Enhancing low-energy absorption band and charge mobility of antiaromatic Ni^{II} norcorroles by their substituents effects

Takuya Yoshida,^a Daisuke Sakamaki,^b Shu Seki^b and Hiroshi Shinokubo^{*a}

^aDepartment of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan ^bDepartment of Molecular Engineering, Graduate School of Engineering, Kyoto University,

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Table of Contents

S 2
S2
S 5
S 8
\$15
516
517
520
\$21

Instrumentation and Materials

¹H NMR (500 MHz), ¹³C NMR (126 MHz) and ¹⁹F NMR (470 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer. Chemical shifts were reported as the delta scale in ppm relative to CDCl₃ (δ = 7.26 ppm) for ¹H NMR and CDCl₃ (δ = 77.16 ppm) for ¹³C NMR and hexafluorobenzene (δ = -164.90 ppm, external standard) for ¹⁹F NMR. UV/vis/NIR absorption spectra were recorded on a JASCO V670 spectrometer. Mass spectra were recorded on a Bruker microTOF using ESI-TOF method for acetonitrile solutions. X-ray data were taken on a Bruker D8 QUEST X-ray diffractometer equipped with PHOTON 100 CMOS active pixel sensor detector and IµS microfocus source using Mo-K α radiation (λ = 0.71073 Å) or a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics using graphite monochromated Mo-K α radiation (λ = 0.71075 Å). Redox potentials were measured by cyclic voltammetry method on an ALS electrochemical analyzer model 612C. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General Procedures

 α, α' -Dibromodipyrrins **4a**-**4f** (Scheme S1a) were used for the synthesis of dissymmetric α, α' -dibromodipyrrin Ni^{II} complexes **3e**-**3i** (Scheme S1b). Dipyrrins **4c**-**4f** were synthesized according to modified literature procedures.¹⁻⁴



Scheme S1. (a) Structures of α, α' -dibromodipyrrins 4a–4f and (b) synthesis of dissymmetric Ni^{II} complexes 3e–3i.

meso-4-Dimethylaminophenyl-α,α'-dibromodipyrrin 4a

A two-necked flask containing *meso*-4-dimethylaminophenyl-dipyrromethane⁵ (1.04 g, 3.92 mmol) was evacuated and then refilled with N₂. To the flask, dry THF (55 mL) was added and the solution was cooled to -78 °C. After *N*-bromosuccinimide (1.40 g, 7.87 mmol) was added to the solution in two portions at a 30 min interval, the mixture was stirred for 1 h. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 891 mg, 3.93 mmol) was added in three portions every 15 min. The resulting mixture was stirred at -78 °C for 10 min and then warmed to room temperature. After stirring for additional 1 h, the reaction mixture was filtered through a short pad of alumina column (CH₂Cl₂ as an eluent) and then evaporated. Purification by silica-gel column chromatography (CH₂Cl₂ as an eluent) afforded the title compound **4a** in 50% (825 mg, 1.96 mmol) as a red solid.

meso-4-Cyanonophenyl-α,α'-dibromodipyrrin 4b

A two-necked flask containing *meso-*4-cyanophenyl-dipyrromethane⁶ (1.24 g, 5.01 mmol) was evacuated and then refilled with N₂. To the flask, dry THF (70 mL) was added and the solution was cooled to -78 °C. After *N*-bromosuccinimide (1.78 g, 10.0 mmol) was added to the solution in two portions at a 30 min interval, the mixture was stirred for 1 h. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.14 g, 5.02 mmol) was added in two portion at a 30 min interval. The resulting mixture was stirred at -78 °C for 10 min then warmed to room temperature. After stirring for additional 1 h, the reaction mixture was filtered through a short pad of alumina column (CH₂Cl₂ as an eluent) and then evaporated. Purification by silica-gel column chromatography (CH₂Cl₂/hexane = 1/1 as an eluent) afforded the title compound **4b** in 80% (1.61 mg, 3.99 mmol) as an orange solid.

Dissymmetric α,α'-dibromodipyrrin Ni^{II} complex 3e

Ni^{II} acetate tetrahydrate (175 mg, 0.703 mmol) dissolved in CH₂Cl₂/MeOH (10 mL/10 mL) was slowly added to a CH₂Cl₂/MeOH (40 mL/10 mL) solution of **4a** (295 mg, 0.700 mmol) and **4e**³ (294 mg, 0.700 mmol) and the mixture was stirred for 1 h at room temperature. After the solvent was removed, silica-gel column chromatography (CH₂Cl₂/hexane = 2/3 as an eluent) was performed to collect the second eluting band. The residue after evaporation was washed with MeOH and the title compound **3e** was obtained in 35% (222 mg, 0.247 mmol) as a green solid.

