# New Conjugated Triazine Based Molecular Materials for Application in Optoelectronic Devices: Design, Synthesis, and Properties

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ABSTRACT: Two novel triazine-based compounds with efficient hole-blocking ability were designed and synthesized, which promoted the performance of electroluminescent devices, especially for PLED even when Al was applied as the cathode. The results indicated that introducing electron-donating groups and extending π-conjugated were facile methodologies to improve the optoelectronic properties of the triazine derivatives.
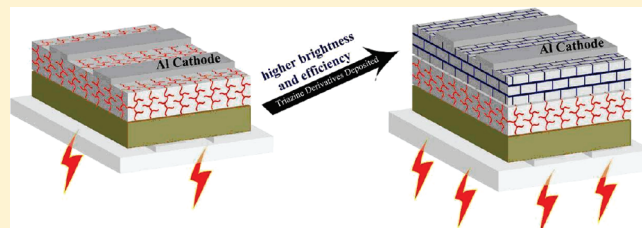
INTRODUCTION

Organic conjugated molecular materials have received great attention in recent decades in optoelectronic applications such as organic (or polymeric) light-emitting diodes (OLED and PLED),[1,2] thin film transistors (TFT),[3] organic photovoltaic cells (OPV),[4] and chemical/biological sensors,[5] because they are low cost and can easily be fabricated to obtain the devices. Within the whole catalogue of the materials, 1,3,5-triazine derivatives have become a focus due to their exceptional properties derived from the unique structure of the 1,3,5-triazine units that show strong electron-accepting ability and high symmetry.[6] Consequently, introducing a 1,3,5-triazine unit into the backbone of the conjugated molecules can not only improve the abilities of electron-injection and electron-transportation of the molecules,[7] but also increase the heat resistance of the molecules.[8] Undoubtedly, from the point of view of the applications of the optoelectronic materials, the organic molecules having both good electron-injection/or transportation ability and high stability are desirable. Thus, in recent years, there has been an increasing interest in the synthesis and investigation of the chemical properties of π-conjugated triazine based small molecules and polymers.[9]

Of the triazine based molecular materials used in OLED, 2,4,6-triphenyl-1,3,5-triazine (TRZ) is popular and its application in OLED as a hole-blocking material can trace back to the last century.[6a] However, its use is limited because it shows poor performance in devices.[10] Much effort has been exerted to improve the properties of the triazine-based materials, mainly concerning introducing different substituents into a triazine ring. Examples of the substituents include naphthalene,[11] phenylnaphthalene,[12] carbazole[13] and pyridine groups.[14] Recently, there are also reports regarding the conjugated polymers containing triazine ring,[15] which were expected to enhance the performance of devices. Nevertheless, satisfactory triazine-based materials are very rare.

A recent work in our group revealed that the fluorene substituted triazine (FTRZ, Scheme 1) showed good properties and could be used as a hole-blocking material in OLED.[9d]

Interestingly, the hole-confinement ability of FTRZ seems to be weaker than that of TRZ because it shows the HOMO levels in an order of FTRZ (-6.25 eV) > TRZ (-6.51 eV), whereas the performance of devices based on them is in a contrary order. Such paradoxical results are probably attributed to the difference of LUMO levels and band gaps between the two compounds. The higher LUMO level of TRZ (-2.70 eV) brings about a large barrier to the electrons, moving from cathode to emitting layer, meanwhile a large band gap of TRZ (3.71 eV) fetters the electron jump or transporting, resulting in very low electron mobility. Therefore, TAZ endows the devices with poor performance, whereas FTRZ has a LUMO level of -2.95 eV and a band gap of 3.30 eV, which are suitable for blocking holes and transporting electrons. Such facts imply that appropriate LUMO levels and band gaps are benefit of 1,3,5-triazine derivatives on the premise of keeping their HOMO levels sufficiently low.

