## **Communications**

## Synthesis, Structures, and Photoluminescent Properties of Cyclometalated Platinum(II) Complexes bearing Upper-Rim Phosphinated Calix[4]arenes

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Summary: A series of upper-rim diphosphinated calixarene receptors bearing various R and R' substituents at the lower rim ( $L^n$ ; n = 1-5) were synthesized, and their reactions with [Pt(Thpy)(HThpy)Cl] afforded the phosphorescent platinum(II)modified calixarene receptors [(PtThpyCl)<sub>2</sub>L<sup>n</sup>]. The structure of [{PtThpy(CH<sub>3</sub>CN)}<sub>2</sub>L<sup>1</sup>](ClO<sub>4</sub>)<sub>2</sub> and [(PtThpyCl)<sub>2</sub>L<sup>5</sup>] were determined by X-ray crystallographic analysis, and the photophysical properties of [(PtThpyCl)<sub>2</sub>L<sup>n</sup>] were investigated.

Calixarenes<sup>1</sup> have been extensively documented as ion carriers, chemical sensors, and models for in vivo reactions of enzymes.<sup>2</sup> Functionalization at the upper rim of calixarenes has expanded this class of molecules into transition-metal-bearing derivatives through metal–ligand coordination,<sup>3,4</sup> which enables the signaling properties conferred by transition-metal complexes

to be incorporated into the calixarene systems. Signaling responses toward targeted guests involving calixarene receptors are commonly analyzed by NMR titration experiments<sup>5</sup> and electrochemistry,<sup>6</sup> yet reporting means using emission measurements have predominantly focused on [Ru(bpy)<sub>3</sub>]<sup>2+</sup>-bearing molecules.<sup>7,8</sup> Examples of optical sensors with luminescent metal complexes integrated into the framework of calixarenes are sparse.<sup>2d,9</sup>

The square-planar geometry of platinum(II) complexes confers photophysical and photochemical properties that are different from those of octahedral  $[Ru^{II}(bpy)_3]^{2+}$  derivatives due to the open Pt(II) coordination sites. Intrusion of guest molecules induces changes in its local environment, leading to a profound impact upon the photoluminescent properties.<sup>10</sup> There is a growing interest in employing Pt(II) luminophores as a signaling moiety in the development of biomolecular chemosensors. Previous reports on cyclometalated platinum(II) complexes bearing Thpy ligands (HThpy = 2-(2'-thienyl)pyridine) revealed that they exhibit intriguing photoluminescent properties (visible emission, long emission lifetime) which are sensitive to the local environment.<sup>11</sup> These properties are advantageous to the development of luminescent sensors.

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Scheme 2. Synthesis of [Pt(Thpy)]<sup>+</sup>-Incorporated Diphosphinated Calixarene Receptors, 1–5



In this work, a series of upper-rim diphosphinated calixarene receptors bearing various R and R' substituents at the lower rim were synthesized (Scheme 1), and their subsequent reactions with [Pt(Thpy)(HThpy)Cl] resulted in coordination of cyclometalated Pt(II) luminophores, [Pt(Thpy)]<sup>+</sup>, at the upper rim of the calixarenes, giving phosphorescent platinum(II)-modified calixarene receptors (Scheme 2).

25,26,27,28-Tetrahydroxycalix[4]arene was prepared by the reaction of *p-tert*-butylcalix[4]arene with phenol and AlCl<sub>3</sub> (step i in Scheme 1),<sup>12</sup> and its reaction with benzyl bromide, 1-iodopropane, or 1-iodobutane (R-Br; step ii in Scheme 1) in the presence of 1 equiv of K<sub>2</sub>CO<sub>3</sub> in acetonitrile afforded dibenzyloxy- (L<sub>Bn</sub>), dipropoxy- (L<sub>C3</sub>), or dibutoxycalix[4]arene (L<sub>C4</sub>), respectively.<sup>13</sup> Bromination was carried out at the para positions of hydroxylated aromatic rings using *N*-bromosuccinimide (NBS) and methyl ethyl ketone (MEK) (step iii in Scheme 1).<sup>14</sup> This was followed by further reaction with benzyl



**Figure 1.** Perspective view of  $[(PtThpyCl)_2L^5]$  (30% probability ellipsoids).

or alkyl bromide (R'-Br; step iv in Scheme 1) to afford various R and R' substituents at the lower rim of the calixarene ligand.<sup>15</sup> Phosphination using Ph<sub>2</sub>PCl at the upper rim of the calixarenes afforded  $L^{1-5}$  (step v in Scheme 1).<sup>15</sup>

The reaction of  $L^{1}-L^{5}$  with [Pt(Thpy)(HThpy)Cl]<sup>11b</sup> in a 1:1 molar ratio in acetonitrile under reflux for 4 h gave [(PtThpyCl)<sub>2</sub> $L^{n}$ ] (**1**–**5**), which are isolated as orange solids in moderate to high yields (Scheme 2). Complexes **1**–**5** were characterized using <sup>1</sup>H, <sup>195</sup>Pt, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, ESI or FAB mass spectrometry, and X-ray crystallography (Supporting Information). They are air- and moisture-stable at room temperature.

