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Speciation in Solution: Silicate Oligomers in Aqueous Solutions Detected by Mass Spectrometry[**]

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Nucleation of solids from solution is one of the most challenging problems in solid-state chemistry. For a better understanding of processes taking place during crystallization, detailed knowledge about the species present in solution, such as particle size distribution and morphology, is mandatory to control the final properties of the solid.[1] However, only very few techniques are suited for such analyses, such as NMR spectroscopy for selected nuclei. Mass spectrometry could be a very versatile technique, since there are in principle no limitations with respect to the elements which can be analyzed. However, surprisingly only a few publications are available, in which mass spectrometry has been used for the analysis of speciation of crystallite precursors in solution. Most of the work reported to date has been limited to the investigation of partially hydrolyzed alkoxide solutions with predominantly alcohol as the solvent.[2] Herein we present for the first time data which show that oligomeric species in aqueous solutions can be reliably analyzed by using mass spectrometry. Electrospray ionization mass spectrometry (ESI-MS) has been used to study oligomer distribution in silicate solutions, since in this system the species can be independently analyzed with ^{29}Si NMR spectroscopy. However, in addition ESI-MS allows one to obtain information on oligomers and to address questions such as charge and degrees of hydrolysis of the species present in solution. Besides the availability of ^{29}Si NMR spectroscopy as an independent technique for analysis, the silicate system was chosen because of the importance of oligomeric species in zeolite synthesis,[3] sol–gel chemistry,[4] and silsesquioxane chemistry.[2c, 5]

Earlier studies showed the distribution of silicate oligomers depends on the alkyl chain length of the added tetraalkylammonium counterion.[3] Silicate solutions containing tetramethylammonium hydroxide (TMAOH) stabilize the cubooctameric double-four-membered ring (D4R), whereas in the presence of tetraethylammonium hydroxide (TEAOH) the formation of the double–three-membered ring (D3R) is preferred. Figure 1 depicts a typical ^{29}Si NMR spectrum and the corresponding negative-ion ESI mass spectrum for an aqueous/methanolic TMAOH solution containing dissolved silica. The ^{29}Si NMR spectrum indicates the high amount of D4R species (88.3%), but there are also D3R (3.8%), monomeric (3.0%), dimeric (1.2%), linear and cyclic trimeric (1.6%), and different tetrameric (1.5%) species present. The species detected in the ^{29}Si NMR are found in the ESI mass spectrum as well. The relative intensities of the peaks attributable to these species are in qualitative agreement for the two techniques. However, the intensity distribution in ESI-MS is somewhat dependent on the cone voltage and type of mass spectrometer used (see below), thus, full quantification is difficult. From the simple singly charged D4R oligomer at m/z 551 a series of peaks with a spacing of $\Delta(m/z)$ 73 to higher masses is observed. These can be assigned to species of higher charged cubic octamers that are clustered to TMA$^+$ ions. The series of peaks extends up to m/z 770, corresponding to a fourfold negatively charged D4R silicate clustered with three TMA$^+$ ions, while the doubly charged species clustered with one TMA$^+$ ion and the triply charged species clustered with two tetramethylammonium cations can be seen at m/z 624 and 697, respectively.

A second series of peaks starts at m/z 551. The following peaks at m/z 565, 579, and 593 shows a mass spacing of $\Delta(m/z)$ 14, which indicates a substitution of up to three hydroxyl groups at the silicon atoms by methoxy groups, which would be expected for highly alkaline solutions containing relatively large amounts of methanol. However, it can not be excluded

