

Supplementary Information

Guest Molecules in a Layered Microporous Tin(IV)

Phosphonate – Phosphate Material: Solid State NMR Studies

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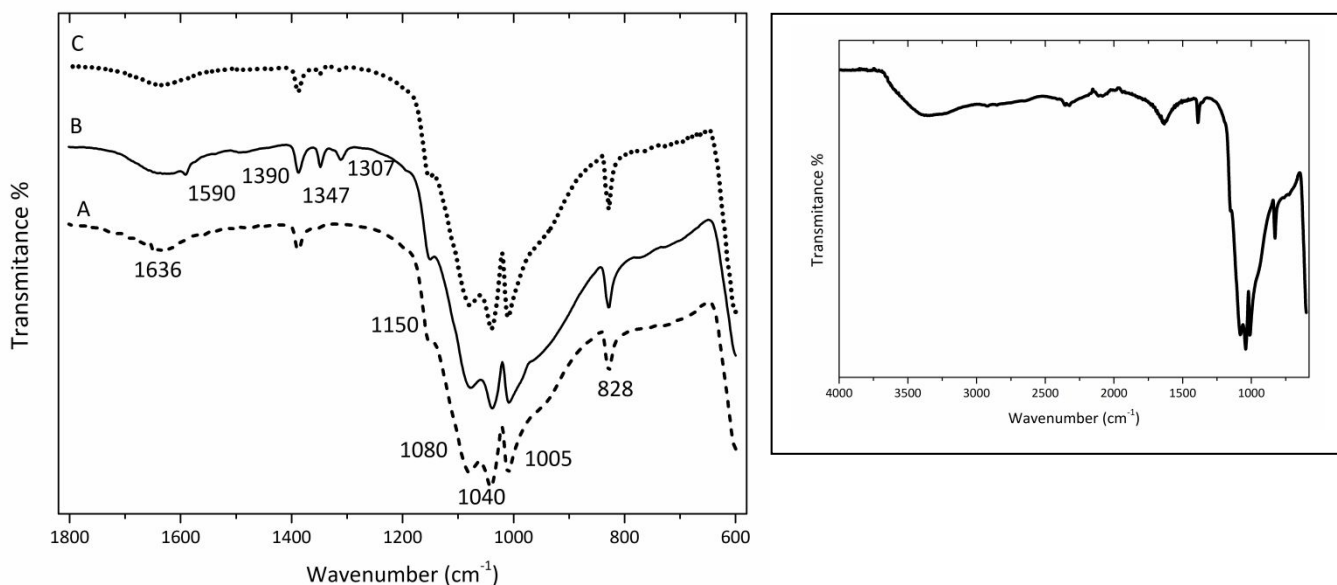


Figure S1. The room-temperature FTIR spectra recorded in the area from 1800 to 650 cm⁻¹: compound **1** (A) and compound **1-Py-1.6** (B); compound **1-Py-1-0.6** (C); the bands at 1590, 1347 and 1307 cm⁻¹ in compounds **1-Py-1.6** and **1-Py-1-0.6** belong to NC₅D₅; the insert shows the full IR spectrum of **1**.

The spectra were recorded from 600 to 1800 cm^{-1} at 40 scans with a FTIR Spectrophotometer IRAffinity-1 equipped with a PIKE MIRacle™ ATR sampling accessory. Compound **1-Py-1-0.6** was obtained by heating a sample of **1-Py-1.6** at 120° C for 18 hours.

Assignments. A broad band between 3600 and 3000 cm^{-1} can be well attributed to O-H stretching modes¹⁻³ in hydrogen bonded groups O-H from water molecules, phosphate groups and phosphonate groups forming the pores; the symmetric and asymmetric P-O-C stretching modes of the phosphonate groups are seen at 828 and 1005 cm^{-1} , respectively; the P-OH stretching mode³ belonging to phosphonate P-OH groups forming the pores is seen at 1040 cm^{-1} ; the P-C stretching region is located at 1150 cm^{-1} ; the band at 1390 cm^{-1} can be attributed to C=C-H stretching; and the peak at 1080 cm^{-1} can be assigned to P=O groups of phosphonic acid moieties forming pores; the large shoulder at ~ 950 cm^{-1} in the IR spectra of compound **1** can be attributed to the P-OH stretching of phosphate groups because of the absence of this band in the IR spectrum of the Sn(IV) phosphonate material; since a wide band at 1636 cm^{-1} was also observed in the IR spectrum of the Sn(IV) phosphonate material, it can be assigned to bending mode associated with water.²

