

Table S1. Mulliken and Natural Bond Orbital(NBO) population analysis (net atomic and natural charges, *q*, bond orbital population, *bop*, and natural electron configuration, *nec*) of the Cu_nH_n (n= 3-6) molecules, computed at various levels of theory.

Compound	Method	<i>q</i> (Cu)		<i>bop</i>		<i>nec</i> (Cu)		
		Mulliken	Natural	Cu-H	Cu-Cu	4s	3d	4p
Cu ₃ H ₃ (<i>D</i> _{3h})	B3LYP/6-311+G(d,p)	0.07	0.54	0.199	0.120	0.50	9.93	0.03
	B3LYP/LANL2DZ	0.05	0.47	0.180	0.074	0.58	9.91	0.04
Cu ₄ H ₄ (<i>D</i> _{4h})	B3LYP/6-311+G(d,p)	-0.02	0.49	0.194	0.163	0.57	9.91	0.02
	B3LYP/LANL2DZ	0.01	0.45	0.188	0.091	0.63	9.88	0.03
Cu ₄ H ₄ (<i>T</i> _d)	B3LYP/6-311+G(d,p)	0.10	0.58	0.149	0.032	0.43	9.94	0.04
	B3LYP/LANL2DZ	0.01	0.45	0.188	0.091	0.63	9.88	0.03
Cu ₅ H ₅ (<i>D</i> _{5h})	B3LYP/6-311+G(d,p)	-0.08	0.48	0.187	0.178	0.59	9.91	0.02
	B3LYP/LANL2DZ	0.06	0.44	0.178	0.019	0.66	9.87	0.02
Cu ₅ H ₅ (<i>C</i> _{2v})	B3LYP/6-311+G(d,p)	0.30	0.49	0.281	0.147	0.57	9.91	0.02
		-0.31	0.48	0.267	0.090			
		-0.11	0.55	0.185	0.040			
		0.43		0.125	0.026			
		-0.08		0.110	0.019			
	B3LYP/LANL2DZ	0.01	0.45	0.188	0.091	0.63	9.88	0.03
Cu ₆ H ₆ (<i>D</i> _{6h})	B3LYP/6-311+G(d,p)	-0.10	0.48	0.189	0.182	0.59	9.90	0.01
	B3LYP/LANL2DZ	0.07	0.43	0.182	0.024	0.86	9.90	0.01
Cu ₆ H ₆ (<i>D</i> _{2h})	B3LYP/6-311+G(d,p)							
	B3LYP/LANL2DZ	0.01	0.45	0.188	0.091	0.63	9.88	0.03