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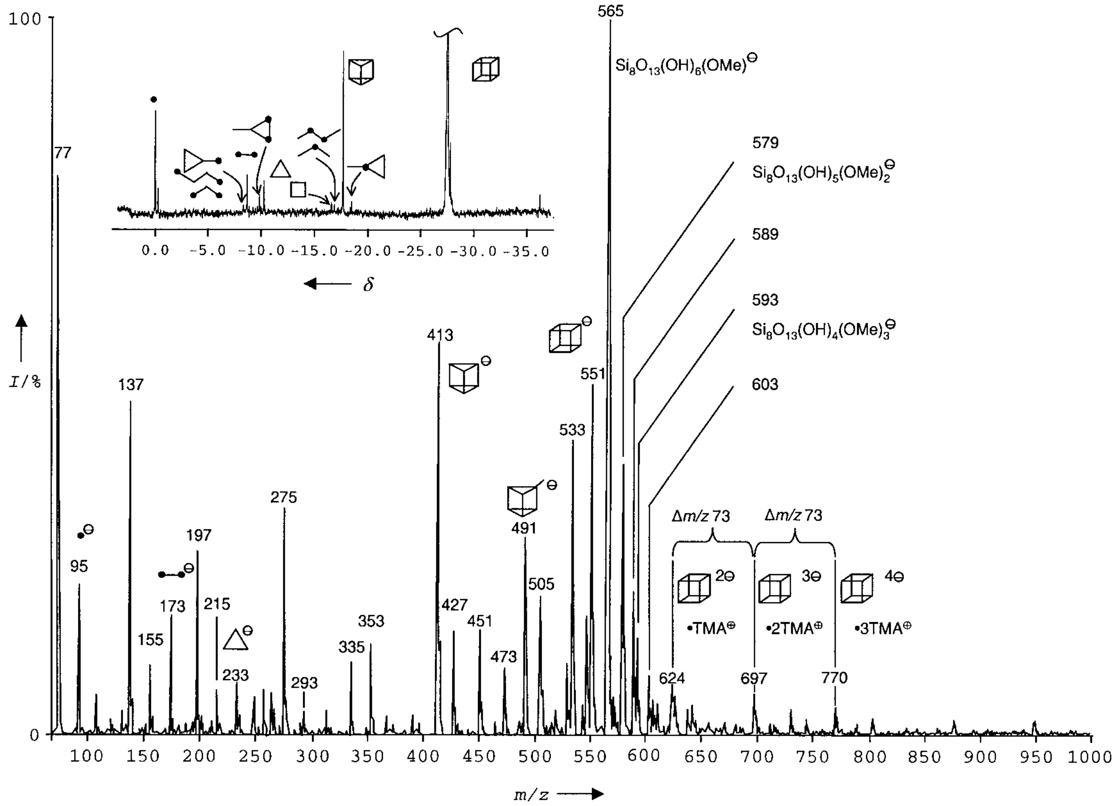


Figure 1. Negative-ion ESI mass spectrum and ^{29}Si NMR spectrum of a silicate solution containing tetramethylammonium (TMA) ions in which the cubic octamer is the predominant species. In the ^{29}Si NMR spectrum, the full intensity of the signal for the cubic octamer is much higher and the scale has been changed to show the peaks of the other oligomers.

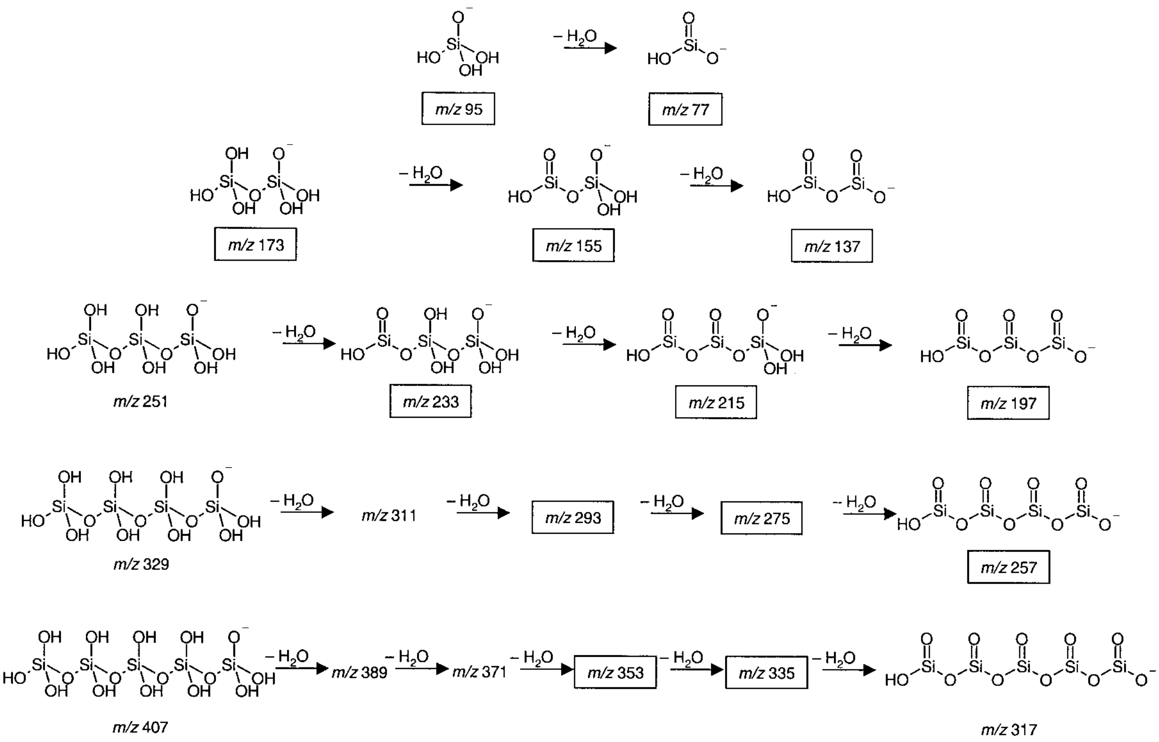
that these methoxylated species are generated during the desorption process or by ligand exchange in the gas phase. The D3R species is also detectable. The signal at *m*/*z* 413 belongs to the singly charged species, whereas the signal at *m*/*z* 491 would appear to belong to a singly charged D3R species that has another $Si(OH)_3$ unit linked to its framework. Again, the analogous species in which a hydroxy group is substituted by a methoxy group are present (*m*/*z* 427 and 505). In contrast to the ^{29}Si NMR spectrum, only the dimer at *m*/*z* 173 can be detected as a fully hydroxylated linear species. The trimer and the tetramer do not appear in the mass spectrum. Instead, signals are detected that on first inspection would not seem to belong to siliceous species. The appearance of these peaks can be explained by the dehydroxylation of these species in the mass spectrometer (Scheme 1). The condensation of two hydroxy groups with the elimination of water leads to the formation of the oxo species. The tendency of these species not to appear as the fully hydroxylated moieties increases with increasing silicate chain length.

