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Solution-processable high-efficiency bis(trifluoromethyl)phenyl functionalized phosphorescent neutral iridium(III) complex for greenish yellow electroluminescence

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ABSTRACT

A novel and highly efficient bis(trifluoromethyl)phenyl functionalized iridium(III) complex is designed and synthesized. The complex shows intensive greenish yellow phosphorescence (525 nm with 563 nm as shoulder), high photoluminescence efficiency (0.90) and moderate full width at half maximum (72 nm). The bulky bis(trifluoromethyl)phenyl moiety introduced into the complex provides the excellent solubility and effective steric hindrance for solution-processed organic light-emitting diodes. The maximum power efficiency and current efficiency of electroluminescence are 4.13 lm/W and 9.54 cd/A, respectively.

Neutral iridium(III) complexes are considered as the excellent candidates for the triplet emitters for phosphorescent organic light-emitting diodes (OLEDs) among various kinds of phosphorescent metal complexes.[1] The greenish yellow emission is the essential chromaticity component for solid-state lighting.[2] The incorporation of complementary greenish yellow color could effectively simplify the device structures of the white electroluminescence. Compared to the phosphors with three primary colors, the developments of phosphors showing complementary greenish yellow emission are less than that of the three primary colors. The mostly used cyclometalated ligand for the design of greenish yellow iridium(III) complexes is 2-aryl-benzothiazole.[3–5] Liu et al. reported benzothiazole-based iridium(III) complexes by incorporating main group elements.[3] Li et al. reported a series of 2-aryl-benzothiazole-based iridium(III) complexes with excellent device performance.[4] Recently, we also realized the highly efficient yellow emission with extremely broad full width at half maximum (FWHM) based on fluorine functionalized 2-phenylquinoline iridium(III) phosphors.[1c] The above mentioned cyclometalated ligands with relatively large π conjugation degrees often suffer from the lower solubility in organic solvents. To meet the requirements of solution-processed organic light-emitting diodes, 2-phenylpyridine could be another choice for the realization of greenish yellow emission. For instance, Wong et al. designed and synthesized high-efficiency greenish yellow iridium(III) complexes by using 2-phenylpyridine containing aromatic sulfonyl group.[6] Based on the above consideration, we select the 2-phenylpyridine derivative as the cyclometalated ligand for the realization of solution-processable greenish yellow-emitting iridium(III) phosphor.

In this letter, we report a novel bis(trifluoromethyl)phenyl functionalized greenish yellow neutral iridium(III) complex **Ir1** by modifying the 2-phenylpyridine with bulky bis(trifluoromethyl) phenyl moiety. The rigid bis(trifluoromethyl)phenyl moiety could not only guarantee the excellent solubility but also give rise to effective steric hindrance for eliminating phosphorescence quenching. The 2-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-5-yl)pyridine was served as the ancillary ligand. The phosphor designed shows bright greenish yellow emission with quite high photoluminescence efficiency (Φ_{PL}) and moderate FWHM suitable for solid-state lighting. The power efficiency (*PE*) and current efficiency (*CE*) of solution-processed greenish yellow OLEDs based on this phosphor are 4.13 lm/W and 9.54 cd/A, respectively.

The bis(trifluoromethyl)phenyl functionalized 2-phenylpyridine cyclometalated ligand was synthesized by two-step Suzuki coupling reactions. The target complex was prepared as glassy yellow crystals in high yields by the facile method (Scheme 1) and fully confirmed by nuclear magnetic resonance (NMR), mass

