

Electronic Supplementary Information

Synthesis of New Copper(I) Based linear 1-D-Coordination Polymers with Neutral Imidazolinium-Dithiocarboxylate Ligands

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Experimental Section

Materials and general methods.

All manipulations were carried out under an anaerobic and anhydrous atmosphere of nitrogen by employing standard Schlenk techniques or working in a glove box. The solvents were dried and degassed prior to use.¹ CuCl and CuBr, were used without further purification as purchased commercially from sigma aldrich. 1,3-Dibenzyl-3-imidazolinium-2-dithiocarboxylate (Bn₂ImCS₂, **1**) was prepared according to the literature.²

Physical measurements.

Spectra were recorded using the following spectrometers. UV: Varian Cary 50. IR and Raman: Bruker Vertex 70. NMR: Bruker Avance 500 (500 and 125 MHz, respectively). The NMR signals were referenced to residual solvents measured relative to TMS. MS (ESI): Waters Synapt 2G (QTOF). Elemental analysis: vario MICRO Cube Elementar.

General method for the synthesis of the copper(I) coordination polymers.

Reaction of Bn₂ImCS₂ (**1**) (1.0 mmol, 326 mg) with copper(I) halides (1 mmol) in 10 mL of abs. MeCN lead to suspensions of a brown solid. These mixtures were stirred over night at room

temperature. The precipitates were collected by filtration, washed with Et₂O and dried in vacuum. Single crystals were obtained by slow diffusion of Et₂O into the mother liquors.

[Cu(Bn₂ImCS₂)Cl]_n (2). With CuCl (1.0 mmol, 99 mg) a dark brown solid was obtained. Yield: 181 mg (43%).

UV/Vis (DCM, λ_{max} [nm] (ε [L mol⁻¹ cm⁻¹])): 538 (1600), 361 (7210), 236 (21600).

IR (KBr, ν̄ [cm⁻¹]): 3437br, 3028w, 2912w, 1597s, 1495w, 1454w, 1437w, 1354w, 1306w, 1244m, 1198w, 1136w, 1105w, 1072w, 1016s, 903w, 822w, 766w, 752w, 698s, 662m, 559w, 465w.

Raman (100 mW, ν̄ [cm⁻¹]): 454m, 481s, 876s, 1004w, 1106m, 1364w, 1559w, 4265w.

¹H-NMR (500 MHz, DMSO, 30 °C, δ [ppm]): 3.70 (s, 8H, CH₂, N-CH₂-CH₂); 4.49 (s, 8H, CH₂, N-CH₂-Ph); 7.33 (m, 20H, CH_{arom.}).

¹³C-NMR (125 MHz, DMSO, 30°C, δ [ppm]): 47.1 (CH₂, N-CH₂-CH₂); 50.4 (CH₂, N-CH₂-Ph); 128.9 (CH_{arom.}); 128.9 (CH_{arom.}); 129.2 (CH_{arom.}); 133.6 (C_q, CH₂-Ph); 167.0 (C_q, C_q-CS₂).

MS-ES⁺ (MeOH, m/z (%)): 389.02 (2.4), 553.07 (1.7), 715.11 (100.0) [Cu(Bn₂ImCS₂)₂]⁺, 815.01 (1.0) [(Cu(Bn₂ImCS₂))₂Cl]⁺.

MS-ES⁻ (MeOH, m/z (%)): 123.91 (10), 134.88 (100) [CuCl₂]⁻, 178.82 (10), 223.81 (81).

Anal. calcd for C₁₈H₁₈ClN₂S₂Cu (425.48): C 50.81, H 4.26, N 6.58, S 15.07 (%); found: C 50.80, H 4.31, N 6.82, S 15.24 (%).

[Cu(Bn₂ImCS₂)Br]_n (3). With CuBr (1.0 mmol, 143 mg) a brown solid was obtained. Yield: 291 mg (62 %).

