

Electronic supplementary information for

Efficient dinuclear Pt(II) complexes based on the triphenylphosphine oxide scaffold for high performance solution-processed OLEDs

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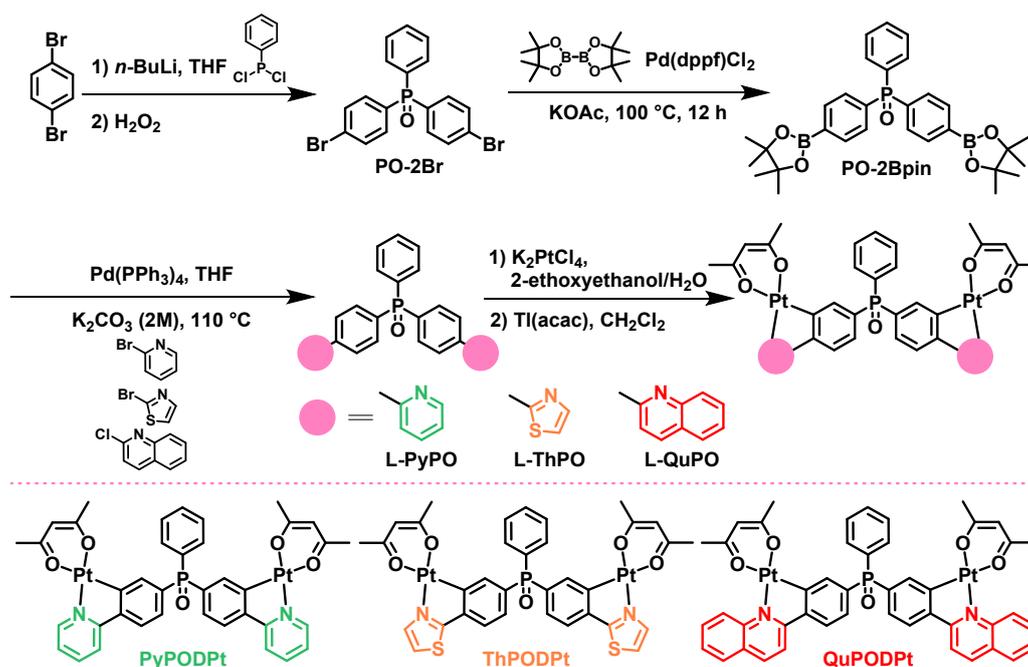
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General information

^1H , ^{13}C , and ^{31}P NMR spectra were measured on a Bruker Avance 400 MHz spectrometer. Mass spectra were recorded on a WATERS I-Class VION IMS Qtof mass spectrometry. The thermal gravimetric analysis was tested with a NETZSCH STA 409C instrument under N_2 at a heating rate of 20 K min^{-1} . The absorption and emission spectra were recorded on a Shimadzu UV-2250 spectrophotometer and an Edinburgh Instruments Ltd (FLSP920) fluorescence spectrophotometer, respectively. Cyclic voltammetry (CV) was performed on the Princeton Advanced Electrochemical System in CH_2Cl_2 solutions. Theoretical calculations were carried out with the density functional theory (DFT) and time dependent-DFT (TD-DFT) method. The basis sets of B3LYP/6-31G(d, p) and B3LYP/LanL2DZ were applied to the non-metal atoms (C, H, N, P, and O) and the metal atom (Pt), respectively.

Synthesis



Scheme S1. Synthetic routes of dinuclear Pt(II) complexes.

