

Electronic Supplementary Information

A [V₆B₂₀]-based architecture incorporating two types of organic amine ligands: innovative additives for enhancing the proton conductivity of Nafion membrane

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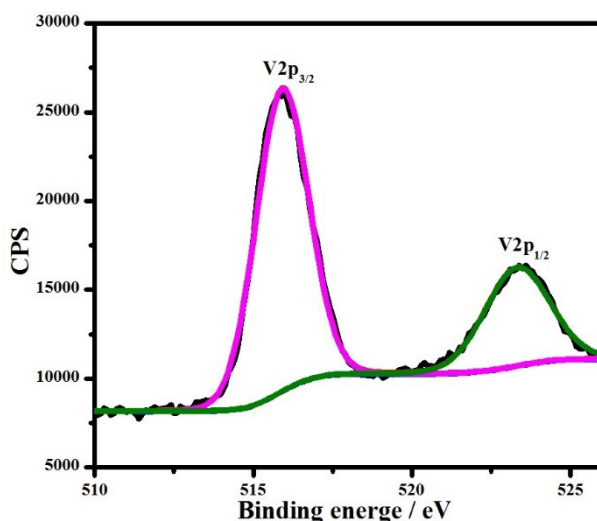


Fig. S1 XPS spectrum of vanadium in VB-1.

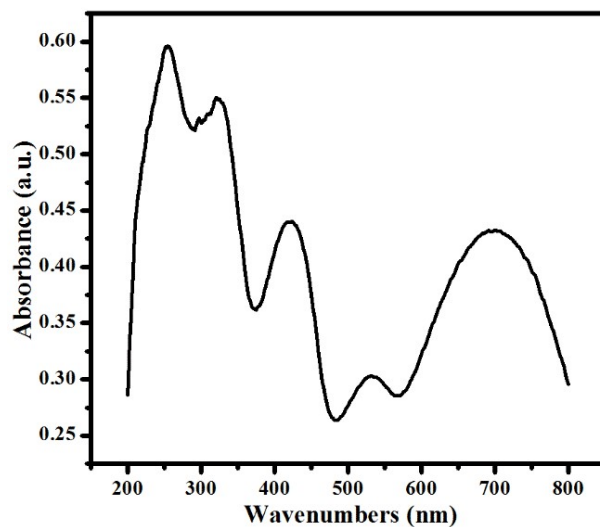


Fig. S2 UV-vis spectrum of VB-1.

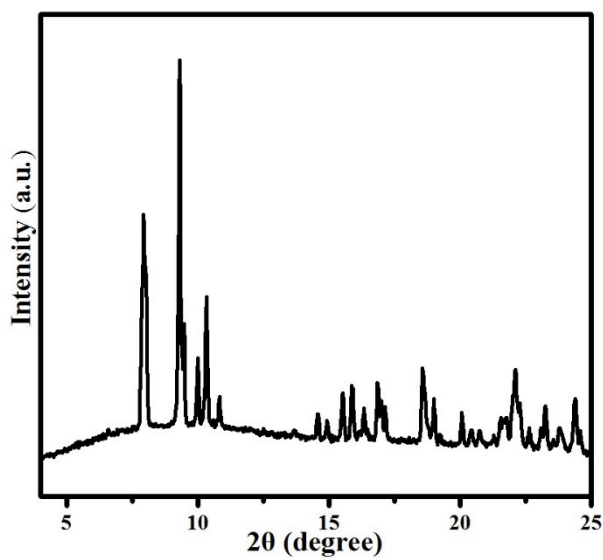


Fig. S3 PXRD pattern of VB-1/Nafion composite with a more limited x-axis range.

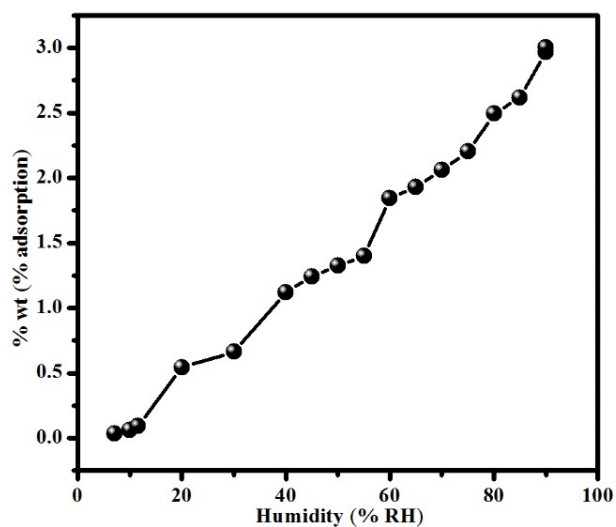


Fig. S4 The water adsorption isotherm of **VB-1** at 293 K.

