Electronic Supplementary Information

The impact of surface structure and band gap on the optoelectronic properties of Cu_2O nanoclusters of varying size and symmetry

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Table S1: Optimised structural parameters of Cu_2O clusters

Clusters	Symmetry	Bond distances (d)/Å		Reported (d)/Å	Angles		Reported
$(Cu_2O)_1$	C_{2v}	$Cu_{2\,CUS}–O_{1\,CUS}^{2}$ $Cu_{3\,CUS}–O_{1\,CUS}^{2}$	1.765^{L} 1.788^{G}	[(a)] 1.75	∠ $Cu_{2\,CUS}–O_{1\,CUS}^{2}–Cu_{3\,CUS}$	$90.9°^{L}$ $93.1°^{G}$	[(a)] 87°
		$Cu_{2\,CUS}–Cu_{3\,CUS}$	2.516^{L} 2.611^{G}	[(a)] 2.41	∠ $O_{1\,CUS}^{2}–Cu_{2\,CUS}–Cu_{3\,CUS}$	$44.5°^{L}$ $43°^{G}$	
$(Cu_2O)_2$	C_{2v}	$Cu_{2\,CSA}–O_{1\,CUS}^{3}$ $Cu_{3\,CSA}–O_{1\,CUS}^{3}$ $Cu_{2\,CSA}–O_{4\,CUS}^{3}$ $Cu_{3\,CSA}–O_{4\,CUS}^{3}$	1.999^{L} 2.026^{G}	[(b)] 1.91	∠ $Cu_{2\,CSA}–O_{1\,CUS}^{3}–Cu_{3\,CSA}$ ∠ $Cu_{2\,CSA}–O_{4\,CUS}^{3}–Cu_{3\,CSA}$	$72.4°^{L}$ $74.2°^{G}$	
					∠ $O_{1\,CUS}^{3}–Cu_{2\,CSA}–O_{4\,CUS}^{3}$ ∠ $O_{1\,CUS}^{3}–Cu_{3\,CSA}–O_{4\,CUS}^{3}$	107.5^{L} 105.3^{G}	[(b)] 109.6°
		$Cu_{6\,CUS}–O_{1\,CUS}^{3}$ $Cu_{5\,CUS}–O_{4\,CUS}^{3}$	1.830^{L} 1.830^{G}	[(b)] 1.76	∠ $O_{1\,CUS}^{3}–Cu_{2\,CSA}–Cu_{3CSA}$ ∠ $O_{1\,CUS}^{3}–Cu_{3\,CSA}–Cu_{2CSA}$ ∠ $O_{4\,CUS}^{3}–Cu_{2\,CSA}–Cu_{3CSA}$ ∠ $O_{4\,CUS}^{3}–Cu_{3\,CSA}–Cu_{2CSA}$	$53.8°^{L}$ $52.9°^{G}$	
		$Cu_{2\,CSA}–Cu_{3\,CSA}$	2.361^{L} 2.445^{G}		∠ $Cu_{2\,CSA}–O_{1\,CUS}^{3}–Cu_{6\,CUS}$ ∠ $Cu_{3\,CSA}–O_{1\,CUS}^{3}–Cu_{6\,CUS}$ ∠ $Cu_{2\,CSA}–O_{4\,CUS}^{3}–Cu_{5\,CUS}$ ∠ $Cu_{3\,CSA}–O_{4\,CUS}^{3}–Cu_{5\,CUS}$	$82.6°^{L}$ $87.4°^{G}$	
$(Cu_2O)_3$	C_{2v}	$Cu_{2\,CSA}–O_{1CSA}$ $Cu_{2\,CSA}–O_{4\,CSA}$ $Cu_{3\,CSA}–O_{1\,CSA}$ $Cu_{3\,CSA}–O_{4\,CSA}$	2.026^{L} 2.057^{G}		∠ $Cu_{2\,CSA}–O_{1\,CSA}–Cu_{3\,CSA}$ ∠ $Cu_{2\,CSA}–O_{4\,CSA}–Cu_{3\,CSA}$	$75.1°^{L}$ $74.4°^{G}$	
					∠ $O_{1\,CSA}–Cu_{2\,CSA}–O_{4\,CSA}$ ∠ $O_{1\,CSA}–Cu_{3\,CSA}–O_{4\,CSA}$	104.8^{L} 105.5^{G}	
					∠ $O_{1\,CSA}–Cu_{2\,CSA}–Cu_{3CSA}$ ∠ $O_{1\,CSA}–Cu_{3\,CSA}–Cu_{2CSA}$ ∠ $O_{4\,CSA}–Cu_{2\,CSA}–Cu_{3CSA}$ ∠ $O_{4\,CSA}–Cu_{3\,CSA}–Cu_{2CSA}$	$52.4°^{L}$ $52.8°^{G}$	

