Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic supplementary information (ESI)

for

A caged tris(2-pyridylmethyl)amine ligand equipped with a $C_{triazole}$-H hydrogen bonding cavity.

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1. Chemical and instrumentation

All reagents were commercial reagent grade and were used without further purification.

Compound **1**,[S1] compound **3**, [S2], and the tris((6-methyl-2-pyridyl)methyl)amine ligand **^{Me3}TPA,** [S3] were obtained according to reported protocols.

Instrumentation

^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance III HD 300 MHz and 400MHz spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts δ are reported in ppm referenced to the protonated residual solvent signal. ESI-HRMS were performed on a SYNAPT G2 HDMS (Waters) mass spectrometer with API and spectra were obtained with TOF analysis. Measurements were realized with two internal standards. Electrochemical experiments were recorded on a Bio-logic SP-150 potentiostat equipped with EC-Lab software. Cyclic voltammetry experiments were conducted in the presence of NBu_4PF_6 as supporting electrolyte and using three-electrode setup which consisted of a Pt working electrode (2 mm), a platinum wire counter electrode and an AgCl/Ag reference electrode. The potentials in the text are referred versus Fc^+/Fc.

2. Computational details

Calculations were performed with the TURBOMOLE program package[S4] at the Density Functional Theory level (DFT). The PBE0 exchange-correlation functional was employed,[S5] together with the empirical dispersion correction D3 (PBE0-D3).[S6]
The basis set is of def2-TZVP quality, accompanied with the corresponding auxiliary basis sets, as the resolution of the identity technique was used throughout.[S7] Solvent effects were taken into account using the COSMO continuum dielectric model for acetonitrile.[S8]
Two structures have been taken into account and fully optimized for **Zn^{II}(Hm-TriA-TPA)(CH$_3$CN)**: the first one displays a C_3 symmetrical environment around the metal center; the second structure was built from the XRD of the **Cu^{II}(Hm-TriA-TPA)(OTf)$_2$** and presents a distorted coordination sphere on the Zn. The first structure is 15.4 kj/mol more stable than the second one.
The XYZ coordinates of the more stable conformation follows. The total energy is reported in a.u.

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Energy = -5160.6603394639

Zn	-2.1284981	-1.7875253	-0.9976660
O	4.2953494	-1.5760409	-1.5198675
O	3.6707803	0.3952836	-3.2811023
O	-0.0495323	0.0626344	4.8209958
O	1.9213958	-1.7055677	4.2174938
O	-0.7202344	4.4729959	-1.6505346
O	-1.7475776	4.5375650	0.8630104
N	-3.6557225	-3.0685006	-1.7125406

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C	4.4519784	1.4035483	0.6840516
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H	3.7016202	2.7612028	-2.3234138
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C	4.7707752	-0.0303895	-4.0842367
H	4.3695071	-0.2270019	-5.0772827
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H	5.5237126	0.7608122	-4.1450153
C	-2.9972773	-4.1267852	-2.4694926
H	-3.7181252	-4.7122258	-3.0479197
H	-2.5183269	-4.8083240	-1.7598259
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C	0.6039083	1.5824341	-3.1468502
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C	0.1501586	4.3546772	-0.6202963
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H	1.9712303	4.1903763	-1.7244134
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C	1.8017743	4.0895804	1.6521236
C	0.4279287	4.3118110	1.7652395
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C	-0.4016485	4.4282801	0.6679749
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C	-4.5275400	-2.2561291	-2.5531278
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H	-6.8249884	-0.8537281	-2.6464214
C	-6.2979838	0.8837181	-1.4888826
H	-7.2562703	1.3764332	-1.5987421
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H	-5.4164417	2.4434526	-0.2999049
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C	-2.9522252	1.5267853	0.0823166
H	-2.0513371	1.4729639	-0.5262450
H	-3.1937684	2.5808640	0.2009364
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H	-1.8290434	2.7020603	2.3637670
C	-1.8896565	0.6921538	3.3843641
C	-1.2743475	0.7878513	4.7358834
H	-1.1467929	1.8306986	5.0312675
H	-1.9214884	0.3097769	5.4707288
C	1.0668898	0.5536965	4.2333700
C	1.2929361	1.8852968	3.9176964
H	0.5344433	2.6207661	4.1537303
C	2.4648502	2.3180060	3.2878017
C	3.4533968	1.3823805	2.9765372
C	3.2503449	0.0564612	3.3644067

H	4.0184984	-0.6863059	3.1781767
C	2.0848592	-0.3745888	3.9657940
C	1.9544587	-2.0766106	5.5950106
H	2.9242307	-1.8221779	6.0325010
H	1.8134778	-3.1559274	5.6269869
H	1.1553473	-1.5849118	6.1526712
C	4.6826519	1.6905439	2.1540468
H	5.0073520	2.7192826	2.2974666
H	5.5026701	1.0588926	2.5033451
C	2.5678108	3.7839632	2.9179278
H	3.6099348	4.0854389	2.8325001
H	2.1435666	4.3749563	3.7328760
C	3.8373971	3.8330877	0.1204176
H	4.4282397	4.1455034	0.9792794
H	4.1488711	4.4672788	-0.7127754
H	0.9053668	-1.1607341	-2.1190472
H	1.5194304	-0.8428796	-3.7261428
H	4.8160424	-2.5943571	0.2311879
H	4.4390657	-3.5427345	-1.2056902
N	-0.6760175	-0.5682156	-0.3165929
C	0.1484325	0.1248713	0.0694185
C	1.1740874	0.9874455	0.5493680
H	1.9006739	1.1691716	-0.2444270
H	0.7367417	1.9366322	0.8634712
H	1.6759486	0.5217799	1.3992087

2. Experimental procedure and characterisation

Synthetic procedure for 2.

A solution of PPTS (0.64 g, 0.026 mol) dissolved in CH_2Cl_2 (10 mL) was added in one portion to a stirred solution of **1** (6.9 g, 0.026 mol) and DHP (3.22 g, 0.038 mol) in THF (100 mL) at room temperature. The solution was stirred overnight at room temperature. The solvent was then evaporated under reduced pressure, and the residue was extracted with diethyl ether. The organic layer was washed twice with brine and then dried over sodium sulfate. The solvent was evaporated under reduced pressure to leave a residue, which was purified by chromatography (Et_2O/pentane: 50/50). Evaporation of the solvent gave compound **2** as a white crystalline material (7.74 g, 84%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (d, 1H, Ar), 6.93 – 6.88 (m, 2H, Ar), 4.74 (d, 1H, propargyl-CH_2), 4.72 (d, 1H, -CH_2-OTHP), 4.68 (m, 1H, THP), 4.44 (d, 1H, -CH_2-OTHP), 3.92 (m, 1H, THP), 3.87 (s, 3H, OCH_3), 3.54 (m, 1H, THP), 2.49 (t, 1H, propargyl-CH), 1.90 -1.48 (m, 6H, THP); **^{13}C NMR** (75 MHz,$CDCl_3$) 149.8, 146.3, 132.4, 120.3, 114.4, 111.9, 97.7, 75.8, 68.8, 62.4, 56.9, 56.0, 30.7, 25.6, 19.8. HRMS (ESI): Calcd for $C_{11}H_{12}O_3$ [M+H]+ : 294.1700, found 294.1700.

