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In order to develop solution-processable organic light-emitting diodes (OLEDs) with improved optical properties, PtAu₃ heterometallic cluster complexes that exhibit narrow-band emission spectra were prepared through a judicious molecular design. The brightly emissive PtAu₃ complexes with robust chemical and thermal stability (> 290 °C) show photoluminescent quantum yields (PLQY) of 80.5%–90.1% in doped films. The dihedral angle between the plane of aromatic acetylide and platinum(II) coordination square plane exerts dramatic influence on the full width at half maximum (FWHM) of phosphorescent emission, in which the better the co-planarity, the narrower the FWHM. Theoretical studies suggest that the more involvment of acetylide-to-Pt ³LMCT state is in favor of attaining narrow-band emission. Solution-processed OLEDs based on narrow-band green emitter gives a maximum current efficiency (CE) of 38.7 cd A⁻¹, power efficiency (PE) of 22.9 lm W⁻¹ and external quantum efficiency (EQE) of 10.3% with FWHM of 42 nm and CIE (0.30, 0.61). The PtAu₃ cluster complex with phenanthrene-fused carbazole-acetylide displays improved device performance due to the enhanced hole-carrier ability withthe peak CE of 62.2 cd A⁻¹, PE of 30.3 lm W⁻¹ and EQE of 16.6 %. The elegant synthetic strategy by combining electron and/or hole transport units enhances not only device performance of PtAu₃ cluster complexes but also charge carrier abilities, which were analyzed through space charge limited current measurements.

Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) based on metal complexes have received growing attention from academic research and commercial industry for full-color flat panel display and energy-efficient lighting devices.1 Nevertheless, some major issues remain in current PhOLEDs to be solved in the practical applications. Great progress has been made to improve the device performance of PhOLEDs, but most of them exhibit broad emission bands with a full width at half maximum (FWHM) typically 80-100 nm. Although a plethora of cyclometalated Pt² and Ir³ complexes for PhOLEDs with high phosphorescent quantum yields (PLQYs) and short emissive lifetimes have been reported, more investigations on emissive dopants are still needed, because they generally exhibit broad emission spectra.⁴ The phosphorescence in those metal complexes originates mostly from the lowest triplet excited states (T₁) contributed by ligand-centered state (³LC) and metal-to-ligand charge transfer character (³MLCT).⁵

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Rational selection of complementary ligands to modulate the shape and the energy of emission spectra results in either broad structureless emission (dominant ³MLCT character)⁶ or emission bands with vibronic features (dominant ³LC character).⁷ The unsatisfactory emissive properties hinder the further development of PhOLEDs by compromising the color purities in displays. Recently, a promising molecular design strategy has been proposed by systematic variation of ligands using pyrazolyl-carbazole groups in tetradentate cyclometalated Pt complexes⁸ so that the FWHM of emission bands could be modulated in the range of 18–85 nm.

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Polynuclear cluster complexes with judicious molecular architectures exhibit distinct phosphorescence nature with high PLQYs (nearly unity), superior solubility, film-forming ability, morphological stability, and balanced charge carrier ability so that they are ideal candidates for solution-processed OLEDs.9-13 More importantly, phosphorescent polynuclear complexes display several advantages cluster over mononuclear complexes, such as (i) high molecular rigidity originated from d⁸-d¹⁰/d¹⁰-d¹⁰ intermetallic contact leading to intense phosphorescence, (ii) emission color tunability by simply changing the bridging and ancillary ligands, (iii) plentiful phosphorescent characteristics related to multiple metal ions as well as intermetallic contacts, and (iv) LMCT/LLCT dependent phosphorescence with narrow band emission bands, typically FWHM of <70 nm, which are much smaller than the utmost of monometallic complexes.14

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Recently, we observed that PtAu₃ heterometallic cluster complexes supported by C_3 symmetrical tris(diphenylphosphinomethyl)phosphine (tdpmp) exhibited distinct structural feature, in which the Pt atom in the PtAu₃ cluster is bound to one of the terminal P donors in tdpmp so that the Pt is situated at one apex in the triangle plane of the PtAu₃ cluster.¹⁵ Since the spatial alignment of aromatic acetylides bound to PtAu₃ backbone can be easily altered to result in improved or suppressed metal-ligand interaction depending on the spatial orientations, our further design strategy focuses n systematic modulation of structure and π conjugation of aromatic acetylides and their charge carrier capability. In this article, five PtAu₃ complexes 1-5 (Scheme 1) with high PLQYs of 80.5%–90.1% in doped films are reported. The photoluminescence spectra of these complexes exhibit structureless narrow to broad emission bands (FWHM = 38-72 nm) in CH₂Cl₂ solution and their structural alignments were analyzed by crystallography and computational calculations. The electroluminescence (EL) performance of solutionprocessed OLEDs based on complex 1 exhibits narrow pure green emission with FWHM of 42 nm, EQE of 10.3 %, CE of 38.7 cd A⁻¹, PE of 22.9 lm W⁻¹ and CIE (0.30, 0.61). Complex 4 having acetylide with phenathrene-functionalized 2-carbazole substituent exhibited excellent device performance with CE of 62.2 cd A⁻¹, PE of 30.3 lm W⁻¹ and EQE of 16.6 %.



Scheme 1Synthetic routes to $PtAu_3$ cluster complexes 1–5.

Results and Discussion

Synthesis and Characterization

The synthetic routes to PtAu₃ heterometallic cluster complexes **1–5** are illustrated in Scheme 1. Complexes **1–5** were prepared by the reactions of Pt(PPh₃)₂(C=CR)(C=CR') (1 eq), tdpmp (2 eq), Au(tht)Cl (3 eq), and NH₄ClO₄ (3 eq) in CH₂Cl₂ solutions. The products were then purified by chromatography on silica gel columns using CH₂Cl₂/MeOH (v : v = 20 : 1) as the eluent to give pure solids in good yields (66–74%). They were satisfactorily characterized by HRMS (ESI) as well as ¹H and

³¹P [¹H] NMR spectroscopy. The structures of complexes 1_0 and 4 were determined by single crystal X-ray differentiate to (Fig. 6P).^{4B} In the ¹H NMR spectra, the three CH₂ protons of tdpmp appeared as two broad singlets in the range of 3.4–4.2 ppm (Fig. S1), which matches with the presence of two different environments in PtAu₃ complexes. The ³¹P [¹H] NMR spectra of PtAu₃ complexes (Fig. S2) exhibit three groups of signals centered at ca. 4.5–5.2 (*J*_{Pt-P} = 2696–2706 Hz), 17.8–22.7 and 29.1–30.4 ppm. The first one is ascribed to one terminal P donor of tdpmp bound to the Pt center, whereas the second one to the central P donor and the last triplet signal to the other two terminal P donors bonded to Au(I) centers.



