



UNIVERSITAT DE  
BARCELONA

**P-Stereogenic ligands  
with the *tert*-butylmethylphosphine fragment.  
Coordination chemistry and catalysis  
of their organometallic complexes**

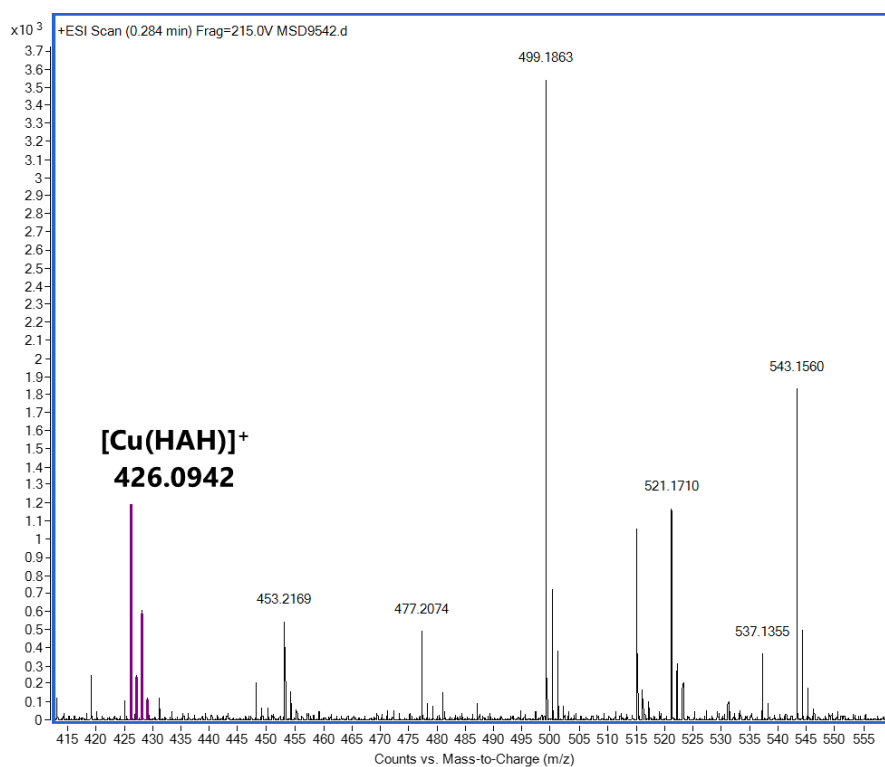
Guillem Vázquez Bigas

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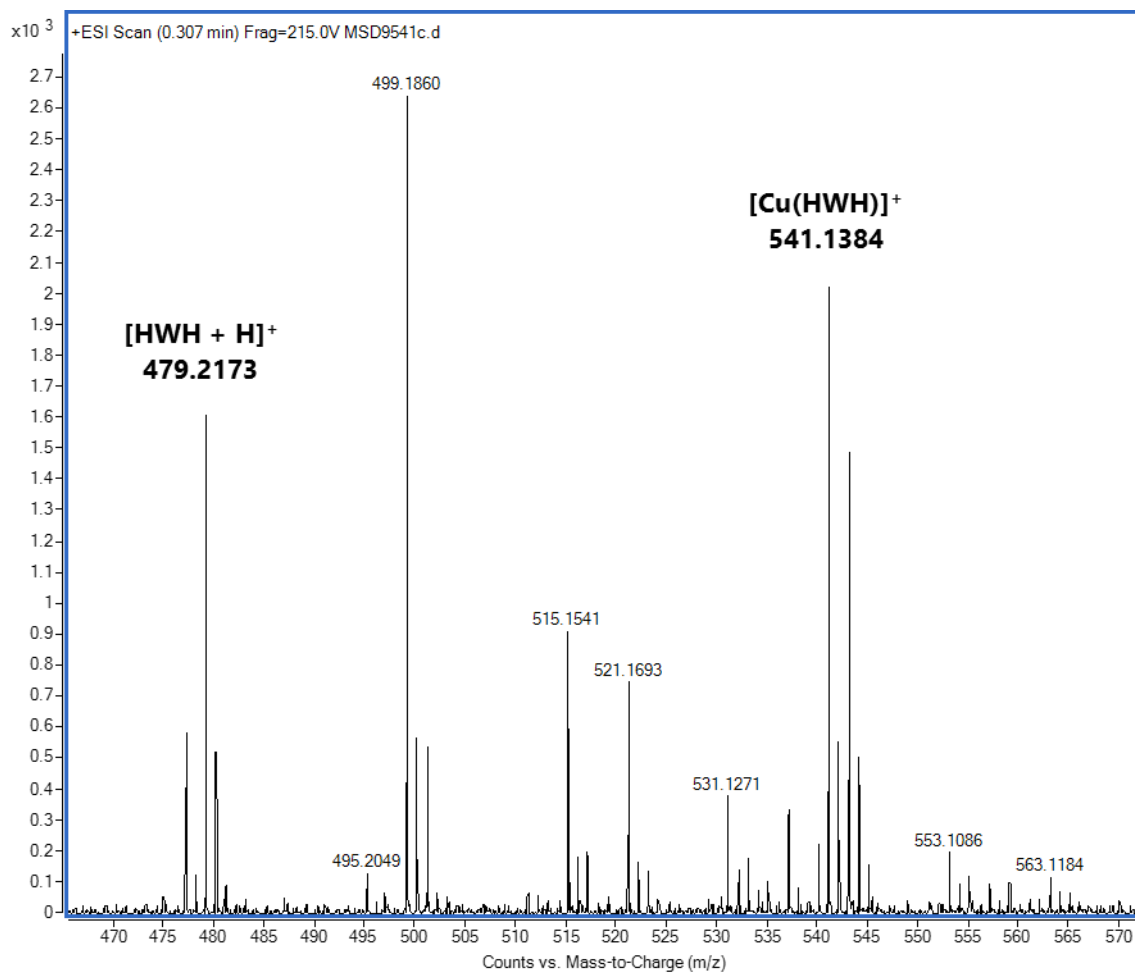
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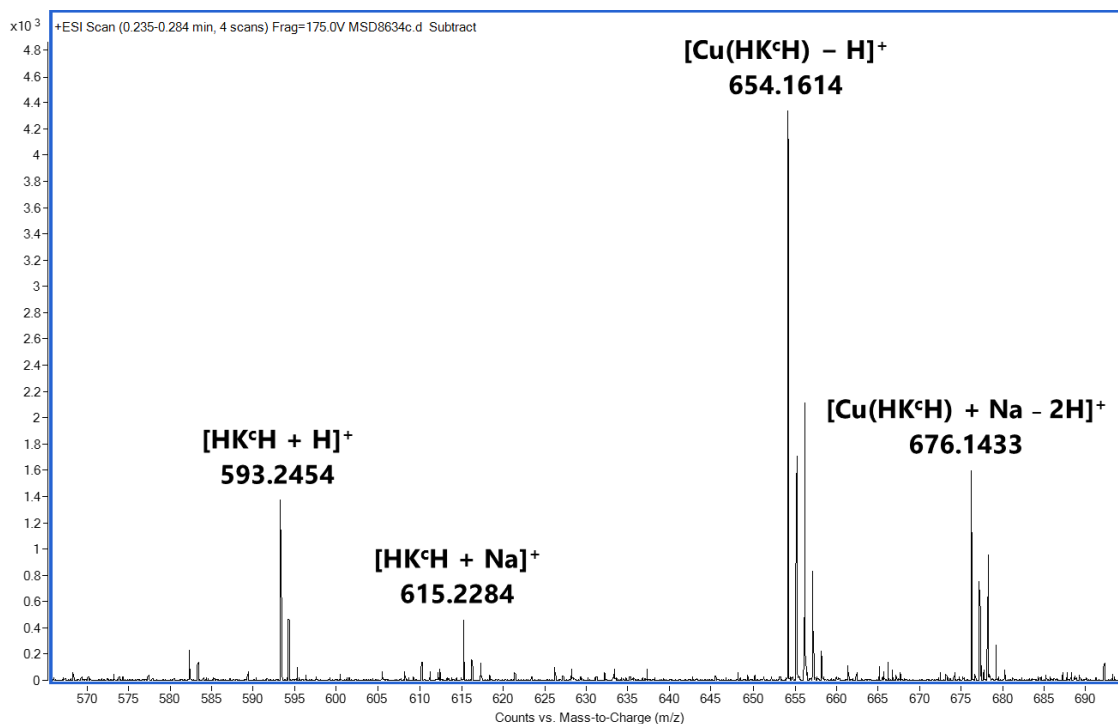
### Chapter 3: Chelation and detection of Cu(II)



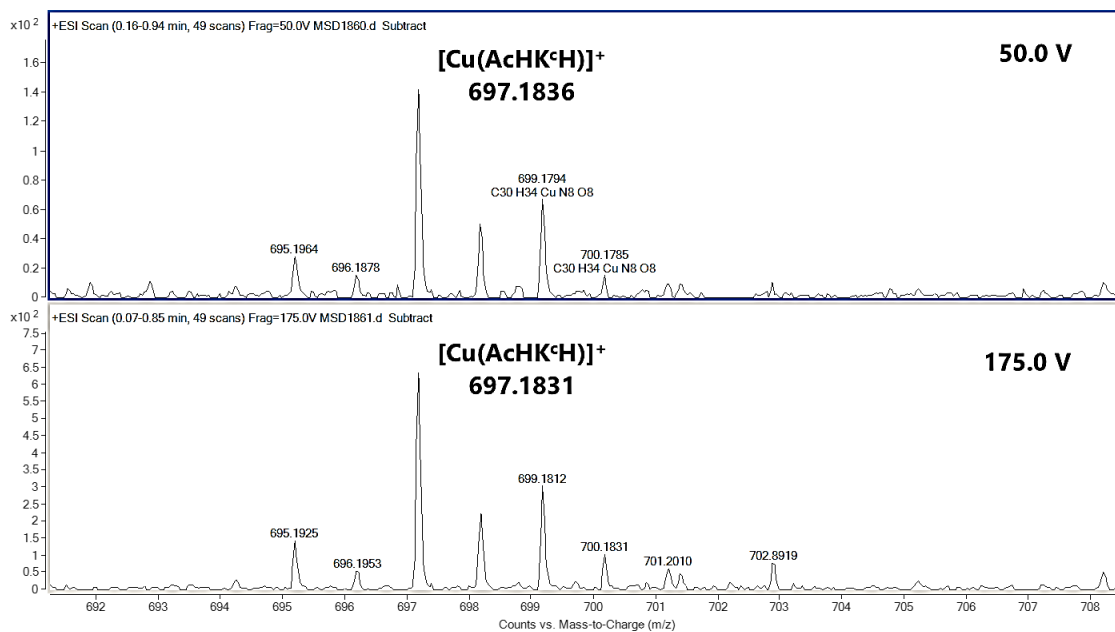
**Figure S3.1:** Mass spectrum of a 1:2 HAH-Cu(II) solution in Milli-Q H<sub>2</sub>O (pH 7.4).



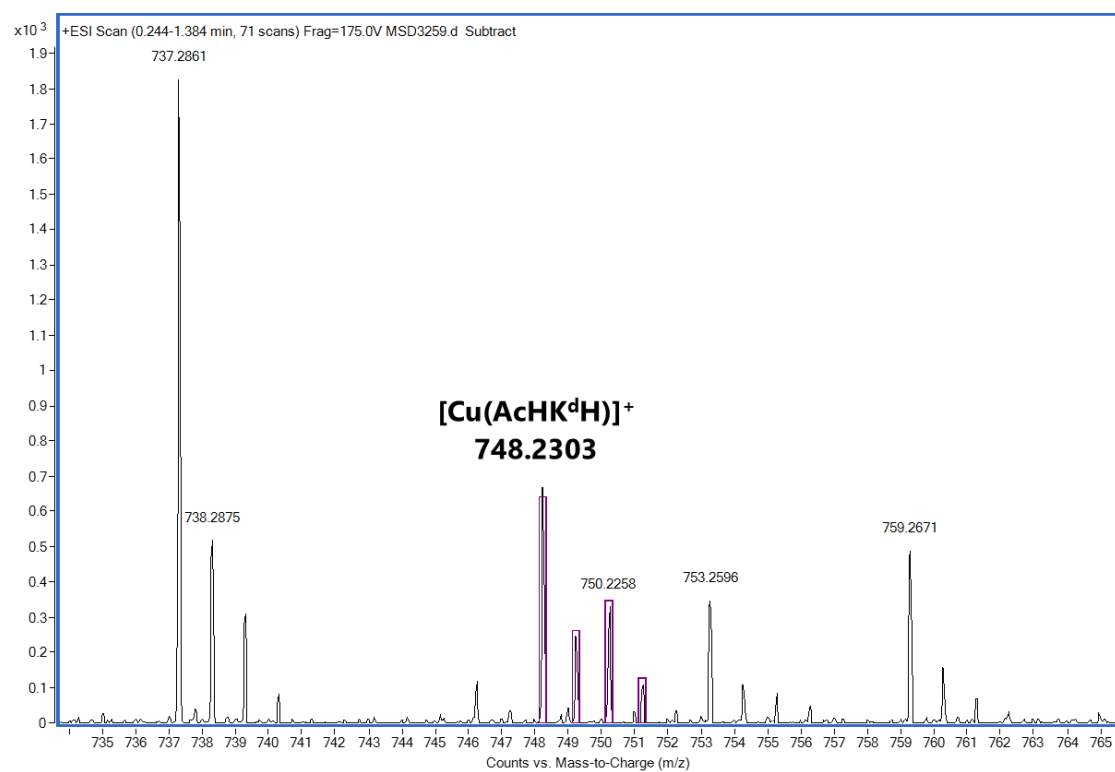
**Figure S3.2:** Mass spectrum of a 1:2 HWH-Cu(II) solution in Milli-Q H<sub>2</sub>O (pH 7.4).



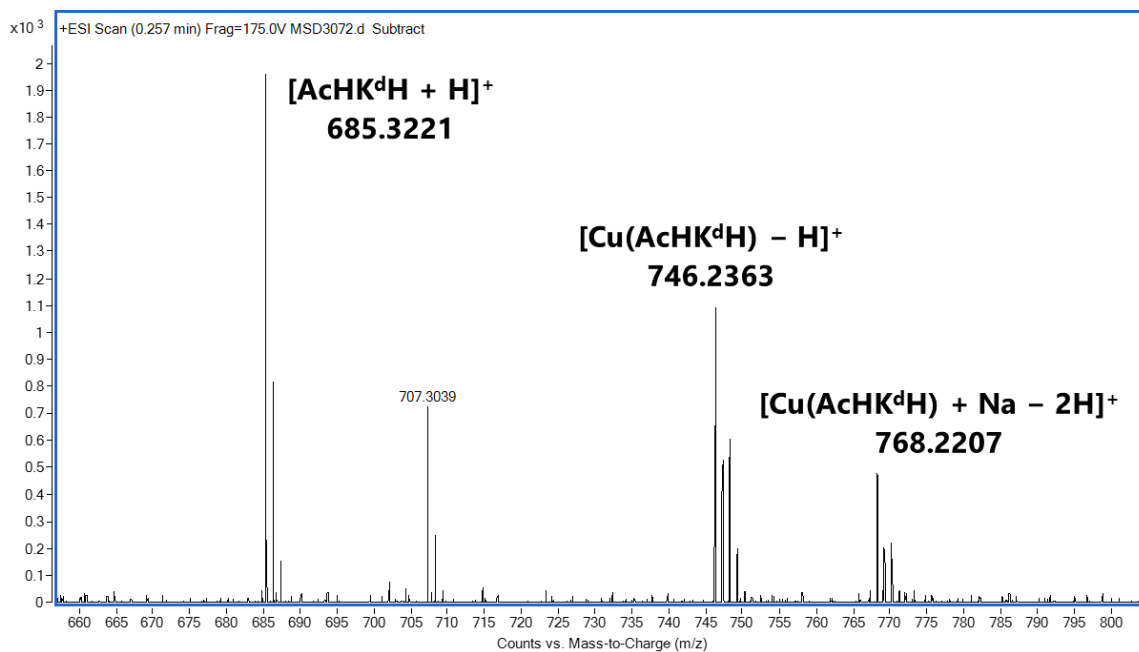
**Figure S3.3:** Mass spectrum of a 1:2 HK<sup>c</sup>H-Cu(II) solution in Milli-Q H<sub>2</sub>O (pH 7.4).



