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DOI: 10.1002/adma.200601958

Photochemical and Chemical Two-Channel Control of Functional Nanogated Hybrid Architectures**

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For many years, scientists working in the field of supramolecular chemistry have been interested in the topology and arrangement of functional groups within molecules.[1,2] Moreover, in many aspects supramolecular chemistry is still designed at the molecular level to reach complementarity between molecular systems in solution. In contrast, functional supramolecular aspects derived from *molecular motion* have been much less studied.[3] However, this can be of importance in the development of new, functional, biomimetic molecular systems.[4] In fact, many biological processes utilize molecular movable mechanisms that are triggered by specific chemical species. However, advanced control using multiple chemical or physical inputs of motion-based functional processes, for example, translocation, reversible mass movement, and controlled molecular transport, on the nanometer level is a landmark subject for the upcoming design of sophisticated molecular and supramolecular architectures.

Moreover, for such systems applications that have been realized by using multiple components in classical modular chemistry are often difficult to achieve. An attractive and suitable alternative approach to enhance functionality is the combination of supramolecular concepts with nanoscopic inorganic solids.[5] This could be achieved by using preorganized nanoscopic solid structures and molecular functional units attached to the surface of the inorganic supports in a synergic fashion. For example, recently reported examples have discovered that the anchoring of molecular entities onto 3D nanoscopic scaffoldings offers the opportunity for development and exploration of new supramolecular concepts that would hardly be achievable on "flat" surfaces (2D systems).[6–8] This is especially true in the field of gated nanochemistry, and its relation with the design of nanoscopic supramolecular architectures incorporating chemical entities that can act as a functional gatelike scaffoldings and allow control over the access to (or from) a certain nanometer-scale site at will.[9–20] This is a timely topic, yet the number of reported examples is still low, and they are usually of limited applicability. In particular there is a lack of multi-channel controlled nanogated systems. Additionally, among different possible external stimuli, the photochemical control of molecular gate-like ensembles is most appealing. However, to our knowledge only one example of gated hybrid materials with a light-driven mechanism has been described, through the use of photodimerization of anchored coumarin molecules in mesoporous materials.[11,12] This photoswitched gate was reported to control delivery of the entrapped guest (cholestane), but its use in *n*-hexane clearly minimizes future applications.

Following our interest in merging supramolecular with nanochemistry concepts, we report here the first two-input (i.e. photochemical and chemical) gated hybrid system, operative in water, and based on photoswitchable molecules anchored on a mesoporous silica support. The switching paradigm relies on the use of the spiropyran photochrome, which can be transformed reversibly between two forms upon the application of an external light source. When the spirocyclic molecule is kept in the dark or irradiated with UV light it isomerizes to the merocyanine form, which is either positively charged at neutral pH, or a zwitterion at high pH. The merocyanine form reverts reversibly to the closed spiropyran either thermally or by irradiation with visible light.[21–24] This is shown schematically in Scheme 1. The designed nanogated architecture is outlined in Scheme 2, and involves the building and disassembly of nanoscopic molecular structures using functional surfaces and reversible photoswitchable supramolecular forces.[25–27] This consists of a mesoporous MCM-41 support containing photoresponsive spiropyran moieties anchored to the pore outlets and a suitable dye, for gating monitoring purposes, in the pore voids. The molecular-gate effect was then achieved by introduction of an additional component to the system, generation 1.5 poly(amidoamine) (G1.5 PAMAM) dendrimers, which would act as nanoscopic molecular stoppers.[28] The closing sequence is light-driven, and stems from electrostatic interactions via the self-assembly of negatively charged dendrimers with the positively charged

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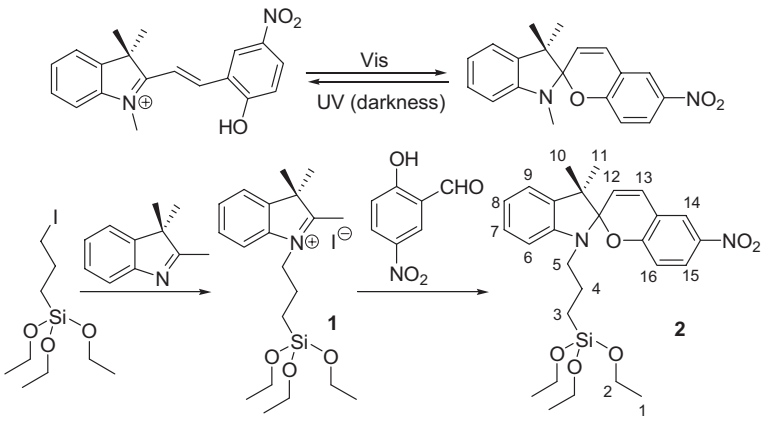
[**] We thank the Ministerio de Ciencia y Tecnología (project CTQ2006-15456-C04-01) for support. E.A. thanks the Ministerio de Educación y Ciencia for a doctoral fellowship. B.G.A. thanks the Generalitat Valenciana for a doctoral fellowship. F.S. also thanks the Ministerio de Educación y Ciencia for a Ramón y Cajal contract.



