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Electronic Supplementary Information

Asymmetric Binuclear Ni(II) And Cu(II) Schiff Base Metallopolymers

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Contents

Synthesis of A. Salicylaldehyde (0.106 mL, 1 mmol) was added to a solution of potassium bicarbonate (0.200 g, 1 mmol) in ethanol (8 mL). After stirring for 15 min, a solution of nickel(II) acetate tetrahydrate (0.144 g, 0.5 mmol) in ethanol (8 mL) was added dropwise to the mixture and the green solution was stirred for 30 min at rt. 3,3'-diaminobenzidine (0.107 g, 0.5 mmol) was dissolved in hot ethanol (13 mL) and added dropwise to the green solution. The mixture was stirred overnight at reflux and a dark brown solid was filtered and washed with cold ethanol (10 mL) and diethyl ether (10 mL). Yield: 94 %. **IR** (KBr, ν/cm^{-1}): 3378, 3272 (vw, ν_{NH2}), 3007, 3070 (vw, $\nu_{C\text{-}Harom}$); 1606 (s, $\nu_{C=N}$); 1617, 1523 (m, $\nu_{C=Carom}$); 757 (m, $\delta_{C\text{-}Harom}$). **^{1}H NMR** (400 MHz, DMSO-d_6, 298 K) δ/ppm: 9.01 (s, 1H, H-C=N), 8.81 (s, 1H, H-C=N), 8.22 (s, 1H, Ar-H), 8.10 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.67 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.59 (d, *J* = 7.9 Hz, 1H, Ar-H), 7.46 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.32 (t, *J* = 7.81 Hz, 1H, Ar-H), 7.30 (t, *J* = 7.91 Hz, 1H, Ar-H), 6.98 (s, 1H, Ar-H), 6.94 (d, *J* = 8.2 Hz, 1H, Ar-H) 6.90-6.87 (m, 2H, Ar-H), 6.68 (t, *J* = 7.81 Hz, Ar-H), 6.66 (t, *J* = 7.91 Hz, 1H, Ar-H), 6.62 (d, *J* = 8.2 Hz, 1H, Ar-H), 4.75 (s, 2H, NH_2), 4.56 (s, 2H, NH_2). **^{13}C NMR** (100 MHz, DMSO-d_6, 298 K) δ/ppm: 165.2 (Ar-O), 164.9 (Ar-O), 156.5 (C=N), 155.4 (C=N), 142.8 (C), 141.2 (C), 140.2 (C), 135.1, 134.9 (CH), 134.2 (CH), 134.0 (CH), 127.3 (C), 124.8 (CH), 120.4 (C), 120.3 (C), 120.2, 120.1 (CH), 116.5 (CH), 116.0 (CH), 115.2 (CH), 114.4 (CH), 112.7 (CH), 112.2 (CH). **Anal. Found (calcd)** for $C_{26}H_{20}N_4NiO_4 \cdot 0.5C_2H_5OH \cdot 1.5H_2O$ (506.18): C 61.97 (61.69) H 4.18 (4.58) N 11.20 (11.07).

Synthesis of B. According to procedure described for **A**, complex **B** was obtained from salicylaldehyde (0.106 mL, 1 mmol) and potassium bicarbonate (0.200 g, 1 mmol) in ethanol (8 mL), copper(II) acetate monohydrate (0.100 g, 0.5 mmol) in ethanol (8 mL) and 3,3'-diaminobenzidine (0.107 g, 0.5 mmol) in ethanol (13 mL). Yield: 93 %. **IR** (KBr, ν/cm^{-1}): 3345, 3281 (w, ν_{NH2}), 3051, 3011 (w, $\nu_{C\text{-}Harom}$); 1609 (s, $\nu_{C=N}$); 1585, 1525 (s, $\nu_{C=Carom}$); 757 (m, $\delta_{C\text{-}Harom}$). **Anal. Found (calcd)** for $C_{26}H_{20}CuN_4O_2 \cdot 0.7H_2O$ (496.44): C 62.70 (62.90) H 4.12 (4.34) N 11.10 (11.29).

Synthesis of 1. A solution of nickel(II) acetate tetrahydrate (0.071 g, 0.25 mmol) in ethanol (5 mL) was added dropwise to a ethanolic solution of 3,5-di-*tert*-butylsalicylaldehyde (0.117 g, 0.5 mmol). This mixture was stirred at reflux and after 30 min a hot solution of **A** (0.120 g, 0.25 mmol) in dimethylformamide (10 mL) was added dropwise. A few drops of phosphoric acid were added and the mixture was left for 48 h at 120 ºC. The solution was filtered and the precipitate washed with dichloromethane and the desired crude product recovered as filtrate. The filtrate was evaporated in vacuum and the solid washed with *n*-hexane. The solid was redissolved in dichloromethane filtered and evaporated to give a redish brown product. Yield: 58 %. **IR** (KBr, ν/cm^{-1}): 3051 (w, $\nu_{C\text{-}Harom}$); 2950, 2903, 2885 (m, $\nu_{CH3\ and\ CH}$); 1610 (s, $\nu_{C=N}$); 1584, 1545 (s, $\nu_{C=Carom}$); 1358 (m, δ_{CH3}); 753 (w, $\delta_{C\text{-}Harom}$). **^{1}H NMR** (400 MHz, DMSO-d_6, 298 K) δ/ppm: 9.09 (s, 1H, H-C=N), 9.00 (s, 1H, H-C=N), 8.93 (s, 1H, H-C=N), 8.85 (s, 1H, H-C=N), 8.54 (s, 1H, Ar-H), 8.50 (s, 1H, Ar-H), 8.27 (d, *J* = 9.0 Hz, 1H, Ar-H), 8.24 (d, *J* = 8.6, 1H, Ar-H), 7.86 (d, *J* = 8.6, 1H, Ar-H), 7.81 (d, *J* = 9.0, 1H, Ar-H), 7,66-7,63 (m, 2H, Ar-H), 7.49 (s, 1H, Ar-H), 7.47 (s, 1H, Ar-H), 7.36 (s, 2H, Ar-H), 7.35-7.31 (m, 2H, Ar-H), 6.93-6.90 (m, 2H, Ar-H), 6.71-6.67 (m, 2H, Ar-H), 1.42 (s, 18H, $C(CH_3)_3$), 1.30 (s, 18H, $C(CH_3)_3$).**^{13}C RMN** (100 MHz, DMSO-d_6, 298 K) δ/ppm: 165.3, 165.2 (Ar-O), 163.3, 163.2 (Ar-O), 156.9 (C=N), 156.7 (C=N), 156.4 (C=N), 156.1 (C=N), 142.9 (C-N), 142.7 (C-N), 142.2 (C-N), 141.9 (C-N), 138.1 (C), 137.3 (C), 135.2, 135.1 (CH), 134.2 (CH), 129.7 (CH), 127.6 (CH), 126.3 (CH), 125.7 (CH), 120.3 (CH), 120.3 (C), 119.8, 119.7 (C), 116.2 (CH), 115.9 (CH), 115.3 (CH), 114.0 (CH), 113.8 (CH), 35.4 ($C(CH_3)_3$), 33.7

($C(CH_3)_3$), 31.1 (CH), 29.6 ($C(CH_3)_3$). **Anal. Found (calcd)** for $C_{56}H_{58}N_4Ni_2O_4 \cdot 0.7H_2O \cdot 0.25C_3H_7NO$ (999,36): C 68.32 (68.20) H 6.33 (6.17) N 5.82 (5.96).

