

Electronic Supplementary Information

A ligand design with modified naphthyridylamide for achieving longest EMACs: the 1st single-molecule conductance of undeca-nickel metal string

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1. Synthesis of H₄bnatpya and EMACs 1–3

Materials.

All reagents and solvents were used as received unless otherwise noted. The precursors, 2-amino-1,8-naphthyridine, was prepared according to the literature procedure.^{1,2}

Physical Measurements.

¹H NMR spectra were recorded in DMSO with a Bruker AMX 400MHz spectrometer. Magnetic susceptibility data was collected with a Quantum Design MPMS7 SQUID magnetometer with an applied magnetic field of 3000 G between 4–300 K. The diamagnetic corrections were calculated using Pascal's constants. Cyclic voltammetry (CHI 440, CH Instruments, Austin, TX, USA) was carried out in dry DMF (*N,N*-dimethylformide) containing 0.1 M TBAP, ca. 1 mM of EMACs, and ferrocene (Fc) which is an internal reference with the redox event of Fc⁺⁰ taking place at 0.544 V against $E_{Ag/AgCl}$ in DMF.³ The working, counter, and reference electrodes were, respectively, a commercially available glassy carbon disk electrode, a platinum wire, and a silver wire as the quasi-reference electrode. MALDI spectra were performed on a MALDI-TOF Voyager DE-STR mass spectrometer. IR spectra were obtained with a Thermo Scientific Nicolet iS5 FT-IR spectrometer.

Synthesis.

***N*-(6-bromopyridin-2-yl)-1,8-naphthyridin-2-amine, L1.** 2-Amino-1,8-naphthyridine (10 g, 69 mmol), 2,6-dibromopyridine (20.3 g, 86 mmol), ^tBuOK (9.66 g, 86 mmol), Pd₂(dba)₃ (1.20 g, 1.3mmol) and dppp (1.03 g, 2.5 mmol) were placed in a flame-dried flask under argon atmosphere. The mixture was stirred and refluxed in toluene (500 mL) for 24 h. The solvent was removed under reduced pressure. The mixture was washed by water and the precipitate was chromatographed on silica gel using CH₂Cl₂/acetone (20 : 1) as the eluent to afford **L1** as a light yellow powder. Yield: 13 g, 65%; ¹H NMR (400 MHz; [D]DMSO): δ = 10.64 (s, NH), 8.85 (m, 1H), 8.76 (d, 1H), 8.23 (m, 2H), 7.76 (t, 1H), 7.39 (m, 1H), 7.21 (m, 1H) ppm.

***N*²,*N*⁶-bis(6-(1,8-naphthyridin-2-ylamino)pyridin-2-yl)pyridine-2,6-diamine (H₄bnatpya), L2.** **L1** (5 g, 16 mmol), 2,6-diaminopyridine (0.75 g, 6.9 mmol), ^tBuOK (1.86 g, 16 mmol), Pd₂(dba)₃ (0.65 g 0.7 mmol), and dppp (0.59 g, 1.4 mmol) were placed in a flame-dried flask under argon atmosphere. The mixture was stirred in refluxed toluene (250 mL) for 72 h. The solvent was removed by filtration and the precipitate was washed with CH₂Cl₂ (100 mL) and methanol (100 mL) to obtain dark yellow powders. Yield: 3.1 g, 82%; ¹H NMR (400 MHz; [D]DMSO): δ = 9.94 (s, 2H), 9.13 (s, 2H), 8.83 (t, 2H), 8.20 (m, 4H), 7.86 (m, 4H), 7.60 (m, 4H), 7.36 (m, 6H) ppm.

[Ni₁₁(bnatpya)₄(Cl)₂]⁴⁺, 1. A mixture of **L2** (0.273 g, 1 mmol), naphthalene (50 g), and Ni(OAc)₂·4H₂O (0.161 g, 1.25 mmol) was placed in an Erlenmeyer flask. The mixture was heated to reflux and stirred for 24 h. The solution then turned dark brown, cooled to about 70 °C, and treated with hexane to dissolve the naphthalene. The precipitate was washed with hexane to remove the residual naphthalene. The metal complex was extracted with CH₂Cl₂ (250 mL), and treated with KPF₆ (92 mg, 0.5 mmol) in CH₂Cl₂ (50 mL). The resulting solution was stirred for 12 h and dried under vacuum. The solid was extracted with methanol and layered with ether. After one week, deep brown crystals were obtained. Yield: 10 mg, 1%; MS (MALDI), m/z: 2898 [M]⁺; IR (KBr): $\nu = 1611, 1548, 1492, 1417, 1370(\text{py}) \text{ cm}^{-1}$.

[Ni₁₁(bnatpya)₄(Cl)₂]²⁺, 2. In a flask, EMAC **1** (50 mg, 17 mmol) was dissolved in CH₂Cl₂ (30 mL) with 10 drops hydrazine and stirred for 0.5 h. The mixture was then filtered and the solution was dried under vacuum. The solid was dissolved in methanol. Brown crystals were obtained by slow diffusion of ether into the solution. Yield: 40 mg, 80%. MS (MALDI), m/z: 2898 [M]⁺.

