Electronic Supplementary Information

Mn^{2+} Cation-Directed Ionothermal Synthesis of an Open-Framework Fluorinated Aluminium Phosphite-Phosphate

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S1. Synthesis of single crystals of DNL-2

A beaker was consecutively charged with [EMIm]Br (100 mmol), H_3PO_3 (10 mmol, 50 wt% in H_2O), $Al(OH)_3$ (2.5 mmol), MnO_2 (2.5 mmol), HF (3 mmol, 40 wt% in H_2O). After stirred at 90 °C for 1 h, the reaction mixture was transferred into a PTFE-lined stainless autoclave (capacity: 30 mL) to crystallize at 160 °C for 21 d. After cooling to room temperature, the product was washed with deionized water, filtered and then dried at 120 °C overnight. A mixture of colourless hexagonal prismatic crystals and white powder was obtained (Fig. S1). Powder X-ray diffraction pattern of DNL-2 (Fig. S2) matched the simulated pattern based on structural analysis well except a slight diffraction peak of $Al(OH)_3$. Energy dispersive X-ray spectroscopy indicated the F/Al/P/Mn molar ratio of 13.9/12.0/18.0/3.40.

S2. Structure determination of DNL-2

A colourless hexagonal crystal with dimensions of 0.1677 mm × 0.1281 mm × 0.0985 mm was carefully selected for the X-ray diffraction experiment. The intensity data was collected on a four-circle kappa diffractometer (Xcalibur, Oxford Diffraction) equipped with a CCD detector and an enhanced X-ray source (graphite monochromatized Mo $K\alpha$ radiation, λ = 0.71073 Å) at room-temperature.

The structure was solved with direct method and refined on $|F|^2$ by full-matrix least squares using SHELXL97.[S1] DNL-2 has a hexagonal space-group $P6_3/m$ (No. 176). Crystallographically independent atoms Al1, P1 and P2 exist in each asymmetric unit, and the corresponding primary building units are $AlO_{4b}F_{2b}$, $H{-}PO_{2b}O_t$/$HO{-}PO_{2b}O_t$ and $H{-}PO_{3b}$/$HO{-}PO_{3b}$ respectively (Fig. S3). Both of the P1 and P2 sites were found to split into two positions P11/P12 and P21/P22. Each P site connected with three O atoms. The sum of P−O bond-valences for each P^{III} is 3.90-4.16. This indicates that the P-centered polyhedra could be assigned as $H{-}PO_3$ groups.[S2] Fourier transform infrared spectrum (FT-IR) also shows the characteristic band at 2430 cm^{-1} corresponding to the stretching vibration of framework P−H bond (Fig. S4).[S3] However, the fourth connected O atoms (O6 and O7 respectively) were found near P11 and P22. Considering the P−O distances (P11−O6: 1.532(9) Å, P22−O7: 1.540(10) Å), O6 and O7 were assigned as O atoms of terminal P−OH groups.[S4] Therefore, P11 and P22 are occupied by P^{III} as well as P^V. The ratios of P^{III}/P^V were determined by the occupancies of O6 and O7 (0.227(15) and 0.138(12) respectively).

Because the extra-framework organics are highly disordered, their structures can not be solved from single crystal X-ray diffraction data. The electron distribution calculated from the difference Fourier map indicates that the organics dynamically locate on the mirror planes perpendicular to the *c*-axis. In each $[6^2 12^3]$ cage, the total electron number of the extra-framework organics approximately equals to 61.9. This result fits well with the 61 electrons

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S1 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112.

S2 a) J. Loub, *Acta Crystallogr. Sect. B*, 1991, **47**, 468; b) S. Fernández-Armas, J. L. Mesa, J. L. Pizarro, J. S. Garitaonandia, M. I. Arriortua and T. Rojo, *Angew. Chem. Int. Ed.*, 2004, **43**, 977.

S3 Y. Ma, N. Li, S. Xiang and N. Guan, *J. Phys. Chem. C*, 2007, **111**, 18361.

S4 J. Yu, K. Sugiyama, S. Zheng, S. Qiu, J. Chen, R. Xu, Y. Sakamoto, O. Terasaki, K. Hiraga, M. Light, M. B. Hursthouse and J. M. Thomas, *Chem. Mater.*, 1998, **10**, 1208.

of one $[EMIm]^+$ cation. The typical vibration bands in the FT-IR of DNL-2 also proved the existence of $[EMIm]^+$ cations (Fig. S4 and Table S1).[S5] Based on above results, we deduce that each cell unit contains two $[EMIm]^+$ cations to balance the framework charge.

In each unit cell, 3.4 Mn^{2+} and 2 $[EMIm]^+$ cations exist in the structure. As a result, 3.2 H atoms were added to the formula to balance the valance of the anionic framework (−12). These H atoms may connect with the dangling $P{-}O_t$ bonds of $H{-}PO_{2b}O_t$/$HO{-}PO_{2b}O_t$ or fill in the channels as H_3O^+ cations.

S5 a) A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y.-M. Tan, T. Welton and J. A. Zora, *J. Chem. Soc., Dalton Trans.*, 1995, 3467; b) S. A. Katsyuba, E. E. Zvereva, A. Vidiš and P. J. Dyson, *J. Phys. Chem. A*, 2007, **111**, 352; c) R. Pei, Y. Xu, Y. Wei, G. Wen, K. Li, L. Wang, H. Ma, Z. Tian and L. Lin, *Chin. J. Catal.*, 2010, **31**, 1083.

