

## Toward the Development of Ionically Controlled Nanoscopic Molecular Gates

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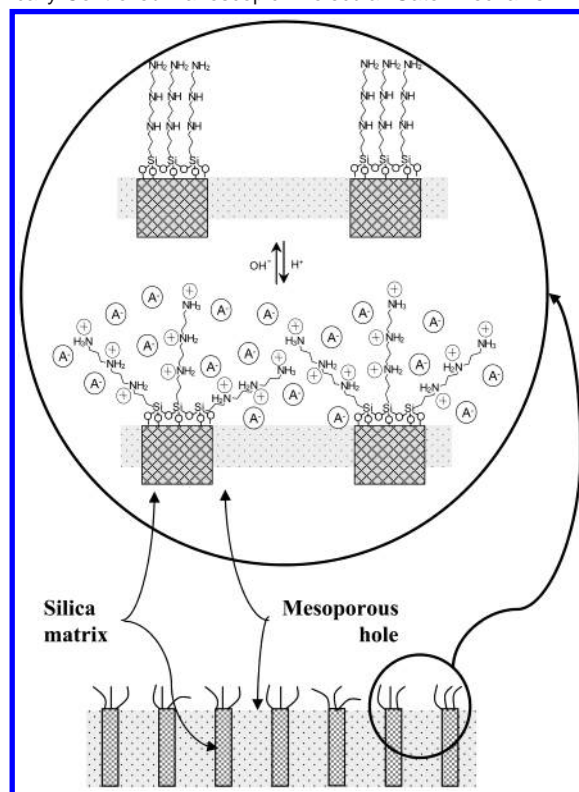
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Although coordination and supramolecular chemistry have been expanding during the past decades, their progress has been mainly limited to the synthesis of molecular receptors and to the study of their interaction with certain guests. A further advanced concept of current interest based on ideas developed within these fields is the design of controlled molecular devices.<sup>1</sup> Those are usually structurally organized supramolecular systems capable of developing specific functions. For instance, some examples have been described in which the control is photochemically, electrochemically, or ionically attained. However, in many cases this has been achieved at the molecular level and more rarely at the nanoscopic scale. Probably one of the more basic and scarcely studied functions in molecular behavior is that of controlled movement. Related to this idea, one basic supramolecular structure is the concept of molecular gate. A gate can be defined as a basic device that modulates the access to a certain site and whose state (opened or closed) can be controlled at will by certain external stimuli. Gates would be essential building blocks for the future construction of nanometric devices.<sup>2</sup> As a further advance in this field, here we show preliminary results on the design of ionically controlled nanoscopic molecular gates by using functionalized mesoporous materials.

Ordered mesoporous MCM-41-type solids<sup>3</sup> were chosen as supports because of two specific properties: their relatively well-known functionalization chemistry<sup>4</sup> and the presence of controlled pore size in the nanometric range. In addition, it is possible to obtain higher accessibility to the inner porous surface by using UVM-75-type materials, which are characterized by their nanometric particle size and bimodal pore system. It was our aim to demonstrate that a simple ionically controlled molecular gate can be created by using functionalized mesoporous materials with pH-responsive groups at the pore outlets. The functionalized solid **S1** was prepared following a two-step procedure. In the first step, (EtO)<sub>3</sub>Si-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SH was added during the synthesis of the mesoporous phase. Before template removal, a second reaction with (EtO)<sub>3</sub>Si-CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>(NHCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> was carried out. This approach was followed to get a preferential anchoring of the amino groups at the external surface while the mercaptothiol groups would remain inside the mesopores.<sup>6</sup> Finally, removal of the template resulted in the bis-functionalized derivative **S1**.

The idealized mechanism of the designed nanoscopic molecular gate is shown in Scheme 1. The open–close protocol would entail simple interactions involving protonated amines. From calculations based on chemical analysis and surface measurements (see Supporting Information), a total of 30 molecules per hole position was estimated, resulting in an occupancy of 22 Å<sup>2</sup> per polyamine moiety. This gives a near monolayer of polyamines at the external surface with an important number of amines around the outlet pore

**Scheme 1.** Representation of Solid **S1** with a Scheme of the Ionically Controlled Nanoscopic “Molecular Gate” Mechanism