PO-2Br Under a N₂ atmosphere, dibromobenzene (5.5 g, 23.3 mmol) was dissolved in dry THF (30 mL). After adding *n*-BuLi (10 mL, 2.5 mol/L) into the solution at -78 °C, the mixture was stirred for 30 min. Then, phenylphosphine dichloride (1.8 g, 10 mmol) was added. The reaction mixture was stirred at room temperature over night. The reaction was quenched by adding water, and then extracted with CH₂Cl₂. The separated organic layer was dried over anhydrous MgSO₄, and concentrated under vacuum. The residual was purified on a silica column to give white solid. Then, the solid (3.6 g, 8.6 mmol) was oxidized by H₂O₂ (5 mL, 30%) in CHCl₃ solution (40 mL) at room temperature for 4 h. After extracted with CH₂Cl₂, the organic layer was dried over anhydrous MgSO₄, and concentrated under vacuum. The residual was purified on a silica column to give color-less oil (3.31 g, 88.7% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.68–7.55 (m, 7H), 7.53–7.46 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 133.52, 133.42, 132.43, 132.40, 132.00, 131.95, 131.88, 131.86, 131.59, 130.54, 128.80, 128.68, 127.48, 127.45; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 28.15.

PO-2Bpin Under a N₂ atmosphere, the mixture of **PO-2Br** (3.2 g, 7.3 mmol), bis(pinacolato)diboron (7.6 g, 30.0 mmol), KOAc (10.0 g, 100 mmol), Pd(dppf)Cl₂ (1.4 g, 2.0 mmol), and dioxane (70 mL) was stirred at 100 °C for 14 h. After cooled to room temperature, the mixture was poured into water and extracted with CH₂Cl₂ several times. The organic layers were combined, dried over anhydrous MgSO₄ and concentrated under vacuum. The residual was purified on a silica column to give pale-yellow solid (3.6 g, 93.0% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.86 (dd, *J*=

4.8, 7.6 Hz, 4H), 7.68–7.60 (m, 6H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.45–7.43 (m, 2H), 1.34 (s, 24H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 135.46, 134.70, 134.56, 134.45, 132.87, 132.10, 132.00, 131.21, 131.12, 128.52, 128.40, 127.67, 83.48, 24.99; ^{31}P NMR (162 MHz, CDCl_3): δ (ppm) 29.03.

General procedure for synthesizing the ligands Under a N_2 atmosphere, the mixture of **PO-2Bpin** (1.0 equiv), 2-bromopyridine (2-bromothiazole or 2-chloroquinoline, 3.0 equiv), and $\text{Pd}(\text{PPh}_3)_4$ (0.12 equiv) were stirred in the mixture of THF (30 mL) and 2 M K_2CO_3 (20 mL) at 110 °C overnight. The reaction mixture was cooled to room temperature, poured into water, and extracted with CH_2Cl_2 several times. The organic layers were combined, dried over anhydrous MgSO_4 and concentrated under vacuum. The residual was purified on self-made TLC to give the target ligands.

L-PyPO (72.6% yield). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.71 (d, $J = 4.4$ Hz, 2H), 8.09 (d, $J = 6.0$ Hz, 4H), 7.84–7.70 (m, 10H), 7.57 (t, $J = 6.8$ Hz, 1H), 7.50–7.46 (m, 2H), 7.30–7.28 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 156.20, 149.92, 142.84, 136.94, 133.27, 132.66, 132.56, 132.16, 132.06, 128.63, 128.51, 127.03, 126.91, 122.91, 121.00; ^{31}P NMR (162 MHz, CDCl_3): δ (ppm) 28.87.

L-ThPO (60.8% yield). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.08 (dd, $J = 6.0$, 8.8 Hz, 4H), 7.92 (d, $J = 3.2$ Hz, 2H), 7.79 (d, $J = 8.4$ Hz, 2H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.73–7.68 (m, 2H), 7.58 (dt, $J = 1.2$, 7.2 Hz, 2H), 7.52–7.48 (m, 2H), 7.41 (d, $J = 3.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 166.79, 144.20, 136.78, 136.75,

134.23, 133.19, 132.81, 132.70, 132.36, 132.31, 132.28, 132.09, 131.98, 131.32, 128.77, 128.64, 126.59, 126.47, 119.99; ^{31}P NMR (162 MHz, CDCl_3): δ (ppm) 28.14.

