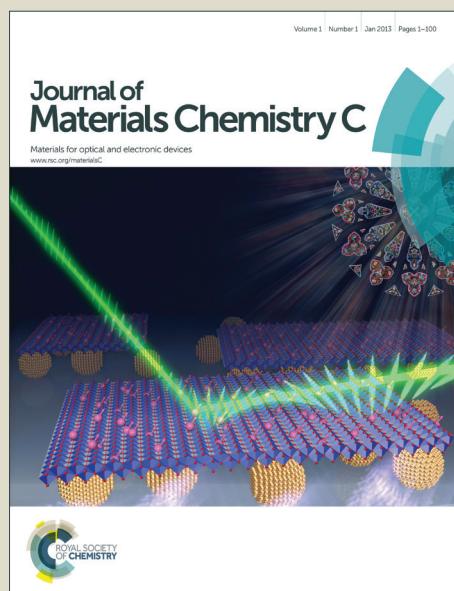


Journal of Materials Chemistry C

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Systematic Study of TCTA Based Star-shaped Host Materials by Optimizing Ratio of Carbazole/Diphenylphosphine Oxide: Achieving Both Low Efficiency Roll-Off and Turn-On Voltage for Blue PHOLEDs

Biao Pan^a, Hong Huang^{a,b}, Xiao Yang^a, Jiangjiang Jin^a, Shaoqing Zhuang,^a Guangyuan Mu^a, Lei Wang^{a*}

^a Wuhan National Laboratory for Optoelectronics, School of Optical and Electronic Information
Huazhong University of Science and Technology

Wuhan, 430074, P. R. China. Tel: +86-27-87793032

^bTCL Corporate Research, Nanshan District, Shenzhen, Guangdong, 518052, P.R.China.

Email: wanglei@mail.hust.edu.cn;

Abstract:

A series of star-shaped host materials **DCzPOTA**, **CzDPOTA** and **TCTA** containing central triphenylamine (TPA) core, peripheral modification with different ratios of p-type carbazole units and n-type diphenylphosphine oxide (DPPO) units were purposefully designed and synthesized. Their electronic nature, electrochemical, thermal and morphological properties were investigated systematically. In a suitable proportion of carbazole and phosphine oxide, blue PhOLEDs based on **DCzPOTA** exhibits a maximum power efficiency of 36.9 lm/W and an ideal turn-on voltage (2.7 V at 1 cd/m²). These results indicate that the electronic nature of host material can be finely adjusted by gradually changing the donor/acceptor ratio.

Keywords: star-shaped, host materials, blue light, carbazole/diphenylphosphine oxide hybrids

1. Introduction

Since the organic light emitting diodes (OLEDs) was firstly commercially successful applied in global markets, phosphorescent organic light-emitting diodes (PHOLEDs) have shown great applicable potentials in digital terminal displays and planar solid-state lighting.¹⁻⁶ However, even as OLEDs sales currently exceed \$1B/yr and grow exponentially, there are outstanding challenges in OLEDs science and technology, notably in improving the efficiency of the devices and their stability at high brightness ($>1000 \text{ Cd/ m}^2$).⁷⁻⁸ In order to achieve this goal, one of the most critical contributions is the materials development, along with innovations and optimizations in the device structure and processing. Therefore, there have been continual studies to improve the device performances of blue PhOLEDs by synthesizing host and dopant materials.⁹⁻¹⁵

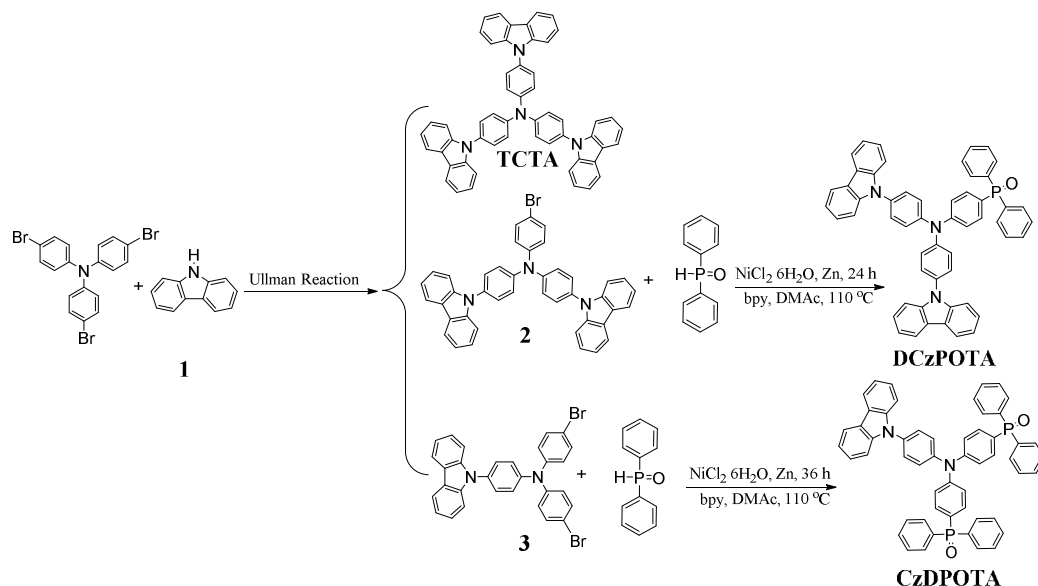
To be an effective host of the blue phosphor suitable for vacuum deposition technology, the triplet energy (E_T) and balanced carrier injecting/transporting property must be considered together. The E_T of the host is required to be higher than 2.70 eV in order to prevent the back energy transfer from the phosphor to the host.¹⁶ On the other hand, bipolar charge-transporting properties are required to increase the balance of the carriers and broaden the excitation recombination zone, which is of paramount importance to maintain the charge balance in the emissive layer so as to improve the device efficiency accompanied by a low roll-off.¹⁷⁻²¹ To fulfill these two basic

requirements, we came up with an appealing strategy including the following two aspects: Firstly, choosing a high-triplet-energy moiety as the core and appropriate electron-donor(D) and acceptor(A) moieties as peripheral groups; Secondly, constructing new materials by altering the proportion of p-type and n-type moieties so as to find the ideal molecular structures.

