

Nanoparticles connected through an ionic liquid-like network

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Silica nanoparticles linked through ionic liquid-like molecules are synthesized by two routes. The first approach utilized a bis(trialkoxysilyl)-substituted imidazolium iodide to link the silica nanoparticles. In the second approach, the silica nanoparticles were first modified by 3-chloropropyltrimethoxysilane and *N*-(3-trimethoxysilylpropyl)imidazole and then coupled through nucleophilic substitution. A comparison of both approaches shows that the second approach results in a more efficient interfacing of nanoparticles.

Introduction

Materials chemistry made two important steps during the last decades with the introduction and development of nanoparticles^{1,2} on the one hand and ionic liquids on the other hand. Although the synthesis of nanoparticles is now well established, the three-dimensional interfacing and organization of nanoparticles remains a preparative challenge.^{3,4} For example, 2D arrays of nanoparticles on solid substrates are of wide interest to the physical and materials science communities because they have unique electronic, magnetic, or photonic properties.^{5,6} Nanoparticle arrays are produced using top-down methods such as e-beam lithography, scanning tunnelling microscopy, or imprint lithography.⁷ Alternative bottom-up methods are based on nanoparticle self-assembly.^{8,9} Because these methods do not require specialised instrumentation they are cheaper and potentially faster.

Ionic liquids, which are low temperature melting salts, are revolutionizing chemistry since their appearance and many syntheses were revisited due to the improved turnover or selectivity in ionic liquid media.^{10–13} Furthermore they are considered “green chemistry” media as they are non-volatile and, at the same time, enable low-temperature ionic chemistry (below 100 °C), thus saving energy.

The combination of properties of nanoparticles and ionic liquids has already been probed by some researchers. Most relevant publications report nanoparticle synthesis in ionic liquid media.^{14–23} Dupont *et al.* demonstrated the improved hydrogen storage properties of an imidazolium ionic liquid in the presence of Ir⁰ nanoparticle catalysts.²⁴ The excellent synergistic effect between metal and ionic liquids²⁵ was applied to palladium nanoparticles, an ionic liquid and a molecular sieve in order significantly enhance the activity, selectivity and durability of olefin hydrogenation.²⁶ Moreover Antonietti *et al.* recently reviewed the remarkable potential of ionic liquids in material synthesis.²⁷

A few articles go a step further, modifying the nanoparticles by ionic liquid-like molecules.²⁸ For example, the ionic liquid 1-methyl-3-(2'-mercaptoacetoxyethyl)imidazolium chloride was used to stabilize palladium nanowires.²⁹ Equivalent thiol-

functionalized ionic liquids were also used to synthesize gold and platinum nanoparticles.³⁰

More than simply using ionic liquids and nanoparticles simultaneously, the work described in this paper demonstrates, to the best of our knowledge, for the first time a way to interface nanoparticles through linking by an ionic liquid-like network.

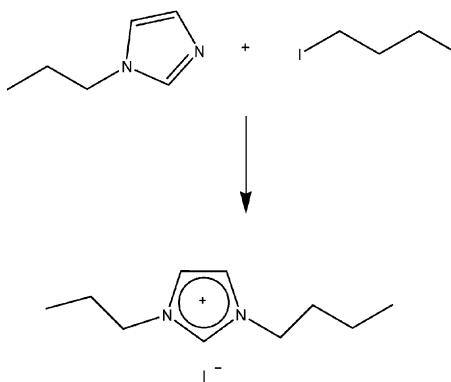
The synthesis method used is based in part on the nucleophilic substitution taking place during the synthesis of imidazolium-based ionic liquids that occurs quantitatively, even without solvent, at room temperature (Scheme 1).³¹

This is combined with known methods for the functionalization of nanoparticles. In the preliminary experiments reported in this paper, silica nanoparticles were chosen due to their easily controllable size thanks to good control of the synthesis parameters;³² furthermore silica nanoparticles are easily modified by functionalized trialkoxysilanes.²⁸ This work has proof-of-principle character and the general concept can be extended to other kinds of nanoparticles.

Experimental

1. Chemicals

All the starting materials were reagent grade and used as purchased. Tetraethoxysilane (TEOS) was purchased from Fluka, chloropropyltrimethoxysilane from ABCR and sodium iodide, imidazole and methanol were obtained from Aldrich.



Scheme 1 Synthesis of 1-propyl-3-butylimidazolium iodide.

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2. Measurements

Nuclear magnetic resonance (NMR). Solution NMR spectra were recorded on a Bruker Avance 300 (^1H at 300.13 MHz) equipped with a 5 mm inverse-broadband probe head with a z-gradient unit. Solid state NMR spectra were recorded on a Bruker DPX 300 (^{13}C at 75.40 MHz, ^{29}Si at 59.65 MHz) equipped with a 4 mm broadband MAS probe head. ^{13}C and ^{29}Si spectra were recorded with ramped CP MAS spectra (cross polarization and magic angle spinning).

Diffraction light scattering (DLS) measurements. For the measurement the solid was dissolved in ethanol. The DLS experiments were carried out without previous sonication of the samples. The run time of the measurements was 10 s. Every size distribution curve was obtained by averaging 10 measurements.

