

# Supporting Information

for

## **Synthesis of rare-earth metal and rare-earth metal-fluoride nanoparticles in ionic liquids and propylene carbonate**

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## **Additional experimental data**

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TEM images, particle size histogram, SAED, EDX and XPS of Er-NPs in [BMIm][NTf<sub>2</sub>]

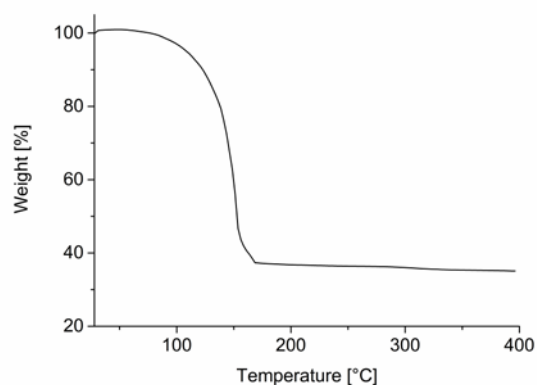
TEM images, particle size histogram, SAED, EDX and XPS of RE-NPs in PC

## Thermogravimetric analysis, TGA of rare earth amidinates and $\text{Eu}(\text{dpm})_3$

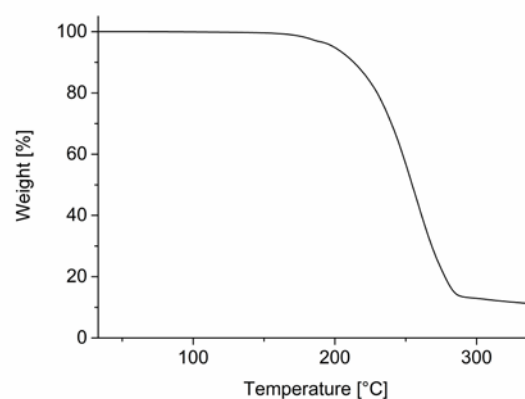
**Table S1:** Thermogravimetric analysis of the rare earth metal amidinates and  $\text{Eu}(\text{dpm})_3$ <sup>a</sup>.

Precursor	Decomposition temperature [°C]	$\Delta m_{\text{TGA}}$ (exptl/calcd)
$\text{Pr}(\text{amd})_3$	160	66/70
$\text{Eu}(\text{dpm})_3$	220	89/79
$\text{Gd}(\text{amd})_3$	230	90/74
$\text{Er}(\text{amd})_3$	220	82/72

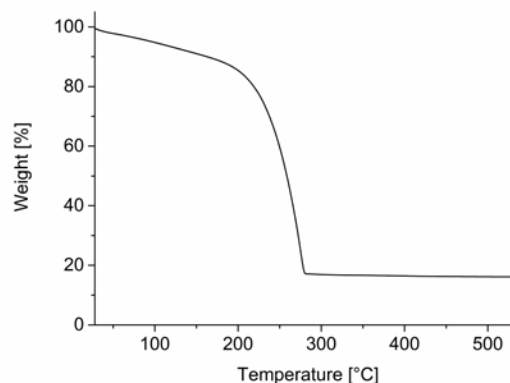
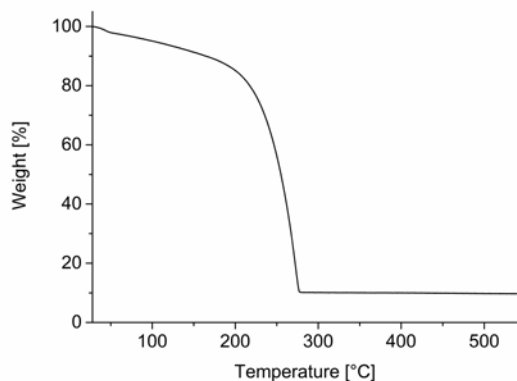
<sup>a</sup> See thermogravimetric diagrams in Figure S2.



**Figure S2a:** TGA  $\text{Pr}(\text{amd})_3$ , 25–400 °C, 5 K/min.

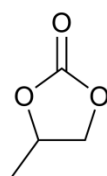
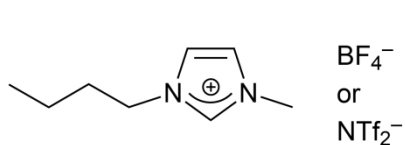


**Figure S2b:** TGA  $\text{Eu}(\text{dpm})_3$ , 25–350 °C, 5 K/min.



**Figure S2c:** TGA  $\text{Gd(amd)}_3$ , 25–550 °C, **Figure S2d:** TGA  $\text{Er(amd)}_3$ , 25–550 °C, 5 K/min.

### Structural formulas of the ionic liquids (ILs) and propylene carbonate (PC)



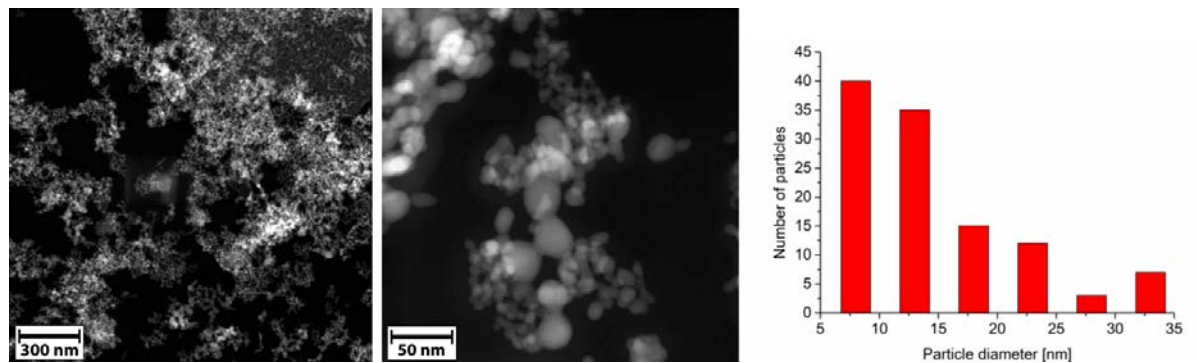
1-*n*-butyl-3-methyl-imidazolium  
- tetrafluoroborate  $[\text{BMIm}][\text{BF}_4]$   
- bistriflimide  $[\text{BMIm}][\text{NTf}_2]$ ,  $\text{NTf}_2^- = [(\text{CF}_3\text{SO}_2)_2\text{N}]^-$

