Fabrication of oriented zeolite L monolayers employing luminescent perylenediimide-bridged silsesquioxane precursor as the covalent linker

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Oriented zeolite L (LTL, $(M)_9[Al_9Si_{27}O_{72}]\cdot nH_2O$ (M = K^+ and Na^+)) monolayers with dense packing and high coverage degree has been obtained by using a luminescent perylenediimide-bridged silsesquioxane precursor as the novel molecular binder.

Organizing building blocks into versatile functional entities has been the focus of interest during the last several decades.[1] Great breakthrough in this regard has been made by arranging of micrometer-sized zeolite crystals into uniformly oriented monolayers on various supports *via* covalent linkers.[2,3] This can be simply realized by tethering organic functional groups onto either the zeolites or the substrates by covalent bonding followed by subsequent chemical linkage between the tethered functional groups and the unmodified surface. The resulting zeolite monolayers, displaying hierarchy of structure order, have served as supramolecularly organized light-harvesting systems[2,3g,4] and as excellent precursors for the preparation of continuous zeolite films with uniform orientations of the nanopores or nanochannels.[5] For instance,[2] unidirectional antenna systems have been realized by the subsequent insertion of different types of dye molecules in an oriented zeolite L monolayer, and this offers unique possibilities for developing photonic devices also comprising dye-sensitized solar cells and luminescent solar concentrators.[2c,6]

So far various types of organic functional groups including silyl groups and isocyanates[2,3] have been attached to the surfaces of zeolite and substrates by silylation and urethanation to yield uniformly oriented monolayers of zeolite A, ZSM-5 and zeolite L., *e.g.*, we have obtained very good oriented zeolite L monolayers with close packing and high degree of coverage by using TES-PCN,CP-TMS and BTESB as the molecular binder.[2] Despite the recent success in the fabrication of oriented zeolite monolayers with dense packing, the covalent linkers employed, including silyl groups and isocyanates, have had limited intrinsic functionalities. Adding additional functionalities such as luminescent properties to the covalent linkers should open a much wider entry for fabricating chemical devices as thus the linkers can transfer electronic excitation energy between the outside and inside of zeolite crystal nanochannels. Substituted perylenediimides, including perylenediimide-bridged silsesquioxane precursors, are one of the most extensively studied classes of organic semiconductor and have found possible applications in optical and electronic devices.[7,8] Perylenediimide-bridged silsesquioxane precursors,[8] tending to self-assembly through π–π interactions between the perylenediimide core, should be a good molecular binder for fabricating zeolite monolayers with luminescent properties. In this communication, we report the promising result regarding the fabrication of densely packed zeolite L monolayers on quartz by using the luminescent molecule, perylenediimide-bridged silsesquioxane precursor **1**, as the covalent linker.

Perylenediimide-bridged silsesquioxane precursor **1** shown in Fig. 1 was synthesized according to the published procedure.[8] The fabrication of closely packed zeolite L monolayer employing **1** as covalent binder was carried out according to the method shown in Scheme 1: typically, two pieces of quartz were immersed in an acetone solution (10 mL) of a perylenediimide-bridged silsesquioxane precursor (0.01 M) and reacted under argon overnight at room temperature (Scheme 1). The treated quartz and dried zeolite L (5 mg) were introduced into toluene (20 mL). The heterogeneous mixture was then sonicated for 10 min. The opaque zeolite L coated quartz was sonicated in a toluene solution for 5 s to remove the physisorbed zeolite L.

Medium-sized cylindrically shaped zeolite L crystals with 1 μm average length of average aspect ratio (length to diameter ratio) 1.0 were used in this study.[9] They have a very flat base as revealed by the SEM images shown in Fig. 2(a).

The quartz remains transparent after treatment with perylenediimide-bridged silsesquioxane precursor **1** and turns opaque upon contact with the zeolite L suspension in dry toluene and vigorous sonication. The opaque quartz turned semitransparent after sonication for 10 s in toluene. The scanning electronic images reveal the zeolite L crystals indeed self-assemble into a perfect oriented monolayer with the *c*-axis perpendicular to the surface of quartz. The degree of coverage is high and the degree of close packing is very high as evidenced by the SEM images shown in Fig. 2(b) where almost all of the zeolite L crystals are standing with the *c*-axis perpendicular to the quartz surface, with only very few zeolite crystals lying on the surface (as marked by rectangle). This

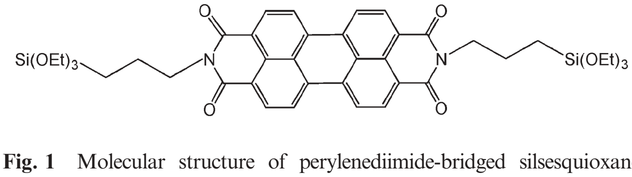

Fig. 1 Molecular structure of perylenediimide-bridged silsesquioxane precursor **1**.

