Electronic Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information

A Series of Alternating Na/M^{3+} (M = Mn, Fe) Covalent and Ionic Chains

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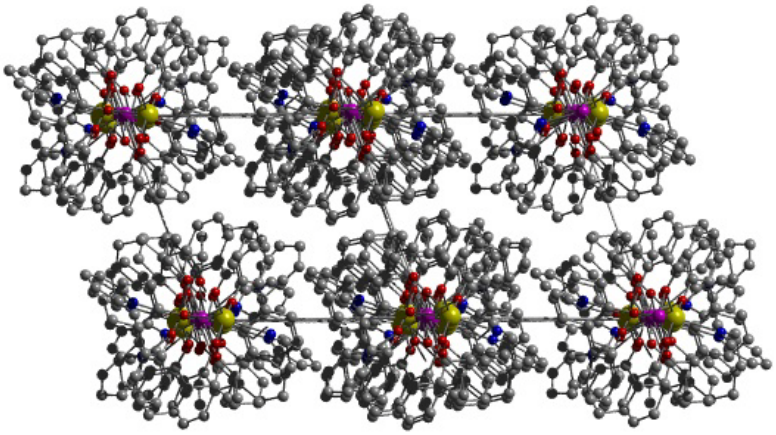

Fig S1: Crystal packing observed in **1** as viewed along the [011] cell face.

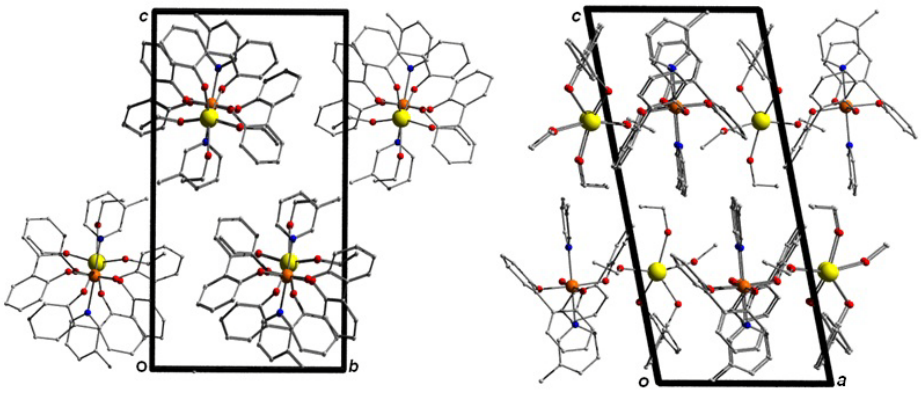

Fig S2: Crystal packing observed in **3** as viewed down the *a* (left) and *b* axis (right) respectively.

