## **ELECTRONIC SUPPORTING INFORMATION**

# Nanocomposites based on Hofmann's clathrate Ni<sup>II</sup>(pz)[Ni<sup>II</sup>(CN)<sub>4</sub>] (pz = pyrazine) nanoparticles for reversible iodine capture.

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### **Experimental Part (supplementary information)**

#### Synthesis of [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>2</sub>[Ni(CN)<sub>4</sub>].

All precursors for the infiltration are commercial except the  $(C_4H_9)_4N[Ni(CN)_4]$  that is prepared by a metathesis reaction. 10 mmol of  $K_2[Ni(CN)_4]$  and 20 mmol of  $(C_4H_9)_4NBr$  (TBABr) are dissolved into the biphasic system (50 vol% of distilled water and 50 vol% of organic solvent –  $CH_2Cl_2$  or  $CHCl_3$ ) and agitation is performed for 1 hour with a rotor driver at room temperature. The organic phase is separated through a separator funnel and dried with MgSO<sub>4</sub>. The organic solvent is evaporated under reduced pressure at P = 300 mbar and T = 50 °C. In order to eliminate the excess of TBABr the compound is purified in hot diethyl ether at 50 °C for 3 H and filtered. The final product is dried in oven at 80 °C. Final aspect: pale orange. IR (KBr, cm<sup>-1</sup>): (cyanide) 2109.

#### Experimental determination of the entrapped amount of iodine.

To perform all entrapment tests in solution with the hybrid materials (kinetics and isotherms), a fixed powder-to-volume ratio was chosen in order to compare all data: 20 mg of material per 20 ml of solution. The entrapments were performed rigorously in round bottom flasks, since iodine showed a certain reactivity toward all plastics and metallic surfaces. The flasks were hermetically closed to avoid evaporation of the solution.

The entrapped amount was determined by UV-VIS spectroscopy, by measuring the maximal absorbance (*A*) at  $\lambda = 525$  nm before and after the entrapment test, in standard cuvettes (width of 1 cm). The concentrations were obtained by dividing the absorbance by the experimental value of 929.61 L.mol<sup>-1</sup>. For concentrations over 10<sup>-3</sup> M a dilution was necessary to avoid saturation at the spectrometer. Then the calculated concentrations were used in the following formula, in order to obtain the entrapped amount in the chosen unit [mmol.g<sup>-1</sup>], *i.e.* mmol of entrapped I<sub>2</sub> per unit mass of employed powder:

$$Q[mmol, g^{-1}] = \frac{(C_1 - C_2) \cdot V}{m} \cdot 1000$$

where  $C_1$  is the iodine concentration before entrapment expressed in [mol.L<sup>-1</sup>];  $C_2$  is the iodine concentration after entrapment expressed in [mol.L<sup>-1</sup>]; *V* is the volume of the solution in [L] and *m* is the mass of the powder expressed in [g].

#### Linearized models for the kinetics and the isotherms in solution.

For the kinetic study a pseudo-second order model was used to describe the trend, since it successfully approximates the sorption processes onto solid adsorbents. In order to fit the experimental Q vs t curve, the following equation was employed:

$$\frac{t}{Q} = \frac{1}{kQ_s^2} + \frac{t}{Q_s}$$

where *t* is the time; *Q* is the entrapped amount at time *t*;  $Q_e$  is the entrapped amount at the equilibrium and *k* is the kinetic constant. By tracing the regression curve the constants  $Q_e$  and *k* can be determined from the slope and the intercept. For the isotherms the Langmuir model was considered suitable to describe the experimental Q vs C curves, since the maximal iodine adsorption was limited at the first monolayer on the solids. The linear shape for the Langmuir model is:

$$\frac{1}{Q} = \frac{1}{Q_{max}} + \frac{1}{KQ_{max}} \frac{1}{C}$$

Where C is the equilibrium concentration; Q is the entrapped amount at concentration C;  $Q_{max}$  is the entrapped amount at saturation conditions and K is the Langmuir constant (or sorption heat). By tracing the regression curve the constants  $Q_{max}$  and K can be determined from the slope and the intercept.



**Figure S1**. Pictures of glass pearls based samples: 1) grafted glass pearls (*Glass*); 2) *Glass@NP*; 3) grafted glass pearls (*Glass*) after iodine uptake; 4) *Glass@NP* after iodine uptake.



b)





**Figure S2.** TGA curves for: a) functionalised mesoporous silica (*Sil*), *Sil@NP* nanocomposite, *Sil@NP* nanocomposite after iodine loading/desorption and the bulk Hofmann clathrate Ni<sup>II</sup>(pz)[Ni<sup>II</sup>(CN)<sub>4</sub>]; b) functionalised glass pearls, *Glass@NP* nanocomposite, *Glass@NP* nanocomposite after iodine loading/desorption and the bulk Hofmann structure Ni<sup>II</sup>(pz)[Ni<sup>II</sup>(CN)<sub>4</sub>]; c) functionalised mesoporous silicas, *Sil@NP* nanocomposite and the bulk Hofmann structure Ni<sup>II</sup>(pz)[Ni<sup>II</sup>(CN)<sub>4</sub>] after iodine uptake; d) functionalised glass pearls, *Glass@NP* nanocomposite and the bulk Hofmann structure Ni<sup>II</sup>(pz)[Ni<sup>II</sup>(CN)<sub>4</sub>] after iodine uptake.

Note that TGA curves indicated that the diamine functionality is stable up to 250 °C and the nanoparticles are stable up to 300 °C. TGA curves of the iodine-loaded materials indicate the start of iodine loss at 250 °C for *Sil* and at 150 °C for *Sil@NP*; the difference is explained by the presence of  $I_3$  in the former and predominantly  $I_2$  in the latter. In the case of glass beads, iodine is desorbed at 150 °C for both, *Glass* and *Glass@NP*, since partial decomposition of  $I_5$  occurs too.



**Fig S3.** Nitrogen adsorption isotherms at 77 K for the glass pearls before, after diamine groups grafting and glass pearls based nanocomposite *Glass@NP*. Inset: pore size distribution for the glass pearls before, after diamine groups grafting and nanocomposite *Glass@NP*.



**Figure S4.** UV-VIS spectra for functionalised glass pearls, Glass@NP nanocomposite and the bulk Hofmann clathrate Ni<sup>II</sup>(pz)[Ni<sup>II</sup>(CN)<sub>4</sub>] before and after iodine uptake.



**Figure S5.** Cyanide bands in the 2250 – 2000 cm<sup>-1</sup> range of the FT-IR spectra of the bulk  $Ni^{II}(pz)[Ni^{II}(CN)_4]$ , *Sil@NP* and *Glass@NP* before and after iodine uptake.



Figure S6. Kinetic curves for the grafted glass pearls, *Glass@NP* nanocomposite, and the bulk clathrate in a cyclohexane solution. The solid lines represent the fits with a pseudo-second order model.



**Figure S7.** Iodine absorption isotherms in a cyclohexane solution for the grafted glass pearls, the *Glass@NP* nanocomposite and the bulk clathrate. The solid lines represent the fit with the Langmuir model.



**Figure S8.** Reversibility of cyanide band v(CN) at thermal desorption of iodine and degradation at 300°C for Sil@NP and Glass@NP.



Figure S9. UV-Vis spectra demonstrating the cycling ability for the *Glass@NP* nanocomposite.