

## Supporting Information for:

### An Original Redox-Responsive Ligand Based on a $\pi$ -Extended TTF Framework

Stefan Dolder,<sup>a</sup> Shi-Xia Liu,<sup>\*,a</sup> Franck Le Derf,<sup>b</sup> Marc Sallé,<sup>\*,b</sup> Antonia Neels,<sup>c</sup> Silvio Decurtins<sup>a</sup>

<sup>a</sup> *Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland.*

<sup>b</sup> *Laboratoire de Chimie, Ingénierie Moléculaire et Matériaux d'Angers, CNRS UMR 6200, Université d'Angers, 2 Bd Lavoisier, 49045 Angers, France.*

<sup>c</sup> *Institut de Microtechnique, Université de Neuchâtel, Rue Jaquet Droz 1, CH-2002 Neuchâtel, Switzerland.*

*Email address: liu@iac.unibe.ch; marc.salle@univ-angers.fr*

## Table of Contents

Experimental section	S2
Procedures for preparation of compounds <b>1</b> , <b>3</b> and <b>4</b>	S3
<sup>1</sup> H and <sup>13</sup> C NMR Spectra of compounds <b>1</b> , <b>3</b> and <b>4</b>	S4-S6
<sup>1</sup> H NMR titration measurements	S7
Crystal packing of Ni <sup>2+</sup> complex with <b>1</b>	S8

## Experimental section

### Materials

The compounds 4,5-ethylenedithio-1,3-dithiole-2-thione, 3-(4,5-ethylenedithio-[1,3]-dithiole-2-ylidene)-3H-isobenzofuran-1-one **2**<sup>7c</sup> and 4,5-bis(cyanoethylthio)-1,3-dithiole-2-thione<sup>8</sup> were prepared according to the literature procedures. All other chemicals and solvents were purchased from commercial sources and were used without further purification.

### Physical measurements

All <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured at 300 and 75.5 MHz, respectively. Chemical shifts  $\delta$  were calibrated against TMS as an internal standard. FT-IR data were collected on a Perkin-Elmer Spectrum One spectrometer. UV-vis spectra were recorded on a Perkin-Elmer Lambda 10 spectrometer. Elemental analyses were performed on a Carlo Erba EA 1110 CHNS apparatus. Cyclic voltammetric measurements were conducted on a EG&G PAR 273A in a three-electrode single-compartment cell equipped with platinum electrodes (diameter 1 mm), a silver wire counter electrode and a Ag/AgCl reference electrode. Cyclic voltammetry was performed under inert atmosphere (Ar-bubbling) at room temperature in CH<sub>2</sub>Cl<sub>2</sub>/acetonitrile (1:1 v/v) solutions containing 0.1 M *n*-Bu<sub>4</sub>N(PF<sub>6</sub>). Potentials were calibrated against ferrocene. Mass spectra were recorded on a Walters Micromass AutospecQ for EI and on a FTMS 4.7T BioAPEX II for MALDI ionisation method.

#### Preparation of **4**

4,5-bis(cyanoethylthio)-1,3-dithiole-2-thione (0.46 g, 1.5 mmol) and phthalic anhydride (0.15 g, 1 mmol) were suspended in 25 ml of dry toluene under N<sub>2</sub>. Then P(OMe)<sub>3</sub> (2.4 ml, 20 mmol) was added and the yellow suspension was refluxed for 4 h at 120 °C. The solvent was evaporated by distillation. Purification of the brownish oily residue by column chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub>/EtOAc (v/v 5:1) yielded **4** as an orange-yellowish solid. Yield 0.20 g (49%). Mp 150-152 °C. Anal. Calc. for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>: C, 50.47; H, 2.99; N, 6.92. Found: C, 50.10; H, 2.85; N, 6.85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.78 (t, J = 7.0 Hz, 4H), 3.14 (t, J = 7.0 Hz, 4H), 7.46 (m, 2H), 7.72 (t, J = 7.5 Hz, 1H), 7.87 (d, J = 7.92 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 18.97, 19.07, 31.06, 31.36, 117.20, 117.31, 121.08, 122.97, 125.53, 126.29, 128.20, 134.74, 135.90, 165.10. Selected IR data (cm<sup>-1</sup>, KBr pellet): 2956, 2250, 1777, 1605, 1494, 1473, 1457, 1423, 1417, 1405, 1347, 1335, 1296, 1263, 1110, 995, 954, 898, 890, 866, 769, 719, 688, 604, 483. Mass spectrum (EI) m/z: 404(**4**<sup>+</sup>).

