ELECTRONIC SUPPLEMENTARY INFORMATION

Control of local structures and photophysical properties of zinc porphyrin-based supramolecular assemblies structurally organized by regioselective ligand coordination

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Synthetic procedures of porphyrin nanocrystals

General information. All reactions involving air- and moisture-sensitive reagents were performed under nitrogen atmosphere in oven-dried or flame-dried glassware. A magnetic stirrer was used in all cases. Thin-layer chromatography (TLC) was carried out using silica gel plates with a fluorescent indicator (Sorbent Technologies) and UV as the detection method. High- and low-resolution mass spectra were collected at a commercial facility. NMR spectra were acquired on a JEOL ECX-400, AL-400, or ALPHA-400 spectrometer, using the solvent peak as the reference standard, with chemical shifts given in parts per million. MALDI-TOF mass spectra were recorded on Bruker Ultra frex.

ZnTCPP was synthesized based on the previously reported synthetic procedure¹ with modification. A typical scheme is as follows.

Scheme S1 A synthesis of ZnTCPP



Synthesis of 5,10,15,20-tetrakis(4-methoxycarbonyl)phenyl)porphyrin (H2TMeCPP).

H₂TCPP (0.19 mmol) and K₂CO₃ (1.9 mmol) were dissolved in dimethylformamide (50 mL), and iodomethane (1.9 mmol) was added to the solution. Then, the reaction mixture was stirred for 12 h at 140 °C. After cooling the mixture to room temperature, the solution was poured into water. Then, the organic layer was extracted with ethyl acetate, washed with H₂O. The collected organic layer was washed with aqueous NaHCO₃ and water, dried over Na₂SO₄, and evaporated. Finally, by silica gel chromatography with only chloroform as eluent, H₂TMeCPP of purple solid was obtained. 158 mg (0.18 mmol; 95%). ¹H NMR (400MHz, CDCl₃): δ (ppm): 8.82 (s, 8H), 8.45 (d, *J* = 8.0 Hz, 8H), 8.30 (d, *J* = 8.0 Hz, 8H), 4.11 (s, 12H), -2.82 (s, 2H).

Synthesis of 5,10,15,20-tetrakis(4-methoxycarbonyl)phenyl)porphinato-zinc (II) (ZnTMeCPP).

H₂TMeCPP (434.0 mg, 0.51 mmol) was dissolved in dry CH₂Cl₂ (40 mL). A solution of Zn(OAc)₂ (38.2 mg, 0.51 mmol) in dry MeOH (10 mL) was added to the solution of H₂TMeCPP, and the reaction mixture was stirred for 12 h at 120 °C. After solvent evaporation, the dried residue was dissolved in CH₂Cl₂. Then, the organic solution was washed with saturated aqueous NaHCO₃ solution and water, dried Na₂SO₄, and evaporated. Finally, by silica gel chromatography with only dichloromethane as eluent, ZnTMeCPP of purple solid was obtained. 398 mg (0.437 mmol; 86%). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm): 8.92 (s, 8H), 8.45 (d, *J* = 8.0 Hz, 8H), 8.30 (d, *J* = 8.0 Hz, 8H), 4.12 (s, 12H).

Synthesis of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinato-zinc(II) (ZnTCPP).

ZnTMeCPP (0.44 mmol) and KOH (8.74 mmol) were dissolved in THF (50 mL). The solution was stirred at 85 °C for 12 h. After distilling the solution, the residue was dissolved in chloroform. Then, aqueous 1N HCl solution was added dropwise onto the solution. The resultant precipitate of ZnTCPP of purple solid was collected by filtration, and washed with water and chloroform. 306 mg (0.36 mmol; 82%). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm): 13.2 (br, 4H), 8.80 (s, 8H), 8.37 (d, *J* = 7.2 Hz, 8H), 8.31 (d, *J* = 7.2 Hz, 8H).



Fig. S1 Steady-state absorption spectrum of porphyrin crystals. In this preparation, freebase porphyrin, 2, 2'-bipyridine and $Zn(NO_3)_2 \cdot 6H_2O$ were added in the solution at once and stirring at 80 °C for 3 h. This is an additional experiment without the first step in solvothermal technique.



Fig. S2 TEM images of (A) ZnPNC-ref and (B) H₂PNC-ref (adapted from ref. 2).



Fig. S3 X-ray diffraction patterns of (a) *m*-cPBC (b) ZnPNC-ref as prepared, (c) simulated pattern from the single crystal of PPF-1 and (d) simulated pattern from the single crystal of starting material (ZnTCPP). The simulated patterns from the single crystal structures of PPF-1 and ZnTCPP were adapted from ref. 3 and ref. 4, respectively.



Fig. S4 Steady-state absorption spectral changes of ZnTMeCPP with different concentrations of DABCO in (A) ca. 400-500 nm (Soret band) and (B) ca. 500-700 nm (Q bands) regions. The isosbestic points are 431 nm (Soret band) and 562 nm (Q bands), respectively. (C) Steady-state fluorescence spectral changes of ZnTMeCPP with different concentrations of DABCO. Excitation wavelength is 562 nm. (D) Scatchard plot^{5, 6} at 432 nm by the titration of 2.5 μ M ZnTMeCPP with different concentrations of DABCO (0–4.9 mM). The association constant was estimated to be 2.4 × 10³ M⁻¹. All measurements were carried out in DMF.



