Supplementary Information

A Rationally Designed Peptoid for the Selective Chelation of Zn$^{2+}$ Over Cu$^{2+}$

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Materials
Rink Amide resin was purchased from Novabiochem. 2-([2,2':6',2''-terpyridin]-4'-yloxy)ethan-1-amine (Netp) has been synthesized as per the literature report\cite{1} where precursor 4'-bromo-2,2':6',2''-terpyridine was purchased from Alfa Aesar and ethanolamine from Acros organics, Israel. Reagents like piperdine, 2-picoly amine, (Aminomethyl)cyclohexane, Amyl amine and allyl amine were purchased from Sigma Aldrich. Benzylamine, 1-(Aminomethyl)naphthalene were purchased from ACROS Organics. (R)-(-)-3,3-Dimethyl-2-butylamine was procured from Alfa Aesar Chemical company. Aryl amine was purchased from Merck. N,N’-diisopropylcarbodiimide (DIC) was purchased from Chem-Impex Int’l Inc. Bromoacetic acid was purchased from Merck and chloro acetic acid was from Acros organics. Metal salts are purchased of analytical grade. All used solvents were HLPC grade of which dimethylforamide (DMF), toluene and dichloromethane (DCM) solvents were purchased from Bio-Lab Ltd. Acetonitrile (ACN) and water were obtained from Sigma-Aldrich.

Instrumentations
Reversed-phase HPLC on a Jasco UV-2075 instrument (analytical C18 column, Luna 5µm, 100 Å, 2.0 x 50 mm) was used to analyze synthesized peptoids. Linear gradient of 5–95% ACN in water with 0.1% TFA (flow rate is 700 µL/min) over 10 min was used. Preparative HPLC was performed using a phenomenex C18 column (Luna 15µm, 100 Å 21.20x100mm) on a Jasco UV-2075 instrument using 5–95% ACN in water with 0.1% TFA as solvent for elution. A linear gradient of the solvent is used over 50 min at a flow rate of 5 mL/min. Mass spectrometry was performed on Waters LCT Premier mass [ESI+, direct probe ACN:H2O (95:5), flow rate 0.2 ml/min] and Advion expression mass under electrospray ionization (ESI) [ESI+, direct probe ACN:H2O (70:30), flow rate 0.3 ml/min]. 1H-NMR spectra were recorded using an AVANCE II 400 MHz Bruker spectrometer. Proton chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to tetramethylsilane ((CH3)4Si, 0.00 ppm). Circular Dichroism experimentation was carried out using Applied Photophysics chirascan spectrophotometer. EPR spectra were using a Bruker EMX-10/12 X-band (ν=9.4 GHz) digital EPR spectrometer. Spectra processing and simulation were carried out with the Bruker WIN-EPR and SimFonia Software. The g factors values were determined using 2,2,6,6- tetramethylpiperidine-N-oxyl (TEMPO) as reference (g = 2.0058). Kaleida Graph is used for data processing.

Preparation of peptoid oligomers
Peptoids (PT-1-9 and PD-1) were manually prepared in fritted syringes by the sub-monomer method on Rink amide resin at room temperature.\cite{2} In a typical synthesis, rink-amide resin (100 mg) was measured
and swallowed in DCM for a period of 40 minutes. De-protection of the resin was carried out by piperidine solution (20%, solvent: DMF) followed by 20 minutes shaking in ambient condition. Next, piperidine was washed by DMF for three times with one minute duration (1 mL/ 25 mg resin each time). Bromoacetylation was done by addition of 20 eq. Bromoacetic acid (1.2 M in DMF, 8.5 mL/g resin) together with 24 eq. of diisopropylcarbodiimide (2 mL g⁻¹ resin), shaking for 20 min in room temperature. Afterwards, the bromoacetylation reagents were properly washed from the resin by DMF (1 mL/ 25 mg resin each time, three times with one minute duration each time). After washing, 20 eq. of the primary amine (1.0 M in DMF, 10 mL/g resin) was added under shaking for next 20 minutes at room temperature and later washed three times by DMF. Bromoacetylations and amine displacement steps were repeated till the desired sequence was loaded on the resin. In case of picolyl amine step, chloroacetic acid was used instead of bromoacetic acid.[3][1] When the synthesis of the desired sequence was finished, they were cleaved from solid support for initial analysis. Approximately 4-6 mg of the resin were dispersed in a cleavage cocktail solution (TFA:DCM:Water= 4.9:4.9:0.2) for 30 minutes.[3][1] Then the cleavage solution was evaporated under nitrogen flow and the residue is suspended in 0.5 mL HPLC grade 1:1 water and acetonitrile mixture. To cleave the entire peptoid oligomers from the solid support for preparative HPLC, the beads were dispersed in the cleavage cocktail solution (TFA:DCM:Water= 4.9:4.9:0.2) for 90 minutes. The solution was evaporated under low pressure, solubilized in 5 mL HPLC grade 1:1 water and acetonitrile mixture and lyophilized overnight.

**Characterization of the peptoid oligomers**

The peptoids (PT-1-9 and PD-1) were characterized by analytical HPLC using a C18 column using a specific solvent gradient of 5% to 95% solvent B (0.1% TFA in HPLC grade acetonitrile) over solvent A (0.1% TFA in HPLC grade water) for 10 minutes under a constant flow rate of 0.7 mL/min with 214 nm UV absorbance. In case of preparative HPLC at 230 nm, C18 column was used where the solvent gradient was 5% to 95% solvent B (0.1% TFA in HPLC grade acetonitrile) over solvent A (0.1% TFA in HPLC grade water), duration 50 minutes, flow rate 5 mL/min. The collected peptoids were lyophilized overnight. The pure peptoids were further analysed by RP-HPLC [C18 column with a linear gradient of 5–95% ACN in water (0.1% TFA) over 10 min at a flow rate of 700 µL/min and 214 nm UV absorbance].

**PT-1** Proton (¹H) NMR (δ in ppm) (400 MHz; ACN-d₃): 9.30(s, 1H, -NH, N-terminal end), 9.18 (m, 3H, Ar-H), 8.84 (d, 1H, Ar-H), 8.77 (d, 1H, Ar-H), 8.63 (m, 3H, Ar-H), 8.27 (d, 1H, Ar-H), 8.06 (m, 2H, Ar-H), 7.92 (m, 1H, Ar-H), 6.30 (m, 2H, -NH₂, C-terminal end), 7.4 (m, 8H, Ar-H), 4.55 (m, 9H, -CH₂ of skeletal and linker), 3.97 (m, 5H, -CH₂ of skeletal and linker) (Fig. S53a).
Table S1. Peptoid oligomer sequences with their molecular weights and UV-Vis signals. [Npm: phenylmethanamine; Nap: naphthalen-1-ylmethanamine; Nchm: cyclohexylmethanamine; Nrtb: (R)-3,3-dimethylbutan-2-amine; Npen: pentan-1-amine; Nall: prop-2-en-1-amine; Nme: 2-methoxyethan-1-amine; Netp: 2-((2,2‘:6’,2’’-terpyridin)-4’-yloxy)ethan-1-amine; Npm: pyridin-2-ylmethanamine; Ac: acetylated]

