Supporting Information
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Regioisomer-Free $C_{4h} \beta$-Tetrakis(tert-butyl)metallophtalocyanines: Regioselective Synthesis and Spectral Investigations
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open_201402093_sm_miscellaneous_information.pdf
Supporting Information

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1. General Method
All solvent and reagents were used without purification. All of the reactions were monitored by thin-layer chromatography (TLC) on 0.25 mm Merck silica gel plates (60F-254). Column chromatography was carried out on a column packed with silica gel 60N (spherical, neutral, size 63-210 μm). $^1$H NMR (300 MHz) spectra were recorded on a Varian Mercury 300. $^1$H NMR (600 MHz) and $^{13}$C NMR (150.9 MHz) spectra for solution in CDCl$_3$ were recorded on AVANCE 600. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane. Infrared (IR), UV/Vis, and steady-state fluorescence spectra were recorded on a JASCO FT/IR-4100 spectrometer, V-530 spectrometer, and FP-6200 spectrofluorimeter, respectively. Fluorescence quantum yields were calculated following the procedure mentioned before. MALDI-TOF mass spectra were taken on a SHIMADZU Axima CFR Plus, GC mass spectra were recorded on a SHIMADZU GCMS-QP5050 and high resolution mass spectrometer (HRMS) were recorded on a Waters, GCT Premier. UV/Vis ATR (attenuated total reflection) spectra of thin films was recorded SIS-5000 (System Instruments Co., Ltd.). Optical waveguide uses quartz waveguide 960016 (System Instruments Co., Ltd.). Synthesized phthalocyanine samples dissolved by chloroform then 4 μl droplet put onto the waveguide surface. Drying after measured using P polarized light and S polarized light respectively.

1. J. Fu, X.-Y. Li, D. K. P. Ng, C. Wu, Langmuir, 2002, 18, 3843-3847.
2. Standard method for synthesis of $\beta$-tetrakis(tert-butyl)phthalocyanines 1

Scheme S1. Standard method for synthesis of $\beta$-tetrakis(tert-butyl)phthalocyanines 1 and structure of four regioisomers
3. Screening desilylation of 4a

Table S1. Screening of desilylation of 4a

| Entry | Reagent       | Solvent      | Temp. (°C) | Yield (%) |
|-------|---------------|--------------|------------|-----------|
| 1     | KOH           | H₂O / EtOH   | 100        | N. R.     |
| 2     | KOH           | H₂O / DMAE   | 150        | N. R.     |
| 3     | TBAF · 3H₂O   | THF          | r.t.       | N. R.     |
| 4     | TBAF · 3H₂O   | DMF          | 135        | complex mixture |
| 5     | CsF           | DMF          | 150        | complex mixture |
| 6     | KF            | THF / H₂O   | 65         | N.R.      |
| 7     | conc. H₂SO₄  | None         | r.t.       | 69        |

Scheme S2. Desilylation of 4a and 5a to 1.

¹H NMR spectra of C₄h⁺1 and mixture of regioisomer 1 are shown in Figure S1 and Figure S2
4. Comparison between $C_{ab}$-I and conventional I by $^1$H NMR and $^{13}$C NMR spectrum
Figure S1. a) $^1$H NMR of $C_{4h}$-$1$ in CDCl$_3$ and Pyridine-$d5$; b) $^1$H NMR of conventional $1$ in CDCl$_3$ and Pyridine-$d5$; c) $^{13}$C NMR of $C_{4h}$-$1$ in CDCl$_3$ and Pyridine-$d5$; d) $^{13}$C NMR of conventional $1$ in CDCl$_3$ and Pyridine-$d5$. 
5. Comparison between 5a and 1 as a mixture of regioisomers by $^1$H NMR

Figure S2. a) $^1$H NMR of 5a; b) $^1$H NMR of 1 as a mixture of regioisomers.
6. Experimental procedure

Synthesis of 4-hexylphthalonitrile

\[
\text{4-(hex-1-ynyl)phthalonitrile}
\]

4-iodophthalonitrile (635 mg, 2.50 mmol), 1-hexyne (0.32 ml, 2.75 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (17.5 mg, 0.0250 mmol), CuI (4.8 mg, 0.0250 mmol) were dissolved in triethylamine (10 ml), THF (10 ml) under nitrogen atmosphere. Reaction mixture was stirred at rt for overnight. After reaction, solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Hex / AcOEt = 90 / 10) to give 4-(hex-1-ynyl)phthalonitrile (502.1 mg, 96% yield) as oil.

\[
\text{C}_{14}\text{H}_{12}\text{N}_2
\]

M.W.: 208.26

\(^1\)H NMR (CDCl\(_3\), 300 MHz): \(\delta = 0.96\) (t, \(J = 6.3\) Hz, 3H), 1.46—1.51 (m, 2H), 1.59—1.63 (m, 2H), 2.46 (t, \(J = 6.3\) Hz, 2H), 7.68—7.73 (m, 2H), 7.77 (s, 1H)

\(^{13}\)C NMR (CDCl\(_3\), 150.9 MHz): \(\delta = 13.9, 19.2, 21.9, 30.1, 77.7, 99.2, 113.5, 114.8, 115.2, 116.0, 130.2, 133.3, 135.7, 136.1\)

