Monolayer Assembly of Zeolite Crystals on Glass with Fullerene as the Covalent Linker

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Abstract: Glass plates tethered with 3-aminopropyl groups were prepared and fullerene (C_{60}) was mounted onto the amine groups via NH insertion of the terminal amine moiety into one of the double bonds of fullerene. Cubic zeolite-A crystals covered with 3-aminopropyl groups on the external surface were independently prepared by treating the crystals with (3-aminopropyl)triethoxysilane. The zeolite-A crystals readily assembled in the form of monolayers on the fullerene-tethering glass substrates when they were allowed to contact in boiling toluene. The assembled zeolite-A monolayers remained intact even after sonication for 5 min in toluene. In contrast, the assembly of zeolite crystals does not occur if the tethering of either 3-aminopropyl or fullerene is omitted. Based on the two contrasting results, the monolayer assembly of zeolite crystals on glass is proposed to occur by formation of a large number of propylamine−fullerene−propylamine covalent linkages between each zeolite crystal and the glass substrate. Scanning electron microscope images revealed that zeolite-A crystals assemble with a face pointing normal to the plane of the substrate. The monolayers consist of small domains comprised of about 110 closely packed zeolite-A crystals aligned in uniform three-dimensional orientation. The same procedure also worked well for the monolayer assembly of larger ZSM-5 crystals. Migration of the weakly bound zeolite crystals over the glass substrate driven by a large number of hydrogen bonds between the surface-bound amine groups on the neighboring crystals is proposed to play an important role in inducing the close packing.

Introduction

Assembly of small molecules in the form of thin films or organization of small molecules into highly ordered arrays of molecules on various supports has been the focus of intense interest during the last three decades as the ability to do so has many implications in material science and in the development of new electronic and optoelectronic devices.[1,2] Scrutiny of the general trend of this area reveals that the sizes of building blocks (molecules) have gradually increased from relatively small molecules such as alkanethiolates[3] and octadecyltrichlorosilane[4] to much larger molecules such as enzymes[5] (several nanometers) and gold particles[6,7] (several tens of nanometers). Extrapolation of the above trend predicts that the sizes of building blocks will soon approach several hundred nanometers or even several micrometers. Under such circumstances, single molecules with extremely large sizes or, more commonly, various types of systems of molecules will be encompassed into a class of building blocks. This signifies that chemists will soon face employing even the complex living organisms such as bacteria and cells as a new class of basic building blocks.[8] In support of our prediction, Whitesides et al.[9] also pointed out the trend of modern chemistry evolving away from the manipulation of sets of individual molecules toward the description and manipulation of systems of molecules, i.e., living cells and materials. The driving force for such a movement can be best explained by Ozin's statement,[10] namely, "to be able to make nanostructures that are useful in electronic, optical, and information processing systems, chemists also have to dream up synthetic methods that have the ability to position objects having nanometer dimensions in appropriately connected organized arrays." Besides, we believe the knowledge accumulated during the course of assembly of very large building blocks, in particular, various micrometer-sized inorganic crystals by use of very small amounts of organic compounds, will help chemists better understand nature's biomineralization processes[11] and apply the acquired knowledge to the advancement of ceramic material science that will lead to the development of various other new valuable materials.[12,13]

In doing so, however, we anticipate many obstacles. For instance, it is expected to be extremely difficult to gain control over the orientation of very large building blocks during their assembly since large substances with the sizes of micrometers are usually not soluble in any solvents. Moreover, very large

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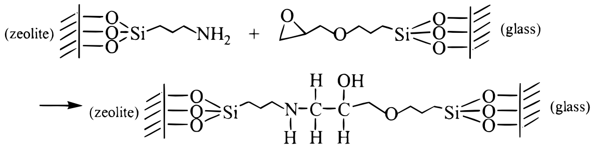
building blocks are generally too inert to be directly interconnected by themselves at moderate reaction conditions since the reactivity of substances generally decreases with increasing size. One way to overcome such poor reactivity of very large building blocks would be to "interweave" them with smaller hence more reactive "molecular wires" or "molecular strings".

On the basis of the above strategy and using zeolite crystals as the prototypical well-defined building blocks, we recently demonstrated facile assembly of cubic zeolite-A crystals of ~0.5 μm and hexagonal prismatic crystals of ZSM-5 of ~15 μm (longest axis) in the form of one-dimensionally oriented monolayer on glass and mica substrates.[14] In the previous report, the assembly of zeolite crystals on the substrates was carried out by a large number of β-hydroxy imine linkages between each zeolite crystal and the substrate according to eq 1.



(1)

In fact, the orientation-controlled assembly of zeolite crystals in the form of well-defined monolayers is of great importance even for its own sake since this is one of the ways to produce various zeolite membranes expected to be widely applied in industry.[15−24] The well-oriented monolayers of zeolite crystals also bear a great potential to be used as versatile media to effectively organize various semiconductor quantum dots in a highly ordered and oriented way.[10,25,26]

However, despite our previous success in developing a covalent molecular wire to organize zeolite crystals on the substrates, we believe further exploration of various other molecular wires and the methodologies to effectively use them should be continued since the strength of the crystal−substrate binding and the future application of the substrate−molecular wire−crystal composite materials will sensitively be affected by the nature of the interconnecting molecular wires.

We now introduce a novel molecular wire based on an amine−fullerene−amine covalent linkage which leads to highly oriented assembly of zeolite crystals on the glass substrate. This paper also discusses a possible mechanism for the observed spontaneous close packing of zeolite crystals on the substrate.

Experimental Section

Materials. Zeolite-A (Na^+ form) and ZSM-5 were synthesized according to the literature procedures.[27] The average size of zeolite-A used in this study was ~0.4 μm and that of ZSM-5 was ~$1.5 \times 1.1 \times 0.6$ μm^3. The template ions such as tetramethylammonium (TMA^+) and tetrapropylammonium (TPA^+) used to synthesize zeolite-A and ZSM-5, respectively, were not removed from the zeolites prior to assembly. (3-Aminopropyl)triethoxysilane from Aldrich was distilled and kept in a Schlenk storage flask under high purity argon. For simplicity, (3-aminopropyl)triethoxysilane and its 3-aminopropylsilyl moiety will be denoted as **APTES** and **APS**, respectively. Fullerene was purchased from Aldrich and was used as received. Cover glasses (18×18 mm^2) were purchased from Marienfeld and dipped into an acid bath consisting of sulfuric acid and ammonium persulfate for 1 h to remove organic residues on the surface. The acid treated glasses were washed with copious amounts of distilled deionized water and then with dilute aqueous ammonia before the final wash with fresh water. The washed glasses were dried at 120 °C for 3 h before undergoing the tethering steps with 3-aminopropyl groups. Fused silica plates of optical grade were purchased from CVI Laser Co. and the surfaces of them were similarly cleaned prior to treatment with APTES. Ninhydrin (1,2,3-triketohydrindene, Aldrich) was used as received. Toluene was treated with sulfuric acid at room temperature until the acid layer remained colorless. The acid-treated toluene was washed with distilled deionized water and dried with $CaCl_2$ prior to distillation over sodium under argon. Benzene and chlorobenzene were purified similarly. The purified solvents were kept in Schlenk storage flasks under argon.