| Entry | Peptoid oligomers | Molecular weight | \( \lambda_{\text{max}} \) (UV-Vis analysis) |
|-------|------------------|-----------------|---------------------------------|
| 1     | PT-1 (Npm- Netp- Npm) | 644.29: 645.35 | 235, 262 and 275 nm |
| 2     | PT-1Ac (Npm- Netp- Npm-Ac) | 686.30: 687.28 | 234, 261, 267 and 277 nm |
| 3     | PT-2 (Nnap- Netp- Nnap) | 694.30: 695.7 | 222, 266 and 280 nm |
| 4     | PT-3 (Nchm- Netp- Npm) | 650.33: 651.61 | 233, 266 and 277 nm |
| 5     | PT-4 (Nrtb- Netp- Npm) | 638.33: 639.44 | 234, 268 and 276 nm |
| 6     | PT-5 (Npen- Netp- Npm) | 624.32: 625.47 | 234, 258, 266 and 277 nm |
| 7     | PT-6 (Nall- Netp- Npm) | 594.27: 595.22 | 234, 266 and 275 nm |
| 8     | PT-7 (Nme- Netp- Npm) | 612.28: 613.67 | 235 and 276 nm |
| 9     | PT-8 (Npm- Netp- Npm) | 643.29: 644.27 | 235 and 276 nm |
| 10    | PD-1 (Netp- Npm) | 497.22: 498.16 | 235, 259, 267 and 277 nm |

Synthesis of Copper/ Zinc peptoid complexes

Lyophilized PT-1 (0.05 mmol) was dissolved in water (2 mL) and stirred for 10 minutes. The solution was colorless. Copper acetate monohydrate or zinc acetate dihydrate (0.05 mmol as solid) was added to the solution of the peptoid under stirring condition and kept for next 4 hours in room temperature. During the reaction with copper, the reaction mixture turns blue while during the reaction with zinc no color change has been observed. The solution was lyophilized to obtain the complex.

Synthesis of ZnPT-1 and CuPT-1 in different temperatures: To a vile containing 500 \( \mu \)L water solution of PT-1 (1mM), one equivalent metal ion (Zn\(^{2+}\) or Cu\(^{2+}\), stock solution in water, 50 mM) was added in either room temperature, 35°C or 50°C and stirred for 24 hours. The reaction was monitored by UV-Vis.

Synthesis of ZnPT-1 and CuPT-1 in different solvents: The reaction was carried out in room temperature for four hours in acetonitrile and/or methanol. Concentration was maintained at 17 \( \mu \)M. The UV-Vis response was remained almost similar other than 2 nm shift in 245 nm peak of ZnPT-1 (H2O) that was shifted to 247 nm in ZnPT-1 (ACN).

Characterization of ZnPT-1: Yield: 92%, ESI-MS: calculated for [Zn\(^{2+}\)-PT-1-OAc] 767.23, found: 767.2338, assigned with proper isotope labelling. UV-Vis characterization (17 \( \mu \)M in water), \( \lambda_{\text{max}} \) for

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ZnPT-1 are 245, 267, 275, 310 and 322 nm. FT-IR peaks (\(\nu, \text{cm}^{-1}\)): 3085, 2948, 1666, 1537, 1440, 1192, 1136, 954, 719, 693. [UV-Vis: Fig. S41, ESI-MS: Fig. S43, FT-IR: Fig. S54c]. \(\lambda_{\text{max}}\) for ZnPT-1 in acetonitrile are 247, 267, 276, 310 and 323 nm; \(\lambda_{\text{max}}\) for ZnPT-1 in methanol are 246, 268, 275, 312 and 323 nm (Fig. S47).

Characterization of CuPT-1: Yield: 88%, ESI-MS: calculated for \([\text{Cu}^{2+}-\text{PT-1}+\text{OAc}^-+\text{K}^+]\) 805.19, found: 805.10, assigned with proper isotope labelling. UV-Vis characterization (17 \(\mu\)M in water), \(\lambda_{\text{max}}\) for CuPT-1 are 253, 259, 279, 318 and 665 (d-d) nm. FT-IR peaks (\(\nu, \text{cm}^{-1}\)): 3093, 2952, 1654, 1597, 1421, 1190, 1140, 1030, 792, 685. Hamiltonian parameter in EPR, for frozen solution \(g_{\|}: 2.22; g_{\perp}: 2.06; A_{\|}: 165 \text{G}\). [UV-Vis: Fig. S42, ESI-MS: Fig. S44, FT-IR: Fig. S54b, EPR: Fig. S55]. \(\lambda_{\text{max}}\) for CuPT-1 in acetonitrile are 253, 260, 279, 318 and 330 nm; \(\lambda_{\text{max}}\) for CuPT-1 in methanol are 253, 259, 279, 318 and 330 nm (Fig. S47).

The UV-Vis peaks of Zn\(^{2+}\)/Cu\(^{2+}\)-peptoids are summarised below:

### Table S2. UV-Vis absorbance data of peptoid oligomers and it Zn\(^{2+}\)/Cu\(^{2+}\) complexes in water.

| SI No | Peptoid oligomers | \(\lambda_{\text{max}}\) (UV-Vis analysis for Zn\(^{2+}\) complex) | \(\lambda_{\text{max}}\) (UV-Vis analysis for Cu\(^{2+}\) complex) |
|-------|-------------------|-------------------------------------------------|-------------------------------------------------|
| 1     | PT-1              | 245, 267, 275, 310 and 322 nm                   | 253, 259, 279, 318, 329 and 665 (d-d) nm        |
| 2     | PT-1Ac            | 243, 267, 272, 309 and 321 nm                   | 241, 255, 266, 275, 315 and 327 nm             |
| 3     | PT-2              | 222, 243, 270, 310 and 322 nm                   | 220, 258, 277, 316 and 328 nm                  |
| 4     | PT-3              | 243, 274, 282, 309 and 322 nm                   | 258, 275, 316 and 328 nm                       |
| 5     | PT-4              | 243, 273, 284, 309 and 322 nm                   | 248, 274, 315 and 327 nm                       |
| 6     | PT-5              | 243, 266, 273, 309 and 322 nm                   | 257, 276, 303, 315 and 327 nm                  |
| 7     | PT-6              | 243, 268, 275, 309 and 321 nm                   | 258, 276, 316 and 328 nm                       |
| 8     | PT-7              | 243, 266, 274, 296, 309 and 321 nm              | 252, 276, 302, 316 and 328 nm                  |
| 9     | PT-8              | 243, 275, 313 and 322 nm                        | 250, 275, 315 and 328 nm                       |
| 10    | PD-1              | 243, 260, 266, 272, 309 and 322 nm              | 240, 268, 275, 315 and 328 nm                  |

**UV-Vis titration experiment for peptoids**

After recording the blank spectrum of water in 200-800 nm range, 10 \(\mu\)L of peptoids (5 mM stock solution) was added into 3mL of water, taken in a standard cuvette used for UV-Vis absorbance analysis to obtain a concentration of 16.61 \(\mu\)M, ~17 \(\mu\)M. Later Zn\(^{2+}\) and Cu\(^{2+}\) was titrated separately to obtain the absorbance of individual complexes for PT-1 by addition of 2 \(\mu\)L metal solution, 2 mM in water stock solution. It shows distinct change in 300-350 nm peak after one equivalent of metal ion addition,
suggesting 1:1 complexation (peptoid:metal). For further insight, ESI-MS of the metal ion titrated solution as obtained from UV-Vis titration was carried out which also shows 1:1 complexation (Fig. S25 and S26b).

