

**N-methylimidazolium containing metal phosphate-oxalates:  
solvent-free synthesis, crystal structure, and proton conduction**

Junfeng Zhang<sup>a</sup>, Qing Lei<sup>b</sup>, Lindong Luan<sup>b,\*</sup>, Hongmei Zeng<sup>b</sup>, Guohong Zou<sup>a</sup>, Zhien  
Lin<sup>a,\*</sup>

<sup>a</sup> *College of Chemistry, Sichuan University, Chengdu 610064, PR China*

<sup>b</sup> *Department of Criminal Investigation, Sichuan Police College, Luzhou 646000, PR  
China*

\* Corresponding authors. E-mail addresses: luanld@scpolicec.edu.cn (L. Luan);  
zhienlin@scu.edu.cn (Z. Lin)

### **Physical measurements:**

Powder X-ray diffraction data were obtained using a Shimadzu XRD-6100 diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Infrared 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<sub>2</sub> with a heating rate of 10 °C/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  $\times$  5 mm  $\phi$ ) 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.<sup>1</sup>

### *Reference*

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

Table S1. Hydrogen bonds for SCU-40

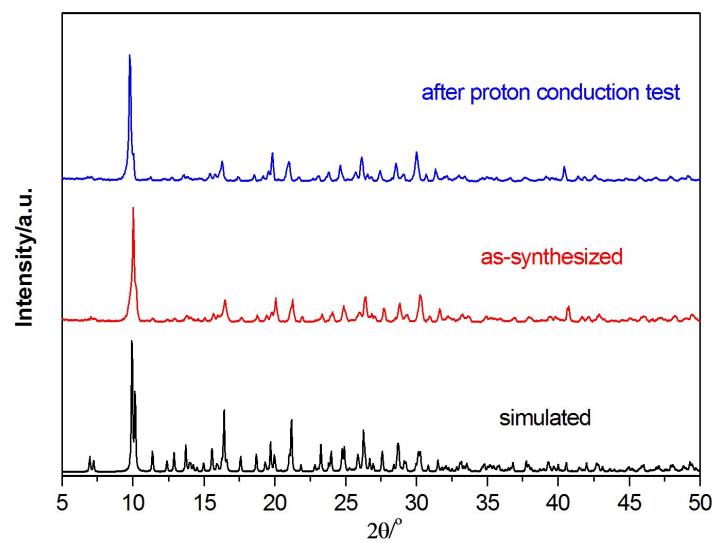
D-H···A <sup>a</sup>	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (deg)
O2-H2···O8#1	0.82	1.76	2.518(4)	152.3
O7-H7···O4#2	0.82	1.83	2.601(5)	156.8
O10-H10···O8#3	0.82	1.66	2.457(4)	163.1
O11-H11···O4#4	0.82	1.79	2.585(4)	161.6
O14-H14···O1#5	0.82	1.76	2.576(4)	171.3
O15-H15···O9	0.82	2.07	2.828(5)	152.5
N2-H2A···O14#6	0.86	2.64	3.162(10)	120.3
N2-H2A···O17#7	0.86	2.64	3.242(9)	128.3
N4-H4A···O15#8	0.86	2.56	3.300(7)	144.2
N4-H4A···O18	0.86	2.62	3.101(7)	116.6

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1 2-X, -Y, 1-Z; #2 1-X, -Y, 1-Z; #3 2-X, 1-Y, -Z; #4 +X, 1+Y, -1+Z; #5 1-X, 1-Y, 1-Z; #6 -1+X, +Y, +Z; #7 -1+X, 1+Y, +Z; #8 1+X, +Y, +Z; #9 +X, 1+Y, +Z.

