

The pKa value of the proximal water molecule *trans* to a high-valent Mn^V=O porphyrin: towards the control of the reactivity by the pH.

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SUPPORTING INFORMATION

Table S1. LC/ESI-MS data of DNA cleavage of duplex DNA at pH = 7.6

Oligo	Retention time (min)	observed m/z (amu) and (z value)	calculated m/z (amu) and (z value)	MW (g/mol) calculated
Oligo A 5'-ACGAAACGCGT	41	1115.7 (z = 3) 1673.9 (z = 2)	1115.75 (z = 3) 1674.1 (z = 2)	3350.25
6-mer (6) 5'-ACGAAAp	33	943.3 (z = 2)	943.12 (z = 2)	1888.24
5-mer (5) 5'- ^{CHO} CGCGT Hydrated aldehyde	32	737.3 (z = 2)	737.5 (z = 2)	1477.00
5-mer (5') 5'- ^{COOH} CGCGT	31	745.2 (z = 2)	745.5 (z = 2)	1493.00
Oligo T 5'-ACGCGTTTCGT	45	1106.5 (z = 3) 1660.6 (z = 2)	1106.73 (z = 3) 1660.6 (z = 2)	3323.20
8-mer (8) 5'-ACGCGTTTp	42	1238.8 (z = 2) 825.7 (z = 3)	1239.3 (z = 2) 825.5 (z = 3)	2480.59
3-mer (3) 5'- ^{CHO} CGT Hydrated aldehyde	28	857.0 (z = 1) 875.2 (z = 1)	857.6 (z = 1) 875.6 (z = 1)	858.61 876.6
?	46	No signal		

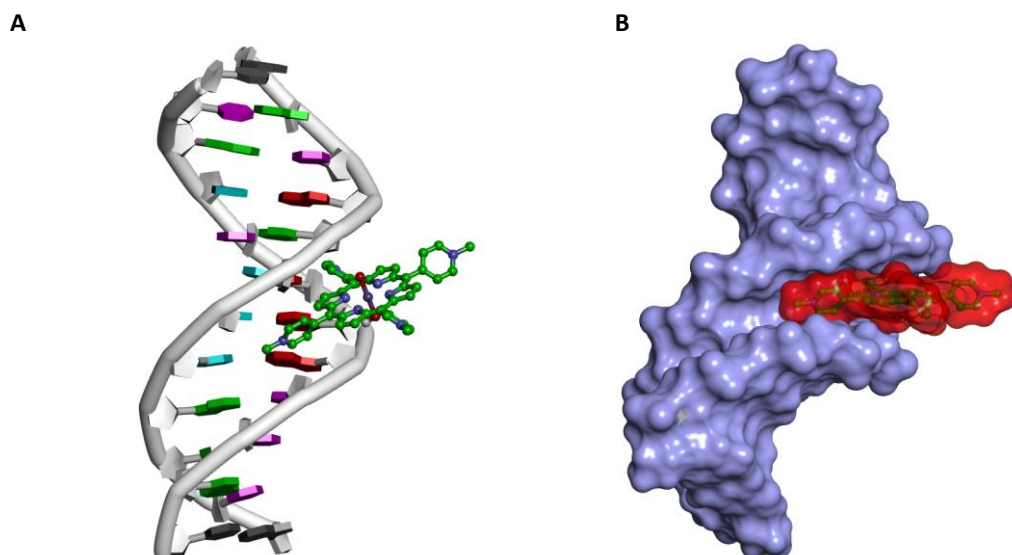


Figure S1. Molecular model of the interaction of the $\text{Mn}^{\text{V}}=\text{O}$ form of Mn-TMPyP4 with the minor groove of double-stranded DNA (Arnaud 2003). A) Cartoon representation with A, T G, C bases in red, blue, cyan, and green color, respectively. B) Solvent accessible surface view.

