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Synthesis and Photophysical Studies of Calix[4]arene-based Binuclear Platinum(II) Complexes: Probing Metal–Metal and Ligand–Ligand Interactions

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A series of calix[4]arene-based binuclear platinum(II) complexes, Pt_2LCl_2 (**1**, $\text{L} = 5,11,17,23$ -tetra-*tert*-butyl-25,27-di[methoxy(4-phenyl)-(C^{^N^N})]-26,28-dihydroxycalix[4]arene, $\text{HC}^{\wedge}\text{N}^{\wedge}\text{N} = 6$ -phenyl-2,2'-bipyridine), $[\text{Pt}_2(\mu\text{-dppC}_n)](\text{ClO}_4)_2$ ($\text{dppC}_n = \text{bis(diphenylphosphino)-methane}$ (**2**, $n = 1$), -ethane (**3**, $n = 2$), -propane (**4**, $n = 3$), and $[\text{Pt}_2\text{L(PPh}_3)_2](\text{ClO}_4)_2$ (**5**), have been designed and synthesized in this work. Spectroscopic investigation demonstrates that *p-tert*-calix[4]arene is capable of assembling the two square-planar $[(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{Pt(II)}]$ units in a face-to-face manner, simultaneously suppressing intermolecular aggregation and increasing the solubility of the studied complexes. Facile replacement of the chloride ligand in **1** by the strongly σ -donating ancillary phosphine ligands affords binuclear platinum(II) complexes with improved photophysical properties. All of the complexes are emissive both in the fluid/glassy solution and in the solid state, except for **1** in the solid state at room temperature. Moreover, the absorption and emission energies of the complexes are sensitive to the ancillary ligands. Varying the tethered phosphine auxiliaries from dppm (**2**) and dppe (**3**) to dppp (**4**) and PPh_3 (**5**) modulates the *intramolecular* metal–metal ($\text{Pt} \cdots \text{Pt}$) and ligand–ligand ($\pi\text{--}\pi$) distances, thereby leading to a switch of $^3\text{MMLCT}$ and excimeric $^3(\pi\pi^*)$ excited states to a common $^3\text{MLCT}$ excited state.

Introduction

Owing to diverse excited states, high-emission quantum yields, and long triplet excited-state lifetimes, platinum(II) polypyridyl complexes have been recently demonstrated to be promising in many fields.^{1–18} In particular, the square-planar d^8 electronic configuration of the platinum(II) complex allows access to the frontier orbital of the metal centers and

ligands as well.^{1,11–18} When two platinum(II) units are in close proximity,¹¹ metal–metal and/or ligand–ligand interactions result in the metal–metal-to-ligand charge transfer ($\text{MMLCT: [d}\sigma^* \rightarrow \pi^*]$) and/or excimeric ligand-to-ligand ($\pi \rightarrow \pi^*$) excited states. Unusual colors and lower-energy emissions relative to the mononuclear species are often the

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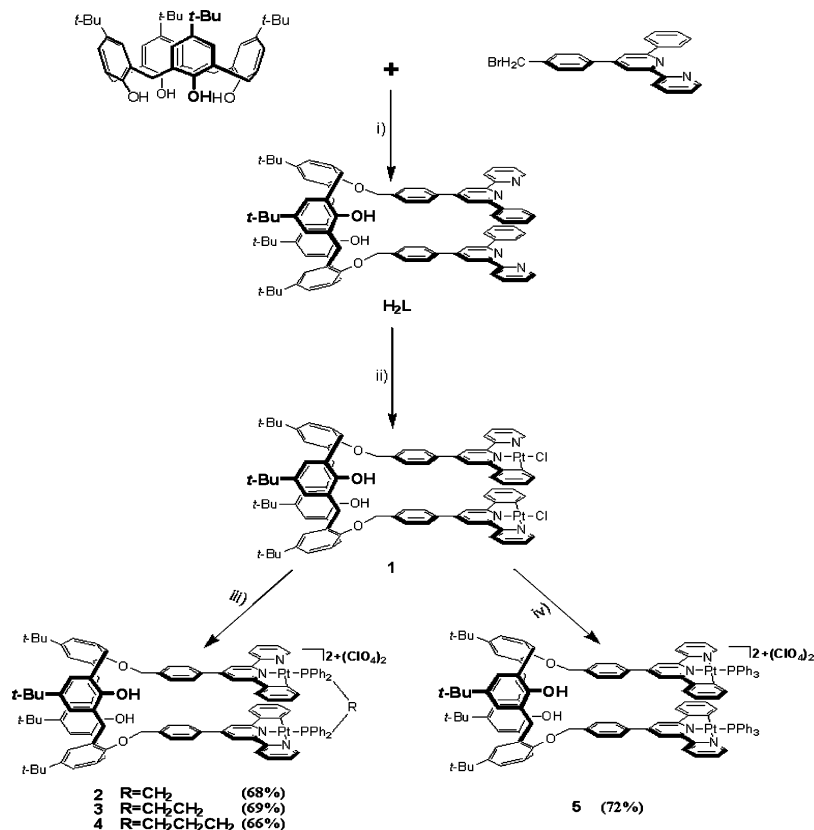
results of metal–metal and ligand–ligand interactions.^{11–18} Because the energies of the metal–metal-to-ligand charge transfer and excimeric ligand-to-ligand excited states are susceptible to the metal–metal and/or ligand–ligand distances,¹¹ several binuclear platinum(II) complexes bridged by bidentate ligands have been characterized to model the interactions of platinum(II) polypyridyl species at the ground state.^{13–15} Gray et al.¹³ observed the emission band of a binuclear platinum(II) terpyridyl complex changing from the ³MLCT excited state to the ³MMLCT state with decreasing Pt••Pt separation, whereas the binuclear platinum(II) com-

plexes were negligibly emissive in fluid solution at room temperature. Thompson et al.¹⁴ made a synthetic control of the Pt••Pt interaction through increasing the steric bulk of the pyrazolate in the boatlike platinum(II) complexes. Che et al.¹⁵ illustrated the structural and spectroscopic properties of bi- and multinuclear cyclometalated platinum(II) complexes tethered by oligophosphine and isocyanide auxiliaries. In comparison with the mononuclear platinum(II) complexes,^{1–10} the strong visible absorption and emission of the binuclear complexes are more attractive as photocatalysts for solar energy conversion, as photoactuated molecular hinges and tweezers for optoelectronics, and as luminescent materials for either OLED or biological applications.^{14–18} Despite the intriguing properties, the chemistry of binuclear platinum(II) complexes has remained relatively unexplored because the preparation always suffers from complicated synthetic procedures, undesired byproducts, and limited solubility.