Tethering APS Groups to the Glass Surface. For this purpose, we prepared a glass incubation chamber consists of a flat-bottomed cylinder (diameter = 10 cm, height = 10 cm) and a top lid (height = 2 cm) attached with a greaseless stopcock. The airtight connection between the top lid and the bottom cylinder was achieved by use of an appropriate O-ring. A round, finely perforated Teflon plate (diameter = 9 cm) with four supporting legs (length = 2 cm) was inserted into the glass chamber. A few (4 or 5) vials (diameter = 2 cm, height = 3 cm) were placed on the top of the Teflon plate and into each a freshly prepared cover glass was placed. On the bottom of the glass chamber, 0.3 mL of APTES was charged. The chamber was then evacuated at 10^{-3} Torr for 30 min at room temperature. The chamber was subsequently transferred into an oven whose temperature was maintained at 100 °C and kept there for 15 min. After being cooled to room temperature, the glass plates tethering 3-aminopropyl groups were removed from the chamber and washed with copious amounts of ethanol and finally with distilled−deionized water. The water-washed glass plates were then dried by blowing them using a gentle stream of high purity N_2. The water-treated glass plate was kept for 30 min in an oven at 120 °C.

Tethering APS Groups to the Zeolite Surface. The zeolites were washed with copious amounts of water until the wash was neutral. Centrifugation was necessary to separate the fine powders of zeolite-A from the aqueous slurry whereas the conventional filtration over filter papers was employed for ZSM-5. The washed zeolites were dried at 120 °C for 3 h before treatment with APTES. Typically, 50 mg of

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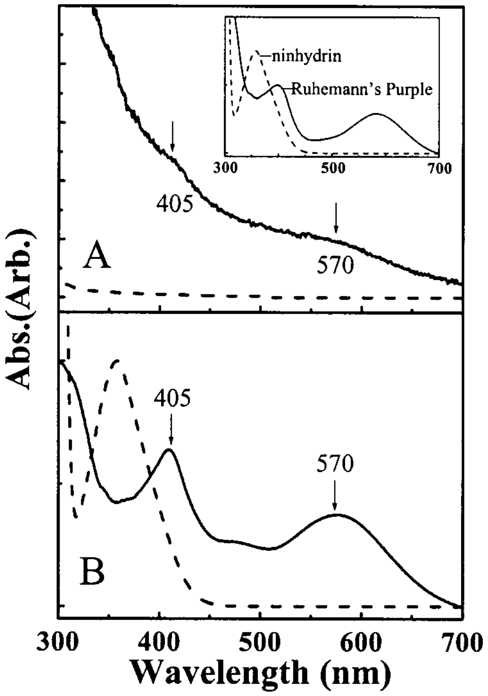


Figure 1. UV−vis absorption spectra of the APTES-treated fused silica plate after treatment with ninhydrin (A) and the supernatant solutions of the reaction mixtures of ninhydrin with APS-coated zeolite-A (—) and plain undoped zeolite-A (- - -) in ethanol (B). The inset shows the absorption spectra of ninhydrin and Ruhemann's Purple (as indicated) in ethanol.

zeolite was introduced into a small round-bottomed Schlenk flask containing 10 mL of dry toluene under the counter flow of dry argon. Into the toluene slurry of zeolite was added 0.3 mL of fresh APTES under an argon flow. The mixture was refluxed for 1 h under an atmosphere of argon. The APTES molecules are not expected to enter the interiors of the zeolites since the estimated minimum cross sectional diameter (kinetic diameter) of the propyltrimethoxysilane moiety (6.8 Å) is much larger than the pore openings of the Na^+-form of zeolite-A (4 Å) and ZSM-5 (5.5 × 5.3 and 5.5 × 5.1 $Å^2$). After being cooled to room temperature, the APS-coated zeolite powders were collected by rapid filtration in the atmosphere over a filter paper. The filter papers were wetted by toluene prior to filtration. Although submicrometer-sized zeolite-A particles readily pass through the filter papers in aqueous solutions, the toluene-soaked filter papers did not allow passage of the ultrafine particles in toluene presumably due to aggregation of the zeolite particles in the nonpolar organic solvent. The filtered powders were then washed with 100 mL of fresh toluene and subsequently with 100 mL of ethanol. The collected powders were then placed in an oven at 120 °C for 30 min.

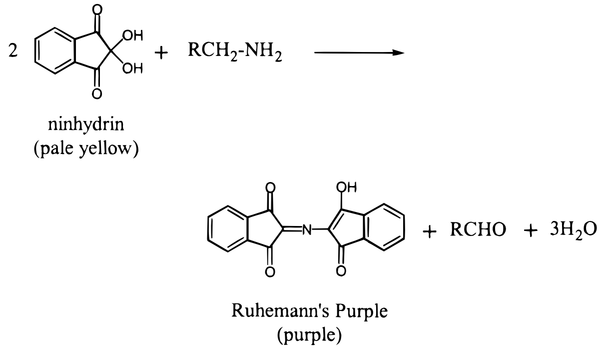
Reaction of Fullerene with Glass-Bound APS Groups. Fullerene (1 mg) and an APS-coated glass plate were introduced into a round-bottomed Schlenk flask containing 15 mL of toluene. The mixture was refluxed for 24 h under an argon atmosphere. After being cooled to room temperature, the fullerene-coated glass plate was removed from the flask and washed with copious amounts of chlorobenzene which has better solubility toward fullerene than toluene.

