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Iodine Capture by Hofmann-Type Clathrate $Ni^{II}(pz)[Ni^{II}(CN)_4]$

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S *Supporting Information*

ABSTRACT: The thermally stable Hofmann-type clathrate framework $Ni^{II}(pz)[Ni^{II}(CN)_4]$ (pz = pyrazine) was investigated for the efficient and reversible sorption of iodine (I_2) in the gaseous phase and in solution with a maximum adsorption capacity of 1 mol of I_2 per 1 mol of $Ni^{II}(pz)[Ni^{II}(CN)_4]$ in solution.

Various processes from the nuclear industry produce an important quantity of radioactive effluents that have to be treated in order to minimize their impact on the environment. Among those, radioactive iodine (I_2) isotopes produced during the fission of ^{235}U, and particularly the γ-ray emitter ^{129}I with a long half-life,[1] are dangerous for health because of their volatility and their persistence in the environment. For this reason, efficient and selective I_2 capture has attracted a great deal of attention in recent years. Several processes consisting of the precipitation of stable and insoluble compounds, like NaI in the scrubbing with alkali solutions, HgI_2 in the "Mercurex process", or $Ba(IO_3)_2$ in the "Iodox process", are currently used in industry.[2] However, they generally possess multistep procedures and cannot be used directly for gas capture. Such treatments also generate an important volume of radioactive wastes, which should then be retreated. Other industrial processes use a silver sorbent, like silver-exchange zeolite,[3] but I_2 diffusion inside the zeolite is slow and limits the adsorption. Moreover, the stability of silver-exchange zeolite is poor.

One of the most promising strategies to direct sequestration of radioiodine from the exhaust gas is to design new thermally stable nanoporous materials, such as zeolite,[4] zeolite-related structures ("zeoballs")[5] or metal−organic frameworks (MOFs),[6−9] able to selectively and efficiently capture I_2. In particular, the latter exhibit high iodine sorption efficiency because of their higher porosity in comparison with the zeolite-like materials. One can cite the three-dimensional $[Cu^{II}(btz)]_n$ MOF[7] [H_2btz = 1,5-bis(5-tetrazolo)-3-oxapentane] able to absorb 0.5 I_2/Cu^{II}, a series of aluminum carboxylate-based functionalized MOFs with a maximum capacity of 0.71 I_2/Al for MIL-100-NH_2,[6] as well as the Zn^{2+}-based zeolitic imidazolate framework (ZIF-8)[8] and the $[Cu_3(btc)_2]_n$ (btc = 1,3,5-benzene tricarboxylate) MOF[9] able to capture volatile I_2 respectively up to 0.76 I_2/Zn and 1.1 I_2/Cu. Recently, I_2 entrapment by another promising nanoporous coordination polymer family called Hofmann-like clathrates has been patented.[10] However, to the best of our knowledge, detailed studies of I_2 sorption by these materials have never been reported.

Hofmann clathrates are a wide family of cyano-bridged coordination polymers of transition-metal ions exhibiting cages in their three-dimensional networks and thus able to capture small guest molecules. The first clathrate of formula $Ni(CN)_2(NH_3)\cdot C_6H_6$ having a guest benzene molecule was reported in 1897 by Hofmann and colleagues.[11] Henceforth, numerous compounds of this family of different compositions and dimensionalities, capable of capturing various tailored molecules, have been investigated.[12] Among those, $Fe^{II}(pz)[M^{II}(CN)_4]$ (pz = pyrazine, M^{2+} = Ni^{2+}, Pd^{2+}, Pt^{2+}) networks have been reported as chemoresponsive porous coordination polymers presenting a switching of the Fe^{II} spin state through guest adsorption processes at room temperature.[13] In such cases, the guest molecules, i.e., gases (N_2, O_2, CO_2, SO_2, H_2) or vapors of alcoholic (MeOH, EtOH), aromatic (toluene, benzene), or miscellaneous solvents [CS_2, $CH_3C(O)CH_3$, CH_3CN], are confined in the pores, interacting weakly with the pyrazine pillar ligands or the Fe^{II} centers. Surprisingly, only one article reports so far the potential aptitude of such networks to host the I_2 molecule, with formation of the $Fe^{II}(pz)[Pt^{II/IV}(CN)_4](I)$ complex synthesized directly in the presence of I_2 and leading to an oxidative addition with formation of a Pt^{IV}−I bond.[14] In this Communication, we report an I_2 adsorption investigation by the $Ni^{II}(pz)[Ni^{II}(CN)_4]$ network, which for the first time demonstrates the efficiency of Hofmann clathrates as high-capacity I_2 absorbents in liquid and gaseous phases.

