Synthesis of flexible nanotweezers with various metals and their application to carbon nanotube extraction

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Materials and methods

Materials

SWNTs (65CoMoCAT and HiPCo) were purchased from Sigma Aldrich and NanoIntegris Technologies Inc., respectively. The nanotweezers $\mathbf{1}_{H2\cdot H2}$, $\mathbf{1}_{Zn\cdot Zn}$, $\mathbf{1}_{Zn\cdot H2}$, and $\mathbf{1}_{Co\cdot Co}$ were prepared according to the methods reported in the literature.[1, 2]

Instruments and measurements

^{1}H NMR spectra were recorded on a Bruker Avance III Nanobay (300 MHz); chemical shifts are expressed in ppm relative to chloroform (7.26 ppm). Mass spectra and accurate mass measurements (HRMS) were obtained on a Bruker Daltonics Ultraflex II spectrometer in the MALDI/TOF reflectron mode using dithranol as a matrix. UV-Vis spectra were recorded on a Varian Cary 1 and a Shimadzu UV3600 spectrophotometers. Bath sonication and centrifugation were carried out by use of Branson 5510 and Avanti J-E (Beckman Coulter, Inc), respectively. Measurements for porphyrin identification were made at the the "*Welience, Pôle Chimie Moléculaire de l'Université de Bourgogne* (*WPCM*)".

Methods

[2,2'-Bis-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-5-yl)diphenylether]Ni_2 $\mathbf{1}_{Ni•Ni}$. Nickel(II) chloride (69 mg, 0.534 mmol) and $\mathbf{1}_{H2•H2}$ (60 mg, 0.0534 mmol) were dissolved in 15 mL of DMF. The resulting solution was then refluxed during 6 h. After evaporation, the crude compound was redissolved in 50 mL of dichloromethane, washed 3 times with 50 mL of water, then dried over $MgSO_4$. The solvent was removed by rotatory evaporation and the crude compound was chromatographed on silica gel using CH_2Cl_2 as eluent. The first red band was collected, evaporated to give $\mathbf{1}_{Ni•Ni}$ in quantitative yield (65.3 mg, 0.0529 mmol). UV-visible (CH_2Cl_2): λ_{max} (nm) (ε x 10^{-3} L mol^{-1} cm^{-1}) = 392 (241), 524 (19), 559 (36). ^1H NMR ($CDCl_3$): δ. 9.52 (s, 2H, meso), 8.11 (br s, 6H, ArH, meso), 7.72 (t, ^3J = 7.5 Hz, 2H, ArH), 7.10 (t, ^3J = 7.5 Hz, 2H, ArH), 6.86 (d, ^3J = 7.5 Hz, 2H, ArH), 3.91 (m, 8H, -CH_2-CH_3), 2.96 (m, 12H, CH_3), 1.57-1.79 (m, 44H). MS (MALDI/TOF): m/z = 1234.32 $[M]^{+•}$, 1234.50 Calcd. for $C_{76}H_{78}N_8ONi_2$. HRMS (MALDI/TOF): m/z = 1234.5074 $[M]^{+•}$, 1234.5000 Calcd. for $C_{76}H_{78}N_8ONi_2$.

[2,2'-Bis-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-5-yl)diphenylether]Cu_2 $\mathbf{1}_{Cu•Cu}$. Copper(II) acetate monohydrate (60 mg, 0.30 mmol) dissolved in 10 mL of absolute methanol was added to a chloroform solution (80 mL) of $\mathbf{1}_{H2•H2}$ (60 mg, 0.053 mmol). The resulting solution was then refluxed during 4 h 30. After evaporation, the compound was redissolved in dichloromethane, washed 3 times with 250 mL of H_2O, then dried over $MgSO_4$. The solvent was removed by rotatory evaporation and the crude compound was chromatographed on silica gel using CH_2Cl_2 as eluent. The first band was collected, evaporated to give $\mathbf{1}_{Cu•Cu}$ in quantitative yield (65 mg, 0.052 mmol). UV-visible (CH_2Cl_2): λ_{max} (nm) (ε x 10^{-3} L mol^{-1} cm^{-1}) = 391 (231), 532 (15), 568 (20). MS (MALDI/TOF): m/z = 1244.43 $[M]^{+•}$, 1244.49 Calcd. for $C_{76}H_{78}N_8OCu_2$. HRMS (MALDI/TOF): m/z = 1244.4922 $[M]^{+•}$, 1244.4885 Calcd. for $C_{76}H_{78}N_8OCu_2$.

[2,2'-Bis-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-5-yl)diphenylether]CoZn $\mathbf{1}_{Co•Zn}$. Cobalt(II) acetate tetrahydrate (80 mg, 0.321 mmol) dissolved in 10 mL of absolute methanol was added to a dichloromethane solution (80 mL) of $\mathbf{1}_{Zn•H2}$ (60 mg, 0.053 mmol). The resulting solution was then refluxed during 4 h 30. After evaporation, the compound was redissolved in dichloromethane, washed 3 times with 250 mL of H_2O, then dried over $MgSO_4$. The solvent was removed by rotatory evaporation and the crude compound was chromatographed on silica gel using CH_2Cl_2 first, then CH_2Cl_2/MeOH 96/4 and finally CH_2Cl_2/MeOH 92/8 as eluent.

The first band was collected, evaporated to give $\mathbf{1}_{Co\bullet Zn}$ in almost quantitative yield (62.1 mg, 0.050 mmol). UV-visible (CH_2Cl_2): λ_{max} (nm) (ε x 10^{-3} L mol^{-1} cm^{-1}) = 390 (130), 538 (11), 570 (9.9). MS (MALDI/TOF): m/z = 1241.47 $[M]^{+\bullet}$, 1241.49 Calcd. for $C_{76}H_{78}N_8OCoZn$. HRMS (MALDI/TOF): m/z = 1241.4949 $[M]^{+\bullet}$, 1241.4917 Calcd. for $C_{76}H_{78}N_8OCoZn$.

