Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Anisotropic ionic liquids built from nonmesogenic cation surfactants and Keggin−type polyoxoanions

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1. Experimental Section

(1). Materials. All chemicals were obtained commercially and used without additional purification. The $H_3PW_{12}O_{40}$, $H_4GeW_{12}O_{40}$, $K_5BW_{12}O_{40}$ were freshly prepared according to the procedure described in the literature[1] and characterized by IR spectra. All other reagents were readily available from commercial sources and used as received without further purification.

(2). Synthesis.

TPW was synthesized as follows: $H_3PW_{12}O_{40}$ was dissolved in aqueous solution and then methylene chloride solution of TOA·Br was added dropwise. The initial molar ratio of TOA·Br to $H_3PW_{12}O_{40}$ was controlled at 3:1. After stirring for 1 hour at room temperature, the organic phase was separated, evaporated, and dried until the weight remained constant. The product obtained was white solid. IR (KBr, cm^{-1}): ν = 2954, 2926, 2852, 1479, 1379, 1081, 981, 898, 818, 595, 515. Anal. Calcd for **TPW** ($C_{96}H_{204}N_3O_{40}PW_{12}$, 4277.67): C, 26.93; H, 4.77; N, 0.98. Found: C, 27.05; H, 4.86; N, 0.91. TGA suggests **TPW** is thermally stable up to ca. 350 ^oC and no significant loss of weight occurs below this temperature. Combining the results of EA and TGA, **TPW** should correspond to a tentative formula: $[(C_8H_{17})_4N]_3[PW_{12}O_{40}]$.

Crystals suitable for single−crystal X−ray crystallography were grown for **TPW** from ethanol/dichloromethane mixture (1:1 by volume, 20 mL) by slow evaporation at room temperature.

TGeW was synthesized following a similar procedure as for **TPW** by using $H_4GeW_{12}O_{40}$ instead. The initial molar ratio of TOA·Br to $H_4GeW_{12}O_{40}$ was controlled at 4:1. The product was white waxy solid. IR (KBr, cm^{-1}): ν = 2955, 2926, 2855, 1468, 1377, 966, 885, 830, 784, 535, 464. Anal. Calcd for **TGeW** ($C_{128}H_{272}N_4O_{40}GeW_{12}$, 4786.25): C, 32.10; H, 5.68; N, 1.17. Found: C, 32.65; H, 5.96; N, 1.12. TGA suggests **TGeW** is thermally stable up to ca. 200 ^oC and no significant loss of

weight occurs below this temperature. Combining the results of EA and TGA, **TGeW** should correspond to a tentative formula: $[(C_8H_{17})_4N]_4[GeW_{12}O_{40}]$.

TBW was synthesized following a similar procedure as for **TPW** by using $K_5BW_{12}O_{40}$ instead. The initial molar ratio of TOA·Br to $K_5BW_{12}O_{40}$ was controlled at 5:1. The product was white waxy solid. IR (KBr, cm^{-1}): ν = 2955, 2925, 2854, 1467, 1378, 991, 948, 899, 823, 724, 530, 506, 423. Anal. Calcd for **TBW** ($C_{160}H_{340}N_5O_{40}BW_{12}$, 5191.31): C, 36.98; H, 6.55; N, 1.35. Found: C, 37.44; H, 6.58; N, 1.34. TGA suggests **TBW** is thermally stable up to ca. 200 ^oC and no significant loss of weight occurs below this temperature. Combining the results of EA and TGA, **TBW** should correspond to a tentative formula: $[(C_8H_{17})_4N]_5[BW_{12}O_{40}]$.

(3). Characterization Methods. The IR spectra in KBr pellets were recorded in the range 400-4000 cm^{-1} with an Alpha Centaurt FT/IR spectrophotometer. Elemental analysis (C, H, N) was performed on a Flash EA1112 from Thermo Quest Italia SPA. Thermal properties of the complexes were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC measurements were performed on a Netzsch DSC 204 at a scanning rate for both heating and cooling of 5 °C min^{-1}. The samples were sealed in aluminum capsules in air, and the holder atmosphere was dry nitrogen. TGA analyses were carried out by using a Perkin-Elmer TGA7 instrument, with a heating rate of 10 °C min^{-1}, under a nitrogen atmosphere. The texture of the compounds was observed by using an Axioskop 40 polarizing optical microscope of (Carl Zeiss Light Microscopy, Germany) equipped with a LINKAM THMS 600 hot stage and a LINKAM CI 94 temperature controller. For variable-temperature XRD measurements, a Bruker AXS D8 ADVANCE X-ray diffractometer using Cu Kα radiation of a wavelength of 0.154 nm with an mri Physikalische Geräte GmbH TC-Basic temperature chamber was used.

