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Three PtAg₂ heterotrinuclear complexes supported by dpmp [dpmp = bis(diphenylphosphinomethyl)phenylphosphine] were prepared using carbazole-functionalized acetylides with hole-transport character as co-ligands. As established by X-ray crystallography, the PtAg₂ array supported by dual dpmp exhibits a centre-symmetric linear arrangement with significant Pt-Ag interaction. They display intense phosphorescence in CH₂Cl₂ solutions ($\Phi_{em} = 56.9\%-65.3\%$) and doping films ($\Phi_{em} = 43.1\%-71.2\%$) at room temperature, originating primarily from ³[π (aromatic acetylides) $\rightarrow \pi^*$ (dpmp)] ³LLCT and ³[π (aromatic acetylides) $\rightarrow s/p$ (PtAg₂)] ³LMCT triplet states mixed with some PtAg₂ cluster centred ³[$d \rightarrow s/p$] character. Upon 8% PtAg₂ complexes doped to blended host materials consisting of hole-transport TCTA and electron-transport OXD-7 as light-emitting layers, high-efficiency solution-processed organic light-emitting diodes were achieved with 67.4 cd A⁻¹ of peak current efficiency and 17.4% of external quantum efficiency.

Introduction

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Since the first two-layer organic light-emitting diodes (OLEDs) was fabricated by Tang and VanSlyke in 1987,¹ tremendous technological progress in the field of electroluminescence has been made through improving device configuration as well as developing more efficient emitting and transport materials.^{2,3} In 1998, the discovery and use of highly phosphorescent platinum(II)⁴ and iridium(III)⁵ complexes by Forrest and coworker as emissive dopants that can take advantage of both singlet and triplet state energy enhanced dramatically electroluminescent efficiency, thus promoting greatly the commercialization process of OLEDs and their practical application in displaying and lighting. Since then, a vast number of phosphorescent metal complexes with $\mathsf{platinum(II)},^{^{6-10}} \text{ iridium(III)},^{^{11-14}} \mathsf{ gold(III)},^{^{15}} \mathsf{ osmium(II)}^{^{16,17}} \mathsf{ and}$ copper(I)^{18,19} etc have been prepared to achieve highefficiency electroluminescence.

Square-planar platinum(II) complexes are frequently phosphorescent at ambient temperature because strong spinorbital coupling of heavy metal coordination facilitates significantly intersystem crossing from singlet to triplet state (ca. 10^{-12} s⁻¹), which it is much faster than typical radiative rate of singlet excited state (ca. 10^{-8} s^{-1}).^{20,21} In order to enhance phosphorescent efficiency in platinum(II) complexes, two viable strategies are usually utilized. One is to raise the energy level of non-radiative d–d state to make it thermally inaccessible by introducing strong-field ligands with C, P or S donors. The other is to reduce the level of emitting state by introducing π -conjugated N-heterocyclic ligands such as 2,2'bipyridine or 2,2':6',2''-terpyridine so that it is significantly lower in energy than that of non-radiative d-d transition.²²

On the other hand, many square-planar platinum(II) complexes with C, P and S donors are weakly phosphorescent at ambient condition because of either flexible structures or high-lying triplet excited states, in which non-radiative vibrational relaxations and d-d transitions are usually dominant.²³ In such cases, introducing another d¹⁰ metal ion [M = copper(I), silver(I) or gold(I)] is one of the feasible approaches to increase phosphorescent efficiency. The formation of Pt-M heterometallic structures not only improves molecular rigidity, but also provides additional Pt-M intermetallic contact with the energy comparable to that of hydrogen bands so that the level in triplet state is largely reduced and obviously lower than that of non-radiative d-d transition.²⁴⁻²⁷ With this idea, a series of diphosphine or triphosphine-supported Pt-M (M = Cu, Ag or Au) heterometallic complexes with alkyl/aryl acetylides or dithiolates were prepared by our group.^{28,29} These d⁸-d¹⁰ complexes display intense room-temperature phosphorescence in most cases, arising normally from charge transfer triplet states with noticeable contribution of Pt-M metallophilic interaction. We have recently demonstrated that PtAu₂ heterotrinuclear acetylide complexes supported with

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 $^{^{+}}$ Electronic Supplementary Information (ESI) available: Tables and figures giving additional photoluminescence, electroluminescence and TD-DFT results, and X-ray crystallographic files in CIF format for $1\text{-}2\text{CH}_2\text{Cl}_2$ (CCDC 1528998). See DOI: 10.1039/x0xx00000x

