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PAPER

Synthesis and optoelectronic properties of a carbazole-modified platinum(II) complex in polymer light-emitting devices[†]

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To improve opto-electronic properties and efficiently suppress excimer emission, a phenylpyridine (ppy)-based platinum(II) complex ($C_{16}OCz$ -ppy)Pt(acac) was synthesized and characterized, where $C_{16}OCz$ -ppy is a 2-phenylpyridine derivative appending a carbazole moiety and three hexadecyloxy methyl units in the parent phenylpyridine, and acac is acetylacetone. This carbazole-modified platinum(II) complex exhibited good thermal stability and three times higher photoluminescent quantum yield than its parent (2-phenylpyridine- C^2 , N)(2,4-pentanedionato-O,O)platinum(II) complex [(ppy)Pt(acac)]. Single-emissive-layer polymer light-emitting devices using (C₁₆OC₇-ppy)Pt(acac) as dopant and a blend of poly(N-vinylcarbazole) and 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1, 3.4-oxadiazole as host matrix presented a maximum current efficiency of $1.51 \text{ cd } \text{A}^{-1}$, which was $1.5 \text{ cd } \text{A}^{-1}$ times higher than that from the (ppy)Pt(acac)-doped device with the same device structure. Little excimer emission and minor aggregation emission were observed in the $(C_{16}OC_7-ppy)$ Pt(acac)-doped PLEDs at different dopant concentrations and applied voltages. This work indicates that introducing a carbazole and three hexadecyloxy methyl groups into the planar platinum(II) complex can reduce molecular aggregation and excimer emissions, thus resulting in high luminance and stable EL spectra in comparison with the parent (ppy)Pt(acac).

Introduction

Phosphorescent cyclometallated complexes have received significant attention for their potential applications in organic light emitting diodes and solar cells.^{1,2} The strong spin-orbital coupling effect of the heavy-metal atom core allows for efficient intersystem crossing from the singlet to the triplet excited state in these cyclometallated complexes. As a result, these cyclometallated complexes can utilize both singlet and triplet excitons for the emission, and to a great extent, theoretically present a 100% internal quantum efficiency.

Since the pioneering work by Thompson,3 cyclometallated complexes, such as Ir(III) and Pt(II) complexes based on 2phenylpyridine (ppy) ligand, have been extensively studied as phosphorescent materials.⁴ Among these cyclometallated complexes, the Pt(II) complexes have square-planar geometry and often exhibit a tendency to form aggregates or excimers through axial coordination, resulting in lower emission efficiency and broad red-shifted emissions. In order to suppress aggregation and excimer emissions for platinum(II) complexes, various strategies

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have been developed. For example, Jabbour et al. reported a class of platinum(II) complexes with polyhedral oligomeric silsesquioxane (POSS) moiety, which presented a reduced interaction and diminished concentration quenching.5 The groups of Wong and Lin incorporated multifunctional bulky chromophores into a platinum complex by conjugation linkage and exhibited good device performance.6,7

To our best knowledge, modifying ppy-type ligand by conjugation linkage, to some extent, can suppress intermolecular interaction and reduce the excimer emission. However, extension of the conjugated π -system readily results in significantly redshifted emission for its platinum(II) complex.8 In light of this consideration, we have designed a modified ppy-based platinum(II) complex (C₁₆OCz-ppy)Pt(acac), which appends a carbazole moiety and three hexadecyloxy methyl substituted groups in the parent 2-phenylpyridine. As shown in Scheme 1, the carbazole unit, which is widely used as hole-transporting and emissive materials for OLEDs,9 is attached into 4-position of the phenyl ring in 2-phenylpyridine via a non-conjugated linkage of a hexyloxy group. We expect that the introduced carbazole by the nonconjugated linkage can improve the hole-transporting property of its platinum(II) complex. Three hexadecyloxy methyl groups attached in the 3,6-positions of carbazole and 4-position of the pyridine ring are expected to improve the dispersibility in the host matrix. The co-effect of carbazole and long-chain hexadecyloxy methyl groups is able to suppress the formation of aggregation

