

Functionalized Periodic Mesoporous Organosilicas: From Metal Free Catalysis To Sensing

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Structural analysis

FT-IR measurements.

Using FT-IR, the obtained materials were compared to the precursors, with the obtained spectra presented in Figure S1 (Pic@PMO) and S2 (Porph@PMO). In Figure S1, it is observed that the Pic@PMO spectrum shows a combination of peaks characteristic for Picolinic acid and for Monoallyl PMO, indicating successful coupling. It has to be noted that the amide peak around 1600 cm^{-1} is coincidental with the C=N stretch of picolinic acid. When studying Figure S2, comparable behavior is noted, but two major TCPH₂ peaks (around 1550 and 1460 cm^{-1}) show a drastically reduced intensity. As those peaks were assigned to the COO⁻ symmetric and antisymmetric stretching frequencies, this is an expected result.

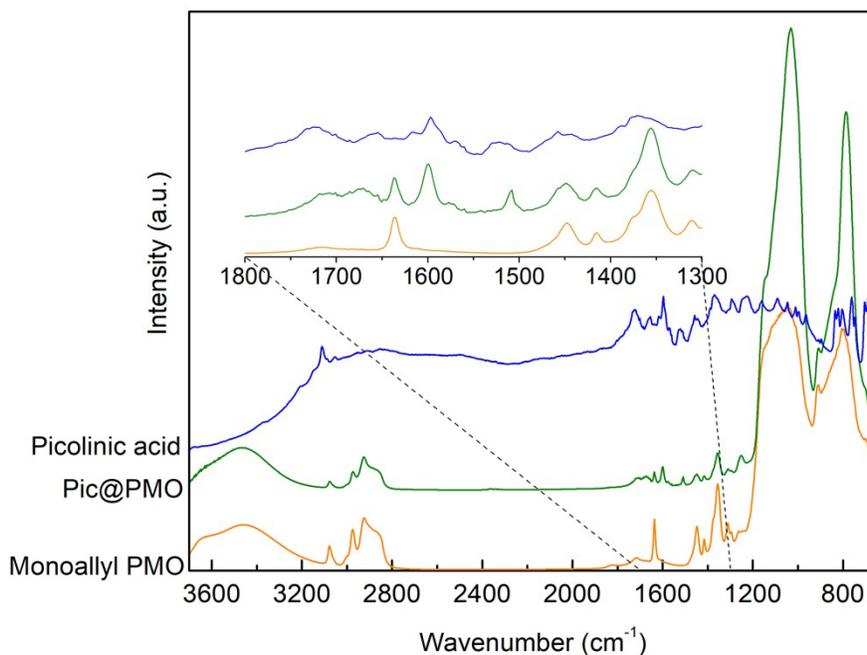


Figure S1. DRIFTS spectra of Monoallyl PMO, Pic@PMO and Picolinic acid, a zoom in on the region of interest for coupling is provided

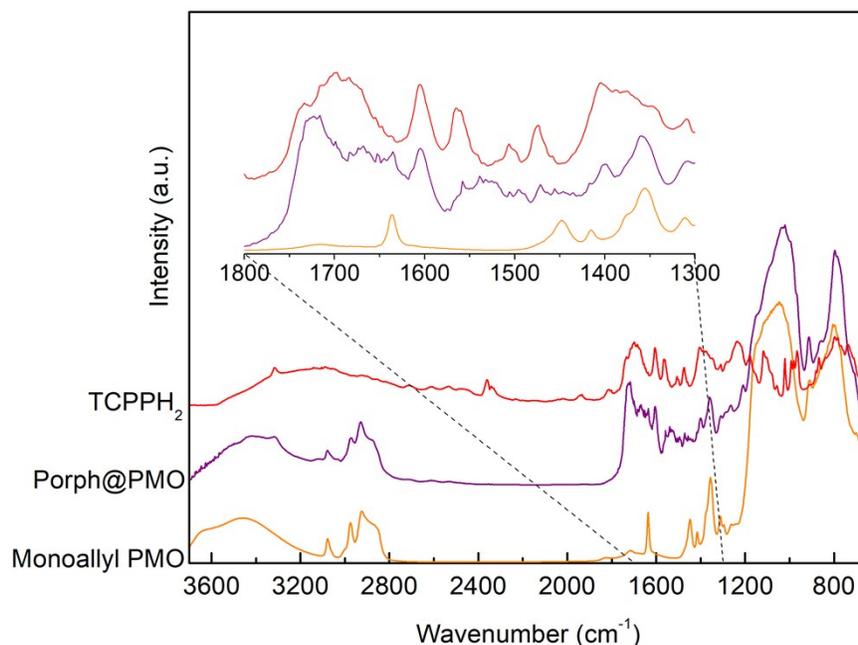


Figure S2. DRIFTS spectra of Monoallyl PMO, Porph@PMO and TCPH₂, a zoom in on the region of interest for coupling is provided

PXRD measurements.