[2,2'-Bis-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-5-yl)diphenylether]Co $\mathbf{1}_{Co\bullet H2}$. 49 mg (0.039 mmol) of the heterobimetallic cobalt zinc complex $\mathbf{1}_{Co\bullet Zn}$ was dissolved in 5 mL of dichloromethane. 3 mL of HCl (5% in water) was added and the solution was stirred at room temperature for 15 min. A hydrogen carbonate solution was then added and the reaction mixture was then washed 3 times with water. The solvent was removed by rotatory evaporation and the crude compound was purified by exclusion chromatography to give the title compound $\mathbf{1}_{Co\bullet H2}$ in 65% yield (30,25 mg, 0.026 mmol). UV-visible (CH_2Cl_2): λ_{max} (nm) (ε x 10^{-3} L mol^{-1} cm^{-1}) = 402 (559), 503 (4.6), 539 (4.5), 573 (3.3), 627 (1.2). MS (MALDI/TOF): m/z = 1180.54 $[M+H]^+$, 1180.46 Calcd. for $C_{76}H_{81}N_8OCo$. HRMS (MALDI/TOF): m/z = 1180.5828 $[M+H]^+$, 1180.5860 Calcd. for $C_{76}H_{81}N_8OCo$.

[2,2'-Bis-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-5-yl)diphenylether]Co(III)Cl Co(III)Cl. $\mathbf{1}_{Co(III)Cl\bullet Co(III)Cl}$. A suspension of heterobimetallic biscobalt complex $\mathbf{1}_{Co\bullet Co}$ (21 mg, 0.016 mmol) in 9 mL of methanol was added concentrated hydrochloric acid (42 µl, 0.40 mmol) and then stirred at room temperature under oxygen during one day. The methanol was removed under reduced pressure and the residue was dissolved in 5 mL of dichloromethane. The organic phase was washed several times with water until the aqueous phase was neutral. The solvent was removed by rotatory evaporation to give the title compound $\mathbf{1}_{Co(III)Cl\bullet Co(III)Cl}$ in 82% yield (17.2 mg, 0.013 mmol). UV-visible (CH_2Cl_2): λ_{max} (nm) = 412, 530, 562. MS (ESI): m/z = 618.54 $[M-2Cl]^{2+}$, 618.25 Calcd. for $C_{76}H_{78}N_8OCo_2$. HRMS (MALDI/TOF): m/z = 1236.4999 $[M-2Cl]^+$, 1236.4957 Calcd. for $C_{76}H_{78}N_8OCo_2$.

Extraction of SWNTs with nanotweezers 1. The dispersion of **1** (10 mg) and SWNTs (10 mg) in methanol (35 mL) was bath-sonicated at 20 °C for 12.5 h and then centrifuged at room temperature in the range of 2469*g* – 2851*g* for 165 min. The supernatant was subjected to the green laser irradiation (Fig. 1) and absorption spectroscopic measurement (Fig. 2 and S1) to confirm the existence of .

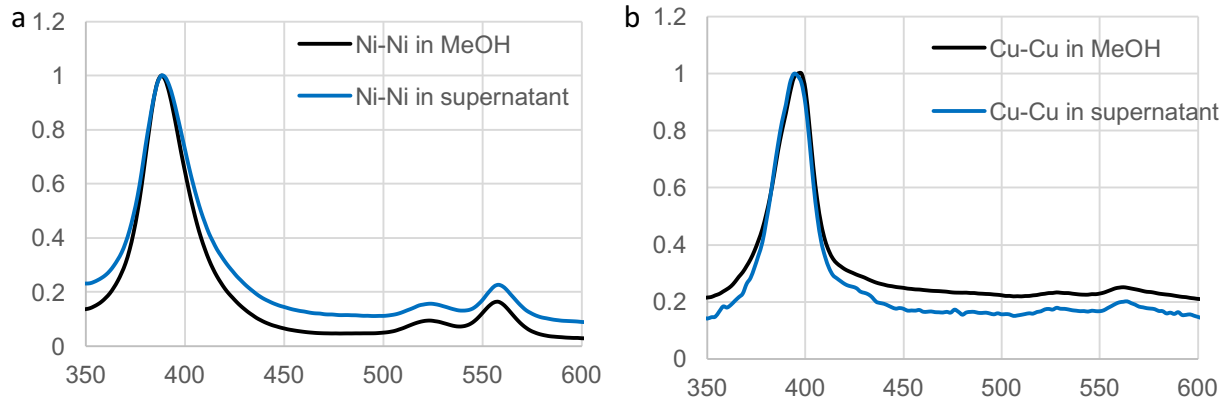


Figure S1: Absorption spectra of nanotweezers $\mathbf{1}_{Ni\cdot Ni}$ (a) and $\mathbf{1}_{Cu\cdot Cu}$ (b) before and after extraction of SWNTs in methanol. The absorbance is normalized at the Soret bands before and after extraction.

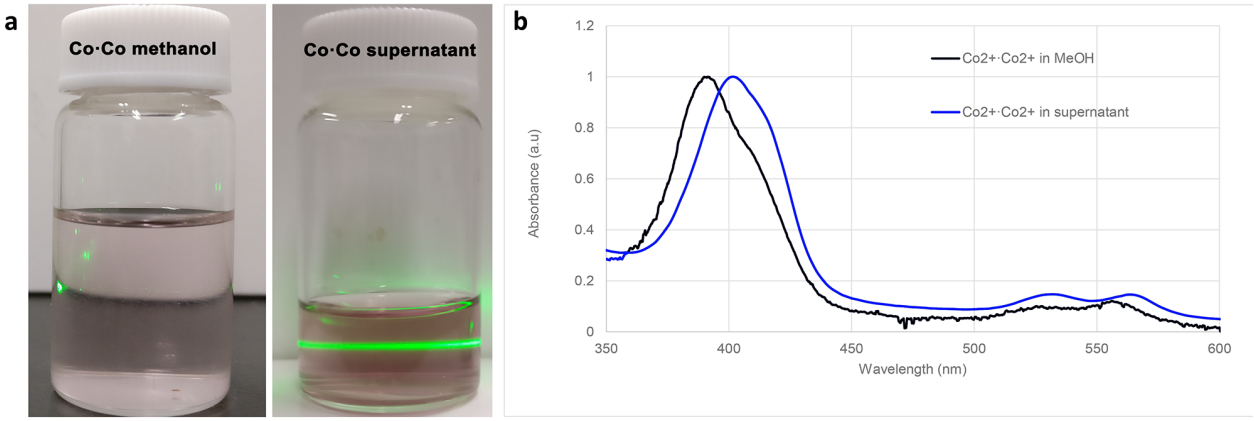


Figure S2: (a) Methanol solutions of $\mathbf{1}_{Co\cdot Co}$ bisporphyrins after sonication (left) without and (right) with HiPCo. (b) Absorption spectra of methanol solution and HiPCo dispersion of $\mathbf{1}_{Co\cdot Co}$ bisporphyrin.

