Tuning the Emission Color of Heavy Metal Complexes by Altering the Ligation of Metal with Carbon of Carbazole Unit

Xiaowei Zhang, Chuluo Yang,* Liang Chen, Kai Zhang, and Jingui Qin
Department of Chemistry, Wuhan University, Wuhan 430072, P. R. China

(Received October 3, 2005; CL-051261; E-mail: clyang@whu.edu.cn)

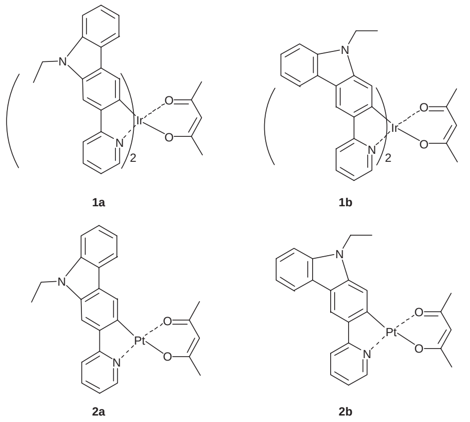
Four novel carbazole-based Ir(III) and Pt(II) complexes exhibiting emission from blue-green to red have been synthesized and characterized. The prominent tuning of emission color has been achieved by altering the ligation of metal with carbon atom at 2 or 3 position of carbazole unit.

Phosphorescent heavy metal complexes as emitters in light-emitting devices are currently under intense investigation because of their ability to harvest both singlet and triplet excited states.[1] Among them, the iridium(III) complexes are the most promising phosphor dyes.[2] The emission frequency of the complexes can usually be tuned by changing the electronic nature and/or position of the substituents on the cyclometalated ligands of phenylpyridine or its analogues,[3] such as benzoisoquinolines,[4] 2-phenylbenzothiazole,[5] benzoimidazole,[6] etc.

Carbazole-based compounds have attracted extensive attention for their distinguished opto-electronic activities. In organic light-emitting diodes (OLEDs), carbazole derivatives are usually be used as host materials for both small molecule OLEDs (such as 4,4′-bis(carbazol-9-yl)biphenyl, CBP) and polymer OLEDs (such as poly(vinylcarbazole), PVK) owing to their high triplet energy and good hole-transporting ability. The carbon atoms at 2/7 and 3/6 positions of carbazole have different electronic density, where the 3/6 position are activated by the nitrogen atom and thus more electron-rich than the 2/7 position.[7] The energy level of carbazole compounds can thus be tuned by substitution at the 3/6 or 2/7 positions.[8] The carbazole derivatives substituted at the 3/6 position have been widely investigated. However, the 2/7-carbazole-based compounds have not received attention until recently.[9] Moreover, there is very few report involving the metal complex by ligation of metal with carbon of carbazole unit.[6]

In this letter, we report four novel carbazole-based cyclometalated Ir(III) and Pt(II) complexes. We expect that the ligation of metal with carbon at 2/7 or 3/6 position of carbazole would result in different bandgap of metal-to-ligand charge transfer (MLCT) in the complexes, consequently tune the emission frequency. In addition, carbazole fragment was included as a part of the ligand framework to improve hole-transporting ability, and thereby to facilitate the charge trapping across the bulk for high performance OLEDs.[10]

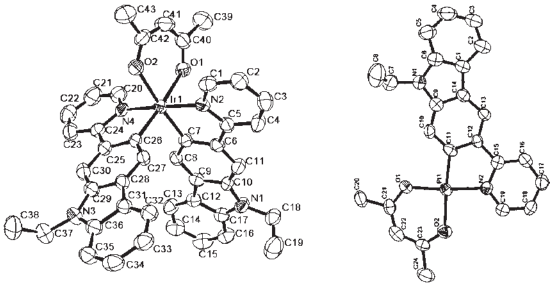
Two carbazole-based ligands, 2-pyridyl-*N*-ethylcarbazole (2-PEC) and 3-pyridyl-*N*-ethylcarbazole (3-PEC) were prepared from corresponding bromo-substituted carbazole and 2-bromopyridine by Negishi cross-coupling reaction. The ligands were then reacted separately with $IrCl_3{\cdot}nH_2O$ and K_2PtCl_4 to give the corresponding cyclometalated μ-chloro-bridged dimers.[3] Further treatment of the dimers with acetylacetone (acac) afforded the desired complexes (Scheme 1). All the complexes were structurally characterized by ^1H NMR, elemental analysis, and mass spectroscopy.