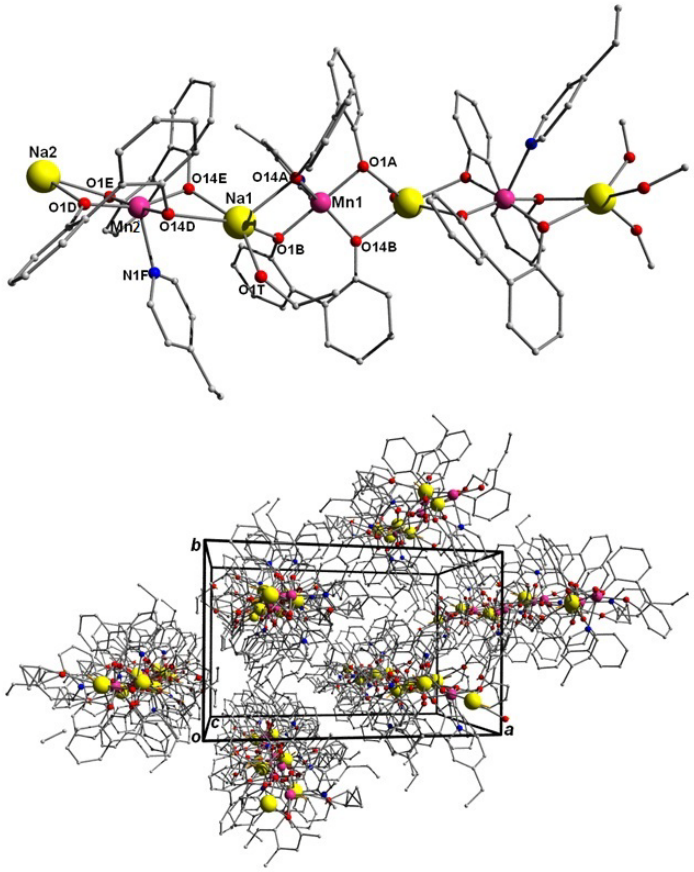

Fig. S3 (top) Part of a 1-D row in chain **6**. Hydrogen atoms have been omitted for clarity. (bottom) View of the chains in **6** propagating along the *c* cell direction.

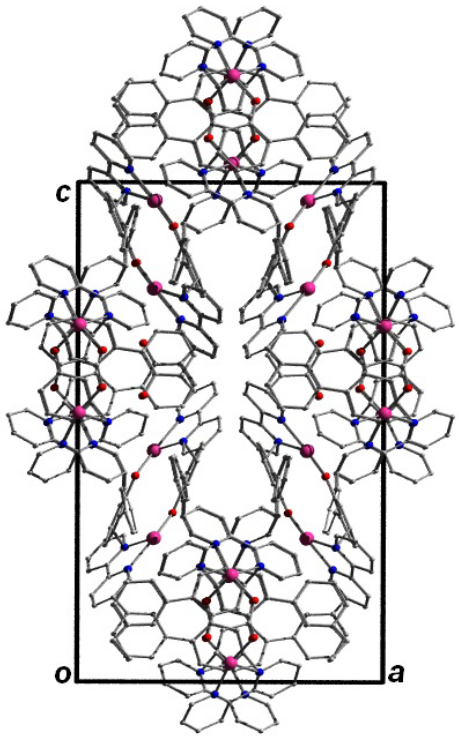

Fig S4: Crystal packing observed in complex **7** as viewed along the *b* axis. The 1-D zig zag rows of $[Mn(biphenH)_2(bipy)_2]$ units propagate along the *a* axis and therefore across the page.

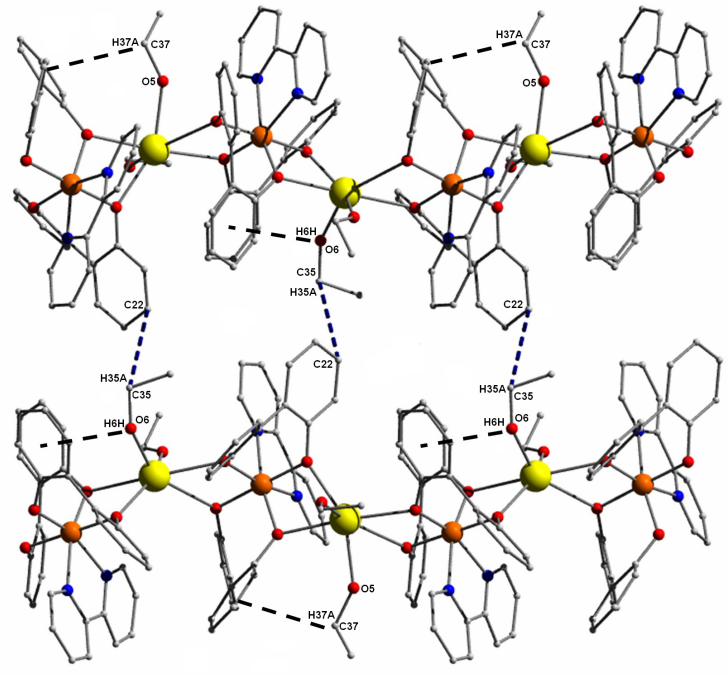

Fig. S5 (top) Crystal structure of **8** showing various intra- and interchain interactions exhibited within the crystal. H atoms have been omitted for clarity.

