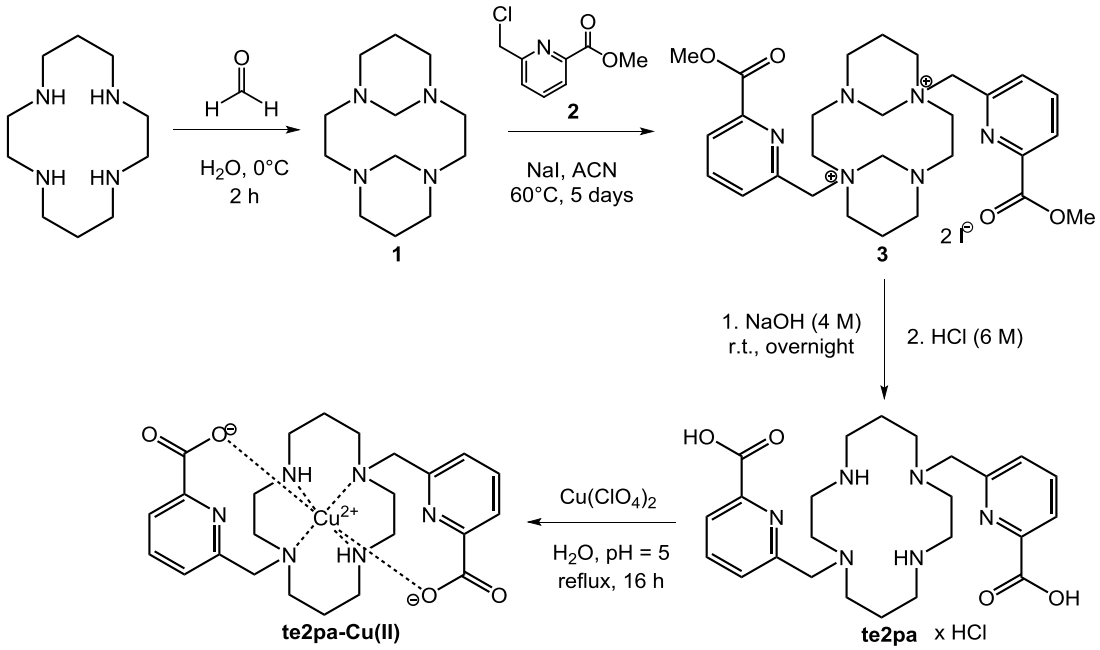
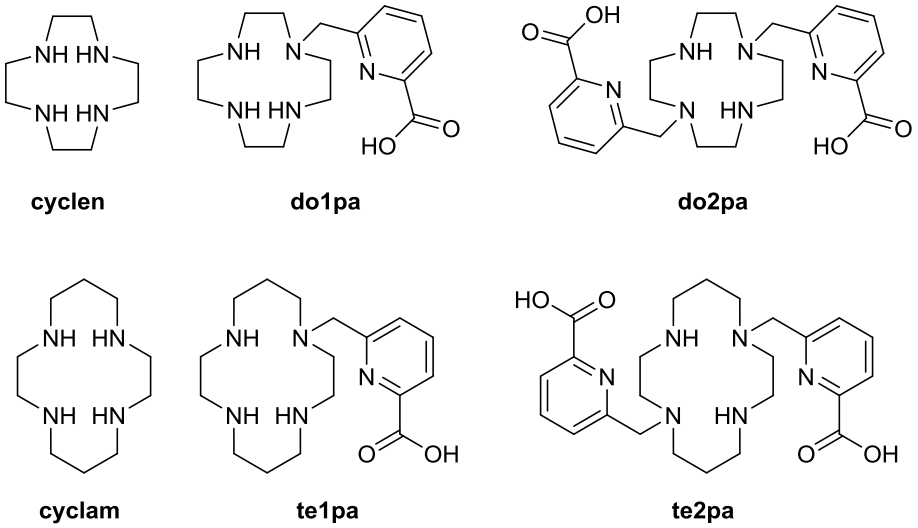
SUPPORTING INFORMATION

1-Synthesis of Cu^{2+}-te2pa complex





Scheme S1. (Top) Synthetic route to the te2pa ligand and its Cu^{2+} complex and (bottom) scheme of the six ligands under study.

Compound 3.

Bisformyl-cyclam (**1**) (200 mg, 0.89 mmol) and NaI (540 mg, 3.57 mmol) were dissolved in 10 mL of freshly distilled acetonitrile. Methyl 6-(chloromethyl)picolinate (**2**) (348 mg, 1.88 mmol) dissolved in 10 mL of acetonitrile was added dropwise to the previous solution and the mixture was stirred at reflux for 5 days. The precipitate was filtered and washed with acetonitrile to obtain compound **3** as a white insoluble salt (686 mg, 98 %) that was used without further purification.

Ligand te2pa

An aqueous solution of NaOH 4 M was added to compound **3** (686 mg, 0.88 mmol). The mixture was stirred at r.t. for 3 days. HCl 6 M was added until pH 2. A white precipitate appeared that was filtered and washed with acetone to give **te2pa** as a hydrochloride salt (491 mg, 80 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (m, 4 H), 7.67 (dd, 2 H, ^{3}J = 6.9 Hz, ^{4}J = 2.1 Hz), 3.98 (s, 4H), 3.37 (bt, 4 H, ^{3}J = 5.1 Hz), 3.02 (m, 4 H), 2.86 (bt, 4 H, ^{3}J = 6.0 Hz), 1.97 (bq, 4 H, ^{3}J = 6.3 Hz).

^{13}C NMR (75.47 MHz, $CDCl_3$): 169.7, 160.0, 149.2, 130.6, 127.7, 60.1, 56.5, 52.1, 46.4, 46.2, 25.8

HR-MS: m/z: 236.1396 $[M + 2H]^{2+}$ calcd. 236.1394 for $C_{24}H_{34}N_6O_4$+ $2H^+$, 471.2718 $[M+ H]^+$ calcd. 471.2714 for $C_{24}H_{34}N_6O_4 + H^+$

Caution! *Although no problem was found during our experiments, salts of perchlorate and their metal complexes are potentially explosive and should be handled with great care and in small quantities.*

Cu-te2pa

Te2pa.xHCl (50 mg, 0.081 mmol) was dissolved in H_2O (5 mL) and the pH adjusted to 5 with a solution of KOH 1 M. $Cu(ClO_4)_2.6H_2O$ (39 mg, 0.11 mmol) was added to the ligand solution. The mixture was refluxed overnight and then concentrated. Acetone was added to precipitate the salts which were removed by filtration. This operation was repeated twice to lead to a purple solid (40.8 mg, 95 %).

ESI-HR-MS (positive, H_2O) *m/z* 266.5967$[M + 2H]^{2+}$ calcd. 266.5963 for $[C_{24}H_{32}CuN_6O_4 + 2H]^{2+}$.