Structurally, FTRZ possesses an extensive π-conjugated system and electron-donating groups compared with TRZ, which may be the source of the superior performance of FTRZ, implying that introducing electron-donating groups to a triazine ring and extending the π-conjugation of the triazine derivative are facile ways to improve the performance of the triazine-based optoelectronic materials. Such an assumption motivated us to design and synthesize two triazine conjugated molecules, **M1** and **M2**, whose structures are shown in Scheme 2. The results showed that **M1** and **M2** can greatly increase the performance both of OLED and PLED. We report the details in this work.
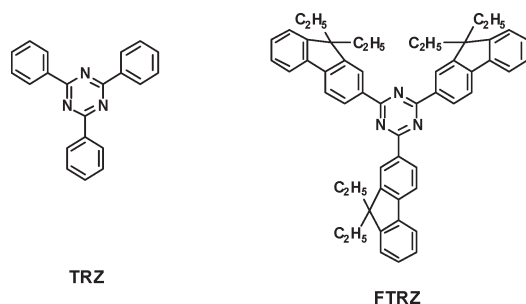
EXPERIMENTAL SECTION

Reagents and Instruments. Commercially available reagents were purchased and used without further purification. All solvents

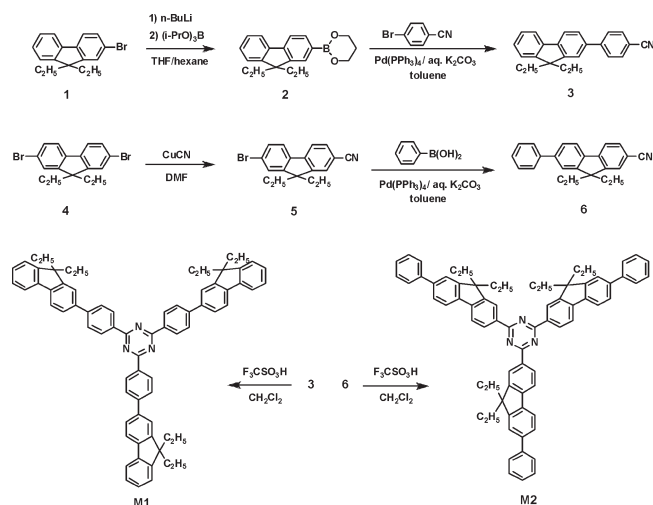**Scheme 1. Chemical Structure of TRZ and FTRZ**

Scheme 2. Procedure for the Preparation of M1 and M2

were dehydrated and distilled under an inert atmosphere before use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX 400 or Varian Mercury 300 spectrometer using CDCl$_3$ as solvent and TMS as internal standard. Mass spectra were taken with an HP 5989A or Finnigan 4021. High resolution mass spectra (HRMS) were obtained by MALDI/DHB. Elemental analysis was performed with a Carlo Erba 1106 elemental analyzer. UV–vis and PL spectra were obtained with a Hitachi UV-2810 and a Hitachi F-4500 spectrophotometer, respectively. Cyclic voltammetry was performed in an acetonitrile solution containing [n-Bu$_4$N]ClO$_4$ (0.10 M) with ferrocene as standard using (0.10 M AgNO$_3$)/Ag and platinum disk electrode as reference and counter electrodes, respectively. A CHI 600B analyzer was used for the cyclic voltammetry. Electroluminescent Properties were recorded on a photometer PR 705 at room temperature in air.

Synthesis. As can be seen from Scheme 1, intermediates 1, 2, 4, and 5 were synthesized following previously reported procedures.[16] The precursors, 3 and 6, were prepared by the standard Suzuki coupling reaction, and then cyclization of the two precursors gave M1 and M2 in a high yield.

4-(9,9-Diethyl-9H-fluoren-2-yl)benzonitrile (3). An aqueous Na$_2$CO$_3$ (2 mL, 2M) solution containing toluene (5 mL) was added to a mixture of 2-(9,9-diethyl-9H-fluoren-2-yl)-1,3,2-dioxaborinane (0.31 g, 1.0 mmol), 4-bromobenzonitrile (0.18 g, 1.0 mmol) and Pd(PPh$_3$)$_4$ (0.058 g, 0.05 mmol) under argon. The resulting solution was kept at reflux for 48 h, and then cooled to room temperature. To the reaction system was added CHCl$_3$

(20 mL), and the organic layer was separated, washed twice with water, dried over anhydrous Na$_2$SO$_4$, and concentrated. The residue was purified by flash chromatography on silica gel (hexane/ethyl acetate 15:1), giving 3 (0.31 g, 0.96 mmol, 96% yield) as a white solid. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.81–7.74 (m, 6H), 7.57 (t, J = 7.2 Hz, 2H), 7.36 (br, 3H), 2.11–2.04 (m, 4H), 0.34 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, CDCl3, δ): 151.0, 150.3, 146.2, 142.3, 140.7, 137.9, 132.6, 127.7, 127.6, 127.1, 126.3, 123.0, 121.6, 120.2, 120.0, 119.1, 110.6, 56.3, 32.8, 8.6. EI-MS (m/z): M$^+$ 323. Calcd for C$_{24}$H$_{21}$N: C 89.12; H 6.54; N 4.33; found: C 89.02, H 6.52, N 4.21.

