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Supporting Information

Metal-Coordination-Assisted Folding and Guest Binding in Helical Aromatic Oligoamide Molecular Capsules

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1. Methods for NMR and X-ray crystallography

Nuclear Magnetic Resonance. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 at 400 MHz and 101 MHz, respectively. Chemical shifts (δ) are given in part per million (ppm) with tetramethylsilane as an internal standard. Coupling constants are given in Hertz (Hz) and the multiplicity of signals is indicated as following: s (singulet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), m (multiplet), br. s (broad singulet). Data processing was performed with Topspin 2.0 software. Samples were not degassed.

Crystallography. The X-ray diffraction measurements for **1**, and **1-Cu** were carried out on a Rigaku FRX rotating anode (2.9 kW) diffractometer at the IECB x-ray facility (UMS 3033 – UMS001). CuKα radiation monochromated with high flux Osmic Varimax mirrors was used for data collections. The x-ray source is equipped with a Dectris Pilatus 200K detector and partial chi goniometer. The Rigaku CrystalClear suite[1] was used to index and integrate data with a multi-scan absorption correction. Both structures were solved with Shelxt and refined by full-matrix least-squares method on F^2 with Shelxl-2014.[2] Hydrogen atoms were placed at idealized position and were refined in the riding-model approximation, with $U_{iso}(H)=1.2U_{eq}$(CH, CH_2, NH) and $U_{iso}(H)=1.5U_{eq}(CH_3)$. Almost all non-hydrogen atoms of the backbones, one chloroform molecule and BF_4 anions were refined with anisotropic temperature parameters. Isotropic displacement parameters were used for other non-hydrogen atoms. FVAR, ISOR, SIMU and DELU instructions were employed to model temperature parameters. The geometry of the molecules was improved with DFIX, SAME, FRAG or AFIX66 commands. Heavily disordered solvent molecules were removed using SQUEEZE[3] procedure. For search and analysis of solvent accessible voids in the structures default parameters were used: grid 0.20 Å, probe radius 1.2 Å and NStep 6. Calculated total potential solvent accessible void volumes and electron counts per unit cell were 15215 $Å^3$ and 4212, and 3363.9 $Å^3$ and 1095 for **1** and **1-Cu**, respectively. Non-merohedral twin, with the twin domains ratio of 88:12, was detected for **1-Cu**. Twin law corresponds to 180° rotation about [1 0 0] direct lattice direction. The final cif files were checked using IUCR's checkcif algorithm. Despite many attempts to collect high quality data, only weak diffraction intensity and data with moderate resolution were obtained due to: radiation damage of the crystals; large volume fractions occupied with disordered solvent molecules; disorder of the isobutoxy substituents; and large size of the foldamer molecules. For these reasons unavoidable A - level and B - level alerts remain in the check cif file but they are inherent to the data quality and refinement procedures and do not reflect errors. These alerts are listed below.

Group 1 alerts illustrate weak quality of the data and refinement statistics if compared to that expected for small molecule structures from highly diffracting crystals:

RFACR01_ALERT_3_A The value of the weighted R factor is > 0.45

THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550

PLAT023_ALERT_3_A Resolution (too) Low [sin(theta)/Lambda < 0.6]

PLAT084_ALERT_3_A High wR2 Value (i.e. > 0.25)

PLAT934_ALERT_3_A Number of (Iobs-Icalc)/SigmaW > 10 Outliers

RFACG01_ALERT_3_B The value of the R factor is > 0.15

RFACR01_ALERT_3_B The value of the weighted R factor is > 0.35

PLAT082_ALERT_2_B High R1 Value ..... 0.19 Report

PLAT084_ALERT_3_B High wR2 Value (i.e. > 0.25)

PLAT234_ALERT_4_B Large Hirshfeld Difference

PLAT241_ALERT_2_B High ’MainMol’ Ueq as Compared to Neighbors

PLAT242_ALERT_2_B Low ’MainMol’ Ueq as Compared to Neighbors

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds

PLAT341_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.02486 Ang.

PLAT910_ALERT_3_B Missing # of FCF Reflection(s) Below Theta(Min) 32 Note

PLAT934_ALERT_3_A Number of (Iobs-Icalc)/SigmaW > 10 Outliers

Group 2 alerts is connected with decision made during refinement and explained below:

PLAT201_ALERT_2_A Isotropic non-H Atoms in Main Residue(s)

Non-H atoms of side chains were refined with isotropic displacement parameters

PLAT410_ALERT_2_B Short Intra H...H Contact H35B .. H1B_6 .. 1.87 Ang.

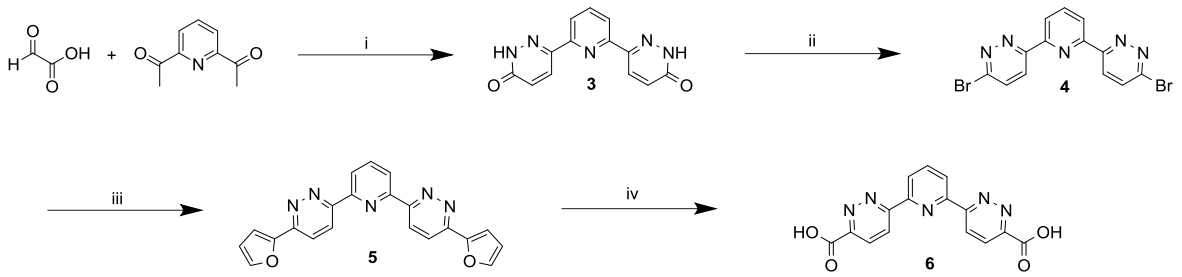
Alert concerns contact of H atom of isobutoxy side chain for which positions of carbon atoms (and hence positions of hydrogen atoms) are determined with low precision.

PLAT930_ALERT_2_B Check Twin Law (1 0 0)[1 0 0] Estimated BASF 0.24

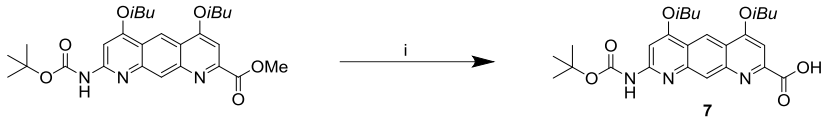
Complex **1**-**Cu** were refined as non-merohedral twin.

2. Materials and Methods for chemical synthesis

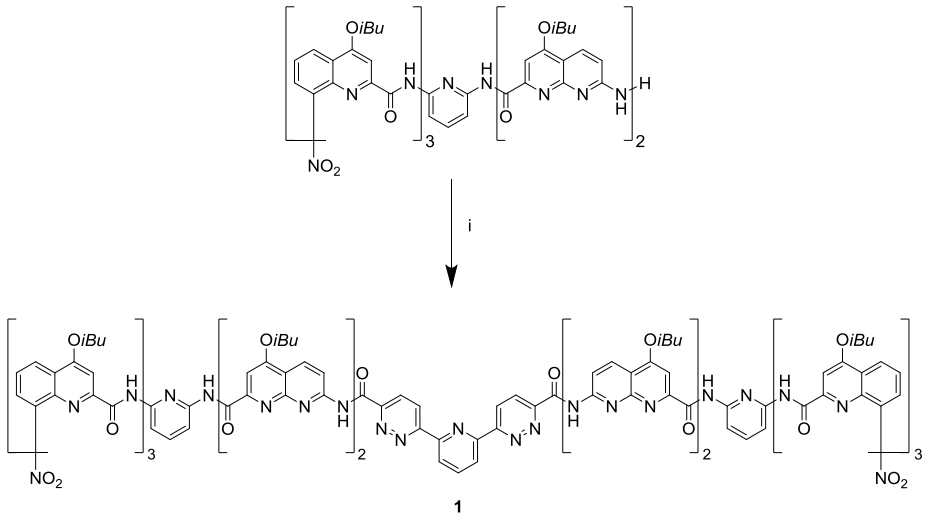
2.1 Synthetic Schemes



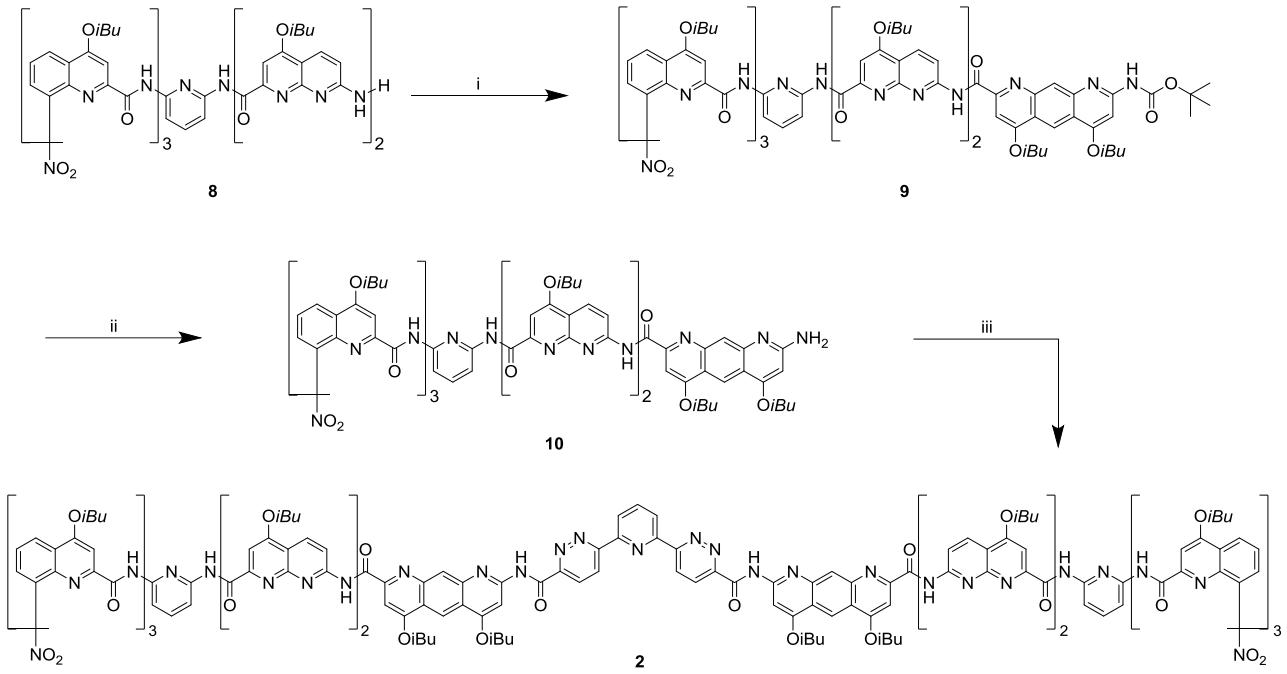
Scheme 1. Synthesis of **6**: i) K_2CO_3 then acetic acid, hydrazine hydrate (91%); ii) $POBr_3$ (56%); iii) furan-2-boronic acid, Et_3N, $Pd(PPh_3)_4$ (59%); iv) $KMnO_4$ (42%).



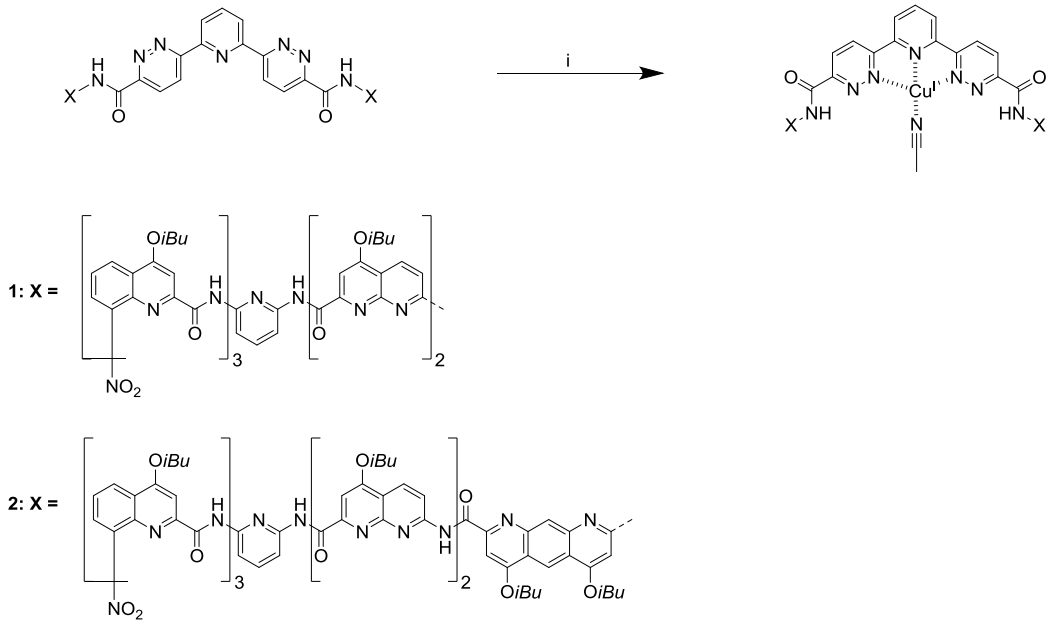
Scheme 2. Synthesis of **7**: i) LiOH (96%).



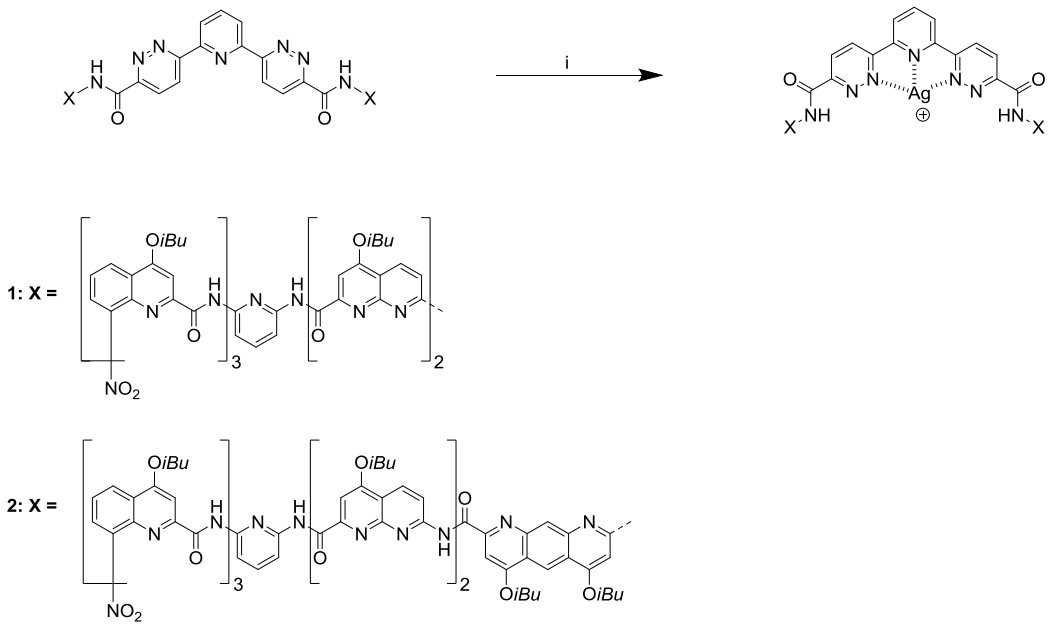
Scheme 3. Synthesis of capsule **1**: i) **6**, DIPEA, PyBOP (53%).



Scheme 4. Synthesis of capsule **2**: i) **7**, DIPEA, PyBOP (88%); ii) TFA (74%); iii) **6**, DIPEA, PyBOP (51%).



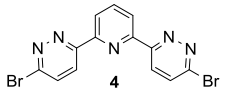
Scheme 5. Complexation of copper by oligomers **1** and **2**: i) $CuBF_4$, MeCN, $CHCl_3$, room temperature (quant.).



