Supplementary Information

In-situ Growth of Luminescent Ln-Imidazolate Dense Frameworks on Functionalized Nanostructured Alumina

Larissa Valerie Meyer, Joachim Vogt, Franziska Andrea Brede, Helmut Schäfer, Martin Steinhart and Klaus Müller-Buschbaum*

Experimental Details

In-situ coating via solventfree melt synthesis

Europium/strontium metal (1*10-3 mol; STREM 99.5 % / Sigma Aldrich 99.95%; ratios: Sr/Eu: x = 1.0: m(Eu) = 152.0 mg; x = 0.5: m(Sr) = 43.8 mg, m(Eu) = 76.0 mg; x = 0.05: m(Sr) = 83.2 mg, m(Eu) = 7.6 mg), 1*H*-imidazole (6 mmol, 408 mg, Acros Organics, 99%) and an AAO membrane of suitable size were sealed in a evacuated DURAN^{TM} glass ampoule (6*10^{-3} mbar). The reaction mixture was heated in a tube oven from room temperature to 220°C with a rate of 50 K/h. The temperature was kept constant for 144 h and then cooled to room temperature within 18 h. Excess 1*H*-imidazole was removed *via* sublimation. The remaining product was a fine yellow powder as well as a coated AAO membrane.
Micro analysis: $^{3}_{\infty}[Sr_{1-x}Eu_x(Im)_2]$,x = 1.0: C 29.23%, H 2.48%, N 22.73%; calc.: C 25.19%, H 2.11%, N 19.58%; $^{3}_{\infty}[Sr_{1-x}Eu_x(Im)_2]$,x = 0.5: C 29.5%, H 2.57%, N 22.93%; calc.: C 28.4%, H 2.38%, N 22.06%; $^{3}_{\infty}[Sr_{1-x}Eu_x(Im)_2]$,x = 0: C 33.35%, H 3.02%, N 25.94%; calc.: C 32.03%, H 2.69%, N 24.9%.
MIR (KBr): $^{3}_{\infty}[Sr_{1-x}Eu_x(Im)_2]$,x = 1.0: (3123 w, 3082 w, 1666 m, 1528 m, 1479 s, 1453 s, 1302 s, 1253 s, 1245 s, 1217 s, 1101 s, 1093 s, 1066 vs, 946 s, 851 s, 828 s, 784 s, 681 vs) cm^{-1}; $^{3}_{\infty}[Sr_{1-x}Eu_x(Im)_2]$,x = 0.5: (3123 w, 3103 w, 3085 w, 1671 m, 1529 w, 1483 s, 1450 s, 1304 m, 1134 m, 1102 s, 1069 vs, 947 s, 923 s, 854 s, 831 s, 776 s, 683 vs) cm^{-1}; $^{3}_{\infty}[Sr_{1-x}Eu_x(Im)_2]$,x = 0: (3105 w, 3084 w, 1672 w, 1611 m, 1533 s, 1480 s, 1456 s, 1301 s, 1250 s, 1217 s, 1105 s, 1075 s, 947 s, 856 s, 833 s, 784 vs, 681 vs) cm^{-1}.

In-situ coating via electride approach

Europium/strontium metal (1*10-3 mol; STREM 99.5 % / Sigma Aldrich 99.95%; ratios: Sr/Eu: x = 0.05: m(Sr) = 83.2 mg, m(Eu) = 7.6 mg), 1*H*-imidazole (6 mmol, 408 mg, Acros Organics, 99%) and an AAO membrane of suitable size were filled in a DURAN^{TM} glass ampoule. 5 ml of ammonia (Linde, 99.999%) were condensed with liquid nitrogen into the ampoule. Subsequently cooling of the reaction mixture was reduced >-78°C. Above the melting point of ammonia the color of the reaction mixture immediately changed to dark blue in the area of the metal pieces. The dark blue color changed to yellow at contact with 1*H*-imidazole in liquid ammonia. Evaporation of ammonia results in the formation of yellow microcrystalline product.
The ampoule was sealed under vacuum (6*10^{-2} mbar) and annealing was carried out in a tube oven by heating up to 220 °C within 10 minutes. Temperature was kept constant for 36 h and then cooled to room temperature within 2 h. Excess 1*H*-imidazole was removed *via* sublimation. The remaining product was a fine yellow powder as well as a coated alumina substrate.
Micro analysis: $^{3}_{\infty}[Sr_{1-x}Eu_x(Im)_2]$,x = 0.05: C 28.89%, H 2.49%, N 22.76%; calc.: C 32.03%, H 2.69%, N 24.9%.
MIR (KBr): $^{3}_{\infty}[Sr_{1-x}Eu_x(Im)_2]$,x =0.05: (3122 w, 3076 w, 1670 w, 1609 w, 1529 s, 1482 s, 1455 s, 1303 m, 1220 s, 1217 s, 1152 s, 1094 s, 947 s, 926 s, 853 s, 770 vs, 682 vs) cm^{-1}.

