

## SUPPORTING INFORMATION

for

**Imidazoporphyrins as supramolecular tectons: synthesis and self-assembling of zinc 2-(4-pyridyl)-1*H*-imidazo[4,5-*b*]porphyrinate**

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Crystallographic data, experiment and refinement details are given in Table S 1. The atomic coordinates and thermal parameters in the crystal structure are filled at the Cambridge Crystallographic Data Center, no. CCDC 1871295.

Table S1. Crystal data and structure refinement for complex **PyPorZn·2C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>**.

Parameter	<b>PyPorZn</b>
CCDC number	1871295
Chemical formula	C <sub>76</sub> H <sub>71</sub> N <sub>7</sub> Zn
Chemical formula moiety	C <sub>62</sub> H <sub>55</sub> N <sub>7</sub> Zn, 2(C <sub>7</sub> H <sub>8</sub> )
Crystal system, space group, <i>Z</i>	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i> , 4
Unit cell dimensions	<i>a</i> = 13.1788(9) Å, <i>b</i> = 21.4947(16) Å, <i>c</i> = 22.2362(18) Å, $\beta$ = 106.952(2)°
Volume, Å <sup>3</sup>	6025.3(8)
Density (calculated), g/cm <sup>3</sup>	1.265
Radiation, $\lambda$ , Å	MoK $\alpha$ , 0.71073
$\mu$ , mm <sup>-1</sup>	0.459
Temperature, K	100(2)
Crystal size, mm	0.3 × 0.2 × 0.08
Data collection range, $\theta$ , °	4.095 – 27.974
Interval of reflection indices	-17 ≤ <i>h</i> ≤ 17, -27 ≤ <i>k</i> ≤ 28, -29 ≤ <i>l</i> ≤ 29
Reflections collected	48812
Unique reflections/ <i>R</i> <sub>int</sub>	14387/0.0876
Reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	8746
Refinement method	Least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	14387/42/771
Weight scheme	$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2 + 3.3075P]$ where $P=(F_o^2+2F_c^2)/3$
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0599, <i>wR</i> 2 = 0.1343
Final <i>R</i> indexes [all data]	<i>R</i> 1 = 0.1195, <i>wR</i> 2 = 0.1594
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.017
Largest diff. peak/ hole, e/Å <sup>3</sup>	1.21/-0.71

Table S2. Selected bond lengths (Å) for **PyPorZn**.

**Bond lengths (Å)**

Zn(1)–N(1)	2.048(2)	N(3)–C(14)	1.373(4)
Zn(1)–N(2)	2.073(2)	N(4)–C(16)	1.375(4)
Zn(1)–N(3)	2.067(3)	N(4)–C(19)	1.376(4)
Zn(1)–N(4)	2.078(3)	N(5)–C(2)	1.386(4)
Zn(1)–N(7) <sup>1</sup>	2.183(3)	N(5)–C(21)	1.341(4)
N(1)–C(1)	1.385(4)	N(6)–C(3)	1.368(4)
N(1)–C(4)	1.379(4)	N(6)–C(21)	1.366(4)
N(2)–C(6)	1.363(4)	N(7)–C(24)	1.346(4)

N(2)–C(9)	1.378(4)	N(7)–C(25)	1.342(4)
N(3)–C(11)	1.374(4)		

<sup>1</sup>2-X, -1/2+Y, 3/2-Z

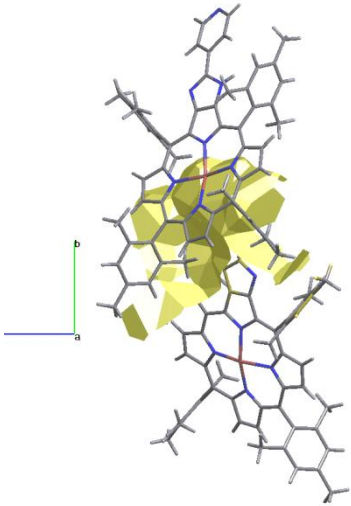
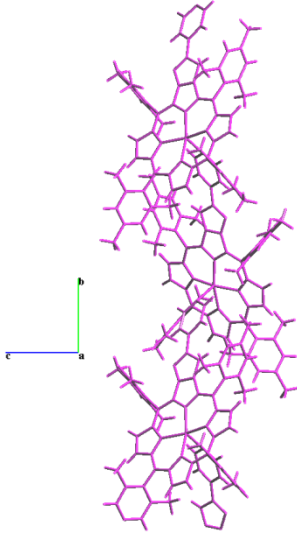
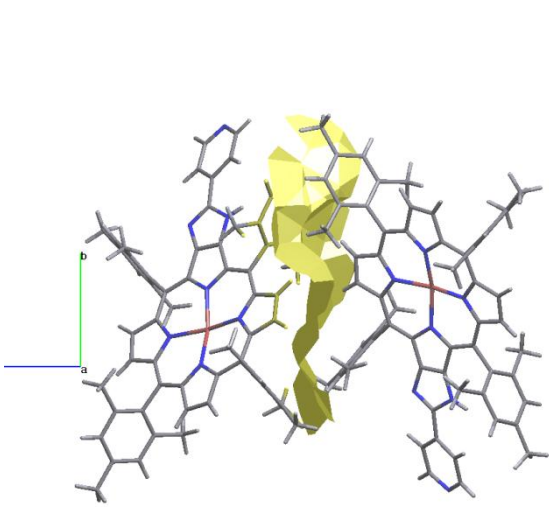
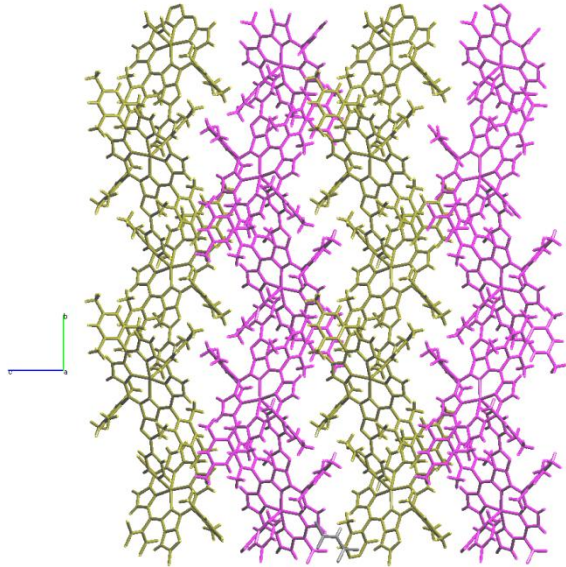
Table S3. Selected bond angles (deg) for **PyPorZn**.