Scheme 6. Complexation of silver by oligomer **1** and **2**: i) $AgBF_4$, MeCN, $CHCl_3$, room temperature (quant.).

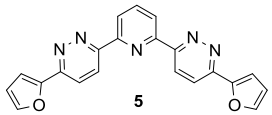
2.2 Experimental procedures

General. Moisture or oxygen sensitive experiments were performed under an argon atmosphere. Solvents used for reactions involving metals such as palladium or nickel were degassed via argon bubbling or freezing-defrosting cycles. All solvents were reagent grade and purified by a MBraun SPS-800 apparatus or according to Perrin procedures (Purification of Laboratory Chemicals 4th Edition, D. D. PERRIN, W.L.F. Armarego (Ed. Butterworth-Heinemann, 1997)). Commercial reagents were purchased from Sigma-Aldrich, Alfa-Aesar, T.C.I., Apollo or Fluorochem and were used without further purification unless otherwise specified. All reactions were monitored by thin layer chromatography (Kieselgel 60F254 Merck). The plates were revealed under UV light. Kieselgel 60 (40-63 µm, Merck) was used for column chromatography. Mass spectra were measured on a DSQ Thermoelectron apparatus by electronic impact (70eV) or by chemical ionisation (gaseous ammonia), either by direct introduction or by GC-MS coupling. High Resolution Mass Spectra (HRMS) were measured by electronic impact or by chemical ionisation on quadripolar spectrometers KRATOS MS 80RF or Micromasse Q T of 1. They were equally measured by electrospray in positive ionization mode (Na+ or K+ ions) on a LTQ-Orbitrap spectrometer (ThermoFisher Scientific) in the Oniris laboratory (Ecole Nationale Vétérinaire, Agroalimentaire et de l'Alimentation de Nantes Atlantique, France) or on a Autoflex III MALDI-TOF spectrometer (Bruker) in positive ionization mode in the service "Biopolymères, Interactions, Biologie Structurale" (INRA, France). The matrix was DHB (2,5-DiHydroxyBenzoic acid) or DCTB (trans-2-(3-(4-t-Butylphenyl)-2-methyl-2-propenylidene)malononitrile). GPC purification was performed on an LC-9130G NEXT setup (Japan Analytical Industry Co., Ltd.) equipped with two preparative columns (Inner diameter of 20mm and length of 600mm): a JAIGEL 2.5H and a JAIGEL 3H, in conjugation with UV-600 NEXT UV detector and an FC-3310 fraction collector. The setup is equipped with a column oven that is set at 37°C. Chloroform (HPLC grade, ethanol stabilized) was used for the separations.



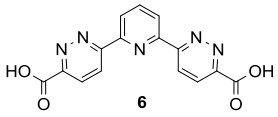
2,6-Bis(6-bromopyridazin-3-yl)pyridine 4. Compound **3**[4] (4.85 g, 18.1 mmol, 1.0 equiv.) was heated in $POBr_3$ (31.2 g, 109 mmol, 6.0 equiv.) at 80°C for 34 h. After cooling, the solid residue was transferred in a 1L flask, diluted in $CHCl_3$

(200 mL) and iced water (200 mL), and neutralized with NaOH (solid) up to pH 4 and then with $NaHCO_3$ (solid) to reach pH 7. The resulting mixture was passed through a pad of alumina and washed with a $CHCl_3$/MeOH (2:1 vol/vol) mixture. Phases were separated and the aqueous layer was extracted twice with $CHCl_3$. The combined organic layers were then dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica gel (eluent: DCM/EtOAc 100:0 to 95:5 vol/vol). Compound **4** was obtained as a white powder in 56% yield (4.01 g). m.p. (°C): 195. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.77 (d, *J* = 7.9 Hz, 2H), 8.51 (d, *J* = 8.9 Hz, 2H), 8.10 (t, *J* = 7.9 Hz, 1H), 7.81 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 157.7, 152.5, 148.8, 139.0, 132.2, 126.5, 123.1. CIMS: m/z 392 ($^{79Br, 79Br}$M + H]$^+$. HRMS (MALDI): m/z calcd. for $C_{13}H_8Br_2N_5$ [M + H]$^+$ 391.9141; found 391.9148.



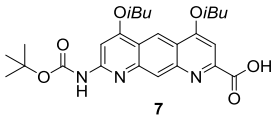
5

2,6-Bis[6-(furan-2-yl)pyridazin-3-yl]pyridine 5. This compound was synthesized according to Kar procedure.[5] A solution of **4** (2.00 g, 5.09 mmol, 1.0 eq), furan-2-boronic acid (2.28 g, 20.4 mmol, 4.0 equiv.), triethylamine (5.50 mL, 40.7 mmol, 8.0 equiv.) and tetrakis(triphenylphosphine)palladium (1.17 g, 1.02 mmol, 0.2 equiv.) in degassed DMF (102 mL) was heated at 110 °C for 13 h until total consumption of starting material. The solution was filtered through a pad of celite which was washed with DCM then with aqueous NH_4OH (25 M). The filtrate was extracted with DCM (4 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and the solvents were removed in vacuo. The crude product was purified by flash chromatography on silica gel (eluent: DCM/Et_2O 100:0 to 90:10 vol/vol) to give compound **5** as a white powder in 59% yield (1.10 g). m.p. (°C): > 230. ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 8.78 (d, *J* = 7.8 Hz, 2H), 8.68 (d, *J* = 8.9 Hz, 2H), 8.05 (t, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 2H), 7.64 (dd, *J* = 0.8, 1.7 Hz, 2H), 7.44 (dd, *J* = 0.8, 3.5 Hz, 2H), 6.63 (dd, *J* = 1.8, 3.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 156.4, 153.2, 152.1, 151.1, 144.8, 138.5, 124.7, 122.3, 122.3, 112.9, 111.1. EIMS: m/z (I %) 367 (M^+, 13), 339 (M^+ - (N_2), 18), 311 (M^+ - ($2N_2$), 5). HRMS (MALDI): m/z calcd. for $C_{21}H_{14}N_5O_2$ [M + H]$^+$ 368.1142; found 368.1147. Elemental analysis: calcd (%) for $C_{21}H_{13}N_5O_2 \cdot 0.4H_2O$: C 67.34, H 3.71, N 18.69; found C 67.69, H 3.95, N 17.37.



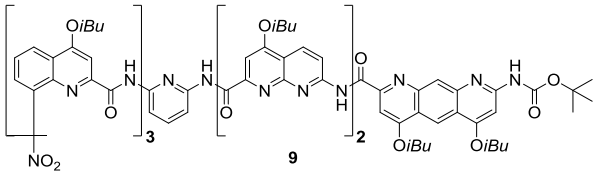
6

6,6'-(Pyridine-2,6-diyl)bis-3-pyridazinylcarboxylic acid 6. To a solution of **5** (680 mg, 1.85 mmol, 1.0 equiv.) in H_2O (30 mL) was added $KMnO_4$ (585 mg, 3.70 mmol, 2.0 equiv.). After stirring at r.t. for 24 h, a new portion of $KMnO_4$ (585 mg, 3.70 mmol, 2.0 equiv.) was added and the solution was further stirred at r.t. for 24 h. The solution was filtered through a pad of celite which was washed with $NaHCO_3$ (satd. aq., 20 mL) and warm H_2O (20 mL, 50°C). The filtrate was acidified to pH 2 with $NaHSO_4$ (2 M aq.), and the resulting precipitate was filtered, washed with H_2O (15 mL) and dried over P_2O_5. The compound **6** was obtained as a white powder with 42% yield (251 mg). m.p. (°C): 199. ^{1}H NMR (400 MHz, DMSO-d_6): δ ppm 8.95 (d, *J* = 8.8 Hz, 2H), 8.81 (d, *J* = 7.8 Hz, 2H), 8.38 (d, *J* = 8.8 Hz, 2H), 8.33 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ ppm 165.1, 158.7, 152.4, 152.2, 139.6, 128.7, 125.4, 123.3. IR, ν (cm^{-1}): 1683 (C=O). EIMS: m/z (I %) 324 (M + H$^+$, 40), 279 (M^+ - (CO_2H), 100), 235 (M^+ - ($2CO_2H$), 69). HRMS (MALDI): m/z calcd. for $C_{15}H_{10}N_5O_4$ [M + H]$^+$ 324.0727; found 324.0737.



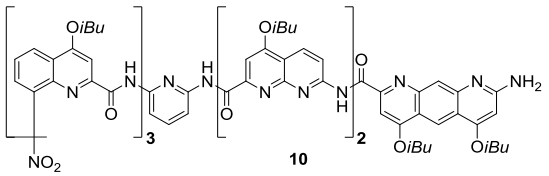
7

1,8-diaza-4,5-diisobutoxy-7-[(tert-butoxycarbonyl)amino]-2-anthracene carboxylic acid 7. Methyl-1,8-diaza-4,5-diisobutoxy-7-[(tert-butoxycarbonyl)amino]-2-anthracene carboxylate[6] (750 mg, 1.5 mmol) was dissolved in THF (16 mL) and methanol (2 mL) at room temperature. Then, distilled water (2 mL) and lithium hydroxide monohydrate (130 mg, 3 mmol) were added successively and the reaction mixture was let to stir at room temperature. After 2 h, the reaction mixture was quenched with a solution of citric acid monohydrate (1.3 g, 6.2 mmol in 30 mL of water). The organic solvents were removed by rotary evaporation and a precipitate was obtained from the remaining aqueous solution. After filtration, the precipitate was washed with distilled water, dissolved in dichloromethane and dried over Na_2SO_4. Then, the dichloromethane was removed under reduced pressure to yield **7** as a yellow solid (96 %, 700 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 9.15 (s, 1H), 8.41 (s, 1H), 7.74 (s, 1H), 7.54 (s, 1H), 4.17 (d, *J* = 6.4 Hz, 2H), 4.12 (d, *J* = 6.3 Hz, 2H), 2.44 – 2.28 (m, 2H), 1.57 (s, 9H), 1.19 (d, *J* = 6.7 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm = 165.92, 164.17, 163.66, 155.34, 152.55, 150.60, 123.02, 120.93, 119.14, 117.87, 96.75, 92.74, 81.94, 75.95, 75.20, 28.48, 28.39, 19.35, 19.22. HRMS (ESI$^+$): *m/z* calcd for $C_{26}H_{34}N_3O_6$ $[M+H]^+$ 484.2442 found 484.2436.

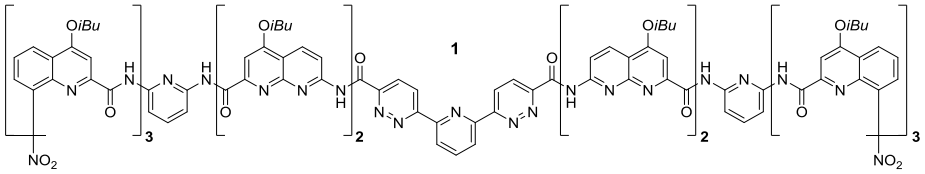


9

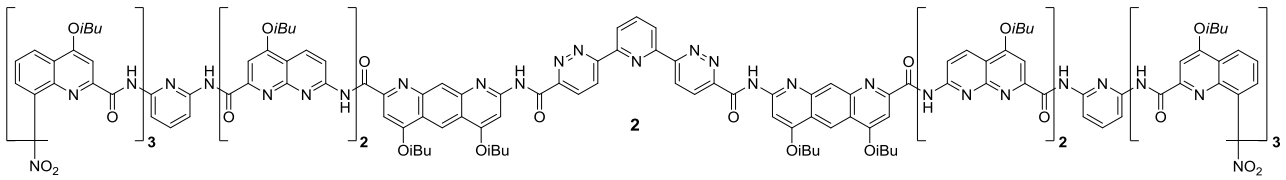
Boc-protected heptamer 9. Amino-hexamer **8**[7] (185 mg, 0.14 mmol, 1.0 equiv.), diazaanthracene acid **7** (73 mg, 0.15 mmol, 1.1 equiv.) and PyBOP (142 mg, 0.27 mmol, 2.0 equiv.) were dissolved in dry $CHCl_3$ (4 mL) then DIPEA (95 µL, 0.27 mmol, 2.0 equiv.) was added at r.t.. After 24 h at 45 °C, PyBOP (71 mg, 0.14 mmol, 1.0 equiv.) was added and the reaction mixture was stirred 12 h at 45°C. After cooling down to r.t., $CHCl_3$ was added. The organic layer was washed with K_2CO_3 (0.5 mol/L aq.), water (3 x), brine and dried over Na_2SO_4, filtered and then concentrated. The crude material was purified by flash chromatography (SiO_2) eluting with $CHCl_3$/MeOH (98:2 vol/vol) to afford **9** as a yellow solid (88%, 221 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 12.03 (s, 1H), 11.75 (s, 1H), 11.53 (s, 1H), 11.34 (s, 1H), 10.37 (s, 1H), 9.97 (s, 1H), 8.92 (d, *J* = 8.9 Hz, 1H), 8.69 - 8.80 (m, 5H), 8.47 (d, *J* = 7.6 Hz, 1H), 8.42 (d, *J* = 7.2 Hz, 1H), 8.16 (quin, *J* = 4.2 Hz, 1H), 7.73 - 7.83 (m, 5H), 7.64 (s, 1H), 7.53 (s, 1H), 7.44 (s, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.19 (s, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.93 (t, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.36 (t, *J* = 8.0 Hz, 1H), 6.25 (s, 1H), 3.87 - 4.33 (m, 10H), 3.25 - 3.59 (m, 4H), 2.11 - 2.49 (m, 7H), 1.57 (s, 9H), 1.09 - 1.32 (m, 42H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 164.6, 164.0, 163.8, 163.6, 163.3, 162.9, 162.9, 162.8, 162.6, 162.2, 161.6, 161.5, 161.0, 154.8, 154.6, 154.3, 154.3, 153.5, 153.4, 153.1, 152.4, 152.4, 151.3, 151.1, 149.8, 149.1, 147.4, 146.3, 146.1, 145.1, 139.7, 139.0, 138.9, 138.4, 134.8, 134.6, 134.1, 127.8, 126.4, 125.8, 125.6, 125.0, 124.0, 123.5, 122.6, 120.9, 119.5, 119.0, 117.9, 116.8, 115.6, 115.4, 115.2, 115.0, 114.8, 114.6, 114.1, 109.3, 108.1, 100.9, 99.3, 98.1, 97.8, 96.5, 95.2, 92.0, 80.8, 75.9, 75.8, 75.4, 75.4, 75.0, 74.8, 74.4, 28.4, 28.4, 28.3, 28.2, 28.1, 27.8, 19.4 - 19.1. CIMS: m/z 1819 $[M + H]^+$. HRMS (ESI+): m/z calcd. for $C_{99}H_{105}N_{18}O_{17}$ $[M + H]^+$ 1817.7900, found 1817.7917.