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a)NaBH₄, toluene, ethanol; b)NaH, DMF, C₁₆H₃₃Br; c)1,6-dibromohexane, K₂CO₃, acetone; d)Carbazole, KOH(50%), toluene; e)POCl₃, ClCH₂CH₂Cl, DMF; f)KOAc, PdCl₂(dppf), DMSO; g)Pd(PPh₃)₄, THF, K₂CO₃(2M); h)K₂PtCl₄, 2-ethoxyethanol, H₂O, 80 °C; i)Acetylactone, 2-ethoxyethanol, Na₂CO₃, 100°C.

Scheme 1 Synthetic route of the (C₁₆OCz-ppy)Pt(acac) and (ppy)Pt(acac) complexes.

and excimer in solid state for its platinum(II) complex. Therefore, this carbazole-modified platinum(II) complex is suggested to exhibit better photo-physical and electroluminescent properties. To confirm this speculation, simple single-emissive-layer (SEL) polymer light-emitting devices (PLEDs) were fabricated by a solution-process using ($C_{16}OCz$ -ppy)Pt(acac) or (ppy)Pt(acac) as dopant and a blend of poly(*N*-vinylcarbazole) (PVK) and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) as matrix. Improved EL performance and decreased aggregation and excimer emissions were obtained in the ($C_{16}OCz$ -ppy)Pt(acac)-doped devices.

Results and discussion

Synthesis

Scheme 1 outlines the synthetic route of the platinum(II) complexes. The carbazole-modified phenylpyridine derivative of $C_{16}OCz$ -ppy was prepared in mild conditions by a Suzuki coupling reaction with a high yield over 80%. Both cyclometallated plat-

inum(II) complexes were synthesized by two-step procedures with a moderate yield of about 40% referring to previous reports for (N^C)Pt(O^O) complexes.^{3b,10} The resulting platinum complexes were characterized by ¹H NMR, ¹³C NMR and elemental analysis to confirm their well-defined chemical structures.

Thermal properties

The thermal properties of the platinum(II) complexes was characterized by thermal gravimetric analysis (TGA) under a nitrogen atmosphere. The recorded TGA graph is shown in Fig. S1 (ESI[†]) and the TGA data are listed in Table 1. The decomposition temperature (T_d) values with a 5% weight loss are 283 and 280 °C for (ppy)Pt(acac) and (C_{16} OCz-ppy)Pt(acac), respectively. The 5% weight loss of the platinum(II) complexes is mostly related to the dissociation of the ancillary acetylacetone ligand.⁷ This indicates that the carbazole-modified platinum(II) complex has almost identical thermal stability to its parent platinum complex. Incorporating a carbazole unit by non-conjugated linkage and attaching three hexadecyloxy methyl groups into the ppy ligand

 Table 1
 UV-vis absorption, PL and thermal properties of the platinum(II) complexes

Compound	$\lambda_{\rm abs}/{ m nm}^a~(arepsilon_{ m max}/{ m dm}^3~{ m mol}^{-1}~{ m cm}^{-1})^b$	$\lambda_{\rm em}({\rm DCM})^c/{\rm nm}$	$\lambda_{\rm em}({\rm film})^d/{\rm nm}$	$arPsi_{ m em}$	$T_{d}^{e}/^{\circ}C$
(ppy)Pt(acac)	278 (20825), 314 (9793), 362 (5554), 399 (2524)	484, 515	500, 528, 570	0.15	283
(C ₁₆ OCz-ppy)Pt(acac)	269 (42915), 299 (29583), 351 (9347), 401 (3758)	500, 528	503, 534, 574	0.48	280

^{*a*} Measured in DCM at RT at a concentration of 10⁻⁵ mol L⁻¹. ^{*b*} Molar extinction coefficient. ^{*c*} Measured in DCM at RT ($\lambda_{ex} = 400$ nm). ^{*d*} Evaluated in the neat films at RT. ^{*e*} 5% weight-loss temperature.

has only a very minor effect on the thermal stability of its platinum(II) complex.