2. IR spectra

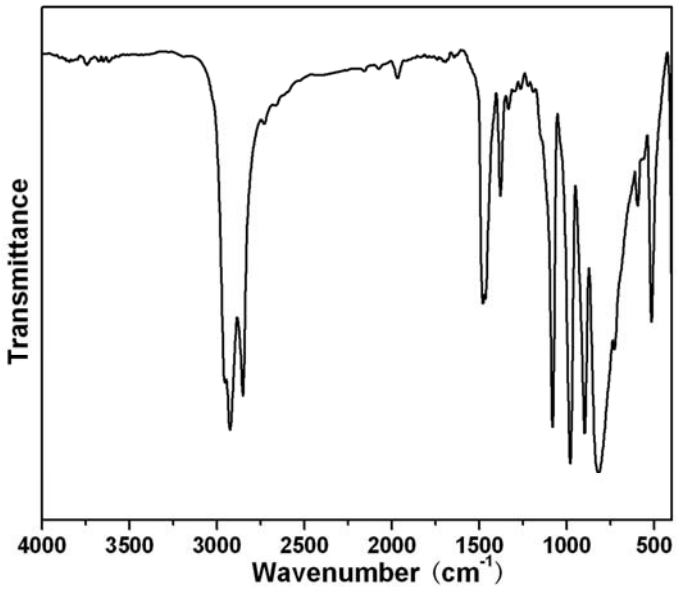

Figure S1. IR spectrum of TPW.

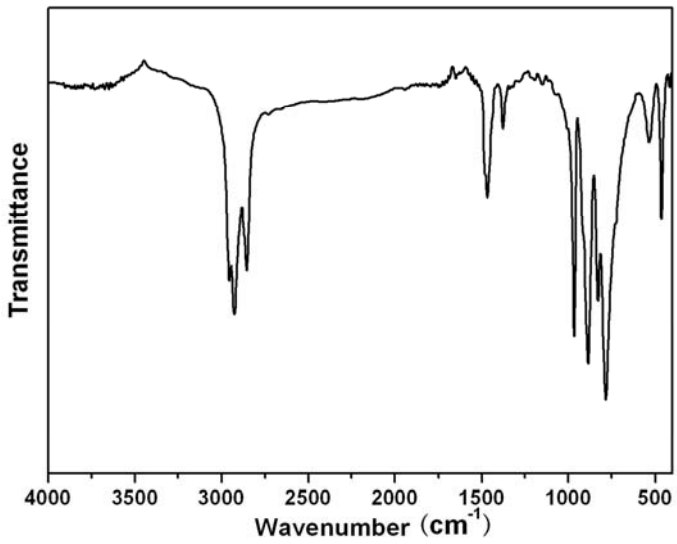

Figure S2. IR spectrum of TGeW.

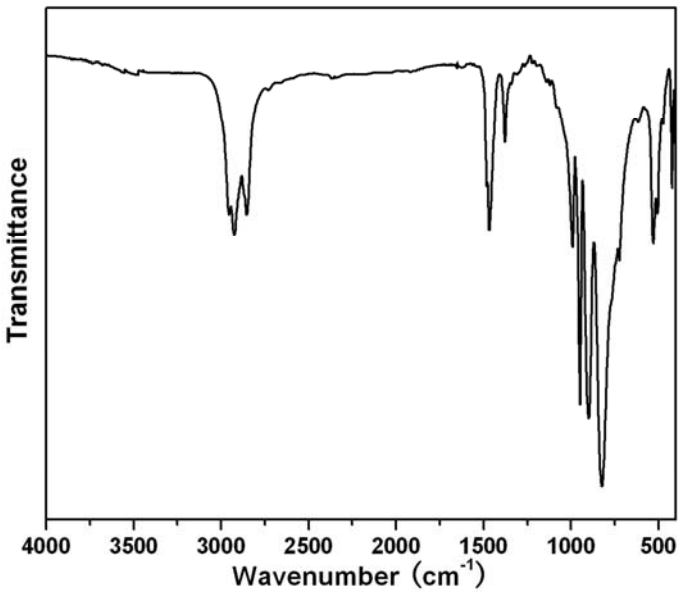

Figure S3. IR spectrum of TBW.

