SUPPORTING INFORMATION
for

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

Inna A. Abdulaeva,[a,b] Kirill P. Birin,[a] Anna A. Sinelshchikova,[a] Mikhail S. Grigoriev,[a] Konstantin A. Lyssenko,[c] Yulia G. Gorbunova,[a,d] Aslan Yu. Tsivadze,[a,d] Alla Bessmertnykh-Lemeune[b]

[a] A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, 119071, Leninsky pr., 31, building 4, Moscow, Russian Federation
[b] Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR CNRS 6302, Université Bourgogne Franche-Comté, 9 Avenue Alain Savary, 21078 Dijon, France.
[c] Department of Chemistry, Lomonosov Moscow State University, 119992 Moscow, Russian Federation
[d] N.S. Kurnakov Institute of General and Inorganic Chemistry RAS, 119991, Leninsky pr., 31, Moscow, Russian Federation

CONTENTS

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·2$C_6H_5CH_3$**.

Parameter	**PyPorZn**
CCDC number	1871295
Chemical formula	$C_{76}H_{71}N_7Zn$
Chemical formula moiety	$C_{62}H_{55}N_7Zn$, 2(C_7H_8)
Crystal system, space group, *Z*	Monoclinic, $P2_1/c$, 4
Unit cell dimensions	*a* = 13.1788(9) Å, *b* = 21.4947(16) Å, *c* = 22.2362(18) Å, β = 106.952(2)°
Volume, Å^3	6025.3(8)
Density (calculated), g/cm^3	1.265
Radiation, λ, Å	MoKα, 0.71073
μ, mm^{-1}	0.459
Temperature, K	100(2)
Crystal size, mm	0.3 × 0.2 × 0.08
Data collection range, θ, °	4.095 – 27.974
Interval of reflection indices	–17 ≤ h ≤ 17, –27 ≤ k ≤ 28, –29 ≤ l ≤ 29
Reflections collected	48812
Unique reflections/R_{int}	14387/0.0876
Reflections with I > 2σ(I)	8746
Refinement method	Least-squares on F^2
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 R indexes [I>=2σ (I)]	R1 = 0.0599, wR2 = 0.1343
Final R indexes [all data]	R1 = 0.1195, wR2 = 0.1594
Goodness-of-fit on F^2	1.017
Largest diff. peak/ hole, e/Å^3	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)^1	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)		

