

Supporting Information

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

M. Golets,^{a,†} M. R. Shimpi,^b Y.-L. Wang,^{c,d} O. N. Antzutkin,^b S. Glavatskih^{d,e} and A.
Laaksonen^{a,f,†}

^{a.} Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden.

^{b.} Chemistry of Interfaces, Luleå University of Technology, S-97187, Luleå, Sweden.

^{c.} Applied Physical Chemistry, Department of Chemistry, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden.

^{d.} System and Component Design, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden.

^{e.} Mechanical Construction and Production, Ghent University, B-9000 Ghent, Belgium.

^{f.} Stellenbosch Institute of Advanced Study (STIAS), Wallenberg Research Centre, Stellenbosch University, Marais Street, Stellenbosch 7600, South Africa.

^{†.} Corresponding authors (e-mail: Mikhail.Golets@mmk.su.se, Aatto.Laaksonen@mmk.su.se).

Liquid-State Nuclear Magnetic Resonance (NMR) Spectroscopy

¹H, ¹³C and ³¹P 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 (CDCl₃, 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).

1H P4448-BOB

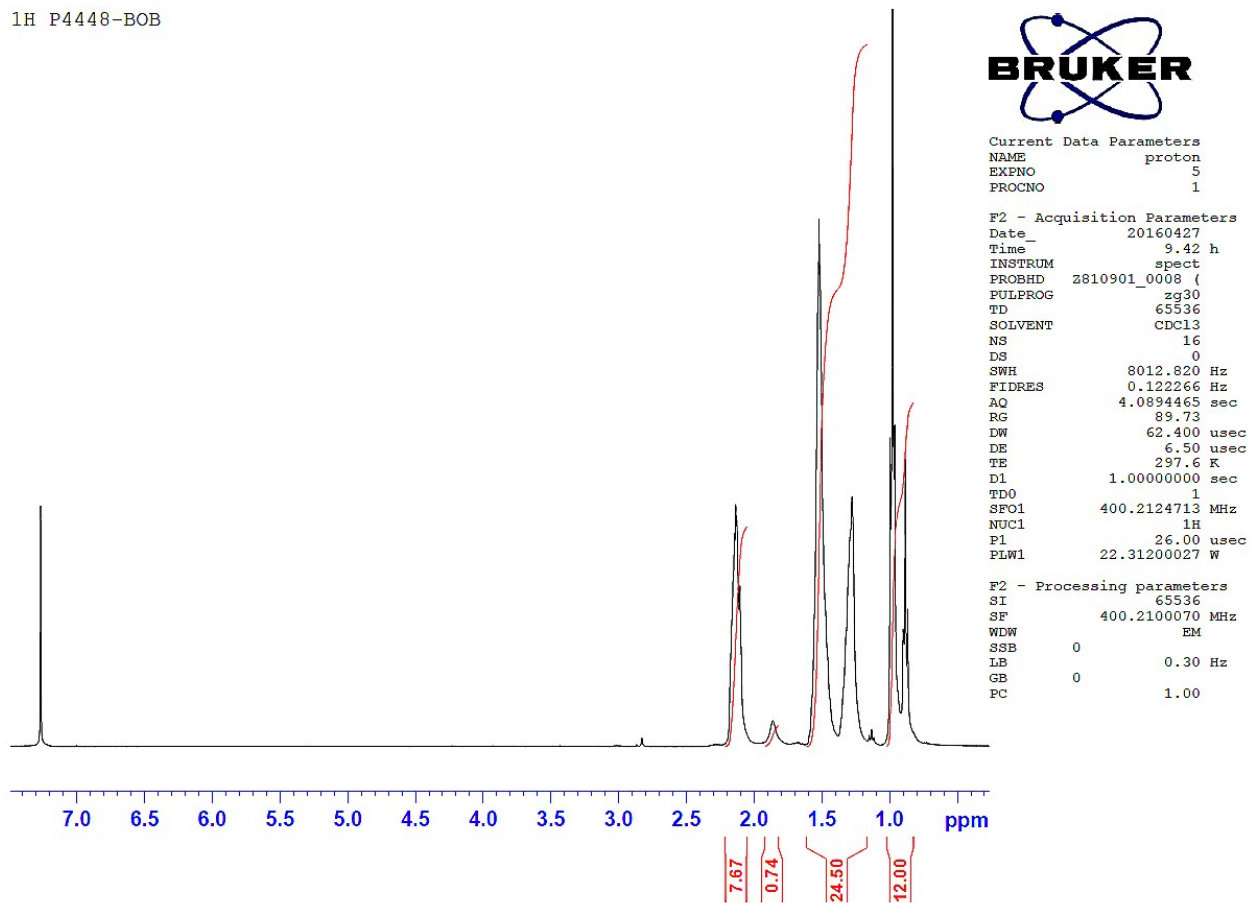


Fig. S1. ¹H NMR of [P_{4,4,4,8}][BOB] (400.21 MHz, CDCl₃): 2.20-2.05 (m, 8H), 1.64-1.18 (m, 24H), 1.0363-0.80 (m, 12H) ppm