In the obtained PXRD spectra (Figure S3), only one intense (100) reflection was observed at very low 2θ values. As PMOs only exhibit pore ordering and no structural ordering, this peak can be attributed to the uniform porous system and corresponds with the pore diameter. As unmodified and modified materials show comparable maximum values for this (100) reflection, it could be concluded that the functionalization of the Monoallyl PMO has no influence on the pore diameter (and uniformity of the porous system).

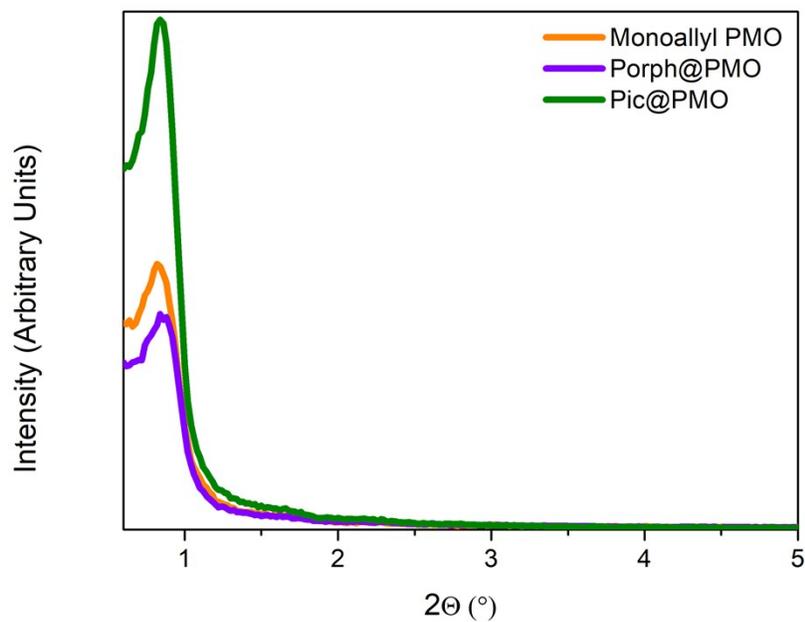


Figure S3. Powder XRD measurements of the PMO materials before and after functionalization. The observed peak is indicative for the (100) reflection of the ordered pores.

STEM-EDX measurements.

To prove homogeneous distribution of the added functional groups over the material, STEM-EDX pictures were made. The distribution of Co and Si over our Co(II) coordinated materials (**Co@Pic@PMO** and **Co@Porph@PMO**) are respectively shown in Figure S4 and Figure S5. As the Co rich zones are coinciding with the PMO material and these ions can only be coordinated to the added functional groups, we could conclude that the used post-modification procedure successfully spread functional groups over the entire material.