Calix[4]arene has a unique cavity-shaped architecture that can be functionalized at four phenolic hydroxyl groups, namely, the lower rim, and at four *para*-phenolic positions, namely, the upper rim. As a versatile molecular scaffold,¹⁹ the functional groups can be directionally preorganized in a calix[4]arene platform. Selective molecular recognition probes and supramolecular self-assemblies have been developed.^{20–22} A binuclear platinum(II) alkynylcalix[4]crown-5 complex was recently reported to show selective sensing for potassium ions.^{22c} Nonetheless, the presence of the polyether linkage at the lower rim of the calix[4]arene, and the presence of sterically bulky *tert*-butyl groups on the polypyridyl ligands prevented the two platinum(II) centers

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Scheme 1. (i) 2 equiv K_2CO_3 , acetone/toluene (v/v) = 5:2, reflux 48 h, 50%; (ii) 2 equiv K_2PtCl_4 , 99.7% ethanol, reflux 72 h, 45%; (iii) 1 equiv dppC_n , acetonitrile/methanol (v/v) = 1:1, argon atmosphere, stir 18 h at room temperature; (iv) 2 equiv PPh_3 , acetonitrile, argon atmosphere, stir 20 h at room temperature



from coming into close proximity, and, as a result, the MMLCT and excimeric ligand-to-ligand ($\pi \rightarrow \pi^*$) excited states were not observed in fluid solution.

To examine whether calix[4]arene could be used as a scaffold for *intramolecular* metal–metal ($\text{Pt} \cdots \text{Pt}$) and ligand–ligand ($\pi-\pi$) interactions, a series of binuclear platinum(II) complexes, Pt_2LCl_2 (**1**, $\text{L} = 5,11,17,23$ -tetra-*tert*-butyl-25,27-di[methoxy(4-phenyl)-(C^NN)]-26,28-dihydroxycalix[4]arene, $\text{HC}^{\text{N}^{\text{N}}\text{N}} = 6$ -phenyl-2,2'-bipyridine), $[\text{Pt}_2\text{L}(\mu\text{-dppC}_n)](\text{ClO}_4)_2$ [dppC_n = bis(diphenylphosphino)-methane (**2**, $n = 1$), -ethane (**3**, $n = 2$), -propane (**4**, $n = 3$)], and $[\text{Pt}_2\text{L}(\text{PPh}_3)_2](\text{ClO}_4)_2$ (**5**), have been designed for understanding the fundamentals in this work (Scheme 1). The $[(\text{C}^{\text{N}^{\text{N}}\text{N}})\text{Pt}(\text{II})]$ moiety was selected as a typical building block because the ease of modification of the $(\text{C}^{\text{N}^{\text{N}}\text{N}})$ ligand would make the synthetic protocol simple. At the same time, the extended π ligand and strongly σ -donating carbanionic moiety would increase the energy gap between the d–d and MLCT excited states,^{1h} thus giving rise to rich photoluminescent properties in fluid solutions at room temperature. It is expected that: (1) the relatively rigid conical *p*-*tert*-butylcalix[4]arene framework could be capable of assembling the two square-planar platinum(II) units in a face-to-face manner, suppressing intermolecular aggregation and increasing the solubility of the studied complexes; (2) spectroscopic investigation may provide valuable information on the metal–metal and ligand–ligand interactions because the absorption and emission energies are very dependent on the degree of such interactions; (3) the coordinated chloride

ligand in this case permits facile substitution by the strongly σ -donating auxiliary phosphine ligands to produce the platinum(II) complexes with enhanced photophysical properties. Moreover, the introduced diphosphine ligand may further keep the conical *p*-*tert*-butylcalix[4]arene framework. A subtle change of the length of the diphosphine ancillary ligand would thus afford a series of binuclear platinum(II) complexes with tunable photophysical properties.

In the present work, we report that the designed binuclear **1–5** can be achieved in moderate-to-high yields. As expected, *p*-*tert*-butylcalix[4]arene acts as the scaffold to maintain a face-to-face arrangement of the two platinum(II) moieties. The absorption and emission energies of the complexes are sensitive to the ancillary ligands. Varying the tethered phosphine auxiliaries from dppm (**2**) and dppe (**3**) to dppp (**4**) and PPh_3 (**5**) modulates the *intramolecular* metal–metal ($\text{Pt} \cdots \text{Pt}$) and ligand–ligand ($\pi-\pi$) interactions, leading to a switch of $^3\text{MMLCT}$ and excimeric $^3(\pi\pi^*)$ excited states to a common $^3\text{MLCT}$ state.

Experimental Section

Materials and Instrumentation. K_2PtCl_4 , PPh_3 , bis(diphenylphosphino)-methane, -ethane and -propane (dppm , dppe , and dppp) were purchased from Acros and used as received. *p*-*tert*-Butylcalix[4]arene was prepared by 4-tetrabutylphenol and formaldehyde in aqueous solution, as reported by Gutsche.²³ 4-(Tolyl)-6-phenyl-2,2'-bipyridine was readily synthesized using appropriate

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enone and 2-pyridacetylpyridinium iodide in the presence of excess ammonium acetate.²⁴ 4-(Bromomethylphenyl)-6-phenyl-2,2'-bipyridine was prepared using *N*-bromosuccinimide and 4-(tolyl)-6-phenyl-2,2'-bipyridine in the presence of PhCOOOCPh. Dichloromethane was treated with concentrated sulfuric acid, 10% sodium hydrogen carbonate, and water, dried by calcium chloride, and distilled over calcium hydride.²⁵ Acetonitrile was distilled over potassium permanganate and calcium hydride.²⁵ 2-Methyltetrahydrofuran (2-MTHF) is of spectroscopic grade and used as received. Chloroform, methanol, and dimethylformamide are of chromatographic grade and used without further purification. All other solvents used are of analytical grade.

