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SUPPORTING INFORMATION

Cyclometalated (boroxinato)gold(III) complexes from arrested transmetalation

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Contents

Experimental

General. (tpy)Au($OCOCF_3$)$_2$ (**1**) was prepared as previously reported,[1] using a CEM Discover microwave, and ppyAu($OCOCF_3$)$_2$ (**2**) was prepared using the same method. 2-*p*-Tolylpyridine (tpy) and phenylpyridine (ppy) were purchased from Sigma Aldrich. Boronic acids were purchased from Frontier Scientific or Sigma Aldrich. Potassium *t*-butoxide was purchased from Acros Organics. All solvents were purchased from Fisher. Unless noted otherwise, all chemicals were used as received. ^{1}H NMR spectra were recorded on a Varian INOVA-400 operating at 400 MHz or a Bruker Ascend-500 operating at 500 MHz. Proton and carbon resonances were referenced to residual solvent signals. When rigorously dry dichloromethane-d was required, solvent from a single-use ampoule was passed over basic alumina in a MBraun glovebox, and the NMR tube and pipettes were dried overnight in a 150 ˚C oven. UV/Vis and luminescence data were recorded with a Cary 5G UV/Vis/NIR spectrometer and a Cary Eclipse spectrometer, respectively. Prior to luminescence measurements, solvents were degassed by bubbling Ar(g) through them for 10 min. Microanalyses were carried out by Midwest Microlabs, LLC (Indianapolis, IN).

(tpy)Au(phenyl)$_2$ boroxine (3). Compound **1** (1 eq., 69.5 mg, 0.118 mmol), phenylboronic acid (2 eq., 30.5 mg, 0.250 mmol), and KOtBu (3 eq., 42.5 mg, 0.379 mmol) were added to a 20-mL vial and suspended in 5-mL toluene. The suspension was stirred for 3 hours. The solvent was stripped by rotary evaporation to give an off-white powder, which was extracted into 10-mL CH_2Cl_2 and filtered through a Celite plug. The solvent was removed by rotary evaporation to yield an off-white powder. The powder was washed with 2x5 mL diethyl ether and dried by vacuum. Yield: 52.3 mg (76%); mp 110 ˚C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (1 H, d, J = 7.0 Hz), 8.22 – 8.16 (4 H, m), 7.98 (1 H, t, J = 8.0 Hz), 7.70 (1 H, d, J = 8.0), 7.66 (1 H, s), 7.46 – 4.43 (7 H, m), 7.37 (1 H, d, J = 8.0 Hz), 7.13 (1 H, d, J = 8.0 Hz), 2.48 (3 H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 1165.9, 146.2, 146.1, 142.7, 142.6, 139.3, 135.3, 135.2, 130.2, 130.0, 129.5, 129.1, 127.7, 124.7, 122.9, 120.2, 22.5. Anal. Calcd for $C_{24}H_{20}AuB_2NO_3$: C, 48.94; N, 2.38; H, 3.42. Found: C, 49.23; N, 2.27; H, 3.60. UV-Vis (2-MeTHF) λ_{max} nm (M^{-1} cm^{-1}): 302 (3353, sh), 317 (5515, sh), 334 (6427); emission (2-MeTHF, λ_{ex} = 364 nm) λ_{max} nm: 416, 472, 495.

(tpy)Au(*p*-isopropoxyphenyl)$_2$ boroxine (4). A 20-mL flask was charged with **1** (1 eq., 45.9 mg, 0.0776 mmol), (4-isopropoxyphenyl)boronic acid (2 eq., 29.6 mg, 0.164 mmol), and

KOtBu (3 eq., 27.1 mg, 0.242 mmol). The solids were suspended in 5-mL toluene and stirred at room temperature in the dark for 3 h. The solvent was removed by rotary evaporation to give an off-white powder. The resulting powder was dissolved in 3-mL methylene chloride, and the solution was filtered through a Celite plug. Rotary evaporation removed the solvent to give an off-white solid. The solid was dissolved in 1-mL diethyl ether and precipitated from solution by the slow addition of pentane to yield a white powder. The powder was dried *in vacuo*. Yield: 37.2 mg (68%); mp 134 ˚C decomp. X-ray diffraction quality crystals were grown by diffusing pentane into a saturated methylene chloride solution. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.40 (1 H, d, *J* = 5.2 Hz), 8.13–8.07 (4 H, m), 7.98 (1 H, t, *J* = 8.0 Hz), 7.71 (1 H, d, *J* = 8.4 Hz), 7.64 (1 H, s), 7.46–7.43 (1 H, m), 7.37 (1 H, d, *J* = 7.6 Hz), 7.13 (1 H, d, *J* = 8.0 Hz), 6.98–6.94 (4 H, m), 4.68–4.61 (2 H, m), 2.47 (3 H, s), 1.38 (6 H, d, *J* = 2.4 Hz), 1.36 (6 H, d, *J* = 2.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 159.8, 159.6, 146.1, 145.7, 142.3, 142.1, 139.4, 136.9, 136.8, 129.4, 128.7, 124.8, 122.6, 120.4, 114.9, 69.7, 22.5, 22.4. Anal. Calcd for $C_{30}H_{32}AuB_2NO_5 \cdot H_2O$: C, 49.83; N, 1.94; H, 4.74. Found: C, 50.20; N, 2.30; H, 4.52. UV-Vis (2-MeTHF) λ_{max} nm (M^{-1} cm^{-1}): 319 (7839), 334 (8288); emission (2-MeTHF, λ_{ex} = 361 nm) λ_{max} nm: 467, 497.

(tpy)Au(*p*-*t*-butylphenyl)$_2$ boroxine (5). To a 20-mL flask was added **1** (1 eq., 30.0 mg, 0.0507 mmol), (4-*t*-butylphenyl)boronic acid (2 eq., 18.1 mg, 0.102 mmol), and KOtBu (3 eq., 16.7 mg, 0.149 mmol). The solids were suspended in 3 mL of toluene. At room temperature, the reaction mixture was stirred in the dark for 3 h. The solvent was removed by rotary evaporation to give an off-white powder. The powder was extracted into 3-mL diethyl ether and passed through a Celite plug. The solvent was removed by rotary evaporation, and the resulting off-white powder was dried *in vacuo*. Yield: 26.0 mg (74%); mp 118 ˚C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.41 (1 H, d, *J* = 4.8 Hz), 8.16–8.10 (4 H, m), 7.97 (1 H, td, *J* = 8.0, 1.6 Hz), 7.70 (2 H, d, *J* = 8.4 Hz), 7.67 (1 H, s), 7.49–7.46 (4 H, m), 7.37 (1 H, d, *J* = 7.6 Hz), 7.12 (1 H, d, *J* = 8.4 Hz), 2.48 (3 H, s), 1.37 (9 H, s), 1.37 (9 H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 153.0, 152.7, 146.2, 145.7, 142.3, 142.2, 139.3, 135.2, 135.1, 129.7, 128.7, 124.6, 124.5, 122.7, 120.3, 35.0, 31.7, 22.4. Anal. Calcd for $C_{32}H_{36}AuB_2NO_3$: C, 54.81; N, 2.00; H, 5.17. Found: C, 54.89; N, 2.01; H, 5.21. UV-Vis (2-MeTHF) λ_{max} nm (M^{-1} cm^{-1}): 320 (8146), 333 (8668); emission (2-MeTHF, λ_{ex} = 356 nm) λ_{max} nm: 466, 496.

(tpy)Au(thiophene-3-yl)$_2$ boroxine (6). A 20-mL flask was charged with **1** (1 eq., 28.1 mg, 0.0475 mmol), 3-thienylboronic acid (2 eq., 13.6 mg, 0.106 mmol), and KOtBu (3 eq., 17.3

mg, 0.154 mmol). The solids were suspended in 3-mL toluene. The reaction mixture was stirred at room temperature in the dark for 3 h. The solvent was removed by rotary evaporation to give an off-white powder, which was washed with 3x5 mL of diethyl ether followed by 3x5 mL of H_2O. The product was dried *in vacuo*. Yield: 22.1 mg (77%); mp 137 ˚C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.38 (1 H, d, *J* = 5.6 Hz), 8.08 (1 H, d, *J* = 2.8 Hz), 8.05–8.00 (2 H, m), 7.75 (1 H, d, *J* = 8.0 Hz), 7.69 (1 H, d, *J* = 4.8 Hz), 7.65–7.64 (2 H, m), 7.48–7.44 (1 H, m), 7.40 (1 H, d, *J* = 8.0 Hz), 7.38–7.34 (2 H, m), 7.16 (1 H, d, *J* = 8.8 Hz), 2.48 (3 H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.6, 161.2, 149.5, 141.9, 140.5, 136.7, 133.2, 133.0, 131.1, 129.5, 127.5, 124.3, 124.2, 123.0, 119.9, 119.9, 22.2. Anal. Calcd for $C_{20}H_{16}AuB_2NO_3S_2$: C, 39.97; N, 2.33; H, 2.68. Found: C, 40.18; N, 2.33; H, 2.74. UV-Vis (2-MeTHF) λ_{max} nm (M^{-1} cm^{-1}): 303 (5390, sh), 320 (7354), 335 (8349); emission (2-MeTHF, λ_{ex} = 365 nm) λ_{max} nm: 467, 498.

(tpy)Au(ferrocenyl)$_2$ boroxine (7). A 20-mL flask was charged with **1** (1 eq., 57.9 mg, 0.0979 mmol), ferroceneboronic acid (2 eq., 47.8 mg, 0.208 mmol), and KOtBu (3 eq., 35.1 mg, 0.313 mmol), and the solids were suspended in 4-mL toluene. The reaction mixture was stirred at room temperature in the dark for 3 h. The solvent was stripped by rotary evaporation to give an orange powder. The orange powder was washed 3x5-mL diethyl ether followed by 3x5 mL H_2O and dried in vacuo. Yield: 57.0 mg (72%); mp 163 ˚C dec. X-ray diffraction quality crystals were grown by layering toluene on a concentrated methylene chloride solution. **7** is mildly hygroscopic. Upon drying a sample under vacuum for 48 h, a water peak is observed in the ^{1}H NMR spectrum in rigorously dried CD_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.42 (1 H, s), 8.08–8.05 (1 H, m), 7.82 (1 H, d, *J* = 6.8 Hz), 7.71 (1 H, s), 7.50–7.37 (2 H, m), 7.20–7.15 (1 H, m), 4.68 (2 H, s), 4.62 (2 H, s), 4.39–4.36 (4 H, m), 4.14 (10 H, s), 2.54 (3 H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.5, 142.6, 142.5, 129.4, 129.3, 128.5, 124.5, 122.8, 120.2, 74.5, 74.4, 71.4, 71.3, 68.8, 68.7, 22.5. Anal. Calcd for $2[C_{32}H_{28}AuB_2Fe_2NO_3]\cdot H_2O$: C, 47.23; N, 1.72; H, 3.59. Found: C, 47.16; N, 1.90; H, 3.57. UV-Vis (2-MeTHF) λ_{max} nm (M^{-1} cm^{-1}): 333 (2906); emission (2-MeTHF, λ_{ex} = 370 nm) λ_{max} nm: 416.

