Electronic Supplementary Information

Investigations on a Series of Novel Ionic Liquids Containing the [*closo*-$B_{12}Cl_{12}$]$^{2-}$ Dianion

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1. Preparation of $Cs_2[B_{12}Cl_{12}]$[1,2]

(1) Preparation of $[NEt_3H]_2[B_{12}H_{12}]$

$Na[BH_4]$ (0.26 mol) in diglyme (40 mL) was charged into a 250 mL three-necked round bottom flask equipped with a 50 mL dropping funnel which should reach under the surface of the reaction mixture, with a pressure equalizing sidearm, a reflux condenser and a bubbler containing silicon oil. Iodine (0.081 mol) was dissolved in 35mL diglyme and added to the dropping funnel. The entire apparatus was flushed with dry argon. The suspension of $Na[BH_4]$ in diglyme was vigorously stirred and heated until the temperature rose to 100 °C. Then iodine was added drop-wise over a period of 30 min. During the addition, the amount of insoluble $Na[BH_4]$ decreased and at the end a yellow color of the reaction mixture was observed. The dropping funnel was disassembled and the reaction mixture was continuously stirred over night at 100 ^oC under an atmosphere of argon to complete the formation of $Na[B_3H_8]$. On the next day the temperature was increased and the reaction mixture was refluxed (temperature of the oil bath was 185 ^oC) over night (16 h) under an atmosphere of dry argon to completely disproportionate $Na[B_3H_8]$ to $Na_2[B_{12}H_{12}]$ (by-product: $Na[BH_4]$). Eventually the reaction mixture was cooled down to the room temperature and the diglyme was distilled off under dynamic vacuum at 140 °C. A large amount of white solid ($Na_2[B_{12}H_{12}]$, $Na[BH_4]$, NaI) remained. The white solid was dissolved in 60 mL of water, 28 mL of concentrated hydrochloric acid were added carefully to the water solution. The acidified clear solution was stored in a fridge (+6 ^oC) over night and colorless crystals (ca. 1.5 g) of boric acid were formed and removed by filtration. The filtrate was treated with 40 mL Et_3N (pH = 9-10) and readily a voluminous white solid precipitated. The cloudy solution was stirred over night (14 h) to complete the precipitation. The white solid (ca. 8 g) was collected by filtration. The solid obtained was suspended in water, heated and then

filtrated while still hot (50 and 60 °C) to remove the more soluble boric acid. The product was dried in vacuum to give $[NEt_3H]_2[B_{12}H_{12}]$ as a white solid (yield: 51%).

(2) Preparation of $Cs_2[B_{12}H_{12}]$

3 equivalents of CsOH was added to a solution of solid $[NEt_3H]_2[B_{12}H_{12}]$ dissolved in water in a polypropylene beaker and it precipitates immediately to give $Cs_2[B_{12}H_{12}]$ after the CsOH addition. (Typically about 100 mL water was used for 10 g $[NEt_3H]_2[B_{12}H_{12}]$).

(3) Preparation of $Cs_2[B_{12}Cl_{12}]$

$Cs_2[B_{12}H_{12}]$ used in this reaction was recrystallized from hot water and dried under vacuum at 80 ^oC for 8 h before use. MeCN was dried with CaH_2, distilled under Ar and stored over molecular sieves in an Ar-filled glovebox. SO_2Cl_2 used in this reaction was fractionally distilled before use. To a suspension of $Cs_2[B_{12}H_{12}]$ (0.25 mmol) in acetonitrile (3 mL) in a Schlenk flask was slowly added SO_2Cl_2 (37 mmol) under Ar. The mixture was heated to reflux. After 24 h, all volatiles were removed under vacuum to give a white solid $Cs_2[B_{12}Cl_{12}]$.

1 V. Geis, K. Guttsche, C. Knapp, H. Scherer and R. Uzun, *Dalton Trans*., 2009, 2687–2694.

2 W. X. Gu and O. V. Ozerov, *Inorg. Chem*., 2011, **50**, 2726–272.

Table S.1 Elemental analysis and electrospray ionization mass spectrometry

Abbreviation	Analysis found (calc.)(%)				ESI-MS	
	C	H	N	Cl	Cation	Anion
$[Hmim]_2[B_{12}Cl_{12}]$	(13.32) 13.91	(1.96) 2.11	(7.77) 7.64	(58.97) 59.11	—	277.37
$[C_2mim]_2[B_{12}Cl_{12}]$	(18.54) 18.92	(2.85) 2.90	(7.21) 7.15	(54.72) 54.95	111.09	277.37
$[C_3mim]_2[B_{12}Cl_{12}]$	(20.86) 21.32	(3.23) 3.39	(6.95) 6.73	(52.89) 52.15	125.10	277.37
$[C_4mim]_2[B_{12}Cl_{12}]$	(23.05) 23.52	(3.63) 3.43	(6.72) 6.56	(51.03) 50.82	139.12	277.37
$[C_8mim]_2[B_{12}Cl_{12}]$	(30.48) 31.39	(3.63) 3.97	(6.72) 5.99	(44.98) 45.29	195.18	277.37
$[C_{10}mim]_2[B_{12}Cl_{12}]$	(33.57) 34.02	(5.42) 5.57	(5.59) 5.59	(42.46) 42.36	223.21	277.37
$[Bnmim]_2[B_{12}Cl_{12}]$	(31.48) 30.95	(3.30) 2.97	(6.12) 6.25	(46.46) 46.68	173.10	277.37
$[C_4C_1mim]_2[B_{12}Cl_{12}]$	(25.09) 25.03	(3.98) 3.99	(6.50) 6.46	(49.37) 49.25	153.14	277.37
$[HEmim]_2[B_{12}Cl_{12}]$	(17.80) 18.25	(2.74) 2.89	(6.92) 6.87	(52.55) 52.35	127.08	277.37
$[N_{2\,2\,2\,4}]_2[B_{12}Cl_{12}]$	(27.55) 27.36	(5.55) 5.65	(3.21) 3.04	(48.80) 49.05	158.18	277.37
$[N_{2\,2\,2\,6}]_2[B_{12}Cl_{12}]$	(31.07) 30.69	(6.08) 6.04	(3.02) 2.71	(45.85) 46.04	186.22	277.37
$[N_{1\,1\,1\,16}]_2[B_{12}Cl_{12}]^a$	(40.60) 41.33	(7.53) 7.46	(2.49) 2.83	(37.84) 37.79	284.32	277.37
$[N_{1\,1\,1\,16}]_2[B_{12}Cl_{12}]^b$	(40.60) 41.01	(7.53) 7.67	(2.49) 2.08	(37.84) 37.11	284.32	277.37
$[N_{2\,2\,2\,HE}]_2[B_{12}Cl_{12}]$	(22.67) 22.64	(4.76) 4.75	(3.30) 3.23	(50.19) 49.99	146.15	277.37
$[PyC_4]2[B_{12}Cl_{12}]$	(26.12) 26.48	(3.41) 3.40	(3.39) 3.40	(51.40) 51.26	136.11	277.37
$[P_{P\,P\,P\,2}]_2[B_{12}Cl_{12}]$	(42.22) 42.47	(3.54) 3.64	—	(37.39) 37.12	291.12	277.37

$[P_{P\,P\,P\,HE}]_2[B_{12}Cl_{12}]$	**(41.07) 42.01**	**(3.45) 3.37**	—	**(36.37) 36.25**	**307.12**	**277.37**

[a] The sample without any further treatment. [b] The sample prepared and further treated with water at the temperature of 60 °C.

Table S.2 ^{1}HNMR chemical shifts (ðppm, *J*Hz) of the reported salts in DMSO-d_6

Imidazolium $[B_{12}Cl_{12}]$	**C(2)-*H***	**C(4)-*H***	**C(5)-*H***	**N-C*H*$_2$-**	**N-C*H*$_3$**	**NCH$_2$-C*H*$_2$**	**N(CH$_2$)$_2$-(C*H*$_2$)$_{n-3}$-**	**N(CH$_2$)$_{n-1}$-C*H*$_3$**
$[Hmim]_2[B_{12}Cl_{12}]$	8.94(s)	7.65(m)	7.60(m)	—	3.85(s)	—	—	—
$[C_2mim]_2[B_{12}Cl_{12}]$	9.25(s)	7.81(m)	7.72(m)	4.21(q) *J*=7.6Hz	3.86(s)	—	—	1.42(t) *J*=6.8Hz
$[C_3mim]_2[B_{12}Cl_{12}]$	9.09(s)	7.76(m)	7.70(m)	4.12(q) *J*=7.1Hz	3.85(s)	1,79(m)	—	0.85(t) *J*=7.4Hz
$[C_4mim]_2[B_{12}Cl_{12}]$	9.17(s)	7.78(m)	7.71(m)	4.17(t) *J*=6.8Hz	3.85(s)	1,77(m)	1.26(m)	0.90(t) *J*=7.6Hz
$[C_8mim]_2[B_{12}Cl_{12}]$	9.14(s)	7.74(m)	7.67(m)	4.12(t) *J*=6.8Hz	3.82(s)	1,75(m)	1.22-1.20 (m)	0.81(t) *J*=6.9Hz
$[C_{10}mim]_2[B_{12}Cl_{12}]$	9.10(s)	7.77(m)	7.70(m)	4.14(t) J=7.6Hz	3.84(s)	1,76(m)	1.27-1.24 (m)	0.86(t) *J*=6.9Hz
$[Bnmim]_2[B_{12}Cl_{12}]$	9.27(s)	7.81(m)	7.80(m)	5.43(s)	3.86(s)	—	7.42-7.43 (m)	—
$[C_4C_1mim]_2[B_{12}Cl_{12}]$	—	7.65(m)	7.62(m)	4.11(t) *J*=7.6Hz	3.75(s)	1.69(m)	1.28(m)	0.91(t) *J*=7.6Hz
$[HEmim]_2[B_{12}Cl_{12}]$	9.09(s)	7.73(m)	7.70(m)	4.21(t) *J*=5.5Hz	3.87(s)	3.71(m)	—	(—OH) 5.18(s)

