Surface Chemistry

DOI: 10.1002/anie.200600075

Facile Monolayer Assembly of Fluorophore-Containing Zeolite Rods in Uniform Orientations for Anisotropic Photoluminescence**

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We have developed methods for organizing zeolite microcrystals in the form of uniformly aligned monolayers on various substrates by inducing well-defined molecular linkages between each microcrystal and the substrates. The resulting monolayers show high degrees of coverage, high degrees of close packing between the attached crystals, strong binding between the crystals and substrates, and high degrees of uniform orientation of the crystals. The zeolite monolayers have served as supramolecularly organized light-harvesting systems and as excellent precursors for the preparation of continuous zeolite films with uniform orientations of the nanopores or nanochannels. The latter property makes the monolayers suitable for applications in molecular sieving membranes and nonlinear optical films. The assembly of monolayers of zeolite microcrystals has also been regarded as one of the future directions of zeolite research.

In our approaches, the monolayers have mostly been assembled by refluxing solutions of bare or functional-group-tethered zeolite crystals in toluene in the presence of substrates bearing functional groups. The solutions were often stirred to keep them dispersed and to give them kinetic energy. More than 24 h were usually required to cover the majority (>90%) of 4 cm² glass plates with closely packed monolayers. High degrees (>98%) of uniform orientation were obtained when the aspect ratios of the zeolite microcrystals were equal to or less than 1. However, the reflux/stirring (RS) method did not produce high coverage and uniform orientation in the case of cylindrical zeolite microcrystals with aspect ratios higher than 1. We recently discovered that sonication of the stacks of bare glass/3-chloropropyl-coated glass (CP-g)/bare glass plates in a toluene solution dispersed with bare zeolite crystals leads to the 4 cm² glass plates being fully covered with very tightly packed monolayers of zeolite microcrystals within two minutes. This method was named “sonication with stacking” (SS). We now report that the SS method is also highly effective for assembling cylindrical zeolite crystals with aspect ratios of up to 3 in vertically oriented monolayers, and that the monolayers give anisotropic photoluminescence in a high dichroic ratio, when fluorescent molecules were incorporated in the channels of zeolite L along the channel directions. The crystals self-assembled into horizontally oriented monolayers when the zeolite L crystals had a hexagonal columnar morphology.

Cylindrical zeolite L crystals with dimensions of 1 × 2–3 μm (diameter × length) and hexagonal columnar zeolite L crystals of 1 × 4–5 μm (width × length) used in the current study were prepared according to procedures described previously. Pyronin B ions (PyB⁻, Figure 1a) were incorporated into the channels of zeolite L crystals by ion exchange of the K⁺ ions of the zeolites with PyB⁻ ions in water. Since the length of the PyB⁻ ion (16.3 Å) is longer than the width of the zeolite L lobe (12.6 Å, Figure 1b), the incorporated PyB⁻ ions are likely to be lined up along the direction of the channel (Figure 1c) with a tilt angle of less than 20°. The surfaces of the PyB⁻-containing zeolite L ([PyB⁻]L) crystals were subsequently treated with (3-aminopropyl)trimethoxysilane (AP-TMS) to tether 3-aminopropyl (AP) groups onto their surfaces and to prevent the egress of the incorporated PyB⁻ ions.

[**] We thank the Ministry of Science and Technology (MOST) and Sogang University for supporting this work through the Creative Research Initiatives (CRI) and the Internal Research Fund programs, respectively. H.C. and H.L. also thank the Quantum Photonics Research Center supported by the Korea Science and Engineering Foundation.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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The X-ray data revealed that the degrees of uniformity of the crystals were very tightly attached onto CP-g plates by the SS method. The CP-g plate covered with (3-chloropropyl)trimethoxysilane (CP-TMS) crystals were attached onto CP-g plates between the bare glass plates (SW method; Figure 2e) but without interposing the CP-g plates (1.88E03 1.8 cm²) were prepared by treating bare glass plates with (3-chloropropyl)trimethoxysilane (CP-TMS). The CP-g plate covered with (3-chloropropyl)trimethoxysilane (CP-TMS) crystals were attached onto CP-g plates between the bare glass plates (SW method; Figure 2e). When cylindrical AP-coated (PyB⁺)L crystals were attached onto CP-g plates by the SS method over two minutes the crystals self-assembled very tightly and for the remark-

