Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

A Quadruply Azulene-fused Porphyrin with Intense Near IR Absorption and Large Two-photon Absorption Cross Section

Kei Kurotobi, Kil Suk Kim, Su Bum Noh, Dongho Kim, and Atsuhiro Osuka**

S1. Detailed experimental procedures

General Procedure. All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. ^{1}H NMR spectra were recorded on a JEOL ECA-600 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.260). The spectroscopic grade CH_2Cl_2 and $CHCl_3$ were used as solvent for all spectroscopic studies. UV/Vis absorption spectra were recorded on a Shimadzu UV-3150 spectrometer and Shimadzu UV-2550 spectrometer. Mass spectra were recorded on a BRUKER micro-TOF spectrometer. Preparative separations were performed by silica gel gravity column chromatography (Wako gel C-200 and C-300). Cyclic voltammogram was obtained with an ALS model 660 voltammetry analyzer versus ferrocene/ferrocenium ion couple. Melting points were measured on Yanaco MICRO MELTIG POINT APPARATUS MP-S3.

4-Formyl-1-methoxycarbonylazulene (3a): 1-Methoxycarbonyl-4-methylazulene (100 mg, 0.50 mmol) and *N*,*N*-dimethylformamide dimethylacetal (0.10 mL, 0.75 mmol) were dissolved in DMF (0.5 mL), and the mixture was stirred at 140 ºC for 1 h. The reaction mixture was cooled to room temperature and concentrated. The residue was purified by column chromatography (alumina, CH_2Cl_2 as an eluent) to get reddish 1-methoxycarbonyl-4-(dimethylaminoethenyl) azulene. Yield: 88%. This product (50 mg, 0.196 mmol) and sodium periodate (126 mg, 0.589 mmol) were added to a mixed solvent (THF/H_2O = 1/1, 1.0 mL) and the reaction mixture was stirred at room temperature for 1 day. After the mixture was filtered, the filtrate was washed with saturated $NaHCO_3$ aqueous solution. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, hexane/AcOEt = 2/1 as an eluent) to get green solid. Yield: 92%; ^{1}H NMR ($CDCl_3$): 3.98 (3H, s, CO_2CH_3), 7.73 (1H, t, *J* = 9.4 Hz, 7-H of azulene), 7.95-8.00 (2H, m, 5-H and 6-H of azulene), 8.17 (1H, d, *J* = 4.1 Hz, 3-H of azulene), 8.62 (1H, d, *J* = 4.1 Hz, 2-H of azulene), 9.81 (1H, d, *J* = 9.6 Hz, 8-H of azulene), and 10.90 ppm (1H, s, CHO). m.p.: 126-127 °C.

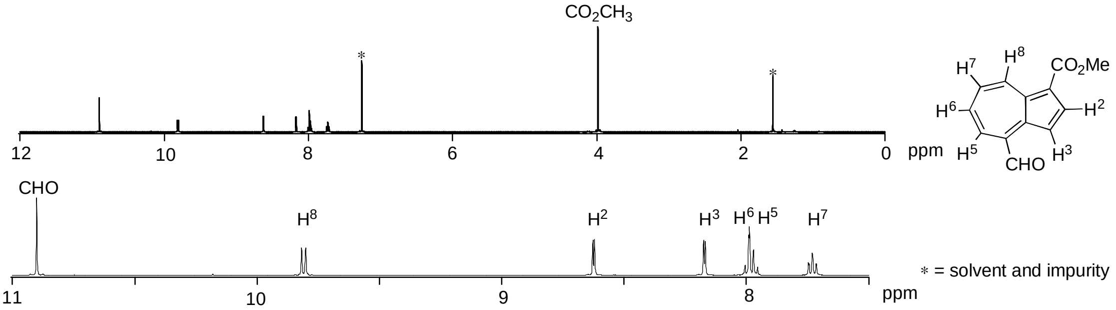

Figure S1. ^{1}H NMR spectrum of **3a**

4-Formyl-1-octyloxycarbonylazulene (3b): 4-Methyl-1-azulene carboxylic acid (650 mg, 3.49 mmol), triethylamine (0.511 mL, 3.67 mmol) and 1-bromooctane (0.603 mL, 3.49 mmol) were dissolved in DMF. The mixture was stirred for 6 h at 60 °C. The reaction was quenched with water and the resulting mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, hexane/AcOEt = 5/1) to get 4-methyl-1-octyloxycarbonylazulene as violet oil. Yield: 67%. 1-Octyloxycarbonyl-4-methylazulene (850 mg, 2.85 mmol) and *N,N*-dimethylformamide dimethylacetal (0.60 mL, 4.5 mmol) were dissolved in DMF (3 mL), and the mixture was stirred at 140 °C for 1 h. The reaction mixture was cooled to room temperature and concentrated. The residue was purified by column chromatography (alumina, CH_2Cl_2 as an eluent) to get reddish 1-