Scheme 1. Structures of the complexes.

The molecular structures of **1a** and **2b** were determined by X-ray crystallography and are depicted in Figure 1.[11] The Ir center locates at a distorted octahedral environment by the two chelating *C–N* ligands with cis-C,C and trans-N,N dispositions. **2b** exhibits a square planar geometry around the Pt(II) center with one 3-PEC ligand and one acac ligand. As we expected, to ligand 2-PEC, the 3-position carbon atom of carbazole unit coordinates to metal center, whereas in case of ligand 3-PEC, the 2-position carbon atom of carbazole unit ligates with metal center.

All complexes show similar electronic absorption spectra with strong $^1\pi$–π^* transition of ligands between 250 and 350 nm and relative weak absorption bands in the range of 350–550 nm, assigned to MLCT band (Table 1 and Figure 2). The emission spectra of **1a** and **1b** in CH_2Cl_2 show emission peak at 594 and 511 nm, respectively. The emission wavelength is tuned by 83 nm. **2a** and **2b** in CH_2Cl_2 emit at maxima of 560 and 493 nm, respectively. There is also a difference of 67 nm between their maximal emissions. For the ligands of 2-PEC



(a) (b)

Figure 1. ORTEP drawings of **1a** (a) and **2b** (b). The thermal ellipsoids for both images represent a 50% probability level.

Table 1. Photophysical and electrochemical properties of the complexes

	Absorbance λ/nm (log ε)[a]	Em λ_{max}/nm[a]	$E_{1/2}{}^{ox}$/V[b]	HOMO/eV[c]	LUMO/eV[d]
1a	289 (5.0), 344 (5.0), 478 (3.8), 518 (3.9)	594	−0.04	−4.69	−2.30
1b	323 (5.2), 420 (4.0), 453 (3.9)	511	0.15	−4.88	−2.02
2a	274 (4.6), 335 (4.5), 383 (4.2), 452 (3.6)	560	0.13	−4.91	−2.49
2b	299 (4.9), 326 (4.8), 373 (4.3), 400 (4.1)	493, 526	0.21	−5.03	−2.34

[a]Measured in CH_2Cl_2. [b]Potential values are reported versus Fc/Fc^+. [c]Determined from the onset oxidation potential. [d]Determined from the onset reduction potential.

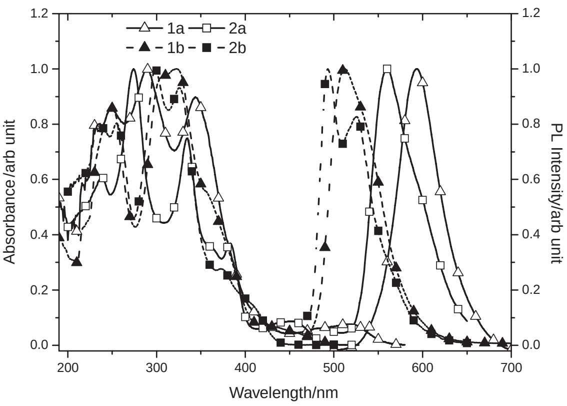


Figure 2. Electronic absorption and PL spectra of the phosphorescent complexes recorded in CH_2Cl_2 solution.

and 3-PEC, Pt complexes show hypsochromic shifts of 34 and 18 nm, respectively, comparing to the corresponding Ir complexes (Figure 2).

Cyclic voltammetry study shows that all the four complexes undergo a reversible one-electron oxidation wave ranging from −0.04 to 0.21 V vs Fc/Fc^+; however, only **1a** exhibits a quasi-reversible reduction wave. According to the density functional theory (DFT) calculations, the HOMO usually consists of a mixture of metal d orbitals and phenyl-based parts, whereas the LUMO is largely localized on the heterocyclic portion for those phenylpyridyl-based complexes.[12] Consistent with this, the more electron-donating 3-position carbon of carbazole pushes up the energy of metal d orbital when ligating to the metal, leading to a higher HOMO than that of the less electron-donating 2-position. In contrast, the connection of pyridine with carbon at less electronic 2-position of carbazole unit more stabilizes the LUMO (Py) than the connection at 3-position. Both effects result in a less energy gap to complexes with the ligand 2-PEC than that with the ligand 3-PEC. This corresponds to a bathochromic shift in the emission of 2-PEC-based complexes with respect to that of 3-PEC-based complexes. The alteration of emission wavelength coincides with the variation of energy gap evaluated from the results of cyclic voltammetry (Table 1).