Dissymmetric α, α' -dibromodipyrrin Ni^{II} complex 3f

 Ni^{II} acetate tetrahydrate (125 mg, 0.502 mmol) dissolved in CH₂Cl₂/MeOH (7 mL/7 mL) was slowly added to a CH₂Cl₂/MeOH (30 mL/7 mL) solution of **4a** (211 mg, 0.501 mmol) and **4f**⁴ (189 mg, 0.500 mmol) and the mixture was stirred for 1 h at room temperature. After the solvent was removed, silica-gel column chromatography (CH₂Cl₂/hexane = 1/1 as an eluent) was performed to collect the second eluting band. The residue after evaporation was washed with MeOH, and the title compound **3f** was obtained in 29% (124 mg, 0.145 mmol) as a green solid.

Dissymmetric α,α'-dibromodipyrrin Ni^{II} complex 3g

 Ni^{II} acetate tetrahydrate (125 mg, 0.502 mmol) dissolved in CH₂Cl₂/MeOH (7 mL/7 mL) was slowly added to a CH₂Cl₂/MeOH (30 mL/7 mL) solution of **4a** (211 mg, 0.501 mmol) and **4b** (202 mg, 0.501 mmol), and the mixture was stirred for 1 h at room temperature. After the solvent was removed, silica-gel column chromatography (CH₂Cl₂/hexane = 2/1 as an eluent) was performed to collect the second eluting band. The residue after evaporation was washed with MeOH, and the title compound **3g** was obtained in 40% (177 mg, 0.201 mmol) as a green solid.

Dissymmetric α, α' -dibromodipyrrin Ni^{II} complex 3h

Ni^{II} acetate tetrahydrate (187 mg, 0.751 mmol) dissolved in CH₂Cl₂/MeOH (11 mL/11 mL) was slowly added to a CH₂Cl₂/MeOH (54 mL/16 mL) solution of **4a** (316 mg, 0.750 mmol) and **4c**¹ (386 mg, 0.751 mmol), and the mixture was stirred for 1 h at room temperature. After the solvent was removed, silica-gel column chromatography (CH₂Cl₂/hexane = 1/1 as an eluent) was performed to collect the second eluting band. The residue after evaporation was washed with MeOH, and the title compound **3h** was obtained in 37% (274 mg, 0.276 mmol) as a green solid.

Dissymmetric α, α' -dibromodipyrrin Ni^{II} complex 3i

Ni^{II} acetate tetrahydrate (175 mg, 0.703 mmol) dissolved in CH₂Cl₂/MeOH (10 mL/10 mL) was slowly added to a CH₂Cl₂/MeOH (40 mL/10 mL) solution of **4a** (295 mg, 0.700 mmol) and **4d**² (328 mg, 0.701 mmol), and the mixture was stirred for 1 h at room temperature. After the solvent was removed, silica-gel column chromatography (CH₂Cl₂/hexane = 1/1 as an eluent) was performed to collect the second eluting band. The residue after evaporation was washed with MeOH, and the title compound **3i** was obtained in 38% (254 mg, 0.269 mmol) as a green solid.

Dissymmetric norcorrole 2e

Dipyrrin complex **3e** (89.8 mg, 0.100 mmol), bis(1,5-cyclooctadiene)nickel (68.8 mg, 0.250 mmol) and 2,2'-bipyridyl (39.0 mg, 0.250 mmol) were dissolved in dehydrated THF (8 mL) and the solution was stirred for 2 h at room temperature inside a glove box. After taking out the flask of the glove box, the reaction mixture was filtered through a short pad of alumina column (CH₂Cl₂ as an eluent) immediately and then evaporated. The residue was purified by silica-gel column chromatography (CH₂Cl₂/hexane = 1/1 as an eluent) and the collected blue band was concentrated and washed with hexane. Recrystallization from CH₂Cl₂/acetonitrile afforded the title compound **2e** in 35% (20.5 mg, 35.4 µmol) as a dark purple solid.