For comparison, Figure 2 shows the mass spectrum and ^{29}Si NMR spectrum of an ethanolic/aqueous silicate solution containing tetraethylammonium ions. The ^{29}Si NMR spectrum confirms the distribution of anions evident in the mass spectrum. As expected, no signals at $m/z > 500$ were detected, proving the absence of D4R ions. Again most of the partially dehydroxylated linear moieties are present.

Finally, Figure 3 shows the same system with a silicate concentration which is 5.6-fold lower. This results in the disappearance of the higher condensed species like the D3R ion, as can easily be seen in the ^{29}Si NMR spectrum. Only the monomeric, dimeric, and cyclic trimeric species are stable in this diluted silicate solution. In the corresponding mass spectrum only the monomer (*m*/*z* 95 and 77) and the dimer (*m*/*z* 173) can be reliably identified. All other species present seem to be unstable intermediates, whose detection is dependent upon the cone-skimmer (declustering) potential.

In order to check the influence of sample injection and ion source geometry, spectra were also recorded in a second ESI-MS system (HP 5989B) which is rather optimized for the detection of higher masses. In this system, species with $m/z < 400$ can be less reliably detected. Figure 4 shows the spectrum which corresponds to the one in Figure 1 measured with the other spectrometer. The signal-to-noise ratio is much lower than in the mass spectrum shown in Figure 1. Thus, only the main species such as the singly charged D4R (*m*/*z* 551) and the following series of peaks with a spacing of $\Delta(m/z)$ 14 to higher mass is observed, indicating the exchange of hydroxy by methoxy groups. The reasons for these differences will be discussed in a forthcoming paper, in which the performance of several different mass spectrometers will be compared.

The results presented show that ESI-MS is a powerful tool for the analysis of species in solution, for example, for silicate oligomers low fragmentation is observed during the desorption process especially at high mass-to-charge ratios. If this approach can be extended to other systems, ESI-MS would be ideally suited for the analysis of higher oligomers, which are the crucial species responsible for nucleation of solids in



Scheme 1. Silicate oligomers that are partly dehydroxylated. Only those *m*/*z* values written in boxes were observed in the ESI-MS experiments.

