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Recent progress of pyrimidine derivatives for high-performance organic light-emitting devices

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Abstract. Pyrimidine is an electron-deficient azaaromatic compound containing two nitrogen atoms at 1, 3-positions that plays a key role as an organic semiconductor or semiconducting material. Because of the high electron-accepting property induced by C═N double bonds and due to its coordination ability, pyrimidine has been incorporated as a building block in phosphorescent emitters, fluorescent emitters, bipolar host materials, and electron transporting materials in organic light-emitting devices (OLEDs). Recently, pyrimidine-based thermally activated delayed fluorescent emitters combined with various electron donors have been developed, and their device performances were far better than those based on conventional fluorescent emitters. In this review, recent progress of pyrimidine-based OLED materials is presented and accompanied by a historical overview, current status, key issues, and outlook for the next generation of high-performance OLED materials. [DOI: 10.1117/1.JPE.8.032108]

Keywords: thermally activated delayed fluorescence; organic light-emitting device; pyrimidine; donor–acceptor molecule.

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1 Introduction

Next generation displays and lighting resources have focused on using organic light-emitting devices (OLEDs) because of their outstanding features, such as having low power consumption and being flat, ultra thin, and light weight.[1–8] Moreover, flexible and transparent OLEDs can be fabricated, and printable OLEDs can also be used in future applications. Until recently, phosphorescent emitters containing platinum heavy metals, such as iridium and platinum, were absolutely required for high-efficiency OLEDs to realize internal quantum efficiency (IQE) of 100% since these rare heavy metals can harvest all electrogenerated molecular singlet and triplet excitons (Fig. 1).[9,10] Phosphorescent OLEDs have achieved a high external quantum efficiency (EQE) of $>30\%$ even at high luminance of over 1000 $\mathrm{cd\,m^{-2}}$.[11–13] Recently, thermally activated delayed fluorescence (TADF) emitters based on pure organic compounds have been considered as an alternate technology to phosphorescent counterparts to realize an IQE of 100%.[14–25] Until recently, several TADF OLEDs have achieved a high EQE of over 30% at maximum.[26–32] The efficiency of the TADF-based OLEDs is expected to exceed that of OLEDs based on phosphorescent emitters due to the unlimited molecular design of pyrimidine derivative-based TADF emitters.

In principle, TADF emitters consist of donor and acceptor units. The emission colors can be easily controlled by modifying the chemical structures. For example, the combination of weak donor/acceptor units gives blue emission due to weak charge-transfer (CT) interaction, whereas the combination of strong donor/acceptor units gives red emission due to strong CT interaction. So far, many kinds of donor and acceptor units for TADF emitters have been reported. For the acceptor unit, triazine is one of the most famous acceptor units.[33–36] Until now, Adachi et al.

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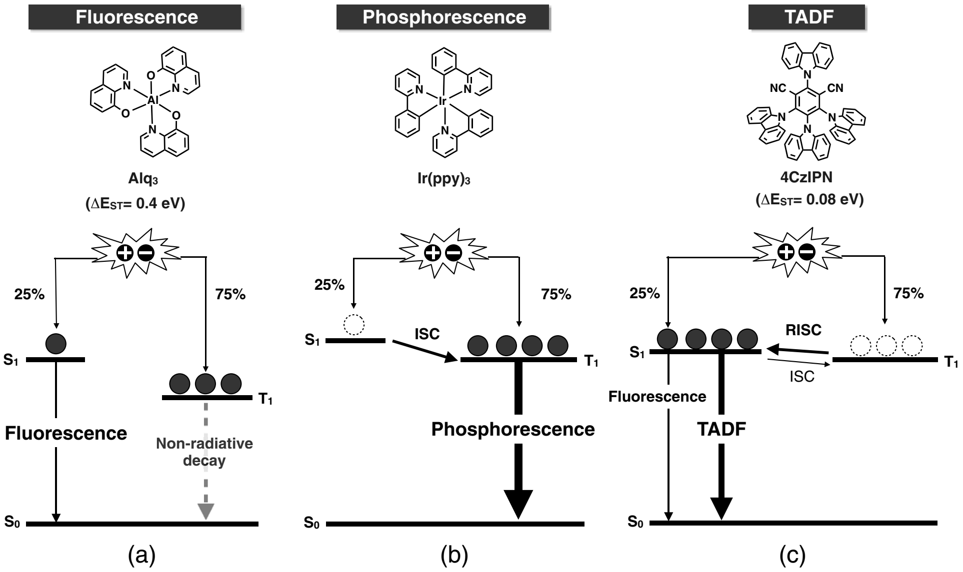


Fig. 1 Emission mechanism of (a) fluorescence, (b) phosphorescence, and (c) TADF-based OLEDs.

reported a series of triphenyltriazine-based emitters that realizes an EQE of over 30% and that emits color range from blue to orange.[33–36] However, the stronger electron-accepting character of triazine compared with other azaaromatic compounds, such as pyridine, pyradine, and pyrimidine, tends to make the emission peak wavelength longer, causing a problem in the development of deep-blue emitters. On the contrary, pyrimidine is a similar electron-deficient azaaromatic compound with two C═N double bonds, and it has a weaker electron-accepting character than that of triazine. Although the differences of chemical structures between pyrimidine and triazine are tiny, only one nitrogen atom, the resulting optoelectronic properties are totally different, and the new chemistry of pyrimidine-based organic semiconductors has been relatively unexplored.

This review presents recent progress in the development of pyrimidine derivatives for OLEDs as well as a historical overview, current status, key issues, and outlook for the next generation of high-performance OLED.

2 Pyrimidine-Based Organic Semiconductor Materials for OLEDs

2.1 *Pyrimidine-Containing Phosphorescent Emitters Based on Iridium*

This first section introduces pyrimidine-containing phosphorescent emitters based on iridium, bipolar host materials, and electron-transport materials (ETMs; Fig. 2). So far, phenylpyridine derivatives have been intensively investigated for the ligands in phosphorescent emitters based on iridium.[37–39] The representative examples are a green emitter, *fac*-tris(2-phenylpyridine) iridium(III) [$\mathrm{Ir(ppy)_3}$],[9] and sky-blue emitter, iridium(III)bis(4,6-(difluorophenyl)pyridinato-*N*, $C^{2'}$)picolinate (FIrpic).[40] In this series of ligands, long-term stability in blue OLEDs remains a big challenge, and replacement of pyridine with pyrimidine unexpectedly provides great improvements of stability in blue OLEDs.[41]

A pyrimidine-containing sky-blue phosphorescent emitter, iridium(III)bis(2-(2,4-difluorophenyl)-pyrimidine-*N*, $C^{2'}$)(picolinate) [$\mathrm{(DFPPM)_2Ir(pic)}$], was originally developed by Ge et al.[42] $\mathrm{(DFPPM)_2Ir(pic)}$ showed an emission peak at 476 nm and had a shoulder peak at 496 nm in the $\mathrm{CH_2Cl_2}$ solution. The emission peak of $\mathrm{(DFPPM)_2Ir(pic)}$ is 6 nm red-shifted compared with that of the pyridine-based FIrpic. Consequently, the replacement of pyridine with pyrimidine leads to a longer emission wavelength. A polymer-based blue OLED showed sky-blue emission with a peak of 491 nm and an EQE of 2.2%. At that time, the OLED efficiency remained very low. However, the situation changed in 2017. A collaboration work of Wu, Chou,