UV-vis absorption properties

The UV-vis absorption spectra of the platinum(II) complexes were measured in dichloromethane (DCM) solution at room temperature (RT) and are depicted in Fig. 1. The pertinent data are collected in Table 1. A UV-vis absorption spectrum with four typical absorption bands is observed in the carbazole-modified platinum(II) complex (C₁₆OCz-ppy)Pt(acac). The intense highlying absorption bands at about 269 and 299 nm are assigned to the spin-allowed π - π * transitions of the ppy and carbazole units, respectively. The weak low-lying absorption bands at about 351 and 401 nm are attributed to the spin-allowed singlet metal-toligand charge transfer (1MLCT) and spin-forbidden triplet metalto-ligand charge transfer (³MLCT) transitions, to a certain extent, together with the contribution of the triplet intraligand (³IL) π - π * transition and ligand-to-ligand charge transfer (LLCT) transition, respectively. Compared to the parent (ppy)Pt(acac), (C₁₆OCzppy)Pt(acac) exhibits an additional absorption band from the carbazole unit and enhanced molar absorption coefficient. The enhanced UV absorption is considered to be available to improve the energy-transfer efficiency from the host matrix to the platinum complex in the PLEDs.



Fig. 1 UV-vis absorption spectra of platinum(II) complexes in DCM solution $(1 \times 10^{-5} \text{ M})$ at RT.

Photoluminescent properties

The photoluminescent (PL) spectra of the platinum(II) complexes in DCM and their neat films are shown in Fig. 2. For comparison, the corresponding data are summarized in Table 1. Intense dual vibronically structured emissive peaks at 500 and 528 nm are observed for ($C_{16}OCz$ -ppy)Pt(acac) in DCM solution (10^{-5} M) under opto-excitation at RT. This inherent structured emission is attributed to a mixed emission from MLCT and LC state.3b Compared to (ppy)Pt(acac), the carbazole-modified ($C_{16}OCz$ ppy)Pt(acac) exhibits a 16 nm bathochromic-shifted PL spectra due to the effect of the introduced carbazole and alkyloxy methyl groups. With increasing concentrations from 10^{-5} to 10^{-3} M, two low-lying emission bands at about 550 and 610 nm are displayed and gradually enhanced for (ppy)Pt(acac). On the contrary, (C₁₆OCz-ppy)Pt(acac) exhibits weaker low-lying emission bands with little change in these conditions. The detailed concentration dependent emission characteristics for the two complexes are shown in Fig. S2 and S3 (ESI[†]). The low-lying emission bands are considered to arise from aggregation and excimer emissions based on the literature.46,11 Therefore, the aggregation and excimer emissions are effectively suppressed for (C₁₆OCz-ppy)Pt(acac) in DCM solution. On the other hand, a more intense broad lowlying emission band at around 540 nm is shown in both platinum complex-based thin films, besides their inherent structured emission. This phenomenon was previously also observed by other groups.^{5,11a,12} However, (C₁₆OCz-ppy)Pt(acac) provides relatively weak low-lying emission compared to the parent (ppy)Pt(acac) in the thin film. This implies that appending carbazole and hexadecyloxy methyl units into the platinum complex, to some extent suppresses aggregation induced emission in the neat films under opto-excitation due to the steric effect of the pendent groups.

In order to further study the influence of carbazole and hexadecyloxy methyl units on PL, the PL quantum yields (Φ_{em}) of both platinum(II) complexes were measured. The measured Φ_{em} values were 0.15 and 0.48 for (ppy)Pt(acac) and (C₁₆OCz-ppy)-Pt(acac) in DCM, respectively. Obviously, (C₁₆OCz-ppy)Pt(acac) exhibits a triplet Φ_{em} level higher than (ppy)Pt(acac). This means that (C₁₆OCz-ppy)Pt(acac) has inhibited aggregation and excimer emissions owing to the steric effect of the pendent units under opto-excitation. Therefore, introducing carbazole and hexadecyloxy methyl units into the platinum complex leads to improved PL efficiency in DCM.