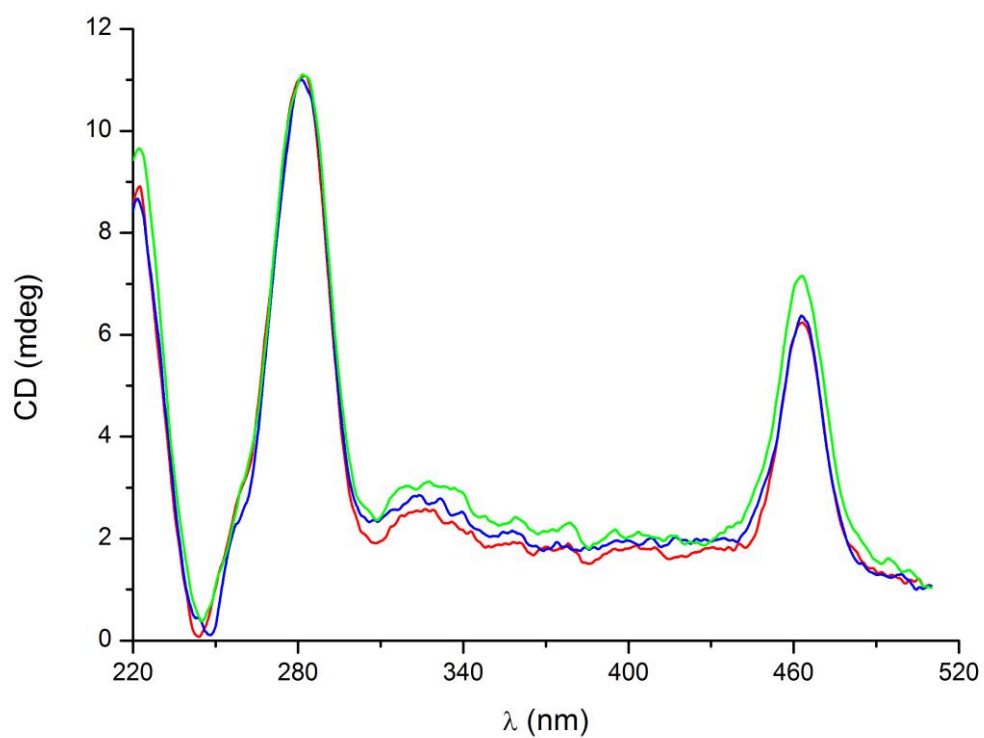
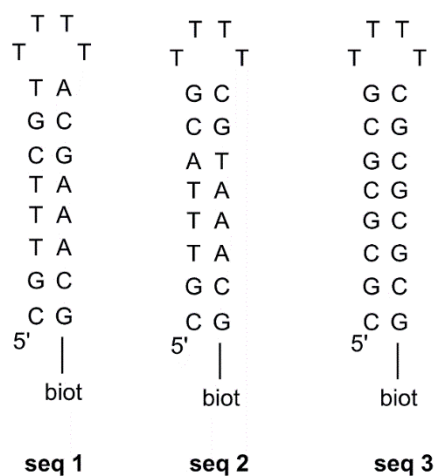


Figure S2. Circular dichroism spectra of oligo-A/oligo-T duplex and Mn-TMPyP4, 1:1 stoichiometry, at pH 6 (green), 7 (blue) and 8 (red). The positive induced CD band in the Soret region is indicative of minor groove binding of Mn-TMPyP4 (Pasternack 2003).



Scheme S1. Sequence of oligonucleotide duplexes used for SPR K_D measurements

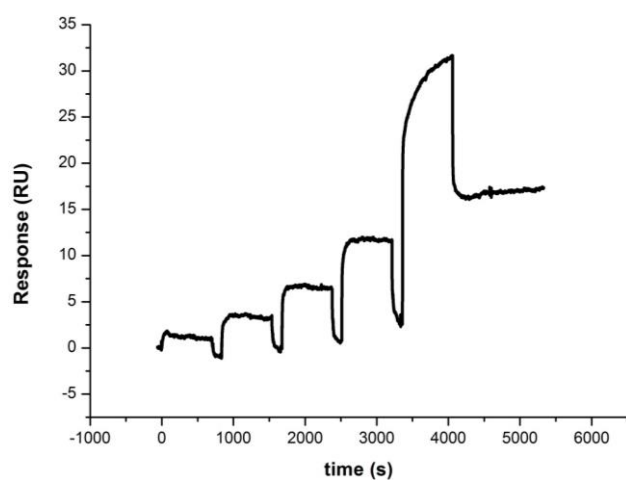
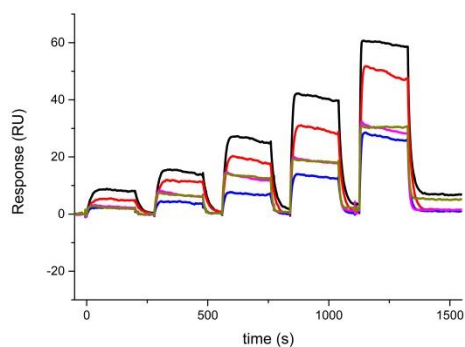
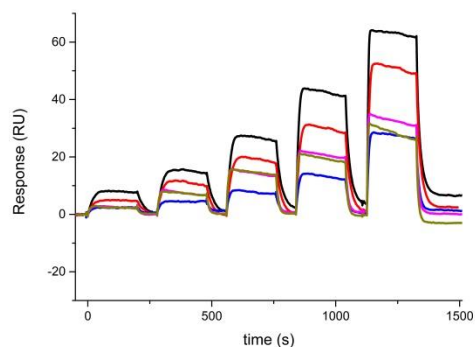


