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Metallomesogens Based on Platinum (II) Complexes: Synthesis, Luminescence and Polarized Emission

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Supporting Information

Experimental

Experimental

General information

All solvents were carefully dried and distilled prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were performed under nitrogen atmosphere and were monitored by thin-layer chromatography (TLC). Flash column chromatography and preparative TLC were carried out using silica gel from Merck (200-300 mesh). All ^{1}H NMR spectra were acquired at a Bruker Dex-400NMR instrument using $CDCl_3$ as a solvent. Elemental analysis was performed on a Harrios elemental analysis instrument. (2-bromopyridin-5-yl)methanol was synthesized based on the procedure described by Feringa.[57]

2-bromo-5-(butoxymethyl)pyridine (C_4OpyBr)

NaH (0.7 g, 29.2 mmol) was added to a solution of (2-bromopyridin-5-yl) methanol (1.9 g, 10.1 mmol) and 1-bromobutane (3.4 g, 25.0 mmol) in DMF (20 mL), and was stirred vigorously for 24 h at RT under a nitrogen atmosphere. The reaction mixture was then poured into 100 mL of water and was extracted with DCM (3 × 50 mL). The mixed organic layer was washed with water and brine, dried over $MgSO_4$ and filtered. The filtrate was evaporated and the residue was purified by dry flash silica gel column using PE / ethyl acetate (7:1) as eluent to gain C_4OpyBr as oil (2.1 g, 84.1 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.31 (s, 1H), 7.55 (d, J = 10.2 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 4.45 (s, 2H), 3.48 (t, 2H), 1.61-1.55 (m, 2H), 1.42-1.33 (m, 2H), 0.92 (t, 3H).

2-bromo-5-(octyloxymethyl)pyridine (C_8OpyBr)

It was synthesized according to the preparation procedure of **C_4OpyBr**. A liquid of **C_8OpyBr** was obtained in 86.9 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.31 (s, 1H), 7.56 (d, J = 10.5 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 4.46 (s, 2H), 3.48 (t, 2H), 1.64-1.57 (m, 2H), 1.41-1.25 (m, 10H), 0.89 (t, 3H).

2-bromo-5-(dodecyloxymethyl)pyridine (C_{12}OpyBr)

It was synthesized according to the preparation procedure of **C_4OpyBr**. A white solid of **C_{12}OpyBr** was obtained in 82.5 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.32(s, 1H), 7.56 (d, J = 10.5 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 4.46(s, 2H), 3.48 (t, 2H), 1.61-1.55(m, 2H), 1.42-1.33(m, 18H), 0.92 (t, 3H).

2-bromo-5-(hexadecyloxymethyl)pyridine (C_{16}OpyBr)

It was synthesized according to the preparation procedure of **C_4OpyBr**. A white solid of **C_{16}OpyBr** was obtained in 78.4 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.32 (s, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 8.2 Hz, 1H), 4.46 (s, 2H), 3.49 (t, 2H), 1.62-1.59 (m, 2H), 1.42-1.25 (m, 26H), 0.92 (t, 3H).

4-bromo-1-butoxybenzene (C_4OpBr)

A mixture of 4-bromophenol (6.9 g, 36.9 mmol), 1-bromobutane (7.9 g, 57.3 mmol), K_2CO_3 (15.0 g, 108.7 mmol), KI (0.5 g, 4.2 mmol) and 100 mL acetone was refluxed under a nitrogen atmosphere for 24 h. The mixture was cooled to RT and filtrated. The filtrate was evaporated to remove the solvent and the residue was

passed through a flash silica gel column using PE as eluent to gain **C_4OpBr** as a colorless liquid (7.5 g, 82.9 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.37-7.34 (m, 2H), 6.79-6.76 (m, 2H), 3.93 (t, 2H), 1.79-1.72 (m, 2H), 1.53-1.43 (m, 2H), 0.99 (t, 3H).

4-bromo-1-octyloxybenzene (C_8OpBr)

It was synthesized according to the preparation procedure of **C_4OpBr**. A colorless liquid of **C_8OpBr** was obtained in 82.9 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.37 (m, 2H), 6.79 (m, 2H), 3.92 (t, 2H), 1.79-1.73 (m, 2H), 1.47-1.40 (m, 2H), 1.32-1.28 (m, 8H), 0.99 (t, 3H).