Table S1 The assignment of typical vibration bands of EMIm cations in the Fourier transform infrared spectrum of DNL-2.

Wave Number / cm^{-1}	Assignment
3159, 3120	the ring C−H stretch
3000~2860	the alkyl C−H stretch
1639, 1576	the C=C stretch
1472	the asymmetric N−C−N stretch
1460~1380	the alkyl bend

Table S2 Gel compositions, crystallization conditions and the crystal phases of the products.

Entry	Gel composition[a]	T / °C	t / d	Product[b]
1	2.5 $Al(OH)_3$: 2.5 MnO_2 : 10 H_3PO_3 : 3 HF : 60 H_2O : 100 [BMIm]Br	160	7	DNL-2 + $Al(OH)_3$
2	2.5 $Al(OH)_3$: 2.5 MnO_2 : 10 H_3PO_3 : 3 HF : 10 MIm : 60 H_2O : 100 [EMIm]Br	160	7	DNL-2
3	2.5 $Al(OH)_3$: 2.5 MnO_2 : 10 H_3PO_3 : 3 HF : 10 TEA : 60 H_2O : 100 [EMIm]Br	160	7	DNL-2
4	2.5 $Al(OH)_3$: 2.5 MnO_2 : 10 H_3PO_3 : 3 HF : 10 TEAC : 60 H_2O : 100 [EMIm]Br	160	7	DNL-2
5	2.5 $Al(OH)_3$: 2.5 MnO_2 : 10 H_3PO_3 : 9 HF : 60 H_2O : 100 [EMIm]Br	160	7	DNL-2 + $Al(OH)_3$
6	2.5 $Al(OH)_3$: 2.5 MnO_2 : 8 H_3PO_3 : 2 H_3PO_4 : 9 HF : 60 H_2O : 100 [EMIm]Br	160	3	DNL-2 + $Al(OH)_3$
7	2.5 $Al(OH)_3$: 2.5 MnO_2 : 6 H_3PO_3 : 4 H_3PO_4 : 9 HF : 60 H_2O : 100 [EMIm]Br	160	3	(clear solution)
8	2.5 $Al(OH)_3$: 2.5 MnO_2 : 4 H_3PO_3 : 6 H_3PO_4 : 9 HF : 60 H_2O : 100 [EMIm]Br	160	3	CHA

[a] [BMIm]Br, 1-butyl-3-methylimidazolium bromide; [EMIm]Br, 1-ethyl-3-methylimidazolium bromide; MIm, 2-methylimidazole; TEA, triethylamine; TEAC, triethylamine hydrochloride.

[b] The crystal phases of the products were determined by their X-ray powder diffraction patterns.

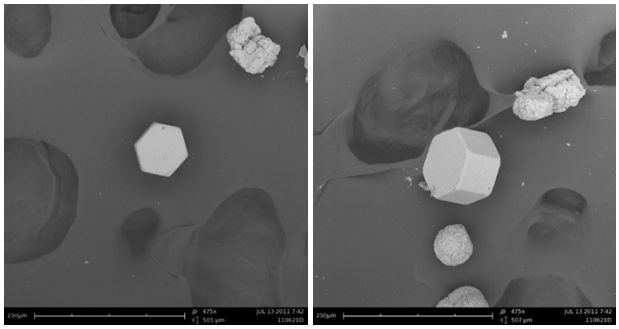

Fig. S1 The scanning electron microscopy of DNL-2.

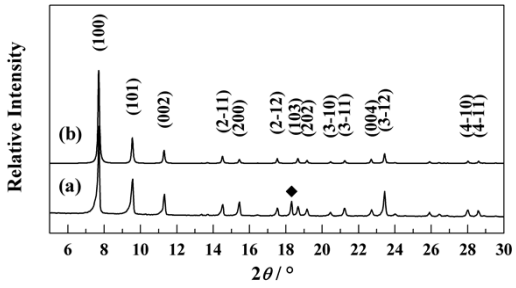

Fig. S2 The experimental (a) and simulated (b) X-ray powder diffraction patterns of DNL-2. ◆ indicates the diffraction peak of $Al(OH)_3$.

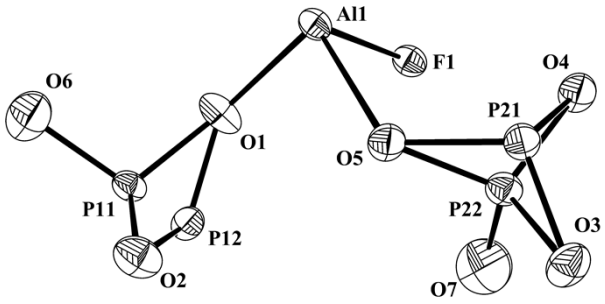

Fig. S3 The connectivity of framework atoms in the asymmetric unit.

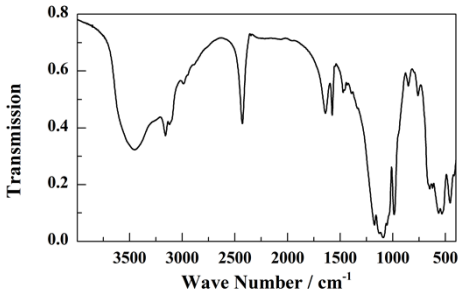

Fig. S4 The Fourier transform infrared spectrum of DNL-2.