Fig 1.Perspective views of cationic $PtAu_3$ complexes1 (a) and 4 (b) with 30% thermal ellipsoids. Phenyl rings on the phosphorus atoms were omitted for clarity.

The crystal structure of complex 1 contains two independent PtAu₃ moieties. As revealed by X-ray crystallography (Fig. 1), the structure of PtAu₃ cluster supported by two tdpmp in a μ_4 -bridging mode shows a triangle-planar arrangement, in which one Au atom is located at the center whereas the Pt and other two Au atoms at the three apexes. The PtAu₃ cluster structure is further stabilized by six five-membered coordination rings, additional Au-Cl-Au linkage and substantial Pt-Au and Au-Au intermetallic contacts. The Pt-Au (2.9633(4) Å for 1 and 2.9348(3) Å for 4) and Au–Au (2.9635(4) - 2.9877(4))Å for 1 and 2.9693(3)-3.0159(3) Å for 4) distances are much shorter than the sum of the van der Waals radii for platinum and gold atoms (3.38 Å) and that for two gold atoms (3.32 Å), respectively, implying significant intermetallic contact and noticeable aurophilicity.¹⁵ The Pt center is surrounded by trans-arranged C₂P₂ donors to give square-planar geometry with the C-Pt-C and P-Pt-P angles of 175.8(3) and 174.94(7)° for 1 and 173.9(2) and 174.90(5) $^{\circ}$ for 4, respectively. The Au atoms are located in T-type environment composed of CIP₂ donors with the P-Au-P angles of 172.65(7)-179.34(7)° for 1 and 163.65(6)–177.30(5) Å for 4. The dihedral angles between the planes of aromatic acetylides and PtC₂P₂ square plane are 13.9 to 45.4° in complex 1, which are much smaller than that

in complex **4** (86.9°). The better co-planarity in complex **1** (FWHM of 49 nm, Table 1) is closely relevant to a much narrower emission band than that in complex **4** (FWHM of 102 nm).



Fig.2 (a) The UV-Vis absorption spectra of complexes **1–5** in CH₂Cl₂ solutions at room temperature. (b) The photoluminescent spectra of PtAu₃ complexes **1–5** in fluid CH₂Cl₂. The solution concentration is 1 × 10⁻⁵ M.

UV-Vis Absorption Properties

The UV-Vis absorption and photoluminescence (PL) spectra of complexes 1-5 in CH₂Cl₂ solutions are shown in Fig. 2. As depicted in Fig. 2a, complexes 1-5 exhibit an intense UV absorption bands in the range of 250-280 nm, originated from tdpmp-centered $\pi \rightarrow \pi^*$ transitions. A band centered at 290–380 nm is ascribed to the π \rightarrow π^{*} transition involving aromatic-acetylides. More importantly, broad low-energy bands centered at above 400 nm (ϵ = 1.2–2.7 imes 10⁴ dm³ mol⁻¹ cm⁻¹) varies with respect to the extended π -conjugation and electron donating ability of aromatic acetylide ligands. Compound 1 with two C=C-4-C₆H₄-(N-phenyl)benzImd ligands on both sides of the Pt center shows absorption band peaked at 416 nm. Compound ${\bm 2}$ with a C=C-4-C₆H₄-(N-phenyl)benzImd on one the side and electron-donating C≡C-3-PhCarb-9 on the other side of Pt center displays a red-shifted absorption band peaked at 440 nm. Compound 3 with C=C-3-PhCarb-9 on both side shows band peaked at 474 nm. Compound 4 with C=C-2-PhenCarb-(N-Me)₂ exhibits a low-energy band at 466 nm, whereas it is red-shifted to 480 nm for **5** with an extended π conjugation from 3-SpiroCz. The low-energy band arises most likely from aromatic acetylide-to-platinum(II) ligand-to-metal charge-transfer (LMCT) as well as aromatic acetylide-to-tdpmp ligand-to-ligand charge-transfer (LLCT) transitions^{14a,14c,16} as further confirmed by TD-DFT calculations (Tables S3–S6).



Fig. 3 Photoluminescence spectra of complexes ${\bf 1}$ and ${\bf 4}$ in doped films at 298 and 80 K, respectively.

Photoluminescence Properties

Complexes 1-5 (Fig. 2b) display Gaussian-like emission bands peaked at 533-578 nm with moderate luminescence intensity in degassed CH₂Cl₂ solutions, but the emission becomes much stronger in solid states (Table 1). The luminescent lifetimes are in the range of 2.1–2.8 μ s in CH₂Cl₂ solutions at room temperature and become 4.2–12.3 μs in mCP : OXD-7 matrixes. The large Stokes shifts with microsecond range of emissive lifetimes are characteristic of triplet excited states. The close resemblance of PL spectra in doped films to those in fluid CH₂Cl₂ solutions indicate that the emission originates from the triplet excited states of unimolecular complexes. The low-temperature emission spectra of complexes 1-5 are similar to those measured at ambient temperature with Gaussian-like shape but with noticeable sharpening of the emission bands (FWHM = 29–58 nm) at 80 K (Fig. 3 and Fig.S3). The photoluminescence origin is assigned to the admixture of ³LMCT and ³LLCT transitions, corresponding to aromatic acetylide-to-PtAu₃ and aromatic acetylide-to-tdpmp charge transfer states, respectively.¹⁵ The PL spectra were sequentially modulated from green to orange wavelength range. The emission wavelengths can be correlated with the π conjugation and electron donating ability of aromatic acetylides. The PL spectra of 1-5 in pure solid state are obviously broader (FWHM = 49-102 nm) with lower PLQY (7.4–41.5%) than those in doping films (Table 1), attributable to the strong molecular aggregation as well as intermolecular interaction.¹⁷ Concentration-dependent PL spectra (Fig. S4 and Table S1) in the doping films of 1 or 4 suggest that the emission spectra show some blue-shift with the decrease in the doping concentration of PtAu₃ species, but the molecular aggregation and concentration guenching are well suppressed to exhibit a nearly constant emission band and FWHM when the doping concentration is lower than 8wt%. The PL spectra of 1-5 (Table 1) in doping films composed of 47.5 wt% mCP : 47.5 wt% OXD-7 : 5 wt% PtAu₃ are peaked at 528, 543, 556, 558 and 572 nm respectively. The quite high PLQY (80.5-90.1 %) of the spin-coated films thus enables them as excellent candidates for solution-processable OLEDs.