2-X-ray diffraction study of Cu2+-te2pa.10H_2O

Table S1. Selected bond lengths (Å) and angles (°) of the metal coordination environment in Cu^{2+}-te2pa. See Figure 1 for labelling.

Cu(1)-N(1)	2.7910(16)
Cu(1)-N(2)	1.9974(13)
Cu(1)-N(3)	2.0462(13)
N(2)-Cu(1)-N(2)#1	180.00(8)
N(2)-Cu(1)-N(1) #1	92.95(6)
N(2)-Cu(1)-N(1)	87.05(6)

Symmetry transformations used to generate equivalent atoms: #1 –x+1, -y+1, -z+1

Table S2. Crystal data and refinement details for **Cu(te2pa).10H_2O**

	Cu(te2pa).10H_2O
formula	$C_{24}H_{52}CuN_6O_{14}$
MW	712.26
crystal system	Monoclinic
space group	$P2_1/c$
T/K	297(2)
a/Å	9.5261(2)
b/Å	12.2915(3)
c/Å	14.3849(4)
β/deg	101.102(2)
V/$Å^3$	1652.81(7)
F(000)	758
Z	2
λ, Å (MoK_α)	0.71073
D_{calc}/g cm^{-3}	1.431
μ/mm^{-1}	0.733
θ range/deg	3.26 to 30.50
R_{int}	0.0232
reflns measd	16365

unique reflns	4955
reflns obsd	3670
GOF on F^2	1.065
R_1[a]	0.0551
wR_2 (all data)[b]	0.1082
Largest differences peak and hole /eÅ^{-3}	0.456 and -0.283

[a] $R1 = \sum \big| |F_o| - |Fc| \big| / \sum |F_o|$. [b] $wR2 = \{\sum[w(|F_o|^2 - |Fc|^2)^2] / \sum[w(F_o^4)]\}^{1/2}$

3-Potentiometric study

Table S3. Stepwise and overall protonation and stability constants of **te2pa**$^{2-}$ and its Cu^{2+}complex at 25.0 ºC and I = 0.10 M in KNO_3.

Equilibrium reaction[a]	**log β_{HiL} / log K_{HiL}**
$L + H^+ \rightleftarrows HL$	11.12 / 11.12 (2)
$HL + H^+ \rightleftarrows H_2L$	21.48 / 10.36 (1)
$H_2L + H^+ \rightleftarrows H_3L$	24.86 / 3.38 (2)
$H_3L + H^+ \rightleftarrows H_4L$	27.49 / 2.63 (1)
	log β_{MHiL} / log K_{MHiL}
$L + Cu^{2+} \rightleftarrows CuL$	23.5 / 23.5 (1)
$CuL + H^+ \rightleftarrows CuHL$	26.47 /2.97 (5)
$CuL \rightleftarrows CuLOH + H^+$	12.47 / -10.93 (6)
pCu[b]	16.8

[a] L denotes the ligand in general; charges of ligand and complex species were omitted for simplicity, [b] Calculated at pH = 7.4 for 100% excess of ligand with $[M^{2+}]_{tot} = 1.0\times10^{-5}$ M

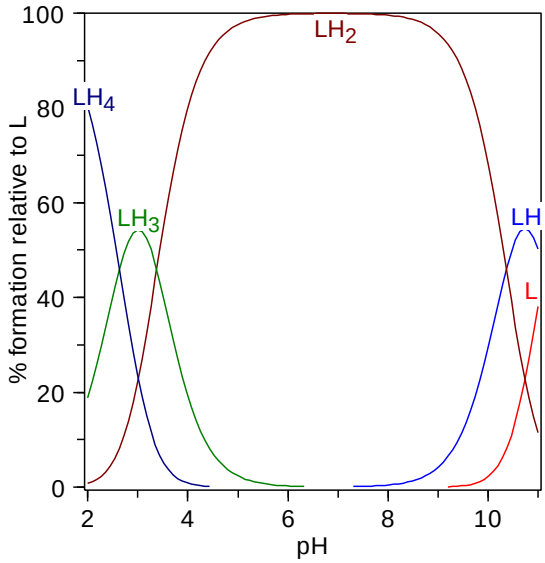


Figure S1. Speciation diagram of the protonated species of **te2pa** in aqueous solution at [L]tot = 10^{-3} M.

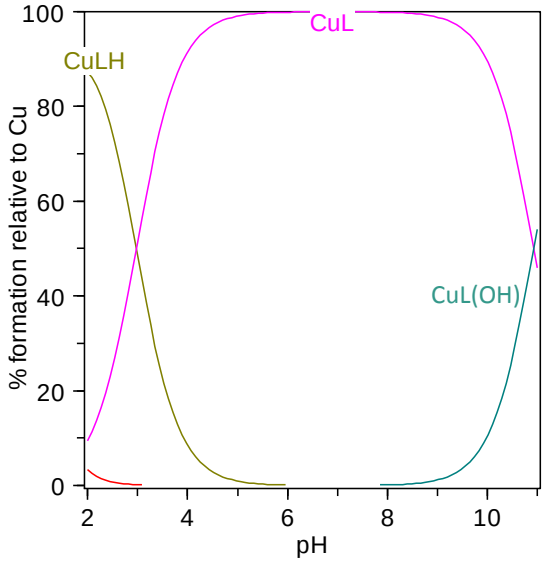


Figure S2. Speciation diagram of **te2pa** in presence of Cu^{2+} in aqueous solution at $[M^{2+}]_{tot} = [L]_{tot} = 10^{-3}$ M.

