Supplementary Information for

Intramolecular Strong Electronic Coupling in a Discretely *H*-Aggregated Phthalocyanine Dimer Connected with a Rigid Linker

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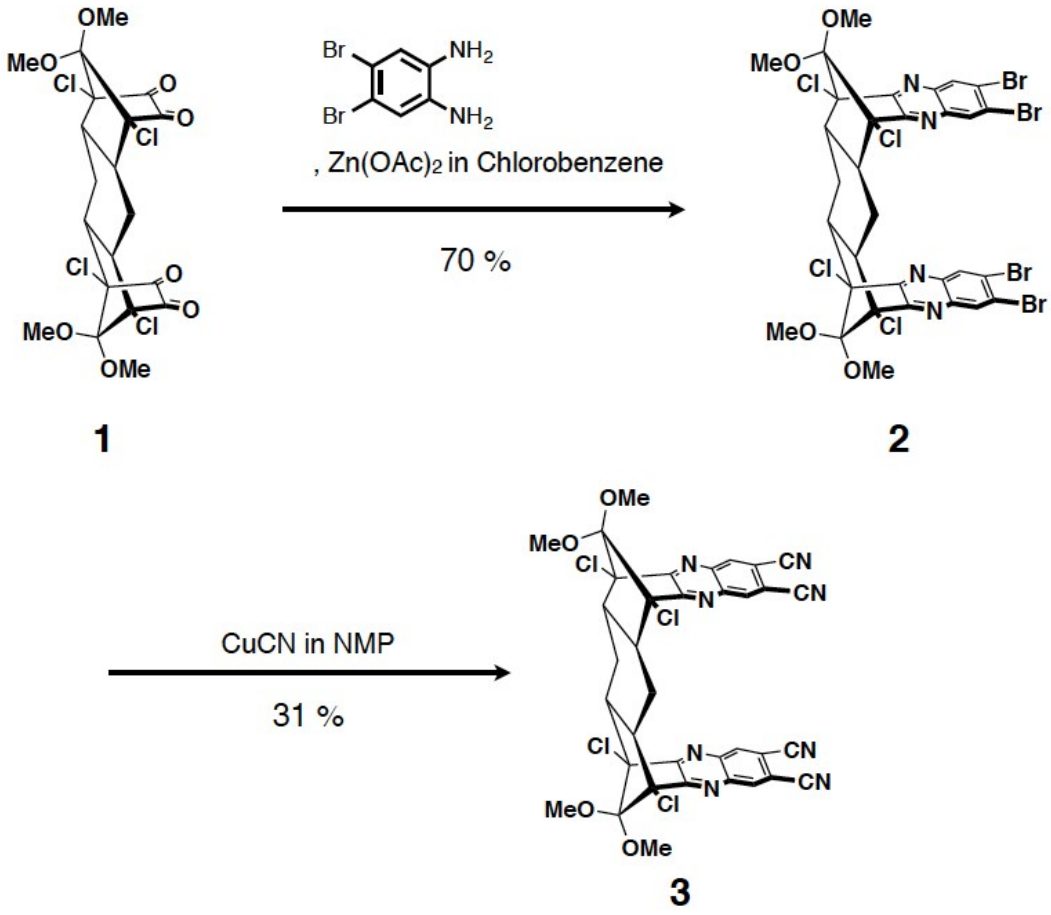
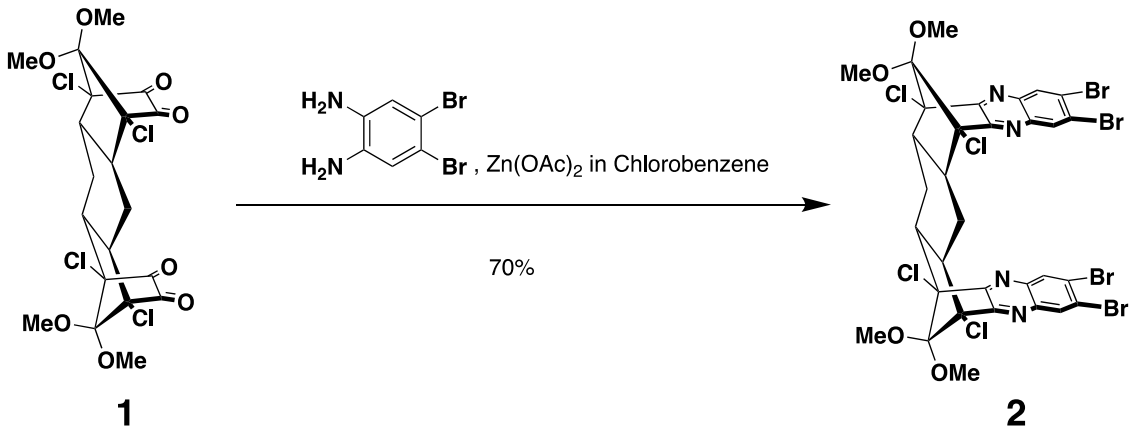
General Methods.

Synthetic procedures were carried out under dry nitrogen atmosphere, unless otherwise specified. All reagents and solvents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. Bis-α-diketone **1**[1], 1,2-di-*n*-octylbenzene[2], and octa-*t*-butylphthalocyanine[3] were synthesized according to the reported procedures. ^{1}H, and ^{13}C spectra were recorded on a JEOL JNM-ECS400 (400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer at a constant temperature of 298 K. Tetramethylsilane (TMS) was used as an internal reference for ^{1}H and ^{13}C-NMR measurements in $CDCl_3$. Elemental analyses were performed on a Yanaco MT-6 analyzer. Silica gel column chromatographies and thin-layer (TLC) chromatography were performed using Merck silica gel 60 and Merck silica gel 60 (F254) TLC plates, respectively. GPC was performed using a JAI LC-9204 equipped with JAIGEL 1H-40/2H-40 columns. ESI mass spectrometry was performed with a Waters LCT-Premier XE Spectrometer controlled using Masslynx software. MALDI-TOF mass spectrometry was performed with a Bruker Ultraflex III. The absorption spectra were recorded with a Hitachi U-4100 spectrophotometer in organic solvent at 20 ± 0.1 °C in 1.0 cm quartz cells.



