Supporting Information

Diazazethrene Bisimide: A Strongly Electron-Accepting π-System Synthesized via the Incorporation of both Imide Substituents and Imine-type Nitrogen Atoms into Zethrene

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1. Instrumentation and materials

¹H NMR (500 MHz, 600 MHz) and ¹³C NMR (126 MHz, 151 MHz) spectra were recorded on a Varian INOVA-500 and JEOL JNM-ECA600II spectrometer. Chemical shifts were reported as the delta scale in ppm relative to CHCl₃ (δ = 7.26 ppm) and DMSO-d₆ (δ = 2.50 ppm) for ¹H NMR, and CDCl₃ (δ = 77.16 ppm) and DMSO-*d*₆ (δ = 39.52 ppm) for ¹³C NMR. UV/vis/NIR absorption spectra were recorded on a JASCO V-670 spectrometer. Emission spectra were recorded on a JASCO FP-6500 spectrometer, and absolute fluorescence quantum yields were measured by the photon-counting method using an integration sphere. Preparative separations were performed by silica gel column chromatography (Wako gel® C-300 or C-400, and FUJISILYSIA CHROMATOREX NH-DM1020). High-resolution atmospheric pressure chemical ionization time-of-flight (APCI-TOF) and electrospray ionization time-of-flight (ESI-TOF) mass spectra were taken on a Bruker micrOTOF instrument using a positive or negative ionization mode. High-resolution matrix-assisted laser desorption and ionization time-of-flight (MALDI-TOF) mass spectra were taken on a Bruker autoflex max using a positive ionization mode. Redox potentials were measured by cyclic voltammetry on an ALS electrochemical analyzer model 612C. X-ray data were obtained using a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics. Dry CH₂Cl₂ was prepared by distillation from CaH₂. Dry THF and 1.4-dioxane were prepared by using GlassContour[™] solvent purification systems. Cobaltocene purchased from a commercial supplier was purified by sublimation. An oil bath was used as a heat source for reactions requiring heating. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. 4-Amino-5-bromo-N-(3-pentyl)-1,8-naphthalenedicarboxylic imide **9b** was synthesized according to the literature.^[S1]

N-(2,4,6-Trimethylphenyl)-4-bromo-5-nitro-1,8-naphthalenedicarboxylic monoamide S1



4-Bromo-5-nitro-1,8-naphthalenedicarboxylic anhydride (3.22 g, 10.0 mmol) and acetic acid (200 mL) were placed in a round-bottom flask. The mixture was stirred at room temperature for 3 min. To the flask, 2,4,6-trimethylaniline (2.67 g, 19.8 mmol) was added. The mixture was refluxed for 13 h. The resulting mixture was cooled to room temperature. The reaction was quenched by the addition of HCl aq. (1 M). The precipitations were collected by filtration and washed with water and MeOH. Recrystallization from CH_2Cl_2 /hexane afforded compound **S1** (2.62 g, 5.94 mmol, 59%) as a beige solid.

¹H NMR (500 MHz, CDCl₃, 298 K): $\delta = 8.77$ (d, J = 7.8 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 7.8 Hz, 1H), 7.05 (s, 2H), 2.36 (s, 3H), 2.08 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃, 298 K): $\delta = 162.35$, 161.60, 151.68, 139.27, 136.19, 135.02, 132.88, 131.85, 131.30, 130.29, 129.67, 125.89, 124.73, 123.75, 122.60, 121.59, 21.30, 17.87 ppm; HRMS (APCI-TOF, positive mode): [M+H]⁺ Calcd for C₂₁H₁₆N₂O₄⁷⁹Br 439.0288; Found 439.0285.

N-(2,4,6-Trimethylphenyl)-4-bromo-5-amino-1,8-naphthalenedicarboxylic monoamide 9a



Compound S1 (1.76 g, 4.00 mmol) and ethanol (80 mL) were placed in a round-bottom flask. The mixture was stirred at room temperature for 3 min. A solution of $SnCl_2$ (3.79 g, 20.1 mmol) in conc. HCl aq. (15 mL) was added slowly to the mixture. The mixture was refluxed for

1 h. The mixture was filtered and washed with water, affording **9a** (1.50 g, 3.68 mmol, 92%) as a yellow solid.

¹H NMR (500 MHz, DMSO- d_6 , 298 K): $\delta = 8.26$ (d, J = 8.6 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.66 (s, 2H), 7.07 (d, J = 8.6 Hz, 1H), 6.99 (s, 2H), 2.29 (s, 3H), 1.93 (s, 6H) ppm; ¹³C NMR (126 MHz, DMSO- d_6 , 298 K): $\delta = 162.74$, 162.09, 153.06, 137.25, 134.99, 134.21, 132.85, 131.97, 131.80, 131.45, 128.67, 126.31, 121.66, 116.68, 111.74, 108.34, 20.62, 17.32 ppm; HRMS (APCI-TOF, positive mode): [M+H]⁺ Calcd for C₂₁H₁₈N₂O₂⁷⁹Br 409.0546; Found 409.0563.

Ethynylene-bridged aminonaphthalene monoimide dimer 10a



A round-bottom flask containing compound **9a** (853 mg, 2.09 mmol), $Pd_2(dba)_3$ •CHCl₃ (108 mg, 0.106 mmol), and triphenylphosphine (110 mg, 0.419 mmol) was purged with N₂ and then charged with dry dioxane (100 mL). Bis(tributylstannyl)acetylene (625 mg, 1.03 mmol) was added to the mixture. The mixture was stirred at 100 °C for 3 h. The resulting mixture was cooled to room temperature. The mixture was filtered, and the residue was washed with hexane. The residue was suspended in CHCl₃ (100 mL), and then hexane (50 mL) was added to the mixture. The precipitates collected by filtration and washed with hexane, affording **10a** (373 mg, 547 µmol, 52%) as a reddish-purple solid.

¹H NMR (500 MHz, DMSO-*d*₆, 298 K): $\delta = 8.51$ (d, J = 7.6 Hz, 2H), 8.32 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 7.6 Hz, 2H), 7.65 (s, 4H), 7.11 (d, J = 8.4 Hz, 2H), 7.02 (s, 4H), 2.31 (s, 6H), 1.96 (s, 12H) ppm; ¹³C NMR (126 MHz, DMSO-*d*₆, 298 K): $\delta = 162.67$, 162.23, 152.96, 137.28, 135.02, 134.27, 132.00, 131.19, 130.48, 128.70, 123.18, 122.83, 118.04, 111.25, 108.61, 98.51, 20.63, 17.34 ppm (One signal is missing due to overlapping); HRMS (MALDI-TOF, positive mode, DIT matrix): [M+H]⁺ Calcd for C₄₄H₃₅N₄O₄ 683.2653; Found 683.2681.

Compound 11a



Compound **10a** (342 mg, 501 μ mol), PdCl₂ (17.7 mg, 99.8 μ mol), and acetonitrile (250 mL) were placed in a round-bottom flask. The mixture was refluxed for 1 h. The resulting mixture was cooled to room temperature. The mixture was filtered, and residue was washed with acetonitrile and hexane, affording **11a** (286 mg, 418 μ mol, 83%) as a reddish brown solid.

¹H NMR (500 MHz, DMSO-*d*₆, 333 K): $\delta = 12.17$ (s, 1H, The signal was weakened by the addition of D₂O), 8.61 (d, *J* = 7.5 Hz, 1H), 8.38 (d, *J* = 8.5 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.03 (s, 2H), 7.01 (d, *J* = 8.5 Hz, 1H, overlapped), 7.00 (s, 2H), 6.92 (s, 1H), 6.47 (s, 2H), 2.33 (s, 3H), 2.32 (s, 3H), 2.01 (s, 6H), 1.96 (s, 6H) ppm; ¹³C NMR (126 MHz, DMSO-*d*₆, 333 K): $\delta = 162.52$, 162.26, 162.07, 161.94, 152.11, 145.08, 144.18, 141.66, 136.96, 136.95, 136.39, 134.75, 134.68, 133.67, 133.28, 133.18, 132.97, 131.81, 131.60, 131.16, 130.42, 128.36, 128.28, 123.20, 116.77, 114.64, 113.04, 111.53, 109.25, 109.04, 108.75, 105.78, 20.66, 17.36, 17.30 ppm (Three signals are missing due to overlapping); HRMS (ESI-TOF, negative mode): [M–H][–] Calcd for C₄₄H₃₄N₄O₄ 681.2496; Found 681.2498.

DAZBI 8a



Compound **11a** (67.8 mg, 99.3 μ mol), [bis(trifluoroacetoxy)iodo]benzene (129 mg, 301 μ mol), and CH₂Cl₂ (50 mL) were placed in a round-bottom flask. The mixture was stirred at room temperature for 2 h. The mixture was filtered over a pad of silica gel eluted with CH₂Cl₂/AcOEt (v/v = 60/1). After removal of the solvent *in vacuo*, the residue was separated by

silica gel column chromatography eluted with CH_2Cl_2 to afford compound **8a** (29.5 mg, 43.5 μ mol, 44%) as a dark green solid.

¹H NMR (500 MHz, CDCl₃, 298 K): $\delta = 9.25$ (d, J = 7.9 Hz, 2H), 8.87 (d, J = 7.9 Hz, 2H), 8.79 (d, J = 7.9 Hz, 2H), 8.27 (d, J = 7.9 Hz, 2H), 7.08 (s, 4H), 2.38 (s, 6H), 2.14 (s, 12H) ppm; ¹³C NMR (126 MHz, CDCl₃, 298 K): $\delta = 162.95$, 162.61, 149.91, 146.01, 139.02, 135.23, 133.89, 133.55, 131.78, 130.94, 130.93, 129.65, 129.11, 126.90, 125.65, 123.41, 122.28, 21.36, 17.99 ppm; HRMS (MALDI-TOF, positive mode, TCNQ matrix): [M+H]⁺ Calcd for C₄₄H₃₁N₄O₄ 679.2340; Found 679.2361.

DAZBI dimer12a



Compound **11a** (68.0 mg, 99.7 μ mol), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (68.1 mg, 300 μ mol), and CH₂Cl₂ (50 mL) were placed in a round-bottom flask. The mixture was stirred for 3 h at 60 °C. The mixture was filtered over a pad of silica gel eluted with CH₂Cl₂/AcOEt (v/v = 40/1). After removal of the solvent *in vacuo*, the residue was separated by silica gel column chromatography eluted with CHCl₃ to afford **12a** (13.6 mg, 10.1 μ mol, 20%) as a black solid and compound **8a** (8.00 mg, 11.8 μ mol, 12%) as a dark green solid.