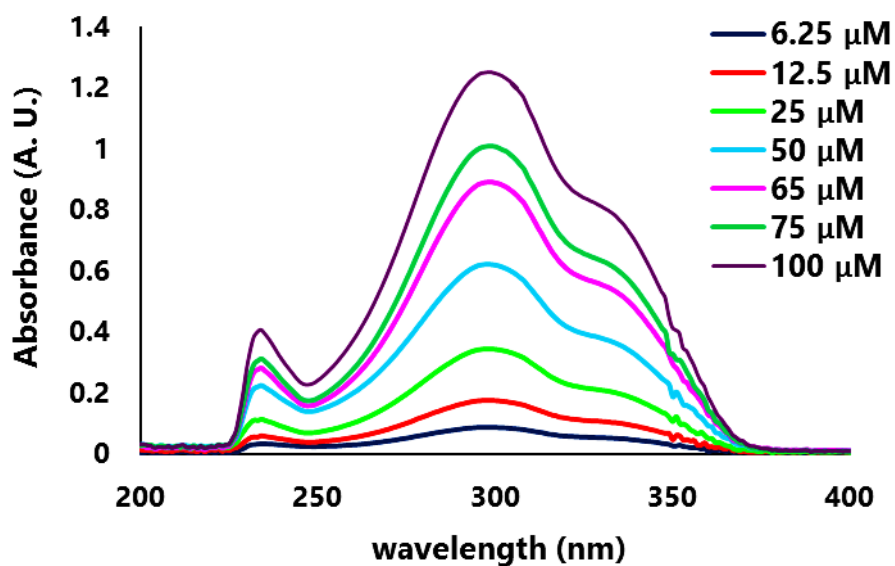
**Figure S3.4:** Mass spectrum of a 1:2 AcHK<sup>H</sup>-Cu(II) solution in Milli-Q H<sub>2</sub>O (pH 7.4).



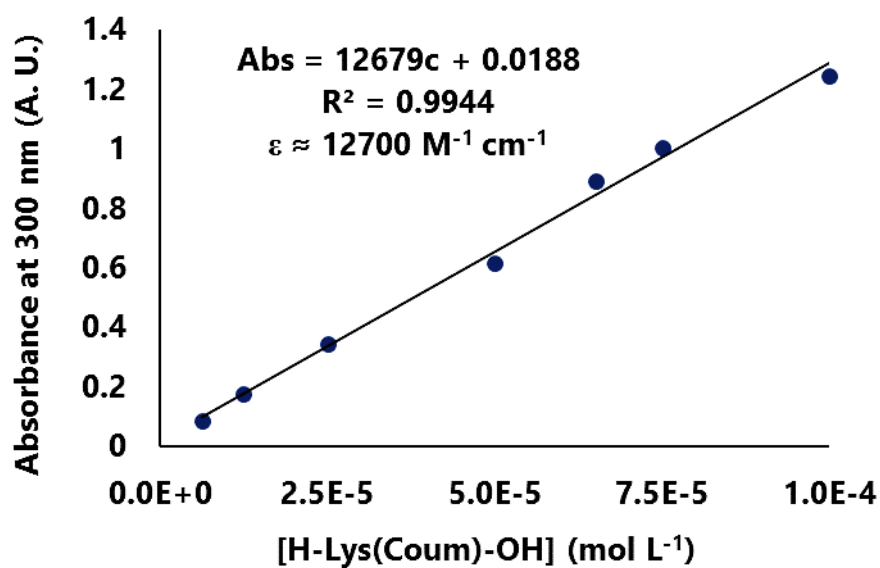
**Figure S3.5:** Mass spectrum of a 1:2 AcHK<sup>dH</sup>-Cu(II) solution in Milli-Q H<sub>2</sub>O (pH 7.4).



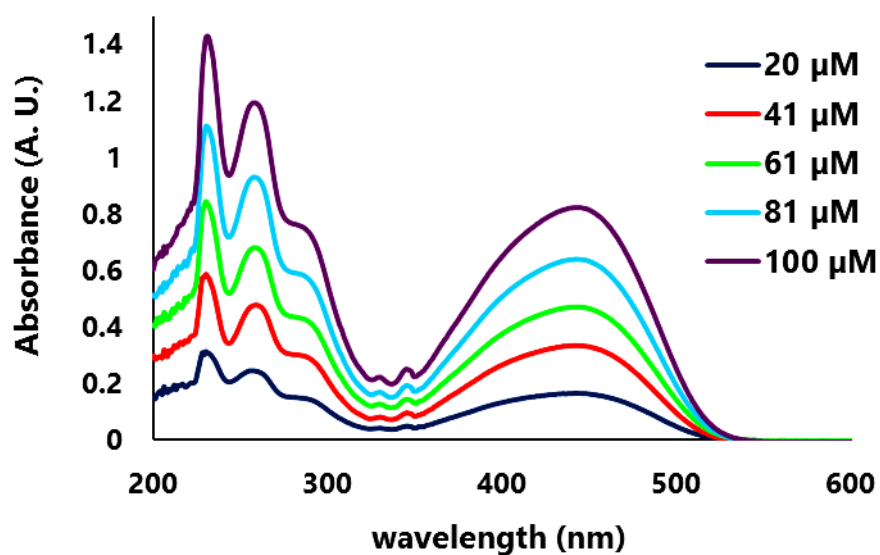
**Figure S3.6:** Mass spectrum of a 1:2 AcHK<sup>d</sup>H-NH<sub>2</sub>-Cu(II) solution in Milli-Q H<sub>2</sub>O (pH 7.4).



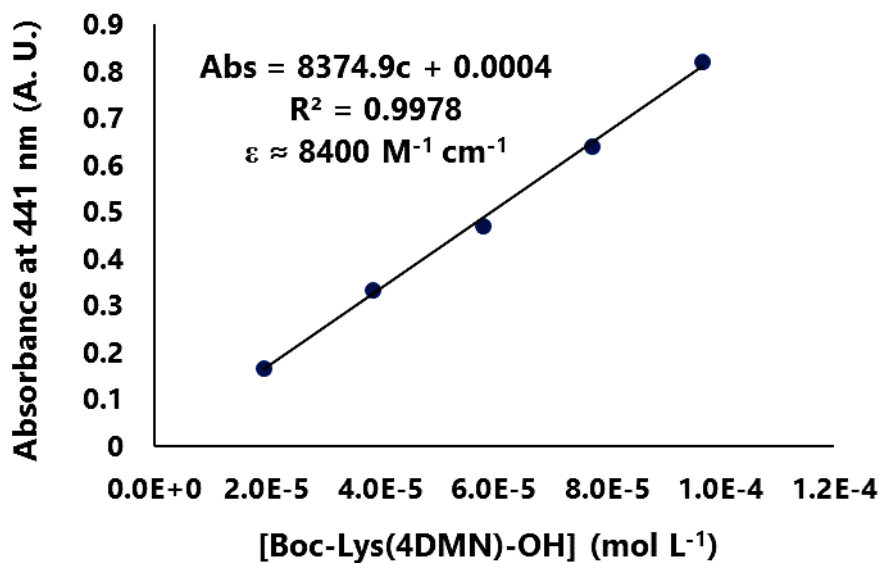
**Figure S3.7:** UV-Vis spectra of H-Lys(Coum)-OH solutions (concentrations 6.25-100 μM) in 100 mM HEPES (pH 7.4).



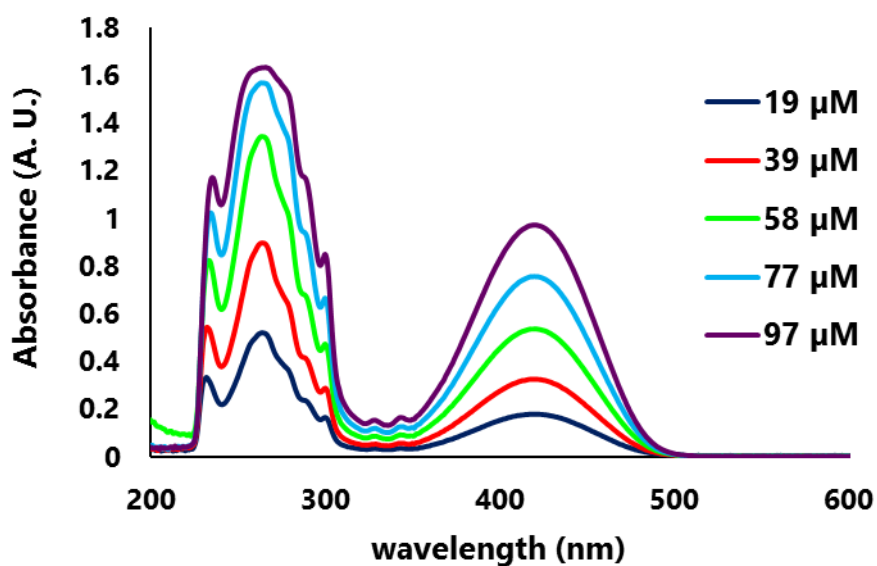
**Figure S3.8:** Absorbance at 300 nm of H-Lys(Coum)-OH solutions (concentrations 6.25-100  $\mu\text{M}$ ) in 100 mM HEPES (pH 7.4).



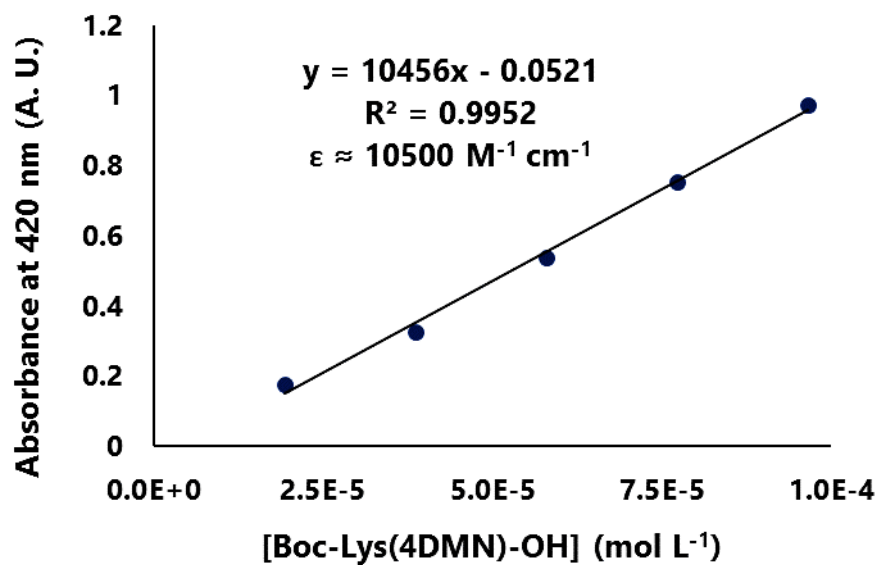
**Figure S3.9:** UV-Vis spectra of Boc-Lys(4DMN)-OH solutions (concentrations 20-100  $\mu\text{M}$ ) in 100 mM HEPES (pH 7.4).



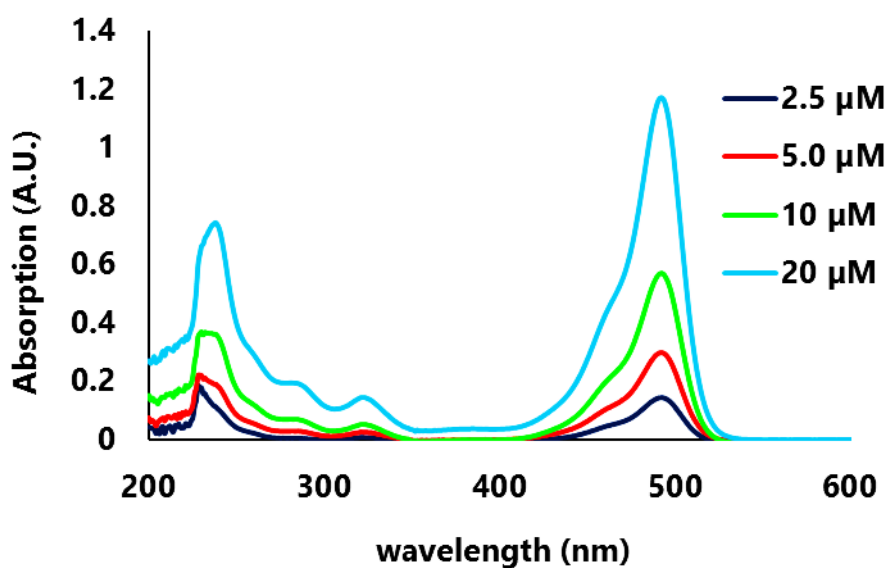
**Figure S3.10:** Absorbance at 441 nm of Boc-Lys(4DMN)-OH solutions (concentrations 20-100  $\mu\text{M}$ ) in 100 mM HEPES (pH 7.4).



**Figure S3.11:** UV-Vis spectra of Boc-Lys(4DMN)-OH solutions (concentrations 19-97  $\mu\text{M}$ ) in DCM.

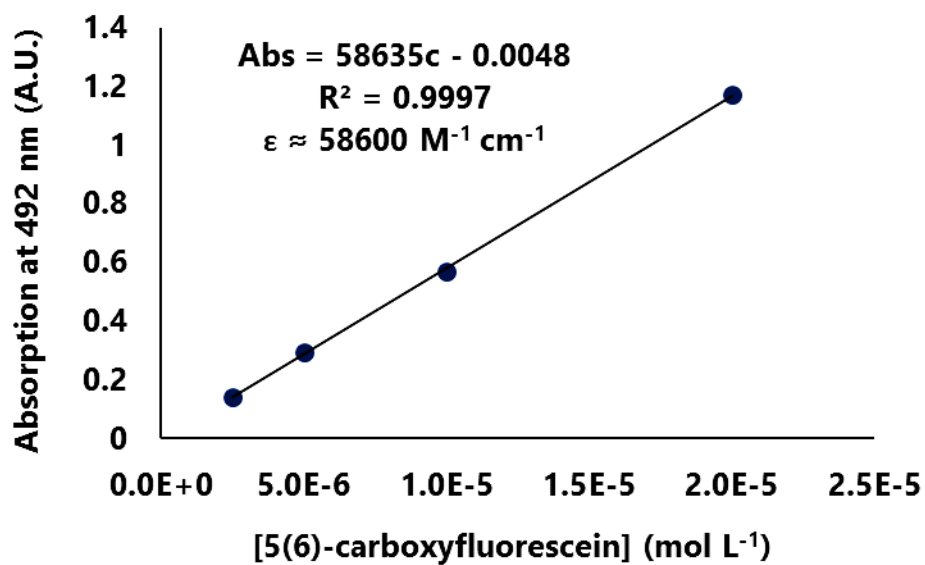


**Figure S3.12:** Absorbance at 420 nm of Boc-Lys(4DMN)-OH solutions (concentrations 19-97  $\mu\text{M}$ ) in DCM.

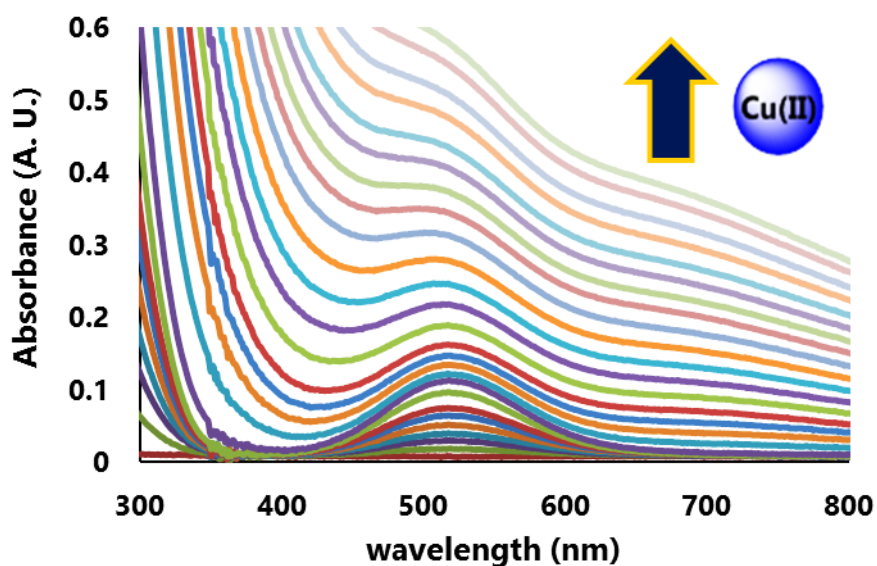


**Figure S3.13:** UV-Vis spectra of 5(6)-carboxyfluorescein solutions (concentrations 2.5-20  $\mu\text{M}$ ) in 100 mM HEPES (pH 7.4).

