Supporting Information

On the Maximum Bond Multiplicity of Carbon: Unusual C≣U Quadruple Bonding in Molecular CUO

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Table S1. Energy decomposition of C-U bonding in selected R_nCUE compounds

	ΔE(Pauli) /eV [a]	ΔE(elect) /eV [b]	ΔE(orb) /eV [c]	BDE/eV[d]
$H_2C{=}\ddot{U}F_2$	25.8809	-8.0185	-22.0219	-4.2
$FC{\equiv}UF_3$	30.1254	-8.5433	-28.7394	-7.2
$HC{\equiv}UF_3$	33.4349	-9.4762	-29.7765	-5.8
$NaC{\equiv}UF_3$	41.7001	-11.7500	-34.8090	-4.9
$^{-}C{\equiv}UF_3$	43.0414	-12.0936	-36.8392	-5.9
$C{\equiv}UN^{-}$	43.9752	-11.8310	-43.6975	-11.6
$C{\equiv}UF_2$	47.0433	-13.2149	-42.6037	-8.8
$C{\equiv}U(OH)^{+}$	52.5665	-14.2837	-46.6299	-8.4
$C{\equiv}UNe^{2+}$	48.3145	-13.9878	-43.1496	-8.8
$C{\equiv}UF^{+}$	51.1906	-14.3855	-46.2595	-9.4
C≣UO	48.8109	-13.4758	-45.5224	-10.2

[a] Energy of Pauli repulsion [b] Energy of electrostatic interaction [c] Energy of orbital interaction [d] The sum of ΔE(Pauli) and ΔE(elect) represents the steric energy (ΔE_{ster}), and BDE = ΔE_{ster} + ΔE(orb).

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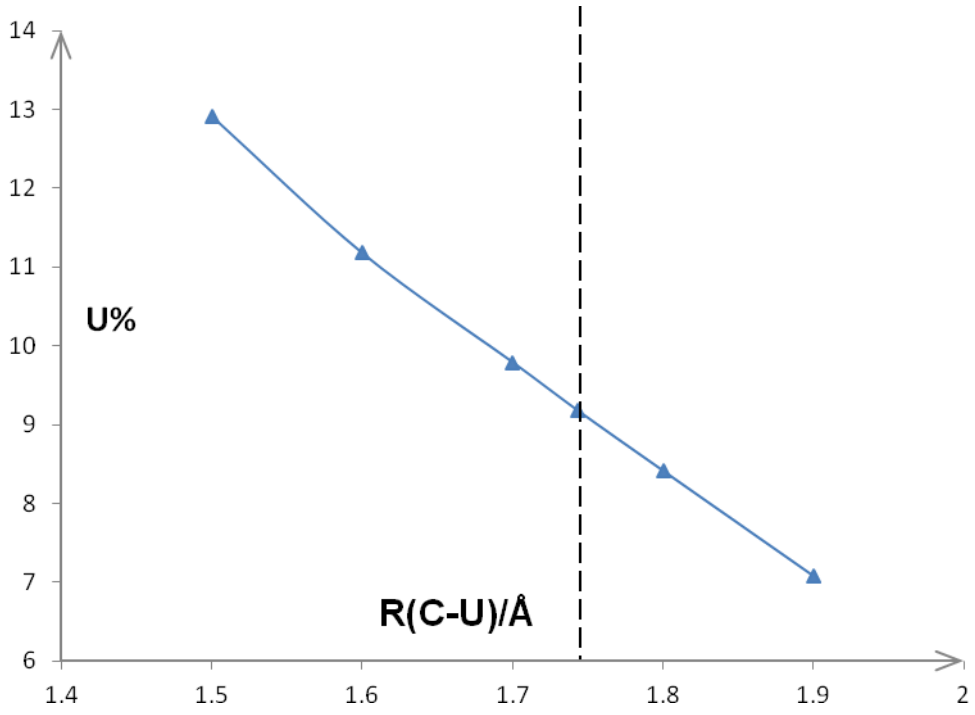

Figure S1. Percentage of U orbitals in the Weinhold natural localized molecular orbitals (NLMO) of the C→U rearward σ-bond, calculated using the B3LYP functional. The vertical dashed bar denotes the optimized C-U distance.

