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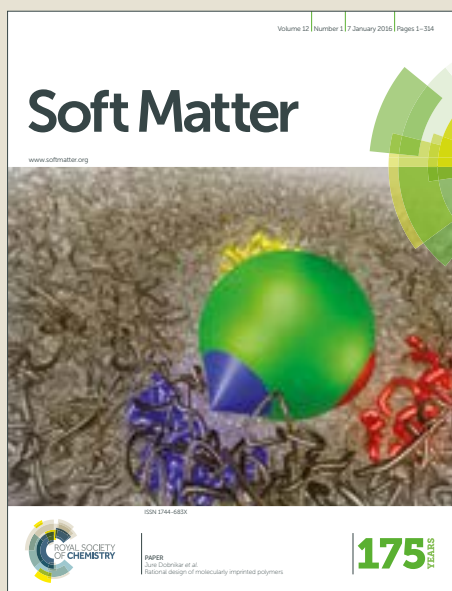
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Phase transfer of TiO₂ nanoparticles from water to ionic liquid triggered by phosphonic acid grafting

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Controlling the interface between TiO₂ nanocrystals and ionic liquids is of high fundamental and applied interest for energy storage and conversion devices. Phase transfer of nanoparticles from a synthesis medium to a processing or an application medium plays a significant role in nanotechnology. Here we demonstrate that surface modification with phosphonic acids bearing cationic end-groups can trigger the phase transfer of TiO₂ nanoparticles from an aqueous sol to a typical water-immiscible ionic liquid, [Emim][NTf₂]. The transfer involves both the grafting of the phosphonic acid moiety and the exchange of the counter ion of the cationic end-group by NTf₂ anions, as demonstrated by solid-state NMR, elemental analysis and independent grafting and ion exchange experiments. Furthermore, the colloidal stability of the TiO₂ sols in [Emim][NTf₂] strongly depends on the hydrophobic character of the cationic end-groups.

The capacity to transfer nanoparticles from their synthesis medium to a processing medium better suited to a specific application greatly widens the applicability of nanoparticles, and phase transfer protocols play a significant role in nanotechnology.¹ In particular, one-step phase transfers avoid the manipulation of dried nanoparticles, which can lead to irreversible aggregation or cause safety issues. Furthermore, phase transfer experiments and colloidal stability studies provide valuable insight on the interactions between the nanoparticles surfaces and their dispersion medium. Much attention was paid to the transfer of noble metal nanoparticles from an aqueous phase to a non-polar, non-miscible, organic solvent or the reverse.¹⁻³ In comparison, only very few studies have been reported dealing with the phase transfer of metal oxide nanoparticles.⁴⁻⁶ Recently, we described the phase transfer of TiO₂ nanoparticles from water to a non-polar solvent such as CH₂Cl₂ or toluene, based on the

surface modification of the TiO₂ nanoparticles with alkylphosphonic acids.⁷ Phosphonic acids appear ideally suited to phase transfer protocols from water to a solvent, as they are stable in aqueous medium and bind to a wide range of metal oxide substrates through strong M-O-P bonds.^{8-10,11}

Due to their outstanding properties such as low vapor pressure, non-flammability, high ionic conductivity and wide electrochemical window, ionic liquids (ILs) have found numerous applications ranging from environmentally friendly solvents for organic synthesis, catalysis, or extraction, to electrolytes for electrochemical devices such as batteries or fuel-cells.^{12, 13} ILs are also attracting increasing interest as synthesis and/or dispersion media of nanoparticles.^{14, 15}

Only a few publications described the transfer of noble metal nanoparticles from an aqueous phase to an IL phase¹⁶⁻¹⁸ or from an IL to an aqueous or organic phase.¹⁹ Nakashima et al. reported that water soluble CdTe nanocrystals covered with cationic thiol derivatives could be transferred into a hydrophobic ionic liquid.²⁰ The spontaneous transport of sulfate-treated polystyrene microparticles across water / IL interfaces has also been described.²¹ The transfer of metal oxide nanoparticles from aqueous sols to an ionic liquid sol has not been reported yet, although it would be of wide scientific and technological interest. Indeed, a broad range of oxide nanoparticles with controlled size and shape can be synthesized in aqueous medium,²²⁻²⁷ and stabilization by electrostatic repulsion allows for low-cost and easily scalable production of concentrated nanoparticle sols in water.

