

Luminescent Metal Complexes and Their Applications

Regioselective Aromatic Substitution Reactions of Cyclometalated Ir(III) Complexes: Synthesis and Photochemical Properties of Substituted Ir(III) Complexes that Exhibit Blue, Green, and Red Color Luminescence Emission

Cyclometalated complexes play central roles as triplet emitters in the production of organic light-emitting diodes (OLEDs), due to their excellent luminescence properties. Iridium(III) complexes such as *fac*-Ir(tpy)₃ **1** and *fac*-Ir(ppy)₃ **2** (tpy = 2-(4'-tolyl)pyridine and ppy = 2-phenylpyridine) shown in Chart 1 have long-lived excited states and high luminescence quantum yields (Φ) of 0.1~0.9, mainly due to low-lying metal to ligand charge transfer (MLCT) (e.g., Φ for **2** has been reported to be 0.4). They are in widespread use in emission materials and also as components of photoreductants, photosensitizer, oxygen sensors, and photoredox catalysts. In addition, several Ir complexes that emit blue- and red-color luminescence have been developed by choosing cyclometalating ligands.

Generally, *fac*-tris-cyclometalated Ir(III) complexes are prepared by the reaction of IrCl₃ or Ir(acac)₃ with the corresponding ligands under high thermal conditions (170-220 °C). On the other hand, regioselective substitution reactions after the preparation of cyclometalated Ir(III) complexes would be an alternative method for preparing functionalized Ir(III) complexes, which are otherwise difficult to prepare. However, successful attempts to functionalize ligands bound to the Ir(III) complexes are few in number.

We recently found the regioselective halogenation, nitration, and formylation of *fac*-Ir(ppy)₃ **1** and *fac*-Ir(tpy)₃ **2** at the 5'-position (*p*-position with respect to the C-Ir bond) of the phenyl ring, and their subsequent conversions to amino, formyl, and cyano groups (**3**, **4**, and **5** in Scheme 1) (*Inorg. Chem.* **2011**, *50*, 806–818). As summarized in Scheme 1, *fac*-Ir(atpy)₃ **3** containing three amino groups at the 5'-position exhibits a red luminescence emission in CH₂Cl₂ at 581 nm, which is a much longer wavelength than that of **2** (green-color emission at 512 nm). In addition, the color of the emission of **12** in aqueous solutions is dependent on the pH of the aqueous solutions. Namely, the red-color (ca. 600 nm) changes to green (at ca. 530 nm) when the amino groups are protonated, possibly the electron-donating NH₂ group is switched to an electron-withdrawing (NH₃)⁺ group.

Scheme 1

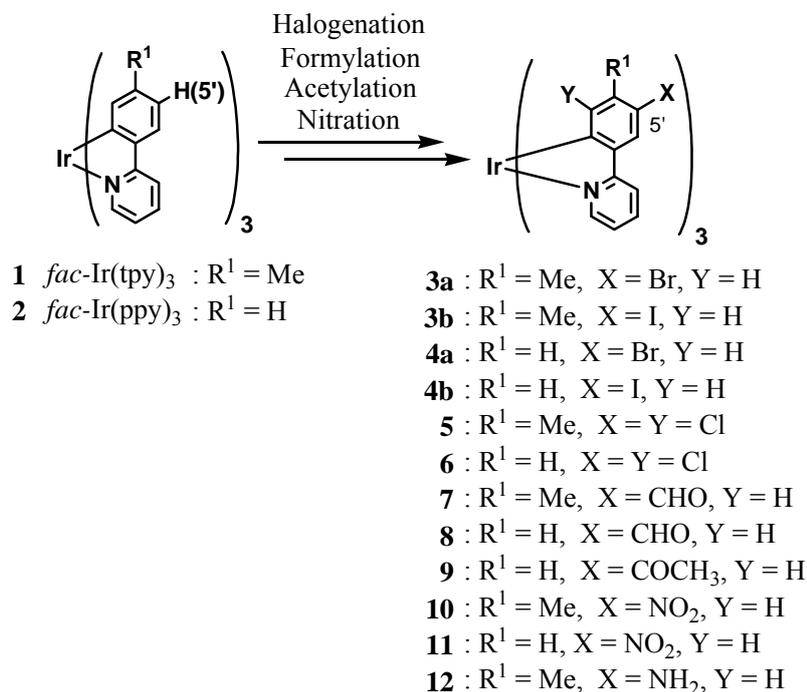
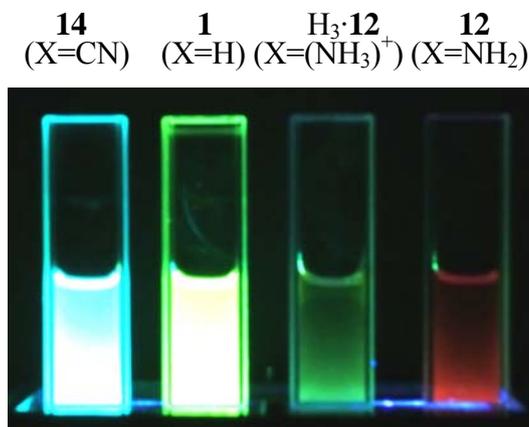