Synthesis of 2. According to procedure described for **1**, complex **2** was obtained from copper(II) acetate monohydrate (0.05 g, 0.25 mmol) in ethanol (5 mL) , 3,5-di-*tert*-butylsalicylaldehyde (0.117 g, 0.5 mmol) in ethanol (5 mL) and **B** (0.121 g, 0.25 mmol) in dimethylformamide (10 mL). Yield: 42 %. **IR** (KBr, ν/cm^{-1}): 3005 (w, $\nu_{C\text{-}Harom}$); 2954, 2904, 2851 (m, $\nu_{CH3\ and\ CH}$); 1612 (s, $\nu_{C=N}$); 1583, 1524 (s, $\nu_{C=Carom}$); 1384 (m, δ_{CH3}); 756 (m, $\delta_{C\text{-}Harom}$). **HR-MS (ESI):** Calcd for $C_{56}H_{59}Cu_2N_4O_4$ $[M+H]^+$ m/z = 977.3123, found m/z = 977.3113. **Anal. Found (calcd)** for $C_{56}H_{59}Cu_2N_4O_4 \cdot 1.1H_2O \cdot 0.1C_3H_7NO$ (1008.13): C 67.31 (67.15) H 6.37 (6.21) N 5.56 (5.72).

Synthesis of 3. A mixture of 3,5-di-*tert*-butylsalicylaldehyde (0.234 g, 1 mmol) and 3,3'-diaminobenzidine (0.021 g, 0.1 mmol) in ethanol (13 mL) was stirred at reflux for 5 h. After 5 h, a solution of nickel(II) acetate tetrahydrate (0.057 g, 0.2 mmol) in ethanol (5 mL) was added dropwise and the mixture was left at reflux for 12 h. The crude product was filtered and washed with *n*-hexane. The solid was dissolved in chloroform, the solution was filtered and evaporated in vacuum to give a red solid as final product. Yield: 90 %. **IR** (KBr, ν/cm^{-1}): 3003 (w, $\nu_{C\text{-}Harom}$); 2954, 2905, 2868 (s, $\nu_{CH3\ and\ CH}$); 1617 (s, $\nu_{C=N}$); 1581, 1524 (s, $\nu_{C=Carom}$); 1385 (m, δ_{CH3}); 787 (m, $\delta_{C\text{-}Harom}$). **^{1}H NMR** (400 MHz, acetone-d_6, 298 K) δ/ppm: 8.89, 8.76 (s, 4H, H_1, H_5), 8.51 (s, 2H, H_6), 8.18, 7.76 (d, 4H, H_7, H_8), 7.48-7.40 (m, 8H, H_2, H_3, H_4), 1.50, 1.33 (s, 18H, *tert*-butil groups). **Anal. Found (calcd)** for $C_{72}H_{90}N_4Ni_2O_4 \cdot C_2H_6O$ (1237.58): C 71.41 (71.76) H 7.71 (7.80) N 4.88 (4.53).

Synthesis of 4. According to procedure described for **3**, complex **4** was obtained from 3,5-di-*tert*-butylsalicylaldehyde (0.234 g, 1 mmol) and 3,3'-diaminobenzidine (0.021 g, 0.1 mmol) in ethanol (13 mL) and copper(II) acetate monohydrate (0.040 g, 0.2 mmol) in ethanol (5 mL). Yield: 93 %. **IR** (KBr, ν/cm^{-1}): 3039 (w, $\nu_{C\text{-}Harom}$); 2997, 2955, 2905 (s, $\nu_{CH3\ and\ CH}$); 1615 (s, $\nu_{C=N}$); 1581, 1522 (s, $\nu_{C=Carom}$); 1357 (m, δ_{CH3}); 789 (m, $\delta_{C\text{-}Harom}$). **HR-MS (ESI):** Calcd for $C_{72}H_{91}Cu_2N_4O_4$ $[M+H]^+$ m/z = 1201.5627, found m/z = 1201.5626. **Anal. Found (calcd)** for $C_{72}H_{91}Cu_2N_4O_4$ (1202.60): C 71.63 (71.91) H 7.66 (7.54) N 4.60 (4.66).

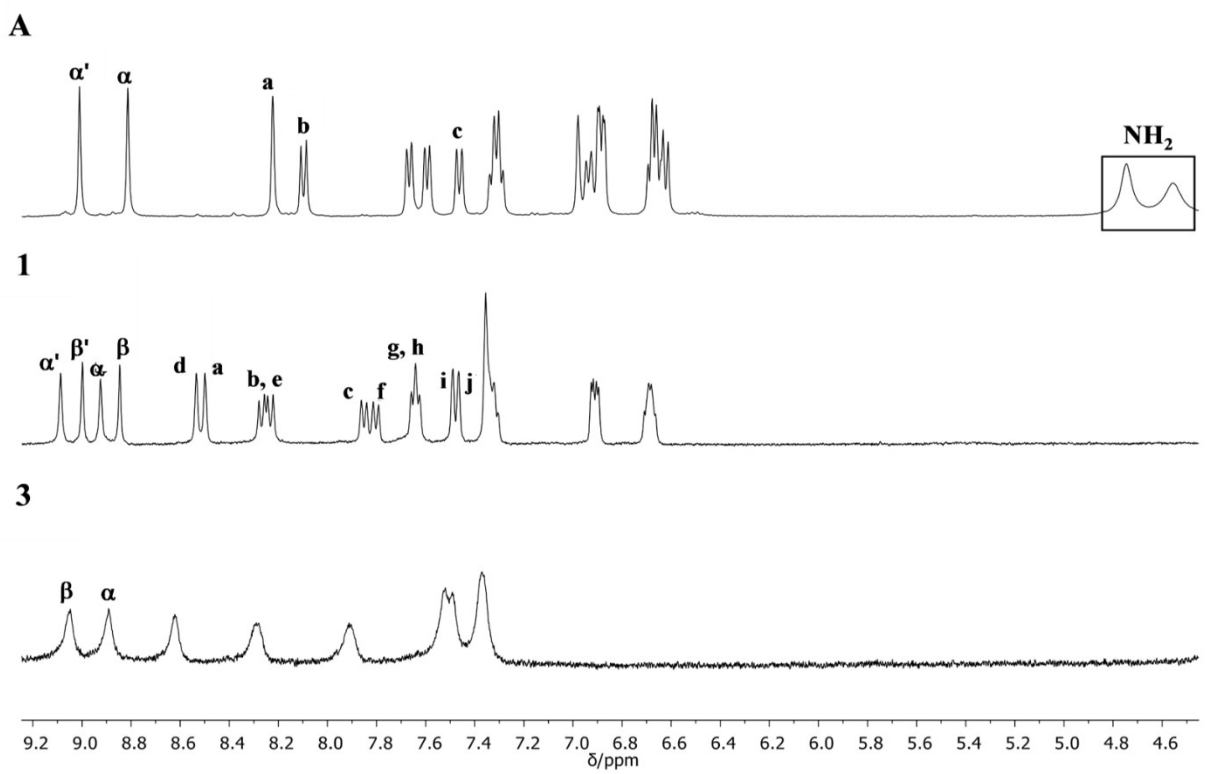


Figure S1. ^{1}H NMR spectra (DMSO-d_6) of complexes **A**, **1** and **3**.

