Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Material for

What Mn K_β Spectroscopy Reveals Concerning the Oxidation States of the Mn Cluster in Photosystem II

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Section S1: Model Compound Descriptions

Table S1: Model Mn compound data of Dau et al., [17], showing oxidation states, ligand environment and $K\beta_{1,3}$ <E> and E_O values. Compounds 1-8 are mono or di- Metal (Mn_2 or Mn,Fe) Mn complexes (see [17], with representative structures given in Fig. **S1** below. Compounds 9-11 are Mn oxides (indicated), with O_6 ligation. Compound 12 is a tetra Mn complex, with mainly O ligation (see [17]). Most Mn co-ordination is sixfold, but compound 5 is penta co-ordinate.

Compound[a]	Ox. States(s)	Ligands	<E> eV	E_0 [b] eV
1	$(II)_2$	$Mn^{II}O_2N_4$	6491.49	6492.44
2	$(III)_2$	$Mn^{III}O_6$	6490.86	6491.97
3	(III)	$Mn^{III}O_5N$	6490.85	6492.03
4	$(III)_2$	$Mn^{III}O_4N_2$	6490.96	6492.14
5	(III)	$Mn^{III}O_3N_2$	6490.82	6491.82
6	(IV)	$Mn^{VI}O_4N_2$	6490.33	6491.08
7	(IV)	$Mn^{VI}O_3N_3$	6490.33	6491.14
8	$(IV)_2$	$Mn^{VI}O_3N_3$	6490.40	6491.06
9	(III)	$Mn^{III}{}_2O_3$	6490.97	6491.88
10	(IV)	$Mn^{VI}O_2$	6490.25	6491.26
11	(II)	$Mn^{II}O$	6491.38	6492.34
12	$(III\text{-}II)_2$	$(Mn^{II}\,Mn^{III})_2O_9\,Cl$	6491.24	6492.34

[a] As listed by Dau [17]. [b] Estimated from Fig. S4 in [17].