L-QuPO (24.9% yield). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.29–8.26 (m, 6H), 8.18 (d, $J = 8.4$ Hz, 2H), 7.92–7.84 (m, 8H), 7.78–7.73 (m, 4H), 7.58–7.54 (m, 3H), 7.52–7.48 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 156.10, 148.27, 143.16, 137.10, 136.05, 133.62, 132.76, 132.66, 132.58, 132.20, 132.11, 129.93, 129.84, 128.66, 128.54, 127.69, 127.56, 127.51, 127.42, 126.80, 119.00; ^{31}P NMR (162 MHz, CDCl_3): δ (ppm) 28.95.

General procedure for synthesizing the dinuclear Pt(II) complexes Under a N_2 atmosphere, organic ligand (1.0 equiv) and K_2PtCl_4 (2.2 equiv) were dissolved in 2-ethoxyethanol and H_2O (3:1, v/v) (30 mL) and stirred at 90 °C for 4 h. When cooled to room temperature, the mixture was extracted with CH_2Cl_2 and the organic layer was dried over anhydrous MgSO_4 . After the removal of solvent, the residual was stirred with thallium(I) acetylacetonate (2.2 equiv) in CH_2Cl_2 (20 mL) at room temperature overnight. Finally, the reaction mixture was concentrated and the residue was purified with self-made silica thin layer chromatography to obtain the target dinuclear Pt(II) complexes.

PyPODPt (13.8% yield). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.99 (d, $J = 5.6$ Hz, 2H), 7.86–7.79 (m, 4H), 7.72 (d, $J = 12.4$ Hz, 2H), 7.68–7.61 (m, 4H), 7.53–7.44 (m, 5H), 7.17 (t, $J = 6.4$ Hz, 2H), 5.36 (s, 2H), 1.96 (s, 6H), 1.72 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 185.75, 184.51, 147.61, 142.50, 138.30, 134.15, 132.61, 132.45, 128.12, 127.46, 127.36, 122.64, 122.52, 122.09, 119.07, 102.35, 28.17, 26.80; ^{31}P NMR

(162 MHz, CDCl₃): δ (ppm) 31.42; ESI-MS (m/z) theoretical [M+H]⁺: 1019.1495, found: 1019.1483.

ThPODPt (4.7% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.96 (d, J = 3.6 Hz, 2H), 7.81–7.71 (m, 4H), 7.60 (t, J = 7.6 Hz, 2H), 7.51–7.42 (m, 5H), 7.36 (d, J = 3.6 Hz, 2H), 5.38 (s, 2H), 1.94 (s, 6H), 1.74 (s, 6H); Due to the poor solubility, the ¹³C NMR could not be obtained properly; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 31.01; ESI-MS (m/z) theoretical [M+H]⁺: 1031.0642, found: 1031.0602.

QuPODPt (9.7% yield). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.56 (d, J = 8.8 Hz, 2H), 8.29 (d, J = 8.4 Hz, 2H), 7.87–7.74 (m, 12H), 7.68 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.6 Hz, 2H), 7.51–7.44 (m, 3H), 5.41 (s, 2H), 1.98 (s, 6H), 1.65 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 185.25, 184.38, 169.10, 149.48, 149.38, 149.35, 139.32, 133.63, 133.47, 133.36, 132.61, 132.51, 132.34, 131.40, 131.11, 128.38, 128.23, 127.77, 127.54, 127.44, 126.89, 126.38, 124.50, 124.37, 116.70, 101.64, 28.30, 26.99; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 31.46; ESI-MS (m/z) theoretical [M+H]⁺: 1119.1808, found: 1119.1774.

OLED Fabrication and Measurements

The ITO glass substrates were pre-cleaned in ultrasonic cleaner with detergent and deionized water, and treated with UV-O₃ for 30 minutes before use. The hole-injection layer was formed by spin-coating poly(ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (3000 rpm) on the pre-cleaned ITO substrates and thermal annealed at 150 °C for 15 min in the air. Then, the poly(9-vinylcarbazole) (PVK) (8 mg/mL, 4000 rpm) was spin-coated and annealed at 120 °C for 10 min in a

glove box to form the hole transport/electron-blocking layer. After that, the CHCl_3 solution containing emitter (1 wt% doping level) and 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (CBP) was spin-coated (1500 rpm) and baked at 90 °C for 10 min to assemble the emissive layer (EML). Finally, the 1,3,5-*tri*(*m*-pyridin-3-ylphenyl)benzene (TmPyPB), LiF, and Al were successively vacuum deposited under a pressure of *ca.* 5×10^{-4} torr to complete the device. The current density-voltage (*I-V*) curves were recorded with a Keithely 2400. The electroluminescent spectra and luminance values were measured using PR788. The EQEs were calculated from the luminance, current density, and EL spectra assuming a Lambertian distribution.¹ All the measurements were carried out under ambient conditions.