		$Cu_{8\,CUS}-O_{1\,CSA}$ $Cu_{9\,CUS}-O_{4\,CSA}$	1.822^{L} 1.828^{G}	(b) 1.78	$\angle Cu_{2\,CSA}-O_{1\,CSA}-Cu_{8\,CUS}$ $\angle Cu_{3\,CSA}-O_{1\,CSA}-Cu_{8\,CUS}$ $\angle Cu_{2\,CSA}-O_{4\,CSA}-Cu_{9\,CUS}$ $\angle Cu_{3\,CSA}-O_{4\,CSA}-Cu_{9\,CUS}$	141.1^{L} 138.7^{G}	
		$Cu_{6\,CSA}-O_{1\,CSA}$ $Cu_{5\,CSA}-O_{4\,CSA}$	1.956^{L} 1.966^{G}		$\angle Cu_{5\,CSA}-O_{4\,CSA}-Cu_{9\,CUS}$ $\angle Cu_{6\,CSA}-O_{1\,CSA}-Cu_{8\,CUS}$	112.8^{L} 119.9^{G}	
		$Cu_{6\,CSA}-O_{7\,CUS}^{2}$ $Cu_{5\,CSA}-O_{7\,CUS}^{2}$	1.832^{L} 1.813^{G}		$\angle O_{4\,CSA}-Cu_{5\,CSA}-O_{7\,CUS}$ $\angle O_{1\,CSA}-Cu_{6\,CSA}-O_{7\,CUS}$	147.7^{L} 147.8^{G}	
		$Cu_{2\,CSA}-Cu_{3\,CSA}$	2.470^{L} 2.488^{G}		$\angle Cu_{5\,CSA}-O_{7\,CUS}-Cu_{6\,CSA}$	$85.8°^{L}$ $87.2°^{G}$	
		$Cu_{5\,CSA}-Cu_{6\,CSA}$	2.493^{L} 2.5^{G}				
$(Cu_2O)_3$	C_{3v}	$Cu_{1\,CSA}-O_{4\,CUS}^{3}$ $Cu_{1\,CSA}-O_{5\,CUS}^{3}$ $Cu_{2\,CSA}-O_{4\,CUS}^{3}$ $Cu_{2\,CSA}-O_{6\,CUS}^{3}$ $Cu_{3\,CSA}-O_{5\,CUS}^{3}$ $Cu_{3\,CSA}-O_{6\,CUS}^{3}$	1.832^{L} 1.912^{G}	(b) 1.91	$\angle Cu_{1\,CSA}-O_{4\,CSA}-Cu_{8\,CUS}$ $\angle Cu_{2\,CSA}-O_{4\,CSA}-Cu_{8\,CUS}$ $\angle Cu_{1\,CSA}-O_{5\,CSA}-Cu_{7\,CUS}$ $\angle Cu_{3\,CSA}-O_{5\,CSA}-Cu_{7\,CUS}$ $\angle Cu_{2\,CSA}-O_{6\,CSA}-Cu_{9\,CUS}$ $\angle Cu_{3\,CSA}-O_{6\,CSA}-Cu_{9\,CUS}$	136.1^{L} 101.2^{G}	(b) 109.6°
		$Cu_{7\,CUS}-O_{5\,CUS}^{3}$ $Cu_{8\,CUS}-O_{4\,CUS}^{3}$ $Cu_{9\,CUS}-O_{6\,CUS}^{3}$	1.762^{L} 1.811^{G}	(b) 1.77	$\angle Cu_{1\,CSA}-O_{4\,CSA}-Cu_{2\,CSA}$ $\angle Cu_{2\,CSA}-O_{6\,CSA}-Cu_{3\,CSA}$ $\angle Cu_{3\,CSA}-O_{5\,CSA}-Cu_{1\,CSA}$	$87.7°^{L}$ $83.2°^{G}$	
		$Cu_{1\,CSA}-Cu_{2\,CSA}$ $Cu_{2\,CSA}-Cu_{3\,CSA}$ $Cu_{1\,CSA}-Cu_{3\,CSA}$	2.539^{L} 2.539^{G}		$\angle O_{4\,CSA}-Cu_{1\,CSA}-Cu_{2CSA}$ $\angle O_{4\,CSA}-Cu_{2\,CSA}-Cu_{1CSA}$ $\angle O_{5\,CSA}-Cu_{1\,CSA}-Cu_{3CSA}$ $\angle O_{5\,CSA}-Cu_{3\,CSA}-Cu_{1CSA}$ $\angle O_{6\,CSA}-Cu_{2\,CSA}-Cu_{3CSA}$ $\angle O_{6\,CSA}-Cu_{3\,CSA}-Cu_{2CSA}$	$46°^{L}$ $48.4°^{G}$	
$(Cu_2O)_3$	C_s	$Cu_{2\,CSA}-O_{1\,CUS}^{2}$ $Cu_{3\,CSA}-O_{1\,CUS}^{2}$	1.776		$\angle Cu_{2\,CSA}-O_{1\,CUS}^{2}-Cu_{3\,CSA}$	114.2°	
		$Cu_{2\,CSA}-O_{4\,CUS}^{3}$ $Cu_{3\,CSA}-O_{7\,CUS}^{3}$	1.839		$\angle Cu_{2\,CSA}-O_{4\,CUS}^{3}-Cu_{6CUS}$ $\angle Cu_{3CSA}-O_{7\,CUS}^{3}-Cu_{8CUS}$	108.3°	

