

# Supporting Information

## Rational design of Lanthanide nano Periodic Mesoporous

## Organosilicas (Ln-nano-PMOs) for near-infrared emission

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## 1. Experimental section

### 1.1 Synthesis of Ln(hfa)<sub>3</sub> complexes

Ln(hfa)<sub>3</sub>•2H<sub>2</sub>O (Ln = Nd and Yb) complexes were carried out as follows. As an example, 4 mmol of NdCl<sub>3</sub>•6H<sub>2</sub>O was dissolved in distilled water (solution 1). A solution of Hfac (12 mmol) was dissolved in 33 mL of diethyl ether and then the resulting solution was neutralized by adding 0.83 mL ammonium hydroxide solution (solution 2). Solution 1 was extracted twice, each time with half volume of solution 2, then the diethyl ether phase was separated. The organic phase was washed with 3.3 mL H<sub>2</sub>O and dried with Na<sub>2</sub>SO<sub>4</sub>, then the diethyl ether was removed by using the vacuum evaporator. The crude products (mixture of oil and crystals) were then extracted several times with boiling hexane solvent. The resulting crystals were obtained by filtration, followed drying for a few hours in air. The compositions of synthesized complexes were characterized by elemental analysis.

Nd(hfa)<sub>3</sub>•2H<sub>2</sub>O (NdC<sub>15</sub>H<sub>10</sub>F<sub>18</sub>O<sub>8</sub>) calculated: 22.49% C; 0.87% H; found: 22.84% C; 0.68% H. Yb(hfa)<sub>3</sub>•2H<sub>2</sub>O (YbC<sub>15</sub>H<sub>10</sub>F<sub>18</sub>O<sub>8</sub>) calculated: 21.60% C; 1.20% H; found: 21.97% C; 1.47% H.

### 1.2 Synthesis of DPA-PMO

The PMO precursor was synthesized according to a previously reported procedure.<sup>1</sup> Firstly, pyridine 2,6-dicarbonyl chloride was dissolved in dry diethyl ether in a round-bottom flask. Subsequently, a mixture of (3-aminopropyl) trimethoxysilane and pyridine in dry diethyl ether was added dropwise under argon atmosphere. The mixed solution was stirred at ambient temperature for 4 h. Then the above solution was filtered. Eventually, the PMO precursor -N,N-bis(trimethoxysilylpropyl)-2,6-pyridine dicarboxamide- was obtained as a yellow oil after removing the diether ether and pyridine by rotary evaporation. The obtained DPA-PMO precursor was

characterized by  $^1\text{H}$  NMR (Figure S1).

The PMO was synthesized by hydrolysis and condensation in aqueous alkaline solution in the presence of surfactant cetrimonium bromide. 1.646 mmol of cetrimonium bromide was dissolved into a solution of 300 mL distilled water and 4.2 mmol NaOH. After having stirred for 30 minutes at 80 °C until the surfactant was fully dissolved, 13.43 mmol of pre-synthesized precursor and tetraethoxysilane (TEOS, 0.2552 mol) in ethanol (1 mL) was added dropwise under vigorous stirring. A white suspension was immediately formed, which was continuously stirred at 80 °C for 2 h. A white powder was obtained by centrifugation and then washed with water (twice) and ethanol (once). Finally, the surfactant was removed by solvent extraction three times to ensure full removal of the surfactant template. The detailed procedure of the solvent extraction was as follows: the as-synthesized material (ca. 1 g) was stirred into a solution which contains 200 mL of ethanol and 0.4 mL of concentrated hydrochloric acid at 65 °C for 6 h.

### 1.3 Synthesis of Am-PMO

The PMO precursors: N-[3-(trimethoxysilyl)propyl]ethylenediamine and 1,2-bis(triethoxysilyl)ethane are commercially available. As the amine precursor is very bulky, the used amount is much lower than 1,2-bis(triethoxysilyl)ethane to obtain the highly ordered structure of the PMO.

The Am-PMO was synthesized by the co-condensation of 10% N-[3-(trimethoxysilyl)propyl]ethylenediamine and 90% 1,2-bis(triethoxysilyl)ethane. 0.5 g of cetrimonium bromide was dissolved in 300 mL of distilled water. Additionally, 3.235 mL of 25% ammonium solution was added to the above solution in an ice water bath, then it was naturally heated to room temperature after stirring 30 minutes. Then mixed solution A was obtained. Next, the precursors N-[3-(trimethoxysilyl)propyl]ethylenediamine (10%) and 1,2-bis(triethoxysilyl)ethane (90%) were dissolved in 10 mL of ethanol to get solution B. Afterwards, the solution B was added dropwise to the solution A, and was left to stir for 3 h at 80 °C. The precipitate was collected by centrifugation and washed with water and acetone. Later it was dried in a vacuum oven at 120 °C overnight. The surfactant was extracted by refluxing the white powder (ca. 1 g) in a mixture of HCl (2 mL) and ethanol (66 mL) for 6 h at 50 °C. The powder was filtered and washed with water and ethanol. The procedure of surfactant removal was repeated 3 times to ensure complete surfactant removal.

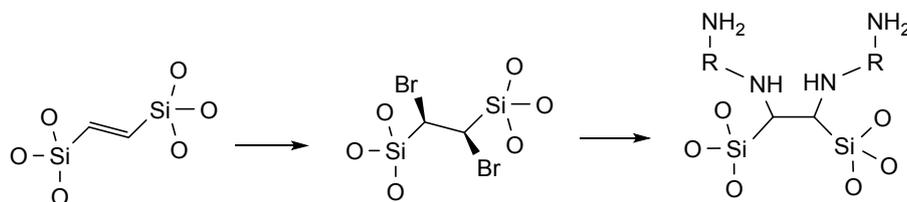
### 1.4 Synthesis of Am-ePMO

The precursor of the ePMO was synthesized by following a published procedure.<sup>2</sup> In a typical synthesis of pure E-diastereoisomer of 1,2-bis(triethoxysilyl)ethene (BTSE),  $(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}$  (Grubb's catalyst 1<sup>st</sup> generation, 0.065 mmol) and vinyltriethoxysilane (42.95 mL) were added to a round bottom flask under argon. The mixture was left to stir for 2 h and subsequently refluxed for an additional 3 h. The unreacted vinyltriethoxysilane was distilled off, after which the BTSE was distilled under vacuum to get a clear colorless liquid.

In order to obtain ethenylene-bridged PMO (ePMO), a solution containing P123 surfactant (1.00 g), HCl (2.12 mL), BuOH (1.17 mL), and 48.70 mL of H<sub>2</sub>O was