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dpmp [bis(diphenylphosphinomethyl)phenylphosphine] exhibit intense room-temperature phosphorescence, which can be used in OLEDs as phosphorescent dopants to achieve high-efficiency electroluminescence.³⁰⁻³²

In our previous research, a series of dpmp-supported complexes with aromatic acetylides were prepared to show weak to moderate phosphorescence. $^{\rm 28c}$ In order to attain more intense photoluminescence for the use in OLEDs, we have designed three new dpmp-supported PtAg₂ complexes taking advantage of carbazole-functionalized acetylides with holetransport character as ligands. These platinum(II)-silver(I) complexes exhibit strong phosphorescence in CH₂Cl₂ solutions $(\Phi_{\rm em} = 56.9-65.3\%)$ and doping films $(\Phi_{\rm em} = 43.1-71.2\%)$. They are first utilized as dopants in emitting layers to achieve highefficiency OLEDs. When 8% PtAg₂ complexes (Scheme 1) are doped to mixed host materials composed of hole-transport TCTA and electron-transport OXD-7 as light-emitting layers, the peak current efficiency (CE) and external quantum efficiency (EQE) in three-layer OLEDs based on complex 1 are as high as 67.4 cd A^{-1} and 17.4%, respectively.



Results and discussion

Synthesis and characterization

PtAg₂ complexes **1–3** (Scheme 1) were prepared by mixing equimolar dpmp and Ag(tht)(ClO₄) in CH₂Cl₂, followed by the addition of 0.5 equiv. Pt(PPh₃)₂(C≡CR)₂. They were purified by silica gel column chromatography to give yellow (**1**), orange (**2**) and pale yellow (**3**) products in 82%, 85% and 70% yield, respectively. Complexes **1–3** were characterized by ESI mass spectrometry (ESI-MS) and ¹H, ¹³C and ³¹P NMR spectra. In the ESI-MS, both [M-ClO₄]⁺ and [M-2ClO₄]²⁺ were observed as high-abundance or base peaks. The ³¹P NMR spectra of complexes **1–3** showed two groups of P signals for each equivalent P donor because of the presence of fluxional structures in solutions arising from labile Ag–C≡C, Ag–OClO₃ or Ag–solvent coordination bonds as revealed previously.^{28c}

The structure of complex **1** was determined by single crystal X-ray diffraction (Fig. 1). The center-symmlet it PtAg_C003ter structure is supported by two dpmp ligands with platinum atom at the middle of Ag–Pt–Ag array. The Pt···Ag [2.9413(8) Å] distance is much shorter than the sum of Van der Waals radii for Pt and Ag (ca. 3.4 Å) atoms, implying a significant metallophilic interaction.²⁸ The platinum(II) center has square-planar environment composed of trans-oriented C₂P₂ donors with C-Pt-P angles of 87.0(2) and 93.0(2)°. The silver(I) atom exhibits a distorted T-shape geometry consisting of CP₂ donors with P3-Ag1-P1, P3-Ag1-C33 and P1-Ag1-C33 angles being 159.19(9), 106.30(18) and 90.31(17)°, respectively. The acetylide displays a μ - η^{-1} , η^{-1} bonding mode bound to Pt and Ag atoms through σ and π coordination, respectively.



Fig. 1. A perspective view of complex 1 showing 30% thermal ellipsoids. Hydrogen atoms and Phenyl rings on the phosphorus atoms are omitted for clarity.



Fig. 2. Plots of the HOMO and LUMO for complexes 1–3 in the triplet state geometry, calculated by TD-DFT method at the PBE1PBE level (isovalue = 0.02).