Reaction of APS-Coated Zeolites with Fullerene-Coated Glass Substrate. Freshly prepared APS-coated zeolite-A or ZSM-5 (~50 mg) and an APS-coated glass plate were introduced into a round-bottomed Schlenk flask containing 20 mL of toluene. The mixture was refluxed for 5 h under an argon atmosphere. The zeolite-coated glass plate was removed from the flask and sonicated in toluene for 2 min to remove physisorbed zeolite crystals.

Instrumentation. The scanning electron microscope (SEM) images of zeolites and the zeolite-coated plates were obtained from a FE-SEM (Hitachi S-4300) at an acceleration voltage of 10 kV. On top of the samples platinum/palladium alloy (in the ratio of 8 to 2) was deposited with a thickness of about 15 nm. The X-ray diffraction patterns were obtained from a Rigaku diffractometer (D/MAX-1C) with the monochromated beam of Cu Kα. The UV−vis spectra of the samples were recorded on a Shimadzu UV-3101PC. The diffuse reflectance UV−vis spectra of solid samples were obtained using an integrating sphere. The water contact angles of the modified glass plates were measured on a contact angle goniometer (rame-hart model 100-00). The values were taken from six different regions within a sample and 10 s after water was dropped. The reported values thus represent the averages. Sonication of the samples was carried out using an ultrasound cleaning bath operated at 28 kHz.

Results and Discussion

I. Confirmation of 3-Aminopropyl Groups on Zeolite and Glass with Ninhydrin. It is well established that Ninhydrin is readily converted to Ruhemann's Purple (diketohydrindylidene-diketohydrindamine) upon reacting with various alkylamines according to eq 2.[28] Ninhydrin has widely been employed as a convenient reagent to detect various alkylamines both qualitatively and quantitatively since the purple color of the resulting Ruhemann's Purple is very intense ($\epsilon = 22\,000$ at $\lambda_{max} = 570$ nm).[28] We also employed ninhydrin as a convenient reagent to confirm the presence of APS groups on the glass and zeolite surfaces after treating them with APTES. Instead of glass plates, fused silica plates were used for direct UV−vis spectrophotometric detection of Ruhemann's Purple on the support, since fused silica plates are optically transparent in the UV as well as in the visible region.



(2)

To allow the APTES-treated fused silica plates to adsorb ninhydrin, they were first dipped into an ethanol solution of ninhydrin (10 mM) for 5 min at room temperature. After removal from the solution, the ninhydrin-adsorbed plates were then gently warmed using a heat gun. Although weak, the UV−vis spectrum of the ninhydrin-adsorbed fused silica plates revealed the presence of the characteristic absorption bands of Ruhemann's Purple at 405 and 570 nm as shown in Figure 1A. In contrast, the plain fused silica plates (not treated with APTES) did not develop the corresponding bands of Ruhemann's Purple as compared by the dashed line in Figure 1A. The APTES-treated glass plates also showed the characteristic absorption bands of Ruhemann's Purple in the UV−vis spectra upon treating them with ninhydrin. On the basis of the two contrasting results, it was concluded that 3-aminopropyl groups readily mount on the top of the glass substrates via siloxane linkages according to Scheme 1, under our experimental conditions. In support of this, the glass plates showed a dramatic increase in the water contact angle from 6° to 73° after treatment with APTES. The measured water contact angle of 73° is in fact

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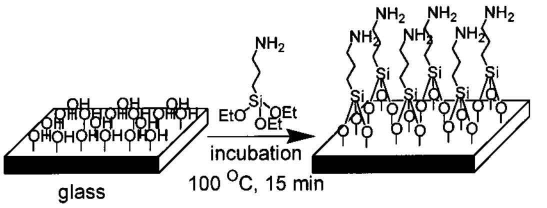
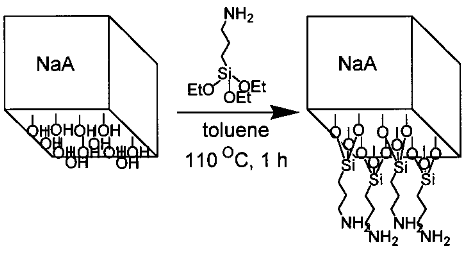
Scheme 1



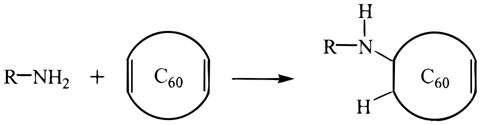
Scheme 2



somewhat larger than the reported values.[29,30] The observed higher water contact angle in our case may arise from the higher and more homogeneous surface coverage of the glass plates with APS, presumably due to the incubation method employed in this work which allows only the monomeric form of APTES to fly and react with the glass surface.

The presence of 3-aminopropyl groups on the zeolite surfaces was confirmed similarly. Thus, upon refluxing the ethanol slurry (50 mL) containing the APTES-treated zeolites (0.5 g) and ninhydrin (0.1 g), the slurry turned pale purple. The UV−vis spectrum of the supernatant solution showed the characteristic bands of Ruhemann's Purple, as shown in Figure 1B. The higher intensity of Ruhemann's Purple observed from the solution than from the fused silica plates is ascribed to a much larger number of APS groups anchored on the larger surface area of zeolite crystals. In contrast, the corresponding solution with the untreated zeolites gave only a single absorption band at 360 nm due to untreated ninhydrin. This result led us to conclude that the APS groups are readily anchored on the external surface of zeolite-A crystals when treated with APTES in boiling toluene according to Scheme 2. Although it is beyond the scope of this paper, the use of ninhydrin may further be developed as a means to quantitatively determine the number of APS groups on various supports.

II. Reaction of Fullerene with the APS Groups Tethered to Glass. It is well-known that alkylamines readily undergo N−H addition into one of the double bonds of fullerene according to eq 3.[30,31] Accordingly, the above reaction was



(3)

employed as a means to attach fullerene molecules onto the glass plates. For this matter, the APS-coated glass plates were refluxed in a fullerene solution of toluene for 1 day. Again, APS-coated fused silica plates were used instead of glass plates for direct UV−vis spectrophotometric detection of the fullerene moieties tethered to the substrate. The UV−vis spectra of the fullerene-tethered APS-coated fused silica plates showed a long tail absorption band that extends over 500 nm as typically shown in Figure 2. The dashed curve in the figure represents the spectrum of the analogous homogeneous reaction mixture of fullerene and 3-aminopropane, which also gives a similar long tail absorption characteristic of the amine-inserted fullerene. In contrast, the untreated fused silica plates showed only the characteristic absorption band of fullerene under the same experimental conditions as shown in the inset. Since saturation of one of the double bonds of fullerene gives rise to a similar long tail band that extends over 500 nm,[32] it was concluded that our experimental procedure also leads to facile mounting of fullerene on each APS group according to Scheme 3, via N−H insertion into one of the double bonds of fullerene. The disappearance of the characteristic bands of fullerene at 330 and ~500 nm (shown in the inset in Figure 2) further supports this since they are known to disappear upon saturating one of the double bonds.[32] Consistent with the fact that the fullerene group is less hydrophilic than the amine group, the water contact angle further increased from 73 to 86° upon introduction of fullerene groups over the amine groups.