4-bromo-1-octyloxy-2-fluorobenzene (C_8OFpBr)

It was synthesized according to the preparation procedure of **C_4OpBr**. A colorless liquid of **C_8OFpBr** was obtained in 60.5 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.25 (d, J = 12.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 6.86 (t, 1H), 4.02 (t, 2H), 1.83-1.79 (m, 2H), 1.46-1.29 (m, 10H), 0.90 (t, 3H).

4-bromo-1-dodecyloxybenzene (C_{12}OpBr)

It was synthesized according to the preparation procedure of **C_4OpBr**. A white solid of **C_{12}OpBr** was obtained in 82.1 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.37 (m, 2H), 6.79 (m, 2H), 3.92 (t, 2H), 1.79-1.72 (m, 2H), 1.45-1.26 (m, 18H), 0.89 (t, 3H).

4-bromo-1-dodecyloxy-2-fluorobenzene (C_{12}OFpBr)

It was synthesized according to the preparation procedure of **C_4OpBr**. A yellow liquid of **C_{12}OFpBr** was obtained in 53.4 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.23 (d, J = 10.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 6.84 (t, 1H), 4.0 (t, 2H), 1.87-1.82 (m, 2H), 1.45-1.26 (m, 18H), 0.89 (t, 3H).

4-bromo-1-hexadecyloxybenzene (C_{16}OpBr)

It was synthesized according to the preparation procedure of **C_4OpBr**. A white solid of **C_{16}OpBr** was obtained in 85.7 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.36 (m, 2H), 6.78 (m, 2H), 3.92 (t, 2H), 1.79-1.72 (m, 2H), 1.43-1.26 (m, 26H), 0.89 (t, 3H).

4-bromo-1-hexadecyloxy-2-fluorobenzene (C_{16}OFpBr)

It was synthesized according to the preparation procedure of **C_4OpBr**. A white solid of **C_{16}OFpBr** was obtained in 62.3 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.23 (d, *J* = 10.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 6.84 (t, 1H), 4.0 (t, 2H), 1.87-1.82 (m, 2H), 1.45-1.26 (m, 26H), 0.89 (t, 3H).

2-(4-butoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (C_4OpB)

A mixture of **C_4OpBr** (2.0 g, 8.9 mmol), bis(pinacolato)diboron (2.4 g, 9.5 mmol), potassium acetate (2.6 g, 26.5 mmol), [1,1'-bis(diphenylphosphino)-ferrocene] dichloropalladium complex with dichloromethane (1:1) (0.27 g, 0.34 mmol), and dimethyl sulfoxide (DMSO, 60 mL) was stirred at 80 °C for 19 h under nitrogen atmosphere. The resulting mixture was cooled to RT, poured into ice-water (200 mL) and then extracted with DCM (3 × 20 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and filtrated. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE / DCM (5:1) as the eluent to give **C_4OpB** as a colorless liquid (1.5 g, 62.1%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.74 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 3.98 (t, 2H), 1.79-1.72 (m, 2H), 1.34 (s, 12H), 1.53-1.43 (m, 2H), 0.90 (t, 3H).

2-(4-octyloxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (C_8OpB)

It was synthesized according to the preparation procedure of **C_4OpB**. A white solid of **C_8OpB** was obtained in 58.7 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.74 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 3.98 (t, 2H), 1.79-1.72 (m, 2H), 1.34 (s, 12H), 1.43-1.26 (m, 8H), 0.90 (t, 3H).

2-(2-fluoro-4-(octyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (C_8OFpB)

It was synthesized according to the preparation procedure of **C_4OpB**. A yellow liquid of **C_8OFpB** was obtained in 48.4 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.51 (d, *J* = 6.4 Hz, 1H), 7.45 (s, 1H), 6.95 (t, 1H), 4.06 (t, 2H), 1.84-1.78 (m, 2H), 1.33 (s, 12H), 1.46-1.29 (m, 10H), 0.90 (t, 3H).

2-(4-dodecyloxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (C_{12}OpB)

It was synthesized according to the preparation procedure of **C_4OpB**. A white solid of **C_{12}OpB** was obtained in 57.5 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.74 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 3.98 (t, 2H), 1.79-1.72 (m, 2H),

1.34 (s, 12H), 1.43-1.26 (m, 18H), 0.90 (t, 3H).

2-(2-fluoro-4-(dodecyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (C_{12}OFpB)

It was synthesized according to the preparation procedure of **C_4OpB**. A brown solid of **C_{12}OFpB** was obtained in 52.1 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.51 (d, *J* = 6.5 Hz, 1H), 7.47 (s, 1H), 6.95 (t, 1H), 4.06 (t, 2H), 1.84-1.78 (m, 2H), 1.34 (s, 12H), 1.45-1.26 (m, 18H), 0.90 (t, 3H).