Synthetic procedure for 4.

Compound **3** (200 mg, 0.87 mmol), was dissolved in DMF (20 mL). Then NaN_3 (73.5 mg, 1.3 equiv.) was added in small portion. The reaction was stirred at room temperature for 16h. The solution was then washed twice with brine and dried over sodium sulfate. The solvent was evaporated under reduced pressure to give a residue, which was purified by column chromatography on silica gel (164 mg, 98%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08(d, 1H), 7.89(t, 1H), 7.59 (d, 1H), 4.64(s, 2H), 4.01(s, 3H). **^{13}C NMR** (400 MHz,$CDCl_3$) 165.65, 158.42, 147.83, 138.17, 125.56, 121.53, 55.7, 51.4. **HRMS (ESI)**: Calcd for $C_8H_8N_4O_2$ [M+H]+ : 193.0720, found 193.0722.

Synthetic procedure for 5.

Compounds **2** (276 mg, 1 mmol) and **4** (192 mg, 1.02 mmol) were dissolved in a 1:1 $CHCl_3$:CH_3CN solvent mixture (30 mL). $CuSO_4{\cdot}5H_2O$ (22.5 mg, 0.09 mmol) and sodium ascorbate (30 mg, 0.1 mmol) were then added and the solution was stirred at room temperature for 24 h. The resulting precipitate was then filtrated and the filtrate concentrated under reduced pressure. The residue was dissolved in $CHCl_3$ (40 mL) and the resulting solution washed with water (2 X 20mL) and brine (20 mL), before to be dried using Na_2SO_4. The solvent was evaporated under reduce pressure and the resulting solid was purified by column chromatography (CH_2Cl_2/MeOH=50:1) to give **5** as a white solid (390 mg, 83%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.06 (d, 1H, pyridine), 7.82 (t, 1H, pyridine), 7.78 (s, 1H, Triazole-H), 7.25 (d, 1H, pyridine), 6.99 – 6.83 (m, 3H, Ar), 5.74 (s, 2H, Pyridine-CH_2), 5.26 (s, 2H, ArO-CH_2), 4.64 (d, 1H, -CH_2-OTHP), 4.62 (m, 1H, THP), 4.40 (d, 1H, -CH_2-OTHP), 4.00 (s, 3H, $COOCH_3$), 3.90 (m, 1H, THP), 3.82 (s, 3H, Ar-OMe), 3.52 (m, 1H, THP), 1.87-1.49 (m, 6H, THP). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 165.2, 155.2, 149.7,148.0,147.1, 145.1, 138.6, 132.1, 125.6, 124.9, 123.6, 120.5, 114.3, 111.9, 97.8, 68.8, 63.4, 62.4, 55.9, 55.7, 53.17, 30.7, 25.5, 19.5 ppm. **HRMS (ESI)**: Calcd for $C_{24}H_{28}N_4O_6$ [M+H]+ : 469.2082, found 469.2080.

Synthetic procedure for 6.

$NaBH_4$ (360 mg, 9.52 mmol) was added to a suspension of **5** (230mg, 0.49 mmol) in anhydrous EtOH (8 mL) at 0°C. The reaction mixture was then refluxed for 2 h and the solvent was removed under reduced pressure. The resulting crude residue was dissolved in CH_2Cl_2 (10 mL), washed with brine (2X10 mL), and with an aqueous saturated Na_2CO_3 solution (2 mL). The organic layer was dried with Na_2SO_4 and concentrated. Recrystallization from CH_2Cl_2/Et_2O (1:1) yielded compound **6** (177 mg, 82%) as a white solid. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75(s, 1H, triazole), 7.66(t, 1H, pyridine), 7.23(d, 1H, pyridine), 6.98-6.83(m, 3H, Ar), 5.63(s, 2H, pyridine-CH_2), 5.27(s, 2H, ArO-CH_2), 4.70 (d, 1H, -CH_2-OTHP), 4.68 (m, 1H, THP), 4.42(d, 1H, -CH_2-OTHP), 3.91(m, 1H, THP), 3.84(s, 3H, OMe), 3.56(m, 1H, THP), 1.90-1.50(m, 6H, THP). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.7, 153.4, 149.7, 147.1, 144.9, 138.1, 132.0, 123.6, 121.0, 120.6, 120.3, 114.3, 111.9, 97.9, 68.9, 64.1, 63.4, 62.5, 56.0, 55.5, 30.7, 25.6, 19.6. **HRMS (ESI):** Calcd for C23H28N4O5 [M+H]+ : 441.2132, found 441.2127.

Synthetic procedure for 7.

A solution of MsCl (233 mg, 2.1 mmol) in CH_2Cl_2 (10 mL) was added slowly, at 0°C, to a stirred solution of **6** (850 mg, 2.0 mmol) and Et_3N (3 ml) in CH_2Cl_2 (100 mL). The solution was stirred overnight at room temperature. The solvent was then evaporated under reduced pressure, and the residue was extracted with CH_2Cl_2. The organic layers were combined and washed twice with brine and then dried over sodium sulfate. The solvent was evaporated under reduced pressure to give a yellow residue, which was purified by chromatography (Et_2O/pentane: 50/50) to yield **7** as a yellow oil (809 mg, 78% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.78(s, 1H, triazole), 7.74(t, 1H, pyridine), 7.42(d, 1H, pyridine), 7.15(d, 1H, pyridine), 7.16-6.84 (m, 3H, Ar), 5.62(s, 2H, pyridine-CH_2), 5.27(s, 2H, ArO-CH_2), 4.70 (d, 1H, -CH_2-OTHP), 4.67 (m, 1H, THP), 4.42(d, 1H, -CH_2-OTHP), 3.91(m, 1H, THP), 3.85(s, 3H, OMe), 3.54(m, 1H, THP), 3.04(s, 3H, OMs), 1.90-1.50(m, 6H). **^{13}C NMR** (75 MHz, CDCl3) δ 154.5, 154.1, 149.7, 147.1, 144.9, 138.4, 132.1, 123.7, 122.3, 122.1, 120.6, 114.2, 111.9, 97.9, 71.1, 68.9, 63.4, 62.5, 56.0, 55.20, 38.2, 30.7, 25.6, 19.6. **HRMS (ESI)**: Calcd for C24H30N4O7S [M+H]+ : 519.1908, found 519.1909.

