Metal Complexes as Precursors for Responsive Films: Electronic Structures and Amphiphilic Properties

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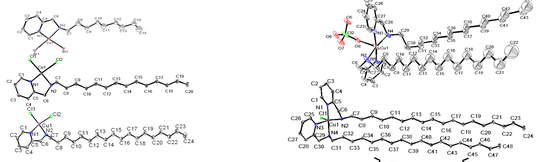
Introduction

One of the main challenges of modern coordination chemistry is to find ways of translating the considerable amount of information learned from small molecules into useful systems that foster the development of new materials. A main step in this process is the need for small molecules to be organized in highly ordered assemblies, and usually the need for transfer onto surfaces. The rich chemistry of transition metal complexes is profuse in systems with well understood, controllable, and tunable properties and the incorporation of these motifs into soft materials—thus allowing for interface and surface organization— is highly desirable. Recent advances in the field of metal-containing soft materials point to successful applications toward molecular electronics, as well as responsive thin films, and hierarchical materials. Other emerging applications focus on metallosurfactants and mesogens, taking advantage of the geometric, redox, and magnetic properties of transition metal centers to build up organized supramolecular architectures based on organic scaffolds.

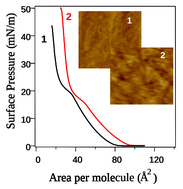
Strategies for Metallosurfactants in LB films

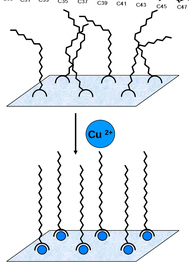
1. Copper Amphiphiles

The complexes $[Cu(L^{CXPy})Cl_2]$ and $[Cu(L^{CXPy})_2](ClO_4)_2$



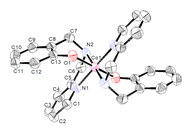
Typical bond lengths (Å): Cu–N = 2.01, Cu–Cl = 2.24, C(6) –N(2) = 1.470(3), $C\text{-}C_{ring\ average}$ = 1.48, $C\text{-}C_{alkyl\ average}$ = 1.52 Å

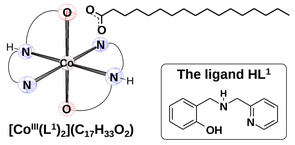




Driscoll, Jayathilake, Wu, Bordenyuk, Heeg, Verani* Benderskii,* da Rocha* *to be submitted*

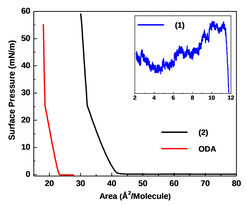
3. Electrolyte-Amphiphile Systems

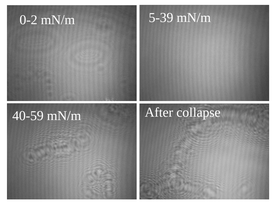




$[Co^{III}(L^1)_2](C_{17}H_{33}O_2)$

The ligand HL^1

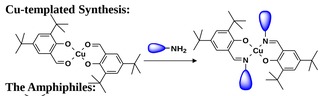




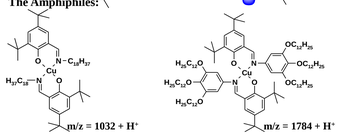
Shakya, Hindo, Tiburcio, da Rocha, Verani* *submitted to Inorg. Chem.* **2007**

5. Template Assembly of Amphiphiles

Cu-templated Synthesis:

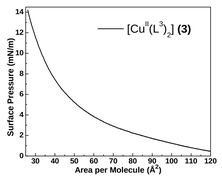


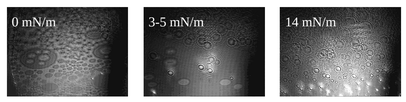
The Amphiphiles:



m/z = 1032 + H⁺

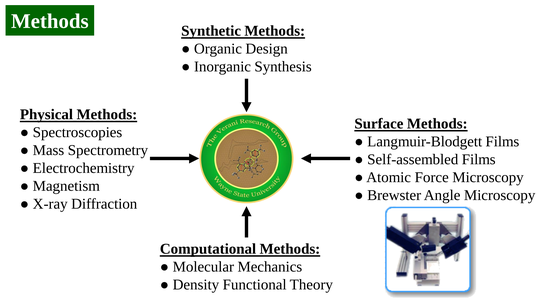
m/z = 1784 + H⁺



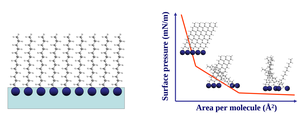


Hindo, Ranulu, Shakya, Heeg, Rodgers, da Rocha, Verani* *to be submitted Inorg. Chem.* **2007**

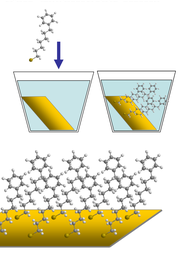
Methods



Langmuir-Blodgett films



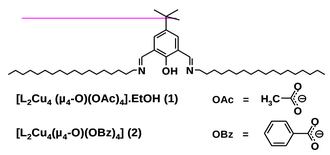
Self-assembled films



➢ Metal-containing Amphiphilic Precursors for Langmuir-Blodgett Films.