#### Preparation of **3**

Compounds **2** (0.16 g, 0.5 mmol) and 4,5-bis(cyanoethylthio)-1,3-dithiole-2-thione (0.22 g, 0.7 mmol) were refluxed at 130 °C under N<sub>2</sub> in 6 ml of P(OEt)<sub>3</sub> for 2 h. Then additional 4,5-bis(cyanoethylthio)-1,3-dithiole-2-thione (0.20 g, 0.6 mmol) was added and the reaction mixture was refluxed for another 3 h. After cooling to r.t., the orange precipitate was filtered and washed with hexane and MeOH. Purification of the orange solid by column chromatography eluting with a gradient of 0-15% EtOAc in CH<sub>2</sub>Cl<sub>2</sub> yielded compound **3** as an orange-brownish solid. Yield 0.08 g (27%). Mp 195 °C dec. Anal. Calc. for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub>OS<sub>8</sub>: C, 45.49; H, 2.78; N, 4.82. Found: C, 45.20; H, 3.14; N, 5.26%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 2.76 (t, J = 7.0 Hz, 2H), 2.77 (t, J = 7.0 Hz, 2H), 3.12 (t, J = 7.0 Hz, 2H), 3.14 (t, J = 7.0 Hz, 2H), 3.35 (s, 4H), 7.40 (broad s, 4H). <sup>13</sup>C NMR (THF-d<sub>8</sub>) δ 19.24, 19.30, 30.50, 30.59, 30.82, 112.42, 113.71, 118.60, 122.23, 122.29, 126.83, 128.92, 129.15, 129.79, 131.87, 131.99, 140.10, 140.64. Selected IR data (cm<sup>-1</sup>, KBr pellet): 3431, 2925, 2855, 2249, 1623, 1595, 1468, 1310, 1109, 1078, 743, 597, 478. Mass spectrum (EI) m/z: 580 (**3**<sup>+</sup>).

Following the same procedure as mentioned above, by using compounds **4** and 4,5-ethylenedithio-1,3-dithiole-2-thione, compound **3** was obtained in 25% yield.