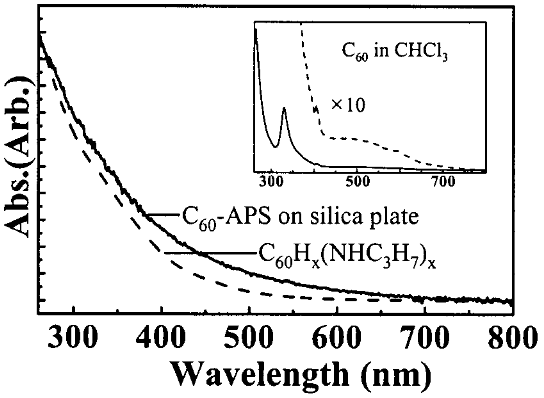
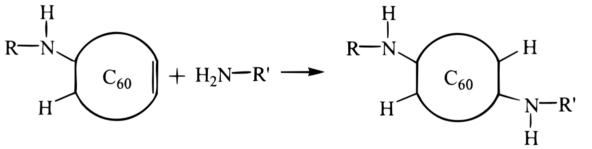


Figure 2. UV−vis absorption spectrum of the APS-covered fused silica plate after treatment with fullerene (—) and the related spectrum of the reaction mixture of fullerene with 3-aminopropane in chloroform (- - -). The inset shows the spectrum of fullerene in chloroform.

III. Assembly of Zeolite-A Monolayer. It has also been known that the amine-inserted fullerene can undergo a second insertion of an amine group as represented in eq 4.[30,31] The



(4)

above reaction was therefore adopted as a means to induce covalent linkage between the amine groups tethered to the zeolite surface and the fullerene groups anchored onto the glass substrates. This was done under the expectation that it will simultaneously lead to monolayer assembly of zeolite-A crystals on the glass substrates via amine−fullerene−amine linkages. Indeed, the glass plates tethered with fullerene turned uniformly opaque after refluxing for 5 h in a toluene slurry of APS-coated zeolite-A (Figure 3A). The SEM images of the opaque glass plates revealed the presence of zeolite-A crystals irregularly aggregated over a uniformly assembled monolayer of zeolite-A

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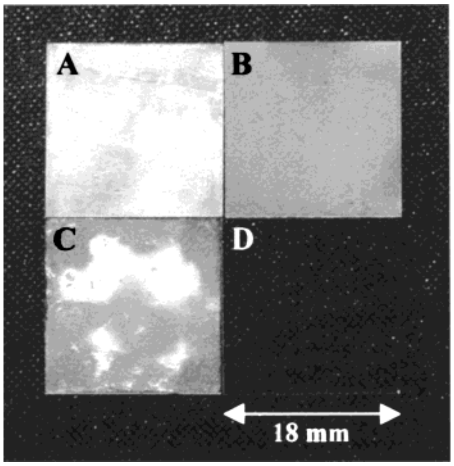
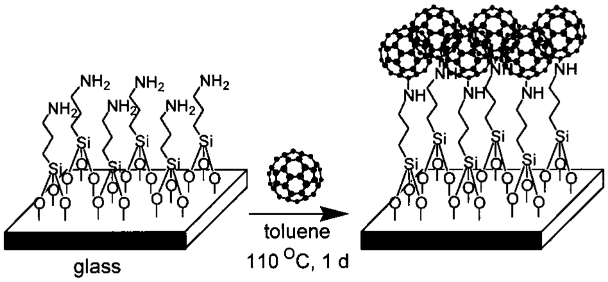


Figure 3. Photographic images of the glass plates covered with zeolite-A crystals from the reaction of the fullerene-tethering glass plate with APS-coated zeolite-A before (A) and after (B) sonication in toluene for 2 min and the corresponding images of the glass plates covered with only APS groups after reaction with APS-coated zeolite-A before (C) and after (D) sonication in toluene for 10 s.

Scheme 3



crystals as typically shown in Figure 4A. The irregular zeolite aggregates were easily removed by sonication for 1 min in toluene. As a result, only a monolayer of zeolite-A crystals was left behind on the glass plate as demonstrated in Figure 4B. Concomitantly, the entire glass plate then turned uniformly semitransparent as shown in Figure 3B. Thorough inspection of every corner of the glass plate with SEM revealed that the entire glass was covered with zeolite-A crystals with the degree of monolayer packing similar to the one shown in Figure 4B with very few defective spots.

Figure 4C shows a typical SEM image in a wider perspective (at lower magnification). This image further demonstrates that the entire glass plate is covered with the uniform zeolite-A monolayer with minor defects. We have repeated the above procedure more than 10 times and found that it is highly reliable and reproducible.

The assembled zeolite-A monolayer remained intact even after sonication in toluene for 5 min or in water for 1 min. This signifies that the binding between each zeolite-A crystal and the glass substrate is strong enough to endure the severe ultrasound-induced vibration of the crystals. Such a strong bonding is proposed to occur due to formation of a large number of amine−fullerene−amine linkages between each zeolite crystal and the glass substrate.