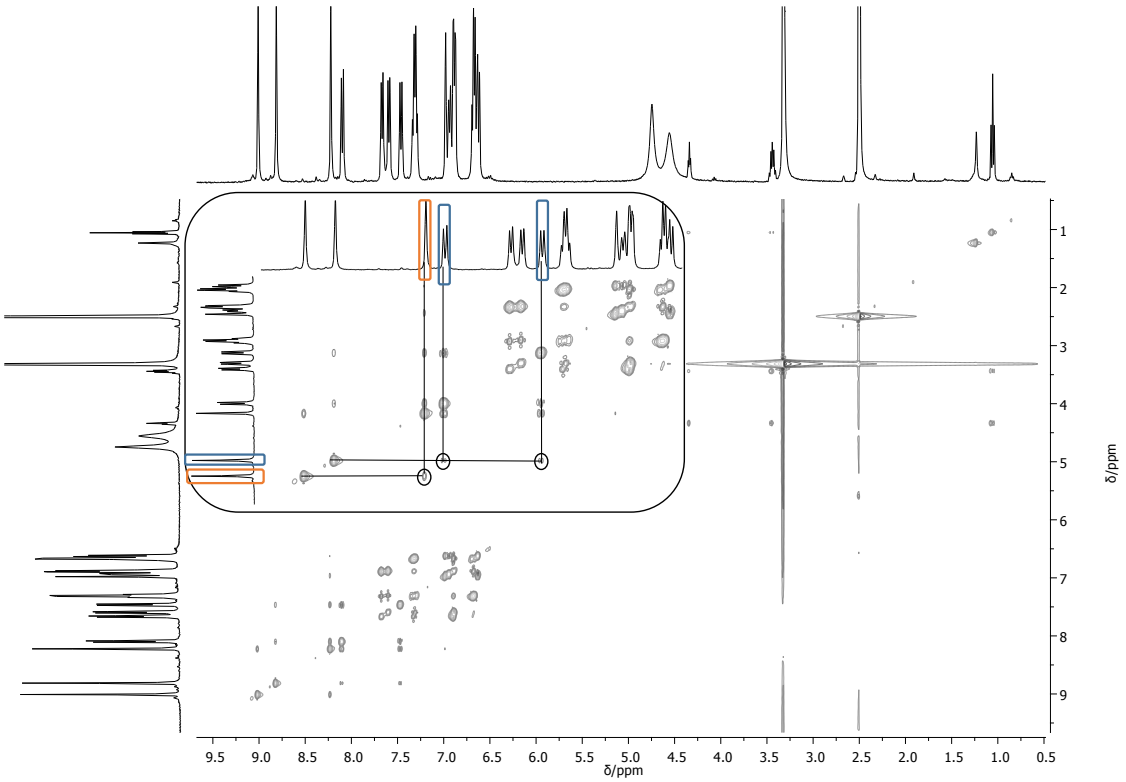


Figure S2. 2D TOCSY (d_6-DMSO) spectrum of complex **A**. Inset: Detailed correlation with the imine protons and DAB subunit protons.

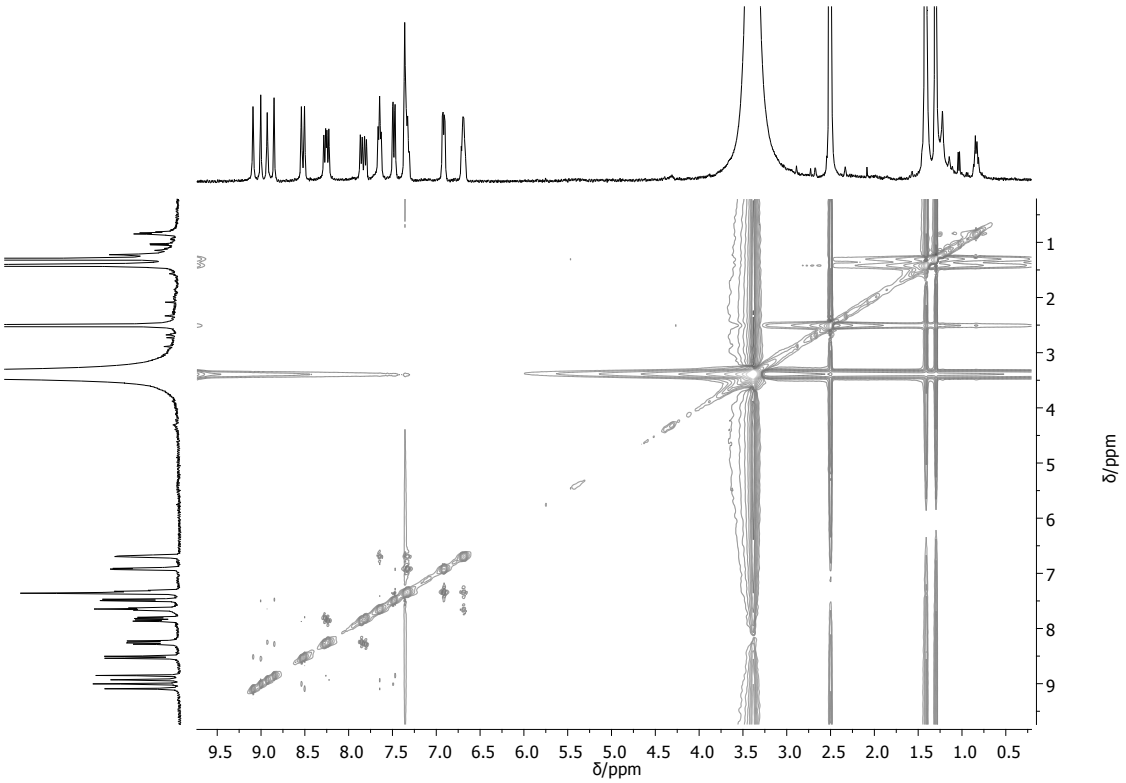


Figure S3. 2D TOCSY d_6-DMSO spectrum of complex **1**.

