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Efficient blue organic light-emitting devices based on novel anthracence derivatives with pronounced thermal stability and excellent film-forming property

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Abstract

A series of anthracene based blue host materials was synthesized and characterized with respect to their chemical, luminescence, film-forming and thermal properties. The anthracene derivatives are strongly blue fluorescent ($\lambda_f = 435$–445 nm) with high fluorescence quantum yields ($\Phi_f = 0.71$–0.85). All of these compounds have excellent film-forming properties and thermal properties. Organic light-emitting devices (OLEDs) fabricated using these three compounds as blue host emitter and using 0.5-wt% tetra (*t*-butyl) perylene (TBPe) dopant in the emitting layer exhibit good light emitting performance with bright blue emission.

1. Introduction

Since the pioneer work of multi-layered organic light-emitting diode (OLED) by Tang et al. [1], OLED has attracted much attention because of its promising applications in full color flat-panel displays [2–6]. For full color displays, three primary colors (red, green, blue) are necessarily. Many new materials with red, green and blue emitting colors have been developed to meet the requirements [7–18]. Apart from developing high efficient materials, another key factor to develop commercializable OLEDs is to optimizing the device structure. It is well recognized that EL efficiency, CIE coordinates and operational stability of OLED can be significantly improved by using host–guest doped emitter system [3]. Good host materials with high thermal stability, good film-forming properties and high quantum fluorescence efficiency are necessary. Comparing with green and red OLED, there are very limited host materials to choose for blue OLED because of the large band gap required for blue emitting materials. 9,10-Di(2-naphthyl) anthracene (ADN) is a major blue host material, which was first developed by Kodak. Tetra (*t*-butyl) perylene (TBPe) doped in ADN has realized efficient of blue luminance efficiency of 3.5 cd/A, a CIE coordinates of $x = 0.15$, $y = 0.23$ and a half-life of 4000 h with initial light output at 700 cd/m^2 [19]. However, it was also reported that the film forming properties of ADN is not acceptable. The thin film of ADN was found to be morphologically unstable, and could accelerate the decay and reduce the lifetime of the device [20–22].

In this letter, we report the synthesis of a series of anthracene derivatives, namely 2-*tert*-butyl-9,10-di(2-naphthyl) anthracene (TBADN), 2-*tert*-butyl-9,10-di(9-phenanthryl) anthracene (TBDHA) and 2-*tert*-butyl-9,10-di(1-pyryl) anthracene (TBDPA). With the purpose of disrupting the symmetry of ADN so that the problematic crystallization in thin film can be suppressed, a *tert*-butyl group at 2-position of the anthracene moiety is introduced. All three compounds have good thermal stability, good film forming property and show blue emission with high fluorescence quantum yield. We report the fabrication and the performance of blue OLEDs using these

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compounds as blue host emitters. In addition, devices using these compounds as host materials and TBPe as blue dopant are also fabricated and performance are also reported here.

2. Experimental section

2.1. Material synthesis

All solvents are purified by routine procedures. Other reagents are used as received from commercial sources, unless otherwise stated. The three compounds were synthesized by a common procedure as described for TBADN.

2.1.1. 2-tert-butyl-9, 10-di(2-naphthyl) anthracene (TBADN)

To 2-bromo-naphthalene (2.08 g, 10 mmol) dissolved in 10 ml tetrahydrofuran (THF), 6.3 ml of *n*-butyllithium (1.6 M in hexane) was added slowly at −78 °C. The suspension was stirring for two hours at this temperature and 2-*tert*-butylanthraquinone (1.32 g, 5 mmol) in 10 ml THF was added drop wise in half an hour. The suspension was kept stirring for additional 2 h at −78 °C and then left to cool down to room temperature. 300 ml of cold water was added and the reaction was kept stirring for another 2 h. The suspension was extracted by ether several times and the combined organic fractions were dried over magnesium sulfate. Ether was removed in vacuum and the residue was obtained. To this residue, 3 g of SnCl2 and 35 ml of acetic acid were added and the mixture was refluxed for 3 h. After cooling, the precipitate was collected and washed with plenty of water. The compound was dried in vacuum and recrystallized in toluene to obtain 1.7 g white powders. (over all yield of 70%). ^{1}H NMR ($CDCl_3$): δ 1.24(s, 9H), 7.26–7.32(m, 2H), 7.47(d, 1H, $J = 9.2$ Hz), 7.62–7.69(m, 5H), 7.72–7.76(m, 5H), 7.98(d, 2H, $J = 5.7$ Hz), 8.03–8.13(m, 6H). MS: m/e 486(M^+).