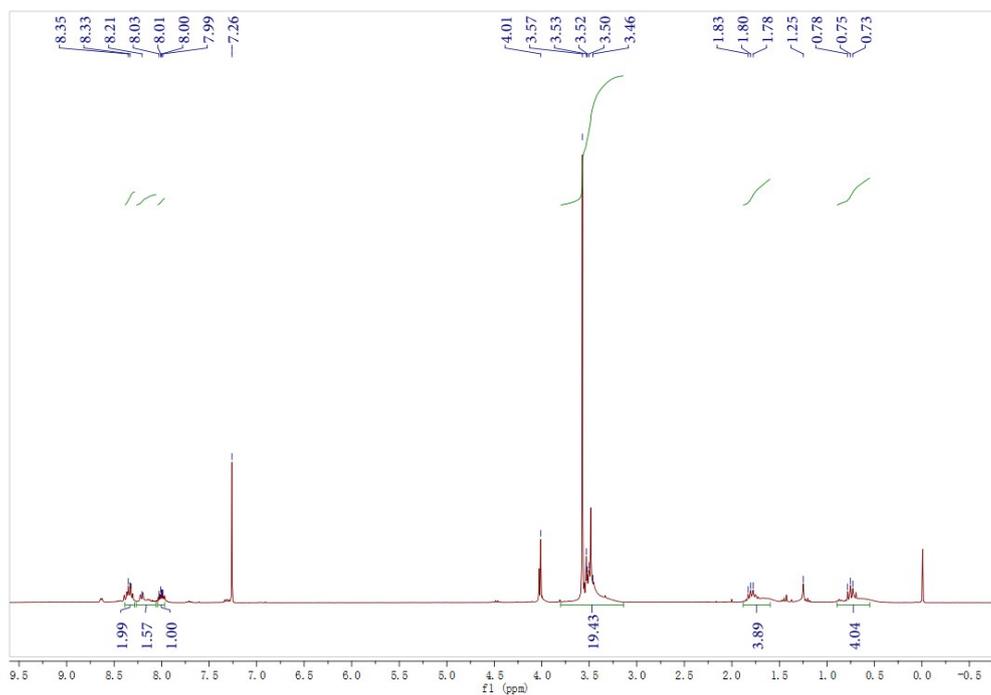
stirred at room temperature for 2 h. Then pure BTSE (1.86 mL) was added dropwise to the above clear solution. The mixture was stirred at 35 °C for 2 h and subsequently aged at 90 °C for 6 h under static conditions. After cooling down, a white powder was collected by filtration and washed with H<sub>2</sub>O. The surfactant was removed by the method of Soxhlet extraction in acetone for 5 h at 100 °C.

The ePMO was then functionalized by a bromination reaction, achieved by adding Br<sub>2</sub> in the gaseous phase to the ePMO. Afterwards, the solid was heated at 120 °C to remove any physisorbed bromine molecules, after which ePMO@Br was obtained. The amount of bromine was determined gravimetrically. Subsequently, the Br was substituted with diethylenetriamine (DETA; 99%) to gain Am-ePMO. In a typical synthesis, 0.1 g of ePMO@Br was mixed with DETA (5 mol equivalents with regard to the amount of bromine) in 50 mL of dimethylformamide (DMF; >99.5%) under an inert atmosphere. After stirring at 100 °C for 5 h, the powder was collected by filtration and washed thoroughly with DMF, distilled water and acetone. Finally, it was dried under vacuum at 90 °C. The material is named as Am-ePMO. The above reactions are depicted in Scheme S1.

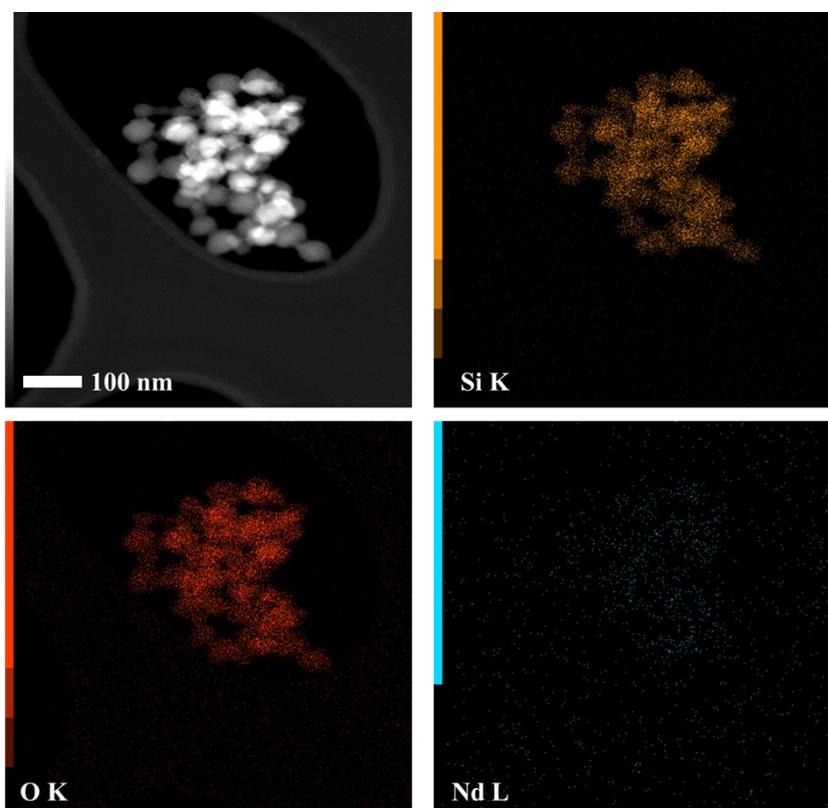


**Scheme S1.** Schematic overview of the modification performed on the ePMO material: (a) bromination of the double bond; (b) substitution with DETA where R represents (CH<sub>2</sub>)<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>

