Supplementary Information

Pyridine-d$_5$ as a ^{2}H NMR Probe for Investigation of Macro Structure and Pore Shapes in a Layered Sn(IV) Phosphonate / Phosphate Material.

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Figures, Table and Experimental Section.

Materials. Compounds **1-Py-1.6** and **1-Py-0.6** were prepared by soaking of **1** (synthesized earlier in[10]) in liquid pyridine-d$_5$ (Sigma-Aldrich) for 30 min and were then placed into an oven at 150 °C for 30 min to yield dry, white powders. The mole fractions of the pyridine were determined, as described in,[10] by the direct excitation ^{13}C{^{1}H} MAS NMR spectra with recycle delays affording full nuclear relaxation and correct integrations of pyridine and phenylene carbons. Then both samples have been self-possessed for two months.

Material **1-Py-0.2** was prepared by placing of compound **1-Py-0.6** into an oven at 150 °C for 6 hours and then investigated by NMR as a freshly-prepared sample.

The samples of **1** loaded with acetone-d$_6$, acetonitrile-d$_3$, water-d$_2$ and benzene-d$_6$ were prepared by the mentioned above method with soaking in the corresponding deuterated solvents (Sigma-Aldrich).

Solid-state NMR. All NMR experiments were carried out with a Bruker Avance-400 solid-state NMR spectrometer (400 MHz for ^{1}H nuclei) equipped with two-channel 4mm MAS probe head. The ^{31}P{^{1}H} MAS NMR single pulse spectra, referenced to 1 M H$_3$PO$_4$, were recorded at a spinning rate of 10 kHz with rf-pulse lengths of 2.5 μs (50°) and recycle delays of 40 s providing full ^{31}P relaxation. The ^{119}Sn{^{1}H} MAS NMR spectra, referenced to 1 M (CH$_3$)$_4$Sn, were collected a spinning rate of 10 kHz, with 50°-rf-pulses and relaxation delays of 40 s. Number of scans was 1800-2000.

The ^{2}H NMR spectra were obtained with the standard Solid-Echo pulse sequence at recycle delays of 1 - 2 s, echo delays of 20 μs and death times of 5 μs to avoid base line distortions. Numbers of scans were 2000-3000.

The variable temperature NMR experiments were performed with a thermocouple calibrated using the ^{1}H NMR spectra of liquid methanol ($\Delta\delta = \delta(OH) - \delta(CH_3)$) placed into a static MAS NMR rotor.

^{31}P T_1 relaxation times were measured by inversion–recovery (180°-τ-90°) experiments using well-calibrated rf- pulses and widely varied τ delays. The Hahn-echo experiments have been used to determine ^{2}H T_2 times. The data obtained were treated with a standard nonlinear fitting computer program on the basis of the Levenberg–Marquardt algorithm to extract $T_{1,2}$.

Solid-line simulations in the static and MAS ^{2}H NMR spectra were performed with a standard Bruker software.

The line shape analysis of the deuterium NMR spectra.

Generally speaking, the exchange between free and bound pyridine molecules, occurring on the NMR time scale is an exchange between the quadrupolar pattern with the splitting of 18 kHz (corresponding to two main singularities of the spectrum with C_Q of 25 kHz) and the isotropic resonance of the liquid-like pyridine (Figure S7). Using a standard dynamic Bruker software, the ^{2}H static NMR spectra in the low-temperature zone have been fitted to a three center exchange model, including two resonances with frequency distances of 18 kHz and the isotropic resonance, as shown in Figure S7. It is obvious that such an approximation will give the same methodical errors in calculations of rate constants $k_{(exch)}$, where dependences $\ln(k_{(exch)}$ versus 1/T will lead to still meaningful $\Delta H^{\neq}$ values, while $\Delta S^{\neq}$ values will be fictitious parameters. We have found that even variations in ratios "bound molecules (P_b) to free molecules (P_{free})" give errors in $\Delta H^{\neq}$ determinations that are ≤ 0.5 kcal/mol.

Table S1. Chemical shifts (ppm) in the room-temperature $^{31}P\{^1H\}$ and $^{119}Sn\{^1H\}$ MAS NMR spectra of materials **1-Py-1.6**, **1-Py-0.6** and **1-Py-0.2** at a spinning rate of 10 kHz.