Ammonium $[B_{12}Cl_{12}]$	**N-C*H*$_2$**	**N-CH$_2$-C*H*$_2$**	**N-(CH$_2$)$_2$-(C*H*$_2$)$_{n-3}$-**	**N-(CH$_2$)$_{n-1}$-C*H*$_3$**	**N-C*H*$_2$^{3}**	**N-C*H*$_3$^{3}**	**—O*H***
$[N_{2\,2\,2\,4}]_2[B_{12}Cl_{12}]$	3.11 (t) *J*=8.2Hz	1.56(m)	1.33(m)	0.94(t) *J*=7.6Hz	3.23(q) *J*=7.6Hz	1.18(m)	–
$[N_{2\,2\,2\,6}]_2[B_{12}Cl_{12}]$	3.12(t) *J*=8.2Hz	1.57(m)	1.31-1.30 (m)	0.88(t) *J*=6.2Hz	3.24(q) *J*=7.6Hz	1.19(m)	–
$[N_{1\,1\,1\,16}]_2[B_{12}Cl_{12}]$	3.25(t) *J*=8.3Hz	1.66(m)	1.29-1.24 (m)	0.86(t) *J*=6.2Hz	–	3.03(s)	–
$[N_{2\,2\,2\,HE}]_2[B_{12}Cl_{12}]$	3.30(m)	—	—	3.34(s)	3.30(m)	1.18(t) *J*=7.6Hz	5.26(s)

Phosphonium $[B_{12}Cl_{12}]$	**P-C*H*$_2$**	**P-CH$_2$-C*H*$_2$-**	**P-(C$_6$*H*$_5$)-o.m**	**P-(C$_6$*H*$_5$)-p**	**—O*H***
$[P_{P\,P\,P\,2}]_2[B_{12}Cl_{12}]$	3.62(m) *J*=7.6Hz	1.23(m) *J*=7.6Hz	7.79-7.78 (m)	7.80(m)	—
$[P_{P\,P\,P\,HE}]_2[B_{12}Cl_{12}]$	3.78(m)	3.78(m)	7.78-7.75 (m)	7.80(m)	5.44(s)

Pyridinium $[B_{12}Cl_{12}]$	**C(2)-*H***	**C(3)-*H***	**C(4)-*H***	**N-C*H*$_2$**	**NCH$_2$-C*H*$_2$**	**N(CH$_2$)$_2$-(C*H*$_2$)$_{n-3}$-**	**N-(CH$_2$)$_{n-1}$-C*H*$_3$**
$[PyC_4]_2[B_{12}Cl_{12}]$	9.10(d) *J*=5.5Hz	8.17(t) *J*=6.8Hz	8.61(t) *J*=7.6Hz	4.61(t) *J*=7.6Hz	1.90(q)	1.29(m)	0.92(t) *J*=7.6Hz

Table S.3 Melting points of the mixture including $[N_{1\ 1\ 1\ 16}]_2[B_{12}Cl_{12}]$ (1) and $[C_4mim]Cl$ (2) are detected, as a function of various quality ratios.

Quality Ratio (m1:m2)	**Melting Point (T_m/^{o}C)**
1:0	104
3:1	93
1:1	69
1:3	31
0:1	41

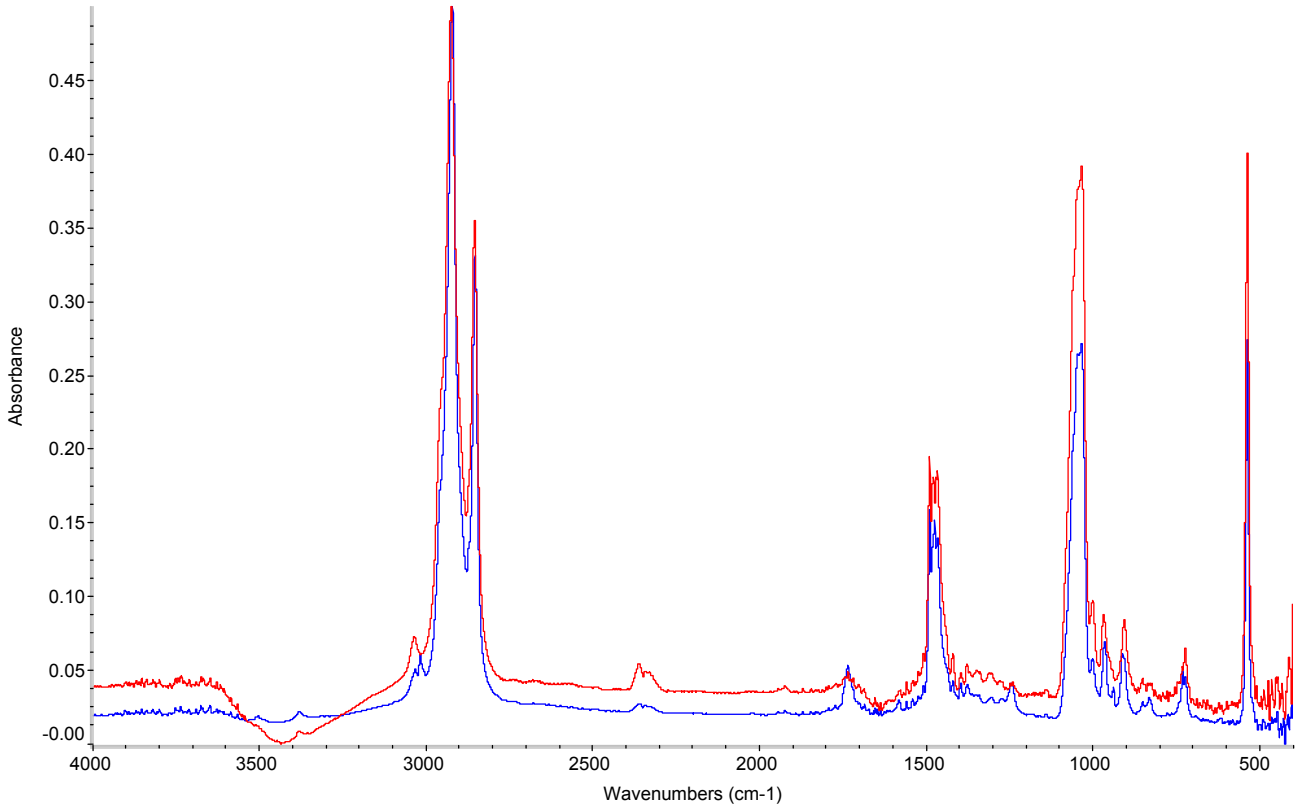
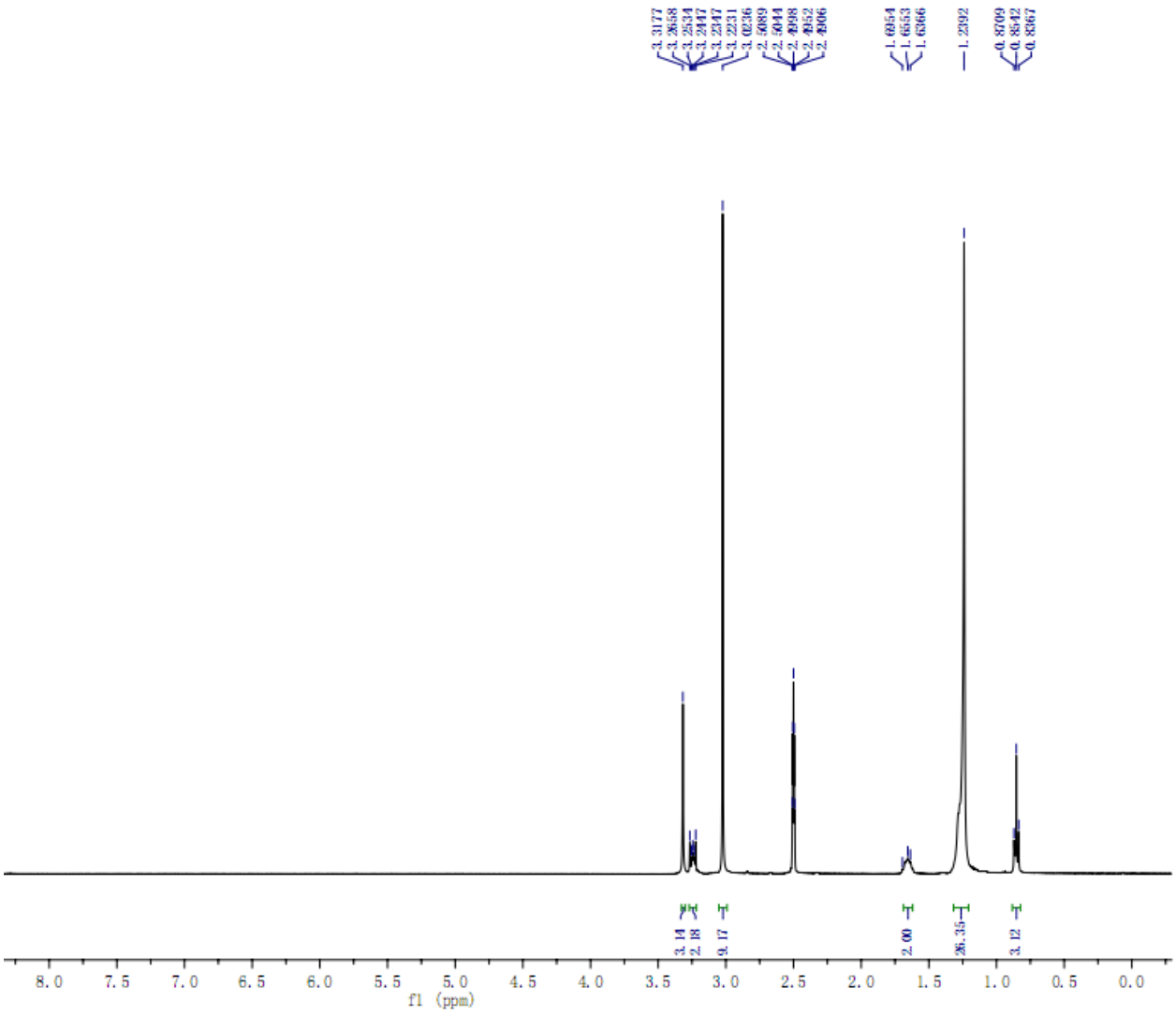
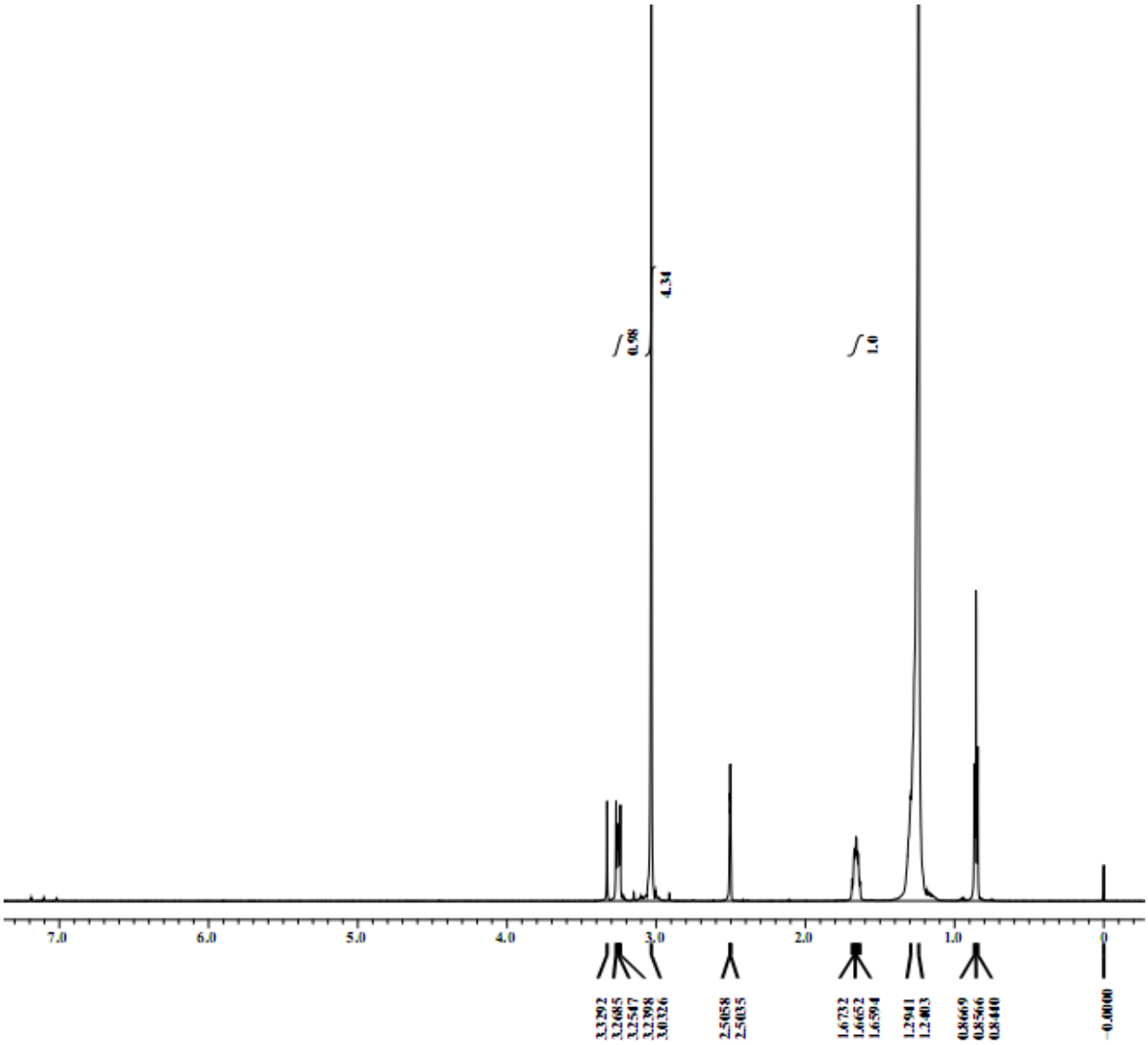


