

ELECTRONIC SUPPORTING INFORMATION

Microfluidics for fast and controlled preparation of organic nanotubes of bent-core based dendrimers

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CONTENT

1.- Reactor specifications

2.- Electronic microscopy details

3.- Reduction protocol for the preparation of AuNPs

4.- Optimization of processing conditions

5.- NMR experiments at variable pH

6.- Additional TEM images of hybrid materials

7.- SEM images of nanostructures deposited onto a glass

8.- Additional SEM images of nanostructures in the filters

9.- Additional SEM images of hybrid materials in the filters

1.- Reactor specifications

A capillary-based flow focusing device with coaxially aligned micro capillaries was employed for the preparation of the nanostructures. It was composed composed by a 150 μ m-diameter inner capillary that contains the organic phase (a 0.5% wt solution of the bent-core dendrimer in THF), whereas the outer capillary diameter was 500 μ m and supplied the aqueous phase aqueous phase (Figure S1a). The organic and aqueous phases were injected using two Harvard PHd syringe pumps to obtain continuous and stable flow rates and mixed at the point of confluence (Figure S1b). The flow rate and the THF/water ratio were controlled by setting different flow rate. The total volume of the reactor was 150 μ L and the outlet stream was collected in a vial. For the deposition of the nanostructures onto the PTFE filters, the outlet stream of the microreactor was connected to a syringe filter and the nanostructures' suspension was made to pass through it as depicted in Figure S1c. The microfluidic system was supported in a polymer housing fabricated by 3D-printing to avoid capillary misalignment and to favour fluid dynamic reproducibility. The organic and aqueous phases were injected using two syringe pumps to obtain continuous and stable flow rates. The shear stress mismatch between the organic and aqueous streams was able to produce turbulence (eddy diffusion) at the point of confluence and this promotes the entrainment of the organic stream in the aqueous one.^[1]

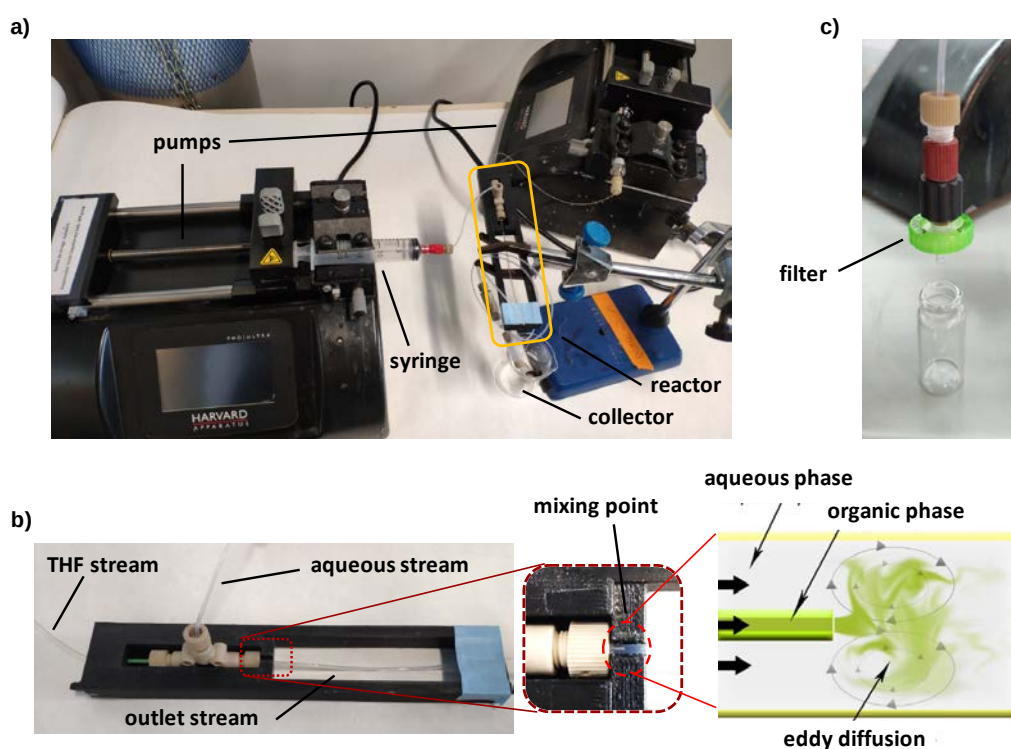


Figure S1. a) Setup of the coaxial microreactor. b) Detail of the reactor and the mixing point. c) Setup of the filter coupled to the outlet stream.

[1] M. Dianat, Z. Yang, D. Jiang, J. J. McGuirk, *Flow Turbulence Combust* **2006**, 77, 205–227.

2.- Electronic microscopy details

TEM images were recorded in a TECNAI G² 20 (FEI COMPANY) microscope using a work voltage of 200 kV (Advanced Microscopy Laboratory (LMA) and Servicio de Apoyo a la investigación, Universidad de Zaragoza (SAI)). Suspensions of the nanostructures collected at the outlet stream of the reactor were deposited onto a copper grid and negatively stained with uranyl acetate prior to observation for better contrast.

