

Supplementary information for

Hybrid functional mesostructured thin films with photo-oxidative properties in the visible range.

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Experimental part:

Ellipsometry measurements were performed on a UV-visible (from 240 to 1000 nm) Variable Angle Spectroscopic Ellipsometer (VASE) from Woolam, and the data analysis was performed with the WVase32 software. Transmission electronic microscopy (TEM) pictures were obtained with a JEOL CX/STEM. XRD patterns were obtained with D8 diffractometer from Bruker instruments (wavelength 0.154 nm). Nitrogen adsorption-desorption volumetry were performed on a Micromeritics ASAP 2010. Transmission spectra of the films were recorded on a Varian Cary 5 spectrometer.

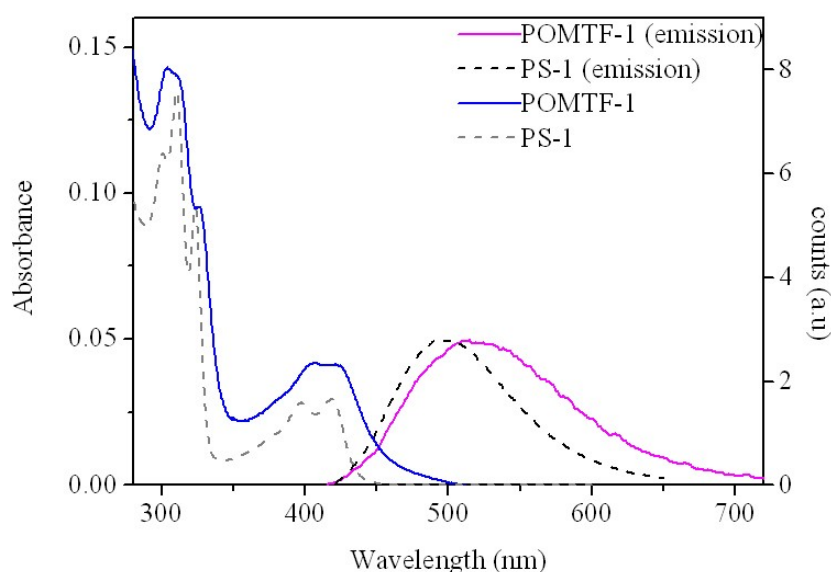


Fig.1 Comparison of the absorption (left) and emission (right) spectra of the POMTF-1 (solid line) and PS-1 in methanol (dotted line). The spectra were recorded in transmission and not in diffuse reflectance mode.

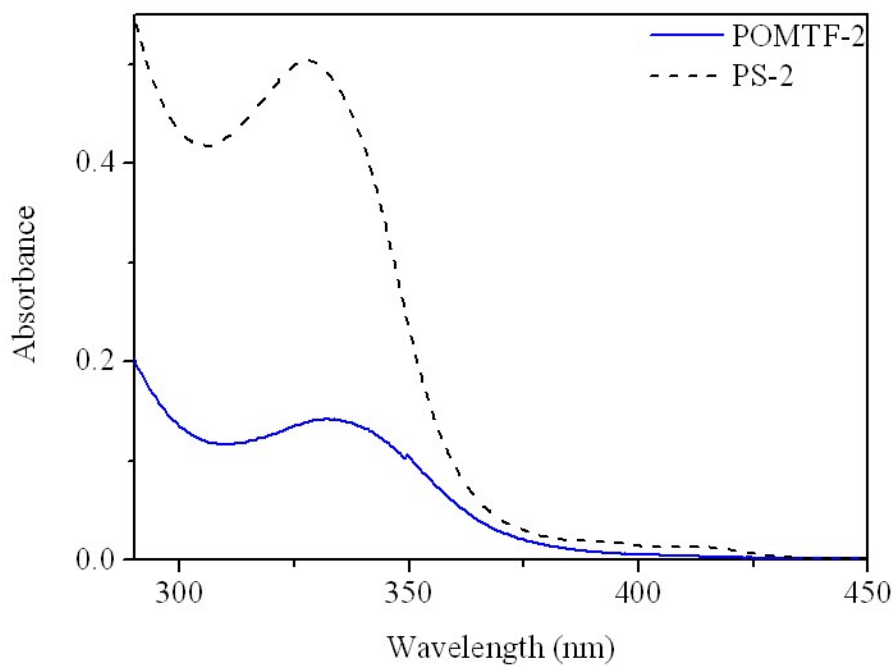


Fig.2 Comparison of the UV spectra of POMTF-2 (solid line) and PS-2 in methanol (dotted line)

