

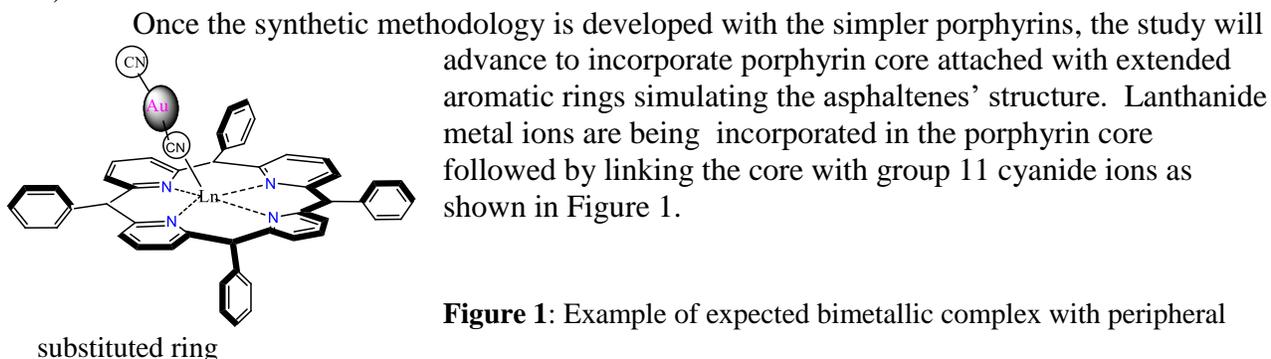
PRF # 55441-UR3

Project Title: Synthesis, Structural, and Spectroscopic Studies of Porphyrin Based Model Asphaltene Lanthanide and Group 11 Bimetallic Complexes: Intra- and Inter-Molecular Excimers and Exciplexes Studies in Solution and Solid State

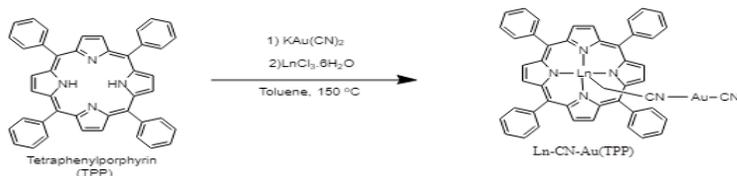
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Introduction

Although porphyrins are widely studied chemical systems because of their application in the field of catalysis, medicine, adsorption and optics our main interest in these systems continues to explore their potential as model complexes that will be used to simulate asphaltene aggregations. Asphaltenes are considered problematic in crude oil compositions, but the oil industry has been showing interest in their utility because of the high composition (~15%) in crude oil. Hence, a deeper understanding of asphaltenes is required to make this shift in the industry. Our primary goal in this project has been the synthesis and characterization of materials involving bimetallic systems containing group 11 transition metals (in particular cyanoaurate complexes) and selected lanthanide ions. The modification of a porphyrin structure by inserting a lanthanide ion into the core generates new porphyrinic compounds with exciting properties and applications. Our objective is to establish a porphyrin based bimetallic structure that contains a lanthanide ion at the core and small metal gold dicyanide linker ion. The lanthanide inserted in the porphyrin core acts as a point of connection allowing the gold dicyanide to act as a spacer and minimizing and/or remove any intermolecular attraction within the porphyrin core (Figure 1).

