Electronic Supplementary Material (ESI) for Soft Matter.


# Supplementary information

## Divalent Metal Ion Modulation of a Simple Peptide-based Hydrogel: Self-Assembly and Viscoelastic Properties

Tsuimy Shao[a,b], Meissam Noroozifar[b], Heinz-Bernhard Kraatz[a,b]*

[a] Department of Chemistry, University of Toronto, 80 St. George Street, M5S 3H6, Toronto, Canada; tsuimy.shao@mail.utoronto.ca

[b] Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1065 Military Trail, M1C 1A4, Scarborough, Canada; tsuimy.shao@mail.utoronto.ca

*Correspondence: bernie.kraatz@utoronto.ca; Tel.: +1-416-287-7197

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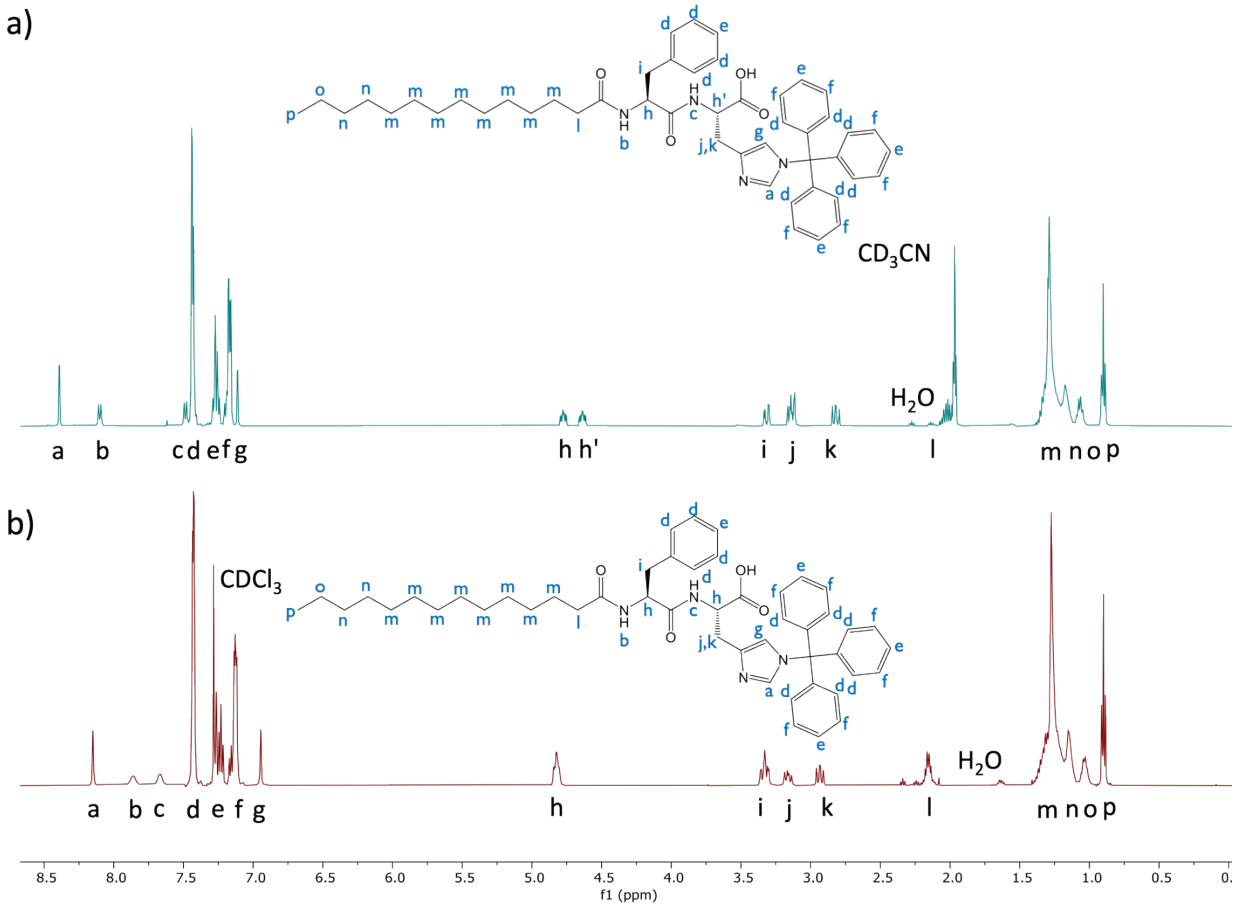


**Figure S1**. $^{1}H$ NMR of 20 mM $C_{14}$-FH(Trt)-OH in a) $CD_3CN$ and b) $CDCl_3$. C-terminal carboxylic acid proton is not seen in spectra with these solvents.