Amino heptamer 10. A solution of heptamer **9** (368 mg, 0.20 mmol, 1.0 equiv.) in $CHCl_3$/TFA (4:1 vol/vol, 10 mL) was stirred for 1 hour at r.t.. Solvents were removed by rotary evaporation using toluene as an azeotrope. The crude material was slurred in DCM and the resulting organic layer was washed with saturated aqueous $NaHCO_3$ (3 x), water and then brine, dried over Na_2SO_4, filtered and concentrated. The crude compound contained 20% starting material. It was purified by flash chromatography on silica gel (eluent: $CHCl_3$/MeOH 100:0 to 95:5 vol/vol). Compound **10** was obtained as a yellow powder in 74% yield (257 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 11.94 (br. s, 1H), 11.60 (br. s, 1H), 11.41 (br. s, 1H), 11.31 (br. s, 1H), 10.26 (br. s, 1H), 9.79 (s, 1H), 8.98 (d, *J* = 8.9 Hz, 1H), 8.87 - 8.73 (m, 3H), 8.64 (d, *J* = 6.9 Hz, 1H), 8.55 (br. s, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.36 (d, *J* = 7.9 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.87 - 7.77 (m, 2H), 7.69 (br. s, 1H), 7.54 (br. s, 1H), 7.47 (br. s, 2H), 7.33 - 7.23 (m, 2H), 7.22 - 7.10 (m, 2H), 7.04 (s, 1H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.48 (s, 1H), 6.29 (t, *J* = 7.7 Hz, 1H), 5.68 (br. s, 1H), 5.30 (br. s, 2H), 4.23 (s, 6H), 3.97 - 3.83 (m, 2H), 3.77 - 3.61 (m, 2H), 3.54 (d, *J* = 6.3 Hz, 2H), 3.40 - 3.19 (m, 2H), 2.51 - 2.02 (m, 7H), 1.43 - 0.58 (m, 42H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 164.7, 164.6, 164.1, 163.7, 163.4, 163.3, 162.8, 162.3, 161.8, 161.7, 161.5, 160.8, 159.1, 155.4, 155.0, 154.5, 154.3, 153.7, 152.7, 151.3, 150.9, 149.3, 149.0, 147.5, 147.1, 144.9, 139.5, 139.4, 139.0, 139.0, 138.5, 134.7, 134.3, 134.1, 128.0, 126.5, 125.9, 125.7, 124.0, 123.5, 122.6, 121.3, 117.9, 117.4, 116.9, 116.0, 115.9, 115.6, 115.3, 115.2, 115.0, 114.4, 109.2, 108.3, 101.0, 99.2, 98.4, 98.4, 98.2, 97.2, 95.0, 91.1, 76.1, 76.0, 75.4, 75.1, 74.7, 74.1, 28.5, 28.4, 28.4, 28.2, 28.1, 28.0, 19.5, 19.4, 19.4, 19.1. CIMS: m/z 1718.7 $[M + H]^+$. HRMS (ESI+): m/z calcd. for $C_{94}H_{97}N_{18}O_{15}$ $[M + H]^+$ 1717.73753, found 1717.7276.



Oligomer 1. Diacid **6** (11 mg, 0.034 mmol, 1.0 equiv.), PyBOP (143 mg, 0.275 mmol, 8.0 equiv.), hexamer amine **8** (93 mg, 0.069 mmol, 2.0 equiv.) and DIPEA (30 µL, 0.172 mmol, 5.0 equiv.) were dissolved in $CHCl_3$ (2 mL) under argon atmosphere. After 70 h at 45°C the resulting mixture was concentrated. The crude material was then diluted in mixture of DCM/MeOH (2:1 vol/vol, 5 mL). The DCM was slowly removed and the precipitate was recovered by filtration and washed with MeOH (15 mL) then diethyl ether (20 mL). The resulting solid was further purified by GPC to afford **1** (55 mg, 53 %) as yellow solid. This compound showed broad resonances which could not be assigned precisely (see main text). HRMS (ESI+): calcd. for $C_{161}H_{151}N_{35}Na_2O_{26}$ $[M + 2Na]^{2+}$ 1518.0682, found 1518.0674.



Oligomer 2. Diacid **6** (30 mg, 0.093 mmol, 1.0 equiv.), PyBOP (195 mg, 0.374 mmol, 4.0 equiv.), heptamer amine **10** (321 mg, 0.187 mmol, 2.0 equiv.) were dissolved in dry $CHCl_3$ (10 mL) then DIPEA (65 µL, 0.374 mmol, 4.0 equiv.) was added at r.t.. After 30 h at 45 °C, PyBOP (71 mg, 0.14 mmol, 1.0 equiv.) was added and the reaction mixture was

stirred 5 days at 45°C. The organic layer was washed with K_2CO_3 (0.5 mol/L aq.), water (3 x), brine and dried over Na_2SO_4, filtered and then concentrated. The crude material was purified by flash chromatography (SiO_2) eluting with $CHCl_3$/MeOH (100:0 to 98:2) to obtain **2** which was further purified by GPC to yield a yellow solid (51%, 176 mg). This compound showed broad resonances which could not be assigned precisely (see main text). HRMS (ESI+): calcd. for $C_{203}H_{197}N_{41}Na_2O_{32}$ $[M + 2Na]^{2+}$ 1883.2416, found 1883.2403.

Preparation of copper (I) and silver (I) foldamer complexes:

Copper complex 1-Cu$^+$. Oligomer **1** (2.99 mg, 1.0 µmol, 1.0 equiv.) was first dissolved in an NMR tube in a mixture of $CDCl_3$/CD_3CN (600 µL, 95:5), then 6 µL of a solution (0.167 M) of $CuBF_4(MeCN)_4$ in CD_3CN (1.0 µmol, 1.0 equiv.) was added. The tube was agitated manually at room temperature and NMR was recorded ten minutes after the addition. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3CN 95:5): δ ppm 11.50 (s, 2H), 11.40 (s, 2H), 10.45 (br. s., 2H), 10.28 (s, 2H), 9.76 (br. s., 2H), 9.39 (s, 2H), 8.80 (d, *J* = 8.7 Hz, 2H), 8.65 (d, *J* = 8.7 Hz, 2H), 8.42 (d, *J* = 8.4 Hz, 2H), 8.33 - 8.25 (m, 5H), 8.22 (d, *J* = 7.1 Hz, 2H), 8.21 (d, *J* = 7.1 Hz, 2H), 8.17 (d, *J* = 7.5 Hz, 2H), 8.05 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.61 (s, 2H), 7.23 - 7.14 (m, 7H), 7.11 – 6.99 (m, 8H), 6.90 (t, *J* = 7.8 Hz, 2H), 6.75 (s, 2H), 6.54 (d, *J* = 7.8 Hz, 2H), 5.96 (t, *J* = 7.7 Hz, 2H), 5.89 (s, 2H), 4.43 - 4.36 (m, 2H), 4.28 - 4.21 (m, 2H), 4.21 - 4.11 (m, 5H), 3.88 - 3.79 (m, 2H), 3.78 - 3.69 (m, 2H), 3.54 - 3.46 (m, 2H), 3.38 - 3.29 (m, 2H), 3.22 - 3.09 (m, 1H), 2.87 - 2.79 (m, 2H), 2.52 - 2.41 (m, *J* = 6.3, 12.5 Hz, 6H), 2.29 - 2.11 (m, 4H), 1.37 - 1.07 (m, 48H), 0.53 (d, *J* = 6.4 Hz, 6H), 0.39 (d, *J* = 6.3 Hz, 6H). HRMS (ESI+): calcd. for $C_{161}H_{152}N_{35}O_{26}Cu$ $[M + Cu + H]^{3+}$ 1018.0315, found 1018.0307.

Silver complex 1-Ag$^+$. Oligomer **1** (2.99 mg, 1.0 µmol, 1.0 equiv.) was first dissolved in an NMR tube in a mixture of $CDCl_3$/CD_3CN (600 µL, 95:5), then 6 µL of a solution (0.167 M) of $AgBF_4$ in CD_3CN (1.0 µmol, 1.0 equiv.) was added. The tube was agitated manually at room temperature and NMR was recorded ten minutes after the addition. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3CN 95:5): δ ppm 11.64 (s, 2H), 11.37 (s, 2H), 10.50 (s, 2H), 10.11 (br. s., 2H), 9.86 (s, 2H), 9.46 (s, 2H), 8.89 (d, *J* = 8.7 Hz, 2H), 8.78 (d, *J* = 8.7 Hz, 2H), 8.45 (d, *J* = 8.5 Hz, 2H), 8.26 (d, *J* = 8.8 Hz, 2H), 8.24 - 8.15 (m, 7H), 8.11 - 8.06 (m, 4H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.81 (s, 2H), 7.31 (s, 2H), 7.28 (br. s., 1H), 7.22 (s, 2H), 7.13 – 6.96 (m, 8H), 6.91 (t, *J* = 7.8 Hz, 2H), 6.76 - 6.68 (m, 4H), 6.65 (s, 2H), 5.96 (t, *J* = 7.8 Hz, 2H), 5.83 (s, 2H), 4.51 - 4.45 (m, 2H), 4.36 - 4.30 (m, 2H), 4.25 - 4.19 (m, 2H), 4.1 - 4.13 (m, 2H), 3.78 - 3.72 (m, 2H), 3.69 - 3.63 (m, 2H), 3.47 - 3.41 (m, 2H), 3.33 - 3.28 (m, 2H), 3.21 - 3.14 (m, 1H), 2.93 - 2.85 (m, 2H), 2.54 - 2.44 (m, 4H), 2.39 - 2.31 (m, 2H), 2.25 - 2.10 (m, 5H), 1.41 - 1.29 (m, 22H), 1.22 (s, 6H), 1.16 - 1.04 (m, 20H), 0.59 (d, *J* = 6.6 Hz, 6H), 0.45 (d, *J* = 6.7 Hz, 6H). HRMS (ESI+): calcd. for $C_{161}H_{152}N_{35}NaO_{26}Ag$ $[M + H + Na + Ag]^{3+}$ 1040.3532, found 1040.3528.

Copper complex 2-Cu$^+$. Oligomer **2** (3.72 mg, 1.0 µmol, 1.0 equiv.) was first dissolved in an NMR tube in a mixture of $CDCl_3$/CD_3CN (600 µL, 95:5), then 6 µL of a solution (0.167 M) of $CuBF_4(MeCN)_4$ in CD_3CN (1.0 µmol, 1.0 equiv.) was added. The tube was agitated manually at room temperature and NMR was recorded ten minutes after the addition. ^{1}H NMR (400 MHz, $CDCl_3$/CD_3CN 95:5): δ ppm 11.57 (s, 2H), 11.34 (s, 2H), 11.12 (br. s., 2H), 10.60 (br. s., 2H), 9.93 (br. s., 2H), 9.72 (br. s., 2H), 9.47 (br. s., 2H), 9.00 (d, *J* = 8.2 Hz, 2H), 8.93 (d, *J* = 6.8 Hz, 2H), 8.80 (d, *J* = 8.2 Hz, 3H), 8.54 (s, 2H), 8.28 (s, 4H), 8.16 (dd, *J* = 1.8, 7.5 Hz, 2H), 7.98 (d, *J* = 6.7 Hz, 2H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.62 (s, 4H), 7.47 (d, *J* = 8.6 Hz, 4H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.19 - 7.24 (m, 4H), 7.11 (s, 2H), 7.02 - 7.09 (m, 4H), 6.99 (d, *J* = 3.3 Hz, 2H), 6.76 (d, *J* = 7.5 Hz, 4H), 6.68 (s, 2H), 6.59 (d, *J* = 6.9 Hz, 2H), 6.32 (br. s., 4H), 6.09 (br. s., 2H), 5.70 (t, *J* = 7.7 Hz, 2H), 4.36 - 4.46 (m, 4H), 4.28 - 4.34 (m, 2H), 4.16 - 4.22 (m, 2H), 4.02 - 4.10 (m, 4H), 3.92 - 3.99 (m, 2H), 3.78 - 3.88 (m, 2H), 3.59 - 3.68 (m, 6H), 3.42 (br. s., 2H), 2.79 (t, *J* = 8.0 Hz, 2H), 2.45 - 2.59 (m, 9H), 2.03 - 2.29 (m, 7H),

1.32 - 1.42 (m, 34H), 1.22 (s, 6H), 1.10 - 1.19 (m, 20H), 0.92 (d, *J* = 6.5 Hz, 12H), 0.41 (d, *J* = 6.3 Hz, 6H), 0.23 (d, *J* = 6.3 Hz, 6H). HRMS (ESI+): calcd. for $C_{203}H_{198}N_{41}O_{32}Cu$ $[M + Cu + H]^{3+}$ 1261.4808, found 1261.4807.

Silver complex 2-Ag$^+$. Oligomer **2** (3.72 mg, 1.0 µmol, 1.0 equiv.) was first dissolved in an NMR tube in a mixture of $CDCl_3/CD_3CN$ (600 µL, 95:5), then 6 µL of a solution (0.167 M) of $AgBF_4$ in CD_3CN (1.0 µmol, 1.0 equiv.) was added. The tube was agitated manually at room temperature and NMR was recorded ten minutes after the addition. ^{1}H NMR (400 MHz, $CDCl_3/CD_3CN$ 95:5): δ ppm 11.59 (s, 2H), 11.38 (s, 2H), 11.05 (s, 2H), 10.68 (br. s., 2H), 9.92 (br. s., 2H), 9.72 (br. s., 2H), 9.56 (br. s., 2H), 9.00 (d, *J* = 8.6 Hz, 2H), 8.86 (d, *J* = 7.7 Hz, 2H), 8.79 (d, *J* = 8.4 Hz, 2H), 8.77 - 8.70 (m, 1H), 8.59 (s, 2H), 8.37 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 8.17 (dd, *J* = 2.1, 7.2 Hz, 2H), 7.97 - 7.88 (m, 0H), 7.69 (s, 2H), 7.66 (s, 2H), 7.51 - 7.40 (m, 6H), 7.28 (br. s., 2H), 7.23 (br. s., 1H), 7.10 - 7.04 (m, 0H), 7.00 (s, 2H), 6.86 (s, 2H), 6.80 (d, *J* = 7.5 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 2H), 6.67 (s, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 7.7 Hz, 2H), 6.24 (t, *J* = 7.3 Hz, 2H), 6.18 (s, 2H), 5.73 (t, *J* = 7.6 Hz, 2H), 4.45 - 4.39 (m, 2H), 4.39 - 4.29 (m, 4H), 4.19 - 4.11 (m, 4H), 4.09 - 4.02 (m, 2H), 3.82 - 3.69 (m, 6H), 3.63 (d, *J* = 3.5 Hz, 4H), 3.44 (t, *J* = 7.7 Hz, 2H), 2.82 (t, *J* = 8.4 Hz, 2H), 2.60 - 2.43 (m, 8H), 2.25 - 2.02 (m, 7H), 1.41 - 1.31 (m, 34H), 1.22 (s, 6H), 1.18 – 1.10 (m, 20H), 0.91 (d, *J* = 6.5 Hz, 12H), 0.41 (d, *J* = 6.1 Hz, 6H), 0.22 (d, *J* = 6.1 Hz, 6H). HRMS (ESI+): calcd. for $C_{203}H_{199}N_{41}O_{32}Ag$ $[M + Ag + 2H]^{3+}$ 1276.4752, found 1261.4742.

3. Solution studies: Nuclear Magnetic Resonance (NMR)

3.1 Determination of dimerization constants

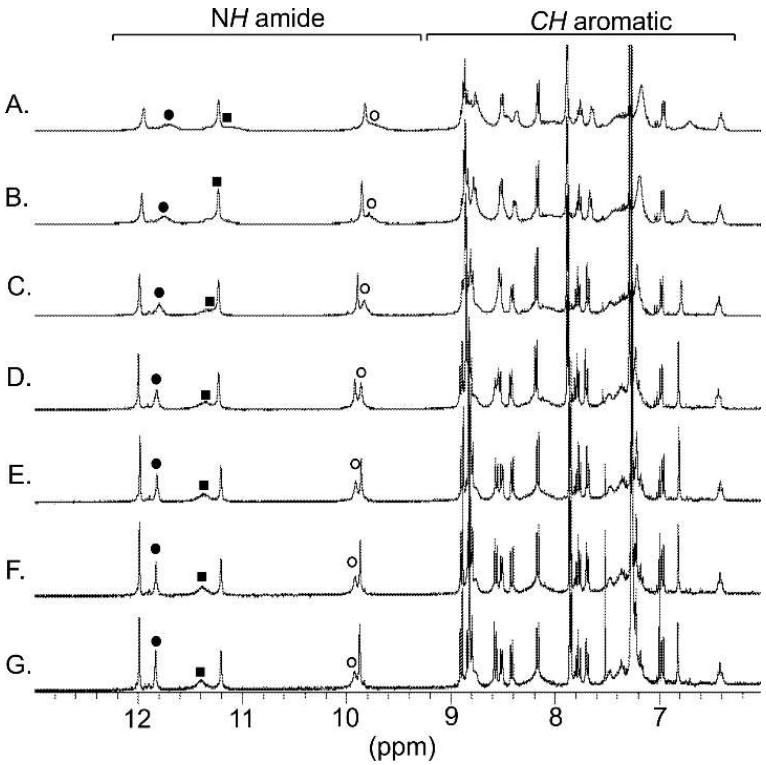


Figure S1. Excerpts of the 400 MHz ^{1}H NMR spectra (298K) of oligomer **1** in $CDCl_3$ showing the amide and aromatic resonances at: (A) 12 mM; (B) 8 mM; (C) 4 mM; (D) 2 mM; (E) 1 mM; (F) 0.5 mM and (G) 0.25 mM.

