Supporting Information

Photophysical and theoretical studies of peripherally halogenated octaphenoxyphthalocyanines

Saad Makhseed[a,*], Basma Ghazal[a], Amr Mohamed Abdelmoniem[a], Veronika Novakova[b] and Petr Zimcik[c]

[a] Department of Chemistry, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait

[b] Department of Biophysics and Physical Chemistry, Faculty of Pharmacy in Hradec Kralove, Charles University in Prague, Heyrovskeho 1203, Hradec Kralove 50005, Czech Republic

[c] Department of Pharmaceutical Chemistry and Drug Control, Faculty of Pharmacy in Hradec Kralove, Charles University in Prague, Heyrovskeho 1203, Hradec Kralove 50005, Czech Republic

Crystal structure of phthalonitrile precursors.

Single crystals of phthalonitrile precursors Pn2 and Pn3 suitable for X-ray diffraction technique were grown by solvent diffusion method. Data collection and structure refinement strategies of these crystals along with their diffraction parameters are discussed in the Supporting information. The structures of both Pn2 and Pn3 obtained from single crystal X-ray diffraction method are in perfect agreement with the proposed ones predicted by synthetic protocol and other characterization techniques like NMR and mass spectroscopy.

The thermal ellipsoid representation of crystal structures derived from Pn2 and Pn3 are depicted in (Figure S1). As expected, the phthalonitrile plane in both of these molecules is oriented perpendicular to the phenoxy rings containing the halogen atoms. The crystal data also indicate that both chloro and bromo derivative of these phthalonitrile precursors exhibited almost the same structural features and 3-dimensional packing pattern (Figure S3).

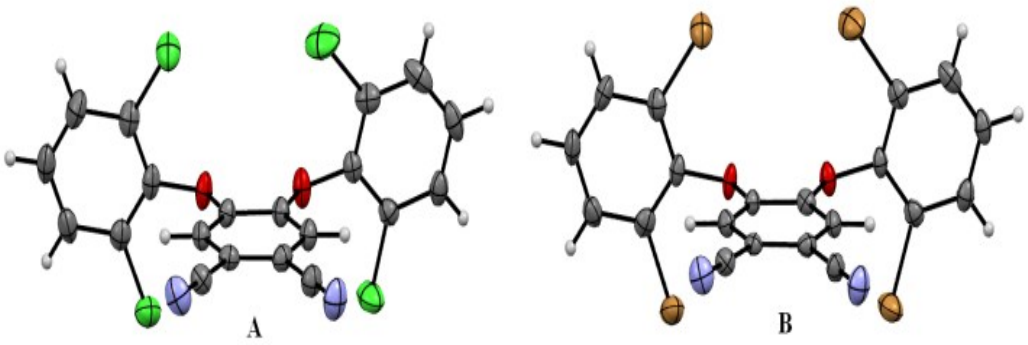


Figure S1. Molecular structures derived from single crystal X-ray diffraction data of phthalonitrile precursors Pn2 (A) and Pn3 (B). Color code: red - oxygen; blue - nitrogen; dark gray –carbon; green - chlorine; yellow - bromine; light gray - hydrogen.

Single crystal X- diffraction analysis of Pn2, **Pn3** and **Pc2-Zn**

Single crystals of both **Pn2** and **Pn3** suitable for diffraction analysis were grown form ethylacetate-hexane mixture by solvent diffusion method. THF-water/DMF mixture (with few drops of pyridine) was employed to grow crystals of **Pc2-Zn**. Table S1 gives description on the physical nature, experimental setup and diffraction data of crystal samples analyzed in the present study.

Table S1. Summary on the nature of the crystals and various diffraction parameters of **Pn2, Pn3** and **Pc2Zn**

Compound	**Pn2**	**Pn3**	**Pc2-Zn**
Crystal Dimension/mm	0.350 x 0.350 x 0.300	0.300 x 0.200 x 0.200	0.400 X 0.300 X 0.050
Crystal Color, Habit	Colorless, Block	Colorless, Block	Green, platelet
Formula weight	$C_{20}H_8Cl_4N_2O_2$	$C_{20}H_8Br_4N_2O_2$	$C_{97}H_{61}Cl_{16}N_9O_{11}Zn$
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group(no.)	$P2_12_12_1$ (#19)	$P2_12_12_1$ (#19)	$P2_1$ (#4)
T/^{o}C	-123.0	-123.0	-123.0
a/Å	11.6044(4)	11.9517(7)	14.7820(4)
b//Å	12.7753(5)	12.7781(7)	21.4253(4
c/Å	13.367(1)	13.519(1)	15.345(1)
V/ Å^3	1981.7(2)	2064.7(2)	4859.2
Z	4	4	2
μ(MOKα)	0.775 cm^{-1}	78.385 cm^{-1}	7.565 cm^{-1}
ρ_{calcd}/g cm^{-3}	1.509	2.020	1.477
$2\theta_{max}$/deg	54.9	54.9	54.9
Reflections collected	19722	20511	48039
Unique reflections	4535	4717	20001
R_{int}	0.0205	0.0422	0.0233
R (I > 2σ)	0.0264	0.0282	0.0473
R (all data)	0.0277	0.0453	0.0511
R_w(all data)	0.0723	0.0583	0.1264
$\lvert\Delta\rho\rvert_{max}$e Å^{-3}	0.39	0.66	1.97

The ball and stick representation of **Pn2** and **Pn3** are depicted in Figure S2. It is clear that the aromatic planes of the phenoxy group containing halogens lie almost perpendicular to the plane of phthalonitrile moiety owing to steric constrains. The calculated torsion angles of the chain of relevant atoms shows the dihedral angles between the phenyl ring containing phthalonitrile functions is about 90 ± 15° to the plane

of those phenoxy substituents (Table S2). The deviation from 90° is almost same for both chloro and bromo derivatives. This deviation is expected to enable efficient packing within the crystal network.

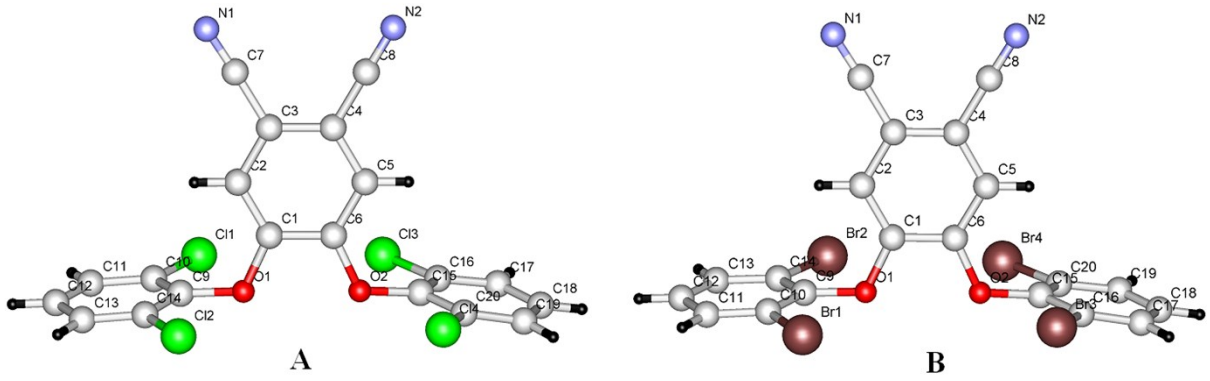


Figure S2. The ball and stick representation of **Pn2** (A) and **Pn3** (B)

Table S2. Torsion angles corresponding to benzene ring containing nitrile functions (or the benzene ring in the Pc core) to plane of phenyl groups contains the halogen moieties.

	Atom chains				Torsion angles
Pc2Zn	C1	O1	C33	C34	85.3(4)
	C1	O1	C33	C38	-99.3(3)
	C2	O2	C39	C40	-102.5(3)
	C2	O2	C39	C44	79.7(4)
	C9	O3	C45	C46	84.2(4
	C9	O3	C45	C50	-99.4(4)
	C10	O4	C51	C52	-64.8(4)
	C10	O4	C51	C56	123.0(3)
	C17	O5	C57	C58	100.2(4)
	C17	O5	C57	C62	-85.5(4)
	C18	O6	C63	C64	-92.6(4
	C18	O6	C63	C68	90.3(4)
	C25	O7	C69	C70	92.8(4)
	C25	O7	C69	C74	-90.5(4)
	C26	O8	C75	C76	-106.9(3)
	C26	O8	C75	C80	79.0(4)
Pn2	C1	O1	C9	C10	79.87(15)
	C1	O1	C9	C14	-105.18(14)
	C6	O2	C15	C16	-77.54(16
	C6	O2	C15	C20	108.07(14)
Pn3	C1	O1	C9	C10	-104.4(4
	C1	O1	C9	C14	79.9(4)
	C6	O2	C15	C16	103.3(4)
	C6	O2	C15	C20	-82.3(4)

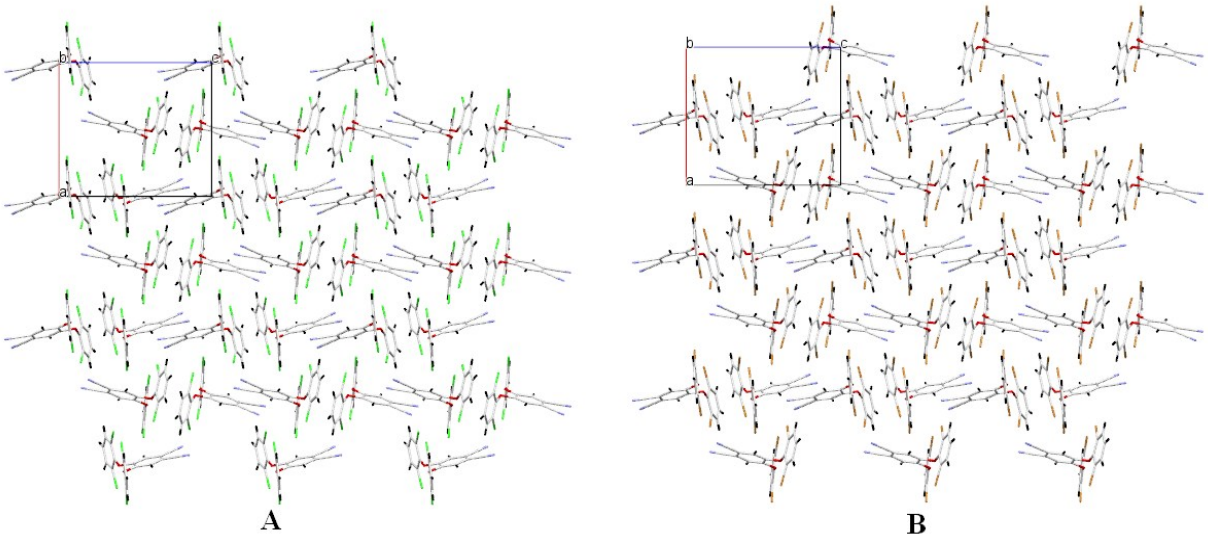


Figure S3. 3-dimensional packing pattern of (A) **Pn2** and (B) **Pn3** viewing along a- direction which demonstrates similar packing pattern of both phthalocyanine precursors in their crystal network

The 3-dimensional packing structures of these molecules are given in Figure S3. Both bromo and chloro derivatives exhibited similar packing pattern in their crystal network. A close examination of their 3-dimensional packing pattern reveals that along the a-, b- and c- directions all the molecules in one row are oriented in the same direction; but their orientation with respect to the molecules in the neighboring rows are in opposite directions. Figure S4 is the demonstration of the 3-dimensional packing of the phthalonitrile groups of **Pn2** along a-,b- and c-directions while other parts of the molecule are kept invisible.