➢ Metal-containing Modular Precursors for Self-assembled Films.

2. Cluster Amphiphiles

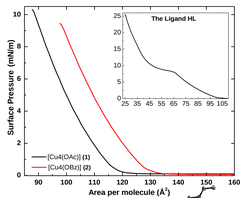


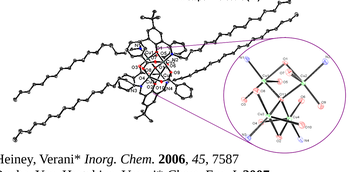
$[L_2Cu_4(\mu_4\text{-}O)(OAc)_4].EtOH$ (1)

$[L_2Cu_4(\mu_4\text{-}O)(OBz)_4]$ (2)

OAc = H_3C

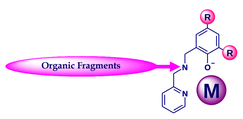
OBz =



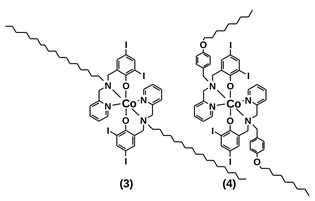


Shakya, Keyes, Heeg, Moussawel, Heiney, Verani* *Inorg. Chem.* **2006**, *45*, 7587
Shakya, Hindo, Wu, Ni, Allard, Heeg, da Rocha, Yee, Hratchian, Verani* *Chem. Eur. J.* **2007**

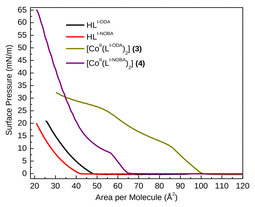
4. Asymmetry in Amphiphiles

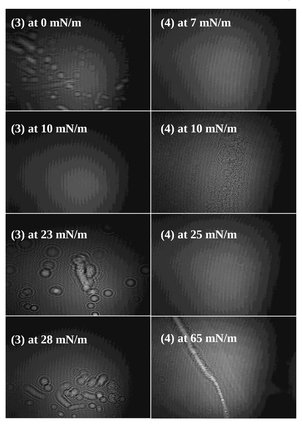


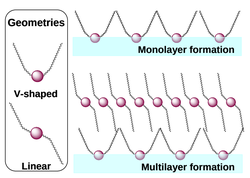
M = Mn, Fe, Co, Ni, Cu, Zn, Ga



(3) (4)



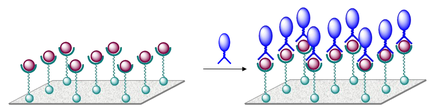




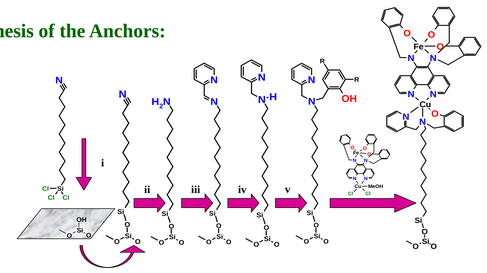
Imbert, Hratchian, Lanznaster, Heeg, Hryhorczuk, McGarvey, Schlegel, Verani,* *Inorg. Chem.* **2005**, *44*, 7414
Shakya, Imbert, Hratchian, Lanznaster, Heeg, McGarvey, Allard, Schlegel, Verani,* *Dalton Trans.*, **2006**, 2517
Shakya, Hindo, Wu, Allard, Heeg, Hratchian, McGarvey, da Rocha, Verani* *submitted to Inorg. Chem.* **2007**
Lesh, Hindo, Driscoll, Heeg da Rocha, Verani* *In preparation* **2007**

Strategies for Self Assembled Films

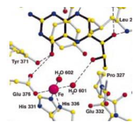
1. Anchoring and Terminal Modules:



2. Synthesis of the Anchors:

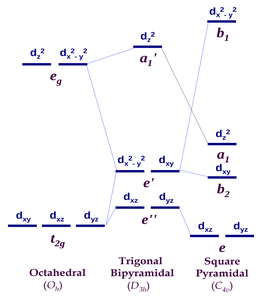


3. A Bioinspired Approach for the Terminal Modules:

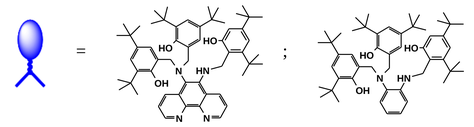


Tyrosine Hydroxylase: Synthesis of Catecholamines

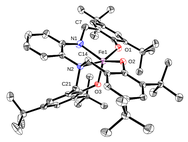
Stevens et al *Biochemistry* ***1998*** *37*, 13437