octyloxycarbonyl-4-(dimethylaminoethenyl) azulene. This product and sodium periodate (1.83 g, 8.56 mmol) were added to a mixed solvent (THF/H_2O = 1/1, 50 mL) and the mixture was stirred at room temperature for 16 h. After the mixture was filtered, the filtrate was washed with saturated $NaHCO_3$ aqueous solution. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, hexane/AcOEt = 5/1 as an eluent) to get desired compound as green solid. Yield: 75%. : ^{1}H NMR ($CDCl_3$): 0.89 (3H, t, *J* = 6.9 Hz, methyl), 1.28-1.52 (10H, m, methylene), 1.84 (2H, f, *J* = 7.1 Hz, methylene), 4.39 (2H, t, *J* = 6.7 Hz, methylene), 7.69-7.74 (1H, m, 7-H of azulene), 7.93-8.00 (2H, m, 5-H and 6-H of azulene), 8.16 (1H, d, *J* = 4.4 Hz, 3-H of azulene), 8.63 (1H, d, *J* = 4.2 Hz, 2-H of azulene), 9.81 (1H, d, *J* = 9.8 Hz, 8-H of azulene), and 10.90 ppm (1H, s, CHO). m.p.: 59-61 °C.

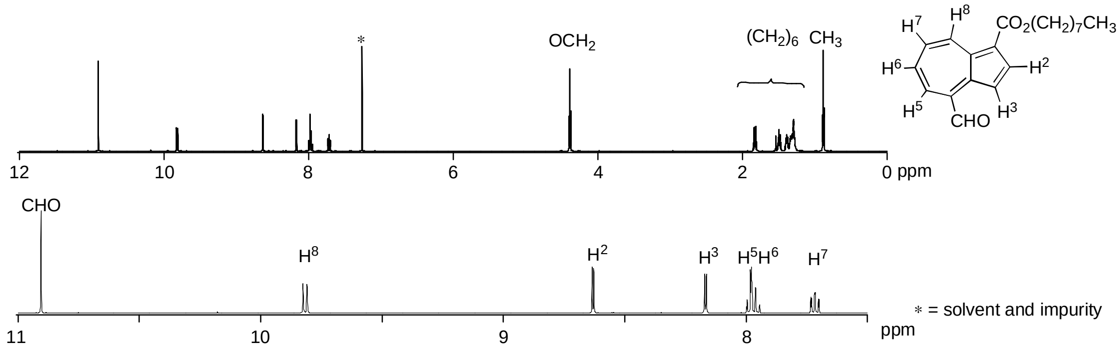

Figure S2. ^{1}H NMR spectrum of **3b**

4-Formyl-1-(2,4,6-tri-*tert*-butylphenoxycarbonyl)-azulene (3c): 4-Methyl-1-azulene carboxylic acid (558 mg, 3.00 mmol), 2,4,6-tri-*tert*-butylphenol (1.55 g, 5.91 mmol) and trifluoroacetic anhydride (0.846 mL, 6.00 mmol) were dissolved in benzene (8 mL). The mixture was stirred at room temperature for 2 days. The reaction was quenched with 2M KOH aqueous solution and the resulting mixture was extracted with ether. The organic layer was washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (silica gel, hexane / AcOEt = 5 / 1 as an eluent) to get 4-methyl-1-(2,4,6-tri-*tert*-butylphenoxycarbonyl)azulene as purple solid. Yield: 38%. 4-Methyl-1-(2,4,6-tri-*tert*-butylphenoxycarbonyl)azulene (493 mg, 1.14 mmol) and *N*,*N*-dimethylformamide dimethylacetal (0.227 mL, 1.71 mmol) were dissolved in DMF (5 mL), and the mixture was stirred at 140 °C for 1 h. The reaction mixture was cooled to room temperature and concentrated. The residue was purified by column chromatography (alumina, CH_2Cl_2 as an eluent) to get reddish 4-(dimethylaminoethenyl)-1-(2,4,6-tri-*tert*-butylphenoxycarbonyl)azulene. This product and sodium periodate (732 mg, 3.42 mmol) were added to a mixed solvent (THF / H_2O = 1 / 1, 20 mL) and the mixture was stirred at room temperature for 1 day. After the mixture was filtered, the filtrate was washed with saturated $NaHCO_3$ aqueous solution. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, hexane / AcOEt = 8 / 1 as an eluent) to get desired compound as green solid. Yield: 45%. ^{1}H NMR ($CDCl_3$): 1.36 (9H, s, *tert*-butyl), 1.38 (18H, s, *tert*-butyl), 7.41 (2H, s, *m*-H of phenyl), 7.75 (1H, dt, *J* = 9.6, 1.4 Hz, 5-H of azulene), 8.00-8.06 (2H, m, 6-H and 7-H of azulene), 8.30 (1H, d, *J* = 4.1 Hz, 3-H of azulene), 8.86 (1H, d, *J* = 4.1 Hz, 2-H of azulene), 9.91 (1H, d, *J* = 9.6 Hz, 8-H of azulene), and 10.94 ppm (1H, s, CHO). m.p.: 218-219 °C.