**Bond angles (deg)**

N(1)–Zn(1)–N(2)	91.45(9)	C(6)–N(2)–C(9)	106.3(2)
N(1)–Zn(1)–N(3)	162.88(10)	C(9)–N(2)–Zn(1)	128.2(2)
N(1)–Zn(1)–N(4)	88.01(9)	C(11)–N(3)–Zn(1)	127.3(2)
N(1)–Zn(1)–N(7) <sup>1</sup>	104.35(10)	C(14)–N(3)–Zn(1)	125.1(2)
N(2)–Zn(1)–N(4)	165.19(10)	C(14)–N(3)–C(11)	106.2(2)
N(2)–Zn(1)–N(7) <sup>1</sup>	99.02(10)	C(16)–N(4)–Zn(1)	126.3(2)
N(3)–Zn(1)–N(2)	87.35(10)	C(16)–N(4)–C(19)	106.3(2)
N(3)–Zn(1)–N(4)	88.82(10)	C(19)–N(4)–Zn(1)	126.9(2)
N(3)–Zn(1)–N(7) <sup>1</sup>	92.70(10)	C(21)–N(5)–C(2)	103.2(2)
N(4)–Zn(1)–N(7) <sup>1</sup>	95.44(10)	C(21)–N(6)–C(3)	105.5(3)
C(1)–N(1)–Zn(1)	127.9(2)	C(24)–N(7)–Zn(1) <sup>2</sup>	116.6(2)
C(4)–N(1)–Zn(1)	122.66(19)	C(25)–N(7)–Zn(1) <sup>2</sup>	118.5(2)
C(4)–N(1)–C(1)	109.3(2)	C(25)–N(7)–C(24)	117.0(3)
C(6)–N(2)–Zn(1)	125.16(19)		

<sup>1</sup>2-X, -1/2+Y, 3/2-Z; <sup>2</sup>2-X, 1/2+Y, 3/2-Z

Table S4. Selected intermolecular contacts in the crystals **PyPorZn<sub>2</sub>C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>**, the boundary surfaces  $S(\text{\AA}^2)$ , center to center distances between contacted porphyrins  $D(\text{\AA})$  and supramolecular assemblies formed.

Boundary surfaces $S(\text{\AA}^2)$ of intermolecular contacts and distances between porphyrin centers $D(\text{\AA})$	Supramolecular organization based on the consideration of the strength level of intermolecular contacts
 <p data-bbox="384 981 592 1093"> <math>S = 113.3 \text{ \AA}^2</math>  <math>D = 12.10 \text{ \AA}</math>                      View along [100]                 </p> <p data-bbox="715 1099 751 1133">(a)</p>	 <p data-bbox="890 994 1369 1066">                     1D polymer chain along [010] direction.                      View along [100].                 </p>
 <p data-bbox="384 1771 592 1883"> <math>S = 81.9 \text{ \AA}^2</math>  <math>D = 11.12 \text{ \AA}</math>                      View along [100]                 </p> <p data-bbox="715 1890 751 1924">(b)</p>	 <p data-bbox="935 1778 1326 1850">                     2D pseudo-layers in (100) plane.                      View along [100] direction.                 </p> <p data-bbox="794 1854 1473 1921">                     Yellow and pink colour corresponds to different polymer chains.                 </p>