[Ni₁₁(bnatpya)₄(NCS)₂]⁴⁺, 3. NaNCS (0.20 mg) was added to a solution of EMAC **1** in CH₂Cl₂ and stirred for 48 h. The mixture then was filtered and dried in vacuum. MS (MALDI), m/z: 2944 [M]⁺; IR (KBr): $\nu = 2066 (\text{NCS}), 1615, 1548, 1521, 1386, 1330 (\text{py}) \text{ cm}^{-1}$.

Determinations of X-ray Structures

For EMACs **1** and **2**, crystallographic data were collected on a Bruker APEX-III D8 Venture diffractometer at 150(2) K with a Mo-K α radiation source ($\lambda = 0.71073$ Å). Cell parameters were retrieved and refined using APEX-III software on all observed reflections. The APEX-III software was also used for the data reduction. An empirical absorption was based on the symmetry-equivalent reflection and absorption corrections were applied with the SADABS program. The structures were solved and refined with SHELX-97 programs by full-matrix least-square fits of the F^2 values. For **2**, some of solvent molecules in the crystal are highly disordered, and attempts to locate and refine these solvent peaks were unsuccessful. Contributions to scattering from some solvent molecules were removed using the SQUEEZE routine of PLATON;⁴ the structure was then refined again using the data. The hydrogen atoms were added to the structure models in calculated positions.

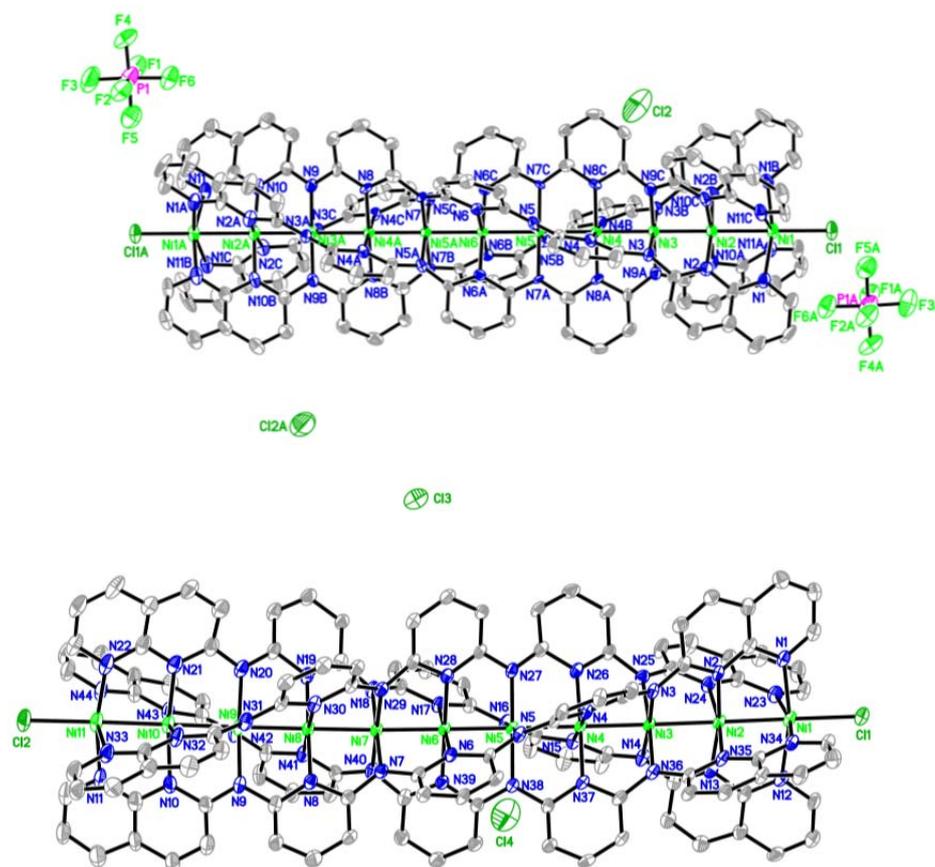


Figure S1. ORTEP views of EMACs (upper, $[\text{Ni}_{11}(\text{bnatpya})_4\text{Cl}_2](\text{PF}_6)\text{Cl}_2$) **1** and (lower, $[\text{Ni}_{11}(\text{bnatpya})_4\text{Cl}_2]\text{Cl}_2$) **2**. Thermal ellipsoids are drawn at the level of 30% probability. Hydrogen atoms are not shown for clarity.

Fitting model for the magnetic measurements.

