

# Supporting information

## Coordination Self-Assembly through Weak Interactions in *Meso*-Dialkoxyphosphoryl-Substituted Zinc Porphyrinates

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## 1. Summary of crystal data and structure refinement for porphyrins Zn5–Zn9.

X-ray structure analysis of **Zn5-Zn9**: Bruker AXS SMART 1000, CCD-detector  $\lambda(\text{MoK}\alpha) = 0.71073\text{\AA}$ , graphite monochromator,  $\omega$ -scanning. Corrections for absorption were made by SADABS [1]. The structure was solved by direct method and refined by full-matrix least squares method for  $F^2$  with anisotropic parameters for all non-hydrogen atoms. All calculations were performed with the use of the SAINT [2] and SHELXTL-97 [3] program packages.

### Special details

#### [Zn5]<sub>n</sub>

The carbons atoms (C35-C36) of ethyl substitutes are disordered at the same sites.

The aryl atoms (C28-C32) are disordered over two sites with occupancies 0.5:0.5.

#### [Zn6]<sub>n</sub>

The n-butyl substitutes are disordered at the same sites.

Two n-butyl C atoms (C39A-C40A) is disordered over two sites with occupancies 0.5:0.5.

#### [Zn7]<sub>n</sub>

The carbons atoms (C36-C37) of ethyl substitutes are disordered at the same sites.

The carbon atom (C34) of other ethyl substitutes is disordered over two sites with occupancies 0.5:0.5

#### [Zn8]<sub>n</sub>

The carbons atoms of ethyl substitutes are disordered at the same sites.

#### [Zn9]<sub>n</sub>

All atoms of Et-and OMe substitutes are disordered at the same sites.

**Table S1.** Crystal data and structure refinement for complexes **Zn5–Zn9**.

Identification code	<b>Zn5</b>	<b>Zn6</b>	<b>Zn7</b>	<b>Zn8</b>	<b>Zn9</b>
CCDC	1844989	1844992	1844991	1844990	1844993
Empirical formula	C <sub>36</sub> H <sub>29</sub> N <sub>4</sub> O <sub>3</sub> PZn	C <sub>40</sub> H <sub>35</sub> N <sub>4</sub> O <sub>3</sub> PZn	C <sub>38</sub> H <sub>27</sub> N <sub>5</sub> O <sub>4</sub> PZn	C <sub>152</sub> H <sub>132</sub> N <sub>16</sub> O <sub>12</sub> P <sub>4</sub> Zn <sub>4</sub>	C <sub>152</sub> H <sub>140</sub> N <sub>16</sub> O <sub>20</sub> P <sub>4</sub> Zn <sub>4</sub>
Formula weight	661.97	716.06	713.98	2760.09	2896.15
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	monoclinic	orthorhombic	monoclinic	tetragonal	tetragonal
Space group	P2 <sub>1</sub>	Pbca	C2/c	P-42 <sub>1</sub> c	P-42 <sub>1</sub> c
a/Å	11.2709(17)	11.4139(14)	33.220(5)	21.1528(7)	20.973(4)
b/Å	10.9305(16)	21.797(3)	10.1145(15)	21.1528(7)	20.973(4)
c/Å	13.289(2)	26.842(3)	23.218(3)	15.1147(6)	15.568(4)
α/°	90	90	90	90	90
β/°	109.961(2)	90	117.342(2)	90	90
γ/°	90	90	90	90	90
Volume/Å <sup>3</sup>	1538.8(4)	6678.0(14)	6929.6(18)	6762.9(5)	6848(3)
Z	2	8	8	2	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.429	1.424	1.369	1.355	1.405
μ/mm <sup>-1</sup>	0.894	0.830	0.803	0.817	0.814
F(000)	684.0	2976.0	2936.0	2864.0	3008.0
Crystal size/mm <sup>3</sup>	0.24 × 0.22 × 0.20	0.24 × 0.22 × 0.20	0.22 × 0.20 × 0.18	0.22 × 0.20 × 0.18	0.22 × 0.20 × 0.18
2θ range for data collection/°	4.95 to 59.99	3.74 to 57.99	4.95 to 60.00	3.85 to 59.99	4.68 to 54.00
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -18 ≤ l ≤ 18	-15 ≤ h ≤ 15, -29 ≤ k ≤ 25, -36 ≤ l ≤ 36	-46 ≤ h ≤ 46, -14 ≤ k ≤ 14, -32 ≤ l ≤ 32	-29 ≤ h ≤ 25, -15 ≤ k ≤ 29, -19 ≤ l ≤ 21	-25 ≤ h ≤ 26, -26 ≤ k ≤ 26, -19 ≤ l ≤ 19
Reflections collected	18125	56745	39845	35445	52423
Independent reflections	8851 [R <sub>int</sub> = 0.0384, R <sub>sigma</sub> = 0.0738]	8878 [R <sub>int</sub> = 0.1202, R <sub>sigma</sub> = 0.0867]	10104 [R <sub>int</sub> = 0.1455, R <sub>sigma</sub> = 0.1464]	9858 [R <sub>int</sub> = 0.0548, R <sub>sigma</sub> = 0.0804]	7469 [R <sub>int</sub> = 0.2027, R <sub>sigma</sub> = 0.1346]
Data/restraints/parameters	8851/3/397	8878/0/402	10104/0/452	9858/0/429	7469/0/435
Goodness-of-fit on F <sup>2</sup>	1.006	1.147	0.957	0.972	1.088
<sup>a</sup> Final R indexes [I ≥ 2σ(I)]	R <sub>1</sub> = 0.0493, wR <sub>2</sub> = 0.1043	R <sub>1</sub> = 0.0736, wR <sub>2</sub> = 0.1661	R <sub>1</sub> = 0.0616, wR <sub>2</sub> = 0.1170	R <sub>1</sub> = 0.0391, wR <sub>2</sub> = 0.0608	R <sub>1</sub> = 0.0872, wR <sub>2</sub> = 0.2020
<sup>a</sup> Final R indexes [all data]	R <sub>1</sub> = 0.0654, wR <sub>2</sub> = 0.1110	R <sub>1</sub> = 0.1366, wR <sub>2</sub> = 0.1946	R <sub>1</sub> = 0.1525, wR <sub>2</sub> = 0.1514	R <sub>1</sub> = 0.0631, wR <sub>2</sub> = 0.0632	R <sub>1</sub> = 0.1645, wR <sub>2</sub> = 0.2377
Largest diff. peak/hole / e Å <sup>-3</sup>	0.84/-0.38	1.63/-1.81	0.59/-0.41	0.88/-0.54	1.19/-0.57

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$$

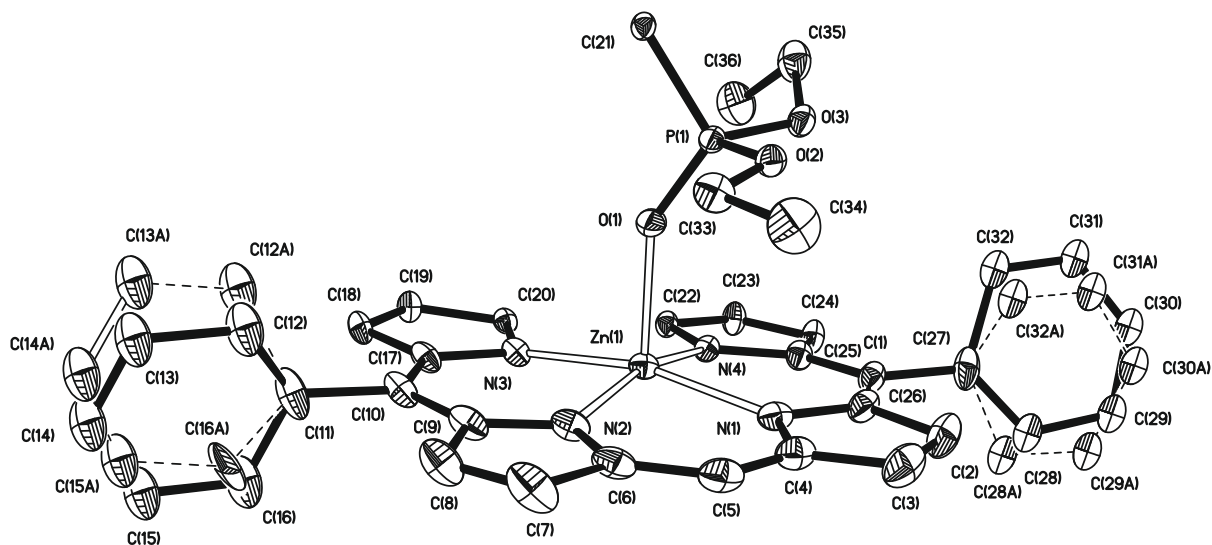
**Table S2.** Selected bond distances and angles in dialkoxyphosphorylporphyrins **Zn5–Zn9**.

Compound	Zn–N [Å]	Zn–O <sup>a</sup> [Å]	Zn/N <sub>4</sub> <sup>b</sup> [Å]	RMSD N <sub>4</sub> <sup>c</sup> [Å]	P/N <sub>4</sub> <sup>d</sup> [Å]	planes N <sub>4</sub> /CP=O dihedral angle [°]	P(O)(OEt) <sub>2</sub> [Å]	planes N <sub>4</sub> /Ar dihedral angle [°]	max C··N <sub>4</sub> <sup>e</sup> [Å]	C–Ar [Å]	Zn/Zn <sup>f</sup> [Å]	N <sub>4</sub> /N <sub>4</sub> planes angle <sup>g</sup> [°]
[Zn5] <sub>n</sub>	2.052(4) 2.060(3) 2.064(4) 2.074(3)	2.071(3)	0.268	±0.015	0.046	8.9	1.469(3) (P=O) 1.564(3) (P–O) 1.570(3) (P–O) 1.790(4) (P–C)	80.9 62.9	-0.242	1.487(3)	7.939	84.8
[Zn6] <sub>n</sub>	2.062(3) 2.064(4) 2.067(3) 2.068(4)	2.113(3)	0.282	±0.028	-0.216	7.4	1.475(3) (P=O) 1.569(3) (P–O) 1.575(3) (P–O) 1.808(4) (P–C)	80.6 60.2	-0.326	1.501(4) 1.506(4)	8.063	88.9
[Zn7] <sub>n</sub>	2.067(3) 2.073(3) 2.074(3) 2.074(3)	2.081(2)	0.333	±0.013	0.056	34.9	1.468(3) (P=O) 1.549(3) (P–O) 1.556(3) (P–O) 1.799(4) (P–C)	75.2 60.1	-0.321	1.498(3)1. 504(3)	7.863	85.8
[Zn8] <sub>4</sub>	2.061(2) 2.070(3) 2.075(3) 2.075(2)	2.072(2)	0.305	±0.010	-0.242	10.3	1.469(2) (P=O) 1.565(2) (P–O) 1.569(2) (P–O) 1.798(3) (P–C)	72.6 71.4	-0.396	1.500(3) 1.510(3)	8.042	86.3
[Zn9] <sub>4</sub>	2.043(11) 2.056(9) 2.069(10) 2.090(10)	2.083(8)	-0.310	±0.000	0.139	9.3	1.456(9) (P=O) 1.543(1) (P–O) 1.56(1) (P–O) 1.750(15) (P–C)	73.7 73.7	0.317	1.516(9)1. 534(9)	8.053	87.8

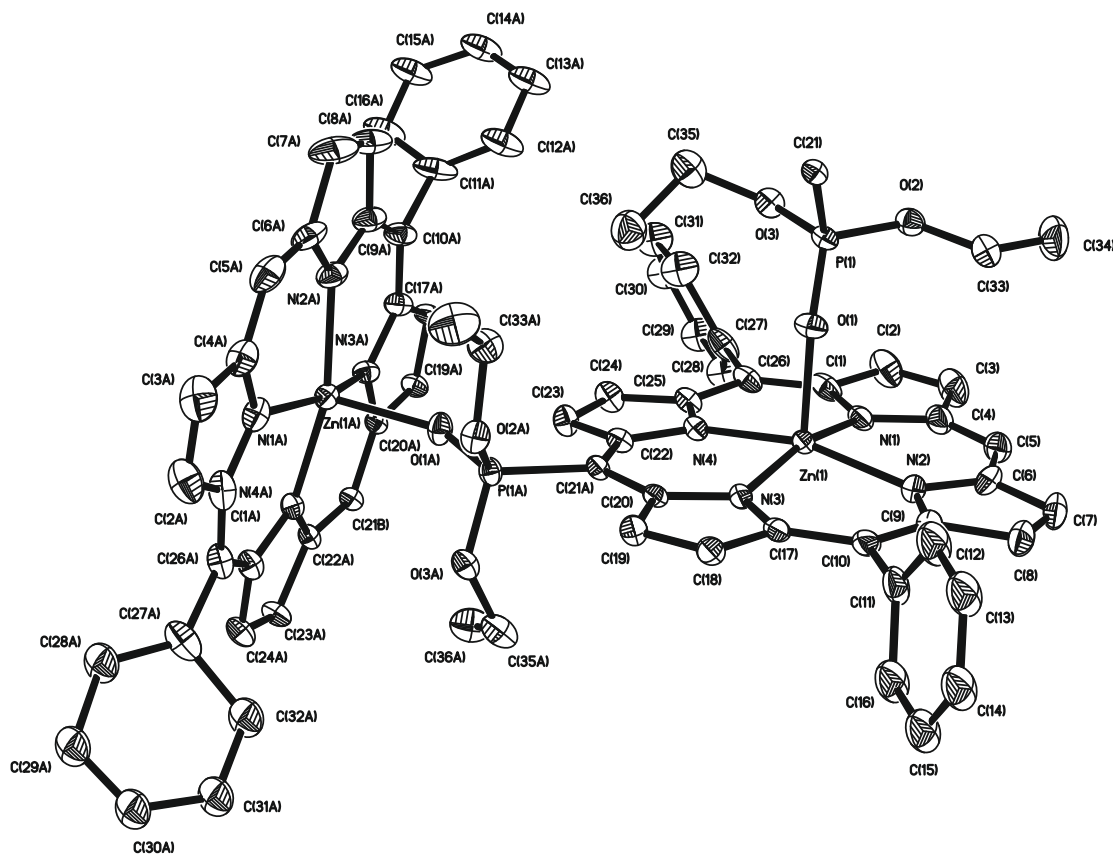
<sup>a</sup> Axial coordination bond.<sup>b</sup> Deviation of the zinc atom from the mean N<sub>4</sub> plane of the macrocycle.<sup>c</sup> RMS deviation of carbon atoms from the mean N<sub>4</sub> plane of the macrocycle.<sup>d</sup> Deviation of the phosphorus atom from the mean N<sub>4</sub> plane of the macrocycle.<sup>e</sup> Maximal deviation of carbon atoms of the macrocycle from the mean N<sub>4</sub> plane of this macrocycle.<sup>f</sup> Distance between two nearest zinc atoms.<sup>g</sup> Dihedral angle formed by the mean N<sub>4</sub> planes of the nearest porphyrin molecules



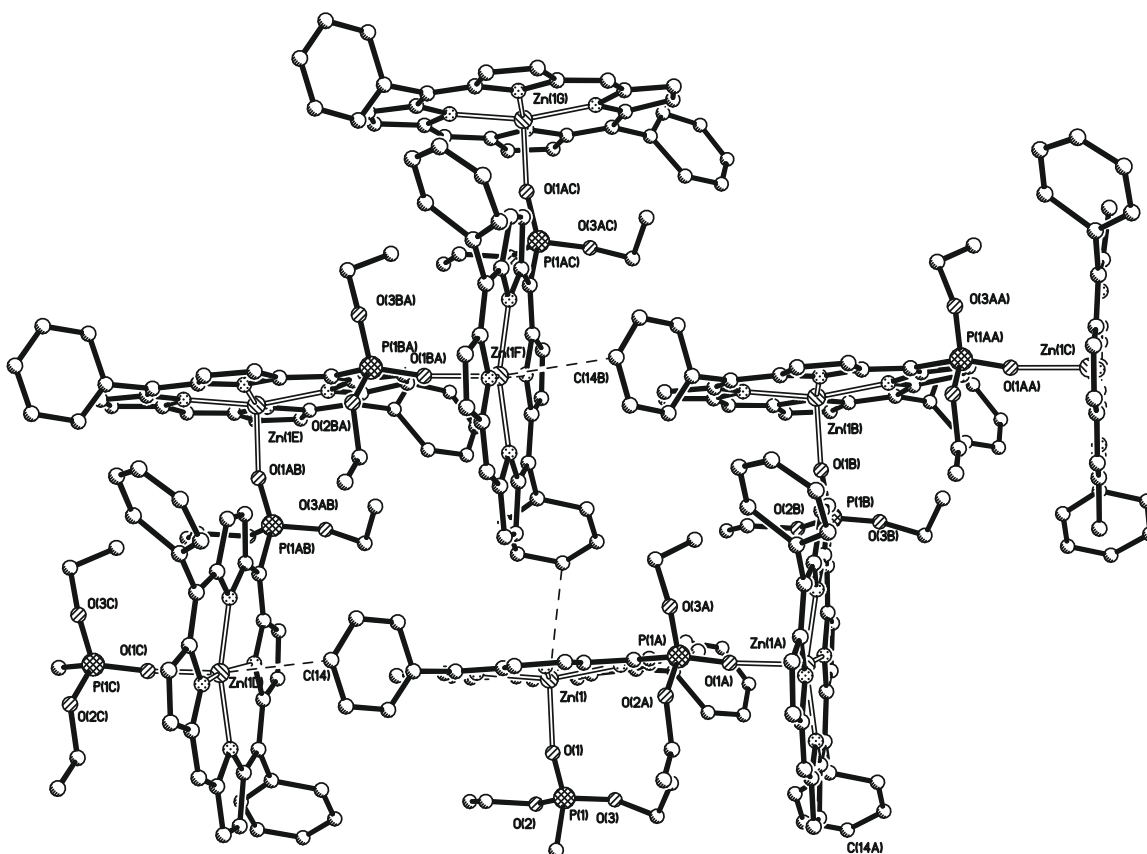
## 2. Crystal data for porphyrin Zn5.