Electrochemical properties

Cyclic voltammetry (CV) was performed using ferrocene as an internal standard to investigate the redox properties of the platinum(II) complexes and estimate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels. The CV results showed that both platinum(II) complexes displayed irreversible oxidation waves (E_{ox}) at 0.48 and 0.52 V vs. Fc/Fc⁺. (C₁₆OCz-ppy)Pt(acac) had a decreased E_{ox} level compared to (ppy)Pt(acac). According to the reported literature, the oxidations originate from the center metal,³⁶ and the irreversible phenomenon is due to rapid solvolysis of the resultant platinum complex species. The reduction potential

Table 2	Electrochemical	properties	of the platinum(II)	complexes
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Compound	E_{g}^{a}/eV	$E_{\rm ox}/{\rm eV}$	$E_{\rm red}{}^{b}/{ m eV}$	$E_{\rm HOMO}^{c}/{\rm eV}$	$E_{\rm LUMO}^{d}/{\rm eV}$
(ppy)Pt(acac)	2.93	0.52	-2.41	-5.32	-2.39
(C ₁₆ OCz-ppy)Pt(acac)	2.92	0.48	-2.44	-5.28	-2.36

^{*a*} Calculated from the optical absorption spectra. ^{*b*} $E_{red} = E_{ox} - E_g$. ^{*c*} $E_{HOMO} = -(4.80 + E_{ox}) \text{ eV.}$ ^{*d*} $E_{LUMO} = -(4.80 + E_{red}) \text{ eV.}$



Fig. 2 PL spectra of platinum(II) complexes (a) in DCM solution $(1 \times 10^{-5} \text{ and } 1 \times 10^{-3} \text{ M})$ and (b) in neat films at RT ($\lambda_{ex} = 400 \text{ nm}$).



Fig. 3 EL spectra of (a) (ppy)Pt(acac)- and (b) (C_{16} OCz-ppy)Pt(acac)- doped devices at dopant concentrations from 1 to 8 wt% under the applied voltage of 10 V.

 $(E_{\rm red})$ can be estimated by the formula of $E_{\rm ox} = E_{\rm g} + E_{\rm red}$, where $E_{\rm g}$ is the optical band gap estimated by the threshold of absorption spectra. On the basis of $E_{\rm ox}$ and $E_{\rm red}$ values, we can calculate the HOMO and LUMO energy levels ($E_{\rm HOMO}$ and $E_{\rm LUMO}$) of the platinum(II) complexes based on the following formula, $E_{\rm HOMO} = -(4.80 + E_{\rm ox})$ eV, $E_{\rm LUMO} = -(4.80 + E_{\rm red})$ eV.¹³ The obtained CV data are summarized in Table 2. It is obvious that ($C_{\rm 16}$ OCz-ppy)Pt(acac) exhibits somewhat increased $E_{\rm HOMO}$ and $E_{\rm LUMO}$ values compared to (ppy)Pt(acac). Therefore, incorporating carbazole and hexadecyloxy methyl units onto the ppy-based ligand can raise the HOMO and LUMO energy levels of its platinum(II) complex.

Electroluminescent properties

To illustrate the electrophosphorescent performance of both platinum(II) complexes, SEL devices with a configuration of ITO/PEDOT:PSS (50 nm)/Pt(II) complex (x wt%) +

