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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
1.1 Oligo-α-pyridylamido ligands and related metal string complexes
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
2.1 Synthesis and structures of the nickel string complexes
2.2 Electron delocalization of the mixed-valence $[Ni_2(napy)_4]^{3+}$ unit
2.3 Single molecular conductance of the nickel string complexes
3 Oligo-α-naphthyridylpyridylamido ligands and related metal string complexes
3.1 Linear hexanuclear metal string complexes
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4 Asymmetric mixed-substituted ligands and related metal string complexes
4.1 2-(Naphthyridylamino)-7-phenylamino-1,8-naphthyridine (H_2napany) ligand
4.2 Novel charge disproportionational asymmetric heptanickel string complex
4.3 Asymmetric 2-naphthyridylphenylamido ligand (Hnpa) and its heterometal string complexes
5 Summary

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

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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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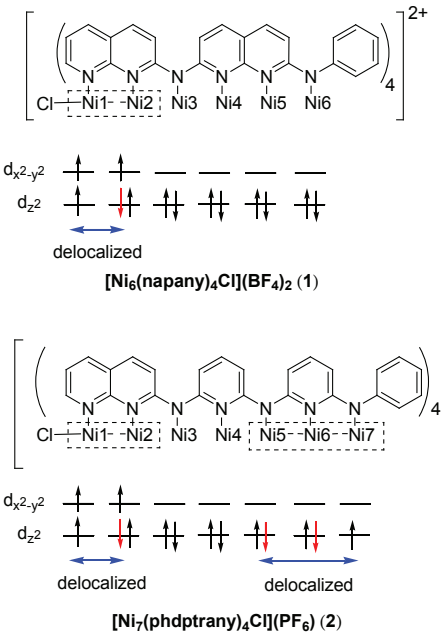
Over the past decade, we have been showing that the combination of 1D linear metal framework with poly-nitrogen ligands gives rise to the unique quadruple helix, which we describe as "*metal string complexes*"[1]. Because the supporting ligands and the axial coordination play an essential role on altering 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**.



[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 : $[Ni_{10}(\mu_{10}$-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*