(tpy)Au(1-naphthyl)$_2$ boroxine (8). A 20-mL flask was charged with **1** (1 eq., 35.1 mg, 0.0594 mmol), 1-naphthylboronic acid (2 eq., 21.0 mg, 0.122 mmol), and KOtBu (3 eq., 19.2 mg, 0.171 mmol), and the solids were suspended in 3-mL toluene. The reaction mixture was stirred at room temperature in the dark for 3 h. And the solvent was stripped by rotary evaporation to give an off-white powder. The powder was extracted into 5-mL methylene

chloride and filtered through a Celite plug. Diethyl ether was vapor diffused into the solution to give fine, white crystals that were dried *in vacuo*. Yield: 31.0 mg (76%); mp 187 ˚C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.53 (1 H, d, *J* = 6.0 Hz), 9.35 (1 H, d, *J* = 7.6 Hz), 9.26–9.23 (1 H, m), 8.43 (1 H, dd, *J* = 7.2, 1.6 Hz), 8.35 (1 H, dd, *J* = 6.8, 1.6 Hz), 8.00 (1 H, td, *J* = 8.0, 1.6 Hz), 7.93–7.86 (5 H, m), 7.76 (1 H, d, *J* = 8.0 Hz), 7.57–7.41 (8 H, m), 7.18 (1 H, d, *J* = 8.4 Hz), 2.45 (3 H, s). Anal. Calcd for $C_{32}H_{24}AuB_2NO_3$: C, 55.77; N, 2.03; H, 3.51. Found: C, 55.71; N, 2.08; H, 3.54. UV-Vis (2-MeTHF) λ_{max} nm (M^{-1} cm^{-1}): 276 (11826), 289 (11261), 298 (sh, 9194), 318 (sh, 4284), 335 (3741); emission (2-MeTHF, λ_{ex} = 369 nm) λ_{max} nm: 406, 467, 497.

(tpy)Au(*p*-styrenyl)$_2$ boroxine (9). A 20-mL flask was charged with **1** (1 eq., 27.6 mg, 0.0467 mmol), 4-vinylphenylboronic acid (2 eq., 14.0 mg, 0.0946 mmol), and KOtBu (3 eq., 16.4 mg, 0.146 mmol). The solids were suspended in 3-mL toluene and stirred at room temperature in the dark for 3 h. The solvent was removed by rotary evaporation to give an off-white powder. The resulting powder was washed with 3x5 mL diethyl ether followed by 3x5 mL H_2O and then dried *in vacuo*. Diffraction quality crystals were grown by layering heptane onto a concentrated methylene chloride solution. Analytically pure material was obtained by recrystallizing **9** twice by vapor diffusion of pentane into methylene chloride and drying the crushed crystals for two days under vacuum. Yield: 27.4 mg (92%); mp 144 ˚C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.37 (1 H, ddd, *J* = 6.0, 1.6, 0.8 Hz), 8.15–8.10 (4 H, m), 7.96–7.92 (1 H, m), 7.66 (1 H, d, *J* = 8.0 Hz), 7.62–7.61 (1 H, m), 7.50–7.44 (4 H, m), 7.44–7.40 (1 H, m), 7.34 (1 H, d, *J* = 8.0 Hz), 7.12–7.10 (1 H, m), 6.84–6.76 (2 H, m), 5.87–5.80 (2 H, m), 5.29–5.25 (2 H, m), 2.46 (3 H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7, 146.2, 146.0, 142.5, 142.5 138.9, 137.7, 137.7, 135.5, 135.4, 129.5, 128.9, 125.6, 124.7, 122.8, 120.3, 114.0, 113.8, 22.5. Anal. Calcd for $2(C_{28}H_{24}AuB_2NO_3)\cdot CH_2Cl_2$ (solvent of crystallization): C, 50.08; N, 2.05; H, 3.69. Found: C, 49.87; N, 2.08; H, 3.83. UV-Vis (2-MeTHF) λ_{max} nm (M^{-1} cm^{-1}): 318 (2090), 336 (2299); emission (2-MeTHF, λ_{ex} = 336 nm) λ_{max} nm: 395.

(tpy)Au(*p*-carbomethoxyphenyl)$_2$ boroxine (10). A 20-mL flask was charged with **1** (1 eq., 29.2 mg, 0.0494 mmol), (4-acetylphenyl)boronic acid (2 eq., 17.7 mg, 0.108 mmol), and KOtBu (3 eq., 16.7 mg, 0.149 mmol), and then the solids were suspended in 3 mL of toluene. The reaction mixture was stirred at room temperature in the dark for 3 h. The solvent was removed the by rotary evaporation to give an off-white powder. The resulting powder was washed with 3x5-mL diethyl ether followed by 3x5 mL H_2O. The product was dried *in vacuo*.

Diffraction quality crystals were grown by diffusing pentane into a concentrated methylene chloride solution. Yield: 22.8 mg (69%); mp 165 ˚C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (1 H, d, *J* = 6.4 Hz), 8.24–8.18 (4 H, m), 8.02–7.97 (5 H, m), 7.69 (1 H, d, *J* = 7.6 Hz), 7.60 (1 H, s), 7.47–7.43 (1 H, m), 7.35 (1 H, d, *J* = 8.0 Hz), 7.13 (1 H, d, 8.8 Hz), 2.67 (3 H, s), 2.65 (3 H, s), 2.46 (3 H, s). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.1, 146.0, 142.8, 142.7, 139.3, 138.4, 138.2, 135.4, 135.2, 129.7, 128.9, 127.5, 124.7, 123.0, 120.3, 27.1, 22.6. Anal. Calcd for $C_{28}H_{24}AuB_2NO_5$: C, 49.96; N, 2.08; H, 3.59. Found: C, 50.01; N, 2.25; H, 3.60. UV-Vis (2-MeTHF) λ_{max} nm (M^{-1} cm^{-1}): 298 (7130), 318 (7108), 335 (8037); emission (2-MeTHF, λ_{ex} = 350 nm) λ_{max} nm: 466, 498.

(tpy)Au(n-propyl)$_2$ boroxine (11). A 20-mL flask was charged with **1** (1 eq., 41.3 mg, 0.0699 mmol), (*n*-propyl)boronic acid (2 eq., 13.8 mg, 0.157 mmol), and KOtBu (3 eq., 24.1 mg, 0.215 mmol). The solids were suspended in 3-mL toluene and stirred for 3 h in the dark at room temperature. The solvent was removed from the reaction mixture by rotary evaporation to yield an off-white powder. The powder was washed with 2x5 mL of diethyl ether(x2) followed by 10-mL H_2O. The resulting white powder was dried *in vacuo*. Yield: 24.7 mg (68%); mp 93 ˚C dec. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.29 (1 H, dd, *J* = 4.5, 1.0 Hz), 8.06 (1 H, td, *J* = 7.5, 1.5 Hz), 7.80 (1 H, d, *J* = 8.0 Hz), 7.58 (1 H, s), 7.49 – 7.25 (1 H, m), 7.44 (1 H, d, *J* = 8.0 Hz), 7.17 (1 H, d, *J* = 8.0 Hz), 2.48 (3 H, s), 1.66 – 1.55 (4 H, m), 1.05 – 0.98 (8 H, m), 0.91 (2 H, t, *J* = 8.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 146.5, 146.1, 142.7, 142.3, 139.3, 129.2, 124.4, 122.7, 120.0, 22.4, 19.3, 19.2, 17.6, 17.5. Anal. Calcd for $C_{18}H_{24}AuB_2NO_3$: C, 41.50; N, 2.69; H, 4.64. Found: C, 41.55; N, 2.68; H, 4.49. ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 146.5, 146.1, 142.7, 142.3, 139.3, 129.2, 124.4, 122.7, 120.0, 22.4, 19.3, 19.2, 17.6, 17.5. UV-Vis (2-MeTHF) λ_{max} nm (M^{-1} cm^{-1}): 319 (9924, sh), 334 (11874), 345 (10527, sh); emission (2-MeTHF, λ_{ex} = 358 nm) λ_{max} nm: 466, 496.

(ppy)Au(4-isopropoxyphenyl)$_2$ boroxine (12). A 20-mL flask was charged with **2** (1 eq., 68.0 mg, 0.118 mmol), (4-isopropoxyphenyl)boronic acid (2 eq., 44.6 mg, 0.248 mmol), and KOtBu (3 eq., 39.3 mg, 0.350 mmol), and the solids were suspended in mL toluene. The reaction mixture was stirred at room temperature for 3 h in the dark. The solvent was removed by rotary evaporation to give an off-white powder. The powder was washed with 2x5 mL diethyl ether followed by 10 mL H_2O and dried by vacuum to give a white powder. Yield: 68.6 mg (84%); mp

142 ˚C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (1 H, d, *J* = 6.0 Hz), 8.06 (4 H, dd, *J* = 12.8, 8.4 Hz), 7.91 (1 H, t, *J* = 7.6 Hz), 7.73 (1 H, d, *J* = 7.6 Hz), 7.66 (1 H, *J* = 8.0 Hz), 7.41 – 7.38 (2 H, m), 7.32 (1 H, td, *J* = 7.6, 0.8 Hz), 7.27 (1 H, d, *J* = 7.6 Hz), 6.95 (4 H, dd, *J* = 8.0, 5.2 Hz), 4.66 (1 H, sept, *J* = 5.2), 4.65 (1 H, sept, *J* = 5.2 Hz), 1.38 (12 H, dd, *J* = 6.0, 1.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5, 159.9, 159.7, 146.4, 146.0, 142.5, 142.2, 136.9, 136.8, 131.4, 128.7, 128.3, 124.8, 123.4, 120.6, 115.0, 69.7, 22.4. Anal. Calcd for $C_{29}H_{30}AuB_2NO_5$: C, 50.40; N, 2.03; H, 4.38. Found: C, 50.22; N, 1.98; H, 4.47. UV-Vis (2-MeTHF) λ_{max} nm (M^{-1} cm^{-1}): 315 (10964), 338 (7361, sh); emission (2-MeTHF, λ_{ex} = 345 nm) λ_{max} nm: 391, 488, 518 (sh).