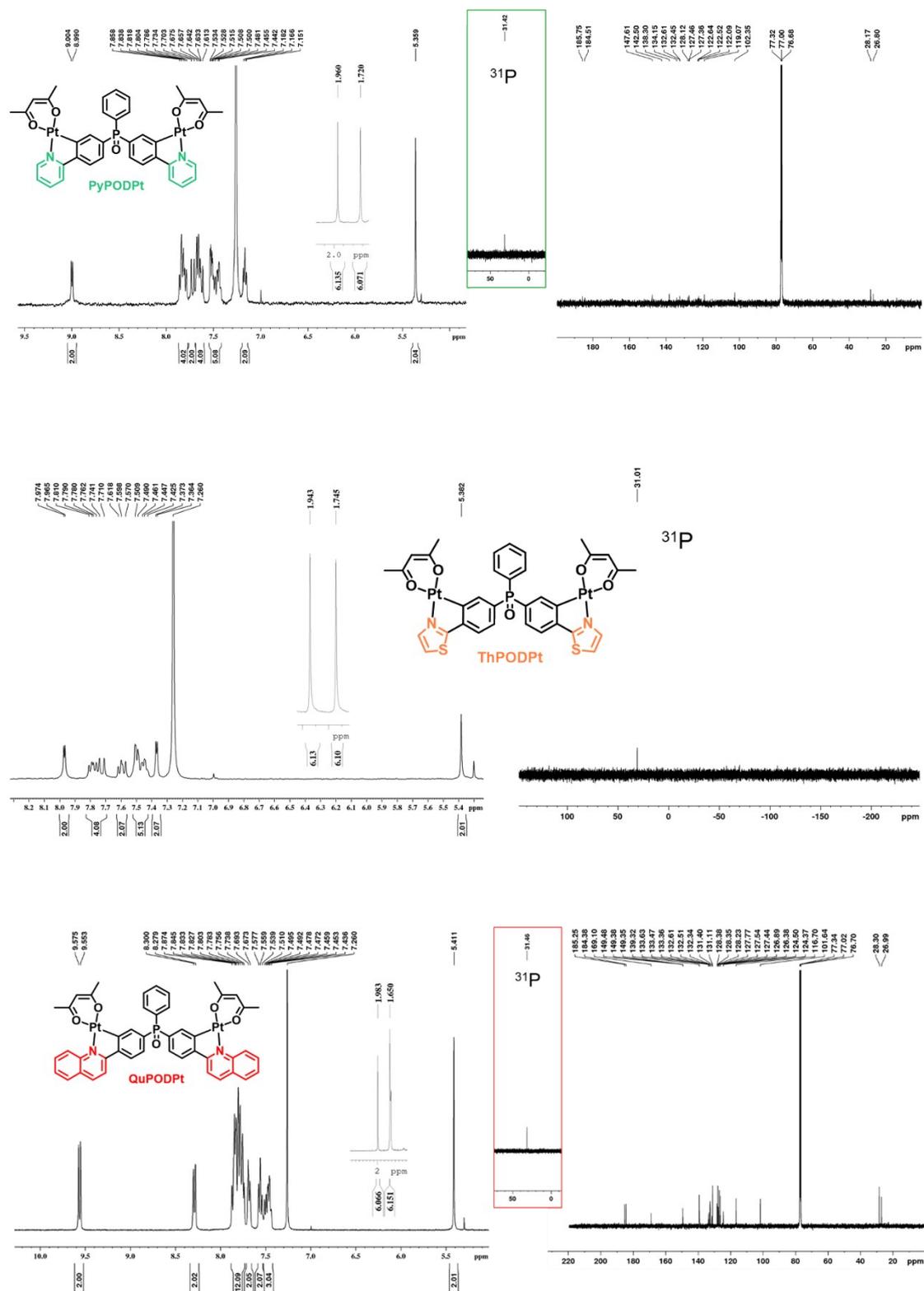


Fig. S1 NMR spectra of PyPODPt, ThPODPt, and QuPODPt.

