Photoluminescence as Complementary Evidence for Short-Range Order in Ionic Silica Nanoparticle Networks

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Recently we published the synthesis of new hybrid materials, ionic silica nanoparticles networks (ISNN), made of silica nanoparticles covalently connected by organic bridging ligands containing imidazolium units owing to a “click-chemistry-like” reaction. Among other techniques small-angle X-ray scattering (SAXS) experiments were carried out to get a better picture of the network extension. It turned out that the short-range order in ISNN materials was strongly influenced by the rigidity of the bridging ligand, while the position of the short-range order peaks confirmed the successful linking of the bridging ligands. The photoluminescence experiments reported in this communication revealed strongly enhanced emission in the hybrid material in comparison with neat imidazolium salts. Moreover the shift of the emission maximum toward longer wavelengths, obtained when varying the aromatic ring content of the bridging ligand, suggested the existence of strong π−π stacking in the hybrid material. Experiments revealed a stronger luminescence in those samples exhibiting the higher extent of short-range order in SAXS.

Introduction

New composites1−9 or hybrid10−23 materials were recently developed, based on the association of imidazolium moieties with an inorganic part, like metallic silver, tin oxide, or mainly silica. These materials were designed in order to take advantage of the highly interesting features of imidazolium moieties and, thus, were developed for numerous applications like catalysis,17,18 anion exchange,10,11 selective gas trapping,12 drug delivery,6 or electrochemistry.5

Self-organization was observed in some genuine imidazolium moieties previously: This organization was first evidenced for imidazolium compounds possessing long alkyl chains, which are ionic liquid crystals 24−26. Self-organization of short-chain imidazolium units by means of π−π stacking of the imidazolium aromatic rings was also observed to a much lower extent.27−31 In numerous of the developed composite materials, or in chemical-bonded imidazolium units, the confinement of the imidazolium moieties within the pores of a matrix forced, and thus enhanced strongly, the π−π stacking of the imidazolium aromatic rings.9,32

Recently we published the synthesis of new hybrid materials, Ionic silica nanoparticles networks, which will hereafter be referred as ISNN.20,21 In those hybrid materials silica nanoparticles are covalently connected by organic bridging ligands containing imidazolium units. The imidazolium unit formation was performed through nucleophilic substitution between the nanoparticle grafted ligands in a “click-chemistry-like” reaction. The covalent grafting of the ligands onto the nanoparticle surface, the formation of the imidazolium unit to link the nanoparticles, was evidenced by combining solid-state NMR, dynamic light scattering, and thermogravimetric analysis.21 In a second stage, to get a better picture of the network extension, small-angle X-ray scattering (SAXS) experiments were carried out. The main result was the observation of short-range order in the hybrid materials.

In light of this observation and of the above cited literature, we put forward the hypothesis that the imidazolium aromatic rings bridging the silica nanoparticles were the driving force for this short-range order, as probably organized by π−π stacking of the imidazolium aromatic rings.33

In this paper, this hypothesis is further confirmed with the aid of first photoluminescence results obtained on various ISNN.

Experimental Section

1. Chemicals. All starting chemicals were reagent grade and used as purchased. 1,4-Bis(chloromethyl)benzene, sodium tetrafluoroborate (NaBF₄), potassium hexafluoroborate (KF₆), and lithium bis(N-trifluoromethylsulfonyl)imide (LiN(SO₂CF₃)₂) were obtained from Aldrich.

2. Measurements. Small-Angle X-ray Scattering (SAXS). SAXS was performed using a rotating anode generator equipped with a pinhole camera (Nanostar from Bruker AXS with Cu Kα radiation from crossed Gōbel mirrors). The X-ray patterns were recorded with an area detector (VANTEC 2000) and radially averaged to obtain the scattering intensity in dependence on the scattering vector q = (4πsinθ)/λ, with 2θ being the scattering angle and λ = 0.1542 nm the X-ray wavelength.

Fluorescence. Fluorescence spectra were recorded at 25 °C with a Horiba Jobin Yvon FluoroMax-4 spectrophluorometer with a xenon arc lamp as excitation source and a photomultiplier tube as detector. The excitation and emission slit widths were 1.0 and 1.0 nm, respectively. Samples were measured, after grinding, in a solid state sample holder in an angle of 60° to the excitation beam to minimize stray light influence.