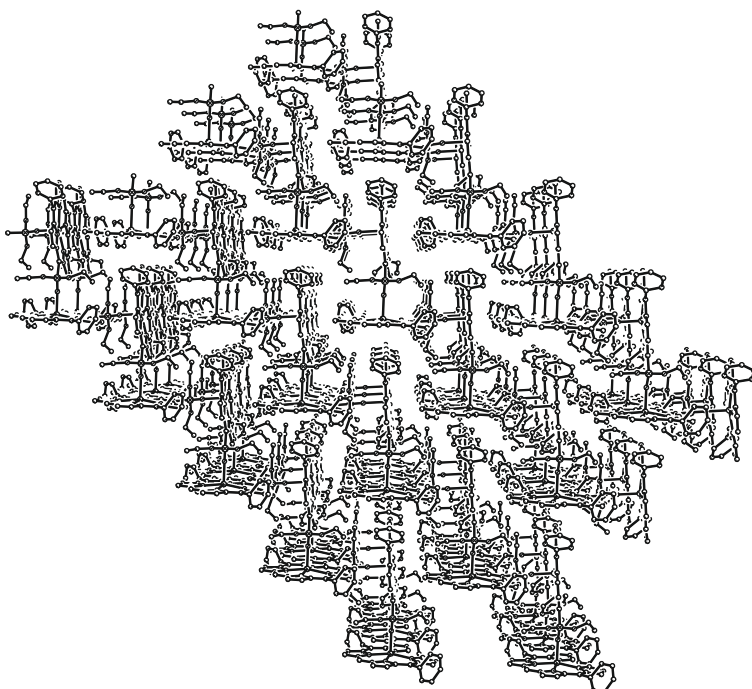
**Figure S1.** Independent part of coordination polymer  $[\text{Zn}5]_n$  (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.



**Figure S2.** Fragment of coordination polymer  $[\text{Zn}5]_n$  (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.



**Figure S3.** Two polymer chains of coordination polymer  $[\text{Zn}_5]_n$  interacting through C–H $\cdots$ Zn,N contacts. Hydrogen atoms are omitted for clarity.



**Figure S4.** Crystal packing of coordination polymer  $[\text{Zn}_5]_n$ . Hydrogen atoms are omitted for clarity.

**Table S3.** Selected bond distances (Å) and angles (deg) for complex [Zn5]<sub>n</sub>.

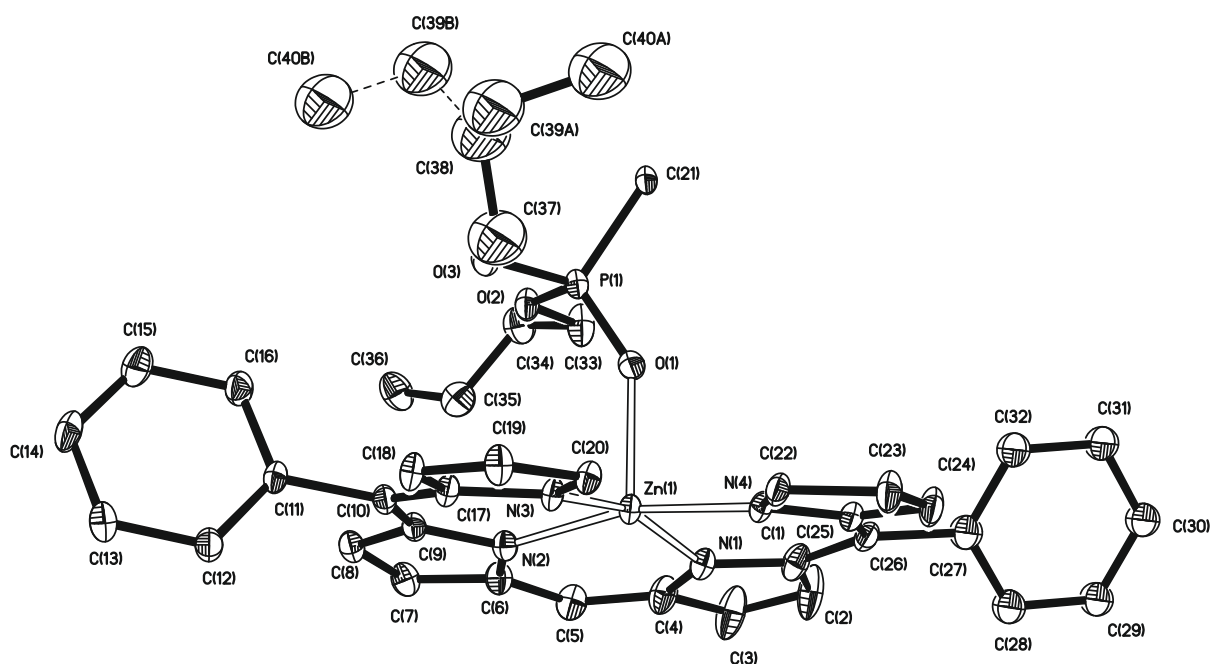
## Bond distances (Å)

Zn(1)-N(4)	2.052(4)	Zn(1)-N(3)	2.060(3)
Zn(1)-N(2)	2.064(4)	Zn(1)-N(1)	2.074(3)
Zn(1)-O(1)	2.071(3)	P(1)-O(1)	1.469(3)
P(1)-O(3)	1.564(3)	P(1)-O(2)	1.570(3)
P(1)-C(21)	1.790(4)	N(1)-C(4)	1.359(6)
N(1)-C(1)	1.382(6)	N(2)-C(9)	1.365(6)
N(2)-C(6)	1.370(6)	N(3)-C(20)	1.370(5)
N(3)-C(17)	1.383(5)	N(4)-C(22)	1.367(5)
N(4)-C(25)	1.380(5)	O(2)-C(33)	1.444(6)
O(3)-C(35)	1.475(7)		

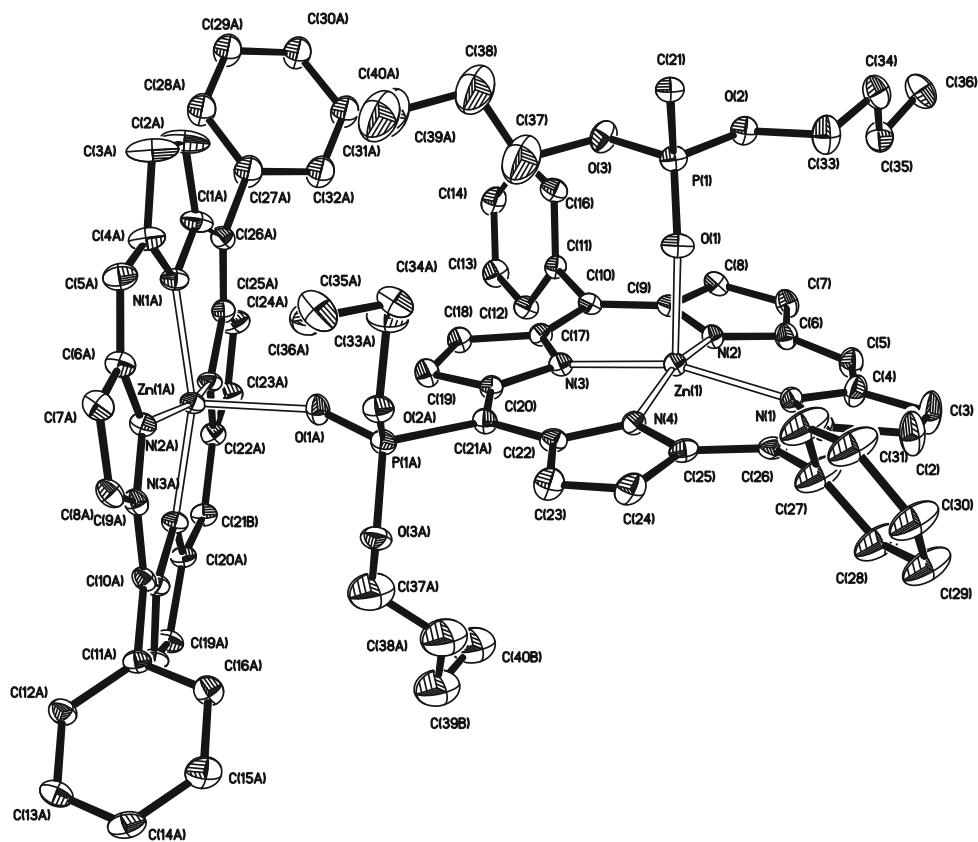
## Bond angles (deg)

N(4)-Zn(1)-N(3)	88.61(13)	N(4)-Zn(1)-N(2)	164.21(14)
N(3)-Zn(1)-N(2)	89.17(14)	N(4)-Zn(1)-O(1)	98.16(14)
N(3)-Zn(1)-O(1)	95.57(13)	N(2)-Zn(1)-O(1)	97.61(15)
N(4)-Zn(1)-N(1)	89.67(16)	N(3)-Zn(1)-N(1)	165.92(14)
N(2)-Zn(1)-N(1)	88.69(16)	O(1)-Zn(1)-N(1)	98.51(13)
O(1)-P(1)-O(3)	114.56(19)	O(1)-P(1)-O(2)	111.91(18)
O(3)-P(1)-O(2)	98.62(17)	O(1)-P(1)-C(21)	112.86(18)
O(3)-P(1)-C(21)	108.41(18)	O(2)-P(1)-C(21)	109.52(18)
C(4)-N(1)-C(1)	106.7(4)	C(4)-N(1)-Zn(1)	126.7(4)
C(1)-N(1)-Zn(1)	125.9(3)	C(9)-N(2)-C(6)	106.8(4)
C(9)-N(2)-Zn(1)	126.4(3)	C(6)-N(2)-Zn(1)	126.0(4)
C(20)-N(3)-C(17)	106.4(3)	C(20)-N(3)-Zn(1)	127.0(3)
C(17)-N(3)-Zn(1)	125.7(3)	C(22)-N(4)-C(25)	106.7(3)
C(22)-N(4)-Zn(1)	127.7(3)	C(25)-N(4)-Zn(1)	125.4(3)
P(1)-O(1)-Zn(1)	148.1(2)	C(33)-O(2)-P(1)	119.7(3)
C(35)-O(3)-P(1)	122.8(3)		

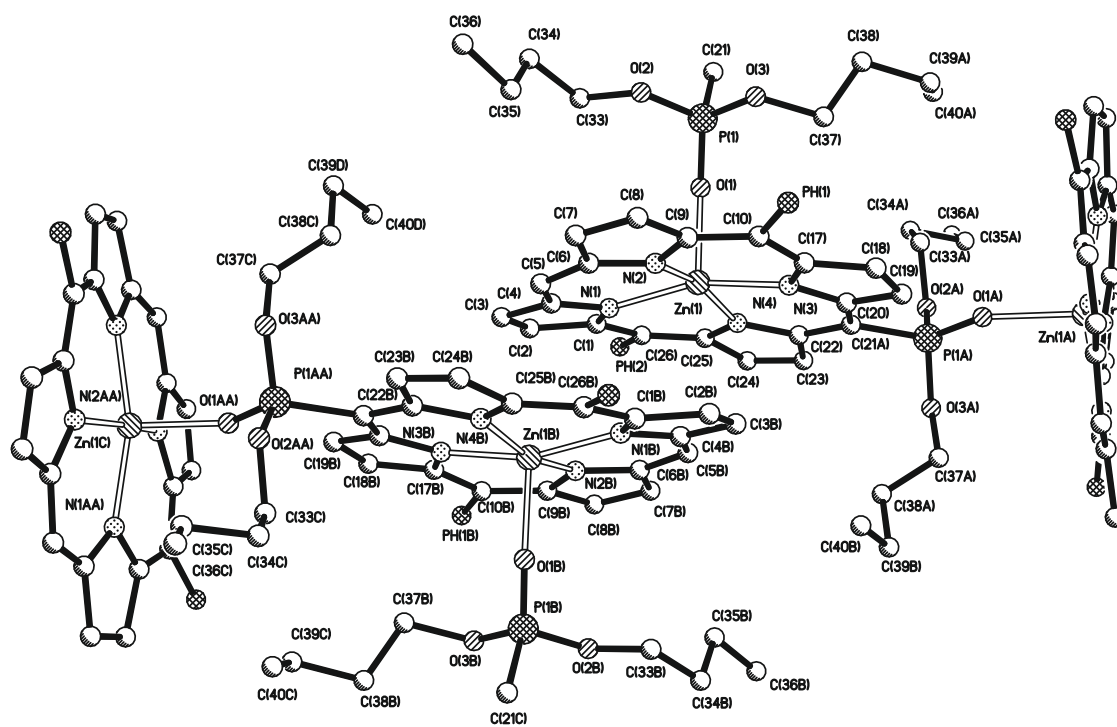
### 3. Crystal data for porphyrin Zn6.



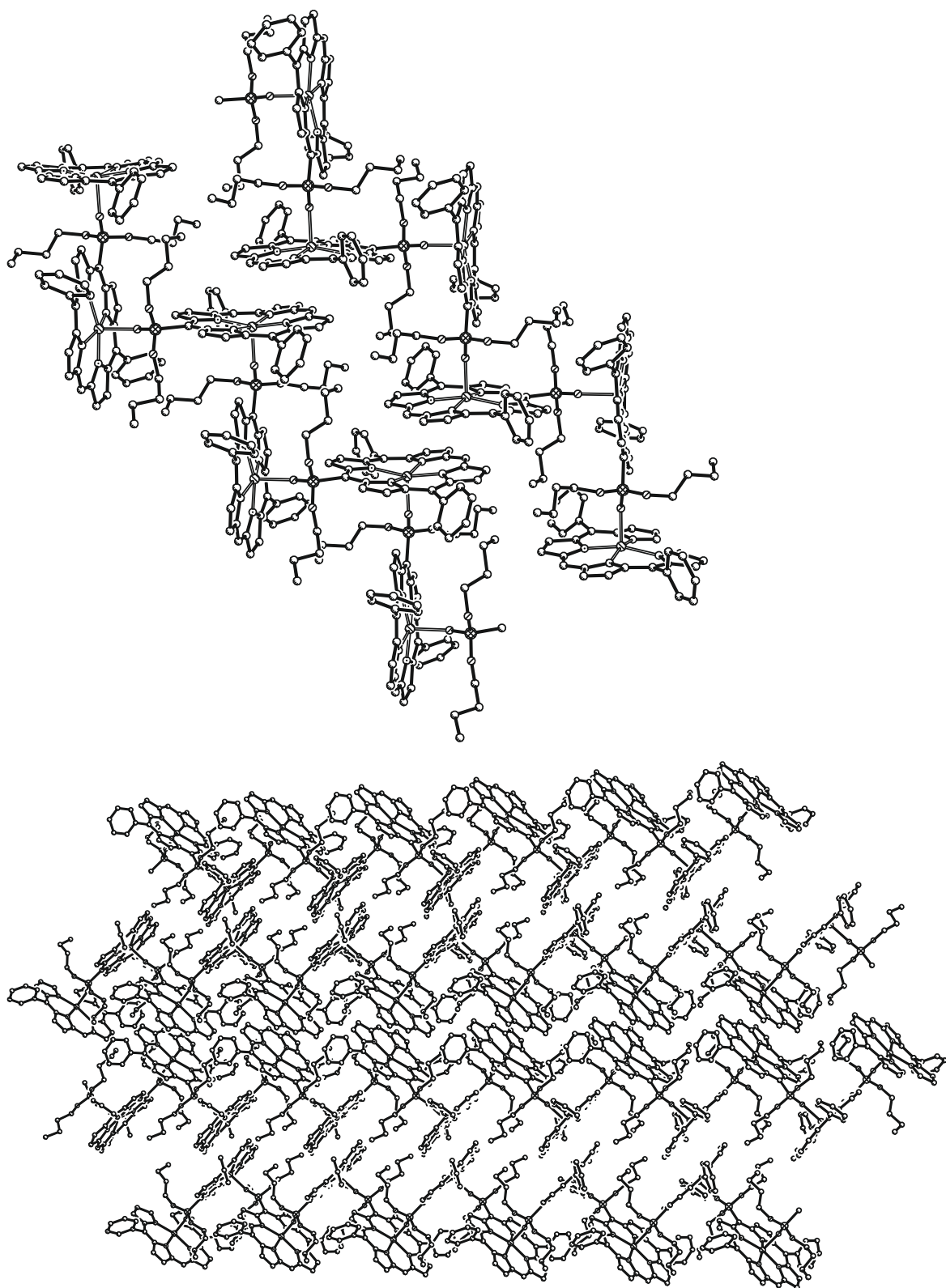
**Figure S5.** Independent part of coordination polymer  $[\text{Zn6}]_n$  (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.



**Figure S6.** Fragment of coordination polymer  $[\text{Zn6}]_n$  (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.



**Figure S7.**  $\pi$ - $\pi$  Contacts between two porphyrin macrocycles in neighboring polymeric chains observed in the crystal of  $[\text{Zn}_6]_n$ . Hydrogen atoms are omitted for clarity.