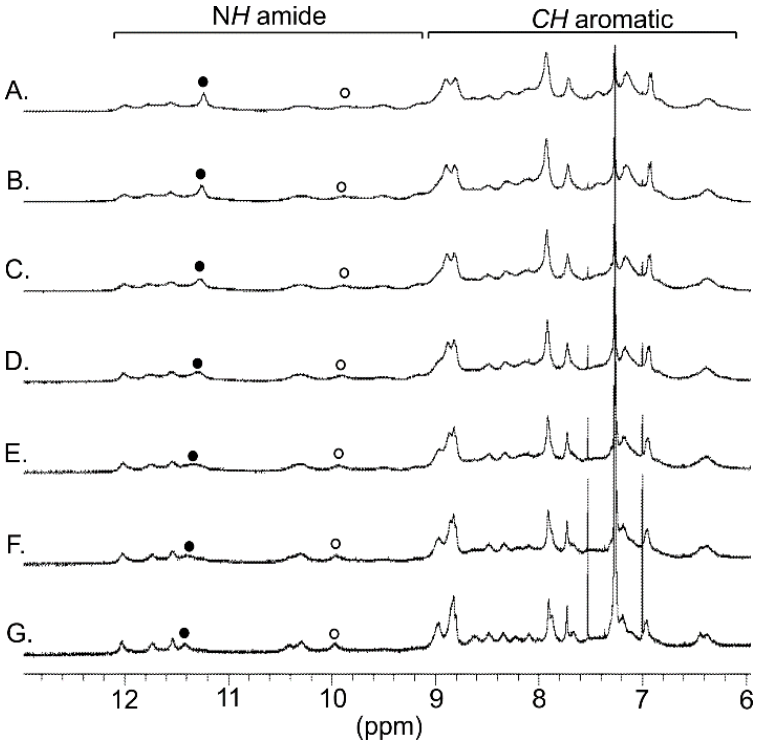


Figure S2. Excerpts of the 400 MHz ^{1}H NMR spectra (298K) of oligomer **2** in $CDCl_3$ showing the amide and aromatic resonances at: (A) 16 mM; (B) 8 mM; (C) 4 mM; (D) 2 mM; (E) 1 mM; (F) 0.5 mM and (G) 0.25 mM.

3.2 ^{1}H NMR titrations

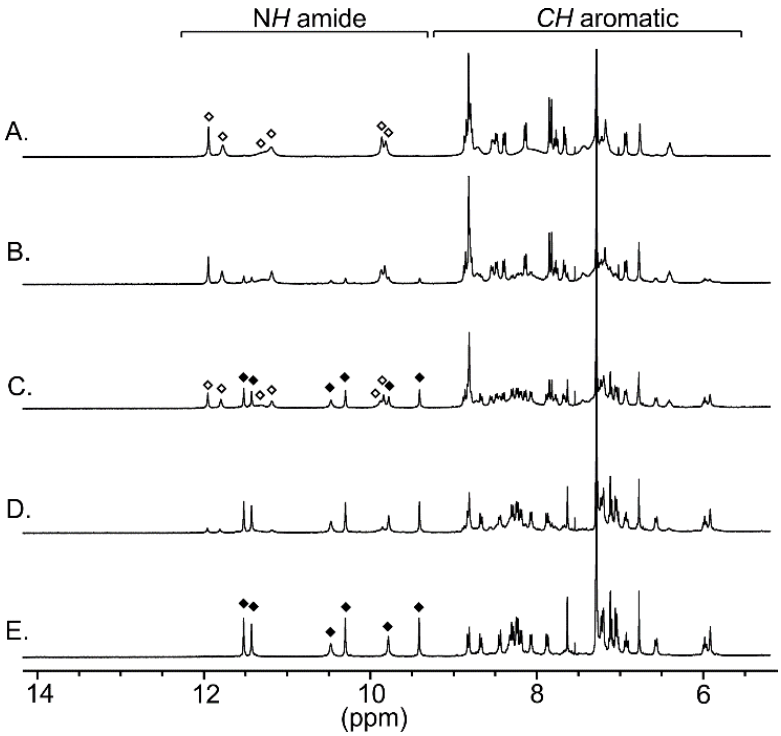


Figure S3. Excerpts of the 400 MHz ^{1}H NMR spectra (298K) showing the amide and aromatic resonances at 1 mM in $CDCl_3/CD_3CN$ (95:5 vol/vol) of oligomer **1** in the presence of increasing amounts of $CuBF_4(MeCN)_4$: (A) 0 equiv.; (B) 0.25 equiv.; (C) 0.5 equiv.; (D) 0.75 equiv.; (E) 1 equiv.

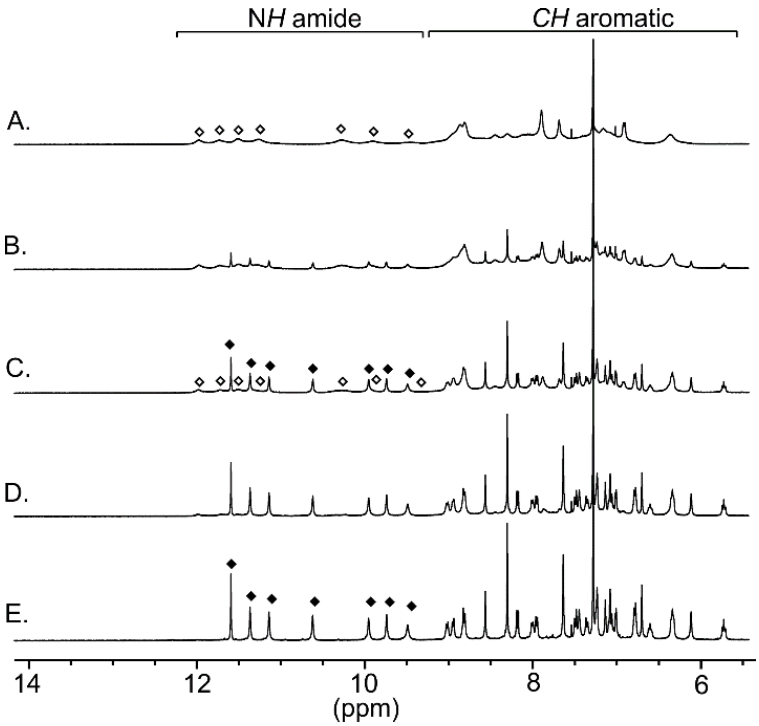


Figure S4. Excerpts of the 400 MHz ^{1}H NMR spectra (298K) showing the amide and aromatic resonances at 1 mM in $CDCl_3/CD_3CN$ (95:5 vol/vol) of oligomer **2** in the presence of increasing amounts of $CuBF_4(MeCN)_4$: (A) 0 equiv.; (B) 0.25 equiv.; (C) 0.5 equiv.; (D) 0.75 equiv.; (E) 1 equiv.

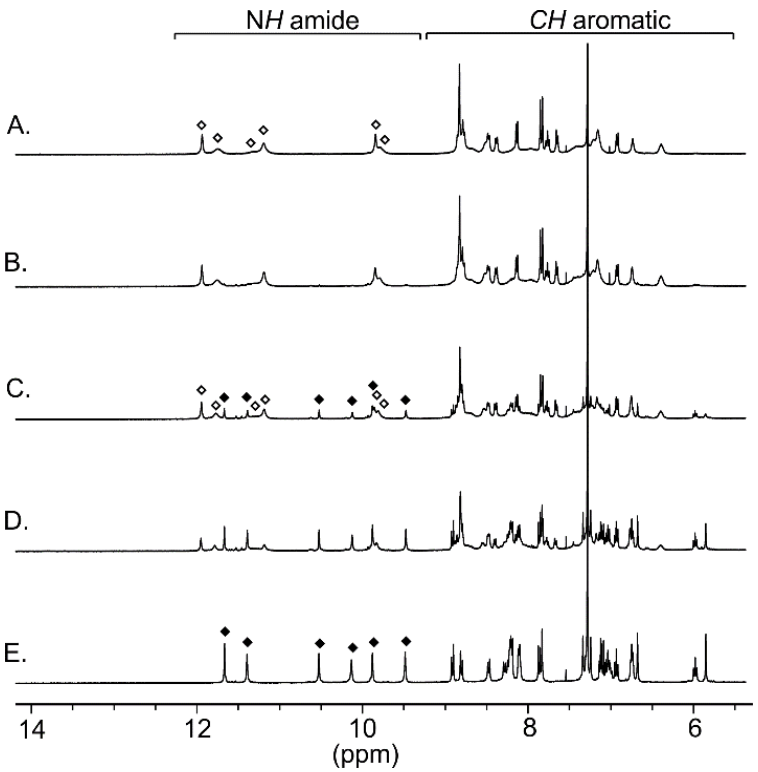


Figure S5. Excerpts of the 400 MHz ^{1}H NMR spectra (298K) showing the amide and aromatic resonances at 1 mM in $CDCl_3/CD_3CN$ (95:5 vol/vol) of oligomer **1** in the presence of increasing amounts of $AgBF_4$: (A) 0 equiv.; (B) 0.25 equiv.; (C) 0.5 equiv.; (D) 0.75 equiv.; (E) 1 equiv.

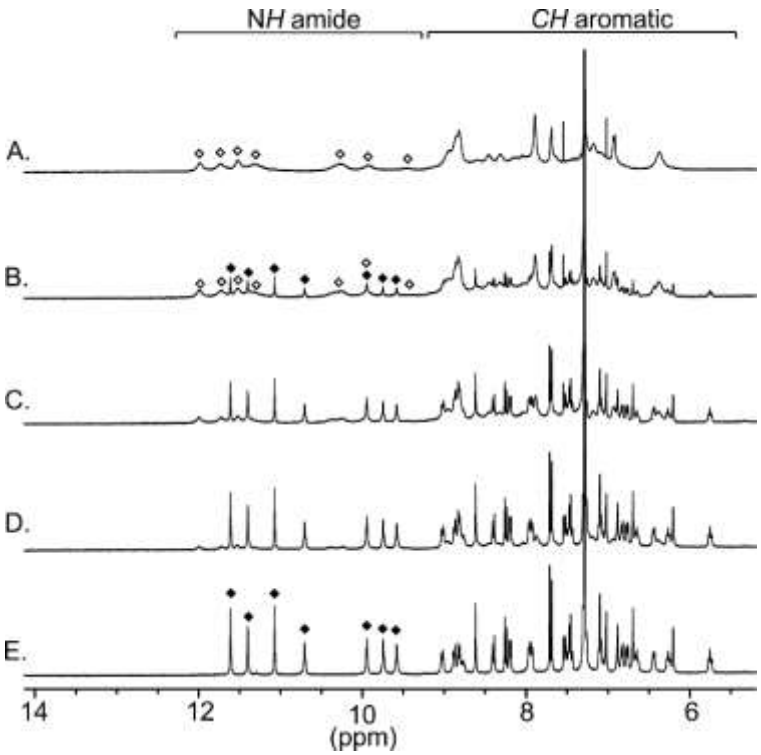


Figure S6. Excerpts of the 400 MHz ^{1}H NMR spectra (298K) showing the amide and aromatic resonances at 1 mM in $CDCl_3/CD_3CN$ (95:5 vol/vol) of oligomer **2** in the presence of increasing amounts of $AgBF_4$: (A) 0 equiv.; (B) 0.25 equiv.; (C) 0.5 equiv.; (D) 0.75 equiv.; (E) 1 equiv.

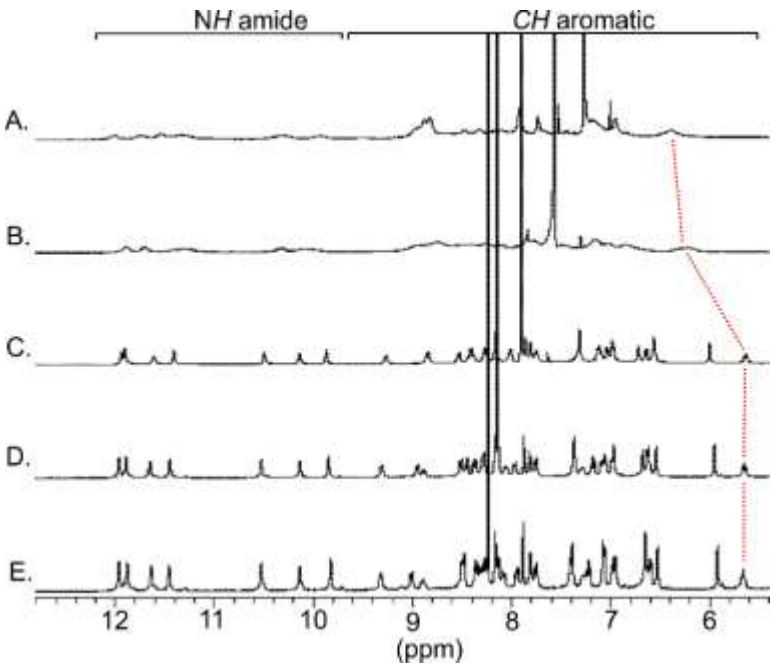


Figure S7. Excerpts of the 400 MHz ^{1}H NMR spectra (298K) showing the amide and aromatic resonances of **2** (2 mM) in $CDCl_3$/[D_6]-DMSO mixtures: (A) 100:0 (vol/vol); (B) 80:20 (vol/vol); (C) 60:40 (vol/vol); (d) 40:60 (vol/vol) and (e) 20:80 (vol/vol). The signal at 5.8 ppm in E is characteristic of helical capsule conformations (for example see reference 7).