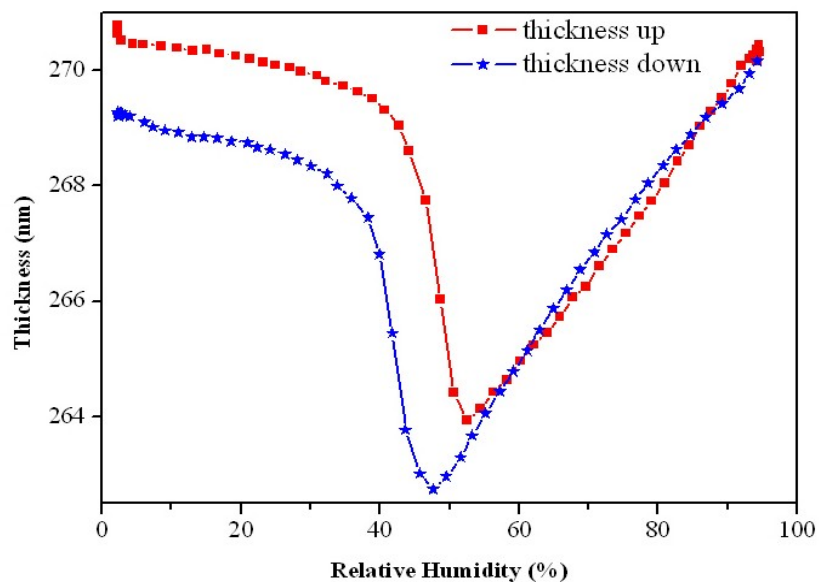


Fig.3 Thickness of the film POMTF-1 measured by ellipsoporimetry with water adsorption (square)/desorption (star) cycle

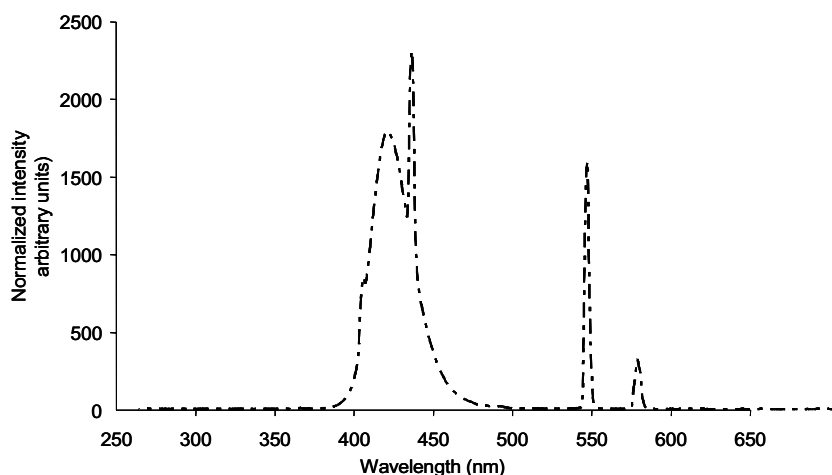


Fig.4 Emission spectra of the 420 nm fluorescent lamp (RPR-4190 A)