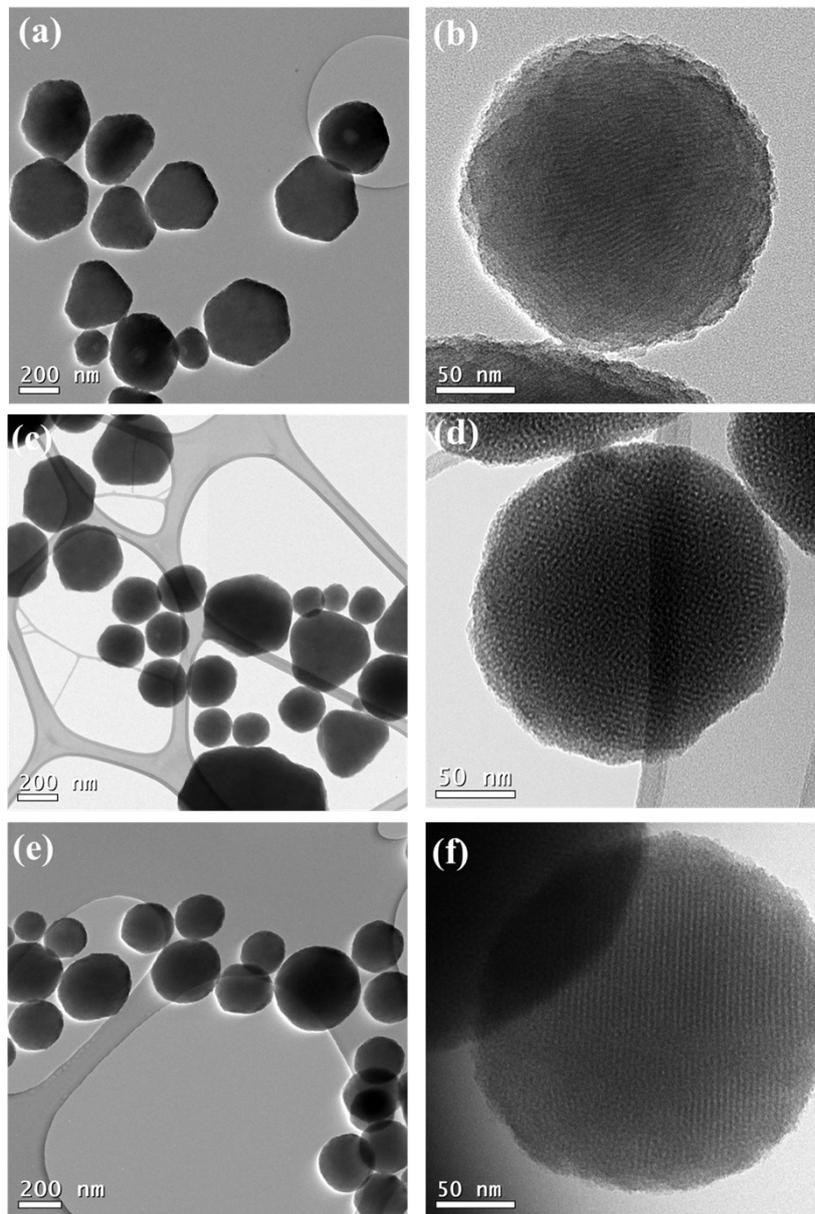
## Supplementary figures and tables



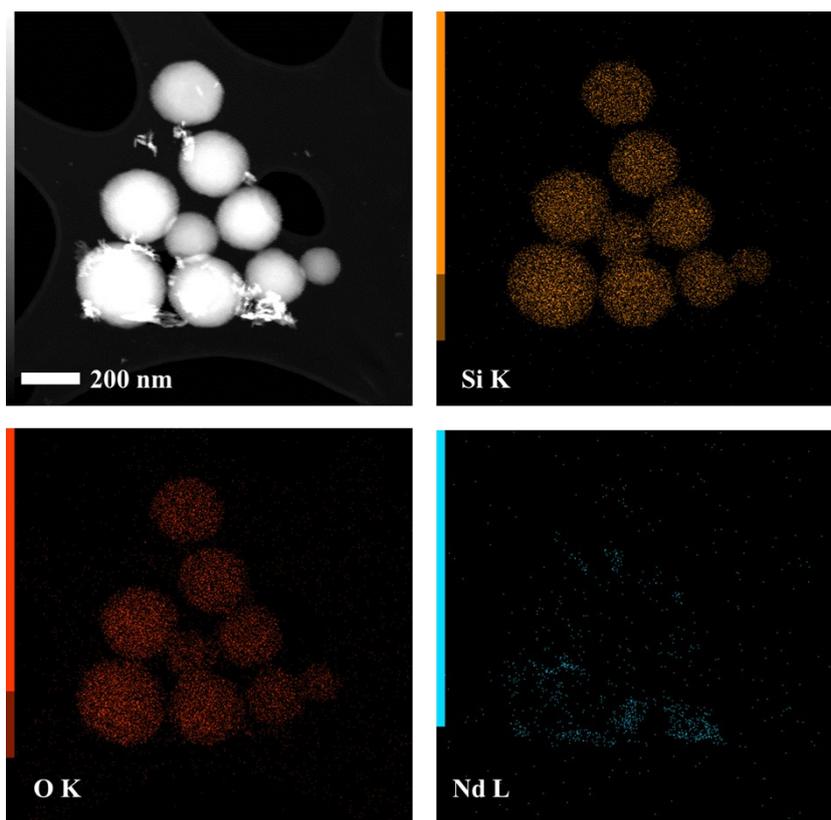
**Figure S1.**  $^1\text{H}$  NMR spectrum of the DPA-Si precursor.



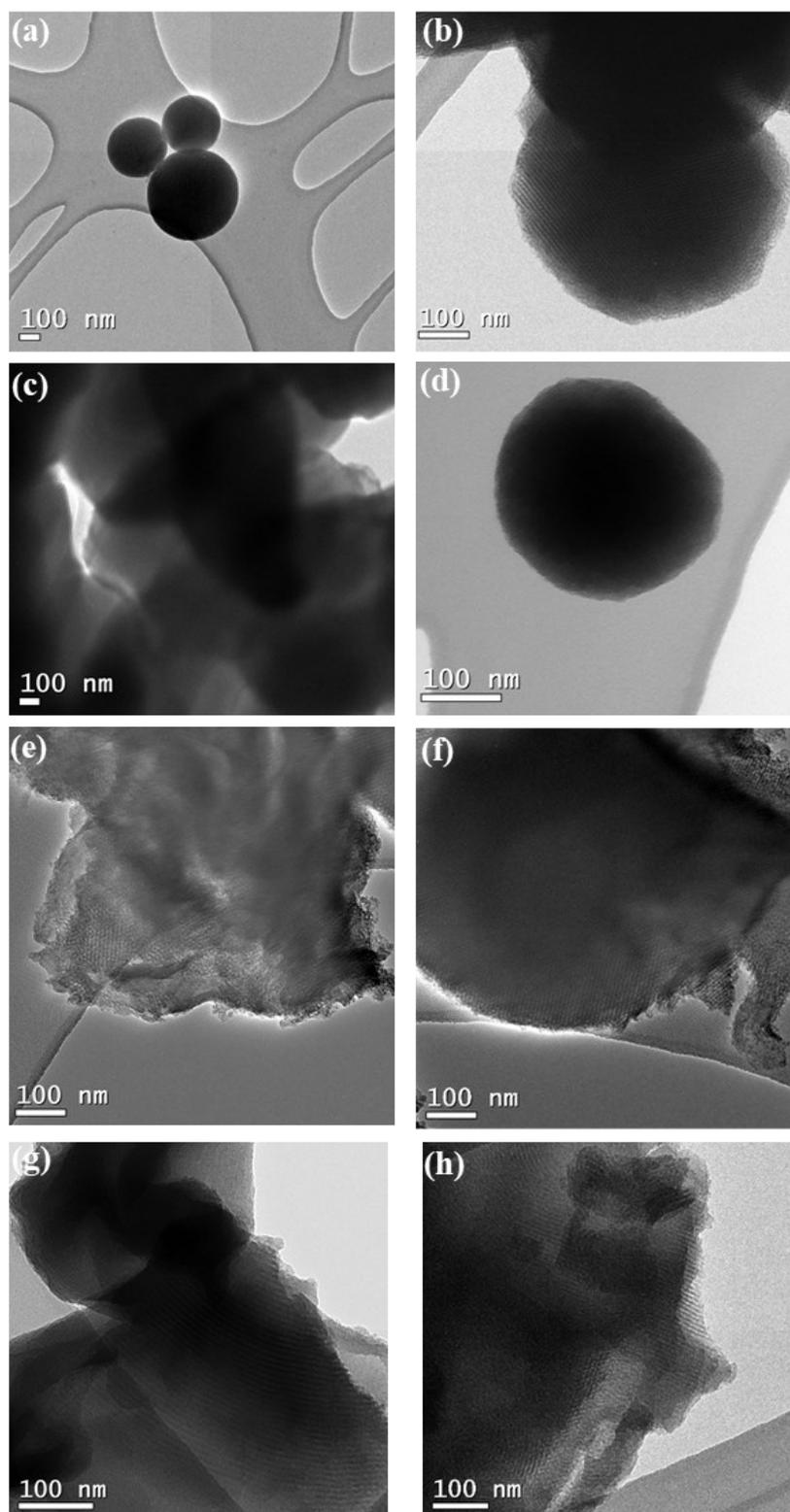
**Figure S2.** TEM-EDX mapping of DPA-PMO@NdCl<sub>3</sub> for the following elements: Si, O, Nd (from top to bottom).



