Electronic Supplementary Information

Selective CO_2 Gas Adsorption in the Narrow Crystalline Cavities of Flexible Peptide Metallo-Macrocycles

Ryosuke Miyake*, Chika Kuwata and Yui Masumoto

Department of Chemistry and Biochemistry, Graduate School of Sciences and Humanities, Ochanomizu University, 2-1-1 Otsuka, Bunkyo-ku, Tokyo 112-8610, Japan

miyake.ryosuke@ocha.ac.jp

Contents:

Experimental Sections

General

The BF_4^- salt[S1] and the NO_3^- salt[S2] of crystalline peptide metallo-macrocycles are synthesized by previously reported methods.

Single Crystal X-ray diffraction measurement

Crystallographic data were collected using a Bruker APEXII CCD detector with Mo-Kα radiation (λ = 0.71075 Å). The structures were solved by direct methods using the program SHELXS. The refinement (on F^2) and graphical calculations were performed using the SHELIXL program suite.[S3, S4] For the measurements at normal humidity, samples were set up in glass capillaries. BF_4^- anions were refined by using SADI (between B and F), SIMU, and ISOR restraints and water molecules were refined by using SIMU and ISOR restraints. In addition, SUMP restraints were used for hardly disordered BF_4^- anions to fix the sum of their occupancy. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CCDC).

Powder X-ray diffraction (PXRD) measurement

The powder X-ray diffraction (PXRD) was measured under CO_2 atmosphere at −80 or −50 °C (193 or 223 K) using Bruker APEXII CCD detector with Mo Kα radiation (λ = 0.71075 Å). The powder pattern was integrated using XRD vaul program (Bruker AXS Co. Ltd.).

The sample was sealed in a glass capillary and used for experiments. For dried sample, the BF_4^- salt in a glass capillary was dried in vacuo for 1h at 100 °C and sealed after cooling to room temperature. For CO_2 loaded sample, the BF_4^- salt after the dried sample process described above was stored under CO_2 gas at −78 °C (195 K) for 1h and sealed using a burner.

Adsorption measurements

The adsorption isotherms of O_2, H_2 at 77 K, and CO_2, CH_4 at 195 K were carried out volumetrically on a BELSORP-mini II (NIHON Bell Co. Ltd.). The adsorption isotherms of N_2, CO_2, CH_4 gases around room temperatures (278-298 K) were carried out gravimetrically on BELSORP-BG-H10 (NIHON Bell Co. Ltd.). H_2, O_2, N_2, CO_2, and CH_4 gases of high purity (>99.999%) were used. Prior to the adsorption isotherm measurements, the samples were dehydrated under vacuum for 1h at 60 °C (NO_3^- salt) or 100 °C (BF_4^- salt). The conditions for dehydration are determined based on thermogravimetric measurements and temperature dependency of IR spectroscopy (for details, refer to ref. S1-2).

Additional information on gas adsorption behavior of crystalline peptide macrocycles

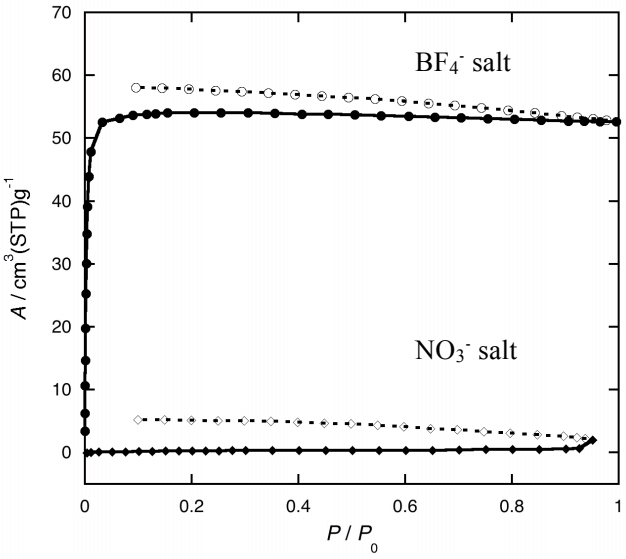

Figure S1. Adsorption isotherms of CO_2 gas for BF_4^- salt (black line) and NO_3^- salt (blue line) at 195 K. (adsorption process: solid line with filled symbol, desorption process: dashed line with empty symbol).

