Supporting Information

Synthesis of meso-Azulenylporphyrins

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General Procedure. All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. Diethylamine and toluene were dried over CaH₂. ¹H-NMR spectra and ¹³C-NMR spectra were recorded on a JEOL ECA-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to CHCl₃ (δ = 7.260 and 77.00 for ¹H-NMR spectra and ¹³C-NMR spectra respectively). The spectroscopic grade CH₂Cl₂ was used as solvent for all spectroscopic studies. UV/Vis absorption spectra were recorded on a Shimadzu UV-3150 spectrometer and Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5300 PC spectrofluorophotometer. Mass spectra were recorded on a JEOL HX-110 spectrometer, using positive-FAB ionization method with accelerating voltage 10 kV and a 3-nitrobenzylalcohol matrix. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-300). Redox potentials were measured by the cyclic voltammetry method on an ALS electrochemical model 660.

5-bromo-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (5)

5,10,15-Tris(3,5-di-*tert*-butylphenyl)porphyrin (277 mg, 0.291 mmol) was dissolved in $CHCl_3$ (150 mL). To the solution pyridine (1 mL) and NBS (52 mg, 0.292 mmol) were added at 0 °C and the mixture was stirred for 30 min. The solvent was evaporated and the product was isolated by column chromatography on silica gel (hexane/AcOEt = 5/1 as eluent). **5** was obtained by precipitation from a mixture of MeOH and CH_2Cl_2 (252 mg, 91% yield).

¹H-NMR (CDCl₃): $\delta = -2.68$ (2H, s, NH), 1.50 (18H, s, *tert*-Bu), 1.53 (36H, s, *tert*-Bu),

7.77 (1H, t, J = 1.8 Hz, p-H of phenyl), 7.80 (2H, t, J = 1.8 Hz, p-H of phenyl), 8.02 (2H, d, J = 1.8 Hz, o-H of phenyl), 8.05 (4H, d, J = 1.8 Hz, o-H of phenyl), 8.85 (4H, s, β -H of pyrrole), 8.93 (2H, d, J = 5.0 Hz, β -H of pyrrole), 9.67 (2H, d, J = 5.0 Hz, β -H of pyrrole); FAB MS: calcd for C₆₂H₇₃BrN₄: 952.5; found: 952.5 [M⁺].

Zn^{II} 5-(1-azulenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (1)

5-Bromo-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin **5** (100 mg, 0.105 mmol), **6** (50 mg, 0.15 mmol), dichlorobis(triphenylphosphine) palladium(II) (7.4 mg, 0.0105 mmol) and barium hydroxide octahydrate (100 mg, 0.317 mmol) were dissolved in DME/H₂O (50/1, 15 mL) under argon atmosphere. The reaction mixture was warmed to 80 °C and stirred for 2 h. The solvent was evaporated and the coupling product **7** was isolated by column chromatography on silica gel (hexane/AcOEt = 5/1 as eluent). The crude **7** was used for the next step without further purification. **7** was dissolved in polyphosphoric acid at 80 °C. The solution was neutralized with 1 M NaOH aqueous solution and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄ and concentrated to give **8**. Then **8** was treated with zinc(II) acetate in CHCl₃/MeOH, washed with water and brine, and dried over anhydrous Na₂SO₄. After the evaporation of the solvent, **1** was obtained by precipitation from a mixture of MeOH and CH₂Cl₂ (76.0 mg, 68% yield).

8 (freebase); ¹H-NMR (CDCl₃): δ = -2.49 (2H, s, NH), 1.51 (18H, s, *tert*-Bu), 1.52 (18H, s, *tert*-Bu), 1.54 (9H, s, *tert*-Bu), 6.96 (1H, t, J = 9.9 Hz, 5- or 7-H of azulene), 7.37 (1H, t, J = 9.9 Hz, 5- or 7-H of azulene), 7.65 (1H, t, J = 9.9 Hz, 6-H of azulene), 7.78 (2H, s, *p*-H of phenyl), 7.80 (1H, s, *p*-H of phenyl), 7.84 (1H, d, J = 3.7 Hz, 3-H of azulene), 8.06 (2H, s, *o*-H of phenyl), 8.10 (2H, m, *o*-H of phenyl), 8.12-8.14 (3H, m, *o*-H of phenyl and 8-H of azulene), 8.63 (2H, d, J = 4.1 Hz, β-H of pyrrole), 8.73 (1H, d, J = 9.6 Hz, 4-H of azulene), 8.80-8.81 (3H, m, β-H of pyrrole and 2-H of azulene), and 8.90 (4H, s, β-H of pyrrole); ¹³C-NMR (CDCl₃): δ = 31.74, 35.03, 114.43, 116.03, 120.90, 120.94, 121.31, 121.46, 123.53, 123.59, 129.61, 129.70, 129.83, 131.41, 137.67, 137.93, 141.26, 141.29, 141.38, 141.90, 144.00, and 148.65; UV (CH₂Cl₂): λ_{max} (ε) = 422 (303000), 521 (17000), 563 (13000), 595 (7000), and 653 (7000) nm; FAB MS: calcd for C₇₂H₈₀N₄: 1000.6; found: 1000.7 [M⁺].

