An experimental and theoretical study of metallorganic coordination networks of tetrahydroxyquinone on Cu(111).

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Figure S1: STM images of three different phases identified after deposition of THQ on Cu(111) at RT. Phase (b) is reported in Figure 1 of the main text. The yellow rhombus outlines the closest tentative coincidence unit cell between overlayer and substrate, identified thanks to the presence of brighter molecules in phases (a) and (c) and thanks to a Moiré pattern visible at voltages higher than 1V for phase (b). Within the coincidence unit cell different molecules occupy different positions with respect the substrate. All images are 20x20 nm^2 ; (a) I=10 nA V=1 V; (b) collage of two images on the same area: lower part I=8 nA, V=0.3 V; upper part I= 8 nA V=1.1 V; (c) I=1 nA V=1V. Arrows indicate the substrate orientation.
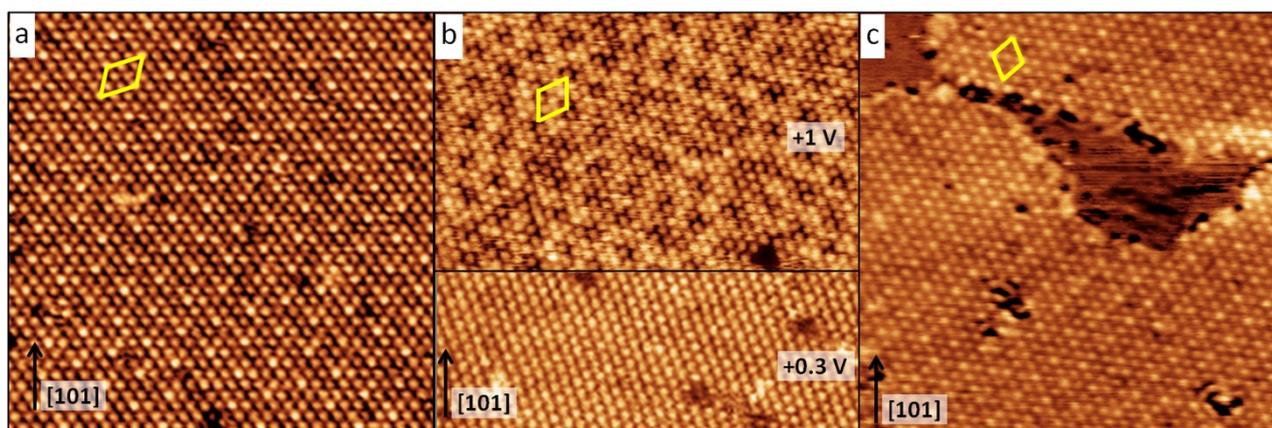
Figure S2: Top (a) and side (b) view representations of the simulated PBE-D2 Cu(111) surface. The different colours are used to highlight the different layers. The red, blue and green hexagonal shapes represent top (T), bridge (B) and hollow (H) chemisorption sites, respectively.

