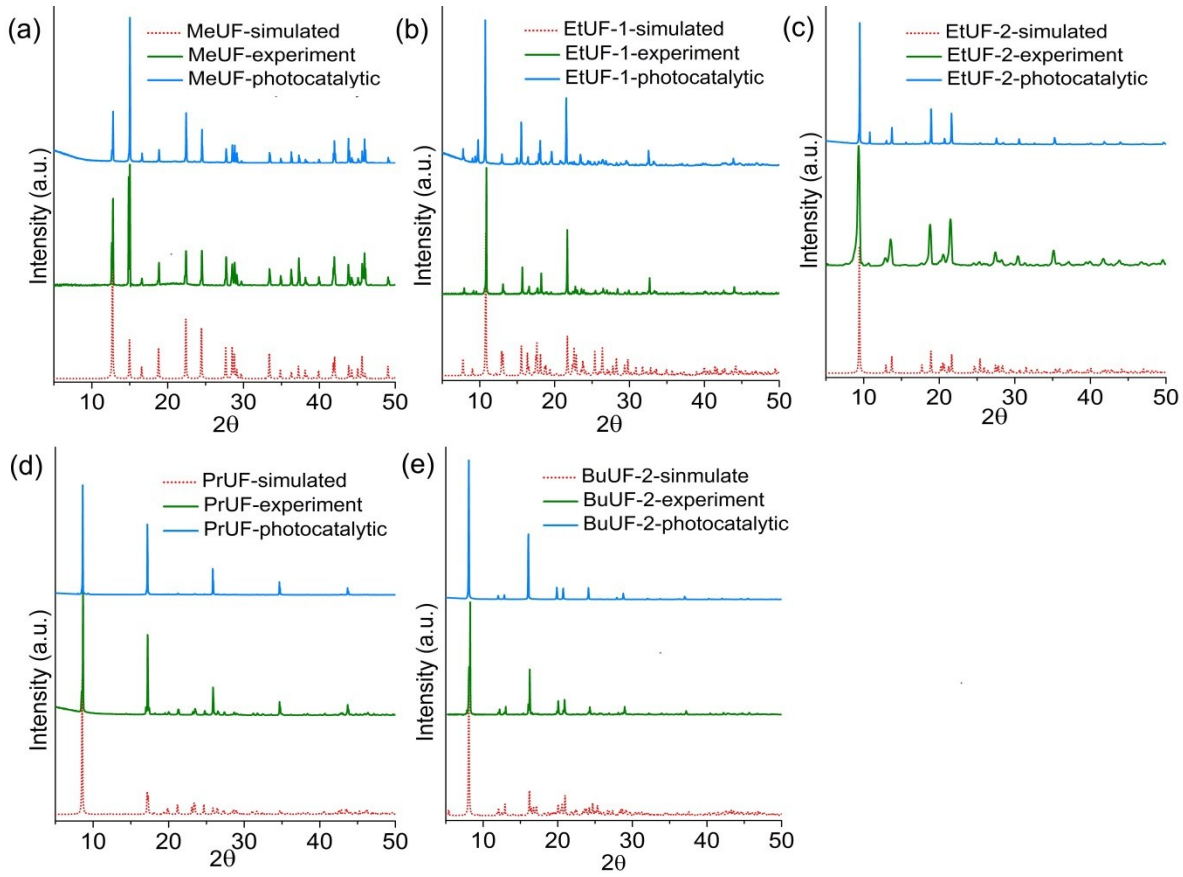

Fig. S9. Powder diffraction patterns of (a) **MeUF**, (b) **EtUF-1**, (c) **EtUF-2**, (d) **PrUF**, and (e) **BuUF-2** before and after photocatalysis experiments.

