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

Guillem Vázquez Bigas

Chapter 3: Chelation and detection of Cu(II)

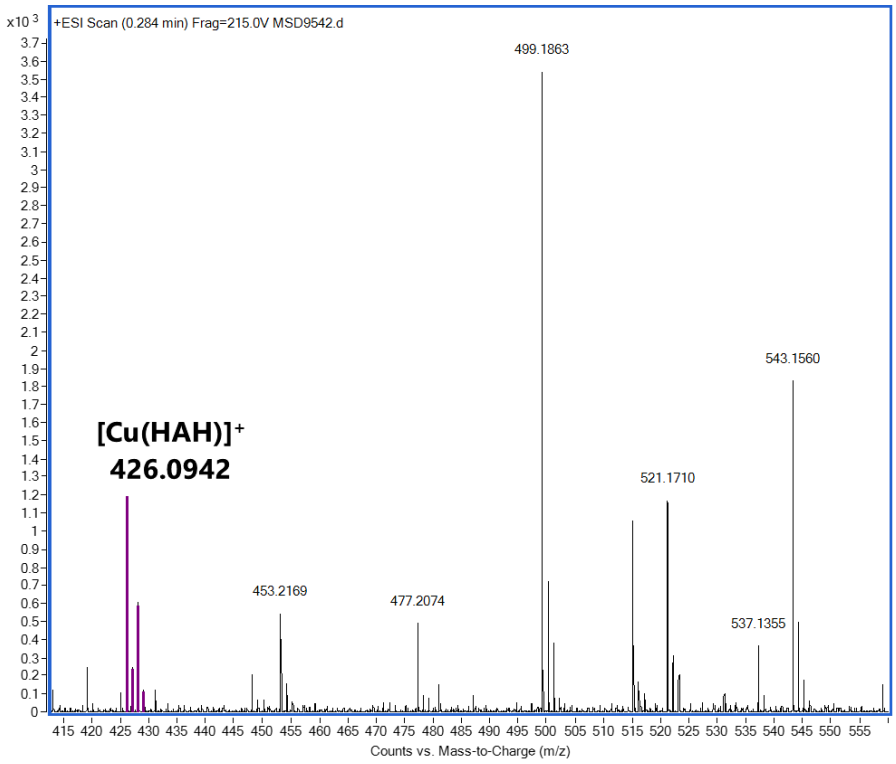

Figure S3.1: Mass spectrum of a 1:2 HAH-Cu(II) solution in Milli-Q H_2O (pH 7.4).

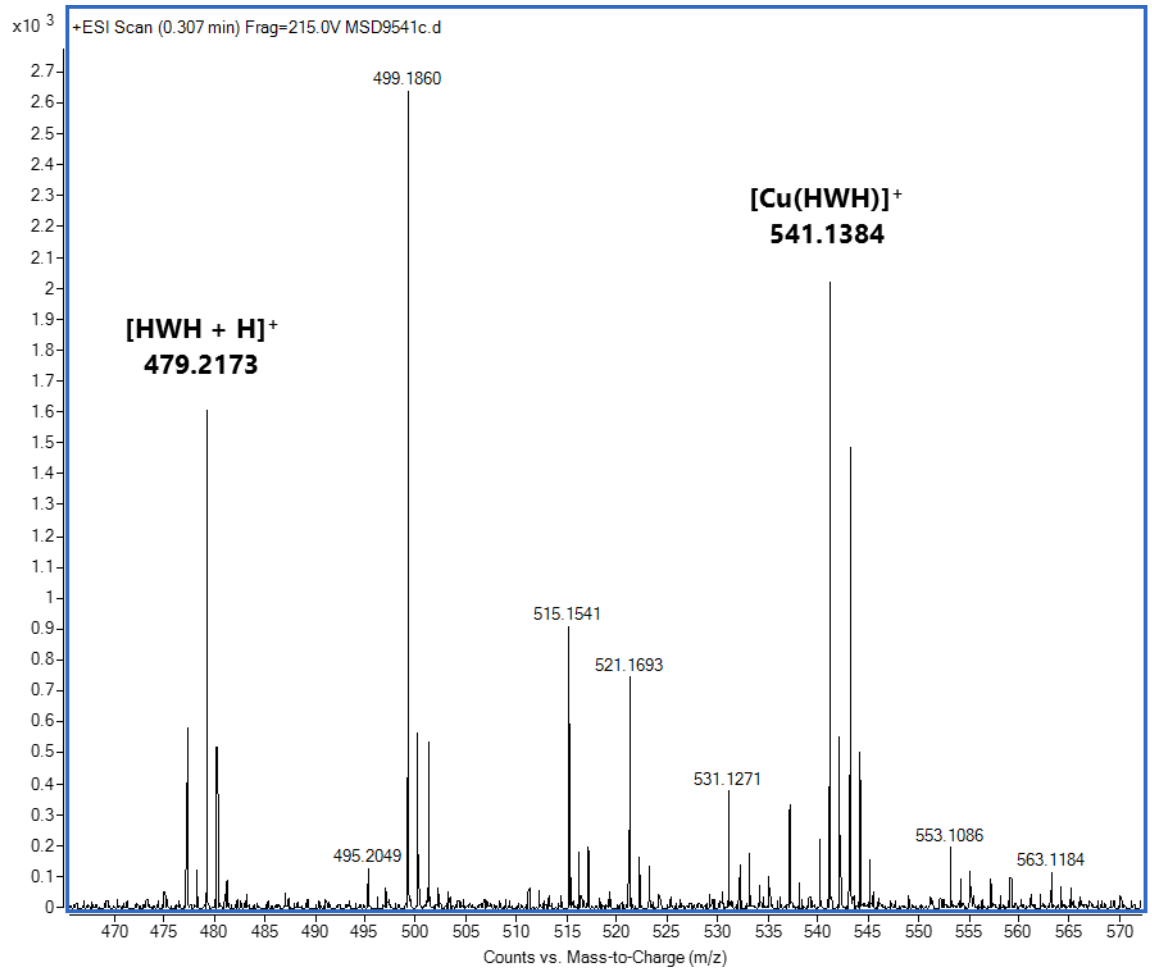

Figure S3.2: Mass spectrum of a 1:2 HWH-Cu(II) solution in Milli-Q H_2O (pH 7.4).

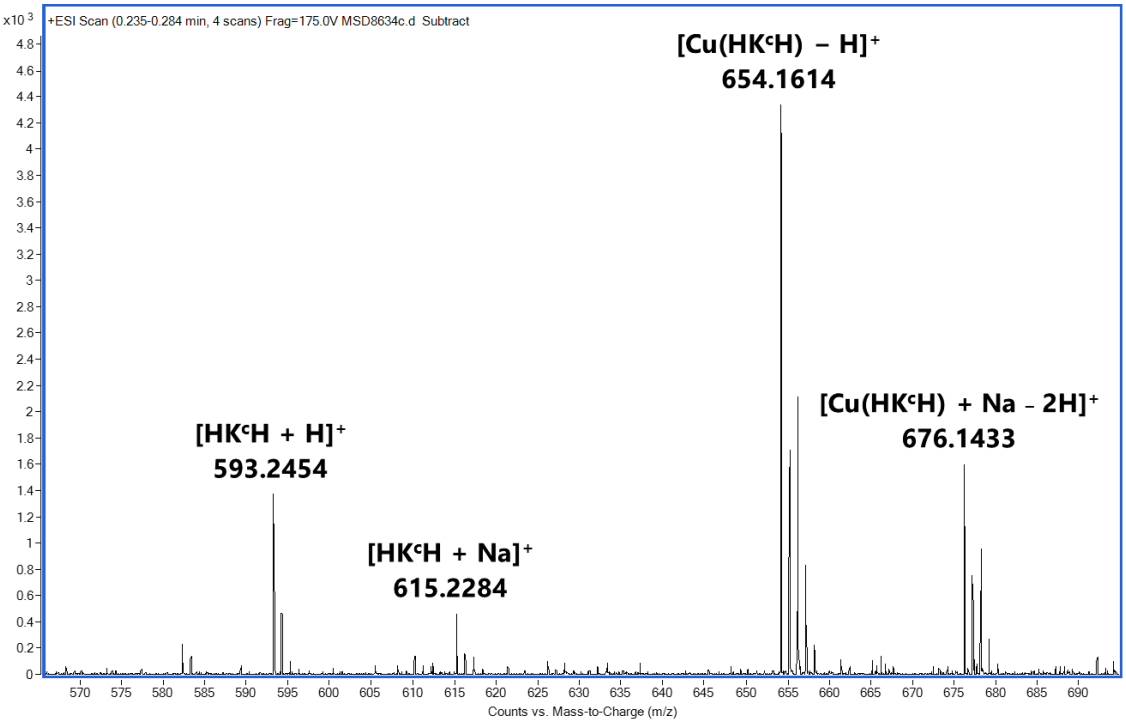

Figure S3.3: Mass spectrum of a 1:2 HK^cH-Cu(II) solution in Milli-Q H_2O (pH 7.4).

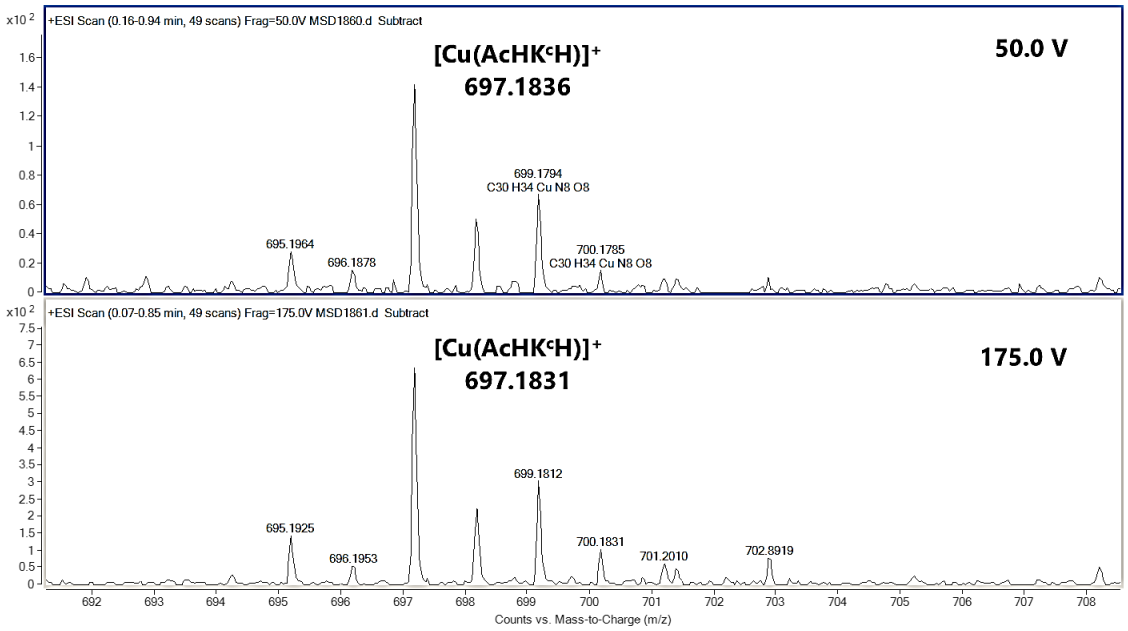

Figure S3.4: Mass spectrum of a 1:2 AcHK^{c}H-Cu(II) solution in Milli-Q H_2O (pH 7.4).

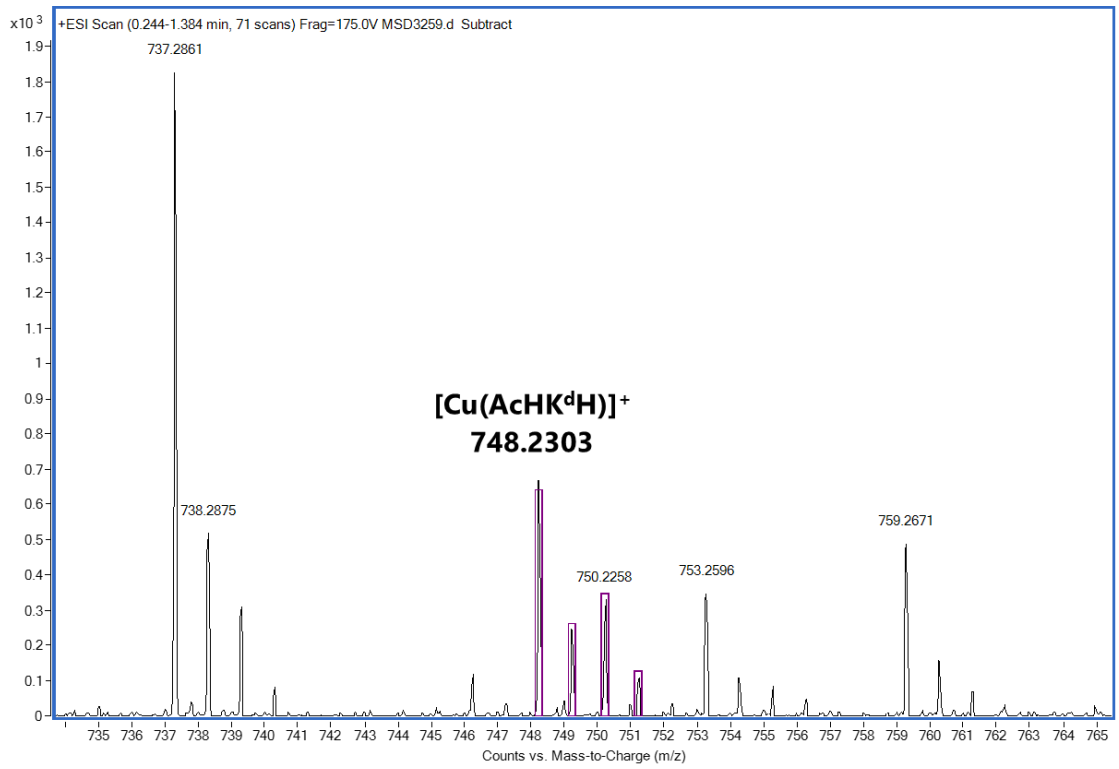

Figure S3.5: Mass spectrum of a 1:2 AcHK^{d}H-Cu(II) solution in Milli-Q H_2O (pH 7.4).

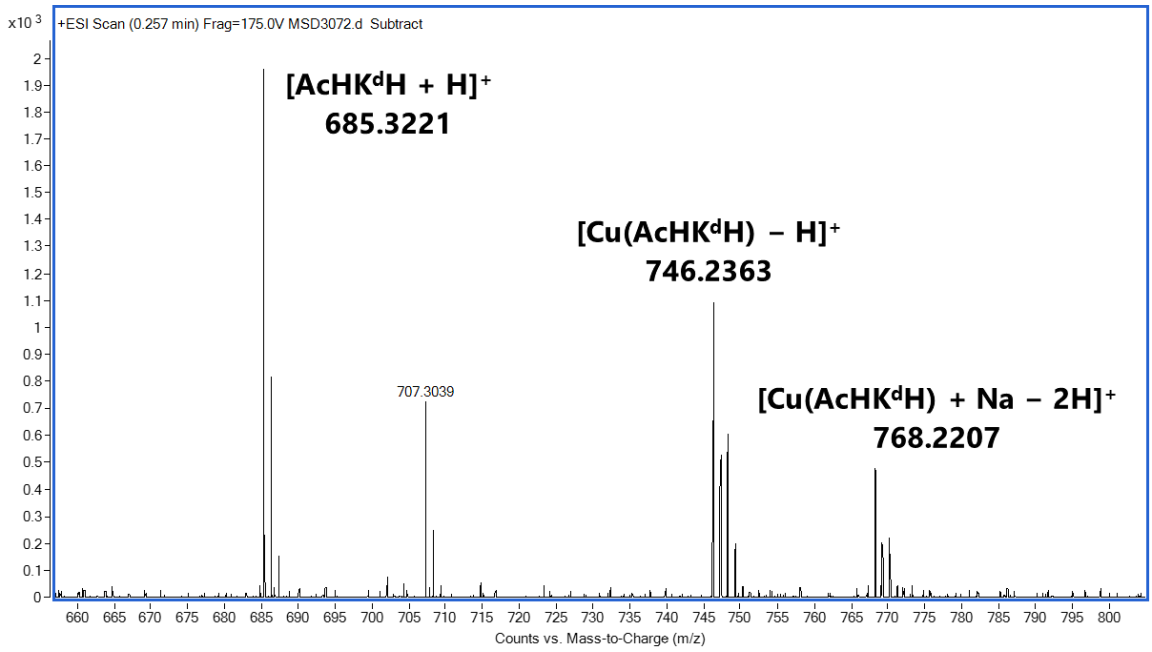

Figure S3.6: Mass spectrum of a 1:2 AcHK^{d}H-NH_2-Cu(II) solution in Milli-Q H_2O (pH 7.4).