Synthetic procedure for 8.

In a 100 mL round-bottom flask, **7** (267 mg, 0.516 mmol) was dissolved in THF (22 mL). Then NH_3 gas was bubbled slowly for an hour. Then Cs_2CO_3 (757 mg, 2.32 mmol) was added in one portion. The reaction was stirred at 90 °C for 3 days. The mixture was then cooled to rt, and THF was removed under vacuum. Then 300 mL of CH_2Cl_2 and 300 mL of H_2O were added. After thoroughly mixing, the organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic layers were dried over Na_2SO_4, and the organic solvent was removed under vacuum. The crude product was purified by column chromatography on silica gel with a 25:1 mixture of CH_2Cl_2:MeOH as eluent to give hemicryptophane precursor **8** as a white oil (493 mg, 73 % yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.75(s, 1H), 7.67(t, 1H), 7.24(d, 1H), 7.05(d, 1H), 6.99-6.84(m, 3H), 5.64(s, 2H), 5.29(s, 2H), 4.74-4.67(m, 4H), 4.43(d, 1H), 3.92(m, 1H), 3.85(s, 3H), 3.53(m, 1H), 1.91-1.51(m, 6 H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.6, 153.4, 149.7, 147.1, 145.0, 138.1, 132.0, 123.6, 120.9, 120.6, 120.3, 114.3, 111.9, 97.9, 77.5, 77.1, 76.7, 68.9, 64.0, 63.4, 62.5, 56.0, 55.5, 30.7, 25.6, 19.6. **HRMS (ESI)**: Calcd for C69H81N13O12 [M+Na]+ : 1306.6020, found 1306.6012.

Synthetic procedure for cage Hm-TriA-TPA.

A solution of hemicryptophane precursor **8** (257 mg, 0.2 mol) in CH_3CN (18 mL) was added dropwise (4 h) under argon at 70°C to a solution of $Sc(OTf)_3$ (125 mg, 0.28 mol) in CH_3CN (50 mL). The mixture was stirred under argon at 70°C for 24 h. The solvent was then evaporated. The crude product was purified by column chromatography on silica gel with 25:1 mixture of CH_2Cl_2:MeOH (with 3 drops of triethylamine) as eluent to give cage **Hm-TriA-TPA** as a white solid (57 mg, 29% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.62(s, 3H), 7.14(t, 3H), 7.04(d, 3H), 6.81(s, 3H), 6.74(d, 3H), 6.58(s, 3H), 5.67(d, 3H), 5.46(d, 3H), 5.37(d, 3H), 5.20(d, 3H), 4.69(d, 3H), 3.66(s, 9H), 3.47(d, 3H), 3.45(d, 3H) 3.12(d, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 159.20, 153.01, 147.85, 146.06, 145.28, 137.35, 132.78, 131.85, 123.45, 123.27, 120.28, 114.85, 113.60, 77.33, 77.01, 76.69, 63.24, 58.61, 56.37, 55.34, 36.57. **HRMS (ESI)**: Calcd for C54H51N13O6 [M+H]+ : 978.4164, found 978.4156.

For ^{1}H NMR; ^{13}C NMR and 2D-NMR spectra, see supplementary figures S2, S3 and S4-5 respectively.

Synthetic procedure for Zn^{II}(Hm-TriA-TPA)(OTf)$_2$.

A solution of Zn^{II}(OTf)$_2$ (6.7 mg, 18,4 µmol, 1.0 equiv.) in CH_3CN (1 mL) was added, at room temperature, to a stirred solution of **Hm-TriA-TPA** (18 mg, 18,4 µmol, 1.0 equiv.) in CH_3CN (2 mL). The resulting white solution was stirred at room temperature for 1 hour and an excess of Et_2O was added. A white precipitate was formed, isolated by filtration, washed with Et_2O, and dried in vacuo to give **Zn^{II}(Hm-TriA-TBTA)(OTf)$_2$** in a 80% yield. ^{1}H NMR (400 MHz, Acetonitrile-*d$_3$*) δ 8.03 (t, 3H), 7.79 (s, 3H), 7.49 (d, 3H), 7.15 (d, 3H), 7.08 (s, 1H), 6.92 (s, 1H), 5.65 (d, 3H), 5.53 (d, 3H), 5.30 (d, 3H), 5.14 (d, 3H), 4.65 (d, 3H), 4.42 (d, 3H), 4.15 (d, 3H), 3.80 (s, 9H), 3.49 (d, 3H). **HRMS** (ESI): Calcd for C54H51ZnN13O6 [M]$^{2+}$: 520.6683 Found: 520.6682 (figure S15).

Synthetic procedure for Cu^{II}(Hm-TriA-TPA)(OTf)$_2$.

To a stirred solution of Cu^{II}(OTf)$_2$ (7.4 mg, 20 µmol, 1.0 equiv.) in CH_3CN (1.0 mL), was added, at room temperature, a solution of **Hm-TriA-TPA** (20 mg, 20 µmol, 1.0 equiv.) in CH_3CN (2.0 mL). The resulting deep blue solution was stirred at room temperature for one additional hour and an excess of Et_2O was added. A blue precipitate was formed, isolated by filtration, washed with Et_2O, and dried in vacuo to give **Cu^{II}(Hm-TriA-TBTA)(OTf)$_2$** in a 74% yield. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether to a CH_3CN solution of **Cu^{II}(Hm-TriA-TBTA)(OTf)$_2$**. **HRMS** (ESI): Calcd for C54H51CuN13O6 [M]$^{2+}$: 520.1685 Found: 520.1684 (figure S8). For UV-vis spectra, see supplementary figure S9.

Preparation of the azido complexes Cu^{II}(L)(OTf)(N$_3$) (L= ^{Me3}TPA or Hm-TriA-TPA).

Azido complexes were obtained, according to reported protocols,[S9] through the addition of NaN_3 (1.7 mg, 26 µmol, 1.2 equiv.) to a stirred solution of the desired **Cu^{II}(L)(OTf)$_2$** complex (L= **^{Me3}PTA** or **Hm-TriA-TPA**, 22 µmol) in acetone. The mixture was sonicated and stirred one hour at room temperature to afford a green solution. An excess of Et_2O was then added to form a green precipitate which was isolated by filtration, washed with Et_2O and dried in vacuo to give the azido complexes **Cu^{II}(L)(OTf)(N$_3$)**, which were further characterized by UV-vis (Figure S10) and IR (Figure S11 and S13) spectroscopies.

