

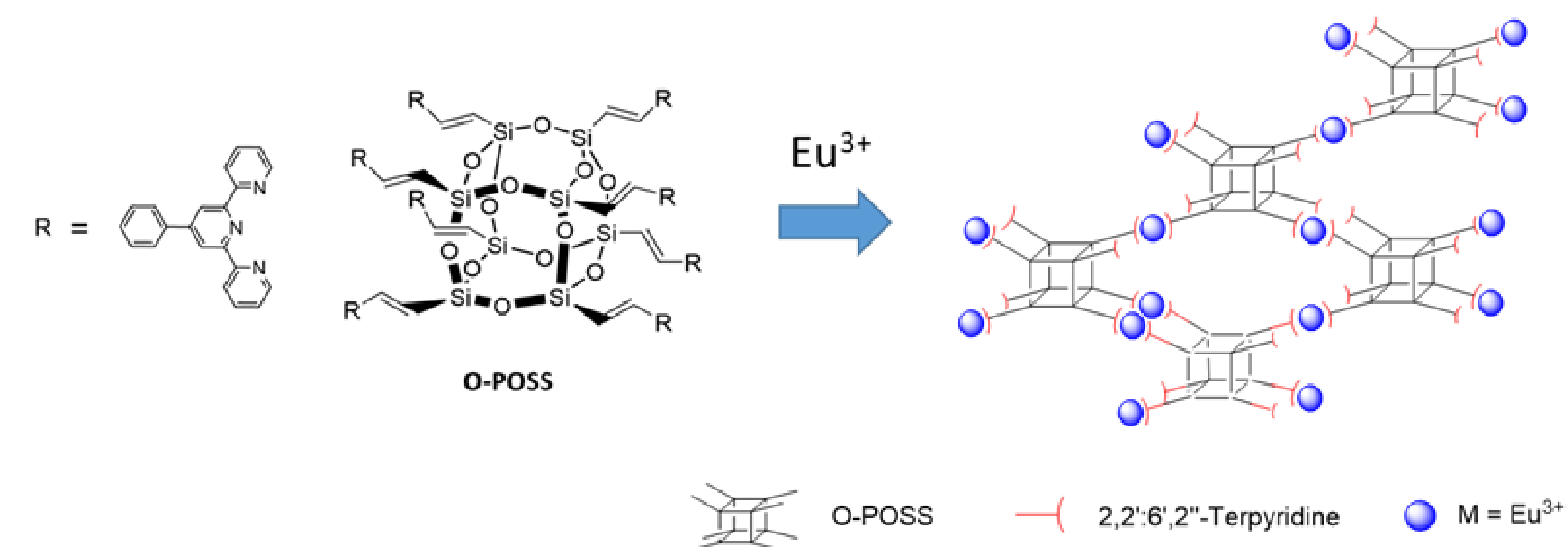
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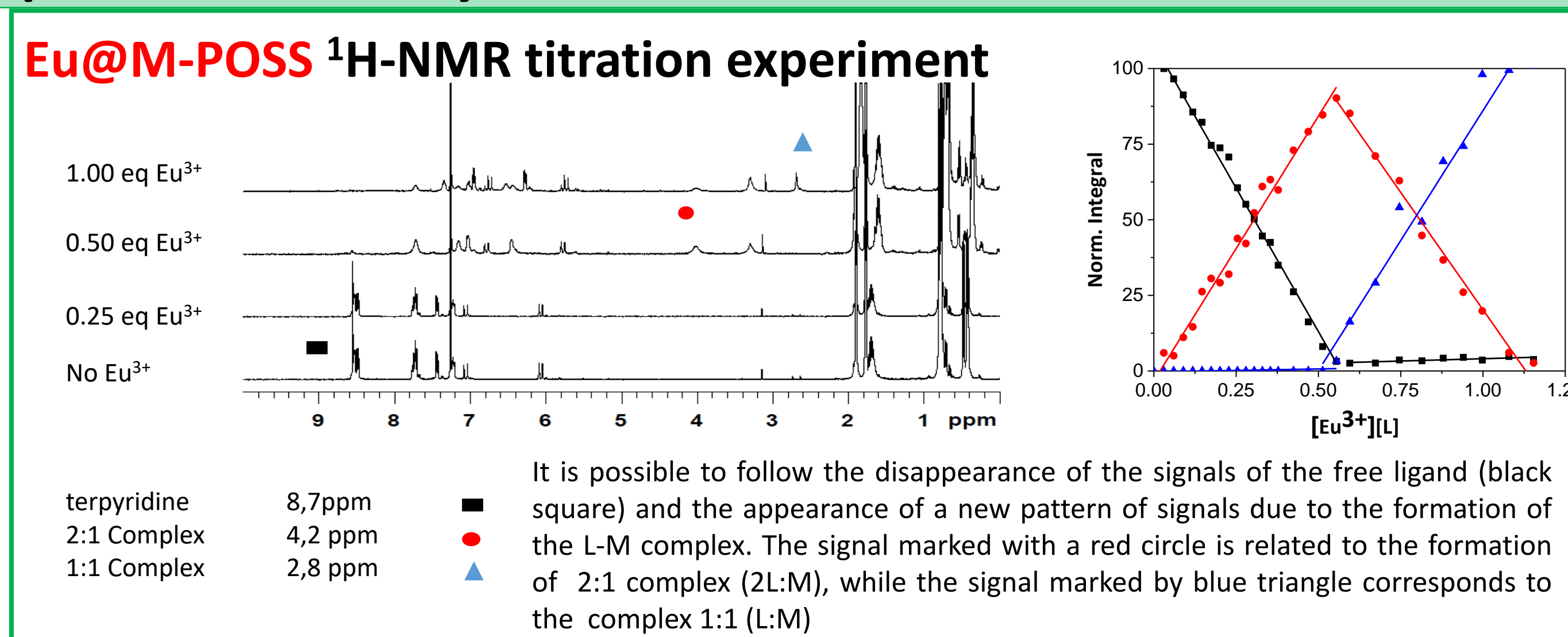
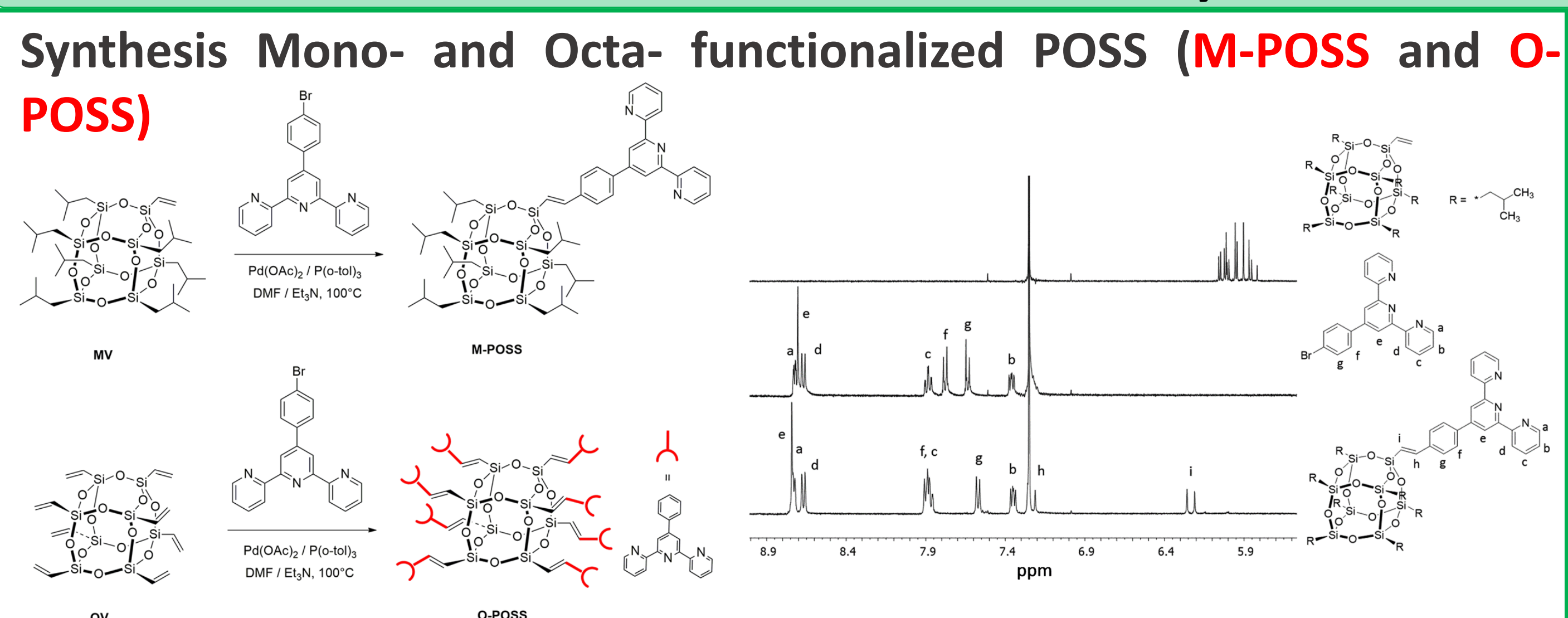
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Abstract: Polyhedral Oligomeric Silsesquioxane (POSS) nanostructures exhibit both organic and inorganic characteristics and a rigid cage-like core whose presence provides a high thermal and mechanical stability. [1,2] Moreover, the organic peripheries 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.