IR (NaCl): 3072, 2959, 2934, 2872, 2229, 1596, 1547, 1489, 1466, 1396, 1329, 1260, 1106, 900, 848, 727, 493 cm\(^{-1}\)

MS (EI): \(m/z = 208\) (M\(^+\))

HRMS (EI) calcd. for C\(_{14}\)H\(_{12}\)N\(_2\) (M\(^+\)): 208.1000 Found: 208.1008

4-hexylphthalonitrile (7b)

4-(hex-1-ynyl)phthalonitrile (468.3 mg, 2.25 mmol) was dissolved in AcOEt. Palladium on carbon (46.8 mg, 10 wt%) was added under nitrogen atmosphere. Reaction flask was replaced with hydrogen. The reaction mixture was stirred at room temperature under H\(_2\) atmosphere (about 275 kPa). After reaction, palladium catalyst was removed by celite filtration, filtrate was
evaporated. The crude product was purified by flash column chromatography on silica gel (Hex / AcOEt = 90 / 10) to give 4-hexylphthalonitrile 7b (450.9 mg, 94% yield) as oil.

C14H16N2
M.W.: 212.29

1H NMR (CDCl3, 300 MHz): ť = 0.89 (t, J = 6.5 Hz, 3H), 1.30 (br, 6H), 1.61—1.66 (m, 2H), 2.72 (t, J = 7.7 Hz, 2H), 7.53 (d, J = 8.3 Hz, 1H), 7.62 (s, 1H), 7.72 (d, J = 8.3 Hz, 1H)

13C NMR (CDCl3, 150.9 MHz): ū = 13.8, 22.3, 28.5, 30.4, 31.3, 35.5, 112.6, 115.4, 115.5, 115.5, 133.3, 133.3, 149.6

Preparation of silylated phthalonitriles

5-tert-butyl-3-(trimethylsilyl)phthalonitrile (3a)

\[
\text{Bu} \quad \text{SiMe}_3 \quad \text{CN} \\
\text{CN} 
\]

To a solution of 2,2,6,6-tetramethyl piperidine (0.12 ml, 0.679 mmol) in THF (2.0 ml) was added 1.23 M solution of n-butyl lithium in hexane (0.55 ml, 0.679 mmol) slowly at 0°C. Reaction mixture was stirred for 30 min at 0°C, cooled to -80°C and solution of 4-tert-butylphthalonitrile (100 mg, 0.543 mmol) in THF (2.0 ml) was dropwised. Dark solution was stirred for 30 min at -80°C, chlorotrimethylsilane (68.9 μl, 0.543 mmol) was dropwised. After stirring 1 h at -80°C, reaction mixture was warmed to room temperature and stirred for 1 h. Then, reaction was quenched by addition of water, and THF was removed under reduced pressure followed by extracted with Et2O for 3 times. The combined Organic phase was washed with brine. Organic phase was dried over Na2SO4, and removed solvent under reduced pressure. The crude product was purified by column chromatography on silica gel (Hex / AcOEt = 90 / 10) to give 5-tert-butyl-3-(trimethylsilyl)phthalonitrile 3a (88.3 mg, 63% yield) as white solid.

C15H20N2Si
M.W.: 256.42

m.p.: 123—124°C

1H NMR (CDCl3, 300 MHz): ť = 0.46 (s, 9H), 1.35 (s, 9H), 7.75 (s, 1H), 7.82 (s, 1H)

13C NMR (CDCl3, 150.9 MHz): ū = -1.6, 30.7, 35.5, 116.3, 116.7, 116.9, 117.4, 130.7, 135.2, 147.1, 155.5

SI-8
To a solution of 2,2,6,6-tetramethyl piperidine (0.57 ml, 3.39 mmol) in THF (10 ml) was added 1.23 M solution of n-butyl lithium in hexane (2.76 ml, 3.39 mmol) slowly at 0 °C. Reaction mixture was stirred for 30 min at 0 °C, cooled to -80 °C and solution of 4-tert-butylphthalonitrile (500 mg, 2.71 mmol) in THF (10 ml) was dropwised. Dark solution was stirred for 30 min at -80 °C, chlorotriethylsilane (0.45 ml, 2.71 mmol) was dropwised. After stirring 1 h at -80 °C, reaction mixture was warmed to room temperature and stirred for 1 h. Then reaction was quenched by addition of water, and THF was removed under reduced pressure followed by extracted with Et₂O for 3 times. The combined Organic phase was washed with brine. Organic phase was dried over Na₂SO₄, and removed solvent under reduced pressure. The crude product was purified by column chromatography on silica gel (Hex / AcOEt = 98 / 2 → 96 / 4) to give 5-tert-butyl-3-(triethylsilyl)phthalonitrile 3b (357 mg, 44% yield) as white solid.

