

Final Report for AOARD Grant AOARD-104050  
"Syntheses, Characterizations, and Applications of Molecular Metal Wires"

August 5, 2011

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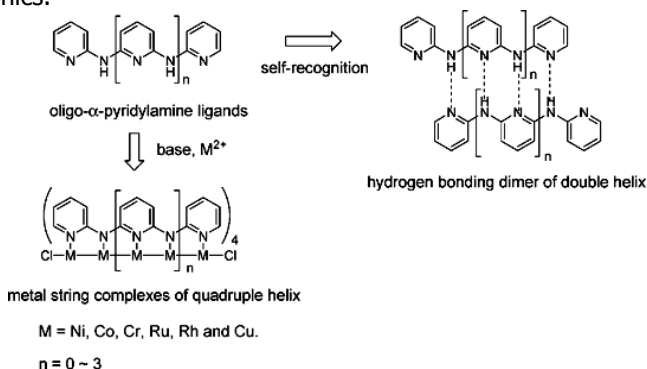
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| 13. SUPPLEMENTARY NOTES                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                                    |                                     |                                    |                                                           |                                    |
| 14. ABSTRACT<br><b>This is the final report of a project on extended metal atom chains, a unique category of metal wires.</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                    |                                     |                                    |                                                           |                                    |
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**Abstract:** Our long-term research interests focus on EMACs (Extended Metal Atom Chains), a unique category of molecular metal wires. A prototypical EMAC is a linear chain of transition metals wrapped helically by four oligo- $\alpha$ -pyridylamido anions. Explored in this AOARD project are novel ligands utilized to synthesize EMACs which inherit interesting physical chemistry, such as crystallographic, structural, magnetic, electrochemical, and electric conductive properties. With the advancement in the synthetic approach over the past years, we prepared pyrazine- (*J. Molecular Structure* **2010**, 973, 116; *J. Chin. Chem. Soc.* **2010**, 57, 765) and naphthyridine-modulated EMACs (*Eur. J. Inorg. Chem.* **2010**, 20, 3153; *Dalton Trans.* **2010**, 3890; *Eur. J. Inorg. Chem.* **2011**, 13, 2025). The latter ligands are less anionic than the prototypical analogues and thus these EMACs tend to form reduced mixed-valence  $[M_2]^{3+}$  dinuclear units which contain a delocalized unpaired electron and, therefore, develop remarkable properties. For example, the naphthyridine-modulated EMACs ligand allows us to prepare a string of 11 nickel atoms, the longest EMAC reported thus far. The  $Ni_{11}$  string contains four mixed-valence  $[Ni_2]^{3+}$  in the sequence of  $Ni_2^{3+}-Ni^{2+}-Ni_2^{3+}-Ni^{2+}-Ni_2^{3+}-Ni^{2+}-Ni_2^{3+}$  that shows all three classes (i.e., characteristics of electron localization, partly delocalization, and delocalization) of the Robin–Day classification of mixed valency (*Angew. Chem. Int. Ed.* **2011**, 50, 2045). Asymmetric EMACs are also an emphasis of this proposal. An unusual charge disproportionate metal chain is prepared by ligands which have phenyl at one terminal and naphthyridine at the other (*Chem. Commun.* **2010**, 46, 5018). Physicochemical properties of trimetal and pentametal EMACs are characterized by methods of IR, Raman spectroscopy and femtosecond transient absorption (*J. Phys. Chem. C* **2011**, 115, 2454; *J. Phys. Chem. C* **2011**, 115, 13919; *ChemPhysChem* **2010**, 11, 466; *ChemPhysChem* **2010**, 11, 517). In 2011, the contribution in the synthesis and characterization of molecular metal wires is recognized by Japan Society of Coordination Chemistry with the 2011 International Award (previous awardees: Michael Grätzel, James P. Collman, Jean-Pierre Sauvage, and Harry B. Gray).

## Introduction:

Comprehensive reviews on EMACs (Extended Metal Atom Chains, scheme 1) from our group and others have been summarized in the *Feature Article* published in *Chem. Commun.* (**2009**, 4323), a monograph in *Nano Redox Sites: Nano-Space Control and its Applications* (ed. T. Hirao, Springer, Berlin, 2006, Ch. 5, pp. 85–117), and an account recently submitted to *Bull. Jpn. Soc. Coord. Chem.* which provide a complete version of the importance and goals of this research. EMACs represent a unique category of molecular wires because most compounds studied in this research field are carbon-based molecules involving conjugated double bond, triple bonds, and aryl groups through which the conducting electrons are expected to transport. Instead of the conjugated framework of carbon-based molecules, for EMACs, the analogous conducting pathways will be the metal-atom chains. Furthermore, these complexes are similar to the electric wires in our macroscopic world as proposed by Cotton's group. Therefore, EMACs are particularly attractive in the field of molecular electronics.



**Scheme 1** Oligo- $\alpha$ -pyridylamine ligands and metal string complexes (*Chem. Commun.* **2009**, 4323).

The prototypical framework of the metal string complexes consists of a one-dimensional linear transition metal backbone in which the metal centers are supported and shrouded by four oligo- $\alpha$ -pyridylamido ligands (Scheme 1). Previous STM measurements showed that resistances of  $[\text{Ni}_3(\text{dpa})_4(\text{NCS})_2]$ ,  $[\text{Co}_3(\text{dpa})_4(\text{NCS})_2]$ ,  $[\text{Cr}_3(\text{dpa})_4(\text{NCS})_2]$ ,  $[\text{Ni}_5(\text{tpda})_4(\text{NCS})_2]$ ,  $[\text{Co}_5(\text{tpda})_4(\text{NCS})_2]$  and  $[\text{Cr}_5(\text{tpda})_4(\text{NCS})_2]$  ranged from 0.9  $M\Omega$  to 24  $M\Omega$ , which are qualitatively well correlated with the metal–metal bond orders. Namely, EMACs with stronger metal–metal interaction exhibit the better conductivity.

One of the goals of designing metal string complexes is for future molecular electronics, including wires and functional devices. Therefore, the development of methods to tune the EMAC properties is of paramount importance. To manipulate the properties of EMACs, two apparent approaches are the selections of metal cores and the modification of the pyridylamido ligands. In this report, the properties of the formers were examined by spectroscopic methods such as vibrational spectroscopy (IR, Raman, and surface enhanced Raman) and femtosecond transient absorption spectroscopy. The latter was carried out via pyrazin- and naphthyridine-modulated ligands which improve the delocalization of unpaired electrons and thus the molecular conductance.

## Experiment:

**General procedures for EMAC synthesis.** Examples of the preparation of pyrazin- or naphthyridine-modulated ligands are described and followed by metallation reactions to obtain the EMACs. Detailed information and procedures, including those for prototypical oligo- $\alpha$ -pyridylamido anions, are referred to the journal articles listed in the publication list.

**H<sub>3</sub>pzp** ( $\text{N}^2$ -(Pyrazin-2-yl)- $\text{N}^6$ -(6-(pyrazin-2-ylamino)pyridin-2-yl)pyridine-2,6-diamine).

A mixture of di(6-amino-2-pyridyl)amine (5.00 g, 24.8 mmol), chloropyrazine (6.84 g, 59.7 mmol),  $\text{Pd}_2(\text{dba})_3$  (0.46 g, 2 mol%), BINAP (0.62 g, 4 mol%) and  $\text{Bu}^t\text{ONa}$  (7.17 g, 74.6 mmol) in dry benzene (230 mL) was refluxed under argon with stirring for 4 days. Then the solvent was removed. The crude product was washed with water, benzene, and methanol and recrystallized from acetone (6.2 g, 70% yield).

