Extremely large cavity assembled by self-interlocking of distorted biconcave porphyrins

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In all drawings of the X-ray structure, whole molecules are shown by symmetry expansion when the molecules occupy special positions. Therefore, the molecular ratios in the figures are not necessarily identical with the molecular compositions of the crystals. In the cases that the PLATON SQUEEZE program was applied, only the Ortep drawing obtained by these results are shown. The Ortep drawings are created by Ortep-3 program and the packing views are created by Mercury program. In the case of free base porphyrin **3**, pyrrolic hydrogen atoms are placed at the all pyrrole moietires with a half occupancy. Bond lengths, angles, and torsion angles are shown in the separated CIF files. The crystallographic data for the individual crystals are summarised in Table S1. The X-ray measurements were performed by Rigaku Raxis-IV (IP) or Rigaku AFC7R-Mercury CCD. The reflection data were created by CrystalClear and processed by CrystalStructure. The structures were refined by teXsan 1.11 or CrystalStructure 3.5.1-3.6.0, in which Shelx-97 programs were installed.

X-ray structure of 5,10,15,20-Tetraphenyl-2,3;7,8;12,13;17,18-tetrakis(9,10-dihydro-9,10-anthraceno)porphyrinato zinc (16)

The single crystals were obtained by slow evaporation of the solvent from a toluene solution. The crystal used for X-ray analysis contained 7 molecules of solvent toluene in the unit cell. As the solvent molecules were not properly modeled, the structure was obtained without the solvent molecules by several cycles of Shelxl-97 and PLATON SQUEEZE refinements

X-ray data for TPTAP-Zn·7PhMe

Empirical Formula	$C_{149}H_{116}N_4Zn$
Formula Weight	2027.96
Crystal Colour	red
Habit	block
Crystal Dimensions	0.55 x 0.20 x 0.20 mm
Crystal System	triclinic
Lattice Type	Primitive
No. of Reflections Used for UnitCell Determination	
(2θ range)	11247 (6.0 - 55.0˚)
Lattice Parameters	*a* = 10.263(1) Å
	b = 16.066(2) Å
	c = 16.779(2)
	α = 82.544(5)˚
	β = 85.022(6)˚
	γ = 80.666(6)˚
	V = 2700.8(5) Å^3
Space Group	*P-1* (#2)
Z value	1
D_{calc}	1.247 g/cm^3
F_{000}	1068.00
μ(MoKα)	2.86 cm^{-1}
Diffractometer	MERCURY
Radiation	MoKα (λ = 0.71070 Å) graphite monochromated
Take-off Angle	2.8˚
Detector Aperture	2.0 - 2.5 mm horizontal
Voltage, Current	50 kV, 100 mA
Temperature	-100.0 °C
Scan Type	ω
$2\theta_{max}$	55.0˚

No. of Reflections Measured	
	Total: 27419
	Unique: 11968 (R_{int} = 0.030)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.8586 -0.9450)
Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F^2
	Shelxl-97
	PLATON SQUEEZE
Function Minimized	Σ w (Fo^2 - Fc^2)^2
Least Squares Weights	
w = 1/ [σ^2 (Fo^2) + (0.1093 · P)^2 + 0.0000 · P]	
where P = (Max(Fo^2,0) + 2Fc^2)/3	
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All)	11968
No. Variables	476
Refl./Param. Ratio	25.14
R (All)	0.055
R1 (I>2.00σ(I))	0.048
wR2 (All)	0.152
Goodness of Fit Indicator	1.001
Max Shift/Error	0.000
Max. peak	0.32 e$^-$/Å^3
Min. peak	-0.32 e$^-$/Å^3

2.