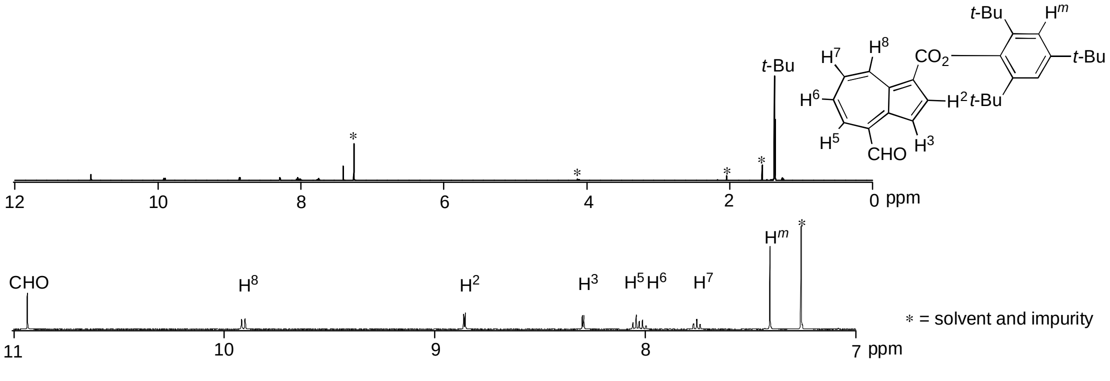

Figure S3. ^{1}H NMR spectrum of **3c**

(1-Methoxycarbonylazulen-4-yl)dipyrromethane (4a): 1-Methoxycarbonyl-4-formylazulene (30 mg, 0.140 mmol) was dissolved in pyrrole (2.0 mL) and TFA (1.0 mL) was added. After the reaction mixture was stirred for 30 min at room temperature, the reaction was quenched with 1 M NaOH aqueous solution. The mixture was extracted with ether, and the organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (silica gel, hexane/AcOEt = 3/1 as an eluent) to get purple solid. Yield: 94%; ^{1}H NMR ($CDCl_3$): 3.93 (3H, s, CO_2CH_3), 5.98 (2H, s, pyrrole), 6.17 (2H, d, *J* = 2.3 Hz, pyrrole), 6.46 (1H, s, CH), 6.71 (2H, s, pyrrole), 7.40 (1H, d, *J* = 10.1 Hz, 5-H of azulene), 7.44-7.48 (2H, m, 3-H and 7-H of azulene), 7.71 (1H, t, *J* = 10.1 Hz, 6-H of azulene), 8.15 (2H, s, NH), 8.27 (1H, d, *J* = 4.1 Hz, 2-H of azulene), and 9.69 ppm (1H, d, *J* = 9.6 Hz, 8-H of azulene). m.p.: 189-190 °C.