**[H<sub>4</sub>pzp]ClO<sub>4</sub>.** A mixture of H<sub>3</sub>pzp (0.10 g, 0.28 mmol) and  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.22 g, 0.61 mmol) was stirred in methanol (50 mL) for 1 day. The resulting yellow solution was filtered. Slow diffusion of the filtrate with ether gave yellow crystals suitable for X-ray diffraction (yield: 85%).

**[Cu(H<sub>3</sub>pzp)(ClO<sub>4</sub>)ClO<sub>4</sub> and [Co(H<sub>3</sub>pzp)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.** A mixture of H<sub>3</sub>pzp (0.10 g, 0.28 mmol) and  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.23 g, 0.61 mmol) and methanol (50 mL) was stirred for 1 day. The resulting green solid was filtered, and then dissolved in acetonitrile. Slow diffusion of the solution with ether gave green crystals suitable for X-ray diffraction (yield: 85%).  $[\text{Co}(\text{H}_3\text{pzp})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  was obtained using a procedure similar to that for  $[\text{Cu}(\text{H}_3\text{pzp})(\text{ClO}_4)]\text{ClO}_4$  except that  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  was used instead of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (yield: 93%).

**[Co(H<sub>3</sub>pzp)(NCS)<sub>2</sub>].** A mixture of H<sub>3</sub>pzp (0.08 g, 0.22 mmol) and  $\text{Co}(\text{NCS})_2$  (0.04 g, 0.23 mmol) and methanol (40 mL) was stirred at 45 °C for 1 day. The resulting solid was filtered off. Slow diffusion of the filtrate with ether gave orange crystals suitable for X-ray diffraction (yield: 83%).

**H<sub>3</sub>tentra** ( $\text{N}^2$ -(2-(1,8-naphthyridin-7-ylamino)-1,8-naphthyridin-7-yl)- $\text{N}^7$ -(1,8-naphthyridin-2-yl)-1,8-naphthyridine-2,7-diamine): The reaction of 2-amino-1,8-naphthyridine (5.8 g, 40 mmol) and bis(2-chloro-1,8-naphthyridin-7-yl)amine (6.84 g, 20 mmol) in the presence of  $\text{Pd}_2(\text{dba})_3$  (0.37 g, 0.4 mmol), dppp (0.33 g, 0.8 mmol) and  $\text{Bu}^t\text{ONa}$  (5.77 g, 60 mmol) in toluene (350 mL) for 60 h gave H<sub>3</sub>tentra. The crude product was washed with water, benzene, and methanol and recrystallized from DMF-ethyl acetate (1:20) and gave pure H<sub>3</sub>tentra as a light-yellow solid (7.22 g, 65% yield).

**[Ni<sub>11</sub>(tentra)<sub>4</sub>Cl<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>.** Anhydrous  $\text{NiCl}_2$  (357 mg, 2.75 mmol), H<sub>3</sub>tentra (559 mg, 1 mmol) and naphthalene (60 g) were placed in an Erlenmeyer flask. The mixture was heated (about 210 °C) under argon overnight and then a solution of potassium *tert*-butoxide (337 mg, 3.0 mmol) in *n*-butyl alcohol (10 mL) was added dropwise. The reaction was continued for another 18 hours. The product was transferred to hexane to wash out the naphthalene after being cooled. The metal complex was extracted with  $\text{CH}_2\text{Cl}_2$  (200 mL), and treated with KPF<sub>6</sub> (500 mg, 2.7 mmol). A dark greenish-brown complex was obtained after evaporation. The single crystals suitable for X-ray diffraction were obtained from diffusion of ether to an acetonitrile solution. Yield: 78 mg, 8.9 %.

**[Ni<sub>11</sub>(tentra)<sub>4</sub>(NCS)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub>.** Solution of NaNCS (115 mg, 1.42 mmol) in  $\text{CH}_3\text{CN}$  (5 mL) was added to a solution of  $[\text{Ni}_{11}(\text{tentra})_4\text{Cl}_2](\text{PF}_6)_4$  (100 mg, 0.028 mmol) in  $\text{CH}_2\text{Cl}_2$  (70 mL). The mixture was stirred for 2 d and then filtered. The filtrate was evaporated to dryness and gave a dark brown compound. The solid was extracted with  $\text{CH}_2\text{Cl}_2$ , and treated with KPF<sub>6</sub> (105 mg, 0.57 mmol) in MeOH (10 mL). The solution was stirred for 12 h, and the solvent was removed under vacuum. The remaining solid was dissolved in  $\text{CH}_2\text{Cl}_2$ . Recrystallization from a  $\text{CH}_2\text{Cl}_2$  solution layered with hexane gave deep brown single crystals suitable for X-ray diffraction. Yield: 83 mg, 82 %.

**Experimental procedures for STM break junction.** The procedures for the conductance measurements are the same as the previous AOARD report. A NanoScope IIIa controller (NanoScope IIIa, Veeco, Santa Barbara, CA) was first operated in the imaging mode with the tunneling current of 1~5 nA. When the imaging showed reasonably stable images of substrates, indicative of a satisfactory tip, the instrument was switched to the mode of STS Plot  $I(s)$  (scanning tunneling spectroscopy). The STM tip was brought into and out of contact with the substrate (8.4~14.0 nm/s, 1.40 Hz) in toluene (TEDIA). The subsequent tip retraction broke the tip-substrate contact and generated a molecular junction where the isothiocyanate headgroup at the termini of the EMACs might bind. While

acquiring current-to-tip stretching profiles,  $I(s)$ , the feedback loop was turned off except at the beginning point of the cycle. Regardless whether the solution contained the molecules of interest,  $I(s)$  traces exhibited a stepwise profile whose steps exhibited multiples of  $G_0$ , the conductance quantum taking place when the cross section of a metallic contact is only that of a single atom ( $G_0 = 2e^2/h$ ,  $\sim(12.9 \text{ k}\Omega)^{-1}$ ).

The concentration of molecules in dichloroethane was typically 1 mM. The stepwise  $I(s)$  traces were obtained at a fixed bias voltage and the magnitudes were orders of magnitude smaller than 1  $G_0$ . To facilitate the determination of peak position, the preparation of the conductance histogram excluded  $I(s)$  traces with simple tunneling decay which was acquired when no molecule bridged between the electrodes. The data points of the stepwise traces were converted to conductance and represented a value on the histogram which indicated qualitatively how the conductance values were distributed and only the range exhibiting peaks was shown. Gaussian function was used to fit the histograms (Origin 7.5). The peak position and standard deviation of the Gaussian curve were utilized to find, respectively, the single-molecule conductance and the error bars.

**Experimental procedures for transient absorption spectroscopy.** The following procedures describe how the experiments were carried out in our published papers (*ChemPhysChem* **2010**, *11*, 517). EMACs were dissolved first in THF, and subsequently with some portion of p-dioxane or acetonitrile separately to prepare solutions with varied polarity. Because of weak absorption of the transient species produced from trinickel complex after irradiation, the sample solution was prepared to have an absorbance up to 0.4 (concentration  $\sim 0.3$  mM) for excitation wavelength 330 nm, and a saturated solution for 600 nm. After each measurement, the UV/Vis absorption of the sample was re-examined to test whether the absorbance variation was less than 10% to ensure no degradation. The steady-state absorption spectra were recorded on a commercial spectrometer (Hitachi U3300).