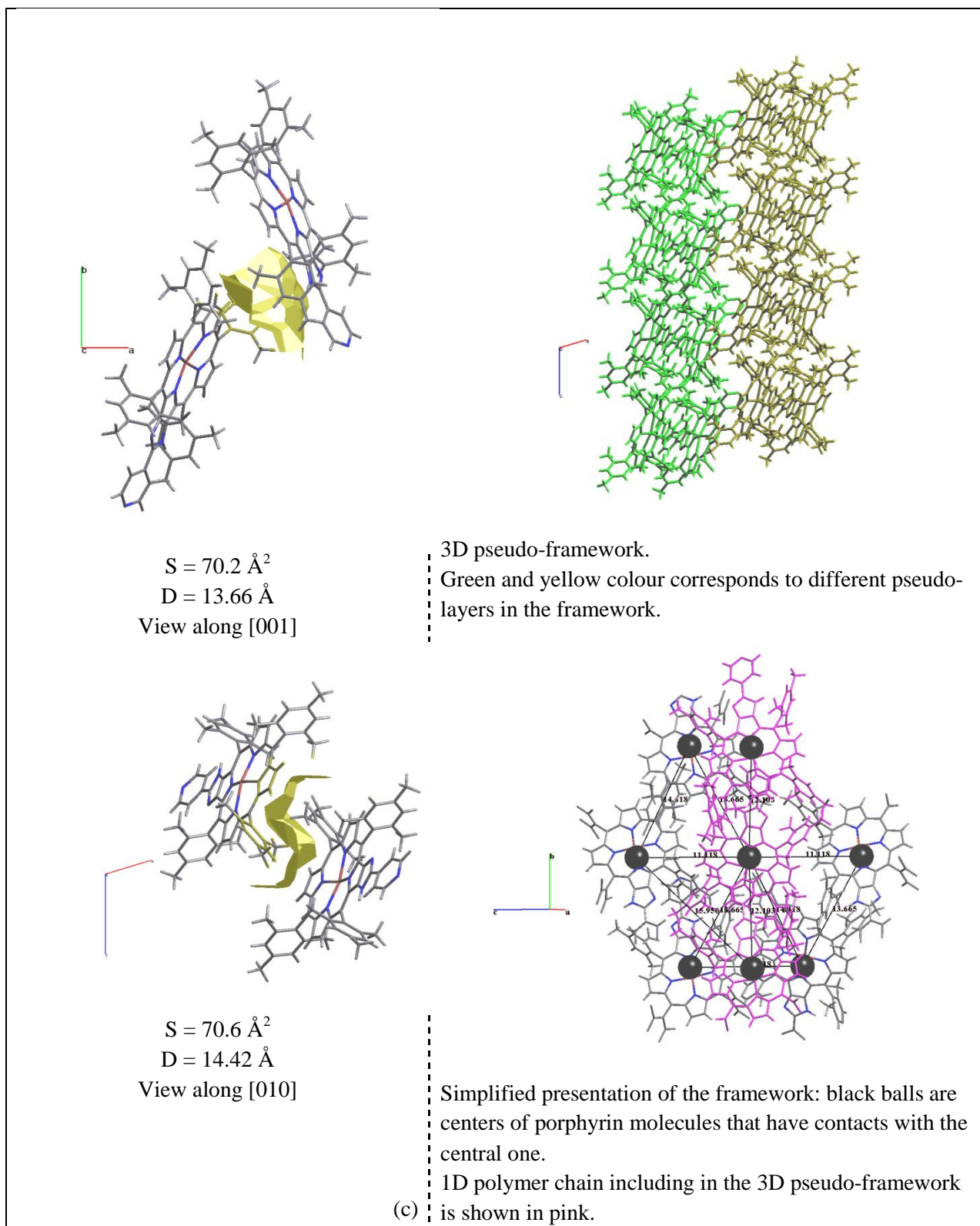


Table S5. Meaningful contacts( $\text{\AA}$ ) between adjacent polymer chains and porphyrin-toluene contacts in the crystals of **PyPorZn·2C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>**. The standard van der Waals radius (VDW) are taken from A. Bondi.<sup>1</sup>

C(32)...C(49) <sup>1</sup>	3.457
C(29)...H(18) <sup>1</sup>	2.928
C(41)...H(2S) <sup>1</sup>	2.944
C(30)...H(17) <sup>1</sup>	2.932

C(13)...H(48) <sup>2</sup>	2.689
C(48)...H(47B) <sup>2</sup>	2.911
C(5S)...H(50C) <sup>2</sup>	2.876
C(49)...H(32C) <sup>3</sup>	2.726
C(51)...H(32C) <sup>3</sup>	2.832
C(40)...H(35B) <sup>4</sup>	2.911
C(35)...H(12) <sup>4</sup>	2.832

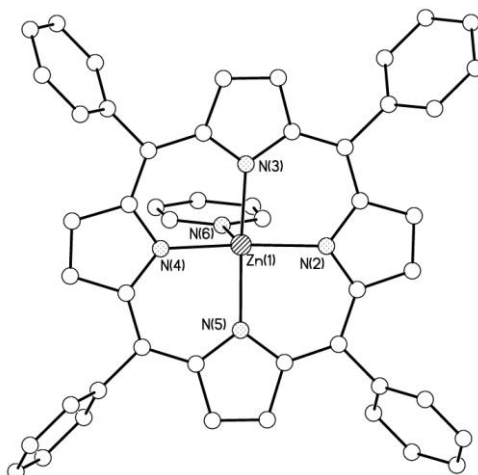
<sup>1</sup>+X, 3/2-Y, 1/2+Z

<sup>2</sup>1-X, 1-Y, 1-Z

<sup>3</sup>+ X, 3/2-Y, -1/2+Z

<sup>4</sup>1-X, 1/2+Y, 3/2-Z

Table S6. Total energy of **TPPZn–Py** as the function of the  $C_{para}$ –N<sub>Py</sub>–Zn angle and selected bond lengths (Å) and angles (deg) according to PBE0/def2-TZVP calculation.