As we know, TCTA has been widely used as a host material for blue, orange, and white OLEDs because of its high morphological stability ($T_g = 152^\circ\text{C}$) and reasonable E_T level ($E_T = 2.85\text{ eV}$)²²⁻²⁴. However, the performances of blue PhOLEDs was relatively poor and suffered from a high efficiency roll-off at high current density, which is presumably due to that TCTA only behaved as a hole-transporting type host material with low capability to transport electrons²⁵. To further optimizing the compound TCTA as the appropriate host for the blue PhOLEDs, J. H. Kwon *et al.* have proposed a series of modified-TCTA materials with electron-deficient *N*- α -carboline moieties and showed very high external quantum efficiency of 25.7% and low onset and driving voltages of 2.47 V²⁶. Our group have reported a new bipolar host material TCTAPO by introducing an electron deficient DPPO group into the TCTA molecule and the maximum power efficiency of blue device based on TCTAPO was achieved at 40.7 lm/W in 2012.²⁷ The results show that the DPPO moiety can lower the lowest unoccupied molecular orbital (LUMO) level and increase the electron-injection property without changing the E_T of TCTA. Meanwhile, it also gives us the enlightenment that we can readily control the carrier injecting/transporting ability of TCTA through changing the ratio of carbazole and

DPPO. In fact, many research groups are concentrating on controllable tuning the ratio between p-type and n-type units in host materials because the minute change of mixing ratio of D/A moieties in host materials could change the resultant device characteristics.²⁸⁻³¹ Nevertheless, up to now, a systematic study elucidating the structure-function relationship of the number and ratio of DPPO and carbazole moieties in TCTA has not been carried out.

In this article, star-shaped TPA-cored and peripheral DPPO/carbazole bipolar hosts, (4-(bis(4-(9H-carbazol-9-yl)phenyl)amino)phenyl) diphenylphosphine oxide **DCzPOTA** and (((4-(9H-carbazol-9-yl)phenyl)azanediyl)bis(4,1-phenylene))bis(diphenylphosphine -oxide) **CzDPOTA** were conveniently synthesized, and the effect of the different ratio of carbazole with DPPO on their thermal, photo physical, electro-chemical, bipolar transporting and device properties were investigated in detail. Both of the two compounds possessed the same kinds of substituted units and showed a topology structure. As expected, the disrupted conjugation via phosphine-oxide linkage can be well-preserved to ensure their high triplet energies, and the charge balance in the emitting layer could be tuned by adjusting the ratio between the carbazole and DPPO units.



Scheme 1. Synthesis routes of the compounds **DCzPOTA**, **CzDPOTA** and **TCTA**.

2. Experimental Section

2.1. General Information

All solvents and materials were used as received from commercial suppliers without further purification. ¹H NMR and ¹³C NMR spectra were measured on a Bruker-AF301 AT 400MHz spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on an Elementar (Vario Micro cube) analyzer. Mass spectra were carried out on an Agilent (1100 LC/MSD Trap) using APCI ionization. UV-Vis absorption spectra were recorded on a Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600). PL spectra were recorded on Edinburgh instruments (FLSP920 spectrometers). Differential scanning calorimetry (DSC) was performed on a PE Instruments DSC 2920 unit at a heating rate of 10 °C/min from 30 to 250 °C under nitrogen. The glass transition temperature (*T_g*) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken with a PerkinElmer

Instruments (Pyris1 TGA). The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10 °C/min from 30 to 700 °C. Cyclic voltammetry measurements were carried out in a conventional three electrode cell using a Pt button working electrode of 2 mm in diameter, a platinum wire counter electrode, and an Ag/AgNO₃ (0.1 M) reference electrode on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature. Reductions CV of all compounds were performed in dichloromethane containing 0.1 M tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. The experimental conditions and equipments used have been described in our previous works.³²

2.2. Computational Details

The geometrical and electronic properties were performed with the Amsterdam Density Functional (ADF) 2009.01 program package. The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functionals)³³⁻³⁴ with the 6-31G(d) atomic basis set. Then the electronic structures were calculated at τ -HCTHhyb/6-311++G(d, p) level.³⁵ Molecular orbitals were visualized using ADF view.

2.3. Device Fabrication and Measurement

The EL devices were fabricated by vacuum deposition of the materials at a base

pressure of 5×10^{-6} Torr onto glass pre-coated with a layer of indium tin oxide (ITO) with a sheet resistance of $20 \Omega/\text{square}$ and transmissivity of 80% in blue light. Before deposition of an organic layer, the clear ITO substrates were treated with oxygen plasma for 5 min. The deposition rate of organic compounds was 0.9-1.1 Å/s. Finally, a cathode composed of LiF (1nm) and aluminum (100nm) was sequentially deposited onto the substrate in the vacuum of 10^{-5} Torr. The L - V - J of the devices was measured with a Keithley 2400 Source meter and PR655. All measurements were carried out at room temperature under ambient conditions. The experimental conditions and equipments used have been described in our previous works.³⁶

2.4. Synthesis

Tris(4-bromophenyl)amine (1). To a solution of triphenylamine (2.5 g, 10.0 mmol) in DMF (25 ml) at 0 °C, NBS (5.2 g, 32.0 mmol) in DMF (10 ml) was added drop-wise. The mixture was stirred for 4 h at room temperature. Then, water was added to the mixture to give a white precipitate. After filtration and drying, the obtained white solid was recrystallized from petroleum to afford tris(4-bromophenyl)amine (**1**) with a yield of 90% (4.3 g). ¹H-NMR (CDCl₃, 400 MHz): δ (ppm) 7.36 ~ 7.34 (m, 6H), 6.93 ~ 6.91 (m, 6H). MS (APCI): calcd for C₁₈H₁₂Br₃N: 481.9, found, 482.9 (M+1)⁺.

