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A spin crossover porous hybrid architecture for potential sensing applications†

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Spin crossover cations have been successfully synthesized in the pores of a mesoporous robust Metal–Organic Framework (MOF) MIL-100(Al) through sequential introduction of Fe(III) cations and a sal$_2$trien ligand. The MIL-100(Al)@Fe(sal$_2$trien) hybrid material retains its crystallinity and partial porosity compared to the parent MOF. The spin state of the Fe(sal$_2$trien)$^+$ cations can be modulated at room temperature through sorption of guest molecules, paving the way to the design of a new generation of sensors based on MOF@spin crossover complex solids.

Metal–Organic Frameworks (MOFs) are ideal materials for the modular design of complex assemblies, as they possess a long-range ordered hybrid structure associated with well-organized micro or mesoporous channels and/or cages.[1] Their large chemical and structural versatility is of great interest for various applications such as gas storage, separation, catalysis, drug delivery, *etc.* Several MOFs can also be considered for sensing small molecules, mainly through the modulation of their emission properties.[2] However, in most cases, their limited stability prevents them from being used in real devices.[3] An alternative for the development of new sensing materials would be to take advantage of electronically bistable materials such as spin-crossover (SCO) compounds capable of switching their spin states [low-spin (LS) ↔ high-spin (HS)] upon exposure to external stimuli such as temperature, pressure, magnetic field and visible light irradiation.[4] This switching phenomenon is accompanied by changes in many physical properties such as color, magnetic susceptibility, dielectric constant *etc.* These features make SCO materials promising candidates for technological applications such as molecular switches and sensors. However, most SCO compounds are not porous and thus lack selective sorption properties that are required for optimal sensing. To date, Hofmann clathrates have been the only family of porous compounds presenting spin transitions close to room temperature.[5] Their potentiality for sensing small molecules such as CS_2 or benzene has been evidenced but their sensitivity to other guests remains limited.[6] Coordination frameworks with tetrazole-based linkers have also been developed recently but their limited porosity restricts their application to small gas molecules such as CO_2.[7]

Taking into account the ability of MOFs to encapsulate various types of guest molecules, we have focused our attention on the inclusion of spin crossover complexes in the pores of water stable large pore MOFs. This strategy should allow combining the stability and selective sorption properties of the host MOF with the sensing ability of the guest SCO complex. The loading of coordination complexes in the pores of MOFs has been studied within the last years, mainly for catalytic or lighting applications.[8] Several strategies can be used, such as the synthesis of the MOF around the existing complexes or the *in situ* synthesis of the coordination complexes in the pores of a pre-formed MOF. The encapsulation of spin crossover complexes in MOFs remains however almost unexplored. Zeolites,[9] oxalate-based coordination frameworks,[10] layered sulfides[11] and mesoporous silica[12] containing spin crossover molecular cations have been widely studied but these materials do not present any permanent porosity. Recently, Abhervé *et al.* have reported the insertion of Fe(III) spin crossover cations into the pores of a preformed oxamate network.[13] However, the sorption properties of this solid have not been reported. Janiak *et al.* have also described the insertion, switching properties and guest sensitivity of an Fe(II) SCO complex in mesoporous NH_2-MIL-101(Al) but the water stability of the host MOF remains limited.[14] In addition, as the windows of this MOF are very large (12–16 Å), it is likely that the complexes might leach out of the pores when in contact with liquids considering the absence of steric hindrance between the complex and the framework. For this study, MIL-100(Al),

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a mesoporous diamagnetic Al(III) tricarboxylate MOF, has then been selected as a host matrix for its remarkable chemical stability (water and organic solvents), surpassing by far that of MIL-101(Al), and its bimodal pore systems with two sets of mesoporous cages of 24 and 27 Å accessible only through 5.5 Å pentagonal and 8.5 Å hexagonal microporous windows. This is a very suitable material to optimize the concept, as the hexagonal windows are both large enough to allow the diffusion of the metal and ligand sources required to prepare the SCO complex and much too small to allow any complex to leach out of the pores. Moreover, the pentagonal windows are too small to allow the diffusion on the ligand, making the associated cages fully accessible for further guest species. Regarding the spin crossover complex, $Fe^{III}(sal_2trien)^+$ has been selected for its good stability in solution and its thermal switching in solution close to room temperature.[15]

