Electronic Supplementary Information

Similarities and differences between Mn(II) and Zn(II) coordination polymers supported by porphyrin-based ligands: Synthesis, structures and nonlinear optical properties

Bo-Wei Xu, Ru-Jie Niu, Quan Liu,* Jun-Yi Yang,* Wen-Hua Zhang* and David J. Young

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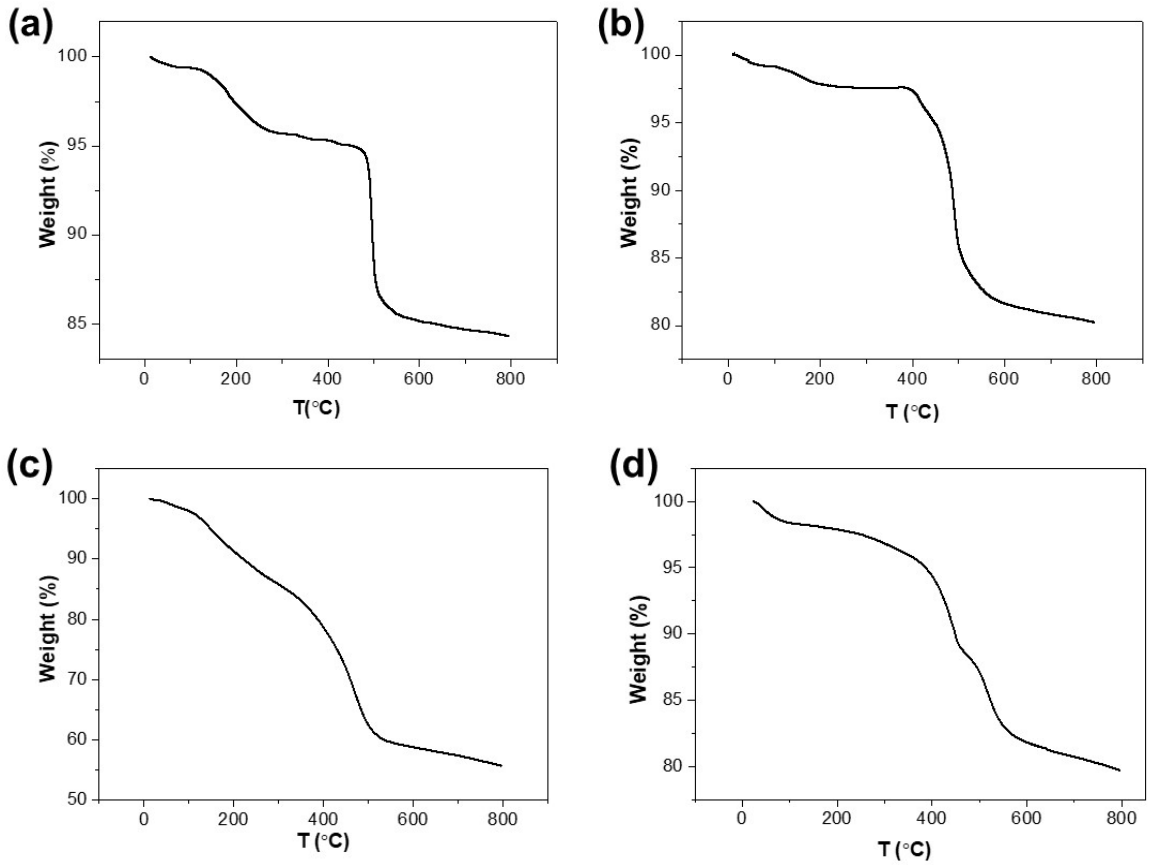

Fig. S1 TGA diagrams of Mn-TMPP (**1**, a), Zn-TMPP (**2**, b), Mn-THPP (**3**, c) and Zn-THPP (**4**, d).