(a) (b)

1st
2nd
3rd
4th
5th
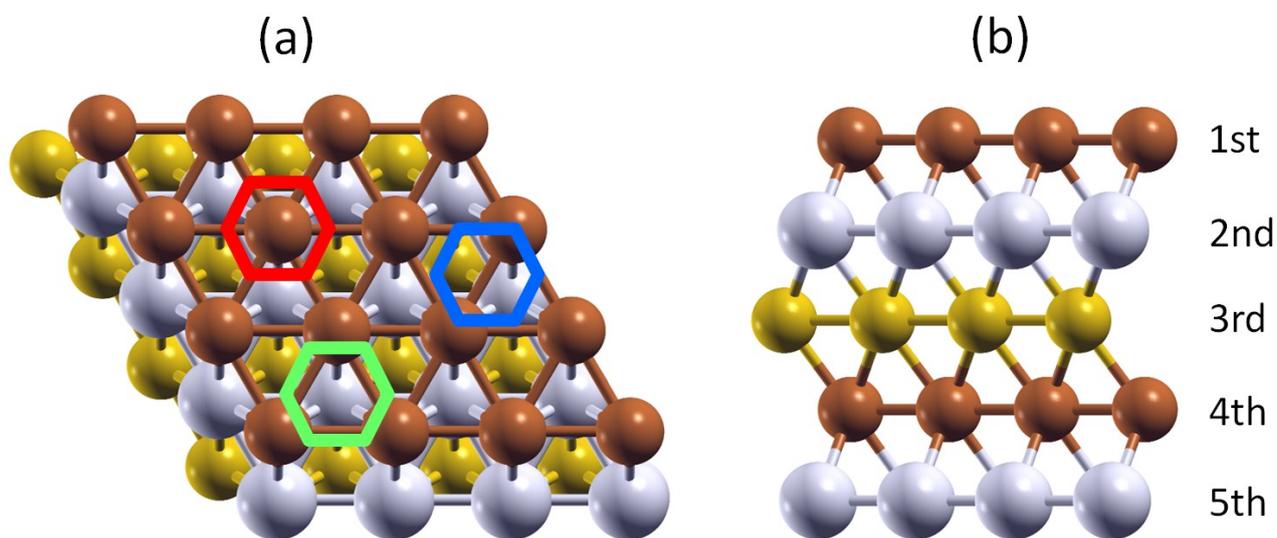
Figure S3: Simulated PBE-D2 molecular models for THQ at T, B and H chemisorption sites. The blue, red and yellow sphere are copper, oxygen and carbon atoms, respectively. Each unit cell contains one THQ molecule.
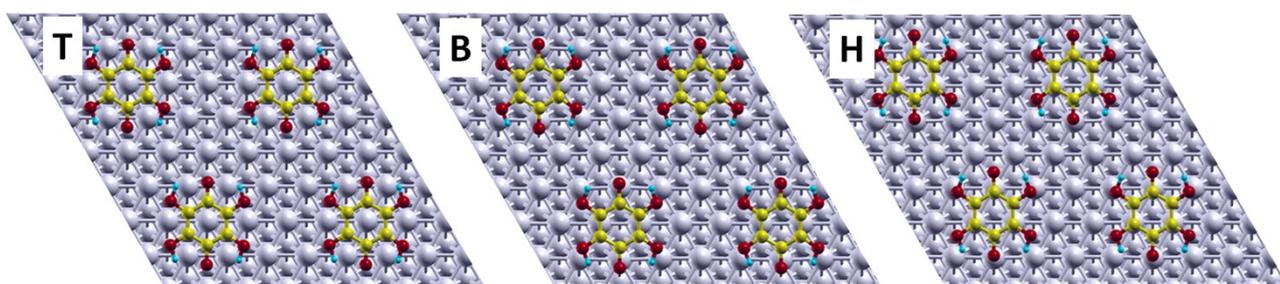
Figure S4: In the top of the Figure the simulated PBE-D2 STM images for TOQ at T, B and H chemisorption sites, while in the bottom of the Figure the respective molecule models. The blue, red and yellow sphere are copper, oxygen and carbon atoms, respectively.
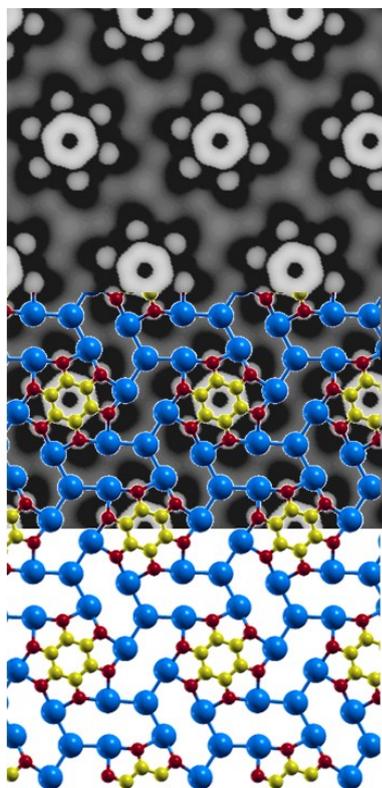
T
