Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Detection of simple inorganic and organic molecules over the Cu-decorated circumcoronene. A combined DFT and QTAIM study

Michal Malček [a,b,*], *Lukáš Bučinský* [b], *Filipe Teixeira* [a], *M. Natália D. S. Cordeiro* [a*]

[a] LAQV@REQUIMTE, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, 4169-007 Porto, Portugal

[b] Institute of Physical Chemistry and Chemical Physics, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

Table S-1 QTAIM spin densities at Cu, oxygen atom/atoms, CC backbone and carbon C5 of all the studied systems in comparison to $Cu(OH)_2$ and CuO_2 molecules and related adsorption energies E_{ads} in eV.

Fig. S-1 Calculated adsorption energies (in eV) on Cu-CC normalized by the number of electrons for all studied adsorbates.

Fig. S-2 Beta PDOS (and DOS) of Cu-C5 bond in Cu-CC + H_2O_2 (a), [Cu-CC + H_2O_2]* (b), Cu-CC + H_2O (c), Cu-CC + O_2 (d) and Cu-CC system. All plots are obtained at the B3LYP level of theory if it is not stated otherwise.

Fig. S-3 PDOS (and DOS) of Cu-C5 bond in Cu-CC + H_2O_2 (a), [Cu-CC + H_2O_2]* (b), Cu-CC + H_2O (c), Cu-CC + O_2 (d) and Cu-CC system. All plots are obtained at the B3LYP level of theory if it is not stated otherwise.

Table S-2 Absolute values of the Scaled Hamiltonian Kinetic Energy (K_S) for Cu, the CC backbone, and the adsorbate [K_S (Cu), K_S (CC), and K_S (Ads), respectively] of all studied systems in comparison to the free adsorbents. All values are given in eV, and were obtained at the B3LYP level of theory if not stated otherwise.

Table S-3 A summary of TD-DFT excitations energies (in eV), wavelengths (in nm) and oscillator strengths obtained for 20 (or 40) lowest excited states

Table S-4 TD-DFT α and β occupied and virtual orbital eigenvalues, and excited states of CC, Cu-CC and Cu-CC + H_2O_2 obtained for B3LYP and CAM-B3LYP functional

Table S-1 QTAIM spin densities at Cu, oxygen atom/atoms, CC backbone and carbon C5 of all the studied systems in comparison to $Cu(OH)_2$ and CuO_2 molecules and related adsorption energies E_{ads} in eV.

System	**QTAIM spin densities**			
	Cu	O	CC	C5
Cu-CC	0.765		0.235	–0.004
$+H_2O_2$ [B3LYP]	0.523	0.241, 0.240	0.003	–0.001
$+H_2O_2$ [PBE0]	0.569	0.221, 0.218	0.000	0.001
$+H_2O_2$ [B97D]	0.395	0.286, 0.286	0.044	–0.001
$+H_2O_2$ [PBE]	0.431	0.277, 0.276	0.023	0.009
$+H_2O_2$ [CAM-B3LYP]	0.580	0.214, 0.213	0.000	–0.001
$+H_2O_2$ [B97D]*	0.341*	0.297*, 0.284*	0.089*	–0.003*
$+H_2O_2$ [PBE]*	0.299*	0.280*, 0.288*	0.139*	–0.009*
$+H_2O$	0.097	0.054	0.816	0.032
$+CH_3OH$	0.070	0.022	0.890	0.040
$+CH_3CH_2OH$	0.034	0.008	0.952	0.031
$+O_2$	–0.002	0.355[a], 0.640[b]	0.007	0.001
$Cu(OH)_2$ [B3LYP]	0.518	0.245, 0.245		
$Cu(OH)_2$ [PBE0]	0.560	0.224, 0.223		
$Cu(OH)_2$ [B97D]	0.409	0.301, 0.301		
$Cu(OH)_2$ [PBE]	0.436	0.286, 0.286		
$Cu(OH)_2$ [CAM-B3LYP]	0.518	0.245, 0.245		
CuO_2	–0.154	0.464, 0.689		