Quantum Yield. Quantum yield measurements were carried out on an Edinburgh Instruments spectrometer (FSP920) with a xenon arc lamp, double grating monochromators, and a
photomultiplier tube equipped with a barium sulfate coated integrating sphere (150 mm internal diameter). All spectra were recorded at room temperature with excitation and emission slit width of 3.0 nm. The dwell time was of 0.5 s, and the recording steps were 0.2 nm. For each spectrum, three scans were registered. The fluorescence yield was calculated by dividing the number of emitted photons by the number of absorbed excitation photons. The number of absorbed photons was determined from the decrease of the scattered excitation light intensity compared to the intensity measured with an empty Suprasil glass cuvette. The spectra were corrected for system-specific effects such as the detector sensitivity, monochromator efficiency, and BaSO4 coating. The spectral distribution of the lamp intensity was corrected using a Si photodiode reference detector.

Digital Photo. Digital photos were made with a 5.0 mega-pixels Canon Digital Ixus 50, on the mode Photo Macro with the highest resolution.

3. Synthesis. In previous works we described the following: the syntheses of silica nanoparticles, the surface functionalization of the silica nanoparticles with chloropropyltrimethoxysilane or N-(3-propyltrimehtoxysilane)imidazole, and their reaction leading to the compound Im/Cl. The anion exchange reaction on Im/Cl to obtain Im/PF6, Im/BF4, or Im/N(SO2CF3)2; the reaction of N-(3-propyltrimehtoxysilane)imidazole modified silica nanoparticles with 1,6-dichlorohexane which led to the product Im/Cl/Hex/Im/Cl.33

Nucleophilic Substitution between N-Propylimidazole Modified Silica Nanoparticles and 1,4-Bis(chloromethyl)benzene. The synthesis is carried out under argon atmosphere. In a 100 mL round-bottom flask, 1.88 g (10.7 mmol) of 1,4-bis(chloromethyl)benzene is added at once to 48 mL of a methanol suspension of silica nanoparticles modified by means of 4.95 mL (21.5 mmol) of N-(3-propyltrimethoxysilane)imidazole. Afterward an additional 20 mL of dry methanol is added. The solution is stirred 24 h at room temperature. The solvent is then removed under reduced pressure (3 mbar), and the crude product is washed twice with 20 mL of deionized water and ethanol, respectively, and dried in a desiccator over P2O5. A white powder is obtained, which will be labeled as Im/Cl/Benz/Im/Cl.

Anion Exchange on Im/Cl/Benz/Im/Cl. The starting compound Im/Cl/Benz/Im/Cl was dispersed in 20 mL of acetone. The salt for the exchange, NaBF4, KPF6, or LiN(SO2CF3)2, was added in a mass ratio of 1:1. The dispersion is stirred for 24 h at room temperature. Then the products are collected by centrifugation and washed with acetone, deionized water, and ethanol, 40 mL each. Afterward the powders are dried in a desiccator over P2O5. White powders are obtained, which will be labeled as Im/BF4/Benz/Im/BF4, Im/PF6/Benz/Im/PF6, and Im/N(SO2CF3)2/Benz/Im/N(SO2CF3)2.

Results and Discussion

Recently published SAXS investigations concerning ionic silica nanoparticle networks have highlighted a short-range order in the ISSN due to a peak in the scattering intensity in the range of the scattering vector \( q \) of about 4 nm\(^{-1}\).33 In Figure 1 the SAXS intensities for seven different silica nanoparticle-based hybrid materials are shown, in the region from \( q = 2 \) to 7 nm\(^{-1}\).

The compound Im/Cl corresponds to bridging ligand containing one imidazolium chloride unit, Im/Cl/Hex/Im/Cl and Im/Cl/Benz/Im/Cl are corresponding to bridging ligands containing two imidazolium chloride units with a hexyl chain (Hex) or a benzene (Benz) group in between (Table 1). In the case of Im/Cl the peak maximum was observed at 5 nm\(^{-1}\), whereas the peak maximum for Im/Cl/Benz/Im/Cl is located at 3.3 nm\(^{-1}\) (Figure 1, Table 1), which corresponds to a longer distance of the objects in real space in comparison with Im/Cl. The maximum of the scattering peak characteristic for short-range order in the ISSN hybrid material, observed in Figure 1 and reported in Table 1, can be related to the length of the ligand introduced to connect the silica nanoparticles. The peak maximum in reciprocal space from the SAXS curves decreases; i.e., the distance in real space increases in accordance with the increasing length of the ligands. This directly confirms the successful bridging of the ligands in the synthesis of the material. Given that the scattering peak is directly related to the length of the nanoparticles bridging ligands, the maximum of the scattering peak did not shift when the chloride anion was exchanged by metathesis reaction toward hexafluorophosphate, tetrafluoroborate, or bis(trifluoromethylsulfonyl)imide (Figure 1, Table 1).34
The short-range order of the hybrid material was shown to be dependent on the rigidity of the bridging ligand. The results obtained for the considered ISNN hybrid materials indicate a stronger short-range order for the Im/Cl/Benz/Im/Cl samples, with rigid bridging units, in comparison to the Im/Cl materials, whereas the ordering in Im/Cl/Hex/Im/Cl, with a highly flexible bridging unit, was much weaker as in Im/Cl (Figure 1).