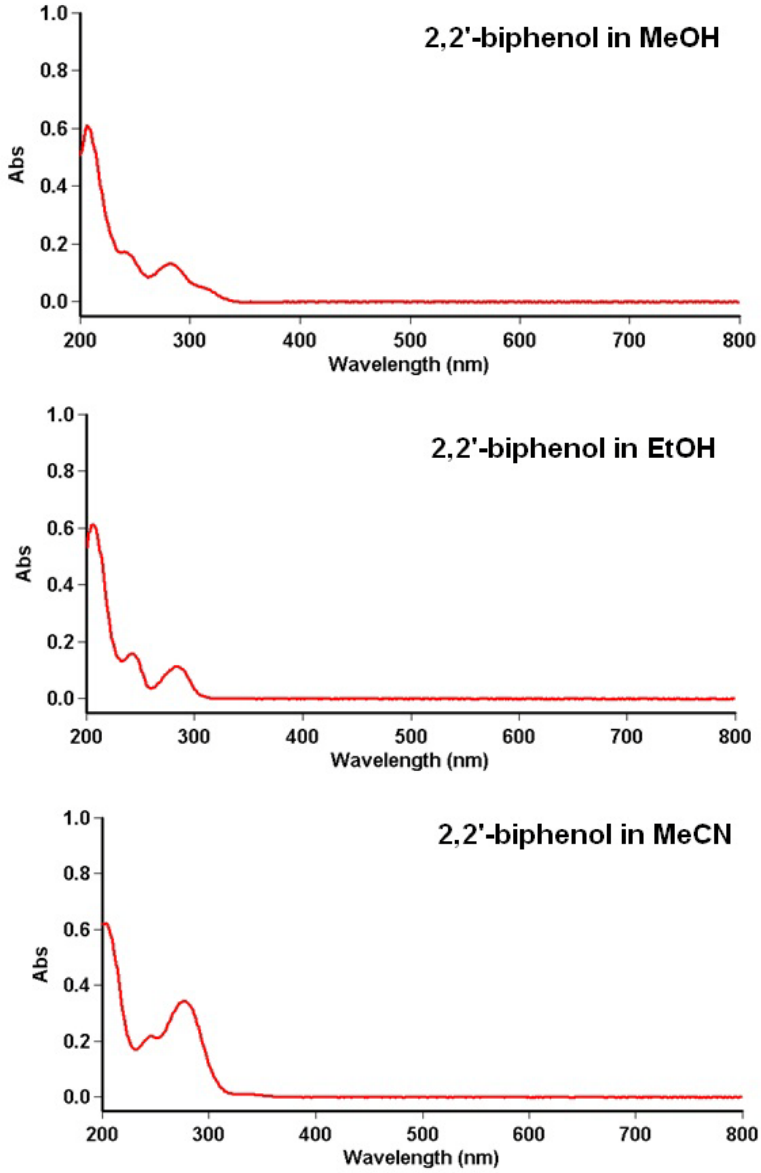

Fig. S6 UV/vis spectra obtained from MeOH (top), EtOH (middle) and MeCN (bottom) solutions of 2,2'-biphenol. UV/vis (MeOH): λ_{max} [nm] (ε_{max} 10^3 dm^3 mol^{-1} cm^{-1}): 206 (37.9), 241 (10.8), 292 (8.2), 318(sh). (EtOH): 207 (38.1), 243 (9.8), 284 (8.3). (MeCN): 203 (38.6), 246 (13.6), 277 (21.2), 319 (2.6).