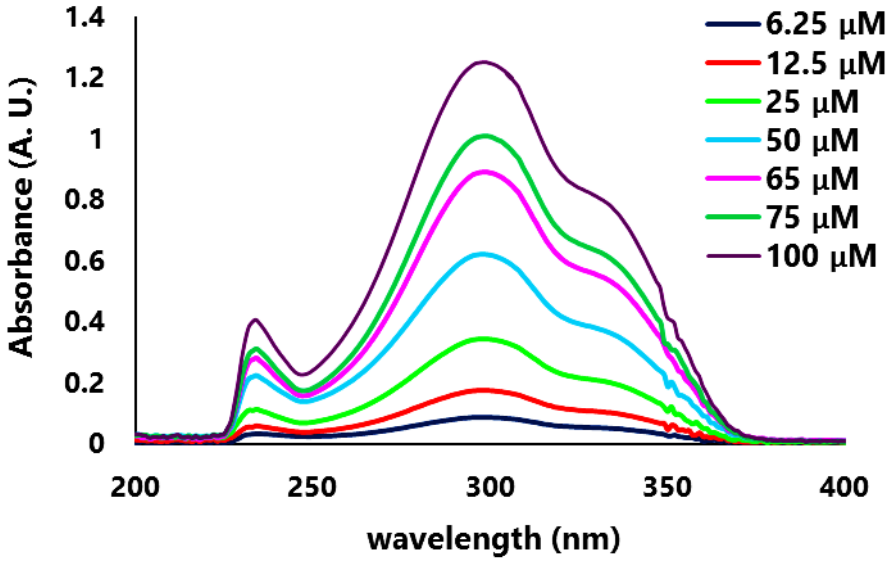

Figure S3.7: UV-Vis spectra of H-Lys(Coum)-OH solutions (concentrations 6.25-100 µM) in 100 mM HEPES (pH 7.4).

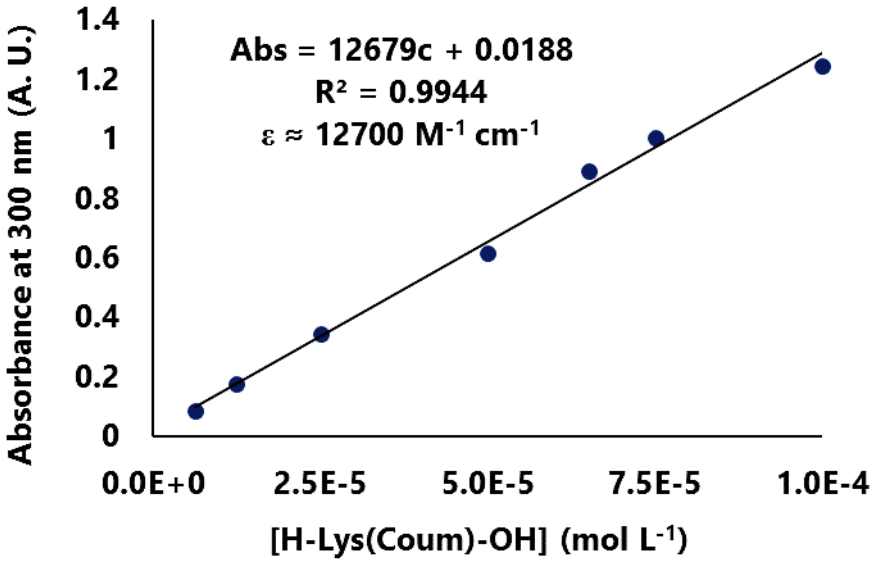

Figure S3.8: Absorbance at 300 nm of H-Lys(Coum)-OH solutions (concentrations 6.25-100 μM) in 100 mM HEPES (pH 7.4).

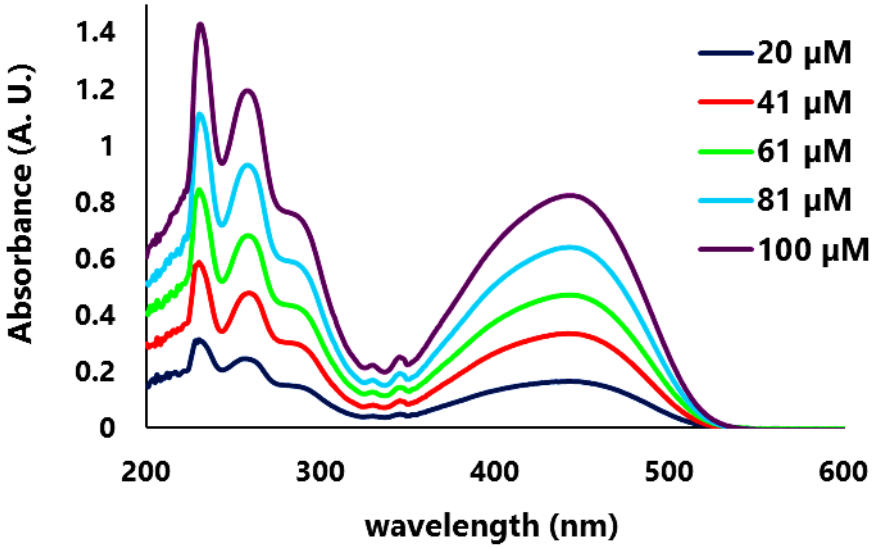

Figure S3.9: UV-Vis spectra of Boc-Lys(4DMN)-OH solutions (concentrations 20-100 μM) in 100 mM HEPES (pH 7.4).

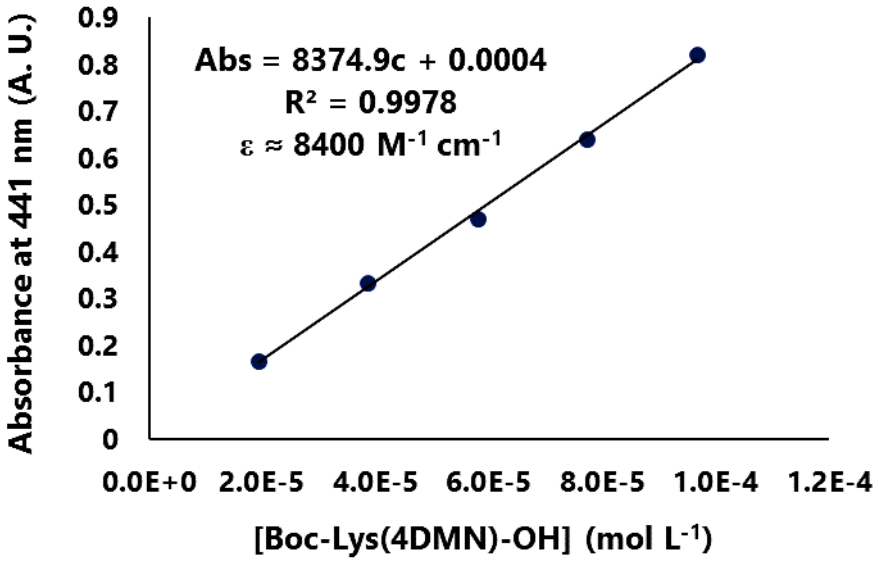

Figure S3.10: Absorbance at 441 nm of Boc-Lys(4DMN)-OH solutions (concentrations 20-100 μM) in 100 mM HEPES (pH 7.4).

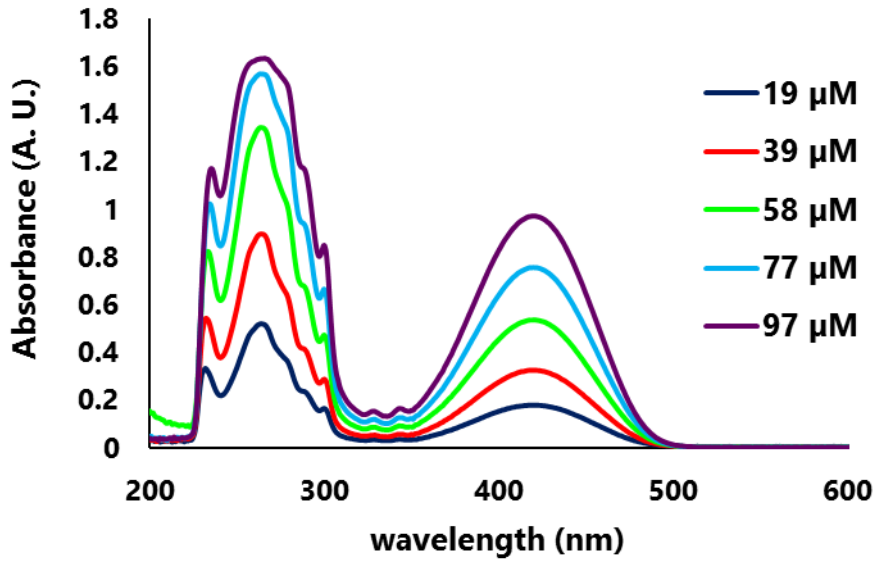

Figure S3.11: UV-Vis spectra of Boc-Lys(4DMN)-OH solutions (concentrations 19-97 μM) in DCM.

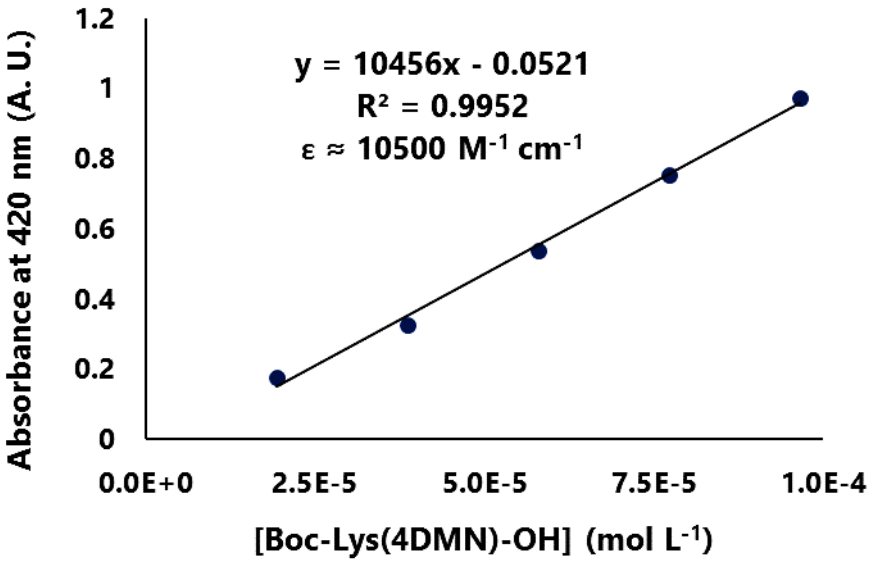

Figure S3.12: Absorbance at 420 nm of Boc-Lys(4DMN)-OH solutions (concentrations 19-97 μM) in DCM.

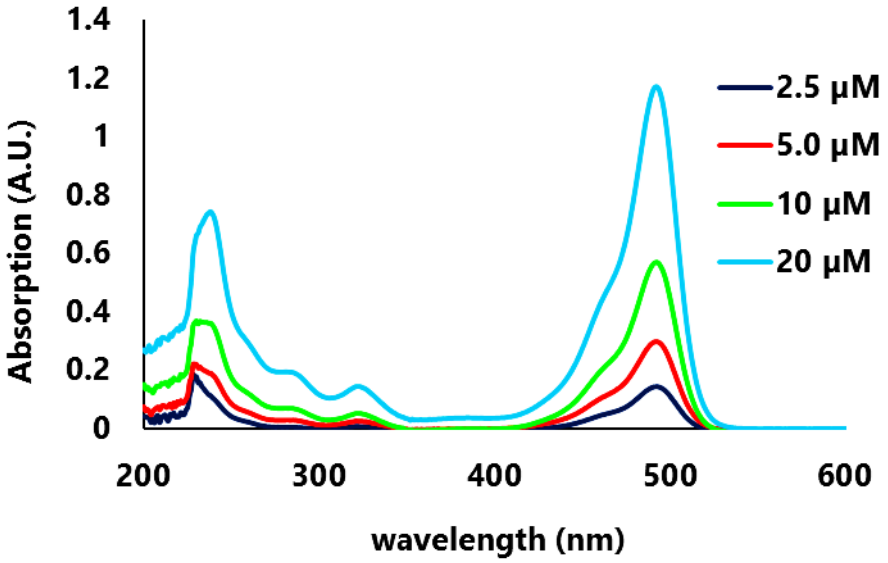

Figure S3.13: UV-Vis spectra of 5(6)-carboxyfluorescein solutions (concentrations 2.5-20 μM) in 100 mM HEPES (pH 7.4).

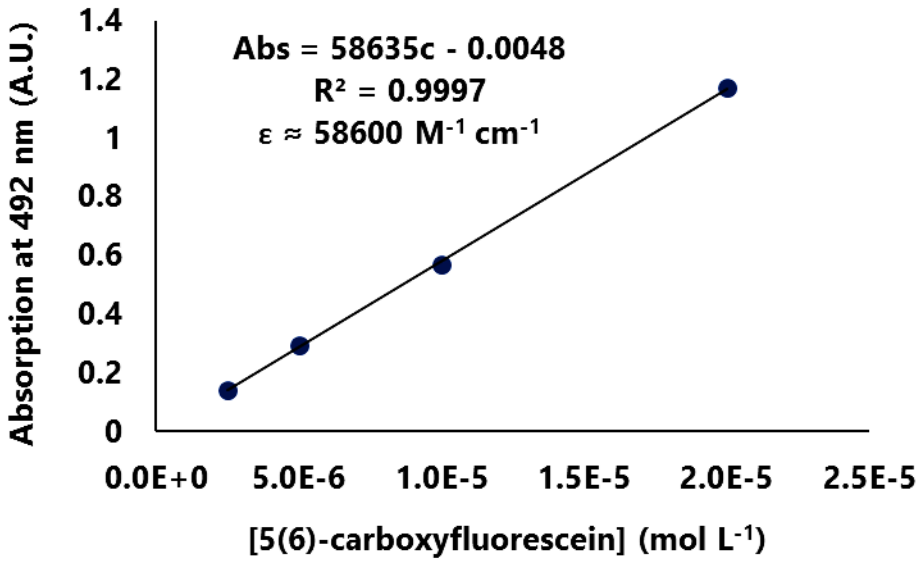

Figure S3.14: Absorbance at 492 nm of 5(6)-carboxyfluorescein solutions (concentrations 2.5-20 μM) in 100 mM HEPES (pH 7.4).

