

## Organic-Inorganic Hybrid of a Lanthanide Doped Di-Ureasil for Integrated Optics

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**Abstract:** In this work, pure urea crosslinked siloxane-based organic-inorganic hybrid and a lanthanide, in this case europium ( $\text{Eu}^{3+}$ ), doped urea crosslinked siloxane based organic-inorganic hybrid materials were synthesized, analyzed and properties compared. The pure and doped materials were synthesized with di-ureasils (Jeffamine 600) / d-U600, zirconium (IV) n-propoxide ( $\text{Zr}(\text{OC}_3\text{H}_7)_4$ ) / ZPO, and methacrylic acid ( $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2\text{H}$ ) / MAA. The reaction between d-U600 and ZPO which was catalyzed by MAA was expected to cause a nucleophilic displacement, with zirconium ion of the ZPO displacing any of the silicon ion ( $\text{Si}^{4+}$ ) grafted at both ends of the tripod siloxane, crosslinked to urea (-NHCO) functionality, then to the variable length poly(ether)-based backbone. However, from the Fourier Transform Infrared Spectroscopy (FTIR) spectra, it seemed that the materials exhibited a non-bonded zirconium ion in the d-U(600)+ZPO(10% molar/SI)+MAA samples as though it were still a pure sample of d-U(600). The pure hybrid sample was strong, tough and rigid, while the  $\text{Eu}^{3+}$  doped material was resilient on compression, showing viscoelastic behaviour. Photoluminescence spectra show that the  $\text{Eu}^{3+}$  doped sample exhibited a moderate emission of blue, green and red, which are the primary colours of white light as opposed to the pure monolith which emitted a high intensity blue light.

**Keywords:** Di-ureasils, Hydrolysis, Jeffamine 600, Photoluminescence, Polycondensation, Thin films.

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### I. Introduction

Organic – inorganic hybrids have presented very interesting properties and applications since the realization of their natural existence in water lilies, sea shells, chameleon skins and butterfly insect wings. Nature made it possible for these hybrid structures to reflect their super nanometric architecture in their inherent properties as hydrophobicity and barrier effects, luminescence, strength and lustre. However, in the case of synthetic routes, the bottom-up approach for nanomaterial assembly as reported by Wang *et al.*, (2005) has been a viable route used to mimic these natural materials in order to obtain novel hybrid non-crystalline materials by the joining of smallest units of organic and inorganic compounds into supra molecular structures. These materials are seen to have intrinsic size dependent properties of interest. The sol gel technique is widely reported as one of the sure ways to synthesize these materials (Sanchez *et al.*, 2005).

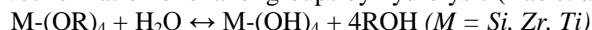
#### 1.1 Organic-Inorganic Monoliths and Thin Films by sol Gel Technique

The sol-gel process is generally based on hydrolysis and polycondensation reactions of metal alkoxide precursors. A sol is obtained when there is a colloidal dispersion of nanoparticles in a solvent carrier, while a highly viscous gel results from ageing, drying or evaporation of the solvent leaving a partially crosslinked soft matter. New materials can be obtained in form of monoliths, fibres, aerogels, powders or selective membranes. This technique has been used to synthesize hybrid organic – inorganic materials at low temperatures (Sanchez *et al.*, 2005). By this technique, the material is tailored to have both an organic and inorganic phases. The chemical strategy in sol-gel chemistry may involve one of bottom-up self – assembly of nanoparticles, in-situ polymerization reactions from nano-building blocks, bio-initiated reactions and reactions used to couple functionalized nanoparticles into stable 3D networks of organic – inorganic bridges. However, achieving the ultimate goal depends on the following (Castelvetto and Cinzia 2004);

- i. The hydrolysis of such metal alkoxides as tetraethoxosilane – TEOS; tetramethoxosilane – TMOS; zirconium IV n-propoxide, or titanium IV butoxide and then polycondensation of functional organosilanes into macro monomers, dimmers, trimmers to tetramers and so on and so forth.

