Electronic Supplementary Information

For

Highly efficient solution-processed pure yellow OLED based on dinuclear Pt(II) complexes

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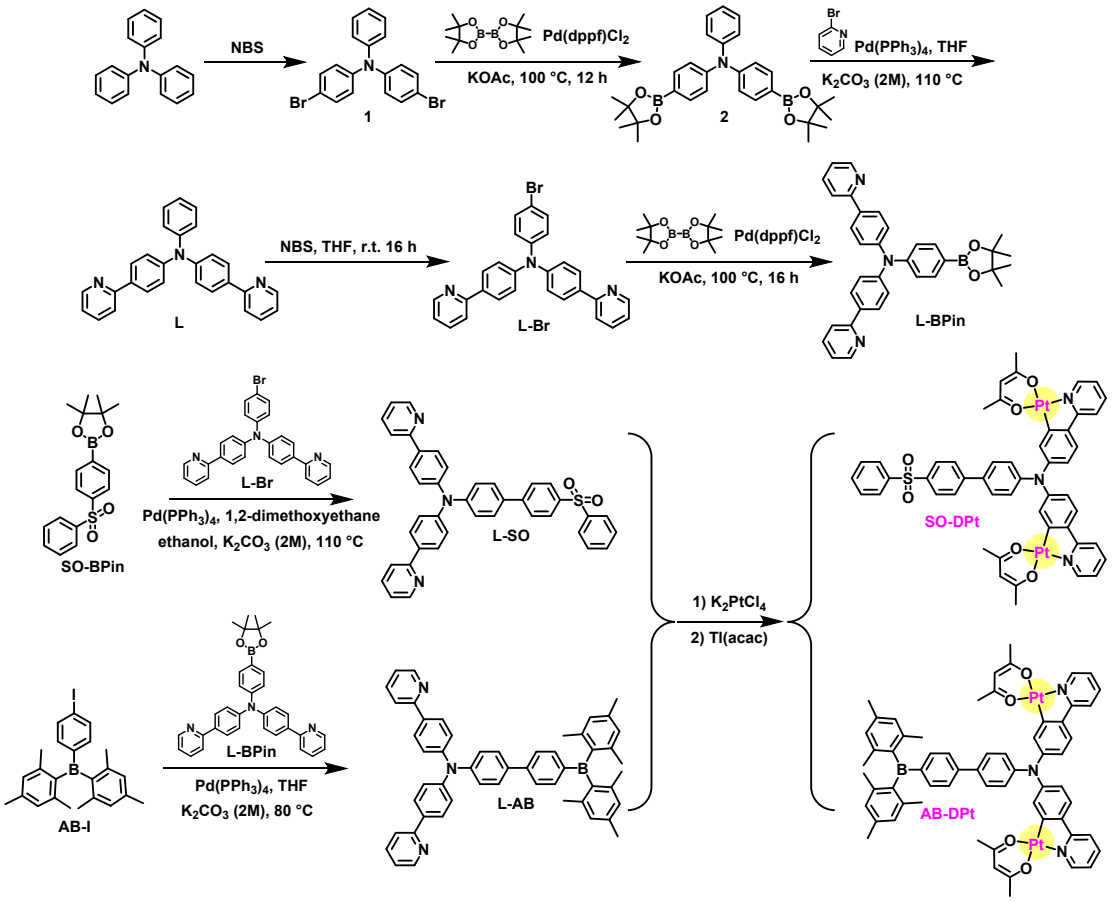
General Information

Commercially available reagents were used directly without further purification. NMR spectra (^{1}H and ^{13}C) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$. Mass spectra were measured on the WATERS I-Class VION IMS Qtof mass spectroscopy. The thermal gravimetric analysis (TGA) was studied with a NETZSCH STA 409C instrument under N_2 at a heating rate of 20 K/min. UV-vis absorption spectra of Pt(II) complexes in CH_2Cl_2 solutions at a concentration of *ca.* 3×10^{-5} M were measured on a Shimadzu UV-2250 spectrophotometer at room temperature. Photoluminescent spectra and lifetimes of Pt(II) complexes in doped films were measured on an Edinburgh Instruments Ltd (FLSP920) fluorescence spectrophotometer. The PLQYs of doped films were tested with an integrating sphere. Cyclic voltammetry curves were recorded with a Princeton Applied Research equipment (PARSTAT 2273) in CH_2Cl_2 solutions using *n*-Bu_4NPF_6 (0.1 M) as the supporting electrolyte and ferrocene/ferrocenium (Fc/Fc^+) couple as the reference. Energy levels of HOMOs (E_{HOMO}) were determined from the onset of oxidation potentials (E_{ox}) according to $E_{HOMO} = -(E_{ox} + 4.8)$ eV and energy levels of LUMOs (E_{LUMO}) were determined from $E_{LUMO} = -(E_{red} + 4.8)$ eV. Theoretical computations based on density functional theory (DFT) and time dependent-DFT (TD-DFT) were carried out for all three dinuclear Pt(II) complexes with Gaussian 09 program. Non-metal atoms of C, H, N, O, S, and B were described by the basis set of B3LYP/6-31G(d, p). The metal atom Pt was described by the B3LYP/LanL2DZ basis set.

