Electronic Supplementary Information (ESI)

Isomorphous Metal 1,3,5-Benzenetriphosphonates MBP-1 with Variable Compositions: Preparation, Crystal Structure, and Electrochemical Properties

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Experimental details

Reagents

BTP was synthesized from 1,3,5-tribromobenzene in a two-step reaction according to the literatures.[1,2] Other reagents and solvents were used as purchased.

Preparation of MBP-1

The preparation procedures of MBP-1 (M: Mn, Zn, Cd, Mg, Ni, Co, and Ca) compounds are basically similar each other except starting metal salts, starting compositions, and temperature of the hydrothermal reactions. Therefore, a representative procedure for MnBP-1 is described below. ZnBP-1 based compounds doped with 5 mol% M(II) designated as M/ZnBP-1 (M : Zn = 5 : 95) were also similarly prepared.

· MnBP-1

A typical preparation procedure is as follows: A mixture of BTP and $MnCl_2{\cdot}4H_2O$ was dissolved in ultrapure water (BTP : Mn source : H_2O = 1 : 2 : 300) and stirred for 30 min at room temperature. The resulting solution was heated at 140 °C for 72 h in a 23-mL Teflon-lined stainless-steel autoclave. After cooling to room temperature, the solid product was filtrated and washed with H_2O for three times to remove the remaining reactants. The resulting white powder was air-dried to obtain MnBP-1. The samples used for further characterization such as elemental analysis and TG-DTA were dried under vacuum prior to the measurement. ICP-AES Found Mn/P = 0.580, Elemental analyses Found C, 17.7; H, 1.3. Calc. for $C_6H_{5.52}P_3O_9Mn_{1.74}$: C, 17.57; H, 1.36%.

MnBP-1 was also hydrothermally prepared using $Mn(O_2CCH_3)_2{\cdot}6H_2O$ as the manganese source. MnBP-1 was obtained also by stirring the aqueous starting mixtures (from either manganese chloride or acetate) at room temperature for 1 day. In order to investigate influence of pH of the starting solution on hydrothermally obtained MnBP-1, LiOH was added to the starting mixture (BTP : LiOH = 1 : 0 – 5.5) in addition to the above procedure. The pH values of the mixture solutions before and after the hydrothermal reactions were roughly measured using pH papers.

·ZnBP-1

BTP : $Zn(NO_3)_2{\cdot}6H_2O$: H_2O = 1 : 3 : 300, 180 °C for 96 h

ICP-AES Found Zn/P = 0.609, Elemental analyses Found C, 16.6; H, 1.2. Calc. for $C_6H_{5.34}P_3O_9Zn_{1.83}$: C, 16.60; H, 1.24%. (white powder)

·CdBP-1

BTP : $Cd(NO_3)_2{\cdot}4H_2O$: H_2O = 1 : 3 : 600, 200 °C for 48 h

EDX Found Cd/P = 0.63, Elemental analyses Found C, 13.3; H, 0.9. Calc. for $C_6H_5P_3O_9Cd_2$: C, 13.37; H, 0.94%. (white powder)

·MgBP-1

BTP : $Mg(NO_3)_2{\cdot}6H_2O$: H_2O = 1 : 3 : 600, 200 °C for 48 h

ICP-AES Found Mg/P = 0.465, Elemental analyses Found C, 20.4; H, 1.4. Calc. for $C_6H_{6.20}P_3O_9Mg_{1.40}$: C, 20.63; H, 1.79%. (white powder)

·NiBP-1

BTP : $Ni(NO_3)_2{\cdot}6H_2O$: H_2O = 1 : 3 : 300, 180 °C for 96 h

ICP-AES Found Ni/P = 0.543, Elemental analyses Found C, 17.6; H, 1.2. Calc. for $C_6H_{5.74}P_3O_9Ni_{1.63}$: C, 17.56; H, 1.41%. (yellow powder)

·CoBP-1

BTP : $Co(NO_3)_2·6H_2O$: H_2O = 1 : 3 : 300, 180 °C for 96 h

ICP-AES Found Co/P = 0.628, Elemental analyses Found C, 17.1; H, 1.2. Calc. for $C_6H_{5.24}P_3O_9Co_{1.88}$: C, 16.95; H, 1.24%. (violet powder)

·CaBP-1

BTP : $Ca(NO_3)_2·6H_2O$ (or mixed with $Ca(OH)_2$) : H_2O = 1 : 3 : 600, 200 °C for 48 h

ICP-AES Found Ca/P = 0.576, Elemental analyses Found C, 16.3; H, 1.9. Calc. for $C_6H_{5.54}P_3O_9Ca_{1.73}·2H_2O$ (air-dried): C, 17.16; H, 2.29%. (white powder)

·M/ZnBP-1

BTP : $Zn(NO_3)_2·6H_2O$: M(II) nitrate (M = Co, Ni, Cd, Mn, or Mg) : H_2O = 1 : 2.85 : 0.15 : 600, 200 °C for 48 h

General Characterization

CHN elemental analysis was performed on a Perkin-Elmer Series II CHNS/O analyser 2400. ICP-AES was measured on a Shimazu ICP-7500. EDX was measured on a Philips XL-30. TG-DTA was measured on a Rigaku Thermo Plus 2 at a heating rate of 10 K min^{-1} under an air flow at 100 mL min^{-1}. Powder X-ray diffraction (PXRD) patterns except the high-resolution data used for the structure solution and indexing were measured on a Rigaku RINT-Ultima+ using monochromated Cu-Kα radiation. Ex-situ XRD measurements for the were performed on a Rigaku Ultima IV using an air-sensitive sample holder. Ex-situ X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Shimazu ESCA 3400 using Al K-α excitation source. The Mn(2p) lines were examined and the binding energies were normalised with respect to the C(1s) line at 284.6 eV.

Crystal structure solution using high-resolution powder XRD data

High-resolution synchrotron diffraction data were collected on the diffractometer with a Debye-Scherrer camera of the BL02B2 beamline at SPring-8 (Hyogo, Japan) or on that of the BL5S2 beamline at Aichi Synchrotron (Aichi, Japan) using powder samples loaded in 0.3–0.5 mm glass capillaries. All the patterns were indexed with hexagonal unit cells using NTREOR[3] implemented in EXPO2014 software[4] and the extinction rule suggested the space groups $P6_3/m$ or $P6_3$. The lattice parameters were refined in the Le Bail method[5] in EXPO2014 to confirm that all the samples were obtained basically as the single phases. In *ab initio* structure solutions of MnBP-1, ZnBP-1, and CdBP-1, most of the non-hydrogen framework atoms in the initial models were found in the direct method by assuming the space group $P6_3/m$ using EXPO2014 from the extracted intensities in the Le Bail method. The aromatic hydrogen atoms of MnBP-1 and ZnBP-1 were found in MEM-based electron density maps using Dysnomia.[6] Since the other hydrogen positions were not confirmed, the compositional information was reflected to the structural models by treating the expected CH and OH groups as virtual atoms at C2 and O1 sites respectively. The structural models were refined in the Rietveld method using Rietan-FP,[7] successfully converged to chemically reasonable structures even with no soft geometrical restraints in the case of MnBP-1 and ZnBP-1. As for CdBP-1 soft geometrical restraints were applied to stabilise the refinement. The population parameters of the metal sites were refined to confirm the metal site vacancies. In the case of OH groups, the number of protic H atoms were constrained to the population parameters of the metal sites (g_M) so as to satisfy the neutrality of the compositions. To stabilise the refinement, some of the isotropic atomic displacement parameters for similar atoms were constrained to be the same. The final crystallographic parameters are listed in Table S1, and the Rietveld plots are shown in Figure S1–S3. The solved structures were visualised using VESTA.[8]

