Electronic Supplementary Information

Alternating Bimetallic Na/Mn Covalent and Ionic 1-D Chains

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All reactions were performed under aerobic conditions at room temperature and all reagents and solvents were used as purchased without further purification. ***Caution:*** Although no problems were encountered during the synthesis of the following compounds, due care and attention should be paid when using the potentially explosive perchlorate and nitrate salts.

Synthesis of $[Na_2Mn_2(biphen)_4(py)_3(EtOH)_2]_n$ (1)

To a solution containing $Mn(ClO_4)_2.6H_2O$ (0.25g, 0.985 mmol) in 40cm^3 EtOH, was added an excess of 2,2'-biphenol (0.73 g, 3.94 mmol). NaOH (0.157 g, 3.94 mmol) and pyridine (1cm^3, 12.4 mmol) were added in quick succession and the solution was stirred for 15 minutes. The resultant deep brown solution was then filtered and left to stand in the fume-cupboard covered by a perforated lid. X-ray quality crystals of **1** were obtained in 20 % yield upon slow evaporation of the mother liquor. Elemental analysis calculated (%) for $C_{67}H_{59}N_3O_{10}Na_2Mn_2$ (**1**): C 65.85, H: 4.87, N: 3.44; Found: C 65.62, H: 4.55, N: 3.07. FT-IR: 3534(w), 3049(w), 1586(w), 1556(m), 1486(s), 1469(s), 1428(s), 1393(m), 1272(s), 1250(s), 1233(s), 1231(sh), 1149(w), 1117(w), 1093(w), 1065(w), 1032(m), 1003(m), 931(m), 854(s), 754(s), 730(s), 707(s).

Synthesis of $[Na(BiphenH_2)(EtOH)_2(H_2O)][Mn(biphen)_2(4\text{-}cnp)_2]_n$ (2)

A 1.456 M aqueous solution of $Mn(NO_3)_2.4H_2O$ (1 cm^3, 1.45 mmol) and an excess of 2,2'-biphenol (1.08 g, 5.8 mmol) were dissolved in 40cm^3 EtOH. NaOH (0.23 g, 5.8 mmol) and 4-cyanopyridine (4-cnp) (0.6 g, 5.8 mmol) were then added in quick succession. The resultant deep brown solution was stirred for 1 h before being filtered and allowed to stand. X-ray quality needle-like crystals of **2** were obtained in 15 % yield upon slow evaporation of the mother liquor. Elemental analysis calculated (%) for $C_{52}H_{47}N_4O_9NaMn$ (**2**): C 65.75, H: 4.99, N: 5.90; Found: C 66.13, H: 4.98, N: 6.04. FT-IR: 3584(w), 3205(wb), 3051(w), 3002(w), 2967(w), 2547(wb), 2238(ms), 1663(w), 1596(m), 1557(w), 1545(w), 1489(s), 1468(s), 1452(s), 1430(s), 1410(s), 1381(m), 1273(m), 1250(s), 1222(s), 1153(m), 1117(m), 1094(m), 1043(m), 1004(m), 966(w), 935(m), 853(s), 827(s), 755(s), 735(s), 708(s). UV/vis (MeOH): λ_{max} [nm] (ε_{max} 10^3 dm^3 mol^{-1} cm^{-}

[1]): 205 (134.2), 241 (41.8), 281(29.3). (EtOH): 204 (117.5), 241 (38.1), 283 (27.3). (MeCN): 210 (90.6), 245(sh), 281 (22.7), 339 (8.6).