TD-DFT computational studies

Time-dependent density functional theory (TD-DFT) calculations were carried out to investigate transition character of the absorption and emission processes of complexes 1-3 (Tables S1-S6, ESI) in the singlet and triplet excited states, respectively. As depicted in Fig. 2, the HOMO is mostly located at aromatic acetylides with some population at PtAg₂ core. The LUMO focuses mainly on dpmp and PtAg₂ core in both lowest-energy singlet and triplet states. The low-

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energy absorption arise primarily from ${}^{1}[\pi$ (aromatic acetylides) $\rightarrow \pi^{*}$ (dpmp)] ligand-to-ligand charge transfer (${}^{1}LLCT$) transition, mixed with some ${}^{1}[\pi$ (aromatic acetylides) \rightarrow s/p (PtAg₂)] ligand-to-metal charge transfer (${}^{1}LMCT$) and PtAg₂ metal-cluster (${}^{1}MC$) centred ${}^{1}[d \rightarrow s/p]$ character. By comparison, the phosphorescent emission is mostly ascribable to ${}^{3}[\pi$ (aromatic acetylides) $\rightarrow \pi^{*}$ (dpmp)] ${}^{3}LLCT$ and ${}^{3}[\pi$ (aromatic acetylides) $\rightarrow s/p$ (PtAg₂)] ${}^{3}LMCT$ triplet states, mixed with minor contribution from PtAg₂ cluster centred ${}^{3}[d \rightarrow s/p]$ transition. Compared with those of complexes 1 and 2, complex 3 exhibits more LMCT state but less PtAg₂ cluster centred character.



Fig. 3. The UV-Vis absorption (solid line) and photoluminescence (dash) spectra of complexes 1-3 in fluid CH₂Cl₂ solutions at ambient temperature.

Photophysical properties

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The UV-Vis absorption and emission data of complexes **1–3** (Fig. 3) are collected in Table 1. The high-energy absorption bands with wavelengths lower than 350 nm are mainly due to ligand-centered transitions mixed with some metal-perturbed character. The low-energy band with wavelength longer than 380 nm is ascribed to $[\pi(\text{aromatic acetylides}) \rightarrow \pi^*(\text{dpmp})]$ LLCT transition together with $[\pi$ (aromatic acetylides) \rightarrow s/p] LMCT state as supported by TD-DFT studies.

Upon excitation at $\lambda_{ex} > 260$ nm, complexes 1--3 show brilliant luminescence in solutions, powders and doping films with micro-second range of emissive lifetimes. As shown in Table 1, quite large energy gap between low-energy absorption and emission spectral bands together with long-lived photoluminescence suggest the phosphorescent character with triplet excited state. The phosphorescent quantum yields are in the range of 56.9%–65.3% in degassed CH_2Cl_2 solutions, 25.4%–34.2% in powders and 43.1%–71.2% in doping films (Table 1).

Compared with those of complexes **1** (λ_{ab} = 435 nm and λ_{em} = 540 nm) and **3** (λ_{ab} = 435 nm and λ_{em} = 545 nm), both lowenergy absorption and emission spectral peaks of complex **2** (λ_{ab} = 455 nm and λ_{em} = 566 nm) display distinct red-shifts in CH₂Cl₂ solutions. Such a trend coincides well with lower HOMO-LUMO gaps in the singlet and triplet states for complex **2** (ΔE_{s} = 3.40 eV and ΔE_{T} = 3.03 eV) than those for **1** (ΔE_{s} = 3.56 eV and ΔE_{T} = 3.15 eV) and **3** (ΔE_{s} = 3.65 eV and ΔE_{T} = 3.22 eV). The para-oriented aminoethyl in 9-ethylcarbazole-3-acetylide for complex **2** exerts stronger electron-donating character relative to that at meta-position in 9-ethylcarbarole \mathbb{R}_{2}^{-1} acetylide for complex **1** or 9-ethylcarbarole \mathbb{R}^{2} is raised and the HOMO-LUMO gap reduced to cause a distinct red-shift of the absorption and emission spectra.

Table 1. UV-Vis Absorption and Luminescence data of $PtAg_2$ complexes 1–3.

	λ_{abs}/nm	$\lambda_{ m em}\left({ m nm} ight)$ / $ au_{ m em}\left({ m \mu s} ight)$ / $arPsi_{ m em}$ (%)		
	(ε/M ⁻¹ ·cm ⁻¹)	$CH_2Cl_2^a$	powder ^b	Film ^c
1	263(99800), 327(64500), 409(23400), 435 (20970)	540/2.7/65.3	546/3.7/34.2	527/5.8/71.2
2	289 (58700), 345 (28700), 455 (18400)	566/4.3/61.1	586/3.1/29.5	548/4.2/62.9
3	264 (67300), 328 (47500), 435 (21700)	545/2.5/56.9	509/4.7/25.4	517/7.8/43.1

^{*a*} Measured In degassed CH₂Cl₂ up excitation at 374 nm for **1**, 369 nm for **2** and 421 nm for **3**. ^{*b*} Up excitation at 468 nm for **1**, 468 nm for **2** and 441 nm for **3**. ^{*c*}The film consists of 46% TCTA, 46% OXD-7 and 8% PtAg₂ complex for **1** or **2** whereas 46% mCP, 46% OXD-7 and 8% PtAg₂ complex for **3**.