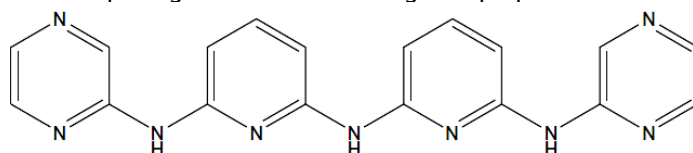
The transient absorption spectra were recorded with another absorption instrument (ExciPro, CDP); the laser was a Ti:sapphire-based amplifier system (Hurricane, Spectra Physics) with output wavelength 800 nm, power 800 mW, and repetition rate 1 kHz. About 70% power of the amplified laser beam was allowed to enter the optical parametric amplifier (OPA, model TOPAS, Light Conversion) to generate the signal light at 1320 and 1200 nm. The excitation beams at wavelengths 330 and 600 nm were generated from the fourth and second-harmonic outputs of the signal beam at 1320 and 1200 nm, respectively. The laser power used for all wavelengths was decreased to 0.5 mJ/pulse to avoid sample decomposition.

The residual 800 nm beam was focused onto a flowing water cell (length 2 mm) to generate continuous white light (400-750 nm) which passed through a wedge reflector and was split into two reflection beams, i.e., reference and probe beams. The pump beam, polarized at the magic angle, traversed the delay line, then was focused and overlapped with the probe beam in the sample cell. The delay stage provided a maximal temporal delay of 2 ns. The sample cell (silica windows, path length of 1 mm) was mounted on a motor (rotational speed 5 Hz) to prevent thermal damage. Two optical fibers collected the residual probe and reference beams after focusing lenses, which were then sent to a monochromator and detected with dual photodiode arrays. A difference in absorption was thus obtained. For the THF solution the instrumental response function, obtained with a Kerrgate method, had a full width at half maximum (fwhm) of 200-300 fs. Measurements were made of the neat solvent under similar conditions to estimate the amplitude and temporal width of XPM occurring through a nonlinear process.

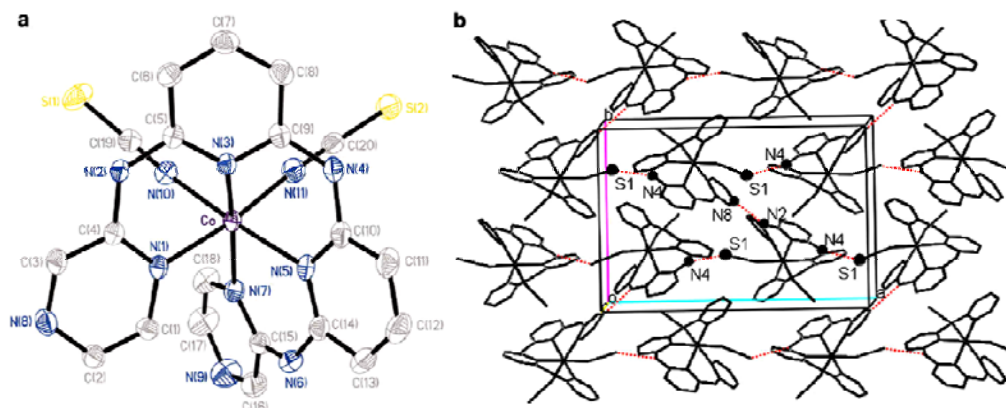
## Results and Discussion:

1. "Study on a pyrazine-modulated tetrapyridyltriamide and its complexes: Synthesis, structure and properties" (*J. Molecular Structure* **2010**, *973*, 116-123).

A pyrazine-modulated oligo- $\alpha$ -pyridylamine ligand  $H_3pzip$  and its mononuclear copper(II) and cobalt(II) complexes have been synthesized and structurally characterized. A pyrazine-modulated oligo- $\alpha$ -pyridylamino ligand  $H_3pzip$  and its mononuclear copper(II) and cobalt(II) complexes have been synthesized and structurally characterized. The protonated ligand cation  $[H_4pzip]ClO_4$  exhibits an anti-anti-anti-anti-syn-anti conformation.  $H_3pzip$  can be a quadridentate ligand and coordinates to metal atoms with all-anti mode in both copper and cobalt mononuclear complexes. The copper(II) ion in  $[Cu(H_3pzip)(ClO_4)]ClO_4$  is five-coordinated in tetragonal pyramid geometry with one of the perchlorate anions being weakly coordinated in the apex position. The cobalt(II) ion in  $[Co(H_3pzip)(H_2O)_2](ClO_4)_2$  and  $[Co(H_3pzip)(NCS)_2]$  is six-coordinated in octahedron geometry. Extensive hydrogen bonds are formed, and construct the complexes  $[H_4pzip]ClO_4$  and  $[Cu(H_3pzip)(ClO_4)]ClO_4$  into 2D networks and  $[Co(H_3pzip)(H_2O)_2](ClO_4)_2$  and  $[Co(H_3pzip)(NCS)_2]$  into 3D networks. X-band EPR spectra of  $[Cu(H_3pzip)(ClO_4)]ClO_4$  showed well-resolved hyperfine structures resulting from the two paramagnetic isotopes  $^{63}Cu$  and  $^{65}Cu$ , resulting in  $g = 2.16$  and  $A^0 = 67 \times 10^{-4} \text{ cm}^{-1}$ . Complexes  $[Co(H_3pzip)(H_2O)_2](ClO_4)_2$  and  $[Co(H_3pzip)(NCS)_2]$  showed spin-orbital coupling and zero-field splitting exhibited in the magnetic properties.



structure of pyrazine-modulated tetrapyridyltriamide



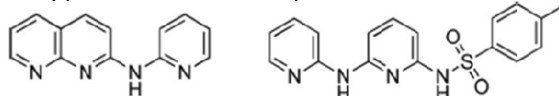
$[Co(H_3pzip)(NCS)_2]$ . (a) The crystal structure of  $[Co(H_3pzip)(NCS)_2]$ . Atoms are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. (b) Hydrogen bonds in 2D portion defined by  $ab$  plane. 3D network is further constructed in  $[Co(H_3pzip)(NCS)_2]$  through hydrogen bonds  $N(6)-H \cdots S(2)$ .

2. "Linear Tetranickel String Complexes with Mixed Supported Ligands and Mixed-Valence Units  $[Ni_2]^{3+}$ : Synthesis, Crystal Structure, and Magnetic Studies" (*Eur. J. Inorg. Chem.* **2010**, 20, 3153-3159).