In this article we report that grafting TiO₂ nanoparticles with phosphonic acids bearing cationic end-groups can trigger the phase transfer from water to a typical water immiscible IL, 1-Ethyl-3-methylimidazolium bistriflimide [Emim][NTf₂]. We find that the transfer also involves the exchange of the counter-anions of the end-groups by NTf₂ anions. In addition, we show that the dispersion and colloidal stability of the grafted TiO₂ sols in [Emim][NTf₂] depends on the length of the alkyl groups linked to the cationic end-groups. TiO₂ nanoparticles are widely used in dye sensitized solar cells and batteries, and ionic liquids have been used to replace conventional

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electrolytes in these devices. Tuning the interactions of TiO₂ and ILs is therefore particularly important for fundamental and applied reasons.^{14, 28, 29}

We used a stable TiO₂ commercial sol (LS101 from Lotus Synthesis, 23 wt% of TiO₂) consisting of small aggregates (hydrodynamic radius 24 ± 3 nm) built of primary particles ca 5 nm in size according to DLS and SAXS characterization.³⁰ This sol is stabilized at low pH by electrostatic repulsion between the positively charged TiO₂ particles. For all experiments this sol was diluted to 1 wt% with ultrapure water. The phase transfer experiments were performed as described in the literature,⁷ but using [Emim][NTf₂] instead of chloroform or toluene.⁷ [Emim][NTf₂] has a density of 1.52 g/cm³ and forms the lower phase in the presence of water. Briefly, the phosphonic acid (0.17 mmol) was dissolved in 2 mL of IL, the resulting solution was added dropwise to 2 mL of the diluted TiO₂ sol in a 10 mL glass jar, then stirred (ca. 1000 rpm) for 1 h at 22 °C. For the photographs given below ca. 1 mL of the IL and aqueous phases were successively transferred with a pipet into a 5 mL hemolysis tube.

Table 1 Structure of the phosphonic acid compounds used.

Acronym	Structure
OPA	
MImDPA	
TMAmPPA	
ODAmDPA	

In the absence of phosphonic acid, no phase transfer of nanoparticles occurs, even after stirring for 24 hours the [Emim][NTf₂] phase remained clear. The hydrophilic TiO₂ nanoparticles remained well dispersed in the water phase, and showed no affinity for the IL phase (Figure 1, left). To trigger the phase transfer, we tested 4 different phosphonic acids (Table 1), bearing either a simple octyl group (OPA), or cationic groups with different structures: a methyl imidazolium end-group with a long dodecyl spacer (MImDPA), a trimethyl ammonium end-group with a short propyl spacer (TMAmPPA), and an octadecyldimethyl ammonium end-group with a dodecyl spacer (ODAmDPA). As shown in Figure 1, grafting with octylphosphonic acid (OPA) did not lead to the phase transfer of the nanoparticles but induced their aggregation in the aqueous phase: the IL phase remained clear and white flocs sedimented at the bottom of the aqueous phase. On the other hand, grafting with phosphonic acids bearing a cationic group led to a complete phase transfer of the nanoparticles to the IL phase, as shown by the clear water phase (Figure 1).

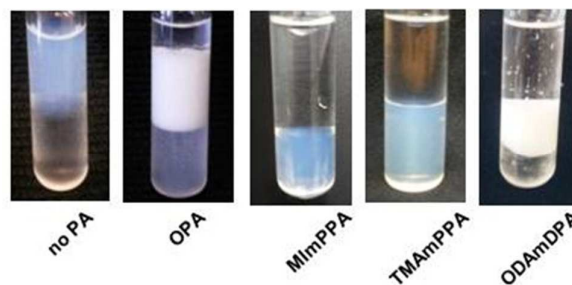


Fig. 1 Photographs of locations of TiO₂ nanoparticles in a water (upper phase)-[Emim][NTf₂] (lower phase) system in the presence of various phosphonic acids. "No PA" stands for "no phosphonic acid".

