

# Microcontact Transfer Printing of Zeolite Monolayers

By Fabio Cucinotta, Zoran Popović, Emily A. Weiss, George M. Whitesides, and Luisa De Cola\*

Zeolites are aluminosilicates that are used in a broad field of applications.<sup>[1–7]</sup> Because of their ion-exchange capabilities, presence of well-defined rigid cavities, and transparency in the UV–vis/NIR region, zeolites can act as water softeners, catalysts, and host systems for a variety of photoactive guests.<sup>[1–7]</sup> In particular, zeolite L, which possesses unidirectional channels, has been shown to be a suitable material for supramolecular organization of different kinds of molecules.<sup>[8–10]</sup>

The size (30 nm to several micrometers) and aspect ratio of L-type zeolite can be controlled synthetically.<sup>[11]</sup> Furthermore, it has been shown recently that they can be organized in monolayers on a silica substrate by chemical functionalization. Interestingly, the orientation of the channels is perpendicular to the surface so that they can be filled after their immobilization.<sup>[12]</sup> However, reports on the formation of well-ordered monolayers on other (conductive) substrates have been very limited and so far it has not yet been possible to transfer them from one surface to another without disruption of the monolayer.<sup>[1,13]</sup> However, the preparation of an oriented monolayer of zeolite L crystals on certain substrates (silicon wafers, ITO, gold) represents an important prerequisite for achieving a controlled architecture of such microsized building blocks for possible optoelectronic applications. Many authors have reported several methods for pursuing this goal by chemical treatment of target surfaces via different kinds of molecular linkers, and in some cases perfect monolayers were achieved, especially for zeolite A.<sup>[12–16]</sup> We report a strategy based on the microcontact printing technique (MCP) to obtain well-ordered and uniformly oriented zeolite L monolayers on conductive surfaces without any chemical modification of the zeolite or the substrate.<sup>[17–20]</sup> MCP, which has been employed by many authors, represents an inexpensive tool for the formation of a wide variety of molecular assemblies, ranging from quantum dots and silicon particles to carbon nanotubes and nanowires, and it has been also applied to pattern materials allowing new applications in device fabrication.<sup>[21–26]</sup>

We have successfully applied this technique to create particular patterns with L-type zeolites that were filled with fluorescent dyes.

We have also demonstrated that it is possible not only to apply the method to cylindrical objects by transferring them and maintaining their orientation, but also to use the anisotropy of the systems to control the different color emissions of zeolites filled with two different dyes by exciting the materials with polarized light.

## Results and discussion

L-type zeolites were prepared according to previously reported methods and with two different aspect ratios: cylinders of 500 nm in diameter and 1  $\mu\text{m}$  in length, and discs of 1500 nm in diameter and 200 nm in height.<sup>[11]</sup> They were organized in monolayers on glass following established procedures.<sup>[14,27]</sup> (see Experimental section for details). In order to visualize the micro-objects and to determine the transfer efficiency at the end of the process, we filled the zeolites with fluorescent dyes.

