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Hybrid xerogels doped with Tb(III) and Eu (III) and a water soluble Pybox ligand

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Introduction

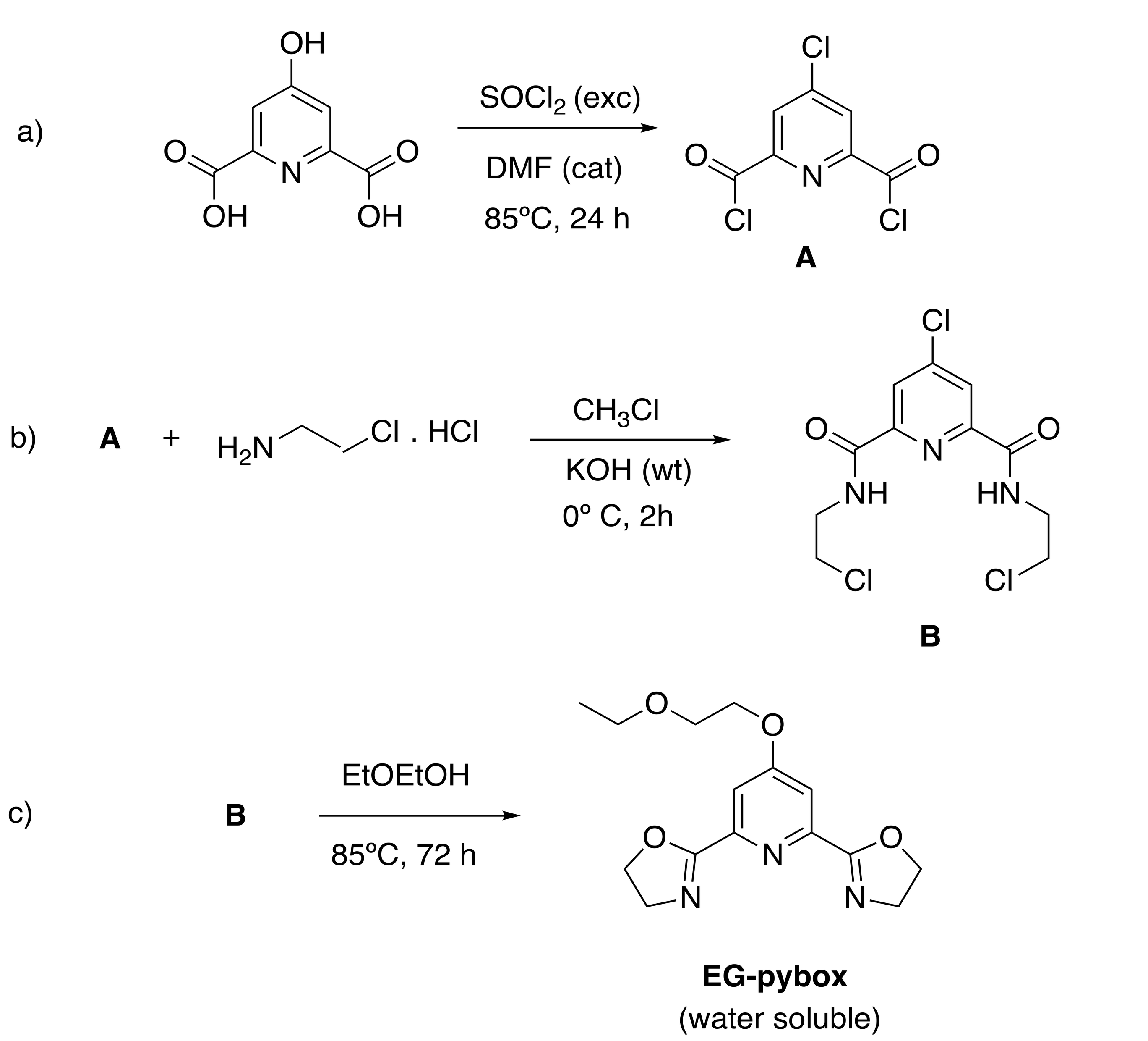
Hybrid organic-inorganic siliceous materials (ORMOSiLs) are a key focus within the nanoscience area as they combine advantages of inorganic materials without losing characteristics intrinsic of organic molecules. In the past years, our research group has designed hybrid siliceous xerogels (HSXG) with porosities and surface chemistries on demand for a range of applications, such as coatings for optic fiber sensors [1]. Although hybrid xerogels are mainly amorphous materials, recent studies by our group have demonstrated that introducing specific organic fragments on the precursors can induce self-organization during the sol-gel process to obtain a series of transparent nanostructured HSXG [2]. In the present work, a step forward is taken in the applicability of this type of HSXG by doping them with Tb(III) or Eu (III) cations and a water-soluble pybox-based antenna ligand (Pybox-EG= 2,2'-(4-(2-Ethoxyethoxy)pyridine-2,6-diyl)bis(4,5-dihydrooxazole)). Inclusion of photoluminescence will provide the materials with new properties and therefore new applications in fiber optic sensors (FOS) or in solar cells devices.