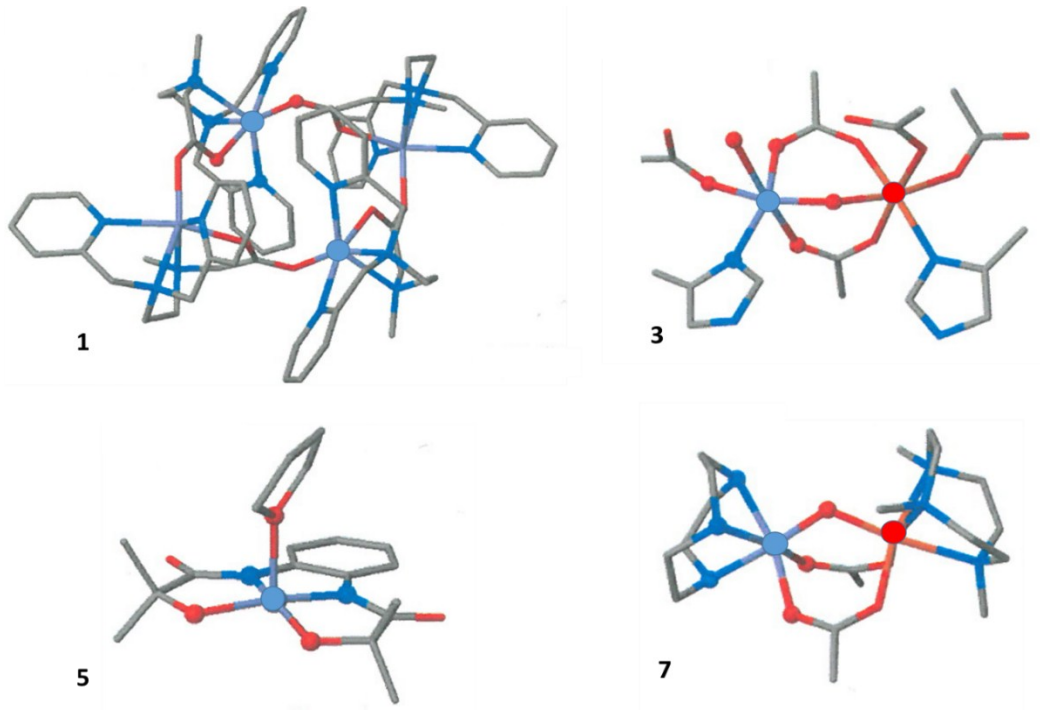

Figure **S1:** Structures of representative examples of O-N ligated Mn Compounds of Dau et al., used for $K\beta_{1,3}$ calibration in [17] (from Fig. S2 in Dau et al.). Compound 5 is 5-co-ordinate. Compounds 3,7 are mixed metal. Colour coding is; Mn (violet), Fe (bright red), O red, N (blue), C (grey). Protons omitted

Table S2: Model Mn compound data of Yachandra et al et al., showing oxidation states, ligand environment and $K\beta_{1,3}$ <E> and E_O values. Data from [12b] for oxo bridged dimeric complexes (compounds 1-5) and for oxo bridged trimeric and tetrameric species (compounds 6-9) [12d]. See Fig **S2** below

Compound[a]	Ox. States(s)	Ligands	<E> eV	E_0 [b] eV
1	$(III)_2$	MnO_2N_4	6490.39	6491.32
2	(III,IV)	MnO_2N_4	6490.18	6490.88
3	$(IV)_2$	MnO_2N_4	6489.96	6490.44
4	(III,IV)	MnO_2N_4	6490.21	6491.12
5	$(IV)_2$	MnO_2N_4	6490.01	6490.70
6	(II,III_2)	$(Mn^{III}O_5N)(Mn^{II}O_6)$	6490.63	-
7	$(III)_3$	MnO_5N	6490.51	-
8	(II,III_3)	MnO_4N_2	6490.54	-
9	$(III)_4$	MnO_4N_2	6490.45	-

[a] Compounds 1-3 mono μ-oxo bridged. Compounds 4-5 di μ-oxo bridged. [b] Estimated from Fig. 8 in [12b].