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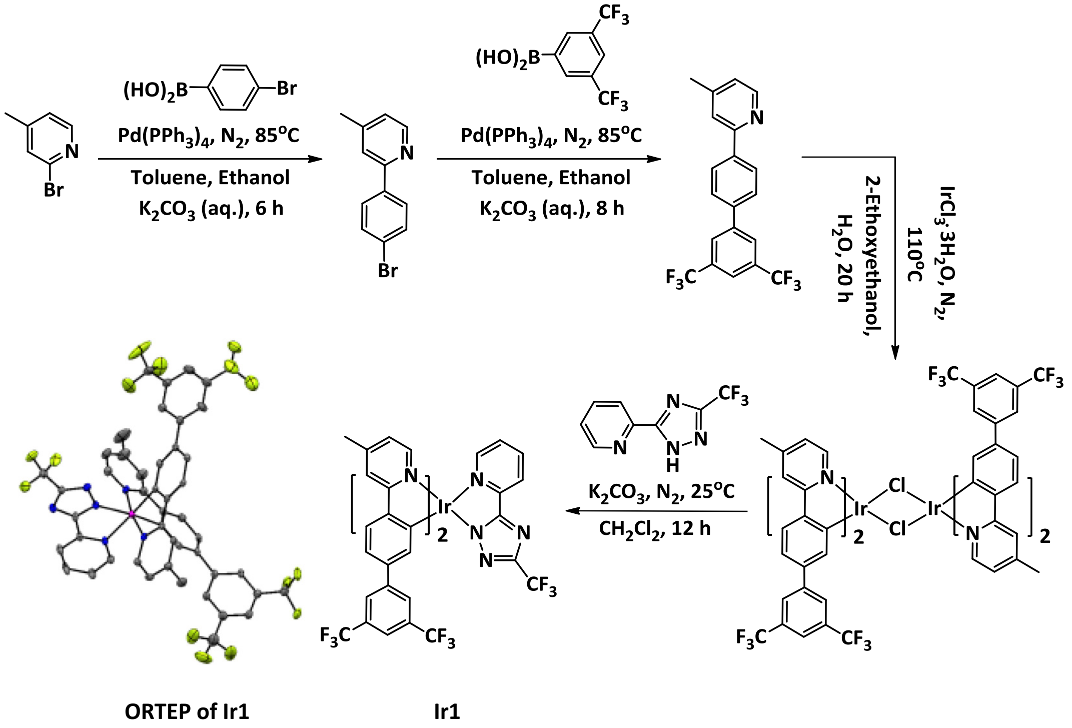

Scheme 1. Synthetic route, chemical structure and ORTEP plot of **Ir1**.

spectra and X-ray single crystal diffraction (Supporting Information).[2a] In the fluorine NMR, three singlets, corresponding to the three kinds of CF_3 groups, originated from the symmetry loss induced by the ancillary ligand. The fluorine NMR signals of the two CF_3 in bis(trifluoromethyl)phenyl moiety were exactly overlapped, implying that the bulky bis(trifluoromethyl)phenyl moiety could rotate freely in solution at room temperature. Single crystals are easily formed from the mixture solvents of methanol and chloroform. Table S1 summarized the crystallographic refinement parameters of complex. Scheme 1 displayed ORTEP plot of the complex, clearly revealing the symmetry loss in **Ir1** as shown in fluorine NMR spectra. Iridium atom adopted slightly distorted octahedral coordination geometry with *cis*-metalated carbon and *trans*-nitrogen atoms, similar to previously reported results.[1d] In crystals, two kinds of weak interactions could be observed (Fig. 1), one is, π-π interactions between phenylpyridine of adjacent complexes beneficial for the phosphorescent emission in aggregation states by the formation of triplet metal-to-ligand-ligand charge-transfer transition, another is F-π interactions between fluorine of bis(trifluoromethyl)phenyl moiety and triazole ring.[7] As shown in Fig. S1, the distance between adjacent iridium centers in the crystal of **Ir1** (11.320 Å in **Ir1**) is significantly longer than that of model complex (7.919 Å in model complex),[1f] supporting the effective steric hindrance in **Ir1**.