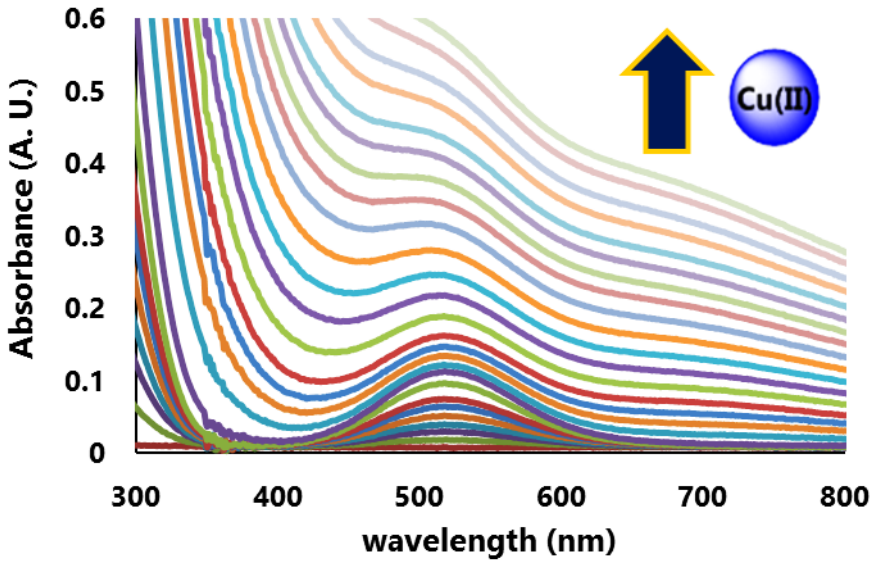

Figure S3.15: UV-Vis spectra of a 1 mM HAH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$.

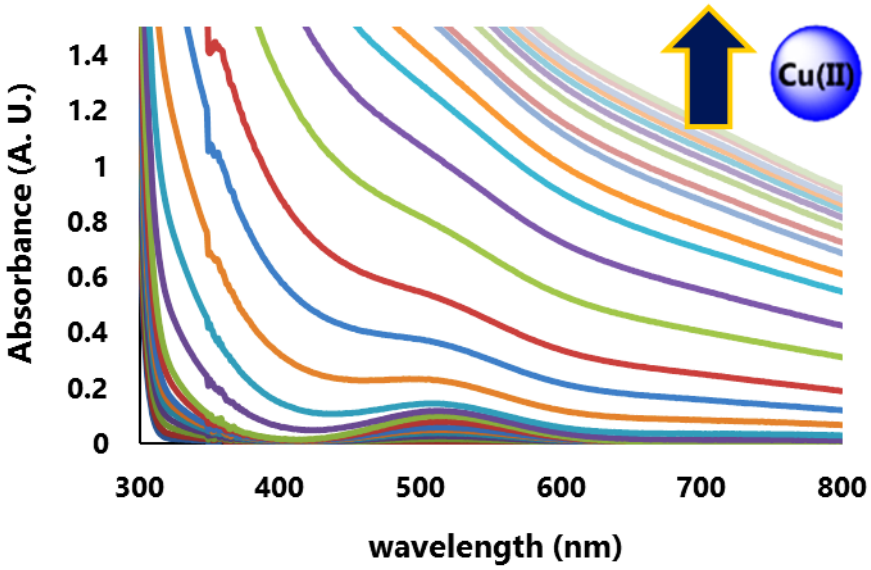

Figure S3.16: UV-Vis spectra of a 1 mM HWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$.

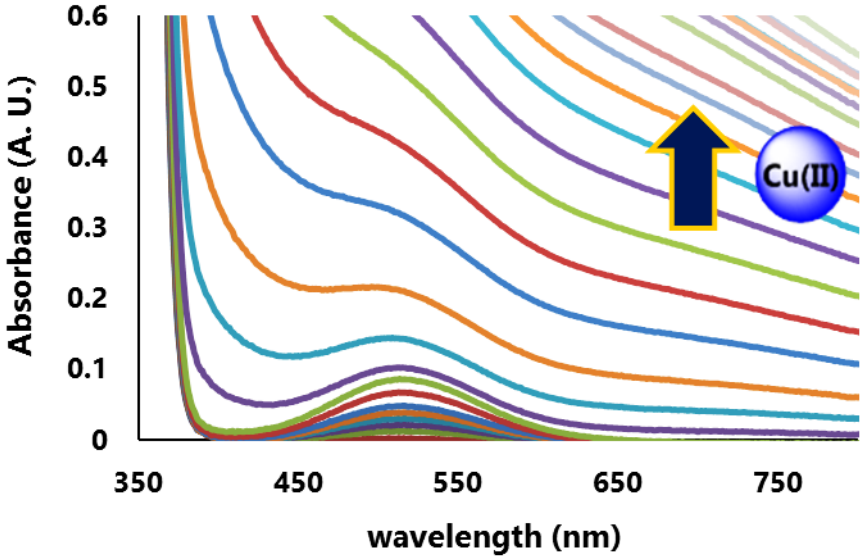

Figure S3.17: UV-Vis spectra of a 1 mM HK^{c}H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$.

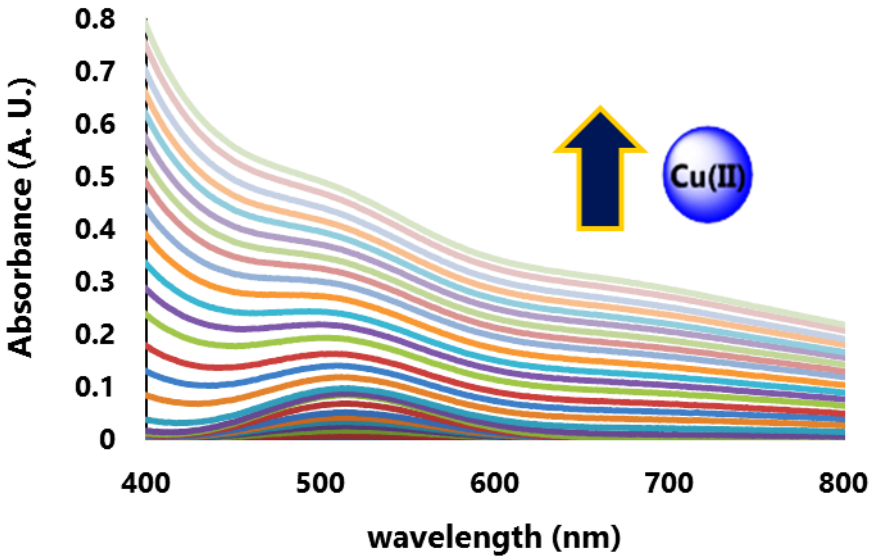

Figure S3.18: UV-Vis spectra of a 1 mM GWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$.

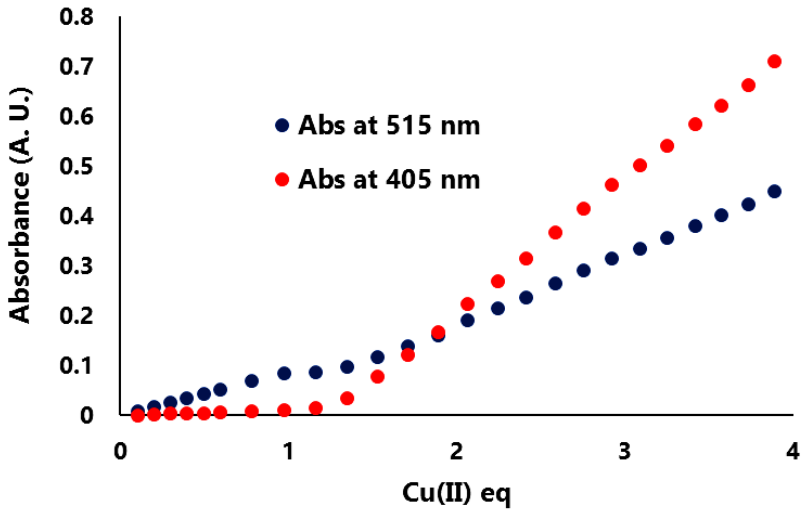

Figure S3.19: Absorbance values (at 405 nm, **red dots**; and 515 nm, **blue dots**) of a 1 mM GWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$.

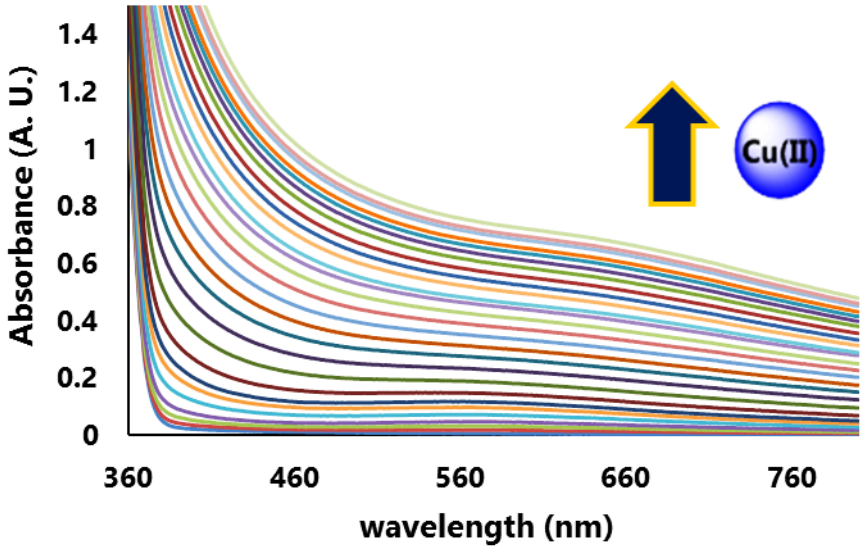

Figure S3.20: UV-Vis spectra of a 1 mM AcHK^{c}H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$.

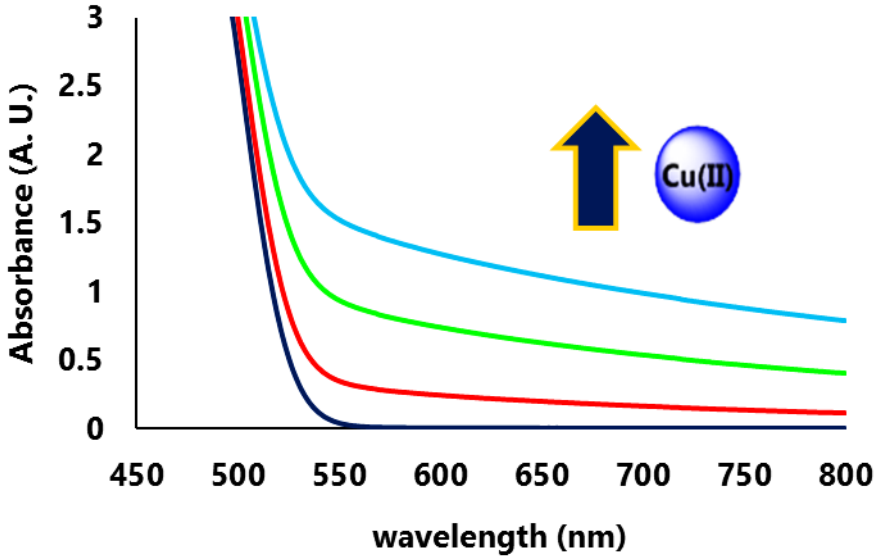

Figure S3.21: UV-Vis spectra of a 1 mM AcHK^{d}H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$.

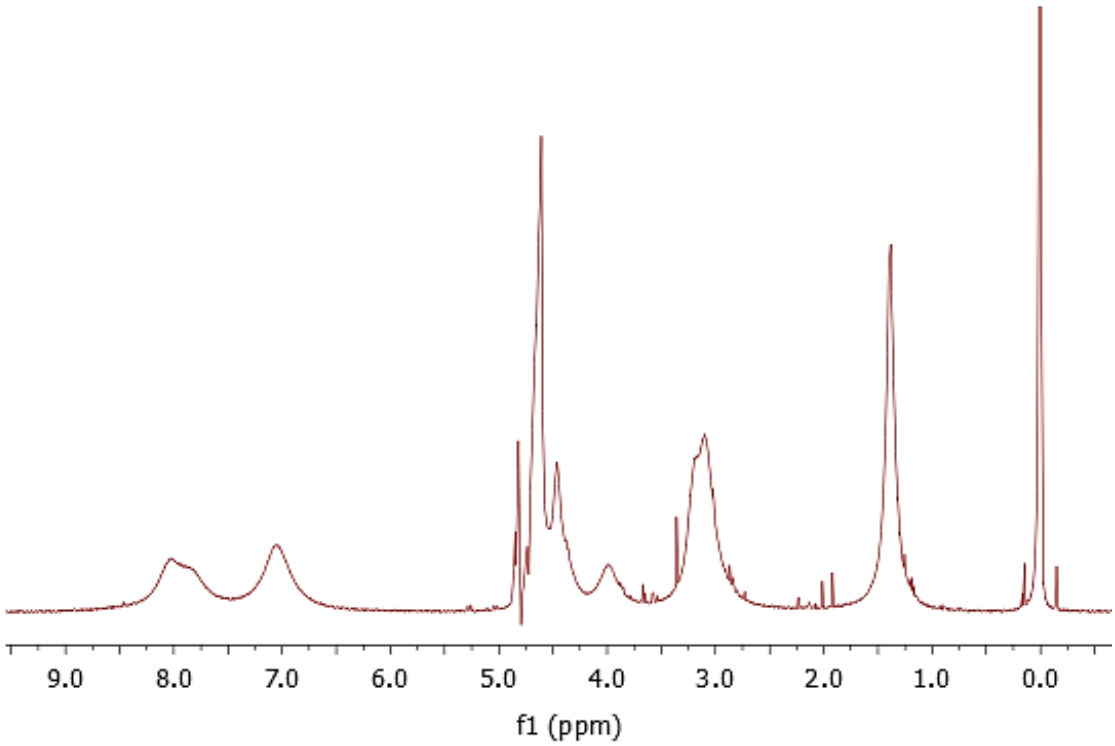

Figure S3.22: ^{1}H NMR spectrum of a 10 mM HAH solution in D_2O containing 1% $CuCl_2$ (pH 7.4).

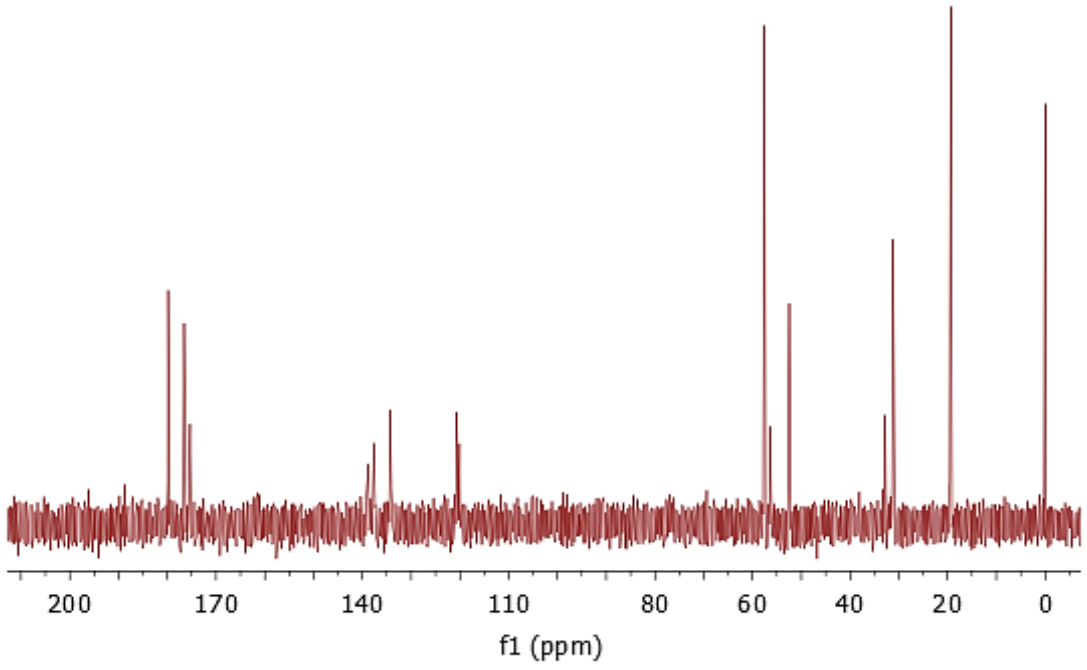

Figure S3.23: ^{13}C NMR spectrum of a 10 mM HAH solution in D_2O containing 1% $CuCl_2$ (pH 7.4).