3. TGA curves

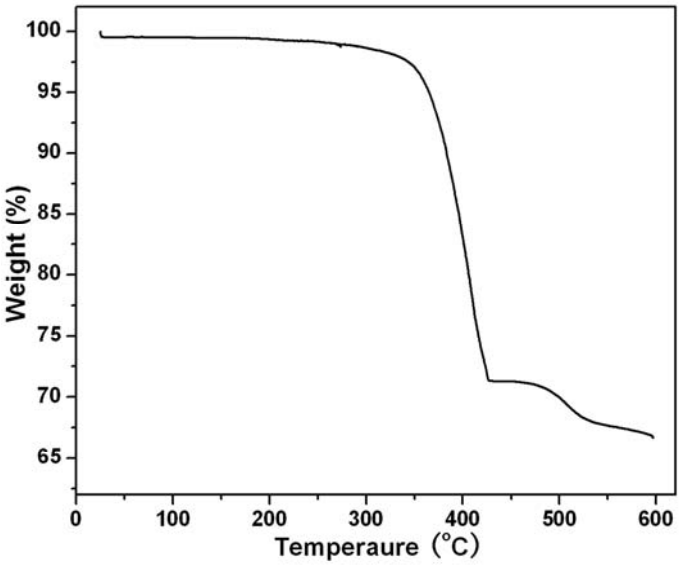

Figure S4. TGA curve of TPW.

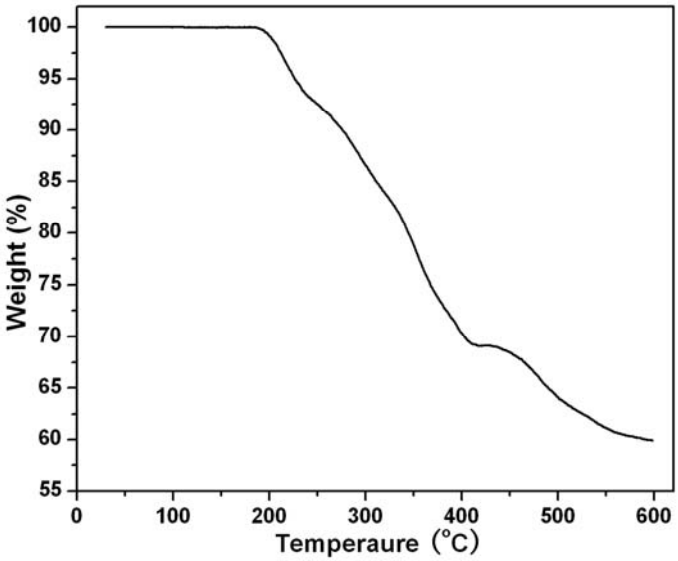

Figure S5. TGA curve of TGeW.

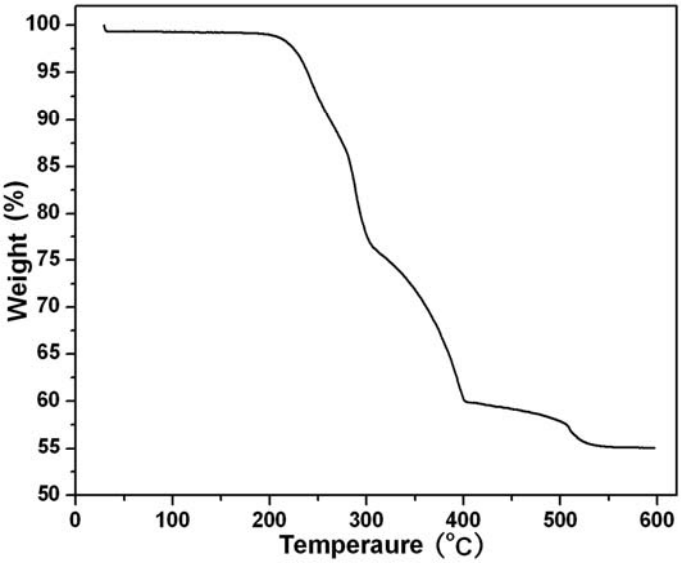

Figure S6. TGA curve of TBW.

