Nanoscopic hybrid systems with a polarity-controlled gate-like scaffolding for the colorimetric signalling of long-chain carboxylates†

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Received (in Cambridge, UK) 5th December 2006, Accepted 30th January 2007
First published as an Advance Article on the web 19th February 2007
DOI: 10.1039/b617703d

Hybrid mesoporous systems containing a gate-like ensemble functionalised with imidazolium groups and a dye are used for the selective colorimetric sensing of long-chain carboxylates.

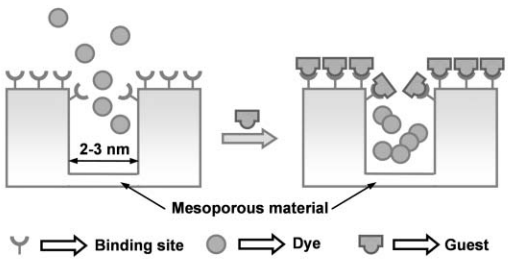
Carboxylates are chemical compounds that play fundamental roles in many different areas and a number of receptors have been designed for the recognition (selective coordination) of target guests containing carboxylic groups.[1] Some of these reported receptors have additionally been designed to display, upon coordination, chromo- or fluorogenic signalling opening the door to the development of probes for target carboxylates. Many carboxylate probes have been designed under the "binding site-signalling subunit" approach using ureas, thioureas, thiouronium and guanidinium as binding sites anchored to suitable dye scaffoldings.[2] Another less explored, but promising protocol for carboxylate detection, makes use of "displacement assays" that utilize receptors containing several binding sites on 1,3,5-triethyl-2,4,6-trimethylbenzene scaffoldings and a suitable dye that is selectively displaced upon guest binding.[3] However, such systems often harbour disadvantages; *i.e.* large synthetic effort, response in non-aqueous solvents, *etc*. Additionally, many of these probes, especially from the former approach, undergo nonspecific chromo-fluorogenic response to the carboxylate functional group and there are few examples for the colorimetric discrimination of individual members or subgroups of carboxylate families.[4]

Apart from developing enhanced selective chemosensors based in the above supramolecular protocols, there is interest in the design of novel functional molecular recognition and signalling concepts. At this respect prominent examples involving the combination of supramolecular ideas and nanoscopic scaffoldings, have recently been reported.[5] In the context of nano-supramolecular enhanced sensing, and as an alternative to the conventional "binding site-signalling subunit" or "displacement" approaches, we report herein the use of nanoscopic molecular gate-like scaffoldings on mesoporous supports and their use for the development of chromogenic or fluorogenic probes.

A nanoscopic gate is a molecular or supramolecular-based device able to control mass transport and that can be "opened" and "closed" by certain target molecules or other external stimuli.[6] The design of pores with stimulus-activated gating mechanism is a potentially fertile research in the nano-chemistry and nano-biotechnology fields. In relation to probe design, the sensing approach relying upon the use of gate-like ensembles is schematically shown in Scheme 1. It entails the use of solid structures containing nanoscopic pores. As suitable systems we focused on mesoporous MCM-41-type solids because of two specific properties: their relatively well-known functionalization chemistry and the presence of controlled pore size in the nanometric range (typically 2–3 nm). The pores of the mesoporous structure are then filled with a dye and the outer surface of the scaffolding functionalised with suitable binding sites. This is an open gate-like system that would allow delivery of the dye to the solution (see Scheme 1). The sensing protocol is based on the concept that addition of certain "key" guests might "close the gate" with the consequent recognition and signalling *via* dye delivery inhibition. This is a novel paradigm that displays a wide range of possibilities that could not be contemplated in classical receptors.[7]

Inspired in this conceptual approach the **MS-Im** solid was designed (*vide infra*) to assess the possibility of developing sensing hybrid gate-like scaffoldings controlled by polarity for the selective sensing of long-chain carboxylates. The **MS-Im** sensing material is a 2.5 nm pore diameter mesoporous MCM-41 support containing imidazolium groups as very simple but suitable binding sites and the $Ru(bipy)_3^{2+}$ complex as dye.

