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Ionothermal synthesis of crystalline metal phosphites using multifunctional protic ionic liquids

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Physical measurements:

Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-rA diffractometer with Cu-Kα radiation (λ = 1.5418 Å). IR spectra (KBr pellets) were recorded on a Nicolet Impact 410 FTIR spectrometer. The thermogravimetric analyses were performed on a Netzsch STA 449c analyzer in a flow of N_2 with a heating rate of 10 ºC/min. Magnetic measurement was performed on the Quantum Design SQUID MPMS XL-7 magnetometer in a magnetic field of 1000 Oe in the temperature range of 2-300 K. Alternating current impedance measurements were carried out with a Solartron SI 1260 impedance/gain-phase analyzer over the frequency range from 0.1 Hz to 10 MHz with an applied voltage of 10 mV. The relative humidity was controlled by a STIK Corp. CIHI-150B incubator. The sample was pressed to form a cylindrical pellet of crystalline powder sample (~2 mm thickness ×5 mm ϕ) coated with C-pressed electrodes. Two silver electrodes were attached to both sides of pellet to form four end terminals (quasi-four-probe method). Single crystal X-ray diffraction data were collected on a New Gemini, Dual, Cu at zero, EosS2 diffractometer at room temperature. The crystal structures were solved by direct methods. The structures were refined on F^2 by full-matrix least-squares methods using the *SHELXTL* program package.[1]

Reference

1. G. M. Sheldrick, Acta Cryst., Sect. A, 2008, 64, 112.

Table S1. Selected bond distances for SCU-17

bond	distance (Å)	bond	distance (Å)
Fe(1)-O(1)	1.981(3)	Fe(2)-O(2)	2.043(3)
Fe(1)-O(1)$^{\#1}$	1.981(3)	Fe(2)-O(2)$^{\#5}$	2.043(3)
Fe(1)-O(3)$^{\#2}$	2.010(2)	Fe(2)-O(4)	2.205(3)
Fe(1)-O(3)$^{\#3}$	2.010(2)	Fe(2)-O(4)$^{\#5}$	2.205(3)
Fe(1)-F(1)	1.938(2)	Fe(2)-F(1)$^{\#3}$	2.072(2)
Fe(1)-F(1)$^{\#1}$	1.938(2)	Fe(2)-F(1)$^{\#4}$	2.072(2)
Σ VB (Fe-O/F)	**3.076**	**Σ VB (Fe-O/F)**	**2.067**

Their sum SVB appears in bold type at the end of the list of the distances around every cation. Symmetry transformations used to generate equivalent atoms: (#1) -x, 1-y, 1-z; (#2) -1+x, +y, +z; (#3) 1-x, 1-y, 1-z; (#4) 1+x, +y, 1+z; (#5) 2-x, 1-y, 2-z.

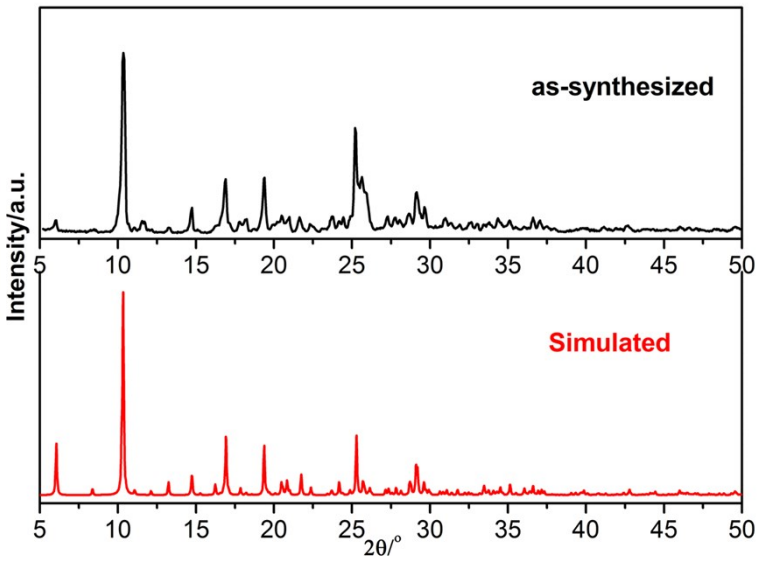

Fig. S1. Experimental and simulated powder XRD patterns of SCU-9.