**Figure S8.** Crystal packing of coordination polymer [Zn6]<sub>n</sub>. Hydrogen atoms are omitted for clarity.

**Table S4.** Selected bond distances (Å) and angles (deg) for complex [Zn6]<sub>n</sub>.

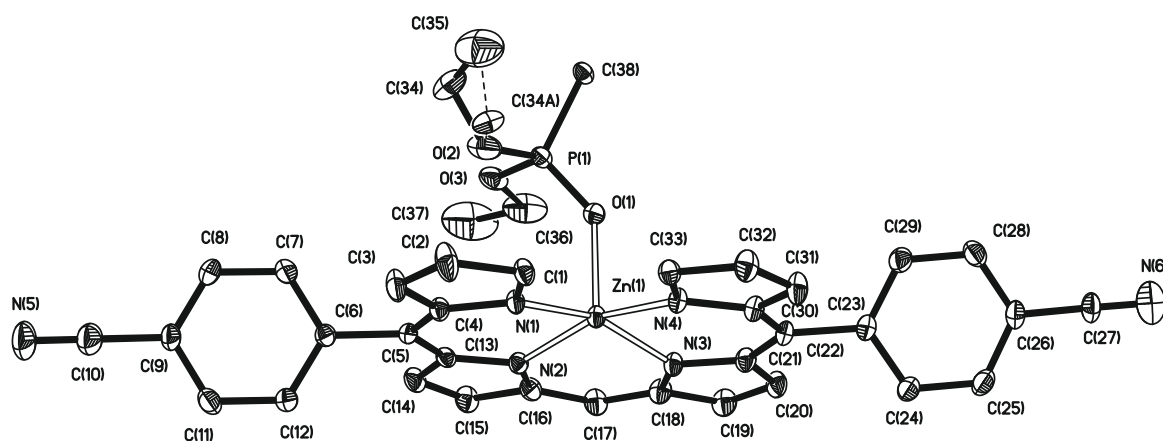
## Bond distances (Å)

Zn(1)-N(4)	2.062(3)	Zn(1)-N(3)	2.064(4)
Zn(1)-N(2)	2.067(3)	Zn(1)-N(1)	2.068(4)
Zn(1)-O(1)	2.113(3)	P(1)-O(1)	1.475(3)
P(1)-O(2)	1.569(3)	P(1)-O(3)	1.575(3)
P(1)-C(21)	1.808(4)	O(2)-C(33)	1.443(6)
O(3)-C(37)	1.481(9)	N(1)-C(1)	1.365(5)
N(1)-C(4)	1.371(6)	N(2)-C(9)	1.361(5)
N(2)-C(6)	1.363(6)	N(3)-C(20)	1.368(5)
N(3)-C(17)	1.388(5)	N(4)-C(22)	1.363(6)
N(4)-C(25)	1.378(5)		

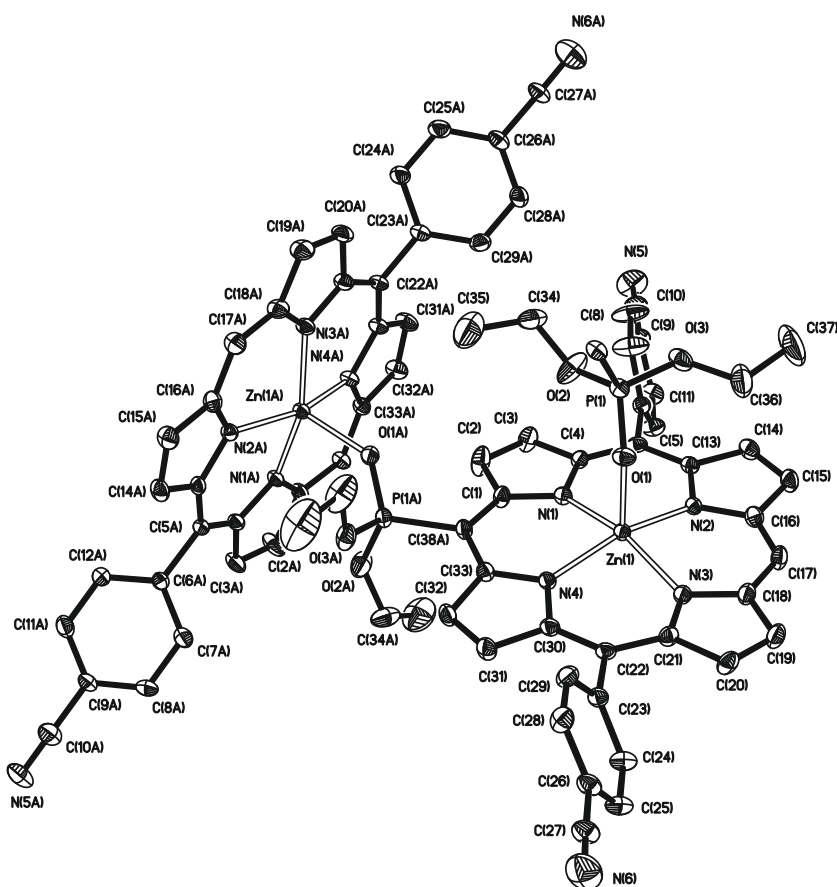
## Bond angles (deg)

N(4)-Zn(1)-N(3)	88.35(13)	N(4)-Zn(1)-N(2)	165.84(14)
N(3)-Zn(1)-N(2)	89.46(13)	N(4)-Zn(1)-N(1)	88.79(14)
N(3)-Zn(1)-N(1)	162.69(15)	N(2)-Zn(1)-N(1)	89.16(14)
N(4)-Zn(1)-O(1)	96.75(13)	N(3)-Zn(1)-O(1)	98.39(14)
N(2)-Zn(1)-O(1)	97.41(13)	N(1)-Zn(1)-O(1)	98.90(14)
O(1)-P(1)-O(2)	113.14(19)	O(1)-P(1)-O(3)	114.4(2)
O(2)-P(1)-O(3)	97.93(18)	O(1)-P(1)-C(21)	113.53(18)
O(2)-P(1)-C(21)	108.0(2)	O(3)-P(1)-C(21)	108.6(2)
P(1)-O(1)-Zn(1)	147.42(19)	C(33)-O(2)-P(1)	119.0(3)
C(37)-O(3)-P(1)	117.1(4)	C(1)-N(1)-C(4)	106.9(4)
C(1)-N(1)-Zn(1)	126.7(3)	C(4)-N(1)-Zn(1)	125.8(3)
C(9)-N(2)-C(6)	106.6(4)	C(9)-N(2)-Zn(1)	125.8(3)
C(6)-N(2)-Zn(1)	126.9(3)	C(20)-N(3)-C(17)	106.2(3)
C(20)-N(3)-Zn(1)	129.2(3)	C(17)-N(3)-Zn(1)	124.4(3)
C(22)-N(4)-C(25)	107.2(3)	C(22)-N(4)-Zn(1)	127.8(3)
C(25)-N(4)-Zn(1)	125.0(3)		

#### 4. Crystal data for porphyrin Zn7.

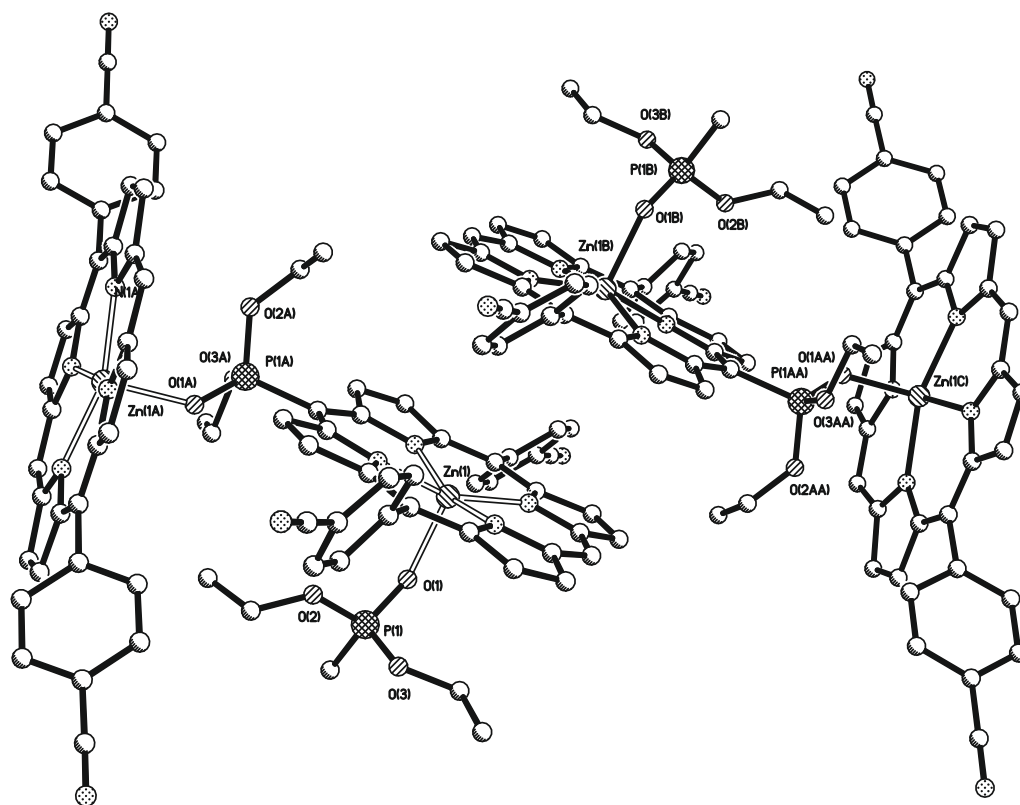


**Figure S9.** Independent part of coordination polymer  $[\text{Zn7}]_n$  (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.

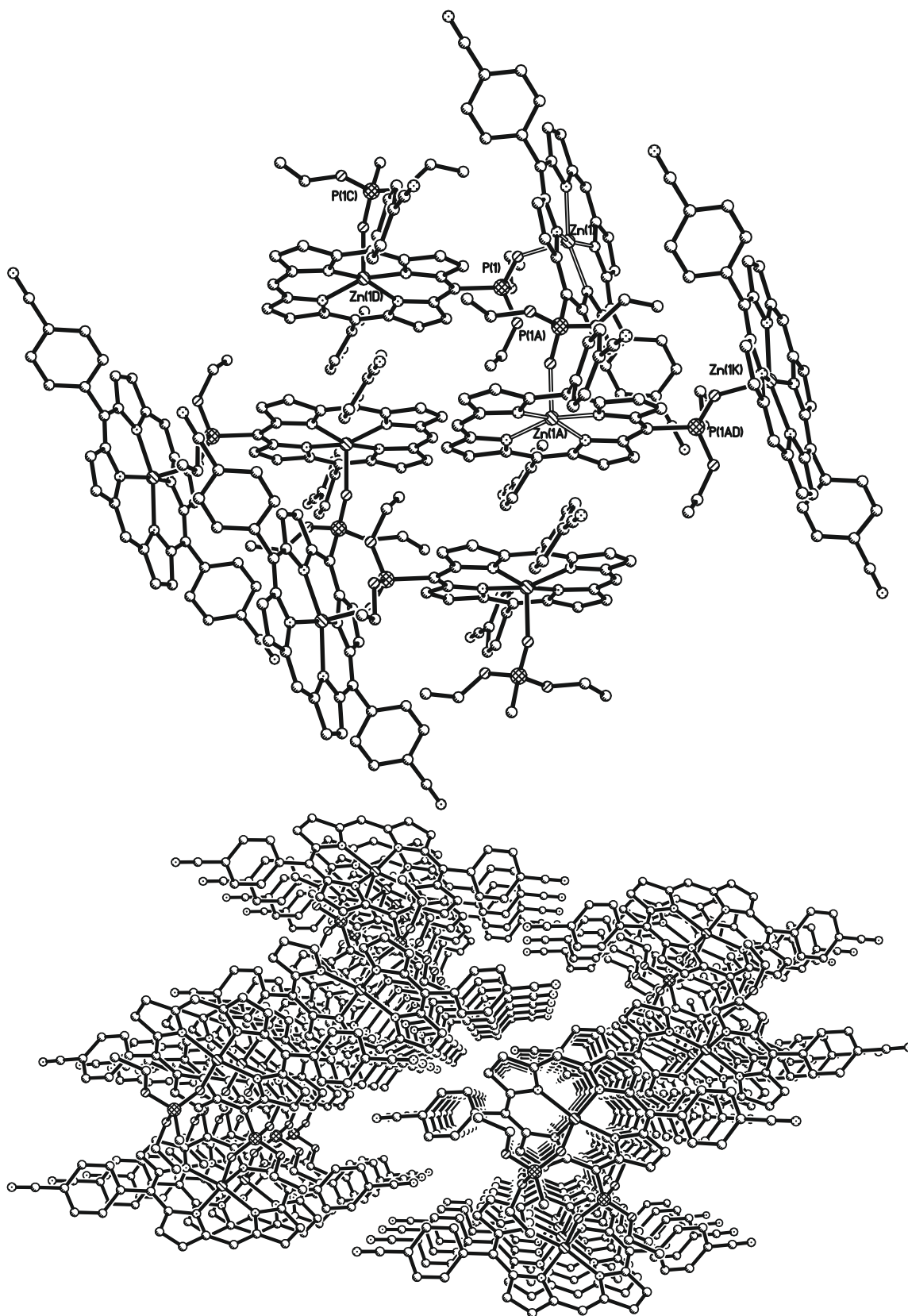


**Figure S10.** Fragment of coordination polymer  $[\text{Zn7}]_n$  (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.





**Figure S11.**  $\pi$ - $\pi$  Contacts between two porphyrin macrocycles in neighboring polymeric chains observed in the crystal of  $[\text{Zn}_7]_n$ . Hydrogen atoms are omitted for clarity.



**Figure S12.** Crystal packing of coordination polymer  $[\text{Zn7}]_n$ . Hydrogen atoms are omitted for clarity.

**Table S5.** Selected bond distances (Å) and angles (deg) for complex [Zn7]<sub>n</sub>.

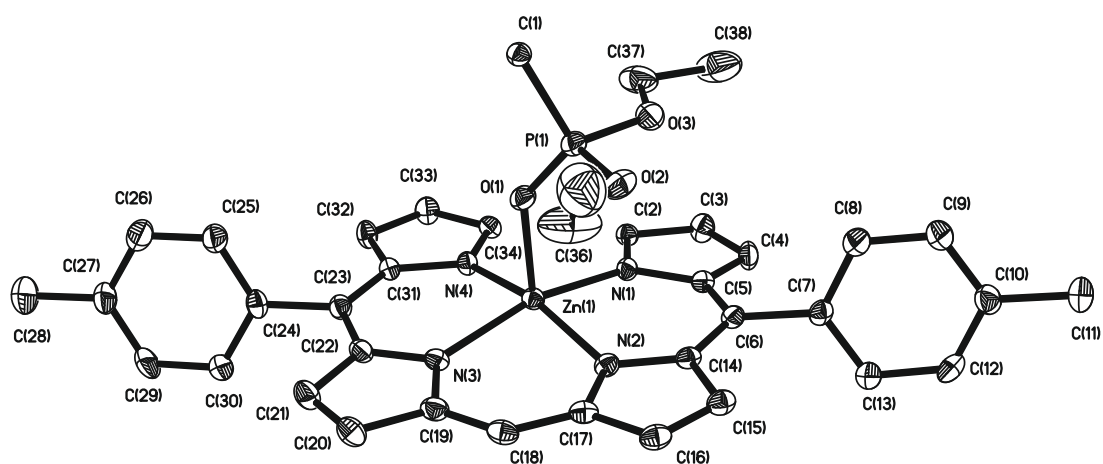
## Bond distances (Å)

Zn(1)-N(1)	2.067(3)	Zn(1)-N(4)	2.073(3)
Zn(1)-N(3)	2.074(3)	Zn(1)-N(2)	2.074(3)
Zn(1)-O(1)	2.081(2)	P(1)-O(1)	1.468(3)
P(1)-O(2)	1.549(3)	P(1)-O(3)	1.556(3)
P(1)-C(38)	1.799(4)	O(2)-C(34A)	1.296(15)
O(2)-C(34)	1.376(7)	O(3)-C(36)	1.452(6)
N(1)-C(1)	1.360(4)	N(1)-C(4)	1.376(4)
N(2)-C(16)	1.363(4)	N(2)-C(13)	1.365(4)
N(3)-C(21)	1.358(4)	N(3)-C(18)	1.363(4)
N(4)-C(33)	1.378(4)	N(4)-C(30)	1.385(4)
N(5)-C(10)	1.147(5)	N(6)-C(27)	1.138(5)

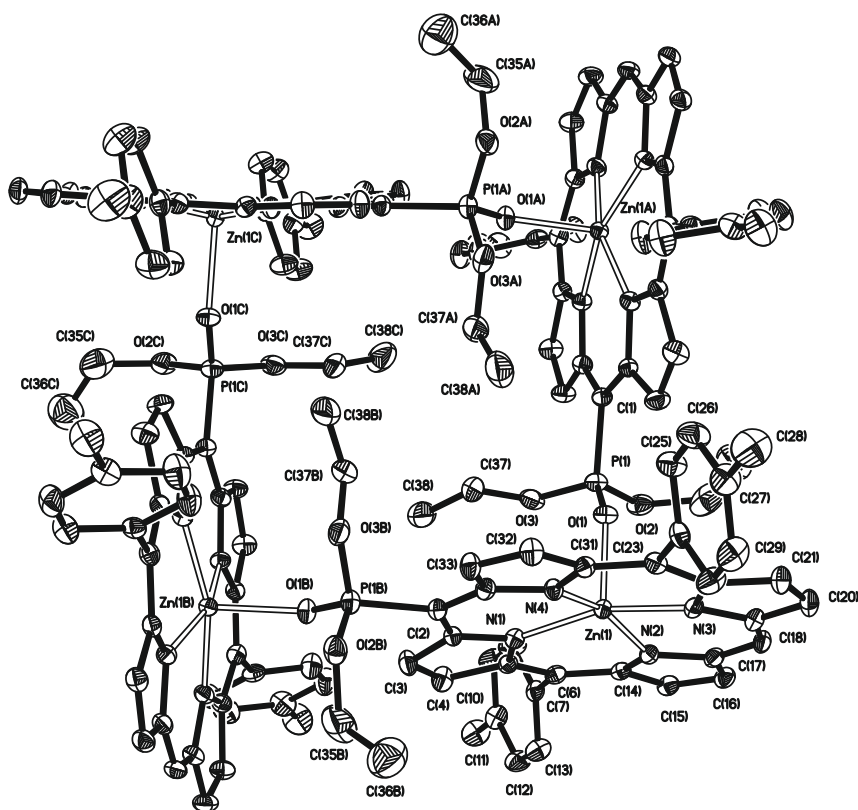
## Bond angles (deg)

N(1)-Zn(1)-N(4)	88.02(11)	N(1)-Zn(1)-N(3)	160.76(12)
N(4)-Zn(1)-N(3)	88.66(11)	N(1)-Zn(1)-N(2)	88.63(11)
N(4)-Zn(1)-N(2)	162.30(11)	N(3)-Zn(1)-N(2)	88.80(11)
N(1)-Zn(1)-O(1)	98.42(11)	N(4)-Zn(1)-O(1)	99.00(10)
N(3)-Zn(1)-O(1)	100.82(11)	N(2)-Zn(1)-O(1)	98.69(10)
O(1)-P(1)-O(2)	112.73(17)	O(1)-P(1)-O(3)	111.13(16)
O(2)-P(1)-O(3)	101.23(19)	O(1)-P(1)-C(38)	111.91(16)
O(2)-P(1)-C(38)	108.16(17)	O(3)-P(1)-C(38)	111.19(16)
P(1)-O(1)-Zn(1)	137.47(16)	C(34A)-O(2)-P(1)	133.5(8)
C(34)-O(2)-P(1)	131.1(4)	C(36)-O(3)-P(1)	118.9(3)
C(1)-N(1)-C(4)	107.1(3)	C(1)-N(1)-Zn(1)	127.0(2)
C(4)-N(1)-Zn(1)	125.2(2)	C(16)-N(2)-C(13)	106.4(3)
C(16)-N(2)-Zn(1)	125.6(2)	C(13)-N(2)-Zn(1)	126.4(2)
C(21)-N(3)-C(18)	106.7(3)	C(21)-N(3)-Zn(1)	126.7(2)
C(18)-N(3)-Zn(1)	125.3(2)	C(33)-N(4)-C(30)	106.7(3)
C(33)-N(4)-Zn(1)	127.5(2)	C(30)-N(4)-Zn(1)	125.6(2)

