Porphyrin and Naphtalenediimide Functionalized Silica-gel Particles. Photophysical Properties

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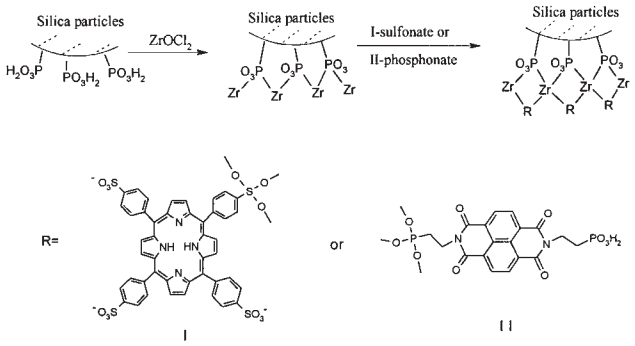
Silica-gel particles were functionalized with *N*,*N*′-bis(2-phosphoethyl)-1,4,5,8-naphthalene diimide (DPN) and *meso*-tetra(4-sulfonatophenyl) porphyrin (TSPP), by using phosphonate/sulfonate zirconium chemistry. The properties of the bound chromophores were shown to differ from their solution properties, with propensity to form either excimer or aggregates at the silica-gel surface for DPN and TSPP, respectively.

Modification of nano and micro-silica particles with photoactive molecules is important to chromatography, solid-state and combinatorial synthesis and photocalysis.[1] Nevertheless, functionalization of these particles is usually made by weak physical adsorption of chromophores in the particle.[2] Complexes between zirconium and phosphonate are known to form strong layered structures.[3–5] Recently these complexes have been used in the construction of self-assembled monolayers and thin films, allowing the incorporation of chromophoric molecules in flat substrates.[4,5] The complex between sulfonate and zirconium is also known to form layered structures.[3] This report describes the application of zirconium phosphonate/sulfonate chemistry to functionalize silica-gel particles with naphtalenediimide and porphryrin derivatives. The photophysical properties of these functionalized silica-gel particles were also investigated.

Silica-gel 60 (50 μm mean diameter, Aldrich) particles were treated with a fuming H_2SO_4: 30% H_2O_2 (7 : 1, v : v) solution and then reacted with 0.4 M of 3-aminopropyl triethoxysilane in 60 mL toluene, under reflux temperature (6 h). The particles were filtered, suspended in an aqueous ethanol solution (1 : 1, v : v) for 2 h at room temperature, washed with acetonitrile, water, and acetone and then dried. The substitution level of 0.7 ± 0.1 mmol of amino group per gram of silica-gel, was determined by the picric acid assay.[6] The particles were then suspended in a acetonitrile solution of $POCl_3$ (0.2 M $POCl_3$ and 0.2 M collidine for 15 min at room temperature), resulting in a coverage of 0.23 ± 0.01 mmol of phosphonic acid per gram of silica-gel as determined by the molybdenum assay.[7] A layer of Zr(IV) was then mounted on the phosphonated silica-gel particles through suspending the particles in an aqueous solution of $ZrOCl_2$ (5 mM) at room temperature for 15 min. The zirconated silica-gel was then suspended in an aqueous solution containing 0.54 mM of DPN or TSPP for 4 h at room temperature. The particles were exhaustively rinsed with water and acetone and dried (Scheme 1). The chromophoric molecules were extracted from the surface of silica-gel particles with a NaF solution (1 M) and the absorption of the resulting solutions was measured at 380 nm (DPN) and 550 nm (TSPP). Using standard curves, coverages of 0.13 ± 0.01 mmol of DPN and 0.04 ± 0.01 mmol of TSPP per gram of silica-gel were obtained. Surface densities of DPN and TSPP were estimated as 1.8 and 0.6 molecules per 100 Å,^{2} considering that only the silica-gel rough surface (60 Å of thickness) was modified (see below).



Scheme 1. Reaction pathways used to functionalize silica-gel particles with TSPP (I) and DPN (II).

Figure 1A shows the fluorescence emission spectra of DPN and DPN-silica-gel particles in aqueous solution. The peaks in the 400 nm region (390 and 414 nm) can be attributed to the emission of DPN in the monomeric form.[8] The emission increase observed with the pH decrease is due to the decrease in intersystem crossing.[8] The emission spectra of DPN-silica particles also present well resolved bands in the 400 nm region added to a red-shifted and unresolved band centered at 520 nm (Figure 1A). This band could be due to the presence of associated DPN molecules, either in the ground state or in the excited state (excimer).[8,9] Two pieces of evidence point to the presence of excimers: i) the absorption spectra of DPN bound to silica-gel are the same as that observed for DPN in solution, suggesting the absence of ground state association (Figure 1B); ii) Fluorescence decay determinations using a nanosecond system (LS1, PTI) showed a fast decay (below the resolution of the apparatus) at 400 nm and a slower component when monitored at 520 nm, which was fitted to a single exponential with lifetime of 2.5 nsec. The time resolved emission spectra obtained in the gated mode without deconvolving the excitation lamp[9] shows the emission build-up at 520 nm with the decrease at 400 nm (Figure 1B, inset). Since the fluorescence lifetime of DPN singlet species is on the sub nanosecond domain, the emission at 400 nm represents basically the lamp decay. The emission profile at 520 nm shows the appearance of an emissive species after the lamp pulse, which is thus assigned to the decay of the excimer (Figure 1A). The increase in emission at 520 nm (Figure 1A) with the pH decrease

