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Atomic Layer Deposition of Cu(I) Oxide films using Cu(II) bis(dimethylamino-2-propoxide) and Water

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Section 1: Experimental Details

Materials AT-cut quartz crystals (Colnatech) were rinsed with acetone and then isopropanol before being blown dry under flowing N_2. Metal precursors tested in this study included trimethylaluminum (TMA, Sigma Aldrich), titanium tetraisopropoxide (TTIP, Strem Chemical Inc.) and Copper (II) bis(dimethylamino-2-propoxide) ($Cu(dmap)_2$, Strem Chemical Inc.). $Cu(dmap)_2$ was heated to 100 °C, as published,[1-2] with no vapor pressure observed at lower temperatures. TTIP was heated to 90 °C. Millipore water (18MΩ, Milli-Q system) and ultra-high purity compressed O_2 were used as oxygen sources for ALD.

ALD Instrumentation. Measurements were carried out on in a Savannah 200 ALD reactor (Cambridge Nanotech, Inc.) under a constant 20 sccm flow of N_2. The lid was modified as previously reported[2] to accommodate two QCM crystals that are oscillated by a commercial thin-film deposition monitor (Inficon, SQM-160). Crystal preparation includes thermal equilibration of the crystal[2] and undercoating with 5 nm Al_2O_3. QCM Crystals were equilibrated at the reactor temperature and under vacuum for ~45 min to ensure optimal thermal stability and full desorption of physisorbed species. Conventional metal oxide deposition "AB cycle" sequence was used (t1-t2-t3-t4) were t1 is the pulse time for the metal precursor, t3 is the pulse time for water, and t2 and t4 are the purge times for the metal precursor and water, respectively. Purge times for t4 (O_2 and water) and TMA (t2) was 30 s. Pulse times (t1 and t3) for TMA, O_2, and water were 15 ms, while $Cu(dmap)_2$ pulse and purge (t1 and t2 respectively) varied as indicated in the text. TTIP was pulsed for 150 ms. All processes have upper ALD window limits of at

least 130°C and in all cases we have used standard dose and purge times as optimized by the tool manufacturer and verified in our lab.

QCM data analysis. Similar to previous studies, data acquired by the *in-situ* QCM tool used for this study used a fixed assumed Cu_2O density value of 6.00 g/cm^2 when converting from mass gain (ng/cm^2) to thickness (Å).[2-3] Additionally, the growth rate was adjusted for the roughness of the unpolished crystals used by measuring against the growth rate of Al_2O_3 by TMA and water. Ellipsometry (A.J.A. Woolam Co. M2000) was performed on the silicon witness chip to confirm the growth rate measured by QCM.

Section 2: Growth rate and *in-situ* QCM study supporting information

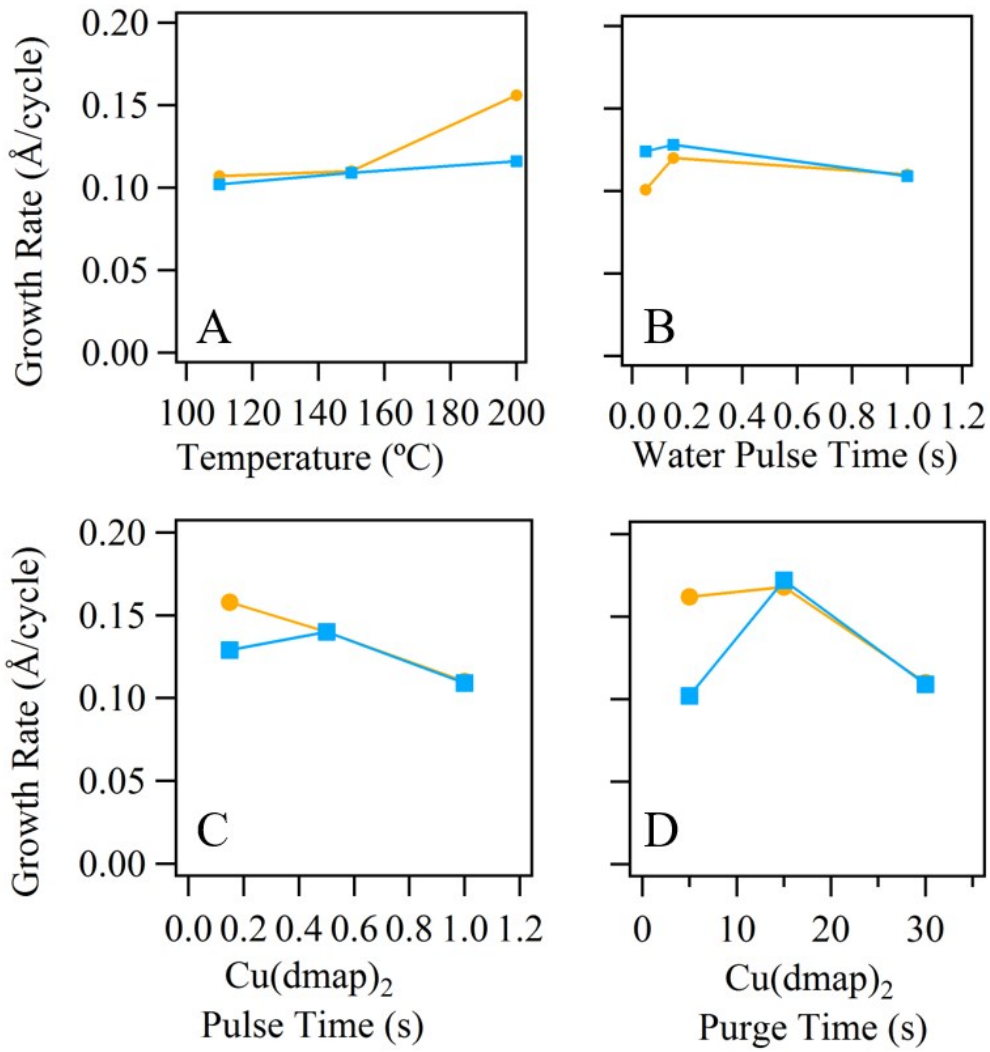

Figure S1: Growth rates of $Cu(dmap)_2$ with water as measured by QCM near the inlet (orange circles) and the outlet (blue squares) of the reactor at various reactor temperatures (A), water pulse time (B), copper precursor pulse time (C), and copper precursor purge time (D).

Figure S1 shows the growth rate measured by QCM of Cu_xO at various reaction conditions. Figure S1-A shows a clear growth profile near the inlet of the reactor at 200 ºC, which is attributed to the decomposition of the $Cu(dmap)_2$ precursor.[3] Figure S1-B shows little to no change in growth rate for

water pulse, with a slight deviation at 15 ms. Figure S1-C and D shows there is only a profile during low $Cu(dmap)_2$ pulse and purging, which is due to the inability to deliver precursor or remove unreacted precursor, respectively. It should be noted all growth rates averaged at 0.12±0.02 Å/cycle and were corroborated using ellipsometry.