C₁₈H₂₆N₂Si

M.W.: 298.5

m.p.: 88—89 °C

¹H NMR (CDCl₃, 300 MHz): ū= 0.99—1.01 (m, 15H), 1.35 (s, 9H), 7.76 (s, 1H), 7.81 (s, 1H)

¹³C NMR (CDCl₃, 150.9 MHz): ū= 2.8, 7.2, 30.7, 35.4, 116.4, 116.7, 117.1, 117.6, 130.6, 136.4, 144.5, 155.3

IR (KBr): 3441, 3064, 2955, 2876, 2229, 1579, 1464, 1392, 1242, 1171, 1011, 899, 842, 797, 738, 699, 512, 413 cm⁻¹

MS (EI): m/z = 298 (M⁺)

HRMS (EI) calcd. for C₁₈H₂₆N₂Si (M)+: 298.1865 Found: 298.1886
5-methyl-3-(trimethylsilyl)phthalonitrile (6a)

To a solution of 2,2,6,6-tetramethyl piperidine (0.68 ml, 4.05 mmol) in THF (55 ml) was added 1.33 M solution of n-butyl lithium in hexane (3.04 ml, 4.05 mmol) slowly at 0 °C. Reaction mixture was stirred for 30 min at 0 °C, cooled to -80 °C and solution of 4-methylphthalonitrile 7a (500 mg, 3.52 mmol) in THF (15 ml) was dropwised. Dark solution was stirred for 30 min at -80 °C, chlorotrimethylsilane (0.45 ml, 3.52 mmol) was dropwised. After stirring 1 h at -80 °C, reaction mixture was warmed to room temperature and stirred for 1 h. Then reaction was quenched by addition of water, and THF was removed under reduced pressure followed by extracted with AcOEt for 3 times. The combined Organic phase was washed with brine. Organic phase was dried over Na₂SO₄ and removed solvent under reduced pressure. The crude product was purified by column chromatography on silica gel (Hex / AcOEt = 80 / 20) to give 5-methyl-3-(trimethylsilyl)phthalonitrile 6a (252.5 mg, 33% yield) as white solid.

C₁₂H₁₄N₂Si M.W.: 214.34 m.p.: 120—121 °C

¹H NMR (CDCl₃, 300 MHz): ₀H = 0.45 (s, 9H), 2.47 (s, 3H), 7.57 (s, 1H), 7.61 (s, 1H)

¹³C NMR (CDCl₃, 150.9 MHz): ₀C = -1.6, 21.6, 116.0, 116.7, 116.9, 117.4, 133.8, 139.1, 142.8, 147.2

IR (KBr): 2970, 2906, 2227, 1866, 1809, 1583, 1552, 1425, 1254, 1120, 1045, 872, 845, 765, 698, 630, 553, 484, 463 cm⁻¹

MS (EI): m/z = 214 (M⁺)

HRMS (EI) calcd. for C₁₂H₁₄N₂Si (M)⁺: 214.0926 Found: 214.0937

5-hexyl-3-(trimethylsilyl)phthalonitrile (6b)

To a solution of 2,2,6,6-tetramethyl piperidine (0.48 ml, 2.83 mmol) in THF (55 ml) was added 1.33 M solution of n-Butyl lithium in hexane (2.13 ml, 2.83 mmol) slowly at 0 °C. Reaction mixture was stirred for 30 min at 0 °C, cooled to -80 °C and solution of 4-hexylphthalonitrile 7b (523 mg, 2.46 mmol) in THF (15 ml) was dropwised. Dark solution was stirred for 30 min at
-80 °C, chlorotrimethylsilane (0.31 ml, 2.46 mmol) was dropwised. After stirring 1 h at -80 °C, reaction mixture was warmed to room temperature and stirred for 1 h. Then reaction was quenched by addition of water, and THF was removed under reduced pressure followed by extracted with Et₂O for 3 times. The combined Organic phase was washed with brine. Organic phase was dried over Na₂SO₄, and removed solvent under reduced pressure. The crude product was purified by column chromatography on silica gel (Hex / AcOEt = 90 / 10) to give 5-hexyl-3-(trimethylsilyl)phthalonitrile 6b (457.7 mg, 65% yield) as oil.

C₁₇H₂₄N₂Si
M.W.: 284.47

¹H NMR (CDCl₃, 300 MHz): δ = 0.45 (s, 9H), 0.90 (br, 3H), 1.32 (br, 6H), 1.63 (br, 2H), 2.69 (t, J = 7.8 Hz, 2H), 7.57 (s, 1H), 7.59 (s, 1H)

¹³C NMR (CDCl₃, 150.9 MHz): δ = -1.7, 13.9, 22.4, 28.7, 30.7, 31.4, 35.7, 116.1, 116.6, 116.9, 117.4, 133.1, 138.4, 147.2, 147.6

IR (NaCl): 2956, 2930, 2858, 2225, 1648, 1582, 1466, 1405, 1254, 1221, 1116, 970, 870, 846, 767, 699, 629 cm⁻¹

MS (EI): m/z = 284 (M⁺)

HRMS (EI) calcd. for C₁₇H₂₄N₂Si (M⁺): 284.1709 Found: 284.1719

2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(trimethylsilyl)phthalocyaninate zinc (II) (4a)

A 5-tert-butyl-3-(trimethylsilyl)phthalonitrile 3a (136.6 mg, 0.533 mmol), Zn(OAc)₂ (24.4 mg, 0.133 mmol) and ethylene glycol (1.0 ml) were added to reaction flask under nitrogen atmosphere. Reaction mixture was stirred at 230 °C for 3 h. The reaction mixture was cooled, quenched by addition of water, and extracted with CH₂Cl₂ for 3 times. Combined organic solvent was washed with brine and dried over with Na₂SO₄. Solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel (Hex / AcOEt = 95 / 5) to give 4a (41.8 mg, 29% yield). Continued elution of the silica gel gave 5a
(14.2 mg, 10% yield).