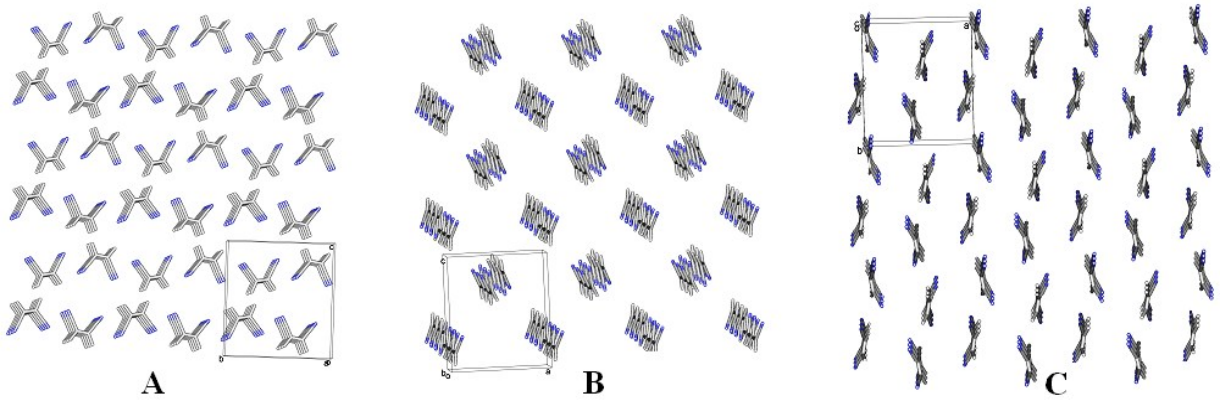


Figure S4: Packing pattern of **Pn2** along a-,b- and c-directions when viewing only the phthalonitrile functions after hiding all other atoms in the molecule.

It is interesting to see that cyano- groups of two neighboring molecules are positioned very close to each other but opposite in orientation along the b-direction. These arrangements enable the structures to avoid vacant spaces as much as possible and also to achieve maximum stabilization through possible non-bonding van der Walls interactions. The unit cell dimension of both **Pn2** and **Pn3** crystals is almost same and hence the density of **Pn3** system is much higher than that of **Pn2** (2.020 and 1.509 g cm^{-3}, respectively)

The ball and stick representation of the crystal structure of **Pc2-Zn** is given in Figure S5. From the molecular structure it is clear that the orientation of the phenyl rings containing chlorine atoms are right angles to the molecular plane of the rest of the phthalocyanine. This make half of the chlorine atoms directed upward with respect to the phthalocyanine plane and the other half is directed downward. The face to face aggregation of Pc units- which is the most notorious drawback of phthalocyanines in its variety of applications- could easily be prevented by this upward and downward orientation of bulky chlorine atoms in this novel system. See Table S2 for the dihedral angles between constitute atoms in the phenoxy ring and the original Pc plane.

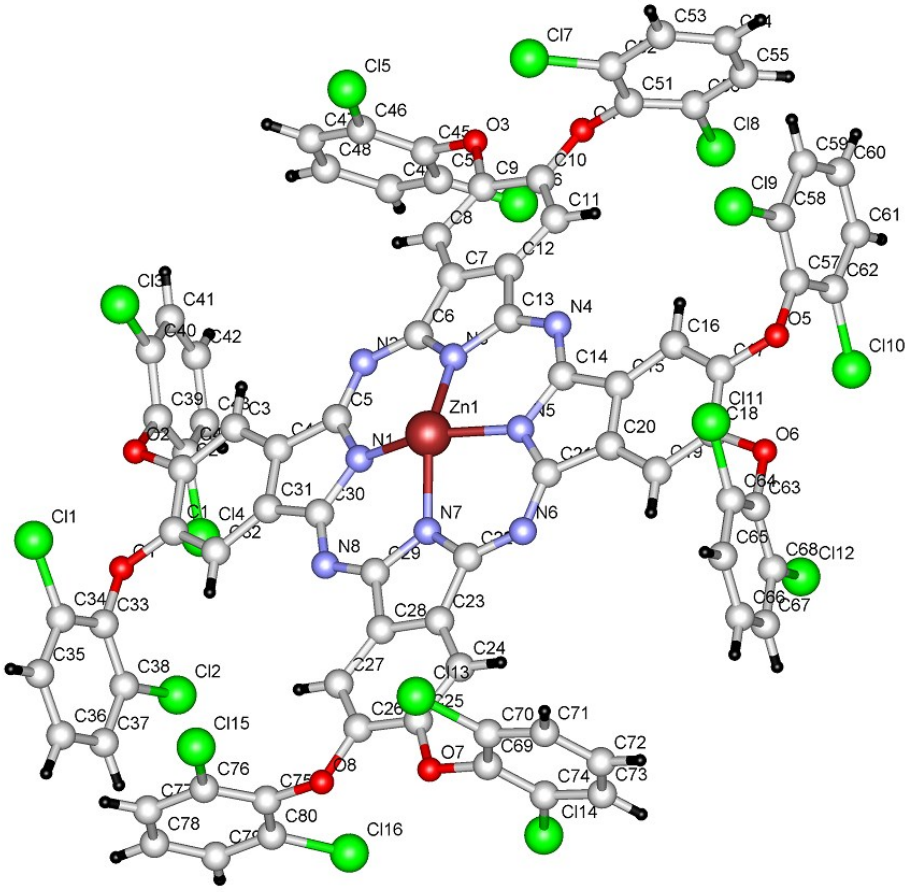


Figure S5. Ball and stick representation of the crystal structure of **Pc2Zn** showing atom labels (for clarity hydrogen atom labels are omitted and both coordinated pyridine and THF molecules are hidden)

The packing pattern of phthalocyanine molecules in the crystal network can be considered as a layer-by layer arrangement parallel to its *b*-direction (**Figure S6 B**). In each layer all **Pc2-Zns** are arranged in same manner with corordinated pyridines pointing either upward or downward direction. In the next layer too all constituent **Pc2-Zn**s have same orientation but opposite with respect to the first layer when considering the orientation of the coordinated pyridines. The third layer follows same orientation of the first layer and hence the crystal packing is an ABAB type layer-by layer arrangement. The packing diagram of **Pc2-Zn** is given in **Figure S6** and **Figure S7**. Along the *a*- and *c*- direction of this crystal all molecules in each row are oriented in same direction. All phthalocyanine and coordinated pyridine in one particular row along *b*-direction are also oriented in one direction. But there is another row of Pc molecules just near to this first row in which the pyridine molecules are coordinated from the opposite direction. This is clear from **figure S7** in which the Pc periphery and solvent molecules are hided for clarity. This arrangement of pc moieties in crystal network was resulted the above mentioned ABAB type layer-by layer propagation.

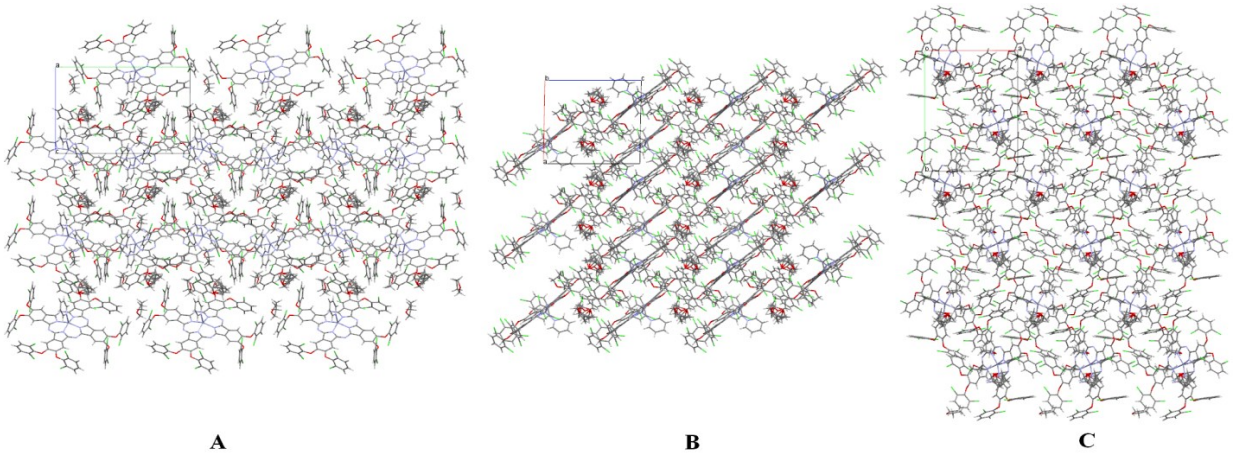


Figure S6. 3-dimensional packing pattern of **Pc2Zn** along (A) *a*-, (B) *b*- and (C) *c*- directions

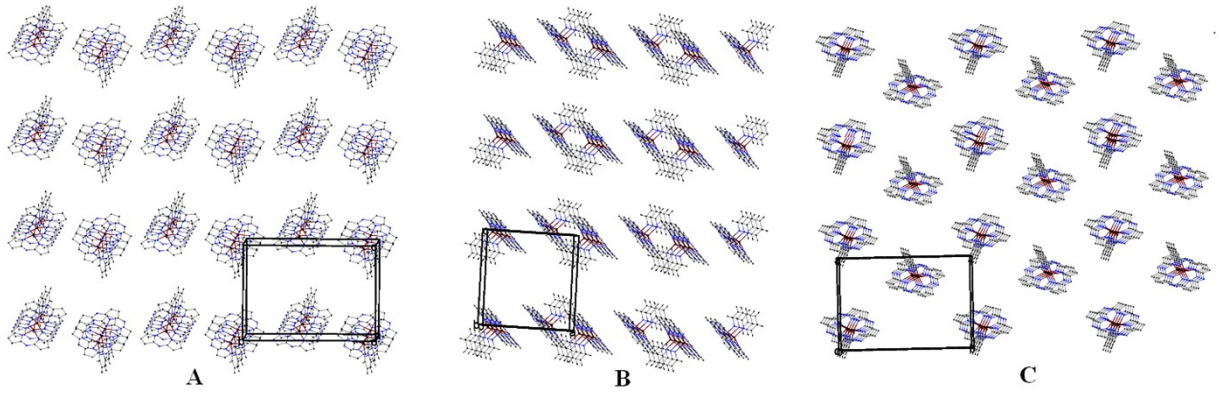


Figure S7. Packing pattern of **Pc2Zn** when viewing the Pc plane and coordinated pyridine only along (A) *a*-, (B) *b*- and (C) *c*- directions

