Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Low-temperature H_2 sensing in self-assembled organotin thin films

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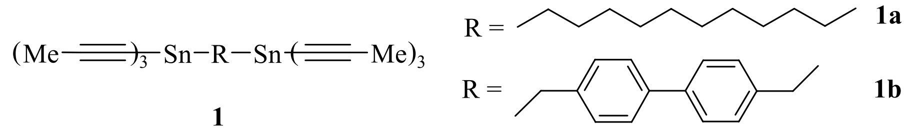
Synthesis of the organotin precursor

The molecular formula of precursors **1** are shown in Scheme 1. 1,4-bis(triprop-1-ynylstannylmethyl)benzene **1b** was synthesized as previously reported.[1] All reactions were carried out under a nitrogen atmosphere. Toluene was distilled from sodium benzophenone ketyl prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DPX-200 or DPX-300 spectrometer in $CDCl_3$ (δ given in ppm relative to tetramethylsilane). MALDI-MS spectra were carried out by the CESAMO (Bordeaux, France) on a Voyager mass spectrometer (Applied Biosystems) equipped with a pulse N2 laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflextron and with an accelerating voltage of 20 kV.

1,10-Bis(tripropy-1-ynyltin)decane 1a

A 2.5M solution of BuLi (4.79 mL, 11.98 mmol) was added to a solution of propyne (0.77 mL, 13.69 mmol) in toluene (10 mL) in a 100-mL 3-necked flask at –78 °C. After stirring for 15 min, a solution 1,10-Bis(trichlorotin)decane[1] (1 g, 1.71 mmol) in 20 mL of toluene was added at –78 °C. After stirring for 15 h at 70 °C, the suspension was filtered over dry $MgSO_4$, the solvent was evaporated under vacuum to give **1a** as a white solid. Yield: 95 %. ^{1}H NMR: δ 1.27 (m, 20H), 1.91 (s, 18H). ^{13}C NMR: δ 5.3 (CH_2-Sn), 15.4 (CH_3), 25.8, 29.2, 29.6, 33.2(CH_2-CH_2-Sn), 76.8 (-C≡*C*-Sn), 107.8 (-*C*≡C-Sn). ^{119}Sn NMR: δ –251.8. HRMS-MALDI: Found (calcd) $[M+Na]^+$ 637.0899 (637.0922).



Scheme S1. Precursor molecules used to prepare the hybrid thin films

(1) B. Jousseaume, H. Riague, T. Toupance, M. Lahcini, P. Mountford, B.R. Tyrrell, *Organometallics,* 2002, **21**, 4590.

Solid state CP-MAS ^{13}C and ^{119}Sn NMR studies

^{13}C and ^{119}Sn CP-MAS NMR measurement were performed on a Bruker Avance 300 spectrometer (300.29 MHz for ^{1}H, 75.52 MHz for ^{13}C and 111.92 MHz for ^{119}Sn) using a 4 mm locked Bruker probe. For both nuclei the contact time is 1 ms. ^{13}C chemical shifts are referenced towards external tetramethylsilane (TMS). ^{119}Sn chemical shifts are referenced towards tetramethyltin (TMT), using tetracyclohexyltin ($\delta = -97.35$ ppm) as a secondary external reference.[2] For ^{119}Sn, two MAS speed (14 and 11.5 kHz) were used to locate the isotropic chemical shifts.

The ^{119}Sn NMR spectra were analyzed with Dmfit,[3] and the ^{119}Sn shielding tensors extracted using the Herzfeld and Berger approach.[4] They are reported as the isotropic chemical shift ($\delta_{iso} = -\sigma_{iso}$), the anisotropy ($\zeta = \sigma_{33} - \sigma_{iso}$), and the asymmetry ($\eta = |\sigma_{22} - \sigma_{11}| / |\sigma_{33} - \sigma_{iso}|$), σ_{11}, σ_{22}, and σ_{33} being the three components of the shielding tensor expressed in its principal axis system with the following convention: $|\sigma_{33} - \sigma_{iso}| > |\sigma_{11} - \sigma_{iso}| > |\sigma_{22} - \sigma_{iso}|$.

Hybrid material from precursor **1a**.

^{13}C CP-MAS NMR: δ_{iso} (ppm) 31.0, 26.5.

^{119}Sn CP-MAS NMR: δ_{iso} (ppm) [ζ (ppm) & η] – 285 [400 & 0.0], – 458 [325 & 0.0], – 470 [312 & 0.35].

