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To design new metal string complexes, several naphthyridyl group modulated oligo-α-pyridylamido ligands have been synthesized in the past five years. Because these ligands are less anionic than pyridylamido ligands, the resulting metal string complexes tend to form reduced mixed-valence $[Ni_2(napy)_4]^{3+}$ dinuclear units which contain a delocalized unpaired electron and thus significantly enhance the conductance of metal string complexes. Furthermore, the asymmetric naphthyridyl group modulated oligo-α-pyridylamido ligands can stabilize the central heteronuclear or charge disproportionational metal frameworks, providing a plausible strategy to build inorganic molecular rectifiers.

1. Introduction
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1.2 Metal-metal bonding in the metal string complexes
1.3 Single molecular conductance of the metal string complexes
2 Oligo-α-naphthyridylamido ligands and related nickel string complexes
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3 Oligo-α-naphthyridylpyridylamido ligands and related metal string complexes
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4.1 2-(Naphthyridylamino)-7-phenylamino-1,8-naphthyridine (H_2napany) ligand
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4.3 Asymmetric 2-naphthyridylphenylamido ligand (Hnpa) and its heterometal string complexes
5 Summary

Keywords: metal-metal bonds; molecular wires; molecular switches

FA4-MS02-P21

Asymmertic Linear Nickel Metal String Complexes: A Manipulation of Electronic Structures through Supporting Ligands. Shao-An Hua[a], Isiah Po-Chun Liu[a,b], Shie-Ming Peng[a,b]. [a]*Department of Chemistry, National Taiwan University, Taipei,106, Taiwan (ROC).* [b]*Institute of Chemistry, Academia Sinica, Taipei,115, Taiwan (ROC).*
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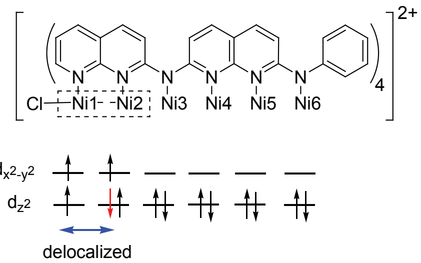
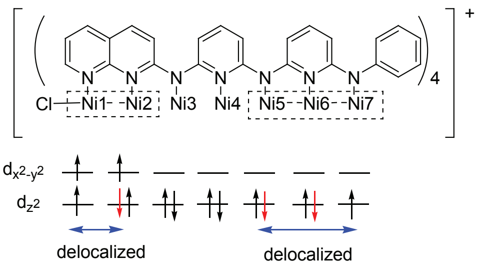
Over the past decade, we have been showing that the combination of 1D linear metal framework with poly-nitrogen ligands gives rise to the unique quadruple helix, which we describe as "*metal string complexes*"[1]. Because the supporting ligands and the axial coordination play an essential role on altering the physical properties of these complexes, we explore the novel electronic structures by introducing asymmetrical ligand system. We present herein two newly synthesized hexa- and heptanickel metal string complexes $[Ni_6(napnay)_4Cl](BF_4)_2$ **(1)** and $[Ni_7(phdptrany)_4Cl]PF_6$ **(2)**.[2] Both of these complexes exhibit an asymmetric *(4,0)*- conformation, which the equatorial ligands align in the same direction with one axial ligand coordinated to the metal chain. Due to the differences of the supporting ligands, **1** and **2** reveal varied physical properties, clearly elucidated by means of crystal structures, magnetism, near-IR spectroscopy and DFT calculations. The complex **1** presenting only one MV $[Ni_2(napy)_4]^{3+}$ dinickel unit (napy = naphthyridyl group) within the metal framework, while an extending of MV units via an intriguing charge disproportionate mechanism is observed for complex **2**.



$[Ni_6(napany)_4Cl](BF_4)_2$ (1)



$[Ni_7(phdptrany)_4Cl](PF_6)$ (2)

[1] C.-Y. Yeh, C.-C. Wang, C.-h. Chen and S.-M. Peng, in *Nano Redox Sites: Nano-Space Control and its Applications*, T. Hirao, Ed.; Springer: Berlin, **2006**, Chapter 5, pp. 85-117. [2] a) I. P.-C. Liu, C.-F. Chen, S.-A. Hua, C.-H. Chen, H.-T. Wang, G.-H. Lee and S.-M. Peng, *Dalton Trans.*, **2009**, DOI: 10.1039/b901675a ; b) S.-A. Hua, G.-C. Huang, I. P.-C. Liu, J.-H. Kuo, C.-H. Jiang, C.-L. Chiu, C.-Y. Yeh, G.-H. Lee and S.-M. Peng, *Chem. Eur. J.*, submitted.