**UV-Vis competition experiments**

The competition experiments of peptoids with metal ions (Cu$^{2+}$, Zn$^{2+}$) were carried out in water medium. The stock solution of peptoid and metal ions were prepared at 5 mM concentration. The UV-Vis of Zn$^{2+}$-peptoid and Cu$^{2+}$-peptoid complex shows signal at different wavelength for these two complexes. Now, a mixture for competition experiment was prepared. In an Eppendorf, 5 µL of Zn$^{2+}$ and 10 µL Cu$^{2+}$ (1:2 ratio) was taken and mixed. Later this mixture was added at-a-time to the cuvette containing the peptoid. Now the UV-Vis of the peptoid with the mixture of metal was recorded. The peak between 300-350 nm was mainly monitored which could show the nature of the complex formed in solution. Finally this solution was monitored by ESI-MS to confirm the complexation.

**Dissociation constants calculations**

The dissociation constants for Zn$^{2+}$ with the peptoids PT-1, PT-2 and PT-3) were measured by using UV-Vis spectroscopy following a competition method. The stock solution of the peptoids, EDTA and Zn$^{2+}$ were prepared at 5 mM concentration in water. For EDTA, the pH was maintained at 7 by adding NaOH (5 mM in water). In a typical competition experiment,[4] each peptoid (individually) and EDTA were mixed in a 1:1 ratio at 26.53 µM (15 µL 5 nM from each solution in 3 mL of water) in a UV-Vis cuvette and gradually titrated with Zn$^{2+}$ up to one equivalent as examined peptoids bind one equivalent of metal ion. The UV-Vis spectra was monitored at 300-350 nm range. Following the method reported by Wedd and Xiao et al, the slope between {([Peptoid]$_{tot}$/[Zn$^{2+}$-Peptoid])−1} and {([EDTA]$_{tot}$/[Zn$^{2+}$-EDTA])−1} was calculated. The value of the slope is equal to $K_{d\text{(Zn}^{2+}\text{-Peptoid)}}K_{a\text{(Zn}^{2+}\text{-EDTA)}}\alpha_{\text{(EDTA)}}$ where $K_{d\text{(Zn}^{2+}\text{-Peptoid)}}$ is the dissociation constant of Zn$^{2+}$-peptoid, $K_{a\text{(Zn}^{2+}\text{-EDTA)}}$ is the association constant of Zn$^{2+}$-EDTA complexation and $\alpha_{\text{(EDTA)}}$ is the pH correction factor for EDTA.

Table S3 is showing an example of how the slope was calculated for Zn$^{2+}$ competition with PT-1 and EDTA. Total concentration of PT-1 and EDTA were kept as 26.53 µM. The absorbance of EDTA free PT-1 (26.53 µM) titrated with Zn$^{2+}$ was used to calculate the unknown concentration of ZnPT-1 formed in presence of EDTA via Beer–Lambert law. The unknown concentration is referred here to Zn-Peptoid in Table S3, 5th column. Total metal ion concentration in each step is known and metal ions those didn’t bind with PT-1 will certainly bind with EDTA. So the concentration of Zn-EDTA could be calculated by subtracting the 5th column from the 2nd column. Now, {([Peptoid]$_{tot}$/[Zn$^{2+}$-Peptoid]) − 1} plotted in X
axis and \( \{[\text{EDTA}]_{\text{tot}}/[\text{Zn}^{2+}-\text{EDTA}] \} - 1 \) was plotted in Y axis. From trend-line option in MS Excel, the straight line was fitted without preset value of intercept. The straight line thus obtained provides the slope that is equal to \( K_{d(Zn^{2+}-\text{Peptoid})} K_{s(Zn^{2+}-\text{EDTA})} \alpha_{(EDTA)} \). Here \( K_{s(Zn^{2+}-\text{EDTA})} \) and \( \alpha_{(EDTA)} \) are known.\([5]\) So \( K_{d(Zn^{2+}-\text{Peptoid})} \) could be obtained.

The values are \( K_{d(Zn^{2+}-\text{Peptoid})} \) for PT-1: \( 1.85 \times 10^{-13} \) M; \( K_{d(Cu^{2+}-\text{Peptoid})} \) for PT-1: \( 2.2 \times 10^{-12} \) M; \( K_{d(Zn^{2+}-\text{Peptoid})} \) for PT-2: \( 2.65 \times 10^{-13} \) M; \( K_{d(Zn^{2+}-\text{Peptoid})} \) for PT-3: \( 4.5 \times 10^{-13} \) M.

Table S3. Competition experiment data of PT-1 and EDTA with Zn\(^{2+}\) via UV-Vis analysis in water.

| [Peptoid]\(_{\text{tot}}\) (µM) | [Zn\(^{2+}\)]\(_{\text{tot}}\) (µM) | [EDTA]\(_{\text{tot}}\) (µM) | Abs of (Peptoid+EDTA)-Zn\(^{2+}\) (µM) | [Zn-Peptoid] (µM) | [Zn-EDTA] (µM) | \([([\text{Peptoid}]_{\text{tot}}/[\text{Zn}^{2+}-\text{Peptoid}] - 1)\) | \([([\text{EDTA}]_{\text{tot}}/[\text{Zn}^{2+}-\text{EDTA}] - 1)\) |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 26.53           | 6.657798614    | 26.53          | 0.043          | 1.902654867    | 4.75513474    | 12.94367442   | 4.579232012    |
| 26.53           | 9.980033992    | 26.53          | 0.0564         | 2.495575221    | 7.484464699   | 9.630815603   | 2.544675681    |
| 26.53           | 13.29787234    | 26.53          | 0.071          | 3.14159292     | 10.15627942   | 7.444760563   | 1.612177049    |
| 26.53           | 16.61129568    | 26.53          | 0.086          | 3.805309735    | 12.80598595   | 5.971837209   | 1.071687421    |
| 26.53           | 19.92031873    | 26.53          | 0.102          | 4.513274336    | 15.40704439   | 4.878215686   | 0.72193961     |
| 26.53           | 23.22495023    | 26.53          | 0.118          | 5.221238938    | 18.00371129   | 4.081169492   | 0.473585061    |
| 26.53           | 26.52519894    | 26.53          | 0.138          | 6.10619469     | 20.41900425   | 3.344768116   | 0.299279812    |

**Protein sample preparation**

PYKCPeciGKSFSQKSDLVKHQRSTHTG (Apo-ZFP) was purchased from PSL, GmbH (Heidelberg, Germany) and used without further purification. It was dissolved in NH\(_4\)OAc buffer (pH 6.5) (1 mM). The disulfide bonds were reduced using dithiothreitol (DTT). CD (circular dichroism) scans was performed at room temperature at concentration of 100µM in buffer solution. The spectra were obtained by averaging four scans per sample in a fused quartz cell (path length = 0.1 cm), over the 370 to 190 nm region at a step of 1 nm (scan rate=1 sec/step). CD scans of Apo-ZFP was measured first followed by stoichiometric addition of Zn\(^{2+}\) with an aim to make Zn-ZFP.\([6]\) The CD of Zn\(^{2+}\) added Apo-ZFP was measured which is same with Zn-ZFP.\([7]\) Chelator (PT-1) was added to the prepared Zn-ZFP in 1:1 equivalent of Zn\(^{2+}\) and CD was measured. In each step along with CD the ESI-MS was also executed which confirms the chelation of Zn\(^{2+}\) (Fig. S60-62). Similar experiment was repeated in SBF medium as well. Identical results have been obtained that suggest the ability of the chelator to bind Zn\(^{2+}\) from protein domain in biological like medium.
**DFT analysis**

