Synthesis, Structural Characterization, and Photophysical Study of Luminescent Face-to-Face Dinuclear Platinum(II) Alkynyl Phosphine Complexes and Their Tetranuclear Mixed-Metal Platinum(II)-Silver(I) and –Copper(I) Complexes[†]

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A series of luminescent face-to-face dinuclear platinum(II) alkynyl phosphine complexes with trimethoxyphenyl and carbazole moieties have been synthesized by phosphine exchange reaction. Two mixed-metal tetranuclear platinum(II)-silver(I) and -copper(I) complexes have also been synthesized. The complexes are well characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy, positive ion FAB mass spectrometry, IR spectroscopy, and elemental analysis. Most of them have been structurally characterized by X-ray crystallography. All the complexes are found to show emissive behavior. Correlations of the emissive property with the $Pt \cdots Pt$ distance, the nature of the alkynyl and bridging phosphine ligands, and the nature of the encapsulated metal ions on the alkynyl ligands have been made. TDDFT/CPCM calculations have been performed to provide further insight into the origin of the absorption and emission properties.

Introduction

Supramolecular chemistry involving metal coordination has been one of the most popular subjects over the past decade.^{1,2} Organometallic supramolecular arrays with transition metal corner and difunctional organic ligand bridges have attracted growing attention.^{2,3} With the unique and interesting spectroscopic and luminescence properties associated with metal-metal interactions, dinuclear d⁸-d⁸ metal complexes have attracted much attention.⁴ Early works by Pringle and Shaw have shown that face-to-face dinuclear platinum(II) alkynyl complexes bridged by bis(diphenylphoshino)methane (dppm) could be isolated by the reaction of $[Pt(dppm-P,P')Cl_2]$ with alkynyllithium.⁵ Extension of the synthesis to various $[Pt_2(\mu-dppm)_2(C \equiv CR)_4]$ derivatives^{6,7} and the use of these face-to-face dinuclear platinum(II) alkynyls as metalloligands to encapsulate metal ions in a tweezer-like/

sandwich fashion^{6a,b} have been reported, and these compounds have been shown by us to show rich luminescence behavior. The $[Pt_2(\mu\text{-dppm})_2(C \equiv CR)_4]$ unit has further been demonstrated to function as versatile building blocks for the construction of multinuclear platinum(II) assemblies through the incorporation of a pyridyl ligating group to give hexanuclear $[Pt_2(\mu-dppm)_2(C \equiv CC_5H_4N)_4 \{Pt(trpy)\}_4](CF_3SO_3)_8 (trpy =$ 2,2':6',2"-terpyridine).^{6c}

ORGANOMETALLICS

While the $[Pt_2(\mu-dppm)_2(C \equiv CR)_4]$ system has been fairly well studied,⁵⁻⁷ corresponding spectroscopic studies involving

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Article

diphosphines other than dppm have not been made. These, together with the previous report by Gladysz and co-workers on the preparation of tetranuclear platinum(II) alkynyls using phosphine exchange reactions,⁸ have prompted us to explore the study of the bis(dimethylphosphino)methane (dmpm) analogues, given the more electron-rich and more optically transparent nature of the dmpm ligand. It is envisaged that the incorporation of dmpm bridging ligands other than that of dppm will provide an opportunity for the systematic variation of the electronic and structural properties of the ligands, which would have an important influence on the spectroscopic properties of this class of compounds. In addition, incorporation of carbazole, a well-known hole-transporting^{9a,b} and electroluminescent molecule^{9c,d} with simple functionization,¹⁰ into the face-to-face dinuclear platinum(II) alkynyl phosphine system has also been explored.

Herein we report the synthesis and photophysical study of several face-to-face dinuclear platinum phosphine alkynyl complexes, $[Pt_2(\mu\text{-dppm})_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (1), $[Pt_2(\mu\text{-dppm})_2(C \equiv CC_6H_4\text{-Carb-9})_4]$ (2), $[Pt_2(\mu\text{-dmpm})_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (3), and $[Pt_2(\mu\text{-dmpm})_2(C \equiv CC_6H_4\text{-Carb-9})_4]$ (4), using the phosphine exchange approach, and their mixed-metal tetranuclear complexes, $[Pt_2(\mu\text{-dppm})_2-\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4\cdot\{Ag(MeCN)\}_2](BF_4)_2$ (5) and $[Pt_2(\mu\text{-dppm})_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4\cdot\{Cu(MeCN)\}_2]$ (PF₆)₂ (6). The influence of the Pt···Pt distance, the nature of the diphosphine and alkynyl ligands, and the metal encapsulation on the spectroscopic and luminescence properties have also been explored and supported by the TDDFT/ CPCM calculations.

Experimental Section

Materials and Reagents. Bis(diphenylphosphino)methane (dppm) and bis(dimethylphosphino)methane (dmpm) were purchased from Strem Chemical Inc. $[Ag(MeCN)_4]BF_4$, $Cu(BF_4)_2$. $6H_2O$, and $PtCl_2$ were purchased from Aldrich Chemical Co. Trimethylsilylacetylene was purchased from GFS Chemical Co. Ltd. $[Cu(MeCN)_4]PF_6^{11}$ and 9-(4-ethynylphenyl)-9*H*-carbazole¹² were prepared according to literature procedures. Tetrahydro-furan (Lab-Scan, AR) was purified by Pure Solv-MD (Multiple Dispensing System, Innovative Technology). Methanol (Merck, GR), acetonitrile (Lab Scan, AR), diethyl ether (Scharlau, AR), and dichloromethane (Lab Scan, AR) were purified and distilled using standard procedures before use. ¹³ All other reagents were of analytical grade and were used as received. Dichloromethane (Sigma-Aldrich, spectrophotometric grade) was used for spectroscopic studies without further purification.

Synthesis and Characterization of the Mononuclear Platinum(II) Alkynyl Precursor Complexes. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques.

trans-[Pt(PPh₃)₂{C=CC₆H₂(OMe)₃-3,4,5)₄}₂]. It was synthesized by the modification of literature procedures.¹ ⁴ cis-[Pt(PPh₃)₂-Cl₂] (1.0 g, 1.27 mmol) was dissolved in HNEt₂ (60 mL) containing CuI (3.8 mg, 0.038 mmol) followed by the addition of 5-ethynyl-1,2,3-trimethoxybenzene (0.73 g, 3.81 mmol). The reaction mixture was then heated to reflux for 8 h with stirring. The white organic ammonium salt formed during the course of the reaction was then filtered off, and the solvent was removed under reduced pressure. Dichloromethane was added to dissolve the yellow residue, and the solution was washed successively with ammonium chloride solution and deionized water to remove the copper(I) catalyst. The organic layer was then dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. Subsequent recrystallization from dichloromethane-diethyl ether afforded pale yellow crystals. Yield: 60.4 mg, 65.0%. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 3.58 (s, 12H, $-OCH_3$ -m), 3.65 (s, 6H, $-OCH_3$ -p), 5.50 (s, 4H, $-C_6H_2$ -), 7.35-7.83 (m, 30H, $-PPh_3$). ¹³C NMR (100.6 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 55.70 (-OCH₃-m), 60.67 (-OCH₃-p), 101.34 (Pt-C≡C-C), 103.56 (Pt-C≡C-C), 105.65, 121.76, 134.10, and 149.25 (-C₆H₂-), 125.45, 126.23, 127.91, and 130.89 (-PPh₃). ³¹P NMR (161 MHz, CDCl₃, 298 K, relative to 85% H_3PO_4): $\delta 18.82$ (s, J(Pt-P) = 2635 Hz). IR (KBr disk, ν/cm^{-1}): 2084 ν (C=C). Positive FAB-MS: ion clusters at m/z 1103 {M}⁺, 913 { $\dot{M} - C \equiv CC_6H_2(OMe)_3-3,4,5$ }⁺, 719 { $\dot{M} - 2C \equiv CC_6-H_2(OMe)_3-3,4,5$ }⁺. Anal. Found (%): C, 63.10; H, 4.70. Calcd for trans-[Pt(PPh₃)₂{C=CC₆H₂(OMe)₃-3,4,5)₄}₂]: C, 63.21; H, 4.76.