SEM images of deposited samples were registered in a Scanning Electron Microscope Carl Zeiss MERLIN with Field Emission Gun working at 5kV (SAI, Universidad de Zaragoza). The morphology of the nanoassemblies was detected using an In-lens high resolution SE detector. An Energy selective backscattered detector (EsB) and an Angular selective backscattered electron detector (AsB) were employed to obtain a compositional contrast of the samples. An Energy-dispersive X-ray spectroscopy (EDS) detector was used to determine the exact atomic composition of the samples.

3.- Reduction protocol for the preparation of AuNPs

A stainless steel, Teflon lined autoclave was fitted with a specially designed Teflon insert to keep the sample at high CO pressure 6 bar for the chemical reduction of Au^{III} to Au⁰. A water heating bath was used to heat the reactor at 50°C during 40 minutes or redox treatment.

4.- Optimization of processing conditions

Evolution over time

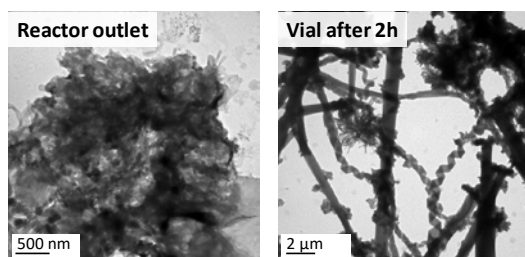


Figure S2. TEM images of nanostructures of **PPI1-B1-4-8** obtained at the reactor outlet or after equilibration during 2h at a vial prepared at THF/water ratios 1/0.70, at a flow rate of 500μL/min (residence time of 18 s) and at a 0.5 % wt.

Flow rate

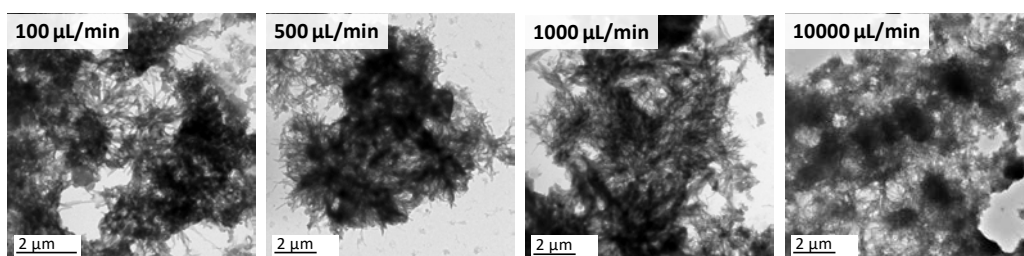


Figure S3. TEM images of nanostructures of **PPI1-B1-4-8** prepared at THF/water ratios 1/0.45 and at residence times 90s (100μL/min), 18s (500μL/min), 9s (1000μL/min) and 0.9s (10000μL/min).

Concentration of PPI1-B1-4-8

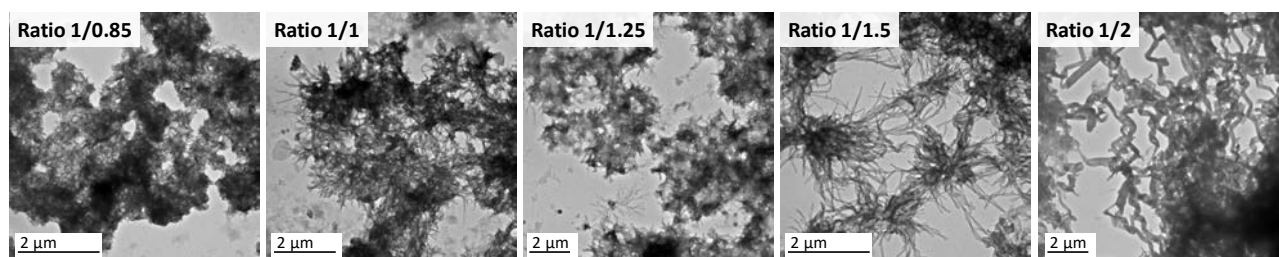


Figure S4. TEM images of nanostructures of **PPI1-B1-4-8** prepared at an amphiphile concentration of 0.2% wt at a flow rate of 500μL/min (residence time of 18s).

Effect of the temperature

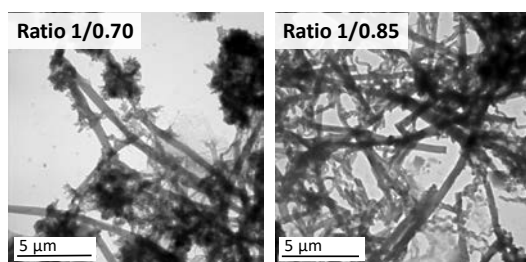


Figure S5. TEM images of nanostructures of **PPI1-B1-4-8** prepared at 50°C at 0.5 % wt and at a flow rate of 500μL/min (residence time of 18s).