References

- (1) Alberti, G.; Casciola, M.; Donnadio, A.; Piaggio, P.; Pica, M.; Sisani, M. Preparation and characterization of a-layered zirconium phosphate sulfophenylphosphonates with variable concentration of sulfonic groups *Solid State Ionics* **2005**, *176*, 2893 – 2898.
- (2) Iozzi, M. F.; Bisio, C.; Regi-Macedo, T.; Airoidi, C.; Cossi, M.; Marchese, L. Structural changes induced by dehydration in the crystalline layered silicate Na-RUB-18: a computational/experimental combined study. *J. Mater. Chem.*, **2009**, *19*, 2610– 2617
- (3) Paul, G.; Bisio, C.; Braschi, I.; Cossi, M.; Gatti, G.; Gianotti, E.; Marchese, L. Combined solid-state NMR, FT-IR and computational studies on layered and porous materials. *Chem. Soc. Rev.* **2018**, *47*, 5684-5739.

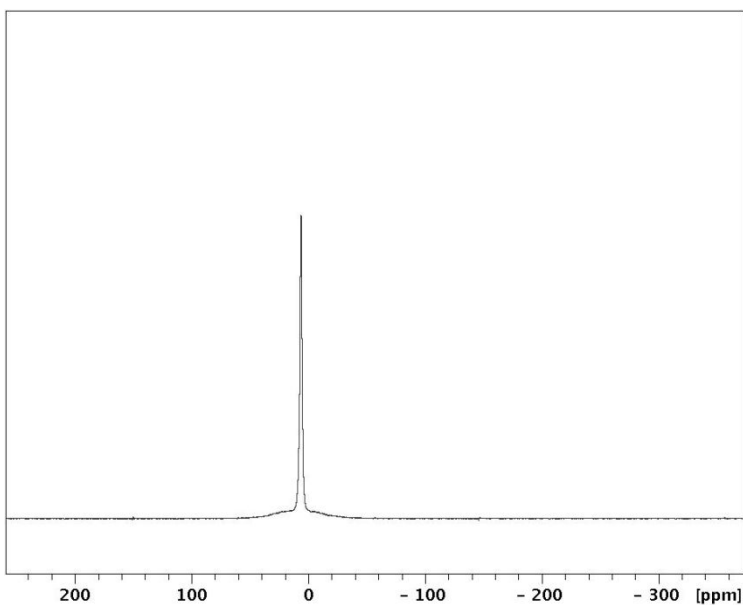


Figure S2. The static ^1H NMR spectrum of compound **1** where the sharp and broad signals belong to water and phenylene protons, respectively.

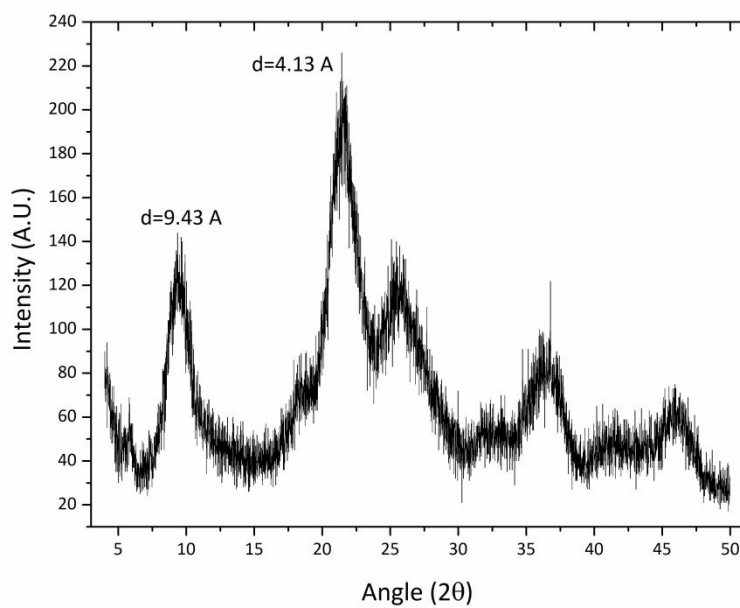


Figure S3. PXRD pattern of compound **1-Py-1.6**. Numbers listed above the peaks are the d-spacing values.

