Final Report for AOARD Grant AOARD-08-4124

"Synthesis, Characterizations and Applications of Molecular Metal Wires and Functional Nanomaterials"

December 22, 2009

Name of Principal Investigators:	Shie-Ming Peng	Co-PI:	Chun-hsien Chen
- e-mail address :	smpeng@ntu.edu.tw		chhchen@ntu.edu.tw
- Institution :	National Taiwan University		National Taiwan University
- Mailing Address :	No. 1, Roosevelt Rd., Sec. 4,		No. 1, Roosevelt Rd., Sec. 4,
-	Taipei, Taiwan 10617		Taipei, Taiwan 10617
- Phone :	+886-2-3366 1655		+886-2-3366 4191
- Fax :	+886-2-8369 3765		

Period of Performance: 08/01/2008 – 07/31/2009

Report Documentation Page	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE **23 DEC 2009**	2. REPORT TYPE **FInal**	3. DATES COVERED **08-08-2008 to 07-09-2009**

4. TITLE AND SUBTITLE **Syntheses, Characterizations, and Applications of Molecular Metal Wires and Functional Nanomaterials**	5a. CONTRACT NUMBER **FA23860814124**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) **Shie-Ming Peng**	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **National Taiwan University,1 Roosevelt Rd Sec 4,Taipei ,Taiwan,TW,106**	8. PERFORMING ORGANIZATION REPORT NUMBER **N/A**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) **AOARD, UNIT 45002, APO, AP, 96337-5002**	10. SPONSOR/MONITOR’S ACRONYM(S) **AOARD**
	11. SPONSOR/MONITOR’S REPORT NUMBER(S) **AOARD-084124**

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
This report is on research into novel extended metal atom chains and their properties, such as crystallographic, structural, magnetic, electrochemical, and electric conductive properties.

15. SUBJECT TERMS
Chemical Synthesis, Molecular Electronics, Inorganic Chemistry

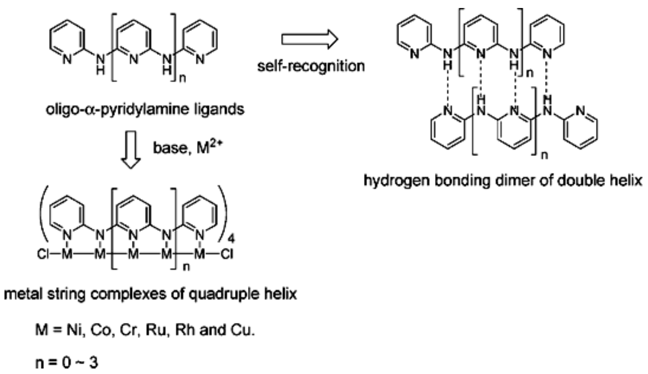
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**14**	

Abstract: Accomplished in this AOARD project are novel EMACs (Extended Metal Atom Chains) and their interesting physical chemistry, such as crystallographic, structural, magnetic, electrochemical, and electric conductive properties. A prototypical EMAC is a linear chain of the first-row transition metals ligated helically by four oligo-α-pyridylamido anions. With the advancement in the synthetic approach over the past years, we prepared $[Ru_5(\mu_5\text{-tpda})_4X_2]$ ($tpda^{2-}$ = tripyridyldiamido dianion, X = Cl and NCS; *J. Am. Chem. Soc.* **2008**, *130*, 10090) in which the metal center is an inert second-row transition metal. The values of single-molecule conductance for such pentaruthenium EMACs, other triruthenium and trirhodium EMACs (*Dalton Trans.* **2009**, 2623) were obtained without and with electrochemical control. The latter along with the selection of the axial ligands contribute means to tune the molecular conductance (*Chem. Commun.* **2010**, accepted in Dec. 2009). New pyrazin-based ligands (*J. Coord. Chem.* **2009**, *62*, 2974; *Eur. J. Inorg. Chem.* **2009**, 2110; *Dalton Trans.* **2008**, 6808) and several naphthyridyl group modulated oligo-α-pyridylamido ligands were designed (*Chem. Commun.* **2009**, 577). These 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 interesting properties (*Dalton Trans.* **2009**, 3571; *Dalton Trans.* **2010**, accepted in Dec. 2009). For example, the dinuclear units contain a delocalized unpaired electron and enhance the conductance of EMACs significantly. Asymmetric naphthyridyl ligands can stabilize the central heterometals or stabilize unevenly distributed charges at the metal frameworks (*Chem. Commun.* **2009**, 577). Therefore, the asymmetric ligands might furnish EMACs a category of inorganic molecular rectifiers (*Chem. Commun.* **2009**, 4323).

Introduction:

Collective work on EMACs (Extended Metal Atom Chains) from our group and others has been reviewed in the *Feature Article* published in *Chem. Commun.* (**2009**, 4323) and a monograph in *Nano Redox Sites: Nano-Space Control and its Applications* (ed. T. Hirao, Springer, Berlin, 2006, Ch. 5, pp. 85–117) which provide a complete version of the importance and goals of this research.

The advocate of molecular electronics beginning in 1974 by Ratner drove the need of unraveling the fundamental issues of molecular wires, one of the most basic building blocks. The design of molecular wires and the follow-up exploration of their properties are essential for the future devices involving electron transport through a molecule which might function like a molecular wire, a voltage-activated switch, or a single-molecule transistor. Among the molecules reported in this research field,[1] EMACs[2] are particularly attractive because these complexes are similar to the electric wires in our macroscopic world and considered to be potential nanomaterials in molecular electronics. The prototypical framework of the metal string complexes consists of a one-dimensional linear transition metal backbone in which the metal centers are supported by four oligo-α-pyridylamido ligands (Scheme 1). These oligo-α-pyridylamine ligands contain numerous pyridino and amino groups, and thus result in the formation of double helix structures in nonpolar solvents due to hydrogen bonding.[3] After deprotonation of oligo-α-pyridylamine ligands, the resulting anions can stabilize the linear metal cores. Up to now, by suitable synthetic strategies, a number of trimetal complexes, *e.g.* $[M_3(dpa)_4Cl_2]$ (M = Ni^{II}, Co^{II}, Cr^{II}, Cu^{II}, Ru^{II}, and Rh^{II}, dpa^{-} = dipyridylamido),[4] pentametal complexes $[M_5(tpda)_4Cl_2]$ (M = Ni^{II}, Co^{II}, Cr^{II} and Ru^{II}, $tpda^{2-}$ = tripyridyldiamido),[5] heptametal complexes $[M_7(teptra)_4Cl_2]$ (M = Ni^{II} and Cr^{II}, $teptra^{3-}$ = tetrapyridyltriamido)[6] and nonametal complexes $[M_9(peptea)_4Cl_2]$ (M = Ni^{II} and Cr^{II}, $peptea^{4-}$ = pentapyridyltetraamido)[7] have been prepared and characterized. Since one of the goals of designing metal string complexes is for future potential molecular-scale wires, their conductance, definitely, should be an interesting topic to study and has been explored quantitatively by STM-BJ (scanning tunneling microscopy-breaking junction).[8,9]



