

SUPPORTING INFORMATION

Eu(III)-DOPED CALCIUM MOLYBDATE NANO- AND MICROSTRUCTURES: MICROFLUIDIC SYNTHESIS AND MORPHOLOGY TUNING VIA SOLVENT DIELECTRIC CONSTANT AND VISCOSITY CONTROL

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Determination of viscosity and dielectric constant of water/ethanol mixtures

Selected equations that allow to express the trend of physico-chemical parameters of binary mixtures of solvents (such as drug solubilization, acid dissociation constant, dielectric constant, viscosity, and surface tension) as a function of their composition and temperature have been reported in the literature. Equation S1 is reported from the work of Jouyban et al.¹

$$\ln(PCP_{m,T}) = x_1 \cdot \ln(PCP_{1,T}) + x_2 \cdot \ln(PCP_{2,T}) + J_0 \left(\frac{x_1 \cdot x_2}{T} \right) + J_1 \left[\frac{x_1 \cdot x_2 (x_1 - x_2)}{T} \right] + J_2 \left[\frac{x_1 \cdot x_2 (x_1 - x_2)^2}{T} \right]$$

Equation S1. Jouyban – Acree equation for the determination chemico-physical properties of liquid mixtures as function of temperature and composition.

PCP = physico – chemical property

x = molar ratio ($x_2 = 1 - x_1$)

m = mixture

T = temperature (K)

1 e 2 = solvent 1 e solvent 2

J_i = expansion coefficients

Determination of the viscosity of water/ethanol mixtures

The viscosity (η_M) of water/ethanol mixtures used in this paper at 20 and -4 °C (Figure S1) was determined using Equation S1. It was observed that by increasing the wt% of ethanol in water/ethanol mixtures, the viscosity of the mixtures increases until about 50 wt% of ethanol, then it decreases. Moreover, at low temperature (-4 °C) viscosity is doubled.

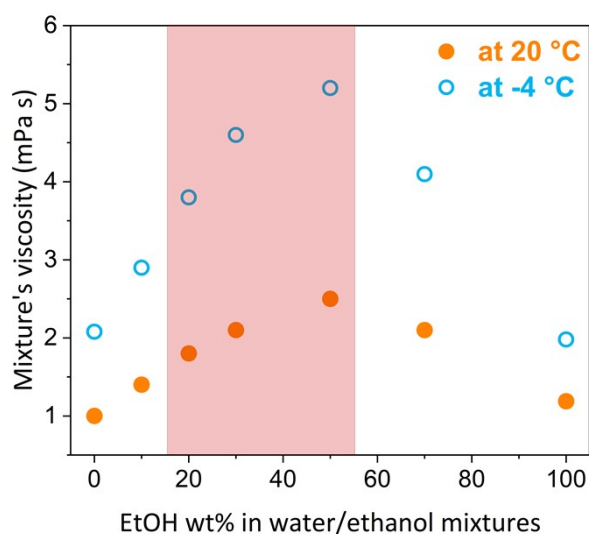


Figure S1. Water/ethanol mixtures viscosity as a function of EtOH wt% at 20 °C (orange) and -4 °C (light blue). Red region highlights the range of EtOH wt% employed in this work.

The following viscosity values of water and ethanol were used (Table S1):²

T (°C)	η_w (mPa·s)	η_E (mPa·s)
20	1.003	1.187
-4	2.08	1.98

Table S1. Viscosity values for water (w) and ethanol (E) at 20 and -4 °C.

The viscosity value for ethanol at -4 °C was determined by equation $\eta = A \exp\left(\frac{B}{T + C}\right)$ from the work of Goncalves et al.³, by assuming A = $6.12 \cdot 10^{-4}$ (mPa s), B = 2961 (K), C = 97.3 (K), T = 269 (K). Viscosity value of water at -4 °C was determined by Hallet⁴.

Expansion coefficient determined by Khattab et al⁵, exploiting the Jouyban – Acree equation (Equation S1), were employed, i.e. $J_0 = 724.652$; $J_1 = 729.357$; $J_2 = 976.050$.