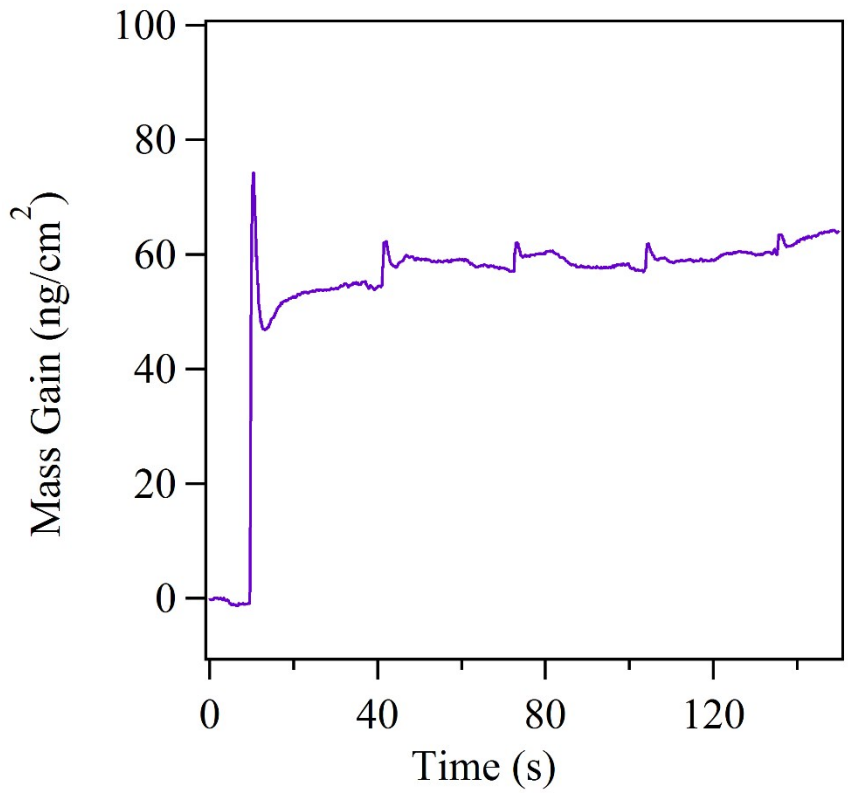

Figure S2: $Cu(dmap)_2$ QCM trace with water exposure on Al_2O_3 undercoat.

Figure S2 shows the deposition of $Cu(dmap)_2$ without water. It is observed that no mass gain beyond the first 2 cycles is observed indicating the $Cu(dmap)_2$ precursor is self-limiting.

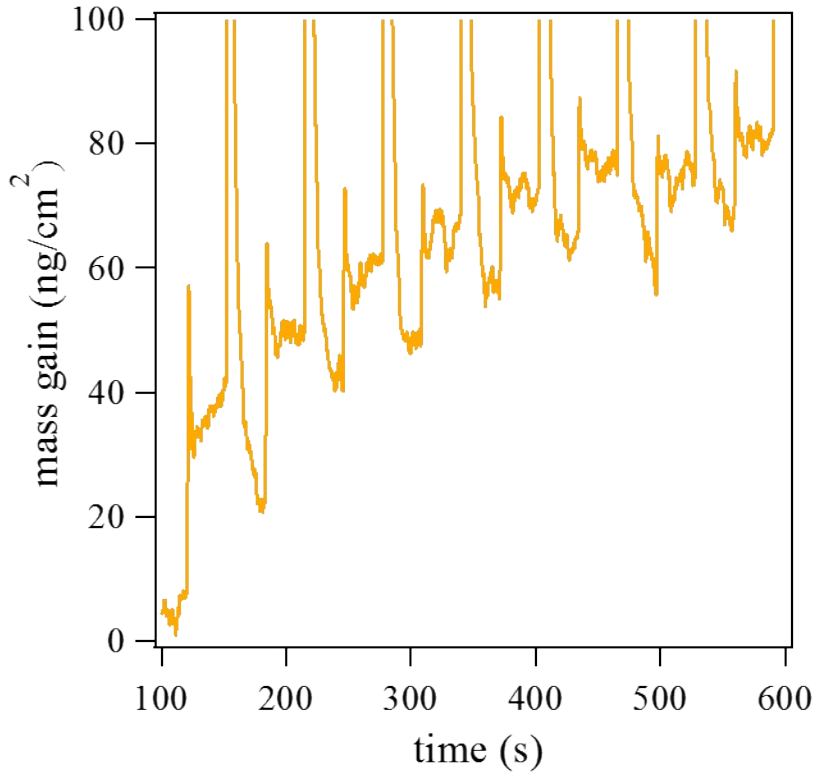

Figure S3: QCM trace of $Cu(dmap)_2$ and water ALD on TiO_2 underlayer.

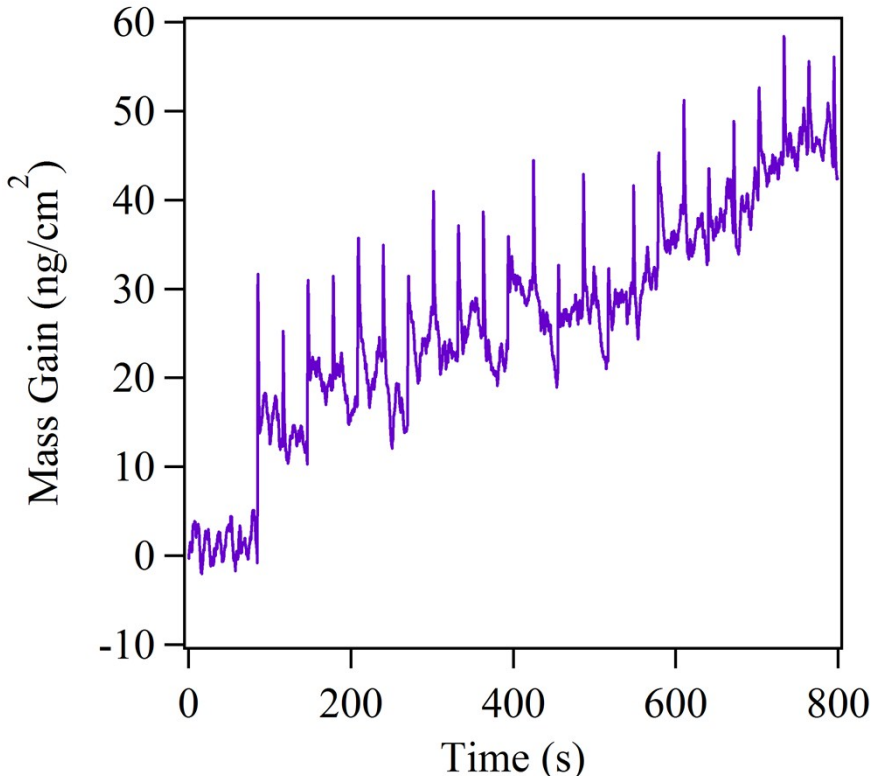

Figure S4: QCM trace of $Cu(dmap)_2$ and water ALD on Cu_XO underlayer.

Figure S3 shows a mass gain of 20 ng/cm^2 for the first $Cu(dmap)_2$ pulse on a TiO_2 undercoated films, which indicated lower surface hydroxo density compared to the first pulse grown on Al_2O_3 shown in figure 3. Furthermore, Figure S4 the first pulse on an as-deposited Cu_xO film, grown using $Cu(dmap)_2$ and water ALD, we see only a 10 ng/cm^2 during the first $Cu(dmap)_2$ pulse, which is within error to the average growth rate of 0.12 Å/cycle. From Figure S4, we can assume the large mass gain during the first pulse of $Cu(dmap)_2$ is not due to loss in vapor pressure during the ALD process, but due to the reduction of surface hydroxos during the reduction ALD reaction.