Effect of the pH

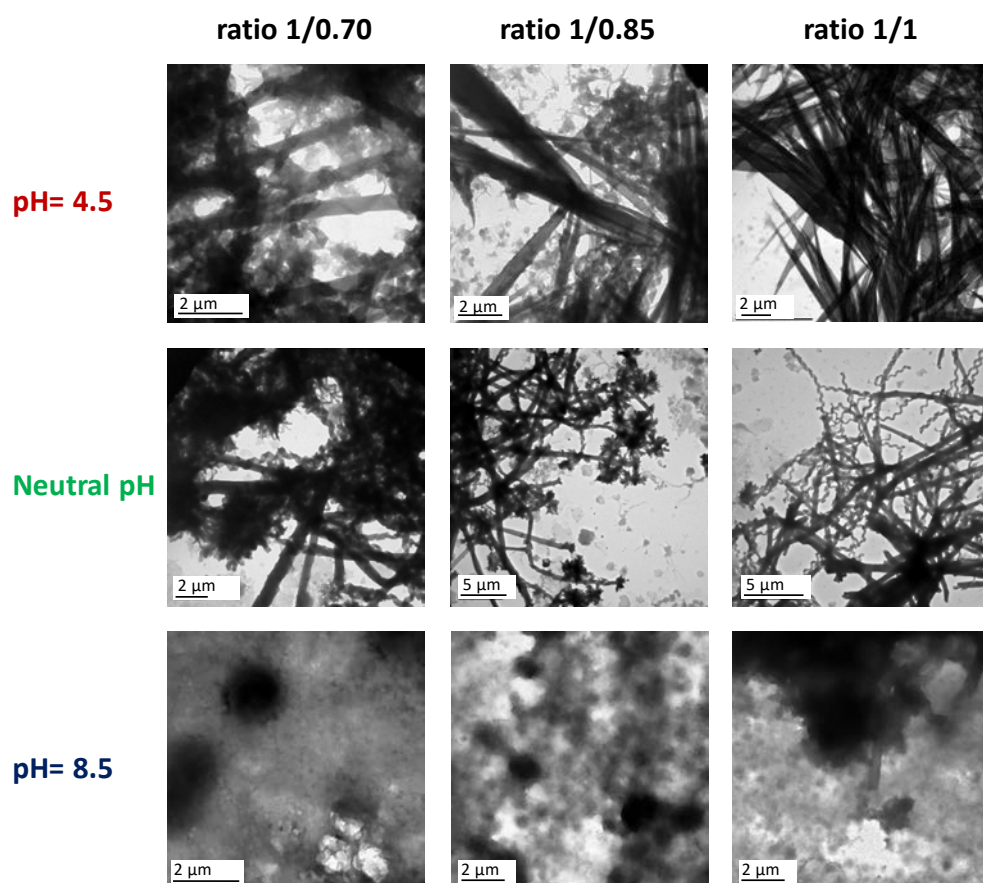


Figure S6. TEM images of nanostructures of **PPI1-B1-4-8** prepared at variable pH at different THF/water ratios, at 0.5 % wt and at a constant flow rate of 500μL/min (residence time of 18s).

5.- NMR experiments at variable pH

Samples were prepared by adding 0.15 mL of an aqueous solution in D₂O (acid media: acetate buffer, 0.1 M, pH = 4; basic media: carbonate buffer, 0.1 M, pH = 9.2) to 0.50 mL of a 0.5% wt solution of PPI1-B1-4-8 in THF-d₈. The ¹H-NMR spectra in the acidic medium showed a down-field shift of signals C and D. COSY experiments allowed these signals to be assigned to the CH₂ groups α to the inner nitrogen atoms. Consequently, we consider that this change is due to the protonation of the inner nitrogen atoms of the PPI dendrimer.

The ¹H-NMR spectra obtained in a basic medium revealed the appearance of a new signal. COSY and HSQC experiments suggest that both the A and A' signals are due to CH₂ groups in the α-position to a primary amine. Thus, we propose that in basic aqueous phases the terminal NH₃⁺ of the PPI dendrimer is partially deprotonated. This explains the splitting of the A signal.

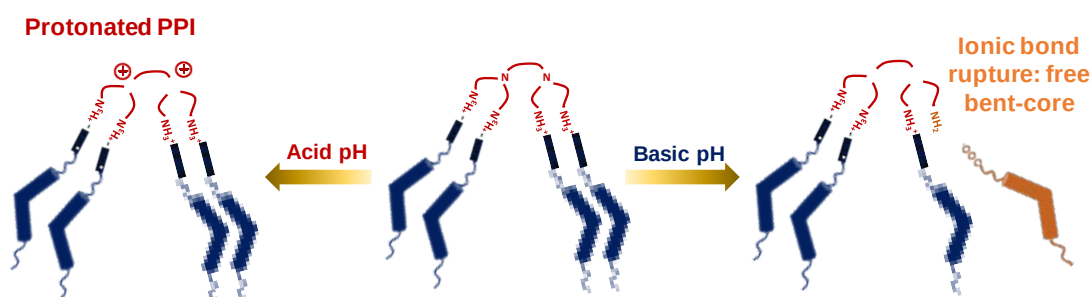


Figure S7. Schematic representation of changes in the ionic dendrimers at variable pH.