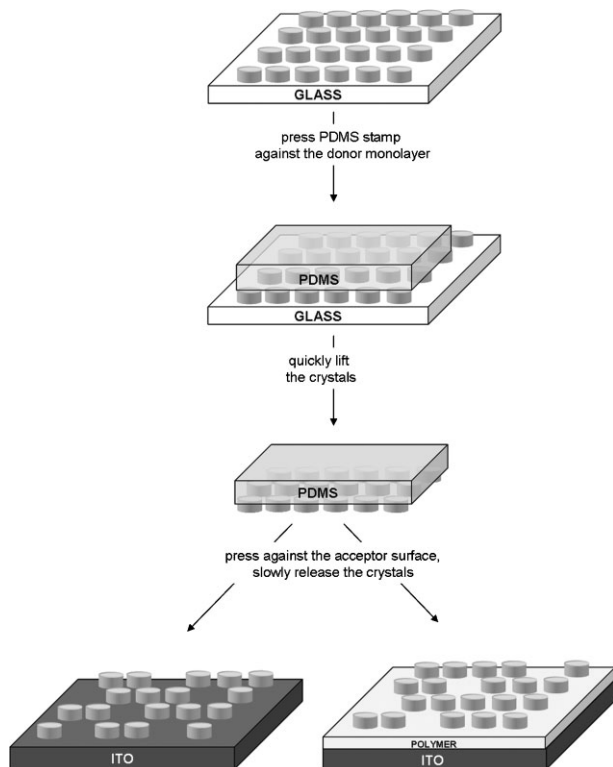
A polydimethylsiloxane (PDMS) elastomeric stamp was brought in close contact with the monolayer and, after applying pressure, was quickly peeled off. The peeled stamp picks up the crystals from the donor in a kinetically controlled step, preserving their orientation.<sup>[20,28]</sup> Finally, the PDMS stamp is pressed against an acceptor-conductive substrate (e.g., indium tin oxide, ITO, or ITO/polymer) and slowly peeled back releasing the crystals on the acceptor surface. The process is depicted in Figure 1.

ITO was chosen as a substrate since it is one of the most often used materials in optoelectronic devices because of its high transparency and conductivity. In principle, other conductive substrates can be used if they have a certain chemical affinity for the zeolites or if a polymeric layer can be spin-coated onto them before stamping. In fact, the polymer layer not only plays the role of a sticky substrate and in some cases smoothes the roughness of the substrate but more importantly increases the surface contact area since the zeolite crystal bases are not perfectly flat. We investigated polyaniline (PANI) and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS), which were spin-coated in 40 and 50 nm thick layers, respectively, onto the ITO surface.

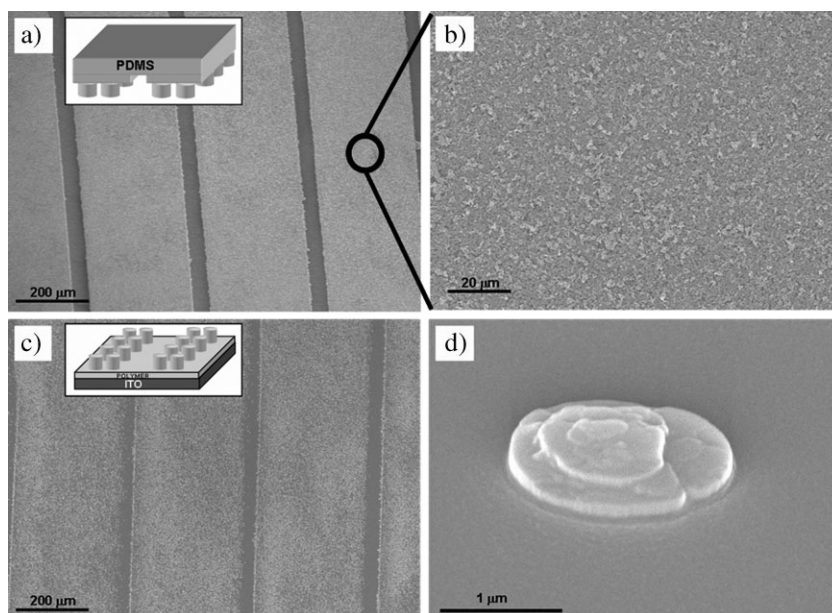
PDMS takes up almost all the crystals from the donor substrate. Air plasma pretreatment of the stamp, which produces hydroxyl groups on its surface, only slightly facilitates this step. In the printing step the transfer depends strongly on the substrate onto which we wish to transfer the monolayers. For bare ITO, the transfer was not complete; on average only a 45% coverage was achieved. The coverage was determined from fluorescent microscopy images (we used pyronine-loaded zeolite monolayers, vide infra) by estimating their bright/dark area ratio.