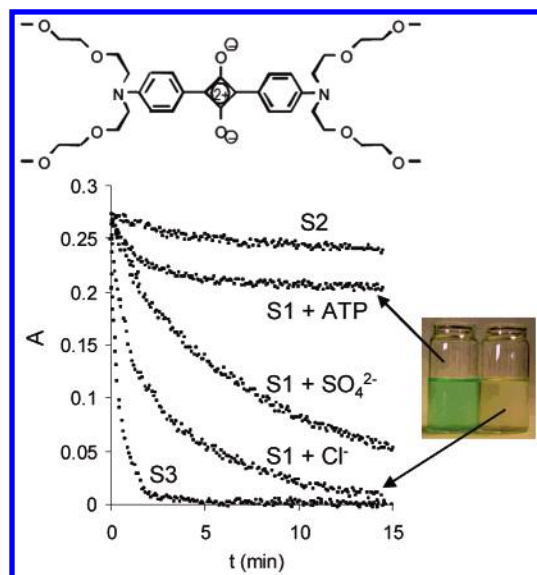


perimeter (see Scheme 1). For the sake of comparison, the solids containing only polyamines, **S2**, and only mercaptopropyl groups on the inner surface, **S3**, were also prepared and included in the study.

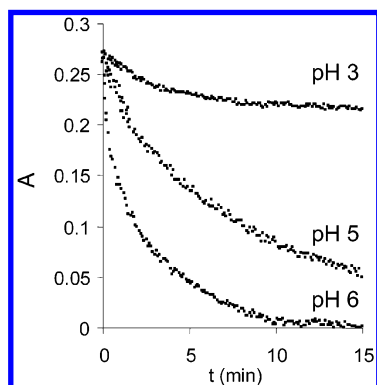
Both pH-controlled and anion-controlled gate effects are expected to occur. The pH-controlled “open–close” mechanism would arise from hydrogen-bonding interactions between amines (open-gate) and Coulombic repulsion between ammonium groups (closed-gate). When protonated, the open-chain polyamines in the external surface would adopt a rigidlike conformation and would be pushed away toward the pore openings (see Scheme 1). Additionally, a synergic anion-controlled outcome would result from the interaction (formation of complexes) between the protonated amines and a certain anion. Thus, for instance, a larger “shielding effect” controlling the access to the pores would be expected in the presence of bulky anions capable of displaying strong interactions with protonated amines than in the presence of small anions poorly coordinated by polyamines.

To study both the pH-controlled and anion-controlled mechanism, mass transport from the solution to the pores was monitored by

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**Figure 1.** Absorbance at 643 nm (squaraine band) vs time at pH 5 for solids **S1** in the presence of ATP, chloride, or sulfate (0.01 M) and **S2** and **S3** in the presence of ATP (0.01 M) in water/acetonitrile 90:10 v/v. The figure also shows a scheme of the used squaraine dye and a photograph of the **S1**-ATP and **S1**-chloride systems after 15 min of reaction.



**Figure 2.** Absorbance at 643 nm (squaraine band) vs time at pH 3, 5, and 6 for solid **S1** in the presence of sulfate (0.01 M) in water/acetonitrile 90:10 v/v. Curves for solids **S2** and **S3** at pH 3 and 6 (not shown) are similar to those in Figure 1.

using a colorimetric reaction consisting in the selective bleaching of a blue squaraine dye (see Figure 1) by reaction with the mercaptopropyl groups in **S1**.<sup>7</sup> In a typical experiment, the corresponding solid was mixed with water containing a certain anion (chloride, sulfate, or ATP at a concentration 0.01 M) and the pH was adjusted to the desired value. Then, an acetonitrile solution of the squaraine was added to give water/acetonitrile 90:10 v/v mixture. The mixture was stirred, and the absorption of the squaraine at 643 nm was measured vs time.

The dual anion and pH gating effect can be seen in Figures 1 and 2, respectively. In Figure 1, the pH is fixed (pH 5) and the absorbance of the squaraine band is measured versus time in the presence of solid **S1** for different anions: chloride, sulfate, or ATP. An anion-controlled shielding effect that tunes the accessibility to the pores was found. This effect can be clearly related to both the anion size and the strength of the polyamine–anion interaction (ATP > sulfate > chloride). Thus, **S1** does not react significantly with the squaraine probe in the presence of ATP (the nanoscopic gate is “closed”). In contrast, a complete bleaching was observed

after a few minutes in the presence of the small and weakly coordinating chloride anion (the nanoscopic gate is “opened”). The anion sulfate showed a behavior between that of chloride and ATP. Figure 1 also shows the reactivity of solids **S2** and **S3** in the presence of ATP (a similar behavior was found in the presence of chloride or sulfate). No reaction occurs between the blue squaraine dye and the thiol-free solid **S2**, whereas solid **S3**, only containing thiols and without any molecular gate mechanism, led to an almost instantly complete bleaching.