* non-linear $Cu(OH)_2$ residue

[a] proximal oxygen atom

[b] distal oxygen atom

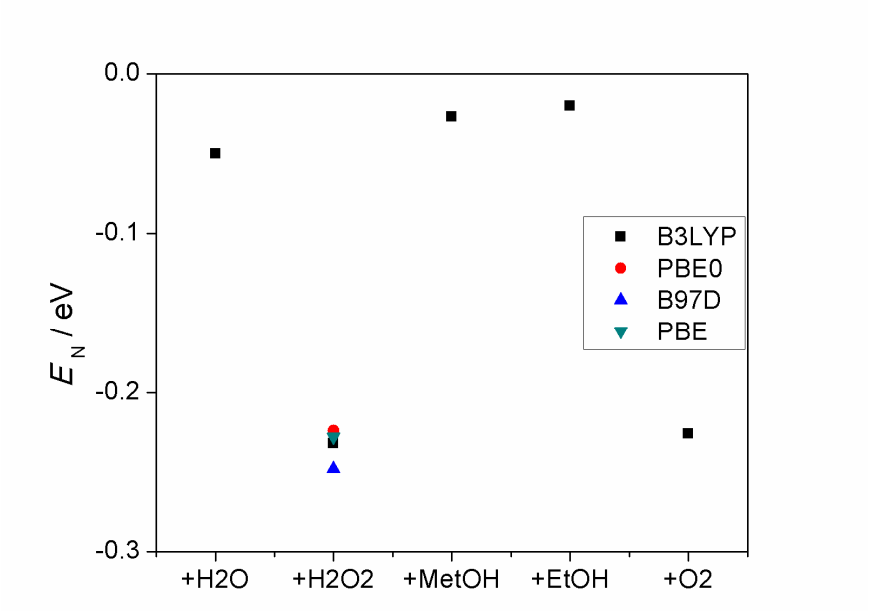

Fig. S-1 Calculated adsorption energies (in eV) of particular adsorbates on Cu-CC normalized by the number of electrons (E_N).