The general view of **TPPZn–Py** with numbering scheme according PBE0/def2-TZVP calculation.

$C_{para}$ –N <sub>Py</sub> –Zn	$E_{total}$ , au	Zn–N <sub>Py</sub>	Zn1–N2	Zn1–N3	Zn1–N4	Zn1–N5	Zn–N <sub>Por</sub> aver.	CN <sub>Py</sub> C
180.0	-3938.448967	2.187	2.068	2.068	2.07	2.07	2.069	119.0
170.0	-3938.448638	2.192	2.070	2.070	2.070	2.065	2.069	118.9
165.0	-3938.448271	2.198	2.069	2.070	2.069	2.064	2.068	118.8
160.0	-3938.447788	2.207	2.069	2.071	2.069	2.062	2.068	118.8
155.0	-3938.447195	2.218	2.069	2.071	2.069	2.061	2.067	118.7
150.0	-3938.446511	2.234	2.068	2.071	2.068	2.059	2.066	118.5
145.0	-3938.445754	2.254	2.067	2.070	2.067	2.057	2.065	118.4
140.0	-3938.444929	2.278	2.066	2.069	2.066	2.056	2.064	118.3
135.0	-3938.444023	2.308	2.064	2.067	2.064	2.054	2.062	118.1
130.0	-3938.443072	2.346	2.063	2.065	2.063	2.052	2.061	118.0
125.0	-3938.442103	2.397	2.060	2.063	2.060	2.050	2.058	117.9
120.0	-3938.441149	2.457	2.058	2.060	2.058	2.048	2.056	117.8



Table S7. Topological parameters of electron density for critical points (3, -1) of Zn–N bonds and energy ( $E_{\text{int}}$ ) of Zn–N bonds estimated by means of CEML.

$V(r)$  – local potential energy density,  $g(r)$  – Lagrangian Form of Kinetic Energy Density, kinetic energy density,  $K(r)$  - Hamiltonian Form of Kinetic Energy Density that is equal to negative electron energy density ( $h_e(r)$ ), Ellip - bond Ellipticity =  $(\text{HessRho\_EigVal}(1) / \text{HessRho\_EigVal}(2)) - 1$

Bond	Rho, $e \cdot \text{\AA}^{-3}$	$v(r)$ , a.u.	$g(r)$ , a.u.	K, a.u.	L, $e \cdot \text{\AA}^{-5}$	Ellip	Eint, kcal/mol
<b><math>C_{\text{para}}\text{NZn}=180</math></b>							
N2 Zn1	0.50	-0.107	0.094	0.013	7.79	0.06	-33.496
Zn1 N3	0.51	-0.108	0.095	0.013	7.86	0.05	-33.878
Zn1 N4	0.50	-0.107	0.094	0.013	7.79	0.06	-33.496
N5 Zn1	0.51	-0.108	0.095	0.013	7.86	0.05	-33.878
Zn1 N6	0.38	-0.072	0.065	0.006	5.71	0.04	-22.476
<b><math>C_{\text{para}}\text{NZn}=170.00</math></b>							
N2 Zn1	0.50	-0.107	0.094	0.013	7.79	0.06	-33.534
Zn1 N3	0.50	-0.107	0.094	0.013	7.82	0.05	-33.669
Zn1 N4	0.50	-0.107	0.094	0.013	7.79	0.06	-33.494
N5 Zn1	0.51	-0.109	0.096	0.013	7.91	0.05	-34.181
N6 Zn1	0.38	-0.070	0.064	0.006	5.61	0.04	-22.019
<b><math>C_{\text{para}}\text{NZn}=165.00</math></b>							
N2 Zn1	0.50	-0.107	0.094	0.013	7.80	0.06	-33.544
Zn1 N3	0.50	-0.107	0.094	0.013	7.81	0.05	-33.624
Zn1 N4	0.50	-0.107	0.094	0.013	7.79	0.06	-33.536
N5 Zn1	0.51	-0.109	0.096	0.014	7.94	0.05	-34.327
N6 Zn1	0.37	-0.068	0.063	0.006	5.49	0.04	-21.448
<b><math>C_{\text{para}}\text{NZn}=160.00</math></b>							
Zn1 N2	0.50	-0.107	0.094	0.013	7.80	0.06	-33.585
Zn1 N3	0.50	-0.107	0.094	0.013	7.80	0.05	-33.568
N4 Zn1	0.50	-0.107	0.094	0.013	7.80	0.06	-33.579
N5 Zn1	0.51	-0.110	0.096	0.014	7.97	0.05	-34.522
N6 Zn1	0.36	-0.066	0.061	0.005	5.32	0.04	-20.667
<b><math>C_{\text{para}}\text{NZn}=155.00</math></b>							
Zn1 N2	0.50	-0.107	0.094	0.013	7.81	0.06	-33.633
Zn1 N3	0.50	-0.107	0.094	0.013	7.79	0.05	-33.564
N4 Zn1	0.50	-0.107	0.094	0.013	7.81	0.06	-33.641
N5 Zn1	0.51	-0.111	0.097	0.014	8.00	0.05	-34.717
N6 Zn1	0.35	-0.063	0.058	0.005	5.10	0.05	-19.695
<b><math>C_{\text{para}}\text{NZn}=150.00</math></b>							
N2 Zn1	0.51	-0.107	0.094	0.013	7.82	0.06	-33.723
N3 Zn1	0.50	-0.107	0.094	0.013	7.79	0.05	-33.583
Zn1 N4	0.51	-0.107	0.094	0.013	7.82	0.06	-33.723
Zn1 N5	0.52	-0.111	0.097	0.014	8.04	0.05	-34.932
N6 Zn1	0.34	-0.059	0.054	0.004	4.83	0.05	-18.482