trans-[Pt(PPh₃)₂(C=CC₆H₄-Carb-9)₂]. The title compound was prepared according to a procedure similar to that described for the preparation of *trans*- $[Pt(PPh_3)_2\{C \equiv CC_6H_2(OMe)_3 3,4,5)_{4}_{2}$, except 9-(4-ethynylphenyl)-9*H*-carbazole (52.0 mg, 0.19 mmol) was used in place of 5-ethynyl-1,2,3-trimethoxybenzene to give a yellow solid. Yield: 54.7 mg, 66.0%. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 6.45 (d, 4H, $J_{HH} = 9.0$ Hz, H's at 5-position of carbazole), 7.08 (d, 4H, H's at 1-position of -C₆H₄-), 7.10-7.30 (m, 8H, H's at 3- and 4-position of carbazole), 7.35 (d, 4H, $J_{HH} = 7.0$, H's at 2-position of $-C_6H_4-$), 7.43-7.92 (m, 30H, $-PPh_3$), 8.10 (d, 4H, $J_{HH} =$ 8.0 Hz, H's at 2-position of carbazole). ¹³C NMR (100.6 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 101.18 (Pt-C≡C-C), 104.25 (Pt-C=C-C), 111.00, 117.27, 119.19, 119.67, 119.88, 120.65, 121.74, 130.86, 132.78, and 140.16 (-C₆H₄-Carb), 128.54, 128.67, 133.47, and 137.56 (-PPh₃). ³¹P NMR (161 MHz, CDCl₃, 298 K, relative to 85% H₃PO₄): δ 18.98 (s, J(Pt-P) = 2624 Hz). IR (KBr disk, ν/cm^{-1}): 2090 $\nu(C \equiv C)$. Positive FAB-MS: ion clusters at m/z $1263 \{M\}^+, 985 \{M - C \equiv CC_6H_4 - Carb - 9\}^+$. Anal. Found (%): C, 73.00; H, 4.43; N, 2.30. Calcd for trans-[Pt(PPh₃)₂(C=CC₆H₄-Carb-9)2]: C, 72.89; H, 4.35; N, 2.24.

Synthesis and Characterization of the Dinuclear Platinum(II) Alkynyl Complexes 1–4. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques.

Pt₂(*μ*-**dppm**)₂{**C**≡**CC**₆**H**₂(**OMe**)₃-3,4,5}₄] (1). The precursor complex *trans*-[Pt(PPh₃)₂{**C**≡**CC**₆H₂(OMe)₃-3,4,5)₄}₂] (50.0 mg, 0.045 mmol) and bis(diphenylphosphino)methane (20.9 mg, 0.054 mmol) were placed in a 250 mL two-necked round-bottomed flask. Degassed THF (160 mL) was transferred into the mixture. The reaction mixture was stirred for two days. The resulting mixture was evaporated to dryness, and the residue was purified by column chromatography on silica gel (70−230 mesh) using dichloromethane – acetone (8:2 v/v) as the eluent. Subsequent diffusion of diethyl ether vapor to the concentrated dichloromethane solution of the product gave **1** as yellow crystals. Yield: 53.7 mg, 62.0%. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 3.39 (s, 24H, $-OCH_3$ -m), 3.72 (s, 12H, $-OCH_3$ -p), 4.62−4.64 (m, 4H, $-PCH_2$ P−), 5.72 (s, 8H, $-C_6H_2$ −), 7.00−7.85 (m, 40H, $-PPh_2$). ¹³C NMR (100.6 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 30.87

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 $(-PCH_2P-)$, 55.76 (−OCH₃-m), 60.68 (−OCH₃-p), 104.56 (Pt-C≡C-C), 105.34 (Pt-C≡C-C), 107.79, 124.43, 135.01, and 152.20 (−C₆H₂-), 127.48, 128.67, 129.82, and 133.90 (−PPh₂). ³¹P NMR (161 MHz, CDCl₃, 298 K, relative to 85% H₃PO₄): δ 2.37 (s, *J*(Pt-P) = 2829 Hz). IR (KBr disk, ν/cm^{-1}): 2097 ν (C≡C). Positive FAB-MS: ion clusters at *m*/*z* 1922 {M}⁺, 1732 {M − C≡CC₆H₂(OMe)₃-3,4,5}⁺, 1541 {M − dppm}⁺, 1159 {M − 2dppm}⁺. Anal. Found (%): C, 58.52; H, 4.88. Calcd for 1: C, 58.69; H, 4.61.

 $[Pt_2(\mu-dppm)_2(C \equiv CC_6H_4-Carb-9)_4]$ (2). The title compound was prepared according to a procedure similar to that described for the preparation of 1, except trans- $[Pt(PPh_3)_2(C \equiv CC_6H_4 - CC_6H_4)]$ Carb-9)2] (50.0 mg, 0.040 mmol) was used in place of trans- $[Pt(PPh_3)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5)_4\}_2]$ to give 2 as a bright yellow solid. Yield: 50.9 mg, 57.2%. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 4.78-4.80 (m, 4H, -PCH₂P-), 6.78 (d, 8H, J_{HH} = 8.4 Hz, H's at 5-position of carbazole), 7.04–7.30 (m, 32H, H's at 3- and 4-position of carbazole, H's at 1- and 2-position of -C₆H₄-), 7.09-7.95 (m, 40H, -PPh₂), 8.04 (d, 8H, $J_{HH} = 7.3$ Hz, H's at 2-position of carbazole). ¹³C NMR (100.6 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 30.89 (-PCH₂P-), 102.56 (Pt-C=C-C), 105.34 (Pt-C=C-C), 109.57, 119.69, 120.12, 123.23, 125.74, 126.43, 128.00, 132.28, 134.44, and 140.66 (-C₆H₄-Carb), 127.50, 128.70, 130.01, and 133.92 (-PPh₂). ³¹P NMR (202 MHz, CDCl₃, 298 K, relative to 85% H₃PO₄): δ 2.59 (s, J(Pt-P) = 2840 Hz). IR (KBr disk, ν/cm^{-1}): 2104 $\nu(C=C)$. Positive FAB-MS: ion clusters at m/z 2224 {M}⁺, 1959 {M -C≡CC₆H₄)-Carb-9}⁺. Anal. Found (%): C, 69.81; H, 4.15; N, 2.99. Calcd for **2**: C, 70.20; H, 4.17; N, 2.89.

 $[Pt_2(\mu-dmpm)_2 \{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4](3)$. The precursor complex *trans*-[Pt(PPh₃)₂{C=CC₆H₂(OMe)₃-3,4,5)₄}₂] (50.0 mg, 0.045 mmol) was placed in a 250 mL two-necked round-bottomed flask. Degassed THF (160 mL) was transferred into the mixture. Bis(dimethylphosphino)methane (12 μ ml, 0.079 mmol) was then added. The reaction mixture immediately turned to a clear yellow solution and was stirred for two days. The resulting mixture was evaporated to dryness under reduced pressure, and the residue was purified by column chromatography on silica gel (70-230 mesh)using dichloromethane-acetone (8:2 v/v) as the eluent. Subsequent diffusion of diethyl ether vapor to the concentrated dichloromethane solution of the product gave 3 as pale yellowgreen crystals. Yield: 45.7 mg, 73.7%. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 2.01 (t, 24H, -PMe₂), 3.06 (m, 4H, -PCH₂P-), 3.54 (s, 24H, -OCH₃-m), 3.76 (s, 12H, -OCH₃-p), 6.51 (s, 8H, $-C_6H_2$ -). ¹³C NMR (100.6 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 15.57 (-PCH₃-), 30.88 (-PCH₂P-), 55.72 $(-OCH_3-m)$, 60.82 $(-OCH_3-p)$, 105.76 (Pt-C=C-C), 106.96 (Pt-C=C-C), 108.22, 124.05, 136.67, and 152.71 ($-C_6H_2-$). ³¹P NMR (161 MHz, CDCl₃, 298 K, relative to 85% H₃PO₄): $\delta - 18.68$ (s, J(Pt-P) = 2517 Hz). IR (KBr disk, ν/cm^{-1}): 2081 ν (C=C). Positive FAB-MS: ion clusters at m/z 1428 {M}⁺, 1237 $\{M - C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(OMe)_3 - 3, 5\}^+, 1045 \{M - 2C \equiv CC_6H_2(Me)_3 - 3,$ $3,4,5\}^+, 853 \{M - 3C \equiv CC_6H_2(OMe)_3 - 3,4,5\}^+$. Anal. Found (%): C, 45.78; H, 5.16. Calcd for 3: C, 45.72; H, 4.87.