The peptoid (PT-1) was optimized by DFT-D3 calculations (considering the dispersion correction) at the level of B3-LYP with def2-SVP for every atoms and COSMO for acetonitrile, using Turbomole software package (OS: MACOSX, V 7.3). The coordinates are directly taken from the CIF (CCDC number 1922716, Fig. S1).\(^8\) Bipyridine group was replaced with terpyridine, the terpyridine CIF was taken from CCDC 263509.\(^9\) After optimizing the PT-1 geometry, the coordinate was taken and metal ions were added with a suggested coordination: (a) terpyridine provides three, (b) picolyl pyridine provides one and (c) acetate provides two for ZnPT-1 and (d) acetate provides one coordination for CuPT-1. Acetate group was taken from acetic acid CIF (database identifier: ACETAC07, deposition number: 131006). The geometries are optimized at the level of DFT-D4 where def2-TZVP for metal ions \([\text{Cu}^{2+}/\text{Zn}^{2+}]\) + def2SVP (C, H, N, O) were used with COSMO for water.

**Figures**

![Figure S1](image_url)

**Figure S1.** (a) Asymmetric unit of the crystal with CCDC number 1922716\(^8\) (color code: red: oxygen, blue: nitrogen, white: hydrogen, grey: carbon, brown: Cu\(^{2+}\)). (b) The chem draw structure of the peptoid in this crystal is shown.
Figure S2. Peptoid oligomers for designing Zn\textsuperscript{2+} chelator; a) achiral and chiral (color choice arbitrary) monomeric units used in the design of the peptoids. b) Chemical sequences of peptoids (PT-1-7 and PD-1) utilised as chelator in this work.
Figure S3. HPLC traces of pure peptoid PT-1.

Figure S4. HPLC traces of pure peptoid PT-1Ac.
**Figure S5.** HPLC traces of pure peptoid PT-2.

**Figure S6.** HPLC traces of pure peptoid PT-3.
Figure S7. HPLC traces of pure peptoid PT-4.

Figure S8. HPLC traces of pure peptoid PT-5.
Figure S9. HPLC traces of pure peptoid PT-6.

Figure S10. HPLC traces of pure peptoid PT-7.
Figure S11. HPLC traces of pure peptoid PT-8.

Figure S12. HPLC traces of pure peptoid PD-1.
Figure S13. ESI-MS of PT-1 in water.

Figure S14. ESI-MS of PT-1Ac in water.

Figure S15. ESI-MS of PT-2 in water.

Figure S16. ESI-MS of PT-3 in water.
Figure S17. ESI-MS of PT-4 in water.

Figure S18. ESI-MS of PT-5 in water.

Figure S19. ESI-MS of PT-6 in water.

Figure S20. ESI-MS of PT-7 in water.
Figure S21. ESI-MS of PT-8 in water.

Figure S22. ESI-MS of PD-1 in water.

Figure S23. (a) UV-Vis spectrum of Terpyridine (Terpy), 2-picoly amine (NPam) and PT-1. Terpy and NPam are in acetonitrile medium and PT-1 is in water (8 µM); (b) UV-Vis titration spectra of PT-1 with Cu²⁺ (17 µM of peptoid, solvent: water titrated with 2µL each time Cu²⁺, stock solution 2 mM in water).
Figure S24. Competition experiment between Zn$^{2+}$ and Cu$^{2+}$ with peptoids (a) PT-1; (b) PD-1; (c) PT-2 and (d) PT-3; (solvent: water, 8 µM). [For PT-1 in Fig. a, Black: PT-1; Red: ZnPT-1 Blue: CuPT-1 Green: 1:4 (Zn$^{2+}$:Cu$^{2+}$). For PD-1 in Fig. b, Red: PD-1; Green: Zn$^{2+}$ - PD-1; Black: Cu$^{2+}$ - PD-1; Violet: 1:2 (Zn$^{2+}$:Cu$^{2+}$). For PT-2 in Fig. c, Red: PT-2; Black: Zn$^{2+}$ - PT-2; Blue: Cu$^{2+}$ - PT-2; Green: 1:2 (Zn$^{2+}$:Cu$^{2+}$). For PT-3 in Fig. d, Red: PT-3; Black: Zn$^{2+}$ - PT-3; Blue: Cu$^{2+}$ - PT-3; Cyan: 1:2 (Zn$^{2+}$:Cu$^{2+}$)].
**Figure S25.** ESI-MS of the aliquot taken from UV-Vis titration of PT-1 with Zn$^{2+}$:Cu$^{2+}$ (1:2) in water (8 µM), could be assigned to [(PT-1)+Zn$^{2+}$+OAc$^-_{}$], calculated mass with chemical formula C$_{38}$H$_{39}$N$_8$O$_6$Zn is 767.23. [Above: Simulated spectrum, below: experimental spectrum].
Figure S26. ESI-MS of the aliquot taken from UV-Vis titration of PT-1 with (a) Zn<sup>2+</sup>:Cu<sup>2+</sup> (1:3) {calculated mass for (PT-1+Zn<sup>2+</sup>+OAc<sup>-</sup>).3H<sub>2</sub>O is 821.26; (PT-1+Cu<sup>2+</sup>+OAc<sup>-</sup>+K<sup>+</sup>) is 805.19} (b) Zn<sup>2+</sup>:Cu<sup>2+</sup> (1:4) in water (8 µM), could be assigned to [(PT-1)+Cu<sup>2+</sup>+OAc<sup>-</sup>+K<sup>+</sup>] calculated mass is 805.19. [Above: Simulated spectrum, below: experimental spectrum for Fig. S26b].
Figure S27. UV-Vis of (a) PD-1, (b) PT-2 and (c) PT-3 with Cu$^{2+}$ and Zn$^{2+}$ (8 µM, solvent: water).

Figure S28. ESI-MS of the aliquot taken from UV-Vis titration of PD-1 with Zn$^{2+}$:Cu$^{2+}$ (1:2) in water (8 µM), could be assigned to [(PD-1)+Cu$^{2+}$+(H$_2$O)]. [Above: Simulated spectrum, below: experimental spectrum].
Figure S29. ESI-MS of the aliquot taken from UV-Vis titration of PT-2 with Zn$^{2+}$:Cu$^{2+}$ (1:2) in water (8 µM), could be assigned to [(PT-2)+Cu$^{2+}$+H$_2$O]. H$_2$O. [Above: Simulated spectrum, below: experimental spectrum].

