

Supporting Information

K β X-ray Emission Spectroscopy as a Probe of Cu(I) Sites: Application to the Cu(I) Site in Preprocessed Galactose Oxidase

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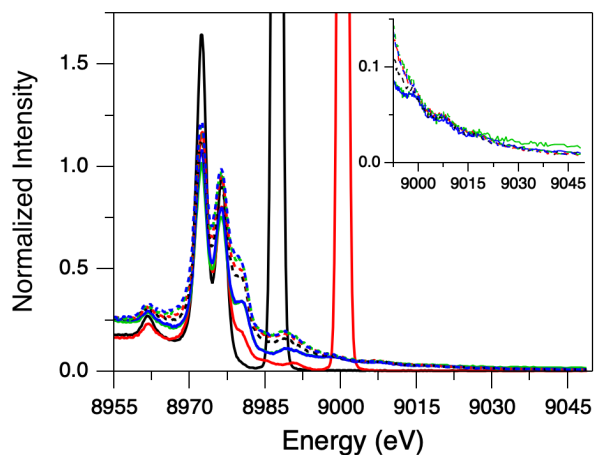


Figure S1. $K\beta$ VtC XES spectra of Cu(I)Cl obtained with excitation energies of 8987 (solid black), 9000 (solid red), 9500 (solid green), 10000 (solid blue), 10500 (dashed black), 11000 (dashed red), 12000 (dashed green), and 13000 eV (dashed blue). The high intensity peaks at 8987 (solid black) and 9000 eV (solid red) are from the elastic scattering of the incident X-ray. Inset shows the expanded $K\beta$ VtC XES spectra for an emission energy range of 8992.5–9050 eV (for excitation energies of 9500–13000 eV).

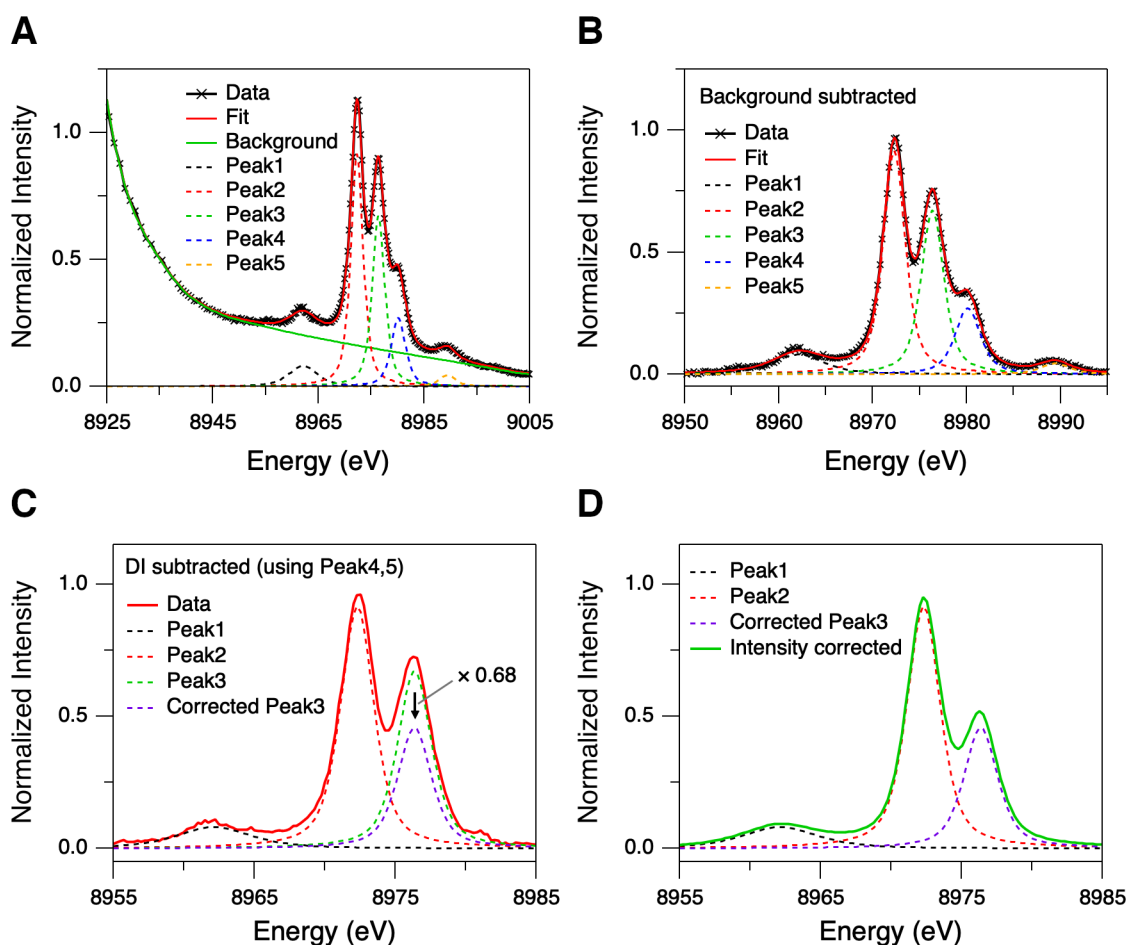


Figure S2. Data processing of the $K\beta$ VtC XES spectrum of Cu(I)Cl obtained with an excitation energy of 10500 eV. (A) Fit to the data, (B) the data after subtraction of the background, (C) the data after subtraction of the background and the DI emission features, and (D) the data after the intensity ratio correction.

Correction method to remove the DI contribution in the $K\beta$ VtC XES spectrum of Cu(I)Cl

Figure S2A shows the fit to the $K\beta$ VtC XES spectrum of Cu(I)Cl obtained with an excitation energy of 10500 eV; the background is modelled with a spline function (solid green spectrum in Figure S2A) while the spectral features are fit with pseudo-Voigt peaks (peaks 1–5 in Figure S2). The peaks 4 and 5 in Figure S2 are used to fit the ~ 8980 eV and the ~ 8989 eV features that originate from the $1s + 3d$ and $1s + 3p$ DIs, respectively. These two peaks are subtracted from the background subtracted spectrum (solid black spectrum in Figure S2B) to remove the DI contribution and the resultant spectrum is shown as the solid red spectrum in Figure S2C. This

resultant spectrum is compared to the data obtained with an excitation energy of 8987 eV (i.e., no DI) in Figure 2A. This comparison shows that, in the red spectrum in Figure 2A (i.e., solid red spectrum in Figure S2C), there still exists the residual 1s + 3d DI contribution in the ~8976 eV feature (see section 2.1) and thus the intensity of the ~8976 eV feature needs to be further corrected. The intensity correction factor is obtained from the intensity ratios of the ~8976 eV to the ~8972 eV features of the black and the red spectra in Figure 2A (see section 2.1; $0.51/0.75 = 0.68$). This correction factor, 0.68, is applied to the peak 3 in Figure S2C to account for the residual 1s + 3d DI contribution (see dashed green (peak 3) to dashed purple (corrected peak 3) peaks in Figure S2C). The intensity ratio corrected spectrum is constructed from the peaks 1, 2 and the corrected peak 3 (Figure S2D). This intensity ratio corrected spectrum is scaled to have the same area under that K β VtC region as the spectrum obtained with an excitation energy of 8987 eV and the resultant spectrum is presented as the green spectrum in Figure 2B.

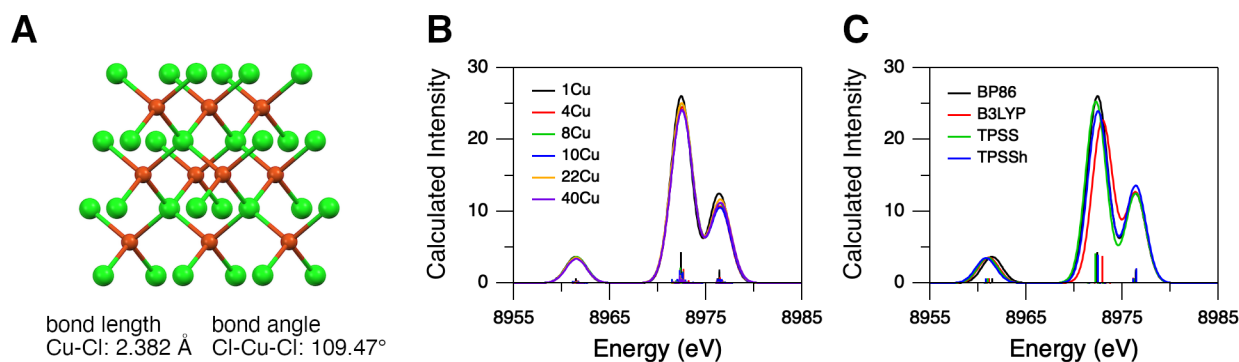


Figure S3. (A) Crystal structure of Cu(I)Cl (Cu in brown and Cl in green). (B,C) DFT calculated K β VtC XES spectra of Cu(I)Cl. For (B), the cluster size varied while the functional was fixed to BP86 (annotation indicates the number of the Cu(I) centers included in the calculation). For (C), the functional varied while the cluster size was fixed to the first coordination sphere of Cu(I) (T_d [Cu(I)Cl₄]³⁻). The DFT calculated spectra have been shifted by 230.5 eV for BP86 and those calculated with the other functionals have been shifted to match the energy of the maximum of the ~8976 eV feature. A 2.5-eV line-broadening has been applied to the calculated transitions.