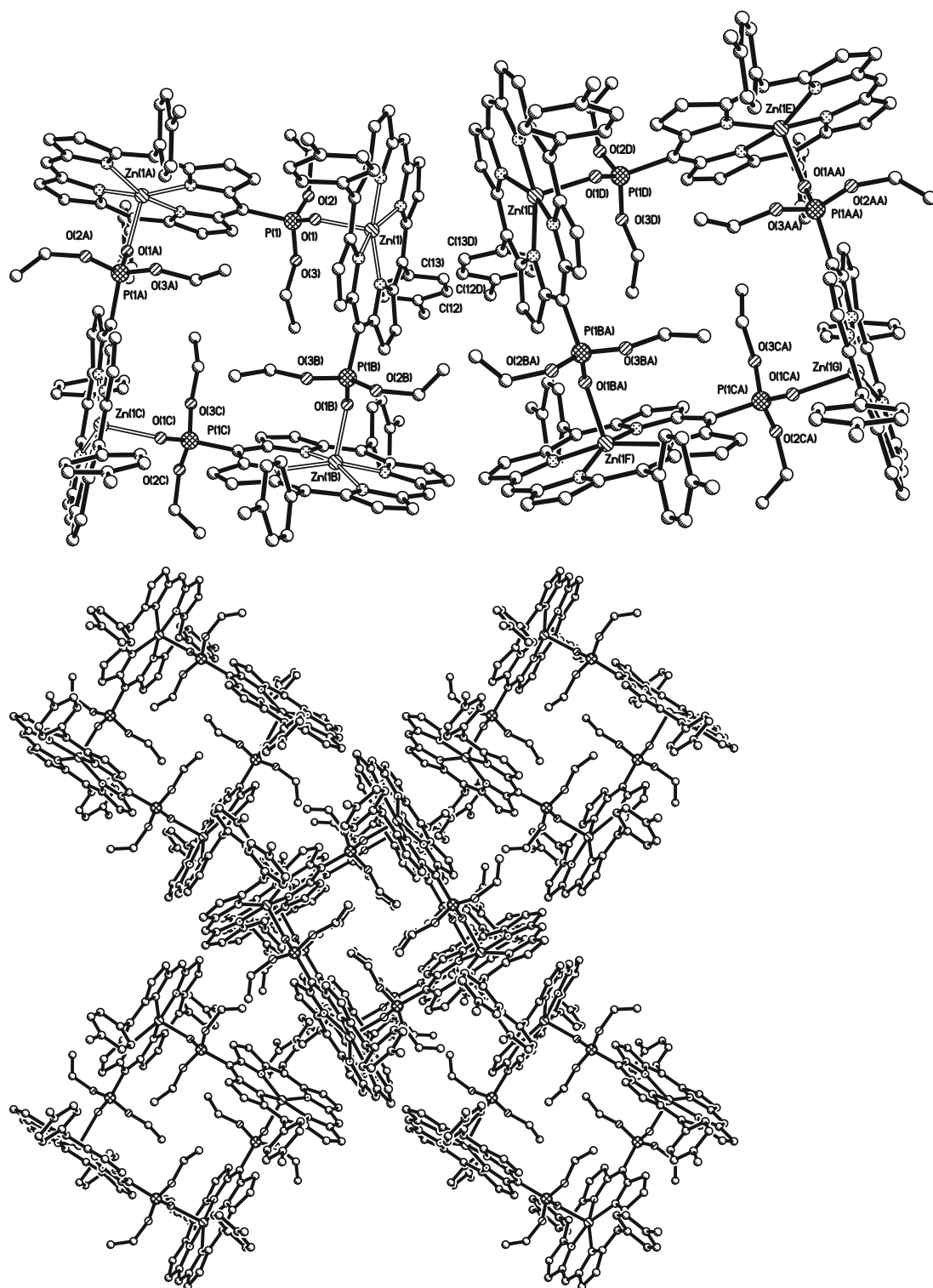
## 5. Crystal data for porphyrin Zn8.



**Figure S13.** Independent part of tetramer  $[\text{Zn}8]_4$  (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.



**Figure S14.** ORTEP view of tetramer  $[\text{Zn}8]_4$  (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.



**Figure S15.** Crystal packing of coordination polymer  $[\text{Zn}_8]_4$ . Hydrogen atoms are omitted for clarity.

**Table S6.** Selected bond distances (Å) and angles (deg) for complex [Zn8]4.

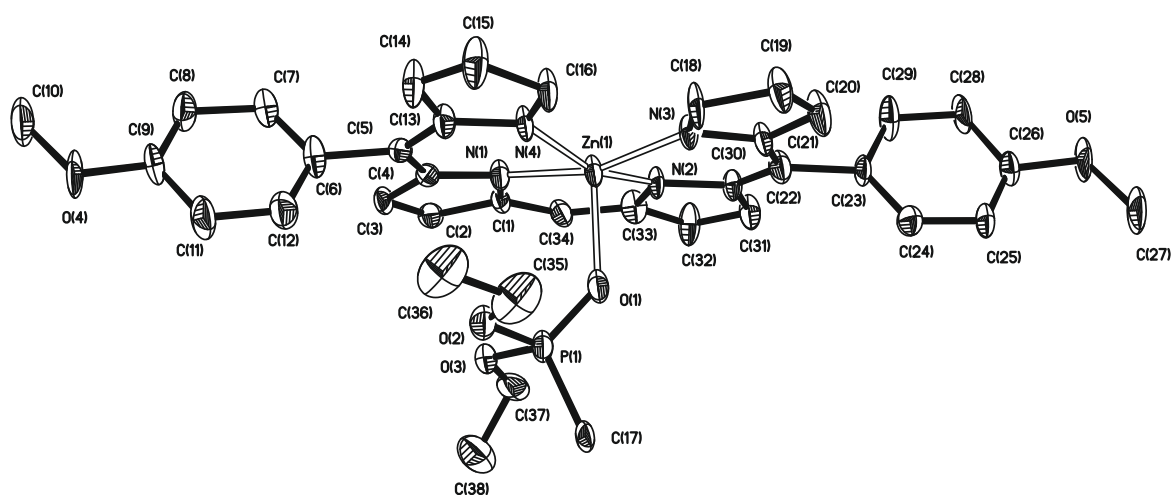
## Bond distances (Å)

Zn(1)-N(4)	2.061(2)	Zn(1)-N(1)	2.070(3)
Zn(1)-O(1)	2.0722(19)	Zn(1)-N(3)	2.075(3)
Zn(1)-N(2)	2.075(2)	P(1)-O(1)	1.469(2)
P(1)-O(2)	1.565(2)	P(1)-O(3)	1.569(2)
P(1)-C(1)	1.798(3)	O(2)-C(35)	1.450(5)
O(3)-C(37)	1.444(4)	N(1)-C(2)	1.378(4)
N(1)-C(5)	1.382(4)	N(2)-C(14)	1.367(4)
N(2)-C(17)	1.370(4)	N(3)-C(22)	1.361(4)
N(3)-C(19)	1.373(4)	N(4)-C(34)	1.358(4)
N(4)-C(31)	1.391(4)		

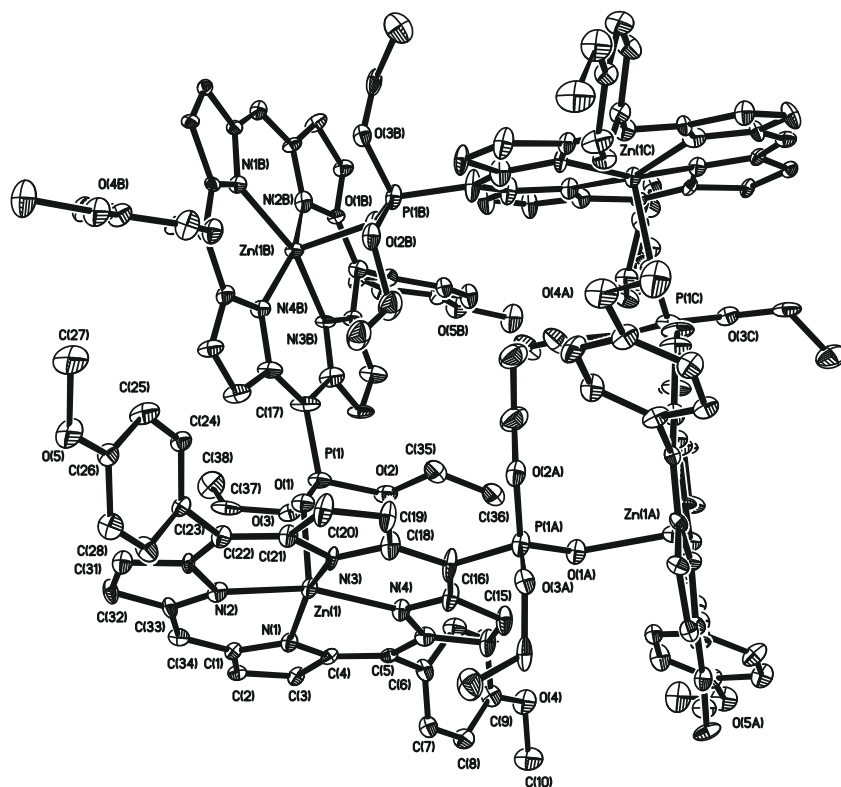
## Bond angles (deg)

N(4)-Zn(1)-N(1)	87.90(10)	N(4)-Zn(1)-O(1)	98.10(9)
N(1)-Zn(1)-O(1)	99.85(9)	N(4)-Zn(1)-N(3)	89.13(10)
N(1)-Zn(1)-N(3)	162.51(10)	O(1)-Zn(1)-N(3)	97.64(9)
N(4)-Zn(1)-N(2)	163.60(10)	N(1)-Zn(1)-N(2)	89.20(10)
O(1)-Zn(1)-N(2)	98.30(9)	N(3)-Zn(1)-N(2)	88.80(10)
O(1)-P(1)-O(2)	115.24(13)	O(1)-P(1)-O(3)	112.83(13)
O(2)-P(1)-O(3)	97.65(14)	O(1)-P(1)-C(1)	112.54(13)
O(2)-P(1)-C(1)	108.52(14)	O(3)-P(1)-C(1)	109.01(14)
P(1)-O(1)-Zn(1)	139.42(13)	C(35)-O(2)-P(1)	118.7(3)
C(37)-O(3)-P(1)	119.2(2)	C(2)-N(1)-C(5)	106.6(3)
C(2)-N(1)-Zn(1)	128.7(2)	C(5)-N(1)-Zn(1)	124.7(2)
C(14)-N(2)-C(17)	106.5(3)	C(14)-N(2)-Zn(1)	126.0(2)
C(17)-N(2)-Zn(1)	125.8(2)	C(22)-N(3)-C(19)	106.6(3)
C(22)-N(3)-Zn(1)	126.9(2)	C(19)-N(3)-Zn(1)	125.6(2)
C(34)-N(4)-C(31)	107.0(2)	C(34)-N(4)-Zn(1)	128.0(2)
C(31)-N(4)-Zn(1)	124.8(2)		

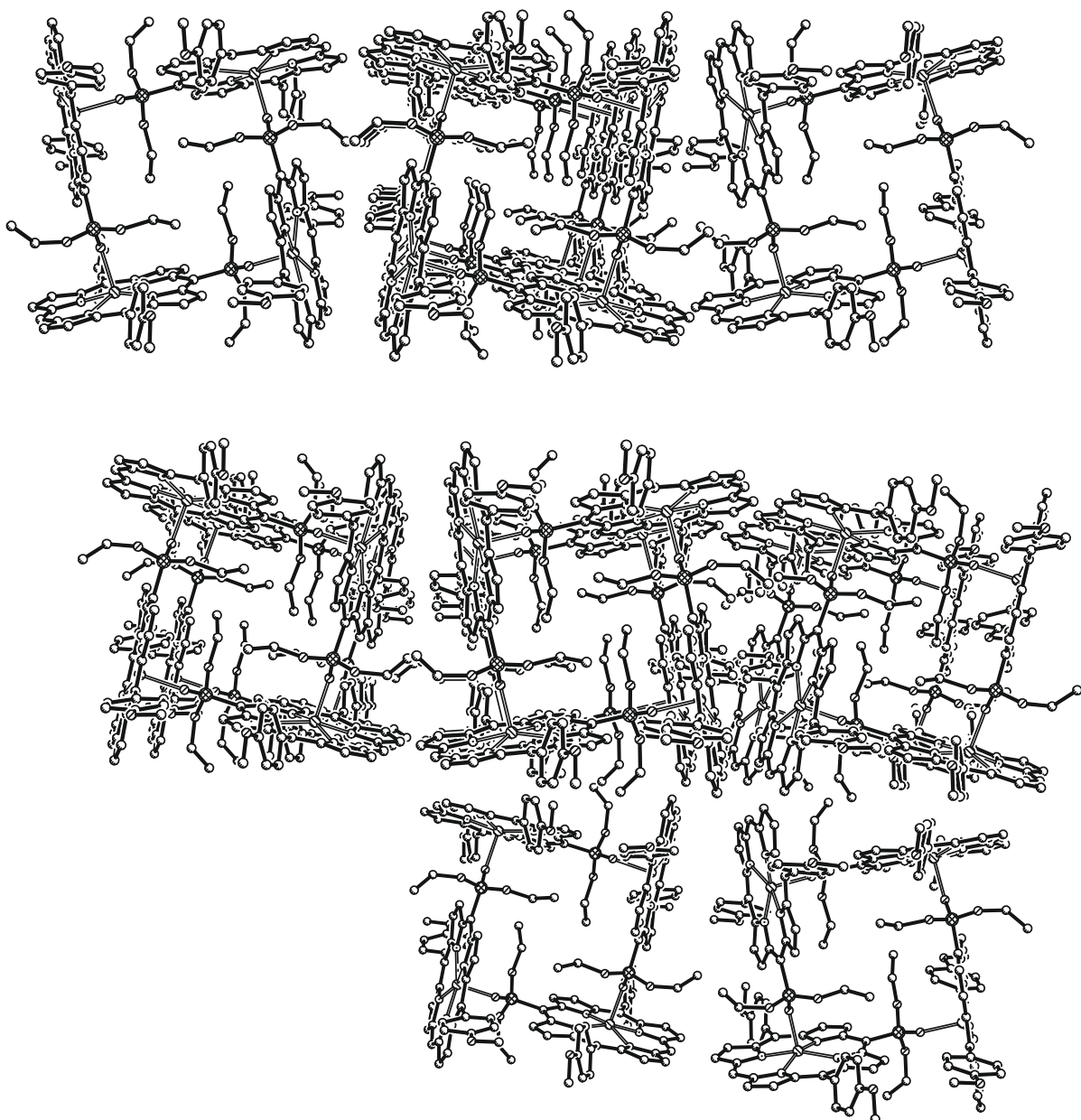
## 6. Crystal data for porphyrins Zn9.



**Figure S16.** Independent part of tetramer  $[\text{Zn9}]_4$  (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.



**Figure S17 .** ORTEP view of tetramer  $[\text{Zn9}]_4$  (30% probability ellipsoids). Hydrogen atoms are omitted for clarity.



**Figure S18.** Crystal packing of coordination polymer  $[\text{Zn}_9]_4$ . Hydrogen atoms are omitted for clarity.



**Table S7.** Selected bond distances (Å) and angles (deg) for complex [Zn9]<sub>4</sub>.

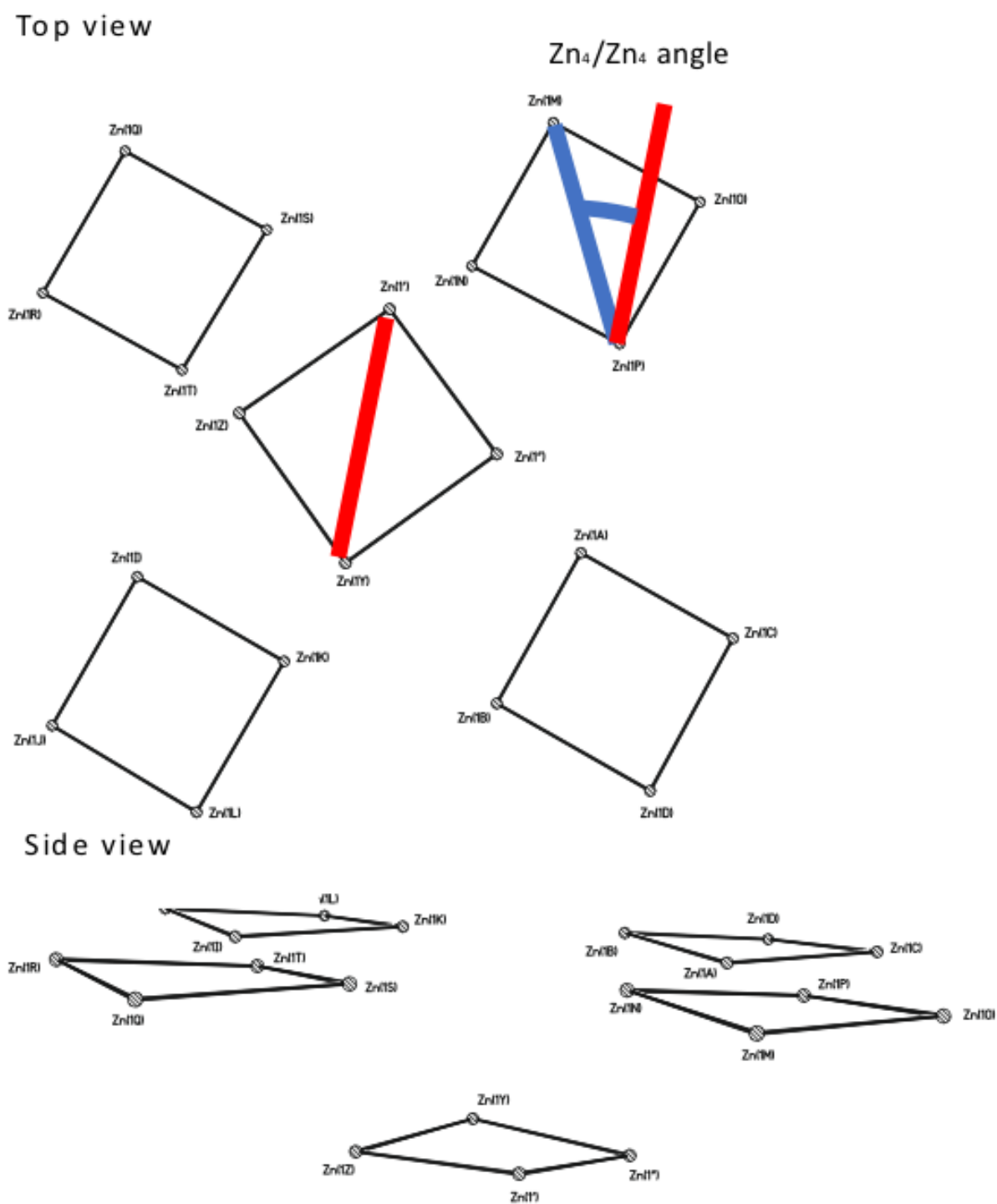
## Bond distances (Å)