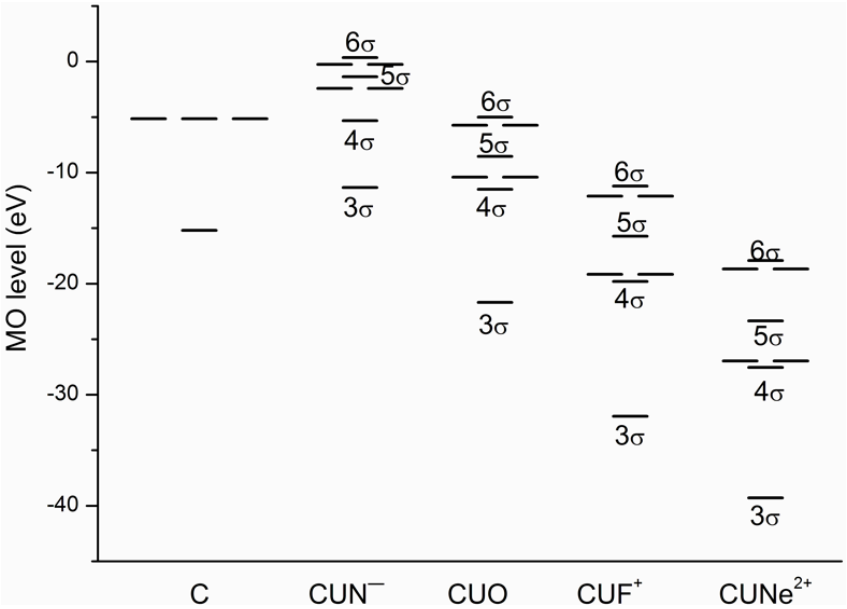

Figure S2 Kohn-Sham occupied orbital energy levels (in eV) of C, CUN^-, CUO, CUF^+ and $CUNe^{2+}$ calculated using B3LYP functional, SR-ZORA Hamiltonian, and TZ2P basis sets. The 3σ and 4σ orbitals are mainly from the heteroatom X 2s and C 2s, respectively.

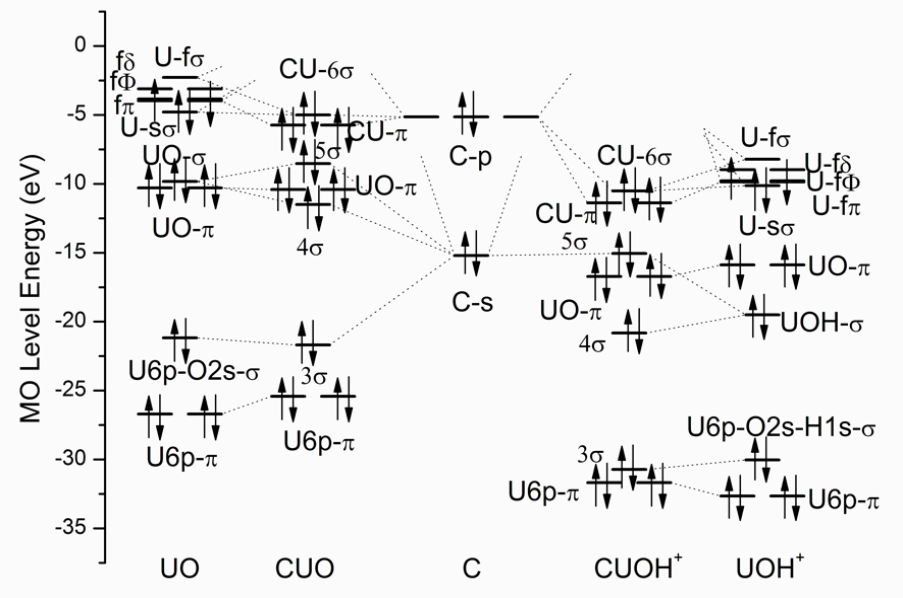

Figure S3 Kohn-Sham orbital energy levels (in eV) calculated using B3LYP functional, SR-ZORA Hamiltonian, and TZ2P basis sets. The 4σ orbital mainly represents the rearward σ-bond involving C 2s orbital. Left panel: C, UO and CUO. Right panel: C, $U(OH)^+$ and $CU(OH)^+$