Elemental analysis: Calcd. for $C_{38}H_{30}$: C, 93.79; H, 6.21. Found: C, 93.65; H, 6.19.

2.1.2. 2-tert-butyl-9,10-di(9-phenanthryl) anthracene (TBDHA)

(Yield: 67%) ^{1}H NMR ($CDCl_3$): δ1.08(s, 9H), 7.37(m, 8H), 7.62(m, 2H), 7.68–7.81(m, 8H), 7.97–8.01(m, 4H), 8.92(d, 3H, $J = 8.4$ Hz).MS: m/e 586(M^+).

Elemental analysis: Calcd. for $C_{46}H_{34}$: C, 94.16; H, 5.84. Found: C, 93.97; H, 5.83.

2.1.3. 2-tert-butyl-9,10-di(1-pyryl) anthracene (TBDPA)

(Yield: 65%) ^{1}H NMR($CDCl_3$): δ1.06(s, 9H), 7.16–7.19(m, 3H), 7.33(d, 1H, $J = 11$ Hz), 7.41–7.47(m, 4H), 7.57(d, 1H, $J = 9$ Hz), 7.64(d, 1H, $J = 11$ Hz), 7.88–7.98(m, 2H), 8.04–8.09(m, 3H), 8.18–8.32(m, 7H), 8.45–8.50(m, 3H). MS: m/e 634(M^+).

Elemental analysis: Calcd. for $C_{50}H_{34}$: C, 94.60; H, 5.40. Found: C, 94.15; H, 5.35.

2.2. Fabrication and performance of OLED

The absorption and fluorescence spectra were recorded using a Hitachi U-3010 UV–Vis spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. TGA measurements were performed on TGA2050 with a heating rate of 20 °C/min. The HOMO values were measured by using ultraviolet photoelectron spectroscopy (UPS) and the LUMO values were calculated from the HOMO values and the band gaps measured from the UV absorption spectra.

Blue OLEDs were fabricated by vacuum deposition on the top of ITO glass substrate with a sheet resistance of $50\ \Omega/\square$. Before deposition, the ITO substrate was thoroughly cleaned, dried in an oven, and finally treated with UV-ozone. The ITO substrate was then loaded into a deposition chamber with a base vacuum less than 10^{-7} Torr. The devices were fabricated by evaporating organic layers onto the ITO substrate sequentially. The evaporation rate of the organic layer was 2–4 Å/s and the Mg:Ag alloy cathode was prepared by co-evaporation of Mg and Ag at a volume ratio of 10:1. EL spectra and CIE color coordinates were measured with a Spectrascan PR650 photometer and the current–voltage–luminescence characteristics were measured with a computer-controlled Keithley 2400 SourceMeter.