Figure S3. Sensorgram of the interaction of Mn-TMPyP4 with **seq 3** at pH 6. Increasing concentrations of Mn-TMPyP4: 100, 250, 500, 1000, 3000 nM (reference channel: streptavidin). The last concentration was not taken into account for the data analysis. Indeed, at high concentration, non-specific interaction is observed, which leads to drift the signal.



A)



B)

Figure S4. Sensorgram of the interaction of Mn-TMPyP4 with **seq 1** (A) and **seq 2** (B) at pH 6 (black), pH 7 (red), pH 7.5 (blue), pH 7.9 (pink), pH 8 (brown). Increasing concentrations of Mn-TMPyP4: 10, 25, 50, 100, 250 nM from pH 6 to 7.5 and 100, 250, 500, 1000, 2000 nM for pH 7.9 and 8. (reference channel: **seq 3**)

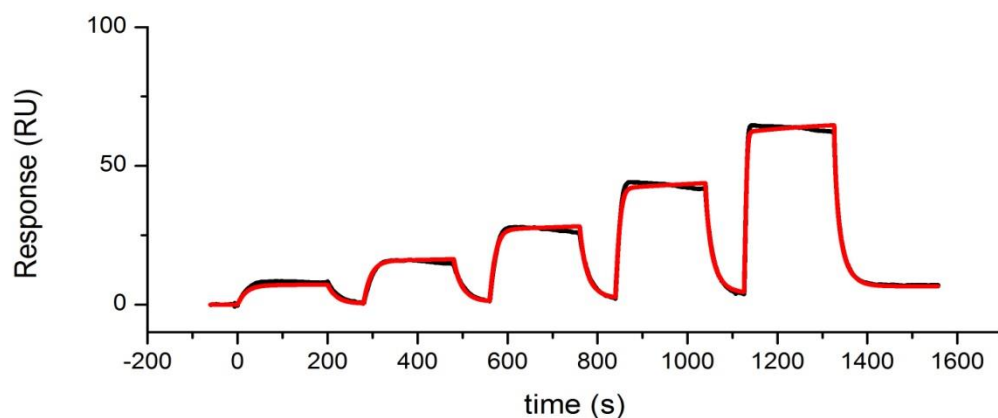


Figure S5. Sensorgram of the interaction of Mn-TMPyP4 with **seq 2** at pH 6 (black) fitted with the 1:1 model (red). Increasing concentrations of Mn-TMPyP4: 10, 25, 50, 100, 250 nM. (reference channel: **seq 3**)