Figure S30. ESI-MS of the aliquot taken from UV-Vis titration of PT-3 with Zn$^{2+}$:Cu$^{2+}$ (1:2) in water (8 µM), could be assigned to [(PT-3)+Cu$^{2+}$+H$_2$O]. H$_2$O. [Above: Simulated spectrum, below: experimental spectrum].
Figure S31. Dissociation constant calculation for (a) PT-1, (b) PT-2, (c) PT-3 by competition with EDTA for Zn$^{2+}$ and (d) PT-1 by competition with EDTA for Cu$^{2+}$ (solvent: water, see experimental section above for details).
Figure S32. UV-Vis of (a) PT-4, (b) PT-5, (c) PT-6, and (d) PT-7 with Cu^{2+} and Zn^{2+} (8 µM, solvent: water).
Figure S33. Competition experiment between Zn$^{2+}$ and Cu$^{2+}$ with peptoids (a) PT-4; (b) PT-5; (c) PT-6 and (d) PT-7; (solvent: water, 8 µM). [For PT-4 in Fig. a, Red: PT-4; Black: Zn$^{2+}$ - PT-4; Blue: Cu$^{2+}$ - PT-4; Cyan: 1:2 (Zn$^{2+}$:Cu$^{2+}$). For PT-5 in Fig. b, Red: PT-5; Blue: Zn$^{2+}$ - PT-5; Black: Cu$^{2+}$ - PT-5; Green: 1:2 (Zn$^{2+}$:Cu$^{2+}$). For PT-6 in Fig. c, Red: PT-6; Black: Zn$^{2+}$ - PT-6; Blue: Cu$^{2+}$ - PT-6; Green: 1:2 (Zn$^{2+}$:Cu$^{2+}$). For PT-7 in Fig. d, Black: PT-7; Blue: Zn$^{2+}$ - PT-7; Red: Cu$^{2+}$ - PT-7; Green: 1:2 (Zn$^{2+}$:Cu$^{2+}$).]
Figure S34. ESI-MS of the aliquot taken from UV-Vis titration of PT-4 with Zn\(^{2+}\):Cu\(^{2+}\) (1:2) in water (8 µM), could be assigned to [(PT-4)+Cu\(^{2+}\)+(OAc\(^{-}\))+K\(^{+}\)]. [Above: Simulated spectrum, below: experimental spectrum].

Figure S35. ESI-MS of the aliquot taken from UV-Vis titration of PT-5 with Zn\(^{2+}\):Cu\(^{2+}\) (1:2) in water (8 µM), could be assigned to [(PT-5)+Cu\(^{2+}\)+H\(_{2}\)O]. H\(_{2}\)O. [Above: Simulated spectrum, below: experimental spectrum].
Figure S36. ESI-MS of the aliquot taken from UV-Vis titration of PT-6 with Zn²⁺:Cu²⁺ (1:2) in water (8 µM), could be assigned to [(PT-6)+Cu²⁺+H₂O].H₂O. [Above: Simulated spectrum, below: experimental spectrum].

Figure S37. ESI-MS of the aliquot taken from UV-Vis titration of PT-7 with Zn²⁺:Cu²⁺ (1:2) in water (8 µM), could be assigned to [(PT-7)+Cu²⁺+OAc⁻+Na⁺]. [Above: Simulated spectrum, below: experimental spectrum].
Figure S38. UV-Vis spectra of (a) PT-1Ac, (b) PT-8 and (c) Terpy and Npam mixture with Cu²⁺ (blue) and Zn²⁺ (red) (d) competition experiment between Zn²⁺ and Cu²⁺ with Terpy and Npam (8 µM, solvent: water for a-b and acetonitrile for c-d).
Figure S39. ESI-MS of the aliquot taken from UV-Vis titration of PT-8 with Zn^{2+}:Cu^{2+} (1:2) in water (8 µM), could be assigned to [(PT-8)+Cu^{2+}+(H_2O)_2]. [Top: simulated, bottom: experimental spectrum].

Figure S40. ESI-MS of the aliquot taken from UV-Vis titration of PT-1Ac with Zn^{2+}:Cu^{2+} (1:2) in water
(8 µM), could be assigned to \([(\text{PT-1Ac})+\text{Cu}^{2+}+\text{H}_2\text{O}].\text{H}_2\text{O}\). [Top: simulated spectrum, below: experimental spectrum].

**Figure S41.** UV-Vis spectrum of ZnPT-1 complex in water (17 µM).

**Figure S42.** UV-Vis spectrum of CuPT-1 complex in water (17 µM), inset shows d-d transition.
Figure S43. ESI-MS of ZnPT-1 complex in water, could be assigned to [(PT-1)+Zn\(^{2+}\)+(OAc\(^{-}\)]\(^{\,+}\). [Top: Simulated spectrum, bottom: experimental spectrum].

Figure S44. ESI-MS of CuPT-1 complex in water, could be assigned to [(PT-1)+Cu\(^{2+}\)+OAc\(^{-}\)+K\(^+\)]. [Top: Simulated spectrum, below: experimental spectrum].
Figure S45. UV-Vis spectrum of ZnPT-1 complex synthesis in water (a) room temperature, (b) 35°C and (c) 50°C (17 µM).

Figure S46. UV-Vis spectrum of CuPT-1 complex synthesis in water (a) room temperature, (b) 35°C and (c) 50°C (17 µM).

Figure S47. UV-Vis spectrum of Zn²⁺/Cu²⁺PT-1 complex in (a) acetonitrile and (b) methanol (17 µM); [black: ZnPT-1 complex in water, red: ZnPT-1 complex in acetonitrile/methanol, blue: CuPT-1 complex in water, cyan: CuPT-1 complex in acetonitrile/methanol].

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Figure S48. ESI-MS of PT-9 in acetonitrile.

Figure S49. $^1$H-NMR (in 400MHz) chemical shift of PT-9 ($C_9H_{18}N_4O_3$) in CD$_3$CN.
Figure S50. $^1$H-NMR (in 400MHz) chemical shift of benzyl amine monomer (Npm) in CD$_3$CN.

Figure S51. $^1$H-NMR chemical shift of terpy (as a surrogate of Netp, the monomer used in synthesis) in CD$_3$CN.
Figure S52. $^1$H-NMR (in 400MHz) chemical shift of 2-picolyl amine monomer (Npam) in CD$_3$CN.
Figure S53. $^1$H-NMR (in 400MHz) chemical shift of (a) PT-1 (C$_{36}$H$_{36}$N$_8$O$_4$) and (b) ZnPT-1 in CD$_3$CN. Chemical shift of Npm assigned near the range of 7-7.5 ppm with less acidic protons of Netp and Npam group (see Fig. S50-52), protons adjacent to pyridine groups assigned at more downfield region near 9.30 ppm. Chemical shift of other protons expected to be similar as obtained with the monomer (see Fig. S50-52). The downfield shifting expected due to coordination with Zn$^{2+}$ ion.$^{[10]}$
Figure S54. Solid phase FT-IR of (a) PT-1 (red), (b) CuPT-1 (black), (c) ZnPT-1 (blue line, obtained from the complex synthesis in water medium) and (d) ZnPT-1 (orange line, obtained after evaporating the CD$_3$CN in NMR analysis), (e) overlaid spectra of PT-1 and ZnPT-1 (as obtained after CD$_3$CN evaporation).
Figure S55. X-band EPR spectra of CuPT-1 in water (frozen solution), red: simulated and blue: experimental spectrum. Hamiltonian parameter $g_{ll}$: 2.22; $g_{ll}$: 2.06; $A_{ll}$: 165G.
Peptoid is electron-donating scaffold\textsuperscript{[11]} that would help in increasing the HOMO-LUMO gap.\textsuperscript{[12]} Zn\textsuperscript{2+} and Cu\textsuperscript{2+} have different electronic configuration, i.e.; d\textsuperscript{10} and d\textsuperscript{9} respectively. The d orbital available for interaction with ligand centre is fully occupied for Zn\textsuperscript{2+} and by one electron for Cu\textsuperscript{2+}. Thus interaction strength of Cu\textsuperscript{2+} with the ligand will be higher than Zn\textsuperscript{2+}.\textsuperscript{[13]} Electron density in HOMO-LUMO orbital shows contribution of the picolyl moiety and peptoid backbone in HOMO and terpyridine in LUMO. Complexation makes lowering the HOMO-LUMO energy (Fig. S56). The LUMO of CuPT-1 is more stabilized than the LUMO of ZnPT-1. Indeed, due to higher interaction energy equatorial ligation of Cu\textsuperscript{2+} with nitrogen of terpyridine and oxygen of acetate ion is stronger that results in shortening the bond distance for Cu-terpyridine than Zn terpyridine in ZnPT-1. The bond distances are as follows: For CuPT-1, Cu49-N46, Cu49-N47, Cu49-N48 and Cu49-O52 are 2.073, 1.958, 2.088 and 1.947Å (see Fig. 6b for atom numbering). For ZnPT-1, Zn49-N46, Zn49-N47, Zn49-N48 and Zn49-O52 are 2.181, 2.080, 2.213 and 2.038 Å (Fig. 6a for atom numbering). The strong interaction stabilized the LUMO of CuPT-1.