MIL-100(Al) has been prepared as previously described by microwave-assisted synthesis.[16] $Fe(sal_2trien)^+$ has been synthesized in the pores of MIL-100(Al) through the "ship-in-a-bottle" technique. Briefly, we have sequentially inserted first the Fe(III) cation, then the ligand in the pores of the MOF and finally thoroughly washed the solid to remove the complexes formed outside the pores (see the ESI†). As mentioned above, the resulting complex in the pores shall remain trapped inside the pores because the windows of the MOF are too small to allow any leaching. The first evidence of the loading is the obvious colour change in the solid, going from yellow to purple upon loading (Fig. S4, ESI†). Moreover, the main characteristic powder X-ray diffraction (PXRD) Bragg peaks of MIL-100(Al) are still observed in the MIL-100(Al)@$Fe(sal_2trien)$ hybrid solid, indicating that the crystallinity of the solid is retained during the loading process (Fig. 1). The relative intensity of the low-angle peaks decreases in MIL-100(Al)@$Fe(sal_2trien)$, which is consistent with the loading of the coordination complex in the pores of the MOF.[17]

The Raman spectrum of the composite material has been recorded at room temperature and compared to those of the parent MOF MIL-100(Al) and the reference molecular compound $Fe(sal_2trien)NO_3$ (Fig. 1). The characteristic peaks of the $Fe(sal_2trien)^+$ complex are clearly observed in the composite, which confirms that the complex has been successfully synthesized in the pores of the MOF. The most intense peaks of MIL-100(Al) are also observed in the composite, but their intensity is significantly lower than that of the complex, while the opposite trend is observed in the infrared spectra (see Fig. S6 in the ESI†). This can be explained by the excitation wavelength used to collect the Raman spectra (514.5 nm), which selectively excites the iron(III) complex.

Nitrogen sorption experiments have been performed on the solids (see Fig. 2). Noteworthily, both the BET surface area ($1620\ m^2\ g^{-1}$) and the nitrogen uptake ($440\ cm^3\ g^{-1}$, $P/P_0 = 0.6$) of MIL-100(Al) are in line with the previously published results.[13] For the MIL-100(Al)@$Fe(sal_2trien)$ composite, both values significantly decrease (a BET surface area of $840\ m^2\ g^{-1}$ and an uptake of $250\ cm^3\ g^{-1}$), in agreement with the successful preparation of the complexes in the pores of the MOF. This is further confirmed by the pore size distribution obtained by DFT calculations, assuming cylindrical pores and an oxide surface (see the inset in Fig. 2), which evidence that only the larger cages of MIL-100(Al) contain SCO complexes. Interestingly, as expected, the intermediate cages remain empty because the pentagonal windows are not large enough to let the ligand diffuse inside these cages. Based on this result and on a combination of EDX and ICP-MS analysis, the loading can be evaluated to be *ca.* 8 Fe(III) complexes per large cage (see the ESI† for the detailed calculation).

The EPR spectrum has been collected at 10 K for the composite material (Fig. 2) in order to characterize the complex inside the MOF. The spectrum of the hydrated compound is characteristic of an LS Fe(III) ($S = 1/2$) that has a pseudo-axial geometry ($g^{\perp} = 2.18$ and $g^{\parallel} = 1.96$), which is further evidence of the presence of $Fe(sal_2trien)^+$ complexes in the composite material.[18] A signal corresponding to the traces of Fe(III) in the HS state is also detected ($g = 4.28$). The dehydration of the solid (thermal treatment at 100 °C under vacuum, see Fig. S2, ESI†)