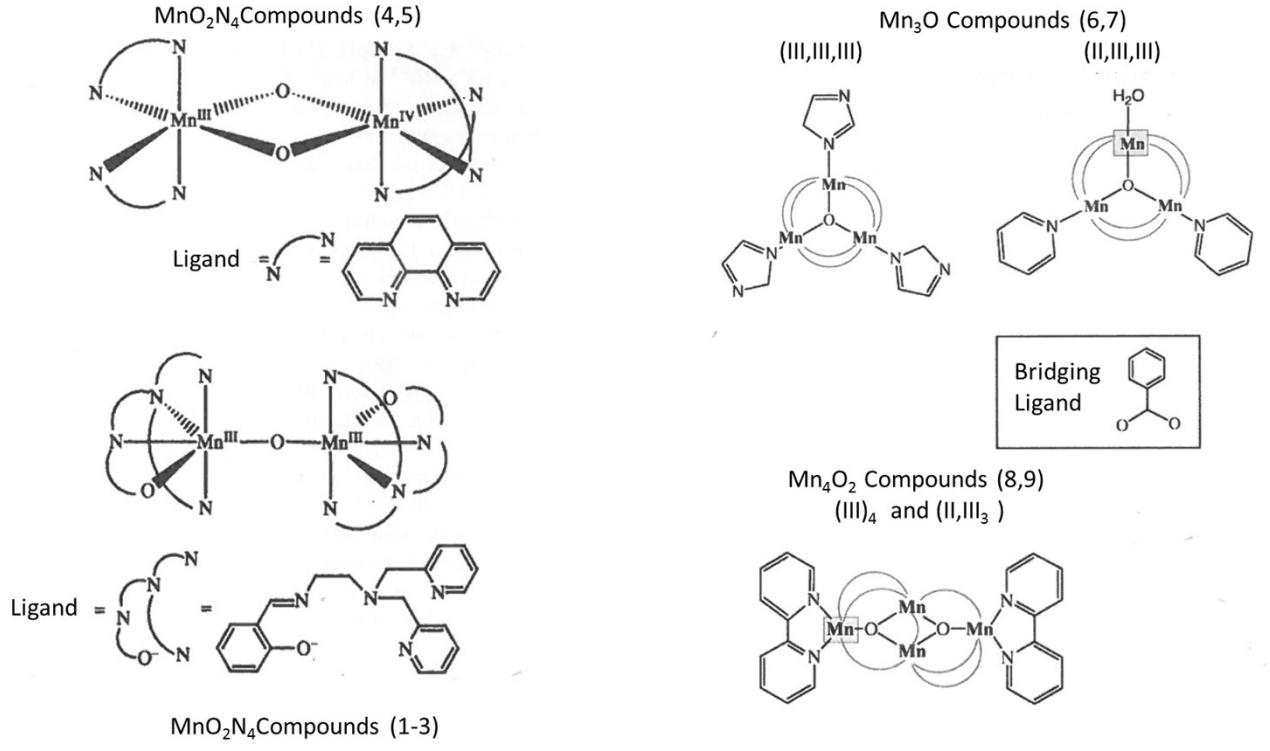

Figure **S2** Structure schematics for O-N ligated Mn Compounds of Yachandra et al., used for $K\beta_{1,3}$ calibration in Figs 4,5 present text. (From Fig. 2 in [12b] and Fig. 2 in [12d]). Numbering as in Table **S2** above. Protons omitted

Table S3: Model Mn compound data of Pushkar al et al. [12f], as for Tables **S1,2** above.

Compound[a]	Ox. States(s)	Ligands	<E> eV	E_0 [b] eV
1	(III,IV)	MnO_2N_4	6490.29	6491.19
2	$(III,IV)_2$	MnO_6	6490.42	-
3	$(III\text{-}IV)_2$	MnO_6	6490.43	-

[a] Compound 1 is equivalent to compound 4 in Table **S2**. Compounds 2,3 have tri μ-oxo bridging and tri phosphinate terminal ligation, see Fig **S3** below. [b] Estimated from Fig. 3 in [12f].

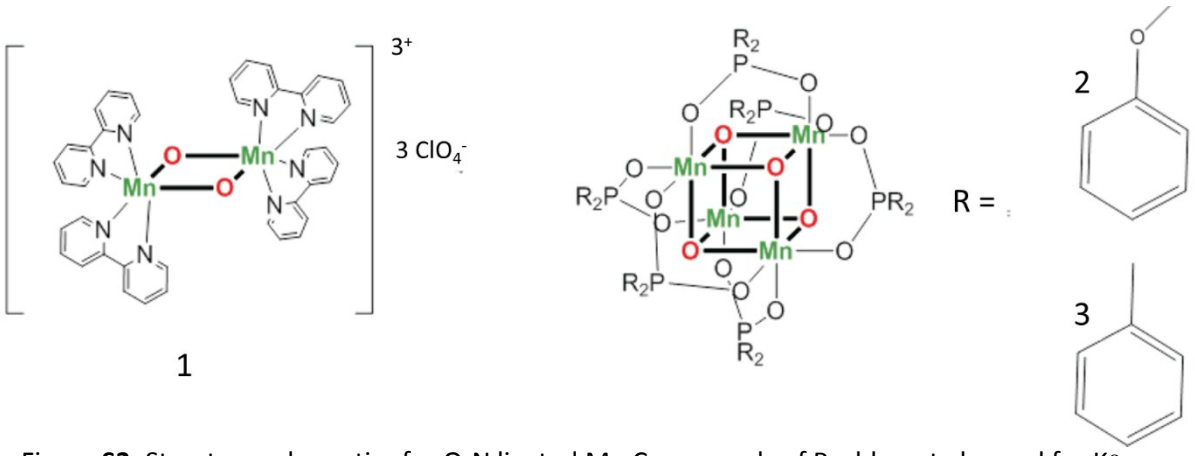

Figure **S3:** Structure schematics for O-N ligated Mn Compounds of Pushkar et al., used for $K\beta_{1,3}$ calibration in Figs 4,5 present text. (From Fig. 1 in [12f]). Numbering as in Table **S3** above. Protons omitted

