# **Electronic Supplementary Information (ESI)**

# Versatile approach to nanoporous polymers with bicontinuous morphology using metal templated synthesis

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### 1) Dealloying of Au<sub>35</sub>Ag<sub>65</sub>

The Au<sub>35</sub>Ag<sub>65</sub> pellets were immersed in 65 % HNO<sub>3</sub> solution and heated to 80 °C during 12 h. After complete dissolution of Ag (as confirmed by weight loss measurements), the dealloyed pellet (np-Au) was rinsed with a mixture of ultrapure water and ethanol at 1:1 (v/v). Figure S1 shows SEM images of the obtained np-Au and the corresponding EDX spectrum.



Figure S1. Top-view SEM images of np-Au template of gyroid-like morphology observed at two different magnifications (A, B), and corresponding EDX spectrum (C).

## 2) Dissolution of Au from polymer-filled np-Au composites

The PS or PCN filled np-Au was immersed during 4 days in an aqueous solution of KI (0.6 mol  $L^{-1}$ , 3 eq.) and I<sub>2</sub> (0.2 mol  $L^{-1}$ , 1 eq.). The resulting np-PS or np-PCN was cleaned with distilled water, dried in open air at room temperature for a few hours before being visualized by SEM. The complete removal of metal framework was confirmed by EDX analysis. Figure presents EDX spectra taken before and after Au removal in KI/I<sub>2</sub> from a np-Au/PS composite. The peak of Au has completely disappeared.



Figure S2. SEM images and EDX spectra of a np-Au/PS composite before [A] and after Au dissolution in KI/I2 to form np-PS [B]. Scale bar: 400 nm. Pt and Pd EDX peaks observed in [B] are due to a 3 nm thick layer of Pt<sub>80</sub>Pd<sub>20</sub> sputtered on np-PS to improve SEM imaging (insulating material).

#### 3) Densities and specific surface areas of the np-polymers

**Densities.** The excess of bulk polymer, often found on a portion of the synthesized np-polymer samples, was a problem in determining the apparent density of np-polymers from mass and volume measurements. The open porosity prevented the use of a pycnometer as well. Consequently, the apparent densities were estimated by calculation from data reported in the literature about the porosity of the np-Au templates (65% with our dealloying conditions), and the density *d* of bulk polymers. Considering that our synthetic method goes through the elaboration of Au/polymer composites for which the np-polymer phase is the exact complementary part of the np-Au phase (template), the porosity of np-polymers after Au dissolution will be 35 % and:

$$d_{np-PS} = 0.65 \ d_{PS} = 0.65 \ x \ 1.05 = 0.68 \ g \ cm^{-3}$$
  
 $d_{np-PCN} = 0.65 \ d_{PCN} = 0.65 \ x \ 1.26 = 0.82 \ g \ cm^{-3}$ 

with  $d_{PS} = 1.05 \text{ g cm}^{-3}$  and  $d_{PCN} = 1.26 \text{ g cm}^{-3}$ .

**Specific surface areas.** The fact that the np-polymer phase is the exact complementary part of the np-Au phase (template) also implies that the two phases have identical surface areas *s*:

$$S_{np-Au} = S_{np-pol}$$

The surface area s (m<sup>2</sup>) is equal to the specific surface area S (m<sup>2</sup> g<sup>-1</sup>) multiplied by the mass *m*:

$$s_{np-Au} = S_{np-Au} m_{Au}$$
  
 $s_{np-pol} = S_{np-pol} m_{pol}$ 

The specific surface areas of Au and the polymer are therefore related according to:

$$S_{np\text{-pol}} = S_{np\text{-}Au} \frac{m_{Au}}{m_{pol}}$$

In the Au/polymer composites, the fraction of Au is 0.35 and the fraction of polymer is 0.65, so the mass ratio is always:

$$\frac{m_{Au}}{m_{pol}} = \frac{0.35d_{Au}}{0.65d_{pol}}$$

 $d_{pol}$  and  $d_{Au}$  being the density (g cm<sup>-3</sup>) of the bulk polymer and bulk Au.

Finally:

$$S_{np-pol} = S_{np-Au} \frac{0.35d_{Au}}{0.65d_{nol}}$$

with:  $d_{Au} = 19.32 \text{ g cm}^{-3}$ 

 $d_{pol} = 1.05 \text{ g cm}^{-3}$  for polystyrene (PS)  $d_{pol} = 1.26 \text{ g cm}^{-3}$  for the polycyanurate (PCN).

Since the np-Au obtained under our dealloying conditions has a specific surface area contained between 2 and 4 m<sup>2</sup> g<sup>-1 [1-3]</sup>, we found:

20 m<sup>2</sup> g<sup>-1</sup> < 
$$S_{np-PS}$$
 < 40 m<sup>2</sup> g<sup>-1</sup>  
17 m<sup>2</sup> g<sup>-1</sup> <  $S_{np-PCN}$  < 33 m<sup>2</sup> g<sup>-1</sup>

#### 4) Optimization of the concentration of PS in THF for the pore-filling step

Figure S3 gives SEM images of three np-PS samples obtained with different PS concentrations in THF, *i.e.* 0.2 [A], 0.5 [B] and 1.0 g mL<sup>-1</sup> [C].



Figure S3. SEM images of np-PS obtained by impregnating np-Au in a solution of PS dissolved in THF at (A) 0.2 g  $L^{-1}$  (ligaments with sponge-like texture); (B) 0.5 g  $L^{-1}$  (ligaments with dense texture); (c) 1.0 g  $L^{-1}$  (the excess of polymer material can be easily observed on the top of figure 3C).

Figure S4 shows two NMR spectra of the DCBE monomer: (a) 1H NMR and (b) 13C NMR.



Figure S4. (a) 1H NMR and (b) 13C NMR spectra of DCBE monomer

#### References

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