Table S1. Emission Energies, Energy Splittings, and Intensity Ratios of Spectral Features in Experimental and Calculated K β VtC XES Spectra of T_d [Cu(I)Cl₄]³⁻ Sites in Cu(I)Cl

	Exp. ^a	BP86 ^b	B3LYP ^b	TPSS ^b	TPSSh ^b
<i>emission energy (eV)</i>					
peak1	8961.7	8961.4	8961.1	8961.0	8960.8
peak2	8972.4	8972.4	8972.9	8972.2	8972.5
peak3	8976.4	8976.4	8976.4	8976.4	8976.4
<i>energy splitting (eV)</i>					
peak2 – peak1	10.7	11	11.8	11.2	11.7
peak3 – peak2	4.0	4.0	3.5	4.2	3.9
<i>intensity ratio^c</i>					
peak3 / peak2	0.51	0.48	0.56	0.49	0.57

^aEnergies are obtained from the fit to the experimental spectrum collected with an excitation energy of 8987 eV. ^bEnergies are obtained from the calculated spectra presented in Figure S3C.

^cIntensities are obtained from the area of the peak which fits each spectral feature.

Table S2. Structural Parameters for DFT Optimized and Crystal Structures of Cu(I) Model Complexes 1–4

bond length (Å)	bond angle (°)	bond length (Å)	bond angle (°)
<i>for DFT optimized structure^a</i>			
complex 1		complex 2	
Cu-N1: 2.222	N1-Cu-N2: 98.37	Cu-N1: 2.192	N1-Cu-N2: 84.22
Cu-N2: 1.921	N1-Cu-N3: 103.91	Cu-N2: 2.001	N1-Cu-N3: 84.04
Cu-N3: 1.920	N2-Cu-N3: 154.79	Cu-N3: 2.005	N1-Cu-N4: 83.70
		Cu-N4: 2.007	N2-Cu-N3: 119.01
			N2-Cu-N4: 118.60
			N3-Cu-N4: 119.14
complex 3		complex 4	
Cu-N1: 2.203	N1-Cu-N2: 84.54	Cu-N1: 2.219	N1-Cu-N2: 81.69
Cu-N2: 1.991	N1-Cu-N3: 84.35	Cu-N2: 2.051	N1-Cu-N3: 80.64
Cu-N3: 2.008	N1-Cu-S: 87.94	Cu-N3: 2.039	N1-Cu-S: 133.06
Cu-S: 2.254	N2-Cu-N3: 120.90	Cu-S: 2.207	N2-Cu-N3: 110.46
	N2-Cu-S: 121.95		N2-Cu-S: 120.25
	N3-Cu-S: 115.39		N3-Cu-S: 120.56
<i>for crystal structure</i>			
complex 1		complex 2	
Cu-N1: 2.227	N1-Cu-N2: 96.71	Cu-N1: 2.185	N1-Cu-N2: 83.50
Cu-N2: 1.912	N1-Cu-N3: 103.28	Cu-N2: 2.004	N1-Cu-N3: 83.03
Cu-N3: 1.902	N2-Cu-N3: 157.04	Cu-N3: 2.011	N1-Cu-N4: 82.47
		Cu-N4: 2.002	N2-Cu-N3: 116.29
			N2-Cu-N4: 119.48
			N3-Cu-N4: 119.83
complex 3		complex 4	
Cu-N1: 2.181	N1-Cu-N2: 83.37	Cu-N1: 2.203	N1-Cu-N2: 82.28
Cu-N2: 1.990	N1-Cu-N3: 83.90	Cu-N2: 2.018	N1-Cu-N3: 79.28
Cu-N3: 2.026	N1-Cu-S: 87.71	Cu-N3: 2.066	N1-Cu-S: 130.11
Cu-S: 2.266	N2-Cu-N3: 128.60	Cu-S: 2.189	N2-Cu-N3: 112.75
	N2-Cu-S: 120.94		N2-Cu-S: 129.69
	N3-Cu-S: 108.00		N3-Cu-S: 110.79

^aDFT optimized structures are shown in Figure 4.

Single crystal X-ray crystallography for [Cu(I)-(BA-OMe)]SbF₆

All reflection intensities were measured at 110(2) K using a KM4/Xcalibur (detector: Sapphire3) with enhance graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) under the program CrysAlisPro version 1.171.34.44 (Oxford Diffraction Ltd., 2010). The CrysAlisPro was used to refine the cell dimensions and for data reduction. The structure was solved with the program SHELXS-97 and was refined on F^2 with the program SHELXL-97.¹ Analytical numeric absorption corrections based on a multifaceted crystal model were applied using the CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 23, AFIX 43, or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times U_{eq} of the attached C atoms. The structure is ordered. The absolute structure configuration was established by anomalous dispersion effects in diffraction measurements on the crystal, and the Flack parameter refines to 0.046(11). Note that, for the DFT calculations of complex **2** in the present study, the -OMe group at the *para* position of the benzyl ring in the crystal structure is replaced by -H using the program Avogadro version 1.2.0 (<http://avogadro.cc>).²

¹Sheldrick, G. M. A short history of *SHELX*. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112–122.

²Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. Avogadro: an advanced semantic chemical editor, visualization, and analysis platform. *J. Cheminf.* **2012**, *4*, 17.

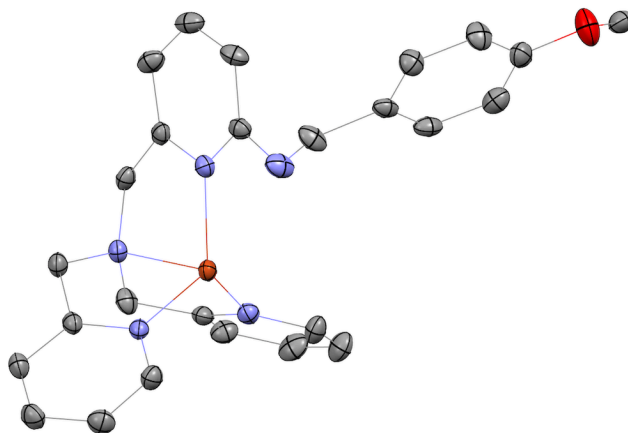


Figure S4. Displacement ellipsoid plot (50% probability level) of [Cu(I)-(BA-OMe)]SbF₆ at 110(2) K (Cu in brown, N in blue, C in grey, and O in red). The H atoms and the counterion are omitted for clarity. [C₂₆H₂₇CuN₅O](SbF₆), formula weight = 724.82 g/mol, yellow block, 0.44 × 0.32 × 0.22 mm³, monoclinic, *Cc* (no. 9), $a = 23.5199(4)$ Å, $b = 8.88829(9)$ Å, $c = 15.2449(3)$ Å, $\beta = 121.459(2)^\circ$, $V = 2718.53(10)$ Å³, $Z = 4$, $D_x = 1.771$ g/cm³, $\mu = 1.847$ mm⁻¹, and T_{\min} – T_{\max} : 0.542–0.725. A total of 23096 reflections were measured up to a resolution of $(\sin \theta/\lambda)_{\max} = 0.65$ Å⁻¹. A total of 6193 reflections were unique ($R_{\text{int}} = 0.0536$), of which 5926 were observed [$I > 2\sigma(I)$]. A total of 363 parameters were refined with 2 restraints. $R1/wR2$ [$I > 2\sigma(I)$]: 0.0260/0.0631. $R1/wR2$ [all reflections]: 0.0272/0.0634. $S = 1.117$. Residual electron density is found between -0.60 and 0.50 e/Å³.

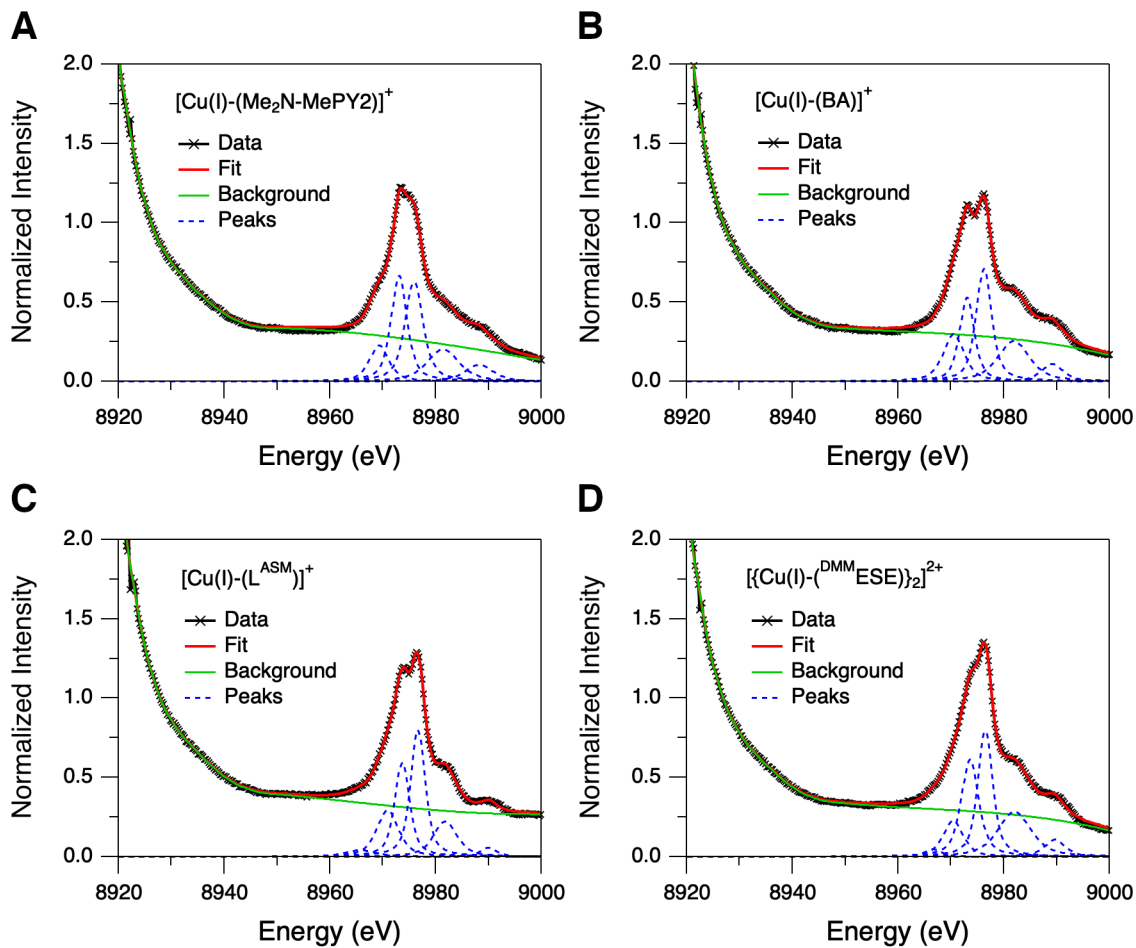


Figure S5. Fits to $\text{K}\beta$ VtC XES spectra of Cu(I) model complexes (A) 1, (B) 2, (C) 3, and (D) 4.