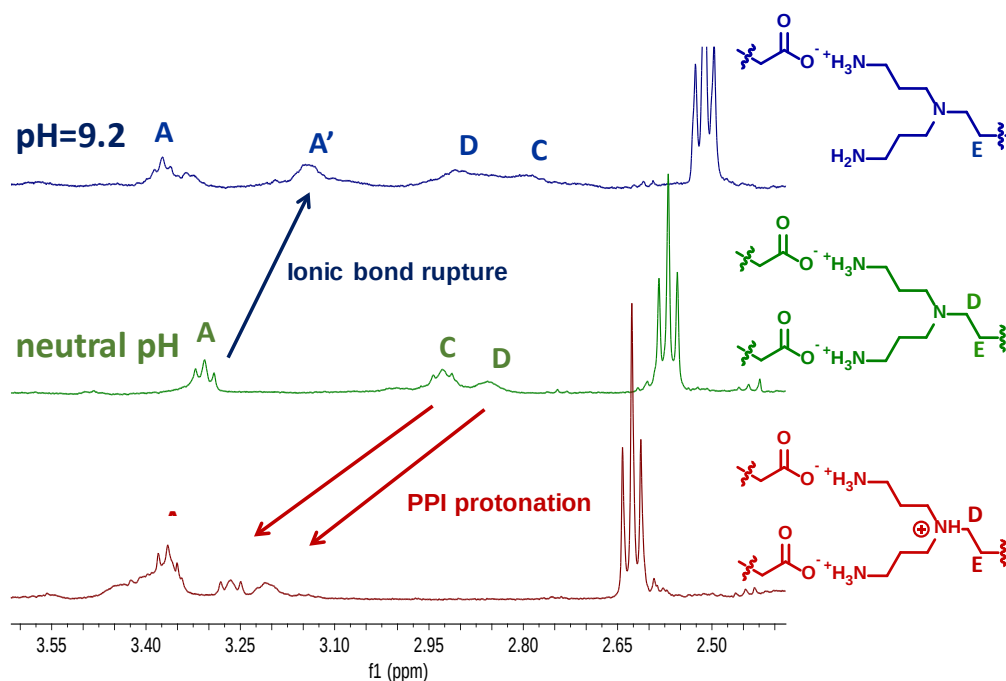


Figure S8. ¹H-NMR of PPI1-B1-4-8 at variable pH. Performed over a 0.5% wt in d₈-THF solution mixed with aqueous buffers. Acid conditions: acetate buffer, 0.1 M, pH = 4; basic conditions: carbonate buffer, 0.1 M, pH = 9.2.

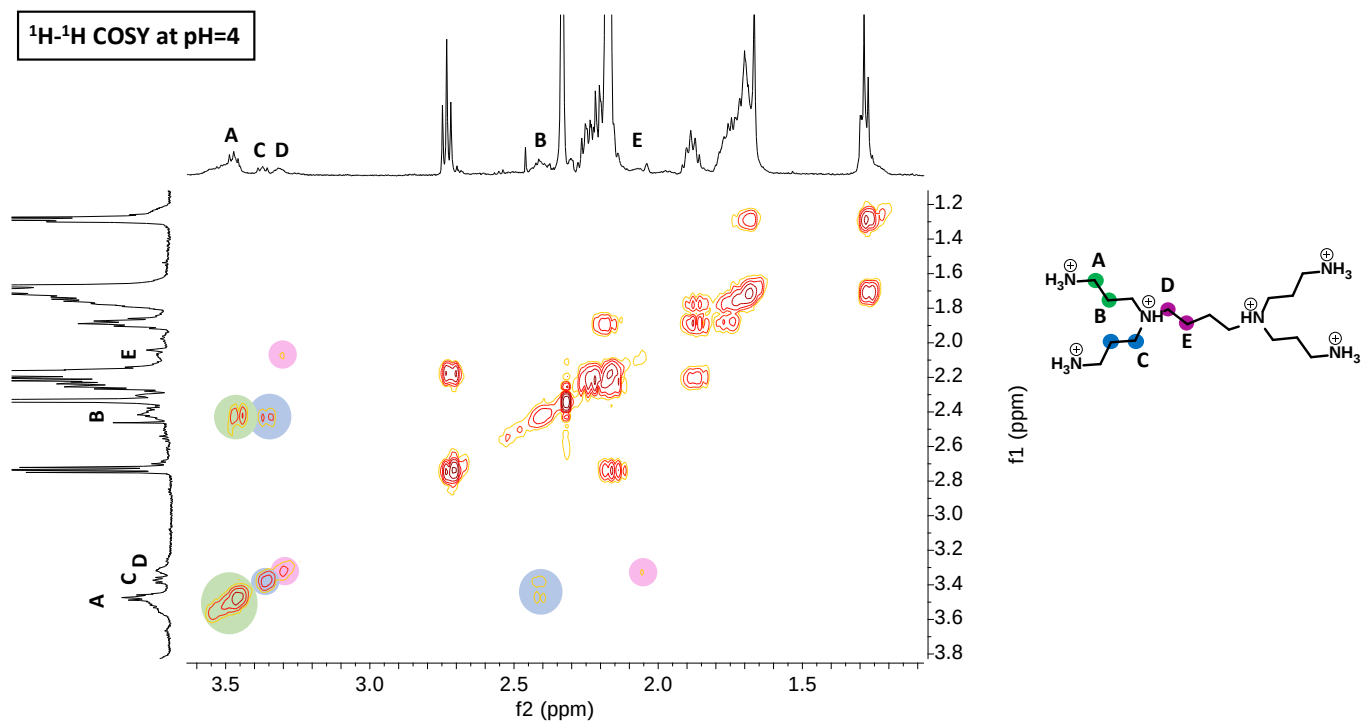


Figure S9. ^1H - ^1H COSY of PP1-B1-4-8 at pH=4.