X-ray Powder Diffraction

Rietveld Refinement of $^{3}{}_{\infty}[Sr_{0.5}Eu_{0.5}(Im)_2]$, carried out according to reference [22].

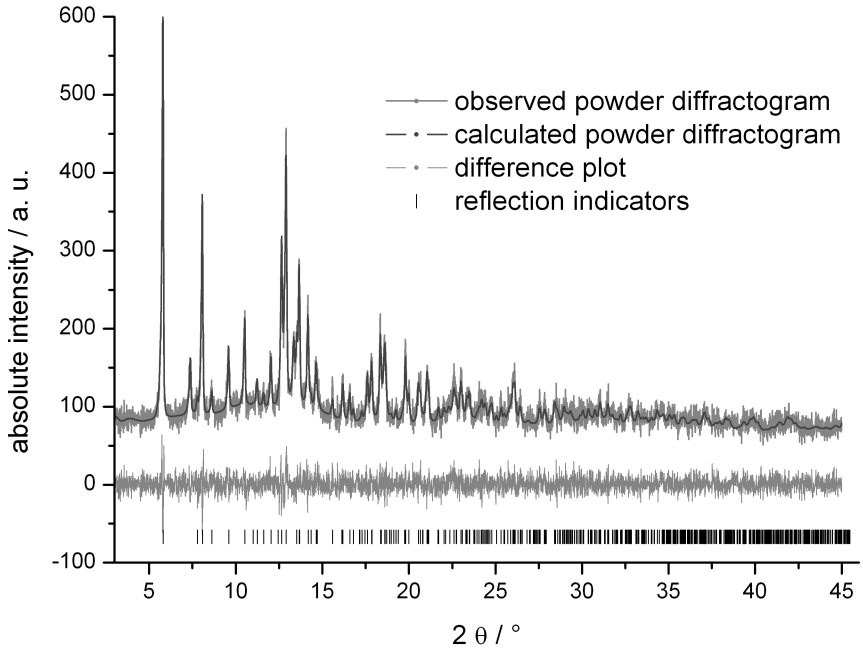

Figure S1: Observed (upper gray line) and calculated (black line) powder X-ray diffractograms from 3° to 46° (2-theta) with difference plot from Rietveld refinement (lower gray line). Reflection positions are given as vertical black lines (bottom).

Electron Microscopy

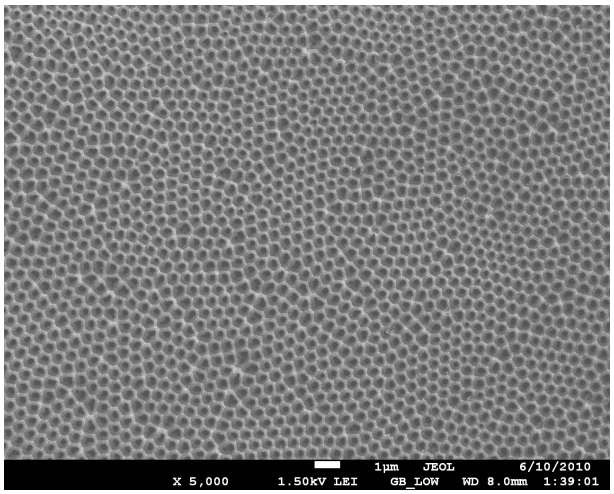

Figure S2: Top view scanning electron microscopy image of AAO having a pore diameter of 400 nm and a pore depth of 100 µm.