#### Preparation of **1**

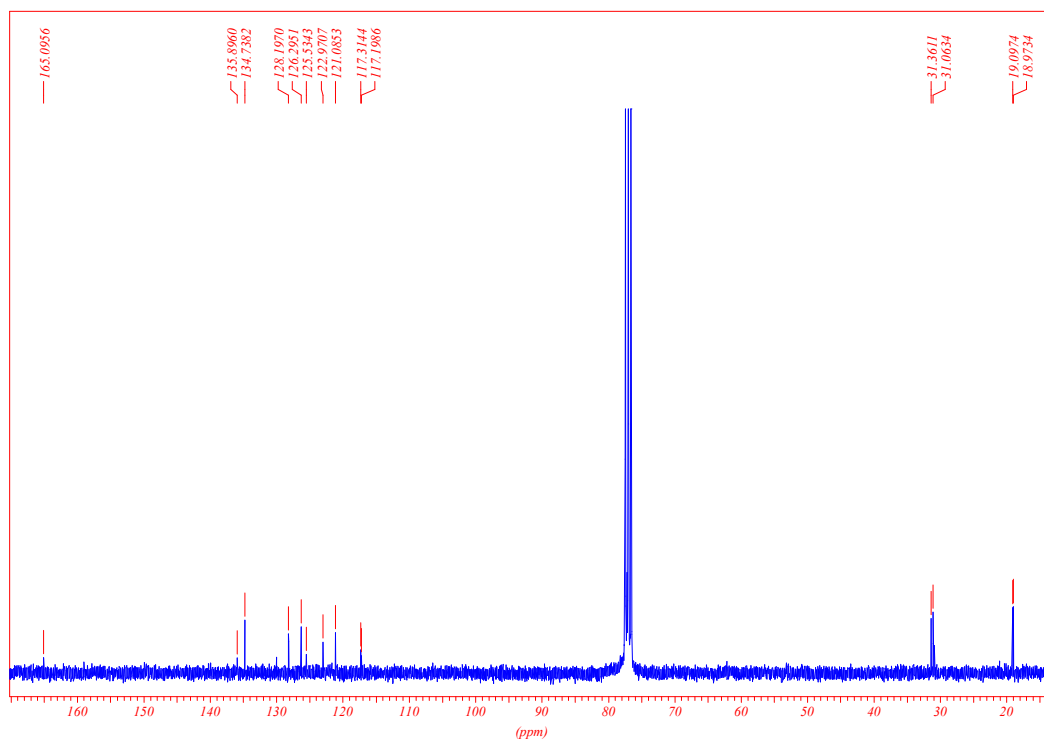
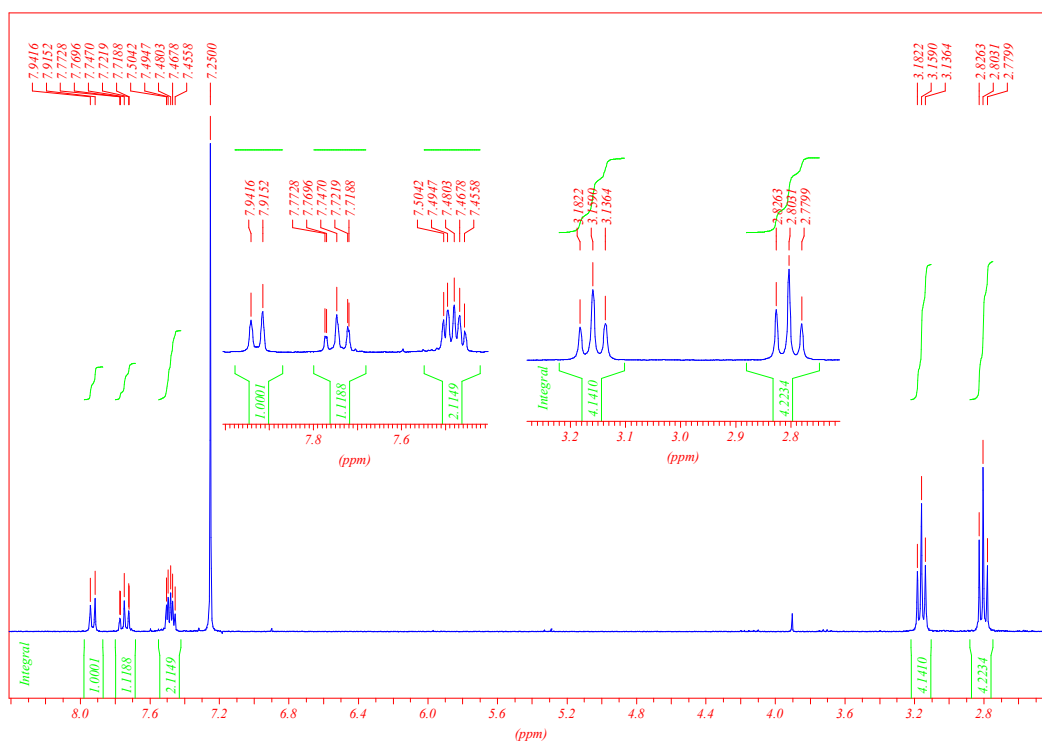
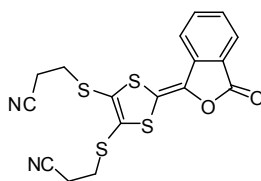
Compound **3** (0.20 g, 0.4 mmol) was suspended in 20 ml of dry EtOH under N<sub>2</sub>. Upon the addition of 1 ml of NaOEt/EtOH solution (~2.4 M), the mixture was stirred for 45 min. at 50 °C. To the deep red solution 2-picolynechloride hydrochloride (0.17 g, 1.1 mmol) was added and the mixture stirred overnight. The suspension was extracted with CH<sub>2</sub>Cl<sub>2</sub> and water. The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub> and the filtrate was evaporated under reduced pressure. Purification of the brown oil by column chromatography eluting with a gradient of 30-60% of EtOAc in CH<sub>2</sub>Cl<sub>2</sub> yielded compound **1** as an orange-brown solid. Yield 0.16 g (67%). Crystals were grown by evaporation of a CH<sub>2</sub>Cl<sub>2</sub> solution. Mp 169-171 °C. Anal. Calc. for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>OS<sub>8</sub>: C, 51.19; H, 3.07; N, 4.26. Found: C, 50.82; H, 3.16; N, 4.06%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 3.35 (s, 4H), 4.05 (s, 2H), 4.09 (s, 2H), 7.15 (m, 2H), 7.27 (m, 3H), 7.36 (m, 3H), 7.61 (m, 2H), 8.52 (m, 2H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 30.22, 30.29, 42.39, 42.52, 112.14, 113.32, 121.41, 121.65, 122.74, 123.60, 123.66, 127.53, 128.06, 128.14, 129.80, 131.14, 131.33, 136.97, 137.00, 139.41, 139.77, 150.02, 157.02, 157.04. Selected IR data (cm<sup>-1</sup>, KBr pellet): 3434, 2923, 2853, 1728, 1618, 1590, 1567, 1467, 1434, 1309, 1283, 1210, 1109, 1075, 993, 743, 596, 477. Mass spectrum (MALDI) m/z: 656 (**1**<sup>+</sup>).

