Self-Templating Amphiphilic Polysiloxane to Design Nanostructured Silica-based Architectures

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Supplementary Information

S1- General Experimental

All reactions were carried out under argon atmosphere using standard Schlenk tube techniques and carius tube. Solvents were purified with the MBRAUN SBS-800 purification system. NMR spectra were recorded with the following spectrometers: 1H, Bruker Avance II 300 (300.13 MHz); 13C, Bruker Avance II 300 (75.47 MHz); 29Si, Bruker Avance II 300 (59.62 MHz). Mass spectra were recorded with a Hewlett-Packard HP 5989 instrument in the electron impact mode (Ei, 70 eV). IR spectra were measured on a Varian 640-IR FT-IR spectrometer. 13C and 29Si CP MAS NMR spectra were acquired on a Bruker Avance 400 WB spectrometer operating at 100 MHz and 79 MHz respectively under cross-polarization conditions. Nitrogen sorption isotherms at 77 K were obtained with an Autosorb-1 apparatus (Quantachrome). Prior to measurement, the samples were degassed for 17 h at 80 °C. The surface area (SBET) was determined from BET treatment in the range 0.04–0.3 p/p0 assuming a surface coverage of the nitrogen molecule estimated to be 13.5 Å2. Thermogravimetric analysis (TGA) was performed on a Pfeiffer Vacuum instrument at a heating rate of 10°C/min under a flow of nitrogen. X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance Bruker AXS system using CuKα radiation with a step size of 0.02° in the 2θ range from 0.3 to 10° for SAXS, and from 0.45 to 87° for WAXS (geometry : Bragg- Brentano, θ/2θ mode). XPS analyses were performed at room temperature with an SSI 301 spectrometer using monochromatic and focused (spot diameter) 600 lm, 100 W) Al K R radiations (1486.6 eV) under a residual pressure of 10.7 Pa. Charge effects were compensated by the use of a flood gun (5 eV). The hemispherical analyzer functioned at constant pass energy of 50 eV. The experimental bands were fitted to theoretical bands (80% Gaussian, 20% Lorentzian) with a least squares algorithm using a nonlinear baseline. Reference binding energy was C1s of CH3 and of the contamination carbon at 284.6 eV. Scanning electronic microscopy (SEM) images were obtained using a JEOL JSM 6700F. Transmission electronic microscopy (TEM) images were obtained using JEOL JEM 2010 at an activation voltage of 200 kV. EDX measurements were carried out using FEI 200F quanta 200F connected to the SEM Hitachi S4500 microscope. Steady-state fluorescence emission spectra and fluorescence anisotropy measurements were performed on a K2 fluorimeter (ISS, Champaign, IL) following excitation of Rhodamine 6G (1.10^{-6} mol.L^{-1}) at 500 nm in the presence and absence of precursor **P1** in ethanol and heptane solutions. Stock solutions of Rhodamine 6G and precursors were prepared in acetone. After mixing the two solutions and evaporation of the solvent, n-heptane was introduced. The solutions were kept under gentle agitation for 24h before measurements.