Synthesis of $[Na_2Mn_2(biphen)_4(3\text{-}cnp)_2(EtOH)_3]$ (3)

A 1.456 M aqueous solution of $Mn(NO_3)_2.4H_2O$ (1 cm^3, 1.45 mmol) and an excess of 2,2'-biphenol (1.08g, 5.8mmol) were dissolved in 40cm^3 EtOH. NaOH (0.23 g, 5.8 mmol) and 3-cyanopyridine (3-cnp) (0.6 g, 5.8 mmol) were then added in quick succession. The resultant deep brown solution was stirred for 1 h before being filtered and allowed to stand. X-ray quality needle-like crystals of **3** were obtained in 15 % yield upon slow evaporation of the mother liquor after 24 hours. Elemental analysis calculated (%) for $C_{66}H_{58}N_4O_{11}Na_2Mn_2$: C 63.98, H: 4.72, N: 4.52; Found: C 63.67, H: 4.41, N: 4.92. FT-IR: 3546(w), 3240(wb), 3060(w), 2966(w), 2545(wb), 2237(ms), 1592(m), 1555(w), 1543(w), 1488(s), 1468(s), 1430(s), 1380(m), 1273(m), 1250(s), 1226(s), 1189(m), 1151(m), 1117(m), 1095(m), 1049(m), 1004(m), 964(vw), 932(m), 878(w), 851(s), 839(s), 763(s), 750(s), 734(s), 709(s), 695(s).

Synthesis of $[Na(BiphenH_2)(EtOH)_3][Mn(biphen)_2(3\text{-}pic)_2]_n$ (4)

To a solution containing $Mn(ClO_4)_2.6H_2O$ (0.25g, 0.985 mmol) in 40cm^3 EtOH, was added an excess of 2,2'-biphenol (0.73 g, 3.94 mmol). NaOH (0.157 g, 3.94 mmol) and 3-picoline (1cm^3, 12.4 mmol) were added in quick succession and the solution was stirred for 15 minutes. The resultant deep brown solution was then filtered and left to stand in the fume-cupboard covered by a perforated lid. X-ray quality crystals of **4** were obtained upon slow evaporation of the mother liquor in 25 % yield. Elemental analysis calculated (%) for $C_{54}H_{60}N_2O_{10}NaMn$: (**4**).$H_2O$: C 66.52, H: 6.20, N: 2.87; Found: C 66.40, H: 6.30, N: 2.92. FT-IR: 3548(w), 3050(w), 2968(w), 1585(w), 1556(m), 1487(s), 1469(s), 1428(s), 1391(m), 1273(s), 1250(s), 1233(sh), 1231(sh), 1150(w), 1118(w), 1094(w), 1035(w), 1002(m), 929(m), 854(s), 753(s), 728(s), 706(s). UV/vis (MeOH): λ_{max} [nm] (ε_{max} 10^3 dm^3 mol^{-1} cm^{-1}): 204 (104.0), 240 (39.0), 284 (24.4). (EtOH): 205 (119.6), 241 (43.0), 285 (26.4). (MeCN): 204 (98.9), 247(sh), 285 (25.2), 335 (11.4).