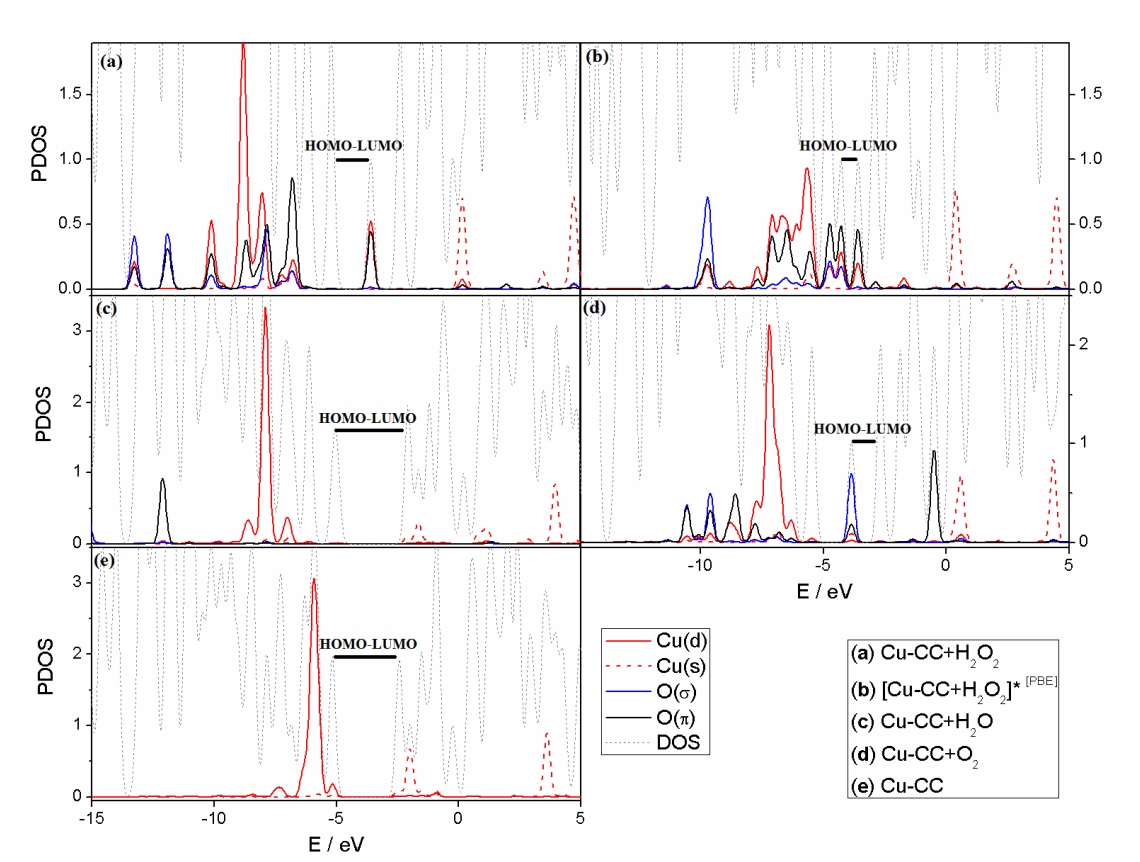

Fig. S-2 β PDOS (and DOS) of Cu-C5 bond in Cu-CC + H_2O_2 (a), [Cu-CC + H_2O_2]* (b), Cu-CC + H_2O (c), Cu-CC + O_2 (d) and Cu-CC system. Particular β HOMO–LUMO band gaps are depicted as well. All plots are obtained at the B3LYP level of theory if it is not stated otherwise.