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$Cu_{6\,CUS}$–$O_{4\,CUS}^{3}$ $Cu_{8\,CUS}$–$O_{7\,CUS}^{3}$	1.857	∠ $Cu_{2\,CSA}$ –$O_{4\,CUS}^{3}$–$Cu_{5\,CUS}$ ∠ $Cu_{3\,CSA}$ –O_{7CUS}^{3}–Cu_{9CUS}	96.6°
$Cu_{5\,CUS}$–$O_{4\,CUS}^{3}$ $Cu_{9\,CUS}$–$O_{7\,CUS}^{3}$	1.872	∠ $Cu_{5\,CUS}$–$O_{4\,CUS}^{3}$–$Cu_{6\,CUS}$ ∠ $Cu_{8\,CUS}$–$O_{7\,CUS}^{3}$–Cu_{9CUS}	86.2°

(a) is from reference 100.

(b) is from reference 101.

Table S2: Partial DOS (PDOS) data of Cu_2O clusters with increasing size at C_{2v} symmetry

Clusters	**Symmetry**	**Peaks**	**MOs. involved in Transition**		**MOs.**	**Contribution of AOs of Cu atom in forming MOs. (%)**			**Contribution of AOs of O atom in forming MOs.(%)**	
			Occupied	Virtual		s	p	d	s	p
$(Cu_2O)_1$	C_{2v}	1	5A1	5B1	5A1	30	2.1	30		34.08
					5B1	50	35.6			13.04
$(Cu_2O)_2$	C_{2v}	1	10B2	17A1	10B2	8		55.5	1.1	28.2
					17A1	61.6	25.5	6.4		21.01
$(Cu_2O)_3$	C_{2v}	1	14A1	13B2	14A1	26		25		44.41
					13B2	57.17	20.27	4.59		13.81

Table S3: Partial DOS (PDOS) data of Cu_2O clusters with fixed size at different symmetries

clusters	**Symmetry**	**peaks**	**MOs. involved in Transition**		**MOs.**	**Contribution of AOs of Cu atom in forming MOs. (%)**			**Contribution of AOs of O atom in forming MOs. (%)**	
			Occupied	Virtual		s	p	d	s	p
$(Cu_2O)_3$	C_s	2	20AAA	22AAA	20AAA	17.9	2.21	35.9		37
					22AAA	59.6	28			9.06
$(Cu_2O)_3$	C_{2v}	2	14A1	13B2	14A1	26		25		44.41
					13B2	57.17	20.27	4.59		13.81
$(Cu_2O)_3$	C_{3v}	2	95A	100A	95A	2.58		40.7		44.3
					100A	62.1	13.6			14.7

Table S4. Vibrational frequencies of clusters of different size and symmetry calculated using GGA as exchange and BLYP as correlation functional.

