

## Modulating coordination microenvironment of uranyl compounds for enhance photocatalytic CO<sub>2</sub> reduction

Zhi-Wei Huang,<sup>a, b</sup> Shu-Wen An,<sup>\*c</sup> Kong-Qiu Hu,<sup>\*b</sup> Xiao-Bo Li,<sup>b</sup> Zhi-Ni Bin,<sup>b</sup> Zhi-Heng Zhou,<sup>b</sup> Lei Mei,<sup>b</sup> Zhi-Jun Guo,<sup>a</sup> Wang-Suo Wu,<sup>a</sup> Zhi-Fang Chai,<sup>d</sup> and Wei-Qun Shi <sup>\*b</sup>

<sup>a</sup> Radiochemistry Laboratory, School of Nuclear Science and Technology, Lanzhou University, Lanzhou 730000, China

<sup>b</sup> Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

<sup>c</sup> College of Nuclear Technology and Automation Engineering, Chengdu University of Technology, Chengdu 610059, China

<sup>d</sup> Engineering Laboratory of Advanced Energy Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

\* E-mail: Shu-Wen An (anshuwen@cdu.edu.cn); Kong-Qiu Hu (hukq@ihep.ac.cn); Wei-Qun Shi ([shiwq@ihep.ac.cn](mailto:shiwq@ihep.ac.cn)).

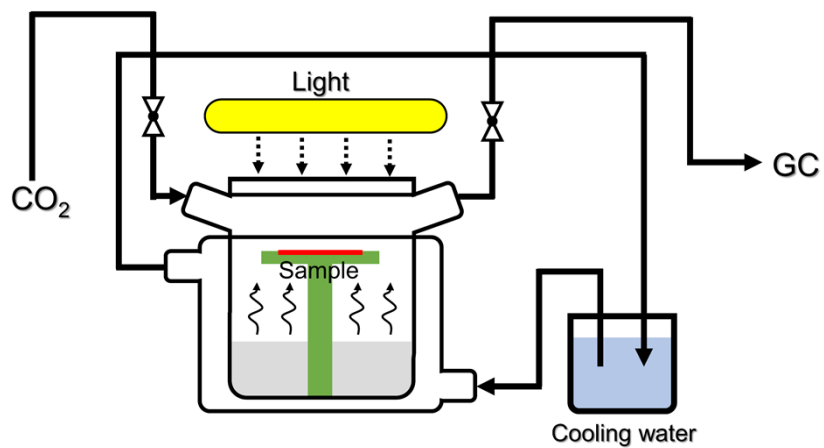


Figure S1. Schematic diagram of CO<sub>2</sub> photo-reduction system.