Intensity ratio correction factors

In section 2.1, it has been found that, for the Cu(I)Cl data obtained with an excitation energy of 10500 eV, the simple subtraction of the 1s + 3d DI emission at ~8980 eV using fits is not sufficient and the additional intensity ratio correction (using factor of 0.68) is necessary (Figure 2). Complexes 1–4 in section 2.3 show this DI emission feature at ~8981 or ~8982 eV (Figures 5B, 7, and S5) and thus its overlap with the ~8976 eV SI feature is expected to be smaller than Cu(I)Cl. In this regard, the intensity ratio correction factor should be larger for the data having the 1s + 3d DI emission at higher energies.

To obtain the proper intensity ratio correction factors for the data having higher 1s + 3d DI emission energies, the overall 1s + 3d DI contribution is first estimated with the Cu(I)Cl data and shown as the blue spectrum in Figure S6. This estimated overall 1s + 3d DI contribution is obtained by combining the pseudo-Voigt peak fitting the apparent ~8980 eV DI feature (dashed purple spectrum) and the residual 1s + 3d DI contribution (dashed orange spectrum) which is obtained from the difference between the spectra with and without the intensity ratio correction (green and red spectra, respectively). Note that the spectral shape of this estimated overall 1s + 3d DI contribution (blue spectrum) does not necessarily represent that of the genuine 1s + 3d DI emission. However, this does give insight into the degree of overlap of the 1s + 3d DI emission with the ~8976 eV SI feature.

The estimated overall 1s + 3d DI contribution (blue spectrum) is upshifted by 1–3 eV in Figure S7B–D. The black spectra in Figure S7 are the sum of this estimated overall 1s + 3d DI contribution (blue spectrum) and the intensity ratio corrected spectrum (green spectrum) which represents the data originating solely from the 1s SI state. As the 1s + 3d DI emission shifts up in energy, it is expected that the pseudo-Voigt peak fits better this DI feature and the residual 1s + 3d DI contribution in the ~8976 eV SI feature decreases. The residual 1s + 3d DI contributions, which would not be simply subtracted using fits, can be approximated with the intensity difference of the ~8976 eV features in the green and the black spectra in Figure S7. The intensity ratio correction factor for the data having the 1s + 3d DI emission at ~8980 eV has been obtained to be 0.68 (in section 2.1) which is the same as the intensity ratio of the ~8976 eV features between the green and the black spectra in Figure S7A. Thus, for the data having the 1s + 3d DI emission at ~8981 to ~8983 eV, the intensity ratio correction factors can be estimated from the intensity ratios of the ~8976 eV features between the green and the black spectra in Figure S7B–D. As the peak widths

of the ~ 8976 eV feature and the residual $1s + 3d$ DI feature would remain similar in this estimation, the intensity ratio correction factors can be approximated from the ratios of the peak heights. This gives the intensity ratio correction factors of 0.68, 0.75, 0.88, and 0.94 for the data having the $1s + 3d$ DI emission at ~ 8980 , ~ 8981 , ~ 8982 , and ~ 8983 eV, respectively (Table 1).

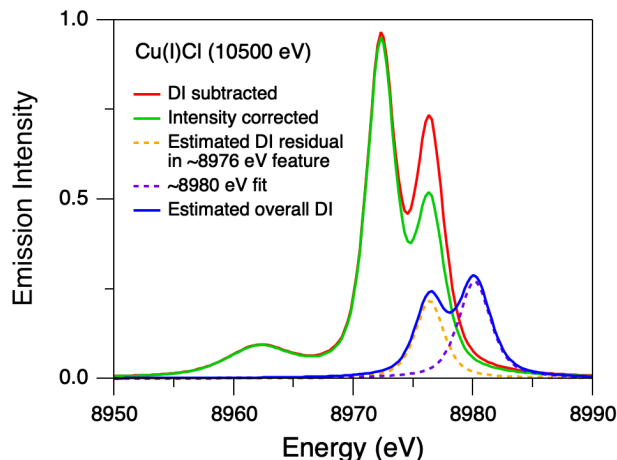


Figure S6. $K\beta$ VtC XES data of Cu(I)Cl for an excitation energy of 10500 eV, reconstructed from the fit with pseudo-Voigt peaks in Figure S2. The red spectrum is constructed with peaks 1–3 in Figure S2, but without peaks 4 and 5 to exclude apparent DI emissions. The green spectrum is obtained from the intensity ratio correction using the factor of 0.68, as discussed in section 2.1, and represents the data solely originating from the $1s$ SI state. The dashed orange spectrum is the result of the subtraction of the green spectrum from the red spectrum and represents the estimated residual $1s + 3d$ DI contribution in the ~ 8976 eV feature. The blue spectrum is the sum of the dashed orange and the dashed purple (peak 4 in Figure S2) spectra and represents the estimated overall $1s + 3d$ DI contribution.

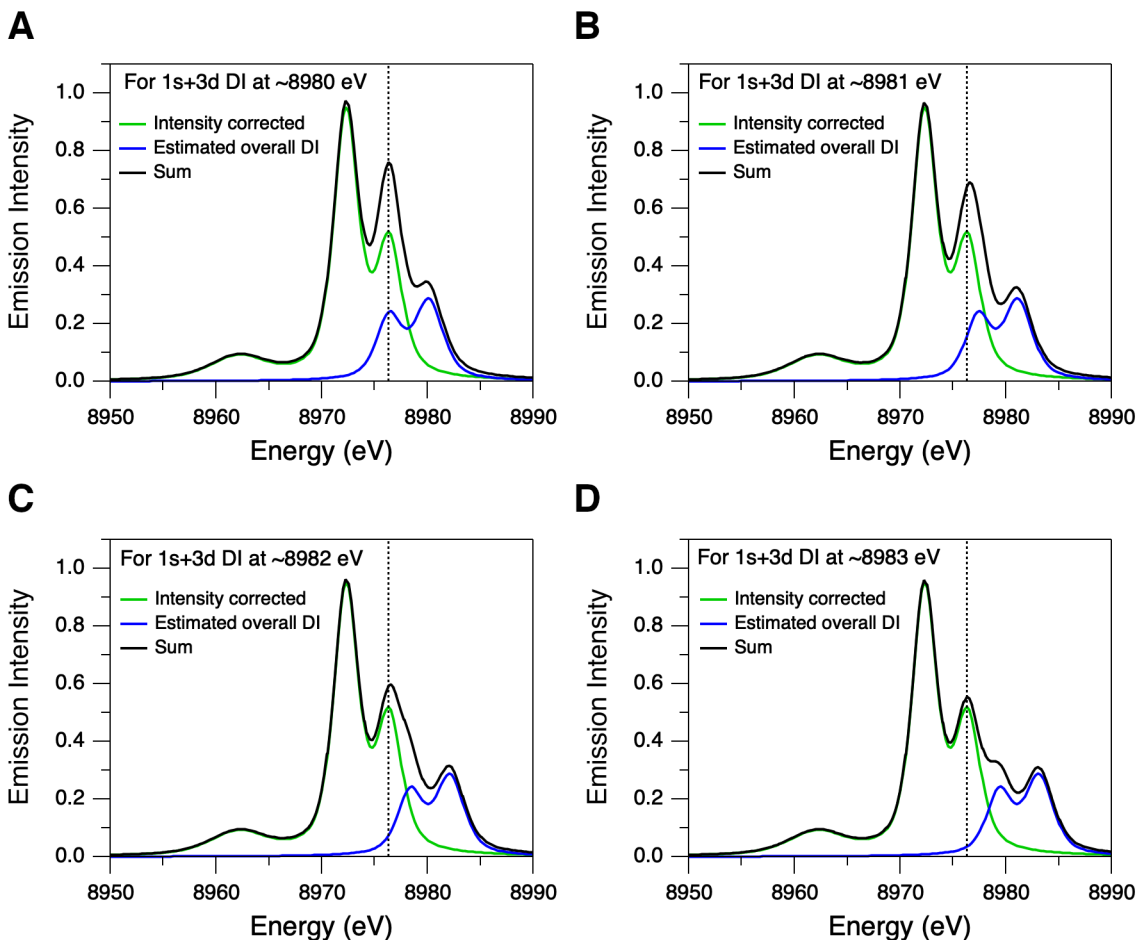


Figure S7. Estimation of the overlap of the 1s + 3d DI contribution with the ~ 8976 eV SI feature, using the Cu(I)Cl data. The green spectra (same as that in Figure S6) are obtained from the intensity ratio correction using the factor of 0.68, as discussed in section 2.1, and represent the data solely originating from the 1s SI state. The blue spectra are the estimated overall 1s + 3d DI contribution which is obtained in Figure S6 and its high energy peak is located at 8980, 8981, 8982, and 8983 eV in (A), (B), (C), and (D), respectively. The black spectra are the sum of the green and the blue spectra and represent the data containing the 1s + 3d DI contribution to the SI features. Dotted lines are drawn on the maximum of the ~ 8976 eV SI feature.