The photophysical properties of complex were explored in dichloromethane and exhibited in Fig. 2a Table 1. The $^1\pi \rightarrow \pi^*$ transition of cyclometalated ligand in complex corresponds to the strong absorption band in the wavelength of 250–350 nm. The weak absorption in the wavelength of 350–450 nm is probably attributed to the triplet and singlet transitions from metal-to-ligand charge-transfer.[1d] The complex shows intensive greenish yellow emission at the wavelength of 525 nm with the 563 nm shoulder emission in dichloromethane under the excitation of 395 nm. The emission energy of the complex is governed by the two opposite effects, one is the red-shift of the emission by partially enlarged π conjugation through the σ bond connection of bis(trifluoromethyl)phenyl ring and phenylpyridine, the other is the blue-shift of triazole-type ancillary ligand. The Φ_{PL} of the complex is quite high up to 0.90, and the lifetime of the complex is 7.29 μs in degassed CH_2Cl_2. The emission exhibited moderate FWHM (72 nm), which is comparable with the reported greenish yellow iridium(III) phosphors.[3–5,8] We noted that the lifetime (7.29 μs) of the complex is much longer than that of the commonly iridium(III) phosphors in solution, which may have negative effect on the performance of electroluminescence caused by the annihilation of triplet excitons.[9] Fig. 2a depicted the emission spectrum at the temperature of 77 K. The spectrum with fine structures of vibronic bands shows slightly blue-shift compared to that at room temperature, the rigidochromic shift of complex is 9 nm. Then, the triplet energy (T_1) of complex was estimated to be 2.40 eV from the highest-energy vibronic sub-band of 77 K emission spectrum.[2a] The cyclic voltammetry in CH_2Cl_2 was carried out to investigate the electrochemical property of complex. As depicted in Fig. 2b, the complex shows reversible oxidation wave and the oxidation potential was calculated to be 0.81 V. The Ir centered oxidation should be responsible for this positive oxidation potential.[1d] The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of complex based on the cyclic voltammetry are estimated to be −5.61 and −3.25 eV, respectively.

To evaluate the electroluminescence (EL) performance, the greenish yellow phosphor was further used to prepare the solution-processed OLEDs. As depicted in Fig. S2, the greenish yellow OLEDs were prepared with the structures of ITO/PEDOT:PSS (30 nm)/emission layer (40 nm)/TmPyPb (60 nm)/LiF (0.8 nm)/Al (100 nm). The indium tin oxide (ITO) acts as the anode, and poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) acts as hole injection layer. The phosphor was doped into a 1:4 wt mixture of hole-transporting host material 4,4′,4″-*tris*(*N*-3-methylphenyl-*N*-phenylamino)triphenylamine (*m*-MTDATA) and bipolar host material 2,6-bis(3-(9*H*-carbazol-9-yl)phenyl)pyr-

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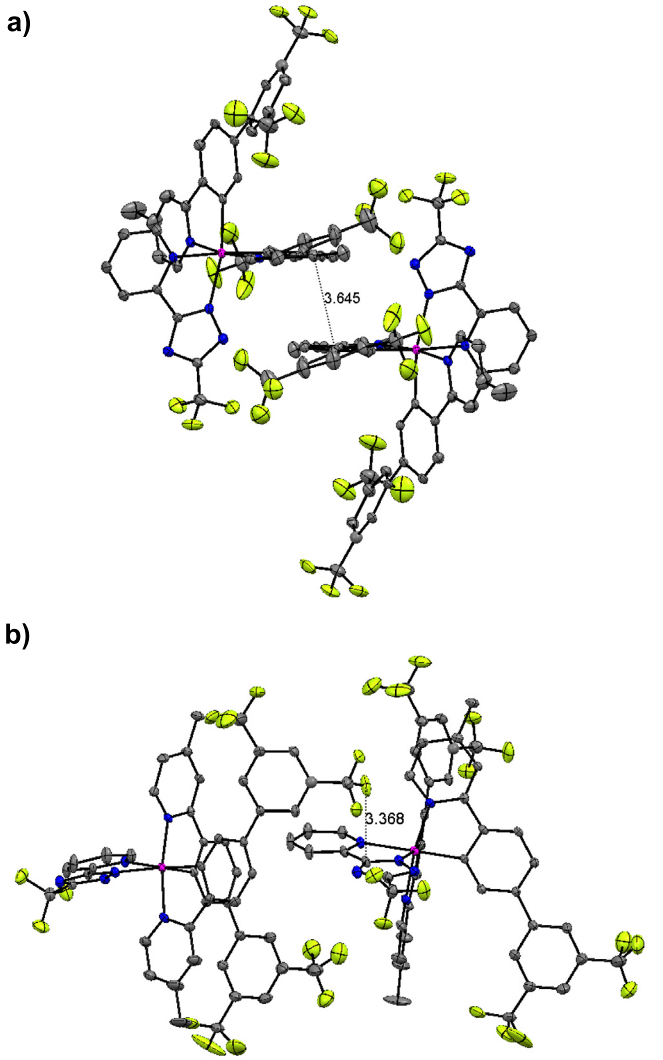