The MALDI-TOF mass spectra were conducted on a BIFLEXIII mass spectrometer. Elemental analyses were performed on a Carlo Erba 1106 analyzer. ¹H (400 MHz) and ³¹P (162 MHz) NMR spectra were measured on a Bruker-400 spectrometer with TMS (¹H), 77% H₃PO₄ (³¹P) as the internal standard, respectively.

Photophysical Measurements. UV-vis absorption spectra were obtained on a Shimadzu UV-1601 PC spectrophotometer, accurate to ± 2 nm. Steady-state emission spectra were recorded on a Hitachi F-4500 spectrophotometer. The low-temperature emission (77 K) spectra were measured in 2-MTHF solution. The solutions for photophysical measurements were optically dilute for steady-state photoluminescence (OD < 0.05) and for emission lifetime determination ($\sim 5 \times 10^{-5}$ M). In most instances, the samples in 1 cm path-length quartz cells were deoxygenated with argon for at least 20 min prior to measurement, whereas the emission spectra for glassy and the solid-state samples were recorded in 5 mm diameter quartz tubes, which were placed in a liquid-nitrogen Dewar equipped with a quartz window.

Luminescence lifetimes were obtained by an Edinburgh LP 920 with the third harmonic (355 nm) of a pulsed Nd:YAG laser as the excitation resource, using the function Exponential Fit in the fluorescence spectrometer software L900. The emission quantum yield was determined by the optical dilute method²⁶ with degassed [Ru(bpy)₃](PF₆)₂ acetonitrile solution as the standard ($\Phi_r = 0.062$) (eq 1), where the subscripts s and r refer to the sample and reference solutions, respectively.

$$\phi_s = \phi_r(B_r/B_s)(n_s/n_r)^2(D_s/D_r) \quad (1)$$

$B = 1 - 10^{-AL}$, A is the absorbance at the excitation wavelength, L is the path length, n is the refractive index of the solvent, and D is the integrated emission intensity. Error limits are estimated: τ ($\pm 10\%$); ϕ ($\pm 10\%$). In the time-resolved emission spectroscopy experiments, the samples were purged with argon for 30 min, which were performed with a 355 nm excitation wavelength on an Edinburgh F900 analytical instrument. A series of luminescence decay curves at specific wavelengths (a decay curve for every 10 nm from 500 to 800 nm was taken, and every decay curve was measured with the same time period of 2 min) were measured using a 1024 channel time-correlated single-photon counting system. The time-resolved emission spectra were obtained using the function TRES in the fluorescence spectrometer software F900.

Syntheses H₂L. A mixture of 4-(bromomethylphenyl)-6-phenyl-2,2'-bipyridine (1.00 g, 2.50 mmol), *p*-tert-butylcalix[4]arene (0.81 g, 1.25 mmol), and K₂CO₃ (0.35 g, 2.50 mmol) in acetone/toluene (50:20 mL) solution was refluxed for 2 days to afford a yellowish suspension. For removal of solvents under reduced pressure, 50 mL of chloroform was added to dissolve the ivory-white solid. The resulting solution was filtered, and the filtrate was subject to column

chromatographic purification with petroleum ether/ethyl acetate (5:1) as eluent. Yield: 0.80 g, 50%. TOF (M+H)⁺ = 1289. Anal. Calcd for C₉₀H₈₈N₄O₄·C₇H₈: C, 83.45; H, 6.96; N, 4.06. Found: C, 83.86; H, 7.23; N, 4.17. ¹H NMR (400 MHz, CDCl₃, δ): 1.02 (s, 18H, *t*-Bu), 1.30 (s, 18H, *t*-Bu), 3.36 (d, 4H, $J = 12.9$ Hz), 4.39 (d, 4H, $J = 12.9$ Hz), 5.21 (s, 4H), 6.90 (s, 4H), 7.09 (s, 4H), 7.25 (m, 2H), 7.36 (m, 6H), 7.65 (s, 2H), 7.69 (s, 4H), 7.74 (d, 4H, $J = 8.0$ Hz), 7.90 (d, 8H, $J = 7.6$ Hz), 8.35 (s, 2H), 8.38 (d, 2H, $J = 7.6$ Hz), 8.59 (d, 2H, $J = 4.0$ Hz).

[Pt₂(L)Cl₂] (1). A mixture of K₂PtCl₄ (0.32 g, 0.78 mmol) and H₂L (0.50 g, 0.39 mmol) in 99.7% EtOH (400 mL) was refluxed for 3 days to give a turbid orange solution. For removal of solvents under the reduced pressure, 60 mL of dichloromethane was added to dissolve the orange-red solid. The resulting solution was filtered, and the filtrate was subject to column chromatographic purification with dichloromethane/ethyl acetate (5:1) as eluent. Yield: 0.23 g, 45%. MALDI-TOF-MS: (M-Cl)⁺ = 1712. Anal. Calcd for C₉₀H₈₆N₄O₄Cl₂Pt₂: C, 61.82; H, 4.92; N, 3.20. Found: C, 61.68; H, 4.89; N, 3.06. ¹H NMR (400 MHz, DMSO-*d*₆, δ): 1.16 (s, 18H), 1.23 (s, 18H), 3.56 (d, 4H, $J = 12.4$ Hz), 4.33 (d, 4H, $J = 12.4$ Hz), 5.14 (s, 4H), 6.50 (m, 1H), 6.79 (m, 1H), 6.95 (m, 3H), 7.05 (m, 2H), 7.23 (m, 8H), 7.35 (d, 1H, $J = 7.6$ Hz), 7.46 (d, 1H, $J = 7.6$ Hz), 7.61 (m, 2H), 7.76 (m, 3H), 7.79 (m, 3H), 7.99 (m, 5H), 8.07 (d, 1H, $J = 8.0$ Hz), 8.19 (m, 3H), 8.32 (s, 1H), 8.48 (s, 1H), 8.67 (d, 1H, $J = 4.4$ Hz), 8.85 (d, 1H, $J = 4.8$ Hz).