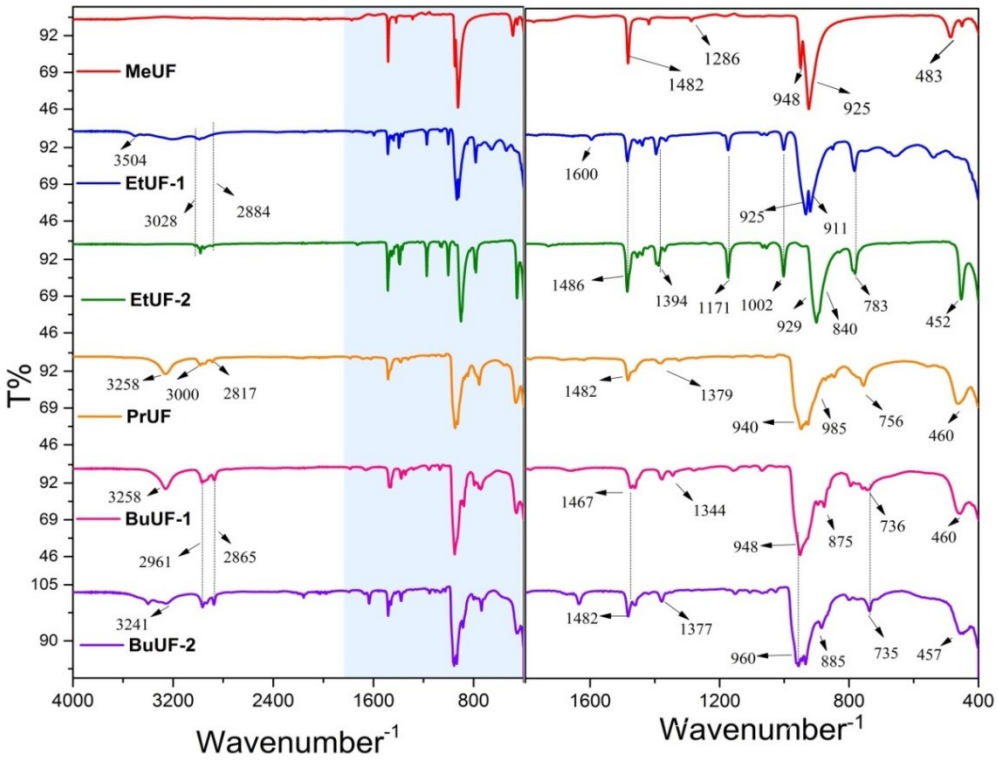

Fig. S10. FTIR spectra of compounds **MeUF-1**, **EtUF-1**, **EtUF-2**, **PrUF-1**, **BuUF-1**, and **BuUF-2**.