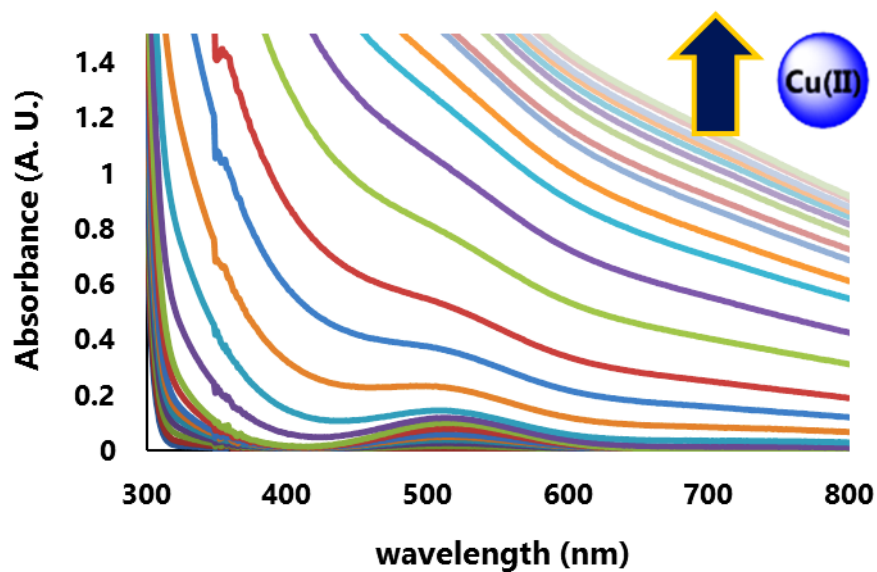




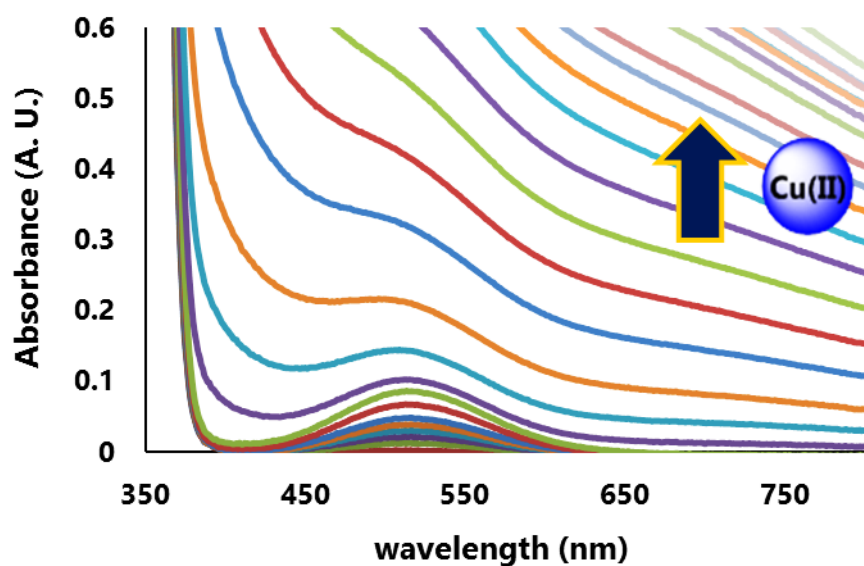
**Figure S3.14:** Absorbance at 492 nm of 5(6)-carboxyfluorescein solutions (concentrations 2.5-20  $\mu\text{M}$ ) in 100 mM HEPES (pH 7.4).



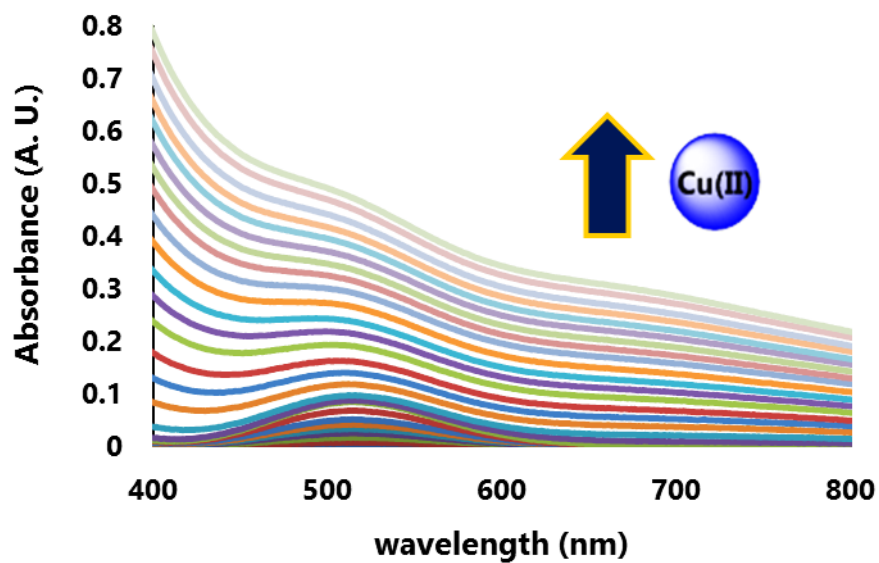
**Figure S3.15:** UV-Vis spectra of a 1 mM HAH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of  $\text{CuCl}_2$ .



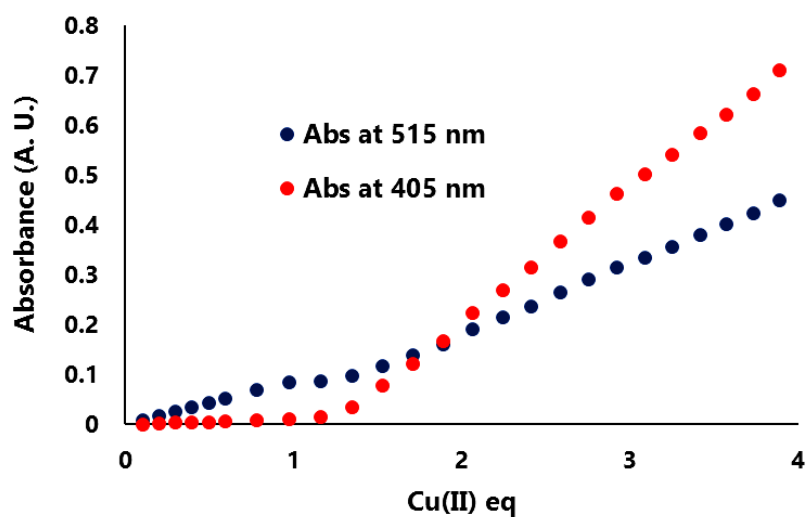
**Figure S3.16:** UV-Vis spectra of a 1 mM HWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of CuCl<sub>2</sub>.



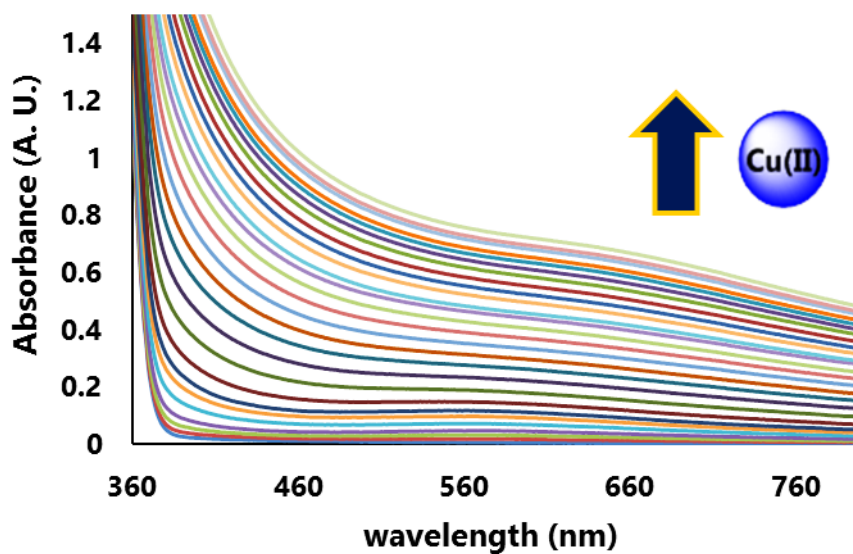
**Figure S3.17:** UV-Vis spectra of a 1 mM HK<sup>c</sup>H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of CuCl<sub>2</sub>.



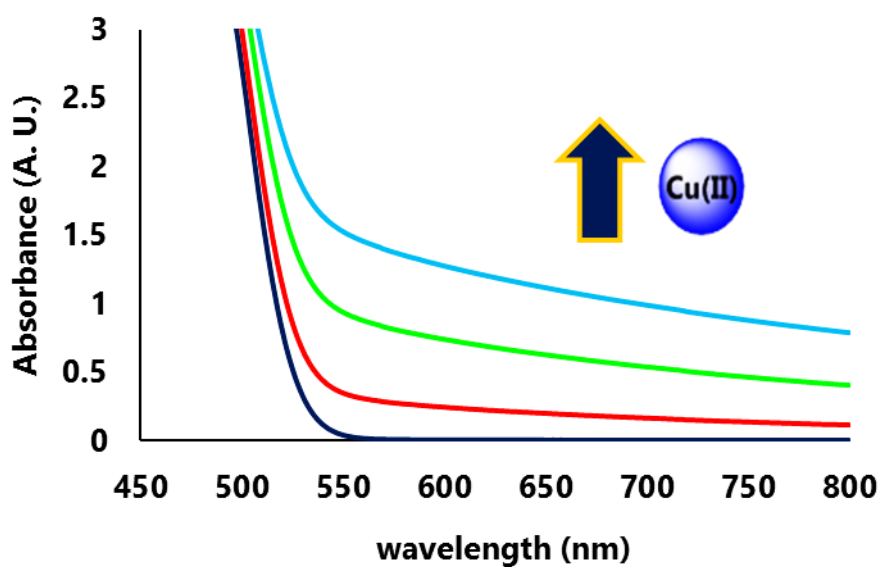
**Figure S3.18:** UV-Vis spectra of a 1 mM GWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of  $\text{CuCl}_2$ .



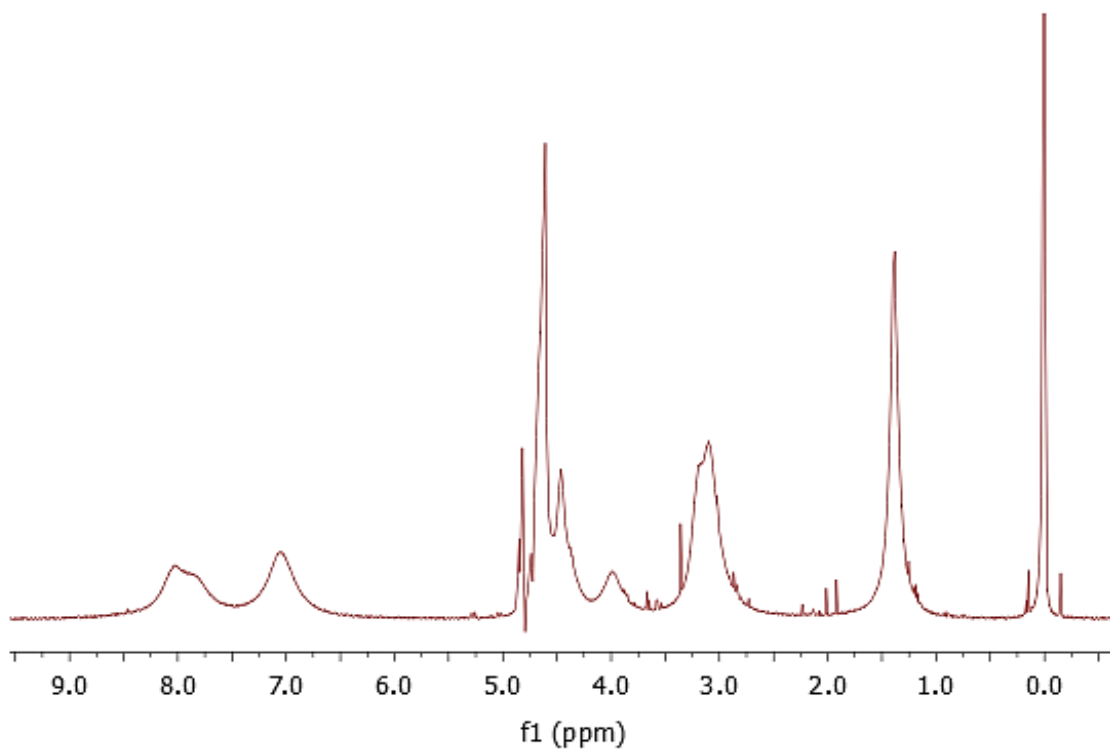
**Figure S3.19:** Absorbance values (at 405 nm, **red dots**; and 515 nm, **blue dots**) of a 1 mM GWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of  $\text{CuCl}_2$ .



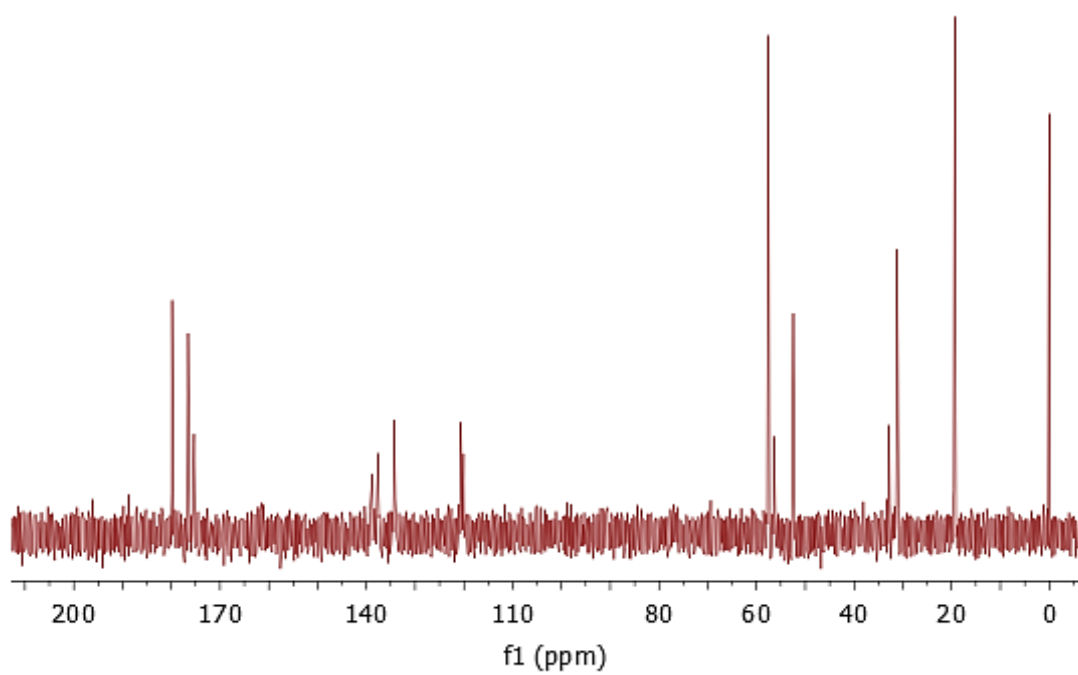
**Figure S3.20:** UV-Vis spectra of a 1 mM AcHK<sup>c</sup>H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of CuCl<sub>2</sub>.



