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Purely Organic and Saturated Red Emitter for Non-doped Electroluminescent Device with An EQE of 6.3% and Low Efficiency Roll-off

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Red organic light emitting diodes (OLEDs) based on purely organic emitters with high efficiency, good colour chromaticity coordinates and low efficiency roll-off features are in high demand for display and lighting applications. Additionally, to simplify the device fabrication processes, it is desirable to develop OLEDs with non-doped emission layers. In this work, three 2,1,3-naphthodiazole-based red emissive model compounds (RMCs) with tailored electron-donating structures were synthesized. In comparison with the orange emissive RMC1 and the near infrared emissive RMC3, RMC2 with moderate electron donating ability demonstrates a pure red peak emission at 625 nm. Moreover, RMC2 shows high fluorescent quantum efficiency (Φf) in both diluted solution (0.76) and neat film (0.41). Non-doped saturated red OLEDs based on RMC2 with a maximum luminous efficiency of 5.3 cd A⁻¹, a maximum external quantum efficiency (EQE) of 6.3% and good CIE coordinates of (0.64, 0.35) is demonstrated. In addition, the device shows a slight efficiency roll-off feature, displaying an EQE of 5.1% at a brightness of 1000 cd m⁻².

Introduction

Organic light-emitting diodes (OLEDs) have quickly spread into our daily lives as a new generation display and lighting technology. Purely organic emitters (POEs) with internal quantum efficiency (IQE) close to 100% have attracted significant attention to substitute the high-cost, noble-metal based phosphorescent emitters. Blue [1-4] and green [5,6] OLEDs employing thermally activated delayed fluorescence (TADF) POEs have been reported with external quantum efficiency (EQE) values around 30%. Many red OLEDs using TADF [7-38] or radicals-based [39] POEs have also been obtained with EQE values beyond 10%. Part of reported red POEs show emission peaks beyond 630 nm [15-39] which is required to realize good colour chromaticity coordinates (CIE: x ≥ 0.62, y ≤ 0.37) for display applications. Among them, most devices show significant efficiency roll-off at high current densities, only a few literatures report EQE values over 5% at a brightness of 1000 cd m⁻² [22,23,30,34,37]. Besides the popular TADF-based POEs, “hot exciton”-based POEs [40] which can convert triplet excitons into singlet excitons from the high-lying excited state (T₂), have been reported with a maximum EQE of 10.5%, 20.2% and 6.8% for blue [41,42], green [43] and red [44] OLEDs respectively.

A dopant-host system is usually adopted to realize efficient electroluminescence (EL) and improved device lifetime. [45] Precise control of the doping concentration is required to suppress serious efficiency roll-off caused by exciton annihilation at high doping concentrations and high current densities. In order to simplify the device structures and fabrication processes, it is desirable to construct highly efficient red OLEDs with non-doped emission layers (EML). [18] TADF-based non-doped red OLEDs with EQE values around 10% have been reported, [25,34] however, they suffer from either poor red colour saturation or significant efficiency roll-off [25], or high turn on voltage [14] issue. And for “hot exciton” based non-doped red OLEDs there is still much room to improve their EQE above the 5% criteria [27,46].

In this work, through tuning the electron-donating ability of previously reported 2,1,3-naphthodiazole (NT) derivatives with “hot exciton” feature in EL process, [47-50] three red emitters (RMC1, RMC2, RMC3) were synthesized as shown in Figure 1. Among them, RMC2 with moderate electron donating ability owns high fluorescent quantum efficiency (Φf) in both diluted solution and solid film. Its neat film exhibits a pure red emission peak at around 625 nm. It realized a trade-off between Φf and colour purity as well as a trade-off between carrier injection and recombination. As a result, non-doped red OLEDs based on RMC2 with a device configuration of ITO/MoO₃/TCTA/EML/TPBI/LiF/Al realized a luminous efficiency (LE) of 3.6 cd A⁻¹, an EQE value of 3.8% and CIE...
coordinates of (0.63, 0.36). Moreover, by introduction of a super thin TPBI layer (1 nm) between hole transporting layer (HTL) and EML to further balance the hole/electron current and confine the carrier recombination zone completely in EML, an optimized device achieved a maximum LE of 5.3 cd A\(^{-1}\), an EQE of 6.3% and CIE coordinates of (0.64, 0.35). In addition, the device demonstrates small efficiency roll-off feature, with an EQE value of 6.3% and 5.1% respectively at the brightness of 100 cd m\(^{-2}\) and 1000 cd m\(^{-2}\).

Results and discussion

Figure 1. Molecular structures of RMC 1-3 (Left); their photographs in 10\(^{-4}\) M toluene solution and in powder under room light and 365-nm UV light irradiation (Right).