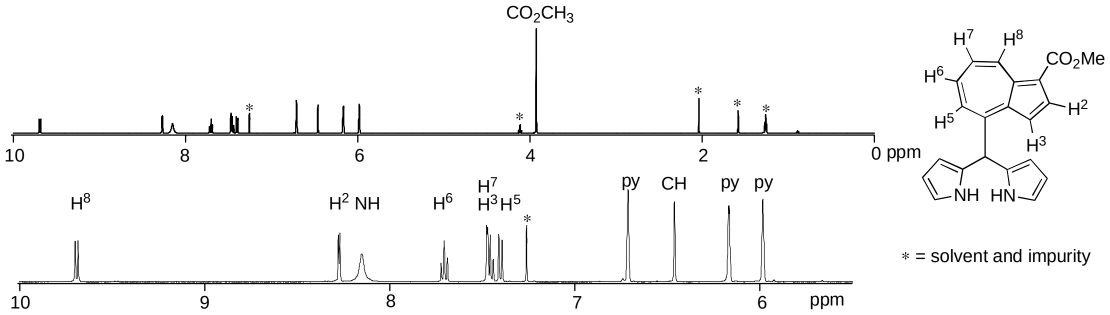

Figure S4. ^{1}H NMR spectrum of **4**

Ni^{II} 5-(1-Methoxycarbonylazulen-4-yl)-10,15,20-tris(3,5-di-*tert*-butylphenyl)porphyrin (6): Dipyrromethanes **4** (155 mg, 0.469 mmol) and **5** (157 mg, 0.469 mmol) and 3,5-di-*tert*-butylbenzaldehyde (205 mg, 0.939 mmol) were dissolved in CH_2Cl_2 (180 mL) under nitrogen atmosphere. TFA (0.14 mL, 1.8 mmol) was added to the mixture. The reaction mixture was stirred for 4 h at room temperature. *p*-Chloranil (461 mg, 1.87 mmol) was added, and the resulting solution was stirred for 18 h at room temperature. The reaction mixture was passed through a short alumina column to remove tarry material. The solvent was evaporated and the product was isolated by column chromatography on silica gel (hexane/AcOEt = 5/1 as an eluent). Ni^{II}-metallation was achieved upon treatment with $Ni(acac)_2$ in toluene at 110 °C. Yield: 16%; ^1H NMR ($CDCl_3$): 1.45 (36H, s, *tert*-butyl), 1.48 (18H, s, *tert*-butyl), 3.95 (3H, s, CO_2CH_3), 6.08 (1H, d, J = 4.1 Hz, 3-H of azulene), 7.70 (2H, s, *p*-H of phenyl), 7.72 (1H, s, *p*-H of phenyl), 7.85 (1H, t, J = 10.1 Hz, 7-H of azulene), 7.97 (1H, t, J = 9.9 Hz, 6-H of azulene), 8.02 (1H, d, J = 4.6 Hz, 2-H of azulene), 8.30 (1H, d, J = 10.1 Hz, 5-H of azulene), 8.48 (2H, d, J = 5.0 Hz, *b*-H of pyrrole), 8.70 (2H, d, J = 5.0 Hz, *b*-H of pyrrole), 8.80 (2H, d, J = 4.6 Hz, *b*-H of pyrrole), 8.82 (2H, d, J = 4.6 Hz, *b*-H of pyrrole), and 10.04 ppm (1H, d, J = 10.1 Hz, 8-H of azulene). The *o*-Ph protons were observed as very broad peak around 7.80 ppm. UV/Vis ($CHCl_3$): l_{max} (e) = 293 (47000), 422 (180000), and 533 (18000) nm; ESI-TOF MS: calcd for $C_{74}H_{80}N_4NiO_2$: 1114.6; found: 1114.5 [M^+]. m.p.: > 300 °C.

Ni^{II} 5,15-bis(1-Methoxycarbonylazulen-4-yl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (7): (1-Methoxycarbonylazulen-4-yl)dipyrromethane (155 mg, 0.469 mmol) and 3,5-di-*tert*-butylbenzaldehyde (103 mg, 0.472 mmol) were dissolved in CH_2Cl_2 (90 mL) under nitrogen atmosphere. TFA (0.070 mL, 0.90 mmol) was added to the mixture. The reaction mixture was stirred for 6 h at room temperature. *p*-Chloranil (461 mg, 1.87 mmol) was added, and the resulting solution was stirred for 10 h at room temperature. The resulting mixture was passed through a short alumina column. The solvent was evaporated and the product was isolated by column chromatography on silica gel (hexane/AcOEt = 5/1 as eluent). Ni^{II}-metallation was achieved upon treatment with $Ni(acac)_2$ in toluene at 110 °C. The porphyrin product was obtained as a mixture of atropisomers. Yield: 15%; ^1H NMR ($CDCl_3$): 1.43 (72H, s, *tert*-butyl), 3.95 (6H, s, CO_2CH_3), 3.97 (6H, s, CO_2CH_3), 5.97 (2H, d, J = 4.1 Hz, 3-H of azulene), 6.24 (2H, *J* = 4.1 Hz, 3-H of azulene), 7.69 (2H, s, *p*-H of phenyl), 7.84-7.89 (6H, m, 7-H of azulene and *p*-H of phenyl), 7.96 (2H, t, *J* = 9.9 Hz, 6-H of azulene), 8.02 (2H, d, *J* = 4.6 Hz, 2-H of azulene), 8.02 (2H, t, *J* = 9.9 Hz, 6-H of azulene), 8.08 (2H, d, *J* = 4.6 Hz, 2-H of azulene), 8.17 (2H, d, *J* = 10.1 Hz, 5-H of azulene), 8.42 (2H, d, *J* = 9.6 Hz, 5-H of azulene), 8.49 (4H, d, *J* = 5.0 Hz, *b*-H of pyrrole), 8.52 (4H, d, *J* = 5.0 Hz, *b*-H of pyrrole), 8.70 (4H, d, *J* = 5.0 Hz, *b*-H of pyrrole), 8.71 (4H, d, *J* = 5.0 Hz, *b*-H of pyrrole), 10.05 (2H, d, *J* = 10.1 Hz, 8-H of azulene) and 10.06 (2H, d, *J* = 9.6 Hz, 8-H of azulene). The *o*-Ph protons were observed as very broad peak around 7.70 ppm. UV/Vis ($CHCl_3$): l_{max} (*e*) = 295 (85000), 426 (160000), and 534 (21000) nm; ESI-TOF MS: calcd for $C_{72}H_{68}N_4NiO_4$: 1110.5; found: 1110.5 [M^+]. m.p.: > 300 °C.