Hybrid material from precursor **1b**.

^{13}C CP-MAS NMR: δ_{iso} (ppm) 138.0, 128.9, 30.0.

^{119}Sn CP-MAS NMR: δ_{iso} (ppm) – 385, – 507, – 592, – 640.[5]

(2) H. Reuter, A. Sebald, *Z. Naturforsch,* 1992, **48B**, 195.

(3) D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, *Magn. Res. Chem.,* 2002, **40**, 70.

(4) J. Herzfeld, A. E. Berger, *J. Chem. Phys.* 1980, **73**, 6021.

(5) Extraction of the ^{119}Sn shielding tensors was not possible. Only the isotropic chemical shifts were obtained.

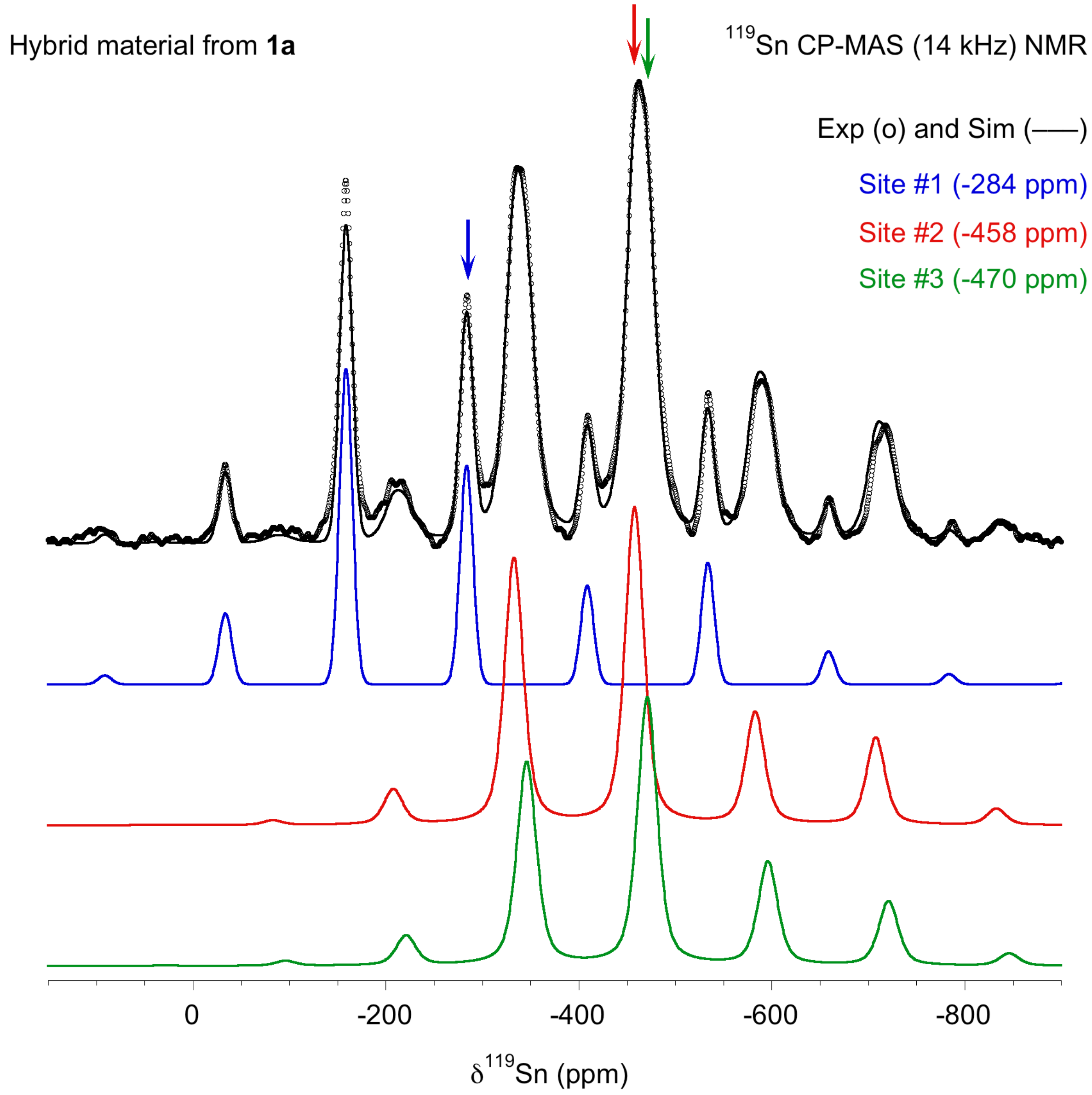


Figure S1A. Experimental and simulated ^{119}Sn CP-MAS spectrum at 14 kHz of the hybrid material prepared from **1a**.