OLED Fabrication and Measurements. The ITO glass substrates were pre-cleaned in ultrasonic cleaner with detergent and deionized water. The substrates were treated with UV-O_3 for 30 minutes before use. Then, PEDOT:PSS was spin-coated on the surface of ITO glass substrates to form a hole-injection layer and annealed at 150 °C for 15 min in the air. The hole transport layer was prepared by spin-coating the chlorobenzene solution of PVK on the surface of PEDOT:PSS layer and annealed at 120 °C for 10 min in a glove box. After spin-coating the chlorobenzene solution of Pt(II) complexes and CBP host (1, 2, or 3 wt% doping level) to form the emissive layer, the TmPyPB (40 nm), LiF 1 (nm), and Al (100 nm) layers were vucuum deposited under a pressure of 5×10^{-4} torr. The current density-voltage (*I-V*) curves were measured by a SourceMeter (Keithely 2400). The EL spectra and luminance values were measured with a PR788 spectra colorimeter. The efficiency and spectra tests were carried out under ambient conditions.



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

Compound **1:** To a solution of triphenylamine (2.45 g, 10.0 mmol) in $CHCl_3$ (30 mL) at 0 °C, *N*-bromosuccinimide (NBS, 3.56 g, 20.0 mmol) was added very slowly. Then the mixture was stirred at room temperature overnight. After being washed with water, the organic layer was separated, dried over anhydrous $MgSO_4$, and concentrated with a rotary evaporator. The residual was purified on a silica column using petroleum ether as the eluent to the target product (3.71 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37−7.31 (m, 4H), 7.29−7.24 (m, 2H), 7.08−7.03 (m, 3H), 6.96–6.92 (m, 4H).

Compound **2:** The mixture of compound **1** (2.02 g, 5.0 mmol), bis(pinacolato)diboron (2.86 g, 11.0 mmol), $Pd(dppf)Cl_2$ (0.48 g, 0.66 mmol), and potassium acetate (3.30 g, 33.7 mmol) were added to dioxane (50 mL) and stirred at

100 °C for 12 h under a N_2 atmosphere. After cooled to room temperature, the mixture was poured into water and extracted with CH_2Cl_2 several times. The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated with a rotary evaporator. The residual was purified on a silica column using a mixture of petroleum ether and CH_2Cl_2 as the eluent to give the target product (1.67 g, 67 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.67 (d, *J* = 8.0 Hz, 4H), 7.28−7.24 (m, 3H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 4H), 1.33 (s, 24H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 150.10, 147.02, 135.86, 129.35, 125.58, 124.96, 123.86, 122.71, 83.60, 24.84.

Compound **L:** Under a N_2 atmosphere, the mixture of compound **2** (1.0 g, 2.0 mmol), 2-bromopyridine (0.66 g, 4.2 mmol), and $Pd(PPh_3)_4$ (0.24 g, 0.21 mmol) were stirred in the 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 with a rotary evaporator. The residual was purified on a silica column using a mixture of petroleum ether and CH_2Cl_2 as the eluent to give the related target product (0.69 g, 86.8% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.66 (d, *J* = 4.4 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 4H), 7.75−7.67 (m, 4H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.25−7.17 (m, 8H), 7.09 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 156.99, 149.60, 148.28, 147.15, 136.66, 133.68, 129.40, 127.81, 125.15, 123.85, 123.67, 121.55, 119.95.