 $[Pt_2(\mu-dmpm)_2(C \equiv CC_6H_4-Carb-9)_4]$ (4). The title compound was prepared according to a procedure similar to that described for the preparation of 3, except trans- $[Pt(PPh_3)_2(C \equiv CC_6H_4 - CC_6H_4)_2(C \equiv CC_6H_4 - CC_6H_4)_2(C \equiv CC_6H_4 - CC_6H_4)_2(C \equiv CC_6H_4 - CC_6H_4)_2(C \equiv CC_6H_4)_2(C \equiv CC_6H_4 - CC_6H_4)_2(C \equiv CC_$ Carb-9)₂] (50.0 mg, 0.040 mmol) was used in place of *trans*- $[Pt(PPh_3)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5)_4\}_2]$ to give 4 as greenishyellow crystals. Yield: 39.9 mg, 60.0%. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 2.19 (t, 24H, -PMe₂), 3.28 $(m, 4H, -PCH_2P-), 7.03 (t, 8H, J_{HH}=8.1 Hz, H's at 4-position$ of carbazole), 7.03 (t, 8H, $J_{HH} = 7.1$ Hz, H's at 3-position of carbazole), 7.21 (d, 8H, $J_{HH} = 8.3$ Hz, H's at 2-position of $-C_6H_4-$), 7.28 (d, 8H, $J_{HH}=$ 6.5 Hz, H's at 5-position of carbazole), 7.50 (d, 8H, $J_{HH} = 8.3$ Hz, H's at 1-position of $-C_6H_4-$), 8.03 (d, 8H, $J_{HH} = 7.7$ Hz, H's at 2-position of carbazole). ¹³C NMR (100.6 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 15.58 (-PCH₃-), 30.92 (-PCH₂P-), 107.86 (Pt-C≡C-C), 109.36 (Pt-C≡C-C), 109.57, 119.69, 120.12, 123.23, 125.74, 126.43, 128.00, 132.28, 134.44, and 140.66 $(-C_6H_4$ -Carb). ³¹P NMR (161 MHz, CDCl₃, 298 K, relative to 85% H₃PO₄): δ –18.70 (s, *J*(Pt–P) = 2480 Hz). IR (KBr disk, ν/cm^{-1}): 2097 ν (C=C). Positive FAB-MS: ion clusters at *m/z* 1729 {M}⁺, 1461 {M – C=CC₆H₄-Carb-9}⁺, 1195 {M – 2C=CC₆H₄-Carb-9}⁺, 921 {M – 3C=CC₆H₄-Carb-9}⁺, 662 {M – 4C=CC₆-H₄-Carb-9}⁺. Anal. Found (%): C, 58.33; H, 4.22; N, 3.90. Calcd for 4·2CH₂Cl₂: C, 58.23; H, 4.25; N, 3.78.

Synthesis and Characterization of the Mixed-Metal Tetranuclear Platinum(II)–Silver(I) and –Copper(I) Alkynyl Complexes 5 and 6. All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques.

 $[Pt_2(\mu-dppm)_2 \{C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}_4 \cdot \{Ag(MeCN)\}_2]$ - $(\mathbf{BF}_4)_2$ (5). This was synthesized by modification of a literature procedure for the related mixed-metal complexes of [Pt2(µ-dppm)2- $(C = CPh)_4$.^{6a} To a yellow suspension of 1 (48.0 mg, 0.025 mmol) in dichloromethane (10 mL) was added dropwise [Ag(MeCN)₄]- BF_4 (19.7 mg, 0.055 mmol) in acetone solution (10 mL). The reaction mixture immediately turned to a clear greenish-yellow solution and was allowed to stir for 30 min. After removal of the solvent under vacuum, a greenish-yellow solid was obtained. Subsequent recrystallization from acetone-n-hexane afforded 5 as air-stable greenish-yellow rod-shaped crystals. Yield: 30.0 mg, 50.4%. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 1.30 (s, 6H, CH₃CN), 3.50 (s, 24H, -OCH₃-m), 3.81 (s, 12H, -OCH₃-p), 5.20-5.22 (m, 4H, -PCH₂P-), 5.47 (s, 8H, -C₆H₂-), 7.35-8.07 (m, 40H, -PPh₂). ³¹P NMR (161 MHz, CDCl₃, 298 K, relative to 85% H₃PO₄): δ 5.16 (s, J(Pt-P) = 2580 Hz). IR (KBr disk, ν/cm^{-1}): 2024 ν (C=C). Positive FAB-MS: ion clusters at *m*/*z* 2033 {M – Ag – 2MeCN}⁺. Anal. Found (%): C, 48.27; H, 4.05. Calcd for **5**: C, 48.50; H, 4.10.

 $[Pt_2(\mu-dppm)_2 \{C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}_4 \cdot \{Cu(MeCN)\}_2]$ $(\mathbf{PF}_6)_2$ (6). This was synthesized by modification of a literature procedure for the related mixed-metal complexes of [Pt2(u-dppm)2- $(C = CPh)_4$].^{6b} To a yellow suspension of 1 (52.8 mg, 0.027 mmol) in dichloromethane (10 mL) was added dropwise [Cu(MeCN)₄]-PF₆ (21.5 mg, 0.058 mmol) in acetone solution (10 mL). The reaction mixture immediately turned to a clear vellow solution and was stirred for 30 min. After removal of the solvent under vacuum, a yellow solid was obtained. Subsequent recrystallization from acetone-n-hexane afforded 6 as air-stable yellow rodshaped crystals. Yield: 35.0 mg, 52.0%. ¹H NMR (400 MHz, CDCl₃, 298 K, relative to Me₄Si): δ 1.81 (s, 6H, CH₃CN), 3.51 (s, 24H, -OCH₃-m), 3.79 (s, 12H, -OCH₃-p), 5.00-5.04 (m, 4H, PCH_2P-), 5.32 (s, 8H, $-C_6H_2-$), 7.26-8.00 (m, 40H, $-PPh_2$). 31 P NMR (400 MHz, CDCl₃, 298 K, relative to 85% H₃PO₄): δ 5.00 (s, J(Pt-P) = 2543 Hz). IR (KBr disk, ν/cm^{-1}): 2005 ν (C=C). Positive FAB-MS: ion clusters at m/z 1988 {M - Cu $- 2MeCN^{+}$, 1025 {M $- 2MeCN^{2+}$. Anal. Found (%): C, 44.08; H, 3.97. Calcd for 6: C, 44.55; H, 3.66.

Physical Measurements and Instrumentation. ¹H, ¹³C, and ³¹P NMR spectra were recorded on either a Bruker DPX300 or a Bruker AV400 FT-NMR spectrometer. The chemical shifts (δ, ppm) were reported relative to tetramethylsilane (Me₄Si) for ¹H and ¹³C NMR and 85% phosphoric acid (H₃PO₄) for ³¹P NMR studies. Positive ion fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT95 mass spectrometer. IR spectra were obtained as KBr disks on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000-400 cm^{-1}). Elemental analyses of the new compounds were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing. UV-vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission and excitation spectra recorded at room temperature and 77 K were obtained on a Spex Fluorolog-2 model F111 fluorescence spectrophotometer equipped with a Hamamatsu R928 photomultiplier tube with or without Corning filters. All solution samples for photophysical studies were degassed on a high-vacuum line in a two-compartment cell consisting of a 10 cm⁻³ Pyrex bulb and a

Table 1.	Crystal and	Structure	Determination	Data
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	1	3	4	5	6
formula	$C_{94}H_{88}O_{12}P_4Pt_2 \cdot 6CH_2Cl_2$	$C_{54}H_{72}O_{12}P_4Pt_2$	$\begin{array}{c} C_{90}H_{76}N_4P_4Pt_2 \cdot \\ 4CH_2Cl_2 \end{array}$	$C_{98}H_{94}Ag_2B_2F_8N_2O_{12}P_4Pt_2 \cdot 4(CH_3)_2CO$	$C_{98}H_{94}Cu_2F_{12}N_2O_{12}P_6Pt \cdot 4(CH_3)_2CO$
fw	2433.26	1427.18	2067.31	2627.48	2655.14
a, Å	13.8451(6)	8.412(1)	11.9617(9)	23.472(2)	23.973(2)
b, Å	15.0585(6)	11.037(2)	12.8784(10)	23.370(2)	22.983(2)
<i>c,</i> Å	15.7499(6)	15.715(3)	15.8100(12)	21.290(2)	21.570(2)
α, deg	61.876(1)	92.82(2)	104.444(1)	90.00	90.00
β , deg	77.895(1)	100.90(2)	100.856(1)	102.184(1)	102.229(2)
γ , deg	64.178(1)	99.52(2)	93.525(1)	90.00	90.00
$V, Å^3$	2606.75(18)	1408.0(4)	2301.2(3)	11415.9(18)	11615(2)
Ζ	1	1	1	4	4
cryst syst	triclinic-P	triclinic-P	triclinic-P	monoclinic-C	monoclinic-C
color/habit	yellow block	yellow block	yellow block	yellow rod	yellow block
space group	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)	<i>P</i> 1 (No. 2)	<i>C</i> 2/ <i>c</i> (No. 15)	<i>C</i> 2/ <i>c</i> (No. 15)
$D_{\rm c},{\rm gcm^{-3}}$	1.550	1.683	1.492	1.529	1.518
<i>T</i> , K	297(2)	301(2)	301(2)	298 (2)	297(2)
μ , mm ⁻¹	3.11	5.14	3.38	2.91	2.93
F(000)	1216	708	5248	5248	5328
no. of reflns	17 798	8190	15665	31 572	29 002
no. of indep reflns	11 532	5234	10 206	10 050	10214
R _{int}	0.0184	0.0279	0.0219	0.0191	0.0223
$R_1,^a w R_2^{\ b} (I > 2(I))$	0.0277, 0.0701	0.0317, 0.0832	0.0388, 0.0984	0.0349, 0.0967	0.0358, 0.1005
R_1 , wR_2 (all data)	0.0328, 0.0729	0.0342, 0.0865	0.0541, 0.1068	0.0443, 0.1056	0.0484, 0.1109
GoF ^c	1.020	1.061	1.016	1.048	1.055