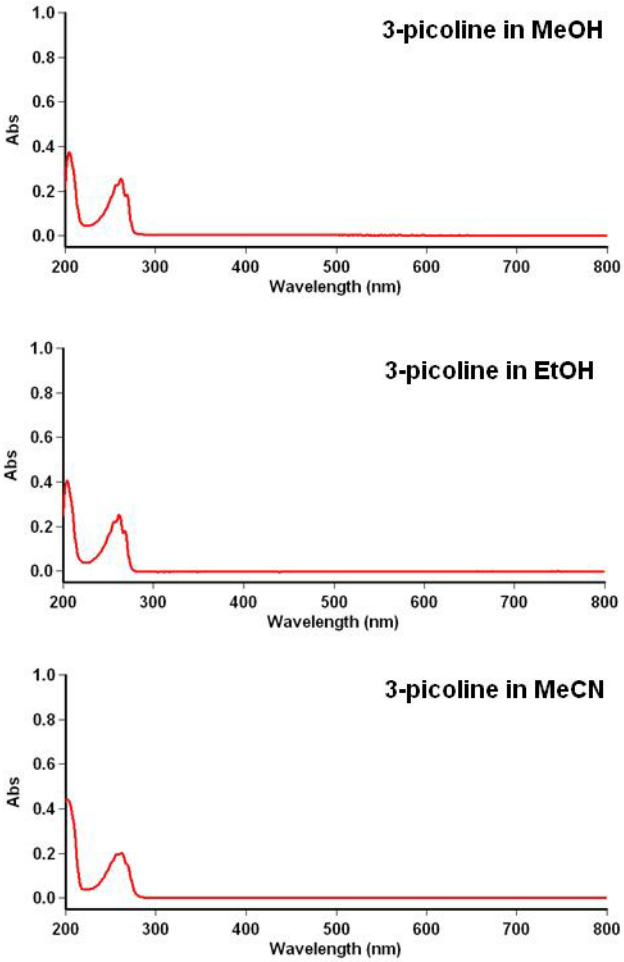

Fig. S7 UV/vis spectra obtained from MeOH (top), EtOH (middle) and MeCN (bottom) solutions of 3-picoline. UV/vis (MeOH): λ_{max} [nm] (ε_{max} 10^3 dm^3 mol^{-1} cm^{-1}): 204 (4.5), 256 (2.7), 262 (3.1), 268 (2.25). (EtOH): 204 (4.95), 250 (1.99), 257 (2.75), 262 (3.06), 269 (2.16). (MeCN): 202 (5.0), 257 (2.37), 262 (2.46), 268 (1.87).