First, the surfactant-free MCM-41 support was prepared following literature procedures.[8] Then the MCM-41 support was suspended in acetonitrile and the dye tris(2,2′-bipyridyl) ruthenium(II) chloride (0.6 g, 0.8 mmol) was added at room



Scheme 1 Guest signalling protocols *via* inhibition of dye delivery using nanoscopic gate-like scaffoldings. (A) Mesoporous systems containing a dye within the pores and binding sites on the external surface (the gate is open), (B) addition of certain guests may eventually close the gate with the corresponding signalling of the target guest *via* dye delivery inhibition.

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† Electronic supplementary information (ESI) available: Synthesis and characterization of solid **MS-Im**. Imidazolium–carboxylate interaction. Colorimetric sensing. See DOI: 10.1039/b617703d

temperature with the aim of loading the pores of the mesoporous scaffolding. After this, imidazolium binding sites were anchored to the siliceous support by reacting with an excess of *N*-methyl-*N′*-propyltriethoxysilylimidazolium chloride (**1**).[9] Following this grafting procedure the imidazolium groups are preferentially attached to the pore outlets; *i.e* the functionalization would take place more easily on the external surface than inside the channels which are filled with the bulky sphere-like Ru(bipy)$_3^{2+}$ dye. That yields the final **MS-Im** material containing dye filled pores and an imidazolium-functionalised external surface. The **MS-Im** solid was characterized following standard procedures. Fig. 1 shows powder X-ray patterns of the calcined MCM-41 support and that of the **MS-Im** sensory material. The PXRD of siliceous MCM-41 as synthesized showed three low-angle reflections typical of hexagonal array that can be indexed as (100), (110) and (200) Bragg peaks with an a_0 cell parameter of 45.31 Å. In curve (b), corresponding to **MS-Im**, the loss of the (110) and (200) reflections reveals a decrease of contrast due to the filing of the pore voids with the ruthenium(II) dye. Nevertheless, the value and intensity of the d_{100} peak in this pattern strongly evidence that the loading process with the dye and further functionalization with imidazolium groups have not damaged the mesoporous 3D MCM-41 scaffolding. The mesoporous structure of the **MS-Im** material was also confirmed by TEM studies. Isothermal adsorption–desorption measurements on **MS-Im** resulted in almost flat curves. The absence of any porosity but at the same time the preservation of the hexagonal ordering (as indicated by the X-ray patterns and TEM images) provide direct evidence of the large loading of the pores with the Ru(bipy)$_3^{2+}$ dye. From thermogravimetric, elemental analysis and X-ray microanalysis, contents of 9 wt% and 17 wt% were found for the imidazolium group and the [Ru(bipy)$_3$]Cl$_2$ dye, respectively.

The capacity of the **MS-Im** solid to deliver the ruthenium(II) dye in the presence of different carboxylates ($CH_3(CH_2)_nCOO^-$, $n = 0$, 2, 4, 6, 8 and 10) was tested in aqueous solution. In a typical experiment, 10 mg of solid **MS-Im** were suspended in 25 mL of water (pH 7.0, HEPES, 10^{-3} mol dm^{-3}) containing the corresponding carboxylate ($C_{\text{carboxylate}} = 10^{-3}$ mol dm^{-3}) and the suspension was stirred until complete diffusion of the Ru(bipy)$_3^{2+}$ complex form the pore voids to the bulk solution was observed (maximum delivery is observed after 30 minutes). Finally the mixture was filtered off. The delivery of the dye is straightforwardly detected through monitorization of the d–π MLCT absorption of the Ru(bipy)$_3^{2+}$ dye ($\lambda_{\max}$ = 454 nm) in the aqueous phase. Because different pore blockage was observed depending on the molecular length, the presence of long-chain carboxylates can be assessed by visual inspection. This effect is shown in Fig. 2 that represents the difference in absorbance at 454 nm for dye delivery from the **MS-Im** solid and for the corresponding **MS-Im**–carboxylate system. This selective response is remarkable and shows the relevance that molecular gate-like ensembles could have in relation to the development of new molecular recognition and sensing paradigms.