Pair Distribution Function (PDF) analysis and Reverse Monte Carlo (RMC) modelling

X-ray total scattering measurements were also carried out with a wavelength of 0.2 Å (BL04B2, SPring-8) to discuss the atomic configuration from the viewpoint of local structure. The scattering data were normalised into Faber-Ziman structure factors $S(Q)$ and then converted into reduced pair distribution function $G(r)$.[9,10] The $S(Q)$ were degraded by convolution taking the box size for RMC modelling into account. First, the obtained $G(r)$ was analysed with PDFgui[11], and then the RMC modelling was performed with RMCProfile using the degraded structure factor $S_{\mathrm{box}}(Q)$ and the Bragg profile.[12]

Electrochemical measurements

For electrochemical measurements, MBP-1 samples (typical preparation conditions are summarised in Table S2) were heated at 420 °C for 2 h under air in covered ceramic vessels to remove water and hydroxyl moieties. In order to fabricate the electrodes, MBP-1 as an active material, acetylene black (FX-35; Denka, abbreviated as AB) or Ketjen black (EC600JD; Lion specialty chemicals, abbreviated as KB) as a conductive agent, and polyvinylidene fluoride (PVDF; Synquest Laboratories) were mixed in a weight ratio of 70:15:15 and dispersed in N-methyl-2-pyrrolidone (NMP; Wako) solvent to form a homogeneous slurry. The slurry was coated on a copper foil (Hosen, thickness: 35 μm), dried in a vacuum oven at 80 °C for 12 h, and punched into a circular shape (φ=16 mm; *i.e.*, the electrode area *ca.* 2 cm^2). Active materials were loaded on 1.5-2.0 mg on the copper foil. Electrochemical measurements were carried out using coin-type half-cells. Coin cells were constructed using an MBP-1 electrode as the working electrode, separator (TEF4030, Nippon Kodoshi), Li metal (Honjo metal, thickness: 0.5 mm) as the counter electrode, and 1 M $LiPF_6$ /EC + DMC (1:1 v/v; Tomiyama Pure Chemical Industry, Ltd., battery grade) as the electrolyte in an argon filled glovebox (Miwa, MDB-1BK-NT1). Cyclic voltammetry (CV) was performed at a potential scanning rate of 0.1 mV s^{-1} between 3.00V and 0.05 V using an electrochemical measurement system (Bio-Logic Science, VSP). All the measurements were conducted at 30 °C. Constant current discharge-charge profiles were recorded at 18.6 mA g^{-1} for the first 3 cycles as pre-cycles and at 62 mA g^{-1} for the following cycles (Hokuto Denko, HJ1001SM8).

References

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Table S1 Crystallographic parameters for Rietveld refinement

Sample	MnBP-1	ZnBP-1	CdBP-1	MnBP-1-4.5eq
CCDC Number	2431043	2431041	2431042	2452711
Formula	$C_2H_1Mn_{0.54}O_3P_1$	$C_2H_1Zn_{0.61}O_3P_1$	$C_2Cd_{0.65}O_3P_1$	$C_2H_1Mn_{0.667}O_3P_1$
Crystal system	hexagonal	hexagonal	hexagonal	hexagonal
Space group	$P6_3/m$	$P6_3/m$	$P6_3/m$	$P6_3/m$
Z	6	6	6	6
a / Å	8.98133(8)	8.85701(6)	9.12216(10)	8.9818(3)
c / Å	7.72133(7)	7.55059(4)	7.84046(9)	7.6950(3)
V / Å^3	539.391(8)	512.962(6)	565.025(10)	537.61(3)
λ / Å	0.79980*	0.79960*	0.79960*	0.80044**
2θ range / °	4.5—78.0	4.5—77.0	5.0—78.0	4.21—78.0
Number of observations	12250	12084	12167	9497
Number of reflections	789	724	825	788
Number of refined parameters	58	48	54	52
R_{wp}	0.0599	0.0299	0.0535	0.0412
R_F	0.0321	0.0365	0.0283	0.0099
R_e	0.0206	0.0144	0.0173	0.0114

* BL02B2, SPring-8, Japan ** BL5S2, Aichi Synchrotron, Japan

Table S2 Typical compositions of starting mixtures and hydrothermal synthesis conditions in preparation of MBP-1 for electrochemical measurements.

Sample	M source	M/BTP	H_2O/BTP	T/°C	Time / h
MnBP-1	$MnCl_2{\cdot}4H_2O$	2	1000	140	72
ZnBP-1	$Zn(NO_3)_2{\cdot}6H_2O$	2	1000	180	48
CoBP-1	$Co(NO_3)_2{\cdot}6H_2O$	2	1000	180	48
CdBP-1	$Cd(NO_3)_2{\cdot}4H_2O$	3	1000	180	48
NiBP-1	$Ni(NO_3)_2{\cdot}6H_2O$	3	1000	180	48
CaBP-1	$Ca(NO_3)_2{\cdot}4H_2O$	3	1000	200	48
MgBP-1	$Mg(NO_3)_2{\cdot}6H_2O$	3	1000	200	48

Table S3 Lattice constants of MBP-1 obtained in the Le Bail analysis by assuming trigonal lattice with space group $P6_3/m$.

M	Ni	Mg	Zn	Co	Mn	Cd	Ca
a / Å	8.807	8.848	8.860	8.860	8.981	9.125	9.227
c / Å	7.516	7.556	7.558	7.590	7.721	7.843	7.860
r_{ion}*/ pm	69	72	74	74.5	83	95	100

* r_{ion}: effective ionic radii of M^{2+} assuming 6-coordinate

Table S4 Estimated compositions of MnBP-1 prepared with LiOH addition.