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}wR_{2} = \left[\sum w(|F_{o}^{2}| - |F_{c}^{2}|)^{2} / \sum w|F_{o}^{2}|^{2}\right]^{1/2}. {}^{c}\text{GoF} = \left[\sum w(|F_{o}| - |F_{c}|)^{2} / (N_{obs} - N_{param})\right]^{1/2}.$

1 cm path length quartz cuvette and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Solution samples were rigorously degassed with no fewer than four successive freeze-pump-thaw cycles prior to the measurements. Low-temperature glass photophysical measurements were carried out with the samples loaded in a quartz tube inside a quartzwalled Dewar flask with liquid nitrogen. Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150-10 pulsed Nd:YAG laser. Luminescence decay signals from a Hamamatsu R928 photomultiplier tube were converted to voltage changes by connecting to a 50 Ω load resistor and were then recorded on a Tektronix model TDS 620A digital oscilloscope. The lifetime τ_0 was determined by a single-exponential fitting of the luminescence decay trace with the relationship $I = I_0 \exp(-t/\tau_0)$, where I and I_0 are the luminescence intensity at time = t and 0, respectively. Solution samples for luminescence lifetime measurements were degassed with no fewer than four successive freezepump-thaw cycles.

X-ray Diffraction Measurement. Single crystals of 1, 3, and 4 suitable for X-ray crystallographic studies were obtained by the diffusion of diethyl ether vapor into a concentrated dichloromethane solution of the respective complexes, while single crystals of 5 and 6 for X-ray crystallographic studies were obtained by the diffusion of diethyl ether vapor into a concentrated acetone solution of the respective complexes. Crystal and structure determination data of 1.6CH₂Cl₂, 3, 4.4CH₂Cl₂, 5.4-(CH₃)₂CO, and 6·4(CH₃)₂CO are summarized in Table 1. Selected bond distances and bond angles of 1 and 3-6 are collected in Tables 2 and 3. The crystals were mounted in a glass capillary, and the intensity data were collected on a Bruker SMART 1000 CCD diffractometer using graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). Raw frame data were integrated using the SAINT¹⁵ program. Semiempirical absorption corrections with SADABS¹⁶ were applied. The structures were solved by direct methods employing the SHELXS-97 program¹⁷ and refined by full-matrix least-squares on F^2 using the SHELXL-97 program.¹⁷ In the final stage of least-squares refinement, non-H atoms of the solvent molecules were refined isotropically; other non-H atoms were refined anisotropically. H atoms were generated by the program SHELXL-97.¹⁷ The positions of H atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of final *R*-indices (see Supporting Information).

Computational Details. Using Gaussian 03,¹⁸ time-dependent density functional theory (TDDFT)¹⁹ at the hybrid Perdew, Burke, and Ernzerhof (PBE0) functional level²⁰ associated with the conductor-like polarizable continuum model (CPCM)²¹ using CH₂Cl₂ as the solvent was employed to compute the first three lowest lying singlet-singlet transitions of $[Pt_2(\mu\text{-dppm})_2-{C=CC_6H_2(OMe)_3-3,4,5}_4]$ (1), $[Pt_2(\mu\text{-dmpm})_2(C=CC_6H_2(OMe)_3-3,4,5}_4]$ (3), and $[Pt_2(\mu\text{-dmpm})_2(C=CC_6H_4\text{-Carb-9})_4]$ (4) on the basis of the experimentally determined geometry obtained from

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Table 2. Selected Bond Distances and Angles with Estimated Standard Deviations in Parentheses

$[Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (1)

Bond Distances (Å)

Pt(1) - P(1)	2.293(1)	C(1) - C(2)	1.206(5)
Pt(1) - P(2)	2.297(1)	C(12) - C(13)	1.220(5)
Pt(1)-C(1)	2.001(3)	P(1) - C(23)	1.837(3)
Pt(1)-C(12)	2.000(3)	P(2)-C(23)	1.832(3)
	Bond Ar	ngles (deg)	
Pt(1)-C(1)-C(2)	172.0(3)	P(1) - Pt(1) - P(2)	174.12(3)
Pt(1)-C(12)-C(13)	174.4(3)	P(1) - Pt(1) - C(12)	84.61(9)
C(1) - Pt(1) - P(1)	92.17(9)	C(1) - Pt(1) - C(12)	170.42(13)

$[Pt_2(\mu-dmpm)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (3)

Bond Distances (Å)

Pt(1)-P(1) 2.290(1) $C(1)-C(2)$	1.222(7)
Pt(1)-P(2) 2.280(1) $C(12)-C(13)$	1.222(7)
Pt(1)-C(1) 1.994(5) P(1)-C(23)	1.826(5)
Pt(1)-C(12) 2.001(5) $P(2)-C(23)$	1.833(5)
Bond Angles (deg)	

Pt(1)-C(1)-C(2)	171.1(4)	P(1)-Pt(1)-P(2)	176.23(4)
Pt(1)-C(12)-C(13)	170.7(4)	P(1) - Pt(1) - C(12)	91.40(14)
C(1) - Pt(1) - P(1)	85.98(14)	C(1) - Pt(1) - C(12)	171.81(18)

$[Pt_2(\mu-dmpm)_2(C \equiv CC_6H_4-Carb-9)_4]$ (4)

Bond Distances (Å)

Pt(1) - P(1) Pt(1) - P(2)	2.284(2) 2.279(2)	C(1)-C(2) C(21)-C(22)	1.217(7) 1.204(7)
Pt(1) - C(1)	1.986(5)	P(1)-C(41)	1.855(8)
Pt(1) = C(21)	1.993(5)	P(2) = C(41)	1.785(7)

Bond Angles (deg)

Pt(1) - C(1) - C(2)	173.0(5)	P(1) - Pt(1) - P(2)	177.65(5)
Pt(1)-C(21)-C(22)	178.0(5)	P(1) - Pt(1) - C(21)	90.39(16)
C(1) - Pt(1) - P(1)	89.99(17)	C(1) - Pt(1) - C(21)	172.98(19)

 $[Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4 \cdot \{Ag(MeCN)\}_2](BF_4)_2 (5)$

Bond Distances (Å)

Pt(1) - P(1)	2.321(1)	Pt(1)-C(1)	2.012(5)
Pt(1) - P(2)	2.303(1)	Pt(1) - C(12)	2.005(5)
Ag(1) - C(1)	2.305(5)	C(1) - C(2)	1.222(7)
Ag(1) - C(2)	2.343(5)	C(12)-C(13)	1.219(7)
Ag(1) - N(1)	2.389(9)	P(1)-C(27)	1.840(5)
	Bond A	ingles (deg)	
P(1) - Pt(1) - P(2)	175.37(4)	P(1) - Pt(1) - C(12)	89.86(14)
P(1) - Pt(1) - C(1)	93.87(15)	P(2) - Pt(1) - C(12)	93.97 (14)
Pt(1)-C(1)-C(2)	165.8(4)	Pt(1)-C(12)-C(13)	168.2 (4)

 $[Pt_2(\mu-dppm)_2 \{C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}_4 \cdot \{Cu(MeCN)\}_2](PF_6)_2$ (6)

Bond Distances (Å)

		. ,	
Pt(1) - P(1)	2.317(1)	Pt(1)-C(1)	2.012(5)
Pt(1) - P(2)	2.304(1)	Pt(1) - C(12)	2.009(5)
Cu(1) - C(1)	2.087(5)	C(1) - C(2)	1.230(7)
Cu(1) - C(2)	2.100(5)	C(12) - C(13)	1.220(7)
Cu(1) - N(1)	2.077(8)	P(1)-C(27)	1.839(5)
	Bond A	Angles (deg)	
P(1) - Pt(1) - P(2)	176.03(5)	P(1)-Pt(1)-C(12)	90.17(14)
P(1) - Pt(1) - C(1)	92.01(16)	P(2) - Pt(1) - C(12)	93.50(14)
Pt(1)-C(1)-C(2)	165.2(5)	Pt(1)-C(12)-C(13)	166.6(4)