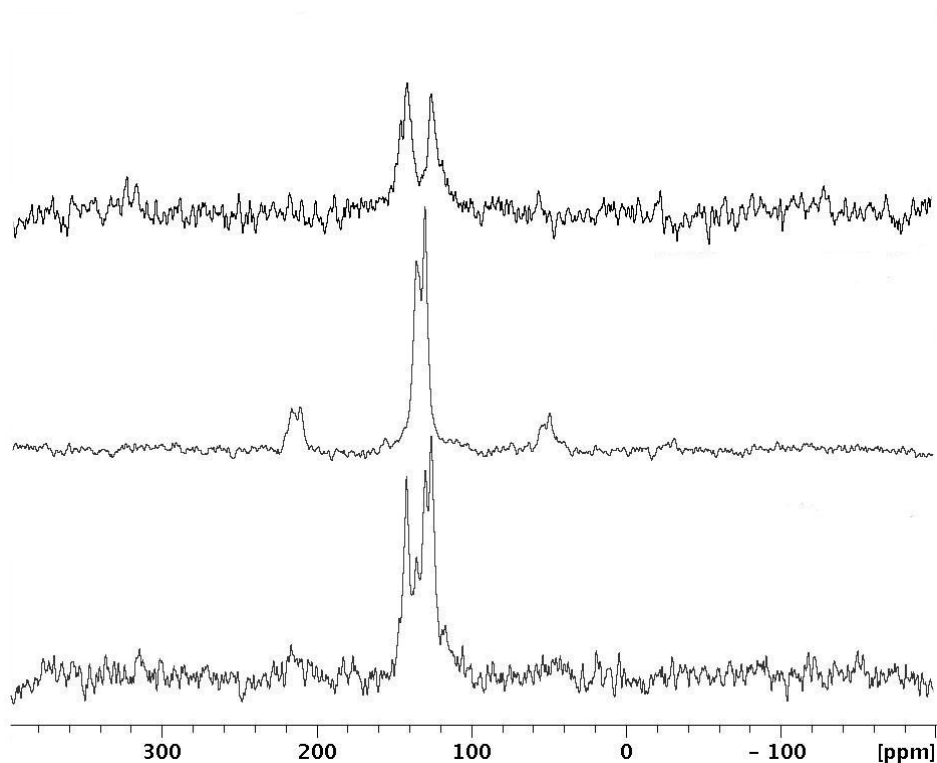


Figure S4. The static $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1-Py-1.6** obtained with direct ^{13}C excitation (top); the $^{13}\text{C}\{^1\text{H}\}$ CP MAS NMR spectrum of **1-Py-1.6** (middle) and $^{13}\text{C}\{^1\text{H}\}$ MAS NMR spectrum of **1-Py-1.6** (bottom) recorded at a spinning rate of 8.2 kHz.

Due to high mobility of pyridine, its ^{13}C resonances are observed in a static sample at 147.1, 137.0 and 124 ppm typical of liquid pyridine (top); the resonances of phenylene rings are observed in the $^{13}\text{C}\{^1\text{H}\}$ CP NMR MAS spectrum (middle); finally, all of these signals are detected in $^{13}\text{C}\{^1\text{H}\}$ MAS NMR spectrum.

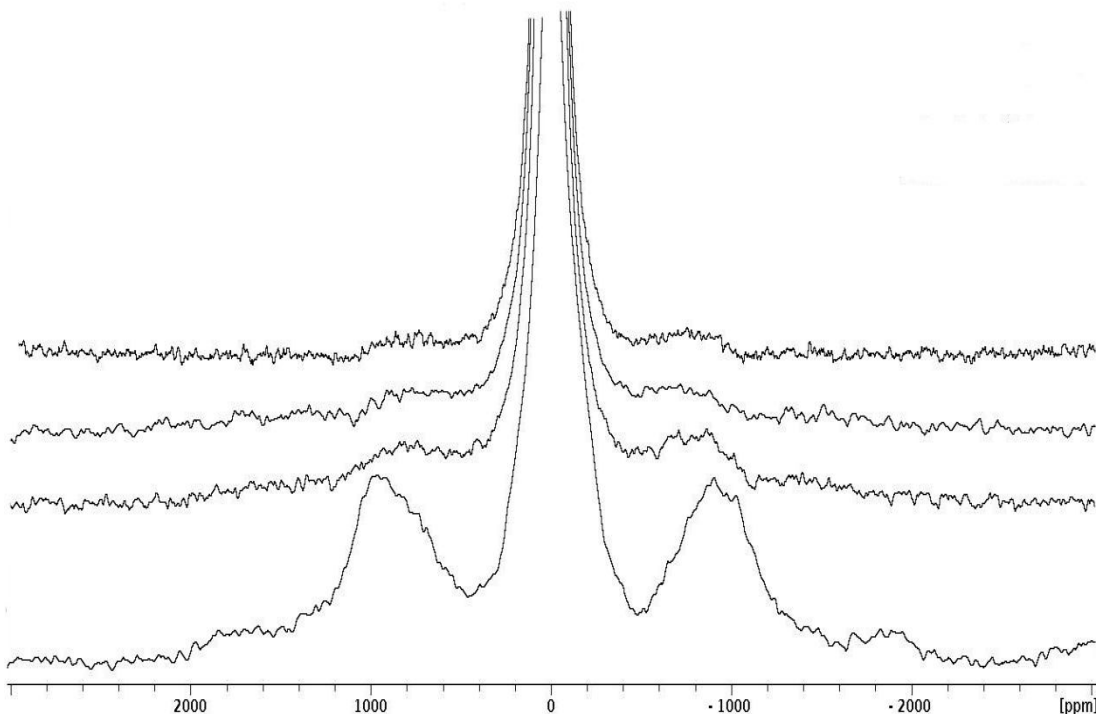


Figure S5. Variable-temperature ^2H NMR spectra recorded in static compound **1-Py-1.6** from top to bottom: 283 K, 273 K, 243 K and 175 K; the spectra scaled to have the same intensity for the isotropic component.