**Table S1** Chemical shifts of aromatic, imidazole, and amide protons in $C_{14}$-FH(Trt)-OH at 5, 10, 20, 25, and 50 mM in $CD_3CN$. $CD_3CN$ solvent residual peak was aligned at 1.94 ppm. Protons are named as labeled in **Figure S1**.

| | [$C_{14}$-FH(Trt)-OH] | | | | |
|---|---|---|---|---|---|
| Proton | 5 mM | 10 mM | 20 mM | 25 mM | 50 mM |
| $H_a$ | 8.33 | 8.35 | 8.36 – 8.37 | 8.37 | 8.38 |
| $H_b$ | 7.97 – 7.99 | 8.02 – 8.05 | 8.06 – 8.08 | 8.08 – 8.09 | 8.09 – 8.10 |
| $H_c$ | 7.35 – 7.36 | Overlap $H_d$ | 7.45 – 7.47 | 7.47 – 7.48 | 7.50 – 7.52 |
| $H_d$ | 7.40 – 7.43 | 7.41 – 7.42 | 7.40 – 7.41 | 7.40 – 7.41 | 7.41 |
| $H_e$ | 7.25 – 7.26 | 7.22 – 7.25 | 7.21 – 7.26 | 7.21 – 7.26 | 7.20 – 7.26 |
| $H_f$ | 7.14 – 7.16 | 7.13 – 7.15 | 7.13 – 7.16 | 7.13 – 7.16 | 7.14 |
| $H_g$ | 7.06 – 7.07 | 7.08 | 7.08– 7.09 | 7.09 | 7.10 |