Section S2: Kβ' and Baseline Offset Effects

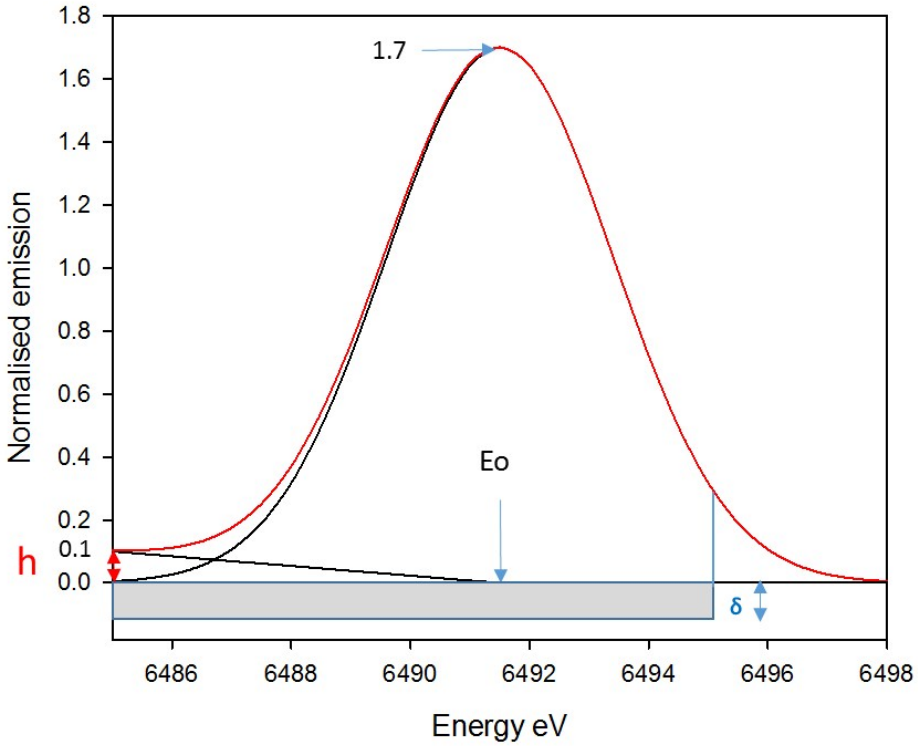

Fig. S4: Illustrates schematically the effects of the Kβ' high energy wing intensity intrusion into the region of the $K\beta_{1,3}$ emission peak and baseline assignment position. The 'pure' $K\beta_{1,3}$ emission (black) is approximated as a simple Gaussian curve (Eo = 6491.5 eV, height A_O = 1.7 units, half height width = 4.5 eV). The Kβ' edge is approximated as a 'wedge' of height **h** at 6485 eV, tapering to zero at Eo. The 'true' baseline for these goes through 0 on the emission axis. The blue rectangle, height δ, represents the additional emission, included in the <E> integral determination (from 6485 to 6495 eV), from variation in assigned baseline. Red curve is the total for Kβ' and $K\beta_{1,3}$ intensities. The 'true' <E> value is Eo, ie 649.50 eV.
The quantitative effects of the Kβ' and baseline effects for the above illustrative example, are indicated below:

let E_O = (Eo – 6485) = 6.50 eV here,

Then for the Kβ' effect, the apparent shift ($\Delta\langle E_O\rangle$) in the estimated <E> value is given by :

$$\Delta\langle E_O\rangle \sim E_O - (h.E_O^2/6 + Area_g.E_O)/(Area_g + h.E_O/2) \quad \ldots\ldots\ldots\ldots \quad 1)$$

where $Area_g$ is the total area of the Gaussian curve up to the upper integration limit of 6495 eV. For the case above this is ~ 8. 0 units (varies somewhat with Eo position)