#### Preparation of [Ni(**1**)Cl<sub>2</sub>] · MeOH · 0.5 CH<sub>2</sub>Cl<sub>2</sub>

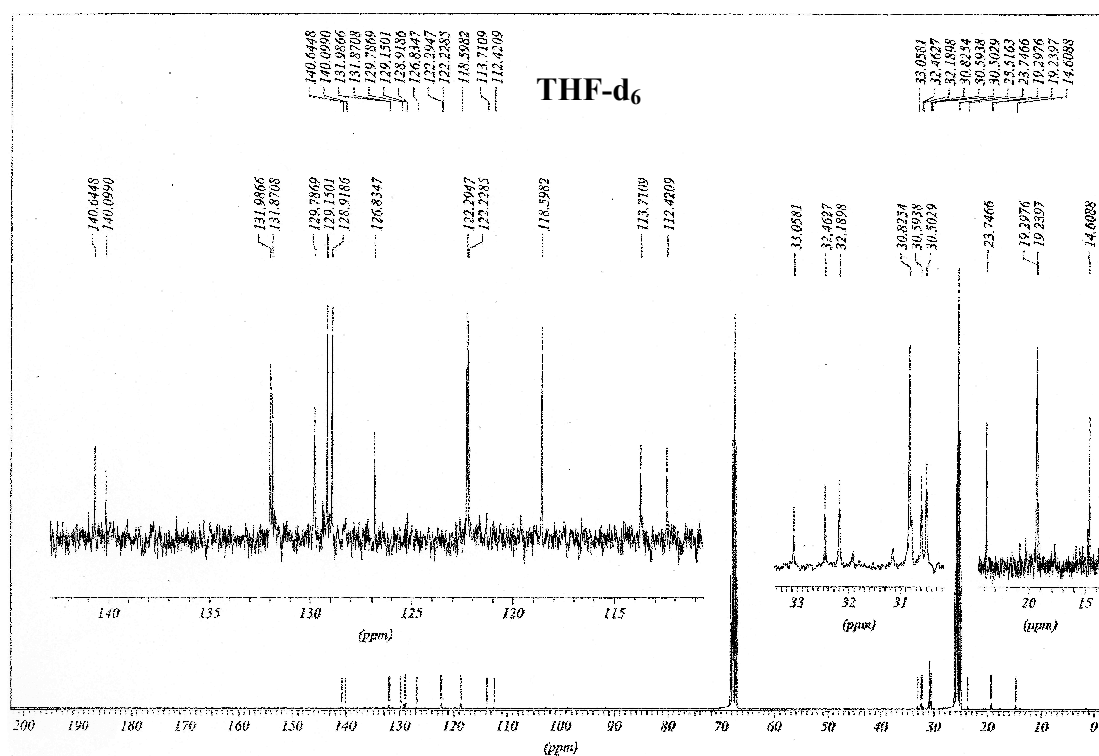
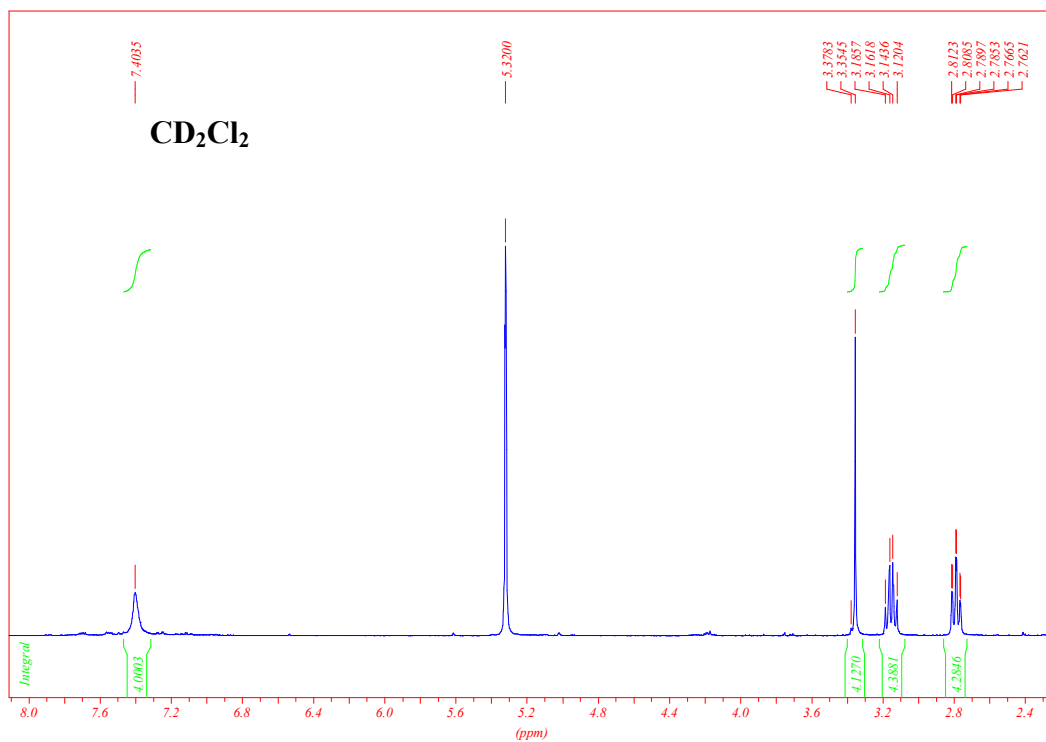
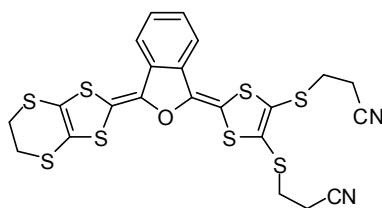
Orange crystals of [Ni(**1**)Cl<sub>2</sub>] · MeOH · 0.5 CH<sub>2</sub>Cl<sub>2</sub> were obtained by layer diffusion. 5 ml of a 2 mM clear solution of **1** were successively superposed by layers of 1 ml of pure CH<sub>2</sub>Cl<sub>2</sub>, 1 ml of pure MeOH and 5 ml of a 3 mM solution of NiCl<sub>2</sub> · 6H<sub>2</sub>O in MeOH. Anal. Calc. for C<sub>28</sub>H<sub>20</sub>N<sub>2</sub>NiOS<sub>8</sub> · CH<sub>2</sub>Cl<sub>2</sub> · MeOH: C, 39.88; H, 2.90; N, 3.10. Found: C, 40.10; H, 2.71; N,