Fig. 1. (a) The intermolecular packing of **Ir1** by π-π interactions (a) and F-π interactions (b) between adjacent molecules in crystals with thermal ellipsoids drawn at the 30% probability level and solvent molecules and H atoms removed for clarity.

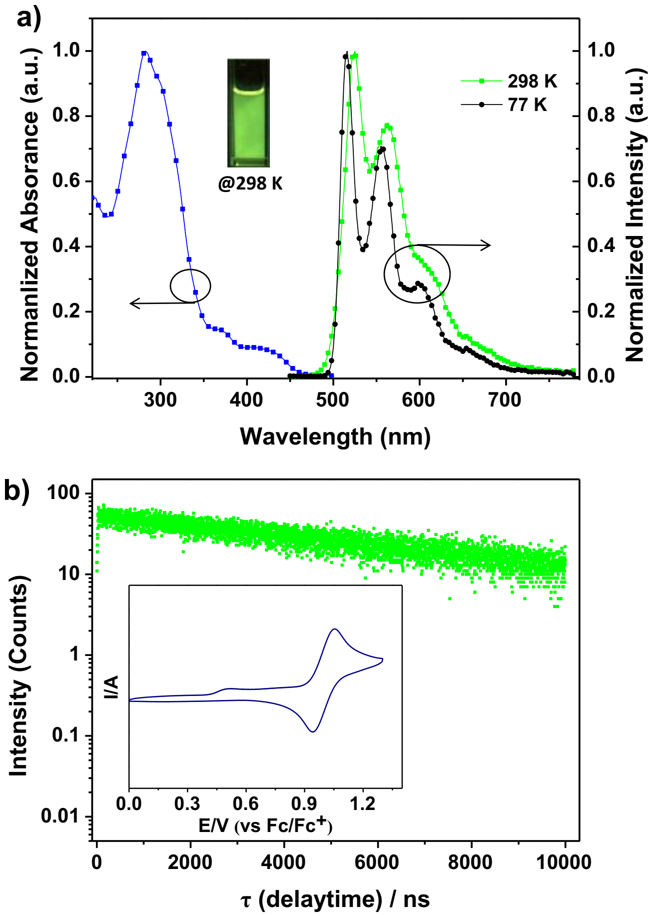

Fig. 2. (a) UV–visible absorption, photoluminescence spectra of **Ir1** at 298 K (in degassed CH_2Cl_2) and at 77 K (in 2-MeTHF); (b) phosphorescent decay of **Ir1** in degassed CH_2Cl_2 at 298 K. Inset: luminescence photograph in CH_2Cl_2 (up) and cyclic voltammogram under a scan rate of 100 mV/s in CH_2Cl_2 (down).

