Electronic Supplementary Information (ESI)

Ligand Chain Length Conveys Thermochromism

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Synthesis of the thermochromic compound.

The thermochromic compounds from the Cu(II) alkanoate have been synthesized in heptane using straight chain amine under refluxing condition. In all the cases, the molar ratio of copper alkanoate and amine has been maintained to be 1 : 2 during the course of synthesis of the thermochromic compounds. Short chain alkanoates (e.g., acetate, propionate) require long chain amines (e.g., DDA, TDA, HDA) to make thermochromic compounds while long chain alkanoates can produce thermochromic compounds with amines of any chain length (short or long). Different physical analyses prove the compounds to be $[Cu(AL)_2(A)_2]$ type.

Copper(II) stearate of 20 mg and tetradecylamine amine (TDA) of 14 mg were added in 10 mL heptane in a 100 mL round bottom flask and refluxed (~99^0C) for 30 minutes using a condenser (with constant water flow) fitted to the round bottom flask. A homogeneous blue solution was obtained during the reflux. Upon cooling, a violet solid $[Cu(St)_2(TDA)_2]$ gradually precipitated out from heptane. The violet solid (yield 94%) was collected via filtration with Whatman 41, washed several times with heptane and dried under vacuum. From elemental analysis, it is found that C is 72.81%, H is 12.62% and N is 2.67% (calculated value of C, H, N is 72.72%, 12.54%, 2.66%, respectively) supporting the formation of $[Cu(St)_2(TDA)_2]$. Copper was estimated titrimetrically [observed 5.95%, calculated 6.01%] corroborating the $[Cu(St)_2(TDA)_2]$ compound.

In the likewise fashion, other thermochromic compounds from copper alkanoates (acetate, propionate etc.) have been synthesized using amines of different chain lengths.

To grow the single crystal, solid crude $[Cu(Ac)_2(TDA)_2]$ product (100 mg) was dissolved in 8 mL dichloromethane (DCM) and kept in a test tube. Then, 8 mL heptane

was slowly added through the side of the test tube. As a result, a blue colored DCM layer at the bottom and colorless heptane layer on DCM were observed. The test tube was then sealed with parafilm to allow slow evaporation and kept undisturbed at 25^0C. After ~15 days, a violet crystalline solid was obtained in colorless heptane. This crystalline solid was isolated and used for single crystal analysis.

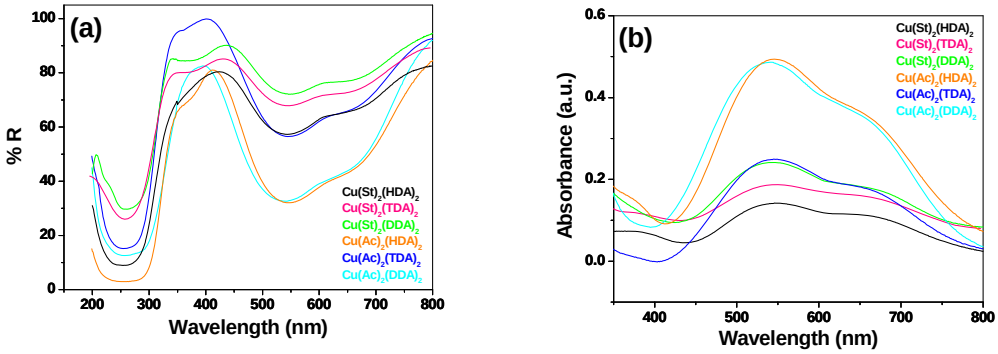

Figure S1: (a) Reflectance and (b) absorption spectra of solid $Cu(AL)_2(A)_2$ compounds at 25 ˚C