Emission Measurements. Steady state Luminescence spectra were measured at 298 K on a Cary Eclipse fluorescence spectrophotometer. Time resolved phosphorescence lifetime data were collected on a nanosecond laser system for which excitation wavelengths were generated as described previously.[2] The emitted light passed through a Triax 320 spectrometer, was dispersed by a blazed grating and detected with a Hamamatsu R928 photomultiplier tube (PMT). The PMT outputs were collected and averaged with a 1 GHz oscilloscope (LeCroy 9382CM). Samples for these measurements were housed in quartz EPR tubes with a high-vacuum adapter and subjected to three freeze-pump-thaw cycles at ~10^{-6} torr. For emission lifetime measurements at 77 K, the EPR tube was immersed in liquid nitrogen in a quartz finger dewar.

Relative emission quantum yields[3] were determined by referencing sample luminescence intensities of 2-methyltetrahydrofuran solutions to that quinine sulfate in 50 mM H_2SO_4(aq).[4] Samples were excited with 450-nm light, and measured luminescence yields were calculated according to:

$$\phi_s = \phi_r \left(\frac{A_r \eta_s^2 D_s}{A_s \eta_r^2 D_r} \right), \quad (1)$$

where *r* and *s* indicate reference and sample, respectively; *A* is the absorbance at λ_{ex}, η is the average refractive index of the solvent, and *D* is the integrated area under the corrected emission spectrum.

Crystallography. Data were collected on a Bruker AXS SMART APEXII CCD diffractometer or a Bruker AXS Quest diffractometer using monochromatic Mo Kα or a Bruker

AXS Prospector CCD diffractometer using monochromatic Cu Kα radiation with omega and/or phi scan techniques. Unit cells were retrieved within the APEX2 Crystallographic Suite. Structures were solved by direct methods and refined by full matrix least squares against F^2 with all reflections using SHELXL2013 and SHELXLE. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and were refined with an isotropic displacement parameter 1.5 (CH_3) or 1.2 (all others) times that of the adjacent carbon atom.

Calculations. Density-functional theory and configuration interaction singles (CIS) calculations were performed with *Gaussian09*.[5] Geometry optimizations proceeded without imposed symmetry or other constraints, and harmonic frequency calculations found converged structures to be local minima of the potential energy hypersurface. The parameter-free exchange and correlation functionals of Perdew, Burke, and Ernzerhof were used for geometry optimizations and TDDFT calculations.[6] The TZVP basis set was applied to nonmetal atoms.[7] For iridium, the SDD effective core potential and accompanying basis set were employed;[8] scalar relativistic effects are treated implicitly. CIS results reflect single-point calculations made on PBE0-optimized structures using tight SCF convergence criteria. Computations include continuum tetrahydrofuran solvation with the integral equation formalism of the polarizable continuum model (IEFPCM).[9–11] Orbital energy level diagrams used the AOMix program of Gorelsky.[12,13]

Figure S1. Thermal ellipsoid diagram of **4** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

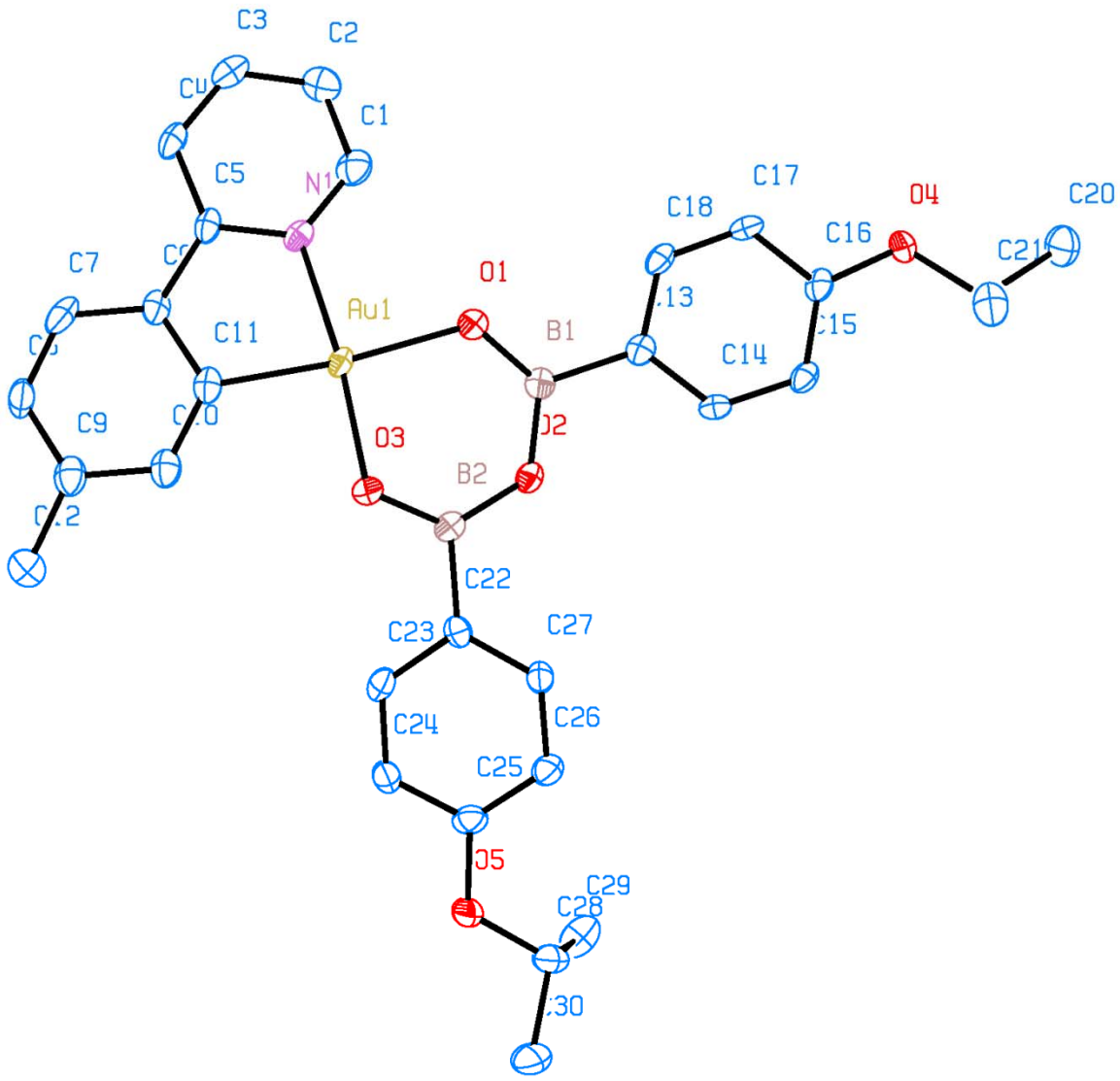


Figure S2. Packing diagram of **4** shown normal to (100) Legend: carbon, blue; boron, pink; oxygen, red; gold, yellow; iron, orange. Hydrogen atoms are omitted for clarity.

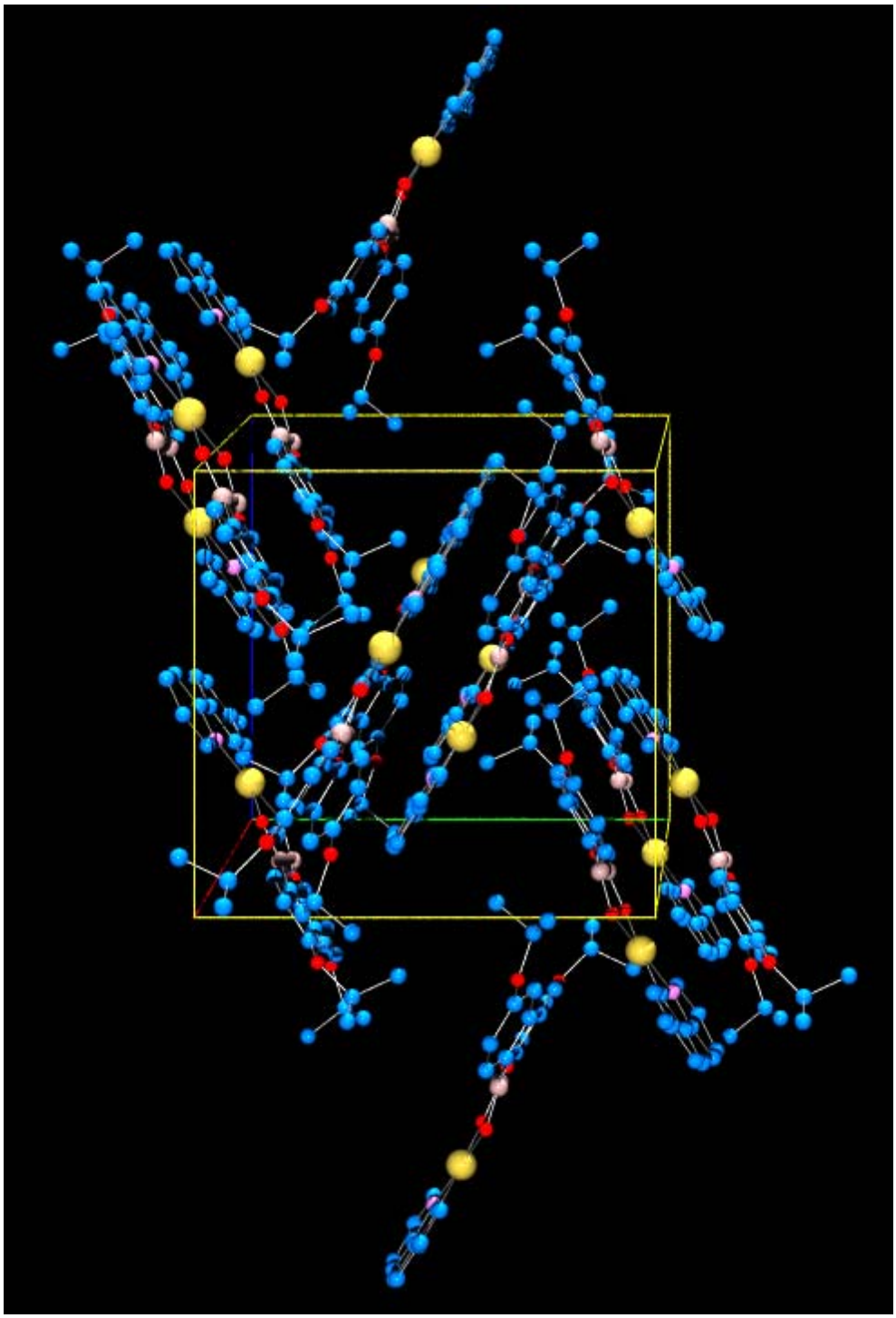


Figure S3. Thermal ellipsoid diagram of **7** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