Ring-closure reaction of 4-azulenylporphyrins. To a solution of **6** (10 mg, 0.0090 mmol) in CH_2Cl_2 (5 mL) was added a solution of $FeCl_3$ (7.3 mg, 0.045 mmol) in nitromethane (1 mL) and the resulting mixture was stirred for 5 min at room temperature. The reaction was quenched by addition of a saturated $NaHCO_3$ solution. The resulting mixture was extracted with CH_2Cl_2 and the organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated and the product was isolated by column chromatography on silica gel (hexane/AcOEt = 5/1 as eluent). Fused product **9** was obtained by precipitation from a mixture of MeOH and CH_2Cl_2. **9**: Yield: 63%; ^{1}H NMR ($CDCl_3$): 1.44 (18H, s, *tert*-butyl), 1.49 (36H, s, *tert*-butyl), 4.04 (3H, s, CO_2CH_3), 7.67 (1H, s, *p*-H of phenyl), 7,70 (1H, s, *p*-H of phenyl), 7.74 (1H, s, *p*-H of phenyl), 7.77 (1H, t, *J* = 9.6 Hz, 7-H of azulenyl), 8.02 (1H, d, *J* = 10.1 Hz, 5-H of azulenyl), 8.29 (1H, t, *J* = 10.3 Hz, 6-H of azulenyl), 8.47 (1H, d, *J* = 4.6 Hz, *b*-H of pyrrole), 8.57 (1H, d, *J* = 5.0 Hz, *b*-H of pyrrole), 8.58 (1H, d, *J* = 4.6 Hz, *b*-H of pyrrole), 8.61 (1H, d, *J* = 5.0 Hz, *b*-H of pyrrole), 8.67 (1H, s, 2-H of azulene), 8.72 (1H, d, *J* = 5.0 Hz, *b*-H of pyrrole), 8.89 (1H, s, *b*-H of pyrrole), 8.92 (1H, d, *J* = 4.6 Hz, *b*-H of pyrrole), and 9.83 ppm (1H, d, *J* = 9.6 Hz, 8-H of azulene). The *o*-Ph protons were observed as a very broad peak around 7.70 ppm. UV/Vis ($CHCl_3$): l_{max} (*e*) = 467 (73000), 526 (27000, sh), 633 (10000), 695 (14000), and 890 (1300) nm; ESI-TOF MS: calcd for $C_{74}H_{78}N_4NiO_2$: 1112.5; found: 1112.5 [M^+]. m.p.: > 300 °C.

The reaction of **7** was carried out under the similar conditions of **6** (10 equiv. of $FeCl_3$ was used).

10: Yield: 84%; ^1H NMR ($C_2D_2Cl_4$, 140 °C): 1.58 (36H, s, *tert*-butyl), 4.08 (6H, s, CO_2CH_3), 7.79 (2H, t, *J* = 9.4 Hz, 7-H of azulene), 7.83 (2H, s, *p*-H of phenyl), 7.91 (4H, s, *o*-H of phenyl), 8.09 (2H, d, *J* = 10.5 Hz, 5-H of azulene), 8.29 (2H, t, *J* = 10.1 Hz, 6-H of azulene), 8.52 (2H, s, 2-H of azulene), 8.56 (2H, d, *J* = 5.0 Hz, *b*-H of pyrrole), 8.77 (2H, d, *J* = 4.6 Hz, *b*-H of pyrrole), 8.86 (2H, s, *b*-H of pyrrole), and 9.81 ppm (2H, d, *J* = 9.6 Hz, 8-H of azulene); UV/Vis ($CHCl_3$): l_{max} (*e*) = 402 (47000), 487 (72000), 545 (62000), 632 (11000), 763 (25000), 898 (19000), and 1014 (19000) nm; ESI-TOF MS: calcd for $C_{72}H_{64}N_4NiO_4$: 1106.4; found: 1106.5 [M^+]. m.p.: > 300 °C.