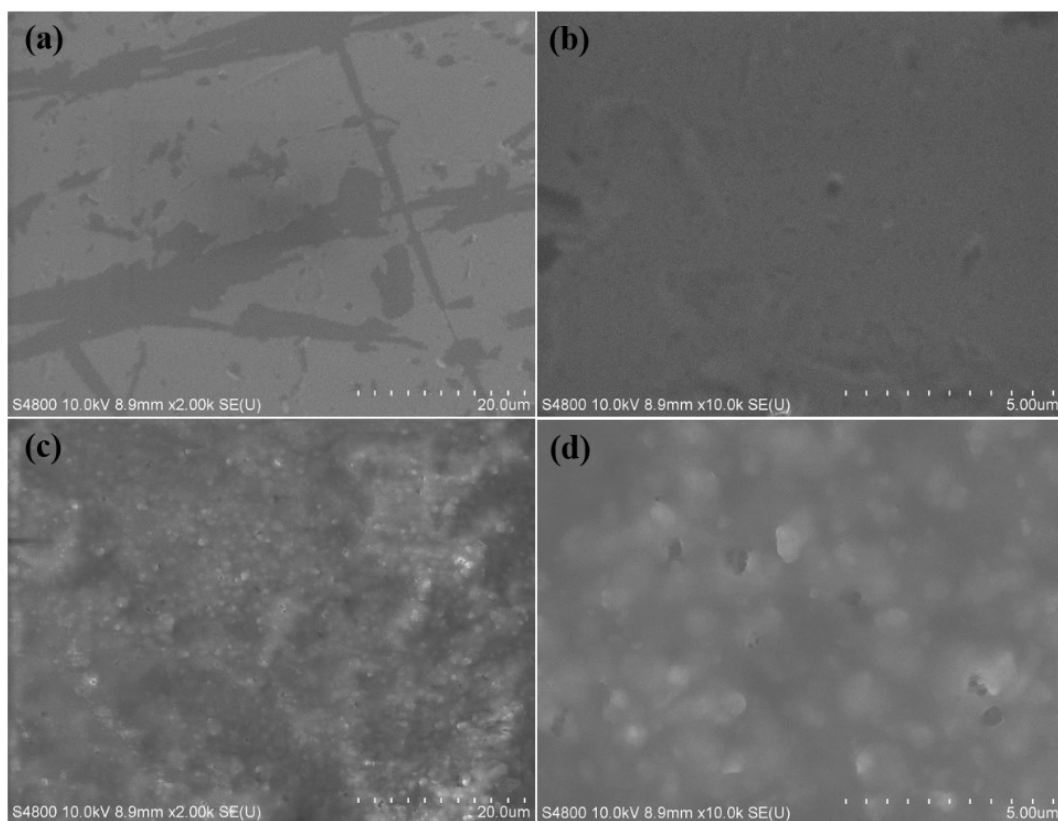


Fig. S5 SEM images of (a, b) Nafion and (c, d) **VB-1**/Nafion composite membranes.