UV/Vis (DCM, λ_{max} [nm] (ε [L · mol⁻¹ · cm⁻¹])): 527 (640), 419 (860), 368 (1170), 298 (sh, 5700), 288 (6620), 243 (52600).

IR (KBr, ν̄ [cm⁻¹]): 3435br, 3030w, 2918w, 2390w, 2284w, 1601m, 1582m, 1549m, 1495w, 1454m, 1437w, 1358w, 1298w, 1250w, 1194w, 1128w, 1051s, 943w, 858w, 770w, 748w, 702m, 671m, 571w, 492w, 455w.

Raman (500 mW, ν̄ [cm⁻¹]): 338w, 354w, 386w, 458w, 471w, 492s, 807w, 859m, 1004w, 1096w, 1358w, 1551w, 1763w.

¹H-NMR (500 MHz, DMSO, 30 °C, δ [ppm]): 3.74 (s, 8H, CH₂, N-CH₂-CH₂); 4.55 (s, 8H, CH₂, N-CH₂-Ph); 7.35 (m, 20H, CH_{arom.}).

^{13}C -NMR (125 MHz, DMSO, 30 °C, δ [ppm]): 47.3 (CH_2 , N- CH_2 - CH_2); 50.5 (CH_2 , N- CH_2 -Ph); 128.9 ($\text{CH}_{\text{arom.}}$); 128.9 ($\text{CH}_{\text{arom.}}$); 129.3 ($\text{CH}_{\text{arom.}}$); 133.6 (C_q , CH_2 -Ph); 166.8 (C_q , C_q , CS_2).

MS-ES⁺ (MeOH, m/z (%)): 239.16 (3.1), 313.08 (1.2), 349.08 (3.4), 389.02 (5.3), 553.07 (3.1), 715.11 (100.0) $[\text{Cu}(\text{Bn}_2\text{ImCS}_2)_2]^+$, 858.96 (9.0) $[(\text{Cu}(\text{Bn}_2\text{ImCS}_2))_2\text{Br}]^+$, 1185.05 (1.0).

MS-ES⁻ (MeOH, m/z (%)): 169.86 (8), 222.77 (100) $[\text{CuBr}_2]^-$, 255.24 (5), 313.70 (12).

Anal. calcd for $\text{C}_{18}\text{H}_{18}\text{BrN}_2\text{S}_2\text{Cu}$ (469.93): C 46.01, H 3.86, N 5.96, S 13.65 (%); found: C 46.12, H 3.99, N 5.98, S 13.59 (%).

General method for the thiol-ene reaction.

The coordination polymers (0.25 mol%) were added to dry acetonitrile or dichloromethane (0.5 mL) followed by the addition of thiophenol (4 equiv.) and styrene (1 equiv.) The resulting mixture was stirred under light for 40 h. Thereafter, the expected phenethyl(phenyl)sulfane was isolated via column chromatography (Pentane/Et₂O, 30:1) as colourless oil. The spectral data were consistent with literature values.³ In case of polymer **2** in acetonitrile a yield of 60% was obtained.

Crystal Structure Analysis.

Bruker AXS SMART APEX CCD diffractometer, graphite monochromator, $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $T = 130(2) \text{ K}$. Data reduction and absorption correction were performed with SAINT and SADABS.⁴ All non-hydrogen atoms were refined anisotropically. All H atom positions were clearly derived from difference Fourier maps and then refined on idealized positions with $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{C})$, C-H distances 0.95-0.99 \AA .

1. ($\text{C}_{18}\text{H}_{18}\text{N}_2\text{S}_2$), red prism, 0.33 x 0.20 x 0.19 mm³, monoclinic, space group C2/c, $a = 18.999(2)$, $b = 7.6609(9)$, $c = 12.3984(15) \text{ \AA}$, $\beta = 113.417(2)^\circ$, $V = 1656.0(3) \text{ \AA}^3$, $Z = 4$, $D_{\text{calc}} = 1.309 \text{ g/cm}^3$, $\mu = 0.319 \text{ mm}^{-1}$, $F(000) = 688$, MoK α radiation $2.3^\circ < \Theta < 27.9^\circ$. The structure was solved by direct methods⁵, and refined on F^2 by full-matrix least-squares⁵ based on 101 parameters and 1972 unique intensities. Refinement converged at $R1(I > 2\sigma(I)) = 0.031$, $wR2(\text{all data}) = 0.083$; residual density min/max = -0.18/0.39 e/ \AA^3 .