1; ¹H-NMR (CDCl₃): δ = 1.52 (18H, s, *tert*-Bu), 1.53 (18H, s, *tert*-Bu), 1.54 (9H, s, *tert*-Bu), 1.55 (9H, s, *tert*-Bu), 6.95 (1H, t, J = 9.6 Hz, 5- or 7-H of azulene), 7.37 (1H, t, J = 9.9 Hz, 5- or 7-H of azulene), 7.64 (1H, t, J = 9.6 Hz, 6-H of azulene), 7.79 (2H, t, J = 1.8 Hz, *p*-H of phenyl), 7.81 (1H, t, J = 1.8 Hz, *p*-H of phenyl), 7.85 (1H, d, J = 3.7 Hz, 3-H of azulene), 8.09 (2H, t, J = 1.8 Hz, *o*-H of phenyl), 8.11 (1H, t, J = 1.8 Hz, *o*-H of phenyl), 8.13-8.14 (3H, m, *o*-H of phenyl), 8.15 (1H, d, J = 10.1 Hz, 8-H of azulene), 8.74 (1H, d, J = 10.1 Hz, 4-H of azulene), 8.75 (2H, d, J = 4.6 Hz, β-H of pyrrole), 8.80 (1H, d, J = 3.7 Hz, 2-H of azulene), 8.92 (2H, d, J = 4.6 Hz, β-H of pyrrole), 9.02 (2H, d, J = 4.6 Hz, β-H of pyrrole), 1³C-NMR (CDCl₃): δ = 31.75, 35.03, 115.53, 115.96, 120.71, 120.76, 122.40, 122.57, 123.41, 129.52, 129.59, 129.64, 129.74, 132.03, 132.12, 132.13, 132.20, 137.71, 137.84, 137.88, 141.20, 141.75, 141.85, 141.90, 144.00, 148.49, 148.51, 150.29, 150.43, and 151.64; UV (CH₂Cl₂): λ_{max} (ε) = 424 (357000), 553 (28000), and 594 (12000) nm; FAB MS: calcd for C₇₂H₇₈N₄Zn: 1062.6; found: 1062.6 [M⁺].



Zn^{II} 5-(2-azulenyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (2)

5-Bromo-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (100 mg, 0.105 mmol), **9** (40 mg, 0.157 mmol), dichlorobis(triphenylphosphine) palladium(II) (7.4 mg, 0.0105 mmol) and barium hydroxide octahydrate (100 mg, 0.317 mmol) were dissolved in DME/H₂O (50/1) 15 mL under argon atmosphere. The reaction mixture was warmed up to 80 °C and stirred for 2 h. The solvent was evaporated and the product **10** was

separated by column chromatography on silica gel (hexane/AcOEt=5/1 as eluent). Then **10** was treated with zinc(II) acetate in CHCl₃/MeOH, washed with water and brine, and dried over anhydrous Na₂SO₄. After the evaporation of the solvent, **2** was obtained by precipitation from a mixture of MeOH and CH₂Cl₂ (78.7 mg, 70% yield).