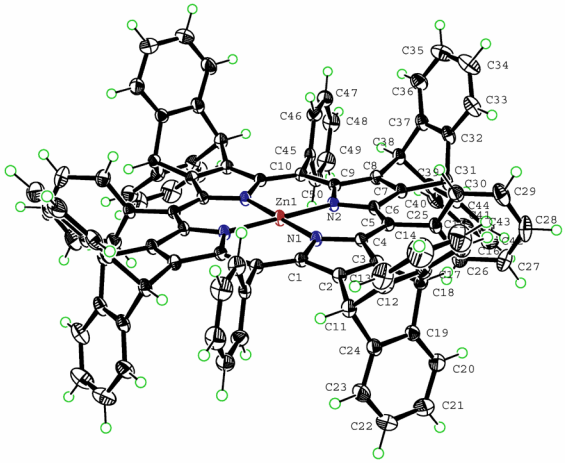

Figure S1. Ortep drawing of **16**·7PhMe (the refined structure is **16**)

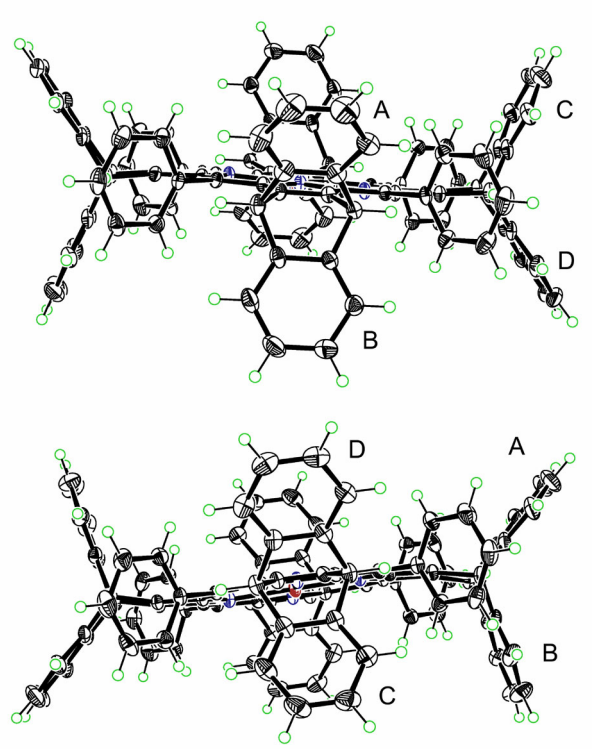

Figure S2. Ortep side views of TPTAP-Zn. The angles toward the porphyrin mean plane are as follows:

Tilting angle of pyrrole 1	3.95(5)˚
Tilting angle of pyrrole 2	2.92(5)˚
Benzene moiety A	45.05(5)˚
Benzene moiety B	77.70(5)˚
Benzene moiety C	69.92(5)˚
Benzene moiety B	52.44(5)˚
5-Phenyl	82.35(5)˚
10-Phenyl	89.54(5)˚

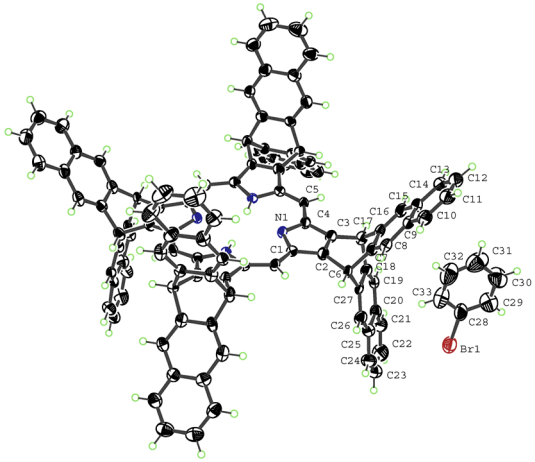

Figure S3. Ortep drawing of **12**·9PhBr (the refined structure is **12**·4PhBr)