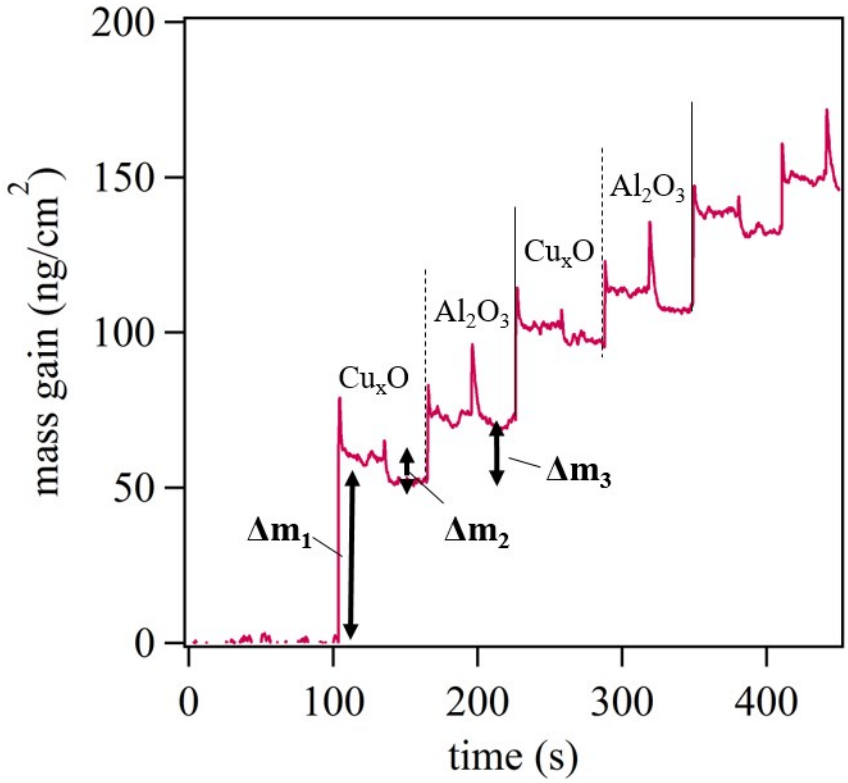

Figure S5: QCM trace of Cu(dmap)$_2$-H$_2$O-TMA-H$_2$O ALD supercycle on Al$_2$O$_3$ underlayer at 150 °C. Cu(dmap)$_2$ (Δm_1) and water (Δm_2) were pulsed for 1 s during the Cu$_x$O subcycle and TMA and water were pulsed for 15 ms during the Al$_2$O$_3$ subcycles (Δm_3). All subcycle steps were purged for 30 seconds.

Figure S5 shows the QCM trace of a Cu(dmap)$_2$-H$_2$O-TMA-H$_2$O supercycle. A supercycles is a cycle that contains multiple AB cycles. In the case of Figure S5, Cu(dmap)$_2$-H$_2$O cycle (labeled Cu$_x$O) is one AB subcycle set, followed by a TMA-H$_2$O (labeled Al$_2$O$_3$) AB subcycle. The first Cu$_x$O subcycle (Δm_2-Δm_1) on Al$_2$O$_3$ underlayer shows a mass gain of ~50 ng/cm^2 which is similar to what was observed in Figure 3. The Al$_2$O$_3$ subcycle (Δm_3) shows a mass gain of ~14 ng/cm^2 on the first Cu$_x$O supercycle, which is less than half the mass gain TMA-H$_2$O grows on Al$_2$O$_3$.[4] The drop in mass gain for the normally reactive TMA-H$_2$O subcycle further indicates far less hydroxo density on Cu$_x$O terminated films. Furthermore, the subsequent Cu$_x$O subscycles showed mass gains of 30 ng/cm^2 after the Al$_2$O$_3$ subcycles, which is a higher mass gain than the average mass gain shown in Figure 3. The trend observed in Figure S5 confirms the low growth rate of the Cu(dmap)$_2$-H$_2$O process is primarily due to a drop in surface hydroxo sites on the Cu$_x$O terminated films, since the Al2O3 deposition showed a much lower mass gain than previously observed, and the Cu$_x$O subcycle showed 3 times the average mass gain on Cu$_x$O films when involved with a supercycle.

Section 3: *Ex-situ* XPS supporting information

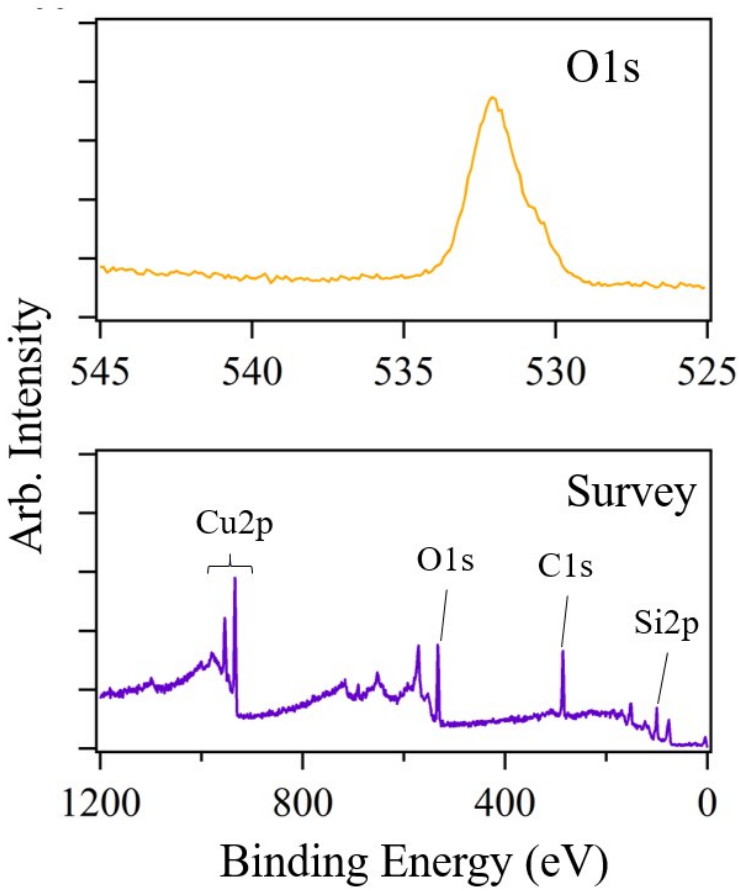

Figure S6: XPS in the O1s region (top) and survey scan (bottom) of 5 nm Cu_xO ALD films grown using $Cu(dmap)_2$ and H_2O as deposited.

Figure S6 shows the XPS survey scan and O1s region of an as-deposited 5 nm Cu_xO film. The clear presence of oxygen further confirms the films grow as Cu_2O, rather than the expected CuO due to the Cu^{2+} charge of the $Cu(dmap)_2$ precursor. Due to the thin nature of the films and the presence of SiO_2 native oxide, we were unable to determine an accurate atomic ratio of the 5 nm Cu_xO film. O 1s peak integration details can be found in Table S1.

Table S1: Fitting details for the O 1s spectrum.

Sample	Peak Energy (eV)	Integration Area (eV)	FWHM (eV)
5 nm Cu_xO as-deposited	532.05	11953.35	1.80
5 nm Cu_xO exposed to air	532.15	14440.08	1.66

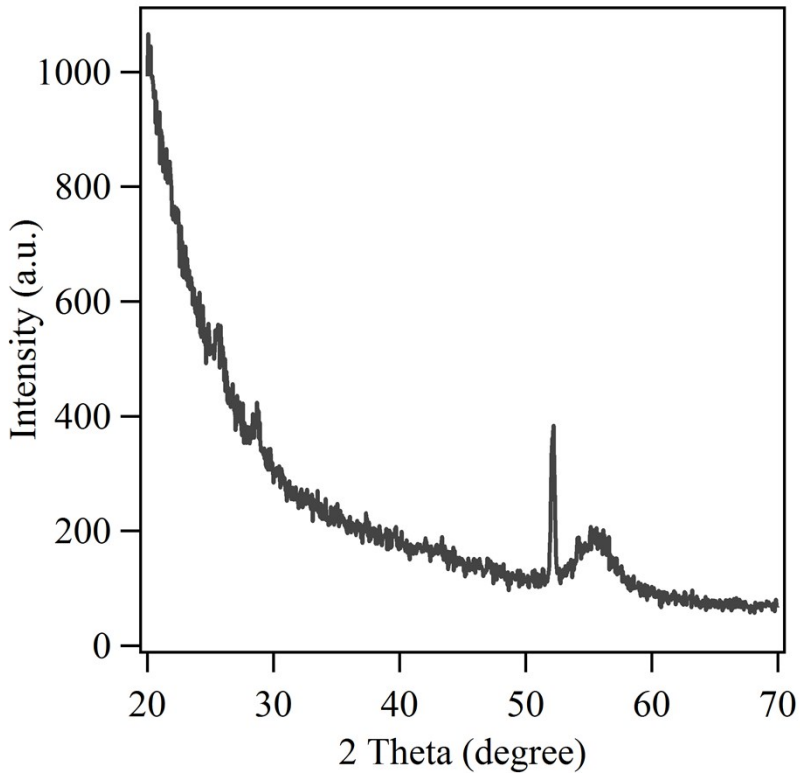

Figure S7: GIXRD of 5 nm Cu_xO deposited by ALD on Si substrate grown using $Cu(dmap)_2$ and H_2O. Features at 50-60 degrees are from the Si substrate and the small features at 20–30 degrees are from the tape used to adhere the sample to the stage.