The apparatus was an ALV/CGS-3 compact goniometer system, equipped with ALV/LSE-5003 light scattering electronics and multiple τ digital correlator, and a 632.8 nm JDSU laser 1145P.

Transmission electron microscopy (TEM) measurements. Samples for transmission electron microscopy measurements were prepared by dispersing the particles in ethanol prior to deposition on a carbon coated TEM Cu grid. TEM measurements were performed on a 200 kV TECNAI F20-S-TWIN apparatus with field emission source or a JEOL JEM-100CX (USTEM, Vienna University of Technology).

Thermogravimetric analysis (TGA). The analyses were carried out with a Shimadzu TGA-50 at heating rates of $5\text{ }^\circ\text{C min}^{-1}$ under air.

3. Synthesis

Synthesis of silica nanoparticles. In a 250 mL round bottom flask, 60 μL (10 mmol) ammonia solution (32%) and 1.98 g (110 mmol) water are added to 100 mL absolute methanol. The solution is stirred for 5 min before adding dropwise 10.41 g (500 mmol) TEOS. The final solution is stirred for three days at ambient temperature.

Synthesis of 3-iodopropyltrimethoxysilane. The synthesis is carried out under argon atmosphere. Sodium iodide (36.9 g, 0.246 mol) is dissolved in 150 mL absolute acetone. 3-Chloropropyltrimethoxysilane (48.9 g, 0.246 mol) is added dropwise under stirring. The mixture is heated under stirring overnight. The precipitate, sodium chloride, is filtered off under argon atmosphere. Then the product is distilled at $80\text{ }^\circ\text{C}$ under vacuum (3 mbar). The resulting 3-iodopropyltrimethoxysilane is a yellowish liquid.

^1H NMR (250 MHz, CDCl_3): δ (ppm) 3.52 (s, 9H, $\text{Si(OCH}_3)_3$); 3.15 (t, 2H, I- CH_2 -); 1.89 (q, 2H, I- $\text{CH}_2\text{-CH}_2\text{-CH}_2$ -); 0.69 (t, 2H, - $\text{CH}_2\text{-Si}$).

Synthesis of *N*-(3-propyltrimethoxysilane)imidazole. The synthesis is carried out under argon atmosphere. Sodium hydride (2.9 g, 0.120 mol) is dissolved in 150 mL absolute THF, the mixture is cooled to around $0\text{ }^\circ\text{C}$ with an ice bath. Imidazole (8.2 g, 0.120 mol) is added dropwise under stirring. After addition, the

ice bath is removed and the mixture is maintained under stirring until no more gas is evacuated (H_2). Then 26.12 g (0.090 mol) of 3-iodopropyltrimethoxysilane are added and the mixture is maintained at reflux overnight. The orange suspension is filtered off and the solvent evacuated. By addition of 150 mL dry dichloromethane a precipitate appears and is filtered off under argon atmosphere. The product is then separated by distillation at $150\text{ }^\circ\text{C}$ under vacuum (1 mbar). *N*-(3-Propyltrimethoxysilane)imidazole is a transparent liquid.

^1H NMR (250 MHz, CDCl_3): δ (ppm) 7.54 (s, 1H, - N-CH-N=); 7.01 (s, 1H, - N-CH-CH-N=); 6.88 (s, 1H, - N-CH-CH-N=); 3.88 (t, 2H, = $\text{N-CH}_2\text{-CH}_2$ -); 3.53 (s, 9H, $\text{Si(OCH}_3)_3$); 1.83 (q, 2H, = $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$); 0.54 (t, 2H, - $\text{CH}_2\text{-Si}$).

^{13}C NMR (250 MHz, CDCl_3): δ (ppm) 136.8 (s, 1C, - N-CH-N=); 128.1 (s, 1C, - N-CH-CH-N=); 120.7 (s, 1C, - N-CH-CH-N=); 56.2 (s, 3C, $\text{Si(OCH}_3)_3$); 55.7 (s, 1C, = $\text{N-CH}_2\text{-CH}_2$ -); 25.1 (s, 1C, = $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$); 7.4 (s, 1C, - $\text{CH}_2\text{-Si}$).

Synthesis of 1,3-di(3-propyltrimethoxysilane)imidazolium iodide. The synthesis is carried out under argon atmosphere. On 1.01 g (4.37 mmol) *N*-(3-propyltrimethoxysilane)imidazole are dropped 1.39 g (4.8 mmol) of 3-iodopropyltrimethoxysilane. The mixture is maintained at $110\text{ }^\circ\text{C}$ overnight. The product is washed with dried toluene. 1,3-Di(3-propyltrimethoxysilane)imidazolium iodide is a viscous yellow liquid.

^1H NMR (250 MHz, CDCl_3): δ (ppm) 10.11 (s, 1H, - N-CH-N=); 7.39 (s, 2H, - N-CH-CH-N=); 4.35 (t, 4H, - $\text{CH}_2\text{-N-CH-CH-N-CH}_2$); 3.56 (s, 18H, $(\text{OCH}_3)_3\text{Si-}-\text{Si(OCH}_3)_3$); 2.00 (q, 4H, - $\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$); 0.63 (t, 4H, $\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$).