2-(4-hexadecyloxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (C_{16}OpB)

It was synthesized according to the preparation procedure of **C_4OpB**. A light yellow solid of **C_{16}OpB** was obtained in 58.6 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.74 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 3.98 (t, 2H), 1.79-1.75 (m, 2H), 1.44-1.42 (m, 2H), 1.33 (s, 12H), 1.43-1.25 (m, 24H), 0.89 (t, 3H).

2-(2-fluoro-4-(hexadecyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (C_{16}OFpB)

It was synthesized according to the preparation procedure of **C_4OpB**. A white solid of **C_{16}OFpB** was obtained in 50.1 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 7.52 (d, *J* = 6.9 Hz, 1H), 7.46 (s, 1H), 6.96 (t, 1H), 4.08 (t, 2H), 1.86-1.81 (m, 2H), 1.34 (s, 12H), 1.49-1.27 (m, 26H), 0.91 (t, 3H).

5-(butoxymethyl)-2-(4-butoxyphenyl)pyridine (C_4OppyH)

To a mixture of **C_4OpB** (1.7 g, 6.1 mmol), **C_4OpBr** (1.0 g, 4.1 mmol) and tetrakis(triphenylphosphine) palladium (86 mg) was added a degassed mixture of toluene (20 mL), ethanol (10 mL) and 2 M potassium carbonate aqueous solution (10 mL). The mixture was refluxed for 24 h under the protection of nitrogen. After cooled to RT, the mixture was poured into water (200 mL) and extracted with DCM (3 × 20 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE / DCM (2:1) as the eluent to give a white solid (1.26 g, 98.1 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.59 (s, 1H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 10.0 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 4.53 (s, 2H), 4.06 (t, 2H), 3.52 (t, 2H), 1.81-1.77 (m, 2H), 1.63-1.59 (m, 2H), 1.54-1.48 (m, 2H), 1.43-1.40 (m, 2H), 1.01-0.91 (m, 6H).

5-(octyloxymethyl)-2-(4-octyloxyphenyl)pyridine (C_8OppyH)

It was synthesized according to the preparation procedure of **C_4OppyH**. A white solid of **C_8OppyH** was obtained in 77.6 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.59 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 4.52 (s, 2H), 4.02 (t, 2H), 3.51 (t, 2H), 1.84-1.77 (m, 2H), 1.64-1.57 (m, 4H), 1.47-1.28 (m, 18H), 0.89 (t, 6H).

2-(4-octyloxy-3-fluorophenyl)-5-(octyloxymethyl)pyridine (C_8OFppyH)

It was synthesized according to the preparation procedure of **C_4OppyH**. A white solid of **C_8OFppyH** was obtained in 59.4 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.61 (s, 1H), 7.79 (m, 3H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.07 (t, 1H), 4.55 (s, 2H), 4.11 (t, 2H), 3.53 (t, 2H), 1.87 (t, 2H), 1.66-1.62 (m, 7H), 1.52-1.30 (m, 15H), 0.90 (t, 6H).

5-(dodecyloxymethyl)-2-(4-dodecyloxyphenyl)pyridine (C_{12}OppyH)

It was synthesized according to the preparation procedure of **C_4OppyH**. A white solid of **C_{12}OppyH** was obtained in 70.5 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.59(s, 1H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 4.55 (s, 2H), 4.05 (t, 2H), 3.53 (t, 2H), 1.84-1.80 (m, 2H), 1.66-1.61 (m, 2H), 1.54-1.27 (m, 36H), 0.91 (m, 6H).

2-(4-dodecyloxy-3-fluorophenyl)-5-(dodecyloxymethyl)pyridine (C_{12}OFppyH)

It was synthesized according to the preparation procedure of **C_4OppyH**. A white solid of **C_{12}OFppyH** was obtained in 64.2 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.63 (s, 1H), 7.80 (m, 3H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.08 (t, 1H), 4.55 (s, 2H), 4.11 (t, 2H), 3.53 (t, 2H), 1.87-1.84 (m, 2H), 1.63-1.26 (m, 38H), 0.91 (t, 6H).

5-(hexadecyloxymethyl)-2-(4-hexadecyloxyphenyl)pyridine (C_{16}OppyH)

It was synthesized according to the preparation procedure of **C_4OppyH**. A white solid of **C_{16}OppyH** was obtained in 72.3 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.64 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 4.53 (s, 2H), 4.02 (t, 2H), 3.51 (t, 2H), 1.83-1.76 (m, 2H), 1.67-1.58 (m, 8H), 1.46-1.25 (m, 46H), 0.89 (m, 6H).

