# Phase transfer of TiO<sub>2</sub> nanoparticles from water to ionic liquid triggered by phosphonic acid grafting

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## **Supporting Information**

### 1. Experimental procedure

#### 1.1. Materials

Four different phosphonic acids were purchased from Sikémia for this study: octylphosphonic acid (OPA), 1-methyl-3-(12-phosphonododecan)-imidazolium bromide (MImDPA), N,N,N-trimethyl-3-phosphonopropan-1-ammonium iodide (TMAmPPA) and N,N-Dimethyl-N-octadecyl-12-phosphonododecan-1-ammonium chloride (ODAmDPA).

The ionic liquid [Emim][NTf<sub>2</sub>], [Emim]Cl and lithium bis(trifluoromethanesulfonyl)-imide, L[iNTf<sub>2</sub>], were purchased from io-li-tec (Heilbronn, Germany) with a purity of 99 %.

The stable aqueous sol of TiO<sub>2</sub> nanoparticles in dilute nitric acid (LS101) (95% anatase, 5% brookite, solid content 23 wt %, pH < 1) was a gift from Lotus Synthesis. The sol was diluted to 1 wt% with ultrapure water before use. Based on the pH value (pH≈1.8) of the diluted sol, the concentration of NO<sub>3</sub><sup>-</sup> anions in the sol was ≈16 mM. The  $\xi$ -potential of these TiO<sub>2</sub> particles at pH 2 was 50 ± 11 mV.

#### 1.2. Methods

### Phase transfer (Figure 1)

The grafting/phase transfer experiments were performed in 10 mL glass bottles, using 2 mL of  $[\text{Emim}][\text{NTf}_2]$  and 2 mL of LS101 colloidal solution diluted to 1 wt% of TiO<sub>2</sub> particles.  $[\text{Emim}][\text{NTf}_2]$  was first introduced in the bottle, then the phosphonic acid (1.7mmol per g of TiO<sub>2</sub>), and finally 2 mL of the diluted sol were added under magnetic stirring. A reference sample was prepared similarly but without phosphonic acid. After stirring (1000 rpm) for 1 hour, the entire solution was transferred to a 5 mL hemolysis tube.

#### Isolation of dried grafted TiO<sub>2</sub> particles

For the solid-state NMR and EDX experiments the grafting/ phase transfer of the TiO<sub>2</sub> particles was performed as described above but using 10 mL of each phase. The grafted particles were isolated by centrifugation after washing with MeOH, then drying at 80 °C for 6 hours under vacuum.

#### Additional grafting and ion exchange experiments (Figure 3)

First, 2 mL of LS101 colloidal solution diluted to1 wt % was taken in a 5 mL hemolysis tube. Then TMAmPPA (1.7 mmol per g of  $TiO_2$ ) was added to the solution and stirred for 1 hour, leading to a

stable colloidal solution of TMAmPPA grafted TiO<sub>2</sub> (**a**). Then LiNTf<sub>2</sub> (3.4 mmol per g of TiO<sub>2</sub>) was added to 1mL of the resulting stable colloidal solution, stirred for 1 hour leading to the formation of the white precipitate (**b**). After that 1 mL of [Emim][NTf<sub>2</sub>] was added to (**b**) and stirred for 30 min affording a well dispersed sol in the ionic liquid phase (**c**).Then 1 mL of CHCl<sub>3</sub> was added to the biphasic solution (**c**) and the grafted TiO<sub>2</sub> particles were transferred to the upper water layer, where they formed a white precipitate (**d**). Finally  $\approx$ 500 µl of the TiO<sub>2</sub> containing water phase was diluted to 1 mL and then 1 g of [Emim]Cl was added to the solution and stirred. A lower [Emim][NTf<sub>2</sub>] phase formed and a stable colloidal sol of grafted TiO<sub>2</sub> particles was obtained in the water phase (**e**). All these steps are detailed in the flow chart below.



### 2. Dynamic light scattering of modified TiO<sub>2</sub> sols in [Emim][NTf<sub>2</sub>]

The average hydrodynamic diameter of the grafted  $TiO_2$  particles in [Emim][NTf<sub>2</sub>] sols was measured by Dynamic Light Scattering (DLS). DLS experiments were carried out on a standard setup (AMTEC goniometer with a BI9400 Brookhaven correlator) with a YAG solid laser (Cobolt Samba 150) operating at 532 nm, incident power 50 mW.

For the DLS experiments the concentration of the PA modified particles in ionic liquid was kept at 0.1 wt% and measurements were done at 20 °C. The viscosity of the pure ionic liquid is 35.5 mPa s at 20 °C.

