

# **EurOgels: A Ferromagnetic Semiconductor with Porous Structure Prepared via the Assembly of Hybrid Nanorods**

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## ELECTRONIC SUPPORTING INFORMATION

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### **Experimental Details**

All the chemicals are of dry, analytical grade and were used without further purification. Due to the reducing nature of  $\text{Eu}^{2+}$  and hygroscopic properties of the hybrids all reactions were performed and products were handled and stored under common inert-gas techniques or in a nitrogen filled glovebox.

**Preparation of the Eu(II)naphtholate precursor:** Eu(II)naphtholate was synthesized as described elsewhere.<sup>1</sup> The europium content of the precursor was determined by TGA in oxygen atmosphere.

**Preparation of the Eu(II)-2,6-di-*tert*-butylphenolate:** Eu(II)-2,6-di-*tert*-butylphenolate<sup>2</sup> was synthesized as described elsewhere. The europium content of the precursor was determined by TGA in oxygen atmosphere.

**Preparation of Eu(III) hybrid nanoparticles:** Typically, 0.4 mmol of Eu(II)aryloxide were dissolved in 5 ml of the corresponding alcohol. The orange solution was transferred to a Teflon lined steel autoclave and heated to 250°C for two days. After cooling the white precipitate was separated from the colorless solution by centrifugation and washed three times with thf.

If additives were used, typically 0.8 mmol of the corresponding additive were added to the reaction solution after the precursor had dissolved.

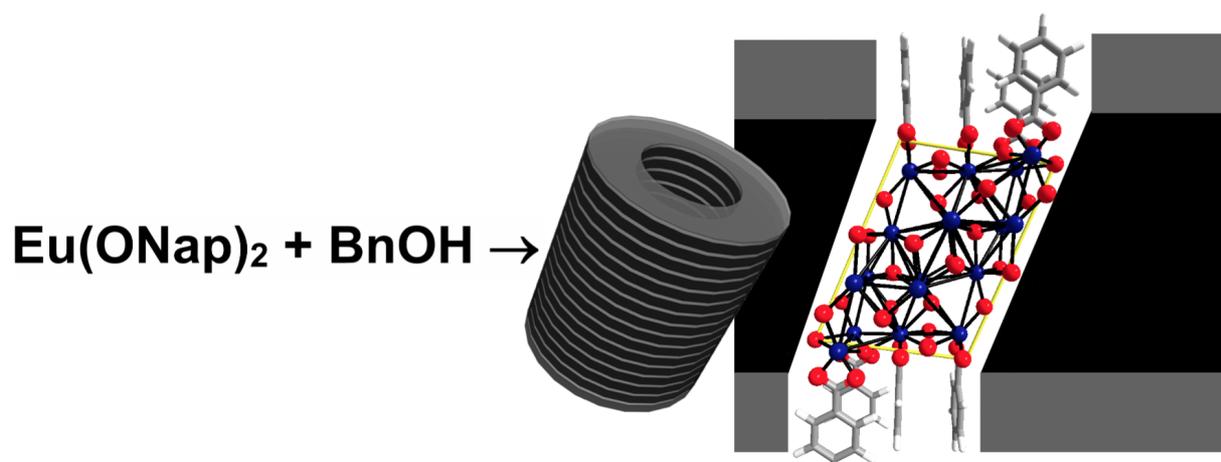
**Preparation of Eu(III) hybrid aerogels:** In a 10 ml beaker 0.4 mmol of Eu(II)naphtholate were dissolved in 5 ml of benzyl alcohol. 0.8 mmol (150.4  $\mu\text{l}$ ) Decanal were added to the solution. Afterwards the beaker was transferred to a Teflon lined steel autoclave and heated to 250°C for two days. After cooling, the solution in the pores is exchanged by acetone by keeping the wet gel in excess of continuously refreshed acetone. By replacing the acetone with liquid  $\text{CO}_2$  and supercritical drying, a monolithic aerogel material could be obtained.

**Chemical transformation to Eu(II)O:** The hybrid structures were placed either beside Eu lumps (powders) or directly on a 0.2 mm thick Eu-foil (Aerogel) in a Mo crucible inside a tube

oven. In a temperature range between 450°C to 750°C and an applied vacuum of  $1 \times 10^{-5}$  mbar the hybrids were transformed to EuO within 4-6 h.

**Characterization:** X-ray diffractions were performed with a Bruker AXS D8 Advance diffractometer using Cu- $K_{\alpha}$  radiation. FT-IR spectra were obtained with a Perkin-Elmer Spectrum 100 with ATR measurement unit. TGA-measurements were performed with a STA (Simultane Thermo Analyse) Modell 429 from Netzsch. N<sub>2</sub>-physisorption measurements were conducted on a Micromeritics Tristar. SEM images were acquired with a Zeiss Crossbeam IS40XB instrument operating at 2-5 kV. (HR)-TEM images were acquired with a JEOL, JEM 2200FS at an accelerating voltage of 200 kV and a Zeiss Libra120 at an accelerating voltage of 100 kV. Photoluminescence spectra were acquired on a FluoTime 300 from Picoquant equipped with a Xenon lamp. Solid UV-vis spectra were acquired on an Agilent Cary 5000 UV-vis-NIR spectrometer. SQUID measurements were performed using a Quantum Design MPMS-XL5 magnetometer.

