

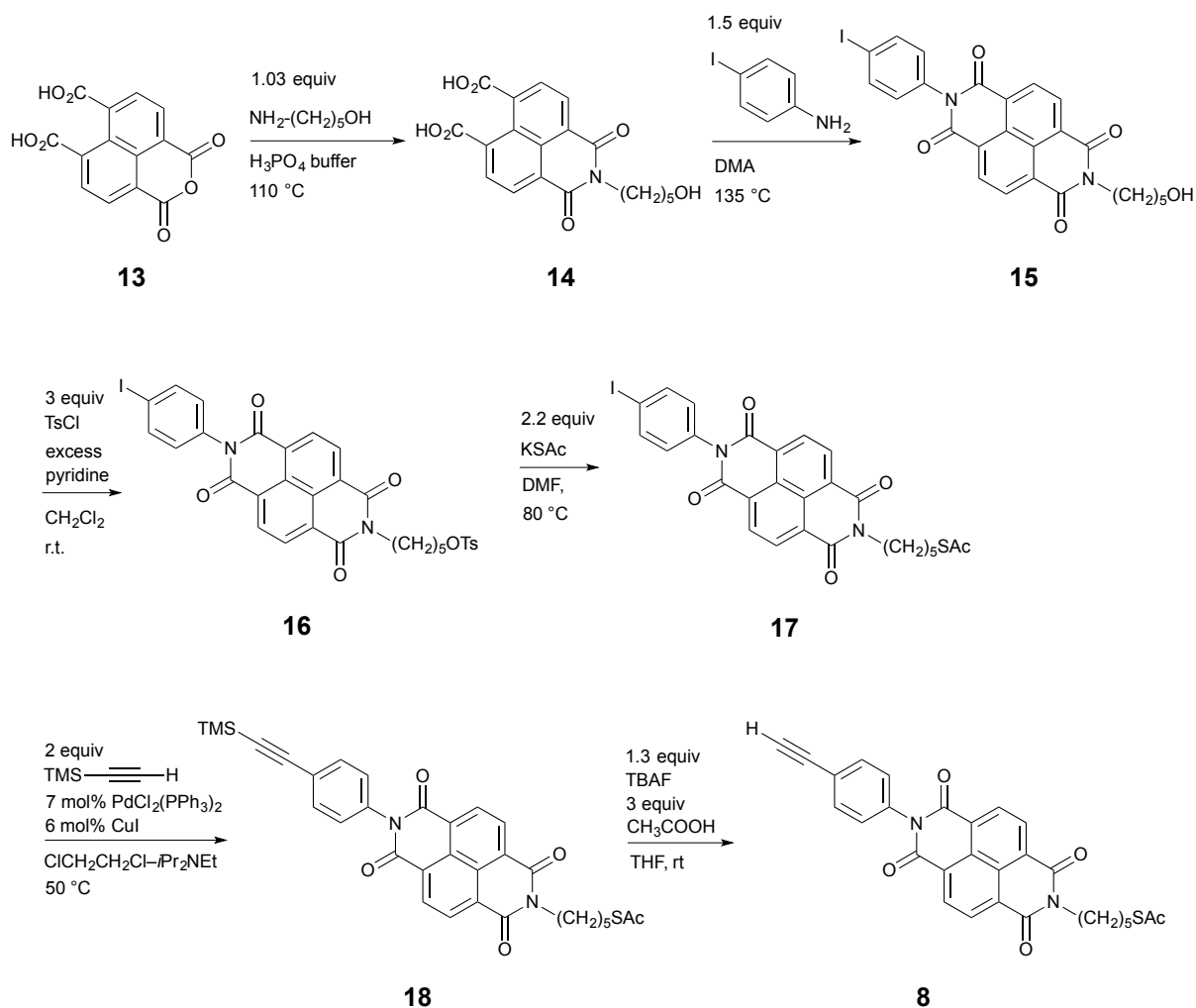
Supplementary Information for

Photoinduced electron transfer of platinum bipyridine diacetylides linked by triphenylamine- and naphthaleneimide-derivatives and its application to photoelectric conversion systems

Synthetic procedures and compound data

General: All the reactions were performed under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer and a JEOL JNM-LA300 spectrometer. FAB-MS and HRMS spectra were recorded on a JEOL JMS-AX-700T spectrometer. Infrared spectra were recorded on KBr plates on a SHIMADZU FTIR-8700 spectrometer. Melting points were measured with a hot-stage apparatus and are uncorrected. Absorption and luminescence spectra were measured with a JASCO V-750 UV-vis spectrometer and a SHIMADZU RF-5300 PC spectrofluorophotometer. Silica gel 60 (100–200 mesh) and aluminium oxide 90 (70–230 mesh, neutral) were used for column chromatography. All commercially available compounds were in a reagent grade and used without further purification. *N,N*-dimethylacetamide (DMA), dichloromethane (CH_2Cl_2), pyridine, *N,N*-dimethylformamide (DMF), 1,2-dichloroethane ($\text{ClCH}_2\text{CH}_2\text{Cl}$), *N*-ethyl-diisopropylamine (*iPr*₂NEt), and diisopropylamine (*iPr*₂NH) were dried and distilled over calcium hydride. Tetrahydrofuran (THF) was dried and distilled in the presence of sodium benzophenone ketyl under an inert atmosphere. 1,3-Dioxo-1*H*,3*H*-benzo[*de*]isochromene-6-carboxylic acid (naphthalene-1,4,5-tricarboxylic acid-4,5-anhydride) (**19**) was prepared from acenaphthene in 3 steps.^{S1}