4-Spectroscopic signatures of the six Cu^{2+} complexes

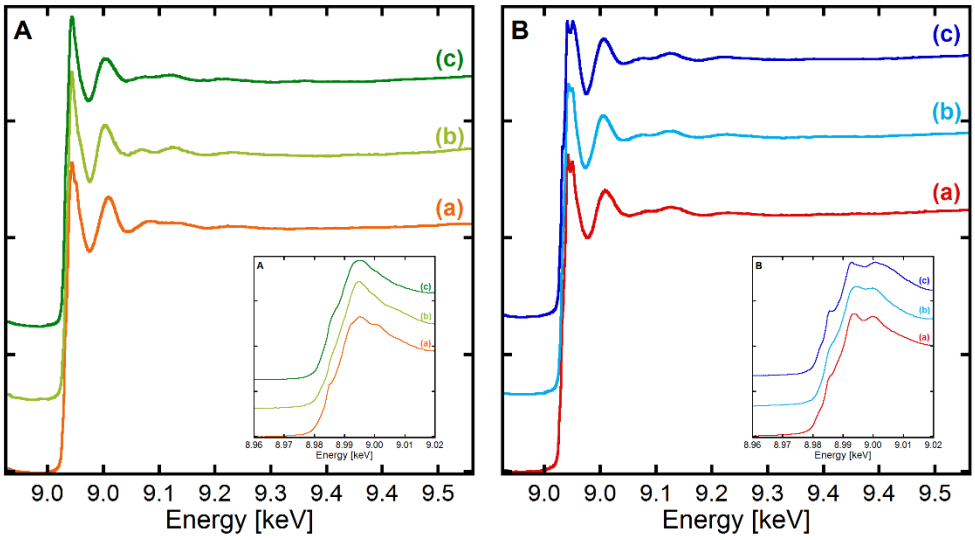


Figure S3. XANES spectra of the different Cu^{2+} complexes. *Panel A*. (a) Cu^{2+}-cyclen, (b) Cu^{2+}-do1pa, (c) Cu^{2+}-do2pa. *Panel B*. (a) Cu^{2+}-cyclam, (b) Cu^{2+}-te1pa, (c) Cu^{2+}-te2pa. [L] = 1 mM, [Cu^{2+}] = 0.9 mM, [HEPES] = 100 mM, pH 7.1. 10% of glycerol was used as cryoprotectant. *T* = 20 K.

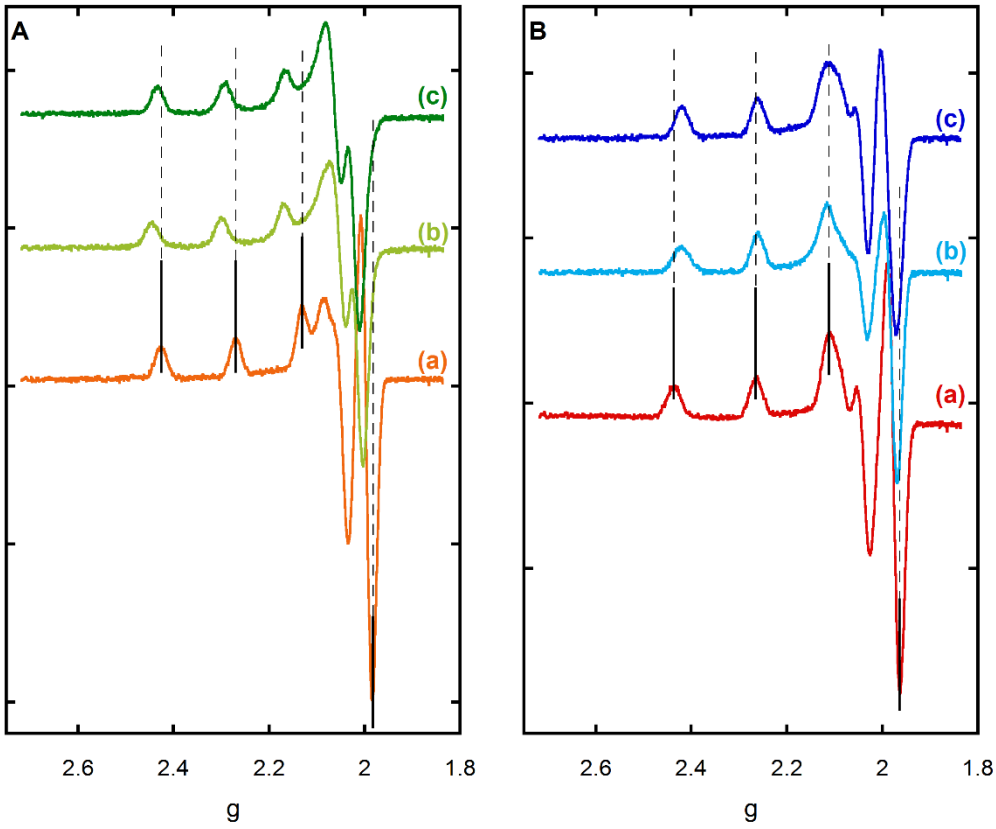


Figure S4. EPR signatures of the different Cu^{2+} complexes. *Panel A*. EPR experiments of (a) Cu^{2+}-cyclen, (b) Cu^{2+}-do1pa, (c) Cu^{2+}-do2pa. *Panel B*. EPR experiments of (a) Cu^{2+}-cyclam, (b) Cu^{2+}-te1pa, (c) Cu^{2+}-te2pa. [L] = 200 µM, [$^{65}Cu^{2+}$] = 190 µM, [HEPES] = 50 mM, pH 7.1. 10% of glycerol was used as cryoprotectant. *T* = 110 K.

5-Cyclic voltammetry signatures of the six Cu^{2+} complexes

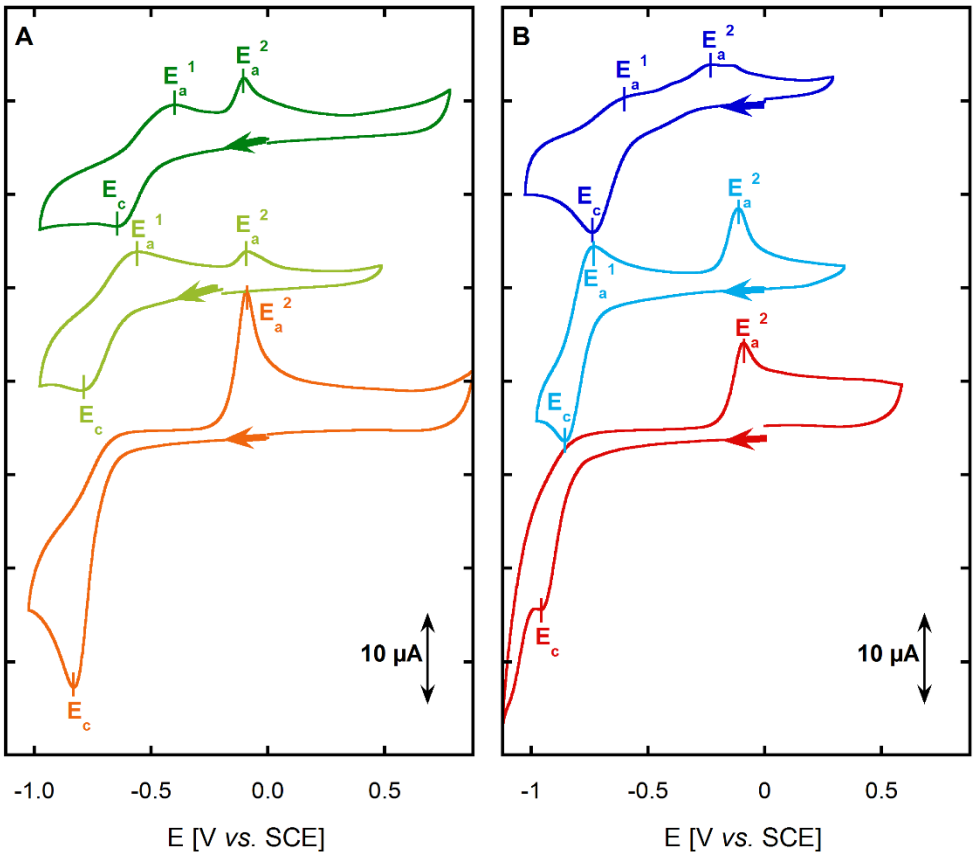


Figure S5. Cyclic voltamograms of the different Cu^{2+} complexes. *Panel A.* Cu^{2+}-cyclen (orange curve), Cu^{2+}-do1pa (light green curve) and Cu^{2+}-do2pa (dark green line).*Panel B.* Cu^{2+}-cyclam (red curve), Cu^{2+}-te1pa (light blue curve) and Cu^{2+}-te2pa (dark blue line). [L] = 1.00 mM, [Cu^{2+}] = 0.96 mM, [phosphate buffer] = 100 mM at pH 7.1. The scanning speed is 0.1 $V.s^{-1}$. Saturated Calomel Electrode was used as a reference.