Determination of the dielectric constant of water/ethanol mixtures

The dielectric constant of water/ethanol mixtures (ϵ_M) used in this work at 20 and -4 °C (Figure S2) was also calculated by applying Equation S1. It was observed that the dielectric constant of water/ethanol mixtures continuously

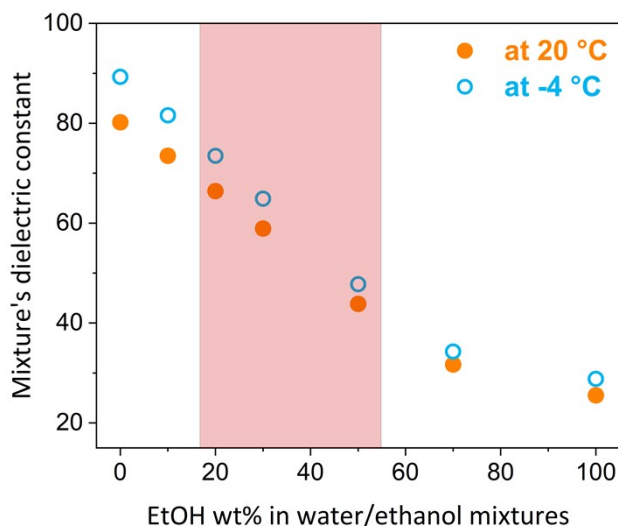


Figure S2. Water/ethanol mixtures dielectric constant as a function of EtOH wt% at 20 °C (orange) and -4 °C (light blue). Red region highlights the range of EtOH wt% employed in this work.

decreases by increasing the ethanol content into the mixture. In addition, at -4 °C the dielectric constant of the mixtures was increased of about 10 % with respect to its value at 20 °C.

In Table S2 reference values for the two pure solvents are reported:

T (°C)	ϵ_w	ϵ_E
20	80,2	25,5
-4	89,3	28,8

Table S2. Dielectric constant values for water (w) and ethanol (E) at 20 and -4 °C.

Dielectric constant values at 20 °C for pure solvent are the one reported into the Handbook of Chemistry and Physics⁶, whereas the values at -4 °C were determined through the equation provided also by the Handbook: $\epsilon(T) = a + bT + cT^2 + dT^3$.

Jouyban determined the expansion coefficients J to be used to calculate the dielectric constant⁷. Since there are lots of parameters which influence the dielectric constant of a liquid, by following the work of Abraham et al⁸, Jouyban inserted the appropriate corrections to Equation S1.