Table 3. Pt···Pt Distances of Dinuclear Pt(II) Alkynyl Complexes with Estimated Standard Deviations in Parentheses

complex	$d(Pt \cdots Pt), Å$
$Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}_4\}$ (1)	3.3686(2)
$Pt_2(\mu-dmpm)_2 \{C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}_4 \}$ (3)	3.3082(5)
$Pt_2(\mu-dmpm)_2(C \equiv CC_6H_4-Carb-9)_4]$ (4)	3.2045(4)
$Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}_4$.	3.2022(2)
$\{Ag(MeCN)\}_{2}(BF_{4})_{2}(5)$	
$Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4$.	3.0117(2)
$\{Cu(MeCN)\}_{2}](PF_{6})_{2}(6)$	

crystallographic data. For complex **6**, calculation was performed on the basis of its X-ray crystal structure with the Cu–N–C and N–C–CH₃ angles in each of the acetonitrile coordinations set at 180°. In the present study, all the C–H bond lengths of the complexes were set at 1.09 Å. The Stuttgart effective core potentials and the associated valence basis set were applied for Pt^{22a} and Cu^{22b} with f polarization functions [$\zeta_f(Pt) = 0.993$ and $\zeta_f(Cu)=3.525$],²³ while the 6-31G(d) basis set²⁴ was used for P, O, N, C, and H atoms. All TDDFT calculations were performed with a larger grid size (99590). Mulliken population analyses were done using MullPop.²⁵

Results and Discussion

Synthesis and Characterization. The face-to-face diplatinum-(II) alkynyl complex [Pt₂(µ-dppm)₂(C≡CPh)₄] was first synthesized by Pringle and Shaw⁵ by the reaction of [Pt(dppm-P, P')-Cl₂] with LiC≡CPh in THF-benzene under reflux conditions for 24 h. In this synthesis, LiC≡CR was generated in situ from the corresponding RC=CH and "BuLi and was added dropwise to $[Pt(dppm-P, P')Cl_2]$ in benzene at -78 °C. Until more recently, an alternative synthetic procedure was reported by Chen and co-workers.' It was suggested that this class of faceto-face diplatinum(II) complexes could be prepared by the stirring of $[Pt(dppm-P, P')Cl_2]$ with the corresponding alkynes in the presence of a base at room temperature for five days without the need for the use of lithiating reagents.⁷ However, this synthetic approach required a relatively long reaction time as compared to the former one. Alternatively, based on the previous experience in phosphine exchange reaction suggested by Gladysz and co-workers,⁸ an improved synthetic route involving two steps that require a common mononuclear platinum(II) bis-alkynyl precursor for the subsequent synthesis of a variety of face-to-face dinuclear platinum(II) alkynyl complexes with various diphosphine ligands has been employed. The first step involves the syntheses of mononuclear platinum-(II) bis-alkynyl complexes with triphenylphosphine as auxiliary ligands, trans-[Pt(PPh₃)₂(C=CR)₂] (R = C=CC₆H₂(OMe)₃-3,4,5 and C=CC₆H₄-Carb-9), according to the well-documented procedures.14 In the second step, the corresponding mononuclear platinum(II) bis-alkynyl intermediate is subjected to a facile phosphine exchange reaction with various diphosphines, which has to be done under very dilute conditions in order to avoid the formation of insoluble polymers. The purification of

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Scheme 2. Synthetic Route of Complexes 5 and 6 by Metal Ion Encapsulation



complexes 1-4 was accomplished by column chromatography on silica gel using dichloromethane as eluent. Subsequent recrystallization from dichloromethane-diethyl ether afforded the products as pure air-stable greenish-yellow crystals. Scheme 1 summarizes the synthetic routes for complexes 1-4.

The structure of the face-to-face dinuclear complexes shows two pairs of adjacent alkynyl ligands that have been preorganized for the ready incorporation of other metal ions through π -coordination.^{6a,b} By the reaction of [Pt₂(μ -dppm)₂- $\{C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}_4\}$ with $[M(MeCN)_4]^+$ (M = Cu or Ag), the tetranuclear mixed-metal platinum(II)-silver(I) and -copper(I) complexes $[Pt_2(\mu-dppm)_2 \{C \equiv CC_6H_2(OMe)_3 3,4,5_4$ {Ag(MeCN)}₂](BF₄)₂ (5) and [Pt₂(μ -dppm)₂{C= $CC_6H_2(OMe)_3-3,4,5_4\{Cu(MeCN)\}_2](PF_6)_2$ (6) have been prepared and isolated, in which the metal ions are sandwiched between the alkynyl groups within the same dinuclear face-to-face complexes (Scheme 2).^{6a,b} In contrast to the homometallic dinuclear platinum(II) face-to-face complexes, which are only sparsely soluble in dichloromethane, the mixed-metal complexes are found to have good solubilities in dichloromethane.

X-ray Crystal Structures. The structures of 1 and 3-6 have been determined by X-ray crystallography. Figures 1 and 2 show the perspective drawings of the dinuclear platinum(II) alkynyl phosphine complexes 1, 3, and 4 and the mixed-metal

tetranuclear platinum(II)-silver(I) and -copper(I) complexes 5 and 6, respectively. The selected bond distances and angles of 1 and 3-6 are summarized in Table 2 and the Pt···Pt distances in Table 3.

In general, the dinuclear platinum(II) alkynyl complexes show a face-to-face arrangement with two mutually eclipsed platinum square planes bridged by two dppm ligands or dmpm ligands to form an eight-membered ring (Pt-P-C-P-Pt-P-C-P). Each platinum atom exhibits a distorted square-planar geometry with the two alkynyl groups $[C-Pt-C, 170.42(13)-172.98(19)^{\circ}]$ and the two bridging dppm or dmpm phosphorus atoms [P-Pt-P, 174.12(3)-177.65(5)°] arranged in a trans disposition. In the mixedmetal complexes 5 and 6, each of the silver(I) and copper(I) centers is π -coordinated to one pair of the preorganized alkynyl groups that serve as η^2 -ligands and is coordinated to one acetonitirile molecule in a trigonal-planar geometry. The average C = C bond distances of complexes 5 and 6 are in the range 1.219(7) - 1.230(7) A, slightly longer than the C=C bond distances (1.206(5)-1.220(5) Å) in the related [Pt₂- $(\mu$ -dppm)₂{C=CC₆H₂(OMe)₃-3,4,5}₄] (1) precursor. The weakening of the C=C bond upon silver(I) or copper(I) coordination is in accord with the π -coordination mode of the alkynyl group and is in agreement with the observation of a lower C=C stretching frequency $\{2024(w) \text{ cm}^{-1}\}$



Figure 1. Perspective drawings of (a) **1**, (b) **3**, and (c) **4** with atomic numbering scheme. The H atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.



Figure 2. Perspective drawings of complex cation of (a) 5 and (b) 6 with atomic numbering scheme. The H atoms, counter-anions and the phenyl rings of dppm have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

in 5; $2005(w) \text{ cm}^{-1}$ in 6 versus 2097 cm⁻¹ in 1} in the IR spectroscopy.

The Pt···Pt distances of 1 and 3–6 are summarized in Table 3. The Pt···Pt distances in the range 3.0117(2)– 3.3686(2) Å, which are comparable to that of the related $[Pt_2(\mu\text{-dppm})_2(C \equiv CPh)_4]$ (Pt···Pt 3.437(1) Å)^{6a} and $[Pt_2-(\mu\text{-dppm})_2(CN)_4]$ (Pt···Pt 3.301(1) Å),^{4d} suggest the presence of weak Pt···Pt interaction. It is interesting to note that the X-ray crystal structure of the dmpm analogue of complex 3 shows a slight decrease in Pt···Pt distance by 0.06 Å when compared to the dppm analogue of complex 1. In addition, it is found that the Pt···Pt distances vary with the nature of the alkynyl ligands. A shorter Pt···Pt distance has been found for complex 4 (Pt···Pt distance 3.2045(4) Å), with the less electron-rich and more bulky carbazole-based alkynyl ligand. The lower electron density and the bulkiness of the alkynyl ligand would cause the two Pt centers to approach each other more closely due to the reduced electron density around the Pt centers as well as the steric crowdedness of the two adjacent alkynyl groups. Comparatively stronger $Pt \cdots Pt$ interactions have been observed in the mixed-metal complexes, 5 [3.2022(2) A] and 6 [3.0117(2) Å], in which the Pt \cdots Pt distances are found to be significantly shorter than in their precursor complex $[Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (1) [3.3686(2) Å]. The substantial decrease in the Pt···Pt distance upon metal ion encapsulation is ascribed to the encapsulation of a silver(I) or copper(I) metal ion into the cleft between the two alkynyl groups, which pushes the platinum atoms into close proximity as a result of the reduced donor strength of the alkynyl ligands as well as the steric demands required upon silver(I) or copper(I) coordination. The larger ionic radius of the silver(I) ion compared to that of the copper(I) ion as well as the weaker Lewis acidity of Ag(I) than Cu(I) may account for the longer $Pt \cdots Pt$ distance in the silver(I) analogue, 5, than that in the copper(I) analogue, 6.