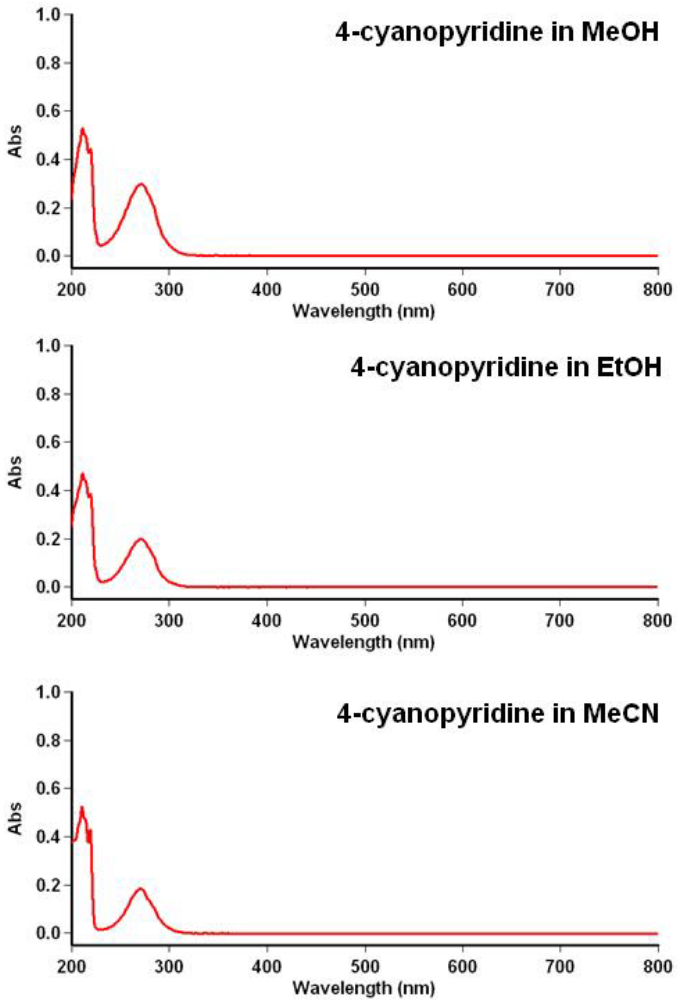

Fig. S8 UV/vis spectra obtained from MeOH (top), EtOH (middle) and MeCN (bottom) solutions of 4-cyanopyridine. UV/vis (MeOH): λ_{max} [nm] (ε_{max} 10^3 dm^3 mol^{-1} cm^{-1}): 211 (9.18), 219 (7.69), 271 (5.16). (EtOH): 211 (8.16), 219 (6.7), 271 (3.44). (MeCN): 210 (9.10), 219 (7.43), 270 (3.21).

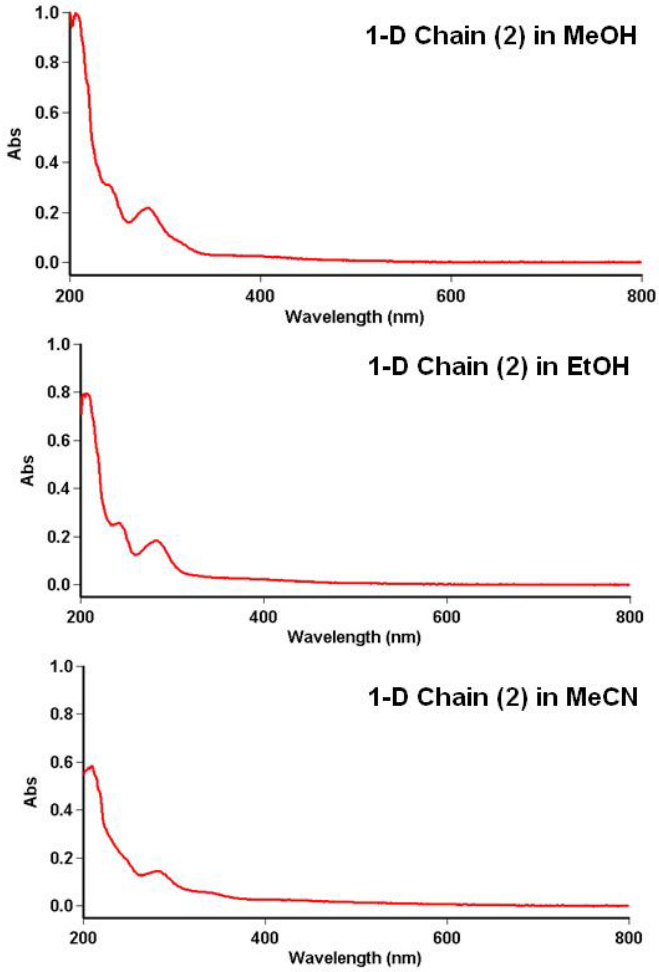

Fig. S9 UV/vis spectra obtained from MeOH (top), EtOH (middle) and MeCN (bottom) solutions of the 1-D chain in **2**.

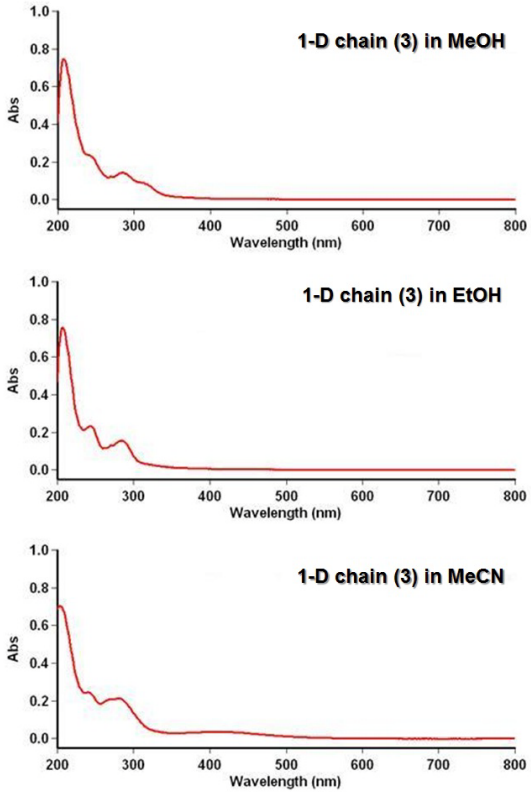

Fig. S10 UV/vis spectra obtained from MeOH (top), EtOH (middle) and MeCN (bottom) solutions of the chain in **4**.