In case of HOMO, Cu\textsuperscript{2+} offers d\textsubscript{z}\textsuperscript{2} orbital (Fig. S56c),\textsuperscript{[14]} which interacts with picolyl nitrogen and eventually raise the energy.\textsuperscript{[15]} Because of the axial interaction, the bond distance is higher in CuPT-1, i.e.; 2.371Å (Cu49-N22) than ZnPT-1, i.e.; 2.176Å (Zn49-N22). Strong interaction makes a better stabilization of ZnPT-1 HOMO, whereas weak interaction leads to a possible destabilization of CuPT-1 HOMO.\textsuperscript{[16]} Lowering the LUMO energy and increasing the HOMO energy for CuPT-1 decreases the HOMO-LUMO gap in comparison with ZnPT-1 and thus makes the ZnPT-1 more stable than CuPT-1. Rational designing of the peptoid scaffold with proper structure directing group might help the peptoid to offer the metal ion to place the picolyl group in axial position, which in turn resulted in a discrimination in interaction eventually the stability.

![Image of HOMO-LUMO for (a) PT-1, (b) ZnPT-1 and (c) CuPT-1](image-url)

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Figure S57. UV-Vis of the PT-1 with (a) Ca$^{2+}$, (b) K$^+$, (c) Mg$^{2+}$, (d) Na$^+$, (e) Fe$^{3+}$, in water, 8 µM, titration was carried out by gradually adding metal ions 2µL each time. Stock solution of PT-1 and metal ions are 5mM in water. In fig. e., the overlaid absorbance spectra of Fe(ClO$_4$)$_3$·2H$_2$O with chelator PT-1 (solid line) and without PT-1 (dashed green line), indicating that the observed rise in the absorption titration spectra in presence of ligands is due to the absorption of the iron salt and not due to binding of the chelator to Fe$^{3+}$, as reported in literature.$^{[17]}

Figure S58. (a) UV-Vis of the PT-1 (purple), ZnPT-1 (blue) and CuPT-1 (black) in SBF (simulated body fluid) (6 µM), reveals that chelator PT-1 is working perfectly in SBF, a biological like medium; (b) ZnPT-1 complex solubilized in SBF at 37°C and monitored for 24 hours (17 µM).
Figure S59. UV-Vis of the PT-1 (red), ZnPT-1 (black) and competition in varying ratio of metal ions (purple and blue, see inset) in simulated body fluid (6 μM).

Figure S60. ESI-MS of Zinc finger protein (PYKCPECGKSFSQKSDLVHKQRTHTG) in 3+ charge. [Above: Simulated spectrum, below: experimental spectrum].
Figure S61. (a) ESI-MS of PT-1 added Zn-ZF solution; it shows the formation of ZnPT-1 complex (b) expanded view of the same ESI-MS file shows the presence of Apo-ZF in 3+ charge. [Top: Simulated spectrum, bottom: experimental spectrum].
Figure S62. CD spectra of Apo-ZF (red line), Zn-ZF (blue line) and Zn²⁺ chelated ZF (green line) in acetate buffer (pH 6.5).

Table S4. Coordinates of PT-1.