Scheme 1. Light-induced merocyanine–spiropyran transformation and synthesis of derivatives **1** and **2**.

merocyanine-functionalized surface. On the other hand, the opening of the pores occurs through merocyanine transformation to the neutral spiropyran form, which would not have affinity for the dendrimers, allowing release of the entrapped molecule to the bulk solution (see Scheme 2).

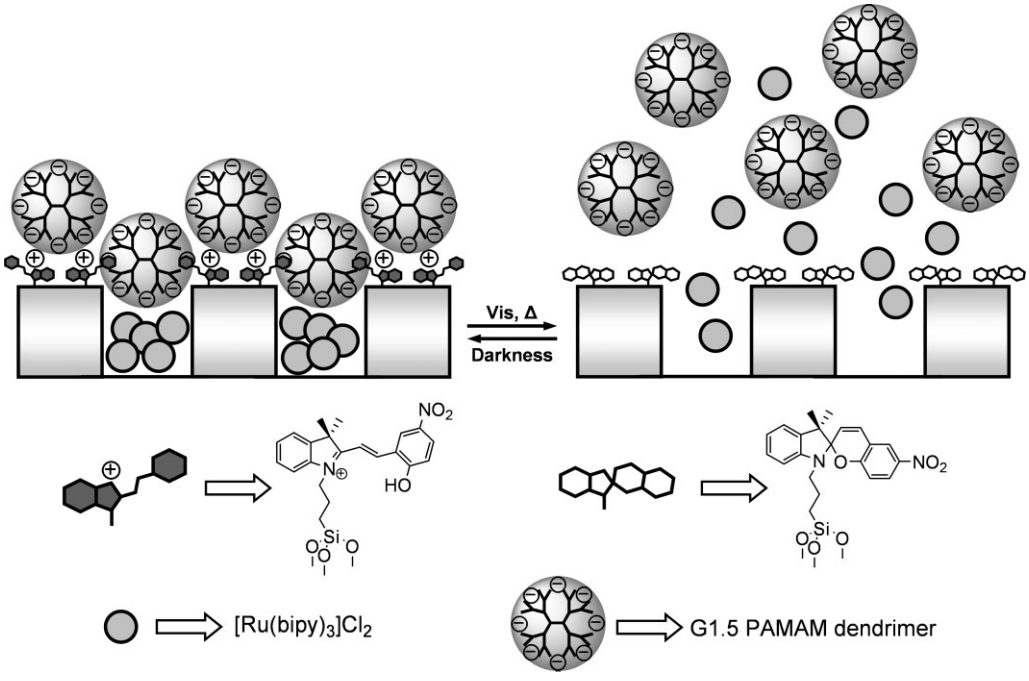
The spirobenzopyran derivative 1'-(3-triethoxysilanpropyl)-3'-3'-dimethyl-6-nitrospiro[2H-1]benzopyran-2,2'-indoline (**2**) was synthesized by a two-step procedure (see Scheme 1) whereas the MCM-41 mesoporous 3D support was prepared following known procedures.[29] The method for obtaining the final **S1** solid containing the $Ru(bipy)_3^{2+}$ dye in the pores and the spirobenzopyran derivative **2** anchored on the pore outlets, is described in more detail in the Experimental section.

As a reference solid **S2**, obtained by simple grafting of **2** onto an MCM-41 support free of the $Ru(bipy)_3^{2+}$ dye, was also prepared.

The light-induced merocyanine–spiropyran switching transformation can be seen in Figure 1, which shows the color transformation from yellow (spiropyran form) to pink-red (merocyanine form) observed in **S2** upon exposure to UV light. The performance of the **S1** material was tested in water at pH 7.2 in the presence of G1.5 PAMAM dendrimers ($c = 5 \times 10^{-5}$ mol dm^{-3}). This neutral pH was selected to keep the merocyanine in its positively charged form. Thus, titration experiments on **S1** allowed calculation of an approximate pK_a value of 8 for the phenolic hydroxyl group of the merocyanine anchored to the silica surface.