Single crystal X-ray Diffraction Data

- **Hm-TriA-TPA** (CCDC 2153939)

Single crystals of $C_{60}H_{66}N_{13}O_{7.5}$ (**Hm-TriA-TPA.**$(Et_2O)_{1.5}$) were crystallized by slow diffusion of Et_2O in a CH_2Cl_2 solution of the compound. A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The crystal was kept at 203.00(10) K during data collection. Using Olex2, [S10] the structure was solved with the Unknown, [S11] structure solution program using Unknown and refined with the ShelXL, [S12] refinement package using Least Squares minimisation.

Empirical formula	$C_{60}H_{66}N_{13}O_{7.5}$
Formula weight	1089.25
Temperature/K	203.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.7425(2)
b/Å	15.3879(3)
c/Å	20.5147(5)
α/°	106.615(2)
β/°	95.925(2)
γ/°	102.708(2)
Volume/Å3	2829.13(11)
Z	2
ρcalcg/cm3	1.279
μ/mm-1	0.705
F(000)	1154.0
Crystal size/mm3	0.28 × 0.26 × 0.03
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.21 to 143.802
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -25 ≤ l ≤ 25
Reflections collected	47874
Independent reflections	10823 [Rint = 0.0514, Rsigma = 0.0350]
Data/restraints/parameters	10823/25/746
Goodness-of-fit on F2	1.037
Final R indexes [I>=2σ (I)]	R1 = 0.0592, wR2 = 0.1529
Final R indexes [all data]	R1 = 0.0863, wR2 = 0.1726
Largest diff. peak/hole / e Å-3	0.58/-0.44

- **Cu^{II}(Hm-TriA-TPA)(OTf)$_2$** (CCDC 2154000)

Single crystals of $C_{174}H_{162}Cu_3F_{18}N_{42}O_{36}S_6$ **[Cu^{II}(Hm-TriA-TPA)(OTf)$_2$(CH_3CN)]**$_3$ were crystallized by slow diffusion of Et_2O in a CH_3CN solution of the compound. A suitable crystal was selected and mounted on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The crystal was kept at 203.01(10) K during data collection. Using Olex2, [S10] the structure was solved with the Unknown, [S11] structure solution program using Unknown and refined with the ShelXL, [S12] refinement package using Least Squares minimisation.

Empirical formula	$C_{174}H_{162}Cu_3F_{18}N_{42}O_{36}S_6$
Formula weight	4142.43
Temperature/K	203.01(10)
Crystal system	triclinic
Space group	P-1
a/Å	13.81820(10)
b/Å	24.6077(3)
c/Å	34.2051(4)
α/°	87.5100(10)
β/°	86.7650(10)
γ/°	81.9360(10)
Volume/Å3	11490.1(2)
Z	2
ρcalcg/cm3	1.197
μ/mm-1	1.552
F(000)	4266.0
Crystal size/mm3	0.32 × 0.22 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.432 to 142.378
Index ranges	-16 ≤ h ≤ 16, -29 ≤ k ≤ 30, -40 ≤ l ≤ 41
Reflections collected	196803
Independent reflections	43691 [Rint = 0.1055, Rsigma = 0.0558]
Data/restraints/parameters	43691/210/2611
Goodness-of-fit on F2	1.065
Final R indexes [I>=2σ (I)]	R1 = 0.0564, wR2 = 0.1576
Final R indexes [all data]	R1 = 0.0696, wR2 = 0.1680
Largest diff. peak/hole / e Å-3	0.49/-0.61

3. Supplementary figures.

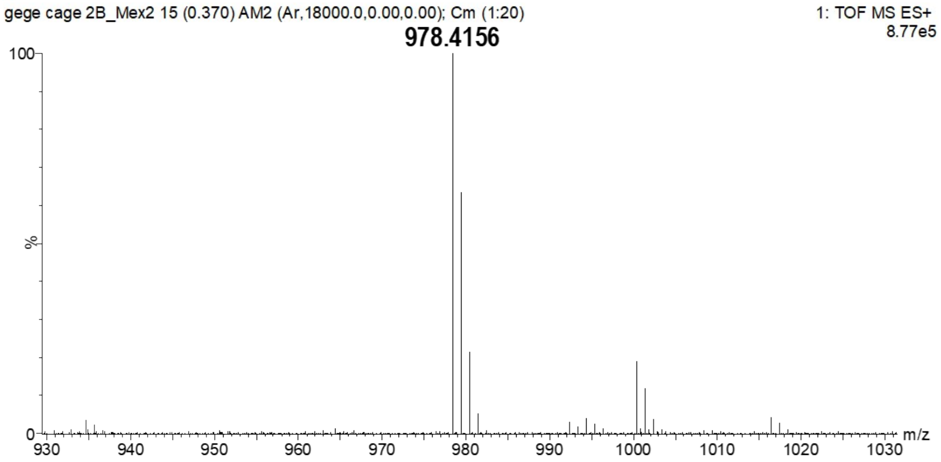

Figure S1. ESI-HRMS spectra of **Hm-TriA-TPA** in CH_2Cl_2 along with the zoom on the isotopic pattern at m/z = 978.4156 that can be attributed to **Hm-TBTA**.H+ (m/z $_{\text{calculated}}$ = 978.4158).