Scheme S1. Synthesis of *syn*-bis-dicyanoquinoxaline **3**.

Synthesis of 2.



1 **2**

To a solution containing **1** (0.51 g, 0.96 mmol) and 1,2-diamino-4,5-dibromobenzene (1.2 g, 4.5 mmol) in chlorobenzene (25 mL) was added $Zn(OAc)_2$ (72 mg, 0.39 mmol). The reaction mixture was stirred at 140 °C for 47 hrs. The solvent was evaporated to give brown solid (1.7 g). The crude products was preabsorbed onto silica gel, and then purified by silica gel column chromatography (4 cm ϕ × 12 cm, hexane : EtOAc : CH_2Cl_2 = 1 : 0 : 3 – 0 : 0 : 1 – 0 : 1 : 0) to afford **2** (0.67 g, 0.68 mmol, 70%) as a colorless solid. Unreacted 1,2-diamino-4,5-dibromobenzene (0.79 g, 3.0 mmol) was recovered. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.14 (s, 4H), 3.71 (s, 6H), 3.31 (s, 6H), 2.92 – 2.84 (m, 4H), 1.98 – 1.94 (m, 2H), -1.12 – -1.22 (m, 2H).

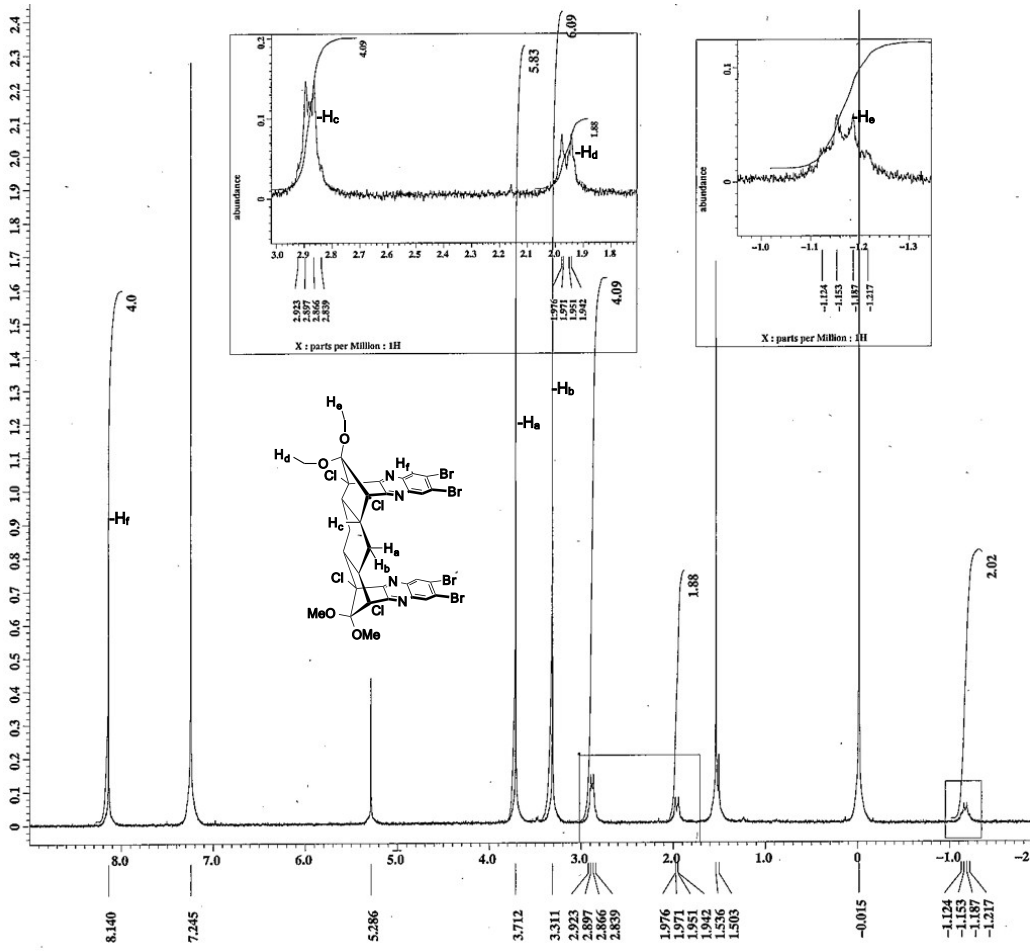
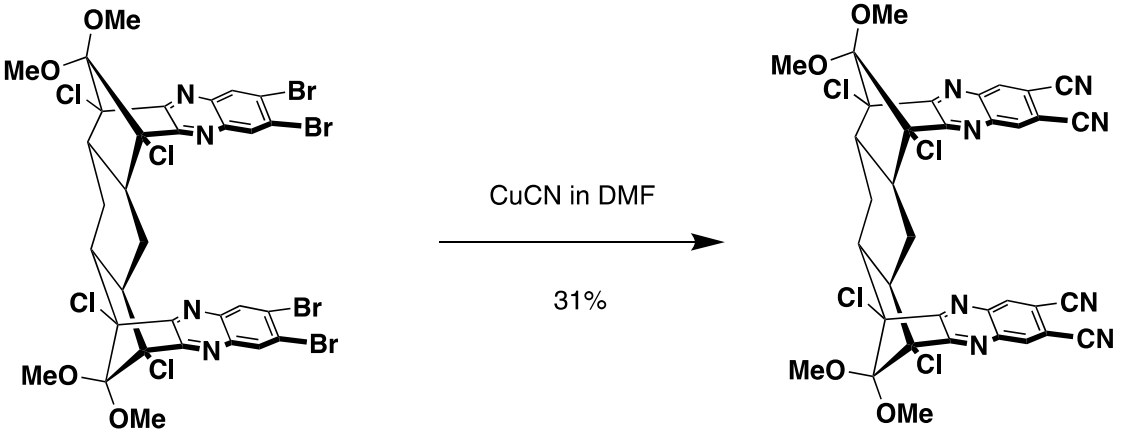


Figure S1. ^{1}H-NMR (400 MHz) Spectrum of **2** in $CDCl_3$.

Synthesis of 3.