3.08%. TGA shows an overall weight loss of 12.81% (calc. for one molecule of MeOH and CH<sub>2</sub>Cl<sub>2</sub>: 12.95%).

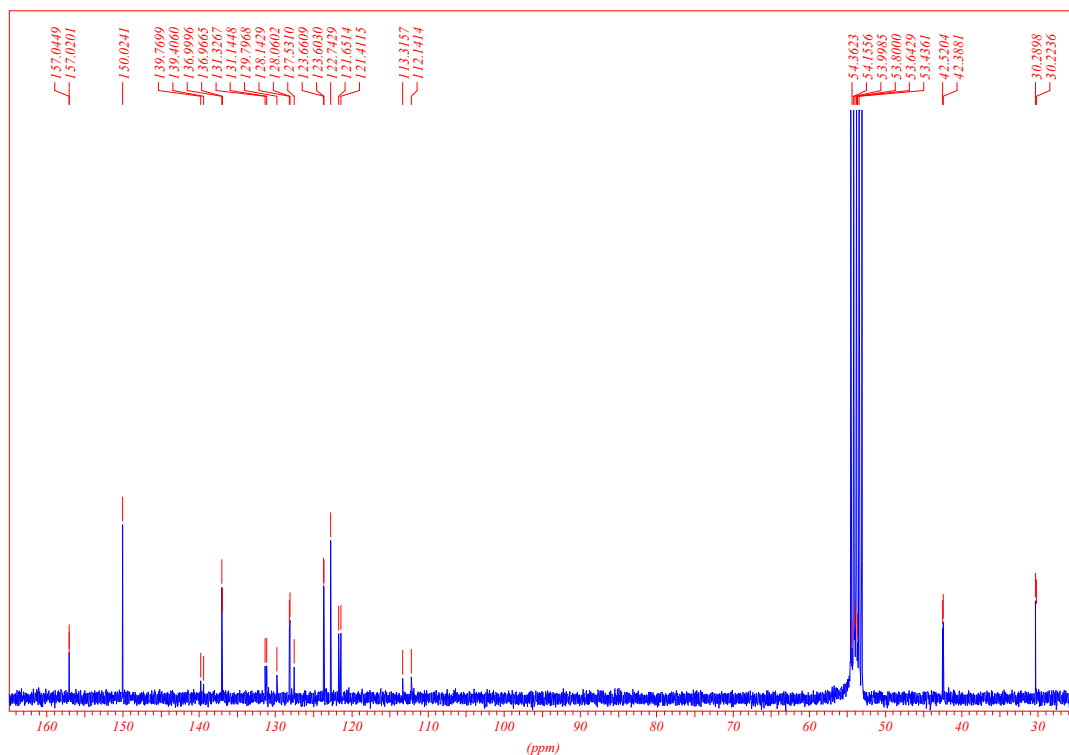
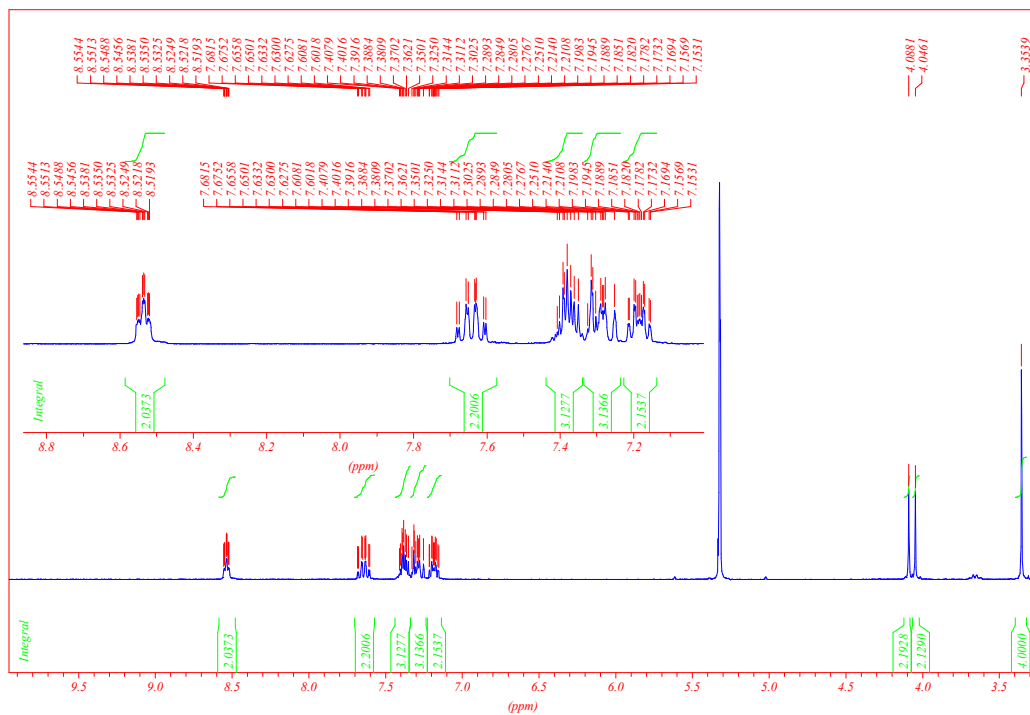
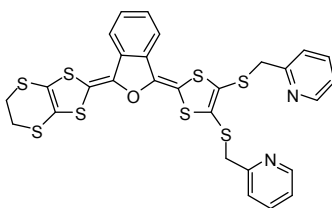
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of 4 in CDCl<sub>3</sub>