N, N-bis(4-(9H-carbazol-9-yl)phenyl)-4-bromoaniline (2). A mixture of tris(4-bromophenyl)amine (**1**) (0.48 g, 1.0 mmol), carbazole (0.33 g, 2.0 mmol), CuI (60.0 mg, 0.3 mmol), 18-crown-6 (80.0 mg, 0.3 mmol), K₂CO₃ (1.38 g, 10 mmol), and

DMPU (3.0 mL) was refluxed under nitrogen for 48 h. After cooling, the mixture was extracted with CH₂Cl₂ and washed with the dilute HCl solution, and then the organic layer was dried over anhydrous Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography on silica gel using CH₂Cl₂ as the eluent to give a white powder. Yield: 38% (0.25 g). ¹H-NMR (CDCl₃, 400MHz): δ (ppm) 8.17 ~ 8.15 (d, *J* = 8.0 Hz, 4H), 7.52 ~ 7.38 (m, 18H), 7.32 ~ 7.28 (m, 4H), 7.22 ~ 7.19 (m, 2H). MS (APCI): calcd for C₄₂H₂₈BrN₃: 653.2, found, 654.4 (M+1)⁺.

***N*-(4-(9H-carbazol-9-yl)phenyl)-4-bromo-*N*-(4-bromophenyl)aniline (3).** The compound **3** was prepared according to the same procedure as the compound **2**. Yield: 45%. ¹H-NMR (CDCl₃, 400MHz): δ (ppm) 8.16 ~ 8.14 (d, *J* = 7.6 Hz, 2H), 7.45 ~ 7.41 (m, 10H), 7.29 ~ 7.27 (m, 3H), 7.26 ~ 7.24 (m, 1H), 7.07 ~ 7.05 (m, 4H). MS (APCI): calcd for C₃₀H₂₀Br₂N₂: 568.3, found, 569.2 (M+1)⁺.

(4-(bis(4-(9H-carbazol-9-yl)phenyl)amino)phenyl)diphenylphosphine oxide (DCzPOTA). To a mixture of NiCl₂·6H₂O (0.07 g, 0.3 mmol), zinc (0.4 g, 6.0 mmol), 2,2'-bipyridine (bpy) (0.09 g, 0.6 mmol) and *N,N*-bis(4-(9H-carbazol-9-yl)phenyl)-4-bromoaniline (**2**) (0.65 g, 1.0 mmol) in DMAc (30.0 ml) solution, biphenylphosphine oxide (0.4 g, 2.0 mmol) were added. The reaction mixture was stirred with a stir bar at 110 °C for 24 hours. After it, the mixture was allowed to cool to room temperature and added with CH₂Cl₂ and water. The organic layer was isolated and the remaining aqueous phase was further extracted with CH₂Cl₂. Then the organic phases were combined and dried with anhydrous MgSO₄, purified by silica gel column chromatography using dichloromethane-methanol as the eluent to afford the

corresponding cross coupled product. Yield: 54%. $^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ (ppm) 8.16 ~ 8.14 (d, $J = 8.4$ Hz, 4H), 7.78 ~ 7.73 (m, 4H), 7.62 ~ 7.54 (m, 8H), 7.52 ~ 7.43 (m, 16H), 7.31 ~ 7.30 (m, 6H). $^{13}\text{C-NMR}$ (CDCl_3 , 100MHz): δ (ppm) 150.67, 145.49, 140.85, 133.84, 133.68, 133.57, 133.27, 132.18, 132.09, 131.93, 131.91, 128.59, 128.47, 128.31, 126.56, 125.98, 123.41, 121.64, 121.52, 120.38, 120.05, 109.75. $^{31}\text{P-NMR}$ (CDCl_3 , 400MHz): δ (ppm) 29.27. MS (APCI): calcd for $\text{C}_{54}\text{H}_{38}\text{N}_3\text{OP}$: 775.3, found, 776.5 ($\text{M}+1$) $^+$. Anal. calcd for $\text{C}_{54}\text{H}_{38}\text{N}_3\text{OP}$ (%):C, 83.59; H, 4.94; N, 5.42; O, 2.06; found: C, 83.46; H, 5.03; N, 5.46;

(((4-(9H-carbazol-9-yl)phenyl)azanediyl)bis(4,1-phenylene))bis(diphenylphosphine oxide) (CzDPOTA). The compound **CzDPOTA** was prepared according to the same procedure as the compound **DCzPOTA**. Yield: 45%. $^1\text{H-NMR}$ (CDCl_3 , 400MHz): δ (ppm) 8.15 ~ 8.13(d, $J = 7.6$ Hz, 2H), 7.74 ~ 7.71 (m, 9H), 7.70 ~ 7.42 (m, 25H), 7.36 ~ 7.34 (m, 3H), 7.29 ~ 7.22 (m, 1H). $^{13}\text{C-NMR}$ (CDCl_3 , 100MHz): δ (ppm) 149.92, 144.89, 140.74, 134.48, 133.71, 133.61, 133.07, 132.15, 132.05, 128.62, 128.50, 128.34, 127.28, 126.00, 123.44, 123.11, 120.38, 120.11, 109.70. $^{31}\text{P-NMR}$ (CDCl_3 , 400MHz): δ (ppm) 29.26. MS (APCI): calcd for $\text{C}_{54}\text{H}_{40}\text{N}_2\text{O}_2\text{P}_2$: 810.3, found, 811.2 ($\text{M}+1$) $^+$. Anal. calcd for $\text{C}_{54}\text{H}_{40}\text{N}_2\text{O}_2\text{P}_2$ (%):C, 79.99; H, 4.97; N, 3.45; found: C, 80.34; H, 5.15; N, 3.42;

3. Results and discussion

3.1. Synthesis and characterization

These bipolar molecules were synthesized by the *Ullmann* and Ni(II)/Zn catalyzed

phosphine oxide coupling reaction in two steps. The synthetic routes and chemical structures of compounds, **DCzPOTA**, **CzDPOTA** and **TCTA** are depicted in Scheme 1. The intermediate tris(4-bromophenyl)amine (**1**) was synthesized according to the literature³⁷. The compounds *N,N*-bis(4-(9H-carbazol-9-yl)phenyl)-4-bromoaniline (**2**) and *N*-(4-(9H-carbazol-9-yl)phenyl)-4-bromo-*N*-(4-bromophenyl)aniline (**3**) were synthesized with the typical *Ullmann* coupling reaction of tris(4-bromophenyl)amine (**1**) and carbazole in the presence of CuI, 18-crown-6 and K₂CO₃. The final products **DCzPOTA** and **CzDPOTA** were synthesized with the Ni(II)/Zn catalyst phosphine oxide coupling reaction in yields of 54% and 45% at the temperature of 110 °C, respectively. All the developed host materials were purified by silica gel chromatography and then repeated thermal gradient vacuum sublimation before characterization and device fabrication. The chemical structures of the compounds **DCzPOTA** and **CzDPOTA** were fully characterized by ¹H NMR, ³¹P NMR and ¹³C NMR spectroscopy, mass spectrometry and elemental analysis. All of the physical properties data were summarized in Table.1 and the data of TCTA were quoted from our previous work²⁷.