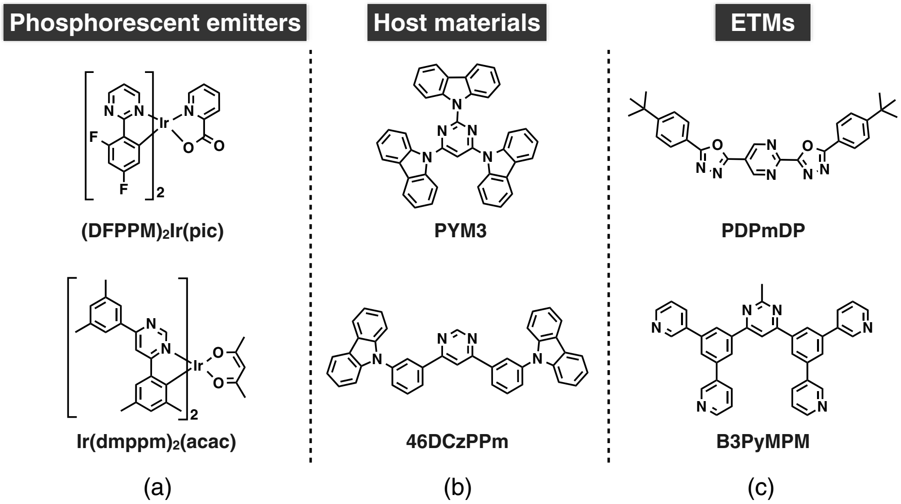


Fig. 2 Chemical structures of pyrimidine-based compounds for OLEDs: (a) phosphorescent emitters, (b) host materials, and (c) ETMs.

and Wong in Taiwan revealed that this sky-blue emitter showed an impressively high EQE and long-term device stability.[41] Surprisingly, an optimized sky-blue OLED exhibited a high EQE of 25% with Commission Internationale de l'Eclairage chromaticity coordinates (CIE) of (0.16, 0.38) and very long operation lifetime at 50% at the initial luminance of 327 $\mathrm{cd\,m^{-2}}$ ($\mathrm{LT_{50}}$, $L_0 = 327\ \mathrm{cd\,m^{-2}}$) of over 2200 h. This value is nearly 1000 times greater than that for the FIrpic. This representative result highlights pyrimidine-based organic semiconductors as promising and stable materials under electrical operation. Similar to pyridine-based iridium complexes, a variety of colors is explored using pyrimidine-based iridium complexes. Cui et al.[43] developed an orange emitter called $\mathrm{Ir(dmppm)_2(acac)}$. This emitter exhibits a high photoluminescent quantum efficiency (PLQE) of 92% and large horizontal transition dipole ratio (Θ) of 78% with respect to the substrate plane. As a result, $\mathrm{Ir(dmppm)_2(acac)}$-based OLED achieved a very high EQE of 28.2%.

The emission color of iridium complex was easily controlled by modifying the chemical structure of pyrimidine substituents. However, pyrimidine-based iridium complexes are relatively unexplored compared with their pyridine derivatives. As described, these excellent results clearly demonstrate the potential advantages of using pyrimidine-based iridium complexes in high-performance phosphorescent OLEDs with long-term stability.

2.2 *Pyrimidine-Containing Hosts*

Among phosphorescent host materials, bipolar host materials containing donor and acceptor units have played an important role in creating superior carrier balance and have generally achieved high-efficiency OLEDs.[44] In addition, pyrimidine-based bipolar hosts combined with the donor units, such as carbazole or diarylamines, have been developed (Fig. 2). The electron-deficient character of pyrimidine compared with benzene and pyridine allows bipolar host materials to have a greater electronically negative character, leading to better electron-transport and injection properties.

Son et al.[45] developed an efficient blue OLED by using a bipolar host material called 2,4,6-tricarbazolo-1,3,5-pyrimidine (PYM3) with high triplet excited energy (E_T) suitable for blue phosphorescent emitters. From the phosphorescent spectrum, the triplet energy level is estimated to be 2.89 eV, which is higher than the triplet energy level of the typical sky-blue emitters, FIrpic (2.64 eV). A FIrpic-based OLED also achieved a lower driving voltage of 6.3 V at 1 $\mathrm{mA\,cm^{-2}}$ and a high EQE of 8.0% at 0.2 $\mathrm{mA\,cm^{-2}}$. These results are attributed to a good exciton confining property and superior carrier injection and transport in the emission layer.

Su et al.[46] developed a bipolar host material called 4,6-bis(3-(carbazol-9-yl)phenyl) pyrimidine (46DCzPPm) with a high E_T of 2.64 eV; this material comprises pyrimidine/carbazole. A blue phosphorescent OLED based on FIrpic exhibited a low turn-on voltage of 3.1 V at 10 cd m^{-2} and a high EQE of 13.5%. Due to superior bipolar ability, 46DCzPPm can be installed into homojunction devices.[47] Su et al.[46] have demonstrated the efficient sky-blue phosphorescent OLEDs with p-i-n homojunction architecture. Using p- and n-doping techniques, the homojunction device was fabricated to achieve a low turn-on voltage of 3 V and a power efficiency (PE) of ~20 lm W^{-1} at a luminance of 100 cd m^{-2}. Moreover, in 2016, using 46DCzPPm, Yamada et al.[48] developed a sky-blue phosphorescent OLED with a high EQE and long device lifetime. The resulting OLED based on 46DCzPPm realized a high EQE of 28% and a long operation lifetime at 90% at the initial luminance of 2000 cd m^{-2} (LT$_{90}$, $L_0 = 2000$ cd m^{-2}) of 160 h at CIE of (0.18, 0.48). These results clearly demonstrate the advantage of using pyrimidine-based bipolar host materials in phosphorescent OLEDs with long-term stability.

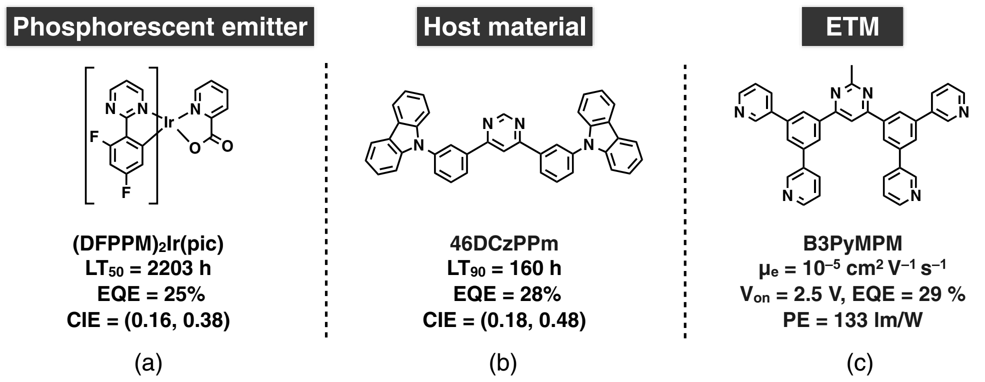
2.3 *Pyrimidine-Containing ETMs*

The electron-deficient character of pyrimidine, compared with benzene and pyridine, allows ETM to have a better electron-injection property. Review articles of *Chemistry of Materials* and *Journal of Materials Chemistry* in 2004 and 2005 show that the research on pyrimidine-based ETMs has been limited.[49,50] However, recently, researchers often use pyrimidine-based ETMs as standard materials (Fig. 2).