Figure S3: Image of the supernatant after the extraction of SWNTs with Co^{3+}-Co^{3+} bisporphyrin, showing no Tyndall effect.

References

1. a) Gros, C. P.; Brisach, F.; Meristoudi, A.; Espinosa, E.; Guilard, R.; Harvey, P. D., Modulation of the Singlet-Singlet Through-Space Energy Transfer Rates in Cofacial Bisporphyrin and Porphyrin-Corrole Dyads. *Inorg. Chem.* **2007,** *46* (1), 125-135. b) Harvey, P. D.; Stern, C.; Gros, C. P.; Guilard, R., Through Space Singlet Energy Transfers in the Light Harvesting Systems and Cofacial Bisporphyrin Dyads. *J. Porphyrins Phthalocyanines* **2010**, *14*, 55-63. c) Gros, C. P.; Aly, S. M.; El Ojaimi, M.; Barbe, J.-M.; Brisach, F.; Abd-El-Aziz, A. S.; Harvey, P. D., Through Space Singlet-Singlet and Triplet-Triplet Energy Transfers in Cofacial Bisporphyrins Held by the Carbazoyl Spacer. *J. Porphyrins Phthalocyanines* **2007**, *11* (3-4), 244-257. d) Chen, P.; Lau, H.; Habermeyer, B.; Gros, C. P.; Barbe, J.-M.; Kadish, K. M., Electrochemistry, Spectroelectrochemistry and Catalytic Activity of Biscobalt Bisporphyrin Dyads Towards Dioxygen Reduction. *J. Porphyrins Phthalocyanines* **2011**, *15*, 467-479.
2. Olaya, A. J.; Schaming, D.; Brevet, P.-F.; Nagatani, H.; Zimmermann, T.; Vanicek, J.; Xu, H.-J.; Gros, C. P.; Barbe, J.-M.; Girault, H. H., Self-Assembled Molecular Rafts at Liquid|Liquid Interfaces for Four-Electron Oxygen Reduction. *J. Am. Chem. Soc.* **2012,** *134* (1), 498-506.

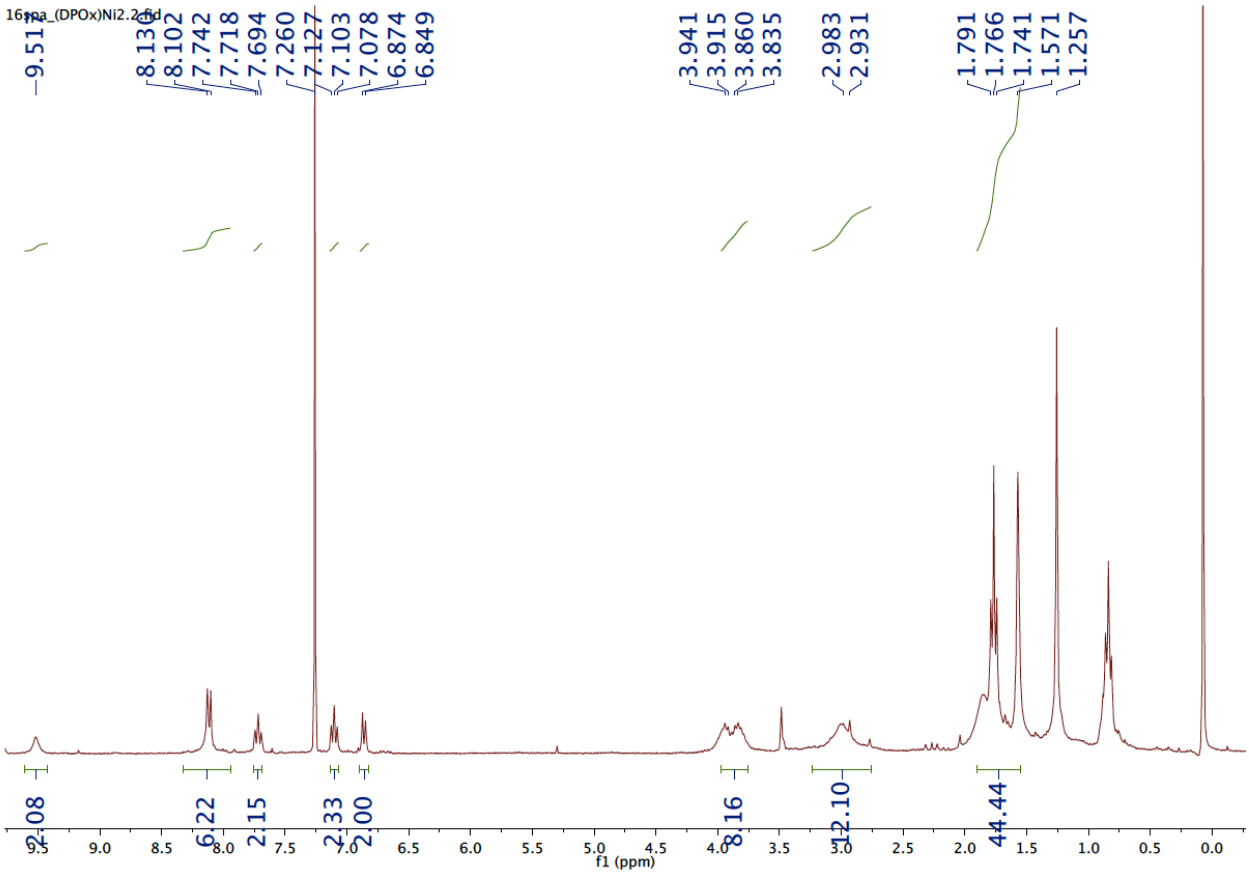


Figure S4: ^{1}H NMR spectrum of $\mathbf{1}_{\mathbf{Ni\text{-}Ni}}$ in $CDCl_3$