The shortest distance (core-to core) between two Pc molecules in this crystal network is observed to be around 12.58Å which is the separation of two neighboring ZnPcs on adjacent layers. In fact, this is the separation of two oppositely oriented Pc molecules along the *b*- direction as depicted in **Figure S8**. The Pc-Pc distance of other directions are also shown in the same figure. Along *a*- direction Pc-Pc core separation in each row is found to be 14.78Å whereas along *c*- direction it is 15.34Å. At the same time, Pc-Pc distance along b- directions which possess similar pyridine orientation is observed to be 21.42Å. The Pc2-Zn moieties in crystal structure have been stabilized by several nonbonding interactions among constituent atoms (all possible short contacts in this crystal structure have also been provided in **Figure S9**. The THF molecules co-crystallised along with phthalocyanine molecules during their crystal growth is also involved in nonbonding interactions with pc moieties and hence contributed to overall stability of the crystals. At the same time, chlorine- chlorine short contact is not observed in the crystal network. The orthogonal orientation of phenoxy substituents which make the chlorine atoms direct upward and downward with respect to the pc core eliminates Cl-Cl contact among adjacent Pcs in each layer. The mutually displaced positions of phthalocyanine units between adjacent layers which prevented pc-pc π stacking caused chlorine atoms to stay apart in this case too. As a result the chlorine atoms are not much close together to make appreciable short contact in these crystals. The shortest Cl-Cl distance observed in this crystal network is 3.54Å which is greater than sum of its Van der Waals radii.

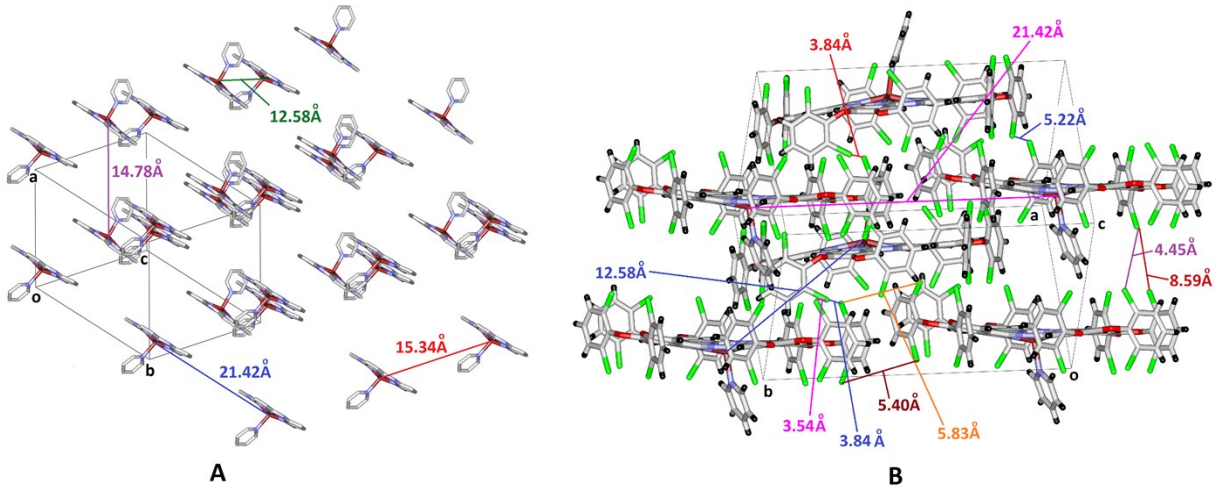


Figure S8. (**A**) Pc-Pc separations calculated from different directions. (B) Unit cell of **Pc2-Zn** showing Pc-Pc distance in each layer as well as between two layers and various Cl-Cl distances.

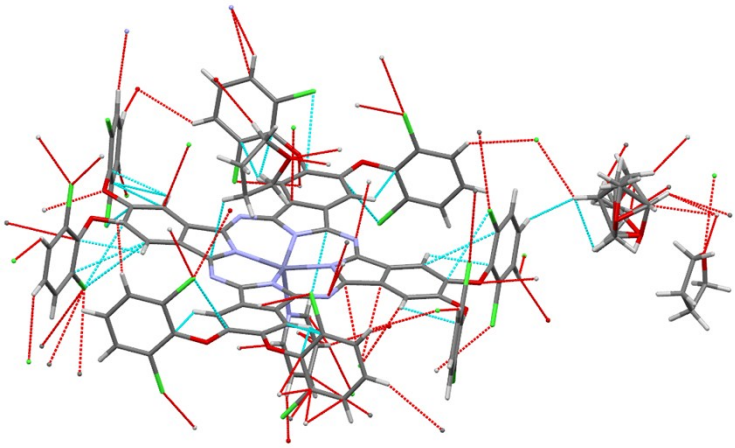


Figure S9. Possible non-bonding contacts calculated for **Pc2-Zn** in its crystal network.

Experimental

Single crystal analysis

The single crystal data collections were made on a Rigaku R-AXIS RAPID diffractometer using filtered Mo-Kα radiation. The data were collected at a temperature of -123 °C (Oxford cryosystems). The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure[2] crystallographic software package except for refinement, which was performed using SHELXL-97[3].

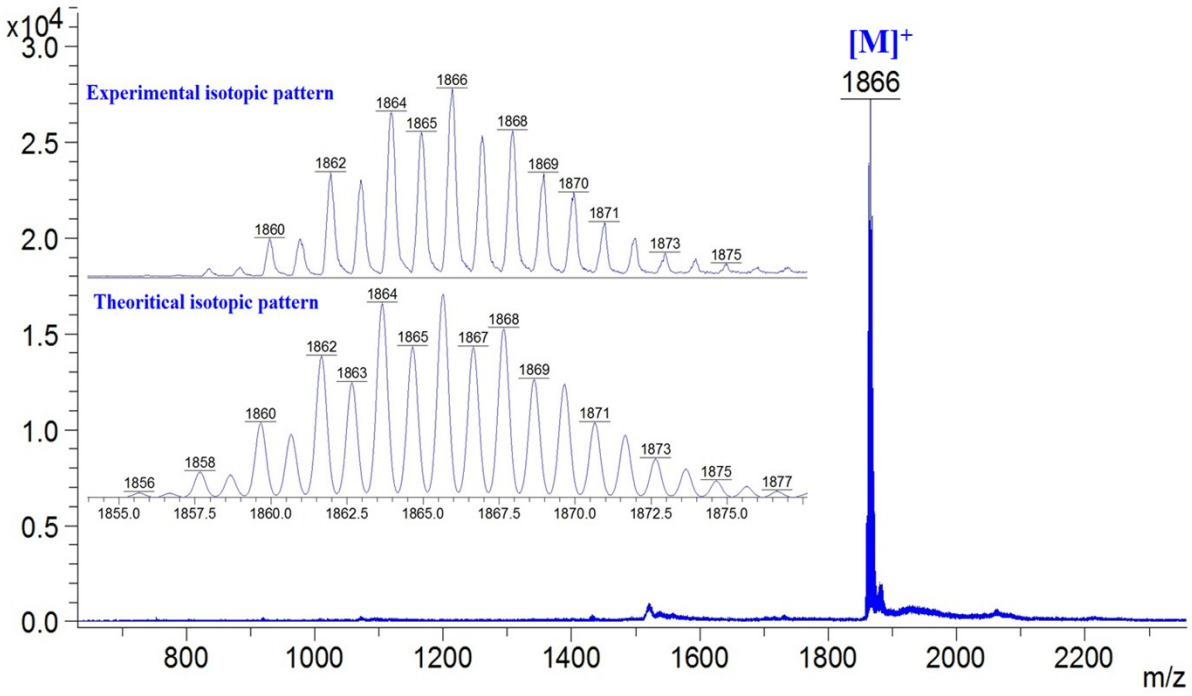


Figure S10. MALDI-TOF spectrum of **Pc2-Zn**.