is probably related with the neutralization of the phosphonate negative charges of DPN, facilitating the approximation of the chromophoric groups and the excimer formation.

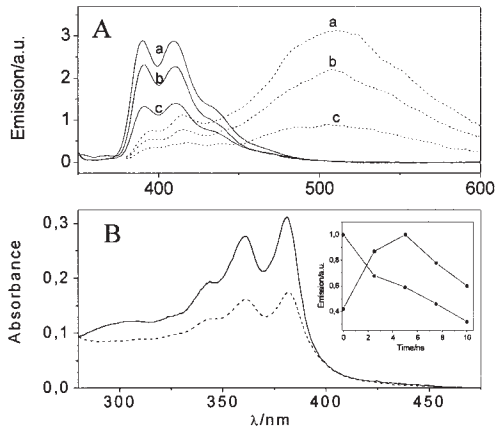


Figure 1. A. Emission spectra of DPN (5×10^{-6} M, solid line) and DPN-silica-gel particles (dashed lines) in water at different pHs: pH = 1.0 (a); pH = 6.8 (b) and pH = 9.3 (c). B. Absorption spectra (pH = 1) of DNP in aqueous solution (solid line) and of DPN-silica-gel particles (dashed line). Inset: Emission intensity at 400 nm (●) and 520 nm (■) as a function of time.

TSPP emission in the silica-gel particle is also different from that observed in homogenous solution (Figure 2A). In aqueous solution, only one peak at 670 nm is observed, which is due to the emission of the TSPP monomer (Figure 2A).[10] In the TSPP-silica-gel particles suspended in water it is observed the splitting of these transitions with peaks centered at 660 nm and 725 nm, which is possibly due to the formation of aggregates in the silica-gel surface. Comparing the excitation spectra of the TSPP in the silica-gel particle with that in aqueous solution (Figure 2B), it is possible to observe a relative increase of the 510 nm band compared with the 410 nm band and a wider 410 nm absorption band in the silica-gel surface. These characteristics have been attributed to the presence of TSPP dimers.[10]

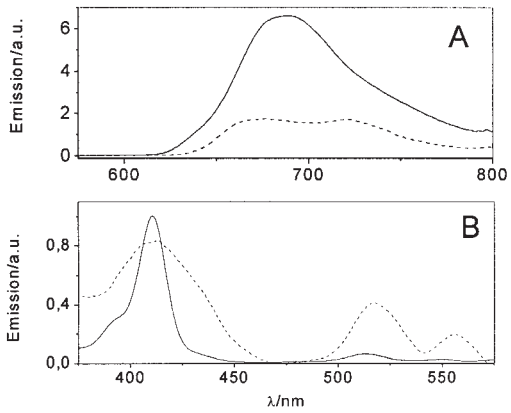


Figure 2. A. Emission spectra of TSPP (1×10^{-6} M, solid line) and of TSPP-silica-gel particles (dashed line) in water, $\lambda_{exc} = 530$ nm. B. Excitation spectra of TSPP in water (1×10^{-6} M, solid line) and of TSPP-silica-gel particles (dashed line) $\lambda_{em} = 650$ nm.

Although being porous solids (average diameter of 60 Å), it is likely that most of the chromophoric substitution took place in the silica surface, because the chromophore dimensions (20–30 Å) are of similar magnitude compared to the pore diameters. Therefore, diffusion of the chromophores into the internal regions of the silica must be restricted. We also observed that the excimer formation is completely suppressed by complexation with poly (diallyldimethylammonium chloride, MW = 150, 000 g · mol^{-1} Data not shown), which is a polyelectrolyte that cannot access the internal regions of the silica-gel particles.

The zirconium based functionalization provides a facile and fast way to furnish chromophore-modified silica-gel particles. DPN and TSPP are forming excimers and dimers species in the silica-gel surface, respectively. In the case of DPN the monomer/excimer ratio was shown to change with pH. These new materials may prove to be valuable for photoconversion because the DPN and TSPP photochemical properties may be tuned depending on the medium properties as well as on the proximity of the chromophores in the silica-gel surface.

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References and Notes

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