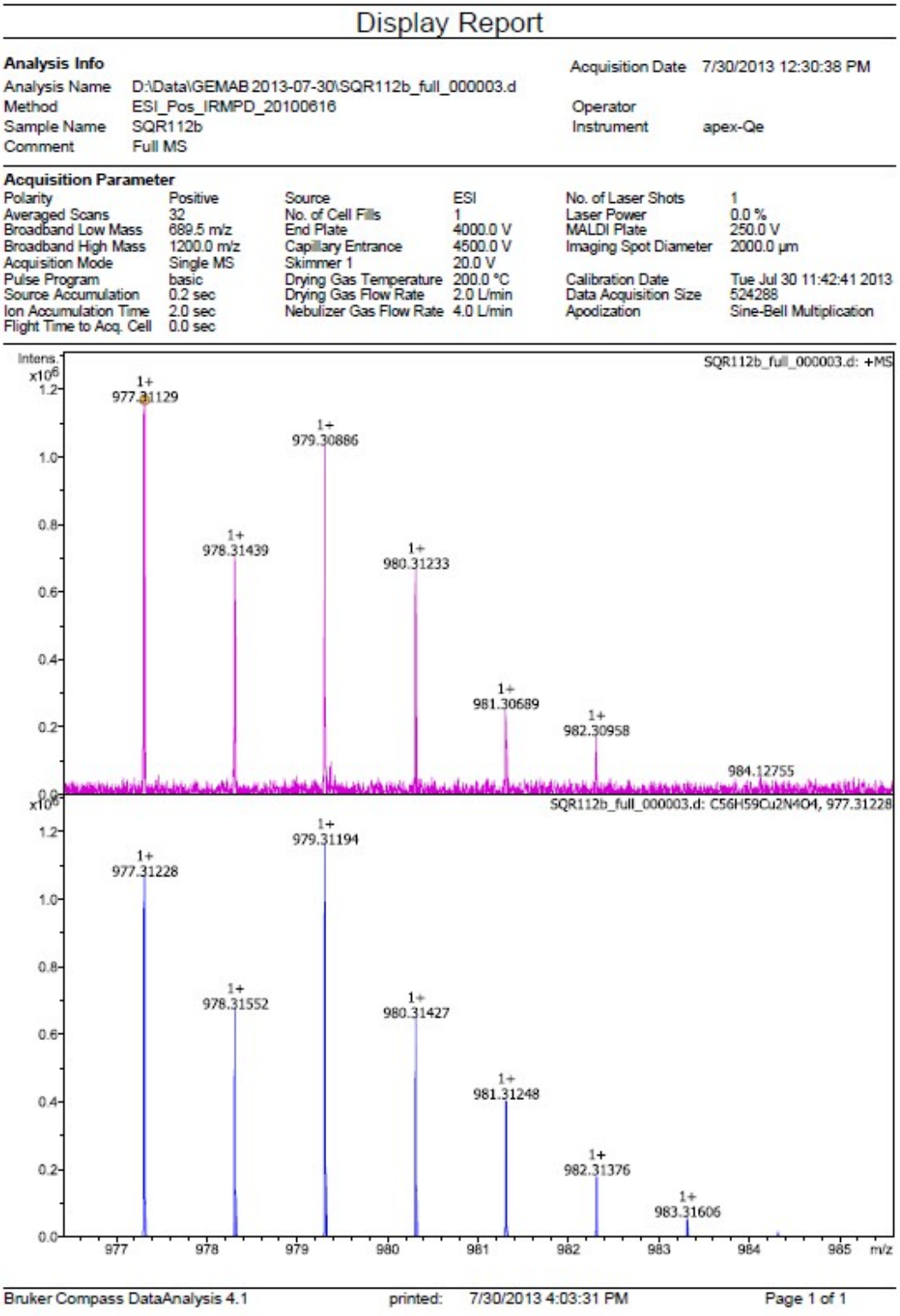


Figure S4. HR-ESI/MS spectrum for complex **2** predicted (bottom) experimental (top).