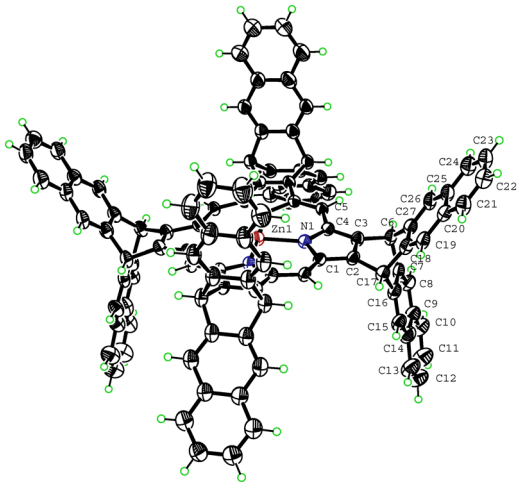

Figure S4. Ortep drawing of **13**·10PhCl (the refined structure is **13**)

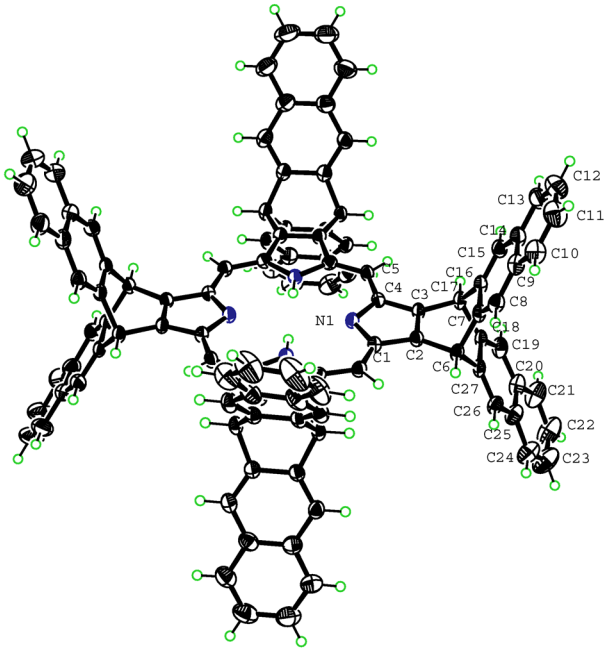

Figure S5. Ortep drawing of **12**·12PhH (the refined structure is **12**)