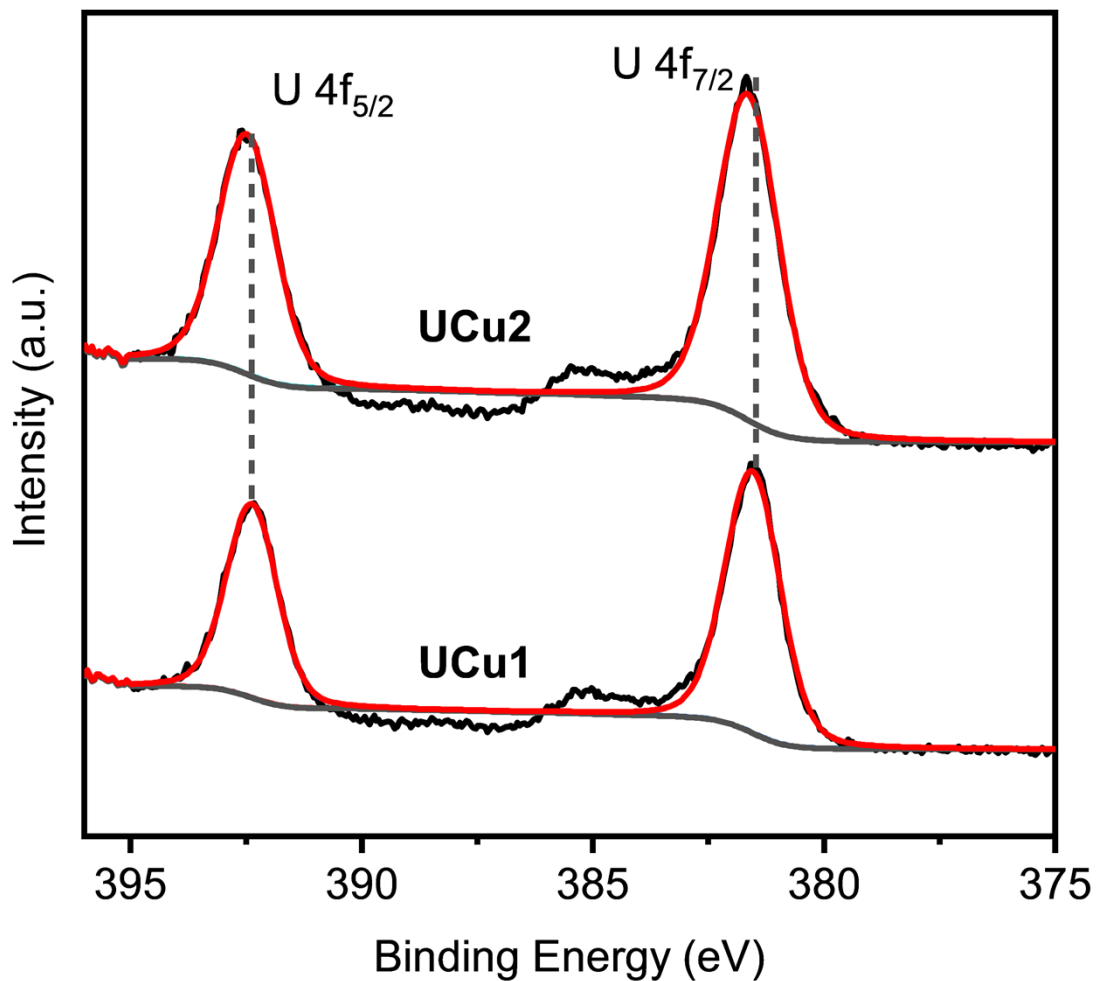


Figure S2. U 4f high resolution XPS spectra of the UCu1 and UCu2.

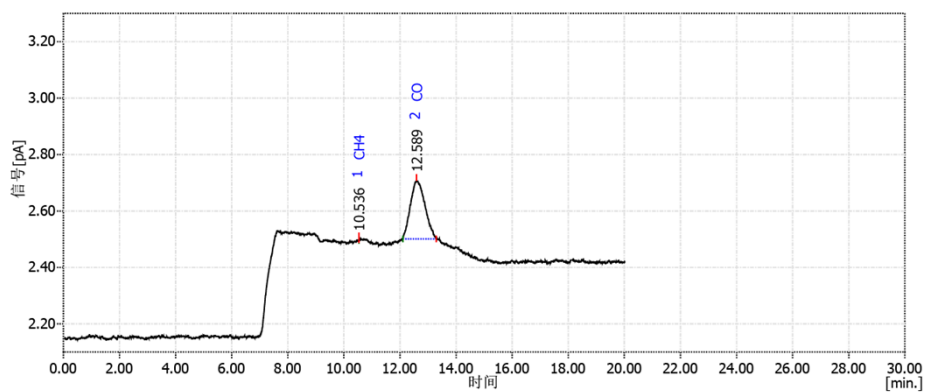


Figure S3. The gas products from photocatalytic CO<sub>2</sub> reduction analyzed by GC with FID detector.

