New In-Se-Cu ternary clusters: synthesis, characterization and applications.

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Palavras Chave: *In-Se-Cu clusters, synthesis, characterization, photocatalytic applications.*

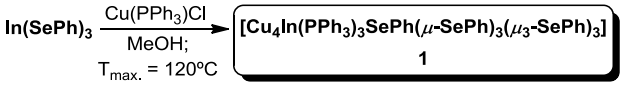
Introduction

Group-III binary chalcogenide materials exist in a number of forms (ME and M_2E_3; M = Ga, In, E = S, Se, Te) and phases. In addition to the binary systems, there is an interesting family of related ternary systems, I-III-VI ($CuME_2$; M = Ga, In; E = S, Se), that are related with significant and promising research for applications in photovoltaics and photocatalysis, especially in association with TiO_2. However, as they have not been studied extensively for this purpose, optimization is still needed.[1]

In order to contribute to this field, the goal of our work is to synthesize new In-Se-Cu ternary clusters using indium(III) selenolates as starting material.

Results and Discussion

Indium(III) phenylselenolate – $In(SePh)_3$ – reacts with $Cu(PPh_3)Cl$, in solvothermal conditions, to give golden crystals of $[Cu_4In(PPh_3)_3SePh(\mu\text{-}SePh)_3(\mu_3\text{-}SePh)_3]$ (**1**), according Scheme 1.



Scheme 1. Synthetic route to obtain compound **1**.

Figure 1 shows the molecular structure of **1**.

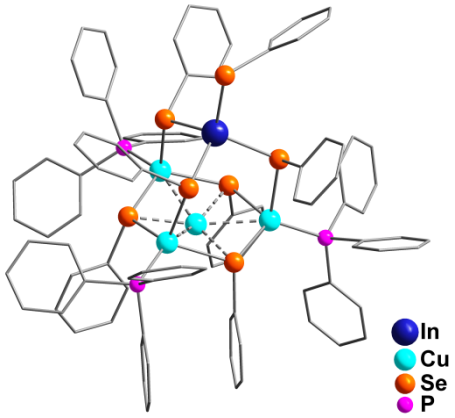
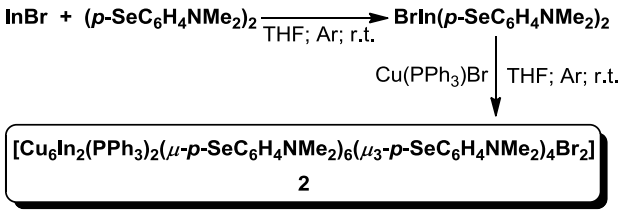


Figure 1. Molecular structure of **1**.

The indium(III) derivative – $BrIn(p\text{-}SeC_6H_4NMe_2)_2$ – can be obtained from the oxidative insertion of InBr into the Se-Se bond of *bis*[(*p*-*N*,*N*-dimethylaminophenyl)] diselenide – $(p\text{-}SeC_6H_4NMe_2)_2$. In the presence of $Cu(PPh_3)Br$, this In^{III} arylchalcogenolate generates $[Cu_6In_2(PPh_3)_2(\mu\text{-}p\text{-}SeC_6H_4NMe_2)_6(\mu_3\text{-}p\text{-}SeC_6H_4NMe_2)_4Br_2]$ (**2**, Figure 2) as shown in Scheme 2.



Scheme 2. Synthetic route to obtain compound **2**.

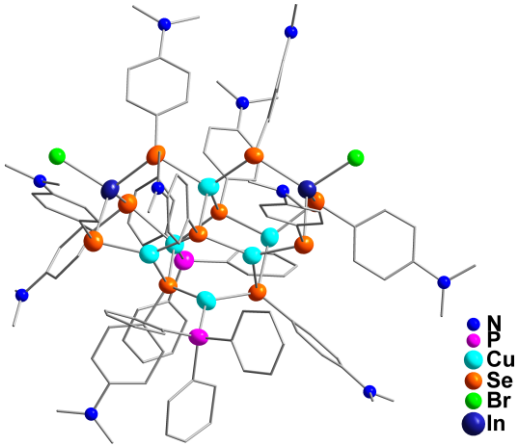


Figure 2. Molecular structure of **2**.

The optical band gap energy (E_g) of compounds **1** and **2** were estimated based on the UV-Vis diffuse reflectance spectra and the material absorption coefficient (α) were related to the sample diffuse reflectance (*r*) by the Kubelka–Munk function.[2] To **1**, E_g is 2.50 eV and to **2**, E_g is 2.51 eV.

Conclusions

Considering the E_g values obtained to the compounds, experiments of hydrogen production using compound **1** as photocatalyst are being performed and preliminary results are promising.

Aknowledgments

We are grateful to CNPq, CAPES and FAPERGS.

[1] Dahl, M.; Liu, Y.; Yin, Y. *Chem. Rev.* **2014**, *114*, 9853.
[2] Tirloni, B.; Lang, E. S.; de Oliveira, G. M.; Piquini, P.; Hörner, M. *New J. Chem.* **2014**, *38*, 2394.