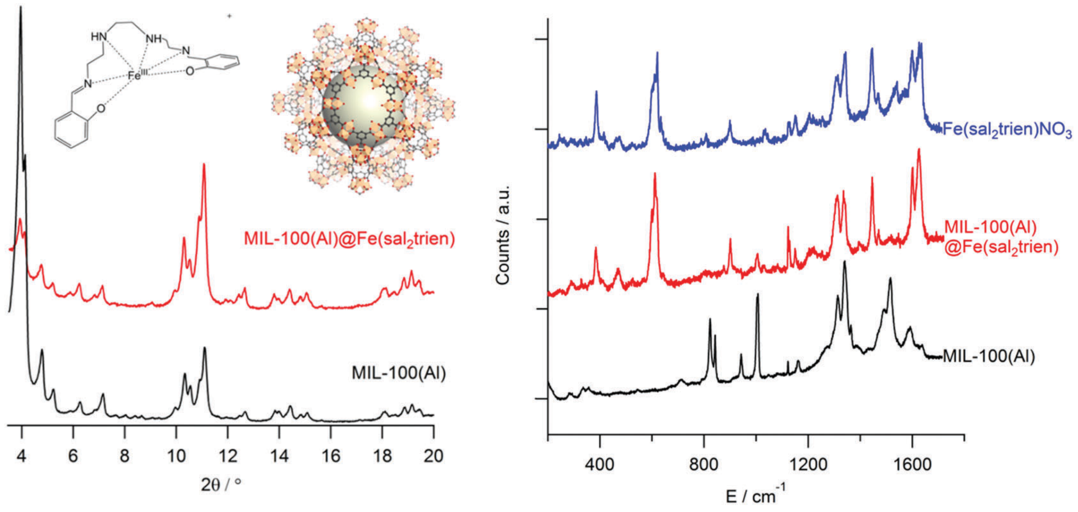

Fig. 1 (left) Comparison of the powder X-ray diffraction patterns of MIL-100(Al) and MIL-100(Al)@$Fe(sal_2trien)$, inset: scheme of the $Fe(sal_2trien)^+$ complex and structure of the MIL-100(Al) large cage; (right) comparison of the Raman spectra of MIL-100(Al), $Fe(sal_2trien)NO_3$ and MIL-100(Al)@$Fe(sal_2trien)$.

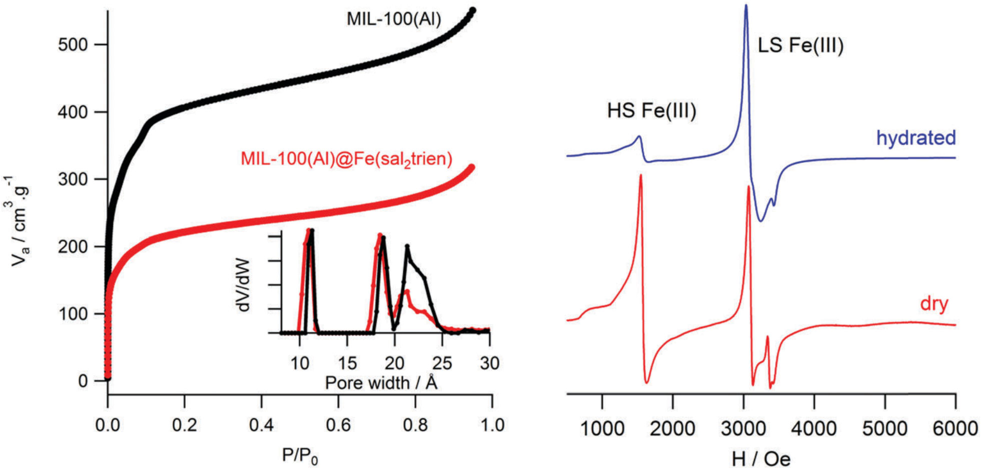

Fig. 2 (left) Comparison of the N_2 sorption isotherms of MIL-100(Al) and MIL-100(Al)@Fe(sal$_2$trien) at 77 K and (inset) pore size distribution obtained by DFT; (right) X-band EPR spectrum of MIL-100(Al)@Fe(sal$_2$trien) recorded at 10 K.

induces important changes in the relative intensities of the LS and HS signals, which indicates that the dehydration induces an increase of the HS fraction in the solid.