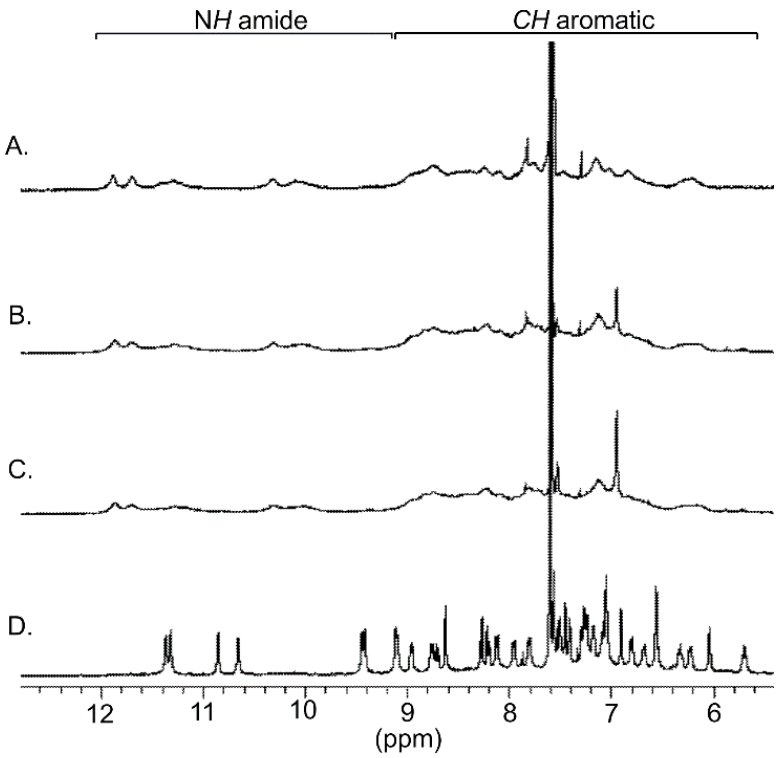


Figure S8. Excerpts of the ^{1}H NMR spectra (400 MHz, 298K) of oligomer **2** (2 mM) in a $CDCl_3$/[D_6]-DMSO mixture, 80:20 (vol/vol) in the presence of: (A) 0 equiv. of imidazole; (B) 0.5 equiv. of imidazole; (C) 1 equiv. of imidazole ; (D) 1.0 equiv. imidazole and 1 equiv. $CuBF_4(MeCN)_4$.

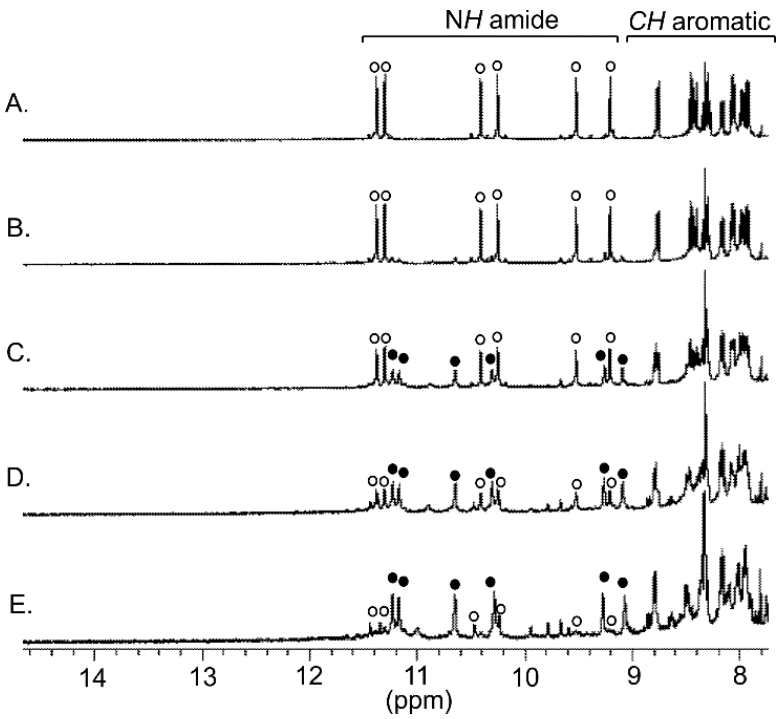


Figure S9. Excerpts of the ^{1}H NMR spectra (400 MHz, 298K) of oligomer **1-Cu**$^{+}$ (2 mM) in a $CDCl_3$/[D_6]-DMSO mixture, 80:20 (vol/vol) in the presence of: (A) 0 equiv. of imidazole; (B) 0.25 equiv. of imidazole, (C) 0.5 equiv. of imidazole; (D) 0.75 equiv. of imidazole and (E) 1 equiv. of imidazole. The amide signals of the empty host and of the host-guest complex are marked with empty (○) and black circles (●), respectively. An affinity constant (K_a) of 6000 L mol^{-1} was determined by integration of the empty host and the host-guest complex resonances.

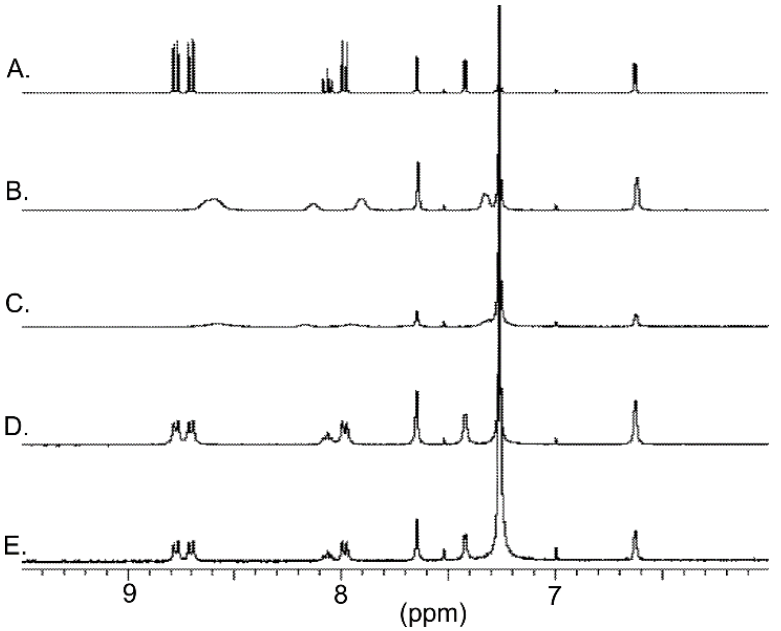


Figure S10. Excerpts of the ^{1}H NMR spectra (400 MHz, 298K) in $CDCl_3$/CD_3CN (95:5 vol/vol) of : (a) compound **5** (2mM, 298K); (b) **5** + $CuBF_4(MeCN)_4$ (0.5 equiv.); (c) **5** + $CuBF_4(MeCN)_4$ (1 equiv.) (d) **5** + $CuBF_4(MeCN)_4$ (0.5 equiv.) + imidazole (0.5 equiv.); (e) **5** + $CuBF_4(MeCN)_4$ (1.0 equiv.) + imidazole (1.0 equiv.).

4. Solid state X-Ray Crystallography

4.1 X-Ray crystallographic data for host-guest complex 1

Table S1. Crystal data and refinement details for **1** complex.

Identification code	**1**
Chemical formula	$C_{161}H_{151}N_{35}O_{26}\cdot 3.72(CHCl_3)\cdot 0.28(H_2O)$
Formula weight	3441.21 g/mol
Temperature	150 (2) K
Wavelength	Cu *K*α
Crystal system	Monoclinic
Space group	*C*2/c
Unit cell dimensions	*a* = 53.339(11) Å, α = 90°
	b = 31.243(6) Å, β = 120.89(3)°
	c = 31.828(6) Å, γ = 90°
Volume	45518 (20) $Å^3$
Z	8, (Z'=1)
Density (calculated)	1.004 Mg/m^3
Absorption coefficient	1.73 mm^{-1}
Absorption correction	Multi-scan
Crystal size	0.10 × 0.04 × 0.03 mm^3
Index ranges	*h* = −53→51, *k* = −30→31, *l* = −31→26
Completeness to theta = 50.43°	98.4%
Reflections collected	77697
Reflections observed [$I > 2\sigma(I)$]	10607
R_{int}	0.15
Data/parameters/restrains	23449/1628/144
Goodness-of-fit on F^2	1.86
Final R indices [I>2sigma(I)]	R1 = 0.1796, wR2 = 0.4085
R indices (all data)	R1 = 0.2573, wR2 = 0.4349
Largest diff. peak and hole	0.89 and -0.58 e $Å^{-3}$
CCDC #	1531704

4.2 X-Ray crystallographic data for host-guest complex 1-Cu

Table S2. Crystal data and refinement details for **1-Cu** complex.

Identification code	**1-Cu**
Chemical formula	$C_{161}H_{151}N_{35}O_{26}Cu \cdot CH_3CN \cdot BF_4 \cdot 1.66(CHCl_3)$
Formula weight	3381.62 g/mol
Temperature	150 (2) K
Wavelength	Cu *K*α
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	*a* = 20.562(1) Å, α = 86.052(4)°
	b = 29.273(2) Å, β = 89.339(5)°
	c = 31.274(2) Å, γ = 89.186(5)°
Volume	18777(2) Å^3
Z	4, (Z'=2)
Density (calculated)	1.196 Mg/m^3
Absorption coefficient	1.44 mm^{-1}
Absorption correction	Multi-scan
Crystal size	0.09 × 0.05 × 0.02 mm^3
Index ranges	$h = -20 \rightarrow 20$, $k = -29 \rightarrow 29$, $l = -31 \rightarrow 31$
Completeness to theta = 51.13°	98.3%
Reflections collected	136687
Reflections observed [$I > 2\sigma(I)$]	19882
R_{int}	0.133
Data/parameters/restrains	38903/3476/526
Goodness-of-fit on F^2	1.64
Final R indices [I>2sigma(I)]	R1 = 0.1916, wR2 = 0.4656
R indices (all data)	R1 = 0.2610, wR2 = 0.5198
Largest diff. peak and hole	1.07 and -0.64 e Å^{-3}
CCDC #	1531703

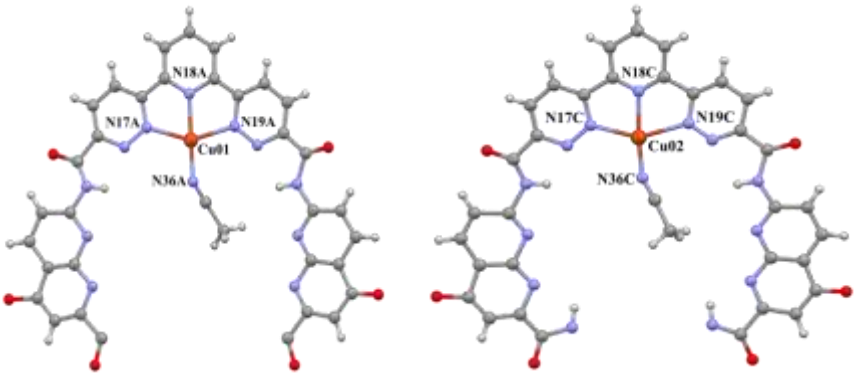
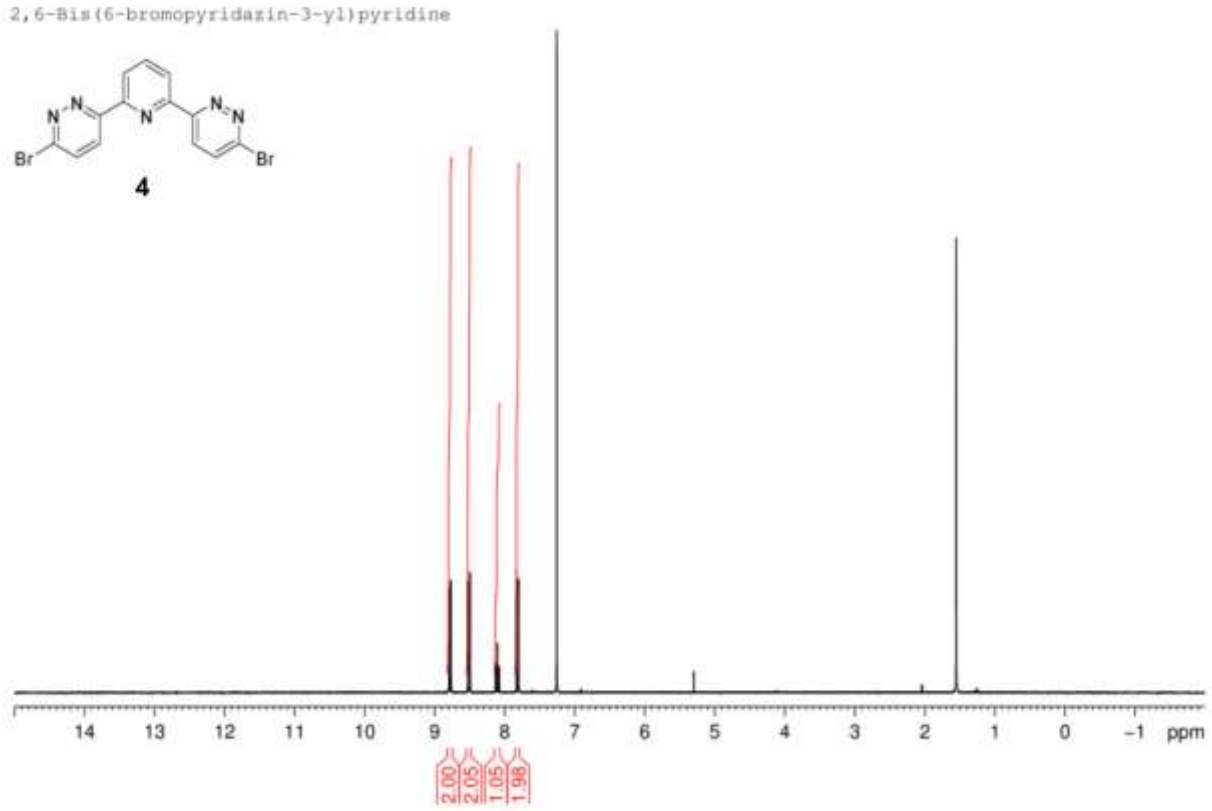


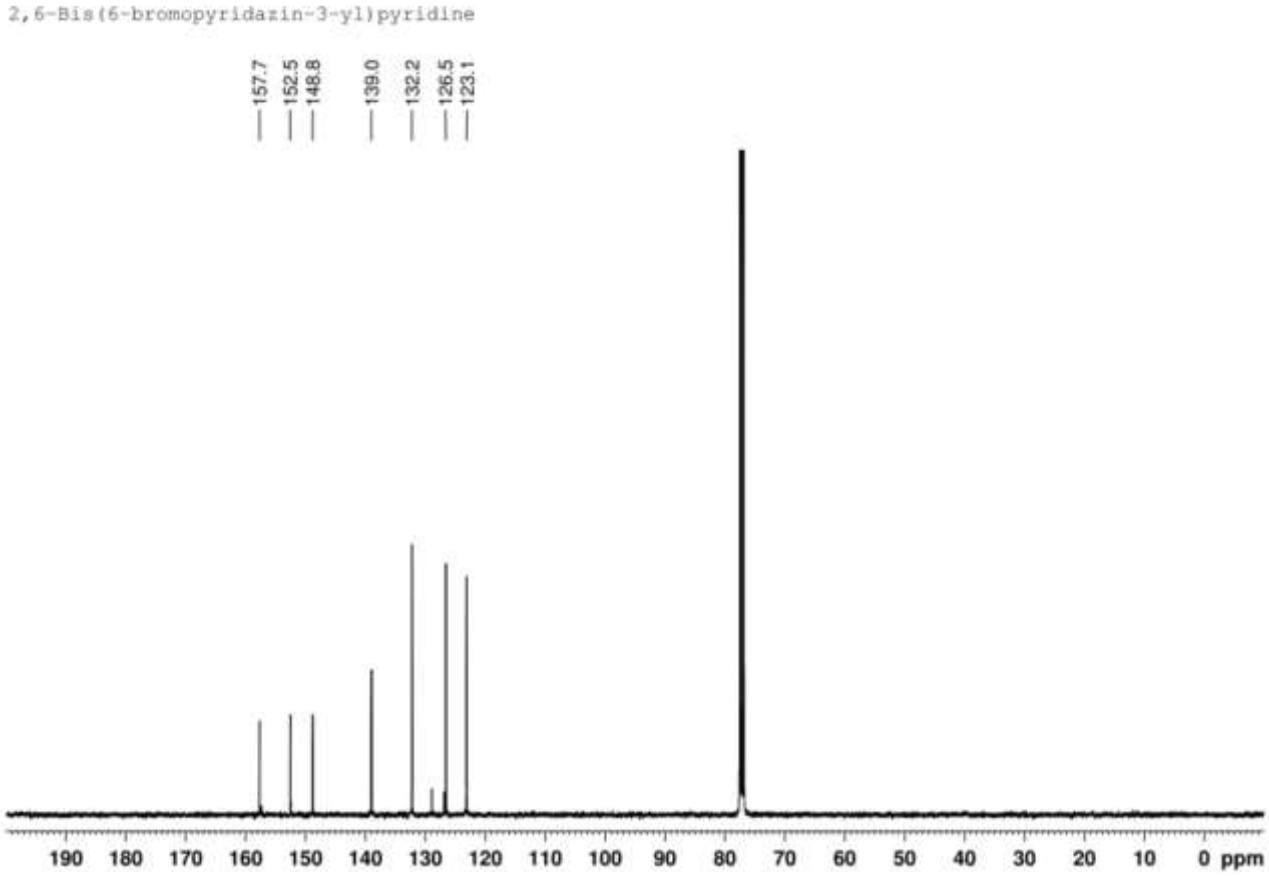
Figure S11. Cu coordination sphere of two symmetry independent molecules in **1-Cu** complex. Atom numbers are those of the cif file. In the asymmetric unit of the **1-Cu** complex, besides solvent molecules, two symmetry independent oligomer **1** molecules coordinated to Cu ions and two BF_4 anions were identified. This might suggest a +1 oxidation state of Cu ions. However, the green color of the crystals and planar coordination of the Cu that is uncommon for Cu^I,[8] and the Cu-N bonds lengths (Tab. S3) concur to indicate a +2 oxidation state. We note that large regions of the structure are occupied with blurred electron density that could not be reasonably modeled and that was removed using the SQUEEZE procedure[3] at the final stages of refinement. It cannot be excluded that other, disordered BF_4 anions were hidden within this "squeezed" electron density and Cu ions are indeed in a +2 oxidation state.