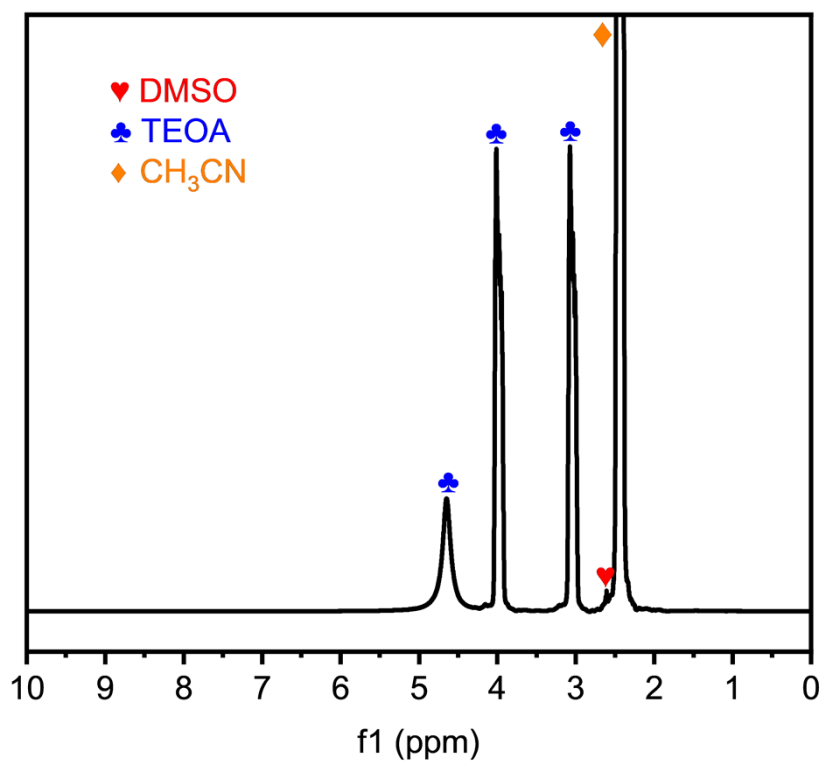


Figure S4. <sup>1</sup>H NMR spectrum of the liquid reaction products.