Synthetic scheme of 8



2-(5'-Hydroxypenpyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6,7-dicarboxylic acid-anhydride (**14**)

Naphthalene-1,4,5,8-tetracarboxylic acid-1,8-anhydride (**13**) (2.00 g, 7.45 mmol) was placed in a 1-L four-necked flask equipped with a refluxed condenser and a dropping funnel. Phosphate buffer solution (pH 6.4, 400 mL) was added to the flask, and the mixture was refluxed for 1 h. A phosphate buffer solution (pH 6.4, 200 mL) of 5-amino-1-pentanol (0.80 mL, 7.68 mmol) was placed in the dropping funnel, and slowly added to the flask for 4 h, then the mixture was refluxed overnight. After cooling to room temperature, an aq. 10% HCl solution was added, and the reaction mixture was stirred for 1 h at room temperature. The generated precipitate was collected by filtration, to give compound **14** as a yellow solid (2.26 g, crude y. 82%) in which a small amount of naphthalenediimide substituted by two hydroxypentyl groups was contained (ca. 13%). Thus obtained crude compound **14** was used for a next step without further purification. **14**: $\text{C}_{19}\text{H}_{17}\text{NO}_7$; M.W. 371.34; mp $157\text{--}158^\circ\text{C}$; ^1H

NMR (300 MHz, DMSO-*d*₆): δ (ppm) 8.56 (d, *J* = 7.5 Hz, 2H), 8.19 (d, *J* = 7.5 Hz, 2H), 4.36 (br, 1H), 4.03 (t, *J* = 7.0 Hz, 2H), 3.38 (t, 2H), 1.67 (m, 2H), 1.41 (m, 4H); IR (KBr/cm⁻¹) 3369, 2951, 2860, 2532, 1705, 1661, 1582, 1518, 1448, 1356, 1337, 1246, 1076, 968, 873, 767, 683, 640; MS (FAB⁺) = 372.1 [M + H⁺].

2-(5'-hydroxypentyl)-7-(4'-iodophenyl)benzo[*lmn*][3,8]phenantrolin-1,3,6,8(2*H*,7*H*)-tetraone (15)

4-Iodoaniline (2.00 g, 9.14 mmol), **14** (2.26 g, crude 6.10 mmol), and dry DMA (25 mL) were taken in a 50-mL two necked flask. The mixture was heated to 140 °C with stirring overnight. After cooling to room temperature, an aq. 10% HCl solution was added, and the generated precipitate was collected by filtration, to give compound **15** (3.69 g, crude y. 104%) as a yellow solid with slight contamination. The compound was used for a next step without further purification. Following data was collected after purification by column chromatography. **15**: C₂₅H₁₉IN₂O₅; M.W. 554.34; mp 277–278 °C; ¹H NMR (300 MHz, DMSO-*d*₆): δ (ppm) 8.70 (d, *J* = 7.6 Hz, 2H), 8.67 (d, *J* = 7.6 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 4.07 (t, *J* = 7.3 Hz, 2H), 3.39 (t, *J* = 6.2 Hz, 2H), 1.68 (m, 2H), 1.45 (m, 4H); IR (KBr/cm⁻¹) 3524, 3090, 2936, 2858, 1703, 1663, 1582, 1485, 1452, 1373, 1346, 1248, 1082, 1049, 1011, 984, 839, 770; High resolution MS: found *m/z* 555.0428; calcd for C₂₅H₁₉IN₂O₅ *m/z* 554.0339.

5-[7'-(4'-Iodophenyl)-1',3',6',8'-tetraoxo-3',6',7',8'-tetrahydrobenzo[*lmn*][3',8']phenantrolin-2'(1*H*)-yl]pentyl 4-methylbenzenesulfonate (16)^{S2}

Compound **15** (3.69 g, crude 6.67 mmol) was dissolved in CH₂Cl₂ (170 mL) and the mixture was cooled to -10 °C in an ice-salt bath. *p*-Toluenesulfonyl chloride (3.82 g, 20.0 mmol) was added to the solution. Then, pyridine (15 mL) was added to the reaction mixture. The ice-salt bath was removed and the reaction mixture was stirred at room temperature for 3 days. The reaction mixture was successively washed by an aq. 10% HCl solution, water, and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH₂Cl₂ then CH₂Cl₂-ethyl acetate (EtOAc) (40:1 ~ 10:1 v/v) as eluents, to give compound **16** (1.85 g, 35% in 3 steps from **13**) as a yellow solid: C₃₂H₂₅IN₂O₇S; M.W. 708.52; mp 211–212 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.71 (d, *J* = 7.7 Hz, 2H), 8.69 (d, *J* = 7.7 Hz, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 4.02 (m, 4H), 2.39 (s, 3H), 1.63 (m, 4H), 1.34 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 162.7 (2C), 144.8, 138.8, 134.3, 133.2, 131.4, 131.1, 130.4, 129.8, 127.9, 126.9 (3C), 126.5, 94.9,

70.2, 40.5, 28.5, 27.3, 22.9, 21.6; IR (KBr/cm⁻¹) 3092, 3061, 2939, 2860, 1993, 1709, 1663, 1371, 1344, 1250, 1211, 1190, 1173, 947, 768, 664.