Wang et al.[51] developed an ETM called 2,5-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yl] pyrimidine (PDPmDP); this ETM contained pyrimidine and oxidiazole units. A phosphorescent OLED using PDPmDP as an ETM achieved an EQE double that of the device with 1,3-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-5-yl]benzene (OXD-7) without the pyrimidine component.

Tanaka et al.[52] developed a pyrimidine-based ETM, bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine (B3PyMPM), based on pyrimidine. B3PyMPM shows an electron mobility of 10^{-5} cm^2 V^{-1} s^{-1} and a good electron-injection property due to the presence of pyrimidine. A green phosphorescent OLED using B3PyMPM achieved a low turn-on voltage of 2.5 V at 100 cd m^{-2}, high EQE of 29%, and extremely high PE of 133 lm W^{-1}. Moreover, bis-4,6-(3,5-dipyridylphenyl)-2-methylpyrimidine (BPyMPM) derivatives exhibit different optoelectronic properties, such as ionization potential, electron affinity, and electron mobility depending on the nitrogen position on the peripheral pyridine rings.[53,54] Interestingly, a 100-fold increase of the electron mobility has been observed based on the nitrogen position of pyridine rings. These series of pyrimidine-based ETMs are also beneficial for exciplex-based high-performance OLEDs, as shown in the next section.

The representative examples of pyrimidine-containing semiconductors are summarized in Fig. 3.



(a) (b) (c)

Fig. 3 Representative pyrimidine-based compounds and OLED performances: (a) phosphorescent emitter, (b) host material, and (c) ETM.

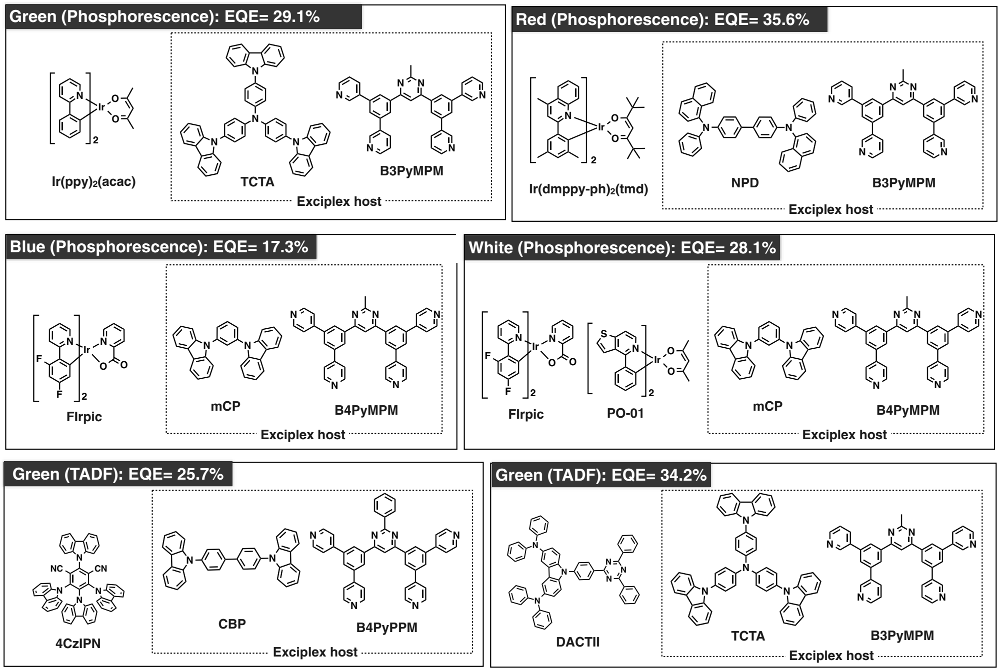


Fig. 4 High performance OLEDs using the exciplex energy transfer system.

2.4 *Pyrimidine-Containing Exciplex Hosts*

An exciplex is an excited complex formed between strong electron-donor and electron-acceptor materials. Different from CT complexes, the exciplex does not show the CT character and absorption band in the ground state. Until recently, exciplex formation was recognized to cause a loss of efficiency in OLEDs.[55] However, by using wide-energy-gap materials for exciplex formation, highly efficient OLEDs can be developed. Among n-type host materials, pyrimidine-containing wide-energy-gap ETMs, such as BPyMPM[52] and 2-phenyl-bis-4,6-(3,5-dipyridylphenyl) pyrimidine (BPyPPM)[56] derivatives, have been widely used as a component of exciplex host, and extremely low power consumption RGBW OLEDs have been developed (Fig. 4).

Park et al.[57] developed highly efficient green phosphorescent OLEDs using energy transfer from exciplex based on B3PyMPM/4,4′-*N*,*N*′-dicarbazolylbiphenyl (CBP), later they introduced more efficient exciplex systems of B3PyMPM/4,4′,4″-tris(*N*-carbazolyl)triphenylamine (TCTA).[58] A green phosphorescent OLED based on bis(2-phenylpyridine)iridium(III)acetylacetonate $[\mathrm{Ir(ppy)_2(acac)}]$ exhibited a PE of 124 $\mathrm{lm\,W^{-1}}$, EQE of 29.1%, and low turn-on voltage of 2.4 V. Similarly, the same group developed red phosphorescent OLEDs using (bis(4-methyl-2-(3,5-dimetylphenyl)quinoline))Ir(III)(tetrametylheptadionate) $[\mathrm{Ir(mphq)_2(tmd)}]$ as a red emitter and B3PyMPM/*N*,*N*′-di(naphthalen-1-yl)-*N*,*N*′-diphenylbenzidine (NPD) as exciplex host material, and a resulting OLED exhibited a very high EQE of 35.6%.[12] The exciplex formation from these hosts can create an almost perfect carrier balance, realizing a low turn-on voltage of 2.1 V and negligible efficiency roll-off (EQE = 30% at 10,000 $\mathrm{cd\,m^{-2}}$).

If a suitable host combination is used, even blue exciplex can be realized.[59,60] Wu et al.[61] developed a blue phosphorescent OLED using B4PyMPM/*N*,*N*-dicarbazoyl-3,5-benzene (mCP) as exciplex host material; an OLED based on FIrpic exhibited a high EQE of 17.3%. Moreover, white OLED combined with an orange phosphorescent emitter (PO-01, bis(4-phenylth-ieno[3,2-c]pyridine)(acetylacetonate)iridium(III)) realized a high EQE of 28.1%.