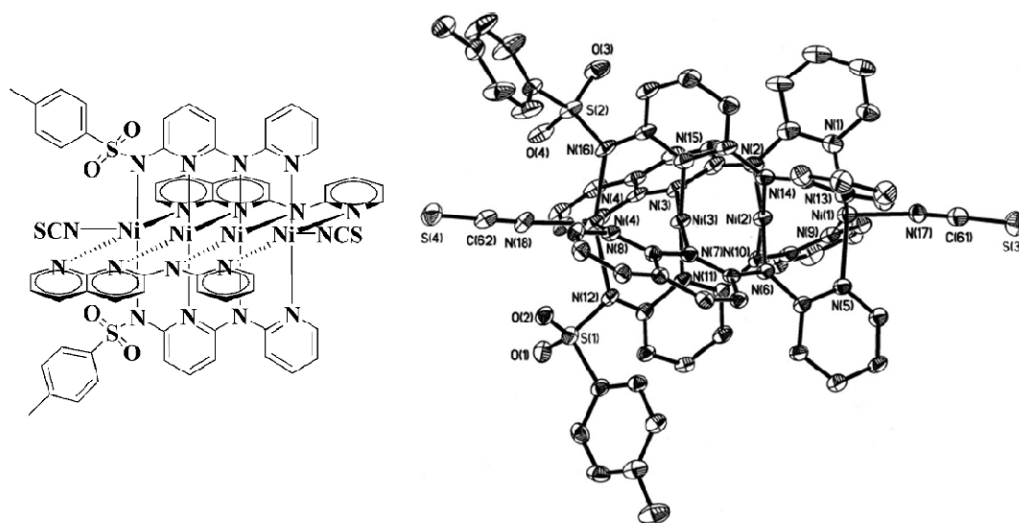
This study presents naphthyridine ligands of 2-( $\alpha$ -pyridylamino)-1,8-naphthyridine ( $Hpyany$ ) and  $N$ -( $p$ -tolylsulfonyl) dipyridyldiamine ( $H_2tsdpda$ ). The ligands were used to synthesize linear tetranickel string complexes whose crystal structures and magnetic properties are examined. In comparing the crystal structure of  $[Ni_4(pyany)_2(tsdpda)_2Cl](1)$  with that of  $[Ni_4(pyany)_2(tsdpda)_2Cl(H_2O)](PF_6)(2)$ , the one-electron-reduced compound 1 displays shorter  $Ni(3)-Ni(4)$  (ca. 2.28 Å) and longer  $Ni(3)-N$  (ca. 2.02 Å) bond lengths. Similar trends have also been observed for axial  $NCS^-$ -substituted derivatives  $[Ni_4(pyany)_2(tsdpda)_2(NCS)](3)$  and  $[Ni_4(pyany)_2(tsdpda)_2(NCS)_2](4)$ . These structural variations indicate the formation of a mixed-valence  $[Ni_2]^{3+}$  unit and a three-electron,

two-center Ni(4)–Ni(3)  $\sigma$  bond. Magnetic measurements of **2** and **4** show that both terminal

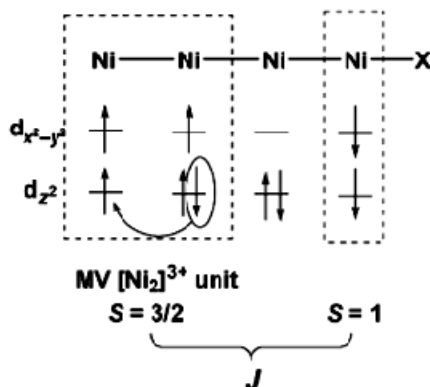
Ni(1) and Ni(4) ions are in the high-spin states ( $S = 1$ ) and are antiferromagnetically coupled. The one-electron-reduced complexes **1** and **3**, however, exhibit a delocalized mixed-valence  $[\text{Ni}_2]^{3+}$  unit ( $S = 3/2$ ), which is antiferromagnetically coupled with the terminal high-spin  $\text{Ni}^{\text{II}}$  ion. The physical properties of even-numbered metal string complexes, could thus be tentatively fine-tuned by utilizing various sets of mixed ligands, which introduces a new approach to the development of future metal string complexes.



structures of 2-( $\alpha$ -pyridylamino)-1,8-naphthyridine (Hpyany) and *N*-(*p*-tolylsulfonyl) dipyridyldiamine (H<sub>2</sub>tsdpda)



Molecular structure of complex  $[\text{Ni}_4(\text{pyany})_2(\text{tsdpda})_2(\text{NCS})_2]$ . Ellipsoids are drawn at 30% probability levels. Hydrogen atoms and interstitial solvent molecules have been omitted for clarity.



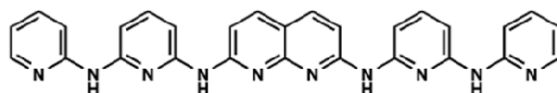
Coupling scheme for complexes  $[\text{Ni}_4(\text{pyany})_2(\text{tsdpda})_2\text{Cl}]$  (**1**) and  $[\text{Ni}_4(\text{pyany})_2(\text{tsdpda})_2(\text{NCS})]$  (**3**).  $J = -121 \text{ cm}^{-1}$  and  $g = 2.12$  for **1**;  $J = -89.3 \text{ cm}^{-1}$  and  $g = 1.97$  for **3**, indicative of a relative stronger antiferromagnetic interaction. The  $[\text{Ni}_2]^{3+}$  unit can be stabilized by only two instead of four



naphthyridyl groups, which might allow us to modulate the physical properties of metal string complexes by modifying the other two ligands.

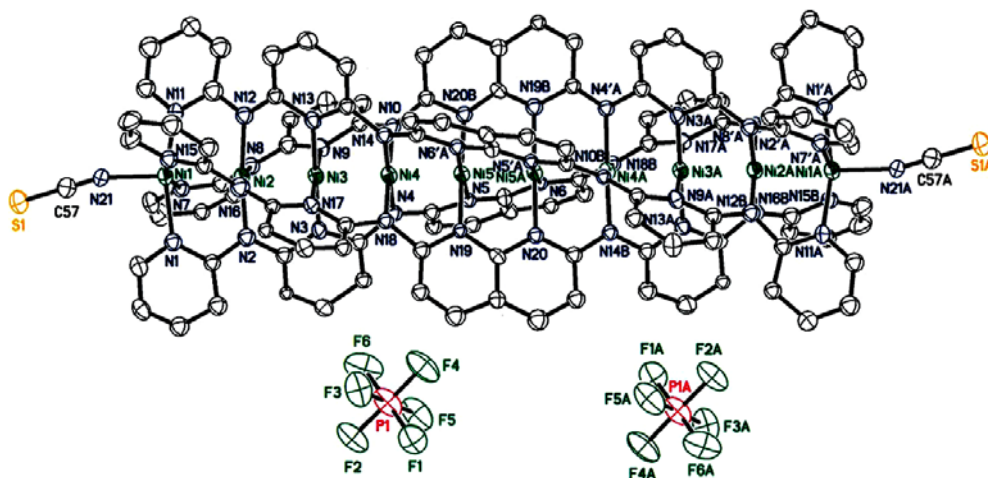
3. "An Extended Metal Chain with the 2,7-Bis(dipyridyldiamino)-1,8-naphthyridine ( $H_4bdpdany$ ) Ligand–The Longest Even-Numbered Metal Chain Complex" (*Eur. J. Inorg. Chem.* **2011**, 13, 2025-2028).