2. ($\text{C}_{18}\text{H}_{18}\text{ClCuN}_2\text{S}_2$)_n, brown needle, 0.45 x 0.04 x 0.04 mm³, triclinic, space group P-1, $a = 6.4888(9)$, $b = 12.0393(16)$, $c = 12.8648(17) \text{ \AA}$, $\alpha = 111.713(2)^\circ$, $\beta = 95.419(3)^\circ$, $\gamma = 100.495(3)^\circ$, $V = 903.6(2) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.564 \text{ g/cm}^3$, $\mu = 1.589 \text{ mm}^{-1}$, $F(000) = 436$, MoK α

radiation $1.7^\circ < \Theta < 27.9^\circ$. The structure was solved by direct methods⁵, and refined on F^2 by full-matrix least-squares⁵ based on 217 parameters and 4293 unique intensities. Refinement converged at $R1(I > 2\sigma(I)) = 0.041$, $wR2(\text{all data}) = 0.071$; residual density min/max = -0.55/0.54 e/Å³.

3. (C₁₈H₁₈BrCuN₂S₂)_n, orange prism, 0.49 x 0.38 x 0.18 mm³, triclinic, space group P-1, a = 6.5715(6), b = 12.1048(11), c = 12.8077(11) Å, $\alpha = 111.257(2)^\circ$, $\beta = 95.214(2)^\circ$, $\gamma = 100.494(2)^\circ$, V = 919.8(1) Å³, Z = 2, D_{calc} = 1.697 g/cm³, $\mu = 3.588 \text{ mm}^{-1}$, F(000) = 472, MoK α radiation $1.7^\circ < \Theta < 27.9^\circ$. The structure was solved by direct methods⁵, and refined on F^2 by full-matrix least-squares⁵ based on 217 parameters and 4366 unique intensities. Refinement converged at $R1(I > 2\sigma(I)) = 0.022$, $wR2(\text{all data}) = 0.058$; $\Delta F_{\text{min/max}} = -0.46/0.40 \text{ e/Å}^3$.

CCDC-1008787, CCDC-1000389, and CCDC-1000390, contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

References.

- 1 J. Leonard, B. Lygo and G. Procter, *Praxis der Organischen Chemie*, Wiley-VCH, Weinheim, 1996.
- 2 A. Blanrue and R. Wilhelm, *Synthesis*, 2009, 583; (b) W. Krasuski, D. Nikolaus, M. Regitz, *Liebigs Ann. Chem.*, 1982, 1451.
- 3 E. L. Tyson, M. S. Ament and T. P. Yoon, *J. Org. Chem.*, 2013, **78**, 2046.
- 4 Bruker (2002). SMART (Version 5.63), SAINT (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
- 5 Sheldrick, G. M. A short history of SHELX, *Acta Cryst.*, 2008, **A64**, 112.

Additional Figures.