propylene  
carbonate, PC

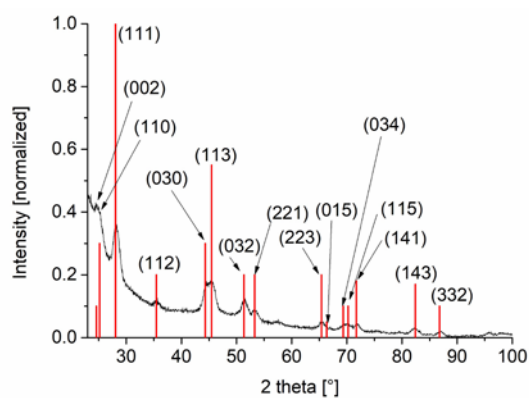
**Figure S3:** Ionic liquids (ILs) and propylene carbonate (PC) used as reaction media and stabilizer for NP syntheses.

## TEM images, particle size histogram, PXRD, SAED, EDX and XPS of $\text{PrF}_3$ -NPs

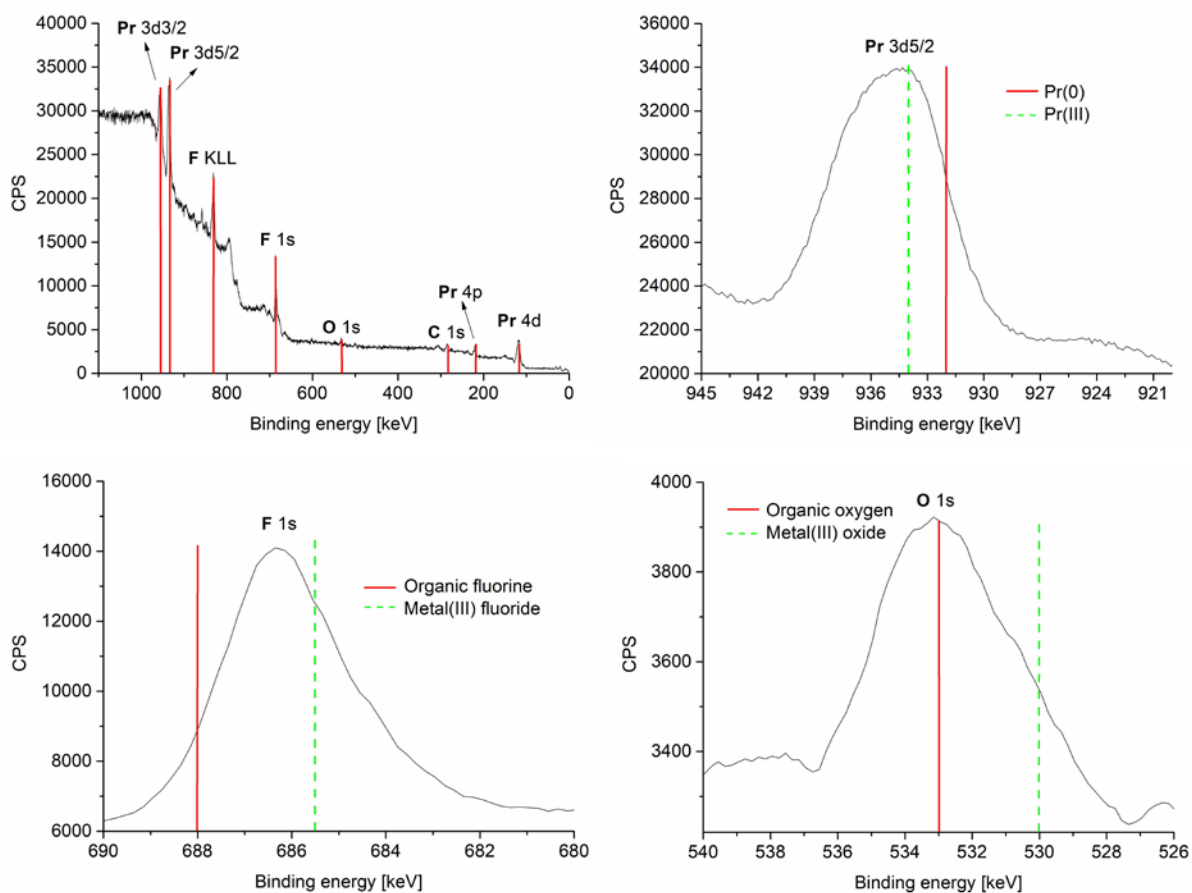
$\text{PrF}_3$ -NPs in  $[\text{BMIm}][\text{BF}_4]$



**Figure S4a:** HAADF-STEM images and particle size histogram of 1.0 wt %  $\text{PrF}_3$ -NPs in  $[\text{BMIm}][\text{BF}_4]$  from  $\text{Pr}(\text{amd})_3$ .