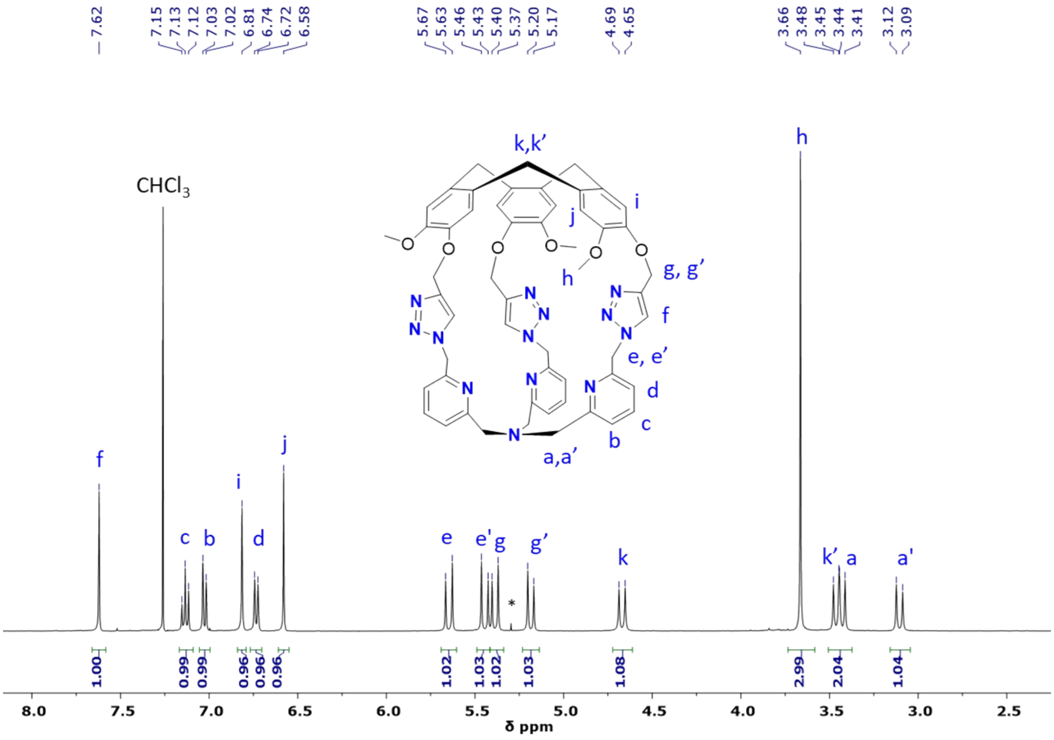

Figure S2. ^1H-NMR spectra ($CDCl_3$, 400 MHz) of **Hm-TriA-TPA**, at 298K (*=CH_2Cl_2).

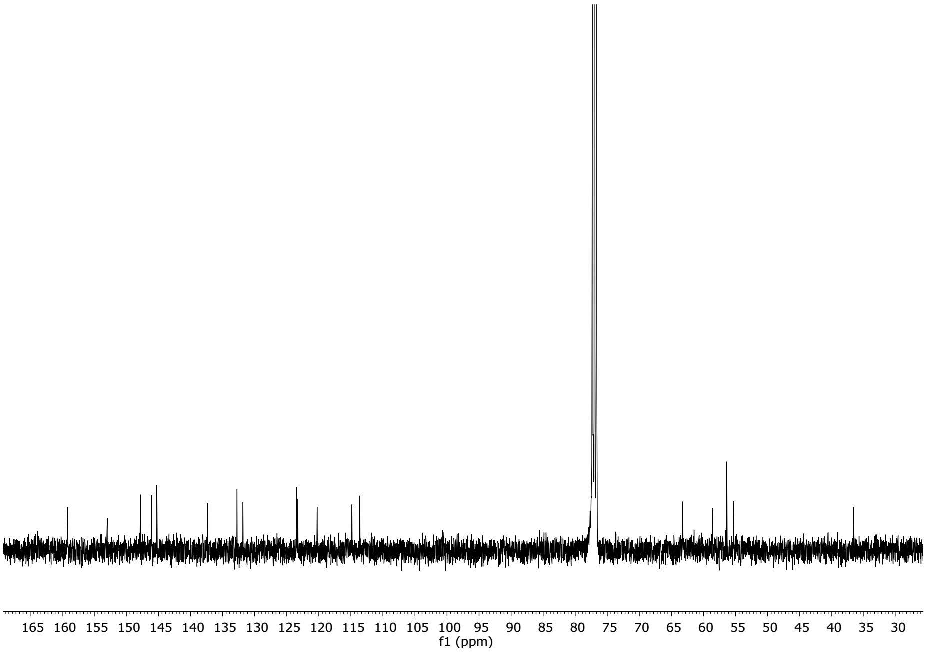

Figure S3. ^{13}C-NMR spectra (CDCl$_3$, 400 MHz) of **Hm-TriA-TPA**, at 298K.

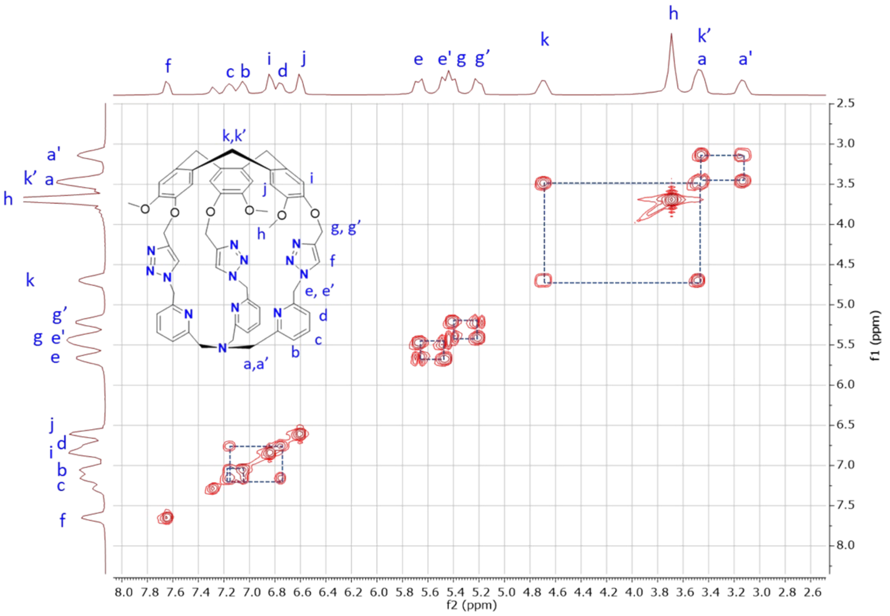

Figure S4. 2D COSY-NMR spectra (CDCl$_3$, 400MHz) of **Hm-TriA-TPA**, at 298K.