2-(4-hexadecyloxy-3-fluorophenyl)-5-(hexadecyloxymethyl)pyridine

(C_{16}OFppyH)

It was synthesized according to the preparation procedure of **C_4OppyH**. A white solid of **C_{16}OFppyH** was obtained in 68.4 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.66 (s, 1H), 7.79 (m, 3H), 7.58 (t, 1H), 7.10 (t, 1H), 4.57 (s, 2H), 4.12 (t, 2H), 3.53 (t, 2H), 1.87-1.84 (m, 2H), 1.63-1.26 (m, 54H), 0.91-0.87 (t, 6H).

Preparation of (C_4Oppy)Pt(acac)

To a mixture of K_2PtCl_4 (0.4 g, 1.0 mmol) and water (5 mL) was added a solution of **C_4OppyH** (0.7 g, 2.3 mmol) and 2-ethoxyethanol (15 mL). The mixture was stirred under inert gas atmosphere at 80°C for 20 h. After cooled to RT, the colored precipitate was filtered off and was washed with water and hexane to gain a **[(C_4Oppy)PtCl]$_2$** dimmer as a yellow solid (0.39 g) directly used in the following process. A mixture of **[(C_4Oppy)PtCl]$_2$** (0.27 g, 0.25 mmol), pentane-2, 4-dione (0.1 g, 1.0 mmol) and sodium carbonate (0.26 g, 2.49 mmol) were stirred in 2-ethoxyethanol (15 mL) under inert gas atmosphere at 100°C for 12-15 h. After cooled to RT, the mixture was extracted with DCM and the mixed organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated to remove the solvent and the residue was passed through a flash silica gel column using PE / DCM (1:2) as eluent to gain **(C_4Oppy)Pt(acac)** as a yellow solid (0.13 g, 86.0 %). ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.85 (s, 1H), 7.72 (d, J = 7.3 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 8.6 Hz, 1H), 7.11 (s, 1H), 6.66 (d, J = 6.9 Hz, 1H), 5.46 (s, 1H), 4.52 (s, 2H), 4.09 (t, 2H), 3.53 (t, 2H), 2.00 (s, 6H), 1.81-1.78 (m, 2H), 1.64-1.60 (m, 2H), 1.45-1.42 (m, 4H), 1.00-0.91 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS), δ(ppm): 185.75, 184.0, 167.34, 159.70, 145.83, 142.60, 137.26, 135.38, 130.94, 124.46, 117.20, 114.98, 110.67, 102.44, 70.55, 69.63, 67.45, 31.76, 31.37, 29.67, 28.20, 27.11, 19.34, 13.91. Anal. Calcd. for $C_{25}H_{33}NO_4Pt$: C 49.50, H 5.48, N 2.31. Found: C 49.80, H 5.82, N 2.17 %.

Preparation of (C_8Oppy)Pt(acac)

It was prepared according to the synthetic procedure of **(C_4Oppy)Pt(acac)**. A yellow solid of **(C_8Oppy)Pt(acac)** was obtained in 49.6 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.84 (s, 1H), 7.73 (d, J = 9.4 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 8.4 Hz, 1H), 7.11 (s, 1H), 6.66 (d, J = 10.8 Hz, 1H), 5.47 (s, 1H), 4.51 (s, 2H), 4.08 (t, 2H), 3.51 (t, 2H), 2.04 (s, 6H), 1.84-1.77 (m, 2H), 1.65-

1.59 (m, 2H), 1.47-1.28 (m, 20H), 0.88-0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS), δ(ppm): 185.73, 184.01, 167.35, 159.70, 145.83, 141.03, 137.31, 137.05, 130.91, 124.46, 117.21, 115.0, 110.65, 102.42, 70.89, 69.63, 67.80, 31.80, 29.71, 29.41, 29.36, 29.32, 29.23, 29.21, 28.23, 27.11, 26.15, 26.09, 22.62, 14.04. Anal. calcd. for $C_{33}H_{49}NO_4Pt$: C 55.14, H 6.87, N 1.95. Found: C 55.25, H 6.92, N 1.92 %.

