Cyclometalated Iridium and Platinum Phosphors in OLEDs

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The photophysics of cyclometalated Pt(II) and Ir(III) complexes (figure 1) have been studied extensively in the past few decades due to their long-lived excited states and high luminescence quantum yields. These complexes have these characteristics as a result of spin-orbit coupling, which results in an effective mixing of the singlet and triplet states. Due to their favorable photophysics, these complexes are now being incorporated into organic light emitting diodes (OLED) to improve the light-emission efficiencies.[1]

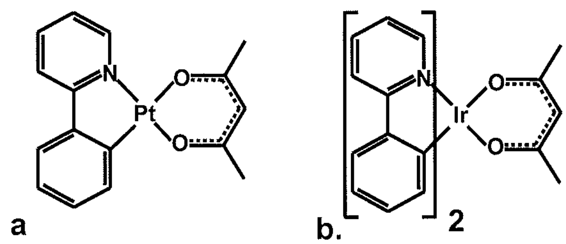

Figure 1. Typical cyclometalated complexes used in OLEDs. a) Platinum(II) (2-phenylpyridinato) acetylacetonate (ppy)Pt(acac) b) $(ppy)_2Ir(acac)$

The first OLED, constructed in 1987 by Tang and VanSlyke of Eastman Kodak,[2] consisted of an anode, an electron transport layer, a hole transport layer and a cathode. Application of a voltage leads to electron-hole recombination and, electroluminescence is observed. The first OLED gave an external quantum efficiency (photons/electrons) of 1%. In 1998, Forest and Thompson constructed the first phosphorescent OLED by incorporating an emissive layer (figure 2) of platinum(II)octaethylporphyrin, resulting in an external quantum efficiency of 4%.[3] Since then, cyclometalated metal complexes have been used, giving external quantum efficiencies as high as 19.2%.[4]

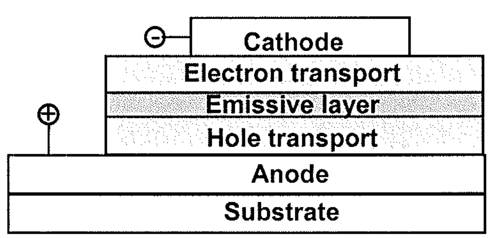

Figure 2. A typical OLED with a doped emissive layer

Recent research has focused on fine-tuning the color of electroluminescence obtained from cyclometalated Ir(III) complexes[5-8] for use in OLEDs. Forrest and Thompson[5,6] as well as Tsuboyama[7] have synthesized a group of iridium complexes based on tris(2-phenylpyridine) iridium ($Ir(ppy)_3$) first studied by Watts.[12] By modifying the phenylpyridine ligand of these complexes, the emission ranges from green to red. The electronic transitions responsible for the emissions are either ligand centered (LC) or metal to ligand (ML) depending on the nature of the ligand. Tsuzki synthesized a group of four iridium complexes based on $(ppy)_2Ir(acac)$ that incorporated a pentafluorophenyl group to either the para or meta position of the pyridine ring or the phenyl ring.[8] These complexes give emission between green and red.

Thompson and coworkers also synthesized cyclometalated platinum complexes with many of the same ligands as the iridium complexes mentioned above.[9] For complexes, such as ppyPt(acac), with transition mainly ML in nature, the emission of the platinum complex was blue shifted relative to the corresponding iridium complex, but for the complexes that are mainly LC, the emission is either unchanged or red shifted slightly. Lee et al. also synthesized a group of cyclometalated platinum complexes based on phenylpyridazine rather then phenylpyridine.[10] Due to the second nitrogen in the ring, the luminescence is red shifted back toward that of the iridium complexes with phenylpyridine. Another class of cyclometalated platinum complexes under study are tridentate phenylbipyridine complexes containing σ-alkyl auxiliaries.[11] These complexes have more sites that can be modified than the phenylpyridine-based complexes, allowing for more fine tuning of the luminescence.

Recent research under way with the complexes mentioned above is their incorporation into conjugated polymers for use in polymer-based LEDs.[13,14] In these devices, the electrons and holes are produced on the polymer chains allowing for the whole device to be constructed in one layer. There are several benefits to using polymer LEDs. Since polymers are soluble in many solvents, ink jet technology can be used to deposit them. In contrast, the OLEDs mentioned above are deposited by vacuum thermal deposition. Polymers are also mechanically flexible, so are suitable for use in flexible displays. Tokito et al. synthesized a group of polymers; each incorporating a highly efficient cyclometalated iridium phosphor.[14] These devices gave much higher efficiencies than polymer-based LEDs without the phosphors added.