Fig. S5 (A) Steady-state absorption and (B) emission spectra of (a) ZnPNC-ref and (b) ZnTCPP monomer. The absorption spectra of ZnTCPP monomer were carried out in DMF ([ZnTCPP] = 2.5 μ M). Emission spectra were measured by excitation source at 555 nm. The Stokes shifts of *n*-cPBC, ZnPNC-ref and ZnTCPP monomer were determined to be 330, 190 and 390 cm⁻¹ (The absorption and fluorescence spectra of *n*-cPBC are shown in Fig. 5).



Fig. S6 Cyclic voltammograms of (A) ZnTCPP, (B) DABCO and (C) BPY in DMF with 0.1 M ^{*n*}Bu₄NPF₆ at 100 mV/s as a scan rate using Pt working electrode, Pt wire counter electrode, and SCE (saturated KCl) reference electrode.



Fig. S7 Phosphorescence emission (red line) and excitation (blue line) spectra of ZnTMeCPP in deaerated diethyl ether/ethanol/toluene (2/1/1, v/v/v) solvent at 77 K. The excitation wavelength is 425 nm in emission measurement and monitored emission wavelength is 773 nm in excitation measurement. ZnTMeCPP was used to determine the energy of excited triplet state of zinc porphyrins because of the limited solubility of ZnTCPP.



Fig. S8 (A) Nano-second transient absorption spectra of ZnTMeCPP in (a) absent and (b) present of DABCO. (B) Time profieles of ZnTMeCPP in (a) absent and (b) present of DABCO. [ZnTMeCPP] = 2.5 μ M and [DABCO] = 1.0 mM in Ar-saturated DMF. Excitation wavelength is 532 nm (ca. 0.41 mJ/pulse).



Fig. S9 Fluorescence lifetimes of (a) *n*-cPBC, (b) ZnPNC-ref and (c) ZnTCPP monomer monitored at 610 nm. The measurements were carried out in DMF. The excitation wavelength is 404 nm. The lifetimes were determined to be 0.77 ns (*n*-cPBC), 1.9 ns (ZnPNC-ref) and 2.1 ns (ZnTCPP monomer) following mono- and double-exponential function described in Experimental Section.



Fig. S10 (A) Fluorescence lifetime measurements of ZnTMeCPP with different concentrations of DABCO in DMF monitored at 610 nm. (B) Concentration dependency on absorbance at 432 nm and quenching properties of excited singlet states of ZnTMeCPP based on the results of Fig. S5 [ZnTMeCPP] = 2.5μ M, [DABCO] = 0-4.9 mM.



Fig. S11 (A) Picosecond transient absorption spectra of *m*-cPDC and (B) Time profiles at 400 and 455 nm. Excitation wavelength is 532 nm.



Fig. S12 Nanosecond transient absorption spectra of (A) *m*-cPDC, (B) *n*-cPBC and (C) ZnPNC-ref. Excitation wavelength is 532 nm (ca. 2.0 mJ/pulse). All measurements were carried out in DMF.



Fig. S13 (A) Nano-second transient absorption spectra of H_2 TMeCPP at 1.0 μ s and 14 μ s and (B) time profieles at 460 nm. The measurement were performed in Ar-saturated DMF.



Fig. S14 The fluorescence spectral changes of (A) *n*-uPDC, (B) *n*-cPBC, (C) H₂PNC-ref and (D) fluorescence decay profiles of (d) ZnPNC-ref by addition of BQ in DMF (see: Table 3).



Fig. S15 Dependence of $(I_0 - I_{obs})^{-1}$ on the reciprocal concentrations of BQ. (A) ZnPNC-ref and (B) H₂PNC-ref.

A. Crystal Data of *m*-cPDC

Empirical Formula	C ₆₀ H ₂₄ N ₈ O ₈ Zn ₃
Formula Weight	1181.04
Crystal Color, Habit	purple, platelet
Crystal Dimensions	$0.240 \times 0.240 \times 0.010 \text{ mm}$
Crystal System	tetragonal
Lattice Type	I-centered
Lattice Parameters	a = 16.679(3) Å c = 17.674(3) Å V = 4917(2) Å ³
Space Group	I4/mmm (#139)
Z value	2
D _{calc}	0.798 g/cm ³
F000	1188.00
m(MoKa)	7.609 cm ⁻¹
R-factor (%)	8.89

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation Voltage, Current	MoKa (l = 0.71075 Å) 50kV, 24mA
Temperature	-170.0°C
Detector Aperture	280 × 256 mm
Data Images	192 exposures
ω oscillation Range (c=45.0, f=0.0)	130.0 - 190.0°
Exposure Rate	45.0 sec./ °
ω oscillation Range (c=45.0, f=180.0)	0.0 - 162.0°
Exposure Rate	45.0 sec./ °
ω oscillation Range (c=45.0, f=90.0)	0.0 - 162.0°
Exposure Rate	45.0 sec./ °
Detector Position	127.40 mm
Pixel Size	0.100 mm
2θ _{max}	50.7°
No. of Reflections Measured	Total: 34462 Unique: 1312 (R _{int} = 0.1258)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.320 - 0.992)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F ²
Function Minimized	$S \le (Fo^2 - Fc^2)^2$
Least Squares Weights	w = 1/ [$s^{2}(Fo^{2}) + (0.1536 \cdot P)^{2} + 8.9878 \cdot P$] where P = (Max(Fo ² ,0) + 2Fc ²)/3
2q _{max} cutoff	50.7°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	1312
No. Variables	75
Reflection/Parameter Ratio	17.49
Residuals: R1 (I>2.00s(I))	0.0889
Residuals: R (All reflections)	0.0976
Residuals: wR2 (All reflections)	0.2511
Goodness of Fit Indicator	1.140
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	2.28 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.68 e ⁻ /Å ³

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