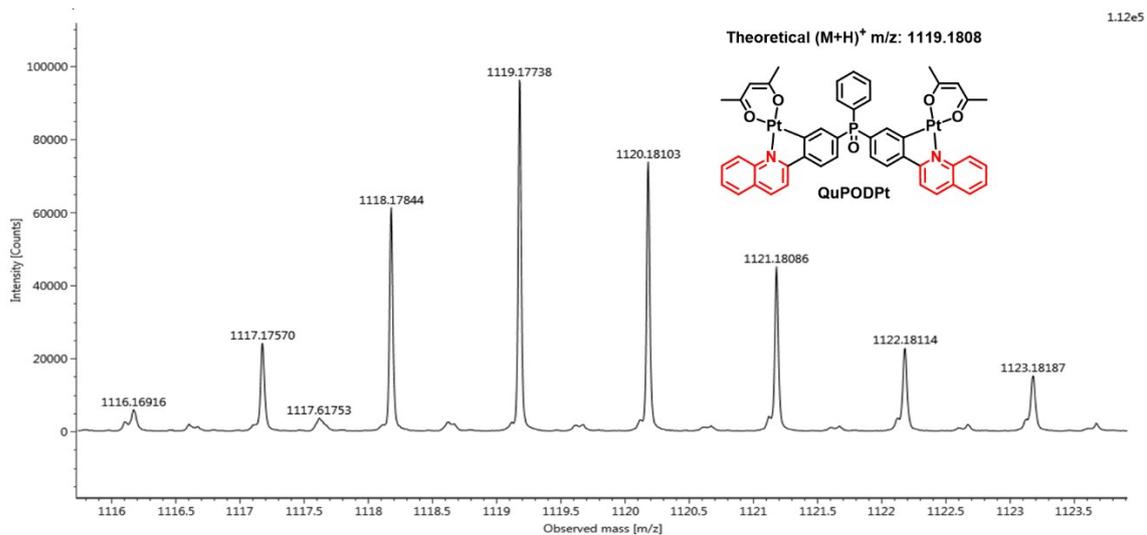
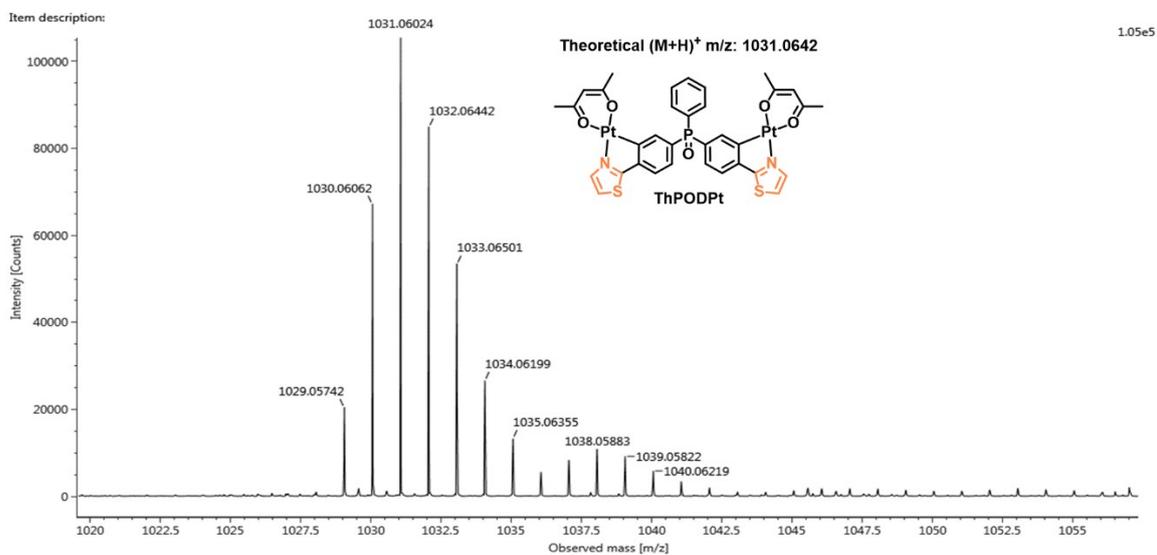