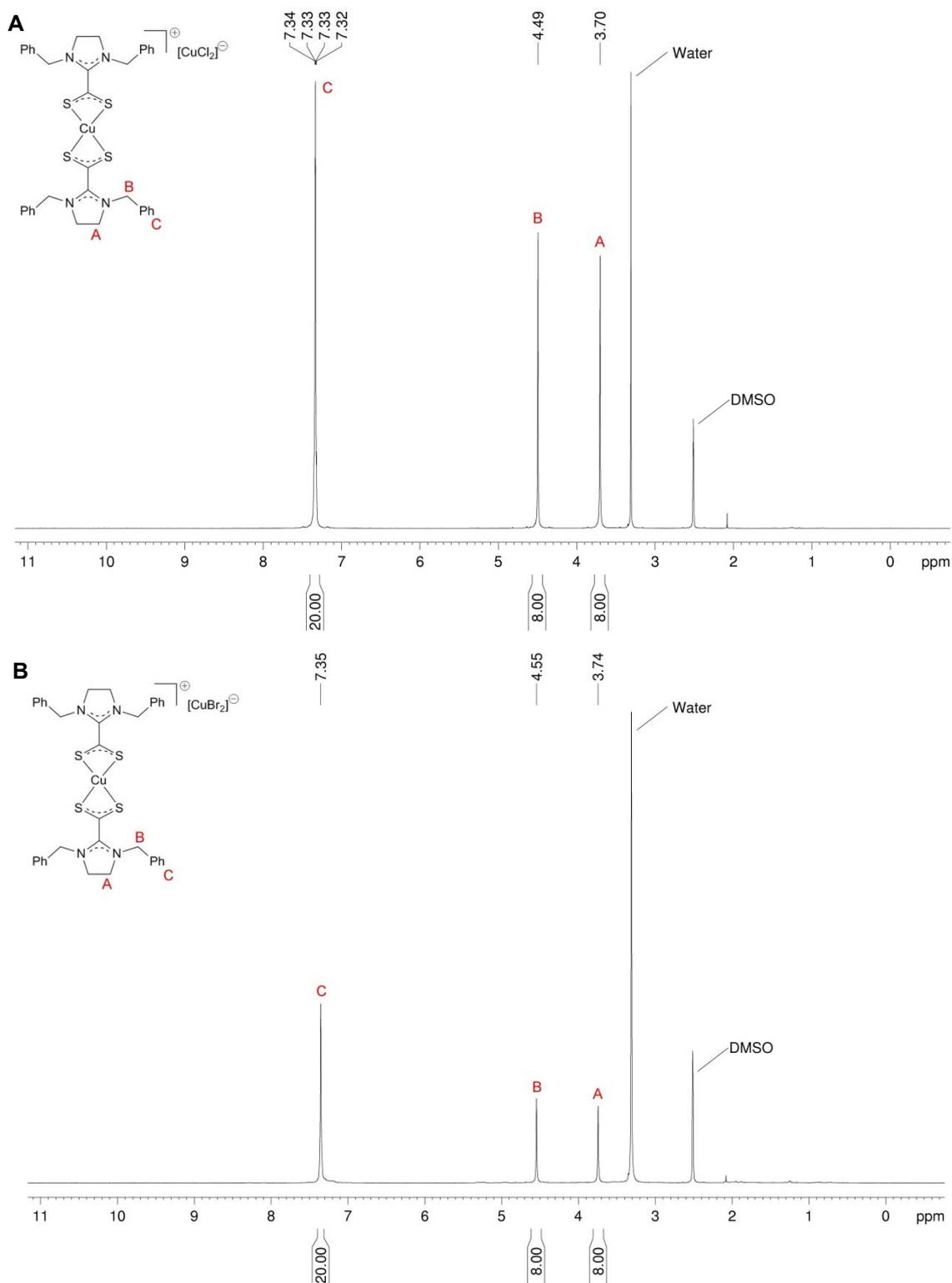


Figure S1 $^1\text{H-NMR}$ spectra of **2** (A) and **3** (B) dissolved in DMSO-d_6 (500 MHz, 30°C). In both cases very sharp proton signals indicate a non-polymeric species. ESI-MS analysis in positive and in negative ionisation mode of **2** and **3** (see below) confirm our proposed structure of the complexes $[\text{Cu}(\text{Bn}_2\text{ImCS}_2)_2][\text{CuX}_2]$ ($\text{X} = \text{Cl}, \text{Br}$).