^{13}C NMR (250 MHz, CDCl_3): δ (ppm) 136.5 (s, 1C, - N-CH-N=); 121.9 (s, 2C, - N-CH-CH-N=); 51.7 (s, 2C, - $\text{CH}_2\text{-N-CH-CH-N-CH}_2$); 50.7 (s, 6C, $(\text{OCH}_3)_3\text{Si-}-\text{Si(OCH}_3)_3$); 24.1 (s, 2C, $\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-N-CH}_2\text{-N-CH}_2\text{-CH}_2\text{-CH}_2\text{-Si}$); 5.9 (s, 2C, $\text{Si-CH}_2\text{-CH}_2\text{-Si}$).

Synthesis of chloropropyltrimethoxysilane modified silica nanoparticles. 16 mL of the previously prepared silica nanoparticles suspension are transferred into a Schlenk tube and degassed in vacuum several minutes to remove excessive ammonia. Then 1.42 g (7.147 mmol) 3-chloropropyltrimethoxysilane are added dropwise. The solution is stirred under argon, at room temperature overnight.

Synthesis of *N*-propylimidazole modified nanoparticles. 16 mL of the previously prepared silica nanoparticles suspension are transferred into a Schlenk tube and degassed in vacuum several minutes to remove excessive ammonia. 1.65 g (7.147 mmol) *N*-(3-propyltrimethoxysilane)imidazole are added dropwise. The solution is stirred under argon, at room temperature overnight.

Grafting of 1,3-di(3-propyltrimethoxysilane)imidazolium iodide on silica nanoparticles. This synthesis is carried out under argon. 1.5 mL of the silica nanoparticles suspension are precipitated with n-hexane and extracted through centrifugation (twice at 6000 rpm) before being re-dissolved in 2 mL dichloromethane. This 2 mL silica nanoparticles suspension is added to 0.654 g (1.26 mmol) of previously synthesized 1,3-di(3-propyltrimethoxysilane)imidazolium iodide dissolved in 7 mL freshly distilled

dichloromethane. Dichloromethane (5 mL) and 3 drops of hydrochloric acid (37%) are then added to the preceding solution. After three days of stirring, the suspension is centrifuged and the yellow solid is washed several times with dichloromethane before drying under vacuum (3 mbar).

Nucleophilic substitution between chloropropyl modified silica nanoparticles and *N*-propylimidazole modified nanoparticles. The synthesis is carried out under argon atmosphere. 5 mL suspension of silica nanoparticles modified with *N*-(3-propyltrimethoxysilane)imidazole and 5 mL suspension of silica nanoparticles modified with 3-chloropropyltrimethoxysilane are introduced into a 50 mL round bottom flask. An additional 10 mL of dry methanol are added. The solution is stirred over 2 days and finally dried under vacuum (3 mbar). A white powder is obtained.

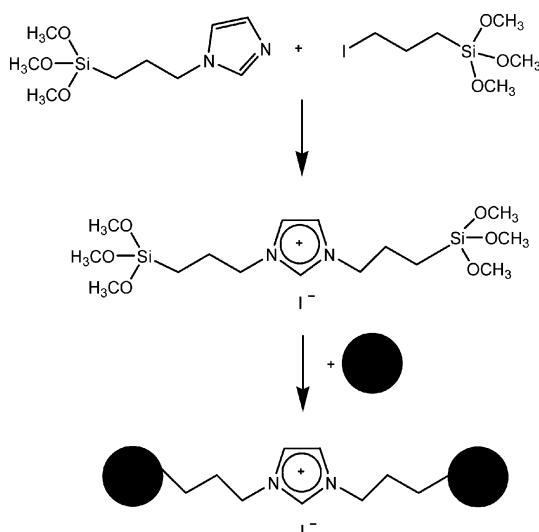
Results and discussion

We investigated two different strategies. The first is a synthesis route in which the nanoparticles were grown starting from a pre-formed trialkoxysilyl-substituted, imidazole-based ionic liquid (Scheme 2). In the second strategy the nanoparticles were first modified and afterwards connected by ionic liquid-like linkers (Scheme 3).

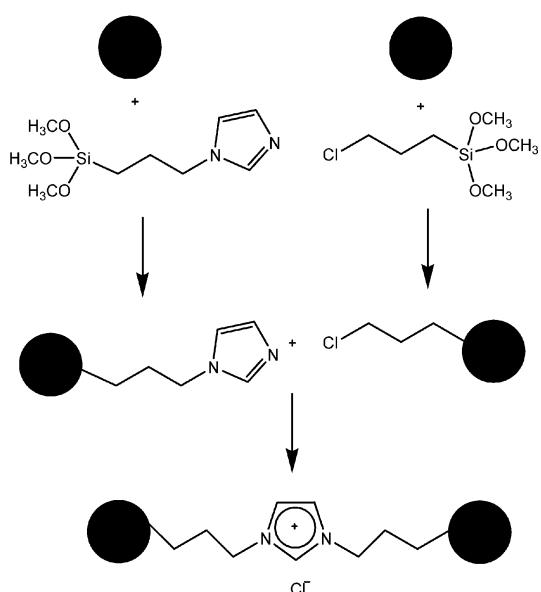
The starting compounds for both approaches were 3-chloropropyltrimethoxysilane and *N*-(3-trimethoxysilylpropyl)imidazole³³ in combination with Stöber silica nanoparticles.³² The silica nanoparticles have an average radius of 10 nm, confirmed by differential light scattering (DLS) (Fig. 1).