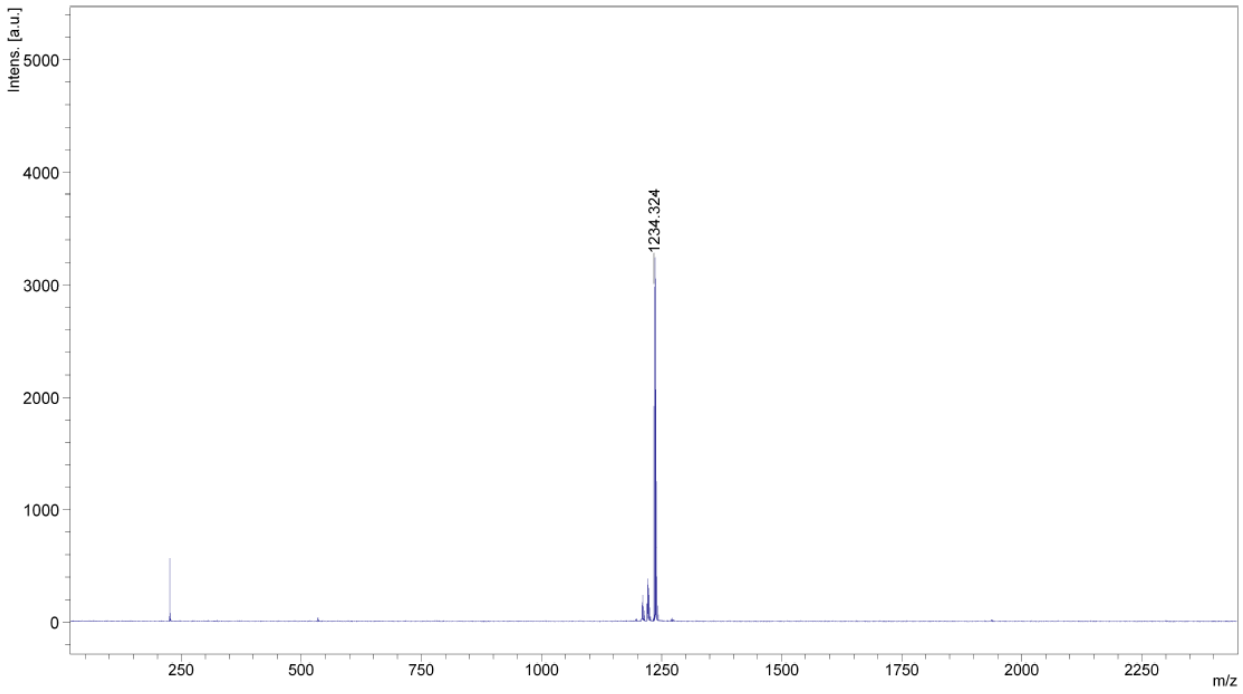
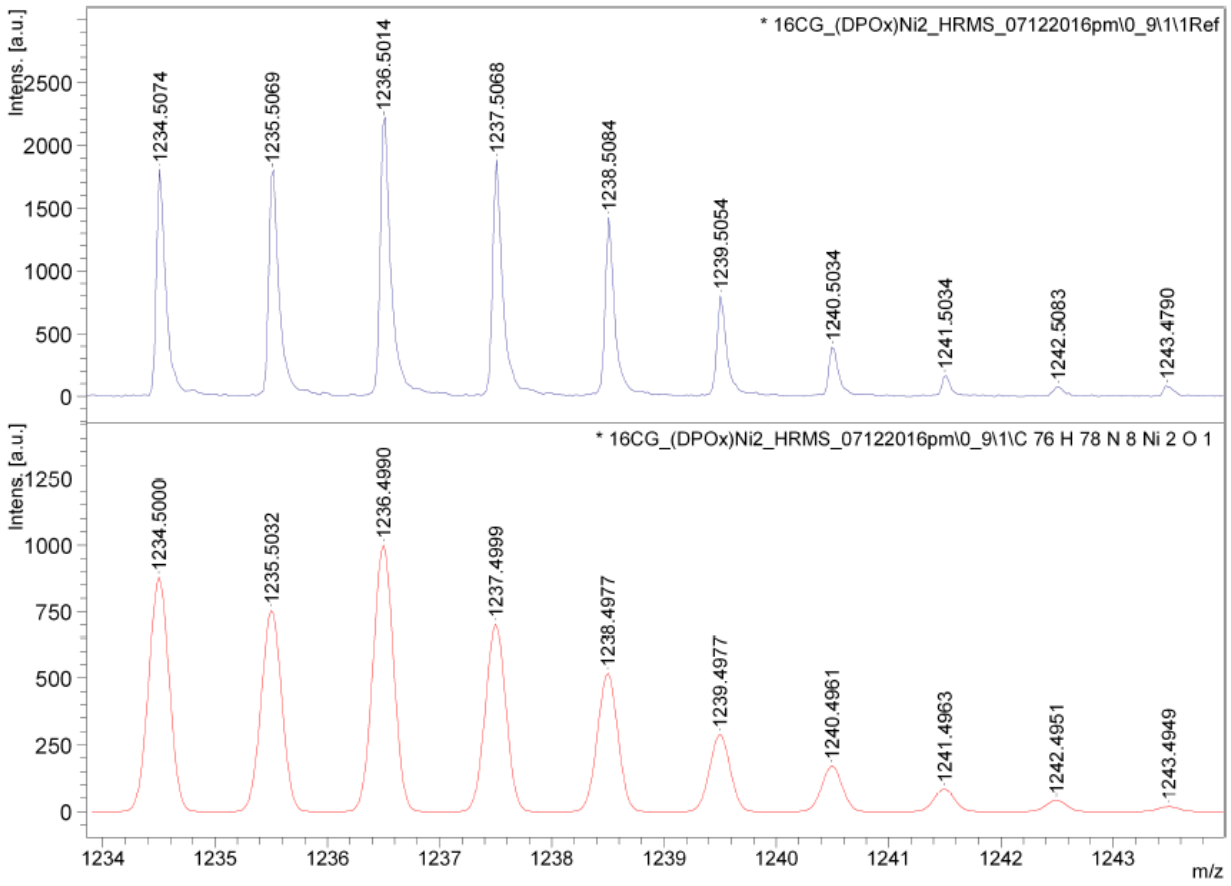


Figure S5: MS (MALDI/TOF) mass spectrum of $\mathbf{1_{Ni\text{-}Ni}}$



Chemical Formula: $C_{76}H_{78}N_8Ni_2O$
Exact Mass: 1234.5000
m/z $_{exp}$ = 1234.5074
δ (ppm) = 5.99

