

## A NEW 3-STATE CATECHOL-BASED FLUORESCENT SWITCH ON SURFACE

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The development of compounds that can be easily and reversibly interconverted between different forms, each one characterized by clearly detectable signals (i.e., molecular switches) is of great interest in fundamental and applied research. Different read-out for such switches can be envisioned although among them, luminescence is a very effective readout signal to monitor the state of the switch. On the other side, organic molecules appear to be potential candidates for the realization of future data-elaboration, -storage, and -communication devices<sup>1</sup>. Among them, catechol-based pH sensors are scarce in spite of their interest. Indeed, catechols have been already shown to have a crucial role in different biological processes, decontamination of soils as part of humic and fulvic acids or even in the field of molecular electronics as components of bistable valence tautomeric complexes.

To overcome this situation, a new catechol derivative exhibiting an acid/base induced switching of the fluorescence in solution was synthesized in our group. The 3-states of the molecule and their respective fluorescence spectra are shown in the Figure 1. However, for this switching behaviour in solution to become a real integrated device, the nanostructuring of the molecules on the surface and the study of their response after acid/base stimuli are highly required.

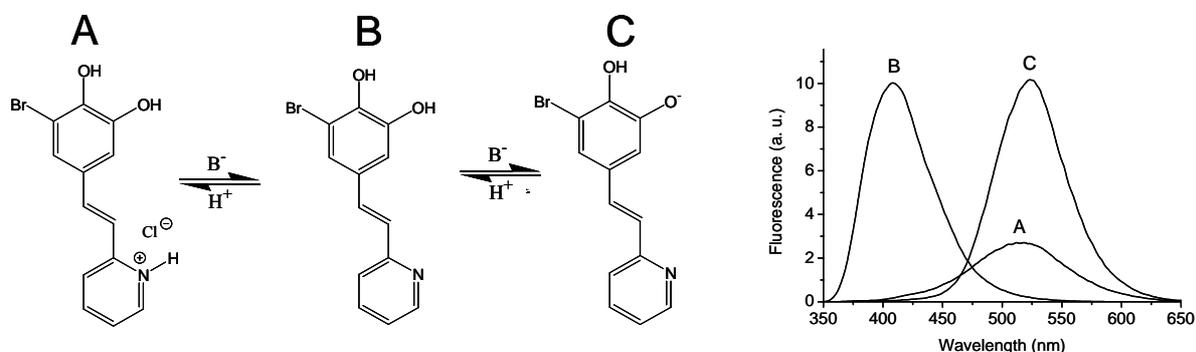


Figure 1. Catechol-based switch, (left) states of the molecule, (right) fluorescent spectra.

Prior to this work, advanced nanofabrication and self-assembly techniques have been used in fabrication of molecular-scale systems<sup>2-3</sup>. Among them, the Lithographically Controlled Wetting (LCW) technique, developed by Biscarini et al.<sup>4</sup>, is a convergent approach based on the stamp-assisted deposition of molecules from a solution together with dewetting phenomena arising from competing interactions between the molecules and the substrate.

Herein we report for the first time the switching behaviour between the three states of the molecules deposited by the LCW technique on Highly Oriented Pyrolytic Graphite (HOPG) and glass. After controlled deposition of the molecule on the surface, the switching was successfully done and followed by confocal microscopy although accompanied by some degradation of the molecular stripes of molecules with repeating cycles of gas bubbling, fact that was confirmed by AFM studies.

Representative images of the switching of the fluorescence upon exposure to the acid/base flow is shown in Figure 2.

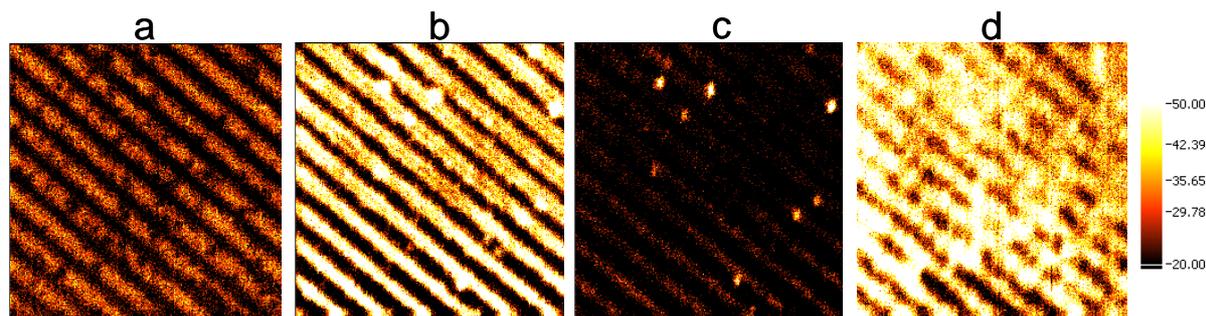


Figure 2. Fluorescence images of  $15 \times 15 \mu\text{m}^2$  areas of a glass substrate with stripes of catechol-based molecules on top after successive exposure of the sample to: (a) air; (b)  $\text{Et}_3\text{N}/\text{N}_2$  flow; (c)  $\text{HCl}/\text{N}_2$  flow; (d)  $\text{HCl}/\text{N}_2$  flow for 5 min. All six images were recorded with the same instrument settings. The fluorescence intensity scale is also equal for all displayed images.

*Experimental.* For this experiment a custom made scanning fluorescence confocal microscope was used. The detection window ( $\lambda_{\text{det}} > 550 \text{ nm}$ ) was set in the way changes between the 3-states can be appreciated (see fluorescence spectra above). Then, flows of acid (HCl) and base ( $\text{Et}_3\text{N}$ ) were used “in situ” by bubbling nitrogen over solutions of these acid and base while the fluorescence images were taken. No liquids were drop on the surface to prevent desorption of molecules.

### References:

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