Figure S7 shows the GIXRD spectrum of 5 nm Cu_xO deposited by ALD on Si Substrate. The features at 50-60 degrees correspond to the Si substrate, and the small features at 20-30 degrees are from the double sided tape used to affix the substrate to the instrument sample stage.

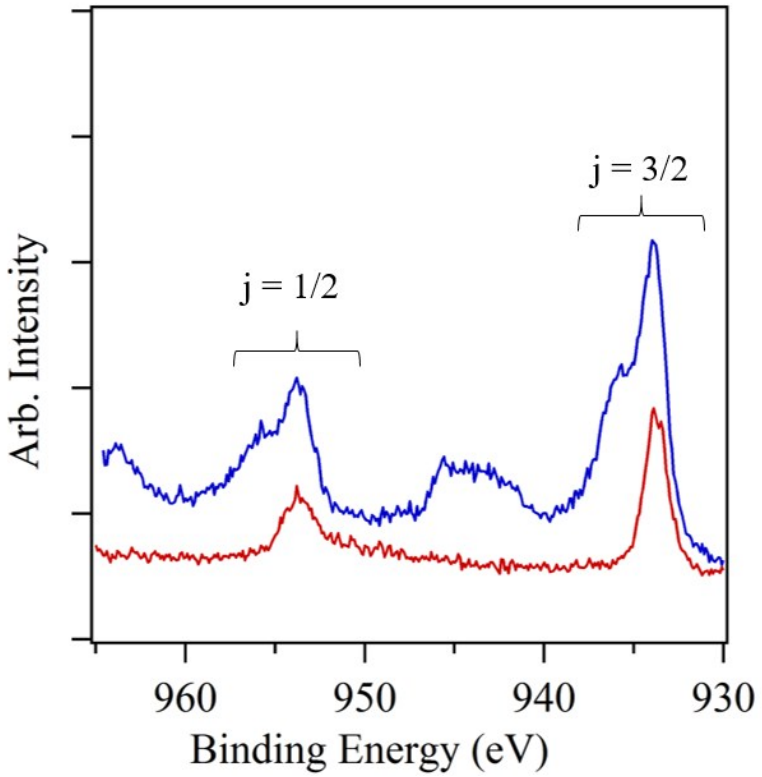

Figure S8: XPS of Cu2p of 5 nm Cu_xO ALD films grown using $Cu(dmap)_2$ and H_2O after 30 minutes in air (blue) and after 10 seconds Ar etch (red).

Figure S8 shows the Cu2p XPS region for 5 nm of Cu_xO after 30 min of air exposure (blue) and after 10 seconds of etching with Ar ions (red). The presence of Cu^{1+} peaks after etching indicate Cu^{2+} is located at the surface of the substrate and is due exclusively to air oxidation.

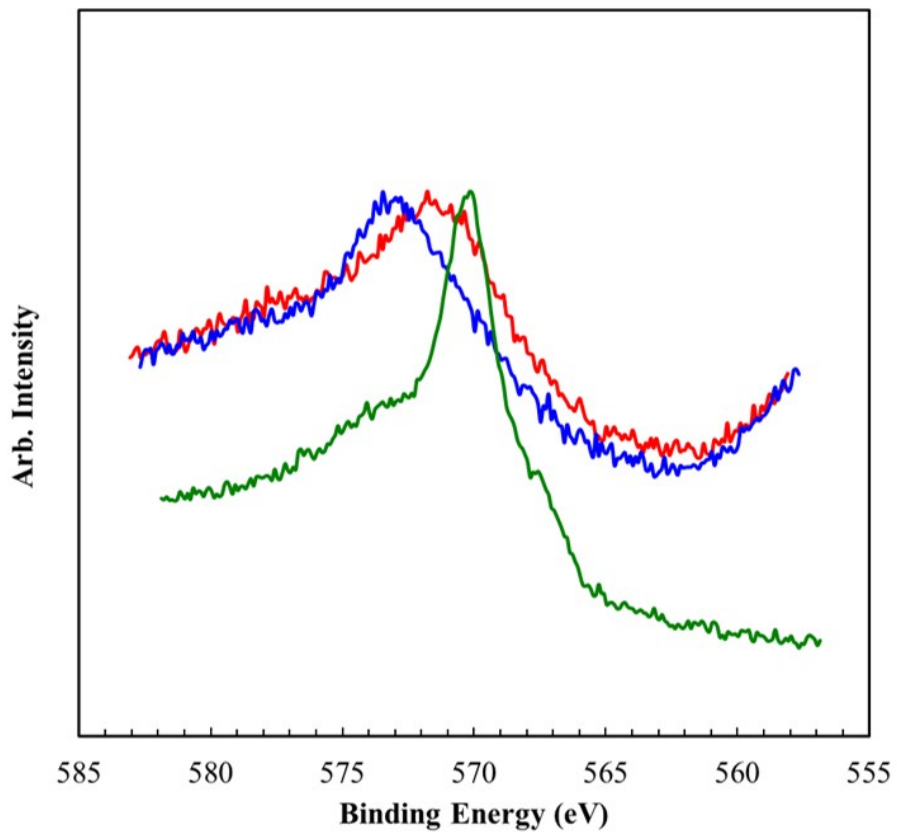

Figure S9: Cu LMM XPS spectrum of air oxidized Cu_xO on AAO (red), after Ar etching (blue), and Cu foil (green).

Figure S9 shows the Cu LMM XPS spectra for Cu_xO films that were deposited by ALD on anodized aluminum oxide (AAO) substrates. The films were exposed to air indicating a peak at 571.48 eV (red), indicating the presence of Cu(II). When the top most film is etched for 30s with Ar, the peaks shift to 572.98 eV revealing the underlying Cu(I) (blue). Comparing to the Cu foil control (green), it can be observed that no Cu (0) is present in the ALD deposited films since there is no peak at 570.18 eV.

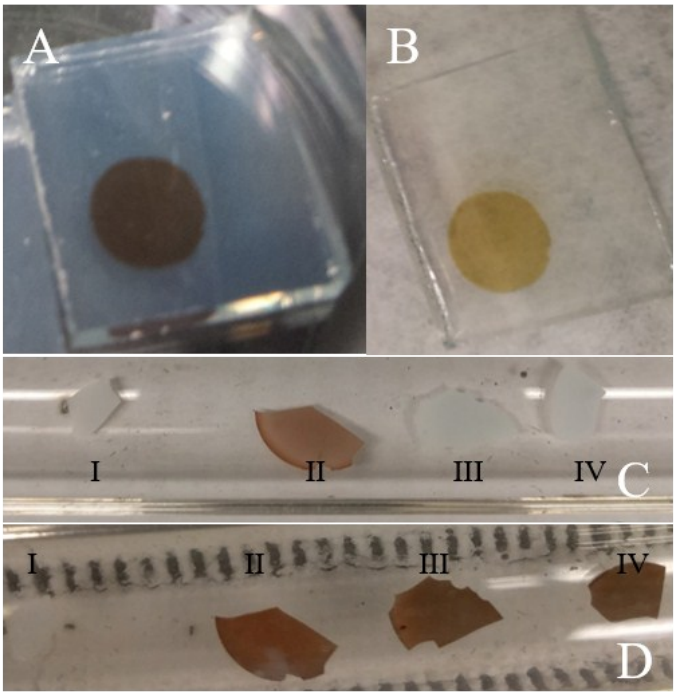

Figure S10: Photographs of Cu_xO deposited by ALD using $Cu(dmap)_2$ and water on a TiO_2 nanoparticle film. The as-deposited films (A) shows a reddish color but once exposed to air (B) the films turn a greenish color. AAO was also used as a substrate for Cu_xO deposition (C). The AAO (C-I) were coated with Cu_xO and protected from air oxidation using a thin layer of Al_2O_3 (C-II), without an Al_2O_3 coating and exposed to air (C-III), and Al_2O_3 protected and annealed at 500 °C for 30 minutes (C-IV). After 10 hours under 5% H_2 in N_2 (20 sccm flow) at 200 °C, the oxidized Cu_xO films turned a reddish color (D).