idine (26Dczppy) to form the emission layer. The doping concentrations of 4%, 6% and 10% in weight were selected to investigate the concentration-dependent device performance respectively. The energy levels and the illustration of device structure of the greenish yellow OLEDs are depicted in Fig. S2. According to the energy level of OLED (Fig. S2a), the HOMO/LUMO levels of the phosphor are all within those of the *m*-MTDATA and 26Dczppy host.[10] Thus, the dominant EL mechanism should be attributed to good carrier trapping in this host-guest system. The performance of the devices were shown in Fig. 3 and Table 2. Under various doping concentrations, the turn-on voltages of these devices in the 4.1–4.6 V and show intensive greenish yellow phosphorescence with wavelength at 525 nm and 563 nm (shoulder). As depicted in Fig. 4, the normalized ELspectra are overlapped quite well, implying that the electroluminescence is independent of the doping concentrations and the phosphorescence originates from the unimolecular iridium(III) complex owing to the bulky bis(trifluoromethyl)phenyl moiety of complexes. Notably, there exists the evident difference between the EL and photoluminescence (PL) spectra, as shown in Fig. S3, the intensity of the shoulder emission of EL is distinctly lower than that of PL in both dichloromethane and film (**Ir1** doped m-MTDATA:26Dczppy). This shoulder emission loss in EL spectra probably originated from weak microcavity effect of the fabricated OLEDs.[11] The 1931 Commission Internationale de L'Eclairage (CIE) coordinates of (0.37, 0.60) are corresponding to the greenish yellow region. The *L-V-J* curves of the greenish yellow-emitting devices can be found in Fig. S4. As listed

Table 1
Photophysical and electrochemical properties for **Ir1**.

Complex	Emission[a]				E_{onset}^{ox} [b] [eV]	E_g [c] [eV]	T_1 [d] [eV]	HOMO/LUMO [eV][c]
	λ_{em} [nm]	FWHM [nm]	τ [μs]	Φ_{PL}				
Ir1	525, 563 (sh)	72	7.29	0.90	0.81	2.36	2.40	−5.61/−3.25

[a] At a concentration of 1.0×10^{-5} mol/L in degassed CH_2Cl_2, $\lambda_{ex} = 395$ nm.
[b] In CH_2Cl_2.
[c] HOMO (eV) = $-e(E_{onset}^{ox} + 4.8)$, $E_g = 1240/\lambda$, LUMO (eV) = E_g + HOMO.
[d] The triplet energy (T_1) was estimated from the highest-energy vibronic sub-band of the phosphorescence spectrum at a concentration of 1.0×10^{-5} mol/L in 2-MeTHF 77 K, $\lambda_{ex} = 395$ nm.

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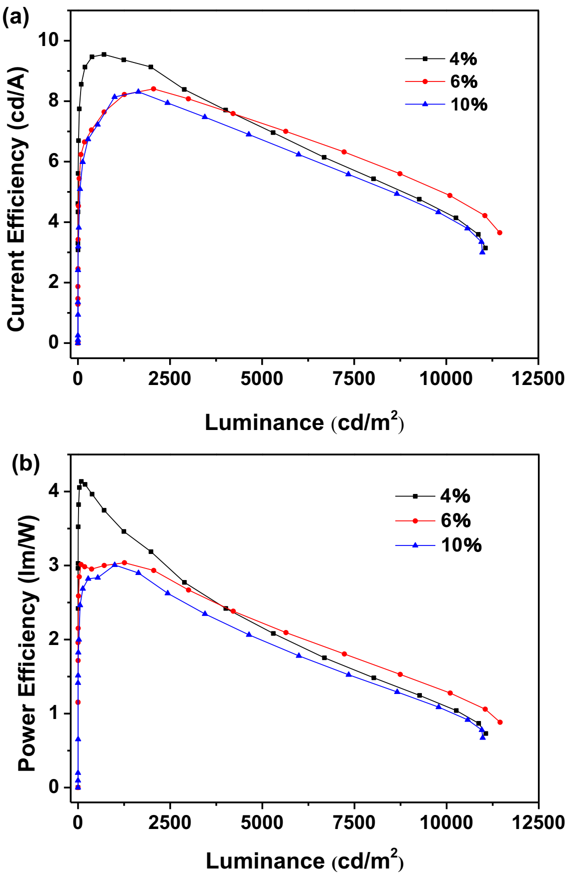

Fig. 3. The *CE-L* curves (a), *PE-L* curves (b) of the greenish yellow-emitting devices.