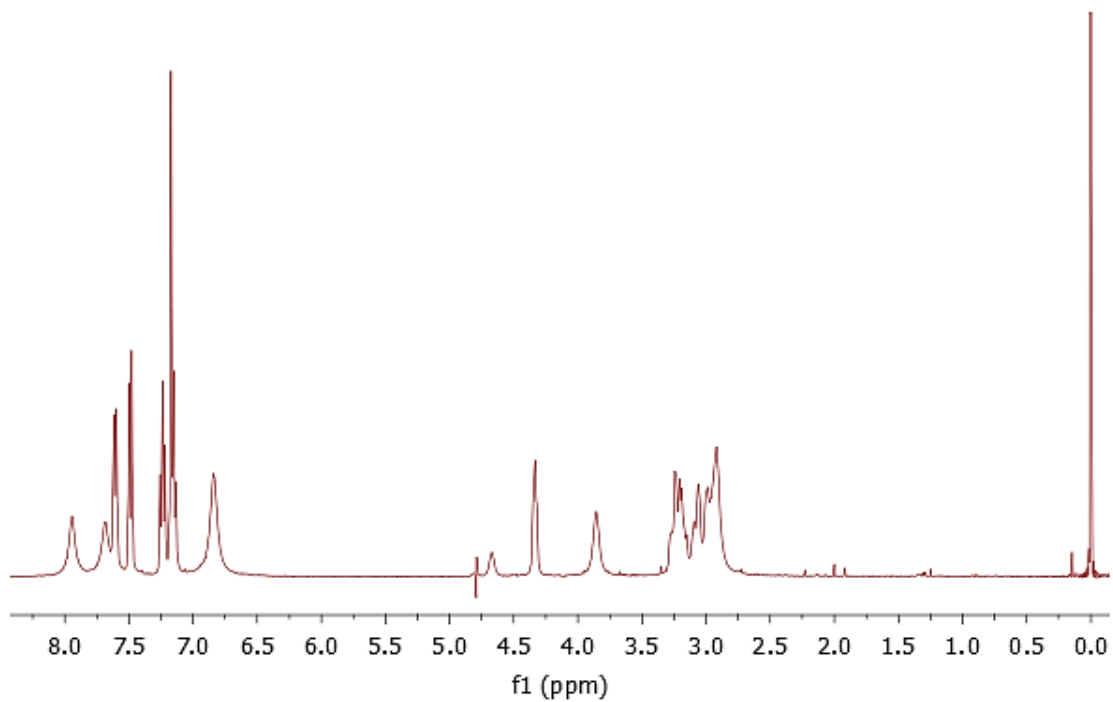
**Figure S3.21:** UV-Vis spectra of a 1 mM AcHK<sup>d</sup>H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of CuCl<sub>2</sub>.



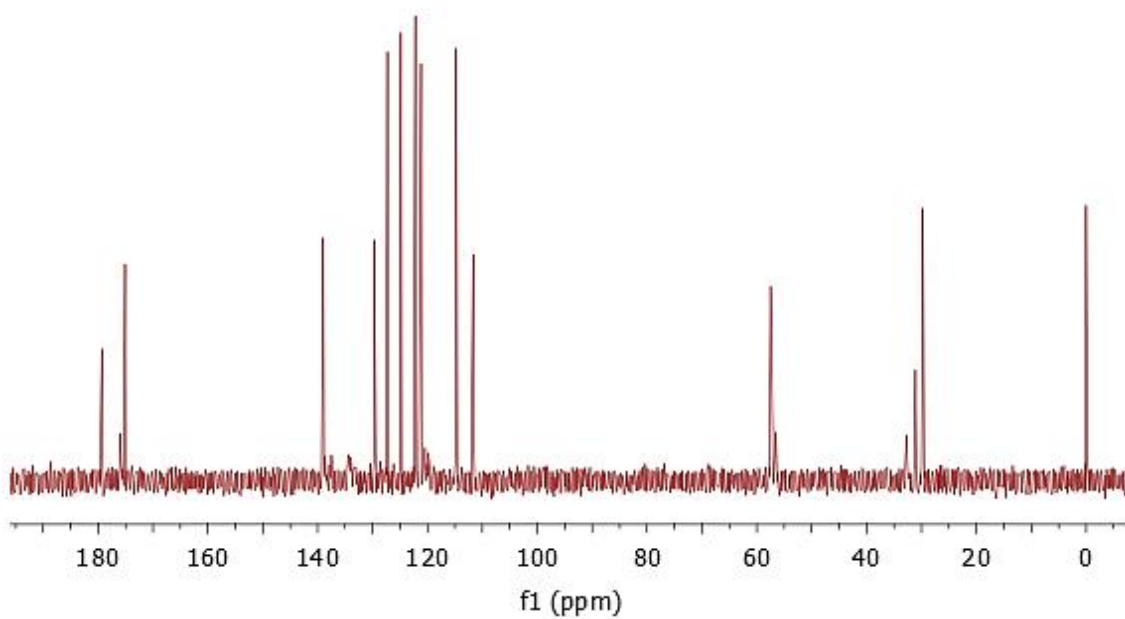
**Figure S3.22:**  $^1\text{H}$  NMR spectrum of a 10 mM HAH solution in  $\text{D}_2\text{O}$  containing 1%  $\text{CuCl}_2$  (pH 7.4).



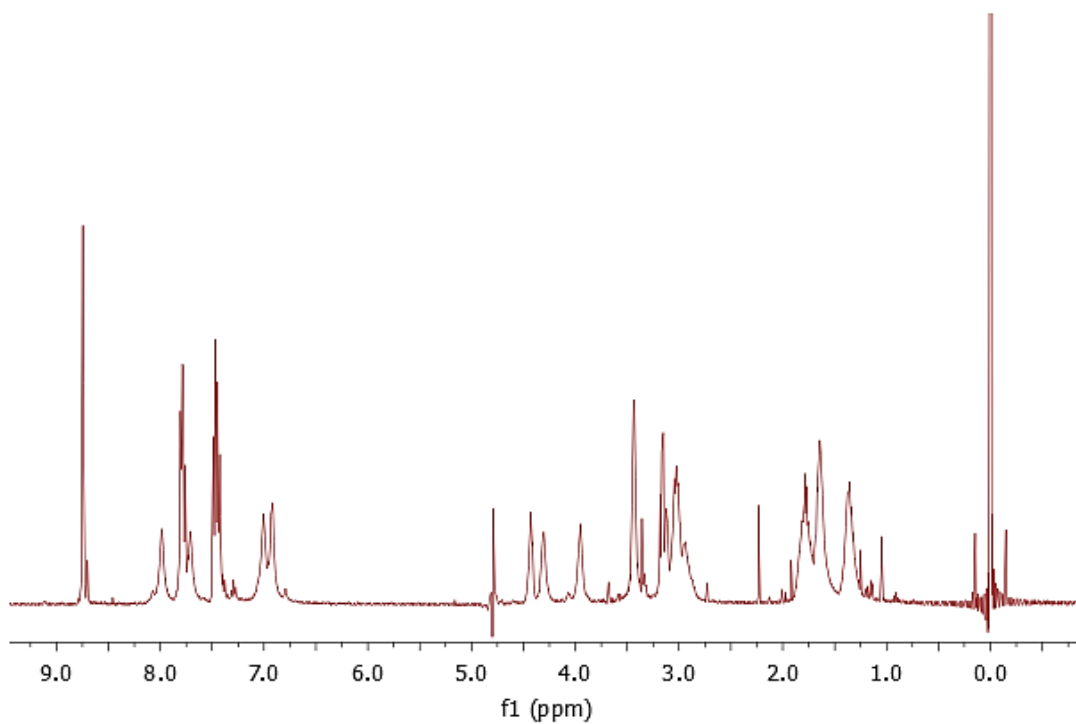
**Figure S3.23:**  $^{13}\text{C}$  NMR spectrum of a 10 mM HAH solution in  $\text{D}_2\text{O}$  containing 1%  $\text{CuCl}_2$  (pH 7.4).



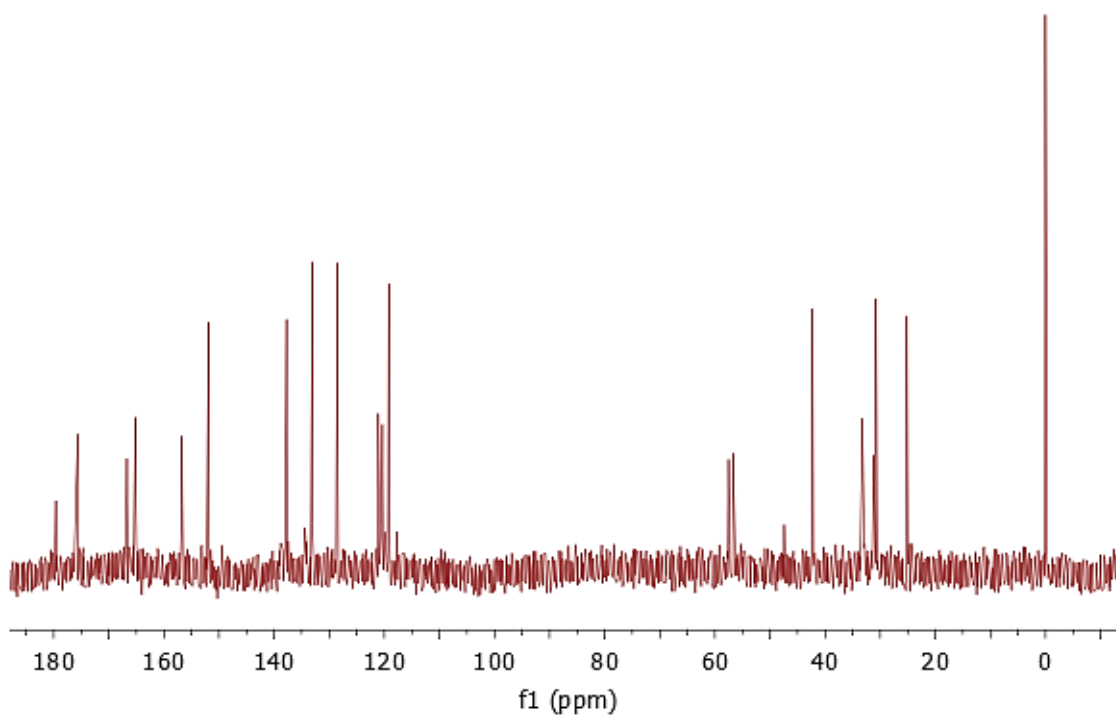
**Figure S3.24:**  $^1\text{H}$  NMR spectrum of a 10 mM HWH solution in  $\text{D}_2\text{O}$  containing 1%  $\text{CuCl}_2$  (pH 7.4).



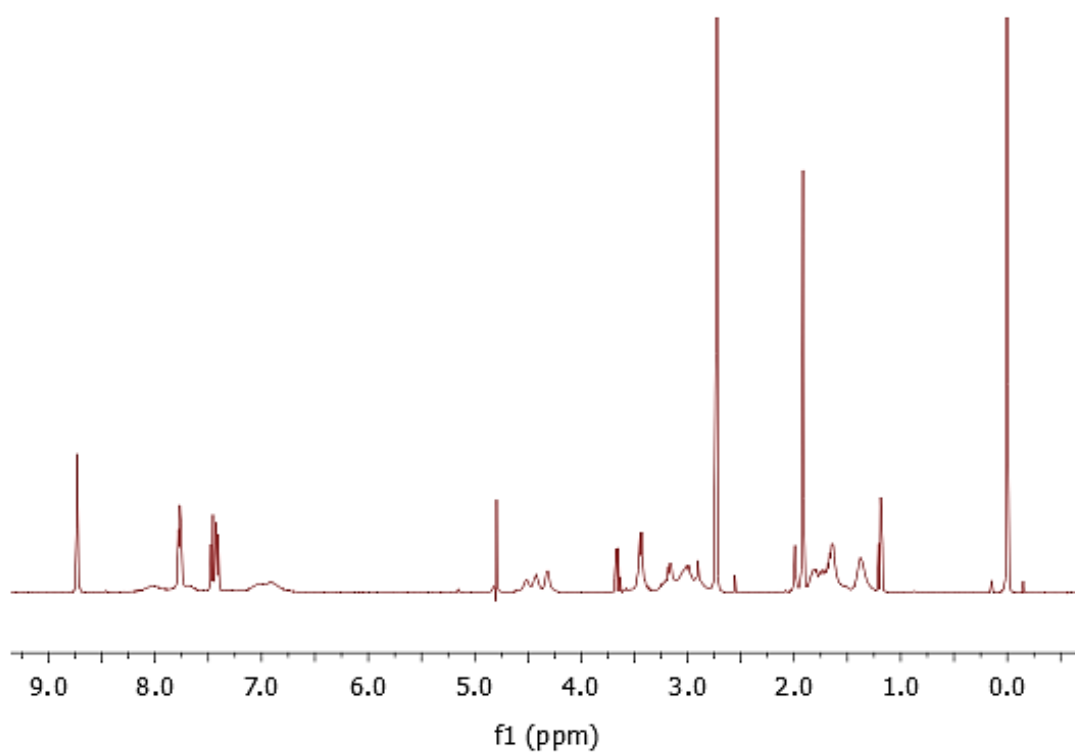
**Figure S3.25:**  $^{13}\text{C}$  NMR spectrum of a 10 mM HWH solution in  $\text{D}_2\text{O}$  containing 1%  $\text{CuCl}_2$  (pH 7.4).



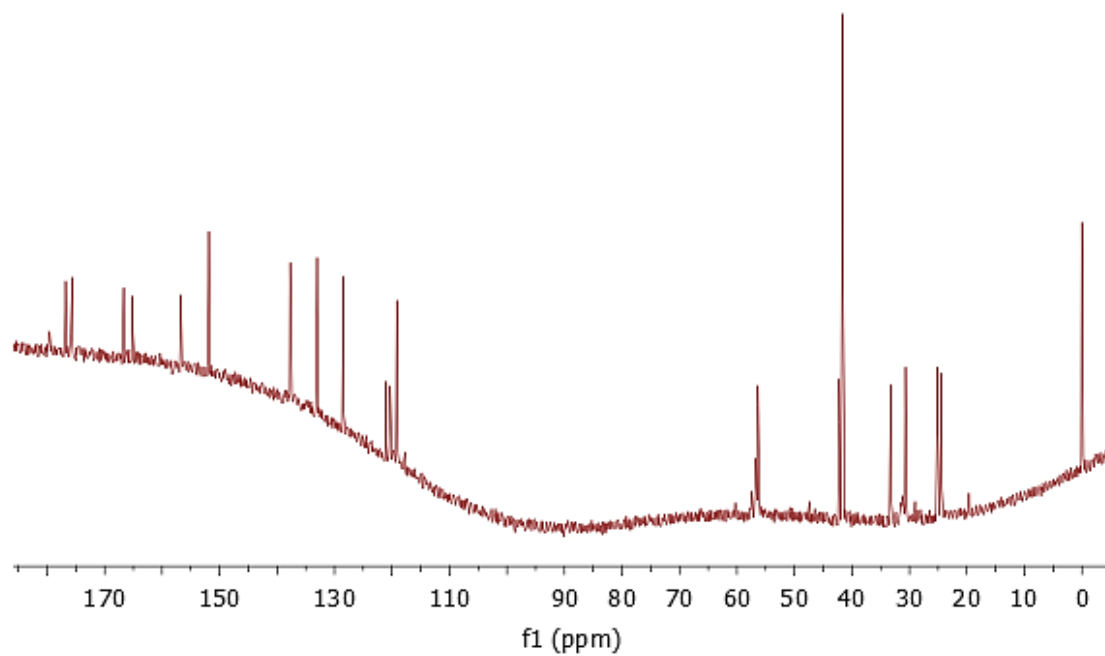
**Figure S3.26:**  $^1\text{H}$  NMR spectrum of a 10 mM  $\text{HK}^{\text{C}}\text{H}$  solution in  $\text{D}_2\text{O}$  containing 1%  $\text{CuCl}_2$  (pH 7.4).



**Figure S3.27:**  $^{13}\text{C}$  NMR spectrum of a 10 mM  $\text{HK}^{\text{C}}\text{H}$  solution in  $\text{D}_2\text{O}$  containing 1%  $\text{CuCl}_2$  (pH 7.4).