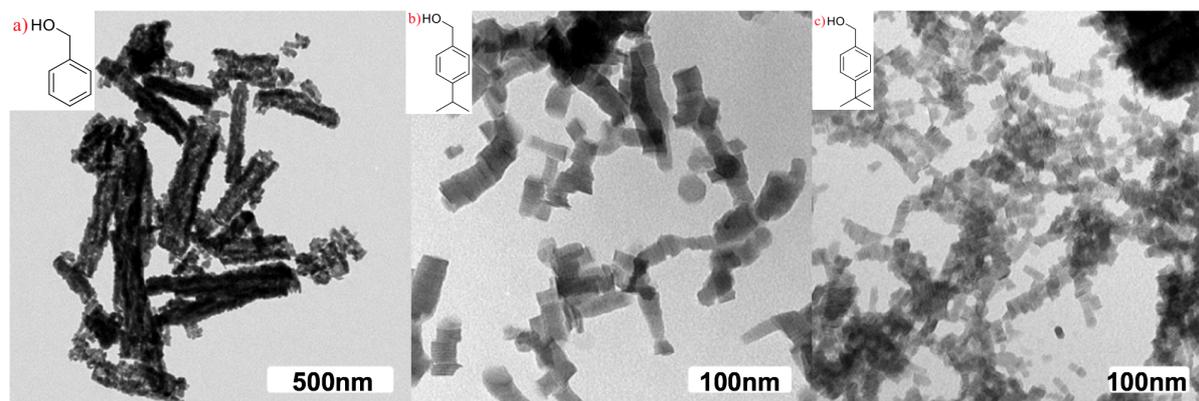
**Fig. S1.**



Organic inorganic phase obtained by the solvothermal treatment of the precursor Europium-bis-naphtolate with benzyl alcohol as a solvent.<sup>3</sup> Disks consisting of monoclinic  $\text{Eu}_2\text{O}_3$  (Eu  $\cong$  blue; O  $\cong$  red; unit cell  $\cong$  yellow line) stabilized by benzoic acid (carbon  $\cong$  dark grey; hydrogen  $\cong$  light grey) form the hollow tubular structure.

**Fig. S2.**

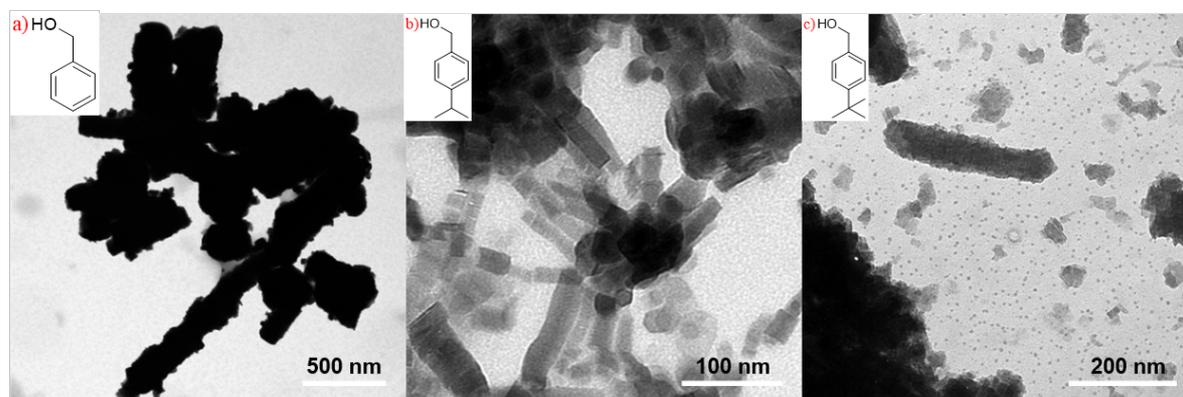
**Precursor:  $\text{Eu}(\text{ONap})_2$**



(a) The known system with hollow  $\text{Eu}_2\text{O}_3$ -benzoate nanotubes as a reference.<sup>3</sup> Particle morphology for 4-isopropyl benzyl alcohol (b) or 4-tertbutyl-benzyl alcohol (c) as a solvent for the solvothermal process. TEM data.