<b><math>C_{para}NZn=145.00</math></b>							
Zn1 N2	0.51	-0.108	0.095	0.013	7.84	0.06	-33.835
Zn1 N3	0.50	-0.107	0.094	0.013	7.80	0.05	-33.670
N4 Zn1	0.51	-0.108	0.095	0.013	7.84	0.06	-33.817
N5 Zn1	0.52	-0.112	0.098	0.014	8.07	0.05	-35.117
N6 Zn1	0.32	-0.055	0.051	0.004	4.51	0.05	-17.126
<b><math>C_{para}NZn=140.00</math></b>							
Zn1 N2	0.51	-0.108	0.095	0.013	7.86	0.06	-33.957
Zn1 N3	0.51	-0.108	0.094	0.013	7.82	0.05	-33.781
N4 Zn1	0.51	-0.108	0.095	0.013	7.86	0.06	-33.969
N5 Zn1	0.52	-0.113	0.098	0.014	8.10	0.05	-35.317
N6 Zn1	0.30	-0.050	0.047	0.003	4.16	0.05	-15.662
<b><math>C_{para}NZn =135.00</math></b>							
N2 Zn1	0.51	-0.109	0.095	0.013	7.89	0.06	-34.125
N3 Zn1	0.51	-0.108	0.095	0.013	7.85	0.05	-33.982
Zn1 N4	0.51	-0.109	0.095	0.013	7.89	0.06	-34.133
Zn1 N5	0.52	-0.113	0.099	0.014	8.13	0.05	-35.506
N6 Zn1	0.28	-0.045	0.042	0.003	3.76	0.05	-14.050
<b><math>C_{para}NZn =130.00</math></b>							
Zn1 N2	0.51	-0.109	0.096	0.014	7.92	0.06	-34.347
Zn1 N3	0.51	-0.109	0.095	0.014	7.88	0.05	-34.195
N4 Zn1	0.51	-0.109	0.096	0.014	7.92	0.06	-34.347
N5 Zn1	0.53	-0.114	0.099	0.015	8.16	0.05	-35.739
N6 Zn1	0.26	-0.039	0.037	0.002	3.32	0.05	-12.307
<b><math>C_{para}NZn = 125.00</math></b>							
N2 Zn1	0.51	-0.110	0.096	0.014	7.96	0.06	-34.619
N3 Zn1	0.51	-0.110	0.096	0.014	7.93	0.05	-34.514
Zn1 N4	0.52	-0.110	0.096	0.014	7.96	0.06	-34.628
Zn1 N5	0.53	-0.115	0.100	0.015	8.20	0.05	-35.991
N6 Zn1	0.23	-0.033	0.031	0.002	2.82	0.05	-10.424

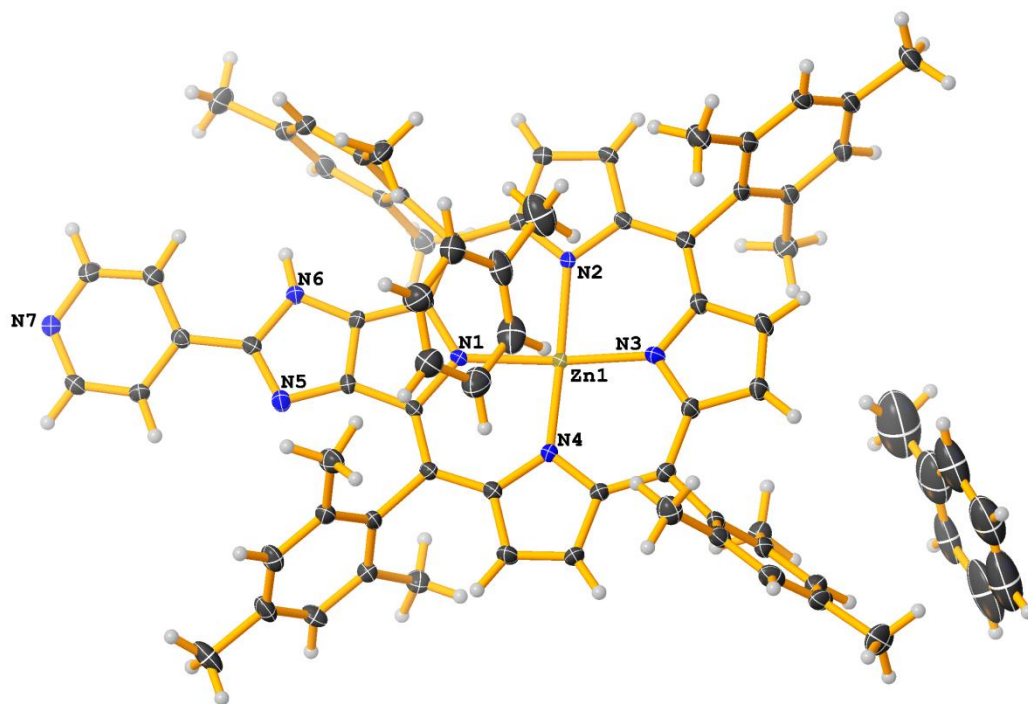


Figure S1. Molecular structure of in **PyPorZn·2C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>**. Thermal ellipsoids are drawn at the 50% probability level.