Grafting with MImDPA or TMAmDPA led to stable translucent sols of TiO₂ nanoparticles in [Emim][NTf₂]. DLS (Supporting Information (SI) Section 2) revealed that the hydrodynamic radius of the particles in the TMAmPPA-grafted TiO₂ sol was the same as in the aqueous sol (ca 17 nm), whereas the MImDPA-grafted particles formed aggregates with a very large size distribution (from 20nm to several microns). In the case of ODAmDPA, flocculation occurred in the IL phase.

The grafted nanoparticles were isolated by centrifugation and thoroughly washed with MeOH, which is a good solvent of the phosphonic acids and is miscible with [Emim][NTf₂]. After drying, the grafted nanoparticles were characterized by ³¹P and ¹⁹F MAS NMR and elemental analysis. ³¹P MAS NMR is a simple method for the study of phosphonic acid-grafted nanoparticles, allowing one to distinguish between grafted, physisorbed, and bulk metal phosphonate species.^{31, 32} However, this method gives no precise information on the bonding modes (monodentate, bidentate or tridentate) of grafted phosphonate species, contrary to ¹⁷O MAS NMR.¹¹ The ³¹P NMR spectra of the grafted TiO₂ particles (Fig. 2) displayed broad resonances in the 20 to 40 ppm range characteristic of phosphonate species grafted onto the nanoparticles surface through Ti-O-P bonds. There are no sharp peaks that would indicate the presence of unreacted phosphonic acid or of a titanium phosphonate phase.^{30, 32} In the case of the TiO₂/TMAmPPA sample, the resonances are shifted upfield by ca 3 ppm compared to the other samples due to the shorter propyl spacer between P and N atoms; indeed, the same trend is found for the starting phosphonic acids (SI Section 3, Tables SI1 and SI2). In addition, the low-field resonance at ca 36 ppm is more intense in the case of the TiO₂/ODAmDPA sample, indicating a different bonding mode or geometry, possibly related to the steric hindrance of the octadecyldimethylammonium end-group. The ¹⁹F MAS NMR spectra of the grafted TiO₂ particles showed an intense resonance at -79 ppm, showing that the counter ions of the imidazolium or ammonium cationic groups were NTf₂ anions, which have a high affinity for these cations.^{33, 34} The width of the ¹⁹F NMR resonances is related to the coulombic interaction of the NTf₂ anion with the cationic end-groups which reflects in the spin-spin relaxation time (*T*₂) (SI Section 3, Table SI3) of the ¹⁹F nucleus: the weaker the interaction, the larger the value of *T*₂ and the narrower the NMR resonances.

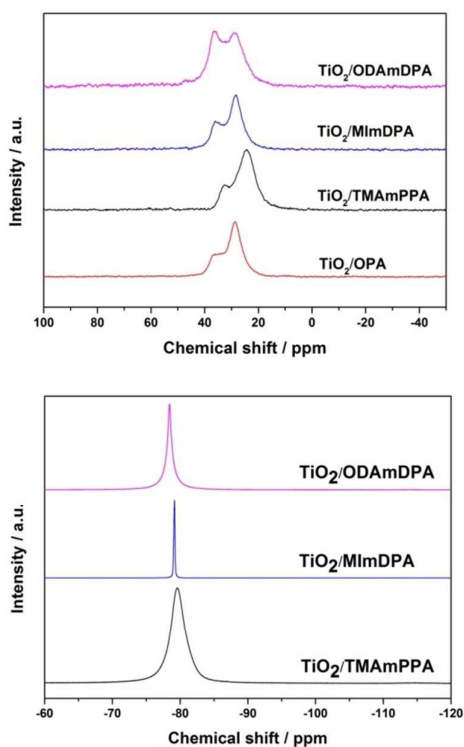


Fig. 2 ^{31}P (top) and ^{19}F (bottom) MAS NMR spectra of the TiO_2 nanoparticles grafted by the different phosphonic acids, after isolation by centrifugation, washing, and drying.