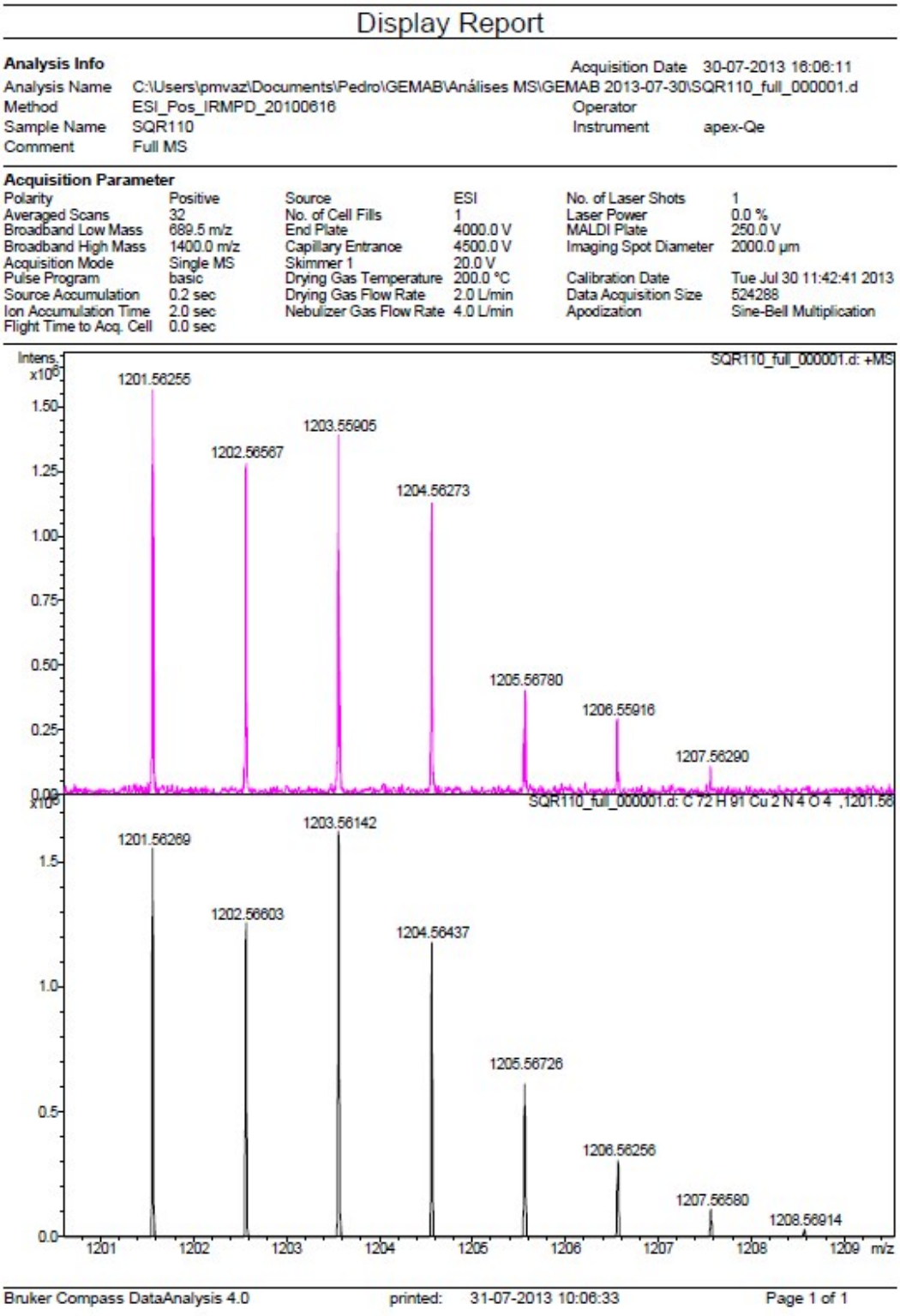


Figure S5. HR-ESI/MS spectrum for complex **4** predicted (bottom) experimental (top).

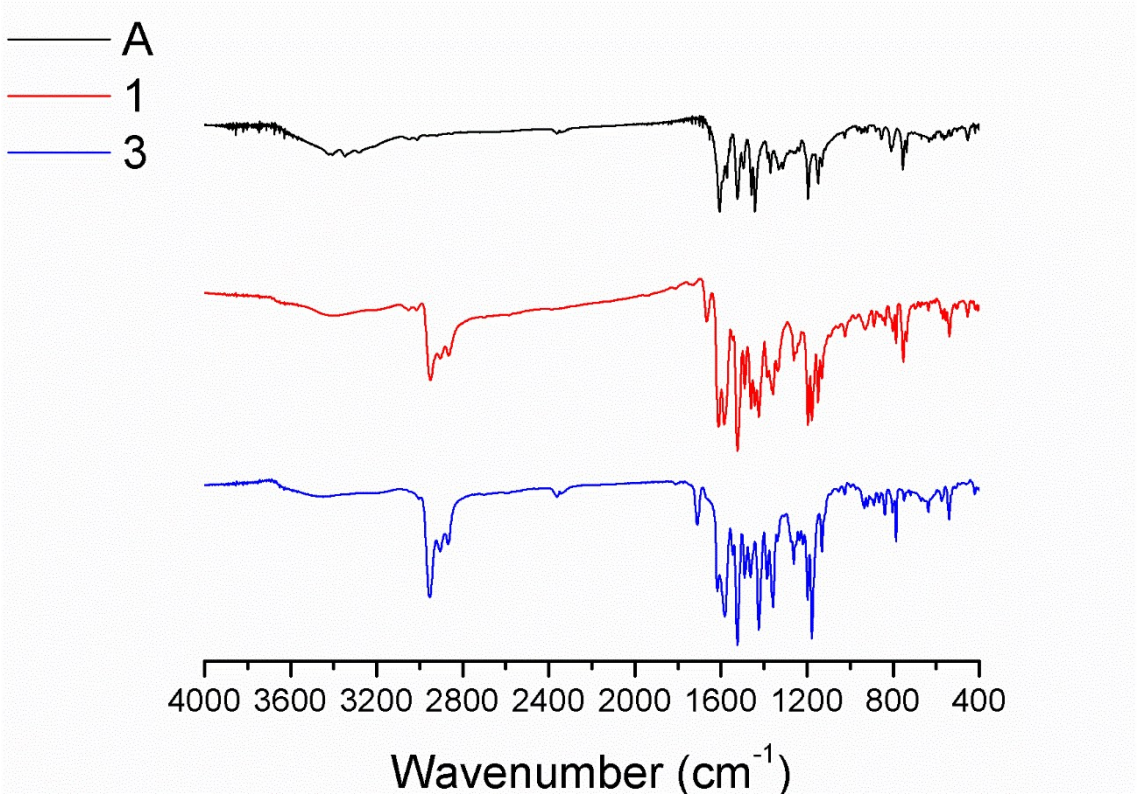


Figure S6. FTIR spectra of Ni(II) complexes.

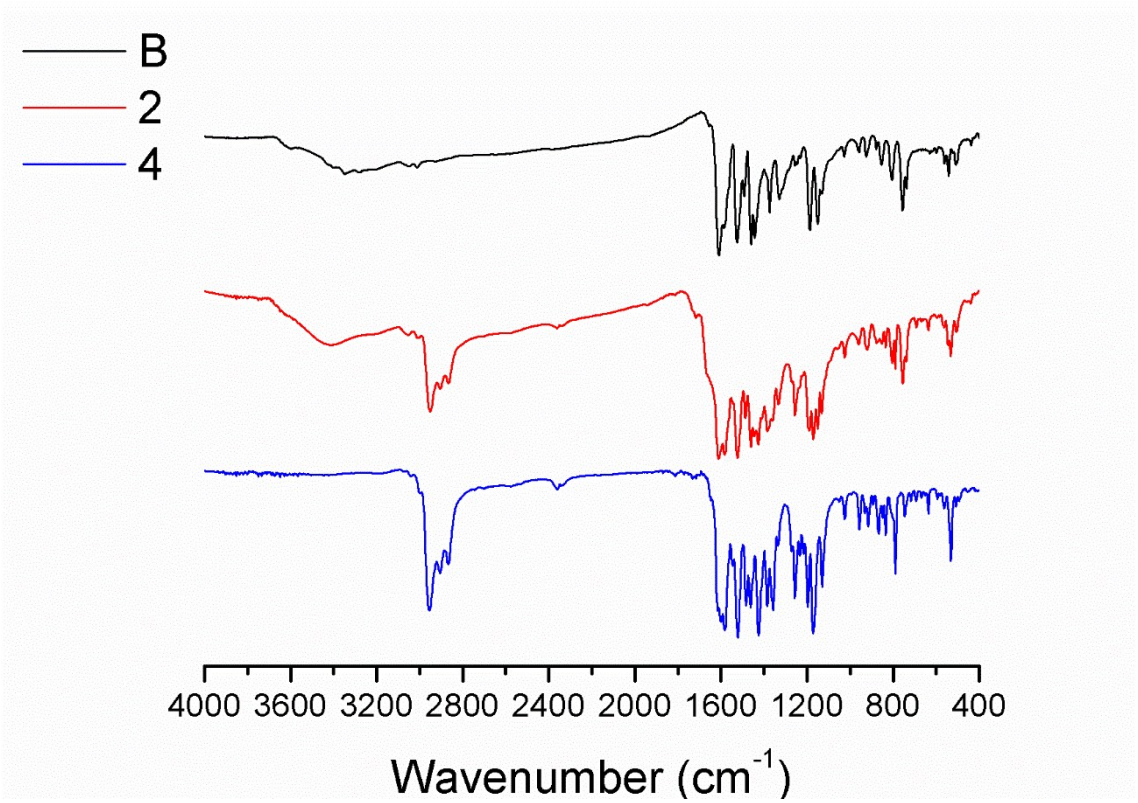


Figure S7. FTIR spectra of Cu(II) complexes.