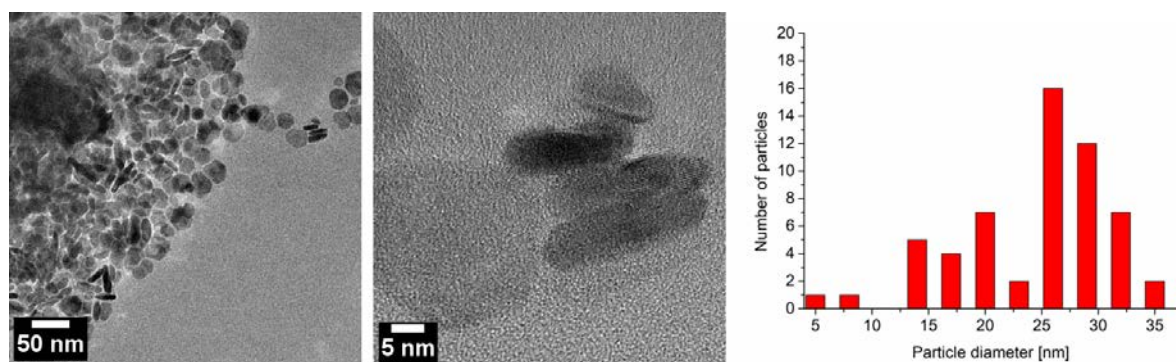


**Figure S4b:** PXRD ( $\text{PrF}_3$  reference peaks in red from COD 1010984, hexagonal with space group  $P6_3/mcm$ ) of 1.0 wt %  $\text{PrF}_3$ -NPs in  $[\text{BMIm}][\text{BF}_4]$  from  $\text{Pr}(\text{amd})_3$ .

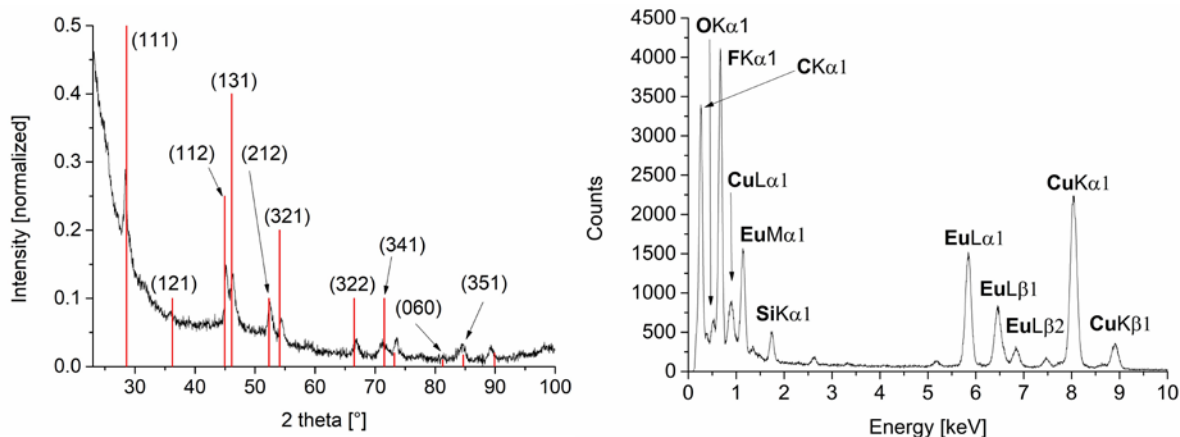


**Figure S4c:** Overview and HR-XPS of 1.0 wt %  $\text{PrF}_3$ -NPs in  $[\text{BMIm}][\text{BF}_4]$  from  $\text{Pr}(\text{amd})_3$ . The red and green bars are a guide to the eye on the binding-energy axis.

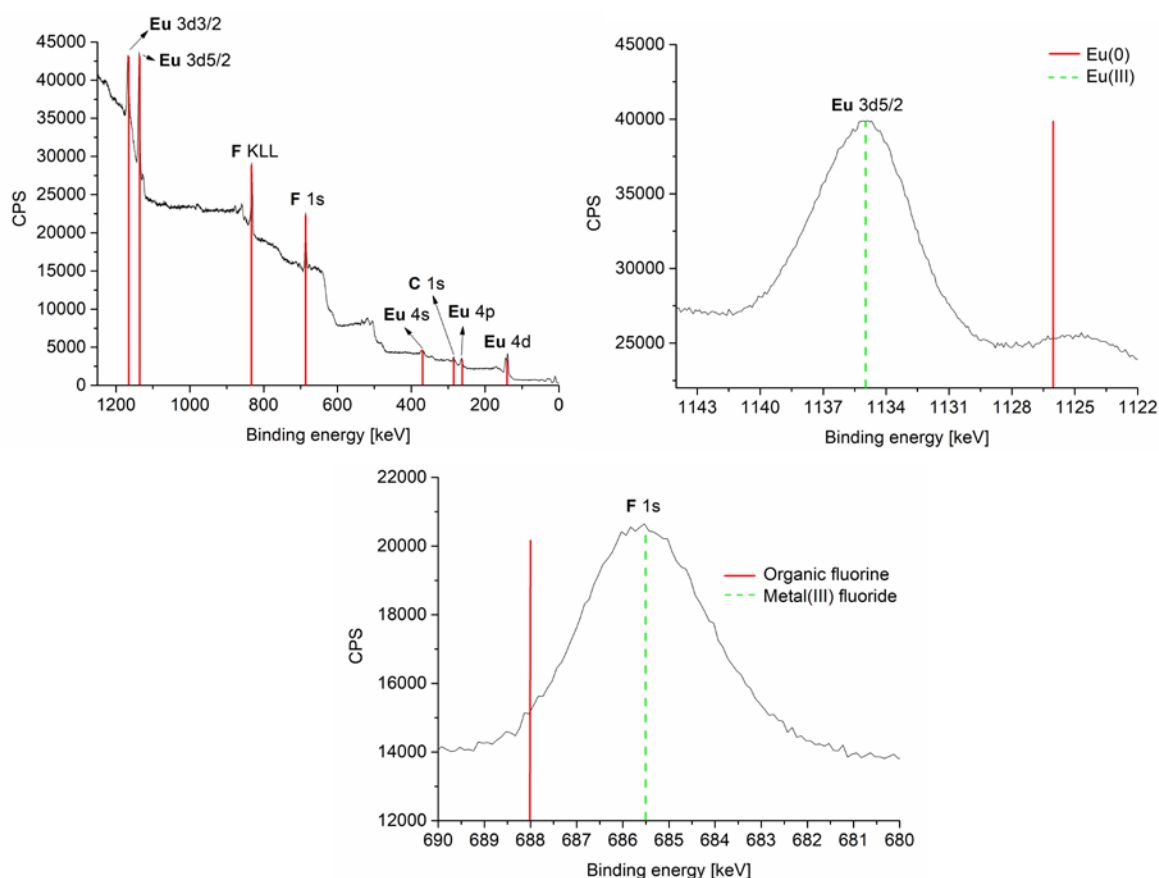
#### *$\text{EuF}_3$ -NPs in $[\text{BMIm}][\text{BF}_4]$*