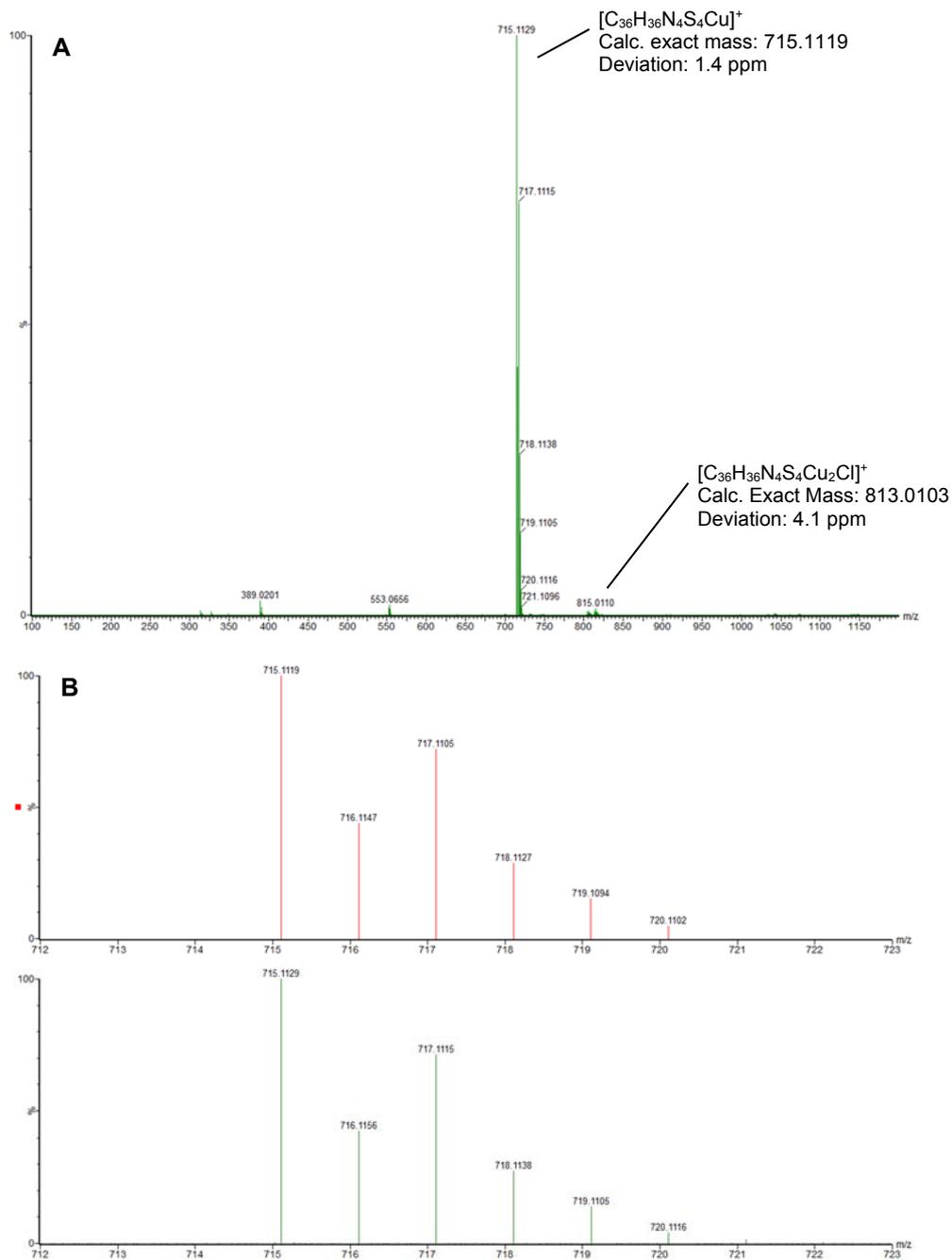


Figure S2 A: ESI-ES spectrum in the positive ionisation mode of **2** in MeOH, B: Comparison of the experimental (green) and calculated (red) isotope pattern of $[Cu(Bn_2ImCS_2)_2]^+$.