***S*-{5-[7'-(4''-Iodophenyl)-1',3',6',8'-tetraoxo-3',6',7',8'-tetrahydrobenzo[*lmn*][3',8']phenantrolin-2'(1*H*)-yl]pentyl} ethanthioate (17)^{S3}**

Compound **16** (2.36 g, 3.34 mmol) and potassium thioacetate (838 mg, 7.34 mmol) were placed in a 500-mL three-necked flask. The mixture was dissolved in dry DMF (125 mL) and stirred at 80 °C overnight. After cooling at room temperature, water and CH₂Cl₂ were added, and the organic layer was separated. The organic layer was successively washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH₂Cl₂ then CH₂Cl₂-EtOAc (40:1 ~ 20:1 v/v) as eluents, to give compound **17** as a yellow solid (1.58 g, 78%). **17**: C₂₇H₂₁IN₂O₅S; M.W. 612.44; mp 238–240 °C; ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.81 (s, 4H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 4.22 (t, *J* = 7.4 Hz, 2H), 2.89 (t, *J* = 7.1 Hz, 2H), 2.3 (s, 3H), 1.79 (m, 2H), 1.68 (m, 2H), 1.54 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 195.7, 162.7, 162.6, 138.8, 134.3, 132.4, 131.5, 131.0, 130.4, 127.0, 126.8, 126.5, 94.8, 40.7, 30.6, 29.2, 28.8, 27.5, 26.2; IR (KBr/cm⁻¹) 3078, 2922, 2856, 1705, 1664, 1581, 1485, 1452, 1371, 1344, 1248, 1194, 1118, 1057, 1009, 978, 953, 881, 837, 767, 729; High resolution MS: found *m/z* 613.0301; calcd for C₂₇H₂₂IN₂O₅S [M⁺ + H] *m/z* 613.0294.

***S*-{5-[1',3',6',8'-Tetraoxo-7'-{4''-[(trimethylsilyl)ethynyl]phenyl}-3',6',7',8'-tetrahydrobenzo[*lmn*][3',8']phenantrolin-2'(1*H*)-yl]pentyl} ethanthioate (18)**

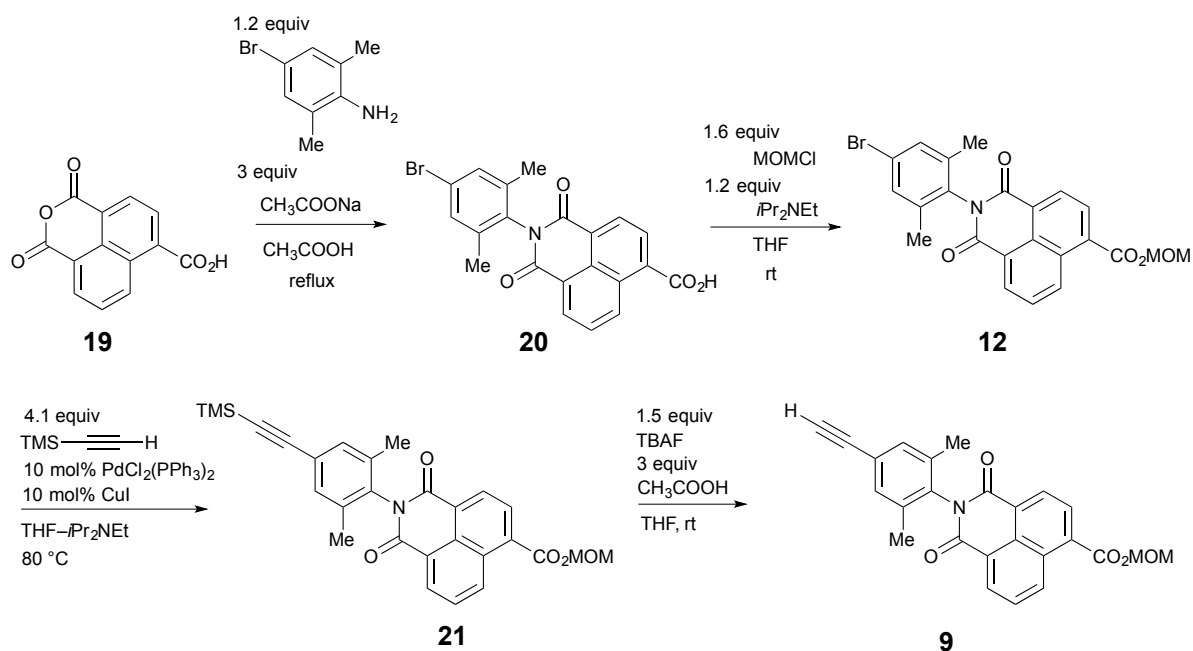
Compound **17** (1.94 g, 3.18 mmol), bis(triphenylphosphine)palladium(II) dichloride (159 mg, 0.227 mmol), copper(I) iodide (44 mg, 0.231 mmol), ClCH₂CH₂Cl (200 mL), *i*Pr₂NEt (10 mL), and trimethylsilylacetylene (0.9 mL, 6.37 mmol) were placed in a 250 mL screw capped tube. The tube was flushed with nitrogen, sealed, and heated at 90 °C overnight. After cooling to room temperature, the mixture was passed through a Celite pad. The pad was washed with CH₂Cl₂. The filtrate was combined and concentrated under reduced pressure. The residue was purified by column chromatography using CH₂Cl₂ then CH₂Cl₂-EtOAc (40:1 ~ 20:1 v/v) as eluents, to give compound **18** as a green yellow solid (1.56 g, 84%). **18**: C₃₂H₃₀N₂O₅SSi; M.W. 582.75; mp: 254–255 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.80 (s, 4H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 4.22 (t, *J* = 7.8 Hz, 2H), 2.89 (t, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 1.79 (m, 2H), 1.88 (m, 2H), 1.53 (m, 2H), 0.28 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 196.0, 162.9, 162.8, 134.5, 133.1, 131.8, 131.1, 128.6, 127.1, 127.0, 126.9, 126.7, 124.4, 104.2, 95.9, 40.8, 30.7, 29.3, 28.9, 27.6, 26.3, 0.0; IR (KBr/cm⁻¹) 3054, 2957, 2939,