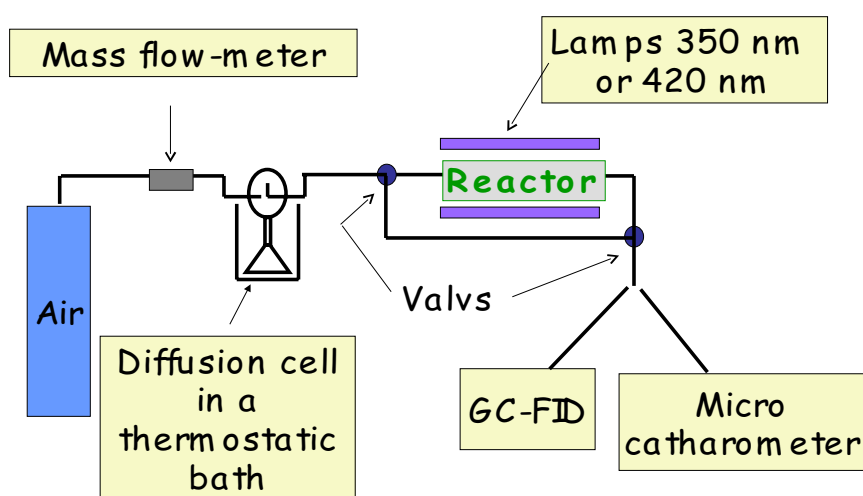


Fig.5 Scheme of the one-pass experiment

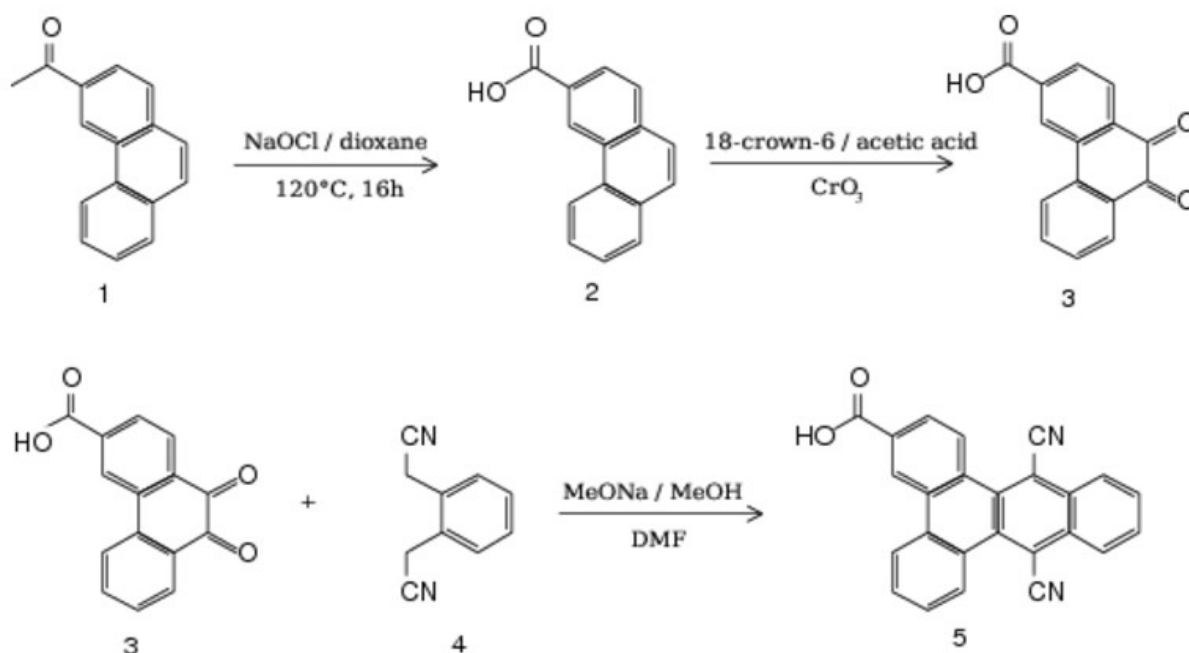
In a first step, air containing pollutant from the diffusion cell flows (fixed pollutant concentration and flow-rate) through the materials in the reactor in the dark. The resulting gas is analysed both by gas-phase chromatography with a flame ionisation detector (FID) and a micro catharometer. Then the lamps around the reactor are switched on and the gas at the outlet of the reactor continuously analysed.

Synthesis of PS-2 from commercial anthraquinone :

1g (3.9 mmol) of commercial anthraquinone-2-carboxylic acid (from Aldrich) was dissolved in the minimal amount of SOCl_2 added dropwise under inert atmosphere in a three neck flask. The mixture was heated for 3 hours at 110°C . The formation of acid chloride was monitored by infrared spectroscopy (ν_{COCl} 1780 cm^{-1}). The excess of SOCl_2 was removed by flushing with nitrogen. The obtained acid chloride was dissolved in 10 mL of dry toluene. Then 1 mL (4.3 mmol) of 3-aminopropyltriethoxysilane (APTES, Aldrich) and 0.6 mL (4.3 mmol) of triethylamine (NEt_3) were added simultaneously. The mixture was stirred for 2 hours at room temperature. Successive precipitations and filtrations of HCl,NEt_3 were achieved in chloroform/hexane or ether/hexane mixtures. The solution containing the product was then evaporated and the final product was crystallised in hexane.

Synthesis of PS-1 :

This synthesis proceeded in three steps.



In the first step 3-phenanthrene carboxylic (**2**) acid was prepared from commercial 3-acetyl phenanthrene (**1**) according to the following method. A solution of 12 mL of NaOCl 13 % in distilled water and 8 mL of distilled water was added to a solution of 3-acetylphenanthrene (**1**) (0.5 g, 2.77 mmol) in 7 mL of dioxan. The mixture was stirred under reflux 24 hours at 120°C, cooled to room temperature, and poured into 125 mL of distilled water. By-products and remaining starting product were extracted twice with 100 mL Et₂O. The aqueous phase was acidified to pH 2 with a concentrated HCl solution. The white solid which precipitated was washed with Et₂O and dried under vacuum. 0.92 g of (**2**) were obtained (yield 92%).