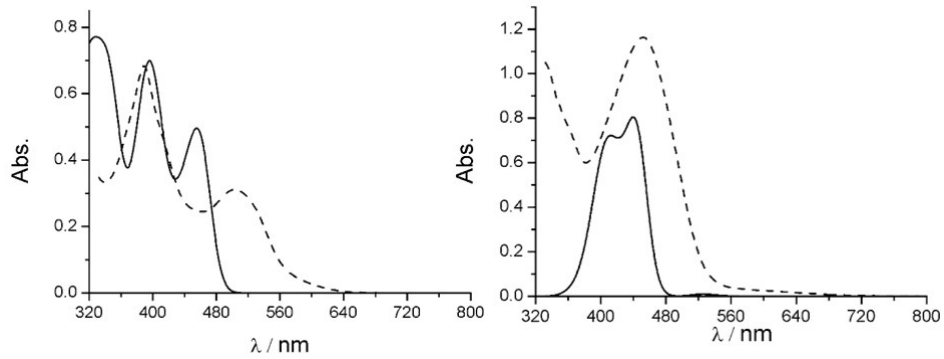


Figure S8. UV-vis spectra of **1** (10^{-5} M, left) and **2** (10^{-6} M, right): in dichloromethane (dashed line), and TD-DFT (solid line, gas-phase).

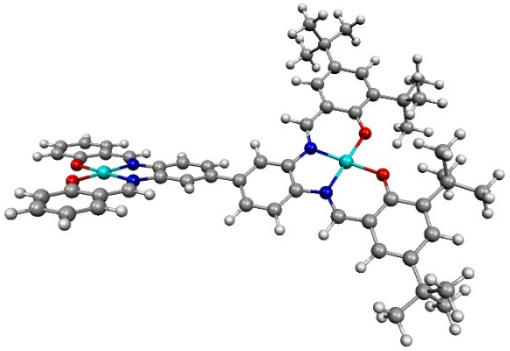


Figure S9. DFT optimised structure of complex **1.**

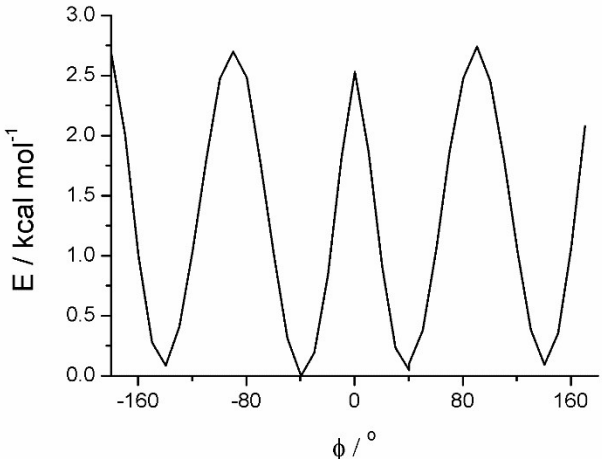


Figure S10. Potential energy scan (kcal mol^{-1}) for varying the dihedral angle, ϕ (°), of the biphenyl bridge in the DAB subunit. Energy maxima correspond to orthogonal arrangements of the ligand and minima to ϕ ~40 °.

Table S1. Excited states, composition, energy, wavelength and oscillator strength from TD-DFT calculations for complex **1**. Corresponding experimental peak wavelengths presented accordingly.

No.	Composition	Energy (eV)	λ (nm)	λ_{exp} (nm)	Oscillator strength
1	H-7 → L+4 (63 %); H-10 → L+4 (35 %);	2.04	608	~600	0.0001
2	H-12 → L+5 (85 %)	2.08	596		0.0001
3	H → L (60 %); H → L+1 (25 %)	2.68	462	504	0.3174
4	H-1 → L (58 %); H-2 → L (21 %)	2.77	444		0.1647
5	H → L+2 (19 %); H-1 → L+1 (18 %); H → L+1 (14 %)	3.08	402	389	0.3456
6	H-3 → L (25 %); H-2 → L+1 (20 %)	3.20	387		0.2699
7	H-4 → L (74 %)	3.57	347	-	0.3543
8	H-5 → L+1 (39 %); H-6 → L (30 %)	3.94	315		0.2284