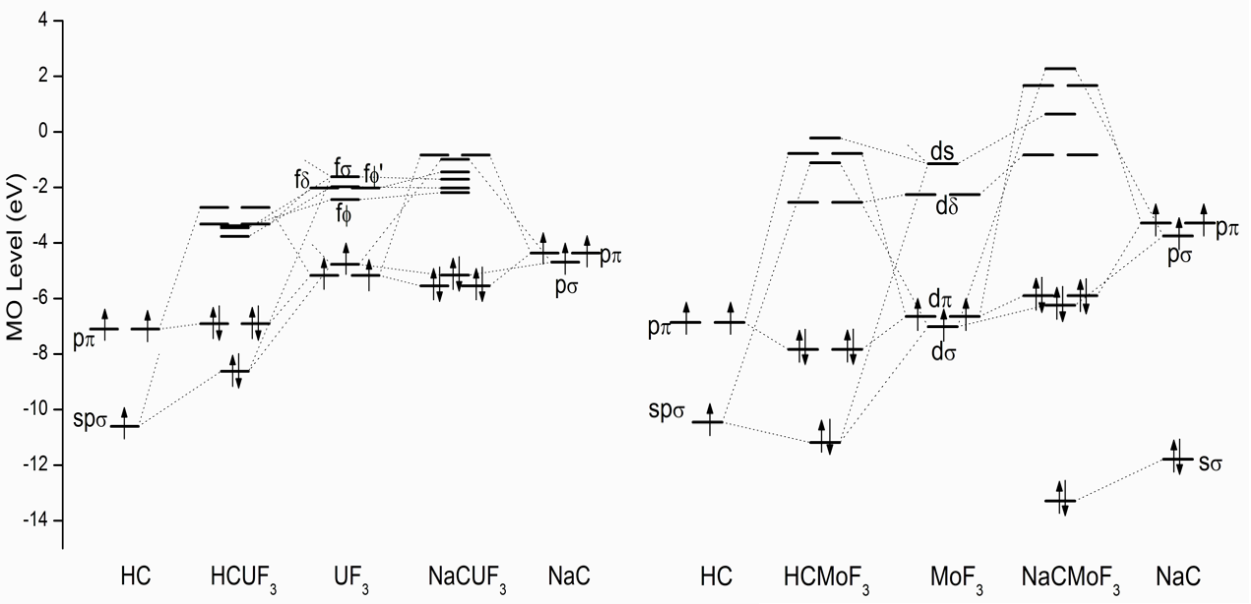

Figure S4 Kohn-Sham orbital energy levels (in eV) calculated using B3LYP functional, SR-ZORA Hamiltonian, and TZ2P basis sets. Left panel: HC, $HC{\equiv}UF_3$, UF_3, $NaC{\equiv}UF_3$ and NaC. Right panel: U substituted by Mo

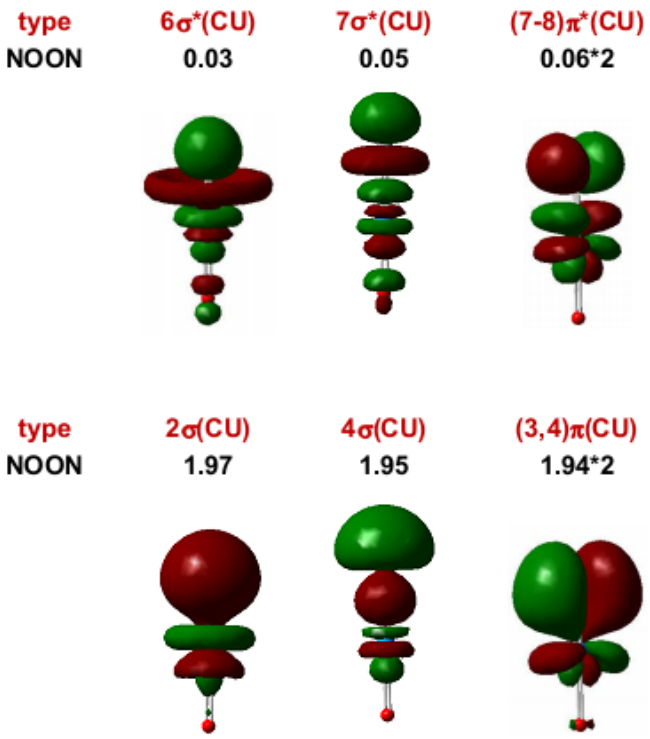

Figure S5 Natural valence orbitals of the CUO molecule (top atom – C, middle – U, bottom O) from CASSCF (8e,8o): orbital types, Löwdin natural orbital occupation numbers NOON, and contour surfaces (0.05 au). The Weinhold bond order from the CAS(8o,8e) calculation is 3.44.

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