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Blue Organic LEDs

Highly Efficient Blue-Emitting Cyclometalated Platinum(II) Complexes by Judicious Molecular Design**

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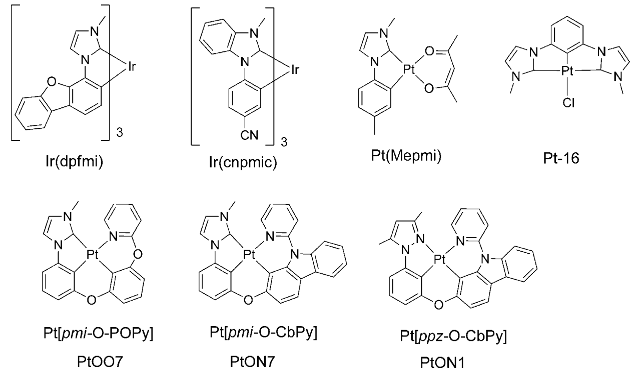
Luminescent properties of cyclometalated Ir and Pt complexes have been the focus of considerable research, driven in large part by their potential use as emitters in organic light-emitting diodes (OLEDs).[1] This class of phosphorescent emitters has demonstrated the ability to harvest both electro-generated singlet and triplet excitons, resulting in a theoretical 100% electron-to-photon conversion efficiency.[2] Driven by the technological need for full-color displays and solid-state lighting applications, the development of stable and efficient Ir and Pt complexes that emit in the range of 400–460 nm (blue region) is vital.[3] Thus far, the approach to achieve efficient blue-phosphorescent OLEDs has focused on Ir-based complexes with either high triplet energy cyclometalated ligands, such as 4,6-difluorophenylpyridine, or electron-withdrawing ancillary ligands, such as picolinate and tetrakis(1-pyrazolyl)borate.[4] There are comparatively few reports on deep blue phosphorescent emitters with fluorine-free cyclometalating ligands,[5–7] despite potential for improved optoelectronic stability compared to fluorinated derivatives.[6]

An example of such a class of materials is metal complexes cyclometalated with the methyl-2-phenylimidazole (pmi) ligand and related analogues that are coordinated to the metal through a neutral carbene.[7] Several Ir complexes have been reported to have efficient deep blue phosphorescent emission at room temperature, including mer-tris(*N*-dibenzofuranyl-*N*-methylimidazole) iridium(III) [Ir(dbfmi)],[7a] tris(1-cyanophenyl-3-methylimidazolin-2-ylidene-C,C2′) iridium(III) [Ir(cnpmic)],[7b] and mer-tris(phenyl-methyl-benzimidazolyl) iridium(III) [*m*-Ir(pmb)$_3$].[7c] However, these complexes suffer from either long luminescent decay or relatively low quantum efficiency compared to Ir complexes based on the cyclometalated 2-phenylpyridine ligand that have quantum efficiency Φ of 0.8–1 and a luminescent lifetime τ of 1–5 μs.[8] This difference can be attributed to the combined effects of a high non-radiative decay rate (k_{nr}) and low radiative decay rate (k_r), which are dictated by the intrinsic properties of the selected metal complex system.[8b] Thus, it will be highly desirable to identify rational design motifs that can improve the luminescent properties of deep blue phosphorescent emitters.

Compared to Ir analogues, there are relatively few reports on platinum complexes cyclometalated with phenylimidazole carbene ligands.[9] However, one such compound, platinum(II) bis(methylimidazolyl)benzene chloride (Pt-16),[9b] has demonstrated impressive device performance with a maximum external quantum efficiency (EQE) of 15.7% and Commission Internationale de L'Éclairage (CIE) coordinates of (0.16, 0.13). Moreover, Pt^{II} complexes can provide additional structural variation owing to the square-planar configuration allowing ligands to be designed that are bidentate, tridentate and tetradentate.[10] These variations can significantly alter the ground and excited state properties of Pt complexes. Herein, we report (pmi)Pt-based complexes that demonstrate a higher luminescent quantum yield and faster radiative decay process than published Ir carbene analogues. A new class of Pt complexes with tetradentate ligands have been synthesized. The complexes have a conventional cyclometalated fragment bridged with oxygen to an LL' chelating group, where LL' is an ancillary chelate, such as, phenoxyl pyridine (POPy) or carbazolyl pyridine (CbPy). The structures of Pt[pmi-O-POPy], Pt[pmi-O-CbPy], and Pt[ppz-O-CbPy] are shown in Scheme 1, and are denoted as PtOO7, PtON7, and PtON1. Along with the photophysical results, a PtON7-based OLED is reported to have a maximum EQE of 23.7% with CIE coordinates of (0.14, 0.15).