**Fig. S3.**

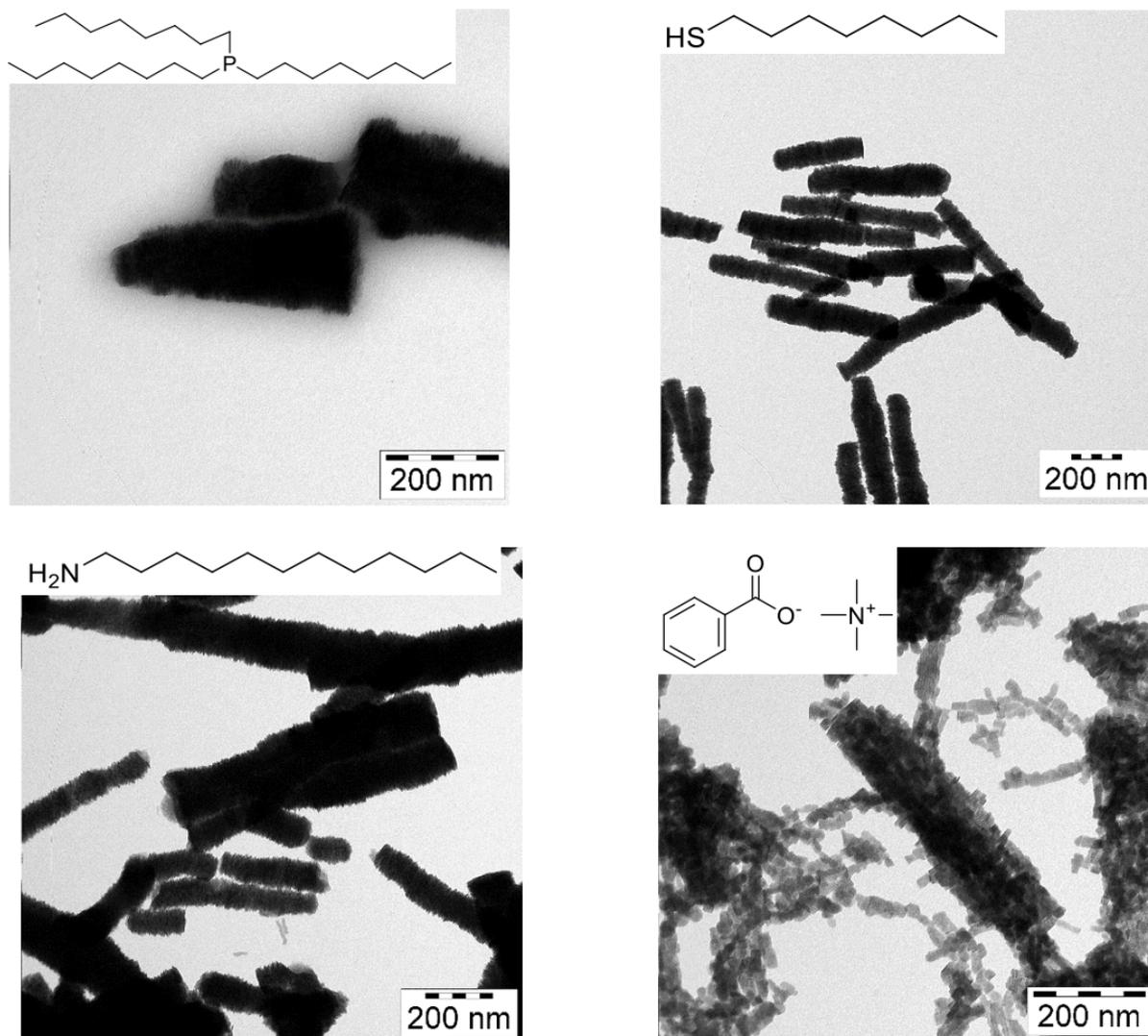
**Precursor:  $\text{Eu}(\text{PPhen})_2$**



Effect of a different ligand attached to the Eu-precursor used for the hydrothermal synthesis with BnOH(a), 4-isopropyl benzyl alcohol (b) or 4-tertbutyl-benzyl alcohol (c). TEM data.

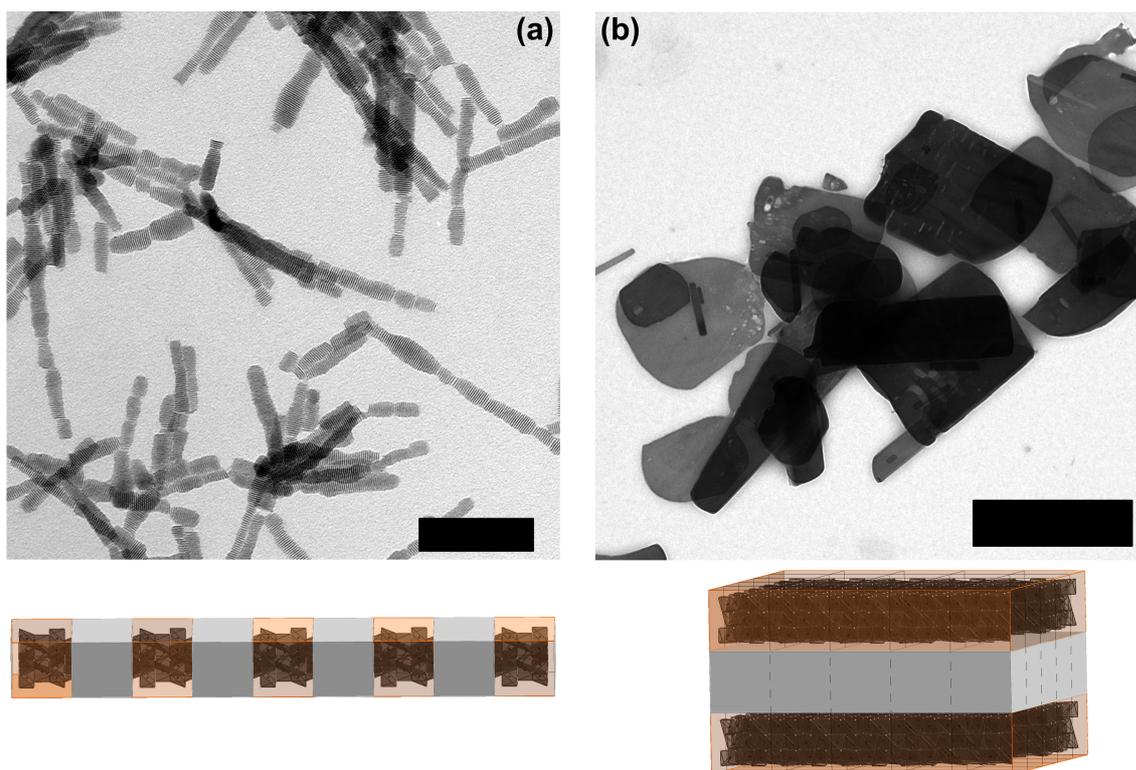
**Fig. S4.**

**Effect of capping agents added to the hydrothermal synthesis using  $\text{Eu}(\text{ONap})_2$  as a precursor and  $\text{BnOH}$  as a solvent.**



