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Deep blue luminescent cyclometallated 1,2,3-triazol-5-ylidene iridium(III) complexes

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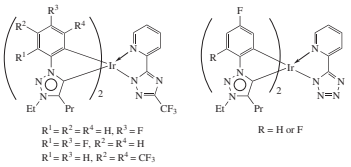
Novel heteroleptic cyclometallated 1,2,3-triazol-5-ylidene Ir^{III} complexes with 2-(5-trifluoromethyl-2*H*-1,2,4-triazol-3-yl)pyridine or 2-(1*H*-tetrazol-5-yl)pyridine as the ancillary ligands demonstrate photoluminescence in green (520 nm) and blue (450–480 nm) regions.

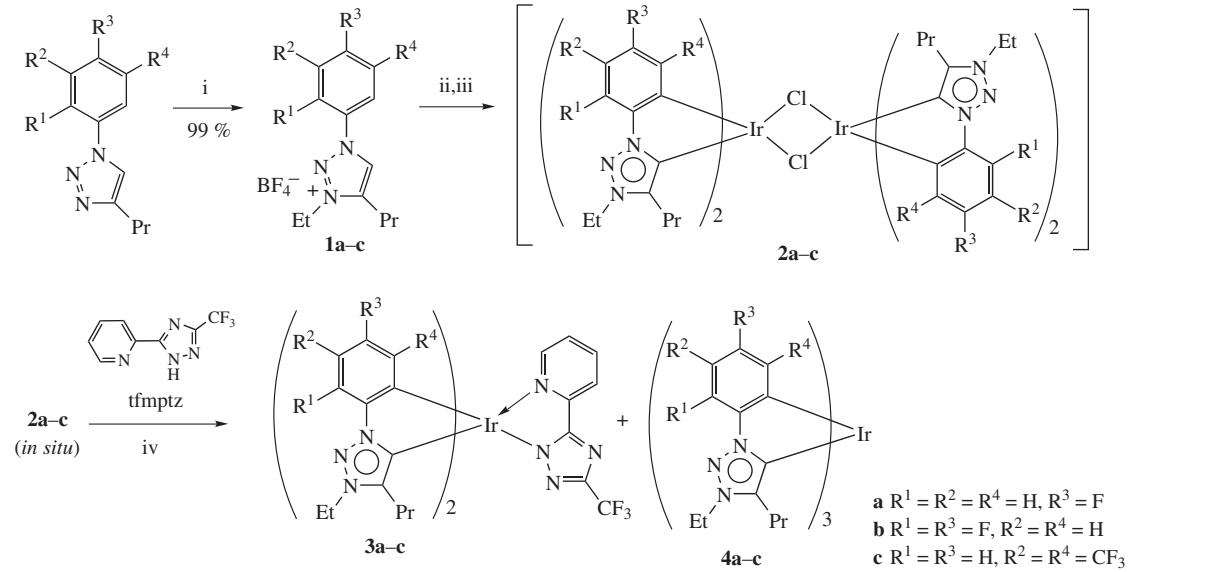


Keywords: iridium complexes, N-heterocyclic carbenes, 1,2,3-triazoles, organofluorine compounds, photoluminescence, quantum yield, OLED.

Phosphorescent cyclometallated iridium(III) complexes are used in highly efficient organic light-emitting diodes (OLEDs)[1] as well as for some photophysical applications.[2] Iridium complexes equipped with N-heterocyclic carbene (NHC) ligands possessing enhanced chemical stability are promising for stable devices emitting in blue region.[1,3]

Recently, we synthesized cyclometallated iridium(III) complexes with mesoionic or abnormal 1,2,3-triazol-5-ylidene carbene (*a*NHC) ligands and found that these ligands can serve as finely tunable platform for the design of phosphorescent iridium(III) complexes.[4] In this study, the *a*NHC ligands were modified with fluorine-containing electron-withdrawing substituents, which can give more insight into the relationship between the ligand structures and the photoluminescence properties.

First, new *a*NHC precursors, 1,2,3-triazolium tetrafluoroborates **1a–c**, were prepared by the N-ethylation of the corresponding 1,2,3-triazoles[5] derived from pent-1-yne and fluorinated aryl azides *via* the copper-catalyzed azide–alkyne cycloaddition (CuAAC) (Scheme 1). Then, 1,2,3-triazolium salts **1a–c** were



Scheme 1 *Reagents and conditions*: i, $Et_3O^+BF_4^-$, CH_2Cl_2, room temperature, 99%; ii, NaI, Ag_2O; iii, $(THT)_3IrCl_3$ (THT is tetrahydrothiophene); iv, tfmptz, Na_2CO_3, *p*-xylene, 136 °C, 48 h.

