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Luminescent Pt(II) Complexes Bearing Dual Isoquinolinyl Pyrazolates: Fundamentals and Applications

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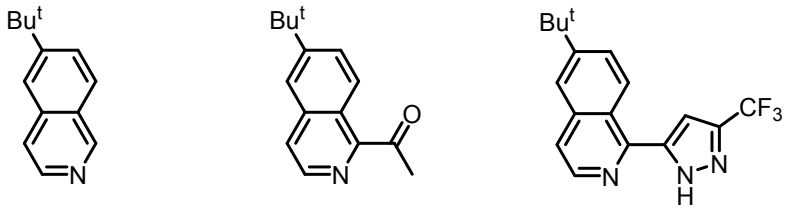
Experimental section

General Procedures. All reactions were performed under nitrogen. Solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification. The required azolate ancillaries were synthesized according to the methods documented in literature. All reactions were monitored by TLC with pre-coated silica gel plates (Merck, 0.20 mm with fluorescent indicator UV254). Compounds were visualized with UV irradiation at 254 or 365 nm. Flash column chromatography was carried out using silica gel obtained from Merck (230 - 400 mesh). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker-400 or INOVA-500 instrument; chemical shifts are quoted with respect to the internal standard tetramethylsilane. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

1. Synthesis of L1



L1-1 L1-2 L1

Synthesis of 6-*tert*-butylisoquinoline (L1-1)

To a 250 mL flask was equipped with a Dean-Stark apparatus and added 4-*tert*-butylbenzaldehyde (10.0 g, 61.7 mmol) and aminoacetaldehyde-dimethylacetal (6.48 g, 61.7 mmol) in 100 mL of toluene. The resulting solution was refluxed for 48 h and the solvent was evaporated. The oily residue was dissolved in $CHCl_3$ (100 mL) and cooled to -10 °C. To this cooled solution was added ethyl chloroformate (5.9 mL, 61.7 mmol) and the resultant solution was stirred for 12 h at room temperature. After that, the resultant solution was cooled to -10°C again. To this mixture was added trimethyl

phosphite (13 mL, 74.1 mmol) and the resultant mixture was allowed to stir at room temperature for 12 h. Then, the resultant mixture was heated to reflux for 24 h and the solvent was evaporated. The resultant oily residue was dissolved in chlorobenzene (100 mL) and $TiCl_4$ (27 mL, 247 mmol) was added and refluxed at 100°C for 48 h. The solvent and $TiCl_4$ were distilled under reduced pressure to leave a residue of crude compound. It was then treated with ice-cold water, basified and extracted with ethyl acetate. The ethyl acetate layer was washed with brine, dried over Na_2SO_4 and concentrated to leave a residue. This was recrystallized from hexane gave a colorless crystal (6.19 g, 54%).

Spectral data of **L1-1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.18 (s, 1 H), 8.46 (d, *J* = 6.0 Hz, 1 H), 7.91 (d, *J* = 8.8 Hz, 1 H), 7.75 ~ 7.65 (m, 2 H), 7.63 (d, *J* = 5.6 Hz, 1 H), 1.40 (s, 9 H).

Synthesis of 2-acetyl-6-*tert*-butylisoquinoline (L1-2)

A solution of iron(II) sulfate heptahydrate (60 mg, 0.22 mmol), para-acetaldehyde (7.2 mL, 53.97 mmol), *tert*-butyl hydroperoxide (3.69 mL of 70 wt % solution in water, 27 mmol), 6-*tert*-butylisoquinoline (2 g, 10.8 mmol) and trifluoroacetic acid (0.83 mL, 10.8 mmol) in MeCN (40 mL) was heated to reflux for 12 h. The solvent was removed by evaporation under vacuum. The residue was dissolved in ethyl acetate and neutralized with Na_2CO_3 solution. The organic phase was washed with brine and dried over Na_2SO_4, the solvent was removed under vacuum to give a crude product. Purification by SiO_2 column chromatography eluting with ethyl acetate and hexane (1:8) afforded a brown solid (1.27 g, 52%).

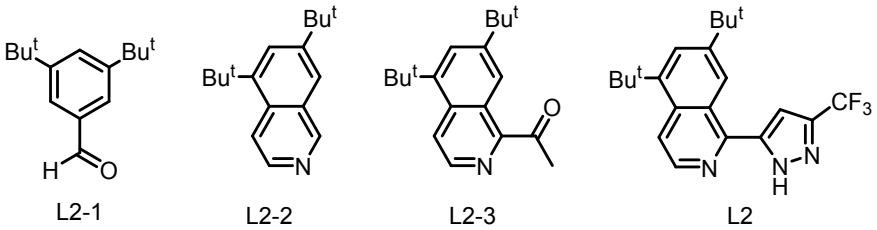
Spectral data of **L1-2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.86 (d, *J* = 8.8 Hz, 1 H), 8.52 (d, *J* = 6.0 Hz, 1 H), 7.80 ~ 7.69 (m, 3 H), 2.85 (s, 3 H), 1.40 (s, 9 H).