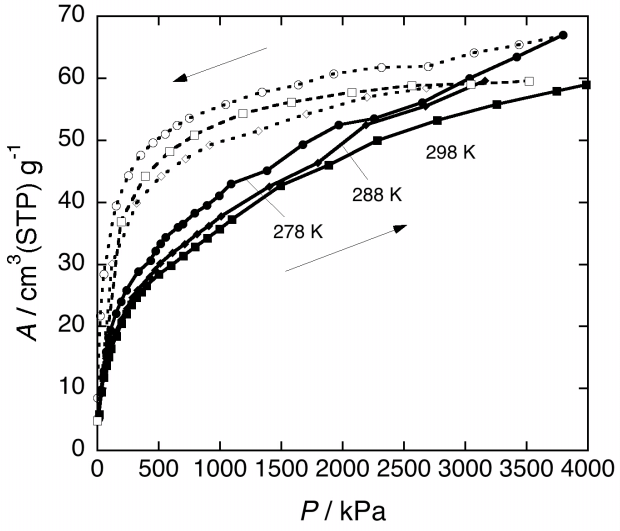

Figure S2. Adsorption isotherm curves of CO_2 gas for the BF_4^- salt at various temperatures (278, 288, and 298 K).

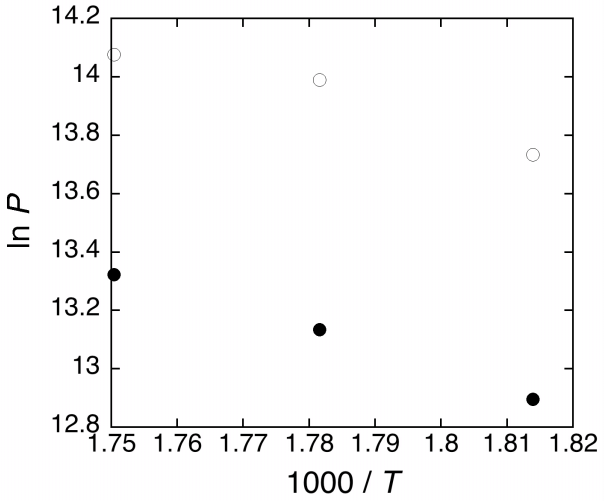

Figure S3. The temperature dependence of CO_2 gas pressure at the adsorption amount of 30 (empty circle) and 40 (solid circle) $cm^3(STP) \cdot g^{-1}$ for the BF_4^- salt (adsorption process).