LiOH /BTP	pH before HR*	pH after HR*	Obs. Mn/BTP	Obs. C/%	Obs. H/%	Estimated compositions**
0.0	1–2	1	1.68	17.1	2.0	$C_6H_{5.64}P_3O_9Mn_{1.68}\cdot 0.8H_2O$
2.0	2–3	2	1.41	16.8	2.0	$C_6H_{6.18}P_3O_9Mn_{1.41}\cdot 1.8H_2O$
3.0	3–4	2–3	1.33	16.3	1.9	$C_6H_{6.34}P_3O_9Mn_{1.33}\cdot 2.1H_2O$
4.0	5–6	4	1.57	16.5	2.5	$C_6H_{5.86}P_3O_9Mn_{1.57}\cdot 2.0H_2O$
4.5	5–6	6	2.04	15.8	1.5	$C_6H_{4.92}P_3O_9Mn_{2.04}\cdot 1.4H_2O$
5.0	6–7	6–7	2.13	15.4	1.7	$C_6H_{4.74}P_3O_9Mn_{2.13}\cdot 2.0H_2O$

*HR: hydrothermal reaction

**The samples were only air-dried.

Table S5 Cationic compositions of M/ZnBP-1 according to EDX.

M	Mg	Mn	Co	Ni	Cd
M/M+Zn mol %	6.7	12.7	7.4	5.6	5.5

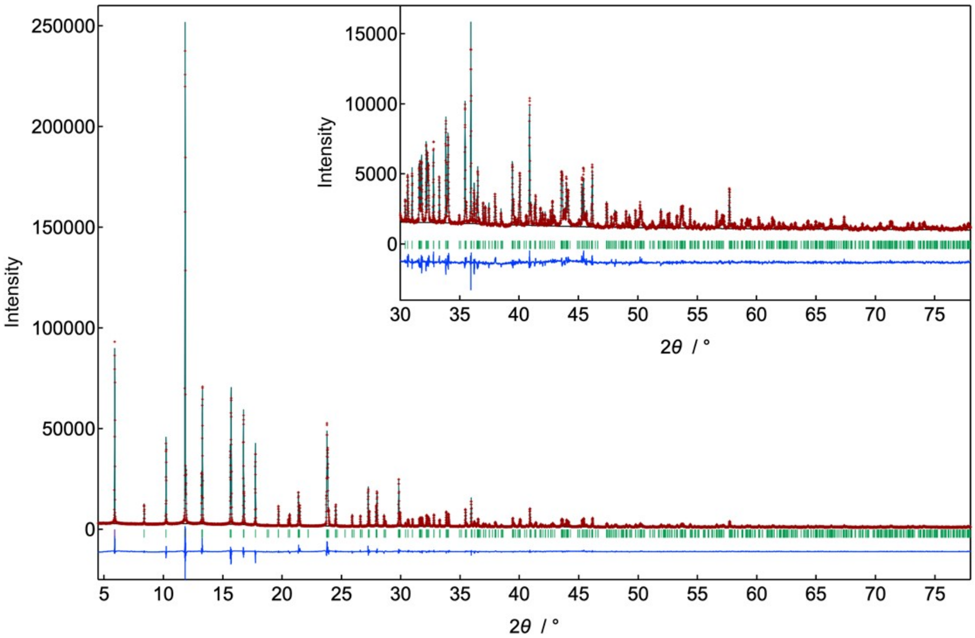

Fig. S1 Observed (red points), calculated (light blue line), and residual (blue line) profile for the Rietveld refinement of MnBP-1

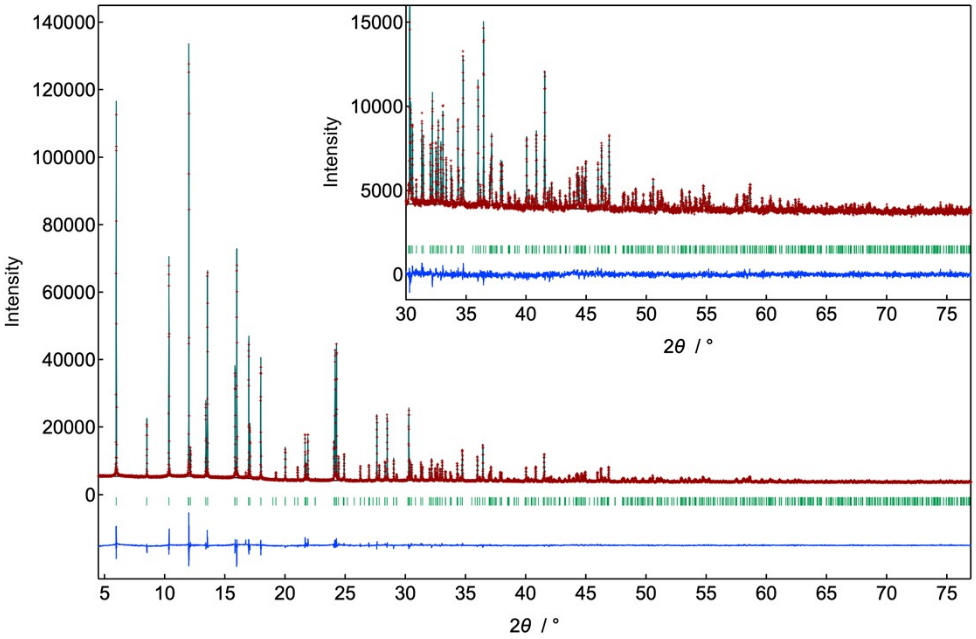

Fig. S2 Observed (red points), calculated (light blue line), and residual (blue line) profile for the Rietveld refinement of ZnBP-1

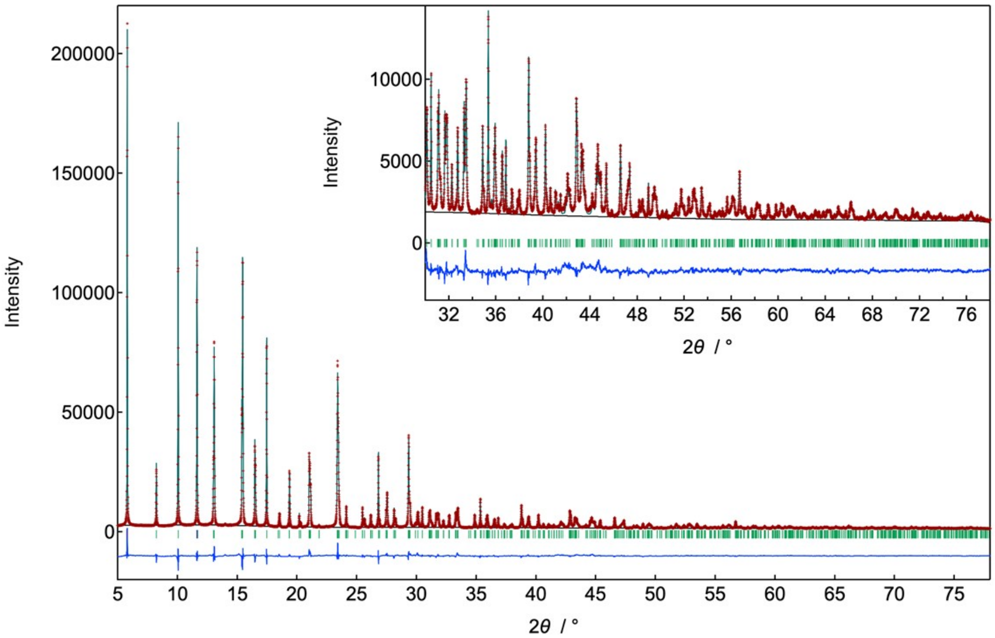

Fig. S3 Observed (red points), calculated (light blue line), and residual (blue line) profile for the Rietveld refinement of CdBP-1