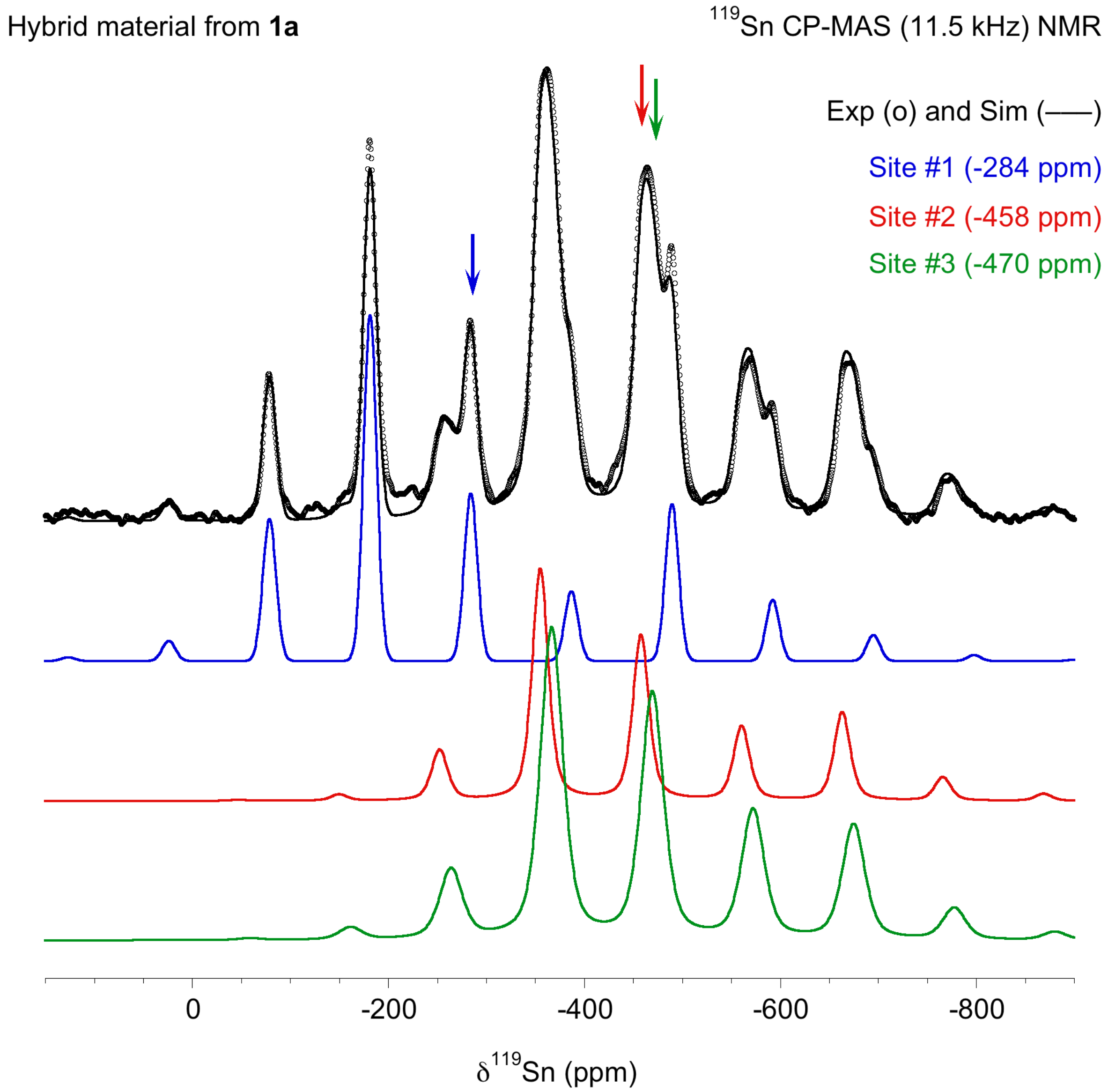


Figure S1B. Experimental and simulated ^{119}Sn CP-MAS spectrum at 11.5 kHz of the hybrid material prepared from **1a**.