The SAXS experiments clearly indicated that the exchange of the chloride anion did not influence the short-range order of the hybrid materials (Figure 1 and Table 1). The diffraction peak intensities are a signature for the extent of short-range order, in other words, the higher the diffraction peak intensity, the stronger the short-range order in the material.

The excitation spectra of the hybrid materials Im/Cl and Im/Cl/Benz/Im/Cl are characterized by a broad band in the region 320–360 nm with maxima at 340 and 350 nm, respectively (Figure 2B). In the case of the hybrid materials Im/Cl/Benz/Im/Cl, a second maximum can be distinguished in the excitation spectrum at 300 nm; this second maximum seems also to be present in the case of Im/Cl, but to a lower extent. The origin of the second maximum in the excitation spectra cannot be assigned at this stage; however the presence of different absorption and fluorescence maxima due to various associated species was already observed in a previous work devoted to fluorescence phenomena in imidazolium ionic liquids. Blue emission is observed for the samples when excited at the wavelength of maximum adsorption. At an excitation wavelength of 340 nm, the hybrid material Im/Cl emits with a maximum at 390 nm, while Im/Cl/Benz/Im/Cl presents an emission maximum at 410 nm after excitation at 350 nm (Figure 2A). It can be noted that the emission spectra of the ISNN hybrid materials remain unchanged when excited at 300 nm, while the intensities are much lower (Figure 2C).

In aromatic-containing compounds, fluorescence phenomena can often be observed as a consequence of the transition of the π* excited state to the π energy level. We interpret the broad excitation and broad emission bands as resulting from various “conjugation lengths” and thus various HOMO–LUMO

![Figure 2](image-url)
energy band gaps occurring in the material. Conjugation length refers to the imidazolium ring stacking, which occurred when networking the silica nanoparticles.33 This interpretation is supported by previous work concerning photoluminescence investigations of imidazolium based ionic liquids35,39–44 and hybrid materials containing those.7

The self-organization of the aromatic heterocycle under “constraint conditions”, like confinement or in the present case due to covalent linking to nanoparticles surface, was already reported and characterized by means of Raman, SAXS or infrared spectroscopy investigations.9,32,45 This self-arrangement tendency was also highlighted by luminescence experiments in the case of silica-confined imidazolium ionic liquids.7,46 The authors pointed out two main features of the emission spectra of confined imidazolium, which were also observed in our ISNN hybrid materials based on covalently bonded imidazolium units. The first observation concerns the excitation wavelength for genuine ionic liquids. For those imidazolium compounds, which are not submitted to any constraint, the wavelength corresponding to the maximal emission is strongly dependent on the excitation wavelength. However in the case of the ISNN the emission maximum is constant, at 410 nm (Figure 2C). The second highly interesting feature, when comparing genuine imidazolium salts and their corresponding hybrid materials, is an enhanced fluorescence. The first measurements indicated, in conformity with the observations reported in the literature, weak luminescence for the genuine imidazolium salts; whereas once confined or in the present case covalently bridging nanoparticles the fluorescence is strongly enhanced (Figure 2A; Table 2). Both observations were explained by the fact that in pure imidazolium salts numerous different lengths for the imidazolium stacking are simultaneously present, while in ISNN, as well as in confined in silica matrixes, this stacking length is much more homogeneous over the whole studied sample.7 Aggregation-induced emission was also already reported for materials derived from triphenylethylene,47 as well as in Zn based metal oxide frameworks containing bipyridinedicarboxylate.48 where the aggregation-induced \( \pi-\pi \) stacking between the aromatic rings originated in strongly enhanced emission.