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

In addition to the potential applications of metal string complexes, much attention has also been paid to the study of multicenter metal–metal bonds.[10] Because of the arrangement of the metal ions, the various interactions between adjacent metal ions significantly extend the scope of the previous research which focused on metal–metal bonds of simple dinuclear metal compounds. Interestingly, the strength of metal–metal bonds does not only reflect the interaction between metal ions, but also correlates qualitatively to the electric conductance. The STM measurements show that resistances of $[Ni_3(dpa)_4(NCS)_2]$, $[Co_3(dpa)_4(NCS)_2]$, $[Cr_3(dpa)_4(NCS)_2]$, $[Ni_5(tpda)_4(NCS)_2]$, $[Co_5(tpda)_4(NCS)_2]$ and $[Cr_5(tpda)_4(NCS)_2]$ were 3.4 MΩ, 1.9 MΩ, 0.9 MΩ, 24 MΩ, 10 MΩ, and 3.2 MΩ, respectively. Considering that the metal–metal bond orders for nickel, cobalt and chromium string complexes are 0, 0.5 and 1.5, it shows that the ET efficiency of metal string complexes is dependent on the extent of charge delocalization along the linear metal framework. Consequently, the metal string complexes with stronger metal–metal interaction exhibit the better conductivity.[9] According to the Robin–Day classification, mixed-valence (MV) compounds with delocalized unpaired electrons belong either to Class II (partly delocalized) or to Class III (fully delocalized) and are expected to transport electrons.[11] Therefore, for prototypical EMACs integrated with an MV moiety, the conductance might be improved due to the easier transport of electrons along the metal chain.

Among the currently available Class II and Class III MV compounds, $[Ni_2(napy)_4(X)_2](BPh_4)$ (napy = 1,8-naphthyridine; X = Cl, Br, I) could represent a good candidate for the synthesis of new metal wires due to the presence of three delocalized electrons in the dinickel core and similar structure conformation with metal string complexes.[12] The coupling of two 1,8-naphthyridine molecules with amino groups provides an alternative to oligo-α-pyridylamido ligands for the synthesis of nickel string complexes based on dinickel mixed-valence units (Scheme 2). The resulting compound $[Ni_5(bna)_4(NCS)_2](NCS)_2$ (bna^- = bisnaphthyridylamido) shows about 40% enhancement of the conductance in comparison with those of the typical pentanickel complex, indicative of great electron mobility within the $[Ni_5]^{8+}$ framework.[13] This exciting result encouraged us to develop novel metal string complexes by designing new naphthyridyl group modulated ligands.[14] In this report, the synthesis of naphthyridyl group modulated ligands and related metal string complexes and those published or accepted by peer-reviewed Journals will be highlighted.

Scheme 2 The concept for designing the naphthyridyl group modulated oligo-α-pyridylamine ligand (*Chem. Commun.* **2009**, 4323).

Experiment:

General procedures for EMAC synthesis. Examples of preparing $[Ru_3(\mu_3\text{-dpa})_4(NCS)_2]$ and are described in the following. The former represents the second-row transition metal coordinated by prototypical pyridylamido ligands. The latter shows examples of EMACs using the new generation ligands containing naphthyridylamido group. Procedures for other EMACs are referred to the journal articles listed in the publication list.

$[Ru_3(\mu_3\text{-dpa})_4(NCS)_2]$. To a 100-mL round bottom flask, Hdpa (171 mg, 1 mmol), $Ru_2(OAc)_4Cl$ (354 mg, 0.75 mmol), and LiCl (100 mg) were dissolved in melted naphthalene (20 g).

The mixture was heated to ~160 ^{o}C for 20 min and then raised to ~220 °C. *t*-BuOK (112 mg, 1 mmol, in *n*-BuOH) was added dropwise into the mixture and the reaction temperature was maintained at ~220 °C for another 1.5 hr. 200-mg NaNCS was then added to this solution to replace the axial ligand. After 30 min, this solution was cooled to ~50 °C and 100-mL hexane was added. After filtration, the crude was washed 3 times with the same amount of hexane to remove naphthalene. 100-mL CH_2Cl_2 was added to extract the product. After filtration, 130-mg dark brown crystals were formed by layering the solution with ether (yield 42%). FAB-MS(m/z): 1100 $[M+H]^+$. IR(KBr, cm^{-1}): 3070 w ($\upsilon_{CH,\ arom}$), 2030 ($\upsilon_{C\equiv N}$, NCS), 1603, 1592 s ($\upsilon_{C=C}$, $\upsilon_{C=N}$), 1460 s, 1425 m, 1362 m, 1311 m, 1156 s, 1025 m, 754 w, 736 m.

$[CuCuM(npa)_4Cl][PF_6]$ (M = Pd or Pt). The Hnpa ligand was prepared by reaction of 2-chloro-1,8-naphthyridine and aniline with a palladium catalyst. Treatment of Hnpa with $CuCl_2$ and K_2PdCl_4 (or K_2PtCl_4) in the presence of *t*-BuOK, followed by excess of KPF_6, generated compound (4,0)$[CuCuPd(npa)_4Cl][PF_6]$ or (4,0)$[CuCuPt(npa)_4Cl][PF_6]$.

Synthesis of 2-naphthyridylphenylamine (Hnpa). Aniline (10 mL, 110 mmol), 2-chloro-1,8-naphthyridine (5.00 g, 30 mmol), *t*-BuOK (5.06 g 45 mmol), $Pd_2(dba)_3$ (0.40 g 0.44 mmol) and dppp (0.50 g, 1.2 mmol) (dba = dibenzylideneacetone; dppp = 1,3-bis(diphenylphosphino)propane). The mixture was stirred and refluxed for 72 h. The solvent was removed under reduced pressure. The mixture was washed with water and the precipitate was extracted by CH_2Cl_2 to obtain a yellow-orange product, Hnpa (yield: 73%). 1H-NMR (400 MHz, $(CD_3)_2SO$): 9.69 (s, 1H), 8.76 (m, 1H), 8.14 (dd, J = 8, 2 Hz, 1H), 8.08 (d, J = 8.8 Hz, 1H), 8.02 (dd, J = 8.8, 1.2 Hz, 2H), 7.31 (m, 3H), 6.98 (t, J = 7.2 Hz, 2H); MS(FAB) m/z 222.1 ($[M + H]^+$).

Synthesis of (4,0)$[CuCuPd(npa)_4Cl][PF_6]$. Hnpa (0.89 g, 4 mmol), $CuCl_2$ (0.27 g, 2 mmol), K_2PdCl_4 (0.33 g, 1 mmol) and 40 g naphthalene (as solvent) were placed in an Erlenmeyer flask. After stirring the mixture at 150 °C for 2 h, *t*-BuOK (0.44 g, 4 mmol) in *t*-BuOH (30 mL) was added dropwise. The resulting solution was then stirred for an additional 3 h. After cooling the mixture to 80 °C, hexane was added and the resulting precipitate was filtered out. The metal complex was extracted with CH_2Cl_2 and treated with KPF_6 (0.36 g, 2 mmol) in CH_2Cl_2 (100 ml). The resulting solution was stirred for a week and dried under vacuum. (4,0)$[CuCuPd(npa)_4Cl][PF_6]$ was extracted with CH_2Cl_2 and recrystallized in DMF–ether (yield: 25%). MS(FAB) m/z: 1147 $[CuCuPd(npa)_4Cl]^+$, 1112 $[CuCuPd(npa)_4]^+$; EA (%): $[CuCuPd(npa)_4Cl][PF_6]\cdot[HCON(CH_3)_2]$: calcd. C 51.80, H 3.46, N 13.31; found: C 52.32, H 3.96, N, 13.46%.