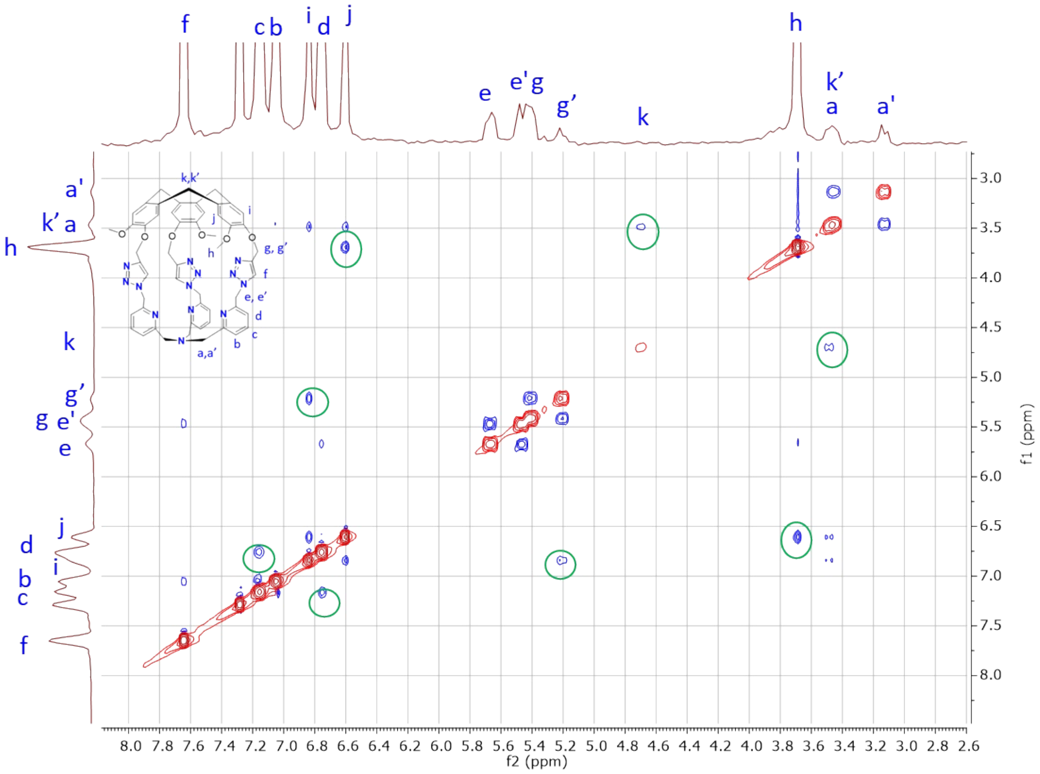

Figure S5. 2D NOESY-NMR spectra ($CDCl_3$, 300MHz) of **Hm-TriA-TPA**, at 298K.

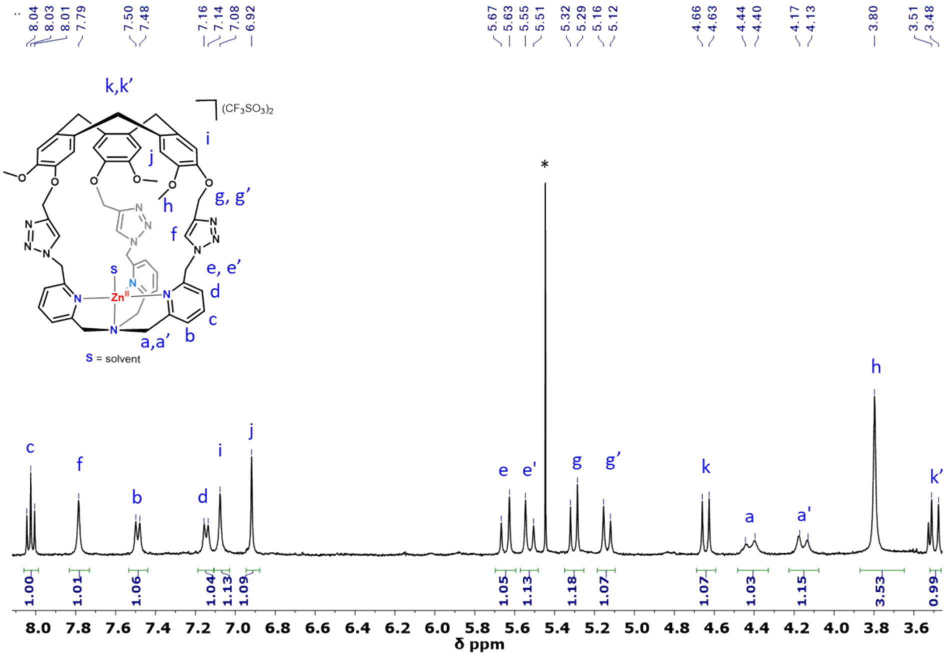

Figure S6. ^{1}H-NMR spectra (CD_3CN, 400 MHz) of **Zn^{II}(Hm-TriA-TPA)(OTf)$_2$**, at 298K (*=CH_2Cl_2). Isolated complex obtained upon precipitation with Et_2O.

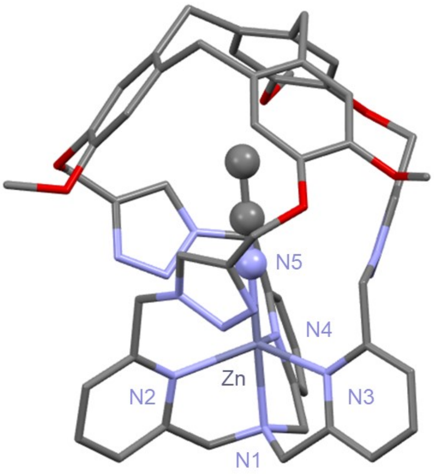

Figure S7. DFT-optimized structure (PBE0-D3/def2-TZVP, COSMO) of **Zn^{II}(Hm-TriA-TPA)(CH_3CN)** showing a distorted trigonal bipyramidal geometry. The trigonal plane comprises the three pyridines (N2, N3 and N4) with Zn-N distances of 2.222 Å. The coordination sphere is completed by the tertiary amine (N1) and one molecule of acetonitrile (N5) with respective Zn-N distances of 2.118 Å and 2.015 Å.