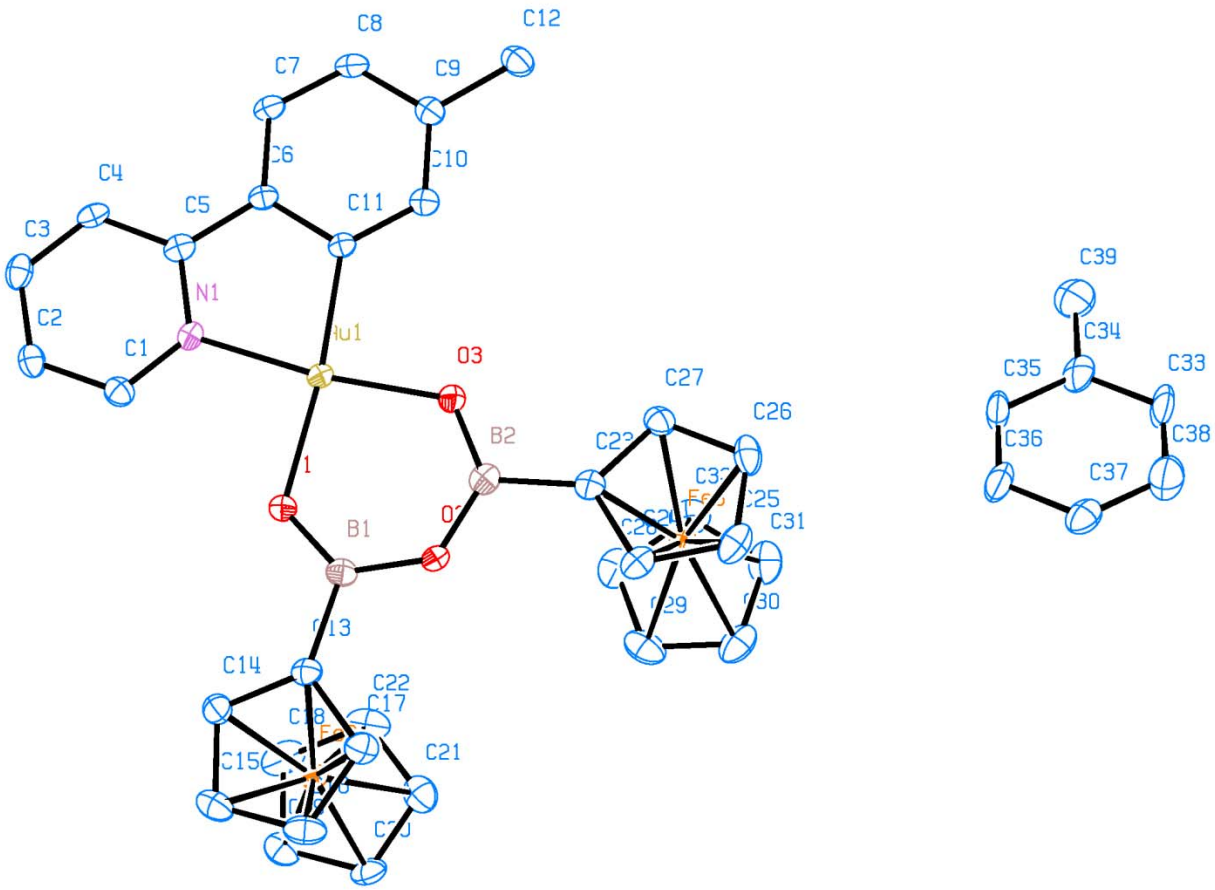


Figure S4. Packing diagram for **7** normal to (010). Legend: carbon, blue; boron, pink; oxygen, red; gold, yellow; iron, orange. Hydrogen atoms are omitted for clarity.

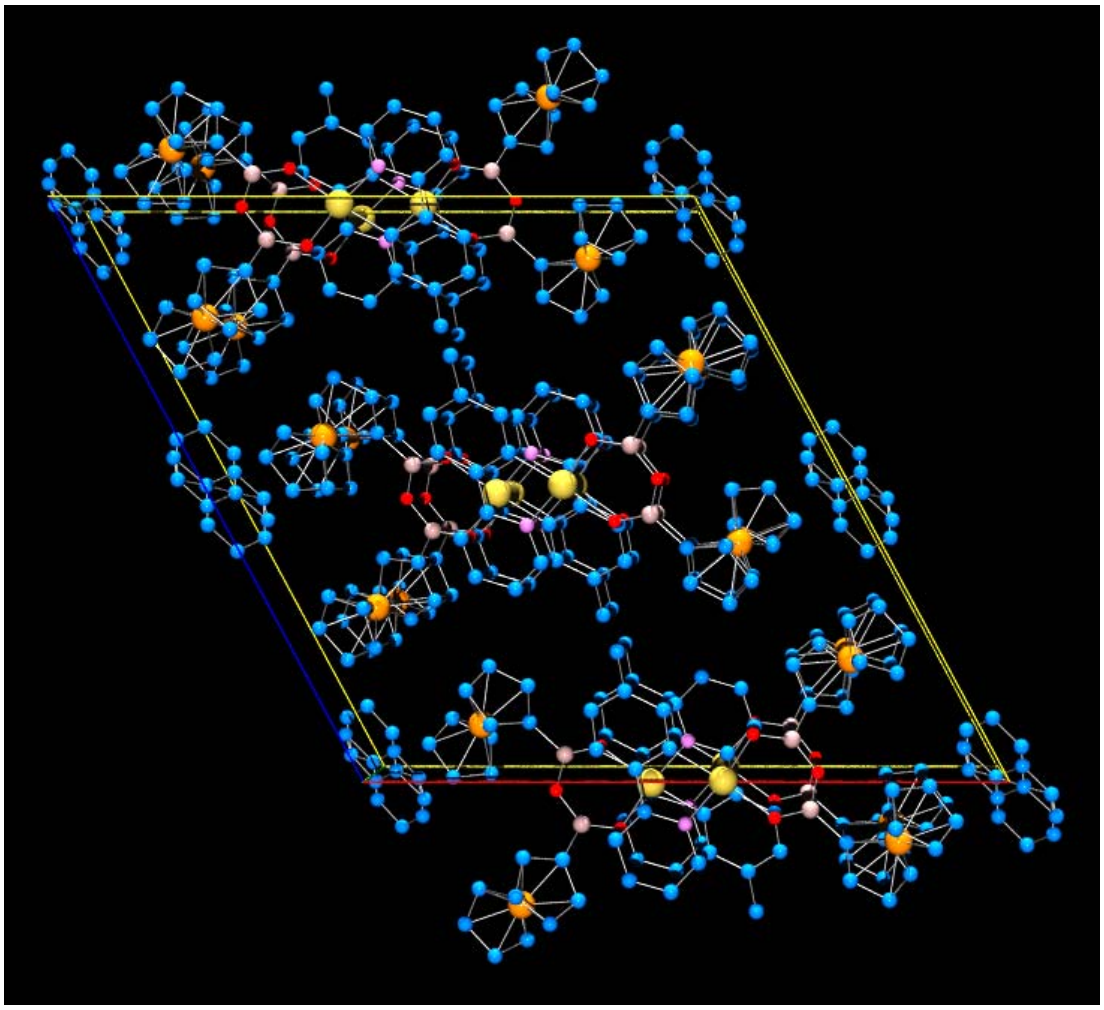


Figure S5 Thermal ellipsoid diagram of **9** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

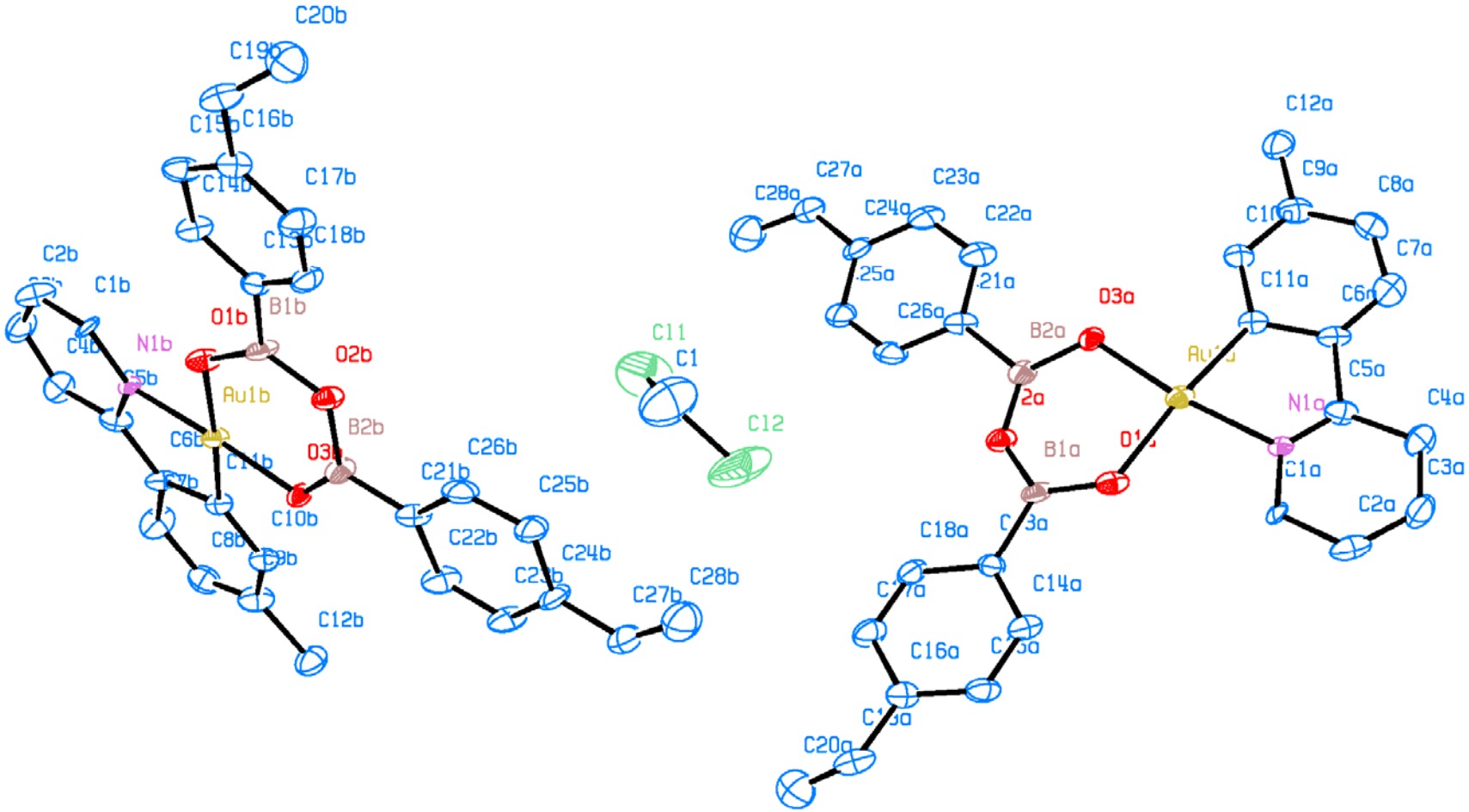


Figure S6. Thermal ellipsoid diagram of **9** showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