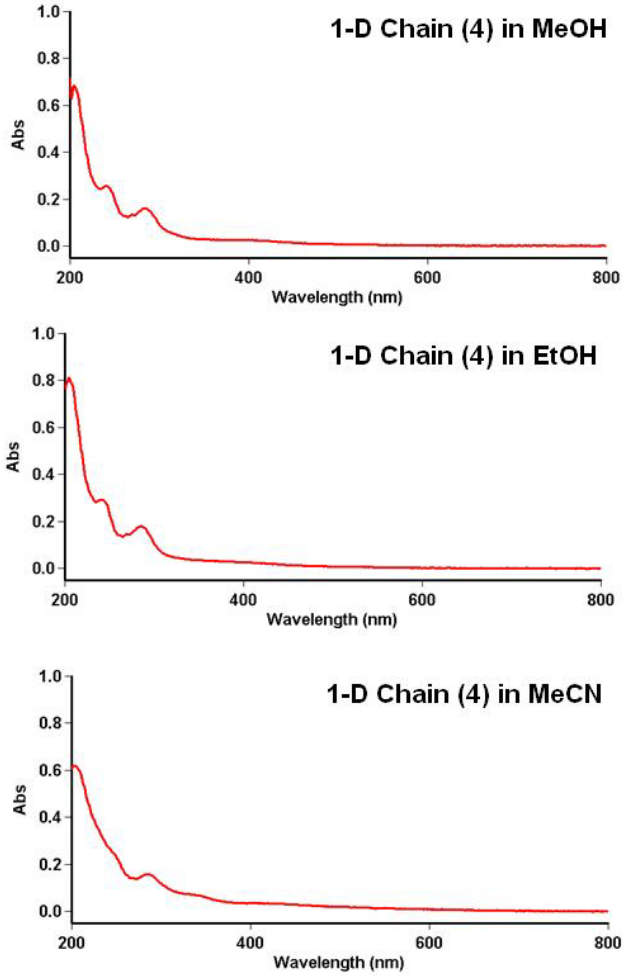

Fig. S11 UV/vis spectra obtained from MeOH (top), EtOH (middle) and MeCN (bottom) solutions of the Fe / Na chain in **5**.

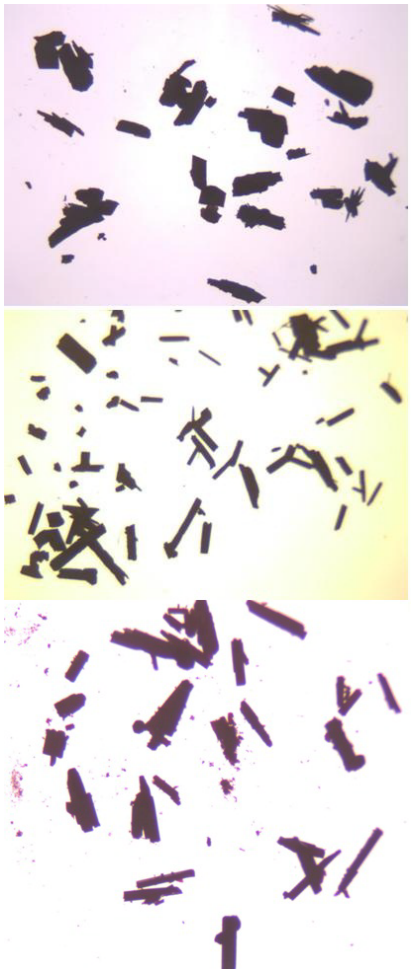

Fig. S12 Microscope images of crystalline products of the covalent Mn / Na chain **1** (top), the ionic Mn / Na chain **4** (middle) and the Fe / Na covalent chain **3** (bottom).