Figure S10 shows photograph of a Cu_xO film deposited by ALD on a TiO_2 nanoparticle film (A-B) and AAO (C-D). The as-deposited film (S10-A) showed a reddish color in a N_2 environment, indicative of Cu(I) present in the films. Once exposed to air (S10-B), the films immediately turned greenish-brown confirming rapid surface oxidation to Cu(II). AAO was also was also used to show the effect of oxidation on the Cu_xO film color (S10-C). The white AAO (S10-C-I) became a deep red color when Cu_xO was deposited on the substrate by ALD. The Cu_xO film was coated with a 1 nm film of Al_2O_3 by ALD to protect it from air oxidation (S10-C-II). When the as deposited Cu_xO film was exposed to air without a Al_2O_3 protective layer, the films turn a very light green color (S10-C-III). If the Al_2O_3 protected Cu_xO film was annealed in air at 500 °C, the film changes from a deep red to the light green (S10-C-IV) indicating films C-III and C-IV are oxidized CuO while films C-II are Cu_2O. When the films are exposed to flowing 5% H_2 in N_2 at 200 °C for 10 hours (S10-D), there is no change to the AAO (S10-D-I) and the Al_2O_3 protected Cu_xO films (S10-D-II). However, the air exposed and annealed Cu_xO films changed to a deep red color (S10-D-III and IV, respectively) indicating the films can be reduced. Once exposed to air the unprotected films (III and IV) were quickly oxidized and returned to a faint green color.

Section 4: Computational methods

Model: For NU-1000, a neutral cluster model formed by one node and eight organic linkers was extracted from previous periodic DFT calculations.[5] The so-called mixed proton topology was used to describe the node, i.e., $[Zr_6(\mu_3\text{-}O)4(\mu_3\text{-}OH)_4(OH)_4(OH_2)_4]^{8+}$. The eight $TBAPy^{4-}$ (1,3,6,8-tetrakis(p-benzoate)pyrene) linkers were truncated to benzoate groups, thereby increasing computational efficiency while maintaining overall charge balance. During the geometry optimization, the organic linkers were kept fixed to account for the rigidity of the solid structure.

Computational Details: All calculations were carried out at the DFT level using the M06-L local density functional[6-8] as implemented in Gaussian 09.[9] Numerical integrations were performed with an ultrafine grid. An automatic density-fitting set generated by the Gaussian program was employed to reduce the computational cost. Stuttgart effective core potentials and associated basis sets (SDD)[10] were used for Cu and Zr atoms, while the 6-31G(d) basis set was used for H, C, N, and O atoms.[11-12] All geometry optimizations were performed for the gas phase. The natures of all stationary points were confirmed by analytic computation of vibrational frequencies at 383.15 K, which were also employed for the computation of thermochemical quantities. All frequencies below 50 cm^{-1} were replaced by 50 cm^{-1} when computing vibrational partition functions.[13]

Section 5: Structures of 3-II and 3-I

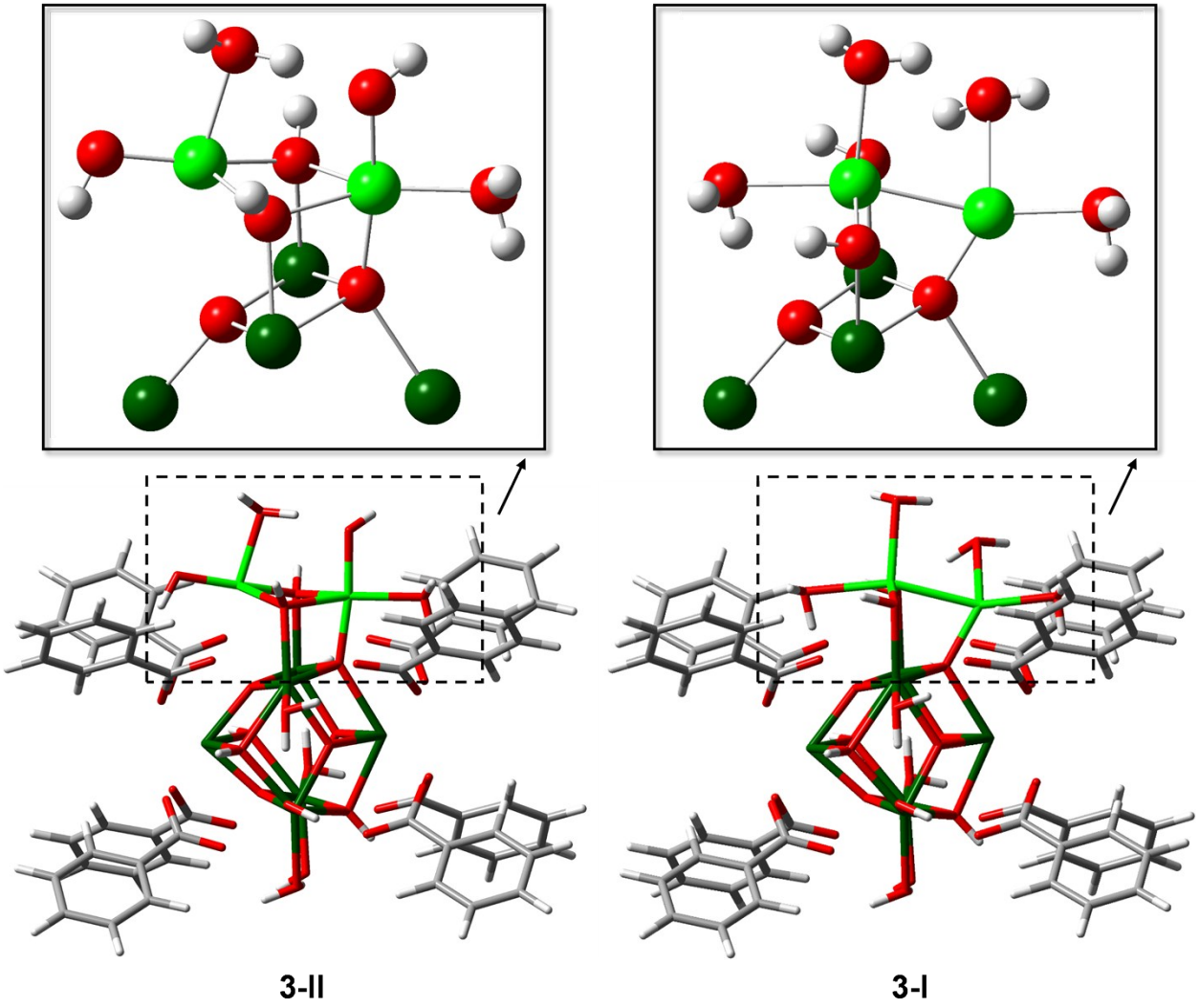

Figure S11. DFT-optimized structure of **3-II** and **3-I**.