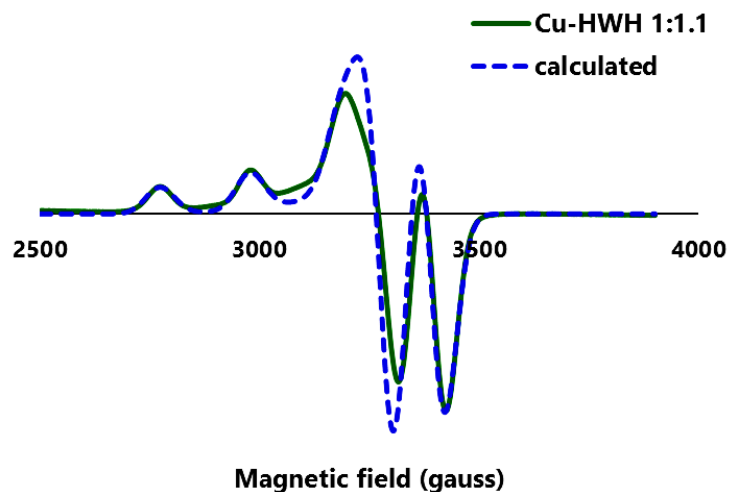


**Figure S3.28:**  $^1\text{H}$  NMR spectrum of a 10 mM AcHK<sup>c</sup>H solution in  $\text{D}_2\text{O}$  containing 1%  $\text{CuCl}_2$  (pH 7.4).

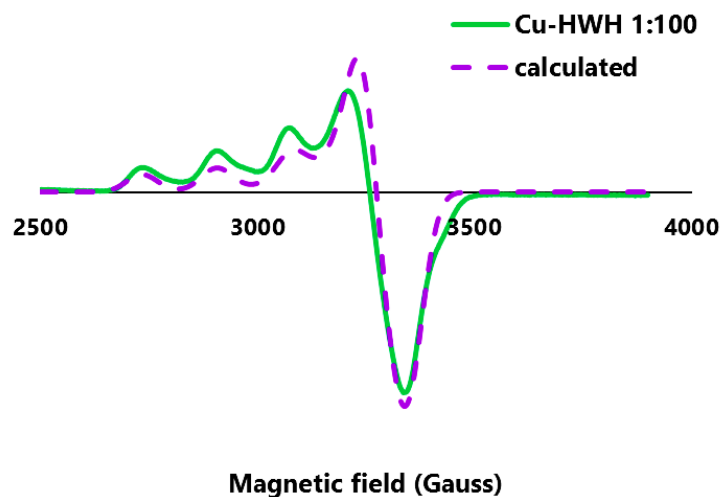


**Figure S3.29:**  $^{13}\text{C}$  NMR spectrum of a 10 mM AcHK<sup>c</sup>H solution in  $\text{D}_2\text{O}$  containing 1%  $\text{CuCl}_2$  (pH 7.4).

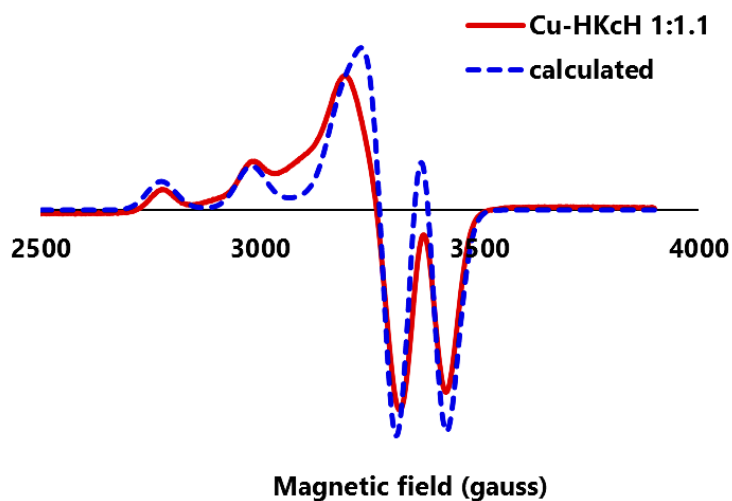




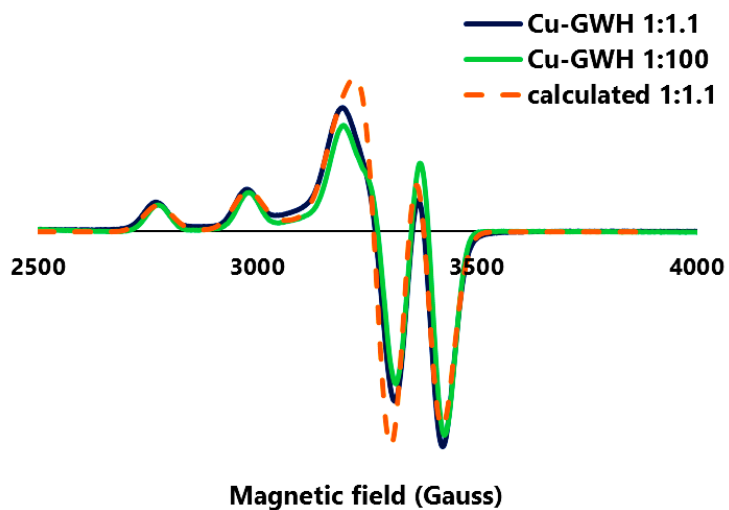
**Figure S3.30:** EPR spectra (obtained, **green line**; calculated, **dashed blue line**) of a 1:1.1 Cu(II)-HWH sample in 100 mM HEPES (pH 7.4) at 77 K.



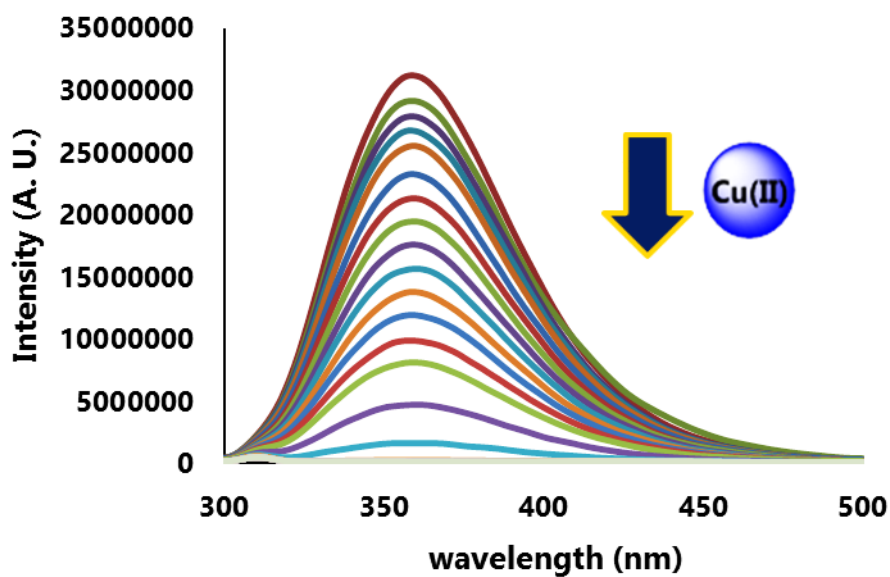
**Figure S3.31:** EPR spectra (obtained, **green line**; calculated, **dashed purple line**) of a 1:100 Cu(II)-HWH sample in 100 mM HEPES (pH 7.4) at 77 K.



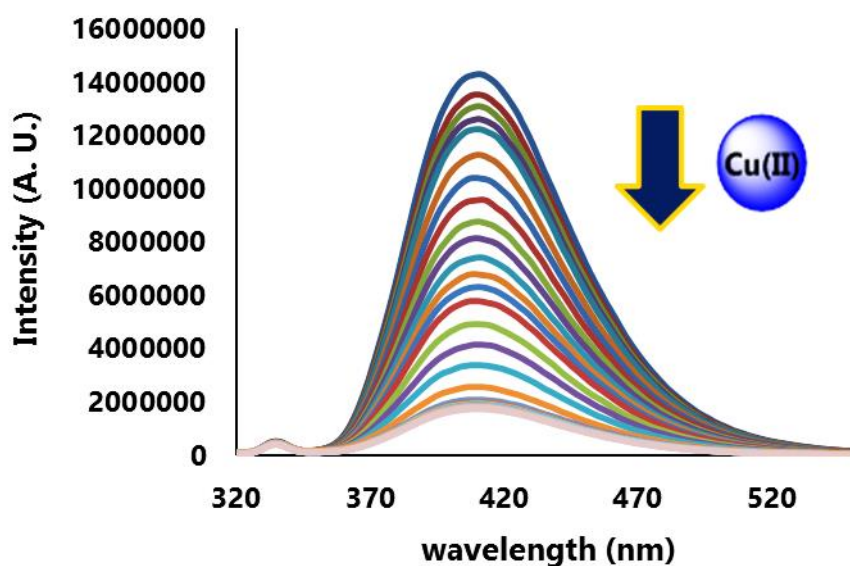
**Figure S3.32:** EPR spectra (obtained, **red line**; calculated, **dashed blue line**) of a 1:1.1 Cu(II)-HK<sup>c</sup>H sample in 100 mM HEPES (pH 7.4) at 77 K.



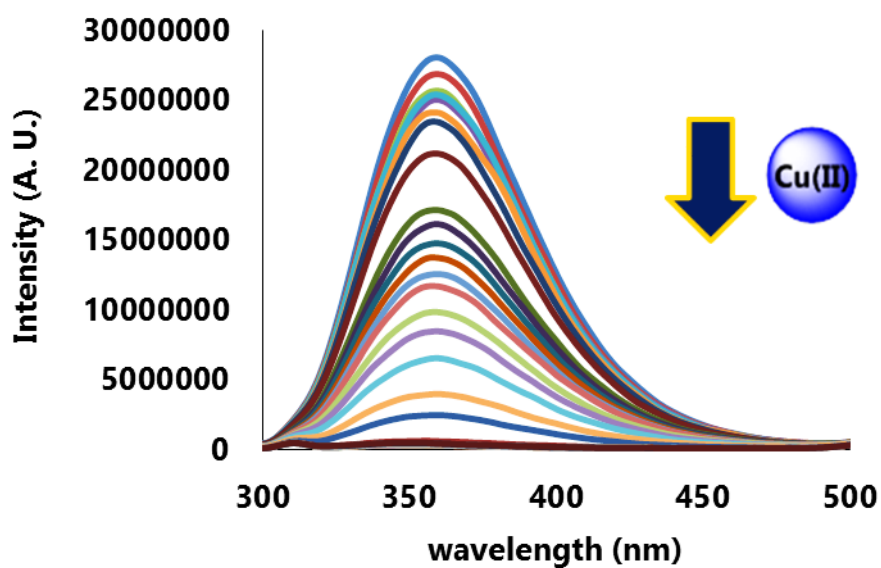
**Figure S3.33:** EPR spectra (obtained for a 1:1.1 sample, **blue line**; obtained for a 1:100 sample, **green line**; calculated for a 1:1.1 sample, **dashed orange line**) of a Cu(II)-GWH sample in 100 mM HEPES (pH 7.4) at 77 K..



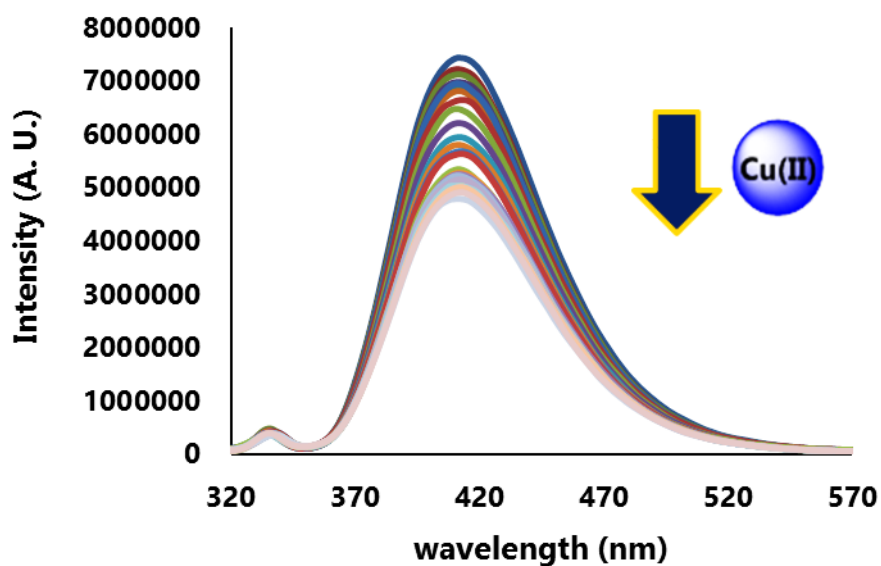
**Figure S3.34:** Fluorescence spectra of a 10  $\mu\text{M}$  HWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of  $\text{CuCl}_2$ .  $\lambda_{\text{exc}} = 280$  nm.



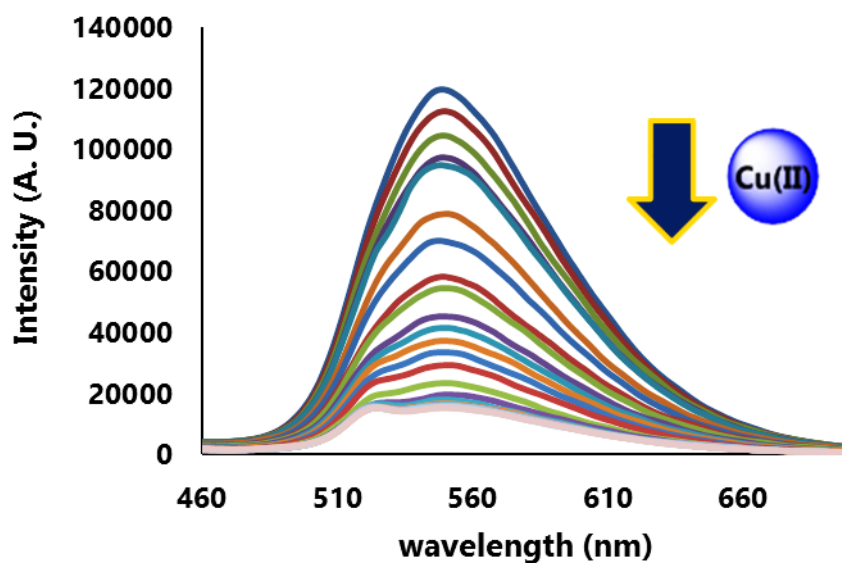
**Figure S3.35:** Fluorescence spectra of a 10  $\mu\text{M}$  HKH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of  $\text{CuCl}_2$ .  $\lambda_{\text{exc}} = 300$  nm.



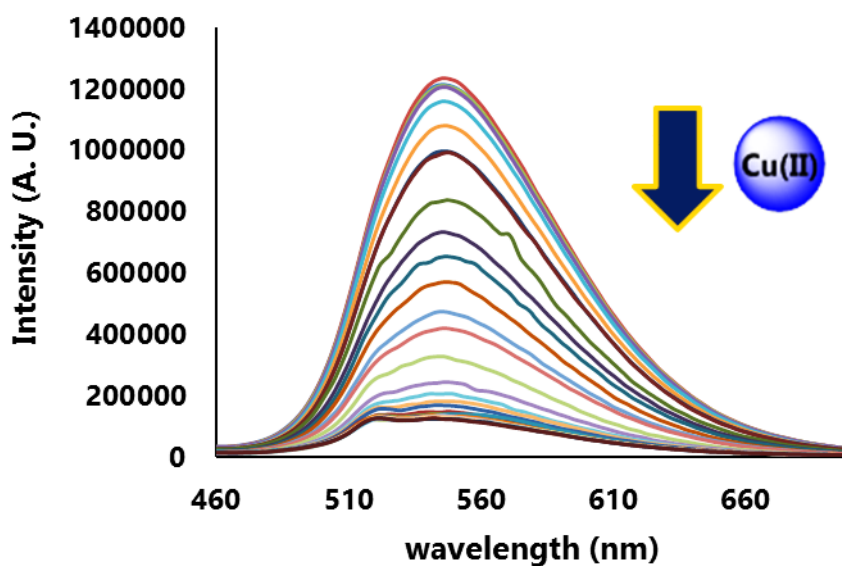
**Figure S3.36:** Fluorescence spectra of a 10 μM GWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of CuCl<sub>2</sub>.  $\lambda_{\text{exc}} = 280$  nm.