S2- Synthesis of P1 and P2

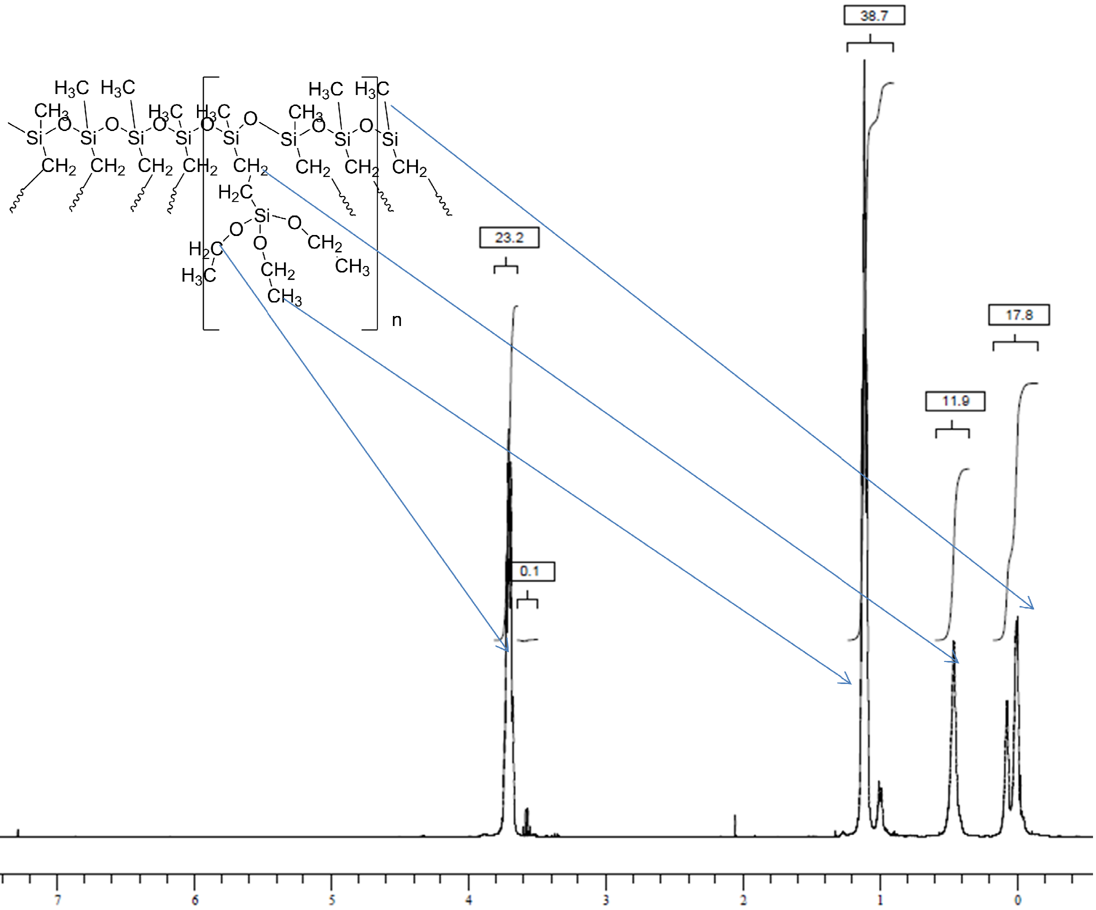
Following the protocole described in A. El Kadib et al., *J. Mater. Chem.*, 2009, 19, 6004-6014, a solution of 0.99 mL of polymethylhydrosiloxane PMHS (n = 29) and vinyltriethoxysilane (2.5 mL; 29 eq.) in toluene (4 mL) was stirred in presence of 1% of Karstedt's catalyst (Pt°) under argon. After 30 seconds, the color turned from yellow to brown indicative of the formation of highly active Pt nanoparticles. After two hours starring at room temperature, the temperature raised to 40°C and an additional stirring for two hours enabled total conversion of the starting materials (~100%) (as monitored by ^{1}H NMR). The solvent was evaporated and the solution was washed three times with anhydrous THF. the crude solution of THF was then passed across a filter of activated carbon, in order to remove the platinum nanoparticles. The resulting solution was evaported under vaccum and the functional siloxane **P1** were obtained as oily compounds.

P1. ^{1}H NMR ($CDCl_3$): 0.17 (s, CH_3Si); 0.47 (m, CH_2Si); 1.19 (t, $SiOCH_2CH_3$); 3.75 (q, $SiOCH_2CH_3$). ^{13}C NMR ($CDCl_3$): 0.9 (CH_3Si); 6.8(CH_2Si-O-); 17($SiOCH_2CH_3$); 57 ($SiOCH_2CH_3$).