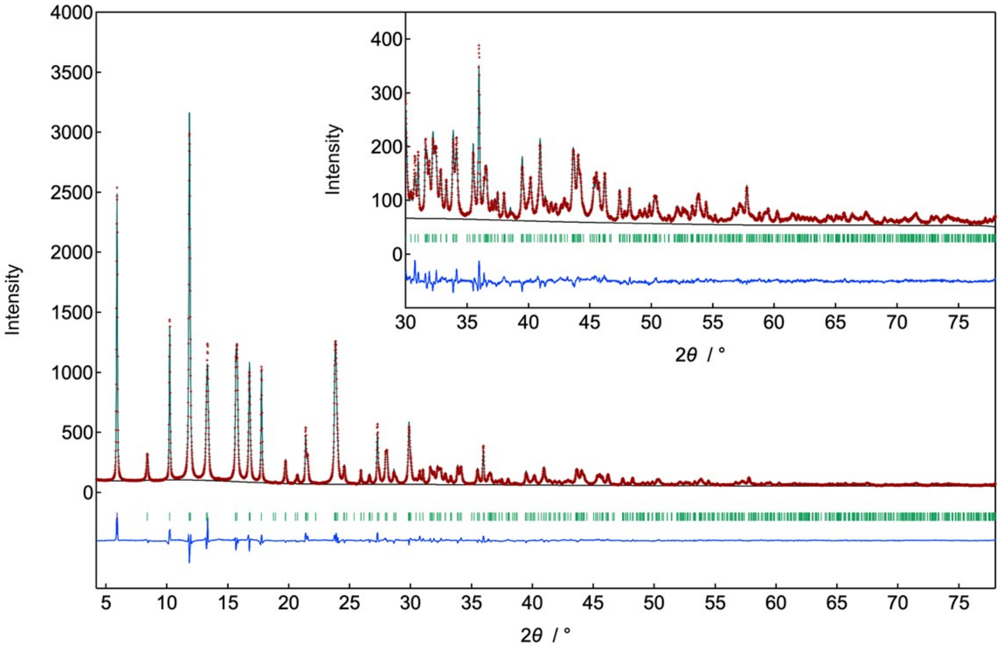

Fig. S4 Observed (red points), calculated (light blue line), and residual (blue line) profile for the Rietveld refinement of MnBP-1 prepared with 4.5 eq LiOH

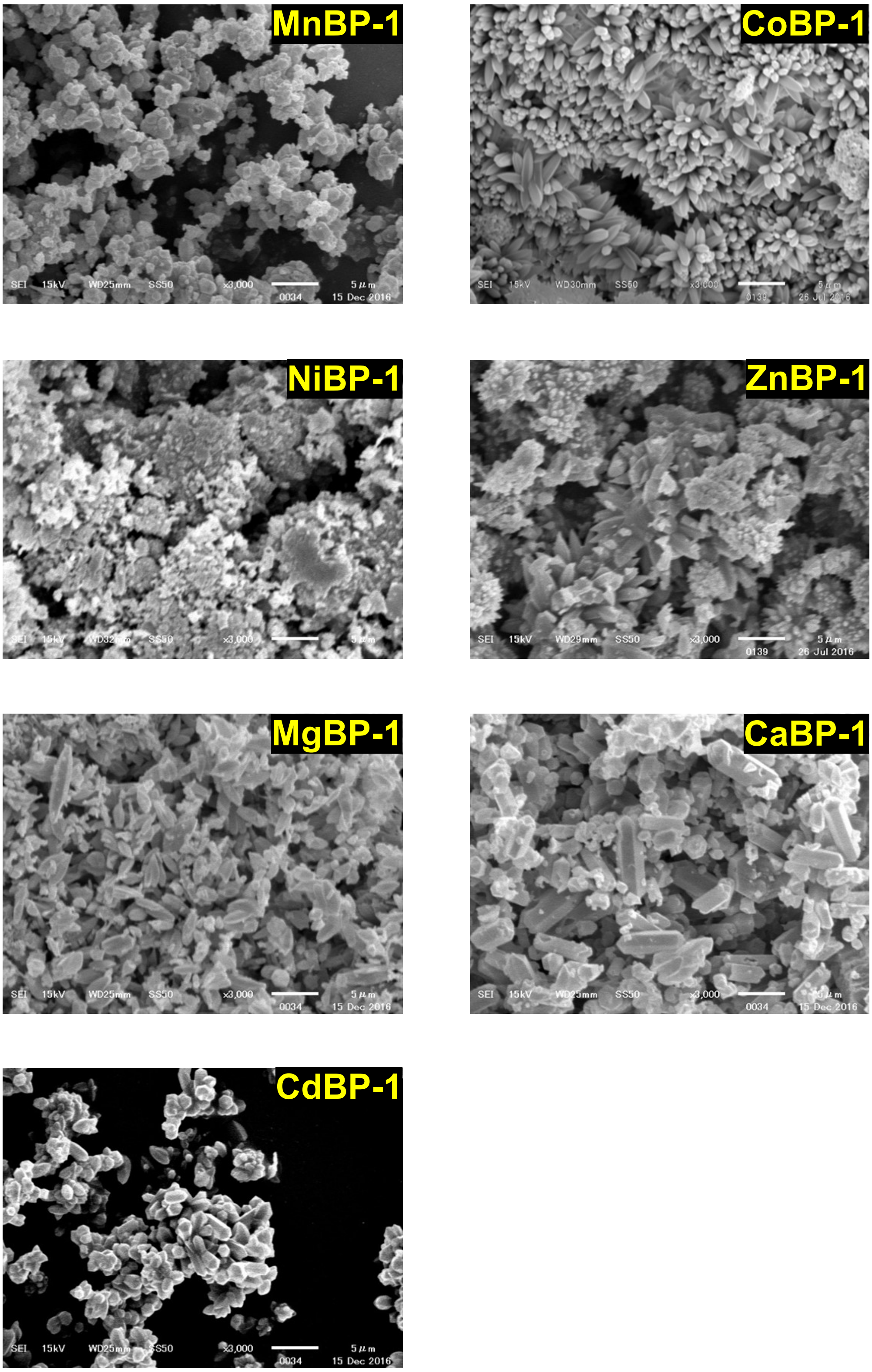

Fig. S5 SEM images of MBP-1 compounds. The white scale bars denote 5 μm.