The <sup>1</sup>H NMR spectra of 1-5 show signals consistent with their chemical formulation; the peak integration shows that the ratio of hydrogens for  $[Pt(Thpy)]^+:L^n$  is 2:1. The <sup>1</sup>H NMR spectra feature characteristic doublets at  $\delta$  2.87-3.05 and 4.15-4.40 due to the AB spin system of ArCH<sub>2</sub>Ar in the calixarene ligand. Typically broad <sup>195</sup>Pt satellites at ~9.61 ppm were observed for 1-5. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 1-5reveal one singlet at  $\delta$  17.43–18.83 with <sup>195</sup>Pt satellites due to one-bond coupling ( ${}^{1}J_{PtP} = 4226 - 4232$  Hz). This is comparable to that of [Pt(Thpy)PPh<sub>3</sub>Cl] (Supporting Information) at  $\delta$  18.62 with  ${}^{1}J_{PtP} = 4236$  Hz, revealing that the phosphorus atoms in [(PtThpyCl)<sub>2</sub>L<sup>1-5</sup>] and [Pt(Thpy)PPh<sub>3</sub>Cl] are in similar environments. The <sup>195</sup>Pt NMR spectra of 1-5 exhibit a doublet of peaks at ca.  $\delta$  -4250 with <sup>1</sup>J<sub>PPt</sub> coupling constants of 4220-4232 Hz. The  ${}^{13}C{}^{1}H$  NMR spectra of 1–5 are well resolved with peaks at  $\delta$  117.0–161.0 corresponding to the aryl protons in the  $[Pt(Thpy)]^+$  and  $L^n$  (n = 1-5) moieties. Their ESI or FAB mass spectra show the  $[(PtThpy)_2L^nCl]^+$  molecular ion. The

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Figure 2. Perspective view of the cation in  $[{PtThpy(CH_3CN)}_2L^1](ClO_4)_2$  (30% probability ellipsoids).

high-resolution ESI-MS of  $[(PtThpyCl)_2L^4]$  in acetonitrile reveals peak clusters centered at m/z 1706.4 corresponding to  $[(PtThpy)_2L^4Cl]^+$ , plus additional peaks centered at m/z856.2 with a peak separation of 0.5 mass unit, which is attributed to  $[(PtThpy)_2L^4(CH_3CN)]^{2+}$  (Figure S2 in the Supporting Information).