Scheme 1. Chemical structures of cyclometalated iridium and platinum complexes discussed herein.

The absorption spectra for Pt-16, PtOO7, and PtON7 are shown in Figure 1a. All of the complexes exhibit very strong

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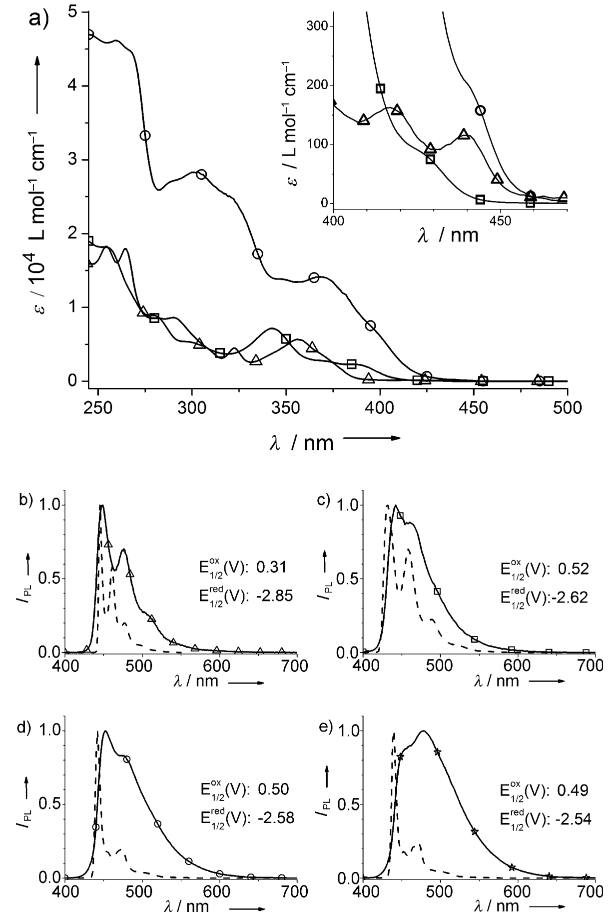

Figure 1. a) Comparison of room-temperature absorption spectra of Pt-16 (△), PtOO7 (□), and PtON7 (○) in CH_2Cl_2. The T_1 absorption transitions are shown in the inset of (a). b)–e) The emission spectra of b) Pt-16, c) PtOO7, d) PtON7, and e) PtON1 in solution at room temperature (——) and at 77 K (-----). Redox potentials for each compound are given in the legends.

Table 1: Photophysical properties of PtON7 and their analogues in a doped PMMA film.

Complex	λ_{max} [nm]	Φ [%]	τ [μs]	k_r [$\times 10^4$ s^{-1}]	k_{nr} [$\times 10^4$ s^{-1}]
PtON7	452	89	4.1	21	2.6
PtOO7	442	58	2.5	23	17
Pt-16[9b]	450	32	5.1	6.3	13.3
Pt(Mepmic)[9a]	419	20	25	0.8	3.2
Ir(cnpmic)$_3$[7b]	425(sh), 450	78	19.5	4	1.1
Ir(dbfmi)[7a]	445	70[a]	19.6	3.6	1.5
PtON1	449	85	4.5	19	3.3

[a] PO9 film was used instead of PMMA film.