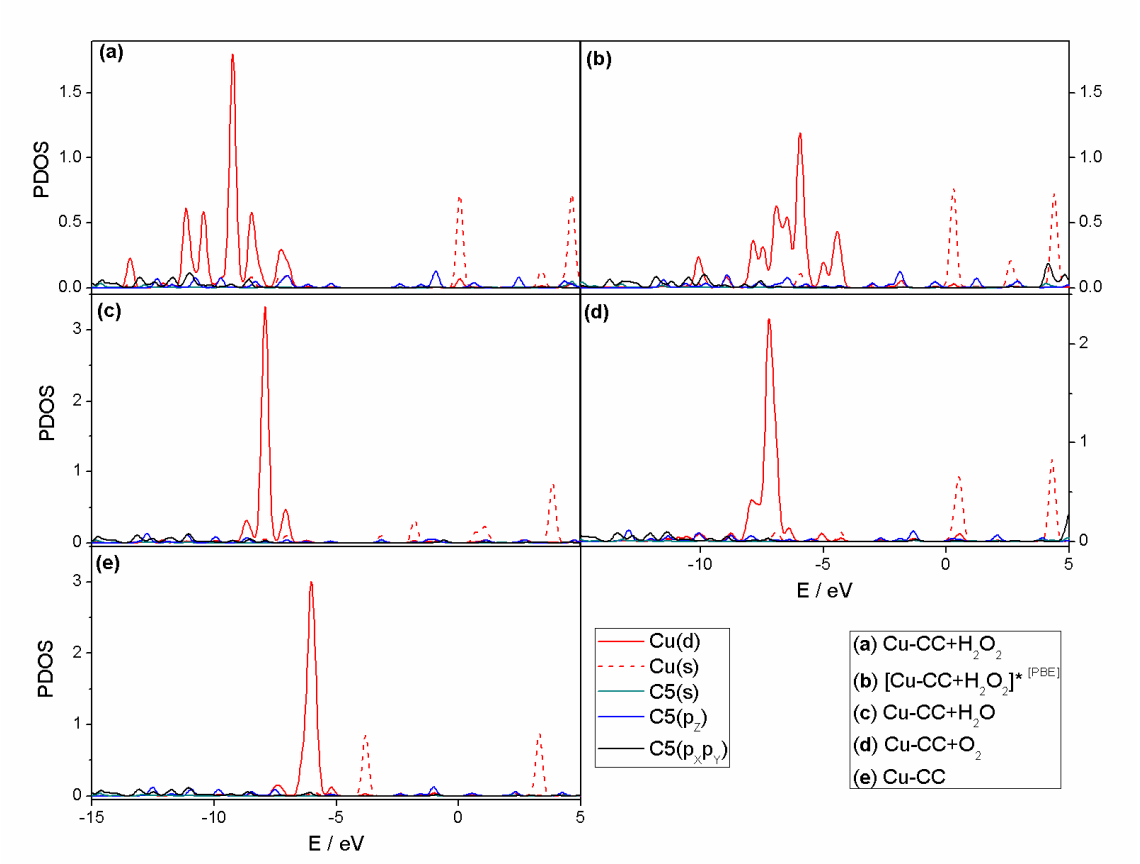

Fig. S-3 α PDOS (and DOS) of Cu-C5 bond in Cu-CC + H_2O_2 (a), [Cu-CC + H_2O_2]* (b), Cu-CC + H_2O (c), Cu-CC + O_2 (d) and Cu-CC system. All plots are obtained at the B3LYP level of theory if it is not stated otherwise.

Table S-2 Absolute values of the Scaled Hamiltonian Kinetic Energy (K_S) for Cu, the CC backbone, and the adsorbate [K_S (Cu), K_S (CC), and K_S (Ads), respectively] of all studied systems in comparison to the free adsorbents. All values are given in eV, and were obtained at the B3LYP level of theory if not stated otherwise.

System	K_S (Cu)	K_S (CC)	K_S (Ads)	K_S (Total)
Cu-CC	–1643.62	–2055.38		–3698.99
$+H_2O_2$ [B3LYP]	–1643.32	–2055.30	–152.11	–3850.73
$+H_2O_2$ [PBE0]	–1642.84	–2053.33	–151.93	–3848.10
$+H_2O_2$ [B97D]	–1644.09	–2053.67	–151.98	–3849.74
$+H_2O_2$ [PBE]	–1642.61	–2053.45	–151.95	–3848.00
$+H_2O_2$ [B97D]*	–1644.05	–2053.72	–151.96	–3849.73
$+H_2O_2$ [PBE]*	–1642.56	–2053.53	–151.92	–3848.01
$+H_2O$	–1643.49	–2055.40	–76.54	–3775.43
$+CH_3OH$	–1643.53	–2055.46	–115.74	–3814.74
$+CH_3CH_2OH$	–1643.56	–2055.53	–154.98	–3854.06
$+O_2$	–1643.43	–2055.39	–150.63	–3849.46
free H_2O_2			–151.58	–151.58
free H_2O			–76.43	–76.43
free CH_3OH			–115.75	–115.75
free CH_3CH_2OH			–155.07	–155.07
free O_2			–150.21	–150.21

Table S-3 A summary of TD-DFT excitations energies (in eV), wavelengths (in nm) and oscillator strengths obtained for 20 (or40) lowest excited states