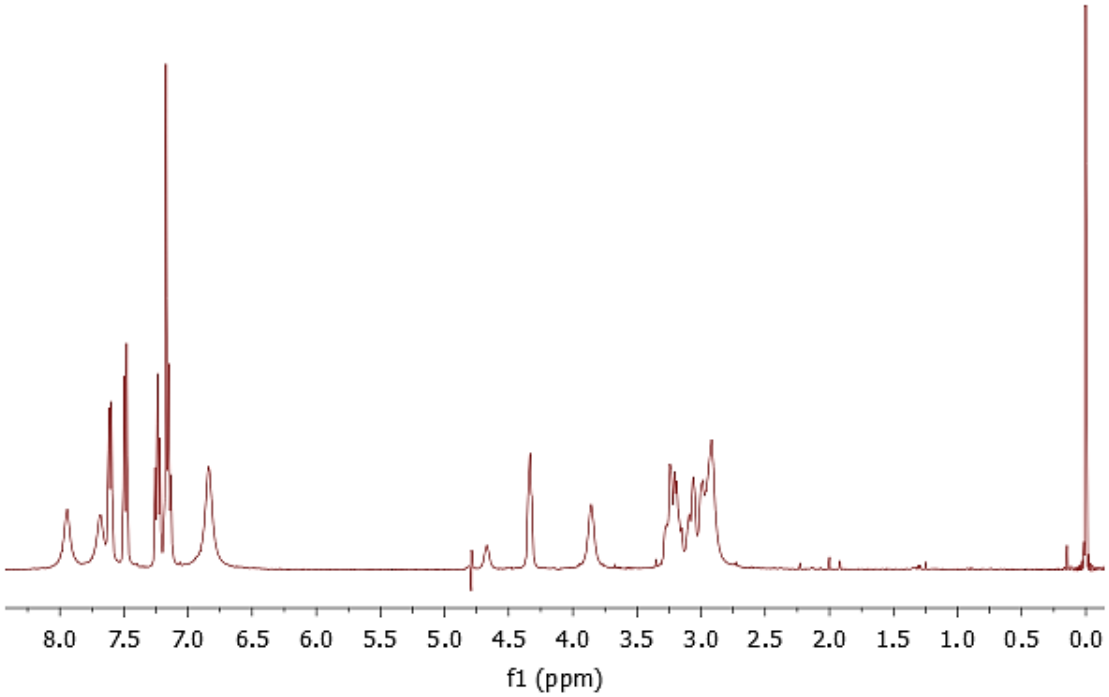

Figure S3.24: ^{1}H NMR spectrum of a 10 mM HWH solution in D_2O containing 1% $CuCl_2$ (pH 7.4)**.**

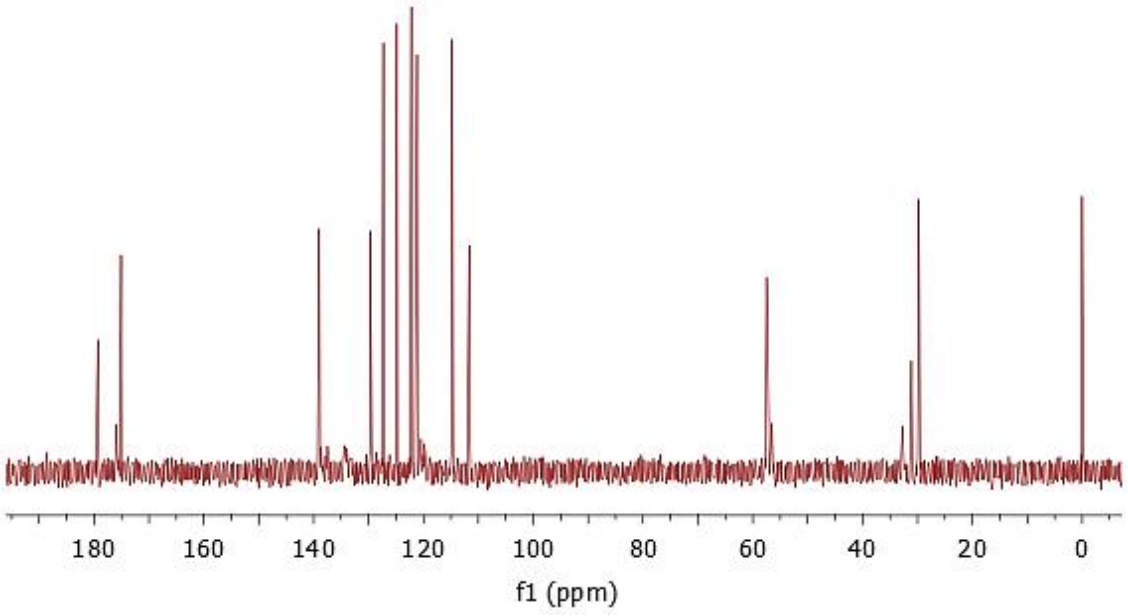

Figure S3.25: ^{13}C NMR spectrum of a 10 mM HWH solution in D_2O containing 1% $CuCl_2$ (pH 7.4)**.**

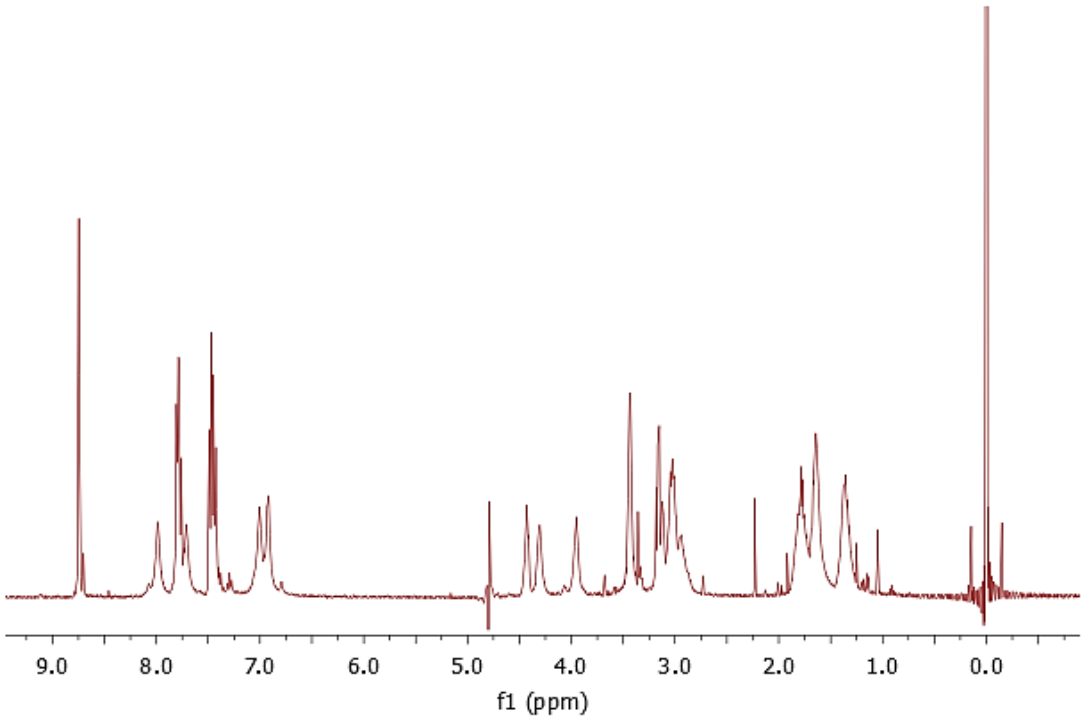

Figure S3.26: ^{1}H NMR spectrum of a 10 mM HK^{c}H solution in D_2O containing 1% $CuCl_2$ (pH 7.4)**.**

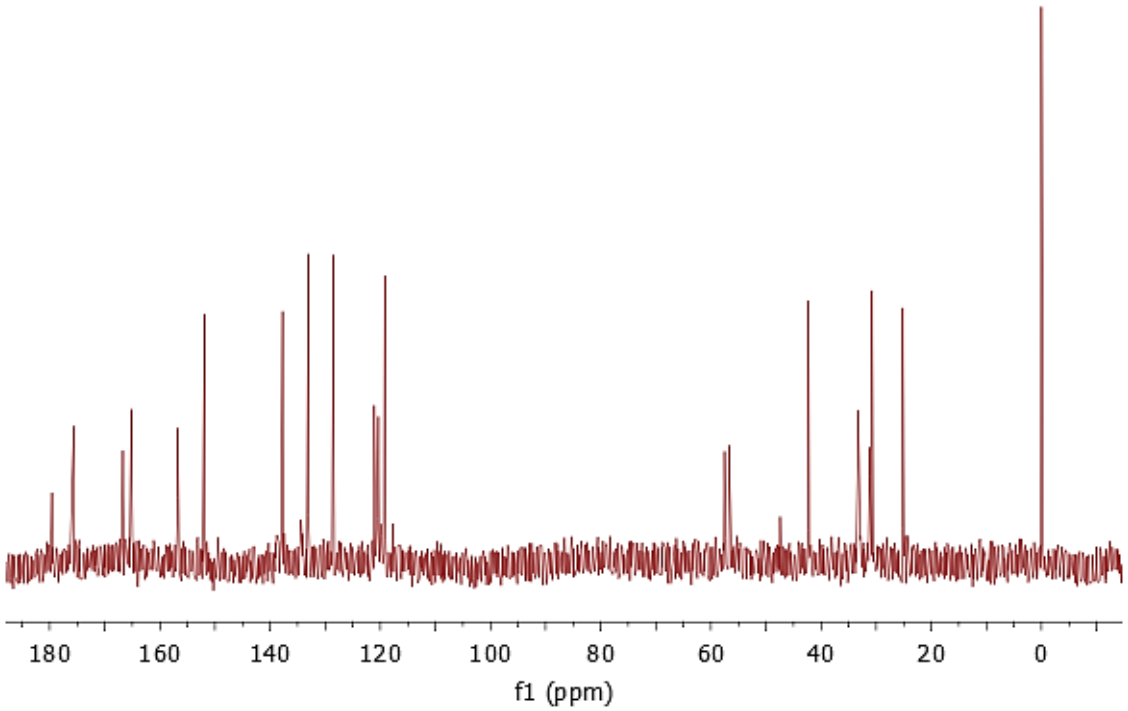

Figure S3.27: ^{13}C NMR spectrum of a 10 mM HK^{c}H solution in D_2O containing 1% $CuCl_2$ (pH 7.4)**.**

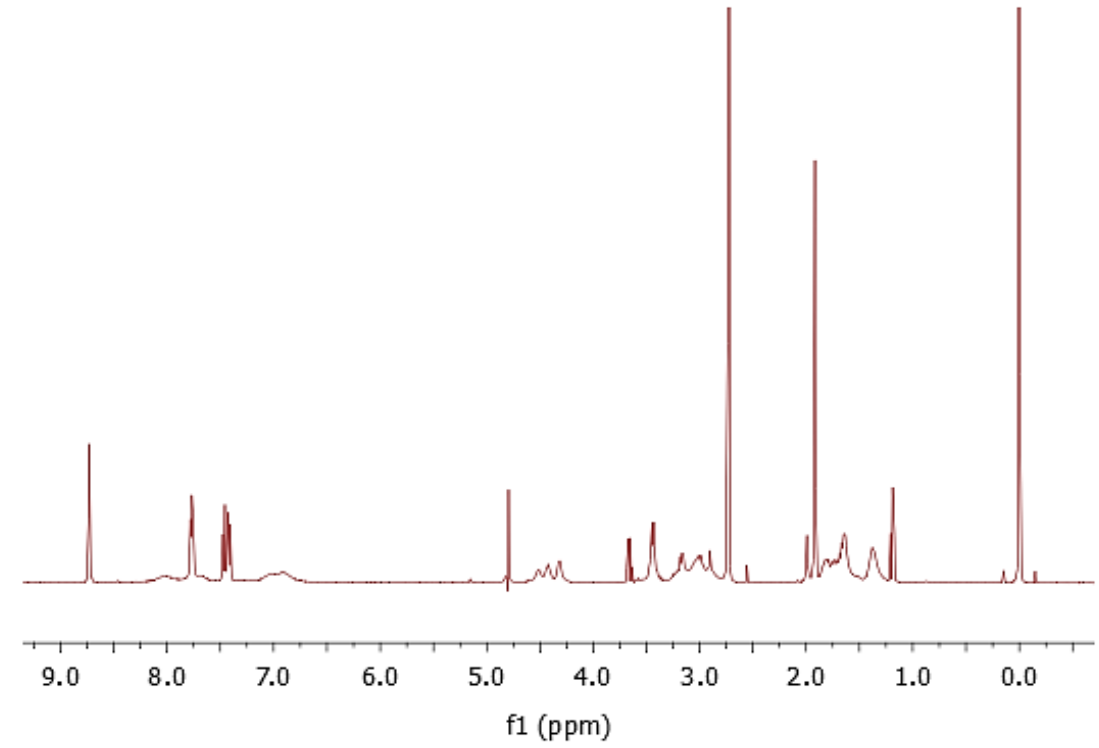

Figure S3.28: ^{1}H NMR spectrum of a 10 mM AcHK^{c}H solution in D_2O containing 1% $CuCl_2$ (pH 7.4)**.**

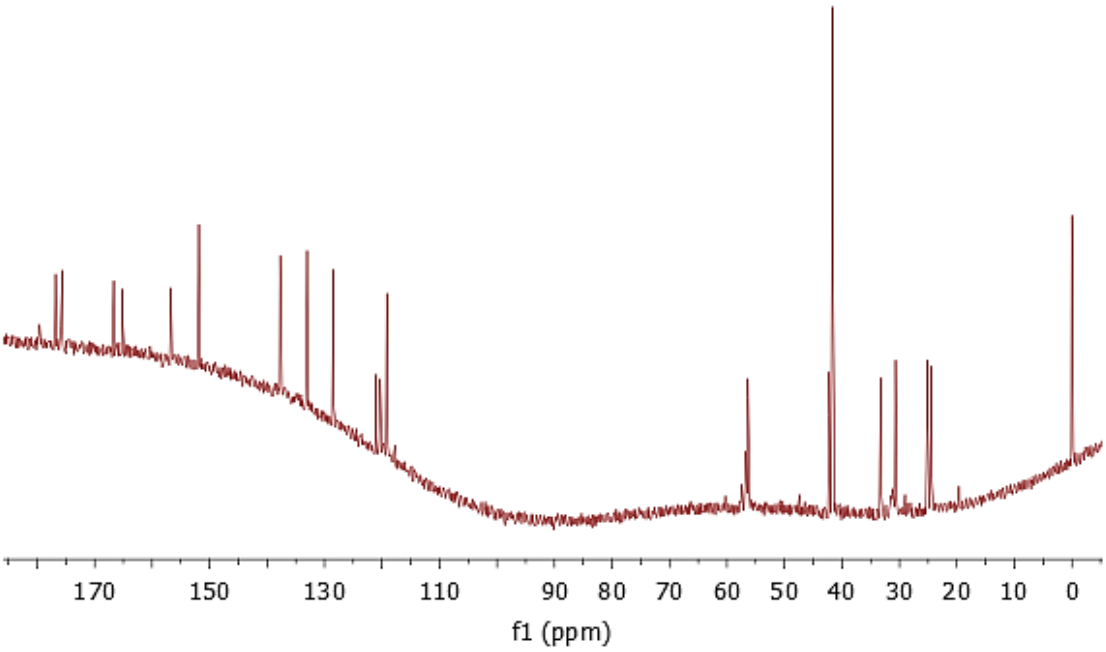

Figure S3.29: ^{13}C NMR spectrum of a 10 mM AcHK^{c}H solution in D_2O containing 1% $CuCl_2$ (pH 7.4)**.**

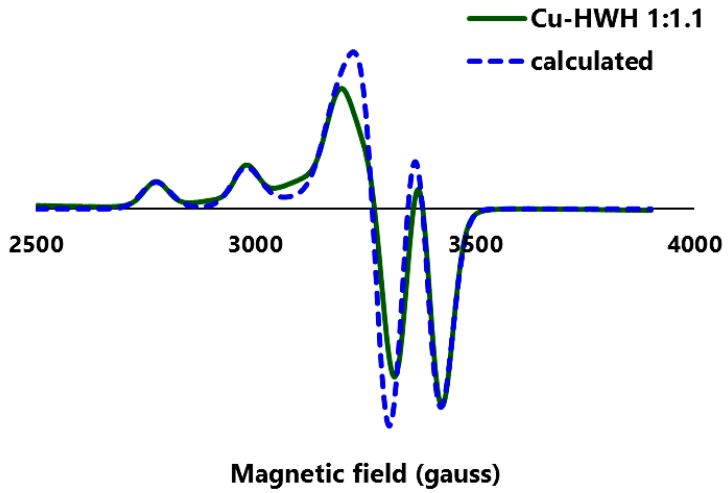

Figure S3.30: EPR spectra (obtained, **green line**; calculated, **dashed blue line**) of a 1:1.1 Cu(II)-HWH sample in 100 mM HEPES (pH 7.4) at 77 K.