C_{60}H_{80}N_8Si_4Zn

M.W.: 1091.06

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 1.17 (s, 36H), 1.81 (s, 36H), 8.50 (s, 4H), 9.73 (s, 4H)

IR (KBr): 3854, 3735, 3650, 3447, 2369, 2344, 1615, 1490, 1394, 1363, 1334, 1281, 1256, 1197, 1146, 1048, 923, 829, 764, 746, 692, 670, 527, 461, 418 cm$^{-1}$

UV / Vis (CH$_2$Cl$_2$, 1.0 × 10$^{-5}$ M): $\varepsilon_{\text{max}}$ (log $\epsilon$) = 347 nm (4.82), 615 nm (4.50), 656 nm (4.51), 683 nm (5.28)

UV / Vis (CF$_3$Ph, 1.0 × 10$^{-5}$ M): $\varepsilon_{\text{max}}$ (log $\epsilon$) = 347 nm (4.79), 614 nm (4.47), 654 nm (4.46), 681 nm (5.26)

UV / Vis (dioxane, 1.0 × 10$^{-5}$ M): $\varepsilon_{\text{max}}$ (log $\epsilon$) = 351 nm (4.87), 612 nm (4.52), 651 nm (4.53), 678 nm (5.31)

Fluorescence (CH$_2$Cl$_2$): $\lambda_{\text{em}}$ = 684 nm, $\Phi_f$ = 0.38; (CF$_3$Ph) $\lambda_{\text{em}}$ = 683 nm, $\Phi_f$ = 0.40 ; (dioxane) $\lambda_{\text{em}}$ = 681 nm, $\Phi_f$ = 0.41

MALDI-TOF MS (dithranol): 1088.36—1095.43 ([M$^+$], isotopic pattern).
2,9,16,23(24)-tetrakis(tert-butyl)-4,11,18,25(22)-tris(trimethylsilyl)phthalocyaninate zinc (II) (5a)

C_{57}H_{72}N_{8}Si_{3}Zn
M.W.: 1018.88

$^1$H NMR (CDCl$_3$ and Pyridine-$d_5$, 600 MHz): $\delta = 1.13$—1.16 (m, 27H), 1.78—1.82 (m, 36H), 8.24—8.28 (m, 1.5H), 8.45—8.46 (m, 2.2H), 9.43 (d, $J = 12$ Hz, 0.8H), 9.50 (d, $J = 6$ Hz, 0.8H), 9.61—9.65 (m, 2.2H), 9.70 (br, 1.5H)

IR (KBr): 3428, 2957, 2927, 2866, 1654, 1480, 1371, 1266, 1109, 940, 888, 836, 752 cm$^{-1}$

MALDI-TOF MS (dithranol): 1016.30—1022.31 ([M$^+$], isotopic pattern).
2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(triethylsilyl)phthalocyaninate zinc (II) (4b)

A 5-tert-butyl-3-(triethylsilyl)phthalonitrile 3b (58.2 mg, 0.195 mmol), Zn(OAc)$_2$ (8.9 mg, 0.0651 mmol) were added to reaction flask under nitrogen atmosphere. Reaction mixture was heated at 200 °C for 3 h. The reaction mixture was cooled and purified by column chromatography (Hex / AcOEt = 95 / 5) on silica gel to give 4b (11.2 mg, 18% yield).

C$_{72}$H$_{104}$N$_8$Si$_4$Zn
M.W.: 1259.38

$^1$H NMR (CDCl$_3$, 300 MHz): $\tilde{\delta}$ = 1.19 (t, $J$ = 7.5 Hz, 36H), 1.81 (s, 36H), 1.94 (q, $J$ = 7.5 Hz, 24Hz), 8.46 (s, 4H), 9.68 (s, 4H)

IR (KBr): 3392, 2956, 2907, 2873, 1598, 1459, 1366, 1341, 1264, 1177, 1105, 1004, 936, 866, 731, 421 cm$^{-1}$

UV / Vis (CH$_2$Cl$_2$, 1.0 $\times$ 10$^{-5}$ M): $\varepsilon_{max}$ (log $\tilde{\delta}$ = 351 nm (4.77), 616 nm (4.42), 656 nm (4.51), 684 nm (5.19), 734 nm (4.75)

UV / Vis (CF$_3$Ph, 1.0 $\times$ 10$^{-5}$ M): $\varepsilon_{max}$ (log $\tilde{\delta}$ = 355 nm (4.85), 615 nm (4.57), 656 nm (4.55), 682 nm (5.34)

UV / Vis (dioxane, 1.0 $\times$ 10$^{-5}$ M): $\varepsilon_{max}$ (log $\tilde{\delta}$ = 353 nm (4.94), 612 nm (4.64), 650 nm (4.61), 678 nm (5.39)

Fluorescence (CH$_2$Cl$_2$): $\Phi_m$ = 0.20; (CF$_3$Ph) $\Phi_m$ = 0.36; (dioxane) $\Phi_m$ = 0.46

MALDI-TOF MS (dithranol): 1256.78—1264.70 ([M$^+$], isotopic pattern).
2,9,16,23(24)-tetrakis(tert-butyl)-4,11,18,25(22)-tris(triethylsilyl)phthalocyaninate zinc (II) (5b)

A 5-tert-butyl-3-(triethylsilyl)phthalonitrile 3b (158.8 mg, 0.533 mmol), Zn(OAc)$_2$ (24.4 mg, 0.133 mmol), ethylene glycol (1.0 ml) were added to reaction flask under nitrogen atmosphere. Reaction mixture was stirred at 230 °C for 3 h. The reaction mixture was cooled, quenched by addition of water, and extracted with CH$_2$Cl$_2$ for 3 times. Combined organic solvent was washed with brine and dried over with Na$_2$SO$_4$. Solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (Hex / AcOEt = 95 / 5) to give 4b (27 mg, 16% yield). Continued elution of the silica gel gave 5b, but it was not fully
characterized due to the difficulty of its purification.