Particles size distribution: bulk vs flow quenching

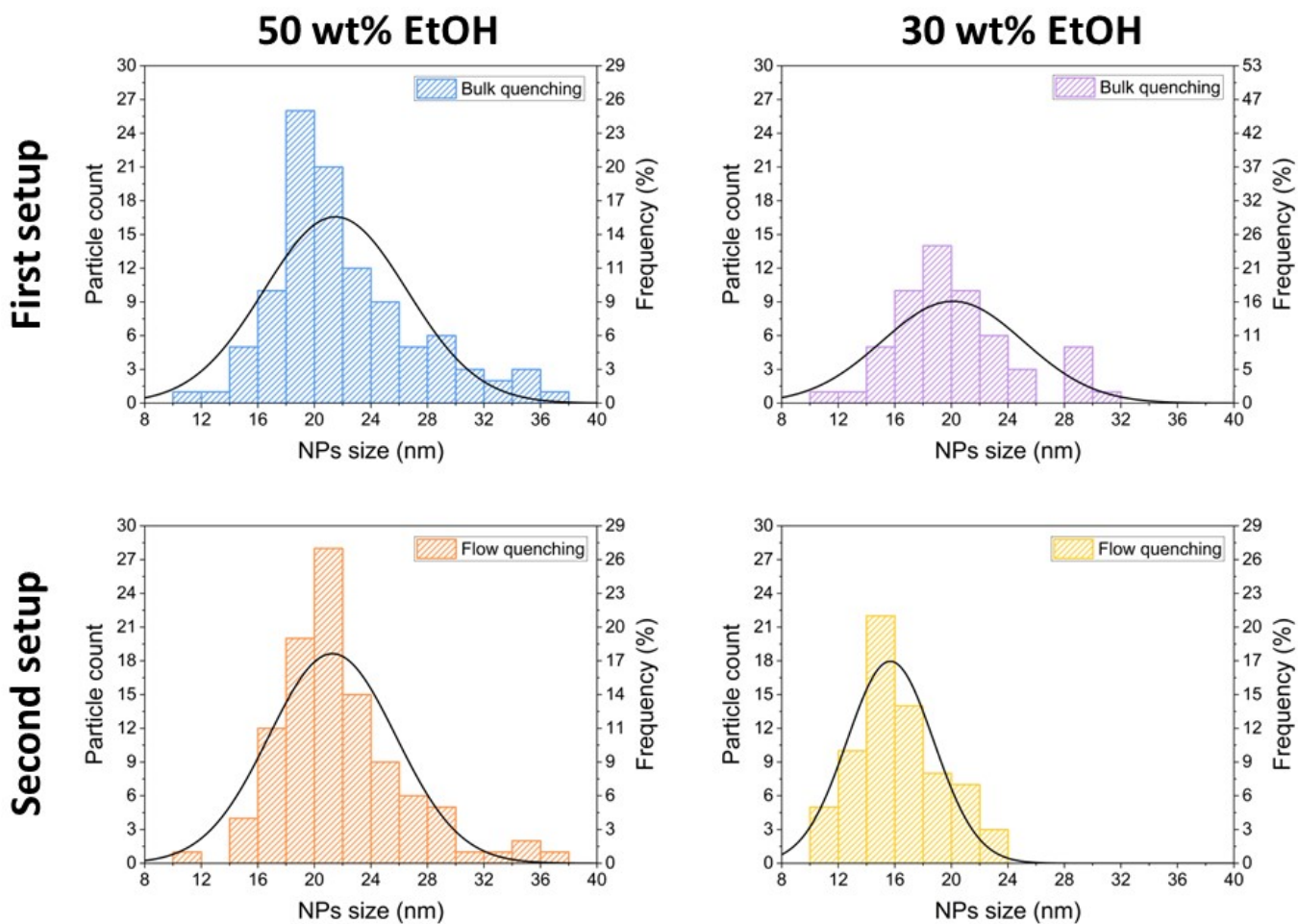


Figure S3. Size distribution of samples prepared at room temperature, with pure ethanol as a quencher. Comparison of bulk vs flow quenching.

Powder X-ray diffraction patterns of Eu(III)-doped samples

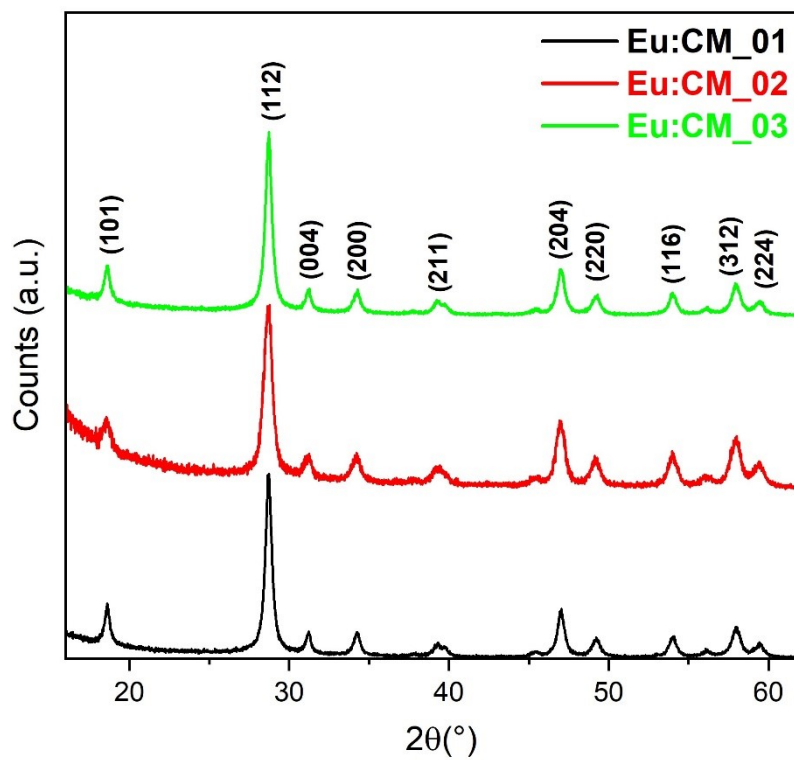


Figure S4. XRD pattern of Eu(III)-doped samples. Miller indexes refers to the *powellite* phase of calcium molybdate.