Crystals of [(PtThpyCl)<sub>2</sub>L<sup>5</sup>] were obtained by layering of *n*-hexane into a dichloromethane solution. However, upon layering of *n*-hexane into a dichloromethane solution of  $[(PtThpyCl)_2L^1]$  in the presence of LiClO<sub>4</sub> in acetonitrile, crystals of [{PtThpy(CH<sub>3</sub>CN)}<sub>2</sub>L<sup>1</sup>](ClO<sub>4</sub>)<sub>2</sub> were obtained. As depicted in the crystal structures (Figures 1 and 2), the platinum atom adopts an approximately square planar geometry. The N-Pt-C angle of ~80.6° is typical for related complexes.<sup>11b</sup> The Pt-N (2.087-2.124 Å) and Pt-C (~2.01 Å) distances of the [Pt(Thpy)]<sup>+</sup> units agree with those reported for [Pt(Thpy)PPh<sub>3</sub>Cl] (2.118(6) and 1.987(8) Å, respectively). For  $[{PtThpy(CH_3CN)}_2L^1]^{2+}$ , the N=CCH<sub>3</sub> groups are nearly linear ( $Pt-N-C = 174^\circ$ ;  $N-C-C = 178^\circ$ ), whereas the Pt-NCCH<sub>3</sub> distances of 2.069(9) and 2.094(8) Å are slightly longer than that of 1.996(14) Å in [Pt- $(trpy)MeCN]^{2+}$   $(trpy = 2,2':6',2''-terpyridine),^{16}$  due to the trans effect of the thienyl carbanion (Figure 2). The Pt-P-C(calixarene) angles of 111.3(3)-119.8(1)° allow good separation between the two phenyl rings in PPh<sub>2</sub> and the [Pt(Thpy)]<sup>+</sup> moiety, in order to avoid steric repulsion. The bond lengths and angles are consistent with those observed for metal complexes featuring such calix[4]arene scaffolds.<sup>15</sup> The four *n*-BuO (Figure 1) or PhH<sub>2</sub>CO moieties (Figure 2) remain at the lower rim to afford modified calixarenes in the cone conformation, and the four oxygen atoms are directed toward the cavity of the calixarenes. There are weak intermolecular interactions including PhCH<sub>2</sub>... CH(Thpy) (2.698–2.886 Å), (L<sup>5</sup>)Ar<sub>2</sub>CH<sub>2</sub>···CH(Ph<sub>2</sub>P) (2.771 Å), and  $(L^5)HC \cdots HC(Ph_2P)$  (2.852 Å) in the crystal structure of [(PtThpyCl)<sub>2</sub>L<sup>5</sup>] (Figure 1). Similarly, there are intermolecular interactions between the  $[{PtThpy(CH_3CN)}_2L^1]^{2+}$ cations as well as between the  $[{PtThpy(CH_3CN)}_2L^1]^{2+}$  and perchlorate ions in the crystal structure of [{PtThpy- $(CH_3CN)$ <sub>2</sub>L<sup>1</sup> $(ClO_4)_2$ . These weak interactions include  $CH_3CN \cdots HC(Ph_2P)$  (2.627 Å), NCCH<sub>3</sub> ··· OClO<sub>3</sub> (2.648 Å), PhCH<sub>2</sub>...OClO<sub>3</sub> (2.497 Å), and (pyridyl)CH...OClO<sub>3</sub> (2.486 Å).

The UV-visible absorption and emission properties of 1-5 have been studied and are listed in the Supporting Information. As examples, the absorption spectra of **3** and **4** in acetonitrile are depicted in Figures 3 and S3 (Supporting Information),



**Figure 3.** Absorption (left) and emission (right;  $\lambda_{ex} = 400$  nm, concentration  $1.55 \times 10^{-5}$  M) spectra of **3** in acetonitrile at 298 K.

respectively. The high-energy, intense absorption bands with  $\lambda_{\rm max}$  at 295–300 nm ( $\epsilon$  = 23 800–29 400 M<sup>-1</sup> cm<sup>-1</sup>) are attributed to spin-allowed intraligand <sup>1</sup>IL:  $\pi$ (Thpy)  $\rightarrow \pi^*$ (Thpy) and  $\pi(L^n) \rightarrow \pi^*(L^n)$  transitions. The moderately intense lowenergy band with  $\lambda_{max}$  at 402–406 nm ( $\varepsilon = 8200-9600 \text{ M}^{-1}$ cm<sup>-1</sup>) is assigned to spin-allowed metal-to-ligand charge transfer <sup>1</sup>MLCT: Pt(5d)  $\rightarrow \pi^*$ (Thpy) transition,<sup>11b</sup> which closely resembles the <sup>1</sup>MLCT absorption of [Pt(Thpy)PPh<sub>3</sub>Cl] with  $\lambda_{max}$ at 398 nm ( $\varepsilon = 3800 \text{ M}^{-1} \text{ cm}^{-1}$ ). Solvatochromic effects for the absorption spectrum of 4 were investigated. The high-energy absorption maximum slightly shifts from 293 nm ( $\varepsilon = 29\ 100$  $M^{-1} \text{ cm}^{-1}$ ) in MeOH to 302 nm ( $\varepsilon = 31\,600 \text{ M}^{-1} \text{ cm}^{-1}$ ) in THF, whereas the low-energy band with  $\lambda_{max}$  at 398 nm ( $\varepsilon$  = 10 000  $M^{-1}$  cm<sup>-1</sup>) in MeOH is red-shifted to 402 nm ( $\varepsilon = 9400$  $M^{-1} \text{ cm}^{-1}$ ) in CH<sub>3</sub>CN and 409 nm ( $\epsilon = 9900 \text{ M}^{-1} \text{ cm}^{-1}$ ) in THF.