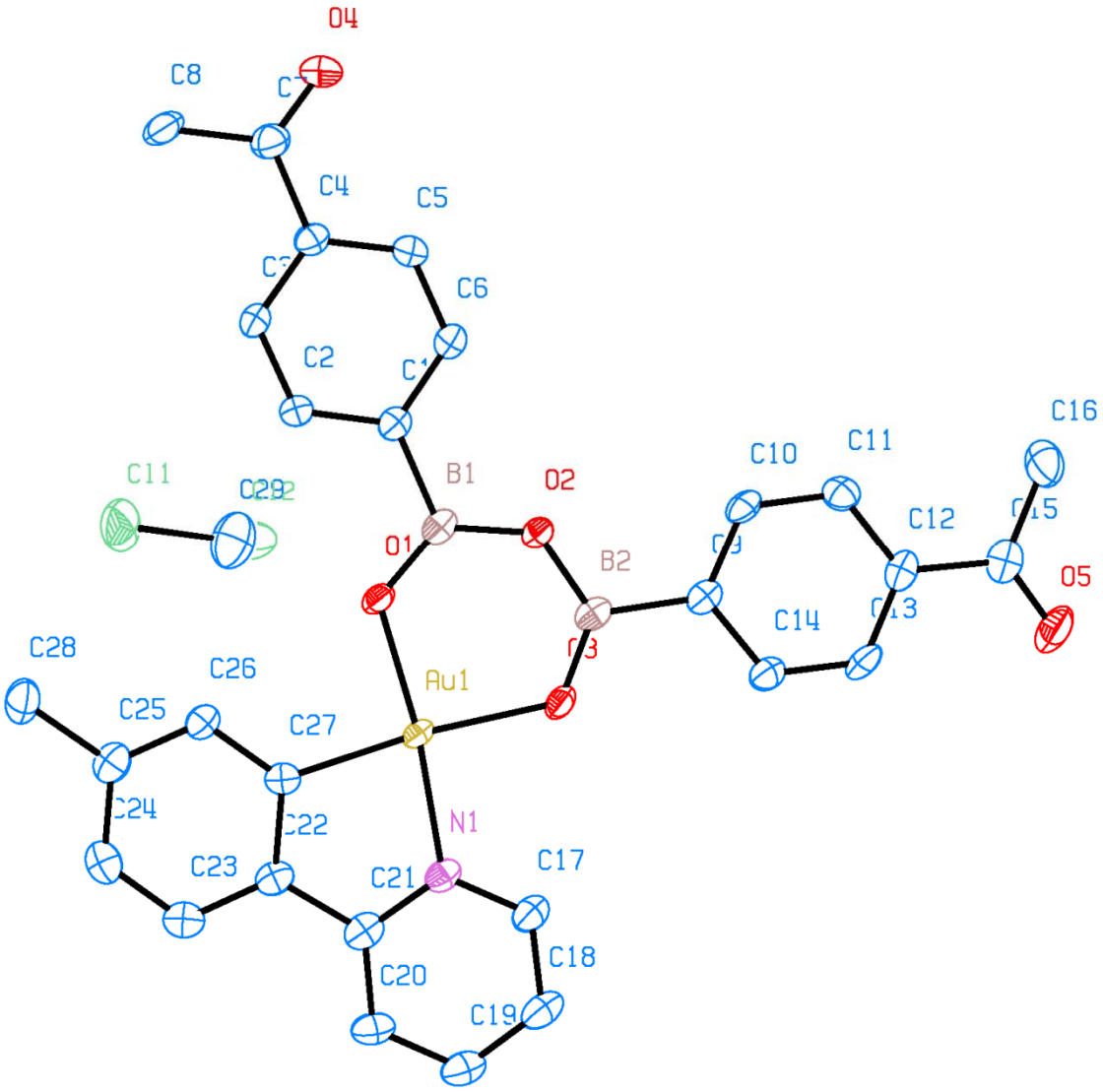


Figure S7. Absorption spectra of new complexes in 2-methyltetrahydrofuran.

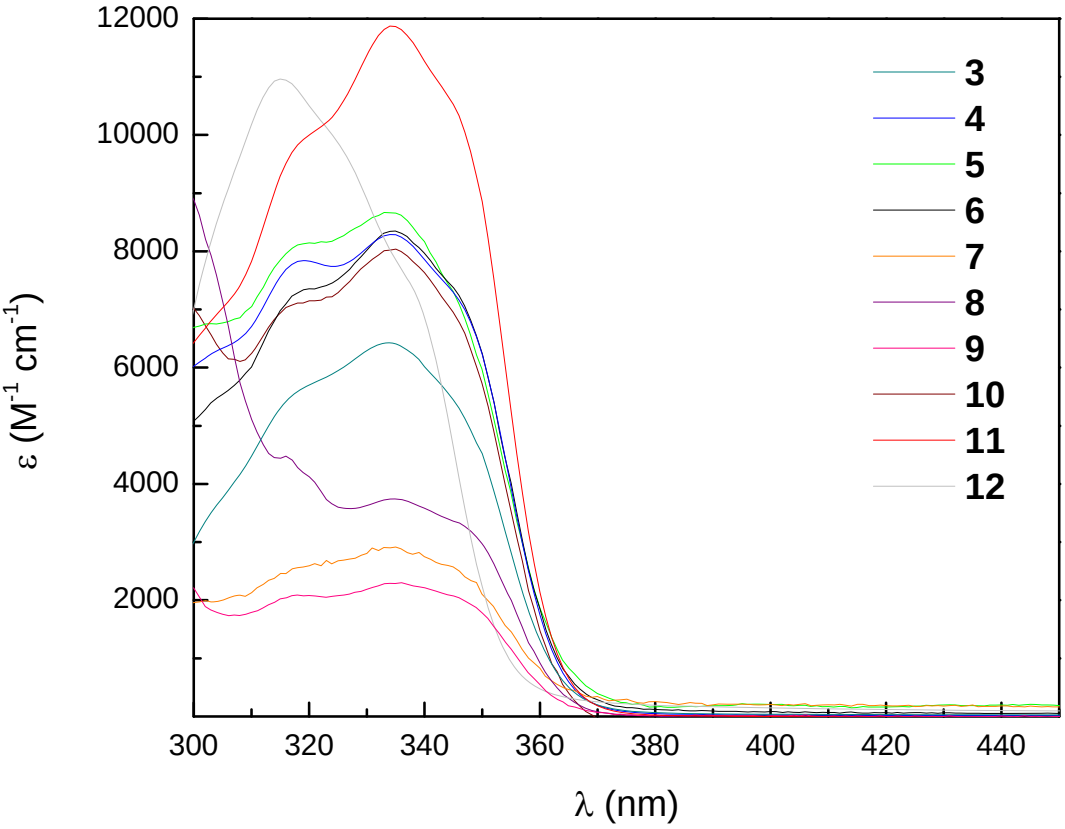


Figure S8. Luminescence spectra of new complexes in 2-methyltetrahydrofuran at 298 K. Excitation wavelengths λ_{ex} are indicated.

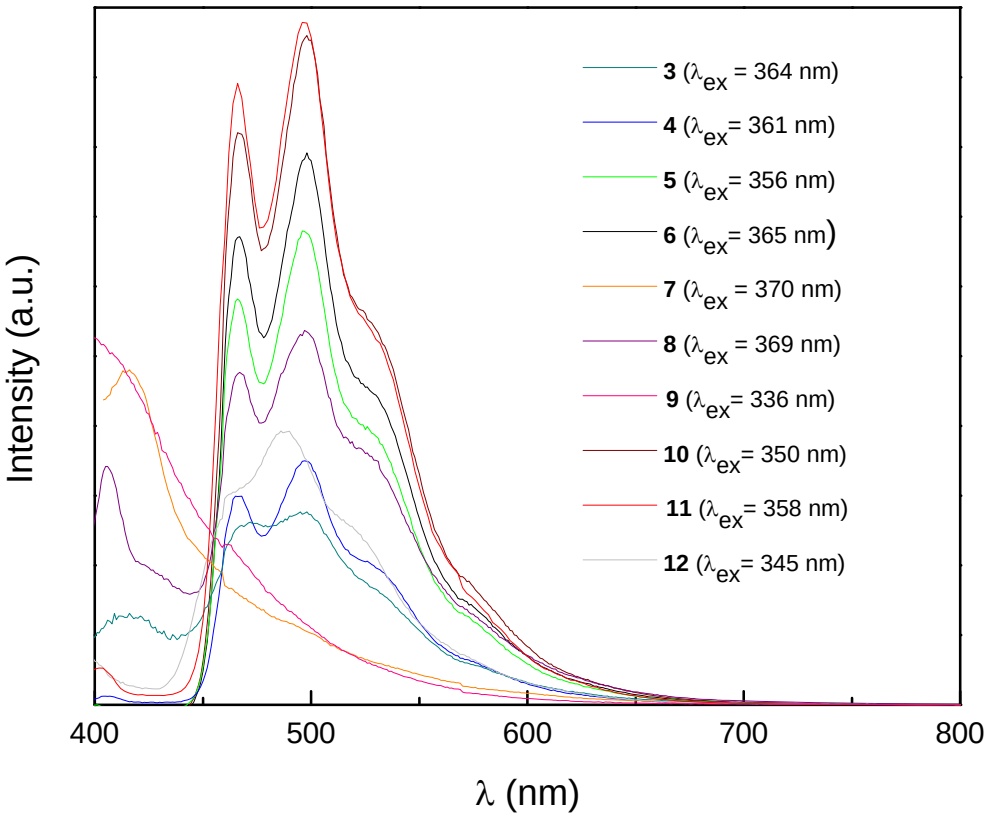


Table S1. Crystallographic data

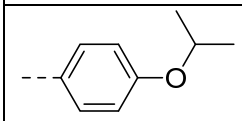
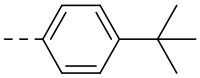
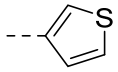
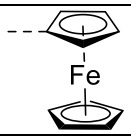
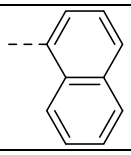
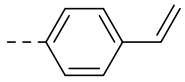
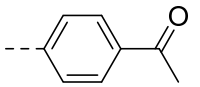
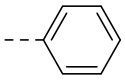
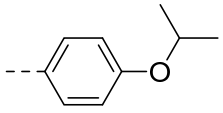
Experiments were carried out at 100 K. H-atom parameters were constrained.