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Table 1.The	Photoluminescence Data for PtA	DOI: 10.1039/C8TC06384B		
	λ _{PL} (nm)	τ (μs)	$arPhi_{PLQY}$ (%)	FWHM (nm)
	CH ₂ Cl ₂ /powder/film ^{b)}	CH ₂ Cl ₂ /powder/film ^{b)}	CH ₂ Cl ₂ /powder/film ^{b)}	CH ₂ Cl ₂ /powder/film ^{b,c)}
1	533/543/528	2.4/5.9/12.3	1.5/41.5/90.1	38/49/41 (29)
2	558/578/543	2.3/2.8/4.3	2.1/16.9./84.2	54/85/56 (45)
3	568/582/556	2.8/2.3/5.1	2.5/7.8/80.5	65/83/75 (57)
4	568/564,599/558	2.1/2.0/5.9	3.2/9.3/87.3	56/102/51 (36)
5	578/604/572	2.5/2.0/4.2	2.8/7.4/82.5	72/94/69 (58)

^aAbsolute quantum yields in CH₂Cl₂ solutions, powder states and doping films were determined by the integrating sphere (142 mm in diameter). ^bComposed of 47.5 wt% mCP : 47.5 wt% OXD-7 : 5 wt% PtAu₃ complex. ^c The data in parentheses were measured at 80 K.

Table 2. The Contributions (%) of Each Fragment in Complexes 1–5 to "Electron" and "Hole" in the Lowest-energy Triplet State in CH₂Cl₂ Solution by SCPA Method with TD-DFT at the PBE1PBE Level.^a

complex		MO contribution (%)							
	_	Pt (s/p/d)	Au (s/p/d)	tdpmp	R-C≡C	Cl			
1	electron	15.99 (61/22/17)	27.80 (55/40/5)	39.95	15.62	0.62			
	hole	11.64 (1/7/92)	3.75 (38/28/34)	4.13	80.17	0.3			
2	electron	22.43(67/16/16)	27.91(43/53/4)	42.23	6.63	0.79			
	hole	11.87(1/9/91)	3.82(45/27/28)	3.56	80.5	0.24			
3	electron	2.32(1/88/10)	38.27(45/44/11)	56.88	2.4	0.12			
	hole	9.64(2/1/97)	1.54(26/38/36)	3.5	85.08	0.24			
4	electron	15.78(68/18/13)	27.30(44/48/8)	43.67	12.84	0.41			
	hole	4.72(4/11/85)	8.09(49/27/24)	5.37	81.48	0.33			
5	electron	8.83(79/17/5)	38.22(41/50/9)	50.93	1.88	0.12			
	hole	10.1(4/5/91)	4.36(55/18/27)	4.35	80.8	0.39			

^a The "electron" and "hole" represent electron accumulation (EA) and electron depletion (ED) in the transition process, respectively.

Table 3. Transferred Electrons in the LLCT and LMCT Processes in the Lowest-energy Triplet States for Complexes 1–5 in CH₂Cl₂ Solutions by SCPA Method with TD-DFT at the PBE1PBE Level.

		LMCT						
complex	LLCT (RC=C \rightarrow tdpmp)	$RC \equiv C \rightarrow Pt$	$RC=C \rightarrow Au$	RC≡C → PtAu₃ (sum)				
1	0.31752	0.11084	0.21241	0.32325				
2	0.33816	0.17362	0.22068	0.3943				
3	0.48319	0.01739	0.3252	0.34259				
4	0.35190	0.12145	0.21006	0.33151				
5	0.41077	0.06953	0.30798	0.37751				

The FWHM (Table 1) for the PL spectra of 1 (38 nm), 2 (54 nm) and 4 (56 nm) in fluid solutions were obviously smaller than those of 3(65 nm) and 5 (72 nm). This trend was also followed in 5 wt% doping films (Table 1) with the FWHM of 41, 56, 75, 51 and 69 nm for complexes 1-5, respectively. Taking advantage of the optimized geometry in the lowest triplet state, the dihedral angles between the plane of aromatic acetylide and PtC₂P₂coordination square plane can be calculated accordingly. The distinctly smaller dihedral angles in 1 (13.6 and 29.5°), 2 (22.2 and 33.7°) and 4 (11.3 and 44.4°) than those in **3** (69.6 and 69.6°) and **5** (38.1 and 69.0°) reveal clearly that the formers display better orbital overlap18 between Pt coordination plane and aromatic acetylide, whereas the lower co-planarity is observed in 3 and 5. Obviously, the better co-planarity between Pt coordination square plane and aromatic acetylide is in favor of giving narrower emission bands.

Theoretical Computational Studies

To factually address the fluctuations in narrow emission behavior with respect to the π -conjugation and electron donating ability of aromatic acetylide, TD-DFT calculations were performed on both the ground and lowest-energy triplet states for complexes 1-5 (Tables S3-S18). It can be seen that the HOMO (Fig.s S5 and S6) focuses predominately on aromatic acetylides (>79 % population) for all these complexes with much less distribution on Pt and Au centers (<18 % population). In contrast, the LUMO is populated over tdpmp, Pt and Au centers and the distribution percentage changes with respect to the π -conjugation extent and electron donating ability of aromatic-acetylide. Accordingly, the electron transition of HOMO→LUMO in both the lowestenergy singlet (S₁) and triplet (T₁) states is mainly featured with π (aromatic acetylide) $\rightarrow \pi^*$ (tdpmp) LLCT and π (aromatic acetylide) \rightarrow s/p (Pt/Au) LMCT states.