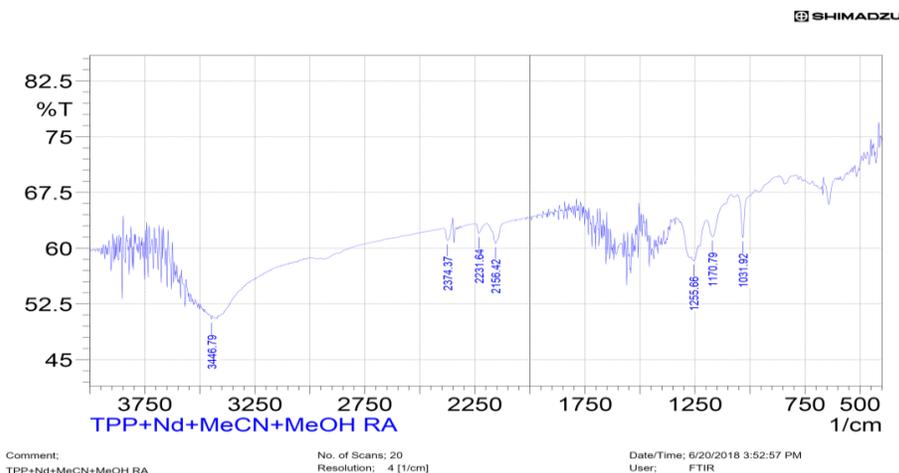


Current study in our laboratory encompasses several porphyrin adduces including meso-tetraphenylporphyrin (TPP), tetrakis(4-carboxyphenyl) porphyrin (TCPP), and tetrakis(phenylsulphanato)porphyrin (TPPS) systems. We have been incorporating several lanthanide ions including Yb, Tm, Er, Gd, and Nd into the porphyrin cores and attempted to link the two groups with the linker $\text{Au}(\text{CN})_2^-$ ion through CN bridging, The general synthetic scheme is shown below. Synthesis of $[(\text{Ln}(\text{TPP})\text{Au}(\text{CN})_2)]$ ($\text{Ln} = \text{Yb}, \text{Nd}, \text{Gd}$)



Spectroscopic studies

FT-IR data for the [Yb(TPP)Au(CN)₂] crystals shows CN peaks at 2145-2156 cm⁻¹ and 2140-2142 cm⁻¹. The FT-IR of KAu(CN)₂ shows that Au-CN peak occurs at 2141 cm⁻¹, hence the peaks around 2142 cm⁻¹ denotes the presence of a free uncoordinated CN. In contrast the FTIR



data for Nd and Tm adducts is different in that a significantly blue shifted band is observed at ~2230 cm⁻¹ corresponding to a CN group linking/bridging two metal ions. Hence, based on the IR data a mono coordination of

the Au(CN)₂⁻ group is inferred for Yb and Er samples whereas bridged dimers or extended chains with alternating Au-CN-Ln groups at the porphyrin site is inferred for Tm and Nd adducts. Crystal structure is being attempted currently but the quality of the crystals has been the major impediment to resolve the structural analysis. In addition Raman and other studies will be conducted in the next round.

Hydrothermal Synthetic Approach

Synthesis of [Ln(TCPP)Au(CN)₂] and [Ln(TPPS)Au(CN)₂] (Ln = Yb, Tb, Gd, Er, Nd)



Figure x: PTFE-lined stainless-steel autoclave setup used for the hydrothermal synthesis

We have recently started using a major hydrothermal synthetic protocol for the porphyrin compounds with the TCPP and TPPS ligands. A mixture of TPPS (60.0 mg, 0.1 mmol), LnCl₃·6H₂O (35.90 mg, 0.1 mmol), and KAu(CN)₂ (30 mg, 0.1 mmol) was placed in a round bottom flask containing 10 mL of deionized water. A 3 mL of 0.1 M NaOH was then added and resulting mixture was transferred into a PTFE-lined stainless-steel autoclave. The hydrothermal reactor was capped securely and placed in the oven. As the initial attempt, the autoclave was inserted into a 150 °C preheated

oven and kept for 48 h. After cooling to room temperature (RT), the products were filtered, washed with water and acetone, and air-dried at RT.

Conclusion: Synthetic effort have been done to prepare new porphyrinic compounds with exciting properties. New approach in hydrothermal synthetic technique has been developed and structural studies are being initiated along with photoluminescence studies to bring this project to a successful completion.