Dissymmetric norcorrole 2f

Dipyrrin complex **3f** (85.6 mg, 0.100 mmol), bis(1,5-cyclooctadiene)nickel (68.8 mg, 0.250 mmol) and 2,2'-bipyridyl (39.0 mg, 0.250 mmol) were dissolved in dehydrated THF (8 mL) and the solution was stirred for 2 h at room temperature inside a glove box. After taking out the flask of the glove box, the reaction mixture was filtered through a short pad of alumina column (CH_2Cl_2 as an eluent) immediately and then

evaporated. The residue was purified by silica-gel column chromatography (CH_2Cl_2 /hexane = 1/1 as an eluent) and the collected blue band was concentrated and washed with hexane. Recrystallization from CH_2Cl_2 /acetonitrile afforded the title compound **2f** in 45% (24.4 mg, 45.5 µmol) as a dark purple solid.

Dissymmetric norcorrole 2g

Dipyrrin complex **3g** (88.1 mg, 0.100 mmol), bis(1,5-cyclooctadiene)nickel (68.8 mg, 0.250 mmol) and 2,2'-bipyridyl (39.0 mg, 0.250 mmol) were dissolved in dehydrated THF (8 mL) and the solution was stirred for 2 h at room temperature inside a glove box. After taking out the flask of the glove box, the reaction mixture was filtered through a short pad of alumina column (CH₂Cl₂ as an eluent) immediately and then evaporated. The residue was purified by silica-gel column chromatography (CH₂Cl₂/hexane = 4/1 as an eluent) and the collected blue band was concentrated and washed with hexane and a small amount of CH₂Cl₂. The title compound **2g** was obtained in 29% (16.1 mg, 28.7 µmol) as a dark purple solid.

Dissymmetric norcorrole 2h

Dipyrrin complex **3h** (99.2 mg, 0.100 mmol), bis(1,5-cyclooctadiene)nickel (68.8 mg, 0.250 mmol) and 2,2'-bipyridyl (39.0 mg, 0.250 mmol) were dissolved in dehydrated THF (8 mL) and the solution was stirred for 2 h at room temperature inside a glove box. After taking out the flask of the glove box, the reaction mixture was filtered through a short pad of alumina column (CH₂Cl₂ as an eluent) immediately and then evaporated. The residue was purified by silica-gel column chromatography (CH₂Cl₂/hexane = 1/2 as an eluent) and the collected green band was concentrated and washed with hexane. Recrystallization from CH₂Cl₂/acetonitrile afforded the title compound **3h** in 25% (16.5 mg, 24.5 µmol) as a dark purple solid.

Dissymmetric norcorrole 2i

Dipyrrin complex **3i** (94.6 mg, 0.100 mmol), bis(1,5-cyclooctadiene)nickel (68.8 mg, 0.250 mmol) and 2,2'-bipyridyl (39.0 mg, 0.250 mmol) were dissolved in dehydrated THF (8 mL) and the solution was stirred for 2 h at room temperature inside a glove box. After taking out the flask of the glove box, the reaction mixture was filtered through a short pad of alumina column (CH₂Cl₂ as an eluent) immediately and then evaporated. The residue was purified by silica-gel column chromatography (CH₂Cl₂/hexane = 2/1 as an eluent) and the collected green band was concentrated and washed with hexane. Recrystallization from CH₂Cl₂/hexane afforded the title compound **2i** in 15% (15.3 mg, 15.3 µmol) as a dark purple solid.

Compounds Data

meso-4-Dimethylaminophenyl-a,a'-dibromodipyrrin 4a

¹H NMR (500 MHz, CDCl₃): δ 12.54 (brs, ¹H, NH), 7.37 (d, J = 8.9 Hz, 2H, aryl), 6.74 (d, J = 8.9 Hz, 2H, aryl), 6.63 (d, J = 4.2 Hz, 2H, β-H), 6.35 (d, J = 4.2 Hz, 2H, β-H), 3.05 (s, 6H, NMe₂) ppm. ¹³C NMR (126 MHz, CDCl₃): δ 151.6, 141.3, 140.3, 133.1, 130.3, 128.1, 123.2, 119.8, 111.2, 40.4 ppm. HR-MS (ESI-MS): m/z = 421.9686, calcd for (C₁₇H₁₆Br₂N₃)⁺ = 421.9686 [(M + H)⁺].