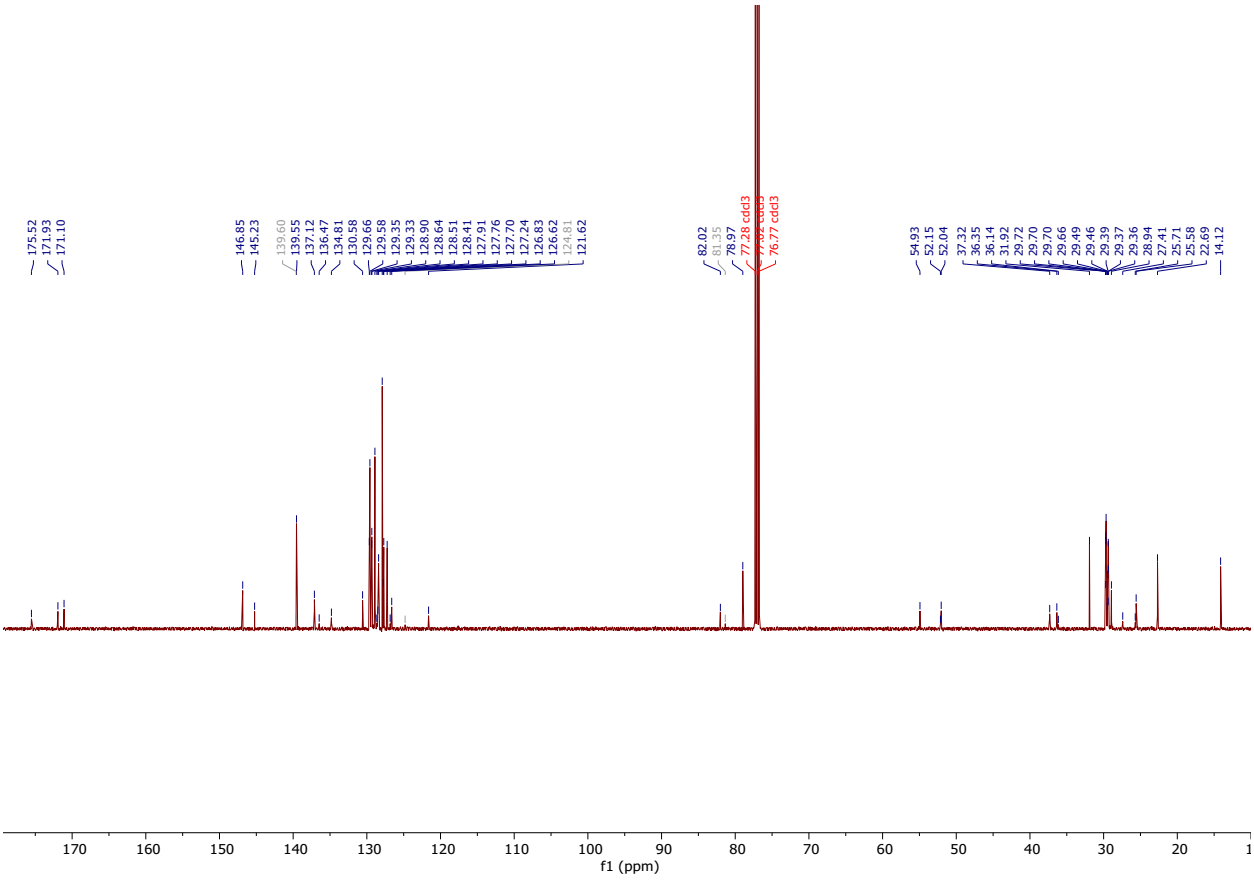


**Figure S2**. $^{13}C$ NMR of $C_{14}$-FH(Trt)-OH.

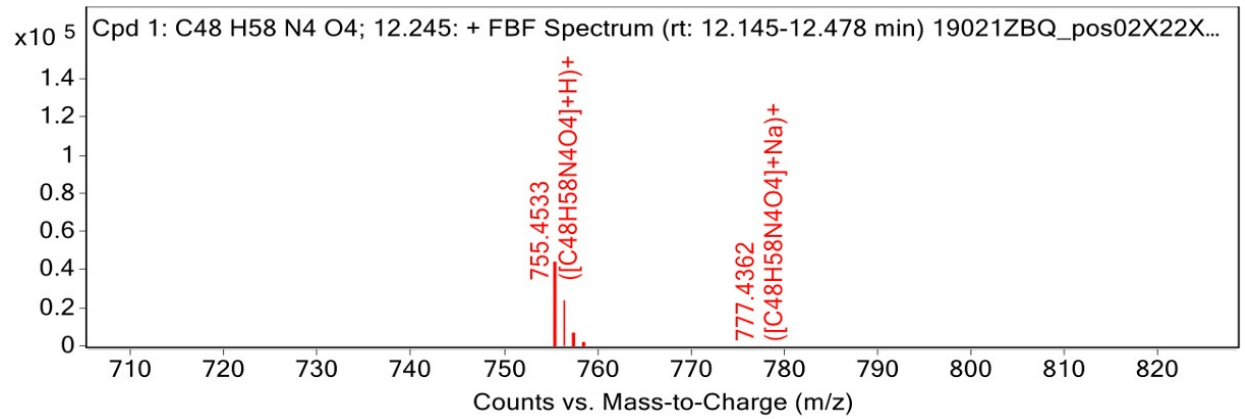


**Figure S3**. Mass spectrum of $C_{14}$-FH(Trt)-OH.

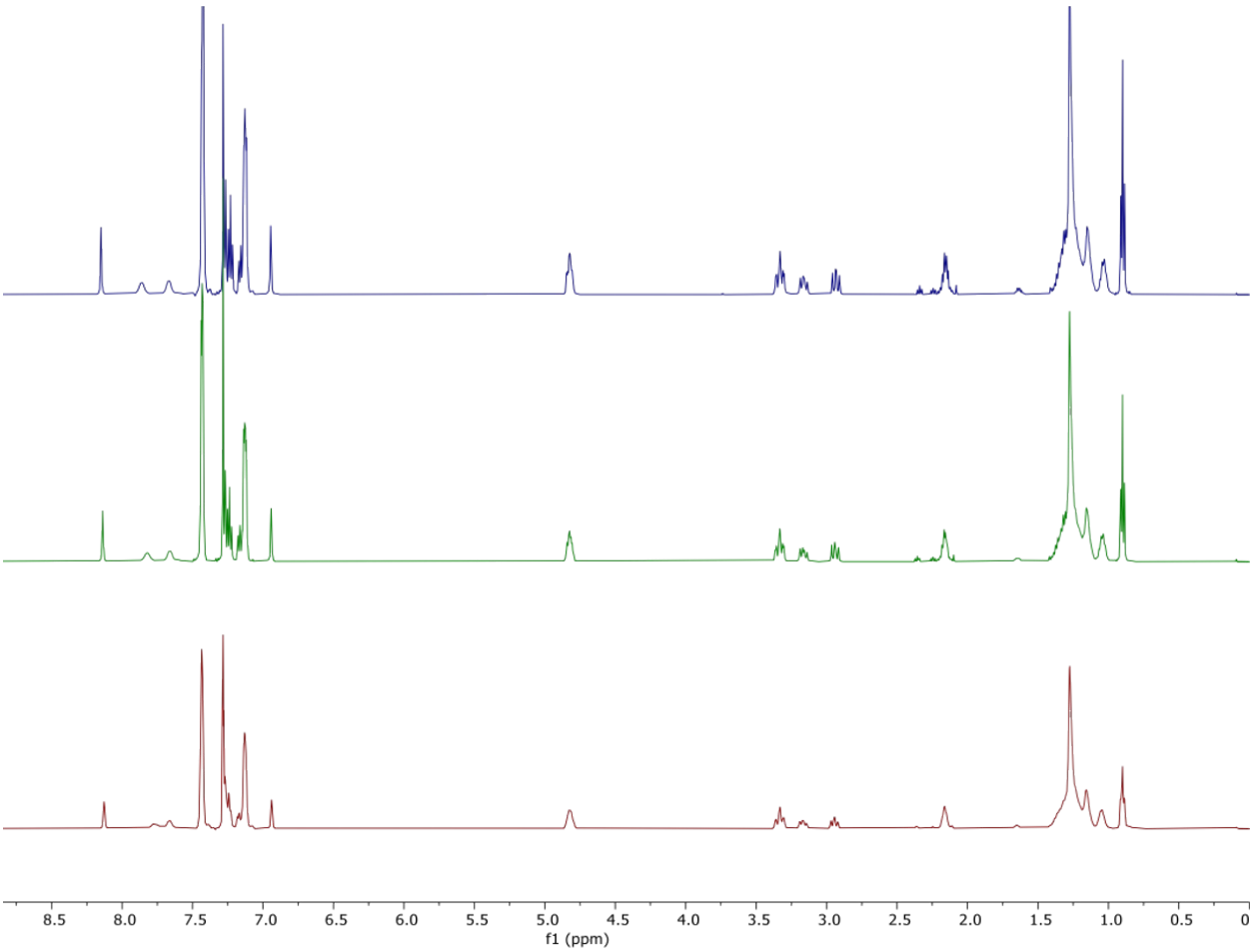


**Figure S4**. $^{1}$H NMR of $C_{14}$-FH(Trt)-OH in $CDCl_3$ at 5, 10, and 20 mM (bottom to top).

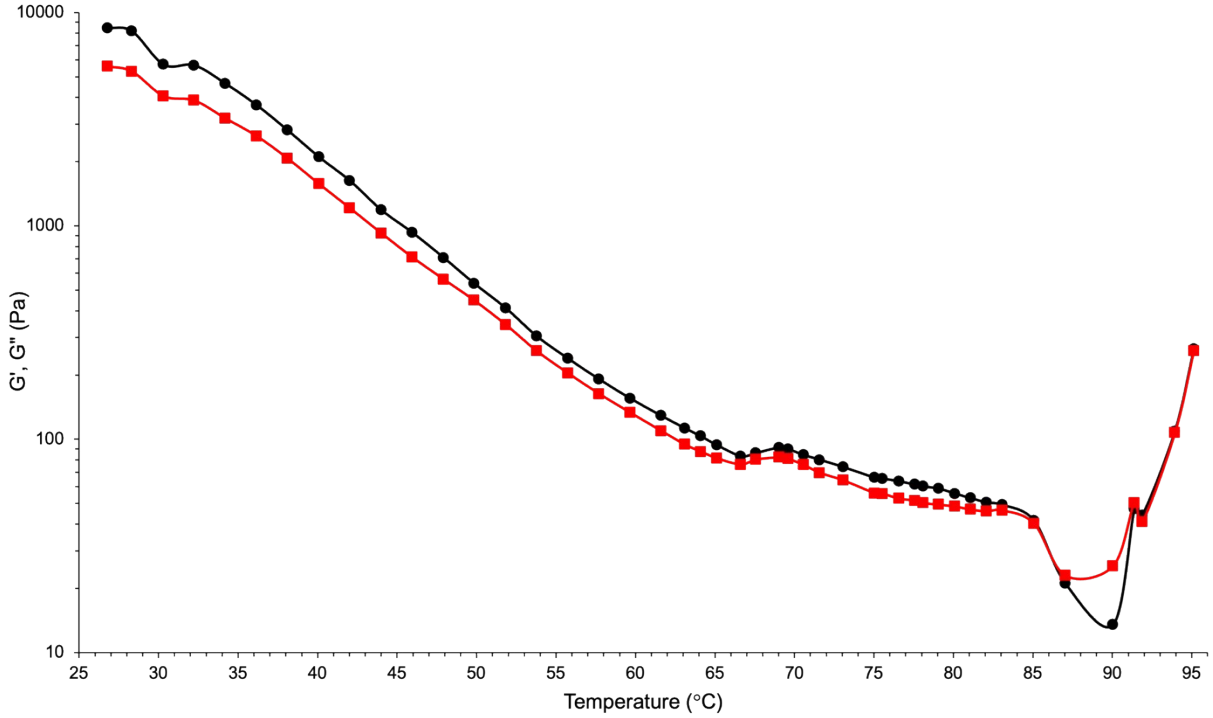


**Figure S5**. Temperature ramp of $C_{14}$-FH(Trt)-OH hydrogel. Melting temperature is determined at the cross over of G' (black