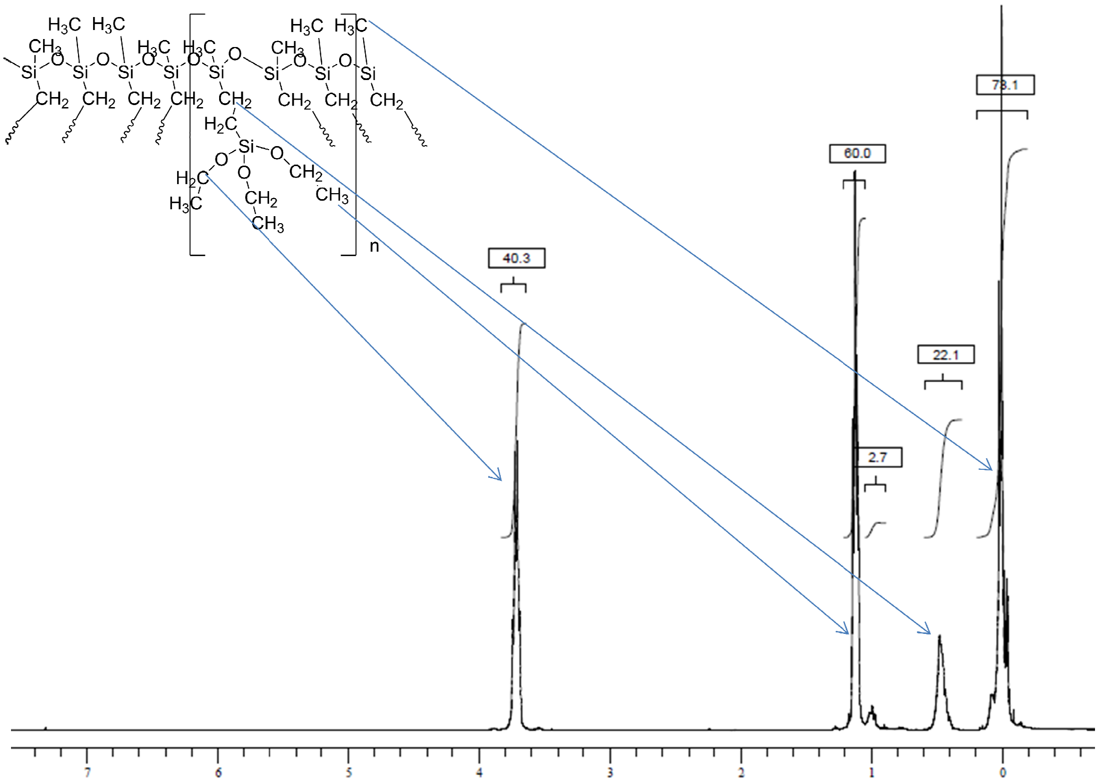
Following the same procedure, the hydrosilylation of low molecular weight PHMS (n = 5) using 5 eq of vinytriethoxysilane. After work-up, the isolated product **P2** exhibits typical signal of functional siloxane.