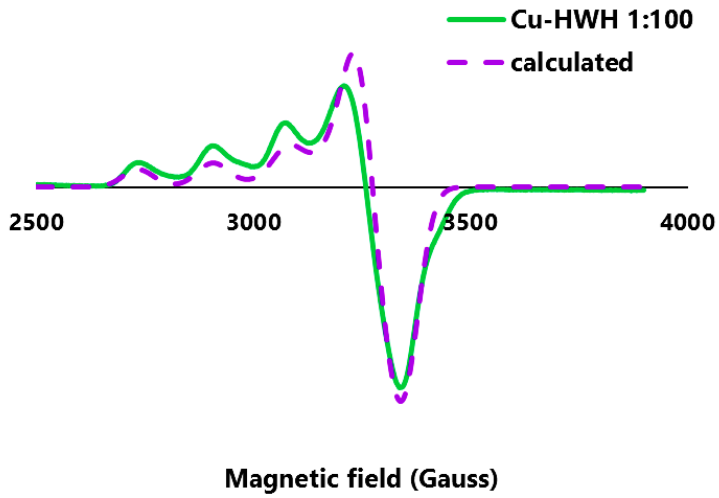

Figure S3.31: EPR spectra (obtained, **green line**; calculated, **dashed purple line**) of a 1:100 Cu(II)-HWH sample in 100 mM HEPES (pH 7.4) at 77 K.

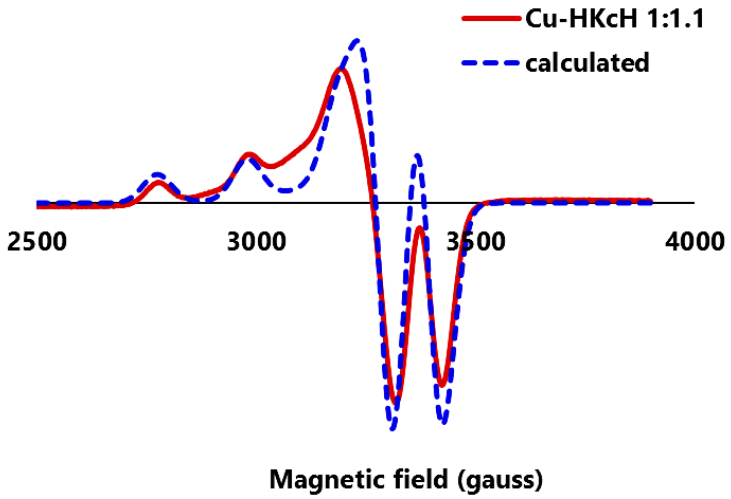

Figure S3.32: EPR spectra (obtained, **red line**; calculated, **dashed blue line**) of a 1:1.1 Cu(II)-HK^{c}H sample in 100 mM HEPES (pH 7.4) at 77 K.

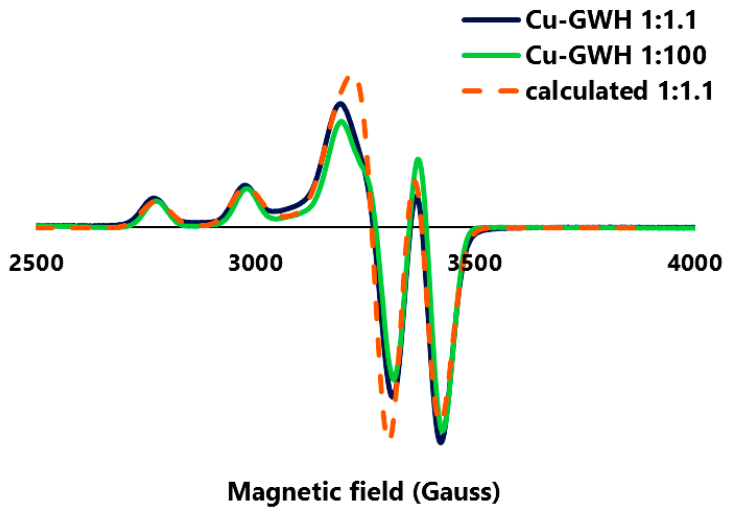

Figure S3.33: EPR spectra (obtained for a 1:1.1 sample, **blue line**; obtained for a 1:100 sample, **green line**; calculated for a 1:1.1 sample, **dashed orange line**) of a Cu(II)-GWH sample in 100 mM HEPES (pH 7.4) at 77 K..

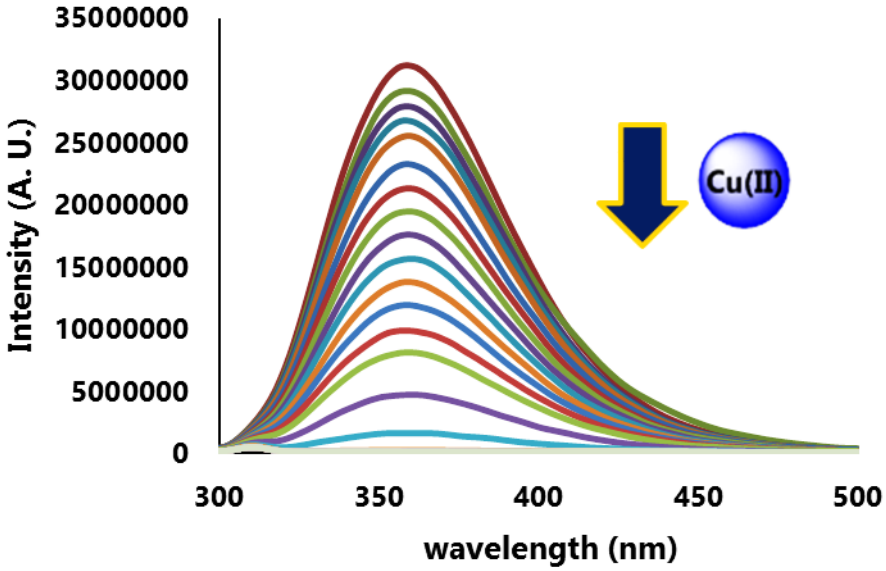

Figure S3.34: Fluorescence spectra of a 10 μM HWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$. λ_{exc} = 280 nm.

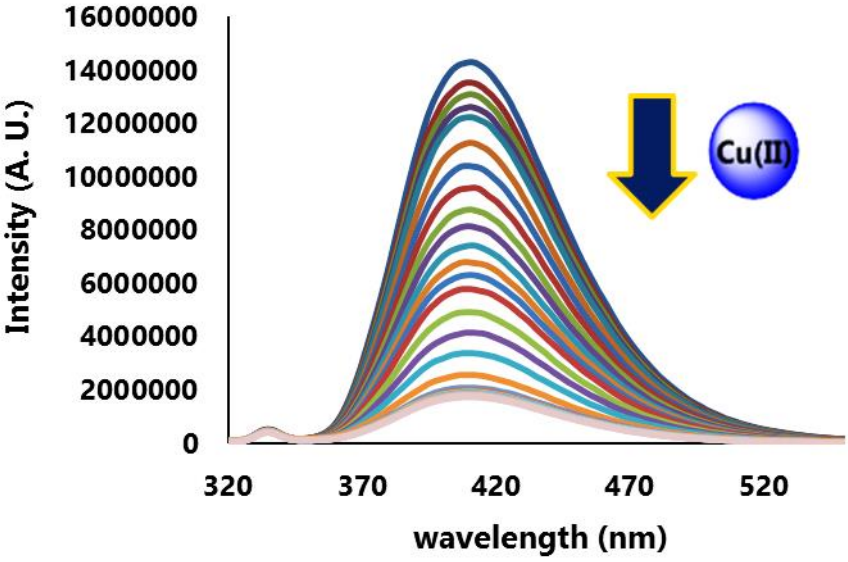

Figure S3.35: Fluorescence spectra of a 10 μM HK^{c}H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$. λ_{exc} = 300 nm.

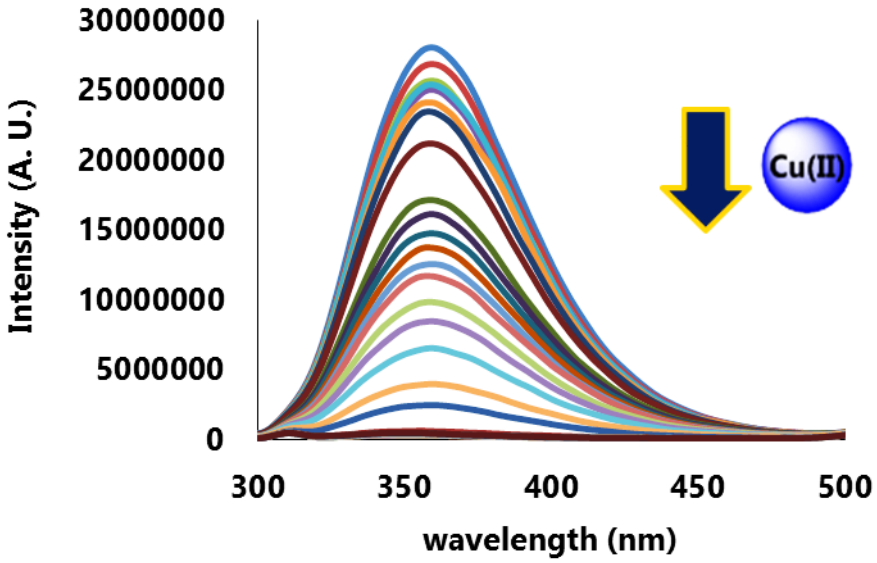

Figure S3.36: Fluorescence spectra of a 10 μM GWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$. λ_{exc} = 280 nm.

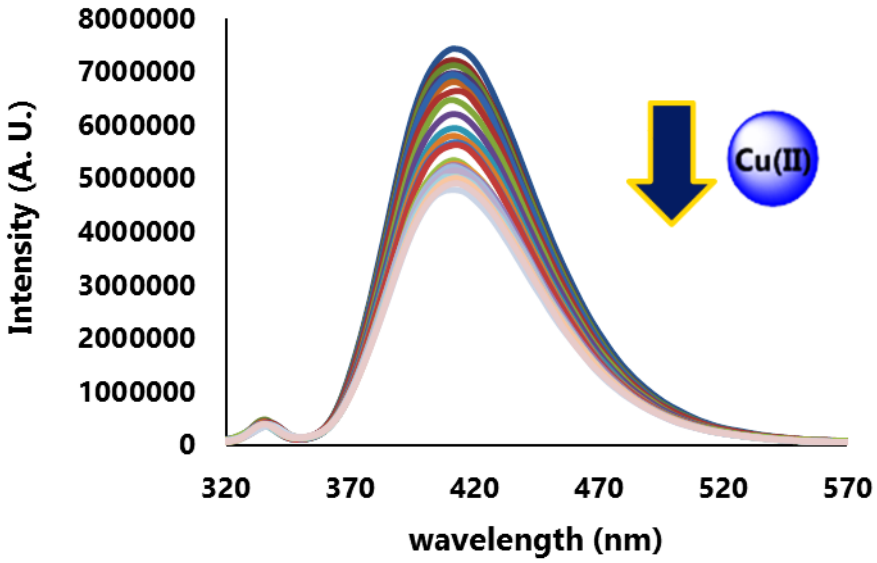

Figure S3.37: Fluorescence spectra of a 10 μM AcHK^{c}H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$. λ_{exc} = 300 nm.

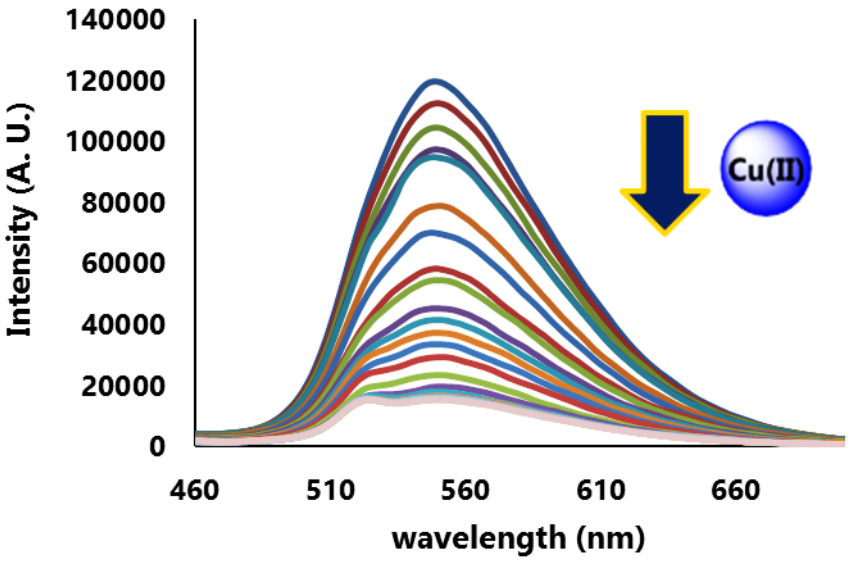

Figure S3.38: Fluorescence spectra of a 10 μM AcHK^{d}H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$. λ_{exc} = 441 nm.

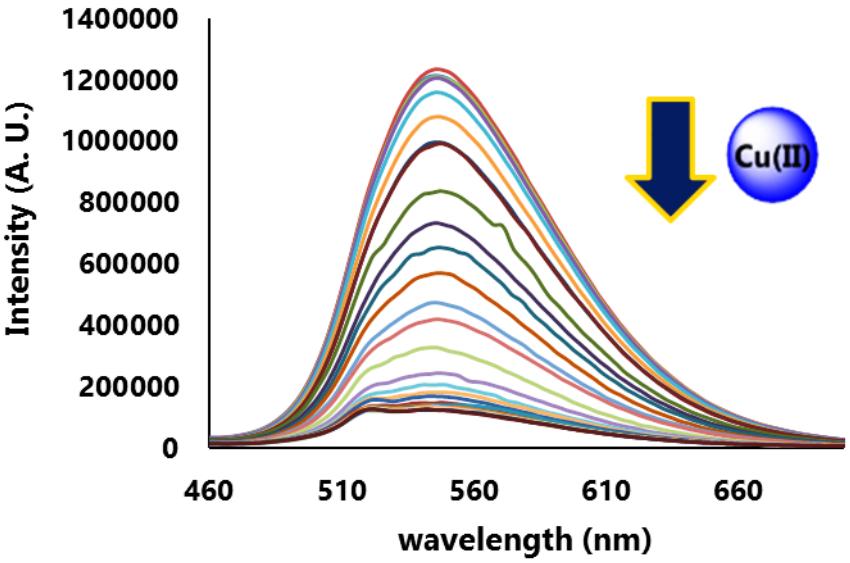

Figure S3.39: Fluorescence spectra of a 10 μM AcHK^{d}H-NH_2 solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$. λ_{exc} = 441 nm.