Keywords: metal-metal bonds; mixed-valence compounds; electronic structure

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Syntheses and Studies of Linear Metal String Complexes : $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2](PF_6)_2$ and $[Ru_2Ni_2(DAniDANy)_3(OAc)_2Cl]$. Jau - Huei Kuo[a], Gin-Chen Huang[a], Shie-Ming Peng[ab]. [a]*Department of*

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Our group was devoted to the research of metal string complexes in past decades. We believe that the thinnest metal wire could be applied to practical applications in molecular electronics in future. We successfully synthesized two kinds of ligand in order to extend the study of metal strings. First, the new decametal string complex $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2](PF_6)_2$ was successfully synthesized with H_4bdpdang ligand. The crystal structure of $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2](PF_6)_2$ shows that all of the bdpdany^{4-} ligands bind metal in all-syn conformation and the X-ray structural studies reveal the internal Ni-Ni bond distance is ca.2.36~2.23 Å. Second, the heteronuclear $[Ru_2Ni_2(DAniDANy)_3(OAc)_2Cl]$ complex was successfully synthesized with H_2DAniDANy ligand. The crystal structure of $[Ru_2Ni_2(DAniDANy)_3(OAc)_2Cl]$ is shown in Figure 1b. Ru(1)-Ru(2) is about 2.288(1) Å. Ru(1)-Cl is 2.469(2) Å . Ru-N distances are 2.04-2.09 Å. Ru(2)-Ni(1) is 2.469(1) Å. This distance is close enough to have some overlap between Ru and Ni. Magnetic study shows it has three unpaired electrons. IVCT band at 890 nm indicates there exists an unoccupied δ* which is similar to Ru_2 dimer. DFT study shows that the three magnetic orbitals are essentially Ru_2 based. Ru_2 and Ni_2 may have weak bonding interaction.

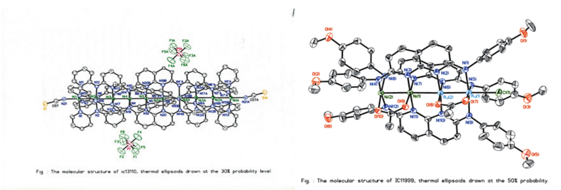

Fig. 1 The crystal structures of $[Ni_{10}(\mu_{10}\text{-bdpdany})_4(NCS)_2](PF_6)_2$ and $[Ru_2Ni_2(DAniDANy)_3(OAc)_2Cl]$.

[1] Gummow R.J., Liles D.C., *Mat. Res. Bull*, **1993**, 28, 1293. [2] Grirrane, A.; Pastor, A.; Galindo, A.; Ienco, A.; Mealli, C. *Chemm. Commun.* **2003**, 512.

Keywords: metal-metal bonds; crystallography; magnetic properties

FA4-MS02-P23

Insight into Crystal Structure/Optical Properties Relationships of New N-Salicylidene Anils.

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N-salicylidene aniline derivatives are highly versatile thermo- and photochromic molecules [1]. These are actively studied for many applications like non linear optics [2], biological activities [3], information storage and display [4], etc. Thermo and photochromism occurring in the solid state thanks to reversible equilibria between the uncoloured *enol*, the yellow *cis-keto* and the red *trans-keto* forms [1] are the main interests of these compounds. All derivatives are described as thermochromic but only a few of them are photochromic. Many authors stress the importance of crystal packing [5] to explain these properties but the molecular environment is also to be considered [6]. Crystallographic study of N-salicylidene aniline derivatives is essential for the understanding of molecular properties in solution or in solid state. In this work, we have observed that the dihedral angle between aromatic rings and the crystal packing are not sufficient to predict the photochromism behaviour of the compounds [7]. This is clearly seen with the N-salicylidene 4-aminopyridine (L4) and 2-(3,5-bis(pyridin-2-yl)-1,2,4-triazole-4-ylimino-methyl)-phenol (ABS). L4, a highly twisted molecule, present an open structure with large intermolecular distances and weak CH-π and ππ stacking interactions. Photo-isomerisation to the *trans-keto* form should be easier thanks to the crystal packing. However, L4 is only thermochromic. In contrast, ABS crystal is formed with highly twisted molecules, packed very closely with strong supramolecular interactions (ππ stacking) but is only photochromic. This observation clearly disagrees with reported conclusions [5]. Finally, a novel interesting molecular conformation has been discovered with the N-salicylidene 4-amino- 1,2,4-triazole (Hsaltrz) which is packed as supramolecular *zig-zag* double chains.

[1] Fujiwara T., Hadara J., Keiichiro O., *J. Phys. Chem. B* **2004**, 108,4035. *[2]* Plaquet A. *et al J. Phys. Chem. C* **2008**, 112, 5638. *[3]* Parashar R.K, Sharma R.C, Kumar A., Mohan G. *Inorg. Chim. Acta* **1988**, 151, *201 .[4]* Feringa B. L., Jager W. F., de Lange B. *Tetrahedron* **1993**, 49/37, 8267. *[5]* Hadjoudis E., Mavridis I.M., *Chem. Soc. Rev.* **2004**, 33, 579. *[6]* Haneda T., Kawano M., Kojima T., Fujita M., *Angew. Chem. Int. Ed.* **2007**, 46, 6643. *[7]* Robert F., Naïk A.D., Tinant B., Robiette R., GarciaY., *in press*

Keywords: supramolecular chemistry; crystal structure; optical properties

FA4-MS02-P24

Cation and Ligand Roles in the Coordination of FeIII Bisdithiolene Complexes.

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Aiming at a better understanding of the role of the cation versus the role of the ligand in the coordination geometry of Fe^{III} bisdithiolene complexes we have been exploring either new $[Fe^{III}(qdt)_2]^-$ salts (qdt=quinoxalinedithiolate) with different cations or new iron bisdithiolates complexes, such as $[Fe(\alpha\text{-tpdt})_2]_2$ (α-tpdt=2,3-thiophenedithiolate). At variance with the large diversity of coordination geometries and oxidation states of bisdithiolene complexes with most metals, the iron complexes with these ligands have been essentially restricted to one stable oxidation state, Fe(III) , and until quite recently all were found to adopt in solid state the same square pyramidal, 4+1, coordination geometry due