**Figure S5a:** TEM images and particle size histogram of 1.0 wt %  $\text{EuF}_3$ -NPs in  $[\text{BMIm}][\text{BF}_4]$  from  $\text{Eu}(\text{dpm})_3$ .

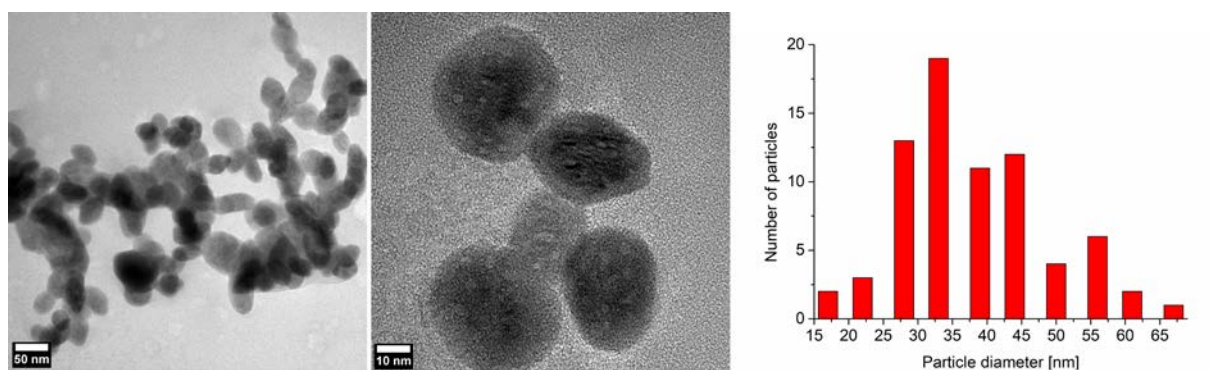


**Figure S5b:** PXRD ( $\text{EuF}_3$  reference peaks in red from COD 1532444, orthorhombic with space group  $Pnma$ ) and EDX of 1.0 wt %  $\text{EuF}_3$ -NPs in  $[\text{BMIm}][\text{BF}_4]$  from  $\text{Eu}(\text{dpm})_3$ .

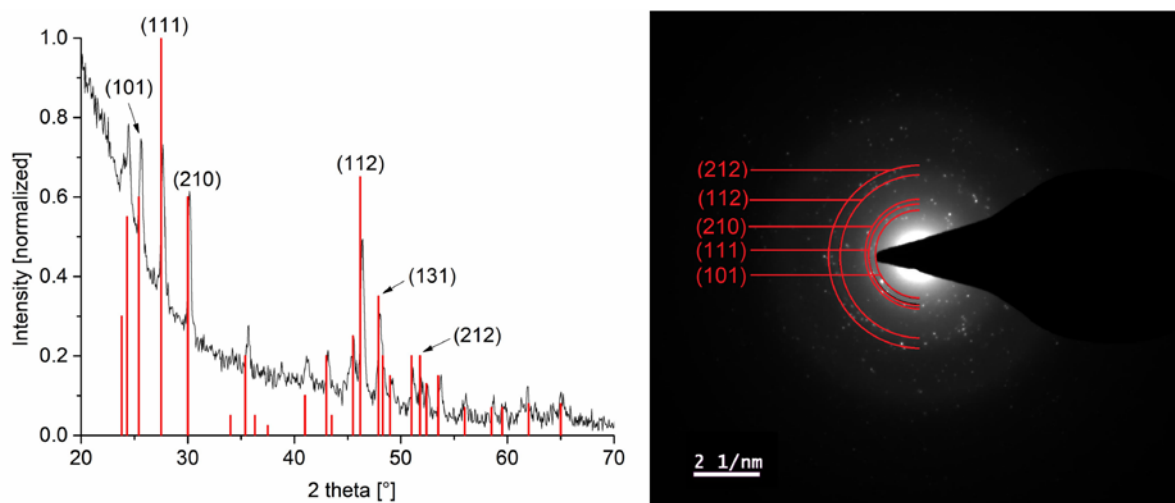


**Figure S5c:** Overview and HR-XPS of 1.0 wt %  $\text{EuF}_3$ -NPs in  $[\text{BMIm}][\text{BF}_4]$  from  $\text{Eu}(\text{dpm})_3$ . The red and green bars are a guide to the eye on the binding-energy axis.