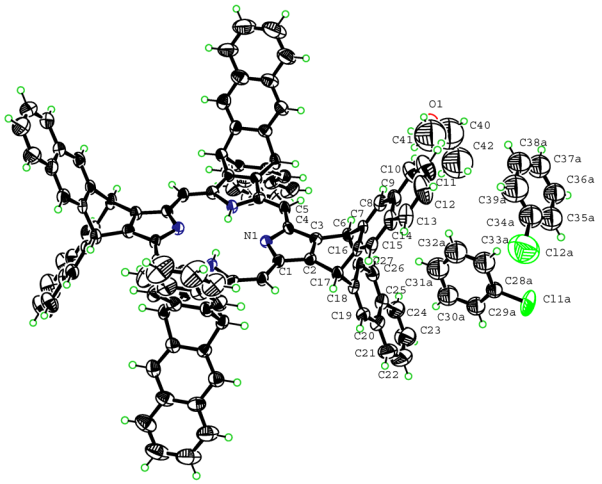

Figure S6. Ortep drawing of **12**·8PhCl·4*i*-PrOH

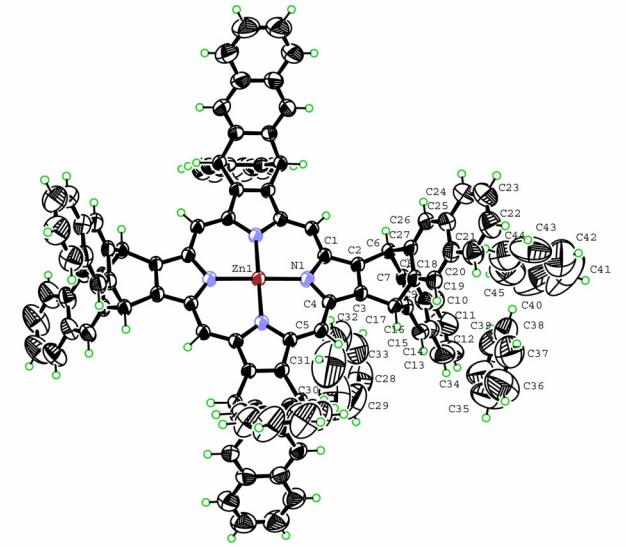

Figure S7. Ortep drawing of **13**·12PhH

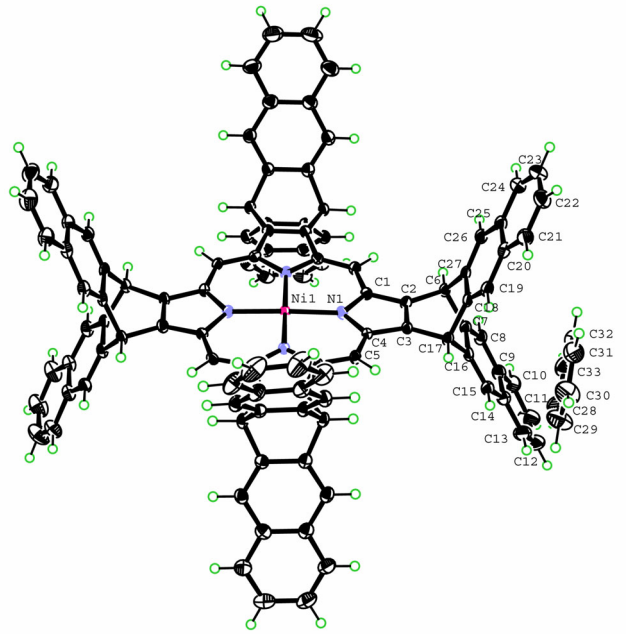

Figure S8. Ortep drawing of **14**·12PhH (the refined structure is **14**·4PhH)

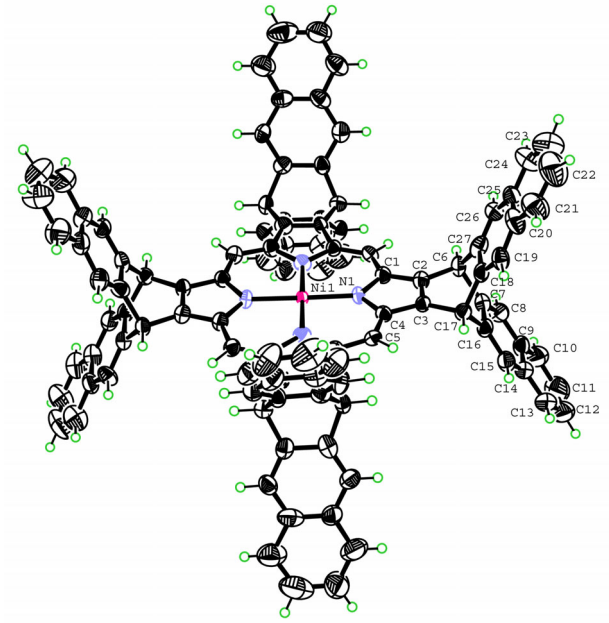

Figure S9. Ortep drawing of **14**·8PhCl·4*i*-PrOH (the refined structure is **14**)

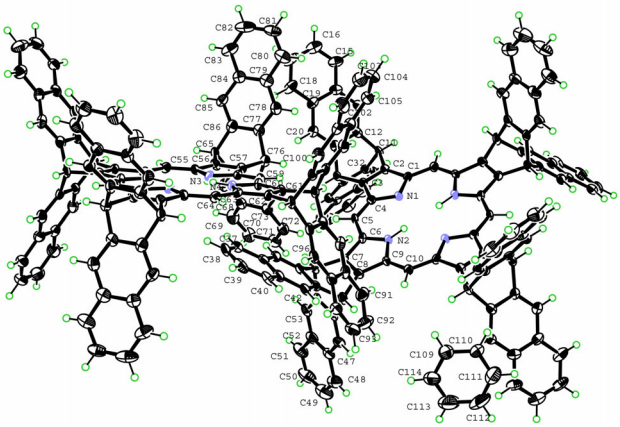

Figure S10. Ortep drawing of **12**·2PhH·7CH_2Cl_2 (the refined structure is **12**·PhH)