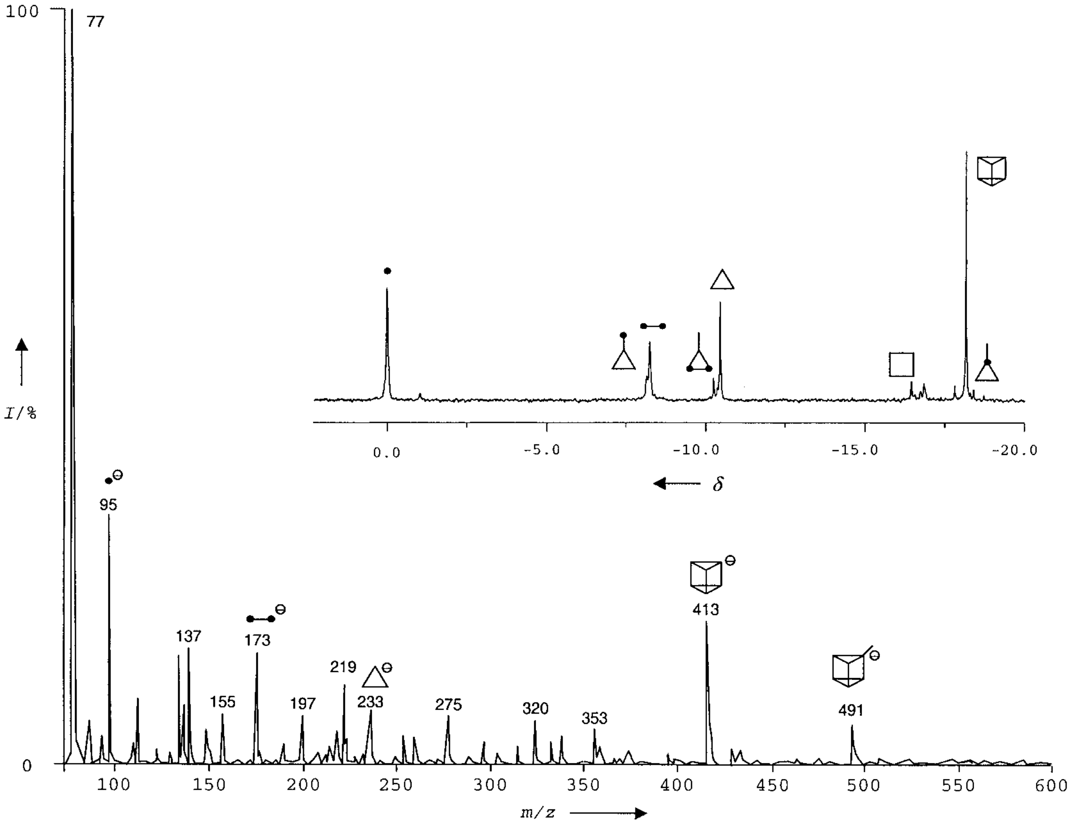


Figure 2. Negative-ion ESI mass spectrum and ^{29}Si NMR spectrum of a silicate solution containing tetraethylammonium ions in which the prismatic hexamer is the predominant species.

solutions. Even for highly alkaline and concentrated (0.5–1.0 M) solutions, which have a high ionic strength, ESI-MS allows the determination of species without strong interference in the system. D4R units with a charge of up to –4 and as a mixture with different degrees of hydroxylation and methoxylation could be detected; such information cannot