	4	**7**	**9**	**10**
	13mz167_0m	Quest14mz023_0m	14mz047_0m	Prosp14mz012_0m
Crystal data				
Chemical formula	$C_{30}H_{32}AuB_2NO_5$	$2(C_{32}H_{28}AuB_2Fe_2NO_3)\cdot C_7H_8$	$C_{57}H_{50}Au_2B_4Cl_2N_2O_6$	$C_{57}H_{50}Au_2B_4Cl_2N_2O_{10}$
M_r	705.15	1701.82	1367.06	1431.06
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
a, b, c (Å)	16.224 (2), 13.4035 (19), 13.0086 (18)	20.8526 (9), 7.7561 (2), 21.4691 (9)	8.007 (4), 17.734 (8), 20.141 (10)	8.6237 (4), 11.2419 (5), 14.8115 (7)
α, β, γ (°)	90, 98.365 (3), 90	90, 118.2832 (11), 90	66.280 (6), 89.959 (7), 77.147 (7)	73.806 (2), 85.564 (2), 72.674 (2)
V (Å^3)	2798.8 (7)	3057.8 (2)	2540 (2)	1316.36 (11)
Z	4	2	2	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	5.30	5.76	5.93	11.77
Crystal size (mm)	0.20 × 0.15 × 0.06	0.30 × 0.05 × 0.02	0.45 × 0.14 × 0.05	0.07 × 0.04 × 0.04
Data collection				
Diffractometer	Bruker AXS *SMART APEX* CCD diffractometer	Bruker AXS D8 Quest CMOS diffractometer	Bruker AXS APEXII CCD diffractometer	Bruker AXS Prospector CCD diffractometer
Absorption correction	Multi-scan TWINABS (Sheldrick, 2012)	Multi-scan Apex2 v2014.1-1 (Bruker, 2014)	Multi-scan Apex2 v2013.4-1 (Bruker, 2013)	Multi-scan Apex2 v2014.1-0 (Bruker, 2014)
T_{min}, T_{max}	0.526, 0.746	0.619, 0.746	0.417, 0.746	0.575, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15283, 7952, 6119	18808, 9021, 7118	33527, 14338, 7751	20434, 4577, 4156
R_{int}	0.042	0.035	0.056	0.033
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.730	0.714	0.732	0.596
Refinement				

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.099, 1.01	0.033, 0.074, 1.02	0.061, 0.180, 1.09	0.021, 0.050, 1.05
No. of reflections	7952	9021	14338	4577
No. of parameters	358	423	457	364
No. of restraints	0	45	22	0
	$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0756P)^2 + 11.8179P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 2.0845P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	3.79, -1.57	3.01, -0.76	7.09, -3.24	1.03, -0.83

Computer programs: Apex2 v2013.4-1 (Bruker, 2013), Apex2 v2014.1-1 (Bruker, 2014), Apex2 v2014.1-0 (Bruker, 2014), *SAINT* V8.30C (Bruker, 2013), *SAINT* V8.34A (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2013), SHELXLE Rev609 (Hübschle *et al.*, 2011), *SHELXL2013* (Sheldrick, 2013), SHELXLE Rev645 (Hübschle *et al.*, 2011), *SHELXTL* (Bruker, 2003).

Table S2. Photophysical Data.

Substituent on boron	λ_{abs} (nm), ε (M^{-1} cm^{-1})	Emission Max (λ_{ex}) nm	τ_{77K} (μs)	τ_{298K} (μs)	Φ_f [b]	k_r (μs^{-1})[c]	k_{nr} (μs^{-1})[d]
	320, 9588 333, 9840	467, 497 (361)	321	1.82	0.0032 ± 0.0005	$3.12x10^{-3}$	0.546
	320, 8146 333, 8668	466, 496 (356)	320	1.50	0.0060 ± 0.0008	$3.13x10^{-3}$	0.664
	320, 7354 335, 8349	467, 498 (365)	315	2.53 [a]	0.0040 ± 0.0002	$3.17x10^{-3}$	0.392
	333, 2906	416 (370)	389 [a]	No signal [a]	0.0004 ± 0.00005	$2.57 x10^{-3}$	-
	276, 11826 289, 11261 335, 3741	406, 467, 497 (369)	[e]	No signal [e]	0.0006 ± 0.00003	-	-
	318, 2090 336, 2299	395 (336)	[f]	-	0.0008 ± 0.00002	-	-
	298, 7130 318, 7108 335, 8037	466, 498 (350)	358 [a]	1.64 [a]	0.0032 ± 0.0003	$2.79 x10^{-3}$	0.607
	334, 6427	472, 495 (364)	325	2.85	0.0060 ± 0.001	$3.08x10^{-3}$	0.348
 ppy	315, 10963	486 (345)	274	1.44	0.0068 ± 0.002	$3.65x10^{-3}$	0.691

Unless otherwise noted, photophysical data were collected in 2-methyltetrahydrofuran.

[a] 1:1 2-MeTHF:CH_2Cl_2

[b] Quantum yields were measured relative to quinine sulfate in 50 mM H_2SO_4(aq). Three samples were run for each compound at a concentration that yielded about 0.05 absorbance. An error of 10% was assumed.

[c] $k_r = 1/\tau_{77K}$

[d] $k_{nr} = (1/\tau_{298K}) - k_r$

[e] At 77K a green emission was observed with a very long lifetime (order of 1-2 seconds). Due to the long lifetime with respect to the laser repetition, no signal could be recorded. At 298 K only a faint blue emission was observed by eye and no signal could be recorded on the instrument.

[f] Data could not be accurately fitted.

Table S3. Composition of excited states of **4** calculated by PBE0 TDDFT.

Singlet states

No.	nm	10^3 cm-1	eV	f	
1	346.0	28.9	3.58	0.0079	HOMO → LUMO (+84%) HOMO − 1 → LUMO (14%)
2	340.2	29.4	3.65	0.0042	HOMO − 1 → LUMO (+84%) HOMO → LUMO (+15%)
3	317.6	31.5	3.90	0.0037	HOMO − 1 → LUMO + 1(+85%) HOMO − 2 → LUMO + 1(7%)
4	317.1	31.5	3.91	0.2429	HOMO − 2 → LUMO (+91%)
5	314.9	31.8	3.94	0.0002	HOMO → LUMO + 1(+90%)
6	298.5	33.5	4.15	0.0002	HOMO − 2 → LUMO + 1(+80%) HOMO → LUMO + 1(7%)
					HOMO − 1 → LUMO + 1(+6%) HOMO − 5 → LUMO + 1(5%)
7	288.9	34.6	4.29	0.0374	HOMO → LUMO + 2(+55%) HOMO − 5 → LUMO (23%)
					HOMO − 1 → LUMO + 2(14%)
8	287.0	34.8	4.32	0.0622	HOMO − 5 → LUMO (+55%) HOMO → LUMO + 2(+29%)
9	282.1	35.4	4.40	0.0109	HOMO − 1 → LUMO + 2(+82%) HOMO → LUMO + 2(+16%)
10	276.8	36.1	4.48	0.0000	HOMO − 5 → LUMO + 1(+75%) HOMO − 2 → LUMO + 1(+8%)
11	274.9	36.4	4.51	0.0015	HOMO − 3 → LUMO (+92%)
12	272.5	36.7	4.55	0.0000	HOMO − 4 → LUMO (+95%)
13	271.6	36.8	4.56	0.0002	HOMO − 6 → LUMO (+91%)
14	264.8	37.8	4.68	0.1775	HOMO − 2 → LUMO + 2(+80%) HOMO − 5 → LUMO (+9%)
15	258.3	38.7	4.80	0.0144	HOMO − 7 → LUMO + 1(+90%)
16	255.4	39.2	4.85	0.0007	HOMO − 4 → LUMO + 1(+71%) HOMO − 8 → LUMO + 1(+16%)
					HOMO − 5 → LUMO + 1(6%)
17	251.7	39.7	4.93	0.0057	HOMO − 3 → LUMO + 1(+84%) HOMO − 4 → LUMO + 1(9%)
18	248.2	40.3	5.00	1.0466	HOMO − 6 → LUMO + 1(+66%) HOMO − 1 → LUMO + 3(+9%)
					HOMO − 1 → LUMO + 4(+5%)
19	247.5	40.4	5.01	0.0100	HOMO − 7 → LUMO (+82%) HOMO − 8 → LUMO + 1(8%)
20	246.3	40.6	5.03	0.0021	HOMO − 8 → LUMO + 1(+55%) HOMO − 4 → LUMO + 1(14%)
					HOMO − 7 → LUMO (+14%) HOMO − 3 → LUMO + 1(5%)

Table S3 (continued).

Triplet states

No.	nm	10^3 cm-1	eV	
1	442.7	22.6	2.80	HOMO − 2 → LUMO (+75%) HOMO − 2 → LUMO + 2(+10%)
2	358.5	27.9	3.46	HOMO − 1 → LUMO + 4(+20%) HOMO − 4 → LUMO + 6(12%)
				HOMO → LUMO + 4(+10%) HOMO − 1 → LUMO + 5(+9%)
				HOMO − 1 → LUMO + 7(+9%) HOMO − 1 → LUMO + 3(+8%)
				HOMO − 4 → LUMO + 5(+6%)
3	357.5	28.0	3.47	HOMO → LUMO + 3(+16%) HOMO → LUMO + 5(14%)
				HOMO → LUMO + 7(10%) HOMO − 3 → LUMO + 6(9%)
				HOMO → LUMO + 4(+8%) HOMO − 3 → LUMO + 7(+7%)
				HOMO − 1 → LUMO + 3(7%) HOMO − 3 → LUMO + 5(6%)
				HOMO − 1 → LUMO + 5(+5%)
4	346.7	28.8	3.58	HOMO → LUMO (+72%) HOMO − 1 → LUMO (9%)
				HOMO − 2 → LUMO + 2(6%)
5	339.8	29.4	3.65	HOMO − 1 → LUMO (+69%) HOMO − 2 → LUMO + 2(11%)
				HOMO − 2 → LUMO (+5%)
6	338.6	29.5	3.66	HOMO − 2 → LUMO + 2(+42%) HOMO → LUMO (+17%)
				HOMO − 1 → LUMO (+15%) HOMO − 11 → LUMO + 2(9%)
				HOMO − 2 → LUMO (8%)
7	330.3	30.3	3.75	HOMO − 1 → LUMO + 1(+59%) HOMO − 2 → LUMO + 1(20%)
				HOMO − 9 → LUMO + 1(7%) HOMO − 5 → LUMO + 1(+6%)
8	324.6	30.8	3.82	HOMO − 5 → LUMO (+77%) HOMO − 5 → LUMO + 2(+6%)
9	322.8	31.0	3.84	HOMO → LUMO + 1(+52%) HOMO − 1 → LUMO + 1(+14%)
				HOMO − 5 → LUMO + 1(13%) HOMO − 2 → LUMO + 1(+11%)
				HOMO − 8 → LUMO + 1(7%)
10	312.7	32.0	3.97	HOMO − 6 → LUMO + 1(+31%) HOMO − 5 → LUMO + 3(13%)
				HOMO − 5 → LUMO + 4(+9%) HOMO − 2 → LUMO + 9(+6%)
				HOMO − 11 → LUMO (6%) HOMO − 5 → LUMO + 2(6%)

Table S4. Composition of excited states of **4** calculated by CIS.