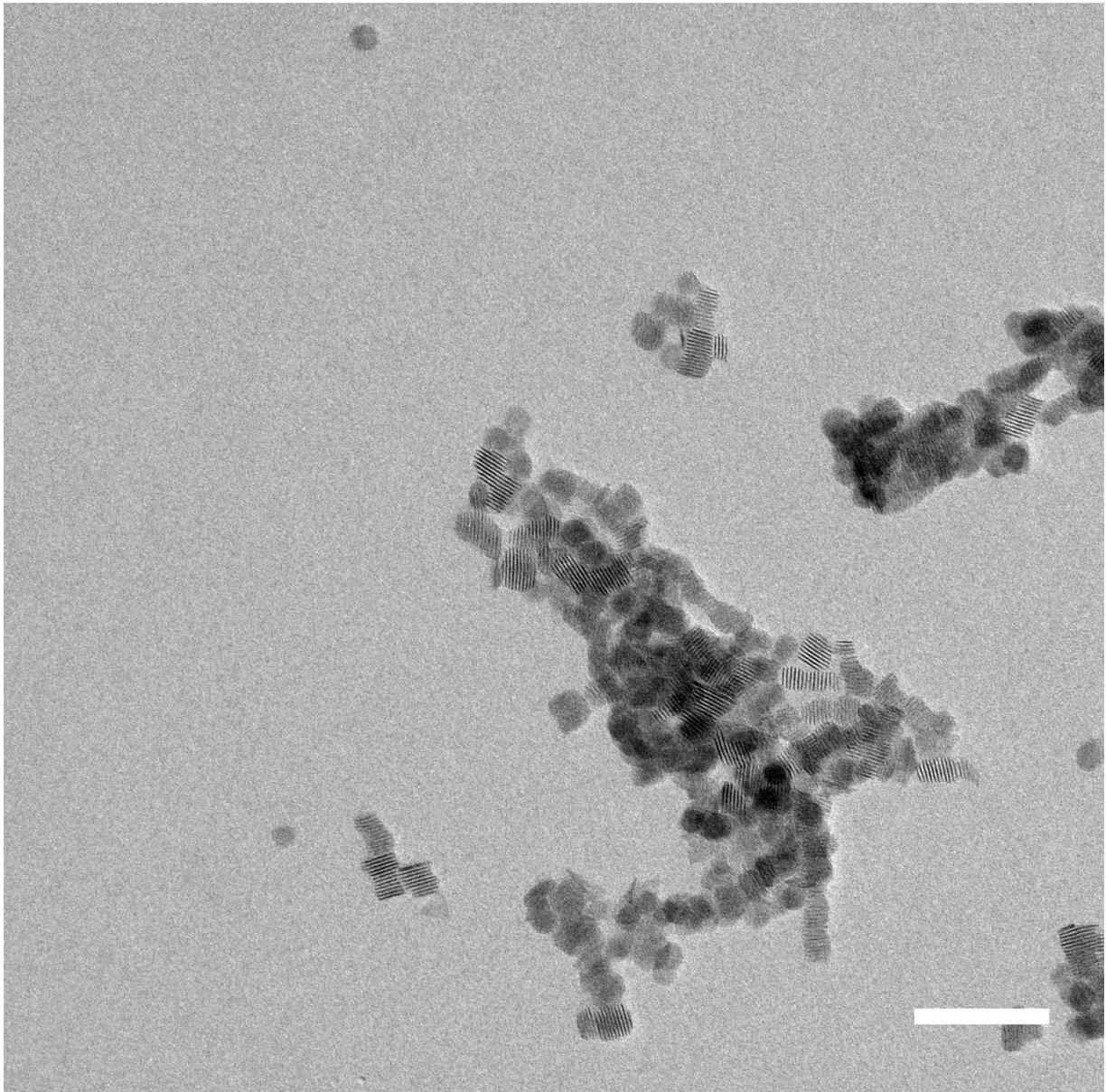
(a) "Inactive" capping agents containing different donor centers.

