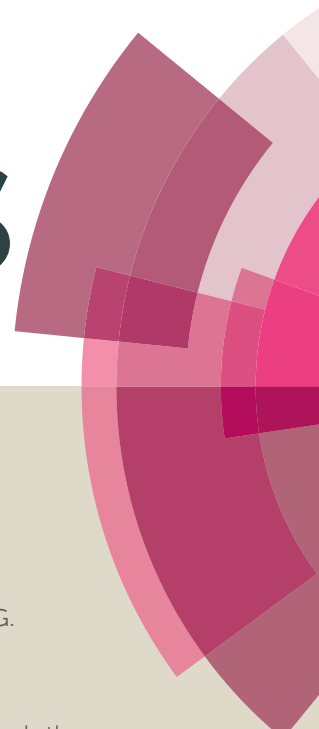


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Synthesis, structure, physical properties and OLED application of pyrazine–triphenylamine fused conjugated compounds

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In this paper, several donor–acceptor compounds using pyrazine and triphenylamine as building units have been synthesized and fully characterized. The physical properties and theoretical calculations were also investigated. In addition, the OLED devices using these compounds as active elements have been fabricated and all devices display very good performance. Specifically, the maximum EQE for **2** is 7.37 %, which is higher than the theoretical limit for fluorescent emitters (5 %), indicating that the mechanism for compound **2** is different from traditional fluorescent dyes. Our results suggest that D–A molecules could be a good approach to improve the performance of OLED devices.

1 Introduction

Organic light emitting diodes (OLEDs) have potential applications in the field of flat-panel display due to their low weight, low power consumption, self-emitting property, high luminous efficiency, wide viewing angle and high contrast.¹ OLEDs normally have three layers including hole–transporting layer, light–emitting layer and electron–transporting layer, which are sandwiched together between two electrodes. The ideal compounds to approach better performance of OLEDs are dipolar D–A molecules, which incorporate both hole–transport units and electron–transport segments. There are two reasons for such design: (1) the hole mobility in the D–A molecules is slightly lower than that in a single hole–transporting layer, thus facilitating the exciton formation inside the layer; and (2) the low-lying LUMO of D–A molecules is helpful to the capture of electrons released from the cathode, which would improve the performance.² In fact, many emissive compounds incorporating anthracene,³ pyrene,⁴ fluorine⁵ and triphenylamine⁶ segments have been synthesized and all compounds displays good performance in OLEDs. It is worthy to note that molecular geometry has two-faced effects on the electroluminescent (EL) efficiency: on one hand, planar geometry is very important to help the delocalization of π –electrons and improve the EL efficiency; on the other hand, non–planar geometry can provide steric hindrance that reduces the molecular aggregation in the solid state, thus increasing the EL efficiency.⁷

As a strong electron donor, triphenylamine has a unique propeller–like structure, and its distorted geometry diminishes the intermolecular interactions and favors efficient fluorescence.⁸ Thus, triphenylamine has been considered as an excellent hole

transport material in OLED devices and memory devices.⁶ On the other hand, pyrazine units have been widely demonstrated as the electron acceptor to construct several electron-deficient structures.⁹ Moreover, pyrazine units can be easy to be functionalized by donor units, acceptor substituents, extended π –conjugation species, or bulky groups to form new conjugated materials.¹⁰ In this work, we are more interested in preparing a series of pyrazine–triphenylamine fused conjugated compounds for applications in OLEDs because (1) the LUMO and bandgap of these D–A molecules could be tuned through choosing the different electron–withdrawing abilities of the acceptor groups; (2) the fluorescence efficiency could also be modified by optimizing the intramolecular charge–transfer (ICT) strength; (3) the introduction of fused aromatic rings into the push–pull system could also lead to an enhanced carrier mobility and a lower band gap.¹¹ Here, we want to investigate how different groups such as strong electron–acceptor cyano groups, moderate electron–acceptor pyridine groups and bulky 9, 9-bis(2-ethylhexyl) fluorine to affect the structures (molecular stacking), physical properties and their performance in OLEDs.

2 Experimental Section

2.1 Materials

Most reagents were purchased from Alfa Aesar or Aldrich and used as received unless otherwise noted. All the solvents used in photophysical measurements and electrochemical measurements were of HPLC grade quality. All other solvents were obtained commercially and purified using standard procedures.