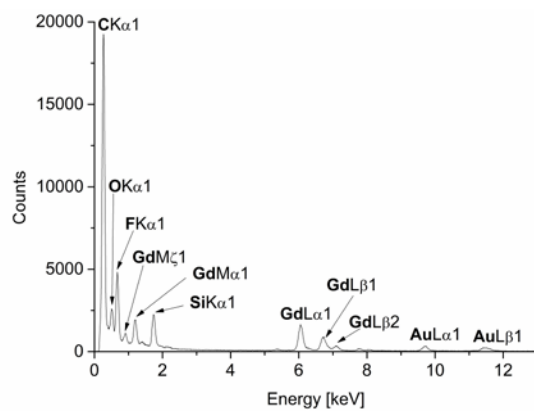
### GdF<sub>3</sub>-NPs in [BMIm][BF<sub>4</sub>]



**Figure S6a:** TEM images and particle size histogram of 1.0 wt % GdF<sub>3</sub>-NPs in [BMIm][BF<sub>4</sub>] from Gd(amd)<sub>3</sub>.

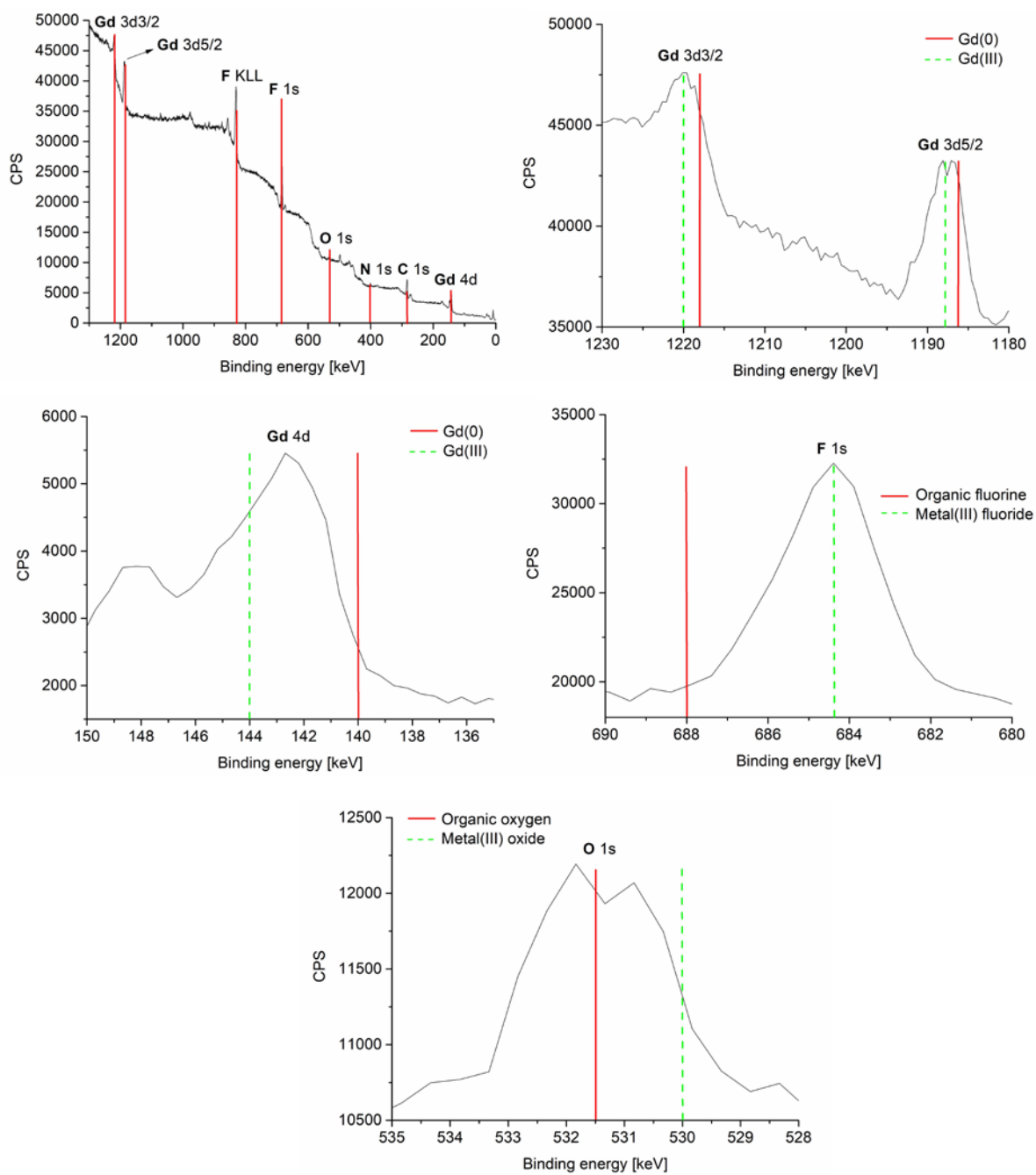


**Figure S6b:** PXRD and SAED (GdF<sub>3</sub> reference peaks in red from ICDD 0120788, orthorhombic with space group *Pnma*) of 1.0 wt % GdF<sub>3</sub>-NPs in [BMIm][BF<sub>4</sub>] from Gd(amd)<sub>3</sub>.