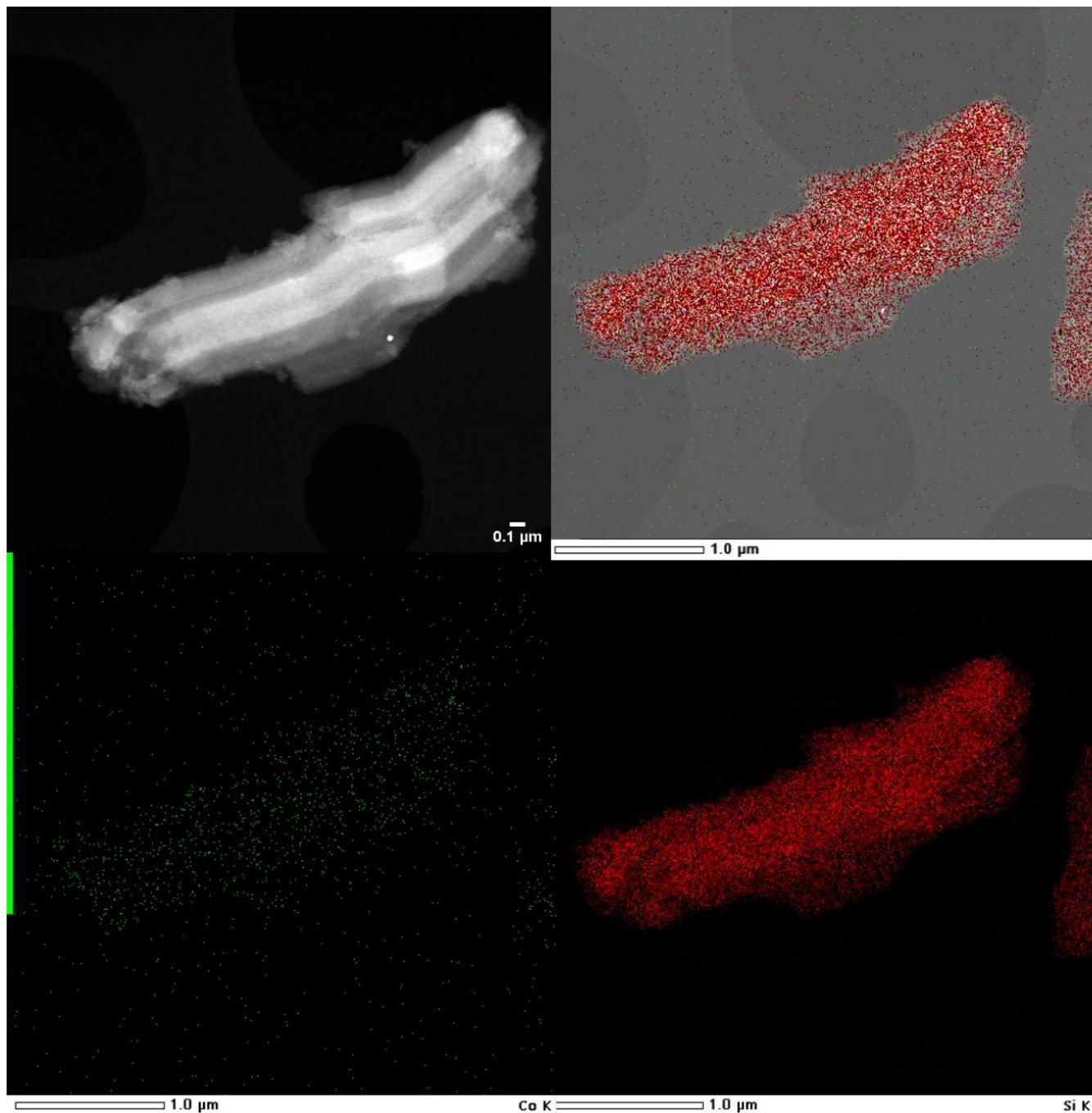


Figure S4. STEM-EDX picture of Co@Pic@PMO. The green dots represent Co (indicative for the coupled functional groups), the red dots represent Si (indicative for the PMO backbone of the material).