Methods

Synthesis of hybrid xerogels doped with pybox-EG

All the hybrid xerogels were prepared with 1:4.75:5.5 molar ratio of (TEOS+RTEOS):EtOH:H_2O (TEOS= tetraethoxyorthosilicate; RTEOS= Chloroalkyltriethoxyorthosilicate, being R= chloromethyl [ClM], 2-chloroethyl [ClE], 3-chloropropyl [ClP], Phenyl [Ph], and 3-[Bis(2-hydroxyethyl)amino]propyl [XNP]) [2]. 0.01 mmol of $Tb(NO_3)_3x6H_2O$ or $Eu(NO_3)_3x6H2O$ and 0.01 mmol of Pybox-EG (Pybox-EG = 2,2'-(4-(2-Ethoxyethoxy)pyridine-2,6-diyl)bis(4,5-dihydrooxazole)) were added to the mixture and the pH was adjusted to 4.5. The alcogel was introduced in an oven at 60 °C until gelation, cured for one week with EtOH and dried at room temperature until there was not significant change in the weight of the monolith.

Synthesis of water soluble pybox-EG [3]



Results

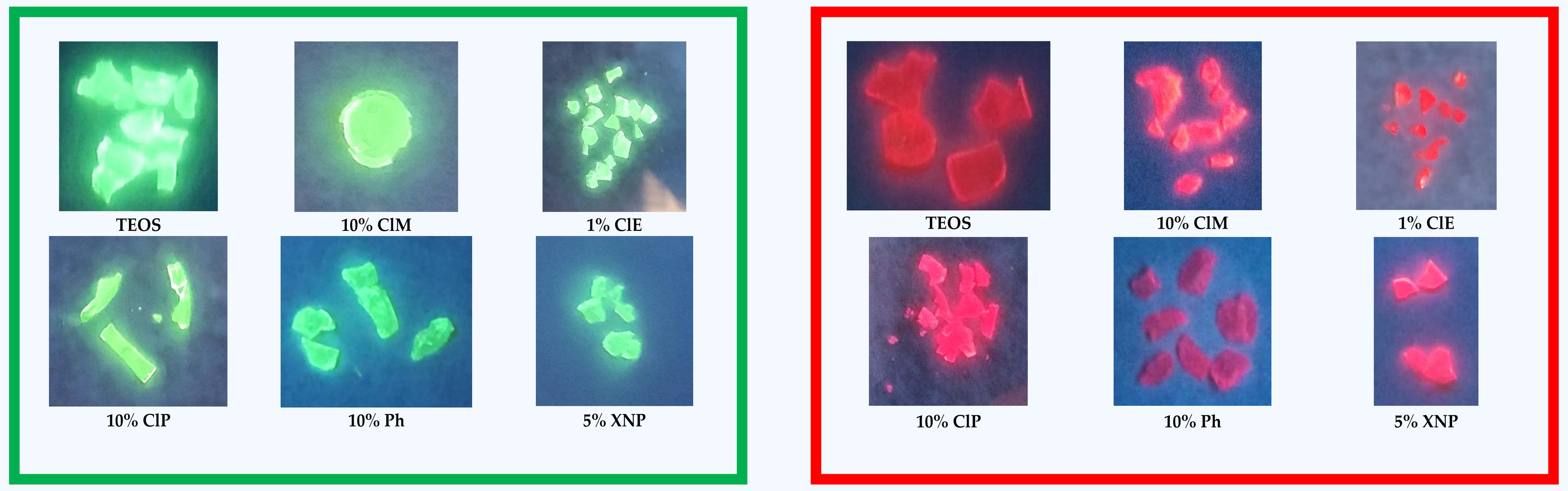


Figure 1. Tb (III) and Eu (III) doped RTEOS:TEOS xerogels under UV lamp

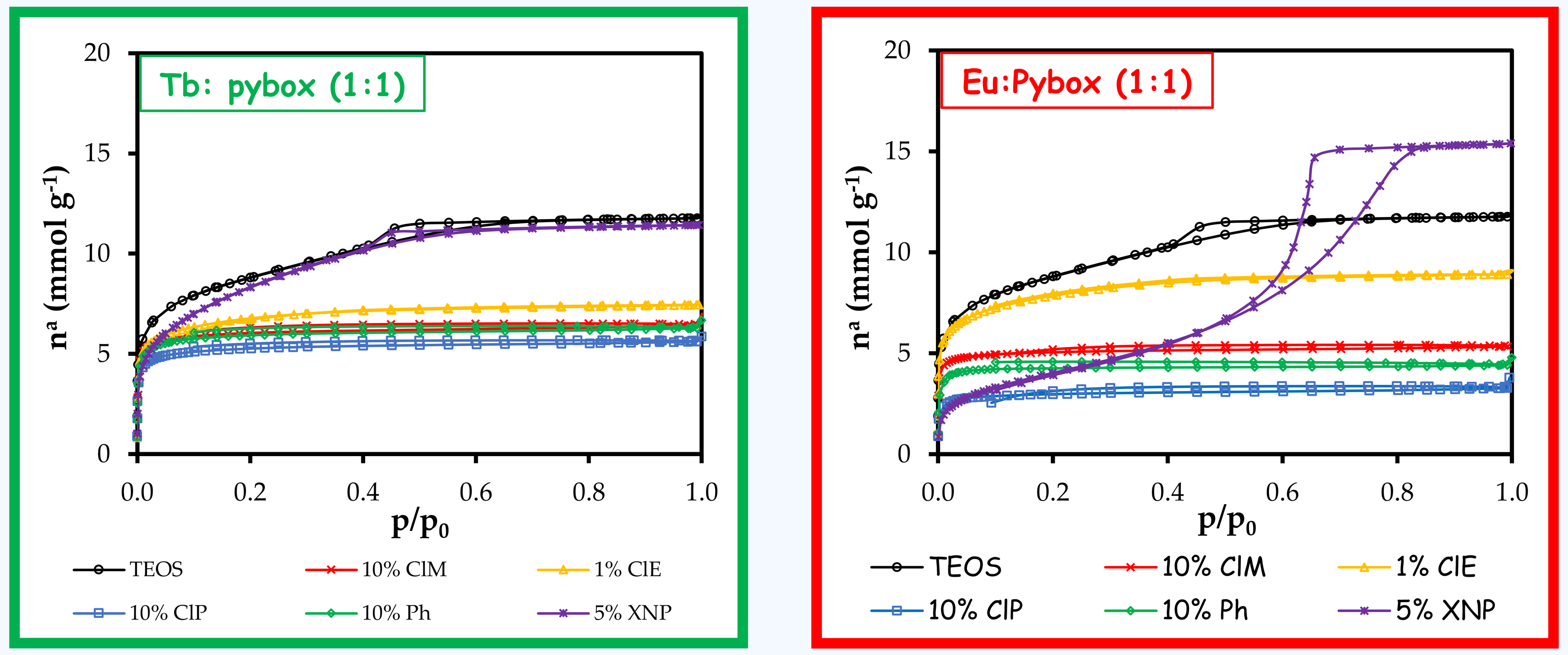


Figure 2. N_2 adsorption isotherms of the Tb (III) and Eu (III) doped RTEOS:TEOS

Lanthanide	RTEOS	RTEOS (%)	a_{lang} ($m^2 g^{-1}$)	a_{BET} ($m^2 g^{-1}$)	a_{DR} ($m^2 g^{-1}$)	V_{micro} [a] ($cm^3 g^{-1}$)	V_{meso} [b] ($cm^3 g^{-1}$)	V_{total} [c] ($cm^3 g^{-1}$)	BJH APS[d] (nm)	E_c [e] (KJ mol^{-1})
None	None	0	-	697	797	0.28	0.07	0.41	2.77	15.27
Eu (III)	ClM	10	518	-	503	0.18	0.01	0.18	3.03	21.98
	ClE	1	878	642	733	0.26	0.02	0.31	3.48	17.27
	ClP	10	316	-	302	0.11	0.01	0.11	2.45	17.48
	Ph	10	429	-	434	0.15	0.00	0.15	1.98	20.78
	XNP	5	-	334	339	0.12	0.33	0.53	5.95	12.00
Tb (III)	ClM	10	624	-	604	0.22	0.01	0.22	3.93	20.06
	ClE	1	730	557	648	0.23	0.01	0.26	3.86	17.52
	ClP	10	546	-	532	0.19	0.01	0.19	2.36	18.21