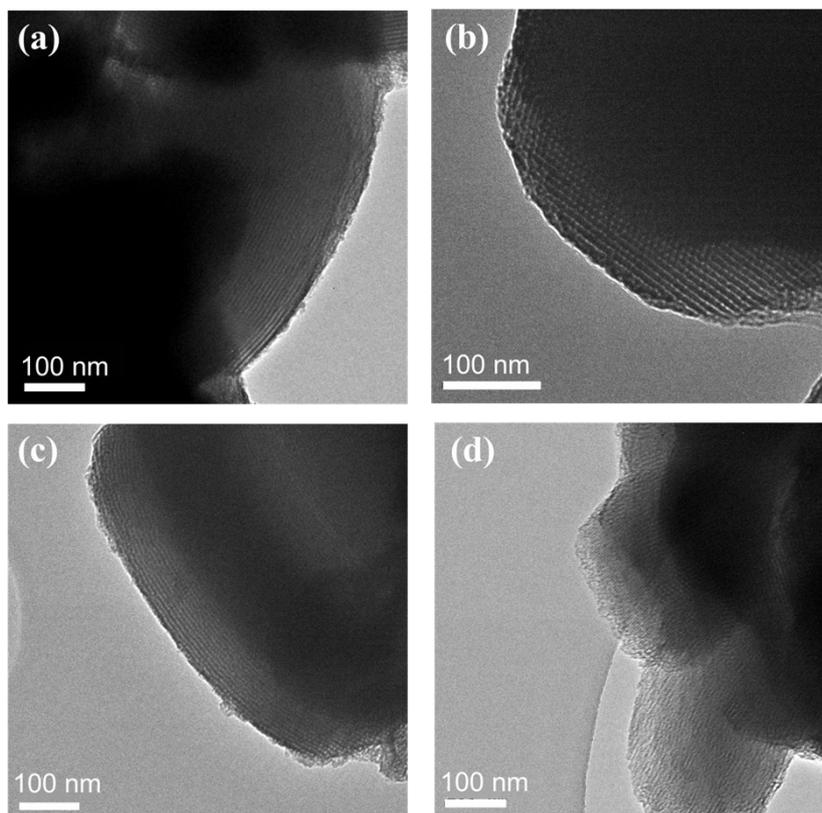
**Figure S3.** TEM images of Am-PMO prepared with different amounts of water employed in the synthesis. (a)(b): 200 mL water; (c)(d): 250 mL water; (e)(f): 300 mL water.



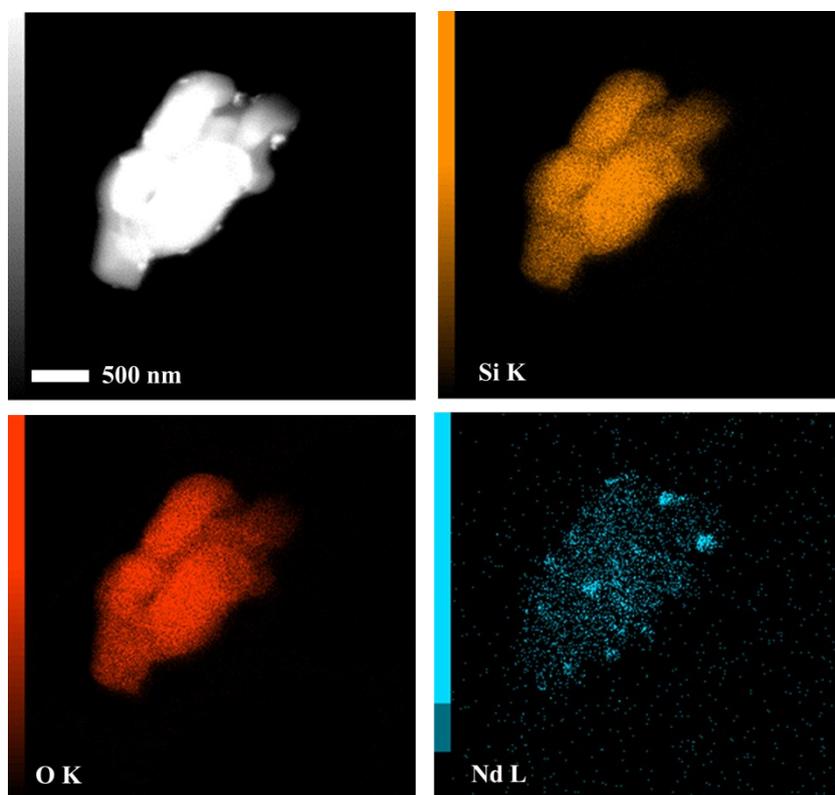
**Figure S4.** TEM-EDX mapping of Am-PMO@NdCl<sub>3</sub> for the following elements: Si, O, Nd (from top to bottom).



**Figure S5.** TEM images of ePMO prepared in different conditions (a)(b)  $V_{\text{HCl}}:V_{\text{BuOH}} = 1.81$ , aged at 90 °C for 6 h; (c)(d)  $V_{\text{HCl}}:V_{\text{BuOH}} = 1.57$ , aged at 90 °C for 6 h; (e)(f)  $V_{\text{HCl}}:V_{\text{BuOH}} = 0.16$ , aged at 90 °C for 6 h; (g)(h)  $V_{\text{HCl}}:V_{\text{BuOH}} = 1.81$ , no aging period. The amount of P123, H<sub>2</sub>O and HCl is fixed at 1g, 48.7 mL and 2.12 mL, respectively.



**Figure S6.** TEM images of (a) ePMO@Br; (b) Am-ePMO; (c)Am-ePMO@o-van; (d) Am-ePMO@NdCl<sub>3</sub>.



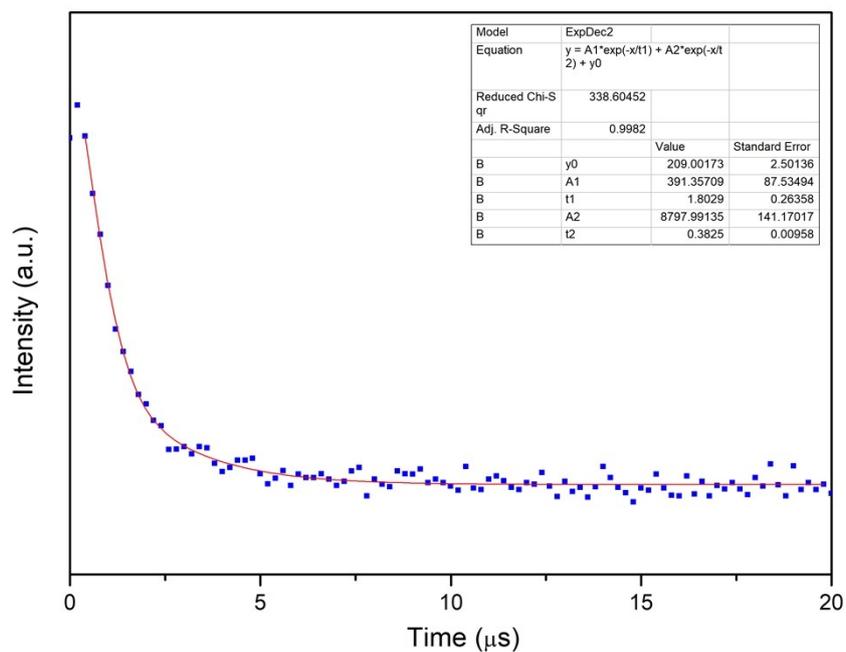
**Figure S7.** TEM-EDX mapping of Am-ePMO@NdCl<sub>3</sub> for the following elements: Si, O, Nd (from top to bottom).

**Table S1.** Physicochemical properties of the PMOs studied in this research. (a determined via the BET equation. b calculated by using BJH model on the desorption branch. c Lattice parameter calculated by  $a_0 = 2d_{100}/\sqrt{3}$ . d Calculated as the difference between  $a_0$  and  $D_p$ .)