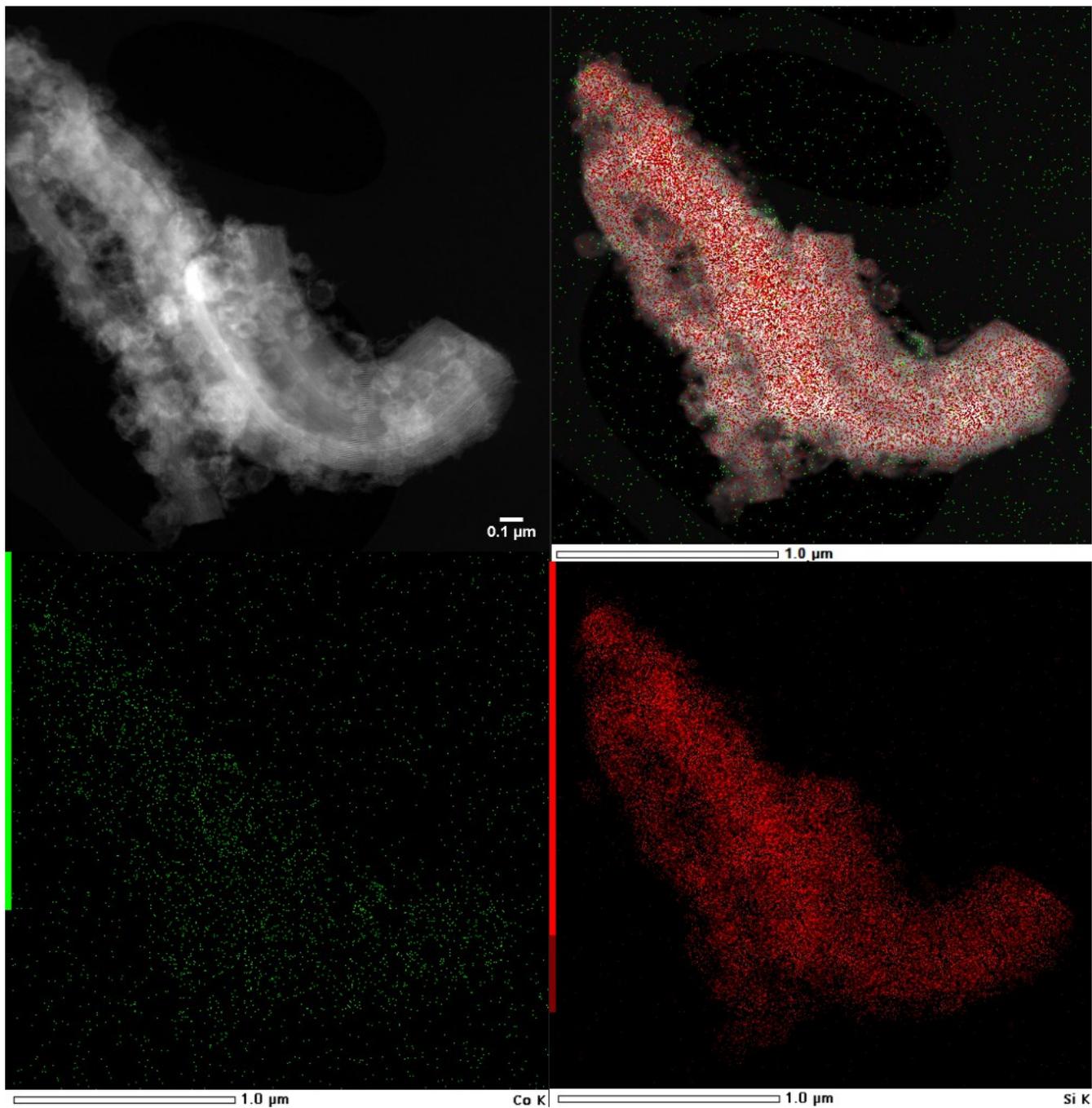


Figure S5. STEM-EDX picture of Co@Porph@PMO. The green dots represent Co (indicative for the coupled functional groups), the red dots represent Si (indicative for the PMO backbone of the material).

UV-VIS absorption.

In order to check the grafting of Yb^{3+} to the porphyrin, UV-VIS absorption measurements were performed. To enable measurements in solution, uncoupled porphyrins were used as a test. In Figure S6, the results for unmodified TCPPh_2 the Yb^{3+} grafted material (Yb@TCPPh_2) are presented. Both materials show very comparable absorption spectra, with a Soret band around 425 nm and 4 Q bands around 525 nm, 550 nm, 600 nm and 650 nm). The observation of 4 different Q bands is characteristic for the reduced symmetry of free base porphyrin,¹ which implies preferential coordination of the Yb^{3+} ions to the peripheral carboxylic acid groups over the porphyrin ring cavity.

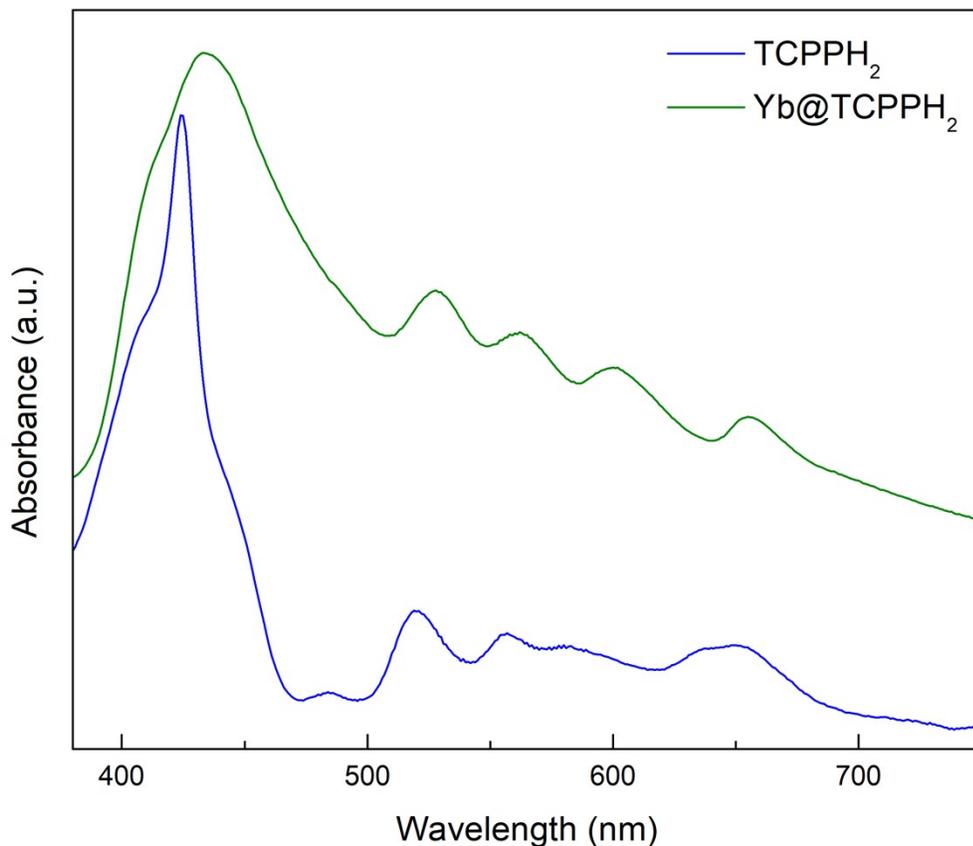


Figure S6. UV-VIS absorption spectra of TCPPh_2 and Yb@TCPPh_2 in water.

Luminescence results

Pic@PMO.

