

# Recent Progress in First-row Luminescent d<sup>6</sup> Complexes

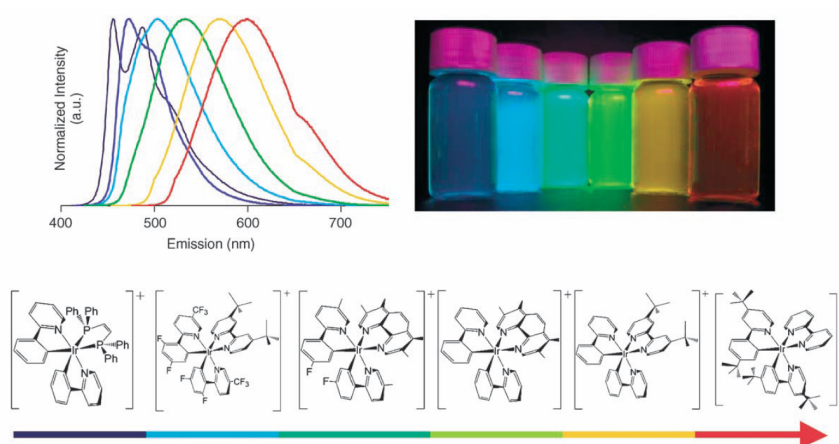
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Luminescent complexes have long attracted research interests for their various applications including light-emitting devices<sup>1</sup>, solar cells<sup>2</sup>, probing sensors<sup>3</sup>, photocatalysts<sup>4</sup>, and biological labeling<sup>5</sup>. In 1959, Paris and Brandt discovered the first luminescent transition-metal complex, [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, opening a new field of luminescent research.<sup>6</sup> However, the intrinsically smaller ligand field splitting of ruthenium as a 4d metal leads to limited color tunability, setting constraints on its real applications, so the research focus moved on to 5d metals, such as: Pt, Re, Au, Os, and Ir.

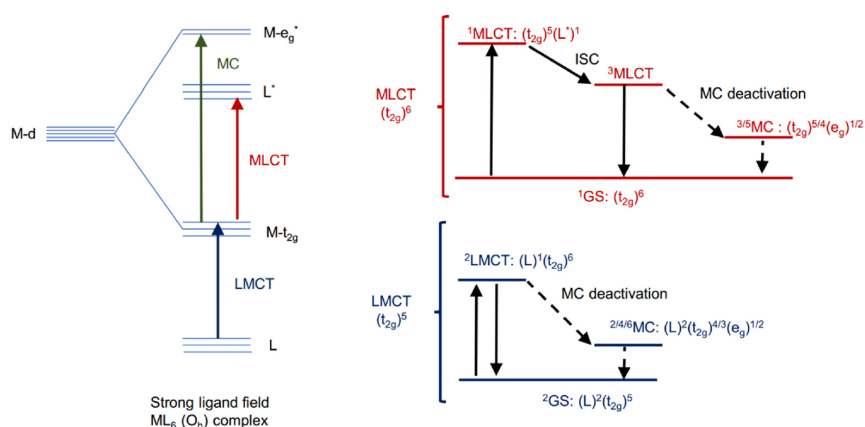
In 1998, Baldo and Forrest et. al. found that incorporation of phosphorescent platinum dyes into organic light-emitting diodes (OLEDs)<sup>7</sup> greatly enhanced the energy transfer efficiency, and therefore a significant increase in the overall OLED efficiency. This discovery attracted considerable attention of chemists, and a variety of phosphorescent dyes with 5d metal centers have sprung up afterwards, especially 5d<sup>6</sup> Ir(III) dyes for their outstanding color tunability. Up until 2007, almost 200 different Ir complexes had been doped into OLED framework and measured the corresponding energy efficiency.<sup>8</sup> Recently, along with commercialization of OLEDs in the display market, the need for cheaper and robust luminescent complexes has become even more important.



**Fig. 1** Color versatility expressed by a series of six iridium (III) complexes<sup>1</sup>

However, since 5d metals are rare in the earth's crust, their prices have always been high, which turned some research interests towards replacing the metal centers with earth-

abundant first-row transition metals.<sup>9</sup> Yet, there are some common obstacles encountered during the development of first-row transition metals. This includes weak ligand field splitting of 3d orbitals, which renders non-emissive excited metal-centered (MC) states easily populated, and inefficient intersystem crossing. These obstacles together make it difficult for metal centers to reach the emissive excited charge-transfer (CT) states, and the short lifetime of emissive states further reduces the chance of luminescence. In general these complexes are either low quantum-yielding or not even considered luminescent at room temperature.