[Pt₂(L)dppm](ClO₄)₂ (2). A mixture of **1** (70.00 mg, 0.04 mmol) and dppm (15.40 mg, 0.04 mmol) in acetonitrile/methanol (10 mL: 10 mL) was carefully deoxygenated with argon bubbled in and then was stirred for 18 h under an argon atmosphere at room temperature. Excess LiClO₄ was added as a solid (**Caution! Perchlorate salts are potentially explosive and should be handled with care and in small amounts**). After filtration, the resultant solution was evaporated to a small volume and then diethyl ether was added to afford a reddish-orange solid, which was further washed with water and diethyl ether to give the desired product. Yield: 61.40 mg, 68%. MALDI-TOF-MS (M-ClO₄)⁺ = 2161, (M-2ClO₄)⁺ = 2061. Anal. Calcd for C₁₁₅H₁₀₈N₄O₁₂Cl₂Pt₂·2H₂O: C, 60.13; H, 4.91; N, 2.44. Found: C, 59.78; H, 4.89; N, 2.55. ¹H NMR (400 MHz, CDCl₃, δ): 0.97 (s, 18H), 1.33 (s, 18H), 3.40 (q, 4H, $J = 12.8$ Hz), 4.29 (q, 4H, $J = 12.8$ Hz), 5.00 (t, 2H, PCH₂, ²*J* (PH) = 13.2 Hz), 5.17 (m, 4H), 6.51 (m, 4H), 6.78 (d, 2H, $J = 10.8$ Hz), 6.86 (m, 6H), 7.11 (m, 6H), 7.43 (m, 8H), 7.50 (s, 6H), 7.74 (m, 4H), 7.90 (m, 10H), 8.07 (m, 8H), 8.30 (s, 4H). ³¹P{¹H} NMR (CD₃CN, δ): 22.18 (¹*J* (PtP) = 4102 Hz, ³*J* (PtP) = 80 Hz).

[Pt₂(L)dppe](ClO₄)₂ (3). **3** was synthesized by the procedure similar to that for **2**, except that dppe (16.00 mg, 0.04 mmol) was used in place of dppm. This product was obtained as an orange solid. Yield: 62.40 mg, 69%. MALDI-TOF-MS (M-ClO₄)⁺ = 2175, (M-2ClO₄)⁺ = 2075. Calcd for C₁₁₆H₁₁₀N₄O₁₂Cl₂Pt₂·2H₂O: C, 60.28; H, 4.97; N, 2.42. Found: C, 60.43; H, 4.83; N, 2.68. ¹H NMR (400 MHz, CD₃CN, δ): 1.19 (s, 18H), 1.28 (s, 18H), 3.60 (q, 4H, $J = 12.8$ Hz), 3.78 ~ 3.87 (m, 4H, PCH₂), 4.39 (q, 4H, $J = 12.8$ Hz), 5.09 (m, 4H), 6.91 (s, 2H), 6.97 (s, 2H), 7.15 (d, 4H, $J = 7.2$ Hz), 7.30 (m, 20H), 7.54 (t, 4H, $J = 6.8$ Hz), 7.73 (s, 4H), 7.94 (m, 14H), 8.05 (m, 6H), 8.15 (m, 1H), 8.34 (s, 1H). ³¹P{¹H} NMR (CD₃CN, δ): 22.62 (¹*J* (PtP) = 4003 Hz).

[Pt₂(L)dppp](ClO₄)₂ (4). **4** was synthesized by the procedure similar to that for **2**, except that dppp (16.40 mg, 0.04 mmol) was used in place of dppm. This product was obtained as a yellow solid. Yield: 60.00 mg, 66%. MALDI-TOF-MS (M-ClO₄)⁺ = 2187, (M-2ClO₄)⁺ = 2088. Calcd for C₁₁₇H₁₁₂N₄O₁₂Cl₂Pt₂·2H₂O: C, 60.34; H, 4.89; N, 2.43. Found: C, 60.34; H, 4.97; N, 2.62. ¹H NMR (400 MHz, CDCl₃, δ): 0.96 (s, 18H), 1.32 (s, 18H), 3.44 (q, 4H, $J =$

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12.8 Hz), 3.52~3.57 (m, 2H, PCH₂CH₂), 3.60~3.68 (m, 4H, PCH₂), 4.29 (q, 4H, *J* = 12.8 Hz), 5.10 (m, 4H), 6.47 (t, 2H, *J* = 7.2 Hz), 6.75~6.82 (m, 6H), 6.85 (s, 4H), 6.92 (d, 2H, *J* = 6.8 Hz), 7.04 (m, 2H), 7.12 (m, 4H), 7.14 (s, 2H), 7.28~7.32 (m, 4H), 7.35 (d, 4H), 7.42~7.52 (m, 6H), 7.70 (m, 4H), 7.78~7.85 (m, 6H), 8.08 (m, 4H), 8.16 (m, 6H), 8.25 (m, 1H), 8.34 (d, 1H, *J* = 7.6 Hz). ³¹P{¹H} NMR (CD₃CN, δ): 22.35 (¹*J* (PtP) = 4002 Hz), 23.42 (¹PtP) = 4013 Hz).