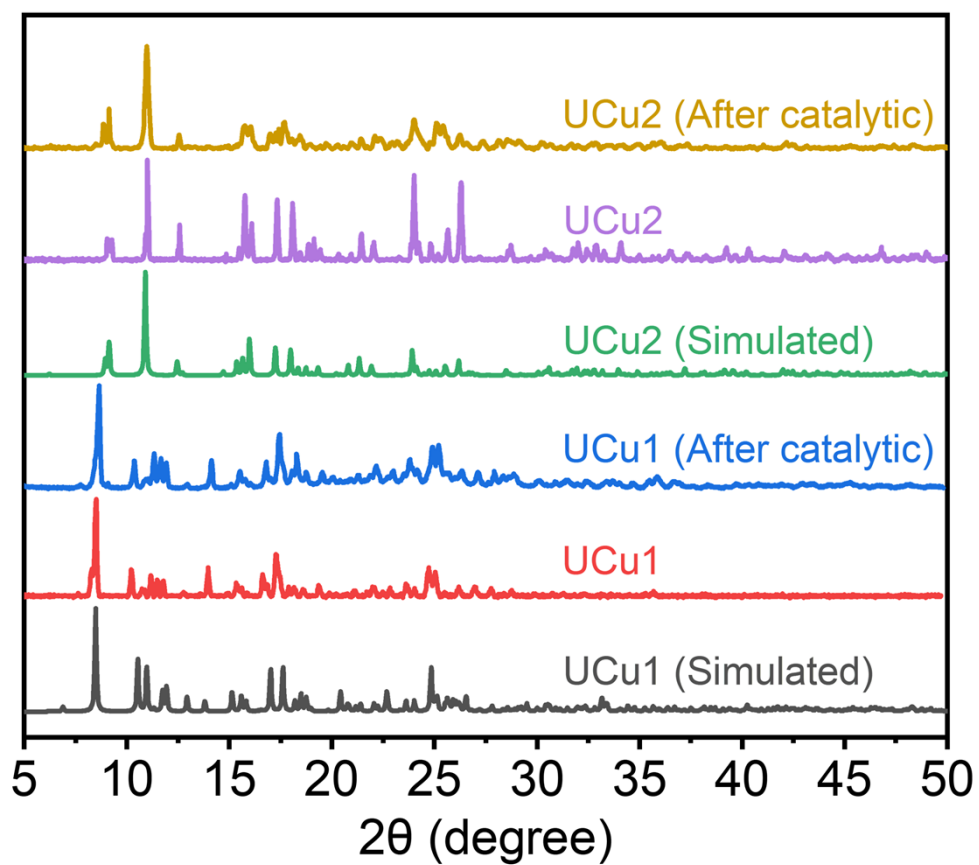
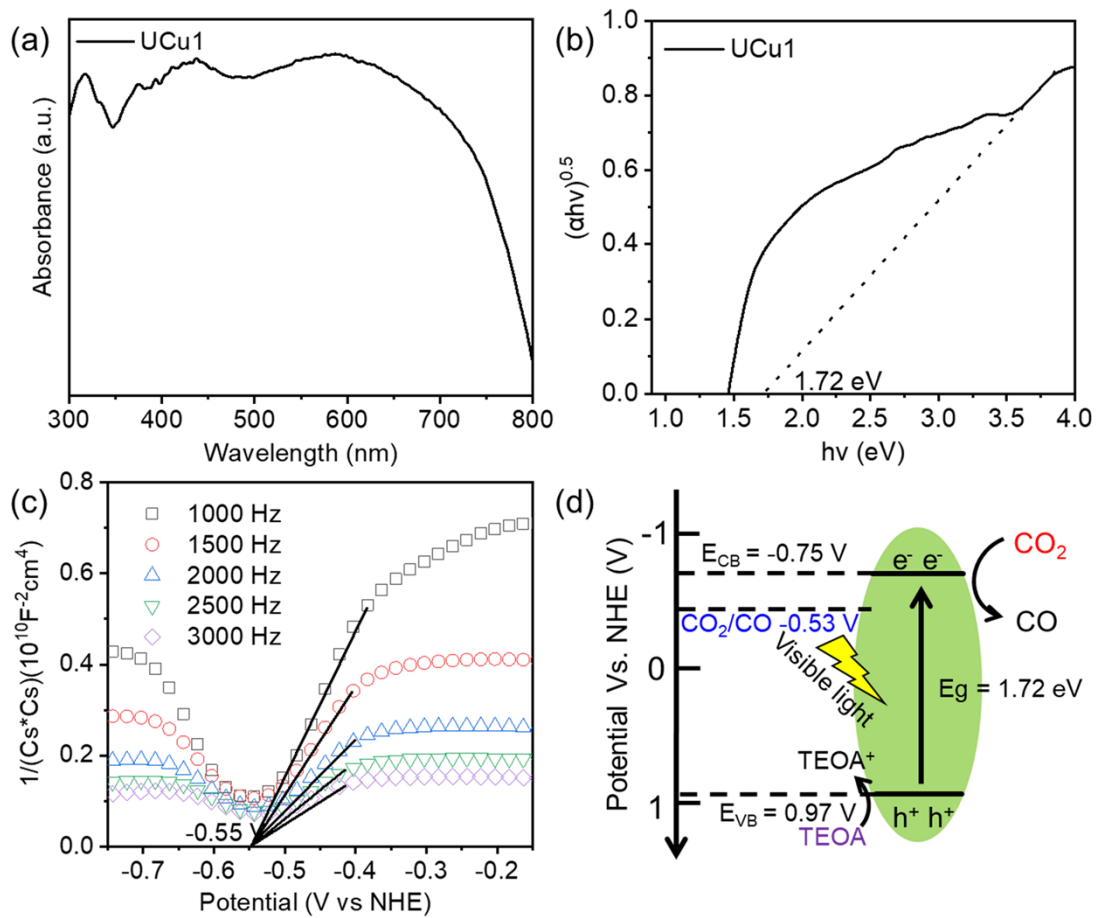


Figure S5. The PXRD patterns for the UCu1 and UCu2 before and after photocatalysis.