Fig. S.1 FT-IR spectrum of $[N_{1\,1\,1\,16}]_2[B_{12}Cl_{12}]$ where the red spectrum represents sample treated with water at the temperature of 60 ^{o}C while the blue spectrum represents the one without any treatment.


3.3177
3.2658
3.2534
3.2447
3.2347
3.2231
3.0236
2.5089
2.5044
2.4998
2.4952
2.4906
1.6654
1.6553
1.6366
1.2392
0.8709
0.8542
0.8367
3.14
2.18
9.17
2.00
26.35
3.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(a)



(b)

Fig. S.2 ^{1}H NMR spectrum of $[N_{1\,1\,1\,16}]_2[B_{12}Cl_{12}]$ in DMSO-d_6 where the former spectrum (a) represents sample treated with water at the temperature of 60 ^{o}C while the latter spectrum (b) represents the one without any treatment.

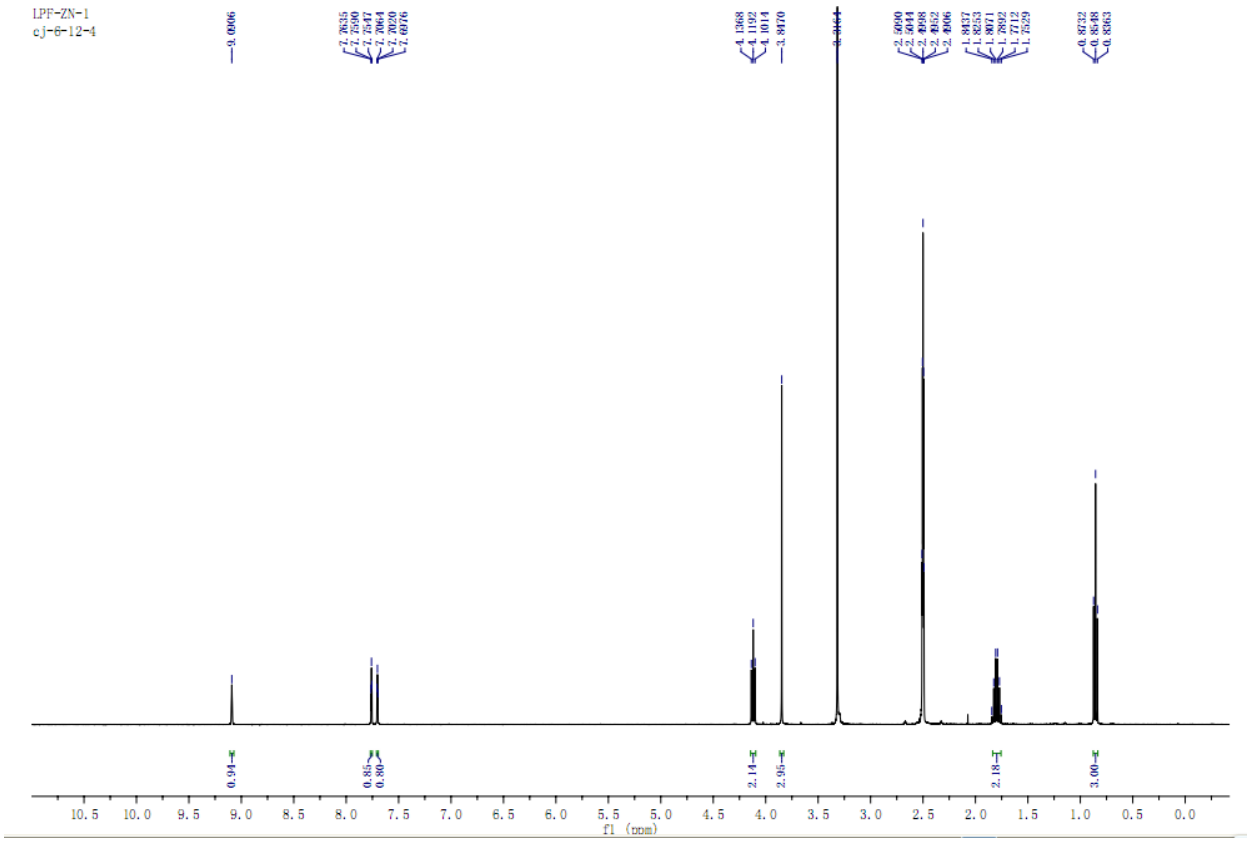


Fig. S.3 ^{1}H NMR spectrum of $[C_3mim]_2[B_{12}Cl_{12}]$ in DMSO-d_6.