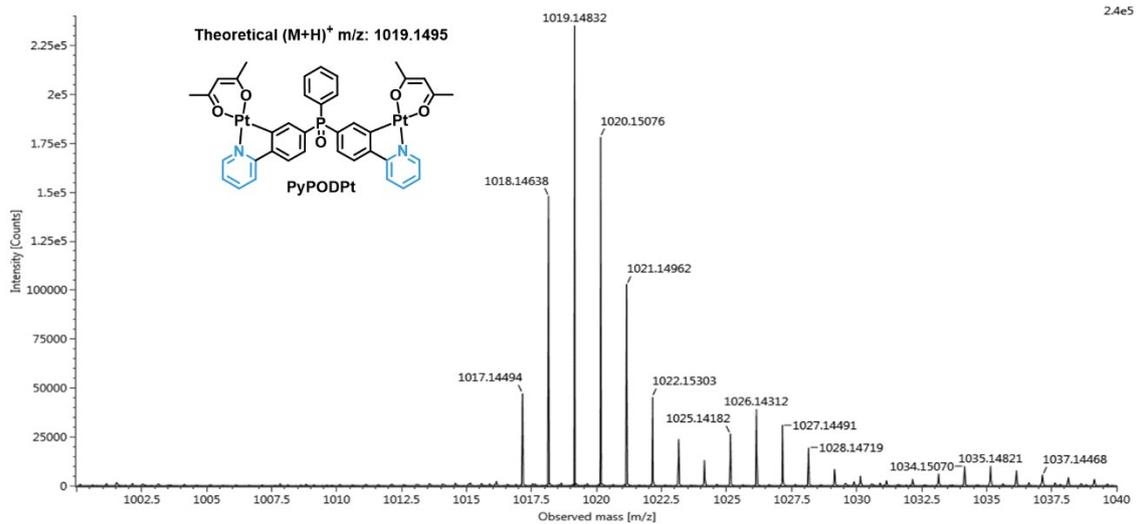