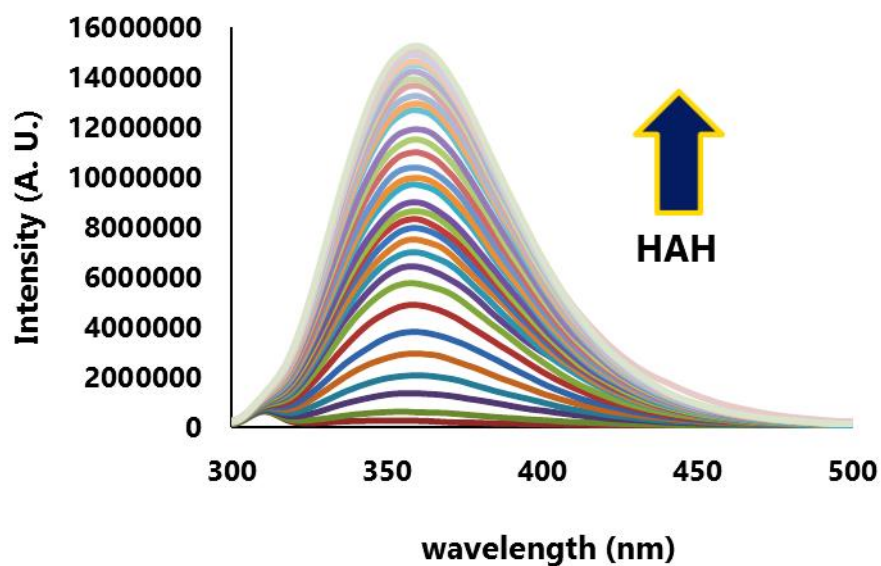
**Figure S3.37:** Fluorescence spectra of a 10 μM AcHK<sup>H</sup> solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of CuCl<sub>2</sub>.  $\lambda_{\text{exc}} = 300$  nm.



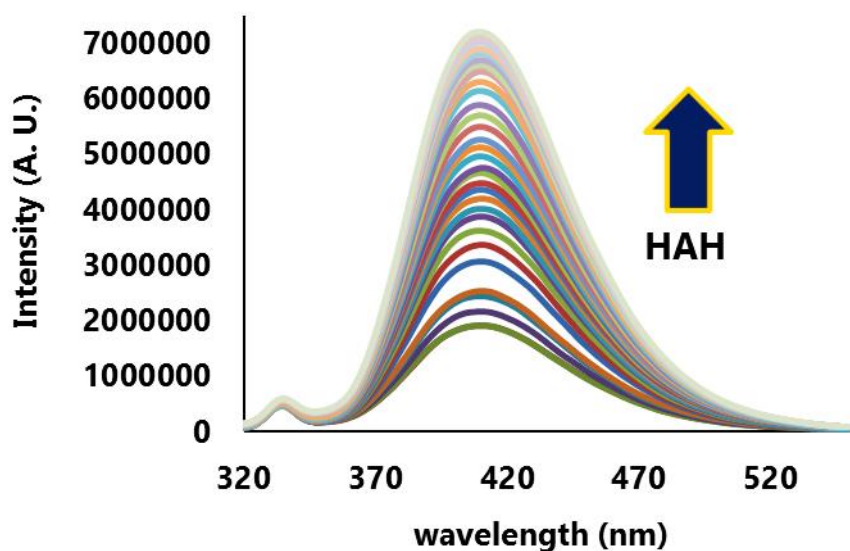
**Figure S3.38:** Fluorescence spectra of a 10 μM ACHK<sup>d</sup>H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of CuCl<sub>2</sub>.  $\lambda_{\text{exc}} = 441$  nm.



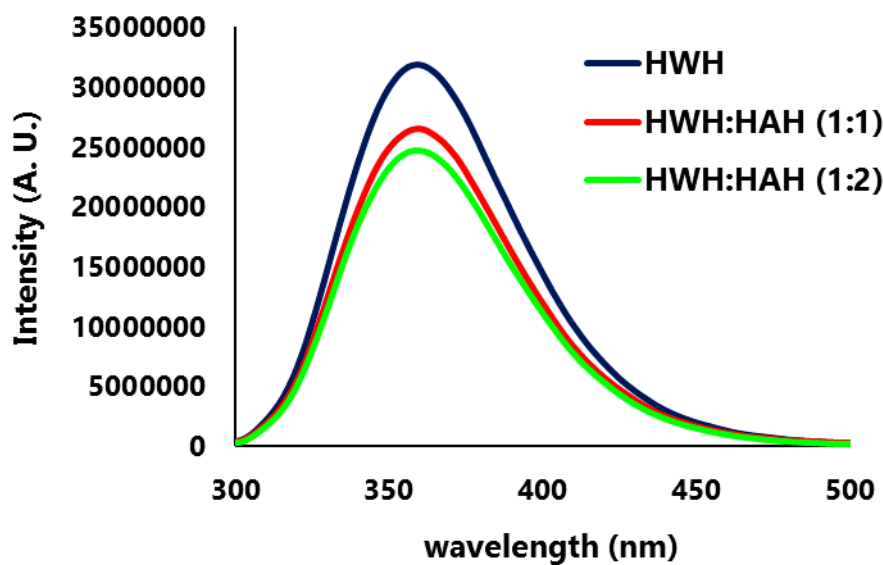
**Figure S3.39:** Fluorescence spectra of a 10 μM ACHK<sup>d</sup>H-NH<sub>2</sub> solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of CuCl<sub>2</sub>.  $\lambda_{\text{exc}} = 441$  nm.



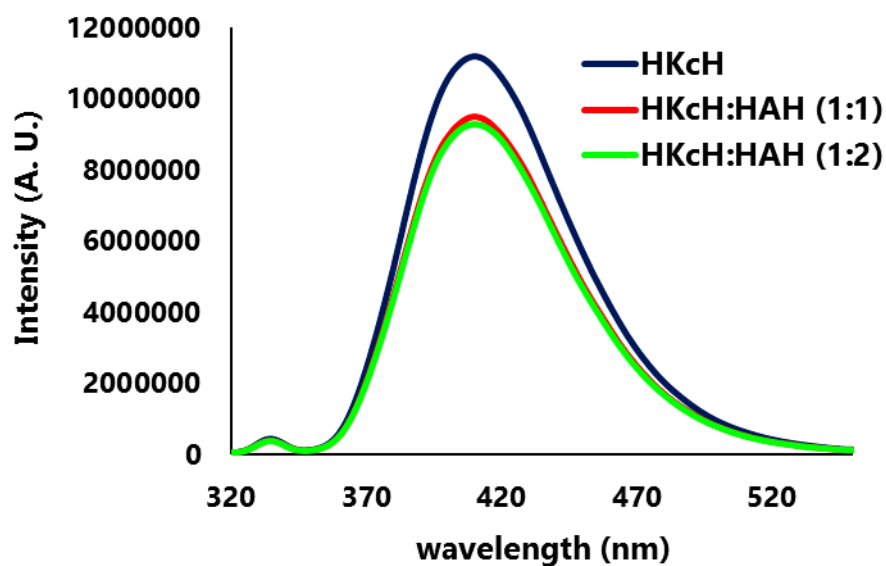
**Figure S3.40:** Fluorescence spectra of a 10  $\mu\text{M}$  Cu-HWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of HAH.  $\lambda_{\text{exc}} = 280$  nm.



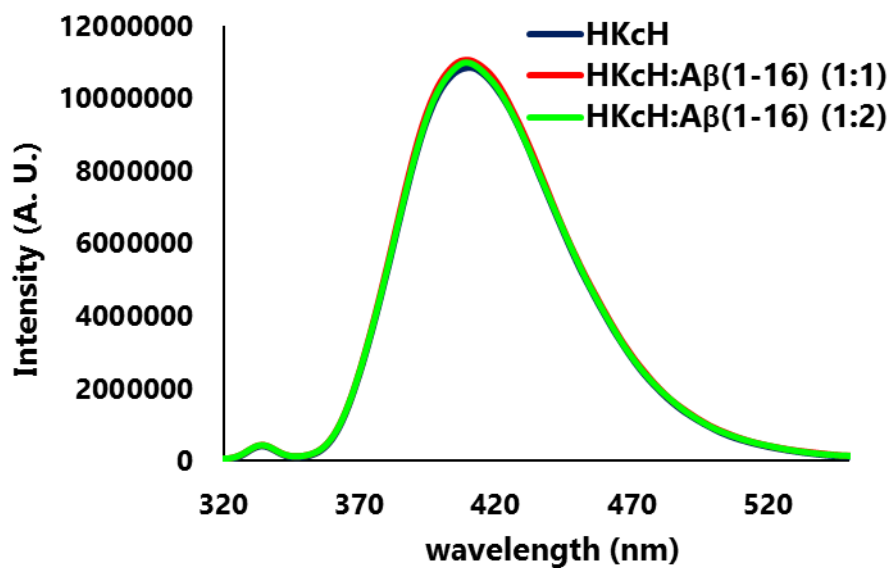
**Figure S3.41:** Fluorescence spectra of a 10  $\mu\text{M}$  Cu-HK<sup>c</sup>H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of HAH.  $\lambda_{\text{exc}} = 300$  nm.



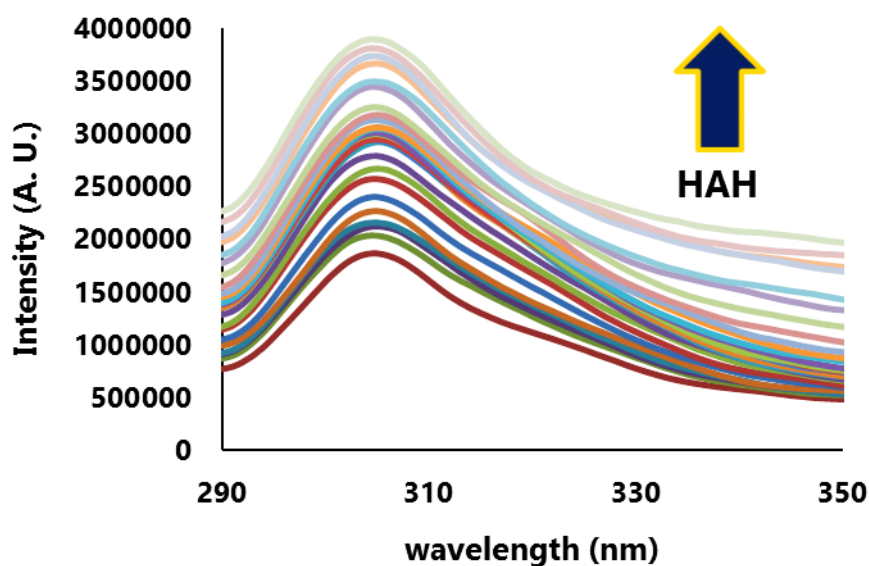
**Figure S3.42:** Fluorescence spectra of a 10 μM HWH solution in 10 mM HEPES (pH 7.4) in the presence of 0, 1 and 2 eq of HAH.  $\lambda_{exc} = 280$  nm.



**Figure S3.43:** Fluorescence spectra of a 10 μM HKcH solution in 10 mM HEPES (pH 7.4) in the presence of 0, 1 and 2 eq of HAH.  $\lambda_{exc} = 300$  nm.

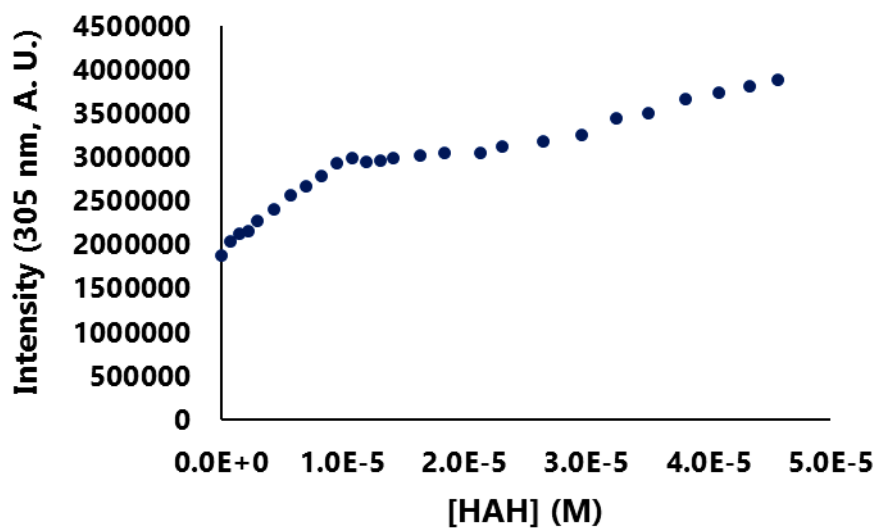


**Figure S3.44:** Fluorescence spectra of a 10  $\mu$ M HK<sup>c</sup>H solution in 10 mM HEPES (pH 7.4) in the presence of 0, 1 and 2 eq of HAH.  $\lambda_{exc}$  = 300 nm.

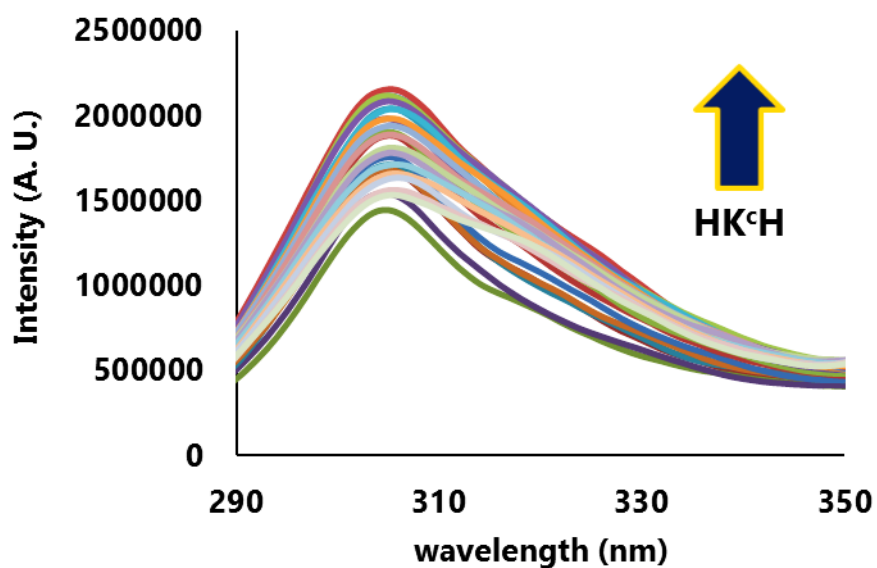


**Figure S3.45:** Fluorescence spectra of a 10  $\mu$ M Cu(II)-A $\beta$ (1-16) solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of HAH.  $\lambda_{exc}$  = 275 nm.

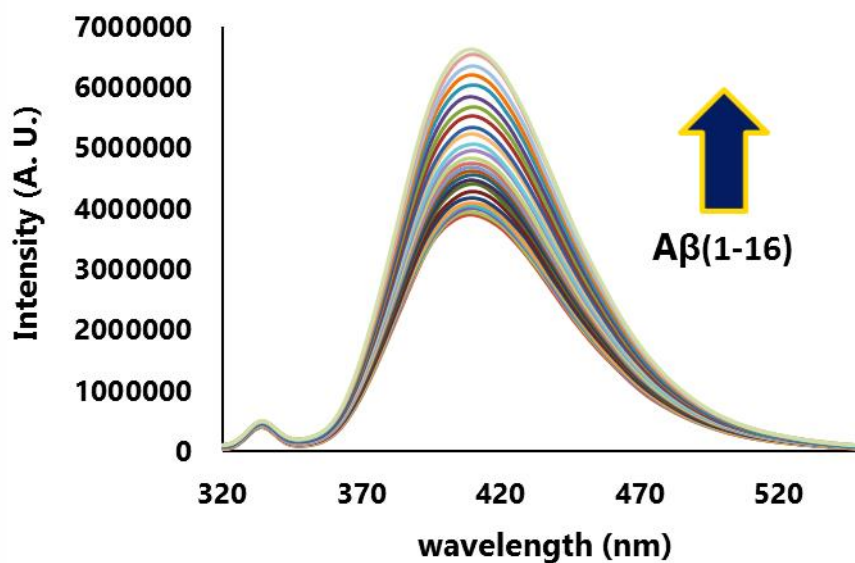




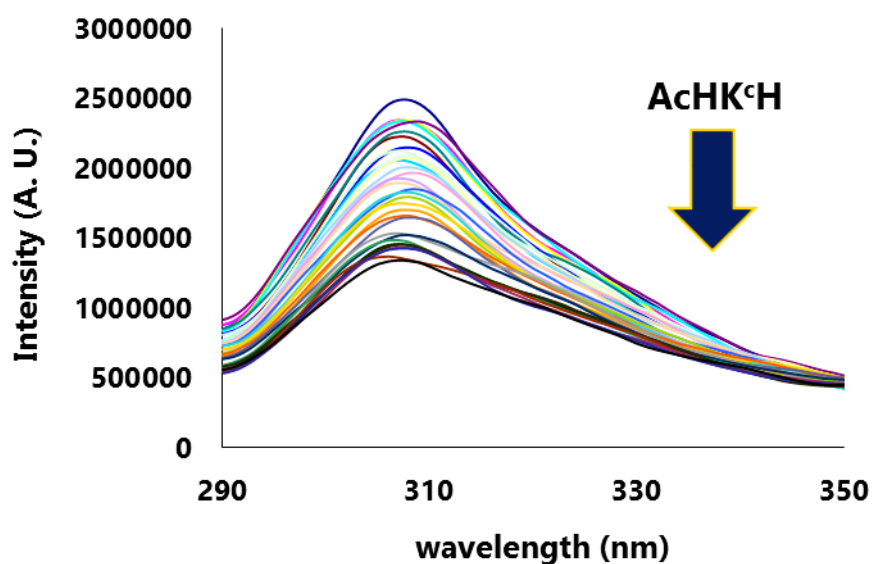
**Figure S3.46:** Fluorescent intensity at 305 nm of a 10  $\mu$ M Cu(II)-A $\beta$ (1-16) solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of HAH.  $\lambda_{\text{exc}} = 275$  nm.