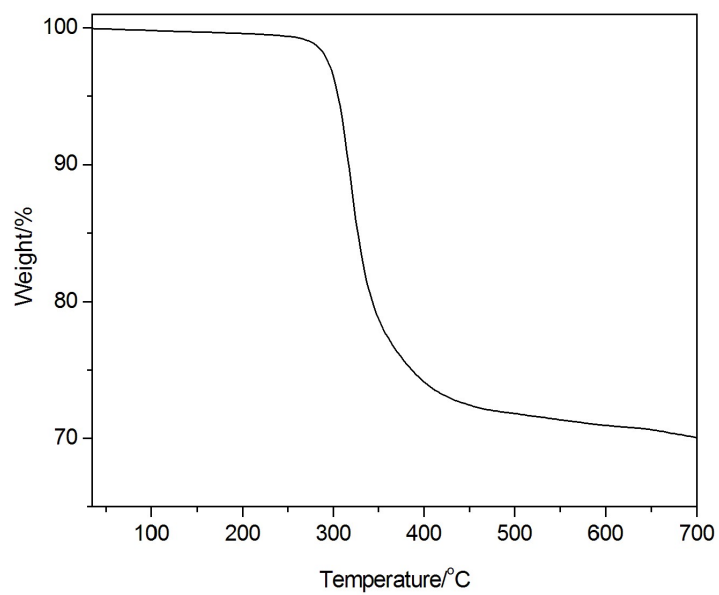
Table S2. Hydrogen bonds for SCU-42

D-H···A <sup>a</sup>	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA) (deg)
O3-H3···O2#1	0.82	1.88	2.688(4)	167.5
O7-H7···O2#2	0.82	1.71	2.486(5)	156.1
O8-H8···O4	0.82	2.16	2.936(5)	157.6
N1-H1···O6	0.86	2.00	2.854(6)	170.2

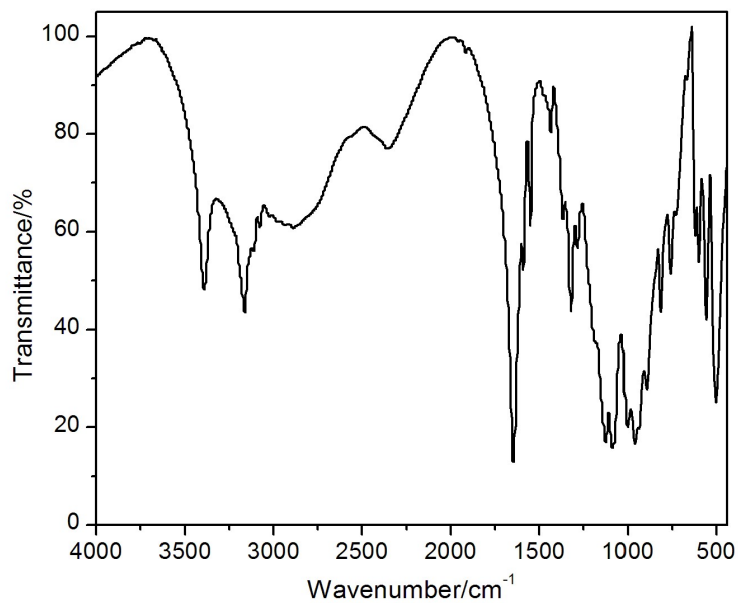
<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1 -X, 2-Y, 1-Z; #2 1-X, 2-Y, 1-Z.



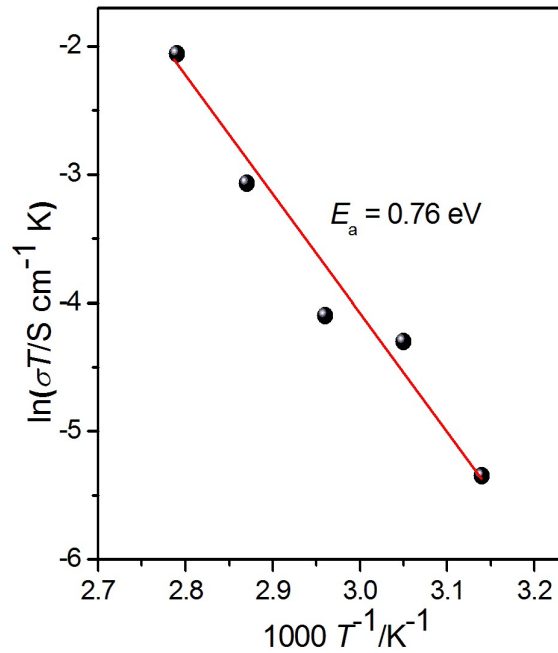
**Fig. S1.** Powder XRD patterns of SCU-40.