**Figure S5.**

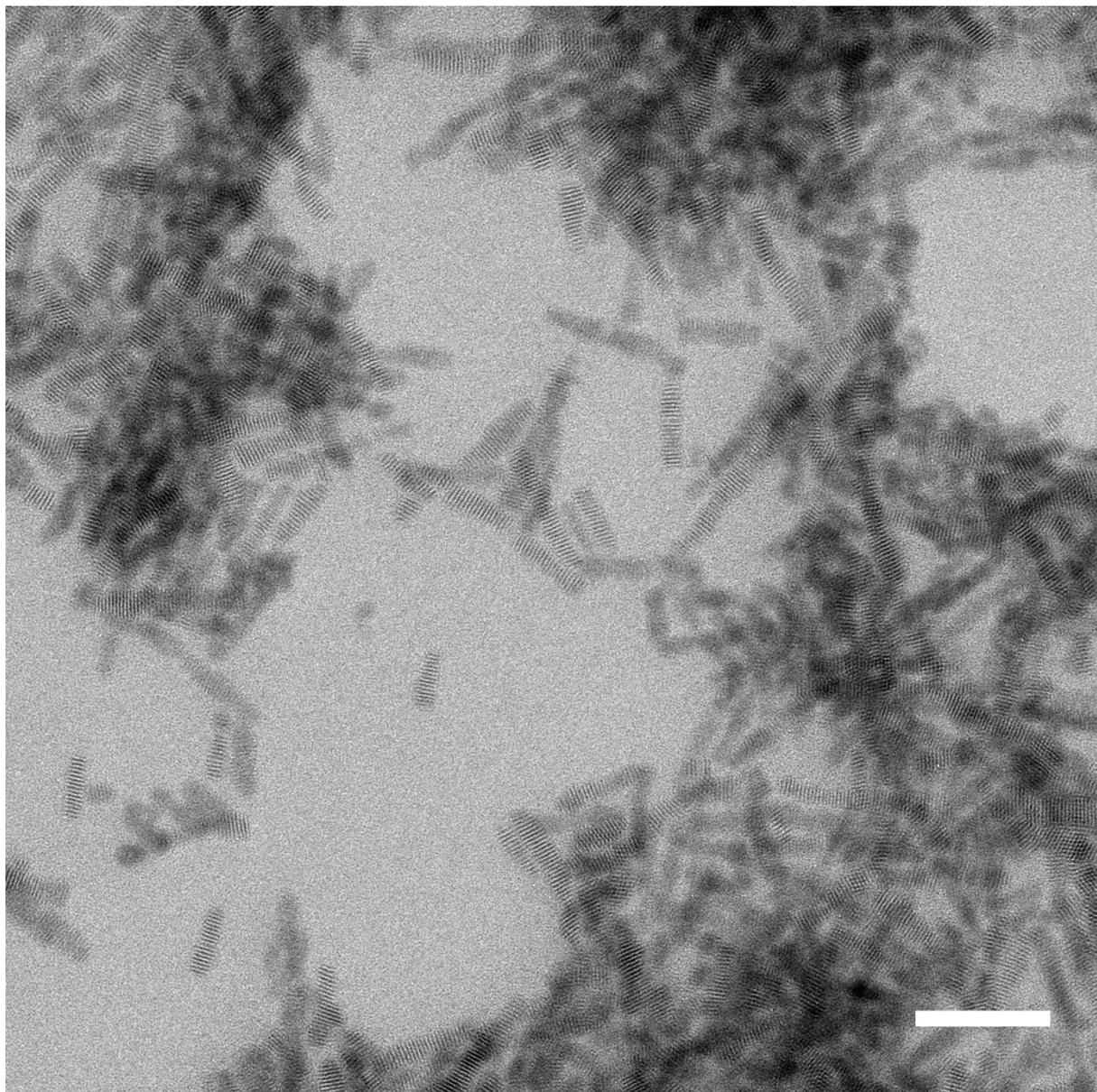


TEM micrographs and scheme of  $\text{Eu}_2\text{O}_3$ -benzoate particles stabilized by benzaldehyde used during synthesis at low (a; scalebar 100nm) and high concentration (b; scalebar;  $1\mu\text{m}$ ). Eu (black) - oxygen (white) coordination polyhedra in monoclinic  $\text{Eu}_2\text{O}_3$ ; benzoate = grey; benzaldehyde = orange.

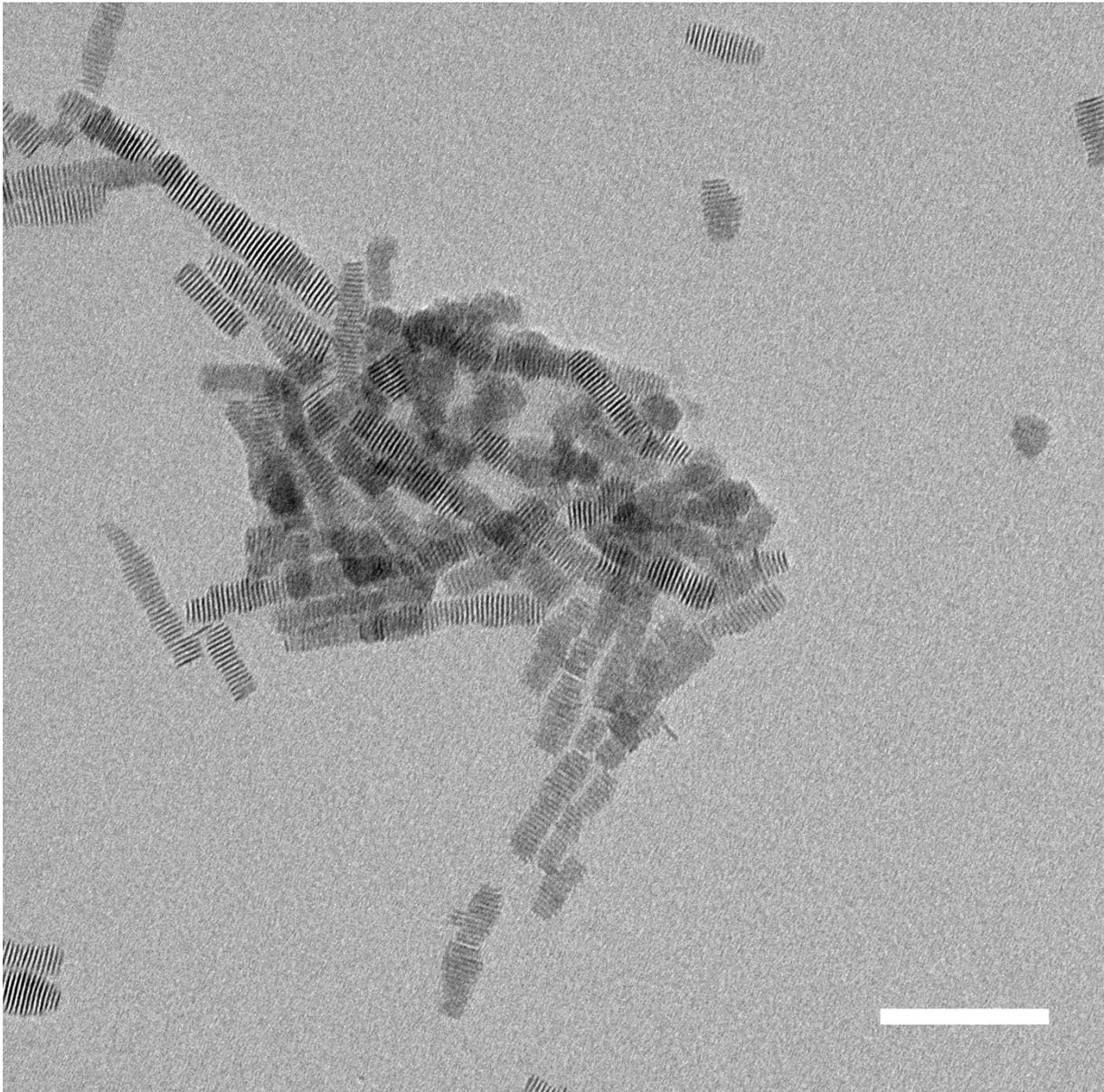
**Fig. S6.** TEM images of  $\text{Eu}_2\text{O}_3$ -benzoate nanorods prepared by aldehydes as capping agents.