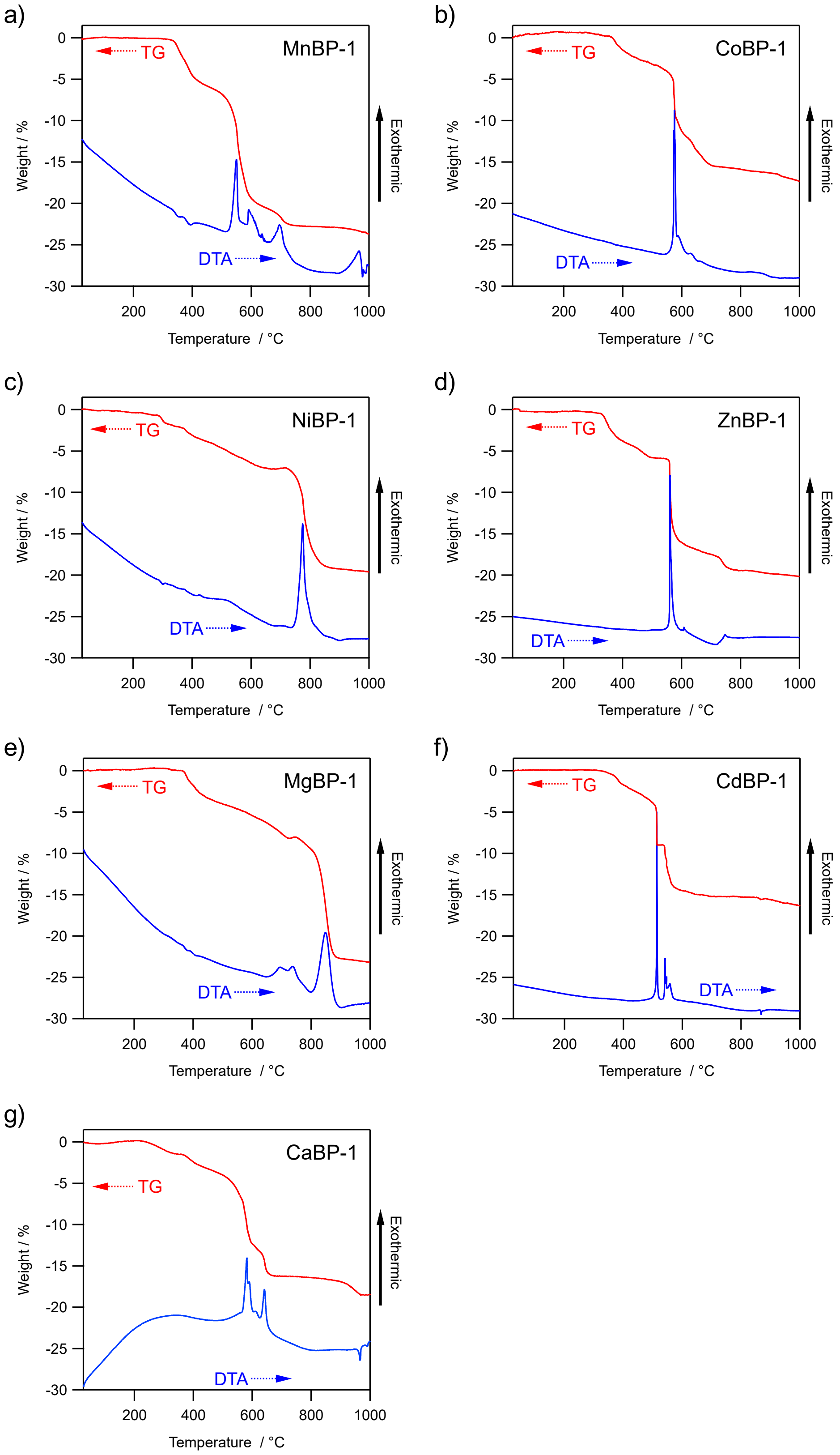

Fig. S6 TG-DTA curves of MBP-1 compounds measured under air. a) MnBP-1, b) CoBP-1, c) NiBP-1, d) ZnBP-1, e) MgBP-1, f) CdBP-1, and g) CaBP-1.