2.2 Characterization

Using CDCl_3 as a solvent and tetramethylsilane (TMS) as the

internal standard, ^1H NMR and ^{13}C NMR spectra were measured on a Bruker Advance 300 MHz NMR spectrometer at ambient temperature. UV/Vis absorption spectra were carried out at room temperature with a Shimadzu UV-3600 spectrophotometer. High resolution mass spectra (HRMS) were recorded on a Waters Q-Tof premierTM mass spectrometer. Cyclic voltammetry measurements were carried out on a CHI660 electrochemical analyzer. Glassy carbon (diameter: 1.6 mm; area 0.02 cm²) was used as a working electrode, platinum wires were used as counter electrode and reference electrode, respectively. Fc^+/Fc was used as an internal standard. Potentials were recorded versus Fc^+/Fc in a solution of anhydrous dichloromethane (DCM) with 0.1M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte at a scan rate of 100 mV s⁻¹.

2.3 Fabrication of the OLED devices

The device structure is ITO/MoO₃(2 nm)/NPB(50 nm)/CBP: X wt.% Dye (20 nm)/Bphen (50 nm)/LiF (1 nm)/ Al (150 nm), where ITO is anode, MoO₃ is hole injection layer, NPB is hole transporting layer, CBP: X wt.% Dye is the emission layer, Bphen is the electron transporting layer, LiF is the electron injection layer and Al is the cathode.¹² The doping concentrations of dye in CBP are 100% (neat dye layer), 50 %, 10 % and 3 %, respectively.

2.4 Synthesis

As shown in scheme 1, the starting material 4, 4'-bis (N, N-diphenylamino) benzil was prepared from TPA and oxalyl chloride through Friedel-Crafts acylation.¹³ And compounds **1-3** are synthesized by condensing 4, 4'-bis (N, N-diphenylamino) benzil and different kinds of diamines and tetraamines including diaminomaleonitrile, 2,3-diaminopyridine and 2,3,6,7-tetraamino-9,9-bis(2-ethylhexyl) fluorene in acetic acid with a catalytic amount of IBX.¹⁴ Note that the 2,3,6,7-tetraamino-9,9-bis(2-ethylhexyl) fluorene cannot react with two equivalents of 4,4'-bis(N,N-diphenylamino)benzil to form two pyrazine units due to the steric hindrance. In fact, it only reacts with one equivalent of 4,4'-bis(N,N-diphenylamino)benzil and one equivalent of acetic acid (solvent) to form compound **3** containing a pyrazine unit and oxazole segment.¹⁵

Synthesis of compound **1**: 4,4'-bis(N,N-diphenylamino)benzil (540 mg, 1.0 mmol) and diaminomaleonitrile (108 mg, 1.0 mmol) were dissolved in anhydrous acetic acid (50 mL) with catalytic amount of 2-iodoxybenzoic acid (IBX). The solution was refluxed for 24 hours under Argon atmosphere. After that the crude product was concentrated in vacuo and purified by column chromatography (CH₂Cl₂/petroleum ether=1/2), affording compounds **1** (542 mg, yield 88%).

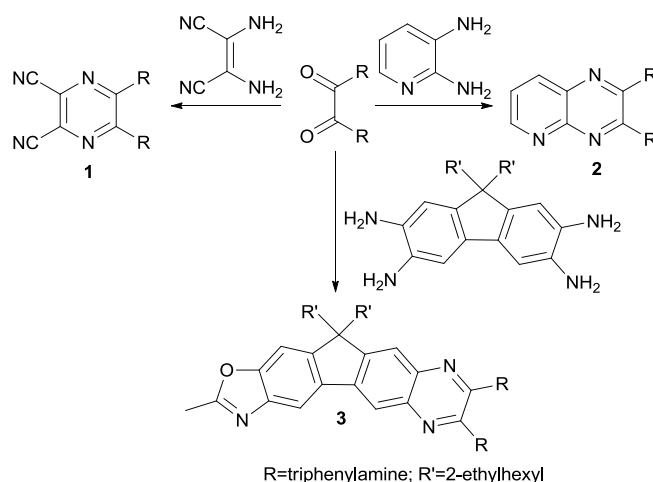
^1H NMR (300 MHz, CDCl₃) δ 7.50 (d, 4 H), 7.34 - 7.29 (m, 8 H), 7.16 - 7.12 (m, 12 H), 6.96 - 6.93 (d, 4 H). ^{13}C NMR (75 MHz, CDCl₃) δ 154.09, 150.78, 146.55, 130.87, 129.76, 128.33, 127.54, 126.09, 124.80, 120.32, 113.77. HRMS (M+1) = 617.2440 (calc. 617.2454).