Fig. S2 MS results of PyPODPt, ThPODPt, and QuPODPt.

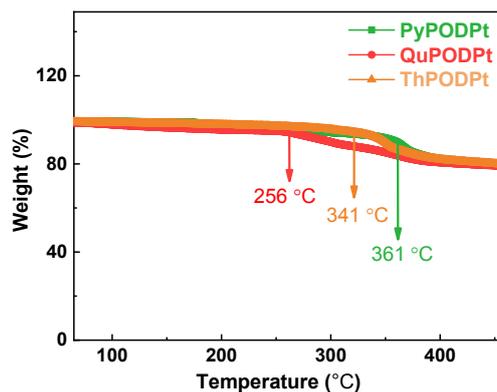


Fig. S3 TGA curves of PyPODPt, ThPODPt, and QuPODPt.

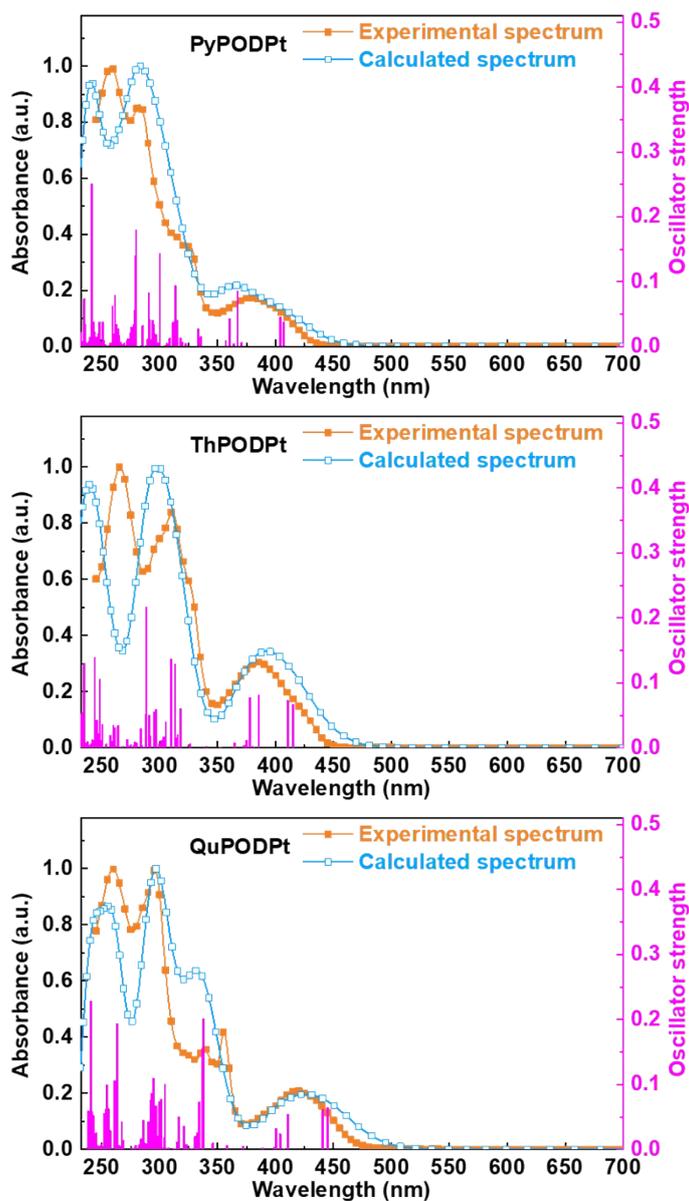


Fig. S4 Comparison of theoretical and experimental UV-visible spectra of PyPODPt, ThPODPt, and QuPODPt.

Table S1 NTO results for **PyPODPt**, **ThPODPt**, and **QuPODPt** based on optimized T₁ geometries

NTOs	Contribution from Pt and ligands to MOs (%)		
	Pt	L-PyPO	acac
PyPODPt			
Particle	6.30	92.72	0.98
Hole	9.12	88.96	1.92
ThPODPt			
Particle2	5.45	93.68	0.87
Particle1	4.93	94.24	0.83
Hole1	15.16	83.62	1.22
Hole2	17.05	81.64	1.31
QuPODPt			
Particle	5.89	93.04	1.07
Hole	21.32	74.86	3.82

Table S2 EL performance of representative OLEDs based on dinuclear Pt(II) complexes

	λ_{EL} (nm)	EQE _{max}	CE _{max} (cd/A)	PE _{max} (lm/W)	Reference
PyPODPt	502, 538	6.85	21.3	11.7	This work ^b
ThPODPt	546, 590	4.52	10.3	6.20	This work ^b
QuPODPt	582, 608	11.2	21.7	11.8	This work ^b
DPt	592	10.5	21.4	12.9	2 ^b
(dfppy)₂Pt₂(C₈OXT)₂	620	8.4	4.2	- ^a	3 ^b
Pt₂L(acac)₂	612	9.9	- ^a	- ^a	4 ^b
Pt₂L¹	660	2.54	1.33	0.76	5 ^b
(2nq)₂Pt₂(l-OXT)₂	670	3.21	- ^a	- ^a	6 ^b
Pt-1	514, 552	21.38	68.31	38.25	7 ^b
3b	480, 320	8.47	24.87	9.88	8 ^c
2	~530	7.0	- ^a	- ^a	9 ^c

^a Not reported. ^b Solution-processed device. ^c Vacuum-deposited device.

Reference

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