- ii. The encapsulation of organic components within sol – gel derived metal oxides.
- iii. The functionalization of nano-fillers, nanoclays or other compounds with lamellar structures.

The first reaction stage involves formation of silanol groups by hydrolysis (Rao *et al.*,2005);



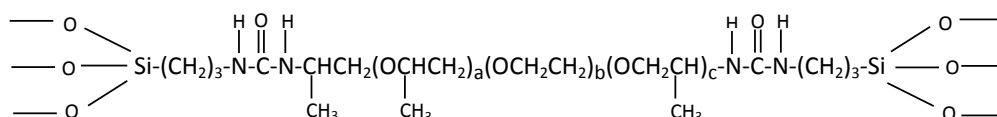
[1 mole of metal alkoxide + 1 mole of water giving 1 mole of silanol + 4 moles of alcohol]

Then follows formation of siloxane networks by a series of polycondensation reactions at the second reaction stage;

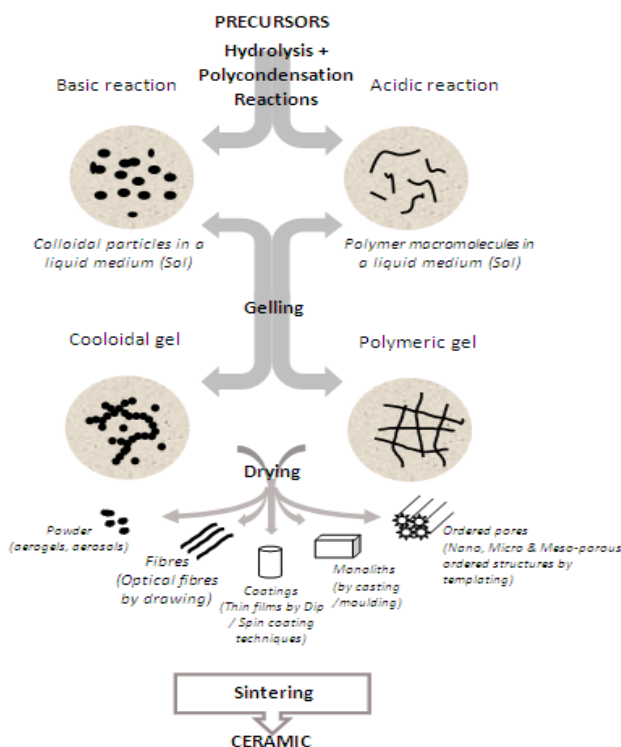


[2 moles of silanol forming 2 moles of siloxane and 4 moles of water]

By carrying out the process in an acidic or basic medium and further varying parameters such as the nature of precursor used, drying temperature, ageing time, dipping and spinning, it is possible to obtain single or multilayer thin film coatings for optical waveguide applications, dense monoliths as gain medium for optical / laser applications, highly cross-linked optical fibres for telecommunications, aerogels and micro or nanoporous membranes for gas and liquid separation. Apart from its low cost, another promising feature of the sol gel technique is the ability to introduce dopants such as lanthanides, fluorescent dye molecules and organic chromophores during synthesis (Righini and Pelli 1997). Novel class II hybrids based on amide crosslinkedalkylene – siloxane have been synthesized by the sol gel technique (Nunes *et al.*,2005). The materials showed a greater percentage of highly bonded amide linkages even though disordered. Furthermore, It has been reported earlier on by Molina *et al.*,(2005), that hybrid hosts formed by poly(ether)-based chains of variable length grafted at both ends to a tripod of siloxane linkages through urea (-NHCO) crosslinks, otherwise called di-ureasils, have shown good transparency and mechanical flexibility. They also offer a wide range of optical applications such as tunable lasers, optical amplifiers, luminescent displays, touch screens and intelligent display panels. The material also was a good host to lanthanide elements as europium (Eu<sup>3+</sup> Eu<sup>2+</sup>); erbium (Er<sup>3+</sup>); cerium (Ce<sup>3+</sup>); neodymium (Nd<sup>3+</sup>); Terbium (Tb<sup>3+</sup>). A hybrid di-ureasil structure is shown in Figure 1, thus;