In strong contrast, the glass plates not doped with fullerene led only to nonuniform coverage over the glass plates even under the identical experimental condition (Figure 3C). Furthermore, the adhered zeolite crystals readily fell off from the glass plates even after a few seconds of sonication in toluene (Figure 3D). A similar negative result was observed when plain zeolite-A crystals (not doped with APS) or the plain glass plates not coated even with the APS groups were employed. On the basis of the

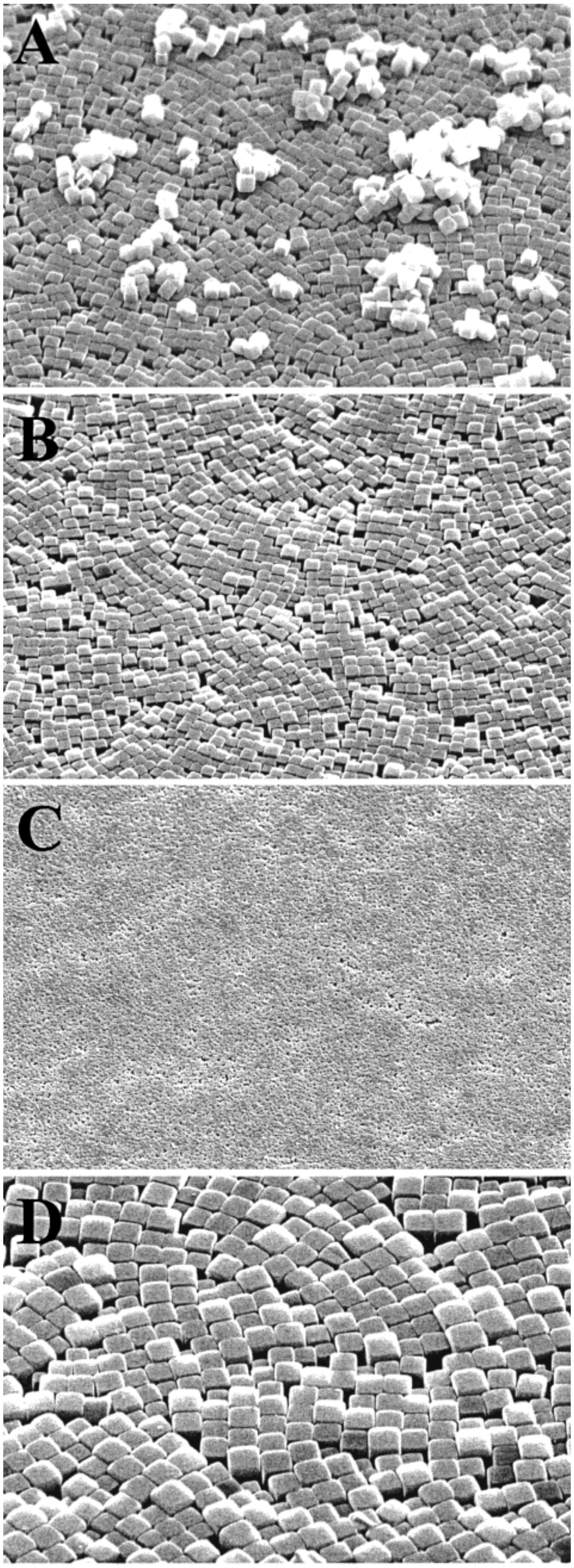


Figure 4. SEM images showing the monolayer of zeolite-A crystals bound to a glass substrate before (A) and after (B) removal of the irregularly aggregated zeolite crystals over the monolayer at the magnification of 7 K. Images C and D represent the monolayer at lower (1 K) and higher (20 K) magnifications, respectively.

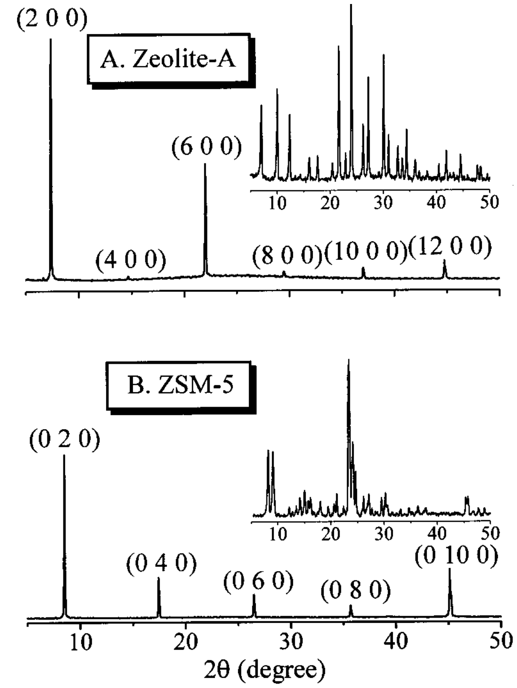
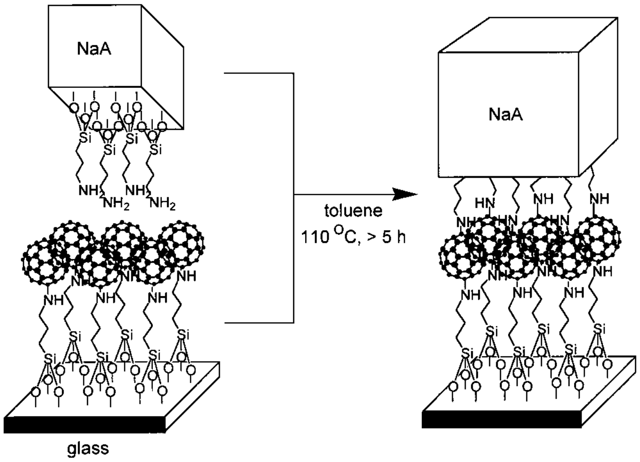


Figure 5. X-ray powder diffraction patterns of zeolite-A (A) and ZSM-5 (B) monolayers assembled on glass substrates showing the unidirectional alignment. The randomly oriented powder patterns are shown in the insets for comparison.

Scheme 4



two sets of contrasting results, it is concluded that zeolite-A crystals readily assemble on the glass plates according to Scheme 4 via a large number of amine−fullerene−amine covalent linkages with the nature of bonding described in eq 4.

Figure 4B further reveals that the cubic zeolite-A crystals invariably assemble with one of their three crystalline axes normal to the surface of the glass substrates. Consistent with the SEM image, the X-ray diffraction pattern of the zeolite-coated glass plates showed only the (h 0 0) reflection planes at $2\theta = 7.4$, 14.7, 22.1, 29.5, 37.1, and 44.8° for $h = 2$, 4, 6, 8, 10, and 12 as demonstrated in Figure 5A. Unlike our previous result,[14] even the (4 0 0) reflection is clearly visible in this case despite the fact that its theoretical intensity is less than 0.5% that of the (2 0 0) reflection.[33]

Interestingly, Figure 4B further reveals a strong tendency of the APS-treated zeolite crystals to pack with the neighboring side faces closely contacting each other. We believe such a tendency arises from the intercrystalline hydrogen bonding between the amine groups tethered on the zeolite surface, as was proposed in our previous report.[14] A similar tendency of close packing has also been observed on the glass substrates during the monolayer assembly of unmodified plain zeolite-A crystals by dip-coating.[16] The hydrogen bonding between the surface hydroxyl groups was also similarly proposed to be responsible for the observed close packing, in support of our proposal.