The pH-induced gating effect is shown in Figure 2, where the response of solid **S1** in the presence of sulfate (0.01 M) at different pH values is plotted. Thus, acidic solutions of squaraine in contact with **S1** remained blue for hours, indicating no reaction with thiols (the gate is closed), whereas bleaching was observed at more basic pH after some few minutes (the gate is opened).

In summary, we have demonstrated the possibility of developing ionically controlled nanoscopic molecular gates by using design concepts based on plain supramolecular ideas. The system shows that control of mass transport can be achieved by using suitable rigid solids and simple pH-responsive molecules. This proof-of-concept might open the door to new ionically tuned tailored materials and devices with a fine control of mass transport at nanoscopic scale for new applications in fields such as drug delivery, selective removal of toxic species, sensing, or catalysis.

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**Supporting Information Available:** Synthetic procedures and characterization of solids **S1**, **S2**, and **S3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) See, for instance: (a) Balzani, V. *Photochem. Photobiol. Sci.* **2003**, *2*, 459–476. (b) Liu, J.; Gómez-Kaifer, M.; Kaifer, A. E. *Struct. Bonding (Berlin)* **2001**, *99*, 141–162. (c) Lehn, J.-M. *J. Inclusion Phenom.* **1988**, *6*, 351–396. (d) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348–3391.
- (2) (a) Mal, N. K.; Fujiwara, M.; Tanaka, Y. *Nature* **2003**, *421*, 350–353. (b) Lai, Ch.-Y.; Trewyn, B. G.; Jeftinija, D. M.; Jeftinija, K.; Xu, S.; Jeftinija, S.; Lin, V. S.-Y. *J. Am. Chem. Soc.* **2003**, *125*, 4451–4459. (c) Zhao, M.; Tokuhisa, H.; Crooks, R. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2596–2598. (d) Liu, N.; Chen, Z.; Dunphy, D. R.; Jiang, Y.-B.; Assink, R. A.; Brinker, C. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 1731–1734. (e) Hernandez, R.; Tseng, H.-R.; Wong, J. W.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2004**, *126*, 3370–3371.
- (3) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710–712.
- (4) Stein, A.; Melde, B. J.; Schoden, R. C. *Adv. Mater.* **2000**, *12*, 1403–1419.
- (5) El Haskouri, J.; Ortiz de Zárate, D.; Guillem, C.; Latorre, J.; Caldes, M.; Beltrán, A.; Beltrán, D.; Descalzo, A. B.; Rodríguez-López, G.; Martínez-Máñez, R.; Marcos, M. D.; Amorós, P. *Chem. Commun.* **2002**, 330–331.
- (6) For similar synthetic procedures for preferential distribution of functionalized groups inside and outside the mesopores, see for instance: (a) Radu, D. R.; Lai, Ch.-Y.; Wiench, J. W.; Pruski, M.; Lin, V. S.-Y. *J. Am. Chem. Soc.* **2004**, *126*, 1640–1641. (b) de Juan, F.; Ruiz-Hitzky, E. *Adv. Mater.* **2000**, *12*, 430–432. (c) Shephard, D. S.; Zhou, W.; Maschmeyer, T.; Matters, J. M.; Roper, C. L.; Parsons, S.; Johnson, B. F. G.; Duer, M. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 2719–2723. (d) Lim, M. H.; Stein, A. *Chem. Mater.* **1999**, *11*, 3285–3295. (e) Feng, X.; Fryxell, G. E.; Wang, L.-Q.; Kim, A. Y.; Liu, J.; Kemner, K. M. *Science* **1997**, *276*, 923–926.
- (7) Ros-Lis, J. V.; García, G.; Jiménez, D.; Martínez-Máñez, R.; Sancenón, F.; Soto, J.; Gonzalvo, F.; Valdecabres, M. C. *J. Am. Chem. Soc.* **2004**, *126*, 4064–4065. Although it cannot be completely ruled out that a small number of thiols could be located on the external surface, the reaction of the squaraine would take place preferentially within the mesopores because of the large amount of thiols inside the pores.

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