In a typical experiment, two samples of solid **S1** (10 mg) were suspended in 25 mL of the aqueous dendrimer-containing solution. One of the samples was irradiated with visible light and the other was kept in darkness

Figure 1. Color modulations of the spiropyran-anchored mesoporous **S2** after exposure to visible light (left) and to UV light or darkness (right).



Scheme 2. Schematic of the photochemical-chemical gating protocol in the hybrid **S1**. The system consists of a mesoporous MCM-41 framework containing a photo-switchable anchored spiropyran, a dye in the inner pores, and carboxylate-terminated G1.5 PAMAM dendrimers as molecular caps.

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(or irradiated with UV light). Both were stirred at room temperature for 2.5 h and then filtered. The release of the Ru^{II} dye from the pore voids to the aqueous solution was easily detected by monitoring the spin-allowed d–π MLCT band of the $Ru(bipy)_3^{2+}$ complex ($\lambda_{max} = 453$ nm). The effect of visible light on the dye delivery can be seen in Figure 2, which shows how the dye release is remarkably greater when irradiated with visible light for the solid containing the spiropyran form.

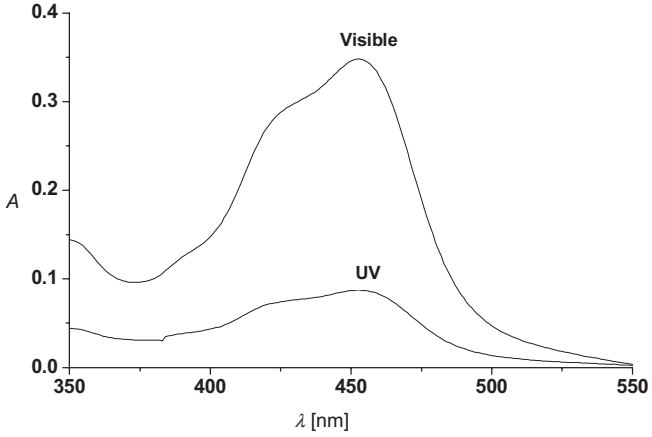

Figure 2. Vis spectra of $Ru(bipy)_3^{2+}$ complex released from **S1** to water at pH 7.2 in the presence of G1.5 PAMAM dendrimers for a solid irradiated with UV light (or kept in the dark) and a solid irradiated with visible light.

This result confirms the gating mechanism outlined in Scheme 2, based on the formation G1.5 PAMAM-capped ensembles via a supramolecular electrostatic interaction that can be photochemically switched at will. Thus, the G1.5 PAMAM dendrimers are acting as "corks in bottlenecks" upon irradiation with UV light (or when in darkness) owing to the electrostatic forces, as explained above. Moreover, some release of the complex under UV light could be observed. This was ascribed to the fact that the G1.5 PAMAM dendrimer is not able to completely block the pores of the hybrid material. However, the effectiveness of the blockage is ca. 80 %. In addition, the functional task of the dendrimers (as caps) can also be switched on/off by simple adjustment of the pH. Thus, at acidic pH (pH ca. 2) G1.5 PAMAM dendrimers do not act as stoppers (large delivery is observed), as they do at neutral pH (vide ante), probably because the protonation of the carboxylate groups at acidic pH prevents the interaction of the dendrimer with the positively charged merocyanine-functionalized surface.

Moreover, to further reveal the role of the G1.5 PAMAM dendrimer in the opening and closing of the pores, dye release from the hybrid material **S1** was studied in water at pH 7.2 in the absence of dendrimers. In this case (under UV or visible light irradiation) a massive $Ru(bipy)_3^{2+}$ delivery was observed. In addition, no notable differences in the delivery process (i.e., in all cases comparable dye release kinetics were found) between visible and UV irradiated **S1** solid were observed in the presence of smaller anions such as chloride, bromide, iodide, nitrate, phosphate, or sulfate, even at concentrations of up to 0.01 mol dm^{-3}. Because of the fairly large pore diameter of the mesoporous MCM-41 support (ca. 2.1 nm) small anions are not sufficient to close the pores by interaction with the merocyanine positively charged surface and larger molecules (i.e., G1.5 PAMAM dendrimers with a diameter of ca. 2.8 nm[30]) had to be used instead.

This double gating control of mass transport, that is, photochemical (merocyanine–spiropyran conversion) and chemical (pH) can be described using a logical-truth-table representation.[31] This is shown in Table 1, which reports the observed output effect (delivery) as a function of the UV irradiation and the pH of an aqueous mixture of **S1** and G1.5 PAMAM dendrimers. Also, it is of significance to note that molecular "logic gates" displaying *molecular motion* as output (i.e., mass transport such as the controlled delivery reported here) have been scarcely studied at the nanoscopic level, in contrast with many of the reported molecular- or supramolecular-based logic gates, which are limited to displaying simple optical signals as output.