References

1.. Baldo, M. A.; Thompson, M. E.; Forrest, S. R. "High-Efficiency Fluorescent Oraganic Light-Emitting Devices Using a Phosphorescent Sensitizer," *Nature* **2000**, *403*, 750-753.

2. Tang, C. W.; VanSlyke, S. A. "Organic Electroluminescent Diodes," *Appl. Phys. Lett.* **1987**, *51*, 913-915.

3. Baldo, M. A., O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. "Highly Efficient Phosphorescent Emission From Organic Electroluminescent Devices," *Nature* **1998**, *395*, 151-154.

4. Ikai, M.; Tokito, S.; Sakamoto, Y.; Suzki, T.; Taga, Y. "Highly Efficient Phosphorescence From Organic Light-Emitting Devices With an Exciton-Block Layer," *Appl. Phys. Lett.* **2001**, *79,* 156-158.

5. Lamanky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Kwong, R.; Tsyba, I.; Bortz, M.; Mui, B.; Bau, R.; Thompson, M. E. "Synthesis and Characterization of Phosphorescent Cyclometalated Iridium Complexes," *Inorg. Chem.* **2001**, *40*, 1704-1711.

6. Lamanky, S.; Djurovich, P.; Murphy, D.; Abdel-Razzaq, F.; Lee, H.; Adachi, C.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. "Phosphorescent Bis-Cyclometalated Iridium Complexes: Synthesis, Photophysical Characterization, and Use in Organic Light Emitting Diodes," *J. Am. Chem. Soc.* **2001**, *123*, 4304-4312.

7. Tsuboyama, A.; Iwawaki, H.; Furugori, M.; Mukaide, T.; Kamatani, J.; Igawa, S.; Moriyama, T.; Miura, S.; Takiquchi, T.; Okada, S.; Hoshino, M.; Ueno, K. "Homoleptic Cyclometalated Iridium Complexes with Highly Efficient Red Phosphorescence and Application to Organic Light-Emitting Diode," *J. Am. Chem. Soc.* 2003, *125*, 12971-12979.

8. Tsuzki, T.; Shirasawa, N.; Suzuki, T.; Tokito, S. "Color Tunable Organic Light-Emitting Diodes Using Pentafluorophenyl-Substituted Iridium Complexes," *Adv. Mater.* **2003**, *15*, 1455-1458.

9. Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. "Synthesis and Characterization of Phosphorescent Cyclometalated Platinum complexes," *Inorg. Chem.* **2002**, *41*, 3055-3066.

10. Lee, S. J.; Kang, S.; Lee, S. H.; Hwang, K. J.; Park, N. K.; Kim, Y. S. "Synthesis and Characterization of Phosphorescent Platinum Complexes Containing Phenylpyridazine," *Mater. Sci. Eng. C* **2004**, *24*, 221-224.

11. Lu, W.; Mi, B.; Chan, C. W.; Hui, Z.; Che, C.; Zhu, N.; Lee, S. "Light-Emitting Tridentate Cyclometalated Platinum(II) Complexes Containing σ-Alkynyl Auxiliaries: Tuning of Photo- and Electophosphorescence," *J. Am. Chem. Soc.* **2004**, *126*, 4958-4971.

12. King, K. A.; Spellane, P. J.; Watts, R. J. "Excited-State Properties of a Triply Ortho-Metalated Iridium(III) Complex," *J. Am. Chem. Soc.* **1985**, *107*, 1431-1432.

13. Lamansky, S.; Kwong, R. C.; Nugent, M.; Djurovich, P. I.; Thompson, M. E. "Molecularly Doped Polymer Light Emitting Diodes Utilizing Phosphorescent Pt(II) and Ir(III) Dopants," *Organic Electronics* **2001**, *2*, 53-62.

14. Tokito, S.; Suzuki, M.; Sato, F.; Kamachi, M.; Shirane, K. "High-Efficiency Phosphorescent Polymer Light-Emitting Devices," *Organic Electronics* **2003**, **4**, 105-111.