Section 6: Cartesian coordinates of all optimized structures

H_2O
E = -76.399606
G(383.15) = -76.401900

O	0.000000	0.000000	0.119300
H	0.000000	0.757360	-0.477199
H	0.000000	-0.757360	-0.477199

$Cu(dmap)_2$ (doublet)
E = -852.767059
G(383.15) = -852.488050

Cu	0.000060	-0.000196	-0.014849
C	2.728285	0.597552	-0.376000
C	2.617562	-0.793257	0.255170
H	2.708616	0.487491	-1.469440
H	3.659383	1.127854	-0.101859
H	2.816339	-0.682192	1.348516
N	1.545243	1.403239	-0.006141
O	1.354159	-1.316185	0.025743
C	3.693321	-1.711486	-0.307044
H	4.705496	-1.333063	-0.108850
H	3.605904	-2.707030	0.140276
H	3.566878	-1.820777	-1.391998
C	1.292004	2.504755	-0.934565
H	0.327725	2.957398	-0.685153
H	2.091806	3.263032	-0.883486
H	1.239569	2.112705	-1.955107
C	1.631634	1.915167	1.364445
H	2.458988	2.638704	1.464574
H	0.685417	2.403714	1.616689
H	1.802948	1.087465	2.060344
O	-1.353858	1.315963	0.028155
C	-2.617736	0.793238	0.255311
C	-2.727888	-0.597220	-0.376731
H	-2.818233	0.681695	1.348285
C	-3.692441	1.711976	-0.308115
N	-1.545367	-1.403272	-0.006032
H	-2.707016	-0.486647	-1.470107
H	-3.659361	-1.127539	-0.103865
H	-4.705005	1.333667	-0.111683
H	-3.605518	2.707275	0.139849
H	-3.564297	1.821791	-1.392819
C	-1.292349	-2.505281	-0.933937
C	-1.632658	-1.914600	1.364708
H	-0.328400	-2.958339	-0.684031
H	-2.092579	-3.263105	-0.882878
H	-1.239291	-2.113647	-1.954605
H	-2.460814	-2.637208	1.464907
H	-0.687062	-2.404146	1.617356
H	-1.803173	-1.086480	2.060296

dmap-H
E = -328.261896
G(383.15) = -328.124461

O	-1.324321	0.675640	1.198098
C	-1.267313	0.255274	-0.149314
C	-0.030938	-0.616041	-0.353304
H	-1.196965	1.136849	-0.819936
C	-2.542334	-0.490320	-0.476000
N	1.157280	0.037012	0.195062
H	-0.175656	-1.553889	0.202238
H	0.096155	-0.880525	-1.424069
H	-2.566746	-0.791452	-1.530276
H	-3.414085	0.141817	-0.278942
H	-2.630688	-1.388093	0.147974
C	2.233291	-0.916695	0.395407
C	1.608052	1.125159	-0.657287
H	3.089395	-0.415550	0.862581
H	2.582968	-1.376225	-0.550768
H	1.898655	-1.719442	1.062001
H	1.888486	0.779721	-1.672825
H	2.483663	1.605660	-0.206280
H	0.823096	1.882381	-0.758492
H	-0.389222	0.770287	1.459569

ketone
E = -327.063150
G(383.15) = -326.950973

O	-2.230890	-0.771472	0.648481
C	-1.375244	-0.221472	-0.017073
C	0.022311	-0.816564	-0.135270
C	-1.636117	1.032022	-0.810259
N	1.072528	0.187514	-0.183203
H	0.156526	-1.555815	0.679781
H	0.047516	-1.379385	-1.082468
H	-0.977621	1.845048	-0.483252
H	-2.681628	1.331801	-0.709038
H	-1.394184	0.871015	-1.868647
C	1.223370	0.811748	1.119885
C	2.330825	-0.399755	-0.603661
H	1.976949	1.605854	1.066129
H	1.531691	0.092981	1.906274
H	0.274574	1.263469	1.436380
H	2.691647	-1.192238	0.083556
H	3.101232	0.378791	-0.653349
H	2.221843	-0.838219	-1.602519

1
E = -4859.050635
G(383.15) = -4858.898097

C	5.668385	2.752687	2.581489
C	-5.704995	2.819602	-2.482672
C	5.663898	2.789916	-2.556609
C	-5.670284	2.831816	2.480715
C	4.329554	2.997376	2.921080
C	-4.361340	3.105373	-2.767477
C	4.324146	3.058130	-2.875230
C	-4.332362	3.106004	2.801205
C	4.030527	4.064522	3.781492
C	-4.060261	4.137888	-3.668078
C	4.035512	4.101788	-3.767167
C	-4.047599	4.137259	3.708085
C	5.046829	4.877835	4.277438
C	-5.080207	4.887789	-4.245877
C	5.059081	4.879952	-4.300962
C	-5.076360	4.896511	4.258793
C	6.393738	4.642753	3.938232
C	-6.431219	4.631834	-3.940395
C	6.405577	4.636061	-3.965877

C	-6.421683	4.644503	3.924666
C	6.683006	3.559607	3.086167
C	-6.722431	3.569500	-3.064217
C	6.686151	3.563570	-3.097513
C	-6.697596	3.585875	3.038728
C	-5.659331	-2.835573	-2.487625
C	5.675451	-2.768923	2.571272
C	-5.698632	-2.828207	2.484774
C	5.687054	-2.728905	-2.590910
C	-4.321317	-3.109242	-2.807927
C	4.337192	-3.046256	2.889320
C	-4.354477	-3.114054	2.766805
C	4.348988	-2.981712	-2.931008
C	-4.033792	-4.139545	-3.714717
C	4.055563	-4.088861	3.785452
C	-4.050774	-4.145191	3.668009
C	4.058639	-4.048030	-3.795716
C	-5.060493	-4.900623	-4.265188
C	5.085391	-4.859000	4.318970
C	-5.069261	-4.894602	4.248943
C	5.080800	-4.854029	-4.291669
C	-6.405609	-4.651443	-3.929921
C	6.430463	-4.608181	3.982584
C	-6.420766	-4.638883	3.945715
C	6.426022	-4.614114	-3.948934
C	-6.684651	-3.592456	-3.045500
C	6.703934	-3.533755	3.113709
C	-6.714874	-3.578213	3.068621
C	6.707527	-3.529317	-3.096153
C	3.241146	2.253286	-2.237661
C	3.245897	2.173932	2.316189
C	3.249067	-2.251070	2.245596
C	-3.261071	-2.349952	2.107456
C	-3.232676	-2.308813	-2.176764
C	-3.266121	2.340973	-2.110365
C	3.258904	-2.169782	-2.319085
C	-3.242171	2.303585	2.173315
H	5.892153	1.929600	1.909986
H	-5.929814	2.011827	-1.792908
H	5.882579	1.976711	-1.871760
H	-5.882713	2.025362	1.785828
H	2.992043	4.258506	4.032220
H	-3.019738	4.341937	-3.900624
H	2.997352	4.308980	-4.009969
H	-3.012310	4.331869	3.972206
H	4.794212	5.707244	4.932922
H	-4.828630	5.689537	-4.935466
H	4.812074	5.694495	-4.976930
H	-4.836245	5.696062	4.954865
H	7.714342	3.354728	2.810389
H	-7.757605	3.339085	-2.825559
H	7.717559	3.343608	-2.833527
H	-7.728152	3.361735	2.775218
H	-5.872941	-2.029217	-1.793128
H	5.888215	-1.955625	1.884683
H	-5.924823	-2.020921	1.794924
H	5.905526	-1.905970	-1.917510
H	-2.997839	-4.331901	-3.977783
H	3.019069	-4.302698	4.029565
H	-3.009643	-4.348505	3.898372
H	3.021854	-4.248480	-4.048575
H	-4.819280	-5.700048	-4.961016
H	4.844300	-5.673919	4.996707
H	-4.816407	-5.695372	4.939171
H	4.833523	-5.683340	-4.949373
H	-7.715956	-3.370864	-2.782766
H	7.733635	-3.306516	2.849323
H	-7.750673	-3.348573	2.832077
H	7.737135	-3.318279	-2.818515
H	7.203076	5.247138	-4.376098
H	-7.225383	5.223523	-4.384261
H	7.231612	-5.214077	4.393299
H	7.221340	-5.244830	-4.332807
H	-7.213780	-5.230367	4.391992
H	-7.222966	5.239104	4.351560
H	-7.205746	-5.248275	-4.355938
H	7.185213	5.277895	4.322882
H	-1.964711	0.054970	-2.855771
H	1.952571	2.868397	0.062878
H	0.960341	-1.652861	4.221651
H	0.025002	-0.380423	4.056998
H	0.762294	-1.632198	-4.397274
H	-0.013614	-4.063566	-0.373053
H	-0.756073	-4.396113	1.624703
H	-0.937419	-4.232904	-1.652178
H	-1.967449	-0.061523	2.854515
H	1.961729	-2.869884	-0.061202
H	0.750442	1.628806	4.399418
H	0.027479	0.374536	-4.057674
H	0.958155	1.649814	-4.223321
H	-0.949488	4.225666	1.650525
H	-0.766697	4.388685	-1.625837
H	-0.024387	4.058279	0.372159
O	1.061761	-0.059872	1.475351
O	3.608148	-1.425483	1.347914
O	3.608088	-1.309430	-1.452717
O	3.600078	1.310808	1.454920
O	2.051193	2.410339	2.679648
O	-0.050088	3.966760	1.387067
O	-2.042322	2.621689	2.441862
O	-2.070014	2.668676	-2.388193
O	-3.602674	1.351402	1.414237
O	-3.616277	1.415685	-1.315028
O	-3.613159	-1.425809	1.311726
O	-3.595548	-1.358596	-1.416493
O	-2.032366	-2.626818	-2.443010
O	-2.064495	-2.676805	2.384144
O	-1.061586	-1.487199	-0.058435
O	-1.387680	-0.071419	2.079299
O	-0.020976	1.253901	3.950230
O	0.059533	-1.395130	3.962234
O	0.058351	1.389329	-3.963434
O	-1.066528	1.482456	0.057588
O	1.391337	2.079566	0.071572
O	2.044965	2.464444	-2.606993
O	0.013719	3.947456	-1.260082
O	3.603627	1.426457	-1.342780
O	0.022976	-3.952581	1.258822
O	-0.038952	-3.971624	-1.388019
O	1.397923	-2.082876	-0.070655
O	2.052932	-2.468074	2.611809
O	2.064862	-2.412426	-2.680848
O	-0.011782	-1.260169	-3.950198
O	-1.384987	0.064645	-2.080541