Strategy 1

For strategy 1, the two trialkoxysilanes are first reacted together to obtain an alkoxy-silyl-modified imidazolium halogenide, *viz.* 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide. The synthesis is carried out in the same way as the nucleophilic substitution taking place in the synthesis of the corresponding ionic liquid 1,3-*N,N*-dipropylimidazolium iodide.³⁴ This synthesis requires



Scheme 2 Strategy 1: synthesis of bis-functionalized imidazolium groups, followed by nanoparticle formation.



Scheme 3 Strategy 2: synthesis of functionalized nanoparticles that react with each other.

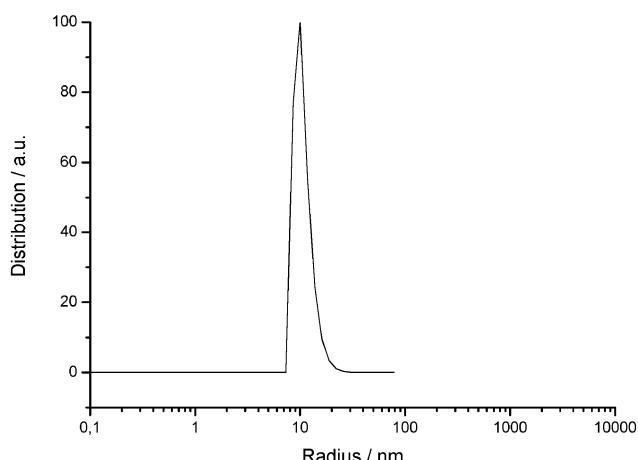


Fig. 1 DLS measurement of the starting SiO_2 nanoparticles.

no solvent and leads to 100% yield. The product was characterized by NMR spectroscopy. The ¹H NMR spectrum is reported in Fig. 2 with the respective proton chemical shifts assignments.

This imidazolium linked bis(trialkoxysilane) was used to modify the silica nanoparticles synthesized by a Stöber sol-gel process^{32,35} in a subsequent step. The purpose of this reaction was to anchor the imidazolium modified trialkoxysilanes on the silica nanoparticles by condensation reaction. This was carried out by mixing, under argon, the pre-formed silica nanoparticles with 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide in methanol, before adding a catalytic amount of an aqueous solution of ammonia.

When heated, the obtained white powder does not decompose below 300 °C. In TGA, the first step, up to 70 °C, corresponds to water desorption, and the small step from 70 °C to 170 °C to silica dehydration (Fig. 3). The second step corresponds to the degradation of the organic part, at 300 °C. Thermal stability of

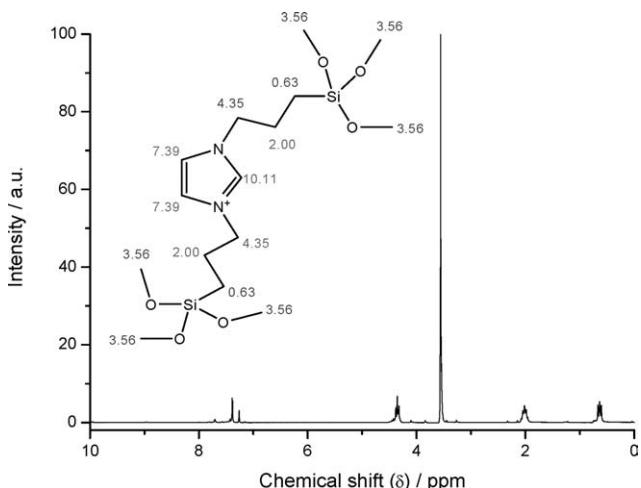


Fig. 2 ^1H NMR spectrum of 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide; (insert) chemical shift identifications of the protons.