Compound **L-Br:** To a solution of compound L (1.0 g, 2.5 mmol) in THF (100 mL) at room temperature, *N*-bromosuccinimide (NBS, 0.46 g, 2.6 mmol) was added very slowly. Then the mixture was stirred overnight. After being washed with water,

the organic layer was separated, dried over anhydrous $MgSO_4$, and concentrated with a rotary evaporator. The residual was purified on a silica column using the mixture of CH_2Cl_2 and ethyl acetate as the eluent to the target product (1.16 g, 97.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.66 (d, *J* = 4.8 Hz, 2H), 7.90 (d, *J* = 8.8 Hz, 4H), 7.75−7.67 (m, 4H), 7.38 (dd, *J* = 5.2, 7.2 Hz, 2H), 7.21−7.18 (m, 6H), 7.05 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 156.78, 149.61,147.74, 146.27, 136.70, 134.18,132.35, 127.93, 126.12, 124.06, 121.68, 119.99, 115.91.

Compound **L-BPin:** The mixture of compound **L-Br** (1.1 g, 2.3 mmol), bis(pinacolato)diboron (0.89 g, 3.5 mmol), Pd(dppf)Cl_2 (0.17 g, 0.23 mmol), and potassium acetate (1.1 g, 11.2 mmol) were added to dioxane (35 mL). The reaction mixture was stirred at 100 ^{o}C for 16 h under a N_2 atmosphere. After cooled to room temperature, the mixture was poured into water and extracted with CH_2Cl_2 several times. The organic layers were combined, dried over anhydrous $MgSO_4$ and concentrated with a rotary evaporator. The residual was purified on a silica column using a mixture of petroleum ether and ethyl acetate as the eluent to give the target product (0.8 g, 66.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.66 (d, *J* = 4.8 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 4H), 7.74−7.67 (m, 6H), 7.23 (d, *J* = 8.8 Hz, 4H), 7.20−7.15 (m, 4H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 156.76, 149.75, 149.49, 147.77, 136.66, 135.91, 134.15, 127.83, 124.52, 122.88, 121.61, 120.00, 83.58, 24.78.

Compounds **SO-BPin** and **AB-I** were synthesized according to our previous studies.[1, 2]

Compound **L-SO:** Under a N_2 atmosphere, the mixture of compound **SO-BPin** (0.42 g, 1.2 mmol), **L-Br** (0.48 g, 1.0 mmol), and $Pd(PPh_3)_4$ (0.07 g, 0.06 mmol) were stirred in the 1,2-dimethoxyethane (20 mL), ethanol (5 mL), and 2 M K_2CO_3 (15 mL) at 110 ^oC 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 with a rotary evaporator. The residual was purified on a silica column using a mixture of petroleum ether and ethyl acetate as the eluent to give the related target product (0.4 g, 65.0% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.67 (d, J = 4.4 Hz, 2H), 7.98 (d, J = 7.2 Hz, 4H), 7.93 (d, J = 8.4 Hz, 4H), 7.76−7.69 (m, 6H), 7.58−7.48 (m, 6H), 7.26−7.12 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 156.83, 149.66, 147.76, 145.45, 139.52, 136.73, 134.48, 133.30, 133.11, 132.03, 129.28, 128.24, 128.18, 128.00, 127.60, 127.30, 124.55, 124.25, 121.75, 120.06.

Compound **L-AB:** Under a N_2 atmosphere, the mixture of **AB-I** (0.4 g, 0.88 mmol), **L-BPin** (0.4 g, 0.76 mmol), and $Pd(PPh_3)_4$ (0.051 g, 0.04 mmol) were stirred in the THF (25 mL) and 2 M K_2CO_3 (15 mL) at 80 ^oC for 5 h. 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 with a rotary evaporator. The residual was purified on a silica column using a mixture of ethyl acetate and CH_2Cl_2 as the eluent to give the related target product (0.25 g, 45.5% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 8.69 (d, J = 4.4 Hz, 2H), 7.95 (d, J = 8.8 Hz, 4H), 7.78−7.71 (m, 4H), 7.63−7.61 (m, 6H), 7.29−7.26 (m, 6H), 7.22 (t, J = 5.6 Hz, 2H), 6.86 (s, 4H), 2.34 (s, 6H), 2.07 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 156.91, 149.63, 147.99, 146.95, 143.57, 140.81, 138.54, 137.17, 136.69,

135.37, 134.06, 128.14, 128.07, 127.90, 126.02, 124.76, 124.20, 121.64, 119.99, 23.47, 21.22.