[1]2-X,-1/2+Y,3/2-Z

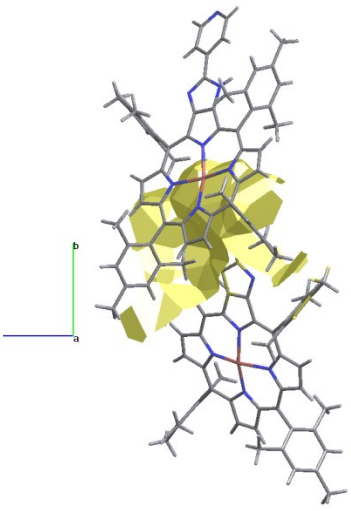
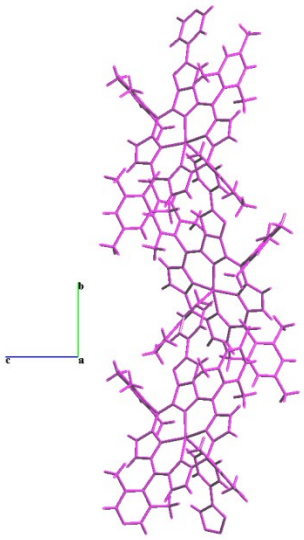
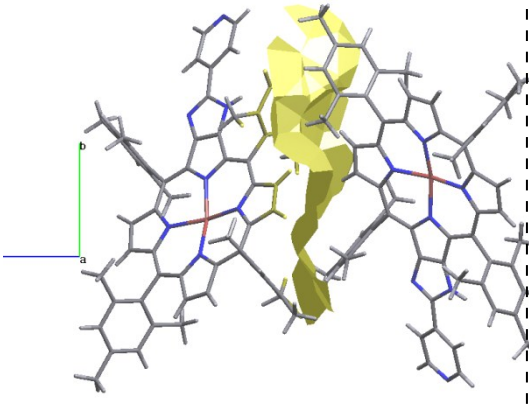
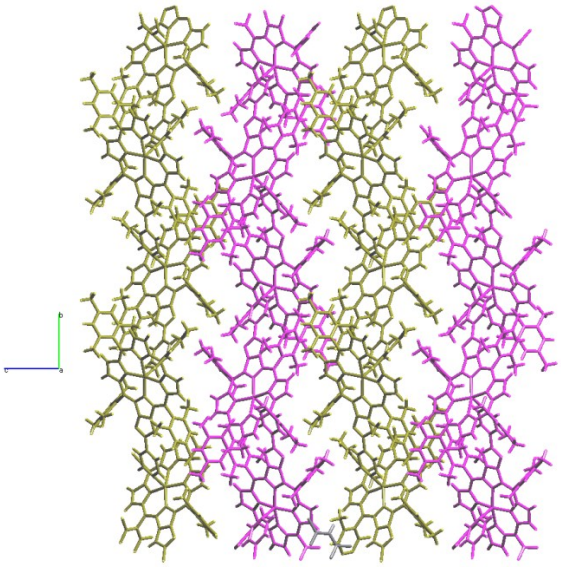
Table S3. Selected bond angles (deg) for **PyPorZn**.

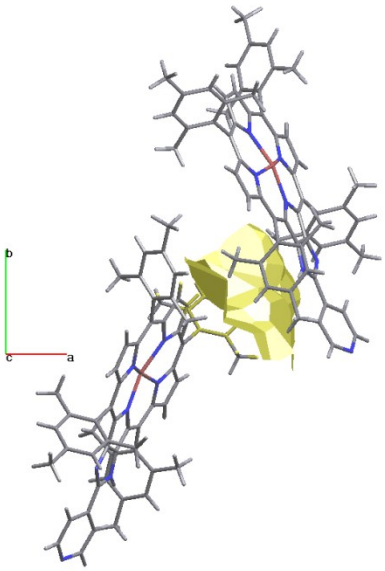
Bond angles (deg)

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)[1]	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)[1]	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)[1]	92.70(10)	C(21)−N(5)−C(2)	103.2(2)
N(4)−Zn(1)−N(7)[1]	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)[2]	116.6(2)
C(4)−N(1)−Zn(1)	122.66(19)	C(25)−N(7)−Zn(1)[2]	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)		

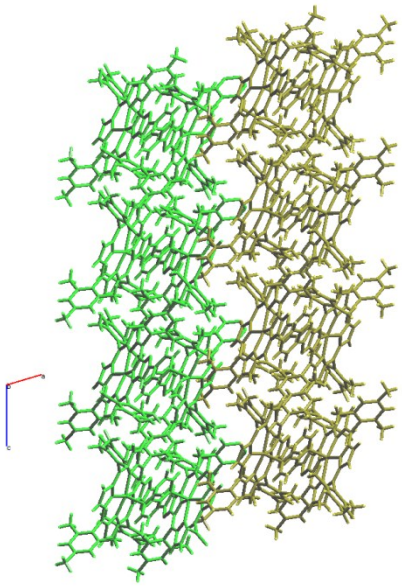
[1]2-X,-1/2+Y,3/2-Z; [2]2-X,1/2+Y,3/2-Z

Table S4. Selected intermolecular contacts in the crystals **PyPorZn·2C$_6$H$_5$CH$_3$**, the boundary surfaces S(Å^2), center to center distances between contacted porphyrins D(Å) and supramolecular assembles formed.

