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An efficient solution processed non-doped red emitter based on carbazole–triphenylamine end-capped di(thiophen-2-yl)benzothiadiazole for pure red organic light-emitting diodes†

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New carbazole–triphenylamine end-capped di(thiophen-2-yl)benzothiadiazole showed high thermal and electrochemical stability, and great potential as a solution processed hole-transporting non-doped red emitter for OLEDs. A pure red device with CIE coordinates and a high luminance efficiency of (0.66, 0.33) and 3.97 cd A^{-1}, respectively, was achieved.

Since the pioneering studies on the first organic light-emitting diodes (OLEDs) by Tang and VanSlyke in 1987,[1] OLEDs have attracted great attention of the scientific community due to their potential for future flat-panel displays and lighting applications.[2] In today's developments of OLED technologies, the trends of OLEDs are mainly focusing both on optimization of device structures and on developing new emitting materials. In terms of the device fabrication, solution-processed OLEDs fabricated using small molecules will have great advantages, because the materials used are easy to synthesize and purify, while the fabrication method is convenient, low cost and allows large-scale manufacturing with less material usage.[3] Clearly the key point of material development for full color-flat displays is to find out materials emitting pure colors such as red, green and blue with excellent emission efficiency and high stability. To date, most of the reported small-molecule red emitters are dopants such as 4-(dicyanomethylene)-2-methyl-6-[2-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)ethenyl]-4*H*-pyran (DCJ, DCM) series,[4] chromene-based and polyacene-based materials,[5] and rare-earth complexes,[6] while the non-doped one is rare, especially the non-doped pure red emitters are very rare.[4a,7] Moreover, OLEDs of these materials are often fabricated using the hole-transporting layer.[4a,8] To this end, we prepare a new solution processed small molecule-based pure red emitter, namely 4,7-bis{5-(*N*,*N*-bis[4-(3,6-di-*tert*-butylcarbazol-9-yl)phenyl]aminophenyl)-thien-2-yl}-2,1,3-benzothiadiazole (**CAPTB**). Our design involved the use of bis(3,6-di-*tert*-butylcarbazol-9-ylphenyl)aniline as an end-capping group and di(thiophen-2-yl)benzothiadiazole as a fluorescent core. The former can suppress aggregation-induced fluorescence quenching of the planar conjugated core as well as increase the hole transporting capability, thermal stability and solubility of the molecule, while with push–pull character of a combined end-capping group and core the molecule will emit in the red region. With this design a simple solution processed hole-transporting non-doped red emitter can be obtained and a simple structure non-doped red OLED can be fabricated. Undoped OLEDs can avoid reproducibility problems of reliably achieving the optimum doping concentration during processing and are easily adapted to a mass production line. Herein, we report a detailed synthesis of **CAPTB** (Scheme 1), and also its physical and photophysical properties. Investigation of solution processed red OLED device fabrication and performance is also reported.

We began with Suzuki coupling of readily obtained compound **1** with 2-thiophene-boronic acid to obtain intermediate **2** in a good yield of 72%. Bromination of **2** with NBS followed by coupling of the resulting bromo compound **3** with 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,1,3-benzothiadiazole gave the target molecule **CAPTB** as a dark red solid in 55% yield. This material shows high solubility in most organic solvents allowing the thin film of **CAPTB** to be fabricated by a solution casting process. The thin film spin-coated from $CHCl_3$:toluene solution analysed using AFM showed a pretty smooth and pinhole-free surface indicating good film-forming property (ESI†).

Quantum chemical calculations performed using the TDDFT/B3LYP/6-31G(d,p) method of **CAPTB** revealed that the end-capped moieties adopt a bulky conformation creating non-planar structure which could help to prevent the close π–π contact between molecules and enhance its thermal stability.[9] In the HOMO, π-electrons are able to delocalize over the entire

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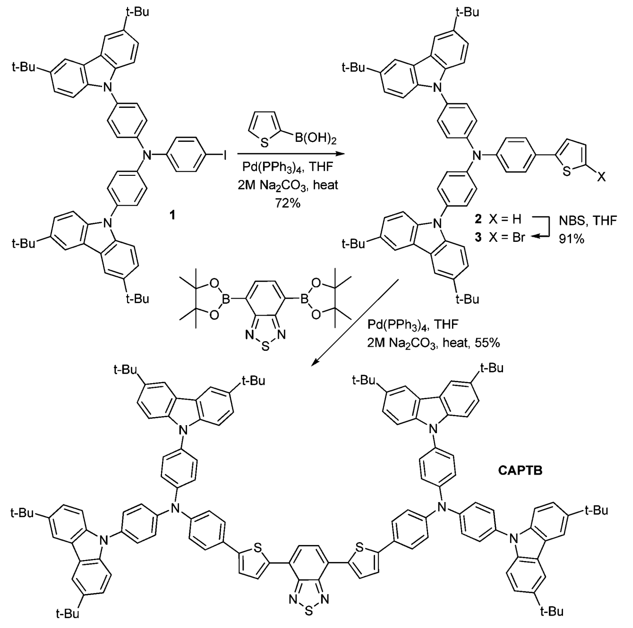