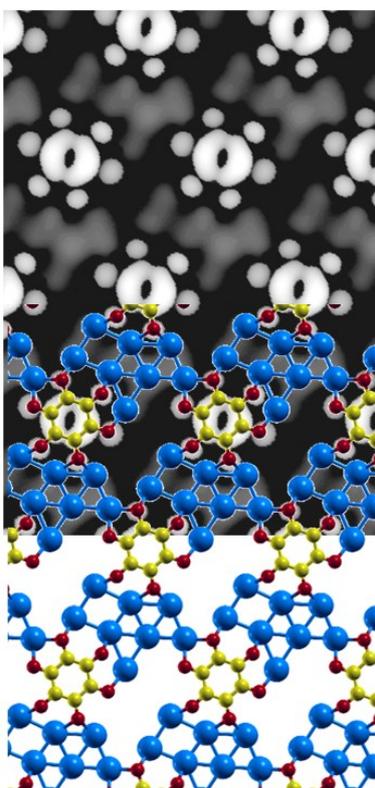
B
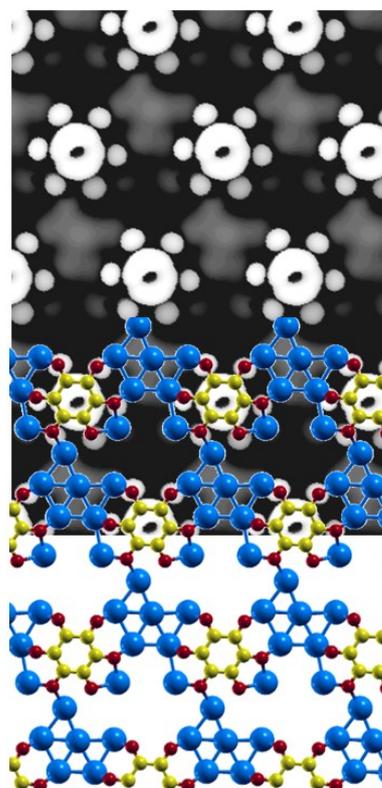
H

Figure S5: Experimental (a) and simulated STM images obtained with (c) and without (d) the inclusion of dispersion corrections for TOQ@T on Cu(111). STM data taken with a bias voltage of V = 0.55 V, on the interface prepared by annealing at 385±5 K. The PBE-D2 optimized geometry (b) has been also reported.
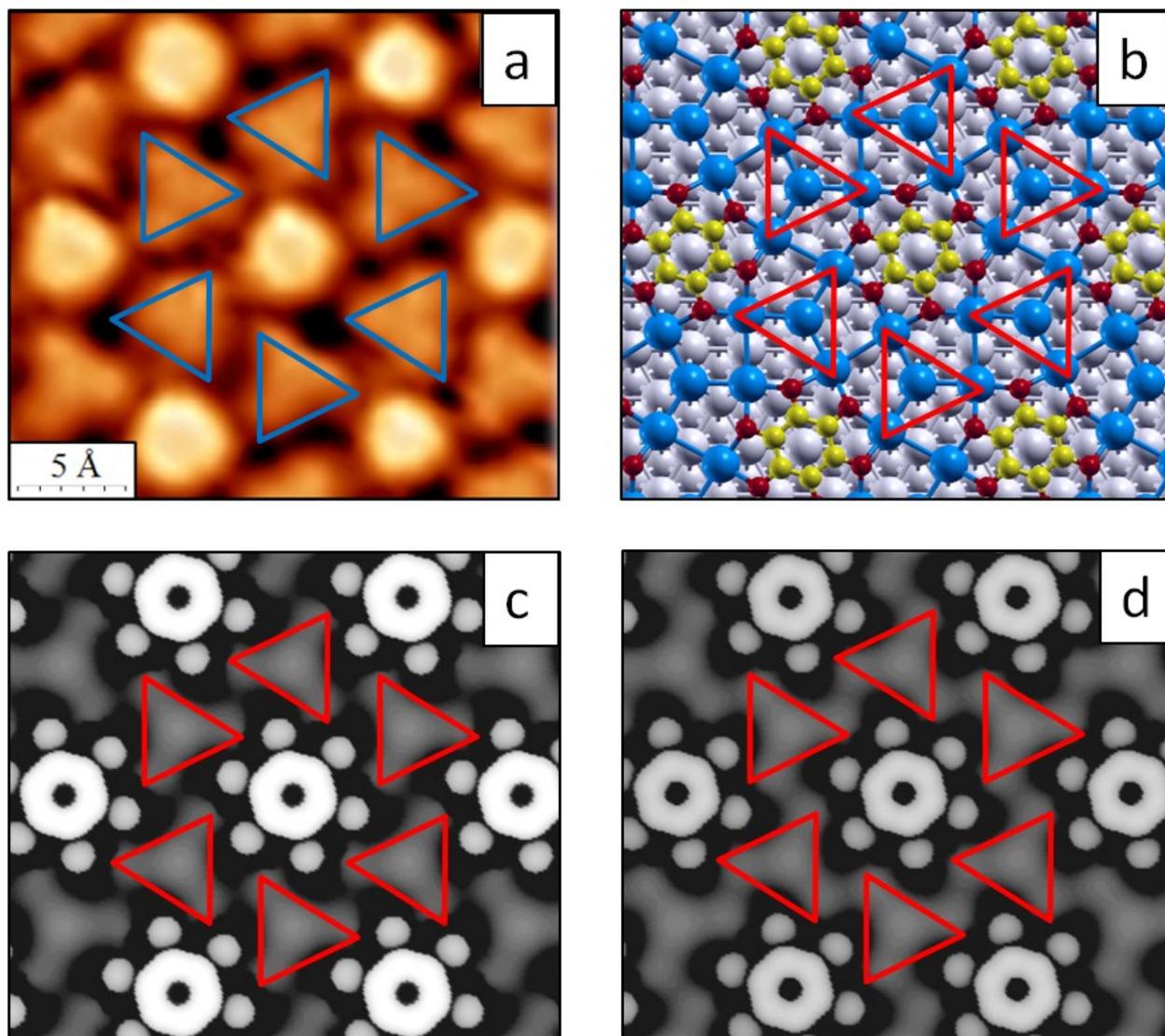
Figure S6: Experimental (solid black lines) and simulated (vertical bars) C K-edge spectra for RT THQ@Cu(111). Simulated spectra are reported for B (blue bars), H (green bars) and T (red bars). The energy