In the second step, a mixture of 18-crown-6 (0.16 g, 0.75 mmol) and of CrO₃ (1.8 g, 18 mmol) was dissolved in 20 mL of acetic acid and 2 mL of distilled water. A solution of (**2**) (1 g, 4.5 mmol) in 40 mL of acetic acid was added to this solution and heated for 10 hours at 60°C. 50 mL of distilled water were then added to the green slurry and the solid filtered, washed twice with a 1/1 solution water/acetic acid, twice with Et₂O and then dried under vacuum. **3** was obtained as an orange solid (0.86 g, yield 76 %).

In the last step a solution of **3** (0.5 g, 1.98 mmol) in 20 mL of freshly distilled dry DMF was added dropwise to a previously stirred (for an hour) solution of 1,2-phenylenediacetonitrile **4** (0.31 g, 1.98 mmol) and sodium methanolate (MeONa, 0.43 g, 8 mmol) in 20 mL of MeOH. The mixture was stirred for 6 hours at 40°C, acidified to pH 4 with 5 ml of concentrated HCl solution, stirred for 30 minutes and filtered. The yellow solid was washed with 50 ml of MeOH and dried under vacuum. It was purified by recrystallisation in a mixture CHCl₃/ MeOH (50/50 V): 0.5 g of yellow crystals (**5**) were obtained (yield 68 %). elemental analysis calculated (%) for C₂₅H₁₂N₂O₂: C 80.6, H 3.22, N 7.5; found: C 79.8, H 3.18, N 7.1. More details will be available in an upcoming submitted work.

Synthesis of Si-powder-1 :

Silicagel powder, purchased from Acros, contained 1.4 mmol g⁻¹ of amine function for a particule size between 40-63 μm, pore size 6-7 nm and a surface of 330 m² g⁻¹ determined by BET technique with an ASAP 2010. Grafting of PS-1 was achieved following the same procedure as described for the POMTF-1.

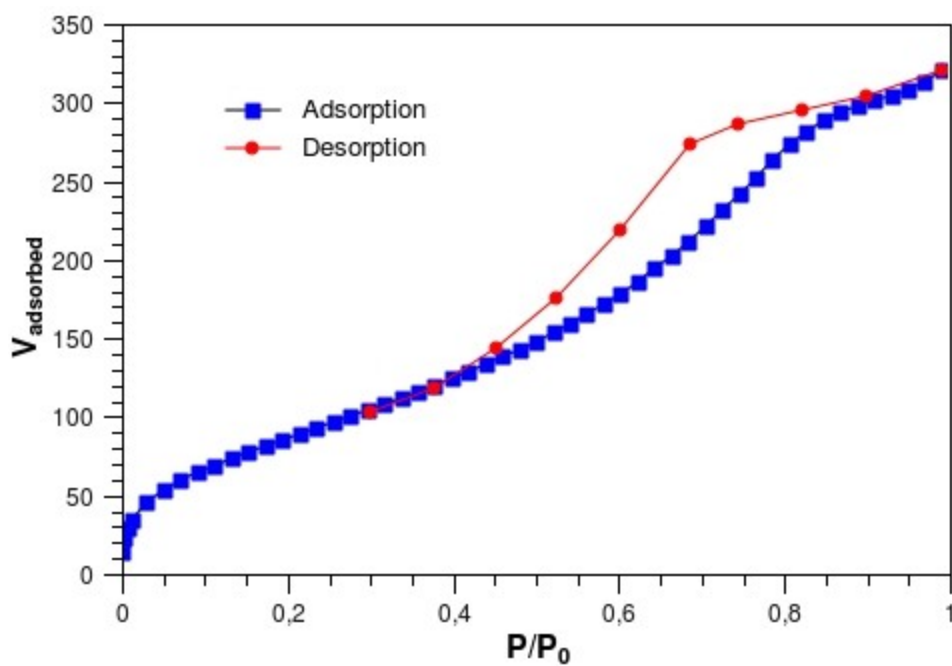


Fig.6 Nitrogen adsorption (square) desorption (circle) isotherm of **Si-powder-1**

References

1. C. Cantau, S. Larribau, T. Pigot, M. Simon, M. T. Maurette, S. Lacombe, *Catal. Today*, 2007, 122, 27-38