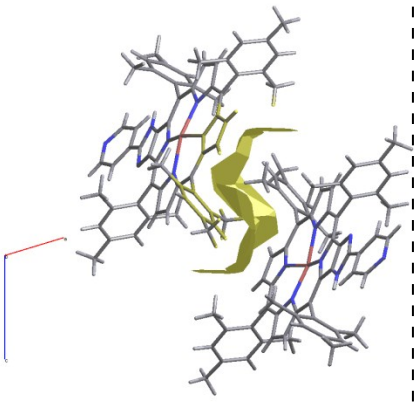
Boundary surfaces S(Å^2) of intermolecular contacts and distances between porphyrin centers D(Å)	Supramolecular organization based on the consideration of the strength level of intermolecular contacts
 S = 113.3 Å^2 D = 12.10 Å View along [100] (a)	 1D polymer chain along [010] direction. View along [100].
 S = 81.9 Å^2 D = 11.12 Å View along [100] (b)	 2D pseudo-layers in (100) plane. View along [100] direction. Yellow and pink colour corresponds to different polymer chains.



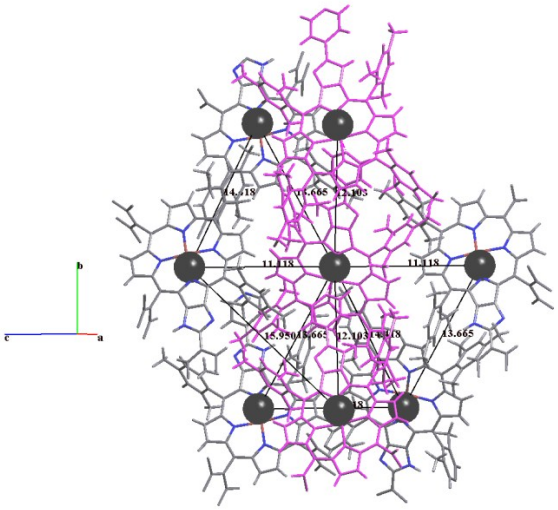
S = 70.2 Å^2
D = 13.66 Å
View along [001]



3D pseudo-framework.
Green and yellow colour corresponds to different pseudo-layers in the framework.



S = 70.6 Å^2
D = 14.42 Å
View along [010]



Simplified presentation of the framework: black balls are centers of porphyrin molecules that have contacts with the central one.
1D polymer chain including in the 3D pseudo-framework is shown in pink.

(c)

Table S5. Meaningful contacts(Å) between adjacent polymer chains and porphyrin-toluene contacts in the crystals of **PyPorZn·2$C_6H_5CH_3$**. The standard van der Waals radius (VDW) are taken from A. Bondi.[1]

C(32)…C(49)[1]	3.457
C(29)…H(18)[1]	2.928
C(41)…H(2S)[1]	2.944

C(30)…H(17)[1]	2.932
C(13)…H(48)[2]	2.689
C(48)…H(47B)[2]	2.911
C(5S)…H(50C)[2]	2.876
C(49)…H(32C)[3]	2.726
C(51)…H(32C)[3]	2.832
C(40)…H(35B)[4]	2.911
C(35)…H(12)[4]	2.832