**Fig. 2** Electronic structure diagram for a quasi-octahedral ( $O_h$ )  $ML_6$  transition metal complex<sup>12</sup>

Nonetheless, with fruitful research results over the past decades, some successful examples of first-row luminescent  $d^6$  complexes have emerged recently.<sup>10-11</sup> In addition, the  $3d^5$  electron configuration was also found to be luminescent while attempting to obtain a  $3d^6$  analogue.<sup>12-13</sup> With those complexes in hand, the ligand design strategies could be summarized into two points. The first is to use extraordinarily strong sigma-donating ligands, and the second is to make the bite angle of multidentate ligands at nearly  $90^\circ$  to ensure a perfect octahedral geometry, maximizing the d-orbital splitting. In these cases, strong sigma-donating motifs were achieved by carbon-based ligands and/or the negatively charged character through resonance structures;  $90^\circ$  bite angle was accomplished with a 6-membered metal-containing ring. This ligand design strategy has proven to be quite promising due to luminescent abilities of their first-row transition metal complexes, but their quantum yield still needs improvement.

To conclude, earth-abundant luminescent first-row  $d^6$  complexes were successfully synthesized by using strongly sigma-donating multidentate ligands, and their photophysical properties were characterized in detail. Though traditionally  $d^6$  is the targeted electron configuration, recent experimental results indicate that  $d^5$  may also be a suitable candidate. The quantum efficiency of these complexes is in general low, but the ligand design strategies are inspiring and should eventually stimulate the future development of relevant binding

motif regarding luminescent complexes.

## References

1. Lowry, M. S.; Bernhard S. Synthetically Tailored Excited States: Phosphorescent, Cyclometalated Iridium (III) Complexes and Their Applications. *Chem. Eur. J.* **2006**, *12*, 7970-7977
2. Kalyanasundaram, K. Photophysics, Photochemistry and Solar Energy Conversion with Tris(bipyridyl)ruthenium(II) and Its Analogues. *Coord. Chem. Rev.* **1982**, *46*, 159-244
3. Higgins, B.; DeGraff, B. A.; Demas, J. N. Luminescent Transition Metal Complexes as Sensors: Structural Effects on pH Response. *Inorg. Chem.* **2005**, *44*, 6662-6669.
4. Teegardin, K.; Day, J. I.; Chan J.; Weaver, J. Advances in Photocatalysis: A Microreview of Visible Light Mediated Ruthenium and Iridium Catalyzed Organic Transformations. *Org. Process Res. Dev.* **2016**, *20*, 1156-1163
5. Ma, D. L.; Wang, M.; Liu, C.; Miao, X.; Kang, T.; Leung, C. H. Metal complexes for the detection of disease-related protein biomarkers. *Coord. Chem. Rev.* **2016**, *324*, 90-105.
6. Paris, J. P.; Brandt, W. W. Charge Transfer Luminescence of a Ruthenium(II) Chelate. *J. Am. Chem. Soc.* **1959**, *81*, 5001-5002.
7. 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
8. Crabtree, R. H.; Mingos, D. M. *Comprehensive Organometallic Chemistry III.* **2007**, *12*, 101-194.
9. Wenger, O. S. Photoactive Complexes with Earth-Abundant Metals. *J. Am. Chem. Soc.* **2018**, *140*, 13522-13533
10. Pal, A. K.; Li C.; Hanan, G. S.; Zysman-Colman, E. Blue-Emissive Cobalt(III) Complexes and Their Use in the Photocatalytic Trifluoromethylation of Polycyclic Aromatic Hydrocarbons. *Angew. Chem. Int. Ed.* **2018**, *57*, 8027-8031
11. Büldt, L. A.; Guo, X.; Vogel, R.; Prescimone A.; Wenger, O. S. A Tris(diisocyanide)-chromium(0) Complex Is a Luminescent Analog of Fe(2,2'-Bipyridine)<sub>3</sub><sup>2+</sup>. *J. Am. Chem. Soc.* **2017**, *139*, 985-992
12. Chábera, P.; Liu, Y.; Prakash, O.; Thyraug E.; Nahhas, A. E.; Honarfar, A.; Essén, S.; Fredin, L. A.; Harlang, T. C. B.; Kjær, K. S.; Handrup, K.; Ericson, F.; Tatsuno, H.; Morgan, K.; Schnadt, J.; Häggström, L.; Ericsson, T.; Sobkowiak, A.; Lidin, S.; Huang, P.; Styring, S.; Uhlig, J.; Bendix, J.; Lomoth, R.; Sundström, V.; Persson, P.; Wärnmark K. A low-spin Fe(III) complex with 100-ps ligand-to-metal charge transfer photoluminescence. *Nature* **2017**, *543*, 695-699

13. Chabera, P.; Kjaer, K. S.; Prakash, O.; Honarfar, A.; Liu, Y. Z.; Fredin, L. A.; Harlang, T. C. B.; Lidin, S.; Uhlig, J.; Sundström, V.; Lomoth, R.; Persson, P.; Wärnmark, K. Fe<sup>II</sup> Hexa N-Heterocyclic Carbene Complex with a 528 ps Metal-to-Ligand Charge-Transfer Excited-State Lifetime. *J. Phys. Chem. Lett.* **2018**, *9*, 459–463.