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Supporting Information

Mechanoluminescence and Efficient White-Emitting OLEDs for Pt(II) Phosphors Bearing Spatially Encumbered Pyridinyl Pyrazolate Chelates

Li-Min Huang,[a] Guan-Min Tu,[a] Yun Chi,*[,a] Wen-Yi Hung,*[,b] Yo-Cheng Song,[b] Mei-Rurng Tseng,[c] Pi-Tai Chou,*[,d] Gene-Hsiang Lee,[d] Ken-Tsung Wong,[d] Shuo-Hsien Cheng,[d] and Wan-Shan Tsai[d]

[a] Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan; E-mail: ychi@mx.nthu.edu.tw

[b] Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung 20224, Taiwan; E-mail: wenhung@mail.ntou.edu.tw

[c] Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu 31040, Taiwan

[d] Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan; E-mail: chop@ntu.edu.tw

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. 2,6-Diisopropylphenyl)boronic acid was prepared from treatment of trimethyl borate with 2-bromo-1,3-diisopropylbenzene, the later was prepared from 2,6-diisopropylaniline using Sandmeyer Reaction. 4-*t*-butyl-2-acetylpyridine was obtained from direct acetylation of 4-*t*-butylpyridine in presence of $FeSO_4 \cdot 7H_2O$, *para*-acetaldehyde, *t*-BuO_2H and CF_3CO_2H.[1] 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. ^1H and ^{19}F NMR spectra were recorded on a Bruker-400 or INOVA-500 instrument. Elemental analysis was carried out with a Heraeus CHN-O Rapid Elementary Analyzer.

Synthesis of L1

Synthesis of 4-(2,6-diisopropylphenyl)pyridine (L1-1)

To a 250 mL round bottom flask was sequentially added a mixture of 1,4-dioxane and water (v/v, 3:1, 160 mL), 4-bromopyridine hydrochloride (3.08 g, 15.8 mmol), $Ba(OH)_2 \cdot 8H_2O$ (20.8 g, 65.9 mmol), (2,6-diisopropylphenyl)boronic acid (2.7 g, 13.2 mmol), and $Pd(PPh_3)_4$ (762 mg, 0.66 mmol). The mixture was refluxed for 1 day under nitrogen and then cooled to RT. The dioxane was evaporated and the residue was dissolved in excess of ethyl acetate. The resulting mixture was filtered, and the filtrate washed with brine, dried over Na_2SO_4, and then concentrated. The solid was first purified using SiO_2 column chromatography eluting with a mixture of

ethyl acetate and hexane (1:7). Recrystallization from CH_2Cl_2 and hexane gave a colorless solid (2.7 g, 85.5%).

Spectral data of **L1-1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.64 (d, *J* = 4.5 Hz, 2 H), 7.36 (t, *J* = 7.8 Hz, 1 H), 7.20 (d, *J* = 7.8 Hz, 2 H), 7.12(d, *J* = 4.5 Hz, 2 H), 2.48 (hept, *J* = 6.9 Hz, 2 H), 1.06 (d, *J* = 6.9 Hz, 12 H).

Synthesis of 4-(2,6-diisopropylphenyl)pyridine N-oxide (L1-2)

A mixture of 4-(2,6-diisopropylphenyl)pyridine (1 g, 4.18 mmol), 30% hydrogen peroxide (10 mL) and glacial acetic acid (10 mL) was refluxed for 24 h. After then, the volatiles were removed under vacuum, and the residue was quenched with 2 M $NaOH_{(aq)}$ solution until pH 8 and extracted three times with CH_2Cl_2. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and filtered. The solution was concentrated under vacuum to yield a pale-yellow solid of 4-(2,6-diisopropylphenyl)pyridine N-oxide (980 mg, 91.9%).

Synthesis of 4-(2,6-diisopropylphenyl)picolinonitrile (L1-3)

A mixture of 4-(2,6-diisopropylphenyl)pyridine N-oxide (500 mg, 1.96 mmol), trimethylsilyl cyanide (0.28 mL, 2.06 mmol) and dimethylcarbamyl chloride (0.18 mL, 1.96 mmol) in 40 mL of CH_2Cl_2 was refluxed for 12 h. After cooled to RT, the content was quenched with saturated Na_2CO_3 solution and the resulting mixture was extracted three times with CH_2Cl_2. The combined organic extract was then washed with brine, dried over Na_2SO_4, and concentrated. The oily product was next purified using SiO_2 column chromatography and eluting with ethyl acetate and hexane (1:5). Recrystallization from a mixed solution of CH_2Cl_2 and hexane gave a colorless solid (407 mg, 78.6%).