Preparation of (C_8OFppy)Pt(acac)

It was prepared according to the synthetic procedure of **(C_4Oppy)Pt(acac)**. A yellow solid of **(C_8OFppy)Pt(acac)** was obtained in 50.2 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.87 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.21 (t, 2H), 5.47 (s, 1H), 4.51 (s, 2H), 4.08 (t, 2H), 3.53 (t, 2H), 2.03 (s, 6H), 1.84-1.77 (m, 2H), 1.65-1.59 (m, 2H), 1.47-1.28 (m, 20H), 0.88-0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS), δ(ppm): 185.77, 183.70, 166.59, 151.47, 149.09, 145.83, 137.38, 136.07, 134.58, 131.54, 117.36, 114.88, 110.62, 102.44, 70.97, 69.52, 68.95, 31.80, 31.79, 30.39, 29.71, 29.66, 29.41, 29.33, 29.21, 28.92, 28.18, 27.05, 26.14, 25.99, 22.94, 22.60, 14.02. Anal. calcd. for $C_{33}H_{48}FNO_4Pt$: C 53.79, H 6.57, N 1.90. Found: C 53.81, H 6.75, N 1.88 %.

Preparation of (C_{12}Oppy)Pt(acac)

It was prepared according to the synthetic procedure of **(C_4Oppy)Pt(acac)**. A yellow solid of **(C_{12}Oppy)Pt(acac)** was obtained in 50.7 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.84 (s, 1H), 7.73 (d, J = 8.2 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 8.5 Hz, 1H), 7.11 (s, 1H), 6.66 (d, J = 10.8 Hz, 1H), 5.47 (s, 1H), 4.51 (s, 2H), 4.08 (t, 2H), 3.51 (t, 2H), 2.00 (s, 6H), 1.82-1.78 (m, 2H), 1.65-1.59 (m, 2H), 1.48-1.26 (m, 36H), 0.89-0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS), δ(ppm): 185.77, 184.06, 167.38, 159.73, 145.87, 141.07, 137.39, 137.07, 130.94, 124.53, 117.29, 114.96, 110.68, 102.51, 70.93, 69.67, 67.81, 31.96, 29.73, 29.66, 29.62, 29.52, 29.47, 29.39, 28.31, 27.19, 26.20, 26.13, 22.72, 14.14. Anal. Calcd. for $C_{41}H_{65}NO_4Pt$: C 59.26, H 7.88, N 1.69. Found: C 59.40, H 8.21, N 1.61 %.

Preparation of (C_{12}OFppy)Pt(acac)

It was prepared according to the synthetic procedure of **(C_4Oppy)Pt(acac)**. A yellow solid of **(C_{12}OFppy)Pt(acac)** was obtained in 49.6 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.86 (s, 1H), 7.77 (d, J = 8.6 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.20 (t, 2H), 5.49 (s, 1H), 4.54 (s, 2H), 4.19 (t, 2H), 3.53 (t, 2H), 2.02 (s,

6H), 1.89-1.83 (m, 2H), 1.57-1.27 (m, 38H), 0.89-0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS), δ(ppm): 185.87, 183.81, 166.77, 151.54, 145.96, 137.48, 136.09, 134.44, 131.55, 117.42, 114.90, 110.67, 110.49, 102.50, 70.97, 69.54, 68.97, 31.87, 29.71, 29.64, 29.61, 29.57, 29.46, 29.38, 29.32, 29.20, 28.23, 27.09, 26.15, 25.98, 22.65, 14.06. Anal. calcd. for $C_{41}H_{64}FNO_4Pt$: C 58.00, H 7.60, N 1.65. Found: C 58.31, H 7.81, N 1.63 %.

Preparation of (C_{16}Oppy)Pt(acac)

It was prepared according to the synthetic procedure of **(C_4Oppy)Pt(acac)** complex. A yellow solid of **(C_{16}Oppy)Pt(acac)** was obtained in 50.9 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.84 (s, 1H), 7.73 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 8.9 Hz, 1H), 7.36 (d, J = 8.8 Hz, 1H), 7.10 (s, 1H), 6.66 (d, J = 8.6 Hz, 1H), 5.46 (s, 1H), 4.51 (s, 2H), 4.08 (t, 2H), 3.51 (t, 2H), 2.04 (s, 6H), 1.82-1.76 (m, 2H), 1.64-1.60 (m, 2H), 1.48-1.24 (m, 52H), 0.89-0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS), δ(ppm): 185.76, 184.04, 167.36, 159.72, 145.86, 141.08, 137.39, 137.07, 130.94, 124.53, 117.28, 114.96, 110.67, 102.51, 70.92, 69.67, 67.81, 53.44, 31.96, 29.77, 29.71, 29.67, 29.62, 29.52, 29.47, 29.39, 28.31, 27.19, 26.20, 26.14, 22.72, 14.15. Anal. Calcd. for $C_{49}H_{81}NO_4Pt$: C 62.39, H 8.66, N 1.48. Found: C 62.95, H 8.92, N 1.42 %.