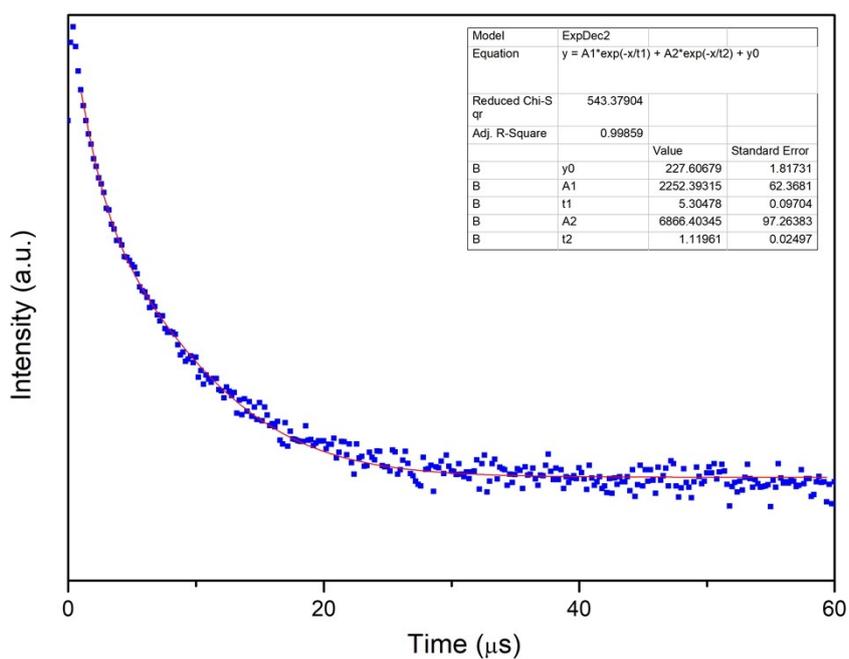
Sample	$S_{BET}^a$ ( $m^2g^{-1}$ )	$V_p^b$ ( $cm^3g^{-1}$ )	$D_p^b$ (nm)	$a_0^c$ (nm)	$d_{100}$ (nm)	Wall thickness $d^d$ (nm)
DPA-PMO	977	0.77	3.00	4.80	4.16	1.80
DPA-PMO@NdCl <sub>3</sub>	835	0.66	2.93	4.76	4.12	1.83
DPA-PMO@Nd(hfa) <sub>3</sub>	542	0.39	2.77	4.63	4.01	1.86
Am-PMO	856	0.66	3.07	6.14	5.32	3.07
Am-PMO@o-van	528	0.34	2.83	6.14	5.32	3.31
ePMO	911	1.07	5.92	11.32	9.81	5.40
ePMO@Br	704	0.79	4.78	10.19	8.83	5.41
Am-ePMO	648	0.76	5.08	10.19	8.83	5.11
Am-ePMO@o-van	553	0.66	4.97	10.19	8.83	5.22
Am-ePMO@NdCl <sub>3</sub>	458	0.60	5.06	-	-	-
Am-ePMO@Nd(hfa) <sub>3</sub>	433	0.54	5.10	-	-	-

**Table S2.** Actual Ln<sup>3+</sup> contents for the Am-PMO@Ln<sup>3+</sup> and Am-ePMO@ Ln<sup>3+</sup> materials determined by ICP-MS analysis.

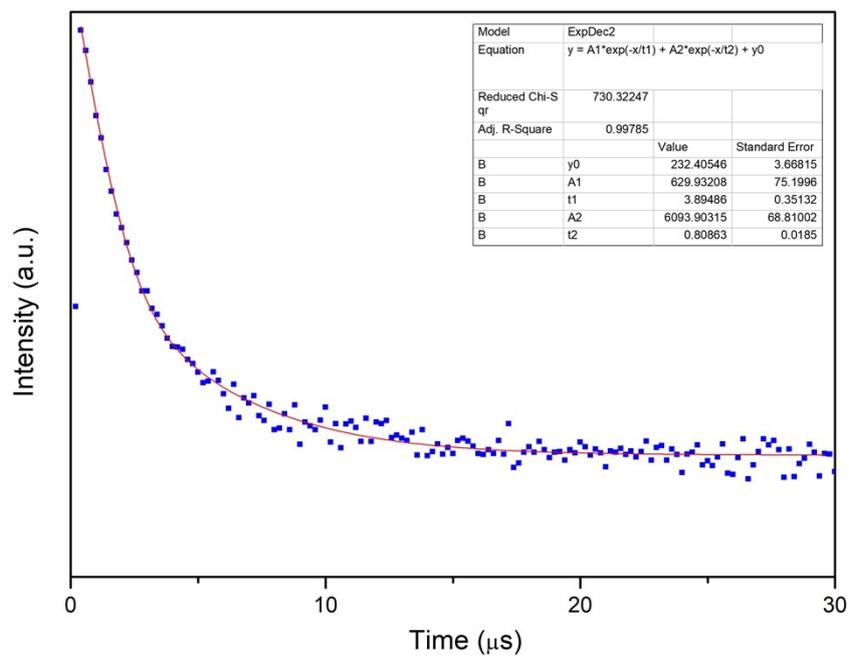
Sample	Nd <sup>3+</sup> (mmol/g)	Yb <sup>3+</sup> (mmol/g)
DPA-PMO@NdCl <sub>3</sub>	0.1058	-
DPA-PMO@Nd(hfa) <sub>3</sub>	0.1477	-
DPA-PMO@YbCl <sub>3</sub>	-	0.1835
DPA-PMO@Yb(hfa) <sub>3</sub>	-	0.2867
Am-PMO@NdCl <sub>3</sub>	0.0189	-
Am-PMO@Nd(hfa) <sub>3</sub>	0.0092	-
Am-PMO@YbCl <sub>3</sub>	-	0.0274
Am-PMO@Yb(hfa) <sub>3</sub>	-	0.008
Am-ePMO@NdCl <sub>3</sub>	0.1177	-
Am-ePMO@Nd(hfa) <sub>3</sub>	0.0843	-
Am-ePMO@YbCl <sub>3</sub>	-	0.1377
Am-ePMO@Yb(hfa) <sub>3</sub>	-	0.1162



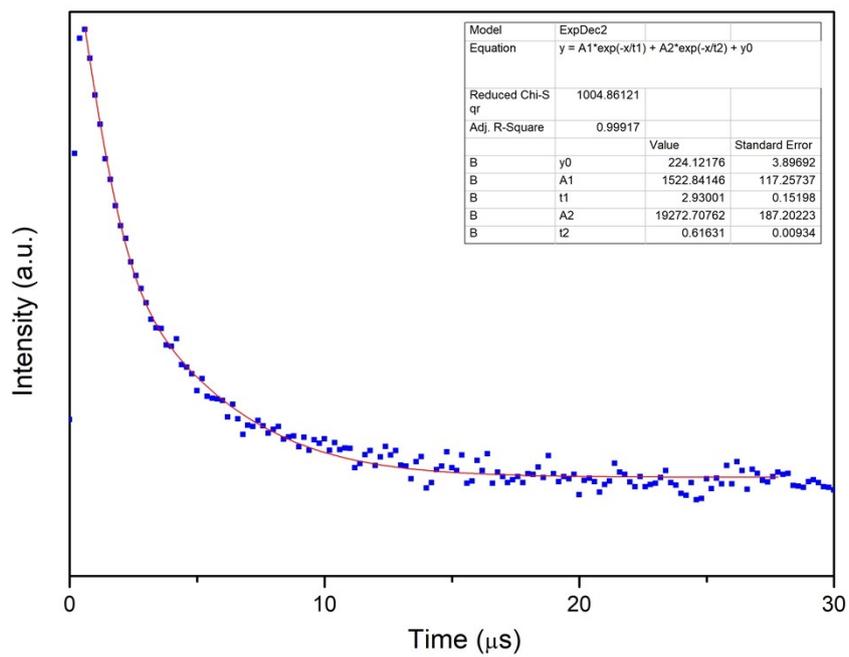
**Figure S8.** Decay profile of DPA-PMO@NdCl<sub>3</sub>.