C₆₆H₉₀N₈Si₃Zn
M.W.: 1145.12
MALDI-TOF MS (dithranol): 1141.48—1146.48 ([M⁺], isotopic pattern).

2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(trimethylsilyl)phthalocyaninate nickel (II) (4a-2)

A 5-tert-butyl-3-(trimethylsilyl)phthalonitrile 3a (50 mg, 0.195 mmol), Ni(OAc)₂ (8.6 mg, 0.0488 mmol) and ethylene glycol (0.5 ml) were added to reaction flask under nitrogen atmosphere. Reaction mixture was stirred at 230 °C for 3 h. The reaction mixture was cooled, quenched by addition of water, and extracted with CH₂Cl₂ for 3 times. Combined organic solvent was washed with brine and dried over with Na₂SO₄. Solvent was removed under
reduced pressure, the crude product was purified by column chromatography (Hex = 100) on silica gel to give 4a-2 (4.8 mg, 9.1% yield).

C_{60}H_{80}N_{8}NiSi_{4}

M.W.: 1084.37

^{1}H NMR (CDCl_{3}, 300 MHz): \( \delta = 1.10 \) (s, 36H), 1.77 (s, 36H), 8.44 (s, 4H), 9.61 (s, 4H)

IR (KBr): 3414, 2960, 2897, 2367, 1529, 1369, 1322, 1271, 1136, 1110, 958, 893, 860, 830, 761 cm\(^{-1}\)

MALDI-TOF MS (dithranol): 1082.32—1089.61 ([M\(^{+}\), isotopic pattern).
2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(trimethylsilyl)phthalocyaninate cobalt (II) (4a-3)

A 5-tert-butyl-3-(trimethylsilyl)phthalonitrile 3a (50 mg, 0.195 mmol), Co(OAc)₂ (8.6 mg, 0.0488 mmol) and 1-chloronaphthalene (0.5 ml) were added to reaction flask under nitrogen atmosphere. Reaction mixture was stirred at 230 °C for 3 h. The reaction mixture was cooled, quenched by addition of water, and extracted with CH₂Cl₂ for 3 times. Combined organic solvent was washed with brine and dried over with Na₂SO₄. Solvent was removed under reduced pressure, the crude product was purified by column chromatography (Hex = 100) on silica gel to give 4a-3 (17.7 mg, 33% yield).

C₆₀H₈₀CoN₈Si₄
M.W.: 1084.61

IR (KBr): 2961, 2902, 1737, 1600, 1458, 1366, 1264, 1110, 838, 760, 689 cm⁻¹

MALDI-TOF MS (dithranol): 1083.54—1087.40 ([M⁺], isotopic pattern).
2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(trimethylsilyl)phthalocyaninate iron (II) \((\text{4a-4})\)

A 5-tert-butyl-3-(trimethylsilyl)phthalonitrile 3a (51.3 mg, 0.200 mmol), FeCl₂ (6.3 mg, 0.0500 mmol) and 1-chloronaphthalene (0.5 ml) were added to reaction flask under nitrogen atmosphere. Reaction mixture was stirred at 230 °C for 3 h. The reaction mixture was cooled, quenched by addition of water, and extracted with CH₂Cl₂ for 3 times. Combined organic solvent was washed with brine and dried over with Na₂SO₄. Solvent was removed under reduced pressure, the crude product was purified by column chromatography (Hex / AcOEt = 90 / 10) on silica gel to give 4a-4 (5.9 mg, 11% yield). C₄₄H₄₄FeN₈Si₄
M.W.: 1081.52
IR (KBr): 3734, 3648, 2957, 2353, 1479, 1367, 1327, 1268, 1100, 943, 889, 834, 760, 670, 620,
473, 423 cm\(^{-1}\)
MALDI-TOF MS (dithranol): 1078.45—1084.58 ([M\(^+\)], isotopic pattern).

\[
2,9,16,23\text{-tetrakis(methyl)-4,11,18,25-tetrakis(trimethylsilyl)}\text{phthalocyaninate zinc (II)} (8a)
\]

A 5-methyl-3-(trimethylsilyl)phthalonitrile 6a (50 mg, 0.233 mmol), Zn(OAc)\(_2\) (10.7 mg, 0.0583 mmol) and ethylene glycol (0.5 ml) were added to reaction flask under nitrogen atmosphere. Reaction mixture was stirred at 230 °C for 3 h. The reaction mixture was cooled, quenched by addition of water, and extracted with CH\(_2\)Cl\(_2\) for 3 times. Combined organic solvent was washed with brine and dried over with Na\(_2\)SO\(_4\). Solvent was removed under
reduced pressure, the crude product was purified by column chromatography (Hex / AcOEt = 90
/10) on silica gel to give 8a (7.5 mg, 14% yield). Continued elution of the silica gel gave 9a (5.8
mg, 12% yield).