Preparation of (C_{16}OFppy)Pt(acac)

It was prepared according to the synthetic procedure of **(C_4Oppy)Pt(acac)**. A yellow solid of **(C_{16}OFppy)Pt(acac)** was obtained in 51.6 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, TMS), δ(ppm): 8.85 (s, 1H), 7.76 (d, J = 7.0 Hz, 1H), 7.39 (d, J = 8.3 Hz, 1H), 7.20 (t, 2H), 5.49 (s, 1H), 4.53 (s, 2H), 4.19 (t, 2H), 3.53 (t, 2H), 2.02 (s, 6H), 1.87-1.84 (m, 2H), 1.63-1.26 (m, 54H), 0.91-0.87 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS), δ(ppm): 185.90, 183.81, 166.73, 151.56, 149.18, 145.98, 137.56, 136.15, 134.69, 131.64, 117.53, 114.86, 110.78, 102.63, 71.09, 69.65, 69.02, 68.26, 31.94, 31.93, 29.84, 29.55, 29.48, 29.36, 29.33, 29.04, 28.35, 27.22, 26.28, 26.13, 22.76, 14.20. Anal. calcd. for $C_{49}H_{80}FNO_4Pt$: C 61.23, H 8.39, N 1.46. Found: C 61.74, H 8.63, N 1.42 %.

Figure S1

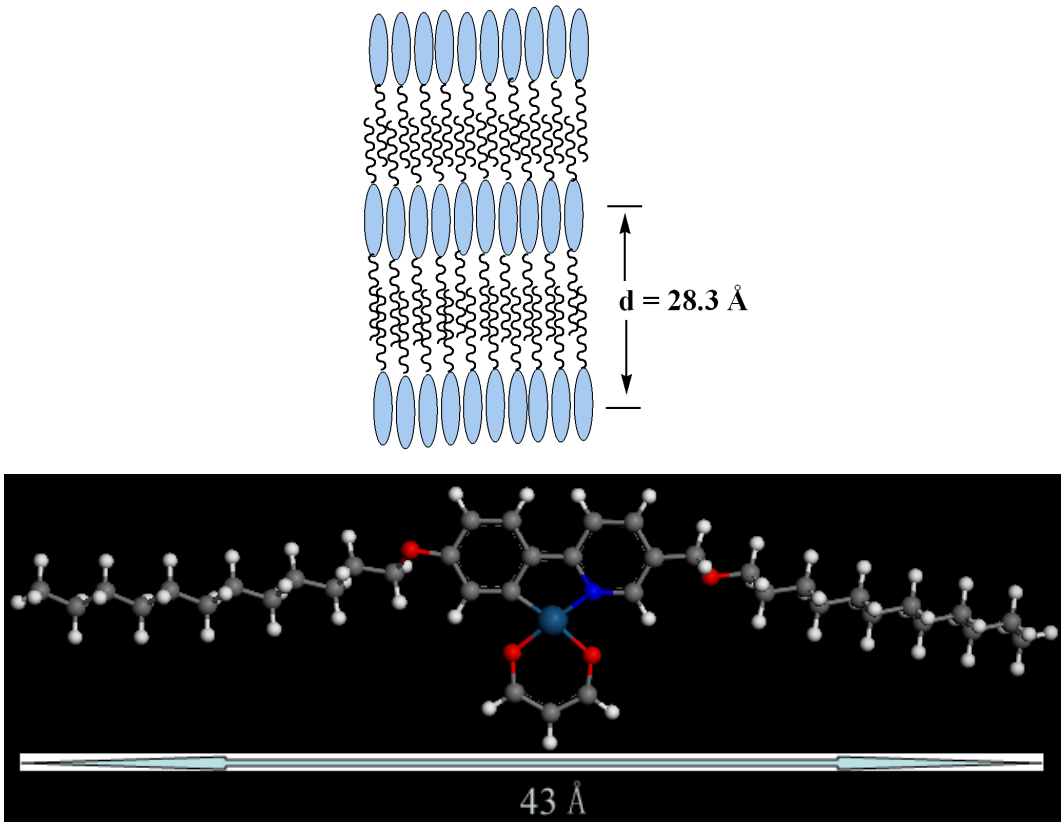

Figure S2