Electron Microscopy and EDX / element mapping

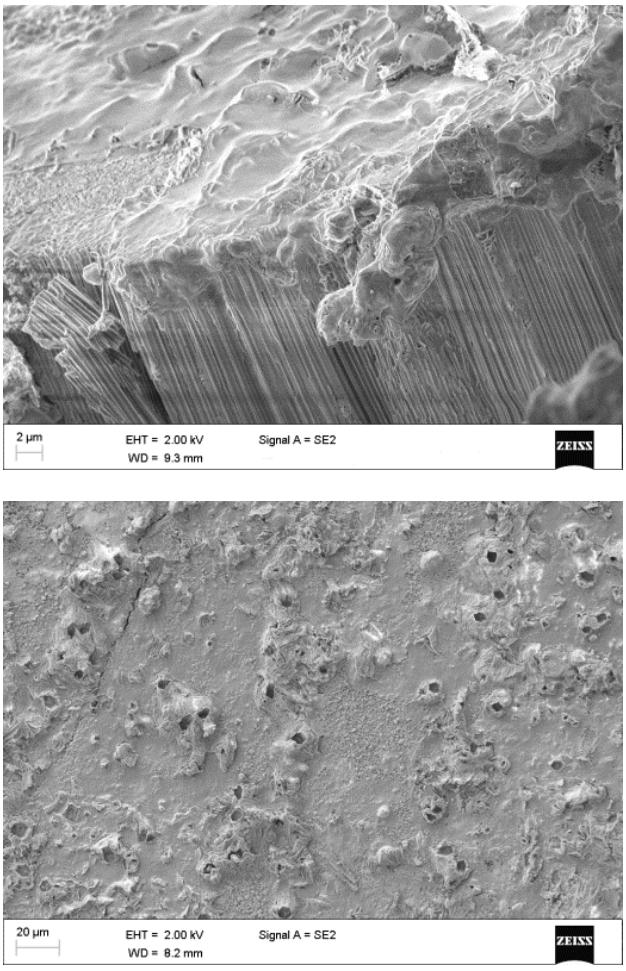

Figure S3: Scanning electron microscopy images of AAO (pore diameter 400 nm; pore depth 100 µm) coated with $^{3}_{\infty}[Sr_{0.5}Eu_{0.5}(Im)_2]$ from melt synthesis.

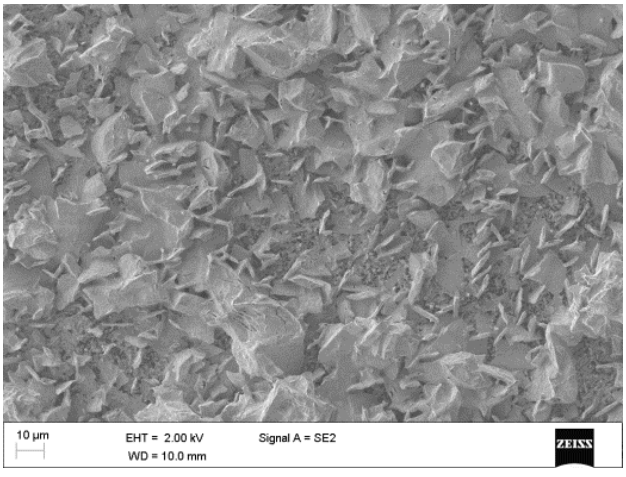

Figure S4: Scanning electron microscopy image of AAO (pore diameter 400 nm; pore depth 100 µm) coated with $^{3}_{\infty}[Sr(Im)_2]$ from melt synthesis.

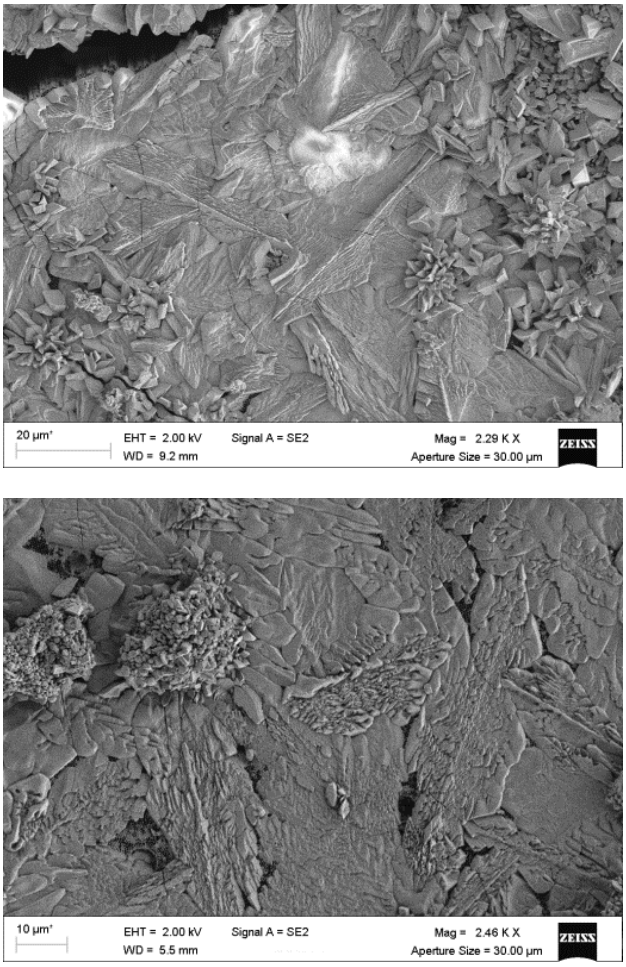

Figure S5: Scanning electron microscopy images of AAO (pore diameter 400 nm; pore depth 100 µm) coated with $^{3}{}_{\infty}[Eu(Im)_2]$ from melt synthesis.