2 **3**

2 (2.0 g, 2.0 mmol), CuCN (3.2 g, 36 mmol), and NMP (66 mL) were added in a 100 mL Schlenk flask. Oxygen was removed by freezing-thaw method by 5 times. The resulting mixture was stirred at 180 °C for 31 hrs. After the mixture was transferred into a 100 mL conical flask with NMP (12 mL) and H_2O (20 mL), 28% aqueous NH_3 (150 mL) was added. The mixture was stirred at room temperature for 11 hrs. H_2O (500 mL) was added to the suspension. The resulting precipitate was collected by suction filtration. The crude solid was dissolved in EtOAc (900 mL). The solution was washed with H_2O (500 mL and 700 mL) and brine (700 mL), dried over anhydrous Na_2SO_4, filtered and evaporated to give black solid (1.5 g). The crude product was purified by silica gel column chromatography (6 cm ϕ × 5 cm, CH_2Cl_2 including 0.1% NEt_3 – EtOAc including 0.1% NEt_3). The main fraction containing the title compound was further purified by reprecipitation from $CHCl_3$ / Et_2O to obtain the title compound (0.29 g, 0.37 mmol, 19%) as a colorless solid. The crude solid obtained from the filtrate mentioned above was purified separately by silica gel chromatography twice (1st: 5 cm ϕ × 8 cm, CH_2Cl_2 : EtOAc = 1 : 0 – 1 : 1 – 0 : 1 including 0.1% NEt_3, 2nd: 5 cm ϕ × 10 cm, CH_2Cl_2 including 0.1% NEt_3), followed by purification by reprecipitation ($CHCl_3$/Et_2O) to afford the title compound (0.19 g, 0.24 mmol, 12%). In total, the title compound was obtained in 31% yield. ^{1}H NMR (400MHz, DMSO-d_6/TMS): δ = 8.76 (s, 4H), 3.69 (s, 6H), 3.25 (s, 6H), 3.22 – 2.13 (m, 4H), 1.78 – 1.74 (m, 2H), –1.39 – –1.56 (m, 2H). ^{13}C NMR (100MHz, DMSO-d_6/TMS): δ = 156.6, 141.9, 136.8, 115.0, 114.5, 111.3, 75.3, 52.5, 41.8, 20.1. ESI-TOF MS (positive); *m/z*

calcd for $[M+Na]^+$ 796; Found 796.

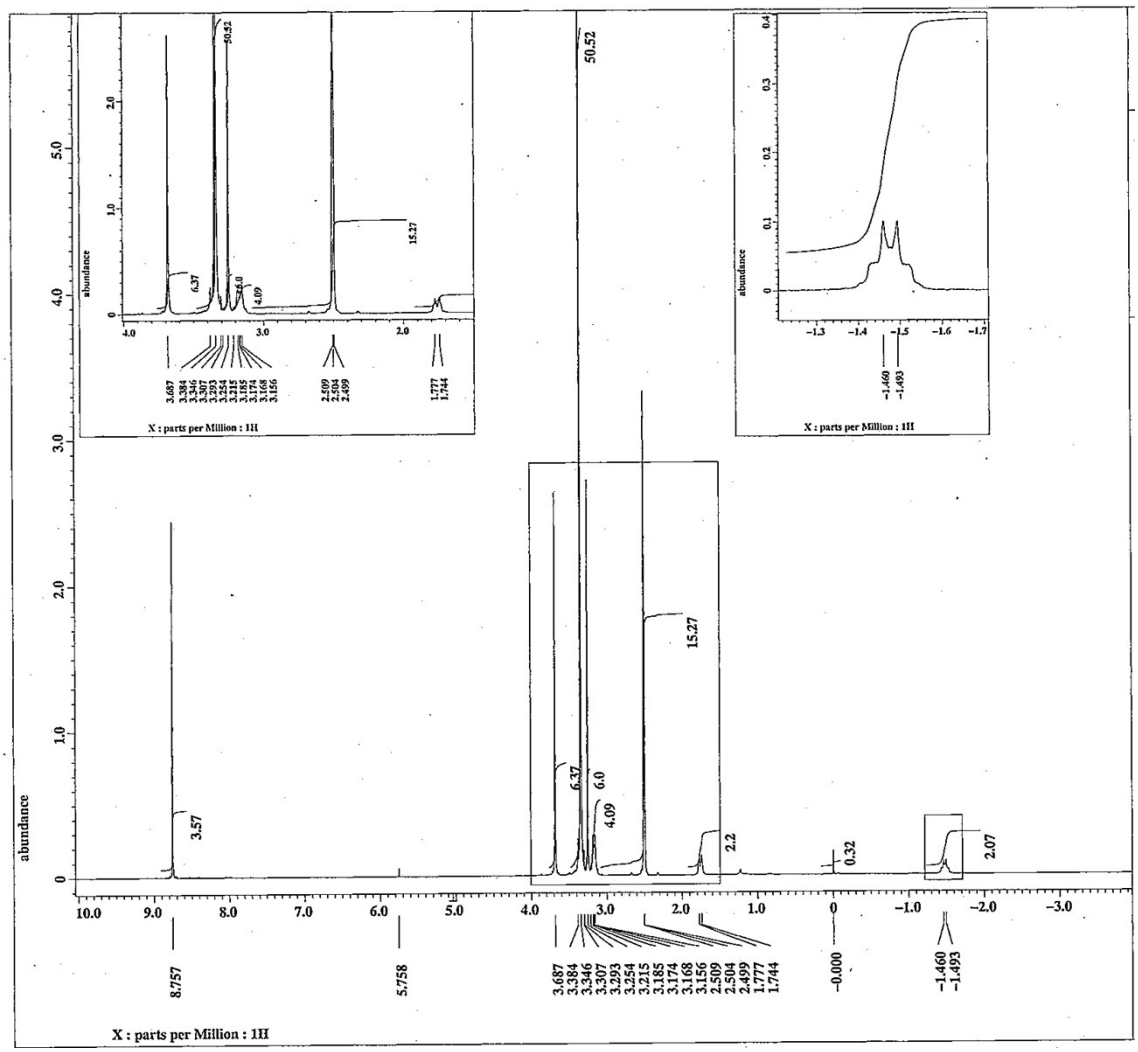


Figure S2. ^{1}H-NMR (400 MHz) Spectrum of **3** in DMSO-d_6.