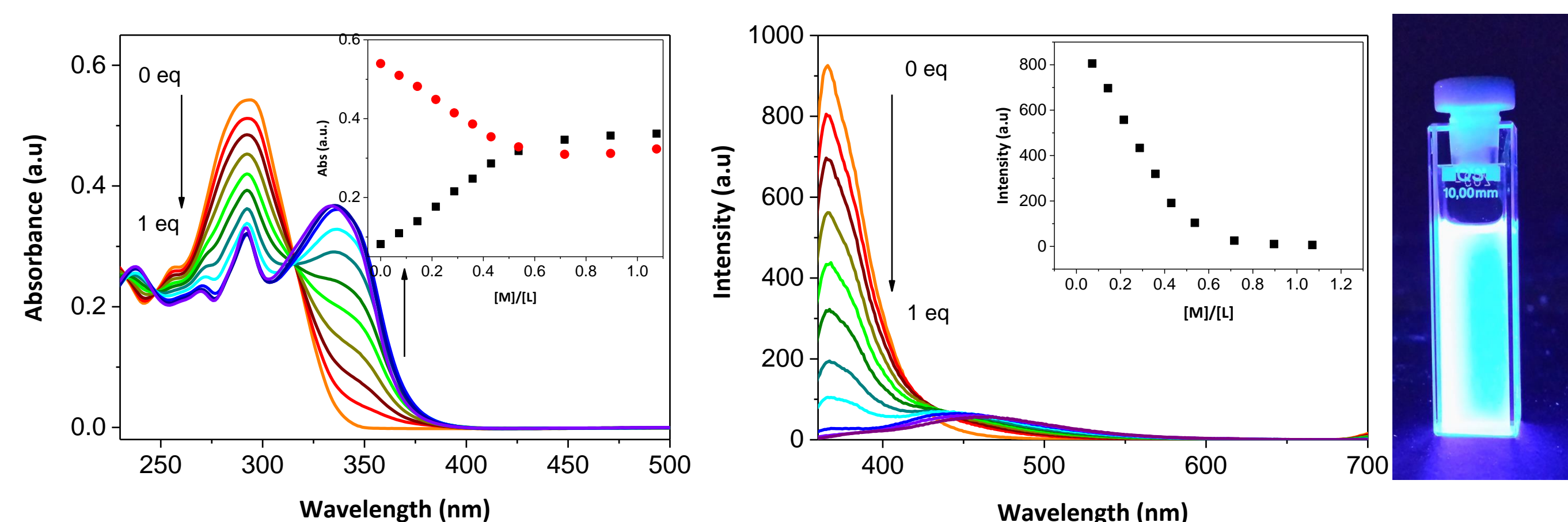
Aim: Here, novel POSS bearing terpyridine moieties (Mono- and Octa- functionalized POSS called M-POSS and O-POSS) were synthesized via Heck coupling reaction^[6] in order to study the formation of 3D supramolecular organizations. The self-assembly processes between M-POSS/O-POSS and Eu³⁺ were investigated by ¹H-NMR as well as 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.