Table 2
EL data for the greenish yellow-emitting devices.

X%	λ_{EL}/nm	CIE(x, y)[a]	V_{ON}[b]/V	L_{max}/ cd·m^{-2}	CE_{max}/ cd·A^{-1}	PE_{max}/ lm·W^{-1}	FWHM/ nm
4	528, 564 (sh)	(0.37, 0.60)	4.1	11,064	9.54	4.13	70
6	528, 564 (sh)	(0.37, 0.60)	4.1	11,453	8.40	3.03	70
10	528, 564 (sh)	(0.37, 0.60)	4.6	10,979	8.30	3.00	70

[a] Current density is 100 mA·cm^{-2}.
[b] Luminance is 1 cd·m^{-2}.

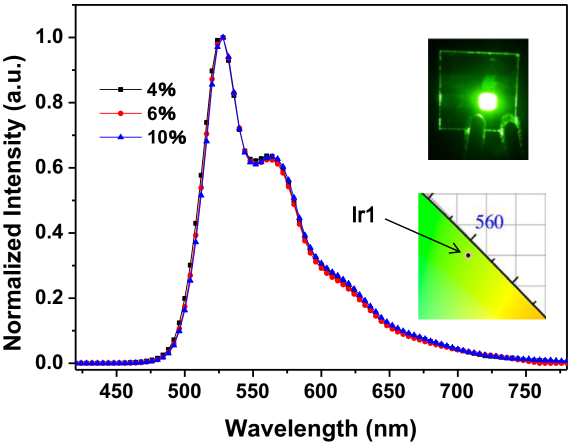

Fig. 4. The EL spectra of the greenish yellow-emitting devices. Inset: 1931 CIE coordinate (up) and EL photograph (down) of device in the doping concentration of 4% at 7 V.

in Table 2, the maximum luminance almost kept the same (~11,000 cd/m^2) in the doping concentrations from 4% to 10%. Device with 4% doping concentration gives the best efficiencies, and the *CE* and *PE* of greenish yellow OLED based on novel phosphor are 9.54 cd/A and 4.13 lm/W, respectively. The relatively low electroluminescence efficiencies could be caused by the quite long excited state lifetime (7.29 μs) of the phosphor. The long lifetime of the phosphor could easily lead to annihilation of triplet excitons formed in the emission layer.[9] These results obtained demonstrated that the excited state lifetime of phosphor is another important factor in determining the performance of light-emitting devices.

To summarize, a novel phenylpyridine-based greenish yellow neutral iridium(III) complex with bulky bis(trifluoromethyl)phenyl moiety was designed and synthesized. Owing to the effective steric hindrance originated from the bulky bis(trifluoromethyl) phenyl moiety, the complex shows bright greenish yellow emission at wavelength of 525 nm and 563 nm (shoulder) with high Φ_{PL} up to 0.90, and the FWHM of complex is moderate (72 nm), which is suitable for the solution-processed white electroluminescence. The relatively low efficiencies (9.54 cd/A) of this solution-processed greenish yellow device could be due to the quite long excite state lifetime (7.29 μs) of the complex. The further works on exploring more suitable bis(trifluoromethyl)phenyl functionalized phenylpyridine-based iridium(III) phosphors toward high-efficiency electroluminescence are going on in our laboratory.

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A. Supplementary data

Supplementary data (details of the complex synthesis, NMR, mass spectra, X-ray crystallography analysis and the device fabrication and testing) associated with this article can be found, in the online version, at https://doi.org/10.1016/j.tetlet.2018.03.073. These data include MOL files and InChiKeys of the most important compounds described in this article.

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