Synthesis of compound **2**: The procedure was the same with above except that diaminomaleonitrile was replaced by 2,3-diaminopyridine (109 mg, 1.0 mmol). This reaction gave compounds **2** (549 mg, yield 89%).

^1H NMR (300 MHz, CDCl₃) δ 9.10 - 9.09 (m, 1 H), 8.47 - 8.44 (m, 1 H), 7.67 - 7.64 (m, 1 H), 7.59 (d, 2 H), 7.49 (d, 2 H), 7.31 - 7.27 (m, 7 H), 7.15-7.13 (m, 8 H), 7.10-7.08 (m, 3 H), 7.07-7.06 (m, 2 H), 7.04-7.00 (m, 3 H). ^{13}C NMR (75 MHz, CDCl₃) δ 156.15, 154.56, 153.25, 149.73, 149.39, 149.18, 147.27, 147.24, 138.16, 136.00, 131.85, 131.45, 131.24, 130.86, 129.56, 125.45, 125.32, 124.76, 123.91, 123.85, 121.99, 121.41. HRMS (M+1) = 618.2673 (calc. 618.2658).

Synthesis of compound **3**: The procedure was the same with above except that 2,3-diaminopyridine was replaced by 2,3,6,7-tetraamino-9,9-bis(2-ethylhexyl) fluorene (596 mg, 1.0 mmol). This reaction gave compounds **3** (787 mg, yield 80%).

^1H NMR (300 MHz, CDCl₃) δ 8.45 (s, 1 H), 8.13 (s, 1 H), 8.09 (s, 1 H), 7.72-7.69 (m, 1 H), 7.54-7.52 (m, 1 H), 7.51-7.44 (m, 5 H), 7.29 (d, 6 H), 7.14 (d, 8 H), 7.09-7.04 (m, 8 H). ^{13}C NMR (75 MHz, CDCl₃) δ 167.90, 164.67, 152.15, 149.17, 148.58, 147.46, 143.96, 141.77, 136.57, 132.62, 131.02, 129.50, 128.95, 125.11, 123.59, 122.32, 117.76, 111.66, 106.33, 68.31, 54.93, 46.33, 38.89, 34.92, 34.87, 33.66, 33.32, 32.07, 30.52, 29.84, 29.59, 29.51, 29.40, 29.24, 29.08, 28.05, 26.95, 26.67, 26.62, 24.90, 23.91, 23.13, 22.84, 22.77, 14.87, 14.26, 14.19, 13.98, 13.95, 11.11, 10.26. HRMS (M+1) = 984.5613 (calc. 984.5508).



80 Scheme 1 Synthesis route for compounds **1-3**. Conditions: anhydrous acetic acid, Ar₂, 2-iodoxybenzoic acid, 120°C, 24 h.

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3 Results and discussion

3.1 Crystal structures

The structures and molecular packing of compounds **1-3** are shown in Figure 1 (CCDC number for compounds **1-3** are 1401901, 1401902, and 1401903, respectively). For compound **1**, the length of C–N bond in cyano group is 1.13–1.14 Å, which is a typical C–N triple bond. The length of C–C bond connecting cyano group to pyrazine ring (1.45 Å) is between the average bond length of C–C single bond (1.54 Å) and aromatic C–C bond (double bond 1.33 Å and aromatic 1.40 Å). For compounds **2** and **3**, the length of C–C bond connecting pyrazine ring to triphenylamine (1.48 Å) are also between the average bond length of C–C single bond and aromatic C–C bond while the length of C–N bond in triphenylamine unit (1.41–1.43 Å) is close to the average aromatic C–N bond length (C–N single bond 1.47 Å; double bond 1.34 Å; aromatic 1.43 Å). These phenomena indicate that strong donor-acceptor interactions exist in these molecules. The lengths of C–N bond of pentagon in compound **3** are 1.281 and 1.400 Å, separately. Note that compound **2** forms dimer via intermolecular N–H hydrogen bond. The adjacent molecules in compound **1** adopt head-to-tail arrangement to reduce the electron coupling effect due to the large molecule dipole moment.