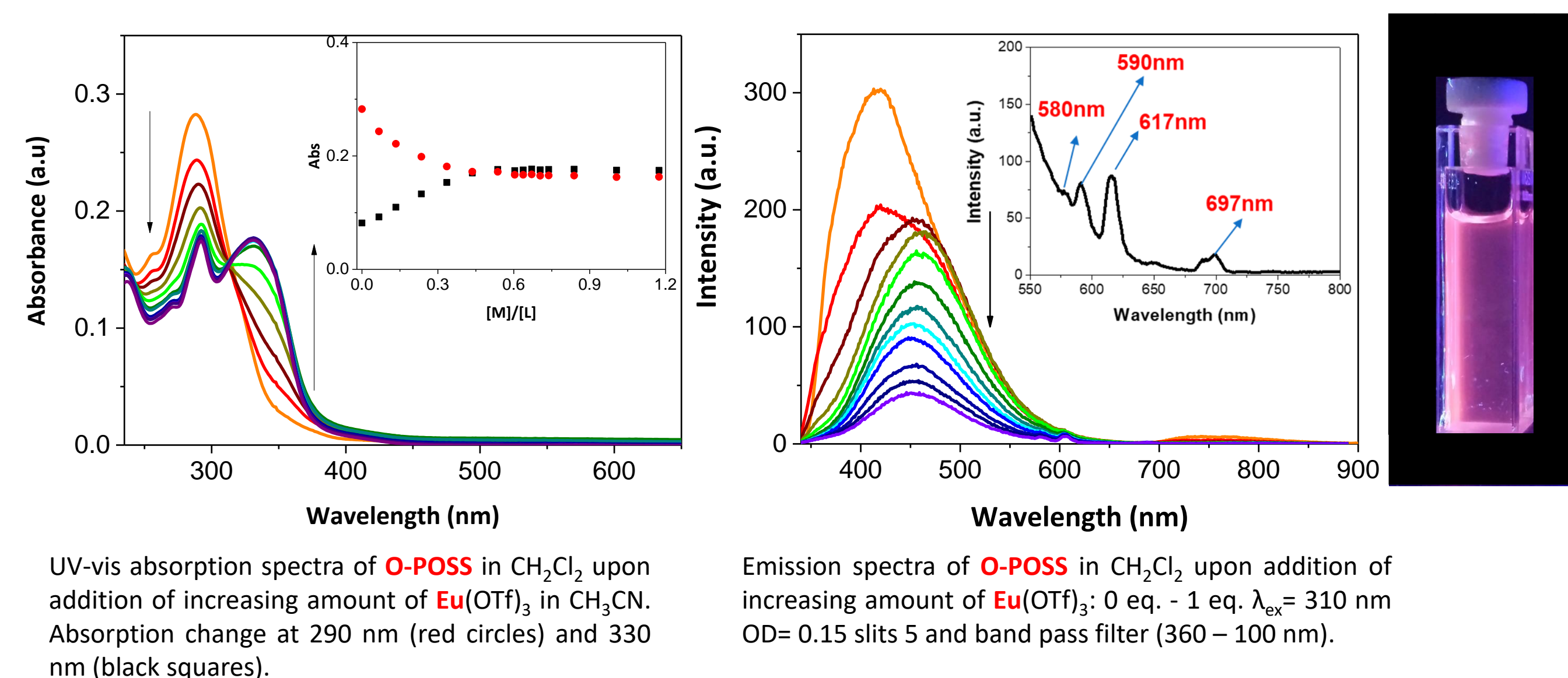
Synthesis and complexometric Study



Eu@M-POSS Titration