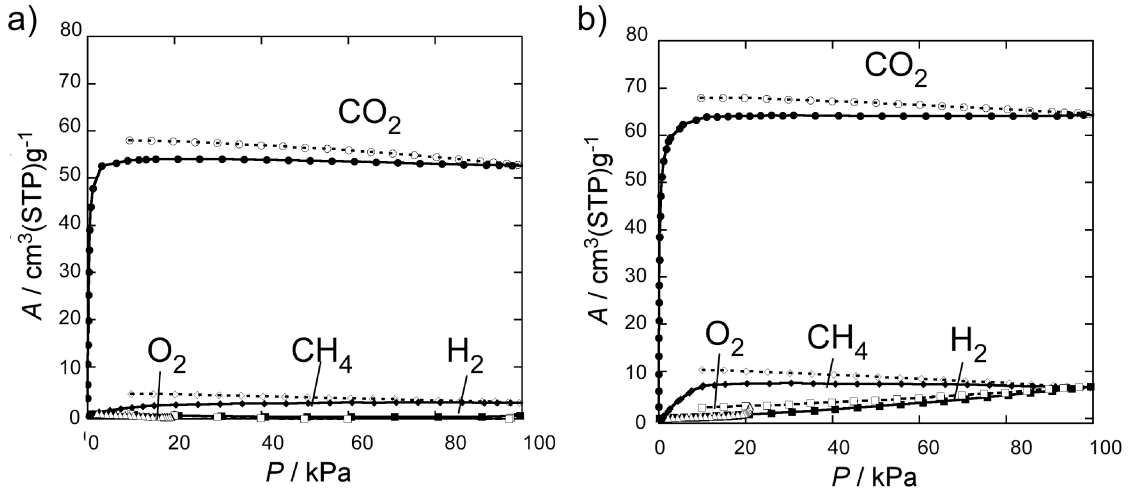

Figure S4. Adsorption isotherm of CO_2 (circle), CH_4 (diamond), H_2 (square), O_2 (triangle) gas for BF_4^- salt at 195 K (CO_2, CH_4 gas) and 77 K (O_2, H_2 gas). The BF_4^- salt was dried in vacuo for 1h at room temperature (a), and 100 °C (b). (adsorption process: solid line with filled symbol, desorption process: dash line with empty symbol).

Additional information about crystal structure of the peptide Ni(II)-macrocycles

Table S1. Crystal data of the BF_4^- salt at various temperatures.

Temperature / °C	-80	-50
Crystal size/ mm	0.024 × 0.012 × 0.012	0.024 × 0.012 × 0.012
Formula[a]	$C_{48}H_{127.61}B_8F_{32}N_{28}Ni_4O_{22.30}$	$C_{48}H_{117.71}B_8F_{32}N_{28}Ni_4O_{17.35}$
M [a]	2383.58	2294.40
Crystal system	*Tetragonal*	*Tetragonal*
Space group	*I-4*	*I-4*
a /Å	15.7784(6)	15.754(2)
b /Å	15.7784(6)	15.754(2)
c /Å	19.7467(15)	19.585(3)
α /°	90	90
β /°	90	90
γ /°	90	90
V /Å^3	4916.1(5)	4860.8(16)
Z	2	2
ρ_{calcd} /g·cm^{-3}	1.610	1.568
F(000)	2460	2361
μ /mm^{-1}	0.890	0.894
θ range /°	1.65-30.15	1.66-30.18
GOF	1.052	1.043
Reflections collected	18856	17913
Independent reflections	7075	7017
Flack parameter	0.016(4)	0.101(11)
R_{int}	0.0205	0.0595
R_{sigma}	0.0355	0.0720
Final R1 ($I > 2\sigma(I)$ (all data))	0.0377(0.0402)	0.0620(0.0754)
wR2 ($I > 2\sigma(I)$ (all data))	0.1105(0.1125)	0.1646(0.1742)
CCDC No.	1033455	1033454

[a] For the formula and molecular weight (M), we included hydrogen atoms of water molecules in the crystal, although we did not determine them in the refined structures.

For detail crystal structure, also refer to reference S1.

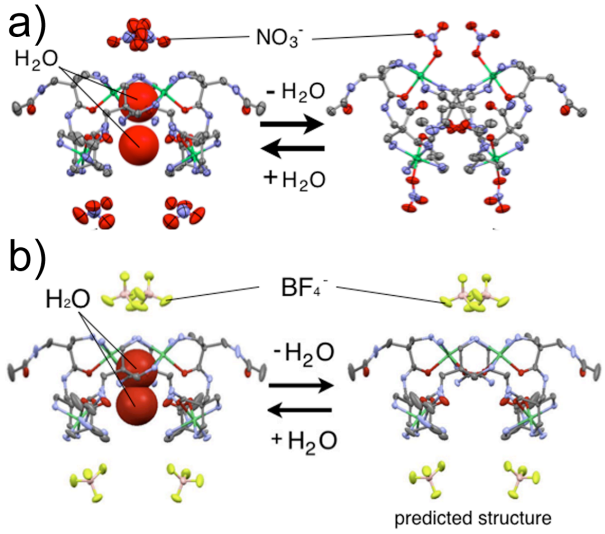

Figure S5. Comparison of the crystal structural changes in the macrocyclic framework between the NO_3^- salt (a), and the BF_4^- salt (b), by removing included water molecules. For the structure of the BF_4^- salt in the dry condition, the predicted structure is shown.