Table 1. Physical data of compounds **DCzPOTA**, **CzDPOTA** and **TCTA**.

Compound	$\lambda_{\text{abs,max}}$ (nm) ^{a)}	$\lambda_{\text{em,max}}$ (nm) ^{a)}	E_g (eV) ^{b)}	HOMO/LUMO (eV) ^{c)}		HOMO/LUMO (eV) ^{d)}		E_T (eV) ^{e)}	$T_g/T_d^f)$ (°C)
DCzPOTA	328/294	432	3.39	-5.44	-2.05	-5.21	-2.12	2.84	148/471
CzDPOTA	333/294	417	3.41	-5.53	-2.12	-5.33	-2.24	2.86	122/476
TCTA	326/293	386	3.46	-5.09	-1.63	-4.99	-2.33	2.85	152/489

^{a)}Measured in CH₂Cl₂; ^{b)}Determined from the onset of oxidation potentials and the E_g = HOMO-LUMO; ^{c)}Measured with the CV; ^{d)}Values from DFT calculation; ^{e)}Measured in 2-methyltetrahydrofuran at 77 K. ^{f)}Obtained from DSC measurements and TGA measurements;

3.2. Thermal properties

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out to examine the thermal properties of these new compounds. **DCzPOTA** shows a high glass transition temperature (T_g) of 148 °C in the DSC heating cycle, which is 26 °C higher than that of **CzDPOTA** (122 °C) indicating that their T_g is influenced by the change of the ratio between the carbazole and phosphine oxide units. The T_g of these three compounds increased as the order of CzDPOTA < DCzPOTA < TCTA with more carbazoles in the peripheral sides of the TPA core, which can be attributed to the increase rigidity of the carbazole compared to the DPPO unit. The high T_g values is prerequisite for their applications in PhOLEDs. We also measured the decomposition temperatures (T_d) of **DCzPOTA** and **CzDPOTA**, determined from the onset points of 5% weight loss, which were found to be 471 °C and 476 °C, respectively (see Figure. 1). Compared with **TCTA** (489 °C), it further confirmed that increasing the number of carbazole is beneficial to improve the thermodynamic stability. The excellent thermal properties indicate that the morphology of the materials is not easily changed at the high temperatures generated by the operation of OLED devices, and it is closely correlated with the lifetime of the device in view of that a high stability of the glassy state is urgently demanded in order to prevent the degradation of devices in applications³⁸.

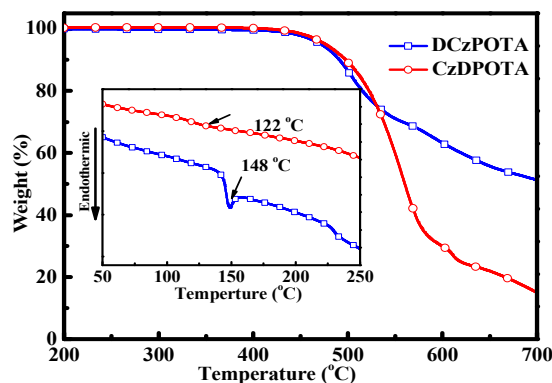


Fig. 1 (a) TGA thermo-grams of the compounds **DCzPOTA** and **CzDPOTA** recorded at a heating rate of 10 °C/min; Inset: DSC traces of the compounds **DCzPOTA** and **CzDPOTA** recorded at a heating rate of 10 °C/min.

3.3. Photophysical properties

The UV absorption and PL spectra of **DCzPOTA** and **CzDPOTA** in CH_2Cl_2 are shown in Figure 2(a). The two compounds exhibit a similar absorption spectra shape, and the absorption peaks at 294 and 328 or 333 nm could be assigned to $n\text{-}\pi^*$, $\pi\text{-}\pi^*$ transition of TPA and carbazole, respectively. The absorption edges of the UV/vis spectra of **DCzPOTA** and **CzDPOTA** are about 366 and 364 nm, respectively, which corresponds to the band gaps at 3.39 and 3.41 eV, respectively. The PL emission peak of **DCzPOTA** and **CzDPOTA** in dichloromethane was observed at 432 and 417 nm, respectively. Compare with TCTA (386nm), both of them exhibited obvious red-shift, which could be ascribed to the strong electron-withdrawing capability of the DPPO unit. The three compounds almost have the same E_T ranging from 2.84 to 2.86 eV, which were determined from the highest energy vibronic sub-band of the phosphorescence spectrum in 2-methyltetrahydrofuran at 77 K in Figure 2(b). The DPPO does not extend the conjugation of the core because of its tetrahedral structure,

allowing it to affect only charge transport properties without degrading the E_T of the TPA core, so the incorporation of DPPO has no influence on E_T of TCTA. In other words, by breaking the conjugation between carbazole and DPPO through the sp^3 -N of TPA core, we successfully get two bipolar hosts for blue phosphorescent that meets the requirement of high triplet energy while simultaneously conserving its thermal stability.