6-ROS production studies

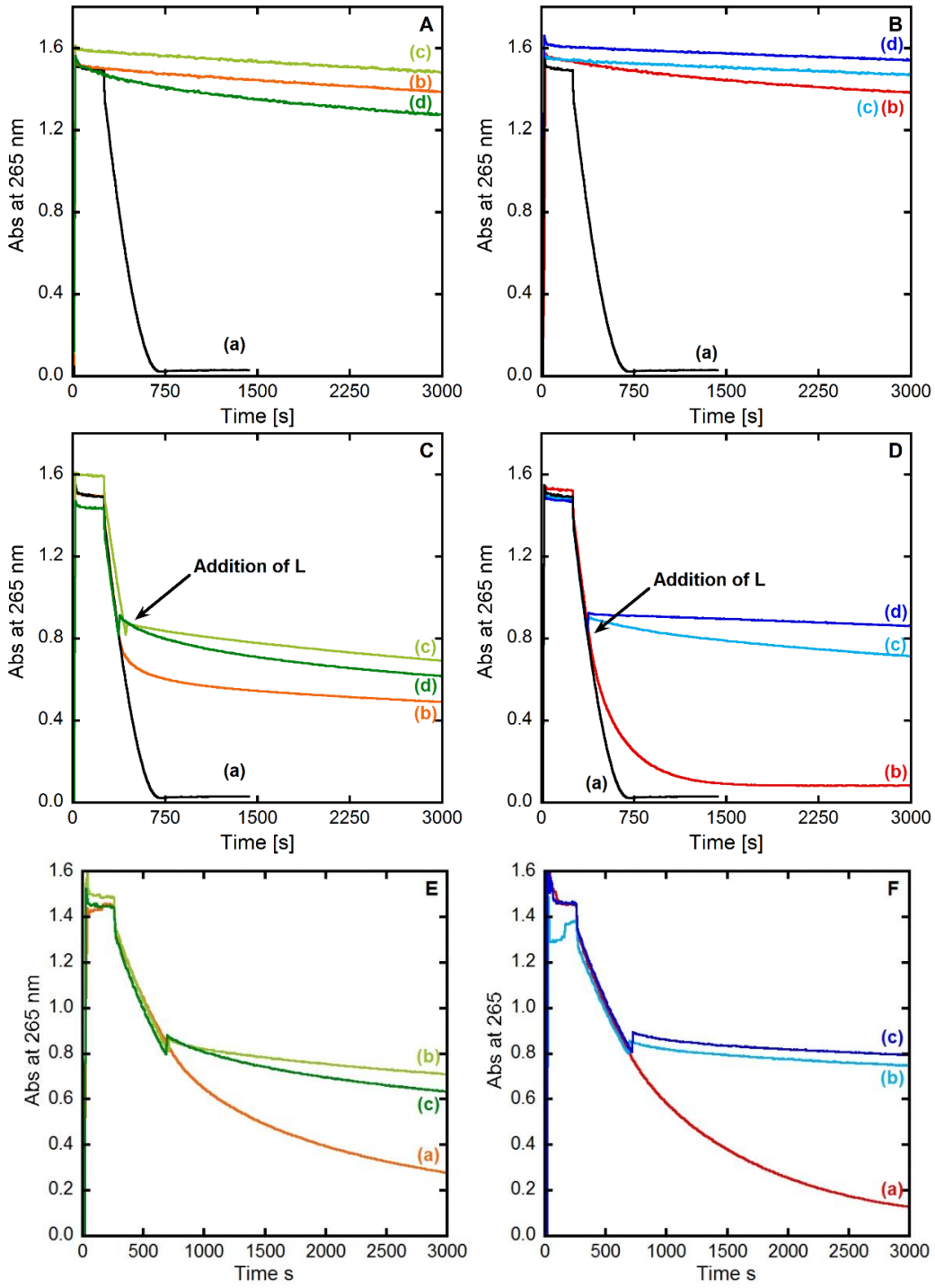


Figure S6. Kinetics of Ascorbate consumption, followed by UV-visible spectroscopy at 265 nm with a background correction at 800 nm. Panel A. (a) Asc + Cu^{2+}, (b) cyclen + Cu^{2+} + Asc, (c) do1pa + Cu^{2+} + Asc, (d) do2pa + Cu^{2+} + Asc. Panel B. (a) Asc + Cu^{2+}, (b) cyclam + Cu^{2+} + Asc, (c) te1pa + Cu^{2+} + Asc, (d) te2pa + Cu^{2+} + Asc. Asc is added long after the first reactants in order to reach the thermodynamic equilibrium. Panel C. (a) Asc + Cu^{2+}, (b) Asc + Cu^{2+} + cyclen, (c) Asc + Cu^{2+} + do1pa, (d) Asc + Cu^{2+} + do2pa. Panel D. (a) Asc + Cu^{2+} (b) Asc + Cu^{2+} + cyclam, (c) Asc + Cu^{2+} + te1pa, (d) Asc + Cu^{2+} + te2pa. Panel E. (a) Asc + Aβ40 + Cu^{2+} + cyclen, (b) Asc + Aβ40 + Cu^{2+} + do1pa, (c) Asc + Aβ40 + Cu^{2+} + do2pa. Panel F. (a) Asc + Aβ40 + Cu^{2+} + cyclam, (b) Asc + Aβ40 + Cu^{2+} + te1pa, (c) Asc + Aβ40 + Cu^{2+} + te2pa. [L] = [Aβ] = 12 µM, [Cu^{2+}] = 10 µM, [Asc] = 100 µM, [HEPES] = 100 mM, pH 7.1.