Synthesis of 5-(6-*tert*-butyl-2-quinolinyl)-3-trifluoromethyl pyrazole (L1)

2-Acetyl-6-*tert*-butylisoquinoline (1.5 g, 6.61 mmol) was slowly added to a stirred suspension of NaOEt (96.6 mg, 11.9 mmol) in dry THF (50 mL) at 0 °C. The resultant solution was stirred for 1 h at RT. Ethyl trifluoroacetate (2.9 mL, 24.4 mmol) was added dropwise at 0 °C and the mixture was refluxed for 12 h. After then, the content was quenched with 2N HCl until pH 5-6 and extracted three times with ethyl acetate. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated under vacuum to yield the crude 1,3-dione. To the crude 1,3-dione was added hydrazine monohydrate (3.2 mL,66.1 mmol) in 60 mL of EtOH and refluxed for 1 day. The solvent was removed by evaporation under vacuum. The residue was dissolved in ethyl acetate and neutralized with Na_2CO_3 solution. The organic phase was washed with brine and dried over Na_2SO_4, the solvent was removed under vacuum to give a crude product. It was then purified by SiO_2 column chromatography and eluting with a mixture of ethyl acetate and hexane (1:2). Recrystallization from a mixed solution of CH_2Cl_2 and hexane gave a white solid (660 mg, 65%).

Spectral data of **L1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 12.82 (br, NH), 8.48 (d, *J* = 5.6 Hz, 1 H), 8.43 (d, *J* = 9.6 Hz, 1 H), 7.82 ~ 7.75 (m, 2 H), 7.66 (d, *J* = 5.6 Hz, 1 H), 7.19 (s, 1 H), 1.42 (s, 9 H). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): *δ* -62.09 (s).

2. Synthesis of L2



L2-1 L2-2 L2-3 L2

Synthesis of 3,5-di-*tert*-butylbenzaldehyde (L2-1)

To a 500 mL round bottom flask was sequentially added 3,5-di-*tert*-butyltoluene (9.3 mL, 39.1 mmol) and solution of cerium ammonium nitrate (93.8 g, 171 mmol) in 140 mL of 50% aqueous HOAc. The resulting solution was heated to 100°C for 1 h under nitrogen. The solvent was removed under vacuum. The residue was dissolved

in ethyl acetate and neutralized with Na_2CO_3 solution. The organic phase was washed with brine and dried over Na_2SO_4, the solvent was removed under vacuum to give a crude product. Purification by SiO_2 column chromatography eluting with ethyl acetate and hexane (1:40) afforded a yellowish solid (2.75 g, 78%).

Spectral data of **L2-1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.99 (s, 1 H), 7.72 ~ 7.68 (m, 3 H), 1.35 (s, 9 H).

Synthesis of 3,5-di-*tert*-butylisoquinoline (L2-2)

Following the procedure described for L1-1, the product was purified using SiO_2 column chromatography with ethyl acetate and hexane (1:3) as the eluent to obtain the yellow oil (22 %).

Spectral data of **L2-2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.19 (s, 1 H), 8.43 (d, *J* = 6.0 Hz, 1 H), 8.09 (d, *J* = 6.4 Hz, 1 H), 7.77 (s, 1 H), 7.71 (s, 1 H), 1.60 (s, 9 H), 1.41 (s, 9 H).

Synthesis of 1-(5,7-di-*tert*-butylisoquinolin-1-yl)ethanone (L2-3)

Following the procedure described for L1-2, the product was purified using SiO_2 column chromatography with ethyl acetate and hexane (1:3) afforded a yellow oil (62 %).

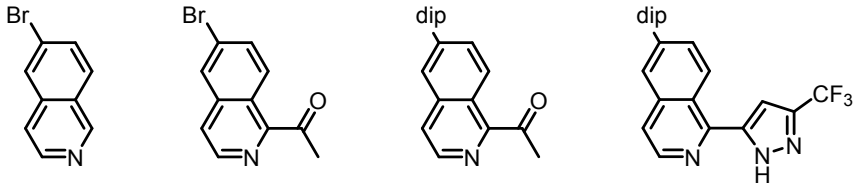
Spectral data of **L2-3**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.64 (s, 1 H), 8.49 (d, *J* = 6.0 Hz, 1 H), 8.29 (d, *J* = 6.0 Hz, 1 H), 7.81 (s, 1 H), 2.83 (s, 3 H), 1.60 (s, 9 H), 1.40 (s, 9 H).