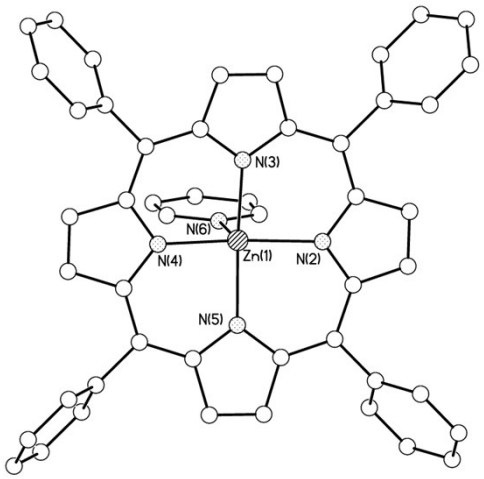
[1]+X, 3/2-Y, 1/2+Z

[2]1-X, 1-Y, 1-Z

[3]+ X, 3/2-Y, -1/2+Z

[4]1-X, 1/2+Y, 3/2-Z

Table S6. Total energy of **TPPZn–Py** as the function of the C_{para}–N_{Py}–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_{Py}–Zn	E_{total}, au	Zn-N_{Py}	Zn1-N2	Zn1-N3	Zn1-N4	Zn1-N5	Zn-N_{Por} aver.	$CN_{Py}C$
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_{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 (he(r)), Ellip - bond Ellipticity = (HessRho_EigVal(1) / HessRho_EigVal(2)) – 1

Bond	**Rho, e·Å-3**	**v(r), a.u.**	**g(r), a.u.**	**K, a.u.**	**L, e·Å-5**	**Ellip**	**Eint, kcal/mol**
C_{para}NZn=180							
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
C_{para}NZn=170.00							
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
C_{para}NZn=165.00							
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
C_{para}NZn=160.00							
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
C_{para}NZn=155.00							
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
C_{para}NZn=150.00							
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

C_{para}NZn=145.00							
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
C_{para}NZn=140.00							
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
C_{para}NZn =135.00							
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
C_{para}NZn =130.00							
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
C_{para}NZn = 125.00							
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

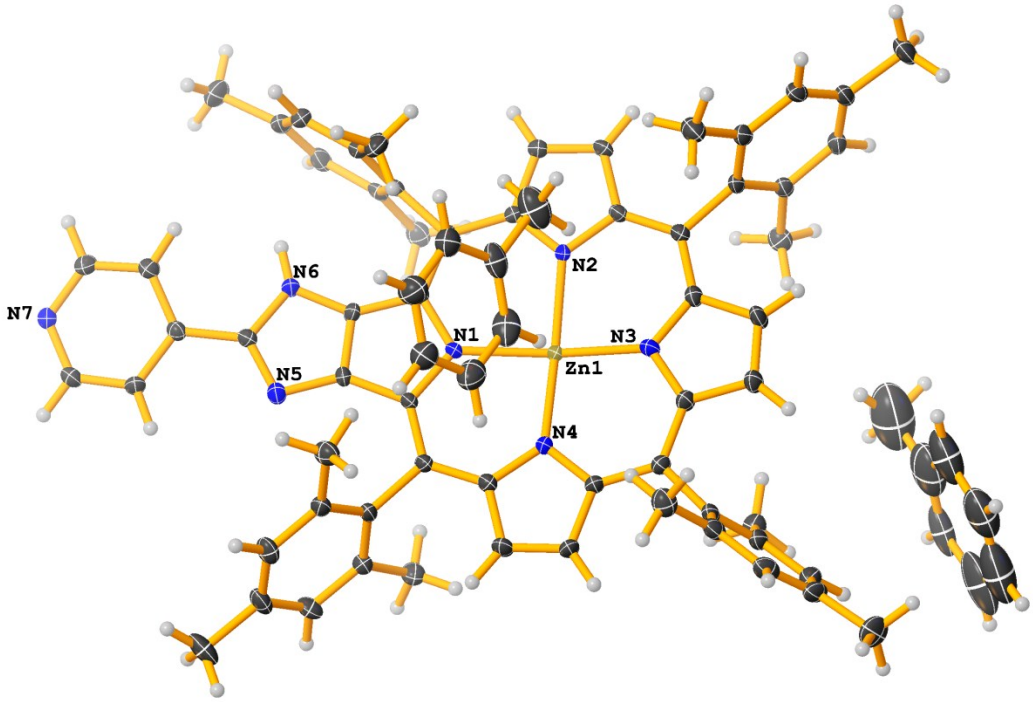


Figure S1. Molecular structure of in **PyPorZn·2C$_6$H$_5$CH$_3$**. Thermal ellipsoids are drawn at the 50% probability level.