TEM micrographs of Eu(III)-doped samples

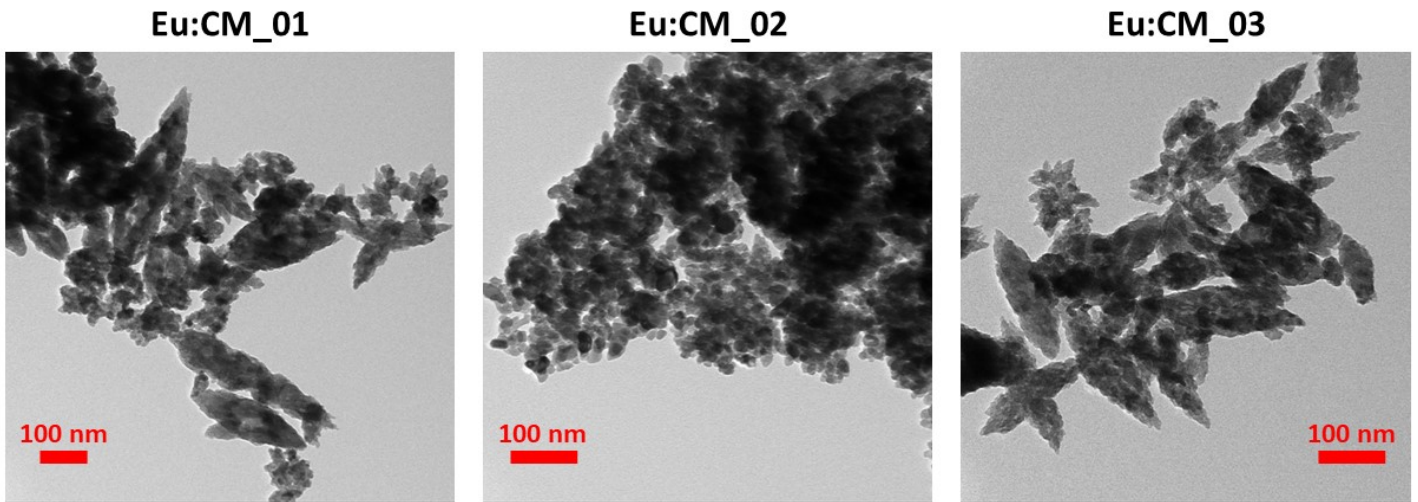


Figure S5. TEM micrographs of Eu(III)-doped samples.