Synthesis of (4,0)$[CuCuPt(npa)_4Cl][PF_6]$. Hnpa (0.89 g, 4 mmol), $CuCl_2$ (0.27 g, 2 mmol), K_2PtCl_4 (0.42 g, 1 mmol) and 40 g naphthalene (as solvent) were placed in an Erlenmeyer flask. After stirring the mixture at 150 °C for 3 h, *t*-BuOK (0.44 g, 4 mmol) in *t*-BuOH (30 mL) was added dropwise. The resulting solution was then stirred for an additional 4 h. After cooling the mixture to 80 °C, hexane was added and the resulting precipitate was filtered out. The metal complex was extracted with CH_2Cl_2 and treated with KPF_6 (0.36 g, 2 mmol) in CH_2Cl_2 (100 mL). The resulting solution was stirred for a week and dried under vacuum. (4,0)$[CuCuPt(npa)_4Cl][PF_6]$ was extracted with CH_2Cl_2 and recrystallized in CH_2Cl_2–ether (yield: 8%). MS(FAB) m/z: 1236 $[CuCuPt(npa)_4Cl]^+$, 1201 $[CuCuPt(npa)_4]^+$; EA (%) $[CuCuPt(npa)_4Cl][PF_6]$: calcd. C 48.61, H 2.91, N 12.15; found: C 47.85, H 2.94, N 12.47%. The crystal structures of (4,0)$[CuCuPd(npa)_4Cl][PF_6]$ and (4,0)$[CuCuPt(npa)_4Cl][PF_6]$ are similar. Their core structures exhibit a $(Cu_2M)^{6+}$ (M = Pd or Pt) chain helically wrapped by four npa^- ligands. The npa^- ligands adopt a (4,0) arrangement with all anilino N ions coordinated to the M atom, and all naphthyridine N atoms coordinated to two Cu atoms, which appears approximated C_4 symmetry. Due to the steric effect of the four phenyl groups, the counter-anion could not approach the M atom in the axial position, which causes the M atom to be square planar coordinated. The coordination environment of the terminal copper forms a distorted square pyramid; the coordination environment of the inner copper is distorted square planar. The interesting feature here is the unique (4,0) conformation, because this conformation may be controlled by utilizing hetero-metal atoms. The M atom prefers to bond to four anilino N ions, which avoids the presence of other regioisomers which result from the inequivalence of the asymmetric ligand. When asymmetric heterometal string complexes are synthesized using the symmetric dpa ligand, a significantly disordered structure results which causes poor X-ray characterization accuracy. (4,0)$[CuCuPd(npa)_4Cl][PF_6]$ and (4,0)$[CuCuPt(npa)_4Cl][PF_6]$ do not possess this problem. The two terminal Cu and M atoms can be clearly identified by X-ray crystallography because of the high asymmetry of the molecules.

Experimental procedures for STM break junction.

Au, Pd, and Pt wires with 0.1-inch in diameter (99.95%, Leesan, Tainan, Taiwan) were mechanically cut by a side cutter and utilized as the STM tips. 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 or thiol headgroup at the termini of the polymethylene chains 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_o, the conductance quantum taking place when the cross section of a metallic contact is only that of a single atom ($G_o = 2e^2/h$, ~$(12.9\ \mathrm{k}\Omega)^{-1}$).[15]

The concentration of molecules in toluene 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_o. 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 *I*(*s*) traces were recorded by a NanoScope built-in program and exported as ASCII files. 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.

To acquire single-molecule *I*-V curves, it is necessary to obtain the values of single-molecule conductance. For example, the single-molecule conductance of $Au\text{-}S(CH_2)_6S\text{-}Au$ was 92.9 nS (vide infra), corresponding to 4.7 nA under a bias voltage of 50 mV, which were the respective settings of $i_{\mathrm{tunneling}}$ and E_{bias} for STM imaging. After the imaging started, the instrument was switched to STS_I(V) mode, the feedback loop was turned off, and the voltage was ramping from 1.0 volt to –1.0 volt at a scan rate of 1.4 Hz. The current as a function of the bias voltage was recorded. Most of the *I*-V curves were simply tunneling between the electrodes. For all headgroup-electrode combinations, approximately 15% of the *I*-V curves contained only one molecule present within the junction. The single-molecule *I*-V curves were reconfirmed by their slopes around zero bias where single molecules appeared ohmic and the slopes laid closely to the value of single-molecule conductance.

Simulations.

Simulations for $(4,0)[CuCuPd(npa)_4Cl][PF_6]$ and $(4,0)[CuCuPt(npa)_4Cl][PF_6]$ are described in the following as examples. Details for other EMACs are referred to the corresponding literature. Calculations and geometry optimizations on $[CuCuM(npa)_4Cl][PF_6]$ (M = Pd or Pt) had been carried out using the Density Functional Theory (DFT) formalism with the spin unrestricted option, as implemented in the Gaussian 03 software, with the B3LYP exchange-correlation functional. All-electron valence double-ζ 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 Cu and the *n*s, *n*p, and *n*d cores of heavier metal atoms ($n = 3$ for Pd, $n = 4$ for Pt). The valence shell of chlorine and all types of metal atoms were described at the double-ζ level (LanL2DZ basis). The antiferromagnetic low-spin state had been characterized and its geometry was optimized using the broken symmetry (BS) approach that was first proposed by Ginsberg, and then developed by Noodleman. The exchange parameter *J* between two magnetic centers A and B is defined as follows by Heisenberg-Dirac-van Vleck (HDvV) Hamiltonian:

$$\hat{H}^{\mathrm{HDvV}} = -J\, \hat{S}_A \bullet \hat{S}_B$$

Since the broken-symmetry solutions were not proper eigenvalues of $\hat{S}$, but a weighted average of the energies of the pure spin multiplets, an approximate projection technique was employed, as proposed and used by Yamaguchi et al. within the ab initio or the DFT frameworks:

$$J = 2({}^{BS}E - {}^{HS}E) / ({}^{HS}\langle S^2\rangle - {}^{BS}\langle S^2\rangle)$$

where ${}^{HS}\langle S^2 \rangle$ and ${}^{BS}\langle S^2 \rangle$ denote the total spin angular momentum calculated in the high spin and in the broken symmetry solutions, respectively.

Simulations for molecular conductance, the optimization of the geometries and calculations of the energies were carried out by using the density functional theory (DFT) method using the Gaussian 03 program, with the Becke's three parameter hybrid functional with Perdew-Wang91 correlation functional (B3PW91), the LANL2DZ relativistic effective core potential for Au, Pd, and Pt, and the 6-31+G* basis set for C, H, N, and S. Each electrode was modeled using a total of 36 atoms composed of a two-layered (3 x 3 x 2) unit cell. The lattice parameters were adapted from those of bulk materials and were fixed throughout the simulations. The calculations of Mayer 2-center bond orders were obtained using AOMix (http://www.sg-chem.net/download.php) to analyze the chemical bonding at the headgroup-electrode contact.[16] DFT/B3LYP analysis was carried out for the EMACs with Gaussian 03w package using LANL2DZ on metal center.

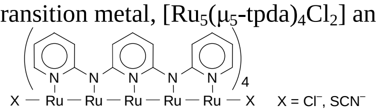
The NEGF-DFT (nonequilibrium Green's function) method implemented in the ATK 2008.10 computational technique was employed to calculate the transmission functions and the current-voltage characteristics for the MMM configurations. Single-ζ plus polarization (SZP) basis was used for the metals with the same electrode structures obtained from Gaussian 03. For C, H, N, and S, double-ζ plus polarization (DZP) basis set was used. Perdew-Zunger local density approximation (LDA) functional is adopted for exchange-correlation. The *I*-V characteristics were obtained for applied biases in the range from 0.0 to 0.5 V.