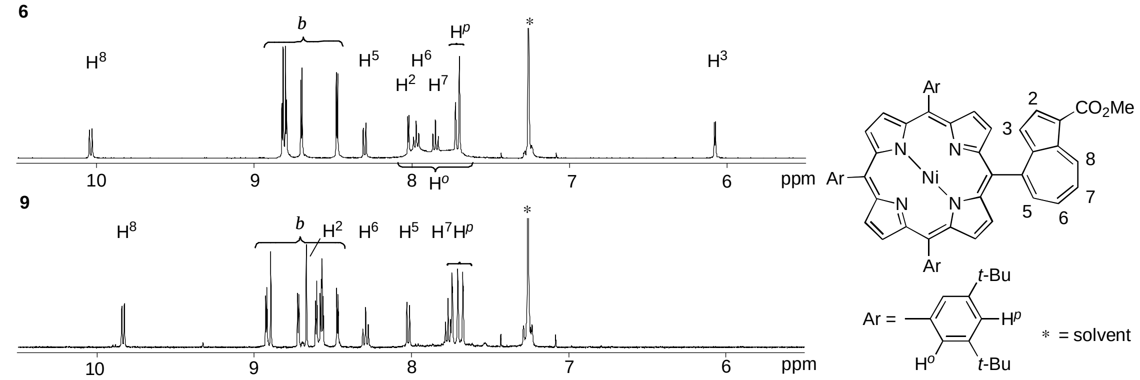

Figure S5. ^1H NMR spectra of **6** and **9**

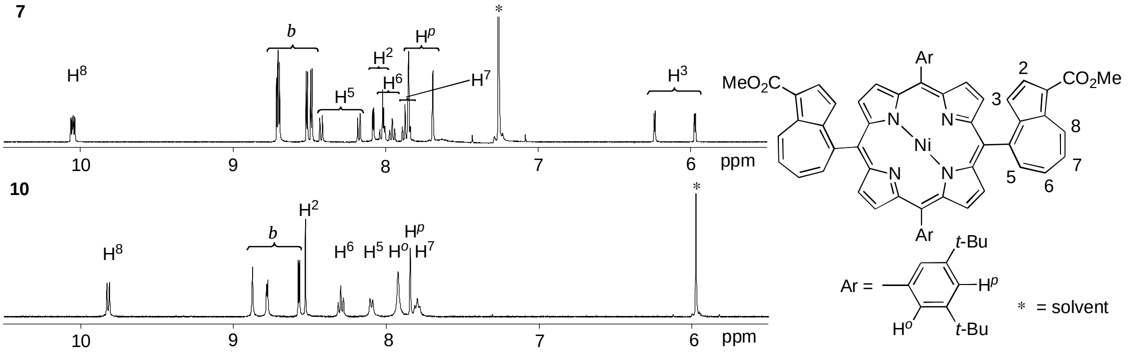

Figure S6. ^{1}H NMR spectra of **7** and **10**

Ni^{II} 5,10,15,20-Tetrakis[1-(2,4,6-tri-*tert*-butylphenoxycarbonyl)-azulen-4-yl]porphyrin (8c) and its fused compound 11. To a solution of **4c** (228 mg, 0.514 mmol) and pyrrole (0.036 mL, 0.519 mmol) in $CHCl_3$ (52 mL) was added $BF_3{\cdot}OEt_2$(0.022 mL, 0.174 mmol) under nitrogen atmosphere. After the reaction mixture was stirred for 9.5 h at room temperature, *p*-chloranil (126 mg, 0.512 mmol) was added, and the resulting solution was stirred for 10 h. The mixture was passed through a short alumina column and the solvent was evaporated. The product was isolated by column chromatography on silica gel (hexane/AcOEt=5/1 as an eluent). Ni^{II}-metallation was achieved upon treatment with Ni(acac)$_2$ in toluene at 110 °C. The porphyrin **8** was obtained as a mixture of atropisomers. Yield 12%. **8**: UV/Vis ($CHCl_3$): l_{max} (e) = 295 (160000), 383 (70000), 437 (140000), 539 (23000), and 573 (20000) nm

To a solution of **8** (4.0 mg, 0.0020 mmol) in CH_2Cl_2 (3 mL) was added a solution of $FeCl_3$ (7.0 mg, 0.043 mmol) in nitromethane (1 mL). The resulting solution was stirred for 30 min at room temperature. The reaction was quenched by addition of a saturated $NaHCO_3$ solution, and the product was extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The product was isolated by column chromatography on silica gel (hexane/AcOEt=5/1 as an eluent). Yield 60%. **11**:

