Supporting Information

Understanding Thermal Decomposition Mechanism of a Halogen-Free Chelated Orthoborate-Based Ionic Liquid: A Combined Computational and Experimental Study

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Liquid-State Nuclear Magnetic Resonance (NMR) Spectroscopy

^{1}H, ^{13}C and ^{31}P NMR spectra of $[P_{4,4,4,8}][BOB]$ were recorded on a Bruker Ascend Aeon WB 400 spectrometer. Spectra were obtained at 25°C using standard Bruker pulse programs. Chemical shifts were expressed in parts per millions (δ) downfield from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ=7.26 ppm) and were reported as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet) and *br* (broad) (Figs. S1-S4). Numbers of atoms in chemical groups are estimated from integrated relative intensities in NMR spectra (indicated in red under corresponding NMR spectra).

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of $[P_{4,4,4,8}][BOB]$ and $[P_{4,4,4,8}][Cl]$ were obtained by means of the Varian 680-IR spectrometer with the Attenuated Total Reflection (ATR) mode. Mid-infrared spectra were recorded in 4000-400 cm^{-1} interval (Figs. S5 and S6). After the analysis, the ATR correction was applied to previously obtained spectra with the refractive index of 0.15 of IL samples.

Quantum Chemical Frequency Calculations

IR spectra are produced by means of the Gaussian software using B3LYP/6-31G(d,p) functional and presented in Figs. S7 and S8. For the $[P_{4,4,4,8}][BOB]$ IR bands are detected at the following intervals: asymmetric stretching of C-H bonds in $[P_{4,4,4,8}]^+$ (3000-3136 cm^{-1}); asymmetric stretching of C-O and C=O bonds in $[BOB]^-$ (1800-1903 cm^{-1}); asymmetric bending of C-H bonds in $[P_{4,4,4,8}]^+$ (1052-1527 cm^{-1}); asymmetric stretching of C-C and C-P bonds in $[P_{4,4,4,8}]^+$ and B-O bonds in $[BOB]^-$ (below 1046 cm^{-1}). In the case of $[P_{4,4,4,8}][Cl]$, IR bands were detected as follows: asymmetric stretching of C-H bonds in $[P_{4,4,4,8}]^+$ (2985-3120 cm^{-1}); asymmetric bending of C-H bonds in $[P_{4,4,4,8}]^+$ (1069-1527 cm^{-1}); asymmetric stretching of C-C bonds in $[P_{4,4,4,8}]^+$ (below 1066 cm^{-1}). Both calculated IR spectra agree with the experimental FTIR results (Figs. S5 and S6).

Differential Thermal Analysis (DTA)

DTA measurement was carried out on a Setaram Labsys TG-DTA instrument (France). The sample of $[P_{4,4,4,8}][BOB]$ weighing around 10 mg was treated from room temperature up to 600°C under argon flow with a heating rate of 10°C/min (Fig. S9).