Figure S6: HRMS (MALDI/TOF) mass spectrum of $\mathbf{1}_{\mathbf{Ni•Ni}}$

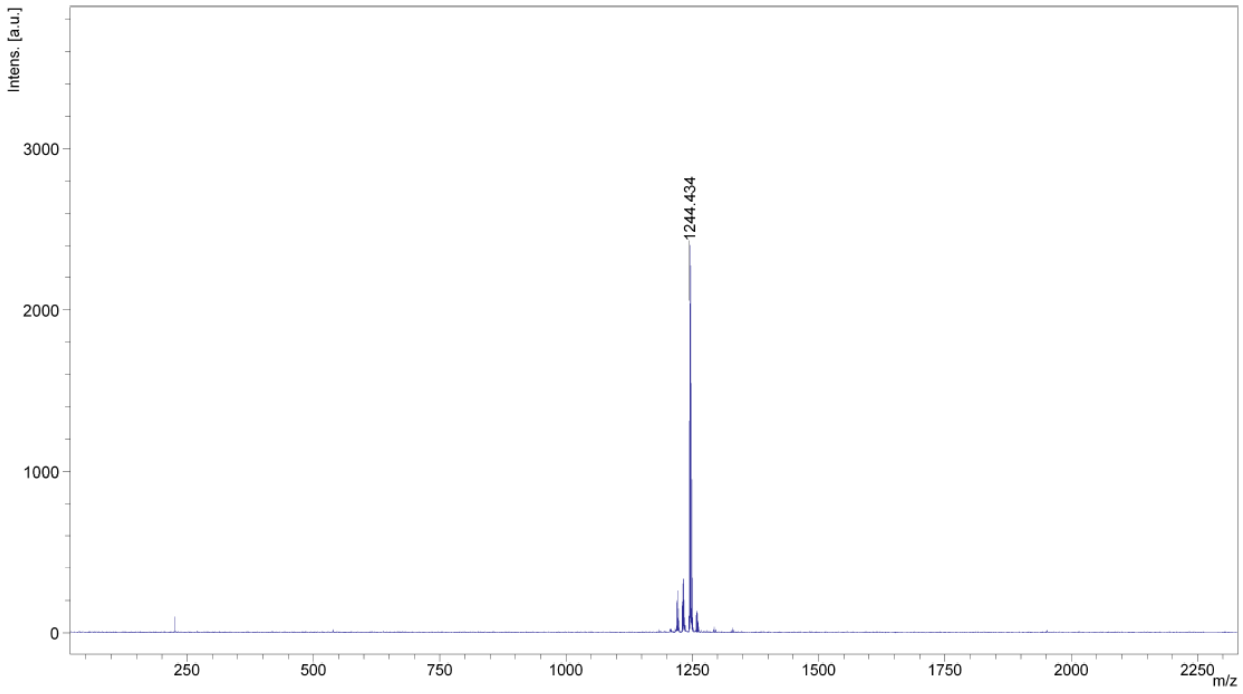
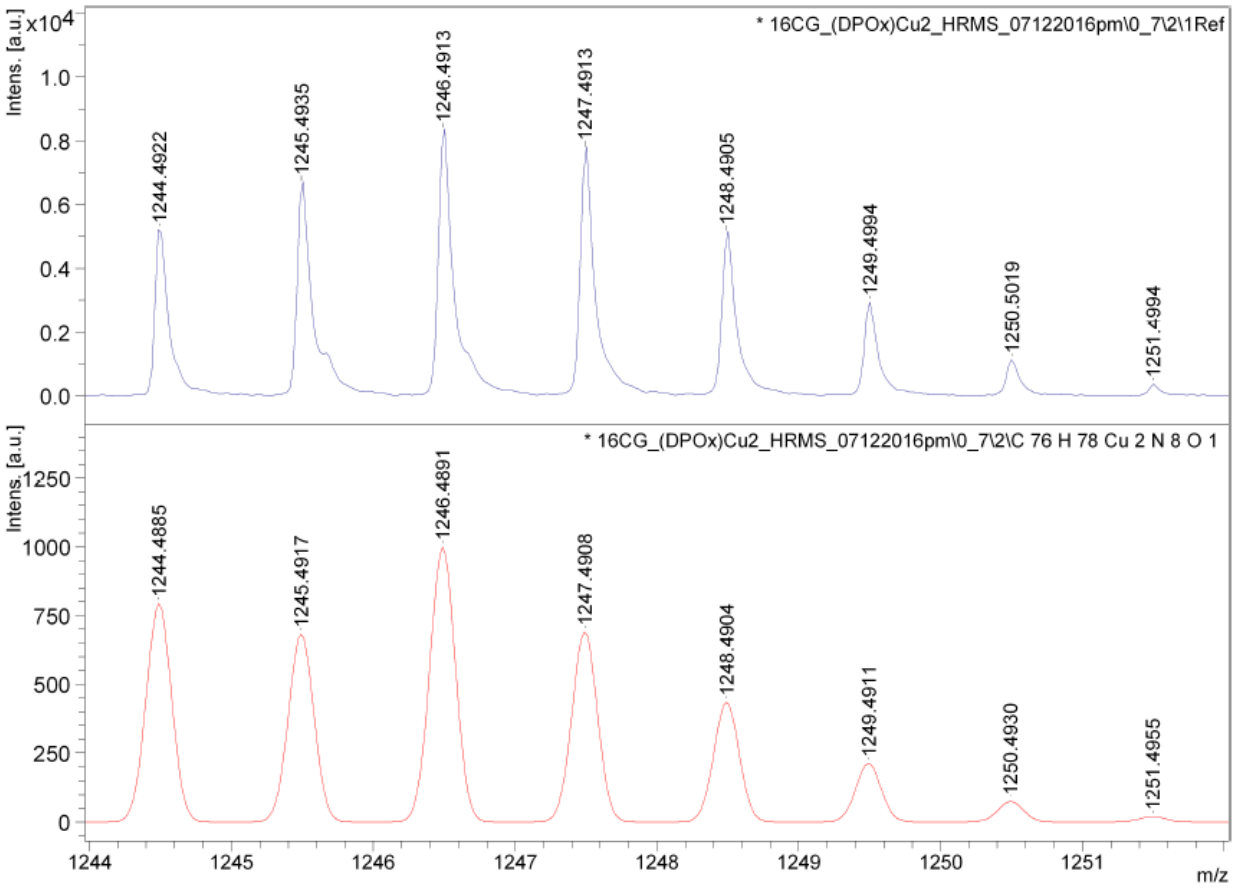
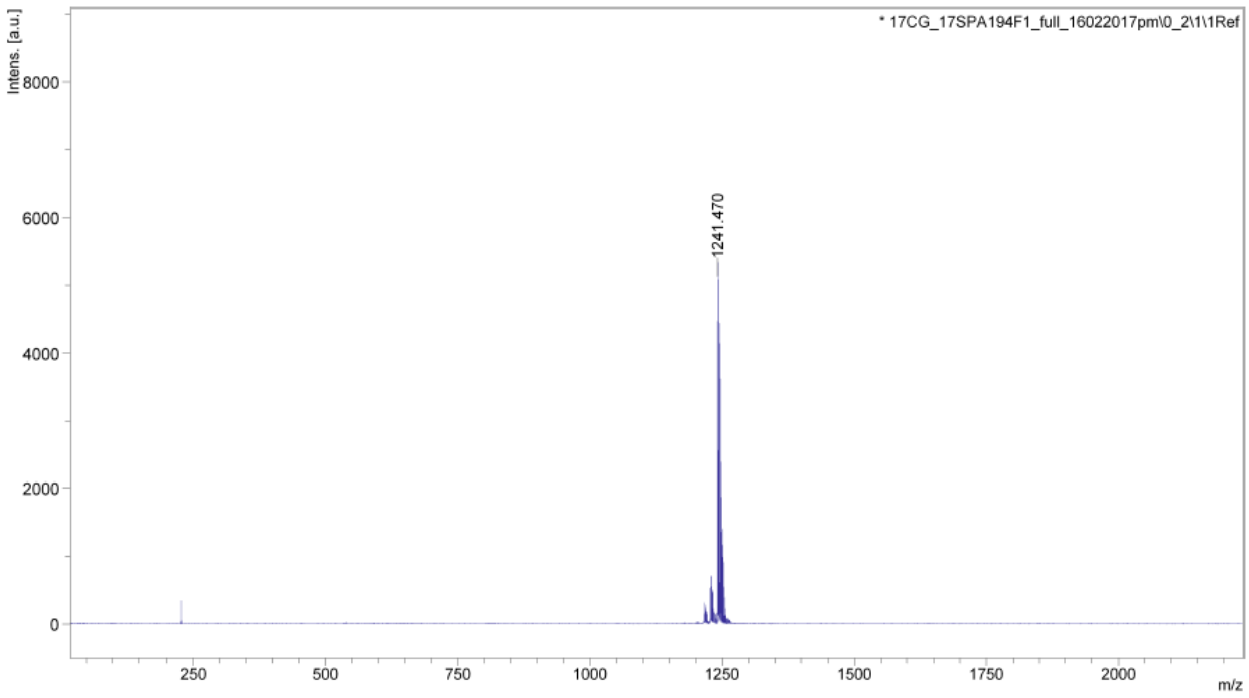