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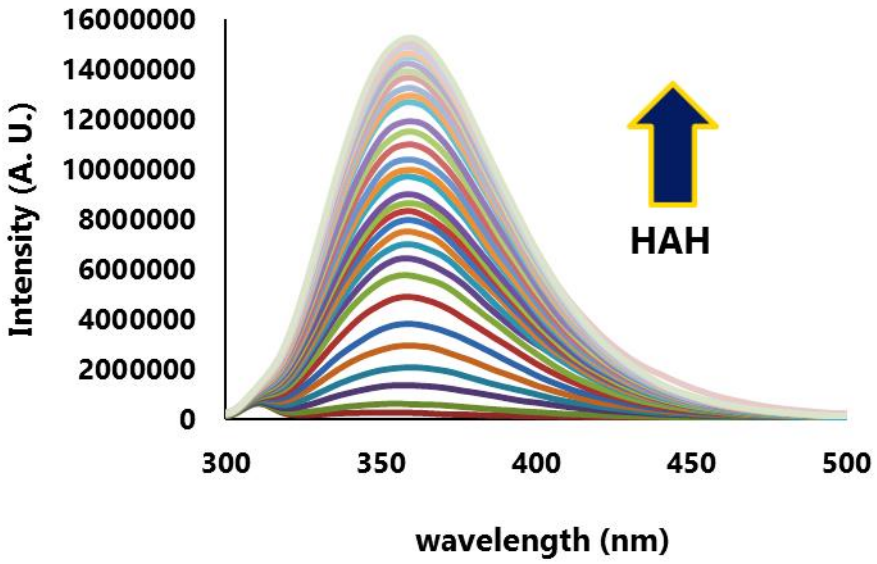

Figure S3.40: Fluorescence spectra of a 10 μM Cu-HWH solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of HAH. λ_{exc} = 280 nm.

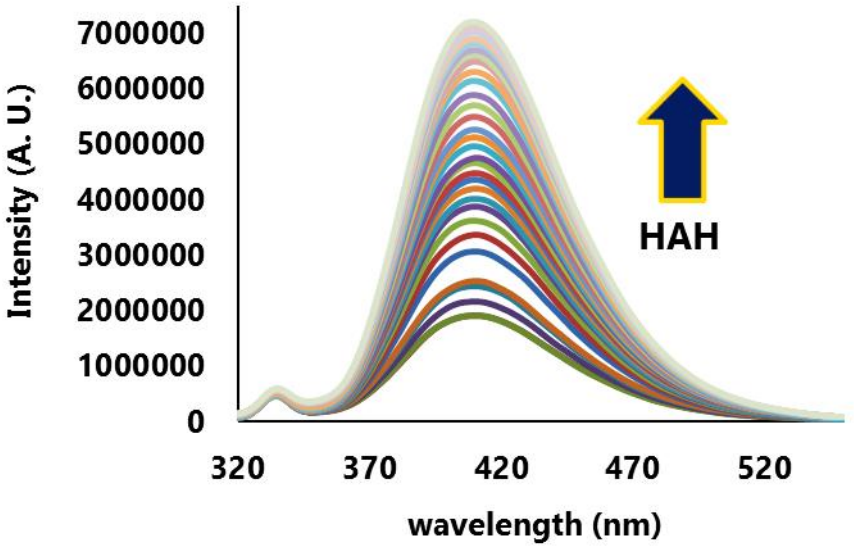

Figure S3.41: Fluorescence spectra of a 10 μM Cu-HK^{c}H solution in 100 mM HEPES (pH 7.4) upon addition of increasing amounts of HAH. λ_{exc} = 300 nm.

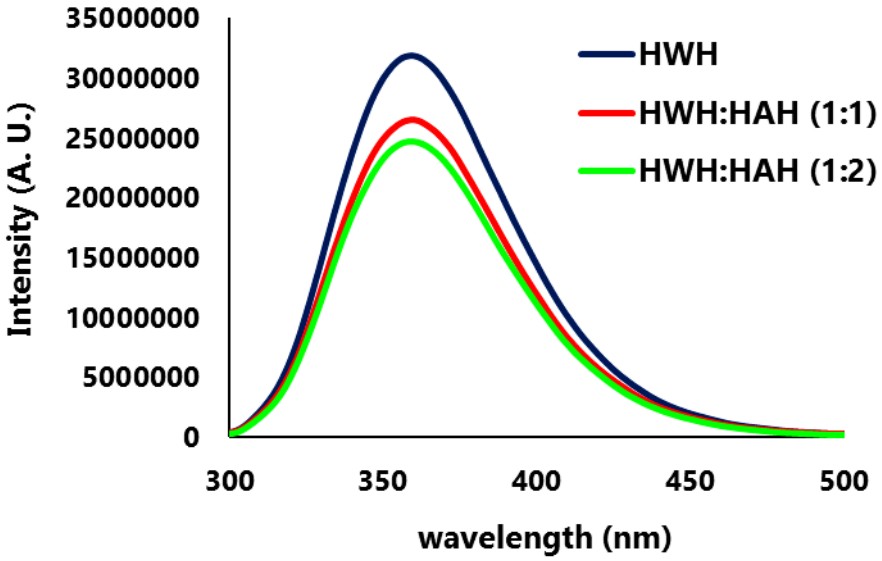

Figure S3.42: Fluorescence spectra of a 10 μM HWH solution in 10 mM HEPES (pH 7.4) in the presence of 0, 1 and 2 eq of HAH. λ_{exc} = 280 nm.

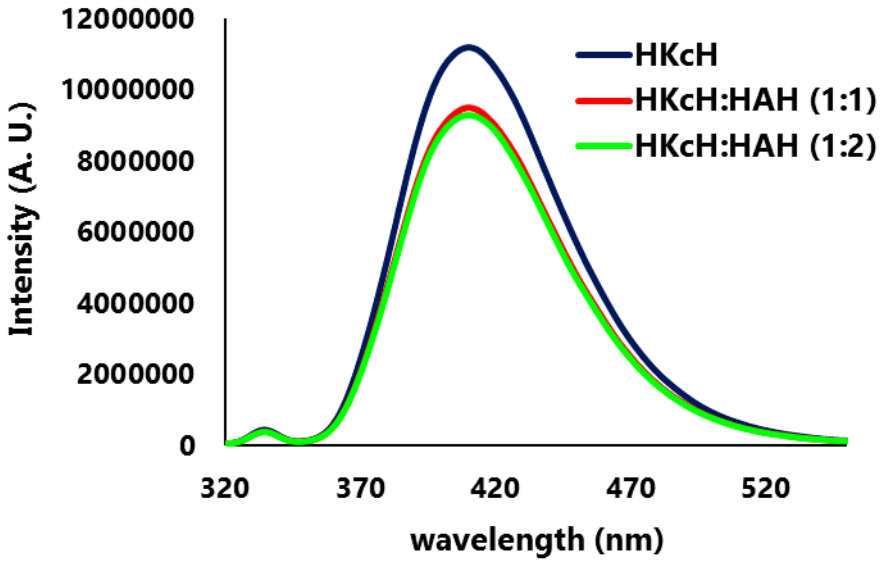

Figure S3.43: Fluorescence spectra of a 10 μM HK^{c}H solution in 10 mM HEPES (pH 7.4) in the presence of 0, 1 and 2 eq of HAH. λ_{exc} = 300 nm.

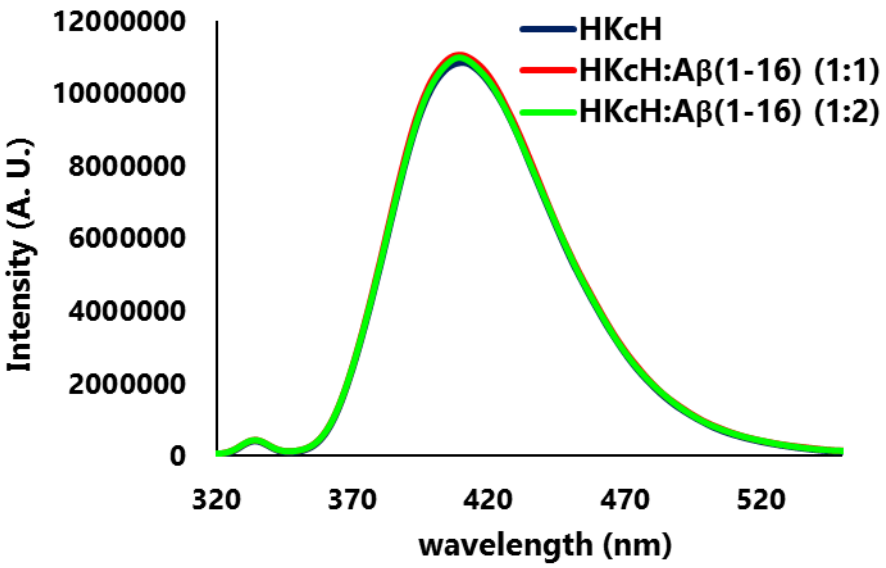

Figure S3.44: Fluorescence spectra of a 10 μM HK^{c}H solution in 10 mM HEPES (pH 7.4) in the presence of 0, 1 and 2 eq of HAH. λ_{exc} = 300 nm.

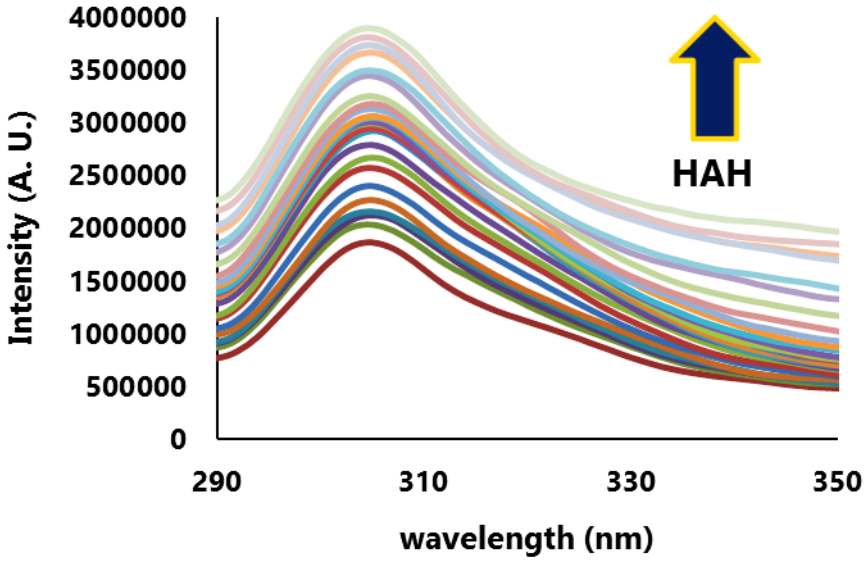

Figure S3.45: Fluorescence spectra of a 10 μM Cu(II)-Aβ(1-16) solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of HAH. λ_{exc} = 275 nm.

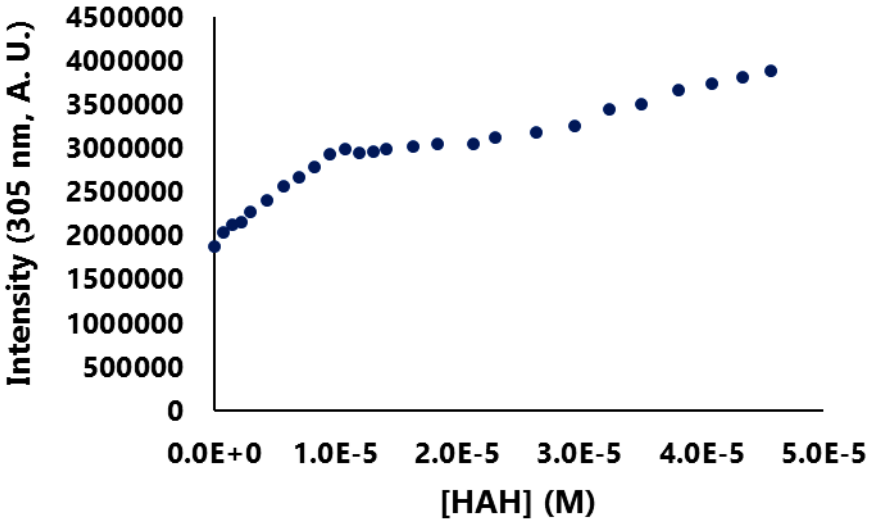

Figure S3.46: Fluorescent intensity at 305 nm of a 10 μM Cu(II)-Aβ(1-16) solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of HAH. λ_{exc} = 275 nm.

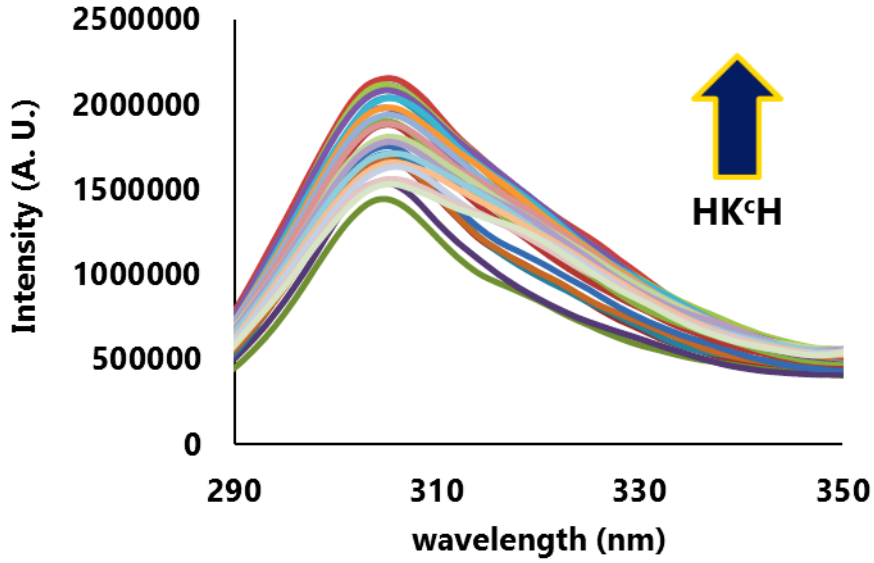

Figure S3.47: Fluorescence spectra of a 10 μM Cu(II)-Aβ(1-16) solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of HK^{c}H. λ_{exc} = 275 nm.

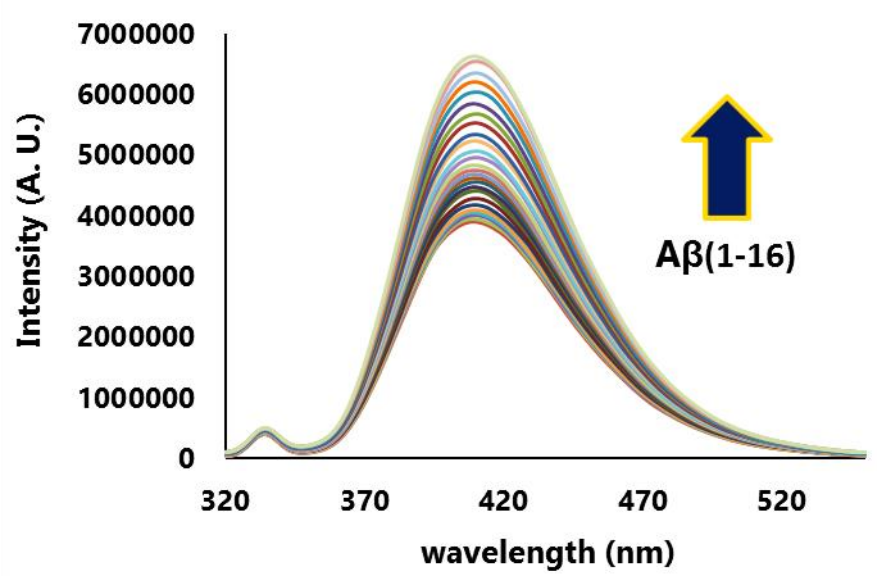

Figure S3.48: Fluorescence spectra of a 10 μM Cu(II)-HK^{c}H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of Aβ(1-16). λ_{exc} = 300 nm.