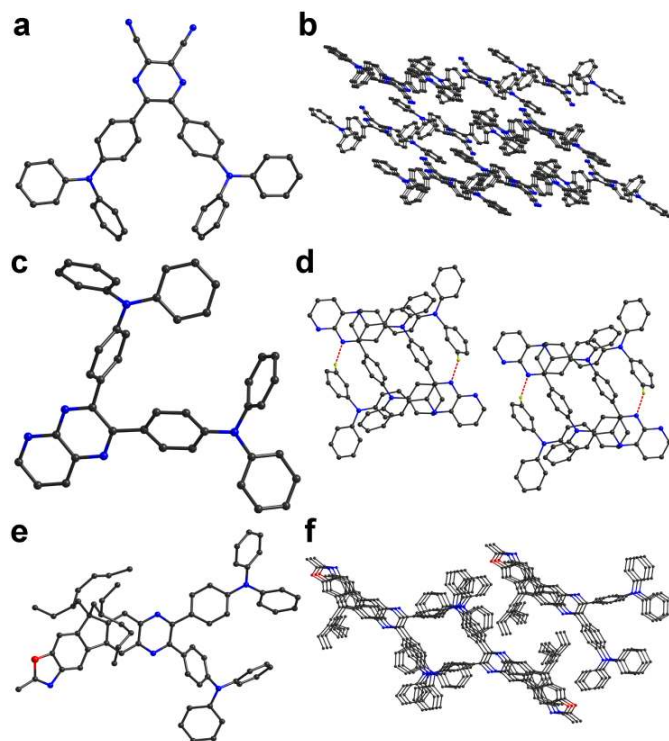


Figure 1 The crystal structures of compounds **1-3** (a, c, e) and the crystal packing diagrams of compounds **1-3** (b, d, f).

3.2 Optical and electrochemical properties

The maximum absorption wavelengths of compounds **1-3** show a trend of **3**<**2**<**1**, reflecting the substituent nature. Fluorene is a weak electron donor, while pyridine is a moderate electron acceptor and cyano group is a strong electron acceptor. With the enhancement of the role of the electron acceptor, the efficiency of intramolecular charge-transfer (ICT) is improved, resulting a bathochromic absorption shift. This trend is also manifested in the emission characteristics. The emission intensity decreases significantly with a concomitant red shift in the emission wavelength from compound **3** to **1**, which suggests that dipolar interactions have a great contribution to the non-radiative decay in these compounds.¹⁶ The lifetime of films of **1**, **2** and **3** are measured by a streak camera system (Table S2). The experimental details are described in reference¹⁷. We can see that the PL decay rate increases from **1**, **2** to **3**, and the lifetime (the time at which the initial PL intensity (I_0) decreases to the (I_0/e)) are extracted to be 4.25, 3.27 and 2.12 ns for **1**, **2** and **3**, respectively.