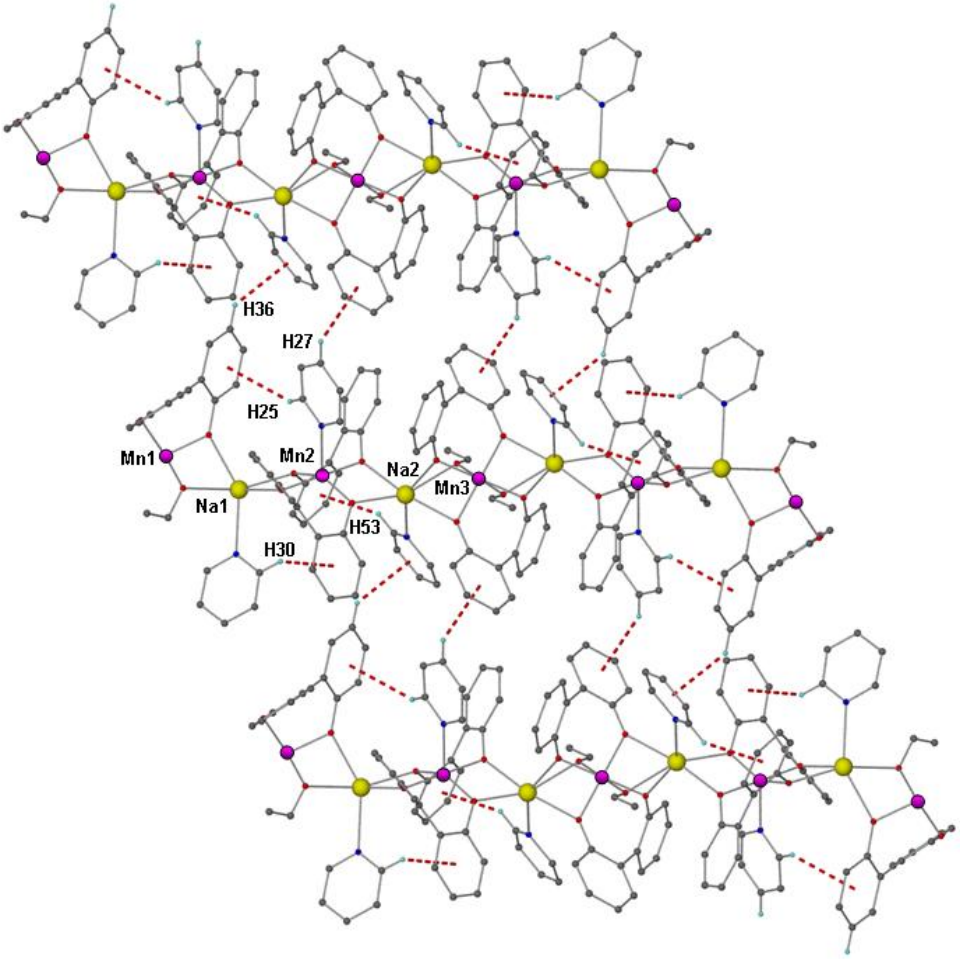

Fig. SI1 Schematic illustrating the intra- and interchain interactions occurring in the coordination polymer **1**. These are represented as dashed lines and have the distances: H27…$\pi_{centroid}$ = 2.907 Å, H46… $\pi_{centroid}$ = 2.850 Å, H25···$\pi_{centroid}$ = 2.995 Å, H53···$\pi_{centroid}$ = 2.768 Å, H30···$\pi_{centroid}$ = 2.913 Å.

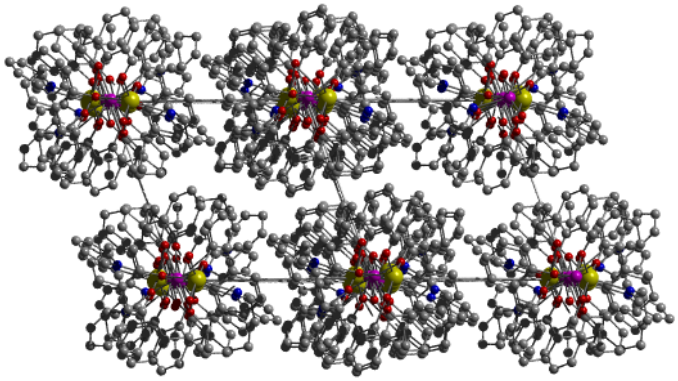

Fig SI2: Crystal packing observed in **1** as viewed along the [011] cell face.