Electroluminescent Performance

Since $PtAg_2$ complexes **1–3** exhibit intense phosphorescence emission with thermal stability of as high as 260 °C (Fig. S3, ESI), they are excellent phosphorescent dopants of solutionprocessed OLEDs. When PAg_2 complexes are doped to organic host materials in 8% concentration, the doping films display higher phosphorescent quantum yields while the fluorescence of host materials is entirely quenched due to effective energy transfer to $PtAg_2$ -based phosphorescent dopants. As a result, the doping concentration of $PtAg_2$ complexes in light-emitting layers was kept at 8% weight ratio while various host materials were utilized to optimize device performances.

Table 2. The Performance Data of Solution-processed OLEDs based on Phosphorescent Complexes 1–3.

complex	1	2	3
host material	TCTA : OXD-7	TCTA : OXD-7	mCP : OXD-7
$\lambda_{\scriptscriptstyle EL}$ (nm)	527	547	526
$V_{\rm on} (V)^b$	4.7	5.7	6.5
$L_{\rm max}$ (cd m ⁻²) ^c	21975	20447	12363
CE_{\max} (cd A^{-1}) ^d	67.4	58.4	25.2
PE_{max} (ml W ⁻¹) ^e	33.0	24.0	9.7
EQE_{max} (%) ^f	17.4	15.3	6.8
EQE (%) at 10^3 cd m ⁻²	16.1	15.2	6.7
CIE	0.30.0.64	0.37.0.59	0.29. 0.63

^a Weight percentages of TCTA/mCP and OXD-7 are 46% and 46% respectively.^b Turn-on voltage at 1 cd m⁻². ^c Maximum luminance. ^d Maximum current efficiency. ^e Maximum power efficiency. ^f Maximum external quantum efficiency.

Taking advantage of three-layer device structure ITO / PEDOT : PSS (50 nm) / host material : 8% complex **1** (50 nm) / TPBi (50 nm) / LiF (1nm) / Al (100 nm), the device performance was improved by optimizing light-emitting layer. Water-soluble PEDOT : PSS was used as hole-injection layer due to its good performance for solution-processed OLEDs. TPBi and LiF were selected as electron-transport and electron-injection layers.

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PEDOT : PSS and light-emitting layers were spin-coated on ITO glass substrates, while TPBi and LiF were deposited through thermal evaporation.

(a)



Fig. 4. (a) Current density (\diamond)-voltage-luminance (∇) (*J*-*V*-*L*) characteristics of **1** (red), **2** (blue) and **3** (green). (b) Current efficiency (\diamond)/external quantum efficiency (∇) *vs* luminance for the devices of **1** (red), **2** (blue) and **3** (green) using 46% TCTA and 46% OXD-7 as blended host materials.



Fig. 5. Photoluminescent emission spectra of the emitting layer 46% TCTA/mCP : 46% OXD-7 : 8% $PTAg_2$ complex toether with electroluminescent spectra of complexes 1–3.

The use of co-host (Table S7, ESI) with both hole-transport (TCTA) and electron-transport (OXD-7) materials resulted in better device performance than that only using hole-transport host material (TCTA). The mixing of TCTA and OXD-7 in 1 : 1 weight ratio gave the higher electroluminescent efficiency. When other hole-transport host materials such as mCP, TAPC or CBP is mixed with OXD-7 as co-host, the device performance is not so good as that of TCTA. Consequently, the device with 8%