PVK:PBD (45 nm)/Ba (4 nm)/Al (150 nm) were fabricated by a spin-coating process, whereas ITO acts as the anode, poly(ethylendioxythiophene)/poly(styrene sulfonic acid) (PE-DOT:PSS) acts as the hole-injection layer, and Ba/Al is employed as a cathode. The emitting layer consists of the phosphorescent Pt(II) complex and a blend of PVK and PBD. The weight ratio of PBD is 30% in the blend of PVK and PBD. Dopant concentrations of platinum(II) complexes were varied from 1 to 8 wt%. Fig. 3 displays EL spectra of the (C₁₆OCz-ppy)Pt(acac)- and (ppy)Pt(acac)doped devices at dopant concentrations from 1 to 8 wt%. Four distinct peaks at about 430, 500, 528 and 563 nm are observed in the EL spectra of the (ppy)Pt(acac)-doped devices, while the (C₁₆OCz-ppy)Pt(acac)-doped devices exhibit three distinct EL peaks at about 430, 502 and 534 at dopant concentrations from 1 to 8 wt%. Among these EL peaks, the high-lying one at about 430 nm is attributed to PVK and significantly decreased with increasing dopant concentrations from 1 to 8 wt%. The mediumlying peaks at about 501 \pm 1 nm and 531 \pm 3 nm are assigned to the emission from the isolated molecular platinum(II) complex. The low-lying one at 563 nm results from aggregation emission, together with some contribution from excimer emission of the platinum(II) complex. In general, differing degree of aggregation can change the relative intensity between the monomer and aggregation emissions, the stronger the aggregation, the broader the EL spectra become.^{7,9a,14} We note that the (ppy)Pt(acac)-doped devices exhibit a more intense and broader low-lying emission band than the (C₁₆OCz-ppy)Pt(acac)-doped devices at different dopant concentrations and driving voltages. This indicates that introducing carbazole and hexadecyloxy methyl groups onto the platinum(II) complex can reduce the intermolecular π -stacking, so inhibiting aggregation and excimer emissions under an electrical field.

In order to study EL spectra stability of both platinum(II) complex-doped devices, the EL spectra of the (ppy)Pt(acac)and ($C_{16}OCz$ -ppy)Pt(acac)-doped devices are shown in Fig. 4 and 5, respectively, at different dopant concentrations and applied voltages. It is obvious that EL spectra are sensitive to the dopant concentrations and applied voltages for all these devices. With increasing applied voltages, the intensity of the low-lying emission significantly increases. On the other hand, minor emission from PVK is also observed in the devices at 1, 2 and 4 wt% dopant concentrations, but almost disappeared at 8 wt% dopant concentration. The results clearly demonstrate that the aggregation emission (even excimer emission) of the planar platinum(II) complexes can be effectively inhibited by modification of carbazole and hexadecyloxy methyl units.

The current density-voltage-luminance (J-V-L) characteristics of the (ppy)Pt(acac)- and (C₁₆OCz-ppy)Pt(acac)-doped PLEDs at various dopant concentrations from 1 to 8 wt% are shown in Fig. S4 (ESI†) and Fig. 6. With increasing dopant concentrations, these devices exhibit an increased brightness and reduced turn-on voltage. The maximum brightness of 733 cd m⁻² and current efficiency of 1.5 cd A⁻¹ were obtained in the (C₁₆OCz-ppy)Pt(acac)-doped PLEDs at 8 wt% doping concentration. This current efficiency level is 1.5 times higher than that from the (ppy)Pt(acac)-doped device with the same device configuration. Therefore, introducing carbazole and three hexadecyloxy methyl units into the parent (ppy)Pt(acac) can also improve the device performance.

Conclusion

In summary, we obtained a carbazole-modified green-emitting platinum(II) complex of ($C_{16}OCz$ -ppy)Pt(acac). Significantly increased PL quantum efficiency in DCM and current efficiency in the SEL PLEDs were achieved for the ($C_{16}OCz$ -ppy)Pt(acac) compared with the corresponding levels for (ppy)Pt(acac). Furthermore, the aggregation and excimer emissions were effectively suppressed in the ($C_{16}OCz$ -ppy)Pt(acac)-doped devices at different dopant concentrations and applied voltages. This work suggests that introducing a carbazole moiety by non-conjugated linkage and further attaching three hexadecyloxy methyl groups into the cyclometallated ligand are beneficial to reduce the aggregation and excimer emissions and improve the EL performance for the corresponding platinum(II) complex.