**Figure S6c:** EDX of 1.0 wt %  $GdF_3$ -NPs in [BMIm][ $BF_4$ ] from  $Gd(amd)_3$ .

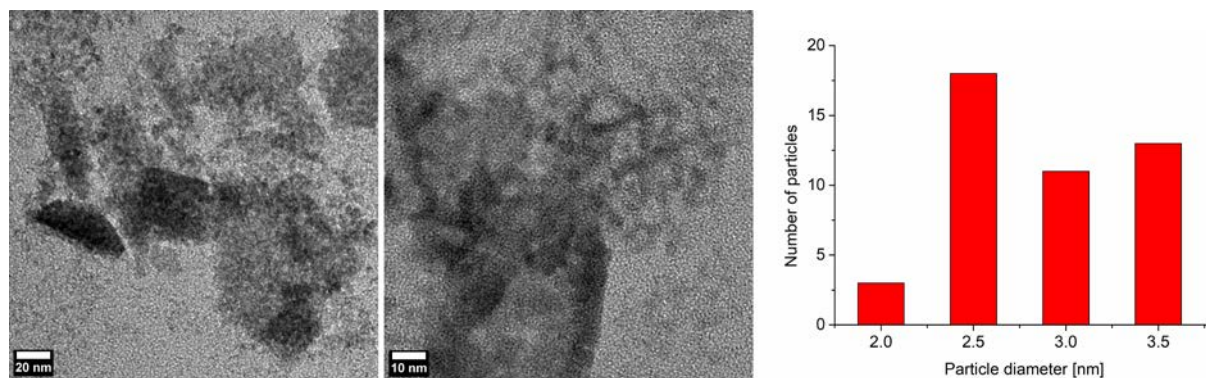




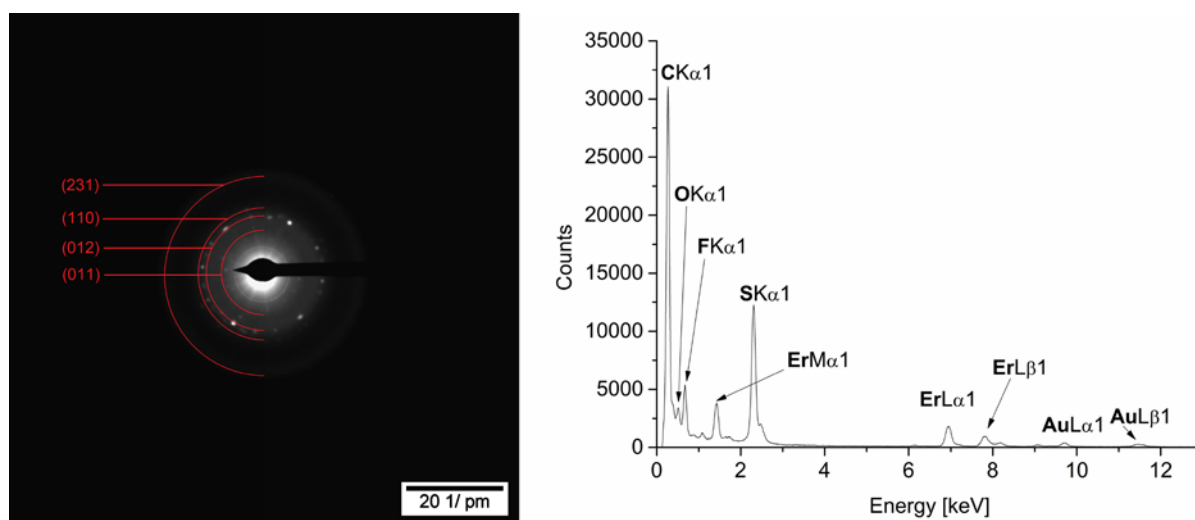
**Figure S6d:** Overview and HR-XPS of 1.0 wt %  $\text{GdF}_3$ -NPs in  $[\text{BMIm}][\text{BF}_4]$  from  $\text{Gd}(\text{amd})_3$ . The red and green bars are a guide to the eye on the binding-energy axis.