Electronic Absorption Study. The electronic absorption spectra of the face-to-face dinuclear platinum(II) phosphine alkynyl complexes and mixed-metal tetranuclear platinum(II)silver(I) and -copper(I) complexes show intense absorption bands at ca. 272-282 and 342-432 nm in dichloromethane solution. A summary of the electronic absorption spectral data is tabulated in Table 4. The high-energy absorption bands at 272-282 nm of complexes 1-2 and 5-6 are assigned as $\pi \to \pi^*$ (phosphine) and $\pi \to \pi^*$ (alkynyl ligand) intraligand (IL) transitions that are slightly perturbed by the metal centers. This is because the free phosphine ligands and alkynyl ligands also absorb strongly in this region. In addition, the very large extinction coefficients of the complexes in this region, which are much larger than those found in the free diphosphine and alkynyl ligands, further support the assignment of the high-energy absorption bands as IL transitions of the diphosphine and alkynyl ligands, resulting from the presence of multiple phosphine and alkynyl moieties.

Table 4. Electronic A	bsorption and	Emission Data
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	absorption	emission	
complex	$\lambda/\mathrm{nm}~(\epsilon/\mathrm{dm^3~mol^{-1}cm^{-1}})$	medium (T/K)	$\lambda/\mathrm{nm}~(au_0/\mu\mathrm{s})$
1	274 sh (117 345), 342 (48 930), 378 (56 090)	CH ₂ Cl ₂ (298)	643 (0.4)
		solid (298)	470 (0.9)
		solid (77)	465 (1.0)
		glass $(77)^a$	460 (5.8)
2	296 (166 315), 312 sh (119 850), 346 sh (94 990), 380 (71 410)	CH ₂ Cl ₂ (298)	648 (0.1)
		solid (298)	615(<0.1)
		solid (77)	660 (4.8)
		glass $(77)^a$	638 (10.2)
3	280 (78 810), 318 sh (28 250), 342 sh (25 855)	CH_2Cl_2 (298)	612 (0.4)
		solid (298)	462 (0.5)
		solid (77)	458 (8.5)
		glass $(77)^a$	453 (6.6)
4	296 (145 530), 316 (106 320), 344 (100 880), 372 sh (46 610)	CH ₂ Cl ₂ (298)	619 (0.2)
		solid (298)	495 (0.3)
		solid (77)	504 (3.8)
		glass $(77)^a$	465 (11.7)
5	282 sh (91 760), 368 (50 500), 404 (59 435)	CH ₂ Cl ₂ (298)	647 (0.3)
		solid (298)	524 (1.3)
		solid (77)	520 (5.1)
		glass $(77)^a$	483 (5.4)
6	282 sh (115 200), 388 (52 610), 432 (74 110)	CH ₂ Cl ₂ (298)	659 (0.2)
		solid (298)	548 (1.4)
		solid (77)	542 (7.2)
		glass $(77)^a$	550 (5.8)

^a In EtOH-MeOH (4:1 v/v).

The lowest energy absorption is found to be sensitive to the nature of the alkynyl ligands, similar to those observed in previous spectroscopic studies,⁶ suggesting the involvement of the $\pi^*(C \equiv CR)$ character in the LUMO. The absorption energy in the order of $[Pt_2(\mu$ -dppm)_2{ $C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (1) (342–378 nm) > $[Pt_2(\mu$ -dppm)_2($C \equiv CC_6H_4$ -Carb-9)_4] (2) (346–380 nm) as well as $Pt_2(\mu$ -dmpm)_2{ $C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (3) (318–342 nm) > $[Pt_2(\mu$ -dmpm)_2($C \equiv CC_6H_4$ -Carb-9)_4] (4) (344–372 nm) seems to be dependent on the π -accepting ability of RC=C, in which R = $C_6H_2(OMe)_3-3,4,5 < C_6H_4$ -Carb-9. The lower π^* orbital energy of $C \equiv CC_6H_4$ -Carb-9 could be attributed to the more extended π -conjugation of the carbazole moiety.

As mentioned previously, a shorter $Pt \cdots Pt$ distance has been found for the carbazole-based complex 4 (Pt $\cdot \cdot \cdot$ Pt distance 3.2045(4) Å) relative to the trimethoxylphenyl-based complexes 1 (3.3686(2) Å) and 3 (3.3082(5) Å). In general, previous spectroscopic works on dinuclear platinum(II) systems⁶ show that a shorter $Pt \cdots Pt$ distance would lead to a smaller HOMO-LUMO gap as a result of a stronger $Pt \cdots Pt$ interaction due to the antibonding overlap of the metal-filled d orbitals in the HOMO and the bonding overlap of the metal empty p orbitals in the LUMO. Computational studies in this system showed that the effect of the Pt···Pt distance on the energy level of the LUMO would be more significant than that of the HOMO, as the antibonding combination of the metal-filled d orbitals is in either π or δ symmetry, while the bonding combination of the metal empty p orbitals is in σ symmetry (vide infra). Both the stronger π -accepting ability of C=CC₆H₄-Carb-9 and the shorter $Pt \cdots Pt$ distance for the carbazole-based complexes would cause a narrowing of the HOMO-LUMO energy gap. Such a red shift of the absorption band appears to be in line with an assignment of the transition that contains a metalto-ligand charge transfer (MLCT) character perturbed by metal d-p character resulting from the metal-metal interaction.

Interestingly, the bridging diphosphine ligands also have been shown to have an effect on the electronic absorption energy. The absorption energy in the order of $[Pt_2(\mu-dmpm)_2-$ $\{C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}_4\}$ (3) (318-342 nm) > $[Pt_2(\mu - dppm)_2 - 4, 5]_4$ $\{C = CC_6H_2(OMe)_3 - 3, 4, 5\}_4]$ (1) (342-378 nm) indicates that the HOMO-LUMO energy gap becomes larger when the bridging diphosphine ligand is changed from dppm to dmpm. A similar trend has also been observed in the carbazole-based alkynyl complexes, in which the energy follows the order $[Pt_2(\mu-dmpm)_2 (C \equiv CC_6H_4 - Carb-9)_4](4)(344 - 372 nm) > [Pt_2(\mu-dppm)_2 - 100) = 1000 mm)_2 - 10000 mm)_2 - 1000 mm)_2 - 1000 mm)_2$ $(C \equiv CC_6H_4$ -Carb-9)₄] (2) (346-380 nm). It is worth mentioning that the dppm and dmpm bridging diphosphine ligands do not alter the structure of the system much, as reflected by the similar Pt···Pt distances observed in the X-ray crystal structures of $[Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}_4]$ (1) (3.3686(2) A) and $[Pt_2(\mu\text{-dmpm})_2\{C \equiv CC_6H_2(OMe)_3, 3, 4, 5\}_4]$ (3) (3.3082(5) Å). Given the less obvious role of the substituent groups on the diphosphine ligands, the effect of the nature of the bridging diphosphine ligands on the low-energy absorption band will be probed by the computational study (vide infra).

Apart from the nature of the alkynyl and bridging ligands, the coordination of d^{10} metal centers, namely, Ag(I) and Cu(I), also has an influence on the energy of the low-energy absorption bands. Figure 3 shows the overlaid electronic absorption spectra of complexes 1, 5, and 6, which indicates a red shift in the low-energy absorption band upon the coordination of Ag(I) and Cu(I). In general, the mixed-metal complexes always show a lower energy absorption band than the dinuclear platinum(II) face-to-face precursor. The red shift of the absorption band upon encapsulation of silver(I) ions in 5 (368–404 nm) and copper(I) ions in 6 (388–432 nm) compared to their precursor complex, $[Pt_2(\mu-dppm)_2(C=$ $CC_6H_2(OMe)_3-3,4,5)_4$ (1), may be ascribed to the narrower HOMO-LUMO energy gap as a consequence of an increase in the alkynyl π -acceptor ability as well as an increase in the Pt···Pt interaction upon metal ion coordination. The Lewis acid Ag(I) and Cu(I) would withdraw electron density from the alkynyl ligands upon coordination. Thus, this would give rise to a lower lying $\pi^*(C \equiv CR)$ orbital for the mixed-metal tetranuclear platinum(II)-silver(I) and -copper(I) complexes.