circles) and G" (red squares), which indicates sol state (G" > G') has been reached from gel state (G' > G").

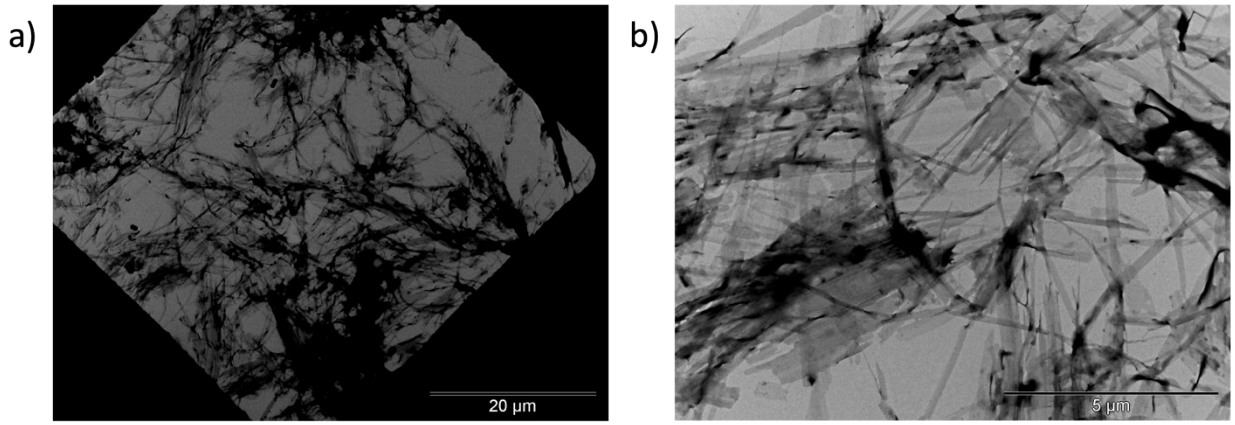


**Figure S6**. TEM imaging of $C_{14}$-FH(Trt)-OH hydrogel. Scale bar a) 20 µm, b) 5 µm.

**Table S2** Chemical shifts of $C_{14}$-FH(Trt)-OH protons with the addition of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4 eq. $Zn^{2+}$ in $CD_3CN$. $CD_3CN$ residual solvent peak was aligned at 1.94 ppm. Protons are named as labeled in **Figure S1**.