Scheme 1 Synthesis of **CAPTB**.

di(thiophen-2-yl)benzothiadiazole core and triphenylamine, while in the LUMO, the excited electrons delocalized over the quinoid-like di(thiophen-2-yl)benzothiadiazole plane, creating a push–pull feature (ESI†). The HOMO–LUMO energy gap was calculated to be 1.78 eV which is slightly lower than that estimated from the absorption onset (2.02 eV). In a CH_2Cl_2 solution, the absorption spectrum of **CAPTB** showed absorption bands at 348 nm assigned to the π–π* electron transition of the end-capping carbazole–triphenylamine moiety and at longer wavelength 528 nm ascribed to a donor to acceptor intramolecular charge transfer (ICT) transition between the end-capping and core units. The PL spectrum displayed a featureless emission peak in the red region (λ_{em} = 640 nm) (Fig. 1a). In solid state, the emission spectrum and the ICT absorption band were slightly red shifted (~4–8 nm) compared with the solution spectrum. This suggests that the bulky molecular structure of the end-capping groups fairly prevent the intermolecular π–π interactions of the fluorescent core in the solid state. Large Stokes shifts are observed in both solution and solid state (~112–118 nm) which are typically associated with compounds that have strong ICT character. This material exhibits red fluorescence with a solution quantum yield (Φ_F) of 0.08. An electrochemical study on **CAPTB** revealed five well defined quasi-reversible oxidation waves at 0.74, 0.80, 1.08, 1.29 and 1.48 V with no distinct reduction process being detected (ESI†). The first two oxidations assigned to removal of electrons from the end-capping carbazole–triphenylamine resulting in radical cations occur at a lower potential value than that for other triarylamine derivatives having *p*-unsubstituted phenyl rings ($E_{1/2}$ = 0.93 V),[10] supporting the existence of π–electron interactions between the triphenylamine and carbazole as revealed by the calculations. Multiple CV scans displayed identical CV curves indicating an electrochemically stable molecule. From these data, the HOMO and LUMO levels of **CAPTB** were calculated to be −5.16 and −3.14 eV, respectively. Thermogravimetric analysis (TGA) revealed that **CAPTB** is thermally stable with a 5% weight loss (T_{5d}) at a temperature well over 339 °C, while the differential scanning calorimetry (DSC) curve showed the endothermic baseline shift owing to both glass transition (T_g) at 255 °C and melting at a higher temperature of 368 °C, and only the base line shift was observed in a repeated scan, indicating a highly stable amorphous material (ESI†). These results prove that the use of bis(3,6-di-*tert*-butylcarbazol-9-ylphenyl)aniline as an end-capping group could fairly reduce the crystallization of a planar conjugated core and improve the amorphous stability of the material and the thin film, which in turn could increase the service time in device operation.[11]

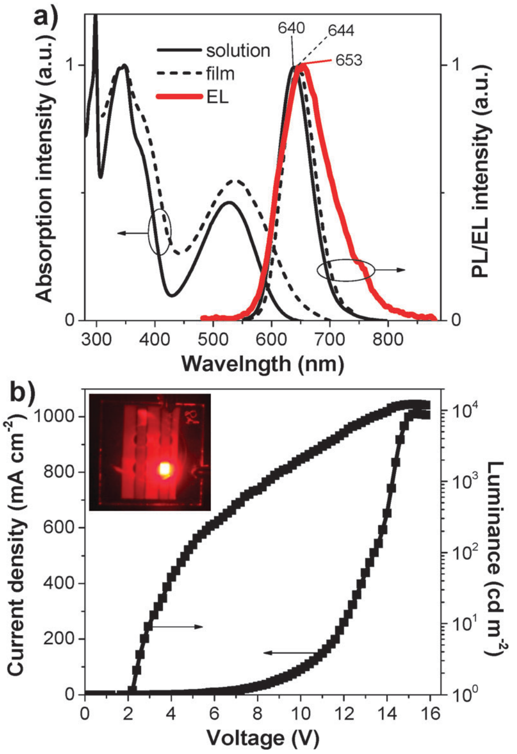

Fig. 1 (a) UV-Vis absorption and PL spectra measured in CH_2Cl_2 and as the thin film, and EL spectrum of the OLED. (b) *J–V–L* characteristics of the OLED device.