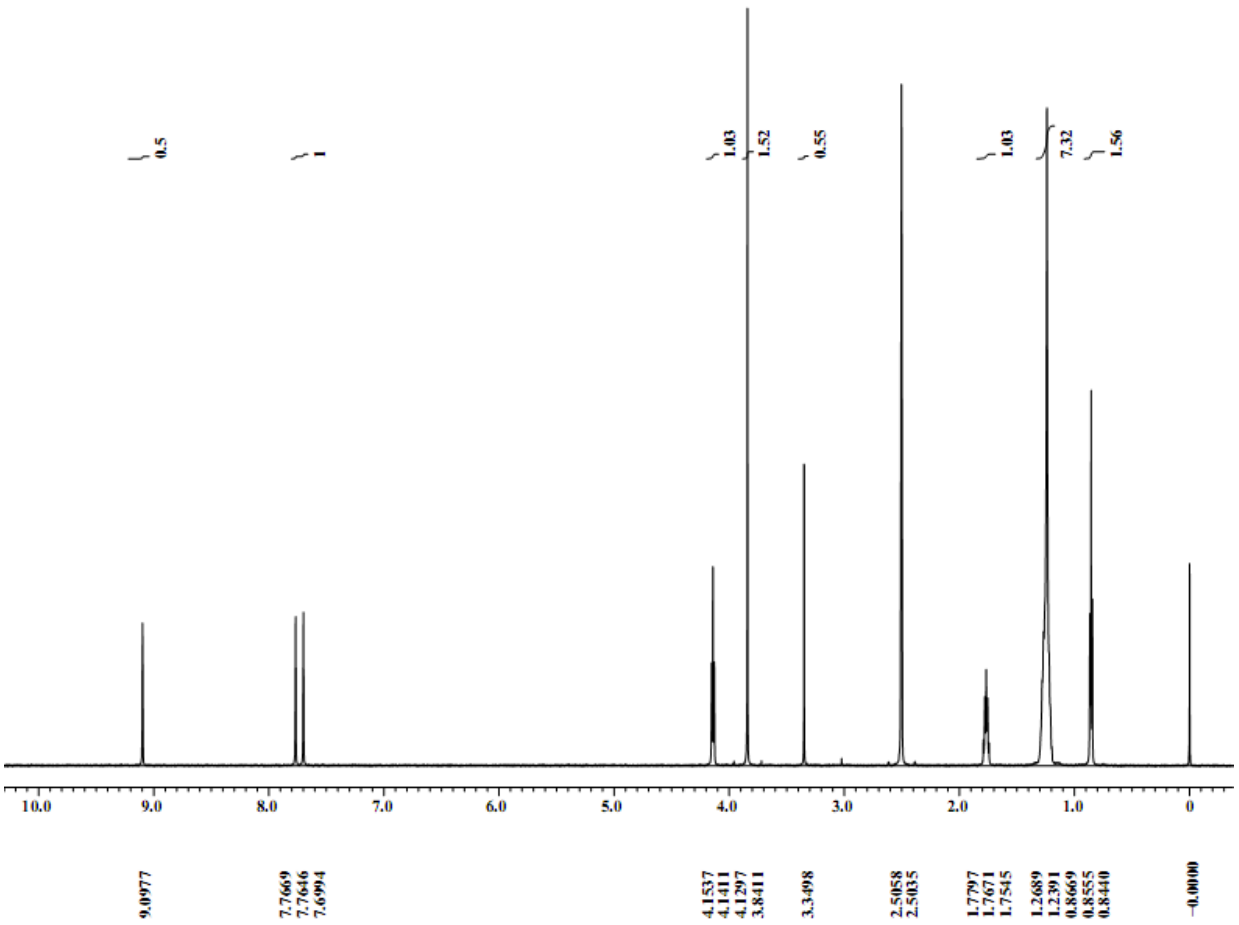


Fig. S.4 ^{1}H NMR spectrum of $[C_{10}mim]_2[B_{12}Cl_{12}]$ in DMSO-d_6.

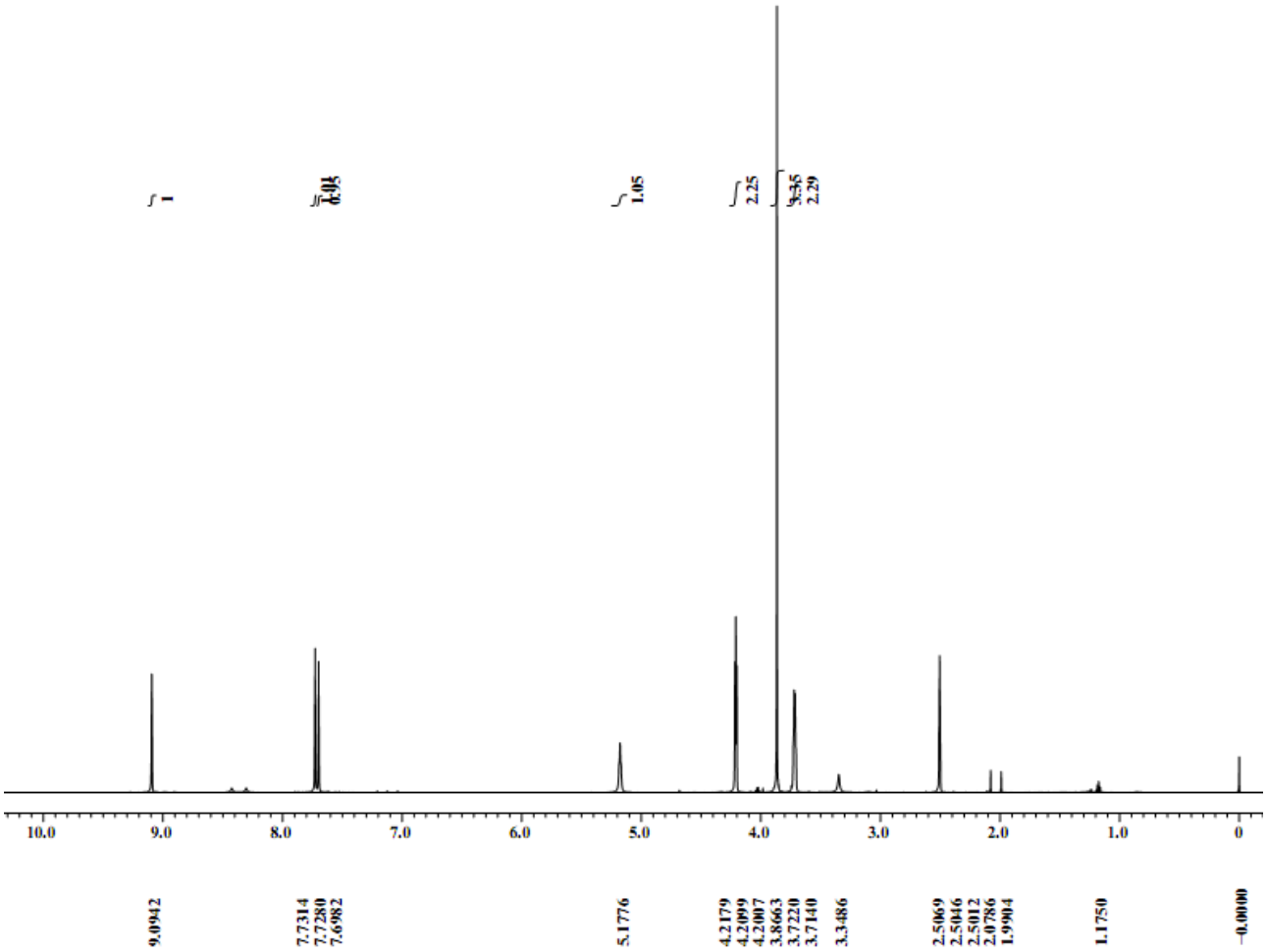


Fig. S.5 ^{1}H NMR spectrum of $[HEmim]_2[B_{12}Cl_{12}]$ in DMSO-d_6.

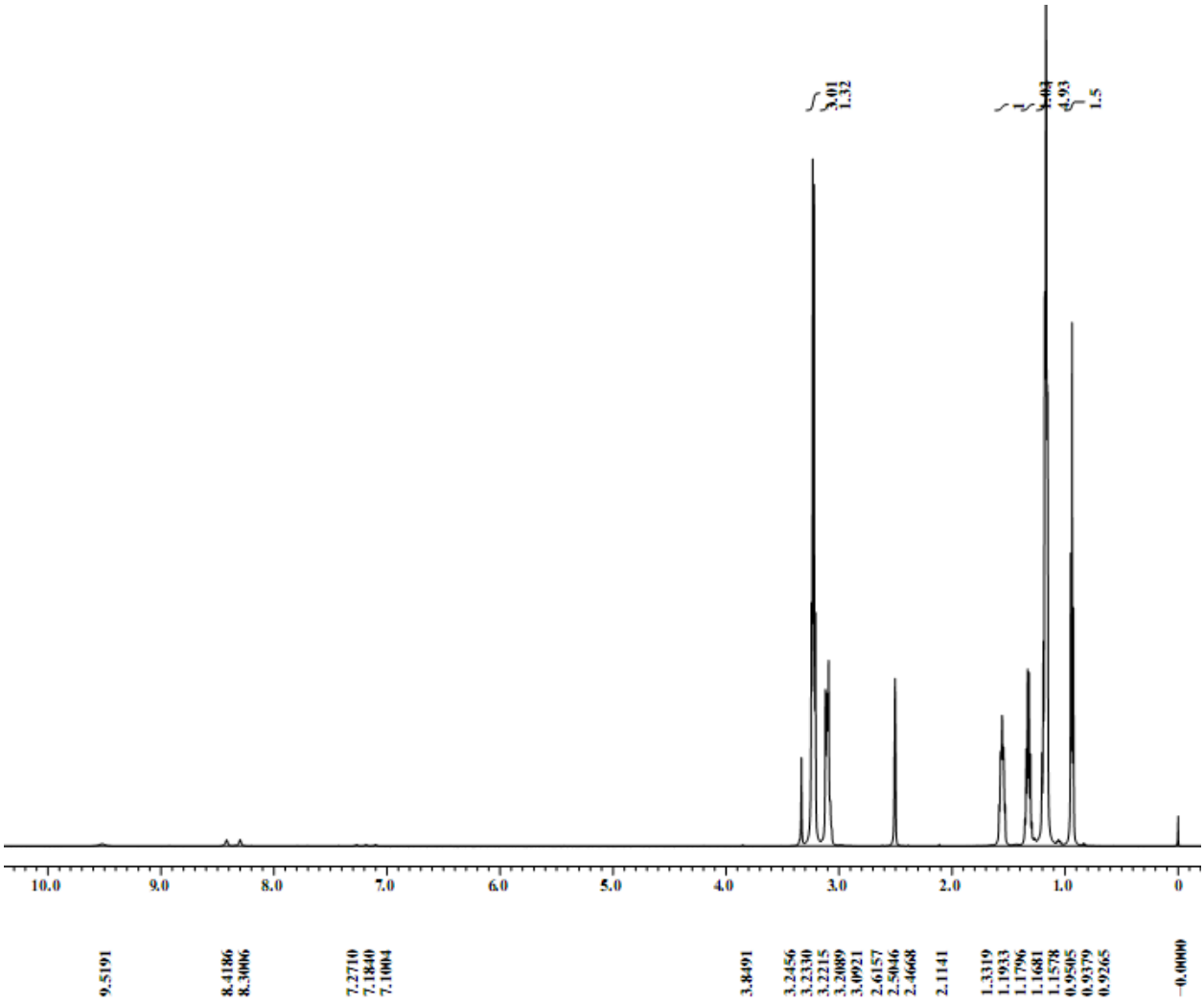


Fig. S.6 ^{1}H NMR spectrum of $[N_{2\,2\,2\,4}]_2[B_{12}Cl_{12}]$ in DMSO-d_6.