¹H NMR (500 MHz, CDCl₃, 333 K): $\delta = 9.51$ (s, 2H), 9.39 (d, J = 8.0 Hz, 2H), 8.99 (d, J = 8.0 Hz, 2H), 8.87 (d, J = 8.0 Hz, 2H), 8.78 (d, J = 7.9 Hz, 2H), 8.62 (d, J = 8.0 Hz, 2H), 8.31 (d, J = 7.9 Hz, 2H), 7.11 (s, 4H), 7.05 (s, 4H), 2.39 (s, 6H), 2.38 (s, 6H), 2.29 (s, 12H), 2.11 (s, 12H) ppm; ¹³C NMR (126 MHz, CDCl₃, 333 K): $\delta = 162.97$, 162.93, 162.78, 162.45, 149.59, 149.54, 146.36, 144.02, 139.40, 139.14, 138.99, 137.64, 135.38, 135.28, 134.58, 133.98, 133.51, 132.10, 131.68, 131.42, 131.20, 131.13, 129.82, 129.63, 129.32, 129.17, 127.46, 127.21, 126.02, 125.96, 123.88, 123.18, 122.43, 122.04, 21.27, 21.26, 18.02, 17.91 ppm; HRMS (MALDI-TOF,

positive mode, TCNQ matrix): [M+H]⁺ Calcd for C₈₈H₅₉N₈O₈ 1355.4450; Found 1355.4458.

Ethynylene-bridged aminonaphthalene monoimide dimer 10b



A round-bottom flask containing compound **9b** (181 mg, 500 μ mol), Pd₂(dba)₃•CHCl₃ (25.2 mg, 24.9 μ mol), and triphenylphosphine (26.1 mg, 99.6 μ mol) was purged with N₂, and then charged dry dioxane (25 mL). Bis(tributylstannyl)acetylene (153 mg, 253 μ mol) was added to the mixture. The mixture was stirred at 100 °C for 3 h. After removal of the solvent *in vacuo*, the residue was separated by silica gel column chromatography eluted with CH₂Cl₂/AcOEt (v/v = 10/1) to afford compound **10b** (49.5 mg, 84.4 μ mol, 34%) as a red solid.

¹H NMR (500 MHz, CDCl₃, 333 K): $\delta = 8.56$ (d, J = 7.6 Hz, 2H), 8.45 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 7.6 Hz, 2H), 6.90 (d, J = 8.2 Hz, 2H), 6.05 (s, 4H), 5.03 (tt, $J_1 = 9.3$ Hz, $J_2 = 5.9$ Hz, 2H), 2.24 (qdd, $J_1 = 7.5$ Hz, $J_2 = 13.8$ Hz, $J_3 = 9.3$ Hz, 4H), 1.92 (qdd, $J_1 = 7.5$ Hz, $J_2 = 13.8$ Hz, $J_3 = 5.9$ Hz, 4H), 0.91 (t, $J_1 = 7.5$ Hz, 12H) ppm.; ¹³C NMR (126 MHz, CDCl₃, 333 K): $\delta = 164.69$, 164.61, 150.21, 134.44, 132.29, 131.37, 130.37, 125.08, 121.96, 118.99, 113.09, 112.13, 98.53, 57.70, 25.36, 11.44 ppm.; HRMS (MALDI-TOF, positive mode, DIT matrix): [M+H]⁺ Calcd for C₃₆H₃₅N₄O₄ 587.2653; Found 587.2642.

Compound 11b



Compound **10b** (95.5 mg, 163 μ mol), PdCl₂ (5.79 mg, 32.7 μ mol), and acetonitrile (80 mL) were placed in a round-bottom flask. The mixture was refluxed for 1 h. After removal of the

solvent *in vacuo*, the residue was washed with acetonitrile and hexane, affording **11b** (84.1 mg, 143 μmol, 88%) as a red solid.

¹H NMR (500 MHz, DMSO-*d*₆, 333 K): δ = 12.01 (s, 1H, The signal was weakened by the addition of D₂O), 8.53 (d, *J* = 7.5 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.81 (s, 1H), 6.34 (s, 2H, The signal was weakened by the addition of D₂O), 5.03 (tt, *J*₁ = 9.5 Hz, *J*₂ = 5.8 Hz, 1H), 4.95 (tt, *J*₁ = 9.6 Hz, *J*₂ = 5.8 Hz, 1H), 2.19 (m, 4H), 1.86 (qdd, *J*₁ = 7.5 Hz, *J*₂ = 11.4 Hz, *J*₃ = 5.8 Hz, 2H), 1.83 (qdd, *J*₁ = 7.5 Hz, *J*₂ = 11.4 Hz, *J*₃ = 5.8 Hz, 2H), 0.83 (t, *J*₁ = 7.5 Hz, 6H), 0.79 (t, *J*₁ = 7.5 Hz, 6H) ppm; ¹³C NMR (126 MHz, DMSO-*d*₆, 298 K): δ = 163.71, 163.63, 163.44, 163.31, 151.40, 144.57, 143.99, 141.00, 136.34, 133.40, 133.09, 133.02, 130.83, 130.54, 129.99, 128.06, 123.32, 122.82, 116.38, 114.32, 113.06, 111.35, 109.30, 109.04, 108.59, 105.46, 55.80, 55.35, 24.22, 24.05, 10.73, 10.66 ppm; HRMS (ESI-TOF, negative mode): [M–H]⁻ Calcd for C₃₆H₃₄N₄O₄ 585.2496; Found 585.2508.

DAZBI 8b



Compound **11b** (35.2 mg, 60.0 μ mol), [bis(trifluoroacetoxy)iodo]benzene (77.5 mg, 180 μ mol), and CH₂Cl₂ (30 mL) were placed in a round-bottom flask. The mixture was stirred at room temperature for 2 h. The mixture was separated by silica gel column chromatography eluted with CH₂Cl₂/AcOEt (v/v = 35/1) to afford compound **8b** (12.0 mg, 20.6 μ mol, 34%) as a green solid.

¹H NMR (500 MHz, CDCl₃, 298 K): $\delta = 9.13$ (d, J = 8.0 Hz, 2H), 8.75 (d, J = 8.0 Hz, 2H), 8.66 (d, J = 7.8 Hz, 2H), 8.14 (d, J = 7.8 Hz, 2H), 5.08 (tt, $J_1 = 9.3$ Hz, $J_2 = 6.0$ Hz, 2H), 2.24 (qdd, $J_1 = 7.5$ Hz, $J_2 = 14.0$ Hz, $J_3 = 9.3$ Hz, 4H), 1.92 (qdd, $J_1 = 7.5$ Hz, $J_2 = 13.8$ Hz, $J_3 = 6.0$ Hz, 4H), 0.91 (t, $J_1 = 7.5$ Hz, 12H) ppm; ¹³C NMR (126 MHz, CDCl₃, 333 K): $\delta = 164.27$, 163.98, 149.95, 145.71, 133.53, 133.03, 131.34, 130.68, 128.70, 126.73, 126.06, 123.82, 122.05, 58.28, 25.38, 11.50 ppm; HRMS (MALDI-TOF, positive mode, TCNQ matrix): [M]⁺ Calcd for C₃₆H₃₀N₄O₄ 582.2262; Found 582.2255.

DAZBI dimer 12b



Compound **3b** (37.4 mg, 63.7 μ mol), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (43.3 mg, 191 μ mol), and CH₂Cl₂ (30 mL) were placed in a round-bottom flask. The mixture was stirred for 3 h at 60 °C. The mixture was filtered over a pad of silica gel eluted with CH₂Cl₂. After removal of the solvent *in vacuo*, the residue was separated by silica gel column chromatography eluted with CH₂Cl₂ to afford **12b** (4.57 mg, 3.93 μ mol, 12%) as a black solid and compound **8b** (3.37 mg, 5.78 μ mol, 9%) as a green solid.

¹H NMR (500 MHz, CDCl₃, 313 K): $\delta = 9.29$ (s, 2H), 9.18 (d, J = 8.0 Hz, 2H), 8.82 (d, J = 8.0 Hz, 2H), 8.66 (t, J = 8.0 Hz, 2H), 8.60 (d, J = 7.9 Hz, 2H), 8.44 (d, J = 8.0 Hz, 2H), 8.13 (d, J = 7.9 Hz, 2H), 5.14 (tt, $J_1 = 9.3$ Hz, $J_2 = 6.0$ Hz, 2H), 4.98 (tt, $J_1 = 9.3$ Hz, $J_2 = 6.0$ Hz, 2H), 2.34 (m, 4H), 2.18 (qdd, $J_1 = 7.5$ Hz, $J_2 = 14.0$ Hz, $J_3 = 9.3$ Hz, 4H), 2.05 (m, 4H), 1.93 (m, 4H), 1.08 (t, J = 7.5 Hz, 12H) 0.90 (d, J = 7.5 Hz, 12H) ppm; ¹³C NMR (126 MHz, CDCl₃, 313 K): $\delta = 164.16, 163.67$ (br, overlapped), 149.09, 149.07, 145.70, 143.37, 139.05, 137.35, 133.80, 133.35, 133.03, 131.61, 131.17, 131.01, 128.59, 128.47, 127.17, 126.87, 125.99, 125.89, 123.74, 122.52, 121.90, 121.83, 58.35, 58.16, 25.30, 25.20, 11.65, 11.49 ppm; HRMS (MALDI-TOF, positive mode, TCNQ matrix): [M+H]⁺ Calcd for C₇₂H₅₉N₈O₈ 1163.4450; Found 1163.4428.

Dianion 13



In an argon-filled glovebox, compound **8a** (13.8 mg, 20.3 μ mol), cobaltocene (9.7 mg, 14 μ mol), and dry THF (4 mL) were placed in a round-bottom flask. The mixture was stirred at room temperature for 1 h. The precipitates were collected by filtration and washed with benzene. Recrystallization from CH₃CN/benzene afforded compound **13** (15.1 mg, 14.3 μ mol, 70%) as a dark green solid.

¹H NMR (500 MHz, DMSO-*d*₆, 298 K): $\delta = 8.14$ (d, J = 8.5 Hz, 2H), 8.09 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 9.0 Hz, 2H), 6.96 (s, 4H), 6.92 (d, J = 9.0 Hz, 2H), 5.80 (s, 20H, Cp), 2.31 (s, 6H), 1.91 (s, 12H) ppm.; ¹³C NMR (126 MHz, DMSO-*d*₆, 298 K): $\delta = 162.17$, 161.04, 150.57, 137.86, 135.49, 135.42, 135.33, 135.23, 135.10, 129.25, 128.90, 128.25, 123.95, 115.17, 110.70, 110.55, 100.25, 84,86 (Cp), 20.64, 17.62 ppm.; HRMS (ESI-TOF, negative mode): $[M^{2-}+H]^{-}$ Calcd for C₄₄H₃₁N₄O₄ 679.2340; Found 679.2323; HRMS (ESI-TOF, positive mode): $[CoCp_2]^{+}$ Calcd for C₁₀H₁₀Co 189.0109; Found 189.0110.

Dihydro-form 14a



(Method A) In an-argon filled glovebox, compound 8a (3.51 mg, 5.17 μ mol), 1,4bis(trimethylsilyl)-1,4-dihydropyrazine (2.0 mg, 8.8 μ mol), and dry THF (2 mL) were placed in a round-bottom flask. The mixture was stirred at room temperature for 30 min. MeOH (2 mL) was added to the reaction mixture. The precipitates were collected by filtration and washed with methanol, affording compound 14a (2.66 mg, 3.91 μ mol, 76%) as a dark green solid.