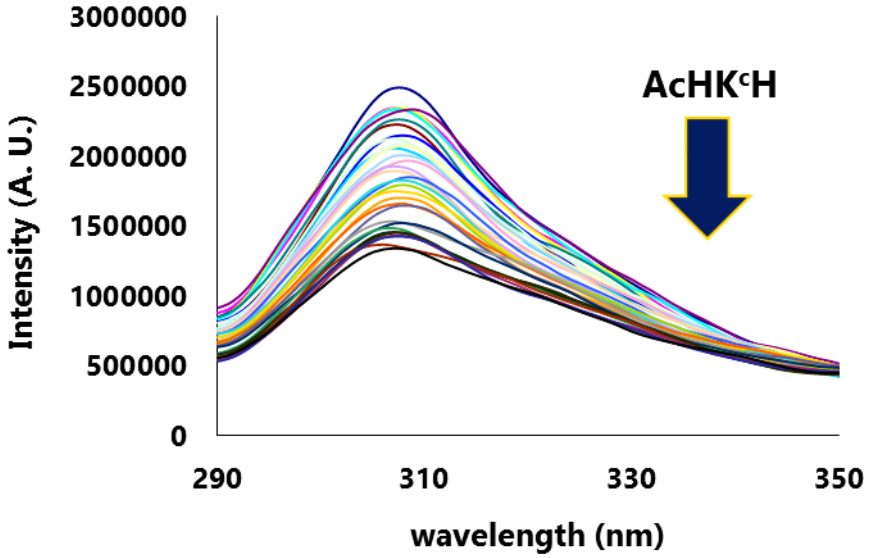

Figure S3.49: Fluorescence spectra of a 10 μM Cu(II)-Aβ(1-16) solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of AcHK^{c}H. λ_{exc} = 275 nm.

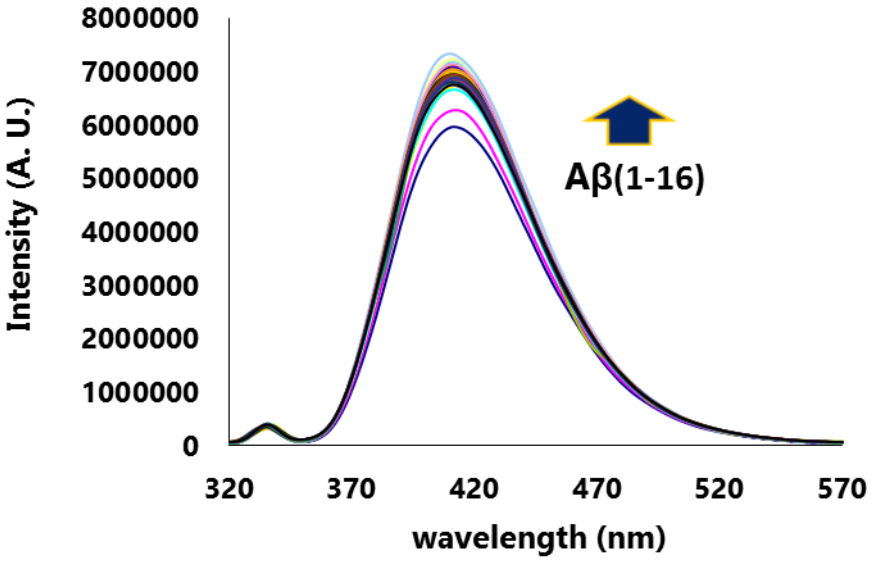

Figure S3.50: Fluorescence spectra of a 10 μM Cu(II)-AcHK^{c}H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of Aβ(1-16). λ_{exc} = 300 nm.

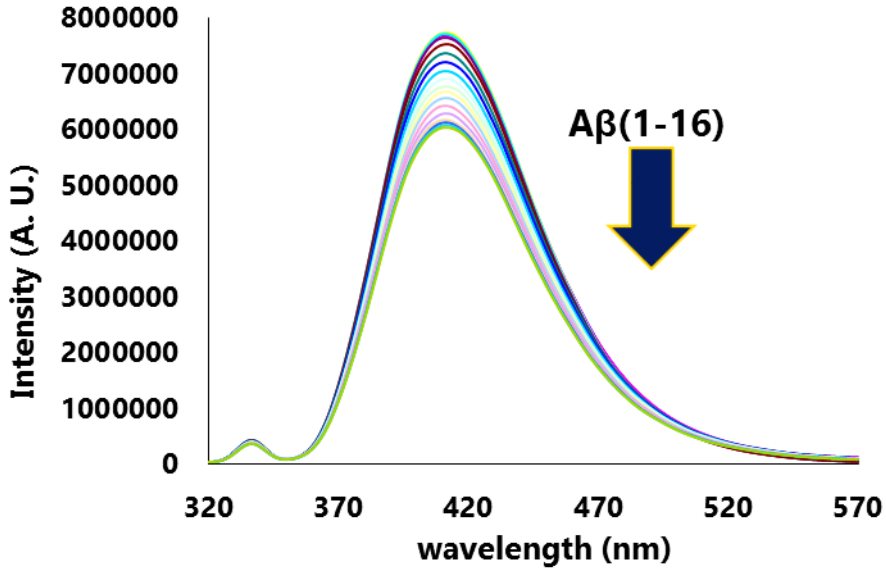

Figure S3.51: Fluorescence spectra of a 10 μM AcHK^{c}H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of Aβ(1-16). λ_{exc} = 300 nm.

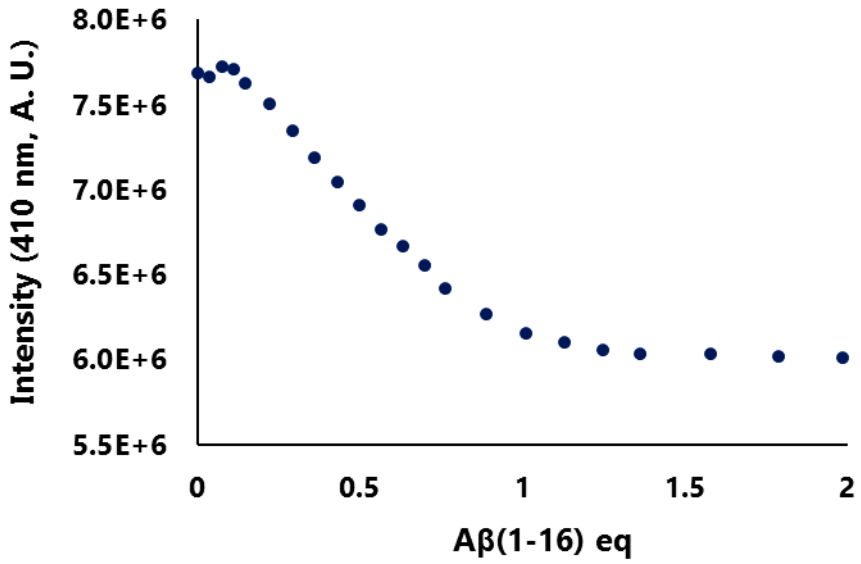

Figure S3.52: Fluorescent intensity at 410 nm of a 10 μM AcHK^{c}H solution solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of Aβ(1-16). λ_{exc} = 300 nm.

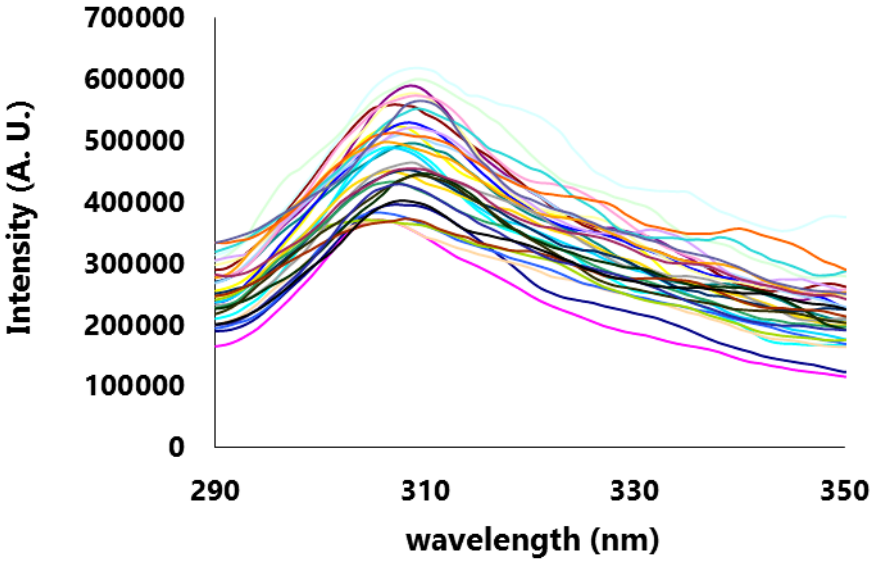

Figure S3.53: Fluorescence spectra of a 10 μM Cu(II)-Aβ(1-16) solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of AcHK^{d}H. λ_{exc} = 275 nm.

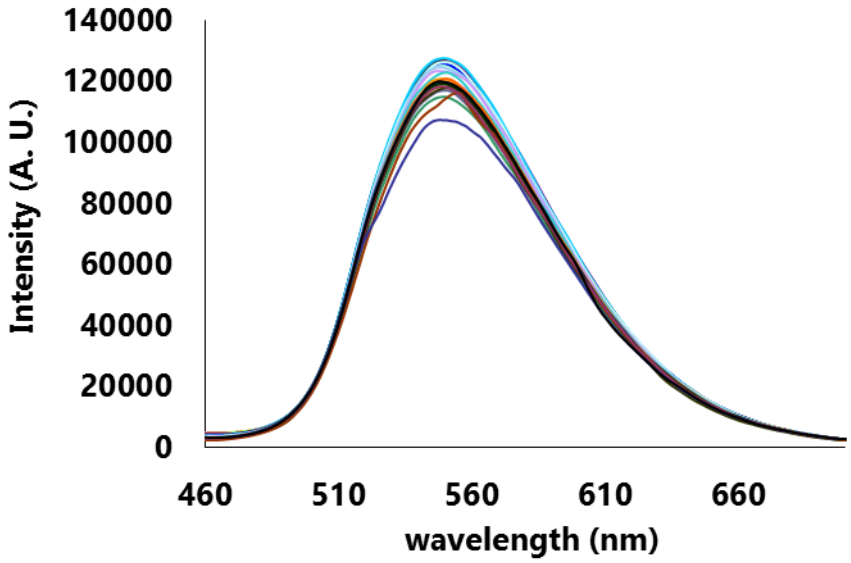

Figure S3.54: Fluorescence spectra of a 10 μM Cu(II)-AcHK^{d}H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of Aβ(1-16). λ_{exc} = 441 nm.

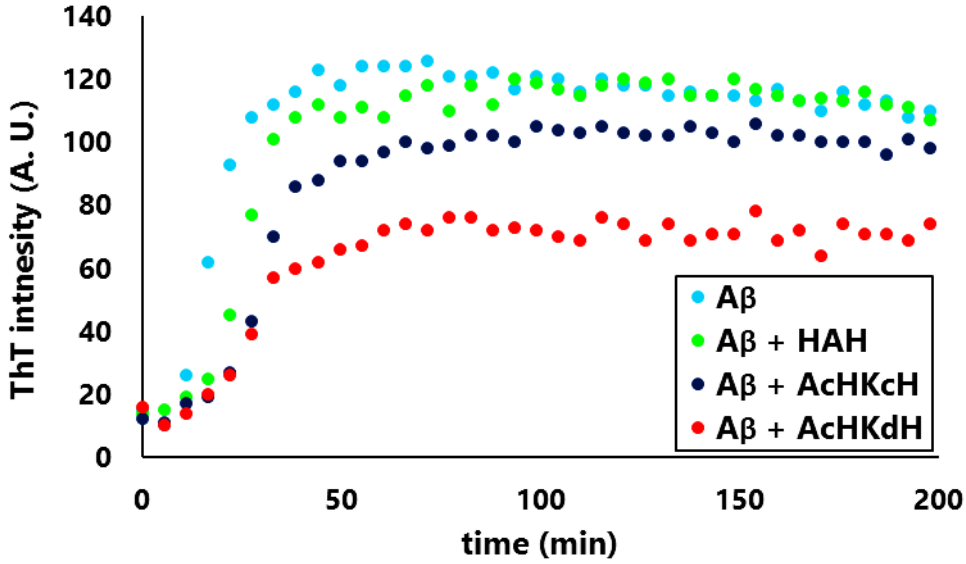

Figure S3.55: Aggregation of 20 μM Aβ(1-40) (light-blue dots) and 20 μM Aβ(1-40) in presence 2 eq of HAH (green dots), AcHK^{c}H (dark-blue dots) or AcHK^{d}H (red dots). Aβ(1-40) aggregation was followed by 25 μM ThT (25 μM) fluorescence emission. 1X PBS (pH 7.4).

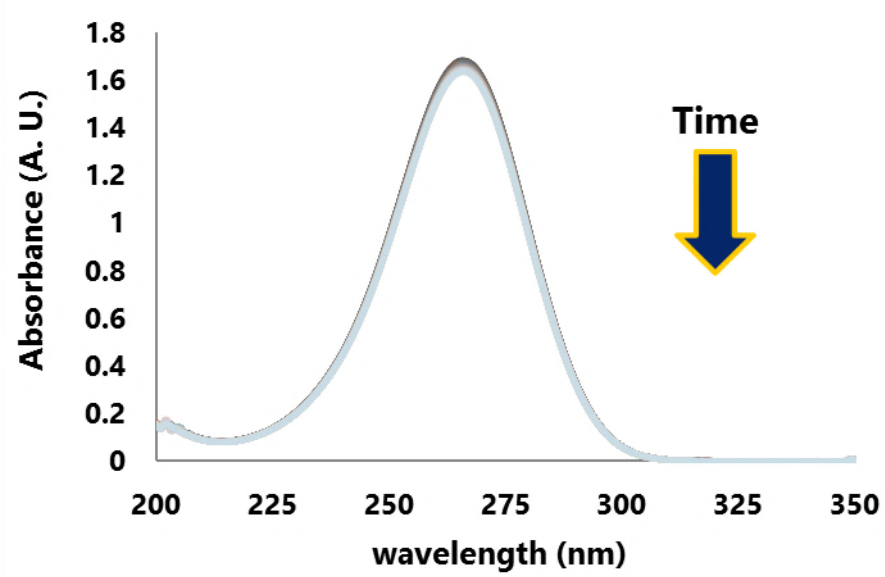

Figure S3.56: UV-Vis spectra of a 100 μM ascorbate solution in 100 mM phosphate buffer (pH 7.4), registered during a period of 30 min.