| | $C_{14}$-FH(Trt)-OH | + x eq. $Zn^{2+}$ | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Proton | 20 mM | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 |
| $H_a$ | 8.36 – 8.37 | 8.53 | 8.56 | 8.53 | 8.50 | 8.49 | 8.49 | 8.49 |
| $H_b$ | 8.06 – 8.08 | 8.42 | 8.44 | 8.41 | 8.39 | 8.39 | 8.38 | 8.38 |
| $H_c$ | 7.45 – 7.47 | 7.70 | 7.58 | * | * | * | * | * |
| $H_d$ | 7.40 – 7.41 | 7.40 – 7.43 | 7.40 – 7.43 | 7.42 – 7.44 | 7.43 – 7.45 | 7.43 – 7.45 | 7.43 – 7.45 | 7.43 – 7.45 |
| $H_e$ | 7.21 – 7.26 | 7.25 – 7.31 | 7.25 – 7.32 | 7.21 – 7.32 | 7.22 – 7.33 | 7.23 – 7.33 | 7.23 – 7.33 | 7.23 – 7.33 |
| $H_f$ | 7.13 – 7.16 | 7.14 – 7.16 | 7.14 – 7.16 | 7.14 – 7.16 | 7.14 – 7.16 | 7.14 – 7.16 | 7.14 – 7.16 | 7.14 – 7.16 |
| $H_g$ | 7.08– 7.09 | 7.08 | 7.08 | 7.08 | 7.08 | 7.08 – 7.11 | 7.08 – 7.10 | 7.08 – 7.11 |
| $H_h$ | 4.72 – 4.77 | 4.70 – 4.75 | 4.69 – 4.73 | 4.67 – 4.71 | 4.67 – 4.70 | 4.67 – 4.70 | 4.67 – 4.71 | 6.66 – 4.69 |
| $H_{h'}$ | 4.59 – 4.63 | 4.46 – 4.50 | 4.42 – 4.46 | 4.37 – 4.40 | 4.34 – 4.40 | 4.33 – 4.40 | 4.33 – 4.40 | 4.33 – 4.40 |
| $H_i$ | 3.27 – 3.31 | 3.25 – 3.29 | 3.24 – 3.28 | 3.22 – 3.26 | 3.22 – 3.30 | 3.21 – 3.30 | 3.21 – 3.30 | 3.21 – 3.30 |
| $H_j$ | 3.09 – 3.14 | 3.06 – 3.18 | 3.05 – 3.18 | 3.04 – 3.20 | 3.04 – 3.17 | 3.04 – 3.17 | 3.04 – 3.17 | 3.04 – 3.17 |
| $H_k$ | 2.77 – 2.82 | 2.82 - 2.87 | 2.84 – 2.90 | 2.87 – 2.91 | 2.88– 2.92 | 2.88 – 2.93 | 2.88 – 2.93 | 2.88 – 2.93 |
| $H_l$ | 1.96 – 2.13 | 2.01 – 2.15 | 2.03 – 2.17 | 2.05 – 2.18 | 2.09 – 2.19 | 2.09 – 2.21 | 2.09 – 2.21 | 2.09 – 2.23 |

*Overlapped with other aromatic protons and not discernable

**Table S3** Chemical shifts of $C_{14}$-FH(Trt)-OH protons with the addition of 0.002, 0.004, 0.006, 0.008, 0.010, 0.012, 0.014, 0.016, 0.018 eq. $Cu^{2+}$ in $CD_3CN$. $CD_3CN$ residual solvent peak was aligned at 1.94 ppm. Protons are named as labeled in **Figure S1**.