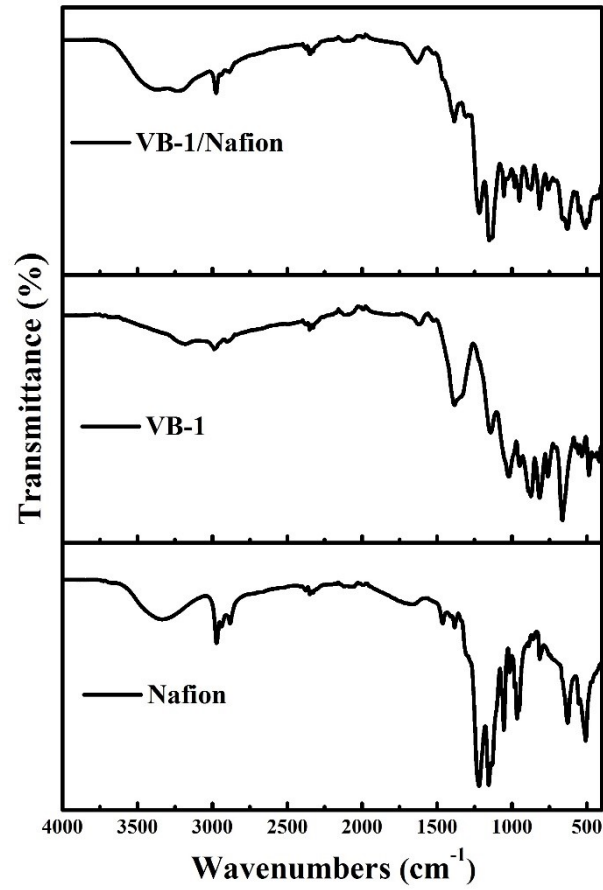


Fig. S6 FT-IR spectra of VB-1, pure Nafion and VB-1/Nafion composite membranes.

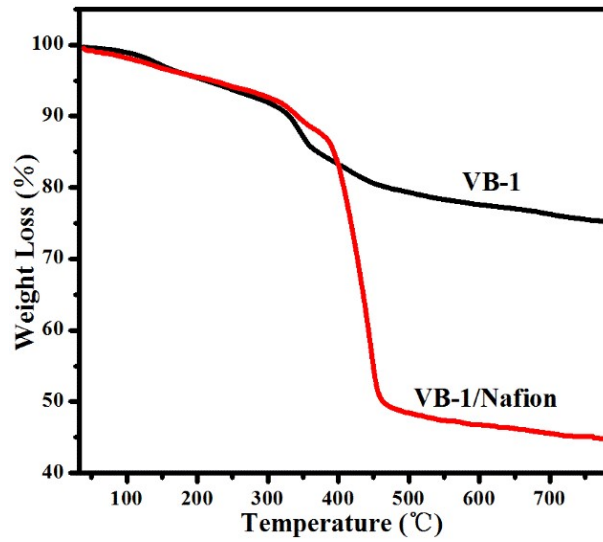


Fig. S7 TG curves of VB-1 and VB-1/Nafion in air.

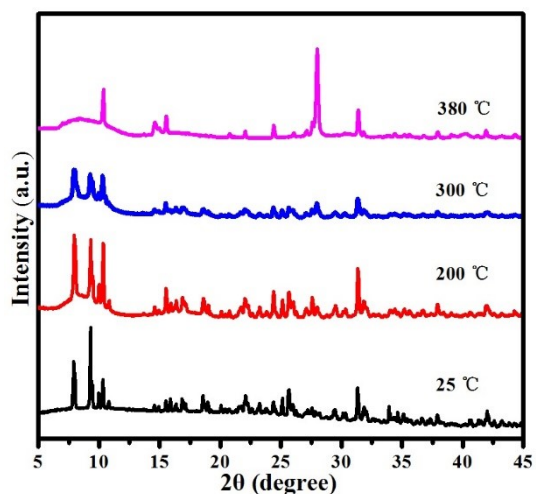


Fig. S8 PXR D patterns of VB-1/Nafion composite after thermal treatment at 200 °C, 300 °C and 380 °C.

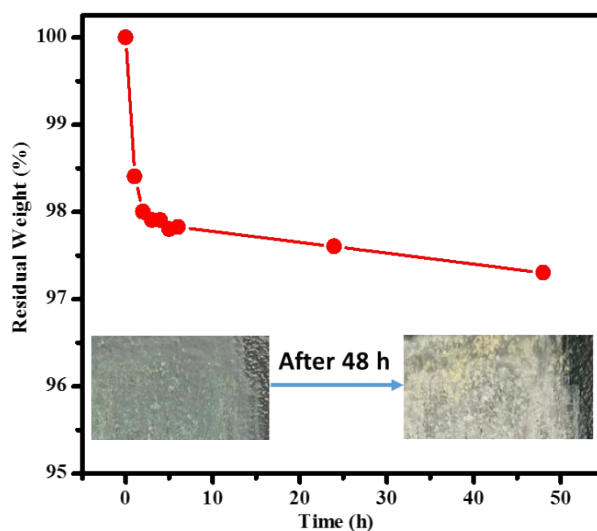


Fig. S9 Oxidative stability and digital photographs of VB-1/Nafion composite before and after Fenton's test at 60 °C for 48 h.