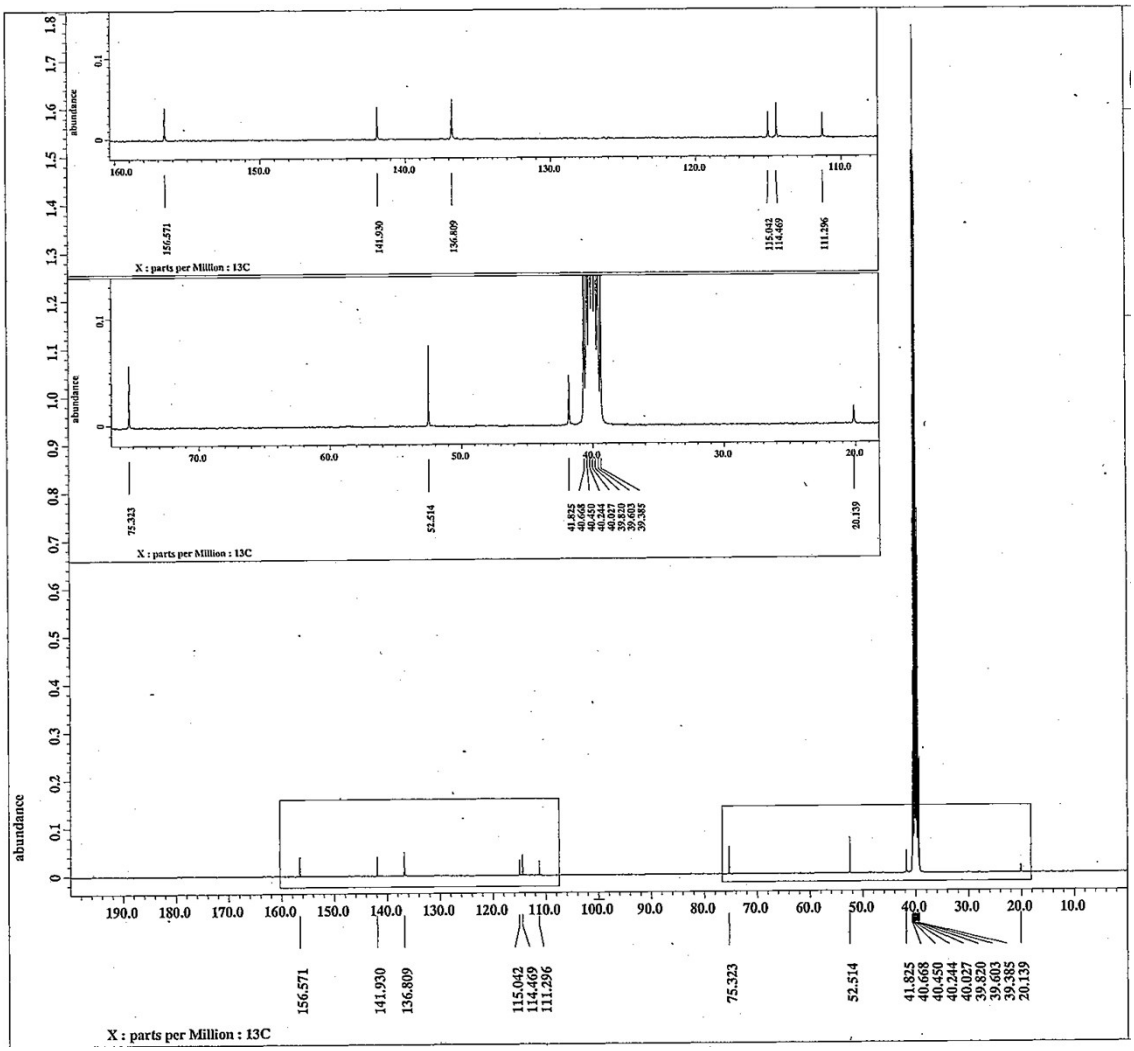
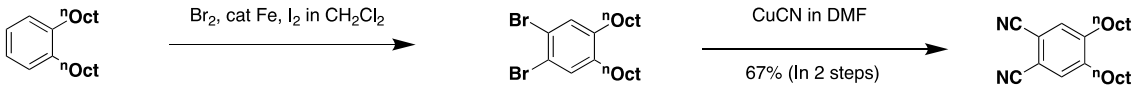


Figure S3. ^{13}C-NMR (100 MHz) Spectrum of **3** in DMSO-d_6.

Synthesis of 4,5-dioctylphthalonitrile



A mixture of 1,2-dioctylbenzene (3.4 g, 11 mmol), Fe (39 mg, 0.69 mmol), and I_2 (49 mg, 0.19 mmol) in CH_2Cl_2 (12 mL) was stirred at room temperature for 1.5 hrs. Then, Br_2 (1.5 mL, 4.7 g, 29 mmol) was added dropwise to the mixture on an ice bath over 20 min. The reaction mixture was stirred at 0 °C for 2hrs, then at room temperature for 13 hrs. The reaction was quenched by addition of saturated aqueous Na_2CO_3. The resulting mixture was extracted with CH_2Cl_2 (150 mL × 2). The combined organic layer was washed with brine (100 mL × 2), dried over $MgSO_4$, filtered and evaporated to give pale yellow oil (5.9 g). The crude product was passed through a silica pad (eluent ; hexane) to obtain colorless oil (5.5 g, 2.0 mmol, 106%). The compound including small amount of mono- and tri- brominated compounds was used for next reaction without further purification. ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.36 (s, 2 H), 2.67 (t, J = 8.0 Hz, 4 H), 1.65 – 1.52 (m, 4H including H_2O), 1.39 – 1.21 (m, 20 H), 0.89 (t, J = 7.0 Hz, 6 H).