**Figure 1:** Jeffamine 600 + polyether; Molecular structure of Jeffamine 600 backbone, a + c = 2.5, b = 8.5 grafted at both ends with triodal siloxane linkages (3-isocyanatopropyl triethoxysilane – ICPTES). A schematic of the various materials obtainable through sol gel process is shown in Figure 2.



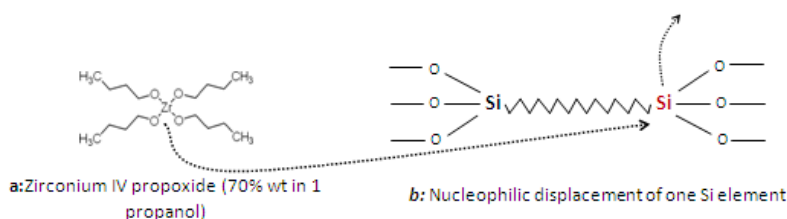
**Figure 2:** Various routes for obtaining different material configurations via sol gel technique.

## 1.2 Thin Films by Spin Coating Technique

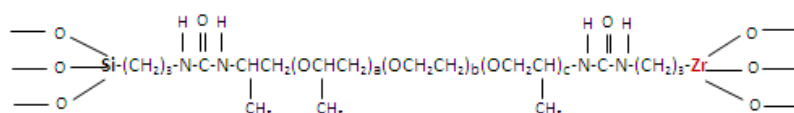
Spin coating, a technique used to coat polymer or glass substrates for planar waveguide applications (Rom 2008), involves manually depositing some drops of a sol of hydrolyzed and poly-condensed precursor, on a metal, glass, plastic or composite material substrate. The sol is sprayed through an injection nozzle onto the substrate, which may be ceramic, plastic or glass. In order to avoid impurities or particles that may affect the quality of the film, the sol is filtered with a sub-micron sized sieve at the injection nozzle. The substrate is accelerated gradually up to 500rpm and then at a higher constant speed. By centrifugal forces generated on the sol coating, it is uniformly spread over the substrate forming a thin film layer. Solvent evaporation dominates at this stage. Final thin film property depends on the nature and viscosity of the resin, solvent drying rate, particle size distribution of nanoparticles and fluid surface tension. Process control parameters include solution viscosity, angular speed, and time (Mellbring *et al.*, 2001). So far, the commercial technologies which depend on this processing technique include the production of Compact Discs (CDs), Digital Video Discs (DVDs) and Compact Disc – Read Only Memory (CD-ROM). Others include flat screen display coatings, magnetic disk coatings, and dielectric insulating layers for microcircuit fabrication.