(Method B) Compound 8a (6.73 mg, 9.99 μ mol) and CH₂Cl₂ (5 mL) were placed in a round-bottom flask. A MeOH solution (1.8 mL) of L-ascorbic acid (6.1 mM) was added to the

reaction mixture. The mixture was stirred for 20 min at room temperature. After removal of the solvent *in vacuo*, the residue was washed with methanol to afford compound **14a** (3.67 mg, $5.39 \mu \text{mol}$, 54%) as a green solid.

¹H NMR (500 MHz, DMSO-*d*₆+CF₃COOH, 298 K): $\delta = 11.14$ (s, 2H, The signal was weakened by the addition of D₂O), 8.39 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.03 (s, 4H), 6.92 (d, *J* = 8.5 Hz, 2H), 2.33 (s, 6H), 2.01 (s, 12H) ppm; ¹³C NMR (126 MHz, DMSO-*d*₆+CF₃COOH, 298 K): $\delta = 162.36$, 161.90, 142.05, 136.90, 134.95, 132.91, 132.26, 131.23, 130.75, 128.68, 122.79, 122.01, 116.37, 114.06, 111.38, 108.38, 106.45, 20.63, 17.44 ppm; HRMS (MALDI-TOF, positive mode, DIT matrix): [M+H]⁺ Calcd for C₄₄H₃₃N₄O₄ 681.2496; Found 681.2520.

Dihydro-form 14b



(Method A) In an argon-filled glovebox, compound **8b** (2.97 mg, 5.10 μ mol), 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (2.3 mg, 10 μ mol), and dry THF (2 mL) were placed in a round-bottom flask. The mixture was stirred at room temperature for 30 min. MeOH (2 mL) was added to reaction mixture. The precipitates were collected by filtration and washed with methanol to afford compound **14b** (2.99 mg, 5.45 μ mol, quant.) as a dark green solid.

(Method B) Compound 8b (5.83 mg, 10.0 μ mol) and CH₂Cl₂ (5 mL) were placed in a round-bottom flask. A MeOH solution (1.8 mL) of L-ascorbic acid (6.1 mM) was added to the reaction mixture. The mixture was stirred for 20 min at room temperature. After removal of the solvent *in vacuo*, the residue was washed with methanol to afford compound 14b (5.42 mg, 9.27 μ mol, 93%) as a green solid.

¹H NMR (500 MHz, DMSO- d_6 +CF₃COOH, 323 K): $\delta = 11.42$ (s, 2H, The signal was weakened by the addition of D₂O), 8.42 (d, J = 8.2 Hz, 2H), 8.21 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 5.02 (m, 2H), 2.20 (m, 4H), 1.85 (sep, J = 7.5 Hz, 4H), 0.81 (d, J = 7.5 Hz, 12H) ppm.; ¹³C NMR (151 MHz, DMSO- d_6 +CF₃COOH, 323 K): $\delta = 162.36$ (br, overlapped), 142.06, 132.54, 130.63, 122.86, 121.99, 117.94, 116.02, 114.10, 112.18, 111.34,

106.63, 55.69, 24.18, 10.99 ppm.; HRMS (MALDI-TOF, positive mode, DIT matrix): $[M+H]^+$ Calcd for $C_{36}H_{33}N_4O_4$ 585.2496; Found 585.2496.



Figure S1. ¹H NMR spectrum of S1 in CDCl₃ at 25 °C.



Figure S2. ¹³C NMR spectrum of S1 in CDCl₃ at 25 °C.



Figure S3. ¹H NMR spectrum of 9a in DMSO- d_6 at 25 °C.



Figure S4. ¹³C NMR spectrum of 9a in DMSO-*d*₆ at 25 °C.



Figure S5. ¹H NMR spectrum of 10a in DMSO-*d*₆ at 25 °C. *: residual solvents.



Figure S6. ¹³C NMR spectrum of 10a in DMSO-*d*₆ at 25 °C.



Figure S7. ¹H NMR spectrum of 11a in DMSO-*d*₆ at 60 °C.



Figure S8. ¹³C NMR spectrum of 11a in DMSO- d_6 at 60 °C.



Figure S9. ¹H NMR spectrum of 8a in CDCl₃ at 25 °C.



Figure S10. ¹³C NMR spectrum of 8a in CDCl₃ at 25 °C.



Figure S11. ¹H NMR spectrum of 12a in CDCl₃ at 60 °C.



Figure S12. ¹³C NMR spectrum of 12a in CDCl₃ at 60 °C.



Figure S13. ¹H NMR spectrum of 10b in CDCl₃ at 25 °C.



Figure S14. ¹³C NMR spectrum of 10b in CDCl₃ at 25 °C.



Figure S15. ¹H NMR spectrum of 11b in CDCl₃ at 25 °C.



Figure S16. ¹³C NMR spectrum of 11b in CDCl₃ at 25 °C. *: residual solvents.



Figure S17. ¹H NMR spectrum of 8b in CDCl₃ at 25 °C.



Figure S18. ¹³C NMR spectrum of 8b in CDCl₃ at 25 °C.



Figure S19. ¹H NMR spectrum of 12b in CDCl₃ at 40 °C.



Figure S20. ¹³C NMR spectrum of 12b in CDCl₃ at 40 °C.



Figure S21. ¹H NMR spectrum of 13 in DMSO-*d*₆ at 25 °C. *: residual solvents.



Figure S22. ¹³C NMR spectrum of 13 in DMSO-*d*₆ at 25 °C. *: residual solvents.



Figure S23. ¹H NMR spectrum of 14a in DMSO-*d*₆ + CF₃COOH at 25 °C. *: residual solvents.


Figure S24. ¹³C NMR spectrum of **14a** in DMSO-*d*₆ + CF₃COOH at 25 °C. *: CF₃COOH signals.



Figure S25. ¹H NMR spectrum of 14b in DMSO- d_6 + CF₃COOH at 50 °C.



Figure S26. ¹³C NMR spectrum of 14b in DMSO- d_6 + CF₃COOH at 50 °C.

*: CF₃COOH signals.

4. Mass spectra



Figure S27. APCI-TOF (positive mode) mass spectrum of S1.



Figure S28. APCI-TOF (positive mode) mass spectrum of 9a.



D:\Data\Shinokubo\tajima\79-20220217-Mes-ethynyldimer\Mes-ethynyldimer\0_A3\1\1Ref

Figure S29. MALDI-TOF (positive mode) mass spectrum of 10a.



Figure S30. ESI-TOF (negative mode) mass spectrum of 11a.



Figure S31. MALDI-TOF (positive mode) mass spectrum of 8a.



Figure S32. MALDI-TOF (positive mode) mass spectrum of 12a.



Figure S33. MALDI-TOF (positive mode) mass spectrum of 10b.



Figure S34. ESI-TOF (negative mode) mass spectrum of 11b.



Figure S35. MALDI-TOF (positive mode) mass spectrum of 8b.



Figure S36. MALDI-TOF (positive mode) mass spectrum of 12b.



Figure S37. ESI-TOF (negative mode) mass spectrum of 13.



Figure S38. ESI-TOF (positive mode) mass spectrum of 13.



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5. Crystal data



Figure S41. (a) HOMA values and (b) bond lengths of **12b** obtained by X-ray diffraction analysis. Thermal ellipsoids are shown at the 50% probability level. 3-Pentyl groups are omitted.



Figure S42. X-ray crystal structure of **8b**. (a) Top view, (b) side view, and (c) packing structure. Thermal ellipsoids are shown at the 50% probability level. Hollow and solid ellipsoids show the disorder over two positions (occupancy: solid spheres/hollow spheres = 0.58/0.42). All hydrogen atoms are omitted for clarity.

compound	8a	8b	12b
Formula	$C_{44}H_{30}N_4O_4$	$C_{36}H_{30}N_4O_4$	$C_{32}H_{26}N_2O_4$
Formula weight	678.75	582.64	15926.7(12)
Crystal system	triclinic	monoclinic	orthorhombic
Space group	<i>P</i> -1 (No. 2)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>Fdd</i> 2 (No. 43)
Crystal color	blue	blue	black
Crystal description	prism	prism	prism
<i>a</i> [Å]	8.0994(3)	20.1187(9)	34.9018(13)
<i>b</i> [Å]	11.7159(8)	16.7884(9)	59.974(3)
<i>c</i> [Å]	21.0793(12)	8.3834(3)	7.6088(3)
α [°]	102.210(5)	90	90
β [°]	97.445(4)	102.468(4)	90
γ [°]	96.128(4)	90	90
V[Å ³]	1919.86(19)	2764.8(2)	15926.7(12)
Ζ	2	4	2
$d_{ m calcd} [{ m g \ cm^{-3}}]$	1.428	1.400	1.324
$R_1 (I > 2\sigma(I))$	0.0840	0.0541	0.0706
wR_2 (all data)	0.2513	0.1605	0.1863
Goodness-of-fit	1.035	1.052	1.015
Temperature [K]	93(2)	93(2)	93(2)
Solvent	<i>o</i> -dichlorobenzene /cyclohexane	toluene/MeOH	o-xylene/octane
CCDC No.	2211115	2211112	2211113

Table S1. Crystallographic data of 8a, 8b, and 12b.

