

Supporting information for:

Compact Hydrogen-Bonded Self-Assembly of

Ni(II)-Salen Derivative Investigated Using Scanning

Tunneling Microscopy

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Experimental procedures

General: 4-(3-hydroformyl-4-hydroxy-5-*tert*-butylphenyl)bezoic acid was synthesized according to reported procedure.^{S1} Starting materials were purchased from Aldrich and all manipulations were performed using materials as received.

Physical measurements. ¹H NMR spectra were recorded on a Bruker 300 MHz. All chemical shifts are reported in ppm and are referenced to deuterated dmsO ($\delta = 2.50$ ppm). Infrared spectra (4000-300 cm^{-1}) were recorded as KBr pellets on a PerkinElmer FTID 1000 spectrometer. Mass analyses in tetrahydrofurane were recorded on a Perseptive Voyager DE STR MALDI TOF-MS spectrometer. Elemental analyses for C, H and N were determined by the Service de Microanalyses, ICSN-CNRS, Gif-sur-Yvette, France.

Synthesis

H₄L. To a solution of 4-(3-hydroformyl-4-hydroxy-5-*tert*-butylphenyl)bezoic acid (269 mg, 0.90 mmol) in ethanol was added ethylenediamine (27.06 mg, 0.45 mmol) and few drops of ethylorthoformate. The reaction mixture was stirred under reflux for two hours. The solvent was removed under reduced pressure. The solid was sonicated with ether, filtrate and dried under vacuum. Yield: 84%. ¹H NMR (DMSO-*d*₆): 1.40 (s, 9H, -C(CH₃)₃), 3.99 (s, 2H, CH₂), 7.58 (s, 1H, Ar-H), 7.65 (d, 2H, Ar-H), 7.69 (s, 1H, Ar-H), 7.96 (d, 2H, Ar-H), 8.71 (s, 1H, -CH=N-). IR ($\nu_{\text{max}}/\text{cm}^{-1}$): 3436(br), 2957(w), 2915(w), 1688(s), 1633(s), 1607(s), 1534(w), 1440(m), 1388(s), 1272(m), 1251(m), 1226(m), 1171(m), 1103(w), 1046(w), 1015(w), 856(m), 776(m), 744(m), 710(w), 444(w). MS (MALDI-TOF, *m/z*): 621.32 (Calcd. for [M+H⁺] = 621.30).

[Ni(H₂L)] (S1). To a solution of the ligand H₄L (93 mg, 0.15 mmol) in dimethylformamide/methanol (15 ml, 15:1 v/v) was added a solution of Ni(OAc)₂ 4H₂O (38 mg, 0.15 mmol) in methanol. The reaction mixture was stirred for 1 h at 80°C, during which gradually a yellow-red precipitated formed. The precipitate was filtered and washed with methanol, and dried in vacuo. Yield: 80%. ¹H NMR (DMSO-*d*₆): 1.40 (s, 9H, -C(CH₃)₃), 3.47 (s, 2H, CH₂), 7.50 (s, 1H, Ar-H), 7.61 (s,

1H, Ar-*H*), 7.69 (d, 2H, Ar-*H*), 7.96 (s, 2H, Ar-*H*), 8.02 (s, 1H, -CH=N-). IR ($\nu_{\max}/\text{cm}^{-1}$): 3435(br), 2947(w), 1691(s), 1625(s), 1602(s), 1537(m), 1439(m), 1421(m), 1397(s), 1334(w), 1318(m), 1287(m), 1278(m), 1230(w), 1174(m), 1126(w), 1094(w), 947(w), 852(m), 775(m), 758(m), 713(w), 546(w), 514(vw). MS (MALDI-TOF, m/z): 677.25 (Calcd. for $[\text{M}+\text{H}^+]$ = 677.22). Anal. Calcd for **1** ($\text{C}_{38}\text{H}_{38}\text{N}_2\text{NiO}_6 \cdot \text{H}_2\text{O} \cdot 0.2\text{DMF}$): C, 65.29; H, 5.88; N, 4.34. Found: C, 64.69; H, 5.73; N, 4.69.