## TEM images, particle size histogram, SAED, EDX and XPS of Er-NPs in [BMIm][NTf<sub>2</sub>]

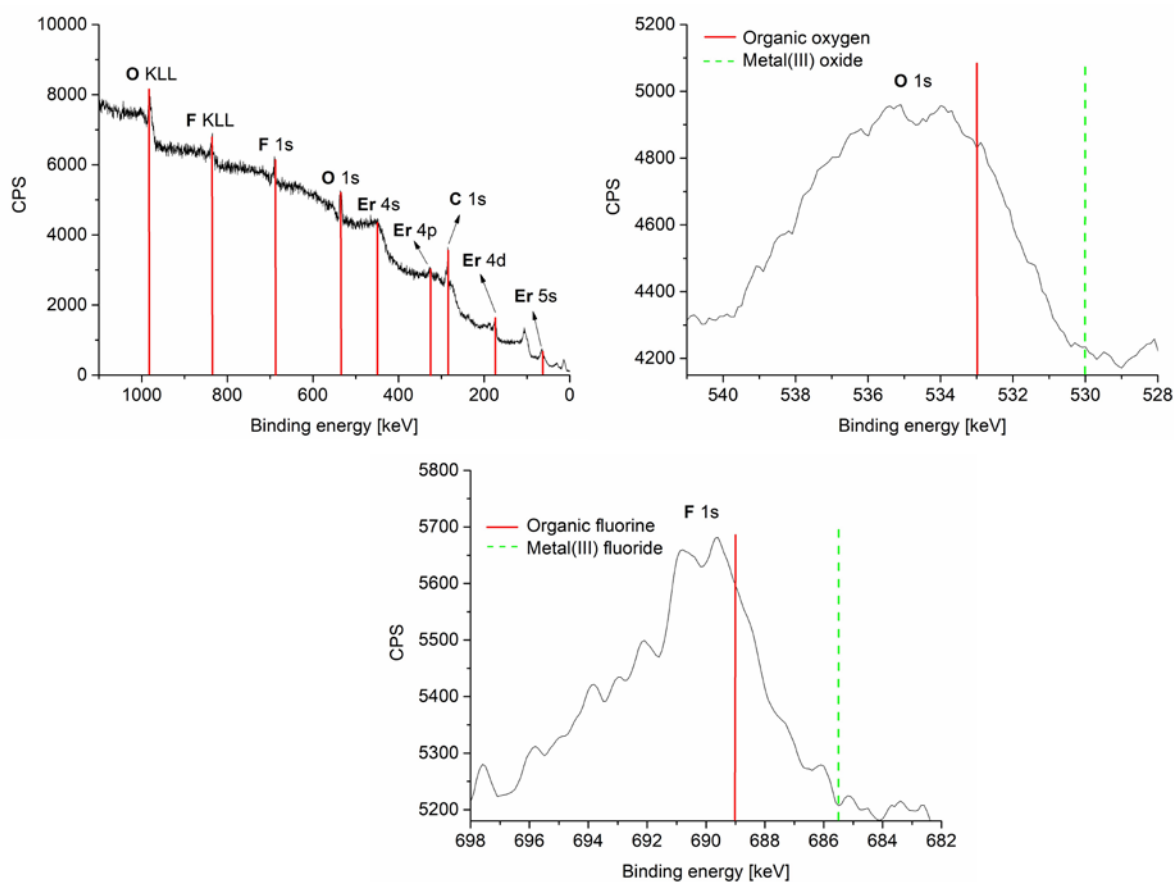
*Er-NPs in [BMIm][NTf<sub>2</sub>]*



**Figure S7a:** TEM images and particle size histogram of 1.0 wt % Er-NPs in [BMIm][NTf<sub>2</sub>] from Er(amd)<sub>3</sub>.



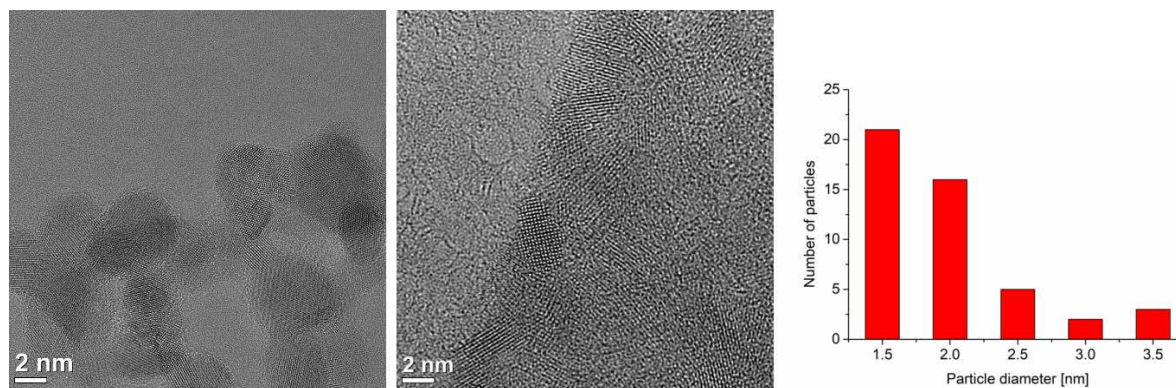
**Figure S7b:** SAED (Er reference peaks in red from COD 9008496, hexagonal with space group  $P6_3/mcm$ ) and EDX of 1.0 wt % Er-NPs in [BMIm][NTf<sub>2</sub>] from Er(amd)<sub>3</sub>.



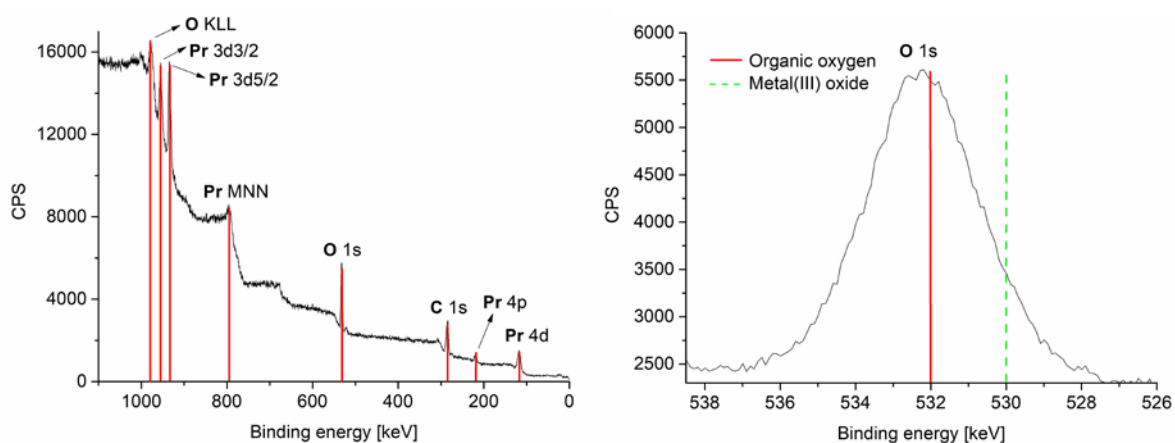
**Figure S7c:** Overview and HR-XPS of 1.0 wt % Er-NPs in [BMIm][NTf<sub>2</sub>] from Er(amd)<sub>3</sub>. The red and green bars are a guide to the eye on the binding-energy axis.