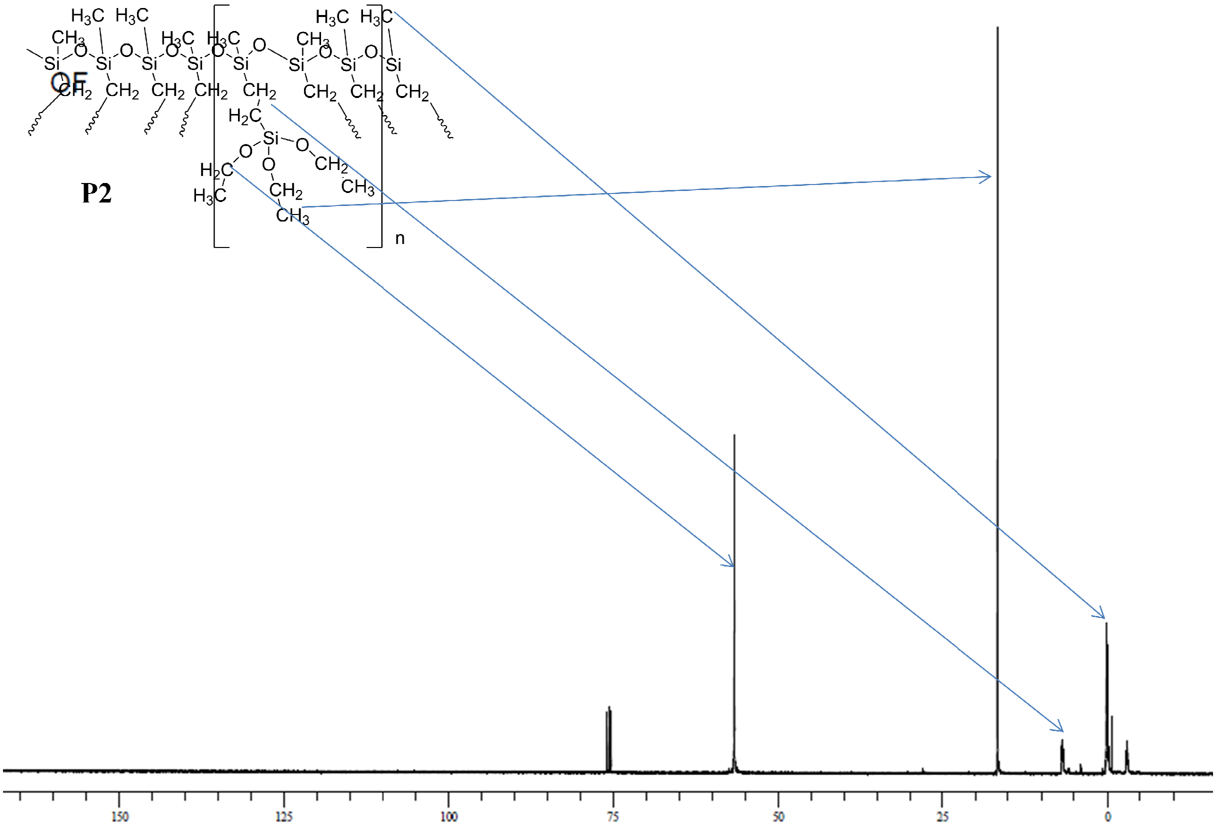
P2. ^{1}H NMR ($CDCl_3$): 0.1 (s, CH_3Si); 0.43 (m, CH_2Si); 1.17 (t, $SiOCH_2CH_3$); 3.78 (q, $SiOCH_2CH_3$). ^{13}C NMR ($CDCl_3$): 0.9 (CH_3Si); 7.2 (CH_2Si-O-); 16.9 ($SiOCH_2CH_3$); 56.9 ($SiOCH_2CH_3$).

P1



P2




P2

S3- Synthesis of M1, M2 and M3

For the synthesis of **M1**, 50 mg of **P1** was dissolved in 10 mL of EtOH and after 15 min, 0.325 mL of TEOS was added. After 15 min of stirring, 2 mL of acidified water HCl/H_2O (0.2 N) was added to induce hydrolysis and condensation of the silicates species. After one hour, the temperature increased to 60°C and the resulting milky solution was stirred for 10 hours. The collected solid was then filtered, washed twice with ethanol and three times with acetone and dried under vacuum for two hours and lastly at 80°C for two hours.

For **M2**, 50 mg of **P1** was dissolved in 10 mL of EtOH and after 15 min, 0.325 mL of TEOS was added. After 15 min of stirring, 2 mL of basic water $NaOH/H_2O$ (0.2N) was added to induce hydrolysis and condensation of the silicates species. After one hour, the temperature increased to 60°C and the resulting milky solution was stirred for 10 hours. The collected solid was then filtered, washed twice with ethanol and three times with acetone and dried under vacuum for two hours and lastly at 80°C for two hours.

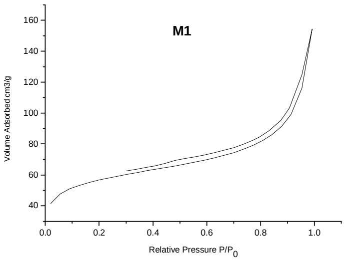
Similar to **M1**, **M3** was prepared adopting the same protocol with 10 mL heptane as solvent.

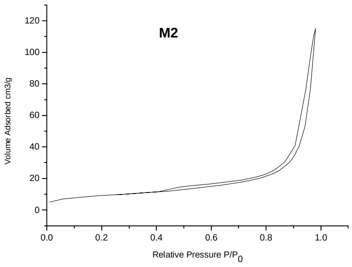
Synthesis of mixed metal oxides in Ethanol and in Heptane.