| | $C_{14}$-FH(Trt)-OH | + x eq. $Cu^{2+}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Proton | 20 mM | 0.002 | 0.004 | 0.006 | 0.008 | 0.010 | 0.012 | 0.014 | 0.016 | 0.018 |
| $H_a$ | 8.36 – 8.37 | 8.31 | 8.32 | 8.33 | 8.35 | 8.30 | 8.31 | 8.31 | 8.31 | 8.31 |
| $H_b$ | 8.06 – 8.08 | 8.00– 8.02 | 8.01 – 8.02 | 8.01 | 8.02 | 8.01 | 8.00 | 8.00 | 8.00 | 7.99 |
| $H_c$ | 7.45 – 7.47 | 7.38 | 7.38 | 7.38 | 7.39 | 7.36 | 7.36 | 7.35 | 7.35 | 7.35 |
| $H_d$ | 7.40 – 7.41 | 7.40 – 7.41 | 7.40 – 7.42 | 7.40 – 7.42 | 7.40 – 7.42 | 7.39 – 7.41 | 7.39 – 7.41 | 7.39 – 7.41 | 7.39 – 7.41 | 7.39 – 7.41 |
| $H_e$ | 7.21 – 7.26 | 7.24 – 7.32 | 7.24 – 7.32 | 7.24 – 7.33 | 7.23 – 7.33 | 7.22 – 7.25 | 7.22 – 7.25 | 7.22 – 7.25 | 7.22 – 7.25 | 7.22 – 7.25 |
| $H_f$ | 7.13 – 7.16 | 7.13 – 7.15 | 7.13 – 7.16 | 7.13– 7.17 | 7.13 – 7.18 | 7.13 – 7.17 | 7.13 – 7.17 | 7.13 – 7.16 | 7.13 – 7.16 | 7.13 – 7.16 |
| $H_g$ | 7.08– 7.09 | 7.07 | 7.07 | 7.08 | 7.08 | 7.07 | 7.06 | 7.06 | 7.06 | 7.06 |
| $H_h$ | 4.72 – 4.77 | 4.73 | 4.73 | 4.73 | 4.74 | 4.73 | 4.73 | 4.73 | 4.73 | 4.73 |
| $H_{h'}$ | 4.59 – 4.63 | 4.60 | 4.60 | 4.60 | 4.61 | 4.60 | 4.59 | 4.59 | 4.60 | 6.60 |
| $H_i$ | 3.27 – 3.31 | 3.26 – 3.29 | 3.26 – 3.28 | 3.26 – 3.29 | 3.26 – 3.28 | 3.25 – 3.28 | 3.25 – 3.27 | 3.25 – 3.28 | 3.25 – 3.28 | 3.25 – 3.28 |
| $H_j$ | 3.09 – 3.14 | 3.07 – 3.13 | 3.07 – 3.13 | 3.07 – 3.13 | 3.08 – 3.13 | 3.08 – 3.12 | 3.08 – 3.12 | 3.08 – 3.12 | 3.08 – 3.12 | 3.08 – 3.12 |
| $H_k$ | 2.77 – 2.82 | 2.77 – 2.82 | 2.77 – 2.82 | 2.77 – 2.82 | 2.77 – 2.82 | 2.77 – 2.82 | 2.77 – 2.82 | 2.77 – 2.82 | 2.77 – 2.82 | 2.77 – 2.82 |

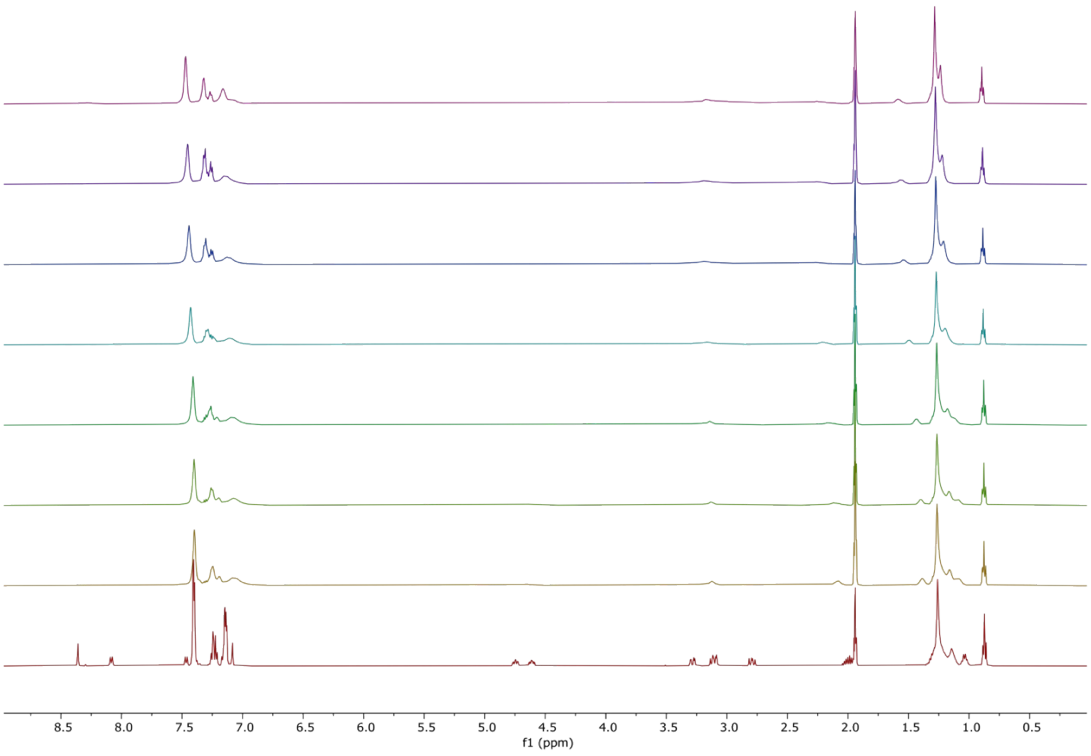


**Figure S7**. $^1H$ NMR of $C_{14}$-FH(Trt)-OH with the addition of 0 – 1.4 eq. $Cu^{2+}$ (bottom to top) at 0.2 eq. intervals resulting in peak broadening and peak disappearance of imidazole, amide, and α-protons.