CC		B3LYP	**CC-Cu**		B3LYP	**H2O2**	B3LYP	
E /eV	λ / nm	f	E /eV	λ / nm	f	E /eV	λ / nm	f
2.2329	555.26	0.0000	0.7838	1581.78	0.0010	0.8446	1467.95	0.0001
2.3785	521.26	0.0000	0.8205	1511.15	0.0055	1.5176	816.98	0.0011
2.8886	429.22	0.9163	1.5594	795.09	0.0049	1.5525	798.61	0.0015
2.8886	429.22	0.9163	1.5723	788.55	0.0003	1.8915	655.50	0.0059
3.0950	400.60	0.0000	1.6854	735.64	0.0006	1.8996	652.69	0.0046
3.0950	400.59	0.0000	1.9330	641.41	0.0083	2.0207	613.57	0.0012
3.1032	399.53	0.0000	1.9928	622.17	0.0021	2.0650	600.42	0.0021
3.1805	389.83	0.0000	2.0079	617.49	0.0018	2.1272	582.85	0.0019
3.2057	386.76	0.0000	2.0545	603.49	0.0006	2.1322	581.48	0.0060
3.2619	380.10	0.0000	2.0581	602.41	0.0011	2.2577	549.15	0.0015
3.2619	380.10	0.0000	2.0720	598.39	0.0022	2.3600	525.35	0.0144
3.5245	351.78	0.0000	2.1066	588.55	0.0000	2.3706	523.01	0.0206
3.5245	351.78	0.0000	2.1257	583.26	0.0015	2.4399	508.15	0.0122
3.5858	345.76	0.0000	2.1415	578.97	0.0019	2.4653	502.92	0.0169
3.6923	335.79	0.0000	2.1656	572.52	0.0015	2.4746	501.02	0.0184
3.6923	335.79	0.0000	2.1808	568.53	0.0001	2.5002	495.89	0.0277
3.7283	332.55	0.0000	2.2010	563.31	0.0002	2.5552	485.22	0.0027
3.7379	331.70	0.0000	2.2535	550.19	0.0008	2.5696	482.50	0.0826
3.7632	329.46	0.0123	2.3705	523.03	0.0002	2.6768	463.18	0.0210
3.7632	329.46	0.0123	2.4132	513.77	0.0003	2.6941	460.21	0.0131
			2.4957	496.79	0.0006	2.7060	458.18	0.0020
			2.5069	494.56	0.0004	2.7420	452.16	0.0234
			2.6399	469.65	0.0884	2.8187	439.87	0.0013
			2.6664	464.99	0.0736	2.8528	434.60	0.2468
			2.7241	455.14	0.0134	2.8631	433.04	0.4021
			2.7495	450.93	0.1116	2.8654	432.69	0.2150
			2.7716	447.34	0.2783	2.8758	431.12	0.4192
			2.8153	440.40	0.0560	2.9184	424.83	0.0489
			2.8237	439.09	0.0208	2.9519	420.01	0.0175
			2.8422	436.23	0.0400	2.9697	417.49	0.0024
			2.8637	432.95	0.0133	2.9891	414.78	0.0017
			2.8730	431.56	0.1543	3.0240	410.00	0.0055
			2.8882	429.27	0.0006	3.0298	409.21	0.0035
			2.8940	428.42	0.0090	3.0570	405.58	0.0156
			2.9262	423.70	0.0134	3.0626	404.84	0.0046
			2.9383	421.96	0.0228	3.0739	403.34	0.0153
			2.9551	419.56	0.0113	3.0875	401.56	0.0025
			2.9689	417.61	0.0143	3.1098	398.68	0.0061
			2.9774	416.41	0.0292	3.1483	393.82	0.0005
			2.9831	415.62	0.0285	3.1749	390.52	0.0033

