Functional hybrid materials based on copper (I) complexes

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Copper (I) complexes displays rich photophysics properties that make them suitable candidates for technological applications including bio-sensoring, catalysis and in OLEDs. Especially the development of sensors is appealing due to reversible photophysical properties of certain copper (I) complexes. Many studies are focused on the characterization of the complex in solid state and solution, however there are few studies for these complexes combined with other materials. When adequately incorporated in a solid matrix, these complexes can present new interesting properties and also enhance characteristics that already exist. In this work we report the photophysical properties of copper (I) complexes incorporated in a mesoporous silica matrix obtained by sol-gel method with an average pore diameter of 10 nm. The complex $Cu_4I_4py_4$ (**1**) incorporated on silica showed a shift in emission of 580 nm to 720 nm due to the distortion of the molecular complex inside the matrix, known as rigidochromic effect[1]. Also, a sensitivity of this hybrid material (1@SiO_2) was observed to oxygen, but not before reported for the solid $Cu_4I_4py_4$. The mesoporous matrix dispersed the molecules of the complex, so as to enable a reversible interaction with oxygen in the center of the cluster (Cu_4I_4) that quenches of luminescence[2] and provides a new functionality to the complex. Already, the new complex $C_{30}H_{28}N_2O_2PCuI$ (**2**) presented vapochromic properties and an emission at 660 nm. Exposed to dichloromethane its color alters from yellow to orange and returns the original color on exposure to acetone, indicating a reversible process. This color change was also observed for the complex 2 incorporated into a mesoporous silica matrix (**2**@SiO_2). The vapochromic effect is usually caused by changes in the structure or molecular packing that modify the distances between the metal atoms, thus influencing the charge transfer mechanism between complexes (Cu-Cu-ligand, MMLCT)[3]. The new functional materials proposed in this study have great potential for applications in luminescent sensor devices for the detection of gases and organic vapors.

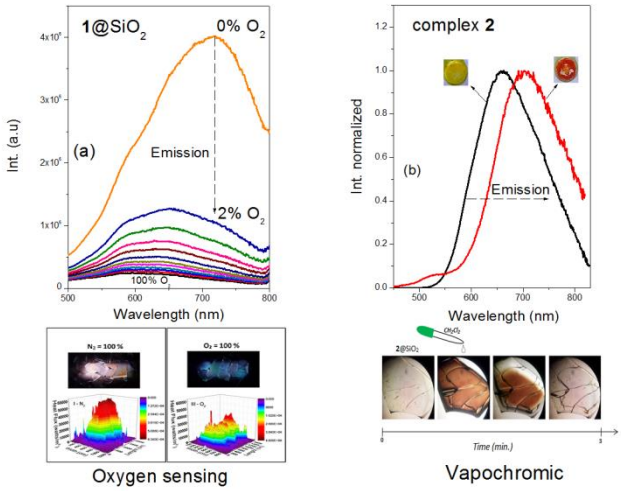

Figure 1. (a) Quenching of luminescence by oxygen for **1**@SiO_2 (λ_{exc} = 330 nm) and (b) emission spectrum (λ_{exc} = 420 nm) for complex **2** and change of color for **2**@SiO_2 after addition of dichloromethane.

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