The coordination polymer $Ni^{II}(pz)[Ni^{II}(CN)_4]\cdot 2H_2O$ was obtained as a microcrystalline powder according to a slightly modified published procedure [see the Supporting Information (SI) and Figure S1].[12,13] Powder X-ray diffraction (PXRD; Figure 1) indicates that the compound is isostructural to the previously reported $Fe^{II}(pz)[Pt^{II}(CN)_4]$ analogue, as shown

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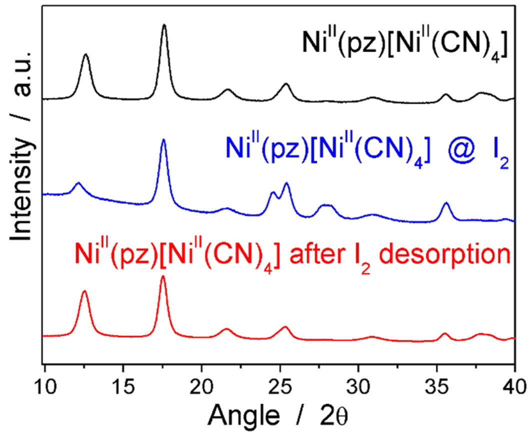

Figure 1. PXRD diffraction for Ni^{II}(pz)[Ni^{II}(CN)$_4$] before (black plot) and after (blue plot) maximal I_2 adsorption in a cyclohexane solution and after I_2 desorption (red plot).

Figure S2 in the SI. Lebail analysis, carried out to model the PXRD data, indicates that the materials crystallize in a tetragonal *P*4/*m* space group with the cell parameter values $a = b = 7.1762(3)$ Å, $c = 7.0316(5)$ Å, and $\alpha = \beta = \gamma = 90.0°$ (Figure S2a,b in the SI). Thermogravimetric analysis (TGA) shows that the investigated material is thermally stable up to 400 °C (red curve in Figure S3 in the SI).

I_2 capture by a thermally activated material at 80 °C under vacuum was performed first in cyclohexane by measuring the residual concentration of I_2 in solution using UV−vis electronic spectroscopy (see the SI). The I_2 sorption kinetic curve performed for a 3×10^{-3} M I_2/cyclohexane solution shows that the process is quite rapid, with equilibrium reached after 2 h (Figure S4 in the SI). The modeling of this curve indicates pseudo-second-order kinetics. The I_2 adsorption isotherm performed at room temperature is shown Figure 2. The curve is concave to the concentration axis, which reflects the ability of the materials for I_2 sorption in a wide range of concentrations. The curve exhibits also a sudden increase at low iodine concentrations, indicating a high affinity of the clathrate for I_2. The material changes its color to dark brown after I_2 filling (Figure 2, inset). The maximum adsorption capacity (Q_{max}), which is indicative of the efficiency of the materials to capture I_2 determined from the plateau of the isotherm, is equal to 3.28 mmol/g (83 wt %) and corresponds to adsorption of about 1 mol of I_2 per 1 mol of clathrate. The isotherm was fitted with the Langmuir model, giving a very close Q_{max} value equal to 3.34 mmol/g (Figure S5 in the SI). The entrapped amount of I_2 was also confirmed by the TGA curve (Figure S3a in the SI). TGA associated with mass spectroscopy analyses showed (Figure S3b in the SI) that I_2, captured both in solution and in gas, is thermally released from the structure at 150 °C. This fact is consistent with the loading of I_2 species in the clathrate cavities.