[\*] Prof. L. De Cola, Dr. Z. Popović, F. Cucinotta  
Physikalisches Institut and Center for Nanotechnology,  
CeNTech, Universität Münster Heisenbergstraße 11,  
48149 Münster (Germany)  
E-mail: decola@uni-muenster.de  
Prof. Dr. G. M. Whitesides, Dr. E. Weiss  
Department of Chemistry and Chemical Biology,  
Harvard University  
12 Oxford Street,  
Cambridge MA 02138 (USA)

DOI: 10.1002/adma.200801751



**Figure 1.** Schematic representation of microcontact transfer printing of a zeolite L-oriented monolayer from a glass (donor) surface to conductive (acceptor) surfaces.



**Figure 2.** Scanning electron microscopy (SEM) images of patterned zeolite L monolayers transferred on PDMS (a,b) and then printed on a PEDOT:PSS-coated ITO surface (c). d) An SEM image at higher magnification of a disc-shaped zeolite used for the monolayers.

The addition of the polymer layer to the ITO substrate typically increased the yield of the transfer up to 65%. Nevertheless, the average coverage was not 100% because of imperfections of the zeolite bases and as a result of the simple method we have employed.

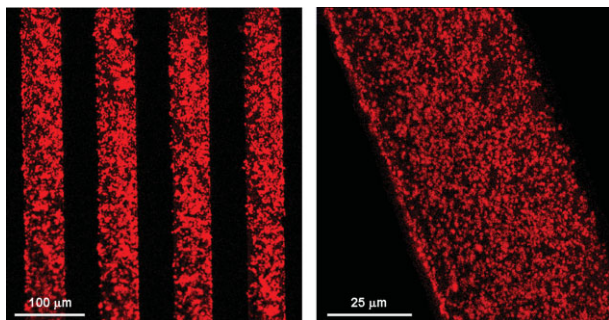
The main advantage of using microcontact printing methods is the ability to pattern molecules and nano-/micro-objects on substrates.<sup>[20–22]</sup> We have exploited this possibility and created zeolite L monolayer patterns on PDMS- and PEDOT:PSS-coated ITO surfaces (Fig. 2).

When using a PDMS stripe-patterned stamp (stripe size 300 μm) and following the same procedure as with flat PDMS, the zeolite crystals were completely transferred from the glass substrate to the PDMS patterned surface upon compression of the stamps on the monolayer. As can be seen clearly in Figure 2, the zeolite crystals are transferred on the stripes only and not on the grooved parts, reproducing the pattern present on the PDMS. The depth of the grooves (20–60 μm) was chosen to ensure that no contact would occur between the zeolite crystals and the groove surface under applied pressure during the transfer-printing process. We found that 1–2 μm deep grooves are not sufficiently deep for achieving a selective transfer of the crystals in a stripe-like geometry. The pattern is then transferred to the ITO or to the polymeric substrate. The use of filled zeolites with fluorescent dyes such as the red-light-emitting thionine dye resulted in fluorescent crystals patterned on ITO, as shown in Figure 3.

As expected the dyes contained in the zeolites had no influence on the transfer process but allowed us to determine the surface coverage and obtain a quantitative estimation of the transfer efficiencies by using fluorescence microscopy.

The narrow channel entrances (0.71 nm) and the rigid crystalline structure of the transparent zeolites provide a perfect basis for establishing the anisotropy of the system by means of light polarization experiments. In fact, it is known that, due to the confinement in the channels, the larger dyes will be frozen in a certain orientation within the channels and their electronic transition moments will also show a fixed orientation.<sup>[29]</sup>