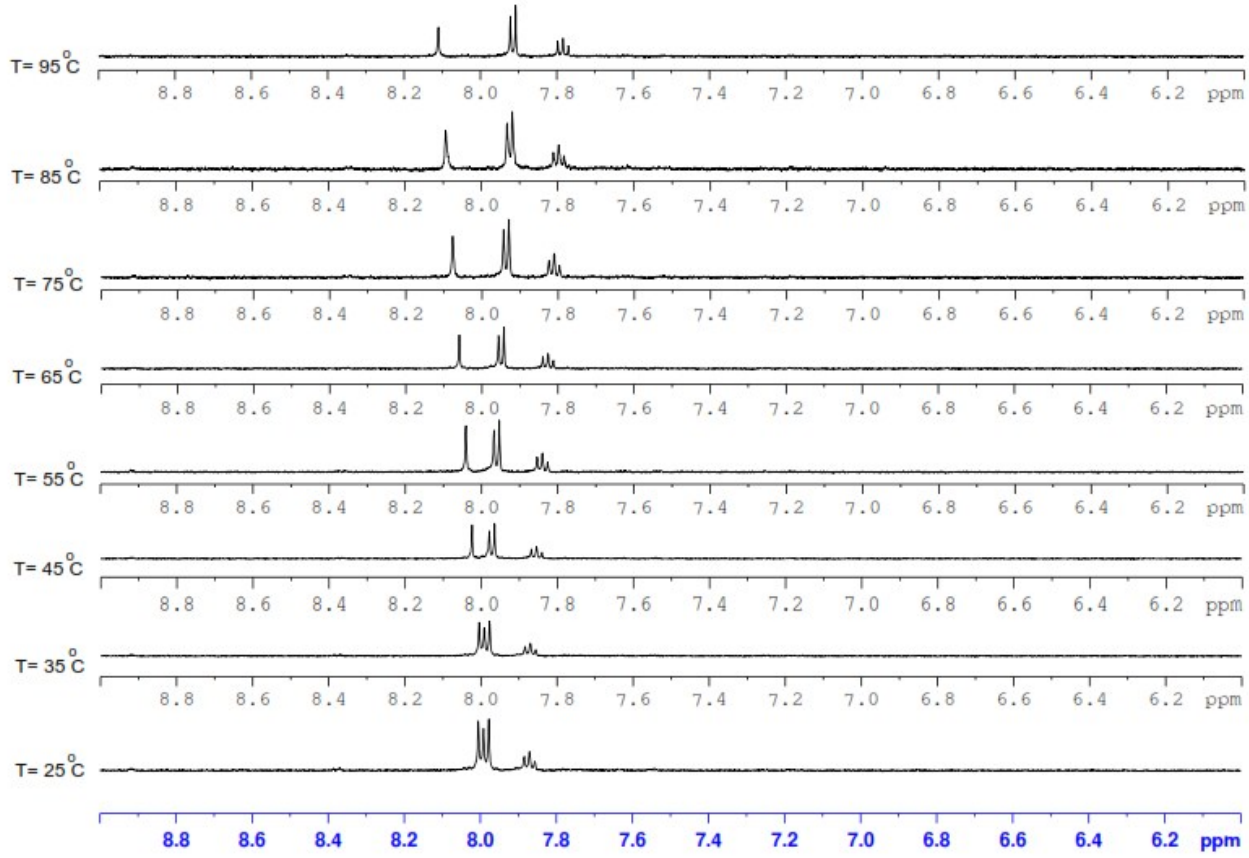
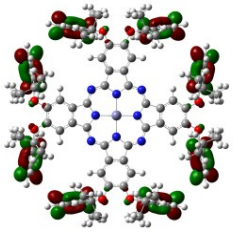
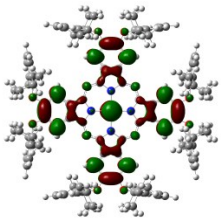
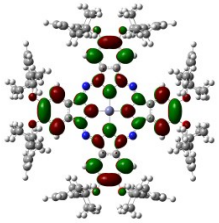
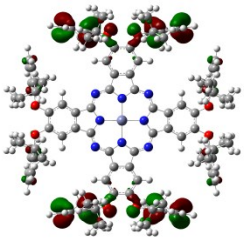
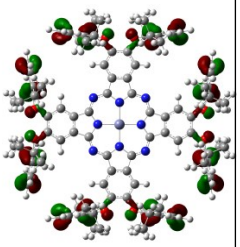
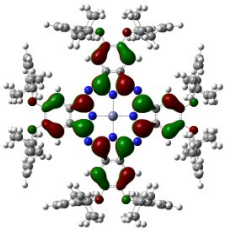
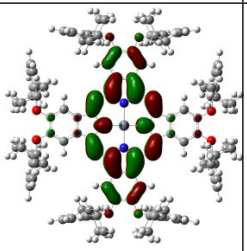
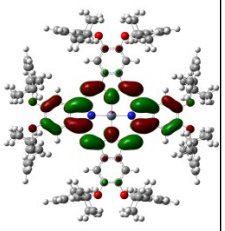
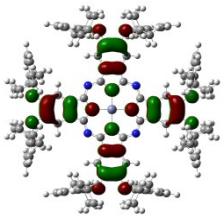
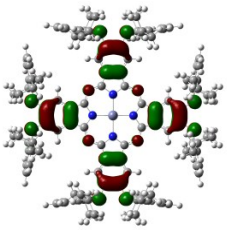
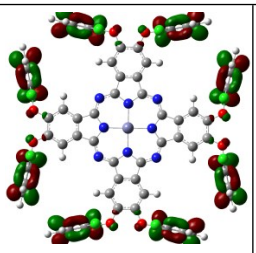
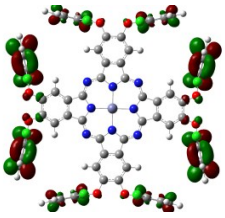
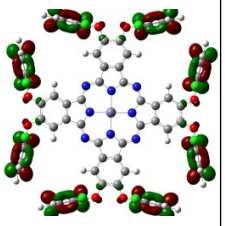
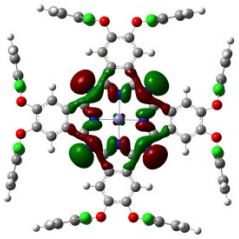
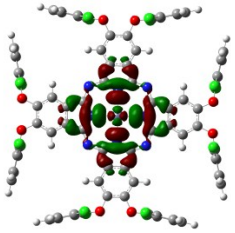
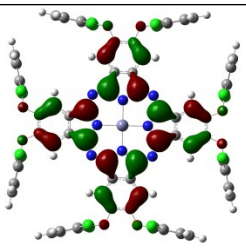
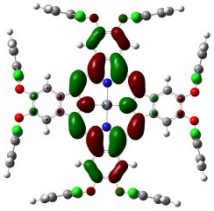
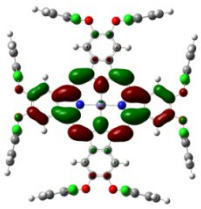
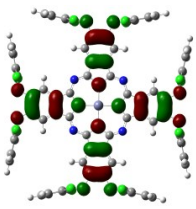
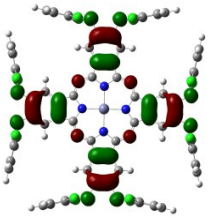


Figure S11. ^{1}H NMR -in DMSO of **Pc2Zn** -at variable temperatures (25-95°C).

				
(LUMO+10, b2g)	(LUMO+4, a2u)	(LUMO+3, b2u)	(HOMO-6, eu)	(HOMO-5, a2g)
				
(HOMO, a1u)	(LUMOs, eg)		(HOMO-1, b2u)	(HOMO-4, a2u)
Pc1-Zn				
				
(LUMO+10, b2g)	(LUMO+4, eu)	(LUMO+3, a1g)	(HOMO-6, b2g)	(HOMO-5, b_{1g})
				
(HOMO, a1u)	(LUMOs, eg)		(HOMO-1, b2u)	(HOMO-4, a_{2u})
Pc2-Zn				

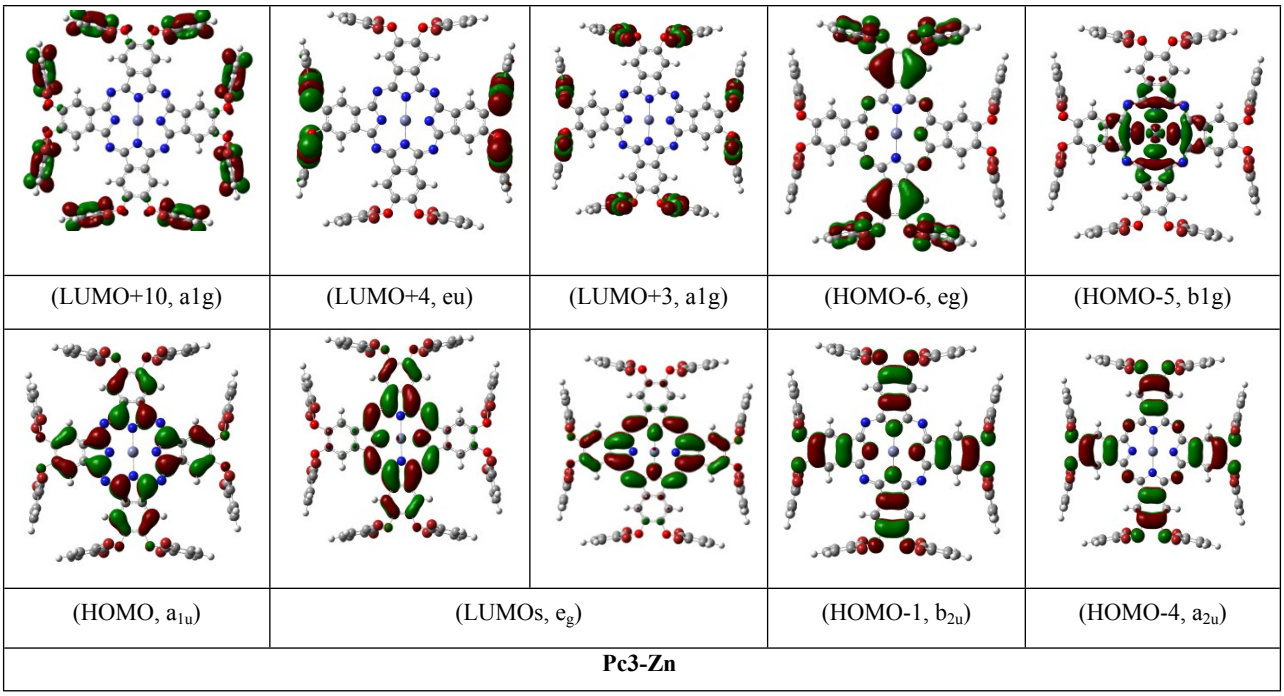


Figure S12. Molecular orbital surfaces near the HOMO and LUMO for **Pc1-Zn**, **Pc2-Zn** and **Pc3-Zn**.

Table S3. Report of the optimized geometry of **Pc1-Zn** calculated by DFT at the B3LYP/SDD level of theory (C128H144N8O8Zn)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.000000	0.000000	0.000000
2	7	0	0.000000	2.008534	0.000000
3	7	0	2.008534	0.000000	0.000000
4	7	0	0.000000	-2.008534	0.000000
5	7	0	-2.008534	0.000000	0.000000
6	6	0	-1.134355	-2.818042	0.000000
7	6	0	-0.708440	-4.220129	0.000000
8	6	0	0.708440	-4.220129	0.000000
9	6	0	1.134355	-2.818042	0.000000
10	6	0	-2.818042	1.134355	0.000000
11	6	0	-4.220129	0.708440	0.000000
12	6	0	-4.220129	-0.708440	0.000000
13	6	0	-2.818042	-1.134355	0.000000
14	6	0	1.134355	2.818042	0.000000
15	6	0	0.708440	4.220129	0.000000
16	6	0	-0.708440	4.220129	0.000000
17	6	0	-1.134355	2.818042	0.000000
18	6	0	2.818042	-1.134355	0.000000
19	6	0	4.220129	-0.708440	0.000000
20	6	0	4.220129	0.708440	0.000000
21	6	0	2.818042	1.134355	0.000000
22	6	0	-1.435324	-5.421429	0.000000
23	6	0	-0.716928	-6.625956	0.000000
24	6	0	0.716928	-6.625956	0.000000
25	6	0	1.435324	-5.421429	0.000000
26	6	0	-5.421429	1.435324	0.000000
27	6	0	-6.625956	0.716928	0.000000
28	6	0	-6.625956	-0.716928	0.000000
29	6	0	-5.421429	-1.435324	0.000000
30	6	0	1.435324	5.421429	0.000000
31	6	0	0.716928	6.625956	0.000000
32	6	0	-0.716928	6.625956	0.000000
33	6	0	-1.435324	5.421429	0.000000
34	6	0	5.421429	-1.435324	0.000000
35	6	0	6.625956	-0.716928	0.000000
36	6	0	6.625956	0.716928	0.000000
37	6	0	5.421429	1.435324	0.000000
38	7	0	2.413791	-2.413791	0.000000
39	7	0	-2.413791	-2.413791	0.000000
40	7	0	-2.413791	2.413791	0.000000
41	7	0	2.413791	2.413791	0.000000
42	1	0	-2.519594	-5.416052	0.000000
43	1	0	2.519594	-5.416052	0.000000
44	1	0	-5.416052	2.519594	0.000000