1,2-Dibromo-4,5-dioctylbenzene obtained above (5.5 g), CuCN (4.8 g, 36 mmol) and DMF (70 mL) were added in a Schlenk flask. Oxygen was removed by freezing-thaw method by 5 times. The solution was stirred at 160 °C for 30 hrs. The reaction mixture was transferred into a 500 mL conical flask containing DMF (10 mL) and H_2O (40 mL). After 28% aqueous NH_3 (200 mL) was added, the mixture was stirred at room temperature for 11 hrs under air. The suspension was extracted with EtOAc (300 mL × 2), and the combined organic layer was washed with H_2O (300 mL × 2) and brine (200 mL × 3), dried over anhydrous Na_2SO_4, filtered and evaporated to give dark brown oil (4.2 g, 106%). The crude product was purified by silica gel column chromatography (1st: 5 cm ϕ × 10 cm, hexane : CH_2Cl_2 = 4 : 1 - 0 : 1, 2nd: 3 cm ϕ × 16 cm, hexane : CH_2Cl_2 = 8 : 1, 3rd: 3 cm ϕ × 20 cm, hexane : EtOAc = 20 : 1, 4th: 3 cm ϕ × 15 cm, hexane : EtOAc = 20 : 1, 5th: 3 cm ϕ × 18 cm, hexane : EtOAc = 20 : 1) to obtain the title compound as a pale blue oil (2.5 g, 7.1 mmol, 63%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 7.55 (s, 2 H), 2.51 (t, J = 8.0 Hz, 4 H), 1.55 – 1.49 (m, 21H

including H_2O), 1.31 – 1.28 (m, 20 H), 0.89 (t, J = 7.0 Hz, 6 H).

Total yield of these two steps was 67%.

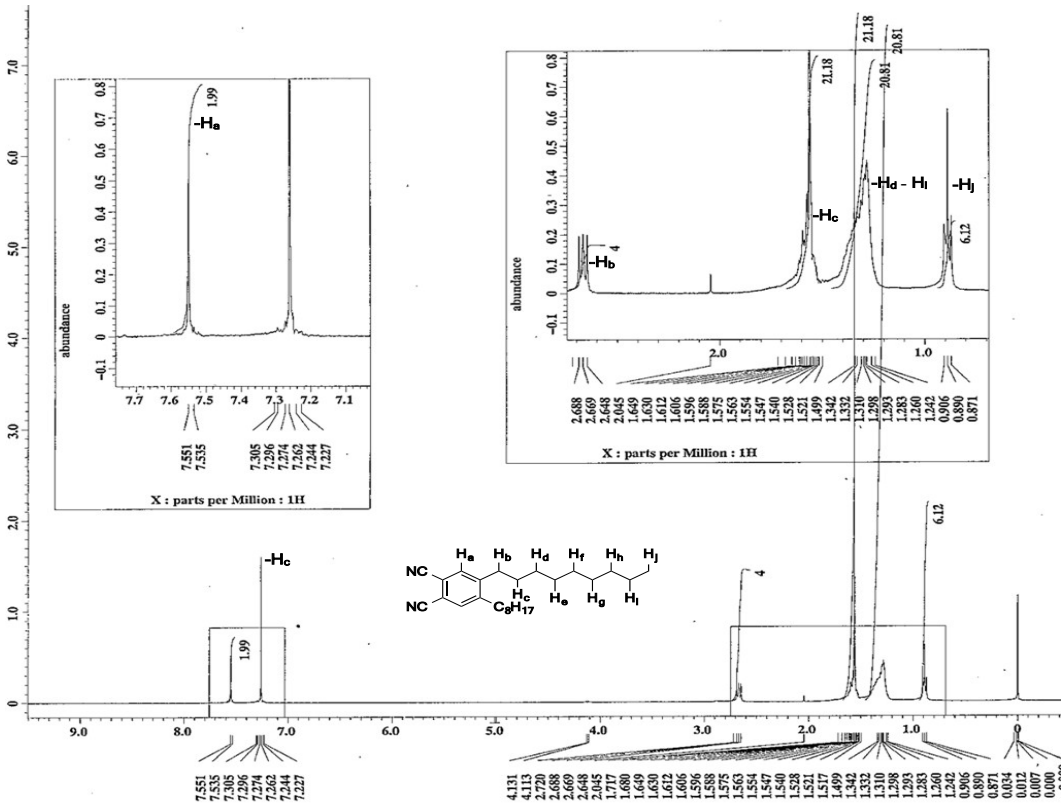
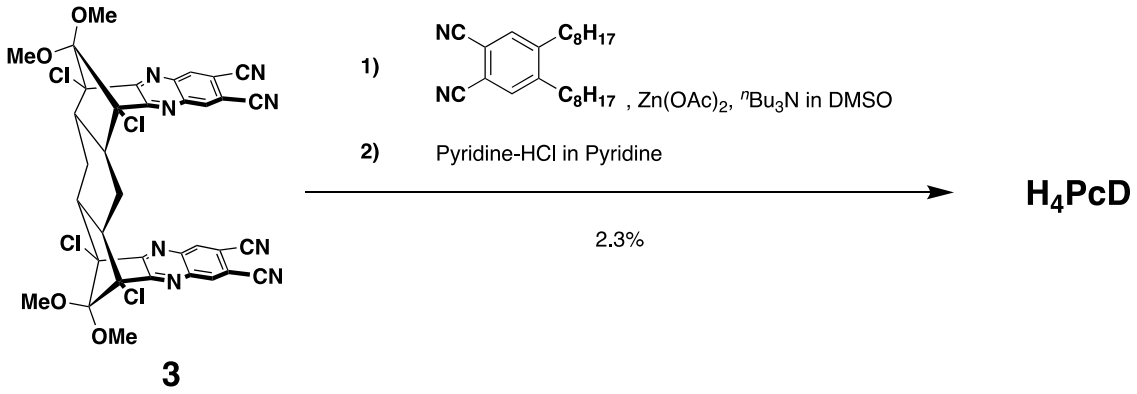


Figure S4. ^{1}H-NMR (400 MHz) Spectrum of 4,5-dioctylphthalonitrile in $CDCl_3$.