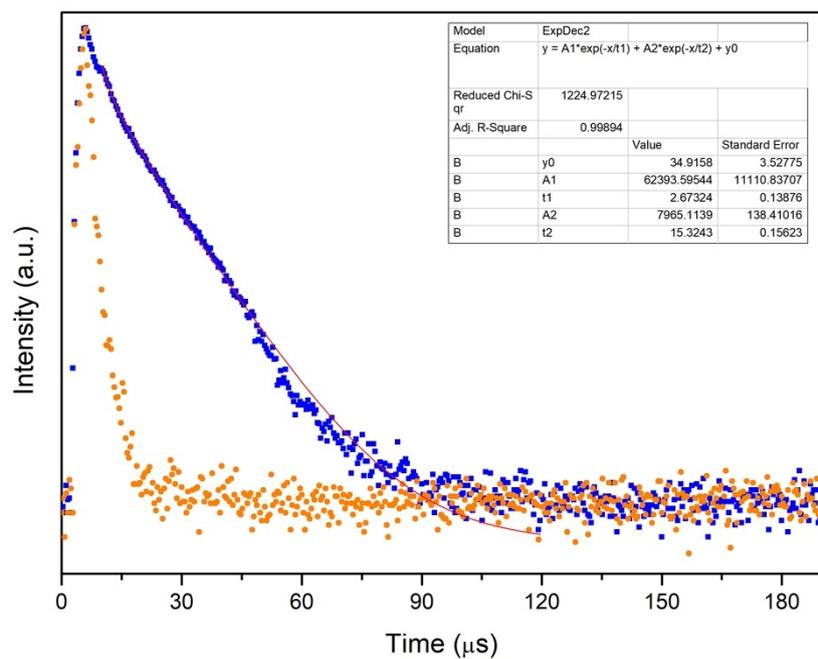
**Figure S9.** Decay profile of DPA-PMO@Nd(hfa)<sub>3</sub>.



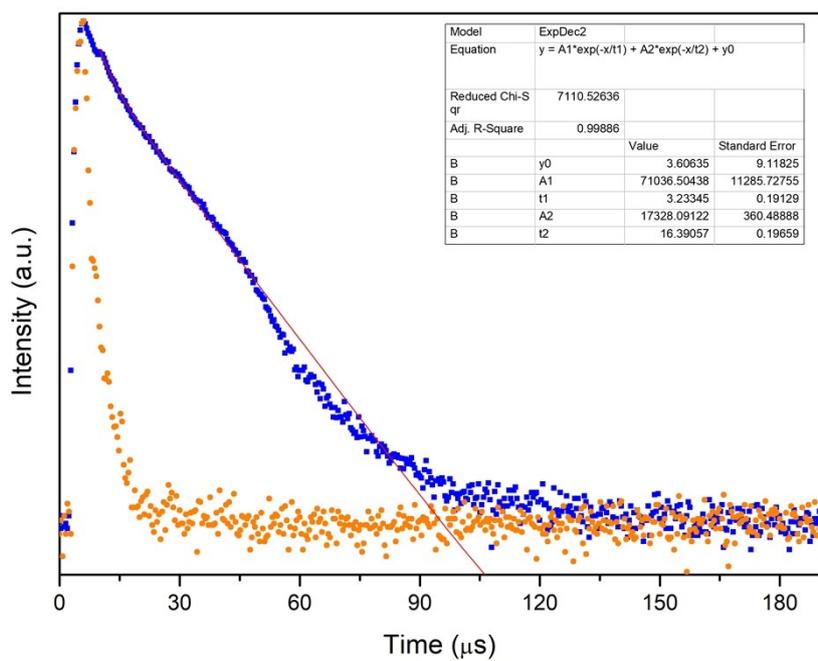
**Figure S10.** Decay profile of Am-ePMO@NdCl<sub>3</sub>.



**Figure S11.** Decay profile of Am-ePMO@Nd(hfa)<sub>3</sub>.



**Figure S12.** Decay profile of DPA-PMO@YbCl<sub>3</sub>. (Orange dots indicates IRF.)



**Figure S13.** Decay profile of DPA-PMO@Yb(hfa)<sub>3</sub>. (Orange dots indicates IRF.)

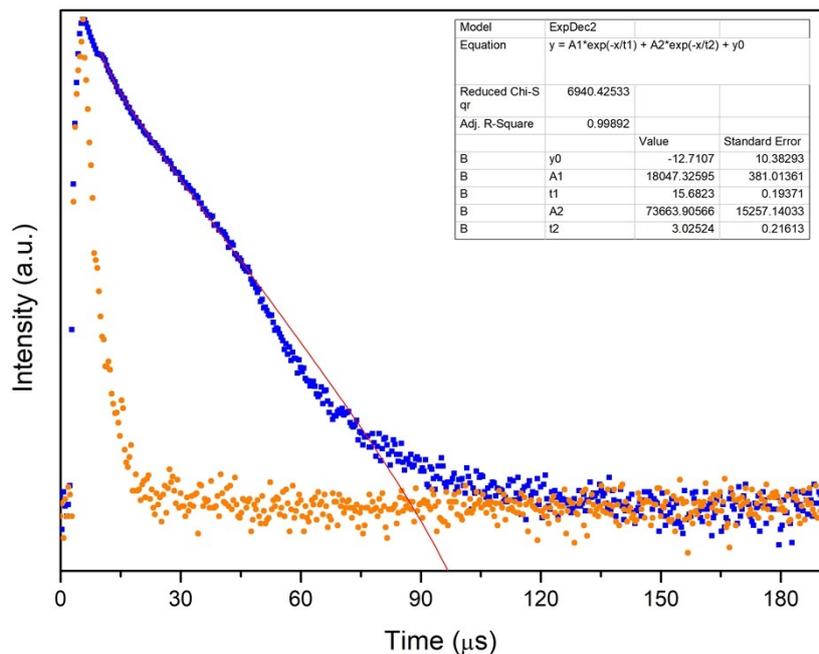


Figure S14. Decay profile of Am-ePMO@YbCl<sub>3</sub>. (Orange dots indicates IRF.)