10 (freebase); ¹H-NMR (CDCl₃): $\delta = -2.53$ (2H, s, NH), 1.53 (54H, s, *tert*-Bu), 7.46 (2H, t, J = 9.9 Hz, 5,7-H of azulene), 7.79 (3H, s, *p*-H of phenyl), 7.80 (1H, t, J = 10.1 Hz, 6-H of azulene), 8.09 (2H, d, J = 1.4 Hz, *o*-H of phenyl), 8.10 (4H, d, J = 1.4 Hz, *o*-H of phenyl), 8.36 (2H, s, 1,3-H of azulene), 8.67 (2H, d, J = 9.2 Hz, 4,8-H of azulene), 8.89 (2H, d, J = 5.0 Hz, β -H of pyrrole), 8.90 (4H, s, β -H of pyrrole), and 9.02 (2H, d, J = 4.6 Hz, β -H of pyrrole); ¹³C-NMR (CDCl₃): $\delta = 31.74$, 35.04, 116.26, 120.94, 120.96, 121.48, 121.61, 124.17, 125.74, 129.66, 129.82, 130.97, 137.00, 137.21, 139.27, 141.31, 141.36, 148.67, and 152.25; UV (CH₂Cl₂): λ_{max} (ϵ) = 427 (350000), 523 (18000), 565 (18000), 595 (8500), and 657 (8500) nm; FAB MS: calcd for C₇₂H₈₀N₄: 1000.6; found: 1000.7 [M⁺].

2; ¹H-NMR (CDCl₃): $\delta = 1.54$ (54H, s, *tert*-Bu), 7.45 (2H, t, J = 9.6 Hz, 5,7-H of azulene), 7.79 (1H, t, J = 10.1 Hz, 6-H of azulene), 7.80 (3H, t, J = 1.8 Hz, *p*-H of phenyl), 8.12 (2H, d, J = 1.8 Hz, *o*-H of phenyl), 8.13 (4H, d, J = 1.8 Hz, *o*-H of phenyl), 8.37 (2H, s, 1,3-H of azulene), 8.67 (2H, d, J = 9.2 Hz, 4,8-H of azulene), 9.02 (2H, d, J = 4.6 Hz, β -H of pyrrole), 9.03 (4H, s, β -H of pyrrole), and 9.14 (2H, d, J = 4.6 Hz, β -H of pyrrole); ¹³C-NMR (CDCl₃): $\delta = 31.76$, 35.04, 117.32, 120.78, 120.73, 122.70, 122.53, 124.10, 125.68, 129.57, 129.69, 132.06, 132.18, 132.40, 136.84, 137.06, 139.18, 141.86, 148.51, 150.13, 150.17, 150.28, 150.46, and 152.98; UV (CH₂Cl₂): λ_{max} (ϵ) = 428 (380000), 554 (27000), and 598 (13000) nm; FAB MS: calcd for C₇₂H₇₈N₄Zn: 1062.6; found: 1062.6 [M⁺].



Figure S2. ¹H-NMR spectrum of **2** in CDCl₃

5-(4-pyridyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (12)

3,5-Di-*tert*-butylbenzaldehyde (2.62 g, 12 mmol), 4-pyridinecarboxaldehyde (0.75 mL, 7.9 mmol), and pyrrole (1.4 mL, 20 mmol) were condensed in refluxing propionic acid (50 mL) for 2h. The acid was evaporated and the product was separated by column chromatography on silica gel (CHCl₃ as eluent). **12** was obtained by precipitation from a mixture of MeOH and CH_2Cl_2 (260 mg, 6% yield).

¹H-NMR (CDCl₃): $\delta = -2.71$ (2H, s, NH), 1.53 (18H, s, *tert*-Bu), 1.53 (36H, s, *tert*-Bu), 7.80-7.81 (3H, m, *p*-H of phenyl), 8.07 (2H, d, J = 1.8 Hz, *o*-H of phenyl), 8.08 (4H, d, J = 1.8 Hz, *o*-H of phenyl), 8.19 (2H, dd, $J_1 = 4.1$ Hz, $J_2 = 1.8$ Hz, 3,5-H of pyridyl), 8.79 (2H, d, J = 4.6 Hz, β-H of pyrrole), 8.91 (4H, s, β-H of pyrrole), 8.93 (2H, d, J =5.0 Hz, β-H of pyrrole), 9.03 (2H, dd, $J_1 = 4.1$ Hz, $J_2 = 1.4$ Hz, 2,6-H of pyridyl); FAB MS: calcd for C₆₇H₇₇N₅: 951.6; found: 951.6 [M⁺].

Typical procedure of the conversion from pyridine moiety to azulene (Ziegler-Hafner method)

5-(4-Pyridyl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (50 mg, 0.053 mmol) was dissolved in toluene (15 mL). Trifluoromethanesulfonic anhydride (0.10 mL, 0.59 mmol) was added to the solution at 0 °C and the mixture was stirred for 5 min. To the reaction mixture, diethylamine (0.2 mL, 1.9 mmol) and sodium cyclopentadienide (0.6 mL, 2 M THF solution) were added at room temperature and then the mixture was refluxed for 10 h. The solvent was evaporated and the product **14** was isolated by

column chromatography on silica gel (hexane/AcOEt=5/1 as eluent). Then it was treated with zinc(II) acetate in CHCl₃/MeOH, washed with water and brine, and dried over anhydrous Na₂SO₄. After the evaporation of the solvent, **4** was obtained by precipitation from a mixture of MeOH and CH₂Cl₂.