**Figure S6.** (a) The UV-Vis DRS spectrum of **UCu1**. (b) The corresponding plots of the  $(\alpha h\nu)^{0.5}$  versus photon energy ( $h\nu$ ) for **UCu1**. (c) The Mott-Schottky plots of **UCu1**. (d) The energy level diagram of **UCu1**.

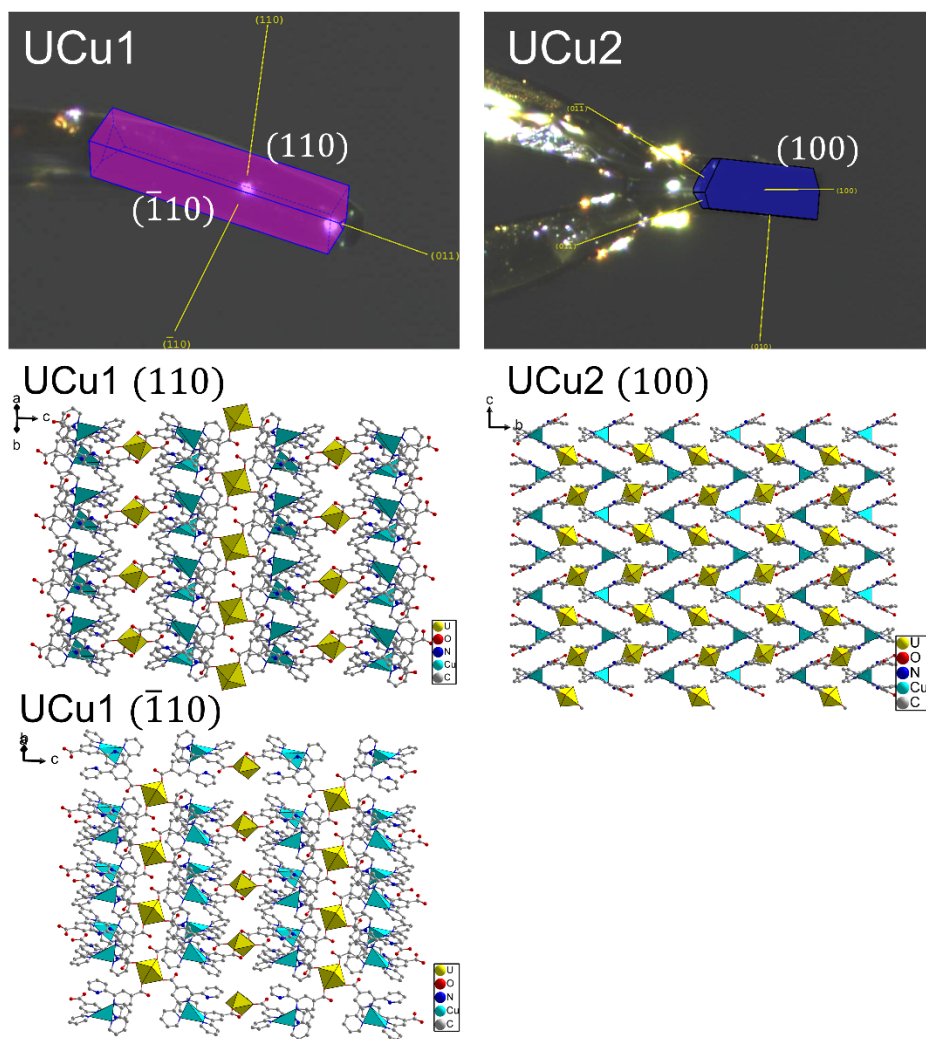
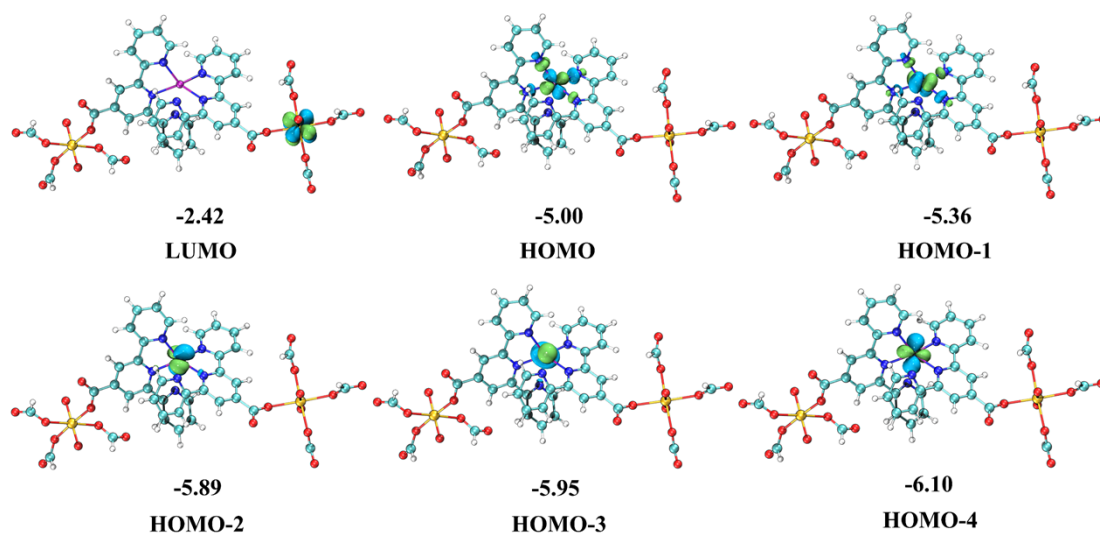
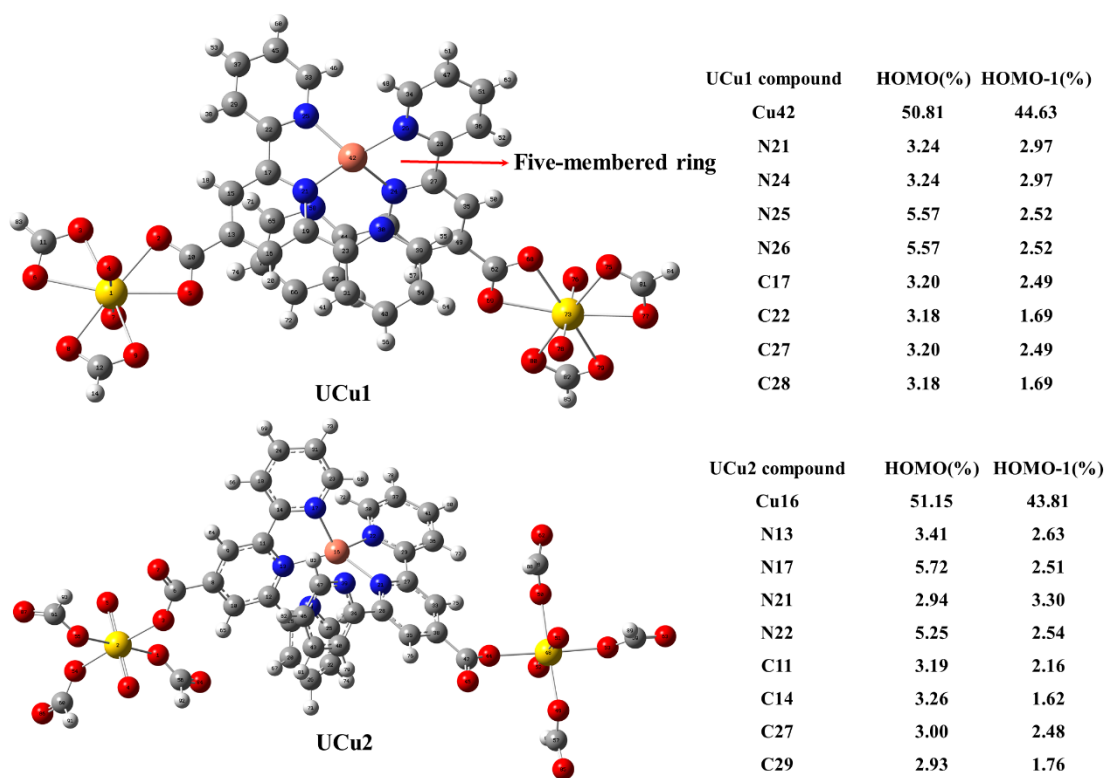


Figure S7. Crystal face index analyses of UCu1 and UCu2.