¹³C P4448-BOB

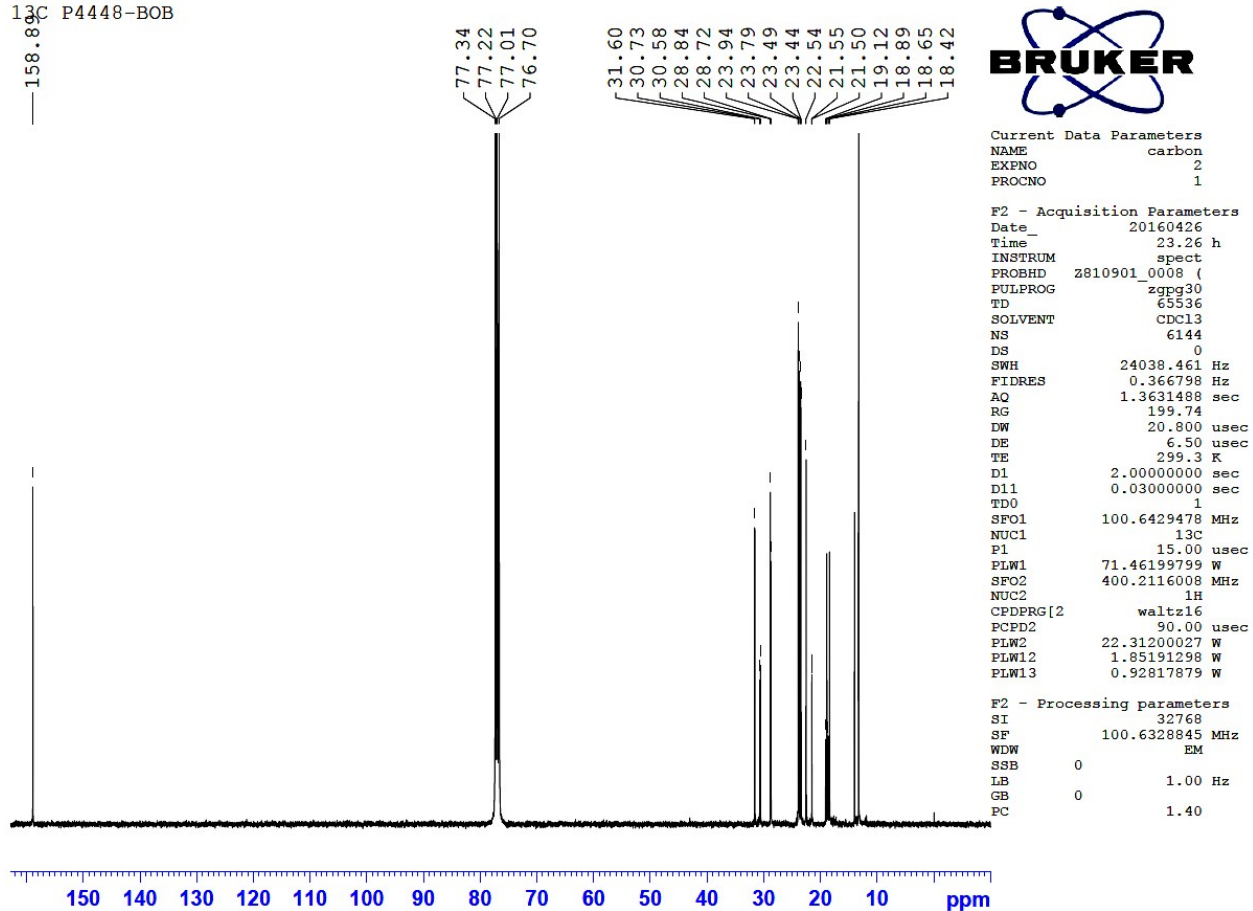
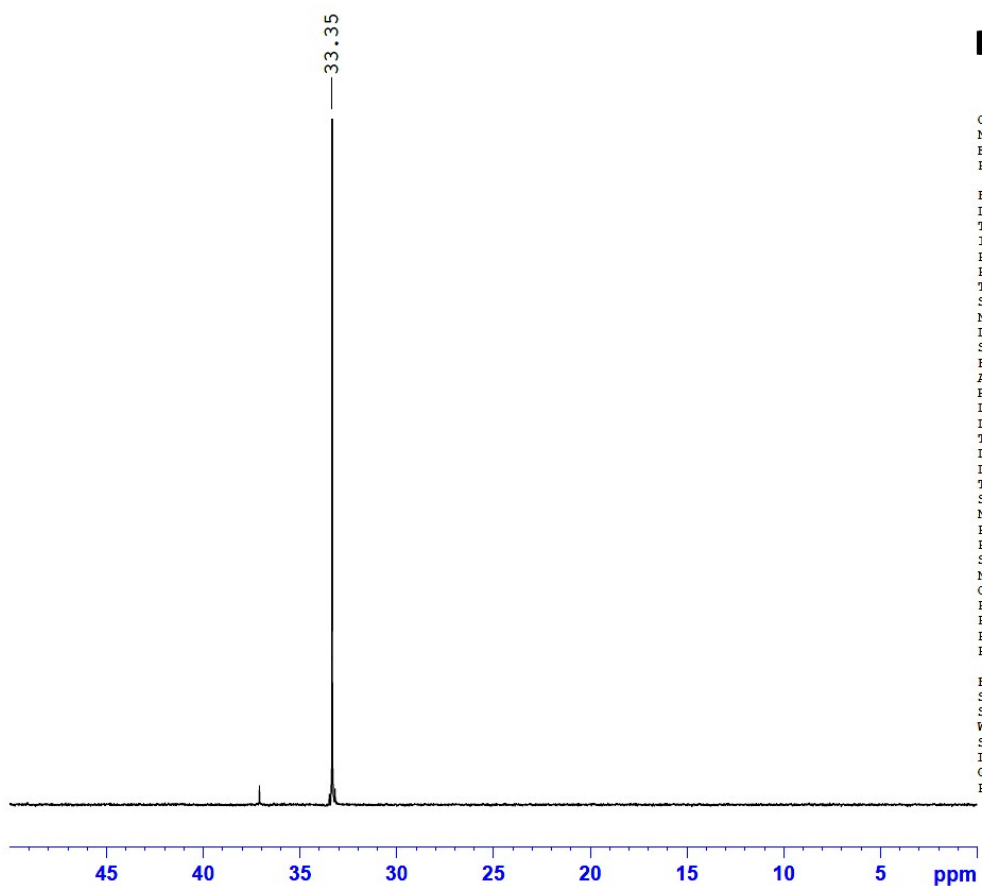


Fig. S2. ¹³C NMR of [P_{4,4,4,8}][BOB]: (100.63 MHz, CDCl₃) 158.88, 31.59, 30.73, 30.58, 28.84, 28.72, 23.93, 23.79, 23.49, 23.44, 22.53, 21.55, 21.50, 19.12, 18.88, 18.65, 18.41, 14.02, 13.27 ppm. (77.33, 77.21, 77.01, 76.70 ppm multiplet is assigned to the solvent CDCl₃).