13 (freebase); ¹H-NMR (CDCl₃): $\delta = -2.62$ (2H, s, NH), 1.52 (36H, s, *tert*-Bu), 1.52 (18H, s, *tert*-Bu), 7.43 (1H, t, J = 9.9 Hz, 7-H of azulene), 7.52 (1H, d, J = 3.2 H, 1-H of azulene), 7.69 (1H, d, J = 3.2 Hz, 3-H of azulene), 7.78-7.80 (3H, m, *p*-H of phenyl), 8.07-8.09 (6H, m, *o*-H of phenyl), 8.13 (1H, t, J = 3.7 Hz, 2-H of azulene), 8.61 (1H, d, J = 10.1 Hz, 6-H of azulene), 8.74 (1H, d, J = 9.6 Hz, 8-H of azulene), 8.85 (2H, d, J = 4.6 Hz, β-H of pyrrole), 8.88 (2H, d, J = 4.6 Hz, β-H of pyrrole), 8.90 (4H, s, β-H of pyrrole), and 9.38 (1H, s, 4-H of azulene); ¹³C-NMR (CDCl₃): $\delta = 31.73$, 35.04, 118.63, 119.55, 119.89, 121.01, 121.60, 121.64, 121.88, 129.66, 129.78, 129.81, 136.57, 136.62, 136.80, 138.25, 140.81, 141.15, 141.28, 141.86, 142.47, 148.71, and 148.74; UV (CH₂Cl₂): λ_{max} (ε) = 426 (400000), 520 (22000), 557 (13000), 595 (8100), and 652 (8100) nm; FAB MS: calcd for C₇₂H₈₀N₄: 1000.6; found: 1000.7 [M⁺].

3; Yield: 10%; ¹H-NMR (CDCl₃): δ = 1.52 (36H, s, *tert*-Bu), 1.53 (18H, s, *tert*-Bu), 7.43 (1H, t, J = 9.9 Hz, 7-H of azulene), 7.50 (1H, d, J = 3.2 H, 1-H of azulene), 7.69 (1H, d, J = 3.7 Hz, 3-H of azulene), 7.78-7.80 (3H, m, *p*-H of phenyl), 8.09-8.10 (6H, m, *o*-H of phenyl), 8.12 (1H, t, J = 3.7 Hz, 2-H of azulene), 8.63 (1H, d, J = 10.1 Hz, 6-H of azulene), 8.75 (1H, d, J = 9.2 Hz, 8-H of azulene), 8.96 (2H, d, J = 4.6 Hz, β-H of pyrrole), 8.99 (2H, d, J = 4.6 Hz, β-H of pyrrole), 9.01 (4H, s, β-H of pyrrole), and 9.39 (1H, s, 4-H of azulene); ¹³C-NMR (CDCl₃): δ = 31.73, 35.03, 111.07, 114.67, 117.08, 118.45, 119.35, 119.68, 119.72, 119.79, 120.81, 122.93, 129.57, 129.65, 129.68, 131.68, 132.26, 132.33, 132.51, 136.72, 137.16, 138.15, 141.73, 141.76, 141.78, 142.30, 148.54, 150.34, 150.43, 150.57, and 150.61; UV (CH₂Cl₂): λ_{max} (ε) = 428 (410000), 552 (25000), and 592 (8400) nm; FAB MS: calcd for C₇₂H₇₈N₄Zn: 1062.6; found: 1062.6 [M⁺].