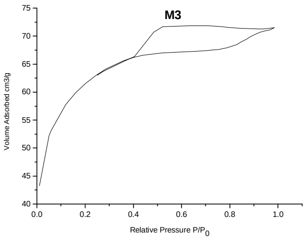
As indicated in table 1 within the manuscript, **M4** to **M6** were prepared using 50 mg of **P1** in dissolved 10 mL of EtOH and after 15 min, 2 mL of water was added to induce hydrolysis and condensation of the silicates species. 1 hour later, 0.29 mmol of the metal source ($Ti(OiPr)_4$, $Zr(OBu)_4$ and $Sn(acac)_2$) was added and left for stirring for an additional hour. The temperature increased to 60°C and the resulting solution was stirred for 10 hours. The collected solid was then filtered, washed twice with ethanol and three times with acetone and dried under vacuum for two hours and lastly at 80°C for two hours.

M7, **M8** and **M9** are prepared following the same experimental procedure as for **M4**, **M5** and **M6** respectively with the main difference being the switch from EtOH to heptane as solvent. All the variants are kept constant and the work-up procedure is exactly the same.

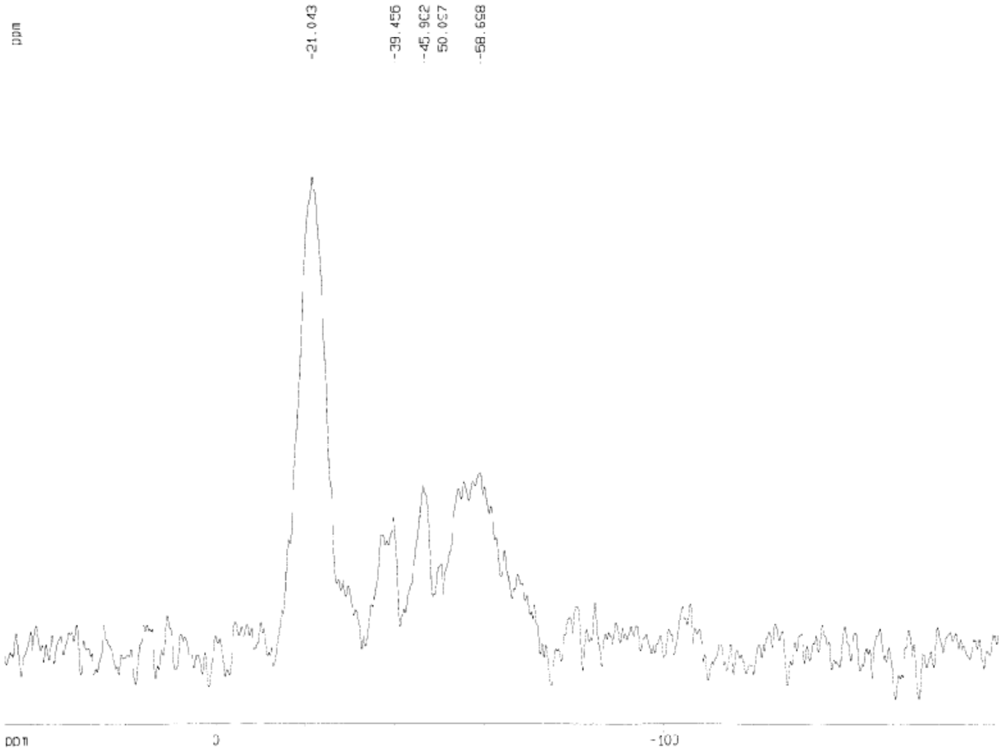
S4-Typical nitrogen sorption profile of siloxane-silica materials.