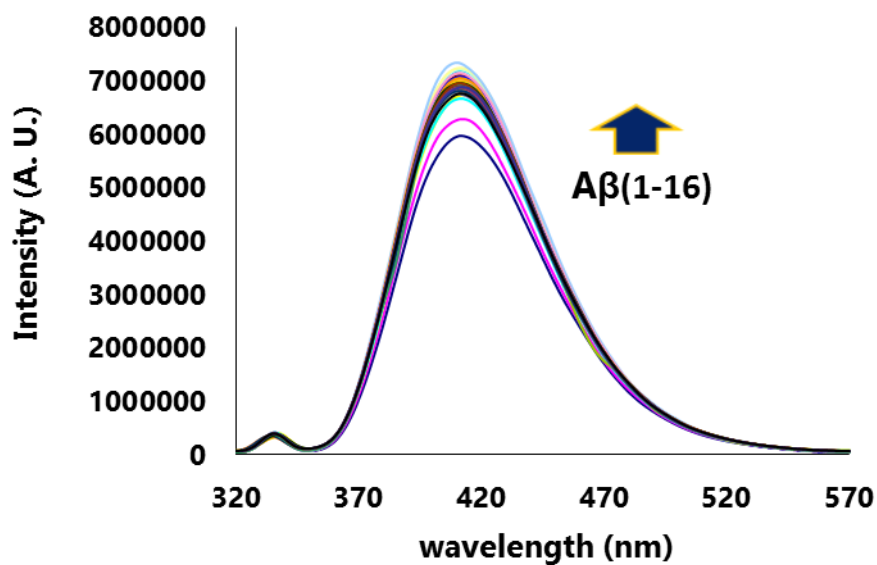
**Figure S3.47:** Fluorescence spectra of a 10  $\mu$ M Cu(II)-A $\beta$ (1-16) solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of HK<sup>c</sup>H.  $\lambda_{\text{exc}} = 275$  nm.



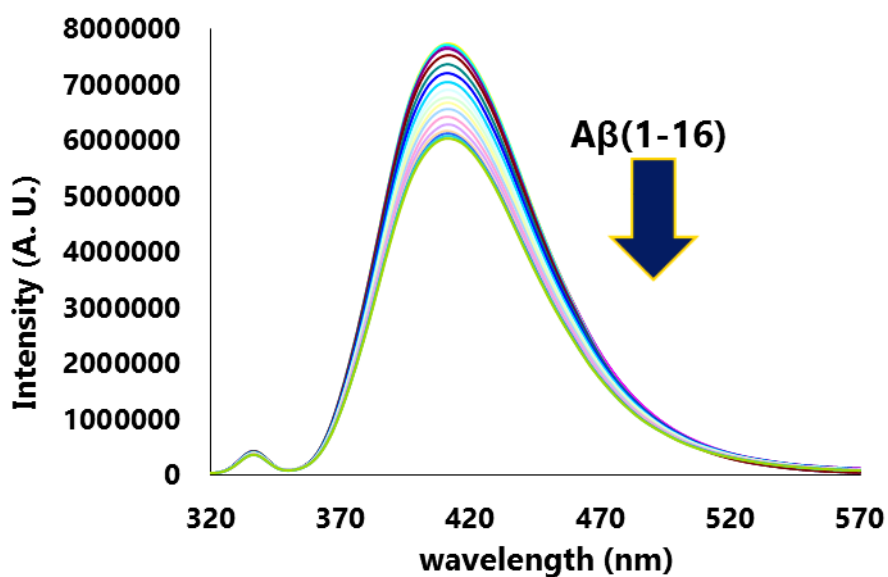
**Figure S3.48:** Fluorescence spectra of a 10  $\mu\text{M}$  Cu(II)-HK<sup>c</sup>H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of A $\beta$ (1-16).  $\lambda_{\text{exc}}$  = 300 nm.



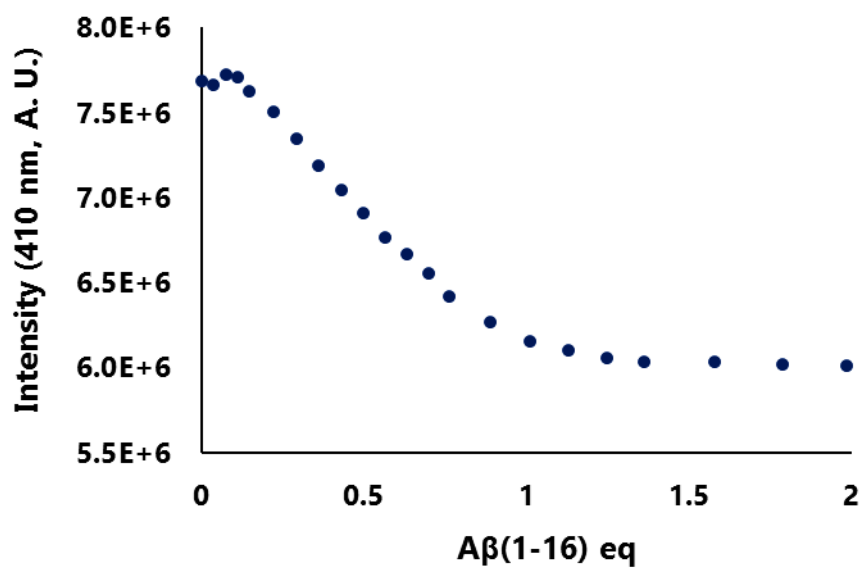
**Figure S3.49:** Fluorescence spectra of a 10  $\mu\text{M}$  Cu(II)-A $\beta$ (1-16) solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of AcHK<sup>c</sup>H.  $\lambda_{\text{exc}}$  = 275 nm.



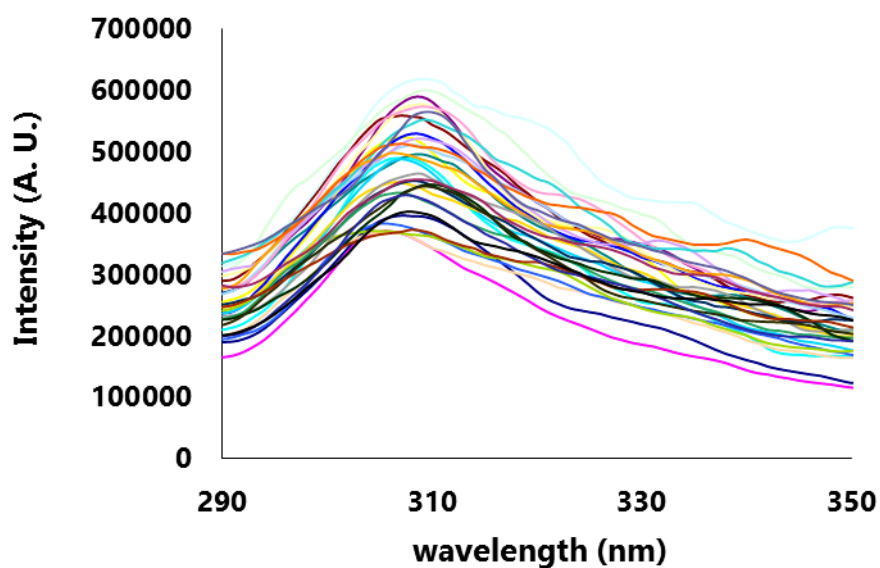
**Figure S3.50:** Fluorescence spectra of a 10  $\mu\text{M}$  Cu(II)-AChK<sup>C</sup>H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of A $\beta$ (1-16).  $\lambda_{\text{exc}}$  = 300 nm.



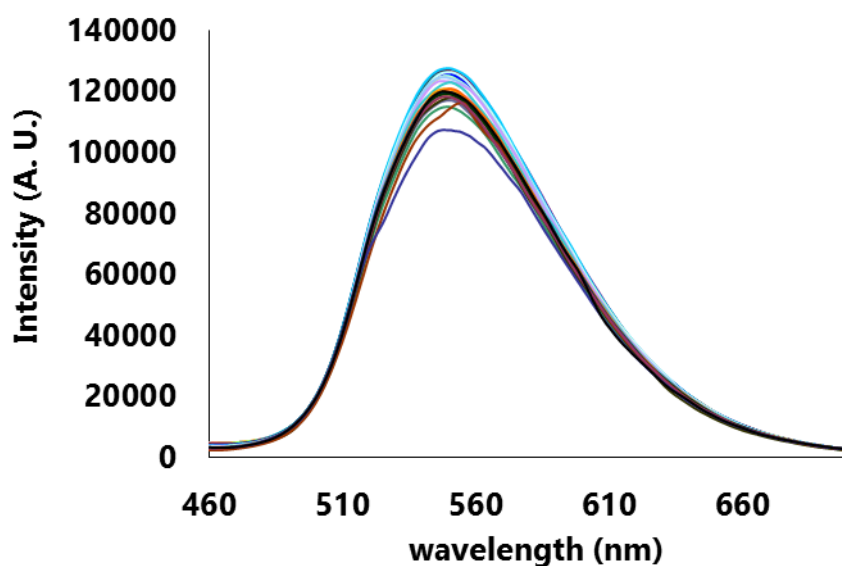
**Figure S3.51:** Fluorescence spectra of a 10  $\mu\text{M}$  AChK<sup>C</sup>H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of A $\beta$ (1-16).  $\lambda_{\text{exc}}$  = 300 nm.



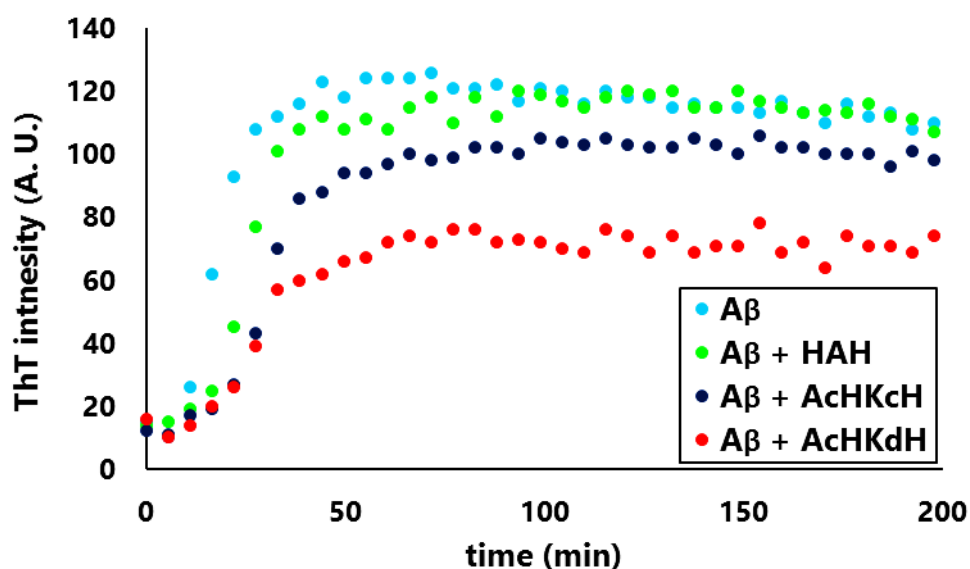
**Figure S3.52:** Fluorescent intensity at 410 nm of a 10  $\mu$ M ACHK<sup>d</sup>H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of A $\beta$ (1-16).  $\lambda_{exc}$  = 300 nm.



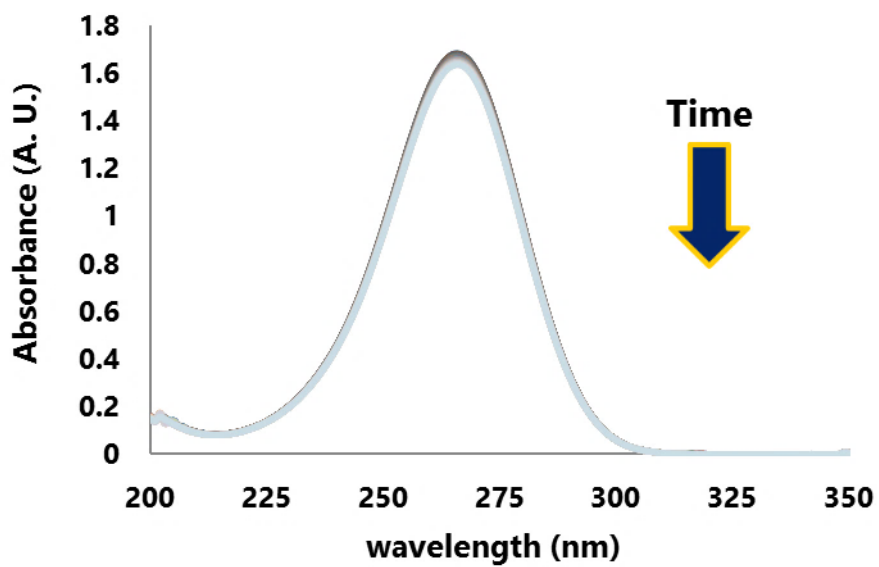
**Figure S3.53:** Fluorescence spectra of a 10  $\mu$ M Cu(II)-A $\beta$ (1-16) solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of ACHK<sup>d</sup>H.  $\lambda_{exc}$  = 275 nm.



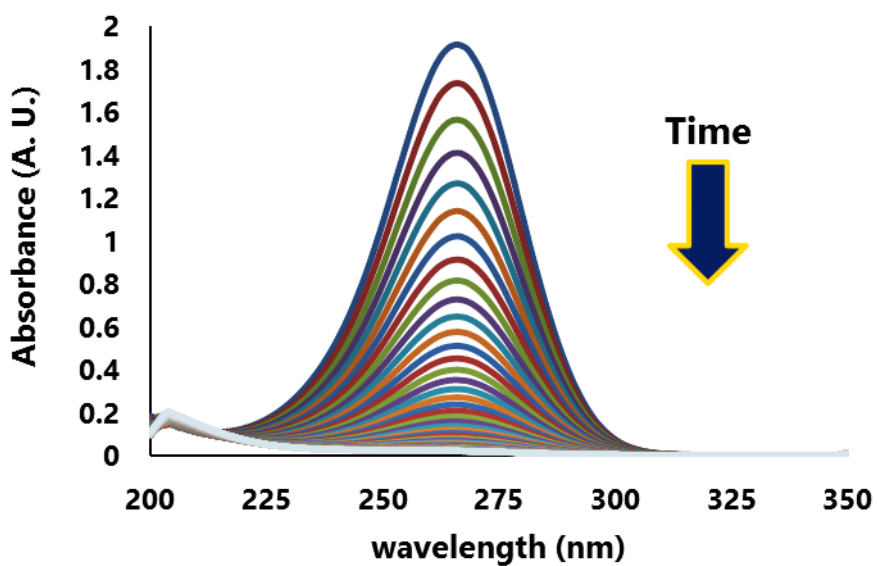
**Figure S3.54:** Fluorescence spectra of a 10  $\mu\text{M}$  Cu(II)-AcHK<sup>d</sup>H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of A $\beta$ (1-16).  $\lambda_{\text{exc}} = 441 \text{ nm}$ .