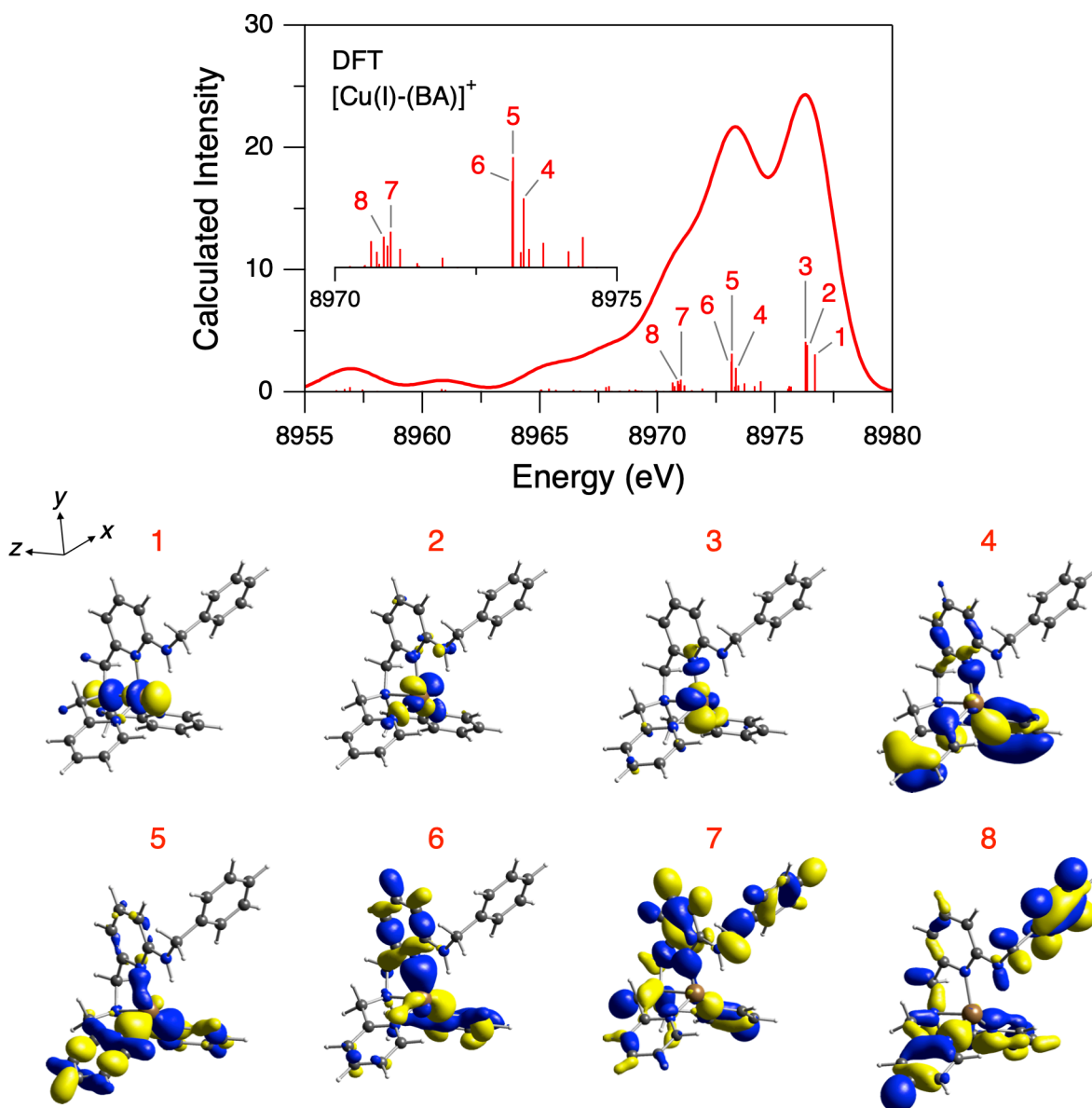


Figure S8. DFT/BP86 calculated K β VtC XES spectrum of complex **2** and contour plots of MOs contributing to calculated transitions denoted as 1–8. The calculated spectrum has been shifted by 230 eV and a 2.5-eV line-broadening has been applied to the calculated transitions. Inset shows the expanded calculated transitions at an emission energy range of 8970–8975 eV for a better visual distinction of transitions 4–8. The molecules are oriented similarly to the structure presented in Figure 4. Note that 1 and 5 are shown in Figure 6.

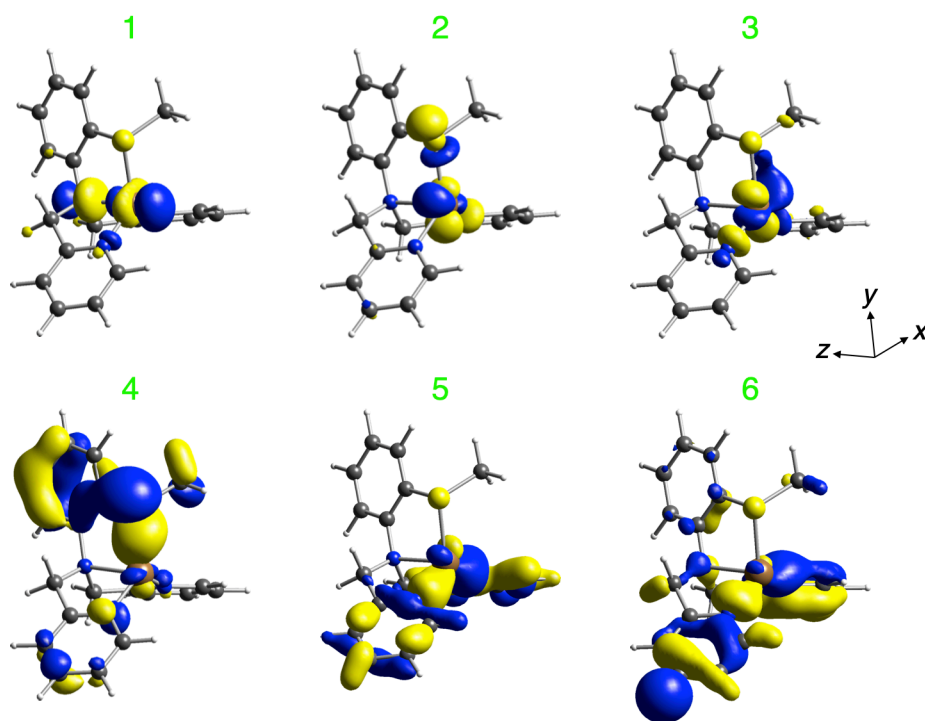
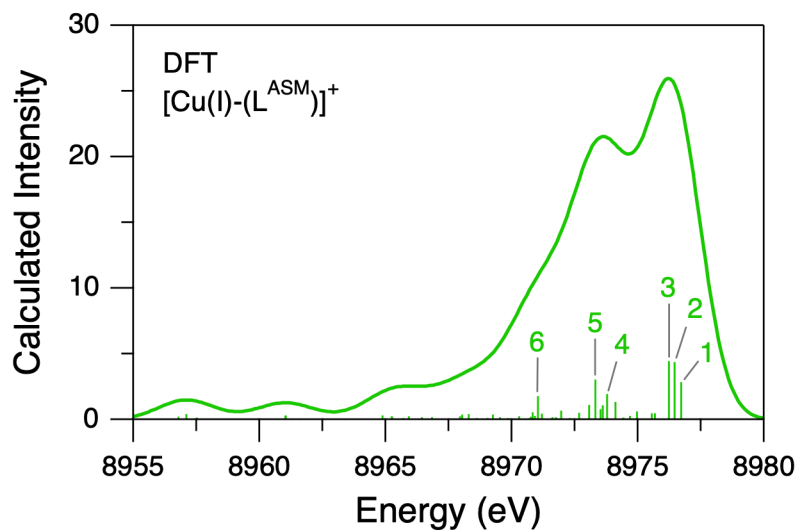


Figure S9. DFT/BP86 calculated $K\beta$ VtC XES spectrum of complex **3** and contour plots of MOs contributing to calculated transitions denoted as 1–6. The calculated spectrum has been shifted by 230 eV and a 2.5-eV line-broadening has been applied to the calculated transitions. The molecules are oriented similarly to the structure presented in Figure 4. Note that 1 and 4 are shown in Figure 6.