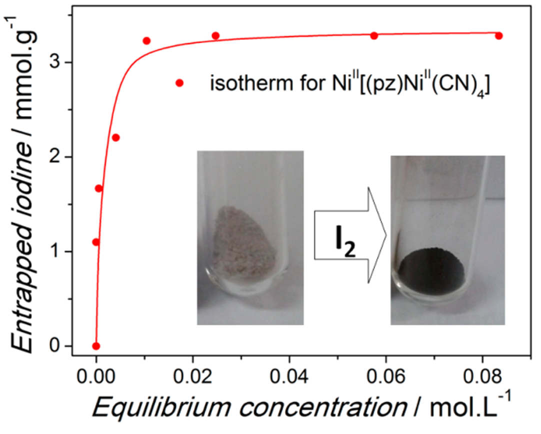

Figure 2. I_2 adsorption isotherm in a cyclohexane solution for Ni^{II}(pz)[Ni^{II}(CN)$_4$]. The solid line represents the fit with the Langmuir model. Inset: from left to right, photographs of thermally activated powders before and after contact with I_2.

I_2 capture by the clathrate network was also investigated in the gaseous phase. The thermally activated compound was exposed to I_2 vapor at 80 °C (I_2 vapor pressure of about 1 kPa) in a closed adsorption chamber during 72 h. The so-obtained material was then thoroughly washed by pentane in order to remove physisorbed I_2 at the surface. I_2 uptake from gas determined from the TGA curve is equal to 2.32 mmol/g (59 wt %), which corresponds to 0.7 mol of I_2 per 1 mol of Ni^{II}(pz)[Ni^{II}(CN)$_4$] (Figure S3 in the SI). This lower absorbed I_2 quantity in the gas phase in comparison to absorption in solution as well as a very slow kinetics (3 days in the gas phase and 2 h in cyclohexane) may be explained by diffusion problems. PXRD performed for the gas-phase I_2-loaded clathrate indicates the same trends as those for entrapment in solution (Figure S6 in the SI). Note that the I_2 adsorption capacities in both solution or the gas phase are comparable to what has already been observed for MOF materials.[6−9]

In order to give microscopic insight into I_2 sorption, Ni^{II}(pz)[Ni^{II}(CN)$_4$]@I_2 samples with maximal I_2 loading were analyzed by means of vibrational spectroscopy, X-ray photoelectron spectroscopy (XPS), and PXRD experiments. First, Fourier transform infrared (FTIR) spectra of samples after I_2 loading in solution or in gas conditions show small shifts of the bands related to the pyrazine ligand (1160, 1129, 1088, and 810 cm^{-1}; Figure S7b in the SI). In addition, the cyanide stretching vibration shifts from 2173 to 2166 cm^{-1} upon I_2 insertion, indicating an increase in the back-donation d−π caused by an interaction between the I_2 and tetracyanonickelate moieties (Figure S7a in the SI). Besides, XPS experiments further show no change in the oxidation state of the Ni^{II} ion after I_2 loading, which clearly indicates an absence of redox processes involving metal centers (Figure S8 in the SI). The Raman spectrum of the I_2-loaded clathrate shows three peaks in the range 100−200 cm^{-1}: at 200 (w), 170, and 103 cm^{-1} (Figure S9 in the SI). The first small peak at 200 cm^{-1} can be associated with vibrations of I_2 in interaction with pyrazine or residual solvent molecules. A large peak at 170 cm^{-1} corresponds to confined I_2 in the solid state (ν_1 symmetric mode) and the peak at 103 cm^{-1} may be assigned to the presence of I_3^-.[15]

PXRD of the Ni^{II}(pz)[Ni^{II}(CN)$_4$]@I_2 sample after contact in solution was treated with Lebail analyses in order to model evolution of the lattice parameters of the unit cell with I_2 filling. The structure still crystallizes in a *P*4/*m* space group with cell parameters $a = b = 7.2605(6)$ Å, $c = 7.0072(5)$ Å, and $\alpha = \beta = \gamma = 90.0°$, indicating essentially a slight increase (i.e., 0.084 Å) of the *a* and *b* cell parameters (Figures 1 and S2b in the SI). All of these results are consistent with the incorporation of predominantly I_2 molecules in the pores of the coordination network through the formation of weak interactions with pyrazine and tetracyanonickelate. A small quantity of pentaiodides may also be present in the cages as a result of a weak interaction between I_3^- and I_2; the former may appear because of the presence of a few lattice defects in the clathrate network.[15c]