Figure 3. Electronic absorption spectra of $[Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (1) (black), $[Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2-(OMe)_3-3,4,5\}_4\cdot \{Ag(MeCN)\}_2](BF_4)_2$ (5) (blue), and $[Pt_2-(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4\cdot \{Cu(MeCN)\}_2](PF_6)_2$ (6) (red) in CH_2CI_2 at 298 K.

Moreover, the antibonding combination of the Pt d orbitals would be higher lying in energy, while the bonding combination of the Pt empty p orbitals would be lower lying in energy when the complexes show a stronger $Pt \cdots Pt$ interaction, as reflected by the shorter $Pt \cdots Pt$ distance observed in the study of the X-ray crystal structures of complexes 1, 5, and 6, in which the Pt···Pt distances are 3.3686(2), 3.2022(2), and 3.0117(2) Å, respectively. As a result, the increase in the π -acceptor ability of alkynyl ligands and the decrease in the Pt · · · Pt distances would cause a narrowing of the HOMO-LUMO energy gap. Such a red shift of the absorption band is in accord with an assignment of the transition that contains MLCT mixed with metal-centered (MC) d-p character. The higher absorption energy of the bands observed in 5 relative to its copper(I) analogue, 6, is ascribed to the weaker Lewis acidity of Ag^I than Cu^I as well as the larger ionic radius of Ag(I) than Cu(I), which would lead to a weaker π -accepting ability of the alkynyl ligands and a longer Pt···Pt separation upon Ag¹ coordination, and hence a higher MLCT/ MC transition energy.

Luminescence Study. Upon excitation at $\lambda > 350$ nm, the carbazole-based complexes 2 and 4 exhibit strong luminescence in room-temperature fluid solution, room- and low-temperature solid state, and low-temperature glass state, while the trimethoxybenzene-based complexes 1, 3, 5, and 6 are found to be weakly emissive in room-temperature fluid solution. In general, all the face-to-face dinuclear platinum(II) phosphine alkynyl complexes 1-6 display emissions at ca. 612-659 nm in degassed dichloromethane solution. 3 and 4, with dmpm as the bridging ligand, are found to exhibit emissions at ca. 612-619 nm, which are more blue-shifted with respect to their dppm analogues 1 and 2, which display the emission at ca. 643–648 nm in the fluid solution. Moreover, mixed-metal tetranuclear platinum(II)silver(I) and -copper(I) complexes 5 (647 nm) and 6 (659 nm) show a red-shifted emission as compared to that of their precursor, 1 (643 nm), in the fluid solution. All complexes exhibit relatively long-lived emissive states in the microsecond range and are suggestive of their triplet parentage. An assignment of the low-energy emission to an excited state of ³MLCT/³MC d-p origin is suggested. The emission and excited-state lifetime data are summarized in Table 4, and selected overlaid emission spectra of the complexes are depicted in Figures 4 and 5. In the solid and glass state at 77 K, the emission spectra are dominated by vibronic structures with vibrational progressional spacings of ca. 1585-1618 and



Figure 4. Normalized emission spectra of $[Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (1) (blue) and $[Pt_2(\mu-dppm)_2(C \equiv CC_6H_4-Carb-9)_4]$ (2) (red) in CH₂Cl₂ at 298 K.



Figure 5. Normalized emission spectra of $[Pt_2(\mu-dppm)_{2^-}(C \equiv CC_6H_2(OMe)_3-3,4,5)_4](1)$ (black), $[Pt_2(\mu-dppm)_2(C \equiv CC_6H_{2^-}(OMe)_3-3,4,5)_4 \cdot \{Ag(MeCN)\}_2](BF_4)_2$ (5) (blue), and $[Pt_2(\mu-dppm)_2(C \equiv CC_6H_2(OMe)_3-3,4,5)_4 \cdot \{Cu(MeCN)\}_2](PF_6)_2$ (6) (red) in the solid state at 298 K.

2012–2142 cm⁻¹, typical of the phenyl ring deformation, $\nu(C = C)$ and $\nu(C = C)$ stretching modes in the ground state, suggesting the involvement of the R-C cmoiety in the emissive state. Similar spectroscopic assignments have also been suggested in other related face-to-face diplatinum(II) systems.⁶

The emission band is also found to be sensitive to the nature of the alkynyl ligands. A red shift in emission energy for complexes 1 (643 nm) and 2 (648 nm) when compared to $[Pt_2(\mu-dppm)_2(C \equiv CPh)_4]$ (620 nm)^{6a} has been observed. This has been similarly rationalized by the presence of the more π -conjugated carbazole-based substituents in 2, which would lower the $\pi^*(C \equiv CR)$ orbital energy, as well as the presence of a shorter $Pt \cdots Pt$ separation in complex 1 (3.36861(18) Å) than that in $[Pt_2(\mu-dppm)_2(C \equiv CPh)_4]$ (3.437 Å).^{5a} Both the increase in the π -accepting ability of the alkynyl group and the shortening of the Pt · · · Pt distance would lead to the narrowing of the HOMO-LUMO energy gap, as discussed in the electronic absorption studies, and thus a lower emission energy is observed for both complexes 1 and 2. Furthermore, it is interesting to note that the emission energy in the fluid solution is in the order of $[Pt_2(\mu-dppm)_2 \{C \equiv CC_6H_2(OMe)_3 - 3, 4, 5\}_4\}$ (1) (643 nm) > $[Pt_2(\mu - dppm)_2 - 4, 5]_4$ $(C \equiv CC_6H_4$ -Carb-9)₄] (2) (648 nm) and $[Pt_2(\mu$ -dmpm)₂{ $C \equiv$ $CC_6H_2(OMe)_3-3,4,5_{4}$] (3) (612 nm) > $[Pt_2(\mu\text{-dmpm})_2(C=$ CC_6H_4 -Carb-9)₄] (4) (619 nm), similar to the trend observed in the electronic absorption studies.



Figure 6. Spatial plot (isovalue value = 0.02) of selected molecular orbitals in 1.

In line with the shift observed in the electronic absorption spectral studies, a lower emission energy of the bands in the dppm analogues (643–648 nm) relative to the dmpm counterparts (612–619 nm) has been observed in the fluid solution. The emission energy in the order of $[Pt_2(\mu-dmpm)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (3) (612 nm) > $[Pt_2(\mu-dppm)_2\{C \equiv CC_6H_2(OMe)_3-3,4,5\}_4]$ (1) (643 nm) in the room-temperature fluid solution indicates a larger transition energy when the bridging diphosphine ligand is changed from dppm to dmpm. A similar trend has also been observed in the carbazole-based alkynyl complexes, in which the emission energy follows the order $[Pt_2(\mu-dmpm)_2(C \equiv CC_6H_4-Carb-9)_4]$ (4) (619 nm) > $Pt_2(\mu-dppm)_2(C \equiv CC_6H_4-Carb-9)_4]$ (2) (648 nm) in the roomtemperature fluid solution.

Upon encapsulation of the Lewis acid metal ions Ag(I) and Cu(I), a lower emission energy of 5 and 6 than the precursor complex 1 in room-temperature fluid solution is observed, consistent with the trend observed in the electronic absorption studies. The coordination of Ag(I) and Cu(I) ions would lead to a shortening of the $Pt \cdots Pt$ distance since the bending of the C-Pt-C bond would force the two Pt centers into close proximity. This, together with the reduction of electron density at the Pt center as a result of the reduction of the donor strength of the alkynyl ligands upon π -donation to Ag(I) and Cu(I), would further bring the two Pt centers into close proximity. In addition, the coordination of the Lewis acidic Ag(I) and Cu(I) centers to the alkynyl unit would also lower the π^* orbital energy of the alkynyls. Both the contraction of the Pt $\cdot \cdot \cdot$ Pt distance and the increase in π -accepting ability of the alkynyl group would result in a narrowing of the HOMO-LUMO energy gap, and hence a lower emission

energy of **5** and **6** was observed. As in the electronic absorption studies, the slightly higher emission energy of the mixedmetal silver(I)-platinum(II) complex **5** (647 nm) than its copper analogue **6** (659 nm) has been similarly ascribed to the weaker Lewis acidity of Ag(I) as well as the larger ionic radius of Ag(I) than Cu(I).