	Ph	10	610	-	597	0.21	0.01	0.22	2.13	18.32
	XNP	5	-	666	771	0.27	0.07	0.40	3.58	11.37

[a] Micropore volume obtained from Dubinin-raduskevich; [b] Mesopore volume obtained from isotherm ($0.8 < p/p_0 < 0.95$);
[c] Total Pore volume obtained from isotherm at p/p0 = 0.95; [d] Average Pore Size; [e] Characteristic energy from Dubinin-raduskevich.

Table 1. Textural parameters of the luminescent hybrid xerogels

Conclusions

Hybrid xerogels doped with Tb (III) or Eu (III) and a water soluble pybox based antenna ligand have been synthesised with various organic precursors. When irradiating with the UV lamp, all the materials emit in the UV range and, in addition, their characterisation shows that these xerogels not only own very different surface chemistries, but also have diverse textural properties.

By way of example, it can be observed that the xerogels synthesised with 10% ClPTEOS have a type Ib isotherm, typical of materials with narrow microporosity. On the other hand, both xerogels synthesised with 5% XPNTEOS have type IV isotherms, the one synthesised with Tb (III) presents a hysteresis loop typical of micro-mesoporous materials, while the hysteresis loop of the one synthesised with Eu (III) corresponds to a mesoporous material.

These materials, in which luminescence is combined with various chemical functionalisation and diverse porosities are very interesting for their use as coatings in FOS. Analytes might interact in a specific and labile way with the chosen xerogel modifying one of the material properties (luminescence or refractive index, among others) which will determine the analyte concentration in the medium.

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