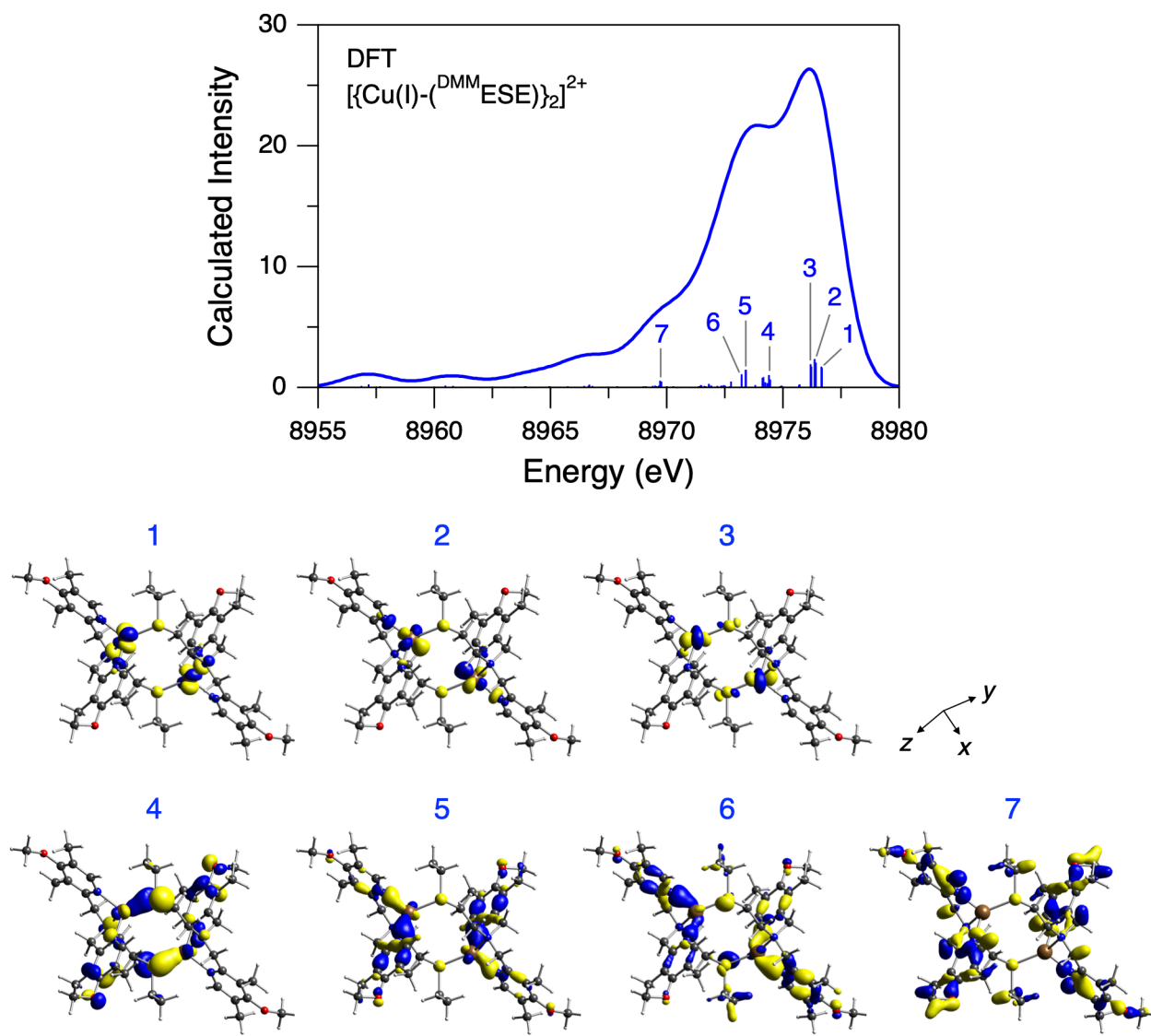


Figure S10. DFT/BP86 calculated $K\beta$ VtC XES spectrum of complex **4** and contour plots of MOs contributing to calculated transitions denoted as 1–7. The calculated spectrum has been shifted by 230 eV and a 2.5-eV line-broadening has been applied to the calculated transitions. The molecules are oriented similarly to the structure presented in Figure 4. As complex **4** is a centrosymmetric dimer, two transitions are calculated at an almost same energy due to in-phase and out-of-phase combinations of two Cu sites. Between these two transitions, the MO that generates the relatively intense transition is shown here. Note that 1 in this figure and the MO for the feature “a” shown in Figure 6 represent the different combinations of two Cu sites; the former is slightly more intense while the latter appears at a slightly higher energy (i.e., HOMO). 4 is also shown in Figure 6.

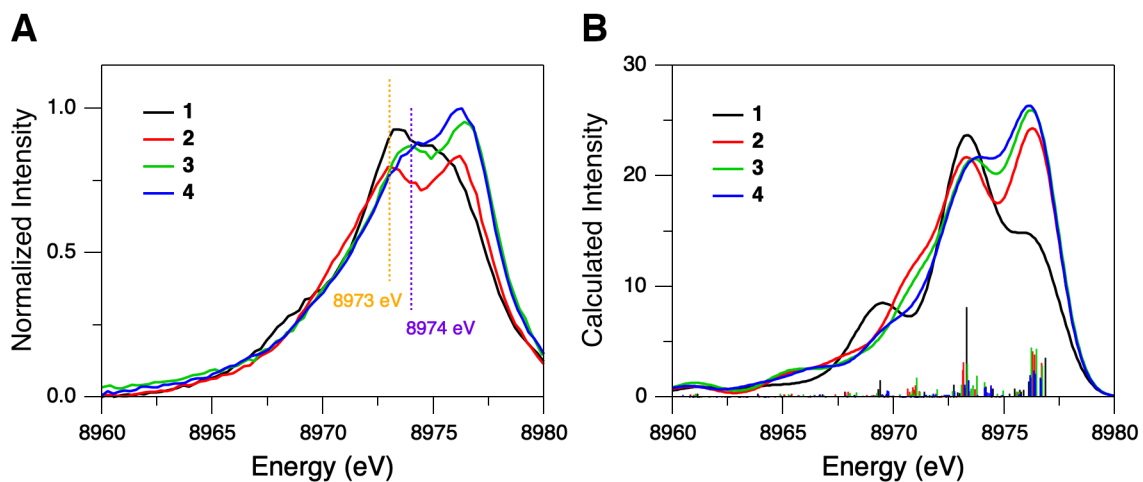


Figure S11. (A) Experimental and (B) DFT/BP86 calculated $K\beta$ VtC XES spectra of complexes 1–4. For the experimental data, the background and the DI emission features have been subtracted using fits in Figure S5. Dotted lines in (A) are drawn on energy positions of 8973 (orange) and 8974 eV (purple). In (B), the calculated spectra have been shifted by 230 eV and a 2.5-eV line-broadening has been applied to the calculated transitions.

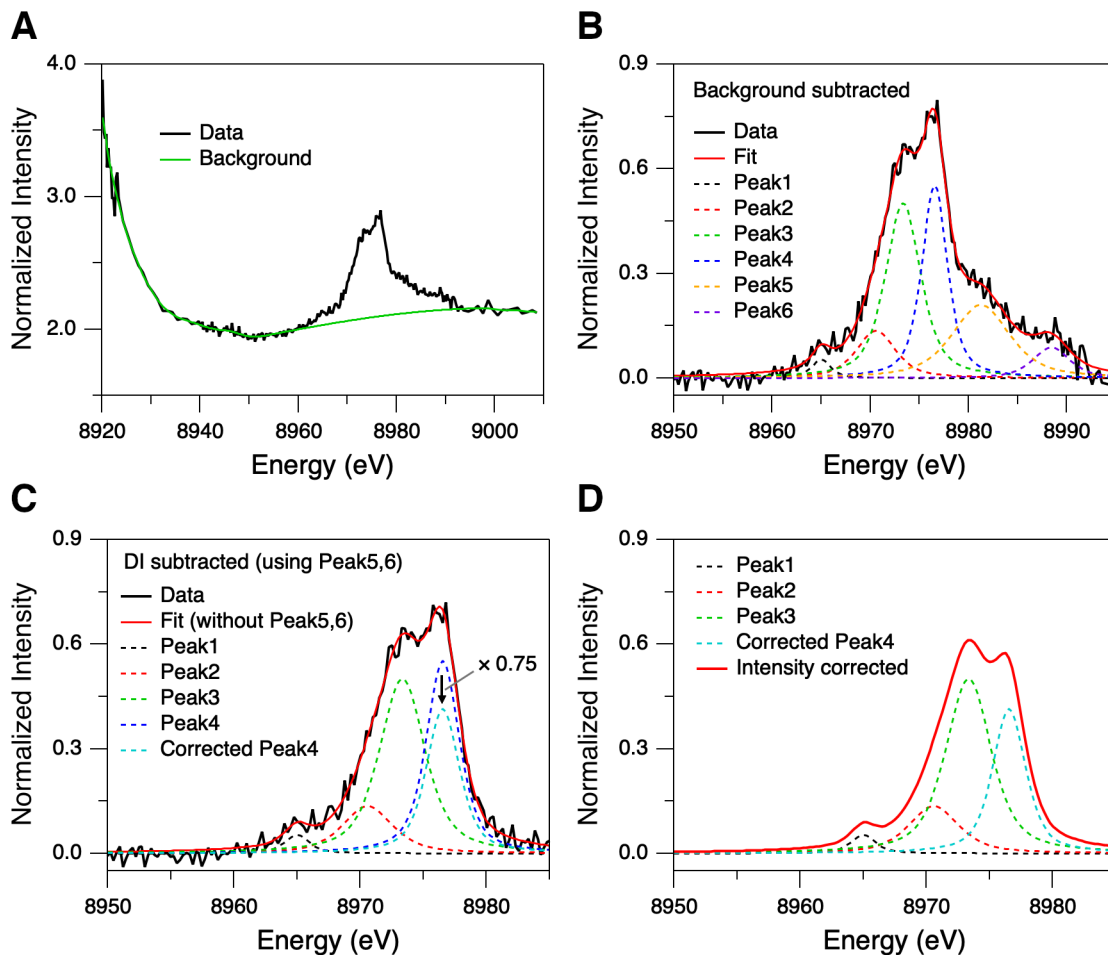


Figure S12. Data processing of the $K\beta$ VtC XES spectrum of $\text{Cu(I)-GO}_{\text{pre}}$. (A) $K\beta$ VtC XES spectrum of $\text{Cu(I)-GO}_{\text{pre}}$ (black) and spline background (green), (B) fit to the background subtracted data, (C) the data after subtraction of the background and the DI emission features, and (D) the data after the intensity ratio correction.