With a novel pyridyl- and naphthyridyl-modulated ligand ( $H_4bdpdany$ ), synthesized is a new decanickel EMAC,  $[Ni_{10}(\mu_{10}-bdpdany)_4(NCS)_2](PF_6)_2$  (**1**), the longest even-numbered EMAC reported to date. The length is approximately 24.48 Å. Analysis of the crystal structure of complex shows that all of the  $bdpdany^{4-}$  ligands bind the metal in an all-*syn* conformation, and structural data reveals short  $Ni\cdots Ni$  distances in the range 2.36–2.23 Å. The electrochemistry of decanuclear complex **1** demonstrates that the metal chain provides four reversible redox couples at  $E_{1/2} = -0.07, +0.52, +0.93,$  and  $+1.30$  V (vs.  $E_{Ag/AgCl}$ ). The coupling constant,  $J_{1,(1A)} = -0.14\text{ cm}^{-1}$ , reveals very weak interaction between the two terminal nickel atoms. Temperature-dependent magnetic measurements performed on two independent high-spin nickel(II) ions of complex **1** demonstrate that the metal chain is antiferromagnetic. The longer distance between the two terminal high-spin nickel(II) ions relative to those in tetranickel and hexanickel strings causes a decrease in the magnitude of the antiferromagnetic interaction.



**$H_4bdpdany$**

Naphthyridine-modulated ligand of 2,7-bis(dipyridyldiamino)-1,8-naphthyridine

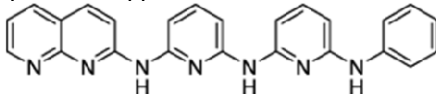


Molecular structure of complex  $[Ni_{10}(\mu_{10}bdpdany)_4(NCS)_2](PF_6)_2$ . Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

4. "Manipulation of electronic structure *via* supporting ligands: a charge disproportionate model within the linear metal framework of asymmetric nickel string  $[Ni_7(phdprrany)_4Cl](PF_6)$ " (*Chem. Commun.* **2010**, 46, 5018-5020).

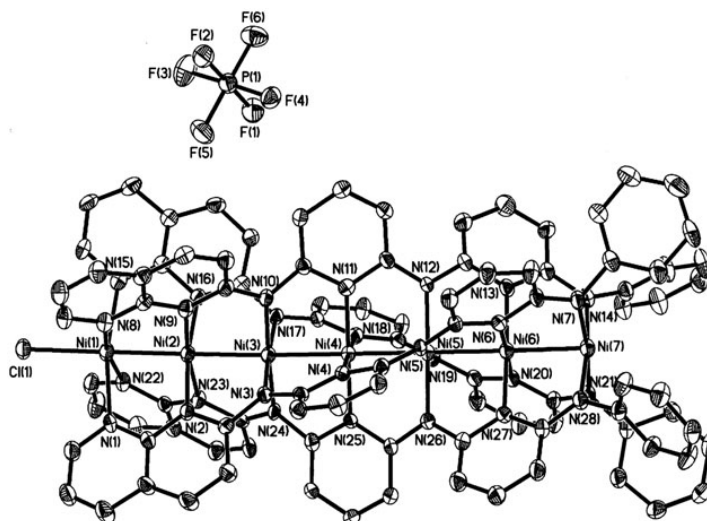
The focus of this study is a unique asymmetric naphthyridine-modulated ligand and its complexes, an asymmetric heptanickel string complex exhibiting a charge disproportionate model along the linear nickel framework. This  $Ni_7$  string is the longest asymmetric EMAC containing two different MV units,  $[Ni_2]^{3+}$  and  $[Ni_3]^{7+}$  arising from its one-electron reduction and oxidation. It is the first example of metal string complexes that possesses this unusual charge disproportionate metal chain. Moreover, the spin distribution shows that the  $[Ni_2]^{3+}$  and  $[Ni_3]^{7+}$  terminus are electronically coupled. This behaviour suggests that compound **1**

not only contains two MV  $[\text{Ni}_2]^{3+}$  and  $[\text{Ni}_3]^{7+}$  units, but also possesses a third extended MV ( $[\text{Ni}_2]^{3+}-[\text{Ni}_3]^{7+}$ ) system. Since mixed-valent units had been proved to be a conductance-enhanced material, this extended MV ( $[\text{Ni}_2]^{3+}-[\text{Ni}_3]^{7+}$ ) system is expected to exhibit higher electronic conductance than traditional MV nickel strings do. It is noteworthy that because of the electronic asymmetry results from charge disproportionation, this complex might also have a potential application as a molecular rectifier.

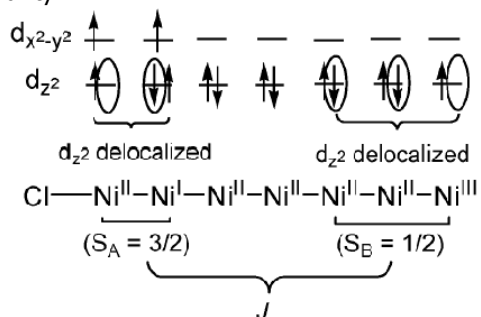


**H<sub>3</sub>phdptryny**

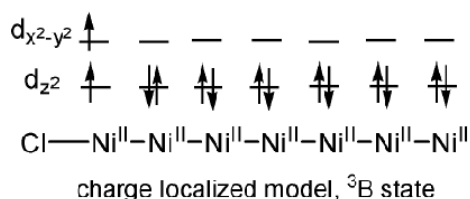
Naphthyridine-modulated ligand of 2-(phenyldipyridyltriamino)-1,8-naphthyridine



Molecular structure of  $[\text{Ni}_7(\text{phdptryny})_4\text{Cl}](\text{PF}_6)$ . Selected bond distances (averaged): Ni(1)–Ni(2) 2.327, Ni(2)–Ni(3) 2.314, Ni(3)–Ni(4) 2.287, Ni(4)–Ni(5) 2.255, Ni(5)–Ni(6) 2.253, Ni(6)–Ni(7) 2.305 Å. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.



charge disproportionate model,  $^5\text{A}$  state

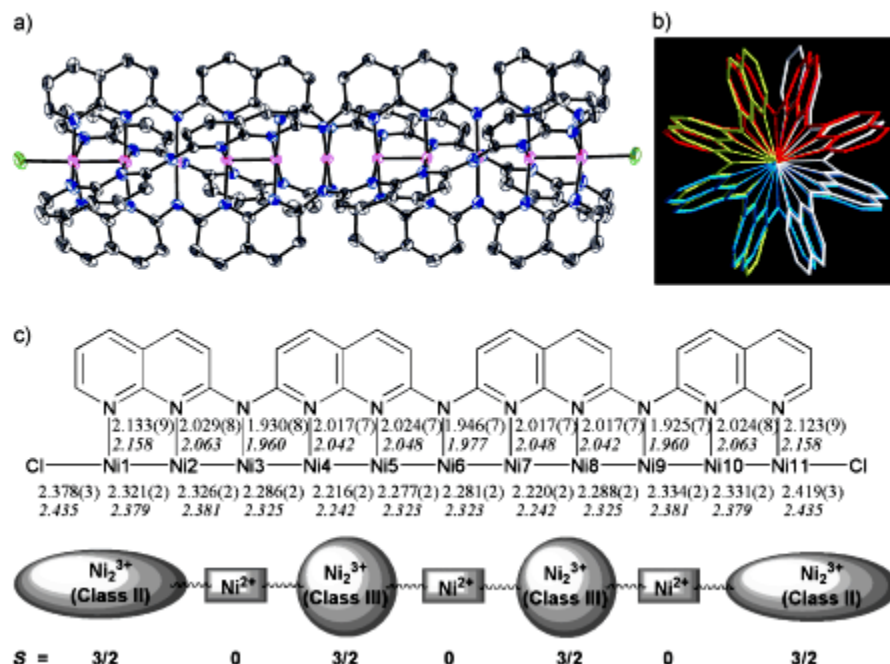


charge localized model,  $^3\text{B}$  state

Calculated electronic configurations of charge disproportionate model and charge localized model for  $[\text{Ni}_7(\text{phdptryny})_4\text{Cl}](\text{PF}_6)$ .