Scheme 1 Procedure for fabricating zeolite L monolayers.

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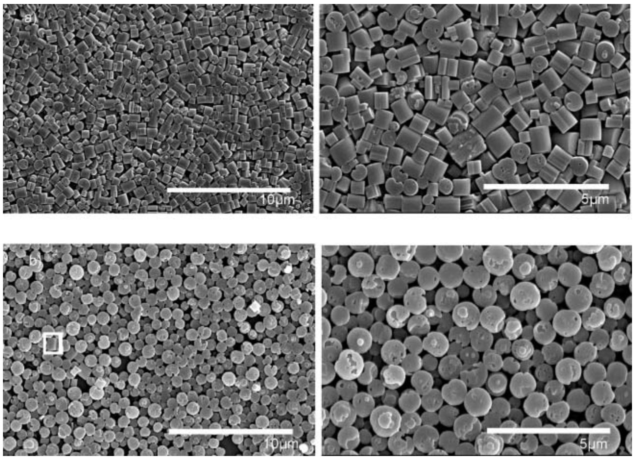

Fig. 2 SEM images of free zeolite L (a) and zeolite L monolayer (b). Simply lying zeolite L crystals on the quartz is marked by a rectangle.

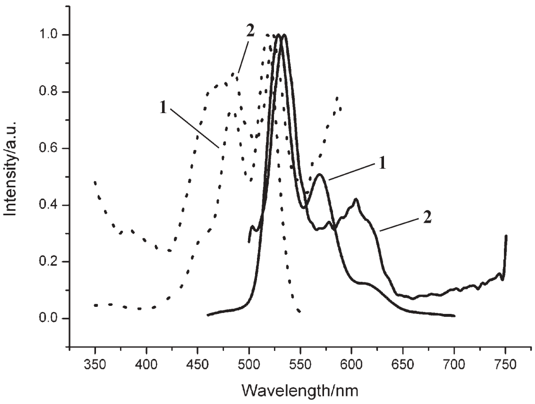

Fig. 3 Excitation (dotted) and emission (solid) spectra of precursor (**1**) in acetone solution and the zeolite L monolayer (**2**). The emission and the excitation spectra of **1** were recorded upon excitation at 460 nm and detection at 560 nm, respectively. Those of **2** were recorded upon excitation at 560 nm and detection at 640 nm, respectively.

is comparable with the result as described in ref. 2 and we can also observe from the SEM images that the size distribution of zeolite L in the monolayer form (see Fig. 2(b)) is narrower than in the free form (see Fig. 2(a)). This means only zeolite L crystals with similar size and morphology can self-assembly into a uniform zeolite L monolayer on the substrate. We should bear in mind that the concentration of the covalent linker used here is much lower than in that ref. 2 and the fabrication of the zeolite L monolayer was done at room temperature. The above result unambiguously means that compound **1** is a very effective covalent linker for the fabrication of densely packed zeolite L monolayers.

The luminescent properties of both the perylenediimide-bridged silsesquioxane precursor **1** in acetone and the oriented zeolite L monolayer **2** were investigated. The excitation (dotted line) and emission (solid line) spectra are shown in Fig. 3. The zeolite L monolayer was immersed into toluene solution to lower the light scattering during the measurement of excitation and emission spectra. Three well-resolved, relatively narrow peaks centered at 454, 483 and 517 nm can be observed from the excitation spectrum of perylenediimide-bridged silsesquioxane precursor **1** in acetone, which are matched by the corresponding emission peaks at 529, 568 and 616 nm. The oriented zeolite L monolayer **2** displays similar luminescence behavior, three less-resolved peaks with red-shift can be observed for both excitation and emission spectra. It is noteworthy that the emission peak centered at 568 nm in the acetone solution red-shifted to 618 nm after the perylenediimide-bridged silsesquioxane precursor was sandwiched between the quartz and zeolite L. This can be attributed to the closer packing of the perylenediimide molecules attached on surfaces of both quartz and zeolite L proceeding by –Si–O–Si– bonds.[8,10] We believe the close packing of perylenediimide molecules on the surface of quartz could be responsible for the fabrication of the densely packed zeolite L monolayer.

We conclude that a perylenediimide-bridged silsesquioxane precursor with luminescent properties was successfully employed to fabricate oriented zeolite L monolayers with a high degree of close packing and coverage on the surface of quartz. This new luminescent covalent linker has promising applications for trapping electronic excitation energy from donor molecules inside the crystal or injecting it to an acceptor inside the channels. This work is currently underway.

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