Zn(1)-N(2)	2.043(11)	Zn(1)-N(3)	2.056(9)
Zn(1)-N(4)	2.069(10)	Zn(1)-N(1)	2.090(10)
Zn(1)-O(1)	2.083(8)	P(1)-O(1)	1.456(9)
P(1)-O(3)	1.543(10)	P(1)-O(2)	1.566(11)
P(1)-C(17)	1.750(15)	O(2)-C(35)	1.54(2)
O(3)-C(37)	1.47(2)	O(4)-C(9)	1.370(14)
O(4)-C(10)	1.458(19)	O(5)-C(26)	1.413(15)
O(5)-C(27)	1.43(2)	N(1)-C(1)	1.366(16)
N(1)-C(4)	1.369(15)	N(2)-C(33)	1.351(16)
N(2)-C(30)	1.407(13)	N(3)-C(18)	1.338(17)
N(3)-C(21)	1.398(14)	N(4)-C(16)	1.361(16)
N(4)-C(13)	1.377(14)		

## Bond angles (deg)

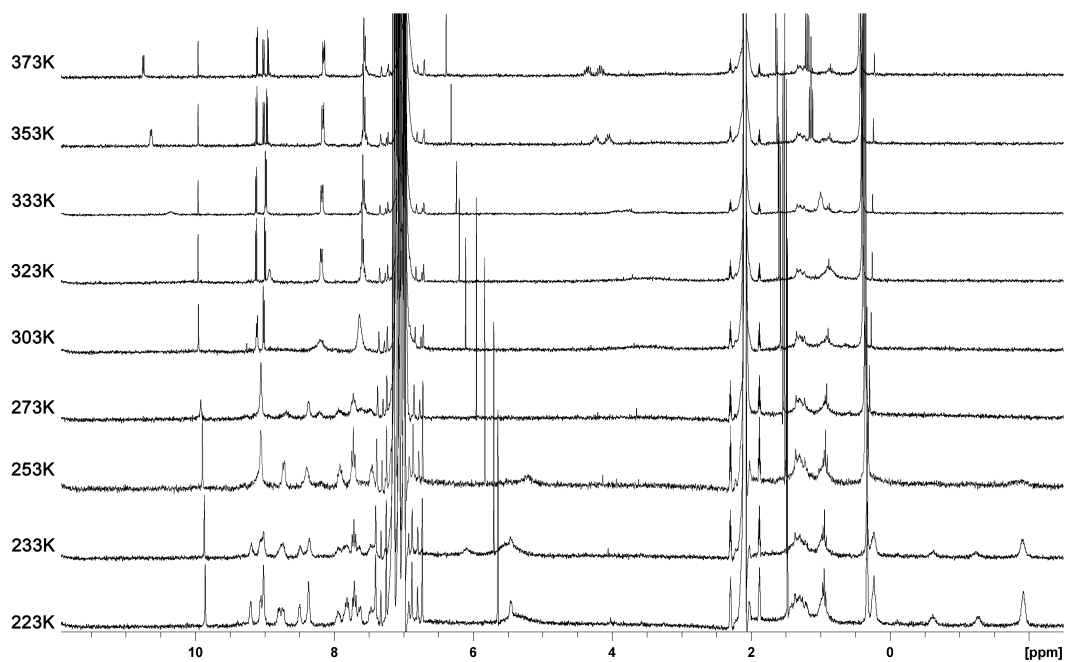
N(2)-Zn(1)-N(3)	89.4(4)	N(2)-Zn(1)-N(4)	162.6(4)
N(3)-Zn(1)-N(4)	88.3(4)	N(2)-Zn(1)-N(1)	89.2(4)
N(3)-Zn(1)-N(1)	162.8(4)	N(4)-Zn(1)-N(1)	88.0(4)
N(2)-Zn(1)-O(1)	95.2(4)	N(3)-Zn(1)-O(1)	98.7(4)
N(4)-Zn(1)-O(1)	102.2(4)	N(1)-Zn(1)-O(1)	98.6(4)
O(1)-P(1)-O(3)	114.3(5)	O(1)-P(1)-O(2)	112.1(6)
O(3)-P(1)-O(2)	98.4(6)	O(1)-P(1)-C(17)	113.0(5)
O(3)-P(1)-C(17)	107.7(7)	O(2)-P(1)-C(17)	110.4(7)
P(1)-O(1)-Zn(1)	135.7(5)	C(35)-O(2)-P(1)	117.3(10)
C(37)-O(3)-P(1)	119.5(8)	C(9)-O(4)-C(10)	114.8(13)
C(26)-O(5)-C(27)	115.0(12)	C(1)-N(1)-C(4)	107.7(9)
C(1)-N(1)-Zn(1)	124.7(7)	C(4)-N(1)-Zn(1)	124.6(8)
C(33)-N(2)-C(30)	104.2(11)	C(33)-N(2)-Zn(1)	127.4(8)
C(30)-N(2)-Zn(1)	126.5(9)	C(18)-N(3)-C(21)	105.8(10)
C(18)-N(3)-Zn(1)	128.5(7)	C(21)-N(3)-Zn(1)	124.9(8)
C(16)-N(4)-C(13)	105.4(10)	C(16)-N(4)-Zn(1)	127.4(7)
C(13)-N(4)-Zn(1)	127.1(9)		

## 7. Schematic representation of crystal packing Zn8 and Zn9.

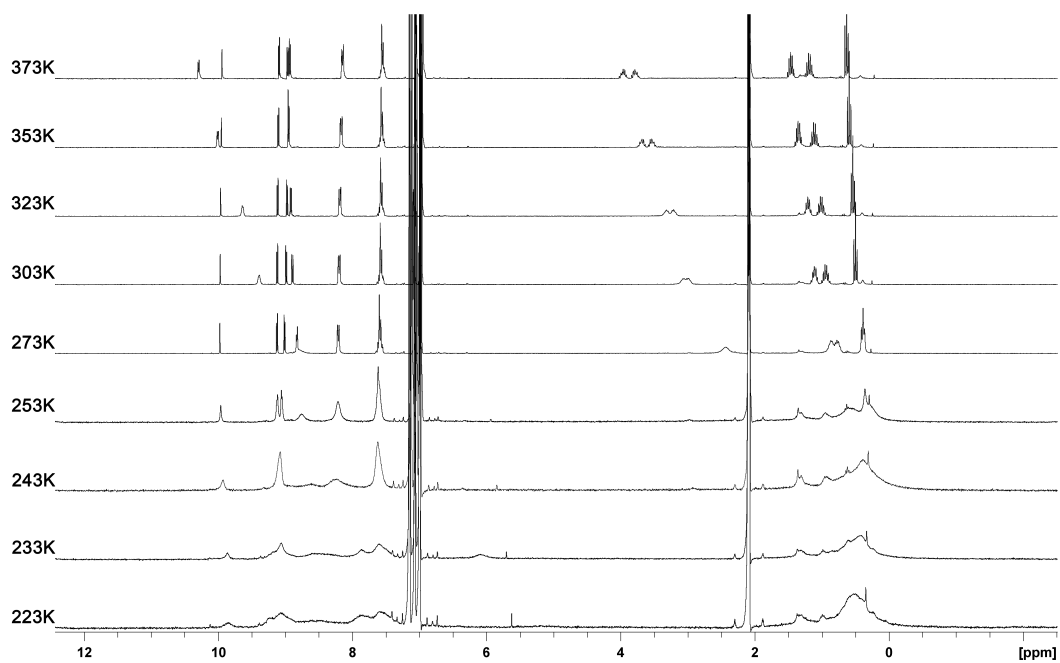


**Figure S19.** Schematic representation of crystal packing of tetramers **Zn<sub>8</sub>** and **Zn<sub>9</sub>** using squares formed by metal atoms.

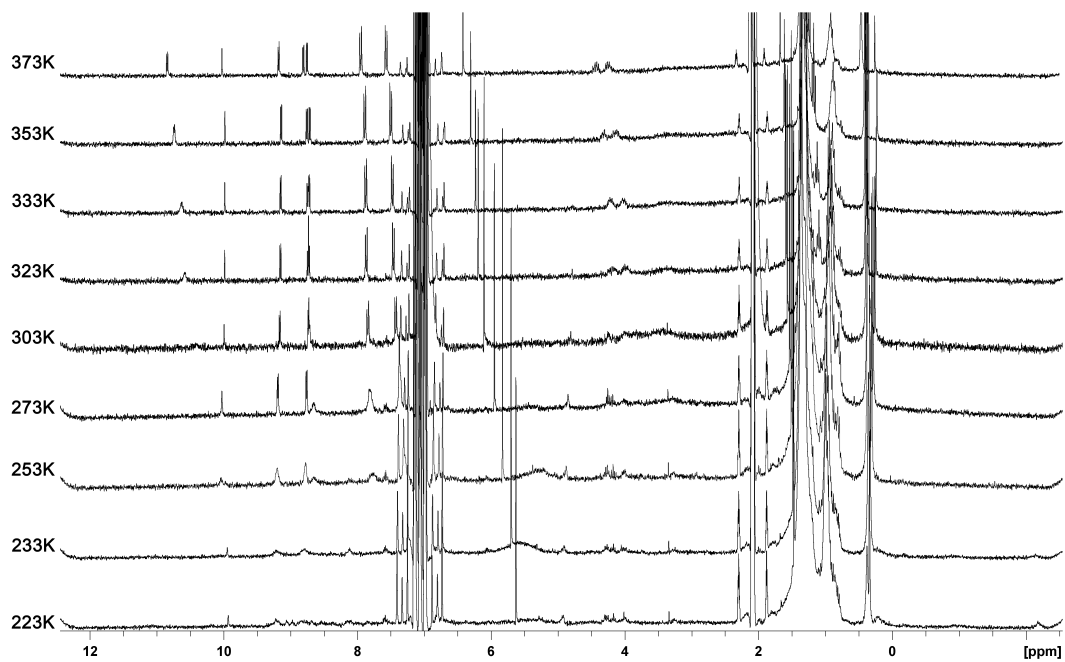
## 8. NMR studies of the self-assembly of porphyrins Zn5–Zn11.



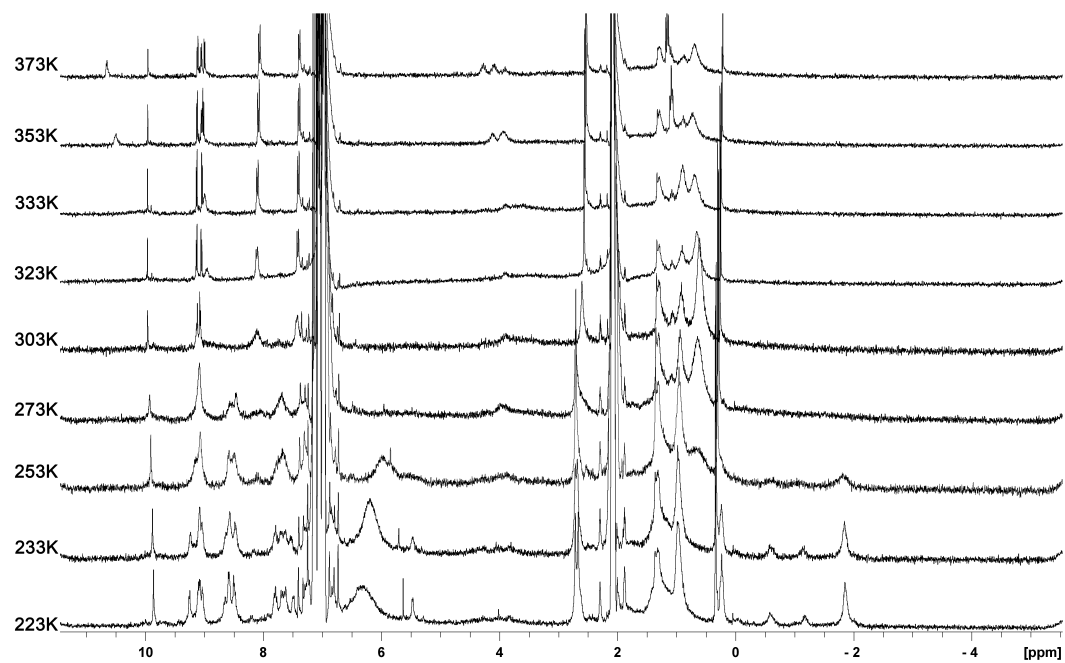
**Figure S20.**  $^1\text{H}$  NMR spectra of Zn5 ( $\text{toluene-d}_8$ ).



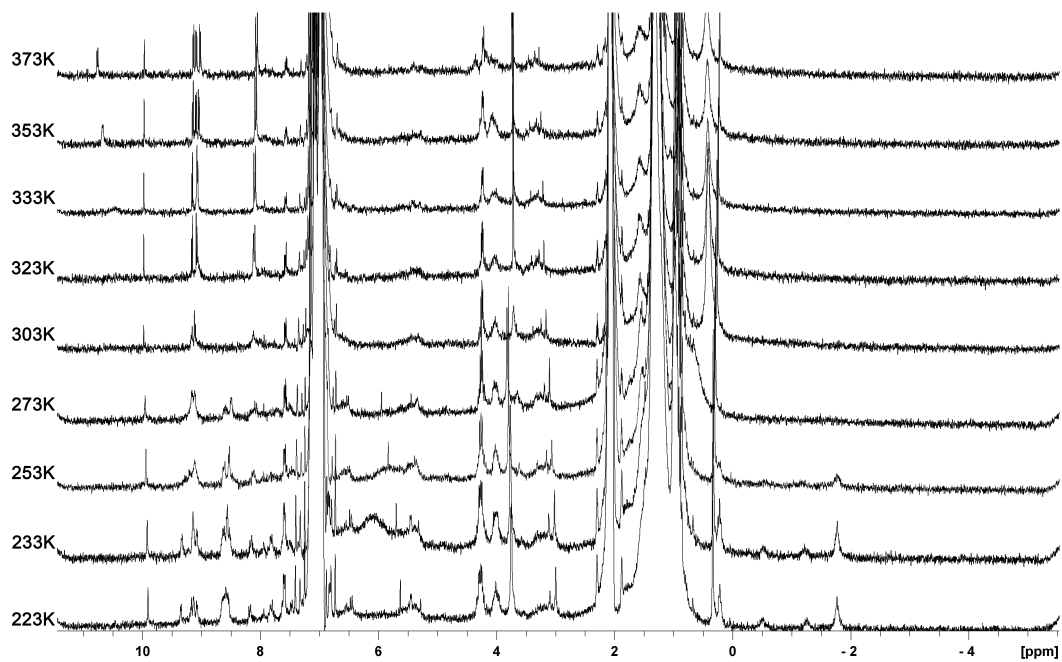
**Figure S21.**  $^1\text{H}$  NMR spectra of Zn6 ( $\text{toluene-d}_8$ ).



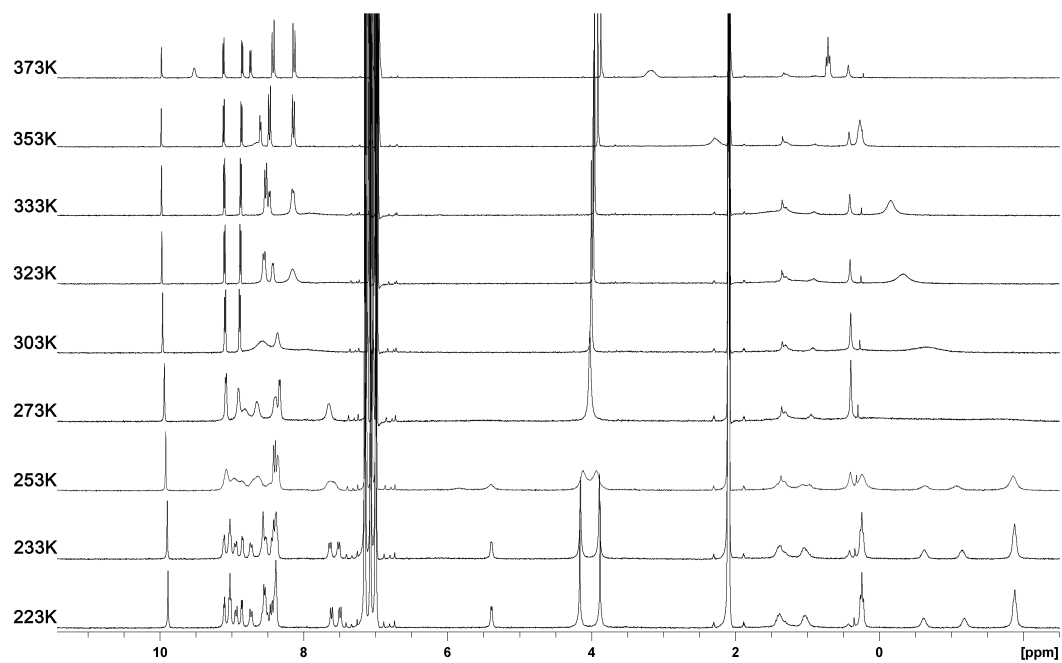
**Figure S22.**  $^1\text{H}$  NMR spectra of **Zn7** ( $\text{toluene-d}_8$ ).



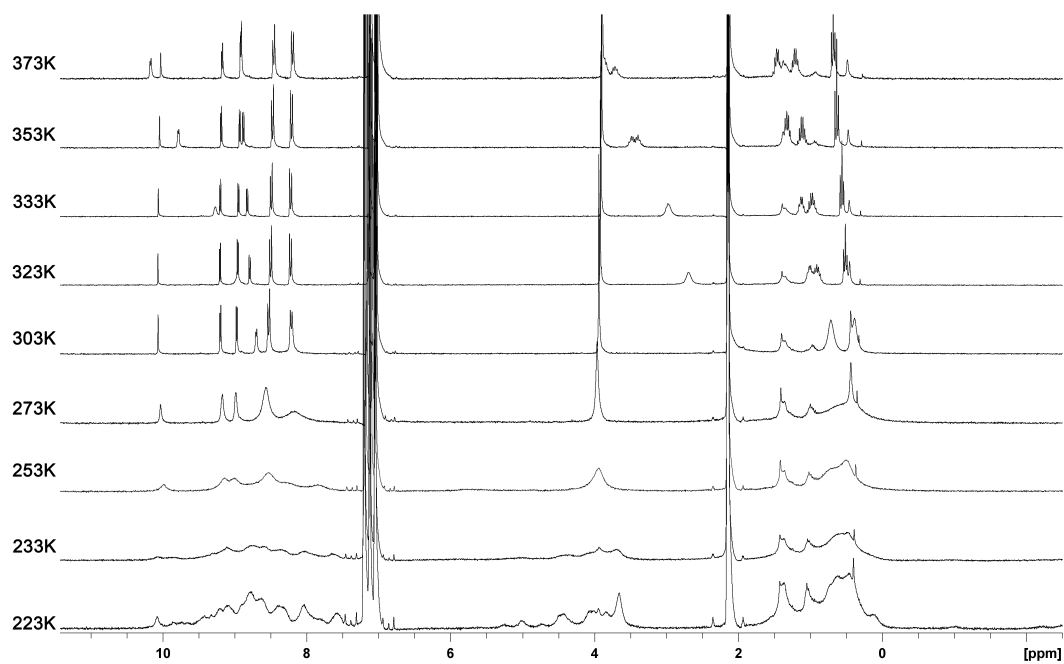
**Figure S23.**  $^1\text{H}$  NMR spectra of **Zn8** ( $\text{toluene-d}_8$ ).