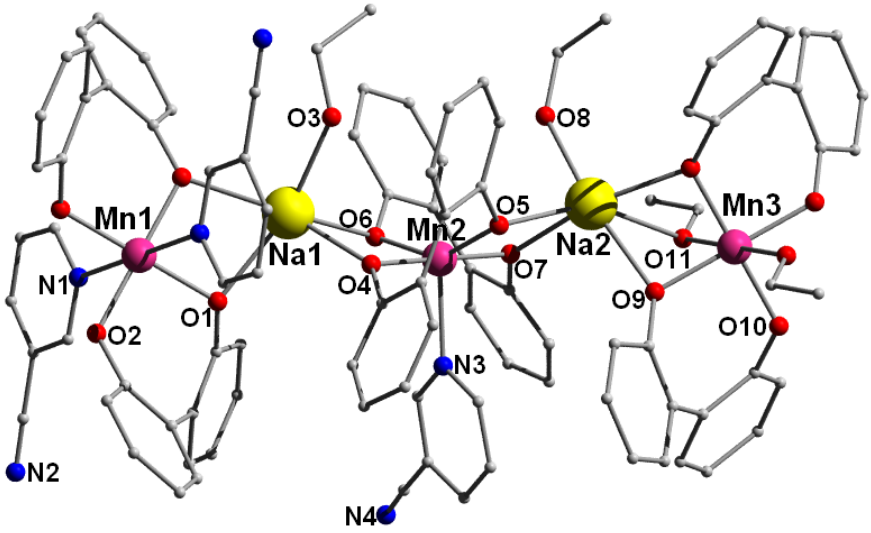

Fig SI3: Asymmetric unit in the covalent polymer **3** illustrating its structural similarities (although *not* isostructural) to that of **1.** Colour code: Yellow (Na), Purple (Mn), Red (O) Blue (N) and Grey (C).

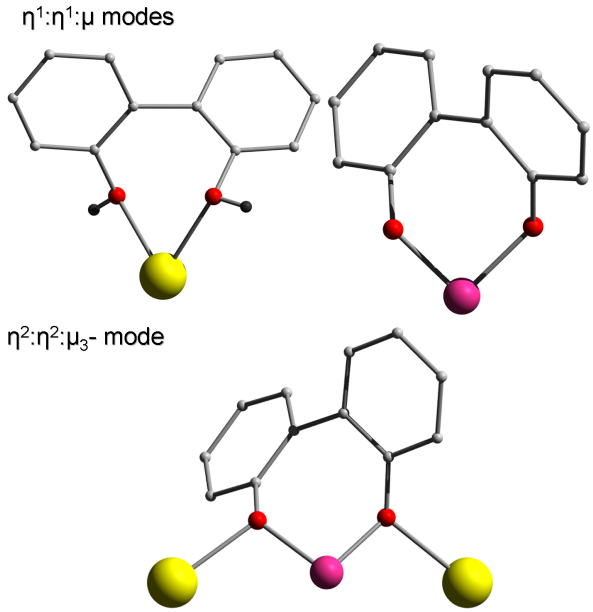

Fig SI4: Schematic illustrating the bonding modes observed in this work. Colour code: Yellow (Na), Purple (Mn), Red (O), Grey (C) and Black (H).

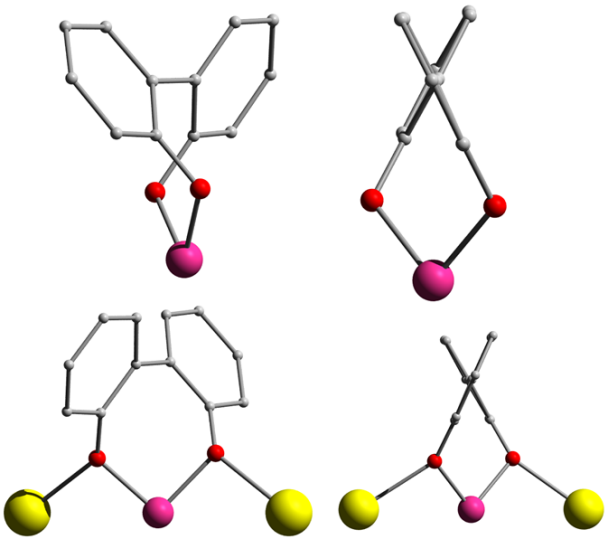

Fig SI5: Schematic illustrating the twisting of the 2,2'-biphenolate anionic ligands when forming **1**-**4** via chelating (top) and bridging (bottom) motifs. Colour code: Yellow (Na), Purple (Mn), Red (O) and Grey (C).