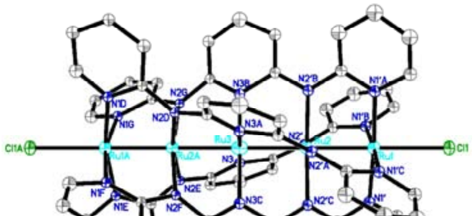
Results and Discussion:

1. Synthetic Challenges.

1-1. "Extended Metal-Atom Chains with an Inert Second Row Transition Metal: $[Ru_5(\mu_5\text{-tpda})_4X_2]$ ($tpda^{2-}$ = tripyridyldiamido dianion, X = Cl and NCS)" (*J. Am. Chem. Soc.* **2008**, *130*, 10090-10092).

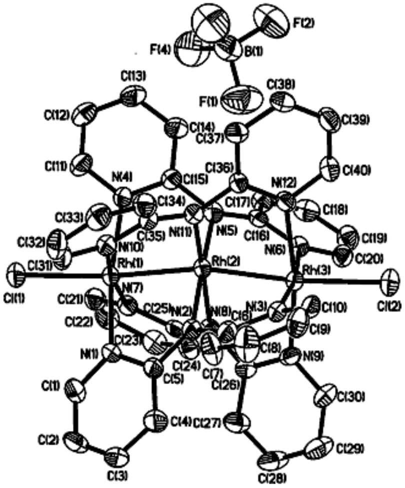
There has been significant advances on the synthesis of EMACs, such as lengthening the chains up to 11 metal atoms thus far, integrating naphthyridine moieties for tuning the charge carried at metal centers, and manipulation of metal−metal interactions. However, the metal centers in EMACs hitherto are limited to first row transition metals which are more labile than those relatively inert ones with electrons filled in the 4d and 5d shells. This study further scrutinizes metal−metal interactions via crystallographic, magnetic, electrochemical, and electrical conducting studies for the first pentanuclear EMACs of second-row transition metal, $[Ru_5(\mu_5\text{-tpda})_4Cl_2]$ and $[Ru_5(\mu_5\text{-tpda})_4(NCS)_2]$.





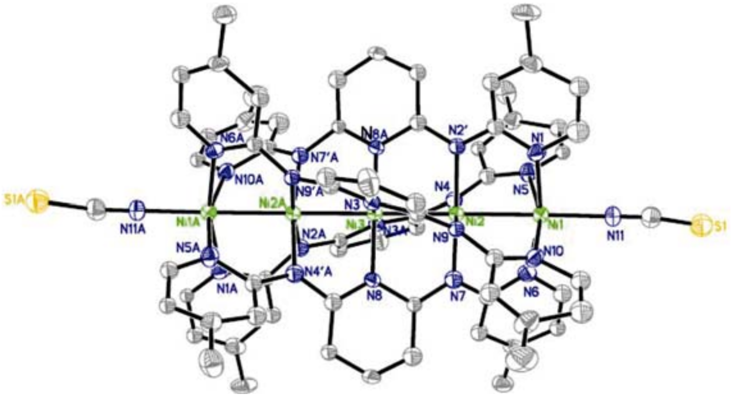
1-2. "Further Investigations of Linear Trirhodium Complexes: Experimental and Theoretical Studies of $[Rh_3(dpa)_4Cl_2]$ and $[Rh_3(dpa)_4Cl_2](BF_4)$ [dpa = bis(2-pyridyl)amido anion]" (*Dalton Trans.* **2009**, 2623-2629).

$Rh_3(dpa)_4Cl_2$ and its one-electron oxidation product, $[Rh_3(dpa)_4Cl_2](BF_4)$ are EMACs with second-row transition metal centers. The magnetic behavior of the neutral form indicates the presence of one unpaired electron, assigned to occupy the σ_{nb} orbital (${}^2A_2$) by DFT calculations. Upon oxidation, a β-spin electron is removed. The resulted $[Rh_3(dpa)_4Cl_2](BF_4)$ is a triplet ground state. DFT calculations and ${}^1H$ NMR spectra suggest that the two unpaired electrons occupy σ_{nb} and δ^* orbitals (${}^3B_1$). Unlike their isoelectronic analogues $[Co_3(dpa)_4Cl_2]$ and $[Co_3(dpa)_4(Cl)_2](BF_4)$, the rhodium EMACs do not exhibit the spin-crossover behavior, which might be attributed to the relative large energy gap between ${}^3B_1$ and open-shell singlet ${}^1B_1$ states.



1-3. "Synthesis, Structure, Magnetism, and electrochemical Properties of a Linear Pentanuclear Ni_5 Compound Derived from an Oligo-α-Pyridylamino Ligand: Ni_5(μ-dmpdda)$_4$(NCS)$_2$" (*J. Coord. Chem.* **2009**, *62*, 2974-2982).

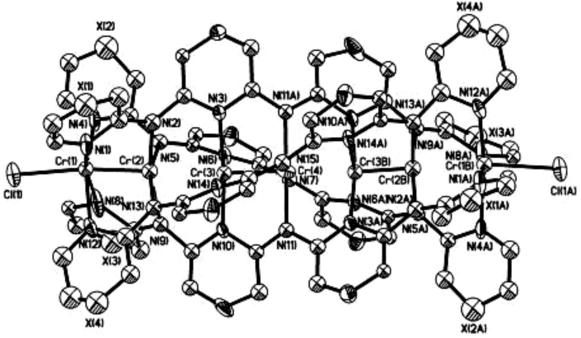
H_2dmpdda [*N*,*N*'-di(4-methylpyridin-2-yl)pyridine-2,6-diamine], a new ligand, and the corresponding pentanickel EMAC were designed and prepared. There are two types of Ni-Ni distances in this complex. Terminal Ni-Ni distances bonded with the axial ligand are longer (2.377 Å); the inner Ni-Ni distances are short at 2.2968 Å. Terminal Ni^{II} ions bonded with the axial ligands are square-pyramidal (NiN_4NCS) with long Ni-N bonds (2.092 Å), consistent with a high-spin Ni^{II} configuration. The inner three Ni^{II} ions have short Ni-N (1.901-1.925 Å) bond distances, consistent with a square planar (NiN_4), diamagnetic arrangement of a low-spin Ni^{II} configuration. This compound exhibits magnetic behavior similar to [Ni_5(μ-tpda)$_4$(NCS)$_2$], indicating an antiferromagnetic interaction of two terminal high-spin Ni^{II} ions.



1-4. "Redox Modification of EMACs Through the Tuning of Ligands: Heptametal(II) Complexes of Pyrazine-Modulated Oligo-α-Pyridylamido Ligands" (*Eur. J. Inorg. Chem.* **2009**, 2110).