According to the above discussed excellent properties, the ability of **CAPTB** as a non-doped red emitting layer (EML) in OLEDs was investigated. Firstly, a single-layer device with the structure of ITO/PEDOT:PSS/**CAPTB** (spin-coating)/LiF(0.5 nm):Al(150 nm) was fabricated. The **CAPTB** layer was spin-coated from $CHCl_3$: toluene (5 : 1) solution with controlled thickness. The electroluminescent (EL) spectra and current density–voltage–luminance (*I–V–L*) characteristics of the device are shown in Fig. S5 (ESI†) and listed in Table 1. Under applied voltage, the device emitted a bright red luminescence with excellent color purity, an emission peak at 652 nm and a full width at half maximum of ~100 nm. The Commission Internationale De L'Eclairage (CIE) coordinates of the emitted light are x = 0.65 and y = 0.33 which are very close to the National Television System Committee (NTSC) standard (0.67, 0.33) for pure red color.[12] This device emits red color with better purity and has less complex device structure than the devices featuring a 1,10-dicyano-substituted bis-styrylnaphthalene derivative (BSN),[13]

Table 1 Electroluminescent data for the red OLEDs

Device structure	λ_{max}^{EL} (nm)	V_{on}/ V_{100}^{a} (V)	L_{max}^{b} (cd m^{-2}, V)	J_{max}^{c} (mA cm^{-2})	η_{max}^{d} (cd A^{-1})	CIE (*x*, *y*)
Single layer	652	2.9/5.7	4522/14.8	732	1.53	0.65, 0.33
Double layer	653	2.2/4.7	12 325/15.2	1009	3.97	0.66, 0.33

[a] Turn-on voltages at 1 and 100 cd m^{-2}. [b] Maximum luminance at applied voltage. [c] Current density at maximum luminance. [d] Luminance efficiency.

(bis(4-(*N*-(1-naphthyl)phenylamino)phenyl)fumaronitrile) (NPAFN)[14] or a star-shaped thieno-[3,4-*b*]-pyrazine (TPNA)[15] as the non-doped material. The EL spectrum of the diode matches the PL spectrum of **CAPTB**. The **CAPTB**-based red OLED showed a high maximum brightness (L_{max}) of 4522 cd m^{-2} at 14.8 V, a maximum luminance efficiency (η_{max}) of 1.53 cd A^{-1}, and a turn-on voltage (V_{on}) of 2.9 V. The high EL efficiency of **CAPTB** despite its low PL quantum yield might arise from a combination of the ICT effect and a good balance of its HOMO and LUMO energy levels.

The efficiency of the single-layer OLED could be further improved by balancing a charge injection in the device. In this case, **CAPTB** is more hole injection EML as its HOMO (−5.16 eV) matches well the work function of the ITO/PEDOT:PSS anode (−5.00 eV), hence an electron injection/hole-blocking layer is required. Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) is known to enhance performance of multi-layer devices fabricated with predominantly hole-transporting emitters.[16] A simple double-layer device of ITO/PEDOT:PSS/**CAPTB** (spin-coating)/BCP(40 nm)/LiF(0.5 nm)/Al(150 nm) was fabricated. The detailed EL and *I–V–L* data are given in Fig. 1 and listed in Table 1. The **CAPTB** spin-coating double-layer device exhibited a high L_{max} of 12 325 cd m^{-2} at 15.2 V, a η_{max} of 3.97 cd A^{-1}, and a low V_{on} of 2.2 V, which is considered to be one of the lowest turn-on voltages for solution processed red and orange-red OLEDs reported so far.[17] The operating voltage at 100 cd m^{-2} was 4.7 V indicating that good performance was achieved. The device emitted a bright red luminescence with an emission peak at 653 nm, a full width at half maximum of ∼100 nm, and CIE coordinates of (0.66, 0.33). No emission shoulder at a longer wavelength due to excimer and exciplex species formed at the interface of the EML and BCP layers, which often occurs in devices fabricated from EMLs with planar molecular structure,[18] was detected. Moreover, stable red emission was obtained from the device and the EL spectra did not change over the entire driven voltages (ESI†). As far as we know, the ability of **CAPTB** as a non-doped red light-emitting layer in red OLEDs, in terms of device performance, solution processability, thermal property, red colour purity, and simple device structure, is outstanding compared with those of solution-processable red fluorescent emitters,[4a,19] and also comparable with those of vacuum-deposited red fluorescent emitters reported in recent years.[4a,14,20] The results clearly demonstrate that **CAPTB** can be a very good candidate for use in solution-processed red OLEDs for display applications.

In summary, we demonstrated the design strategy and synthesis of **CAPTB** as a non-doped solution processed red light-emitter for OLEDs. By using bis(3,6-di-*tert*-butylcarbazol-9-ylphenyl)aniline as an end-capping group, we were able to reduce the crystallization and retain the high red emissive ability of a planar fluorescent core in the solid state, as well as improve the amorphous stability and solubility of the material. A double-layer OLED using **CAPTB** as EML emits stable red light at 653 nm with a luminance efficiency of 3.97 cd A^{-1}, a low turn-on voltage of 2.2 V and CIE coordinates of (0.66, 0.33) which is close to the pure red color. This report offers a useful strategy to adorn the highly efficient but planar fluorophore to be suitable for application in solution-processable and non-doped OLEDs.

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