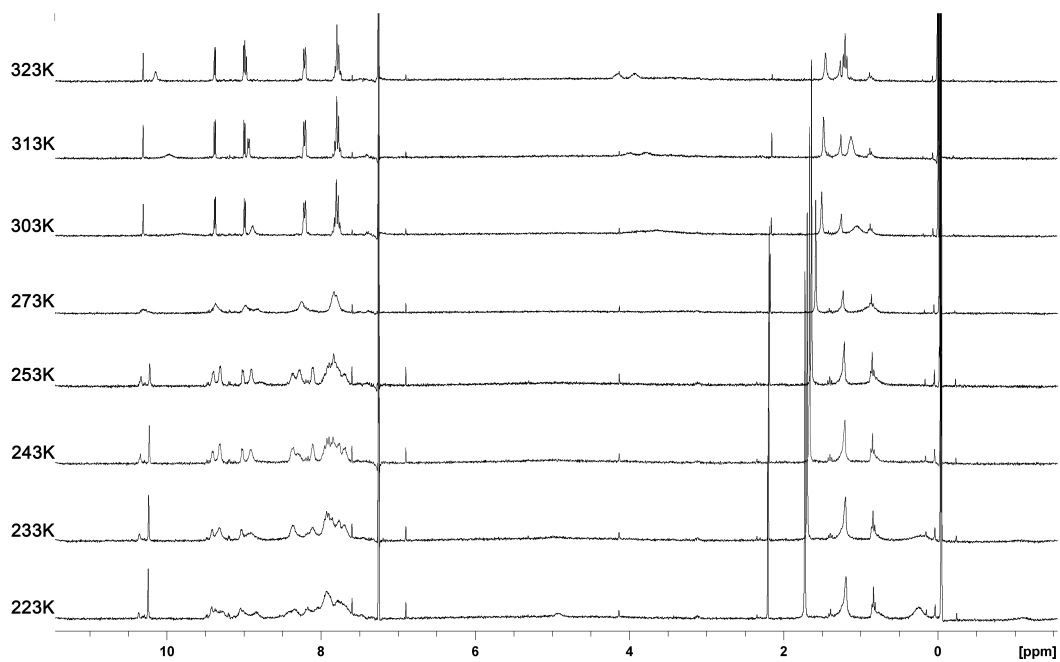
**Figure S24.**  $^1\text{H}$  NMR spectra of **Zn9** ( $\text{toluene-d}_8$ ).



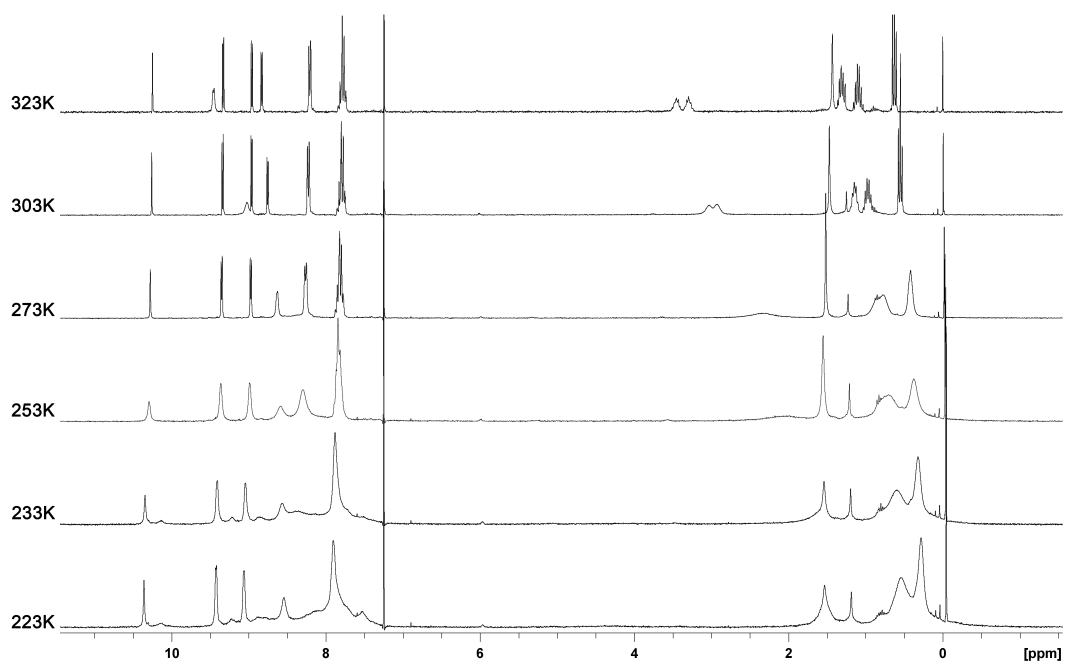
**Figure S25.**  $^1\text{H}$  NMR spectra of **Zn10** ( $\text{toluene-d}_8$ ).



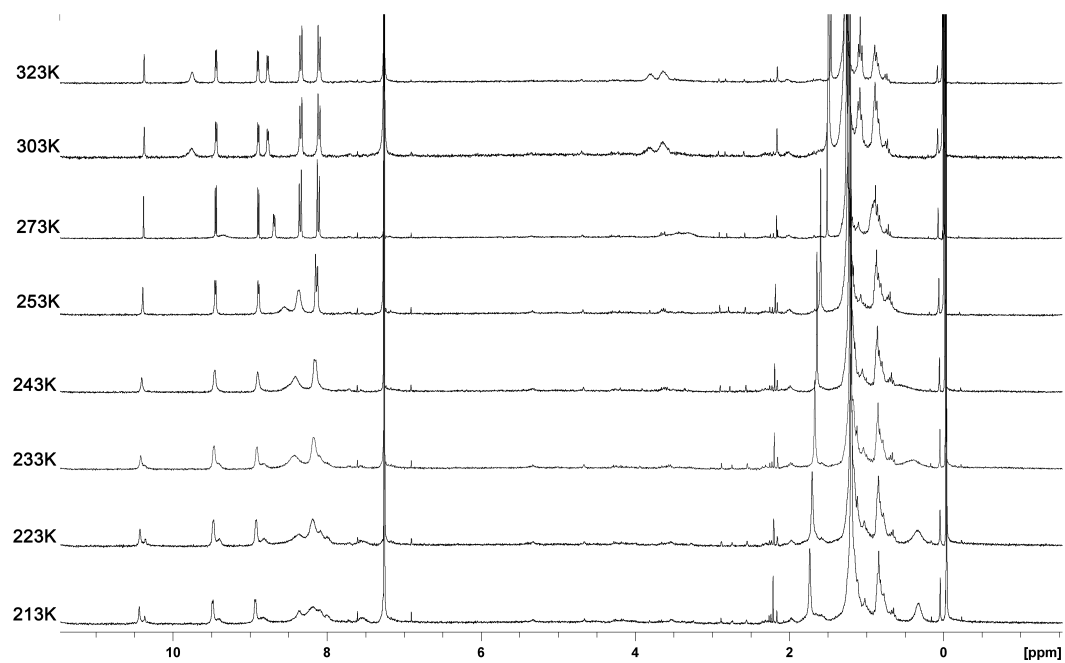
**Figure S26.**  $^1\text{H}$  NMR spectra of **Zn11** ( $\text{toluene-d}_8$ ).



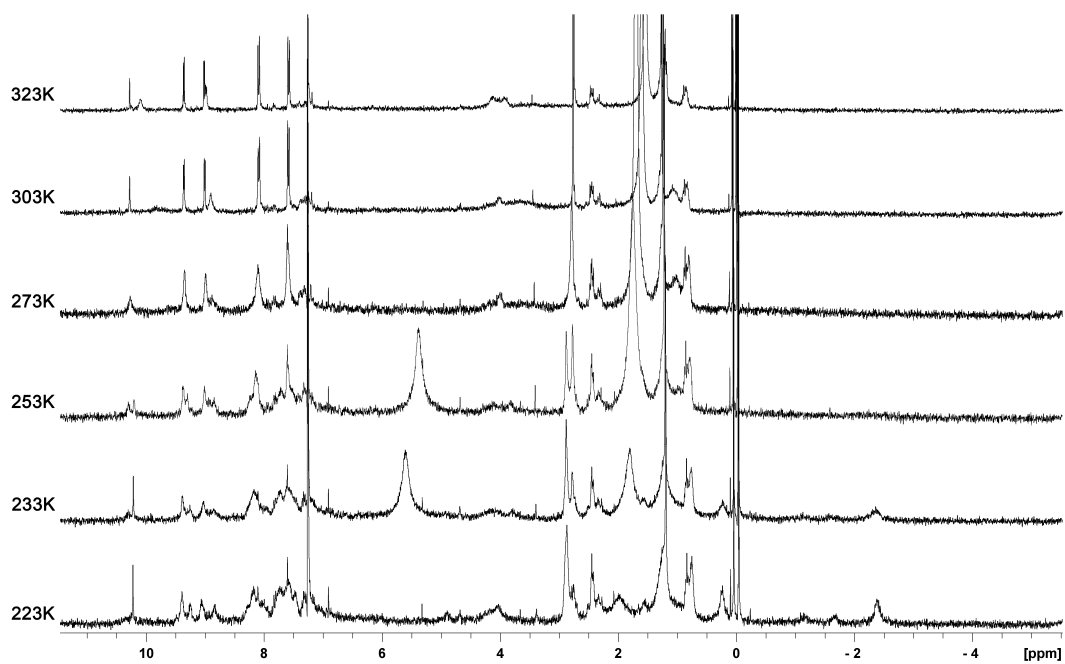
**Figure S27.**  $^1\text{H}$  NMR spectra of **Zn5** ( $\text{CDCl}_3$ ).



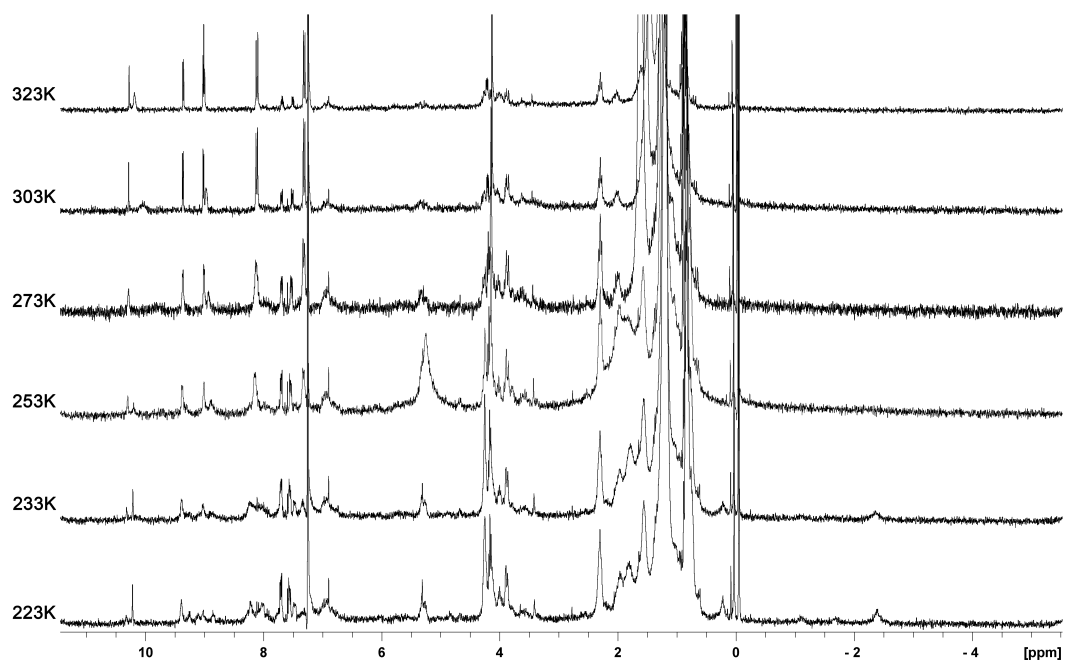
**Figure S28.**  $^1\text{H}$  NMR spectra of **Zn6** ( $\text{CDCl}_3$ ).