^{1}H NMR ($CDCl_3$): 1.39 (36H, s, *tert*-butyl), 1.42 (36H, s, *tert*-butyl), 1.53 (36H, s, *tert*-butyl), 7.40 (4H, s, *m*-H of phenyl), 7.43 (4H, s, *m*-H of phenyl), 7.93 (4H, t, *J* = 9.4 Hz, 7H of azulene), 8.45 (4H, t, *J* = 9.9 Hz, 6H of azulene), 8.64 (4H, d, *J* = 10.1 Hz, 5H of azulene), 8.74 (4H, s, 2-H of azulene), 9.12 (4H, s, *b*-H of pyrrole), and 9.89 ppm (4H, d, *J* = 9.6 Hz, 8-H of azulene); UV/Vis ($CHCl_3$): l_{max} (e) = 338 (90000), 400 (77000), 574 (43000, sh), 684 (65000), 1000 (29000), and 1136 (54000) nm; ESI-TOF MS: calcd for $C_{136}H_{140}N_4NiO_8$: 2017.0057; found: 2017.0052 [M^+]. m.p.: > 300 °C.

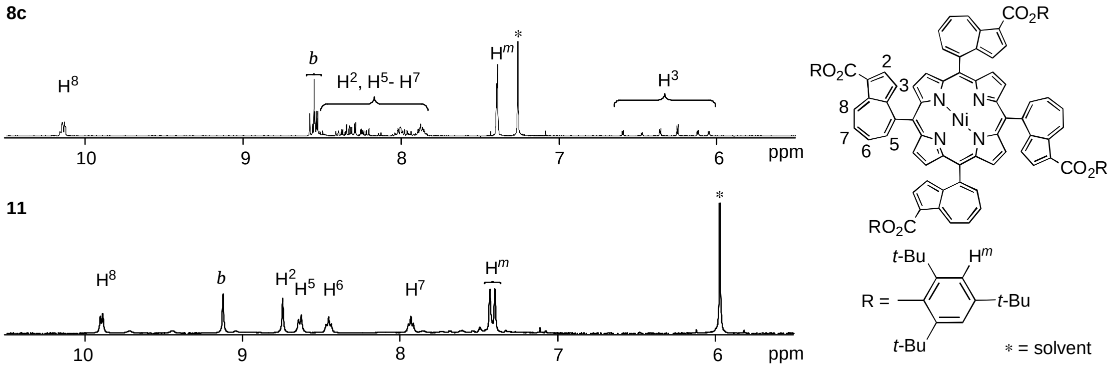

Figure S7. ^{1}H NMR spectra of **8c** and **11**.

S2. Cyclic voltammograms of NiTDBPP, 6, 9, 10, and 11.

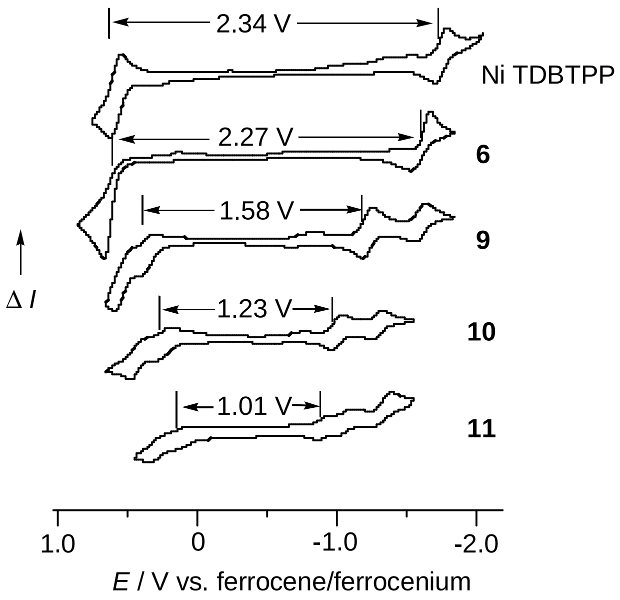

Figure S8. Conditions; benzonitrile, tetrabutylammonium perchlorate, Pt working electrode, Pt counter electrode, versus ferrocene/ferrocenium ion couple.

S3. Two-photon absorption cross-section measurements of 9, 10, and 11.