31P-P4448-BOB



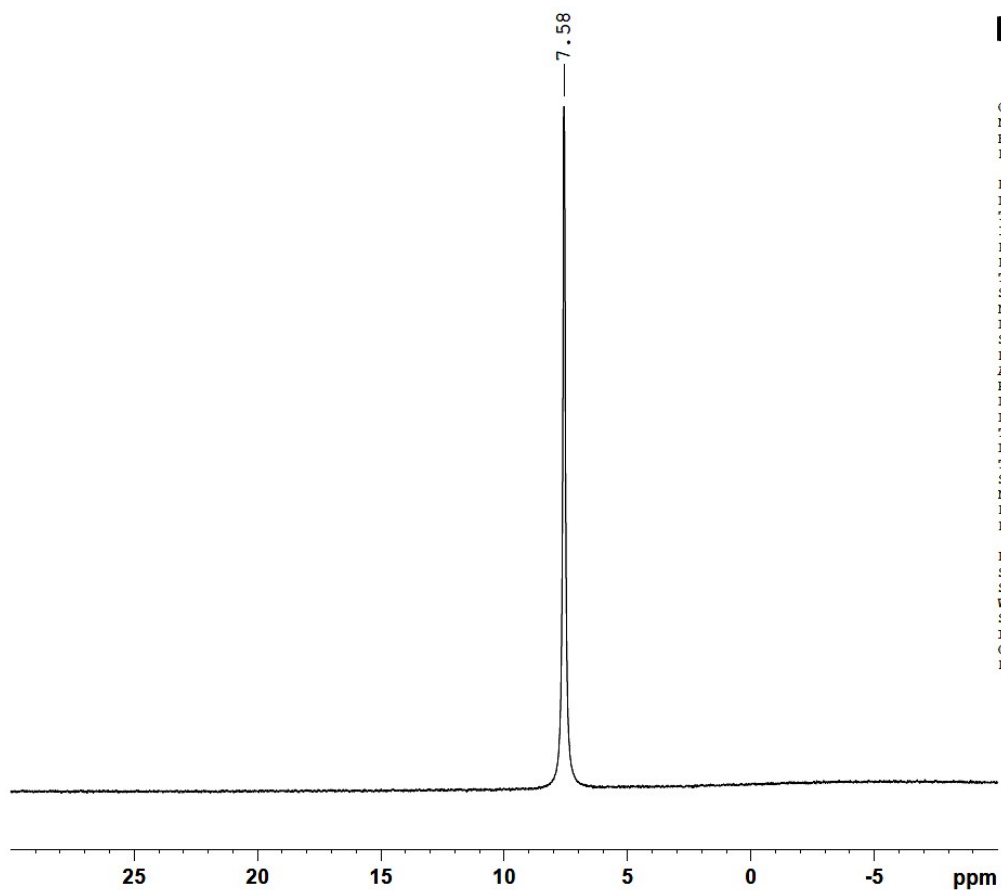
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PROCNO   1

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PULPROG  zgpg30
TD       65536
SOLVENT  CDCl3
NS       16
DS       0
SWH      64102.563 Hz
FIDRES   0.978127 Hz
AQ       0.5111808 sec
RG       199.74
DW       7.800 usec
DE       6.50 usec
TE       297.8 K
D1       2.00000000 sec
D11      0.03000000 sec
TD0      1
SF01     161.9998772 MHz
NUC1     31P
P1       30.00 usec
PLW1     31.04199982 W
SFO2     400.2116008 MHz
NUC2     1H
CPDPRG[2] waltz16
PCPD2    90.00 usec
PLW2     22.31200027 W
PLW12    1.85191298 W
PLW13    0.92817879 W

F2 - Processing parameters
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SF       162.0079776 MHz
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SSB      0
LB       1.00 Hz
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PC       1.40
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Fig. S3. ³¹P NMR of [P_{4,4,4,8}][BOB] (162.00 MHz, CDCl₃): 33.35 ppm. A small intensity resonance line at *c.a.* 37 ppm corresponds to a phosphorous-containing impurity.