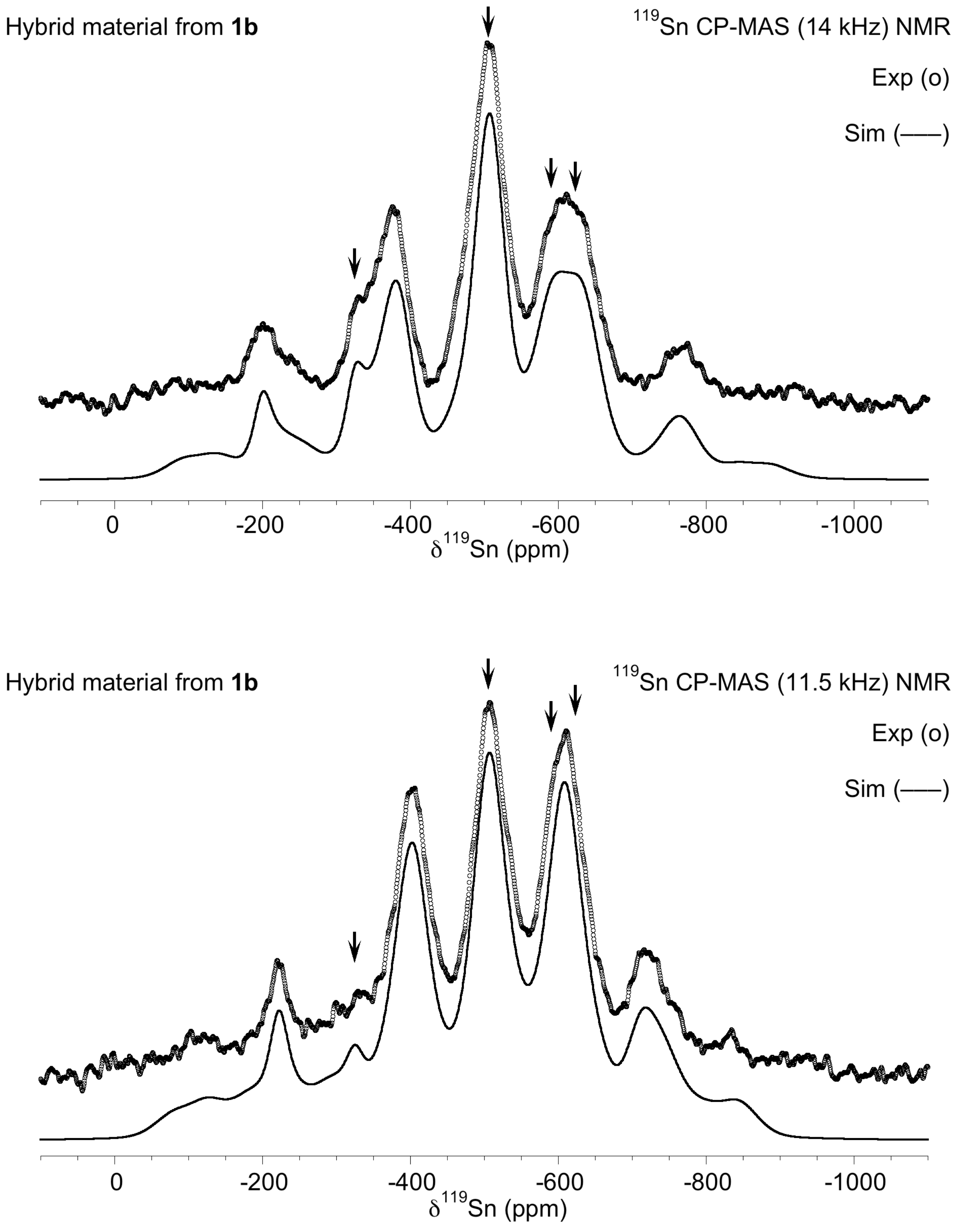


Figure S2. Experimental and simulated ^{119}Sn CP-MAS spectra at 14 kHz (top) and 11.5 kHz (bottom) of the hybrid material prepared from **1b**.

Film preparation

Glass substrates (2cm x 2cm) were washed in refluxing $CHCl_3$ (analytical grade, Aldrich) for 15 min. Then, they were exposed to UV-ozone (home-made apparatus, $\lambda = 254$ nm) for 30 min on each side. In a typical experiment, a mixture of water (0.21 g, 11 mmoles), HCl 1N (0.021 g) and THF (2 g) was added to precursors **1** (0.15 mmole) in THF (2g). The resulting solution (5 drops) was immediately spin-coated (8000 round/min/s then 1000 round/min) for 10 s. After drying in air for 15 min, the layers were annealed at 120°C for 1 (**1a**) or 4h (**1b**) to achieve the hydrolysis-condensation process as evidenced by the disappearance of the 2169 cm^{-1} band assigned to the triple bond stretching vibration of the propynyl group (FTIR).