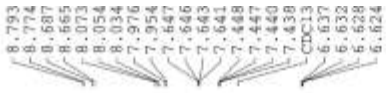
Table S3. Cu-N bond lengths (Å) in in **1-Cu** complex complex. Atom numbers are those of the cif file.

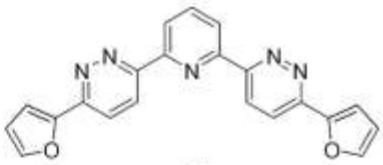
Cu01—N17A	2.224 (11)	Cu02—N17C	2.189 (11)
Cu01—N18A	2.075 (8)	Cu02—N18C	2.070 (14)
Cu01—N19A	2.210 (8)	Cu02—N19C	2.283 (13)
Cu01—N36A	1.860 (18)	Cu02—N36C	1.822 (16)

5. ^{1}H NMR and ^{13}C NMR spectra of new synthetic compounds

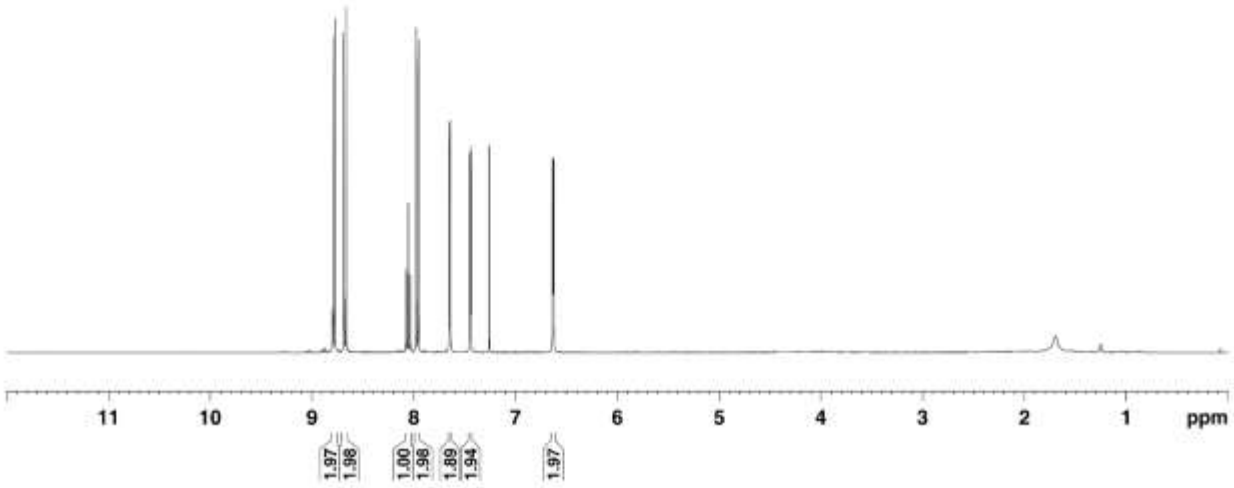




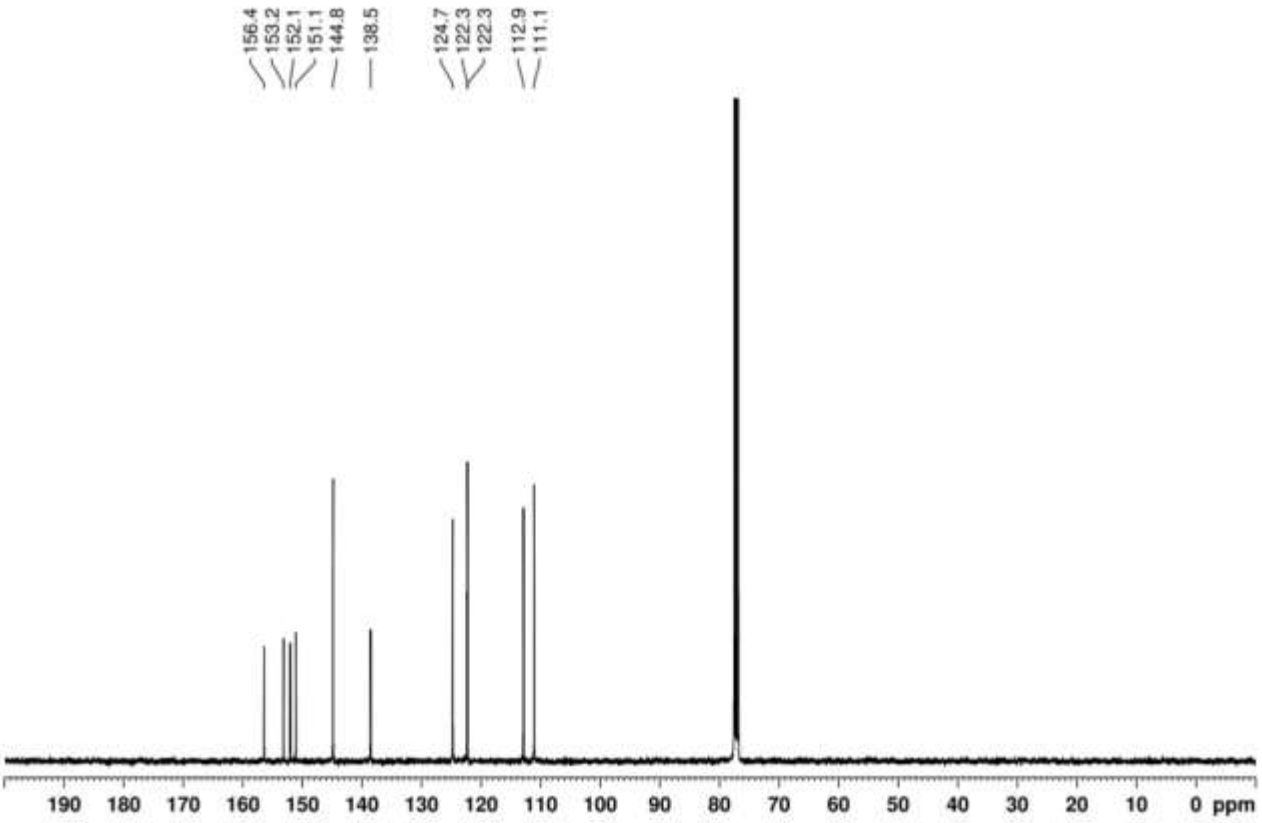




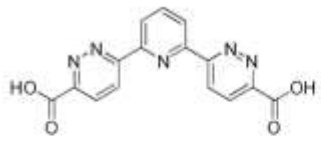
5



2,6-Bis[6-(furan-2-yl)pyridazin-3-yl]py



6,6'-(Pyridine-2,6-diyl)bis-3-pyridazinylcarboxylic acid



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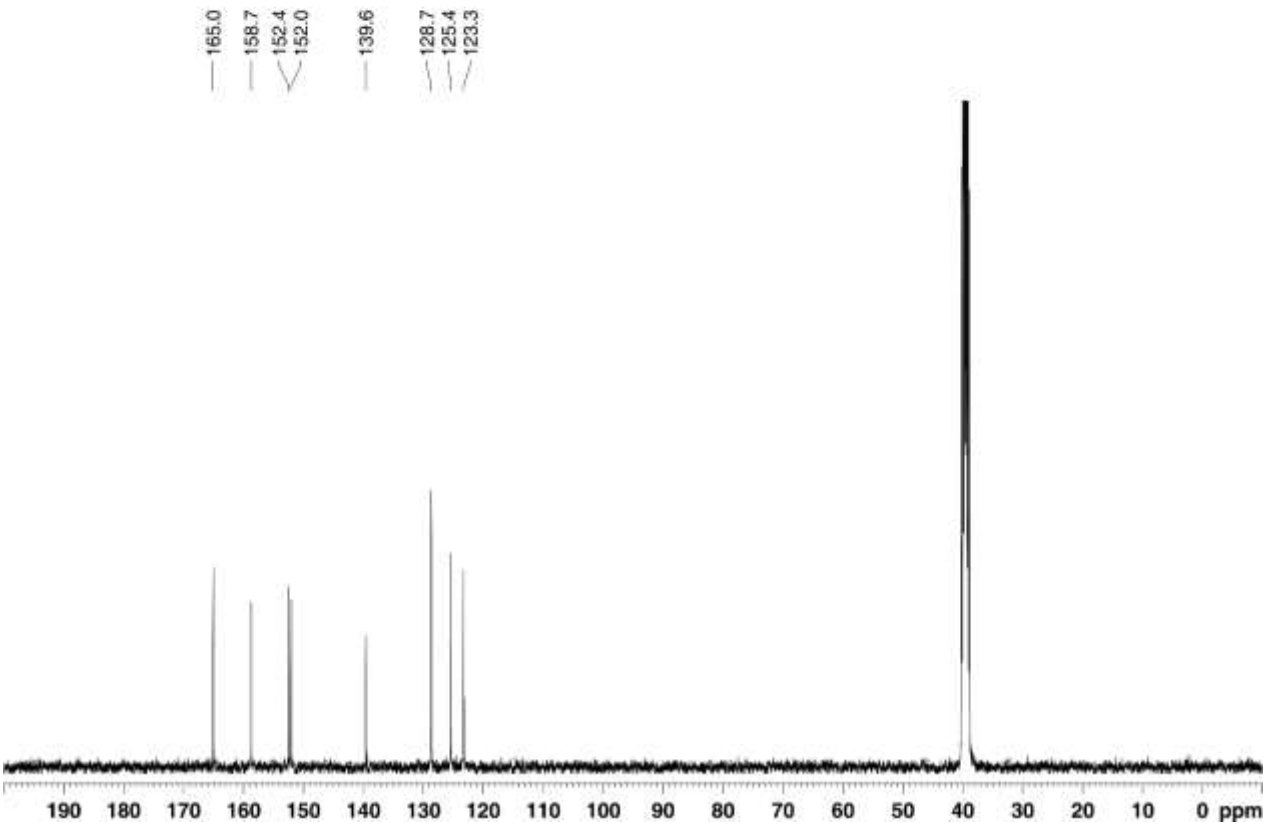