11B P4448-BOB



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Current Data Parameters
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EXPNO     3
PROCNO    1

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PULPROG   zg
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SOLVENT   CDCl3
NS         64
DS         0
SWH       25510.203 Hz
FIDRES    0.389255 Hz
AQ         1.2845056 sec
RG         199.74
DW         19.600 usec
DE         6.50 usec
TE         297.7 K
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NUC1       11B
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F2 - Processing parameters
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WDW        EM
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Fig. S4. ^{11}B NMR of $[\text{P}_{4,4,4,8}][\text{BOB}]$ (128.40 MHz, CDCl_3): 7.58 ppm.

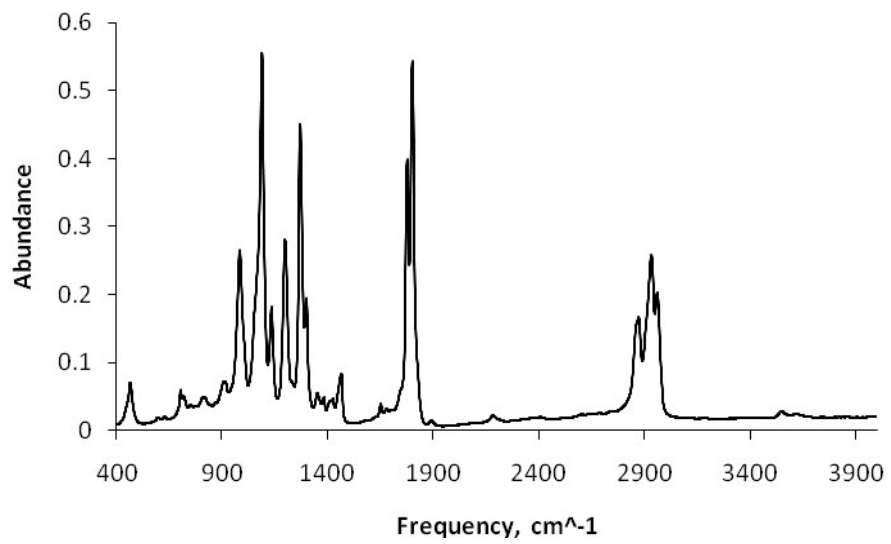


Fig. S5. Experimental FTIR spectra of [P_{4,4,4,8}][BOB].

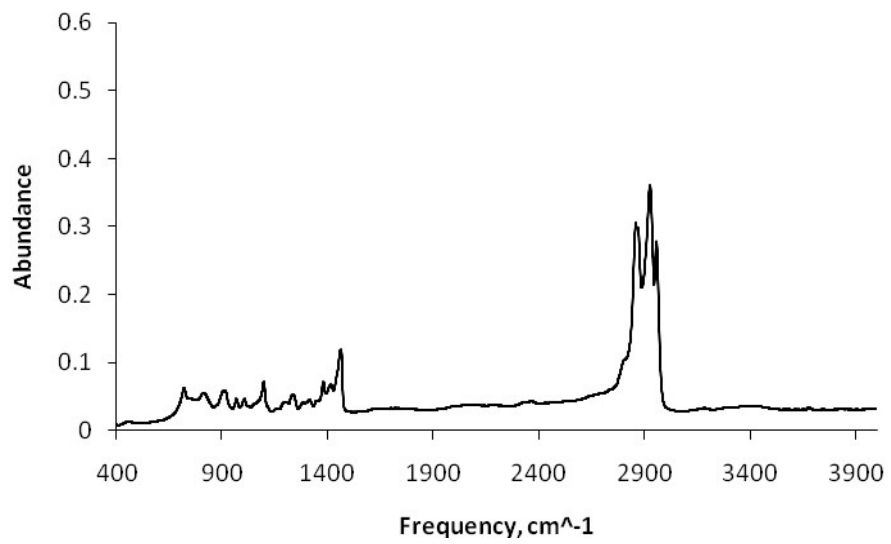


Fig. S6. Experimental FTIR spectra of [P_{4,4,4,8}][Cl].