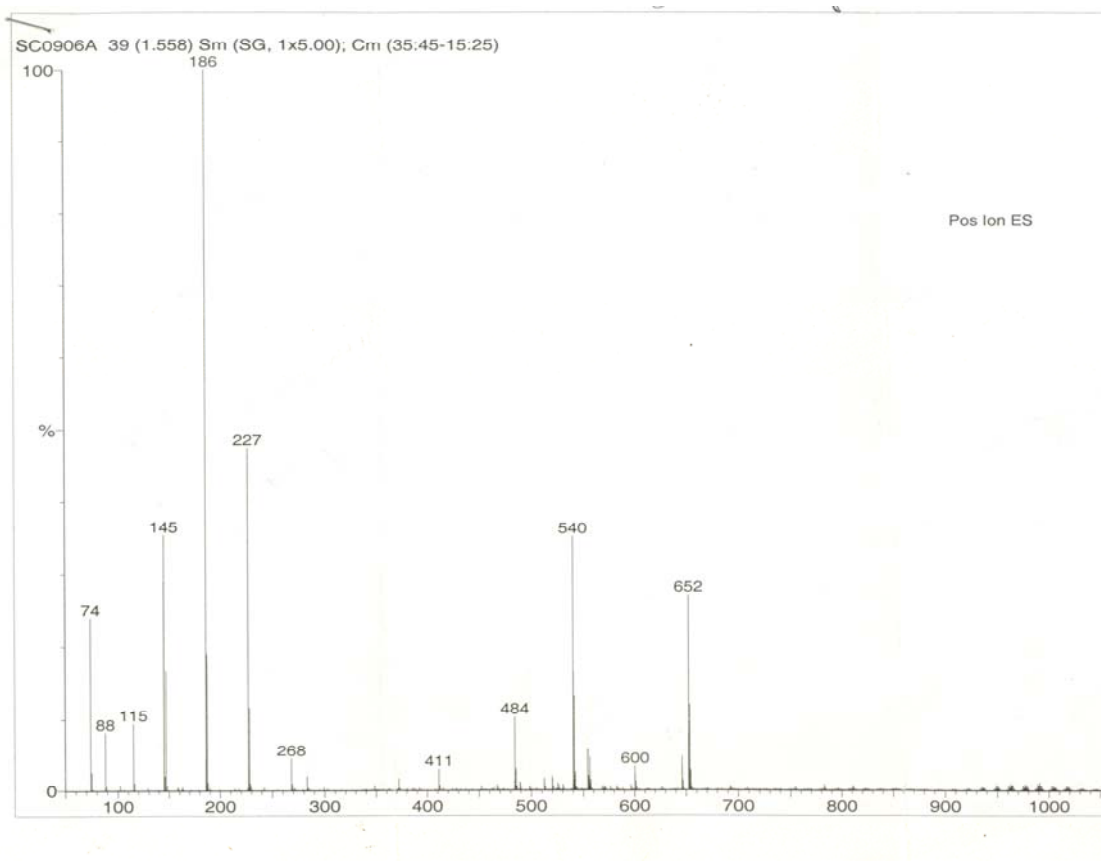

Figure S2: Mass spectrum of $Cu(St)_2(DDA)_2$ compound.