Comments on changes in the ^2H NMR spectra of compound 1-Py-1.6 detected after its holding for 10 days.

Figure S6 shows the VT ^2H NMR spectra of a static sample of **1-Py-1.6** recorded 10 days later after preparation. Comparison with Figure 9 in the main text reveals a remarkable increase in the relative intensity of the quadrupolar pattern at low temperature corresponding immobile pyridine molecules. At the same time, the $^{31}\text{P}\{^1\text{H}\}$ and $^{119}\text{Sn}\{^1\text{H}\}$ MAS NMR spectra, the IR spectrum and the PXRD pattern of this sample do not change. We believe that the pyridine causes a slow reorganization of pore surface in **1**. Similarly, as it has recently been reported, the metal-organic frame work MIL-53(Cr) undergoes a contraction upon benzene adsorption.¹

Reference

(1) D. I. Kolokolov, H. Jobic, S. Rives, P. G. Yot, J. Olivier, P. Trens, A. G. Stepanov, G. Maurin. *J. Phys. Chem. C*, **2015**, *119*, 8217-8225.

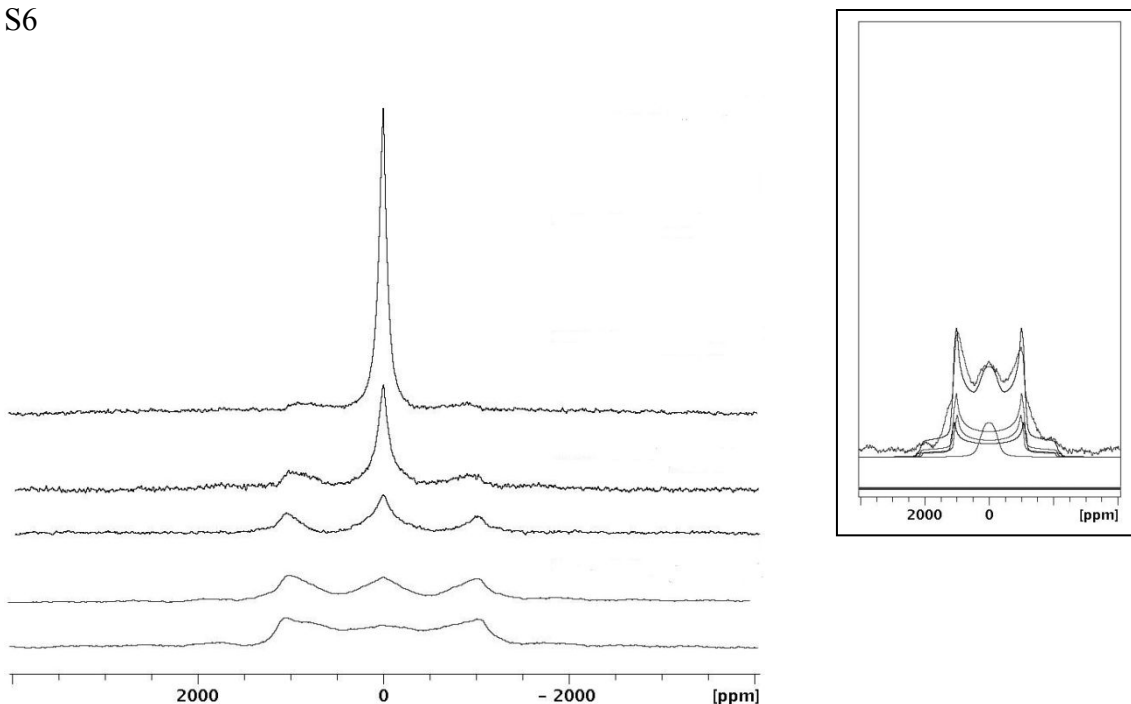


Figure S6. Variable-temperature ^2H NMR spectra of a static sample of **1-Py-1.6** recorded 10 days later after preparation from top to bottom: 273 K, 243 K, 213 K, and 175 K; the insert: the ^2H NMR spectrum at 193 K simulated as a combination of four sub-spectra corresponding to mobile pyridine (the central component) and the full size anisotropy of a quadrupolar tensors with static quadrupolar constants of 170, 175 and 185 kHz ($\eta = 0.1$).