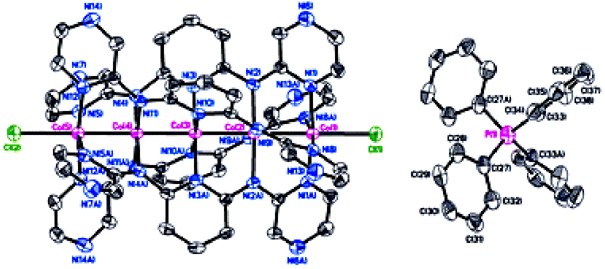
New ligands of pyrazine-modulated oligo-α-pyridylamido anions were designed and prepared. H_3pzpz {N^2-(pyrazin-2-yl)-N^6-[6-(pyrazin-2-ylamino)pyridin-2-yl]pyridine-2,6-diamine} and H_3tpz {N^2-(pyrazin-2-yl)-N^6-[6-(pyridin-2-ylamino)pyridin-2-yl]pyridine-2,6-diamine} were employed to synthesize linear heptametal EMACs, [M_7(μ_7-L)$_4X_2$] [L = pzpz^{3-}, M = Ni^{II}, X = Cl^-, NCS^-; M = Cr^{II}, X = Cl^-, NCS^-; L = tpz^{3-}, M = Cr^{II}, X = Cl^-, NCS^-]. Electrochemical studies showed that heptanickel complexes can undergo one reversible oxidation at +0.46 V and +0.52 V for axial ligands of Cl^- and NCS^-, respectively. [Cr_7(μ_7-pzpz)$_4Cl_2$] exhibited two reversible, one-electron oxidation peaks at +0.61 and +0.88 V, and [Cr_7(μ_7-tpz)$_4Cl_2$] exhibited three reversible, one-electron oxidation peaks at

+0.40, +0.68 and +1.07 V. The redox peaks shifted positively when axial ligands changed from chloride to thiocyanate anions, at +0.67 and +0.92 V for $[Cr_7(\mu_7\text{-pzpz})_4(NCS)_2]$ and +0.44, +0.73 and +1.11 V for $[Cr_7(\mu_7\text{-tpz})_4(NCS)_2]$. The introduction of electron-withdrawing pyrazine rings to the spacer ligand retarded oxidation of the heptametal EMACs and stabilized the complexes. In the two nickel species, both terminal nickel atoms exist in spin state $S = 1$ whereas all the inner nickel atoms exist in spin state $S = 0$. Temperature-dependent magnetic research revealed an antiferromagnetic interaction between the two terminal atoms through a superexchange pathway along metal cores with a parameter of about 4 cm^{-1}. Chromium EMACs showed a localized structure consisting of three quadruple Cr-Cr bonds and a single terminal Cr^{II} atom. Magnetic study revealed a quintet ground state resulting from the isolated, high-spin Cr^{II} atom.



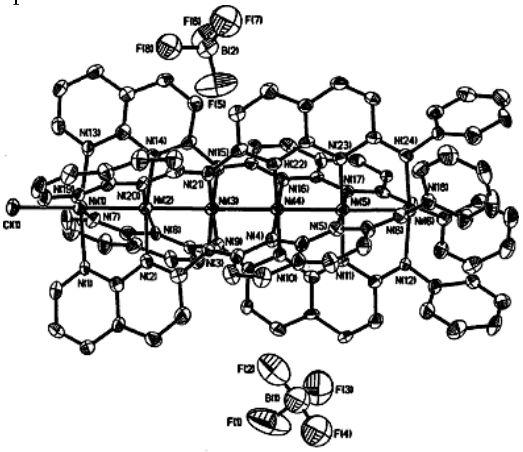
1-5. "First Stable Reduced Form of $[Co_5]^{10+}$: Fine Tuning of Linear Pentacobalt(II) Complexes Containing Delocalized Metal-Metal Bonds through Ligand Modification" (*Dalton Trans.* **2008**, 6808).

A new ligand of pyrazine-modulated tripyridyldiamine ligand was employed to prepare pentacobalt EMAC exhibiting a stable 1-electron reduced form. The ligand is H_2dpzpda, [*N*,*N*'-di(pyrazin-2-yl)pyridine-2,6-diamine]. The structures of the neutral forms ($[Co_5(\mu_5\text{-dpzpda})_4Cl_2]$, $[Co_5(\mu_5\text{-dpzpda})_4(NCS)_2]$) and reduced forms ($(Ph_4P)[Co_5(\mu_5\text{-dpzpda})_4Cl_2]$, $(Ph_4P)[Co_5(\mu_5\text{-dpzpda})_4(NCS)_2]$) showed direct Co–Co bonds with Co–Co distances in the range 2.2385(7)–2.2888(15) Å, and valence electrons delocalized through the whole metal chain with distances of longer than 9.06 Å. The distances of the inner Co–Co bonds and the Co–axial ligands became longer after reduction, whereas no significant change was observed in the distances of the outer Co–Co bonds and Co–N (supporting ligand) bonds, which was consistent with the MO analysis. Electrochemical studies on the neutral forms showed one reversible oxidation and one reversible reduction at $E_{1/2}$ = +0.82 and −0.05 V for $[Co_5(\mu_5\text{-dpzpda})_4Cl_2]$, and at $E_{1/2}$ = +0.89 and +0.02 V for $[Co_5(\mu_5\text{-dpzpda})_4(NCS)_2]$, respectively. The redox reactions of the thiocyanate complex $(Ph_4P)[Co_5(\mu_5\text{-dpzpda})_4(NCS)_2]$ happened at higher potentials than the chloride complex $(Ph_4P)[Co_5(\mu_5\text{-dpzpda})_4Cl_2]$. Magnetism measurements revealed anomalous magnetic behavior similar to that of heptacobalt EMACs, and a deviation from the Curie–Weiss law was observed. The $\chi_M T$ value at 300 K is 0.84 and 1.16 emu K mol^{-1} for $[Co_5(\mu_5\text{-dpzpda})_4Cl_2]$ and $[Co_5(\mu_5\text{-dpzpda})_4(NCS)_2]$, respectively, suggesting spin-equilibrium or a spin-admixture between doublet and quartet states arising from the Boltzmann distribution over different energy levels. Similar results were obtained for the reduced forms, showing intermediate $\chi_M T$ values between a diamagnetic and a triplet state of 0.15–0.96 emu K mol^{-1} in the temperature range 5–300 K. The structural and magnetic results were interpreted through an EHMO study.



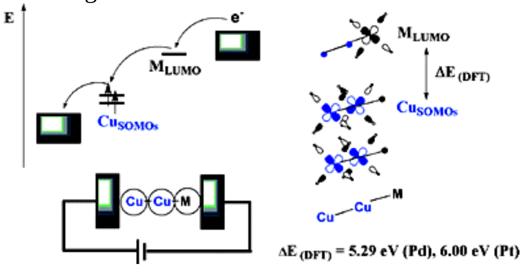
1-6. "Clear Evidence of Electron Delocalization: Synthesis, Structure, Magnetism, EPR and DFT Calculation of the Asymmetric Hexanickel String Complex Containing a Single Mixed-Valence $(Ni_2)^{3+}$ Unit" (*Dalton Trans.* **2009**, 3571-3573).

To explore whether the $(Ni_2)^{3+}$ mixed-valence unit can be a tool to enhance the conductance of EMACs, $(4,0)[Ni_6(napany)_4Cl](BF_4)_2$ was designed and synthesized. This compound contains a unique $(Ni_2)^{3+}$ mixed-valence unit which can provide direct evidence for electron delocalization. The crystal structure, magnetic measurement and EPR spectrum suggest that the three unpaired electrons of the $(Ni_2)^{3+}$ unit are partly delocalized between two Ni ions and the thermal energy to activate this delocalized process is very small. DFT calculation supports the experimental results and demonstrates that the stabilization of the S = 3/2 state is due to electron delocalization. Hence, we consider that this compound may have potential applications in molecular electronic devices. It should be noted that most of the research of metal string complexes has, up to now, focused mainly on symmetric molecules. The extended asymmetric EMAC that possesses a delocalized $(Ni_2)^{3+}$ mixed-valence unit is a suitable candidate for building novel asymmetric inorganic molecular wires and for broadening the scope of molecular electronic devices.



1-7. "Asymmetric heterometal string complexes: stereochemical control of the unique isomer of $(4,0)[CuCuPd(npa)_4Cl][PF_6]$ and $(4,0)[CuCuPt(npa)_4Cl][PF_6]$" (*Chem. Commun.* **2009**, 577).