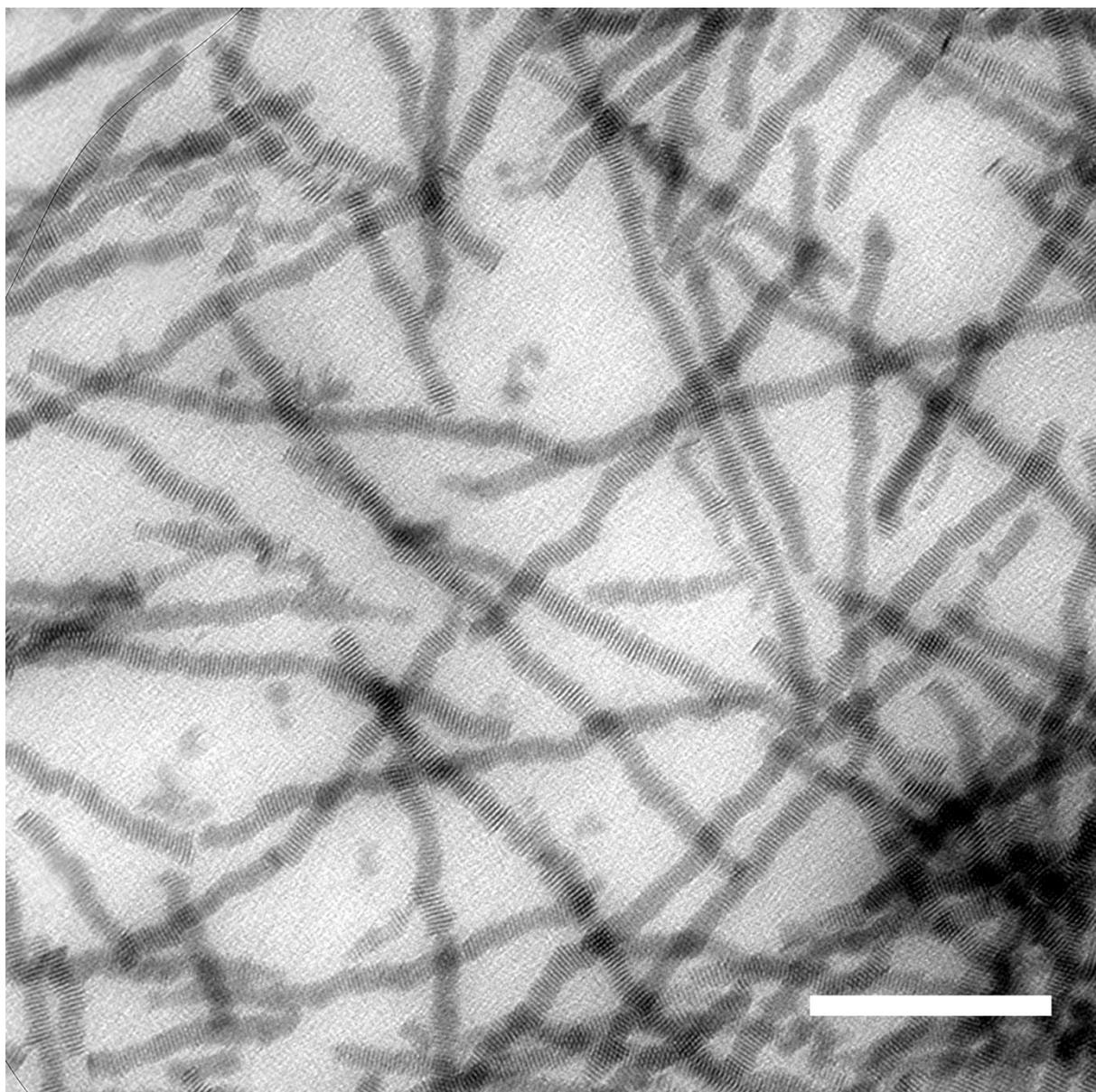
(a) n-butyl aldehyde; scalbar 50nm.



(b) Cyclohexaldehyde; scalbar 50nm.

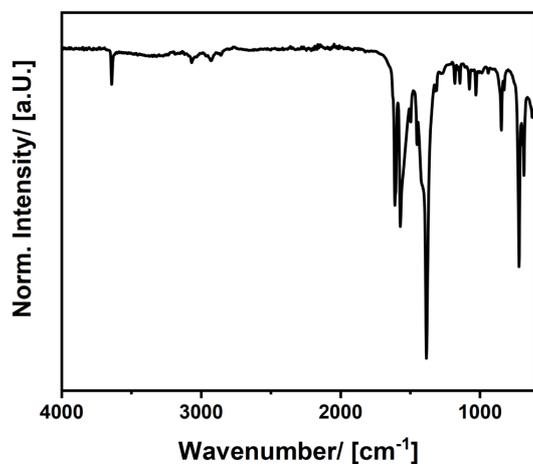


(c) isobutyl aldehyde; scale bar 50nm.