absorption bands below 300 nm assigned to $^1\pi$–π^* transitions localized on the cyclometalating ligands (^{1}LC). The intense bands in the 300–420 nm region are attributed to metal-to-ligand charge-transfer (^{1}MLCT) transitions. Weaker absorption bands between 420–450 nm can be identified as the triplet absorption on the basis of the small energy shift between absorption and emission at room temperature. Compared to the tridentate structure, Pt-16, both PtOO7 and PtON7 demonstrate stronger MLCT transitions at longer wavelengths (between 380–410 nm). Moreover, both PtOO7 and PtON7 possess a less-resolved triplet absorption band (Figure 1 a inset). Among the three Pt complexes, PtON7 demonstrates the most intense absorption for all of three types of transitions (^{1}LC, ^{1}MLCT and$S_0 \rightarrow T_1$).

The room-temperature and low-temperature (77 K) solution emission spectra and solid-state emission spectra at 5 wt% in an optically inert polymethylmethatcrylate (PMMA) matrix were recorded for both PtOO7 and PtON7 and their analogues (Table 1 and Supporting Information). The emission spectra for Pt-16, PtOO7, PtON7, and PtON1 at room temperature and 77 K are shown in Figure 1 b–e. Unlike previously reported bidentate Pt(Mepmi) and tridentate Pt-16, which have structured luminescent spectra with resolved vibronic progressions,[9] both PtOO7 and PtON7 have a less vibronically structured room-temperature emission spectra, resembling their Ir analogues, for example, tris-cyclometalated Ir(dpfmi) and Ir(cnpmic).[7] Moreover, both PtOO7 and PtON7 have much greater radiative decay rates ($>20\times10^4$ s^{-1}) than Pt and Ir analogues with similar emitting ligands (Table 1). The less-resolved T_1 absorption band, supressed vibronic structure in the room temperature solution emission spectra, and faster radiative process indicate tetradentate Pt complexes like PtON7 may have more ^{1}MLCT/^{3}MLCT character in their lowest excited states.[4b] This can be attributed to the structural changes of metal complexes by adding the ancillary POPy and CbPy chelates. Between the two structures described here, PtON7 has much lower non-radiative decay rate than PtOO7, resulting in a higher quantum efficiency (0.89). Therefore PtON7 is considered a desirable candidate as a blue emissive material for OLED applications.

Devices employing Pt-16, PtOO7, and PtON7 as emitters were fabricated in the following device structure (type I): ITO/PEDOT:PSS/NPD (30 nm)/TAPC (10 nm)/2% emitter:26 mCPy (25 nm)/PO15 (40 nm)/LiF/Al (NPD = *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4''-diamine, TAPC = di-[4-(*N,N*-ditolyl-amino)phenyl]cyclohexane, 26 mCPy = 2,6-bis(N-carbazolyl)pyridine, and PO15 = 2,8-bis(diphenylphosphoryl) dibenzothiophene.[11] The corresponding EL spectra and CIE coordinates for each device are displayed in Figure 2 a,b, and EQE versus current density plots are shown in Figure 2 d. A summary of device performance at the brightness of 100 cd m^{-2} and 1000 cd m^{-2} are presented in Table 2. Unlike tridentate Pt-16, PtON7 and PtOO7 do not show evidence of excimer formation. Both PtON7 and PtOO7 devices demonstrate EL spectra similar to their room temperature solution emission spectra, confirming that the EL spectra are generated exclusively from the emitters themselves. The CIE coordinates of the PtON7 device are (0.14, 0.19) and its peak device efficiency exceeds 16%.

PtON7 device performance was further improved by increasing the dopant concentration and using a different hole injection material, 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HATCN) and a different electron-transporting material, diphenylbis[4-(pyridin-3-yl)phenyl]silane (DPPS).