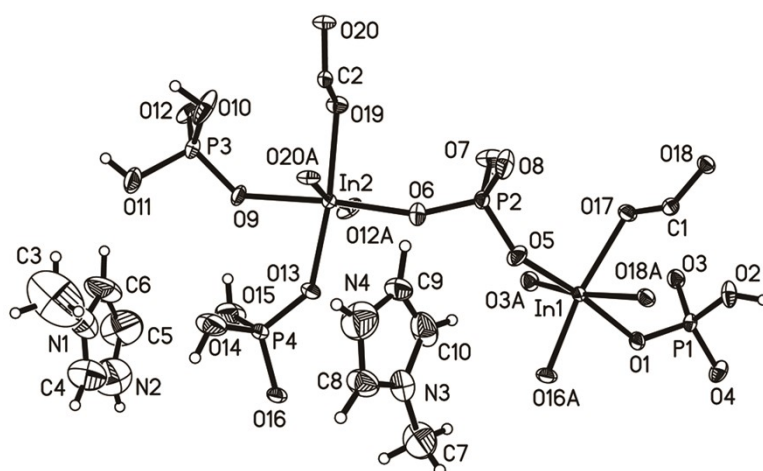
**Fig. S2.** TGA curve of SCU-40.



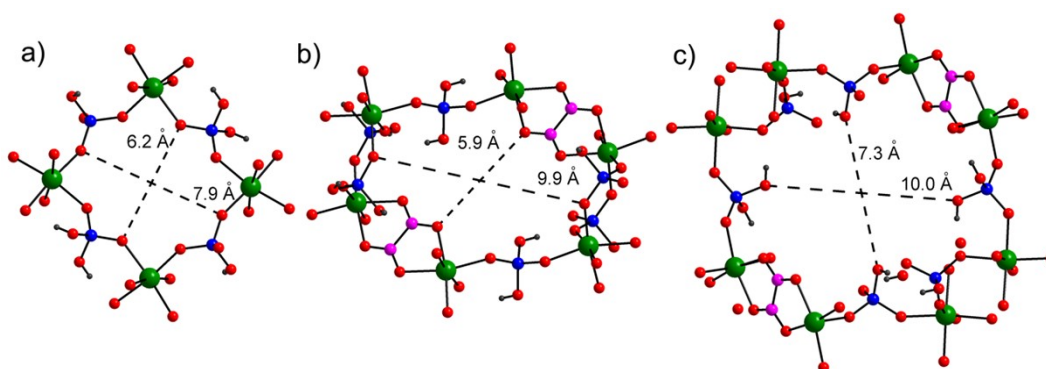
**Fig. S3.** IR spectrum of SCU-40.