## 1.3 Theoretical Background and aim of study

Lanthanide doped di-ureasils and light emitting diodes have been synthesized in previous studies (Fu *et al.*, 2007; Nunes *et al.*, 2006; Binnemans 2009; De Bettencourt-Dias 2007). In the conventional sol-gel approach, lanthanides doping involves dissolving rare-earth salts which may contain  $\text{Nd}^{3+}$ ,  $\text{Eu}^{3+}$  (Sá Ferreira *et al.*, 2010; Carlos *et al.*, 2004; Fernandes *et al.*, 2008),  $\text{Er}^{3+}$ ,  $\text{Te}^{3+}$  (Wang and Yan 2006; Lima *et al.*, 2009), within an organic precursor – sol, and polycondensed into a gel. In this study europium II chloride ( $\text{EuCl}_2$ ) salt may be introduced in the initial sol of dispersed hydrolyzed metal alkoxide which is 3-isocyanatopropyl triethoxysilane – (ICPTES) compounds as espoused by Sanchez *et al.*, (2003). Practically grafting zirconium ion ( $\text{Zr}^{2+}$ ) from zirconium IV n-propoxide ( $\text{Zr}(\text{OC}_3\text{H}_7)_4$ ) unto the polyether backbone on the urea linkage as a replacement for one of the silicon ( $\text{Si}^{4+}$ ) ions in the di-ureasil compound catalyzed by methacrylic acid (MAA), while controlling impurity level, may offer more promising properties. Figure 3 illustrate this reaction scheme while Figure 4 shows the intended molecular structure of the new hybrid material. It is further suggested that the refractive index of the synthesized material may be controlled with the addition of zirconium (IV) n-propoxide. This study explores the possibility of producing  $\text{Eu}^{3+}$  doped optical waveguides based on di-ureasils. Recall that a *passive waveguide* is a material that allows the smooth passage of light waves like the optic fibre while an *active waveguide* is a material which is able to amplify light by stimulated or spontaneous emission of radiation (Paschotta 2008; Sá Ferreira *et al.*, 2010). This is achieved by introducing any of the lanthanides (Carlos *et al.*, 2011);  $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ , ruby, which is able to emit light near the infrared (IR) range in an optical cavity by the excitation of its ground state photons. For each photon excited from the ground state, there is a release of additional photon until there is a coherent emission of light through the cavity. This process is able to develop an amplified light or signal at the end of the cavity.



**Figure 3:** Reaction scheme of zirconium IV propoxide and Jeffamine 600



**Figure 4:** Intended new molecular structure of hybrid material,  $a + c = 2.5$ ,  $b = 8.5$

## II. Materials and Methods

The procedure used for the sol-gel synthesis is as elucidated by Molina *et al.*, (2005b). All reagents were of analytical grade and marked “for analysis”.

## 2.1 Synthesis of doped di-ureasil

As 8.4mL of Jeffamine 600 (Sigma-Aldrich) was put in a beaker under continuous stirring. 37.8mL of tetrahydrofuran (THF) was added while stirring continued. After 5mins of stirring, 6.11mL of ICPTES (Fluka) poured into the mixture. Stirring continued while 1.22mL of zirconium IV propoxide (Sigma-Aldrich) was added carefully into the mixture after 30mins followed by addition of 2.5mL of methacrylic acid (MAA) (Sigma-Aldrich). The experiment was set up using a reflux condenser. The contents were continuously heated under constant stirring. The temperature was however equilibrated with an oil bath at 82°C and maintained for 24hrs after which, the sol was allowed to cool down from 80°C to 45°C. THF solvent was then recovered from the solution by using the Rotavapor R-114 (BUCHI water bath B-480) at 60°C. About 22ml of THF was recovered. The resultant viscous solution was then poured into a beaker. A little quantity of the mixture was tested for Zr by using water. This test was to ascertain the effectiveness of the zirconium IV n-propoxide during the nucleophilic reaction involving Jeffamine 600 and ICPTES in the sol.

However, three hybrid mixtures were synthesized with the addition of 2mls of butanol and 0.03g of europium III chloride dopant. The third hybrid material without the addition of europium III chloride dopant was used as a control experiment.

## 2.2 Spin coating hybrid di-ureasil thin films and molding hybrid di-ureasil monoliths

The 3 synthesized hybrid sol were used for the spin coating process by using each sample to coat one borosilicate glass and one soda lime glass. The spin coater was programmed to spin at 1000 rotations per minute (rpm) for 30 seconds for each coating process. Aside from spin coating borosilicate and soda lime glasses, 3 different formulations were collected for the gelation stage and moulded into monoliths. The spin coated glasses and monoliths were aged and oven dried in a laboratory oven for 5 days at 60°C.