meso-4-Cyanonophenyl-α,α'-dibromodipyrrin 4b

¹H NMR (500 MHz, CDCl₃): δ 12.37 (brs, 1H, NH), 7.76 (d, J = 8.5 Hz, 2H, aryl), 7.56 (d, J = 8.5 Hz, 2H, aryl), 6.36 (d, J = 4.3 Hz, 2H, β-H), 6.35 (d, J = 4.3 Hz, 2H, β-H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ 140.3, 139.9, 136.5, 131.9, 131.4, 130.8, 129.7, 121.3, 118.3, 113.4 ppm. HR-MS (ESI-MS): m/z = 403.9204, calcd for (C₁₆H₁₀Br₂N₃)⁺ = 403.9216 [(M + H)⁺].

Dissymmetric α, α' -dibromodipyrrin Ni^{II} complex 3e

HR-MS (ESI-MS): m/z = 897.8537, calcd for $(C_{35}H_{30}Br_4N_5Ni)^+ = 867.8540 [(M + H)^+]$.

Dissymmetric α, α' -dibromodipyrrin Ni^{II} complex 3f

HR-MS (ESI-MS): m/z = 855.8057, calcd for $(C_{32}H_{24}Br_4N_5Ni)^+ = 855.8070 [(M + H)^+]$.

Dissymmetric α, α' -dibromodipyrrin Ni^{II} complex 3g

HR-MS (ESI-MS): m/z = 880.8031, calcd for $(C_{33}H_{23}Br_4N_6Ni)^+ = 880.8023 [(M + H)^+]$.

Dissymmetric α, α' -dibromodipyrrin Ni^{II} complex 3h

HR-MS (ESI-MS): m/z = 991.7821, calcd for $(C_{34}H_{22}Br_4F_6N_5Ni)^+ = 991.7818 [(M + H)^+]$.

Dissymmetric α,α'-dibromodipyrrin Ni^{II} complex 3i

HR-MS (ESI-MS): m/z = 945.7604, calcd for $(C_{32}H_{19}Br_4F_5N_5Ni)^+ = 945.7599$ [(M + H)⁺].

Dissymmetric norcorrole 2e

¹H NMR (500 MHz, CDCl₃): δ 6.35 (s, 2H, Mes), 6.09 (d, J = 9.0 Hz, 2H, aryl), 5.95 (d, J = 9.0 Hz, 2H, aryl), 2.79 (s, 6H), 2.78 (s, 6H), 2.76 (d, J = 4.2 Hz, 2H, β -H), 2.26–2.25 (m, 4H, β -H), 2.17 (d, J = 4.2 Hz, 2H, β -H), 1.89 (s, 3H, *ortho*-Me) ppm.

¹³C NMR (126 MHz, CDCl₃): δ 167.2, 164.7, 159.5, 156.4, 154.0, 146.0, 145.2, 136.9, 134.1, 130.5, 129.4, 128.1, 126.9, 122.9, 119.4, 114.3, 113.7, 109.1, 40.0, 20.8, 18.1 ppm.

UV/vis/NIR (CH₂Cl₂): λ_{max} (ε [M⁻¹cm⁻¹]) = 262 (34000), 426 (40000), 623 (34000) nm.

HR-MS (ESI-MS): m/z = 577.1790, calcd for $(C_{35}H_{29}N_5Ni)^+ = 577.1771$ [(M)⁺].

Single crystals were obtained by vapor diffusion of acetonitrile into a chlorobenzene solution of **2e**. $C_{35}H_{29}N_5Ni$, $M_w = 578.34$, monoclinic, $P2_1/c$, a = 11.547(4) Å, b = 7.327(2) Å, c = 32.081(9) Å, $\beta = 96.234(5)^\circ$, V = 2698.4(14) Å³, Z = 4, R = 0.0320 ($I > 2.0 \sigma(I)$), $R_w = 0.0917$ (all data), GOF = 1.077.