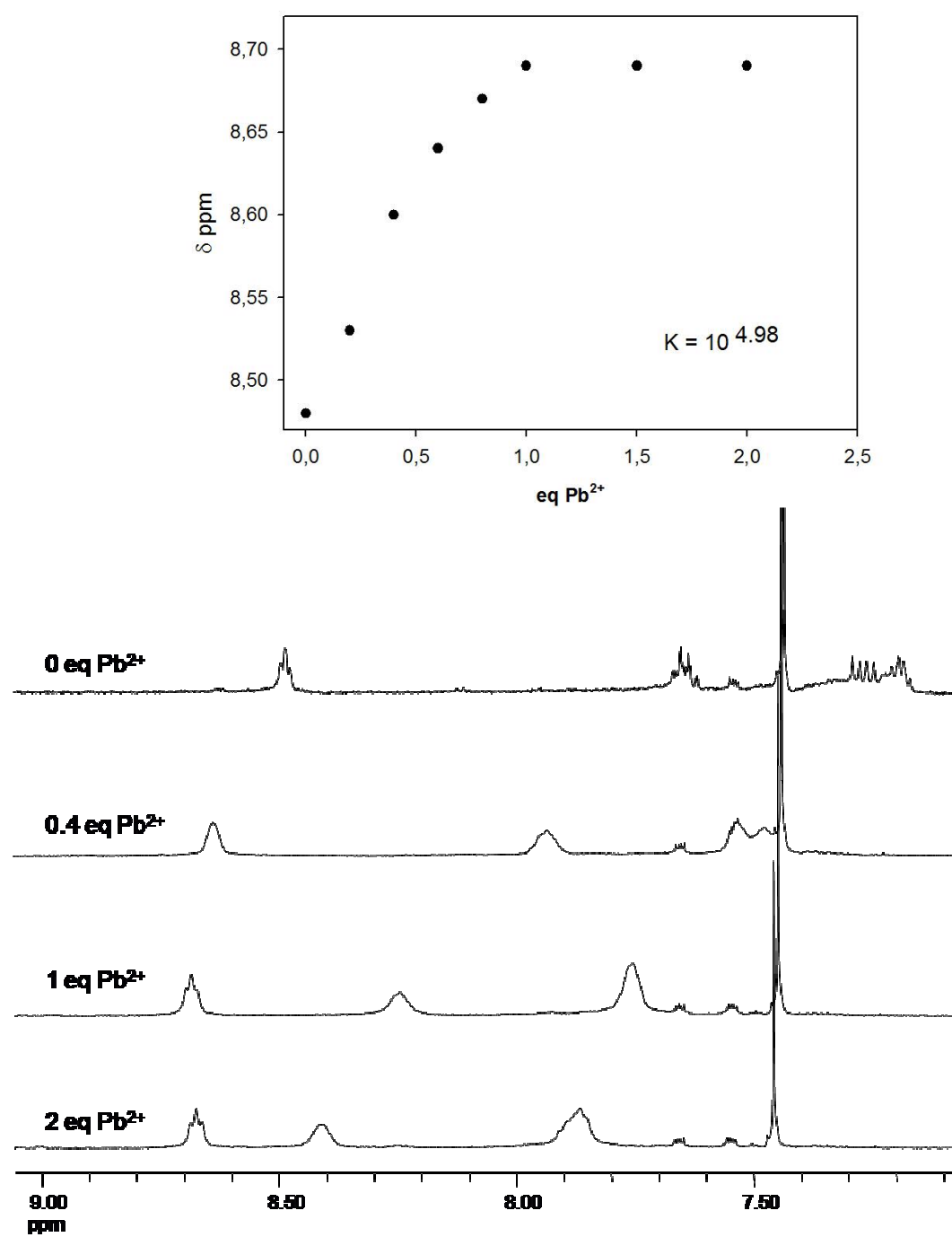
# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3**