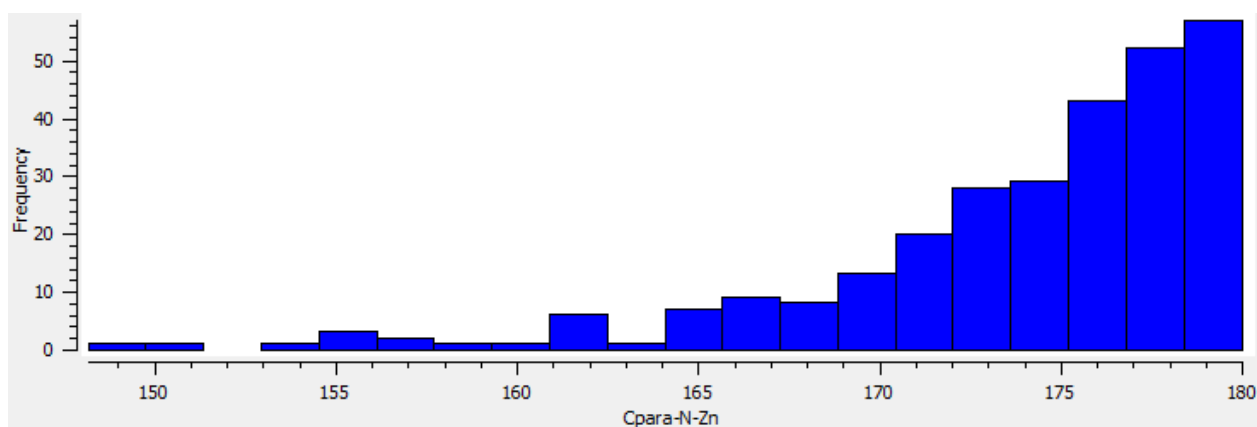


Figure S2. Histogram of  $C_{para}$ -N<sub>py</sub>-Zn angle in zinc porphyrinates according CSD analysis.

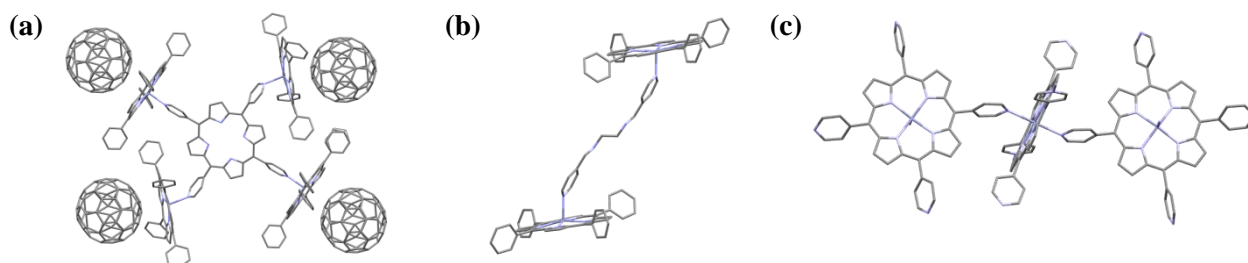


Figure S3. Schematic representation of porphyrins in which the  $C_{para}$ -N-Zn angle significantly deviates from  $180^\circ$  (CSD refcodes BIBVUE, BABBEM, BURJEE).  $C_{para}$ -N-Zn angle is equal to  $148.2^\circ$  (a)<sup>2</sup>,  $154.5^\circ$  (b)<sup>3</sup> and  $153.3^\circ$  (c)<sup>4</sup>.

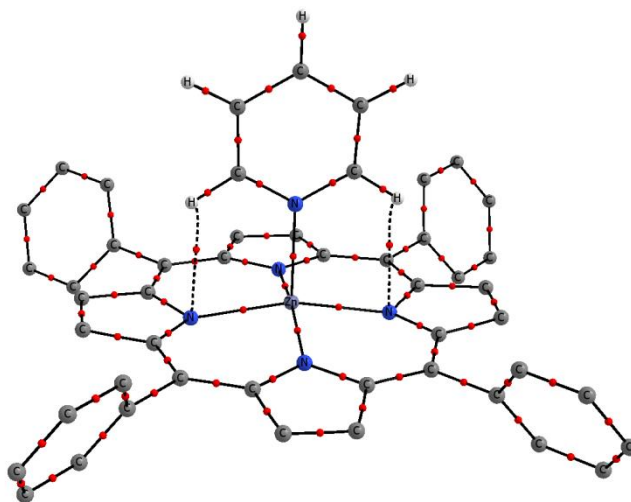


Figure S4. The molecular graph of **TPPZn-py**. The hydrogen atoms of porphyrin and corresponding CP (3,-1) for C-H bonds as well as CP (3,+1) are omitted for clarity. The CP (3,-1) are shown by red spheres.