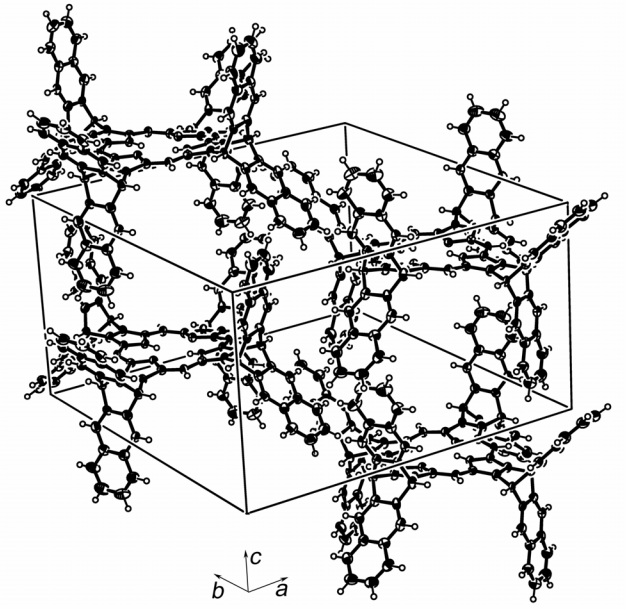

Figure S11. Packing diagram of **12**·9PhBr (the refined structure is **12**)

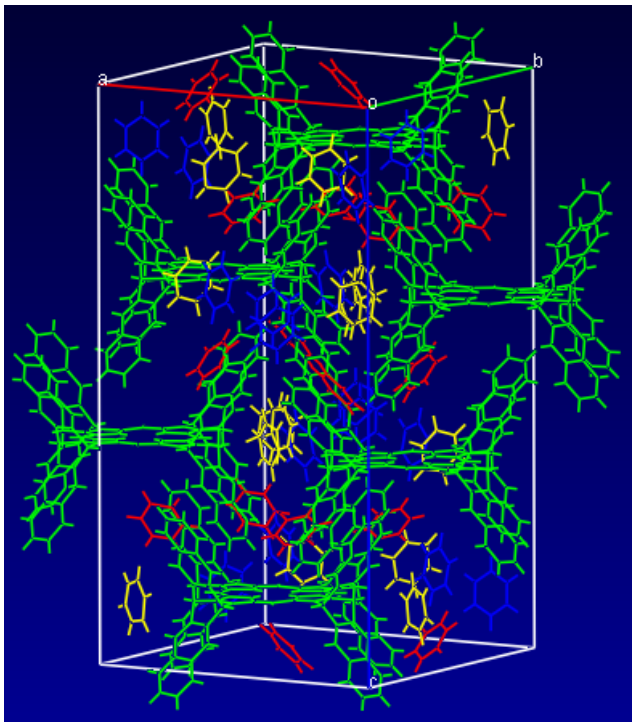

Figure S12. Packing diagram of **12**·12PhH. Green: **12** and Red, Blue and Yellow: PhH.