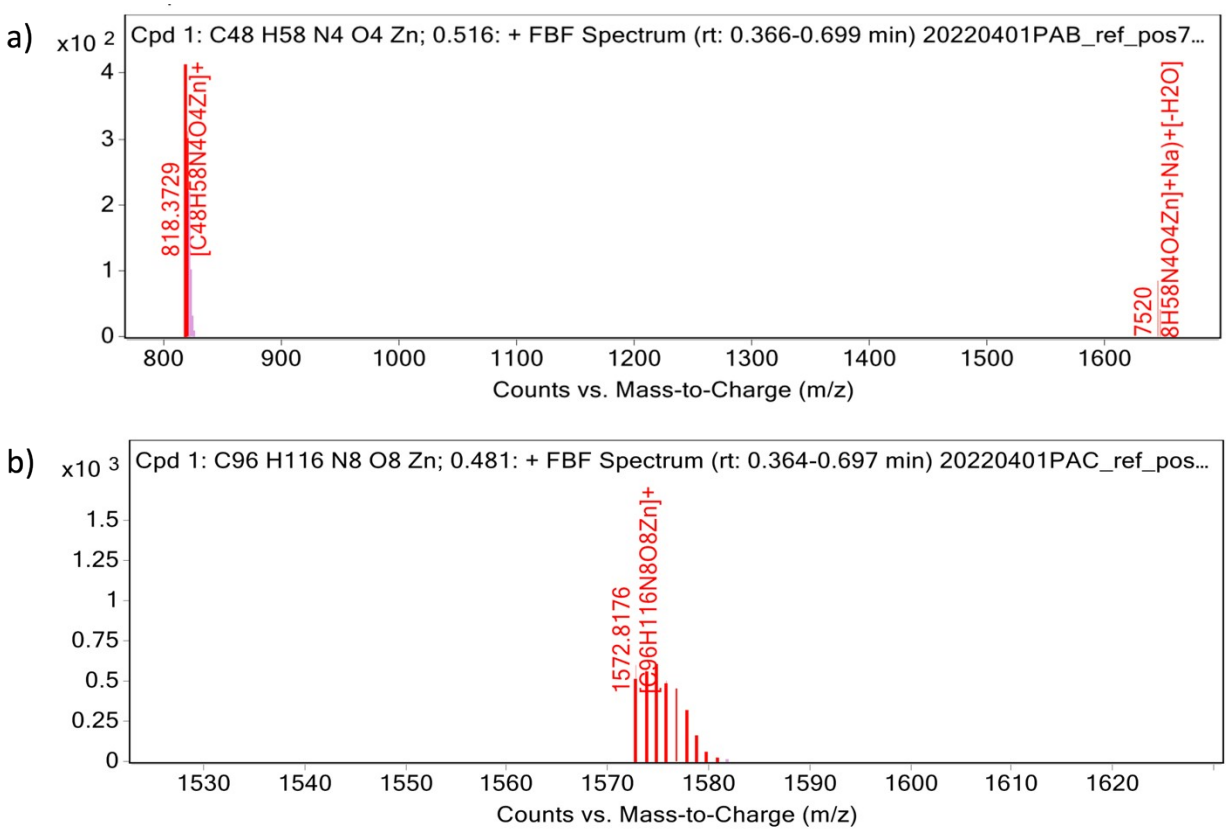


**Figure S8**. Mass spectra of a) 1:1 $C_{14}$-FH(Trt)-OH:Zn and b) 2:1 $C_{14}$-FH(Trt)-OH:Zn species found in $Zn^{2+}$-$C_{14}$-FH(Trt)-OH hydrogel.