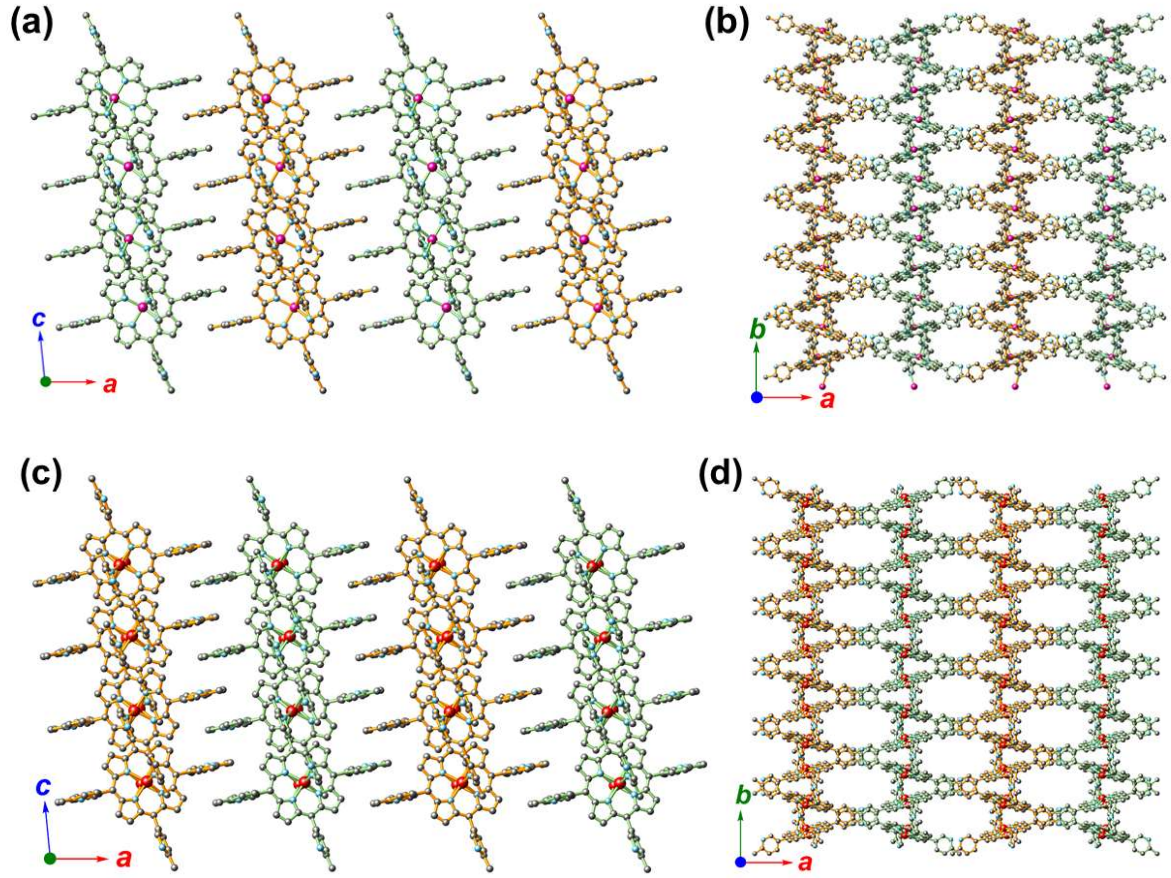

Fig. S2 The crystal packing diagrams of Mn-TMPP (**1**, a, b) and Zn-TMPP (**2**, c, d) showing the nearly identical packing patterns when looking along the crystallographic *b* direction (a, c) and *c* direction (b, d). Colour codes: Mn (dark magenta), Zn (red), C (gray), N (cyan). The bond colors of adjacent layers are also distinguished by orange and bamboo for clarity. All disordered domain and H atoms are omitted.