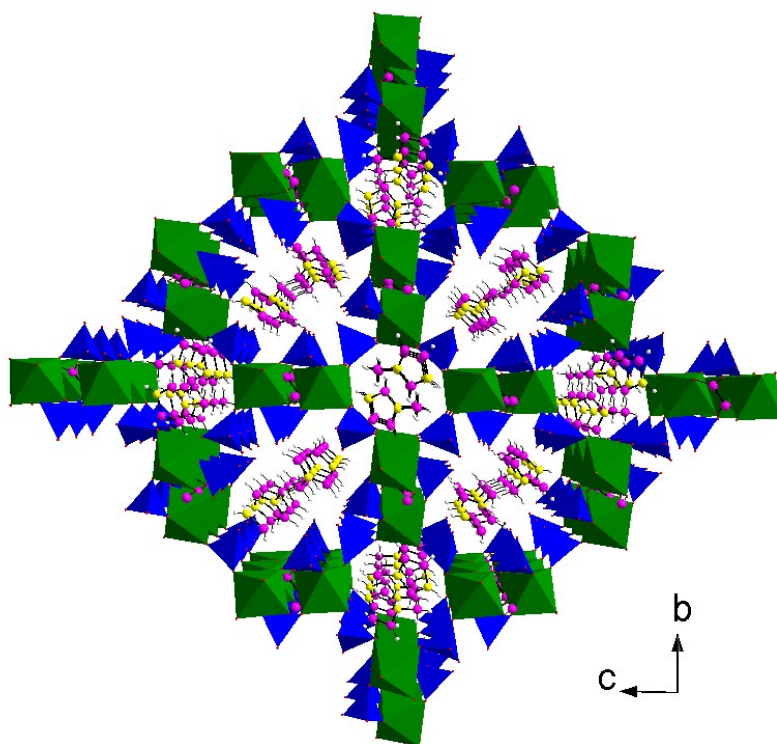
**Fig. S4.** Arrhenius plot of the proton conductivity of SCU-40.



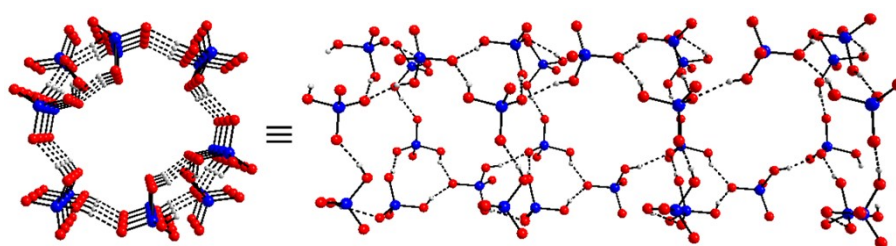
**Fig. S5.** ORTEP plot of the asymmetric unit of SCU-40, showing the labeling scheme and the 50% probability displacement ellipsoid. Atom labels with “A” refer to symmetry-generated atoms.



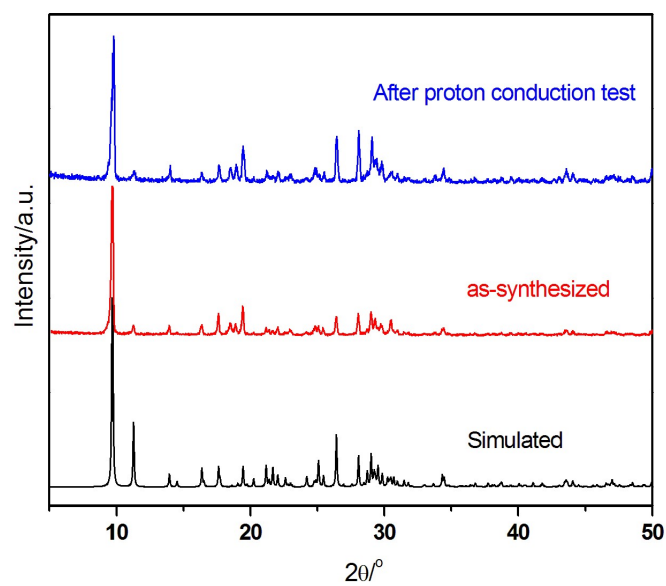
**Fig. S6.** Ball-and-stick representations of (a) 8-ring, (b) 12-ring, and (c) 16-ring windows in SCU-40.