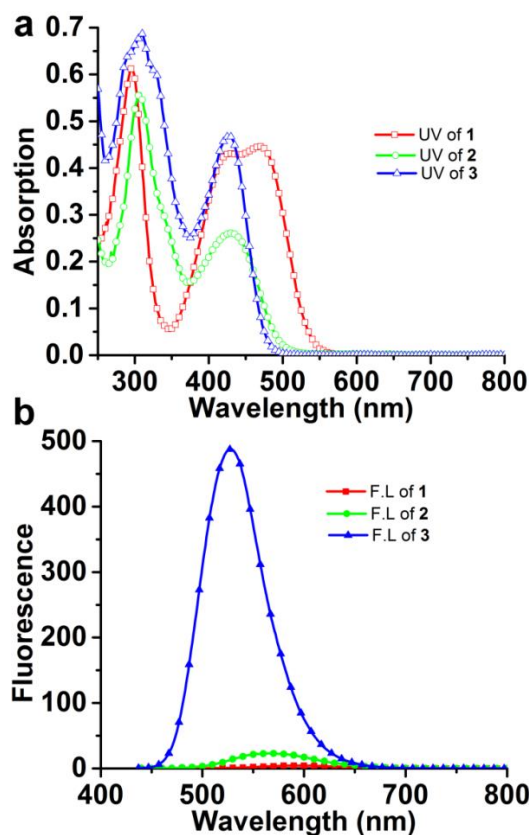


Figure 2 The UV-Vis (a) and fluorescence (b) spectra of compounds **1-3**. They are measured in dichloromethane with the concentration of 10^{-5} M and 10^{-6} M, respectively.

Table 1. The UV-Vis and fluorescence data of compounds 1-3

| | Abs λ_{\max} (nm) | ϵ (M ⁻¹ ·cm ⁻¹) | Fluor λ_{\max} (nm) | Φ_{fl} |
|---|---------------------------|---|-----------------------------|-------------|
| 1 | 468 | 39540 | 593 | 0.02 |
| 2 | 430 | 23540 | 568 | 0.09 |
| 3 | 428 | 46900 | 528 | 0.99 |

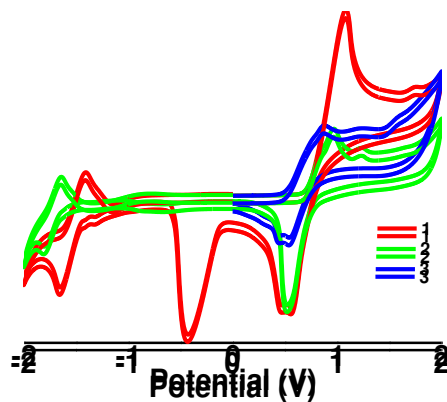


Figure 3 The CV spectra of compounds 1-3.

- As shown in Figure 3, for compound **1**, one reversible reduction wave and one irreversible reduction wave were investigated, while for compound **2**, only one reversible reduction wave was found. Because the electron affiliation of cyano group is stronger than that of pyridine, the reduction potentials of compounds **1** are higher than that of compound **2**.

Table 2. The CV data of compounds 1-3

| | E_{ox}^1/V | E_{ox}^2/V | E_{red}^1/V | E_{red}^2/V | HOMO | LUMO | E_g (eV) |
|---|--------------|--------------|---------------|---------------|-------|-------|------------|
| 1 | 0.52 | 1.50 | -0.29 | -1.62 | -5.32 | -2.17 | 3.15 |
| 2 | 0.53 | 1.01 | -1.74 | - | -5.33 | -1.92 | 3.41 |
| 3 | 0.35 | 0.89 | - | - | -5.15 | -1.85 | 3.30 |

3.3 Theoretical calculation

The optimization for geometric structures of compounds **1-3** is carried out by Gaussian 09 program at the B3LYP/6-31G* level. The electronic distributions in the HOMO and LUMO for these compounds are shown in Figure 4. The HOMOs of compounds **1** and **2** are delocalized over the whole molecule but the HOMO of compound **3** are delocalized over the triphenylamine groups. The LUMOs are delocalized on the cyano group, pyridine or quinoxaline. With the acceptor strength increasing in the order from compound **3** to compound **1**, the donor-acceptor interactions are enhanced gradually, which induce a higher dipole moment and stabilize the HOMO and LUMO energy level. Since the LUMO is more sensitive than the HOMO in our case, the band gap becomes narrower.

