Electronic Supplementary Information

A F-Bridged Mn(II) Molecular Square

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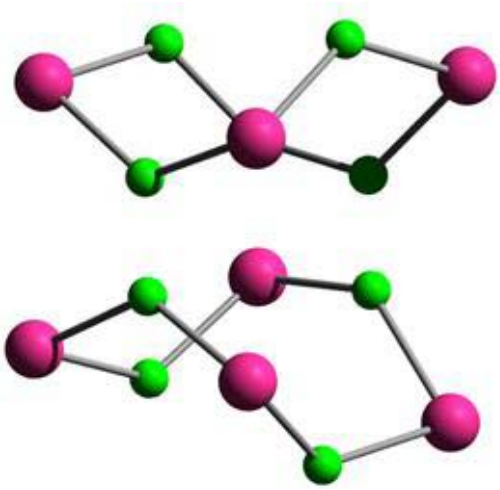

Fig. SI1 Structures of the $\{Mn_4F_4\}$ square core in **1**. Colour code: Mn (pink), F (green).

Table SI1: BVS calculations undertaken for Mn1 in $[Mn_4(\mu_2\text{-}F)_4(1,10\text{-phen})_8](NO_3)_4$ **(1)**

Calculated as:	**Mn1**
Mn(II)	2.34
Mn(III)	2.27
Mn(IV)	2.20

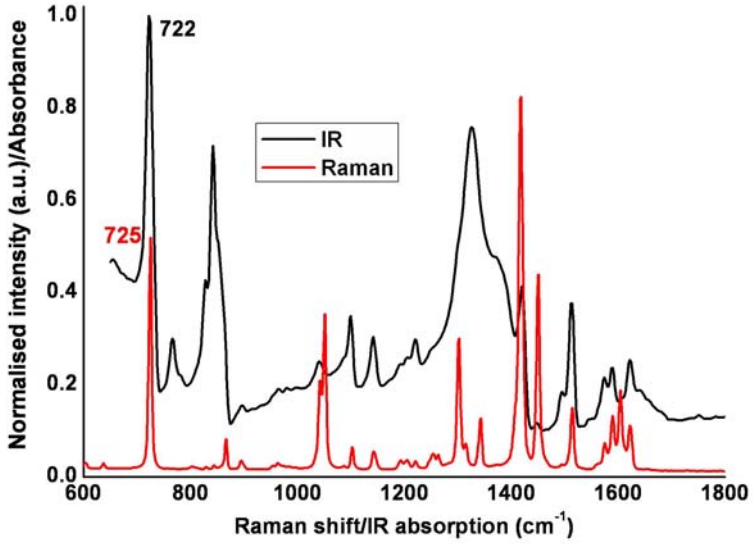

Fig. SI2 Infra-Red (black line) and Raman spectra (red line) obtained from crystalline sample of **1.**