A computational approach based on an energy minimization procedure[16] was employed to determine a plausible crystal structure of the fully loaded $Ni^{II}(pz)[Ni^{II}(CN)_4]@I_2$ sample. Grand canonical Monte Carlo (GCMC) simulations were further performed at 25 °C to calculate the I_2 adsorption isotherm. Similar to previous studies on MOFs,[7] the I_2/host interactions included only short-range van der Waals terms with parameters taken from the universal force field[17] (see the SI). Calculations revealed that the optimal maximal uptake is 1 mol of I_2 per unit cell, confirming the experimentally achieved saturation capacity of the material in solution. Analysis of the preferential arrangements of I_2 issued from these simulations evidenced that the I_2 molecules (i) interact with both the Ni^{2+} ion of the $[Ni(CN)_4]^{2-}$ moiety (distances ranging from 3.32 to 3.71 Å) and the pyrazine (3.52−3.74 Å), in agreement with the experimental observation reported above and (ii) tend to orient along the direction of the tunnel, with distances separating each other over 4 Å (Figure 3).

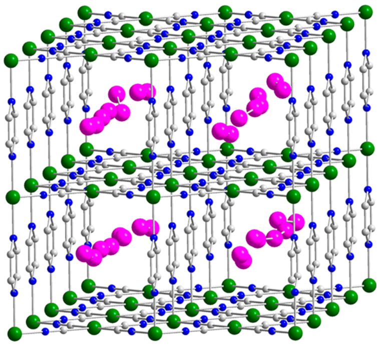

Figure 3. GCMC-optimized distribution of I_2 in $Ni^{II}(pz)[Ni^{II}(CN)_4]@I_2$ corresponding to a loading of 1 molecule per unit cell, C. Color code: green, Ni; gray, C; blue, N, purple, I.

Finally, I_2 adsorption by Hofmann clathrate is perfectly reversible. As the fully loaded material $Ni^{II}(pz)[Ni^{II}(CN)_4]@I_2$ is treated for 2 h at 300 °C under a continuous flux of argon, I_2 is totally removed from the framework, giving an empty clathrate in both cases. The FTIR spectroscopy data (Figure S7 in the SI) as well as PXRD (Figures 1 and S6 in the SI) obtained after heat treatment are in accordance with such a reversible process. Entrapments both in solution and in the gaseous phase were repeated two more times (three uptake/desorption cycles in total), indicating comparable capacities for the third cycle: 3.32 mmol/g (84 wt %), equal to 1 mol I_2 per 1 mol of clathrate, for the uptake in solution and 2.84 mmol/g (72 wt %), equal to 0.85 I_2 per 1 mol of clathrate, for capture in the gaseous phase. PXRD patterns after three cycles of entrapment in both conditions and after respective desorption indicate good structural stability and complete recovery of the framework (Figure S10 in the SI).

In summary, we have presented here for the first time the study of I_2 capture within the Hofmann clathrate framework $Ni^{II}(pz)[Ni^{II}(CN)_4]$ from either the cyclohexane solution or the gaseous phase, with a maximum capacity of 1 mol of I_2 per 1 mol of $Ni^{II}(pz)[Ni^{II}(CN)_4]$ for the capture in solution. Structural and spectroscopic investigations combined with molecular simulations indicate that adsorption of I_2 is mainly due to the insertion of I_2 molecules within the network cages through synergetic interactions with both the pyrazine pillar ligand and the cyanometallate moiety, together with the possible presence of a small amount of pentaiodides. I_2 uptake is fully reversible by applying heat treatment, recovering the starting material, and several I_2 sorption/desorption cycles may be performed without material decomposition.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, characterizations, and iodine loading conditions in cycloxehane and gas. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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