According to our previous works,\(^{[51,52]}\) we selected NT units as electron acceptor because it possesses stronger electron withdrawing ability due to one more benzene ring fused in its molecular structure compared to benzothiadiazole (BT) unit. The emission wavelength of its derivatives can be effectively red-shifted.\(^{[53-55]}\) More importantly, the fused ring structure leads to enhanced molecular rigidity, which is beneficial for achieving high \(\Phi_F\) in solution state. Benzene, 3,6-di-tert-butyl-9H-carbazolobenzene (t-BuCzB) and N,N-di-(4-methylphenyl)aminobenzene (DMPAB) were chosen as the donor units with sequentially increased electron-donating ability. Benzene is a weak donor. DMPAB is a strong donor due to the lone pair electrons of nitrogen atom. In comparison with DMPAB, t-BuCzB unit is a moderate electron donor because the dihedral angle between the carbazole moiety and phenyl bridge is relatively larger than that of diphenylamine and phenyl bridge. Part of the charge of the nitrogen lone pair will be delocalized in carbazole moiety, so its electron donating strength is less than triphenylamine derivatives.\(^{[56]}\) Bulky tert-butyl groups were introduced to the C-3 and C-6 position of carbazole to further suppress the aggregation in solid state. The detailed synthetic routes and characterization data of the three RMCs are described in Supporting Information (SI).

The photophysical, electrochemical, and thermal properties of the RMCs are shown in Figure 2 and the corresponding data are listed in Table 1. In diluted toluene solution, the absorption/emission peaks of RMC1, RMC2 and RMC3 are 476/553 nm, 493/593 nm and 537/649 nm, respectively. Their absorption, emissive peaks and Stokes shifts are gradually increased. These are consistent with their intramolecular charge transfer ability. In neat film state, their absorption/emission peaks are bathochromic shifted to 487/569 nm, 503/622 nm and 561/691 nm. The redshift should be due to the aggregation effect of the compounds. Interestingly, RMCI also display another strong absorption peaks at 515 nm. The first peak at 487 nm can be ascribed to the absorption of RMC1 monomer. The later at 515 nm should be the absorption of RMC1 J-dimer, due to its good molecular planarity. To verify the speculation, we acquired the absorbance of RMC1 in doped polystyrene (PS) film (10 wt%) as shown Figure S1a. There is only one absorption peak around 466 nm. No other longer wavelength absorption was detected. Compared with doped films, the neat films of three RMCs show bathochromic shifted absorption. Among them, the absorption of RMC2 only red-shifts about 11 nm, which is much smaller than that of RMC1 (21/47 nm) and RMC3 (23 nm), implying the aggregation effect of RMC2 is effectively suppressed. As a result, the \(\Phi_F\) of the RMC2 in neat film remains as high as 41%, while, the \(\Phi_F\) of RMC1 and RMC3 neat film is decreased to 15% and 9%, respectively.

Cyclic voltammetry (CV) measurements were conducted to investigate the electrochemical properties of the RMCs (Figure 1c). Their onset oxidation voltages and onset reduction voltages as well as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels are listed in Table 1. These RMCs possess almost the same LUMOs of around -3.40 eV because they have the same electron withdrawing unit. While, due to the improved electron donating ability of RMC1, RMC2 and RMC3, their HOMO energy levels gradually increase from -5.82 eV to -5.58 eV and -5.21 eV. The results agree with their photophysical properties very well.

The thermal properties of the RMCs were acquired by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). It can be seen in Figure 2d that RMC1 has a sharp and intense crystalline transition at around 275 °C without glass transition. RMC3 exists a glass transition at around 155 °C as well as a cold crystallization process and a crystalline transition at around 167 °C and 308 °C, respectively. RMC2 has no cold crystallization process and crystalline transition during the measurement temperature range, indicating it is under amorphous state. The DSC results are consistent with solid state appearance of the RMCs, which is needle-like red crystal for RMC1, fluffy orange-red solid for RMC2 and semi-crystalline purple solid for RMC3. This phenomenon confirms restricted self-aggregation of RMC2 in solid state. It can be ascribed to the more twisted molecular conformation and existence of bulky tert-butyl groups. The high thermal decomposition temperature (394 °C, Figure S2) of RMC2 further guarantee its thermal stability in EL devices. All these indicate RMC2 is a good candidate for non-doped red electroluminescence. RMC1 and RMC3 are not suitable for non-doped red device due to their orange-red or near-infrared emissive color and low PL efficiency in neat film.
Figure 2. The absorption and PL spectra in toluene solution (a) and film state (b) as well as CV (c) and DSC (d) curves of the RMCs.