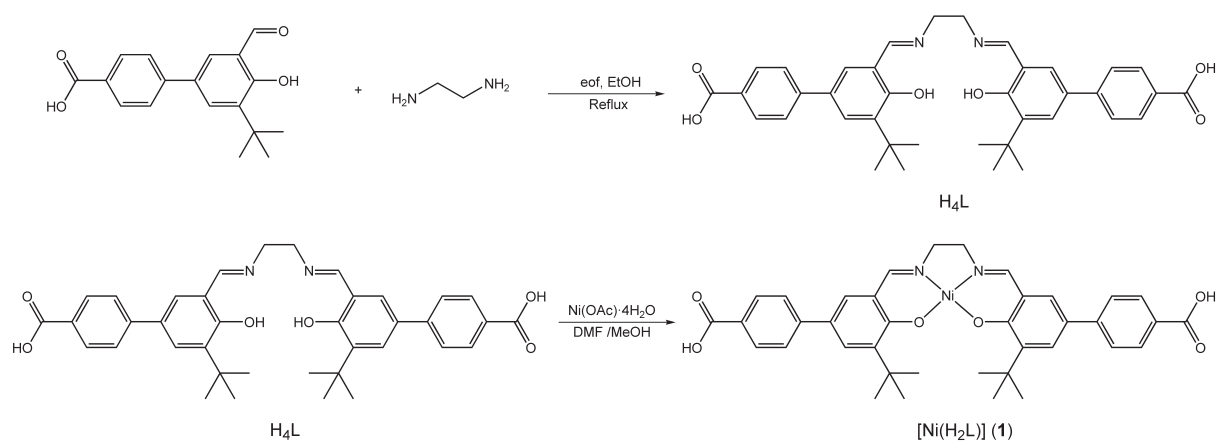


Figure S1: Scheme 1

References

(S1) Patterson, J. B.; Lonergan, D. G. *PCT Int. Appl.* **2008**, 437, 2008154484.