Experiments: Absorption and Emission

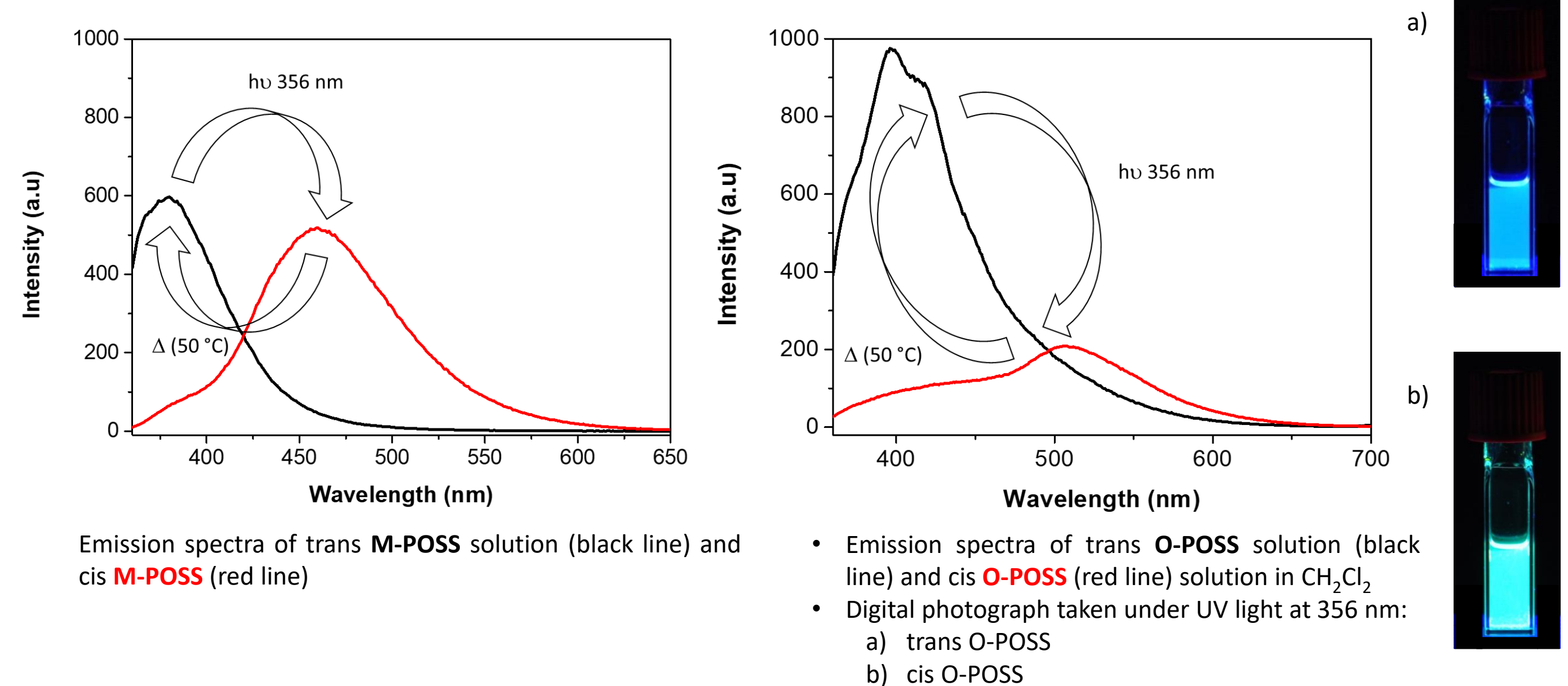


Eu@O-POSS Titration