The positive charge in $\text{TiO}_2/\text{MImDPA}$ is delocalized over the imidazolium ring system and therefore less available for interaction with the NTf_2 anion, leading to the highest T_2 and narrowest resonance. For $\text{TiO}_2/\text{TMAmPPA}$ there is no delocalization of charge and steric hindrance of the alkyl groups surrounding the charge is also low, allowing strong coulombic interaction leading to the lowest T_2 thus to the broadest resonance, while in $\text{TiO}_2/\text{ODAmDPA}$ steric hindrance of the octadecyl group lowers the interaction leading to a resonance with an intermediate line broadening.

The P and S contents measured by EDX (Table S14) confirmed the significant grafting of phosphonic acids (>50%) and exchange of halide or nitrate anions by NTf_2 anions (>75%).

Bare TiO_2 nanoparticles are hydrophilic and, according to the literature, they can be better dispersed in a "hydrophilic" (i.e. water miscible) IL (e.g. $[\text{Emim}][\text{BF}_4]$) than in a "hydrophobic" (i.e. immiscible with water) IL such as $[\text{Emim}][\text{NTf}_2]$.²⁹ However, our results show that making the TiO_2 nanoparticles hydrophobic by grafting OPA does not trigger the transfer to the $[\text{Emim}][\text{NTf}_2]$ phase, but merely led to flocculation of nanoparticles in the aqueous phase, through hydrophobic interactions.³⁰ This result shows that transfer to IL is not simply a matter of hydrophobicity: particles can get unstable in water without showing any affinity for the water-immiscible IL phase. Phase transfer was only observed for phosphonic acids bearing a cationic group, independently of the nature of this group (imidazolium or ammonium), of the counter ion (Cl^- , Br^- , or I^-), or of the length of the spacer (propyl or dodecyl).

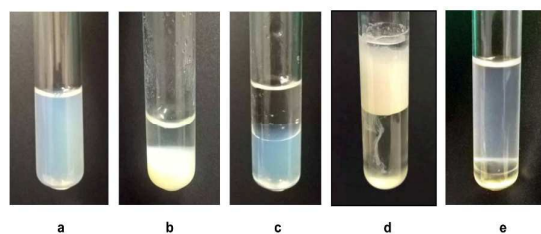


Fig. 3 Successive experiments illustrating the role of anion in the phase transfer and its reversibility. (a): Aqueous TiO_2 sol + TMAmPPA; (b): (a) + $\text{Li}[\text{NTf}_2]$; (c): (b) + $[\text{Emim}][\text{NTf}_2]$; (d): (c) + CHCl_3 ; (e): aqueous layer of (c) + $[\text{Emim}][\text{Cl}]$.

In addition, solid state NMR and elemental analysis suggest that the phase transfer involves not only the anchoring of the cationic groups but also the exchange of the starting halide counter-ions by NTf_2 ions. To confirm this hypothesis we performed a series of additional experiments (Figure 3, SI Section 1.2 flow chart).