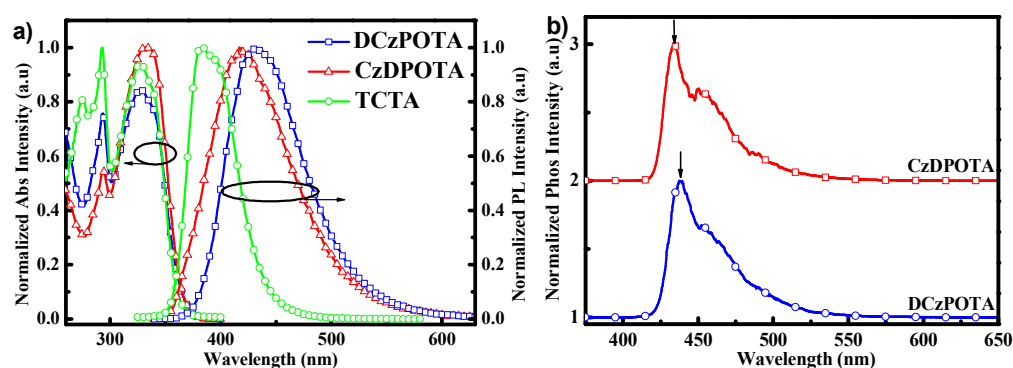


Figure 2. (a) Absorption and PL-emission spectra of TCTA, DCzPOTA and CzDPOTA in CH_2Cl_2 ; (b) The phosphorescence spectra of DCzPOTA and CzDPOTA in a frozen 2-methyltetrahydrofuran matrix at 77 K.

3.4. Electrochemical Properties

The electrochemical properties of these compounds were measured by cyclic voltammetry (CV) (Figure 3). The compounds exhibit reversible oxidation behaviors, which can be assigned to the oxidation of the carbazole and TPA moieties. The highest occupied molecular orbital (HOMO) determined from the onsets of the oxidation potentials by comparing with ferrocene (Fc) is $-5.44 \sim -5.53$ eV ($HOMO = -(E_{ox} + 4.8)$ eV). And the lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the HOMO values and the energy gaps (E_g), which is in

the range of -2.05 ~ -2.12 eV. The HOMO levels of these compounds are adjacent to that of widely used hole transport material NPB (-5.4 eV)³⁹, which means the hole-injection barriers from NPB to the compounds is small. The LUMO level of **DCzPOTA** (-2.05 eV) is slightly higher than that of **CzDPOTA** (-2.12 eV), but has a significant difference with **TCTA** (-1.63 eV), which could be attributed to the electron-withdrawing nature and increasing numbers of DPPO units.

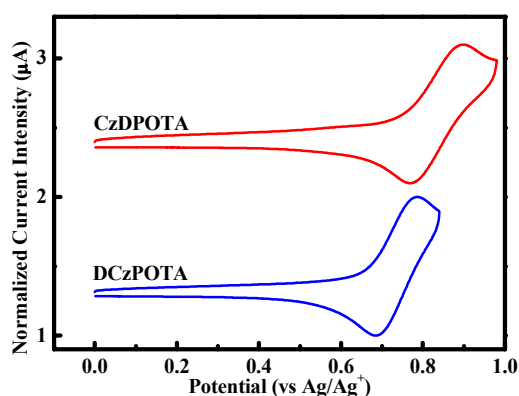
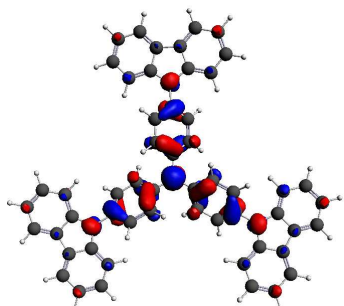
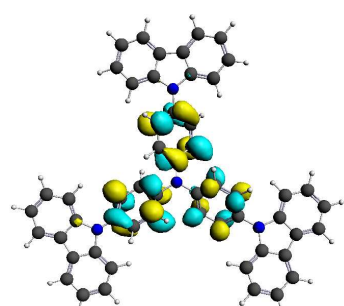
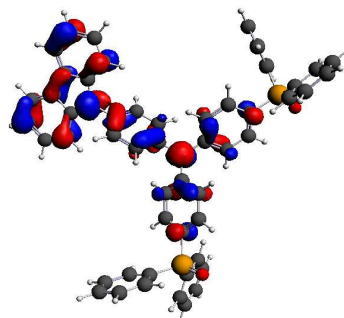
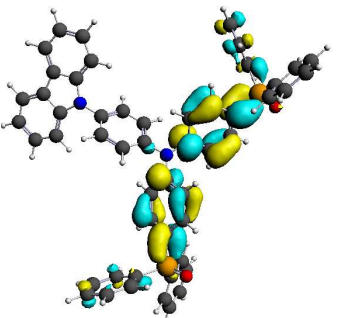


Figure 3. CV curves of **DCzPOTA** and **CzDPOTA**. Working electrode: Pt button; reference electrode: Ag/Ag⁺. Oxidation CV was performed in dichloromethane containing 0.1 M *n*-Bu₄NPF₆ as the supporting electrolyte at a scan rate of 100 mV/s.

3.5. Quantum Chemical Calculations

Theoretical calculations on the electronic nature of these compounds were carried out at the DFT//B3LYP/6-31G level in the Amsterdam Density Functional (ADF) 2009.01 program to acquire a better understanding of the bipolar properties. As shown in Figure 4, the HOMO orbitals for **CzDPOTA** and **DCzPOTA** are mainly located on the electron-donating carbazole moiety or TPA moiety, while the LUMO orbitals are mainly dispersed in the electron-accepting DPPO unit and the benzenes

linked to it directly. The separated HOMO and LUMO distribution of **CzDPOTA** and **DCzPOTA** and are largely different with overlapped distribution for **TCTA** indicating the donating or withdrawing properties of the moieties have great influence on the distribution of the frontier energy levels. These new designed compounds have almost complete separation of the HOMO and LUMO orbital at the carbazole and DPPO moieties, respectively, which can be rationalized by the disruption of the π -conjugation between the electron-donor and electron-accepter moieties because of the special conjugated configuration of the DPPO group. The separated frontier molecular orbitals of **CzDPOTA** and **DCzPOTA** indicate their potential ambipolar characteristics, which is preferable for balanced hole- and electron- transporting properties².