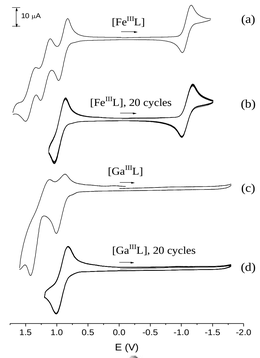
4. The Terminal Module and its Archetype:

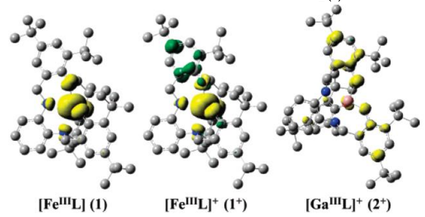


5. The Archetype:



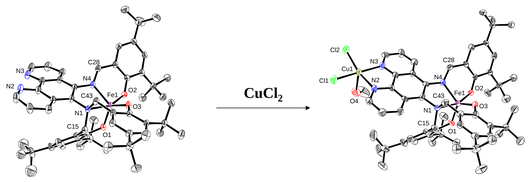
$[Fe^{III}L]$: Fe1-O1 = 1.887(1), Fe1-O2 = 1.868(1), Fe1-O3 = 1.871(1), Fe1-N1 = 2.148(2), Fe1-N2 = 2.233(2), **C7-N1 (1) = 1.414(3)** Å





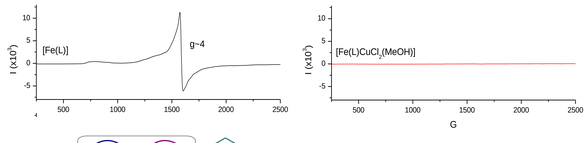
$[Fe^{III}L]$ (1) $[Fe^{III}L]^+$ (1^+) $[Ga^{III}L]^+$ (2^+)

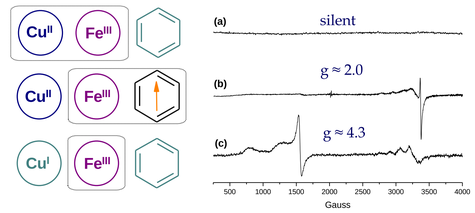
6. The Terminal Module:



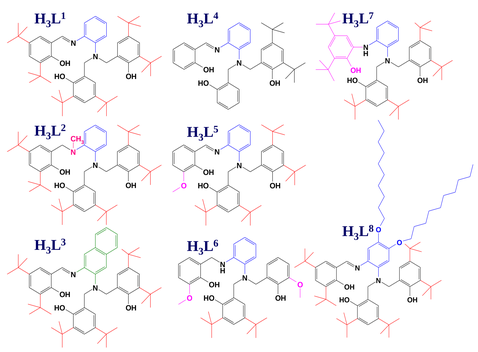
$CuCl_2$

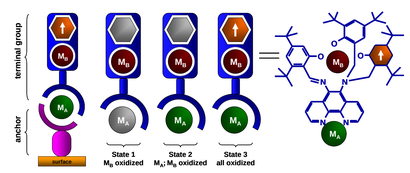
$[Fe(L')]_{ox}$:Fe-O1: 1.853, Fe-N1: 2.307, C28=N4: 1.315, Fe-O2: 1.917, Fe-N4: 2.043, C15-N1: 1.500, Fe-O3: 1.873, C43-N1: 1.498; Cu – Fe ~ 8.0 Å





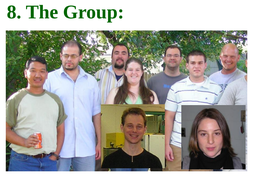
7. Other Systems:





Lanznaster, Hratchian, Heeg, Hryhorczuk, McGarvey, Schlegel, Verani* *Inorg. Chem.* **2006**, *45*, 955.
Lanznaster, Heeg, Yee, McGarvey, Verani* *Inorg. Chem.* **2007**, *46*, 72.
Allard, Darland, Hratchian, Heeg, Verani* *in preparation* **2007**

8. The Group:



Present Members: Marco Allard, Jeff Driscoll, Sarmad Hindo, Frank Lesh, Rajendra Shakya, Rama Shanmugan Dajena Tomco

Past Members: Camille Imbert, Mauricio Lanznaster, Azzam Moussawel

9. Financial Support:

Wayne State University · NSF · ACS PRF

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