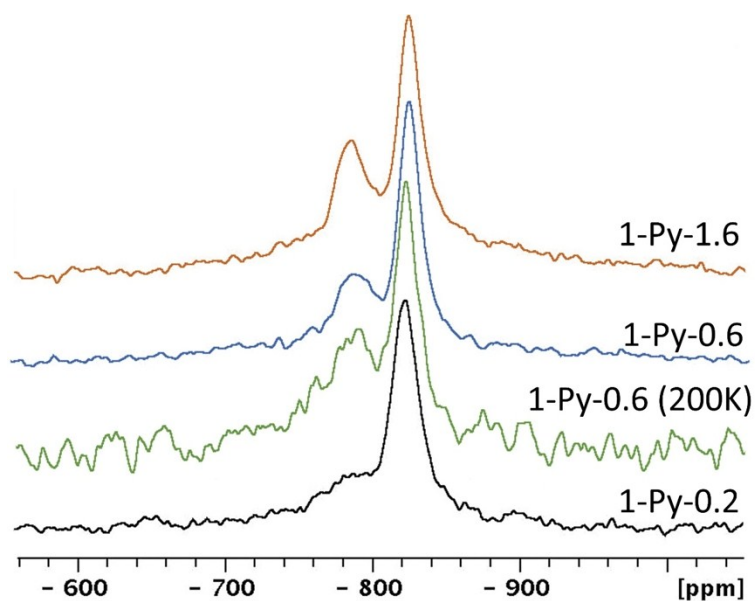| Compound	$\delta^{31}P$ (PPhP)	$\delta^{31}P$ (POH)	$\delta^{119}Sn$ (SnOPOH)	$\delta^{119}Sn$ (SnOPPhP)
1-Py-1.6	3.2	-14.7	-784	-822
1-Py-0.6	3.4	-14.9	-786	-822
1-Py-0.2	4.0	-14.8	-787 (wide)	-822

Figure S1. The room temperature $^{119}Sn\{^1H\}$ MAS NMR spectra, recorded at a spinning rate of 10 kHz for compounds investigated.

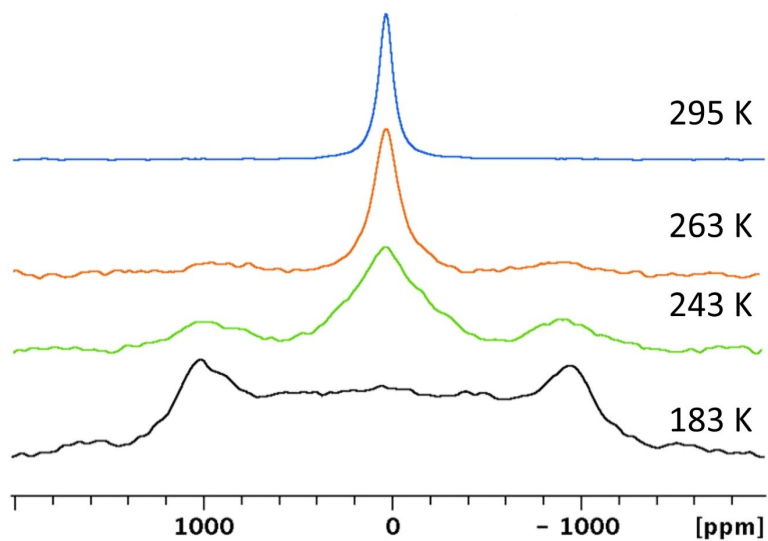**Figure S2.** A part of the variable-temperature static ^{2}H NMR spectra recoded for material **1-Py-1.6**.
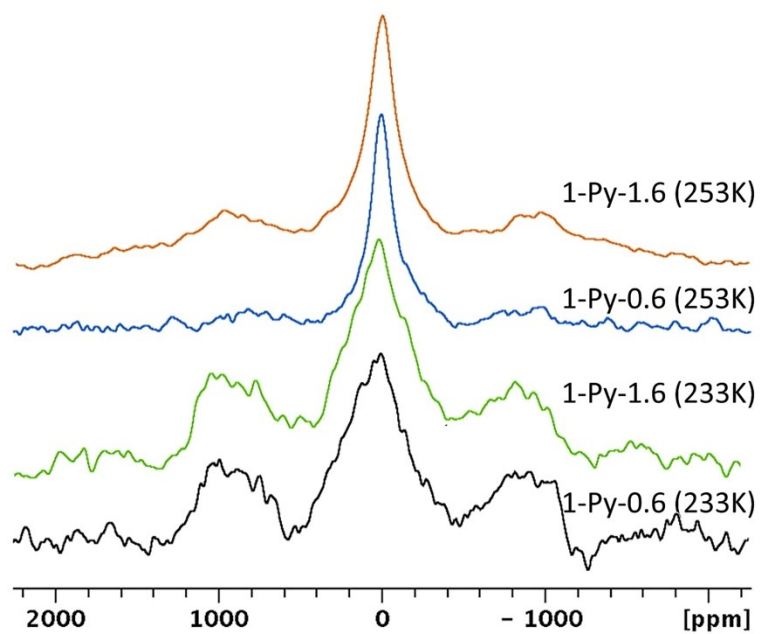