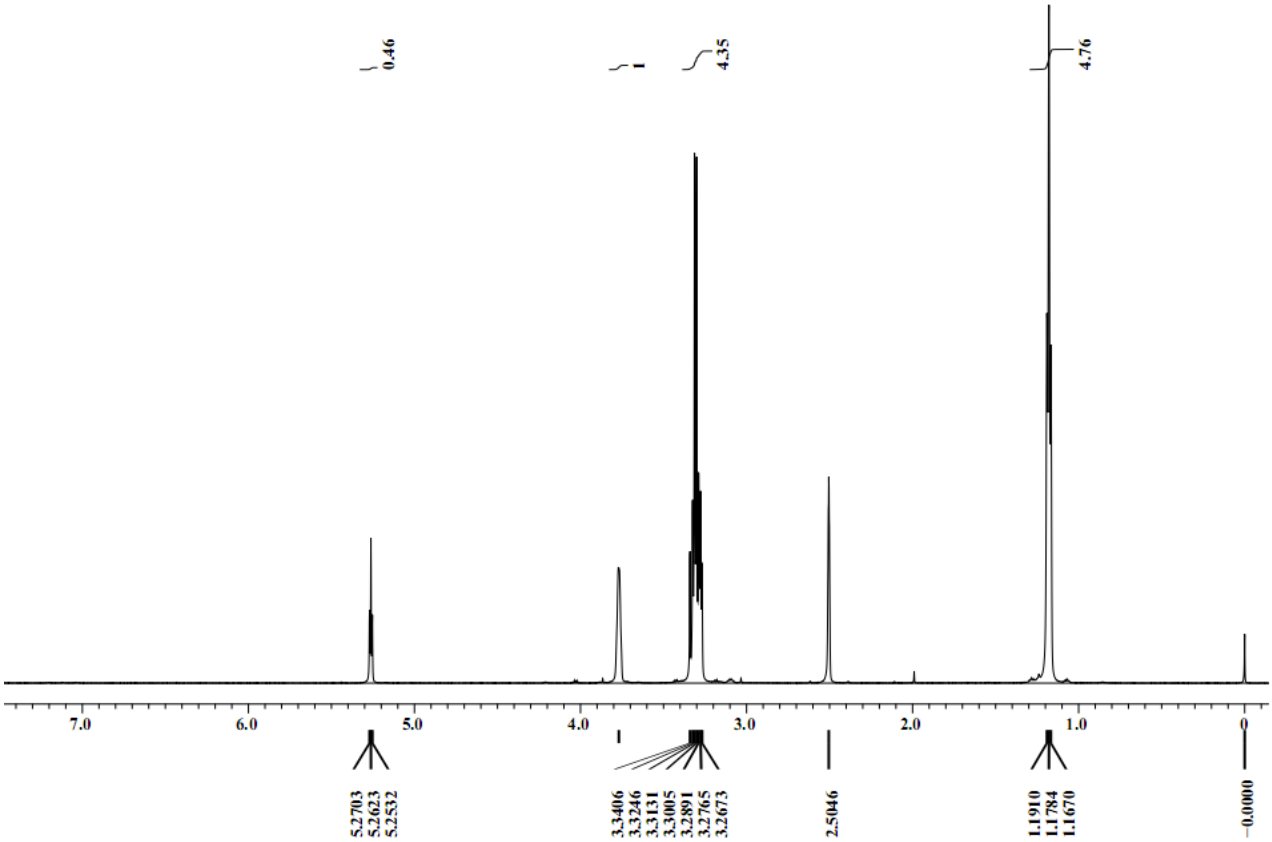


Fig. S.7 ^{1}H NMR spectrum of $[N_{2\,2\,2\,HE}]_2[B_{12}Cl_{12}]$ in DMSO-d_6.

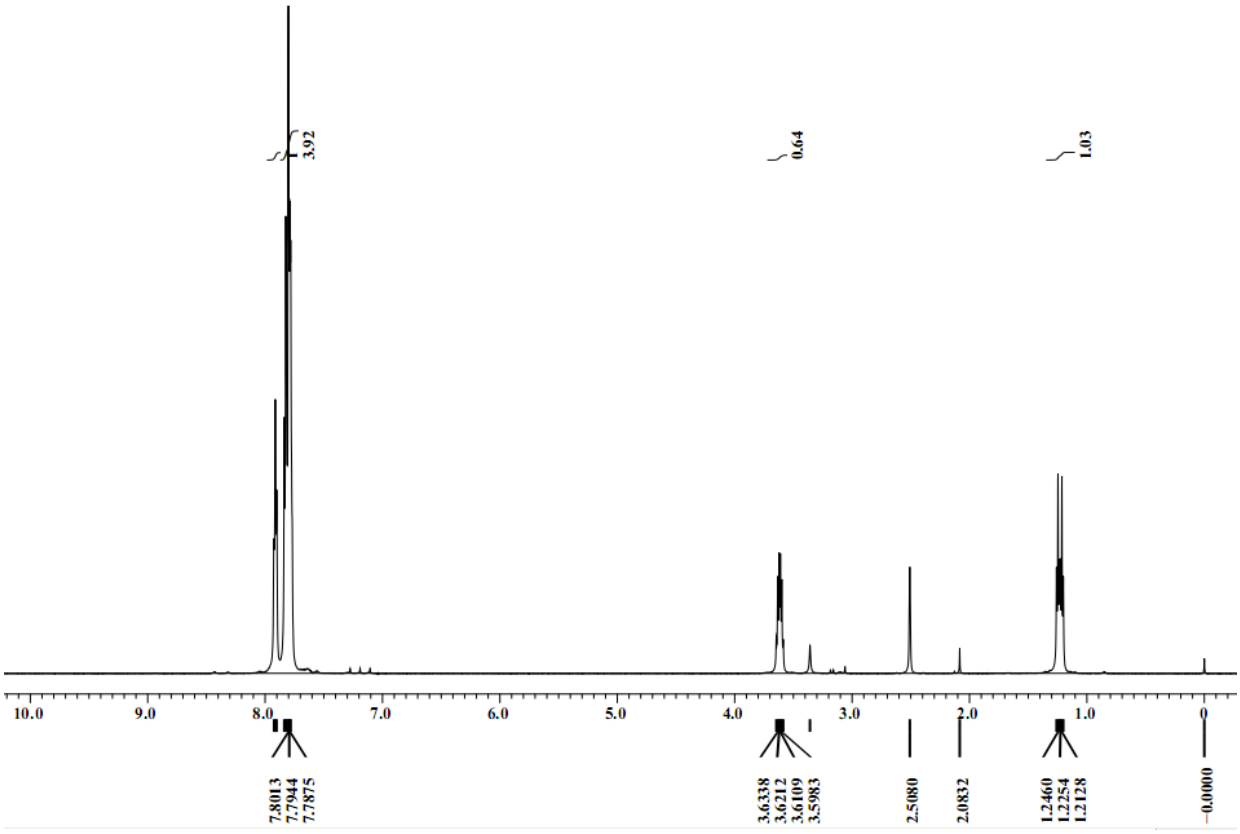


Fig. S.8 ^{1}H NMR spectrum of $[P_{P\,P\,P\,2}]_2[B_{12}Cl_{12}]$ in DMSO-d_6.

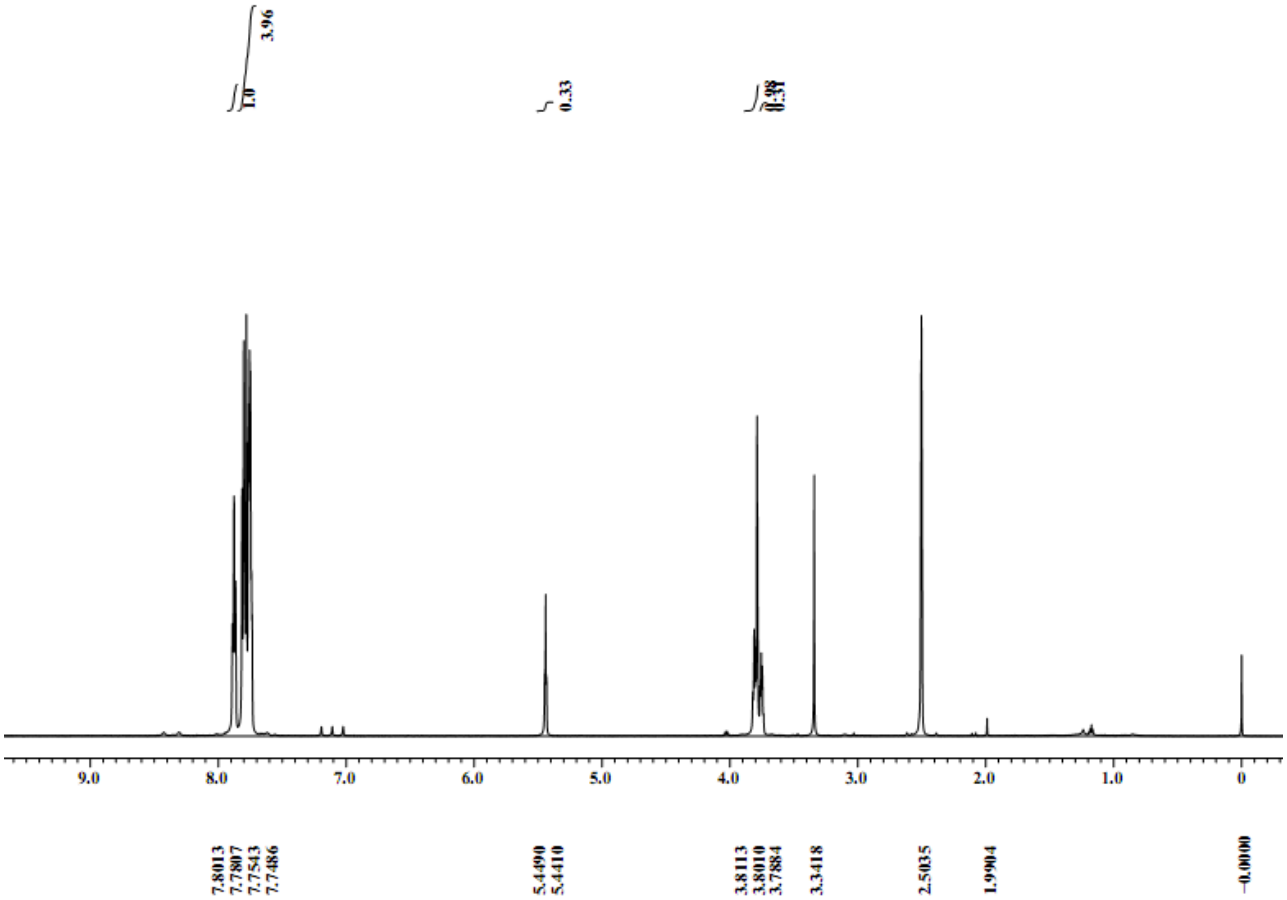


Fig. S.9 ^{1}H NMR spectrum of $[P_{P\ P\ P\ HE}]_2[B_{12}Cl_{12}]$ in DMSO-d_6.