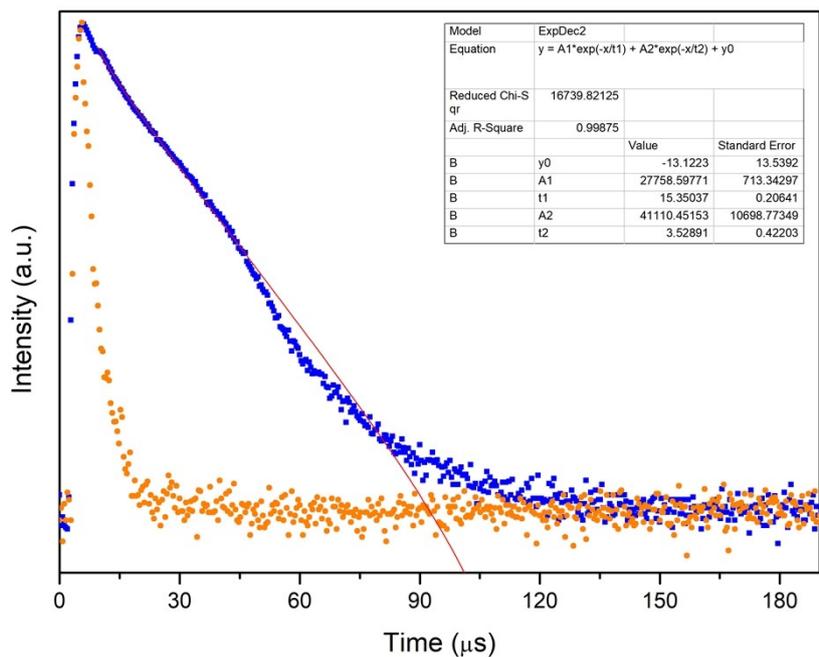
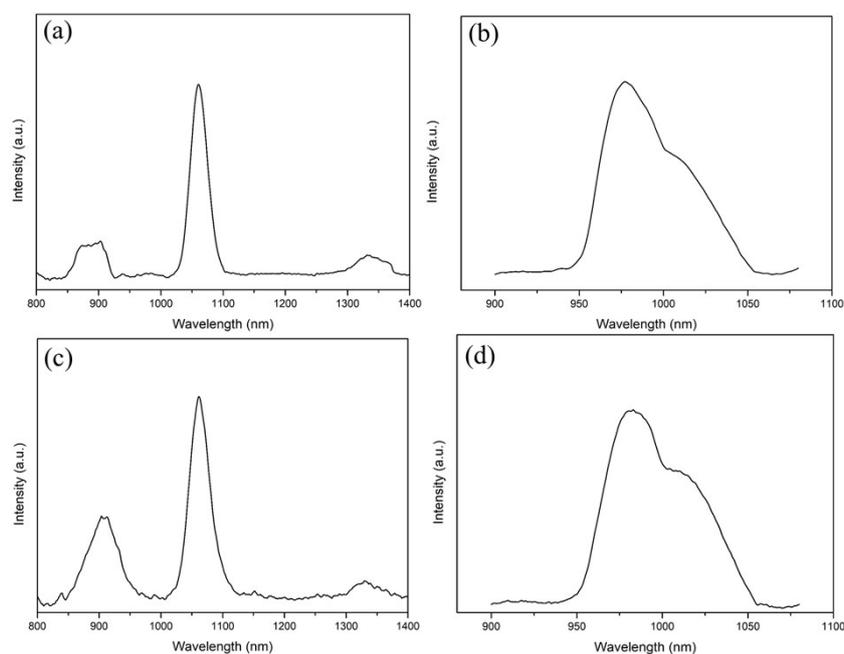


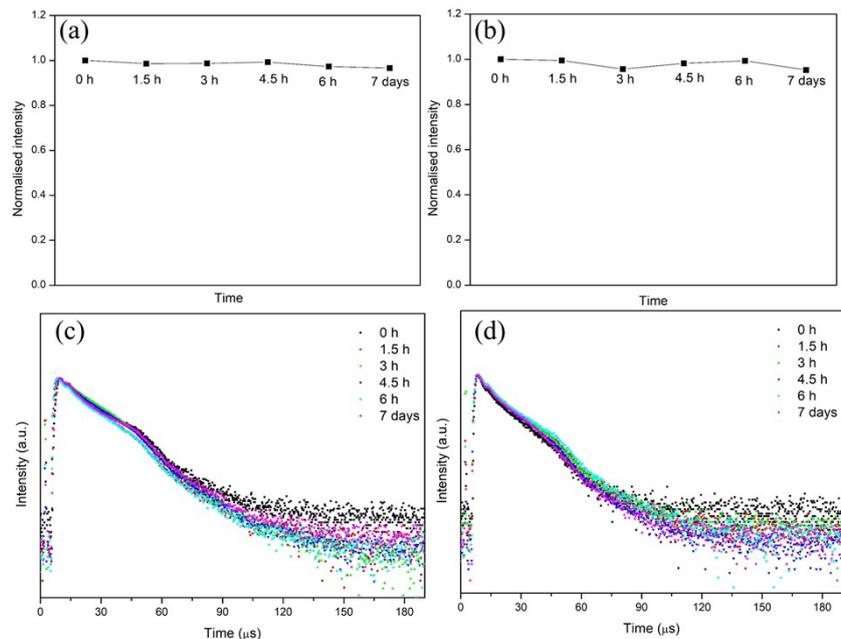
Figure S15. Decay profile of Am-ePMO@Yb(hfa)<sub>3</sub>. (Orange dots indicates IRF.)

**Table S3.** Fitting results of the decay curves of the studied hybrid mesoporous materials.

Samples	Ln	$\tau_1$ ( $\mu\text{s}$ )	$\tau_2$ ( $\mu\text{s}$ )	$\tau_{ave}$ ( $\mu\text{s}$ )
DPA-PMO@LnCl <sub>3</sub>	Nd	1.80	0.38	0.62
	Yb	2.67	15.32	8.02
DPA-PMO@Ln(hfa) <sub>3</sub>	Nd	5.30	1.11	3.66
	Yb	3.23	16.39	10.51
Am-ePMO@LnCl <sub>3</sub>	Nd	3.89	0.80	1.83
	Yb	15.68	3.02	10.11
Am-ePMO@Ln(hfa) <sub>3</sub>	Nd	2.93	0.61	1.25
	Yb	15.35	3.53	12.35

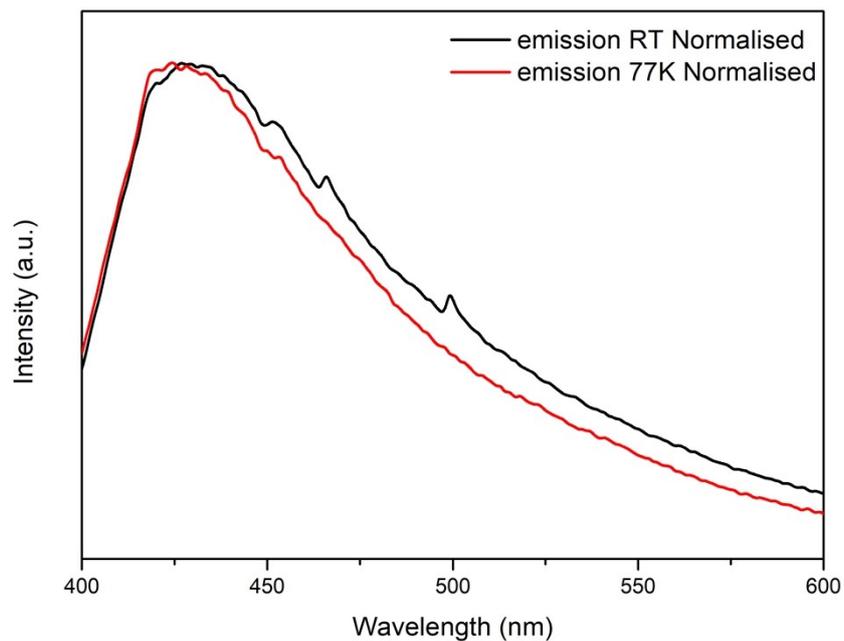


**Figure S16.** Emission spectra of (a) DPA-PMO@Nd(hfa)<sub>3</sub>; (b) DPA-PMO@Yb(hfa)<sub>3</sub>; (c) Am-ePMO@Nd(hfa)<sub>3</sub> and (d) Am-ePMO@Yb(hfa)<sub>3</sub> recorded in water suspension. The spectra were recorded upon excitation at 323 nm (a, b, c) and 372 nm (d).