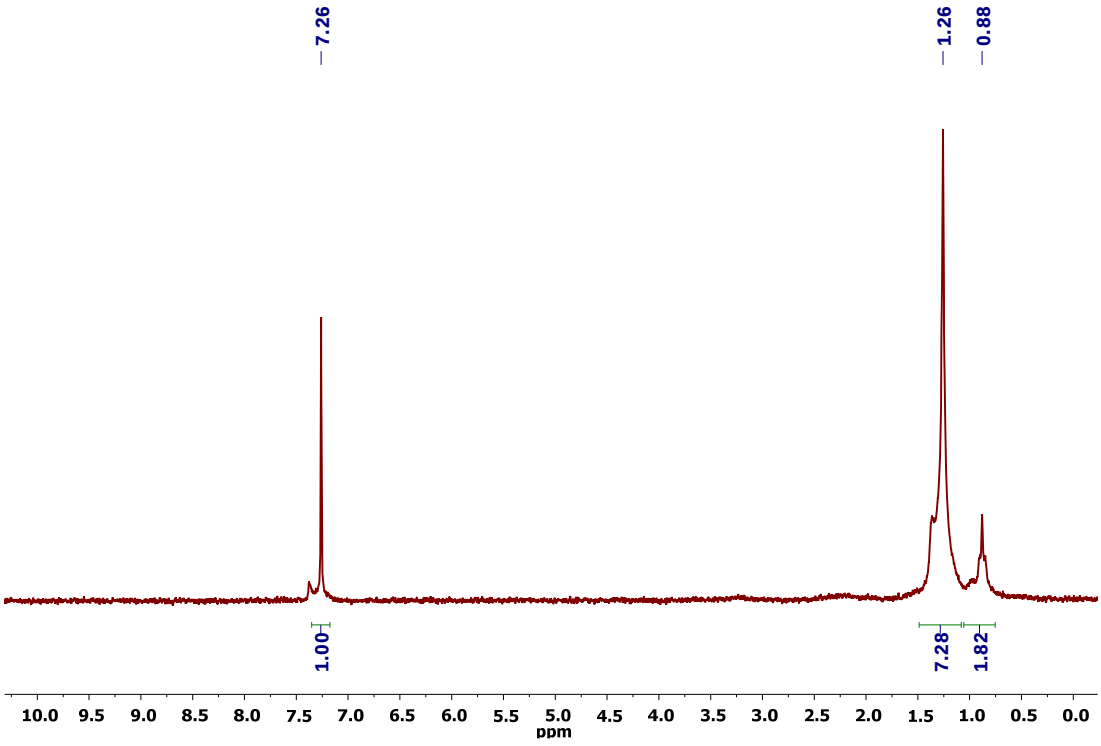

Figure S3: ^{1}H NMR spectrum of $Cu(Ac)_2(TDA)_2$ in $CDCl_3$.

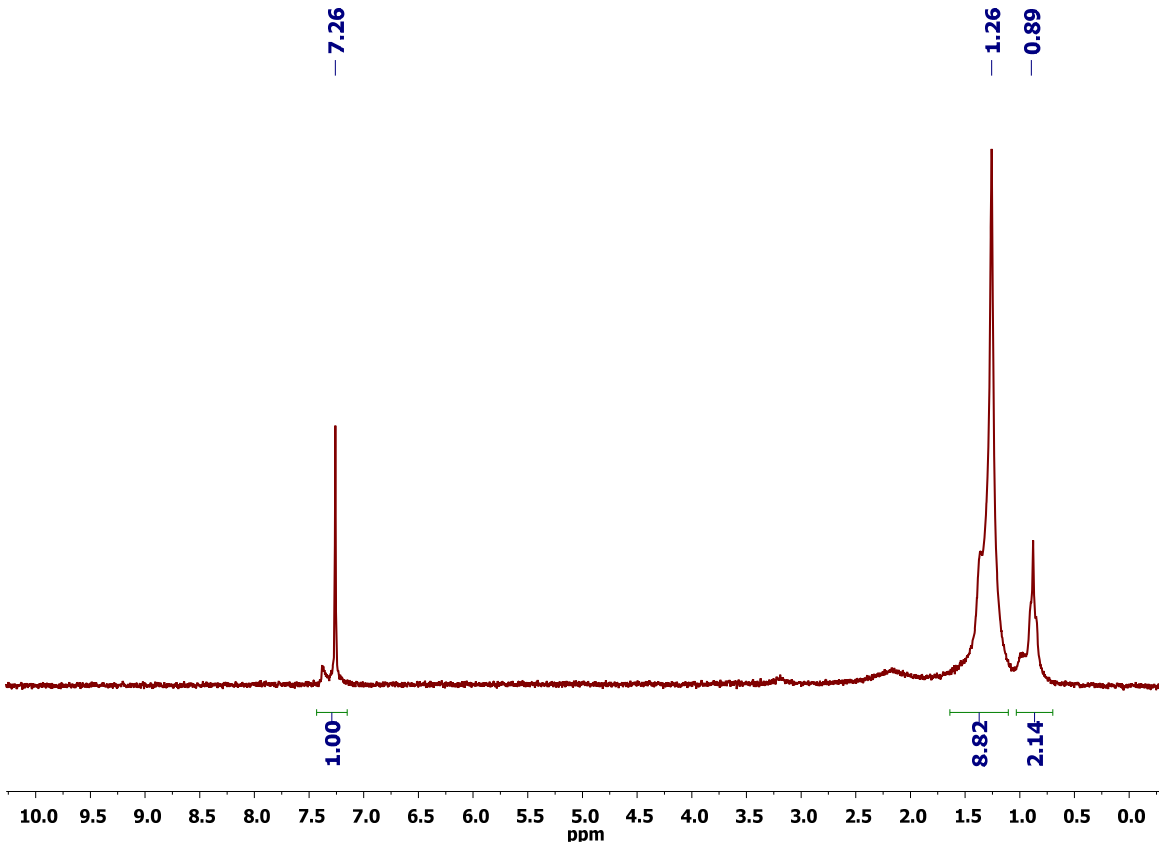

Figure S4: ^{1}H NMR spectrum of $Cu(Ac)_2(DDA)_2$ in $CDCl_3$.