PtAg₂ complex 1 doped to 46% TCTA and 46% OXD₂Z₁as₂light₋ emitting layer produced the best performance 1978king USE86f optimized device configuration ITO / PEDOT : PSS (50 nm) / TCTA (46%) : OXD-7 (46%) : 8% PtAg₂ complex (50 nm) / TPBi (50 nm) / LiF (1nm) / Al (100 nm), the turn-on voltage (V_{on}), peak luminance (L_{max}) , current efficiency (CE_{max}) , power efficiency (PE_{max}) and external quantum efficiency (EQE_{max}) are 4.7 V, 21975 cd m⁻², 67.4 cd A⁻¹, 33.0 lm W⁻¹ and 17.4% for complex **1** and 5.7 V, 20447 cd m^{-2} , 58.4 cd A^{-1} , 24.0 lm W^{-1} and 15.3% for complex 2, respectively. Table 2 summarizes the optimized performance data of solution-processed OLEDs based on complexes 1-3. Current density-voltage-luminance characteristics and CE/EQE versus luminance for OLEDs based on complexes 1-3 are depicted in Fig. 4. At a luminance of 1000 cd m⁻² in practical application for lighting and displaying, the EQE is 16.1% for the device of complex 1 and 15.2% for that of complex 2 with efficiency roll-off only being 7.4% for the former and 0.7% for the latter.

For complex **3**, since 46% mCP and 46% OXD-7 as blended host materials resulted in higher photoluminescent quantum yield than that with TCTA and OXD-7 as co-host, the doping film of 46% mCP : 46% OXD-7 : 8% complex **3** was thus used as light-emitting layer in OLED based on complex **3**. Taking advantage of device structure ITO / PEDOT : PSS (50 nm) / mCP (46%) : OXD-7 (46%) : 8% PtAg₂ complex **3** (50 nm) / TPBi (50 nm) / LiF (1nm) / Al (100 nm), the L_{max} , CE_{max} , PE_{max} and EQE_{max} are 12363 cd m⁻², 25.2 cd A⁻¹, 9.7 lm W⁻¹ and 6.8%, respectively. The *EQE* is 6.7% at a luminance of 1000 cd m⁻² in practical application with only 1.5% efficiency roll-off.

The much lower *EQE* for complex **3** (6.8%) in comparison with those for complexes **1** (17.4%) and **2** (15.3%) can be rationalized by the obviously lower photoluminescent quantum yield in light-emitting layer for **3** ($\Phi_{em} = 43.1\%$) than those for **1** ($\Phi_{em} = 71.2\%$) and **2** ($\Phi_{em} = 62.9\%$). As depicted in Fig. 5, the electroluminescent spectra agree well with the corresponding photoluminescent spectra in light-emitting layers, indicating unambiguously the same emissive origin between electroluminescence and photoluminescence.

Conclusions

The dpmp-supported PtAg₂ cluster complexes with 9ethylcarbazole-acetylides display rigid structures through acetylides bound to Pt and Ag centres in μ - η^1 , η^1 bonding mode. They display intense room-temperature phosphorescence in CH_2Cl_2 solutions (Φ_{em} = 56.9%–65.3%) and doping films ($\Phi_{\rm em}$ = 43.1%–71.2%) at room temperature, from ³[9-ethylcarbazole-acetylides arising mostly dpmp/PtAg₂] ³LLCT/³LMCT triplet states mixed with PtAg₂ cluster centred 3 [d \rightarrow s/p] character as demonstrated experimentally and theoretically. Using 8% PtAg₂ complexes as phosphorescent dopants, solution-processed OLEDs achieved high-efficiency electroluminescence with peak EQE of 17.4%, 15.3% and 6.8% for complexes 1-3, respectively. This investigation paves a viable avenue to attain high-efficiency OLEDs adopting Pt-Ag heterometallic cluster complexes as phosphorescent emitters.

Experimental

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General Procedures and Materials

All operations were carried out in a dry argon atmosphere using Schlenk techniques and vacuum-line systems unless specified. Bis(diphenylphosphinomethyl)otherwise phenylphosphine (dpmp) was prepared by synthetic procedure described in literature.³³ 2-Ethynyl-9-ethylcarbazole (HC=C-2-Etcarb-9), 3-ethynyl-9-ethylcarbazole (HC=C-3-Etcarb-9) or 4ethynyl-9-ethylcarbazole (HC=C-4-Etcarb-9) were prepared by the reaction of 2-bromo-9-ethylcarbazole, 3-bromo-9ethylcarbazole or 4-bromo-9-ethylcarbazole with ethynyltrimethylsilane in the presence of Pd(PPh₃)₂Cl₂ and Cul. Other reagents were purchased from commercial sources and used as received unless stated otherwise. The precursor complexes Pt(PPh₃)₂(C=C-2-Etcarb-9)₂, Pt(PPh₃)₂(C=C-3-Etcarb-9)₂ and Pt(PPh₃)₂(C=C-4-Etcarb-9)₂ were prepared by reactions of Pt(PPh₃)₂Cl₂ (0.5 mmol), alkynyl ligands (1.1 mmol), CuI (1 mg) and NEt₃ (1 mL) in chloroform (50 mL) with stirring at 50° C for 5 h. The products were purified by chromatography on silica gel columns using CH₂Cl₂-petroleum ether as eluent.