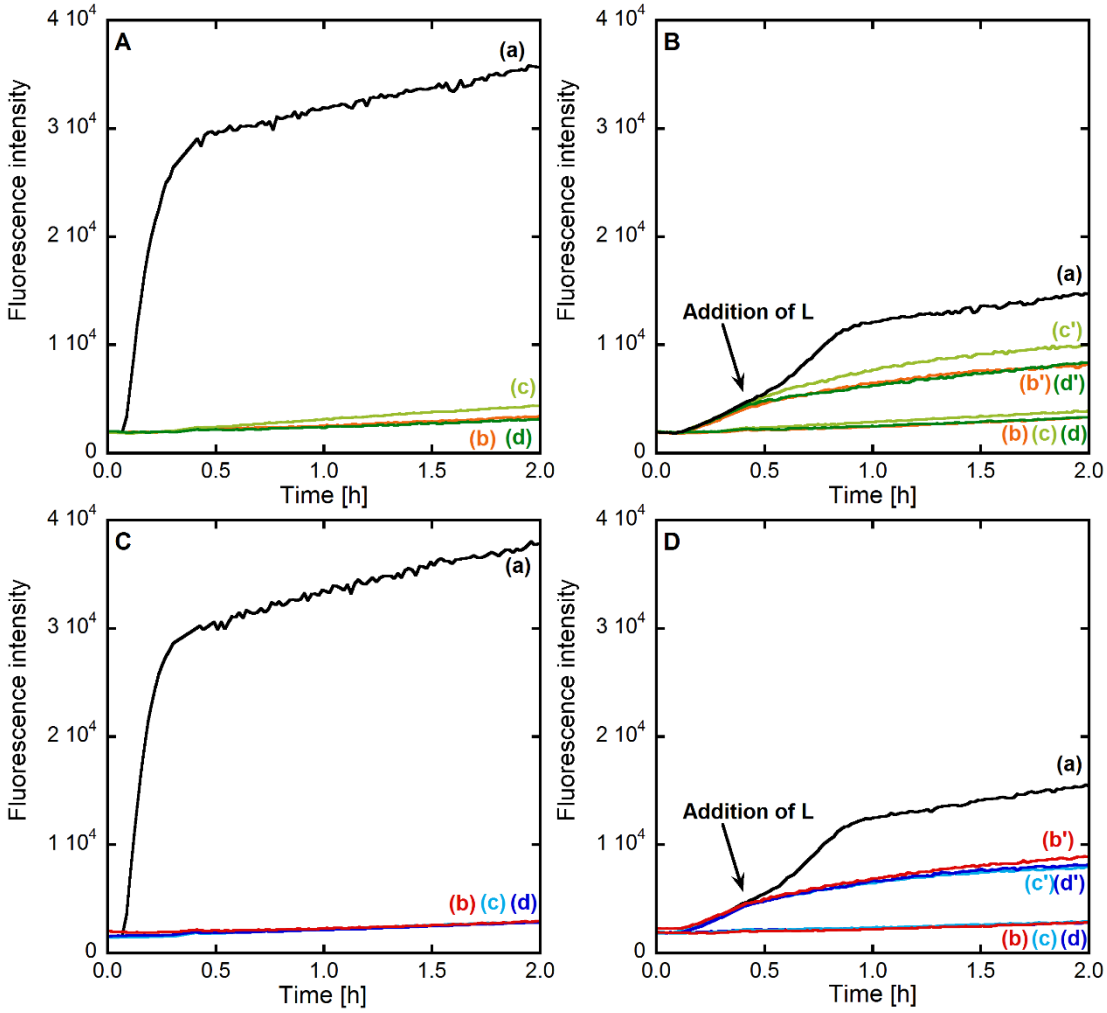
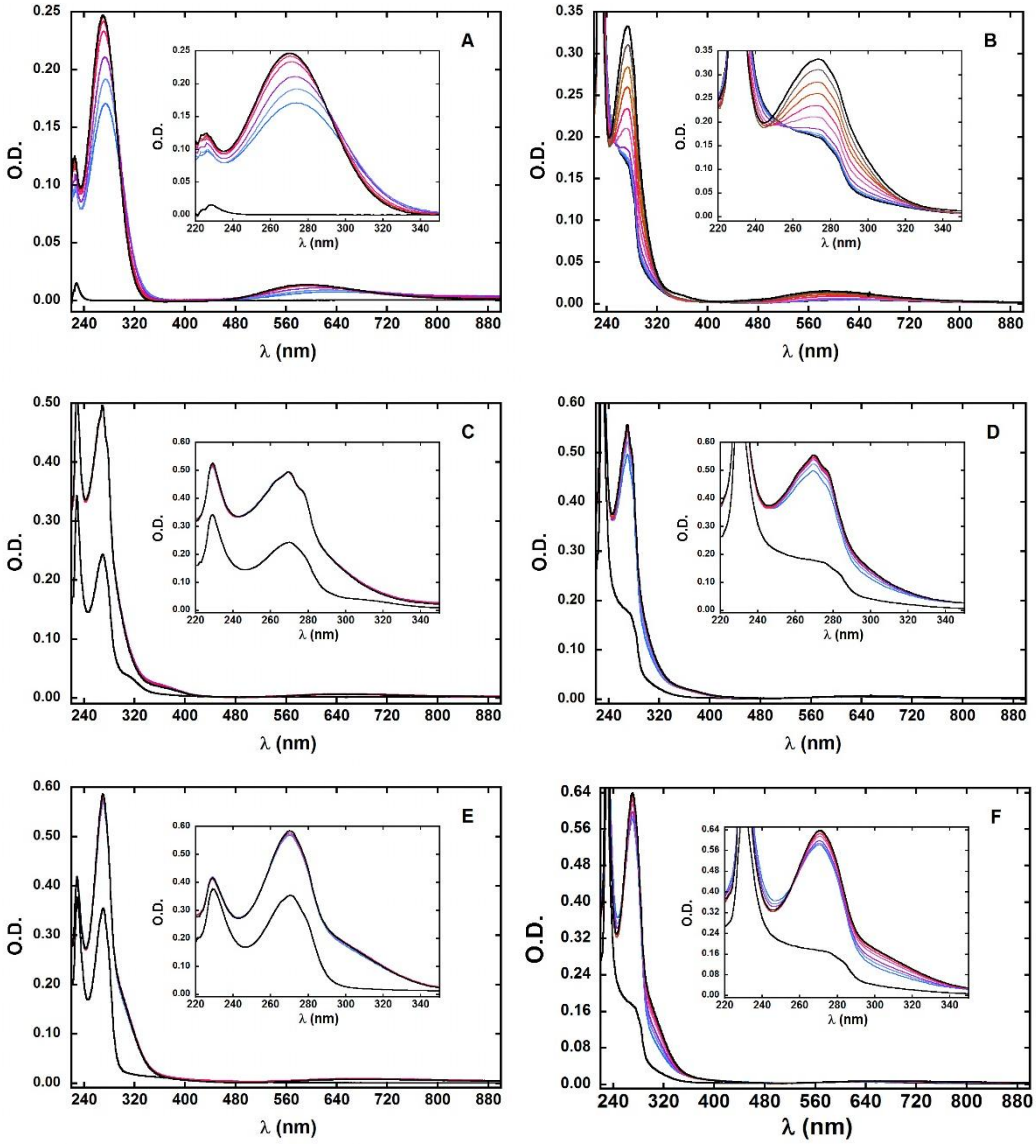