Formula $C_{64}H_{50}N_4O_4Co_2$ Formula weight1056.99Crystal systemmonoclinicSpace group $P2_1/c$ (No. 14)Crystal colorgreenCrystal descriptionprism a [Å]9.5098(2) b [Å]20.5556(3) c [Å]15.4387(2) a [°]90 β [°]95.024(2) γ [°]90 V [ų]3006.36(9) Z 2 d_{calcd} [g cm ⁻³]1.371 R_1 ($I > 2\sigma(I)$)0.0685 wR_2 (all data)0.2028Goodness-of-fit1.033Temperature [K]93(2)	compound	13	
Formula weight1056.99Crystal systemmonoclinicSpace group $P2_1/c$ (No. 14)Crystal colorgreenCrystal descriptionprism a [Å]9.5098(2) b [Å]20.5556(3) c [Å]15.4387(2) a [°]90 β [°]95.024(2) γ [°]90 V [ų]3006.36(9) Z 2 d_{calcd} [g cm ⁻³]1.371 R_1 ($I > 2\sigma(I)$)0.0685 wR_2 (all data)0.2028Goodness-of-fit1.033Temperature [K]93(2)	Formula	$C_{64}H_{50}N_4O_4Co_2\\$	
Crystal system monoclinic Space group $P2_1/c$ (No. 14) Crystal color green Crystal description prism a [Å] 9.5098(2) b [Å] 20.5556(3) c [Å] 15.4387(2) a [°] 90 β [°] 95.024(2) γ [°] 90 \mathcal{V} [ų] 3006.36(9) Z 2 d_{calcd} [g cm ⁻³] 1.371 R_1 ($I > 2\sigma(I)$) 0.0685 wR_2 (all data) 0.2028 Goodness-of-fit 1.033 Temperature [K] 93(2)	Formula weight	1056.99	
Space group $P2_1/c$ (No. 14) Crystal color green Crystal description prism a [Å] 9.5098(2) b [Å] 20.5556(3) c [Å] 15.4387(2) a [°] 90 β [°] 95.024(2) γ [°] 90 \mathcal{V} [ų] 3006.36(9) Z 2 d_{calcd} [g cm ⁻³] 1.371 R_1 ($I > 2\sigma(I)$) 0.0685 wR_2 (all data) 0.2028 Goodness-of-fit 1.033 Temperature [K] 93(2)	Crystal system	monoclinic	
Crystal color green Crystal description prism a [Å] 9.5098(2) b [Å] 20.5556(3) c [Å] 15.4387(2) a [°] 90 β [°] 95.024(2) γ [°] 90 V [ų] 3006.36(9) Z 2 d_{calcd} [g cm ⁻³] 1.371 R_1 ($I > 2\sigma(I)$) 0.0685 wR_2 (all data) 0.2028 Goodness-of-fit 1.033 Temperature [K] 93(2)	Space group	$P2_1/c$ (No. 14)	
Crystal description prism a [Å] 9.5098(2) b [Å] 20.5556(3) c [Å] 15.4387(2) a [°] 90 β [°] 95.024(2) γ [°] 90 V [ų] 3006.36(9) Z 2 d_{calcd} [g cm ⁻³] 1.371 R_1 ($I > 2\sigma(I)$) 0.0685 wR_2 (all data) 0.2028 Goodness-of-fit 1.033 Temperature [K] 93(2)	Crystal color	green	
a [Å]9.5098(2) b [Å]20.5556(3) c [Å]15.4387(2) a [°]90 β [°]95.024(2) γ [°]90 V [Å]3006.36(9) Z 2 d_{calcd} [g cm ⁻³]1.371 R_1 ($I > 2\sigma(I)$)0.0685 wR_2 (all data)0.2028Goodness-of-fit1.033Temperature [K]93(2)	Crystal description	prism	
b [Å]20.5556(3)c [Å]15.4387(2) α [°]90 β [°]95.024(2) γ [°]90 V [Å]3006.36(9) Z 2 d_{calcd} [g cm ⁻³]1.371 R_1 ($I > 2\sigma(I)$)0.0685 wR_2 (all data)0.2028Goodness-of-fit1.033Temperature [K]93(2)	<i>a</i> [Å]	9.5098(2)	
c [Å]15.4387(2) α [°]90 β [°]95.024(2) γ [°]90 V [ų]3006.36(9) Z 2 d_{calcd} [g cm ⁻³]1.371 R_1 ($I > 2\sigma(I)$)0.0685 wR_2 (all data)0.2028Goodness-of-fit1.033Temperature [K]93(2)	<i>b</i> [Å]	20.5556(3)	
α [°] 90 β [°] 95.024(2) γ [°] 90 V [Å ³] 3006.36(9) Z 2 d_{calcd} [g cm ⁻³] 1.371 R_1 ($I > 2\sigma(I)$) 0.0685 wR_2 (all data) 0.2028 Goodness-of-fit 1.033 Temperature [K] 93(2)	<i>c</i> [Å]	15.4387(2)	
β [°]95.024(2) γ [°]90 V [ų]3006.36(9) Z 2 d_{calcd} [g cm ⁻³]1.371 R_1 ($I > 2\sigma(I)$)0.0685 wR_2 (all data)0.2028Goodness-of-fit1.033Temperature [K]93(2)	α [°]	90	
γ [°]90 V [ų]3006.36(9) Z 2 d_{calcd} [g cm ⁻³]1.371 R_1 ($I > 2\sigma(I)$)0.0685 wR_2 (all data)0.2028Goodness-of-fit1.033Temperature [K]93(2)	β [°]	95.024(2)	
V [ų]3006.36(9) Z 2 d_{calcd} [g cm ⁻³]1.371 R_1 ($I > 2\sigma(I)$)0.0685 wR_2 (all data)0.2028Goodness-of-fit1.033Temperature [K]93(2)	γ [°]	90	
Z 2 $d_{calcd} [g cm^{-3}]$ 1.371 $R_1 (I > 2\sigma(I))$ 0.0685 wR_2 (all data) 0.2028 Goodness-of-fit 1.033 Temperature [K] 93(2)	V[Å ³]	3006.36(9)	
$d_{calcd} [g cm^{-3}]$ 1.371 $R_1 (I > 2\sigma(I))$ 0.0685 wR_2 (all data) 0.2028 Goodness-of-fit 1.033 Temperature [K] 93(2)	Ζ	2	
$R_1 (I > 2\sigma(I))$ 0.0685 wR_2 (all data) 0.2028 Goodness-of-fit 1.033 Temperature [K] 93(2)	$d_{\rm calcd} [{ m g \ cm^{-3}}]$	1.371	
wR_2 (all data)0.2028Goodness-of-fit1.033Temperature [K]93(2)	$R_1 (I > 2\sigma(I))$	0.0685	
Goodness-of-fit1.033Temperature [K]93(2)	wR_2 (all data)	0.2028	
Temperature [K] 93(2)	Goodness-of-fit	1.033	
	Temperature [K]	93(2)	
Solvent acetonitrile/toluene	Solvent	acetonitrile/toluene	
CCDC No. 2211114	CCDC No.	2211114	

 Table S2. Crystallographic data of 13.

6. Electrochemistry

Cyclic and differential pulse voltammograms were obtained under the following conditions; solvent: CH₂Cl₂ or THF. electrolyte: 0.1 M Bu₄NPF₆, working electrode: glassy carbon, counter electrode: Pt, reference electrode: Ag/AgNO₃, scan rate: 0.1 V/s.



Figure S43. Cyclic and differential pulse voltammograms of 8a in CH₂Cl₂.



Figure S45. Cyclic and differential pulse voltammograms of 8a in THF.



Figure S46. Cyclic and differential pulse voltammograms of 14b in THF.

7. DFT calculations



Figure S47. Calculated molecular orbitals of **1**, **4**, **2**, and **8c** (isovalue = 0.02). Calculation levels: B3LYP/6-31G(d).



Figure S48. Calculated molecular orbitals of 8c and 12c (isovalue = 0.02). Calculation levels:

B3LYP/6-31G(d).



Figure S49. Calculated molecular orbitals of perylene, 6, anthanthrene, 7, 1, and 8c (isovalue =





Figure S50. Simulated absorption spectra of (a) 8c and (b) 12c. Calculation levels: TD-cam-B3LYP/6-31+G(d,p).



Figure S51. Simulated absorption spectra of (a) 8c and (b) 12c. Calculation levels: TD-cam-B3LYP/6-31+G(d,p) for 14c and $8c^{2-}$ and TD-ucam-B3LYP/6-31+G(d,p) for $8c^{-}$.

8. IR spectra



Figure S53. FT-IR spectra of 8a (red line) and 14a (blue line).



Figure S⁵⁴. Simulated IR spectra of **8c** (red line) and its dianion (blue line). Calculation levels: B3LYP/6-31+G(d)//B3LYP/6-31+G(d). Simulated spectra are output with 10 cm¹ of half-width at half height.



Figure S55. Simulated IR spectra of **8c** (red line) and **14c** (blue line). Calculation levels: B3LYP/6-31+G(d)//B3LYP/6-31+G(d). Simulated spectra are output with 10 cm⁻¹ of half-width at half height.



Figure S56. Change in the absorption spectrum of **8a** in THF (9.9×10^{-6} M) upon addition of cobaltocene. (a) from 0 eq. to 1.2 eq. and (b) from 1.2 eq. to 2.4 eq. The spectrum after the addition of 2.4 eq. of cobaltocene (blue line) is broad due to the precipitation of dianion **13**. Dianion **13** dissolved by the following addition of 10 vol% DMSO (green line); λ : wavelength.



Figure S57. Absorption spectra of **8a** upon application of a voltage in THF in the presence of nBu_4NPF_6 as electrolyte (a) from 0 V to -0.3 V and (b) from 0 V to -0.8 V (vs. Ag/Ag⁺).



Figure S58. Absorption, fluorescence ($\lambda_{ex} = 630 \text{ nm}$), and excitation spectra ($\lambda_{em} = 730 \text{ nm}$) of (a) dianion **13** in DMSO and (b) dihydro-form **14a** in DMSO with one drop of TFA; λ = wavelength.

	solvent	λ_{Abs}/nm	λ_{FL}/nm	Stokes shift/cm ⁻¹	$arPsi_{ m FL}$	τ/ns	$k_{\rm r}/10^7 {\rm \ s}^{-1}$	$k_{\rm nr} + k_{\rm ISC} / 10^8 {\rm s}^{-1}$
8 a	CH_2Cl_2	633	664	738	0.13	2.0	6.5	5.0
13	DMSO	664	679	333	0.53	6.3	12	0.39
14a	DMSO ^[a]	655	673	408	0.40	4.6	8.7	1.3

Table S3. Photophysical properties of 8a, 13, and 14a

[a]: with one drop of TFA.

10. OFET devices

For fabricating thin-film OFETs, the substrates modified with self-assembled monolayers (SAMs) of 12-cyclohexyldodecylphosphonic acid (CDPA) were used. SAM-modified substrates were prepared as described in literature^{S6}. Heavily n-doped Si wafers with a 300 nm-thick thermally grown SiO₂ layer were used as substrates. The Si/SiO₂ substrates were cleaned with deionized water, acetone, and 2-propanol for 10 min in an ultrasonic bath. Substrates were dried with a flow of N₂ gas and then treated by UV-O₃ cleaner (Filgen UV253V8) for 45 min. A solution of Al(NO₃)₃·9H₂O in ethanol (0.1 M) was spin-coated (5000 rpm, 40 s) on cleaned substrates in an N₂ glovebox, and the substrates were annealed at 300 °C for 30 min in the air to form Al₂O₃ layer. The Al₂O₃-coated substrates were treated by UV-O₃ cleaner for 45 min and then soaked in a solution of CDPA in 2-propanol (1.5 mM) at room temperature for 12 h. Finally, substrates were washed with 2-propanol and deionized water, and then dried with a flow of N₂ gas to afford SAM-modified substrates. The average capacitance per unit area of the dielectric layer (C_i) of the insulating layer prepared by this method was measured to be 10 nF cm^{-2 S2}. The active layer was prepared with the vacuum-deposition method using a solid of 8b for 500 Å at 0.3-0.8 Å/s under the pressure of $\sim 5 \times 10^{-4}$ Pa. The top contact source and drain electrodes of gold films (thickness = 300 Å) were vacuum deposited under the pressure of $\sim 5 \times 10^{-4}$ Pa through a shadow mask on the active layer. The drain-source channel length (L) and width (W) were 50 μ m and 1000 μ m, respectively. The output and transfer characteristics of the OFETs were measured using a vacuum prober system (Thermal Block Company, SB-MCPS-NAT) and a Keithley 2400 semiconductor characterization system under vacuum at the pressure of $\sim 3 \times 10^{-1}$ Pa and atmospheric conditions. The field-effect mobilities (μ) of the OFETs were determined from the forward transfer curve in the saturation regime ($V_{\rm DS} = 60$ V) and linear regime ($V_{\rm DS} = 5$ V) using the following each equation,

 $I_{\rm DS} = \mu W C_{\rm i} (V_{\rm G} - V_{\rm th})^2 / 2L$ (saturation regime)

 $I_{\rm DS} = \mu W C_i V_{\rm DS} \{2(V_{\rm G} - V_{\rm th}) - V_{\rm DS}\}/2L$ (linear regime)

Where I_{DS} is the drain-source current and V_{DS} , V_G , and V_{th} are the drain-source voltage, gate voltage, and threshold voltage, respectively. The on/off ratios (I_{on}/I_{off}) were determined from the I_{DS} at $V_G = 0$ V (I_{off}) and $V_G = 60$ V (I_{on}). The averaged μ values ($\mu_{average}$) of the thin-film OFETs were calculated from six devices for **8b**. The polarized optical microscope images were obtained using Zeiss Axio Scope.A1 microscope. The atomic force microscope images were obtained

using Shimadzu SPM-9700 in the tapping mode. Out-of-plane XRD measurement of the vacuum deposited film was performed using a Rigaku SmartLab X-ray diffractometer with a Cu-K α source ($\lambda = 1.5418$ Å) in the 2θ scan mode at a fixed incidence angle of 0.58°. Photoelectron yield spectroscopy measurement was performed using a Riken Keiki AC-3 photoelectron spectrometer.