For the baseline effect, the corresponding $\Delta\langle E_O\rangle$ value is given by :

$$\Delta\langle E_O\rangle \sim E_O - [(50.\delta + Area_g.E_O)/(Area_g + 10.\delta)] \quad \ldots\ldots\ldots\ldots \quad 2)$$

If h ~ 0.1 and δ/A_O ~ 0.1, (see main text), then both equations 1) and 2) separately predict $\Delta\langle E_O \rangle$ values of ~ 0.2-0.3 eV, depending on the precise Eo position, actual Gaussian width etc. In both cases, the perturbations produce an apparent <E> value which is **Lower** that the 'true' E_O value, ie correspond to an apparently *Higher* Mn oxidation state.

Section S3: Turnover Difference Baseline Levelling

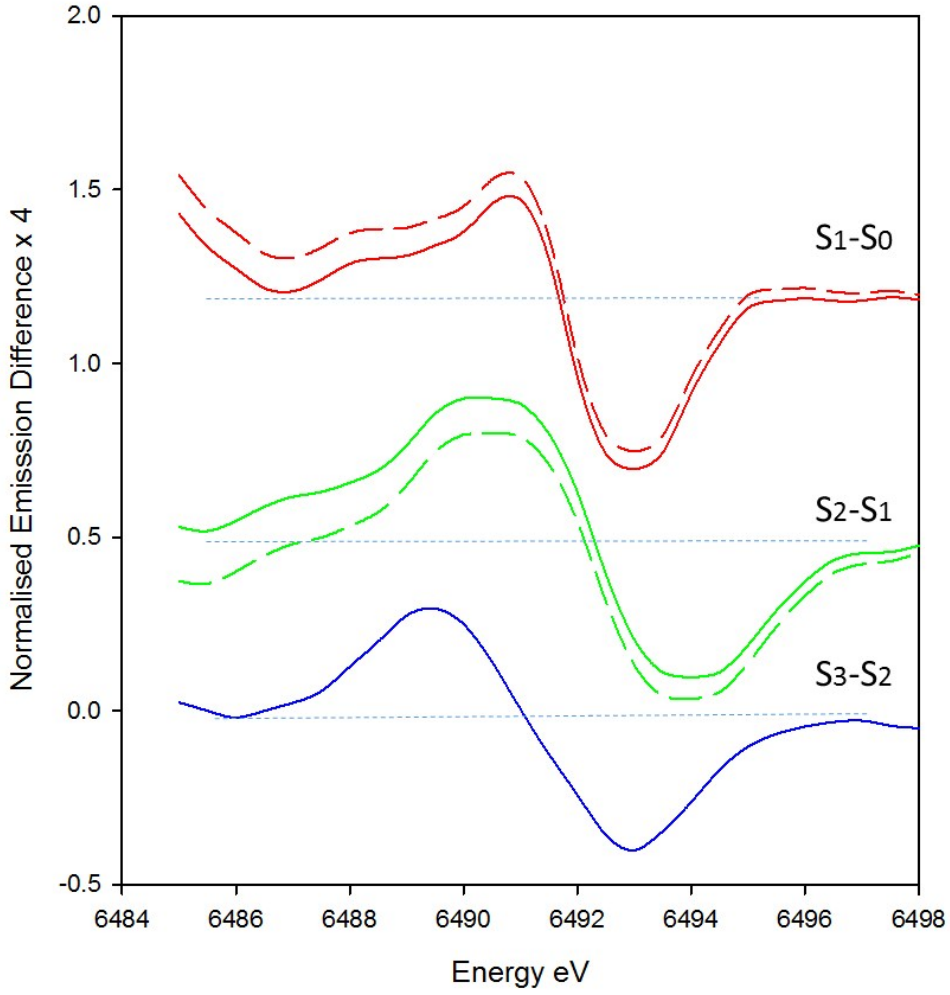

Fig. S5: Shows levelled curves (full) and raw unlevelled curves (dashed) for S state turnover difference spectra of Dau et al. [17] (see also main text). Levelling was by linear baseline adjustment, as indicated by dotted lines. This is reasonable for the S_2-S_1 spectrum, but the S_1-S_0 spectrum likely