Figure S7: MS (MALDI/TOF) mass spectrum of $\mathbf{1}_{\mathbf{Cu\cdot Cu}}$



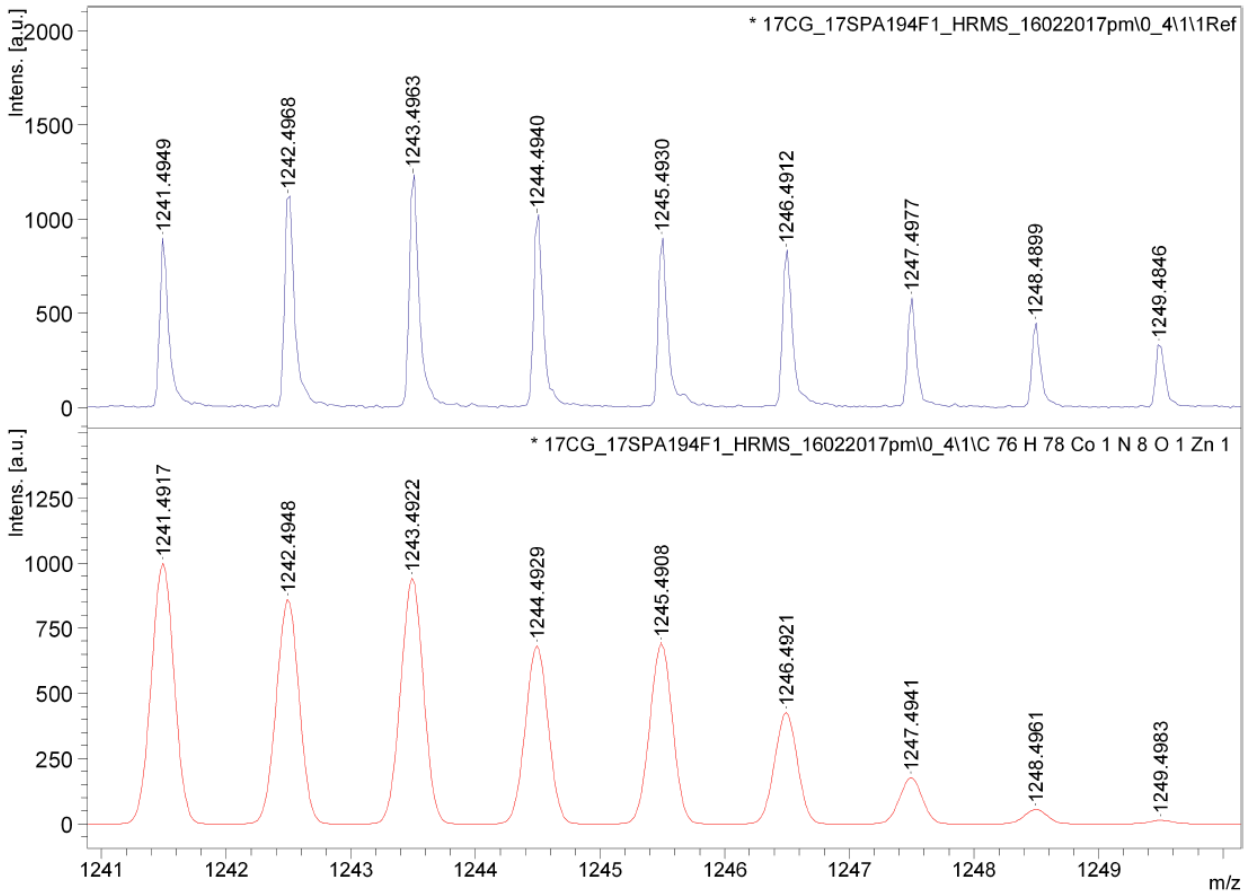
Chemical Formula: $C_{76}H_{78}Cu_2N_8O$
Exact Mass: 1244.4885
m/z $_{exp}$ = 1244.4922
δ (ppm) = 2.97