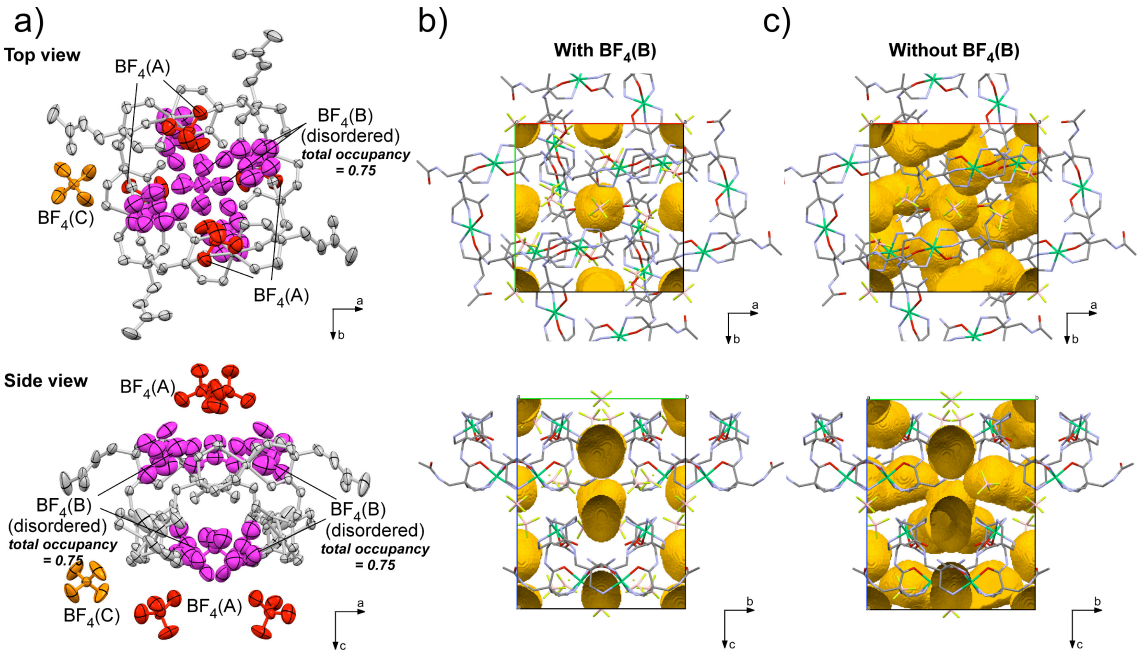

Figure S6. Crystal structure showing the position of counter anions (a), and void spaces with (b) and without (c) considering the BF_4^- anions whose occupancy is 0.75. The void spaces are calculated using mercury, by setting the probe radius at 1.72 Å. For disordered anions, only one of the positions was considered to calculate the void volume.

Estimation of the void volume in the BF_4^- salt

For the calculation of void volume in the BF_4^- salt at 293 K, the weighted averages of the void volumes, with BF_4(B) and without the BF_4(B), were applied as follows. The values of void volume were calculated by setting the probe radius and the approximate grid spacing at 1.72 Å (value for CO_2 gas) and 0.1 Å, respectively. We used one of the positions for disordered BF_4^- anion (i.e. BF_4(B)) which gives the largest voids. For BF_4(B), refer to Figure S6.