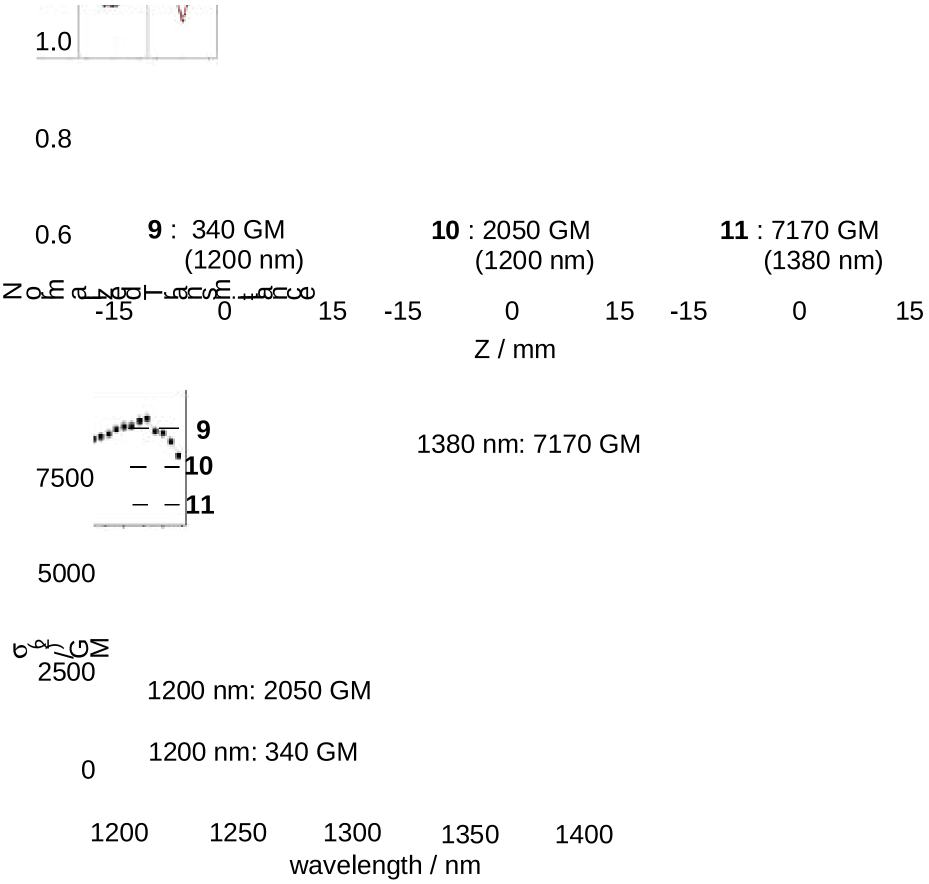

Figure S9. The open aperture Z-scan traces (circles) of **9, 10**, and **11** and two-photon absorption spectra in toluene measured under the same experimental conditions. The sample concentration is 0.250 mM. The peak irradiance at the focal point is 60 GW/cm^2. The solid lines are the best fitted curves of experimental data.

S4. Excited-state decays of 9, 10, and 11.

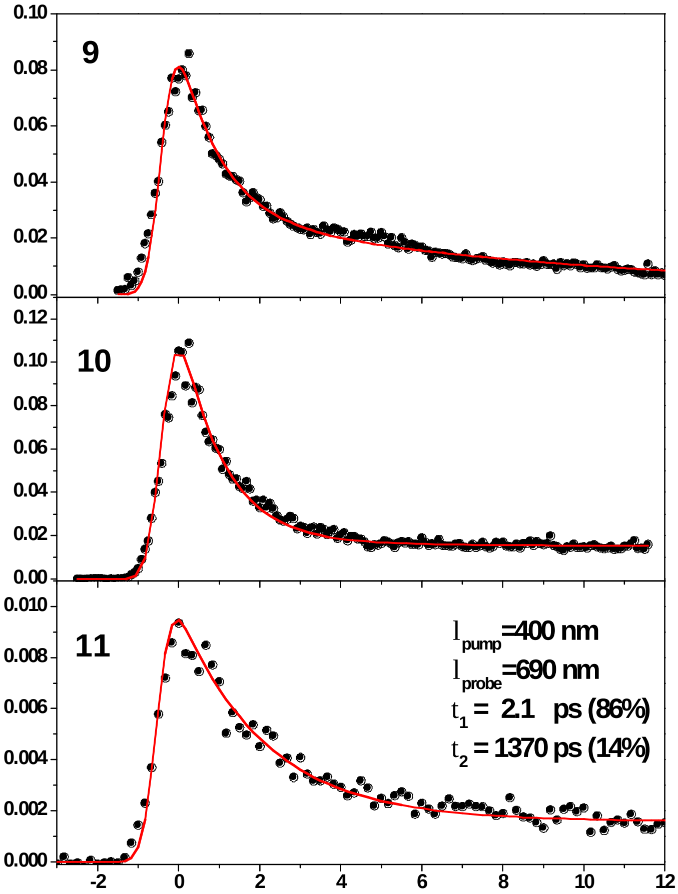

Figure S10. Transient absorption decays of **9**, **10**, and **11** measured by picosecond time-resolved laser-system. Each decay following a biexponential functions with a fast decay component (1-2 ps) and a relatively slow component.