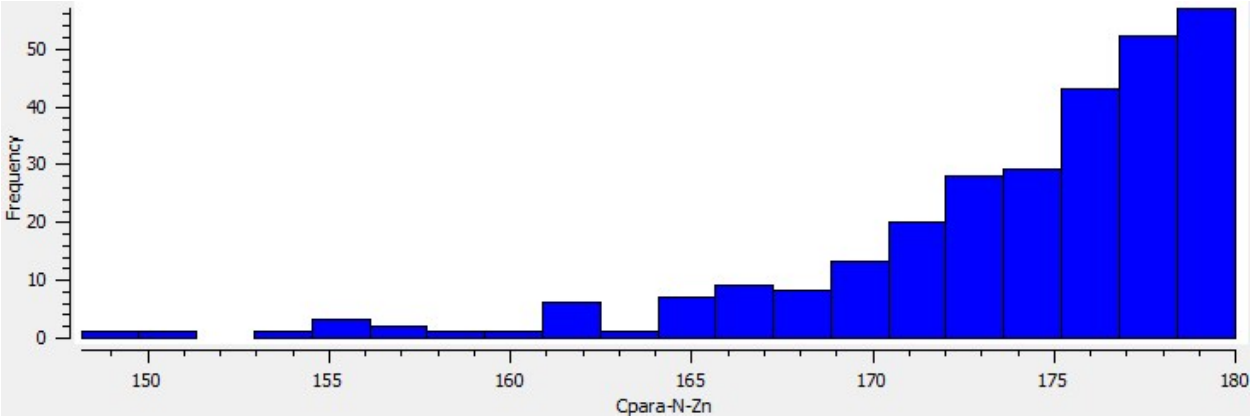


Figure S2. Histogram of C$_{para}$–N$_{Py}$–Zn angle in zinc porphyrinates according CSD analysis.

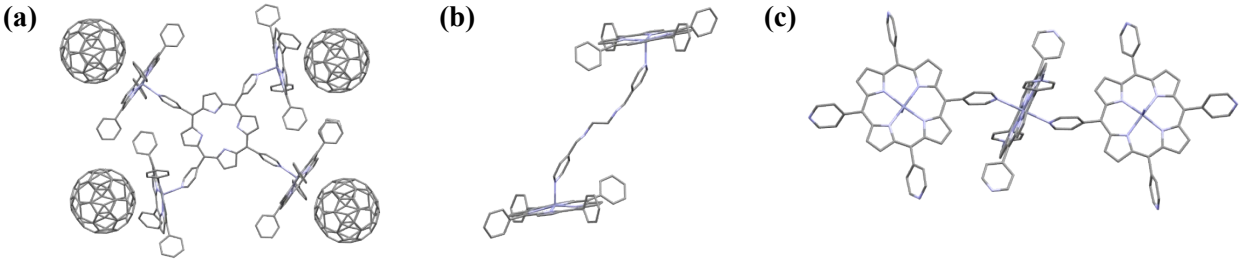


Figure S3. Schematic representation of porphyrins in which the C$_{para}$–N–Zn angle significantly deviates from 180° (CSD refcodes BIBVUE, BABBEM, BURJEE). C$_{para}$–N–Zn angle is equal to 148.2º (a) [2], 154.5º (b) [3] and 153.3º (c) [4].