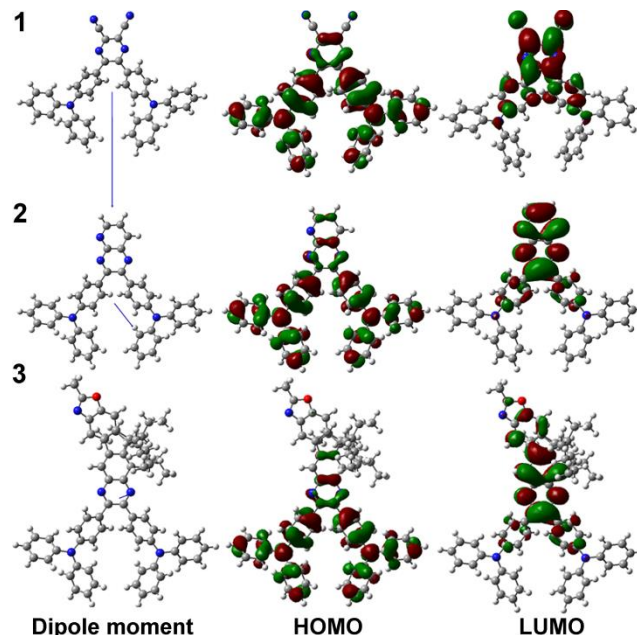


Figure 4 The dipole moment and molecular orbitals of compounds 1-3.

Table 3. The calculated data of compounds 1-3

| | HOMO (eV) | LUMO (eV) | Gap (eV) | Dipole moment (D) |
|---|-----------|-----------|----------|-------------------|
| 1 | -5.25 | -2.49 | 2.76 | 11.92 |
| 2 | -4.95 | -2.04 | 2.91 | 1.0259 |
| 3 | -4.85 | -1.86 | 2.99 | 0.9586 |

3.4 OLED performance

As shown in Figure 5, the turn-on voltages for the devices range from 2.9 V to 3.6 V, which are within the normal range for OLEDs. For doped emission layers, maximum brightness levels around or higher than 10,000 cd/m² were achieved. All the dyes show good efficiencies (with EQE above 2 %). Among them, compounds **1** and **2** show better performance. The maximum EQE for compounds **1** and **2** are 4.01 % and 7.37 %, respectively, both achieved at low doping concentration (less than 10 wt.%). Especially for compound **2**, the EQE is higher than the theoretical limit for fluorescent emitters (5 %),¹⁸ indicating that the mechanism for compound **2** is different from traditional fluorescent dyes. The mechanism is still under investigation. The concentration dependence of device EQE for the dyes also shows some difference. For compounds **1** and **2**, the concentration quenching effect is much stronger than compound **3**. This can also be inferred from the concentration dependent electroluminescence (EL) spectrum. (Figure S3-2) For compounds **1** and **2**, their EL spectra shows larger redshift compared with that of compound **3**. These results indicate that the introduction of bulk substituted groups can reduce the aggregation caused quenching (ACQ) effect by sacrificing the efficiency or raising the turn-on-voltage.¹⁹

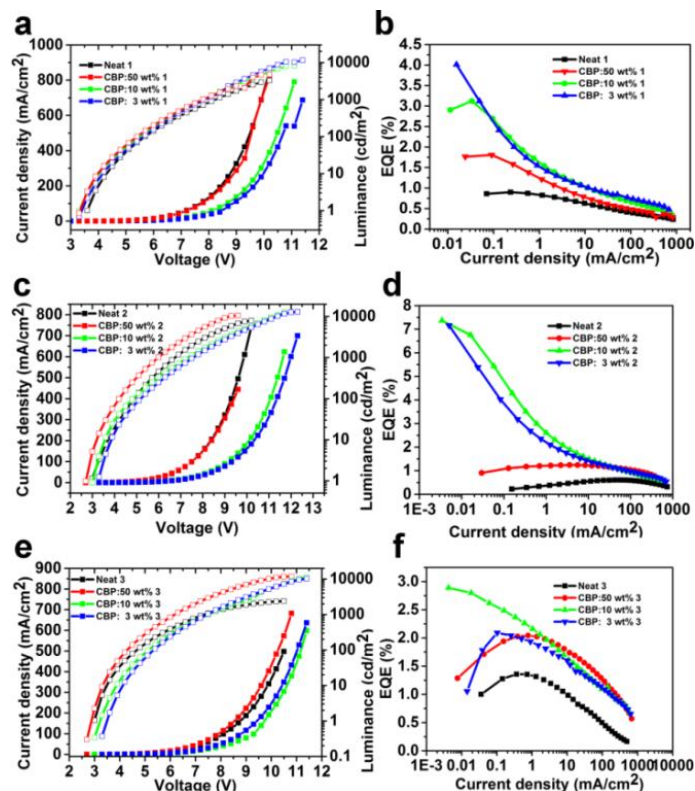


Figure 5 The current density-voltage-luminance curves (a, c, e) and external quantum efficiency curves (b, d, f) of compounds 1-3