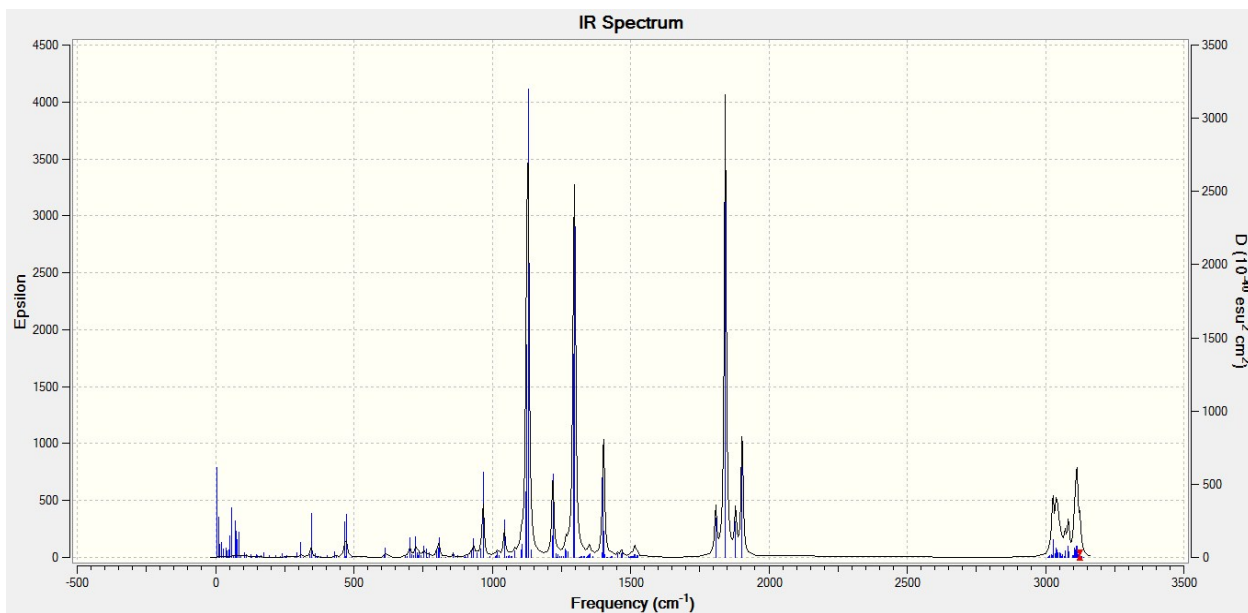


Fig. S7. Calculated IR spectra of $[P_{4,4,4,8}][BOB]$.

