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Introduction

- > The real-time sensing of volatile organic compounds (VOCs) is an active research area because of the relevance of the detection of these compounds in ambient air, atmosphere or breath
- > Several transduction methods have been employed with optical sensors being among the most wide-spread ones.^[1] Advantage of luminescence techniques: they offer multiple information and high sensitivity
- > Key issue: search for a suitable solid-state platform to guarantee a rapid response toward the analytes of interest

Approach

- > A mesoporous silica matrix, **UVM-7**,^[2] is chosen as support
- > A phenoxazinone^[3] dye acts as the indicator. This fluorophore shows intense emission in the red region of the spectrum (at ca. 600 nm) and is influenced by polarity of the environment
- > The dye is covalently anchored onto the mesoporous silica walls
- > After dye attachment, passivation of remaining silanol groups is carried out in order to optimize sensor response

Experimental

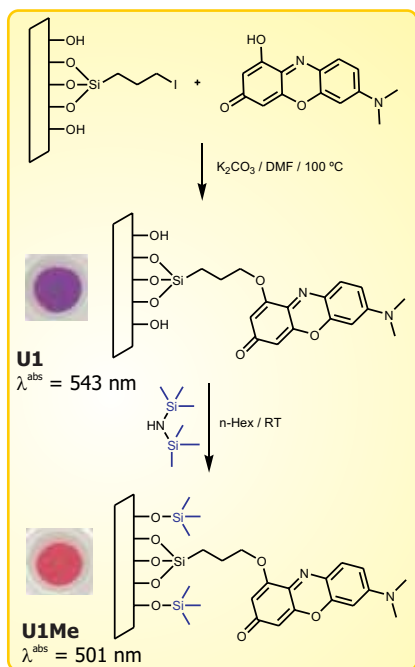


Fig. 1. Synthetic route for the preparation of materials **U1** and **U1Me**

The phenoxazinone dye is linked to a **UVM-7** silica containing alkyl iodide groups via a phenolic function. Then, the surface of the polar solid **U1** obtained is passivated with hexamethyldisilazane to yield a highly hydrophobic material, **U1Me**.

The different polarity of the materials is shown by the difference in color for both solids **U1** (violet) and **U1Me** (pink)

Literature

- [1] See for example N.A. Rakow and K.S. Suslick, Nature 2000, 406, 710.
 [2] J.E. Haskouri et. al., Chem. Commun. 2002, 330.
 [3] A.B. Descalzo et. al., J. Am. Chem. Soc. 2003, 125, 3418.

Results

U1Me characterization

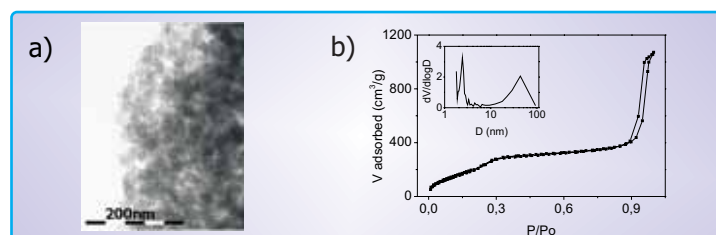


Fig. 2. a) TEM image and b) N_2 adsorption-desorption isotherms and pore size distribution (inset) for solid **U1Me**

- Bimodal pore system with pore diameter of 2.27 nm and 34.8 nm
- BET specific surface of $815 \text{ m}^2 \text{ g}^{-1}$
- DRX peak at angle $2\theta = 2.2^\circ$
- $\text{Si}(\text{CH}_3)_3$ IR bands at 2964, 849 and 759 cm^{-1}
- Chromophore content: $5 \times 10^{-3} \text{ mmol g}^{-1}$ (UV-vis photometrie)

Sensor response

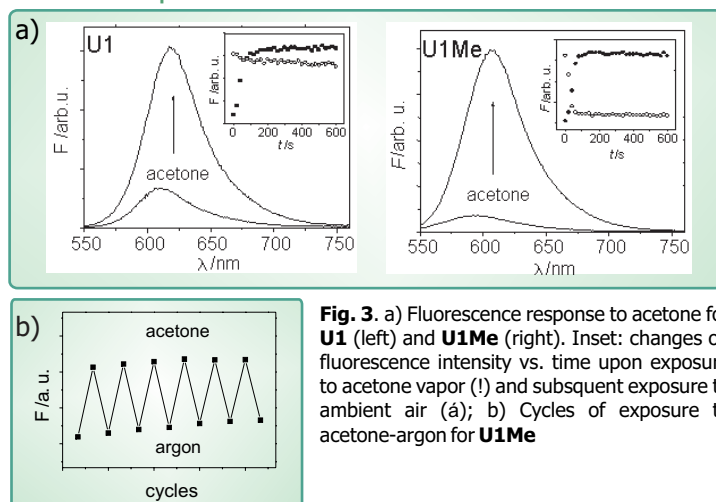


Fig. 3. a) Fluorescence response to acetone for **U1** (left) and **U1Me** (right). Inset: changes on fluorescence intensity vs. time upon exposure to acetone vapor (!) and subsequent exposure to ambient air (a); b) Cycles of exposure to acetone-argon for **U1Me**

- Increase on fluorescence upon exposure to acetone
- Fast recovery of the original signal for the **U1Me** solid, but slow for **U1**
- **Higher solvatochromism for U1Me** than for **U1**. For example, upon exposure to MeOH vapors there is a red shift in absorption of 41 nm for **U1Me** but only of 22 nm for **U1**
- Water quenches the fluorescence of **U1** but has no effect in the hydrophobic material **U1Me**
- The materials possess a long-term stability (> 2 years)

Conclusions

- > New vapor sensing materials based on the use of mesoporous silica scaffoldings and a solvatochromic dye have been described
- > Control of the surface polarity allows to tune the optical response
- > **U1Me** shows better performance as optical sensor material for organic vapors than **U1** (larger spectroscopical changes upon VOCs exposure, indication of the vapors over a larger polarity range, faster response times, better reversibility and minimal interference from environmental humidity)

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