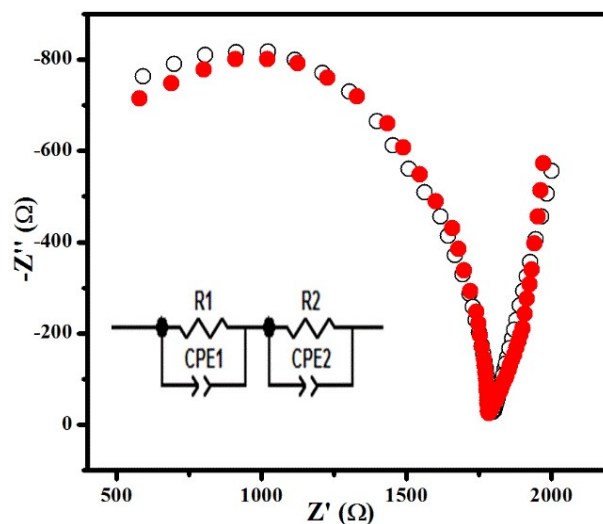


Fig. S10 Equivalent circuits used to fit the impedance data.

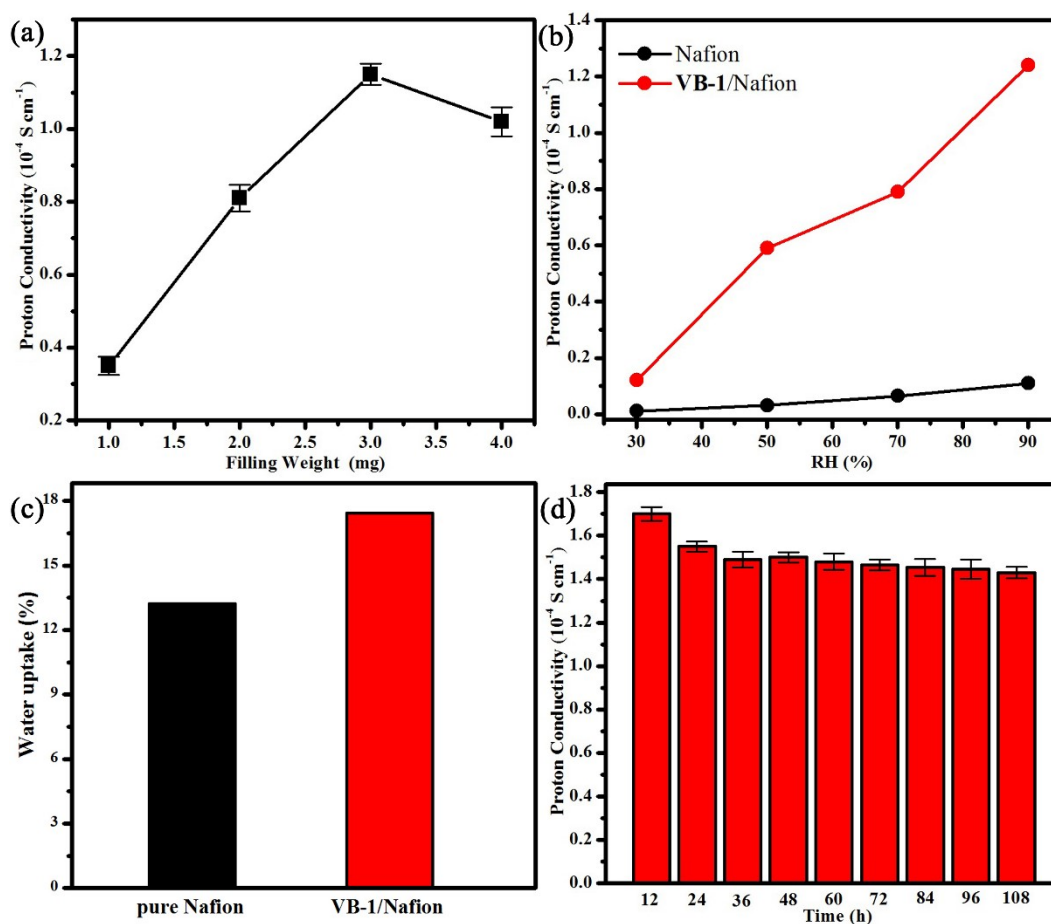


Fig. S11 Proton conductivities of VB-1/Nafion composite membranes investigated under different conditions: (a) varying weight loadings of VB-1 at 293 K, (b) different RHs at 343 K, (d) various time points during water immersion tests at 343 K; (c) the water uptake ratio of pure Nafion and VB-1/Nafion membranes.