Figure S59. Schematic description of the thin-film OFET device composition.



Figure S60. Transfer characteristics in the linear regime of thin-film OFET properties of **8b** under (a) vacuum and (b) ambient conditions. Black line: forward sweeping. Red line: backward sweeping.

Table S4. Properties of thin-film OFET devices of 8b.

	Saturatio	on regime	Linear regime		
in vacuum		in air	in vacuum	in air	
$\mu_{ m max} \ [{ m cm}^2 { m V}^{-1} { m s}^{-1}]$	6.7×10^{-3}	5.4×10 ⁻³	5.4×10 ⁻³	4.8×10 ⁻³	
$\mu_{\mathrm{average}} \ [\mathrm{cm}^2 \mathrm{V}^{-1} \mathrm{s}^{-1}]$	$(6.1\pm0.5)\times10^{-3}$	$(4.6\pm0.7)\times10^{-3}$	$(4.9\pm0.3)\times10^{-3}$	$(4.1\pm0.6)\times10^{-3}$	
$V_{\rm th}$ [V]	2.5±0.5	3.8±1.8	6.2±1.5	7.5 ± 1.9	
$I_{ m on}/I_{ m off}$ [-]	$(3.4\pm1.8)\times10^{3}$	$(5.2\pm9.7)\times10^{3}$	$(3.0\pm3.6)\times10^3$	$(3.3\pm5.3)\times10^{3}$	

All potentials are standardized by ferrocene. [a]: in CH₂Cl₂ solution. [b]: in THF solution.



Figure S61. (a,b) Polarized optical micrographs and (c) AFM image of a vacuum-deposited film of **8b**. (RMS roughness: 8.5 nm)



Figure S<mark>62</mark>. Thin film out-of-plane X-ray diffraction patterns of a vacuum-deposited film of **8b**.



Figure S63. Photoelectron spectroscopy measurement of 8b in a vacuum-deposited thin film.



Figure S64. UV/vis absorption spectra of a vacuum-deposited film of 8b and a CH₂Cl₂ solution of 8b. λ = wavelength.


Figure S₆₅. Packing pattern of **8b**. Arrows indicate the direction of transfer integrals. (a) Top view and (b) side view.

	direction	8b–A and 8b–A ^[a] [meV]	8b–A and 8b–B ^[a] [meV]	8b–B and 8b–B ^[a] [meV]
LUMO	t_1	+89.1	+7.62	+37.2
	t_2	+1.63	-0.38	+0.88
	t_3	+2.54	+5.31	+0.89
НОМО	t_1	+65.0	-6.56	+15.3
	t_2	+1.68	-0.92	-0.16
	t_3	+0.08	-0.07	-0.16

 Table S5. Transfer integrals of the 8b calculated at the PBEPBE/6-31G(d) level of theory.

[a]: **8b–A** is one of the disordered structures with an occupancy of 0.58, and **8b–B** is another one with an occupancy of 0.42.



Scheme S1. Possible reaction mechanism of generation of 12a and 12b.



Figure S66. ¹H NMR spectra of 8a in CDCl₃. (a) The spectrum after treatment with 1.0 equiv of DDQ at 60 °C. (b) The spectrum of the as-prepared sample.



Figure S67. (a) Change in absorption spectra of 13 in DMSO under ambient conditions. (b) The plot of change in absorbance at 602 nm of 13 in DMSO under ambient conditions. Curve fitting was conducted by exponential approximation; λ = wavelength.



Figure S68. (a) Change in absorption spectra of 14a in DMSO under ambient conditions. (b) The plot of change in absorbance at 602 nm of 14a in DMSO under ambient conditions. Curve fitting was conducted by exponential approximation; λ = wavelength.



Figure S69. Absorption spectra of **13** in DMSO without TFA (black line) and with one drop of TFA (red line).



Figure S70. ¹H NMR spectra of 14a in DMSO-*d*₆. (a) The spectrum of the as-prepared sample.
(b) The spectrum after treatment with one drop of D₂O. *: residual solvent.



Figure S71. ¹H NMR spectra of 14a and 13 in DMSO-*d*₆. (a) The spectrum of 14a after treatment with one drop of TFA. (b) The spectrum of 13 after treatment with one drop of TFA.
(c) The spectrum of the as-prepared sample of 13. *: residual solvent.

Table S6. Cartesian coordinate of 8c.