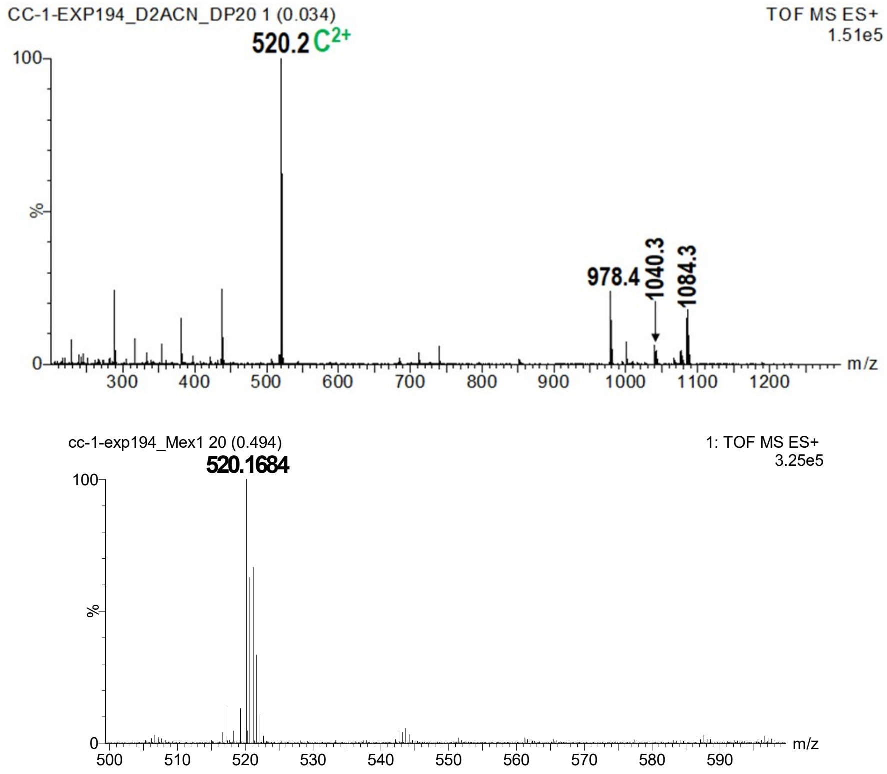

Figure S8. ESI-HRMS spectra of **Cu^{II}(Hm-TriA-TPA)$(OTf)_2$** in CH_3CN along with the zoom on the isotopic pattern at m/z = 520.1684 that can be attributed to **Cu^{II}(Hm-TriA-TPA)$^{2+}$** (m/z $_{calculated}$ = 520.1685). Isotopic pattern at m/z = 978.4 could be attributed to the free ligand due to common partial metal-ion decomplexation in the condition of analysis (electrospray ionization).

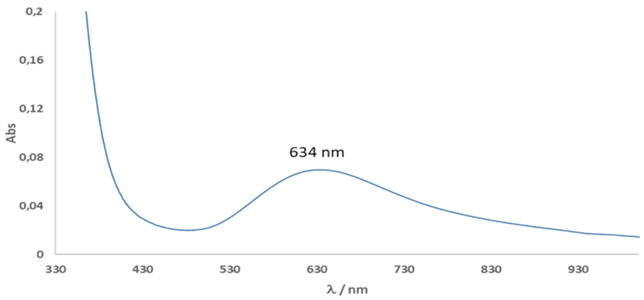

Figure S9. UV-vis spectra of **Cu^{II}(Hm-TriA-TPA)$(OTf)_2$** at 0,5 mM in acetone at 298K (λ_{max} = 634nm, ε = 139 M^{-1} cm^{-1}).

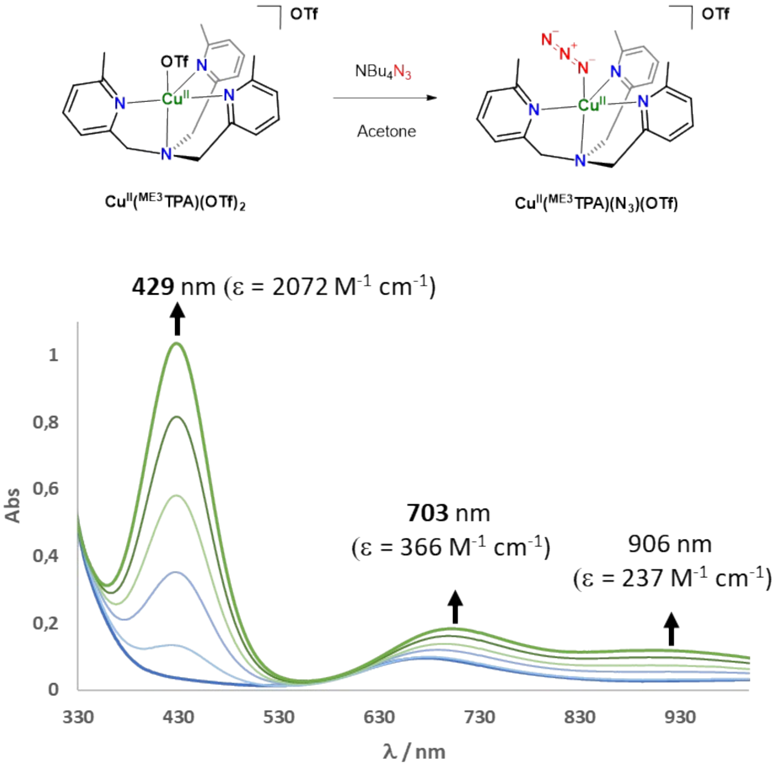

Figure S10. UV-vis monitoring of the addition of NBu_4N_3 (0 to 1.0 equiv.) to a 0,5 mM solution of **$Cu^{II}(^{Me3}TPA)(OTf)_2$** in acetone at 298K ($\lambda_{max}$ = 429nm, ε = 2072 M^{-1} cm^{-1}).

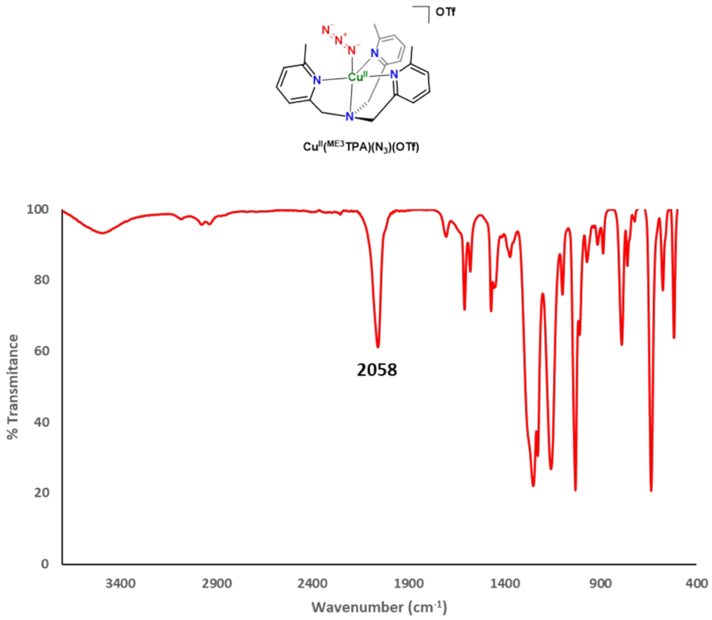

Figure S11. Infrared spectra of **$Cu^{II}(^{Me3}TPA)(N_3)(OTf)$**, the characteristic N≡N stretch is observed at 2058 cm^{-1}.