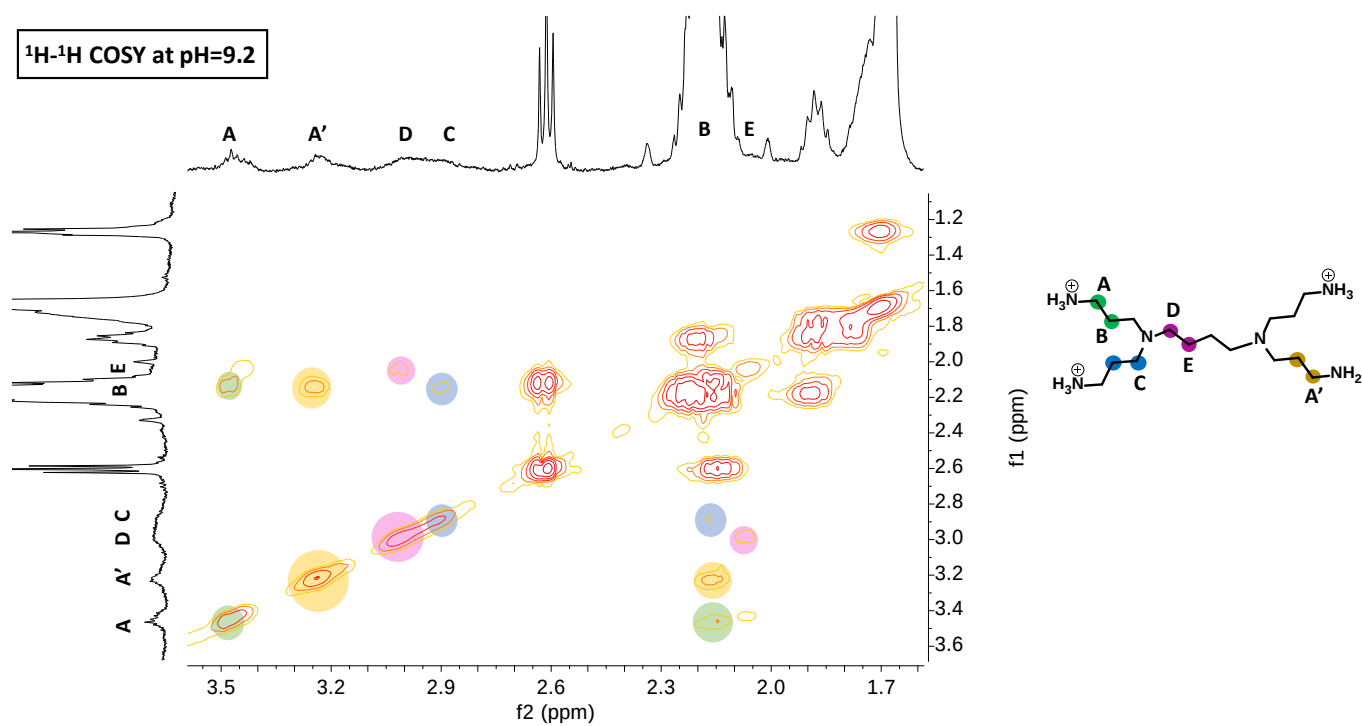


Figure S10. ^1H - ^1H COSY of PP1-B1-4-8 at pH=9.2.