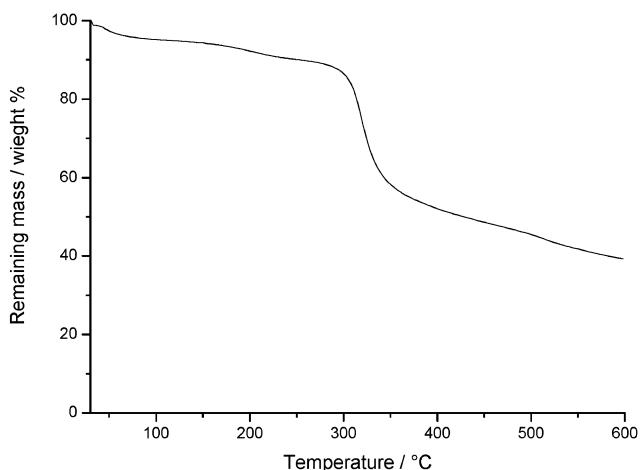


Fig. 3 TGA of SiO_2 nanoparticles linked by 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide (strategy 1).

a compound with organic groups until 300 °C is very remarkable and indicates that the obtained hybrid organic–inorganic material possesses a thermal stability comparable to that of dialkyimidazolium halogenide ionic liquids, reported at around 300 °C.^{36,37} If the dialkyimidazolium link in the obtained materials was not intact after condensation onto the silica nanoparticles, degradation would occur below 300 °C.

In the CP MAS ^{13}C NMR spectrum of the resulting powder (Fig. 4), the characteristic peaks of the 1,3-dipropylimidazolium link are still observed. At 133 and 120 ppm are the signals from the three imidazolium ring carbon atoms. The broad signal at 45 ppm corresponds to the very few methyl groups that remain in the product but mainly corresponds to residual methanol used as solvent. This peak area, as the spectrum is recorded with the cross-polarisation method, is largely over-evaluated. The reason for this over-evaluation of the concerned carbon atoms is that they are surrounded by many more hydrogen atoms than the other carbon atoms of the molecule. The three remaining signals between 5 ppm and 18 ppm correspond to the carbon atoms of the alkyl chain between the nitrogen and the silicon atoms.

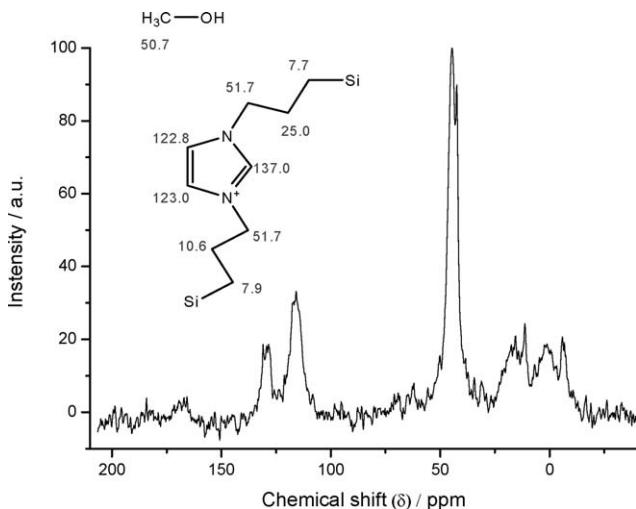


Fig. 4 CP MAS ^{13}C NMR spectrum of SiO_2 nanoparticles linked by means of 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide (strategy 1); (insert) chemical shift identifications of the carbons.

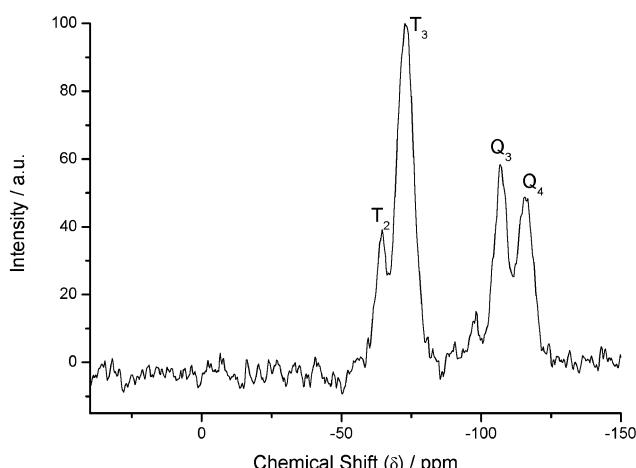


Fig. 5 CP MAS ^{29}Si NMR spectrum of SiO_2 nanoparticles linked by 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide (strategy 1).

Both TGA results and the CP MAS ^{13}C NMR spectrum of the product are consistent with the concept that the dialkyimidazolium link is retained in the resulting hybrid material after the condensation reaction of the trialkoxysilane groups.

NMR characterization of the product was completed by CP MAS ^{29}Si NMR (Fig. 5) in which two regions have to be distinguished. One is located between –100 and –120 ppm corresponding to Q_i units originating from the silica nanoparticles (Q_2 , Q_3 and Q_4 located at –97, –106 and –116 ppm respectively). The second region, between –50 and –80 ppm, corresponds to the T_n units, originating from the 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide precursor (T_2 and T_3 situated at –64 and –72 ppm respectively). Considering that this spectrum was registered by a cross-polarization experiment, T_2 units are overestimated in comparison with T_3 units, we can conclude that the T units are well condensed, *i.e.* that the modified precursor was condensed to the surface of the silica nanoparticles. This conclusion confirms that the peak at 45 ppm in Fig. 4 thus corresponds to residual methanol in the product.