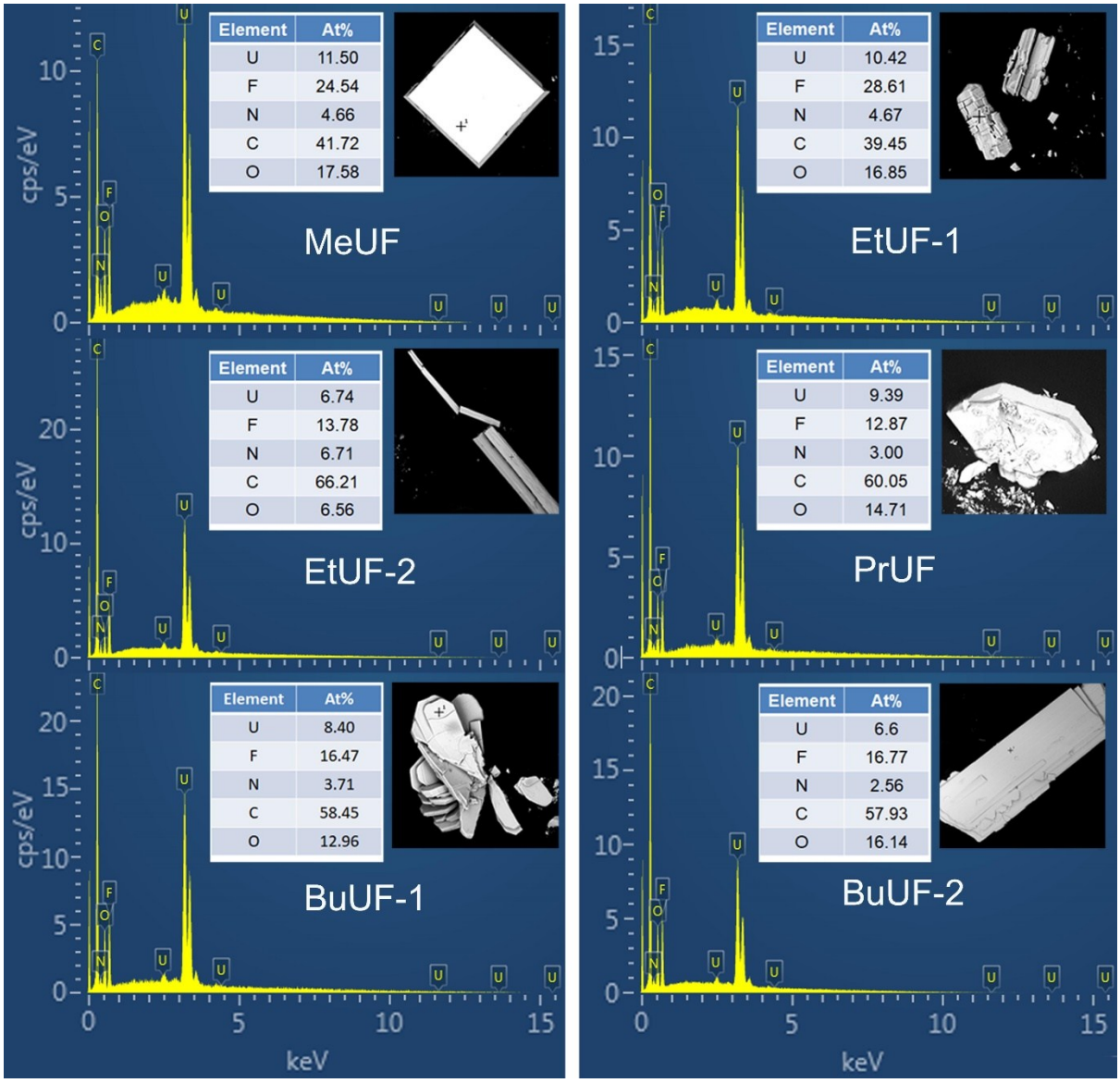

Fig. S11. SEM images and EDS spectra of **MeUF-1**, **EtUF-1**, **EtUF-2**, **PrUF**, **BuUF-1**, and **BuUF-2**.

Table S1. Crystallographic data for **MeUF-1**, **EtUF-1**, **EtUF-2**, **PrUF-1**, **BuUF-1**, and **BuUF-2**.

Compound	**MeUF**	**EtUF-1**	**EtUF-2**	**PrUF**	**BuUF-1**	**BuUF-2**
Formula	$U_2O_4F_5NC_4H_{12}$	$U_4O_{11}F_{10}N_2C_{16}H_{40}$	$UO_2F_3NC_8H_{20}$	$U_3O_8F_7$	$U_3O_7F_7C_{16}H_{36}$	$U_7O_{20}F_{16}N_2C_{32}H_{72}$
Colour	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
Habit	Block	Plate	Plate	Plate	Plate	Plate
Space Group	$I4_1/amd$	$P2_1/n$	$C2/c$	$Pbcm$	$P2/c$	P-1
a (Å)	7.2721(10)	13.8413(18)	14.5685(15)	9.8238(11)	11.9218(12)	9.7727(10)
b (Å)	7.2721(10)	15.531(2)	12.8961(13)	12.5892(16)	9.8442(10)	17.5281(19)
c (Å)	23.668(4)	16.556(2)	14.6415(14)	20.661(3)	12.5378(12)	19.726(2)
α (°)	90	90	90	90	90	73.920(5)
β (°)	90	98.762(4)	110.215(3)	90	101.924(3)	87.943(4)
γ (°)	90	90	90	90	90	78.166(4)
V (Å^3)	1251.6(4)	3517.7(8)	2581.4(4)	2555.2(5)	1439.7(2)	3177.0(6)
Z	4	4	8	4	2	2
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Maximum 2θ (°)	27.468	27.573	27.578	27.436	27.643	27.652
ρ_{calcd} (g cm^{-3})	3.764	2.981	2.353	2.493	2.772	2.851
μ (Mo Kα) (mm^{-1})	25.905	18.458	12.596	19.018	16.908	17.874
GoF on F^2	1.086	1.184	1.044	1.130	1.069	1.061
R_1,[a] wR_2 [$I > 2\sigma(I)$][b]	0.0302, 0.0661	0.0315, 0.0747	0.0246, 0.0655	0.0213, 0.0426	0.0342, 0.0656	0.0420，0.1161
R_1,[a] wR_2 (all data)[b]	0.0404, 0.0697	0.0414, 0.0774	0.0287, 0.0672	0.0321, 0.0449	0.0571, 0.0710	0.0608, 0.1275
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/e (Å^{-3})	1.793, -1.557	1.977, -2.347	1.741, -1.387	1.325, -1.505	1.940, -1.647	3.054，-3.256