Film characterization

Infrared spectra were recorded in the absorption mode using a FTIR Perkin-Elmer spectrophotometer. Contact angles were determined on a Krüss DAS 100 apparatus (Drop Shape System DAS 10 Mk2) at room temperature in static mode. The results correspond to the average value of at least three measurements. The values of the polar (γ_S^p) and dispersive (γ_S^d) components of the surface energy (γ_S) were calculated according to the Owens-Wendt theory using the contact angles determined for diiodomethane, ethylene glycol and water.[6] The surface morphology of the films was studied by scanning electron microscopy (SEM) with a JEOL JSM-6700F microscope. AFM images were recorded in the tapping-mode phase imaging using a standard silicon cantilever (≈ 20 N/m) on a commercial ICON AFM (DI-Veeco). XRD investigations were performed by a Seifert PTS 3003 using a Cu anode, an X-ray mirror, a long soller slit and a secondary monochromator.

Sensor tests

To investigate the sensing characteristics of the hybrids, they were processed as thin films without addition of any binder or activation layers as well as without thermal activation on suitable substrates. The dc electrical measurements were performed to monitor the sensor response to H_2 (200, 1000, 10000 ppm) in dry N_2 in absence of oxygen and in $O_2 + N_2$ mixture (10000 ppm oxygen), and to oxygen (2500, 5000 and 10000 ppm) in dry N_2. The sensor signal (S) is given as the resistance ratio R_0/R_{gas}, where R_{gas} and R_0 denote the sensors' resistances in and without the presence of an analyte gas, respectively.

(6) D.K. Owens, R. C. Wendt, *J. Appl. Sci.,* 1969, **13**, 1741.

Contact angle and surface energy determination

Precursor	θ (deg)	γ_s^d (mJ.m^{-2})	γ_s^p (mJ.m^{-2})	γ_s (mJ.m^{-2})
1a	82.4 ± 0.2	27.7 ± 0.1	5.3 ± 0.1	33.0 ± 0.2
1b	94.3 ± 0.2	24.2 ± 0.2	2.6 ± 0.1	26.8 ± 0.1

Table S1. Contact angle with water (θ) measurements and polar and dispersive components of the surface energy.

Infrared spectrum after the detection of hydrogen

The FTIR spectra of the hybrid films prepared from **1a** and **1b** after gas sensing tests are shown in Figure S3.

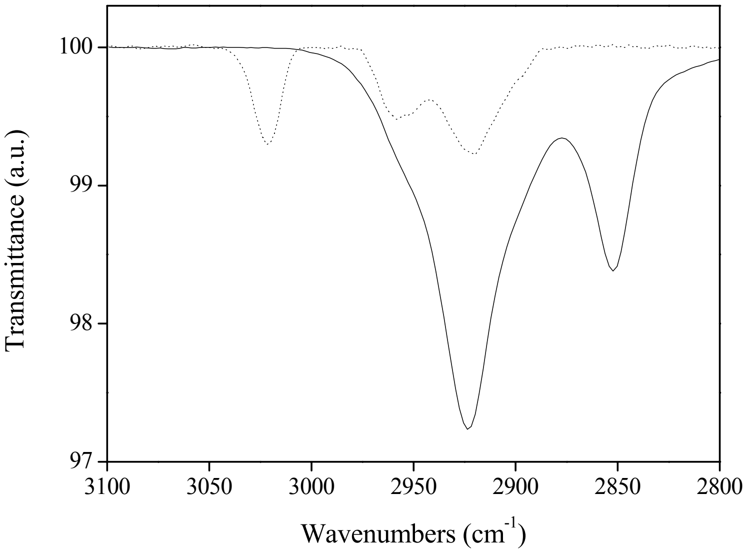
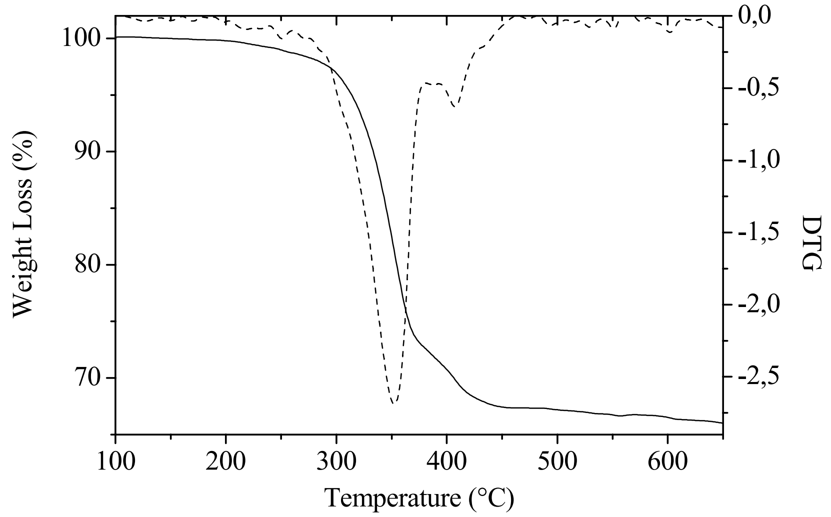