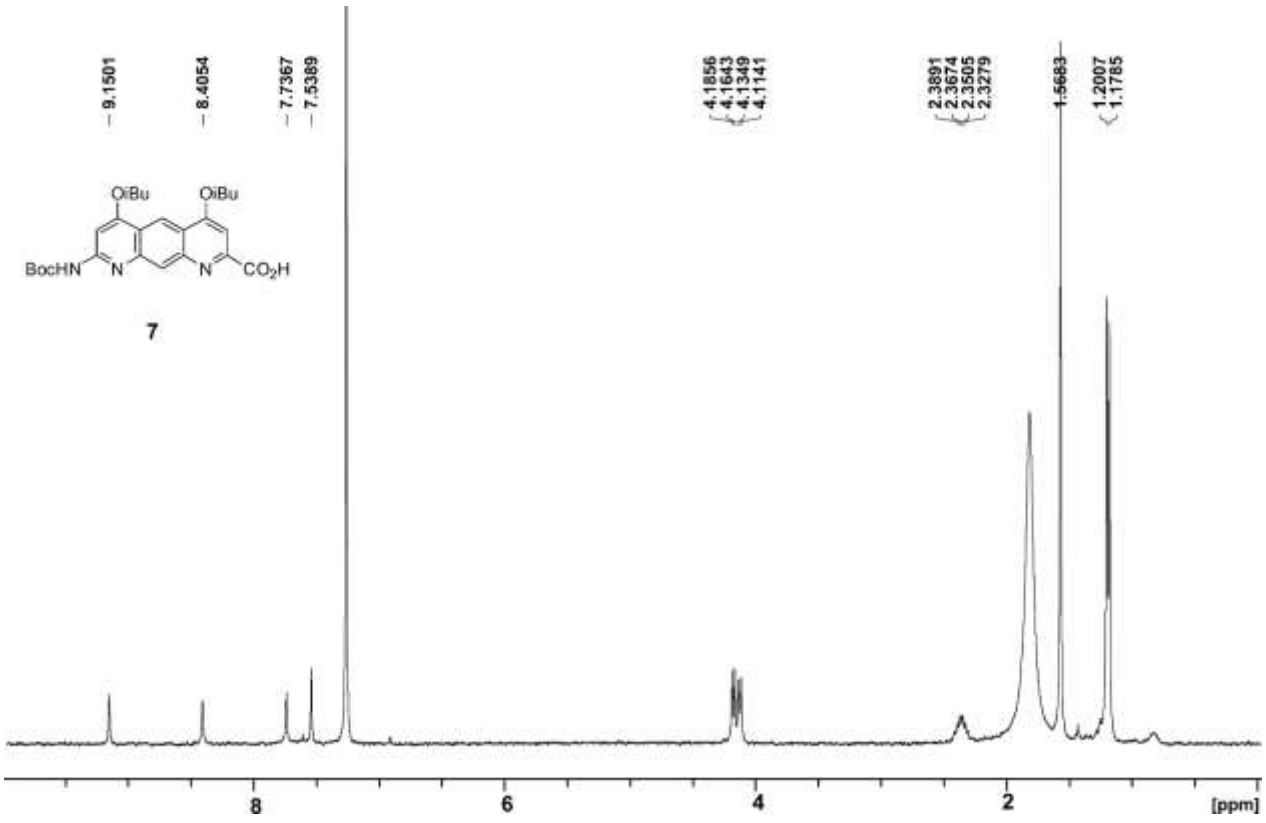
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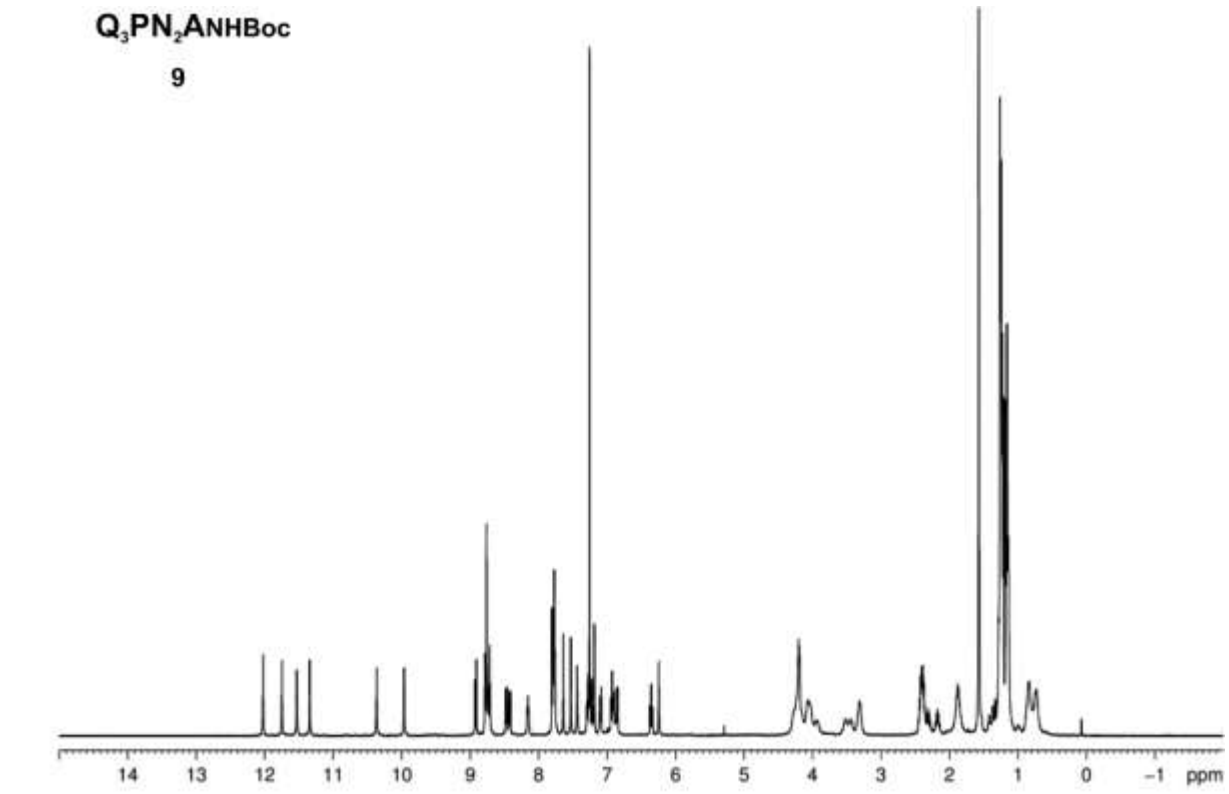
7.7367
7.5389
4.1856
4.1643
4.1349
4.1141
2.3891
2.3674
2.3505
2.3279
1.5683
1.2007
1.1785
OiBu
OiBu
BocHN
N
N
CO2H
7
8
6
4
2
[ppm]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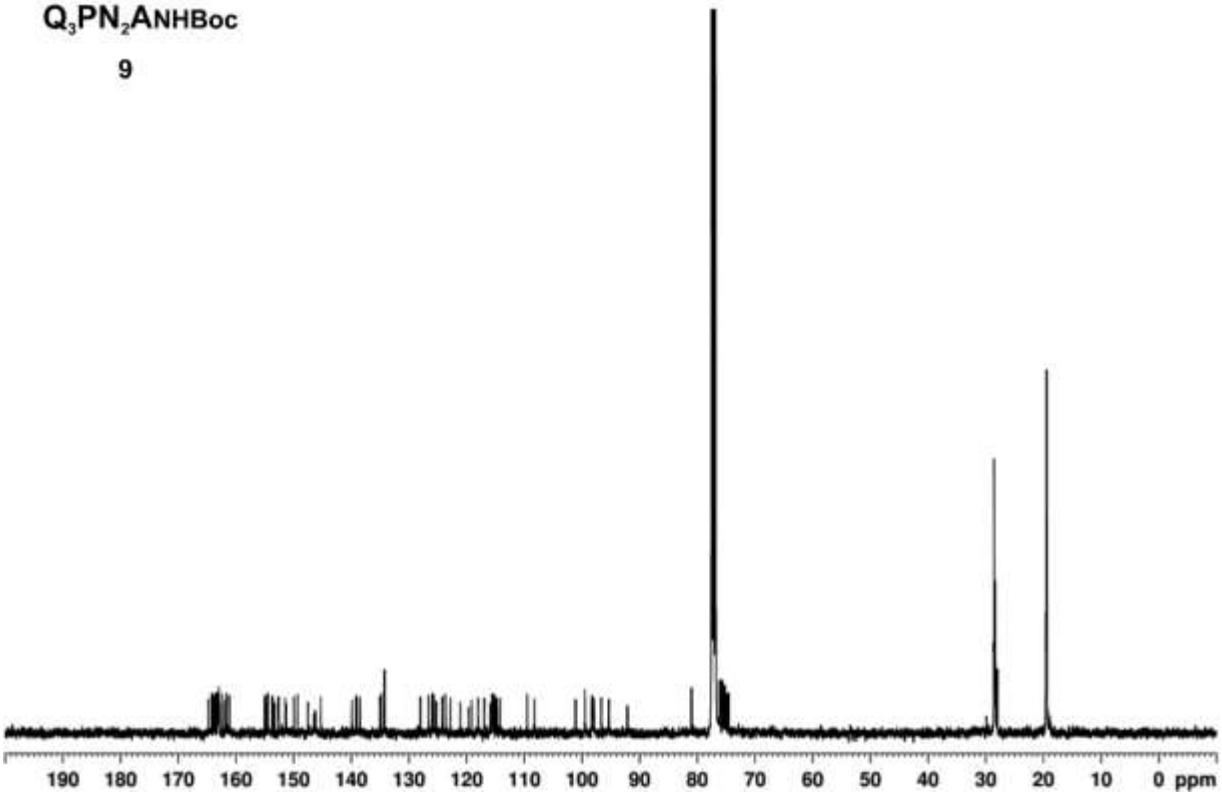
9
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm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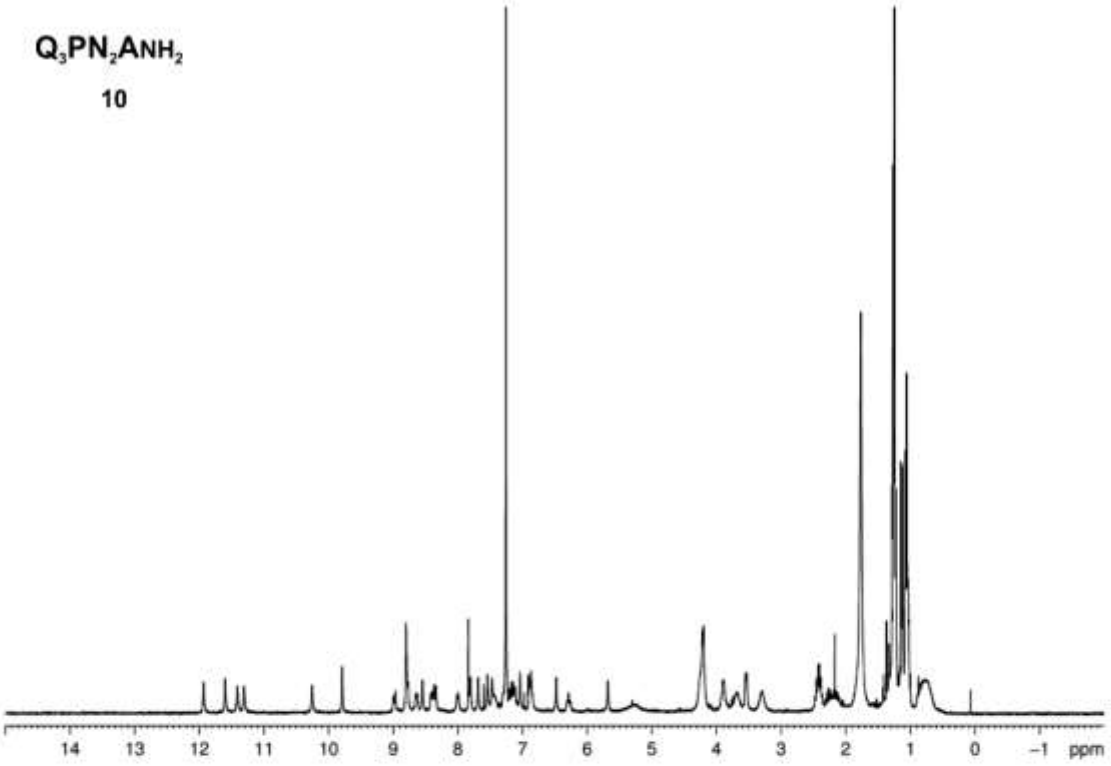
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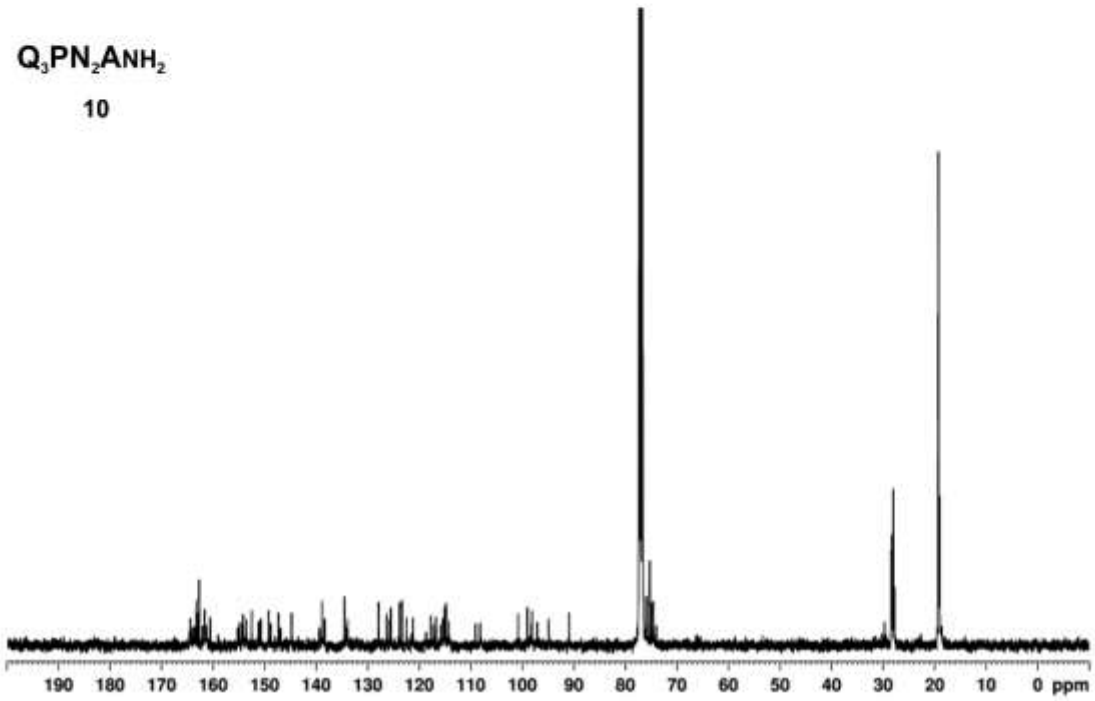
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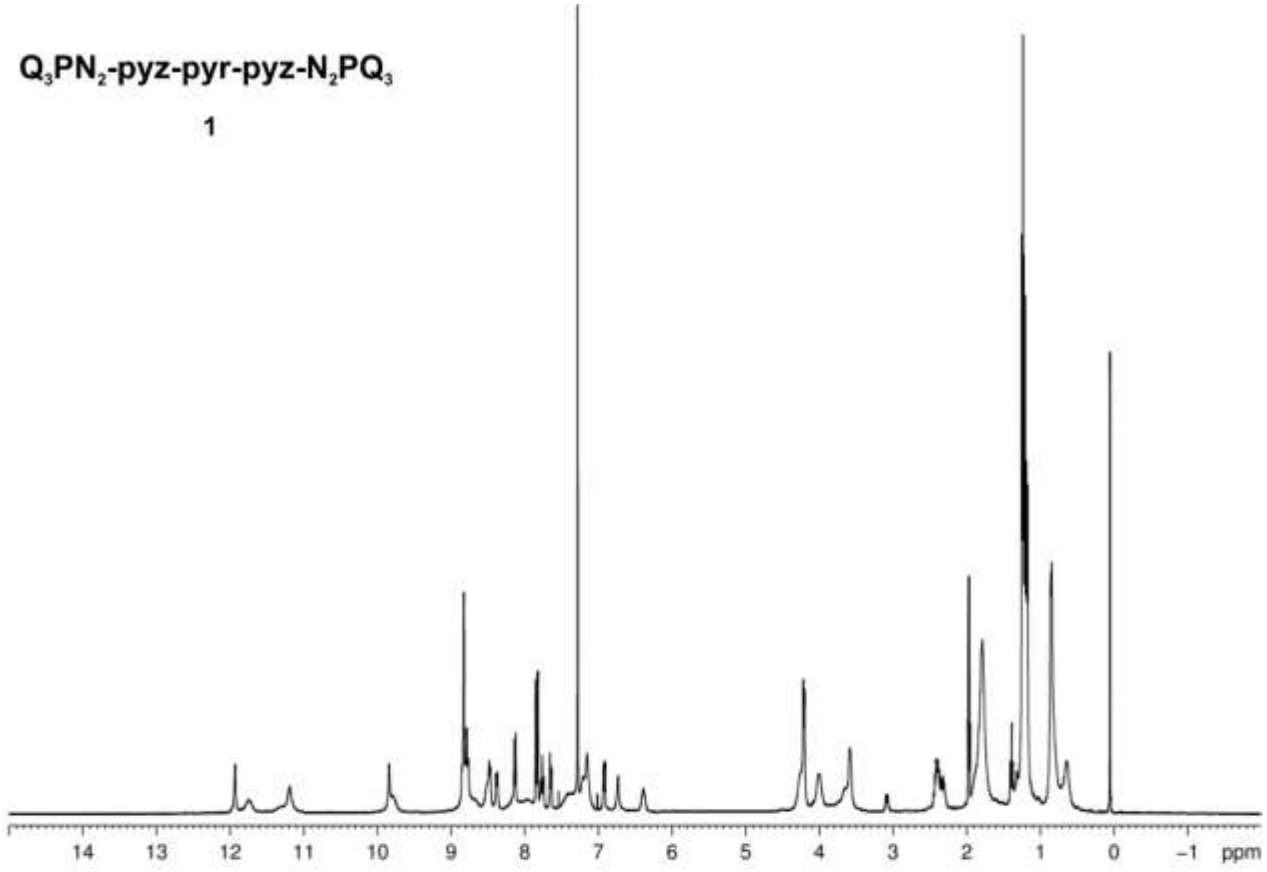
