A sky blue thermally activated delayed fluorescent emitter to achieve efficient white light emission through in situ metal complex formation

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We developed two types of 2,6-pyrazine-based sky blue-to-green thermally activated delyaed fluorescent (TADF) emitters, of which the green emitter helped realize high-performance organic light-emitting devices (OLEDs) with an external quantum efficiency (η_{ext}) of over 20%, whereas the sky-blue emitter outperformed conventional fluorescent emitters with an η_{ext} of over 10%. Moreover, this sky-blue emitter was able to form an in situ metal complex in the form of CuI(I) and it exhibited efficient white light emission with $\eta_{\mathrm{ext,\ max}}$ of 11%. To our best knowledge, this is the first report on TADF emitters realizing the in situ formation of a metal complex.

Since Adachi and co-workers reported a series of TADF materials, the so-called third-generation emitters, aiding realization of high-efficiency OLEDs with a maximum external quantum efficiency ($\eta_{\mathrm{ext,max}}$) of nearly 20%, significant efforts have been directed toward the development of high-efficiency TADF OLEDs.[1] In recent times, extremely efficient TADF OLEDs with a $\eta_{\mathrm{ext,max}}$ exceeding 30% for the three primary colors,[2–8] very low-power consuming OLEDs comparable to phosphorescent counterparts,[9–11] and long-lifetime OLEDs at high brightness[12–14] have been reported.

In principle, TADF materials are based on molecules consisting of electron-donor and electron-acceptor units with a small energy difference between the singlet and triplet excited states (ΔE_{ST}) that allows efficient reverse intersystem crossing (RISC), which is crucial to harvesting all electrically generated molecular excitons. Some electron-acceptor units such as pyridines, bipyridines, and terpyridines have a strong coordination ability toward metal ions enabling the potential generation of supramolecular building blocks and superior emissive materials.[15] However, there is a limited number of studies on OLEDs reporting the use of such an attractive coordination functionality of acceptor units.[16–22]

In 2011, Thompson and co-workers reported a co-deposition route to produce copper iodide (I) (CuI)–pyridine coordination complexes for efficient OLEDs.[16] They used 3,5-bis(carbazol-9-

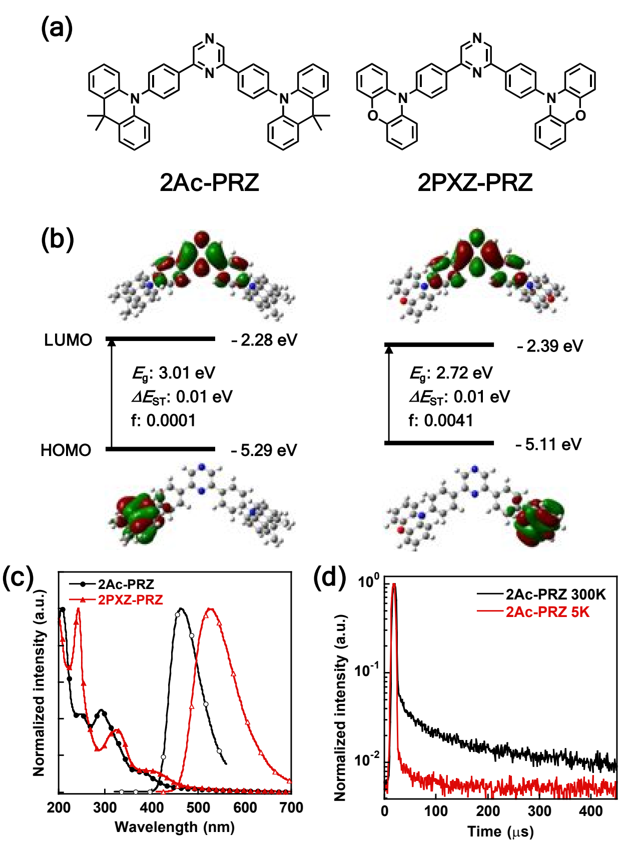

Figure 1 (a) Chemical structure of 2,6-pyrazine derivatives. (b) HOMO and LUMO distributions, energy levels, optical energy gaps (E_g), energy differences between the singlet and triplet excited states (ΔE_{ST}), and oscillator strengths (*f*) of 2,6-pyrazine derivatives. (c) UV/Vis absorption and PL spectra of 2,6-pyrazine derivatives in solid state. (d) Transient PL decay curves of 2Ac-PRZ-doped DPEPO film at 5 K and 300 K.