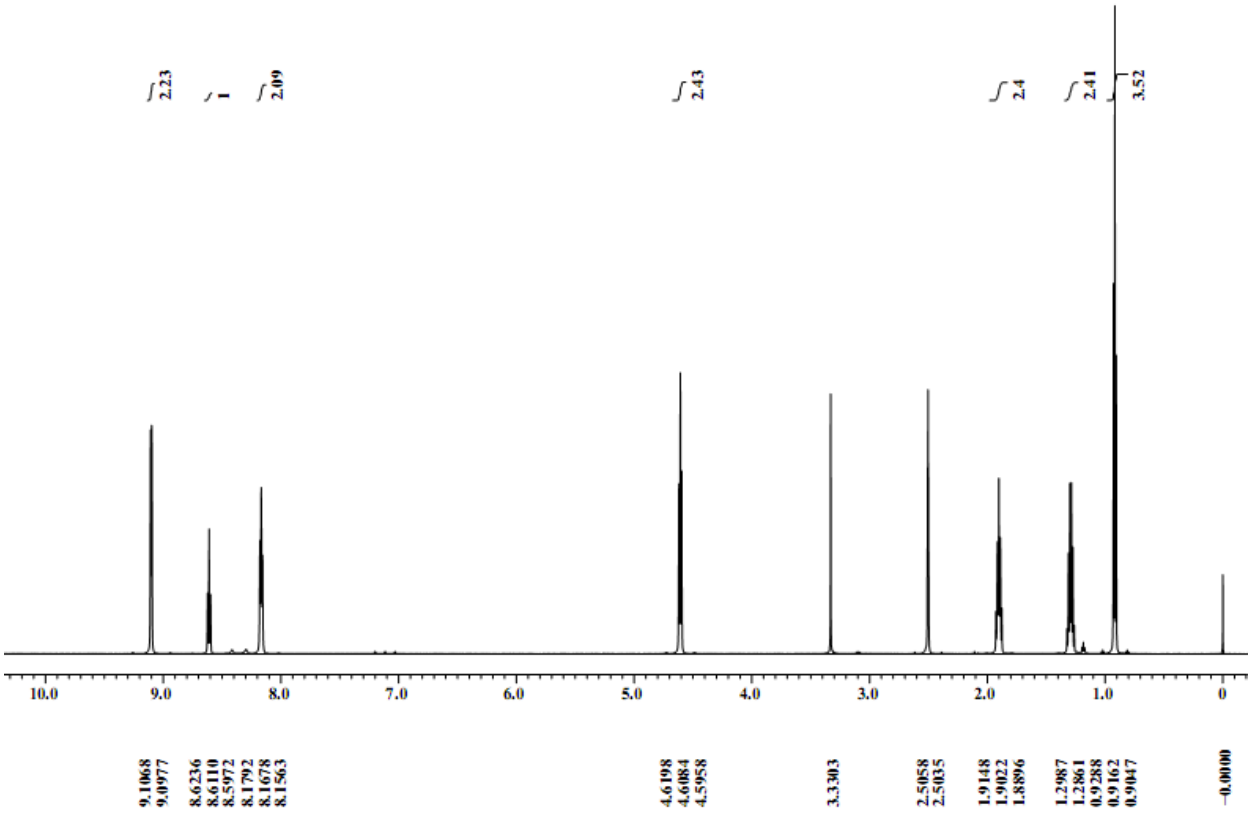


Fig. S.10 ^{1}H NMR spectrum of $[PyC_4]_2[B_{12}Cl_{12}]$ in DMSO-d_6.

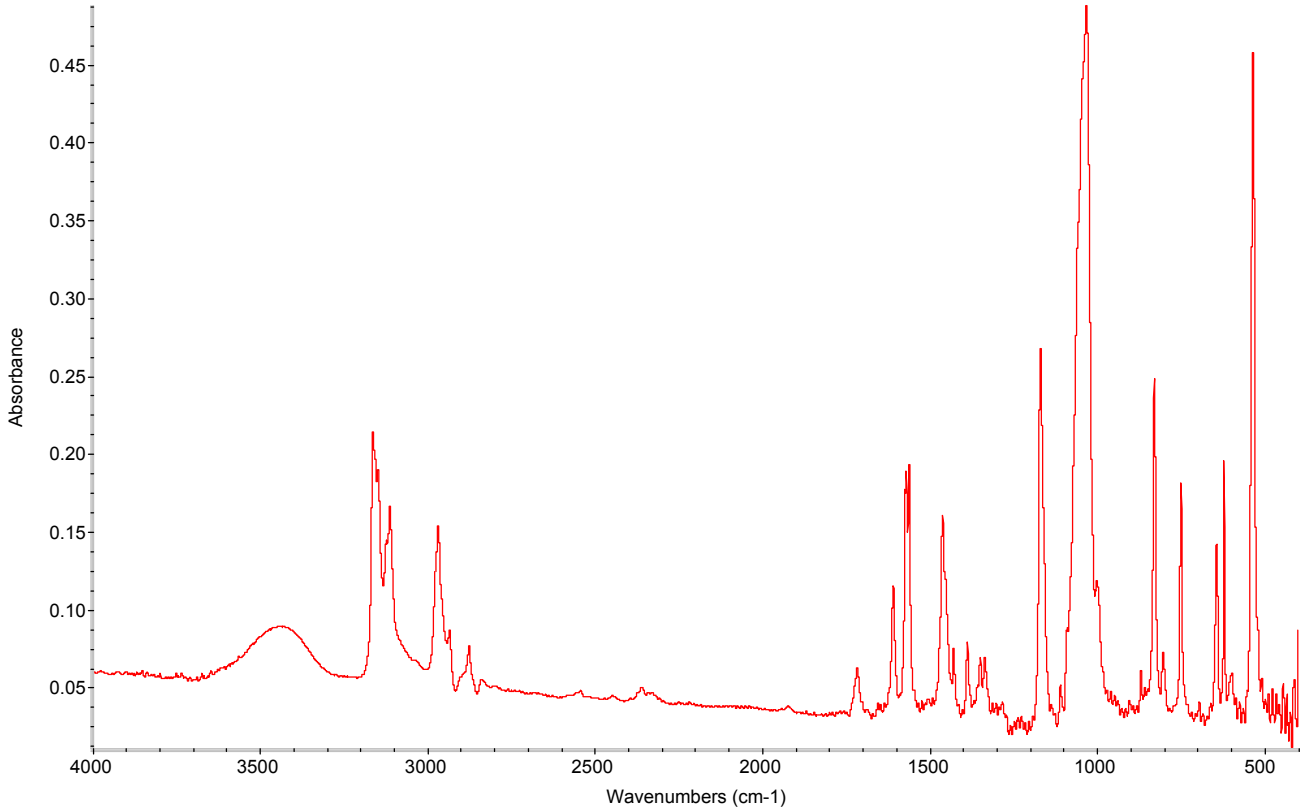


Fig. S.11 FT-IR spectrum of $[C_3mim]_2[B_{12}Cl_{12}]$.

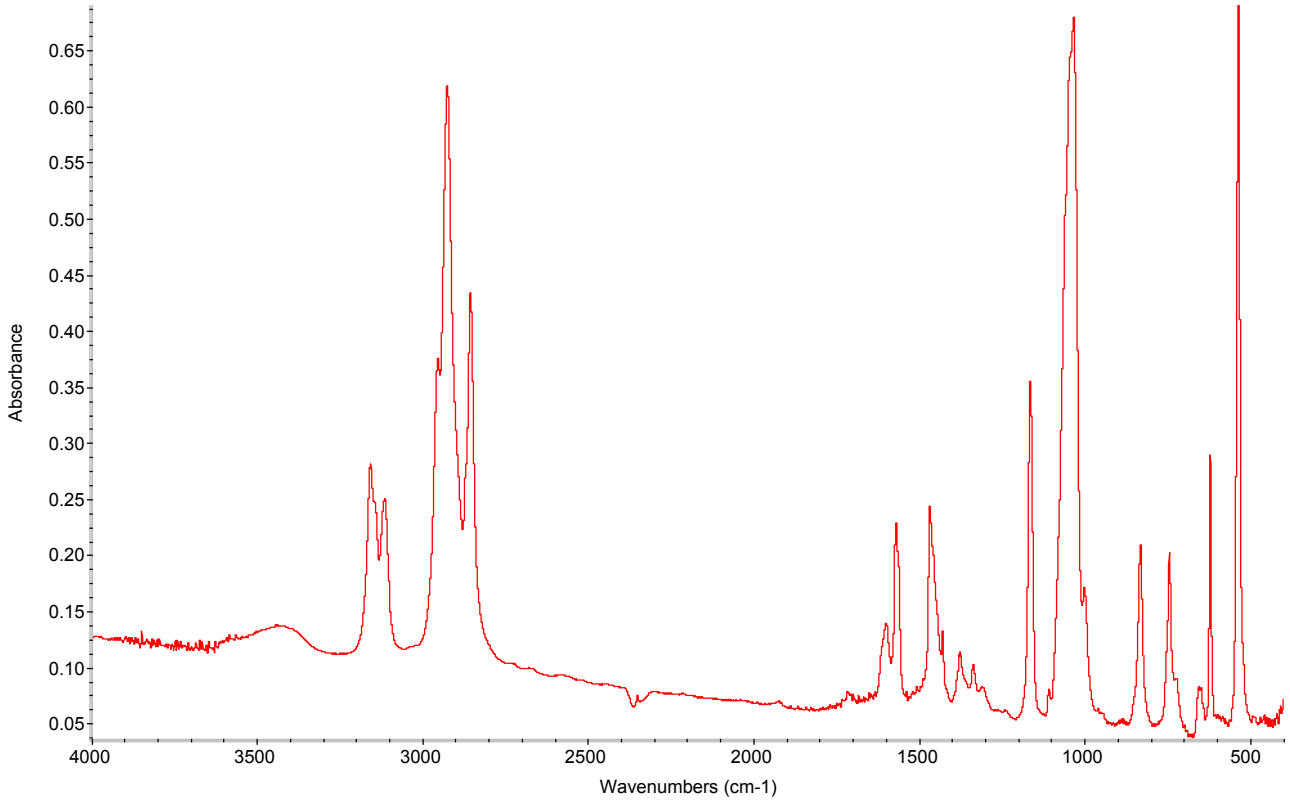


Fig. S.12 FT-IR spectrum of $[C_{10}mim]_2[B_{12}Cl_{12}]$.