C 4.743540 -1.2473402 -0.0001261 C 4.1669403 -2.5108199 -0.0003208 H 4.8199207 -3.3772714 -0.000372 C 2.7733510 -2.6599701 -0.0000372 C 1.03918663 -1.5421599 -0.0000433 C 1.6802127 0.9130251 -0.0001598 C 2.2662098 2.1824432 -0.0003814 H 1.16211490 3.054023 -0.000732 C 3.358212 2.3221865 -0.000773 C 3.4485634 1.2027984 -0.000773 C 3.521071 -0.0226367 -0.0000732 C 3.521071 -0.0263645 -0.0000346 C 0.2323215 0.7021612 -0.0000572 C -4.743524 1.2473600 0.0000283 C 0.2323215 0.7021612 -0.0000572 C -4.743524 1.2473600 0.0000283 C -4.743524 1.2473600 0.0000283 <tr< th=""><th></th><th></th><th></th><th></th></tr<>				
C 4.169403 -2.5108199 -0.0002068 H 4.8199207 -3.3772714 -0.000373 C 2.2733515 2.62699701 -0.0000372 C 1.9318663 -1.5421599 -0.000198 C 1.0318621 0.9130251 -0.000198 C 2.2662098 2.1824432 -0.0001814 H 1.6211400 3.0540233 -0.0001763 C 3.3548312 2.3221865 -0.0001763 C 3.3541917 -0.0001763 -0.0001763 C 3.2510171 -0.0026287 -0.0000173 C 3.2510171 -0.0026287 -0.0000173 C 3.2510171 -0.0026287 -0.0000173 C 3.2510171 -0.0001733 -0.0001733 C -3.582312 3.773875 0.0000184 C 0.2584021 -1.1484364 -0.0001332 C -4.7433423 2.6599703 -0.0001852 C -4.763242 2.659973 -0.0001854	С	4.7443540	-1.2473402	-0.0001261
H (4.8199207 -3.372714 (-0.0003673 C 2.7733510 -2.6599701 -0.000398 H 2.316898 -3.6443297 0.0000572 C 1.680127 0.9130251 -0.0001898 C 2.2662098 2.1824432 -0.000314 H 1.6121490 3.0540233 -0.000731 C 3.6582312 2.3221865 -0.000773 C 3.6582312 2.3221865 -0.000773 C 3.456343 1.2027984 -0.000773 C 3.9210171 -0.023645 -0.0001733 C 3.9210171 -0.023645 -0.0001733 C 2.5084021 -0.236345 -0.0001733 C 3.9210171 -0.0236345 -0.0003874 C 3.9210171 -0.0236345 -0.0001733 C 4.2182474 -1.1045836 -0.0003846 C -2.5084021 0.721612 -0.0005875 C -4.743524 1.2473600 0.0000382 <tr< td=""><td>С</td><td>4.1669403</td><td>-2.5108199</td><td>-0.0002068</td></tr<>	С	4.1669403	-2.5108199	-0.0002068
C 2.713310 -2.6599701 -0.0000398 H 2.3168958 -3.643297 0.0000572 C 1.6802127 0.9130251 -0.0000438 C 2.2662098 2.1824432 -0.0000814 H 1.6211490 3.0540233 -0.000273 C 3.6582312 2.3221865 -0.0004786 H 4.1192765 3.3041924 -0.000773 C 3.9210171 -0.0926287 -0.0000733 C 2.5084021 -0.2363645 -0.0000136 C 6.2182474 -1.1045836 -0.0000384 C 0.2323215 0.7021612 -0.0000872 C -4.743524 1.2473600 0.0000233 C -4.743524 1.2473600 0.0000332 C -4.743524 1.247360 0.0001852 C -2.733423 2.6599703 -0.001843 C -1.9318645 1.5421533 -0.0001430 C -1.9318645 1.5421533 -0.000346	Н	4.8199207	-3.3772714	-0.0003673
H 2.3168938 3.6443297 0.0000572 C 1.9318663 1.521599 -0.0001598 C 2.2662098 2.1824432 -0.0003814 H 1.6121490 3.0540233 -0.0005251 C 3.658212 2.23221865 -0.0004756 H 4.1192765 3.3041924 -0.000773 C 3.4856334 1.2027984 -0.000773 C 3.9210171 -0.0926365 -0.00001763 C 2.5084021 -0.2363645 -0.0001381 C 2.5182647 -1.1045836 -0.0000382 C 0.232215 0.7021612 -0.0000587 C -4.7443524 1.2473600 0.0000283 C -4.7443524 1.2473600 0.0000382 C -4.7443524 1.2473600 0.0000382 C -4.73423 2.6599703 -0.001819 H -4.319979 3.372875 0.000366 C -2.73423 2.6599703 -0.0001862 <t< td=""><td>С</td><td>2.7733510</td><td>-2.6599701</td><td>-0.0000398</td></t<>	С	2.7733510	-2.6599701	-0.0000398
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C1.68021270.9130251-0.0001598C2.26620982.1824432-0.000814H1.62114903.0540233-0.000251C3.65823122.3221865-0.0004786H4.11927653.3041924-0.000173C3.9210171-0.0026287-0.000173C3.9210171-0.0262685-0.0000133C6.2182647-1.1045836-0.000034C5.96092681.3780233-0.0000887C0.23232150.7021612-0.0000887C-4.74435241.24736000.0000887C-4.74435242.51083390.0000382C-4.74435242.51083390.0000382C-4.7435242.51083390.0000386C-7.7734232.6599703-0.0001819H-1.93186451.5421533-0.0001403C-1.93186451.5421533-0.0001403C-1.6802120-0.91302920.0002846C-1.6802120-0.91302920.000386C-3.6582360-2.32217370.0004103H-1.621584-3.05402960.0003868C-3.92102110.0926386-0.0001200C-5.969329-1.37803540.0003214C-3.92102110.0926386-0.0001200C-5.969329-1.37803540.0001321C-6.978403-0.202438-0.0001200C-6.978403-0.202438-0.0001200C-6.978403-	С	1.9318663	-1.5421599	-0.0000463
C 2.2662098 2.1824432 0.0005814 H 1.6211490 3.0540233 0.000786 C 3.6582312 2.3221865 0.0004786 H 4.1192765 3.3041924 0.000773 C 3.9210171 0.0926287 0.0000133 C 2.5084021 0.2363645 0.0000384 C 0.2323215 0.7021612 0.0000887 C -4.7443524 1.2473600 0.0000832 C -4.7443524 1.2473600 0.0000832 C -2.7733423 2.659703 0.001819 H -4.8199099 3.3772875 0.0000382 C -1.9318645 1.5421533 0.001403 C -1.6802120 -0.913022 0.0000243 C -2.2662115 -2.321737 0.00002539 H -1.6521584 -3.0540296 0.0003686 C -3.9210211 0.0926386 -0.00001610 C -3.9210211 0.0926386 -0.00001241 <td>С</td> <td>1.6802127</td> <td>0.9130251</td> <td>-0.0001598</td>	С	1.6802127	0.9130251	-0.0001598
H 1.6211490 3.0540233 -0.0002511 C 3.6582312 2.3221865 -0.0004786 H 4.1192765 3.3041924 -0.000773 C 3.9210171 -0.0926287 -0.0000792 C 2.5084021 -0.2363645 -0.000034 C 6.2182647 -1.1045836 -0.0000384 C 0.2323125 0.7021612 -0.000083 C 4.7443524 1.2473600 0.0000283 C -4.1669324 2.5108339 0.0000882 C -2.7733423 2.6599703 -0.0001892 C -1.9318645 1.5421533 -0.0001403 C -1.6802120 -0.9130292 0.0000244 C -2.2662115 -2.182437 0.0002539 H -1.6211584 -3.0540296 -0.000366 C -3.6582360 -2.3221737 0.0001403 C -3.6582360 -1.027851 0.000146 C -3.9210211 0.0926386 -0.0001690	С	2.2662098	2.1824432	-0.0003814
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H 4.1192765 3.3041924 0.000773 C 4.4856334 1.0207984 0.000792 C 3.921011 0.0926287 0.0000792 C 2.5084021 0.2363645 0.0000384 C 6.2182647 -1.1045836 0.000384 C 0.02323215 0.7021612 -0.0000887 C -4.7443524 1.2473600 0.0000283 C -4.1669324 2.518339 0.00001852 C -4.7733423 2.6599703 -0.0001819 H -2.3168747 3.6443245 -0.0001346 C -1.9318645 1.5421533 -0.000182 C -1.9318645 -1.9130292 0.0001263 C -2.2662115 -2.182437 0.0002539 H -1.6211584 -3.0540296 0.0003868 C -3.9210211 0.0926386 -0.0000140 C -2.350436 0.2363608 -0.0000150 C -4.4856396 -1.2027851 0.0001426	С	3.6582312	2.3221865	-0.0004786
C 4.4856334 1.2027984 0.0001763 C 3.3210171 0.036645 0.0000732 C 2.5084021 0.145836 0.000334 C 0.2323215 0.7021612 0.000384 C 0.2323215 0.7021612 0.000383 C -4.7443524 1.2473600 0.0000283 C -4.7443524 1.2473600 0.0000382 C -4.7443524 1.2473600 0.0000382 C -4.7483524 1.2473600 0.0000382 C -4.7483524 1.2473600 0.0000382 C -4.7483524 1.2473600 0.0000382 C -4.7483524 1.2473600 0.0000382 C -2.7733423 2.6599703 0.001834 C -1.6802120 -0.9130292 0.0000244 C -1.6802120 -0.9130292 0.0000368 C -1.2662115 -3.3041790 0.0007358 C -3.521021 -0.0203546 -0.001056 </td <td>Н</td> <td>4.1192765</td> <td>3.3041924</td> <td>-0.0007773</td>	Н	4.1192765	3.3041924	-0.0007773
C 3.9210171 0.0926287 0.0000792 C 2.5084021 0.2363645 0.0000334 C 6.2182647 1.1045836 0.000384 C 0.2323215 0.7021612 0.0000887 C -4.7443524 1.2473600 0.0000832 C -4.7443524 1.2473600 0.0000832 C -4.7443524 2.5108339 0.0000832 C -2.773423 2.6599703 0.001852 C -2.773423 2.6599703 -0.0001843 C -1.9318645 1.5421533 -0.0001846 C -1.9318645 1.5421533 -0.000124 C -2.2662115 -2.182437 0.0002539 H -1.6511584 -3.0540296 0.0003586 C -3.921021 0.0026386 -0.0001426 C -3.921021 0.002783 0.0001538 C -4.4856396 -1.2027851 0.0001538 C -3.921021 0.0026386 -0.0000657	С	4.4856334	1.2027984	-0.0001763
C 2.5084021 0.2363645 0.000133 C 6.2182647 -1.1045836 0.000384 C 5.9609268 1.378033 -0.0000887 C 0.2323215 0.07021612 -0.0000887 C -4.7443524 1.2473600 0.0000283 C -4.1669324 2.5108339 0.00001852 C -2.7733423 2.6599703 -0.0001819 H -2.3168747 3.6443245 -0.0001346 C -1.6802120 -0.913024 0.000244 C -2.2662115 -2.182437 0.0002539 H -1.6211584 -3.0540296 0.0003686 C -3.6582360 -2.3221737 0.0004133 H -1.6211584 -3.3041790 0.0007358 C -3.658236 -0.2027851 0.0001242 C -2.5084036 0.2363608 -0.0001260 C -2.5084036 0.2363608 -0.0001261 C -0.5075439 -1.7384354 -0.00016312	С	3.9210171	-0.0926287	-0.0000792
C 6.2182647 1.045836 0.0003046 C 5.9609268 1.3780233 3.0.0000384 C 0.2323215 0.7021612 -0.0000587 C -4.7434524 1.2473600 0.0000283 C -4.7434524 2.5108339 0.0000832 C -4.7434524 2.6599703 -0.001852 C -2.733423 2.6599703 -0.0001843 C -1.9318645 1.5421533 -0.0001403 C -1.6802120 -0.9130292 0.0000244 C -2.3662115 -2.1824437 0.000259 H -1.615845 -3.054026 0.000366 C -3.6582360 -2.3221737 0.0004103 H -4.1192815 -3.3041790 0.0007358 C -3.9210211 0.0926368 -0.0001260 C -3.9210211 0.0926368 -0.0001260 C -5.9609329 -1.3780354 0.0001332 C -0.0323186 -0.7021681 -0.0002614	С	2.5084021	-0.2363645	-0.0000133
C 5.9609268 1.3780233 0.000384 C 0.2323215 0.7021612 -0.0000873 C -4.7443524 1.2473600 0.0000383 C -4.1669324 2.5108339 0.0000385 C -2.7733423 2.6599703 -0.0001819 H -2.3168747 3.6443245 -0.0003346 C -1.6802120 -0.9130292 0.0000244 C -1.6802120 -0.9130292 0.0000244 C -2.2662115 -2.3221737 0.00001403 H -1.6211584 -3.0540296 0.0003686 C -3.5582360 -2.3221737 0.0001403 H -4.1192815 -3.041790 0.0007378 C -4.865396 -1.0227851 0.0001246 C -5.969329 -1.3780354 0.0001321 C -5.969329 -1.3780354 0.0000321 C -0.2323186 -0.7021681 -0.0006591 N 0.6737439 1.7384854 -0.0003202	С	6.2182647	-1.1045836	-0.0003046
C 0.2323215 0.7021612 0.000587 C -4.7443524 1.2473600 0.0000283 C -4.1669324 2.5108339 0.000082 H -4.8199099 3.3772875 0.0001819 H -2.3168747 3.6443245 -0.000346 C -1.9318645 1.5421533 -0.0001403 C -1.6802120 -0.9130292 0.0000244 C -2.2662115 -2.1824437 0.0002539 H -1.6211584 -3.0540296 0.0003686 C -3.6582360 -2.3221737 0.0004103 H -4.1192815 -3.3041790 0.0007358 C -4.485636 -1.027851 0.0001426 C -3.5910211 0.0926386 -0.0001260 C -2.5084036 0.2363608 -0.0001260 C -0.2323186 -0.7021681 -0.0006691 N 0.5675451 -1.7384952 -0.00005302 O 6.9789402 -2.0629547 -0.0003502	С	5.9609268	1.3780233	-0.0000384
C -4.7443524 1.2473600 0.0000283 C -4.1669324 2.5108339 0.0000382 H -4.8199099 3.3772875 0.0001852 C -2.713423 2.6599703 0.001819 C -1.7318645 1.5421533 -0.0001346 C -1.9318645 1.5421533 -0.0001403 C -1.9318645 1.5421533 -0.0001244 C -2.2662115 -2.182437 0.0002539 H -1.6211584 -3.3041790 0.0007358 C -3.658236 -2.3221737 0.0004103 H -4.1192815 -3.3041790 0.0007358 C -3.9210211 0.0926386 -0.000057 C -2.5084036 0.2363608 -0.0001260 C -5.909329 -1.3780534 0.0001320 C -0.2323186 -0.7021681 -0.0000651 N 0.5675451 -1.7384932 -0.0001266 N 0.5675453 -1.7384932 -0.0001832	С	0.2323215	0.7021612	-0.0000587
C -4.1669324 2.5108339 0.000382 H -4.8199099 3.3772875 0.0001852 C -2.7733423 2.6599703 -0.0001819 H -2.3168747 3.6443245 -0.0003346 C -1.9318645 1.5421533 -0.0001403 C -1.6802120 -0.9130292 0.0000244 C -2.2662115 -2.1824437 0.0002539 H -1.6211584 -3.0541790 0.0007358 C -3.658260 -2.3221737 0.0004103 K -4.4856396 -1.2027851 0.0007358 C -4.4856396 -1.2027851 0.0001426 C -3.9210211 0.0926386 -0.0001260 C -2.5084036 0.2363608 -0.0001320 C -0.2182540 1.1045741 0.000132 C -0.2023186 -0.7021681 -0.0001669 N 0.5675439 1.1378454 -0.0001682 N -0.67781026 -2.0629438 -0.0001572	С	-4.7443524	1.2473600	0.0000283
H4.81990993.37728750.0001852C2.77334232.65997030.001819H2.31687473.64432450.003346C-1.93186451.54215330.001403C-2.2662115-2.18244370.0002539H-1.6211584-3.05402960.0003686C-3.6582360-2.32217370.0004103H-4.1192815-3.30417900.0007358C-3.92102110.0926386-0.000057C-3.92102110.0926386-0.000057C-5.9609329-1.37803540.0001320C-5.9609329-1.37803540.0001321C-0.2323186-0.7021681-0.0000691N0.5675451-1.7384932-0.0000657N0.5675453-1.7384932-0.0001246N-6.7301267-0.2029438-0.0001820O-6.48342742.4841218-0.000346O-6.9789402-2.0629471-0.000346O-6.4834331-2.48412270.0019321O-6.9789402-2.0629434-0.0001832O-6.4834331-2.4841218-0.000346O-6.9789402-2.0629347-0.000346O-6.4834331-2.4841218-0.000346O-6.4834331-2.48412170.0004573H8.6036640-0.17193440.884336H8.6036640-0.17193440.884336H8.6039581-0.1260328-0.088786H<	С	-4.1669324	2.5108339	0.0000382
C 2.7733423 2.6599703 0.001819 H -2.3168747 3.6443245 -0.0003366 C -1.9318645 1.5421533 -0.0001403 C -1.6802120 -0.21824437 0.0002539 C -2.2662115 -2.1824437 0.0003666 C -3.5582360 -2.3221737 0.0004103 H -4.192815 -3.3041790 0.0007358 C -3.582360 -2.3221737 0.00001426 C -3.582360 -2.3221737 0.00001426 C -3.9210211 0.0926386 -0.000057 C -4.4856396 -1.2027851 0.0001320 C -3.9210211 0.0926386 -0.0000691 C -2.5084036 0.2363608 -0.0001320 C -0.2323186 -0.7021681 -0.0000691 N 0.5675451 -1.7384932 -0.0000530 N -0.5675439 1.7384854 -0.001260 N -6.7301267 -0.2029438 -0.0001832 </td <td>Н</td> <td>-4.8199099</td> <td>3.3772875</td> <td>0.0001852</td>	Н	-4.8199099	3.3772875	0.0001852