Table 1 Photoluminescence properties of iridium(III) complexes **3** and **5**.[a]

Complex	λ_{max}/nm	Φ_{PL} (%)
3a	477	10.9
3b	468	40
3c	476	5.6
5a	480	7
5b	450	46

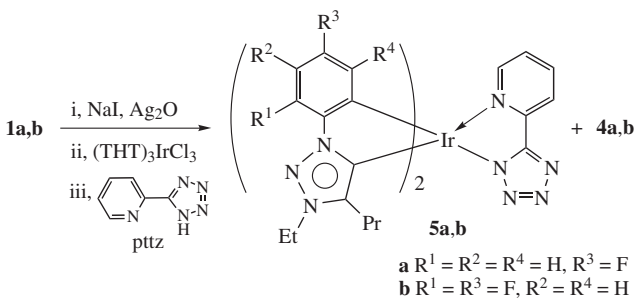
[a] Emission spectra, CH_2Cl_2, room temperature, quantum yields were determined using Coumarin-460 as a standard (ref. 8).

used for the preparation of novel heteroleptic Ir^{III} complexes **3a–c** with *a*NHCs as the key cyclometallating ligands and with 2-(5-trifluoromethyl-2*H*-1,2,4-triazol-3-yl)pyridine (tfmptz) as the auxiliary ligand. We have elaborated an efficient one-pot synthetic protocol involving the reaction of salts **1a–c** with silver(I) oxide in the presence of sodium iodide to afford intermediate 1,4-disubstituted 1*H*-1,2,3-triazol-5-ylidene silver(I) complexes [(*a*NHC)AgI] (stage ii) followed by transmetallation with $Ir(THT)_3Cl_3$ (THT is tetrahydrothiophene)[6] (stage iii) affording cyclometallated iridium(III) complexes $[(NHC)_2IrCl]_2$ **2a–c** (this stage proceeds *via* C–H activation[7]). The *in situ* obtained complexes **2a–c** on treatment with tfmptz underwent nucleophilic substitution of chlorine atoms (stage iv, see Scheme 1) to give the desired heteroleptic iridium complexes **3a–c** along with homoleptic $Ir(NHC)_3$ complexes **4a–c** as side products. In all cases, complexes **3a–c** and **4a–c** were easily separated by column chromatography.

Photoluminescence properties of $(NHC)_2Ir(tfmptz)$ complexes **3a–c** are summarized in Table 1. They exhibit maximum peaks in emission spectra in the range of 468–477 nm. Thus, the presence of *ortho* and *para* fluorine substituents in phenyl ring at position 1 of 1,2,3-triazol-5-ylidene moiety leads to a significant blue shift compared to the previously reported unsubstituted complex.[4] Complex **3c** bearing fluorinated substituents at *meta* position of the phenyl ring showed the lowest quantum yield (Φ_{PL} 5.6%).

In order to achieve luminescence in the deep blue region (450–460 nm), we decided to modify the structure of complexes **3a**,**b** by replacement of the auxiliary ligand tfmptz with more electron deficient 2-(1*H*-tetrazol-5-yl)pyridine (pttz) one. Complexes **5a**,**b** were synthesized (Scheme 2) using a protocol similar to that for the preparation of **3a–c**. New complexes **5a**,**b** were obtained in 16 and 23% yields, respectively. We noticed that the reaction mixtures contained large amounts of undissolved material. Fortunately, the replacement of *o*-xylene with polar DMSO not only simplified the synthetic procedure but also increased the yields of complexes **5a**,**b** up to 33 and 31%, respectively. Some amounts of homoleptic complexes **4a**,**b** were also formed (see Scheme 2).

Examination of photoluminescence properties of **5a**,**b** showed that their emission maximums are located in the blue region (see Table 1), thus making compounds of this type promising materials for OLED device fabrication. Photoluminescence study showed that replacement of auxiliary ligand tfmptz with pttz had no effect on the emission maximum of complex **5a** compared to **3a**, whereas the emission maximum of complex **5b** was shifted to the blue region relative to complex **3b**. Homoleptic iridium(III) complexes



Scheme 2

4a–c exhibit maximum peaks in emission spectra in the green region: **4a** – 543 nm, Φ_{PL} 4%; **4b** – 522 nm, Φ_{PL} 23%; **4c** – 521 nm, Φ_{PL} 6% (see Online Supplementary Materials).

In conclusion, five heteroleptic (**3a–c**, **5a**,**b**) and three homoleptic (**4a–c**) iridium(III) complexes were synthesized. Heteroleptic complexes exhibit photoluminescence in blue (450–480 nm) region, novel homoleptic iridium(III) complexes exhibit photoluminescence in green (520–540 nm) region. Complex **5b** bearing two fluorine atoms in phenyl ring at position 1 of 1,2,3-triazol-5-ylidene ligand manifested the highest quantum yield (46%). Hence, the photoluminescence properties of complex **5b** make it promising for OLED applications.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.11.009.

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