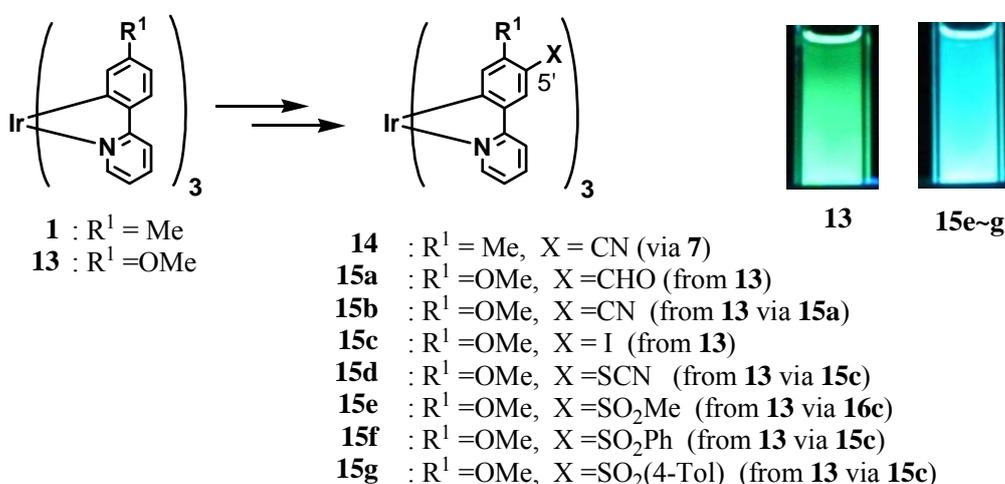
Figure 1. Photograph showing solutions of Ir(ctpy)₃ (**14**) (30 μM), Ir(tpy)₃ (30 μM), H₃·Ir(atpy)₃ (H₃·**12**) (100 μM), and acid-free Ir(atpy)₃ (**12**) (100 μM) in degassed DMSO/CH₂Cl₂ (1/5) at 25 °C (excitation at 365 nm).



Ref) Shin Aoki, Yasuki Matsuo, Shiori Ogura, Hiroki Ohwada, Yosuke Hisamatsu, Shinsuke Moromizato, Motoo Shiro, and Masanori Kitamura, “Regioselective Aromatic Substitution Reactions of Cyclometalated Ir(III) Complexes: Synthesis and Photochemical Properties of Substituted Ir(III) Complexes that Exhibit Blue, Green, and Red Color Luminescence Emission.” *Inorganic Chemistry*, **2011**, 50 (3), 806–818 (DOI: 10.1021/ic101164g)

On the other hand, the introduction of electron-withdrawing groups such as CHO, CN, and sulfonyl groups (SO₂Me, SO₂Ar) at the 5'-position of **6** induces ca. a 30 nm blue-shift in the luminescence emission, resulting in a blue-colored emission (463 nm to 465 nm) without the fluorine substituent on the ligands (Scheme 2). These results suggest that modifications at the 5'-position of the tpy ligand of **2** can be effective for the color-tuning of Ir(III) complexes (*Eur. J. Inorg. Chem.* **2011**, 5360-5369).

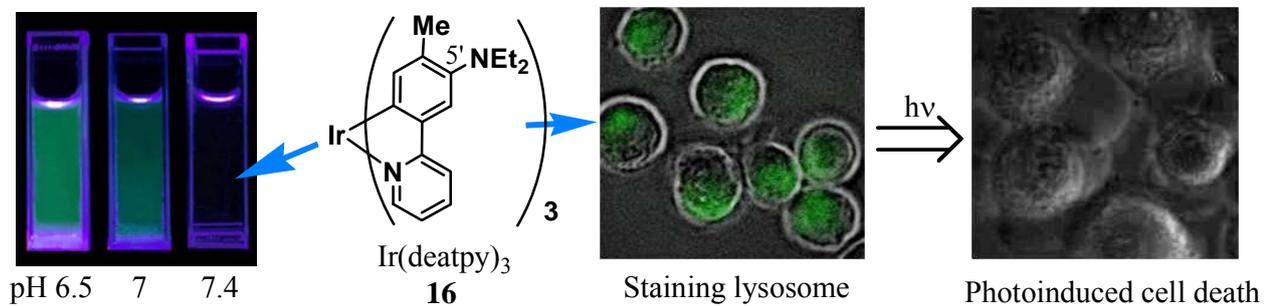
Scheme 2



Ref) Yosuke Hisamatsu, and Shin Aoki, "Design and Synthesis of Blue-Color Emitting Cyclometalated Iridium(III) Complexes Based on Regioselective Functionalization." *European Journal of Inorganic Chemistry* **2011**, 5360-5369 (DOI: 10.1002/ejic.201100755) (Selected as EurBest in Eur. JIC)

These successful results prompted us to design and synthesize a new pH-sensitive cyclometalated Ir(III) complex containing a 2-(5'-N,N-diethylamino-4'-tolyl)pyridine (deatpy) ligand, *fac*-Ir(deatpy)₃ **17**. The complex exhibits a considerable change in emission intensity between neutral and slightly acidic pH (pH 6.5~7.4). Luminescence microscopic studies using HeLa-S3 cells indicate that **17** can be used to selectively stain lysosome, an acidic organelle in cells. Moreover, complex **17** is capable of generating singlet oxygen in a pH-dependent manner and inducing the death of HeLa-S3 cells upon photoirradiation at 377 nm or 470 nm (*Inorg. Chem.* **2012**, 51, 12697-12706).

Scheme 3.



Ref) Shinsuke Moromizato, Yosuke Hisamatsu, Toshihiro Suzuki, Yasuki Matsuo, Ryo Abe, and Shin Aoki, “Design and Synthesis of a Luminescent Cyclometalated Iridium(III) Complex Having *N,N*-Diethylamino Group that Stains Acidic Intracellular Organelles and Induces Cell Death by Photoirradiation”.

Inorganic Chemistry **2012**, 51, 12697-12706 (DOI: 10.1002/ic301310q).