Fig. 4 Plots of the "hole" (green part) and "electron" (purple part) (isovalue = 0.0004) in the lowest-energy triplet states for PtAu₃ cluster complexes **1–5** in CH_2Cl_2 solutions by TD-DFT method at the PBE1PBE level. The process of single-electron excitation can be described as an electron leaving from "hole" and going to "electron" part.

To get more insight into the influence of the substitution on the excited-state transition process and the FWHM of the emission band, analysis of hole-electron distribution was introduced to overcome the defect by analyzing the transition of multiple MO pairs with corresponding weighting coefficients. The process of single-electron excitation can be described as an electron leaving "hole" and going to "electron". According to the definition of "hole" and "electron" by Lu et al,¹⁹ the analysis of hole and electron distribution and inter-fragment charge transfer (IFCT) by using Multiwfn program is an effective approach to examine the electronic excitation process. The contribution of each fragment to the "electron" and "hole" in the lowest-energy triplet states of complexes **1–5** in CH_2Cl_2 is summarized in Table^{O2.10}The^{9/}framsferred electron between individual fragments in the LLCT and LMCT processes are also presented in Table 3.

As depicted in Fig. 4, the hole (electron loss) in PtAu₃ cluster complexes 1-5 focuses mostly on aromatic acetylides (> 80%, Table 2), whereas the transferred electron is spread over PtAu₃ cluster (40.59%-50.34%) and tdpmp (39.95%-56.88%). Noticeably, the transferred electron is less populated on tdpmp in 1 (39.95%), 2 (42.23%) and 4 (43.67%) than that in 3 (56.88%) and 5 (50.93%), so that 1 (0.31752), 2 (0.33816) and 4 (0.35190) (Table 3) exhibit obviously less LLCT character than that in 3 (0.48319) and 5 (0.41077). On the other hand, the transferred electron is more populated on Pt and less on Au for 1 (15.99% on Pt and 27.80% on Au), 2 (22.43% on Pt and 27.91% on Au), and 4 (15.78% on Pt and 27.30% on Au) than that for 3 (2.32% on Pt and 38.27% on Au) and 5 (8.83% on Pt and 38.22% on Au). On this basis, complexes 1 (0.11084), 2(0.17362) and 4 (0.12145) display more aromatic acetylideto-Pt LMCT character than that in3 (0.01739) and 5 (0.06953) as indicated in Table 3. As a result, the distinctly narrower FWHM of the emission bands for complexes 1 (38 nm), 2 (54 nm) and 4 (56 nm) than those for3 (65 nm) and 5 (72 nm) in CH₂Cl₂ solutions are well correlated to the more aromatic acetylide-to-Pt LMCT character (0.11084 for 1, 0.17362 for 2 and 0.12145 for 4 versus 0.01739 for 3 and 0.06953 for 5) but less aromatic acetylide-to-tdpmp LLCT percentage in the formers.18

Solution-Processed OLEDs

The EL performance (Table 4) of complexes 1-5 as phosphorescent dopants was achieved in solution-processed OLEDs. As depicted in Fig.5, employing 5 wt% 1-5 : mCP : OXD-7 (wt%, 1 : 1) doping films as emitting layers (EML), three-layer devices were fabricated with the structure ITO/PEDOT : Poly-TPD (50 nm) / EML (50 nm) / ETL (50 nm) / LiF (1 nm) / Al (100 nm). The poly(3,4-ethylenedioxythiophene) : poly(4butylphenyldiphenylamine) (PEDOT: Poly-TPD) was used as hole-injection layer through spin-coating in an aqueous solution. The emissive layer was prepared by spin-coating a solution of mCP : OXD-7 (1:1) : PtAu₃ complex (5 wt%) blend in dichloromethane. To improve the charge balance and achieve better exciton recombination zone, an additional layer with BmPyPb was introduced to serve as electron transport/hole blocking layer, which was then capped with LiF/Al cathode.

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Table 4. The Performance D	View Article Online					
					DOI: 10.1039/C8TC0	6384B
complex	1	2	3	4	5	
λ_{EL} /nm	527	539	565	556	568	
FWHM/nm	42	62	92	59	83	
Von ^{b)} /V	3.0	3.4	3.5	4.2	5.4	
L _{max} ^{c)} /cd m ⁻²	10415	17079	14755	6539	12702	
CE _{max} ^d /cd A ⁻¹	38.7	55.6	45.5	62.2	57.1	
PE _{max} ^{e)} /Im W ⁻¹	22.9	35.1	28.3	30.3	20.1	
EQE _{max} f)/%	10.3	14.8	14.1	16.6	13.1	
CIE	0.30, 0.61	0.33, 0.60	0.47, 0.52	0.54, 0.32	0.46, 0.54	

^{*a*})Device structure is ITO / PEDOT : Poly-TPD (50 nm) / mCP (24 wt%) : OXD-7 (47 wt%) : PtAu₃ complex (5 wt%) (50 nm) / BmPyPb (50 nm) / LiF (1 nm) / Al (100 nm). ^{*b*})Turn-on voltage at 1 cd m⁻². ^{*c*})Maximum luminance. ^{*d*})Maximum current efficiency. ^{*e*})Maximum power efficiency. ^{*h*}Maximum external quantum efficiency.



Fig.5 (a) Energy level diagram of the transport materials and emitting compounds 1–5 used in the devices, (b) current efficiency vs luminance, (c) EQE vs luminance, and (d) EL spectra of the devices based on PtAu₃ complexes 1–5.