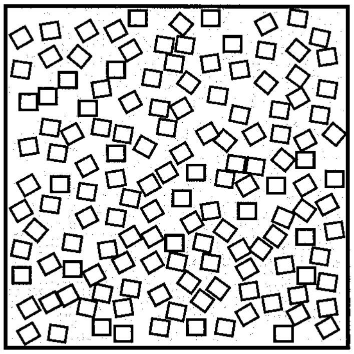


Figure 6. The imagined pattern of zeolite-A assembly on the substrate under the condition of no intercrystalline attractive forces.

The SEM image shown in Figure 4B further reveals that the zeolite-A monolayer actually consists of small domains in which all the zeolite-A crystals are not only closely packed but also three-dimensionally oriented. Thus, all three (*a*, *b*, *c*) axes of each zeolite crystal point to the same direction in the small domains. The average number of three-dimensionally packed crystals in the domains was counted to be about 110. This number corresponds to about 5 times of that of the zeolite-A monolayer assembled by our previous method. It is therefore concluded that amine−fullerene−amine linkage is more efficient in preparing a zeolite-A monolayer with a higher degree of three-dimensional orientation than the previously reported β-hydroxy imine linkage. We believe the slower reaction rate for the second amine insertion into fullerene (5 h) than that of nucleophilic attack of amine to epoxide (1 h) gives rise to such a difference.

The boundaries between the three-dimensionally oriented local domains are more distinctively visible at higher magnification shown in Figure 4D. If no attractive forces operate between the crystals, the pattern of crystal assembly should be random as depicted in Figure 6 rather than being compact, considering the steric factors. It is therefore appropriate to discuss the possible mechanisms for the observed close packing phenomenon of close packing among the zeolite crystals. Two possible mechanisms can be considered at this moment to account for the close packing phenomenon.

First, as illustrated in Scheme 5A, some of the zeolite crystals initially land over the glass substrate in a randomly scattered way and become firmly bound to the glass substrate through a large number of amine−fullerene−amine linkages. The randomly bound crystals then act as seed or template crystals to attract the subsequently landing crystals next to them via strong intercrystalline attractive forces. Thus, the subsequently landing zeolite crystals first adhere to the previously anchored crystals through a large number of hydrogen bonds between the zeolite-tethered amine groups and then undergo the bond-forming processes with the glass-bound fullerene units. For this mechanism to be viable, the bond-forming process between the zeolite-tethered amine groups and the glass-bound fullerene units should be sufficiently slow. If this is the case, the zeolite crystals adhered to the template crystals can provide a longer chance

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[33] Treacy, M. M. J.; Higgins, J. B.; von Ballmoons, R. *Collection of Simulated X-ray Powder Patterns for Zeolites*; Elsevier Science Inc.: New York, 1996.

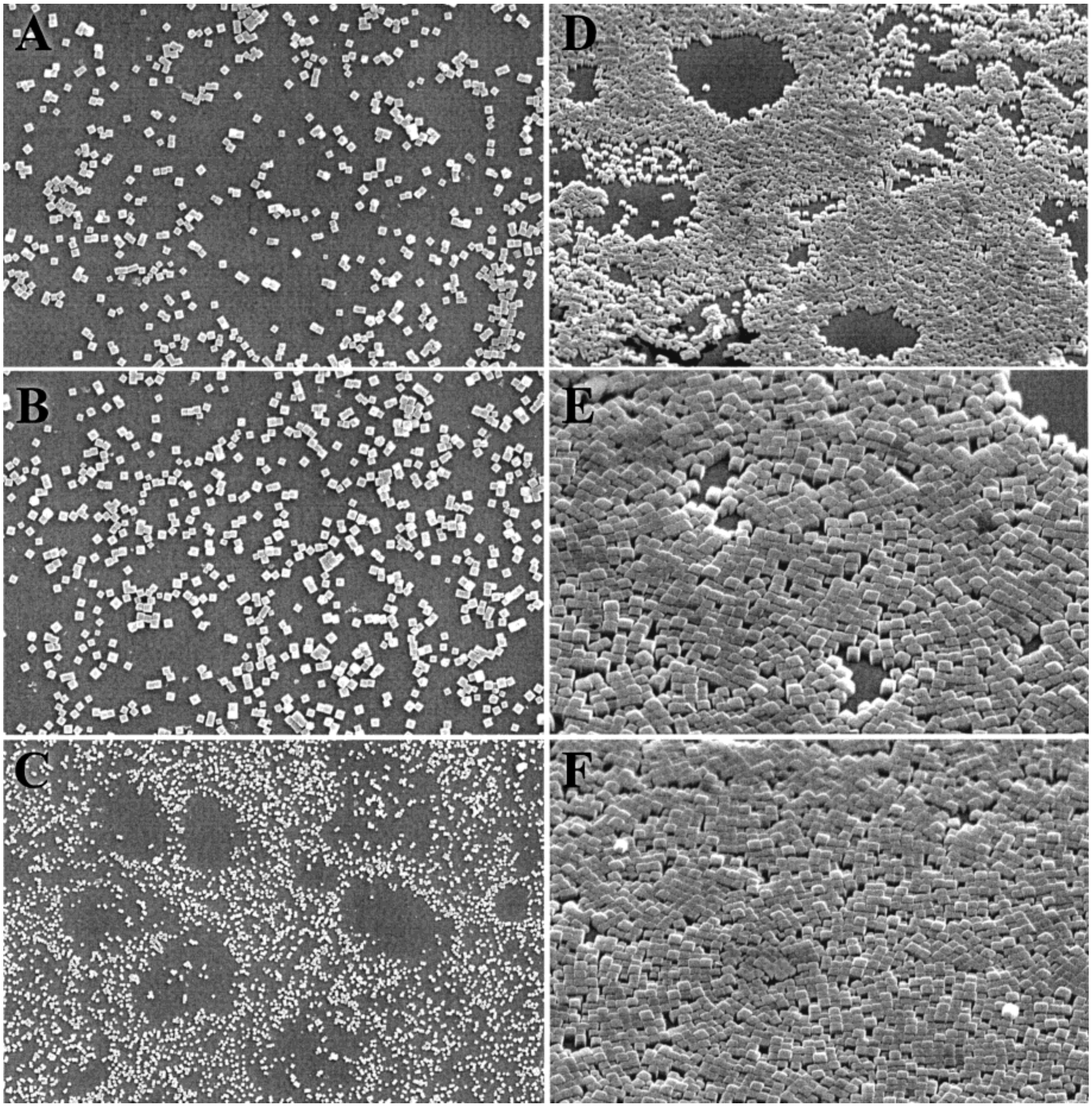
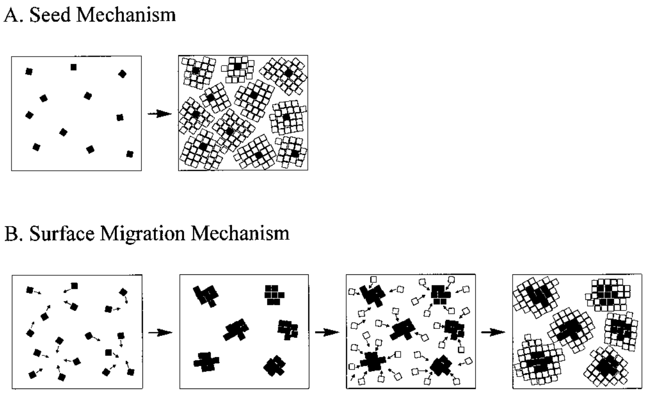