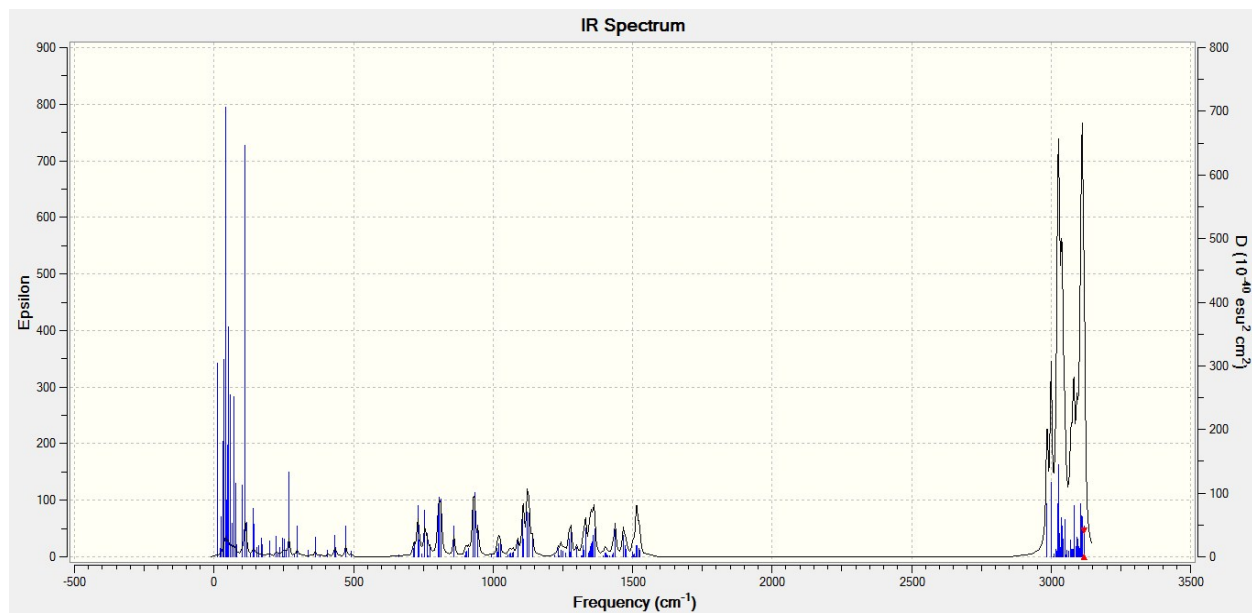


Fig. S8. Calculated IR spectra of [P_{4,4,4,8}][Cl].

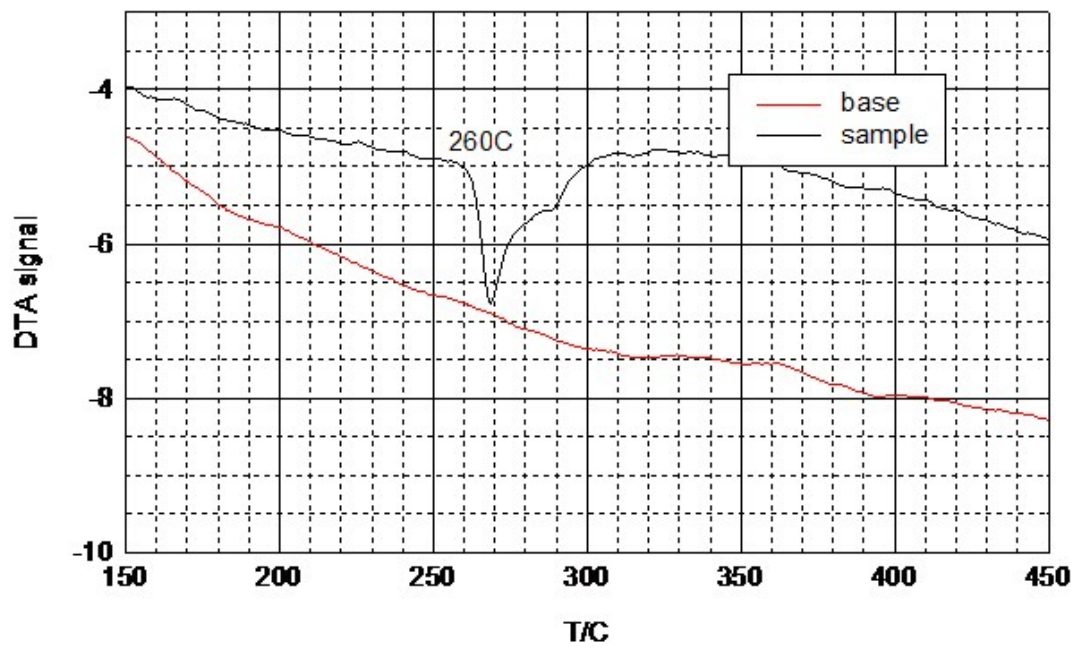


Fig. S9. The differential thermal analysis (DTA) curve of $[P_{4,4,4,8}][BOB]$. Black line corresponds to the DTA curve.