[Pt₂(L)(PPh₃)₂](ClO₄)₂ (**5**). **5** was synthesized by the procedure similar to that for **2**, except that PPh₃ (20.80 mg, 0.08 mmol) and acetonitrile were used in place of dpmp and acetonitrile/methanol, respectively. This product was obtained as a bright-yellow solid. Yield: 69.00 mg, 72%. MALDI-TOF-MS (M-ClO₄)⁺ = 2301, (M-ClO₄-PPh₃)⁺ = 2037. Anal. Calcd for C₁₂₆H₁₁₆N₄O₁₂Cl₂P₂Pt₂·H₂O: C, 62.47; H, 4.78; N, 2.33. Found: C, 62.15; H, 4.68; N, 2.70. ¹H NMR (CDCl₃, 400 MHz, δ): 1.03 (s, 18H), 1.28 (s, 18H), 3.32 (d, 4H, *J* = 12.8 Hz), 4.26 (d, 4H, *J* = 12.8 Hz), 5.19 (s, 4H), 6.37~6.60 (m, 4H), 6.79~6.99 (m, 8H), 7.09 (m, 6H), 7.74 (m, 20H), 7.81 (m, 16H), 7.99 (s, 8H), 8.29~8.48 (m, 4H). ³¹P{¹H} NMR (CD₃CN, δ): 26.37 (¹*J*(PtP) = 4036 Hz).

Results and Discussion

Synthesis. The synthesis of the ligand **H₂L** was carried out under a typical Williamson etherification. As described by Shinkai,²⁷ 1,3- vs. 1,2-etherification of the calix[4]arene is mainly affected by the base used. Therefore, when *p*-tert-butylcalix[4]arene backbone was reacted with 4-(bromomethylphenyl)-6-phenyl-2,2'-bipyridine under weak base condition, 1,3-etherified ligand **H₂L** was obtained in a moderate yield (Scheme 1). Refluxing **H₂L** and K₂PtCl₄ in a mixture of CH₃CN and H₂O (1:1) solution for 36 h failed to give any desired binuclear platinum(II) **1**. As an alternative, using 99.7% EtOH in place of CH₃CN and H₂O (1:1) solution afforded **1** in a reasonable yield. Facile displacement of the chloride group in binuclear **1** by the diphosphine ligands or PPh₃ under anaerobic conditions produced **2–5** with moderate to good yields at room temperature. Significantly, **1–5** obtained in this work are soluble in considerable organic solvents.

MS spectrometry, ¹H NMR (³¹P NMR) spectroscopy, and satisfactory elemental analyses confirmed the identities of **1–5**. The methylene-bridged protons on the *p*-tert-butylcalix[4]arene of binuclear **1–5** exhibit two typical peaks around 4.4–4.2 and 3.6–3.3 ppm in ¹H NMR spectra, indicating that the complexes are symmetric with cone conformation.²⁸ Similar to that observed by Che in calix[4]arene-free binuclear complexes,^{15a} the ³¹P NMR spectrum of **2** displays the typical peak with ¹⁹⁵Pt satellites due to one- and three-bond couplings. **3** and **5** contain one signal with ¹⁹⁵Pt satellites due to one-bond couplings, whereas **4** with a relatively flexible dpmp ligand displays two sets of signals with ¹⁹⁵Pt satellites. These spectral patterns indicate the presence of a binuclear Pt₂(PPh₃)₂ or Pt₂(μ-dppC_n) unit with chemically equivalent phosphorus atoms,^{15a} which are consistent with the signals corresponding to (M-ClO₄)⁺ as

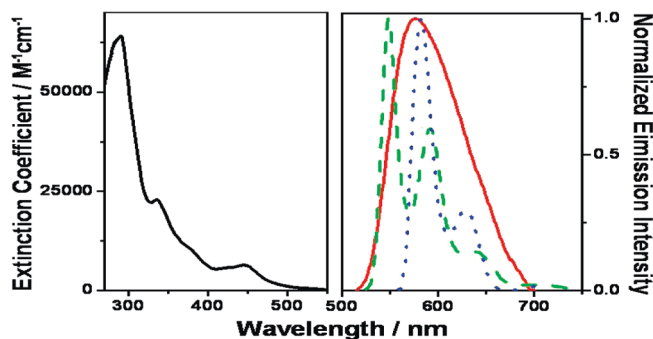


Figure 1. The absorption (left) and emission (right) spectra of **1** in CH₂Cl₂ at 298 K (—), 2-MTHF at 77 K (----), and in the solid state at 77 K (·····), (λ_{ex} 450 nm).

Table 1. UV-vis spectral data for **1–5** in CH₂Cl₂ at room temperature

complex	λ _{max} /nm (ε/M ⁻¹ cm ⁻¹)
1	291 (67 500), 336 (25 700), 446 (5800), 515 (730)
2	292 (53 600), 327 (42 800), 518 (1570)
3	290 (59 100), 331 (44 900), 439 (1980)
4	289 (60 900), 332 (42 900), 373 (17 000), 429 (630)
5	291 (65 500), 332 (49 300), 375 (15 000), 432 (1010)

well as (M-2ClO₄)⁺ fragments observed in MALDI-TOF mass spectra for **2–5**. Single crystals of **1** have been obtained by slow evaporation of concentrated DMF solution and determined by X-ray diffraction. Unfortunately, the crystal quality was poor for detailed analysis, but it suggests that the conic *p*-tert-butylcalix[4]arene backbone aligns the two [(C[^]N[^]N)PtCl] moieties in a cofacial arrangement on the lower rim (Figure S1, Table S1). Such alignment may be suitable for investigation of the intramolecular metal–metal (Pt···Pt) and ligand–ligand (π–π) interactions.