H2.31687473.64432450.000346C-1.93186451.5421533-0.0001403C-1.6802120-0.91302920.0000244C-2.2662115-2.18244370.0002539H-1.6211584-3.05402960.0003686C-3.6582360-2.32217370.0004103H-4.1192815-3.30417900.0007358C-3.92102110.0926386-0.000057C-3.92102110.0926386-0.00001260C-3.92102110.0926386-0.0001260C-2.50840360.2363608-0.0001260C-2.50840360.2363608-0.0001260C-2.50840360.2363608-0.0001260C-2.50840360.2363608-0.0001260C-2.50840360.2363608-0.0001260C-2.50840360.2363608-0.0001260C-2.5084036-0.7021681-0.000651C-0.2323186-0.7021681-0.000659N0.5675451-1.7384954-0.0001246N6.73013060.20293170.0008588N-6.7301267-0.2029438-0.0005302O6.48342742.4841218-0.0003696O-6.97894872.06294240.0010960O-6.97894872.06294240.0010960O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H	С	-2.7733423	2.6599703	-0.0001819
C 1.9318645 1.5421533 0.001403 C 1.6802120 0.9130292 0.0000244 C 2.2662115 2.1824437 0.0002539 H -1.6211584 3.0540296 0.0003686 C 3.6582360 2.3221737 0.0001103 H -4.1192815 3.3041790 0.0007358 C -4.4856396 -1.2027851 0.0001426 C -3.9210211 0.0926386 -0.000057 C -2.5084036 0.2363608 -0.00001260 C -2.5084036 0.2363608 -0.0001260 C -2.5084036 0.2363608 -0.000051 C -0.2323186 -0.7021681 -0.0000651 N 0.5675451 -1.7384932 -0.0000651 N -0.5675439 1.7384854 -0.0001246 N -6.7301267 -0.2029438 -0.0001260 O 6.9789402 -2.0629547 -0.001832 O 6.64834274 2.4841218 -0.0	Н	-2.3168747	3.6443245	-0.0003346
C 1.6802120 0.9130292 0.0000244 C 2.2662115 2.1824437 0.0002539 H 1.6211584 3.0540296 0.0003686 C 3.6582360 2.3221737 0.0004103 H 4.419215 3.3041790 0.0007358 C 4.4856396 1.2027851 0.0001426 C 3.9210211 0.0926368 0.000057 C 3.5084036 0.23263608 0.0001260 C 5.9609329 1.3780354 0.0001332 C -0.02323186 -0.7021681 -0.0000651 N 0.5675451 -1.7384932 -0.0000510 N 0.5675451 -1.7384932 -0.0000651 N -6.7301267 -0.2029438 -0.0001280 O 6.9789402 -2.0629547 -0.0003214 O -6.7301267 -0.2029438 -0.0003921 O -6.9789402 -2.0629547 -0.0010832 O -6.9789487 2.0629424	С	-1.9318645	1.5421533	-0.0001403
C 2.2662115 2.1824437 0.0002539 H -1.6211584 3.0540296 0.0003686 C 3.6582360 2.3221737 0.0004103 H -4.1192815 3.3041790 0.0007358 C -4.4856396 -1.2027851 0.0001426 C -3.9210211 0.0926386 -0.000057 C -2.5084036 0.2363608 -0.0001260 C -2.5084036 0.2363608 -0.0001240 C -2.50840329 -1.3780354 0.0001332 C -0.2323186 -0.7021681 -0.0000651 N 0.5675439 1.7384932 -0.0001246 N 0.5675439 1.7384932 -0.0001246 N -0.57301306 0.2029317 0.008658 N -6.7301267 -0.2029438 -0.0001332 O 6.4834274 2.4841218 -0.0001832 O -6.4834331 -2.4841227 0.0004921 C 8.1929368 0.3237131 0.0007574<	С	-1.6802120	-0.9130292	0.0000244
H1.62115843.05402960.0003686C3.65823602.32217370.0004103H4.11928153.30417900.0007358C4.4856396-1.20278510.0001426C3.92102110.0926386-0.000057C2.50840360.2363608-0.0001260C2.50840360.2363608-0.0001261C2.50840360.2363608-0.0001261C2.50840360.2363608-0.0001261C2.50840360.2363608-0.0001261C5.9609329-1.37803540.0001322C-0.2323186-0.7021681-0.000651N0.5675451-1.7384952-0.000651N0.56754591.17384854-0.0001246N0.6.73013060.20293170.0008658N-6.7301267-0.2029438-0.0003946O6.48342742.4841218-0.0003946O-6.47894872.06294240.0010960O-6.47894872.06294240.0010960O-6.4834331-2.4841218-0.0003946O-6.4834331-2.48412180.001972C8.19293680.32371310.0015732H8.6041980-0.1610106-0.8870878H8.6041980-0.1610106-0.8870878H-8.60395810.16093720.8879243H-8.60395810.16093720.8834681H-8.60395850.1720828-0.8834681 <t< td=""><td>С</td><td>-2.2662115</td><td>-2.1824437</td><td>0.0002539</td></t<>	С	-2.2662115	-2.1824437	0.0002539
C 3.6582360 2.3221737 0.0004103 H 4.1192815 3.3041790 0.0007358 C 4.4856396 1.2027851 0.0001426 C 3.9210211 0.0926386 0.000057 C 2.5084036 0.2363608 0.0001260 C 6.2182540 1.1045741 0.0003214 C 5.9609329 -1.3780354 0.0001332 C -0.2323186 -0.7021681 -0.0000669 N 0.5675451 -1.7384932 -0.0000651 N -0.5675439 1.7384854 -0.0001246 N -0.5675439 1.7384854 -0.0001246 N -0.5675439 -0.2029317 0.0008658 N -0.67301306 0.2029317 -0.001832 O -6.7301267 -0.2029438 -0.001832 O -6.483431 -2.4629547 -0.001832 O -6.4834331 -2.4841218 -0.001960 O -6.4834331 -2.4841227 0.	Н	-1.6211584	-3.0540296	0.0003686
H4.11928153.30417900.0007358C4.48563961.20278510.0001426C3.92102110.09263860.000057C-2.50840360.2363608-0.0001260C-6.21825401.10457410.0003214C-5.9609329-1.37803540.0001332C-0.02323186-0.7021681-0.000669N0.5675451-1.7384932-0.000651N-0.56754391.7384854-0.001246N6.73013060.20293170.0008658N-6.7301267-0.2029438-0.0003202O6.648342742.4841218-0.001392O-6.4834331-2.48412270.001960O-6.4834331-2.48412270.0004921C8.19293680.32371310.001573H8.6036640-0.17193440.884396H-8.60395810.16093720.0078748H-8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.60387860.1720828-0.8834681H-8.60387860.1720828-0.8834681	С	-3.6582360	-2.3221737	0.0004103
C 4.4856396 1.2027851 0.0001426 C 3.9210211 0.0926386 0.000057 C 2.5084036 0.2363608 0.0001260 C 6.2182540 1.1045741 0.0003214 C 5.9609329 1.3780354 0.0001332 C 0.2323186 0.7021681 0.000669 N 0.5675451 1.7384932 0.0001246 N -0.5675439 1.7384854 0.0001246 N -0.5675439 1.7384854 0.0001246 N -0.5675439 1.7384854 0.0001246 N -0.5675439 1.7384854 0.001246 N -0.5675439 1.7384854 -0.0001832 O -6.7301267 -0.2029438 -0.001282 O -6.7301267 -0.02029438 -0.0010832 O -6.7301267 -0.02029438 -0.0010832 O -6.739847 2.0629424 0.0010960 O -6.4834331 -2.4841217	Н	-4.1192815	-3.3041790	0.0007358
C3.92102110.09263860.000057C-2.50840360.2363608-0.0001260C-6.21825401.10457410.0003214C-5.9609329-1.37803540.0001332C-0.2323186-0.7021681-0.000669N0.5675451-1.7384932-0.0000651N-0.56754391.7384854-0.0001246N-0.56754391.7384854-0.0001246N-0.56754391.7384854-0.0001246N-6.7301267-0.2029438-0.0005302O6.9789402-2.0629547-0.0010832O6.48342742.4841218-0.0003946O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6039581-0.3237153-0.0008938H8.60395810.16093720.8879243H-8.60395810.16093720.8879243H-8.60395810.16093720.8834681H-8.60387860.1720828-0.8834681H-8.60387860.1720828-0.8834681H-8.60387860.1720828-0.8834681	С	-4.4856396	-1.2027851	0.0001426
C2.50840360.23636080.0001260C6.21825401.10457410.0003214C5.9609329-1.37803540.0001332C-0.2323186-0.7021681-0.0000669N0.5675451-1.7384932-0.0000651N-0.56754391.7384854-0.0001246N6.73013060.20293170.0008588N-6.7301267-0.2029438-0.0005302O6.9789402-2.0629547-0.0010832O6.48342742.4841218-0.0003946O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6041980-0.1610106-0.8870875H8.43782291.38320010.0078748C-8.1929332-0.3237153-0.0008938H-8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.60387860.1720828-0.8834681H-8.60387860.1720828-0.8834681	С	-3.9210211	0.0926386	-0.0000057
C6.21825401.10457410.0003214C5.9609329-1.37803540.0001332C-0.02323186-0.7021681-0.000669N0.5675451-1.7384932-0.0000651N-0.56754391.7384854-0.0001246N6.73013060.20293170.0008658N-6.7301267-0.2029438-0.0005302O6.9789402-2.0629547-0.0010832O6.48342742.4841218-0.0003946O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6036640-0.1610106-0.8870875H8.6036640-0.1610106-0.8870875H8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.60387860.1720828-0.8834681H-8.6337865-1.3831943-0.0072381	С	-2.5084036	0.2363608	-0.0001260
C5.96093291.37803540.0001332C-0.2323186-0.7021681-0.000669N0.5675451-1.7384932-0.0000651N-0.56754391.7384854-0.0001246N6.73013060.20293170.0008658N-6.7301267-0.2029438-0.0003920O6.9789402-2.0629547-0.0010832O6.48342742.4841218-0.0003946O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6041980-0.1610106-0.8870875H8.6303640-0.1610106-0.8870875H8.63378610.16093720.8879243H-8.60395810.16093720.8834681H-8.60387860.1720828-0.8834681H-8.4378675-1.3831943-0.0072381	С	-6.2182540	1.1045741	0.0003214
C0.23231860.70216810.0000699N0.5675451-1.7384932-0.0000651N-0.56754391.7384854-0.0001246N6.73013060.20293170.0008658N-6.7301267-0.2029438-0.0005302O6.9789402-2.0629547-0.0010832O6.48342742.4841218-0.0003946O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6041980-0.1610106-0.8870875H8.43782291.38320010.0078748C-8.1929332-0.3237153-0.0008938H-8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.60387860.1720828-0.8834681H-8.4378675-1.3831943-0.0072381	С	-5.9609329	-1.3780354	0.0001332
N0.56754511.73849320.000651N-0.56754391.7384854-0.0001246N6.73013060.20293170.0008658N-6.7301267-0.2029438-0.005302O6.9789402-2.0629547-0.0010832O6.48342742.4841218-0.0003946O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6041980-0.1610106-0.8870875H8.43782291.38320010.0078748C-8.1929332-0.3237153-0.0008938H-8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.4378675-1.3831943-0.0072381	С	-0.2323186	-0.7021681	-0.0000669
N0.56754391.73848540.0001246N6.73013060.20293170.0008658N-6.7301267-0.2029438-0.0005302O6.9789402-2.0629547-0.0010832O6.48342742.4841218-0.0003946O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6041980-0.1610106-0.8870875H8.43782291.38320010.0078748C-8.1929332-0.3237153-0.0008938H-8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.4378675-1.3831943-0.0072381	N	0.5675451	-1.7384932	-0.0000651
N6.73013060.20293170.0008658N-6.7301267-0.2029438-0.0005302O6.9789402-2.0629547-0.0010832O6.48342742.4841218-0.0003946O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6041980-0.1610106-0.8870875H8.43782291.38320010.0078748C-8.1929332-0.3237153-0.0008938H-8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.4378675-1.3831943-0.0072381	N	-0.5675439	1.7384854	-0.0001246
N 6.7301267 0.2029438 0.0005302 O 6.9789402 -2.0629547 0.010832 O 6.4834274 2.4841218 -0.0003946 O -6.9789487 2.0629424 0.0010960 O -6.4834331 -2.4841227 0.0004921 C 8.1929368 0.3237131 0.0015732 H 8.6036640 -0.1719344 0.8843396 H 8.6041980 -0.1610106 -0.8870875 H 8.4378229 1.3832001 0.0078748 C -8.1929332 -0.3237153 -0.0008938 H -8.6039581 0.1609372 0.8879243 H -8.6038786 0.1720828 -0.8834681 H -8.4378675 -1.3831943 -0.0072381	N	6.7301306	0.2029317	0.0008658
O6.97894022.06295470.0010832O6.48342742.4841218-0.0003946O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6041980-0.1610106-0.8870875H8.43782291.38320010.0078748C-8.1929332-0.3237153-0.0008938H-8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.4378675-1.3831943-0.0072381	N	-6.7301267	-0.2029438	-0.0005302
O6.48342742.48412180.0003946O-6.97894872.06294240.0010960O-6.4834331-2.48412270.0004921C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6041980-0.1610106-0.8870875H8.43782291.38320010.0078748C-8.1929332-0.3237153-0.0008938H-8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.4378675-1.3831943-0.0072381	0	6.9789402	-2.0629547	-0.0010832
O6.97894872.06294240.0010960O6.48343312.48412270.0004921C8.19293680.32371310.0015732H8.60366400.17193440.8843396H8.60419800.16101060.8870875H8.43782291.38320010.0078748C-8.1929332-0.3237153-0.0008938H-8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.4378675-1.3831943-0.0072381	0	6.4834274	2.4841218	-0.0003946
O 6.4834331 2.4841227 0.0004921 C 8.1929368 0.3237131 0.0015732 H 8.6036640 0.1719344 0.8843396 H 8.6041980 0.1610106 0.8870875 H 8.4378229 1.3832001 0.0078748 C 8.1929332 0.3237153 0.0008938 H -8.6039581 0.1609372 0.8879243 H 8.6038786 0.1720828 0.8834681 H -8.4378675 -1.3831943 -0.0072381	0	-6.9789487	2.0629424	0.0010960
C8.19293680.32371310.0015732H8.6036640-0.17193440.8843396H8.6041980-0.1610106-0.8870875H8.43782291.38320010.0078748C-8.1929332-0.3237153-0.0008938H-8.60395810.16093720.8879243H-8.60387860.1720828-0.8834681H-8.4378675-1.3831943-0.0072381	0	-6.4834331	-2.4841227	0.0004921
H8.60366400.17193440.8843396H8.60419800.16101060.8870875H8.43782291.38320010.0078748C8.19293320.32371530.0008938H-8.60395810.16093720.8879243H-8.60387860.17208280.8834681H-8.4378675-1.3831943-0.0072381	С	8.1929368	0.3237131	0.0015732
H8.60419800.16101060.8870875H8.43782291.38320010.0078748C8.19293320.32371530.0008938H8.60395810.16093720.8879243H8.60387860.17208280.8834681H8.43786751.3831943-0.0072381	Н	8.6036640	-0.1719344	0.8843396
H8.43782291.38320010.0078748C8.19293320.32371530.0008938H8.60395810.16093720.8879243H8.60387860.17208280.8834681H8.43786751.3831943-0.0072381	Н	8.6041980	-0.1610106	-0.8870875
C 8.1929332 0.3237153 0.0008938 H 8.6039581 0.1609372 0.8879243 H 8.6038786 0.1720828 0.8834681 H 8.4378675 1.3831943 0.0072381	Н	8.4378229	1.3832001	0.0078748
H8.60395810.16093720.8879243H8.60387860.17208280.8834681H8.43786751.38319430.0072381	С	-8.1929332	-0.3237153	-0.0008938
H-8.60387860.1720828-0.8834681H-8.4378675-1.3831943-0.0072381	Н	-8.6039581	0.1609372	0.8879243
Н –8.4378675 –1.3831943 –0.0072381	Н	-8.6038786	0.1720828	-0.8834681
	Н	-8.4378675	-1.3831943	-0.0072381