A combined emission-excitation spectrum of pure Pic@PMO has been recorded (Figure S7). The material is easily excited around 350-400 nm, which yields a broad emission peak from 400-600 nm. The sharp peaks observed between 420 and 480 nm originate from the Xenon excitation source and are thus not a feature of the material.

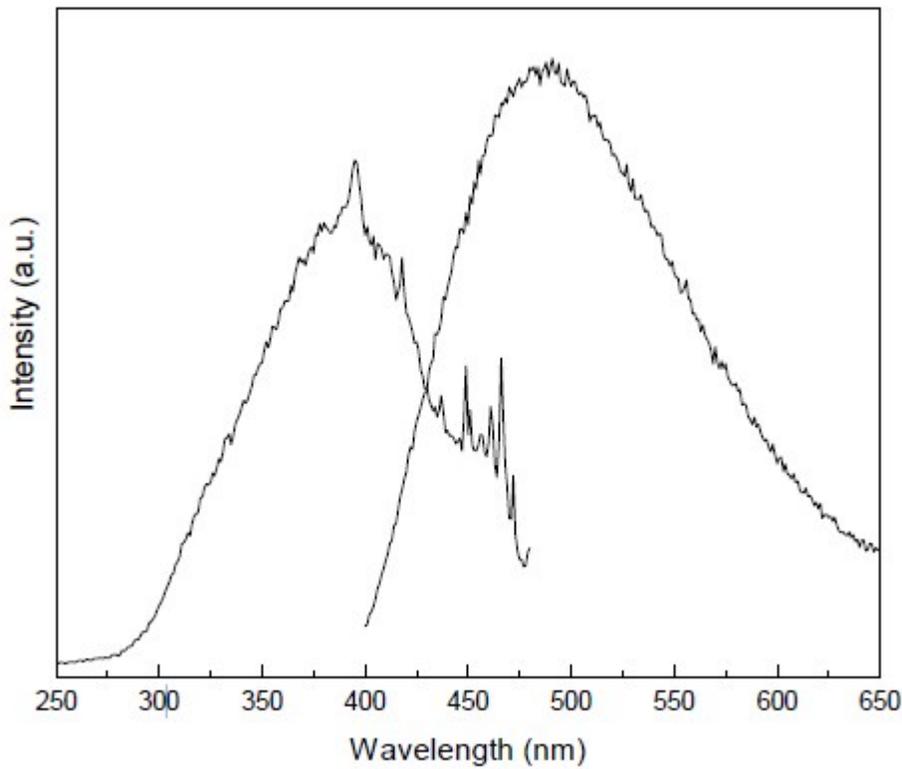


Figure S7. Excitation emission spectrum of pure Pic@PMO

In Figure S8, a plot of S_r in function of the temperature (between 273 and 373 K) is presented. It could be observed, that the maximum value of S_r is situated at 273 K with a value of 2.1078 % K⁻¹. A solid line fitting the experimental points was added as a guide for the eyes.

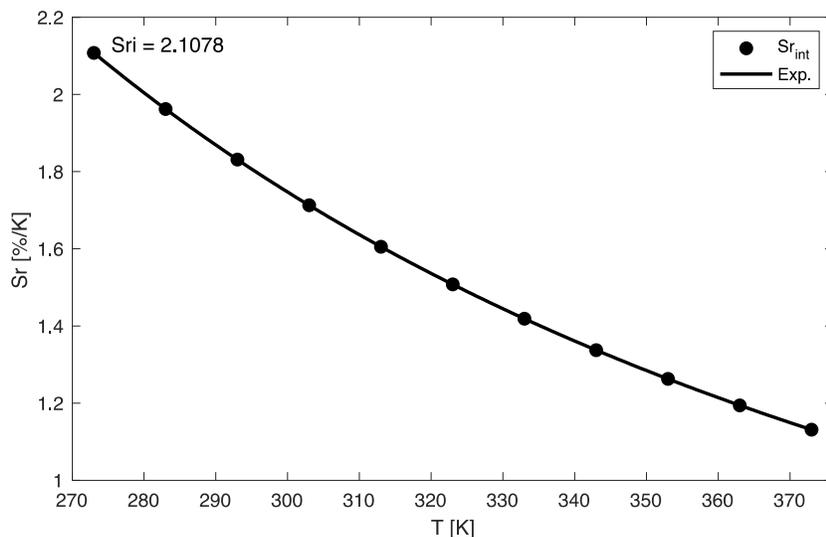


Figure S8. Plot representing the relative sensitivity (S_r) in function of temperature, with the max value for S_r indicated as 2.1078. The solid line is a guide for the eyes.

Porph@PMO.

Luminescent data for Yb@TCPPH₂ were collected for comparison and are shown in Figure S9.