values in parentheses are the adsorption energies. The reported adsorption energy is computed from the formula: $E_{ads} = E_{tot} - E_{slab} - E_{mol}$, where E_{tot} is the total energy of the surface containing the adsorbed molecule, E_{slab} is the total energy of the bare surface, and E_{mol} is the energy of the free molecule. Simulated spectra for B, H and T sites are shifted by 1.48, 1.51, 1.42 eV, respectively for superimposed them at the experimental C K-edge spectrum. For sake of clarity, only the p-polarization is reported in the Figure.
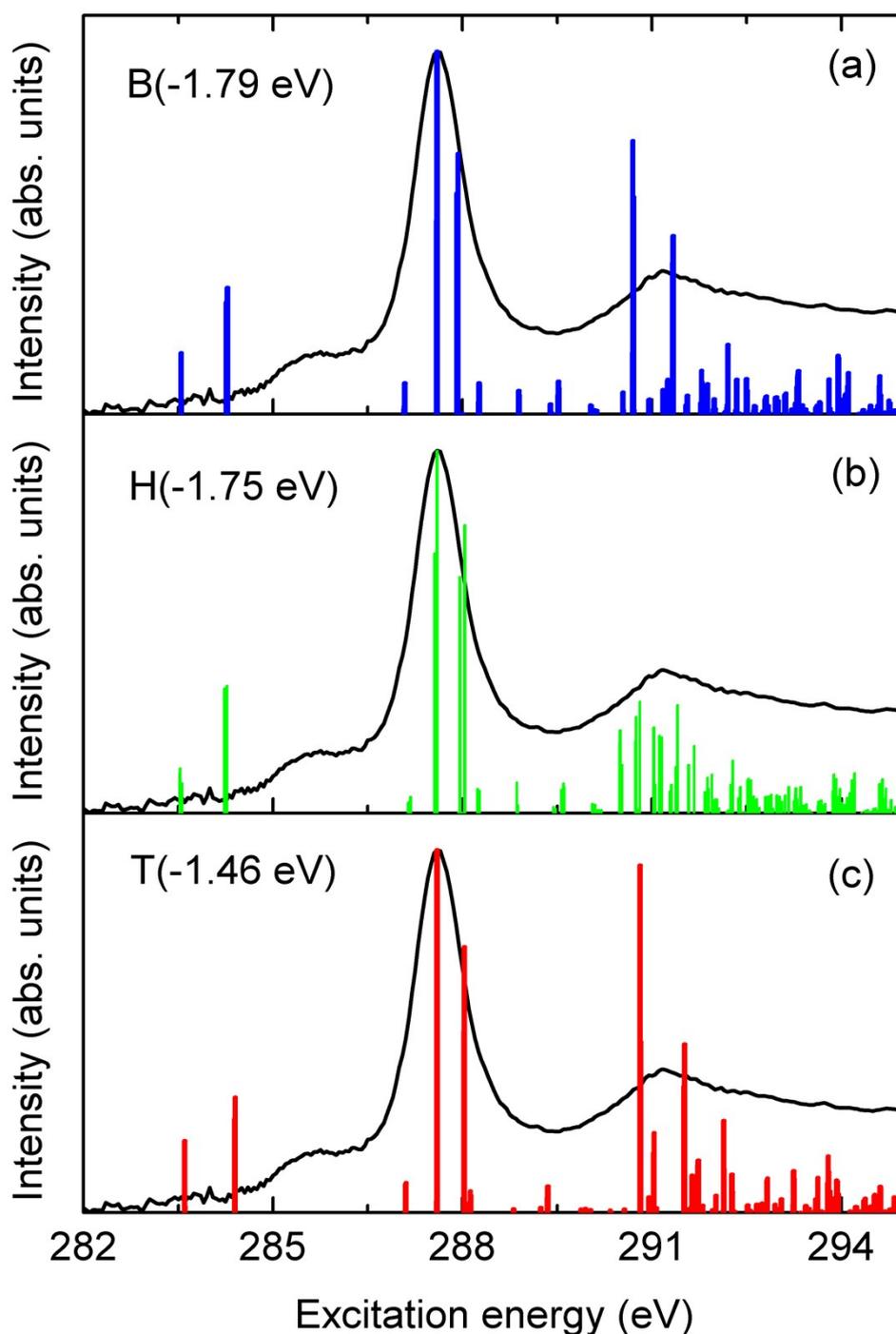