[a] $R(F) = \sum \| F_o | - | F_o \| / \sum | F_o |$. [b] $R_w(F_o^2) = \left[\sum \left[w(F_o^2 - F_c^2)^2 \right] / \sum w F_o^4 \right]^{1/2}$

Table S2. Selected bond distances for **MeUF-1**, **EtUF-1**, **EtUF-2**, **PrUF-1**, **BuUF-1**, and **BuUF-2**.

	U(1)-O(1)	1.757(8)						
	U(1)-O(1)#1	1.758(8)						
	U(1)-F(1)	2.281(1)						
MeUF-1	U(1)-F(2)#2	2.322(6)						
	U(1)-F(2)#3	2.322(6)						
	U(1)-F(2)	2.337(6)						
	U(1)-F(2)#1	2.337(6)						
	U(1)-O(5)	1.764(6)	U(2)-O(8)	1.753(6)	U(3)-O(4)	1.767(6)	U(4)-O(7)	1.764(6)
	U(1)-O(3)	1.768(6)	U(2)-O(2)	1.769(6)	U(3)-O(6)	1.778(6)	U(4)-O(1)	1.771(6)
	U(1)-F(7)	2.194(4)	U(2)-F(2)	2.277(4)	U(3)-F(10)	2.178(6)	U(4)-F(5)	2.284(5)
EtUF-1	U(1)-F(9)	2.283(5)	U(2)-F(6)	2.284(5)	U(3)-F(6)	2.319(5)	U(4)-F(1)	2.284(4)
	U(1)-F(5)#1	2.309(5)	U(2)-F(9)	2.293(5)	U(3)-F(1)	2.340(4)	U(4)-F(3)	2.290(4)
	U(1)-OW2	2.426(5)	U(2)-F(3)#2	2.356(4)	U(3)-F(4)	2.343(4)	U(4)-F(4)	2.334(4)
	U(1)-OW1	2.544(5)	U(2)-F(8)	2.374(4)	U(3)-OW3	2.459(5)	U(4)-F(8)#3	2.394(4)
	U(1)-O(2)	1.791(4)						
	U(1)-O(1)	1.792(4)						
	U(1)-F(3)	2.162(4)						
EtUF-2	U(1)-F(2)	2.305(4)						
	U(1)-F(1)	2.319(3)						
	U(1)-F(1)#1	2.323(4)						
	U(1)-F(2)#2	2.341(3)						
	U(1)-O(3B)	1.658(8)	U(2)-O(1)#1	1.748(4)	U(3)-O(2)	1.751(4)		
	U(1)-O(3A)	1.863(8)	U(2)-O(1)	1.748(4)	U(3)-O(2)#1	1.751(4)		
PrUF-1	U(1)-F(7)	2.238(4)	U(2)-F(5)#3	2.265(4)	U(3)-F(7)#5	2.271(4)		
	U(1)-F(5)	2.282(4)	U(2)-F(1)	2.312(3)	U(3)-F(6)	2.291(4)		
	U(1)-F(1)	2.325(3)	U(2)-F(4)#4	2.329(3)	U(3)-F(3)	2.332(3)		