**Figure S8.** Frontier molecular orbital diagrams of **UCu1** complex in ACN solution at the B3LYP/ECP60MWB/def2-TZVP level of theory and the corresponding energies (eV). Yellow, purple, red, blue, cyan, and white balls represent U, Cu, O, N, C, and H atoms, respectively.



**Figure S9.** The structures of **UCu1** and **UCu2** compounds with the atom labels and the corresponding atom compositions of the HOMO and HOMO-1 orbitals.



**Table S1.** Selected Bond Lengths for **UCu1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
U1	O1	2.282(3)	Cu1	N1	2.032(3)
U1	O2	1.773(3)	Cu1	N2	2.088(3)
U1	O4 <sup>1</sup>	2.276(3)	Cu1	N5	2.063(3)
Cu1	N6	2.065(3)			

<sup>1</sup>2-X,-1/2+Y,1/2-Z;**Table S2.** Selected Bond Angles for **UCu1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1 <sup>1</sup>	U1	O1	180.0	N1	Cu1	N6	109.31(12)
O2	U1	O1	88.66(14)	N1	Cu1	N5	149.89(13)
O2	U1	O1 <sup>1</sup>	91.34(14)	C6	N2	Cu1	110.4(2)
O4 <sup>2</sup>	U1	O1	87.79(11)	C5	N2	Cu1	125.8(2)
O4 <sup>2</sup>	U1	O1 <sup>1</sup>	92.21(11)	C1	O4	U1 <sup>4</sup>	145.7(3)
O4 <sup>3</sup>	U1	O2	89.00(16)	C28	N6	Cu1	113.5(2)
O4 <sup>3</sup>	U1	O2 <sup>1</sup>	91.00(16)	C32	N6	Cu1	127.5(3)
C25	O1	U1	149.6(3)	C22	N5	Cu1	126.2(2)
N6	Cu1	N2	138.12(12)	C27	N5	Cu1	112.7(2)
N5	Cu1	N2	111.82(11)	C7	N1	Cu1	114.0(2)
N5	Cu1	N6	80.35(11)	C11	N1	Cu1	128.0(3)
N1	Cu1	N2	80.56(11)				

<sup>1</sup>2-X,-Y,1-Z; <sup>2</sup>+X,1/2-Y,1/2+Z; <sup>3</sup>2-X,-1/2+Y,1/2-Z; <sup>4</sup>+X,1/2-Y,-1/2+Z

**Table S3.** Selected Bond Lengths for **UCu2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
U1	O3	2.441(3)	U1	C9	2.867(3)
U1	O2	1.750(4)	U1	C17	2.799(7)
U1	O4	2.545(3)	N2	Cu1	2.069(3)
U1	O1	1.752(4)	Cu1	N1	2.035(3)
U1	O5	2.449(3)			

**Table S4.** Selected Bond Angles for **UCu2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O3 <sup>1</sup>	U1	O4	114.64(9)	C6	N2	Cu1	127.7(2)
O3	U1	O5 <sup>1</sup>	121.82(10)	N2 <sup>2</sup>	Cu1	N2	116.19(16)
O3	U1	O5	173.25(12)	N1 <sup>2</sup>	Cu1	N2	138.82(11)
O2	U1	O1	179.4(2)	N1	Cu1	N1 <sup>2</sup>	110.34(17)
O4 <sup>1</sup>	U1	O4	165.81(12)	C12	N1	Cu1	113.9(2)
O5	U1	O4	123.44(9)	C16	N1	Cu1	128.2(2)
C11	N2	Cu1	111.5(2)				

<sup>1</sup>1-X,+Y,+Z; <sup>2</sup>3/2-X,+Y,1/2-Z