Compound	HOMO	LUMO
TCTA		
CzDPOTA		

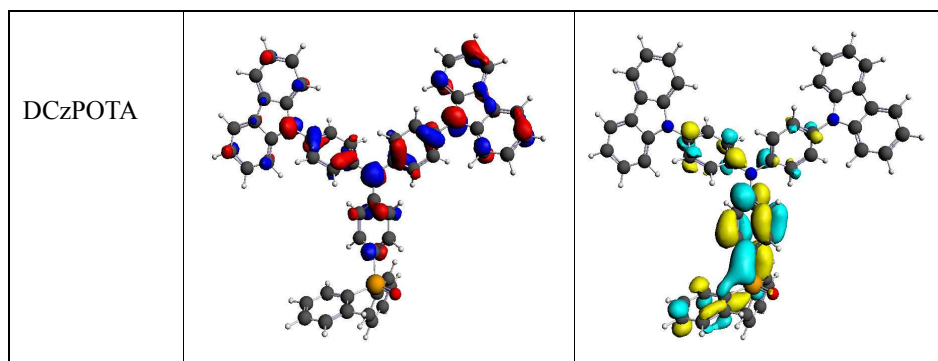


Figure 4. The molecular-orbital surfaces of HOMO and LUMO of the compounds **TCTA**, **DCzPOTA** and **CzDPOTA**.

3.6. Carrier-Transport Properties

The charge-carrier properties of two compounds were investigated in hole-only and electron-only devices. The hole-only device with the following structure: ITO/NPB (10 nm)/host (30 nm)/NPB (10 nm)/Al (100 nm) and the electron-only device with the structure of ITO/BCP (30 nm)/host (30 nm)/BCP (30 nm)/LiF (1 nm)/Al (100 nm). It can be assumed that only single carriers are injected and transported in the devices due to the LUMO of the NPB is low and the HOMO of the BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) is high enough to block electron and hole injection, respectively.⁴⁰ As shown in Figure 5, the remarkable current densities are obviously to prove the bipolar properties of the two compounds. The current density of the **CzDPOTA** based electron-only device is higher than that of the **DCzPOTA** at the same voltages, which implies that the number of DPPO groups and electron-injecting/transporting ability are proportional. In stark contrast to electron-only device, the current density of the **DCzPOTA** based hole-only device is

higher than that of the **CzDPOTA**, indicates that the number of carbazole groups and hole-injecting/transporting ability are proportional. It could be ascertained that tuning the ratio of the carbazole and DPPO could authentically modulate carrier-transport properties.

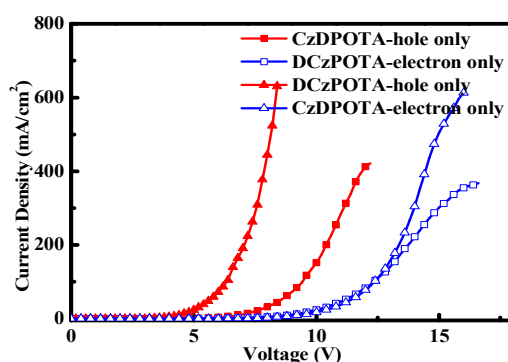


Figure 5. The current density versus voltage curves of the hole-only and electron-only devices for the compounds **DCzPOTA** and **CzDPOTA**.

3.7. Electroluminescent Devices

To assess which of **DCzPOTA** and **CzDPOTA** will give the better balanced performance as bipolar host materials in blue PhOLEDs, FIrpic-doped devices were fabricated with a simple configuration of ITO/MoO₃ (10 nm)/NPB (40 nm)/mCP (5 nm)/Host: 6 wt % FIrpic (20 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (150 nm), (Host: **CzDPOTA** for Device A; **DCzPOTA** for Device B; **TCTA** for Device C.). For comparison, the control device C was also prepared. NPB is the hole-transporting layer and mCP is the exciton blocking layer. FIrpic doped host was used as the emitting layer, the best electroluminescence (EL) performance was achieved with 6 wt % FIrpic for all the hosts. TmPyPB served as both electron-transporting layer and hole-blocking layer. MoO₃ and LiF (lithium fluoride) served as the hole- and

electron-injecting layers, respectively. The schematic energy level diagrams of the three devices are shown in Figure 6.

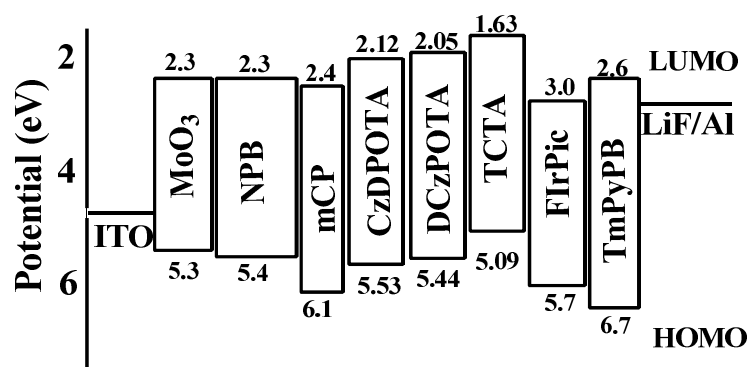
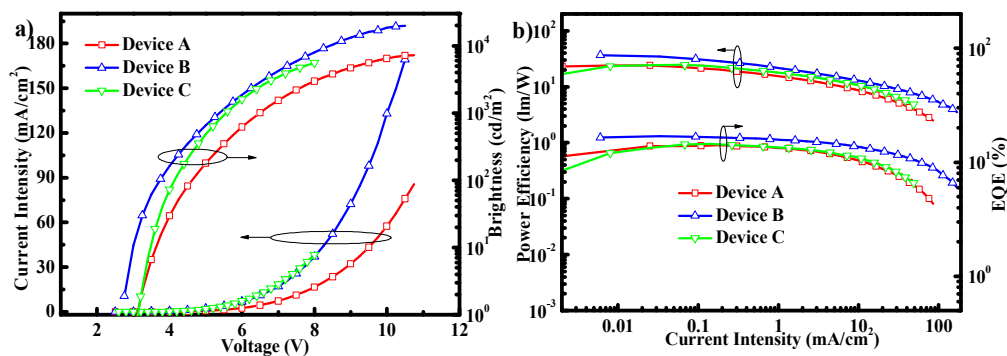


Figure 6. Energy level diagram of HOMO and LUMO levels (relative to vacuum level) for materials investigated in this work.