Table 1. The photophysical, electrochemical and thermal properties of the RMCs.

|       | λ_{abs} | λ_{emi} | Φ_{f} | E_{onset red} [V] | E_{LUMO} [eV] | E_{onset oxd} [V] | E_{HOMO} [eV] | E_{g} [eV] | T_{g} [°C] | T_{m} [°C] | T_{d} [°C] |
|-------|---------|---------|-------|-------------------|--------------|-------------------|--------------|-----------|-----------|-----------|-----------|
| RMC1  | 476/487 | 553/569 | 91/15 | -1.01             | -3.39        | 1.42              | -5.82        | 2.43      | n.a.      | 275       | 447       |
| RMC2  | 493/503 | 593/622 | 76/41 | -0.99             | -3.41        | 1.18              | -5.58        | 2.17      | n.a.      | n.a.      | 394       |
| RMC3  | 537/561 | 649/691 | 35/9  | -1.03             | -3.37        | 0.81              | -5.21        | 1.84      | 155       | 308       | 242       |

[a] Measured in around 10⁻⁶ M toluene solution and neat film respectively. [b] Tested in using 0.1 mol L⁻¹ (n-C₄H₉)₄NClO₄ CH₂Cl₂ solution. [c] Extracted from the second heating curves. [d] Temperature at 5% weight loss.

In order to investigate the EL properties of RMC2, we first fabricated type A device with a simple structure of ITO/RMC2/TPBI/LiF(1nm)/Al(100 nm). Here, TPBI stands for 1,3,5-tris(N-phenylbenzimiazole-2-yl)benzene, which is employed as electron transporting layer (ETL) and hole blocking layer (HBL). The energy level alignments of the device are illuminated in Figure 3. The thickness of the non-doped EML and TPBI layer is optimized to be 40 nm and 20 nm, respectively. The current density-LE, current density-EQE curves and EL spectra of the device are shown in Figure 4. The device performance is listed in Table 2. It realized a maximum LE of 1.5 cd A⁻¹, a power efficiency (PE) of 1.6 lm W⁻¹ and an EQE of 2.6% with an emission peak at 654 nm and CIE coordinates of (0.67, 0.33).

Since the HOMO energy level of RMC2 is about -5.6 eV, which is much lower than the work function of UV-Ozone treated ITO (-5.0 eV), the hole injection of the device should be inefficient due to the large energy barrier. MoO₃ buffer layer and Tris[4-carbazoyl-9-ylphenyl]amine (TCTA) HTL were introduced to fabricate type B device with improved hole-injection efficiency. MoO₃ is an efficient hole injection layer for optoelectronic devices. Although with a wide band-gap of about 3.1 eV, mid-gap states in MoO₃ film can be formed by partial filling of unoccupied 4d orbitals of molybdenum atoms due to the existence of oxygen vacancies in thermal evaporated MoO₃ thin film. The gap states align well with the HOMO level of organic HTL layer and thus lower the hole injection barrier at the HTL/MoO₃ interface. TCTA exhibits almost the same HOMO level (-5.7 eV) as that of RMC2, the hole-injection energy barrier at the HTL/EML interface is negligible. As a result, the maximum brightness was greatly improved from 2512 cd m⁻² of device A to 10270 cd m⁻² of
device B with a configuration of ITO/MoO$_3$(10 nm)/TCTA(40 nm)/RMC(20 nm)/TPBI(40 nm)/LiF(1 nm)/Al(100 nm). The optimized device achieved a maximum LE of 3.6 cd A$^{-1}$, a PE of 3.1 lm W$^{-1}$ and an EQE of 3.8% with an emission peak at 646 nm and CIE coordinates of (0.63, 0.36).

The good device performance could be attributed not only to the fine-tuned photophysical properties of RMC2 in PL process but also the good charge recombination efficiency in EL process. Non-doped red OLEDs based on aryl amine derivatives usually show predominantly hole-carrier transporting feature,$^{[59,60]}$ leading to unbalanced hole-and electron carrier flow and unwanted exciton recombination zone located at the EML/ETL interface. Replacing aryl amine by carbazole may lead to more balanced hole and electron charger carrier. We fabricated single-carrier device based on RMC2 and RMC3 to verify the speculation. The hole-only device structure is ITO/MoO$_3$(5 nm)/TCTA(20 nm)/EML(70 nm)/TCTA(20 nm)/MoO$_3$(5 nm)/Al. The electron-only device structure is ITO/TPBI(20 nm)/EML(70 nm)/TPBI(20 nm)/LiF(1 nm)/Al. Their current density-voltage curves are shown in Figure 4d, insert figure is the calculated ratio of hole/electron carrier. It can be seen that RMC3 with triphenyl amine donor group show much larger hole/electron current ratio than that of RMC2 with carbazole donor unit. This demonstrates the hole/electron current indeed becomes more balanced in RMC2 based device. On the view of material design, although both the hole and electron current of RMC2 is inferior to that of RMC3, while the more balanced hole-electron carrier may lead to higher recombination efficiency, achieving better trade-off between charge injection and recombination efficiency in EL process.