General procedure for synthesizing dinuclear Pt(II) complexes: Under a N_2 atmosphere, the mixture solution of 2-ethoxyethanol and H_2O (3:1, v/v) (25 mL), organic ligand (1.0 equiv), and K_2PtCl_4 (ca. 2.1 equiv) were stirred at 90 °C for 4 h. After cooled to room temperature, the mixture was extracted with CH_2Cl_2 several times. The collected organic layers were dried over anhydrous $MgSO_4$ and concentrated with a rotary evaporator. Then, the residual was mixed with thallium(I) acetylacetonate (ca. 2.1 equiv) in CH_2Cl_2 (20 mL), and stirred at room temperature overnight under a N_2 atmosphere. Finally, the solvent was removed, and the residual was purified on self-made silica TLC to give the target dinuclear Pt(II) complexes.

SO-DPt (19.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.93 (d, *J* = 5.6 Hz, 2H), 8.01−7.98 (m, 4H), 7.77 (t, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.60−7.50 (m, 7H), 7.39−7.35 (m, 6H), 7.05 (t, *J* = 6.4 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.40 (s, 2H), 1.99 (s, 6H), 1.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 185.62, 184.13, 167.72, 148.03, 147.47, 147.17, 145.92, 141.90, 139.86, 139.40, 139.14, 137.94, 133.06, 132.82, 129.26, 128.18, 127.75, 127.59, 127.17, 125.36, 125.21, 123.99, 120.14, 119.78, 117.89, 102.36, 28.22, 26.96; ESI-MS (*m/z*) theoretical $[M]^+$: 1201.20, found: 1201.20.

AB-DPt (18.9 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.90 (d, *J* = 5.2 Hz, 2H), 7.73 (t, *J* = 7.2 Hz, 2H), 7.58−7.56 (m, 6H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.38−7.32 (m, 6H), 7.01 (t, *J* = 6.0 Hz, 2H), 6.92 (dd, *J* = 6.0, 8.4 Hz, 2H), 6.83 (s, 4H), 5.38 (s, 2H),

2.32 (s, 6H), 2.04 (s, 12H), 1.96 (s, 6H), 1.74 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 185.53, 184.24, 167.84, 165.03, 147.70, 147.15, 144.25, 143.79, 140.80, 139.78, 138.99, 138.46, 137.87, 137.18, 135.08, 128.12, 127.73, 126.03, 125.83, 124.92, 123.93, 119.98, 119.45, 117.82, 102.32, 28.22, 26.96, 23.48, 21.22; ESI-MS (*m/z*) theoretical $[M]^+$: 1309.38, found: 1309.38.