Figure S7: Energy and 3D contour plot for the relevant FMOs for THQ@Cu(111) for B site. Isosurface value: 0.03 e$^{1/2}$/Å$^{3/2}$.

MOs	Energy (eV)	Symmetry Reminiscent	3D Plot
44a (HOMO)	-11.52	E_{1g}	
45a (LUMO)	-11.09	E_{1g}	
46a	-7.56	E_{2u}	
47a	-7.23	E_{2u}	
52a	-4.12	B_{2g}	
53a	-4.03		
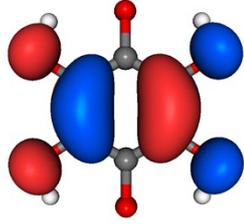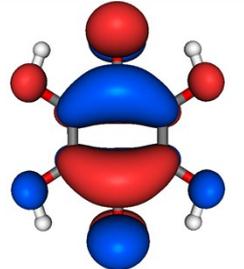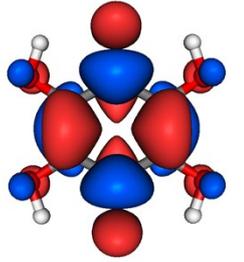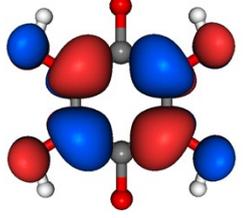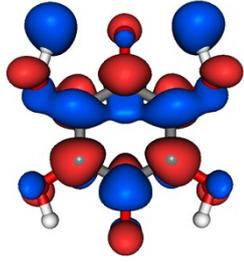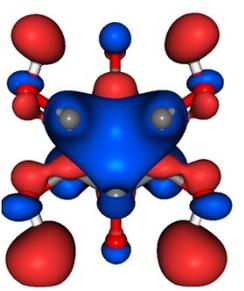
Figure S8: Energy and 3D contour plot for the relevant FMOs for TOQ@Cu(111) for T site. Isosurface value: 0.3 $e^{1/2}/Å^{3/2}$.