Figure SI1 shows that the concentration fluctuations of  $TiO_2$  particles relax faster in [Emim][NTf<sub>2</sub>] when the particles are modified by TMAmPA than when they are modified by MImDPA. The correlation function of TMAmPA/TiO<sub>2</sub> was analyzed by cumulant analysis and leads to an average hydrodynamic diameter of 31 nm and a very low polydispersity. The correlation function of MImDPA shows two modes in the distribution of correlation times, which translates in size into a mode at 37nm and another one at 149nm. The intensity of the slow mode correspond to about 60% of the intensity of the rapid mode which suggest that if the second mode corresponds to large particles they should be in a very small amount. Distribution of hydrodynamic diameter analyzed by NNLS a presented in the second graph. The conclusion that can be drawn from DLS, is that  $TiO_2$  particles have a diameter of 30nm in both case but that MImDPA modified  $TiO_2$  particles slightly attract each other in [Emim][NTf<sub>2</sub>] while TMAmPA modified particles are more stable in [Emim][NTf<sub>2</sub>].



Figure SI1: Correlation functions for  $TiO_2/TMAmPPA$  (blue) and  $TiO_2/MImDPA$  (red) sols in  $[Emim][NTf_2]$ 



**Figure SI2:** Distribution of diameter for TiO<sub>2</sub>/TMAmPPA (blue) and TiO<sub>2</sub>/MImDPA (red) sols in [Emim][NTf<sub>2</sub>]. T=20°C; Viscosity η[EMim]NTF<sub>2</sub>=35.5 mPa.s (20 °C).

#### 3. NMR results

The liquid-state <sup>31</sup>P NMR measurements were performed in Bruker Spectrometer Avance 300 with permanent field strength of 7.4 T, using QNP probe and equipped with Avance I console.

Solid-state NMR measurements were performed using a Varian spectrometer VNMRS 600 with permanent field strength of 14.09 T. Varian  $T_3$  MAS probe was used with 3.2 mm ZrO<sub>2</sub> rotors. The spinning frequency was 20 kHz.

**Table SI1:** solution <sup>31</sup>P NMR chemical shifts of the starting phosphonic acids in MeOH (provided by Sikémia)

Phosphonic acid	<sup>31</sup> P chemical shift (ppm)
OPA	30.42
MImDPA	30.28
TMAmPPA	26.92
ODAmDPA	30.40

**Table SI2:** solid state <sup>31</sup>P MAS-NMR chemical shift data for the phosphonic acid-modified TiO<sub>2</sub> nanoparticles

Sample	peak 1	peak 2
TiO <sub>2</sub> /OPA	28.57	35.87
TiO <sub>2</sub> /MImDPA	28.57	35.87
TiO <sub>2</sub> /TMAmPPA	24.55	32.56
TiO <sub>2</sub> /ODAmDPA	28.91	36.39

**Table SI3:** <sup>19</sup>F MAS-NMR analysis data and calculated  $T_2$  values for <sup>19</sup>F nucleus. The dmfit software was used for peak fitting.

	Position	Width	T <sub>2</sub>	Peak Model	%
	(ppm)	(ppm)	(ms)		
TiO <sub>2</sub> /MImDPA	-79.16	0.20	2.87	"Gaus/Lor"	100
TiO <sub>2</sub> /TMAmPPA	-79.61	2.48	0.23	"Gaus/Lor"	100
	-78.47	1.77	0.32	"Gaus/Lor"	61.9
	-78.44	0.51	1.11	"Gaus/Lor"	38.1

The spectra of samples TiO<sub>2</sub>/MImDPA and TiO<sub>2</sub>/TMAmPPA could be fitted with single Gaussian. However to fit peak of the sample TiO<sub>2</sub>/ODAmDPA two different Gaussian/ Lorentzian combinations were needed. This suggests different modes of interaction of the <sup>19</sup>F nucleus with the positive charge of the ODAmDPA.

#### 4. Elemental analysis results

EDX measurements were performed with a FEI Quanta FEG 200 scanning electron microscope fitted with Silicon Drift Detector (SDD)-X-Max.

Sample	at%Ti	at%P	at%S	P/Ti	S/P	
TiO <sub>2</sub> /OPA	91.0	9.0	0	0.099	0	
TiO <sub>2</sub> /MImDPA	73.3	5.8	20.9	0.079	3.5	
TiO <sub>2</sub> /TMAmPPA	85.5	5.7	8.8	0.067	1.5	
TiO <sub>2</sub> /ODAmDPA	78.9	6.9	14.2	0.087	2.1	

Table SI4: Ti, P, and S atomic contents (normalized to 100 at %) determined by EDX analysis.

Taking into account the amount of phosphonic acid reacted (1.7 mmol/g TiO<sub>2</sub>), a quantitative grafting would lead to a P/Ti atomic ratio of  $\approx$ 0.14, and a complete exchange of halide or nitrate anions by NTf<sub>2</sub> anions would lead to an S/P ratio of 2. Considering the precision of EDX analysis on powders, the values reported in Table SI1 indicate significant grafting (>50%) and anion exchange (>75%).