2901, 2860, 2160, 1709, 1667, 1582, 1506, 1452, 1371, 1344, 1245, 1219, 1192, 1134, 1113, 866, 842, 768, 629, 549.

***S*-{5-[7-(4-Ethynylphenyl)-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenantrolin-2(1*H*)-yl]pentyl} ethanthioate (**8**)**

Compound **18** (1.54 g, 2.65 mmol) was dissolved in THF (45 mL) in a 200-mL three-necked flask. To this solution, acetic acid (0.45 mL 7.86 mmol) and 1.0 M THF solution of tetra-*n*-butylammonium fluoride (TBAF) (3.5 mL, 3.5 mmol) were added and the mixture was stirred at room temperature for 90 min. CH₂Cl₂ and water were added to the mixture, the organic layer was separated. The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using CH₂Cl₂ then CH₂Cl₂-EtOAc (40:1 ~ 20:1 v/v) as eluents, to give compound **8** as a green yellow solid (1.27 g, 94%). **8**: C₂₉H₂₂N₂O₅S; M.W. 510.56; mp 190–191 °C (dec) ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.81 (s, 4H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.19 (t, *J* = 7.9 Hz, 2H), 3.17 (s, 1H), 2.90 (t, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.79 (m, 2H), 1.68 (m, 2H), 1.59 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm): 196.0, 162.9, 162.8, 134.9, 133.4, 131.6 (2C), 128.8, 127.2, 127.1, 126.7 (2C), 123.5, 82.85, 78.7, 40.9, 30.8, 29.4, 29.0, 27.7, 26.3; IR (KBr/cm⁻¹) 3265, 2939, 2860, 1707, 1662, 1582, 1456, 1373, 1344, 1250, 1220, 1198, 1063, 978, 884, 835, 768, 708, 629.

Synthetic scheme of 9



2-(4-Bromo-2,6-dimethylphenyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-6-carboxylic acid (**20**)

Compound **19** (2.00 g, 8.25 mmol), 4-bromo-2,6-dimethylaniline (1.96 g, 9.93 mmol), sodium acetate (2.04 g, 24.9 mmol), and acetic acid (30 mL) were placed in a 200-mL round-bottomed flask. The mixture was refluxed for 6 h. After cooling to room temperature, an aq. 10% HCl solution was added to the mixture, forming a precipitate, which was collected, to give desired **20** (3.50 g, 100%) as a gray solid. The compound was used for a next step without further purification. **20**: C₂₁H₁₄BrNO₄; M.W. 424.25; mp > 300 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 9.27 (d, *J* = 8.5 Hz, 1H), 8.63 (d, *J* = 7.8 Hz, 1H), 8.62 (d, *J* = 7.6 Hz, 1H), 8.41 (d, *J* = 7.8 Hz, 1H), 8.04 (dd, *J* = 8.5 and 7.6 Hz, 1H), 7.50 (s, 2H), 2.05 (s, 6H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ (ppm) 167.6, 162.6, 162.1, 138.3, 134.2, 133.4, 132.7, 131.5, 130.7, 130.4, 129.9, 129.2, 128.6, 128.5, 124.7, 122.1, 121.4, 17.1; IR (KBr/cm⁻¹) 3082, 2984, 2922, 1713, 1682, 1666, 1593, 1510, 1472, 1435, 1366, 1348, 1273, 1242, 1196, 1032, 914, 862, 787, 777; MS (FAB⁺) = 424.2 [M⁺ + H]; High resolution MS: found *m/z* 424.0185; calcd for C₂₁H₁₅BrNO₄ [M⁺ + H] *m/z* 424.0184.