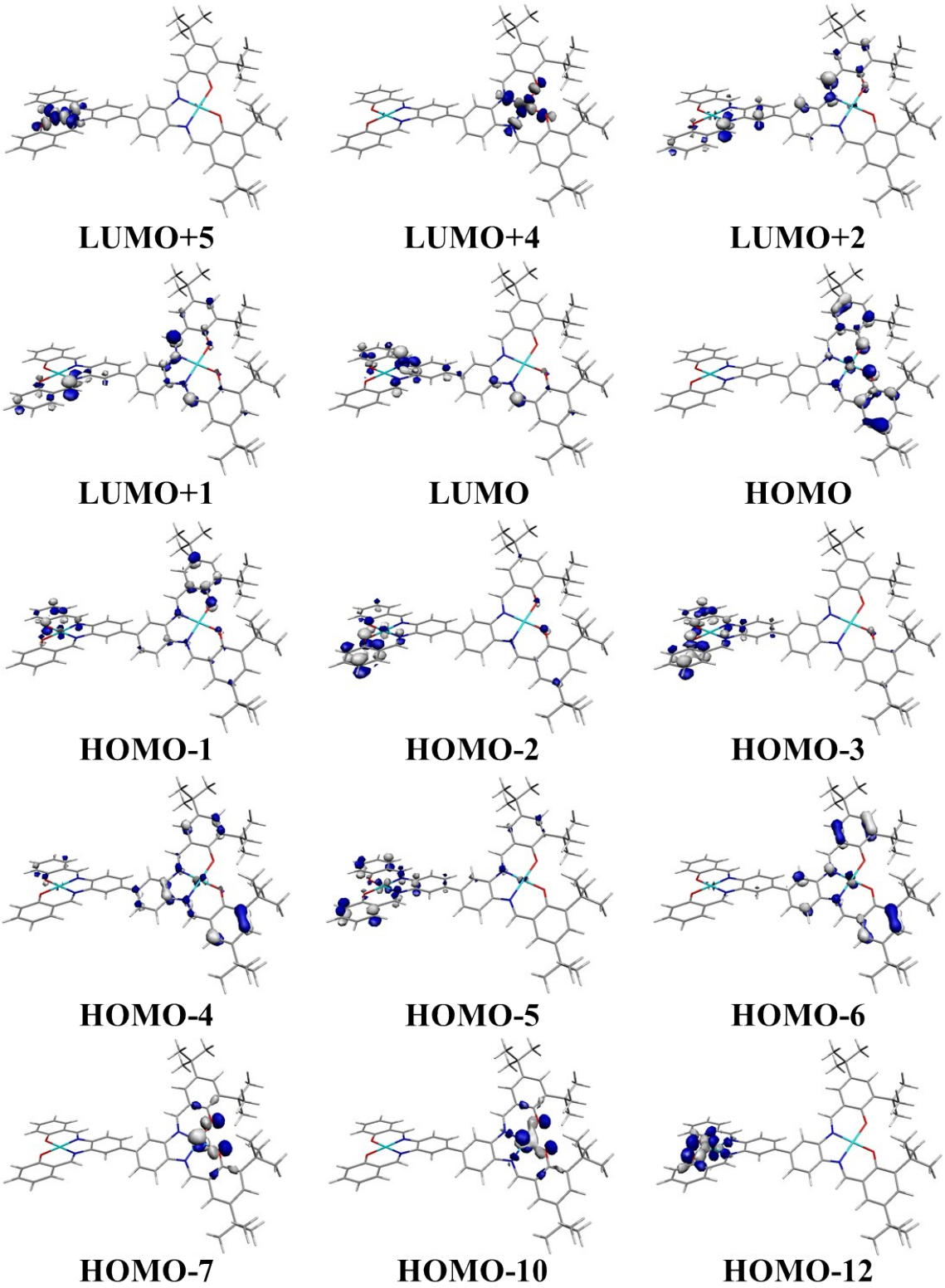


Figure S11. Molecular orbitals of complex **1**.

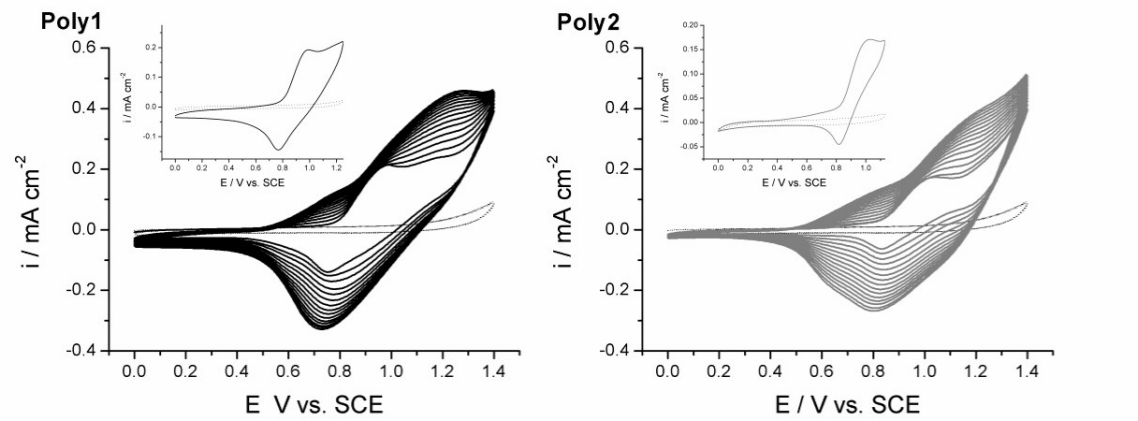


Figure S12. Cyclic voltammograms collected during the potentiodynamic growth of **Poly1** and **Poly2** films on Pt from 1 mM dichloromethane solutions of **1** and **2** using 0.1 M $TBAPF_6$ as supporting electrolyte (dotted line), ν = 50 mV s^{-1}, 15 cycles.

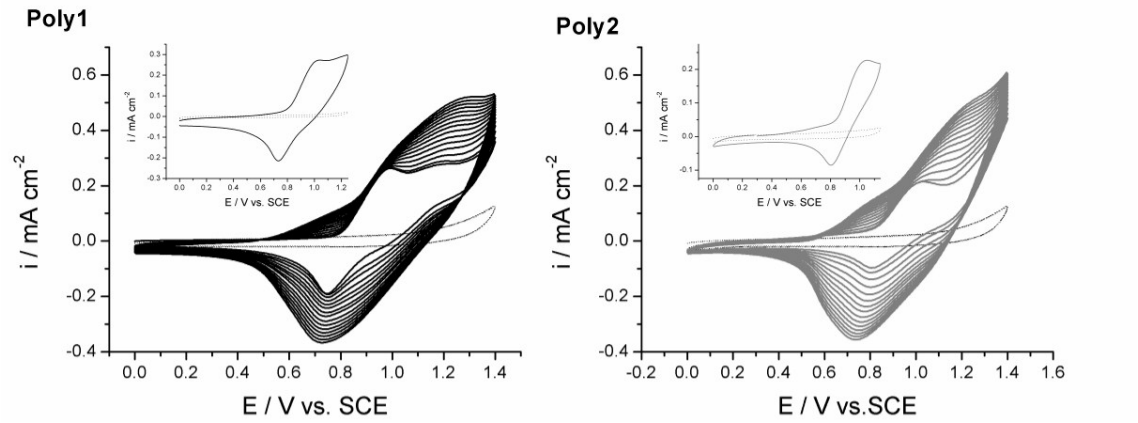
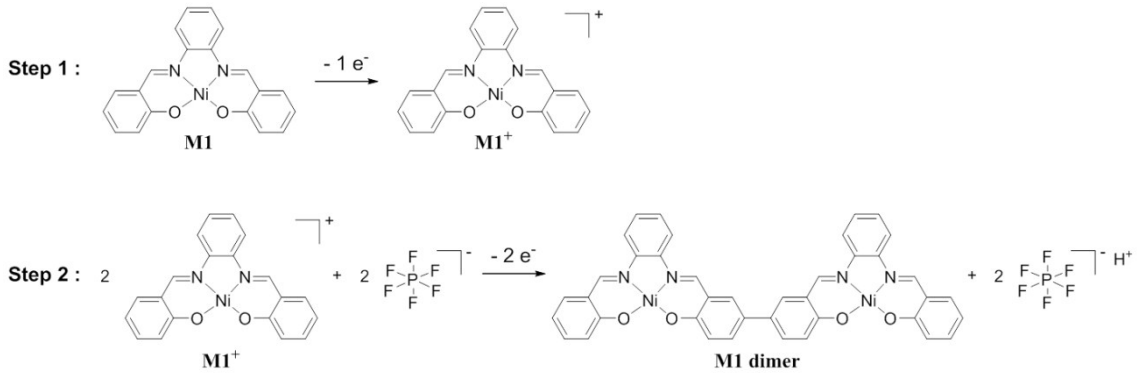


Figure S13. Cyclic voltammograms collected during the potentiodynamic growth of **Poly1** and **Poly2** films on Pt from 1 mM dichloromethane solutions of **1** and **2** using 0.1 M TBAPF6 as supporting electrolyte (dotted line), ν = 100 mV s^{-1}, 15 cycles.