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Table 1 Thermal and photophysical properties.

Compound	$T_g/T_m/T_{d5}$ [a] [°C]	$I_p/E_a/E_g$ [b] [eV]	$E_S/E_T/\Delta E_{ST}$ [c] [eV]	τ_d [d] [μsec]	η_{PL} [e] (%)
2Ac-PRZ	-/292/428	–5.80/–2.94/2.86	2.94/2.58/0.36[f]	134[f]	48[f]
2PXZ-PRZ	115/246/451	–5.63/–3.05/2.58	2.73/2.52/0.21[g]	54[g]	65[g]

[a] T_g and Tm were measured using DSC; T_{d5} was measured using TGA. [b] I_p was measured using PYS; E_g was taken as the point of the intersection of the normalized absorption spectra; E_a was calculated using I_p and E_g. [c] The onset of phosphorescence of 10 wt% emitter-doped host film, measured using a streak camera. [d] Delayed fluorescence lifetime of 10 wt% emitter-doped host film. [e] Photoluminescence quantum yield of 10 wt% emitter-doped host film. [f] DPEPO used as a host. [g] CBP used as a host.

yl)pyridine as a coordination ligand, and realized green OLEDs with a $\eta_{ext,max}$ of 4.4%. Subsequent to this pioneering work, in 2014, they significantly improved the $\eta_{ext,max}$ to 15.7% by using a newly designed pyridine-containing ligand, 3-(carbazol-9-yl)-5-((3-carbazol-9-yl)phenyl)pyridine (**CPPyC**).[17] Therefore, in situ phosphorescent copper (I) complex production shows great promise toward realizing high-efficiency OLEDs. Another approach premised on using the coordination ability of pyridine to enhance the luminescence properties of TADF emitters has been reported by Yasuda and Matsuo.[22] They used an intramolecularly coordinated boryl group to achieve increased TADF behavior. The boryl-substituted phenylpyridine derivative exhibited a $\eta_{ext,max}$ of 22.7% in a sky-blue OLED.

In this context, a combination of in situ formation of copper (I) complex and the electron-acceptor unit in TADF molecule is very intriguing because based on it, the luminescent properties of the emitters can be drastically altered; however, this is as yet an unexplored avenue. In this study, we developed two pyrazine-based TADF emitters with a metal coordination site, namely 2,6-bis[4-(9,9-dimethyl-9,10-dihydroacridine)-phenyl]pyrazine (**2Ac-PRZ**) and 2,6-bis[10-phenoxazine-phenyl]pyrazine (**2PXZ-PRZ**). The **2Ac-PRZ**-based TADF OLED exhibited sky-blue emissions with Commission Internationale de l'Eclairage (CIE) coordinates of (0.19, 0.31) and a $\eta_{ext,max}$ of 12%. On the other hand, the **2PXZ-PRZ**-based OLED displayed green emissions with CIE coordinates of (0.31, 0.55) and a $\eta_{ext,max}$ of 21.4%; in addition, this emitter exhibited the metal coordination ability to form a metal complex via in situ doping of CuI(I) thereby displaying an orange emission with a peak wavelength of 583 nm. When CuI(I) was doped into the **2Ac-PRZ** layer, the resulting emission was white with dual EL emission peaks at 463 nm and 583 nm, and the realized white OLED had CIE coordinates of (0.46, 0.49) and a very high $\eta_{ext,max}$ of over 10%.

Based on the previous reports of Thompson and co-workers, the in situ formation of a copper (I) complex using the vacuum evaporation process can be achieved using less sterically hindered ligands with pyridines,[16,17,20] pyradines,[18] and quinolines.[19] Hence, we designed 2,6-diphenylpyradine as an acceptor unit, in which the nitrogen atom at the 4-position was coordinated with CuI(I) easily to form a copper (I) complex. To develop TADF emitters, we introduced 9,9-dimethyl-9,10-dihydroacridine (**Ac**) and phenoxazine (**PXZ**) as an electron-donor unit. These electron-donor units held out the potential to realize a small energy difference between the singlet and triplet excited states (ΔE_{ST}) owing to steric repulsion between the phenyl linkers. Therefore, we designed two types of TADF emitters named **2Ac-PRZ** and **2PXZ-PRZ** (**Figure 1(a)**). Density functional theory (DFT) calculations were performed to estimate ΔE_{ST} and the energy gap (E_g) of these two compounds prior to their syntheses (**Figure 1(b)**). The electron cloud distribution in **Figure 1(b)** indicates that the highest occupied molecular orbital (HOMO) extends over the entire substituted donor moieties such as **Ac** and **PXZ**, whereas the lowest unoccupied molecular orbital (LUMO) is located on the 2,6-diphenylpyrazine moiety. These two compounds were calculated to have a small ΔE_{ST} of 0.01 eV, consistent with the expectation of TADF behavior.