Synthesis of 5-(3,5-di-*tert*-butyl-2-quinolinyl)-3-trifluoromethyl pyrazole (L2)

Following the procedure described for L1, the product was purified using SiO_2 column chromatography with ethyl acetate and hexane (1:4) as eluent. Recrystallization from a mixed solution of CH_2Cl_2 and hexane gave a white solid (44 %).

Spectral data of **L2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 11.78 (br, NH), 8.48 (d, *J* = 6.2 Hz, 1 H), 8.30 (s, 1 H), 8.20 (d, *J* = 6.2 Hz, 1 H), 7.86 (s, 1 H), 7.09 (s, 1 H), 1.63 (s, 9 H), 1.43 (s, 9 H). ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): *δ* -62.20 (s).

1. Synthesis of L3



L3-1 L3-2 L3-3 L3

Synthesis of (2,6-diisopropylphenyl)boronic acid

To a 100 mL flask was added 2-bromo-1,3-diisopropylbenzene (5 g, 20.7 mmol) under nitrogen. Dry THF (50 mL) was added and the solution was cooled to -78 °C. After the addition of *n*-BuLi (2.80 mL, 2.5 M in *n*-hexane), the solution was stirred at -78 °C for 1 h whereupon trimethyl borate (2.80 mL, 24.8 mmol) dissolved in 10 mL of dry THF was added. The solution was allowed to warm to RT overnight. After that the reaction was quenched with 2N HCl (10 mL). The solvent was removed under vacuum. The residue was dissolved in ethyl acetate and neutralized with saturated Na_2CO_3 solution. The organic phase was washed with brine and dried over Na_2SO_4, and the solvent was removed under vacuum. The residue was dissolved in excess of ethyl acetate. The resulted biphasic solution was extracted with ethyl acetate (2 × 50 mL), and the filtrate washed with brine, dried over Na_2SO_4, and then concentrated. Recrystallization from hexane gave a white solid (5.76 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.29 (t, *J* = 7.8 Hz, 1 H), 7.12 (d, *J* = 7.8 Hz, 2 H), 4.69 (s, 2 H), 2.87 (hept, *J* = 6.8 Hz, 2 H), 1.25 (d, *J* = 6.8 Hz, 12 H).

Synthesis of 6-bromoisoquinoline (L3-1)

Following the procedure described for L1-1, the product was purified using SiO_2 column chromatography with ethyl acetate: Hexane (1:3) as eluents to afford the title

compound. Recrystallization from hexane and CH_2Cl_2 gave a white solid (28 %).

Spectral data of **L3-1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 9.21 (s, 1H), 8.53 (d, *J* = 6.0 Hz, 1H), 7.99 (s, 1H), 7.84 (d, *J* = 8.8 Hz 2H), 7.68 (dd, *J* = 8.4 Hz, 1.2 Hz 1H), 7.55 (d, *J* = 6.0 Hz 1H).

Synthesis of 1-(6-bromoisoquinolin-1-yl)ethanone (L3-2)

Following the procedure described for L1-2, the product was purified using SiO_2 column chromatography with ethyl acetate and hexane (1:6) afforded a yellow oil (71%).

Spectral data of **L3-2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.87 (d, *J* = 9.2 Hz, 1H), 8.59 (d, *J* = 8.6 Hz, 1H), 8.02 (s, 1H), 7.74 ~ 7.70 (m, 2H), 2.84 (s, 3H).

Synthesis of 1-(6-(2,6-diisopropylphenyl)isoquinolin-1-yl)ethanone (L3-3)

To the 100 mL round bottom flask was sequentially added 1,4-dioxane and water (v/v, 3:1, 60 mL), (2,6-diisopropylphenyl)boronic acid (1.06 g, 5.21 mmol), $Ba(OH)_2{\cdot}8H_2O$ (6.31 g, 19.96 mmol), 1-(6-bromoisoquinolin-1-yl)ethanone (1.00 g, 3.99 mmol) and $Pd(PPh_3)_4$ (231 mg, 0.22 mmol). The solvent was removed under vacuum. The residue was dissolved in ethyl acetate and neutralized with Na_2CO_3 solution. The organic phase was washed with brine and dried over Na_2SO_4, and the solvent was removed under vacuum. Then, the residue was purified using SiO_2 column chromatography eluting with ethyl acetate and hexane (1:6). Recrystallization from CH_2Cl_2 and hexane gave a white solid (1.05 g, 79%).