Data processing of the $K\beta$ VtC XES spectrum of $\text{Cu(I)-GO}_{\text{pre}}$

Due to the Compton scattering contribution, the background in the $K\beta$ VtC XES spectrum of $\text{Cu(I)-GO}_{\text{pre}}$ is high in intensity and increases toward higher emission energy with a different shape from that generally associated with the tail of the $K\beta$ main peak (see black spectrum in Figure S12A). This background is reasonably modelled with a spline function (green spectrum in Figure S12A). Pseudo-Voigt peaks (peaks 1–6 in Figure S12) are used to fit the spectral features and the peaks 5 and 6 in Figure S12B model the $1s + 3d$ and the $1s + 3p$ DI emission features, respectively. These two peaks are subtracted from the background subtracted spectrum (solid black spectrum in Figure

S12B) to remove the DI contribution. The resultant spectrum is shown as the solid black spectrum in Figure S12C and also presented in Figure 9A. Since the 1s + 3d DI emission feature is fit with the pseudo-Voigt peak centered on ~8981 eV (peak 5 in Figure S12B), the intensity correction factor, 0.75 (Table 1), is applied to the peak 4 in Figure S12C to account for the residual 1s + 3d DI contribution in the ~8976 eV feature (see dashed blue (peak 4) to dashed light blue (corrected peak 4) peaks in Figure S12C). The intensity ratio corrected spectrum is constructed from the peaks 1–3 and the corrected peak 4 (Figure S12D). This intensity ratio corrected spectrum is scaled as conducted for Cu(I)Cl (see section 2.1) and the resultant spectrum is presented in Figure 9B.

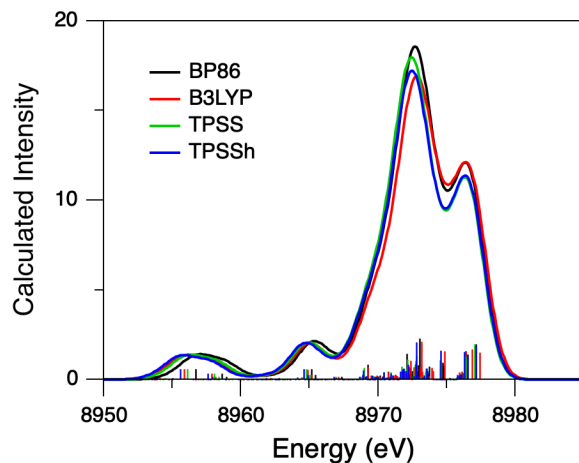


Figure S13. DFT calculated $K\beta$ VtC XES spectra of Cu(I)-GO_{pre} using the optimized structure shown in Figure 8 but with different functionals. The DFT calculated spectrum has been shifted by 230.4 eV for BP86 and those calculated with the other functionals have been shifted to match the energy of the maximum of the ~ 8976 eV feature. A 2.5-eV line-broadening has been applied to the calculated transitions.

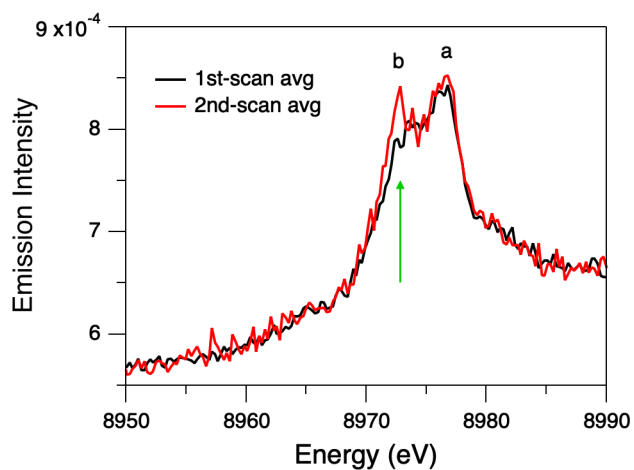


Figure S14. Photodamage in $K\beta$ VtC XES spectra of Cu(I)-GO_{pre}. Two consecutive scans were measured at one sample spot, and black and red spectra are averages of the first and second scans, respectively. A green arrow shows that photodamage leads to an increase of the feature “b” intensity without the noticeable change in the feature “a” intensity.

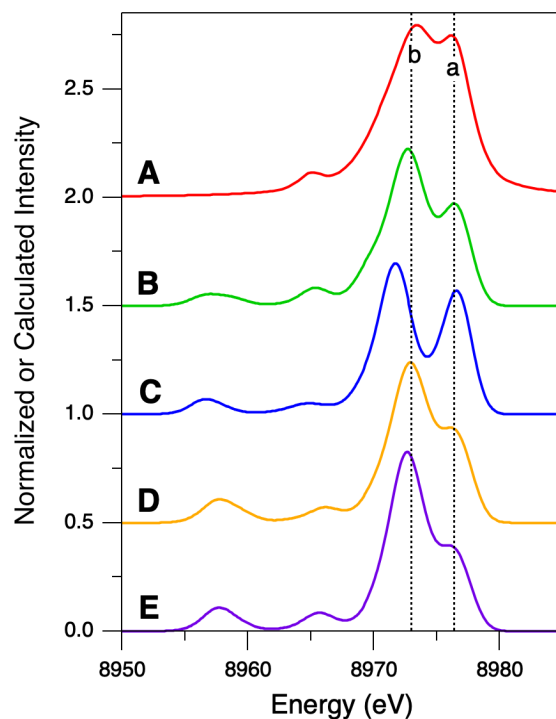


Figure S15. $K\beta$ VtC XES spectra of Cu(I)-GO_{pre} for (A; red) experimental data after subtraction of the background and the DI emission features, and the further intensity ratio correction, and (B–E) DFT/BP86 calculations using optimized structures having the Cu(I) center coordinated with (B; green) Tyr272/His496/His581 (same as Figure 9C), (C; blue) Tyr272/Tyr495/His581 (both Tyr deprotonated), (D; orange) Tyr272/Tyr495/His581 (only Tyr272 deprotonated), and (E; purple) Tyr495/His581. Dotted lines are drawn to show the relative energy positions of the features “a” and “b”.

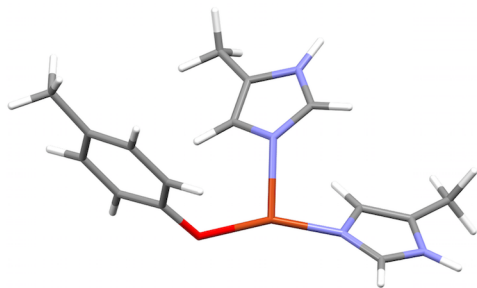
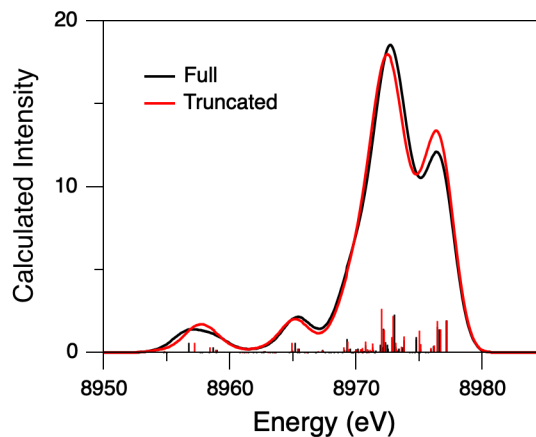
A**B**

Figure S16. (A) Truncated Cu(I)-GO_{pre} structure which contains only the first coordination sphere of Cu(I) (tyrosine and histidine are simplified to phenolate and imidazole, respectively) (Cu in brown, N in blue, C in grey, O in red, and H in white). (B) DFT/BP86 calculated K β VtC XES spectra from the full (black) and the truncated (red) Cu(I)-GO_{pre} structures. The calculated spectra have been shifted by 230.4 eV and a 2.5-eV line-broadening has been applied to the calculated transitions.