| total energy: -2129.91304869579 Hartree |
|-----------------------------------------|
| C  9.0373210  6.8370819    2.5545684   |
| C  10.3187623  6.6881271    3.0837788   |
| C  10.9599853  7.8274421    3.5793465   |
| C  10.3035310  9.0526687    3.5164519   |
| C  9.0184681   9.1044549    2.9533527   |
| C  8.2703886   10.4192118   2.9045022   |
| C  6.1944419   11.5223508   2.3144937   |
| C  5.6108753   11.8001891   3.7100857   |
| C  6.1679948   14.2127279   3.4728946   |
| C  7.6960869   14.3536776   3.3730844   |
| C  7.7385211   15.5119377   5.5775021   |
| C  9.7719367   15.3342673   4.1306527   |
| C  10.6320002  14.2113819   4.7232611   |
|   |       |       |       |
|---|-------|-------|-------|
| C | 4.8494358 | 13.3500395 | 5.4268025 |
| C | 5.2423114  | 12.6500761 | 6.7276394 |
| N | 8.4007874  | 8.0134273  | 2.4875527 |
| N | 6.9880437  | 10.3146508 | 2.2347218 |
| N | 5.6718257  | 13.0627902 | 4.2404423 |
| N | 8.3472412  | 15.0650218 | 4.3266817 |
| N | 10.6899806 | 13.0924974 | 3.9730079 |
| O | 5.0540195  | 10.8870360 | 4.3195729 |
| O | 6.6296152  | 12.8122837 | 7.0300457 |
| O | 8.3000116  | 13.8768855 | 2.4060593 |
| O | 11.1837080 | 14.3432633 | 5.8135220 |
| N | 12.0313908 | 11.1216986 | 5.8093411 |
| N | 9.4800951  | 9.8395714  | 6.4498622 |
| N | 8.6720966  | 7.1683690  | 6.2812828 |
| C | 13.3406509 | 11.3860504 | 5.8677112 |
| C | 13.9627174 | 11.9253478 | 6.9964285 |
| C | 13.1732839 | 12.2129832 | 8.1118665 |
| C | 11.8049249 | 11.9474131 | 8.0542912 |
| C | 11.2727801 | 11.3949842 | 6.8826684 |
| C | 9.8118456  | 11.0988185 | 6.7660180 |
| C | 8.8751256  | 12.1174579 | 6.9674390 |
| C | 7.5132459  | 11.0871166 | 6.8332168 |
| C | 7.1647703  | 10.4888189 | 6.5257334 |
| C | 8.1805492  | 9.5425311  | 6.3286909 |
| C | 7.8152688  | 8.1456300  | 5.9454217 |
| C | 6.6172724  | 7.8846611  | 5.2555060 |
| C | 6.3024818  | 6.5676065  | 4.9245240 |
| C | 7.1899046  | 5.5524251  | 5.2832703 |
| C | 8.3628855  | 5.9121003  | 5.9548365 |
|   |   |   |   |
|---|---|---|---|
| H | 8.4927654 | 5.9642315 | 2.1761688 |
| H | 10.7911724 | 5.7041211 | 3.1213932 |
| H | 11.9550415 | 7.7596193 | 4.0266875 |
| H | 10.7693506 | 9.9425211 | 3.9413953 |
| H | 8.8895625 | 10.1627714 | 2.3733587 |
| H | 8.1936335 | 10.8002017 | 3.9466173 |
| H | 6.7950712 | 12.3560571 | 1.9383716 |
| H | 5.3105367 | 11.4242279 | 1.6585283 |
| H | 5.7401006 | 15.1177076 | 3.9159642 |
| H | 5.8070490 | 14.1755107 | 2.4369141 |
| H | 8.5653511 | 15.6859149 | 6.2830545 |
| H | 7.1609018 | 14.6947066 | 6.0238118 |
| H | 10.0288011 | 16.2674333 | 4.6449961 |
| H | 9.9636059 | 15.4429185 | 3.0550491 |
| H | 3.8000559 | 13.0739281 | 5.2251195 |
| H | 4.8725982 | 14.4359677 | 5.5792024 |
| H | 4.6865929 | 13.1276240 | 7.5481956 |
| H | 4.9621473 | 11.5945376 | 6.6966627 |
| H | 6.4772541 | 9.5078675 | 2.5904238 |
| H | 11.1447383 | 12.2613838 | 4.3596597 |
| H | 10.1273419 | 13.0344596 | 3.1280749 |
| H | 13.9238242 | 11.1662593 | 4.9665030 |
| H | 15.0374233 | 12.1190010 | 6.9934958 |
| H | 13.6172594 | 12.6389832 | 9.0151001 |
| H | 11.1537367 | 12.1581205 | 8.9047707 |
| H | 9.1960337 | 13.1339371 | 7.1947728 |
| H | 6.1293670 | 10.1892900 | 6.4145007 |
| H | 5.9633499 | 8.7032223 | 4.9500136 |
| H | 5.3831778 | 6.3411336 | 4.3788711 |
|   |          |          |          |
|---|----------|----------|----------|
| H | 6.9899070 | 4.5062806 | 5.0418038 |
| H | 9.0865968 | 5.1395427 | 6.2413261 |
| C | 6.8937872 | 16.7659053| 5.4714765 |
| C | 7.0211956 | 17.6619839| 4.4021866 |
| C | 6.2367076 | 18.8195774| 4.3499948 |
| C | 5.3159270 | 19.0928338| 5.3663228 |
| C | 5.1813600 | 18.2001840| 6.4361788 |
| C | 5.9645912 | 17.0440133| 6.4861940 |
| H | 7.7298022 | 17.4515563| 3.5977858 |
| H | 6.3455293 | 19.5089946| 3.5088051 |
| H | 4.7009893 | 19.9953095| 5.3232089 |
| H | 4.4594193 | 18.4015897| 7.2317481 |
| H | 5.8537533 | 16.3477708| 7.3228890 |

**Table S5.** Coordinates of ZnPT-1.

total energy: -4137.48324721934 Hartree
|     | X     | Y     | Z     |
|-----|-------|-------|-------|
| C   | 8.5510389 | 16.0580308 | 1.1721683 |
| C   | 7.2202678  | 16.1752765 | 0.7529972  |
| C   | 6.2751377  | 16.7482681 | 1.6092551  |
| C   | 6.6576697  | 17.1907081 | 2.8804458  |
| C   | 10.6918633 | 16.7193307 | 5.3325128  |
| C   | 11.4358741 | 16.6763074 | 6.6680735  |
| C   | 6.6104095  | 12.9878043 | 7.1452142  |
| C   | 7.6996143  | 12.2391054 | 7.9118013  |
| N   | 9.8070999  | 10.2250729 | 0.9384671  |
| N   | 7.5180179  | 12.7804723 | 2.3106583  |
| N   | 7.0188668  | 13.6363703 | 5.8974320  |
| N   | 9.2436890  | 16.5552119 | 5.4149582  |
| N   | 10.7956742 | 17.2188014 | 7.7184944  |
| O   | 6.6411558  | 11.7316604 | 4.7182769  |
| O   | 7.9233610  | 10.9153785 | 7.3970829  |
| O   | 9.6043772  | 14.5690283 | 6.4149919  |
| O   | 12.574694  | 16.2237338 | 6.7189255  |
| C   | 13.0227045 | 12.3752000 | 2.4714502  |
| C   | 13.5566816 | 13.5441443 | 3.0193118  |
| C   | 13.0840975 | 13.9711133 | 4.2613121  |
| C   | 12.1011486 | 13.2218945 | 4.9123975  |
| C   | 11.620351  | 12.0625472 | 4.2988816  |
| C   | 10.5817370 | 11.1854047 | 4.9069223  |
| C   | 9.7769936  | 11.5667722 | 5.9770951  |
| C   | 8.7968073  | 10.6634027 | 6.4213721  |
| C   | 8.7007928  | 9.3967642  | 5.8128628  |
| C   | 9.5329412  | 9.1092921  | 4.7379994  |
| C   | 9.4930586  | 7.8442782  | 3.9531249  |
| C   | 8.7358673  | 6.7305146  | 4.3288932  |
C  8.7843491  5.5847561  3.5326905
C  9.5859421  5.5800792  2.3896020
C 10.3071964  6.7351425  2.0826466
N 12.0822574 11.6628470  3.0958752
N 10.4358371 10.0011465  4.3063483
N 10.2539841  7.8302786  2.8420925
Zn 11.3068388  9.7340334  2.4360711
C 14.8422000  8.0622823  1.3877848
C 13.5676337  8.6588825  1.9393014
O 12.7127049  9.1185296  1.0952130
O 13.3463456  8.7126212  3.1662650
H 15.4012080  8.8381584  0.8405859
H  9.1392707  8.8079326 -2.0554704
H  7.0086831 10.1338449 -1.7450587
H  6.7602982 11.5266239  0.3321142
H  9.5839790 12.2692356  2.5150598
H  8.4060992 11.1383801  3.2025980
H  8.4581454 14.0847416  3.7141393
H  6.7933414 14.4675534  3.2732020
H  6.8713813 15.5085627  6.8044694
H  6.8137142 15.5481926  5.0534582
H  8.9099141 18.4646369  4.6799431
H  7.4687447 17.6931436  5.3129080
H  9.9703920 16.3957376  2.7519732
H  9.2987353 15.6192332  0.5064812
H  6.9227205 15.8232009 -0.2378313
H  5.2336432 16.8431118  1.2925871
H  5.9094176 17.6226849  3.5508981
H 10.9035151 17.6900968  4.8632938
Table S6. Coordinates of CuPT-1.