Synthesis of H_4PcD



3 (200 mg, 227 μmol), 4,5-dioctylphthalonitrile (191 mg, 541 μmol), $Zn(OAc)_2$ (274 mg, 1.50 mmol), N^nBu_3 (1.30 mL, 5.47 mmol), and DMSO (4.0 mL) were added in a Schlenk flask. Oxygen was removed by freezing-thaw method by 4 times. The resulting mixture was stirred at 180 °C for 4 days. MeOH (50 mL) was added to the suspension and the generated precipitate was collected by suction filtration. The crude product was purified by silica gel column chromatography (1st: 5 cm ϕ × 10 cm, hexane : CH_2Cl_2 = 4 : 1 - 0 : 1, 2nd: 3 cm ϕ × 16 cm, hexane : CH_2Cl_2 = 8 : 1, 3rd: 3 cm ϕ × 20 cm, hexane : EtOAc = 20 : 1) to obtain the desired dinuclear zinc complex **Zn_2PcD** (190 mg, 63 μmol, 28% as pure **Zn_2PcD**) (included small amount of impurity). This was used for the next reaction without purification. ^{1}H-NMR spectrum of this sample showed significant broadening, presumably due to the fast exchange of the axial H_2O of the Zn^{2+} center of **Zn_2PcD** as shown in Figure S5. MALDI-TOF MS of this sample was shown in Figure S6.

A mixture containing **Zn_2PcD** (190 mg, 63 μmol) obtained above, pyridine-HCl (2.5 g, 22 mmol), and pyridine (5 mL) was stirred at 110 °C for 9 days. Water (40 mL) was added to the suspension and the generated precipitate was collected by filtration. The filtrate was extracted with $CHCl_3$ (80 mL) and the organic layer was washed with brine (50 mL × 2), dried over anhydrous Na_2SO_4, filtered, and evaporated to give a green solid. Totally, 0.19 g crude product was obtained. The combined crude product was purified by silica gel column chromatography (1st: 4 cm ϕ × 12 cm, hexane : CH_2Cl_2 = 1 : 4 - 0 : 1, 2nd: 3 cm ϕ × 16 cm). The crude solid obtained from the fraction was further purified by recycling GPC (JAIGEL, 2.5 H–2.5 H, $CHCl_3$) and

reprecipitation (1st: CH_2CH_2/MeOH, 2nd: CH_2CH_2/Et_2O, 3rd: $CHCH_3$/MeOH) to obtain the target product **H_4PcD** as a blue solid (15 mg, 5.2 μmol, 8.3%). ^{1}H NMR (400 MHz, $CDCl_3$/TMS): δ = 9.60 (s, 4 H), 8.81 (s, 4 H), 8.54 (s, 4 H), 8.46 (s, 4 H), 3.86 (s, 6 H), 3.42 (s, 6 H), 3.42-3.01 (m, 24 H including MeOH), 2.80 (m, 4 H), 2.56 (m, 2 H), 2.36 (m, 4 H), 2.20 (m, 4 H), 2.11 (m, 8 H), 2.02 – 1.41 (m, 148H including H_2O), 1.05 – 0.80 (m, 32 H), –0.48 (m, 2 H), –3.19 (m, 4 H). MALDI-TOF MS (positive): *m/z* calcd. for $[M+H]^+$ 2893.8; Found 2893.6. Anal. Calcd for $C_{182}H_{252}Cl_4N_{20}O_6$ (M + $2CH_3OH$) : C, 73.90; H, 8.59; N, 9.47. Found: C, 74.24; H, 8.72; N, 9.15 (0.32% error).