Figure S3. ¹H-NMR spectrum of **3** in CDCl₃

14 (freebase); ¹H-NMR (CDCl₃): $\delta = -2.63(2H, s, NH)$, 1.52 (36H, s, *tert*-Bu), 1.52 (18H, s, *tert*-Bu), 7.70 (2H, d, J = 4.1 Hz, 1,3-H of azulene), 7.78-7.79 (3H, m, *p*-H of phenyl), 8.07-8.08 (6H, m, *o*-H of phenyl), 8.13 (1H, t, J = 3.7 Hz, 2-H of azulene), 8.20 (2H, d, J = 9.6 Hz, 5,7-H of azulene), 8.59 (2H, d, J = 9.6 Hz, 4,8-H of azulene), 8.83 (2H, d, J = 4.6 Hz, β-H of pyrrole), 8.87 (2H, d, J = 4.6 Hz, β-H of pyrrole), and 8.89 (4H, s, β-H of pyrrole); ¹³C-NMR (CDCl₃): $\delta = 31.73$, 35.04, 119.27, 121.04, 121.65, 121.89, 121.93, 129.65, 129.75, 130.12, 133.33, 137.72, 139.67, 141.12, 141.26, 148.70, 148.74, and 151.60; UV (CH₂Cl₂): λ_{max} (ε) = 425 (370000), 519 (23000), 556 (13000), 595 (7800), and 650 (7800) nm; FAB MS: calcd for C₇₂H₈₀N₄: 1000.6; found: 1000.7 [M⁺]

4; Yield: 55%; ¹H-NMR (CDCl₃): δ = 1.53 (36H, s, *tert*-Bu), 1.53 (18H, s, *tert*-Bu), 7.70 (2H, d, J = 3.7 Hz, 1,3-H of azulene), 7.79-7.80 (3H, m, *p*-H of phenyl), 8.10 (6H, d, J = 1.8 Hz, *o*-H of phenyl), 8.13 (1H, t, J = 3.9 Hz, 2-H of azulene), 8.22 (2H, d, J = 10.1 Hz, 5,7-H of azulene), 8.60 (2H, d, J = 10.1 Hz, 4,8-H of azulene), 8.94 (2H, d, J = 4.6 Hz, β-H of pyrrole), 8.99 (2H, d, J = 4.6 Hz, β-H of pyrrole), 9.01 (2H, d, J = 4.6 Hz, β-H of pyrrole), and 9.02 (2H, d, J = 4.6 Hz, β-H of pyrrole); ¹³C-NMR (CDCl₃): δ = 31.74, 35.03, 119.14, 120.84, 122.70, 122.92, 123.03, 129.57, 129.62, 130.07, 131.48, 132.21, 132.34, 132.53, 133.27, 137.56, 139.65, 141.71, 141.76, 148.57, 149.58, 150.34, 150.48, 150.65, and 152.29; UV (CH₂Cl₂): λ_{max} (ε) = 427 (473000), 551 (32000), and 590 (8700) nm; FAB MS: calcd for C₇₂H₇₈N₄Zn: 1062.6; found: 1062.6 [M⁺]



Figure S4. ¹H-NMR spectrum of 4 in CDCl₃



Figure S5. ¹H-NMR spectra in low field (1-4). Assignments of the protons have been done by extensive 2D-COSY experiments.

Tetrakis(6-azulenyl)porphyrin (16)

Tetra(4-pyridyl)porphyrin (100 mg, 0.162 mmol) and 1-chloro-2,4-dinitrobenzene (288 mg, 1.42 mmol) were dissolved in CHCl₃/MeOH (4/1, 15 mL) and the mixture was refluxed for 3 days. Diethylamine (1.5 mL, 14.5 mmol) was added to the reaction mixture at room temperature, and it was stirred for 2 days. The solvent was evaporated and the residue was dissolved in toluene (15 mL). Sodium cyclopentadienide (1.0 mL, 2M THF solution) was added and then the mixture was refluxed for 3 days. The solvent was evaporated and the product was separated by column chromatography on silica gel

(CH₂Cl₂ as eluent). The product was recrystallized from MeOH and CH₂Cl₂.

Yield: 1%; ¹H-NMR (CDCl₃): $\delta = -2.54$ (2H, s, NH), 7.70 (8H, d, J = 4.1 Hz, 1,3-H of azulene), 8.14 (8H, d, J = 10.1 Hz, 5,7-H of azulene), 8.14 (4H, m, 2-H of azulene), 8.59 (8H, d, J = 10.1 Hz, 4,8-H of azulene), and 8.84 (8H, s, β -H of pyrrole); UV (CH₂Cl₂): $\lambda_{max} = 443$, 525, 561, 597, and 653 nm; FAB MS: calcd for C₆₀H₃₈N₄: 814.3; found: 814.3 [M⁺].



Figure S6. ¹H-NMR spectrum of **16** in CDCl₃



Figure S7. (a, b) Fluorescence spectra of 1-4 and 17 taken for excitation at 428 nm in CH_2Cl_2 .