$[PtAg_{2}(dpmp)_{2}(C=C-2-Etcarb-9)_{2}](ClO_{4})_{2}(1)$

To a CH₂Cl₂ (40 mL) solution of dpmp (101.2 mg, 0.2 mmol) was added Ag(tht)(ClO₄) (59.0 mg, 0.2 mmol) with stirring for 30 min. Upon the addition of $Pt(PPh_3)_2(C \equiv C-2-Etcarb-9)_2$ (115.5 mg, 0.1 mmol), the solution became yellow after stirring at ambient temperature for 4 h. The solution was concentrated to 2 mL and the crude product was purified on a silica gel column using CH₂Cl₂-CH₃OH (10:1) as eluent to afford the product as a yellow solid. Yield: 82%. Anal. Calcd. for $C_{96}H_{82}N_2O_8P_6Cl_2Ag_2Pt,\ C,\ 55.99;\ H,\ 4.01;\ N,\ 1.36;\ Found:\ C$ 55.66, H 4.24, N 1.25. ESI-MS m/z (%): 1957.1 (100) [M-ClO₄]⁺, 928.9 (37.6) [M-2ClO₄]²⁺. IR (KBr, cm⁻¹): 2092w (C≡C), 1082s (ClO₄). ¹H NMR (400 MHz, CD₃CN, δ [ppm]): 8.13 (d, 1H, J = 7.7 Hz), 8.09 (d, 1H, J = 7.8 Hz), 7.87-7.79 (m, 5H), 7.78-7.68 (m, 4H), 7.57-7.48 (m, 18H), 7.43-7.37 (m, 10H), 7.25-7.21 (d, 13H, J = 7.6 Hz), 7.12-7.08 (d, 2H, J = 7.5 Hz), 7.02 (s, 1H), 6.98-6.93 (m, 4H), 6.85-6.77 (m, 2H), 6.67 (d, 1H, J = 8.0 Hz), 6.62 (s, 1H), 6.53 (d, 1H, J = 8.0 Hz), 4.31-4.21 (m, 8H), 4.02-3.89 (m, 4H), 1.35-1.27 (m, 6H). ¹³C NMR (141.2 MHz, DMF-d₇, δ [ppm]): 140.75, 139.72, 134.32, 132.65, 131.86, 131.46, 131.10, 129.96, 129.46, 129.01, 127.71, 126.26, 123.48, 122.71, 122.08, 120.62, 120.22, 119.37, 111.82, 111.12, 109.40, 79.19, 37.43, 37.32, 13.80. ³¹P NMR (162.0 MHz, CD₃CN, δ [ppm]): 13.8 and 8.7 (m, 2P, J_{Pt-P} = 2548 Hz, J_{P-P} = 44.0 Hz), 1.5 and -2.6 (m, 4P, J_{Ag-P} = 484 Hz, J_{P-P} = 40.7 Hz).

$[PtAg_{2}(dpmp)_{2}(C \equiv C-3-Etcarb-9)_{2}](ClO_{4})_{2}(2)$

This compound was prepared by the same procedure as that of **1** except for the use of Pt(PPh₃)₂(C=C-3-Etcarb-9)₂ in place of Pt(PPh₃)₂(C=C-2-Etcarb-9)₂. Yield: 85%. Anal. Calcd. for C₉₆H₈₂N₂O₈P₆Cl₂Ag₂Pt, C, 55.99; H, 4.01; N, 1.36; Found: C 55.50, H 4.23, N 1.27. ESI-MS m/z (%): 1958.0 (100) [M-ClO₄]⁺, 929.6 (41.1) [M-2ClO₄]²⁺. IR (KBr, cm⁻¹): 2082w (C=C), 1092s (ClO₄). ¹H NMR (400 MHz, CDCl₃, δ [ppm]): 7.98-7.74 (m, 14H), 7.73-7.68 (d, 2H, *J* = 7.6 Hz), 7.62-7.46 (m, 14H), 7.44-7.36 (m,