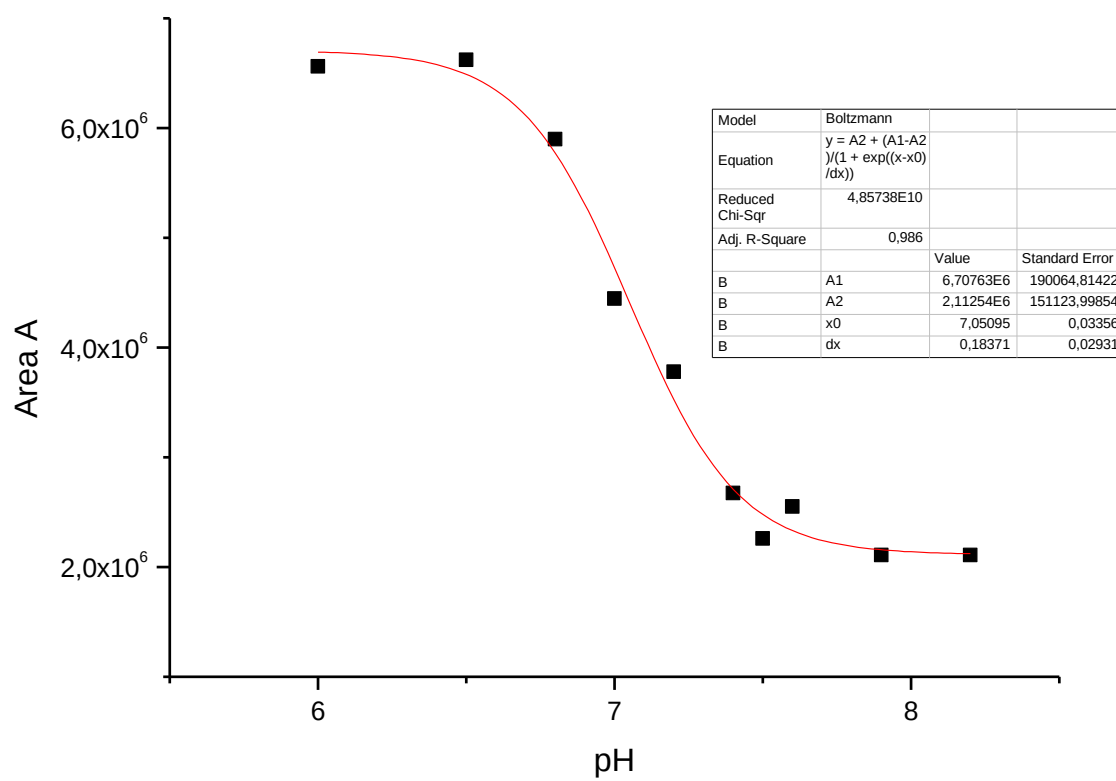


Figure S6. Fitting for the determination of pKa value of Figure 2.

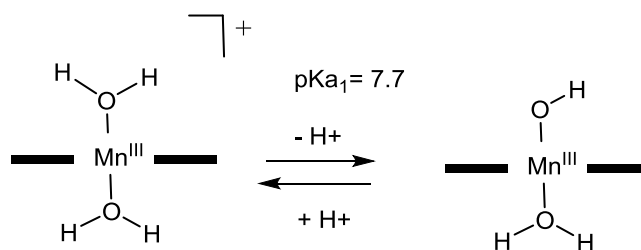
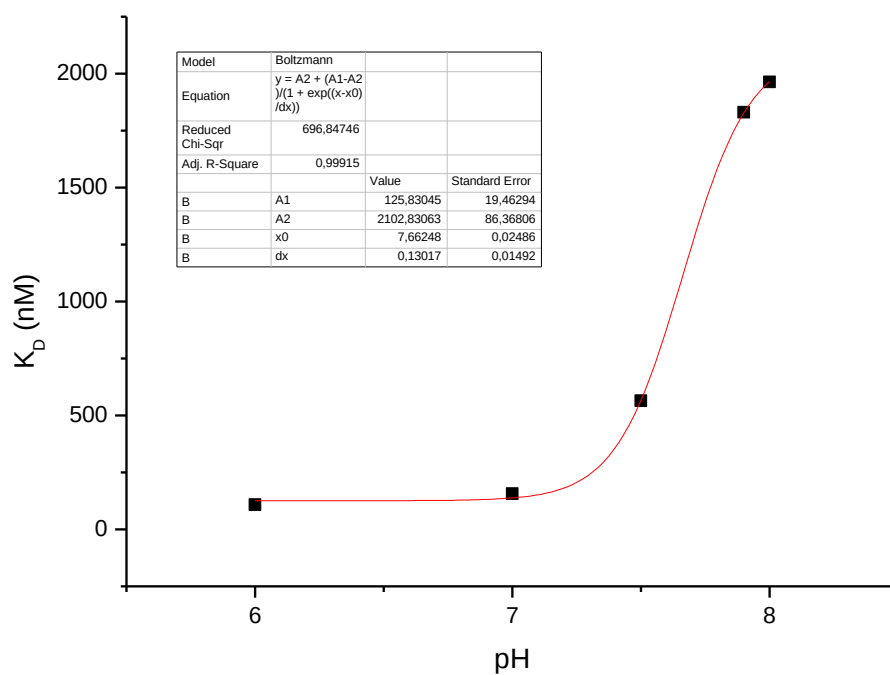


Figure S7. SPR determination of the pKa of axially bound water molecule of Mn-TMPyP4 by SPR. K_D measured with **seq 1**. The porphyrin macrocycle is simplified. Only the charges of the metallic core of the porphyrin are shown.

References

Pasternack, R. F. *Chirality* **2003**, *15*, 329.

Arnaud P., Zakrzewska, K., Meunier, B. J. *Comput. Chem.* **2003**, *24*, 797