45	1	0	-5.416052	-2.519594	0.000000
46	1	0	2.519594	5.416052	0.000000
47	1	0	-2.519594	5.416052	0.000000
48	1	0	5.416052	-2.519594	0.000000
49	1	0	5.416052	2.519594	0.000000
50	8	0	-7.889342	-1.318592	0.000000
51	8	0	-7.889342	1.318592	0.000000
52	8	0	-1.318592	-7.889342	0.000000
53	8	0	1.318592	-7.889342	0.000000
54	8	0	7.889342	-1.318592	0.000000
55	8	0	7.889342	1.318592	0.000000
56	8	0	1.318592	7.889342	0.000000
57	8	0	-1.318592	7.889342	0.000000
58	6	0	2.743894	-8.007487	0.000000
59	6	0	3.400717	-8.117271	1.246388
60	6	0	3.400717	-8.117271	-1.246388
61	6	0	4.794749	-8.334403	1.219399
62	6	0	4.794749	-8.334403	-1.219399
63	6	0	5.485014	-8.438538	0.000000
64	1	0	5.342147	-8.419970	2.153037
65	1	0	5.342147	-8.419970	-2.153037
66	1	0	6.559786	-8.604344	0.000000
67	6	0	-2.743894	-8.007487	0.000000
68	6	0	-3.400717	-8.117271	1.246388
69	6	0	-3.400717	-8.117271	-1.246388
70	6	0	-4.794749	-8.334403	1.219399
71	6	0	-4.794749	-8.334403	-1.219399
72	6	0	-5.485014	-8.438538	0.000000
73	1	0	-5.342147	-8.419970	2.153037
74	1	0	-5.342147	-8.419970	-2.153037
75	1	0	-6.559786	-8.604344	0.000000
76	6	0	8.007487	-2.743894	0.000000
77	6	0	8.117271	-3.400717	1.246388
78	6	0	8.117271	-3.400717	-1.246388
79	6	0	8.334403	-4.794749	1.219399
80	6	0	8.334403	-4.794749	-1.219399
81	6	0	8.438538	-5.485014	0.000000
82	1	0	8.419970	-5.342147	2.153037
83	1	0	8.419970	-5.342147	-2.153037
84	1	0	8.604344	-6.559786	0.000000
85	6	0	8.007487	2.743894	0.000000
86	6	0	8.117271	3.400717	-1.246388
87	6	0	8.117271	3.400717	1.246388
88	6	0	8.334403	4.794749	-1.219399
89	6	0	8.334403	4.794749	1.219399
90	6	0	8.438538	5.485014	0.000000
91	1	0	8.419970	5.342147	-2.153037
92	1	0	8.419970	5.342147	2.153037
93	1	0	8.604344	6.559786	0.000000
94	6	0	-8.007487	-2.743894	0.000000
95	6	0	-8.117271	-3.400717	1.246388

96	6	0	-8.117271	-3.400717	-1.246388
97	6	0	-8.334403	-4.794749	1.219399
98	6	0	-8.334403	-4.794749	-1.219399
99	6	0	-8.438538	-5.485014	0.000000
100	1	0	-8.419970	-5.342147	2.153037
101	1	0	-8.419970	-5.342147	-2.153037
102	1	0	-8.604344	-6.559786	0.000000
103	6	0	-8.007487	2.743894	0.000000
104	6	0	-8.117271	3.400717	-1.246388
105	6	0	-8.117271	3.400717	1.246388
106	6	0	-8.334403	4.794749	-1.219399
107	6	0	-8.334403	4.794749	1.219399
108	6	0	-8.438538	5.485014	0.000000
109	1	0	-8.419970	5.342147	-2.153037
110	1	0	-8.419970	5.342147	2.153037
111	1	0	-8.604344	6.559786	0.000000
112	6	0	-2.743894	8.007487	0.000000
113	6	0	-3.400717	8.117271	-1.246388
114	6	0	-3.400717	8.117271	1.246388
115	6	0	-4.794749	8.334403	-1.219399
116	6	0	-4.794749	8.334403	1.219399
117	6	0	-5.485014	8.438538	0.000000
118	1	0	-5.342147	8.419970	-2.153037
119	1	0	-5.342147	8.419970	2.153037
120	1	0	-6.559786	8.604344	0.000000
121	6	0	2.743894	8.007487	0.000000
122	6	0	3.400717	8.117271	-1.246388
123	6	0	3.400717	8.117271	1.246388
124	6	0	4.794749	8.334403	-1.219399
125	6	0	4.794749	8.334403	1.219399
126	6	0	5.485014	8.438538	0.000000
127	1	0	5.342147	8.419970	-2.153037
128	1	0	5.342147	8.419970	2.153037
129	1	0	6.559786	8.604344	0.000000
130	6	0	8.071862	2.604501	2.553117
131	6	0	7.559506	3.421744	3.760498
132	6	0	9.474321	2.003901	2.849172
133	1	0	7.384234	1.761424	2.410652
134	1	0	6.587343	3.886657	3.551965
135	1	0	7.441697	2.763200	4.630777
136	1	0	8.264221	4.213862	4.046356
137	1	0	9.804244	1.363556	2.023884
138	1	0	10.215641	2.802441	2.988152
139	1	0	9.447227	1.399060	3.765559
140	6	0	8.071862	2.604501	-2.553117
141	6	0	9.474321	2.003901	-2.849172
142	6	0	7.559506	3.421744	-3.760498
143	1	0	7.384234	1.761424	-2.410652
144	1	0	9.804244	1.363556	-2.023884
145	1	0	9.447227	1.399060	-3.765559
146	1	0	10.215641	2.802441	-2.988152

147	1	0	6.587343	3.886657	-3.551965
148	1	0	8.264221	4.213862	-4.046356
149	1	0	7.441697	2.763200	-4.630777
150	6	0	8.071862	-2.604501	-2.553117
151	6	0	7.559506	-3.421744	-3.760498
152	6	0	9.474321	-2.003901	-2.849172
153	1	0	7.384234	-1.761424	-2.410652
154	1	0	6.587343	-3.886657	-3.551965
155	1	0	7.441697	-2.763200	-4.630777
156	1	0	8.264221	-4.213862	-4.046356
157	1	0	9.804244	-1.363556	-2.023884
158	1	0	10.215641	-2.802441	-2.988152
159	1	0	9.447227	-1.399060	-3.765559
160	6	0	8.071862	-2.604501	2.553117
161	6	0	9.474321	-2.003901	2.849172
162	6	0	7.559506	-3.421744	3.760498
163	1	0	7.384234	-1.761424	2.410652
164	1	0	9.804244	-1.363556	2.023884
165	1	0	9.447227	-1.399060	3.765559
166	1	0	10.215641	-2.802441	2.988152
167	1	0	6.587343	-3.886657	3.551965
168	1	0	8.264221	-4.213862	4.046356
169	1	0	7.441697	-2.763200	4.630777
170	6	0	2.604501	8.071862	2.553117
171	6	0	2.003901	9.474321	2.849172
172	6	0	3.421744	7.559506	3.760498
173	1	0	1.761424	7.384234	2.410652
174	1	0	1.363556	9.804244	2.023884
175	1	0	1.399060	9.447227	3.765559
176	1	0	2.802441	10.215641	2.988152
177	1	0	3.886657	6.587343	3.551965
178	1	0	4.213862	8.264221	4.046356
179	1	0	2.763200	7.441697	4.630777
180	6	0	-2.604501	8.071862	2.553117
181	6	0	-3.421744	7.559506	3.760498
182	6	0	-2.003901	9.474321	2.849172
183	1	0	-1.761424	7.384234	2.410652
184	1	0	-3.886657	6.587343	3.551965
185	1	0	-2.763200	7.441697	4.630777
186	1	0	-4.213862	8.264221	4.046356
187	1	0	-1.363556	9.804244	2.023884
188	1	0	-2.802441	10.215641	2.988152
189	1	0	-1.399060	9.447227	3.765559
190	6	0	2.604501	8.071862	-2.553117
191	6	0	3.421744	7.559506	-3.760498
192	6	0	2.003901	9.474321	-2.849172
193	1	0	1.761424	7.384234	-2.410652
194	1	0	3.886657	6.587343	-3.551965
195	1	0	2.763200	7.441697	-4.630777
196	1	0	4.213862	8.264221	-4.046356
197	1	0	1.363556	9.804244	-2.023884

198	1	0	2.802441	10.215641	-2.988152
199	1	0	1.399060	9.447227	-3.765559
200	6	0	-2.604501	8.071862	-2.553117
201	6	0	-2.003901	9.474321	-2.849172
202	6	0	-3.421744	7.559506	-3.760498
203	1	0	-1.761424	7.384234	-2.410652
204	1	0	-1.363556	9.804244	-2.023884
205	1	0	-1.399060	9.447227	-3.765559
206	1	0	-2.802441	10.215641	-2.988152
207	1	0	-3.886657	6.587343	-3.551965
208	1	0	-4.213862	8.264221	-4.046356
209	1	0	-2.763200	7.441697	-4.630777
210	6	0	-8.071862	2.604501	-2.553117
211	6	0	-7.559506	3.421744	-3.760498
212	6	0	-9.474321	2.003901	-2.849172
213	1	0	-7.384234	1.761424	-2.410652
214	1	0	-6.587343	3.886657	-3.551965
215	1	0	-7.441697	2.763200	-4.630777
216	1	0	-8.264221	4.213862	-4.046356
217	1	0	-9.804244	1.363556	-2.023884
218	1	0	-10.215641	2.802441	-2.988152
219	1	0	-9.447227	1.399060	-3.765559
220	6	0	-8.071862	-2.604501	-2.553117
221	6	0	-9.474321	-2.003901	-2.849172
222	6	0	-7.559506	-3.421744	-3.760498
223	1	0	-7.384234	-1.761424	-2.410652
224	1	0	-9.804244	-1.363556	-2.023884
225	1	0	-9.447227	-1.399060	-3.765559
226	1	0	-10.215641	-2.802441	-2.988152
227	1	0	-6.587343	-3.886657	-3.551965
228	1	0	-8.264221	-4.213862	-4.046356
229	1	0	-7.441697	-2.763200	-4.630777
230	6	0	-8.071862	2.604501	2.553117
231	6	0	-9.474321	2.003901	2.849172
232	6	0	-7.559506	3.421744	3.760498
233	1	0	-7.384234	1.761424	2.410652
234	1	0	-9.804244	1.363556	2.023884
235	1	0	-9.447227	1.399060	3.765559
236	1	0	-10.215641	2.802441	2.988152
237	1	0	-6.587343	3.886657	3.551965
238	1	0	-8.264221	4.213862	4.046356
239	1	0	-7.441697	2.763200	4.630777
240	6	0	-8.071862	-2.604501	2.553117
241	6	0	-7.559506	-3.421744	3.760498
242	6	0	-9.474321	-2.003901	2.849172
243	1	0	-7.384234	-1.761424	2.410652
244	1	0	-6.587343	-3.886657	3.551965
245	1	0	-7.441697	-2.763200	4.630777
246	1	0	-8.264221	-4.213862	4.046356
247	1	0	-9.804244	-1.363556	2.023884
248	1	0	-10.215641	-2.802441	2.988152