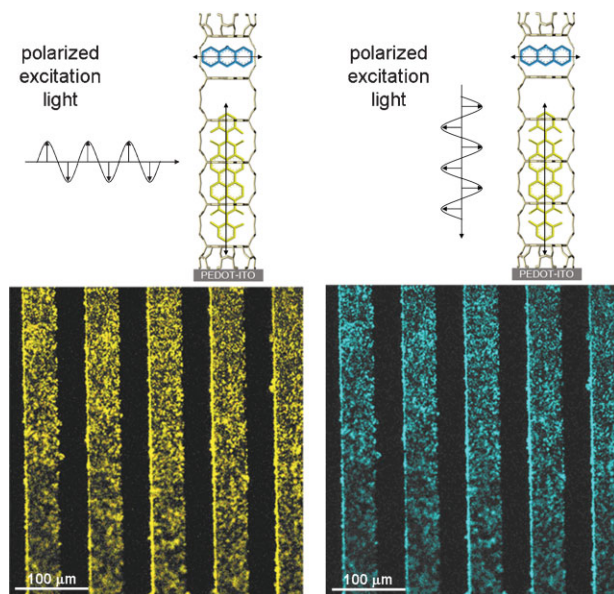
We have therefore decided to explore the possibilities of creating patterned stripes that have different emission colors by changing the polarization of the excitation light. To achieve this goal, we filled the zeolites with two different dyes possessing perpendicular electronic transition moments once entrapped in the channels. The *N,N'*-bis(2,6-dimethylphenyl)-perylene-3,4,9,10-tetracarboxylic diimide (DXP) dye, which shows a yellow emission upon 20% loading into the zeolites, is oriented parallel to the channels, and therefore perpendicular to the surface once the zeolites form the monolayers. The blue-emitting acridine dye and its methylated analogues possess an electronic transition moment perpendicular to the channels and therefore parallel to the surface.<sup>[9]</sup>



**Figure 3.** Fluorescence microscopy images of patterned thionine-loaded zeolite L monolayers printed on a PEDOT:PSS-coated surface.

After formation of the monolayer on glass, the zeolites were transferred using a patterned PDMS stamp to ITO with the strategy discussed above. The stripes obtained are of course fluorescent but, very interestingly, upon irradiation with polarized light, the color switches from blue to yellow. In fact, upon excitation with polarized light, only one of the two types of dye can absorb the light due to the coincident orientation of its electronic transition moment, leading to one-color emission. The process and the fluorescence images are depicted in Figure 4. Any modulation of the color can be obtained using different emission wavelengths of different dyes and we are exploiting several combinations for optical applications.

We have demonstrated that we are able to transfer a patterned monolayer of zeolite L from one substrate to another, different one without any chemical functionalization. The appropriate choice of fluorescent dyes trapped in the channels results in a pattern, for which we can modulate the color of the emission by changing the polarization of the excitation light.



**Figure 4.** Fluorescence microscopy images of patterned DXP- and acridine-loaded zeolite L monolayers printed on PEDOT:PSS-coated surface, illuminated under different light polarization conditions.

## Experimental

**Materials:** Disc-shaped (1500 nm in diameter and 200 nm in height) and cylindrical (500 nm in diameter and 1000 nm in length) zeolite L crystals were synthesized according to [11]. 3-Chloropropyl-trimethoxysilane (CP-TMS), 97+%, and polyaniline (emeraldine salt, 10 ml) were purchased from Aldrich, PDMS was obtained from Dow Corning Corporation (184 silicon elastomer base, SYLGARD), PEDOT:PSS (1:6 dispersion in water, Al4083) was purchased from HC Starck, toluene (stored over molecular sieves, puriss.,  $H_2O \leq 0.005\%$ ) and DXP were obtained from Fluka. Pyronine was synthesized according to [30]. Thionine and acridine were purchased from Sigma-Aldrich. Glass plates (1 cm × 1 cm, 0.2 cm thickness) used for starting zeolite L monolayers were obtained from Lionix and ITO plates were purchased from Präzisions Glas & Optik GmbH.