Calculated value (probe radius: 1.72 Å, approx. grid spacing: 0.1 Å)
Void volume with BF_4(B) : 173.10 $Å^3$ (with 5 BF_4^- per macrocycle)
Void volume without BF_4(B): 450.32 $Å^3$ (with 9 BF_4^- per macrocycle)
Calculated void volume for BF_4^- salt: 173.10 x 3/4 + 450.32 x 1/4 = 242 $Å^3$

Additional discussion for void space in the BF_4^- salt

The values of void space were observed to decrease with decrease of the value of grid spacing (Table S2), suggesting that the BF_4^- salt has tangled spaces. Since the powder diffraction pattern of the crystal after CO_2 adsorption is similar to that of the water included crystal (hydrated form), the reorientation of the BF_4^- salt and conformational changes of the peptide framework should play an important role in the adsorption of 6 CO_2 molecules per macrocycle, although the calculated void volume is enough for the observed amount of CO_2 gas adsorption.

Table S2 Estimated void volume with various approx. grid. spacing

Value of grid spacing	Void volume with BF_4(B)[a]	Void volume without BF_4(B)[a]
0.1	173.10 $Å^3$	450.32 $Å^3$
0.3	152.76 $Å^3$	385.82 $Å^3$
0.7	147.07 $Å^3$	279.09 $Å^3$

Probe radius: 1.72 Å (the value for CO_2 gas)
[a]: The value was estimated using mercury program (CCDC).

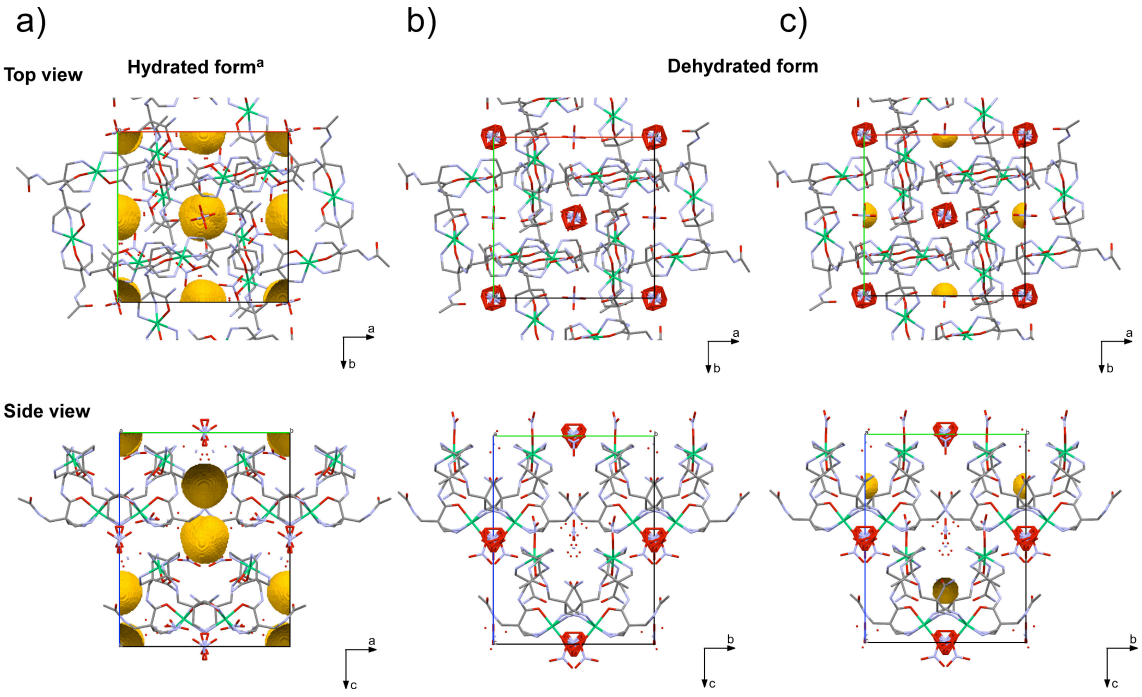

Figure S7. Crystal structure of the NO_3^- salt in hydrated form (a) and dehydrated form (b) showing void spaces The void spaces are calculated using mercury, by setting the probe radius at 1.72 Å for (a) and (b) and 1.2 Å for (c) (approx. grid. spacing is set at 0.1 Å). The estimated void volume are 385 (a), 0 (b), 8 (c) $Å^3$ per macrocycle.