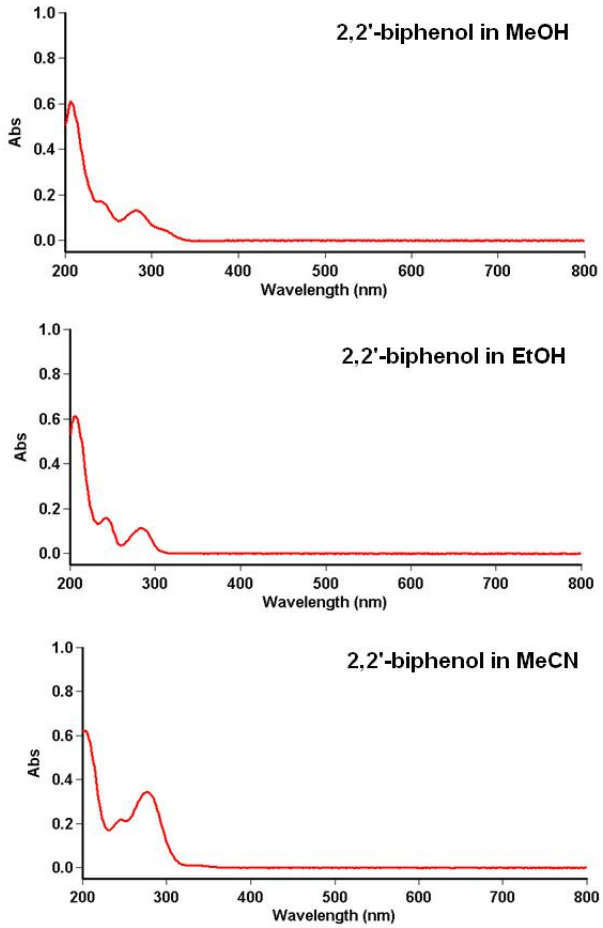

Fig. SI6 UV/vis spectra obtained from MeOH (top), EtOH (middle) and MeCN (bottom) solutions of 2,2'-biphenol. UV/vis (MeOH): λ_{max} [nm] (ε_{max} 10^3 dm^3 mol^{-1} cm^{-1}): 206 (37.9), 241 (10.8), 292 (8.2), 318(sh). (EtOH): 207 (38.1), 243 (9.8), 284 (8.3). (MeCN): 203 (38.6), 246 (13.6), 277 (21.2), 319 (2.6).