Table S1 Bond lengths [Å] for **VB-1**

V1 V2	3.0425(15)	O16 B8	1.543(8)
O7 B5	1.511(8)	V3 O22	1.967(4)
V1 V31	3.0547(14)	O16 B10	1.480(9)
O7 B10	1.475(9)	V3 O23	1.610(5)
V1 O101	1.959(4)	O17 B10	1.438(8)
O8 B4	1.381(9)	O1 B1	1.371(9)
V1 O19	1.959(4)	O18 B8	1.414(8)
O9 B4	1.366(10)	O2 B1	1.352(9)
V1 O20	1.939(4)	O18 B9	1.436(8)
O9 B5	1.468(9)	O2 B9	1.457(8)
V1 O221	1.970(5)	O19 B8	1.459(8)
O10 B5	1.485(8)	O3 B1	1.374(9)
V1 O25	1.620(4)	O20 B9	1.452(8)
O11 B5	1.435(9)	O3 B2	1.469(9)
V2 V3	3.0477(15)	O21 B2	1.459(8)
O11 B6	1.427(9)	O4 B2	1.441(9)
V2 O101	1.973(5)	O22 B3	1.483(8)
O12 B6	1.478(8)	O4 B3	1.411(9)
V2 O121	1.956(4)	N1 C1	1.520(10)
O13 B6	1.470(8)	O5 B2	1.522(9)
V2 O20	1.964(4)	N2 C3	1.500(16)
O13 B7	1.360(10)	O5 B9	1.535(9)
V2 O21	1.944(4)	N3 C4	1.491(10)
O14 B7	1.379(9)	O5 B10	1.484(8)
V2 O24	1.604(5)	N4 C5	1.494(10)
O15 B7	1.358(9)	O6 B3	1.459(9)
V3 O121	1.960(4)	C1 C2	1.513(10)
O15 B8	1.468(8)	O6 B4	1.352(9)
V3 O191	1.963(4)	C2 C3	1.476(10)
O16 B6	1.525(8)	O7 B3	1.538(9)
V3 O21	1.957(4)	C4 C5	1.518(10)

Table S2 Bond angles [deg] for **VB-1**

V2 V1 V31	120.42(4)	C2 C1 N1	120.8(17)
V21 O12 V31	102.22(19)	O101 V2 V1	39.13(12)
O101 V1 V2	39.47(13)	C3 C2 C1	122.2(18)
B6 O12 V21	125.2(4)	O101 V2 V3	118.03(14)
O101 V1 V31	117.55(14)	C2 C3 N2	120.7(14)
B6 O12 V31	129.0(4)	O121 V2 V1	117.03(14)
O101 V1 O221	91.17(19)	N3 C4 C5	118(3)