The EL performance parameters of PtAu₃ complexes 1–5 are listed in Table 4.The current efficiency (CE) vs luminance, external quantum efficiency (EQE) vs luminance and the EL spectra of the devices are depicted in Fig.5. The turn-on voltages of these devices are relatively low, ranging from 3.0-5.4 V (Table 4) and the OLEDs exhibit intense green to yellowish orange electroluminescence with the emission bands peaked at 527-568 nm. The EL spectra of the optimized devices are virtually identical to the corresponding PL spectra of the doping films. No residual emission from the host materials was observed when the doping concentration of 5% PtAu₃ complexes was used. The excitons were completely confined within the emissive layer and charge carrier recombination took place only in the emissive layers of the devices. Of the devices based on PtAu₃ complexes with the same architecture, the devices based on complex 1 exhibited pure green electroluminescence and the narrowest emission band with the FWHM of 42 nm, the peak EQE of 10.3%, CE of

38.7 cd A⁻¹, PE of 22.9 lm W⁻¹, and the CIE (0.30, 0.61). Such a narrow-band emission with EQE over 10% represents superior device performance for solution-processed OLEDs. The device based on complex 2 also exhibit green emission peaked at 539 nm and CIE (0.33, 0.60) with the peak CE of 55.6 cd A⁻¹, PE of 35.1 lm W⁻¹ and EQE of 14.8%, but a broader emission band with the FWHM of 62 nm. The distinctly improved efficiency for 2 compared with that for 1 arises likely from the bipolar character in the presence of both hole-transport (C=C-4-C₆H₄-(N-phenyl)benzImd) and electron-transport (C=C-3-PhCarb-9) ligands, in which the devices achieve a better balance of electron and hole carriers at the interface of the emissive layer.²⁰ The PtAu₃ cluster complexes having acetylides with 2or 3-carbazole (3), structurally fused phenathrene (4) and spiro-carbazole (5) connected to the Pt showed dramatic variations in contour of the EL spectra and device performance. Complexes 3 and 5 contain acetylides with 3-carbazole substituent exhibited FWHM of 92 and 83 nm, CE of 45.5 and

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57.1 cd A⁻¹ as well as EQE of 14.1 and 13.1 %, respectively, while acetylides with 2-carbazole unit in complex **4** exhibited FWHM of 59 nm, CE of 62.2 cd A⁻¹ and EQE of 16.6 %. The slight broadening observed in the EL spectra relative to those in the doping films is possibly due to π - π interaction of PtAu₃ species with host molecules.²¹ It is noteworthy that the emission bands in PtAu₃ complexes having the acetylides with 2-carbazole units are obviously narrower than those having the acetylides with 3-carbazole units.

The impressive device performances should be closely related to the design concept that the use of ethynyl ligands with the 2-carbazole groups supports the structural coplanarity with Pt coordination square plane so as to give narrower emission bands, which can also provide enhanced charge carrier transport ability in PtAu₃ complexes to improve EL efficiency. Upon carefully examining the emission bands in the recently reported PtM_2 (M = Au or Ag) complexessupportedby dpmp (bis(diphenylphosphinomethyl)phenylphosphine),^{14a,14e} we can find the similar phenomenon, in which the emission bands in PtM₂ complexes having acetylides with 2-carbazole ligands are much narrower than those having acetylides with 3-carbazole or 4-carbazole ligands. Consequently, it is evident that merely enhancing the coplanarity of aromatic acetylide with Pt coordination square plane could improve the orbital contribution of Pt in charge transfer processes so that more acetylide-to-Pt LMCT character is achieved to give narrower emission bands.

Charge Transport Properties

In order to understand the influence of structural variation on device performance, the charge carrier mobility of complexes 1-4 was investigated by the space-charge limited current (SCLC) technique.²²⁻²⁴ Fig.6a shows current density-voltage (J-V) characteristics of complexes 1-4 in electron-only devices with the configuration of ITO/LiF (2 nm)/EML (60 nm)/LiF (2 nm)/Al (100 nm) and hole-only devices with the configuration of ITO/PEDOT:PSS (70 nm)/EML (60 nm)/MoO₃ (2 nm)/Al (100 nm) under ambient conditions. It can be seen that the J-V behavior is ohmic and the dependence of current density on voltage is linear at low voltages. While raising the applied voltage, injection of charge carrier took place and the current became space charge limited, which is quadratic dependence on the voltage. In this regime, the SCLC characteristics are generally described by the following Mott-Gurney equation:

$$J = 9\varepsilon_0 \varepsilon_r \mu E/8L \qquad (1$$

Where J is current density, ε_{o} is the free space permittivity (8.85×10⁻¹⁴ C V⁻¹ cm⁻¹), ε_{r} is the relative dielectric constant (calculated to be 99 by using Tonghui TH2828 precision LCR meter), *E* is the electric field, and *L* is the thickness of the active layer. In general, the carrier mobility (μ) depends on the electric field (*E*) and is thus described by the Poole-Frenkel formalism:

$$\mu = \mu_0 \exp(\gamma \sqrt{E}) \qquad (2)$$

where γ is the field dependence parameter and μ_{Pels} the zeros field mobility. In this case, the expression for the SCECCAN BE approximated by using the empirical Murgatroyd equation:

$$J = 9\varepsilon_0\varepsilon_r V^2 \mu_0 \exp(0.891\gamma \sqrt{V/L}) / 8L^3$$
(3)

where V is voltage. The values of μ_0 and γ were obtained by fitting the experimental J-V curves of electron- and hole-only devices in SCLC region according to equation (3).



Fig.6 (a) J-V characteristics of electron-only and hole-only devices of complexes 1–4. (b) Electron and hole mobility of complexes 1–4 in the electric field of 1.5×10^6 V cm⁻¹ calculated by SCLC technique.

The charge mobility at a given field then can be calculated according to Equation (2). As shown in Fig. 6b, the electron mobility shows a stepwise decrease in the order 3.94×10^{-7} (1) > 3.24×10^{-7} (2) > 1.76×10^{-7} (3) > 0.18×10^{-7} cm² V⁻¹ cm⁻¹ (4) at an electric field of 1.5×10⁶ V cm⁻¹. In contrast, the hole mobility exhibits a reversed order following 0.37×10^{-7} (1) < 0.79×10^{-7} (2)< 1.71×10^{-7} (3) < 2.11×10^{-7} cm² V⁻¹ s⁻¹ (4). The comparable hole and electron mobility in these PtAu₃ complexes provides an excellent carrier balance in the emitting layers so that superior electroluminescence performance with the CE over 38 cd A⁻¹ and the EQE over 10% can be achieved in solutionprocessed devices. On the other hand, it is known that benzo[d]imidazole and carbazole are favorable electron- and hole-transport groups, respectively. Since complexes 1, 2, and 3 contain two benzo[d]imidazole, one benzo[d]imidazole and one carbazole, and two carbazole groups, respectively, it is easy to understand the order of electron mobility 1 > 2 > 3 and

that of hole mobility 1 < 2 < 3. In view of a larger π -conjugation system in dibenzo[a,c]carbazole than that in carbazole, the former is a better hole-transport moiety than that of the latter. Thus, it is reasonable that complex **4** with two dibenzo[a,c]carbazole moieties provides a higher hole mobility than that of complex **3** with two carbazole groups.