Figure 7. shows the current density-voltage-brightness (J - V - L) characteristics, efficiency versus current density curves for the devices and all of the EL spectra of the devices. The EL data of the devices are summarized in Table 2. The highest efficiency was achieved for device B based on **DCzPOTA**, giving a maximum external quantum efficiency (EQE) of 16.9% and a maximum power efficiency (η_p) of 36.9 lm/W. In comparison, obviously lower efficiencies of 14.1% and 24.1 lm/W were obtained at 82.0 cd/m² for device A based on **CzDPOTA**. Device C exhibits a η_p of 24.0 lm/W and a EQE of 14.5 %, and its turn-on voltage (V_{on}) is 3.2 V. The η_p in the device B was increased about 53.8% compared to the device C, which can be attributed to the improved charge balance by the bipolar nature of **DCzPOTA**. Nevertheless, the efficiency of Device A is equal to the Device C, and the maximum value was reached at higher brightness which can be caused by the unbalanced charge and larger hole injection barrier between **CzDPOTA** and NPB. From the perspective of V_{on} , it is obviously that device C has a higher turn-on voltage compared to device A and B,

which can be ascribed to the bipolar transporting property and the suitable HOMO and LUMO energy levels of the two compounds. It is worth noting that the device B has a low turn-on voltage of 2.7 V, at a brightness of 1.91 cd/m^2 . Considering that the E_T of Flrpic is about 2.65 eV, the turn-on voltage value of the device B has already reached the limit of the Flrpic-based blue PhOLEDs. With regard to efficiency roll-off, device A and B also have excellent performance: the EQE of device B remains 16.9%, and 14.8% at 100 and 1000 cd/m^2 , respectively. Compared with TCTA, the EQE efficiency roll-off of device based on **DCzPOTA** is weaker. The slightly reduced efficiency for the devices based on **DCzPOTA** should also be attributed to the reduced carrier balance recombined in the EML. Finally, EL spectra of the blue phosphorescent OLEDs based on **CzDPOTA** and **DCzPOTA** peak at 473 nm with a shoulder at 500 nm, which are identical to those reported previously, indicating an effective exothermic energy transfer from host to guest Flrpic. From the blue device results, we can conclude that a better charge balance shall be attained in DPPO-substituted TCTA while the ratio of DPPO with carbazole is 1:2.



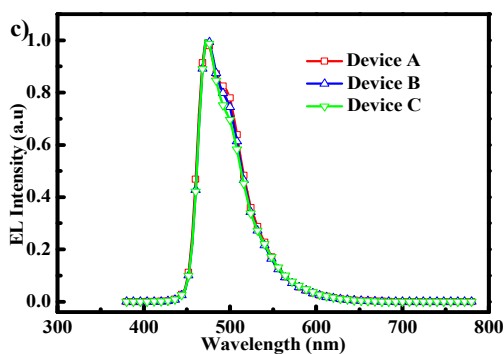


Figure 7. (a) Current density-voltage-brightness (J - V - L) characteristics for devices A-C; (b) external quantum efficiency and power efficiency versus current density curves for devices A-C and (c) the EL spectra of the devices A-C.

Table 2. Electroluminescence properties of the devices A-C

Device	host	V_{on} (V) ^a	L_{max} [cd/m ²] (V at L_{max} , V)	η_c^b [cd/A]	η_p^b [lm/W]	EQE ^b [%]	EQE ^c [%]	CIE [x, y] ^d
A	CzDPOTA	3.10	7287(10.8)	27.4	24.1	14.1	11.9	(0.14, 0.32)
B	DCzPOTA	2.70	19910(10.5)	33.0	36.9	16.9	14.8	(0.14, 0.32)
C	TCTA	3.20	5560 (8.0)	29.4	24.4	14.5	12.4	(0.15, 0.31)

^aAbbreviations: V_{on} : turn-on voltage at 1 cd/m²; L_{max} : maximum luminance; V: voltage at the maximum brightness; η_c : current efficiency; η_p : power efficiency; CIE [x, y]: Commission International de l'Eclairage coordinates. ^b maximum efficiency. ^c EQE at brightness 1000 cd/m². ^d Measured at 8 V

4. Conclusions

In conclusion, we have designed and synthesized a series of bipolar hosts based on the conventional blue host material TCTA with convergent modulation of the ratio between carbazole and DPPO units. The photo-physical and electrochemical properties of the hosts can be tuned through introduction of moieties with different electronegativity. The rigidity structure of the carbazole units effectively suppresses close molecular packing in the solid state so that all the compounds exhibit excellent thermal stability and amorphous ability. Devices using **DCzPOTA** as the host

exhibited a maximum power efficiency of 36.9 lm/W and an ideal turn-on voltage (2.7 V at 1.91 cd/m²). Our findings provided a valuable strategy for readily controlling the carrier injecting/transporting ability of the star-shaped molecules through changing the number, ratio, and type of the functional groups and the molecular configurations.

ACKNOWLEDGEMENTS

This research work was supported by the NSFC/China (21161160442, 51203056), the National Basic Research Program of China (973 Program 2013CB922104) and the Analytical and Testing Centre at Huazhong University of Science and Technology.