MOs	Energy (eV)	Symmetry Reminiscent	3D Plot
127a (LUMO)	-10.83		
128a	-9.74	E_{1g}	
129	-9.73	E_{1g}	
134a	-8.03		
135a	-7.71		
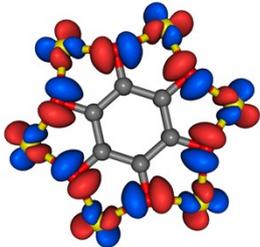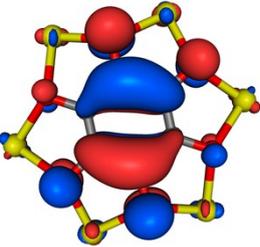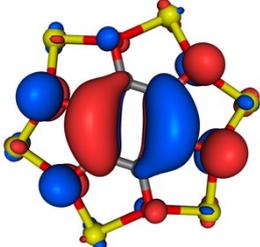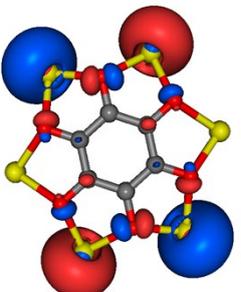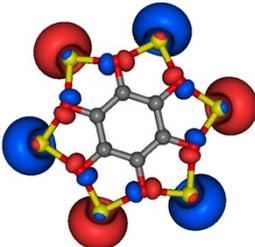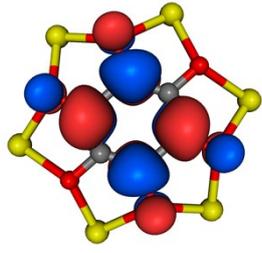
136a	-5.84	E$_{2u}$	
137a	-5.83	E$_{2u}$	
153a	-2.46	B$_{2g}$	
154a	-2.12		
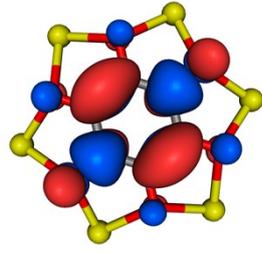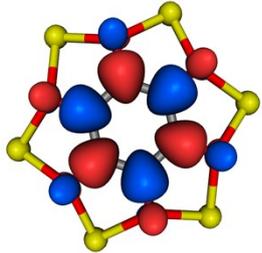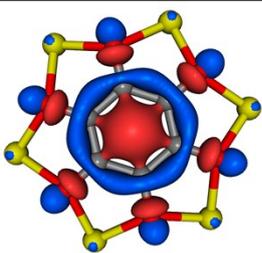
Figure S9: Experimental (solid red lines) and simulated (black bars) O K-edge spectra for HT TOQ@Cu(111) at the T site. Simulated outcomes are shifted of 9.5 eV to superimposed the highest energy peak (B). For sake of clarity, only the p-polarization is reported in the Figure.