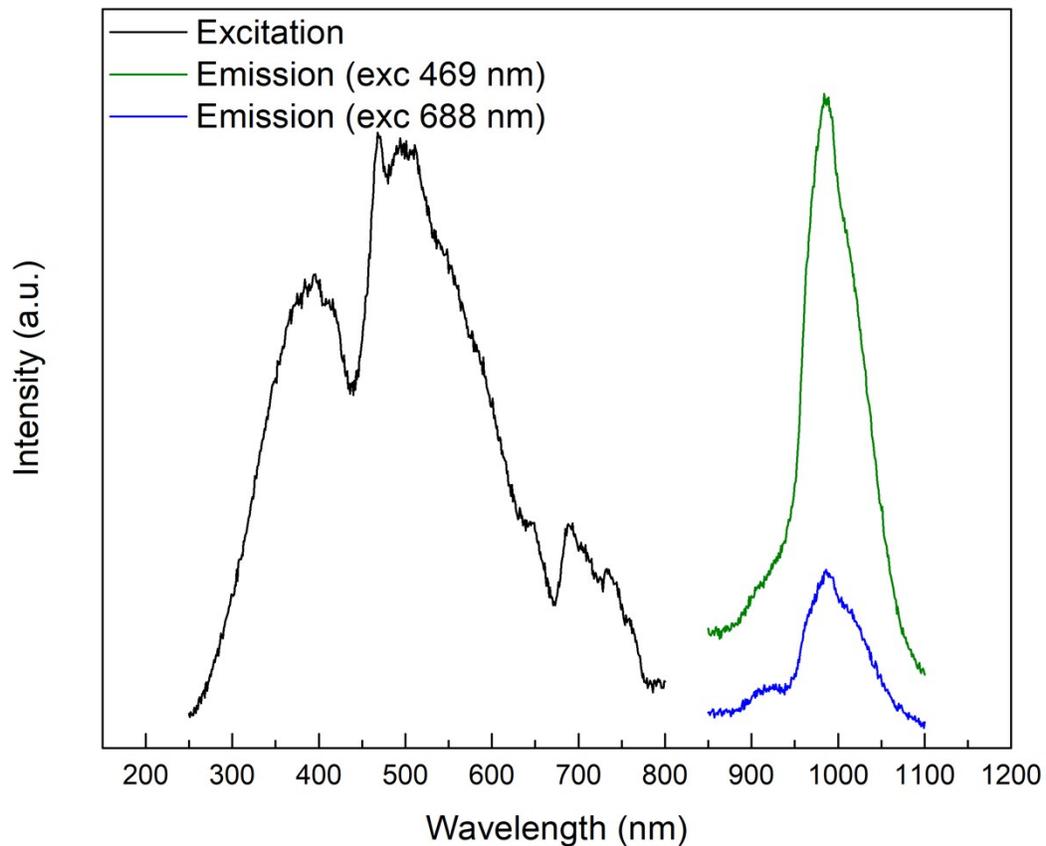


Figure S9. Combined luminescence spectrum of Yb@TCPPH₂, the excitation spectrum is presented in black. Two emission spectra are presented, one obtained by excitation into the Soret band (at 469 nm) in green and one obtained by excitation in the Q bands (at 688 nm) in blue.

The excitation spectrum of Yb@Porph@PMO was recorded and is presented in Figure S10.