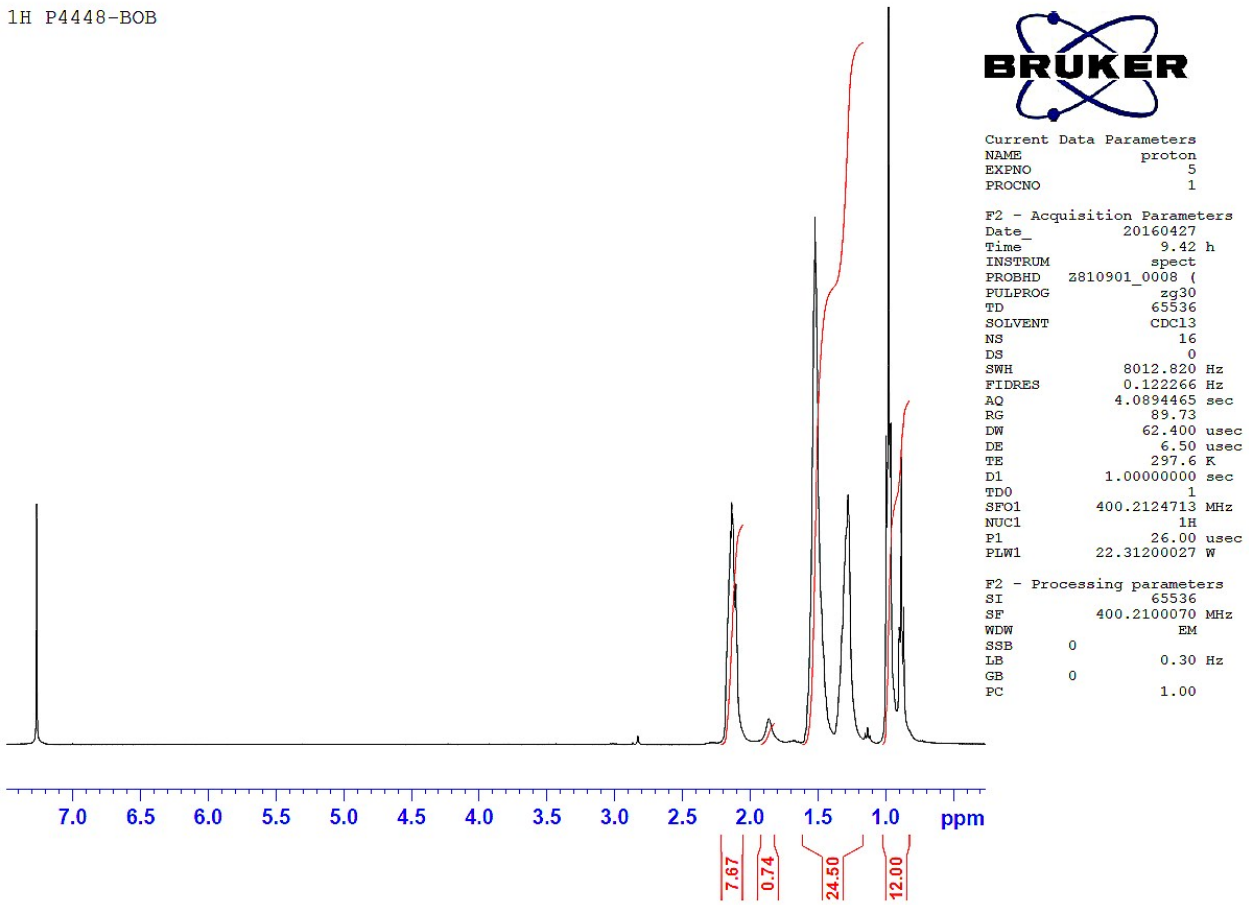

Fig. S1. ^{1}H NMR of $[P_{4,4,4,8}][BOB]$ (400.21 MHz, $CDCl_3$): 2.20-2.05 (m, 8H), 1.64-1.18 (m, 24H), 1.0363-0.80 (m, 12H) ppm