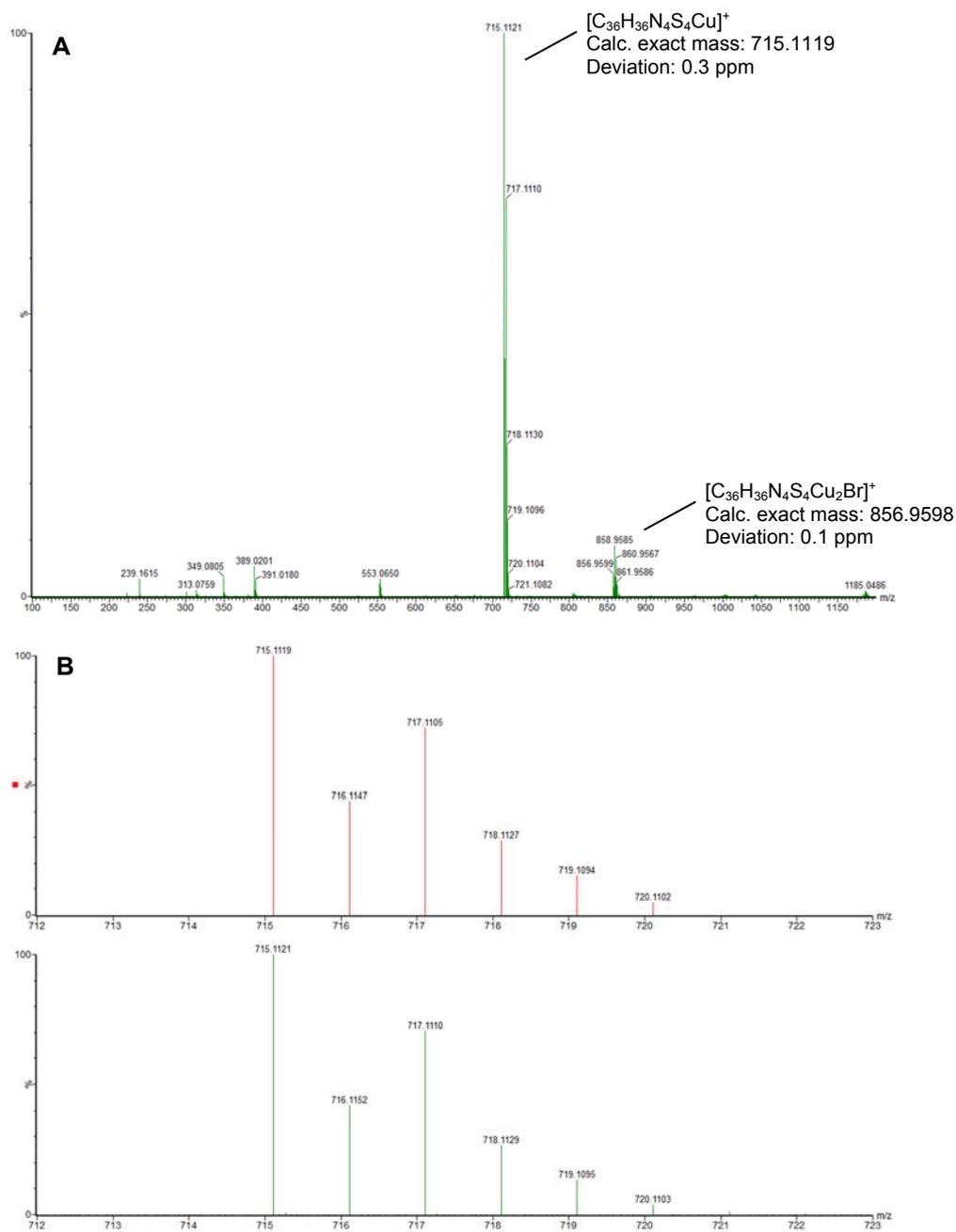


Figure S3 A: ESI-MS spectrum in the positive ionisation mode of **3** in MeOH, B: Comparison of the experimental (green) and calculated (red) isotope pattern of $[Cu(Bn_2ImCS_2)_2]^+$.