In the first step, the particles in the aqueous sol were reacted with TMAmPPA for 1 h leading to a stable sol (Figure 3a), showing that as long as the counter anions have not been exchanged by NTf_2 anions the particles grafted by TMAmPPA were hydrophilic. When $\text{Li}[\text{NTf}_2]$ was added, the particles precipitated in the water phase (Figure 3b), indicating that after exchange of the counter anions of the trimethylammonium groups by NTf_2 anions the particles become hydrophobic. Upon addition of an $[\text{Emim}][\text{NTf}_2]$ phase and stirring, the grafted and ion-exchanged particles spontaneously transferred to the IL phase and redispersed, leading to a stable sol (Figure 3c). Interestingly, the particles can be transferred back to the aqueous phase by adding one volume of chloroform to the biphasic system (Figure 3d). Chloroform is miscible with the $[\text{Emim}][\text{NTf}_2]$ phase, its addition to the IL favors the formation of ion pairs and hinders the solvation of the nanoparticles by the IL,³ leading to phase transfer and to a precipitate in the water phase. Finally, upon addition of $[\text{Emim}][\text{Cl}]$ to the aqueous layer (Figure 3e), ion exchange leads to the formation of an $[\text{Emim}][\text{NTf}_2]$ lower phase and to TiO_2 particles functionalized by trimethylammonium groups with a chloride counter anion, which are hydrophilic and readily disperse in the water phase. These results evidence the importance of the counter anion on the transfer: before exchange by NTf_2 anions the ammonium-functionalized particles are hydrophilic and have thus no affinity for $[\text{Emim}][\text{NTf}_2]$, while after exchange they become hydrophobic³⁵ and compatible with the IL phase, which triggers the transfer to the IL phase. Similarly, Mevellec et al. reported the water to IL phase transfer of rhodium nanoparticles stabilized by a cationic surfactant based on the exchange of the chloride counter ions by $[\text{NTf}_2]$ anions using $\text{Li}[\text{NTf}_2]$.¹⁸

The dispersion of the nanoparticles in the $[\text{Emim}][\text{NTf}_2]$ phase strongly depends on the structure of the phosphonic acid compound. A well-dispersed sol was obtained in the case of TMAmPPA, which bears only short alkyl chains. It is well known that the miscibility between IL and alkanes is low and decreases as the alkyl chain length increases.³⁶ In our case, the

presence of long alkyl chains (dodecyl, octadecyl) as spacer or/and terminal group increases attractive van der Waals interactions between the nanoparticles, whereas the affinity toward the short chain [Emim][NTf₂] ionic liquid is not improved. As a result, aggregation (MImDPA) or flocculation (ODAmDPA) took place. In the case of MImDPA, attractive interactions between imidazolium rings could also account for the aggregation.

In summary, we have described an original method for the transfer of TiO₂ nanoparticles from water to [Emim][NTf₂] ionic liquid, involving surface functionalization with phosphonic acids bearing cationic groups and counter-anion exchange. Considering the range of inorganic materials (oxides, metals, but also phosphates, hydroxides, carbonates, sulfides, etc.) that can be grafted with phosphonic acids, this simple method can be generalized to the production of a wide variety of sols of inorganic particles in ionic liquids. The nanoparticles dispersion and sol stability are highly sensitive to the structure of the grafted phosphonic acids and provide valuable insights on the nanoparticles/IL interactions. In turn, control of these interactions by surface modification with appropriate phosphonic acids should allow to tune the structure of ionic-liquid-based materials, for applications for instance in separation,³⁶ catalysis,³⁷ solar cells, fuel cells and lithium-ion batteries.³⁸ In addition, the transfer of hydrophilic objects toward a water-immiscible ionic liquid phase may open new opportunities notably in extraction and separation technologies.

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Conflicts of interest

There are no conflicts to declare.

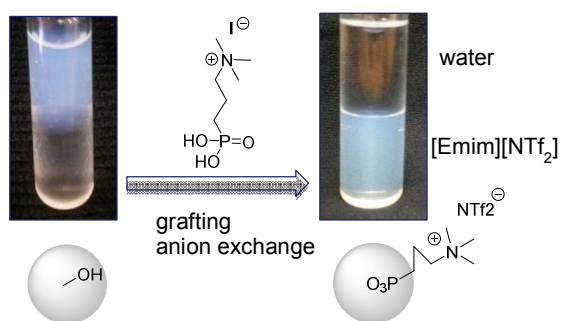
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Hydroxylated TiO_2 nanoparticles can be transferred from water to $[\text{Emim}][\text{NTf}_2]$ ionic liquid by reaction with a phosphonic acid bearing a cationic group; this phase transfer involves both grafting and anion exchange.