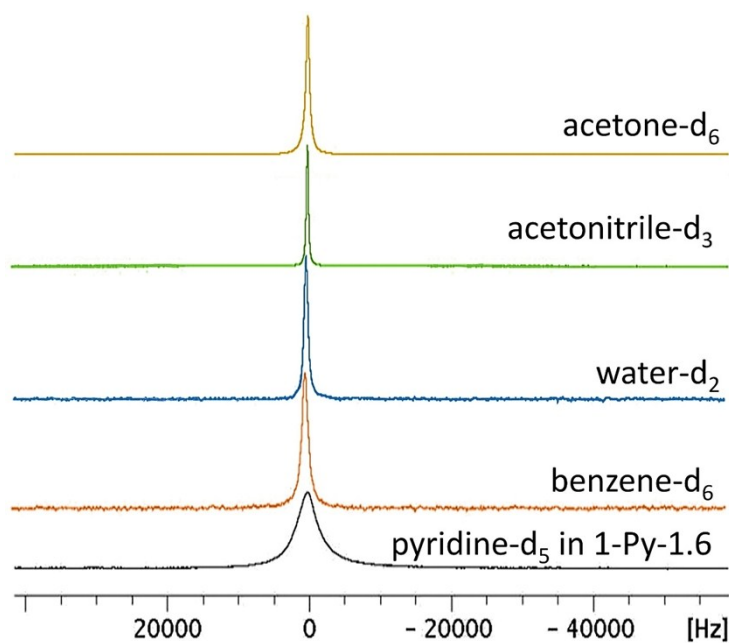**Figure S3.** The static ^{2}H NMR spectra of the shown compounds.

Figure S4. The static ^{2}H NMR spectra, recorded for sample of **1** containing acetone-d$_6$, acetonitrile-d$_3$, water-d$_2$, benzene-d$_6$ and pyridine-d$_5$ in **1-Py-1.6**.
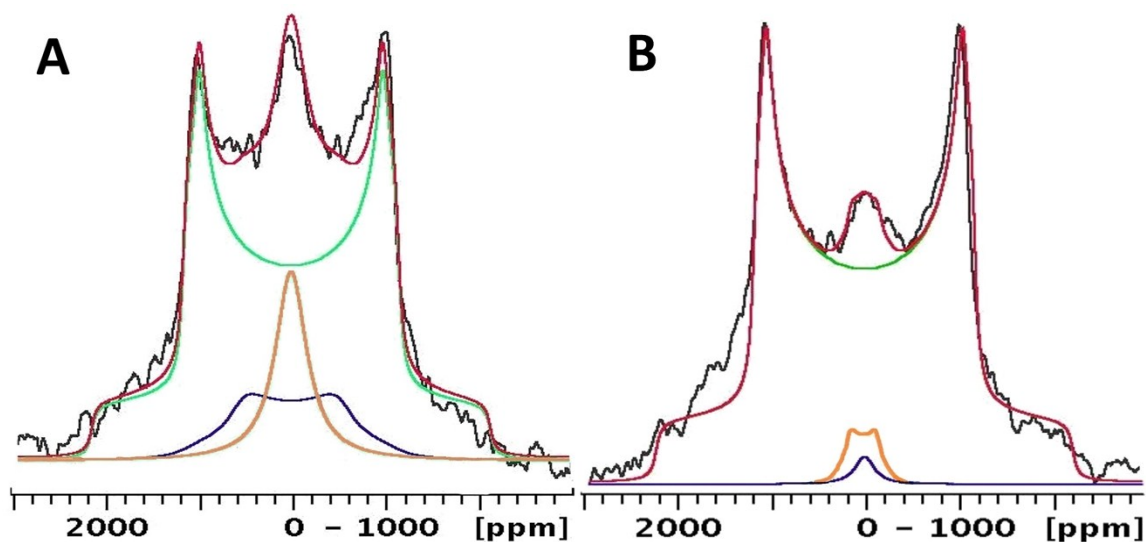