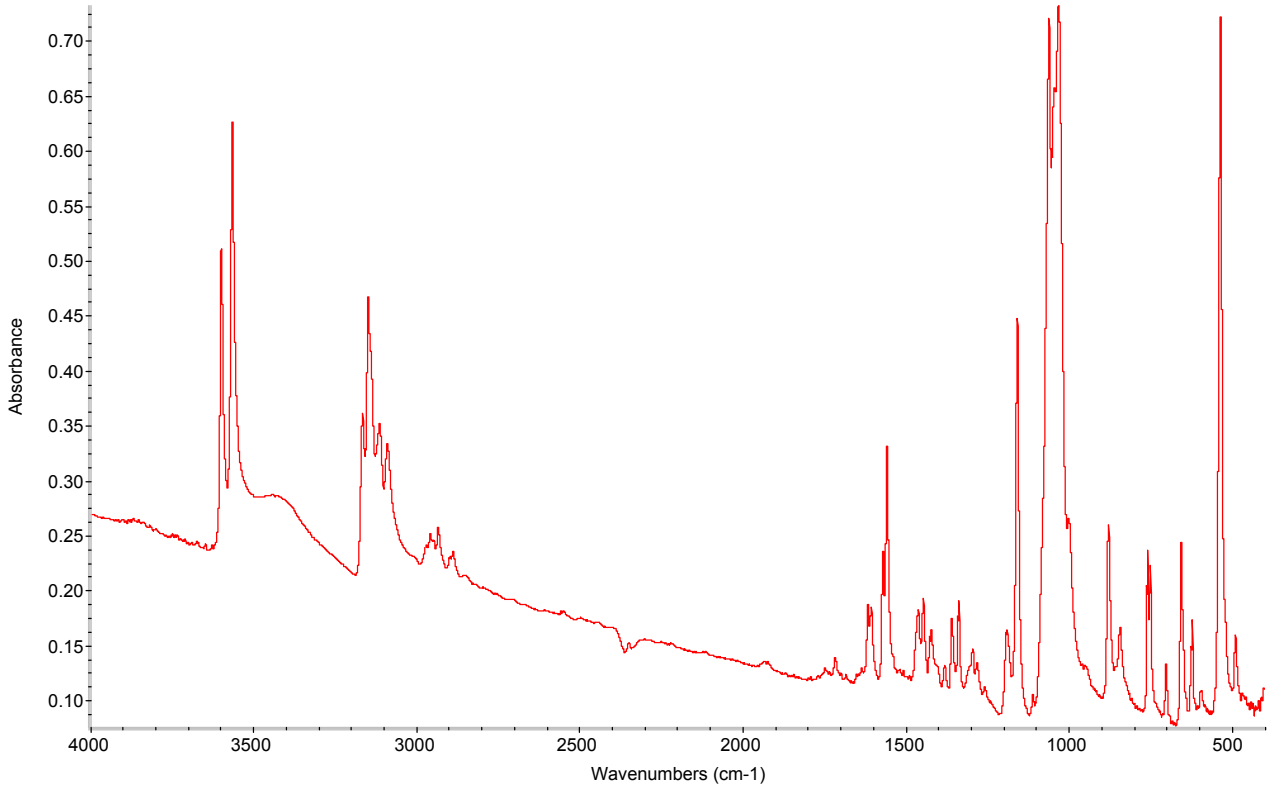


Fig. S.13 FT-IR spectrum of $[HEmim]_2[B_{12}Cl_{12}]$.

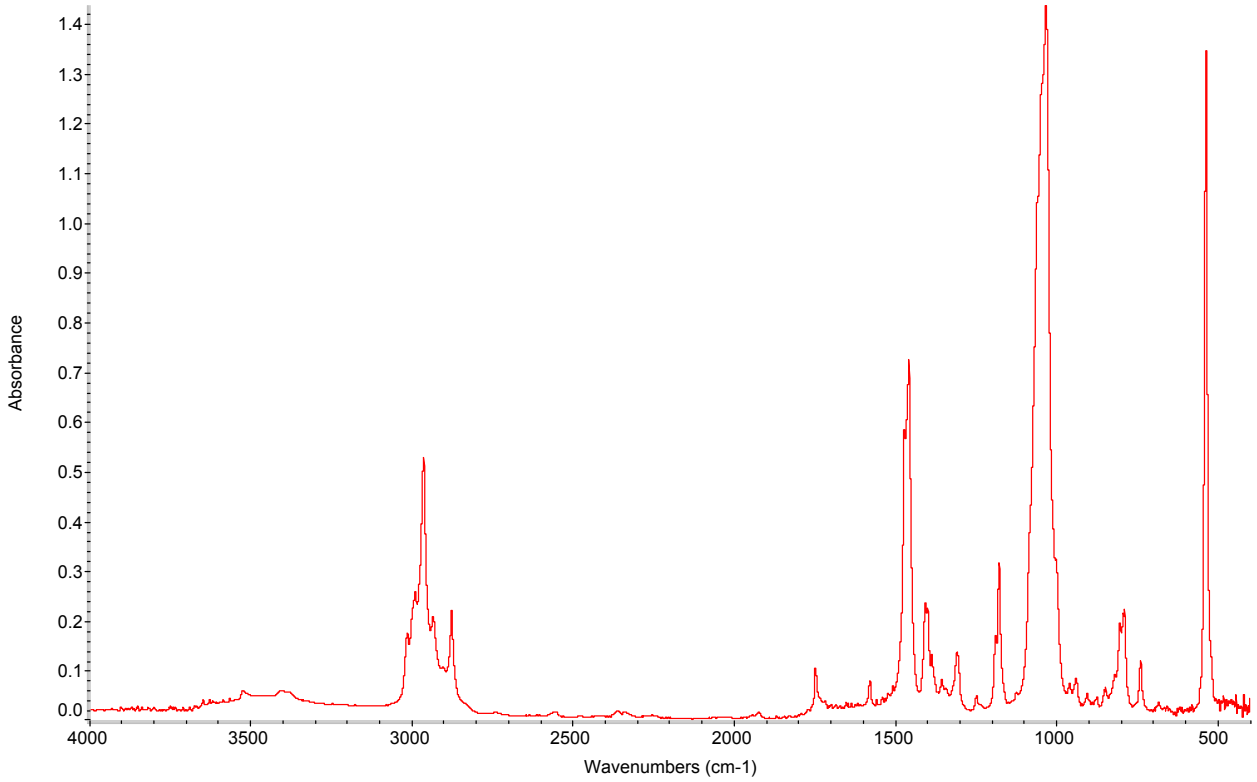


Fig. S.14 FT-IR spectrum of $[N_{2\,2\,2\,4}]_2[B_{12}Cl_{12}]$.

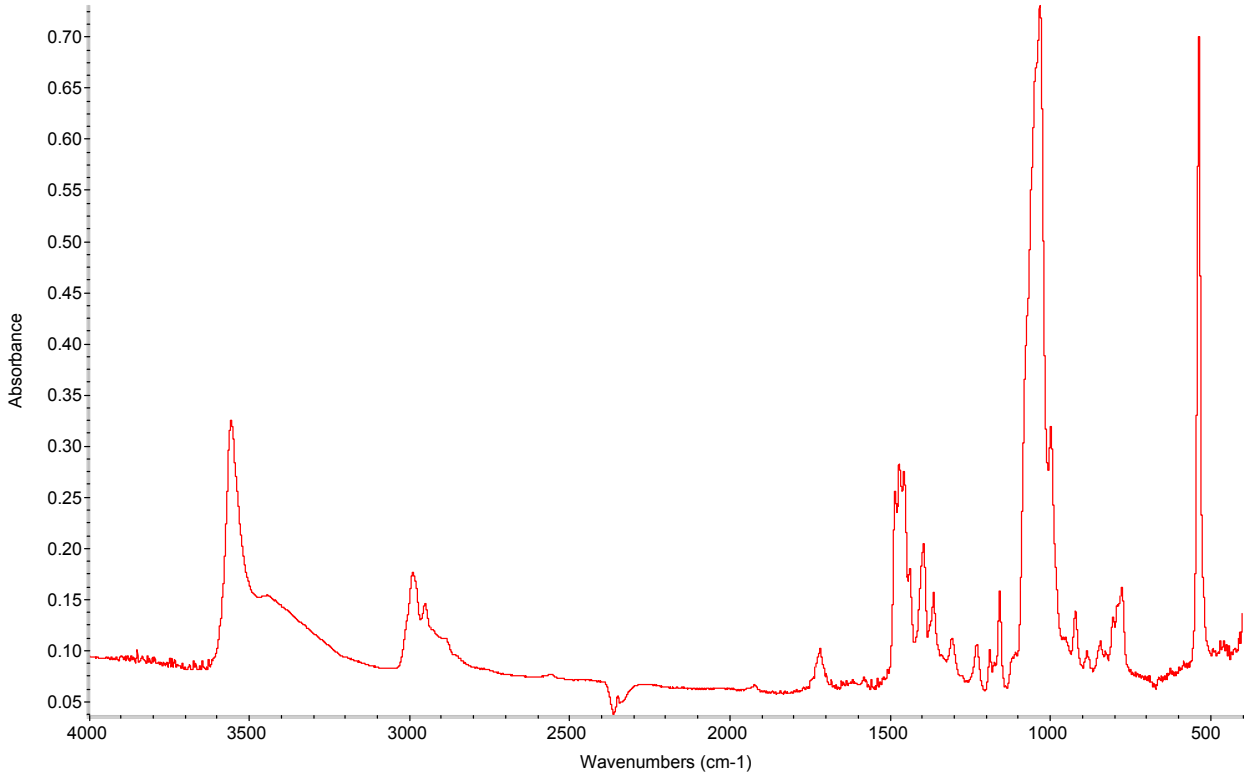


Fig. S.15 FT-IR spectrum of $[N_{2\,2\,2\,HE}]_2[B_{12}Cl_{12}]$.