The synthesis of these compounds was very easy and as such required a two-step procedure comprising Suzuki-Miyaura coupling and Buchwald-Hartwig amination reaction (see ESI in detail). The obtained compounds were purified by silica gel column chromatography on silica gel and train sublimation before fabrication of OLEDs. Their thermal properties were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). A weight loss of 5% (T_{d5}) was observed at temperatures exceeding 420°C, indicating high thermal stability. The optical properties were obtained using UV/vis absorption and photoluminescence (PL) spectra in vacuum using a deposited thin solid film (**Figure 1(c), S1-2**). A weak absorption band was observed around 350-450 nm, which could be attributed to intramolecular charge transfer (ICT) from the electron-donor unit to the electron-accepter unit. The emission peak for **2Ac-PRZ** was observed at 466 nm showing sky-blue emission, whereas the emission peak for **2PXZ-PRZ** was observed at 510 nm showing green emission. The physical properties of the compounds were evaluated in their solid state. Ionization potentials (I_p) were measured by

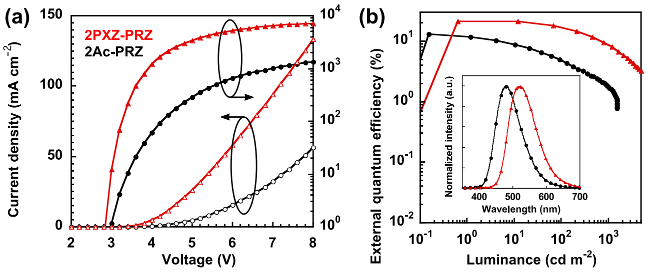

Figure 2 (a) Current density–voltage–luminance (*J*–*V*–*L*) characteristics, and (b) external quantum efficiency–luminance (η_{ext}–*L*) characteristics of OLEDs. Inset: EL spectra at 0.1 mA.

photoelectron yield spectroscopy (PYS) and observed at –5.80 eV for **2Ac-PRZ** and at –5.63 eV for **2PXZ-PRZ**. Electron affinities (E_a) were estimated using I_p and E_g and were found to be –2.94 eV for **2Ac-PRZ** and –3.05 eV for **2PXZ-PRZ**.

Before fabrication of OLEDs, we evaluated the photophysical properties of the doped films in the host matrices of bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) and 4,4'-bis(carbazol-9- yl)biphenyl (CBP). The emission peak of 10 wt% **2Ac-PRZ**-doped DPEPO films was located at 475 nm and its η_{PL} value was recorded to be 48%. On the other hand, the emission peak of 10 wt% **2PXZ-PRZ**-doped CBP film was located at 519 nm and its η_{PL} value was observed to be 65%. The TADF characteristic of both films was tested on the basis of PL transient decay curves at 5 K and 300 K. The delayed PL intensities of both the films increased at 300 K, confirming the presence of TADF (**Figure 1(d)**). Transient PL decay curves of these doped films exhibited a double-exponential decay with a delayed lifetime (τ_d) of 134 μs for **2Ac-PRZ** and 54 μs for **2PXZ-PRZ**. The ΔE_{ST} values were estimated based on the onset of the prompt and delayed emission components to be 0.36 eV for **2Ac-PRZ** and 0.21 eV for **2PXZ-PRZ** at 5 K (**Figure S2**). All thermal and photophysical properties of the two emitters are summarized in **Table 1**.