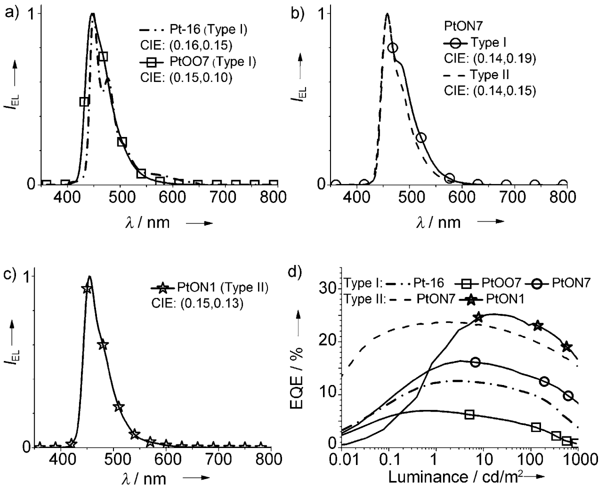

Figure 2. a–c) Plots of electroluminescent spectra for devices based on Pt-16, PtOO7, PtON7, and PtON1 with corresponding CIE coordinates. d) Plots of external quantum efficiency (EQE) versus luminance for devices of the various emitters. Device type I: PEDOT:PSS/NPD/TAPC/26mCPy:emitter(2%)/PO15/LiF/Al; device type II: ITO/HATCN/NPD/TAPC/26mCPy:emitter(6%)/DPPS/LiF/Al. The EL spectra were measured at 100 cd m^{-2}.

Table 2: A summary of device characteristics at 100 cd m^{-2} and 1000 cd m^{-2} for the devices with two different structures.[a]

Device type	Emitter	@100 cd m^{-2}				@1000 cd m^{-2}	
		CIE *x*	CIE *y*	EQE [%]	P.E. [Lm/W]	EQE [%]	P.E. [Lm/W]
I	Pt-16	0.16	0.15	10.1	9.0	3.8	2.4
I	PtOO7	0.15	0.10	4.1	3.7	0.5	0.25
I	PtON7	0.14	0.19	13.5	14.3	8.35	6.6
II	PtON7	0.15	0.14	20.4	16.8	15.4	10.2
II	PtON1	0.15	0.13	23.3	20.6	16.8	11.7

[a] Device type I: PEDOT:PSS/NPD/TAPC/26mCPy: emitter(2%)/PO15/LiF/Al. Device type II: ITO/HATCN/NPD/TAPC/26mCPy: emitter(6%)/DPPS/LiF/Al.

Despite the weak electron-transporting capabilities of DPPS, its high bandgap and deep HOMO level has allowed a demonstrated performance of nearly 100% IQE for deep blue emitting devices.[12] Through the device structure (type II), ITO/HATCN(10 nm)/NPD(40 nm)/TAPC(10 nm)/6% PtON7:26 mCPy(25 nm)/DPPS(40 nm)/LiF/Al, a maximum forward viewing EQE of $\eta_{ext} = 23.7\%$ was achieved at a luminance of 2 cd m^{-2} and this only decreases to 20.4% and 15.4% at 100 and 1000 cd m^{-2}, respectively. This device also gives a maximum forward power efficiency of $\eta_p = 26.9$ Lm W^{-1} but this drops to $\eta_p = 16.8$ Lm W^{-1} at 100 cd m^{-2}, which is attributed to the weak electron-transporting capabilities of DPPS. Moreover, a narrower EL spectrum was observed, yielding highly desirable CIE coordinates of (0.14, 0.15) for the PtON7 devices. A similar improvement was observed for phenylpyraole-based Pt complexes, such as PtON1 (Scheme 1, Figure 1, Figure 2, Table 1, and Table 2) reaching a maximum forward viewing EQE of $\eta_{ext} = 25.2\%$. The color quality and device efficiency of the PtON7 and PtON1 devices are better than the best reported deep blue phosphorescent OLEDs with fluorine-free Ir-based complexes (a maximum EQE of 18.6% and CIE coordinates of (0.15, 0.19) for the Ir(dbfmi) device) in a similar device setting.[7a] Furthermore, PtON7 and PtON1 device performances are also comparable or superior to the best reported deep blue phosphorescent OLEDs, which employed the fluorinated complex, iridium(III) bis(3′,5′-difluoro-4′-cyanophenylpyridinato-N,C$^{2'}$) picolinate (FCNIrpic) as an emissive material (a maximum EQE of 24.2% and CIE coordinates of (0.14, 0.20)).[13] It is also notable that 26 mCPy, a carbazole-based host materials with an estimated triplet energy of 2.9 eV, can be used for deep blue phosphorescent OLEDs.