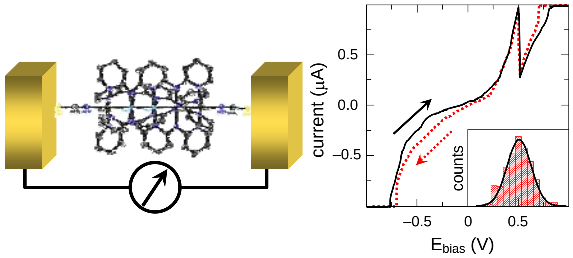
This paper describes the synthesis and physical properties of $(4,0)[CuCuPd(npa)_4Cl][PF_6]$ and $(4,0)[CuCuPt(npa)_4Cl][PF_6]$ in which the metal centers are supported by the anion of new asymmetric 2-naphthyridylphenylamine (Hnpa). The insertion of one or several heterometal(s) in EMACs represents a new avenue by which novel metal string complexes may be developed. We previously synthesized heterometal EMACs by employing the symmetric dipyridylamide (dpa^-) ligand, *e.g.* $[CoPdCo(\mu_3\text{-}dpa)_4Cl_2]$ (*Eur. J. Inorg. Chem.* **2008**, 1767). The introduced metal atoms (M = Pd and Pt) have a tendency to coordinate to the amido N, attributed to the different ligand field strengths of an amido N and a pyridino N and suggesting that an asymmetric heterometallic framework could be designed. The magnetic measurements and DFT calculations suggest that the unpaired electrons of the Cu atoms are antiferromagnetically coupled. Because of the energy barrier between the d-orbitals of neighboring hetero-atoms, these molecules may exhibit rectifier-like behavior and are suitable candidates for future inorganic molecular rectifiers.



2. Conductance of single molecules: heterometal EMACs, under electrochemical controls, and contact resistance.

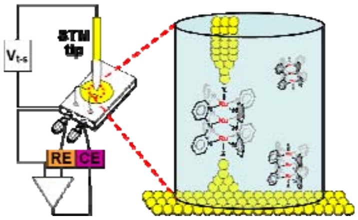
2-1. "Negative Differential Resistance of a Heteropentanulcear Extended Metal-Atom Chain [Ni-Ru_2-Ni_2(tripyridyldiamido)$_4$(NCS)$_2$]: Tuning the Frontier Molecular Orbitals" *Manuscript in preparation*.

In this study we show that, by incorporating a diruthenium moiety into a string of nickel cores, the heteropentametal Ni-Ru-Ru-Ni-Ni EMAC has a single-molecule conductance of 6.3 (± 1.0) MΩ, 4-fold superior to that of the pentanickel analogue (23.3 (± 4.1) MΩ) at the ohmic region and results in NDR characteristics, unobserved for its analogues of pentanickel or pentaruthenium EMACs. Spin-unrestricted DFT/B3LYP analysis shows that the frontier molecular orbitals are contributed by the [Ru_2] unit which reduces the HOMO-LUMO gap to 1.14 eV, significantly smaller than that of 3.03 eV for pentanickel EMAC. More importantly, the [Ru_2] unit is accounted for discrete HOMO levels that lead to the NDR behavior as a result of the energy alignment with the electrode Fermi.



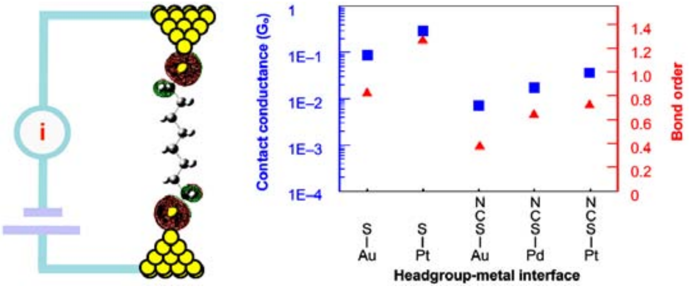
2-2. "On the Tuning of Electric Conductance of Extended-Metal-Atom-Chains via Axial Ligands for [$Ru_3(\mu_3\text{-dpa})_4(X)_2]^{0/+}$ (X = NCS^-, CN^-)" (*Chem. Commun.* **2010**, accepted in Dec. 2009).

The influence of a π-acid cyanide axial ligand on the metal-metal interactions of [$Ru_3(\mu_3\text{-dpa})_4(X)_2]^{0/+}$ (X = NCS^-, CN^-) is manifested by the measurements of single-molecule conductance coupled with *in-situ* electrochemical control. Quantitative values of single-molecule conductance for $[Ru_3(dpa)_4(NCS)_2]^{0/+}$ and $[Ru_3(dpa)_4(CN)_2]^{0/+}$ were obtained. The former appears innocent to the reaction of one-electron redox while the latter exhibited an interesting bistable switching behaviour. DFT calculations illustrated that the metal-metal interactions of Ru_3 EMACs was axial-ligand dependent. Hence, the axial ligand is more than the contact clip to bind onto electrodes in molecular electronics but provide a mean to modulate the electrical behavior of the molecular framework.



2-3. "Superior Contact for Single-Molecule Conductance: Electronic Coupling of Thiolate and Isothiocyanate on Pt, Pd, and Au" (*J. Am. Chem. Soc.* **2010**, accepted in Nov. 2009).

One of the critical issues for the realization of molecular electronics is the development of ideal molecule-electrode contacts that render efficient charge transportation and thus attenuate the unwanted voltage drop and power loss. The conductance at the single-molecule level has long been expected to be correlated strongly with the electrode materials. However, other than gold, systematic studies of a homologous series of molecules to extract the headgroup-metal contact conductance ($G_{n=0}$) have not been reported. Carefully examined herein are the conductance of alkanedithiols anchored onto electrode materials of Au and Pt as well as the conductance of alkanediisothiocyanates on Au, Pd, and Pt by utilizing the method of STM-BJ (scanning tunneling microscopy break junction). In comparison with Au substrate, Pd and Pt are group 10 elements with stronger *d*-orbital characteristics, and larger local density of states near the Fermi level. The model compounds, $SCN(CH_2)_nNCS$ (n = 4, 6, and 8), are studied because the isothiocyanate (−NCS) headgroup is a versatile ligand for organometallics, an emerging class of molecular wires, and can bind to substrates of noble metals to complete a metal-molecule-metal configuration for external *I*–V measurements. Also studied include alkanedithiols, one of the most scrutinized systems in the field of single-molecule conductance. The results show that the conductance for single molecules bridged between a pair of Pt electrodes is about 3.5 folds superior to those between Au electrodes. On all electrode materials, observed are two sets of conductance values, with the smaller set being one order of magnitude less conductive. These findings are ascribed to the degree of electronic coupling between the headgroup and the electrode.



Concluding Remarks:

In summary, fundamental understanding of the electron transport through a molecule between metal electrodes is essential for the development of the emerging technology of molecular electronics, such as molecular wires, voltage-activated switches, and single molecular transistors. Prior to the studies of conductance, magnetism, and spintronics, a range of new EMACs should be explored, prepared, purified, and characterized in detail, including x-ray crystallography, magnetic susceptibility, electrochemistry, and *I–V* characteristics. It is our wish to continue (1) the synthesis of novel EMACs with innovative experimental designs, (2) measurements of the 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.