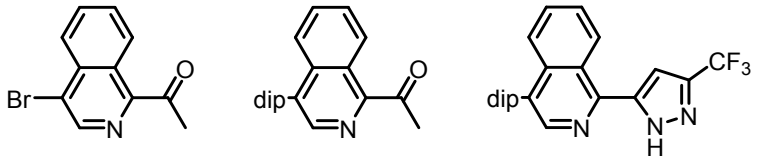
Spectral data of **L3-3**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.99 (d, *J* = 8.8 Hz, 1 H), δ 8.62 (d, *J* = 5.6 Hz, 1 H), 7.82 (d, *J* = 5.2 Hz, 1 H), 7.68 (s, 1 H), 7.54(dd, *J* = 5.2 Hz, *J* = 1.6 Hz, 1 H), 7.26 (s, 2 H), 2.90 (s, 3 H), 2.52 (hept, *J* = 6.9 Hz, 2 H), 1.07 (d, *J* = 6.8 Hz, 12 H).

Synthesis of 6-(2,6-diisopropylphenyl)-1-(3-(trifluoromethyl)-1H-pyrazol-5-yl) isoquinoline (L3)

Following the procedure described for L1, the product was purified using SiO_2 column chromatography with ethyl acetate and hexane (1:5). Recrystallization from a mixed solution of CH_2Cl_2 and hexane gave a white solid (52%).

Spectral data of **L3**: ^{1}H NMR (400 MHz, d_6-acetone, 298 K): δ 13.53 (br, 1 H, NH), 8.69 (d, *J* = 8.8 Hz, 1 H), 8.68 (d, *J* = 5.2 Hz, 1 H), 7.94 (d, *J* = 4.4 Hz, 1 H), 7.92 (s, 1 H), 7.64 (d, *J* = 8.8 Hz, 1 H), 7.52 (s, 1 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 2.57 (hept, *J* = 6.9 Hz, 2 H), 1.09 (d, *J* = 6.8 Hz, 12 H). ^{19}F NMR (376 MHz, d_6-acetone, 298 K): δ -62.32 (s).

4. Synthesis of L4



L4-1 L4-2 L4

Synthesis of 1-(4-bromoisoquinolin-1-yl)ethanone (L4-1)

Following the procedure described for L1-2, the product was purified using SiO_2 column chromatography with ethyl acetate and hexane (1:5) afforded a white powder (73%).

Spectral data of **L4-1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 8.99 (d, *J* = 8.4 Hz, 1H), 8.78 (s, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 2.84 (s, 3H)

Synthesis of 1-(4-(2,6-diisopropylphenyl)isoquinolin-1-yl)ethanone (L4-2)

Following the procedure described for L3-5, the product was purified using SiO_2 column chromatography with ethyl acetate and hexane (1:8) afforded a brown powder (63%)

Spectral data of **L4-2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 9.03 (d, *J* = 8.4 Hz, 1 H), δ 8.39 (s, 1 H), 7.65 (t, *J* = 5.0 Hz, 1 H), 7.57 (t, *J* = 7.6 Hz , 1 H), 7.47(t, *J* = 7.8 Hz, 1 H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 2.91 (s, 3 H), 2.23 (hept, *J* = 6.8 Hz, 2 H), 1.04 (d, *J* = 6.8 Hz, 6 H), 0.92 (d, *J* = 6.8 Hz, 6 H).

Synthesis of 4-(2,6-diisopropylphenyl)-1-(3-(trifluoromethyl)-1H-pyrazol-5-yl) isoquinoline (L4)

Following the procedure described for L1, the product was purified using SiO_2 column chromatography with ethyl acetate and hexane (1:4). Recrystallization from a mixed solution of CH_2Cl_2 and hexane gave a white solid (52%).

Spectral data of **L4**: ^{1}H NMR (400 MHz, d_6-acetone, 298 K): δ 11.81 (br, 1 H, NH), 8.56 (d, *J* = 8.4 Hz, 1 H), 8.38 (s, 1 H), 7.71 (t, *J* = 7.7 Hz, 1 H), 7.64 (t, *J* = 8.2 Hz, 1 H), 7.49-7.46 (m, 2 H), 7.32 (s, 1 H), 7.30 (s, 1 H), 7.27 (s, 1 H), 2.29 (hept, *J* = 6.8 Hz, 2 H), 1.05 (d, *J* = 6.8 Hz, 6 H), 0.96 (d, *J* = 6.9 Hz, 6 H). ^{19}F NMR (376 MHz, d_6-acetone, 298 K): δ -62.05 (s).