The exciplex host can be used not only for phosphorescent OLEDs but also for TADF counterparts. The first report using B3PyMPM/mCP exciplex as a host for TADF OLED was reported by Sun et al.[26] They used a green TADF emitter, 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)[14] and realized a highly efficient OLED with a PE of 89 $\mathrm{lm\,W^{-1}}$. Seino et al.[62] developed a green TADF OLED using a B4PyPPM/CBP exciplex formed at the emission layer and ETM interface. This green OLED exhibited a high PE of 100 lm W^{-1}, low turn-on voltage of 2.3 V, and a high EQE of 26%. Moon et al.[31] developed green TADF OLEDs using B3PyMPM/TCTA as the exciplex host materials. A green device based on 9-[4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl]-*N*,*N*,*N*′,*N*′-tetraphenyl-9*H*-carbazole-3,6-diamine (DACT-II) exhibited a high PE of 121 lm W^{-1} and a high EQE of 34.2%.

Another types of pyramidine-based n-type host are used in stable deep-red OLEDs with EL emission wavelength of 670 nm. Nagai et al.[63] developed dibenzothiophene-containing n-type host materials named 2-(3′-(dibenzo[b,d]thiophene-4-yl)-[1,1′-biphenyl]-3-yl)-4,6-diphenylpyrimidine (4DBT46PM) and 4-(3′-(dibenzo[b,d]thiophene-4-yl)-[1,1′-biphenyl]-3-yl)-2,6-diphenylpyrimidine (4DBT26PM). Deep-red phosphorescent OLEDs using bis(2,3-diphenylquinoxaline)iridium(dipivaloylmethane) $[(DPQ)_2Ir(dpm)]$ as a deep-red emitter and 4DBT46PM or 4DBT26PM/NPD as exciplex hosts exhibited high EQEs of over 15% and long operation lifetime at 70% at the initial luminance of 170 cd m^{-2} (LT_{50}, $L_0 = 327$ cd m^{-2}) of over 250 h.

As shown in this section, pyrimidine derivatives are very useful for organic semiconductor materials as ligands for phosphorescent emitters, bipolar hosts, and ETMs due to their high-efficiency and long-term stability.

3 Pyrimidine-Containing Conventional Fluorescent Blue Emitters

Before generating TADF technology, the researchers focused on developing conventional fluorescent emitters (Fig. 5).[64] So far, researchers developed several kinds of pyrimidine-based blue emitters with high PLQE and observed unique photophysical phenomena due to the asymmetric structure.

Wu et al.[65] developed a fluorescent blue emitter called 2,7-bis[2-(4-tert-butylphenyl)pyrimidine-5-yl]-9,9’-spirobifluorene, which consists of pyrimidine and spirobifluorene; the emitter realized a high PLQE of 80%, and it should be noted that this conventional fluorescent OLED realized a nearly theoretical maximum EQE of 4.0%.

Itami et al.[66] reported syntheses and unique fluorescent properties of a series of π-conjugated pyrimidine compounds. The authors synthesized several pyrimidine compounds and showed that the combination of pyrimidine and electron-donating moiety such as dimethyl amine is important to achieve high PLQE. Interestingly, triphenylpyrimidine itself showed significantly low PLQE of 1%, but the introduction of dimethylamine moiety onto the 4-position of pyrimidine ring showed a much higher PLQE of 63%. By contrast, introducing dimethylamine moiety into the 2-position of pyrimidine ring caused a lower PLQE of 5% (Fig. 5).

Skardziute et al.[67] reported the syntheses and optical properties of a series of pyrimidine/carbazole conjugated molecules. These compounds showed strong intramolecular CT characteristics in the excited states; this was proven by solvatochromic dynamics and was supported by

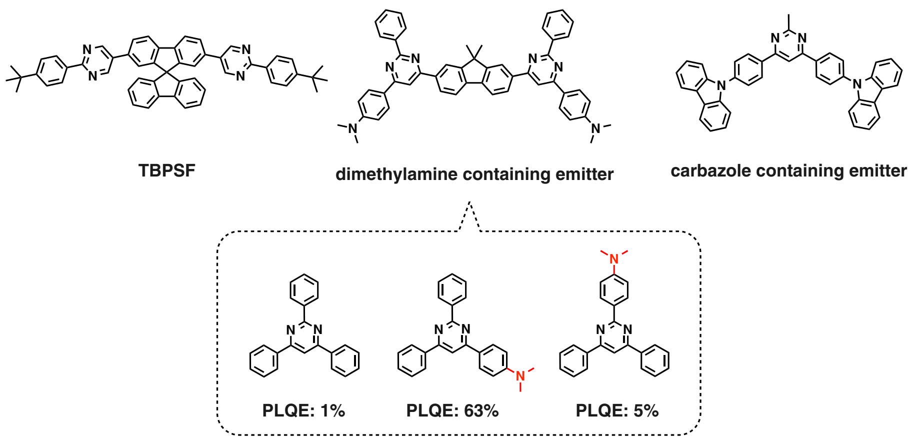


Fig. 5 Chemical structures of pyrimidine-based conventional fluorescent emitters.

density functional theory (DFT) calculations. A pyrimidine–carbazole containing emitter exhibited a high PLQE of 65% and a deep-blue emission wavelength of 402 nm.

As mentioned, pyrimidine-containing fluorescent emitters clearly exhibited blue emission and high PLQE, and they also exhibited unique photophysical properties due to the asymmetric chemical structure. However, OLED performances of these emitters are mostly unexplored.

4 Pyrimidine-Containing TADF Emitters

4.1 *Molecular Design Strategy of Pyrimidine Derivatives as TADF Emitters*

Although conventional pyrimidine-based fluorescent blue emitters composed of donor moieties, such as alkyl amines and cabazoles, have been well known throughout the past decade as efficient fluorescence emitters with high PLQE values, the pyrimidine moiety has not been used as a component of TADF emitters. While developing TADF emitters, the energy difference between the singlet and triplet excited states (ΔE_{ST}) must be small (approximately <0.3 eV) to obtain the TADF character.[14–25] Figure 6(a) shows the molecular structure of 4CzIPN,[14] which is the most famous TADF emitter, and the typical requirements for efficient TADF emitters. TADF emitters are composed of donor and acceptor units, and a small ΔE_{ST} can be achieved by creating a highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) separation. This HOMO and LUMO separation can be achieved by introducing steric hindrance between the donor and acceptor units. Small ΔE_{ST} enhances exciton up-conversion from triplet excited state to singlet excited state, leading to 100% of the IQE in the OLEDs. In fact, the 4CzIPN-based TADF OLED exhibited an EQE of 19%, which is four times higher than that exhibited by fluorescent emitters.[14] The emission color is correlated to the energy gap between the HOMO of the donor and the LUMO of the acceptor units. In Fig. 6(b), the reported molecular design strategy of pyrimidine derivatives as TADF emitters is shown. Pyrimidine-based TADF emitters are mainly categorized into donor–acceptor–donor (D-A-D)[68–72] and donor–acceptor (D-A)[29,73–76] types, where the pyrimidine backbone is used as the acceptor unit, and phenoxazine, acridine, and carbazole derivatives are frequently used as donor units. Among D-A-D types, the donor unit is attached to the 4,6-position of pyrimidine, whereas among D-A types, the donor unit is attached to the 2-position or the 4-position of pyrimidine. Consequently, a large variety of pyrimidine-based blue TADF emitters can be developed due to the structural asymmetry and the weaker electron-accepting property of the pyrimidine in comparison with that of the triazine.