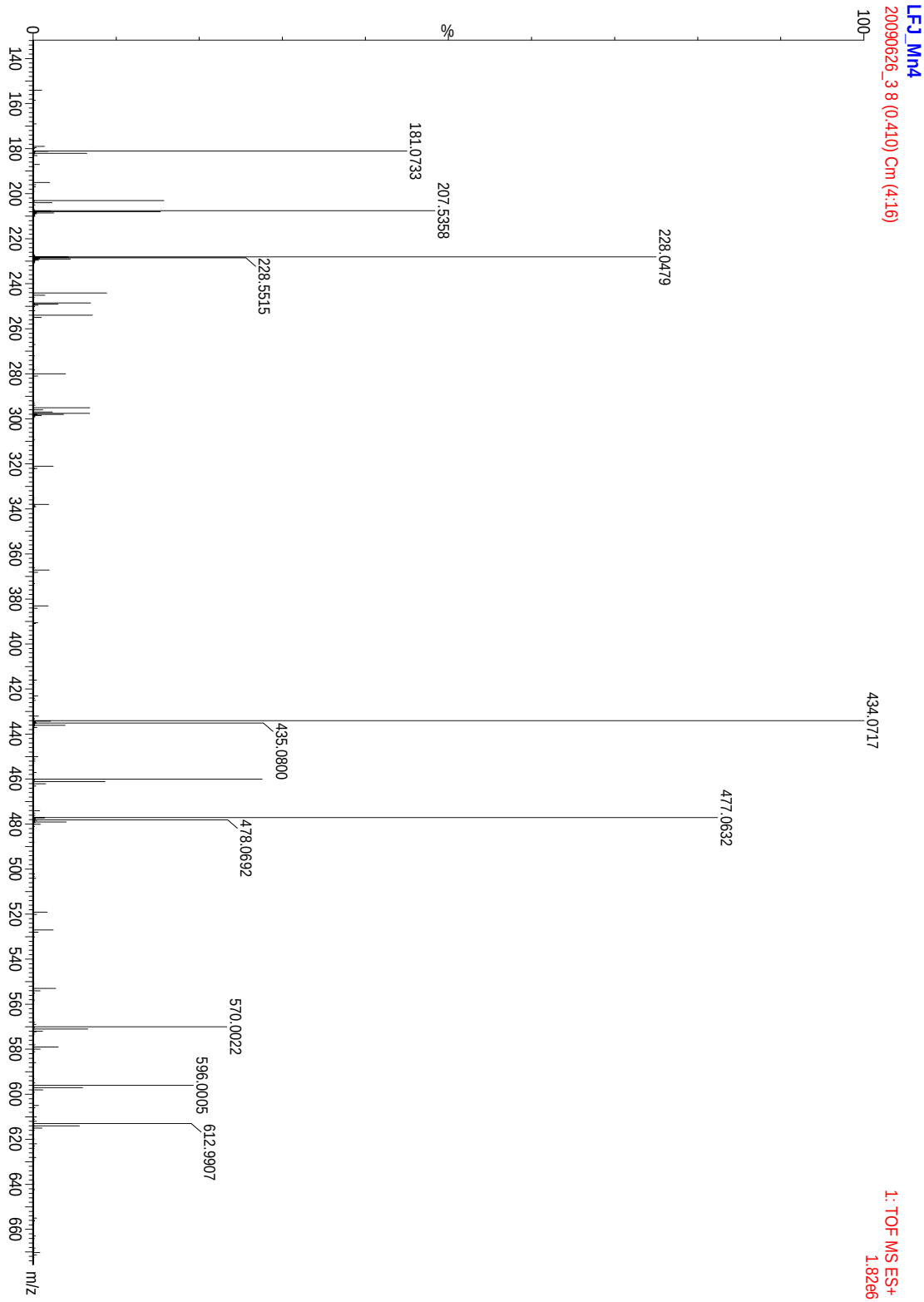

Fig. SI3 Mass spectrum of **1** from MeCN solution. TOF MS-ES (%) m/z: 181.1 (40, $[L+H]^+$), 227 (70, [65, $^{55}Mn(L)_2(F)_2 + 2H^+]^{2+}$), 254 (18, $[^{55}Mn(L)(F)]^+$) 434 (95, $[^{55}Mn_4(F)_4(L)_8]^{4+}$ *or* $[^{55}Mn(F)(L)_2]^+$), 453 (20, $[^{55}Mn(F)_2(L)_2\text{-}H]^+$), 477 (85, $[^{55}Mn(F)_2(L)_2\text{-}Na]^+$), 570 (25, $[^{55}Mn_2(F)_3(L)_2\text{-}(CH_3CN)]^+$), 613 (20, $[^{55}Mn_2(F)_3(L)_2\text{-}(CH_3CN)_2^+$).

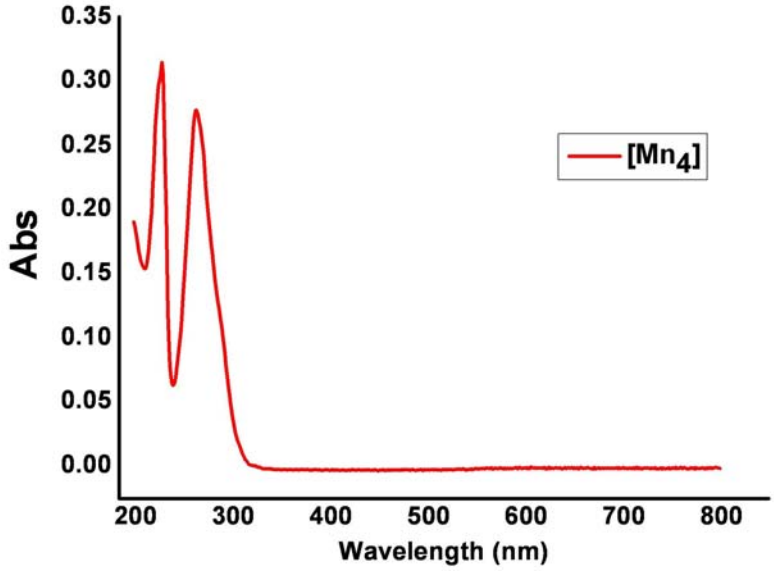

Fig. SI4 UV/vis spectrum obtained from an CH_3CN solution of $[Mn_4(\mu_2\text{-}F)_4(1,10\text{-phen})_8](NO_3)_4$ (**1**).

X-ray diffraction details on the collection of [Mn_4] (1)

The structure of **1** was collected on an Xcalibur S single crystal diffractometer (Oxford Diffraction) using an enhanced Mo source**.** The data reduction was carried out on the CrysAlisPro software package. The structure was 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 were placed in calculated positions. The non hydrogen atoms were refined anisotropic except for the oxygen atoms of the H_2O solvent molecules of crystallisation (which were left isotropic).

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.