Absorption and Emission Spectroscopy of Binuclear

1. The absorption spectrum of **1** in CH₂Cl₂ solution displays intense absorptions at λ < 350 nm with extinction coefficients on the order of 10⁴ M⁻¹ cm⁻¹ and a moderately intense low-energy absorption band at λ_{max} = 446 nm with an extinction coefficient on the order of 10³ M⁻¹ cm⁻¹ (Figure 1, Table 1.) These spectral properties obey Beer's Law at concentrations below 3.5 × 10⁻⁴ M, suggesting no intermolecular aggregation occurred under such conditions. With reference to previous spectroscopic works on the cyclometallated platinum(II) complexes,^{15a} the absorptions at λ < 350 nm are assigned to the intraligand (IL) π→π* transitions of the (RC[^]N[^]N) ligand, whereas the low-energy absorption at 446 nm is ascribed to the ¹MLCT [(5d)Pt→π*(RC[^]N[^]N)] transition.

1 is emissive in fluid and glassy solutions. Upon excitation, **1** exhibited a weakly broad emission at λ_{max} 577 nm in CH₂Cl₂ at room temperature, whereas well-defined vibronic structured emission bands were detected at λ_{max} 549–591 nm in 2-MTHF at 77 K (Figure 1). The vibrational spacing of 1294 cm⁻¹ corresponding to the skeletal stretching of the (RC[^]N[^]N) ligand suggests that the origin of the emission is derived from the ³MLCT excited state in nature. **1** is nonemissive in the solid state at room temperature, whereas its emission is red-shifted from solution to 583–629 nm upon cooling to 77 K, which derived from the ³MLCT excited state mixing with the excimeric ³(ππ*) state (Table S2 in the

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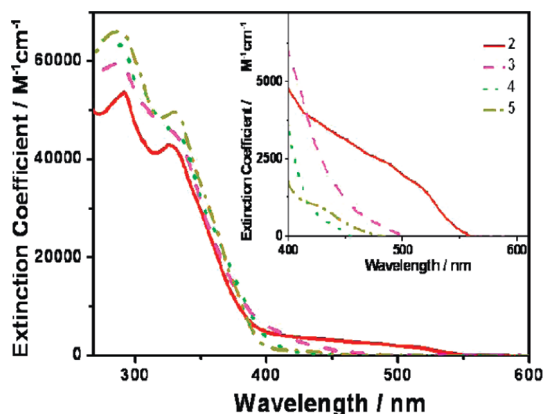


Figure 2. The absorption spectra of **2** (—), **3** (---), **4** (·····), and **5** (-·-·-) in CH_2Cl_2 at room temperature. Inset: Plot of extinction coefficient versus wavelength for **2**–**5** in the range of 400–610 nm.

Supporting Information). Evidently, the relatively flexible framework of calix[4]arene and low-energy d-d excited state involved make for the weak emission of **1** in fluid solution.

Binuclear 2–5 with Phosphine Ancillary Ligand. To examine whether the calix[4]arene could be served as a bridge to construct a series of binuclear platinum(II) complexes, the C_1 , C_2 , and C_3 diphosphine **2**–**4** as well as phosphine congener **5** have been designed and synthesized. The strongly σ -donating auxiliary phosphine ligands are expected to increase the energy difference between the MLCT and d-d states, giving rise to platinum(II) complexes with enhanced photophysical properties. On the other hand, the introduced diphosphine ligand would further keep the conical calix[4]arene framework, suppress the nonradiative decay via molecular vibration, and modulate the distance of the two face-to-face platinum(II) moieties. As the metal–metal separation is increased by C_1 , C_2 , and C_3 diphosphine ligands, spectroscopic investigation would provide valuable information on the *intramolecular* metal–metal and ligand–ligand interactions.

Table 1 lists the absorption wavelength (λ_{max}) of **2**–**5** in CH_2Cl_2 . It is apparent that the lowest-energy absorption band of **2** in CH_2Cl_2 is in the range of 510–560 nm, which is absent for the mononuclear platinum(II) analogues as well as the other complexes studied in this work under the same conditions (Figure 2). Because the absorption is independent to the concentration of **2**, the unique cone-shaped structure of the calix[4]arene backbone is likely to be responsible for the two closely interacting $[(\text{RC}^{\wedge}\text{N}^{\wedge}\text{N})\text{Pt}(\text{II})]$ groups. The long tail around 500 nm is assigned to a $^1\text{MMLCT}$ [$\text{d}\sigma^* \rightarrow \pi^*(\text{RC}^{\wedge}\text{N}^{\wedge}\text{N})$] transition arising from the *intramolecular* $\text{Pt} \cdots \text{Pt}$ contacts. In contrast, the absorptions of **3** and **4** are distinctly different from that of **2**. Obviously, the lowest absorption energies of **2**–**4** in fluid solution depend on the carbon chain between the phosphorus atoms. The shorter the carbon chain of the complex is, the lower energy of the absorption will be (Table 1).

The luminescence response toward the distance between the phosphorus atoms of the complexes was found to be even more pronounced. The binuclear platinum(II) complexes studied in this work are emissive in fluid and glassy solutions

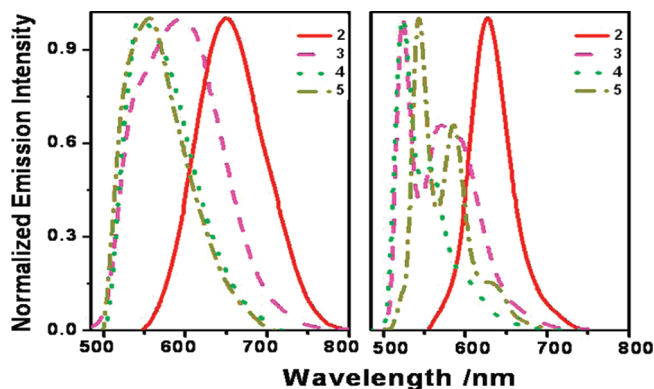


Figure 3. Emission spectra of **2** (—), **3** (---), **4** (·····), and **5** (-·-·-) in CH_2Cl_2 at room temperature (left) and in 2-MTHF at 77 K (right), respectively (λ_{ex} 450 nm).