In conclusion, we have developed four novel carbazole-based heavy metal complexes that exhibit emission from blue-green to red region. The remarkable color tuning was easily realized by control of the ligation of metal with carbon of carbazole unit. This represents an alternative for color tuning of the phosphorescent heavy metal complexes. The electroluminescent properties of these complexes are in progress.

This work was supported by the National Natural Science Foundation of China (Nos. 20371036 and 20474047) and the Program for New Century Excellent Talents in University, the Ministry of Education of China.

References and Notes

1 a) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151. b) Y. Cao, I. D. Parker, A. J. Heeger, *Nature* **1999**, *397*, 414.

2 a) M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **1999**, *75*, 4. b) C. Adachi, M. A. Baldo, S. R. Forrest, M. E. Thompson, *Appl. Phys. Lett.* **2000**, *77*, 904.

3 a) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H. E. Lee, C. Adachi, P. E. Buttows, S. R. Forrest, M. E. Thompson, *J. Am. Chem. Soc.* **2001**, *123*, 4304. b) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau, M. E. Thompson, *Inorg. Chem.* **2001**, *40*, 1704.

4 Y. J. Su, H. L. Huang, C. L. Li, C. H. Chien, Y. T. Tao, P. T. Chou, S. Datta, R. S. Liu, *Adv. Mater.* **2003**, *15*, 884.

5 I. R. Laskar, T. M. Chen, *Chem. Mater.* **2004**, *16*, 111.

6 W. S. Huang, J. T. Lin, C. H. Chien, Y. T. Tao, S. S. Sun, Y. S. Wen, *Chem. Mater.* **2004**, *16*, 2480.

7 J. F. Ambrose, L. L. Carpenter, R. F. Nelson, *J. Electrochem. Soc.* **1975**, *122*, 876.

8 K. Brunner, A. V. Dijken, H. Borner, J. J. Bastiaansen, N. M. Kiggen, B. M. Langeveld, *J. Am. Chem. Soc.* **2004**, *126*, 6035.

9 a) M. Sonntag, P. Strohriegl, *Chem. Mater.* **2004**, *16*, 4736. b) J.-F. Morin, N. Drolet, Y. Tao, M. Leclerc, *Chem. Mater.* **2004**, *16*, 4619.

10 a) M. R. Robinson, M. B. O'Reganand, G. C. Bazan, *Chem. Commun.* **2000**, 1645. b) J. C. Ostrowski, M. R. Robinson, A. J. Heeger, G. C. Bazan, *Chem. Commun.* **2002**, 784.

11 Crystal data for **1a**: $C_{43}H_{37}IrN_4O_2$, (CH_2Cl_2) [$M_r = 918.89$]: Monoclinic, space group $P2_1/c$, $D_{calcd} = 1.573\,g/cm^3$, $Z = 4$, $a = 11.678(5)$, $b = 17.976(7)$, $c = 18.621(7)$ Å, $\alpha = 90$, $\beta = 96.851(7)$, $\gamma = 90°$, $V = 3881(3)$ Å^3. $R_{int} = 0.0843$, final $R(F) = 0.0391$ ($I > 2\sigma(I)$), $wR(F^2) = 0.0874$. Crystal data for **2b**: $C_{24}H_{22}N_2O_2Pt$, [$M_r = 565.53$]: Monoclinic, space group $P2_1/c$, $D_{calcd} = 1.835\,g/cm^3$, $Z = 4$, $a = 13.6986(19)$, $b = 12.3557(17)$, $c = 12.9513(18)$ Å, $\alpha = 90$, $\beta = 110.993(2)$, $\gamma = 90°$, $V = 2046.6(5)$ Å^3. $R_{int} = 0.0469$, final $R(F) = 0.0427$ ($I > 2\sigma(I)$), $wR(F^2) = 0.1211$.

12 a) P. J. Hay, *J. Phys. Chem. A* **2002**, *106*, 1634. b) J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, M. E. Thompson, *Inorg. Chem.* **2002**, *41*, 3055.