The chromogenic response is related with the ability of positively charged imidazolium groups to form complexes with carboxylates.[10] From Fig. 2 it is noticeable that there is not a gradual pore blockage, but a rather "on"–"off" behavior; *i.e.* complete dye delivery for small carboxylates (from acetate to octanoate) that are not able to "close the gate" and complete blockage for longer carboxylates that act as molecular taps in the gate-like ensemble.

This open–closed protocol most likely has a dual character related with the size of the carboxylates and with the hydrophilic/hydrophobic nature of the formed monolayer (see Scheme 2). Coordination of small or medium carboxylates such as octanoate (or smaller) are not able to inhibit dye release from the pores to the bulk solution. On the other hand, dodecanoate would form, upon coordination with the imidazolium groups, a highly hydrophobic layer around the pore outlets that inhibit the delivery of the rather hydrophilic ruthenium(II) dye from the inner pores to the water phase. The formation of a highly hydrophobic layer around the pore outlets seems to be essential in the mechanism of the gate rather than the volume of the carboxylate. This could be observed when the delivery process was carried out in the presence of pivaloate and pentanoate because both carboxylates induced the same delivery of ruthenium(II) complex. This remarkable colorimetric "on"–"off" discrimination of long-chain carboxylates *via* the use of size- and polarity-controlled gate-like scaffolding, as far as we know, has never been reported and would be hardly achievable using conventional molecular probes.

The interaction of octanoate and docecanoate with imidazolium surfaces was studied in more detail with the **MS-Im** solid and with an analogous fumed silica support containing anchored imidazolium groups (but lacking the mesoporous structure). From

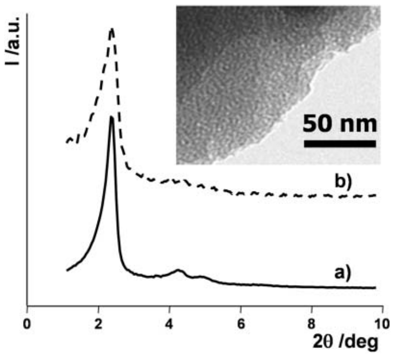


Fig. 1 XRD patterns of (a) MCM-41 calcined and (b) imidazolium-functionalized dye-containing material (**MS-Im**). The inset shows a TEM image of the **MS-Im** solid.

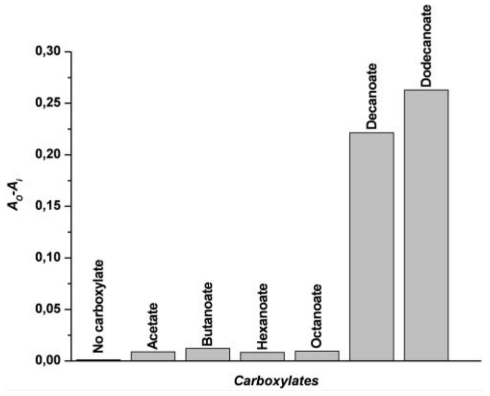
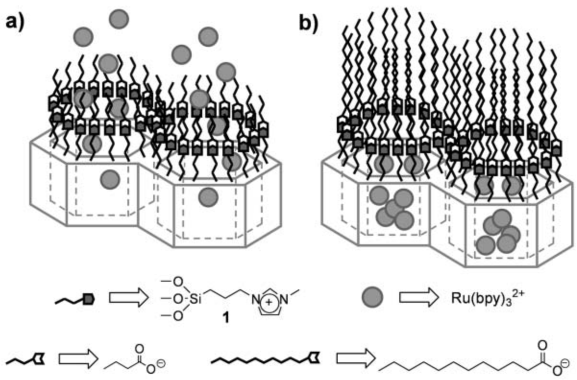


Fig. 2 Colorimetric response of the **MS-Im** sensory material in the presence of carboxylates of different length at neutral pH in water. The figure shows the difference in absorbance for the **MS-Im** system alone (A_o) and the absorbance for the corresponding **MS-Im**–carboxylate system (A_I).