References:

1. (*a*) *Atomic and Molecular Wires*, ed. C. Joachim and S. Roth, NATO Applied Science, Kluwer, Boston, 1997, vol. 341; (*b*) *Molecular Electronic: Science and Technology*, ed. A. Aviram and M. Ratner, *Ann. N. Y. Acad. Sci.*, 1998, vol. 852; (*c*) *Introduction to Molecular Electronics*, ed. M. C. Petty, M. R. Bryce and D. Bloor, Oxford University Press, New York, 1995; (*d*) *Molecular Wires: From Design to Perspectives*, ed. L. De Cola, *Top. Curr. Chem.*, 2005, p. 257; (*e*) K. Krogmann, *Angew. Chem.*, 1969, **81**, 10; (*f*) J. M. Williams, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 235; (*g*) J. R. Ferraro and J. M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic Press, San Diego, 1987, Ch. 4; (*h*) J. K. Bera and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 2002, **41**, 4453; (*i*) S. Roth, *One-Dimensional Metals*, VCH, New York, 1995; (*j*) *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum, New York, 1982.
2. (*a*) J. F. Berry, F. A. Cotton, P. Lei, T. Lu and C. A. Murillo, *Inorg. Chem.*, 2003, **42**, 3534; (*b*) L.-G. Zhu and S.-M. Peng, *Wuji Huaxue Xuebao*, 2002, **18**, 117; (*c*) C.-Y. Yeh, C.-C. Wang, C.-h. Chen and S.-M. Peng, in *Nano Redox Sites: Nano-Space Control and its Applications*, ed. T. Hirao, Springer, Berlin, 2006, Ch. 5, pp. 85–117.
3. M.-k. Leung, A. B. Mandal, C.-C. Wang, G.-H. Lee, S.-M. Peng, H.-L. Cheng, G.-R. Her, I. Chao, H.-F. Lu, Y.-C. Sun, M.-Y. Shiao and P.-T. Chou, *J. Am. Chem. Soc.*, 2002, **124**, 4287.
4. (*a*) S. Aduldecha and B. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1991, 993; (*b*) G. J. Pyrka, M. El-Mekki and A. A. Pinkerton, *J. Chem. Soc., Chem. Commun.*, 1991, 84; (*c*) L.-P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. Hathaway, C. Simmons and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1990, 3835; (*d*) F. A. Cotton, L. M. Daniels, C. A. Murillo and I. Pascual, *J. Am. Chem. Soc.*, 1997, **119**, 10223; (*e*) J.-T. Sheu, C.-C. Lin, I. Chao, C.-C. Wang and S.-M. Peng, *Chem. Commun.*, 1996, 315; (*f*) E.-C. Yang, M.-C. Cheng, M.-S. Tsai and S.-M. Peng, *J. Chem. Soc., Chem. Commun.*, 1994, 2377; (*g*) F. A. Cotton, L. M. Daniels and G. T. Jordan IV, *Chem. Commun.*, 1997, 421; (*h*) F. A. Cotton, L. M. Daniels, G. T. Jordan IV and C. A. Murillo, *J. Am. Chem. Soc.*, 1997, **119**, 10377.
5. (*a*) C.-C. Wang, W.-C. Lo, C.-C. Chou, G.-H. Lee, J.-M. Chen and S.-M. Peng, *Inorg. Chem.*,

1998, **37**, 4059; (*b*) S.-J. Shieh, C.-C. Chou, G.-H. Lee, C.-C. Wang and S.-M. Peng, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 56; (*c*) H.-C. Chang, J.-T. Li, C.-C. Wang, T.-W. Lin, H.-C. Lee, G.-H. Lee and S.-M. Peng, *Eur. J. Inorg. Chem.*, 1999, 1243; (*d*) F. A. Cotton, L. M. Daniels, T. Lu, C. A. Murillo and X. Wang, *J. Chem. Soc., Dalton Trans.*, 1999, 517; (*e*) C.-Y. Yeh, C.-H. Chou, K.-C. Pan, C.-C. Wang, G.-H. Lee, Y. O. Su and S.-M. Peng, *J. Chem. Soc., Dalton Trans.*, 2002, 2670; (*f*) C. Yin, G.-C. Huang, C.-K. Kuo, M.-D. Fu, H.-C. Lu, J.-H. Ke, K.-N. Shih, Y.-L. Huang, G.-H. Lee, C.-Y. Yeh, C.-h. Chen and S.-M. Peng, *J. Am. Chem. Soc.*, 2008, **130**, 10090.

6. (*a*) S.-Y. Lai, T.-W. Lin, Y.-H. Chen, C.-C. Wang, G.-H. Lee, M. Yang, M. Leung and S.-M. Peng, *J. Am. Chem. Soc.*, 1999, **121**, 250; (*b*) Y.-H. Chen, C.-C. Lee, C.-C. Wang, G.-H. Lee, S.-Y. Lai, F.-Y. Li, C.-Y. Mou and S.-M. Peng, *Chem. Commun.*, 1999, 1667.
7. S.-M. Peng, C.-C. Wang, Y.-L. Jang, Y.-H. Chen, F.-Y. Li, C.-Y. Mou and M.-k. Leung, *J. Magn. Magn. Mater.*, 2000, **209**, 80.
8. L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara, J. M. Tour and P. S. Weiss, *Science*, 1996, **271**, 1705.
9. (*a*) S.-Y. Lin, I-W. P. Chen, C.-h. Chen, M.-H. Hsieh, C.-Y. Yeh, T.-W. Lin, Y.-H. Chen and S.-M. Peng, *J. Phys. Chem. B*, 2004, **108**, 959; (*b*) I-W. P. Chen, M.-D. Fu, W.-H. Tseng, J.-H. Yu, S.-H. Wu, C.-J. Ku, C.-h. Chen and S.-M. Peng, *Angew. Chem., Int. Ed.*, 2006, **45**, 5814.
10. (*a*) J. F. Berry, F. A. Cotton, L. M. Daniels, C. A. Murillo and X. Wang, *Inorg. Chem.*, 2003, **42**, 2418; (*b*) *Multiple Bonds Between Metal Atoms*, ed. F. A. Cotton, C. A. Murillo and R. A. Walton, Springer, New York, 3rd edn, 2005; (*c*) M.-M. Rohmer and M. Bénard, *J. Cluster Sci.*, 2002, **13**, 333; (*d*) P. Kiehl, M.-M. Rohmer and M. Bénard, *Inorg. Chem.*, 2004, **43**, 3151; (*e*) M.-M. Rohmer, I. P.-C. Liu, J.-C. Lin, M.-J. Chiu, G.-H. Lee, M. Bénard, X. López and S.-M. Peng, *Angew. Chem., Int. Ed.*, 2007, **46**, 3533; (*f*) J. F. Berry, F. A. Cotton, L. M. Daniels and C. A. Murillo, *J. Am. Chem. Soc.*, 2002, **124**, 3212 and references therein.
11. (*a*) M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247; (*b*) *Mixed Valence Compounds*, ed. D. M. Brown, D. Reidel, Dordrecht, Holland, 1980.
12. (*a*) D. Gatteschi, C. Mealli and L. Sacconi, *J. Am. Chem. Soc.*, 1973, **95**, 2736; (*b*) L. Sacconi, C. Mealli and D. Gatteschi, *Inorg. Chem.*, 1974, **13**, 1985; (*c*) A. Bencini, D. Gatteschi and L. Sacconi, *Inorg. Chem.*, 1978, **17**, 2670; (*d*) A. Bencini, E. Berti, A. Caneschi, D. Gatteschi, E. Giannasi and I. Invernizzi, *Chem.–Eur. J.*, 2002, **8**, 3660.
13. I. P.-C. Liu, M. Bénard, H. Hasanov, I-W. P. Chen, W.-H. Tseng, M.-D. Fu, M.-M. Rohmer, C.-h. Chen, G.-H. Lee and S.-M. Peng, *Chem.–Eur. J.*, 2007, **13**, 8667
14. (*a*) C.-H. Chien, J.-C. Chang, C.-Y. Yeh, L.-M. Fang, Y. Song and S.-M. Peng, *Dalton Trans.*, 2006, 3249; (*b*) C.-H. Chien, J.-C. Chang, C.-Y. Yeh, G.-H. Lee, L.-M. Fang and S.-M. Peng, *Dalton Trans.*, 2006, 2106; (*c*) T.-B. Tsao, S.-S. Lo, C.-Y. Yeh, G.-H. Lee and S.-M. Peng, *Polyhedron*, 2007, **26**, 3833.
15. (*a*) J. L. Costa-Kramer, *Phys. Rev. B*, 1997, **55**, R4875; (*b*) J. Li, T. Kanzaki, K. Murakoshi and Y. Nakato, *Appl. Phys. Lett.*, 2002, **81**, 123; (*c*) H. Ohnishi, Y. Kondo and K. Takayanagi, *Nature*, 1998, **395**, 780.
16. (*a*) S. I. Gorelsky, AOMix: Program for Molecular Orbital Analysis; University of Ottawa, 2009, http://www.sg-chem.net/; (*b*) S. I. Gorelsky and A. B. P. Lever, *J. Organomet. Chem.*, 2001, **635**, 187.