Figure S7. Fluorescence kinetics of CCA experiments. *Panel A*. (a) Cu^{2+} + Asc, (b) Cu^{2+}-cyclen + Asc, (c) Cu^{2+}-do1pa + Asc, (d) Cu^{2+}-do2pa + Asc. *Panel B.* (a) Aβ16 + Cu^{2+} + Asc, (b) Aβ16 + Cu^{2+} + cyclen + Asc, (b') Aβ16 + Cu^{2+} + Asc + cyclen, (c) Aβ16 + Cu^{2+} + do1pa + Asc, (c') Aβ16 + Cu^{2+} + Asc + do1pa, (d) Aβ16 + Cu^{2+} + do2pa + Asc, (d') Aβ16 + Cu^{2+} + Asc + do2pa. *Panel C*. (a) Cu^{2+} + Asc, (b) Cu^{2+}-cyclam + Asc, (c) Cu^{2+}-te1pa + Asc, (d) Cu^{2+}-te2pa + Asc. *Panel D.* (a) Aβ16 + Cu^{2+} + Asc, (b) Aβ16 + Cu^{2+} + cyclam + Asc, (b') Aβ16 + Cu^{2+} + Asc + cyclam, (c) Aβ16 + Cu^{2+} + te1pa + Asc, (c') Aβ16 + Cu^{2+} + Asc + te1pa, (d) Aβ16 + Cu^{2+} + te2pa + Asc, (d') Aβ16 + Cu^{2+} + Asc + te2pa. If Asc is the last reactant, it was added 5 min after the beginning of the measurement. For the experiments A(b), A(c), A(d), B(b), B(c), B(d), C(b) and D(b), the samples were prepared 1 to 2 days before the addition of Asc. [L] = [Aβ16] = 12 μM, [Cu^{2+}] = 10 μM, [CCA] = 500 μM, [Asc] = 500 μM, [phosphate buffer] = 50 mM, pH 7.3.

7-Kinetic study



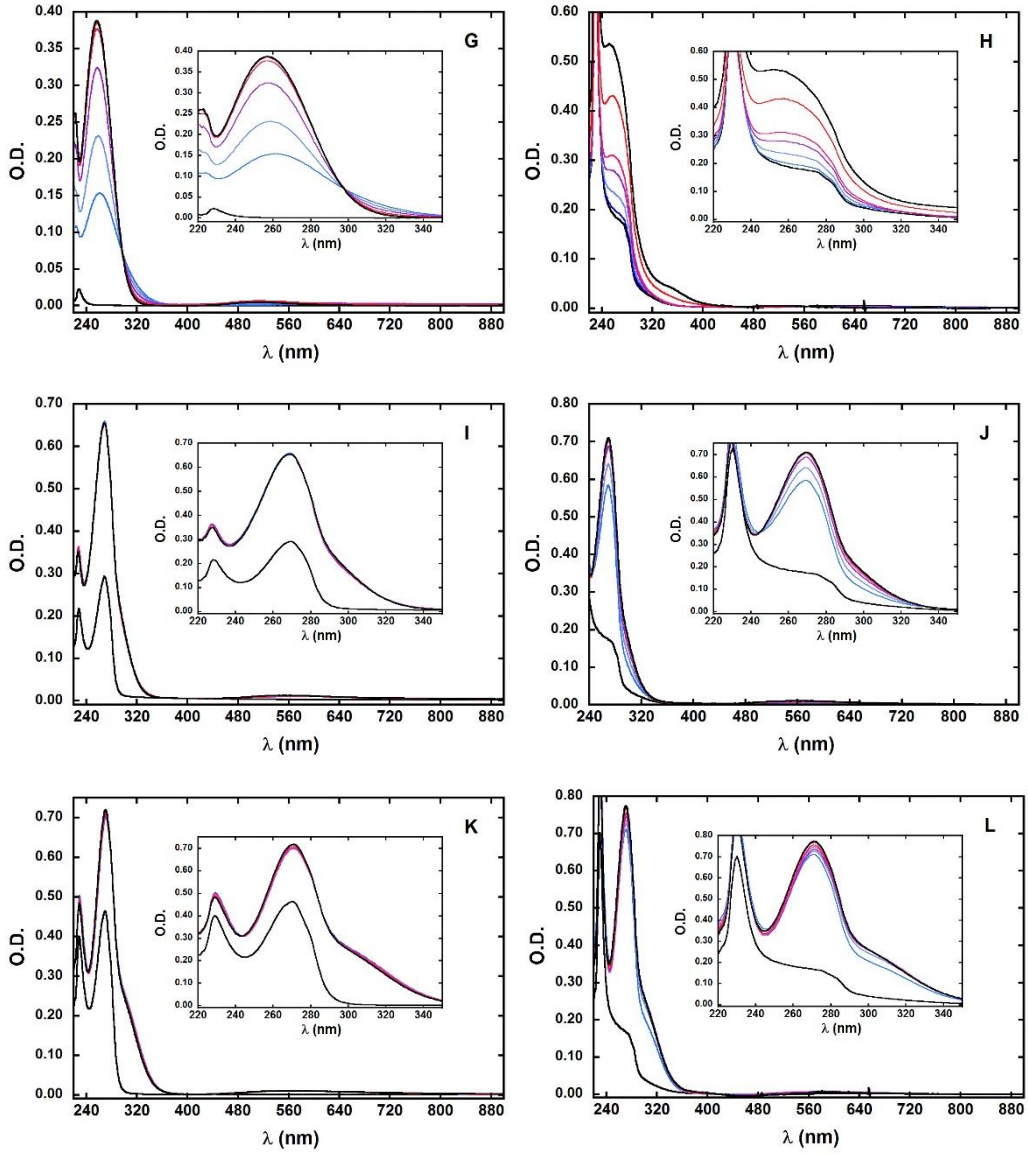


Figure S8. Kinetics of Cu^{2+} binding (Panels A, C, E, G, I, K) and Cu^{2+} removal from Aβ (Panles B, D, F, H, J, L). cyclen (panel A) or do1pa (panel C) or do2pa (panel E) + Cu^{2+}; Cu^{2+}-Aβ16 + cyclen (panel B) or do1pa (panel D) or do2pa panel F); cyclam (panel G) or te1pa (panel I) or te2pa (panel I) + Cu^{2+} ; Cu^{2+}-Aβ16 + cyclam (panel H) or te1pa (panel J) or te2pa (panel L). [L] = [Aβ16] = [Cu^{2+}] = 50 µM, [HEPES] = 100 mM, pH 7.1. Additions are performed at t = 100 s, bold black lines correspond to the spectra before additions and the last spectra. For panels A, C, E, I, K, spectra were taken 10, 30, 100, 400, 900, 1900 and 2900 s after the mixing ; for panel G, spectra were taken 10, 30, 100, 400, 900, 1300 s after the mixing ; for panel B, spectra were taken 10, 30, 100, 400, 900, 1900, 2900, 9800 and 59800 s after the mixing, for panel H, spectra were taken 300, 800, 1800, 2800, 9800 and 59800 s after the mixing ; for panels D, F, J, L spectra were taken 310, 30, 100, 400, 900, 1900, 2900 s after the mixing.