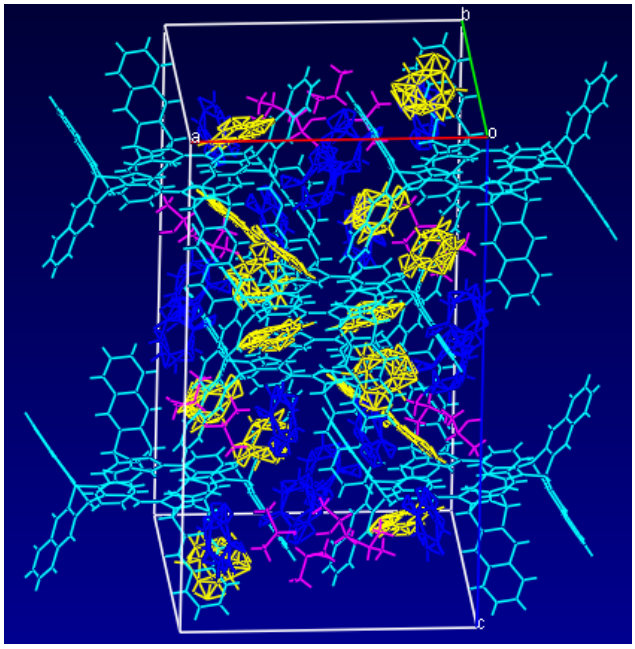

Figure S13. Packing diagram of **12**·8PhCl·4*i*-PrOH. Light blue: **12**; Blue and Yellow: disordered PhCl; and Purple: *i*-PrOH around -4 symmetric position.

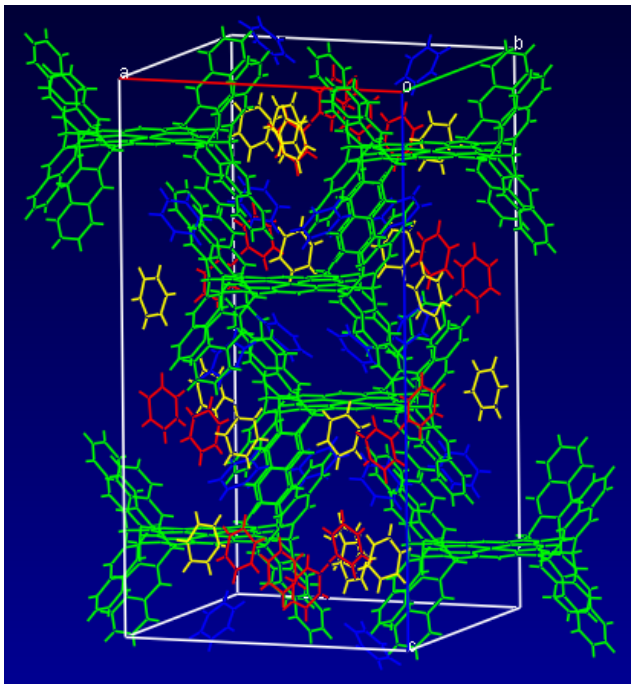

Figure S14. Packing diagram of **13**·12PhH. Green: **13** and Red, Blue and Yellow: PhH.

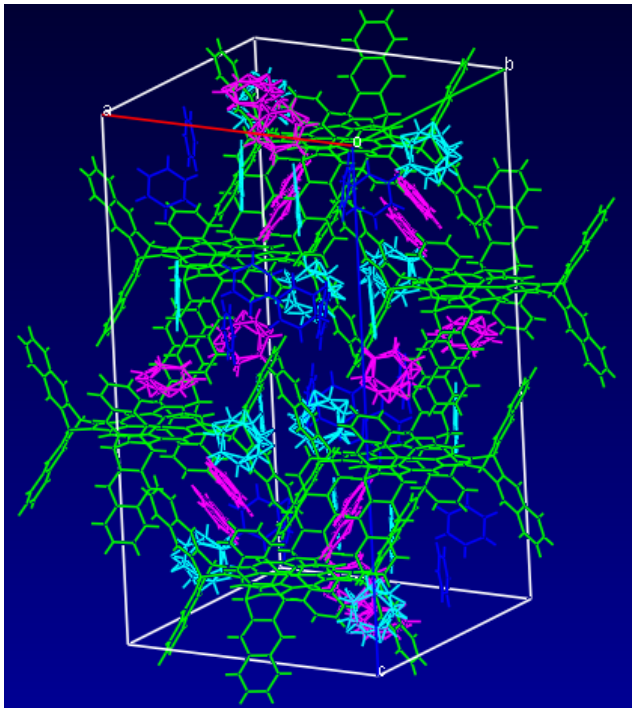

Figure S15. Packing diagram of **14**·12PhH. Green: **14**; Blue: PhH refined in the PLATON SQUEEZE and Shelxl-97 refinement; and Purple and Yellow: disordered PhH.