**Figure S29.**  $^1\text{H}$  NMR spectra of **Zn7** ( $\text{CDCl}_3$ ).

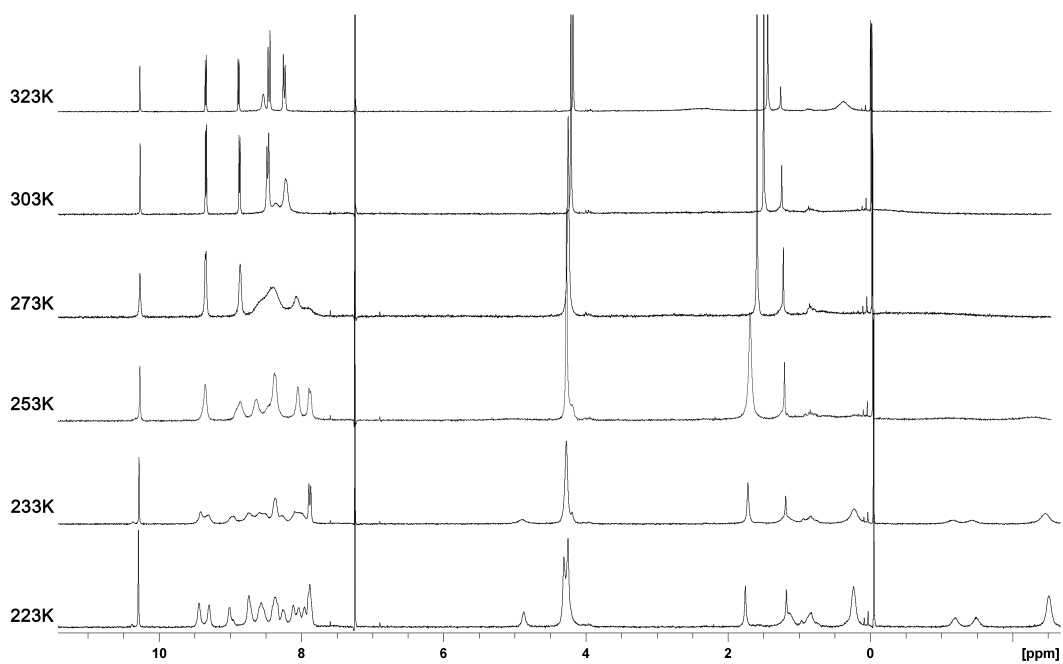


**Figure S30.** <sup>1</sup>H NMR spectra of **Zn8** (CDCl<sub>3</sub>).

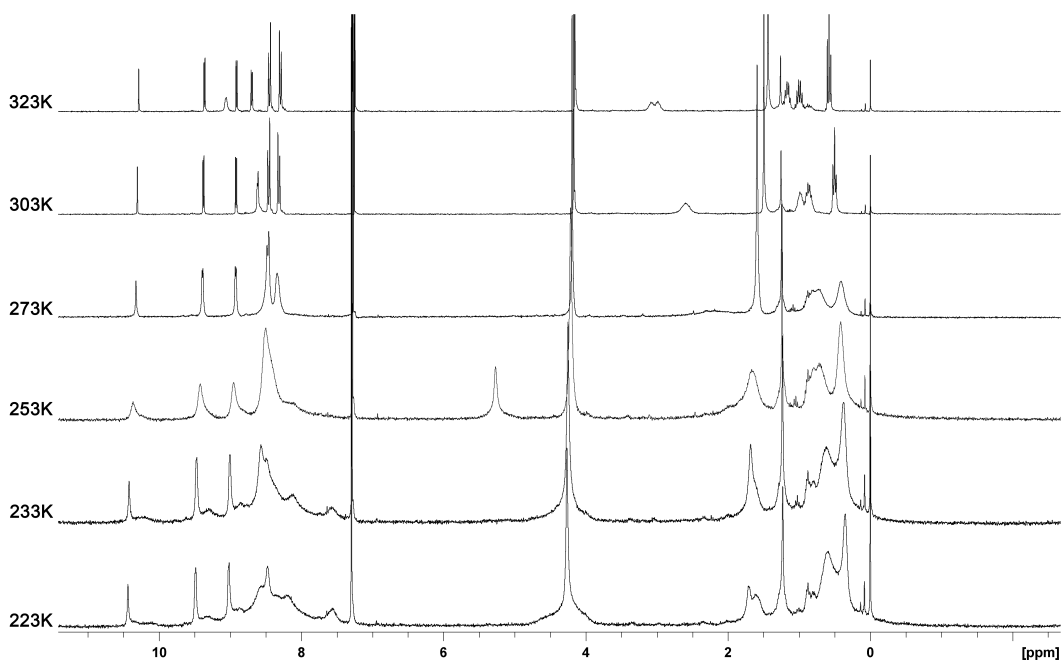


**Figure S31.** <sup>1</sup>H NMR spectra of **Zn9** (CDCl<sub>3</sub>).

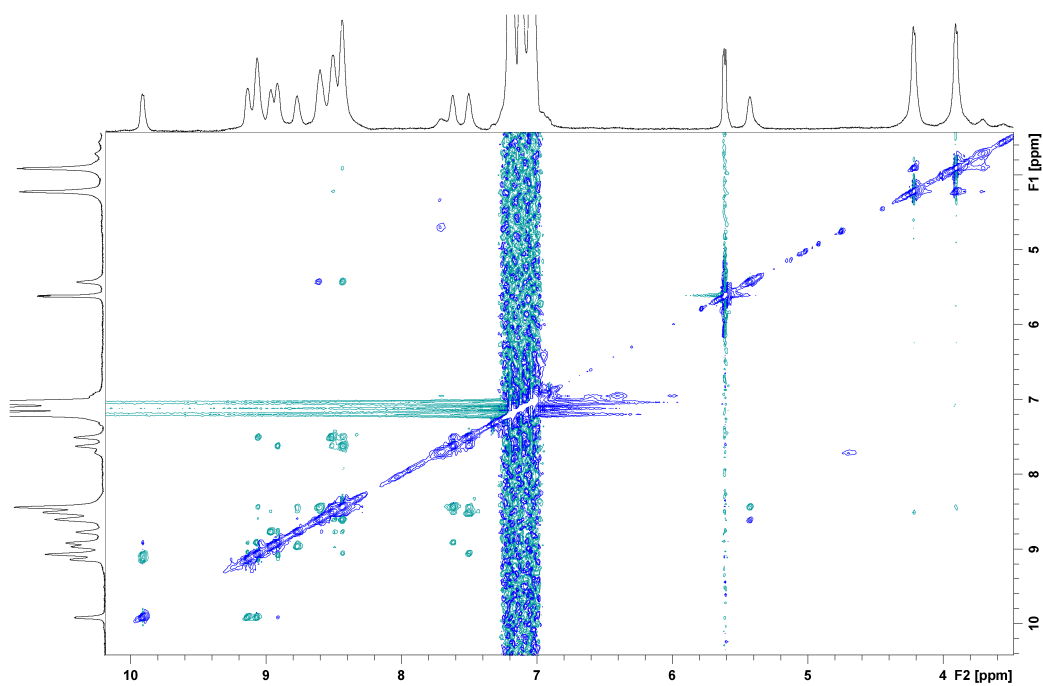




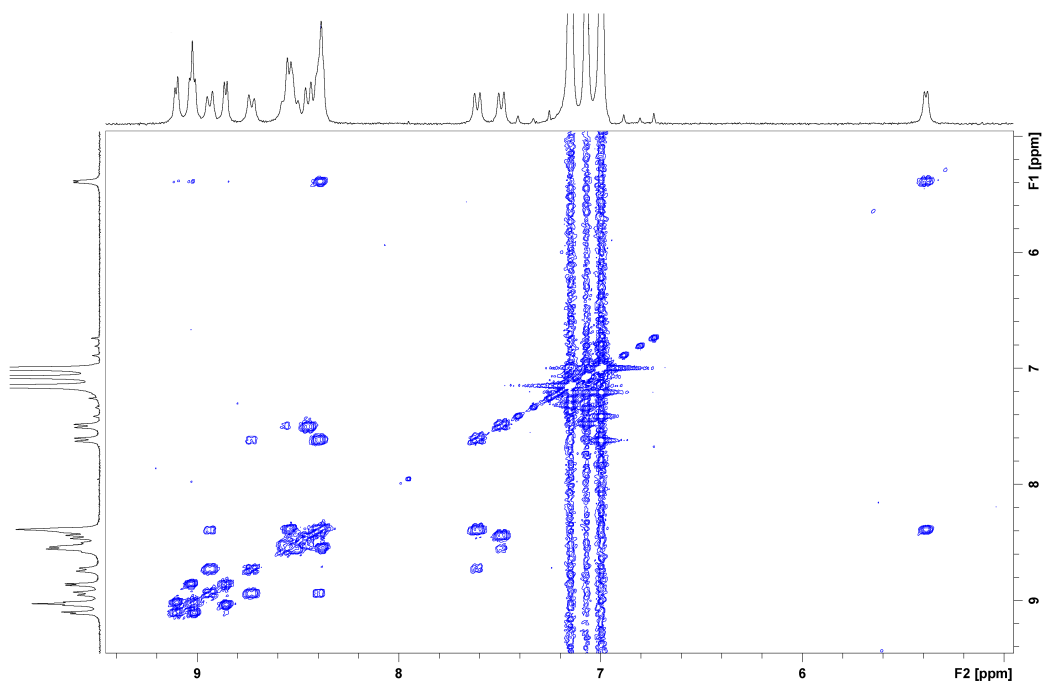
**Figure S32.**  $^1\text{H}$  NMR spectra of Zn10 ( $\text{CDCl}_3$ ).



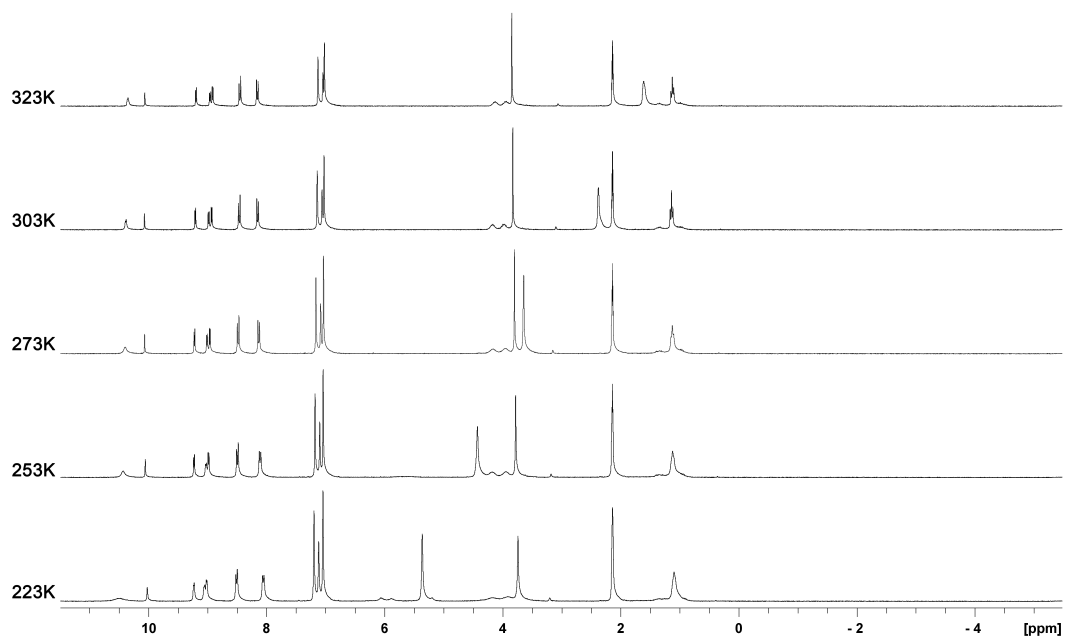
**Figure S33.**  $^1\text{H}$  NMR spectra of Zn11 ( $\text{CDCl}_3$ ).



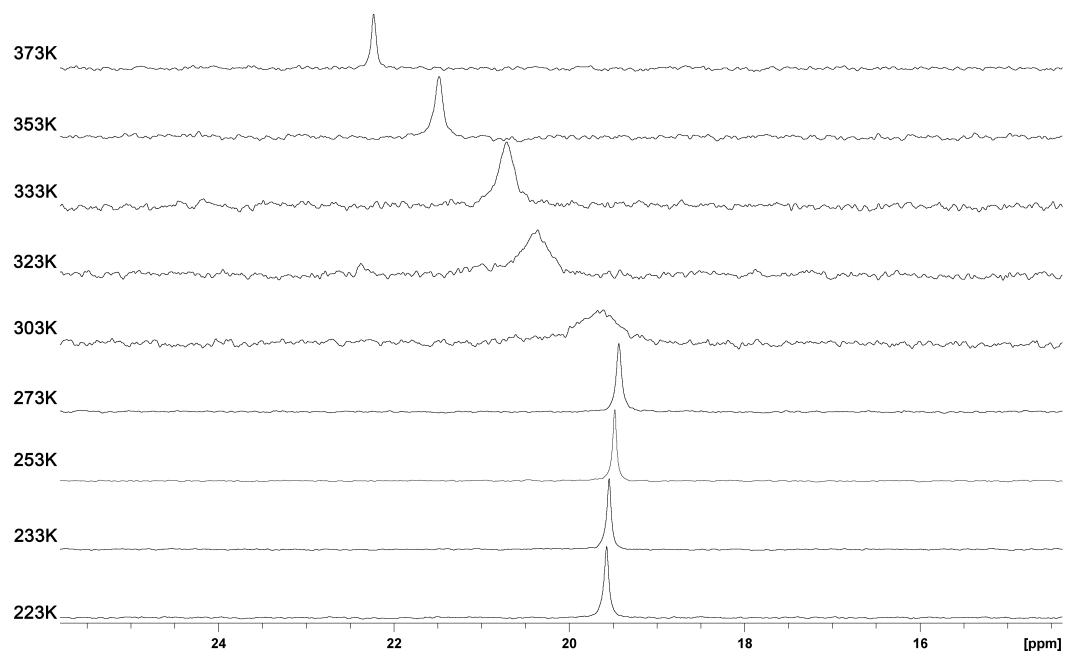
**Figure S34.**  $^1\text{H}$ - $^1\text{H}$  ROESY spectrum of **Zn10** at 223K (toluene- $\text{d}_8$ ).



**Figure S35.**  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of **Zn10** at 223K (toluene- $\text{d}_8$ ).

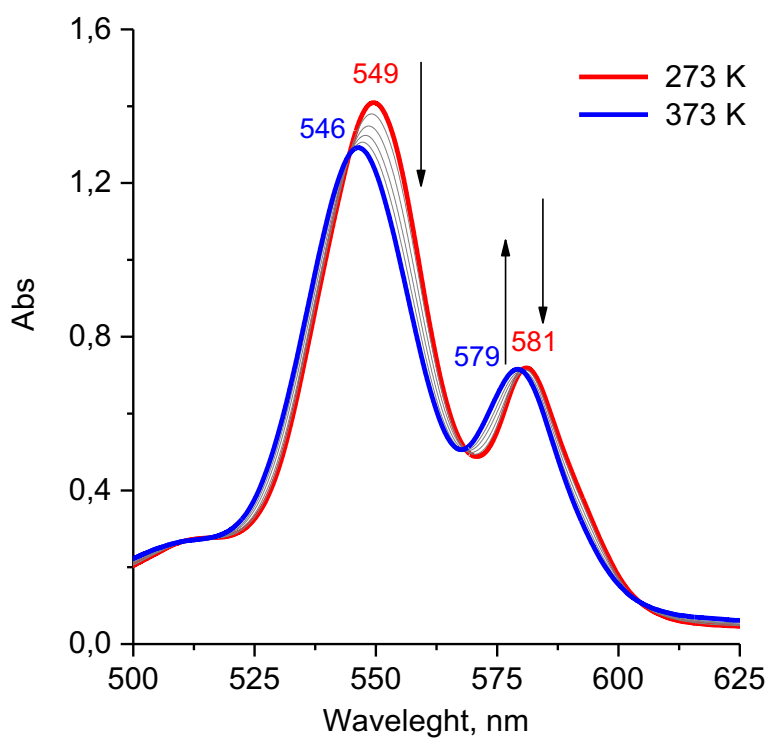


**Figure S36.** <sup>1</sup>H NMR spectra of **Zn10** (toluene-d<sub>8</sub>/MeOD 25:1 v/v).

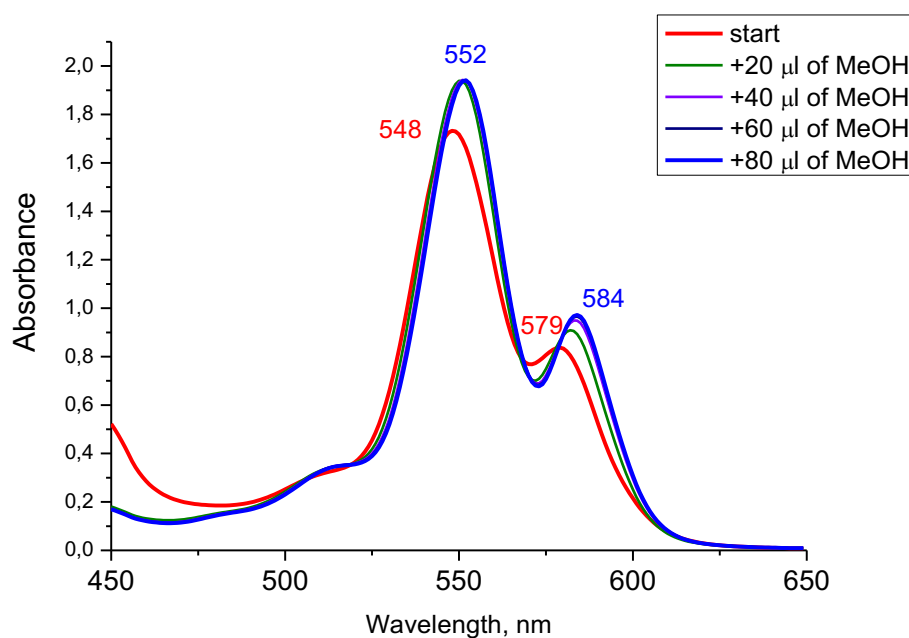


**Figure S37.** <sup>31</sup>P NMR spectra of **Zn10** (toluene-d<sub>8</sub>).

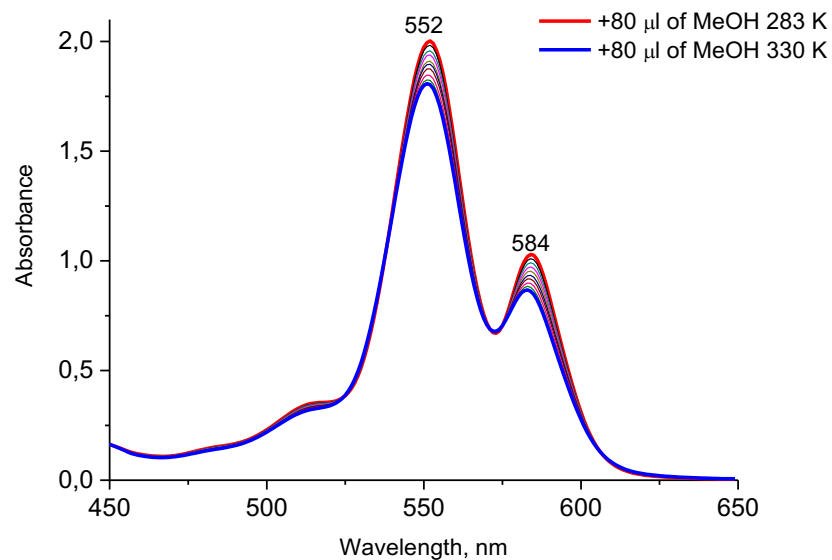
## 9. UV-vis studies of complex Zn10.



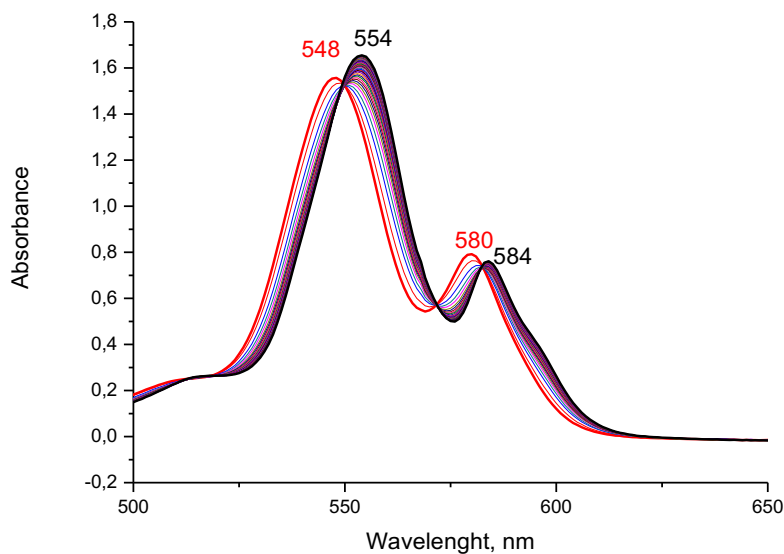
**Figure S38.** Q bands region of variable-temperature UV-vis spectra of complex **Zn10** in chloroform ( $c = 10^{-5}$  M).



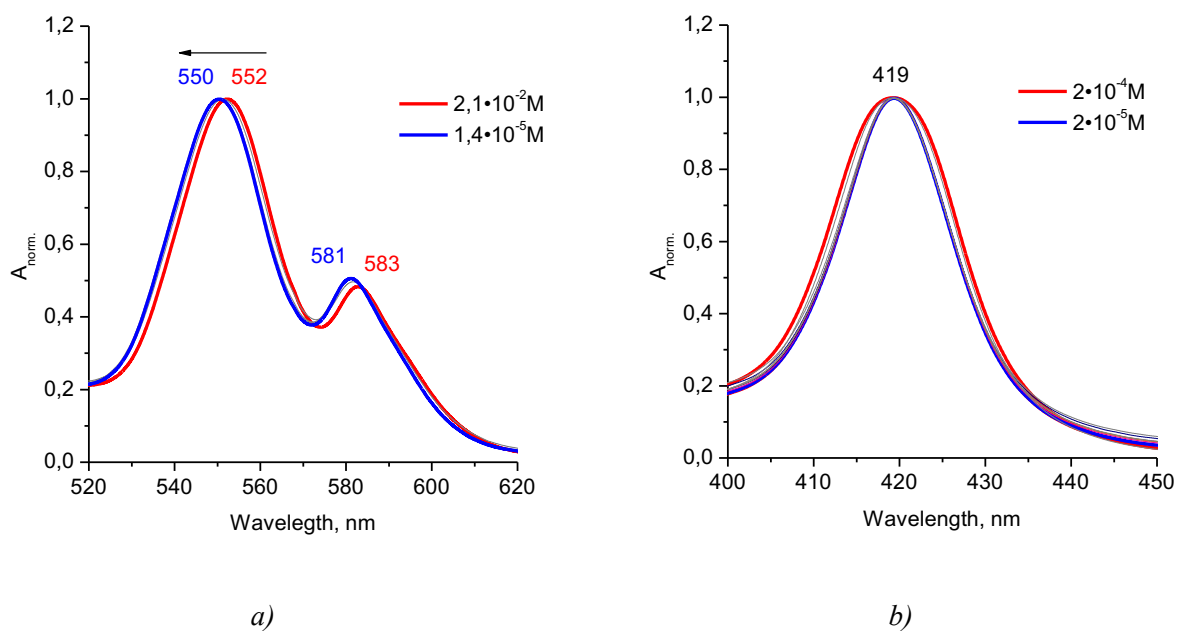
**Figure S39.** Q bands region of UV-vis spectrum of complex **Zn10** in toluene and its changes after addition of methanol ( $c = 10^{-4}$  M,  $T = 298$  K).



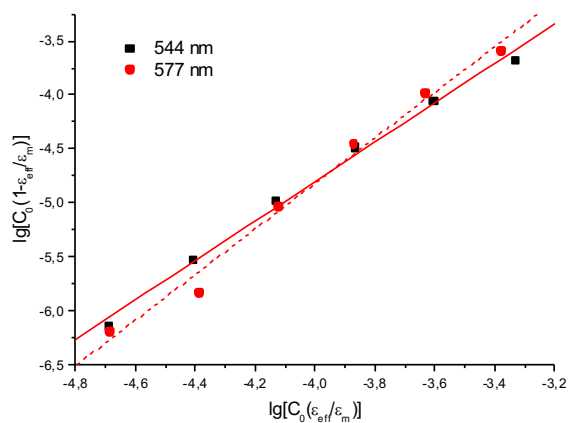
**Figure S40.** Q bands region of variable-temperature UV-vis spectra of complex **Zn10** in toluene/methanol solution (prepared by the addition of 80  $\mu\text{L}$  of MeOH to 3 mL of  $10^{-4}$  M solution of complex **Zn10** in toluene).