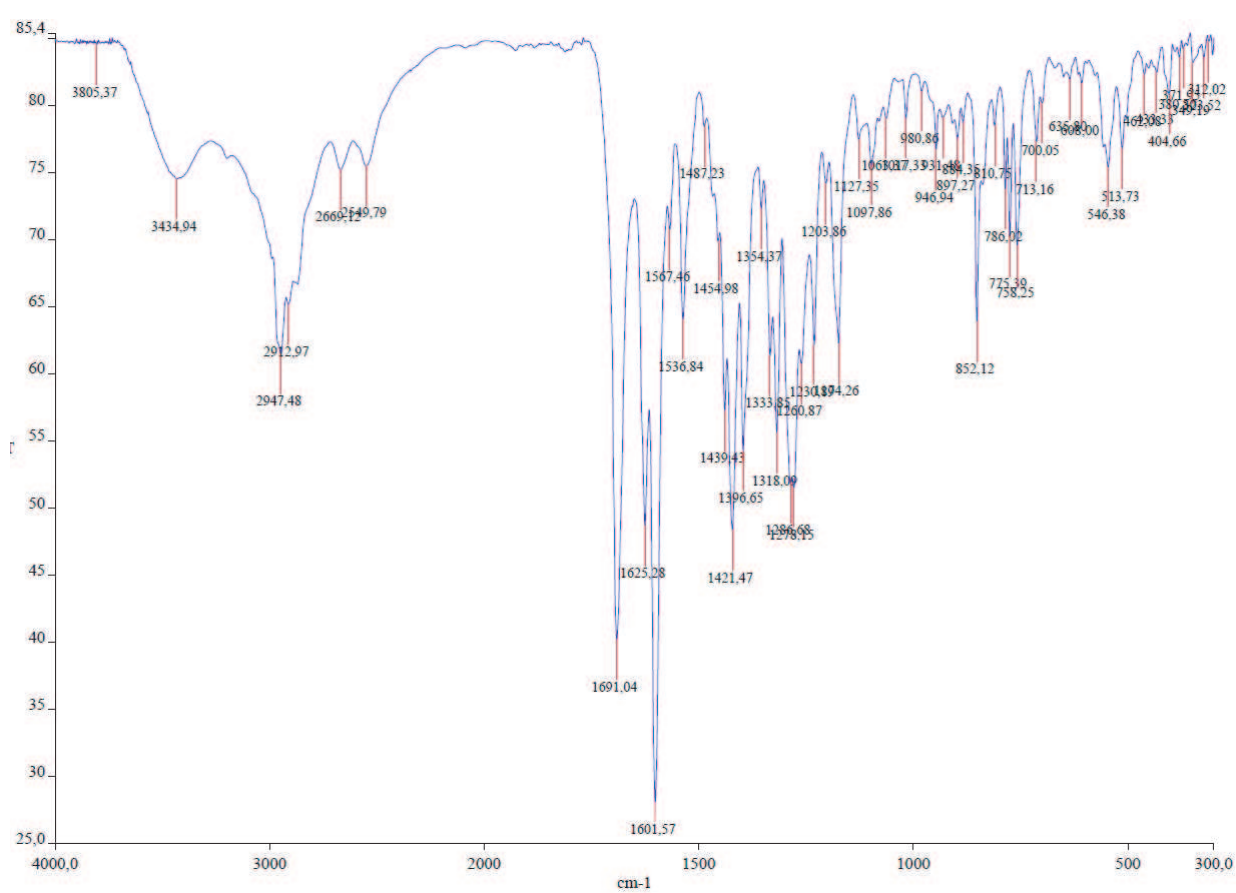


Figure S2: IR spectrum of complex **1**

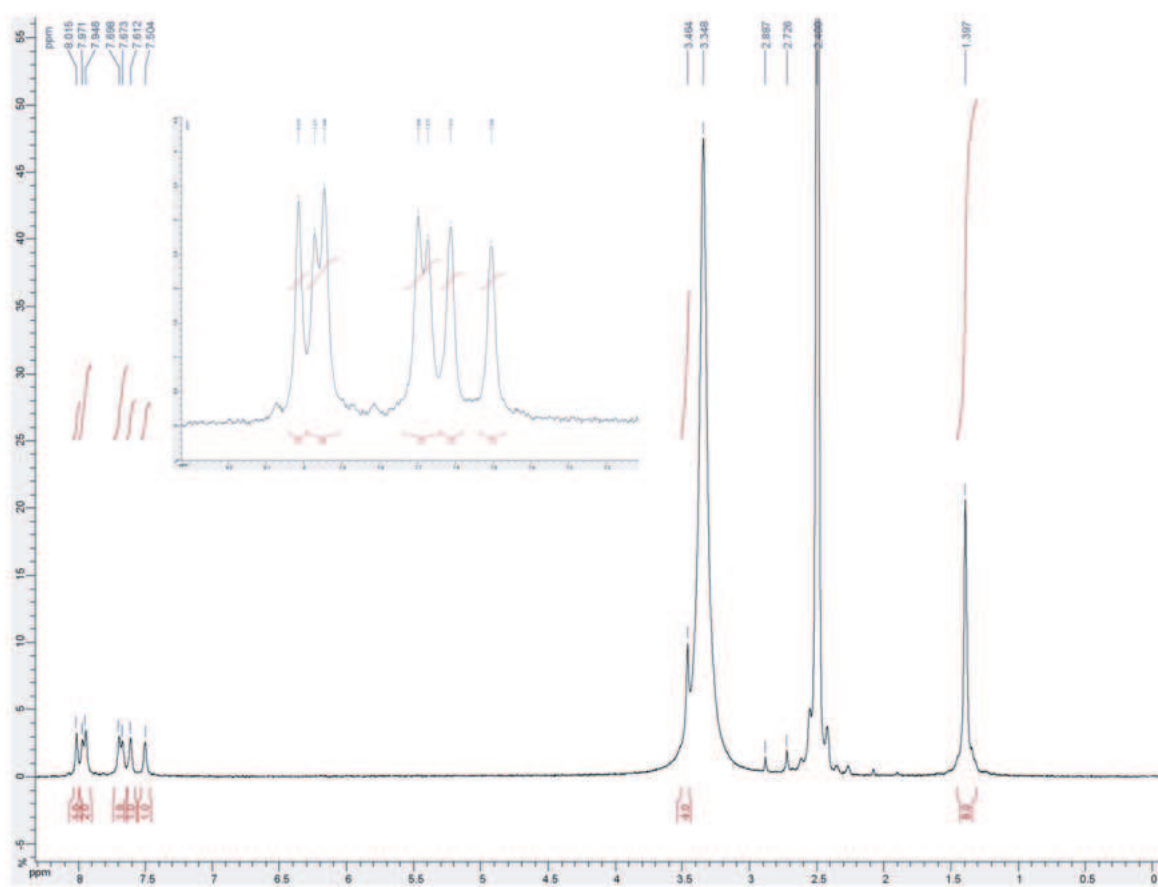