No negative frequency

Sum of electronic and thermal free energies = -1595.457896 Hartree.

 Table S7. Cartesian coordinate of 12c.

С	-0.090742	0.060005	-0.039438
С	-0.065483	0.091163	3.673408
С	0.560501	0.075315	1.221026
С	-0.044203	-0.560139	2.412981
С	1.825846	0.702523	1.321825
С	-0.604512	-1.856637	2.311502
С	2.439618	1.301126	0.237557
С	-1.173902	-2.498454	3.394799
С	2.424681	1.884657	-2.152913
С	-1.775895	-2.50992	5.780576
С	1.787163	1.866745	-3.39079
С	-1.799881	-1.867805	7.016317
С	0.53414	1.266182	-3.532723
С	-1.264504	-0.585766	7.159249
С	-0.098229	0.667422	-2.437169
С	-0.689346	0.073303	6.066923
С	0.54026	0.669919	-1.170291
С	-0.650443	-0.567446	4.801972
С	1.808208	1.290502	-1.032204
С	-1.205112	-1.865602	4.663113
С	-1.40989	0.031982	-2.54028
С	-0.119455	1.414665	6.171672
С	-3.27185	-0.573038	-3.784448
С	0.383807	3.306746	7.415848
С	-3.929438	-0.574251	-5.020509
С	0.338156	3.967978	8.649212
С	-5.186666	-1.174633	-5.165752
С	0.881255	5.250703	8.797762
С	-5.809918	-1.786204	-4.084316
С	1.481172	5.894508	7.722251
С	-5.781443	-2.423582	-1.705089
С	2.156786	5.886602	5.353434
С	-5.135198	-2.436944	-0.472721
С	2.216647	5.235445	4.124681
С	-3.883132	-1.833168	-0.315741
С	1.668018	3.958795	3.96368
С	-3.257846	-1.204722	-1.398183
С	1.048762	3.311828	5.038536
С	-3.899135	-1.192236	-2.661927
С	0.990825	3.956366	6.299207
С	-5.171236	-1.803172	-2.818202
С	1.545028	5.25378	6.458979
С	-1.951068	-0.556704	-1.302132
С	0.45689	1.978903	4.938206
С	3.75748	1.958281	0.41479
С	-1.757717	-3.849712	3.225738
С	3.754603	2.527226	-2.013976
С	-2.351189	-3.872868	5.648594
С	-7.138711	-2.420096	-4.261195
С	2.057141	7.248153	7.895036
С	-7.11152	-3.065831	-1.850945
С	2.743387	7.244382	5.495828
С	5.644236	3.172981	-0.619065
L	1		

С	-2.866132	-5.795747	4.187035
С	-9.015281	-3.665886	-3.245339
С	3.219385	9.174973	6.958914
N	-1.331231	-0.520993	-0.148205
N	0.457461	1.357095	3.784827
N	-2.034663	0.024115	-3.692058
N	-0.154923	2.043175	7.320867
N	-7.70173	-3.022578	-3.121115
N	2.652533	7.834614	6.766991
N	4.335182	2.518975	-0.737406
N	-2.298209	-4.454387	4.37013
0	4.31546	2.022484	1.502532
0	-1.788135	-4.431103	2.148766
0	-7.722145	-2.424382	-5.336411
0	2.029577	7.850431	8.959693
0	4.33706	3.049844	-2.953939
0	-2.847694	-4.462692	6.597841
0	-7.68573	-3.613409	-0.919819
0	3.277496	7.821947	4.559255
Н	-1.28386	-0.079084	8.117592
Н	-2.243858	-2.385455	7.859923
Н	-0.583111	-2.37986	1.364916
Н	2.346865	0.711767	2.26962
Н	1.726057	3.45139	3.007711
Н	2.700889	5.740583	3.295895
Н	0.84691	5.763535	9.753215
Н	-0.127135	3.457802	9.486201
Н	-5.624692	-2.928273	0.36142
Н	-3.378059	-1.853197	0.643036
Н	-5.69581	-1.175759	-6.123668
Н	-3.436956	-0.098785	-5.862372
Н	0.029601	1.25253	-4.492296
Н	2.284894	2.330036	-4.236149
Н	3.646708	9.492745	6.010787
Н	2.435314	9.865648	7.27827
Н	3.986596	9.142877	7.736012
Н	-2.097582	-6.471981	3.805758
Н	-3.231562	-6.135321	5.153279
Н	-3.681152	-5.756932	3.460296
Н	-9.336851	-3.565112	-4.279221
Н	-8.937192	-4.719309	-2.966581
Н	-9.728292	-3.183944	-2.57204
Н	5.561351	4.222259	-0.912305
Н	5.963896	3.089424	0.416929
Н	6.360586	2.685678	-1.284536

No negative frequency

Sum of electronic and thermal free energies = -3189.719267 Hartree.

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