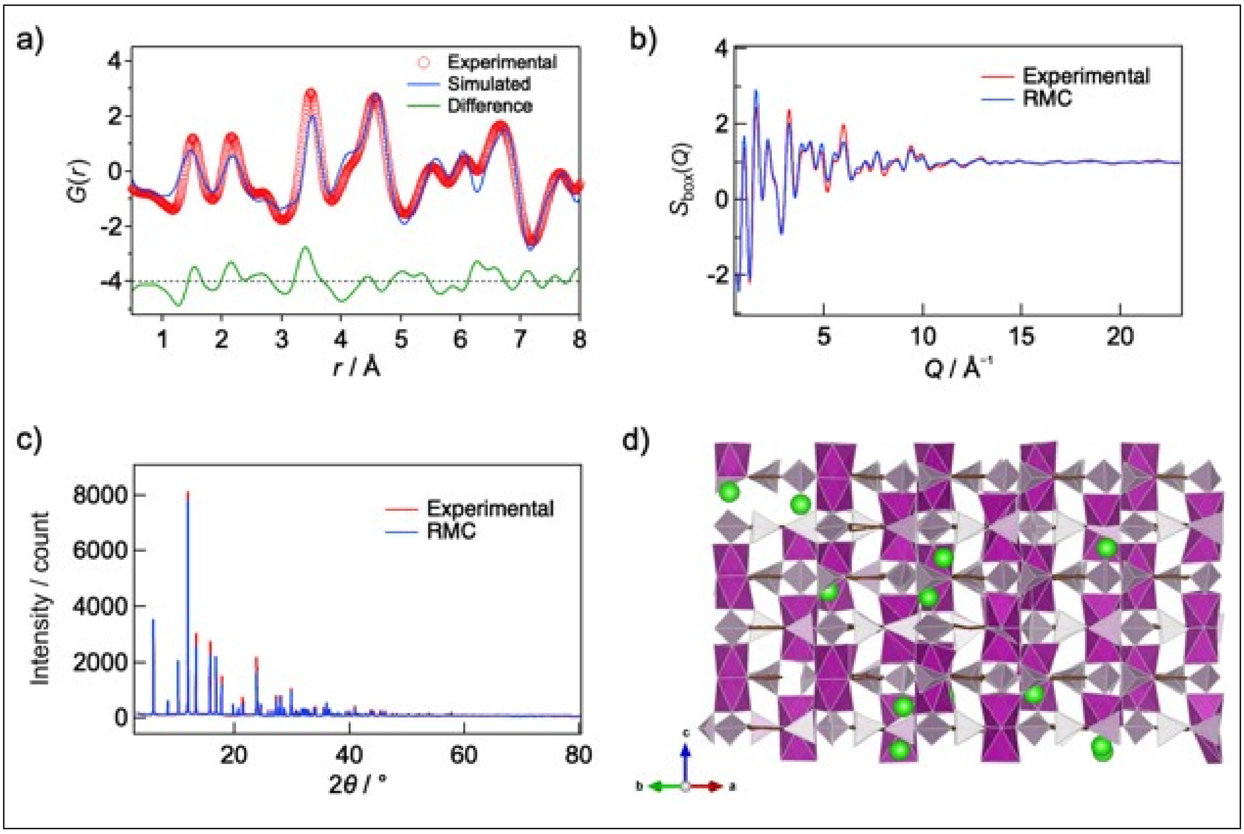

Fig. S7 (a) A reduced pair distribution function (PDF) of MnBP-1 The red circle represents the experimentally-obtained *G*(*r*) and the blue line represents the simulated *G*(*r*) using the refined unit cell. (b) X-ray structure factors $S_{\mathrm{box}}(Q)$, (c) Bragg profile, and (d) atomic configuration simulated by reverse Monte Carlo (RMC) modelling. Dark violet octahedra, pale violet tetrahedra, brown sticks, and green balls denote MnO_6, PCO_3, C-C bonds, and Mn site vacancies, respectively.

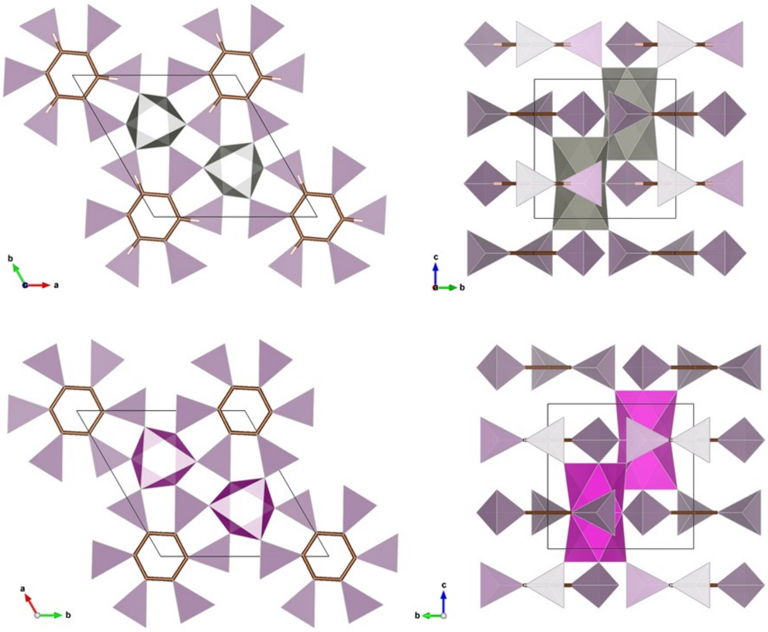

Fig. S8 Crystal structure of ZnBP-1 (upper) and CdBP-1 (lower) viewed along the *c*-axis (left) and the *a*-axis (right)

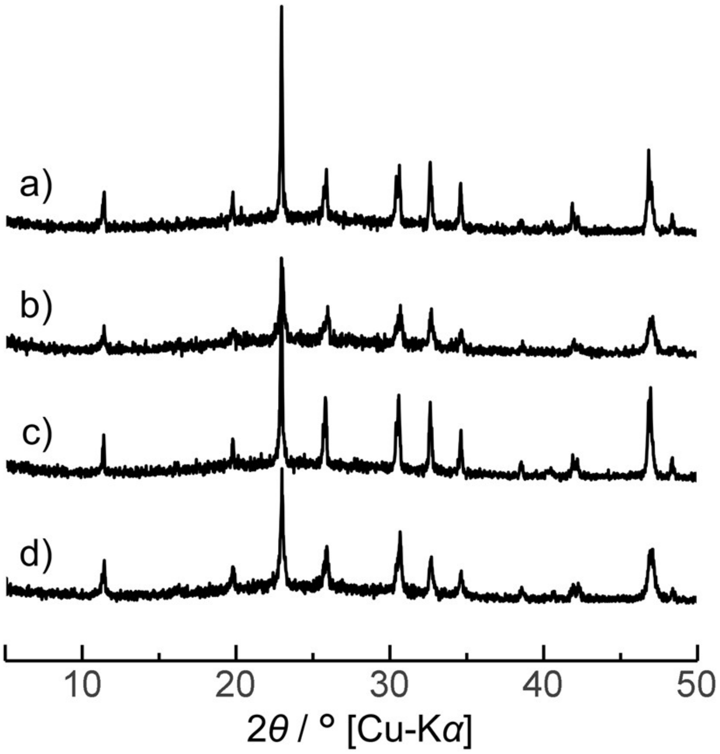

Fig. S9 PXRD patterns of MnBP-1 prepared at room temperatures (a, b) and in hydrothermal conditions (c, d) using chloride (a, c) and acetate (b, d) salts as the manganese (II) source.

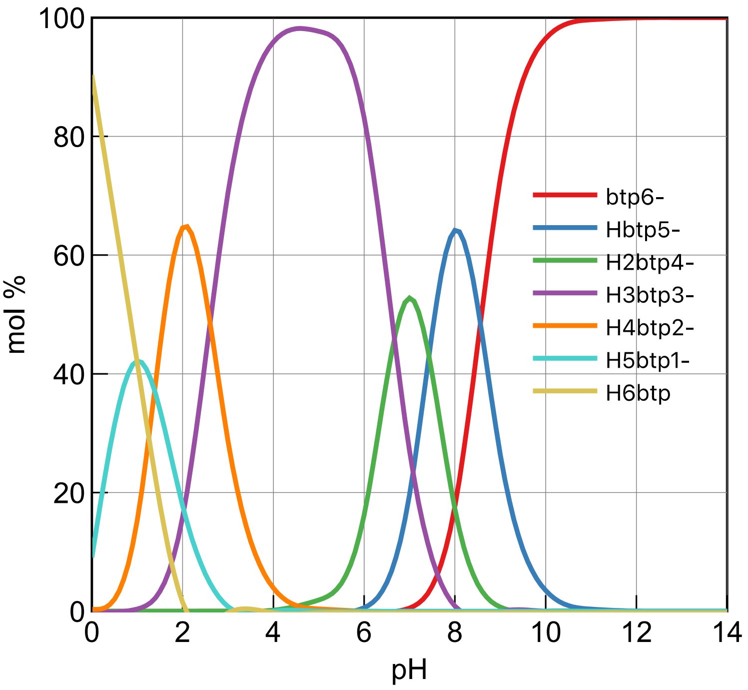

Fig. S10 The pH-dependence of BTP-derived deprotonated species in an aqueous solution.