**Figure S41.** UV-vis spectra of **Zn10** in chloroform ( $c = 9 \cdot 10^{-5}$  M) at 298K before and after gradual addition of  $\text{Ph}_3\text{P}=\text{O}$  (0–1000 equiv., red line – without  $\text{Ph}_3\text{P}=\text{O}$ , black lines – titration with  $\text{Ph}_3\text{PO}$ , bold black line – final solution).



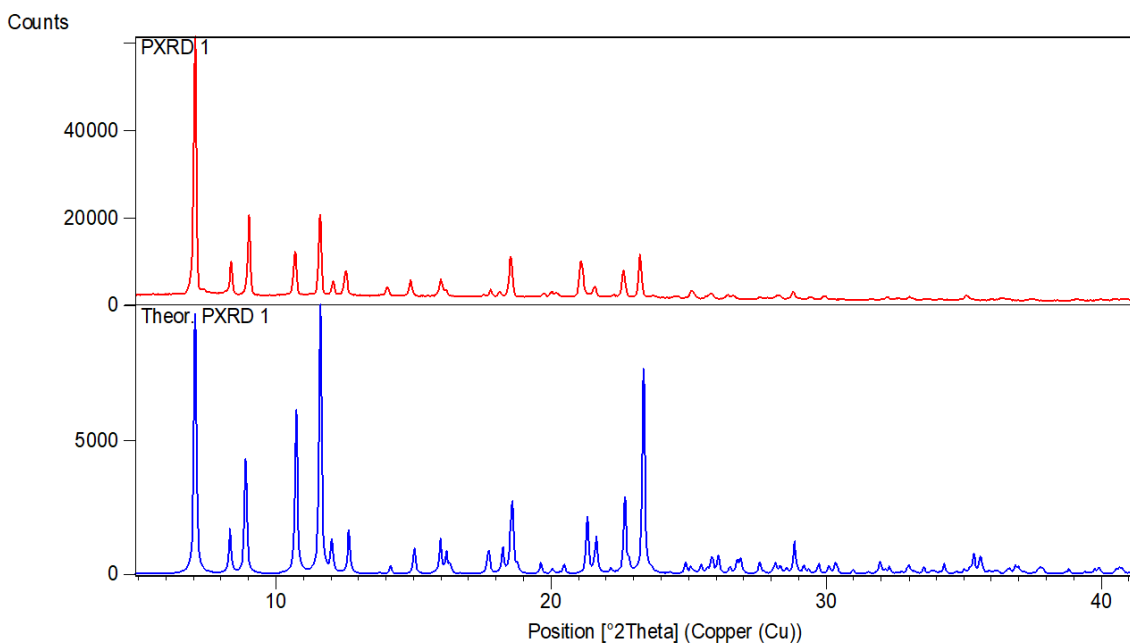
**Figure S42.** UV-vis spectra of  $2.1 \cdot 10^{-2}$  M (red line) and  $1.4 \cdot 10^{-5}$  M (blue line) solutions of complex **Zn10** in chloroform at 298 K. **Left panel:** Q bands region. **Right panel:** Soret band region.



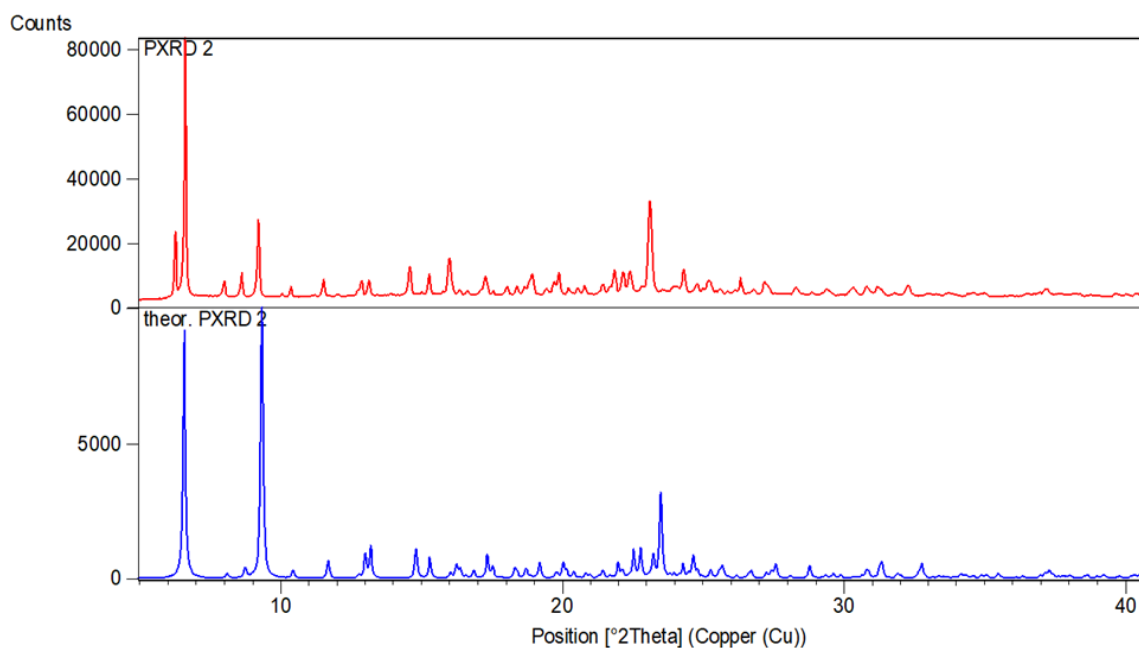
**Figure S43.** Graphical analysis of  $\epsilon_{eff}$  values for determination of aggregation number  $n$ , obtained for Q bands at 544 nm:  $y = (1.822 \pm 0.070) x + 2.486$ ,  $R^2 = 0.994$  and 577 nm:  $y = (2.106 \pm 0.115) x + 3.607$ ,  $R^2 = 0.988$ .

## 10. Powder X-ray diffraction analysis of Zn5-Zn9.

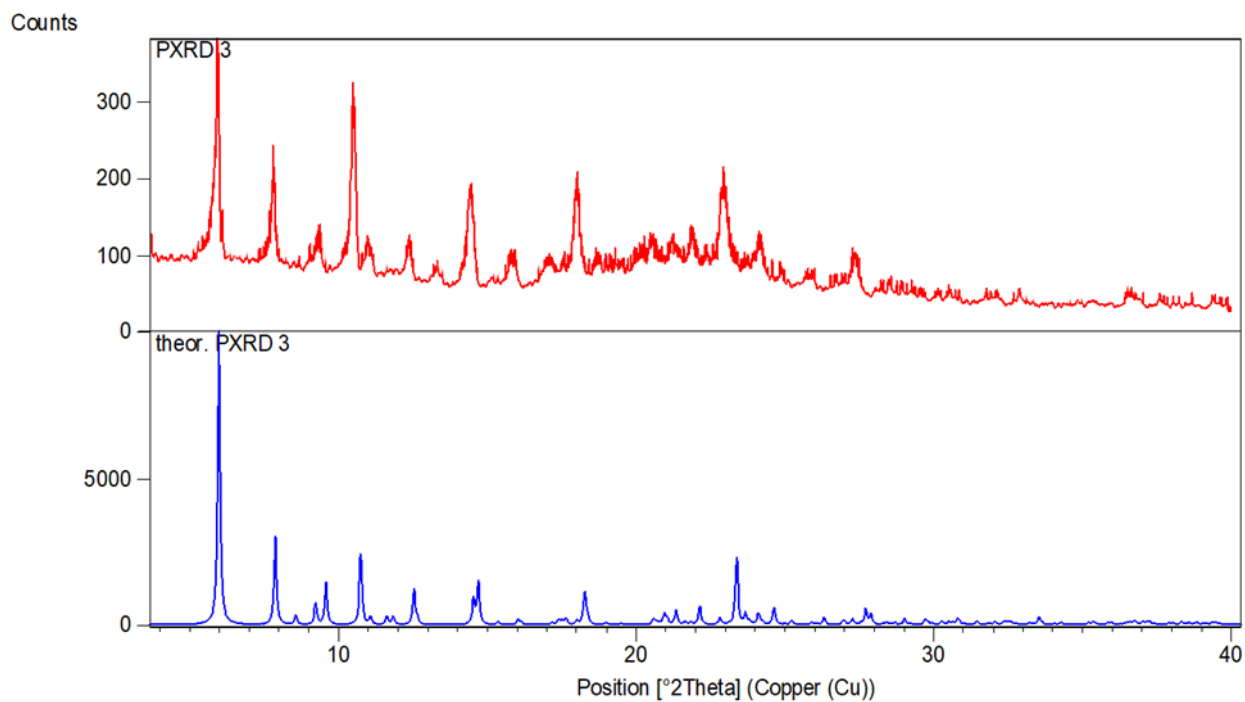
The PXRD patterns of the compounds **Zn1-Zn6** are in good agreement with structures obtained in single crystal experiment. Figs show the comparison of PXRD pattern (red top pattern) with the theoretical pattern calculated from cif-file (blue bottom pattern). Only bulky sample of compound **6** shows amorphous PXRD pattern, which could not be compared with theoretical pattern.



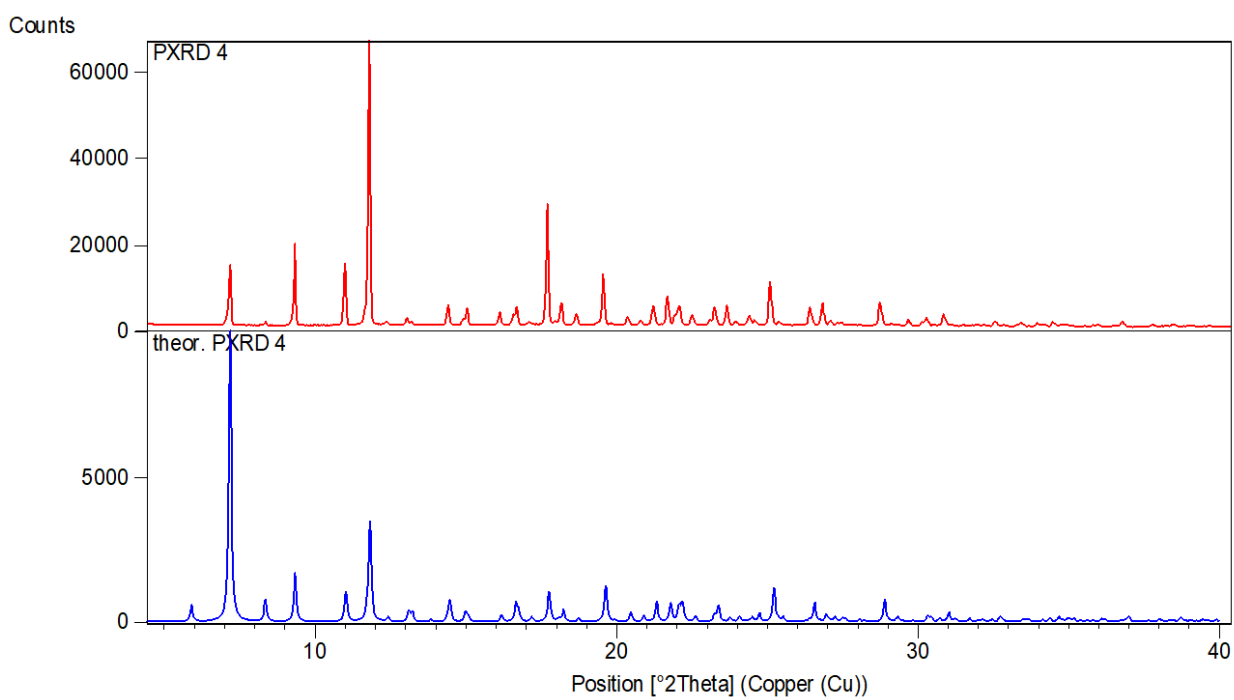
**Figure S44.** Powder X-ray diffraction analysis of **Zn5**.



**Figure S45.** Powder X-ray diffraction analysis of **Zn6**.

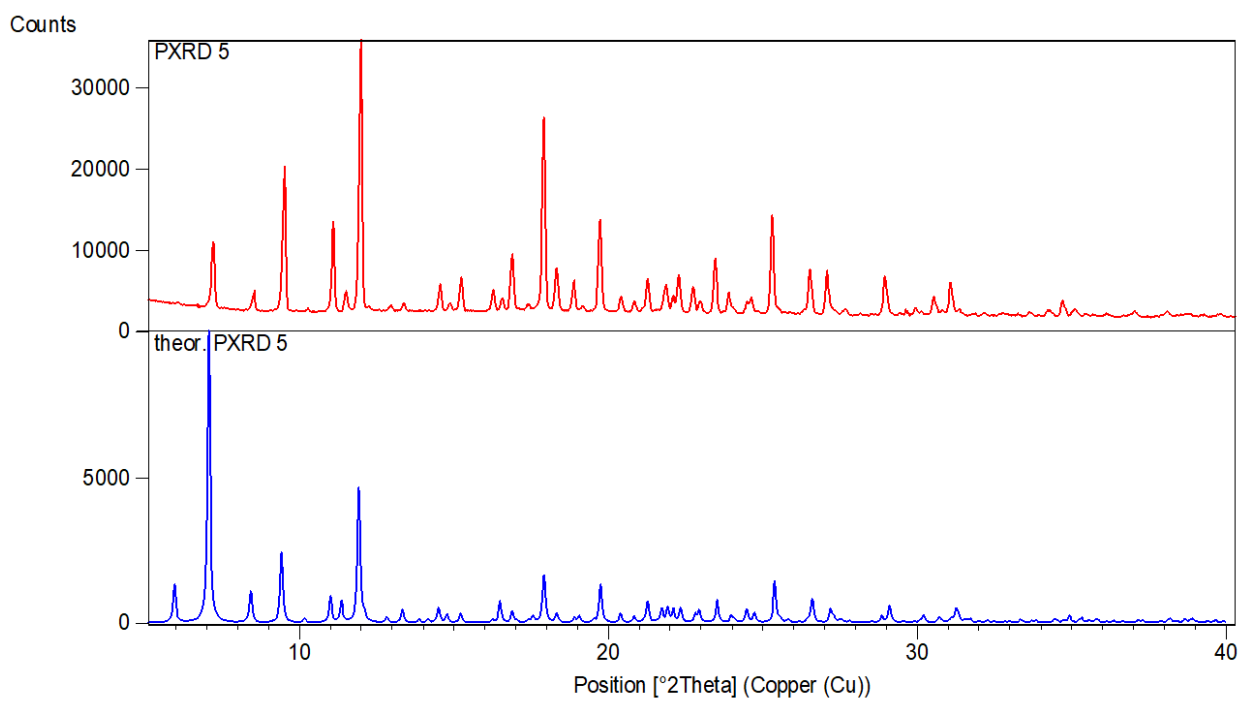


**Figure S46.** Powder X-ray diffraction analysis of **Zn7**.



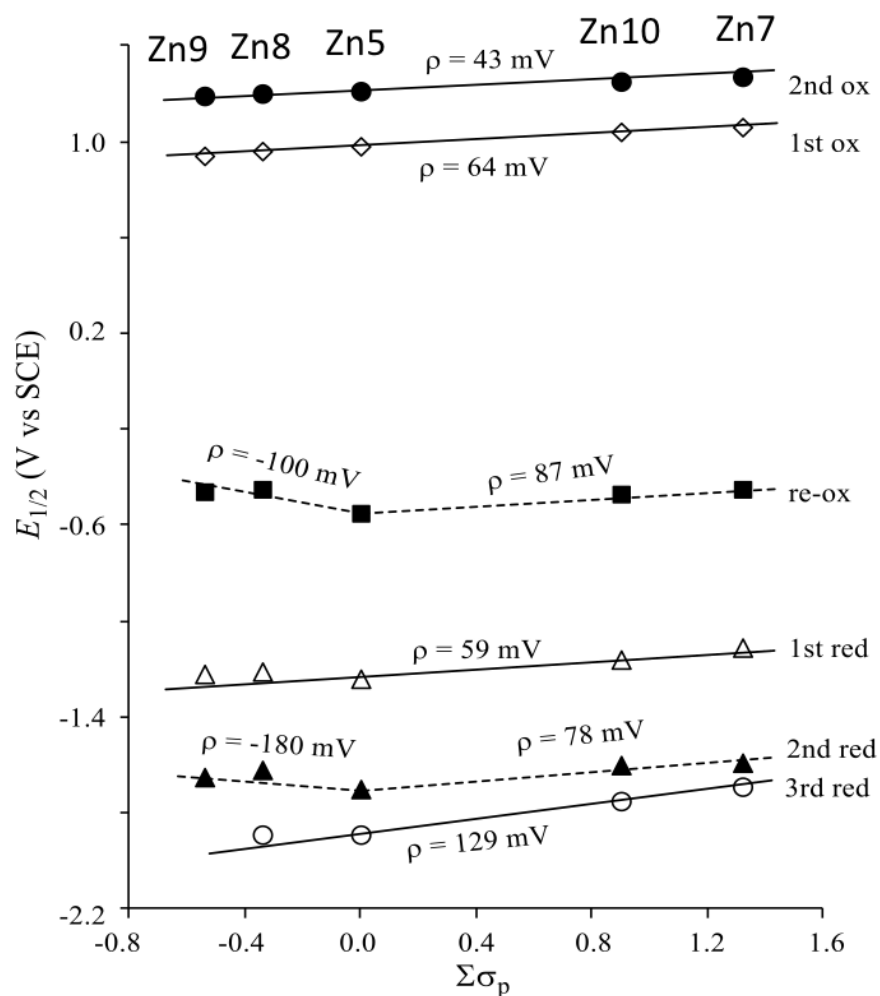
**Figure S47.** Powder X-ray diffraction analysis of **Zn8**.





**Figure S48.** Powder X-ray diffraction analysis of **Zn9**.

## 10. Electrochemical data for Zn10.



**Figure S49.** Correlation between redox potentials and Hammett substituents on the *meso*-phenyl groups of the porphyrin **Zn10** and referenced compounds **Zn5** and **Zn7-Zn9**, previously reported in Ref [4]. PhCN was used as a solvent.

## 11. References.

- [1] G.M. Sheldrick, SADABS, 1997, Bruker AXS Inc., Madison, WI-53719, USA.
- [2] SMART V5.051 and SAINT V5.00, Area detector control and integration software, 1998, Bruker AXS Inc., Madison, WI-53719, USA.
- [3] G.M. Sheldrick, SHELXTL-97 V5.10, 1997, Bruker AXS Inc., Madison, WI-53719, USA.
- [4] Y. Fang, X. Jiang, K. M. Kadish, S. E. Nefedov, G. A. Kirakosyan, Yu. Yu. Enakieva, Yu. G. Gorbunova, A. Y. Tsivadze, C. Stern, A. Bessmertnykh-Lemeune, R. Guillard, *Inorg. Chem.*, **2019**, submitted.