C₄₈H₅₆N₈Si₄Zn

M.W.: 922.74

¹H NMR (CDCl₃, 300 MHz): δ = 1.13 (s, 36H), 3.01 (s, 12H), 8.22 (s, 4H), 9.42 (s, 4H)

IR (KBr): 2949, 2361, 1477, 1352 1311, 1251, 1217, 1113, 950, 891, 845, 747, 622 cm⁻¹

MALDI-TOF MS (dithranol): 919.11—927.22 ([M⁺], isotopic pattern).
2,9,16,23(24)-tetrakis(methyl)-4,11,18,25(22)-tris(trimethylsilyl)phthalocyaninate zinc (II) (9a)

C_{63}H_{48}N_{13}Si_{13}Zn
M.W.: 850.56

$^1$H NMR (CDCl$_3$, and Pyridine-$d_5$, 600 MHz): $\delta =$ 1.10—1.12 (m, 27H), 2.98 (s, 12H), 7.98—8.00 (m, 1H), 8.16 (s, 2.7H), 9.30—9.37 (m, 2H), 9.40 (s, 2H), 9.42 (d, $J = 6$Hz, 1.3H)

IR (KBr): 3734, 3648, 2921, 1716, 1598, 1478, 1309, 1218, 1104, 952, 887, 841, 748, 624 cm$^{-1}$

MALDI-TOF MS (dithranol): 847.69—853.68 ([M$^+$], isotopic pattern).
A 5-hexyl-3-(trimethylsilyl)phthalonitrile 6b (56.8 mg, 0.200 mmol), Zn(OAc)$_2$ (9.2 mg, 0.0500 mmol) and ethylene glycol (0.5 ml) were added to reaction flask under nitrogen atmosphere. Reaction mixture was stirred at 230 °C for 3 h. The reaction mixture was cooled, quenched by addition of water, and extracted with CH$_2$Cl$_2$ for 3 times. Combined organic solvent was washed with brine and dried over with Na$_2$SO$_4$. Solvent was removed under reduced pressure, the crude product was purified by column chromatography (Hex / AcOEt = 95 / 5) on silica gel to give 8b (9.3 mg, 15% yield). Continued elution of the silica gel gave 9b (6.7 mg, 12% yield).

C$_{68}$H$_{96}$N$_8$Si$_4$Zn
M.W.: 1203.28

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 0.99 (t, $J$ = 6.9 Hz, 12H), 1.14 (s, 36H), 1.45—1.56 (br, 16H), 1.66—1.68 (br 8H), 2.08—2.13 (br, 8H), 3.27 (br, 8H), 8.22 (s, 4H), 8.47 (s, 4H)

IR (KBr): 3735, 3649, 2925, 2853, 2366, 1598, 1475, 1320, 1246, 1117, 956, 891, 841, 750, 619, 425 cm$^{-1}$

MALDI-TOF MS (dithranol): 1197.54—1205.64 ([M$^+$], isotopic pattern).
2,9,16,23-tetrakis(hexyl)-4,11,18,25-tris(trimethylsilyl)phthalocyaninate zinc (II) (9b)

C$_{65}$H$_{88}$N$_8$Si$_3$Zn
M.W.: 1131.09

$^1$H NMR (CDCl$_3$, and Pyridine-$d_5$, 600 MHz): $\delta = 0.99$ (t, $J = 6$ Hz, 10H), 1.11—1.12 (m, 27H), 1.44—1.45 (m, 7.3H), 1.48—1.53 (m, 7.7H), 1.66—1.67 (m, 8.5H), 2.08—2.09 (m, 11.5H), 3.23—3.25 (m, 7H), 7.99 (d, 1.4H), 8.16 (s, 2.5H), 9.34—9.41 (m, 2.5H), 9.44 (br, 2.6H)
IR (KBr): 3648, 2927, 2855, 1685, 1557, 1457, 1318, 1248, 1104, 895, 841, 748 cm⁻¹
MALDI-TOF MS (dithranol): 1127.69—1132.94 ([M⁺], isotopic pattern).

2,9,16,23-tetrakis(tert-butyl) phthalocyaninate zinc (II) (C₄h₁)

2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(trimethylsilyl)phthalocyaninate zinc (II) 4a
(41.8 mg, 0.03831 mmol) was dissolved in conc. H₂SO₄ (5.0 ml), stirred at room temperature for 5 h. Reaction was neutralized by 1.0 M aqueous NaOH and extracted with Et₂O for 3 times. Combined organic phase was washed with brine and dried over Na₂SO₄. Solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel (Hex / Acetone = 85 / 15) to give C₄h₁ (21.2 mg, 69% yield).