H2O	B3LYP		**O2**	B3LYP		**MetOH**	B3LYP	
E /eV	λ / nm	f	E /eV	λ / nm	f	E /eV	λ / nm	f
0.3408	3638.50	0.0008	0.4295	2886.77	0.0000	0.3094	4007.55	0.0006
0.6489	1910.58	0.0273	0.7062	1755.66	0.0000	0.6994	1772.61	0.0128
1.0754	1152.92	0.0287	0.7493	1654.60	0.0001	1.0416	1190.28	0.0091
1.0783	1149.76	0.0072	1.1207	1106.26	0.0001	1.1056	1121.41	0.0236
1.4308	866.51	0.0255	1.1289	1098.27	0.0001	1.4465	857.15	0.0473
1.4970	828.20	0.0411	1.4283	868.07	0.0002	1.4857	834.52	0.0220
1.6266	762.22	0.0009	1.5106	820.77	0.0000	1.5798	784.80	0.0009
1.6852	735.73	0.0006	1.5992	775.29	0.0001	1.6420	755.06	0.0009
1.7888	693.10	0.0169	1.8447	672.11	0.0000	1.8109	684.66	0.0181
1.9050	650.83	0.0101	1.8943	654.53	0.0033	1.8766	660.70	0.0129
2.1052	588.94	0.0016	1.9041	651.14	0.0029	2.1032	589.51	0.0078
2.1545	575.46	0.0545	1.9255	643.92	0.0000	2.1803	568.65	0.0632
2.1816	568.33	0.0311	1.9443	637.68	0.0014	2.2037	562.61	0.0274
2.3556	526.34	0.0015	1.9546	634.31	0.0001	2.3734	522.39	0.0010
2.3902	518.71	0.0012	1.9982	620.48	0.0001	2.4364	508.88	0.0015
2.4756	500.82	0.0339	2.0782	596.59	0.0008	2.5391	488.29	0.0076
2.5207	491.86	0.0276	2.0794	596.26	0.0005	2.5897	478.76	0.1676
2.5220	491.61	0.0143	2.0907	593.04	0.0000	2.6166	473.83	0.0599
2.6039	476.15	0.0002	2.1577	574.60	0.0005	2.6437	468.98	0.0198
2.6261	472.13	0.0061	2.2322	555.44	0.0001	2.6791	462.78	0.0087
2.7931	443.89	0.0008	2.3445	528.82	0.0003			
2.8349	437.36	0.5354	2.3534	526.83	0.0000	**EtOH**	B3LYP	
2.8385	436.79	0.6240	2.3667	523.86	0.0008	E /eV	λ / nm	f
2.8738	431.43	0.0531	2.3697	523.20	0.0002	0.2860	4335.28	0.0003
2.9272	423.56	0.0991	2.4185	512.65	0.0000	0.8242	1504.28	0.0055
2.9822	415.75	0.0216	2.4658	502.82	0.0002	0.9969	1243.66	0.0101
2.9875	415.01	0.0039	2.4713	501.70	0.0001	1.0413	1190.70	0.0221
3.0500	406.50	0.0070	2.5107	493.81	0.0001	1.4123	877.87	0.0571
3.0696	403.91	0.0078	2.5989	477.06	0.0023	1.4718	842.39	0.0087
3.0851	401.88	0.0008	2.6887	461.13	0.0009	1.5646	792.46	0.0028
3.0936	400.77	0.0046	2.7331	453.64	0.0001	1.6105	769.86	0.0010
3.1044	399.38	0.0002	2.7763	446.59	0.0021	1.8246	679.53	0.0246
3.1281	396.36	0.0169	2.8354	437.27	0.5526	1.8383	674.46	0.0143
3.1369	395.25	0.0004	2.8405	436.48	0.6830	2.0802	596.02	0.0240
3.1400	394.86	0.0032	2.8546	434.33	0.3198	2.2036	562.64	0.0763
3.1872	389.00	0.0004	2.9080	426.36	0.0002	2.2392	553.69	0.0148
3.2192	385.14	0.0039	2.9703	417.41	0.0098	2.3448	528.77	0.0005
3.2382	382.89	0.0084	2.9755	416.69	0.0106	2.5343	489.23	0.0006
3.2783	378.20	0.0025	3.0038	412.76	0.0035	2.5526	485.71	0.0096
3.2930	376.51	0.0034	3.0234	410.08	0.0083	2.6583	466.40	0.0084
						2.6947	460.10	0.4153
						2.7233	455.28	0.0921
						2.7499	450.87	0.3410