Conclusions

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The structural uniqueness of tetraphosphine-supported PtAu₃ cluster complexes encourages us to design and synthesize acetylide various aromatic ligands to modulate phosphorescent emission properties. The structural difference of aromatic acetylides modifies the spatial alignment of the PtAu₃ cluster complexes so that the band width of emission spectra could be modulated. Both structural and theoretical studies indicate that the co-planarity of aromatic acetylide with Pt coordination square plane is in favor for acetylide-to-Pt ³LMCT state to achieve narrow-band emission. The PtAu₃ cluster complexes not only exhibit excellent solubility in organic solvents with robust chemical and thermal stability, but also show bright phosphorescence with PLQY up to 80.5%-90.1% in doping films. Highly efficient solutionprocessed OLEDs were fabricated when 5wt% PtAu₃ complexes were doped with blended host materials of mCP and OXD-7 as the emitting layers. The devices with peak CE of 38.7 cd A⁻¹ and EQE of 10.3% and FWHM of 42 nm, and CE of 62.2 cd A^{-1} , EQE of 16.6% and FWHM of 59 nm were realized for complexes 1 and 4, respectively, which are the ones among excellent narrow-band emissive devices based on the solutionprocessed OLEDs.

Experimental Section

General Procedures and Materials

Aromatic acetylide ligands including (2-(4-ethynylphenyl)-1phenyl-1H-benzo[d]imidazole) $(HC \equiv C - 4 - C_6 H_4 (N - M_6))$ phenyl)benzImd), 3-ethynyl-9-phenyl-9H-carbazole (HC=C-3-Ph-9-Carb), 11-ethynyl-9-methyl-9H-dibenzo[a,c]carbazole (HC≡C-2-PhenCarb(NMe)) and 2'-ethynyl-5'-methyl-5'Hspiro[fluorene-9,11'-indeno[1,2-b]carbazole] (HC=C-3-SpiroCarb(NMe)) were synthesized according to the modified procedures²⁵⁻²⁷ and the experimental details are shown in Supporting Information (Scheme S1). All the reactions were conducted under dry argon using Schlenk technique and vacuum-line system. All solvents were carefully dried and distilled from appropriate drying agents prior to use. The precursor complexes $Pt(PPh_3)_2(C \equiv C - 4 - C_6H_4 - (N - C_6H_4))_2$ phenyl)benzImd)₂, Pt(PPh₃)₂(C=C-4-C₆H₄-(N-phenyl)benzImd)-(C≡C-3-Ph-9-Carb), Pt(PPh₃)₂(C≡C-3-Ph-9-Carb)₂, Pt(PPh₃)₂(C≡C-2-PhenCarb(NMe))₂ and Pt(PPh₃)₂(C≡C-3-SpiroCarb(NMe))₂ were prepared by the reactions of Pt(PPh₃)₂Cl₂ (0.5 mmol), corresponding acetylide ligands (1.1 mmol), Cul (1 mg) and NEt₃ (1 mL) in chloroform (50 mL) with stirring for 5 h at 50 °C. The products were purified by chromatography on silica gel (100-200 mesh) columns using CH₂Cl₂-petroleum ether as eluent. The procedure_{Art}for the synthesis of tris((diphenylphosphind))métro()phosphine (tdpmp) followed the method reported in the literature.²⁸

 $[PtAu_3(\mu-Cl)(tdpmp)_2(C=C-4-C_6H_4-(N-phenyl)benzImd)_2]$ (ClO₄)₂ (1). A mixture of $Pt(PPh_3)_2(C \equiv C-4-C_6H_4-(N-1))_2$ phenyl)benzImd)2 (65.2 mg, 0.05 mmol), tdpmp (62.7 mg, 0.1 mmol), Au(tht)Cl (48 mg, 0.15 mmol) and NH₄ClO₄ (18 mg, 0.15 mmol) was added to CH₂Cl₂ (30 mL) with stirring at ambient temperature for 8 h. The product was then purified by chromatography on a silica gel column using CH₂Cl₂/MeOH (20 : 1) as eluent. Yield: 70%. HRMS (ESI): m/z calculated for C₁₂₀H₉₈Au₃ClN₄P₈Pt [M-2ClO₄]²⁺: 1332.1989; found: 1332.2010. ¹H NMR (CDCl₃, ppm): 7.89–7.91 (m, 8H), 7.80–7.82 (m, 10H), 7.57-7.61 (m, 12H), 7.45-7.49 (m, 18H), 7.34-7.36 (m, 6H), 7.26–7.29 (m, 18H), 6.99 (t, 6H, J = 7.2 Hz), 6.94 (d, 4H, J = 8.4 Hz), 5.30 (d, 4H, J = 8.4 Hz), 4.07 (br, 4H), 3.54 (br, 4H), 3.46 (br, 4H). ³¹P NMR (CDCl₃, ppm): 30.4 (t, 4P, J_{P−P} = 31 Hz), 22.6 (m, 2P, J_{P-P} = 30 Hz), 3.9 (t, 2P, J_{P-P} = 29 Hz, J_{Pt-P} = 2686 Hz). IR (KBr, cm⁻¹): 2092w (C≡C), 1100s (ClO₄⁻).