9,9-Diethyl-7-phenyl-9H-fluorene-2-carbonitrile (6). A similar procedure for preparation of 3 was employed. The pure product was obtained as a white powder (0.25 g, 0.77 mmol, 96% yield) after flash chromatography on silica gel (hexane/ethyl acetate 15:1). ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.81 (t, J = 7.1 Hz, 2H), 7.69–7.58 (m, 6H), 7.49 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.1 Hz, 1H), 2.13–2.06 (t, 4H), 0.34 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, CDCl3, δ): 151.3, 150.9, 145.8, 142.2, 141.1, 138.8, 131.5, 128.9, 127.6, 127.3, 126.6, 126.5, 121.8, 121.1, 120.2, 119.9, 109.9, 55.7, 32.6, 8.5. MALDI-MS (m/z): M$^+$ 323.2. Calcd for C$_{24}$H$_{21}$N: C 89.12; H 6.54; N 4.33; found: C 88.61, H 6.52, N 4.18.

2,4,6-Tris(4-(9,9-diethyl-9H-fluoren-2-yl)phenyl)-1,3,5-triazine (M1). A solution of 3 (0.29 g, 0.9 mmol) in anhydrous CH$_2$Cl$_2$ (10 mL) was added to a solution of trifluoromethanesulfonic acid (1.5 g, 10 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL). After being stirred for 10 h at room temperature, an aqueous NaHSO$_3$ solution was added dropwise until the appearance of the solution is colorless. The mixture was extracted with CHCl$_3$ (30 mL) and the organic phase was separated, washed twice with water, dried over anhydrous Na$_2$SO$_4$, and concentrated. The residue was purified by flash chromatography on silica gel (hexane/ethyl acetate 20:1) to afford to a white solid (0.27 g, 0.28 mmol, 93% yield). ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.92 (d, J = 8.1 Hz, 6H), 7.94–7.70 (m, 18H), 7.35 (br, 9H), 2.14–2.10 (t, 12H), 0.41 (t, J = 7.2 Hz, 18H) ^{13}C NMR (100 MHz, CDCl$_3$, δ): 171.3, 150.7, 150.2, 145.6, 141.6, 141.0, 139.2, 135.0, 129.5, 127.3, 126.9, 126.2, 122.9, 121.6, 120.0, 119.8. FT-IR (KBr, cm^{-1}): ν = 3067, 2962, 1606, 1568, 1512, 1371, 814. HRMS (MALDI, m/z): [M + H]$^+$ calcd for C$_{72}$H$_{64}$N$_3$, 970.5095; found, 970.5070.

2,4,6-Tris(9,9-diethyl-7-phenyl-9H-fluoren-2-yl)-1,3,5-triazine (M2). M2 was prepared by using the analogous procedure for preparation of M1. The crude product was purified by flash chromatography on silica gel (hexane/ethyl acetate 20:1), giving M2 (0.29 g, 0.30 mmol, 90% yield) as a white powder. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.91 (d, J = 7.8 Hz, 3H), 8.80 (s, 3H), 7.98 (d, J = 7.8 Hz, 3H), 7.92 (d, J = 7.5 Hz, 3H), 7.73 (d, J = 7.5 Hz, 6H), 7.67 (m, 6H), 7.51 (t, J = 7.4 Hz, 6H), 7.40 (t, J = 7.1 Hz, 3H), 2.27 (q, 12H), 0.48 (t, J = 7.1 Hz, 18H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 171.7, 151.8, 150.6, 145.6, 141.4, 141.1, 140.0, 135.2, 128.8, 127.3, 127.2, 126.2, 123.2, 121.8, 120.8, 119.8, 56.4, 32.8, 8.7. FT-IR (KBr, cm^{-1}): ν = 3064, 3026, 2963, 1608, 1577, 1516, 1372, 817. HRMS (MALDI, m/z): [M + H]$^+$ calcd for C$_{72}$H$_{64}$N$_3$, 970.5095; found, 970.5083.