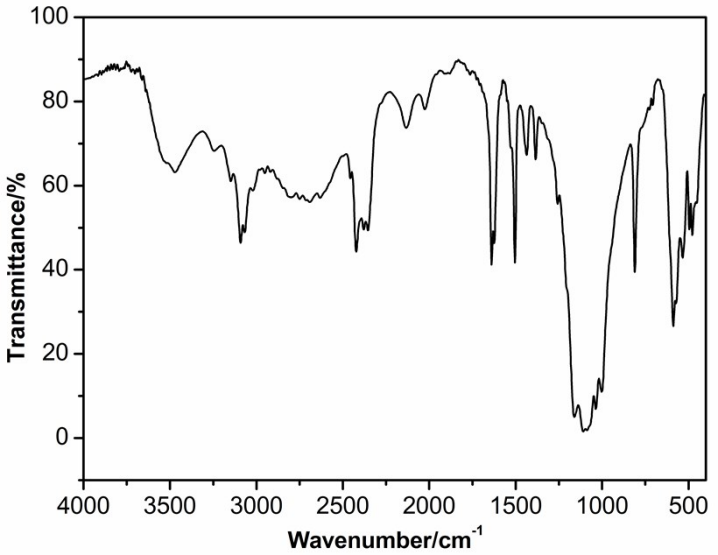

Fig. S2. IR spectrum of SCU-9.

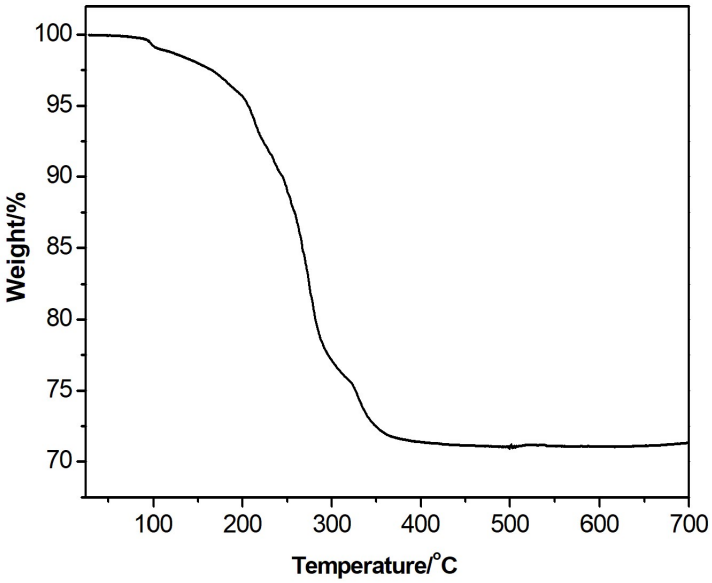

Fig. S3. TGA curve of SCU-9.

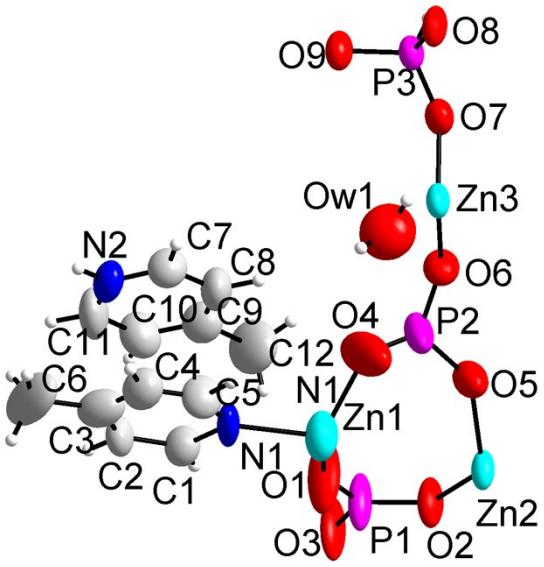

Fig. S4. ORTEP plot of the asymmetric unit of SCU-9, showing the labeling scheme and the 50% probability displacement ellipsoid.