We evaluated the OLED performance first using the sky-blue **2Ac-PRZ** as an emitter (**Figure S3**, **S4**). *N,N*-dicarbazoyl-3,5-benzene (mCP) and DPEPO were used as the host materials. Di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (TAPC) was used as the hole transport layer (HTL) and 3,3'',5,5'-tetra(3- pyridyl)-1,1';3',1''-terphenyl (B3PyPB)[23] was used as the electron transport layer (ETL). All these materials have higher E_T values than that of **2Ac-PRZ** (E_T = 2.58 eV), and that permitted effective suppression of the quenching of triplet excitons in the emission layer. OLED with a structure of [ITO/triphenylamine-containing polymer: 4-isopropyl-4'-methyldiphenyl-iodonium tetrakis(pentafluorophenyl)borate (PPBI)[24] (20 nm)/TAPC (20 nm)/10 wt% **2Ac-PRZ**:mCP (10 nm)/10 wt% **2Ac-PRZ**:DPEPO (10 nm)/B3PyPB (50 nm)/LiF (0.5 nm)/Al (100 nm)] was fabricated. Here, we used double emission layer (DML) strategy to obtain better performances.[25] The CIE coordinates were evaluated to be (0.19, 0.31) and the $\eta_{ext,\ max}$ was greater than 11%, thereby outperforming the theoretical limit of fluorescent materials (**Figure 2**). For the **2PXZ-PRZ**-based green emission device, tris(4-carbazoyl-9-ylphenyl)amine (TCTA) and CBP were used as the host materials (**Figure S3**, **S4**). The CIE coordinates for this device were evaluated as (0.31, 0.55) and its $\eta_{ext,\ max}$ recorded a high value of over 21%.

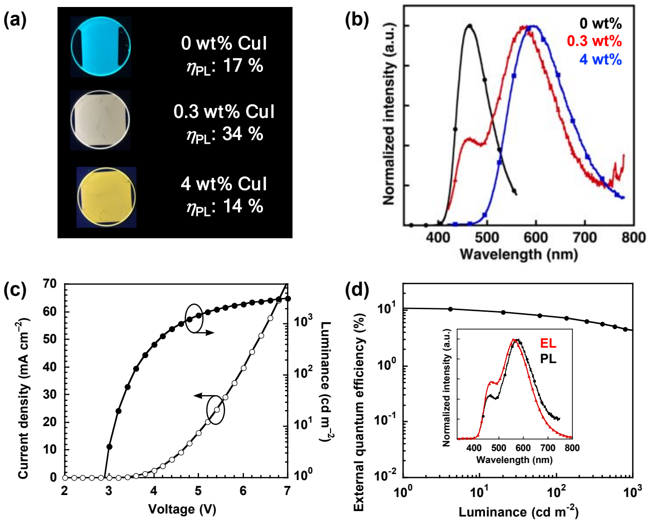

Figure 3 (a) Photographs of CuI-doped **2Ac-PRZ** films on quartz substrates under UV irradiation (365 nm), (b) PL spectra of CuI-doped **2Ac-PRZ** films, (c) *J–V–L* characteristics, and (d) η_{ext}–*L* characteristics of 0.3 wt% CuI(I)/**2Ac-PRZ**-based devices. Inset: PL and EL spectra at 5 mA.

As demonstrated above, **2Ac-PRZ** exhibited sky-blue emission and evident TADF behavior. We then assessed the photophysical properties of co-deposited CuI(I)/**2Ac-PRZ** films with different CuI(I) doping concentrations ranging from 0.3 to 4 wt%. **Figure 3(a)** and **(b)** show the photographs and PL spectra of CuI(I)-doped **2Ac-PRZ** films on quartz substrates. A new orange emission with a peak wavelength of 583 nm was noticed with a corresponding decrease in the intensity of the sky-blue emission from **2Ac-PRZ** (**Figure 3(b)**, **S5**). This new emission can be attributed to the CuI(I) complex. The 4 wt% doped CuI(I)/**2Ac-PRZ** film too exhibited an orange emission with the peak wavelength of 583 nm and a η_{PL} value of 14%. This CuI(I)/**2Ac-PRZ** film showed no TADF characteristics, and a decrease in PL intensity was observed at the higher temperature of 300 K compared with 5 K, indicating that the emission came from the phosphorescence with a lifetime of 8.25 μs (**Figure S6**). Interestingly, the 0.3 wt%-doped CuI(I)/**2Ac-PRZ** film showed white emission with dual emission peaks at 463 nm and 583 nm and a η_{PL} of up to 34%, which is twice that of a pure **2Ac-PRZ** film with a η_{PL} of 17%. This white emission is generated from a combination of sky-blue emission and orange emission. For higher doping of CuI(I), the spectra showed only orange emission without sky-blue emission from **2Ac-PRZ**. Note that co-deposited CuI(I)/**2PXZ-PRZ** films also formed in-situ metal complex (**Figure S7**). We then fabricated a white OLED (WOLED) using 0.3 wt%-doped CuI(I)/**2Ac-PRZ** film (**Figure 3**).