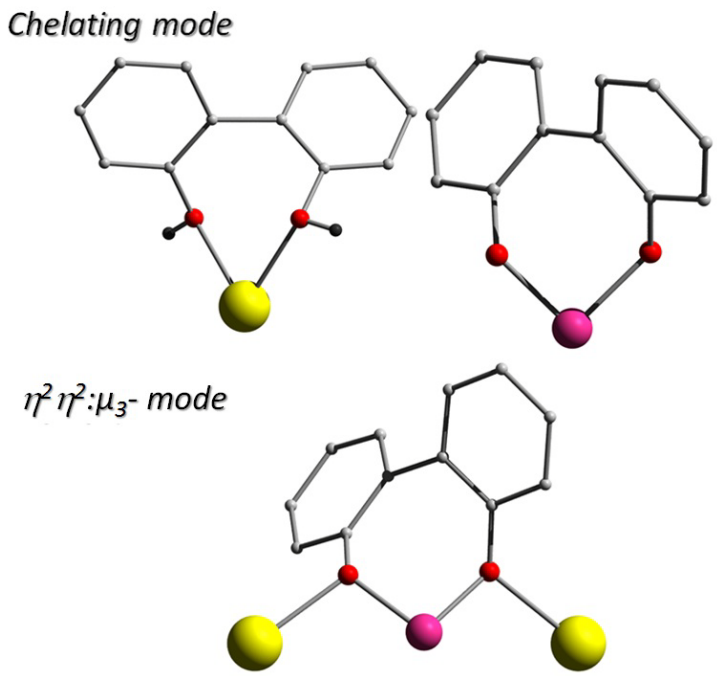

Fig. S13: Bonding modes observed in this work. Colour code: Yellow (Na), Pink (Mn), Red (O), Grey (C), Black (H).

Table S1 Crystallographic data for complexes **1-4**

	1	**2**	**3**	**4**
Formula[a]	$C_{67}H_{59}N_3O_{10}Mn_2Na_2$	$C_{54}H_{58}N_2O_9MnNa$	$C_{54}H_{58}N_2O_9FeNa$	$C_{52}H_{46}N_4O_9MnNa$
M_W	1222.03	956.95	957.86	946.86
Crystal System	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	$P2_1/n$
a/Å	11.814(2)	10.350(2)	10.342(2)	10.377(2)
b/Å	12.513(3)	11.989(2)	12.133(2)	21.331(4)
c/Å	22.786(5)	21.671(4)	21.457(4)	23.121(5)
α/°	96.06(3)	86.90(3)	86.03(3)	90.00
β/°	98.11(3)	78.51(3)	78.40(3)	99.53(3)
γ/°	115.49(3)	69.14(3)	68.86(3)	90.00
V/Å^3	2957.6(10)	2462.1(9)	2459.9(9)	5047.4(18)
Z	2	2	2	4
T/K	150(2)	150(2)	150(2)	150(2)
λ[b]/Å	0.7107	0.7107	0.7107	0.7107
D_c/g cm^{-3}	1.372	1.291	1.293	1.249
Meas./indep.(R_{int}) refl.	10822 / 6185 (0.0477)	9016 / 6299 (0.0491)	9008 / 3555 (0.1151)	9233 / 5854 (0.0424)
wR2 (all data)	0.1411	0.1634	0.1951	0.2652
$R1$[d,e]	0.0599	0.0610	0.0863	0.0725
Goodness of fit on F^2	0.966	1.065	0.951	1.058

[a] Includes guest molecules. [b] Mo-Kα radiation, graphite monochromator. [c] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|^2]^{1/2}$. [d] For observed data. [e] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.