5. "Two Linear Undecanickel Mixed-Valence Complexes: Increasing the Size and the Scope of the Electronic Properties of Nickel Metal Strings" (*Angew. Chem. Int. Ed.* **2011**, *50*, 2045-2048).

$N^2$ -(2-(1,8-naphthyridin-7-ylamino)-1,8-naphthyridin-7-yl)- $N^7$ -(1,8-naphthyridin-2-yl)-1,8-naphthyridine-2,7-diamine ( $H_3$ tentra), a new tetranaphthyridyl triamine ligand, is used to prepared two undecanickel complexes of the deprotonated tentra trianion,  $[Ni_{11}(\text{tentra})_4Cl_2](PF_6)_4$  and  $[Ni_{11}(\text{tentra})_4(NCS)_2](PF_6)_4$ . Metal-metal distances usually decrease from the end to the center of the chain in EMACs of oligo- $\alpha$ -pyridyl-amido ligand. However, for the  $Ni_{11}$ c complexes, terminal  $Ni1-Ni2$  distances are slightly shorter than the next  $Ni2-Ni3$  distances, whereas the other naphthyridyl-bridged  $Ni4-Ni5$  distance is significantly shorter than the innermost metal-metal contact,  $Ni5-Ni6$ . These trends might result from partial metal-metal bonds between the nickel atoms bonded to naphthyridyl units.

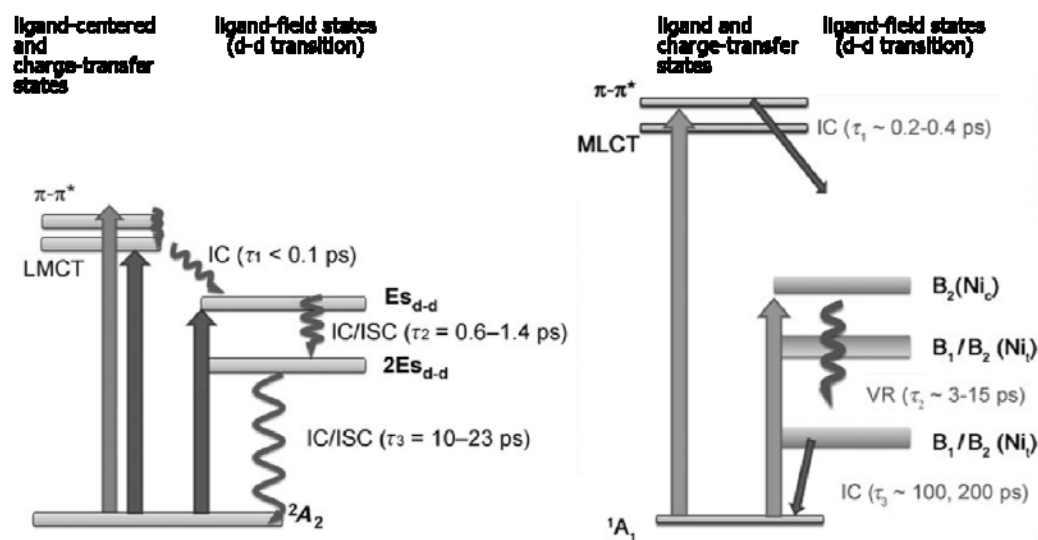


Molecular structure of complex  $[Ni_{11}(\text{tentra})_4Cl_2]^{4+}$ . (a) Thermal ellipsoids are set at 30% probability. The hydrogen atoms are omitted for clarity (Ni pink, N blue, Cl green, C black). (b) View illustrating the quadruple helix along the metal-chain axis. (c) Top: Selected interatomic distances observed and computed (B3LYP calculations, *italic*) for  $[Ni_{11}(\text{tentra})_4Cl_2](PF_6)_4$ . Bottom: The proposed valence and spin-state representation for nickel atoms in  $[Ni_{11}(\text{tentra})_4Cl_2]^{4+}$ .

$[Ni_{11}(\text{tentra})_4Cl_2](PF_6)_4$  and  $[Ni_{11}(\text{tentra})_4(NCS)_2](PF_6)_4$  are four-electron reduced species whose metal core can be described, according to crystallographic analysis and DFT calculations, as a series of four mixed-valence  $[Ni_2(\text{napy})_4]^{3+}$  units each separated by a square-planar  $Ni^{2+}$  unit, in the sequence  $Ni_2^{3+}-Ni^{2+}-Ni_2^{3+}-Ni^{2+}-Ni_2^{3+}-Ni^{2+}-Ni_2^{3+}$ . Temperature-dependent magnetic susceptibility curves are consistent with a system of four magnetic centers with  $S = 3/2, 3/2, 3/2, 3/2$ , each associated with a  $Ni_2^{3+}$  unit which is considered as a single center. Relatively strong antiferromagnetic couplings between mixed-valence  $Ni_2^{3+}$  units above 30 K were fitted for  $[Ni_{11}(\text{tentra})_4Cl_2](PF_6)_4$  by the set of parameters  $g = 2.09$ ,  $J_{12} = J_{34} = -40.83 \text{ cm}^{-1}$  and  $J_{23} = -58.26 \text{ cm}^{-1}$ .  $[Ni_{11}(\text{tentra})_4Cl_2](PF_6)_4$  and  $[Ni_{11}(\text{tentra})_4(NCS)_2](PF_6)_4$  are the first examples of metal string complexes gathering within a single molecule all three classes of the Robin-Day classification of mixed valency, i.e., with the characteristics of conductors, semiconductors, and insulators.

6. " Excited-State Dynamics of the Metal String Complex  $\text{Co}_3(\text{dpa})_4(\text{NCS})_2$  and  $\text{Ni}_3(\text{dpa})_4\text{X}_2$  from Femtosecond Transient Absorption Spectra" (*ChemPhysChem* **2010**, *11*, 466-473 & 517-524).

Transient absorption spectroscopy is used to study the excited-state dynamics of  $\text{Co}_3(\text{dpa})_4(\text{NCS})_2$ ,  $\text{Ni}_3(\text{dpa})_4(\text{NCS})_2$ , and  $\text{Ni}_3(\text{dpa})_4\text{Cl}_2$  where dpa is the ligand dipyridylamido. The  $\pi\text{-}\pi^*$ , charge-transfer, and d-d transition states are excited upon irradiation at wavelengths of 330, 400 and 600 nm, respectively. Similar transient spectra are observed under the experimental temporal resolution and the transient species show weak absorption. We thus propose that a lowlying metal-centered d-d state is accessed immediately after excitation. Analyses of the experimental kinetic traces reveal rapid conversion from the ligand-centered  $\pi\text{-}\pi^*$  and the charge-transfer states to this metal-centered d-d state within 100 fs for  $\text{Co}_3(\text{dpa})_4(\text{NCS})_2$  and for  $\text{Ni}_3(\text{dpa})_4(\text{NCS})_2$  from a ligand-centered  $\pi\text{-}\pi^*$  state to a metal-centered d-d state in 0.1-0.4 ps. For  $\text{Co}_3(\text{dpa})_4(\text{NCS})_2$ , the excited molecule then crosses to a second d-d state within the ligand-field manifold, with a time coefficient of 0.6-1.4 ps. Because the ground-state bleaching band recovers with a time coefficient of 10-23 ps, we propose that an excited molecule crosses from the low-lying d-d state either directly within the same spin system or with spin crossing via the state  $2\text{B}$  to the ground state  $^2\text{A}_2$  (symmetry group  $\text{C}_4$ ). In this trimetal string complex, relaxation to the ground electronic surface after excitation is thus rapid. For  $\text{Ni}_3(\text{dpa})_4\text{X}_2$ , vibrational cooling occurs with a time coefficient of 3.0-15.9 ps. From the spectral shift observed in the transient spectra relative to the steady-state spectra, the dd state is assigned as  $\text{B}_1/\text{B}_2(\text{Ni}_t)$ . This d-d state eventually converts to the electronic ground state, in about 100 ps for the isothiocyanate complex and 200 ps for the chloride. In this trimetal string complex, relaxation to the ground electronic surface after excitation is therefore rapid.