## 2.3 FTIR measurements

Bruker Optics FTIR equipment with beam splitter KBr/Gloablar lamp detector at 100 scans done in transmittance mode, was used to determine the nature of chemical bonds and functional groups between ICPTES and Jeff 600-Zirconium propoxide in the gel. By interpreting the infrared (IR) absorption spectrum, the chemical bonds present in the material were determined. The spectra obtained from the analysis were compared with predetermined spectra of pure compounds. Several infrared spectra of pure compounds (organic and inorganic) already exist in IR spectra libraries for comparison.

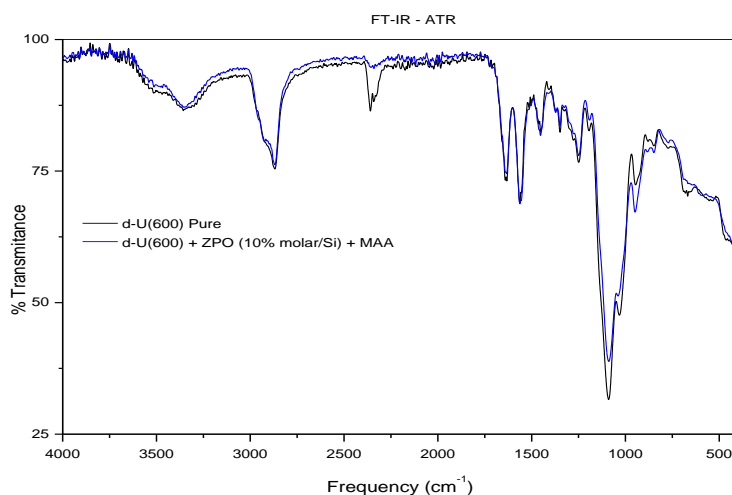
## 2.4 Photoluminescence measurements

Photoluminescence was recorded at ambient temperature with a TRIAX monochromator coupled to R928 Hamamatsu photomultiplier. Each spectrum was obtained using the front face acquisition mode for the pure and doped hybrid di-ureasil thin films and monoliths synthesized with di-ureasil (d-U600) + 10% molar ZPO + MAA and the second material doped with 1%  $\text{Eu}^{3+}$  respectively.

## III. Results and Discussions

### 3.1. Results of FTIR

Here we analyzed the different chemical compositions, bond possibilities and functional groups. The FTIR transmittance spectrum is shown in Figure 5.