Clusters	**Symmetry**	**Frequencies (cm^{-1})**
$(Cu_2O)_1$	C_{2v}	ν_1= 99.011, ν_2 = 566.589, ν_3 = 594.664
$(Cu_2O)_2$	C_{2v}	ν_1 = 15.04, ν_2 = 49.45, ν_3 = 59.767, ν_4 = 74.66, ν_5 = 123.785, ν_6 = 150.66, ν_7 = 165.108, ν_8 =241.094, ν_9 =317.499, ν_{10} = 413.617, ν_{11} =525.733, ν_{12} =547.473
$(Cu_2O)_3$	C_{2v}	ν_1 = i13.422, ν_2 =17.442, ν_3 = 25.247, ν_4 = 45.538, ν_5 = 60.975, ν_6 = 97.623, ν_7 = 99.626, ν_8 = 103.112, ν_9 = 116.452, ν_{10} = 153.383, ν_{11} =195.809, ν_{12} = 197.193, ν_{13} = 199.533, ν_{14} = 206.058 ν_{15} =221.477, ν_{16} = 316.122, ν_{17} = 334.313, ν_{18} = 506.849, ν_{19} = 597.349, ν_{20} = 607.34, ν_{21} =612.904.
$(Cu_2O)_3$	C_{3v}	ν_1 = i17.692, ν_2 =10.035, ν_3 =11.067, ν_4 = 21.395, ν_5 = 27.751, ν_6 = 30.145, ν_7 = 103.919, ν_8 = 104.917, ν_9 = 133.134, ν_{10} = 147.902, ν_{11} = 148.521, ν_{12} = 200.889, ν_{13} = 342.961, ν_{14} = 344.991, ν_{15} = 408.415, ν_{16} = 449.01, ν_{17} = 484.134, ν_{18} = 486.374, ν_{19} = 563.883 ν_{20} = 566.764, ν_{21} = 584.341.
$(Cu_2O)_3$	C_s	ν_1 = i11.756, ν_2 = i1.781, ν_3 = 7.733, ν_4 = 12.833, ν_5 = 26.312, ν_6 = 34.469, ν_7 = 43.984 ν_8 = 86.646, ν_9 = 107.612, ν_{10} = 119.286, ν_{11} = 141.953, ν_{12} = 144.674, ν_{13} = 193.337, ν_{14} = 421.759, ν_{15} = 425.993, ν_{16} = 442.952, ν_{17} = 472.448, ν_{18} = 517.353, ν_{19} = 529.809, ν_{20} = 590.120, ν_{21} = 714.755.

Table S5: Partial DOS (PDOS) data of larger Cu_2O clusters with different size at fixed symmetries

clusters	**Symmetry**	**peaks**	**MOs. involved in Transition**		**MOs.**	**Contribution of AOs of Cu atom in forming MOs. (%)**			**Contribution of AOs of O atom in forming MOs.(%)**	
			Occupied	**Virtual**		***s***	***p***	***d***	***s***	***p***
$[Cu_{28}O_{15}]^{6+}$	T_d	1	71T2	38A1	71T2			40		47
					38A1	74.86		15.45		10.75
$[Cu_{44}O_{15}]^{6+}$	T_d	1	19A1	43T2	19A1	76.07		20.9		
					43T2	62.08		2.24		15.01