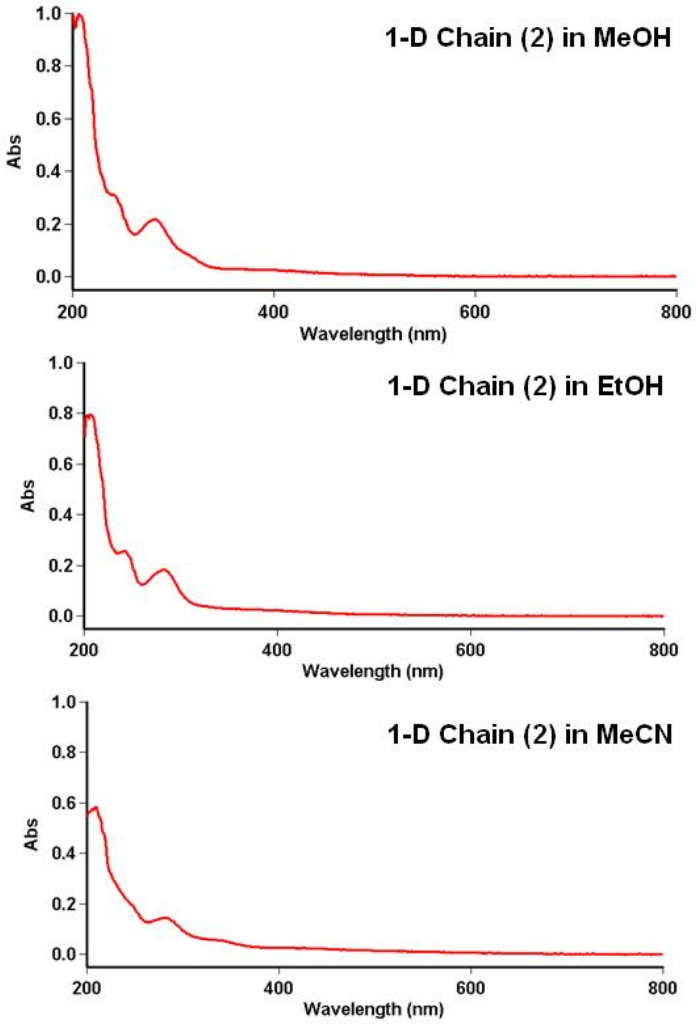

Fig. SI7 UV/vis spectra obtained from MeOH (top), EtOH (middle) and MeCN (bottom) solutions of the 1-D chain in **2**.

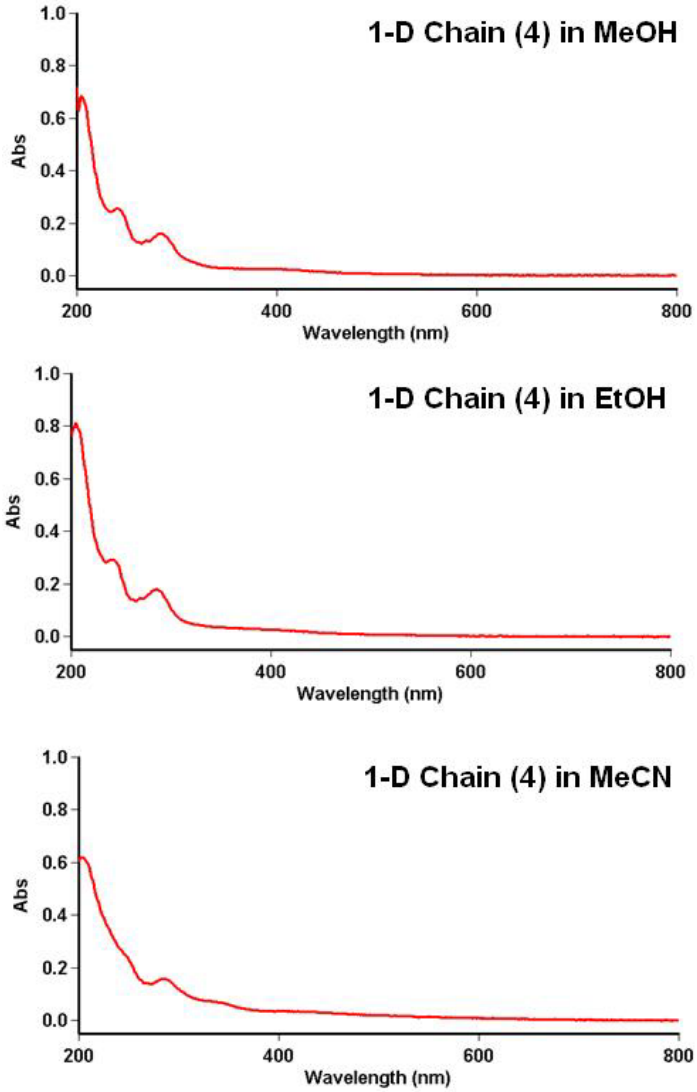

Fig. SI8 UV/vis spectra obtained from MeOH (top), EtOH (middle) and MeCN (bottom) solutions of the 1-D chain in **4**.