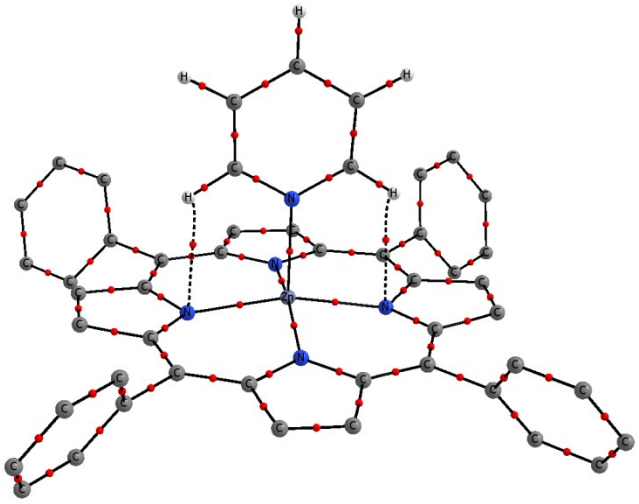


Figure S4. The molecular graph of **TPPZn–py**. The hydrogen atoms of porphyrin and corresponding CP (3,-1) for C–H bonds as well as CP (3,+1) are omitted for clarity. The CP (3,-1) are shown by red spheres.