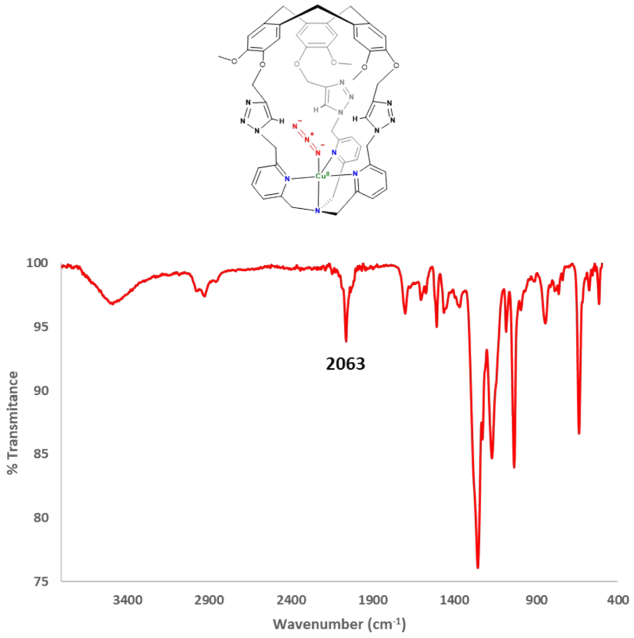

Figure S12. Infrared spectra of **Cu^{II}(Hm-TriA-TPA)(OTf)(N$_3$)**, the characteristic N≡N stretch is observed at 2063 cm^{-1}.

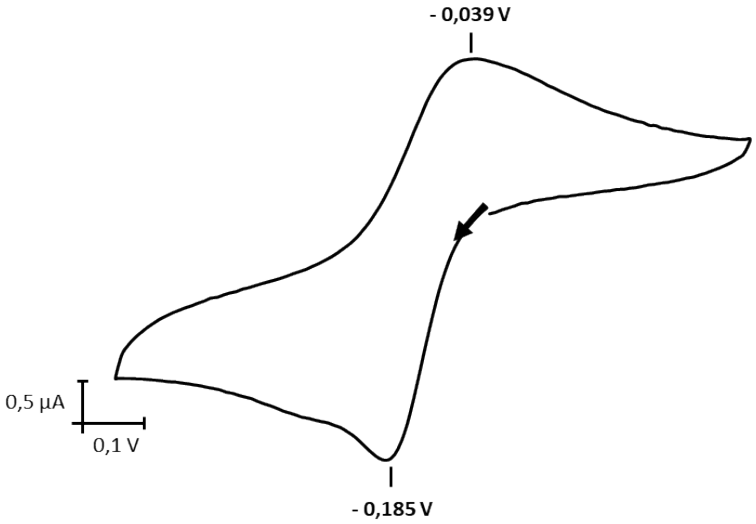

Figure S13. Cyclic voltammogram of **Cu^{II}(Hm-TriA-TPA)(OTf)** (-0.2 V to 0.8 V; 1.5 mM; 100 mV.s^{-1}; CH_3CN; 0.15 M NBu_4PF_6; platinum WE ∅ = 2mm; E vs. Fc/Fc$^+$).

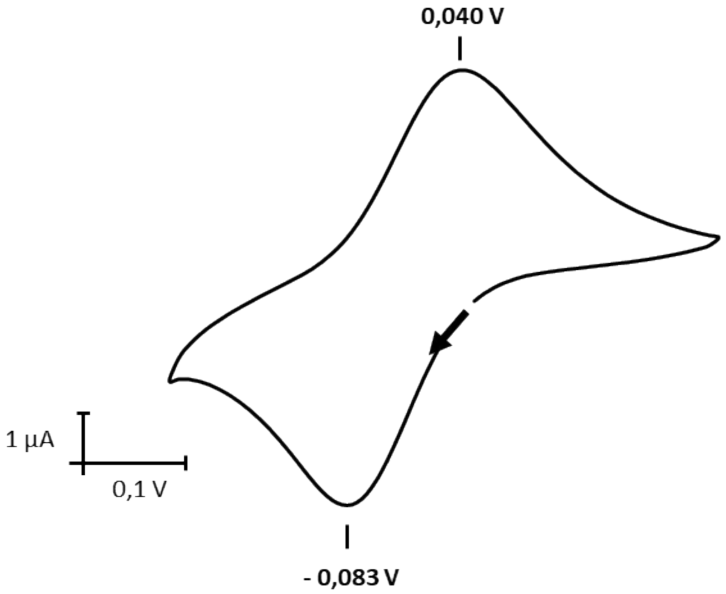

Figure S14. Cyclic voltammogram of **Cu^{II}(^{Me3}TPA)(N$_3$)(OTf)** (-0.2 V to 0.8 V; 2.5 mM; 100 mV.s^{-1}; CH$_3$CN; 0.25 M NBu$_4$PF$_6$; platinum WE ∅ = 2mm; E vs. Fc/Fc$^+$).

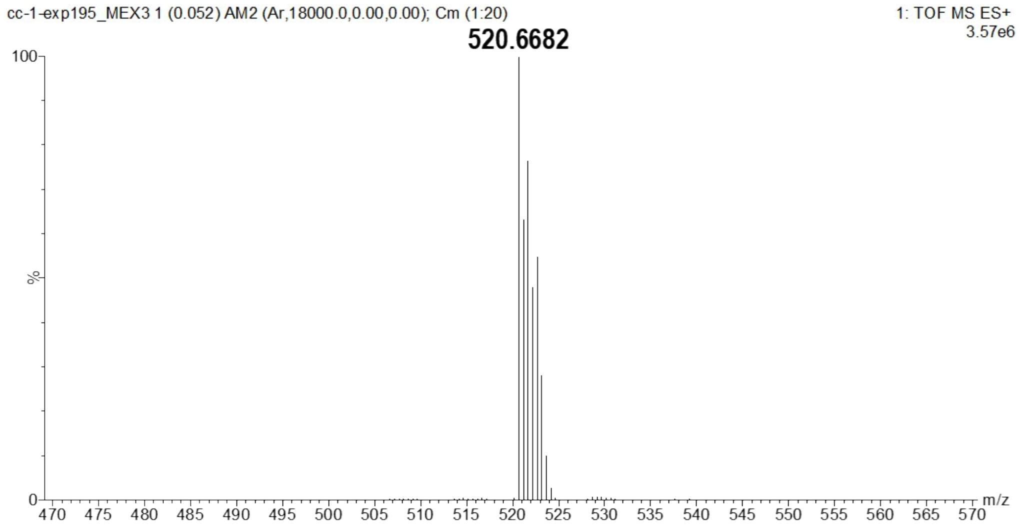

Figure S15. ESI-HRMS spectra of **Zn^{II}(Hm-TriA-TPA)(OTf)$_2$** in CH$_3$CN, the isotopic pattern at m/z = 520.6682 can be attributed to **Zn^{II}(Hm-TriA-TPA)$^{2+}$** (m/z $_{\text{calculated}}$ = 520.6683).

5. Supplementary references.

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