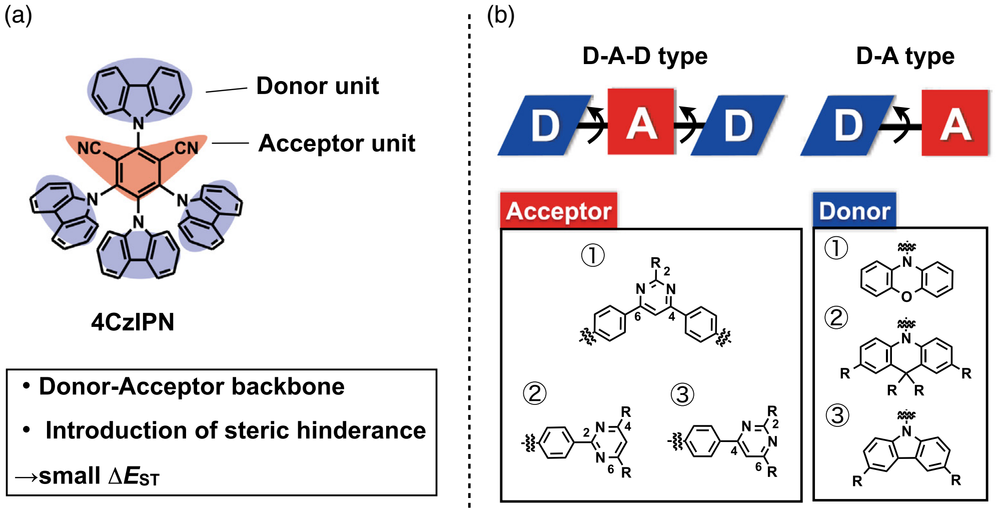


Fig. 6 (a) The molecular structure of 4CzIPN and (b) a molecular design strategy of pyrimidine derivatives as TADF emitters.

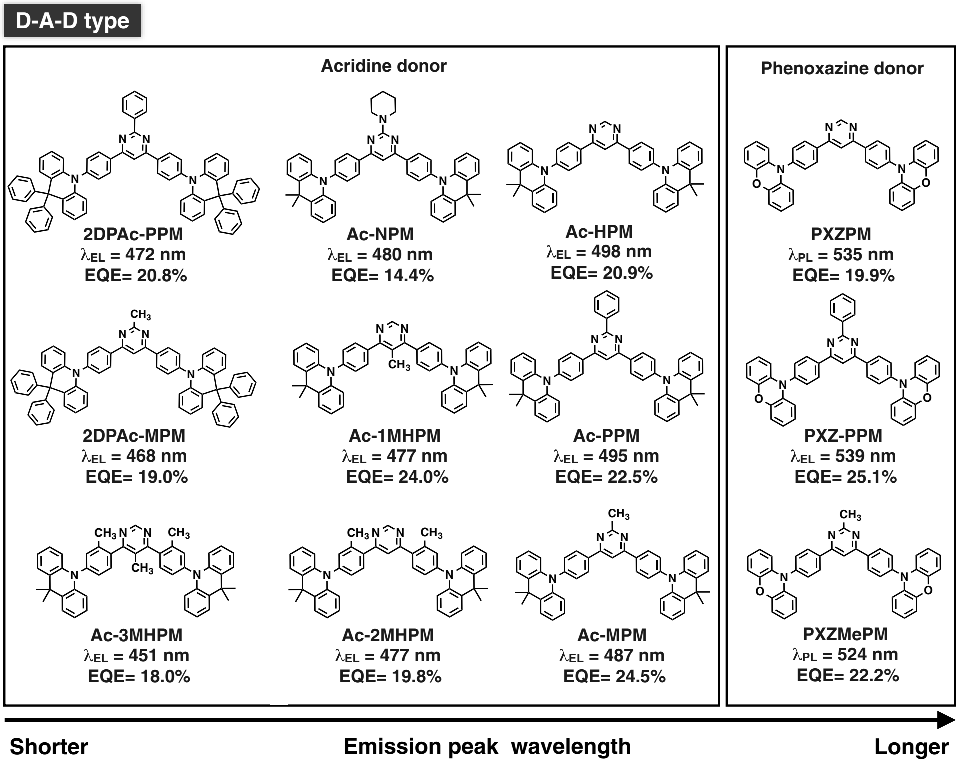


Fig. 7 Chemical structures of D-A-D type pyrimidine derivatives as TADF emitters.

4.2 *D-A-D Type Emitters*

In many cases, D-A-D type emitters exhibit more efficient triplet-to-singlet exciton up-conversion characteristics than the D-A type emitters.[77,78] The ΔE_{ST} of D-A-D type TADF emitters tends to become smaller in comparison with that of the D-A type because of the stronger CT characteristics. Although the emission peak wavelength tends to become longer, from the perspective of efficiency, the D-A-D type emitters generally exhibit a superior EQE. Figure 7 presents a summary of the D-A-D type emitters.

In early 2016, Komatsu et al.[68] reported a series of highly efficient TADF emitters composed of pyrimidine/acridine. Three TADF emitters called 2-functionalized-4,6-bis[4-(9,9-dimethyl-9,10-dihydroacridine)-phenyl]pyrimidine (Ac-RPM) derivatives (Ac-HPM, Ac-PPM, and Ac-MPM, where R═H, phenyl, and CH_3, respectively) were developed. The emission peaks of Ac-HPM, Ac-PPM, and Ac-MPM doped bis[2-(diphenylphosphino) phenyl]ether oxide (DPEPO) films were located at 498, 498, and 489 nm, respectively. All the films showed high PLQE values of ~80% and small ΔE_{ST} values of <0.20 eV with fluorescent delayed lifetime (τ_{d}) of 21 to 26 μs. Ac-HPM and Ac-PPM based devices showed a high EQE of ~20% and light green emission with CIE of (0.21, 0.44). In addition, the Ac-MPM based device realized an EQE of 25%, a low turn-on voltage of 2.80 V, a PE of 61.6 $\mathrm{lm\,W^{-1}}$, and sky-blue emission with CIE of (0.19, 0.37). This is the first report of pyrimidine derivatives as TADF emitters.

Later, Wu et al.[69] developed a series of phenoxazine-based green TADF emitters called 4,6-bis(4-(10H-phenoxazin-10-yl)phenyl)-2-phenylpyrimidine (PXZ-PPM), 4,6-bis(4-(10H-phenoxazin-10-yl)phenyl)pyrimidine (PXZPM), and 4,6-bis(4-(10H-phenoxazin-10-yl)phenyl)-2-methylpyrimidine (PXZMePM). They introduced methyl, hydrogen, and phenyl moiety into the diarylpyrimidine unit. The emission peaks of PXZ-PPM, PXZPM, and PXZMePM doped CBP films are located at 524 to 535 nm, which is 40 nm longer than the emission peaks of films with an acridine donor. All the films showed very small ΔE_{ST} values of <0.1 eV with delayed lifetimes (τ_d) of <3 μs. All the devices showed high EQE values over 20% with small EQE-roll-off values.