Photoluminescence decay of Eu(III)-doped samples

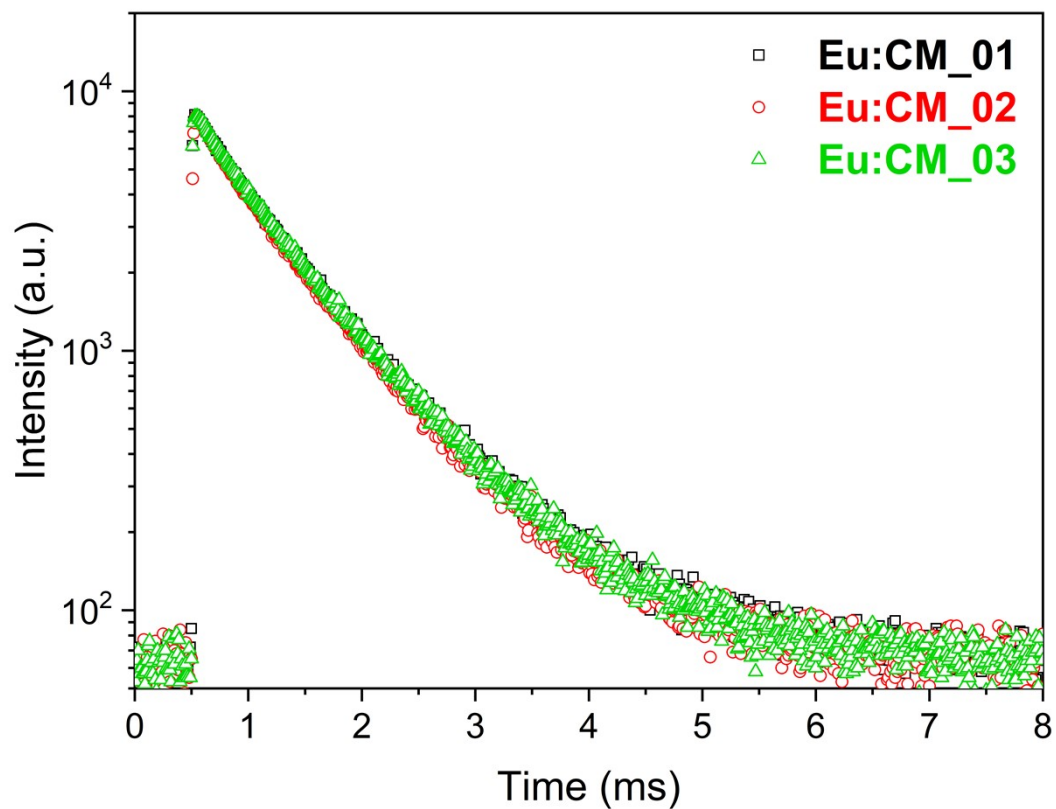


Figure S6. Experimental photoluminescence decay of Eu(III)-doped samples.

20 wt% EtOH

30 wt% EtOH

50 wt% EtOH

EtOH/H₂O as q.

T_{amb}

EtOH as q.

T_{amb}

Flow EtOH as q.

T_{amb}

EtOH/H₂O in
ice as q.

T = -4 °C

EtOH in ice
as q.

T = -4 °C

Eu(III)-doped
samples

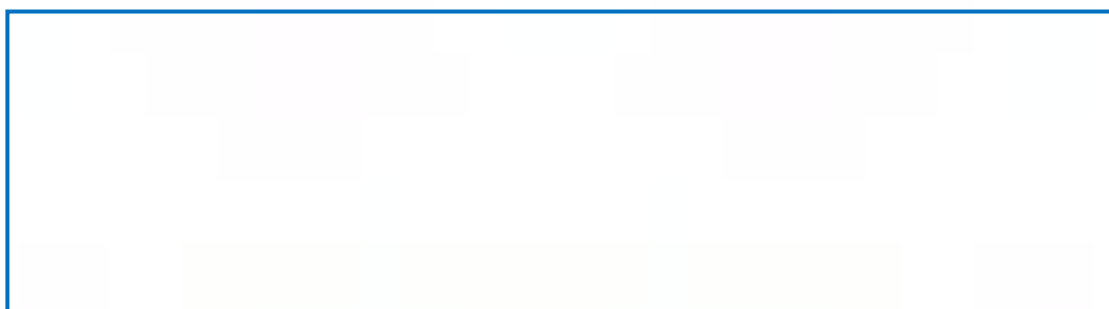


Figure S7. Fitted XRD pattern of the samples reported in the paper

Lattice parameters of calcium molybdate

As a result of the fitting of XRD patterns of the CM samples with the Pawley method we obtained the lattice parameters:

$$a = 5.23 \text{ \AA}$$

$$c = 11.46 \text{ \AA}$$

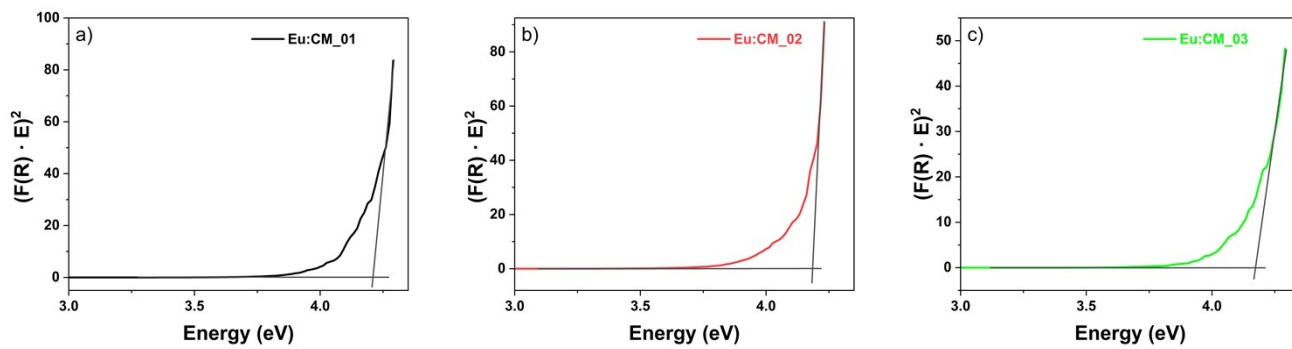


Figure S8. Tauc plots of Eu(III)-doped samples, a) Eu:CM_01, b) Eu:CM_02, c) Eu:CM_03

References

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