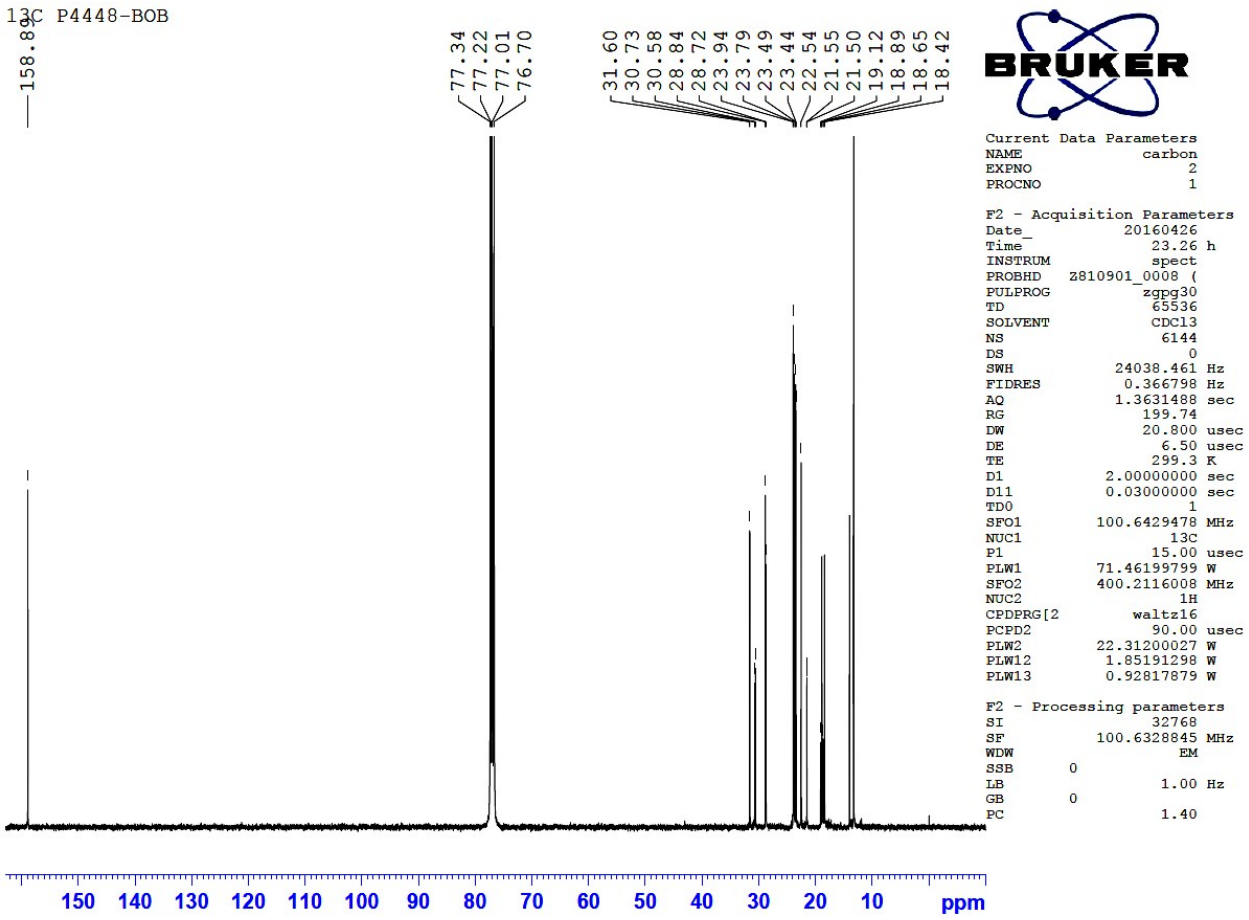

Fig. S2. ^{13}C NMR of $[P_{4,4,4,8}][BOB]$: (100.63 MHz, $CDCl_3$) 158.88, 31.59, 30.73, 30.58, 28.84, 28.72, 23.93, 23.79, 23.49, 23.44, 22.53, 21.55, 21.50, 19.12, 18.88, 18.65, 18.41, 14.02, 13.27 ppm. (77.33, 77.21, 77.01, 76.70 ppm multiplet is assigned to the solvent $CDCl_3$).