Spectral data of **L1-3**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.75 (d, *J* = 5 Hz, 1 H), 7.53 (s, 1 H), 7.39 (t, *J* = 7.8 Hz, 1 H), 7.35 (d, *J* = 5 Hz, 1 H), 7.22 (d, *J* = 7.8 Hz, 2 H), 2.34 (hept, *J* = 6.8 Hz, 2 H), 1.08 (d, *J* = 6.8 Hz, 6 H), 1.06 (d, *J* = 6.8 Hz, 6 H).

Synthesis of 1-(4-(2,6-diisopropylphenyl)pyridin-2-yl)ethanone (L1-4)

To a stirred solution of 4-(2,6-diisopropylphenyl)picolinonitrile (200 mg, 0.84 mmol) in dry THF (30 mL) was added methylmagnesium bromide (0.42 mL, 3.0 M in diethyl ether) slowly at -78 ^{o}C. The mixture was stirred at this temperature for 2 h and then at RT for another 12 h, before quenched with 2 N HCl solution. The mixture was extracted with ethyl acetate, and the organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum to obtain a pale yellow solid (138 mg, 64.8%).

Spectral data of **L1-4**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.72 (d, *J* = 4.8 Hz, 1 H), 7.89 (s, 1 H), 7.37 (t, *J* = 7.8 Hz, 1 H), 7.30 (d, *J* = 4.8 Hz, 1 H), 7.21 (d, *J* = 7.8 Hz, 2 H), 2.77 (s, 3 H), 2.34 (hept, *J* = 2.6 Hz, 2 H), 1.06 (d, *J* = 2.6 Hz, 6 H), 1.04 (d, *J* = 2.6 Hz, 6 H).

Synthesis of 4-(2,6-diisopropylphenyl)-2-(3-trifluoromethyl-1H-pyrazol-5-yl) pyridine (L1)

To a stirred suspension of sodium hydride (94 mg, 3.91 mmol) in dry THF (30 mL) was slowly added 1-(4-(2,6-diisopropylphenyl)pyridin-2-yl)ethanone (500 mg, 1.96 mmol) and ethyl trifluoroacetate (0.46 mL, 3.91 mmol) at 0^{o}C. The mixture was refluxed for 12 h. After then, the content was quenched with 2 N 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 (1 mL, 20 mmol) in 30 mL of EtOH and refluxed for 1 day. After then, the solution was concentrated and the residue was redissolved in ethyl acetate. The solution was washed with brine, dried over Na_2SO_4, and concentrated. Finally, the crude product was purified by SiO_2 column chromatography and eluting with a mixture of ethyl acetate and hexane (1:5).

Recrystallization from a mixed solution of CH_2Cl_2 and hexane gave a colorless solid (293 mg, 40.1%).

Spectral data of **L1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 12.10 (br, 1 H), 8.70 (d, *J* = 5 Hz, 1 H), 7.50 (s, 1 H), 7.41 (t, *J* = 7.8 Hz, 1 H), 7.25 (d, *J* = 7.8 Hz, 2 H), 7.18 (d, *J* = 5 Hz, 1H), 6.91 (s, 1 H), 2.51 (hept, *J* = 5.8 Hz, 2 H), 1.11 (d, *J* = 5.8 Hz, 6 H), 1.09 (d, *J* = 5.8 Hz, 6 H). ^{19}F NMR (400 MHz, $CDCl_3$, 298 K): δ -62.39.

Synthesis of L2

Synthesis of 3-(2,6-diisopropylphenyl)pyridine (L2-1)

Following the procedure described for **L1-1**, the product was purified using SiO_2 column chromatography with ethyl acetate and hexane (1:3) as eluent. Recrystallization from a mixed solution of CH_2Cl_2 and hexane gave a colorless solid (650 mg, 85.5%).