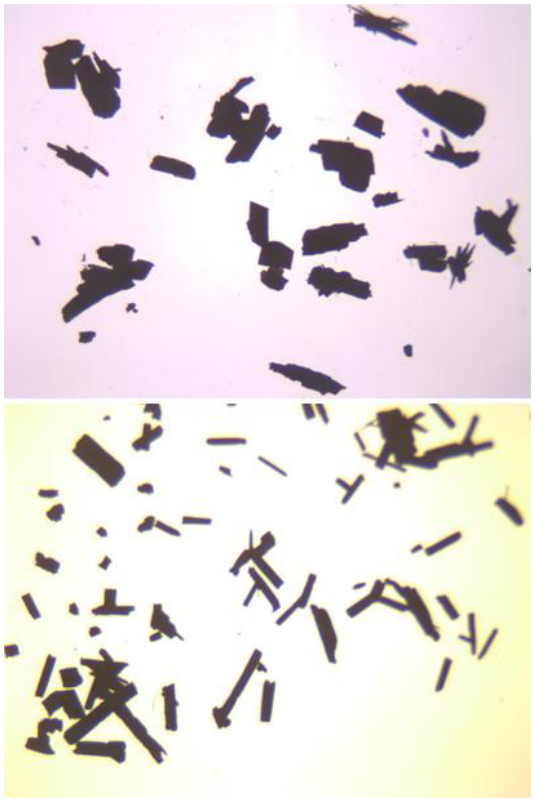

Fig. SI9 Microscope images of crystalline products of the covalent chain **1** (top) and ionic chains **2** (bottom).

Table SI1 Intra-chain metal…metal distances in the 1-D chains **1-4**

(1)	
Mn2···Na2	3.306
Mn2···Na1	3.339
Mn1···Na1	3.153
Mn3···Na2	3.142
(2)	
Mn1···Na1	5.256
(3)	
Mn1···Na1	3.182
Mn3···Na2	3.075
Mn2···Na2	3.294
Mn2···Na1	3.231
(4)	
Mn1···Na1	5.251

Table SI2 BVS calculations on Mn ions in **1-4**

Chain		**Atom label and BVS result**
1	**Calculated as:**	**Mn1**
	Mn^{2+}	3.38
	Mn^{3+}	3.11
	Mn^{4+}	3.05
	Calculated as:	**Mn3**
	Mn^{2+}	3.04
	Mn^{3+}	3.10
	Mn^{4+}	3.36
2	**Calculated as:**	**Mn1**
	Mn^{2+}	3.30
	Mn^{3+}	3.05
	Mn^{4+}	2.99
3	**Calculated as:**	**Mn1**
	Mn^{2+}	3.24
	Mn^{3+}	2.99
	Mn^{4+}	2.93
	Calculated as:	**Mn3**
	Mn^{2+}	3.46
	Mn^{3+}	3.19
	Mn^{4+}	3.13
4	**Calculated as:**	**Mn3**
	Mn^{2+}	3.19
	Mn^{3+}	2.94
	Mn^{4+}	2.89

X-ray diffraction details on the collection of 1-4

The structures of **1-4** were collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source. Each data reduction was carried out on the CrysAlisPro software package. The structures were solved by direct methods (SHELXS-97)[1] and refined by full matrix least squares using SHELXL-97.[2] SHELX operations were automated using the OSCAIL software package.[3] All hydrogen atoms within the covalent chains **1** and **3** were assigned to idealised positions. The majority of the hydrogen atoms in the ionic chains of **2** and **4** were also assigned to ideal positions however the H-bonding H atoms (H5A-H8A in **2** and H5A-H9A in **4**) were located in the difference map and restrained to no less than 0.85(1) Å from their corresponding O atoms (O5-O8 in **1**, O5-O9 in **4**) using the DFIX parameter. The bridging EtOH labelled O5-C35-C36 in **1** was successfully modelled as disordered over two sites (60:40) using the PART function. The H atoms (H5A and H10) of the two bridging EtOH ligands were assigned to idealised positions. The proton (H11A) of the one EtOH ligand that bridges Na2 and Mn3 in **3** was assigned to an idealised position using a riding model in an identical fashion to the bridging EtOHs in **1** described above.

1. G. M. Sheldrick, *Acta. Crystallogr., Sect. A: Found. Crystallogr.,* 1990, **A46**, 467.
2. G. M. Sheldrick, SHELXL-97, A computer programme for crystal structure determination, University of Gottingen, 1997.
3. P. McArdle, P. Daly and D. Cunningham, *J. Appl. Crystallogr.*, 2002, **35**, 378.