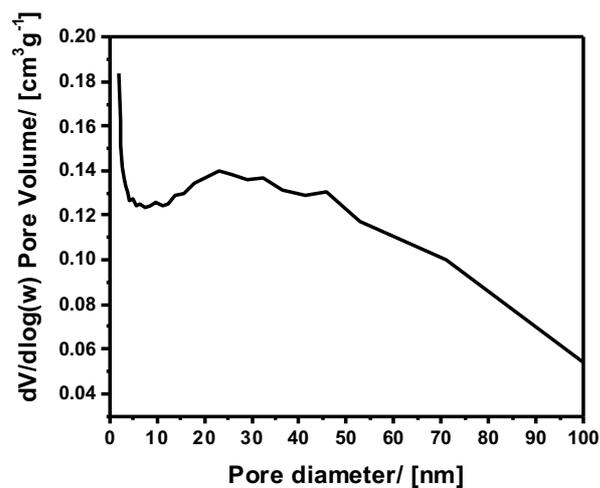


(d) n-decyl aldehyde; scalebar 100nm

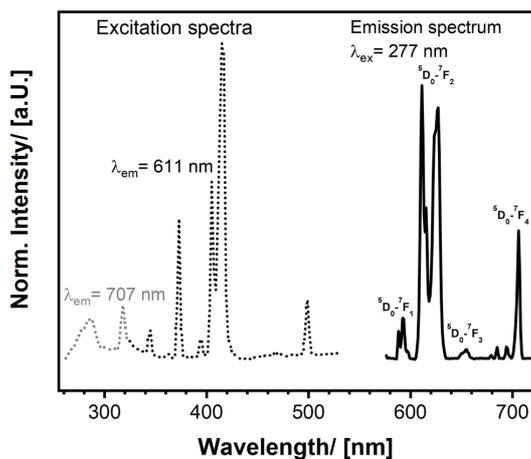
**Fig. S7. Additional data for the hybrid benzoate-Eu<sub>2</sub>O<sub>3</sub> aerogel.**



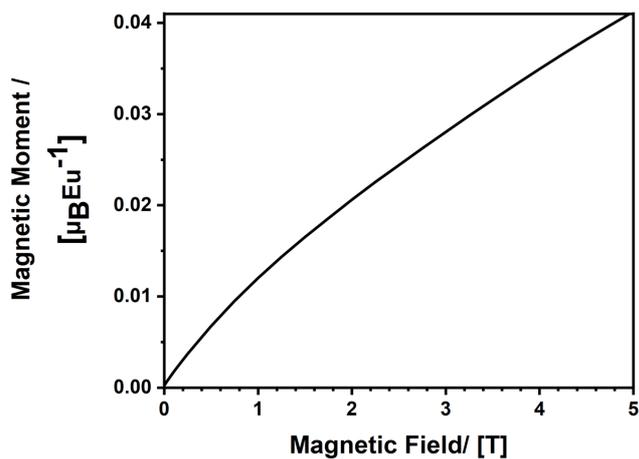
(a) FT-IR spectrum. Eu-OH vibration mode at (3655 cm<sup>-1</sup>); C-H vibration mode of the phenylring ( $\approx 3062$  cm<sup>-1</sup>); symmetrical and anti-symmetrical valence vibrational modes of the carboxylate (1515 cm<sup>-1</sup>; 1402 cm<sup>-1</sup>).



(b) Pore-size distribution function determined from N<sub>2</sub> physisorption measurements.

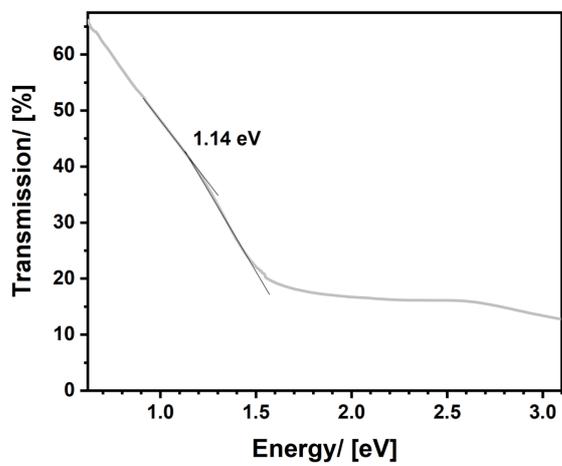


(c) Photoluminescence properties. The photoluminescence properties can be explained by Eu<sup>III</sup> in an asymmetric ligand field.<sup>4-5</sup>