The best devices of PtON7 and PtON1 (type II) were also tested for device lifetime at 2 mA cm^{-2}, which corresponds to a normal operational brightness in the range of 400–500 cd m^{-2}. For comparison, devices were fabricated with the stable and efficient green emitter, fac-Ir(ppy)$_3$, in the same structure as well as the known stable structure: ITO/HATCN(10 nm)/NPD(40 nm)/6% Ir(ppy)$_3$:CBP(25 nm)/BAlq(10 nm)/Alq(40 nm)/LiF/Al (CBP = 4,4′-bis(*N*-carbazolyl)biphenyl, BAlq = bis(2-methyl-8-quinolinolato)(biphenyl-4-olato)aluminum, and Alq = tris-(8-hydroxyquinoline)aluminum).[14] In Figure 3, the relative luminance versus time is plotted for 10 h of constant operation. It is encouraging that the devices of both PtON7 and PtON1 retained a significant percentage of their initial luminance for over an hour, and in particular that PtON1 emitted a non-negligible relative luminance up to 10 h. Furthermore, it is evident from the comparison of Ir(ppy)$_3$ devices between the two structures that the reduced device lifetimes in the type II devices can be greatly attributed to the degradation of either the electron or hole blockers, TAPC and DPPS respectively, or the 26 mCPy host. Therefore, it is challenging to create any significant conclusions about the stability of these complexes until stable host and charge blocking materials are developed for deep

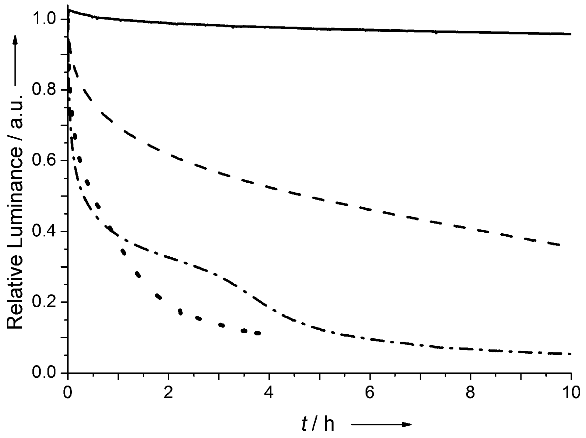

Figure 3. Plot of relative luminance against time for devices based on Ir(ppy)$_3$ (-----), PtON7 (•••••), and PtON1 (–•–•) with the structure ITO/HATCN/NPD/TAPC/6% emitter:26mCPy/DPPS/LiF/Al. Also plotted are the lifetime data for the device ITO/HATCN/NPD/6%Ir(ppy)$_3$:CBP/BAlq/Alq/LiF/Al (——). The devices were run at a constant current of 2 mA cm^{-2}.

blue phosphorescent devices. Efforts towards using these phosphorescent emitters with stable hosts and blockers are currently under significant study, and an improvement of more than two orders of magnitude in device operational lifetime can be expected, which will be presented in future publications.

In conclusion, three deep blue platinum complexes are reported based on a tetradentate ligand design. The compounds PtON1 and PtON7 show excellent photophysical properties and a high PLQY and radiative rate. An OLED employing PtON7 is reported to have a maximum device efficiency of 23.7% with CIE coordinates of (0.14, 0.15). The photophysical properties and device performance of PtON7 are much improved compared to its Pt and Ir analogues with similar emitting ligands reported previously. The device operational lifetimes of these complexes were also studied. Continued characterization and development of this class of materials should provide a viable route to develop stable and efficient deep blue phosphorescent emitters for display and lighting applications.

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