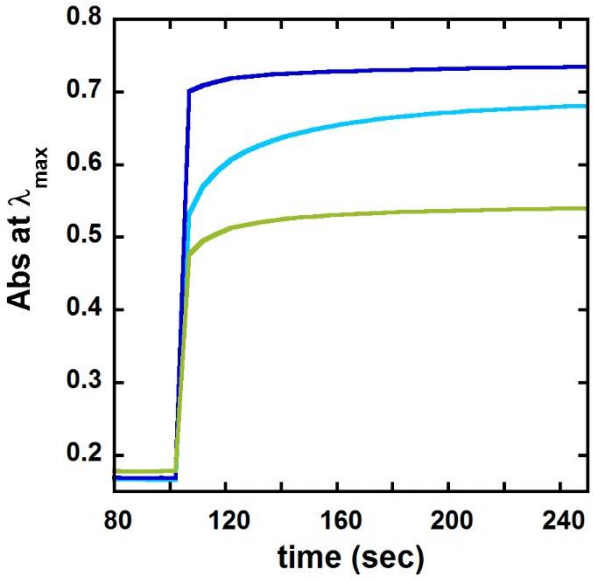


Figure S9. Kinetics of Cu^{2+} binding to the ligands after pre-incubation with Aβ at the wavelength of maximum intensity: do1pa (light green), te1pa (light blue) and te2pa (dark blue).[L] = [Aβ16] = [Cu^{2+}] = 50 µM, [HEPES] = 100 mM, pH 7.1. Additions are performed at t = 100.

8-Experimental details

Synthesis. Reagents were purchased from ACROS Organics and from ALDRICH Chemical Co. Cyclam was purchased from Chematech (Dijon, France). Bisformyl-Cyclam (**1**)[1] and methyl 6-(chloromethyl)picolinate (**2**)[2] were synthesized as previously described. The solvents were freshly distilled prior to use and according to the standard methods. NMR spectra (^{1}H and ^{13}C) were recorded at the core facilities of the University of Brest, with Bruker Avance 500 (500 MHz) or Bruker AMX-3 300 (300 MHz) spectrometers. The HR-MS analyses were performed at the Institute of Analytic and Organic Chemistry, ICOA in Orléans.

Reagents, except the different ligands, were commercially available and were used as received. All the solutions were prepared in milliQ water (resistance: 18.2 MΩ.cm).

The Cu^{2+} ion source was $CuSO_4.5H_2O$, bought from Sigma-Aldrich.

HEPES buffer (sodium salt of 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid) was bought from Sigma-Aldrich. A stock solution was prepared at 500 mM, pH = 7.1.

Phosphate buffer was bought from Sigma-Aldrich. Two stock solutions, K_2HPO_4 and KH_2PO_4, were prepared at 500 mM, and they were mixed until to reach a stock solution at pH = 7.1.

Sodium ascorbate was bought from Sigma-Aldrich. A stock solution was prepared at 5 mM each day because of the quick degradation of the ascorbate.

Coumarin-3-carboxilic acid (CCA) was bought from Acros Organics. A stock solution at 5 mM was prepared in phosphate buffer at 500 mM, pH = 7.1. The stock solution was stored at 4°C.

Thioflavin T (ThT) was bought from Acros Organics. A stock solution of ThT at 250 µM was prepared in water without any further purification.

Peptides. Aβ16 (DAEFRHDSGYEVHHQK) was bought from Genecust. A stock solution of about 10 mM was prepared and titrated using the Tyr chromophore, with ε = 1410 cm^{-1} M^{-1} at acidic pH. The stock solution was stored at 4°C.

Aβ40 (DAEFRHDSGYEVHHQKLVFFAEDVGSNKGAIIGLMVGGVV) was bought from Genecust. Around 6 mg were dissolved in approx. 400 µL of NaOH 50 mM. This solution was purified by FPLC, with a Superdex 75 column and NaOH 15 mM as eluent, with a flow rate at 0.9 mL min^{-1}. The collected fractions were titrated using the Tyr chromophore, with ε = 2400 cm^{-1} M^{-1} at basic pH. The stock solution was directly used for the ThT experiments.

Single crystal X-ray diffraction measurements. Single-crystal X-ray diffraction data were collected at 170 K on an X-CALIBUR-2 CCD 4-circle diffractometer (Oxford Diffraction) with graphite-monochromatized MoK_α radiation (λ = 0.71073). Crystal data and structure refinement details are given in Table 5. Unit-cell determination and data reduction, including interframe scaling, Lorentz, polarization, empirical absorption and detector sensitivity corrections, were carried out using attached programs of Crysalis software (Oxford Diffraction).[3] Structures were solved by direct methods and refined by full matrix least squares method on F^2 with the SHELXL[4] suites of programs. The hydrogen atoms were identified at the last step and refined under geometrical restraints and isotropic U-constraints.[5] CCDC number 1540075 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Equipment and Work Conditions

The potentiometric setup consisted of a 50 mL glass-jacketed titration cell sealed from the atmosphere and connected to a separate glass-jacketed reference electrode cell by a Wilhelm type salt bridge filled with 0.1 M KNO_3 electrolyte. An Orion 720A+ measuring instruments fitted with a Metrohm 6.0123.100 glass electrode and a Metrohm 6.0733.100 Ag/AgCl reference electrode was used for the measurements. Batch points were measured with a Metrohm 6.0233.100 combined glass electrode. The ionic strength of the experimental solutions was kept at 0.10 ± 0.01 M with KNO_3; temperature was controlled at 298.2 ± 0.1 K using a Huber CC3-K6 compact cooling and heating bath thermostat and a previously calibrated Orion 91-70-06 ATC-probe. Atmospheric CO_2 was excluded from the titration cell during experiments by slightly bubbling purified nitrogen on the experimental solution. Titrant solutions were added through capillary tips at the surface of the experimental solution by a Metrohm Dosimat 665 automatic buret. Titration procedure is automatically controlled by software after selection of suitable parameters, allowing for long unattended experimental runs. The titrant was a KOH solution prepared at *ca.* 0.1 M from a commercial ampule of analytical grade, and its accurate concentration was obtained by application of the Gran's method[6] upon titration of a standard HNO_3 solution. Ligand solution was prepared at *ca.* 2.0×10^{-3} M, and the Cu^{2+} solution was prepared at *ca.* 0.05 M from analytical grade nitrate salts and standardized by complexometric titrations with H_4edta (ethylenediaminetetraacetic acid).[7] Sample solutions for titration contained approximately 0.04 mmol of ligand in a volume of 30.00 mL. In complexation titrations metal cations were added at 0.9 equiv of the ligand amount. In competition titrations H_4edta was additionally added at 1.2 equiv. Batch titrations were prepared in a similar way with approximately 0.08 mmol of the ligand in a total volume of 3.00 mL, with Cu^{2+} and H_4edta added

respectively at 1 and 2.3 equiv. of the ligand amount. Increasing amounts of standardized KOH solution at ca. 0.1 M were added to each one. Batch titration points were incubated in tightly closed vials at 25 °C until potential measurements attained complete stability.