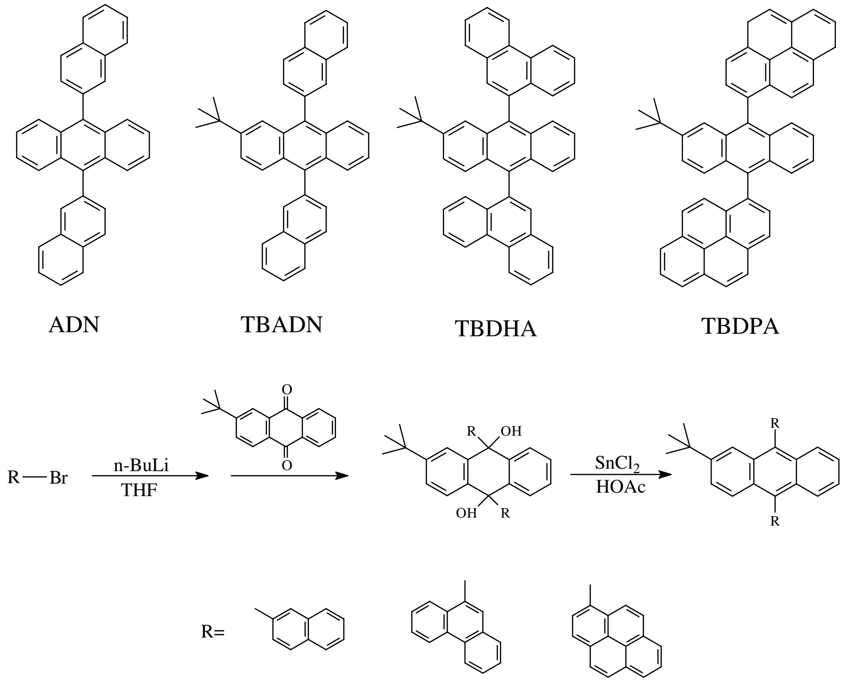
3. Results and discussion

The anthracene derivatives synthesized for this work are shown in Scheme 1 and the synthetic route utilized for these compounds illustrates in the scheme. The three compounds can be synthesized according to the synthetic route with reasonably high yields of 65–70%. Molecular structures of TBADN, TBDHA and TBDPA were confirmed with ^{1}H nuclear magnetic resonance (^{1}H NMR), mass spectrometry (MS) and element analysis (EA).

3.1. Thermal and film-forming properties

The thermal properties of the three compounds were determined by TGA measurements. The TGA scans for the three compounds are shown in Fig. 1 and that of ADN is also included in this figure for comparison purpose. All of the compounds are thermally stable up to 320 °C in air. It is clearly observed that the decomposition temperature (T_d) of TBADN is lower than that of ADN. The decrease of the T_d of TBADN compared with ADN could be attributed to the *tert*-butyl substituted in the 2-position of anthracence. However, the phenanthryl and pyryl instead in the C-9, 10 position of 2-*tert*-butyl anthracene, the decomposition temperature is increased substantially and is much higher than that of ADN. Relevant thermal data of the three compounds and ADN are listed in Table 1.

In order to achieve good light-emitting performance, thin films formed from the materials used in OLED should



Scheme 1. Chemical structure of the anthracene derivatives and Synthetic route of the anthracene derivatives.

be amorphous and uniform. The properties of the film are critical to the performance of OLED and especially have a big effect on the lifetimes of OLED. To study the film-forming properties of the three compounds, thin films with same thickness on indium tin oxide (ITO) were prepared by vacuum deposition. The surface morphologies of these films are characterized by atomic-force microscopy (AFM). For comparison, ADN film at the same thickness was also measured by AFM. The AFM images of the thin films of these compounds are shown in Fig. 2. As shown in Fig. 2a, the surface of ADN film is quite rough and many small crystallites are detected on the surface. The average roughness (R_a) of the ADN film is 8.49 nm. Though some pinholes exist in the TBADN film (Fig. 2b), the R_a of the film is only 0.43 nm. By Comparing TBADN film with ADN film, it is concluded that the film-forming property of TBADN is much better than that of ADN. As illustrated in Fig. 2c and d, the films of TBDHA and TBDPA are quite amorphous and uniform with average roughness of 0.45 nm and 0.44 nm, respectively. It is concluded that by introducing *tert*-butyl and large aryl groups in anthracene can improve the film-forming properties.

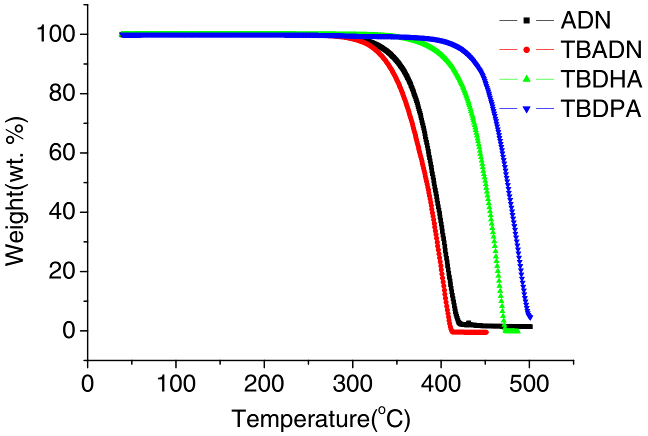


Fig. 1. TGA curves of ADN, TBADN, TBDHA, and TBDPA.