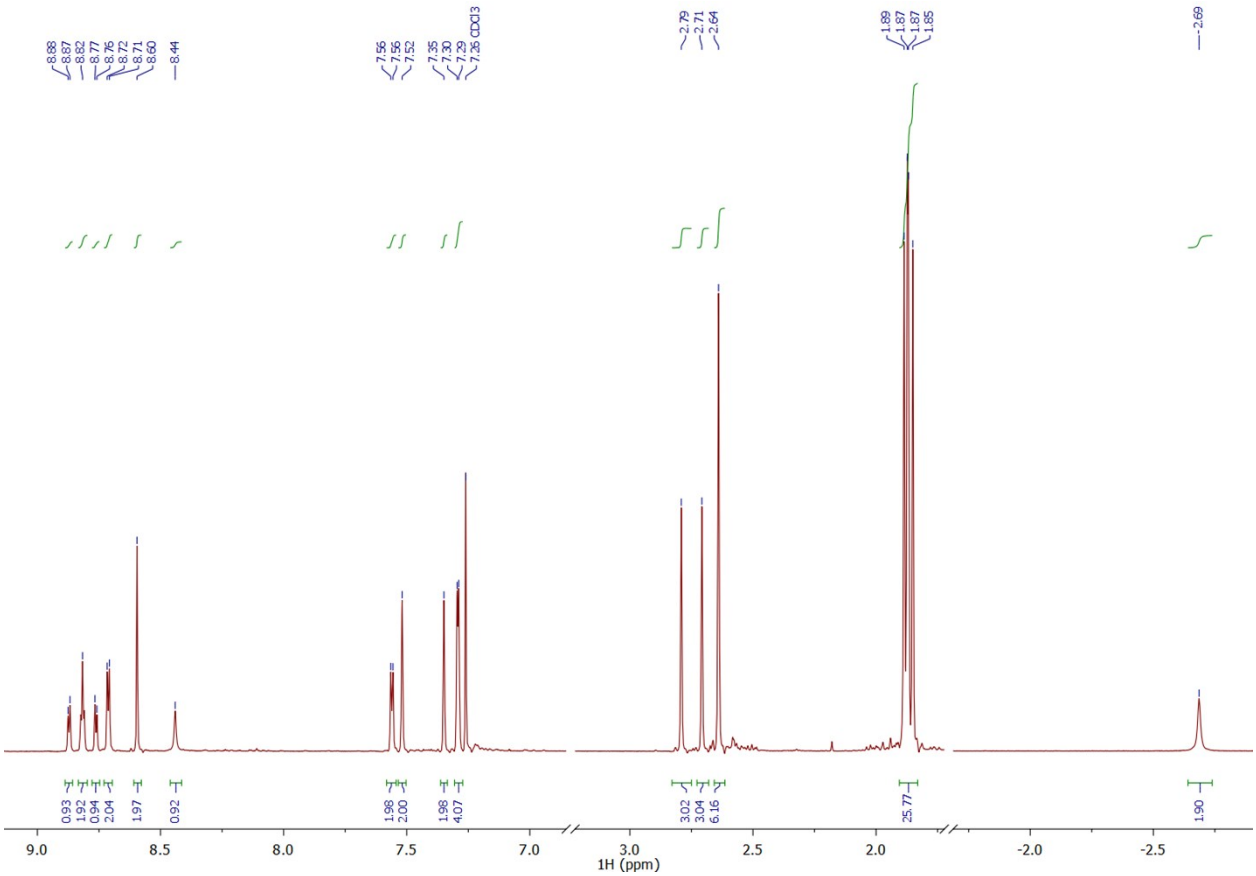


Figure S5. ^{1}H NMR spectrum of **PyPor** in $CDCl_3$.