Measurements

The electromotive force of the sample solutions was measured after calibration of the electrode by titration of a standard HNO_3 solution at 2.0×10^{-3} M in the work conditions. The $[H^+]$ of the solutions was determined by measurement of the electromotive force of the cell, $E = E^{\circ\prime} + Q \log [H^+] + E_j$. The term pH is defined as $-\log[H^+]$. $E^{\circ\prime}$ and Q were determined by acid region of the calibration curves. The liquid-junction potential, E_j, was found to be negligible under the experimental conditions used. The value of $K_w = [H^+][OH^-]$ was found to be equal to $10^{-13.78}$ by titrating a solution of known hydrogen-ion concentration at the same ionic strength in the alkaline pH region, considering $E^{\circ\prime}$ and Q valid for the entire pH range. The protonation constants of H_4edta and the thermodynamic stability constants of its Cu^{2+} complex used in competition titration refinements were taken from the literature.[8] Each titration consisted of 50–70 equilibrium points in the range pH 2.5-11.5, and at least two replicate titrations were performed for each particular system.

Calculations

The potentiometric data were refined with the HYPERQUAD software,[9] and speciation diagrams were plotted using the HySS software.[10] The overall equilibrium constants β_i^H and β_{MmHhLl} are defined by $\beta_{MmHhLl} = [M_mH_hL_l]/[M]^m[H]^h[L]^l$ ($\beta_i^H = [H_hL_l]/[H]^h[L]^l$ and $\beta_{MH-1L=} \beta_{ML(OH)} \times K_w$). Differences, in log units, between the values of protonated (or hydrolyzed) and nonprotonated constants provide the stepwise (log K) reaction constants (being $K_{MmHhLl} = [M_mH_hL_l]/[M_mH_{h-1}L_l][H]$). The errors quoted are the standard deviations calculated by the fitting program from all the experimental data for each system.

Electron Paramagnetic Resonance.

Electron Paramagnetic Resonance (EPR) data were recorded using an Elexsys E 500 Bruker spectrometer, operating at a microwave frequency of approximately 9.5 GHz. Spectra were recorded under non-saturating conditions across a sweep width of 120 mT (centred at 310 mT) with modulation amplitude of 1.0 mT. Experiments were carried out at 110 K using a liquid nitrogen cryostat.

EPR samples were prepared from stock solution of ligand diluted down to 0.2 mM in H_2O. 0.95 eq. of $^{65}Cu^{2+}$ was added from 25 mM $^{65}Cu(NO_3)_2$ stock solution home-made from a ^{65}Cu foil. If necessary, pH was adjusted with H_2SO_4 or NaOH solutions. Samples were frozen in quartz tube after addition of 10% glycerol as a cryoprotectant and stored in liquid nitrogen until used.

Electrochemistry. Cyclic voltamogram were recorded on an Autolab PGSTAT302N at 25°C. Saturated Calomel Electrode was used as a reference, Platine electrode was the counter electrode and the working electrode was a glassy carbon electrode. This last electrode was carefully polished before each measurement on a red disk NAP with 1 µm AP-A suspension under abundant distillate water flow during at least three minutes (Struers). The solution was deoxygenated by bubbling Argon before each measurement. Any support electrolyte was added because of the high concentration of phosphate buffer in the solution. The scanning speed was 0.1 $V.s^{-1}$. The

samples were prepared from stock solutions of ligand and Cu^{2+} down to approx. 1 mM and 0.9 mM respectively in a buffered solution.

UV-Visible spectrophotometry.

UV-vis kinetics were recorded on a spectrophotometer Agilent 8453 at 25°C in 1 cm path length quartz cuvette, with an 800 rpm stirring. The samples were prepared from stock solutions of ligand, peptide and Cu^{2+} diluted down to 12, 12 and 10 µM respectively in 100mM HEPES solution, pH = 7.1. Ascorbate is diluted down to 100 µM. UV-Vis kinetic monitoring of the Cu^{2+} binding or Cu^{2+} removal from Aβ by the six ligands were recorded on a spectrophotometer Agilent 8453 at 25°C in 1 cm path length quartz cuvette, with an 800 rpm stirring. The samples were prepared from stock solutions of Cu^{2+}, peptide and ligand diluted down to 50, 50 and 50 µM respectively in 100mM HEPES solution, pH = 7.1.

Fluorescence experiments.

CCA experiments were recorded on a FLUOstar OPTIMA BMG LABTECH at 25°C in a 96-well plate bought from Dutscher SAS. CCA was excited at 390 nm and the fluorescence was recorded at 450 nm. The gain was 1350. The samples were prepared from stock solutions of ligand, peptide and Cu^{2+} diluted down to 12, 12 and 10 µM respectively in phosphate solution, pH = 7.1. CCA was added at a resulting concentration of 500 µM. Injector was used for the addition of ascorbate diluted down to 500 µM, 5 min after the beginning of the experiment.

ThT experiments were recorded on a FLUOstar OPTIMA BMG LABTECH at 37°C in a 384-well plate bought from Dutscher SAS. ThT was excited at 440 nm and the fluorescence was recorded at 490 nm. The gain was 1200. The samples were prepared from stock solutions of ligand, peptide and Cu^{2+} diluted down to 20, 20 and 18 µM respectively in HEPES buffer, pH = 7.1. ThT was added at a resulting concentration of 10 µM.

Transmission electron microscopy.

Specimens were prepared for electron microscopy using the conventional negative staining procedure. 20 µL of solution was absorbed on Formvar-carbon-coated grids for 2 min, blotted, and negatively stained with uranyl acetate (1%) for 1 min. Grids were examined with a TEM (Jeol JEM-1400, JEOL Inc, Peabody, MA, USA) at 80 kV. Images were acquired using a digital camera (Gatan Orius, Gatan Inc, Pleasanton, CA, USA) at a x 25 000 magnification.

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