Supporting Information

Eu@COK-16, a host sensitized, hybrid luminescent metal-organic framework

Danilo Mustafa,[a,b,*] Ivan G. N. Silva,[a] Sneha R. Bajpe,[b,‡] Johan A. Martens,[b] Christine E. A. Kirschhock,[b] Eric Breynaert [b,*] and Hermi F. Brito[a].

FINAL DOI reference

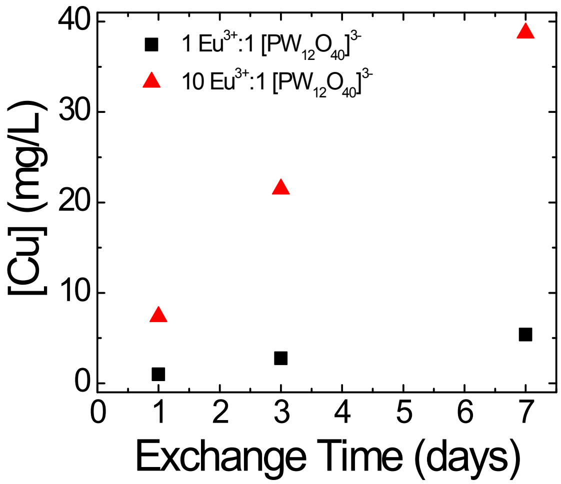

Figure S1: Elemental analysis performed on the supernatant solution after exchange. The exchanged Cu concentration increases in the samples with more Eu^{3+} and for longer exchange time.

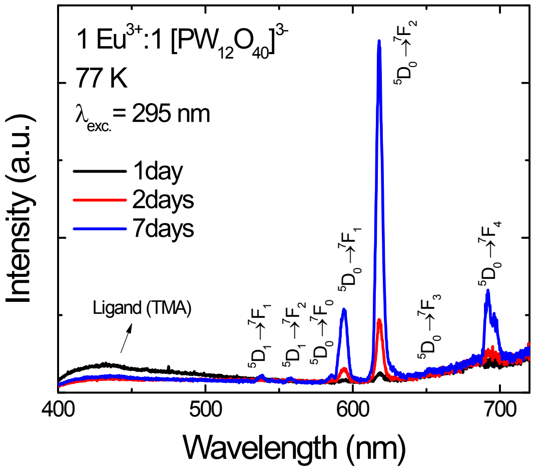

Figure S2: Emission spectra using a 295 nm excitation wavelength for the Eu@COK-16 (1 Eu^{3+}: 1 $[PW_{12}O_{40}]^{3-}$) sample as function of the equilibration time. The increase in the emission intensity of the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ (618 nm) upon extension of the equilibration time of COK-16 in the Eu^{3+} ion containing solution is related to an increase in the exchanged fraction. This is corroborated by the inverse ratio between the equilibration time dependent concentration of Eu^{3+} in the framework and Cu^{2+} ion in the exchange solution respectively (Figure S1).

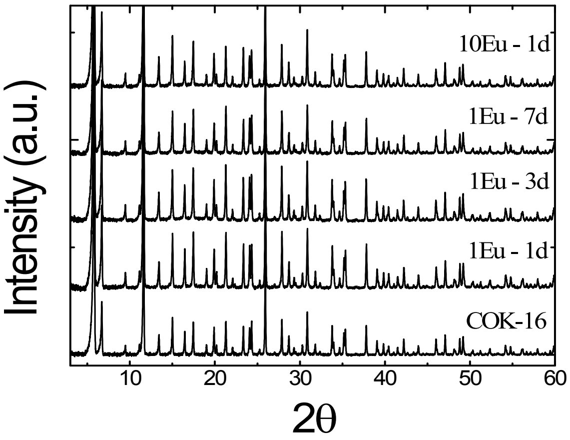

Figure S3: Powder XRD patterns of the COK-16 with Eu^{3+} for different Eu concentrations and exchange time.

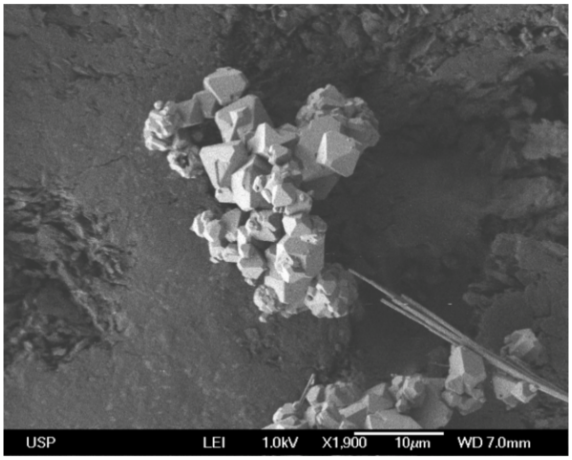

Figure S4: Scanning Electron Microscopy of the COK-16 with Eu^{3+} (10 Eu^{3+}: *1*$[PW_{12}O_{40}]^{3-}$ exchanged for 7 days).