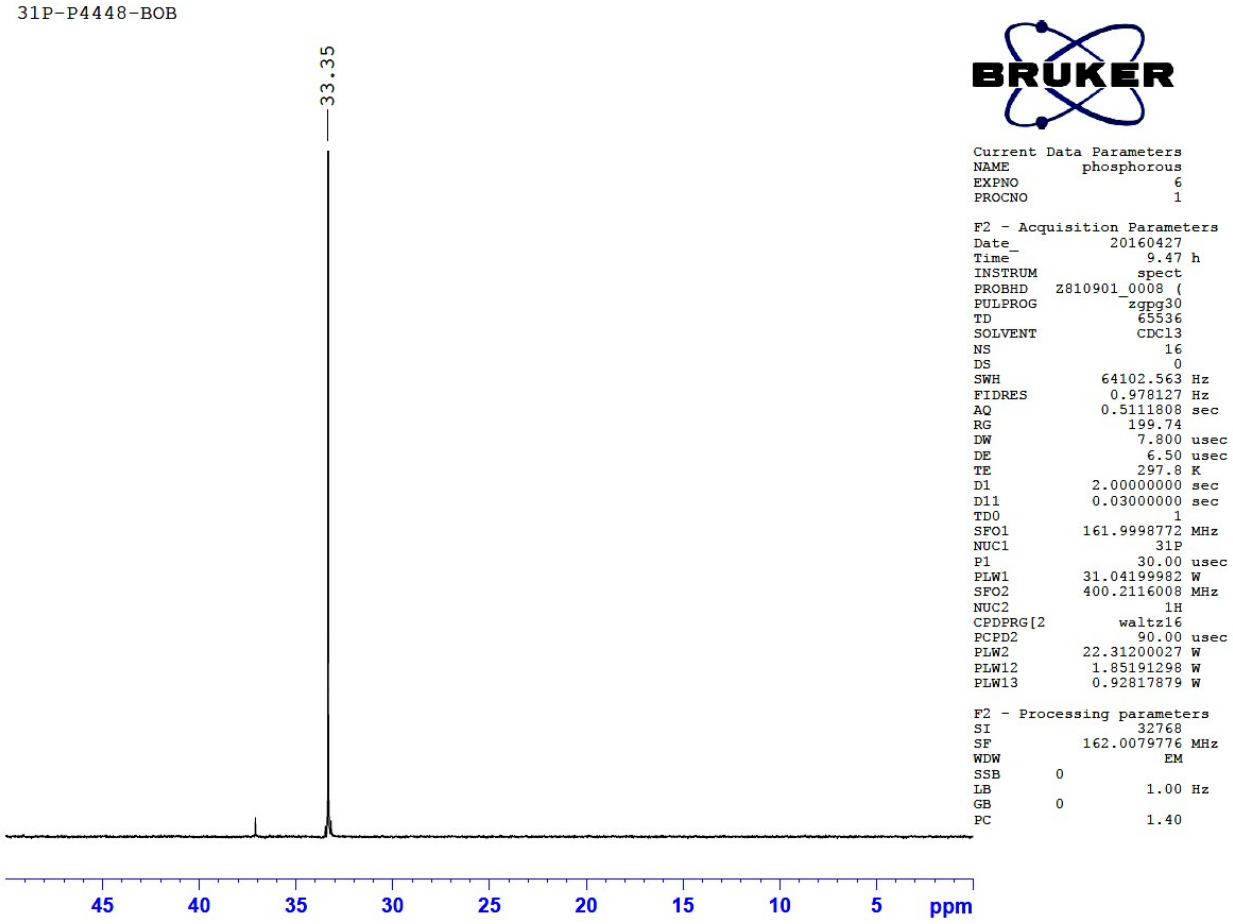

Fig. S3. ^{31}P NMR of $[P_{4,4,4,8}][BOB]$ (162.00 MHz, $CDCl_3$): 33.35 ppm. A small intensity resonance line at *c.a.* 37 ppm corresponds to a phosphorous-containing impurity.