4. DSC Measurements

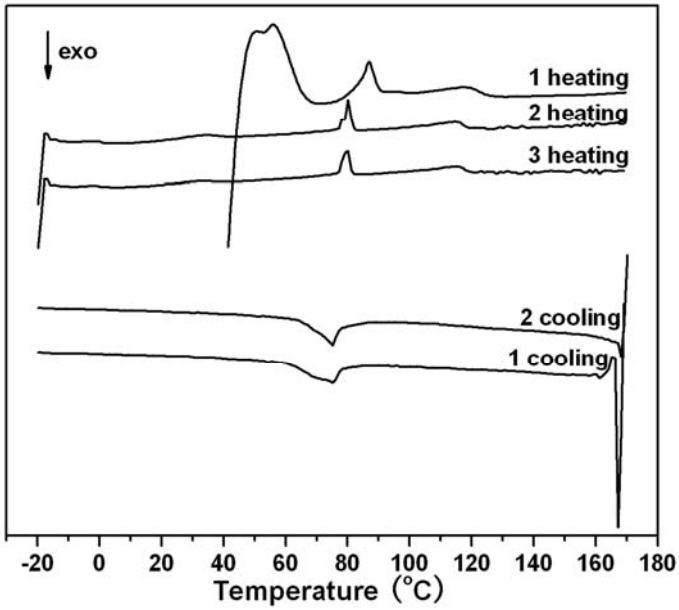

Figure S7. DSC curves of TGeW at a scanning rate of 5 ^{o}C min^{-1}.

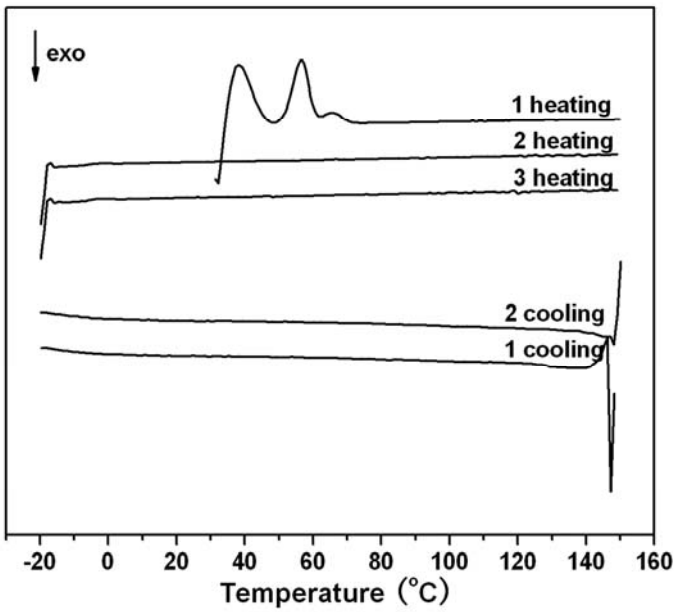

Figure S8. DSC curves of TBW at a scanning rate of 5 ^{o}C min^{-1}.

5. Temperature dependent FT−IR spectra of TGeW

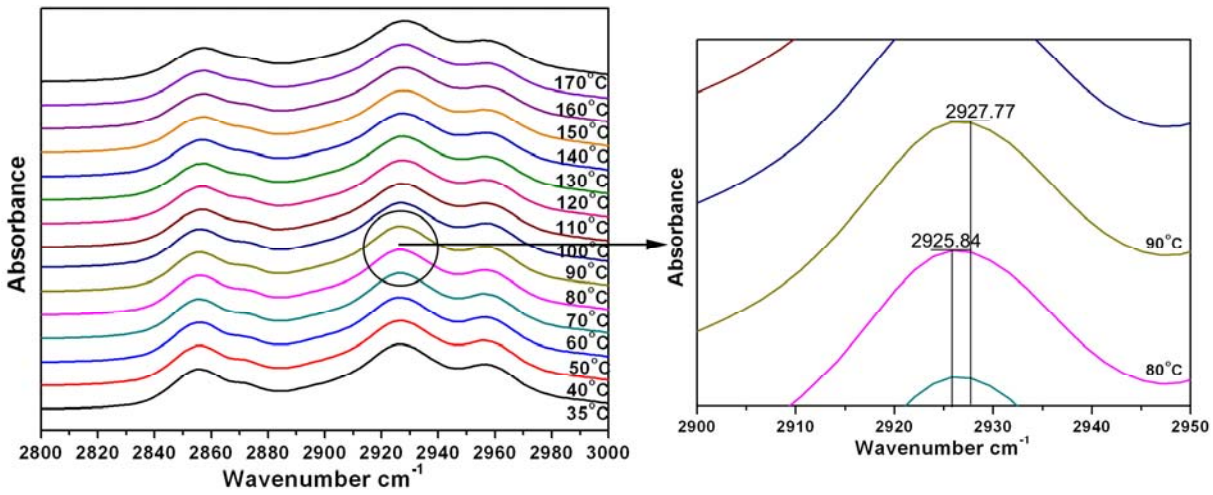

Figure S9. Temperature dependent FT−IR spectra of TGeW.