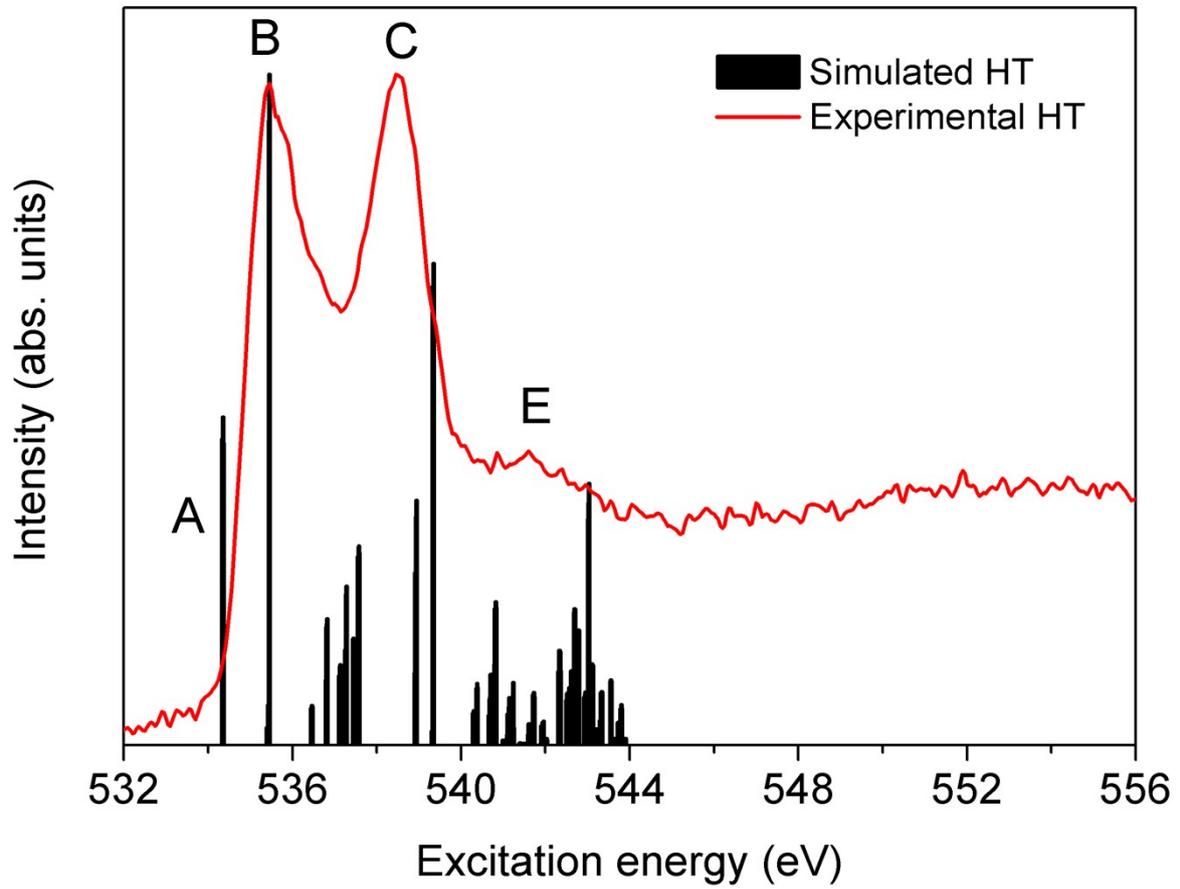
Table S1: Energies and oscillator strengths for all irreducible representations in C K-edge spectrum (B site) calculated at RT with LB94 functional. Only the transitions with oscillator strengths higher than 6×10^{-3} are reported. C_i and X_f represent the initial and final states of the excitations. Labeled peak are reported in Figure 3.

Peak	C_i	X_f	Energy (eV)	$f \times 10^3$	Transitions
A	C(-OH)	O	282.1	6.4	11a→ 45a (99%)
A	C(=O)	O	282.8	11.7	8a→ 45a (100%)
A	C(=O)	O	282.8	13.1	7a→45a (100%)
C	C(-OH)	C(-OH)	286.1	7.1	12a→47a (61%) + 10a→47a (26%)
C	C(-OH)	C(-OH)	286.1	20.2	11a→ 47a (67%) + 9a→47a (18%)
C	C(-OH)	C(-OH)	286.1	21.9	10a→47a (61%) + 12a→47a (29%)
C	C(-OH)	C(-OH)	286.1	37.7	9a→47a (71%) + 11a→47a (20%)
C	C(=O)	C(=O)	286.4	23.0	8a→46a (99%)
C	C(=O)	C(=O)	286.5	27.1	7a→46a (99%)
D	C(-OH)	C	289.2	28.5	11a→52a (40%) + 11a→53a (34%)
D	C(-OH)	C	289.2	12.8	10a→52a (42%) + 10a→53a (37%)
D	C(-OH)	C	289.2	22.6	9a→52a (44%) + 9a→53a (40%)
D	C(=O)	C	289.9	15.8	7a→52a (55%) + 7a→53a (41%)
D	C(=O)	C	289.9	18.6	8a→53a (55%) + 8a→52a (42%)

Table S2: Energies and oscillator strengths for all irreducible representations in C K-edge spectrum (T site) calculated at HT with LB94 functional. Only the transitions with oscillator strengths higher than 1.5×10^{-2} are reported. X_f represent the final states of the excitations. All initial and final levels are beta. Labeled peak are reported in Figure 3.