CC	CAM-B3LYP		**CC-Cu**	CAM-B3LYP		**H2O2**	CAM-B3LYP	
E /eV	λ / nm	f	E /eV	λ / nm	f	E /eV	λ / nm	f
2.6287	471.65	0.0000	0.4045	3065.07	0.0000	0.4045	3065.07	0.0000
2.8180	439.97	0.0000	1.0726	1155.96	0.0001	1.0726	1155.96	0.0001
3.4885	355.41	1.4521	1.3452	921.71	0.0000	1.3452	921.71	0.0000
3.4885	355.41	1.4521	1.5942	777.70	0.0002	1.5942	777.70	0.0002
3.6197	342.53	0.0000	1.6154	767.53	0.0000	1.6154	767.53	0.0000
3.6200	342.50	0.0000	2.3191	534.63	0.0008	2.3191	534.63	0.0008
3.6200	342.50	0.0000	2.3248	533.31	0.0009	2.3248	533.31	0.0009
3.8377	323.07	0.0000	2.4533	505.39	0.0000	2.4533	505.39	0.0000
3.8377	323.07	0.0000	2.4601	503.98	0.0000	2.4601	503.98	0.0000
3.9471	314.11	0.0000	2.4878	498.37	0.0001	2.4878	498.37	0.0001
3.9787	311.62	0.0000	2.4897	498.00	0.0000	2.4897	498.00	0.0000
4.3268	286.55	0.0000	2.5095	494.06	0.0000	2.5095	494.06	0.0000
4.3391	285.74	0.0000	2.5712	482.20	0.0200	2.5712	482.20	0.0200
4.3628	284.18	0.0000	2.5980	477.22	0.0006	2.5980	477.22	0.0006
4.4011	281.71	0.1474	2.6313	471.19	0.0003	2.6313	471.19	0.0003
4.4011	281.71	0.1474	2.8199	439.67	0.0001	2.8199	439.67	0.0001
4.4397	279.26	0.0030	3.0424	407.52	0.0000	3.0424	407.52	0.0000
4.4397	279.26	0.0030	3.3359	371.67	0.0013	3.3359	371.67	0.0013
4.5576	272.04	0.0000	3.3632	368.65	0.0088	3.3632	368.65	0.0088
4.5577	272.04	0.0000	3.4436	360.04	0.0341	3.4436	360.04	0.0341

Table S-4 TD-DFT α and β occupied and virtual orbital eigenvalues, and excited states of CC, Cu-CC and Cu-CC + H_2O_2 obtained for B3LYP and CAM-B3LYP functional