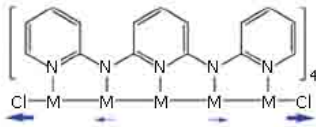
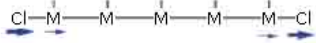
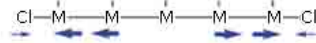
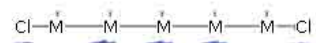


Proposed relaxation pathways for (left)  $\text{Co}_3(\text{dpa})_4(\text{NCS})_2$  and (right)  $\text{Ni}_3(\text{dpa})_4\text{X}_2$ .

7. "Metal-Metal Bonding of Metal-String Complexes: Tripyridylidamido Pentanickel, Pentacobalt, Pentachromium, and Heptachromium from IR, Raman, and Surface-Enhanced Raman Scattering Spectra" (*J. Phys. Chem. C* **2011**, *115*, 2454-2461 & 13919-13926).

The spectroscopic studies of Raman, IR, and SERS show that both  $\text{Co}_5(\text{tpda})_4\text{X}_2$  and  $\text{Ni}_5(\text{tpda})_4\text{X}_2$  ( $\text{X} = \text{Cl}^-$  and  $\text{NCS}^-$ ) have only symmetric metal-metal bonding near 295 K, distinct from  $\text{Co}_3(\text{dpa})_4\text{Cl}_2$ . In  $\text{Ni}_5$  EMACs, the inner and outer Ni have dissimilar coordination to yield varied breathing wavenumbers for the pyridyl rings in ligands. The following table summarizes the assignment of vibrational normal modes and comparison with spectra for four pentanuclear complexes, the  $\text{Ni}_5$  and  $\text{Co}_5$ . Overall, Co-Co has a stronger bond than

Ni-Ni in the pentanuclear complexes and hence  $\text{Co}_5$  is expected to be electrically more conductive than  $\text{Ni}_5$ .

| Vibrational mode                                                                                         | $\text{Ni}_5(\text{tpda})_4\text{Cl}_2$<br>Exp./Cal. | $\text{Co}_5(\text{tpda})_4\text{Cl}_2$<br>Exp./Cal. |
|----------------------------------------------------------------------------------------------------------|------------------------------------------------------|------------------------------------------------------|
| <br>M-Cl sym. str.      | 216/210<br>(Raman)                                   | 197/189<br>(Raman)                                   |
| <br>M-Cl asym. str.     | 206/175<br>(IR)                                      | 188/194<br>(IR)                                      |
| <br>M-M(in) sym. str.   | 257/254<br>(Raman)                                   | 287/265<br>(Raman)                                   |
| <br>M-M(out) asym. str. | 255/270<br>(IR)                                      | 319/309<br>(IR)                                      |
| <br>M-M(out) sym. str.  | 302/302<br>(Raman)                                   | 355/348<br>(Raman)                                   |
| <br>M-M asym. str.     | 297/297<br>(IR)                                      | 391/388<br>(IR)                                      |

Vibrational motions and wavenumbers ( $\text{cm}^{-1}$ ) involving metals for  $\text{Ni}_5(\text{tpda})_4\text{Cl}_2$  and  $\text{Co}_5(\text{tpda})_4\text{Cl}_2$ .

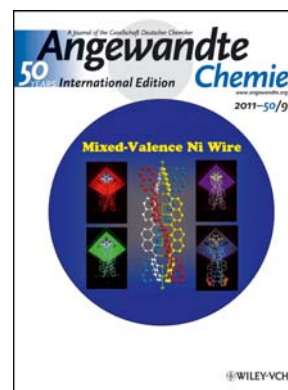
For  $\text{Cr}_5$  and  $\text{Cr}_7$  EMACs, the vibrational peak at  $280\text{ cm}^{-1}$  is assigned to the symmetric stretching mode of Cr-Cr in the s-form for the  $\text{Cr}_5$  complex. The vibrational wavenumber for the stretching motion of the Cr-Cr quadruple bond is  $570\text{ cm}^{-1}$  for  $\text{Cr}_3$  and  $\text{Cr}_5$  complexes and  $554/571\text{ cm}^{-1}$  for  $\text{Cr}_7$  complexes. These three metal-string complexes have Cr-Cr quadruple bonding with approximately equal strength. The metal-string complexes with metal ions arranged linearly display a large absorption coefficient for the d-d band in the visible range. For the  $\text{Cr}_3$  and  $\text{Cr}_5$  EMACs at  $632.8\text{ nm}$ , the absorption coefficient is  $5000\sim 7000\text{ cm}^{-1}\text{M}^{-1}$  greater than that of chromium acetate. This condition might enable resonant enhancement of the Raman intensity for the metal-related modes, especially the metal-metal stretching band. For the  $\text{Cr}_7$  complex, the d-d bands may red shift to the near-IR range. Weak enhancement in spectral intensity is observed for the metal-related modes. The experimental data show that the  $\text{Cr}_5$  complex in both s- and u-structures exists in their crystalline forms. In solution phase when the complex is bound to the metal surface of nanoparticles, no major structural variation is observed, according to the recorded Raman lines. We assumed the complex to be in thermal equilibrium. The s-form is accordingly present in a large proportion. The u-form is thermally accessible via the s-form, indicating that the s-form is the ground state. For  $\text{Cr}_7$  complexes, the u-form is identified in SERS spectra and exists in addition to the more stable s-form. X-ray diffraction is unable to distinguish these two structures for such large metal-string complexes. The  $\text{Cr}_7$  complexes of pyrazine-modulated oligo- $\alpha$ -pyridylamido ligands show localized structures consisting of three quadruple Cr-Cr bonds and a single terminal Cr(II) atom, according to the results of X-ray diffraction. With varied ligands, these complexes show variation on the bonding of metal ions and multiple oxidation forms.