C₂₈H₄₈N₈Zn
M.W.: 802.34

$^1$H NMR (CDCl$_3$ and Pyridine-$d_5$, 600 MHz): $\delta = 1.79$ (s, 36H), 8.26 (d, $J = 6.0$ Hz, 4H), 9.47 (d, $J = 6.0$ Hz, 4H), 9.55 (s, 4H)

$^{13}$C NMR (CDCl$_3$ and Pyridine-$d_5$, 150.9 MHz): $\delta = 32.0$, 35.9, 119.0, 122.4, 127.1, 136.4, 138.8, 153.0, 153.9, 154.1

IR (KBr): 3735, 3650, 3447, 2960, 2900, 2869, 2369, 2320, 1615, 1490, 1394, 1363, 1334, 1281, 1256, 1197, 1146, 923, 829, 764, 746, 692, 670, 527, 418 cm$^{-1}$

UV / Vis (CH$_2$Cl$_2$, 1.0 x 10$^{-5}$ M): $\lambda_{max}$ (log $\epsilon$) = 350 nm (4.87), 611 nm (4.57), 648 nm (4.54), 678 nm (5.34)

UV / Vis (CF$_3$Ph, 1.0 x 10$^{-5}$ M): $\lambda_{max}$ (log $\epsilon$) = 350 nm (4.77), 606 nm (4.46), 645 nm (4.42), 672 nm (5.26)

UV / Vis (dioxane, 1.0 x 10$^{-5}$ M): $\lambda_{max}$ (log $\epsilon$) = 349 nm (4.77), 606 nm (4.46), 645 nm (4.42), 672 nm (5.26)

Fluorescence (CH$_2$Cl$_2$): $\lambda_{em}$ = 683 nm, $\Phi_f$ = 0.49; (CF$_3$Ph) $\lambda_{em}$ = 681 nm, $\Phi_f$ = 0.50; (dioxane) $\lambda_{em}$ = 677 nm, $\Phi_f$ = 0.58

MALDI-TOF MS (dithranol): 799.22—805.23 ([M$^+$], isotopic pattern).
2,9,16(17),23(24)-tetrakis(tert-butyl)phthalocyaninate zinc (II) (I as a mixture of regioisomers)

\[
\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{Zn} \\
\text{N} \\
\text{N} \\
\text{N} \\
\text{tBu} \\
\end{array}
\]

2,9,16,23(24)-tetrakis(tert-butyl)-4,11,18-tris(trimethylsilyl)phthalocyaninate zinc (II) 5a (15.3 mg, 0.0150 mmol) was dissolved in conc. H₂SO₄ (3.0 ml), stirred at room temperature for 5 h. Reaction was neutralized by 1.0 M aqueous NaOH and extracted with Et₂O for 3 times. Combined organic phase was washed with brine and dried over Na₂SO₄. The crude product was purified by column chromatography on silica gel (Hex / Acetone = 85 / 15) to give I as a mixture of regioisomers (8.4 mg, 70% yield).

C₅₅H₄₈N₈Zn
M.W.: 802.34

¹H NMR (CDCl₃ and Pyridine-d₅, 600 MHz): ¹H = 1.79 ¹.80 (m, 36H), 8.26 (d, J = 12 Hz, 4H), 9.45 (dd, J = 27 Hz, 6 Hz, 1.5H), 9.45 (dd, J = 24Hz, 6 Hz, 1.5H), 9.46 (d, J = 12 Hz, 1.5H), 9.55 (s, 2H), 9.57 (s, 1.5H)

IR (KBr): 3300, 2957, 2920, 2854, 1607, 1491, 1325, 1259, 1089, 922, 833, 760, 689 cm⁻¹

MALDI-TOF MS (dithranol): 799.70—806.74 ([M⁺], isotopic pattern).
7. $^1$H NMR and $^{13}$C NMR spectra
$^{1}$$H$ NMR (CDCl$_3$)

3a

$^{1}$$H$ NMR (CDCl$_3$)

3b

$^{1}$$H$ NMR (CDCl$_3$)
$6a$
$^1H$ NMR (CDCl$_3$)

$6b$
$^1H$ NMR (CDCl$_3$)
$^{1}H$ NMR (CDCl$_3$)

$^{1}H$ NMR (CDCl$_3$ and Pyridine-$d_5$)
$^{1}\text{H NMR (CDCl}_3\text{)}$

$4b$

$^{1}\text{H NMR (CDCl}_3\text{)}$

$4a-2$

$^{1}\text{H NMR (CDCl}_3\text{)}$
$^{1}H$ NMR (CDCl$_3$ and Pyridine-d$_5$)

Mixture of regioisomers 1
$^{1}H$ NMR (CDCl$_3$ and Pyridine-d$_5$)
$^{13}$C NMR spectra

$^{13}$C NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

3a

3b

$^{13}$C NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

**6a**

$^{13}$C NMR (CDCl$_3$)

**6b**

$^{13}$C NMR (CDCl$_3$)
8. UV/Vis spectra of phthalocyanine

**Figure S3.** UV/Vis spectra of 2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(trimethylsilyl)phthalocyaninate zinc (II) 4a in 1.0 × 10^{-5} M (blue: CH2Cl2, pink: CF3Ph, green: dioxane)