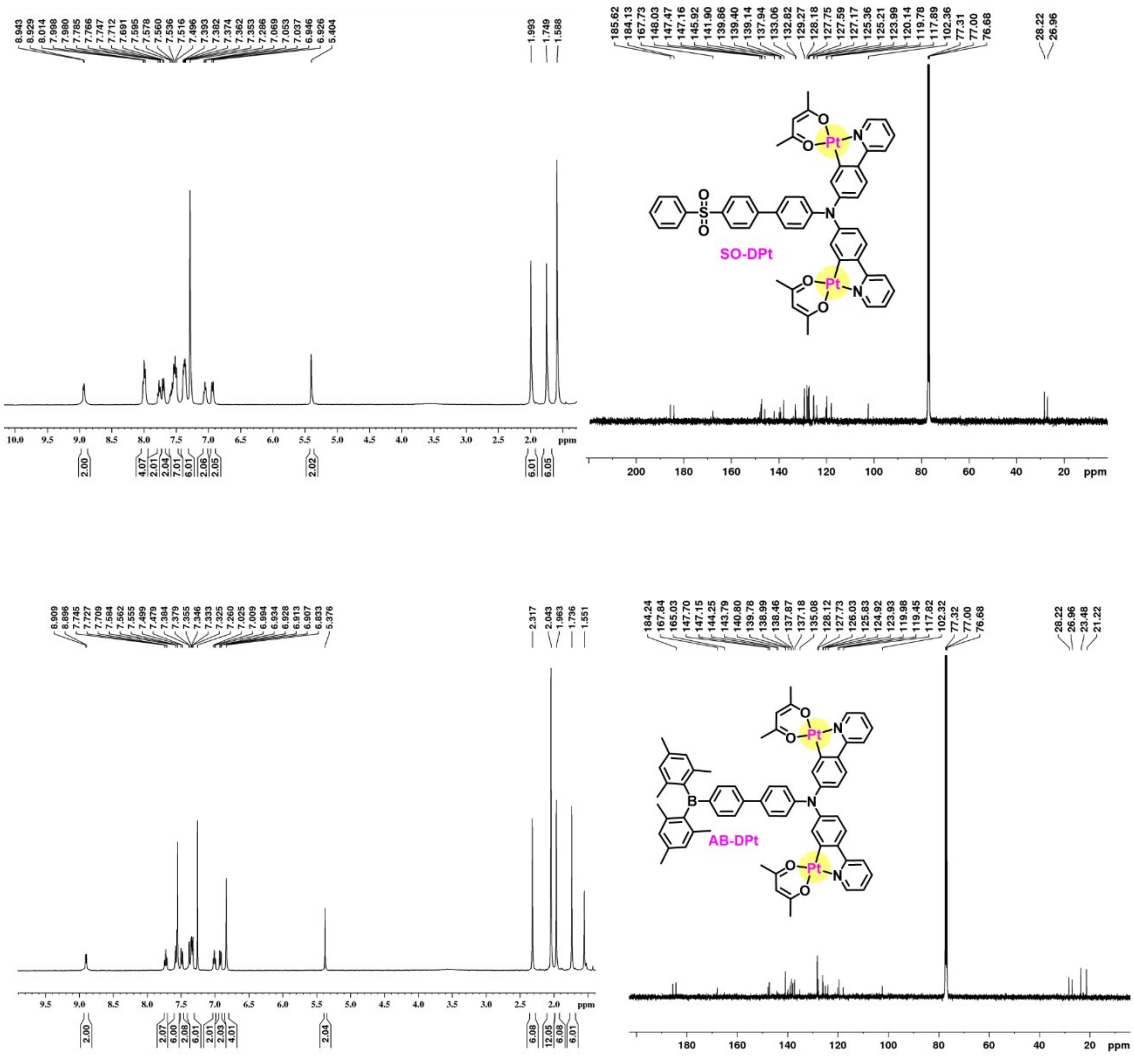


Fig. S1 NMR spectra of **SO-DPt** and **AB-DPt**.