Dissymmetric norcorrole 2f

¹H NMR (500 MHz, CDCl₃): δ 6.96 (t, J = 7.4 Hz, 1H, Ph), 6.77 (m, 2H, Ph), 6.18 (dd, J = 1.3, 8.4 Hz, 2H, Ph), 6.13 (d, J = 9.1 Hz, 2H, aryl), 5.96 (d, J = 9.1 Hz, 2H, aryl), 2.87 (d, J = 4.2 Hz, 2H, β -H), 2.79 (s, 6H, NMe₂), 2.68 (d, J = 4.2 Hz, 2H, β -H), 2.37 (d, J = 4.2 Hz, 2H, β -H), 2.35 (d, J = 4.2 Hz, 2H, β -H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ 167.3, 164.5, 159.3, 156.9, 154.0, 145.8, 145.0, 131.9, 131.5, 130.9, 130.2, 127.9, 123.2, 121.8, 119.4, 114.3, 113.6, 109.1, 40.0 ppm.

UV/vis/NIR (CH₂Cl₂): λ_{max} (ε [M⁻¹cm⁻¹]) = 261 (32000), 426 (39000), 628 (36000) nm. HR-MS (ESI-MS): m/z = 535.1295, calcd for (C₃₂H₂₃N₅Ni)⁺ = 535.1301 [(M)⁺].

Single crystals were obtained by pouring hexane into a chloroform solution of **2f**. $C_{32}H_{23}N_5Ni$, $M_w = 536.26$, monoclinic, $P2_1/n$, a = 14.9222(10) Å, b = 10.1071(7) Å, c = 16.9856(11) Å, $\beta = 111.902(2)^\circ$, V = 2376.9(3) Å³, Z = 4, R = 0.0301 ($I > 2.0 \sigma(I)$), $R_w = 0.0819$ (all data), GOF = 1.092.

Dissymmetric norcorrole 2g

¹H NMR (500 MHz, CDCl₃): δ 7.05 (d, *J* = 8.6 Hz, 2H, aryl), 6.22 (d, *J* = 8.6 Hz, 2H, aryl), 6.04 (d, *J* = 9.1 Hz, 2H, aryl), 5.89 (d, *J* = 9.1 Hz, 2H, aryl), 2.76 (s, 6H, NMe₂), 2.65 (d, *J* = 4.0 Hz, 2H, β -H), 2.32 (d, *J* = 4.2 Hz, 2H, β -H), 2.14 (d, *J* = 4.0 Hz, 2H, β -H), 2.10 (d, *J* = 4.2 Hz, 2H, β -H) ppm.

UV/vis/NIR (CH₂Cl₂): λ_{max} (ε [M⁻¹cm⁻¹]) = 259 (32000), 430 (35000), 645 (35000) nm.

HR-MS (ESI-MS): m/z = 560.1250, calcd for $(C_{33}H_{22}N_6Ni)^+ = 560.1254$ [(M)⁺].

Single crystals were obtained by vapor diffusion of methanol into a chloroform solution of **2g**. $C_{16.5}H_{11}N_3Ni_{0.5}$, $M_w = 280.64$, monoclinic, C2/c, a = 10.7913(16) Å, b = 23.085(4) Å, c = 9.7956(12) Å, $\beta = 98.370(14)^\circ$, V = 2414.3(6) Å³, Z = 8, R = 0.0902 ($I > 2.0 \sigma(I)$), $R_w = 0.2609$ (all data), GOF = 1.070.

Dissymmetric norcorrole 2h

¹H NMR (500 MHz, CDCl₃): δ 7.41 (s, 1H, aryl), 6.65 (s, 2H, aryl), 6.11 (d, *J* = 9.1 Hz, 2H, aryl), 5.91 (d, *J* = 9.1 Hz, 2H, aryl), 2.89 (d, *J* = 4.2 Hz, 2H, β -H), 2.56 (d, *J* = 4.3 Hz, 2H, β -H), 2.39–2.37 (m, 4H, β -H) ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ –66.6 ppm. UV/vis/NIR (CH₂Cl₂): λ_{max} (ε [M⁻¹cm⁻¹]) = 260 (29000), 430 (33000), 649 (32000) nm.

HR-MS (ESI-MS): m/z = 671.1056, calcd for $(C_{34}H_{21}F_6N_5Ni)^+ = 671.1049$ [(M)⁺].

Single crystals were obtained by vapor diffusion of hexane into a 1,2-dichloroethane solution of **2h**. $C_{51}H_{31.5}F_9N_{7.5}Ni_{1.5}, M_w = 1008.40$, monoclinic, $P2_1/c, a = 17.128(4)$ Å, b = 11.539(2) Å, c = 21.492(4) Å, $\beta = 94.759(4)^\circ, V = 4233.1(14)$ Å³, Z = 4, R = 0.0695 ($I > 2.0 \sigma(I)$), $R_w = 0.1885$ (all data), GOF = 1.083.