Table 2 Summery of OLED performances.

Emitter	$V_{on}/\eta_{p,on}/\eta_{c,on}/\eta_{ext,on}$ [a] [V/lm W^{-1}/cd A^{-1}/ %]	$V_{100}/\eta_{p,100}/\eta_{c,100}/\eta_{ext,100}$ [b] [V/lm W^{-1}/cd A^{-1}/ %]	$V_{1000}/\eta_{p,1000}/\eta_{c,1000}/\eta_{ext,1000}$ [c] [V/lm W^{-1}/cd A^{-1}/ %]	*CIE*[d] (*x*, *y*)
2Ac-PRZ	2.96/25.1/23.6/11.9	4.24/7.03/9.49/4.79	6.96/1.43/3.18/1.76	0.19, 0.31
2PXZ-PRZ	2.81/76.0/67.9/21.4	3.24/53.1/54.6/17.3	3.90/22.4/27.7/8.77	0.31, 0.55
2Ac-PRZ:CuI(I)	2.83/32.7/29.4/11.1	3.51/18.1/20.1/7.60	4.59/7.59/11.1/4.27	0.46, 0.49

[a] Voltage (V), power efficiency (η_p), current efficiency (η_c), and external quantum efficiency (η_{ext}) at 1 cd·m^{-2}. [b] V, η_p, η_c, and η_{ext} at 100 cd·m^{-2}. [c] V, η_p, η_c, and η_{ext} at 1000 cd·m^{-2}. [d] CIE at 100 cd·m^{-2}.

Table 2 provides a summary of the OLED performances. The EL spectra showed white emission with two complementary emission peaks at 469 nm and 558 nm and CIE coordinates of (0.46, 0.49). This device was operated using a low-drive-voltage of 2.8 V at 1 cd m^{-2}, and it exhibited a $\eta_{\rm ext,\,max}$ of 11%. A relatively low efficiency roll-off with a stable $\eta_{\rm ext}$ of 4.3% at a brightness of 1000 cd m^{-2} was observed. The $\eta_{\rm ext}$ values of this preliminary device were relatively low because of the low $\eta_{\rm PL}$ of CuI(I)-doped **2Ac-PRZ** film ($\eta_{\rm PL}$ = 34%). To improve the performances, we should realize much higher $\eta_{\rm PL}$ of CuI(I)-doped film. This simple CuI(I)-doping into TADF emitters evidently then affords a promising approach toward realizing high-efficiency WOLEDs.[25] At this preliminary white device, we observed spectral changes at different voltages (**Figure S8**). However, further device optimization and materials improvement should realize stable white light emission.

To conclude, we developed two types of 2,6-pyrazine-based TADF emitters. Of the two, the green emitter **2PXZ-PRZ** helped realize high-performance OLEDs with a $\eta_{\rm ext}$ of over 20%, whereas the sky-blue emitter **2Ac-PRZ** outperformed conventional fluorescent emitters with a $\eta_{\rm ext}$ of over 10%. Moreover, **2Ac-PRZ** was able to form an in situ metal complex with CuI(I) through the co-evaporation process helping achieve an efficient WOLED with CIE coordinates of (0.46, 0.49) and a $\eta_{\rm ext,\,max}$ of 11%. To our best knowledge, this is the first report of TADF emitters realizing in situ formation of a metal complex. We believe that further improvement in the efficiency of WOLEDs is achievable through sophisticated molecular design and pertinent studies on the same are underway in our laboratory.

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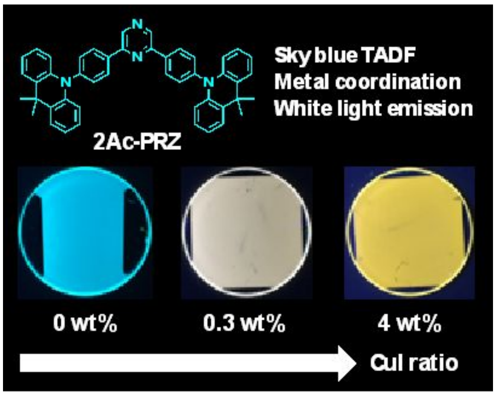

A pyradine-containing sky blue fluorescent emitter can achieve efficient white light emission through in situ metal complex formation.