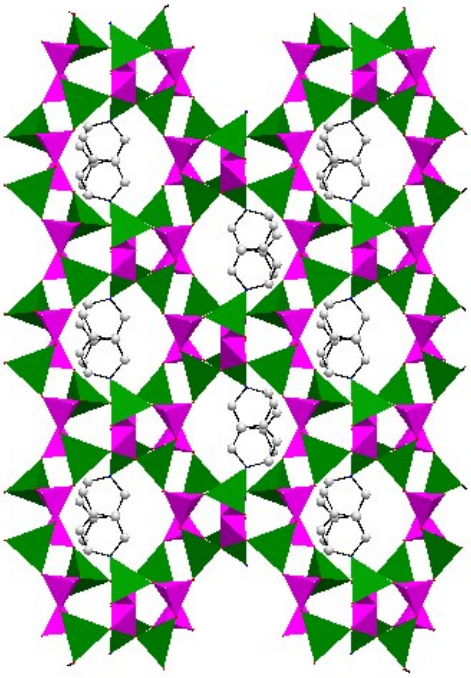

Fig. S5. View of the structure of SCU-9 with 12 MR channels along the [001] direction.

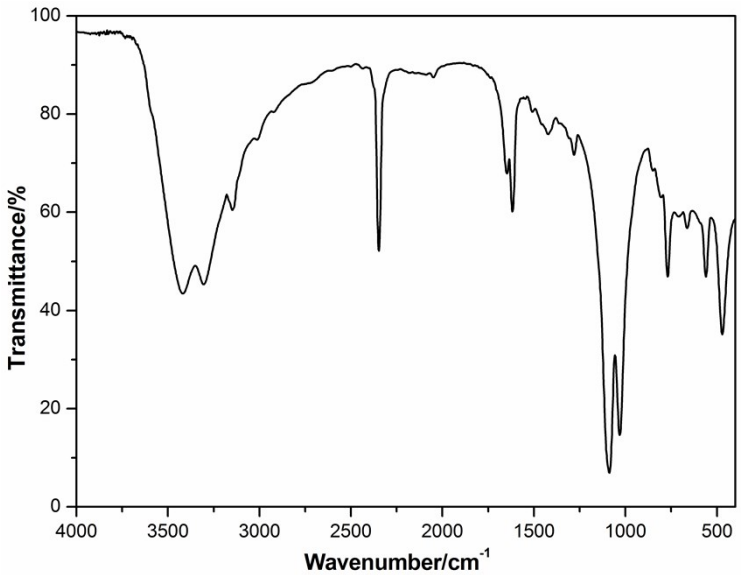

Fig. S6. IR spectrum of SCU-17.

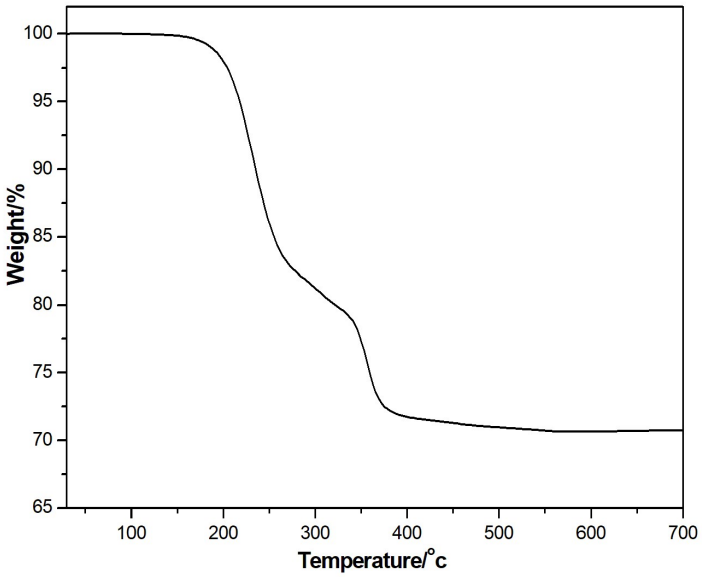

Fig. S7. TGA curve of SCU-17.