Figure 7. SEM images showing various spots with different degrees of coverage on a glass plate partially covered with zeolite-A crystals, at the magnifications of 3 (A), 4 (B), 1.5 (C), 3 (D), and 6 K (E, F).

Scheme 5



for their surface-bound amine groups to undergo slow bond-forming processes with the glass-bound fullerene units.

Alternatively, the zeolite crystals may initially loosely bind to the glass surface then undergo the subsequent close packing processes through migration over the glass surface as described in Scheme 5B. This mechanism requires the premise that the initial number of amine−fullerene covalent bonds between each zeolite crystal and the glass substrate is not large enough to prevent the bond breaking that allows migration of the crystals over the surface. The microscopic roughness of both surfaces may limit the actual number of initially formed amine−fullerene bonds between the glass substrate and each zeolite crystal. Accordingly, the overall strength of the molecular wires to hold each zeolite crystal onto the glass substrate may not be strong enough to prevent migration or escape of the crystal from one site to another through multiple bond breaking. If this is the case, then the zeolite crystals initially bound onto the surface may continuously migrate by repeated bond breaking and bond forming until they are finally held by more tightly bound crystals by a large number of hydrogen bonds between the surface-bound amine groups.

To obtain an idea about the mechanism for the close packing, several glass plates were removed from the reaction flasks before completion of zeolite assembly and their SEM images were analyzed. Interestingly, even within a partially covered glass plate, various spots with varying degrees of surface coverage were observed, as shown in Figure 7. Thus, the degree of coverage varies from very scarce (Figure 7A) to very dense (Figure 7F) together with varying degrees of intermediate coverage (Figure 7B through 7E). This result first reveals that zeolite assembly does not proceed homogeneously over the entire glass plate. Subsequent control experiments revealed that the glass plates removed shortly after reaction ($<$30 min) are dominated by the scarcely covered regions (Figure 7A) while the glass plates removed much later ($>$3 h) are dominated by the densely packed regions.

Scrutiny of Figure 7A reveals that two or three crystals already exist in the packed form even at very low coverage. Upon increasing the coverage, only the number of isolated single zeolite crystals increases while that of the closely packed crystals remains nearly the same. This phenomenon seems to eliminate the possibility of a “seed mechanism” depicted in Scheme 5A.

As the coverage keeps increasing, an interesting pattern of circles with the diameters of about 15 μm generally develops over the entire glass plate and the zeolite crystals start aggregating along the peripheries of the circles while the insides remain nearly empty (Figure 7C). At the early stage of circle formation, the degree of intercrystalline close packing still does not progress very much despite the fact that the absolute number of the zeolite crystals has increased substantially. This result further suggests that the seed mechanism in Scheme 5A is again less probable to account for the general phenomenon of close packing. However, based on the undeniable fact that a large number of zeolite crystals have migrated by any means from the insides of the circles to the peripheries, we are rather inclined to propose that the close packing occurs via the “surface migration mechanism” depicted in Scheme 5B. We think the bubbles with sizes of 10–15 μm that develop on the glass plates play a significant role in forming such circles.

As the number of zeolite crystals further increases, they tend to closely pack only along the periphery of the circles as shown in Figure 7D. From the wider perspective view, it was noticed that the number of empty circles generally increases on going from the edges of the glass plate toward the center. At the stage of Figure 7D, the boundary between the highly packed region and the empty central area becomes quite apparent. This figure also demonstrates the merging of the circles as the thickness increases. From the near absence of zeolite crystals at the centers of circles, the solvent bubbles are inferred to readily sweep the zeolite crystals away from the central area to the periphery of the packed circles. The area of the empty center keeps decreasing as the degree of coverage keeps increasing as shown in Figure 7E. Accordingly, the fully covered monolayer of zeolites usually carries the vestiges of circled patterns as typically shown in Figure 7E. Such a circled pattern is also clearly visible in Figure 4D.

When the assembly is carried out at a slightly lower temperature (90 °C) to suppress formation of solvent bubbles, the degree of circled pattern on the glass plate reduces significantly. Even in the absence of solvent bubbles, the tendency of the crystals to pack was still apparent. However, even at very high surface coverage, the resulting degree of intercrystalline close packing was observed to be less.

On the basis of the above results and discussions, we propose that surface migration of zeolite crystals gives rise to close packing of zeolite-A crystals during the monolayer assembly on the glass substrate by amine–fullerene–amine linkages. This surface migration mechanism is likened to the well-established surface crystallization processes of alkanethiolates adsorbed on gold substrates.[2,34] The micro solvent bubbles are also proposed to play important roles in assisting the surface migration of the zeolite crystals.