249	1	0	-9.447227	-1.399060	3.765559
250	6	0	2.604501	-8.071862	2.553117
251	6	0	3.421744	-7.559506	3.760498
252	6	0	2.003901	-9.474321	2.849172
253	1	0	1.761424	-7.384234	2.410652
254	1	0	3.886657	-6.587343	3.551965
255	1	0	2.763200	-7.441697	4.630777
256	1	0	4.213862	-8.264221	4.046356
257	1	0	1.363556	-9.804244	2.023884
258	1	0	2.802441	-10.215641	2.988152
259	1	0	1.399060	-9.447227	3.765559
260	6	0	-2.604501	-8.071862	2.553117
261	6	0	-2.003901	-9.474321	2.849172
262	6	0	-3.421744	-7.559506	3.760498
263	1	0	-1.761424	-7.384234	2.410652
264	1	0	-1.363556	-9.804244	2.023884
265	1	0	-1.399060	-9.447227	3.765559
266	1	0	-2.802441	-10.215641	2.988152
267	1	0	-3.886657	-6.587343	3.551965
268	1	0	-4.213862	-8.264221	4.046356
269	1	0	-2.763200	-7.441697	4.630777
270	6	0	-2.604501	-8.071862	-2.553117
271	6	0	-3.421744	-7.559506	-3.760498
272	6	0	-2.003901	-9.474321	-2.849172
273	1	0	-1.761424	-7.384234	-2.410652
274	1	0	-3.886657	-6.587343	-3.551965
275	1	0	-2.763200	-7.441697	-4.630777
276	1	0	-4.213862	-8.264221	-4.046356
277	1	0	-1.363556	-9.804244	-2.023884
278	1	0	-2.802441	-10.215641	-2.988152
279	1	0	-1.399060	-9.447227	-3.765559
280	6	0	2.604501	-8.071862	-2.553117
281	6	0	2.003901	-9.474321	-2.849172
282	6	0	3.421744	-7.559506	-3.760498
283	1	0	1.761424	-7.384234	-2.410652
284	1	0	1.363556	-9.804244	-2.023884
285	1	0	1.399060	-9.447227	-3.765559
286	1	0	2.802441	-10.215641	-2.988152
287	1	0	3.886657	-6.587343	-3.551965
288	1	0	4.213862	-8.264221	-4.046356
289	1	0	2.763200	-7.441697	-4.630777

Table S4. Report of the optimized geometry of **Pc2-Zn** calculated by DFT at the B3LYP/SDD level of theory (C80H32Cl16N8O8Zn)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.000000	0.000000	0.000000
2	7	0	0.000000	2.008401	0.000000
3	7	0	2.008401	0.000000	0.000000
4	7	0	0.000000	-2.008401	0.000000
5	7	0	-2.008401	0.000000	0.000000
6	6	0	-1.134113	-2.816759	0.000000
7	6	0	-0.708348	-4.218832	0.000000
8	6	0	0.708348	-4.218832	0.000000
9	6	0	1.134113	-2.816759	0.000000
10	6	0	-2.816759	1.134113	0.000000
11	6	0	-4.218832	0.708348	0.000000
12	6	0	-4.218832	-0.708348	0.000000
13	6	0	-2.816759	-1.134113	0.000000
14	6	0	1.134113	2.816759	0.000000
15	6	0	0.708348	4.218832	0.000000
16	6	0	-0.708348	4.218832	0.000000
17	6	0	-1.134113	2.816759	0.000000
18	6	0	2.816759	-1.134113	0.000000
19	6	0	4.218832	-0.708348	0.000000
20	6	0	4.218832	0.708348	0.000000
21	6	0	2.816759	1.134113	0.000000
22	6	0	-1.436039	-5.418792	0.000000
23	6	0	-0.713168	-6.616203	0.000000
24	6	0	0.713168	-6.616203	0.000000
25	6	0	1.436039	-5.418792	0.000000
26	6	0	-5.418792	1.436039	0.000000
27	6	0	-6.616203	0.713168	0.000000
28	6	0	-6.616203	-0.713168	0.000000
29	6	0	-5.418792	-1.436039	0.000000
30	6	0	1.436039	5.418792	0.000000
31	6	0	0.713168	6.616203	0.000000
32	6	0	-0.713168	6.616203	0.000000
33	6	0	-1.436039	5.418792	0.000000
34	6	0	5.418792	-1.436039	0.000000
35	6	0	6.616203	-0.713168	0.000000
36	6	0	6.616203	0.713168	0.000000
37	6	0	5.418792	1.436039	0.000000
38	7	0	2.413340	-2.413340	0.000000
39	7	0	-2.413340	-2.413340	0.000000
40	7	0	-2.413340	2.413340	0.000000
41	7	0	2.413340	2.413340	0.000000
42	1	0	-2.520430	-5.409551	0.000000
43	1	0	2.520430	-5.409551	0.000000
44	1	0	-5.409551	2.520430	0.000000

45	1	0	-5.409551	-2.520430	0.000000
46	1	0	2.520430	5.409551	0.000000
47	1	0	-2.520430	5.409551	0.000000
48	1	0	5.409551	-2.520430	0.000000
49	1	0	5.409551	2.520430	0.000000
50	8	0	-7.890079	-1.305321	0.000000
51	8	0	-7.890079	1.305321	0.000000
52	8	0	-1.305321	-7.890079	0.000000
53	8	0	1.305321	-7.890079	0.000000
54	8	0	7.890079	-1.305321	0.000000
55	8	0	7.890079	1.305321	0.000000
56	8	0	1.305321	7.890079	0.000000
57	8	0	-1.305321	7.890079	0.000000
58	6	0	2.691469	-8.042350	0.000000
59	6	0	3.400344	-8.195084	1.208514
60	6	0	3.400344	-8.195084	-1.208514
61	6	0	4.771091	-8.488351	1.221790
62	6	0	4.771091	-8.488351	-1.221790
63	6	0	5.453274	-8.635996	0.000000
64	1	0	5.288332	-8.604619	2.168404
65	1	0	5.288332	-8.604619	-2.168404
66	1	0	6.513007	-8.873783	0.000000
67	6	0	-2.691469	-8.042350	0.000000
68	6	0	-3.400344	-8.195084	1.208514
69	6	0	-3.400344	-8.195084	-1.208514
70	6	0	-4.771091	-8.488351	1.221790
71	6	0	-4.771091	-8.488351	-1.221790
72	6	0	-5.453274	-8.635996	0.000000
73	1	0	-5.288332	-8.604619	2.168404
74	1	0	-5.288332	-8.604619	-2.168404
75	1	0	-6.513007	-8.873783	0.000000
76	6	0	8.042350	-2.691469	0.000000
77	6	0	8.195084	-3.400344	1.208514
78	6	0	8.195084	-3.400344	-1.208514
79	6	0	8.488351	-4.771091	1.221790
80	6	0	8.488351	-4.771091	-1.221790
81	6	0	8.635996	-5.453274	0.000000
82	1	0	8.604619	-5.288332	2.168404
83	1	0	8.604619	-5.288332	-2.168404
84	1	0	8.873783	-6.513007	0.000000
85	6	0	8.042350	2.691469	0.000000
86	6	0	8.195084	3.400344	-1.208514
87	6	0	8.195084	3.400344	1.208514
88	6	0	8.488351	4.771091	-1.221790
89	6	0	8.488351	4.771091	1.221790
90	6	0	8.635996	5.453274	0.000000
91	1	0	8.604619	5.288332	-2.168404
92	1	0	8.604619	5.288332	2.168404
93	1	0	8.873783	6.513007	0.000000
94	6	0	-8.042350	-2.691469	0.000000
95	6	0	-8.195084	-3.400344	1.208514

96	6	0	-8.195084	-3.400344	-1.208514
97	6	0	-8.488351	-4.771091	1.221790
98	6	0	-8.488351	-4.771091	-1.221790
99	6	0	-8.635996	-5.453274	0.000000
100	1	0	-8.604619	-5.288332	2.168404
101	1	0	-8.604619	-5.288332	-2.168404
102	1	0	-8.873783	-6.513007	0.000000
103	6	0	-8.042350	2.691469	0.000000
104	6	0	-8.195084	3.400344	-1.208514
105	6	0	-8.195084	3.400344	1.208514
106	6	0	-8.488351	4.771091	-1.221790
107	6	0	-8.488351	4.771091	1.221790
108	6	0	-8.635996	5.453274	0.000000
109	1	0	-8.604619	5.288332	-2.168404
110	1	0	-8.604619	5.288332	2.168404
111	1	0	-8.873783	6.513007	0.000000
112	6	0	-2.691469	8.042350	0.000000
113	6	0	-3.400344	8.195084	-1.208514
114	6	0	-3.400344	8.195084	1.208514
115	6	0	-4.771091	8.488351	-1.221790
116	6	0	-4.771091	8.488351	1.221790
117	6	0	-5.453274	8.635996	0.000000
118	1	0	-5.288332	8.604619	-2.168404
119	1	0	-5.288332	8.604619	2.168404
120	1	0	-6.513007	8.873783	0.000000
121	6	0	2.691469	8.042350	0.000000
122	6	0	3.400344	8.195084	-1.208514
123	6	0	3.400344	8.195084	1.208514
124	6	0	4.771091	8.488351	-1.221790
125	6	0	4.771091	8.488351	1.221790
126	6	0	5.453274	8.635996	0.000000
127	1	0	5.288332	8.604619	-2.168404
128	1	0	5.288332	8.604619	2.168404
129	1	0	6.513007	8.873783	0.000000
130	17	0	-2.515949	-8.017151	-2.777945
131	17	0	-2.515949	-8.017151	2.777945
132	17	0	2.515949	-8.017151	-2.777945
133	17	0	2.515949	-8.017151	2.777945
134	17	0	-8.017151	-2.515949	-2.777945
135	17	0	-8.017151	-2.515949	2.777945
136	17	0	8.017151	-2.515949	-2.777945
137	17	0	8.017151	-2.515949	2.777945
138	17	0	8.017151	2.515949	-2.777945
139	17	0	8.017151	2.515949	2.777945
140	17	0	-8.017151	2.515949	-2.777945
141	17	0	-8.017151	2.515949	2.777945
142	17	0	-2.515949	8.017151	2.777945
143	17	0	-2.515949	8.017151	-2.777945
144	17	0	2.515949	8.017151	2.777945
145	17	0	2.515949	8.017151	-2.777945