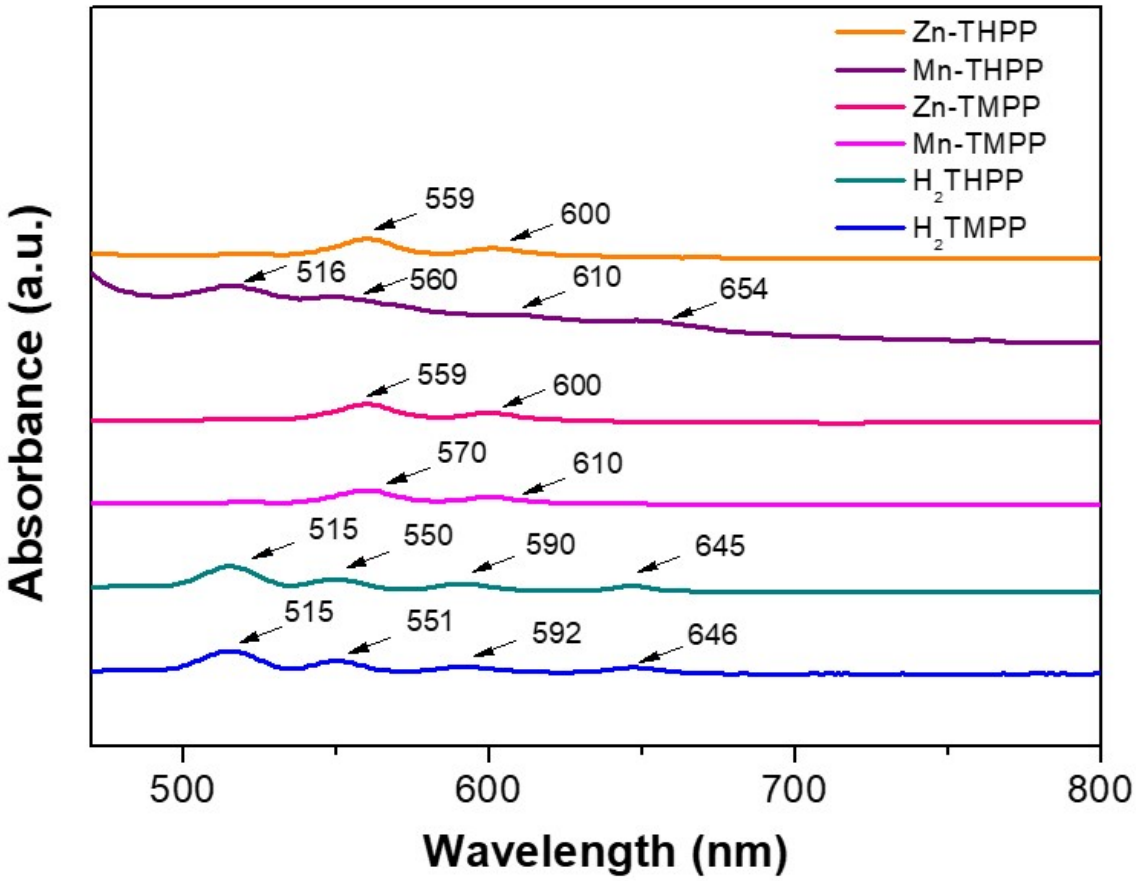

Fig. S3 Expanded UV-Vis spectra showing the Q-band region of CPs **1**–**4** and their respective free-bases TMPP and THPP for comparison.

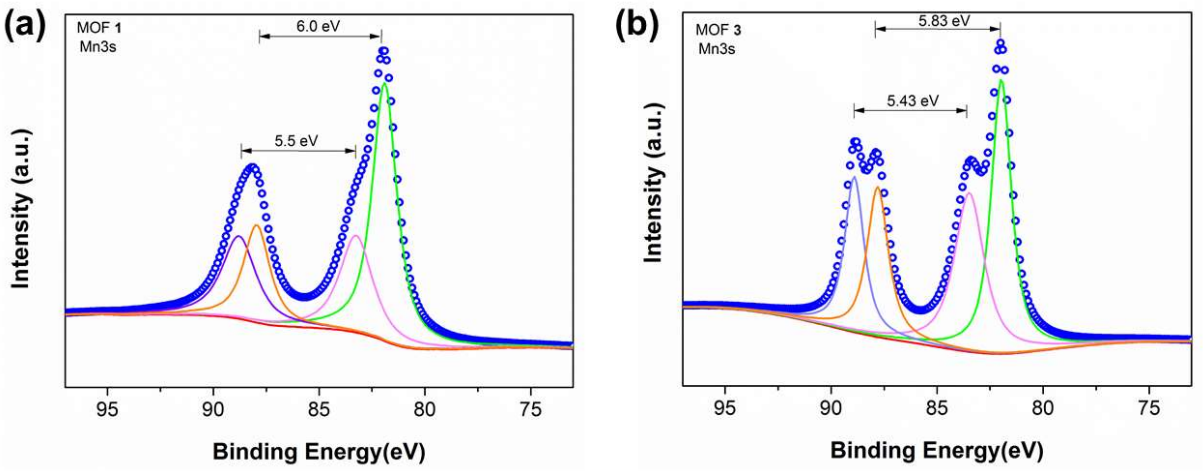

Fig. S4 XPS spectra of MOFs **1** and **3** showing the presence of both Mn(II) and Mn(III) in the bulk samples.