**Concluding Remarks:**

Based on the framework of the prototypical oligo- $\alpha$ -pyridylamine, we recently developed new families of pyrazine- and naphthyridine-modulated ligands by substituting the pyridine (py) rings. Particularly interesting is the naphthyridine group which is rigid and potentially redox active and can stabilize nickel ions in a low oxidation state. Mixed-valent  $[\text{Ni}_2(\text{napy})_4]^{3+}$  as well as a series of stable, low-oxidation-state-nickel string complexes combining mixed-valency can therefore be prepared. This MV property is important in the tuning and the development of novel electronic materials. In the period of the AOARD project, spectroscopic studies of prototypical nickel, cobalt, and chromium EMACs unveil that, upon excitation for the trimetal complexes, the ground electronic state is rapidly recovered. Therefore, EMACs are expected to be stable and little reactive, and should have potential use as rapidly responding molecular wires. It is our long-term goals to continue (1) the synthesis of novel EMACs with innovative experimental designs, (2) measurements of the spectroscopic, electrical, and energy transfer properties for unique compounds promising for molecular electronics and, in particular, (3) theoretical studies of the underlying physics controlling the electron transfer and transport processes.

## List of Publications:

1. Tsai, T.-W.; Huang, Q.-R.; Peng, S.-M.; Jin, B.-Y. "Smallest Electrical Wire Based on Extended Metal-Atom Chains" *J. Phys. Chem. C* **2010**, *114*, 3641-3644.
2. Cheng, C.-H.; Hung, R.-D.; Wang, W.-Z.; Peng S.-M.; Chen, I.-C. "Excited-State Dynamics of the Metal String Complex  $\text{Co}_3(\text{dpa})_4(\text{NCS})_2$  from Femtosecond Transient Absorption Spectra" *ChemPhysChem* **2010**, *11*, 466-473.
3. Cheng, C.-H.; Hung, R.-D.; Wang, W.-Z.; Peng, S.-M.; Chen, I.-C. "Excited-State Dynamics of Metal String Complex  $\text{Ni}_3(\text{dpa})_4\text{X}_2$  from Femtosecond Transient Absorption Spectra" *ChemPhysChem* **2010**, *11*, 517-524.
4. Wang, W.-Z.; Ismayilov, R. H.; Lee, G.-H.; Wen, Y.-S.; Peng, S.-M. "Study on a pyrazine-modulated tetrapyridyltriamide and its complexes: Synthesis, structure and properties" *J. Molecular Structure* **2010**, *973*, 116-123.
5. Wang, W.-Z.; Ismayilov, R. H.; Lee, G.-H.; Peng, S.-M. "Supramolecular Structure of an Unsymmetrical Pyrazine-modulated Tetrapyridyltriamide and Its Complexes" *J. Chin. Chem. Soc.* **2010**, *57*(4B Sp. Iss. SI), 765-770.
6. Yeh, C.-W.; Liu, I. P.-C.; Wang, R.-R.; Yeh, C.-Y.; Lee, G.-H.; Peng, S.-M. "Linear Tetranickel String Complexes with Mixed Supported Ligands and Mixed-Valence Units  $[\text{Ni}_2]^{3+}$ : Synthesis, Crystal Structure, and Magnetic Studies", *Eur. J. Inorg. Chem.* **2010**, *20*, 3153-3159.
7. Hua, S.-A.; Huang, G.-C.; Liu, I. P.-C.; Kuo, J.-H.; Jiang, C.-H.; Chiu, C.-L.; Yeh, C.-Y.; Lee, G.-H.; Peng, S.-M. "Manipulation of electronic structure *via* supporting ligands: a charge disproportionate model within the linear metal framework of asymmetric nickel string  $[\text{Ni}_7(\text{phdptry})_4\text{Cl}](\text{PF}_6)_3$ ", *Chem. Commun.* **2010**, *46*, 5018-5020.
8. Shih, K.-N.; Huang, M.-J.; Lu, H.-C.; Fu, M.-D.; Kuo, C.-K.; Huang, G.-C.; Lee, G.-H.; Chen, C.-H.; Peng, S.-M. "On the tuning of electric conductance of extended metal atom chains via axial ligands for  $[\text{Ru}_3(\mu_3\text{-dpa})_4(\text{X})_2]^{0/+}$  ( $\text{X} = \text{NCS}^-, \text{CN}^-$ )", *Chem. Commun.* **2010**, 1338-1340.
9. Hua, S.-A.; Liu, I. P.-C.; Hasanov, H.; Huang, G.-C.; Ismayilov, R. H.; Chiu, C.-L.; Yeh, C.-Y.; Lee, G.-H.; Peng, S.-M. "Probing the electronic communication of linear heptanickel and nonanickel string complexes by utilizing two redox-active  $[\text{Ni}_2(\text{napy})_4]^{3+}$  moieties", *Dalton Transactions* **2010**, 3890-3896. (Cover Picture)
10. Kuo, C.-T.; Yu, J.-Y.; Huang, M.-J.; Chen, C.-h. "On the Size Evolution of Gold-Monolayer-Protected Clusters by Ligand Place-Exchange Reactions: The Effect of Headgroup-Gold Interactions", *Langmuir* **2010**, *26*, 6149-6153.
11. Ko, C.-H.; Huang, M.-J.; Fu, M.-D.; Chen, C.-h., "Superior Contact for Single-Molecule Conductance: Electronic Coupling of Thiolate and Isothiocyanate on Pt, Pd, and Au", *J. Am. Chem. Soc.* **2010**, *132*, 756-764.
12. Ismayilov, R.-H.; Wang, W.-Z.; Lee, G.-H.; Yeh, C.-Y.; Hua, S.-A.; Song, Y.; Rohmer, M.-M.; Bénard, M.; Peng, S.-M. "Two Linear Undecanickel Mixed-Valence Complexes: Increasing the Size and The Scope of the Electronic Properties of Nickel Metal Strings", *Angew. Chem. Int. Ed.* **2011**, *50*, 2045-2048. (Back Cover)
13. Kuo, J.-H.; Tsao, T.-B.; Lee, G.-H.; Lee, H.-W.; Yeh, C.-Y.; Peng, S.-M. "An Extended Metal Chain with the 2,7-Bis(dipyridyldiamino)-1,8-naphthyridine ( $\text{H}_4\text{bdpdany}$ ) Ligand - The Longest Even-Numbered Metal Chain Complex", *Eur. J. Inorg. Chem.* **2011**, *13*, 2025-2028.
14. Huang, Y.-M.; Lai, S.-H.; Lee, S. J.; Chen, I.-C.; Huang, C. L.; Peng, S.-M.; Wang, W.-Z. "Metal-Metal Bonding and Structures of Metal-String Complexes: Tripyridyldiamido



- Pentanickel and Pentacobalt from IR, Raman, and Surface-Enhanced Raman Scattering Spectra", *J. Phys. Chem. C* **2011**, *115*, 2454-2461.
15. Huang, Y.-M.; Tsai, H.-R.; Lai, S.-H.; Lee, S. J.; Chen, I.-C.; Huang, C. L.; Peng, S.-M.; Wang, W.-Z. "Bonding between Chromium Atoms in Metal-String Complexes from Raman Spectra and Surface-Enhanced Raman Scattering: Vibrational Frequency of the Chromium Quadruple Bond", *J. Phys. Chem. C* **2011**, *115*, 13919-13926.
16. Lee, S.-L.; Huang, M.-J.; Chen, C.-h.; Wang, C.-I.; Liu, R.-S., "Diode-like *I*-*V* Characteristics of a Nonplanar Polyaromatic Compound: a Spectroscopic Study of Isolated and Stacked Dibenzo[*g,p*]chrysene", *Chem.-Asian J.* **2011**, *6*, 1110. (Inside Cover)

**DD882:** There is no material from this project required to fill in Form DD882 (the inventions disclosure form).