Figure 1. a) Molecular structure of the PyB⁺ ion. The estimated length is 16.3 Å. b) The zeolite L channel consists of 7.5 Å long lobes with a pore opening of 7.1 Å. The internal width of a lobe is 12.6 Å, which is smaller than the length of the PyB⁺ ion. c) Illustrations of PyB⁺-containing cylindrical (left) and hexagonal columnar (right) zeolite L crystals with their dimensions. The red cylinders represent PyB⁺ ions positioned in the channel direction. The middle diagram illustrates the imagined position of a PyB⁺ ion positioned in the channel direction. d) The diffuse-reflectance absorption spectrum of the dry (PyB⁺)L-g crystals and the fluorescence spectra of (PyB⁺)L crystals dispersed in glycerol (solid blue curve, λmax = 550 nm), the absorption spectrum of PyB⁺ in methanol (green curve, λmax = 551 nm), and the isotropic fluorescence spectrum of PyB⁺-containing zeolite L crystals dispersed in glycerol (red curve, λmax = 567 nm).

Figure 4a shows the anisotropic fluorescence spectra for SVV and SVA. The inset shows the angle-dependent change of Iνν/IVHH, where Iνν represents the intensity of the spectrum of v-(PyB⁺)L-g at λνν at various angles (θ) under vertical excitation. The Iνν/IVHH ratio was 8.9:1, which is about double that obtained by Tolbert and co-workers (4.5:1) for polymer-containing mesoporous silica.[28,29] Thus, this current study demonstrates a novel and highly effective way of preparing supramolecularly organized systems that give strongly anisotropic photoluminescence. Figure 4c shows the anisotropic fluorescence spectra of the SHH and SSH components. The inset shows the angle-dependent change of IHH/IIHH, where IHH represents the intensity of the spectrum of v-(PyB⁺)L-g at λHH at various values of θ under horizontal excitation.
The CP-g plate covered with hex-AP-(PyB\textsuperscript{+})\textsubscript{L} crystals on both sides in horizontal orientations is denoted as h-(PyB\textsuperscript{+})\textsubscript{L}-g. The four polarized fluorescence spectra obtained from a stack of three h- (PyB\textsuperscript{+})\textsubscript{L}-g crystals are denoted as $S_{hHH}$, $S_{hHV}$, $S_{hVV}$, and $S_{hVH}$ (see the Supporting Information for spectra). The corresponding intensities at $\lambda_{\text{exc}}$ are denoted as $I_{hHH}$, $I_{hHV}$, $I_{hVV}$, and $I_{hVH}$. The $I_{hHH}/I_{hHV}$ ratio was 3.0:1. The reason for the $I_{hHH}/I_{hHV}$ ratio being about 1/3 of that of $I_{hHV}/I_{hVH}$ (8.9:1) is because the hex-AP-(PyB\textsuperscript{+})\textsubscript{L} crystals are oriented randomly on the glass plane, even though they are all horizontally attached to the glass plane, and the integration of $(\cos \theta)^2$ over the angle range 0–180° gives 1/3. If the hex-AP-(PyB\textsuperscript{+})\textsubscript{L} crystals were uniformly oriented in the $x$ and $y$ directions as well, then the $I_{hHH}/I_{hHV}$ ratio would be approximately 9:1.