[PtAu₃(μ -Cl)(tdpmp)₂(C=C-4-C₆H₄-(N-phenyl)benzImd)(C=C-3-Ph-9-Carb)](ClO₄)₂ (2). This compound was prepared by the same synthetic procedure as that of **1** except for the use of Pt(PPh₃)₂(C=C-4-C₆H₄-(N-phenyl)benzImd)(C=C-3-Ph-9-Carb) instead of Pt(PPh₃)₂(C=C-4-C₆H₄-(N-phenyl)benzImd)₂. Yield: 74 %. HRMS (ESI): m/z calculated for C₁₁₉H₉₇Au₃ClN₃P₈Pt [M-2ClO₄]²⁺: 1318.6934; found: 1318.6961. ¹H NMR (CDCl₃, ppm): 8.02-8.06 (m, 4H), 7.74-7.81 (m, 16H), 7.65-7.69 (m, 8H), 7.58-7.62 (m, 6H), 7.04-7.06 (m, 4H), 6.93-6.95 (m, 4H), 6.72 (d, 1H, J = 8.4 Hz), 6.01 (s, 1H), 5.70 (d, 1H, J = 8.0 Hz), 5.42 (d, 2H, J = 8.0 Hz), 4.04 (br, 4H), 3.86 (br, 4H), 3.69 (br, 4H). ³¹P NMR (CDCl₃, ppm): 29.4 (t, 4P, J_{P-P} = 31 Hz), 17.9 (m, 2P, J_{P-P} = 31 Hz), 5.5 (t, 2P, J_{P-P} = 30 Hz, J_{Pt-P} = 2686 Hz). IR (KBr, cm⁻¹): 2104w (C= C), 1100s (ClO₄⁻).

[PtAu₃(µ-Cl)(tdpmp)₂(C=C-3-Ph-9-Carb)₂](ClO₄)₂ (3). This compound was prepared by the same synthetic procedure as that of **1** except for the use of trans-Pt(PPh₃)₂(C=C-3-Ph-9-Carb)₂ instead of Pt(PPh₃)₂(C=C-4-C₆H₄-(N-phenyl)benzImd)₂. Yield: 66%. HRMS (ESI): m/z calculated for C₁₁₈H₉₆Au₃ClN₂P₈Pt [M-2ClO₄]²⁺: 1305.1880; found: 1305.1909. ¹H NMR (CDCl₃, ppm): 8.01-8.03 (m, 8H), 7.74-7.77 (m, 10H), 7.66-7.69 (m, 10H), 7.51-7.55 (m, 12H), 7.43-7.49 (m, 12H), 7.37-7.41 (m, 16H), 6.95 (m, 10H), 6.78 (d, 2H, *J* = 8.4 Hz), 6.02 (s, 2H), 5.78 (d, 2H, *J* = 8.4 Hz), 4.13 (br, 4H), 4.03 (br, 4H), 3.65 (br, 4H). ³¹P NMR (CDCl₃, ppm): 29.6 (t, 4P, *J*_{P-P} = 32 Hz), 18.1 (m, 2P, *J*_{P-P} = 30 Hz), 6.2 (t, 2P, *J*_{P-P} = 30 Hz, 6.2 (t, 2P, *J*_{P-P} = 30 Hz, *J*_{Pt-P} = 2726 Hz). IR (KBr, cm⁻¹): 2099w (C=C), 1100s (ClO₄⁻).

[PtAu₃(μ -Cl)(tdpmp)₂(C=C-2-PhenCar(NMe))₂](ClO₄)₂ (4). This compound was prepared by the same synthetic procedure as that of **1** except for the use of trans- Pt(PPh₃)₂(C=C-2-PhenCarb (NMe))₂ instead of Pt(PPh₃)₂(C=C-4-C₆H₄-(Nphenyl)benzImd)₂. Yield: 72%. HRMS (ESI): m/z calculated for C₁₂₄H₁₀₀Au₃ClN₂P₈Pt [M-2ClO₄]²⁺: 1343.2036; found: 1343.2141. ¹H NMR (CDCl₃, ppm): 8.93 (d, 2H, *J* = 9.2 Hz), 8.84 (d, 2H, *J* = 8.0 Hz), 8.79 (d, 2H, *J* = 8.4 Hz), 8.73 (d, 2H, *J* = 9.2 Hz), 8.64 (d, 2H, *J* = 7.6 Hz), 8.02–8.08 (m, 8H), 7.84 (t, 4H, *J* = 7.6 Hz), 7.72–7.78 (m, 16H), 7.62–7.68 (m, 6H), 7.44–7.48 (m, Published on 28 January 2019. Downloaded by Gothenburg University Library on 1/28/2019 1:36:11 PM

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22H), 7.00–7.08 (m, 12H), 5.99 (d, 2H, J = 8.0 Hz), 5.49 (s, 2H), 4.07 (br, 4H), 3.98 (s, 6H), 3.73 (br, 4H), 3.55 (br, 4H). ³¹P NMR (CDCl₃, ppm): 29.8 (t, 4P, $J_{P-P} = 32$ Hz), 18.2 (m, 2P, $J_{P-P} = 31$ Hz), 6.5 (t, 2P, $J_{P-P} = 30$ Hz, $J_{Pt-P} = 2744$ Hz). IR (KBr, cm⁻¹): 2099w (C=C), 1100s (ClO₄⁻).

[PtAu₃(µ-Cl)(tdpmp)₂(C=C-3-SpiroCarb(NMe))₂](ClO₄)₂ (5). This compound was prepared by the same synthetic procedure as that of 1 except for the use of trans-Pt(PPh₃)₂(C=C-3- $Pt(PPh_3)_2(C \equiv C - 4 - C_6H_4(N - C_6H_4))_2(C \equiv C - 4 - C_6H_4(N - C_6H_4))_2(C \equiv C - 4 - C_6H_4)_2(N - C_6H_4)_2(C \equiv C - 4 - C_6H_4)_2(N - C_6H_4)_2(C \equiv C - 4 - C_6H_4)_2(N - C_6H$ SpiroCarb(NMe))₂ instead of phenyl)benzImd)2. Yield: 66%. HRMS (ESI): m/z calculated for C146H112Au3CIN2P8Pt [M-2ClO₄]²⁺: 1481.7506; found: 1481.7545. ¹H NMR (CDCl₃, ppm): 8.22 (d, 4H, J = 8.8 Hz), 8.02 (d, 2H, J = 7.6 Hz), 7.76-7.79 (m, 8H), 7.68-7.71 (m, 6H), 7.50-7.56 (m, 18H), 7.44-7.48 (m, 10H), 7.21-7.27 (m, 6H), 7.13 (t, 6H, J = 7.6 Hz), 7.01–7.04 (m, 12H), 6.84 (d, 4H, J = 7.6 Hz), 6.72–6.76 (m, 10H), 6.58 (t, 4H, J = 7.2 Hz), 5.56 (d, 2H, J = 8.4 Hz), 5.41 (s, 2H), 4.04 (br, 8H), 3.90 (s, 6H), 3.56 (br, 4H). ³¹P NMR (CDCl₃, ppm): 30.4 (t, 4P, J_{P-P} = 33 Hz), 19.2 (m, 2P, J_{P-P} = 31 Hz), 5.7 (t, 2P, J_{P-P} = 30 Hz, J_{Pt-P} = 2744 Hz). IR (KBr, cm⁻¹): 2099w (C≡C), 1100s (ClO₄⁻).

