NEW ADVANCES IN PHOTOCHEMICAL - CHEMICAL CONTROL OF FUNCTIONAL NANOGATED HYBRID ARCHITECTURES

Elena Aznar, Carmen Coll, María Comes, Beatriz García-Acosta, Rosa Casasús, Félix Sancenón, María Dolores Marcos, Ramón Martínez-Máñez
Instituto de Química Molecular Aplicada, Universidad Politécnica de Valencia, Camino de Vera s/n E-46022, Valencia, Spain
elazgi@doctor.upv.es

The control via multiple chemical or physical inputs of motion-based functional processes such as translocation, reversible mass movement, controlled molecular transport, etc. at nanometric level is a landmark subject to further advances in the upcoming design of molecular and supramolecular sophisticated architectures.

The anchoring of molecular entities on 3D nanoscopic scaffoldings offers the opportunity to develop and explore new functional supramolecular concepts that would be hardly achieved on "flat" surfaces (2D systems). This is especially so in the field of gated nanochemistry and its relation with the design of nanoscopic supramolecular architectures that incorporate chemical entities which can act as a functional gate and allow to control the access of (or from) a certain nanosite at will [1,2].

The designed nanogated architecture consists of a mesoporous MCM-41 support containing photo-responsive spiropyran moieties anchored to the pore outlets and a suitable dye $[Ru(bipy)_3]^{2+}$ in the pore voids, for gating monitoring purposes. The molecular gate effect was achieved by introduction of G1.5 PAMAM dendrimers that act as nanoscopic molecular stoppers [3]. The closing sequence is light-driven and stems from electrostatic interactions via the self-assembly of negatively-charged dendrimers with the positively-charged merocyanine-functionalised surface. The opening of the pores occurs via merocyanine transformation to the neutral spiropyran form that have not affinity for the dendrimers allowing release of the entrapped molecule to the bulk solution [4,5].

This new two-input (i.e. photochemical and chemical) gated hybrid system is a further step in the development of tunable nanoscopic systems which are assumed to have a high potential for advances in new hybrid functional designs.

References:

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