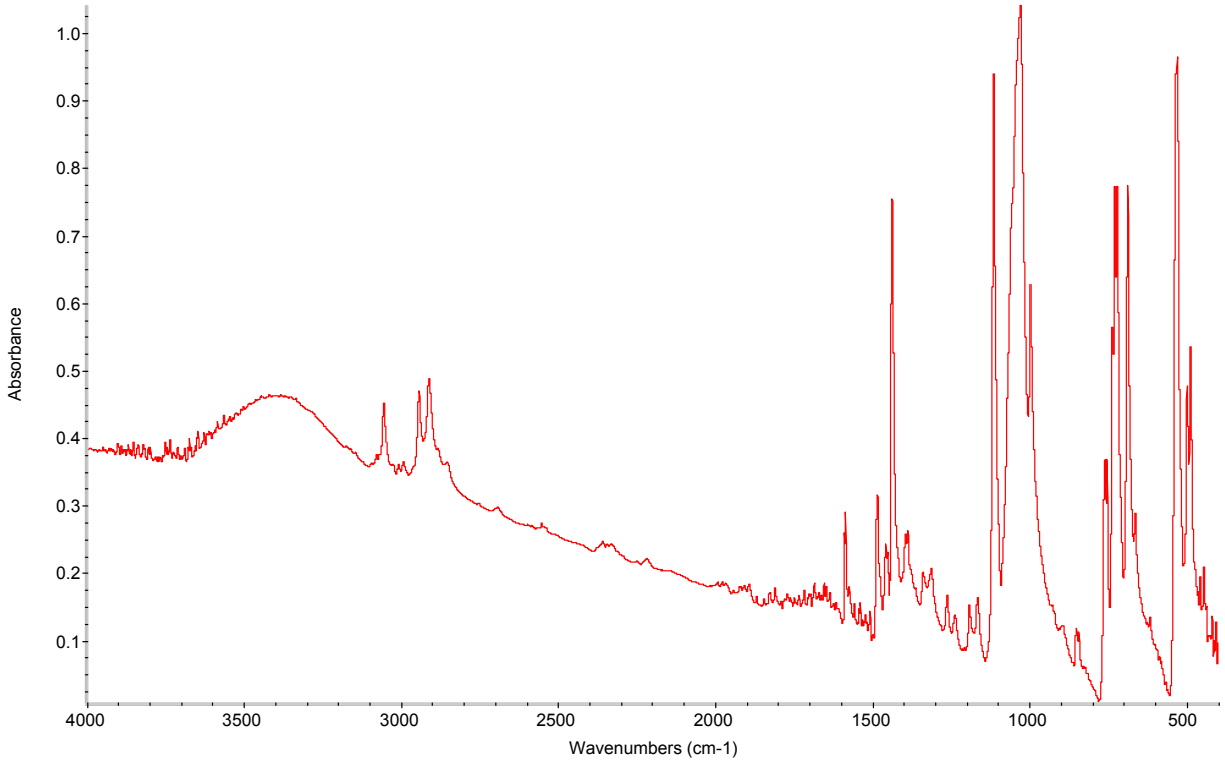


Fig. S.16 FT-IR spectrum of $[P_{P\,P\,P\,2}]_2[B_{12}Cl_{12}]$.

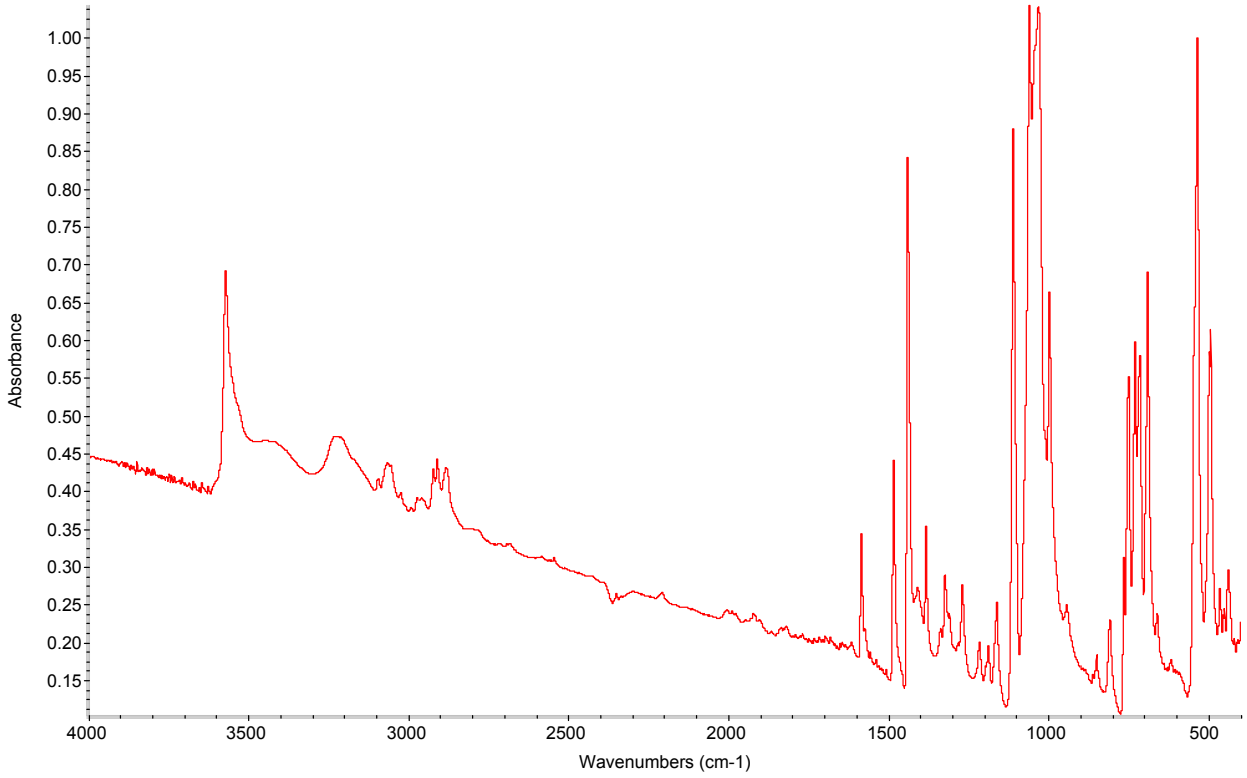


Fig. S.17 FT-IR spectrum of $[P_{P\,P\,P\,HE}]_2[B_{12}Cl_{12}]$.

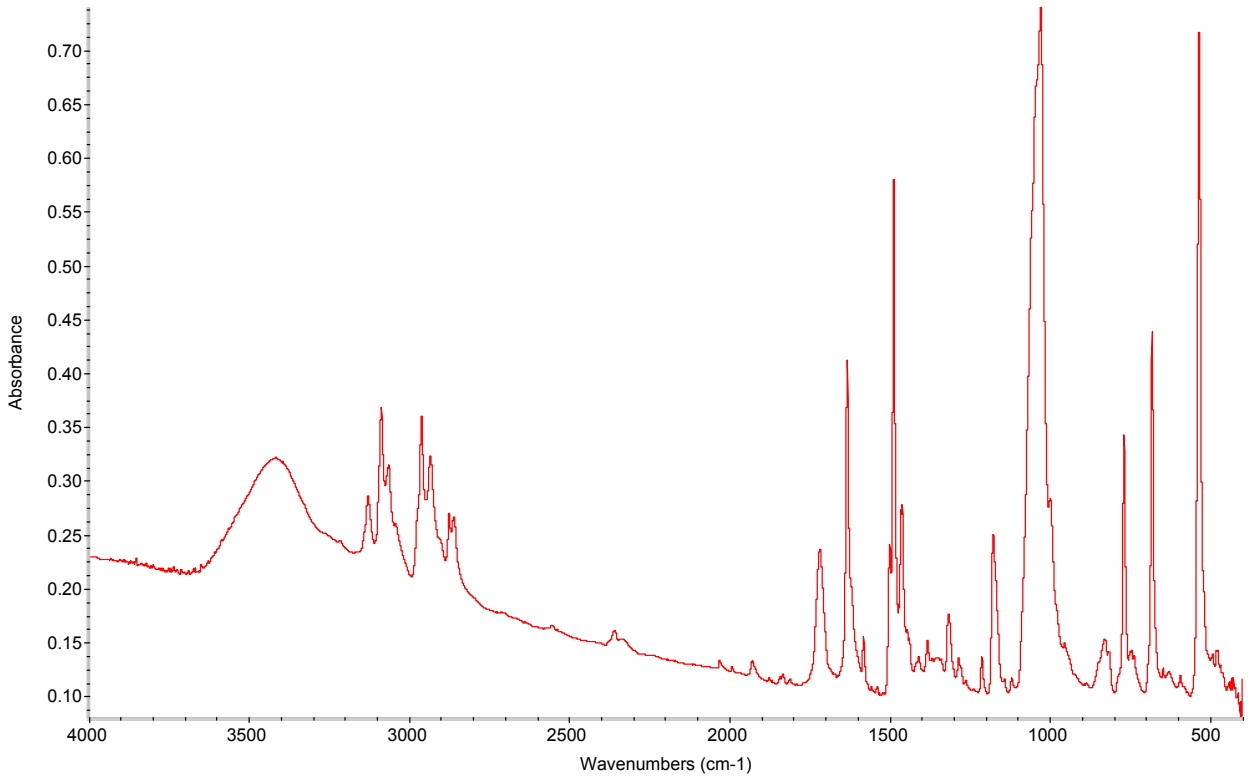


Fig. S.18 FT-IR spectrum of $[PyC_4]_2[\ B_{12}Cl_{12}]$.