Table S5. Report of the optimized geometry of **Pc3-Zn** calculated by DFT at the B3LYP/SDD level of theory (C80H32Br16N8O8Zn)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	30	0	0.000000	0.000000	0.000000
2	7	0	0.000000	2.008353	0.000000
3	7	0	2.008353	0.000000	0.000000
4	7	0	0.000000	-2.008353	0.000000
5	7	0	-2.008353	0.000000	0.000000
6	6	0	-1.134153	-2.816799	0.000000
7	6	0	-0.708345	-4.218895	0.000000
8	6	0	0.708345	-4.218895	0.000000
9	6	0	1.134153	-2.816799	0.000000
10	6	0	-2.816799	1.134153	0.000000
11	6	0	-4.218895	0.708345	0.000000
12	6	0	-4.218895	-0.708345	0.000000
13	6	0	-2.816799	-1.134153	0.000000
14	6	0	1.134153	2.816799	0.000000
15	6	0	0.708345	4.218895	0.000000
16	6	0	-0.708345	4.218895	0.000000
17	6	0	-1.134153	2.816799	0.000000
18	6	0	2.816799	-1.134153	0.000000
19	6	0	4.218895	-0.708345	0.000000
20	6	0	4.218895	0.708345	0.000000
21	6	0	2.816799	1.134153	0.000000
22	6	0	-1.436087	-5.418728	0.000000
23	6	0	-0.713342	-6.616628	0.000000
24	6	0	0.713342	-6.616628	0.000000
25	6	0	1.436087	-5.418728	0.000000
26	6	0	-5.418728	1.436087	0.000000
27	6	0	-6.616628	0.713342	0.000000
28	6	0	-6.616628	-0.713342	0.000000
29	6	0	-5.418728	-1.436087	0.000000
30	6	0	1.436087	5.418728	0.000000
31	6	0	0.713342	6.616628	0.000000
32	6	0	-0.713342	6.616628	0.000000
33	6	0	-1.436087	5.418728	0.000000
34	6	0	5.418728	-1.436087	0.000000
35	6	0	6.616628	-0.713342	0.000000
36	6	0	6.616628	0.713342	0.000000
37	6	0	5.418728	1.436087	0.000000
38	7	0	2.413338	-2.413338	0.000000
39	7	0	-2.413338	-2.413338	0.000000
40	7	0	-2.413338	2.413338	0.000000
41	7	0	2.413338	2.413338	0.000000
42	1	0	-2.520525	-5.409425	0.000000
43	1	0	2.520525	-5.409425	0.000000
44	1	0	-5.409425	2.520525	0.000000
45	1	0	-5.409425	-2.520525	0.000000

46	1	0	2.520525	5.409425	0.000000
47	1	0	-2.520525	5.409425	0.000000
48	1	0	5.409425	-2.520525	0.000000
49	1	0	5.409425	2.520525	0.000000
50	8	0	-7.890322	-1.306824	0.000000
51	8	0	-7.890322	1.306824	0.000000
52	8	0	-1.306824	-7.890322	0.000000
53	8	0	1.306824	-7.890322	0.000000
54	8	0	7.890322	-1.306824	0.000000
55	8	0	7.890322	1.306824	0.000000
56	8	0	1.306824	7.890322	0.000000
57	8	0	-1.306824	7.890322	0.000000
58	6	0	2.694298	-8.040836	0.000000
59	6	0	3.400161	-8.189202	1.213574
60	6	0	3.400161	-8.189202	-1.213574
61	6	0	4.775183	-8.471239	1.221143
62	6	0	4.775183	-8.471239	-1.221143
63	6	0	5.459088	-8.611188	0.000000
64	1	0	5.298311	-8.586312	2.164652
65	1	0	5.298311	-8.586312	-2.164652
66	1	0	6.520875	-8.839957	0.000000
67	6	0	-2.694298	-8.040836	0.000000
68	6	0	-3.400161	-8.189202	1.213574
69	6	0	-3.400161	-8.189202	-1.213574
70	6	0	-4.775183	-8.471239	1.221143
71	6	0	-4.775183	-8.471239	-1.221143
72	6	0	-5.459088	-8.611188	0.000000
73	1	0	-5.298311	-8.586312	2.164652
74	1	0	-5.298311	-8.586312	-2.164652
75	1	0	-6.520875	-8.839957	0.000000
76	6	0	8.040836	-2.694298	0.000000
77	6	0	8.189202	-3.400161	1.213574
78	6	0	8.189202	-3.400161	-1.213574
79	6	0	8.471239	-4.775183	1.221143
80	6	0	8.471239	-4.775183	-1.221143
81	6	0	8.611188	-5.459088	0.000000
82	1	0	8.586312	-5.298311	2.164652
83	1	0	8.586312	-5.298311	-2.164652
84	1	0	8.839957	-6.520875	0.000000
85	6	0	8.040836	2.694298	0.000000
86	6	0	8.189202	3.400161	-1.213574
87	6	0	8.189202	3.400161	1.213574
88	6	0	8.471239	4.775183	-1.221143
89	6	0	8.471239	4.775183	1.221143
90	6	0	8.611188	5.459088	0.000000
91	1	0	8.586312	5.298311	-2.164652
92	1	0	8.586312	5.298311	2.164652
93	1	0	8.839957	6.520875	0.000000
94	6	0	-8.040836	-2.694298	0.000000
95	6	0	-8.189202	-3.400161	1.213574
96	6	0	-8.189202	-3.400161	-1.213574

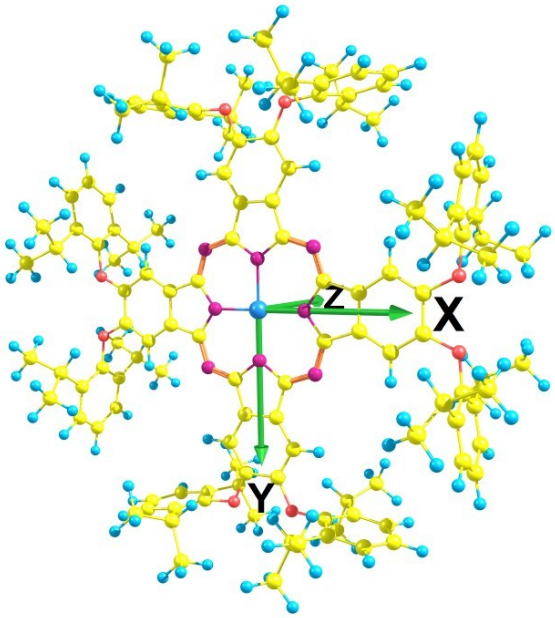
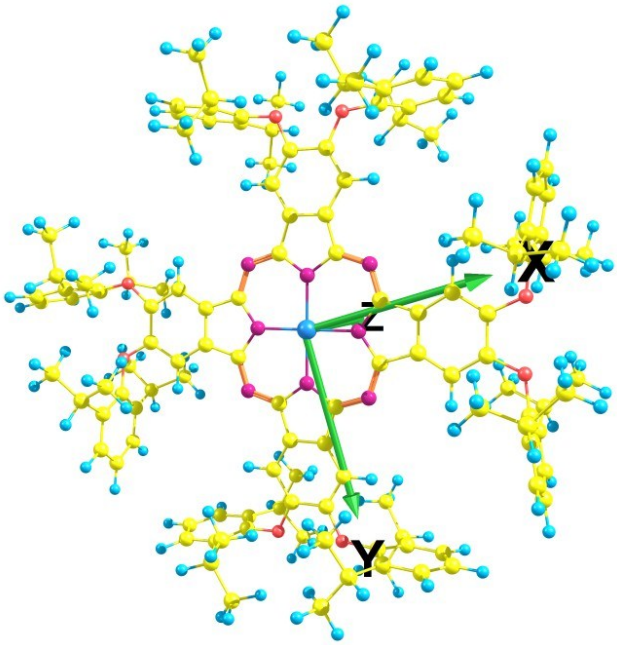
97	6	0	-8.471239	-4.775183	1.221143
98	6	0	-8.471239	-4.775183	-1.221143
99	6	0	-8.611188	-5.459088	0.000000
100	1	0	-8.586312	-5.298311	2.164652
101	1	0	-8.586312	-5.298311	-2.164652
102	1	0	-8.839957	-6.520875	0.000000
103	6	0	-8.040836	2.694298	0.000000
104	6	0	-8.189202	3.400161	-1.213574
105	6	0	-8.189202	3.400161	1.213574
106	6	0	-8.471239	4.775183	-1.221143
107	6	0	-8.471239	4.775183	1.221143
108	6	0	-8.611188	5.459088	0.000000
109	1	0	-8.586312	5.298311	-2.164652
110	1	0	-8.586312	5.298311	2.164652
111	1	0	-8.839957	6.520875	0.000000
112	6	0	-2.694298	8.040836	0.000000
113	6	0	-3.400161	8.189202	-1.213574
114	6	0	-3.400161	8.189202	1.213574
115	6	0	-4.775183	8.471239	-1.221143
116	6	0	-4.775183	8.471239	1.221143
117	6	0	-5.459088	8.611188	0.000000
118	1	0	-5.298311	8.586312	-2.164652
119	1	0	-5.298311	8.586312	2.164652
120	1	0	-6.520875	8.839957	0.000000
121	6	0	2.694298	8.040836	0.000000
122	6	0	3.400161	8.189202	-1.213574
123	6	0	3.400161	8.189202	1.213574
124	6	0	4.775183	8.471239	-1.221143
125	6	0	4.775183	8.471239	1.221143
126	6	0	5.459088	8.611188	0.000000
127	1	0	5.298311	8.586312	-2.164652
128	1	0	5.298311	8.586312	2.164652
129	1	0	6.520875	8.839957	0.000000
130	35	0	-2.450395	-8.024207	-2.905585
131	35	0	-2.450395	-8.024207	2.905585
132	35	0	2.450395	-8.024207	-2.905585
133	35	0	2.450395	-8.024207	2.905585
134	35	0	-8.024207	-2.450395	-2.905585
135	35	0	-8.024207	-2.450395	2.905585
136	35	0	8.024207	-2.450395	-2.905585
137	35	0	8.024207	-2.450395	2.905585
138	35	0	8.024207	2.450395	-2.905585
139	35	0	8.024207	2.450395	2.905585
140	35	0	-8.024207	2.450395	-2.905585
141	35	0	-8.024207	2.450395	2.905585
142	35	0	-2.450395	8.024207	2.905585
143	35	0	-2.450395	8.024207	-2.905585
144	35	0	2.450395	8.024207	2.905585
145	35	0	2.450395	8.024207	-2.905585

Table S6. Comparison analysis between theoretical and experimental parameters based on X-ray diffraction of **Pc2-Zn** calculated at B3LYP/SDD.