| Atom | X   | Y   | Z    |
|------|-----|-----|------|
| H    | 11.1416484 | 15.9364525 | 4.7066453 |
| H    | 5.7924009   | 12.2863226 | 6.9266290 |
| H    | 6.2173319   | 13.7675106 | 7.8127967 |
| H    | 8.6311633   | 12.8190797 | 7.9526618 |
| H    | 7.3460885   | 12.0744599 | 8.9386777 |
| H    | 7.6224134   | 13.3843708 | 1.4958042 |
| H    | 11.2341876  | 17.2111383 | 8.6339046 |
| H    | 9.8401306   | 17.5475307 | 7.6457208 |
| H    | 13.3573180  | 11.9951801 | 1.5022275 |
| H    | 14.3240775  | 14.0999676 | 2.4782768 |
| H    | 13.4598924  | 14.8788661 | 4.7385445 |
| H    | 11.7170573   | 13.5488768 | 5.8764883 |
| H    | 9.8530941   | 12.5687111 | 6.3893129 |
| H    | 7.9387217   | 8.7020885 | 6.1626366 |
| H    | 8.1252263   | 6.7491902 | 5.2315115 |
| H    | 8.2033424   | 4.7019466 | 3.8079637 |
| H    | 9.6554904   | 4.7027130 | 1.7447240 |
| H    | 10.9517864  | 6.7856636 | 1.2008788 |
| H    | 10.8779850  | 8.9210026 | -0.2600840 |
| H    | 14.5965060  | 7.2693560 | 0.6643931 |
| H    | 15.4693981   | 7.6553204 | 2.1910972 |

total energy: -3998.58066618600 Hartree
|   | C   | 8.5459190 | 11.7953912 | 2.4514853 |
|---|-----|-----------|------------|-----------|
| C | 7.4245300 | 13.6372700 | 3.5503049 |
| C | 6.9791416 | 12.9394371 | 4.8337292 |
| C | 7.3498958 | 15.1102009 | 5.9476252 |
| C | 8.8506553 | 15.4124697 | 5.8912187 |
| C | 8.3518516 | 17.5367316 | 4.6814906 |
| C | 7.8864149 | 17.0819374 | 3.3098874 |
| C | 8.7808388 | 16.5120122 | 2.3903006 |
| C | 8.3307240 | 16.0514811 | 1.1504049 |
| C | 6.9771037 | 16.1583722 | 0.8088958 |
| C | 6.0811051 | 16.7374861 | 1.7124887 |
| C | 6.5352765 | 17.1956544 | 2.9541939 |
| C | 10.7014661 | 16.7484094 | 5.1797229 |
| C | 11.5162754 | 16.7289362 | 6.4737203 |
| C | 6.6871074 | 13.0584762 | 7.2508729 |
| C | 7.7954287 | 12.2957863 | 7.9732998 |
| N | 9.7569727 | 10.1998188 | 1.0752064 |
| N | 7.4596911 | 12.7572365 | 2.4044541 |
| N | 7.0550533 | 13.6869513 | 5.9808737 |
| N | 9.2597674 | 16.5897841 | 5.3434438 |
| N | 10.9341147 | 17.2921768 | 7.5465404 |
| O | 6.6154784 | 11.7692744 | 4.8469023 |
| O | 7.9872693 | 10.9730917 | 7.4406208 |
| O | 9.6665646 | 14.6161560 | 6.3523026 |
| O | 12.6579305 | 16.2733709 | 6.4716611 |
| C | 13.1865727 | 12.1384812 | 2.5193495 |
| C | 13.6850877 | 13.3680871 | 2.9580461 |
| C | 13.1502809 | 13.9304041 | 4.1179124 |
| C | 12.1350920 | 13.2548253 | 4.8006173 |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 11.6894354 | 12.0307983 | 4.3017243 |
| C       | 10.6293382 | 11.2085673 | 4.9334880 |
| C       | 9.8264675  | 11.6061897 | 5.9966080 |
| C       | 8.8432056  | 10.7106234 | 6.4556935 |
| C       | 8.7321189  | 9.4359273  | 5.8604312 |
| C       | 9.5609292  | 9.1273032  | 4.7914040 |
| C       | 9.5560344  | 7.8643029  | 4.0144509 |
| C       | 8.7420109  | 6.7687192  | 4.3043911 |
| C       | 8.8427814  | 5.6269743  | 3.5059890 |
| C       | 9.7494600  | 5.6117675  | 2.4450702 |
| C       | 10.5254507 | 6.7493025  | 2.2145194 |
| N       | 12.2207220 | 11.4954282 | 3.1771243 |
| N       | 10.4670822 | 10.0148048 | 4.3523398 |
| Cu      | 11.4161441 | 9.6512642  | 2.6782342 |
| C       | 14.7697250 | 8.1011237  | 0.9007966 |
| C       | 13.6861050 | 8.5885060  | 1.8421382 |
| O       | 12.6512427 | 9.1191328  | 1.2701173 |
| O       | 13.7917319 | 8.4851746  | 3.0703974 |
| H       | 15.1413093 | 8.9434658  | 0.2958775 |
| H       | 9.0291429  | 8.6104936  | -1.8183525 |
| H       | 6.8641217  | 9.8746835  | -1.4935121 |
| H       | 6.6420412  | 11.3649452 | 0.5218711 |
| H       | 9.5386816  | 12.2746835 | 2.5746317 |
| H       | 8.3882454  | 11.1631163 | 3.3362708 |
| H       | 8.4070581  | 14.1138575 | 3.7494409 |
| H       | 6.7269327  | 14.4606758 | 3.3368800 |
| H       | 6.9586972  | 15.5728553 | 6.8664068 |
| H       | 6.8142253  | 15.5862507 | 5.1195583 |

52 | Supporting Information
|   | 1st Column | 2nd Column | 3rd Column |
|---|------------|------------|------------|
| H | 8.8917035  | 18.4919196 | 4.6055446  |
| H | 7.4857506  | 17.7338270 | 5.3278376  |
| H | 9.8387444  | 16.4130487 | 2.6399808  |
| H | 9.0404311  | 15.6082594 | 0.4472070  |
| H | 6.6235903  | 15.7931545 | -0.1585496 |
| H | 5.0224373  | 16.8248334 | 1.4563030  |
| H | 5.8255011  | 17.6323837 | 3.6624380  |
| H | 10.8888125 | 17.7101318 | 4.6823003  |
| H | 11.1162101 | 15.9545080 | 4.5429895  |
| H | 5.8465829  | 12.3715422 | 7.0754574  |
| H | 6.3403146  | 13.8507889 | 7.9290381  |
| H | 8.7338223  | 12.8658563 | 7.9832127  |
| H | 7.4788938  | 12.1272996 | 9.0115169  |
| H | 7.5378351  | 13.3352406 | 1.5684197  |
| H | 11.4217793 | 17.3020302 | 8.4367419  |
| H | 9.9772233  | 17.6235757 | 7.5187591  |
| H | 13.5660076 | 11.6510925 | 1.6178977  |
| H | 14.4774497 | 13.8646068 | 2.3959523  |
| H | 13.5028481 | 14.8876662 | 4.5086251  |
| H | 11.6966249 | 13.6863560 | 5.6987586  |
| H | 9.9157242  | 12.6101917 | 6.4022890  |
| H | 7.9733911  | 8.7455129  | 6.2262149  |
| H | 8.0433964  | 6.8018851  | 5.1405802  |
| H | 8.2172815  | 4.7565845  | 3.7146514  |
| H | 9.8592862  | 4.7376906  | 1.8015251  |
| H | 11.2469241 | 6.7949515  | 1.3955460  |
| H | 10.8315594 | 8.8824456  | -0.0961981 |
| H | 14.3500912 | 7.3610258  | 0.2013514  |
| H | 15.6006045 | 7.6537060  | 1.4615580  |
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