Figure S5. The ^{2}H NMR spectra of pyridine-d$_5$ in material 1-Py-0.6: (A) the static spectrum at 208 K (red), simulated in the presence of an immobile pyridine with C$_Q$ = 180 kHz (green), a bound mobile pyridine with C$_Q$ of 90 kHz (blue) and an isotropically moving pyridine (orange); (B) the static spectrum at 203 K, simulated in the presence of an immobile pyridine with C$_Q$ = 180 kHz (green), a bound mobile pyridine with C$_Q$ of 25 kHz (a D in *para* position is not shown)(orange) and an isotropically-moving pyridine (blue).

Table S2. The temperature dependence of the linewidth (Δv) measured for the Lorentz-shaped resonance or the central component in the static ^{2}H NMR spectra of pyridine-d$_5$ in compound **1-Py-0.6**; equilibrium constants K_{eq} ($K_{eq}=P_b/P_{free}$) characterize bound and free pyridine molecules; rate constants $k_{(exch)}$ (s^{-1}) are obtained for the chemical exchange between free and bound pyridine molecules.

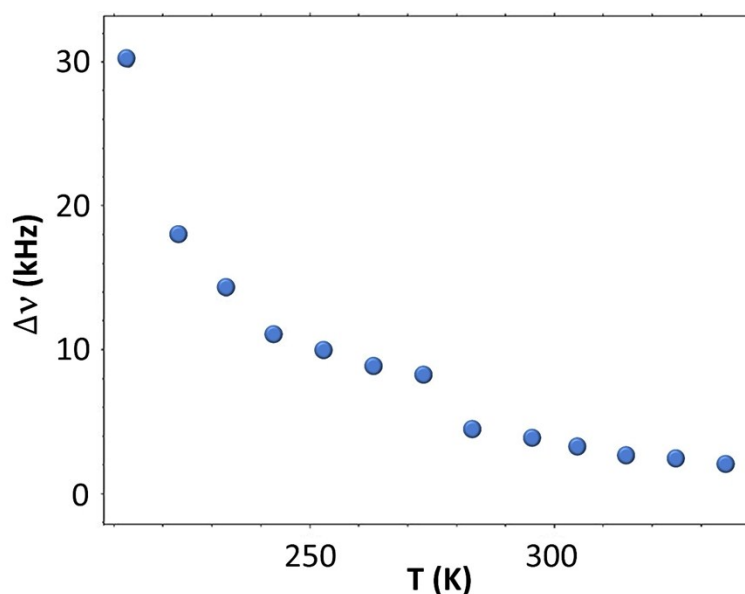| T (K)	Δv (kHz)	K_{eq}	T (K)	Δv (kHz)	$k_{(exch)} \times 10^5$
335	2.1	0.099	273	8.1	1.00
325	2.3	0.12	263	9	0.55
315	2.7	0.14	253	10	0.32
305	3.3	0.18	243	11.1	0.18
295	3.8	0.22	233	14.1	0.12
283	4.4	0.27	223	18	--