**Table S2.** Result of UV/Vis spectra of 2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(trimethylsilyl)phthalocyaninate zinc (II) 4a

| Concentration  | λ (nm) | ε (M^{-1} cm^{-1}) |
|---------------|--------|---------------------|
| 1.0 × 10^{-5} M in CH2Cl2, (blue) | 347 (4.82) | 615 (4.50) | 656 (4.51) | 683 (5.28) |
| 1.0 × 10^{-5} M in CF3Ph, (pink) | 347 (4.79) | 614 (4.47) | 654 (4.46) | 681 (5.26) |
| 1.0 × 10^{-4} M in dioxane, (green) | 351 (4.87) | 612 (4.52) | 651 (4.53) | 678 (5.31) |
Figure S4. UV/Vis spectra of 2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(triethylsilyl)phthalocyaninate zinc (II) 4b in 1.0 × 10⁻⁵ M (blue: CH₂Cl₂, pink: CF₃Ph, green: dioxane)

| Table S3. Result of UV/Vis spectra of 2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(triethylsilyl)phthalocyaninate zinc (II) 4b |
|---|---|---|---|---|---|
| 1.0 × 10⁻³ M in CH₂Cl₂, (blue) | 351 (4.77) | 616 (4.42) | 656 (4.51) | 684 (5.19) | 734 (4.75) |
| 1.0 × 10⁻² M in CF₃Ph, (pink) | 355 (4.85) | 615 (4.57) | 656 (4.55) | 682 (5.34) |
| 1.0 × 10⁻⁴ M in dioxane, (green) | 353 (4.94) | 612 (4.64) | 650 (4.61) | 678 (5.39) |
Figure S5. UV/Vis spectra of 2,9,16,23-tetrakis(tert-butyl)phthalocyaninate zinc (II) $C_{4h}$-I in 1.0 $\times$ 10$^{-5}$ M (blue: CH$_2$Cl$_2$, pink: CF$_3$Ph, green: dioxane)

Table S4. Result of UV/Vis spectra of 2,9,16,23-tetrakis(tert-butyl)phthalocyaninate zinc (II) $C_{4h}$-I

| Concentration | Wavelength | Absorbance |
|---------------|-------------|-------------|
| 1.0 $\times$ 10$^{-5}$ M in CH$_2$Cl$_2$, (blue) | 350 (4.87) | 611 (4.57) | 648 (4.54) | 678 (5.34) |
| 1.0 $\times$ 10$^{-5}$ M in CF$_3$Ph, (pink) | 350 (4.70) | 609 (4.40) | 645 (4.37) | 676 (5.20) |
| 1.0 $\times$ 10$^{-5}$ M in dioxane, (green) | 349 (4.77) | 606 (4.46) | 645 (4.42) | 672 (5.26) |
9. Steady-state emission spectra of phthalocyanines

Figure S6. Steady-state emission spectra of 2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(trimethylsilyl)phthalocyaninate zinc (II) 4a in 1.0 × 10⁻⁵ M (blue: CH₂Cl₂, pink: CF₃Ph, green: dioxane)

Table S5. Result of steady-state emission spectra of 2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(trimethylsilyl)phthalocyaninate zinc (II) 4a

| Medium          | λ_{em} (nm) | Φ_t  |
|-----------------|------------|------|
| CH₂Cl₂ (blue)   | 684        | 0.38 |
| CF₃Ph (pink)    | 683        | 0.40 |
| dioxane (green) | 681        | 0.41 |
**Figure S7.** Steady-state emission spectra of 2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(triethylsilyl)phthalocyaninate zinc (II) 4b in 1.0 × 10^{-5} M (blue: CH_{2}Cl_{2}, pink: CF_{3}Ph, green: dioxane)

**Table S6.** Result of steady-state emission spectra of 2,9,16,23-tetrakis(tert-butyl)-4,11,18,25-tetrakis(triethylsilyl)phthalocyaninate zinc (II) 4b

|     | λ_{em} (nm) | Φ_t   |
|-----|-------------|-------|
| CH_{2}Cl_{2} (blue) | 737   | 0.20  |
| CF_{3}Ph (pink)     | 685   | 0.36  |
| dioxane (green)     | 682   | 0.46  |
Figure S8. Steady-state emission spectra of 2,9,16,23-tetrakis(tert-butyl)phthalocyaninate zinc (II) $C_{4h}$-1 in $1.0 \times 10^{-5}$ M (blue: CH$_2$Cl$_2$, pink: CF$_3$Ph, green: dioxane)

Table S7. Result of steady-state emission spectra of 2,9,16,23-tetrakis(tert-butyl)phthalocyaninate zinc (II) $C_{4h}$-1

|          | $\lambda_{em}$ (nm) | $\Phi_t$ |
|----------|---------------------|----------|
| CH$_2$Cl$_2$ (blue) | 683                 | 0.49     |
| CF$_3$Ph (pink)     | 681                 | 0.50     |
| dioxane (green)     | 677                 | 0.58     |
10. UV/Vis ATR spectra of \( C_{4h} \)-1 of thin film

**Figure S9.** UV/Vis ATR spectra of \( C_{4h} \)-1 of thin film (green: s-polarized light; light green: p-polarized light), conventional 1 of thin film (blue: s-polarized light; light blue: p-polarized light).

**Table S8.** Result of UV/Vis ATR spectra of \( C_{4h} \)-1 and conventional 1

|                        | Q-band (nm) |
|------------------------|-------------|
| \( C_{4h} \)-1 (green: s-polarized light) | 689         |
| \( C_{4h} \)-1 (light green: p-polarized light) | 685         |
| conventional 1 (blue: s-polarized light blue) | 686         |
| conventional 1 (light blue: p-polarized light blue) | 685         |