Methoxymethyl 2-(4-bromo-2,6-dimethylphenyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-6-carboxylate (**12**)^{S4}

Compound **20** (3.50 g, 8.24 mmol), THF (15 mL), and *i*Pr₂NEt (1.7 mL, 10.2 mmol) were placed in a 50-mL round-bottomed flask. Chloromethylmethylether (1.0 mL, 13.2 mmol) was added to the mixture and the mixture was stirred for 2.5 h. After removing the solvent under

reduced pressure, the residue was dissolved in CH_2Cl_2 , which was successively washed with water and brine. The organic layer dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using hexane– CH_2Cl_2 (1:1 ~ 20:1 v/v) then CH_2Cl_2 as eluents, to give compound **12** as a yellow solid (3.36 g, 87% in 2 steps from **19**). **12**: $\text{C}_{23}\text{H}_{18}\text{BrNO}_5$; M.W. 468.30; mp 172–174 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.37 (d, $J = 8.6$ Hz, 1H), 8.73 (d, $J = 7.3$ Hz, 1H), 8.70 (d, $J = 7.6$ Hz, 1H), 8.49 (d, $J = 7.6$ Hz, 1H), 7.94 (dd, $J = 8.6$ and 7.3 Hz, 1H), 7.39 (s, 2H), 5.64 (s, 2H), 3.65 (s, 3H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 165.5, 163.0, 162.5, 137.7, 132.8, 132.7, 132.4, 132.1, 131.5, 130.34, 130.29, 130.1, 129.2, 128.6, 126.0, 122.7, 122.6, 91.9, 58.2, 17.7; IR ($\text{KBr}/\text{cm}^{-1}$) 3431, 2966, 2945, 2825, 1730, 1709, 1668, 1591, 1472, 1427, 1367, 1354, 1273, 1261, 1244, 1194, 1163, 1086, 1047, 984, 916, 903, 862. 775; MS (FAB^+) = 468.2 [$\text{M}^+ + \text{H}$]; High resolution MS: found m/z 468.0432; calcd for $\text{C}_{23}\text{H}_{19}\text{BrNO}_5$ [$\text{M}^+ + \text{H}$] m/z 468.0447.

Methoxymethyl {2,6-dimethyl-4-[(trimethylsilyl)ethynyl]phenyl}-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-6-carboxylate (21)

Compound **12** (3.00, 6.41 mmol), tetrakis(triphenylphosphine)palladium(0) (755 mg, 0.65 mmol), copper(I) iodide (123 mg, 0.64 mmol), THF (40 mL), $i\text{Pr}_2\text{NEt}$ (20 mL), and trimethylsilylacetylene (3.75 mL, 26.5 mmol) were placed in a screw capped tube. The tube was flushed with nitrogen, sealed, and heated at 80 °C overnight. After cooling to room temperature, the mixture was passed through a Celite pad, which was washed with CH_2Cl_2 . The filtrates were combined and concentrated under reduced pressure. The residue was purified by column chromatography using hexane– CH_2Cl_2 (1:1 ~ 1:5 v/v) then CH_2Cl_2 as eluents, to give compound **21** as a pale yellow solid (2.00 g, 64%). **21**: $\text{C}_{28}\text{H}_{27}\text{NO}_5\text{Si}$; M.W. 485.61; mp 199–200 °C; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.37 (d, $J = 8.8$ Hz, 1H), 8.72 (d, $J = 7.3$ Hz, 1H), 8.69 (d, $J = 7.6$ Hz, 1H), 8.49 (d, $J = 7.6$ Hz, 1H), 7.93 (dd, $J = 8.8$ and 7.3 Hz, 1H), 7.35 (s, 2H), 5.65 (s, 2H), 3.65 (s, 3H), 2.11 (s, 6H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 165.6, 163.0, 162.6, 135.8, 134.0, 132.8, 132.4, 132.1, 132.0, 130.4, 130.3, 130.2, 129.3, 128.6, 126.1, 123.8, 122.7, 104.8, 94.5, 91.9, 58.3, 17.7, 0.0; IR ($\text{KBr}/\text{cm}^{-1}$) 2957, 21367, 932, 2897, 2824, 2158, 1728, 1711, 1670, 1591, 1516, 1475, 1439, 1402, 1367, 1356, 1267, 1250, 1236, 1196, 1163, 1123, 1088, 1051, 986, 936, 918, 906, 864, 845, 827, 787, 773, 762, 683; MS (FAB^+) = 486.3 [$\text{M}^+ + \text{H}$]; High resolution MS: found m/z 486.1743; High resolution MS: found m/z 486.1743; calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_5\text{Si}$ [$\text{M}^+ + \text{H}$] m/z 486.1737.