Experiments: Absorption and Emission

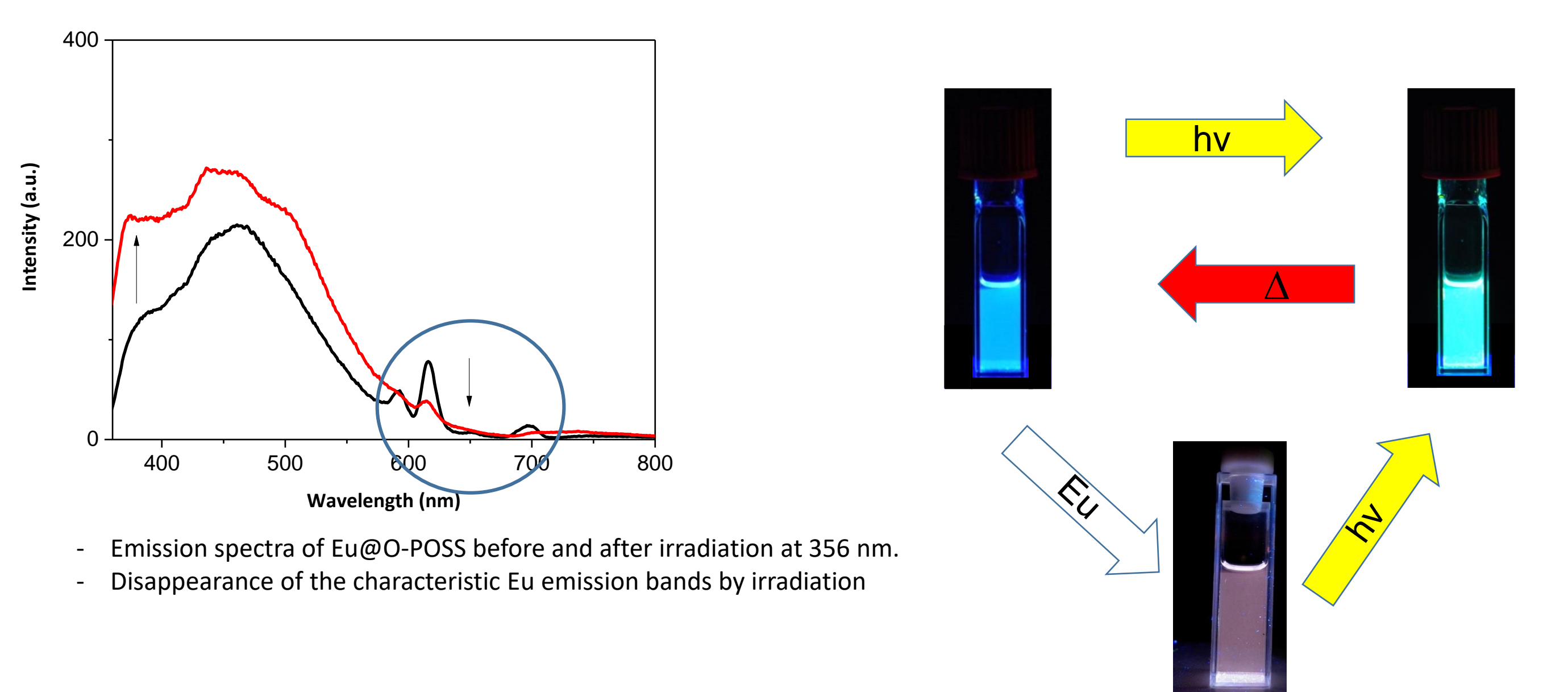


Reversible isomerization