Discussion of structural changes under CO_2 gas

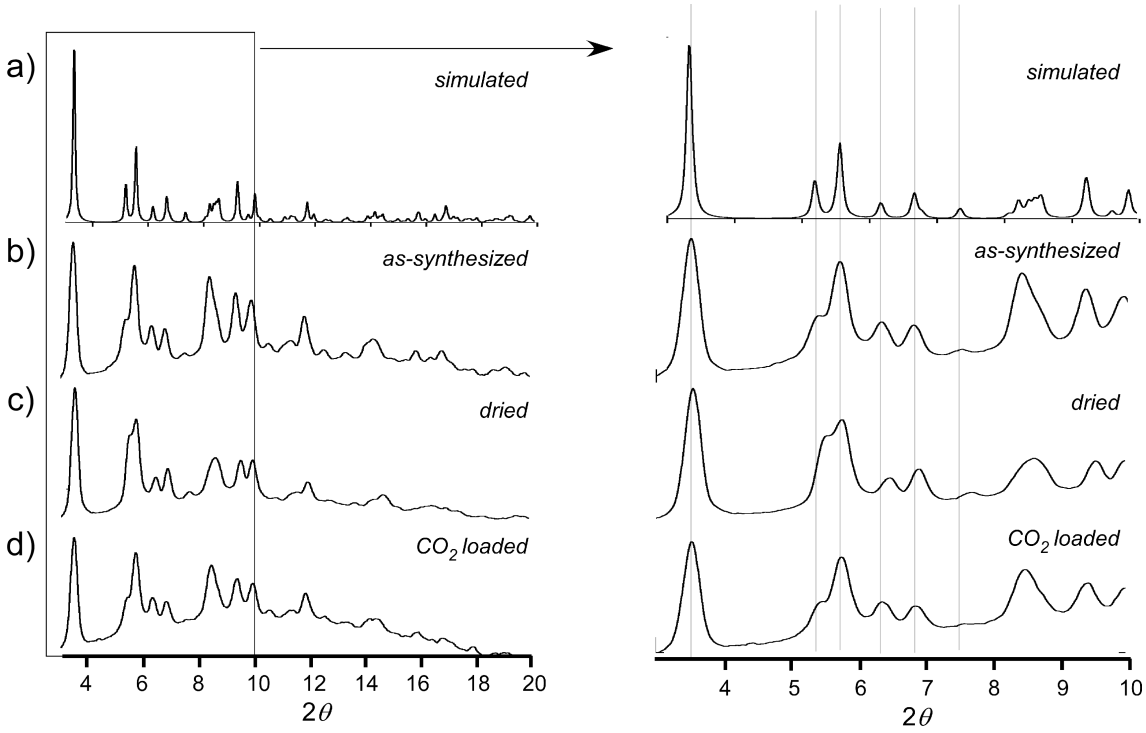

Figure S8. Powder X-ray diffraction pattern of the BF_4^- salt. (a) A simulated pattern of the BF_4^- salt at −80 °C (193 K). (b) A pattern of the as-synthesized sample. (c) A pattern of the sample dried at 100 °C in vacuo. (d) A pattern of the sample sealed with CO_2 gas. All diffraction patterns were measured at -80 °C using a glass capillary.