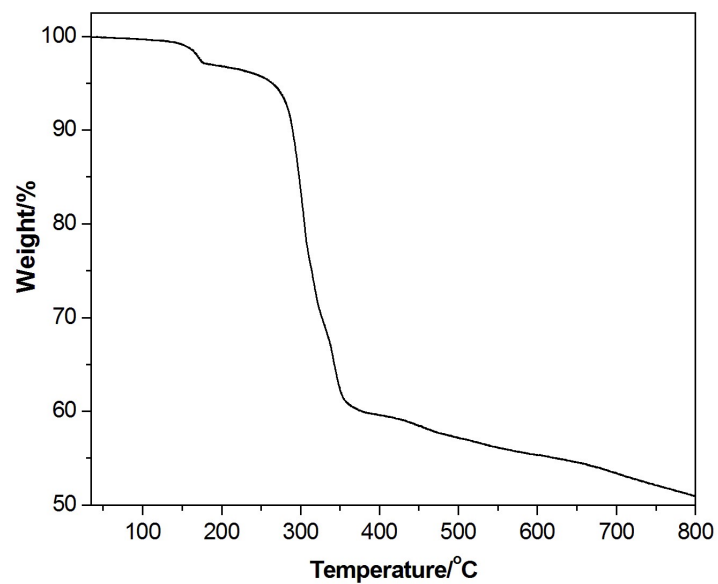
**Fig. S7.** A view of the structure of SCU-40 containing N-methylimidazolium within its channels.



**Fig. S8.** A view of a hydrogen-bonded tubule constructed from  $\text{HPO}_4$  and  $\text{H}_2\text{PO}_4$  units in SCU-40.