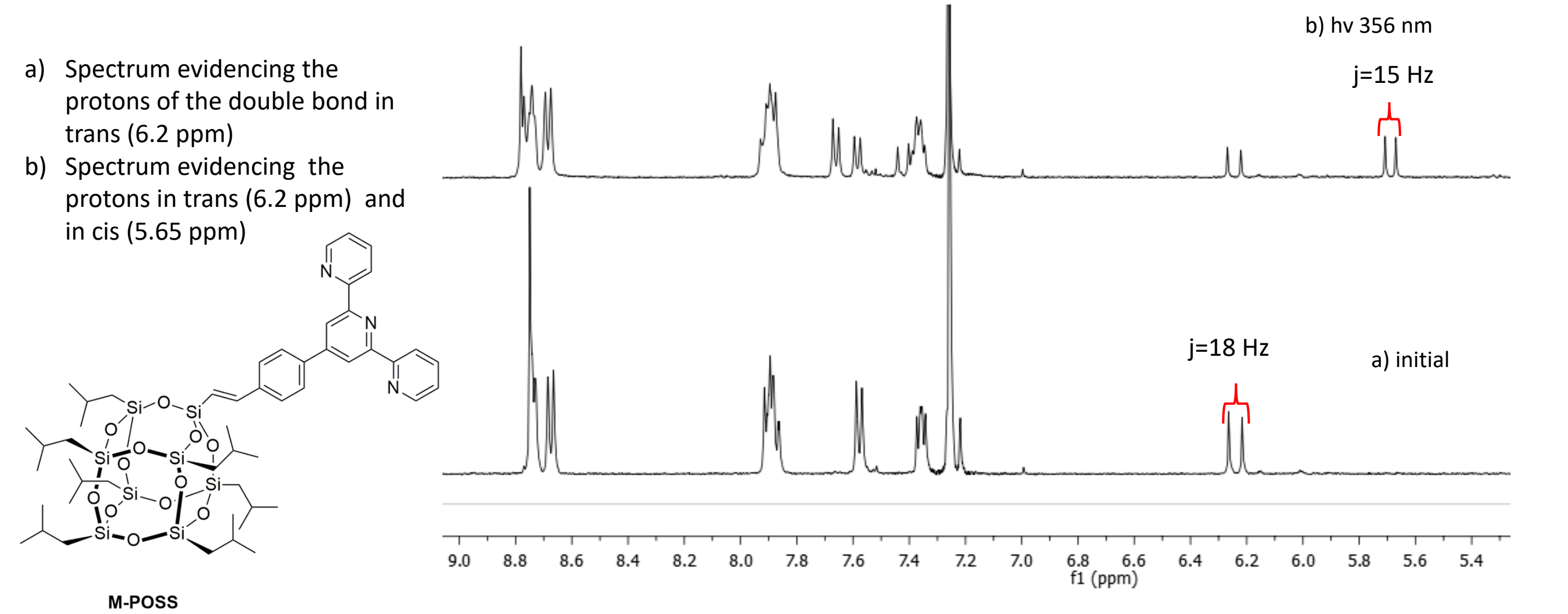
M-POSS & O-POSS: trans to cis reversible isomerization



