

## Electronic Supplementary Information

# Clear Evidences of the Electron Delocalization: Synthesis, Structure, Magnetism, EPR and DFT Calculation of the Asymmetric Hexanickel String Complex Containing a Single Mixed-Valence $(\text{Ni}_2)^{3+}$ Unit

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### *Synthesis of 2-(naphthyridylamino)-7-phenylamino-1,8-naphthyridine ( $\text{H}_2\text{napany}$ ).*

Aniline (1 mL, 10 mmol), 2,7-dichloro-1,8-naphthyridine (1.98 g, 10 mmol), 2-amino-1,8-naphthyridine (1.45 g, 10 mmol),  $\text{NaNH}_2$  (0.78 g 20mmol),  $\text{Pd}_2(\text{dba})_3$  (0.10 g 0.11 mmol) and dppp (0.13 g, 0.3 mmol). The mixture was stirred and refluxed in toluene (100 mL) for 96 hrs. The solvent was removed under reduced pressure. The mixture was washed by water and the precipitate was extracted by  $\text{CH}_2\text{Cl}_2$  to obtain the solid. Column chromatography was performed on silica gel using  $\text{CH}_2\text{Cl}_2/\text{Aceton}$  (5:1) as eluent affording the light yellow product,  $\text{H}_2\text{napany}$  (yield: 46 %).  $^1\text{H-NMR}$  (400 MHz,  $\text{d}_6\text{-DMSO}$ ):  $\delta$  10.3(s,1H), 9.5(s,1H), 8.9(s,1H), 8.7(d,1H), 8.5(d,2H), 8.2(d,1H), 8(d,3H), 7.7(d,1H), 7.35(t,2H), 7.4(d,1H), 7(t,2H); MS(FAB)  $m/z$  365 ( $[\text{M}]^+$ ).

*Synthesis of  $(4,0)[\text{Ni}_6(\text{napany})_4\text{Cl}](\text{BF}_4)_2$  (1).* A mixture of  $\text{H}_2\text{napany}$  (364 mg, 1 mmol), naphthalene (50 g) and  $\text{NiCl}_2$  (195 mg, 1.5 mmol) were placed in an

Erlenmeyer flask. The mixture was heated (about 200°C) for 15 hrs. A solution of t-BuOK (224 mg, 2 mmol) in n-butanol (20 mL) was added dropwise. The solution then turned to dark green. The mixture was heated for another 10 hrs, cooled to about 70°C, and treated with hexane to precipitate the metal complexes. The precipitate was washed with hexane to remove the residual naphthalene. The metal complex was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and treated with NaBF<sub>4</sub> (549 mg, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (250 mL). The resulting solution was stirred for a week and dried at vacuum. The solid was extracted with CH<sub>2</sub>Cl<sub>2</sub> and layered with hexane. After 1 week, the deep green crystals were obtained. (yield: 30%). MS(FAB) m/z: 1859 [M]<sup>+</sup>, EA (%):[Ni<sub>6</sub>(napany)<sub>4</sub>Cl](BF<sub>4</sub>)<sub>2</sub>·2(CH<sub>2</sub>Cl<sub>2</sub>): calcd. C 49.57, H 2.77, N 14.42; found.: C 48.61, H 2.55, N, 15.64.

**Computational details:** Calculations and geometry optimizations on **1** had been carried out using the Density Functional Theory (DFT) formalism with the spin unrestricted option, as implemented in the Gaussian03 software, with the B3LYP exchange-correlation functional. All-electron valence double- $\zeta$  basis sets (D95V) were used to describe C, N, and H atoms. Los Alamos core potentials were used to model the neon cores of Cl and Ni. The valence shell of chlorine and nickel were described at the double- $\zeta$  level (LanL2DZ basis). The antiferromagnetic low-spin state ( $S_{Ni1} = 1$ ,  $S_{Ni2} = -1/2$ ,  $S_{Ni1} + S_{Ni2} = S = 1/2$ ) of **1** has been characterized and using the broken symmetry (BS) approach first proposed by Ginsberg, and then developed by Noodleman.<sup>1</sup> The energy difference between BS ( $S = 1/2$ ) and HS ( $S = 3/2$ ) states is defined as  ${}^{BS}E - {}^{HS}E$ .

**X-ray Structure Determinations:** Crystallographic data were collected at 150(2) K on a NONIUS Kappa CCD diffractometer using graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell parameters were retrieved and refined using *DENZO-SMN* software on all observed reflections. Data reduction was performed with the *DENZO-SMN* software.<sup>2</sup> An empirical absorption was based on the symmetry-equivalent reflection and absorption corrections were applied with the SORTAV program.<sup>3</sup> The structures were solved and refined with *SHELX* programs.<sup>4</sup> The hydrogen atoms were included in calculated positions and refined using a riding mode.

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