Table 4 OLED device characteristics of compounds 1-3

| X (wt. %) | V_{on} (V) | L_{max} (cd/m^2) | Max efficiency | | | Efficiency @ 100 cd/m^2 | | | Efficiency @ 1000 cd/m^2 | | | CIE (x, y) | |
|--------------|-----------------|---------------------------|----------------|-----------|-----------|---------------------------|-----------|-----------|----------------------------|-----------|-----------|------------|-------------|
| | | | EQE (%) | CE (cd/A) | PE (lm/W) | EQE (%) | CE (cd/A) | PE (lm/W) | EQE (%) | CE (cd/A) | PE (lm/W) | | |
| 1 | 100 | 3.6 | 3270 | 0.89 | 1.48 | 1.23 | 0.57 | 1.03 | 0.63 | 0.22 | 0.60 | 0.36 | (0.59,0.40) |
| | 50 | 3.4 | 4775 | 1.81 | 3.64 | 3.39 | 0.87 | 1.75 | 1.02 | 0.48 | 0.97 | 0.40 | (0.56,0.43) |
| | 10 | 3.3 | 8202 | 3.12 | 9.23 | 8.05 | 1.31 | 2.20 | 3.93 | 0.78 | 2.31 | 0.93 | (0.49,0.50) |
| | 3 | 3.3 | 11550 | 4.01 | 16.12 | 15.35 | 1.30 | 4.57 | 2.51 | 0.84 | 2.95 | 1.14 | (0.40,0.57) |
| 2 | 100 | 3.0 | 7916 | 0.60 | 2.04 | 1.10 | 0.50 | 1.69 | 1.09 | 0.60 | 2.03 | 0.96 | (0.41,0.56) |
| | 50 | 2.7 | 10520 | 1.24 | 4.43 | 4.13 | 1.23 | 4.41 | 3.30 | 1.18 | 4.23 | 2.21 | (0.39,0.58) |
| | 10 | 3.0 | 12650 | 7.37 | 26.65 | 27.90 | 2.60 | 9.41 | 6.16 | 1.24 | 4.50 | 1.90 | (0.33,0.61) |
| | 3 | 3.3 | 12860 | 7.16 | 24.66 | 23.47 | 2.10 | 7.20 | 4.01 | 1.22 | 4.15 | 1.70 | (0.29,0.61) |
| 3 | 100 | 3.0 | 2378 | 1.36 | 3.93 | 3.51 | 1.22 | 3.51 | 2.40 | 0.61 | 1.78 | 0.75 | (0.24,0.55) |
| | 50 | 2.9 | 11860 | 2.04 | 6.24 | 5.64 | 2.02 | 6.18 | 4.60 | 1.64 | 5.02 | 2.51 | (0.22,0.58) |
| | 10 | 3.3 | 11120 | 2.89 | 7.98 | 8.35 | 2.05 | 5.68 | 3.50 | 1.42 | 3.93 | 1.64 | (0.19,0.51) |
| | 3 | 3.6 | 10200 | 2.09 | 5.13 | 4.13 | 1.81 | 4.45 | 2.63 | 1.33 | 3.27 | 1.37 | (0.17,0.44) |

⁵ V_{on} is turn-on voltage (the voltage when luminance reaches 1 cd/m^2); L_{max} is maximum luminance; EQE is external quantum efficiency; CE is current efficiency; PE is power efficiency.

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4 Conclusion

In summary, using one-step reaction between 1, 2-diamine and 1, 2-diketones, a series of D–A molecules containing triphenylamine segment and pyrazine unit have been synthesized and fully characterized. The modification of the pyrazine unit with different substituted groups such as strong electron-acceptor cyano groups, moderate electron-acceptor pyridine groups and large steric functional group 9,9-bis(2-ethylhexyl) fluorine gave different patterns of D–A compounds with different photoelectric properties. The OLED devices based on these compounds exhibit good efficiencies. In particular, CBP-doped devices using compounds **1** and **2** as active layers show maximum external quantum efficiency of 4.01 % and 7.37 %, respectively. These results indicate that these compounds have good applications in OLED devices.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: [details of experimental section]. See DOI: 10.1039/b000000x/
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