O	1.063465	0.056157	-1.474337
Zr	-2.502366	-0.003792	-0.000643
Zr	0.026422	1.697452	1.891495
Zr	-0.023966	-1.891729	1.698263
Zr	0.033986	-1.702578	-1.891650
Zr	2.512691	-0.001496	0.001293
Zr	-0.027744	1.886350	-1.698884

2 (triplet)
E = -5908.075325
G(383.15) = -5907.635237

C	-5.808007	-3.410919	-2.688778
C	5.730083	1.263805	-2.841911
C	-5.629353	1.716603	-2.967461
C	5.527735	-3.690675	-2.621154
C	-4.478635	-3.806022	-2.899327
C	4.400280	1.579199	-3.158674
C	-4.276574	1.977519	-3.232291
C	4.183062	-3.979198	-2.897811
C	-4.196329	-4.725557	-3.920744
C	4.141990	2.439300	-4.236327
C	-3.945739	2.808945	-4.312959
C	3.879956	-4.924029	-3.888987
C	-5.219176	-5.225502	-4.723330
C	5.189644	2.946668	-4.998889
C	-4.941379	3.338834	-5.129004
C	4.898374	-5.544007	-4.607694
C	-6.556519	-4.830976	-4.522465
C	6.526449	2.608973	-4.710833
C	-6.301206	3.060574	-4.887652
C	6.251169	-5.243169	-4.353740
C	-6.829540	-3.919338	-3.484545
C	6.775345	1.774996	-3.604676
C	-6.623585	2.253952	-3.779294
C	6.544395	-4.317651	-3.334355
C	5.618068	1.538600	2.805661
C	-5.879698	-3.138492	2.825655
C	5.489320	-3.427108	3.032668
C	-5.716288	2.013461	2.542770
C	4.288521	1.915775	3.046085
C	-4.556311	-3.487299	3.135481
C	4.133130	-3.650458	3.313489
C	-4.370722	2.320319	2.797003
C	4.019713	2.879494	4.028661
C	-4.317430	-4.341808	4.222744
C	3.787019	-4.491135	4.381718
C	-4.063688	3.225014	3.825118
C	5.055407	3.431049	4.776653
C	-5.373697	-4.803682	5.003304
C	4.776393	-5.069362	5.171154
C	-5.077960	3.792223	4.593356
C	6.391258	3.039846	4.561497
C	-6.703582	-4.435086	4.719003
C	6.140296	-4.823670	4.919527
C	-6.431064	3.483237	4.351999
C	6.652683	2.097395	3.549094
C	-6.934859	-3.609568	3.601350
C	6.476350	-4.008143	3.822805
C	-6.728457	2.589806	3.304808
C	-3.225231	1.343205	-2.384224
C	-3.384910	-3.199065	-2.090843
C	-3.437758	-2.918499	2.325532
C	3.071706	-2.992200	2.504658
C	3.188669	1.283984	2.261680
C	3.274559	0.995847	-2.378924
C	-3.292316	1.634911	2.029609
C	3.105354	-3.278091	-2.140425
H	-6.018611	-2.694062	-1.901243
H	5.921931	0.606059	-1.999663
H	-5.880631	1.078680	-2.126095
H	5.754030	-2.965746	-1.845511
H	-3.164705	-5.019561	-4.088837
H	3.112402	2.696332	-4.464960
H	-2.897524	3.006905	-4.517532
H	2.838691	-5.162556	-4.084763
H	-4.979121	-5.927631	-5.517549
H	4.970975	3.605416	-5.835466
H	-4.662089	3.966783	-5.971088
H	4.644289	-6.268874	-5.376760
H	-7.853305	-3.600047	-3.306651
H	7.799082	1.513291	-3.349492
H	-7.665842	2.035026	-3.561007
H	7.580562	-4.078180	-3.109113
H	5.817547	0.799914	2.035780
H	-6.059543	-2.484579	1.978200
H	5.748191	-2.784233	2.196925
H	-5.947711	1.309414	1.749598
H	2.991054	3.185651	4.194587
H	-3.292368	-4.609790	4.461642
H	2.736377	-4.676884	4.581725
H	-3.021420	3.452319	4.027599
H	4.828466	4.171656	5.539176
H	-5.165263	-5.449623	5.852337
H	4.490944	-5.712037	6.000049
H	-4.818351	4.479881	5.394125
H	7.677053	1.790337	3.353893
H	-7.952290	-3.322209	3.348200
H	7.522182	-3.817295	3.596145
H	-7.764308	2.336793	3.093360
H	-7.077137	3.467599	-5.527937
H	7.342074	2.997637	-5.312083
H	-7.525235	-4.789752	5.332793
H	-7.220316	3.922822	4.953280
H	6.910752	-5.267471	5.541876
H	7.044499	-5.724174	-4.916849
H	7.198262	3.466893	5.148268
H	-7.353020	-5.218831	-5.149327
H	-1.998879	-0.981484	-2.839913
H	-1.218297	-5.013744	1.834349
H	-0.252419	-4.929173	0.574946
H	0.000073	3.728017	2.126283
H	-0.096865	-0.336258	4.062427
H	0.567755	-2.344738	4.493134
H	0.894560	0.895006	4.147767
H	1.801070	-3.781694	0.233146
H	-2.051689	-0.609642	2.863092
H	-0.972746	-5.326251	-1.416717
H	0.016309	3.576164	-2.210706
H	0.863223	-2.691831	-4.100814
H	0.830187	0.512219	-4.336562
H	-0.030095	-1.384165	-3.971334
O	-1.192612	-2.313951	0.139491
O	-3.756504	-2.049704	1.453842
O	-3.660486	0.740744	1.206318