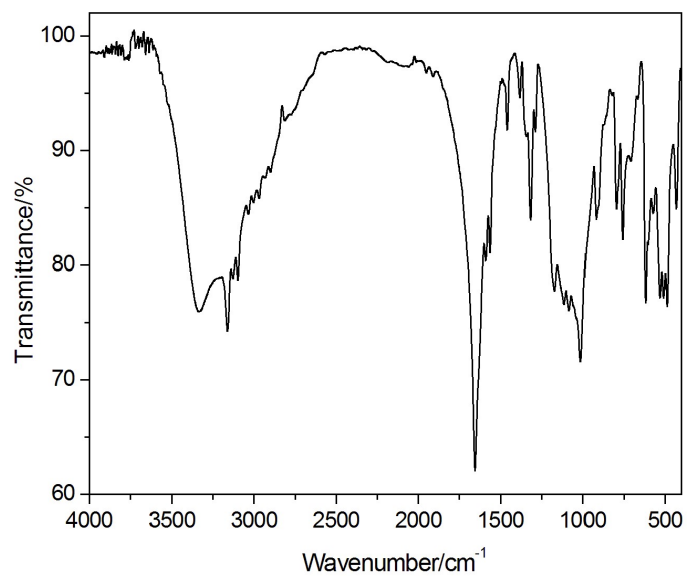


**Fig. S9.** Powder XRD patterns of SCU-42.

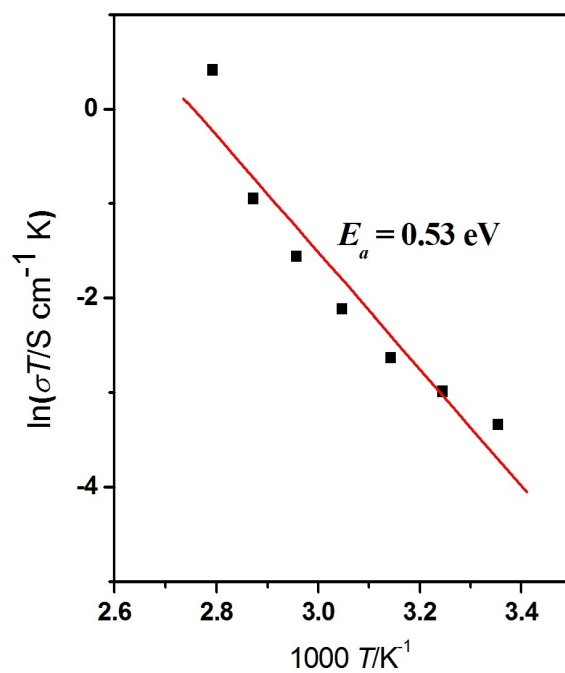


**Fig. S10.** TGA curve of SCU-42.

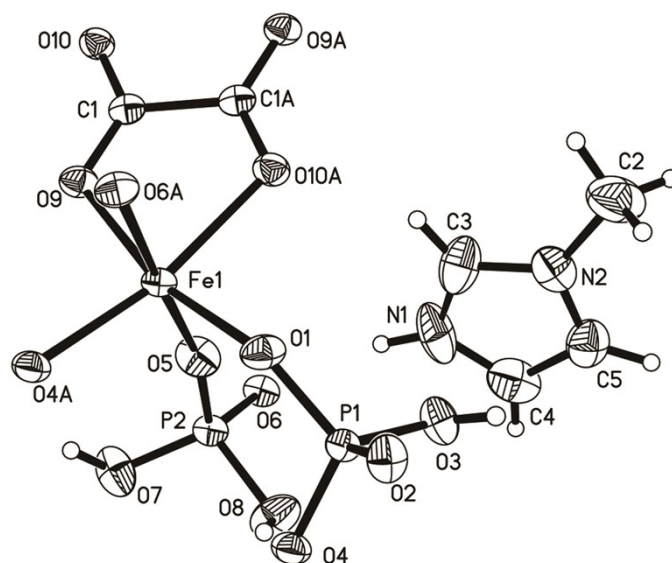




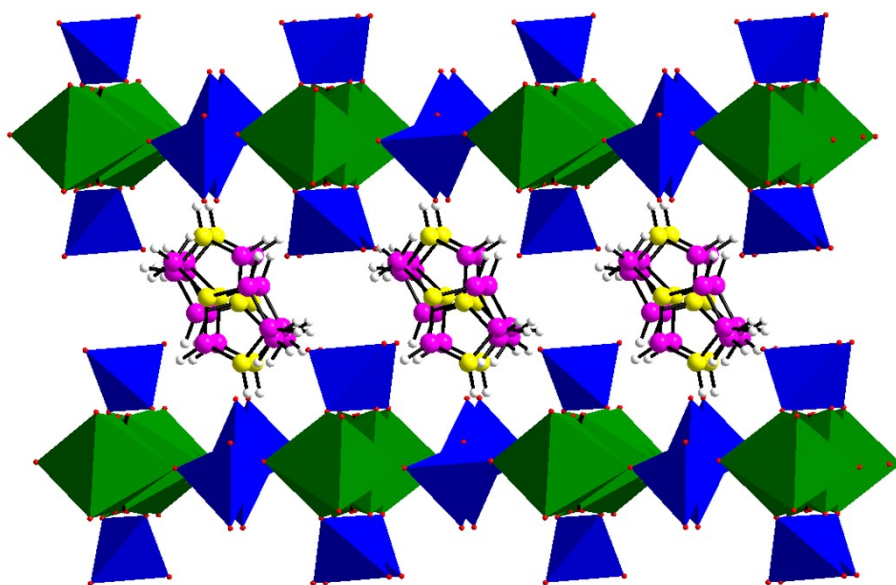
**Fig. S11.** IR spectrum of SCU-42.



**Fig. S12.** Arrhenius plot of the proton conductivity of SCU-42.



**Fig. S13.** ORTEP plot of the asymmetric unit of SCU-42, showing the labeling scheme and the 50% probability displacement ellipsoid. Atom labels with “A” refer to symmetry-generated atoms.



**Fig. S14.** View of the two-dimensional structure of SCU-42 intercalated with Hmim cations.