Dissymmetric norcorrole 2i

¹H NMR (500 MHz, CDCl₃): δ 5.91 (d, J = 9.1 Hz, 2H, aryl), 5.83 (d, J = 9.1 Hz, 2H, aryl), 2.75 (s, 6H, NMe₂), 2.28 (d, J = 4.2, 2H, β -H), 1.84 (d, J = 4.3 Hz, 2H, β -H), 1.75 (d, J = 4.2 Hz, 2H, β -H), 1.71 (d, J = 4.3 Hz, 2H, β -H) ppm.

¹⁹F NMR (470 MHz, CDCl₃): δ –140.1, –156.7, –163.0 ppm.

UV/vis/NIR (CH₂Cl₂): λ_{max} (ε [M⁻¹cm⁻¹]) = 261 (31000), 433 (39000), 645 (33000) nm.

HR-MS (ESI-MS): m/z = 625.0842, calcd for $(C_{32}H_{18}F_5N_5Ni)^+ = 625.0830$ [(M)⁺].

Single crystals were obtained by vapor diffusion of hexane into a dichloromethane solution of **2i**. $C_{32}H_{18}Cl_2F_5N_5Ni$, $M_w = 697.12$, monoclinic, $P2_1/c$, a = 16.003(2) Å, b = 10.6329(14) Å, c = 17.070(2) Å, $\beta = 100.125(4)^\circ$, V = 2859.4(7) Å³, Z = 4, R = 0.0694 ($I > 2.0 \sigma(I)$), $R_w = 0.1479$ (all data), GOF = 1.078.





Figure S1. ¹H NMR (500 MHz) spectrum of 4a in CDCl₃.



S8





Figure S3. ¹H NMR (500 MHz) spectrum of 4b in CDCl₃.



Figure S4. ¹³C NMR (126 MHz) spectrum of 4b in CDCl₃.



Enhancing low-energy absorption band and charge mobility of antiaromatic Ni^{II} norcorroles

Figure S6. ¹³C NMR (126 MHz) spectrum of 2e in CDCl₃.





Figure S8. ¹³C NMR (126 MHz) spectrum of 2f in CDCl₃.





Figure S9. ¹H NMR (500 MHz) spectrum of 2g in CDCl₃.



Figure S10. ¹H NMR (500 MHz) spectrum of 2h in CDCl₃.



Figure S11. ¹H NMR spectra (500 MHz) of **2h** in solutions in CDCl₃ with various concentrations.



Figure S12. ¹⁹F NMR (470 MHz) spectrum of 2h in CDCl₃.



Figure S14. ¹⁹F NMR (470 MHz) spectrum of 2i in CDCl₃.



Absorption Spectra in Various Solvents





Spectroelectrochemical Analyses



Figure S16. Spectral change of 2h (left) and 2e (right) in CH₂Cl₂ during electrochemical oxidation upon applying 0 V to 0.6 V (blue line to red line). analyte: 0.3 mM, electrolyte: 0.1 M of tetrabutylammonium tetrafluoroborate, working electrode: Pt, counter electrode: Pt, reference electrode: Ag⁺/Ag. See also Figure S17.

Cyclic Voltammograms

Cyclic voltammograms of 2e-2i were recorded on ALS electrochemical analyzer 612C. Measurements were performed in freshly distilled dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as electrolyte. A three-electrode system was used and consisted of a grassy carbon working electrode, a platinum wire and Ag/AgClO₄ as the reference electrode. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.



Figure S17. Cyclic voltammograms (0.1 V•s⁻¹) of **1** and **2e-2i** in CH_2Cl_2 (0.1 M TBAPF₆). Working electrode: grass carbon, counter electrode: Pt, reference electrode: Ag/AgClO₄. The data for **1** was taken from our previous paper.⁷