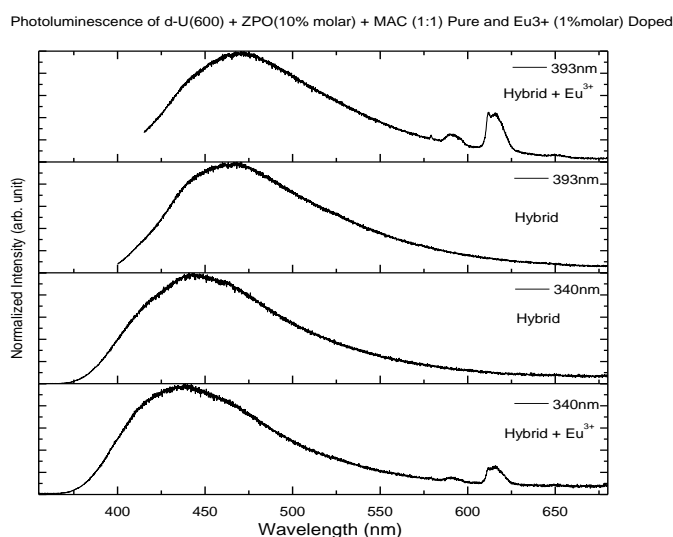


**Figure 5:** FTIR spectra of pure di-ureasil and zirconium propoxide doped di-ureasil

The presumed chemical composition of the hybrid material as earlier reported in this work are 2 siliceous backbones, di-urea groups (amide linkages I & II), silanols, methyl groups ( $-\text{CH}_3$ ), carbonyl ( $\text{C}=\text{O}$ ) linkages, polyether ( $\text{R}-\text{O}-\text{R}'$ ) backbone and  $\text{Zr}-\text{O}_3$  linkages. Usually, the bands at  $1720\text{cm}^{-1}$ ,  $1683\text{cm}^{-1}$  and  $1660\text{cm}^{-1}$  are assigned to hydrogen bonded carbonyl group ( $\text{C}=\text{O}$ ) (Nunes *et al.* 2006). The FTIR spectrum confirm these compositions. The spectrum for pure d-U(600) hybrid has several peaks at about  $3300\text{cm}^{-1}$ ,  $2800\text{cm}^{-1}$ ,  $2300\text{cm}^{-1}$ ,  $1720\text{cm}^{-1}$ ,  $1683\text{cm}^{-1}$ ,  $1380\text{cm}^{-1}$ ,  $1180\text{cm}^{-1}$ ,  $1080\text{cm}^{-1}$ . This also corresponded to that shown by d-U(600)+ZPO(10% molar/SI) + MAA. Furthermore, shoulders appear between  $3650 - 3550\text{cm}^{-1}$  in both cases. The difference in the two spectra is seen in their intensities which show the pure hybrid having a higher intensity than the doped hybrid material.

#### Photoluminescence Results

Photoluminescence spectra were obtained for the pure hybrid material synthesized with ureasil 600 + 10% molar ZPO + MAA and the second hybrid material doped with 1%  $\text{Eu}^{3+}$ . As a result of pumping at two wavelengths; 340nm and 393nm, the following spectra shown in Figure 6, were obtained.



**Figure 6:**Photoluminescence spectra

From Figure 6, luminescence of blue light was observed between 435 – 460nm for the pure hybrid material when pumped at 340 and 393nm respectively as represented by the different peaks. The doped material however exhibited 3 peak levels at about 475nm, 585nm and 617nm with the 393nm pumped  $\text{Eu}^{3+}$  doped hybrid material and 340nm pumped  $\text{Eu}^{3+}$  doped hybrid material respectively, showing a stronger luminescence of white light; red, blue and green, compared to the pure hybrid materials. This may be attributable to the presence of electron holes and energy transfer between the organic-inorganic hybrid host and the  $\text{Eu}^{3+}$  ions. Interestingly, these were under normalized intensities.

#### IV. Conclusion

We have reported a sol gel technique used to synthesize pure urea crosslinked siloxane based organic-inorganic hybrid and europium ( $\text{Eu}^{3+}$ ) doped urea crosslinked siloxane based organic-inorganic hybrid materials. The pure and doped samples were synthesized with di-ureasils (Jeffamine 600) / d-U600, Zirconium (IV) n-propoxide ( $\text{Zr}(\text{OC}_3\text{H}_7)_4$ ) / ZPO, and methacrylic acid ( $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2\text{H}$ ) / MAA. A thin film was successfully coated on the hybrid materials via spin coating technique. The materials have been characterized using FTIR and photoluminescence techniques. Fourier Transform Infrared Spectroscopy (FTIR) and photoluminescence were carried out on both samples to obtain spectra for characterization. From FTIR spectra, it was obvious that the materials exhibited a non-bonded zirconium ion in the d-U(600)+ZPO(10% molar/SI)+MAA samples as though it were still a pure sample of d-U(600). The pure hybrid sample was strong, tough and rigid. On the other hand, the  $\text{Eu}^{3+}$  doped material was resilient on compression, showing viscoelastic behaviour. The acquired kinetic energy in the as synthesized doped sample was high, giving the material ability to rebound several times. On rebound, the kinetic energy may be dissipated through various means without direct impact on the synthesized material. Therefore, there seems to be an effect of the  $\text{Eu}^{3+}$  ion on the rheological property of the bulk hybrid host. From the photoluminescence results, the  $\text{Eu}^{3+}$  doped sample exhibited a moderate emission of blue, green and red, which are the primary colours of white light as opposed to the pure hybrid material which

emitted a high intensity blue light. These properties may be very useful for cell-phones that may experience several falls during their lifetime, having energy saving screens of organic light emitting diodes (OLED).