Experimental

General information

The solvents were carefully dried and distilled by standard procedures before use. All chemicals, unless otherwise stated, were obtained from commercial sources and used as received. The Suzuki coupling and cyclometallated reactions were car-



Fig. 4 EL spectra of the (ppy)Pt(acac)-doped devices at different dopant concentrations and applied voltages.



Fig. 5 EL spectra of the (C_{16} OCz-ppy)Pt(acac)-doped devices at different dopant concentrations and applied voltages.



Fig. 6 Current density-voltage-luminance (J-V-L) curves of the $(C_{16}OCz$ -ppy)Pt- (acac)-doped device at different dopant concentrations.

ried out in inert gas atmosphere and monitored by thin-layer chromatography (TLC). NMR spectra were recorded on a Bruker Dex-400 (MHz) NMR instrument using CDCl₃ or DMSO d_6 as a solvent and tetramethylsilane as an internal standard. Elemental analysis was performed on a Harrios elemental analysis instrument. UV absorption spectroscopy was measured by a Shimadzu UV-265 spectrometer. Photoluminescent (PL) spectra were recorded on Perkin-Elmer LS50B luminescence spectrometer. The emission quantum yields were determined by the optical dilution method using (ppy)Pt(acac) as a standard in 2-MeTHF $(\Phi = 0.15)$.^{3b} For electrochemical measurements a conventional three-electrode configuration, consisting of a platinum working electrode, a Pt-wire counter electrode, and a calomel electrode reference electrode, was used. The supporting electrolyte was 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate (Bu₄NPF₆) in DCM. Electroluminescence (EL) spectra were recorded with an Instaspec IV CCD system (Oriel). Luminance was measured with

a Si photodiode and calibrated by using a PR-705 Spectrascan spectrophotometer (Photo Research).

Compounds 1, 2 and 3 were synthesized following literature methods.15 The cyclometallated platinum(II) complexes were also synthesized according to the literature.3b,10 A mixture of K₂PtCl₄, C^AN-chelate ligand C₁₆OCz-ppy (or ppy) (2.5 equiv.), 2-ethoxyethanol and distilled water (3:1, v/v) was stirred under nitrogen atmosphere at 80 °C for 24 h. After being cooled to RT, the resulting precipitate was collected by filtration and washed successively with water, ethanol and hexane. The dried chlorobridged dimer was obtained. This dimer was suspended in 2ethoxyethanol and treated with acetylacetone (2.5 equiv.) and anhydrous Na₂CO₃ (10 equiv.). The mixture was stirred under nitrogen atmosphere at 100 °C for 16 h. After cooling to RT, the resulting precipitate was filtered off and washed with water, ethanol and hexane, respectively. The residue was purified by flash chromatography on silica gel using dichloromethane/hexane(1:1, v/v) as eluent.

Syntheses

9-(6-(4-Bromophenoxy)hexyl)-9*H***-carbazole (4).** A mixture of compound **3** (7.5 g, 22.32 mmol), carbazole (6.5 g, 38.90 mmol) and NaOH (50%, 80 mL) in 80 mL toluene was heated to reflux under stirring for 20 h. After being cooled to RT, the mixture was filtered and the solid was washed three times by DCM. The combined solution was then concentrated under reduced pressure. The residue was purified by silica gel column chromatography using dichloromethane–petroleum ether (1:2; v/v) as eluent to provide a white solid (6.5 g, 69.0%). ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 8.10 (d, J = 7.80 Hz, 2H), 7.47–7.39 (m, 4H), 7.34 (d, J = 8.64 Hz, 2H), 7.25–7.21 (m, 2H), 6.71 (d, J = 8.68 Hz, 2H), 4.32 (t, J = 7.10 Hz, 2H), 3.85 (t, J = 6.36 Hz, 2H), 1.93–1.70 (m, 4H), 1.49–1.44 (m, 4H).