Table S2 Crystallographic data for complexes **5**-**8**

	5	**6**	**7**	**8**
Formula[a]	$C_{66}H_{58}N_4O_{11}Mn_2Na_2$	$C_{75}H_{77}N_3O_{11}Mn_2Na_2$	$C_{44}H_{34}N_4O_4Mn$	$C_{38}H_{36}N_2O_6FeNa$
M_W	1239.02	1352.26	737.69	695.53
Crystal System	Triclinic	Monoclinic	Tetragonal	Orthorhombic
Space group	P-1	$P2_1/c$	$I4_1/a$	Pbca
a/Å	11.293(2)	21.3738(6)	16.357(2)	20.326(4)
b/Å	15.606(3)	12.8753(4)	16.357(2)	12.942(3)
c/Å	17.596(4)	24.8333(8)	26.747(5)	24.997(5)
α/°	84.81(3)	90	90	90
β/°	77.73(3)	104.246(3)	90	90
γ/°	81.07(3)	90	90	90
V/Å^3	2988.3(10)	6623.8(3)	7156(2)	6576(2)
Z	2	4	8	8
T/K	150(2)	150(2)	150(2)	150(2)
λ[b]/Å	0.7107	1.5418*	0.7107	0.7107
D_c/g cm^{-3}	1.377	1.356	1.369	1.405
Meas./indep.(R_{int}) refl.	10920 / 5906 (0.0779)	62976 / 13175 (0.0684)	3076 / 1770 (0.0785)	6010 / 2535 (0.0832)
wR2 (all data)	0.1698	0.0906	0.1119	0.0358
$R1$[d,e]	0.0814	0.0391	0.0497	0.0389
Goodness of fit on F^2	1.036	0.895	0.868	0.661

[a] Includes guest molecules. [b] Mo-Kα radiation, graphite monochromator. [c] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2 / \Sigma w|F_o^2|^2]^{1/2}$. [d] For observed data. [e] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. *Measured using a SuperNova (Cu) X-ray source.

Table S3 Intra-chain metal…metal distances in the 1-D chains **1-6** and **8**

(1)	
Mn2···Na2	3.307
Mn2···Na1	3.339
Mn1···Na1	3.153
Mn3···Na2	3.142
(2)	
Mn1···Na1	5.251
(3)	
Fe1···Na1	5.242
(4)	
Mn1···Na1	5.257
(5)	
Mn1···Na1	3.183
Mn3···Na2	3.074
Mn2···Na2	3.295
Mn2···Na1	3.231
(6)	
Mn1···Na1	3.310
Mn1···Na2	3.293
Mn2···Na1	3.273
Mn2···Na2	3.327
(8)	
Fe1···Na1	3.439

Table S4 BVS calculations on the Mn ions described in this work.

Chain		**Atom label and BVS result**
(1)	**Calculated as:**	**Mn1**
	Mn^{2+}	3.39
	Mn^{3+}	3.13
	Mn^{4+}	3.09
	Calculated as:	**Mn3**
	Mn^{2+}	3.38
	Mn^{3+}	3.11
	Mn^{4+}	3.05

(2)	**Calculated as:**	**Mn1**
	Mn^{2+}	3.23
	Mn^{3+}	2.98
	Mn^{4+}	2.92
(4)	**Calculated as:**	**Mn1**
	Mn^{2+}	3.30
	Mn^{3+}	3.04
	Mn^{4+}	2.98
(5)	**Calculated as:**	**Mn1**
	Mn^{2+}	3.24
	Mn^{3+}	2.99
	Mn^{4+}	2.93
	Calculated as:	**Mn3**
	Mn^{2+}	3.48
	Mn^{3+}	3.20
	Mn^{4+}	3.14
(7)	**Calculated as:**	**Mn1**
	Mn^{2+}	1.88
	Mn^{3+}	1.74
	Mn^{4+}	1.70

X-ray diffraction details on the collection of 1-8

The structures of **1-5** and **7** and **8** 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 **5** 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 hydrogen atoms (H5A-H8A in **2** and H5A-H8A 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 **2**) 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 **5** was assigned to an idealised position using a riding model in an identical fashion to the bridging EtOHs in **1** described above. The structure of **6** was collected with Cu radiation (l = 1.5418 A˚) on an Oxford Diffraction SuperNova Dual wavelength diffractometer with an Atlas CCD detector. All hydrogen atoms within this covalent chain were assigned to idealised positions.

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.