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13H), 7.36-7.30 (m, 5H), 7.24-7.18 and 7.03-6.94 (m, 9H), 7.04 and 6.86 (s, 2H), 6.81-6.72 (t, 3H, J = 7.3 H2), 16.69 and 6.54 (d, 2H, J = 8.4 Hz), 5.28-5.11 and 4.88-4.69 (m, 4H), 4.39-4.28 (m, 4H), 4.18-4.01 (m, 4H), 1.49-1.39 (m, 6H). ¹³C NMR (141.2 MHz, CD₂Cl₂, δ [ppm]): 140.18, 139.14, 134.03, 133.06, 132.99, 132.89, 131.65, 131.16, 129.78, 129.36, 127.85, 126.03, 124.79, 122.37, 122.34, 120.54, 119.36, 114.43, 111.01, 108.68 107.93, 77.24, 37.63, 37.56, 13.79. ³¹P NMR (162.0 MHz, CDCl₃, δ [ppm]): 13.1 and 12.3 (m, 2P, $J_{Pt-P} = 2548$ Hz, $J_{P-P} = 35.8$ Hz), 4.83 and 4.41 (m, 4P, $J_{Ag-P} = 517$ Hz, $J_{P-P} = 46$ Hz).

[PtAg₂(dpmp)₂(C=C-4-Etcarb-9)₂](ClO₄)₂(3)

This compound was prepared by the same procedure as that of 1 except for the use of $Pt(PPh_3)_2(C=C-4-Etcarb-9)_2$ in place of Pt(PPh₃)₂(C=C-2-Etcarb-9)₂. Yield: 70%. ESI-MS m/z (%): 1958.0 (100) [M-ClO₄]⁺, 930.1 (82.2) [M-2ClO₄]²⁺. Anal. Calcd. for C₉₆H₈₂N₂O₈P₆Cl₂Ag₂Pt, C, 55.99; H, 4.01; N, 1.36; Found: C 55.91, H 4.09, N 1.25. IR (KBr, cm⁻¹): 2095w (C≡C), 1099s (ClO₄). ¹H NMR (400 MHz, CD₃CN, δ [ppm]): 8.74-8.30 (d, 2H, J = 7.6 Hz), 7.91-7.74 (m, 6H), 7.71-7.53 (m, 10H), 7.53-7.32 (m, 20H), 7.28-7.16 (m, 9H), 7.11-7.05 (m, 2H), 7.05-6.98 (t, 5H, J = 7.1 Hz), 6.91-6.77 (m, 5H), 6.60-6.52 (m, 2H), 6.50-6.42, 6.29-6.21 (m, 1H), 5.89-5.79 (m, 1H), 5.50, 5.38 (t, 1H, J = 6.0 Hz), 4.54-4.35 (m, 4H), 4.33-3.90 (m, 8H), 0.94-0.86 (m, 6H). ¹³C NMR (141.2 MHz, CD₃CN, δ [ppm]): 139.84, 138.09, 133.77, 133.61, 132.99, 132.17, 131.66, 131.34, 131.15, 130.99, 129.53, 129.27, 128.87, 125.47, 122.22, 121.05, 119.71, 115.71, 108.42, 107.81 105.99, 77.81, 37.26, 37.30, 14.65. ³¹P NMR (162.0 MHz, CD₃CN, δ [ppm]): 12.0 and 8.0 (m, 2P, J_{Pt-P} = 2585 Hz, J_{P-P} = 42.0 Hz), 1.1 and -2.1 (m, 4P, J_{Ag-P} = 436 Hz, J_{P-P} = 38.4 Hz).

Physical measurements

The ¹H and ³¹P NMR spectra were collected on a Bruker Avance III (400 MHz) spectrometer. Electrospray ionization mass spectrometry (ESI-MS) was recorded on a Finnigan DECAX-30000 LCQ mass spectrometer using dichloromethane and methanol mixtures as mobile phases. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851e under a N₂ atmosphere at a heating rate of 10 °C min⁻¹. Elemental analysis (C, H, N) was carried out on a Perkin-Elmer model 240 C elemental analyzer. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. Photoluminescence (PL) spectra and lifetimes were measured using an Edinburgh FLS-920 fluorescence spectrometer. Absolute photoluminescent quantum yields (PLQY) in CH₂Cl₂ solutions, powders and films were measured in argon atmosphere by using an integrating sphere (142 mm in diameter) on an Edinburgh FLS-920 fluorescence spectrometer.

