Supporting Materials

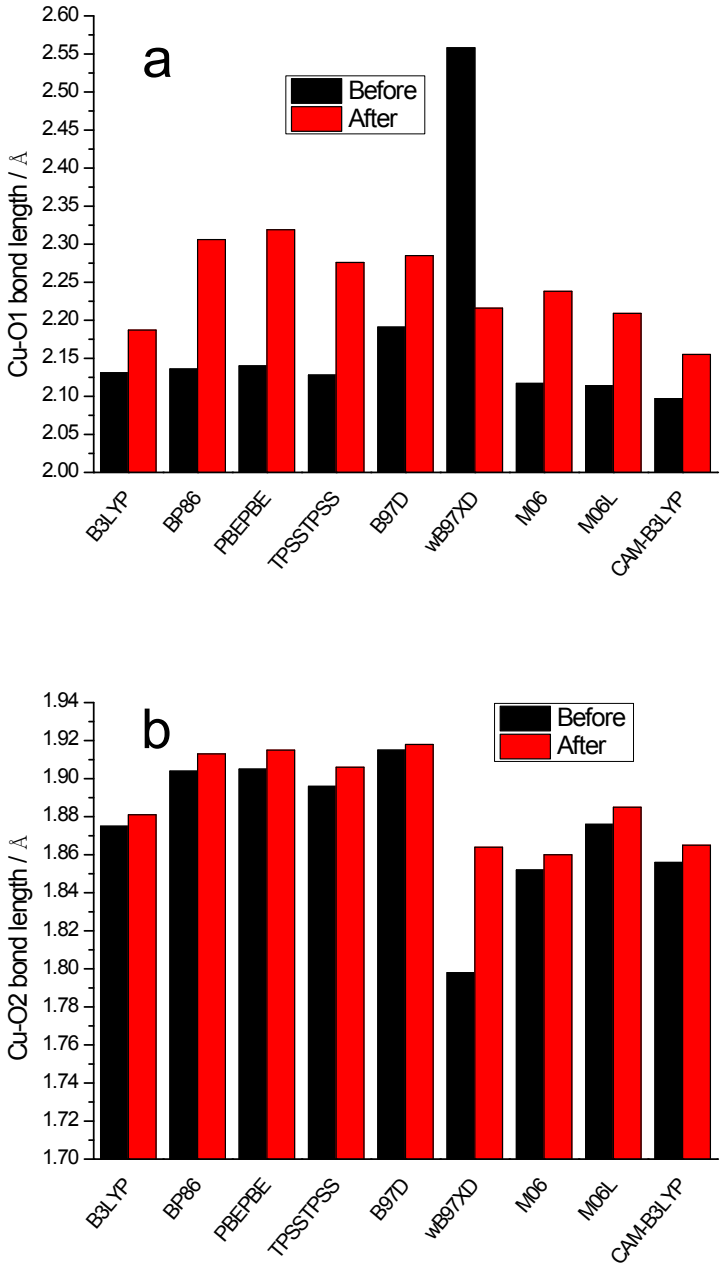

Figure S1. The bond length of Cu-O1 (a) and that of Cu-O2 (b) before and after the interaction calculated with the nine functionals using the mixed basis set 6-311+G(d,p)+LANL2DZ.

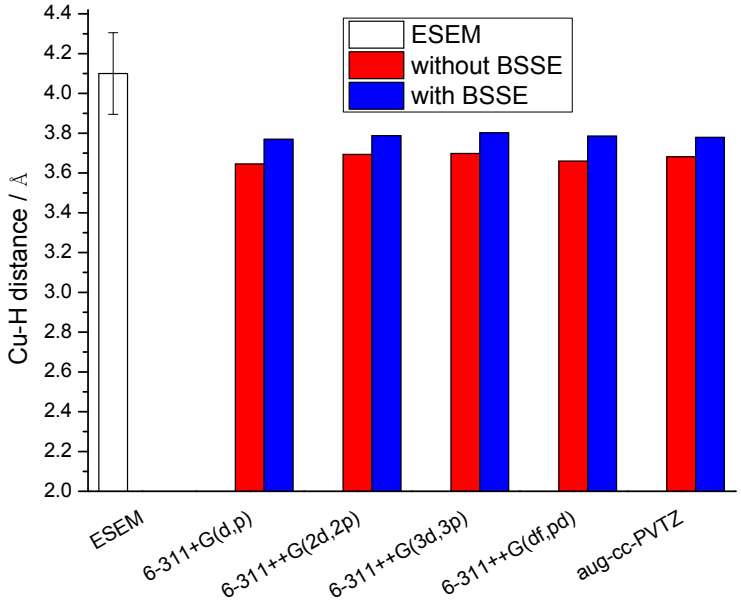

Figure S2. The calculated Cu-H distances by B3LYP using 6-311+G(d,p), 6-311++G(2d,2p), 6-311++G(3d,3p), 6-311++G(df,pd) and aug-cc-pVTZ with and without the BSSE correction.

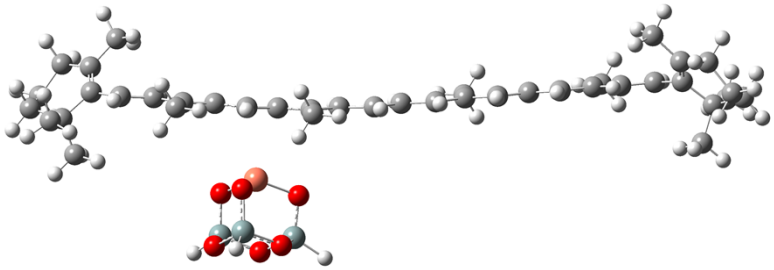

Figure S3. The optimized structure of Cu^{2+}-**I** with Cu^{2+} interacting with C11=C12 double bond, which is calculated by B3LYP with the BSSE correction using the mixed basis set (6-311+G(d) for Cu, 6-31G(d) for **I**, and the three oxygen atoms coordinated to Cu^{2+}, and 3-21G for the remaining atoms). H: light gray, O: red, Cu: orange and C: dark gray. Si: blue-gray.