Compared with the corresponding triazine derivatives, another advantage of pyrimidine derivatives is to easily modify the molecular structure to finely tune the optoelectronic properties. To investigate the structure-property relationships among pyrimidine conjugate emitters, Komatsu et al.[70] developed functionalized pyrimidine emitters called Ac-NPM and PXZ-PPM by chemically modifying the acceptor and donor units. Ac-NPM possessed a piperidine moiety at the 2-position of pyrimidine, and the stronger electron-donating piperidine is expected to increase the LUMO levels, leading to a higher singlet excited energy. PXZ-PPM has the same chemical structure, as previously reported by Yang et al.,[24] and it has the phenoxazine unit as a donor. The mission peaks of Ac-NPM and PXZ-PPM doped DPEPO films are located at 476 and 540 nm, respectively, and the Ac-NPM and PXZ-PPM doped DPEPO films showed PLQE values of 63% and 78%, ΔE_{ST} values of 0.25 and 0.08 eV, and τ_{d} values of 79 and 9 μs, respectively. The Ac-NPM based device showed an EQE of 14% with a blue emission peak at CIE of (0.17, 0.29), whereas the PXZ-PPM based green OLED showed an impressive 25% EQE, 103 $\mathrm{lm\,W^{-1}}$, and 2.6 V at 100 $\mathrm{cd\,m^{-2}}$ with a CIE of (0.36, 0.58). The results show that the performance of PXZ-PPM is comparable with the phosphorescent counterparts.

Park et al.[71] focused on the diphenylacridine donor unit and developed a series of pure blue TADF OLEDs emitters called 2DPAc-MPM and 2DPAc-PPM. Diphenylacridine has deeper HOMO levels than dimethylacridine and phenoxazine donor units. Therefore, the corresponding pyrimidine emitters are expected to exhibit larger HOMO/LUMO energy gaps and bluer emissions. The emission peaks of 2DPAc-MPM and 2DPAc-PPM doped 2,8-bis(diphenylphosphine oxide)dibenzofuran (PPF) films are located around 460 nm with PLQE values of over 90%, ΔE_{ST} values of ca. 0.25 eV, and long τ_{d} values of 210 to 330 μs. These emitters showed EQE values of around 20% and pure blue emission peaks with CIE values of (0.16, 0.24) for 2DPAc-PPM and CIE of (0.16, 0.21) for 2DPAc-MPM, respectively.

In addition to pure blue emitters, deep-blue emitters are required for high color rendering index white OLEDs for general lighting or TV applications. In this context, Komatsu et al.[72] designed and synthesized a series of twisted pyrimidine derivatives as TADF emitters. These emitters are called Ac-XMHPMs ($X = 1$, 2, and 3), and they contain different numbers of bulky methyl substituents at acceptor moieties, increasing the excited singlet and triplet state energies. The emission peaks of Ac-1MHPM, Ac-2MHPM, and Ac-3MHPM doped DPEPO films are located at 477, 477, and 454 nm, respectively. Ac-1MHPM and Ac-2MHPM based films showed high PLQE values of 75% and 71%, respectively, whereas an Ac-3MHPM based film showed a lower PLQE value of 47%. These emitters showed ΔE_{ST} values of ca. 0.23 eV and τ_{d} values around 45 μs. Among Ac-RPMs, Ac-3MHPM with a high triplet state energy of 2.95 eV exhibited a high peak EQE of 18% with CIE of (0.16, 0.15). This is among the highest EQE values in deep-blue TADF OLEDs.

4.3 *D-A Type Emitters*

Compared with D-A-D type emitters, D-A type emitters tend to exhibit weaker CT characteristics. Thus, it is easier for D-A type emitters to obtain bluer emission than D-A-D type emitters from the CT interaction point of view. However, for the efficient TADF process, more delicate molecular design should be required by considering the important interplay between CT, $\pi\pi*$, and $n\pi*$ transitions. Figure 8 shows the D-A type pyrimidine emitters that have been reported so far.

Gomez-Bombarelli et al.[73] used a high-throughput virtual screening and experimental approach for the molecular design of TADF emitters, and they found that several pyrimidine-based emitters are promising candidates. They explored a search space of 1.6 million molecules and screened over 400,000 of them using time-dependent DFT. These emitters are named 9-(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-*N*,*N*-diphenyl-9H-carbazol-3-amine (J1) and 9-(4-(4,6-diphenylpyrimidin-2-yl)phenyl)-*N*,*N*-diphenyl-9H-carbazol-3-amine (J2). J1 attached diphenylamine modified carbazole donor into the 4-positon of the pyrimidine unit, and the device exhibited a larger EQE value of 22% compared with that of the J2 (EQE = 13%) with the same donor unit in the 2-positon of the pyrimidine unit. One of the major reasons for the different performances of these two devices is the different PLQE values, and the PLQE values of J1 and J2 were 67% and 40%, respectively, in the toluene solution.

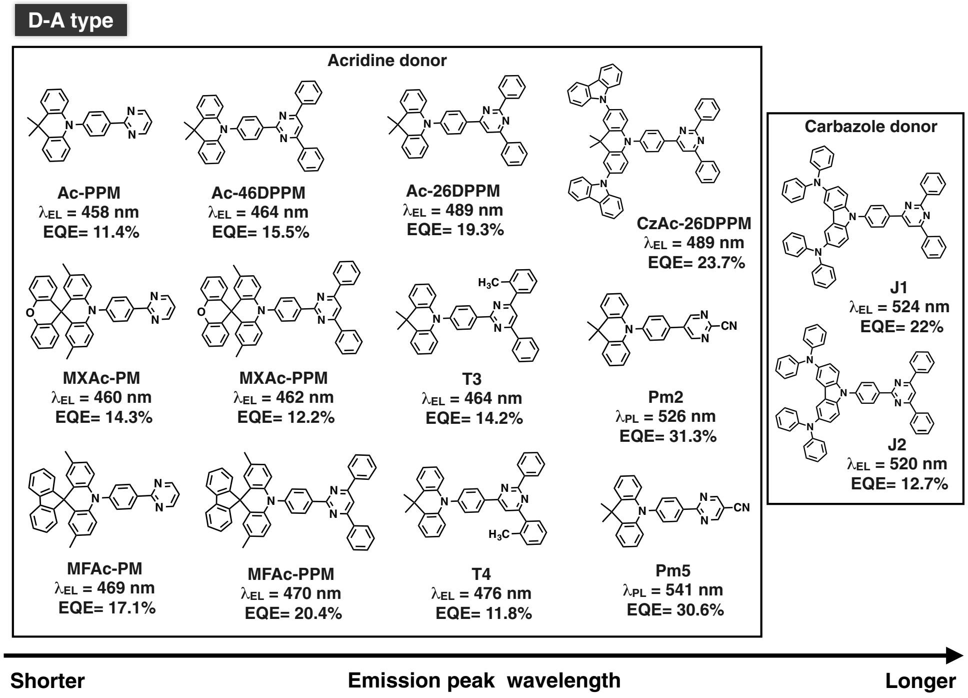


Fig. 8 Chemical structures of D-A type pyrimidine derivatives as TADF emitters.

Gomez-Bombarelli et al.[73] also reported an acceptor–donor–acceptor (A-D-A) type TADF emitter, named 5,8-bis(4-(2,6-diphenylpyrimidin-4-yl)phenyl)-5,8-dihydroindolo[2,3-c]carbazole (L1); that emitter is discussed in the next section. In the near future, this high-throughput approach will become a major way to find an appropriate combination of TADF emitters.