3,6-Diformoxyl-9-(6-(4-bromophenoxy)hexyl)-9*H***-carbazole** (5). Compound 5 was synthesized by Vilsmeier formylation reaction according to the reported literature¹⁶ as a yellow solid in a yield of 43.5%. ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 10.14 (s, 2H), 8.68 (s, 2H), 8.08 (d, *J* = 8.64 Hz, 2H), 7.55 (d, *J* = 8.56 Hz, 2H), 7.35 (d, *J* = 8.76 Hz, 2H), 6.71 (d, *J* = 8.60 Hz, 2H), 4.42 (t, *J* = 6.94 Hz, 2H), 3.87 (t, *J* = 5.90 Hz, 2H), 1.99–1.26 (m, 8H).

3,6-Dihydroxymethyl-9-(6-(4-bromophenoxy)hexyl)-9*H***-carbazole (6).** Compound **6** was synthesized according to the reported literature¹⁵ as a white solid in a yield of 86.3%. ¹H NMR (400 MHz, DMSO, TMS), δ (ppm): 8.10 (s, 2H), 7.50 (d, *J* = 8.36 Hz, 2H), 7.39–7.36 (m, 4H), 6.80 (d, *J* = 8.66 Hz, 2H), 5.11 (t, *J* = 5.54 Hz, 2H), 4.62 (d, *J* = 5.47 Hz, 4H), 4.35 (t, *J* = 6.35 Hz, 2H), 3.85 (t, *J* = 6.06 Hz, 2H), 1.76–1.22 (m, 8H).

3,6-Dihexadecyloxymethyl-9-(6-(4-bromophenoxy)hexyl)-9*H***-carbazole (7).** Compound 7 was synthesized according to the reported literature¹⁵ as a white solid in a yield of 46.4%. ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 8.05 (s, 2H), 7.44 (d, *J* = 8.40 Hz, 2H), 7.35 (d, *J* = 8.48 Hz, 4H), 6.72 (d, *J* = 8.77 Hz, 2H), 4.67 (s, 4H), 4.31 (t, *J* = 6.85 Hz, 2H), 3.86 (t, *J* = 6.21 Hz, 2H), 3.52 (t, *J* = 6.62 Hz, 4H), 1.92–1.63 (m, 8H), 1.58–1.28 (m, 56H), 0.88 (t, *J* = 6.59 Hz, 6H).

3,6-Dihexadecyloxymethyl-9-(6-(4-(4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)phenoxy)hexyl)-9H-carbazole (8). A nitrogenflushed three-neck round bottom flask was charged with compound 7 (2.8 g, 3.05 mmol), bis(pinacolato)diboron (0.85 g, 3.36 mmol), potassium acetate (0.90 g, 9.16 mmol), Pd(dppf)Cl₂(CH₂Cl₂) adduct, (74.7 mg, 0.09 mmol), and dimethyl sulfoxide (DMSO, 60 mL), respectively. The mixture was bubbled with nitrogen for 15 min, and stirred at 80 °C for 24 h. After being cooled to RT, the mixture was poured into ice-water (200 mL) and extracted with DCM. The combined organic layer was dried over anhydrous MgSO4 and then concentrated under reduced pressure. The residue was purified by silica gel column chromatography using ethyl acetate-petroleum ether (1:15, v/v) as the eluent to give a white solid (1.27 g, 43.2%). ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 8.05 (s, 2H), 7.73 (d, J = 8.37 Hz, 2H), 7.44 (d, J =8.33 Hz, 2H), 7.36 (d, J = 8.39 Hz, 2H), 6.85 (d, J = 8.41 Hz, 2H), 4.67 (s, 4H), 4.31 (t, J = 6.90 Hz, 2H), 3.94 (t, J = 6.35 Hz, 2H), 3.51 (t, J = 6.66 Hz, 4H), 1.89-1.57 (m, 8H), 1.49-1.37 (t, 56H), 1.33 (s, 12H), 0.88 (t, J = 6.69 Hz, 6H).

