Design of ionically-controlled nanoscopic molecular gates by using mesoporous materials and their applications

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Mesoporous silica of MCM-41S family discovered by Mobil researchers in 1992 has been paid much attention due to their scientific importance and great potential applications such as adsorption, catalysis, sensing, drug delivery or nanotechnology. Those silica materials own several features such as stable mesoporous structure, large surface areas, biocompatibility, and tunable pore size and volume at the nanometer scale. In order to achieve desired applications, often it is necessary the functionalization of mesoporous silica with active functional groups. The fine control of the functionalization of mesoporous materials might allow the design of controlled molecular devices. Those are usually structurally organized supramolecular systems capable of developing specific functions that can be controlled willfully by certain external stimuli. In this sense, it is possible to define the concept of molecular gate can be defined as a basic device that modulate the entrance or the release to a certain site and whose state (opened or closed) can be controlled at will by certain external stimuli.

Our group has been studying the design of ionically-controlled nanoscopic molecular gates by using mesoporous materials **[1]**. We have design a molecular gate by anchoring polyamine molecules onto the entrance of mesoporous silica materials of the MCM-41 type. The open – close protocol would entail interactions involving protonation of the polyamines.
These systems show that the control of mass transport from the solution to the a solid matrix can be achieved by using suitable rigid solids and simple pH-responsive molecules. A further advanced concept based on these ideas is the design of molecular devices that can be used as both mass transport control and sensing devices.

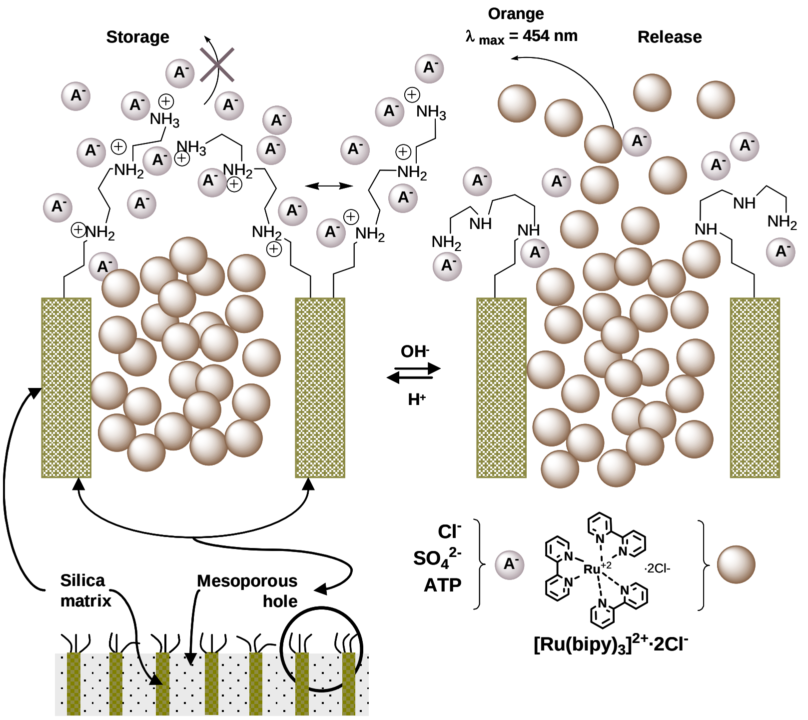
In our study the gate effect can be modulated by: •the type of amine used; •the pH of the solution; •the presence of different anions (Cl^-, SO_4^{-2}, PO_4^{-3}, and ATP); •the topology of silica used as support. In the first place we show a molecular gate able to control the release of different molecules or ions. The (Tris(2,2'-bipyridyl)ruthenium(II) cation has been used to follow the operation of the open-close mechanism of the pH and anion-controlled gate. The idealized mechanism of the nanoscopic molecular gate is shown in **Scheme 1**. Secondly we report a sensing application for colorimetric discrimination of ATP among ADP, GMP and other inorganic anions. It has been achieved by using the first tuneable hybrid sensory system based on controlled mass transport and molecular gate concepts (**Scheme 2).** The presence of certain anions that could interact with the charged polyamines might induce certain degree of pore blockage with the subsequent modulated release of the loaded dye. This mechanism allows to detect the presence of big anions as the ATP when often smaller anions are also present in the solution. ATP is the one able to completely avoid the release of the dye.

References:

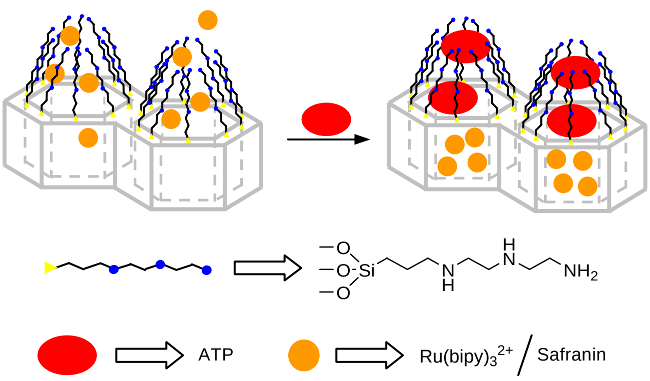
[1] Rosa Casasús, María Dolores Marcos, Ramón Martínez-Máñez, José V. Ros-Lis, Juan Soto, Luis A. Villaescusa, Pedro Amorós, Daniel Beltrán, Carmen Guillem, and Julio Latorre, J. Am. Chem. Soc., **126** (2004) 8612.

[2] R. Casasús, M. D. Marcos, R. Martínez-Máñez, and J. Soto., Chem. Comm., *(Submitted).*

Figures:



Scheme 1 Mechanism of polyamines as molecular gates.



Scheme 2 ATP sensing by using polyamines as molecular gates.