Methoxymethyl (4-ethynyl-2,6-dimethylphenyl)-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-6-carboxylate (9)

Compound **21** (2.41 g, 4.97 mmol) was dissolved in THF (10 mL) in a 100-mL round-bottomed flask. To this solution, acetic acid (0.16 mL, 2.80 mmol) and a 1.0 M solution of tetra-*n*-butylammonium fluoride (TBAF) (7.5 mL, 7.5 mmol) were added and the mixture was stirred at room temperature for 3 h. CH₂Cl₂ and water were added to the mixture, the organic layer was separated. The organic layer was dried over sodium sulfate, then filtered and concentrated under reduced pressure. The residue was purified by column chromatography using CH₂Cl₂ as eluent, to give compound **9** as a pale yellow solid (1.69 g, 82%). **9**: C₂₅H₁₉NO₅; M.W. 413.43; mp 207–208 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.38 (d, *J* = 8.8 Hz, 1H), 8.73 (d, *J* = 7.3 Hz, 1H), 8.70 (d, *J* = 7.6 Hz, 1H), 8.49 (d, *J* = 7.6 Hz, 1H), 7.94 (dd, *J* = 8.8 and 7.3 Hz, 1H), 7.37 (s, 2H), 5.65 (s, 2H), 3.65 (s, 3H), 3.08 (s, 1H), 2.13 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 165.5, 163.0, 162.5, 135.9, 134.3, 132.8, 132.4, 132.2, 132.0, 130.4, 130.2, 130.1, 129.2, 128.6, 126.0, 123.0, 122.6, 91.9, 82.3, 77.4, 58.2, 17.7; IR (KBr/cm⁻¹) 3246, 2953, 2928, 2825, 2100, 1730, 1707, 1666, 1616, 1591, 1514, 1472, 1437, 1402, 1367, 1335, 1265, 1246, 1196, 1159, 1119, 1088, 1051, 984, 934, 914, 903, 874, 866, 840, 826, 804, 789, 773, 727, 706, 654, 606, 559; MS (FAB⁺) = 414.0 [M⁺ + H]; High resolution MS: found *m/z* 414.1339; calcd for C₂₅H₂₀NO₅ [M⁺ + H] *m/z* 414.1341.

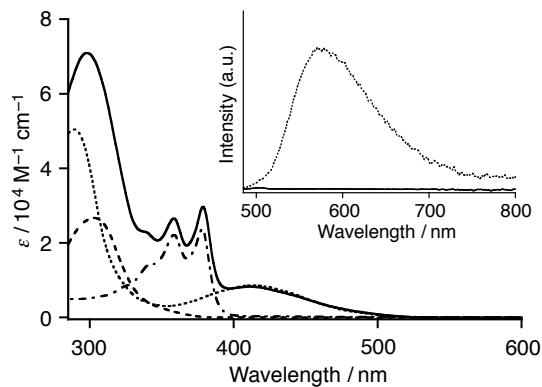
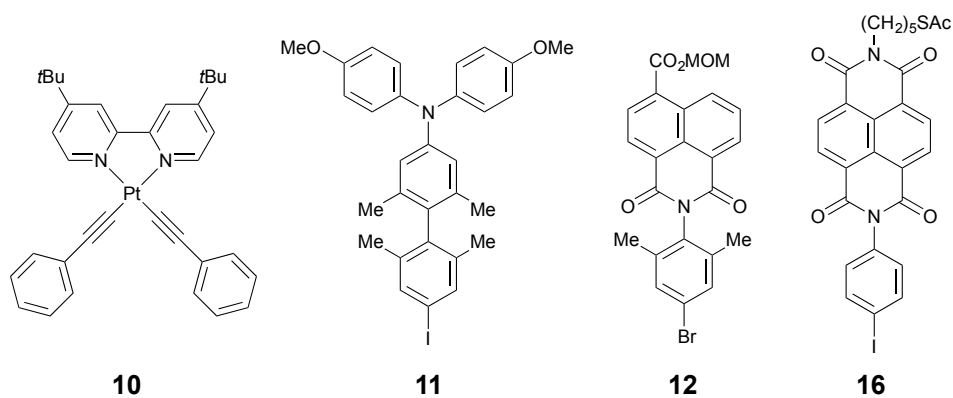


Fig. S1. UV-visible and phosphorescence (inset) spectra of **3** and reference compounds in toluene: triad **3** (solid line), platinum complex **10** (dotted line), triphenylamine **11** (dashed line), naphthalenediimide **16** (dashed-dotted line). Inset: The phosphorescence spectra of **3** (solid line, nearly base line) and **10** (dotted line) are compared at the same absorption intensity with the excitation wavelength of 440 nm.

Table S1. Redox potentials of **3** and **5**, and reference compounds^a

	$E_{\text{ox}2}^b$	$E_{\text{ox}1}^b$	$E_{\text{red}1}^b$	$E_{\text{red}2}^b$	$E_{\text{red}3}^b$
3	+0.87 ^c	+0.16	-1.06	-1.47	-1.88
5	+0.87 ^c	+0.16	-1.46	-1.88 ^d	
10		+0.59 ^c	-1.86		
11		+0.16			
12			-1.46	-1.86	
16			-1.06	-1.47	

^a Measured in CH₂Cl₂ in the presence of 0.1 M tetra-*n*-butylammonium perchlorate as supporting electrolyte. ^b V vs Fc/Fc⁺. ^c Peak potential (irreversible). ^d Two-electron reduction process.