shows evidence of a non linear intrusion of Kβ' intensity into the energy region below ~6488 eV, which is substantially greater in the S_1 spectrum than in the S_0 spectrum. This effect is essentially absent in the other two turnover difference spectra, suggesting that the extra Kβ' intensity largely cancels between successive S states up to S_3 (i.e. is equally present in those states). All of these effects however, have very little influence on the estimation of the central inflection point energies (typically < 0.1 eV).

Section S4: PS II RIXS Data of Yachandra et al. [13].

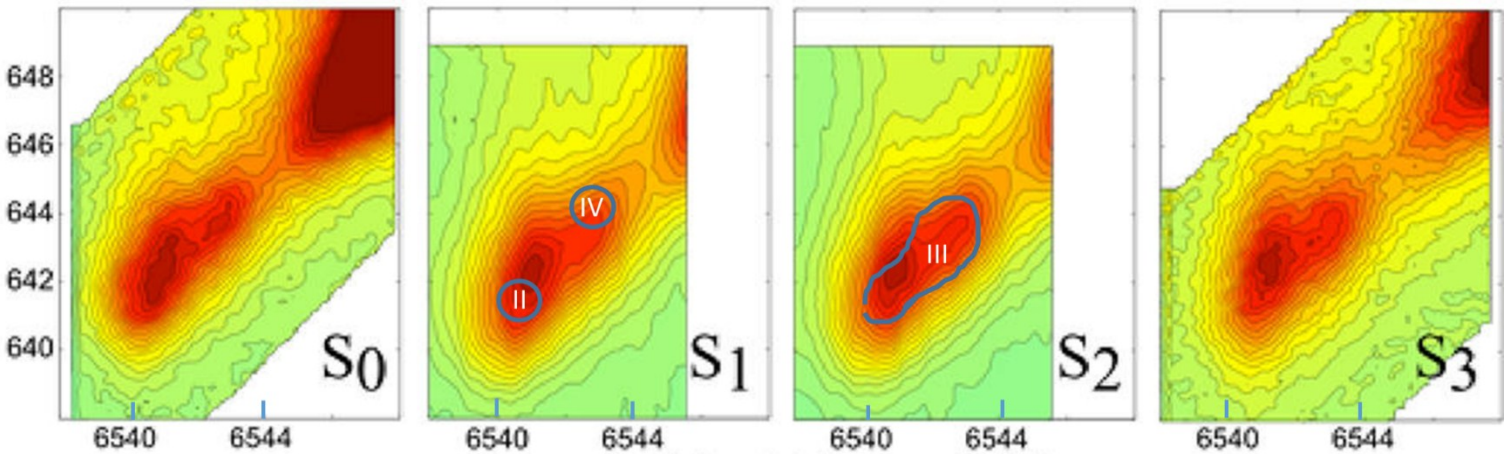

Fig **S6**: Reproduced Mn RIXS plots for the de-convoluted S states of PS II, with axis identifications as described in main text and refs [13]. Overlaid on the S_1 plot are the principal RIXS peak positions for Mn(II) (MnO) and Mn(IV) compounds from [13b], with mainly O ligation (see main text). The extended region overlaying the S_2 plot is for Mn_2O_3 (Mn(III) , from [13a].