The dinuclear model with a Hamiltonian^{5,6} $\mathbf{H} = -2J_{1,1A}S_1S_{1A}$ is used for fitting the χ_M curve of EMACs **1** and **2**. For two equivalent magnetic centres with $S_1 = S_2 = 1$ and $S_1 = S_2 = 3/2$, the van Vleck equation can be developed as Equations 1 and 2, respectively.

$$\chi_M = \frac{Ng^2\beta^2}{kT} \times \frac{2e^{\frac{J}{kT}} + 10e^{\frac{3J}{kT}}}{1 + 3e^{\frac{J}{kT}} + 5e^{\frac{3J}{kT}}} \quad (1)$$

$$\chi_M = \frac{Ng^2\beta^2}{kT} \times \frac{2e^{\frac{J}{kT}} + 10e^{\frac{3J}{kT}} + 28e^{\frac{6J}{kT}}}{1 + 3e^{\frac{J}{kT}} + 5e^{\frac{3J}{kT}} + 7e^{\frac{6J}{kT}}} \quad (2)$$

N is Avogadro's constant, g is the Landé factor, β is the Bohr magneton, k is the Boltzmann constant, and T is temperature.

Cyclic voltammetry.

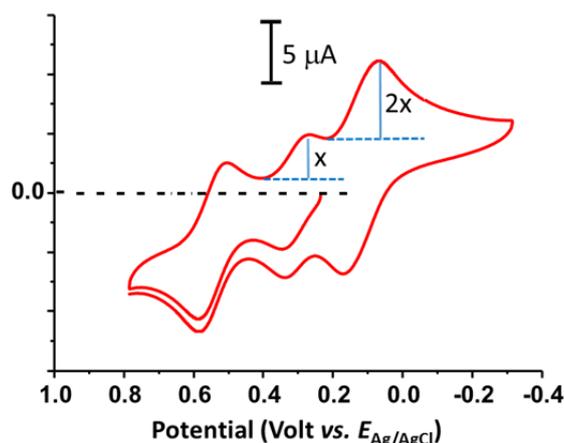
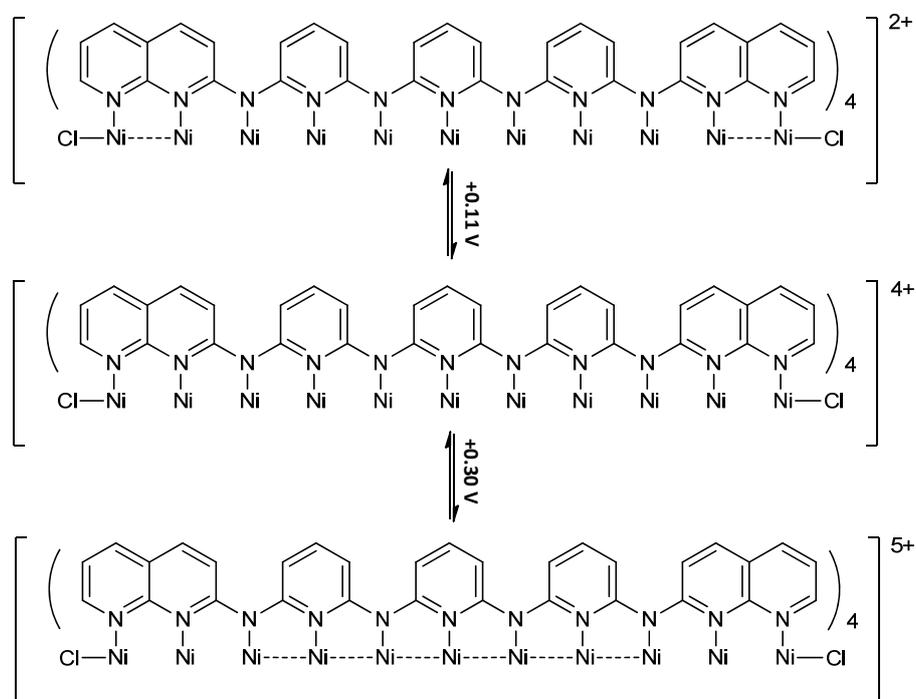


Figure S2. Cyclic voltammogram of EMAC **1**. The potential of zero net current was found at ca. 0.2 V against $E_{\text{Ag}/\text{AgCl}}$. Therefore, peaks of $E_{1/2}$ at +0.11 V and +0.30 V are attributed to the redox reactions of $[\text{Ni}_{11}]^{22+/20+}$ and $[\text{Ni}_{11}]^{23+/22+}$, respectively, where the relative peak currents are consistent with the assigned charges. The internal reference standard used was Fc (ferrocene) whose redox potential was 0.54 V against $E_{\text{Ag}/\text{AgCl}}$. The experiment was deaerated and carried out under N_2 environment. Other conditions: solvent, DMF; supporting electrolyte, 0.1 M tetrabutyl ammonium perchlorate; scan rate, 0.1 V/s; working electrode, glassy carbon electrode (3 mm in diameter); reference electrode: Ag wire; counter electrode: Pt wire.



Scheme S1. Proposed metal-metal bonds and the associated oxidation states.

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