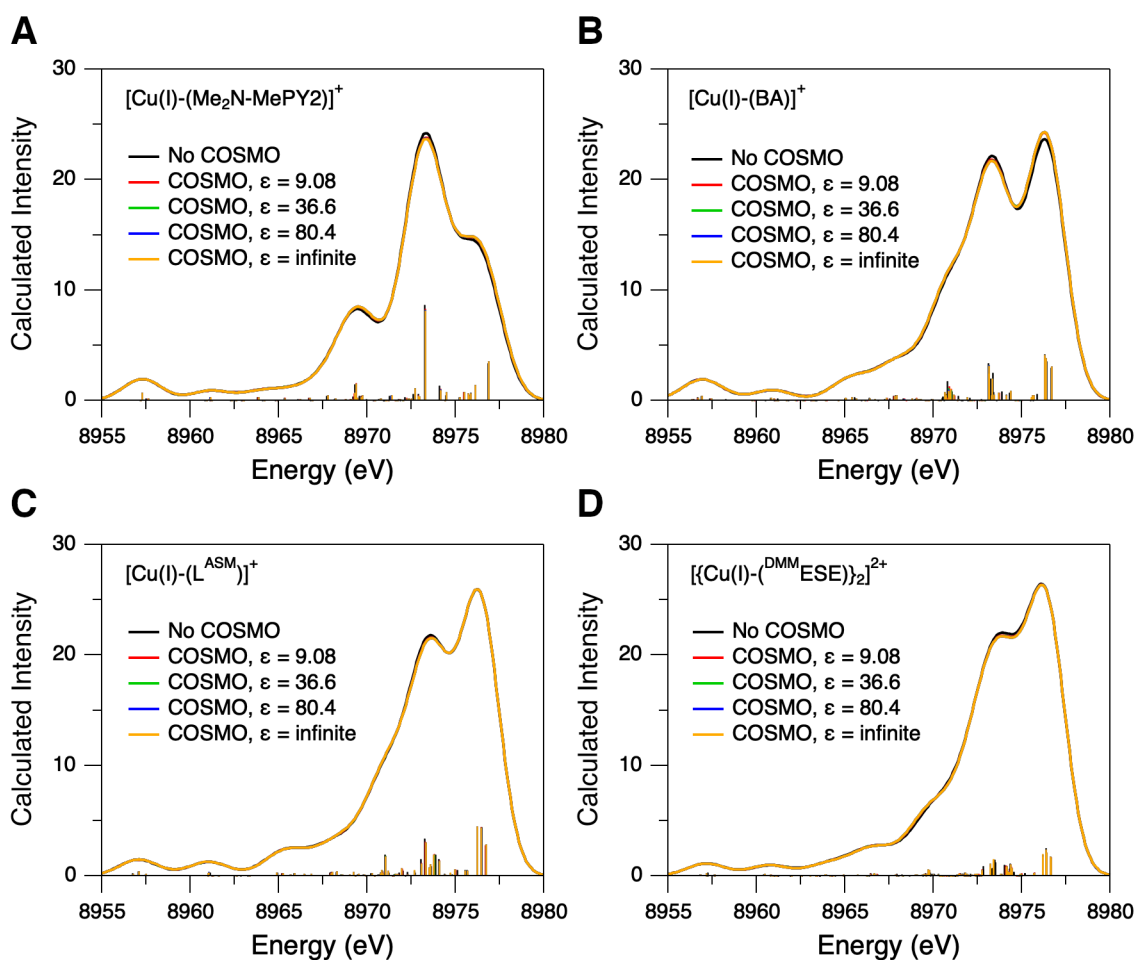


Figure S17. DFT/BP86 calculated $\text{K}\beta$ VtC XES spectra of complexes (A) **1**, (B) **2**, (C) **3**, and (D) **4**. Black spectra were calculated without the COSMO. Red, green, blue, and orange spectra were calculated using the COSMO with a dielectric constant (ϵ) of 9.08 (dichloromethane), 36.6 (acetonitrile), 80.4 (water), and infinite, respectively. The calculated spectra have been shifted by 230 eV and a 2.5-eV line-broadening has been applied to the calculated transitions.

Cartesian coordinates for the optimized structure of [Cu(I)-(Me₂N-MePY2)]⁺ (1)

Cu	0.00000	0.00000	0.00000	C	-1.43295	0.85048	2.41103
N	-0.24288	1.37527	-1.72810	H	-0.50905	0.57223	2.91894
N	1.25057	-1.31426	-0.62843	C	-5.99694	2.54793	2.41889
N	3.25727	-4.67937	-2.17160	H	-5.81949	3.26011	1.59825
N	-1.46369	0.63426	1.06982	H	-6.70488	3.00257	3.11845
N	-4.75869	2.24603	3.13234	H	-6.45747	1.63861	1.99892
C	0.57257	2.60221	-1.63963	C	-4.70846	2.42240	4.58162
H	0.46197	3.23392	-2.54213	H	-4.61477	1.45754	5.10659
H	1.63306	2.35116	-1.51857	H	-5.63348	2.90586	4.90974
H	0.26048	3.18107	-0.76114	H	-3.86278	3.06291	4.87550
C	0.16823	0.53426	-2.87971				
H	0.13289	1.14069	-3.80728				
H	-0.57663	-0.26786	-2.99307				
C	1.57260	-0.08186	-2.75821				
H	1.90883	-0.32972	-3.77434				
H	2.28152	0.67888	-2.39158				
C	1.72488	-1.32402	-1.91084				
C	2.38262	-2.42663	-2.44123				
H	2.72677	-2.37018	-3.47184				
C	2.61198	-3.59672	-1.66832				
C	2.12263	-3.55919	-0.33344				
H	2.24748	-4.39926	0.34614				
C	1.46652	-2.43374	0.11814				
H	1.08425	-2.40456	1.13844				
C	3.72206	-4.68547	-3.55693				
H	2.88352	-4.58890	-4.26537				
H	4.23176	-5.63332	-3.75297				
H	4.43319	-3.86573	-3.74446				
C	3.44472	-5.87282	-1.34895				
H	4.02451	-5.64579	-0.44077				
H	3.99504	-6.61871	-1.92996				
H	2.47964	-6.31005	-1.04640				
C	-1.68479	1.72780	-1.83901				
H	-1.97999	1.76632	-2.90304				
H	-1.82410	2.74053	-1.43617				
C	-2.62707	0.76407	-1.08574				
H	-3.64818	0.92596	-1.45838				
H	-2.36083	-0.27951	-1.32574				
C	-2.61326	0.96631	0.40872				
C	-3.71655	1.49342	1.06617				
H	-4.60296	1.72337	0.47852				
C	-3.69299	1.72512	2.46863				
C	-2.48460	1.37586	3.13407				
H	-2.36727	1.50216	4.20798				

Cartesian coordinates for the optimized structure of [Cu(I)-(BA)]⁺ (2)

Cu	0.00000	0.00000	0.00000	C	1.33531	5.13745	5.74627
C	0.65251	-2.92579	0.44989	C	0.82760	4.20087	6.65440
H	1.48866	-2.55393	1.04281	H	0.71736	4.46404	7.70805
C	0.48629	-4.28916	0.22313	C	0.45238	2.92845	6.21369
H	1.19710	-4.99866	0.64594	H	0.04988	2.20484	6.92732
C	-0.59172	-4.71277	-0.55666	N	-0.19120	-1.99130	-0.04314
H	-0.74803	-5.77137	-0.76651	N	-1.61091	-0.03510	-1.48628
C	-1.46502	-3.75283	-1.07068	N	1.03887	0.90896	-1.45450
H	-2.31579	-4.04401	-1.68809	N	-1.31524	1.06833	1.07530
C	-1.25005	-2.40220	-0.79042	N	-0.07707	0.98307	3.02049
C	-2.23701	-1.34234	-1.26054	H	0.62273	0.55896	2.41279
H	-2.78134	-1.71276	-2.14729	H	1.62459	6.13287	6.08751
H	-2.98935	-1.21538	-0.46461				
C	-0.89073	0.09882	-2.75707				
H	-1.52623	0.49387	-3.56949				
H	-0.57983	-0.91226	-3.06779				
C	0.36934	0.94444	-2.63717				
C	0.84729	1.67633	-3.72544				
H	0.27363	1.69517	-4.65308				
C	2.05212	2.37247	-3.61386				
H	2.43789	2.94869	-4.45544				
C	2.74690	2.32023	-2.40387				
H	3.69124	2.84623	-2.26618				
C	2.20527	1.58492	-1.35305				
H	2.71314	1.52614	-0.38995				
C	-2.43020	1.12425	-1.10910				
H	-3.46613	1.05401	-1.48536				
H	-1.98190	2.01024	-1.58819				
C	-2.44633	1.37673	0.39193				
C	-3.54959	1.95551	1.01084				
H	-4.44812	2.17460	0.43481				
C	-3.46788	2.25585	2.37869				
H	-4.31307	2.71891	2.89005				
C	-2.31196	1.96320	3.08672				
H	-2.23118	2.19694	4.14680				
C	-1.23718	1.34592	2.40565				
C	0.21782	1.15464	4.43029				
H	1.05591	0.47966	4.65897				
H	-0.63174	0.79725	5.03504				
C	0.58369	2.56996	4.86306				
C	1.09088	3.51367	3.96062				
H	1.18993	3.25179	2.90555				
C	1.46336	4.78991	4.39764				
H	1.85425	5.51411	3.68040				

Cartesian coordinates for the optimized structure of [Cu(I)-(L^{ASM})]⁺ (3)

Cu	0.00000	0.00000	0.00000
N	-0.09421	0.67421	1.88916
N	-1.29862	1.72208	-0.44888
N	1.23655	0.83036	-1.32182
S	-1.69768	-1.34140	-0.63338
C	0.20661	0.02359	3.03385
H	0.70998	-0.93760	2.92399
C	-0.09927	0.53440	4.29319
H	0.16502	-0.03230	5.18565
C	-0.74931	1.76644	4.37774
H	-1.01425	2.19272	5.34589
C	-1.05977	2.44532	3.19732
H	-1.56511	3.41139	3.22357
C	-0.71444	1.88065	1.96945
C	-0.94046	2.62521	0.66613
H	-1.67473	3.43298	0.81693
H	0.00924	3.11341	0.39277
C	-0.78834	2.16336	-1.76702
H	-1.00524	3.22798	-1.96175
H	-1.32776	1.58479	-2.53345
C	0.69892	1.90825	-1.94905
C	1.46155	2.72179	-2.78852
H	0.99948	3.58911	-3.26183
C	2.80405	2.41285	-3.01227
H	3.41322	3.03724	-3.66667
C	3.35098	1.29614	-2.37691
H	4.39427	1.01506	-2.51825
C	2.53913	0.53885	-1.53759
H	2.93022	-0.33299	-1.01237
C	-2.67947	1.28521	-0.47479
C	-2.99345	-0.09030	-0.56312
C	-4.33545	-0.49307	-0.63992
H	-4.57814	-1.55196	-0.73689
C	-5.36383	0.44754	-0.58535
H	-6.40177	0.11543	-0.63285
C	-5.05901	1.80851	-0.47990
H	-5.85686	2.55162	-0.44794
C	-3.72639	2.21818	-0.43382
H	-3.49125	3.28198	-0.37168
C	-2.20164	-2.46716	0.71694
H	-3.15008	-2.95713	0.47107
H	-2.27348	-1.91935	1.66280
H	-1.40815	-3.22232	0.77685