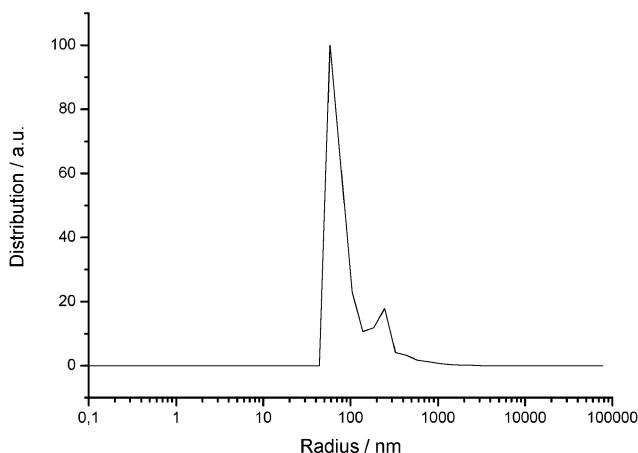


Fig. 6 DLS measurement of SiO_2 nanoparticles linked by using 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide (strategy 1).

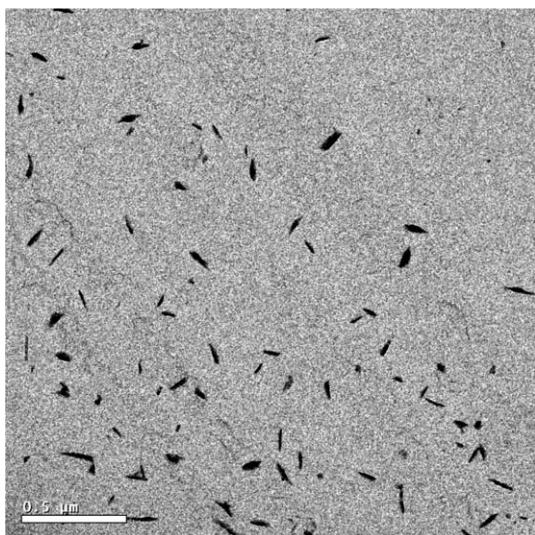


Fig. 7 TEM micrograph of SiO_2 nanoparticles linked by 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide (strategy 1).

The obtained powder was dispersed in ethanol to be investigated by DLS. The curve shown in Fig. 6 is the average of ten measurements each measurement being recorded over 10 s. This method is based on the assumption of spherical entities. For this reason the conclusions drawn by this characterization are limited to the “non-observation” of a diffraction peak around 10 nm, the size of the starting silica nanoparticles (Fig. 1), indicating that all starting silica nanoparticles did react.

Linking of the nanoparticles through the ionic liquid-like bond was confirmed by TEM, by observation of “islands” instead of the single 10 nm diameter silica nanoparticles (Fig. 7).

The “islands” have a maximum size of around 100 nm (Fig. 8), meaning that not more than 10 nanoparticles were linked to each other. The islands, *i.e.* the linked nanoparticles, are predominantly linear and with an average length of around 70 nm.

Strategy 2

Pre-formed silica nanoparticles, with an average radius of 10 nm (Fig. 1), were functionalized with either *N*-propylimidazole

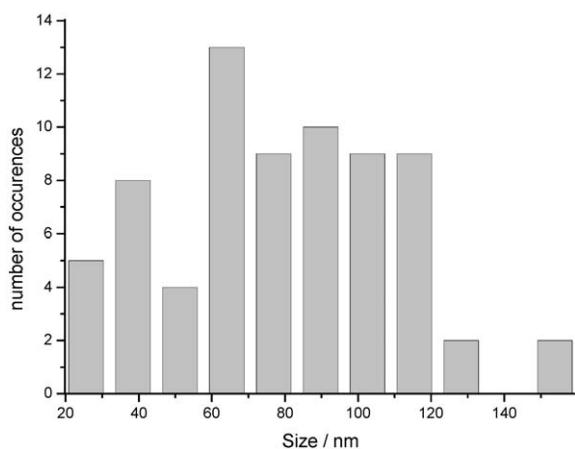


Fig. 8 Bar chart of SiO_2 nanoparticles linked by 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide (strategy 1) evaluated from four different TEM pictures.

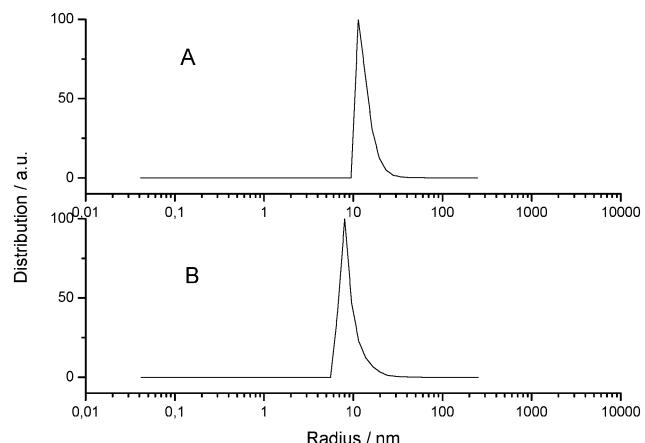


Fig. 9 DLS measurements of SiO_2 nanoparticles modified with *N*-propylimidazole trimethoxysilane (A) and SiO_2 nanoparticles modified with chloropropyltrimethoxysilane (B).

trimethoxysilane or chloropropyltrimethoxysilane. The obtained modified nanoparticles have still an average radius of around 10 nm (Fig. 9).