## TEM images, particle size histogram, SAED, EDX and XPS of RE-NPs in PC

### Pr-NPs in PC

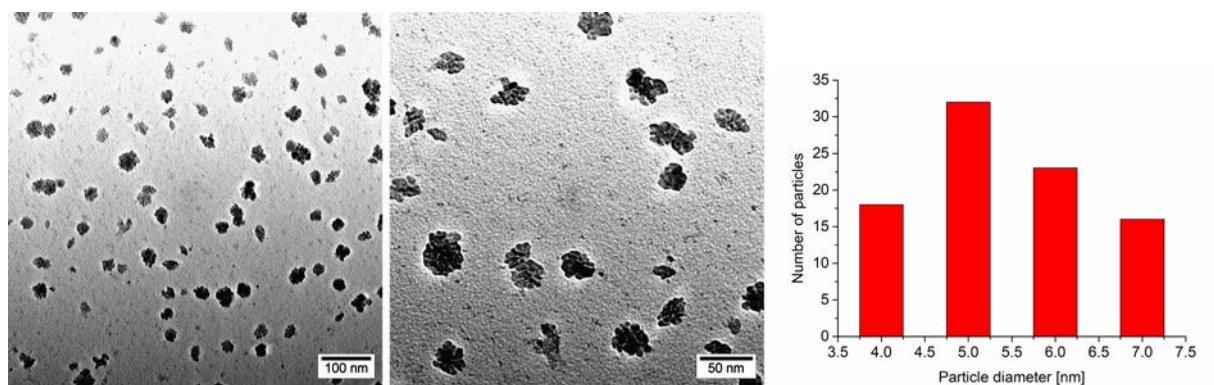


**Figure S8a:** TEM images and particle size histogram of 1.0 wt % Pr-NPs in PC from Pr(amd)<sub>3</sub>.

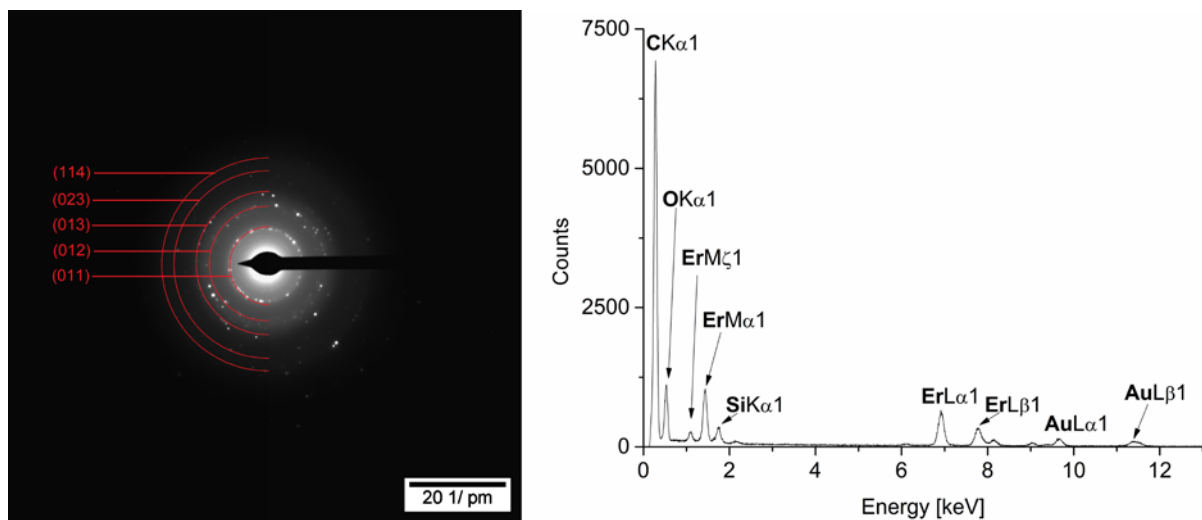


**Figure S8b:** Overview and HR-XPS of 1.0 wt % Pr-NPs in PC from Pr(amd)<sub>3</sub>. The red and green bars are a guide to the eye on the binding-energy axis.

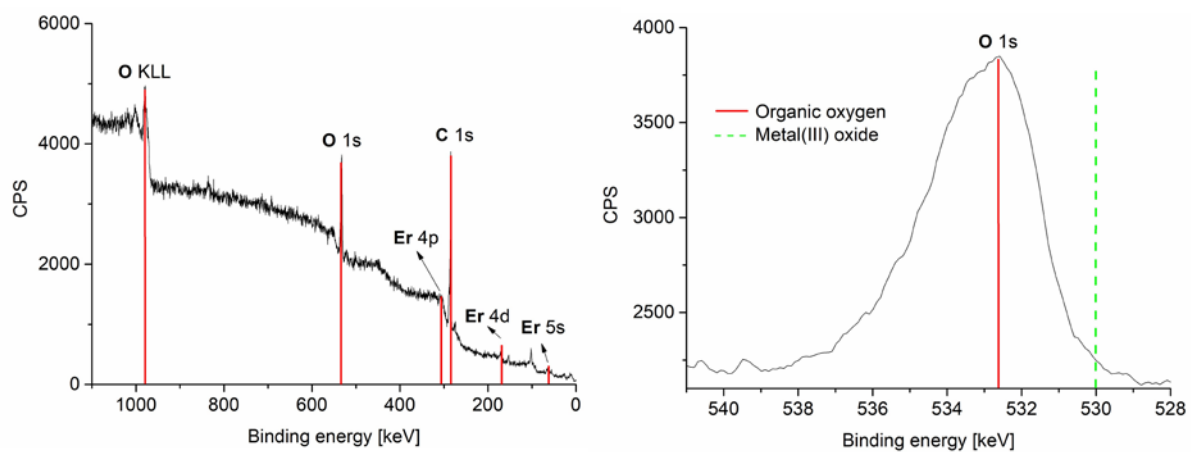
### Er-NPs in PC



**Figure S9a:** TEM images and particle size histogram of 1.0 wt % Er-NPs in PC from  $\text{Er}(\text{amd})_3$ .



**Figure S9b:** SAED (Er reference peaks in red from COD 9008496, hexagonal with space group  $P6_3/mcm$ ) and EDX of 1.0 wt % Er-NPs in PC from  $\text{Er}(\text{amd})_3$ .



**Figure S9c:** Overview and HR-XPS of 1.0 wt % Er-NPs in PC from  $\text{Er}(\text{amd})_3$ . The red and green bars are a guide to the eye on the binding-energy axis.