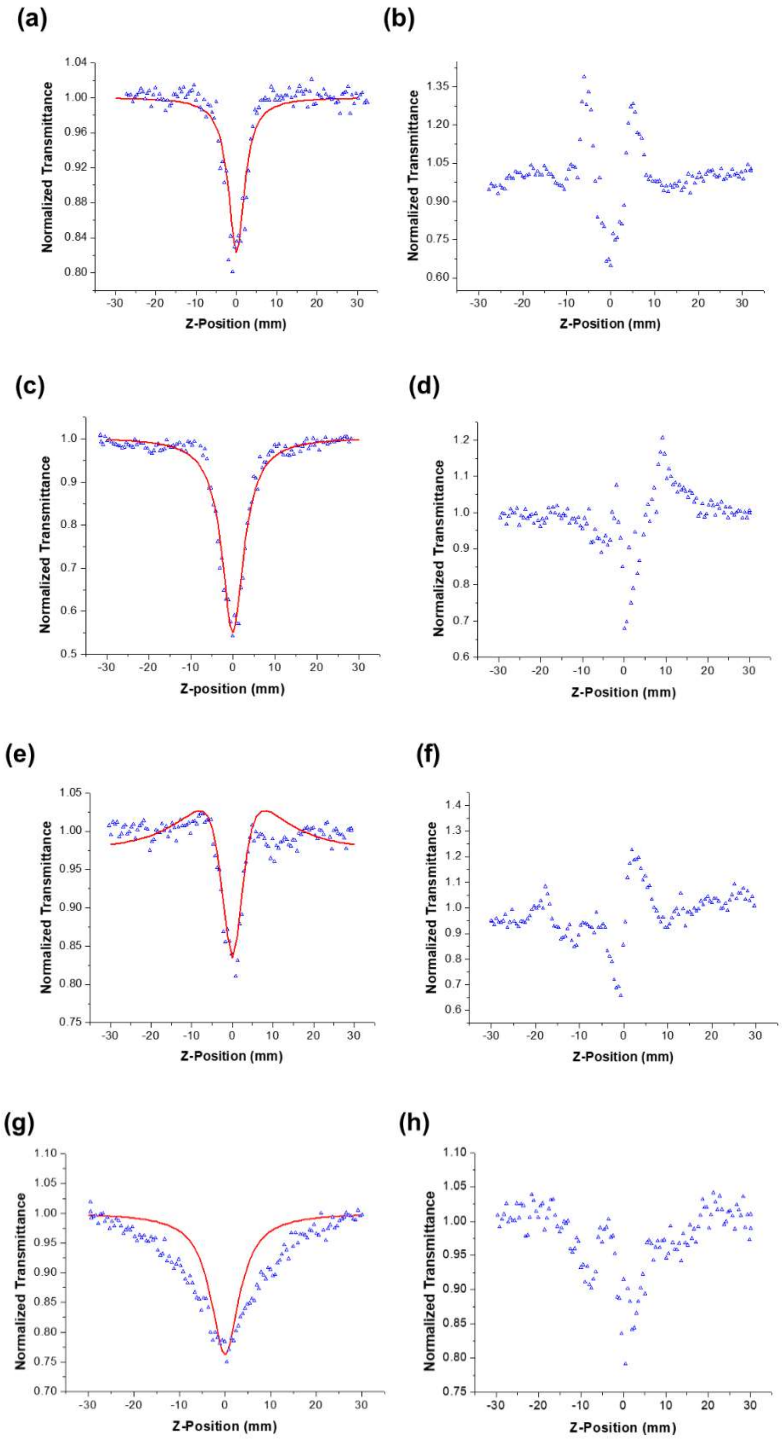

Fig. S5 *Z*-scan data of **1**–**4** (1.0×10^{-5} mol·L^{-1}, DMF solution) at 532 nm. Normalized *Z*-scan data under open-aperture conditions for **1**–**4** (a, c, e, and g). Curves obtained by dividing the normalized *Z*-scan data under closed aperture configuration by that in a, c, e, g (b, d, f, and h). The blue triangles are the experimental data, and the red solid curve is the theoretical fit.

Table S1 Selected bond lengths (Å) and bond angles (°) for CPs **1**–**4**.