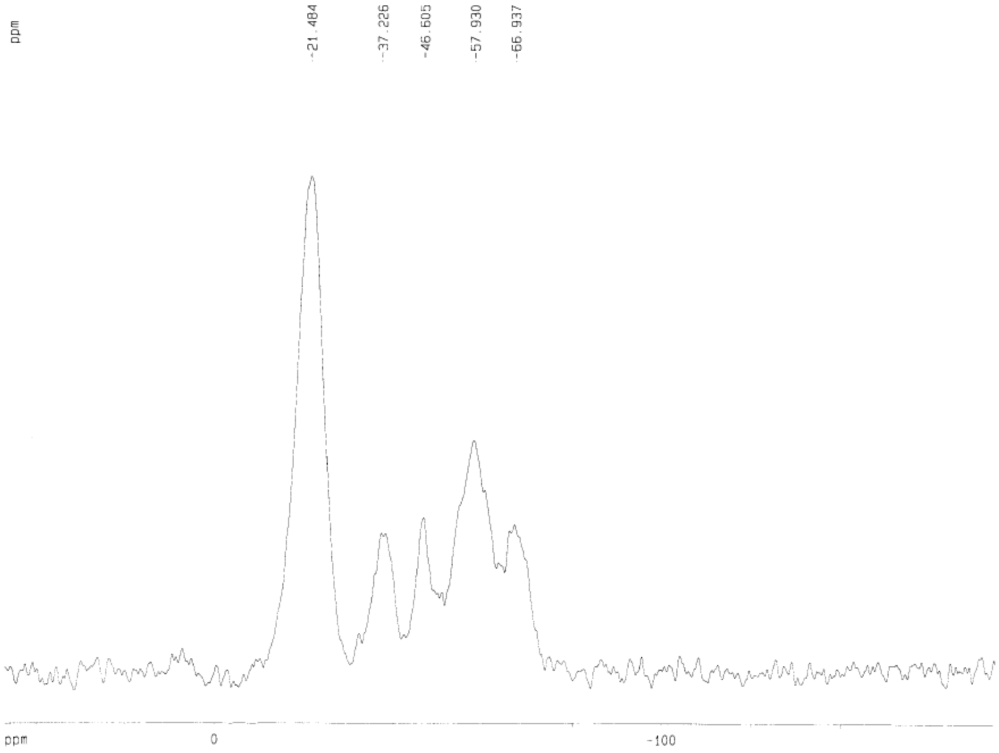




S5- Typical ^{29}Si NMR spectra of mixed metal oxides

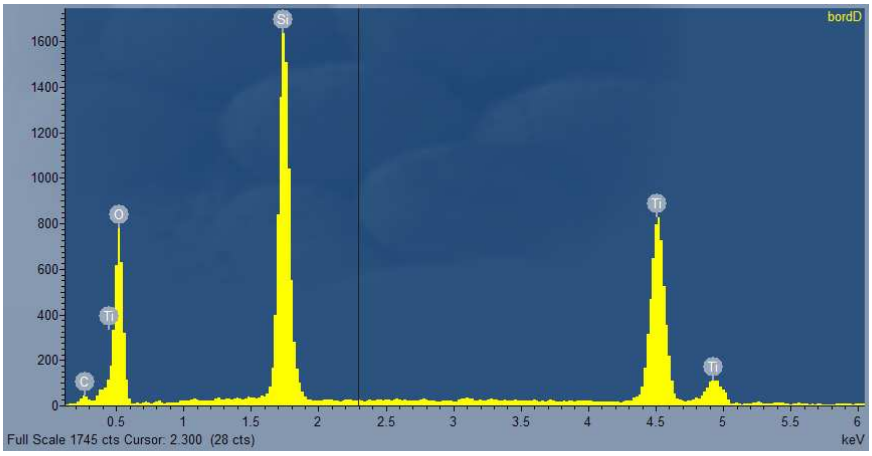


^{29}Si NMR of M4

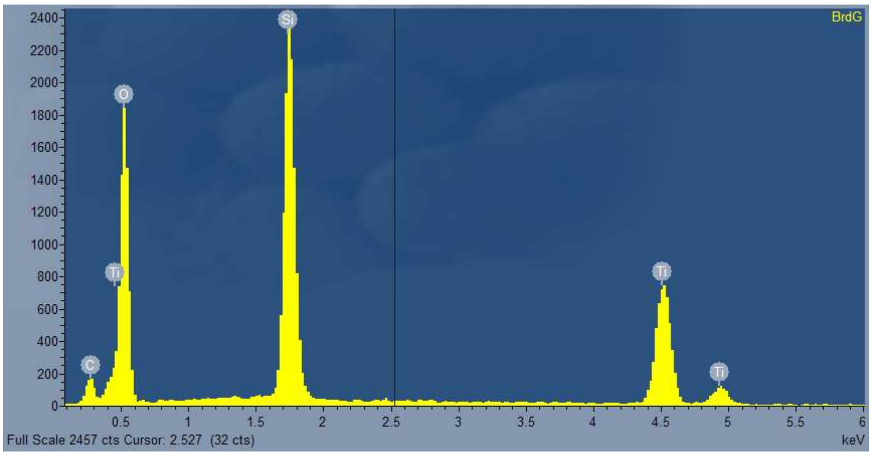


^{29}Si NMR of M8

S6. Typical EDX of mixed oxide materials

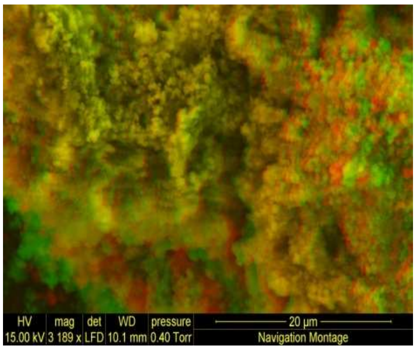


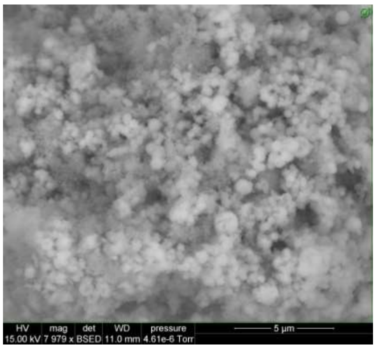
Typical analysis by EDX of **M4** showing the presence of titanium within the material network. EDX coupled to SEM shows that the same ratio Si/Ti is found in different zones of the material ruling out any appreciable phase separation or material heterogeneity.

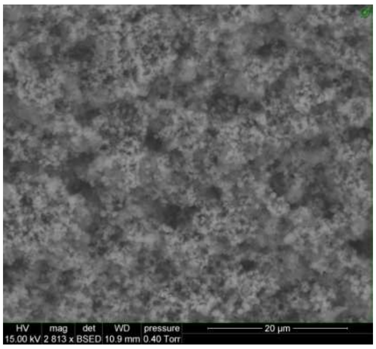


Typical analysis of **M7** by EDX showing the presence of titanium within the material network.

S7. SEM of mixed metal oxide materials







M4 **M5** **M6**

S8. Steady-state fluorescence

Stock solutions of Rhodamine 6G and precursors were prepared in acetone. After mixing the two solutions and evaporation of the solvent, n-heptane was introduced. The solutions were kept under gentle agitation for 24h before measurements.