The modified nanoparticles were then reacted with each other through the nucleophilic substitution occurring normally between chloroalkyl and imidazole groups present on the ligands. Reactions were carried out in methanol, the two nanoparticle dispersions being mixed in a molar ratio between the chloride and the imidazole of 1 : 1.

As for strategy 1, the DLS analysis (Fig. 10) is used only to visualize that the spherical functionalized silica nanoparticles did react, as no peak corresponding to the initial 10 nm nanoparticles remains. No conclusion on the size of the nanohybrid material can be drawn from this curve as DLS is suitable only for spherical entities.

The thermal stability of the starting modified nanoparticles and that of the final product (Fig. 11) show a small weight loss below 100 °C, corresponding to water desorption, and a loss step between 100 and 200 °C that corresponds to the silica dehydration. The silica nanoparticles modified with chloropropyl

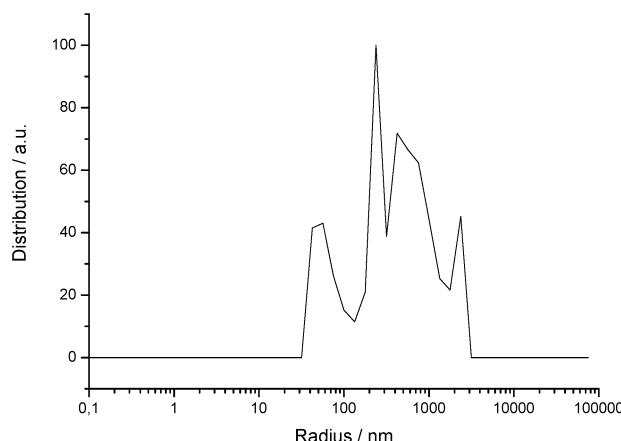


Fig. 10 DLS measurement of the dispersion obtained by reaction of chloropropyl-modified nanoparticles and propylimidazole-modified nanoparticles.

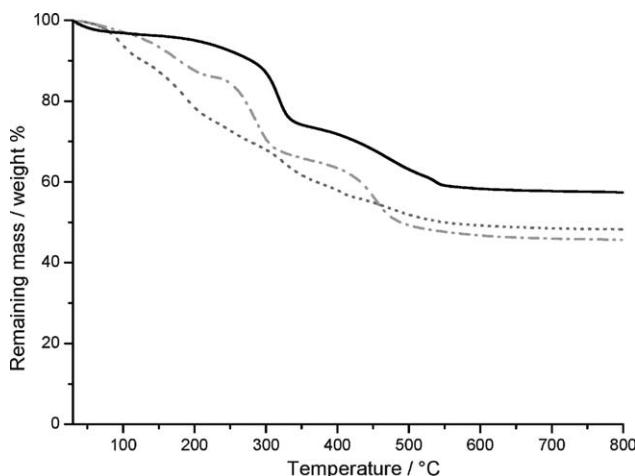


Fig. 11 TGA analysis. Dotted line: silica nanoparticles modified with chloropropyl ligands; dashed-dotted line: silica nanoparticles modified with propylimidazole ligands; solid line: product of the reaction between chloropropyl modified nanoparticles and propylimidazole modified nanoparticles.

ligands start to decompose around 120 °C by degradation of the organic ligand (dotted line in Fig. 11). The silica nanoparticles modified by propylimidazole ligands are more stable, and start to degrade around 250 °C (dashed-dotted line in Fig. 11).

The thermal stability profile of the compound, resulting from linking of the two types of modified silica nanoparticles (Scheme 3), shows a mass change occurring around 300 °C (solid line in Fig. 11). The thermal stability of the resulting compound is much higher than that of the starting modified silica nanoparticles. A characteristic of ionic liquid molecules is to have a higher thermal stability than the corresponding organic groups used for their formation. Thus the high thermal stability of the final material is a clear proof that the halogenide dialkylimidazolium link is formed. Thermal degradation of the organic part of the resulting linked nanoparticles takes place from 300 °C to 500 °C. Above 500 °C, only silica remains, corresponding to around 58 wt% of the material.

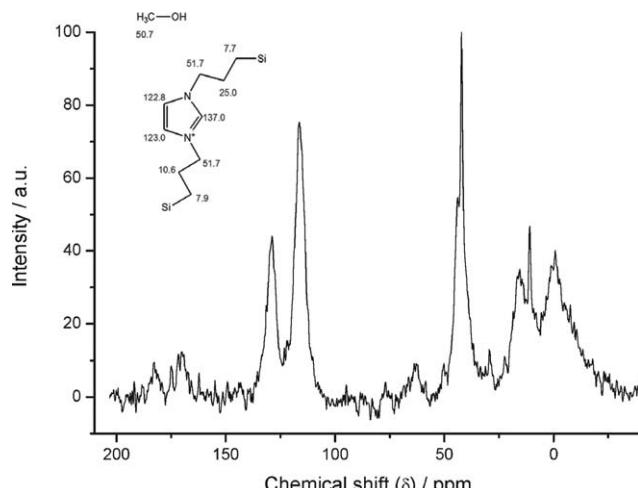


Fig. 12 CP MAS ^{13}C NMR spectrum of SiO_2 nanoparticles linked by means of 1,3-di(3-trimethoxysilylpropyl)imidazolium chloride (strategy 2); (insert) chemical shift identifications of the carbons.