Figure 3. The device configurations and energy level alignments of device A, B and C as well as the chemical structure of TPBI and TCTA.

Figure 4. The current density-luminous efficiency (a), current density-external quantum efficiency (b) curves and EL spectra (c) of RMC2 based device structures A, B and C as well as the current density-voltage curves of single carrier devices based on RMC2 and RMC3 (d).
According to the single-carrier device, it can be seen that replacing triphenyl amine by carbazole units is indeed beneficial for the hole-electron carrier balance, but it is still inadequate. It can be verified by the EL spectra of device B (Figure 4c), which displays a tail emission around 400 nm arising from TPBI ETL. This indicates part of the exciton was generated in TPBI layer, due to the improved hole injection ability. Other hole blocking/electron transporting materials, such as 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) has smaller HOMO level, may supply more efficient hole blocking ability, while the electron mobility is lower than TPBI. Employing it as HBL layer of non-doped red OLED produces even inferior device performance. To resolve this problem, we fabricated device C by utilizing a super thin TPBI layer inserted between TCTA layer and EML (see in Figure 3) of device C to fine control the hole injection without affecting the electron transporting. The thickness of thin TPBI layer was optimized to 1 nm. The maximum brightness of device C decreased to 4850 cd m\(^{-2}\) because of limited hole current. While, the LE and EQE of device C was greatly improved to 5.3 cd A\(^{-1}\) and an EQE of 6.3%, suggesting increased carrier recombination efficiency in the EL process. The EQE still remains a high value of 5.1% at the brightness of 1000 cd m\(^{-2}\). Following two reasons should be attributed for the superior device performance. First, the fine-tuned hole injection ability leads to more balanced hole-electron carrier. Second, the recombination zone is well confined in the EML, which can be proved by the disappeared TPBI tail emission in the EL spectrum of device C. As a result, the CIE coordinates of the red electroluminescence was also optimized from (0.63, 0.36) of device B to (0.64, 0.35) of device C at a driving voltage of 7.0 V, which is closed to the standard red (0.64, 0.33) of NTSC (National Television System Committee).

The EQE of a device based on fluorescent materials is the product of charge recombination efficiency (\(\eta_1\)), the singlet ratio of generated exciton (\(\eta_2\)), the radiative decay efficiency of the singlet exciton (\(\eta_3\)) and light out-coupling efficiency (\(\eta_4\)) of the emission. Usually, the \(\eta_4 \approx 1/(2\pi)^2 \approx 20\%\) for a glass substrate with a refraction index (n) of 1.5. Assuming the \(\eta_1\) of our device is 100%, the \(\eta_2\) of neat RMC2-based device C is calculated to be 77%, considering the PL efficiency (\(\eta_3\)) of RMC2 neat film is 41%. It is relatively higher than the 25% singlet exciton generation ratio for conventional fluorescent emitters. According to the previously reported NT derivative-based red OLEDs, the high singlet exciton generation ratio of RMC2 is probably ascribed to the hybrid local and charge-transfer (HLCT) transition mechanism, which provides a reverse intersystem crossing (RISC) process through intramolecular \(T_1\) to \(S_0\) state, and induces the terminal singlet exciton ratio to exceed 25% of spin statistic in OLEDs.

### Conclusions

In summary, through tuning the electron donating ability of 2,1,3-naphthodiazole derivatives, we obtained a saturated red emitter RMC2 with superior PL efficiency/color purity trade-off feature in PL process and charge injection/recombination efficiency trade-off feature in EL process. Optimized red OLEDs based on neat RMC2 realized a maximum LE of 5.3 cd A\(^{-1}\), a maximum EQE value of 6.3% and good CIE coordinates of (0.64, 0.35). What’s more, the red OLEDs exhibits relatively low efficiency roll-off property. At a high luminance of up to 1000 cd m\(^{-2}\), it remains 81% of the maximum EQE value. Our results also reveal that it is important to fine tune the balance of hole injection and transporting ability so as to improve the device performance of non-doped red OLEDs.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

We gratefully acknowledge support of this work by the Hundred Talents Program of Sun Yat-Sen University (76190-18841211) and the National Natural Science and Foundation of China (NSFC, 61905206).

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