Parameter	D_{4h}	Experimental
Zn1-N1	2.008	2.019
Zn1-N5	2.008	2.019
Zn1-N3	2.008	2.029
Zn1-N7	2.008	2.046
Cl2-C38	1.8102	1.727
Cl4-C44	1.8102	1.735
Cl1-C34	1.8102	1.731
Cl3-C40	1.8102	1.722
Cl6-C50	1.8102	1.731
Cl8-C56	1.8102	1.748
Cl5-C46	1.8102	1.741
Cl7-C52	1.8102	1.726
Cl10-C62	1.8102	1.732
Cl12-C68	1.8102	1.722
Cl9-C58	1.8102	1.719
Cl11-C64	1.8102	1.727
Cl16-C80	1.8102	1.719
Cl14-C74	1.8102	1.731
Cl13-C70	1.8102	1.738
Cl15-C76	1.8102	1.730
N1-Zn1-N3	90.000	87.580
N1-Zn1-N7	90.000	86.950
N3-Zn1-N5	90.000	87.970
N5-Zn1-N7	90.000	86.920
C2-O2-C39	121.200	116.230
C10-O4-C51	121.200	120.030
C18-O6-C63	121.200	116.530
C26-O8-C75	121.200	118.930
C1-O1-C33	121.200	117.430
C9-O3-C45	121.200	118.130
C17-O5-C57	121.200	117.230
C25-O7-C69	121.200	116.930

Table S7. Relative energies of the target compounds and number of negative frequencies calculated at B3LYP/SDD.

	ΔE (KJ/mol - D_{4h})	Nu. Of imaginary frequency (D_{4h})	ΔE(KJ/mol - Nosymm)	No. Of imaginary frequency
Pc1-Zn	-16358182.69	8	-16358181.88	0
Pc2-Zn	-30710027.75	5	-30710027.36	0
Pc3-Zn	-11940781.14	5	-11940780.99	3

D_{4h}	**Nosymm**
	
Pc1-Zn	

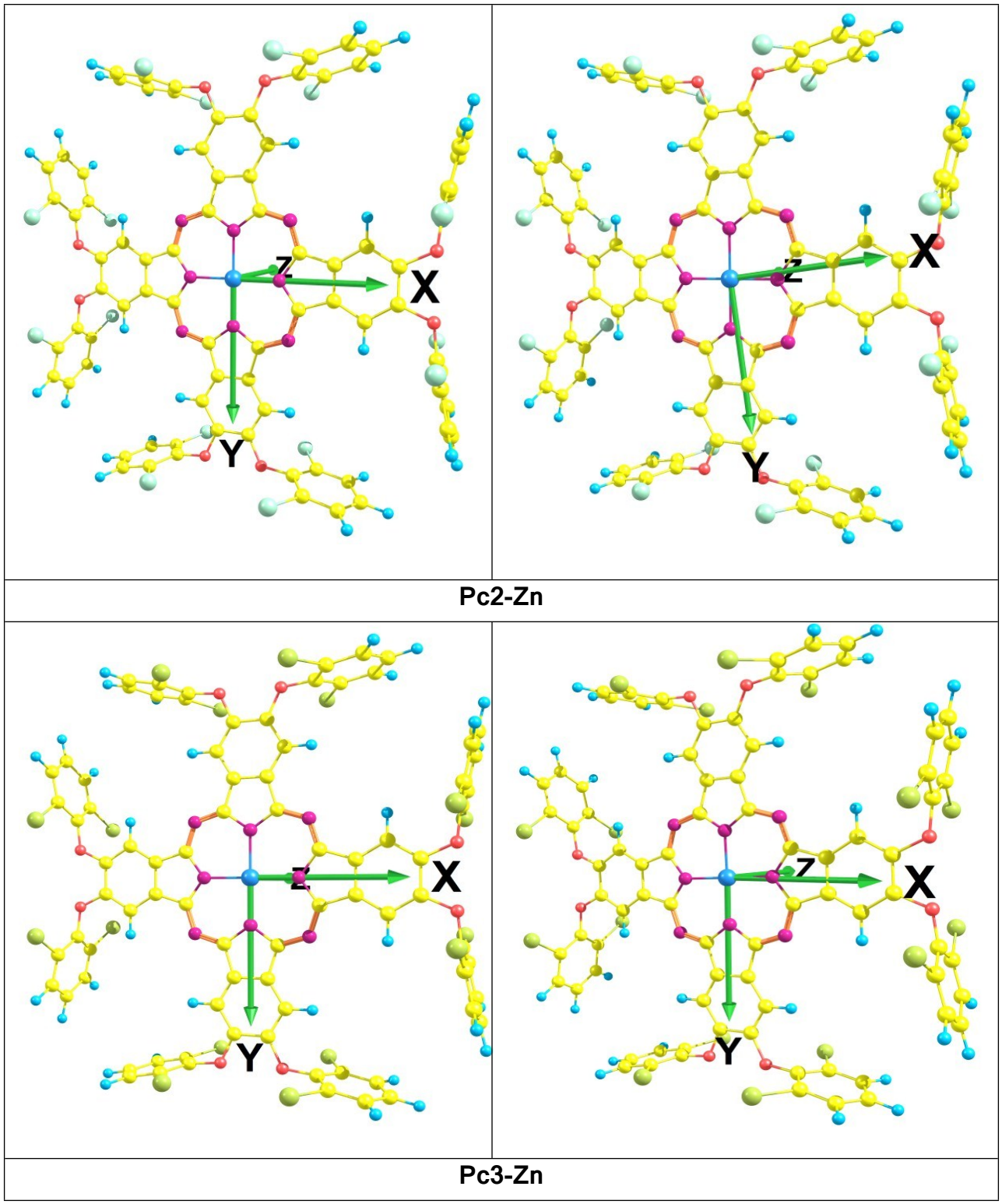


Figure S13. Optimized geometry of **Pc1-Zn**, **Pc2-Zn** and **Pc3-Zn** without symmetry constraint, the arrows represents the X-Y and Z direction.

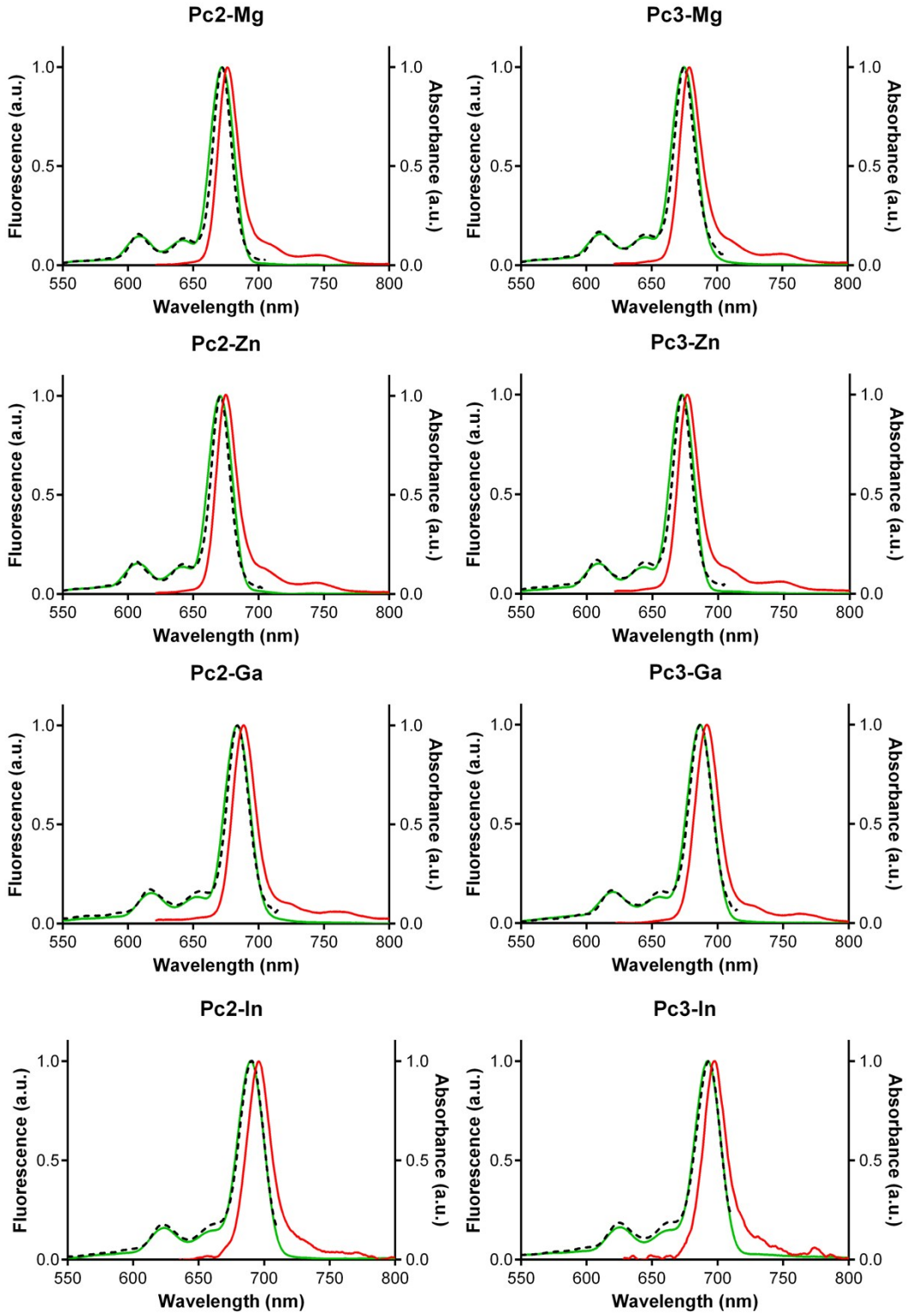


Figure S14. Normalized absorption (green), emission (red, λ_{exc} = 610 nm) and excitation (black dashed, λ_{em} = 720 nm) spectra of studied Pcs in THF.

References

(1) SIR2008: M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna (2007)

(2) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2010). Tokyo 196-8666, Japan.

(3) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.