Eu@O-POSS Reversible isomerization: Emission Spectra



¹H-NMR spectra of M-POSS solution before (a) and after (b) irradiation

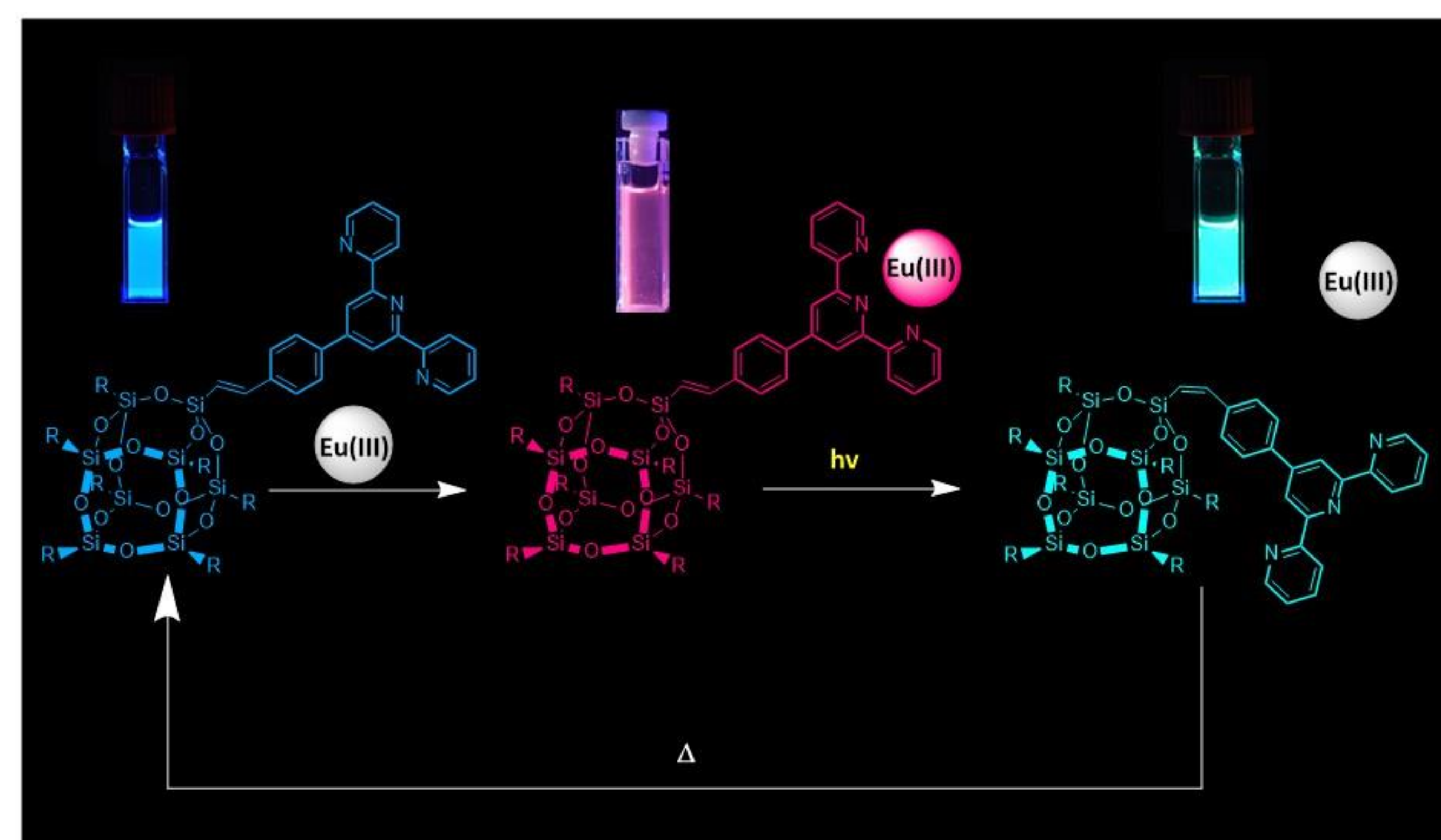


Conclusions

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.

Acknowledgements

C.V. gratefully acknowledges the University of Palermo and University of Namur for a co-founded PhD fellowship. This research uses the resources of the nuclear magnetic resonance service located at the University of Namur. This service is part of the "Plateforme Technologique Physico-Chimical Characterization" - PC².



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