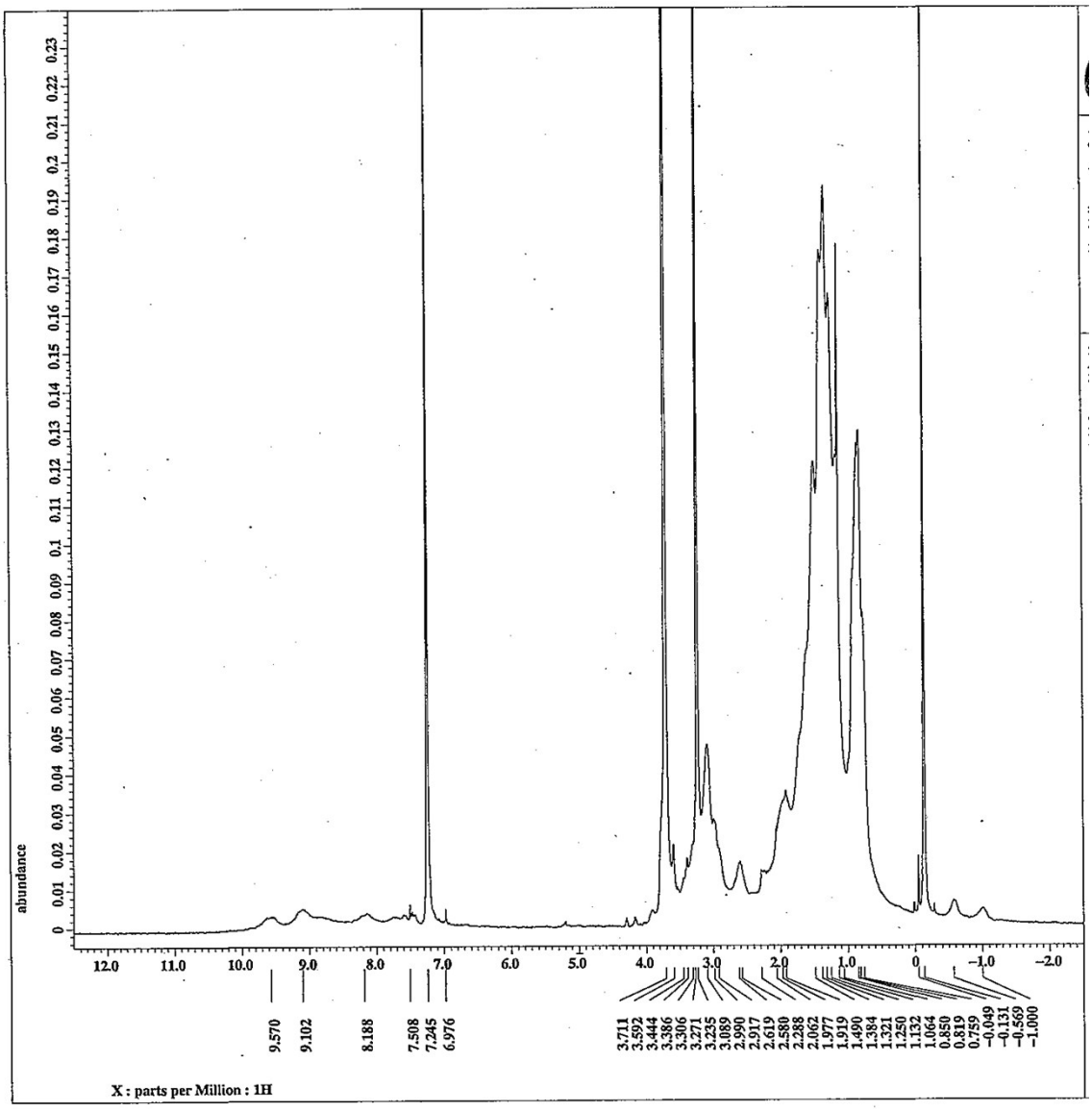


Figure S5. ^{1}H-NMR (400 MHz) Spectrum of **Zn_2PcD** in $CDCl_3$.

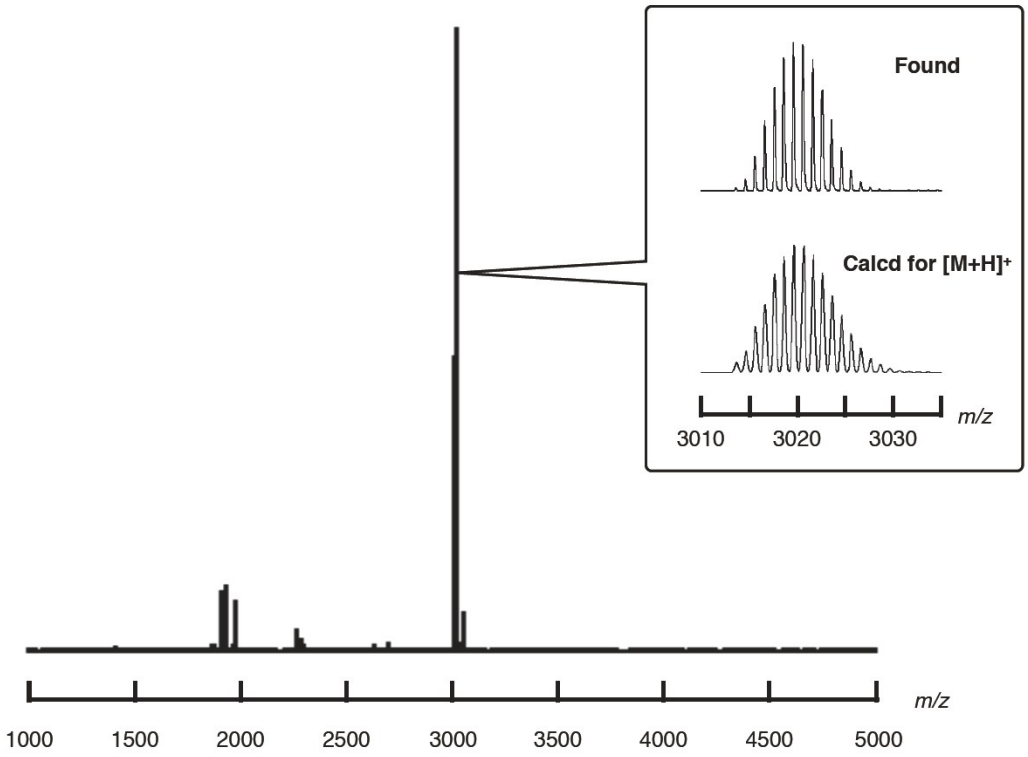


Figure S6. MALDI-TOF MS Spectrum of **Zn_2PcD**. Inset: Comparison of the observed spectrum with the calculated isotopic distribution pattern for [**Zn_2PcD**+H]$^{+}$ ($C_{180}H_{241}Cl_4N_{20}O_4Zn_2$).

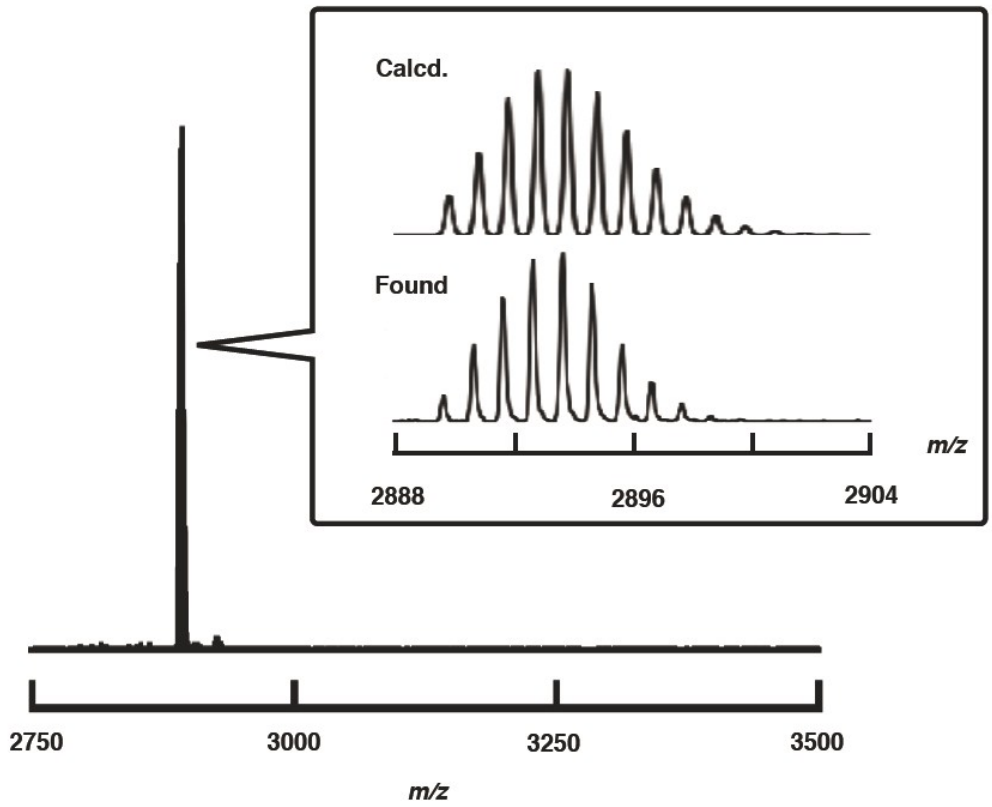


Figure S7. MALDI-TOF MS Spectrum of **H_4PcD**. Inset: Comparison of the observed spectrum with the calculated isotopic distribution pattern for [**H_4PcD**+H]$^+$ ($C_{180}H_{245}Cl_4N_{20}O_4$).