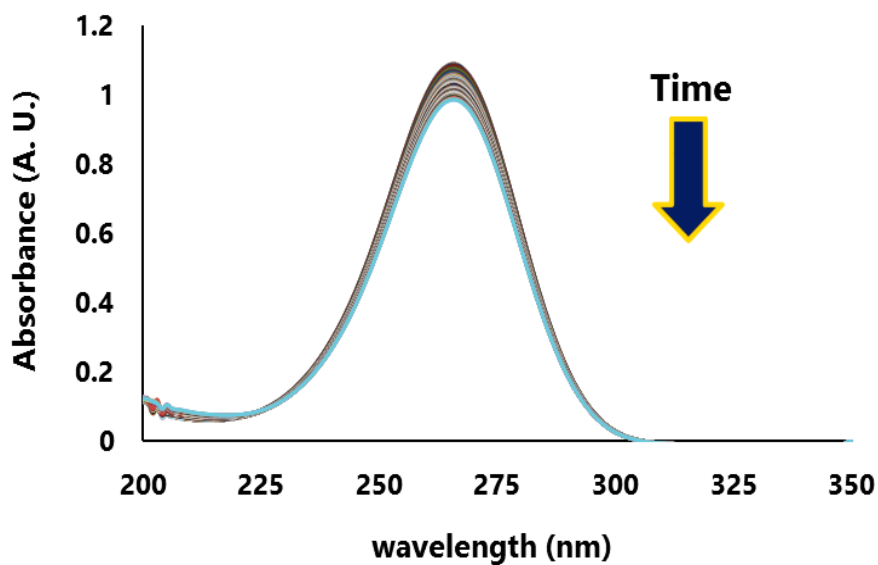
**Figure S3.55:** Aggregation of 20  $\mu\text{M}$  A $\beta$ (1-40) (light-blue dots) and 20  $\mu\text{M}$  A $\beta$ (1-40) in presence 2 eq of HAH (green dots), AcHK<sup>c</sup>H (dark-blue dots) or AcHK<sup>d</sup>H (red dots). A $\beta$ (1-40) aggregation was followed by 25  $\mu\text{M}$  ThT (25  $\mu\text{M}$ ) fluorescence emission. 1X PBS (pH 7.4).



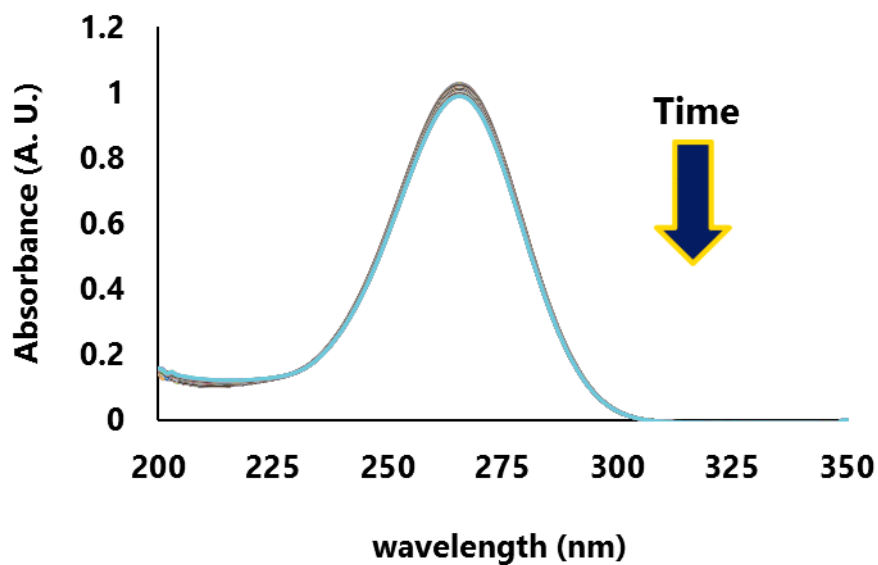
**Figure S3.56:** UV-Vis spectra of a 100  $\mu\text{M}$  ascorbate solution in 100 mM phosphate buffer (pH 7.4), registered during a period of 30 min.



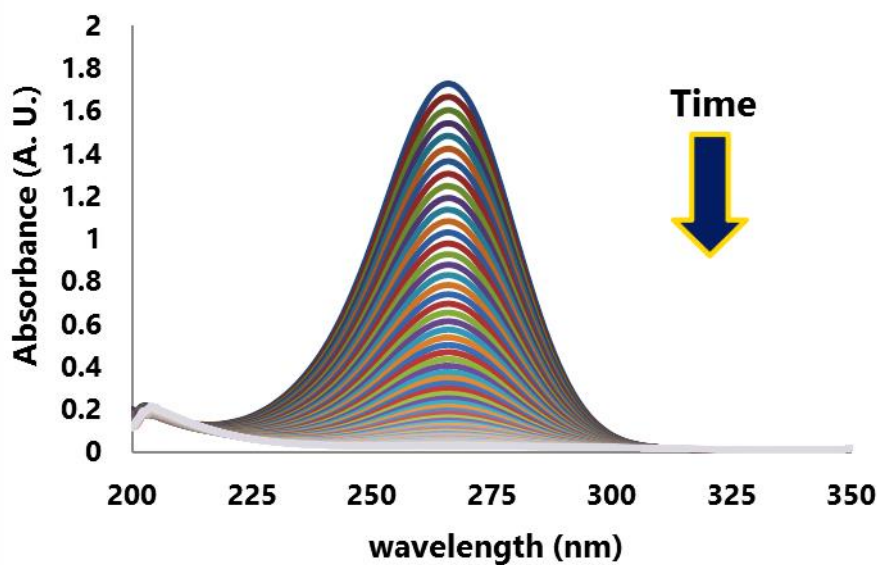
**Figure S3.57:** UV-Vis spectra of a 100  $\mu\text{M}$  ascorbate solution in 100 mM phosphate buffer (pH 7.4) in the presence of 1%  $\text{CuCl}_2$ , registered during a period of 30 min.



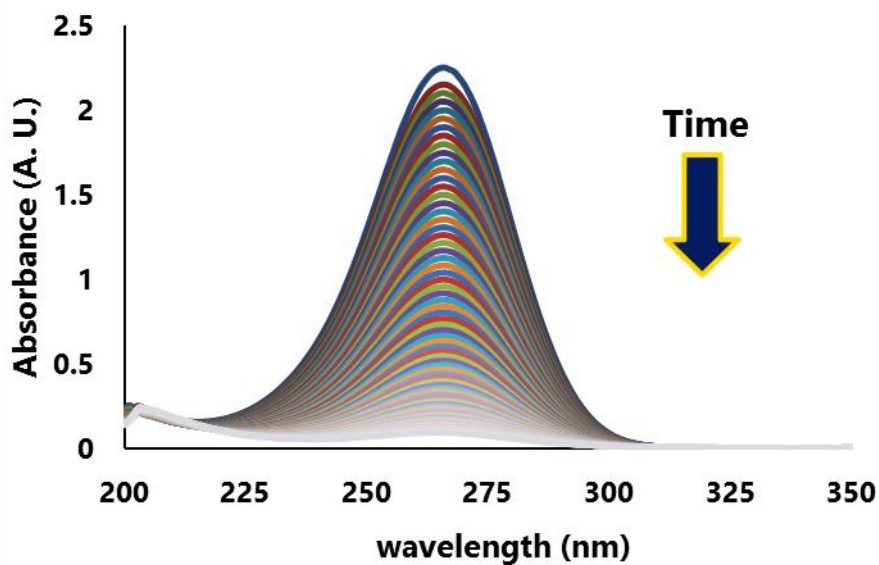
**Figure S3.58:** UV-Vis spectra of a 100  $\mu\text{M}$  ascorbate solution in 100 mM phosphate buffer (pH 7.4) in the presence of 1%  $\text{CuCl}_2$  and 1.1% HAH, registered during a period of 30 min.



**Figure S3.59:** UV-Vis spectra of a 100  $\mu\text{M}$  ascorbate solution in 100 mM phosphate buffer (pH 7.4) in the presence of 1%  $\text{CuCl}_2$  and 1.1% HWH, registered during a period of 30 min.

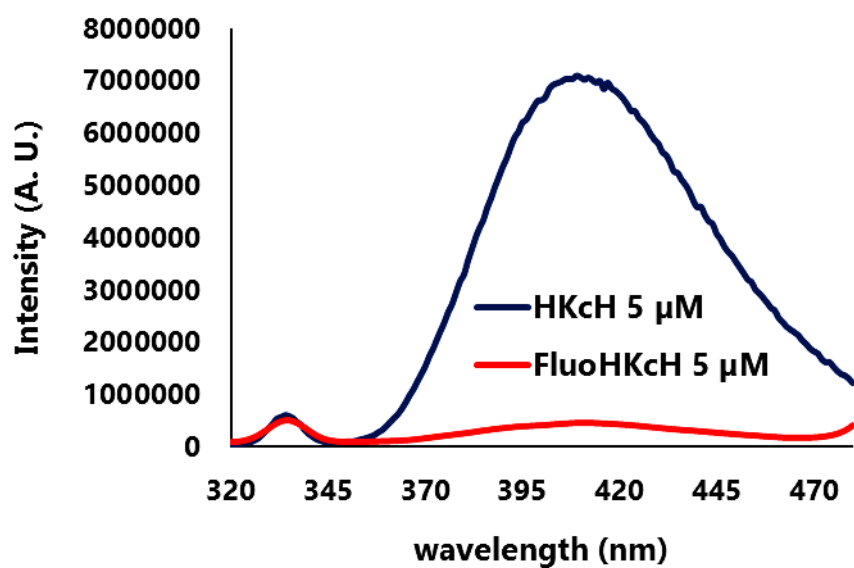


**Figure S3.60:** UV-Vis spectra of a 100 μM ascorbate solution in 100 mM phosphate buffer (pH 7.4) in the presence of 1% CuCl<sub>2</sub> and 1.1% AcHK<sup>d</sup>H, registered during a period of 30 min.

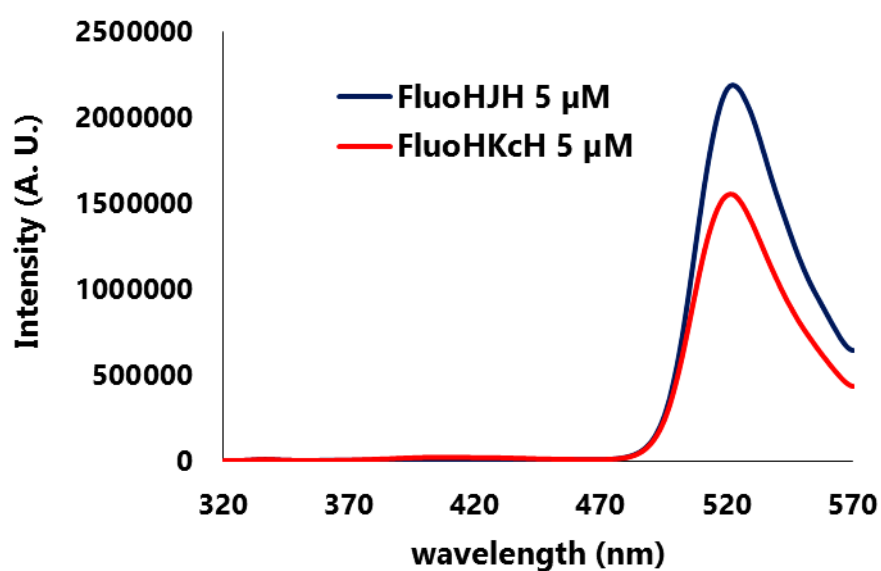


**Figure S3.61:** UV-Vis spectra of a 100 μM ascorbate solution in 100 mM phosphate buffer (pH 7.4) in the presence of 1% CuCl<sub>2</sub> and 1.1% AcHK<sup>d</sup>H, registered during a period of 30 min.

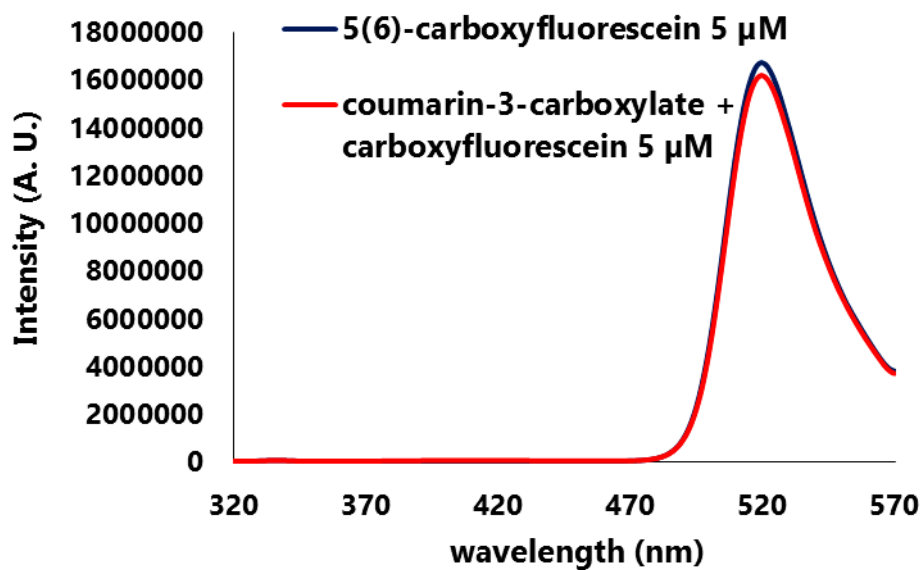




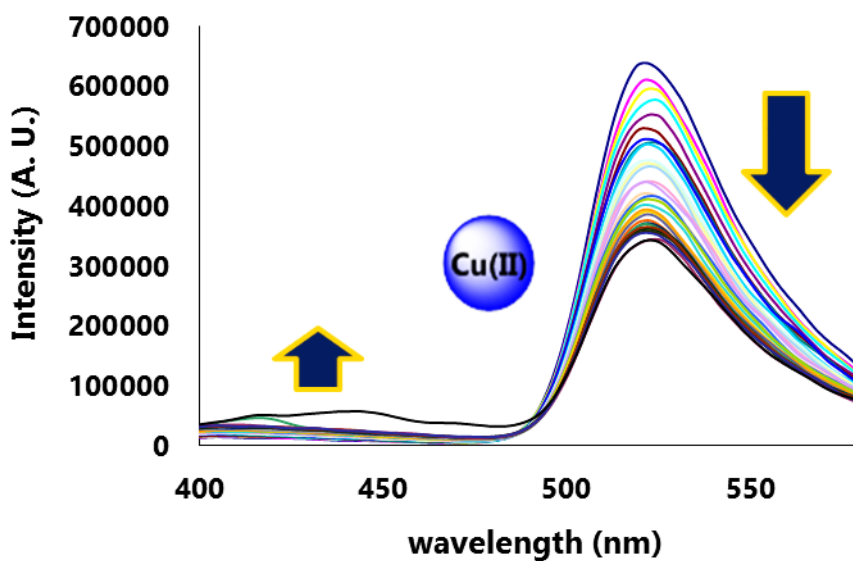
**Figure S3.62:** Fluorescence spectra of 5  $\mu\text{M}$  FluoHK<sup>c</sup>H (red line) and 5  $\mu\text{M}$  HK<sup>c</sup>H (blue line) solutions in 10 mM HEPES (pH 7.4).  $\lambda_{\text{exc}} = 300$  nm.



**Figure S3.63:** Fluorescence spectra of 5  $\mu\text{M}$  FluoHK<sup>c</sup>H (red line) and 5  $\mu\text{M}$  FluoHJH (blue line) solutions in 10 mM HEPES (pH 7.4).  $\lambda_{\text{exc}} = 300$  nm.



**Figure S3.64:** Fluorescence spectra of solutions containing 5 μM coumarin-3-carboxylate (**blue line**) and 5 μM coumarin-3-carboxylate in the presence of 1 eq of 5(6)-carboxyfluorescein (**red line**) in 10 mM HEPES (pH 7.4).  $\lambda_{exc} = 300$  nm.



**Figure S3.65:** Fluorescence spectra of a 10 μM FluoHK<sup>C</sup>H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of CuCl<sub>2</sub>.  $\lambda_{exc} = 300$  nm.