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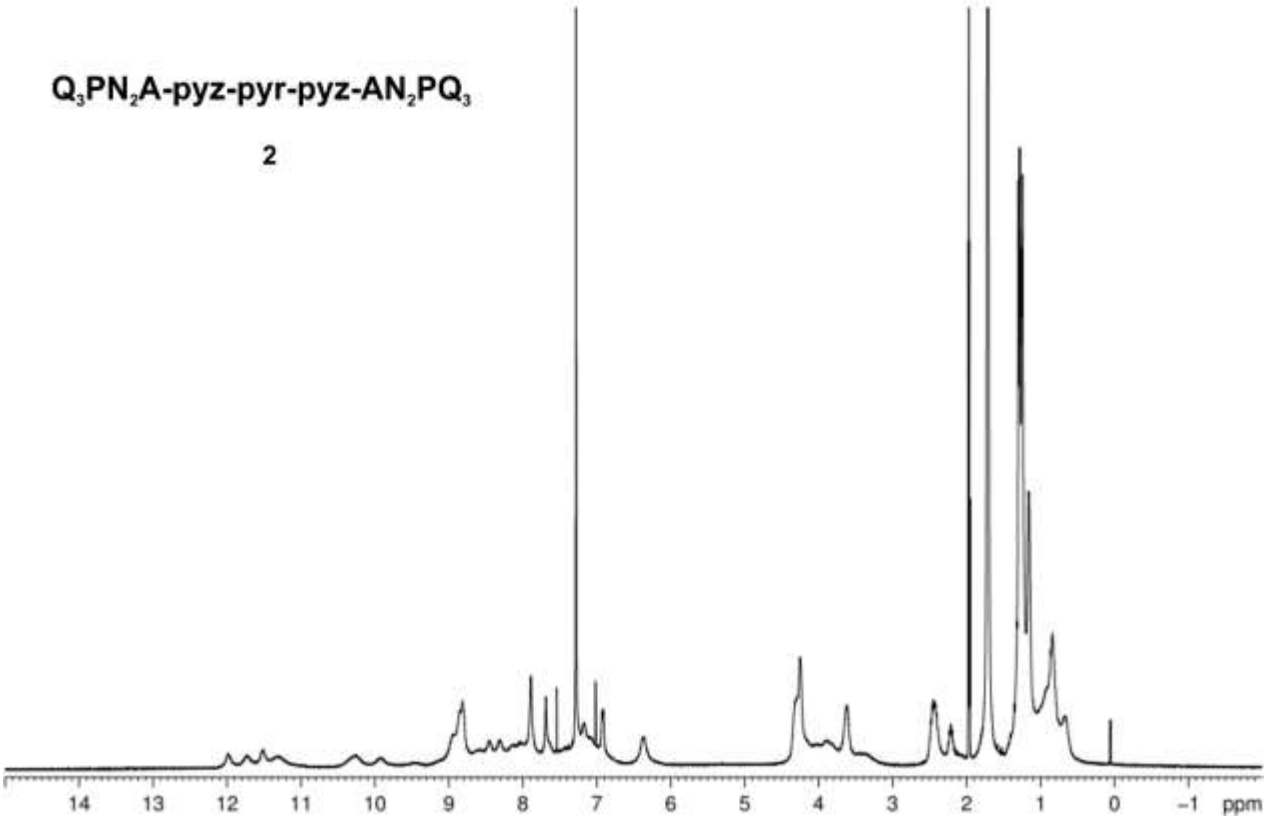
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2
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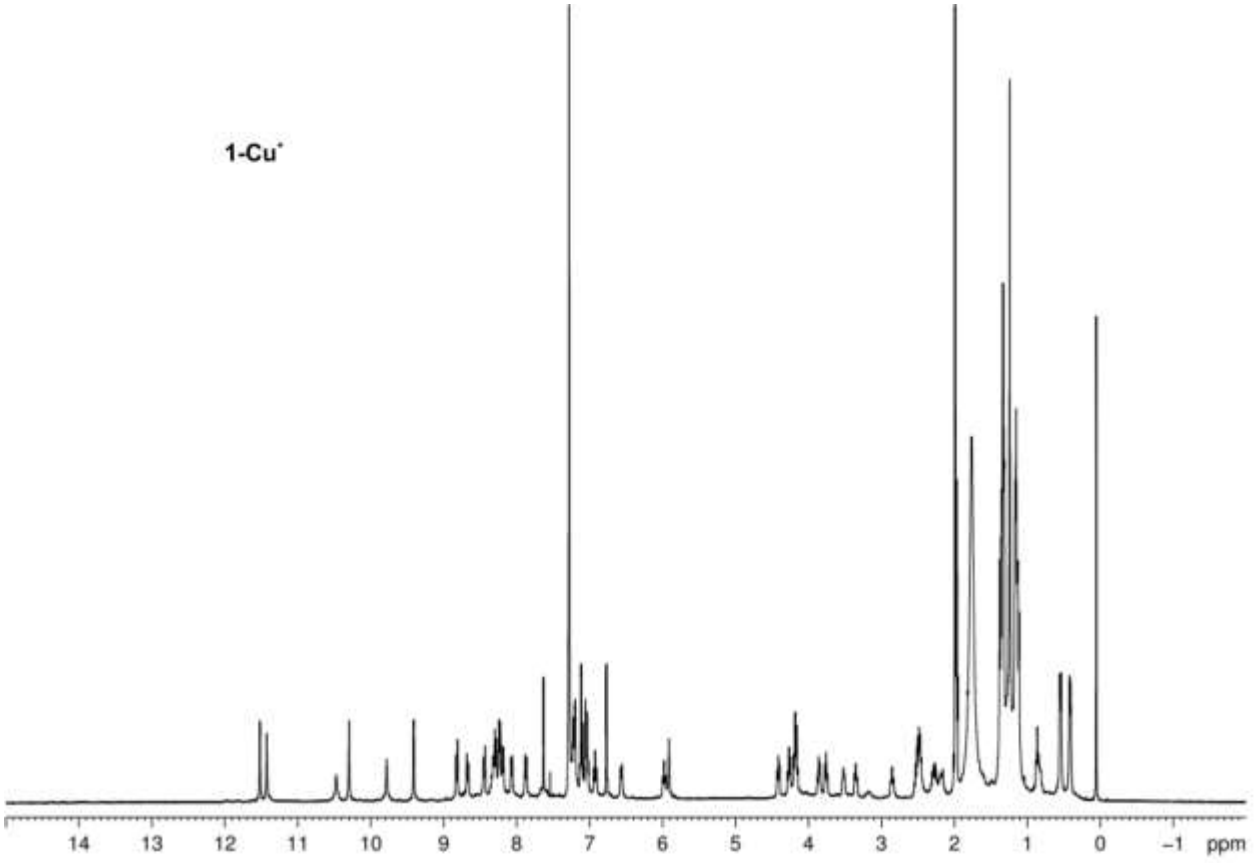
1-Cu•
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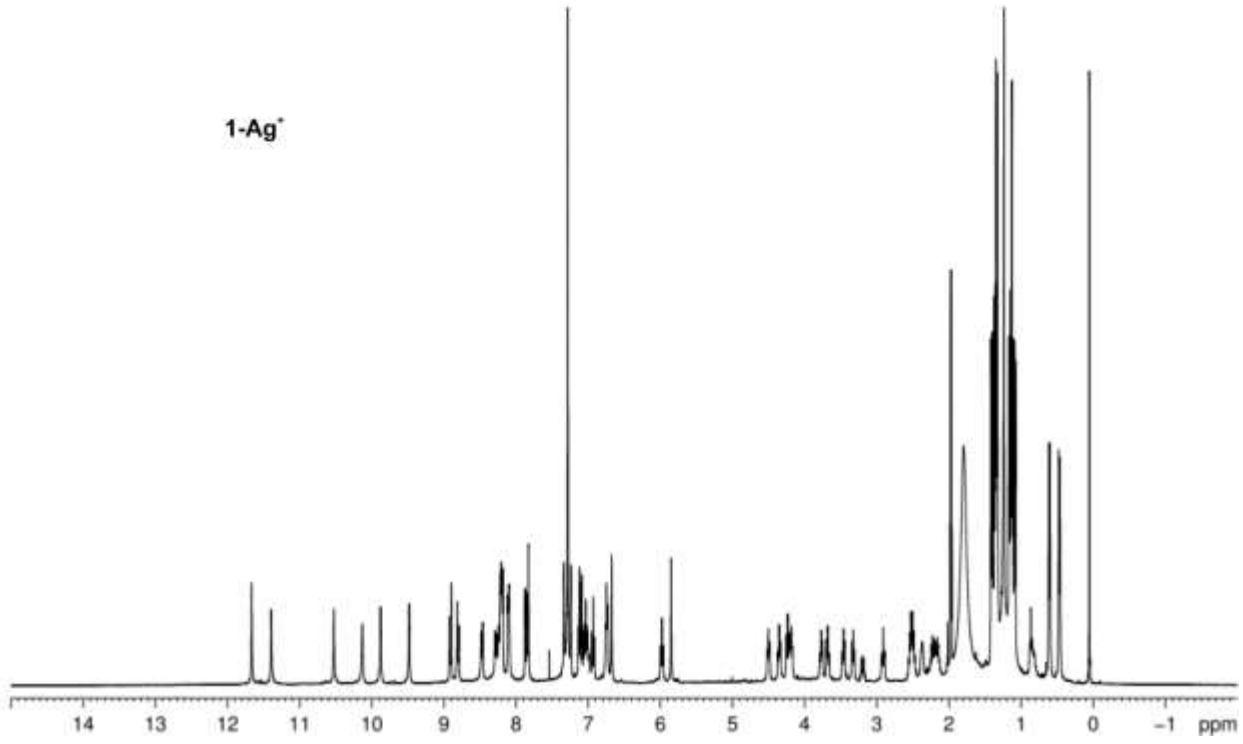
1-Ag•
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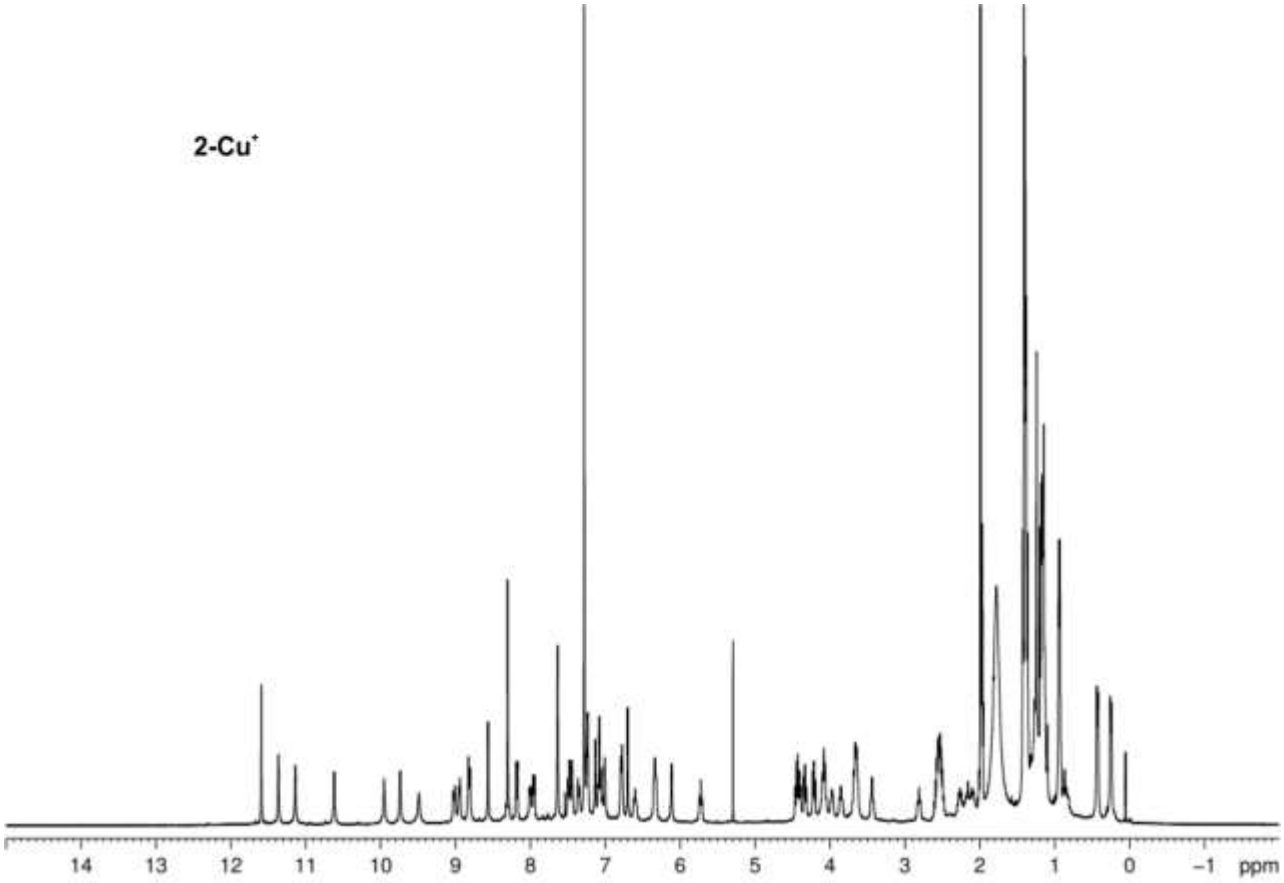
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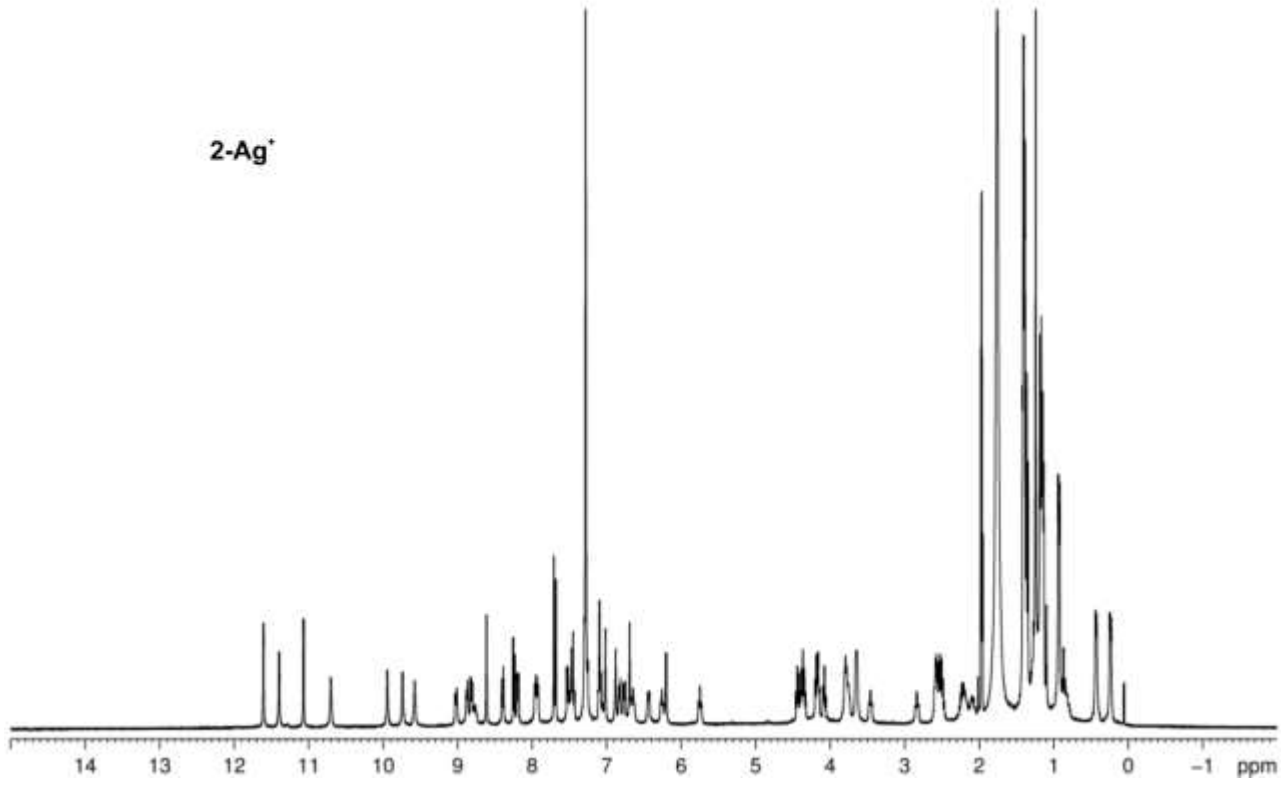
2-Ag+
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 ppm

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