Estimated energy Diagram of 3

The energy for the CS states (E_{CS} in eV) relative to the ground states in toluene and THF were roughly estimated using the Weller approximation (Eq 1),^{S5} where the ΔG_s is a correction term for the solvent of different polarity (Eq 2).

$$E_{CS} = e[E_{ox}(D) - E_{red}(A)] + \Delta G_s \quad (\text{Eq 1})$$

$$\Delta G_s = (e^2/4\pi\epsilon_0) \cdot [(1/2r_D + 1/2r_A) \cdot (1/\epsilon - 1/\epsilon_r) - 1/\epsilon R_{DA}] \quad (\text{Eq 2})$$

In the equations, D, A and Pt showed MTA and NDISAc moieties, and platinum complex moiety, respectively. The CS states are considered as a solvent-separated ion-pair with a center(+)-to-center(-) distance R_{DA} (in angstrom) and the effective radii r_D and r_A (in angstrom). ϵ_0 refers to vacuum permittivity. ϵ is a relative dielectric constant of the solvent ($\epsilon = 2.38$ for toluene, 7.58 for THF) and ϵ_r is that of the reference solvent ($\epsilon_r = 8.93$ for CH_2Cl_2) in which the redox potentials are measured. From the molecular model calculated at the PM6 level,^{S6} the distances between donors and acceptors were estimated as follows: $R_{DA} = 18.0 \text{ \AA}$, $R_{Pt-A} = 12.4 \text{ \AA}$, $R_{D-Pt} = 13.2 \text{ \AA}$. The effective radii were assumed to be $r_{Pt} = r_D = r_A = 4.5 \text{ \AA}$, which is frequently used as a typical value.^{S5b,S7} The triplet state energies of naphthalenediimide ($^3\text{NDISAc}^*$) were around 2.0 eV,^{S8} respectively, which were determined by the literature. The energy of $^3\text{Pt}^*$ (2.16 eV) estimated from wavelength of maximum emission ($\lambda_{em} = 574 \text{ nm}$) in **10** was higher than that of $^3\text{NDISAc}^*$ but lower than that of $^3\text{MTA}^*$, suggesting the lowest triplet energy is 2.0 eV assigned to $^3\text{LE}_{\text{NDI}}$. The estimated energy diagrams are shown in Fig. S2.

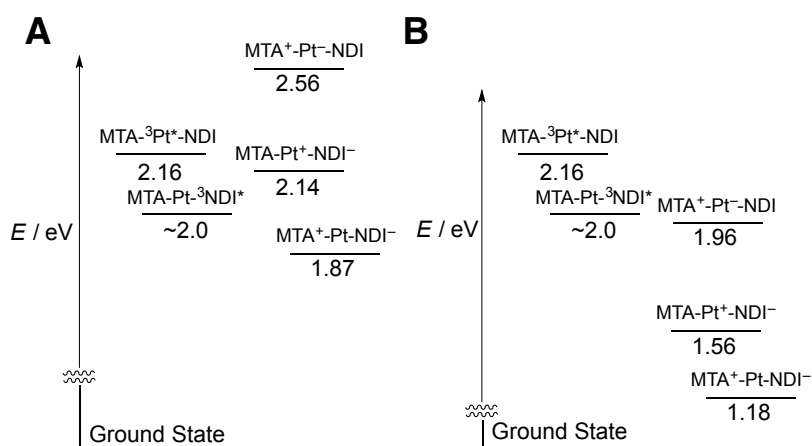


Fig. S2. The energy levels of excited states and CS states for **3** (NDI = NDISAc) in toluene (A) and in THF (B).

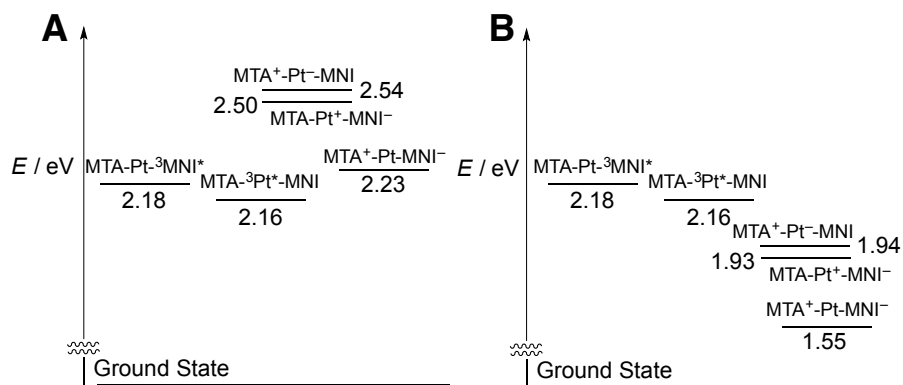


Fig. S3. The energy levels of excited states and CS states for **5** (MNI = MNICOOMOM) in toluene (A) and in THF (B).