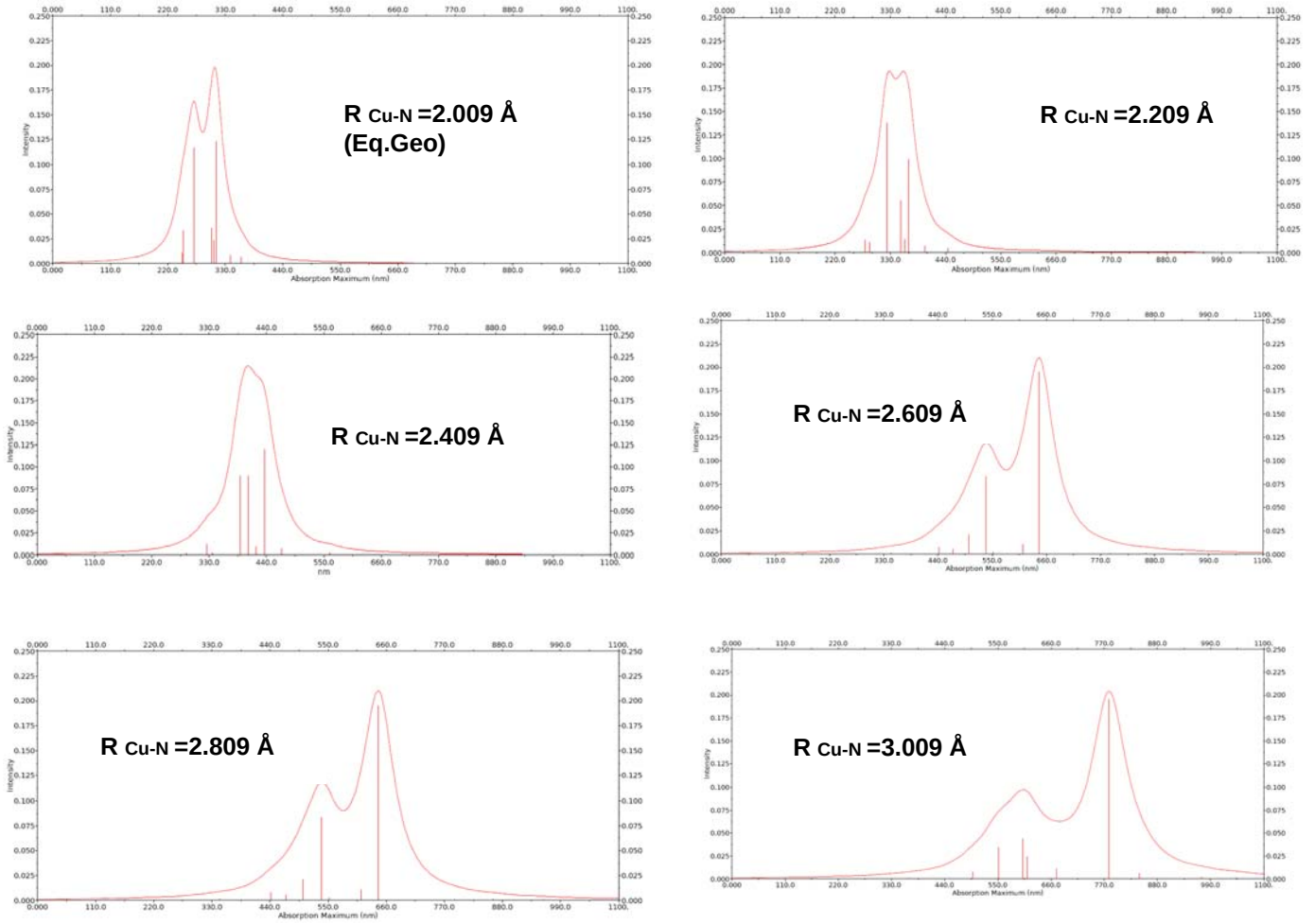

Figure S5: TD-DFT-simulated absorption spectra of the model complex $Cu(Ac)_2$(methyl amine)$_2$ complex with one water molecule.

