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Pt^{II}(C^N)(N-donor ligand)Cl-type complexes showing highly sensitive aggregation-induced phosphorescent emission (AIPE) behavior fulfilled by long-size ligands and distorted molecular configuration

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Synthesis

Procedures for the Synthesis of CN1-Br

Under the N\textsubscript{2} atmosphere, 2-bromo-9,9-diethyl-7-iodo-9H-fluorene (5.0 g, 11.7 mmol), diphenylamine (2.2 g, 12.9 mmol), CuI (0.25 g, 1.29 mmol) were heated in p-xylene (35 mL) at 100 °C for 20 min. Then, KOH (5.00 g, 88.90 mmol) was added and the reaction mixture was heated to 130 °C for 48 h. After cooling to room temperature, the reaction was poured into ice water (50 mL). The mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3×30 mL). The organic phase was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}. After removing solvent, the residue was purified on silica column with petroleum ether as eluent to obtain the product as white solid (3.8 g, 70%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \textit{\delta}): 7.52 (d, \textit{J} = 8.4 Hz, 1H), 7.47 (d, \textit{J} = 8.0 Hz, 1H), 7.44-7.41 (m, 3H), 7.26-7.24 (m, 4H), 7.12 (d, \textit{J} = 7.6 Hz, 4H), 7.08-7.02 (m, 3H), 1.96-1.84 (m, 4H), 0.34 (t, \textit{J} = 7.4 Hz, 6H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, \textit{\delta}): 152.03, 151.12, 147.99, 147.53, 140.48, 135.69, 130.30, 129.54, 129.36, 129.11, 126.14, 124.44, 124.08, 123.85, 123.77, 123.66, 122.95, 122.75, 122.48, 120.59, 120.45, 120.25, 119.14, 56.42, 32.66, 8.64.

Procedures for the Synthesis of CN2-Br

Following the same procedure for synthesis of CN1-Br with starting material of bis(4-methoxyphenyl)amine. The yield of this reaction is 69%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \textit{\delta}): 7.46 (d, \textit{J} = 8.0 Hz, 2H), 7.41 (d, \textit{J} = 9.6 Hz, 2H), 7.06 (d, \textit{J} = 8.8 Hz, 4H), 6.95 (s, 1H), 6.90-6.87 (m, 1H), 6.83 (d, \textit{J} = 8.8 Hz, 4H), 3.89 (s, 6H), 1.95-1.82 (m, 4H), 0.33 (t, \textit{J} = 7.4 Hz, 6H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, \textit{\delta}): 155.44, 151.74, 150.66, 148.47, 141.22, 140.46, 133.41, 129.72, 125.92, 125.82, 120.44, 120.00, 119.89, 119.48, 115.94, 114.46, 56.28, 32.61, 8.66.

Procedures for the Synthesis of CN1-1

Under the N\textsubscript{2} atmosphere, CN1-Br (2.1 g, 4.5 mmol), 2-(tributylstannyl)pyridine (1.81 g, 4.9 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (0.26 g, 0.23 mmol) were heated in toluene (25 mL) at 110 °C for 20 min. The reaction mixture was heated to 110 °C for 18 h. After cooling to room temperature, the solvent as removed under reduced pressure and the residue was purified on silica column with CH\textsubscript{2}Cl\textsubscript{2}:petroleum ether (1:1, v:v) as eluent to obtain the product as pale yellow solid (1.3 g, 64%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \textit{\delta}): 8.71 (d, \textit{J} = 4.6 Hz, 1H), 7.99-7.60 (m, 6H), 7.29-6.98 (m, 13H), 2.09-1.94 (m, 4H), 0.39 (t, \textit{J} = 7.4 Hz, 6H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, \textit{\delta}): 152.03, 151.12, 147.99, 147.53, 140.48, 135.69, 130.30.
130.30, 129.54, 129.36, 129.11, 126.14, 124.44, 124.08, 123.85, 123.77, 123.66, 122.95, 122.75, 122.48, 120.59, 120.45, 120.25, 119.14, 56.42, 32.66, 8.64.

**Procedures for the Synthesis of CN1-2**

Following the same procedure for synthesis of CN1-1 with starting material of CN2-Br. The yield of this reaction is 62%.\(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 8.71 (d, \(J = 4.6\) Hz, 1H), 7.96-7.91 (m, 2H), 7.81-7.76 (m, 2H), 7.67 (d, \(J = 8.0\) Hz, 1H), 7.52 (d, \(J = 8.0\) Hz, 1H), 7.23-7.19 (m, 1H), 7.08 (d, \(J = 8.8\) Hz, 4H), 6.98 (s, 1H), 6.93-6.82 (m, 5H), 3.82 (s, 6H), 2.09-1.89 (m, 4H), 0.38 (t, \(J = 7.4\) Hz, 6H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)): 157.77, 155.34, 151.66, 150.18, 149.47, 148.39, 142.59, 141.30, 136.88, 136.54, 134.21, 125.90, 125.74, 121.55, 120.99, 120.36, 120.31, 118.81, 116.22, 114.56, 56.77, 55.51, 32.75, 8.69.