Device Fabrication. Indium tin oxide (ITO) with a sheet resistance of about 15 ohm/square was cleaned with isopropyl alcohol, acetone and deionized water then treated with UV/ozone. Then, 20 nm NPB (N,N'-bis(naphthalen-1-yl)-N,N'-bis-(phenyl)benzidine) and 40 nm Alq were thermal evaporated sequentially on ITO for OLED. For PLED, a layer of PEDOT: PSS (Baytron AI 4083, Bayer) film with thickness of 50 nm was
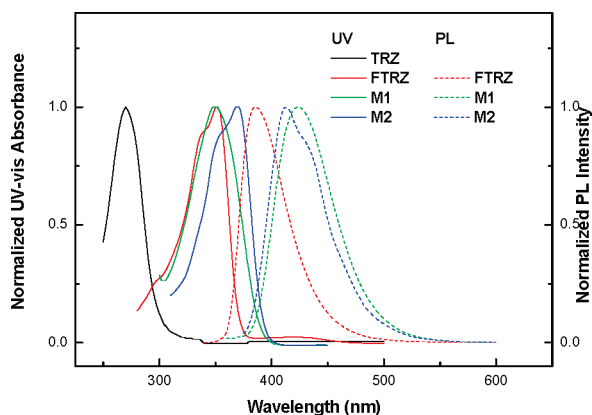
Figure 1. UV−vis and PL spectra of TRZ, FTRZ, **M1**, and **M2**.

Table 1. Optical and Electrochemical Properties of TRZ, FTRZ, M1, and M2

compounds	$\lambda_{\max \text{ abs}}$(nm)[a] solution film	$\lambda_{\max \text{ em}}$(nm)[b] solution film	LUMO (eV)[c]	HOMO (eV)[d]	E_g^{opt} (eV)[e]
TRZ	270, 279	−, −	−2.80	−6.51	3.71
FTRZ	352, 358	385, 417	−2.95	−6.25	3.30
M1	350, 349	424, 436	−2.96	−6.10	3.14
M2	370, 372	412, 424	−2.94	−6.07	3.13

[a] Maximum UV−vis absorption peaks. [b] Maximum PL emission peaks. [c] Evaluated from their reduction onset potentials versus ferrocene (Fc) as the internal standard. [d] HOMO = LUMO − E_g^{opt}. [e] Optical band gap, estimated from the onset wavelength of the absorption spectra in the solid film.

spin-coated from its aqueous dispersion and dried at 180 °C for 10 min. MEH-PPV (M_n 150,000−250,000, Aldrich) layer was formed by spin-coating at 3000 rpm from its solution in cyclohexanone (10 mg/mL), and then by heating at 60 °C for 2 h in a glovebox. Finally, triazine compounds (20 nm), LiF (2 nm) and Al (100 nm) were deposited sequentially by thermal evaporation at a pressure below 10^{-4} Pa for both OLED and PLED. The control devices without triazine compounds were also fabricated using an aforementioned analogous procedure.

■ RESULTS AND DISCUSSION

The basic photophysical characteristics of **M1** and **M2** were investigated by UV−vis and photoluminescent (PL) spectra, and the data are shown in Figure 1 and Table 1. For comparison, the optical data of TRZ and FTRZ are also listed. Because fluorene is an electron-donating group and shows an expansion of the π-conjugation system, compared with phenyl group, FTRZ shows a UV−vis peak red-shifted by about 80 nm from 270 nm of TRZ. Analogously, **M1** and **M2** also show the red shift compared with TRZ. Interestingly, the UV−vis peak of **M2** red-shifts about 20 nm, compared with 350 nm of **M1**. Such a result may be attributed to the presence of a charge-transferred (CT) electronic state in **M2**, caused by the action between electron-donating fluorene group and electron-accepting triazine group.[17] In contrast to **M2**, the presence of a phenyl space between fluorene group and triazine ring in the molecule may weaken the CT action and results in the UV−vis peak of **M1** is located at lower wavelength.
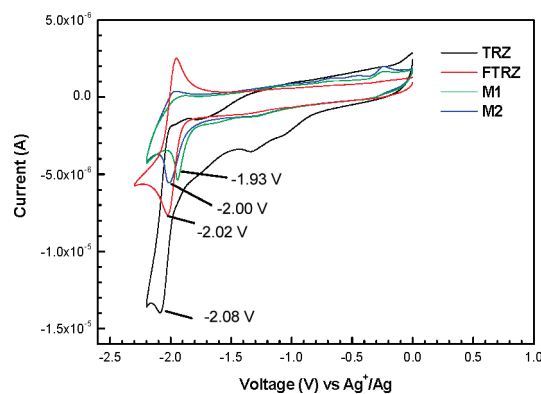

Figure 2. CV curves of TRZ, FTRZ, **M1**, and **M2**.