B7 O13 B6	122.1(5)	O121 V2 V3	38.94(13)
O19 V1 V2	116.80(13)	N4 C5 C4	98.6(8)
B7 O15 B8	122.8(6)	O121 V2 O101	90.95(19)
O19 V1 V31	38.87(13)	O1 B1 O3	120.2(7)
B6 O16 B8	115.5(5)	O121 V2 O20	140.51(19)
O19 V1 O101	142.60(19)	O2 B1 O1	117.2(7)
B10 O16 B6	121.7(5)	O20 V2 V1	38.48(13)
O19 V1 O221	77.25(18)	O2 B1 O3	122.6(6)
B10 O16 B8	122.8(5)	O20 V2 V3	115.94(13)
O20 V1 V2	39.09(12)	O3 B2 O5	106.9(6)
B8 O18 B9	116.6(5)	O20 V2 O101	77.12(17)
O20 V1 V31	115.79(13)	O4 B2 O3	112.6(6)
V1 O19 V31	102.35(19)	O21 V2 V1	115.71(13)
O20 V1 O101	78.05(18)	O4 B2 O5	107.5(5)
B8 O19 V1	124.8(4)	O21 V2 V3	38.79(13)
O20 V1 O19	89.35(18)	O4 B2 O21	111.2(6)
B8 O19 V31	129.6(4)	O21 V2 O101	141.57(19)
O20 V1 O221	141.88(19)	O21 B2 O3	109.9(5)
V1 O20 V2	102.43(19)	O21 V2 O121	77.38(18)
O221 V1 V2	117.96(14)	O21 B2 O5	108.6(5)
B9 O20 V1	126.2(4)	O21 V2 O20	88.88(18)
O221 V1 V31	39.07(12)	O4 B3 O6	111.2(6)
B9 O20 V2	129.2(4)	O24 V2 V1	119.98(19)
O25 V1 V2	116.98(17)	O4 B3 O7	108.9(5)
V2 O21 V3	102.73(19)	O24 V2 V3	119.34(18)
O25 V1 V31	122.60(17)	O4 B3 O22	112.5(5)
B2 O21 V2	128.3(4)	O24 V2 O101	108.3(2)
O25 V1 O101	106.5(2)	O6 B3 O7	107.8(5)
B2 O21 V3	126.7(4)	O24 V2 O121	108.9(2)
O25 V1 O19	110.8(2)	O6 B3 O22	108.9(5)
V3 O22 V11	101.80(19)	O24 V2 O20	110.6(2)
O25 V1 O20	107.5(2)	O22 B3 O7	107.3(5)
B3 O22 V11	128.5(4)	O24 V2 O21	110.2(2)
O25 V1 O221	110.6(2)	O6 B4 O8	119.4(7)
B3 O22 V3	124.2(4)	V2 V3 V11	118.90(4)
V1 V2 V3	120.68(4)	O6 B4 O9	124.3(6)
O9 B4 O8	116.3(7)	O121 V3 V11	115.57(14)
O121 V3 V2	38.85(13)	O2 B9 O5	107.9(5)
O9 B5 O7	108.4(5)	B2 O5 B9	114.7(5)
O121 V3 O191	89.29(19)	O18 B9 O2	109.8(5)
O9 B5 O10	109.7(5)	B10 O5 B2	122.9(5)
O121 V3 O22	141.64(19)	O18 B9 O5	107.9(5)
O10 B5 O7	107.2(5)	B10 O5 B9	122.4(5)
O191 V3 V11	38.78(12)	O18 B9 O20	113.0(6)

O11 B5 O7	109.3(5)	B4 O6 B3	121.9(6)
O191 V3 V2	115.52(13)	O20 B9 O2	110.5(5)
O11 B5 O9	110.3(5)	B5 O7 B3	116.5(5)
O191 V3 O22	77.22(17)	O20 B9 O5	107.5(5)
O11 B5 O10	111.8(6)	B10 O7 B3	121.7(5)
O21 V3 V11	114.72(13)	O7 B10 O5	107.8(5)
O11 B6 O12	112.5(5)	B10 O7 B5	121.3(5)
O21 V3 V2	38.48(13)	O7 B10 O16	108.2(5)
O11 B6 O13	111.5(5)	B4 O9 B5	120.9(5)
O21 V3 O121	76.98(18)	O16 B10 O5	107.9(5)
O11 B6 O16	108.3(5)	V11 O10 V21	101.39(19)
O21 V3 O191	138.92(19)	O17 B10 O5	110.1(6)
O12 B6 O16	107.6(5)	B5 O10 V11	128.6(4)
O21 V3 O22	89.87(18)	O17 B10 O7	111.2(6)
O13 B6 O12	108.6(5)	B5 O10 V21	124.9(4)
O22 V3 V11	39.13(13)	O17 B10 O16	111.5(5)
O13 B6 O16	108.1(5)	B6 O11 B5	117.4(5)
O22 V3 V2	117.07(14)	O23 V3 O22	109.1(2)
O13 B7 O14	118.1(6)	O18 B8 O19	113.8(5)
O23 V3 V11	121.58(19)	B1 O2 B9	121.6(6)
O15 B7 O13	123.0(6)	O19 B8 O15	110.7(5)
O23 V3 V2	119.52(19)	B1 O3 B2	122.4(6)
O15 B7 O14	118.9(7)	O19 B8 O16	107.3(5)
O23 V3 O121	109.3(2)	B3 O4 B2	117.8(5)
O15 B8 O16	106.6(5)	O23 V3 O21	110.2(2)
O23 V3 O191	110.9(2)	O18 B8 O16	107.8(5)
O18 B8 O15	110.4(5)		

Symmetry transformations used to generate equivalent atoms: ¹2-X,1-Y,2-Z