Crystal structure determination

Single crystals of complex 1.2CH₂Cl₂ were grown by layering nhexane onto the CH₂Cl₂ solution of complex **1**. The X-ray diffraction data were collected on a Mercury CCD diffractometer, used graphite-monochromated Mo-K_{α} (λ = 0.71073 Å) radiation. The structures were solved by direct method employing SHELXS-97 software package.³⁴ The heavy

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atoms Pt and Ag were located from E-map, most of nonhydrogen atoms were found in subsequent Fourier maps, the positions of other non-hydrogen atoms were found after successful refinement by full-matrix least-squares. All nonhydrogen atoms were refined anisotropically, while the hydrogen atoms were generated geometrically and refined with isotropic thermal parameters.

TD-DFT Calculation

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All the calculations were implemented by using Gaussian 09 program package.³⁵ Firstly, the structures of complexes **1-3** as isolated molecules in the ground state (S_0) and lowest-energy triplet state (T₁) were optimized, respectively, by the restricted and unrestricted density functional theory (DFT) method without symmetry constraint. The gradient corrected correlation functional form PBE1PBE³⁶ was used to describe the exchange and correlation interaction. The initial structure of complex 1 was extracted from determined geometry by Xray crystallography, while those of complexes 2 and 3 were obtained from the modification in the structure of complex **1**. To analyse the spectroscopic properties, 80 singlet and 6 triplet excited-states were calculated in dichloromethane solution based on the optimized ground state (G₀) and lowestenergy triplet state (T₁) structures, respectively, to determine the vertical excitation energies by time-dependent density functional theory (TD-DFT)³⁷ with the same functional used in the optimization processes. The solvent effects were taken into account by performing the self-consistent reaction field (SCRF) calculations using the polarizable continuum model method (PCM).³⁸ In these calculations, the Stuttgart-Dresden (SDD) basis set and the effective core potentials (ECPs) was used to describe the Pt and Ag atoms, ³⁹ while other non-metal atoms of P, N, C and H were described by the all-electron basis set of 6-31G*. Visualization of the frontier molecular orbitals were performed by GaussView. Ros & Schuit method⁴⁰ (Csquared population analysis method, SCPA) was supported to analyze the partition orbital composition by using Multiwfn 3.3.8 program.⁴¹

Device fabrication and characterization

The electroluminescent (EL) devices were prepared on 29.4 × 29.4 mm² indium-tin-oxide (ITO) glass with a sheet resistance of 15 $\Omega \cdot sq^{-1}$. ITO substrates were cleaned by sonication in acetone, isopropanol and de-ionized water, dried in an oven, and then treated with UV-ozone for 15 min. PEDOT : PSS was filtered through a 0.22 μ m filter and spin-coated at 3000 rmp onto the pre-cleaned ITO substrates, then dried at 140 °C for 20 min to give a 50 nm neat film. Subsequently, the CH₂Cl₂ solution (5.5 mg mL⁻¹) of emitting layer was filtered and spincoated at 1500 rmp. Then TPBi, LiF and Al cathode were deposited through vacuum thermal evaporation with a thickness of 50, 1 and 100 nm, respectively. The electroluminescence (EL) spectra were recorded on an Edinburgh FLS-920 spectrometer. The current density-voltageluminance (I-V-L) curves of the devices were recorded on a Keithley 2400/2000 source meter and a calibrated silicon Page 6 of 8

photodiode. All measurements of the devices were carried out DOI: 10.1039/C7TC00382J under ambient conditions.

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Title: High-Efficiency Organic Light-Emitting Diodes of Phosphorescent PtAg₂ Heterotrinuclear Acetylide Complexes Supported with Triphosphine

Authors: Yi-Peng Li, Xin-Xia Fan, Yue Wu, Xian-Chong Zeng, Jin-Yun Wang, Qiao-Hua Wei* and Zhong-Ning Chen

Platinum(II)-silver(I) heterometallic cluster complexes is used as a new type of phosphorescent dopants to achieve high-efficiency OLEDs with 67.4 cd A⁻¹ of peak current efficiency (CE) and 17.4% of external quantum efficiency (EQE).