Figure S8: HRMS (MALDI/TOF) mass spectrum of $\mathbf{1_{Cu•Cu}}$



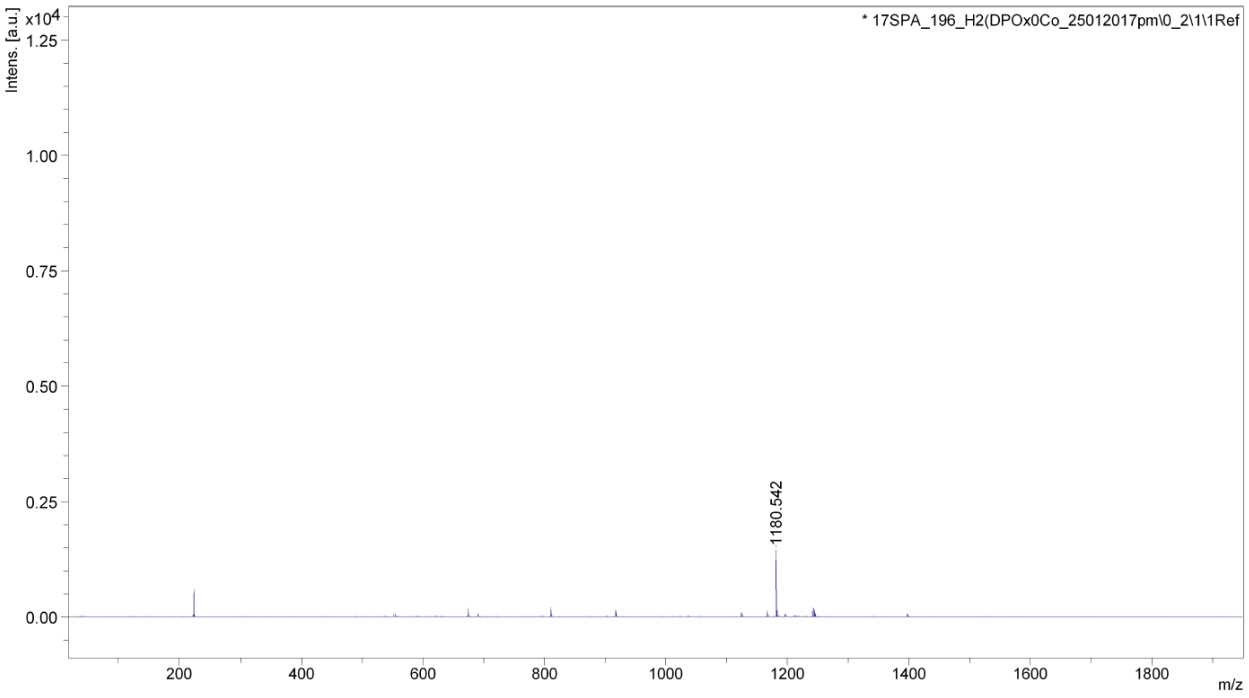
Chemical Formula: $C_{76}H_{78}CoN_8OZn$
Exact Mass: 1241,4922
Molecular Weight: 1243,8282

Figure S9: MS (MALDI/TOF) mass spectrum of $\mathbf{1}_{\mathbf{Zn\cdot Co}}$



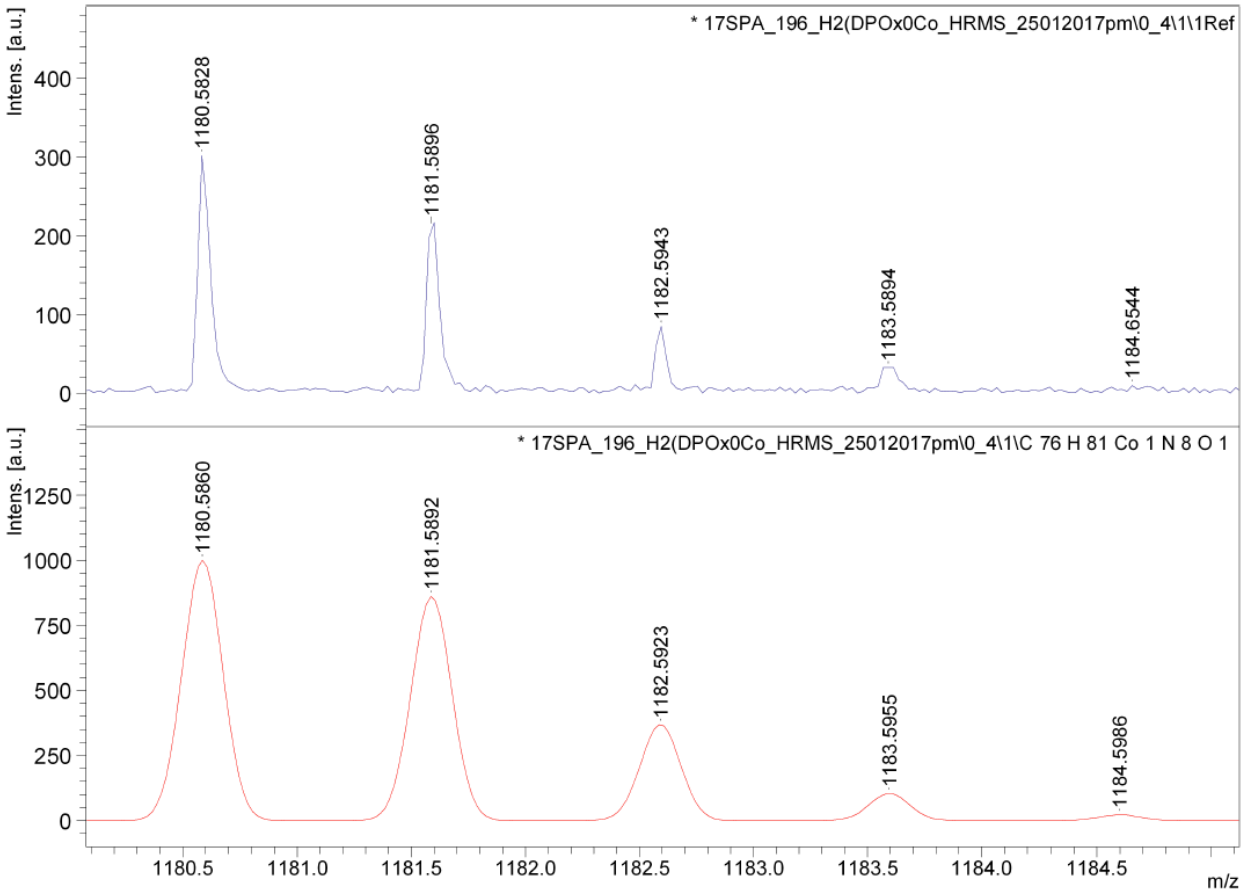
Chemical Formula: $C_{76}H_{78}CoN_8OZn$
Exact Mass: 1241.4917
m/z $_{exp}$ = 1234. 4949
δ (ppm) = 2.61