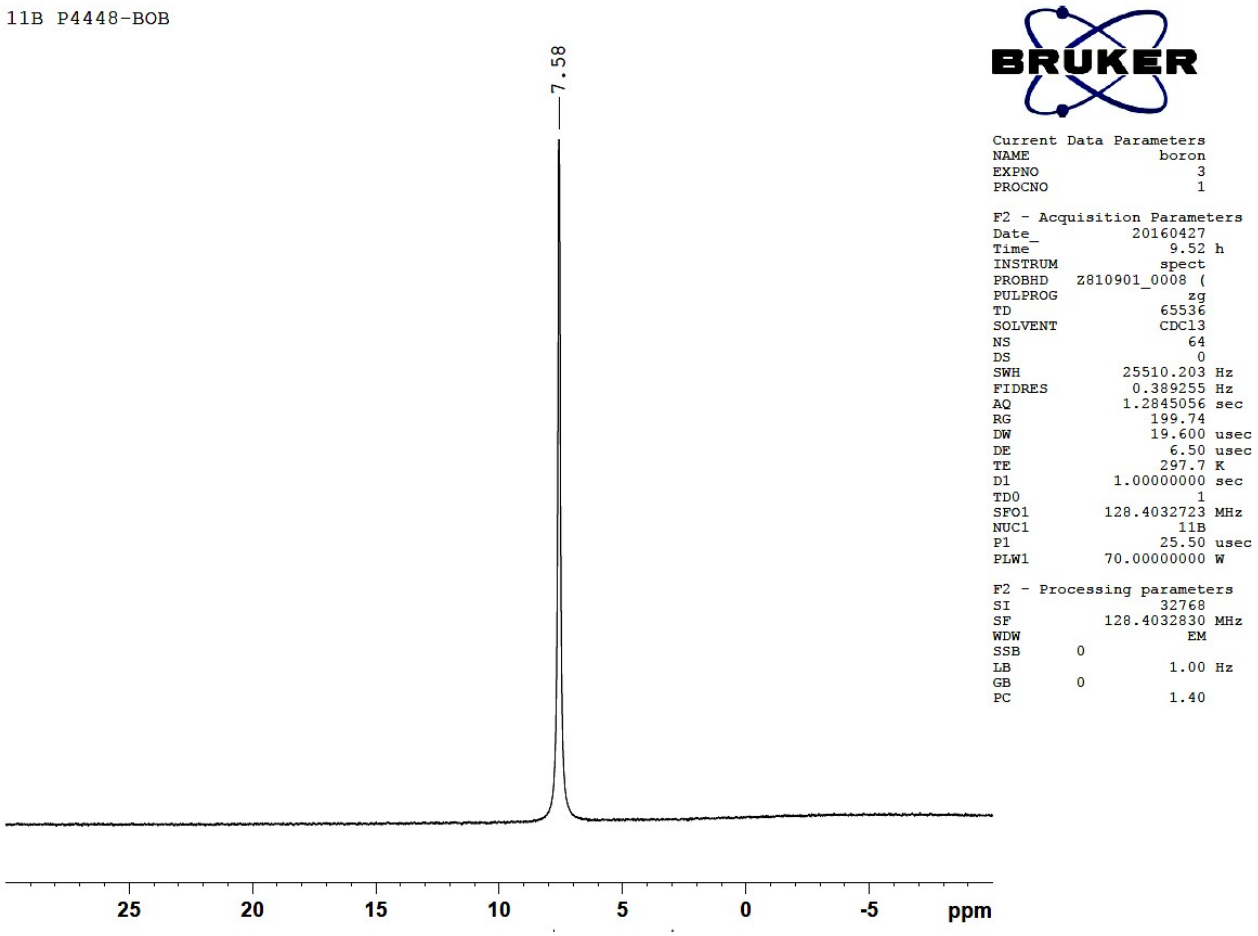

Fig. S4. ^{11}B NMR of $[P_{4,4,4,8}][BOB]$ (128.40 MHz, $CDCl_3$): 7.58 ppm.

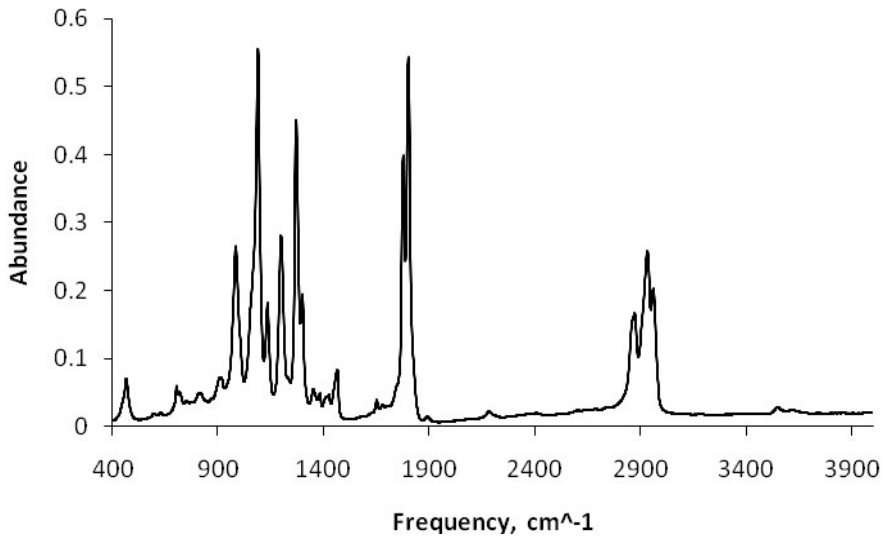

Fig. S5. Experimental FTIR spectra of $[P_{4,4,4,8}][BOB]$.