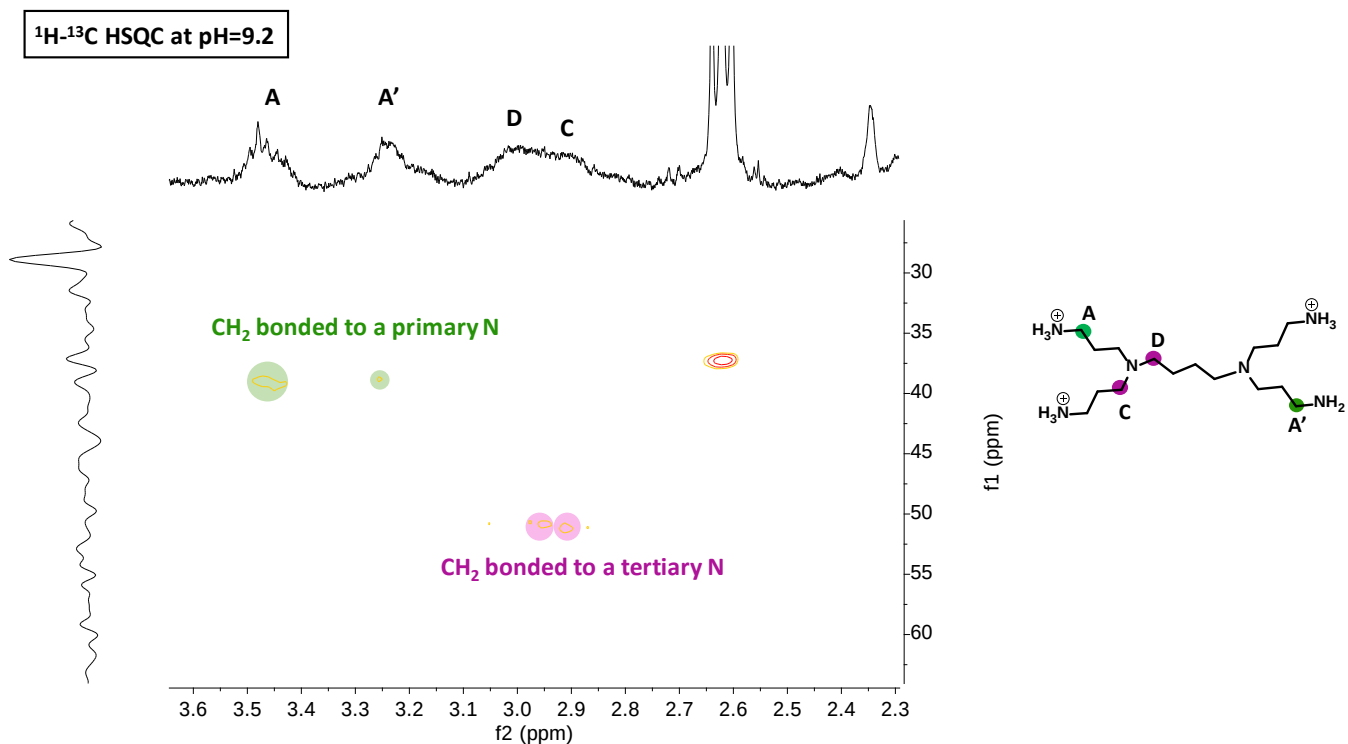


Figure S11. ^1H - ^{13}C HSQC of **PP1-B1-4-8** at pH=9.2.

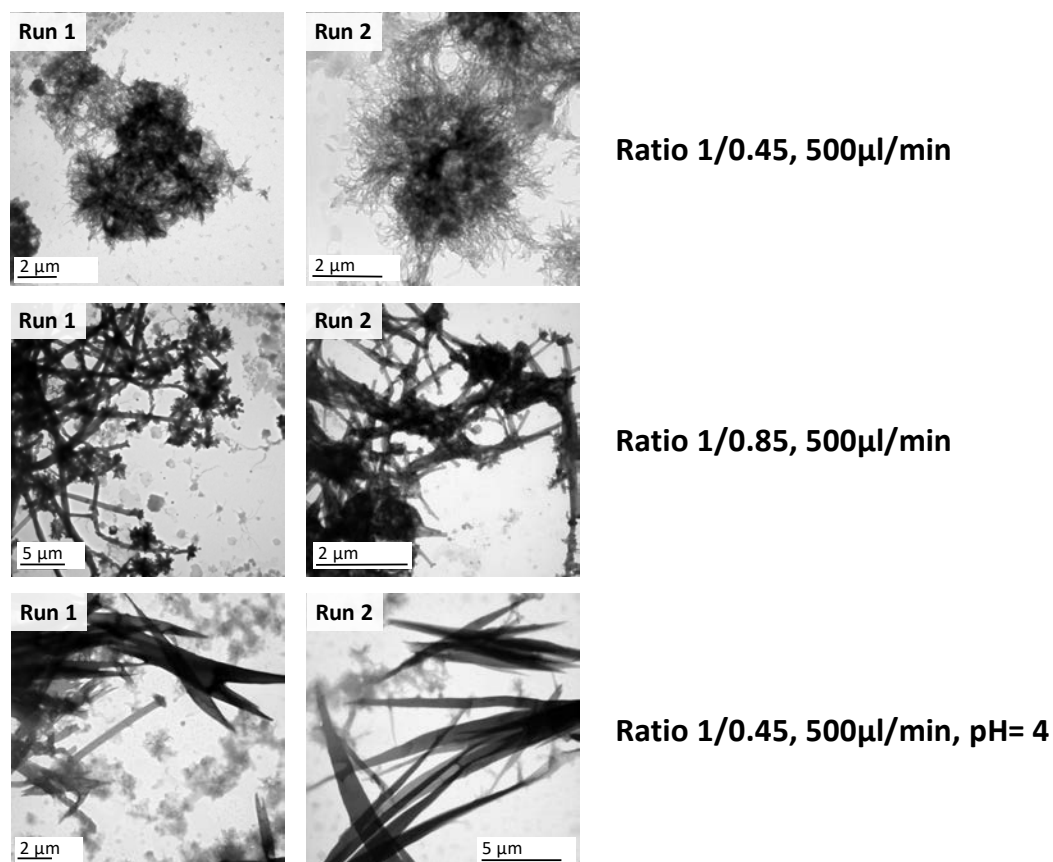


Figure S12. Comparative TEM images of nanostructures of **PP1-B1-4-8** prepared in two different runs at the same conditions.