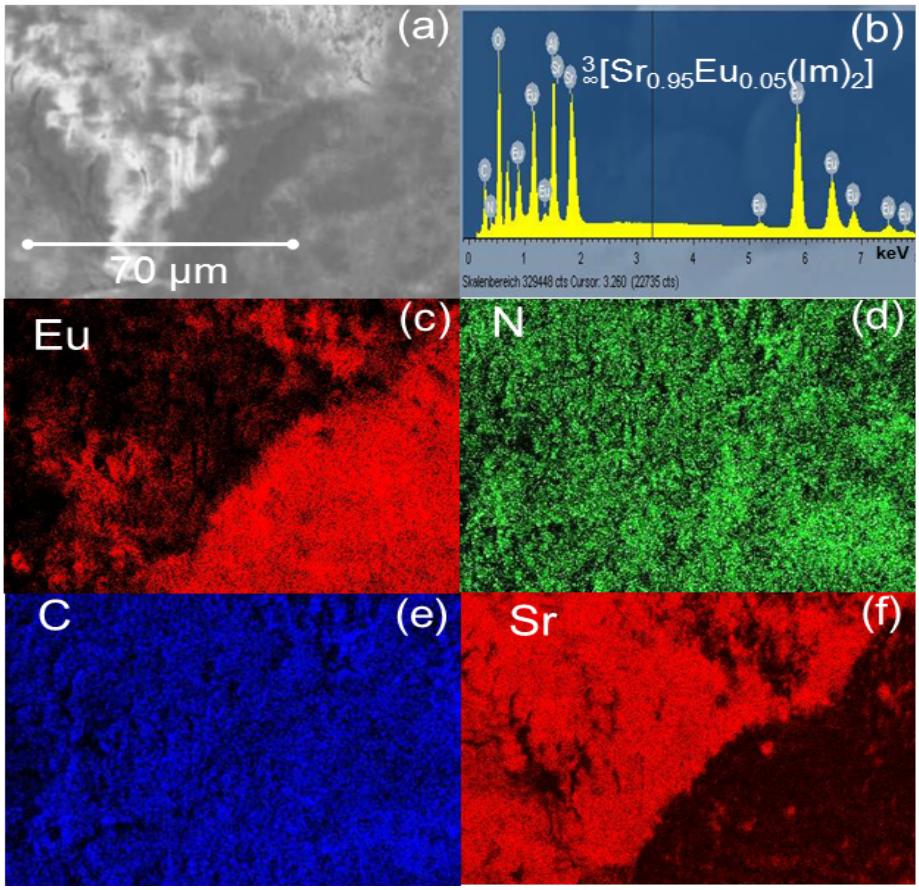

Figure S6: SEM and EDX element mapping of $^3_\infty[Sr_{0.95}Eu_{0.05}(Im)_2]$ from liquid ammonia

Sorption Experiments / BET

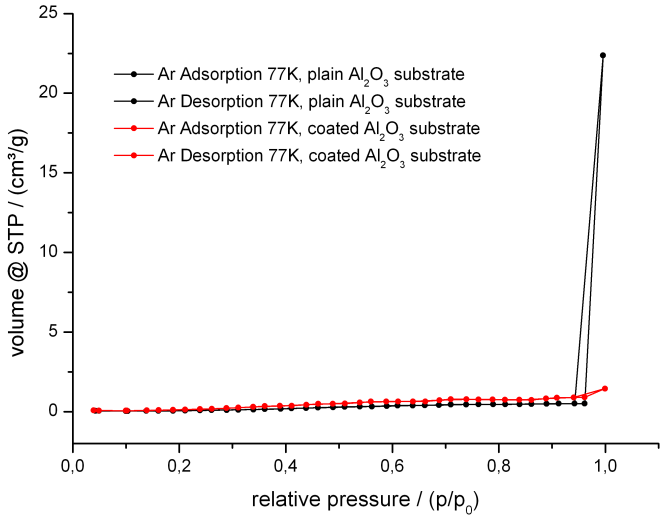

Figure S7: Argon adsorption on plain and coated AAO membranes (pore diameter 400 nm, pore depth 100 µm) according to the BET theory.