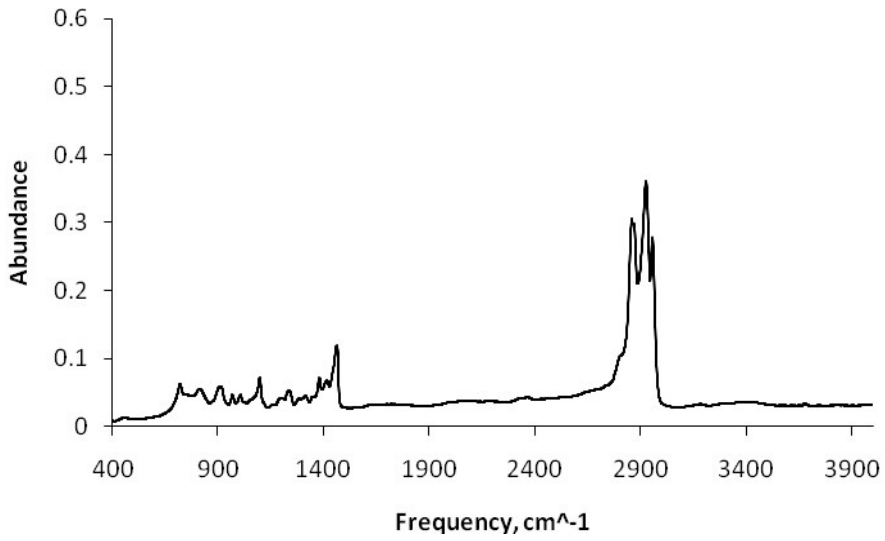

Fig. S6. Experimental FTIR spectra of $[P_{4,4,4,8}][Cl]$.

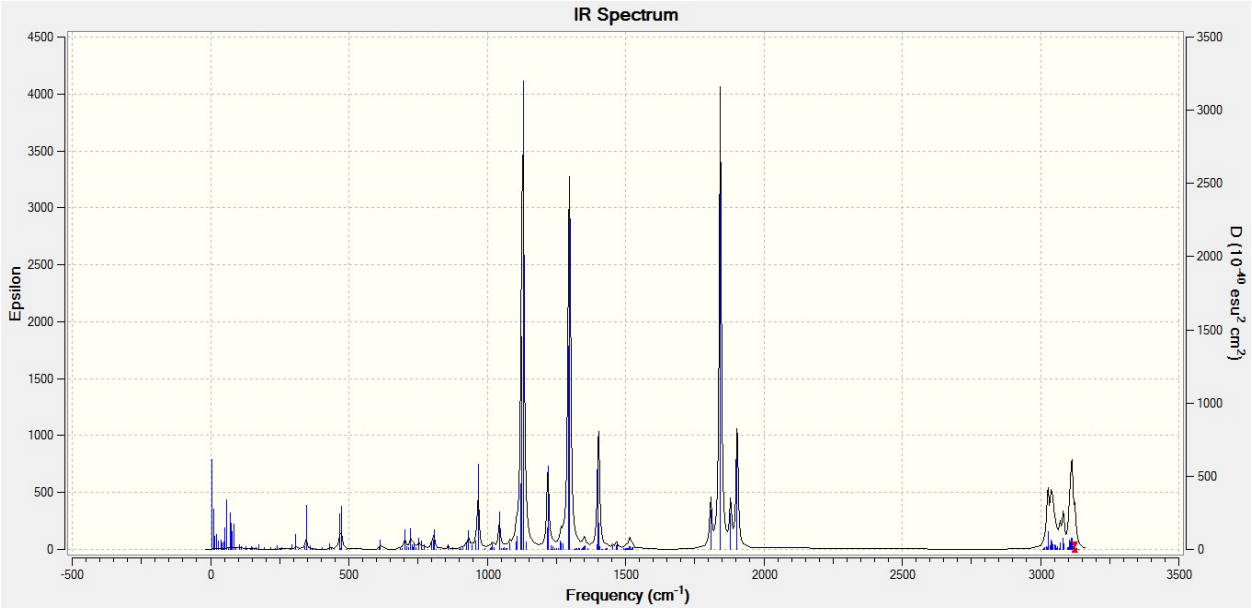

Fig. S7. Calculated IR spectra of $[P_{4,4,4,8}][BOB]$.