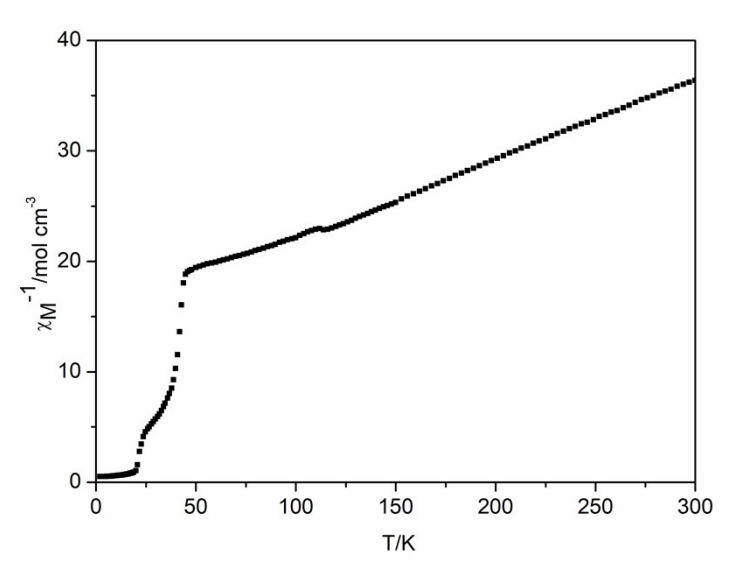

Fig. S8. Temperature dependence of χ_M^{-1} for SCU-17.

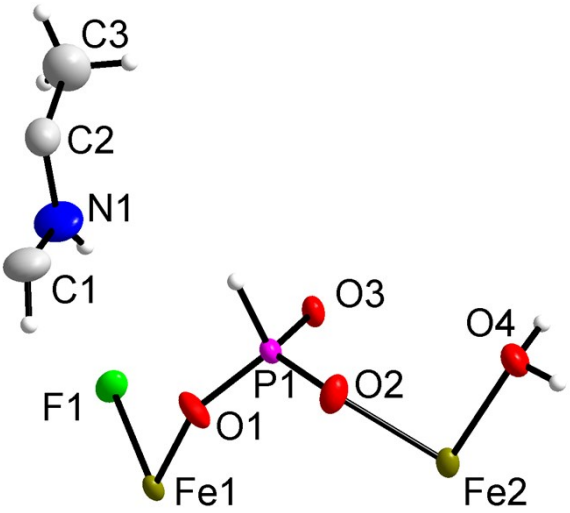

Fig. S9. ORTEP plot of the asymmetric unit of SCU-17, showing the labeling scheme and the 50% probability displacement ellipsoid.

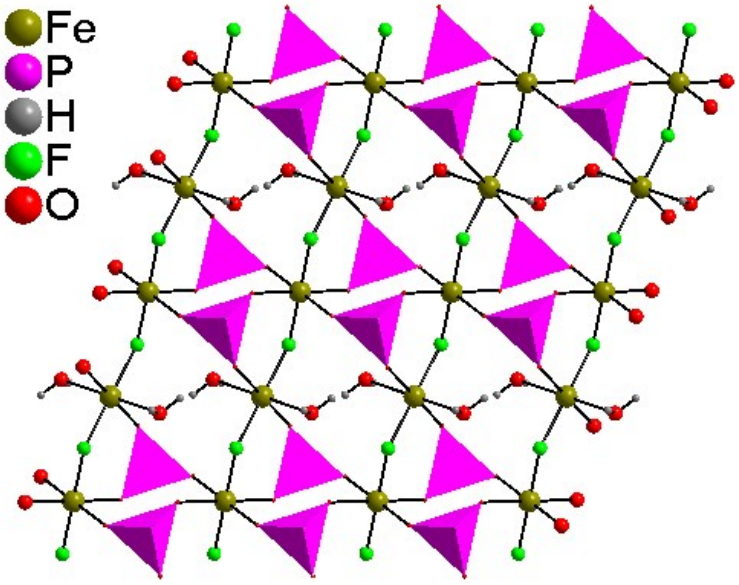

Fig. S10. View of the layered structure of SCU-17 showing infinite Fe-F-Fe linkages.