Cartesian coordinates for the optimized structure of $[\{\text{Cu(I)}-(\text{DMM}^{\text{E}}\text{SE})\}_2]^{2+}$ (4)

Cu	0.00000	0.00000	0.00000	C	-2.57710	-1.90927	0.02722
S	-4.46377	-1.67087	-1.97011	H	-3.25073	-2.56913	0.60740
C	2.29470	-0.35838	1.95386	H	-2.05627	-2.54096	-0.70774
H	2.69922	0.51748	1.44175	C	-3.41126	-0.85273	-0.69354
C	3.02540	-0.94354	2.98754	H	-2.77311	-0.09440	-1.16268
C	2.45042	-2.07917	3.60098	H	-4.10473	-0.35217	-0.00411
C	1.21347	-2.58999	3.14009	C	-6.00298	-0.66907	-1.83243
C	0.57930	-1.91278	2.08799	H	-6.36865	-0.81328	-0.80537
C	-0.72752	-2.41241	1.50331	H	-6.70217	-1.18288	-2.50697
H	-0.50096	-3.13480	0.70147	C	-5.86611	0.80385	-2.18710
H	-1.30556	-2.96518	2.26432	H	-5.51426	0.93377	-3.21947
C	-2.11734	-0.46235	1.96642	H	-6.84641	1.29530	-2.09406
H	-1.47663	-0.54840	2.85924	H	-5.17019	1.32573	-1.51544
H	-3.10914	-0.83742	2.26907	N	1.10957	-0.81239	1.50616
C	-2.18053	1.01110	1.60311	N	-1.53423	-1.32315	0.90471
C	-3.11048	1.87431	2.21298	N	-1.24922	1.45226	0.73127
C	-3.02745	3.24120	1.88326	O	3.06263	-2.78724	4.59444
C	-2.07776	3.71025	0.95625	O	-3.92954	4.13814	2.41310
C	-1.21350	2.76097	0.41447	Cu	-3.63346	-1.49573	-4.00782
H	-0.45137	3.06272	-0.30735	S	0.83244	0.17204	-2.03701
C	4.38952	-0.39851	3.32058	C	-5.92706	-1.13580	-5.96240
H	4.70587	0.30994	2.54407	H	-6.33135	-2.01238	-5.45138
H	5.13609	-1.20381	3.37252	C	-6.65699	-0.55015	-6.99634
H	4.40755	0.13292	4.28269	C	-6.08200	0.58626	-7.60829
C	3.61747	-2.08561	5.73423	C	-4.84601	1.09765	-7.14556
H	4.68049	-1.85981	5.58280	C	-4.21255	0.41993	-6.09334
H	3.50751	-2.76993	6.58377	C	-2.90667	0.91974	-5.50672
H	3.05699	-1.16269	5.93369	H	-3.13457	1.64013	-4.70345
C	0.60732	-3.82417	3.75711	H	-2.32875	1.47474	-6.26622
H	-0.41436	-3.63003	4.11591	C	-1.51564	-1.02868	-5.97325
H	1.20912	-4.16851	4.60369	H	-2.15655	-0.94152	-6.86582
H	0.54415	-4.64468	3.02624	H	-0.52414	-0.65243	-6.27544
C	-4.15368	1.36892	3.17458	C	-1.45167	-2.50274	-5.61243
H	-3.70452	1.05070	4.12788	C	-0.52083	-3.36443	-6.22307
H	-4.68639	0.49857	2.76460	C	-0.60338	-4.73192	-5.89569
H	-4.89410	2.14827	3.38630	C	-1.55380	-5.20309	-4.97051
C	-3.55604	4.67127	3.70717	C	-2.41895	-4.25519	-4.42774
H	-3.46799	3.86819	4.45436	H	-3.18185	-4.55843	-3.70736
H	-4.35797	5.35967	3.99528	C	-8.02039	-1.09561	-7.33158
H	-2.60230	5.21660	3.64147	H	-8.33777	-1.80432	-6.55573
C	-2.00350	5.15669	0.55536	H	-8.76715	-0.29056	-7.38466
H	-1.76138	5.80094	1.41359	H	-8.03666	-1.62688	-8.29383
H	-2.96739	5.50414	0.15601	C	-7.24510	0.59270	-9.74348
H	-1.23287	5.30532	-0.21190	H	-8.30831	0.36598	-9.59473

H	-7.13357	1.27725	-10.59265
H	-6.68346	-0.32977	-9.94177
C	-4.24011	2.33281	-7.76087
H	-3.21806	2.13964	-8.11913
H	-4.84151	2.67759	-8.60755
H	-4.17794	3.15262	-7.02911
C	0.52289	-2.85700	-7.18302
H	0.07446	-2.53800	-8.13641
H	1.05457	-1.98671	-6.77154
H	1.26417	-3.63549	-7.39489
C	-0.07179	-6.15907	-7.72117
H	-0.15880	-5.35513	-8.46755
H	0.73056	-6.84711	-8.00896
H	-1.02561	-6.70450	-7.65746
C	-1.62765	-6.65027	-4.57223
H	-1.86480	-7.29358	-5.43250
H	-0.66500	-6.99681	-4.16904
H	-2.40142	-6.80126	-3.80859
C	-1.05661	0.41492	-4.03162
H	-0.38426	1.07741	-4.61029
H	-1.57763	1.04364	-3.29419
C	-0.22059	-0.64283	-3.31487
H	-0.85749	-1.40369	-2.84804
H	0.47263	-1.14056	-4.00678
C	2.36853	-0.83456	-2.17289
H	2.73862	-0.68776	-3.19800
H	3.06713	-0.32583	-1.49389
C	2.22518	-2.30829	-1.82428
H	1.86882	-2.44073	-0.79376
H	3.20420	-2.80270	-1.91504
H	1.53031	-2.82544	-2.50065
N	-4.74263	-0.68141	-5.51320
N	-2.09922	-0.17006	-4.91006
N	-2.38340	-2.94587	-4.74204
O	-6.69365	1.29441	-8.60211
O	0.29988	-5.62747	-6.42593

Cartesian coordinates for as-truncated Cu(I)-GO_{pre}

Cu	0.00000	0.00000	0.00000
O	-0.81580	1.69874	0.46046
N	0.30882	-0.96857	1.90006
N	1.72310	-1.78323	3.39124
N	1.35085	-1.00420	-1.01567
N	2.60245	-2.26897	-2.31158
C	1.02263	-2.03066	2.24174
C	0.55552	-0.00053	2.87141
C	1.43523	-0.48186	3.79662
C	2.60075	-1.17678	-0.41897
C	3.39126	-1.96619	-1.20609
C	1.38559	-1.66980	-2.15949
C	4.76581	-2.50857	-1.01229
H	5.35242	-2.08171	-0.19107
C	2.02654	0.17681	4.97940
C	-1.67816	1.81886	1.49046
C	-1.55494	2.88099	2.40915
C	-2.36116	2.94545	3.54058
C	-3.33610	1.97825	3.80976
C	-3.50203	0.96563	2.85997
C	-2.69539	0.88195	1.72752
C	-4.14955	2.01857	5.08114
H	-4.93721	1.26309	5.06563
H	-3.52755	1.82564	5.96105
H	-4.62384	2.99351	5.22628
H	3.11636	0.24387	4.91302
H	1.63952	1.19213	5.05348
H	1.77965	-0.33927	5.91181
H	-4.27194	0.21504	3.00467
H	-2.84247	0.07670	1.01738
H	-0.80404	3.64055	2.23270
H	-2.22073	3.76581	4.23692
H	1.08621	-2.94955	1.69063
H	2.34266	-2.42140	3.86025
H	0.08556	0.96441	2.83712
H	0.58761	-1.73921	-2.87334
H	2.89239	-2.81784	-3.10302
H	2.83256	-0.69331	0.51023
H	4.70420	-3.56889	-0.73644
H	5.34542	-2.45328	-1.93740

Cartesian coordinates for trigonal planar Cu(I)-GO_{pre}

Cu	0.00000	0.00000	0.00000
O	-0.99647	1.66439	-0.01061
N	0.39799	-1.00219	1.86573
N	0.75285	-2.54158	3.40757
N	0.79580	-0.67667	-1.66542
N	1.02249	-1.07632	-3.82495
C	0.60683	-2.29629	2.07625
C	0.41239	-0.40154	3.11325
C	0.63408	-1.34400	4.09418
C	1.98997	-1.34999	-1.88375
C	2.15288	-1.60790	-3.22728
C	0.23479	-0.52500	-2.86341
C	3.23817	-2.28489	-3.99233
H	4.02283	-2.62208	-3.30403
C	0.73806	-1.23924	5.57736
C	-2.16120	1.87631	0.57181
C	-2.71979	3.18704	0.61280
C	-3.95679	3.43681	1.20416
C	-4.72213	2.41302	1.79485
C	-4.17957	1.11855	1.75933
C	-2.94139	0.84927	1.17000
C	-6.05655	2.69983	2.44309
H	-6.55814	1.76824	2.74266
H	-5.95120	3.32230	3.34773
H	-6.73579	3.23986	1.76370
H	1.71701	-1.58541	5.94381
H	0.61379	-0.19331	5.88338
H	-0.03785	-1.83438	6.08347
H	-4.74517	0.29331	2.20464
H	-2.54388	-0.17040	1.15898
H	-2.14930	4.00272	0.16048
H	-4.34342	4.46132	1.20800
H	0.65336	-3.07063	1.31785
H	0.91799	-3.45253	3.82498
H	0.25404	0.66570	3.22807
H	-0.70763	-0.02853	-3.06701
H	0.81468	-1.08532	-4.81900
H	2.65803	-1.59826	-1.06578
H	2.86381	-3.16489	-4.53793
H	3.70063	-1.60801	-4.72727