Figure S3: NMR spectrum of complex **1**

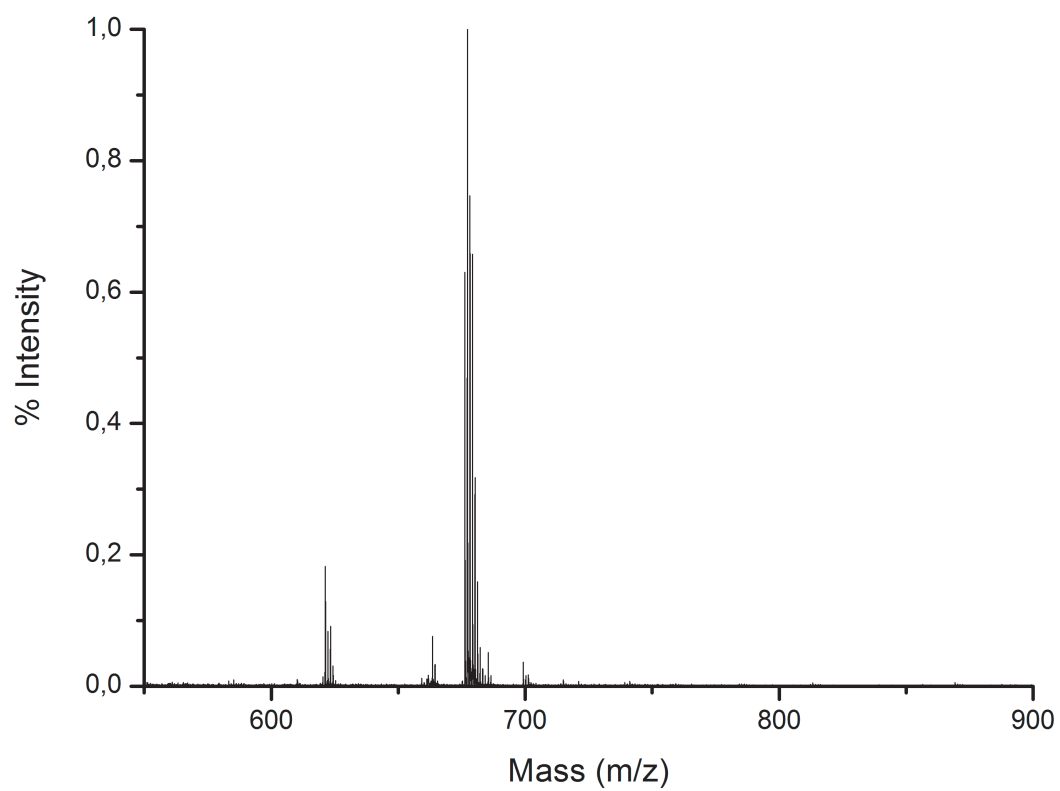


Figure S4: MALDI spectrum of complex **1**