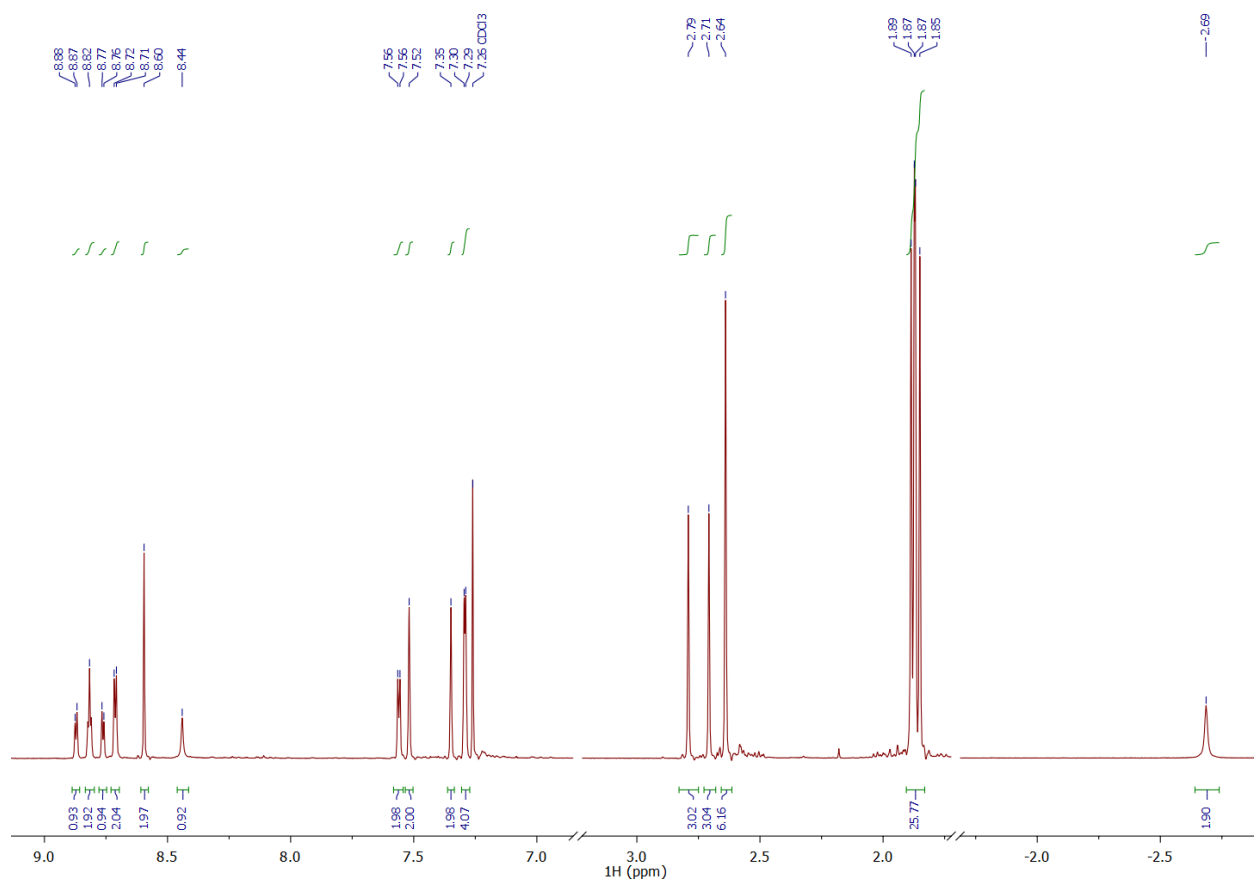


Figure S5. <sup>1</sup>H NMR spectrum of **PyPor** in CDCl<sub>3</sub>.