# <sup>1</sup>H and <sup>13</sup>C NMR Spectra of 1 in CD<sub>2</sub>Cl<sub>2</sub>



$^1\text{H}$  NMR titration of **1** with  $\text{Pb}^{2+} (\text{ClO}_4^-)_2$  ( $[\text{L}] = 0.0122 \text{ M}$ ;  $\text{CDCl}_3 / \text{CD}_3\text{CN}$  1:1)



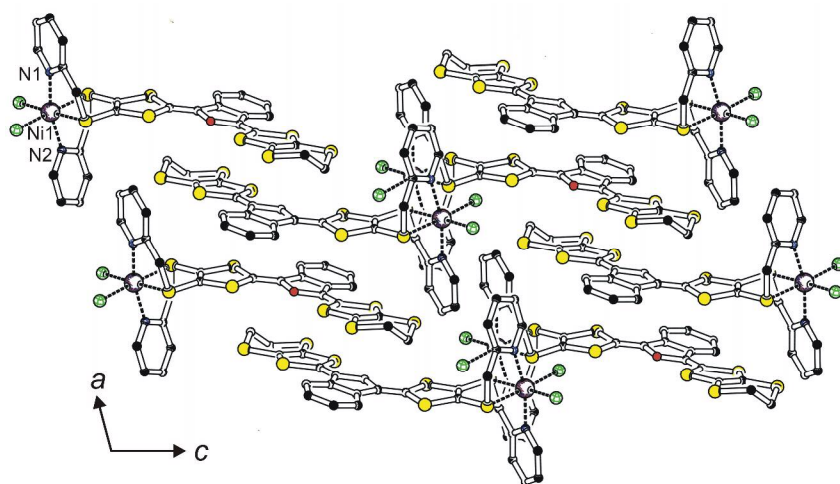


Figure S1. *ac* Projection of the crystal structure of  $[\text{Ni}(\mathbf{1})\text{Cl}_2]\cdot\text{CH}_3\text{OH}\cdot(\text{CH}_2\text{Cl}_2)_{0.5}$ . Stacking along the *a*-axis forms alternating organic and inorganic layers. Hydrogen atoms and solvent molecules are omitted for clarity.