The CT action is also observed in the PL spectra of the triazine molecules. For example, TRZ without a donor−acceptor structure is not photoluminescent, whereas its analogues, FTRZ, **M1**, and **M2**, show photoluminescence. As seen from Figure 1 and Table 1, the maximum emission peaks are in an order of FTRZ (385 nm) < **M2** (412 nm) < **M1** (424 nm) in solution. In the solid state, their emission maxima show a slight red shift, and the values of red-shifting maintain an order of FTRZ > **M1** = **M2**, indicating the existence of partial π-staking structure in the three compounds. However, the degree of π-staking in **M1** and **M2** is lower than that in FTRZ, suggesting the attachment of more groups with large steric-hindrance can suppress the molecular aggregation. It is noted that **M1** shows a Stokes shift of 74 nm, relative to 33 nm for FTRZ and 42 nm for **M2**. This result indicates that the Donator−space−Acceptor molecular structure of **M1** produces greater conformational relaxation and more conformational disorder in the excited state.[18]

The redox behavior of TRZ, FTRZ, **M1**, and **M2** was characterized by cyclic voltammetry (CV) at a platinum disk electrode versus a (0.1 M AgNO$_3$)/Ag reference electrode in 0.1 M (n-Bu$_4$N)ClO$_4$/acetonitrile and the results are described in Figure 2. From their reduction onset potentials, the LUMO levels of **M1**, **M2**, FTRZ, and TRZ are estimated as −2.96, −2.94, −2.95, and −2.80 eV, respectively. On the basis of the LUMO levels and the optical band gap, HOMO levels of **M1**, **M2**, FTRZ, and TRZ are evaluated with the value of −6.10, −6.07, −6.25, and −6.51 eV, respectively. In comparison with TRZ and FTRZ, **M1**, and **M2** achieved the appropriate band gaps and adequately low HOMO energy levels, meeting the requirement of the original molecular design.

To confirm the above-mentioned assumption regarding the relationship between the molecular structure and the properties, five electroluminescent devices were designed and fabricated with the following configuration: ITO/NPB/Alq/compounds containing triazine units/LiF/Al, where a 40 nm thickness of Alq was used as the emitting layer and TRZ, FTRZ, **M1**, and **M2** were used as the electron-transporting/hole-blocking materials with a thickness of 20 nm. Considering that Alq is also an effective electron-transporting material,[1a] a comparative device was fabricated with a configuration of ITO/NPB/Alq/Alq/LiF/Al, and the thickness of the Alq used as electron-transporting layer was the same as that of the triazine compounds, e.g., 20 nm.

Due to the dual functions of Alq, the maximum luminance of the control device Alq/Alq is more than 19 000 cd m^{-2}, meanwhile device Alq/FTRZ (16000 cd m^{-2}), device Alq/**M1** (13 000 cd m^{-2}) and device Alq/M2 (18 000 cd m^{-2}) also keep
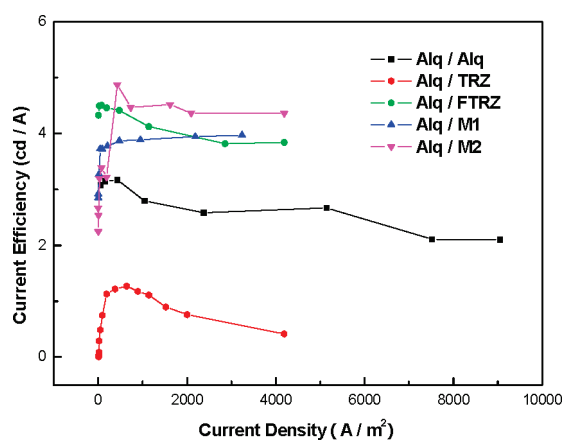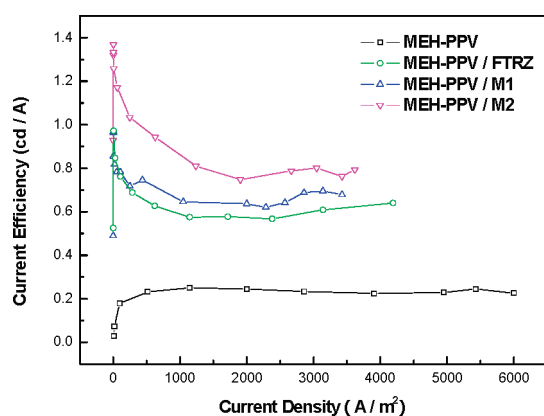
Figure 3. Efficiency curves of OLEDs.