Peak	X_f	Energy (eV)	$f(10^2)$	Transitions
A	C/O	282.2	1.5	39a→129a (50%) + 37a→129a (16%)
C	C	286.2	11.9	41a→137a (48%) + 40a→136a (23%)
D	C	289.6	3.0	37a→153a (44%) + 42a→153a (19%)
D	C	289.6	4.1	37a→153a (29%) + 42a→153a (19%) + 38a→153a (15%)

Table S3: Energies and oscillator strengths for all irreducible representations in O K-edge spectrum (T site) calculated at HT with LB94 functional. Only the transitions with oscillator strengths higher than 2×10^{-3} are reported. X_f represent the final states of the excitations. All initial and final levels are beta, except the first one of C peak. Labeled peak are reported in Figure 4.

Peak	X_f	Energy (eV)	$f(10^3)$	Transitions
A	Cu $(dx_{2-y2} + d_{xy})$/O	524.9	2.7	36a→127a (100%)
A	Cu $(dx_{2-y2} + d_{xy})$/O	524.9	2.9	35a→127a (100%)
A	Cu $(dx_{2-y2} + d_{xy})$/O	524.9	2.5	34a→127a (100%)
A	Cu $(dx_{2-y2} + d_{xy})$/O	524.9	2.8	33a→127a (100%)
A	Cu $(dx_{2-y2} + d_{xy})$/O	524.9	2.5	32a→127a (100%)
A	Cu $(dx_{2-y2} + d_{xy})$/O	524.9	2.6	31a→127a (100%)
B	C/O	526.0	5.4	36a→129a (96%)
B	C/O	526.0	5.0	32a→128a (83%) + 32a→129a (16%)
B	C/O	526.0	5.0	34a→ 129a (70%) + 34a→128a (30%)
B	C/O	526.0	5.4	35a→129a (96%)
B	C/O	526.0	5.8	33a→129a (70%) + 33a→128a (30%)
B	C/O	526.0	5.9	31a→128a (83%) + 31a→129a(17%)
C	C	529.5	2.1	33a (α)→137a (96%)
C	C	529.9	4.0	36a→136a (53%) + 36a→137a (43%)
C	C	529.9	3.8	35a→136a (53%) + 35a→137a (43%)
C	C	529.9	3.9	32a→136a (65%) + 32a→137a (31%)
C	C	529.9	4.1	34a→137a (96%)

C	C	529.9	4.1	33a→137a (96%)
C	C	529.9	4.1	31a→136a (65%) + 31a→137a(31%)
E	C/Cu/O	533.6	2.3	32a→154a (93%)
E	C/Cu/O	533.6	2.1	31a→154a (94%)

Table S4: Energies and oscillator strengths for all irreducible representations in O K-edge spectrum (B site) calculated at RT with LB94 functional. Only the transitions with oscillator strengths higher than 4×10^{-3} are reported. O_i and X_f represent the initial and final states of the excitations. Labeled peak are reported in Figure 4.

Peak	O_i	X_f	Energy (eV)	$f(10^3)$	Transitions
B	=O	C/O	525.7	15.6	6a→ 45a (100%)
B	=O	C/O	525.7	16.0	5a→ 45a (100%)
C	=O	C	529.1	8.8	6a→46a (100%)
C	=O	C	529.1	8.6	5a→46a (100%)
D	-OH	C	530.2	4.4	4a→47a (100%)
D	-OH	C	530.2	4.5	3a→ 47a (100%)
D	-OH	C	530.2	4.6	2a→47a (100%)
D	-OH	C	530.2	4.6	1a→ 47a (100%)
E	=O	O	537.4	2.5	6a→101a (92%)
E	=O	O	537.4	2.6	5a→101a (91%)
E	-OH	C	537.5	4.7	4a→ 87a (95%)
E	-OH	C	537.5	4.8	3a→87a (95%)
E	-OH	C	537.5	4.5	2a→87a (95%)
E	-OH	C	537.5	4.6	1a→87a (95%)