Nano-second laser flash photolysis for **3**

Fig. S4 shows the nanosecond transient absorption of **3** in toluene and THF with laser excitation at 532 nm (FWHM: 4 ns). The laser light selectively excites the platinum complex moiety. In the transient absorption, sharp absorption at 480, 610, and 750 nm were observed in both solution. The absorption at 480 and 610 nm was assigned to the naphthalenediimide radical anion,^{S9} while that at 750 nm was assigned to triphenylamine radical cation (750 nm).^{S9} The transient spectra were clearly assigned to the CS state. The decay curve at 480 nm was best estimated as a single exponential in toluene ($\tau_{CR} = 730$ ns), and as a biexponential curve in THF [$\tau_{CR1} = 61$ ns (0.7) and $\tau_{CR2} = 170$ ns (0.3)]. The origin of the biexponential decay in THF is probably due to conformational isomers based on the arrangement around the acetylenic bonds.^{S9} These results are consistent with those of **1**,^{S9} indicating efficient generation of charge separated state.

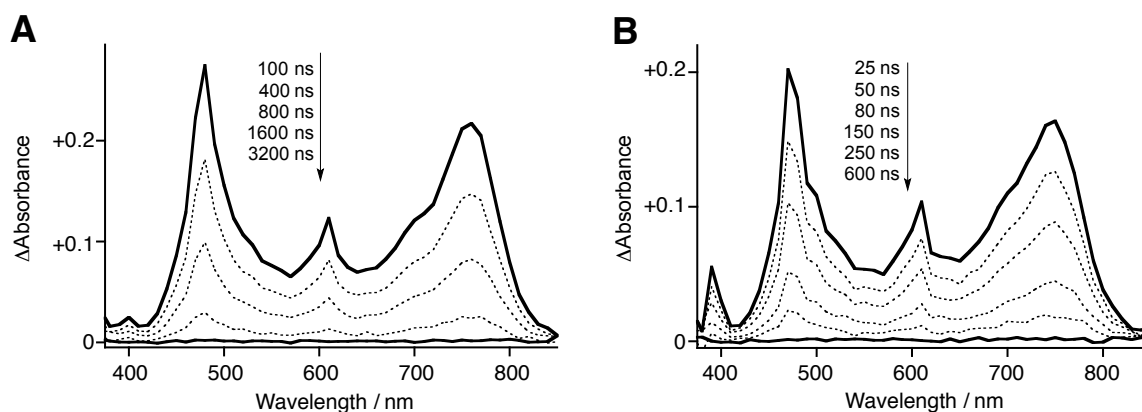


Fig. S4 The nanosecond transient absorption spectra of **3** in toluene (A) and THF (B) under 532 nm laser excitation (FWHM: 4 ns) at room temperature.

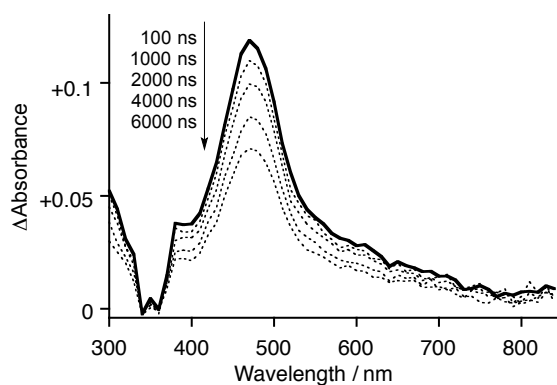


Fig. S5 Nanosecond transient absorption of **12** in toluene under 355 nm laser excitation (FWHM: 4 ns) at room temperature. The absorption at 470 nm was assigned to $^3\text{MNICOOMOM}^*$.

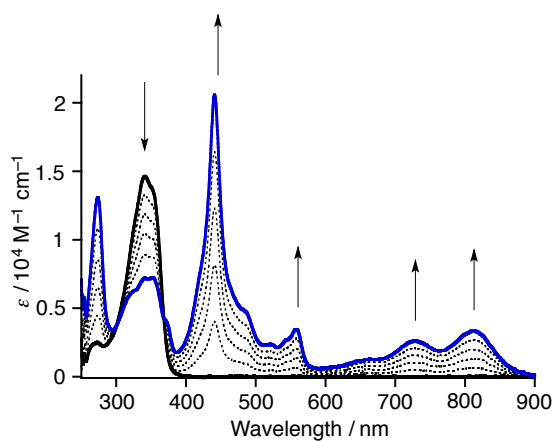


Fig. S6 UV-visible spectra of the electrochemically generated radical anion $\mathbf{12}^{\bullet-}$ in DMF. The black solid, dotted, and blue solid lines show the initial, intermediate, and final states, respectively.

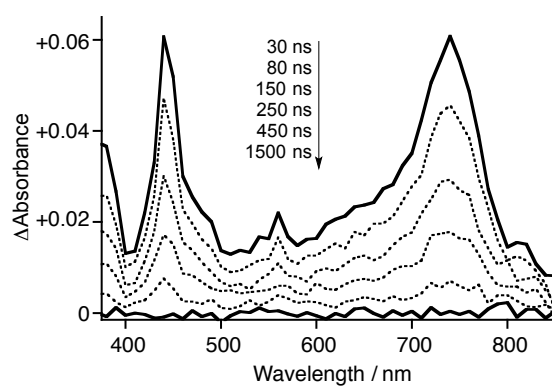


Fig. S7 The nanosecond transient absorption spectra of **5** in THF under 532 nm laser excitation (FWHM: 4 ns) at room temperature.

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