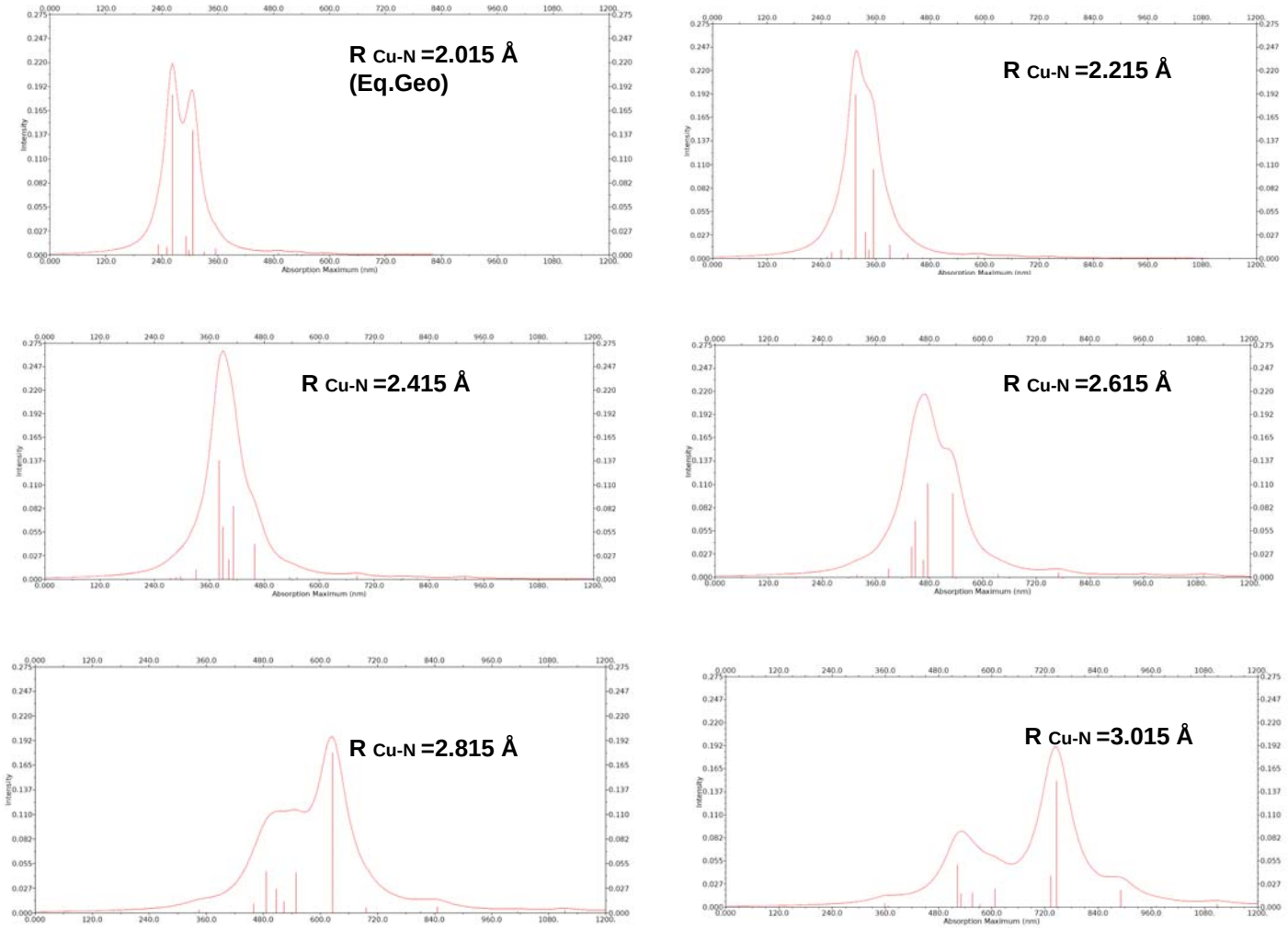

Figure S6: TD-DFT-simulated absorption spectra of the model complex $Cu(Ac)_2(DA)_2$ complex with one water molecule.