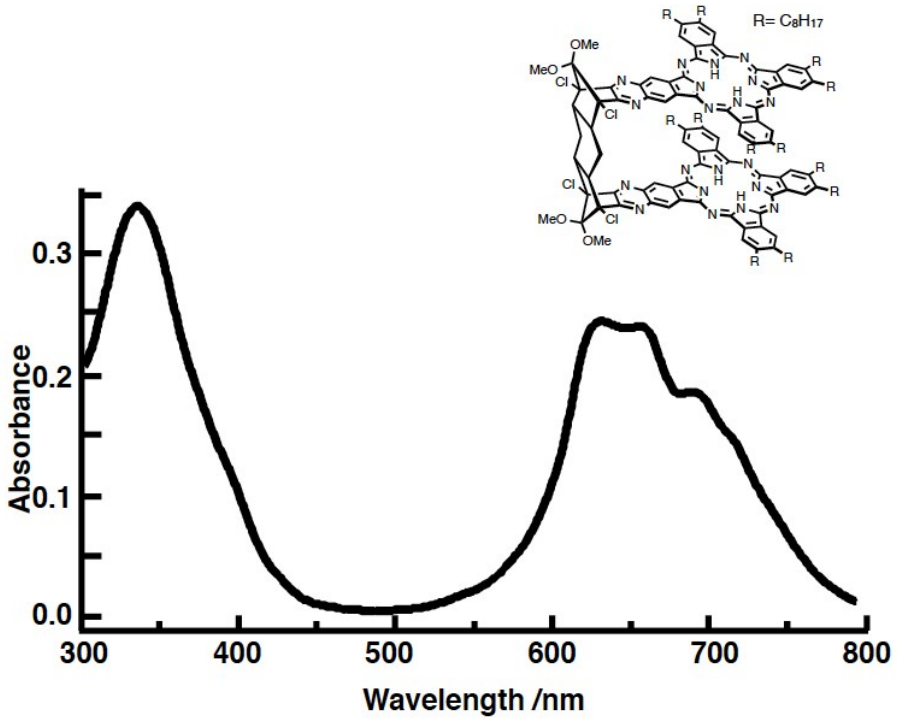


Figure S8. UV-Vis absorption spectrum of **H_4PcD** (1.0 μM) in CH_2Cl_2 at 20 °C.

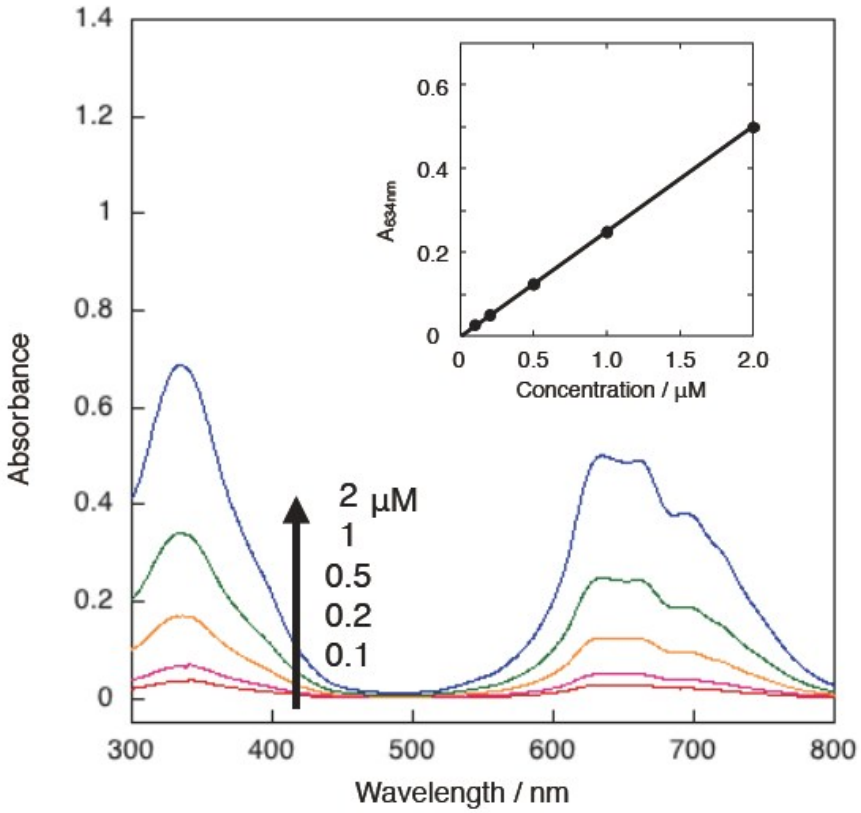


Figure S9. Concentration dependence of the UV-Vis absorption spectrum of **H_4PcD** (0.1–2.0 μM) in CH_2Cl_2 at 20 °C. Inset: Change in the absorption of **H_4PcD** at 634 nm.

References

1. T.-C. Chou, K.-C. Liao, and J.-J. Lin, *Org. Lett.,* **2005**, *22*, 4843–4846.
2. N. R. S. Gobo, T. J. Brocksom, J. Zukerman-Schpector, and K. T. de Oliveira, *Eur. J. Org. Chem.*, **2013**, 5028–5031.
3. W. Cui, Y. Zhao, H. Tian, Z. Xie, Y. Geng, and F. Wang, *Macromolecules*, **2009**, *42*, 8021–8027.