Mn-TMPP (**1**)					
Mn(1)-N(4)	2.110(7)	Mn(1)-N(3)	2.121(7)	Mn(1)-N(1)	2.114(7)
Mn(1)-N(2)	2.126(7)	Mn(1)-N(7)#1	2.236(8)		
N(4)-Mn(1)-N(3)	85.9(3)	N(4)-Mn(1)-N(1)	87.7(3)	N(3)-Mn(1)-N(1)	151.5(3)
N(4)-Mn(1)-N(2)	151.5(3)	N(3)-Mn(1)-N(2)	86.6(3)	N(1)-Mn(1)-N(2)	85.8(3)
N(4)-Mn(1)-N(7)#1	110.1(3)	N(3)-Mn(1)-N(7)#1	107.2(3)	N(1)-Mn(1)-N(7)#1	101.0(3)
N(2)-Mn(1)-N(7)#1	98.4(3)				
#1 –*x* + 1/2, *y* + 1/2, –*z*.					
Zn-TMPP (**2**)					
Zn(1)-Zn(1)#1	1.241(2)	Zn(1)-N(2)	2.045(3)	Zn(1)-N(1)#1	2.129(3)
Zn(1)-N(1)	2.157(3)	Zn(1)-N(2)#1	2.203(3)	Zn(1)-N(4)#2	2.246(4)
N(2)-Zn(1)-N(1)#1	88.17(12)	N(2)-Zn(1)-N(1)	86.15(13)	N(1)#1-Zn(1)-N(1)	146.35(7)
N(2)-Zn(1)-N(2)#1	146.28(7)	N(1)#1-Zn(1)-N(2)#1	83.00(13)	N(1)-Zn(1)-N(2)#1	83.56(13)
N(2)-Zn(1)-N(4)#2	106.94(18)	N(1)#1-Zn(1)-N(4)#2	99.06(18)	N(1)-Zn(1)-N(4)#2	114.33(18)
N(2)#1-Zn(1)-N(4)#2	106.57(16)				
#1 –*x* + 3/2, –*y* + 1/2, –*z* + 1; #2 *x*, –*y*, *z* – 1/2.					
Mn-THPP (**3**)					
Mn(1)-N(1)	2.080(5)	Mn(1)-N(1)#1	2.080(5)	Mn(1)-N(2)	2.105(5)
Mn(1)-N(2)#1	2.105(5)	Mn(1)-O(1)#2	2.310(6)	Mn(1)-O(1)#3	2.310(6)
N(1)-Mn(1)-N(1)#1	180.0	N(1)-Mn(1)-N(2)	90.2(2)	N(1)#1-Mn(1)-N(2)	89.8(2)
N(1)-Mn(1)-N(2)#1	89.8(2)	N(1)#1-Mn(1)-N(2)#1	90.2(2)	N(2)-Mn(1)-N(2)#1	180.0(3)
N(1)-Mn(1)-O(1)#2	87.7(2)	N(1)#1-Mn(1)-O(1)#2	92.3(2)	N(2)-Mn(1)-O(1)#2	91.3(2)
N(2)#1-Mn(1)-O(1)#2	88.7(2)	N(1)-Mn(1)-O(1)#3	92.3(2)	N(1)#1-Mn(1)-O(1)#3	87.7(2)
N(2)-Mn(1)-O(1)#3	88.7(2)	N(2)#1-Mn(1)-O(1)#3	91.3(2)	O(1)#2-Mn(1)-O(1)#3	180.0
#1 –*x* + 1, –*y* + 1, –*z* + 1; #2 *x* + 1/2, –*y* + 1/2, *z* + 1/2; #3 –*x* + 1/2, *y* + 1/2, –*z* + 1/2.					
Zn-THPP (**4**)					
Zn(1)-N(4)	2.045(3)	Zn(1)-N(4)#1	2.045(3)	Zn(1)-N(3)#1	2.068(3)
Zn(1)-N(3)	2.068(3)	Zn(1)-O(1)#2	2.265(3)	Zn(1)-O(1)#3	2.265(3)
N(4)-Zn(1)-N(4)#1	180.0	N(4)-Zn(1)-N(3)#1	89.57(13)	N(4)#1-Zn(1)-N(3)#1	90.43(13)
N(4)-Zn(1)-N(3)	90.43(13)	N(4)#1-Zn(1)-N(3)	89.57(13)	N(3)#1-Zn(1)-N(3)	180.0
N(4)-Zn(1)-O(1)#2	87.76(12)	N(4)#1-Zn(1)-O(1)#2	92.24(12)	N(3)#1-Zn(1)-O(1)#2	88.44(12)
N(3)-Zn(1)-O(1)#2	91.57(12)	N(4)-Zn(1)-O(1)#3	92.24(12)	N(4)#1-Zn(1)-O(1)#3	87.76(12)
N(3)#1-Zn(1)-O(1)#3	91.56(12)	N(3)-Zn(1)-O(1)#3	88.43(12)	O(1)#2-Zn(1)-O(1)#3	180.00(13)
Symmetry codes: #1 –*x*, –*y* + 2, –*z* + 1; #2 *x*, –*y* + 3/2, *z* + 1/2; #3 –*x*, *y* + 1/2, –*z* + 1/2.					