The magnetic properties of the MIL-100(Al)@Fe(sal$_2$trien) composite solid have then been investigated (see Fig. S3, ESI†) and compared to those of the parent Fe(sal$_2$trien)NO_3, which is in the LS state at every temperature.[19] The observed magnetic susceptibility, either without solvent molecules inside the pores or loaded with *ca.* 30 wt% water (see Fig. S2 in the ESI†), shows a significant difference between the dried and loaded composites: the magnetic susceptibility of MIL-100(Al)@Fe(sal$_2$trien) is much higher at every temperature for the dehydrated compound, indicating a larger HS fraction. This observation is in line with the EPR spectra recorded at 10 K. Above room temperature, both hydrated and dehydrated compounds start to undergo a gradual thermal spin crossover, which remains incomplete at 350 K. This result evidences how the sorption of water molecules in the pores of the MOF can influence the switching properties of the guest complexes and can be related to the solvent dependence of the spin state of Fe(sal$_2$trien)$^+$ in solution at room temperature. Indeed, Wilson *et al.* have demonstrated that the spin state of the complexes can be correlated with the ability of the solvent to interact through H-bonding.[20] In MIL-100(Al)@Fe(sal$_2$trien), the water sorption in the pores of the MOF is likely to induce a change in the environment of Fe(sal$_2$trien)$^+$ through the formation of H-bonds between the water molecules and the NH groups of the sal$_2$trien ligand, therefore influencing the spin state switching properties of the complex inserted into the pores.

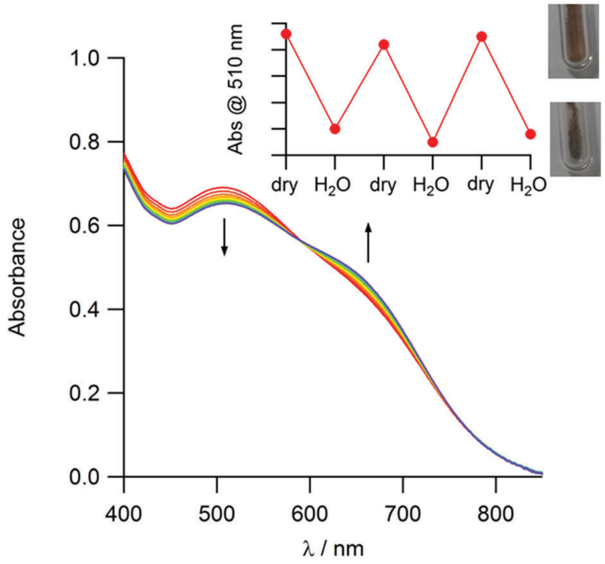

Fig. 3 Evolution of the optical absorption spectrum of MIL-100(Al)@Fe(sal$_2$trien) upon water sorption; inset: evolution of the absorption at 510 nm upon several water sorption/desorption cycles.

Finally, the evolution of the optical absorption spectrum at room temperature upon water sorption has been monitored (Fig. 3 and Fig. S5, ESI†). The spectrum of the dehydrated compound presents an absorption band at 510 nm, corresponding to a LMCT transition of Fe(sal$_2$trien)$^+$ in the HS state, along with a shoulder at 660 nm that can be attributed to a LMCT transition of Fe(sal$_2$trien)$^+$ in the LS state.[21] Therefore, the dehydrated MIL-100(Al)@Fe(sal$_2$trien) compound is mainly HS at room temperature, which is consistent with both EPR and magnetic measurements. Upon water sorption at room temperature, the intensity of the LS absorption band increases at the expense of the HS one, on a timescale of *ca.* one hour (Fig. S5, ESI†), which evidences that adsorbing water in the pores of the MOF can modulate the spin state of the host complex. This phenomenon is fully reversible upon several hydration/dehydration cycles, illustrating the good water stability of both the MOF and the guest Fe(III) complex.

In conclusion, we report for the first time a strategy dealing with the trapping, through an *in situ* synthesis, of an Fe(III) spin crossover complex into a water stable bimodal pore MOF (MIL-100(Al)). The composite material retains its crystallinity and partial porosity compared to the parent MOF, while the spin state of the inserted Fe^{III}(sal$_2$trien)$^+$ cations can be modulated at room temperature by water sorption in the pores of the MOF. The impact of the nature of the guest molecules and their sensing selectivity and sensitivity are currently under investigation. Considering the growing number of mesoporous water stable diamagnetic MOFs and the large diversity of SCO complexes, this paves the way to the design of a new generation of sensing devices based on MOF@spin crossover complex composites.

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Conflicts of interest

There are no conflicts to declare.

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