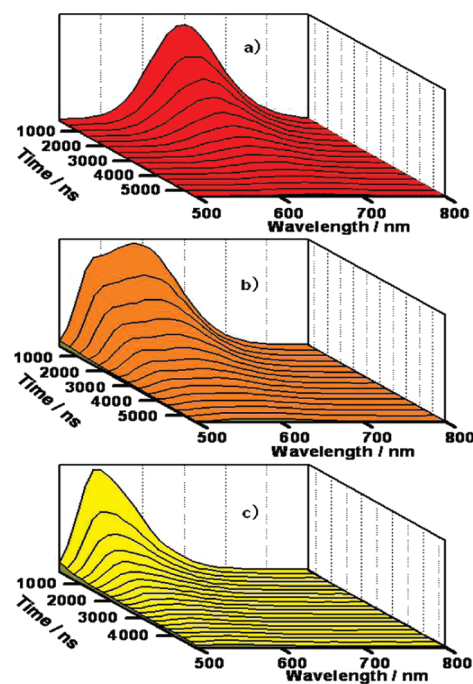


Figure 4. Time-resolved emission spectra of **2** (a), **3** (b), and **4** (c) in CH_2Cl_2 at 298 K (λ_{ex} 355 nm).

(Figure 3). Upon excitation at $\lambda > 450$ nm, **2** displayed a broad emission band at 650 nm in CH_2Cl_2 solution at room temperature. The respective emission energy, lifetime, and quantum yield of **2** are sensitive to the polarity of solvents (Table S3 in the Supporting Information). As reported in $[(\text{C}^{\wedge}\text{N}^{\wedge}\text{N})\text{Pt}(\text{II})]_2(\mu\text{-dppm})(\text{ClO}_4)_2$,^{15a} the emission of **2** is attributed to a $^3\text{MMLCT}$ excited-state with the *intramolecular* $\text{d}^8\text{-d}^8$ interactions. **3** ($n = 2$) shows the broad emission centered at 602 nm with a distinct shoulder at 536 nm. The intermolecular interactions are precluded because the emission is insensitive to the concentration of **3** in the range of 10^{-6} to 10^{-3} M. The excitation spectra, monitored at $\lambda < 550$ nm and $\lambda > 610$ nm, are similar, but the latter shows a higher extinction absorption coefficient at $\lambda > 410$ nm than the former (Figure S2 in the Supporting Information). In the case of **4** bearing a longer carbon chain ($n = 3$) between the diphosphine ligand, an intense emission at 543 nm, a typical $^3\text{MLCT}$ transition, was detected in CH_2Cl_2 . The emission

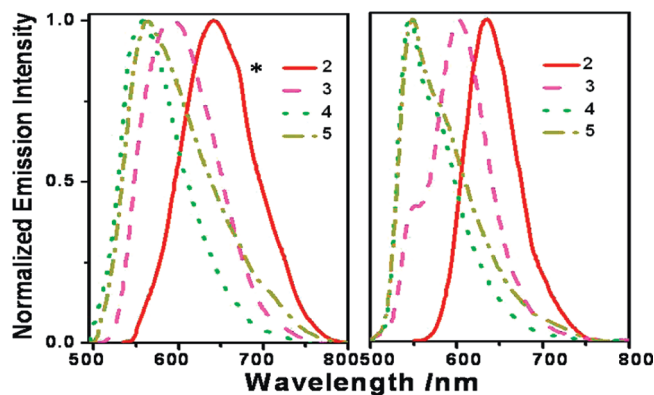


Figure 5. Emission spectra of **2** (—), **3** (---), **4** (·····), and **5** (-·-·-) in the solid state at room temperature (left) and 77 K (right), respectively (λ_{ex} 450 nm, * denotes an instrumental artifact).

Table 2. Photophysical properties of **1–5** in CH_2Cl_2 at 298 K and in 2-MTHF at 77 K, respectively

complex	298 K ($\lambda_{\text{max}}/\text{nm}$; $\tau_0/\mu\text{s}$; ϕ_0)	77 K ($\lambda_{\text{max}}/\text{nm}$)
1	577; 0.21; 0.0044	549 (max), 591, 640
2	650; 1.86; 0.15	628
3	602 (max), 536 (shoulder); 1.06; 0.14	523, 607
4	543; 0.52; 0.045	524 (max), 557, 604
5	550; 0.28; 0.0062	541 (max), 585, 630

maxima observed at 543–550 nm for **4** and **5** correlate with the bulky groups of dppp and PPh_3 , which keep from undergoing effective *intramolecular* metal–metal and ligand–ligand interactions.

To shed more light on the emission characteristic in nature, time-resolved emission spectra of **2–4** were also recorded at room temperature. As shown in Figure 4, **2** ($n = 1$) emits at $\lambda_{\text{max}} = 650$ nm with a lifetime of 1.86 μs and **4** ($n = 3$) is at $\lambda_{\text{max}} = 543$ nm that has a lifetime of 0.52 μs . Despite of the fact that the broad emission centered at 590 nm with a distinct shoulder at 540 nm was clearly detected throughout the measurement, the time-resolved emission spectra of **3** ($n = 2$) remain essentially constant during the decay, reflecting that the emissions for 536 and 602 nm have the same decay rate constant ($\tau = 1.02$ μs).