Figure 4. Efficiency curves of PLEDs.

high luminance. But the maximum luminance of the device Alq/TRZ is only 1700 cd m^{-2}.

Alternatively, as shown in Figure 3, the maximum current efficiencies of the devices containing FTRZ or **M1** or **M2** are remarkably improved from 3.1 cd A^{-1} of the comparative device to 4.5, 4.0, and 4.9 cd A^{-1}, respectively. However, device TRZ shows poor performance with a maximum current efficiency of 1.2 cd A^{-1}. These results indicate that the application of FTRZ, **M1**, and **M2** enables the devices to improve the balance between hole and electron transporting. In particular, the promotion is superior to the utilization of Alq, which has been proven to be an available electron transporting material.

The excellent performance of **M1** and **M2** in OLED inspires us to investigate the probability of application of the compounds in PLED. Recently, although there are many reports about introducing small molecules to PLED for improvement of the performance, the results basically are not satisfactory.[19] The main reason is as follows: (1) doping small molecules to PLED usually brings about phase separation and unfavorable interfacial effect that may decline the performance of devices;[20] (2) although depositing small molecules on the surface of PLED is a good way, the choice of the small molecular materials is limited. On the basis of the aforementioned situation, we chose the depositing way to study the behavior of the triazine molecules in PLED. Because MEH-PPV is a famous PLED material, and its performance should be improved, thus, it was used as a light emitting layer in our case. The devices were fabricated with the configurations

Table 2. Electroluminescent Properties of the Devices

devices	η_{max} (cd A^{-1}) [a]	V_{max} (V) [b]	B_{max} (cd m^{-2}) [c]	η_{Bmax} (cd A^{-1}) [d]
Alq/Alq	3.1	13	19 040	2.1
Alq/TRZ	1.3	21	1740	0.4
Alq/RTRZ	4.5	13	16 100	3.8
Alq/**M1**	4.0	15	12 860	4.0
Alq/**M2**	4.9	16	18 290	4.4
MEH-PPV	0.25	10	1358	0.23
MEH-PPV/FTRZ	0.97	12	2683	0.64
MEH-PPV/**M1**	0.97	12.5	2327	0.68
MEH-PPV/**M2**	1.37	10.5	2871	0.79

[a] Maximum current efficiency. [b] Breakdown voltage. [c] Maximum luminance. [d] Current efficiency at maximum luminance.

of ITO/PEDOT:PSS/MEH-PPV/hole-blocking layer/LiF/Al. Here, triazine molecules were applied as hole-blocking materials and a stable and low-cost cathode Al was employed as cathodes. Meanwhile, a device without a hole-blocking layer was also fabricated for comparison. The utilization of Al is based on the following facts: the common cathode in PLED is Ca or Ba, which can usually improve the performance of PLED, however, their utilization brings out the complication of the encapsulation procedure and raises the cost due to their air-sensitivity.

As shown in Figure 4 and Table 2, the maximum luminance of device FTRZ, **M1** and **M2** are promoted from 1358 cd m^{-2} (comparative device MEH-PPV) to 2683, 2327, and 2871 cd m^{-2}, respectively. Furthermore, Devices FTRZ, **M1**, and **M2** show maximum current efficiencies of 0.97, 0.97, and 1.37 cd A^{-1}, respectively, which are more than four times higher than 0.25 cd A^{-1} of device MEH-PPV. These results suggest that these triazine derivatives possess excellent hole-blocking capacity. Compared with device FTRZ, devices **M1** and **M2** exhibit good performance, conforming that the new triazine molecular materials can also improve the performance of PLED.

■ CONCLUSIONS

In summary, two new conjugated triazine-containing molecular materials, **M1** and **M2**, were synthesized and used to improve the performance of OLED and PLED. The results showed that **M1** and **M2** can greatly increase the performance both of OLED and PLED, which supports a concept for molecular design that introducing more electron-donating groups and extended π-conjugation into a triazine ring can turn the optimal energy levels and band gaps of the molecules, resulting in the improvement of the optoelectronic properties of the molecules. Such a concept for molecular design may useful for developing and exploring new 1,3,5-triazine derivatives with excellent optoelectronic properties.

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