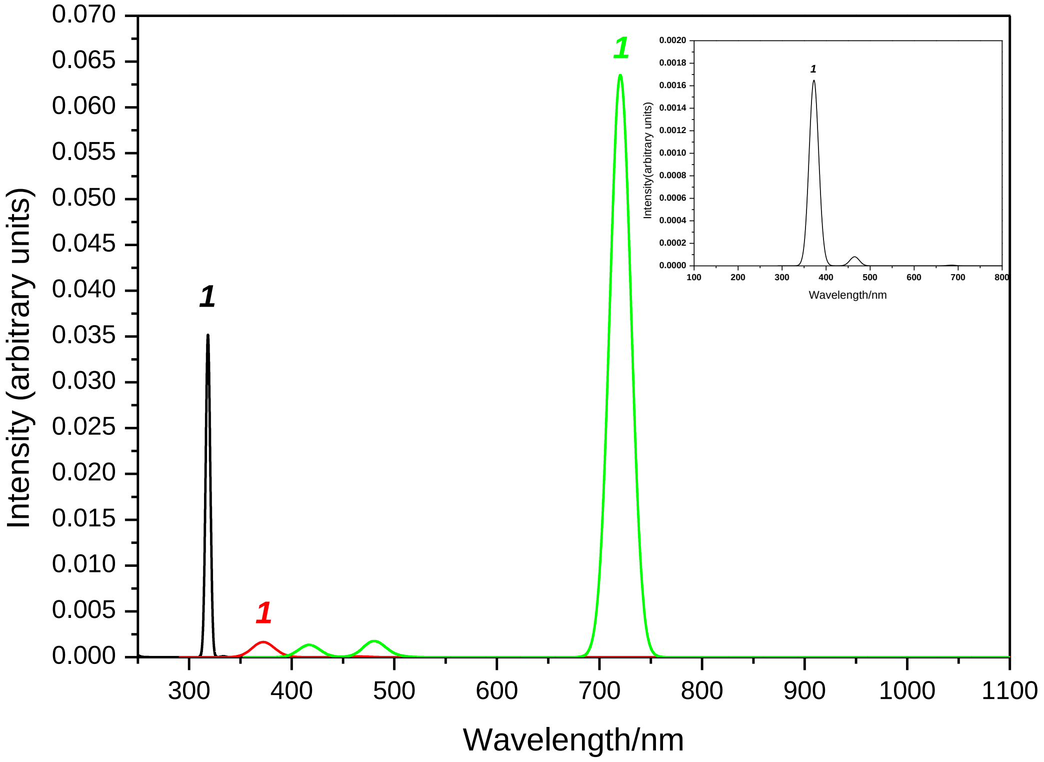

Figure S1: TDDFT valence excitation spectra (intensity vs wavelength) of $(Cu_2O)_1$ (black), $(Cu_2O)_2$ (red) and $(Cu_2O)_3$ (green) clusters having same symmetry (C_{2v}). Only the most intense discrete transitions are reported and labelled as 1. In the inset the intensity of peak ***1*** of $(Cu_2O)_2$ is displayed distinctly.

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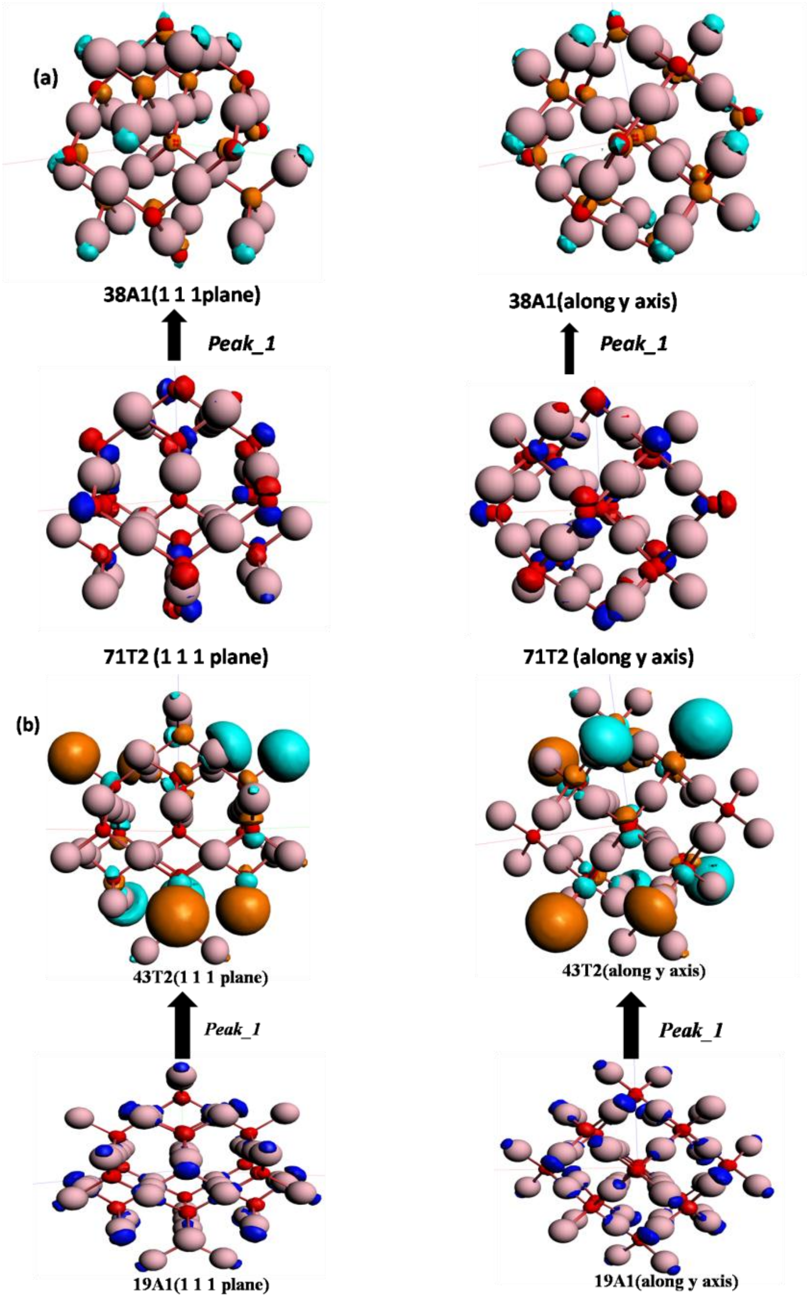

Figure S2: The representation of MOs participating in the electronic transitions to form the most intense peaks labelled as ***1*** (a) $[Cu_{28}O_{15}]^{6+}$ and (b) $[Cu_{44}O_{30}]^{6+}$ in T_d symmetry.