Figure S3. FTIR spectrum (CH stretching vibration region) of the hybrid films prepared from **1a** (full line) and **1b** (dotted line).

Thermogravimetric analysis

Thermogravimetric analyses (Figure S4) of hybrid powders prepared from precursors **1a** and **1b** were recorded between 100 and 650°C under an argon or a nitrogen flow at a heating rate of 10°C/min with a Netzsch STA simultaneous analyzer.



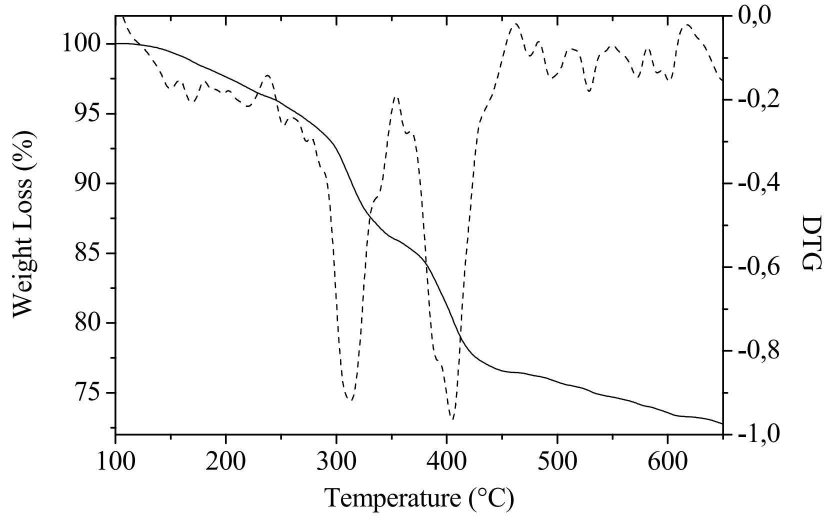


Figure S4. TG and DTG traces of the hybrid powders synthesized from **1a** (top) and **1b** (bottom).

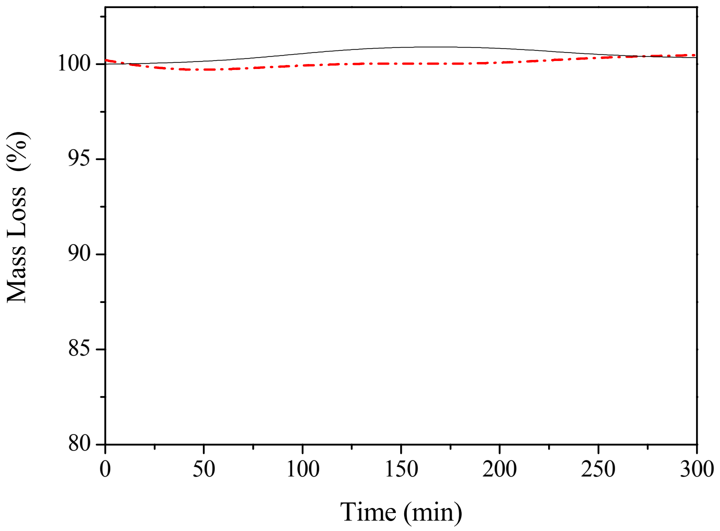


Figure S5. Mass loss as a function of time of the hybrid materials prepared from **1a** (black, full) and **1b** (red, dash) annealed at 200°C under a nitrogen flow.