Figure S10: HRMS (MALDI/TOF) mass spectrum of $\mathbf{1_{Zn\cdot Co}}$



Chemical Formula: $C_{76}H_{80}CoN_8O$
Exact Mass: 1179,5787
Molecular Weight: 1180,4642

Figure S11: MS (MALDI/TOF) mass spectrum of $\mathbf{1_{Co•H2}}$



Chemical Formula: $C_{76}H_{81}CoN_8O$
Exact Mass: 1180. 5860
m/z $_{exp}$ = 1180. 5828 $[M+H]^+$
δ (ppm) = 2.70

Figure S12: HRMS (MALDI/TOF) mass spectrum of $\mathbf{1_{Co•H2}}$

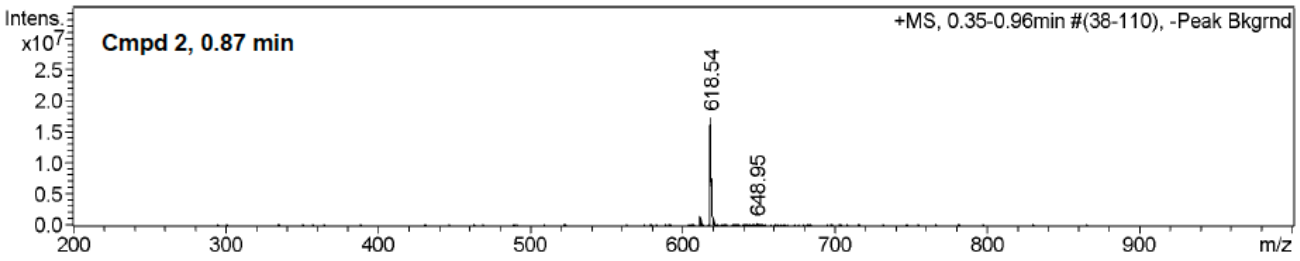


Figure S13: MS (ESI) mass spectrum of $\mathbf{1}_{Co(III)Cl \bullet Co(III)Cl}$

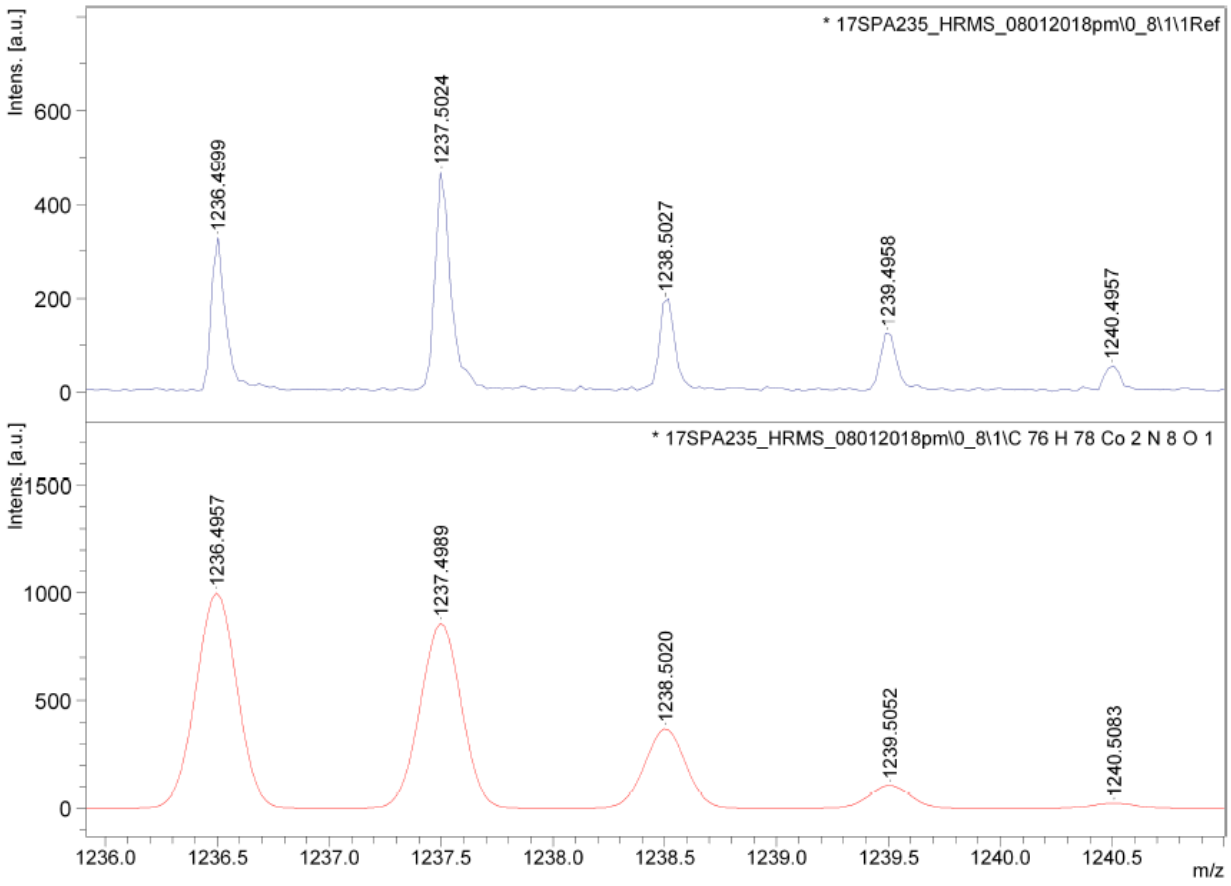


Figure S14: HRMS (MALDI-TOF) mass spectrum of $\mathbf{1}_{Co(III)Cl \bullet Co(III)Cl}$