**Zeolite loading:** The zeolite crystals were loaded with the above-mentioned organic laser dyes according to well established procedures [8]. For cationic dyes, the desired amount of pyronine and thionine was added to a watery zeolite suspension while stirring and the suspension was heated under reflux for 2–24 h; after the ion-exchange reaction was completed, the zeolites were washed, typically with butanol, until the supernatant showed no fluorescence. For neutral dyes, acridine and DXP were inserted by a gas-phase reaction, filling a glass ampoule with zeolite powder and the required amount of dye and dehydrating the ampoule under controlled vacuum ( $10^{-6}$  mbar) for 2–8 h; the ampoule was then sealed and heated in a rotating oven to the sublimation temperature of the dye, respectively 110 °C for acridine and 300 °C for DXP; after the insertion was completed, the ampoule neck was broken and the zeolites were washed with butanol until the supernatant showed no fluorescence.

**Monolayers on glass:** Starting zeolite L monolayers were prepared according to a previously reported procedure [12]. Shortly after glass plates were cleaned with “piranha solution” ( $H_2SO_4/H_2O_2$ , 3:1) by refluxing at 100 °C for 1 h, the plates were washed with copious amounts of bidistilled water, then washed with ethanol, and finally dried at 80 °C. Next, the clean substrates were fixed in a Teflon support to avoid any surface overlap and the system was placed in a 100 mL round bottom flask containing toluene (20 mL). CP-TMS was added (0.8 ml) and the flask placed in an oil bath at 115 °C for 3 h. The treated plates were dried in air and placed in a  $1 \text{ mg ml}^{-1}$  separate suspension of disc-shaped zeolite L crystals in toluene that were previously sonicated for 30 min. Following another sonication step for 15 min, the plates were taken out, sonicated for additional 1 s in fresh toluene, and dried in air.

**Zeolite Transfer:** PDMS elastomer stamps were prepared by mixing silicon elastomer base and the curing agent in a 10:1 weight ratio. The mixture was homogenized and placed in a vacuum chamber in order to remove formed bubbles. The mixture was then poured in a Petri-dish forming a 5 mm thick layer and stored at 60 °C for 3 h. For the preparation of patterned PDMS stamps, the elastomer mixture was poured in a Petri-dish containing a prepatterned silicon wafer mask bearing different stripes-like geometry:  $50 \mu\text{m} \times 50 \mu\text{m}$  (width × depth) and  $300 \mu\text{m} \times 50 \mu\text{m}$ . The stamps were finally cut from a solid formed layer and then air-plasma treated for 1 min immediately prior to the transfer process. The ITO target substrates ( $1.5 \text{ cm} \times 1.5 \text{ cm}$ , 1.1 cm thickness) were precleaned with a sequence of solvents (soap, water, isopropanol, ethanol, and acetone) and coated with polymers. Polyaniline was spin-coated with a speed of 4000 rpm for 10 s resulting in a layer thickness of 40 nm, while PEDOT:PSS was spin-coated with a speed of 1200 rpm for 10 s and a layer thickness of 50 nm was obtained. The transfer of zeolite crystals from the starting monolayer on glass to the PDMS stamp was performed by pressing the PDMS stamp extensively with a thumb against the monolayer for 1 min, which was followed by a fast peeling of the stamp. In the printing step, the obtained PDMS-zeolite stamps were brought in contact with the ITO-polymer plates for 1 min (in the same manner as in the first step) and finally the PDMS was slowly peeled off, leaving the crystals attached to the polymer-coated ITO surface.

**Characterization:** The morphology of the zeolite monolayers was investigated using a Zeiss 1540 EsB dual beam focused ion beam/field emission scanning electron microscope with a working distance of 8 mm

and an electronic high tension (EHT) of 3 kV. Fluorescence microscopy was carried out with an Olympus BX-41 equipped with a Hg high pressure lamp, air objective 100 × 1.0, MBFL3, MWU2, U-MWB2, and U-MWG2 excitation cubes, a color camera, and a polarizer.

## Acknowledgements

Supported by the Westfälische Wilhelms-Universität Münster, Marie-Curie Research Training Network 'Nanomatch' [Grant No. MRTN-CT-2006-035884]. Supporting Information is available online from Wiley InterScience or from the author.

Received: June 23, 2008

Published online: December 4, 2008

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