	U(1)-F(6)#2	2.342(4)	U(2)-F(2)	2.368(3)	U(3)-F(4)	2.333(3)		
	U(1)-O(4)	2.516(6)	U(2)-F(3)	2.390(3)	U(3)-F(2)	2.384(3)		
	U(1)-O(4)#1	2.516(6)						
	U(1)-O(3)#1	1.712(8)	U(2)-O(2)	1.736(9)				
	U(1)-O(3)	1.712(8)	U(2)-O(1)	1.780(8)				
	U(1)-F(4)	2.271(5)	U(2)-F(4)#2	2.252(5)				
BuUF-1	U(1)-F(4)#1	2.271(5)	U(2)-F(1)	2.292(4)				
	U(1)-F(1)#1	2.338(4)	U(2)-F(3)	2.3245(11)				
	U(1)-F(1)	2.339(4)	U(2)-F(2)	2.345(4)				
	U(1)-OW1	2.412(9)	U(2)-F(2)#3	2.377(4)				
	U(1)-O(1)	1.755(6)	U(2)-O(12)	1.763(8)	U(3)-O(6)	1.776(8)	U(4)-O(8)	1.769(8)
	U(1)-O(5)	1.778(8)	U(2)-O(11)	1.765(9)	U(3)-O(14)	1.776(8)	U(4)-O(7)	1.777(8)
	U(1)-F(8)	2.256(5)	U(2)-F(12)	2.274(5)	U(3)-F(12)	2.297(5)	U(4)-F(6)	2.277(5)
	U(1)-F(7)	2.326(5)	U(2)-F(11)	2.301(5)	U(3)-F(8)	2.317(5)	U(4)-F(4)	2.304(5)
	U(1)-F(14)	2.335(5)	U(2)-F(14)	2.335(5)	U(3)-F(6)#2	2.320(5)	U(4)-F(10)#2	2.327(5)
	U(1)-F(1)	2.358(5)	U(2)-F(5)#1	2.344(5)	U(3)-F(11)#3	2.328(5)	U(4)-F(3)	2.359(5)
BuUF-2	U(1)-F(3)	2.382(5)	U(2)-F(5)	2.378(5)	U(3)-OW2	2.449(7)	U(4)-F(1)	2.374(5)
	U(5)-O(9)	1.765(9)	U(6)-O(10)	1.773(7)	U(7)-O(13)	1.756(9)		
	U(5)-O(3)	1.774(9)	U(6)-O(4)	1.775(7)	U(7)-O(2)	1.765(9)		
	U(5)-F(9)	2.277(5)	U(6)-F(4)	2.277(5)	U(7)-F(15)	2.276(5)		
	U(5)-F(16)	2.309(6)	U(6)-F(7)#5	2.312(5)	U(7)-F(10)	2.317(5)		
	U(5)-F(13)#4	2.340(5)	U(6)-F(15)#2	2.330(5)	U(7)-F(16)	2.341(6)		
	U(5)-F(13)	2.345(5)	U(6)-F(9)	2.371(5)	U(7)-F(2)	2.388(5)		
	U(5)-F(2)	2.380(5)	U(6)-OW1	2.456(6)	U(7)-OW3	2.471(7)		

Table S3 Kinetic parameters of the pseudo-second-order model for **MB**$^{+}$ adsorption on **PrUF** and **BuUF-2**.

	c_0	M/V	q_0	Removal	Second-order kinetic model			
	($mg \cdot kg^{-1}$)	($mg \cdot g^{-1}$)	($mg \cdot g^{-1}$)	(%)	q_e ($mg \cdot g^{-1}$)	h ($mg \cdot g^{-1} \cdot h^{-1}$)	k ($g \cdot mg^{-1} \cdot h^{-1}$)	R^2
PrUF	4	5	0.8	70.0	0.5359	0.1267	0.4413	0.9861
BuUF-2	4	5	0.8	96.6	0.7725	1.5918	2.6675	0.9992

S3. REFERENCES

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