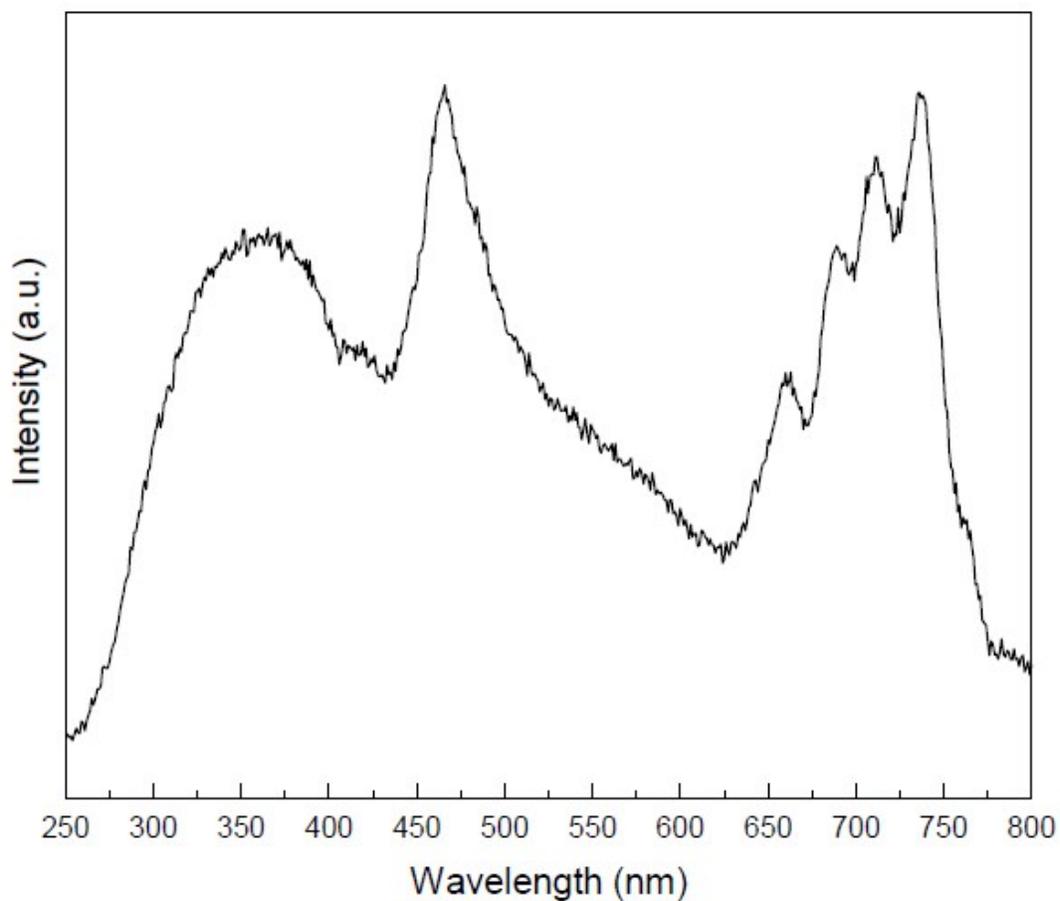


Figure S10. Excitation spectrum of Yb@Porph@PMO (excited at 467 nm and observed in the $\text{Yb}^{3+} \ ^2\text{F}_{(5/2)} \rightarrow \ ^2\text{F}_{(7/2)}$ transition peak), the sample shows intense peaks at 450 nm and between 650 and 800 nm.

Luminescent decay.

Decay profiles of all investigated luminescent samples were measured and are presented in Figure S11-S13.

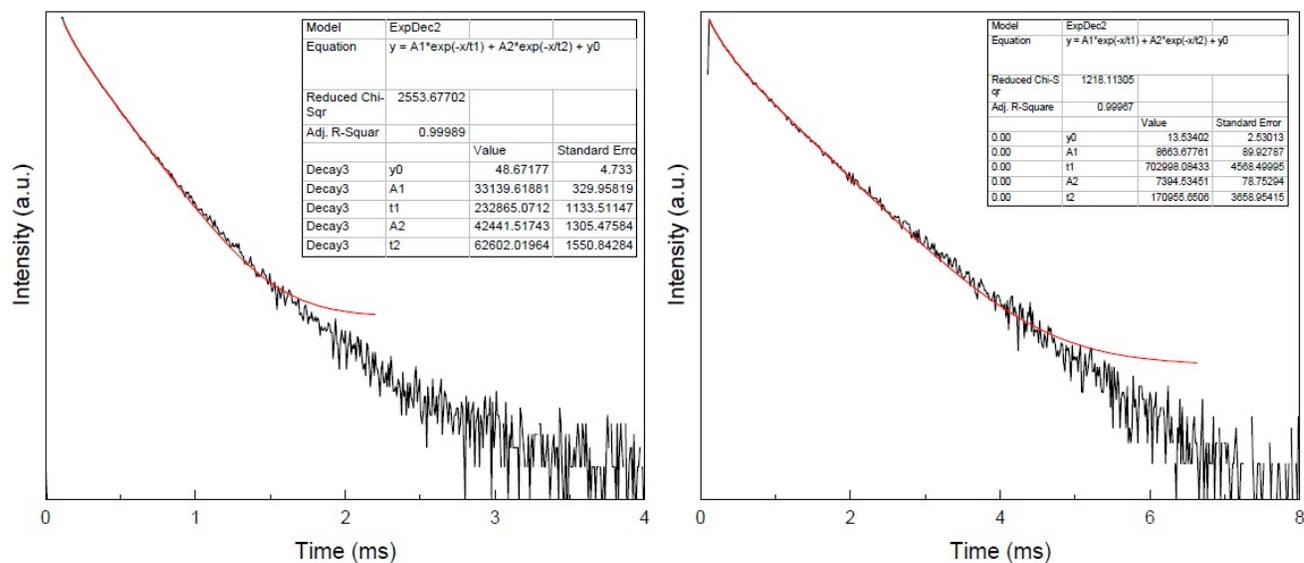


Figure S11. Decay profiles of Eu@Pic@PMO (left) and Tb@Pic@PMO (right)