Scheme S1. Two step model dimerization reaction: oxidation of the monomer (Step 1) and formation the new C-C bond with release of protons in the presence of $[PF_6]^-$ (Step 2).

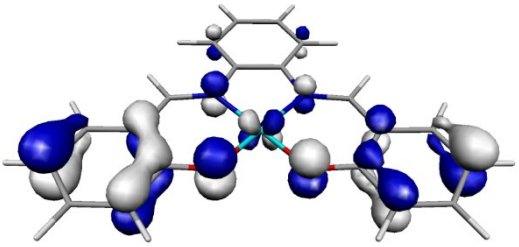


Figure S14. Representation of the SOMO of the **M1**$^{+}$ model.

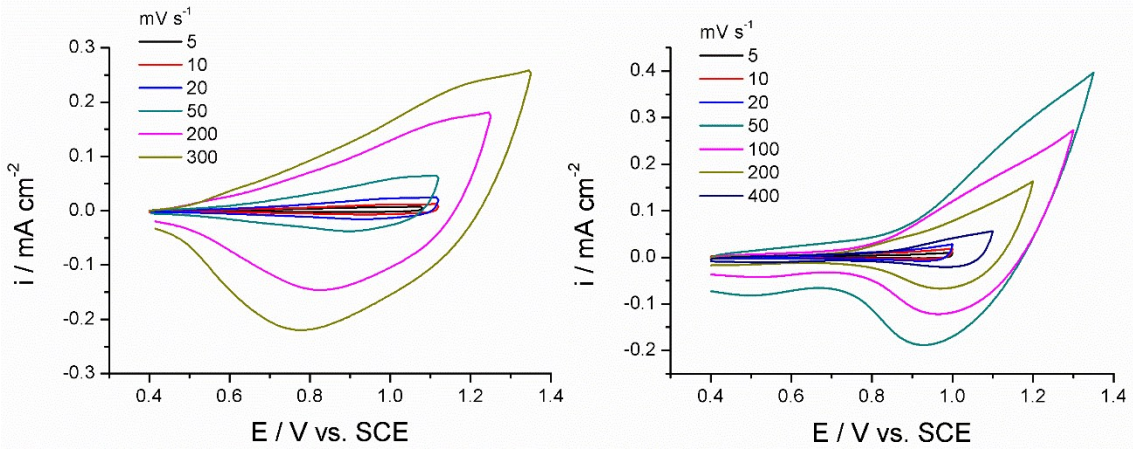


Figure S15. Redox behaviour of **Poly1** (left) and **Poly2** (right) at different scan rates both polymerised at 200 mV s^{-1}.

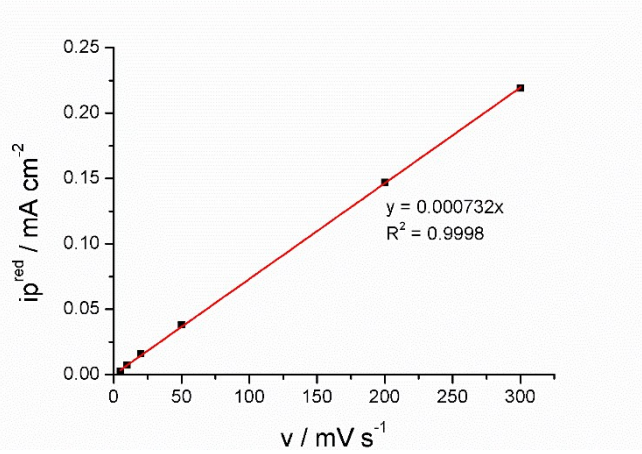


Figure S16. Relationship between reduction peak current and scan rate for **Poly1** grown at 200 mV s^{-1}.

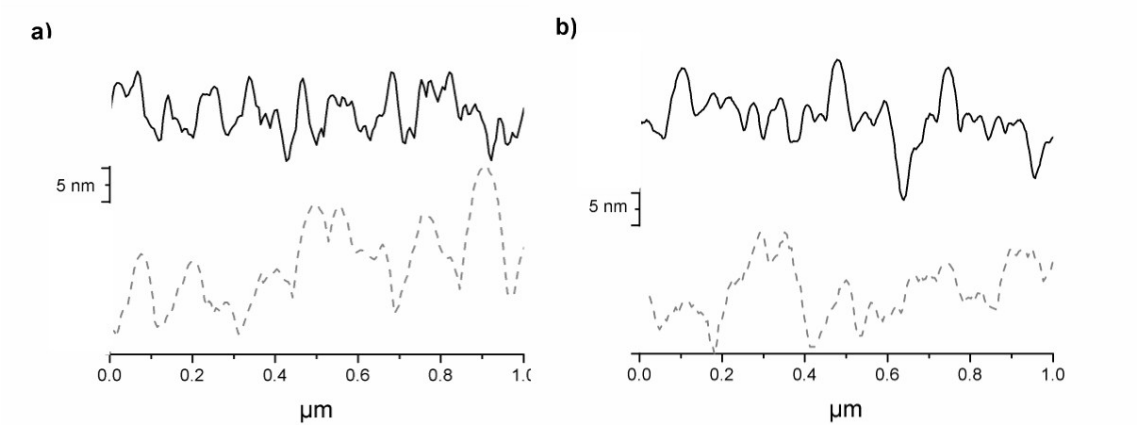


Figure S17. Topographic profiles of **Poly1** (black line) and **Poly2** (dashed line) grown at a) 50 and b) 100 mV s^{-1}.

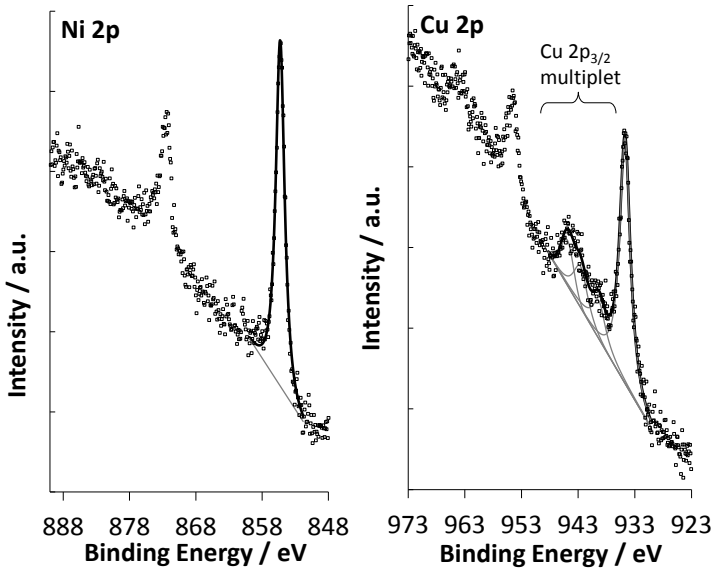


Figure S18. XPS spectra for Ni 2p and Cu 2p in Poly1 (left) and Poly2 (right).