Figure S6. The temperature dependence of linewidths (Δv), obtained for the deuterium isotropic pyridine-d$_5$ resonance, observed in static material **1-Py-0.6**.
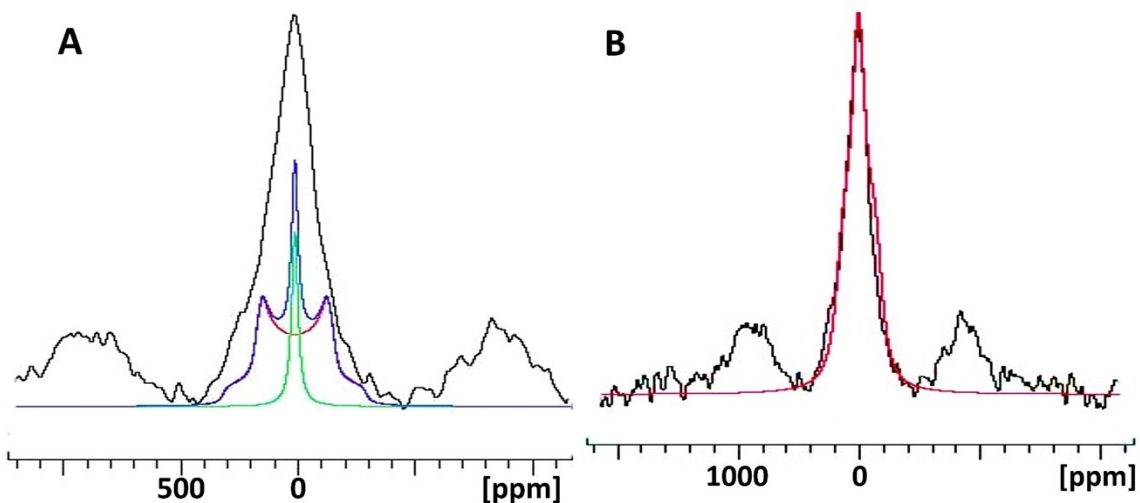
Figure S7. The ^{2}H NMR spectrum of material **1-Py-0.6** at 243 K: (A) illustration of a chemical exchange between a quadrupolar pattern with C_Q of 25 kHz (red) and an isotropic resonance (green); (B) the fitting procedure carried out for the central component of the spectrum.

Table S3. Temperature dependence of the equilibrium constant, $K_{eq} = P_{immob}/P_{mob}$, found via the fraction of immobile pyridine molecules in 1-Py-06 where P_{mob} is the fraction of isotropically-moving molecules.

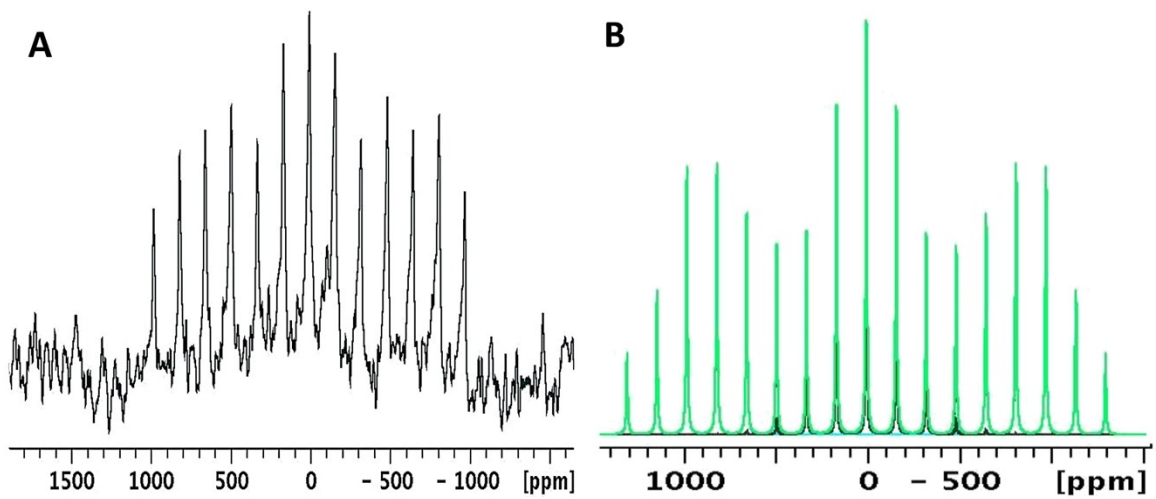| T (K)	K_{eq}
206	7.36
213	4.25
223	2.13
233	1.28
243	0.84

Figure S8. The spectrum of the freshly-obtained material **1-Py-0.2**, (A) spinning at a rate of 10 kHz (295 K); (B)simulated as two sub-spectra with the parameters (see the text).