O	-3.719850	-2.286550	-1.273994
O	-2.200461	-3.612816	-2.293941
O	-0.034273	-2.401680	-3.864860
O	1.900950	-3.521422	-2.461569
O	2.092366	1.297385	-2.735207
O	3.480086	-2.487029	-1.220343
O	3.586639	0.234104	-1.412710
O	3.461415	-2.253247	1.548944
O	3.536760	0.467727	1.353269
O	1.994731	1.604342	2.550259
O	1.862739	-3.213124	2.828118
O	0.972783	-0.822871	1.558374
O	1.223455	-3.005627	0.206454
O	-0.189120	-4.892333	-1.049594
O	-0.304278	-4.795224	1.586892
O	0.060131	3.043518	-1.401890
O	0.989036	-1.054125	-1.445199
O	-1.458444	-1.000667	-2.037321
O	-2.014964	1.662236	-2.596450
O	-0.008107	0.247874	-3.930557
O	-3.627522	0.501050	-1.521137
O	-0.206034	-1.987791	4.032921
O	-0.021860	0.666749	3.914609
O	-1.498538	-0.689127	2.072868
O	-2.257311	-3.313555	2.575475
O	-2.089645	1.968052	2.271061
O	0.223267	3.177703	1.353528
O	1.325174	1.142273	-0.104512
O	-1.181268	0.694478	-0.099882
Zr	2.411313	-0.918741	0.050860
Zr	-0.148999	-2.850447	-1.588126
Zr	-0.140010	-2.522332	1.994872
Zr	-0.027176	1.012613	1.593860
Zr	-2.602970	-0.813446	-0.007425
Zr	0.023323	0.745190	-1.857716
Cu	-1.000586	3.995579	0.094716
C	-2.683619	6.216749	-0.226922
C	-2.393772	6.129083	1.269030
H	-1.899720	6.823553	-0.704461
H	-3.286081	5.704911	1.779769
Cu	1.925119	3.021715	-0.377215
O	3.796827	2.909408	-0.105226
C	4.447662	4.128454	-0.003169
C	3.683275	5.173291	-0.806253
H	4.497438	4.471159	1.057060
C	5.880381	4.014532	-0.505841
N	2.249165	5.119362	-0.432509
H	3.750362	4.913983	-1.873566
H	4.065268	6.202889	-0.670652
H	6.442316	4.943017	-0.334674
H	6.390213	3.200415	0.020838
H	5.897831	3.783604	-1.578865
C	1.448523	5.880163	-1.388696
C	2.043707	5.668020	0.920395
H	0.390121	5.839899	-1.092746
H	1.756320	6.939412	-1.416473
H	1.568290	5.455521	-2.393041
H	2.474117	6.681885	0.987378
H	0.971008	5.713613	1.139586
H	2.530829	5.022674	1.657446
C	-2.147182	7.515413	1.846223
H	-1.284249	7.982586	1.352404
H	-3.019241	8.171256	1.722911
H	-1.922053	7.441516	2.914822
H	-3.661081	6.674373	-0.461420
C	-2.469306	4.939234	-2.286689
H	-3.379135	5.352930	-2.750500
H	-1.621498	5.589638	-2.535809
H	-2.291175	3.934002	-2.678554
C	-3.776733	4.052987	-0.450925
H	-3.612405	3.002877	-0.706805
H	-3.929015	4.118734	0.630572
H	-4.681368	4.414277	-0.965971
N	-2.601919	4.862445	-0.830442
O	-1.281369	5.320801	1.460302

3-II (triplet)
E = -5557.170583
G(383.15) = -5556.983937

C	-5.753436	2.475527	3.118159
C	5.711181	-2.337527	2.484872
C	-5.654335	-2.610025	2.390989
C	5.584988	2.567391	3.234818
C	-4.421577	2.798880	3.416932
C	4.372439	-2.685699	2.718807
C	-4.309485	-2.940977	2.615086
C	4.240840	2.819487	3.547310
C	-4.140581	3.496202	4.601542
C	4.085948	-3.735142	3.604478
C	-4.006533	-3.972876	3.515922
C	3.937366	3.557622	4.700593
C	-5.167465	3.847343	5.474765
C	5.114880	-4.399686	4.264919
C	-5.021634	-4.634751	4.201234
C	4.954289	4.007613	5.538130
C	-6.507424	3.522791	5.185519
C	6.460540	-4.035357	4.063598
C	-6.373593	-4.291307	4.003544
C	6.306041	3.738862	5.245578
C	-6.778784	2.836284	3.986366
C	6.737667	-3.005823	3.144741
C	-6.667985	-3.278238	3.070787
C	6.600338	3.025348	4.068296
C	5.676875	-1.502001	-3.108326
C	-5.749321	3.286672	-2.343557
C	5.624521	3.413875	-2.361486
C	-5.665875	-1.823398	-3.071631
C	4.345537	-1.801955	-3.432881
C	-4.416599	3.666369	-2.564222
C	4.275967	3.711142	-2.608552
C	-4.321270	-2.098088	-3.365878
C	4.076822	-2.550409	-4.587900
C	-4.149457	4.712535	-3.460640
C	3.957760	4.750118	-3.495632
C	-4.012910	-2.789180	-4.547557
C	5.115006	-2.963043	-5.417530
C	-5.187409	5.336131	-4.147724
C	4.966857	5.454236	-4.145525
C	-5.024153	-3.177962	-5.423145
C	6.453215	-2.644520	-5.114939
C	-6.526550	4.942120	-3.956048
C	6.323211	5.140615	-3.931373
C	-6.375937	-2.898900	-5.141270
C	6.713802	-1.922608	-3.934911

C	-6.786102	3.918321	-3.024064
C	6.631319	4.120914	-3.011544
C	-6.675265	-2.222165	-3.943067
C	-3.236772	-2.171361	1.919054
C	-3.325330	2.342740	2.517811
C	-3.318392	2.931129	-1.868493
C	3.193386	2.925988	-1.956117
C	3.243861	-1.316505	-2.552675
C	3.266810	-1.941992	2.055364
C	-3.244245	-1.594294	-2.466812
C	3.164017	2.298514	2.655321
H	-5.963151	1.930032	2.203326
H	5.924857	-1.531358	1.789710
H	-5.883981	-1.815857	1.687636
H	5.811790	2.004118	2.335010
H	-3.107285	3.733860	4.835541
H	3.049486	-4.014070	3.766775
H	-2.964489	-4.225149	3.689595
H	2.896998	3.771254	4.927434
H	-4.928624	4.376578	6.393601
H	4.874457	-5.205265	4.954025
H	-4.763838	-5.419829	4.907367
H	4.699796	4.572585	6.431156
H	-7.804457	2.575608	3.737902
H	7.768725	-2.717026	2.957253
H	-7.703644	-3.003001	2.887668
H	7.636021	2.816632	3.812320
H	5.876041	-0.931468	-2.206667
H	-5.951015	2.483035	-1.642404
H	5.861778	2.615775	-1.664694
H	-5.898354	-1.283935	-2.158752
H	3.046276	-2.800463	-4.822111
H	-3.117217	5.004285	-3.630911
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H	-4.957230	6.131764	-4.851663
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O	-2.434725	3.268106	-1.894300
O	-2.005420	-1.926487	-2.815494
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O	1.341040	-1.489634	-0.272839
O	-1.187744	-1.237624	-0.189798
Zr	2.283623	0.612752	0.071384
Zr	-0.314463	1.952228	2.083323
Zr	-0.286243	2.450348	-1.499910
Zr	-0.006143	-1.120390	-1.922625
Zr	-2.654264	0.219074	0.048168
Zr	0.027302	-1.628795	1.545911
Cu	2.508220	-3.025622	-0.416460
Cu	0.175282	-3.919278	-0.867903
H	-0.530871	-3.445717	-3.123700
H	-0.581086	-4.213084	1.457952
O	4.661323	-2.953639	-0.623868
H	4.666406	-1.976718	-0.553635
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H	-2.143022	-3.078051	-0.421582
H	-2.554729	-4.081987	-1.503368
H	4.914434	-3.118859	-1.547164
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H	1.824843	-4.555492	1.212280
H	3.393894	-4.768140	1.301212
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H	0.039205	-6.460370	-0.157643

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