**Procedures for the Synthesis of CN1-3**

Under the N\(_2\) atmosphere, CN1-Br (1.5 g, 2.9 mmol), 4-pyridylboronic acid (0.68 g, 3.5 mmol), Pd(PPh\(_3\))\(_4\) (0.2 g, 0.17 mmol) were heated in toluene (15 mL) and 2M K\(_2\)CO\(_3\) (15 mL) at 110 °C for 18 h. After cooling to room temperature, the reaction mixture was extracted with CH\(_2\)Cl\(_2\) (3×25 mL). The organic phase was dried over anhydrous Na\(_2\)SO\(_4\). After removing solvent, the residue was purified on silica column with CH\(_2\)Cl\(_2\):EA (5:1, v:v) as eluent to obtain the product as white solid (1.1 g, 69%). \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 8.75 (d, \(J = 4.4\) Hz, 2H), 7.99-7.60 (m, 5H), 7.29-6.98 (m, 13H), 2.11-1.96 (m, 4H), 0.38 (t, \(J = 7.4\) Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\), \(\delta\)): 150.14, 148.09, 147.83, 140.58, 136.19, 131.20, 129.66, 129.15, 127.34, 125.26, 124.33, 123.59, 123.36, 123.12, 122.82, 122.36, 121.79, 120.95, 120.31, 120.02, 119.52, 57.44, 32.61, 8.67.

**Procedures for the Synthesis of CN2-1**

Under the N\(_2\) atmosphere, CN1-Br (2.0 g, 4.3 mmol), bis(pinacolato) diboron (1.2 g, 4.7 mmol), Pd(dppf)Cl\(_2\) (0.24 g, 0.21 mmol) and AcOK (1.26 g, 12.8 mmol) were heated in dioxane (30 mL) at 110 °C for 18 h. After cooling to room temperature, the solvent as removed under reduced pressure and the residue was purified on silica column with CH\(_2\)Cl\(_2\):petroleum ether (1:3, v:v) as eluent to obtain the crude intermediate compound as white solid (1.33 g, 64%). Under the N\(_2\) atmosphere, crude intermediate compound (0.8 g, 1.5 mmol), 1-chloroisouquinoline (0.26 g, 1.6 mmol), Pd(PPh\(_3\))\(_4\) (0.1 g, 0.09 mmol) were heated in toluene (15 mL) and 2M K\(_2\)CO\(_3\) (15 mL) at 110 °C for 18 h. After cooling to room temperature, the reaction mixture was extracted with CH\(_2\)Cl\(_2\) (3×20 mL). The organic phase was dried over anhydrous Na\(_2\)SO\(_4\). After removing solvent, the residue was purified on
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silica column with CH\textsubscript{2}Cl\textsubscript{2}: petroleum ether (4:1, v:v) as eluent to obtain the product as pale yellow solid (0.6 g, 81%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \textdelta): 8.65 (d, \textit{J} = 6.0 Hz, 1H), 8.12 (d, \textit{J} = 8.4 Hz, 1H), 7.90 (d, \textit{J} = 8.0 Hz, 1H), 7.76 (d, \textit{J} = 8.0 Hz, 1H), 7.73-7.61 (m, 5H), 7.58-7.54 (m, 1H), 7.28-7.26 (m, 3H), 7.24 (s, 1H), 7.16 (d, \textit{J} = 8.0 Hz, 5H), 7.07 (d, \textit{J} = 4.0 Hz, 1H), 7.00 (t, \textit{J} = 8.0 Hz, 2H), 2.06-1.89 (m, 4H), 0.43 (t, \textit{J} = 7.4 Hz, 6H).

**Procedures for the Synthesis of CN2-2**

Following the same procedure for synthesis of CN2-1 with starting material of CN2-Br. The yield of this reaction is 62\%. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, \textdelta): 8.64 (d, \textit{J} = 6.0 Hz, 1H), 8.13 (d, \textit{J} = 8.4 Hz, 1H), 7.90 (d, \textit{J} = 8.0 Hz, 1H), 7.75 (d, \textit{J} = 8.0 Hz, 1H), 7.72-7.53 (m, 6H), 7.11-7.09 (m, 4H), 7.02 (d, \textit{J} = 2.4 Hz, 1H), 6.95 (d, \textit{J} = 4.4 Hz, 1H), 6.86-6.84 (m, 4H), 3.83 (s, 6H), 2.05-1.87 (m, 4H), 0.43 (t, \textit{J} = 7.4 Hz, 6H).
Figure S1. NMR spectra for the Pt$^{II}$(C$^\equiv$N)(N-donor ligand)Cl-type complexes.
Figure S2. TGA curves for these Pt\textsuperscript{II}(C^\text{N})(N-donor ligand)Cl-type complexes.
Figure S3. Patterns of the key MOs for these Pt\textsuperscript{II}(C\textsuperscript{N})(N-donor ligand)Cl-type complexes.
Figure S4. Prompt and delayed (50 ns) PL spectra in CH$_2$Cl$_2$ for P1, P2, P3 and P5 at 293 K.
Figure S5. Excitation spectra at different emission wavelengths for P1, P2, P3 and P5 in CH₂Cl₂ at 293 K.
Figure S6. Delayed (50 ns) PL spectra in THF-H$_2$O mixture for P1, P2, P3 and P5 at 293 K.
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