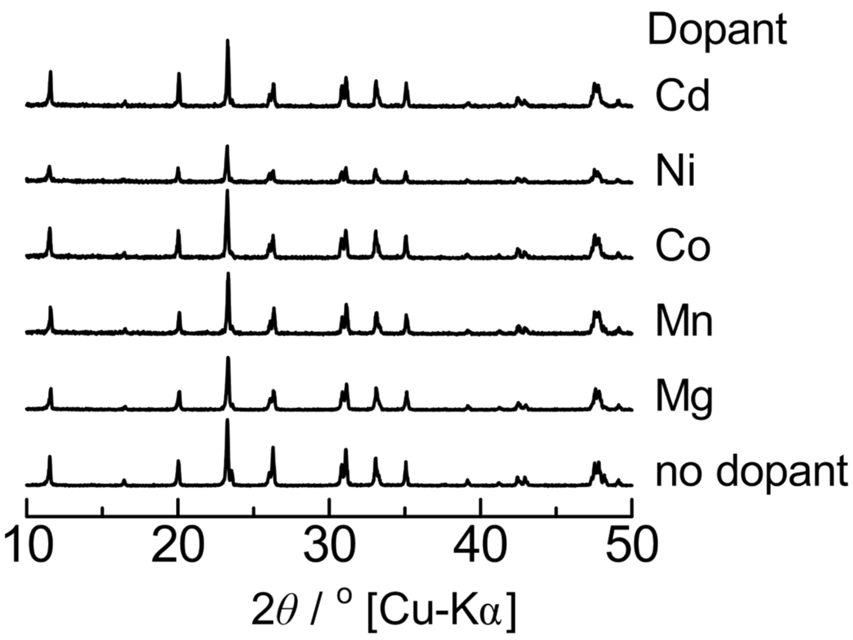

Fig. S11 XRD patterns of M/ZnBP-1 doped with 5 mol % divalent metal (M) cations.

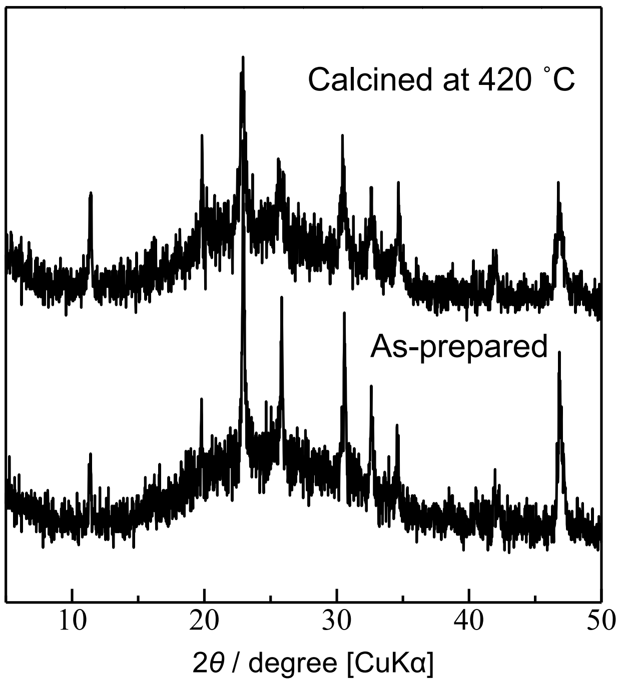

Fig. S12 XRD patterns of MnBP-1 samples as-prepared and calcined at 420 °C for 2 h under air.

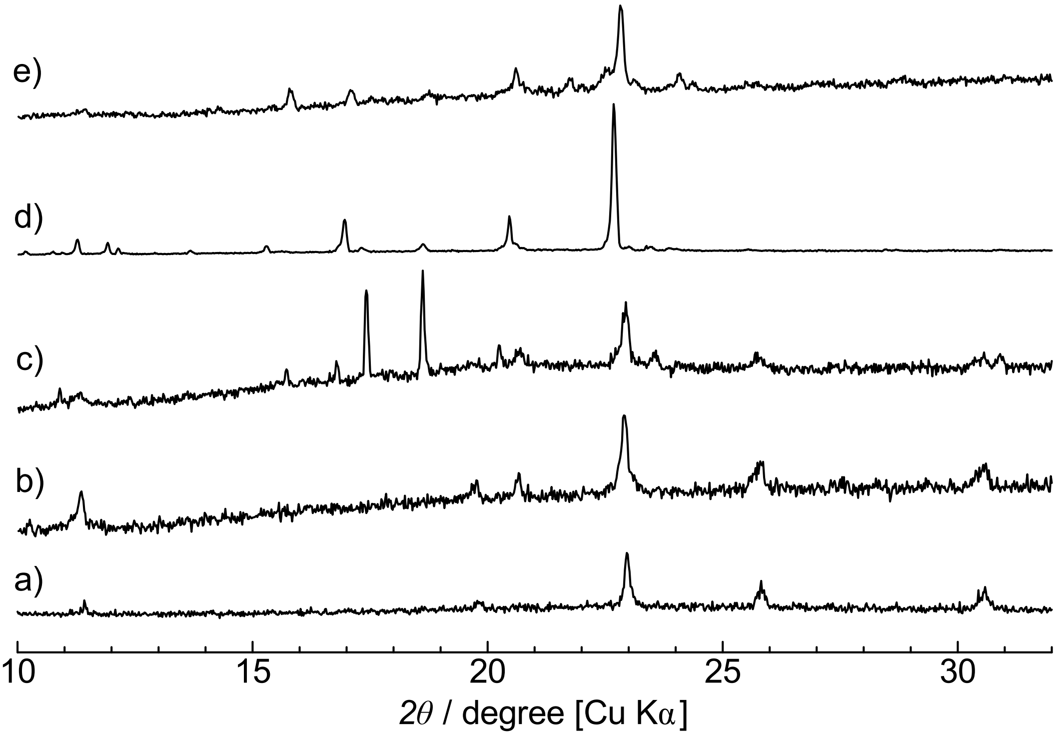

Fig S13 Ex situ XRD of MnBP-1 electrode; a) MnBP-1, b) pristine electrode, c) electrode after contacting with Li metal and rinsing with the electrolyte solution, d) after the first charge process, and e) after the first discharge process.