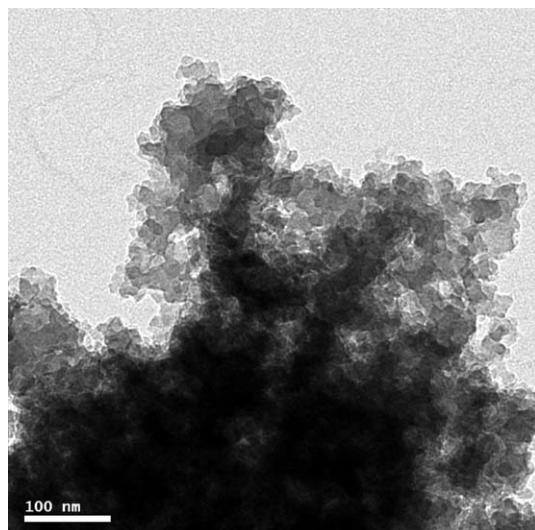


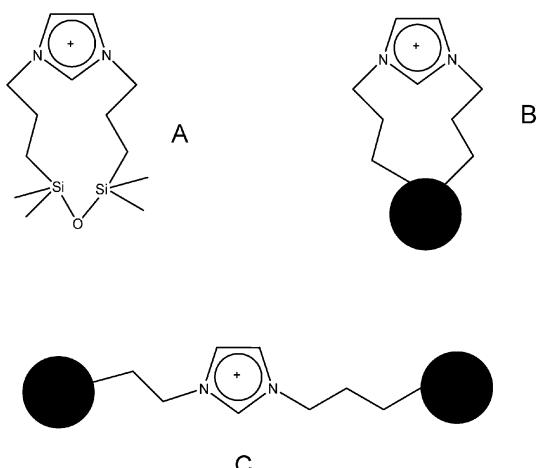
Fig. 13 TEM of linked SiO_2 nanoparticles (strategy 2).

The successful nucleophilic substitution appearing between the chloropropyl and propylimidazole ligands, leading to 1,3-dipropylimidazolium, is confirmed by solid state ^{13}C NMR (Fig. 12).

The obtained powder was dispersed in ethanol to be observed by electron microscopy. The material appears to be made of linked nanoparticles (Fig. 13).

Comparison of the two strategies

Both strategies intent to build a nanoparticle network based on ionic liquid-like connections. In each approach, the ionic liquid-like linker is based on the 1,3-dipropylimidazolium iodide or 1,3-dipropylimidazolium chloride, respectively. The choice to use iodide for strategy 1 is because iodide is a better leaving group than chloride. However, 3-chloropropyltrimethoxysilane, used in strategy 2, is commercially available.



Scheme 4 Three different condensation possibilities of 1,3-di(3-trimethoxysilylpropyl)imidazolium iodide; A: homocondensation; B: condensation of the two trialkoxysilyl groups on one silica nanoparticle; C: condensation of the two trialkoxysilyl groups on two different silica nanoparticles.

In both cases, the TEM micrographs alone could result either from agglomerated nanoparticles or from linked nanoparticles. The reason allowing us to eliminate the hypothesis of having agglomerated nanoparticles comes from the combined observation of the TGA and NMR characterizations. Those figures prove the presence in the final material of dialkylimidazolium, meaning that the nanoparticles, covered by functional groups, reacted with one another to form the dialkylimidazolium group.

Consequently, the results obtained by both strategies indicate that the aim of the work was reached: synthesizing a new hybrid organic–inorganic material made of nanoparticles linked with each other through ionic liquid-like entities.

By comparing the TEM of the resulting materials it appears that the second strategy is much more efficient than the first one, given that the network size is much bigger. The reason for this difference may come from the possibility for the alkoxyisilyl groups, attached to the dialkylimidazolium groups, to react in three different ways. First, they can react with each other by homocondensation, leading to no nanoparticle linkage at all (Scheme 4A) but to the formation of silsesquioxane. Second, the two trialkoxysilyl groups can react on the surface of only one silica nanoparticle, also not leading to nanoparticle linkage (Scheme 4B). The third possibility is the reaction of each trialkoxysilyl group with a different silica nanoparticle, leading to nanoparticle linkage (Scheme 4C).

In the second strategy, the functionalized nanoparticles are first functionalized and then the functional groups dangling from the nanoparticles surface react together. The higher efficiency of this method, in comparison with the first, can be explained by the fact that the modified nanoparticles have just one choice to react, namely to form the imidazolium link.

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