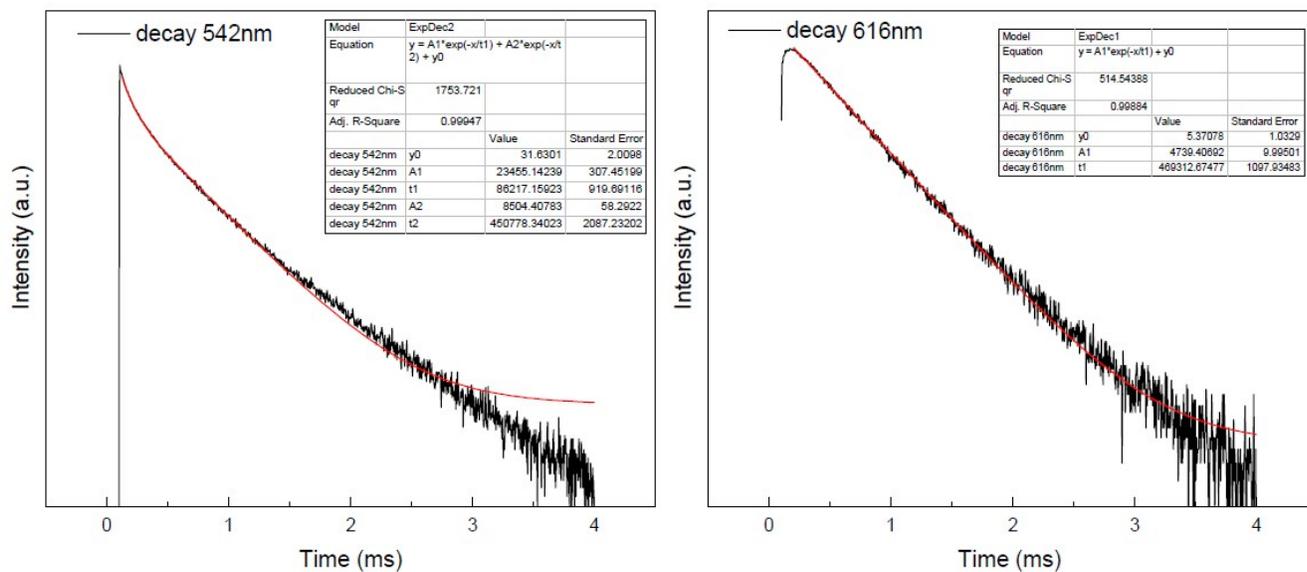


Figure S12. Decay profile of Eu,Tb@Pic@PMO, left decay of the 542 nm peak, right decay of the 616 nm peak

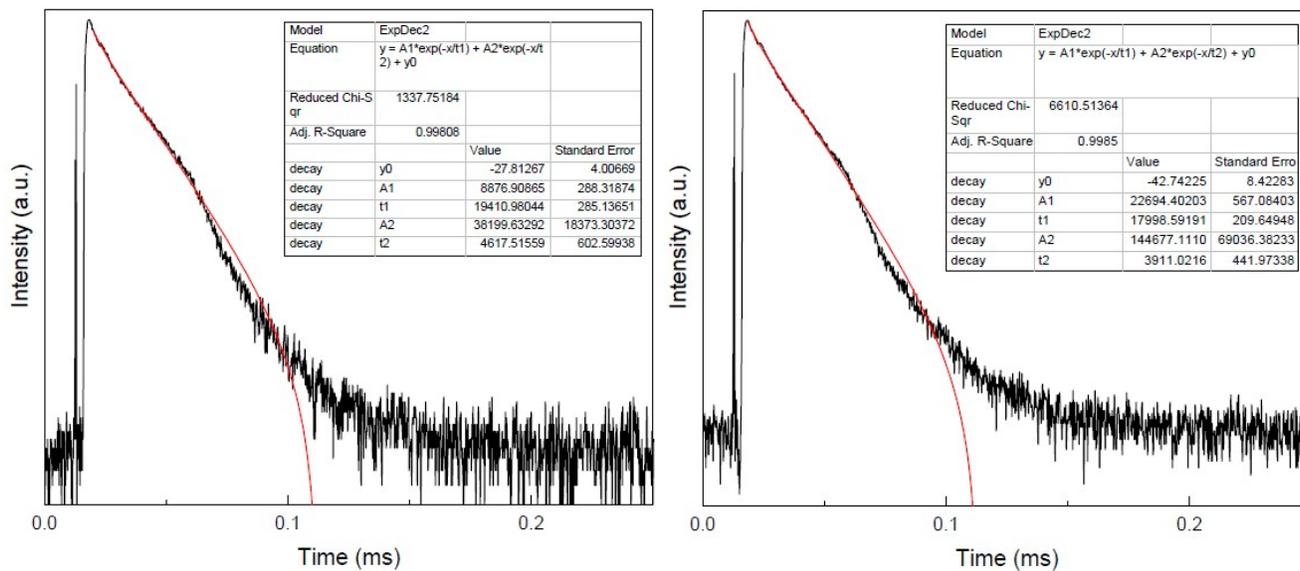


Figure S13. Luminescence decay profile of Yb@Porph@PMO (left: excited at 467 nm, right: excited at 650 nm)

REFERENCES

- (1) Gouterman, M. in *The Porphyrins, Vol. III*; Dolphin D.; Academic Press, New York **1978**, Chapter 1.