Considering the emission spectra of the two ISNN hybrid materials \( \text{Im}/\text{Cl} \) and \( \text{Im}/\text{Cl}/\text{Benz}/\text{Im}/\text{Cl} \), a clear shift of the emissions toward longer wavelengths can be observed; the maxima are at 390 and 410 nm, respectively (Figure 2A). A red-shifted luminescence is typical for the presence of extensive \( \pi-\pi \) stacking between adjacent aromatic rings.36,48,49 It has to be noted that the bridging unit in \( \text{Im}/\text{Cl}/\text{Benz}/\text{Im}/\text{Cl} \) is not fully conjugated; the presence of the CH\(_2\) groups between the imidazolium and benzene units hinders the conjugation between the aromatic groups (Table 1). As a consequence, increased \( \pi-\pi \) stacking can only originate if the ligands in the ISNN hybrid materials exhibit a stronger short-range order.

The observation of almost no emission for the sample \( \text{Im}/\text{Cl}/\text{Hex}/\text{Im}/\text{Cl} \) (Figure 2A) speaks also for a minimum short-range order of the ligands as criterion for an increased

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**TABLE 2: Quantum Yields for the Hybrid Materials and Their Precursors**

| bridging units/sample names | quantum yields |
|-----------------------------|----------------|
| BMI Br                      | 0.05           |
| BMI PF\(_6\)                | 0.07           |
| Im/Cl                       | 0.07           |
| Im/Br                       | 0.26           |
| Im/PF\(_6\)                 | 0.26           |
| Im/Cl/Benz/Im/Cl            | 0.01           |
| Im/Cl/Benz/Im/Cl            | 0.12           |
| Im/BF\(_4\)/Benz/Im/BF\(_4\)| 0.26           |
| Im/PF\(_6\)/Benz/Im/PF\(_6\)| 0.23           |
| Im/(SO\(_2\)CF\(_3\))\(_2\)/Benz/Im/(SO\(_2\)CF\(_3\))\(_2\) | 0.14 |

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Figure 3. Emission and excitation (insert) spectra of (top) \( \text{Im}/\text{X} \) and (bottom) \( \text{Im}/\text{X}/\text{Benz}/\text{Im}/\text{X} \) hybrid materials. The excitation wavelength for the emission spectra was the wavelength of maximal absorption in the excitation spectra.
fluorescence. Indeed, the SAXS measurements on Im/Cl/Hex/Im/Cl revealed a very weak ordering (Figure 1, dots). We interpret this weak ordering, and as a consequence the very weak fluorescence, by the flexibility of the dichlorohexane which can “backbite” on the same nanoparticle instead of bridging two different silica nanoparticles.33 This “backbite” phenomenon hinders the π−π stacking between adjacent ligands. The quantum yields reported in Table 2 decrease in the order Im/Cl > Im/Cl/Benz/Im/Cl > Im/Cl/Hex/Im/Cl. The very low value obtained for Im/Cl/Hex/Im/Cl, can be explained by the fact that the material is so poorly organized, due to the flexible hexane linker, that only very few π−π stacking is possible. This observation was confirmed by the SAXS results (Figure 1). The difference in the quantum yield values measured for Im/Cl and Im/Cl/Benz/Im/Cl, 0.13 and 0.26, respectively, are in accordance with the results published by Carlos et al. indicating first that the morphology of the hybrid materials influences the quantum yield values52–54 and second that a too high degree of organization induced a decrease in the emission quantum yield.52–54 The reported quantum yield decrease could be assigned to aggregation quenching.54 The difference in the degree of organization of those two hybrid materials was given by the extent of short-range order from SAXS measurements (the peak intensities in Figure 1), i.e., Im/Cl/Benz/Im/Cl > Im/Cl. The observation of simultaneously: the necessity of a high degree of molecular order from molecular self-assembly for becoming an efficient energy transfer and a decrease of the quantum yield value when self-aggregation is too pronounced hindered the π−π stacking. The stability of the π−π stacking is confirmed by SAXS experiments, where the short-range order peak was correlated to the length of the bridging chain and remains unchanged even after anion exchange. These results, in combination with SAXS measurements, confirmed our previous results suggesting a short-range order in the materials originating from π−π stacking interactions.

Some open questions have remained, e.g., the influence of the anion exchange on the quantum yield of the hybrid material, and will be investigated further.

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