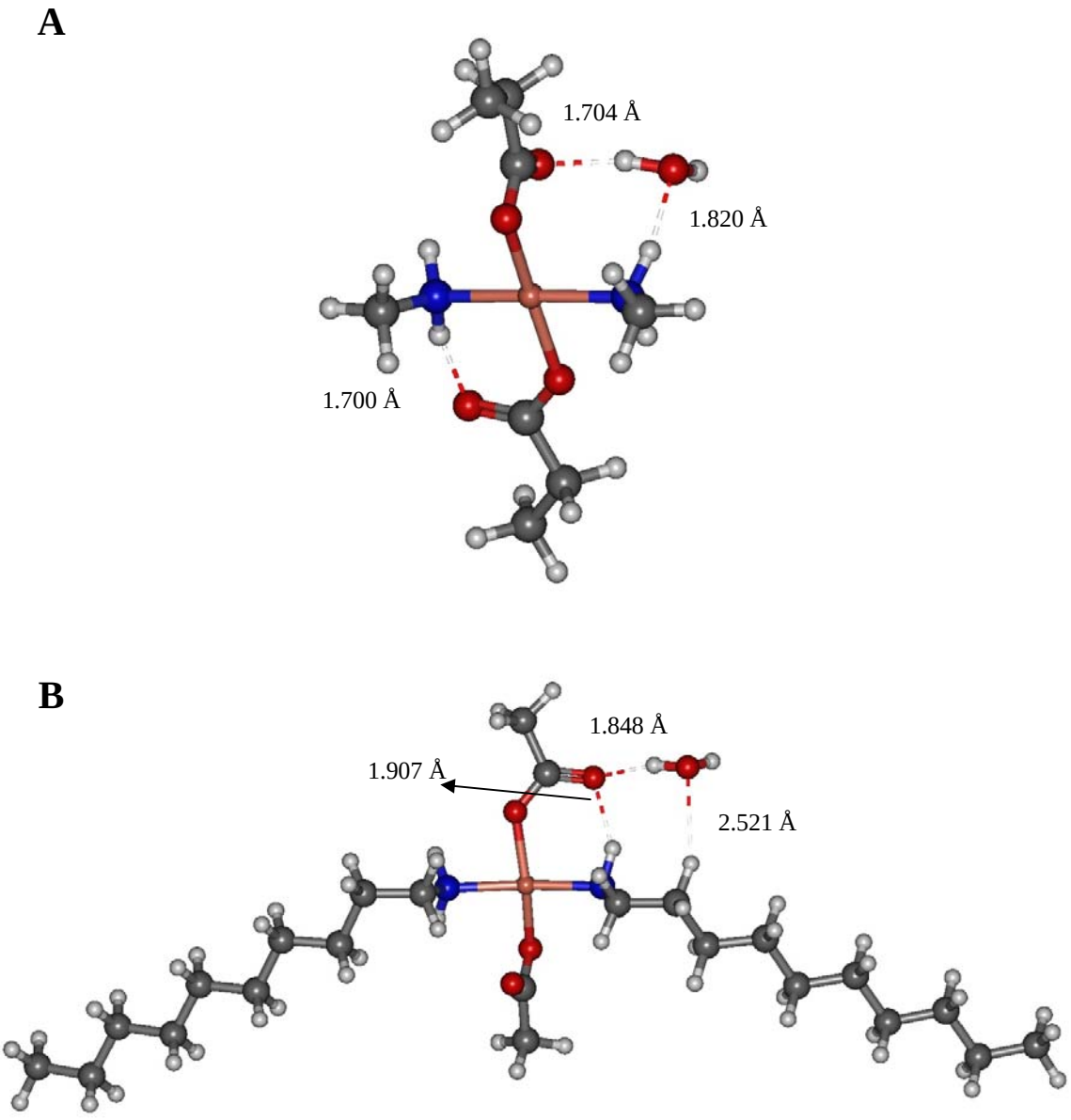

Figure S7: Water molecular interaction with the model complexes, (A) $Cu(Ac)_2$(methyl amine)$_2$ and (B) $Cu(Ac)_2(DA)_2$ complex and the corresponding hydrogen bonding interaction is shown as dotted line along with their distances.