Although the assembly of monolayers of zeolite rods in a vertical orientation has been recognized as being important because of the applicability of the aligned zeolite rods to second harmonic generation, molecular sieve membranes, and macroscopic alignments of guest molecules, only a few examples have been reported. Caro et al. developed a method driven by an electric field to vertically orient the related long MFI-type zeolite rods.\textsuperscript{30} Chao and co-workers used anodized alumina discs to grow vertical metal-doped aluminumphosphate molecular sieves.\textsuperscript{31} However, the degrees of close packing and uniform orientation achieved by the above cases cannot compete with those of v-(PyB\textsuperscript{+})\textsubscript{L}-g.

In conclusion, we have described how zeolite L monolayers can be prepared on glass in two orientations. The organized monolayers can be applied as novel supramolecularly organized systems for the demonstration of anisotropic photoluminescence in high dichroic ratios,\textsuperscript{32} to study energy-transfer dynamics between internally and externally placed fluorophores,\textsuperscript{33,34} and to develop zeolite-based advanced materials. The vertically assembled zeolite L monolayers also have the potential to be transformed into continuous films with one-dimensional channels all oriented perpendicular to the substrate, an arrangement that has been shown to be very difficult to obtain.\textsuperscript{35}
**Experimental Section**

Materials: The cylindrical and hexagonal columnar zeolite L crystals were prepared according to procedures described previously.[26] PyB\(^+\)FeCl\(_4\)/Co, AP-TMS, CP-TMS, dimethylsulfoxide (DMSO), and glycerol were purchased from Aldrich and used as received. PyB\(^+\) ions were incorporated into zeolite L crystals (3 g) by aqueous ion exchange of K\(^+\) ions in zeolite L with PyB\(^+\)FeCl\(_4\)/Co (180 mL, 0.1 M) under reflux (90 min). After rigorously washing the PyB\(^+\)-exchanged zeolite L with distilled deionized water, it was further washed with DMSO by soxhlet extraction for more than 24 h until no further PyB\(^+\)FeCl\(_4\)/Co was detected in the DMSO. The washing step with DMSO is highly recommended to rigorously remove the physisorbed PyB\(^+\)FeCl\(_4\)/Co salts from the external surfaces of the zeolite powders.

Analysis of the amount of PyB\(^+\) ions according to the method of Minkowski and Calzaferri[36] revealed that the incorporated amount corresponded to 1.7 ions per channel. Although the incorporated amount was rather low, the incorporated PyB\(^+\) ions were aligned with the channel direction as reported by Calzaferri et al.[21] (see the Supporting Information for more evidence).

The AP-tethered PyB\(^+\)-containing zeolite L crystals and CP-tethered glass (CP-g) plates were prepared according to the standard method developed in our group.[14] v-(PyB\(^+\))L-g and h-(PyB\(^+\))L-g were prepared by the SS method according to the procedure described in the Supporting Information.[19]

**Keywords:** fluorophores · luminescence · monolayers · zeolites

Received: January 8, 2006  
Revised: May 17, 2006  
Published online: July 11, 2006

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**Figure 3.** Schematic illustration of the morphology-dependent change of the orientation of zeolite L crystals during assembly of the monolayer by the SS method. While the cyl-AP-(PyB\(^+\))L crystals assemble into a vertically oriented monolayer, the hex-AP-(PyB\(^+\))L crystals assemble into a horizontally oriented monolayer on CP-g plates.

**Figure 4.** Anisotropic fluorescence spectra and dichroic ratios: a) Normalized anisotropic fluorescence spectra (S\(_{vVV}\), S\(_{vVH}\), S\(_{vHV}\), and S\(_{vHH}\)) of v-(PyB\(^+\))L-g and the fluorescence spectrum of the 1 μM solution of PyB\(^+\) ions in glycerol (S\(_{GL}\)). The inset shows the peak positions of the spectra.  
b) S\(_{vV}\) and S\(_{vHH}\). c) S\(_{vVH}\) and S\(_{vHV}\). The insets in (b) and (c) show the angle-dependent changes of I\(_{vVV}/I_{vHH}\) and I\(_{vVH}/I_{vHV}\), respectively.