

Light-induced trans-cis isomerization of terpyridine functionalized POSS nanostructures self-assembled in presence of Eu³⁺ ions.



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Abstract: Polyhedral Oligomeric Silsesquioxane (POSS) nanostructures exhibit both organic and inorganic characteristics and a rigid cage-like core whose presence provides a high thermal and mechanical stability. ^[1,2] Moreover, the organic peripheries can be easily functionalized allowing a facile tuning of the POSS properties. ^[3,4,5] The rational design of the organic moieties may favor specific interaction allowing the self-assembly of the POSS nanostructures.

Aim: Here, novel POSS bearing terpyridine moieties (Mono- and Octa- functionalized POSS called M-POSS and O-POSS) were synthetized via Heck coupling reaction^[6] in order to study the formation of 3D supramolecular organizations. The self-assembly processes between M-POSS/O-POSS and Eu³⁺ were investigated by ¹H-NMR as well as $R = \langle C \rangle$ absorbance and emission spectroscopy. The O-POSS forms extended 3D architectures after interaction with Eu³⁺ displaying interesting photo-physical properties. Moreover, the O-POSS-based structures show reversible cis-trans isomerization also in presence of europium species.



500

400

600

Wavelength (nm)

700

800

900

Synthesis and complexometric Study



400

Wavelength (nm)

300

500

600

Wavelength (nm) UV-vis absorption spectra of M-POSS in CH_2Cl_2 (1.3 x 10⁻⁵ M) Emission spectra of O-POSS in CH₂Cl₂ upon addition of Emission spectra of M-POSS in CH₂Cl₂ upon titration UV-vis absorption spectra of **O-POSS** in CH₂Cl₂ upon upon addition of increasing amount of $Eu(OTf)_3$ in CH_3CN with Eu(OTf)₃: 0 eq. - 1 eq. λ_{ex} = 310 nm OD= 0.27 slits addition of increasing amount of $Eu(OTf)_3$ in CH_3CN . increasing amount of Eu(OTf)₃: 0 eq. - 1 eq. λ_{ex} = 310 nm (1.4 x 10-3 M). Inset shows the normalized absorption at 2.5-5 and band pass filter (360 – 100 nm). Inset shows OD= 0.15 slits 5 and band pass filter (360 - 100 nm). Absorption change at 290 nm (red circles) and 330 290nm (red circles) and 330nm (black squares). the normalized absorption at 366nm (black squares). nm (black squares). **Reversible isomerization** M-POSS & O-POSS: trans to cis reversible isomerization **Eu@O-POSS** Reversible isomerization: Emission Spectra a) 1000 1000 իս 356 nm 800 800 hv իս 356 nm Intensity (a.u) Intensity (a.u) 600 -600 400 -200 - Δ (50 °C 200 Δ (50 °C) b) 600 500 550 450 500 400 650 600 400 500 700 400 Wavelength (nm) Wavelength (nm) Wavelength • Emission spectra of trans **O-POSS** solution (black Emission spectra of Eu@O-POSS before and after irradiation at 356 nm. Emission spectra of trans M-POSS solution (black line) and line) and cis **O-POSS** (red line) solution in CH₂Cl₂ - Disappearance of the characteristic Eu emission bands by irradiation cis M-POSS (red line) • Digital photograph taken under UV light at 356 nm: a) trans O-POSS b) cis O-POSS ¹H-NMR spectra of M-POSS solution before (a) and after (b) irradiation b) hv 356 nm a) Spectrum evidencing the

protons of the double bond in

300

250

350

Wavelength (nm)

450

500

400

500

600

700

j=15 Hz



Conclusions

Two POSS based nanostructure functionalized with terpyridine moiety were successfully synthesized. Both nanostructures were able to efficiently complex Eu(III) cations exhibiting (after complexation) a bright-red luminescence under UV light at room temperature. Moreover, the solutions display a reversible trans to cis isomerization of the vinyl moiety. By exploiting this behaviour it is possible to modulate the fluorescence emission of O-POSS in presence of Eu(III) under UV irradiation.

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