6.- Additional TEM images of hybrid materials

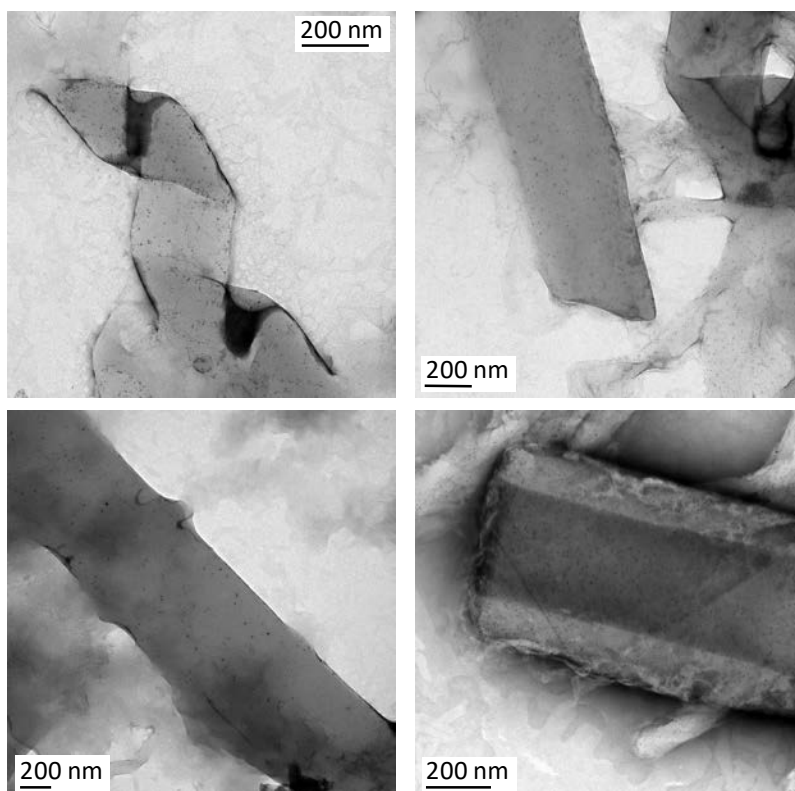


Figure S13. TEM images of hybrid materials of **PP1-B1-4-8** covered with AuNPs. Organic nanostructures were prepared in the microreactor. Nanoparticles were prepared by addition of AuCl_3 to the nanostructures prepared at 0.5 % wt and at a flow rate of $500\mu\text{L}/\text{min}$ (residence time of 18s) and subsequent reduction with CO.

7.- SEM images of nanostructures deposited onto a glass

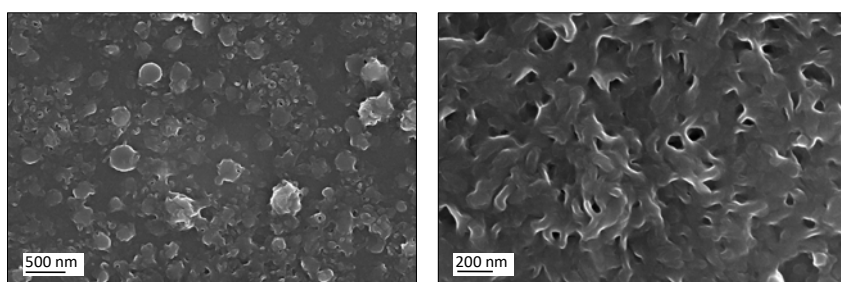


Figure S14. SEM images of **PP11-B1-4-8** drop-casted onto a glass cover.