Singlet states

No.	nm	10^3 cm-1	eV	f	
1	267.4	37.4	4.64	0.6086	HOMO − 2 → LUMO (+82%)
2	233.0	42.9	5.32	0.0002	HOMO − 5 → LUMO + 6(+14%) HOMO − 5 → LUMO + 4(11%) HOMO − 2 → LUMO + 6(+9%) HOMO − 46 → LUMO + 6(8%) HOMO − 2 → LUMO + 4(7%) HOMO − 46 → LUMO + 4(+5%)
3	225.5	44.3	5.50	0.2654	HOMO − 5 → LUMO (+32%) HOMO − 2 → LUMO + 3(9%) HOMO − 2 → LUMO + 2(+6%)
4	222.1	45.0	5.58	0.0709	HOMO − 2 → LUMO + 3(11%) HOMO − 2 → LUMO + 2(+8%) HOMO − 5 → LUMO (+7%) HOMO − 10 → LUMO + 6(+6%)
5	221.4	45.2	5.60	0.0003	HOMO − 8 → LUMO + 6(14%) HOMO − 8 → LUMO + 4(+10%) HOMO − 12 → LUMO + 6(5%) HOMO − 17 → LUMO + 6(5%)
6	212.4	47.1	5.84	0.0186	HOMO − 2 → LUMO + 2(+23%) HOMO − 5 → LUMO (17%) HOMO − 2 → LUMO + 3(10%) HOMO − 7 → LUMO (9%) HOMO − 7 → LUMO + 2(+5%) HOMO − 2 → LUMO + 8(+5%)
7	211.8	47.2	5.85	0.0765	HOMO − 25 → LUMO + 6(8%) HOMO − 25 → LUMO + 4(+5%)
8	210.7	47.5	5.89	0.1398	HOMO − 1 → LUMO + 9(+21%) HOMO → LUMO + 9(20%) HOMO → LUMO + 10(+13%) HOMO − 4 → LUMO + 11(7%) HOMO − 4 → LUMO + 7(7%)
9	210.3	47.6	5.90	0.0652	HOMO − 1 → LUMO + 10(+25%) HOMO → LUMO + 10(+12%) HOMO → LUMO + 9(+11%) HOMO − 3 → LUMO + 7(7%) HOMO − 3 → LUMO + 8(+5%)
10	209.5	47.7	5.92	0.3550	HOMO − 1 → LUMO + 11(26%) HOMO → LUMO + 7(+22%) HOMO → LUMO + 8(7%) HOMO − 3 → LUMO + 9(+7%) HOMO − 4 → LUMO + 10(+6%) HOMO → LUMO + 10(5%)
11	208.2	48.0	5.95	0.2402	HOMO → LUMO + 11(27%) HOMO − 1 → LUMO + 7(+23%) HOMO − 1 → LUMO + 8(10%) HOMO − 3 → LUMO + 10(+10%) HOMO − 4 → LUMO + 9(+9%)
12	192.4	52.0	6.44	1.0479	HOMO − 5 → LUMO + 8(+13%) HOMO − 5 → LUMO (+12%) HOMO − 2 → LUMO + 3(+10%) HOMO − 7 → LUMO (9%) HOMO − 5 → LUMO + 7(+8%) HOMO − 5 → LUMO + 3(+7%) HOMO − 2 → LUMO + 15(+6%) HOMO − 2 → LUMO + 8(+6%)
13	192.0	52.1	6.46	0.0086	HOMO − 2 → LUMO + 1(+61%) HOMO − 2 → LUMO + 4(26%)
14	185.5	53.9	6.69	0.4666	HOMO − 8 → LUMO (+20%) HOMO − 2 → LUMO + 8(+11%)

					HOMO − 2 → LUMO + 7(+8%) HOMO − 7 → LUMO + 3(7%)
					HOMO − 5 → LUMO (+6%) HOMO − 2 → LUMO + 15(6%)
					HOMO − 7 → LUMO + 2(+6%)
15	183.8	54.4	6.74	0.0194	HOMO → LUMO + 1(+56%) HOMO → LUMO + 4(+13%)
					HOMO − 1 → LUMO + 5(7%)
16	183.1	54.6	6.77	0.0012	HOMO − 2 → LUMO + 6(+27%) HOMO − 1 → LUMO + 1(+27%)
					HOMO − 2 → LUMO + 5(7%) HOMO − 2 → LUMO + 4(7%)
17	182.5	54.8	6.80	0.0012	HOMO − 1 → LUMO + 1(+29%) HOMO − 2 → LUMO + 6(19%)
					HOMO − 1 → LUMO + 4(+8%) HOMO → LUMO + 5(5%)
					HOMO − 2 → LUMO + 4(+5%) HOMO − 2 → LUMO + 5(+5%)
18	175.2	57.1	7.08	2.4373	HOMO − 3 → LUMO + 10(+14%) HOMO − 4 → LUMO + 9(+11%)
					HOMO − 6 → LUMO + 6(+11%) HOMO − 6 → LUMO + 4(9%)
					HOMO − 8 → LUMO (8%)
19	174.7	57.3	7.10	2.0518	HOMO − 7 → LUMO (+12%) HOMO − 8 → LUMO (+10%)
					HOMO − 8 → LUMO + 2(10%) HOMO − 5 → LUMO + 8(+8%)
					HOMO − 5 → LUMO + 3(+8%) HOMO − 5 → LUMO + 7(+5%)
20	172.8	57.9	7.18	1.6643	HOMO − 4 → LUMO + 10(+24%) HOMO − 3 → LUMO + 9(+22%)
					HOMO → LUMO + 7(8%) HOMO − 3 → LUMO + 10(+6%)
					HOMO − 1 → LUMO + 11(+5%)

Table S4 (continued).

Triplet states

No.	nm	10^3 cm-1	eV	
1	423.4	23.6	2.93	HOMO − 2 → LUMO (+53%) HOMO − 2 → LUMO + 3(8%)
				HOMO − 7 → LUMO + 15(6%) HOMO − 5 → LUMO + 8(+5%)
2	362.2	27.6	3.42	HOMO → LUMO + 7(18%) HOMO − 1 → LUMO + 11(+15%)
				HOMO − 4 → LUMO + 10(13%) HOMO − 3 → LUMO + 9(8%)
				HOMO − 1 → LUMO + 9(8%) HOMO → LUMO + 8(+8%)
3	362.1	27.6	3.42	HOMO − 3 → LUMO + 10(+16%) HOMO − 1 → LUMO + 7(+16%)
				HOMO → LUMO + 11(15%) HOMO − 4 → LUMO + 9(+9%)
				HOMO − 1 → LUMO + 8(9%) HOMO → LUMO + 9(+8%)
4	318.4	31.4	3.89	HOMO − 7 → LUMO + 2(+12%) HOMO − 7 → LUMO + 3(12%)
				HOMO − 8 → LUMO (+11%) HOMO − 2 → LUMO + 15(8%)
				HOMO − 2 → LUMO + 2(+8%) HOMO − 2 → LUMO + 3(8%)
				HOMO − 5 → LUMO + 8(5%)
5	302.2	33.1	4.10	HOMO − 7 → LUMO (+21%) HOMO − 2 → LUMO (+20%)
				HOMO − 2 → LUMO + 2(14%) HOMO − 5 → LUMO + 8(6%)
				HOMO − 2 → LUMO + 3(+5%) HOMO − 7 → LUMO + 2(5%)
6	272.0	36.8	4.56	HOMO − 5 → LUMO (+44%) HOMO − 5 → LUMO + 15(+9%)
7	266.0	37.6	4.66	HOMO − 46 → LUMO + 6(8%) HOMO − 17 → LUMO + 6(+8%)
				HOMO − 8 → LUMO + 6(+6%) HOMO − 46 → LUMO + 4(+6%)
				HOMO − 17 → LUMO + 4(5%)
8	264.6	37.8	4.69	HOMO − 5 → LUMO (13%) HOMO − 6 → LUMO + 6(7%)
				HOMO − 5 → LUMO + 3(+6%) HOMO − 15 → LUMO + 6(+5%)
9	261.6	38.2	4.74	HOMO − 8 → LUMO (12%) HOMO − 5 → LUMO + 8(12%)
				HOMO − 5 → LUMO + 7(7%) HOMO − 5 → LUMO + 3(7%)
				HOMO − 2 → LUMO + 2(+5%) HOMO − 2 → LUMO + 3(5%)
10	259.6	38.5	4.78	HOMO → LUMO + 10(21%) HOMO − 1 → LUMO + 10(19%)
				HOMO − 1 → LUMO + 11(11%) HOMO → LUMO + 7(+6%)
				HOMO → LUMO + 11(6%) HOMO − 3 → LUMO + 10(5%)
				HOMO − 1 → LUMO + 7(+5%)

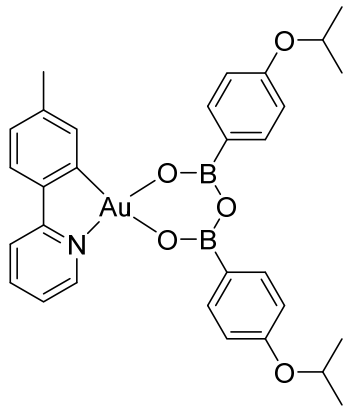


Table S5. Optimized Cartesian coordinates (Å) of **4**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	79	0	-2.085747	-1.053424	-0.055625
2	7	0	-1.058496	0.679475	-0.349208
3	6	0	0.288945	0.577987	-0.250076
4	6	0	1.064548	1.716216	-0.437506
5	6	0	0.451073	2.923539	-0.718976
6	6	0	-0.933086	2.991047	-0.812679
7	6	0	-1.663740	1.836469	-0.619850
8	1	0	2.141754	1.650681	-0.362039
9	1	0	1.052555	3.812961	-0.865441
10	1	0	-1.444002	3.919180	-1.030976
11	1	0	-2.745759	1.788960	-0.672249
12	6	0	0.766471	-0.763803	0.052597
13	6	0	2.105110	-1.118895	0.200683
14	1	0	2.889886	-0.378368	0.091726
15	6	0	2.444324	-2.431261	0.487191
16	1	0	3.489886	-2.698148	0.597839
17	6	0	1.467432	-3.416019	0.633841
18	6	0	0.123899	-3.055332	0.481149
19	1	0	-0.658829	-3.799714	0.584244
20	6	0	-0.220781	-1.752381	0.197153
21	6	0	1.838761	-4.828829	0.965417
22	1	0	2.903290	-5.008128	0.808332
23	1	0	1.613350	-5.051189	2.013058
24	1	0	1.273987	-5.538585	0.356912
25	8	0	-2.895691	-2.839396	0.258394
26	5	0	-4.228855	-3.063205	0.239270
27	8	0	-5.203161	-2.111963	0.012660
28	5	0	-5.070868	-0.749758	-0.258195
29	8	0	-3.896070	-0.115593	-0.350621
30	6	0	-4.716355	-4.537138	0.497683
31	6	0	-6.068520	-4.876659	0.443660
32	6	0	-3.818081	-5.572964	0.787105
33	6	0	-6.522183	-6.172293	0.661324
34	1	0	-6.795444	-4.102895	0.219325
35	6	0	-4.243760	-6.867391	1.011682
36	1	0	-2.757259	-5.350786	0.838189