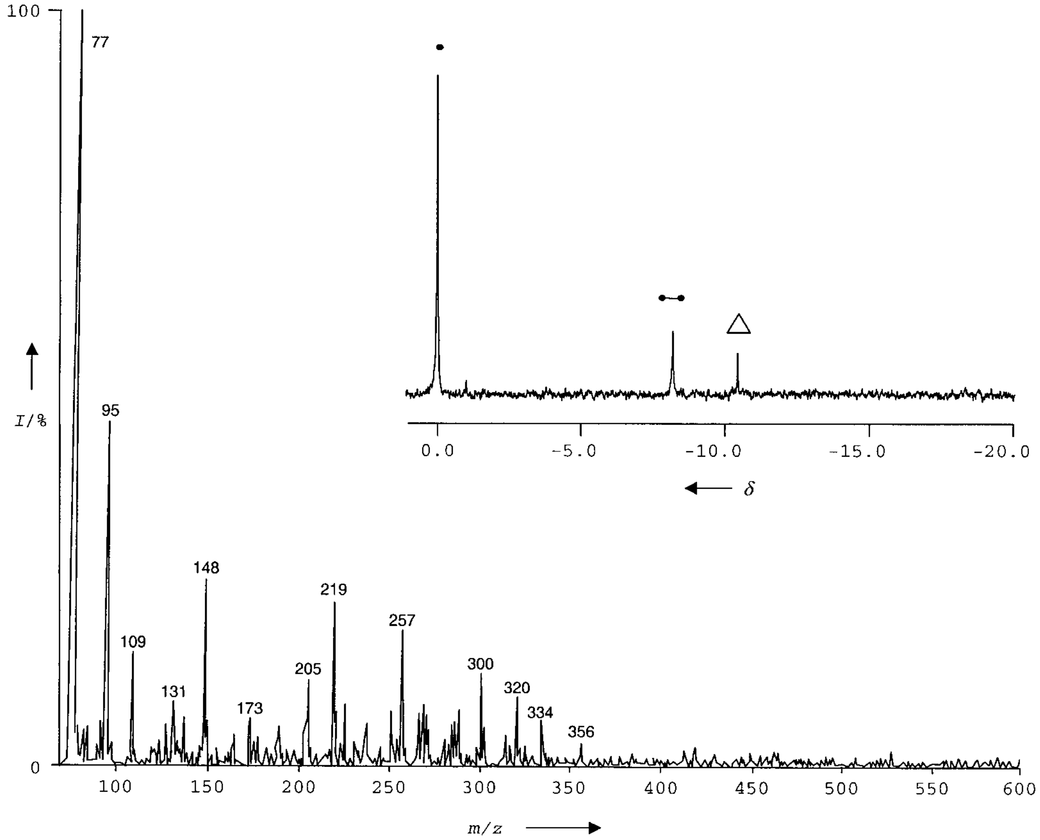


Figure 3. Negative-ion ESI mass spectrum and ^{29}Si NMR spectrum of a silicate solution of lower concentration containing only smaller oligomers.

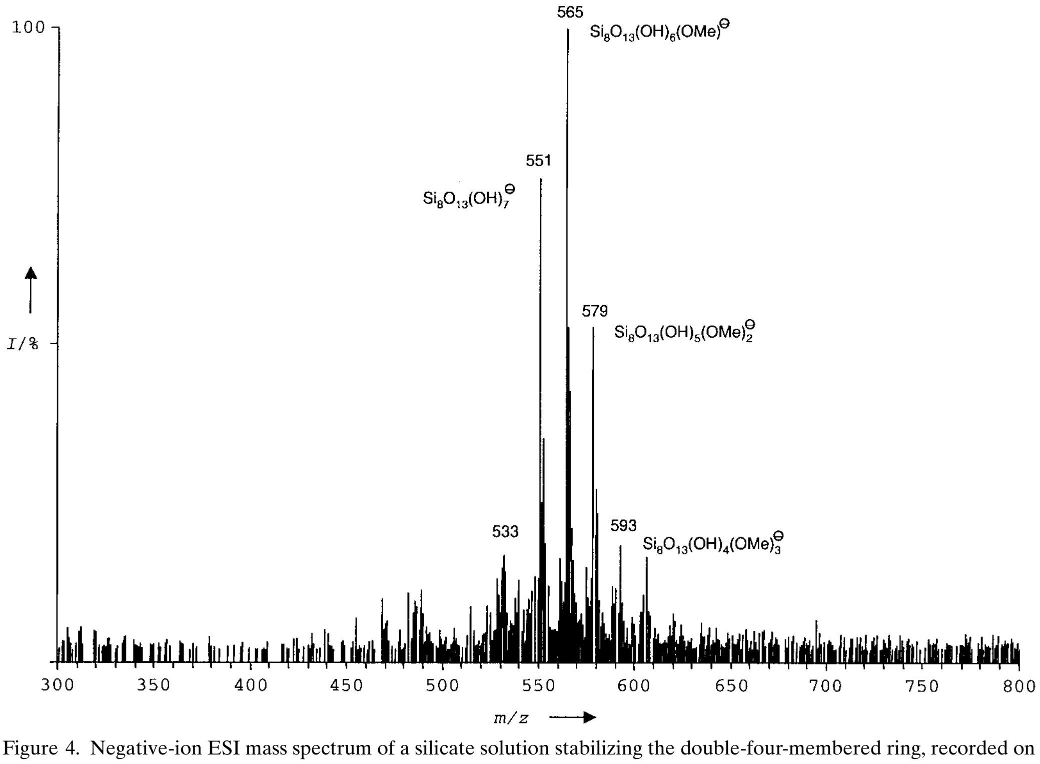


Figure 4. Negative-ion ESI mass spectrum of a silicate solution stabilizing the double-four-membered ring, recorded on a Hewlett Packard HP 5989B mass spectrometer.

be obtained by NMR spectroscopy. However, the power of mass spectrometry will become even more obvious in systems in which NMR spectroscopy fails due to the lack of suitable nuclei.