8.- Additional SEM images of nanostructures in the filters

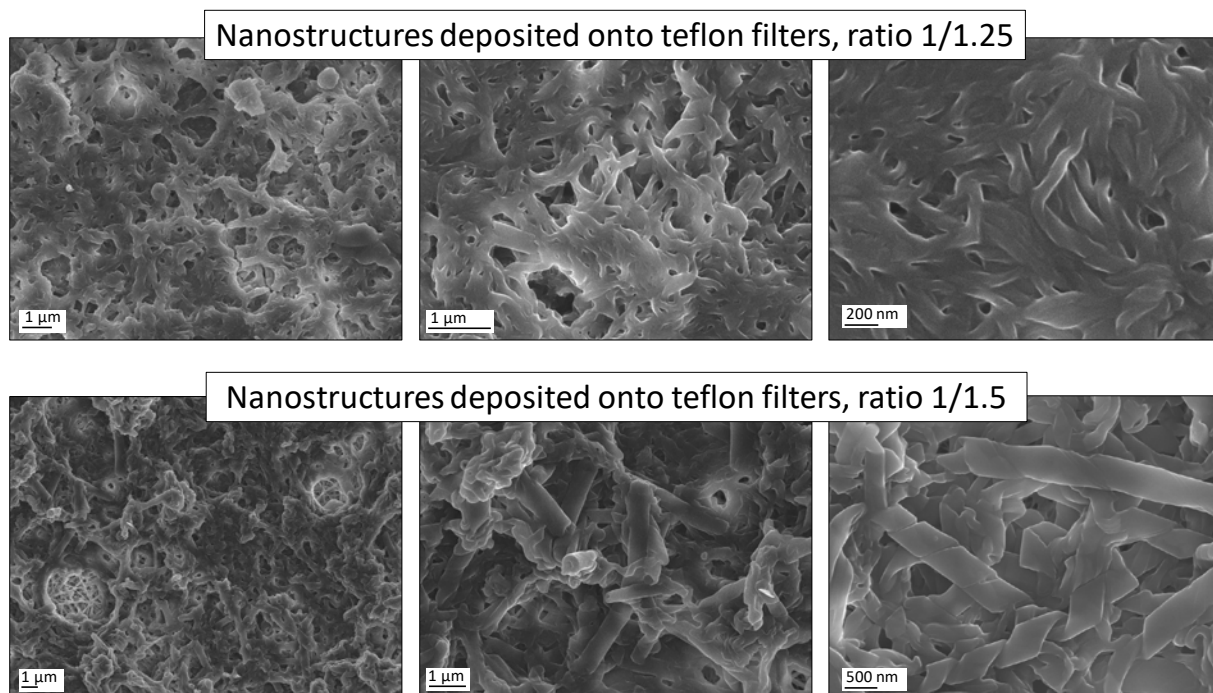


Figure S15. Additional SEM images of **PPI1-B1-4-8** deposited onto a Teflon filter at THF/water ratio 1/1.25 (top) and 1/1.5 (down).

9.- Additional SEM images of hybrid materials in the filters

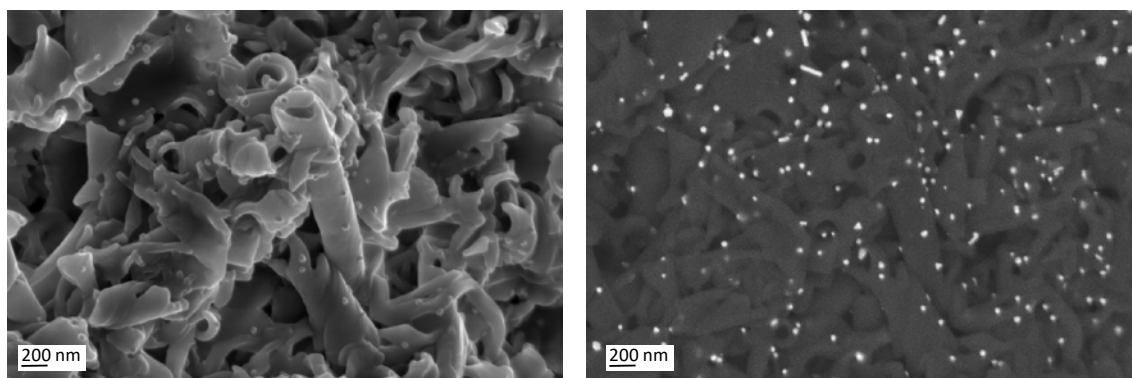


Figure S16. Additional SEM images of hybrid materials of **PPI1-B1-4-8** covered with AuNPs deposited onto a Teflon filter at THF/water ratio 1/1.5. *Left:* Image taken with the InLens detector. *Right:* Image taken with the Low energy backscattered electrons detector.

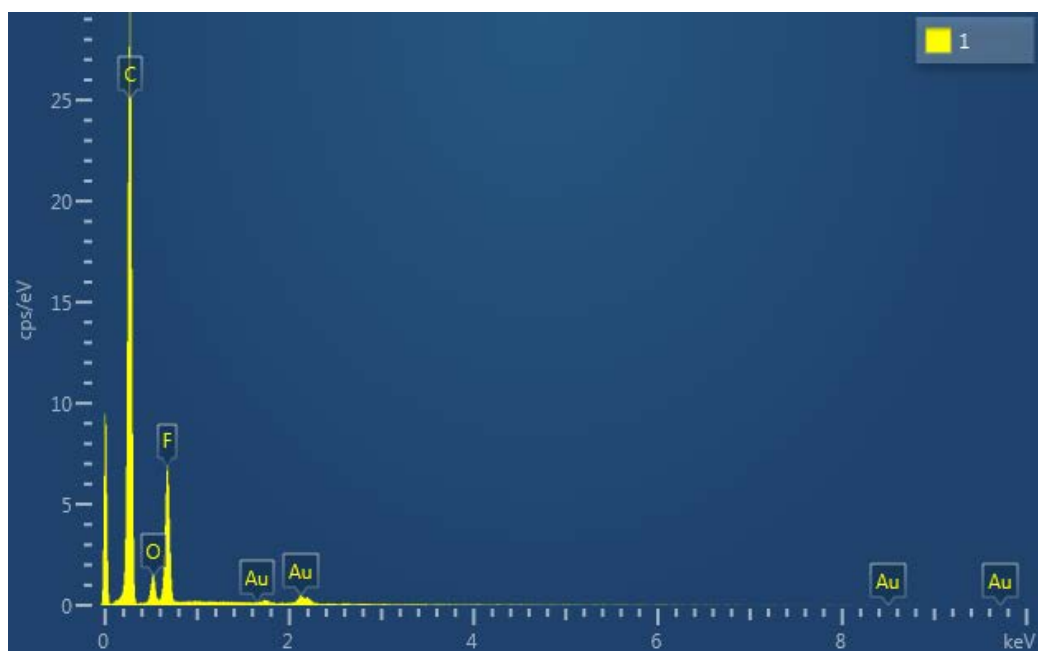


Figure S17. Energy-dispersive X-ray spectroscopy spectrum of the hybrid materials deposited onto a Teflon filter. Signals of carbon and oxygen from the **PPI1-B1-4-8** nanostructures and Au from the nanoparticles can be observed. Also fluorine signals from the filter is detected.