Flash-Photolysis Time-Resolved Microwave Conductivity Measurements⁸

Transient photoconductivity was measured by flash-photolysis time-resolved microwave conductivity (FP-TRMC) method. A resonant cavity was used to obtain a high degree of sensitivity in the measurement of conductivity. The resonant frequency and the microwave power were set at ~9.1 GHz and 3 mW, respectively, so that the electric field of the microwave was sufficiently small not to disturb the motion of charge carriers. The value of conductivity is converted to the product of the quantum yield ϕ and the sum of charge carrier mobilities $\Sigma \mu$, by $\phi \Sigma \mu = \Delta \sigma (eI_0 F_{\text{light}})^{-1}$, where e, I_0, F_{light} , and $\Delta \sigma$ are the unit charge of a single electron, incident photon density of excitation laser (photons/m²), a correction (or filling) factor (/m), and a transient photoconductivity, respectively. The sample was set at the highest electric field in a resonant cavity. FP-TRMC experiments were performed at room temperature. The charge carriers were injected into the samples via photo-ionization by direct excitation with a third harmonic generation ($\lambda = 355$ nm) light pulses from a Nd: YAG laser (spectra Physics, INDI-HG). The excitation density was tuned at 9.1 × 10¹⁵ cm⁻² photons per pulse.



Figure S18. Time-resolved microwave conductivities **2e–2i**. Crystalline samples were used for measurement of **2e**, **2f**, **2h** and **2i**, and a powder sample was used for measurement of **2g**.

Theoretical Calculations

All calculations were carried out using the *Gaussian 09* program.⁹ Initial geometries of **2e** and **2i** were obtained from their X-ray structures. Full optimizations were performed with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP)¹⁰ and a basis set consisting of SDD¹¹ for Ni and 6-31G(d) for the rest (denoted as 631SDD). The calculated absorption wavelengths and oscillator strengths were obtained with the TD-DFT method at the B3LYP/631SDD level.

Energy (eV)



Figure S19. MO diagrams for norcorroles 1, 2e and 2i calculated at the B3LYP/631SDD level.



Figure S20. Theoretical and experimental absorption spectra of norcorroles 2e and 2i calculated at the B3LYP/631SDD level.

Table S1. Calculated exited wavelengths (λ) and oscillator strengths (*f*) of selected transitions of **2e** and **2i**.

Compound	λ (nm)	f	Composition (%)	Assignment
2e	1424	0.0000	HOMO->LUMO (100%)	forbidden transition
	542	0.5200	HOMO-3->LUMO (94%)	СТ
2i	1573	0.0003	HOMO->LUMO (100%)	forbidden transition
	570	0.5113	HOMO-3->LUMO (92%)	СТ

Structural Analysis of X-ray Structures

	Norcorrole–Ar ¹	Norcorrole–Ar ²
	(4-dimethylaminophenyl)	
2e	38.3	78.9
2f	34.5	43.3
2g	49.8	47.8
2h (centre)	38.5	38.5
2h (edges)	47.0	49.0
2i	40.5	69.6

Table S2. Dihedral angles between norcorrole cores and Ar^1 or Ar^2 in the X-ray structures of **2e–2i**.

References

- 1 H. Omori, S. Hiroto, H. Shinokubo, Chem Commun., 2016, 52, 3540-3543.
- S. Shimizu, Y. Ito, K. Oniwa, S. Hirokawa, Y. Miura, O. Matsushita, N. Kobayashi, *Chem Commun.*, 2012, 48, 3851–3853.
- 3 Y. Matano, T. Shibano, H. Nakano, H. Imahori, Chem. Eur. J., 2012, 18, 6208-6216.
- R. Nozawa, H. Tanaka, W.-Y. Cha, Y. Hong, I. Hisaki, S. Shimizu, J.-Y. Shin, T. Kowalczyk, S. Irle,
 D. Kim, H. Shinokubo, *Nat. Commun.*, 2016, 7, 13620 (doi: 10.1038/ncomms13620).
- 5 E. N. Durantini, *Molecules*, 2001, **6**, 533–539.
- 6 H. Chen, X.-B. Shao, X.-K. Jiang, Z.-T. Li, *Tetrahedron*, 2003, **59**, 3505–3510.
- 7 T. Ito, Y. Hayashi, S. Shimizu, J.-Y. Shin, N. Kobayashi, H. Shinokubo, *Angew. Chem. Int. Ed.*, 2012, 51, 8542–8545.
- 8 S. Seki, A. Saeki, T. Sakurai, D. Sakamaki, Phys. Chem. Chem. Phys., 2014, 16, 11093–11113.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 10 (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100; (b) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
- 11 M. Dolg, U. Wedig, H. Stoll, H. Preuss, J. Chem. Phys., 1987, 86, 866-872.