Computational Study. In order to provide an in-depth understanding of the origin of the low-energy electronic absorption band of the face-to-face dinuclear platinum(II) complexes, time-dependent density functional theory (TDDFT) calculations associated with the conductor-like polarizable continuum model (CPCM) were performed to compute the first three lowest lying singlet—singlet transitions of $[Pt_2(\mu-dppm)_2-{C=CC_6H_2(OMe)_3-3,4,5}_4]$ (1), $[Pt_2(\mu-dmpm)_2{C=CC_6H_2-(OMe)_3-3,4,5}_4]$ (3), and $[Pt_2(\mu-dmpm)_2(C=CC_6H_4-Carb-9)_4]$ (4) on the basis of the experimentally determined geometries obtained from X-ray crystallographic diffraction data (for details, see the Experimental Section).

In general, the first four highest lying occupied orbitals in each of 1, 3, and 4 are dominated by the four linear combinations of the highest occupied π orbitals of the four C=CR ligands. In the HOMO and HOMO-1 orbitals, orbital mixing from the metal $d\pi$ orbitals in an out-of-phase fashion can be found. The LUMO is the σ -bonding combination of the empty metal p orbitals from the two metal centers with the P-C σ^* orbitals²⁶ of the bridging diphosphine ligands and π^* orbitals of the alkynyl ligands contributing in a bonding fashion. Figure 6 and Figure S1 depict these orbitals for complexes 1, and 3 and 4, respectively.

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Table 5. TDDFT/CPCM Vertical Excitation Wavelength (nm) of the First Three Lowest Lying Singlet Excited States of 1, 3, and 4

complex	S _n	excitation ^a	transition coefficient	f^b	vertical excitation wavelength (nm)
1	S_1	$H-1 \rightarrow L$	0.68	0.000	362
	S_2	$H \rightarrow L$	0.68	0.590	362
	S_3	$H-2 \rightarrow L$	0.65	0.184	338
3	S_1	$H \rightarrow L$	0.68	0.323	341
	S_2	$H-1 \rightarrow L$	0.67	0.000	337
	S_3	$H-3 \rightarrow L$	0.65	0.000	325
4	S_1	$H \rightarrow L$	0.67	0.001	365
	S_2	$H-1 \rightarrow L$	0.63	1.221	357
	S_3	$H-2 \rightarrow L$	0.62	0.809	344

^{*a*}Orbitals involved in the major excitation (H = HOMO and L = LUMO). ^{*b*}Oscillator strengths.

The computed singlet—singlet transitions and the percentage composition of selected molecular orbitals for 1, 3, and 4 are listed in Tables 5 and 6, respectively. These transitions involve the excitation from the π orbitals of the alkynyl ligand mixed with the metal d orbitals to the LUMO. The transitions for 1 (S₀ \rightarrow S₂) and 3 (S₀ \rightarrow S₁) with the largest oscillator strength are mainly the excitation from the HOMO to the LUMO, while for 4 the S₀ \rightarrow S₂ transition with the largest oscillator strength involves the HOMO–1 \rightarrow LUMO excitation. The excitation wavelengths for the transitions in 1, 3, and 4 are computed to be 362, 341, and 357 nm, respectively. The red shift of the calculated transitions upon going from 3 to 1 and from 3 to 4 is in agreement with the trend of the low-energy absorption band observed in the electronic absorption spectra.

The energy level of the LUMO in 3(-0.87 eV) is found to be higher lying than that of 1 (-0.98 eV). Based on the calculated percentage composition of the molecular orbitals in Table 6, the contribution of the bridging diphosphine ligands to the LUMO in 1 is larger than that in 3. As mentioned above, the LUMO is composed of the P–C σ^* antibonding orbitals of the diphosphine ligands. The mixing of the π^* orbitals from the phenyl rings into the P–C σ^* antibonding orbitals would stabilize the LUMO in the dppm system. It is interesting to note that the HOMO level in 3 (-5.29 eV) is found to be lower lying in energy than that in 1 (-5.12 eV). This is in contrast to the expectation that the stronger σ -donating dmpm ligand when compared to the dppm ligand would raise the HOMO that contains the metal and alkynyl characters. These unexpected findings might be ascribed to the greater degree of conjugation in the complexes with the phenyl rings attached to the P atoms in the dppm ligands, which is in contrast to the methyl groups in the dmpm ligands. Both the decrease in the HOMO level and the increase in the LUMO level in 3 would increase the transition energy. For 4, the red shift of the transition energy relative to 3 is due to the fact that the LUMO level in 4(-1.11 eV)is lower in energy than that in 3. More alkynyl contribution to the LUMO for 4 relative to 3 is found (Table 6), consistent with a stronger π -accepting ability of the carbazole-containing alkynyl ligand.

The coordination of the Lewis acid metal ions Ag^+ and Cu^+ to the alkynyl ligands of **1** would lead to the decrease of both the energy level of the filled and unfilled orbitals, due to the electron-withdrawing properties of the cations. However, since the LUMO consists of the bonding combination of the metal p orbitals with the π^* orbitals of the alkynyl

Table 6. Mulliken Percentage Compositions of Selected Molecular Orbitals (H = HOMO and L = LUMO) of the Complexes^{*a*}

	1			3			4		
	Pt	dppm	C≡CR	Pt	dmpm	C≡CR	Pt	dmpm	C≡CR
	22	48	31	36	28	37	29	20	51
Н	15	1	84	12	1	87	14	0	86
I-1	13	1	86	10	1	89	19	1	81
I-2	13	5	82	13	3	84	21	3	76
I-3	1	4	95	16	2	82	1	1	98

^{*a*} The compositions were expressed in terms of contributions from the two Pt metal centers (Pt), four alkynyl ligands ($C \equiv CR$), and two bridging diphosphine ligands (dppm for 1 and dmpm for 3 and 4).

ligand, the decrease in the $Pt \cdots Pt$ separation and increase in the contribution of the alkynyl ligand upon coordination of the metal ions would decrease the LUMO level to a more significant extent relative to the decrease in the HOMO level, leading to the red shift of the low-energy absorption and emission bands upon coordination of the metal ions. As the acetonitrile ligands in the X-ray crystal structures of the mixed-metal complexes 5 and 6 showed cross-like disorder, with the acetonitrile ligands largely deviated from linear geometry, showing average N-C-CH₃ angles of 158° for 5 and 150° for 6, and a bent coordination to the metal center with average M-N-C angles of 130° and 131° for 5 and 6, respectively, attempts have been made to perform the TDDFT/CPCM calculation for 6 on the basis of its X-ray crystal structure with the Cu-N-C and N-C-CH₃ angles in each of the acetonitrile coordination set at 180°. While the computational results have reproduced the trend in the electronic absorption spectral shift of 6 relative to that of 1 and the larger decrease in the LUMO level relative to the HOMO level upon coordination of the metal ion, the calculated data based on the crystal structure of 6 did not provide a good match with the experimental data, probably due to the distorted solid-state structure, which could not well represent the structure in solution.²⁷

On the basis of the spectroscopic studies and TDDFT/ CPCM calculations, the lowest energy absorption of the faceto-face diplatinum alkynyl complexes can be assigned as an admixture of the MLCT transition from the Pt d orbitals to the π^* orbitals of the alkynyl ligands and the P-C σ^* orbitals of the bridging diphosphine ligands and the intraligand $\pi - \pi^*$ transition of the alkynyl ligands. For these transitions, some mixing of the MC d-p transition can also be found. Similarly, the lowenergy emission has been assigned to be derived from triplet states of a mixture of MLCT, IL, and MC character.

Conclusion

In summary, the synthesis, structures, and luminescent behavior of a series of face-to-face dinuclear platinum(II) alkynyl complexes bridged by the two diphosphine ligands together with their mixed-metal tetranuclear platinum(II)– silver(I) and –copper(I) complexes have been studied. The origin and the energy of the lowest energy absorption and emission in the complexes depend on the nature of both the alkynyl and bridging diphosphine ligands, the Pt···Pt

⁽²⁷⁾ The first singlet-singlet transition of 6 was computed at 374 nm, which is mainly contributed from the HOMO \rightarrow LUMO excitation, and was found to show a red shift when compared to 1 (362 nm), in line with the trend observed in the electronic absorption spectra. The small shift of the calculated transitions from 1 to 6 was probably due to the fact that the crystal structure for 6 could not represent the structure in solution.

separation, and the nature of the encapsulated metal ions on the alkynyl ligands. In general, stronger π -accepting abilities of the alkynyl ligands, greater degree of π -conjugation of the substituent groups attached to the P atoms of the bridging diphosphine ligands, and shorter Pt····Pt separations will lead to a red shift in the lowest energy absorption and emission. The TDDFT/CPCM calculations support the spectroscopic assignments.

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Supporting Information Available: Crystallographic data and details for complexes 1, and 3–6. Figure S1, containing selected molecular orbitals for complexes 3 and 4. This material is available free of charge via the Internet at http://pubs.acs.org.