REFERENCE

1. K. T. Kamtekar, A. P. Monkman and M. R. Bryce, *Adv. Mater.*, 2010, **22**, 572-582.
2. K. S. Yook and J. Y. Lee, *Adv. Mater.*, 2012, **24**, 3169-3190.
3. H. Sasabe and J. Kido, *J. Mater. Chem.*, C. 2013, **1**, 1699-1707.
4. L. Ying, C.-L. Ho, H. B. Wu, Y. Cao and W.-Y. Wong, *Adv. Mater.*, 2014, **26**, 2459-2473.
5. X. L. Yang, G. J. Zhou and W.-Y. Wong, *J. Mater. Chem. C.*, 2014, **2**, 1760-1778.
6. G. J. Zhou, W.-Y. Wong and S. Suo, *J. Photoch. Photobio. C.*, 2010, **11**, 133-156.
7. C. Murawski, K. Leo and M. C. Gather, *Adv. Mater.*, 2013, **25**, 6801-6827.
8. S. F. Chen, Q. Wu, M. Kong, X. F. Zhao, Z. Yu, P. P. Jia and W. Huang, *J. Mater. Chem.C.*, 2013, **1**, 3508-3524.
9. Y. J. Cho and J. Y. Lee, *J. Phys. Chem. C.*, 2011, **115**, 10272-10276.
10. H. Huang, X. Yang, B. Pan, L. Wang, J. S. Chen, D. G. Ma and C. L. Yang, *J. Mater. Chem.*, 2012, **22**, 13223-13230.
11. H. Sasabe, J.-I. Takamatsu, T. Motoyama, S. Watanabe, G. Wagenblast, N. Langer, O. Molt, E. Fuchs, C. Lennartz and J. Kido, *Adv. Mater.*, 2010, **22**, 5003-5007.
12. H. Sasabe, N. Toyota, H. Nakanishi, T. Ishizaka, Y.-J. Pu and J. Kido, *Adv. Mater.*, 2012, **24**, 3212-3217.
13. L. X. Xiao, Z. J. Chen, B. Qu, J. X. Luo, S. Kong, Q. H. Gong and J. Kido, *Adv. Mater.* 2011, **23**, 926-952.
14. C.-L. Ho and W.-Y. Wong, *New. J. Chem.* 2013, **37**, 1665-1683.
15. L. S. Cui, Y. Liu, X. D. Yuan, Q. Li, Z. Q. Jiang and L. S. Liao, *J. Mater. Chem. C.*, 2013, **1**, 8177-8185.

16. M.-H. Tsai, H.-W. Lin, H.-C. Su, T.-H. Ke, C.-C. Wu, F.-C. Fang, Y.-L. Liao, K.-T. Wong and C.-I. Wu, *Adv. Mater.*, 2006, **18**, 1216-1220.
17. A. Chaskar, H. F. Chen and K.-T. Wong, *Adv. Mater.*, 2011, **23**, 3876-3895.
18. F. So and D. Kondakov, *Adv. Mater.*, 2010, **22**, 3762-3777.
19. C.-T. Chen, Y. Wei, J.-S. Lin, M. V. R. K. Moturu, W.-S. Chao, Y.-T. Tao and C.-H. Chien, *J. Am. Chem. Soc.*, 2006, **128**, 10992-10993.
20. X. B. Xu, X. L. Yang, J. S. Dang, G. J. Zhou, Y. Wu, H. Li and W.-Y. Wong, *Chem. Commun.*, 2014, **50**, 2473-2476.
21. Y. Zhou, S. T. Han, G. J. Zhou, W.-Y. Wong and V. A. L. Roy, *Appl. Phys. Lett.*, 2013, **102**, 083301.
22. G. F. He, M. Pfeiffer, K. Leo, M. Hofmann, J. Birnstock, R. Pudzich and J. Salbeck, *Appl. Phys. Lett.*, 2004, **85**, 3911-3913.
23. Q. Wang, J. Q. Ding, D. G. Ma, Y. X. Cheng, L. X. Wang, *Appl. Phys. Lett.*, 2009, **94**, 103503.
24. N. C. Erickson and R. J. Holmes, *Appl. Phys. Lett.*, 2010, **97**, 083308.
25. S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem and K. Leo, *Nature*, 2009, **459**, 234-238.
26. Y. H. Son, Y. J. Kim, M. J. Park, H.-Y. Oh, J. S. Park, J. H. Yang, M. C. Suh and J. H. Kwon, *J. Mater. Chem. C*, 2013, **1**, 5008-5014.
27. X. Yang, H. Huang, B. Pan, M. P. Aldred, S. Q. Zhuang, L. Wang, J. S. Chen and D. G. Ma, *J. Phys. Chem. C*, 2012, **116**, 15041-15047.
28. C. M. Han, Z. S. Zhang, H. Xu, G. H. Xie, J. Li, Yi Zhao, Z. P. Deng, S. Y. Liu and P. F. Yan, *Chem. Eur. J.*, 2013, **19**, 141-154.
29. H. Liu, G. Cheng, D. H. Hu, F. Z. Shen, Y. Lv, G. N. Sun, B. Yang, P. Lu and Y. G. Ma, *Adv. Funct. Mater.*, 2012, **22**, 2830-2836.
30. C. M. Han, Z. S. Zhang, H. Xu, J. Li, G. H. Xie, R. F. Chen, Y. Zhao and W. Huang, *Angew. Chem. Int. Ed.*, 2012, **51**, 10104-10108.
31. D. D. Zhang, L. Duan, Y. L. Li, H. Y. Li, Z. Y. Bin, D. Q. Zhang, J. Qiao, G. F. Dong, L. D. Wang, and Y. Qiu, *Adv. Funct. Mater.*, 2014, **24**, 3551-3561.
32. B. Pan, B. Wang, Y. X. Wang, P. Xu, L. Wang, J. S. Chen and D. G. Ma, *J. Mater. Chem. C*, 2014, **2**, 2466-2469.
33. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
34. J. M. Soler, P. A. Serena and N. Garcia, *Phys. Rev. B*, 1988, **37**, 8701-8706.
35. A. D. Boese and N. C. Handy, *J. Chem. Phys.*, 2002, **116**, 9559-9569.
36. S. Q. Zhuang, R. G. Shangguan, J. J. Jin, G. Tu, L. Wang, J. S. Chen, D. G. Ma and X. J. Zhu, *Org. Electron.*, 2012, **13**, 3050-3059.
37. J. Q. Ding, Q. Wang, L. Zhao, D. G. Ma, L. X. Wang, X. B. Jing and F. S. Wang, *J. Mater. Chem.*, 2010, **20**, 8126-8133.
38. T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker and J. Salbeck, *Chem. Rev.*, 2007, **107**, 1011-1065.
39. M.-H. Tsai, Y.-H. Hong, C.-H. Chang, H.-C. Su, C.-C. Wu, A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius, J. V. Grazulevicius and C.-P. Hsu, *Adv. Mater.*, 2007, **19**, 862-866.
40. H.-H. Chou and C.-H. Cheng, *Adv. Mater.*, 2010, **22**, 2468-2471.