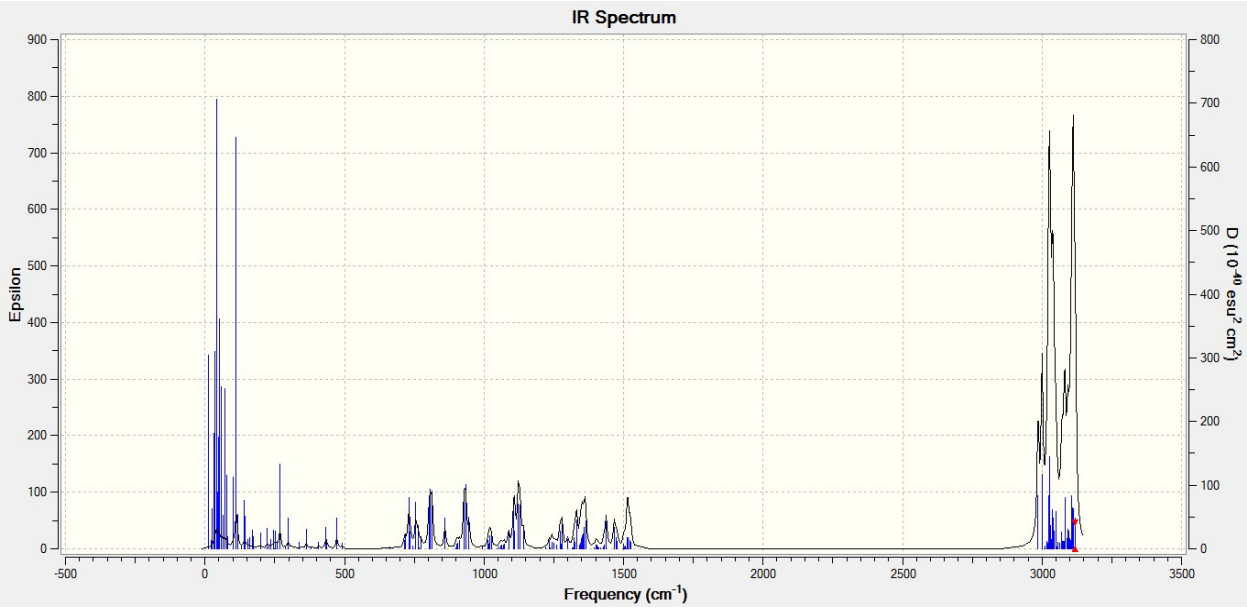

Fig. S8. Calculated IR spectra of $[P_{4,4,4,8}][Cl]$.

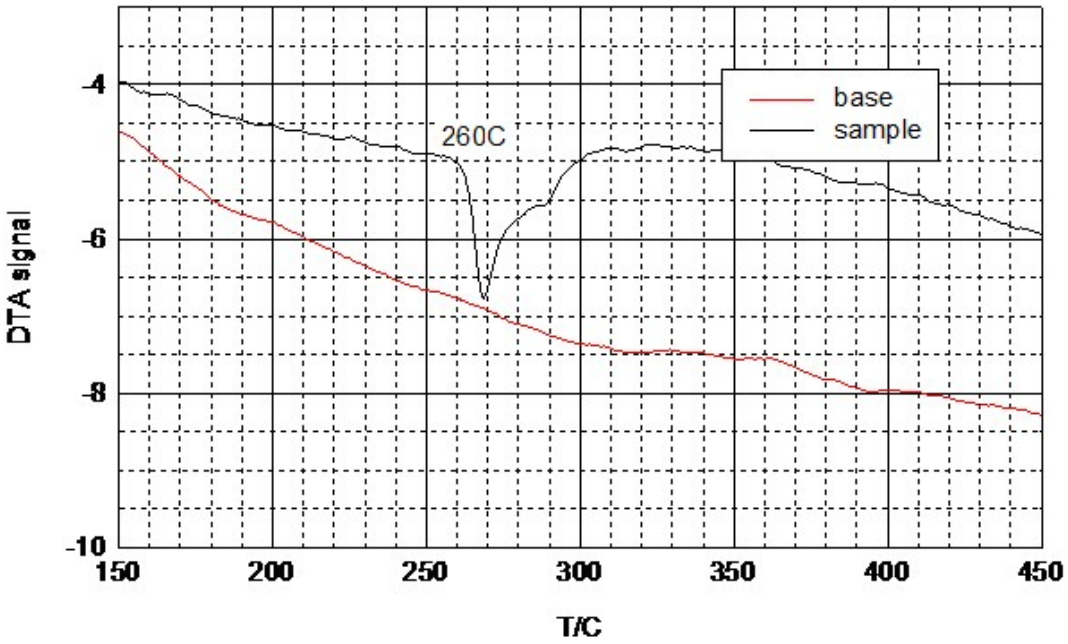

Fig. S9. The differential thermal analysis (DTA) curve of $[P_{4,4,4,8}][BOB]$. Black line corresponds to the DTA curve.