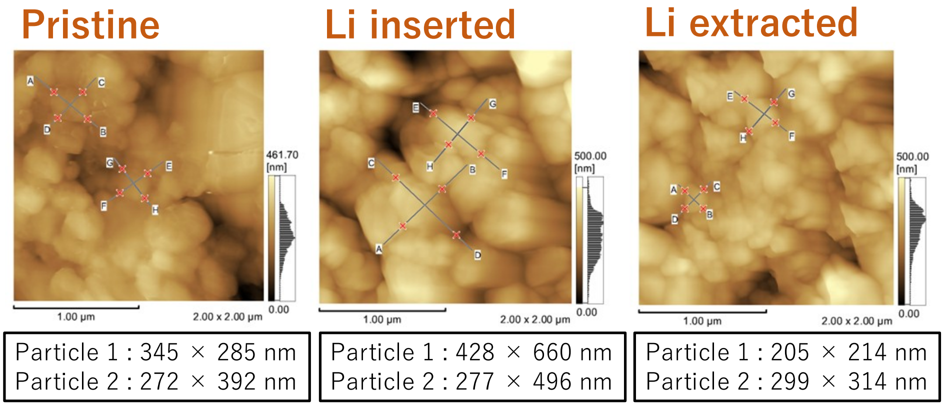

Fig S14 Scanning probe microscopy of MnBP-1 during the Li insertion-extraction cycle.

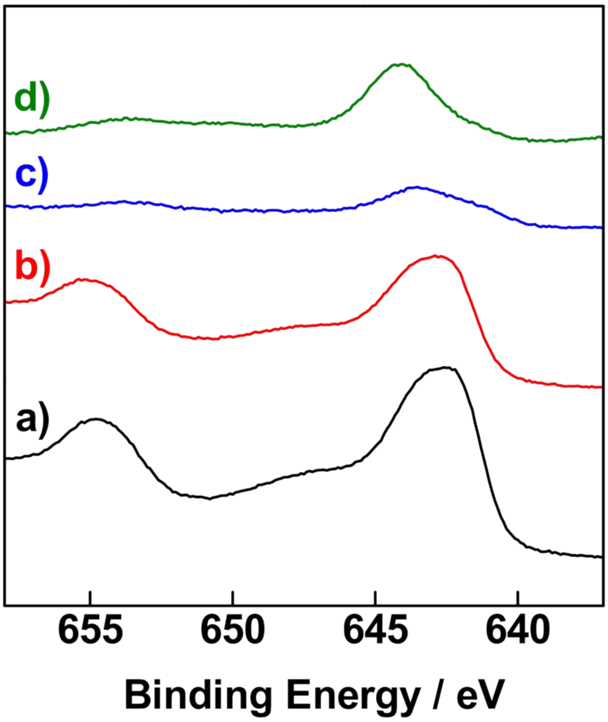

Fig S15 XPS spectra of the Mn $2p_{3/2}$ region of a) MnBP-1, b) pristine electrode, c) electrode after the second charge process, and d) after the second discharge process.

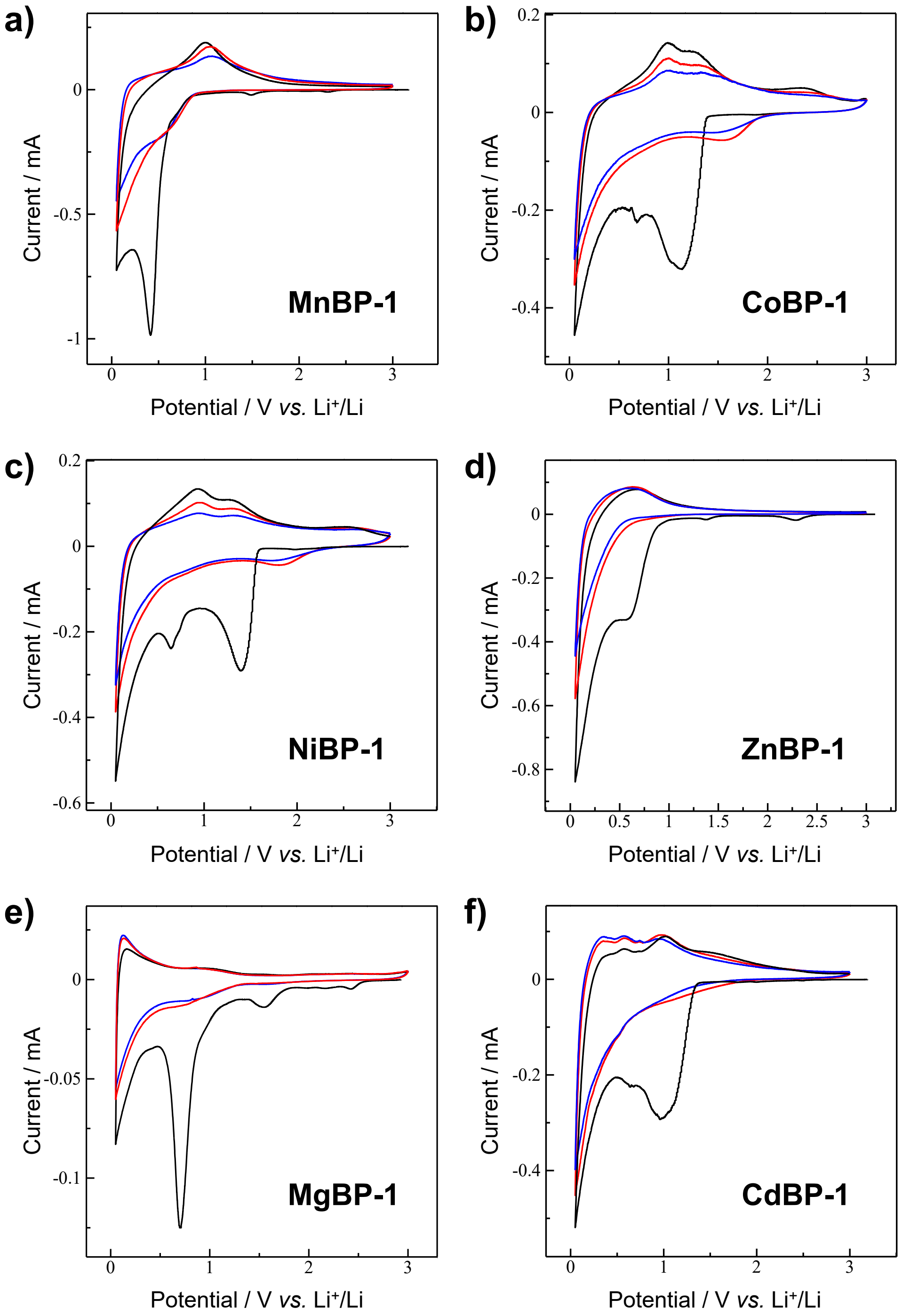

Fig. S16 Cyclic voltammetry (CV) curves of MBP-1 electrodes. a) MnBP-1, b) CoBP-1, c) NiBP-1, d) ZnBP-1, e) MgBP-1, and f) CdBP-1. Black, red, and blue lines denote the first, second, and third cycle, respectively.