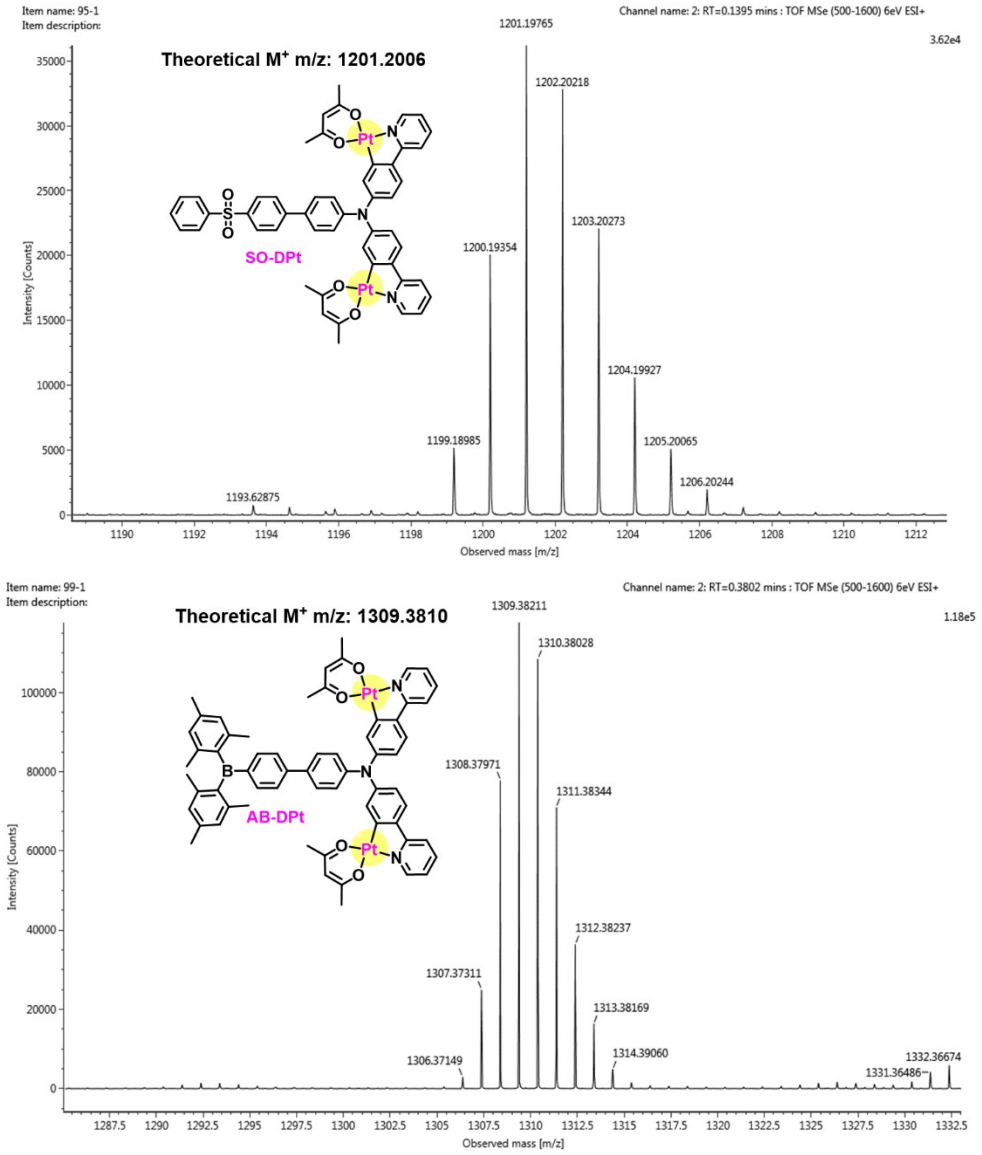


Fig. S2 Mass spectra of **SO-DPt** and **AB-DPt** complexes.

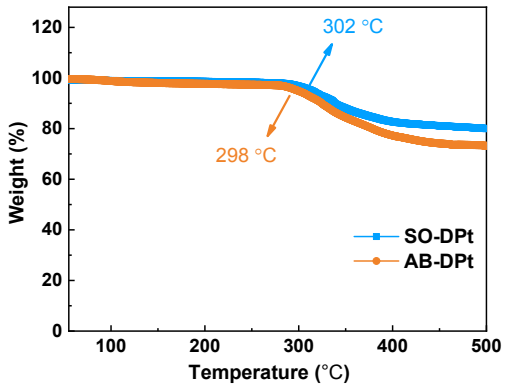


Fig. S3 TGA curves of **SO-DPt** and **AB-DPt**.

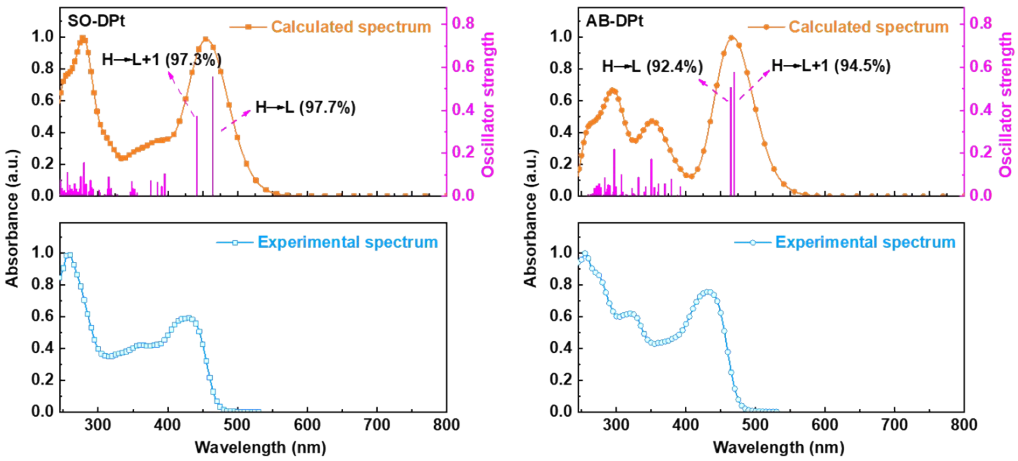


Fig. S4 Caltulation results of absorptions for **SO-DPt** and **AB-DPt**.