List of Publications:

Synthetic Challenges.

1. "New Generation of Metal String Complexes: Strengthening Metal-Metal Interaction via Naphthyridyl Group Modulated Oligo-α-Pyridylamido Ligands" Liu, I. P.-C.; Wang, W.-Z.; Peng, S.-M. *Chem. Commun.* **2009**, 4323-4331.
2. "Asymmetric Heterometal String Complexes: Stereochemical Control of the Unique Isomer of $(4,0)[CuCuPd(npa)_4Cl][PF_6]$ and $(4,0)[CuCuPt(npa)_4Cl][PF_6]$" Liu, I. P.-C.; Chen, C.-H.; Chen, C.-F.; Lee, G.-H.; Peng, S.-M. *Chem. Commun.* **2009**, 577-579.
3. Synthesis, Structure, Magnetism, and Electrochemical Properties of a Linear Pentanuclear Ni_5 Compound Derived from an Oligo-α-Pyridylamino Ligand: $Ni_5(\mu\text{-dmpdda})_4(NCS)_2$" Yin, C.-X.; Su, J.; Huo, F.-J.; Ismayilov, R.-H.; Wang, W.-Z.; Lee, G.-H.; Yeh, C.-Y.; Peng, S.-M. *J. Coord. Chem.* **2009**, *62*, 2974-2982.
4. "Clear Evidence of Electron Delocalization: Synthesis, Structure, Magnetism, EPR and DFT Calculation of the Asymmetric Hexanickel String Complex Containing a Single Mixed-Valence $(Ni_2)^{3+}$ Unit" Liu, I. P.-C.; Chen, C.-F.; Hua, S.-A.; Chen, C.-H.; Wang, H.-T.; Lee, G.-H.; Peng, S.-M. *Dalton Trans.* **2009**, 3571-3573.
5. "Further Investigations of Linear Trirhodium Complexes: Experimental and Theoretical Studies of $[Rh_3(dpa)_4Cl_2]$ and $[Rh_3(dpa)_4Cl_2](BF_4)$ [dpa = bis(2-pyridyl)amido anion]" Huang, G.-C.; Liu, I. P.-C.; Kuo, J.-H.; Huang, Y.-L.; Yeh, C.-Y.; Lee, G.-H.; Peng, S.-M. *Dalton Trans.* **2009**, 2623-2629.
6. "Redox Modification of EMACs Through the Tuning of Ligands: Heptametal(II) Complexes of Pyrazine-Modulated Oligo-α-pyridylamido Ligands" Ismayilov, R. H.; Wang, W.-Z.; Lee, G.-H.; Chien, C.-H.; Jiang, C.-H.; Chiu, C.-L.; Yeh, C.-Y.; Peng, S.-M. *Eur. J. Inorg. Chem.* **2009**, 2110-2120.
7. "First Stable Reduced Form of $[Co_5]^{10+}$: Fine Tuning of Linear Pentacobalt(II) Complexes Containing Delocalized Metal-Metal Bonds through Ligand Modification" Wang, W.-Z.; Ismayilov, R. H.; Wang, R.-R.; Huang, Y.-L.; Yeh, C.-Y.; Lee, G.-H.; Peng, S.-M. *Dalton Trans.* **2008**, 6808-6816.
8. "Stabilization of Long Cationic EMACs by Reduction or Loss of One Metal Ion" Ismayilov, R. H.; Wang, W.-Z.; Wang, R.-R. Huang, Y.-L.; Yeh, C.-Y.; Lee, G.-H.; Peng, S.-M. *Eur. J. Inorg. Chem.* **2008**, 4290-4295.
9. "Extended Metal-Atom Chains with an Inert Second Row Transition Metal: $[Ru_5(\mu_5\text{-tpda})_4X_2]$ ($tpda^{2-}$ = tripyridyldiamido dianion, X = Cl and NCS)" Yin, C.; Huang, G.-C.; Kuo, C.-K.; Fu, M.-D.; Lu, H.-C.; Ke, J.-H.; Shih, K.-N.; Huang, Y.-L.; Lee, G.-H.; Yeh, C.-Y.; Chen, C.-h.; Peng, S.-M. *J. Am. Chem. Soc.* **2008**, *130*, 10090-10092.
10. "Probing the Electronic Communication of Linear Heptanickel and Nonanickel String Complexes by Utilizing Two Redox-Active $[Ni_2(napy)_4]$ Moieties", 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. *Dalton Trans.* **2010**, accepted in Dec. 2009.
11. "Manipulation of Electronic Structure via Supporting Ligands: a Charge Disproportionate Model within the Linear Metal Framework of Asymmetric Nickel String $[Ni_7(phdptrany)_4Cl](PF_6)$", 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. *Chem. Commun.* submitted.

Conductance of Single Molecules: Heterometal EMACs, under Electrochemical Controls, and Contact Resistance.

12. "Negative Differential Resistance of a Heteropentanulcear Extended Metal-Atom Chain $[Ni\text{-}Ru_2\text{-}Ni_2(tripyridyldiamido)_4(NCS)_2]$: Tuning the Frontier Molecular Orbitals" Fu, M.-D.; Huang, G.-C.; Yin, C.; Ko, J.-H.; Huang, M.-J.; Kuo, C.-K.; Lee, G.-H.; Peng, S.-M.; Chen, C.-h. Manuscript in preparation.
13. "On the Tuning of Electric Conductance of Extended-Metal-Atom-Chains via Axial Ligands for $[Ru_3(\mu_3\text{-dpa})_4(X)_2]^{0/+}$ ($X = NCS^-, CN^-$)" 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. *Chem. Commun.* **2010**, accepted in Dec. 2009.
14. "Superior Contact for Single-Molecule Conductance: Electronic Coupling of Thiolate and Isothiocyanate on Pt, Pd, and Au" Ko, C.-H.; Huang, M.-J.; Fu, M.-D.; Chen, C.-h. *J. Am. Chem. Soc.* **2010**, accepted in Nov. 2009.

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