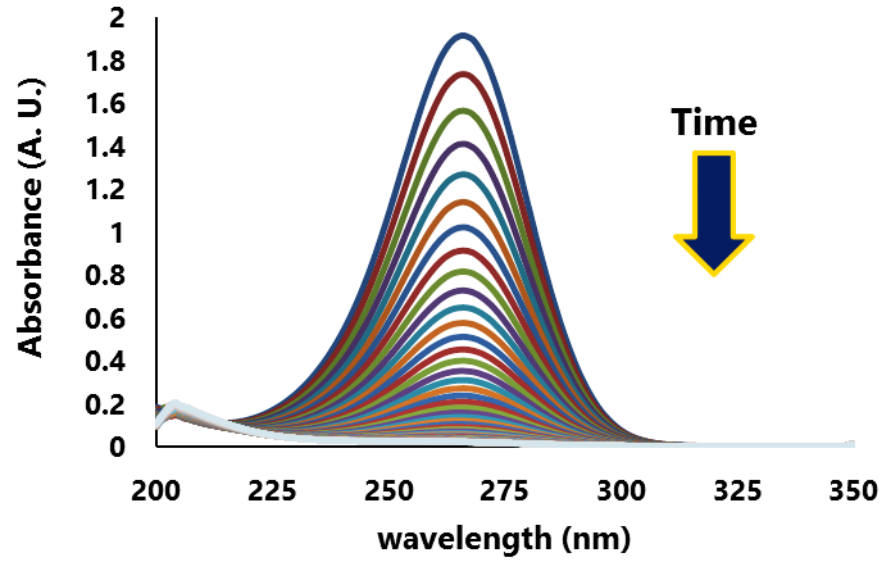

Figure S3.57: UV-Vis spectra of a 100 μM ascorbate solution in 100 mM phosphate buffer (pH 7.4) in the presence of 1% $CuCl_2$, registered during a period of 30 min.

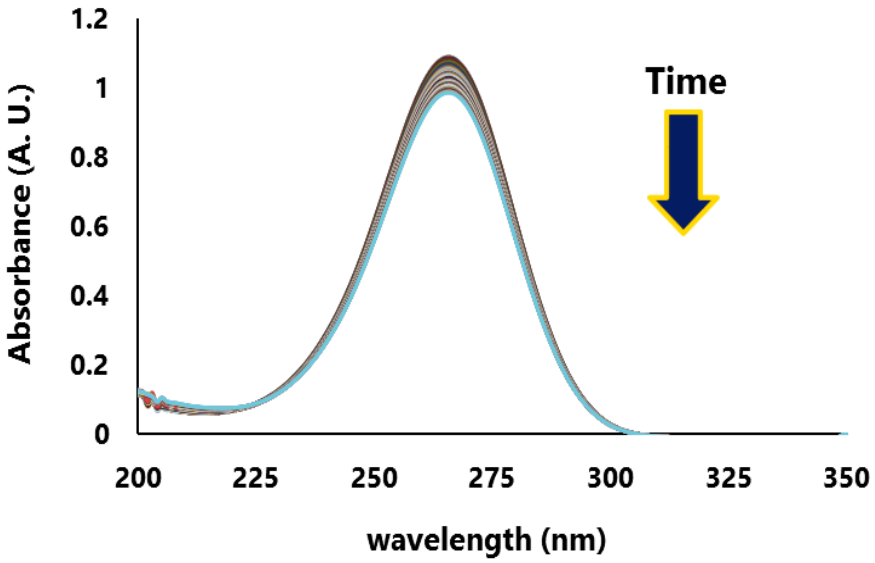

Figure S3.58: UV-Vis spectra of a 100 μM ascorbate solution in 100 mM phosphate buffer (pH 7.4) in the presence of 1% $CuCl_2$ and 1.1% HAH, registered during a period of 30 min.

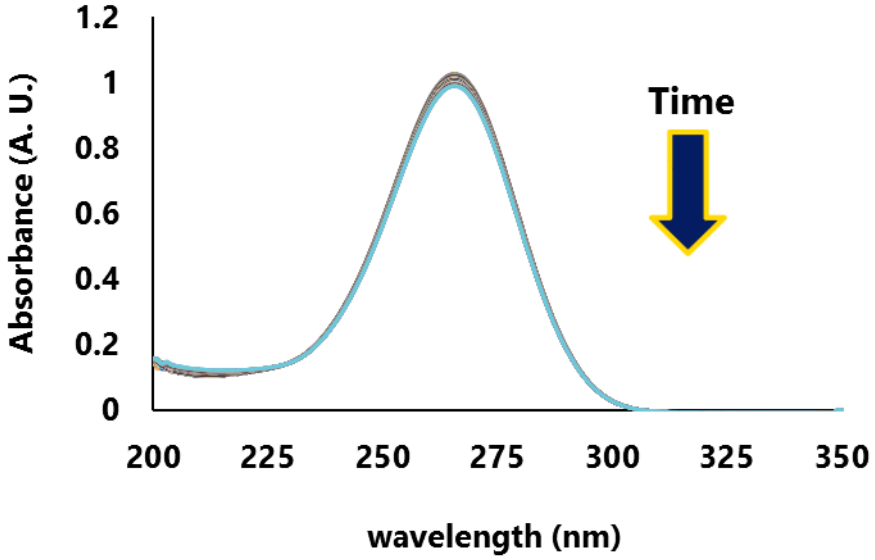

Figure S3.59: UV-Vis spectra of a 100 μM ascorbate solution in 100 mM phosphate buffer (pH 7.4) in the presence of 1% $CuCl_2$ and 1.1% HWH, registered during a period of 30 min.

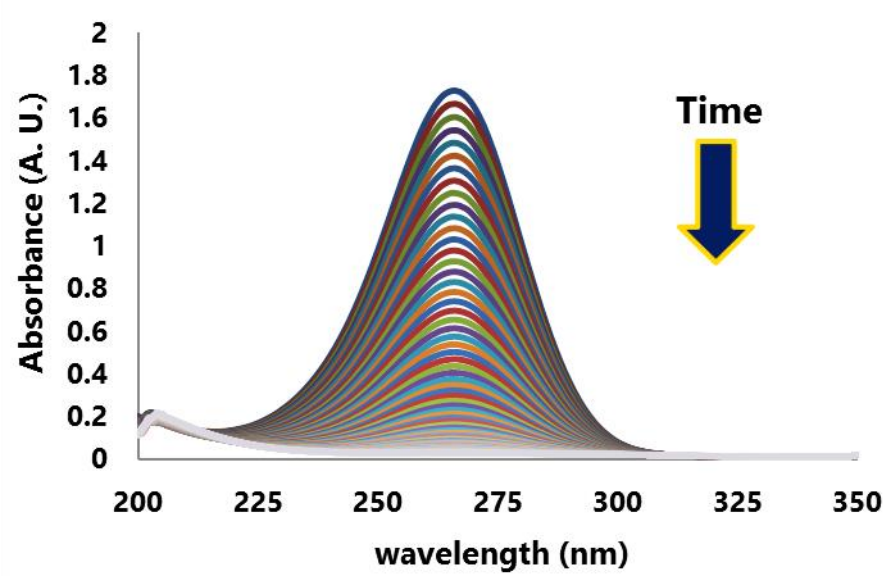

Figure S3.60: UV-Vis spectra of a 100 μM ascorbate solution in 100 mM phosphate buffer (pH 7.4) in the presence of 1% $CuCl_2$ and 1.1% AcHK^{c}H, registered during a period of 30 min.

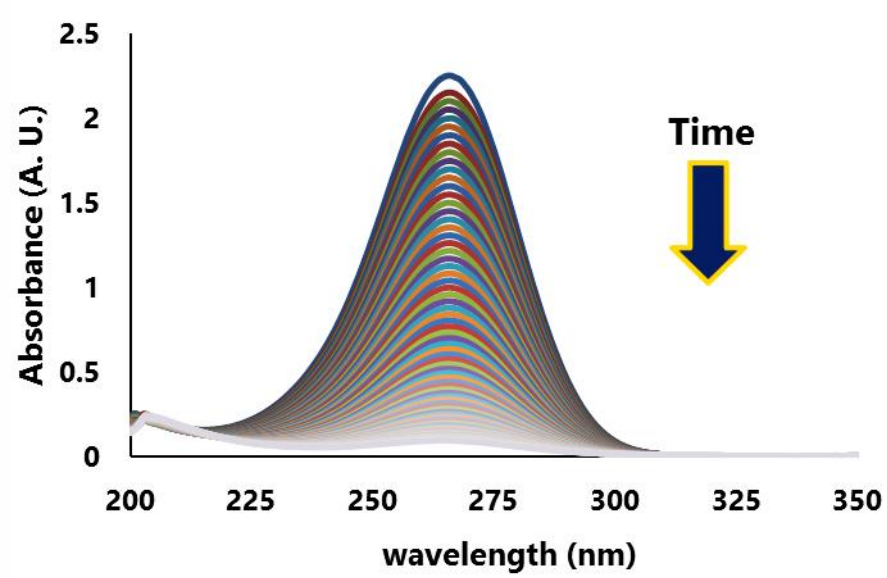

Figure S3.61: UV-Vis spectra of a 100 μM ascorbate solution in 100 mM phosphate buffer (pH 7.4) in the presence of 1% $CuCl_2$ and 1.1% AcHK^{d}H, registered during a period of 30 min.

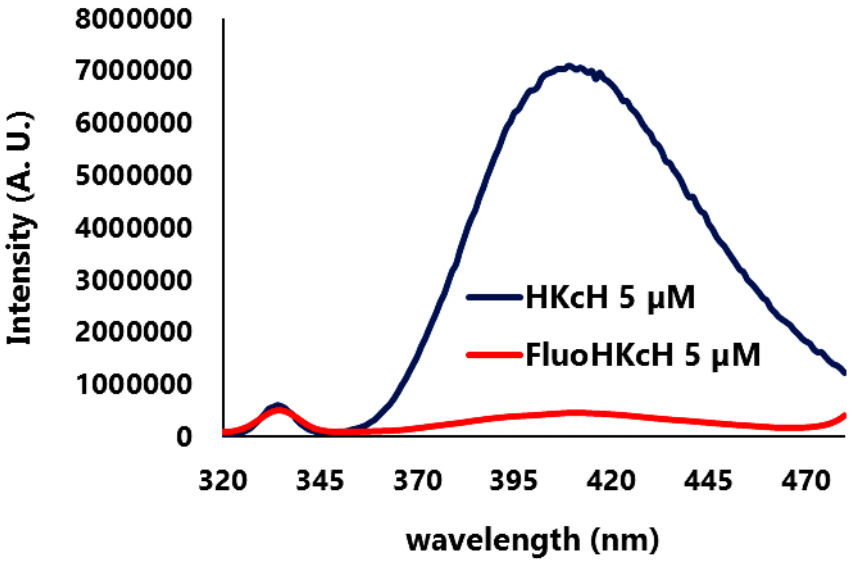

Figure S3.62: Fluorescence spectra of 5 µM FluoHK^{c}H (**red line**) and 5 µM HK^{c}H (**blue line**) solutions in 10 mM HEPES (pH 7.4). λ_{exc} = 300 nm.

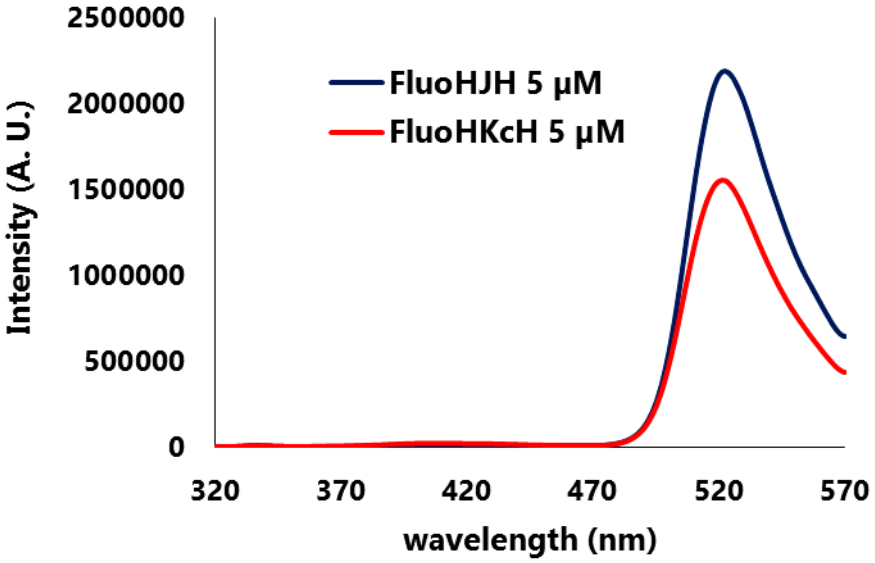

Figure S3.63: Fluorescence spectra of 5 µM FluoHK^{c}H (**red line**) and 5 µM FluoHJH (**blue line**) solutions in 10 mM HEPES (pH 7.4). λ_{exc} = 300 nm.

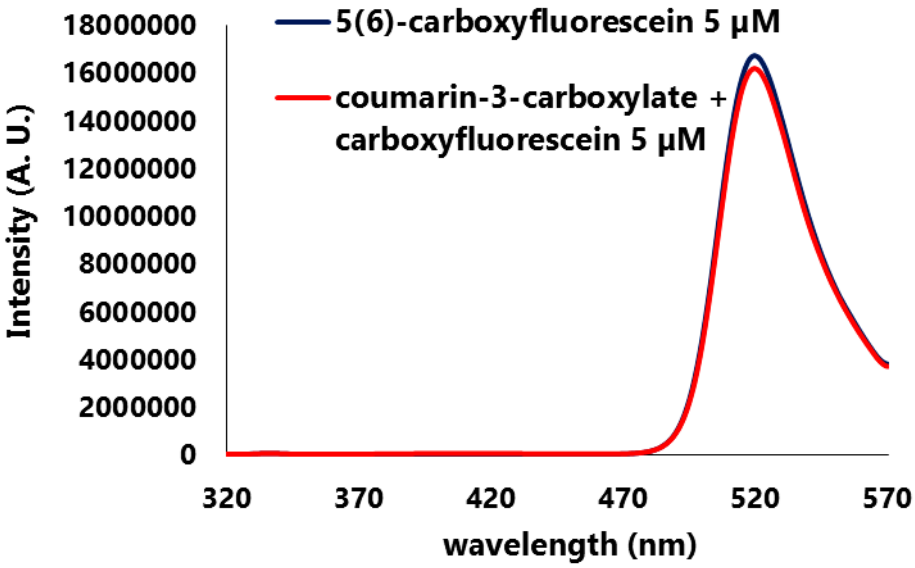

Figure S3.64: Fluorescence spectra of solutions containing 5 µM coumarin-3-carboxylate (**blue line**) and 5 µM coumarin-3-carboxylate in the presence of 1 eq of 5(6)-carboxyfluorescein (**red line**) in 10 mM HEPES (pH 7.4). λ_{exc} = 300 nm.

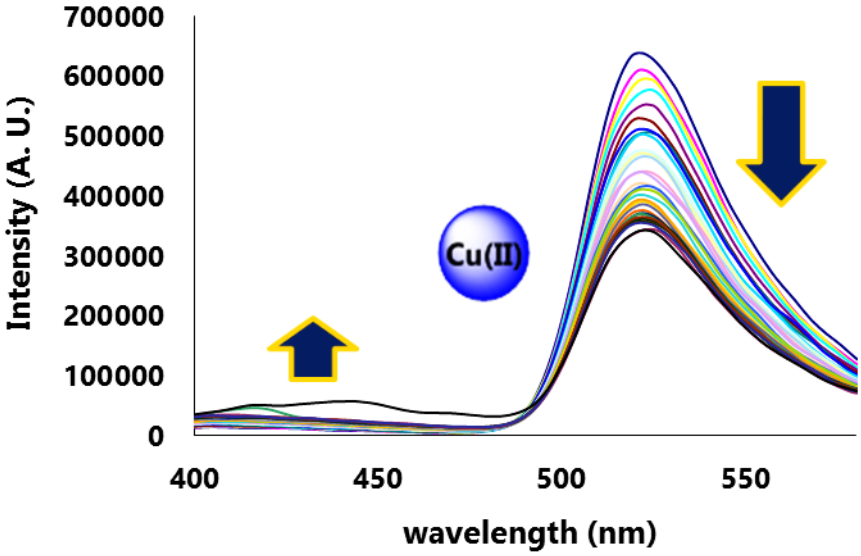

Figure S3.65: Fluorescence spectra of a 10 µM FluoHK^{c}H solution in 10 mM HEPES (pH 7.4) upon addition of increasing amounts of $CuCl_2$. λ_{exc} = 300 nm.