Scheme 2 A representation of the sensory hybrid material **MS-Im** and the interaction of the gate-like ensemble with (a) butanoate (the "gate" remains "open") and with (b) dodecanoate (the "gate" is "closed").

these studies (involving elemental and thermogravimetric analysis) it was evident that both carboxylates trend to form a self-assembly monolayer on the imidazolium surface. These results suggest that the difference observed for dodecanoate and octanoate in relation to the delivery of the ruthenium(II) dye from the pores of the **MS-Im** support (see Fig. 2) is not just because different densities of the **MS-Im**-carboxylate at the pore outlets, but most likely due to the "gate-like" effect described above. This different behaviour displayed by octanoate and dodecanoate can also be seen in Fig. 3 that shows absorption *vs.* log $C_{\text{carboxylate}}$ curves for dodecanoate and octanoate using the sensory material **MS-Im** in water. As can be seen, dodecanoate is capable to completely inhibit dye delivery form the **MS-Im** solid at mM level, whereas octanoate (and also shorter carboxylates, not shown) do not have any effect even at very high concentrations up to 10^{-2} M. Also in preliminary results the presence of other anions or cations (*i.e.* chloride, bromide, carbonate, nitrate, sulfate, phosphate, sodium, potassium and calcium) does not inhibit dye delivery from the **MS-Im** material.

Finally, we were particularly concerned with the possibility that the observed effect was caused by a simple interaction of the carboxylates with the silica surface. To eliminate this possibility the delivery experiments were repeated using a MCM-41 support loaded with the dye but not functionalized with the imidazolium groups. This solid shows no selectivity and for all the carboxylates a similar dye release kinetic is observed. In an additional experiment, we found that the colorimetric signalling in Fig. 1 is only attainable using 3D supports and a similar paradigm could not be achieved on functionalized "flat" 2D silica supports; *i.e.* a solid prepared from fumed silica (not including the mesoporous structure) containing anchored imidazolium groups and a certain amount of adsorbed $Ru(bipy)_3^{2+}$ dye, does not display any sensing ability. Thus, it can be concluded that the colorimetric signalling discrimination to the naked eye of long-chain carboxylates is only observed for solids containing both, nanoscopic pores and coordinating groups at the pore outlets.

In resume, we have shown here the use of size- and polarity-controlled gate-like scaffolding for the development of new long-chain carboxylates recognition/signalling systems. The studies shown here may contribute to the rational design of selective chromo-fluorogenic probes for target guests based on the combination of functional nanoscopic properties (nanometrically organised solids) and supramolecular (gate-like scaffoldings) concepts.

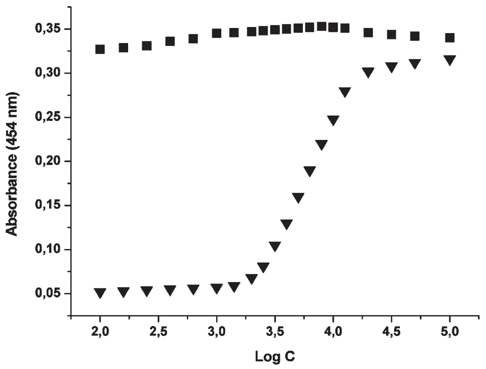


Fig. 3 Variation in the absorption (at 454 nm) *vs.* the logarithm of the concentration for dodecanoate (▼) and octanoate (■) using the sensory material **MS-Im** in water.

We thank the Ministerio de Ciencia y Tecnología (project CTQ2006-15456-C04-01/BQU) and Generalitat Valenciana (project GV06/101). C. C. thanks the UPV for a Fellowship.

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