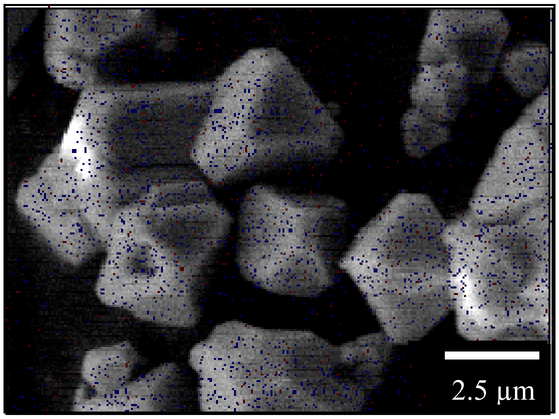

Figure S5: SEM and EDX image of the Eu@COK-16 (blue: Cu L and red: Eu M).

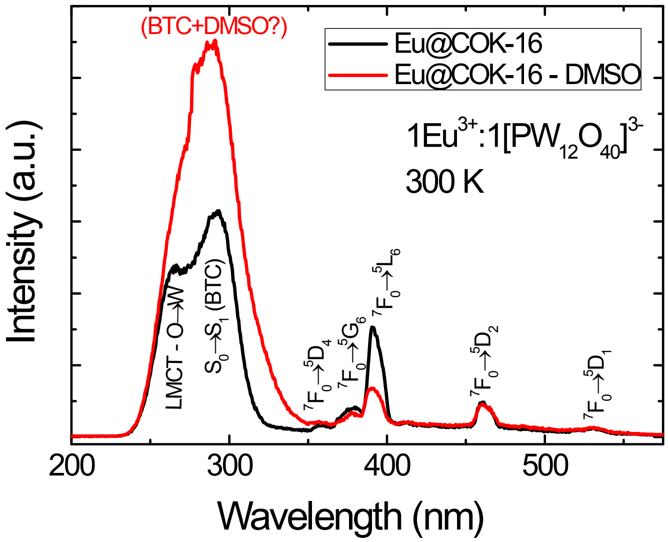

Figure S6: Excitation spectra of Eu@COK16 (1Eu7d) before and after impregnation with DMSO and consequent drying at 393K (monitoring the hypersensitive 5D0→7F2 transition at 618 nm).

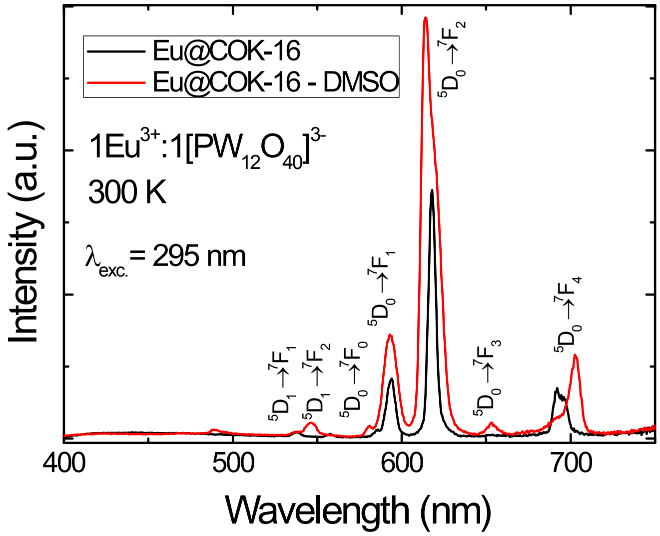

Figure S7: Emission spectra Eu@COK16 (1Eu7d) before and after impregnation with DMSO and consequent drying at 393K.

The excitation and emission spectra shown in Figure S6 and S7 demonstrate a distinct change in the spectral properties of Eu@COK16 (1Eu7d) before and after impregnation with DMSO and consequent drying at 393K. While the increase in absolute intensity could be related to additional antenna effects from DMSO, the change in the relative intensities of the $^5D_0\rightarrow{}^7F_3$ and $^5D_0\rightarrow{}^7F_4$ transitions clearly indicate a modification in the local symmetry of the Eu^{3+}. While the impregnation approach should limit unintended alteration of the MOF structure, it must be noted that HKUST-1 solubility can be significantly altered in presence of solvents such as DMSO. Since such enhanced solubility could result into a recrystallization into EuBTC, ideally a complete structural analysis would be required for each solvent.