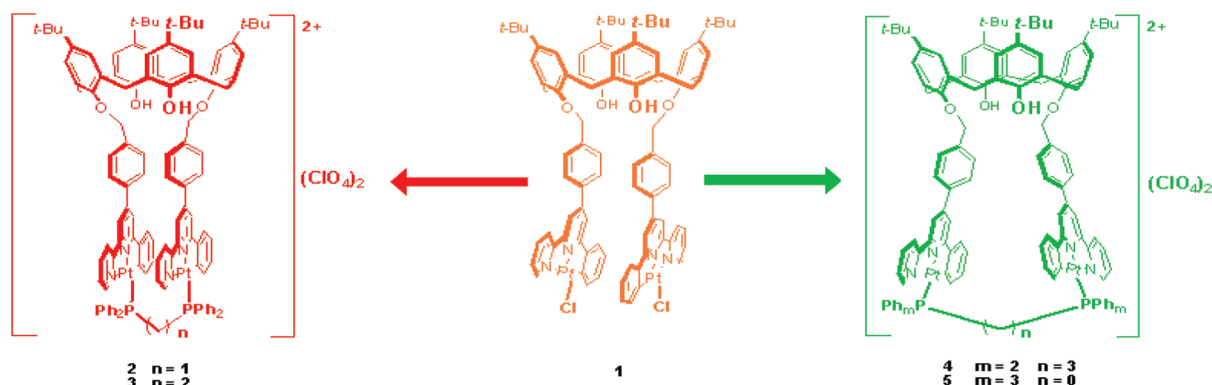
Upon cooling to 77 K, **3** becomes structured with the most intense peak at 523 nm and a moderate broadband at 607 nm, whereas **2** shows a broad $^3\text{MMLCT}$ emission centered at 628 nm and **4** (524 nm) and **5** (541 nm) displays the typical $^3\text{MLCT}$ excited state in 2-MTHF (Figure 3, Figure S3 in the Supporting Information). Notably, the excitation spectra

of **3**, monitored at $\lambda < 550$ nm and $\lambda > 590$ nm, are evidently different. The noticeably enhanced low-energy band intensity of the latter suggests the different emissive excited states involved in **3** (Figure S4 in the Supporting Information). Considering that the absorption energy of **3** is lower relative to **4** but much higher than that for **2**, the concentration-independent emission of **3** is assigned to the $^3\text{MLCT}$ excited state with excimeric $^3(\pi\pi^*)$ emission that results from the *intramolecular* π – π interaction. The emissive behaviors of **2–5** in the solid state have been studied. Trends arising from the different nature of auxiliary ligands are also apparent. The shape and energy for **2–5** emissions in the solid state, analogous to those observed in CH_2Cl_2 solution at room temperature (Figure S5 in the Supporting Information), indicate that intermolecular aggregation is suppressed and the *intramolecular* face-to-face configuration is well retained. The dominant low-energy emission at 603 nm for **3** in the solid state may be interpreted by the fact that the *intramolecular* separation of the two platinum(II) units decreases to operate a stronger *intramolecular* π – π interaction at 77 K (Figure 5).

Table 2 summarizes the photophysical properties of **2–5**, together with the parent **1**. As expected, incorporation of the phosphine ancillary ligand to calix[4]arene-based binuclear **1** leads to the higher emission quantum yield and longer lifetime observed. More interestingly, the absorption and emission energies are very sensitive toward the length of the carbon chain between the diphosphine ligand. The shorter carbon chain ($n = 1$) presented in **2** affords the emission occurring at lower energy relative to those of **3** ($n = 2$) and **4** ($n = 3$). Considering a long carbon chain involved, the separation between the two $[(\text{RC}^{\wedge}\text{N}^{\wedge}\text{N})\text{Pt}(\text{II})]$ units in **4** should be greater than that of **2**. From a spectroscopic point of view, the $[(\text{RC}^{\wedge}\text{N}^{\wedge}\text{N})\text{Pt}(\text{II})]$ fragments in **4** are expected to behave as discrete noninteracting moieties. This is further strengthened by the fact that the $^3\text{MLCT}$ emission observed for **5** with bulky PPh_3 groups, which hinder the two platinum(II) centers to approach either in solution or in the solid state at room temperature or 77 K (Figures 3–5).

In view of the cone-shaped binuclear **1–5**, it could be speculated that the origin of the excited states can be changed over by the introduced ancillary ligands (Scheme 2). **2** and **3** display $^3\text{MMLCT}$ or excimeric $^3(\pi\pi^*)$ excited states from a pair of the $[(\text{RC}^{\wedge}\text{N}^{\wedge}\text{N})\text{Pt}(\text{II})]$ groups that exist prior to

Scheme 2



excitation. When the distance between the two [(RC[^]N[^]N)-Pt(II)] centers is beyond the region of metal–metal and/or ligand–ligand interactions, **4** and **5** with the bulky groups exhibit ³MLCT emission. Therefore, the *p*-*tert*-butylcalix[4]-arene as a hinge is promising to align two [(RC[^]N[^]N)Pt(II)] groups parallel to each other, thereby optimizing the electronic communication between the *intramolecular* metal–metal (Pt···Pt) and ligand–ligand (π – π) interactions and producing a series of binuclear platinum(II) complex with tunable photophysical properties.

Conclusions

Calix[4]arene-based binuclear platinum(II) **1–5** have been achieved with moderate-to-good yields in this work. Spectroscopic investigation demonstrates that the binuclear complexes are capable of assembling the two [(C[^]N[^]N)-Pt(II)] units in a face-to-face manner, simultaneously suppressing intermolecular aggregation and increasing the solubility of the complexes. The coordinated chloride ligand in **1** allows facile replacement by the strongly σ -donating auxiliary phosphine ligands to produce binuclear platinum(II) complexes with enhanced photophysical properties. More importantly, the absorption and emission energies of the binuclear complexes are sensitive to the ancillary ligands.

Varying the tethered phosphine auxiliaries from dppm (**2**) and dppe (**3**) to dppp (**4**) and PPh₃ (**5**) modulates the *intramolecular* metal–metal (Pt···Pt) and ligand–ligand (π – π) interactions, leading to a switch of ³MMLCT and excimeric ³($\pi\pi^*$) excited states to a common ³MLCT state. These results imply that a conical *p*-*tert*-butylcalix[4]arene spacer permits a fine-tuning distance separating the two [(C[^]N[^]N)Pt(II)] units in the cofacial arrangement. The easy modification of the ancillary ligand in the binuclear platinum(II) complexes opens up interest in this new system for exploring applications in optoelectronics and chemical biology.

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Supporting Information Available: Crystal structure of **1** and the detailed spectroscopic spectra of **1–5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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