Experimental Section

The solution in which double-four ring (D4R) silicate oligomers are stabilized was prepared by dissolving Aerosil 130 (Degussa) (0.75 g, 12.45 mmol) in aqueous tetramethylammonium hydroxide (TMAOH) solution (5.0 g; 25 wt %; Aldrich), ultra-purified water (4.67 g; Millipore), and methanol (5.625 g, 175.55 mmol; Fluka, p.a.). Double-three ring (D3R) containing solutions were prepared by dissolving Aerosil 130 (0.193 g, 3.21 mmol) in aqueous tetraethylammonium hydroxide (5.0 g; 35 wt %; Aldrich), ultra-purified water (0.146 g; Millipore), and ethanol (1.817 g, 39.5 mmol; Fischer & Rintelen, puriss.). All solutions were stirred for 30 min and then heated at 70 °C for 18 h. The clear solutions were then filtered through a polyether sulfone membrane (Nalgene) with a pore width of 0.2 μm before being injected into the mass spectrometer.

The mass spectra were recorded with a Fisons VG Platform II instrument with a quadrupole analyzer. The sample was injected directly through a Rheodyne valve. Skimmer cone voltages were varied between 30 and 100 V. In order to obtain an independent verification of the findings, a second series of experiments was carried out on a quadrupole mass spectrometer (Hewlett Packard HP MS-Engine 5989B), fitted with an Analytica of Brandford ESI-source. The solutions were injected by direct infusion and measured with an ESI voltage of 3640 V, a flow rate of 40 μL min^{-}, a desolvation temperature of 150 °C, a CapEx voltage of -133 V, and a skimmer voltage of -31.5 V.

^{29}Si NMR spectra were recorded with an AMX 400 Bruker spectrometer operating at 79.483 MHz. Samples containing D_2O for the deuterium locking frequency were placed in a 10-mm PTFE NMR tube liner without a glass sample tube to minimize the silicon background from the glass. The pulse sequence used to acquire the spectra was a ^{29}Si{^{1}H} inverse-gated experiment with a waltz16 composite pulse program for proton decoupling. Generally for the ^{29}Si determination a 13.6 μs pulse with a 8 s relaxation delay was used between each acquisition. The number of acquisitions ranged from 15000 to 30000 depending on the concentration of the solutions.

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Stepwise Assembled Photoactive Films Containing Donor-Linked Fullerenes**

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The construction of molecular devices such as photoelectrochemical cells for use in solar energy conversion is a very useful but challenging task.[1] Most common problems relate to the interfacial diffusion of the donor and acceptor molecules or the lack of semiconductor materials with large band gaps that give an efficient light response in the visible region.[2, 3]

Herein we present the supramolecular organization of donor-linked fullerenes as a viable alternative for the assembly of photoactive indium tin oxide (ITO) electrodes which exhibit an efficient generation of photocurrent.[4] The fundamental advantage of the fabrication of these tailored architectures is the control that can be exerted at a molecular level over the thickness and composition of the assembled films.[5] Equally important is the specific alignment and the orientation of the incorporated donor–acceptor systems so as to facilitate the electron transfer among adjacent layers.[6] Thus, the efficiency of the generated photocurrents is expected to depend on the cooperative interaction of these individual parameters (film thickness, alignment, and orientation).

In the following we describe the layer-by-layer deposition of a positively charged fulleropyrrolidinium ion (**1**) and a series of positively charged ruthenium(II)–polypyridyl–fullerene donor–acceptor dyads (**2** and **3**, the counterion is PF_6^- in both cases, Scheme 1) on solid substrates (quartz or semiconducting ITO electrodes). The ruthenium(II)–polypyridyl complexes employed show a marked red-shift in their absorption maxima while maintaining a high photopotential.[7, 8] Both parameters are essential in order to guarantee an elevated monochromatic photon-to-current conversion efficiency at longer wavelength. More importantly, the use of

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