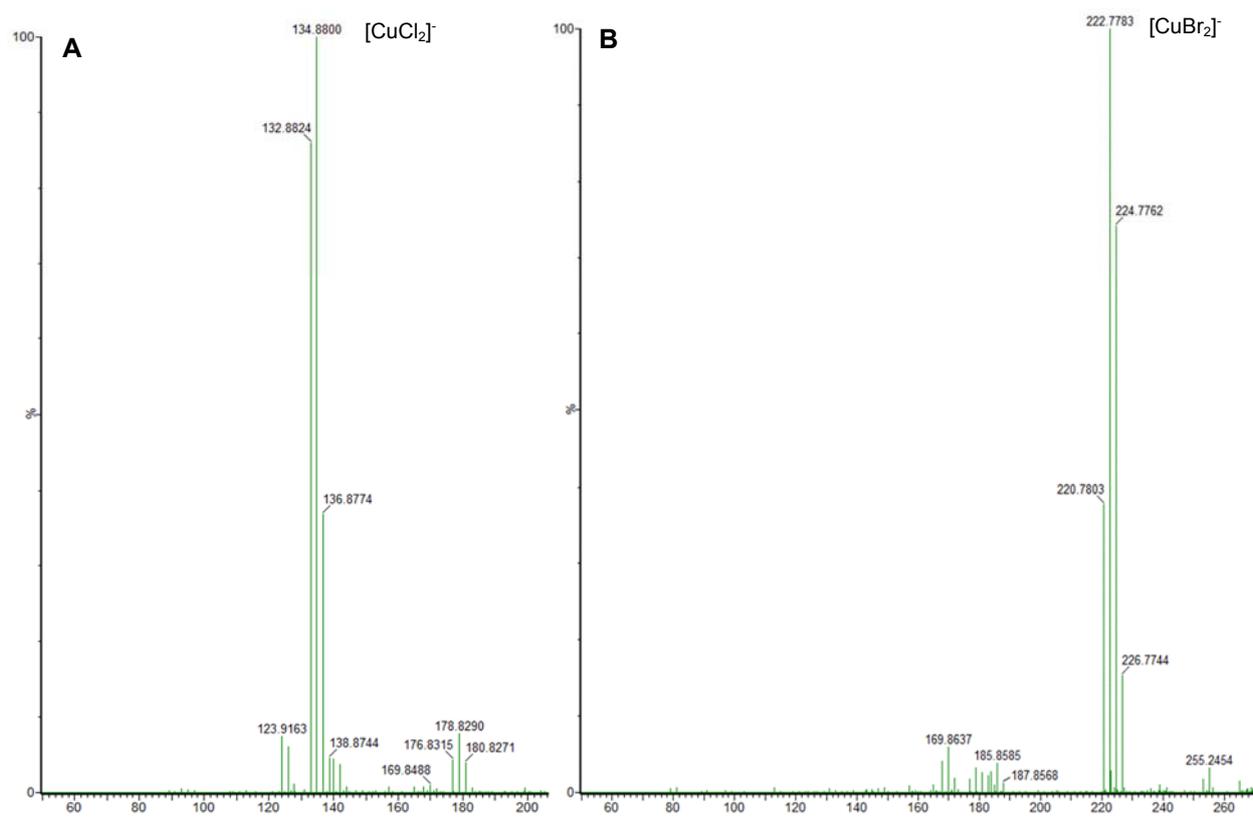


Figure S4 ESI-MS spectrum in the negative ionisation mode of **2**(A) and **3** (B) (in MeOH). In both cases we found the [CuX₂]⁻ molecules with the characteristic isotpe pattern.