Spectral data of **L2-1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.60 (d, *J* = 4.8 Hz, 1 H), 8.44 (s, 1 H), 7.50 (d, *J* = 5.9 Hz, 1 H), 7.33 ~ 7.39 (m, 2 H), 7.22 (d, *J* = 7.8 Hz, 2 H), 2.51 (hept, *J* = 6.9 Hz, 2 H), 1.07 (d, *J* = 6.9 Hz, 6 H), 1.05 (d, *J* = 6.9 Hz, 6 H).

Synthesis of 1-(5-(2,6-diisopropylphenyl)pyridin-2-yl)ethanone (L2-2)

A solution of iron(II) sulfate heptahydrate (19 mg, 0.07 mmol), para-acetaldehyde (2.3 mL, 17.4 mmol), *tert*-butyl hydroperoxide (1.2 mL of 70 wt % solution in water, 8.46 mmol), 3-(2,6-diisopropylphenyl)pyridine (810 mg, 3.38 mmol), and trifluoroacetic acid (0.26 mL, 3.38 mmol) in MeCN (20 mL) was heated at reflux for 3 h. The reaction mixture was cooled to room temperature, concentrated by rota-evaporation, dissolved in ethyl acetate and neutralized with saturated aqueous 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 yellow oil. Purification by SiO_2

column chromatography eluting with ethyl acetate and hexane (1:5) afforded a yellow oil (598 mg, 62.8%).

Spectral data of **L2-2**: ^{1}H NMR (400 MHz, d_6-acetone, 298 K): δ 8.54 (d, *J* = 4 Hz, 1 H), 8.10 (d, *J* = 7.9 Hz, 1 H), 7.84 (d, *J* = 7.9 Hz, 1 H), 7.42 (t, *J* = 8.1 Hz, 1 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 2.70 (s, 3 H), 2.48 (hept, *J* = 6.8 Hz, 2 H), 1.10 (d, *J* = 6.8 Hz, 6 H), 1.07 (d, *J* = 6.8 Hz, 6 H).

Synthesis of 5-(2,6-diisopropylphenyl)-2-(3-trifluoromethyl-1H-pyrazol-5-yl) pyridine (L2)

Following the procedure described for **L1**, the product was purified by SiO_2 column chromatography and using ethyl acetate and hexane (1:3) as the eluent. Recrystallization from a mixed solution of CH_2Cl_2 and hexane gave a colorless solid (516 mg, 48.3%).

Spectral data of **L2**: ^{1}H NMR (400 MHz, d_6-acetone, 298 K): δ 13.44 (br, 1 H), 8.47 (s, 1 H), 8.05 (d, *J* = 8 Hz, 1 H), 7.79 (d, *J* = 8 Hz, 1 H), 7.40 (t, *J* = 7.8 Hz, 1 H), 7.33 (s, 1 H), 7.28 (d, *J* = 7.8 Hz, 2 H), 2.57 (hept, *J* = 6.8 Hz, 2 H), 1.09 (d, *J* = 6.8 Hz, 6 H), 1.08 (d, *J* = 6.8 Hz, 6 H). ^{19}F NMR (400 MHz, d_6-acetone, 298 K): δ -62.57.

Synthesis of L3

Synthesis of 1-(4-(*tert*-butyl)pyridin-2-yl)ethanone (L3-1)

Following the procedure described for **L2-2**, the product was chromatographed on SiO_2 using ethyl acetate and hexane (1:1) as the eluent to obtain a yellow oil (3.28 g, 50.1%).

Spectral data of **L3-1**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.62 (d, *J* = 5.2 Hz, 1 H), 8.09 (s, 1 H), 7.53 (d, *J* = 5.2 Hz, 1 H), 2.77 (s, 3 H), 1.34 (s, 9 H).

Synthesis of 4-(*tert*-butyl)-2-(3-trifluoromethyl-1H-pyrazol-5-yl)pyridine (bpfpzH) (L3)

Following the procedure described for **L1**, the product was purified by SiO_2 column chromatography and using ethyl acetate and hexane (1:3) as the eluent. Recrystallization from a mixed solution of CH_2Cl_2 and hexane gave a colorless solid (1.15 g, 58.6%).

Spectral data of **L3**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 12.76 (br, 1 H), 8.54 (d, *J* = 5.5 Hz, 1 H), 7.70 (s, 1 H), 7.40 (d, *J* = 5.5 Hz, 1 H), 7.05 (s, 1 H), 1.37 (s, 9 H). ^{19}F NMR (400 MHz, $CDCl_3$, 298 K): δ -62.27.