CC [B3LYP]	**CC [CAM-B3LYP]**
Alpha occ. eigenvalues -0.23126 -0.22529 -0.22529 -0.19036 -0.19036	Alpha occ. eigenvalues -0.27962 -0.27079 -0.27079 -0.22588 -0.22588
Alpha virt. eigenvalues -0.08678 -0.08678 -0.05487 -0.05487 -0.04379	Alpha virt. eigenvalues -0.05345 -0.05345 -0.01289 -0.01289 0.00210
Excited State 3: 2.8886 eV 429.22 nm f=0.9163	Excited State 3: 3.4885 eV 355.41 nm f=1.4521
170 -> 172 0.27815	170 -> 173 0.49130
170 -> 173 0.39983	171 -> 172 0.49129
171 -> 172 0.39981	
171 -> 173 -0.27815	
Excited State 4: 2.8886 eV 429.22 nm f=0.9163	Excited State 4: 3.4885 eV 355.41 nm f=1.4521
170 -> 172 0.39982	170 -> 172 0.49130
170 -> 173 -0.27815	171 -> 173 -0.49129
171 -> 172 -0.27814	
171 -> 173 -0.39982	
CC-Cu [B3LYP]	**Cu-CC + H2O [B3LYP]**
Alpha occ. eigenvalues -0.21879 -0.21306 -0.19145 -0.19044 -0.13632	Alpha occ. eigenvalues -0.21929 -0.21690 -0.18431 -0.18391 -0.11153
Alpha virt. eigenvalues -0.08611 -0.08569 -0.05557 -0.05511 -0.04225	Alpha virt. eigenvalues -0.05565 -0.05514 -0.01590 -0.01521 0.00043
Beta occ. eigenvalues -0.21683 -0.21258 -0.21007 -0.19016 -0.18919	Beta occ. eigenvalues -0.21910 -0.21584 -0.21507 -0.18134 -0.17663
Beta virt. eigenvalues -0.08667 -0.08567 -0.06820 -0.05499 -0.05337	Beta virt. eigenvalues -0.08100 -0.07624 -0.06671 -0.04830 -0.04630
Excited State 2: 0.8205 eV 1511.15 nm f=0.0055	Excited State 2: 0.6489 eV 1910.58 nm f=0.0273
186A -> 187A 0.73235	191A -> 193A 0.98298
186A -> 188A -0.67227	191A -> 194A 0.19079
Excited State 3: 1.5594 eV 795.09 nm f=0.0049	191A <- 193A -0.10319
186A -> 189A 0.93957	Excited State 3: 1.0754 eV 1152.92 nm f=0.0287
186A -> 190A 0.26730	191A -> 193A -0.19304
186A -> 194A -0.10087	191A -> 194A 0.96310
	191A -> 197A 0.10743

Cu-CC + H2O2 [B3LYP]	**Cu-CC + O2 [B3LYP]**
Alpha occ. eigenvalues -0.22631 -0.21274 -0.20840 -0.19557 -0.19283	Alpha occ. eigenvalues -0.23378 -0.20142 -0.20098 -0.18529 -0.15684
Alpha virt. eigenvalues -0.09394 -0.09337 -0.06369 -0.06216 -0.050319	Alpha virt. eigenvalues -0.09781 -0.09715 -0.06916 -0.06681 -0.0529
Beta occ. eigenvalues -0.23014 -0.21823 -0.20430 -0.19525 -0.19483	Beta occ. eigenvalues -0.23624 -0.23071 -0.20129 -0.19981 -0.14122
Beta virt. eigenvalues -0.10337 -0.09346 -0.08175 -0.06321 -0.06062	Beta virt. eigenvalues -0.09779 -0.09740 -0.06913 -0.06689 -0.05301
Excited State 4: 1.8915 eV 655.50 nm f=0.0059	Excited State 10: 1.8943 eV 654.53 nm f=0.0033
194A -> 196A -0.23869	191A -> 196A 0.10610
195A -> 196A -0.29731	193A -> 195A 0.51195
195A -> 197A -0.25267	193A -> 196A 0.80646
181B -> 195B 0.10862	191B -> 195B -0.12308
181B -> 197B 0.10772	192B -> 195B -0.13041
184B -> 195B 0.12235	193B -> 199B 0.11989
187B -> 195B -0.14712	Excited State 11: 1.9041 eV 651.14 nm f=0.0029
187B -> 197B -0.11988	191A -> 196A 0.15679
193B -> 195B 0.65176	193A -> 195A 0.77648
193B -> 196B -0.20891	193A -> 196A -0.49880
194B -> 195B 0.38570	191B -> 195B -0.22748
Excited State 5: 1.8996 eV 652.69 nm f=0.0046	193B -> 199B -0.15304
194A -> 197A -0.14787	
195A -> 196A 0.35705	
195A -> 197A -0.26995	
187B -> 195B 0.18906	
187B -> 197B 0.15335	
192B -> 195B -0.21824	
193B -> 195B 0.57587	
193B -> 196B 0.23332	
194B -> 195B -0.41115	