The emission spectra of **3** and **4** in acetonitrile at 298 K exhibit a low-energy structured emission with peak maxima at ~558 and 602 nm (Figures 3 and S3). The microsecond emission lifetimes (~1.20–1.43  $\mu$ s) of **1–5** in dichloromethane solutions indicate the emissions to be phosphorescence. Similar emission properties of analogous [Pt(Thpy)]<sup>+</sup> complexes<sup>11b</sup> and of [Pt(Thpy)PPh<sub>3</sub>Cl]<sup>17</sup> have been reported. In comparison with the absorption data, solvatochromic effects on the emission energy of **4** is minor, as the emission  $\lambda_{max}$  does not alter upon

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changing the solvent from dichloromethane to acetonitrile. Instead, the lifetime increases from 0.77  $\mu$ s in CH<sub>3</sub>CN to 2.09  $\mu$ s in DMSO, and the emission quantum yield increases from 0.0074 in CH<sub>3</sub>CN to 0.045 in CH<sub>3</sub>OH. The emission data reveal that the emissive excited state is largely <sup>3</sup>IL in nature, although mixing with <sup>3</sup>MLCT cannot be excluded.

The solid-state emission spectra of 1-5 at 298 K show structured emission bands with peaks at ~559, 580, and 603 nm, which become more resolved with slightly blue-shifted  $\lambda_{max}$  to 557 nm upon cooling to 77 K. Importantly, the emission lifetimes of solid samples of 1-5 significantly increase to  $13.9-21.2 \ \mu s$  at 77 K. The emission spectra of 1-5 in butyronitrile glassy solution show vibronically resolved peaks at 550-655 nm and emission lifetimes of  $42.1-44.1 \ \mu s$ . The significant temperature dependence for the emission lifetimes of solid samples of 1-5 is consistent with the d-d excited states being responsible for the nonradiative decay of the emission.

To examine the effects of auxiliary ligands upon the emission properties of [PtThpy]+ luminophores, we synthesized [Pt(Thpy)PPh<sub>3</sub>(CH<sub>3</sub>CN)]ClO<sub>4</sub> (6) by reacting [Pt(Thpy)-PPh<sub>3</sub>Cl] with AgClO<sub>4</sub> in acetonitrile. The low-energy <sup>1</sup>MLCT absorption band of **6** at 389 nm ( $\varepsilon = 2400 \text{ M}^{-1} \text{ cm}^{-1}$ ) is blue-shifted from that (398 nm;  $\varepsilon = 3800 \text{ M}^{-1} \text{ cm}^{-1}$ ) in [Pt(Thpy)PPh<sub>3</sub>Cl] (Supporting Information). Interestingly, the emission  $\lambda_{max}$  values of [Pt(Thpy)PPh<sub>3</sub>Cl] and **6** in acetonitrile solutions are virtually the same. However, both the emission quantum yield and lifetime of 6 remarkably increase to 0.17 and 26.2  $\mu$ s, respectively, from [Pt(Thpy)PPh<sub>3</sub>Cl] ( $\Phi = 0.020$ ;  $\tau = 6.8 \ \mu s$ ). Similar phenomena were observed when  $[(PtThpyCl)_2L^4]$  (4) was treated with AgClO<sub>4</sub> in acetonitrile; namely, a blue-shifted <sup>1</sup>MLCT absorption band (402 to 390 nm) and substantial enhancement in emission quantum yield (0.0074 to 0.21) and lifetime  $(0.77 \text{ to } 28.9 \,\mu\text{s})$  were detected. We postulate that the increased cationic charge on the [Pt(Thpy)PPh<sub>3</sub>]<sup>+</sup> luminophore, upon replacing the coordinated chloride ligand by acetonitrile, causes an increase in the energy of the d-d excited state, which consequently leads to increases in the emission intensity and lifetime.

In conclusion, we have prepared phosphorescent platinum(II)-modified calixarene receptors by coordination of [Pt-(Thpy)]<sup>+</sup> moieties by the pendant phosphine groups at the upper rim of calix[4]arenes. The electronic and spectroscopic properties of the [Pt(Thpy)]<sup>+</sup> units can be systematically varied by changing the bidentate cyclometalated ligands. Furthermore, the chloride and acetonitrile ligands in [(Pt-ThpyCl)<sub>2</sub>L<sup>5</sup>] and [{PtThpy(CH<sub>3</sub>CN)}<sub>2</sub>L<sup>1</sup>](ClO<sub>4</sub>)<sub>2</sub>, respectively, would allow modification of the platinum(II)-incorporated calixarene receptors by ligand substitution reactions. All these can significantly affect the mixed <sup>3</sup>MLCT/<sup>3</sup>IL emissive excited states, together with the deactivating d-d states, leading to a new class of luminescent calix[4]arene-based sensory molecules. Our studies on the binding reactions of  $[(PtThpyCl)_2L^n]$  with neutral and anionic hydrophobic analytes are in progress.

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**Supporting Information Available:** Text, figures, tables, and CIF files giving experimental details, spectroscopic data, crystallographic data, and selected photophysical spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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