Physical Measurements. The ¹H and ³¹P NMR spectra were performed on a Bruker Avance III (400 MHz) spectrometer with SiMe₄ as the internal reference and H_3PO_4 as the external reference, respectively. Splitting patterns are designated as singlet (s), doublet (d), and triplet (t). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m) and broad (br). The UV-Vis absorption spectra were measured on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer using a 10 mm path quartz cell. The infrared spectra (IR) were recorded on a Magna 750 FT-IR spectrophotometer. The high-resolution mass spectrometry (HRMS) was conducted on an Impact II mass spectrometer using dichloromethane and methanol mixtures as mobile phases. The emission and excitation spectra together with the emissive lifetimes were measured on Edinburgh FLS-920 fluorescence spectrometer. The emission spectra were recorded by exciting the samples at their excitation spectral maxima unless otherwise mentioned. All the experiments in solutions were performed at a concentration of 1.0×10^{-5} M. The luminescent quantum yield (Φ_{em}) in degassed dichloromethane solutions, powder samples and films at room temperature were determined by the integrating sphere (142 mm in diameter) using Edinburgh FLS-920 fluorescence spectrometer. The cyclic voltammetry was measured on CHI 660E electrochemical workstation (Shanghai CH Instruments) in CH₂Cl₂ solution using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The experiments were performed at room temperature at 1 mM concentration with a three-electrode cell that consists of a Pt wire as an auxiliary electrode, a saturated Ag/Ag⁺ reference electrode and a Pt working electrode. Ferrocene/ferrocenium (Fc/Fc+) was used as an internal standard. The thermogravimetric analysis (TGA) was performed under a continuous nitrogen flow using a TA Instruments Q50 at a heating rate of 10 °C min ⁻¹.

Crystal Structural Determination. X-ray single-crystal diffraction data were collected on a Bruker D8 Venture

diffractometer using IµS 3.0 microfocus source ride for a computer with the Bruker SAINT software package (V8.38A) using a SAINT algorithm. Data were corrected for absorption effects using the multi-scan method (SADABS).²⁹ All the structures were solved and refined using the Bruker SHELXTL Software Package, a computer program for automatic solution of crystal structures, and refined by the full-matrix least-squares method with ShelXle Version 4.8.6, a Qt graphical user interface for the SHELXL.³⁰

Computational Details. To understand the electronic and spectroscopic properties, the calculations were implemented by using Gaussian 09 program package³¹ for complexes 1–5. The geometrical structures as isolated molecules in the ground state and the lowest-energy triplet state were firstly optimized, respectively, by the restricted and unrestricted density functional theory (DFT) method with the gradient corrected correlation functional PBE1PBE.32 During the optimization process, the convergent values of maximum force, root-meansquare (RMS) force, maximum displacement and RMS displacement were set by default. To analyse the spectroscopic properties, 80 singlet and 6 triplet excited-states were calculated, respectively, based on the optimized structures in the ground state and lowest-energy triplet state to determine the vertical excitation energies by time-dependent density functional theory (TD-DFT)³³ with the same functional used in the optimization process. In the calculation of excited states, the polarizable continuum model method (PCM)³⁴ with CH₂Cl₂ as solvent was employed. The self-consistent field (SCF) convergence criterions of RMS density matrix and maximum density matrix were set by default in the excited-state calculation. The iterations of excited states continue until the changes on energies of states were no more than 10⁻⁷a.u. between the iterations, and then convergences reached in all the excited states. In these calculations, the Stuttgart-Dresden (SDD)³⁵ basis set and the effective core potentials (ECPs) were used to describe the Pt and Au atoms, while other non-metal atoms of Cl, P, N, C and H were described by the all-electron basis set of 6-31G**. Visualization of the frontier molecular orbitals and the hole-electron distribution were performed by GaussView. The contributions of fragments to "hole" and "electron" and InterFragment Charge Transfer (IFCT)¹⁹ in the electronic excitation process were analysed by the Ros&Schuit method³⁶ (C-squared population analysis method, SCPA) in Multiwfn 3.3.8 program.³⁷

Device Fabrication and characterization. ITO substrates were cleaned by detergent and deionized water, then successively washed by ethanol, acetone, and isopropanol under ultrasonic, respectively, followed by UV-ozone treatment for 15 min. A PEDOT : PSS solution was spin-coated on the ITO substrates at 4800 r/min for 1 min, which were then dried at 140 °C for 20 min. The emitting layers were prepared using filtered CH_2Cl_2 solutions (5 mg/mL) composed of host and PtAu₃ compound through spin-coating at 2000 r/min for 30 s. Subsequently, ETL (0.3 mm/s), LiF (0.05 nm/s) and Al (3 mm/s) were thermally evaporated in a vacuum chamber at a base pressure lower than 4.0×10^{-4} Pa. The

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current density-voltage-brightness (I-V-B) characteristics of the devices were measured on a Keithley 2400/2000 source meter with a calibrated silicon photodiode. All the measurements of the devices were performed at dry and ambient conditions with humidity lower than 30%.

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PtAu₃ Cluster Complexes with Narrow-band Emission for Solution-Processed Organic Light Emitting Diodes

Nagarajan Natarajan,^{II} Lin-Xi Shi,^{II} Hui Xiao, Jin-Yun Wang,* Li-Yi Zhang, Xu Zhang, and Zhong-Ning Chen*

Solution-processed OLEDs based on PtAu₃ cluster complexes show high-efficiency electroluminescence with narrow emission bands through enhancing the co-planarity between aromatic acetylide and platinum(II) coordination square plane.