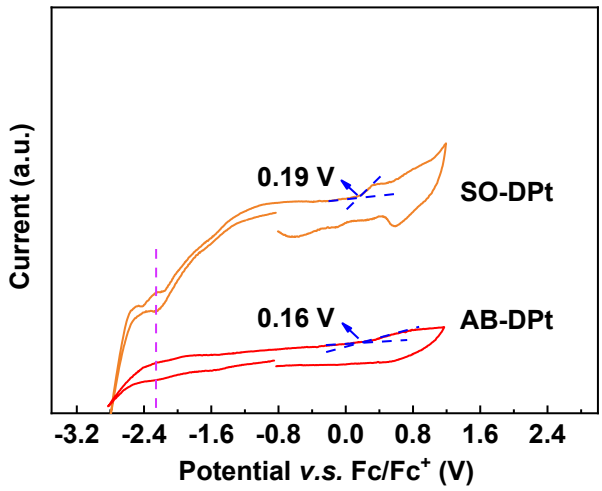


Fig. S5 CV curves of **SO-DPt** and **AB-DPt**.

Table S1 NTO results for **SO-DPt** and **AB-DPt**

	NTOs	Contribution from Pt and ligands to MOs (%)		
SO-DPt		**Pt**	**L-SO**	acac
	Particle	4.62	94.65	0.73
	Hole	3.87	95.71	0.42
AB-DPt		**Pt**	**L-AB**	acac
	Particle	4.61	94.66	0.73
	Hole	3.52	96.08	0.40

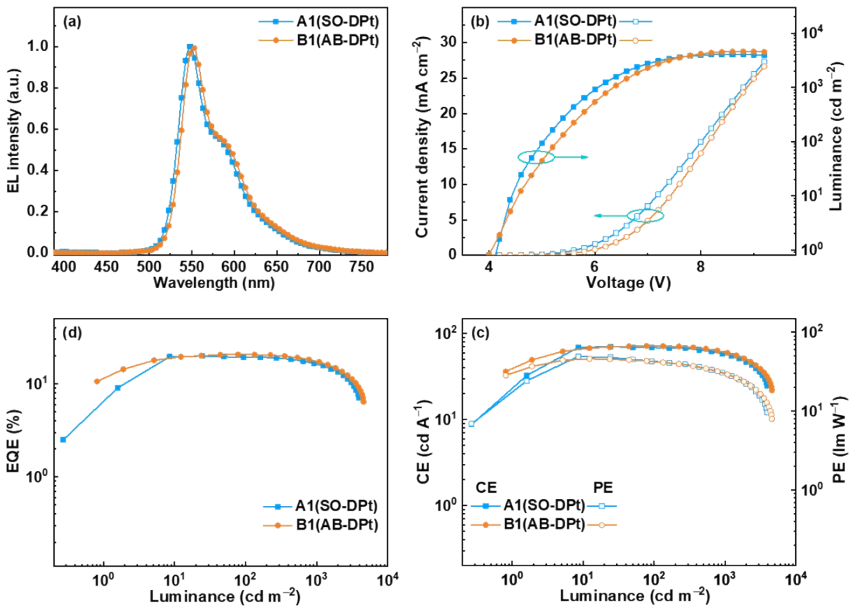


Fig. S6 EL performance of devices A1 and B1: (a) EL spectra, (b) *J*-*V*-*L* characteristics, (c) CE/PE vs luminance, and (d) EQE vs luminance.