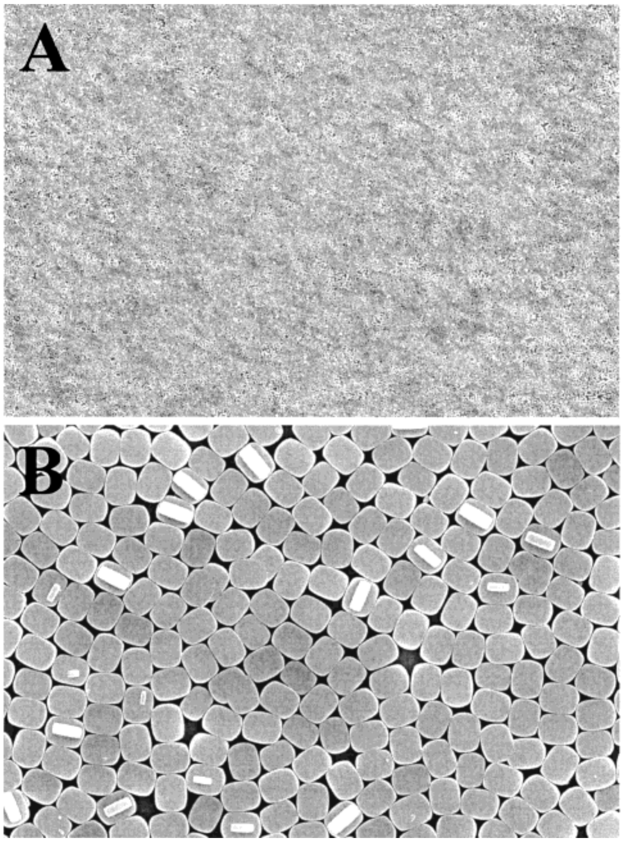


Figure 8. SEM images showing the monolayer of ZSM-5 crystals bound to a glass substrate at the magnifications of 0.3 and 5 K, respectively.

IV. Assembly of the ZSM-5 Monolayer. ZSM-5 crystals with an average size of 1.5 × 1.1 × 0.6 μm^3 were similarly assembled over the glass plates in the form of monolayer by applying the above methodology. Despite that the size was much larger than cubic zeolite-A (~0.4 μm) and the crystal edges were rather round, the above experimental procedure also worked very well for this zeolite. Panels A and B in Figure 8 demonstrate the closely packed monolayer of ZSM-5 on the glass substrate at the lower (×300) and higher (×5000) magnifications, respectively. As can be noticed in Figure 8A, the amine–fullerene–amine linkage is also highly effective in assembling the larger crystals on the entire glass plate with minor defective spots. Figure 8B further demonstrates the strong tendency of the procedure to induce close packing of zeolite crystals despite each crystal being strongly bound onto the substrate via covalent linkages. Figure 5B shows the X-ray diffraction pattern of the glass plate covered with ZSM-5. The appearance of only (0 *k* 0) reflections accords well with the SEM image (Figure 8B) showing that all the crystals are aligned with the *b* axis normal to the plane.

Great efforts have been made to provide insight into the orientation control of the zeolite or the related molecular sieve crystals during the preparation of continuous thin films, single crystals, and layers of preformed crystals on various substrates.[15–24] During the course of continuous thin film preparation, the orientation and morphology of the thin films have been found to be sensitively affected by the chemical composition of the precursor gel,[18c] synthesis time (film thickness),[16b,17a,b,18c]

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[34] Fenter, P.; Eisenberger, P.; Liang, K. S. *Phys. Rev. Lett.* **1993**, *70*, 2447.

roughness (morphology) of the substrate surface,[23] and nature of the chemical modification on the substrate.[23] Up to now, however, no general trends have been established on the control of the orientation and morphology of the resulting thin films and this still remains state of the art.

The orientation control of the resulting crystals in thin films has been shown to be easier if deposition of layers of preformed colloidal seed crystals on the substrates is carried out prior to successive film growth in the synthesis gel.[16a,17a] This is often referred to as secondary growth of thin films.[16,17] The orientation of the precursor seed crystals on the substrate has a strong orientation-directing effect on the orientation of the final film. Accordingly, the orientation control of the precursor seed crystals laid on the substrates has to be achieved to gain control over the orientation of the final continuous film. So far, dipping of the glass substrate into the aqueous slurry of seed crystals is the only reported method that gives rise to one-dimensional orientation of the laid seed crystals on the substrate.[16,24] During dip-coating, the removal speed[16] and tilt angle[24] (against the water level) of the substrate should be carefully controlled to achieve a satisfactory degree of uniform orientation of the laid crystals.

The surface coverage of the substrates with seed crystals is usually not high if only one cycle of the dipping procedure is carried out.[16] Accordingly, it is usually necessary to repeat the procedure several times until the surface coverage reaches a satisfactory degree for the subsequent film synthesis since the surface coverage also strongly affects the kinetics of the film growth. Before repetition of the dipping procedure, the substrates coated with seed crystals were calcined at high temperatures (>500 °C) to induce strong adhesion between the crystals and the substrate. Otherwise, the dip-coated seed crystals tend to fall off the substrates during the successive dipping processes. In this regard, the covalently linking procedure introduced in this work can be said to have many advantages over the dipping procedure with respect to high surface coverage, perfect one-dimensional orientation, and high degree of intercrystalline close packing.

Interestingly, the gold plates modified with metal phosphonate multilayer films have been shown to give rise to highly oriented crystals of zincophosphate[15a] and aluminophophate ($AlPO_4$-5)[15b] with the (111) and (001) planes normal to the substrate, respectively. The applied electric potential has also been found to be effective in aligning long columnar crystals of ZSM-5 and $AlPO_4$-5.[21] However, the latter is limited to those crystals with aspect ratios larger than 5 and not applicable to isometric crystals.

Overall, this paper demonstrates a novel procedure for assembly of closely packed monolayers of zeolite-A and ZSM-5 on glass plates by a large number of amine−fullerene−amine linkages. In the case of zeolite-A, the newly introduced covalent linkage yields much higher degrees of three-dimensional orientation of the assembled crystals than the previously reported β-hydroxy imine linkage.[14] The phenomenon of close packing between the assembled zeolite crystals is attributed to the surface migration of the weakly bound crystals. We believe the methodology introduced in this paper will serve as an experimental basis to prepare novel well-defined porous membranes useful for industrial purposes,[15−24] to provide ideal media for organization of semiconductor quantum dots necessary to develop novel optoelectronic materials,[10] and to develop well-defined nanoreactors to explore photochemistry and the related fine chemistry under the highly confined and organized conditions.[35] In addition, this work will lead to conceptual development of “the chemistry of crystal assembly” necessary to understand nature’s biomineralization and to develop the ceramic material science.

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