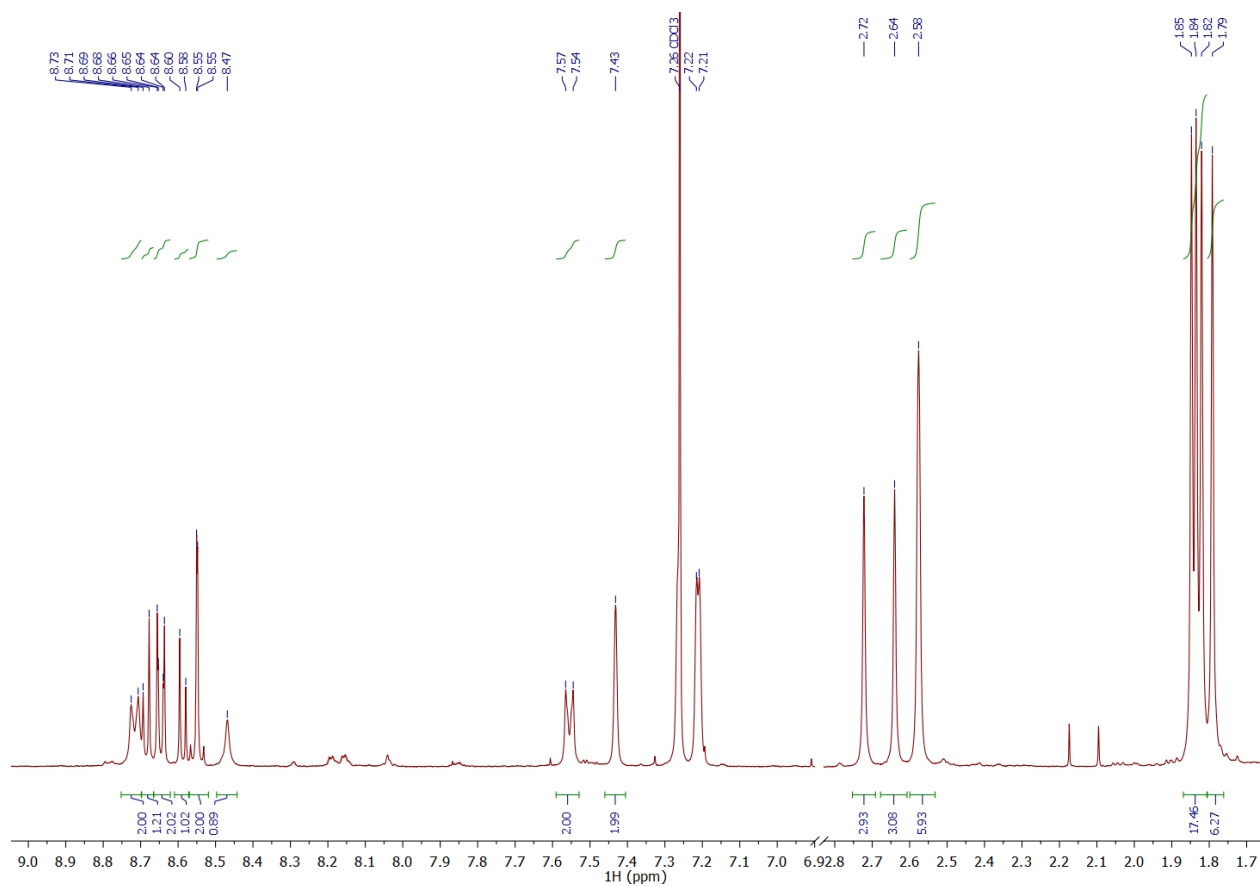


Figure S6. <sup>1</sup>H NMR spectrum of **PyPorNi** in CDCl<sub>3</sub>.

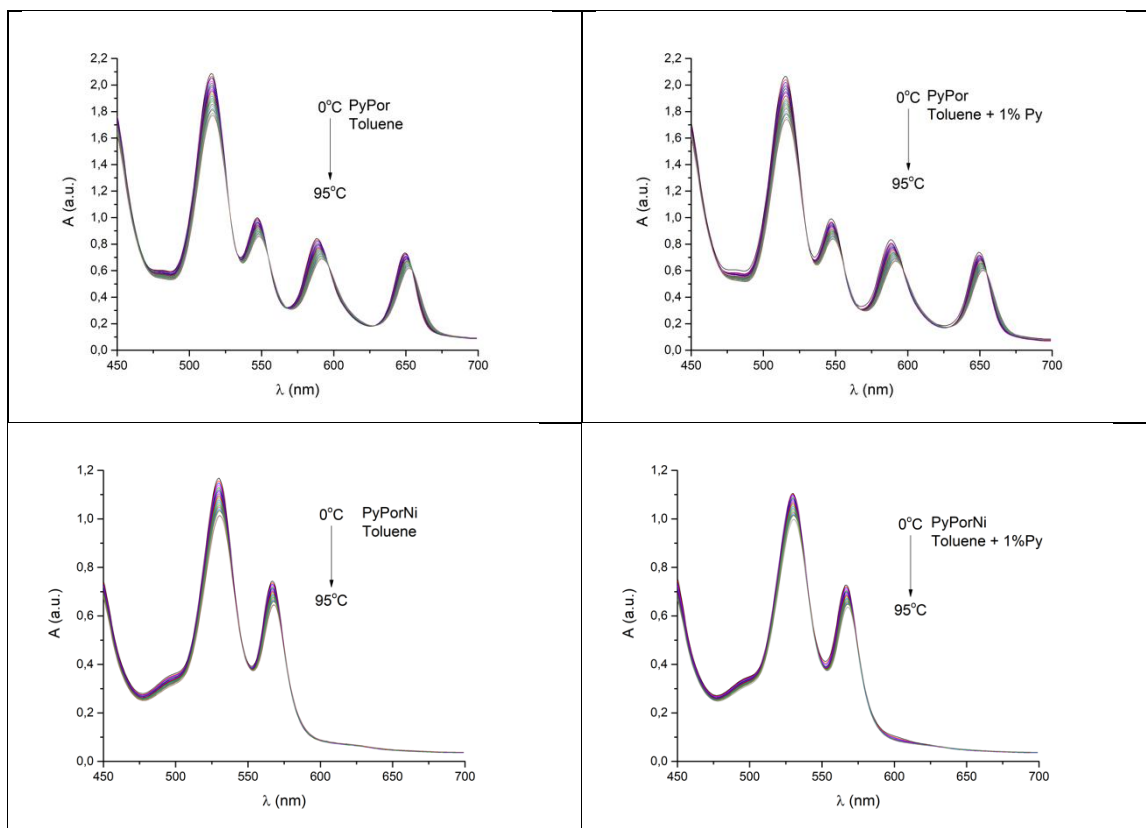


Figure S7. UV-Vis spectra of **PyPor** and **PyPorNi** upon variation of the temperature.

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