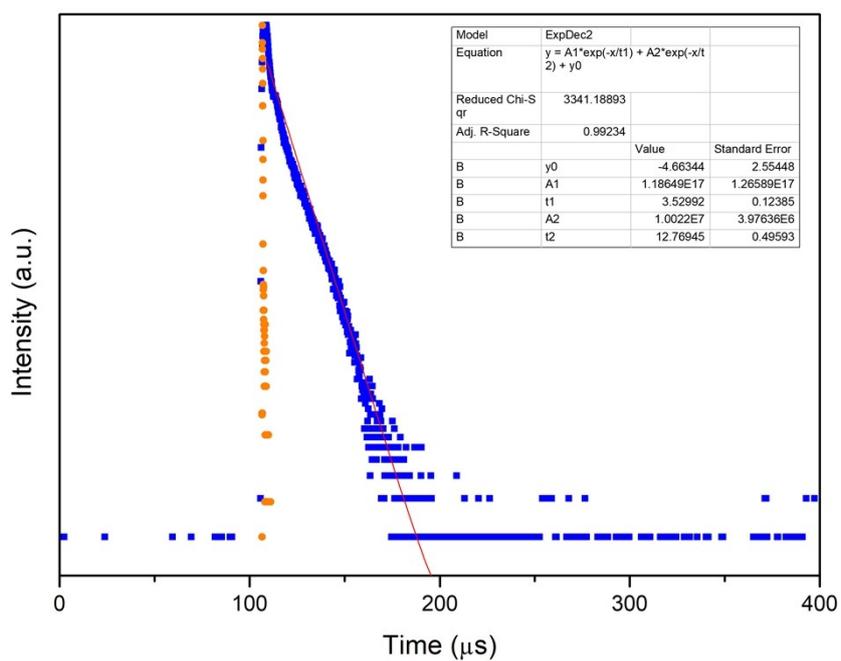


**Figure S17.** Emission intensity versus time (1.5 hours, 3 hours, 4.5 hours, 6 hours and 7 days): (a) DPA-PMO@Yb(hfa)<sub>3</sub>, (b) Am-ePMO@Yb(hfa)<sub>3</sub>; Decay time profiles versus time: (c) DPA-PMO@Yb(hfa)<sub>3</sub>, (d) Am-ePMO@Yb(hfa)<sub>3</sub>.

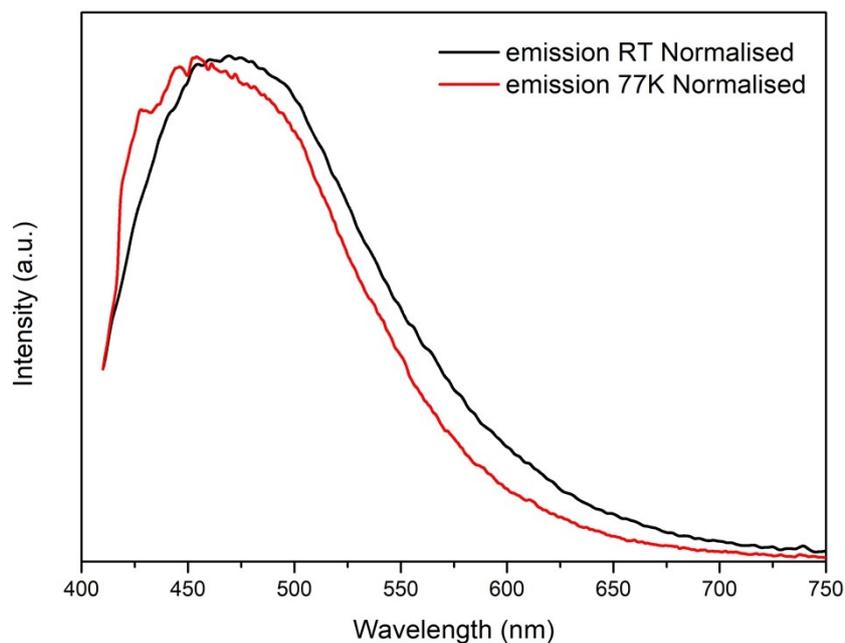
To confirm that the lowest triplet levels of PMO materials are well above the accepting levels of lanthanide ions Nd<sup>3+</sup> and Yb<sup>3+</sup>. The emission spectra of DPA-PMO and Am-ePMO grafted with GdCl<sub>3</sub> at 77 K in ethanol/methanol mixture (4:1) were measured to determine the triplet levels of the PMO materials.<sup>3</sup> One band can be distinguished when measured at 77 K in Figure S18, as well as in Figure S20. Subsequently, the maximum decay time was recorded and observed microsecond range lifetimes, confirming the band belongs to the triplet level of the PMO materials (Figure S19 and S21). The triplet level of the PMO material corresponds to the high-energy edge of the band, the lowest triplet levels are therefore located around 410 nm (DPA-PMO) and 428 nm (Am-ePMO), respectively.



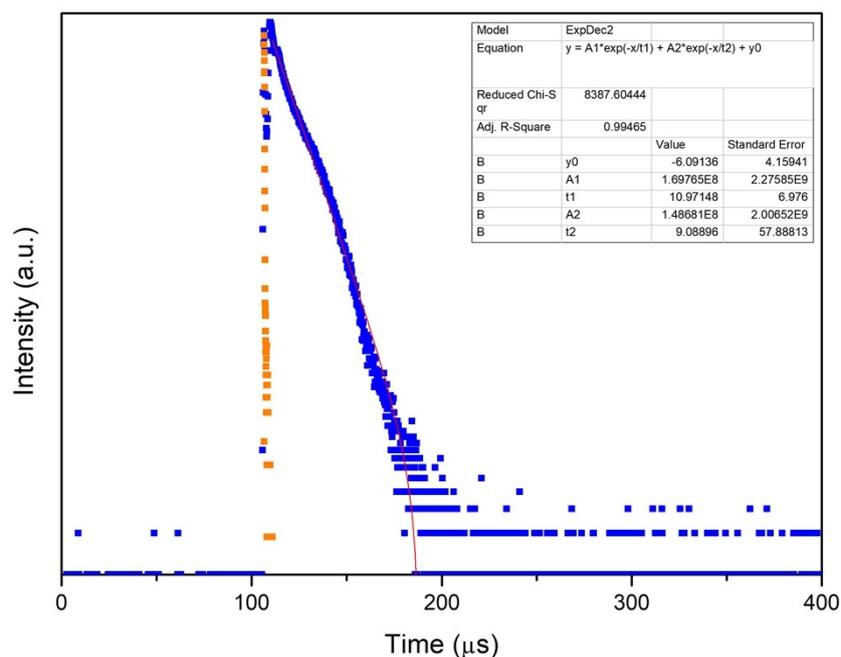
**Figure S18.** Emission spectra of DPA-PMO grafted with  $\text{GdCl}_3$  ( $\text{DPA-PMO@GdCl}_3$ ), measured in ethanol:methanol (4:1) solution at RT (black line) and at 77 K (red line).



**Figure S19.** Luminescence decay time of  $\text{DPA-PMO@GdCl}_3$  recorded at 410 nm. (Orange dots indicates IRF.)



**Figure S20.** Emission spectra of Am-ePMO grafted with  $\text{GdCl}_3$  (Am-ePMO@ $\text{GdCl}_3$ ), measured in ethanol:methanol (4:1) solution at RT (black line) and at 77 K (red line).



**Figure S21.** Luminescence decay time of Am-ePMO@ $\text{GdCl}_3$  recorded at 428 nm. (Orange dots indicates IRF.)

## Supplementary References

- 1 N. Yuan, Y. Liang, E. S. Erichsen and R. Anwander, *RSC Adv.*, 2015, **5**, 83368-83376.
- 2 C. Vercaemst, M. Ide, B. Allaert, N. Ledoux, F. Verpoort and P. Van Der Voort, *Chem. Commun.*, 2007, 2262-2263.
- 3 A. M. Kaczmarek, Y. Liu, M. K. Kaczmarek, H. Liu, F. Artizzu., L. D. Carlos and P. Van Der Voort, *Angew. Chem., Int. Ed.*, 2020, **59**, 1932-1940.