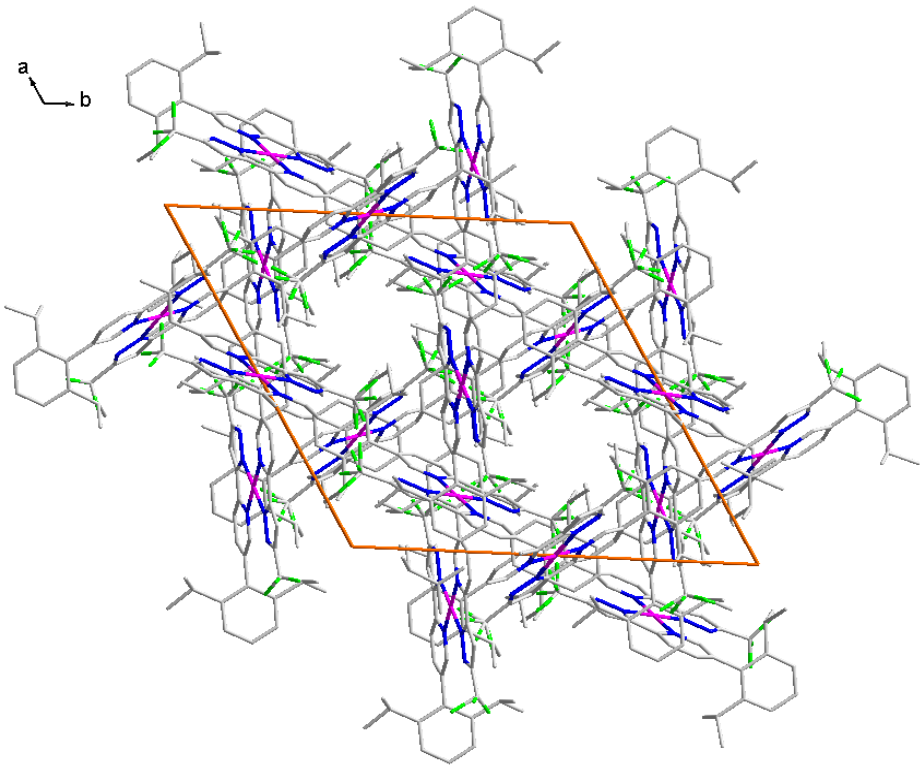

Figure S1. Molecular packing of Pt(II) complex **2** alone the c-axis of unit cell.

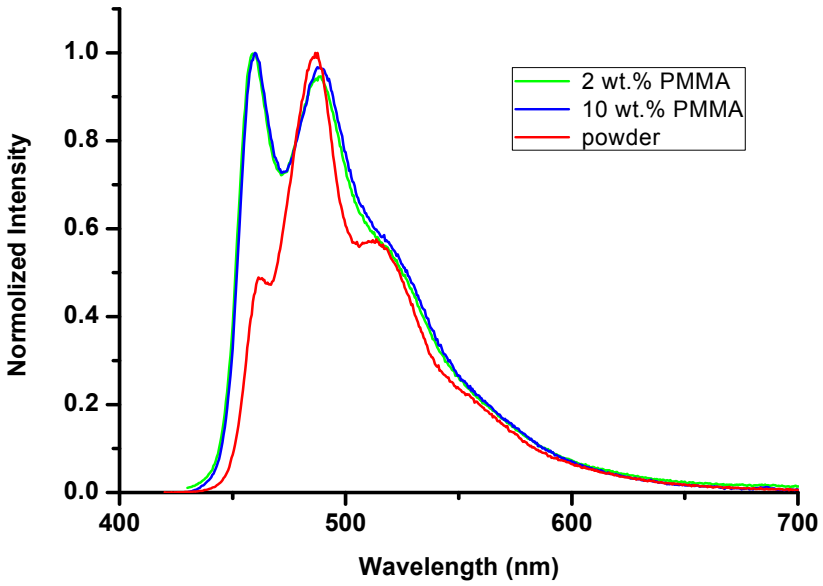

Figure S2. Photoluminescent spectra of the PMMA thin films with concentration of Pt(II) complex **2** at 2 wt.% and 10 wt.% and that of powdery sample as reference.