In ethanol, typical Rhodamine 6G emission characteristics are observed with a maximum of the fluorescence band at 550 nm and a fluorescence anisotropy of 0.02. The photophysical properties of Rhodamine 6G are not affected by the presence of precursor **P1** (similar maximum emission wavelength, fluorescence intensity, anisotropy value are obtained), indicating that the polar fluorescence probe is not encapsulated into the apolar core of the micellar aggregate. In n-heptane solution free from precursor **P1**, no emission could be measured. The presence of precursor **P1** induces an intense fluorescence of Rhodamine 6G (Figure S1) characterized by a high anisotropy (0.23). This clearly indicates the incorporation of the probe molecule into the polar and constrained medium constituting the micellar core of the aggregate in this solvent.

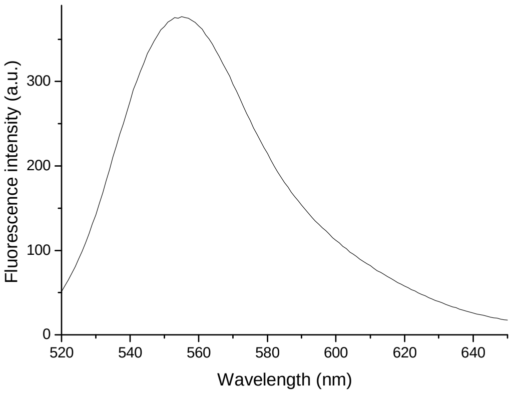


Figure S1: emission spectrum of Rhodamine 6G in solution containing precursor **P1** and n-heptane (λ_{ex} = 500nm).