Table 1. Logical gate (NAND) in relation to mass transport (delivery) in solid **S1** and two input signals: photochemical (UV light) and chemical (pH).

UV light (Input 1)	Neutral pH[a] (Input 2)	Delivery (Output)
0	0	1
1	0	1
0	1	1
1	1	0

[a] Input "1" and "0" denote pH 7.2 and pH 2, respectively.

In summary, the results shown here demonstrate how the use of suitable building blocks allows the development of functional multichannel-controlled gatelike ensembles on nanoscopic hybrid systems. This is a new functional gating scaffold that is photochemically and chemically controlled in pure water. **S1** and similar multichannel nanoscopic systems are attractive new functional materials, which might find remarkable novel applications in areas such as the control of mass delivery, sensing, catalysis, or related fields in which a fine control of mass movement at nanoscopic level would be required.

Experimental

*Synthesis of 1'-(3-triethoxysilanpropyl)-3'-3'-dimethyl-6-nitrospiro[2H-1]benzopyran-2,2'-indoline (**2**)*: The spirobenzopyran derivative **2** was synthesized by a two-step procedure (see Scheme 1) via reaction of 2,3,3-trimethylindolenine (1.96 mL, 12 mmol) and (3-iodopropyl)-trimethoxysilane (4.96 mL, 24 mmol) in refluxing ethanol (40 mL) for 24 h. The product 1-(3-triethoxysilanpropyl)-2,3,3-trimethyilindolenine (**1**) precipitated from ethyl ether. In a further step, reaction of **1** (2.55 g, 7 mmol) with 2-hydroxy-5-nitrobenzaldehyde (1.50 g, 9 mmol) and triethylamine (9 mL) in refluxing ethanol (135 mL) for 4 h yielded the triethoxysilyl derivative **2**, which was purified in a sili-

ca gel column using ethyl acetate/hexane 2:1 as eluent (0.85 g , 17 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.55$ (t, 2H; 3-H), 1.16 (t, 9H; 1-H), 1.25 (s, 6H; 10-H and 11-H), 1.72 (qn, 2H; 4-H), 3.75 (q, 6H; 2-H), 3.81 (t, 2H; 5-H), 5.84 (d, 1H; 12-H), 6.58 (d, 1H; 9-H), 6.73 (d, 1H; 16-H), 6.84 (t, 1H; 7-H), 6.87 (d, 1H; 13-H), 7.06 (d, 1H; 6-H), 7.14 (t, 1H; 8-H), 7.97 (s, 1H; 14-H), 8.00 ppm (d, 1H; 15-H).

Synthesis of ***S1***: The MCM-41 mesoporous 3D support was prepared using tetraethylorthosilicate (TEOS) as the hydrolytic inorganic precursor and the surfactant hexadecyl trimethylammonium bromide (CTAB) following known procedures [29]. After removal of the surfactant by calcination, the MCM-41 solid was suspended in 25 mL of anhydrous acetonitrile and heated in a Dean-Stark apparatus to remove the adsorbed water via azeotropic distillation. The dye tris(2,2'-bipyridyl)ruthenium(II) chloride (0.3 g, 0.4 mmol) was then added to the suspension and stirred for 24 h with the aim of loading the pores of the MCM-41 scaffolding. After this, an excess of **2** (0.85 g, 2.4 mmol) was added and the suspension was stirred for 24 h. The final orange solid (**S1**) was filtered, washed with acetonitrile, and dried. This synthetic procedure somehow assured a preferential grafting of the spiropyran at the pore outlets rather than inside the pore walls, which are basically filled by the $Ru(bipy)_3^{2+}$ dye. As we have reported in other systems, these procedures (filling the pores and anchoring) do not significantly affect the mesoporous structure [8]. Thus, both the powder X-ray pattern of the solid and the TEM images show that the filling process with $Ru(bipy)_3^{2+}$ and the anchoring of the spiropyran at the pore outlets did not change the MCM-41 structure. The final solid contained 2 wt % and 17 wt % of the spiropyran and $[Ru(bipy)_3]Cl_2$, respectively (both values from thermogravimetric and elemental analysis). As a reference, solid **S2** obtained by simple grafting of **2** onto an MCM-41 support free of the $Ru(bipy)_3^{2+}$ dye was also prepared.

Received: August 29, 2006
Revised: January 12, 2007
Published online: July 26, 2007

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