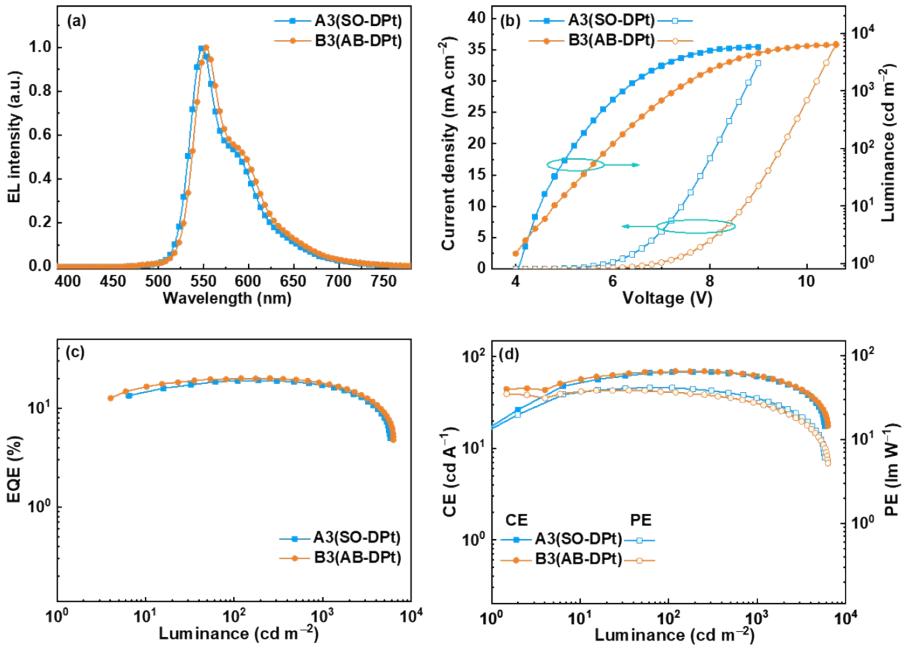


Fig. S7 EL performance of devices A3 and B3: (a) EL spectra, (b) *J*-*V*-*L* characteristics, (c) CE/PE vs luminance, and (d) EQE vs luminance.

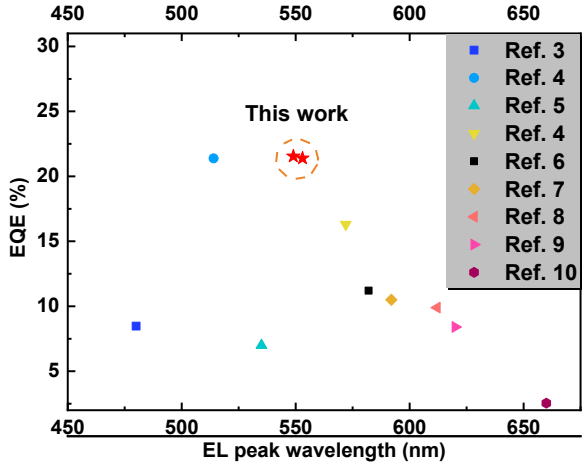


Fig. S8 Summary of EQEs vs EL peaks of OLEDs based on dinuclear Pt(II) complexes.[3-10]

Table S2 EL performance of highly efficienct solution-processed yellow OLEDs

Complex	Center metal	λ_{EL} (nm)	EQE_{max} (%)	CE_{max} (cd/A)	PE_{max} (lm/W)	CIE (x, y)	Reference
SO-DPt	Pt	549	21.54	76.64	52.33	(0.43, 0.56)	This work
AB-DPt	Pt	553	21.39	74.35	48.08	(0.45, 0.54)	This work
2-FBNO	Ir	- [a]	18.9 [b]	65.7 [b]	64.4 [b]	(0.45, 0.54)	11
Complex 4	Pt	550	7.2	7.5	24.0	(0.41, 0.57)	12
Y1	Ir	578	7.55	15.1	- [a]	(0.53, 0.45)	13
$Ir(SFXpy)_3$	Ir	542	12.1	46.2	36.3	(0.45, 0.54)	14
BPyPmIr	Ir	568	18.7	62.8	60.9	- [a]	15
$Ir(TPABPBI)_2(acac)$	Ir	568	15.0	30.0	6.80	(0.507, 0.486)	16
FCF3BNO	Ir	- [a]	22.7 [c]	82.5 [c]	49.2 [c]	(0.43, 0.56)	17
m-LIrpic	Ir	572	17.1	43.9	23.0	(0.528, 0.469)	18
(Et-Cz-BTz)2Ir(EO2-pic)	Ir	~550	19	60	- [a]	(0.467, 0.524)	19
Complex 1	Ir	570	19.20	40.10	- [a]	(0.493, 0.500)	20
PO-01	Ir	564	23 [b]	71 [b]	72 [b]	- [a]	21
$Ir(FP)_3$	Ir	- [a]	12.7	41.7	12.5	- [a]	22
IrST-3F	Ir	580	12.3	27.5	17.3	(0.57, 0.43)	23
PyTPt	Pt	557	16.92	56.74	29.09	(0.47, 0.52)	24

[a] Not report. [b] Recorded at a luminance of 100 cd m^{-2}. [c] Recorded at a luminance of 1000 cd m^{-2}.

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