The donor position critically influences the photophysical properties of pyrimidine emitters. Thus, Nakao et al.[74] systematically investigated a series of pyrimidine derivatives as TADF emitters, and those emitters are called Ac-26DPPM, Ac-46DPPM, and CzAc-26DPPM. Among these emitters, a small structural difference of nitrogen positions significantly influences the photophysical events and OLED performances. The emission peaks of Ac-26DPPM, Ac-46DPPM, and CzAc-26DPPM doped DPEPO films are located at 468, 491, and 488 nm, respectively, and Ac-46DPPM and CzAc-26DPPM based films showed the same PLQE values of 81%, whereas an Ac-26DPPM based film showed a lower PLQE value of 61%. Interestingly, there is a large difference in the τ_d values between Ac-26DPPM and Ac-46DPPM. Ac-46DPPM ($\tau_d = 178\ \mu s$) had a τ_d value almost double that of the Ac-26DPPM ($\tau_d = 87\ \mu s$). Ac-46DPPM showed an EQE of 15.5% with a CIE of (0.16, 0.21), and sky-blue emitters, Ac-26DPPM and CzAc-26DPPM, showed EQE values of 19.3% and 23.7%, respectively.

Later, a collaboration group of Ganesan et al.[75] developed a series of blue emitters composed of acridine and pyrimidine named T1 to T4. T1 and T2 had the same chemical structures with Ac-46DPPM and Ac-26DPPM developed by Nakao et al.,[74] respectively. In addition, T3 and T4 had reduced π-conjugation than that of T1 and T2, which have an orthomethyl substituent on the triphenylpyrimidine unit. These emitters showed interesting mechanochromism phenomena in the solid state. These OLEDs exhibited TADF behaviors, and the T2-based device showed the highest EQE of 14.2% with a sky-blue emission at CIE of (0.20, 0.39).

Park et al.[76] developed a new family of pyrimidine-based blue emitters using spiroacridine as a donor unit. 2,4,6-Triphenyl pyrimidine and 2-phenyl pyrimidine are used for the acceptor units, and the emission peaks of MFAc-PPM, MXAc-PPM, MFAc-PM, MXAc-PM, and Ac-PM doped PPF films are located at the range of 457 to 466 nm. All the films showed high PLQE up to 91%. In particular, the Ac-PM based device showed deep-blue emission with a CIE of (0.15, 0.15) and an EQE of 11%, whereas the MFAc-PPM based device showed a high EQE of 20% and pure blue emission with a CIE of (0.16, 0.23).

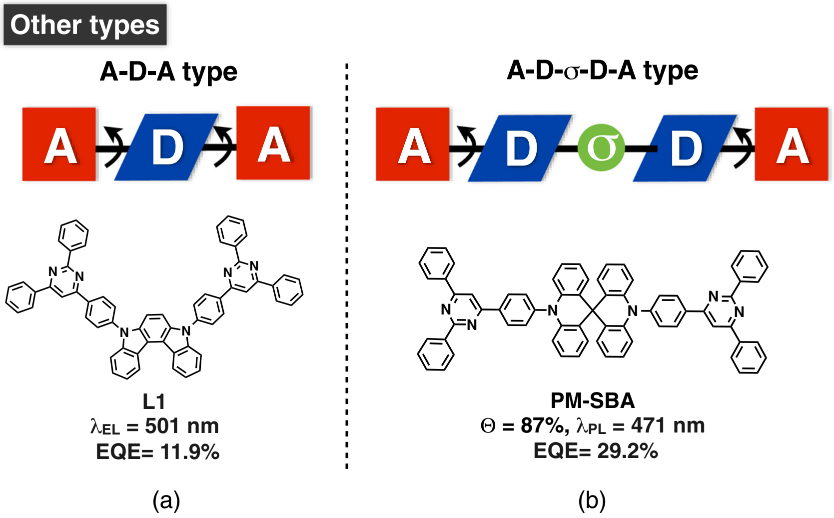


Fig. 9 Chemical structures of other types of pyrimidine derivatives as TADF emitters. (a) A-D-A type and (b) A-D-σ-D-A type.

Pan et al.[29] group developed TADF emitters with CN-substituted pyrimidines called Pm2 and Pm5. Due to the stronger acceptor character induced by the CN group, the enhanced CT emission showed very large PLQE values up to 100%. The emission peaks of Pm2 and Pm5 doped 9-(3-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole-3-carbonitrile (mCPCN) films are located at 526 and 541 nm, and these greenish-yellow OLEDs exhibited an impressively high EQE of 31%.

4.4 *Other Type Emitters*

As described previously, the strength of CT character and TADF behavior of pyrimidine emitters can be easily tuned by the donor position and functionalization of the pyrimidine ring. Compared with the D-A-D and D-A types discussed, few A-D-A and acceptor-donor-sp^3-carbon (σ-bond)-donor-acceptor (A-D-σ-D-A) type emitters have been reported (Fig. 9).[30,73]

Gomez-Bombarelli et al.[73] developed an A-D-A type emitter based on indolocarbazole skeleton, and the device showed sky-blue emission with an EQE of 12%. Recently, a collaboration team of Liu et al.[30] developed spirobiacridine-based sticklike TADF emitters called PM-SBA with the structure of A-D-σ-D-A. In addition, the emission peak of PM-SBA doped DPEPO film is located at 471 nm. The film showed a high PLQE of 73%, ΔE_{ST} of 0.07 eV, and τ_{d} of 23 μs. Moreover, due to the sticklike structure, this emitter exhibited very high horizontal transition dipole ratio (Θ) of 87%. This Θ value is one of the highest among ever reported phosphorescent and TADF emitters. The sky-blue device based on PM-SBA realized a very high EQE of 29% with a CIE of (0.17, 0.28). As described, A-D-A and A-D-σ-D-A type TADF emitters can become one of the promising alternate structures to conventional D-A-D and D-A types TADF emitters; however, there are only a few examples reported in the scientific literature so far.

5 Conclusion and Outlook

In this review, we have demonstrated the recent progress of pyrimidine-based OLED materials and have also demonstrated how pyrimidine-based materials can play a more important and unique role in OLEDs in comparison with other building blocks, such as triazine and pyridine. So far, pyrimidine-containing phosphorescent emitters, conventional fluorescent emitters, bipolar host materials, and ETMs have been developed, and high-performance OLEDs have been realized. Different from the other building blocks, even though several pyrimidine-based OLED materials, such as phosphorescent emitters, have generated high-performance OLEDs with long-term stability, pyrimidine-based materials are relatively unexplored, especially for blue emitters, including conventional fluorescent, phosphorescent, and TADF systems. Among three types of emitters, researchers have recently focused on the TADF system, and several pyrimidine-based blue TADF emitters have been developed in the past several years. Almost all the pyrimidine derivatives as TADF emitters are categorized into D-A-D and D-A type molecules. Fortunately, these TADF emitters have outperformed conventional fluorescent emitter systems. As the representative examples of blue emitters, a D-A-D type emitter, Ac-3MHPM, exhibited EQE of 18.0% at CIE of (0.16, 0.15), and a D-A type emitter, MFAc-PM, realized EQE of 17.1% at CIE of (0.16, 0.21). Additionally, a sticklike emitter, PM-SBA, achieved very high EQE of 29.2% at CIE of CIE (0.17, 0.28). This EQE is comparable to the state-of-the-art phosphorescent counterparts (Fig. 10).[30,72,76] However, there are several big challenges that remain with