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### Cited Works

- [1]. Bettencourt-Dias, A De. 2007. "Lanthanide-Based Emitting Materials in Light-Emitting Diodes." *Dalton Transactions*, no. 22: 2229–41.
- [2]. Binnemans, Koen. 2009. "Lanthanide-Based Luminescent Hybrid Materials." *Chemical Reviews* 109 (9): 4283–4374. <https://doi.org/10.1021/cr8003983>.
- [3]. Carlos, Luís D, Rute A Sá Ferreira, De Zea Bermudez, Beatriz Julian-Lopez, and P Escribano. 2011. "Progress on Lanthanide-Based Organic-Inorganic Hybrid Phosphors." *Chemical Society Reviews* 40 (2): 536–49. <https://doi.org/10.1039/c0cs00069h>.
- [4]. Carlos, Luís D, Rute A. Sá Ferreira, M C Gonçalves, and V. de Zea Bermudez. 2004. "Local Coordination of Eu(III) in Organic/Inorganic Amine Functionalized Hybrids." *Journal of Alloys and Compounds* 374 (1–2): 50–55. <https://doi.org/http://dx.doi.org/10.1016/j.jallcom.2003.11.063>.
- [5]. Castelvetro, V., and Vita de Cinzia. 2004. "Nanostructured Hybrid Materials from Aqueous Polymer Dispersions." *Advances in Colloid and Interface Science* 108–109: 167–85.
- [6]. Fernandes, M., V. de Zea Bermudez, R.a. Sá Ferreira, L.D. Carlos, and N.V. Martins. 2008. "Incorporation of the Eu(Tta)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> Complex into a Co-Condensed d-U(600)/d-U(900) Matrix." *Journal of Luminescence* 128 (2): 205–12. <https://doi.org/10.1016/j.jlumin.2007.07.009>.
- [7]. Fu, L, R A Sa' Ferreira, S S Notre, Luís D Carlos, and João Rocha. 2007. "In-Situ Synthesis of Lanthanide Complex in Urea Crosslinked Organic-Inorganic Di-Ureasil Hybrids via Carboxylic Acid Solvolysis." *Journal of Luminescence* 122–123: 265–67.
- [8]. Lima, P P, Rute A. Sá Ferreira, S A Junior, O L Malta, and Luís D Carlos. 2009. "Terbium (III)-Containing Organic-Inorganic Hybrids Synthesized through Hydrochloric Acid Catalysis." *Journal of Photochemistry and Photobiology A: Chemistry* 201 (2–3): 214–21.
- [9]. Mellbring, O, S Kihlman Øiset, A Krozer, J Lausmaa, and T Hjertberg. 2001. "Spin Coating and Characterization of Thin High-Density Polyethylene Films." *Macromolecules* 34 (21): 7496–7503. <https://doi.org/10.1021/ma000094x>.
- [10]. Molina, C., P. J. Moreira, R. R. Gonçalves, R. a. Sá Ferreira, Y. Messaddeq, S. J. L. Ribeiro, O. Soppera, et al. 2005a. "Planar and UV Written Channel Optical Waveguides Prepared with Siloxane-poly(Oxyethylene)-zirconia Organic-inorganic Hybrids. Structure and Optical Properties." *Journal of Materials Chemistry* 15 (35–36): 3937. <https://doi.org/10.1039/b505081m>.
- [11]. ———. 2005b. "Planar and UV Written Channel Optical Waveguides Prepared with Siloxane-poly(Oxyethylene)-zirconia Organic-inorganic Hybrids. Structure and Optical Properties." *Journal of Materials Chemistry* 15 (35–36): 3937. <https://doi.org/10.1039/b505081m>.