37	6	0	-5.604572	-7.181367	0.951321
38	1	0	-7.582684	-6.379285	0.598767
39	1	0	-3.539420	-7.660326	1.238537
40	6	0	-6.414032	0.047630	-0.457917
41	6	0	-7.661437	-0.559831	-0.312373
42	6	0	-6.413841	1.409586	-0.787488
43	6	0	-8.854773	0.132821	-0.481756
44	1	0	-7.704883	-1.613383	-0.056143
45	6	0	-7.585012	2.120324	-0.964523
46	1	0	-5.463967	1.920387	-0.908871
47	6	0	-8.821780	1.487389	-0.810386
48	1	0	-9.793548	-0.391463	-0.359447
49	1	0	-7.571517	3.174429	-1.219606
50	8	0	-5.918847	-8.473479	1.206382
51	6	0	-7.277961	-8.920090	1.105123
52	6	0	-7.359606	-10.192923	1.918290
53	6	0	-7.664650	-9.135474	-0.345830
54	1	0	-7.929916	-8.167371	1.562176
55	1	0	-7.080690	-10.008129	2.957087
56	1	0	-8.378586	-10.584587	1.897811
57	1	0	-6.690106	-10.952152	1.506586
58	1	0	-7.547912	-8.224453	-0.935037
59	1	0	-7.039162	-9.914817	-0.788245
60	1	0	-8.708039	-9.451854	-0.412449
61	8	0	-9.909236	2.276403	-0.982126
62	6	0	-11.227409	1.718151	-0.893874
63	6	0	-11.590264	0.990255	-2.174450
64	6	0	-12.153298	2.880435	-0.610841
65	1	0	-11.259380	1.027058	-0.044162
66	1	0	-10.886926	0.186110	-2.396691
67	1	0	-12.588164	0.554548	-2.086930
68	1	0	-11.591920	1.689103	-3.014662
69	1	0	-11.871521	3.384134	0.315406
70	1	0	-12.116045	3.605147	-1.427858
71	1	0	-13.180858	2.524526	-0.512696

Table S6. Cartesian coordinates (Å) of partly optimized, stacked $(\mathbf{4})_2$. Non-hydrogen atoms were held in crystallographic positions; H atoms were optimized in a PBE0/6-31G(d) calculation with imposed C_i symmetry. Please see "Experimental and Computational Details."

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	79	0	0.018062	0.030539	0.526547
2	8	0	0.068343	-0.168900	2.568142
3	8	0	2.479608	-0.229157	2.664150
4	8	0	1.984593	0.075718	0.296997
5	8	0	0.983720	-0.830099	8.979439
6	8	0	8.416331	0.777247	0.181900
7	7	0	-2.021454	0.018799	0.540000
8	6	0	-2.727709	-0.000365	1.673796
9	6	0	-4.113207	0.009723	1.649979
10	6	0	-4.751126	0.032103	0.412494
11	6	0	-4.001605	0.059716	-0.756220
12	6	0	-2.608488	0.063838	-0.684693
13	6	0	-1.668470	0.132078	-1.797274
14	6	0	-2.026810	0.192624	-3.146881
15	6	0	-1.041112	0.292706	-4.119836
16	6	0	0.315634	0.340546	-3.776333
17	6	0	0.670900	0.261098	-2.423142
18	6	0	-0.303423	0.160751	-1.447878
19	6	0	1.372476	0.520212	-4.827209
20	6	0	1.185493	-0.469118	4.811720
21	6	0	2.360292	-0.577031	5.563020
22	6	0	2.351680	-0.712115	6.950198
23	6	0	1.130723	-0.739427	7.629121
24	6	0	-0.061633	-0.646676	6.900561
25	6	0	-0.025375	-0.511658	5.522306
26	6	0	2.124670	-1.058118	9.803829
27	6	0	1.701300	-0.679306	11.211100
28	6	0	2.573967	-2.509420	9.711686
29	6	0	4.362482	0.195996	1.052128
30	6	0	4.814145	0.825178	-0.120021
31	6	0	6.163778	1.020461	-0.371077
32	6	0	7.123725	0.562705	0.541684
33	6	0	6.703303	-0.073424	1.714105
34	6	0	5.339583	-0.237891	1.953537
35	6	0	9.476184	0.356747	1.036200
36	6	0	9.672525	1.346709	2.176333
37	6	0	10.703690	0.250946	0.150105
38	5	0	1.216077	-0.284476	3.248488
39	5	0	2.826448	0.002145	1.351503
40	1	0	-2.132073	-0.019490	2.581799
41	1	0	-4.664689	0.025546	2.583031
42	1	0	-5.836298	0.037342	0.357453
43	1	0	-4.488116	0.087522	-1.725010

44	1	0	-3.071836	0.160701	-3.446481
45	1	0	-1.327615	0.336638	-5.168278
46	1	0	1.714794	0.286491	-2.121685
47	1	0	1.616563	1.585303	-4.932664
48	1	0	1.038349	0.154712	-5.804039
49	1	0	2.294987	-0.005412	-4.560611
50	1	0	3.315793	-0.551679	5.044190
51	1	0	3.293014	-0.788191	7.484131
52	1	0	-1.001370	-0.679237	7.445396
53	1	0	-0.959111	-0.428217	4.971991
54	1	0	2.935410	-0.387459	9.485372
55	1	0	2.527732	-0.833061	11.912741
56	1	0	0.855446	-1.297311	11.530964
57	1	0	1.396563	0.370718	11.254815
58	1	0	2.814993	-2.789657	8.682146
59	1	0	1.774488	-3.169062	10.066310
60	1	0	3.461766	-2.676833	10.331549
61	1	0	4.080997	1.172199	-0.844524
62	1	0	6.509780	1.508498	-1.278084
63	1	0	7.419091	-0.441508	2.441883
64	1	0	5.024165	-0.723212	2.874100
65	1	0	9.240321	-0.638877	1.437527
66	1	0	10.486994	1.022098	2.833182
67	1	0	8.764235	1.444085	2.779449
68	1	0	9.926172	2.332842	1.771732
69	1	0	10.937367	1.225478	-0.291935
70	1	0	10.530050	-0.461802	-0.661329
71	1	0	11.568951	-0.083610	0.731680
72	79	0	1.475315	3.234900	4.091818
73	8	0	1.425034	3.434339	2.050222
74	8	0	-0.986231	3.494596	1.954215
75	8	0	-0.491216	3.189721	4.321368
76	8	0	0.509657	4.095538	-4.361075
77	8	0	-6.922954	2.488192	4.436465
78	7	0	3.514831	3.246640	4.078364
79	6	0	4.221087	3.265804	2.944569
80	6	0	5.606584	3.255717	2.968386
81	6	0	6.244503	3.233337	4.205871
82	6	0	5.494982	3.205723	5.374585
83	6	0	4.101865	3.201601	5.303058
84	6	0	3.161847	3.133361	6.415639
85	6	0	3.520187	3.072815	7.765246
86	6	0	2.534489	2.972733	8.738201
87	6	0	1.177744	2.924893	8.394698
88	6	0	0.822478	3.004342	7.041507
89	6	0	1.796800	3.104688	6.066242
90	6	0	0.120901	2.745227	9.445574
91	6	0	0.307884	3.734557	-0.193356
92	6	0	-0.866915	3.842470	-0.944655
93	6	0	-0.858303	3.977554	-2.331834
94	6	0	0.362654	4.004866	-3.010756
95	6	0	1.555011	3.912115	-2.282197

96	6	0	1.518752	3.777098	-0.903941
97	6	0	-0.631293	4.323557	-5.185464
98	6	0	-0.207922	3.944745	-6.592735
99	6	0	-1.080590	5.774859	-5.093321
100	6	0	-2.869105	3.069443	3.566237
101	6	0	-3.320768	2.440261	4.738386
102	6	0	-4.670400	2.244978	4.989442
103	6	0	-5.630347	2.702734	4.076681
104	6	0	-5.209925	3.338863	2.904260
105	6	0	-3.846206	3.503330	2.664827
106	6	0	-7.982807	2.908693	3.582165
107	6	0	-8.179148	1.918730	2.442032
108	6	0	-9.210312	3.014494	4.468260
109	5	0	0.277300	3.549915	1.369877
110	5	0	-1.333070	3.263294	3.266862
111	1	0	3.625450	3.284929	2.036565
112	1	0	6.158067	3.239894	2.035333
113	1	0	7.329675	3.228098	4.260912
114	1	0	5.981493	3.177918	6.343375
115	1	0	4.565213	3.104738	8.064846
116	1	0	2.820992	2.928801	9.786643
117	1	0	-0.221417	2.978949	6.740050
118	1	0	-0.123186	1.680136	9.551029
119	1	0	0.455029	3.110727	10.422403
120	1	0	-0.801610	3.270851	9.178975
121	1	0	-1.822416	3.817118	-0.425825
122	1	0	-1.799637	4.053630	-2.865767
123	1	0	2.494747	3.944676	-2.827031
124	1	0	2.452488	3.693656	-0.353626
125	1	0	-1.442033	3.652898	-4.867008
126	1	0	-1.034355	4.098500	-7.294376
127	1	0	0.637931	4.562750	-6.912600
128	1	0	0.096814	2.894721	-6.636450
129	1	0	-1.321615	6.055096	-4.063781
130	1	0	-0.281110	6.434501	-5.447945
131	1	0	-1.968388	5.942272	-5.713185
132	1	0	-2.587620	2.093240	5.462889
133	1	0	-5.016403	1.756942	5.896449
134	1	0	-5.925714	3.706947	2.176482
135	1	0	-3.530787	3.988652	1.744264
136	1	0	-7.746944	3.904317	3.180838
137	1	0	-8.993617	2.243341	1.785183
138	1	0	-7.270858	1.821354	1.838916
139	1	0	-8.432794	0.932598	2.846633
140	1	0	-9.443990	2.039961	4.910299
141	1	0	-9.036673	3.727242	5.279693
142	1	0	-10.075573	3.349049	3.886684

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