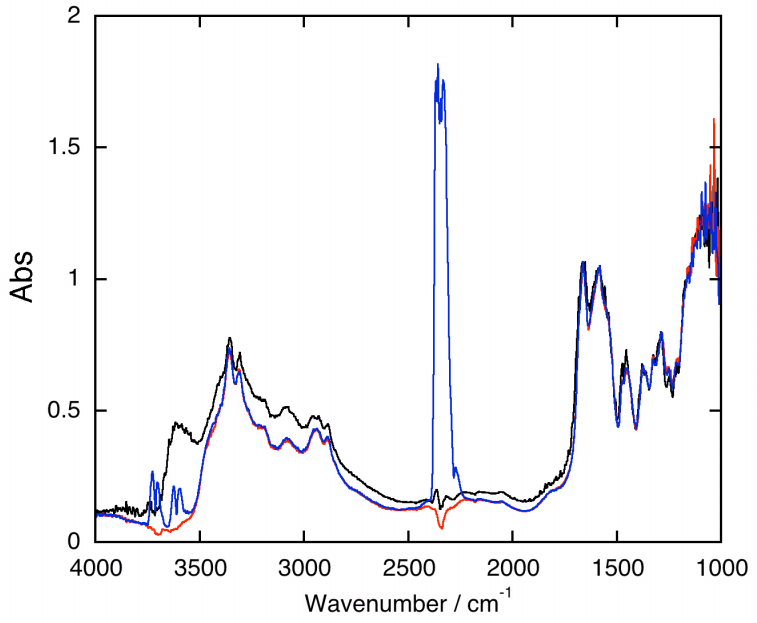

Figure S9. IR spectrum of the BF_4^- salt at room temperature. (Black line: as synthesized BF_4^- salt; Red line: dried BF_4^- salt: Blue line: dried sample under CO_2/N_2 mixture gas (v/v =1).)

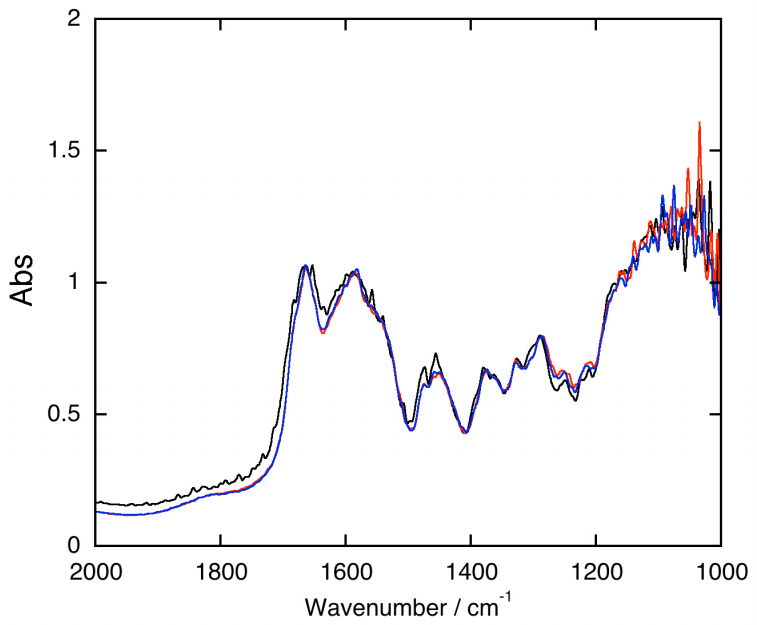

Figure S10. Extended IR spectra of the BF_4^- salt at room temperature. (For extra explanation, refer to the caption of Figure S9.)

References

S1: R. Miyake and M. Shionoya, *Inorg. Chem.* 2014, **53**, 5717.
S2: R. Miyake and M. Shionoya, *Chem. Commun.* 2012, **48**, 7553.
S3: G.M. Sheldrick, *SHELXL-2013*, Program for refinement of crystal structures, University of Göttingen (Germany), **2013**.
S4: G.M. Sheldrick, SADABS, Program for scaling and correction of area detector data, University of Göttingen (Germany), **1996**.