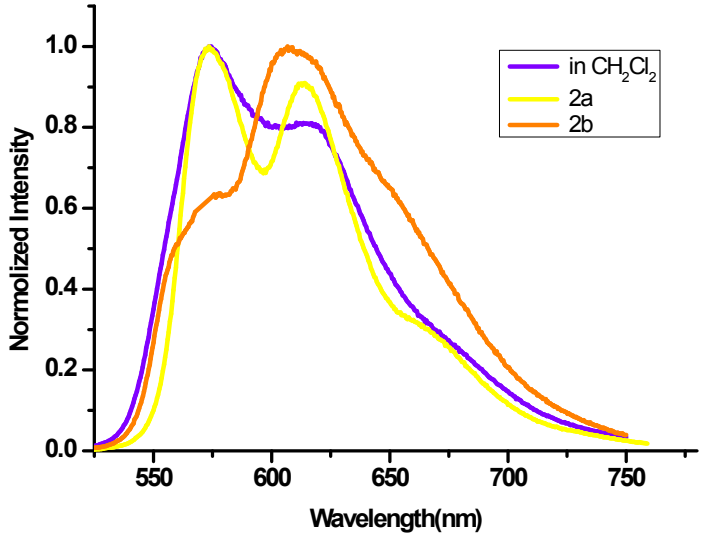


Figure S1. Emission spectral of **2** were recorded in neat powder (**2a**), after grinding with mortar and pestle (**2b**) and in CH_2Cl_2 at conc. of 10^{-5} M.

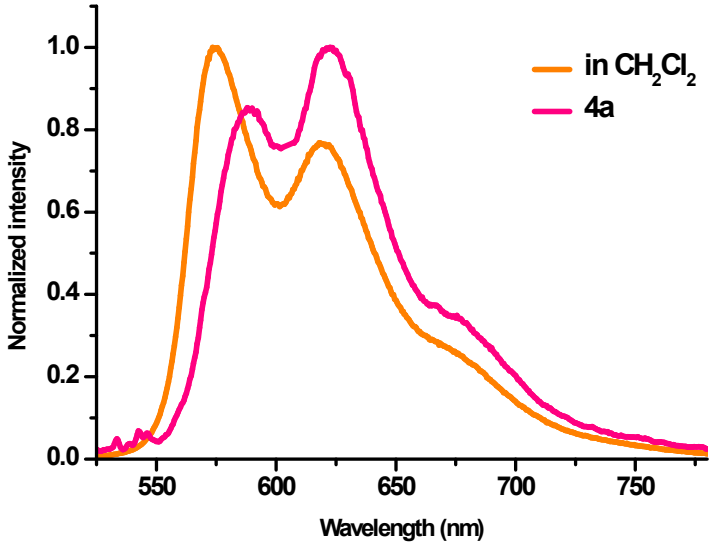


Figure S2. Emission spectral of **4** were recorded in neat powder (**4a**) and in CH_2Cl_2 at conc. of 10^{-5} M.

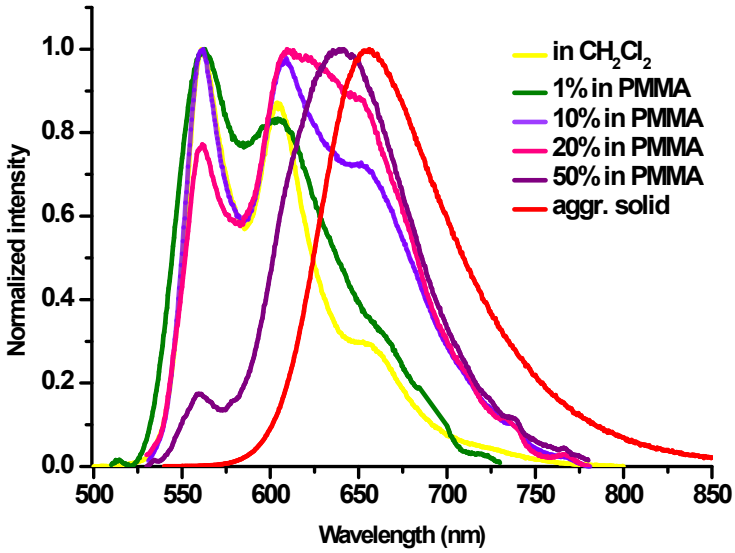


Figure S3. Emission spectral of Pt(II) complex **1** in CH_2Cl_2 solution, in PMMA matrix, and in strongly aggregated solid state.

HYK-132
10.54
10.53
8.48
8.46
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7.78
7.58
7.56
7.22
10.54
10.53
8.48
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