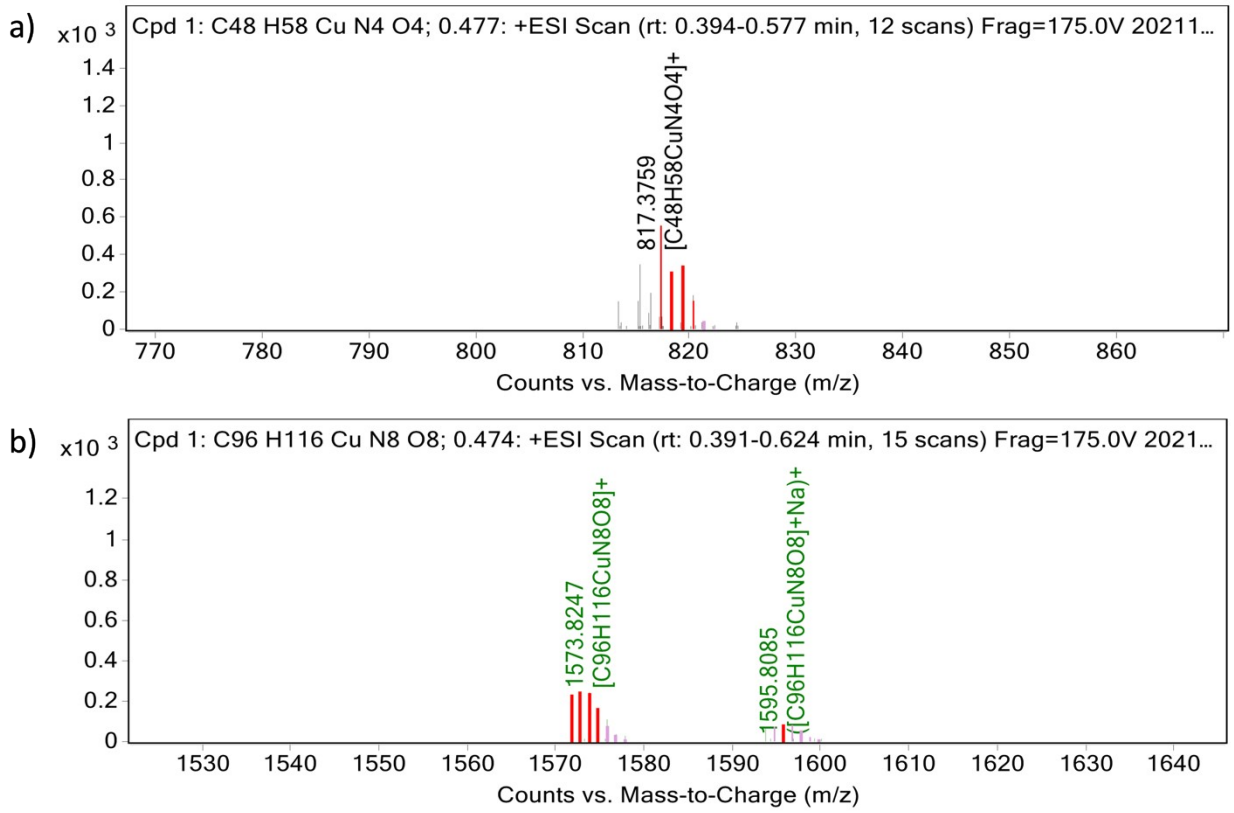


**Figure S9**. Mass spectra of a) 1:1 $C_{14}$-FH(Trt)-OH:Cu and b) 2:1 $C_{14}$-FH(Trt)-OH:Cu species found in $Cu^{2+}$-C14-FH(Trt)-OH hydrogel.

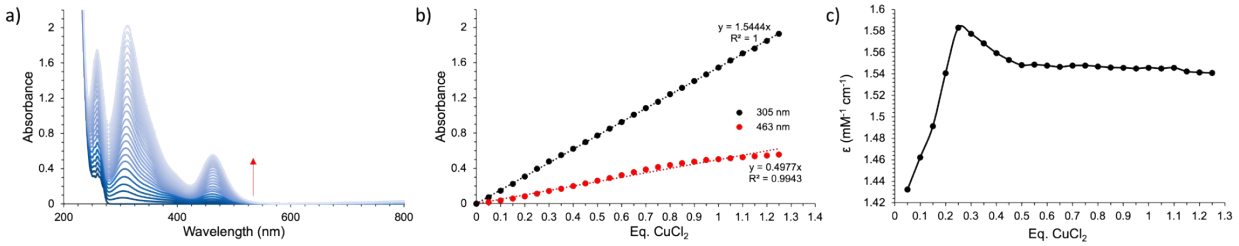


**Figure S10**. UV-vis spectra of 0.4 mM $C_{14}$-FH(Trt)-OH in acetonitrile with a) 0.05-1.25 eq. $Cu^{2+}$ added. Absorbance was plotted for b) 305 nm (black) and 463 nm (red) to determine the molar extinction coefficients. For the absorbance at 463 nm, the molar extinction coefficients c) plateau at 0.50 eq of $Cu^{2+}$.

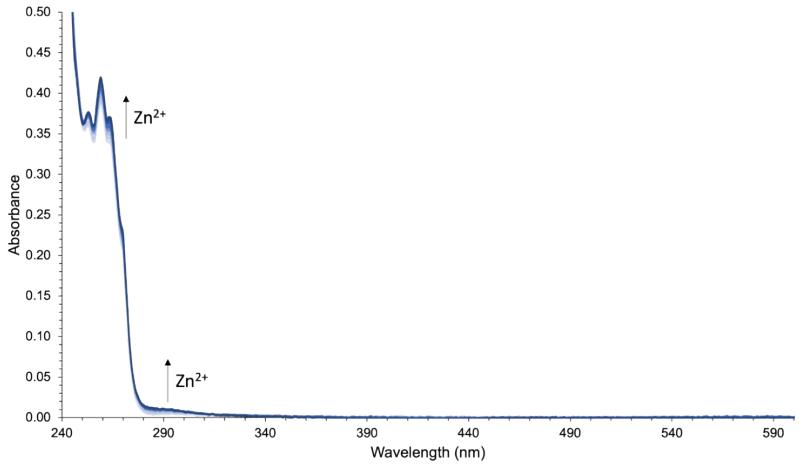


**Figure S11**. UV-vis spectra of 0.4 mM $C_{14}$-FH(Trt)-OH with 0-1.0 eq. $Zn^{2+}$ added. Minor increases of absorbance are seen in peptide peaks at 253, 259, and 264 nm and at 290 nm.