6. X−ray diffraction of TBW

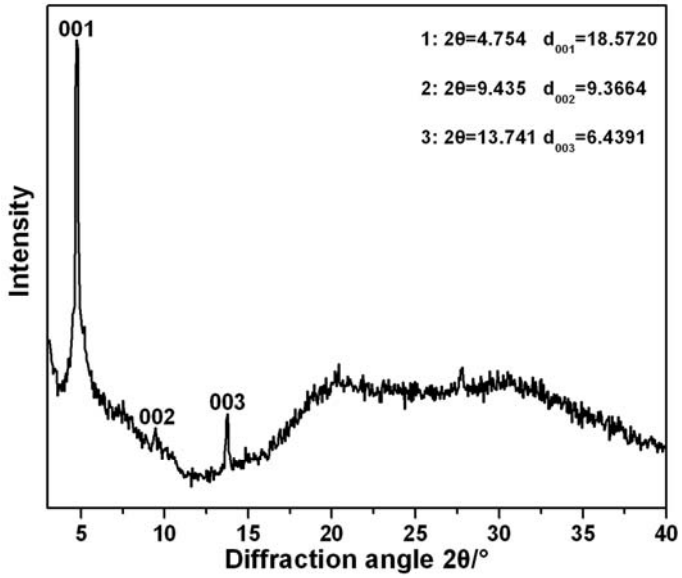

Figure S10. X−ray characterization of TBW at room temperature.

7. X−ray Structural Studies.

Single−crystal diffractometry of **TPW** was conducted on a Bruker Smart Apex CCD diffractometer with Mo Kα monochromated radiation (λ = 0.71073 Å) at room temperature. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from the International Tables for X−Ray Crystallography.[2] Empirical absorption

corrections were applied. The structures were solved by using the direct method and refined through the full-matrix least−squares method on $F2$ using SHELXS−97.[3] Anisotropic thermal parameters were used to refine all non−hydrogen atoms. Hydrogen atoms on the TOA cations were placed on calculated positions and included in the refinement riding on their respective parent atoms. CCDC−788692 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44−1223/336−033; e-mail: deposit@ccdc.cam.ac.uk). The crystal data and structure refinement results of **TPW** are summarized in Table S1.

Table S1. Crystal Data and Structural Refinement for Compounds **TPW**

	TPW
Formula	$C_{96}H_{204}N_3O_{40}PW_{12}$
Formula weight ($gmol^{-1}$)	4277.67
T (K)	296
Wavelength (Å)	0.71073
Crystal system	trigonal
Space group	R -3c
a (Å)	24.4709(18)
b (Å)	24.4709(18)
c (Å)	39.112(3)
V(Å^3)	20283(3)
Z	6
D_{calc} ($mg\ m^{-3}$)	2.101
μ(mm^{-1})	10.241
F(000)	12144.0

Crystal size (mm)	0.20×0.18×0.16
Goodness−of−fit on F^2	0.997
Final R indices[$I>2\sigma(I)$]	$R_1{}^a = 0.0319$， $wR_2{}^a = 0.0521$
R indices (all data)	$R_1{}^a = 0.0655$， $wR_2{}^a = 0.0605$

$R_1{}^a = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2{}^a = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

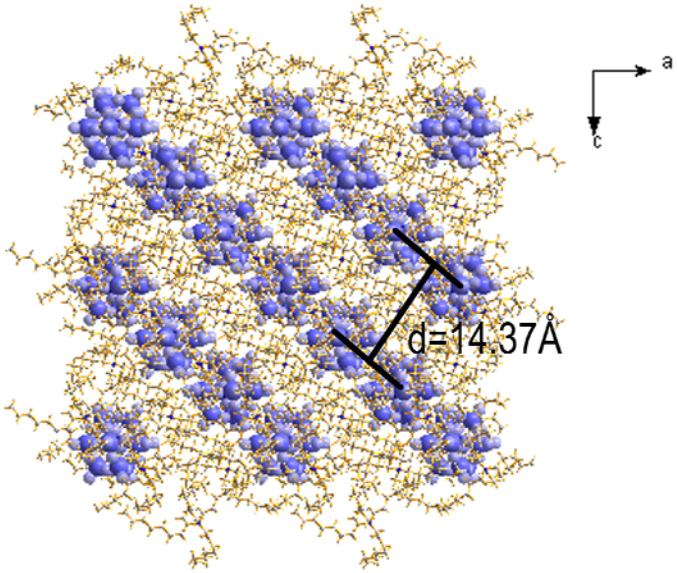

Figure S11. Layered structure in the crystal of **TPW** (view is along the *b* axis, d = 14.37 Å).

References

1. R. D. Claude, F. Michel, F. Raymonde and T. René, *Inorg. Chem.,* 1983, **22,** 207.

2. N. F. M. Henry and K. Lonsdale (Eds.), International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1952.

3. G. M. Sheldrick, SHELXS-97: Programs for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.