- [12]. Nunes, S. C., V. de Zea Bermudez, J. Cybinska, R. a. Sá Ferreira, J. Legendziewicz, L. D. Carlos, M. M. Silva, M. J. Smith, D. Ostrovskii, and J. Rocha. 2005. "Structure and Photoluminescent Features of Di-Amide Cross-Linked Alkylene-siloxane Hybrids." *Journal of Materials Chemistry* 15 (35–36): 3876. <https://doi.org/10.1039/b505372m>.
- [13]. Nunes, S.C., V. de Zea Bermudez, D. Ostrovskii, and L.D. Carlos. 2006. "FT-IR and Raman Spectroscopic Study of Di-Urea Cross-Linked Poly(Oxyethylene)/Siloxane Ormolytes Doped with Zn<sup>2+</sup> Ions." *Vibrational Spectroscopy* 40 (2): 278–88. <https://doi.org/10.1016/j.vibspec.2005.11.003>.
- [14]. Paschotta, R. 2008. "Photonics." *Encyclopedia of Laser Physics and Technology*. RP Photonics Consulting GmbH. <http://www.rp-photonics.com/photoluminescence.html>.
- [15]. Rao, Kota Sreenivasa, Khalil El-Hami, Tsutomu Kodaki, Kazumi Matsushige, and Keisuke Makino. 2005. "A Novel Method for Synthesis of Silica Nanoparticles." *Journal of Colloid and Interface Science* 289 (1): 125–31. <http://www.ncbi.nlm.nih.gov/pubmed/15913636>.
- [16]. Righini, Giancarlo C, and Stefano Pelli. 1997. "Sol Gel Glass Waveguides." *Journal of Sol Gel Science and Technology* 8: 991–97.
- [17]. Rom, C D. 2008. "Spin Coat Theory." Columbia Centre for Integrated Science and Engineering. 2008. <http://www.clean.cise.columbia.edu/process/spintheory.pdf>.
- [18]. Sá Ferreira, Rute A, Paulo Sergio de Brito Andre, and Luis D Carlos. 2010. "Organic-inorganic Hybrid Materials towards Passive and Active Architectures for the next Generation of Optical Networks." *Optical Materials* 32 (11): 1397–1409. <https://doi.org/http://dx.doi.org/10.1016/j.optmat.2010.06.019>.
- [19]. Sá Ferreira, Rute A, D C Oliveira, L Q Maia, C M S Vicente, Paulo Sergio de Brito Andre, V. de Zea Bermudez, S. J. L. Ribeiro, and Luís D Carlos. 2010. "Enhanced Photoluminescence Features of Eu<sup>3+</sup>-Modified Di-Ureasil-Zirconium Oxocluster Organic-inorganic Hybrids." *Optical Materials* 32 (12): 1587–91. <https://doi.org/http://dx.doi.org/10.1016/j.optmat.2010.05.028>.
- [20]. Sanchez, C, B Lebeau, F Chaput, and J P Boilot. 2003. "Optical Properties of Functional Hybrid Organic-Inorganic Nanocomposites." *Advanced Materials* 15 (23): 1969–94. <https://doi.org/10.1002/adma.200300389>.
- [21]. Sanchez, Clément, Beatriz Julián, Philippe Belleville, and Michael Popall. 2005. "Applications of Hybrid Organic-inorganic Nanocomposites." *Journal of Materials Chemistry* 15 (35–36): 3559. <https://doi.org/10.1039/b509097k>.
- [22]. Wang, Qian-Ming, and Bing Yan. 2006. "Terbenium/Zinc Luminescent Hybrid Siloxane-Oxide Materials Bridged by Novel Ureasils Linkages." *Journal of Organometallic Chemistry* 691 (4): 545–50.
- [23]. Wang, X., J. Zhuang, Q. Peng, and A. Li. 2005. "A General Strategy for Nano Crystal Synthesis." *Nature* 437: 121–24.

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