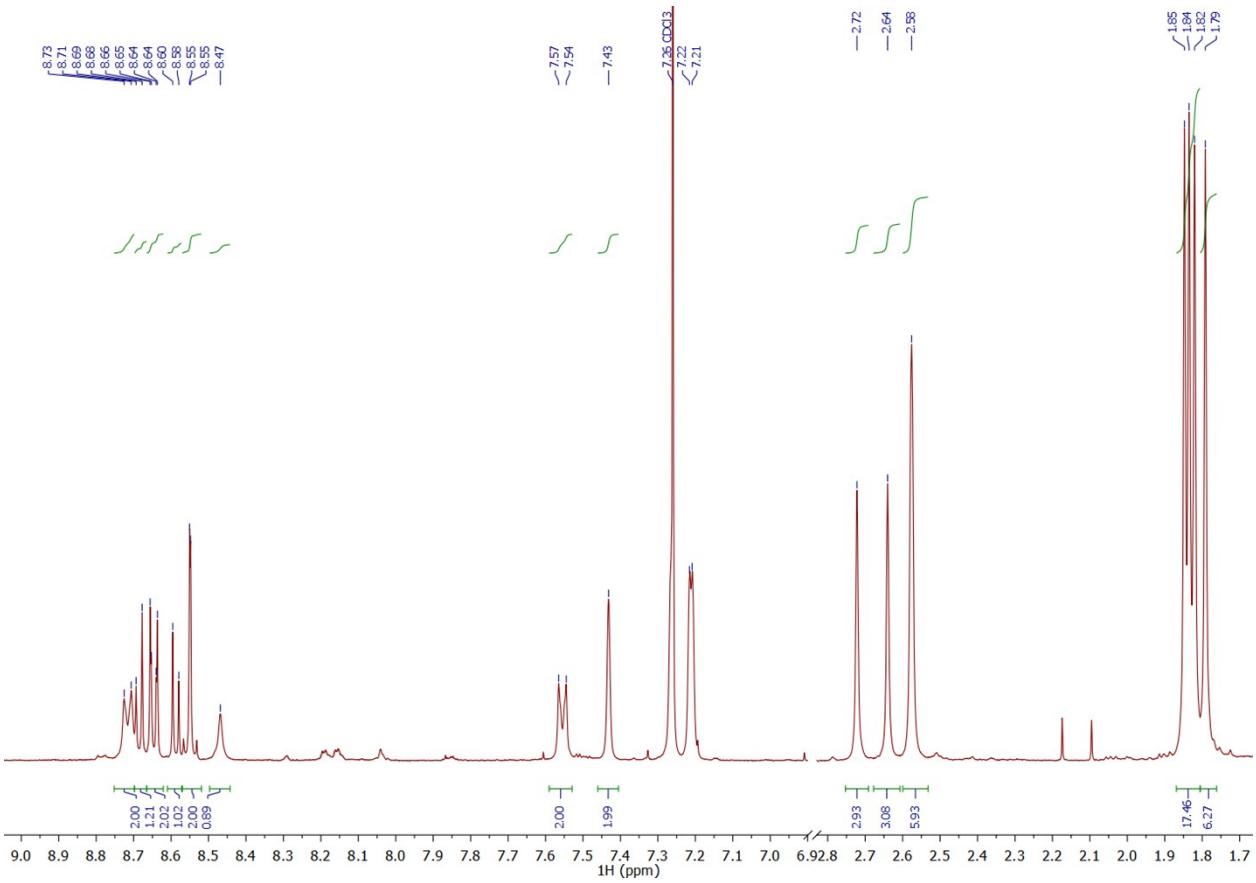


Figure S6. ^{1}H NMR spectrum of **PyPorNi** in $CDCl_3$.

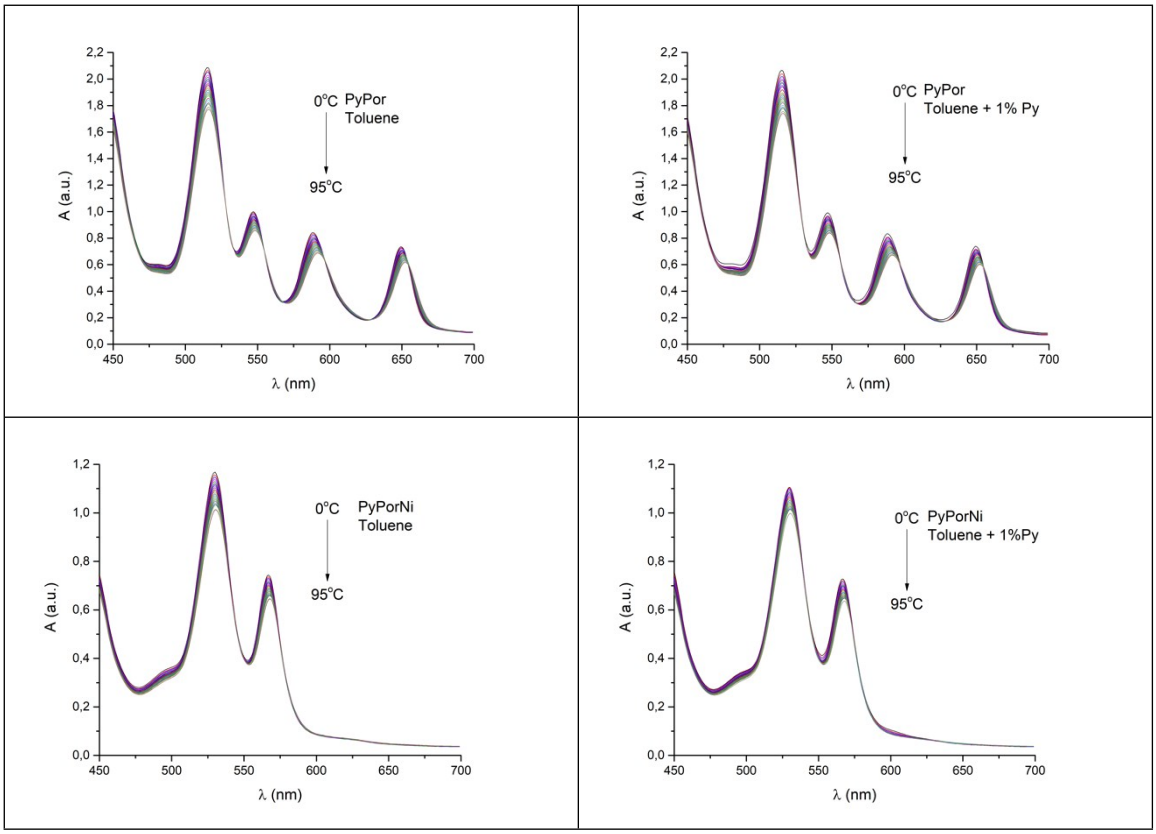


Figure S7. UV-Vis spectra of **PyPor** and **PyPorNi** upon variation of the temperature.

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