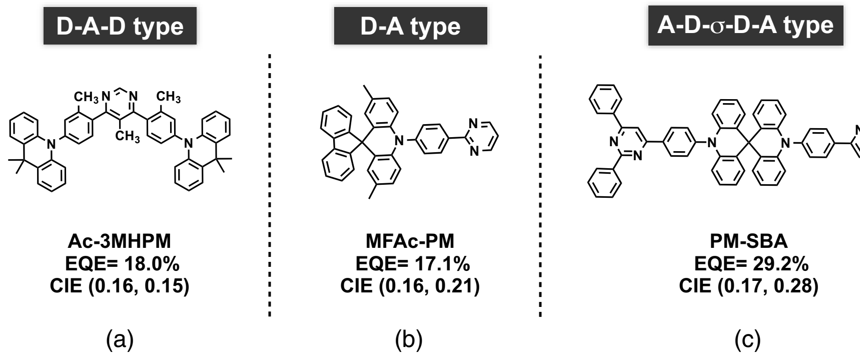


Fig. 10 Representative examples of pyrimidine derivatives as TADF emitters and OLED performances: (a) D-A-D type, (b) D-A type, and (c) A-D-σ-D-A type.

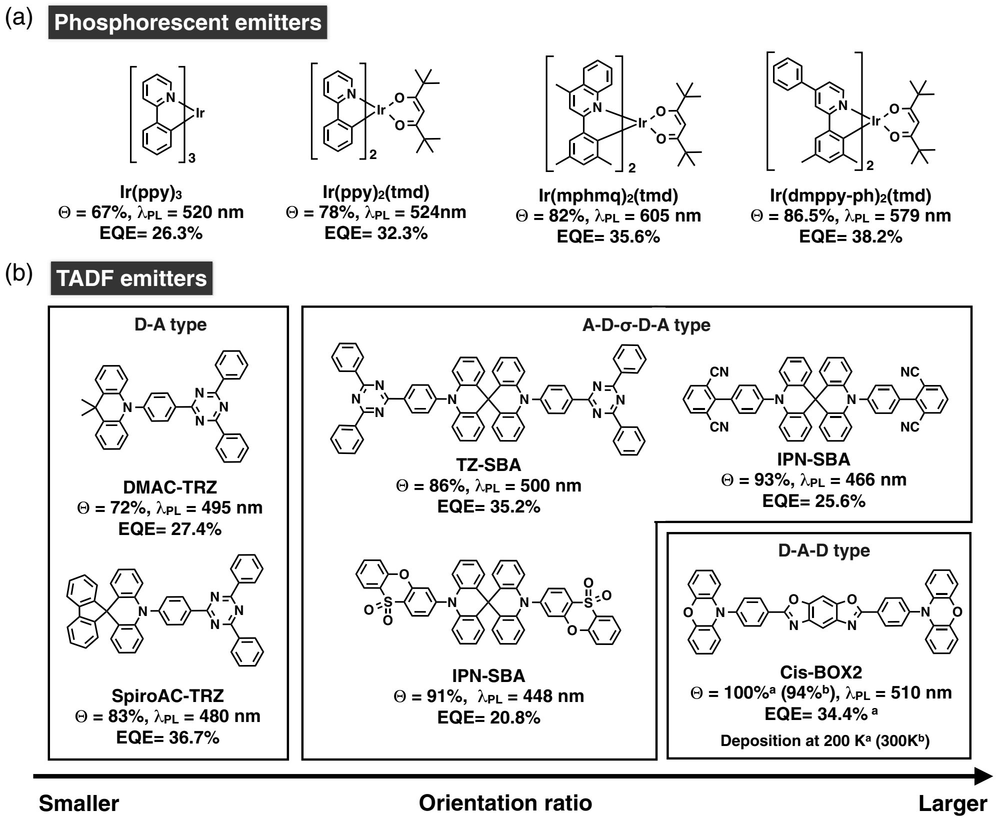


Fig. 11 Summary of oriented emitters in vacuum-deposited film: (a) phosphorescent emitters and (b) TADF emitters.

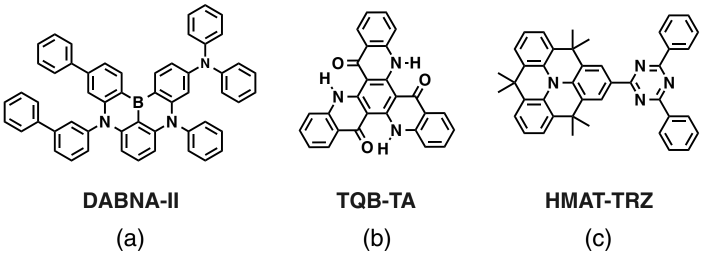


Fig. 12 Chemical structures of planer type TADF emitters: (a) DABNA-II, (b) TQB-TA, and (c) HMAT-TRZ.

pyrimidine-based blue TADF OLEDs at this stage: (i) long-term stability at practical luminance, (ii) efficiency roll-off at high brightness, and (iii) low-driving voltage.

For the next generation of pyrimidine derivatives as TADF emitters, further improvements of efficiency should be required. To obtain more light from the plane substrate, horizontal orientation of the emitter must be necessary because perfect horizontal orientation can boost EQE up to 45%, which is 1.5 times greater than that for the random orientation.[79,80] In this context, TADF emitters have a significant advantage compared with phosphorescent emitters based on iridium because sticklike chemical structure, which is beneficial to realizing horizontal orientation, is easily obtainable from TADF molecule (Fig. 11).[11,12,27,28,30,81] Actually, a high Θ of up to 100% have been reported using sticklike TADF molecules, such as *Cis*-BOX2 ($\Theta = 100\%$ at substrate temperature $= 200$ K) and IPN-SBA ($\Theta = 93\%$).[28,30] These values are much higher than the reported Θ of iridium complex with a sphere-like structure. Moreover, the planer structure TADF molecule is very attractive and should be investigated for pyrimidine-based emitters from the perspective of long-term stability and small structural relaxation energy, which can realize narrow emission band and shorter τ_d (Fig. 12).[82–84] A representative example of 9-([1,1′-biphenyl]-3-yl)-*N*,*N*,5,11-tetraphenyl-5,9-dihydro-5,9-diaza-13b-boranaphtho[3,2,1-*de*]anthracen-3-amine (DABNA-2) developed by Hatakeyama et al.[82] realized a high EQE of 20% and a very narrow full-width at half-maximum of 28 nm. Furthermore, Mamada et al.[83] presented a whole new type of planar TADF emitter based on the use of excited-state intramolecular proton transfer without conventional D-A structures.

Consequently, the unlimited molecular design of pyrimidine derivatives as TADF emitters can open a new way for the next generation of high-performance OLEDs as well as a whole new category for material science for the sustainable future.

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