3,6-Bis(hexadecyloxymethyl)-9-(6-(4-(5-(hexadecyloxymethyl)pyridin-2-yl)phenoxy)hexyl)-9*H***-carbazole (9). A mixture of 2** (0.48 g, 1.2 mmol), **8** (1.27 g, 1.3 mmol), tetrakis(triphenylphosphine)palladium (90 mg), K_2CO_3 (2 M, 10 mL), and THF (30 mL) was refluxed for 40 h under a nitrogen atmosphere. After being cooled to RT, the mixture was extracted with DCM. The combined organic layer was dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel column chromatography using ethyl acetate–petroleum ether (1 : 7, v/v) as eluent to obtain a yellow liquid (1.11 g, 80.3%). ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 8.59 (s, 1H), 8.05(s, 2H), 7.92 (d, *J* = 8.58 Hz, 2H), 7.72– 7.64 (m, 2H), 7.45–7.33 (m, 4H), 6.95 (d, *J* = 8.62 Hz, 2H), 4.67 (s, 4H), 4.53 (s, 2H), 4.32 (t, *J* = 6.88 Hz, 2H), 3.97 (t, *J* = 6.24 Hz, 2H), 3.51 (t, *J* = 5.21 Hz, 6H), 1.91–1.60 (m, 15H), 1.59–1.25 (m, 77H), 0.88 (t, *J* = 6.60 Hz, 9H).

(**ppy**)**Pt(acac).** (ppy)Pt(acac) was synthesized by the method described above for the general synthesis of the platinum complex. Yellow solid (40.2%). ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 9.00 (d, J = 5.60 Hz, 1H), 7.80 (t, J = 7.61 Hz, 1H), 7.62 (t, J = 6.39 Hz, 2H), 7.45 (d, J = 7.54 Hz, 1H), 7.22 (t, J = 7.23 Hz, 1H), 7.12–7.09 (m, 2H), 5.48 (s, 1H), 2.02 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, TMS), δ (ppm): 185.79, 184.18, 168.47, 147.34, 144.64, 138.98, 138.05, 130.65, 129.26, 123.55, 122.97, 121.11, 118.29, 102.43, 28.22, 27.06. Anal. Calc. for C₁₆H₁₅NO₂Pt: C 42.86, H 3.37, N 3.12. Found: C 43.05, H 3.42, N 3.10%.

(C₁₆OCz-ppy)Pt(acac). Yellow-orange solid (31.5%). ¹H NMR (400 MHz, CDCl₃, TMS), δ (ppm): 8.86 (s, 1H), 8.06 (s, 2H), 7.74 (d, J = 8.14 Hz, 1H), 7.46 (d, J = 8.32 Hz, 3H), 7.35 (t, J = 8.56 Hz, 3H), 7.11 (s, 1H), 6.65–6.63 (m, 1H), 5.47 (s, 1H), 4.68 (s, 4H), 4.53 (s, 2H), 4.32 (t, J = 6.80 Hz, 2H), 4.06 (t, J = 6.06 Hz, 2H), 3.52 (t, J = 6.56 Hz, 6H), 2.02 (s, 3H), 2.00 (s, 3H), 1.93–1.65 (m, 15H), 1.60–0.88 (m, 77H), 0.89 (t, J = 6.49 Hz, 9H). ¹³C NMR (100 MHz, CDCl₃, TMS), δ (ppm): 185.71, 183.98, 167.33, 159.58, 145.83, 141.11, 140.40, 137.27, 137.17, 130.99, 129.12, 126.03, 124.45, 122.79, 120.08, 117.20, 115.08, 110.57, 108.55, 102.40, 73.52, 70.92, 70.22, 69.63, 67.45, 43.10, 31.90, 29.86, 29.73, 29.68, 29.63, 29.57, 29.53, 29.47, 29.33, 29.17, 28.90, 28.21, 27.11, 27.00, 26.26, 26.16, 25.92, 22.65, 14.04. Anal. Calc. for C₈₅H₁₃₆N₂O₆Pt: C 69.12, H 9.28, N 1.90. Found: C 69.20, H 9.31, N 1.94%.

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