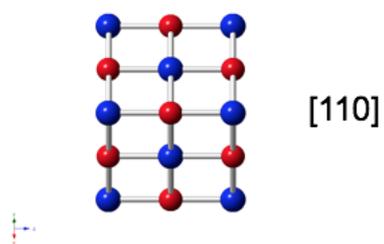
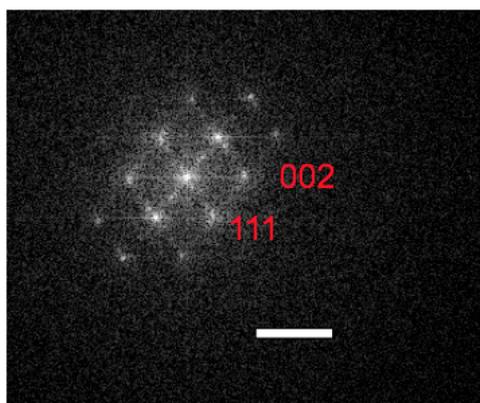
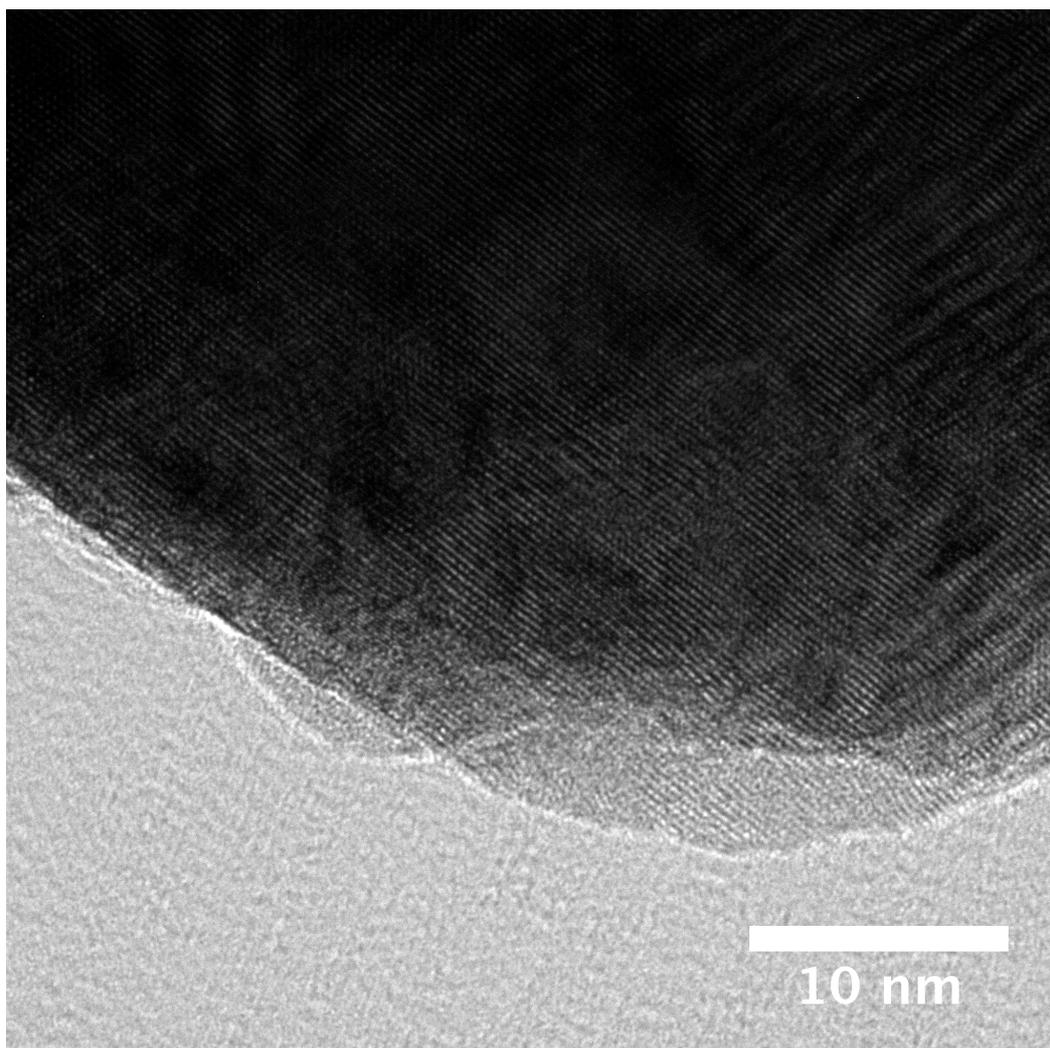


(d) SQUID measurements at T = 1.8K. The paramagnetic behaviour is in agreement with magnetically decoupled Eu<sup>III</sup> centers in Eu<sub>2</sub>O<sub>3</sub>.<sup>6</sup>

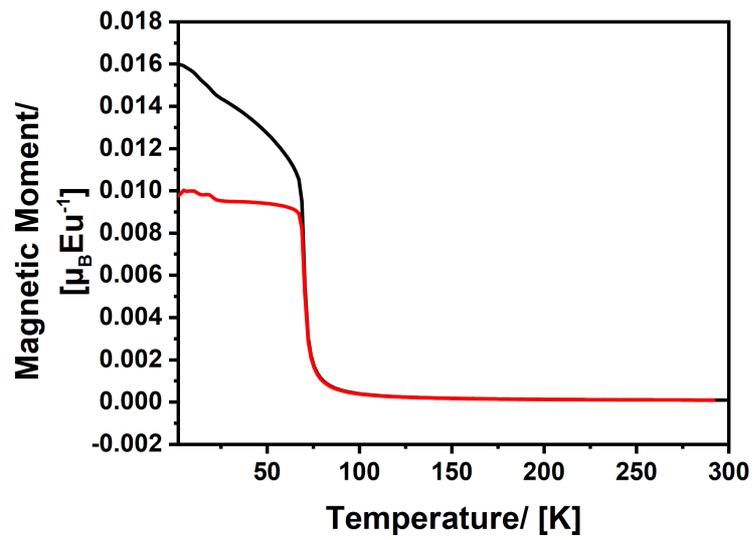
**Fig. S8. Additional data for the hybrid EuO aerogel.**



(a) UV-Vis measurement.



(b) HRTEM micrograph and selected-area FFT-pattern.



(c) T-dependent SQUID measurements; zero-field cooled data = red (100 Oe applied magnetic field at warming); field-cooled data = black (applied magnetic field 100 Oe).

## References.

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