Table 1
Physical data of anthracene derivatives

Compd.	T_d, °C	$\lambda_{max,abs}$, nm	λem(nm)(Φ_f)	λem[a] , nm	HOMO/LUMO, ev
ADN	335	377	427(0.79)	435	5.88/2.87
TBADN	324	377	435(0.79)	443	5.83/2.95
TBDHA	392	376	419, 437(0.71)	430	5.85/2.91
TBDPA	423	377	445(0.85)	457	5.73/2.85

T_d: temperature at 5 wt% loss in TGA measurements. Absorption and emission spectra were measured in CH_2Cl_2 solution.

[a] Film samples. Fluorescence quantum efficiencies were measured in CH_2Cl_2 solution comparable to that of 9,10-dinaphthylanthracene ($\Phi_f \sim 0.9$). HOMO level obtained from UPS experiment. LUMO estimated from the relationship E_g = HOMO–LUMO, where E_g was obtained from the edge of the electronic absorption band.

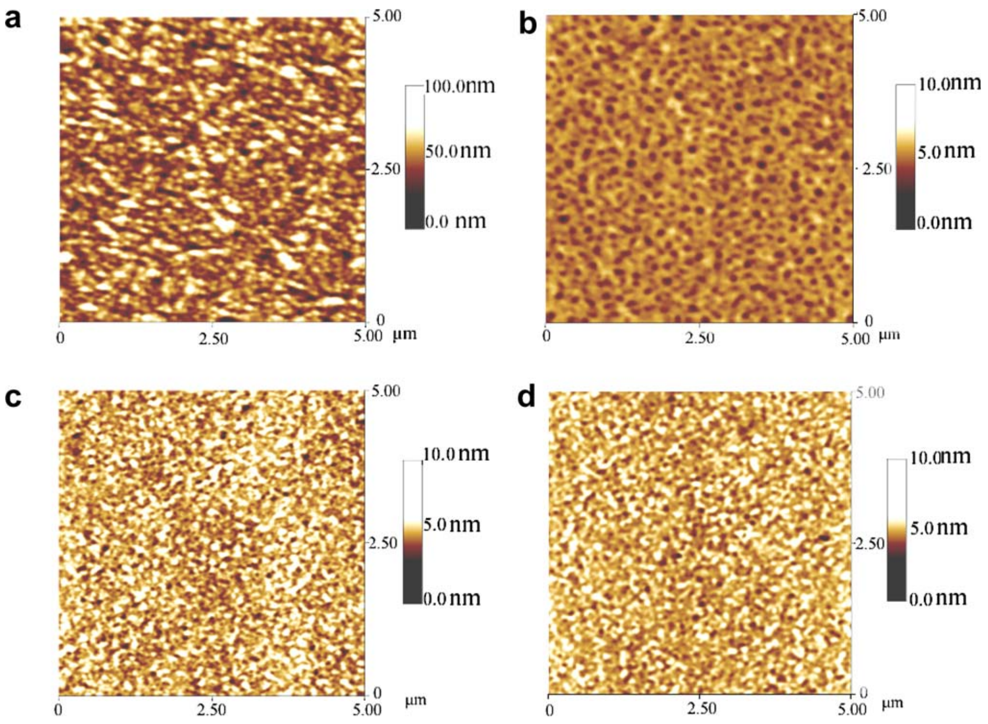


Fig. 2. AFM images of (a) ADN film (b) TBADN film (c) TBDHA film (d) TBDPA film.

3.2. Optical properties

The absorption and fluorescence spectra of the compounds were measured in dilute dichloromethane solution and as a solid film on a quartz plate obtained by thermal evaporation. Photo-physical data of the three compounds and ADN are also listed in Table 1. Absorption and emission spectra of the three compounds are shown in Fig. 3. The absorption spectra of TBADN and TBDHA are almost identical and show the characteristic vibration pattern of the anthracene group ($\lambda_{\max} = 340, 360, 378, 396$ nm) in solution. The absorption spectrum of TBDPA consists of the overlap of characteristic vibration pattern of the pyrene and anthracene group. These results suggest that the substituents of these three anthracene compounds are poorly conjugation between the anthracene core and substituted aryl groups in ground states. Upon photo-excitation, the three compounds are strongly fluorescent in dilute solutions and the emission wavelength ranged from 435 nm to 445 nm. Photo luminescence data of the thin film of the three compounds are list in Table 1. The red shift of the PL spectra between film samples and solution are attributed to the difference of dielectric constant of the environment [23]. Fluorescence quantum yields of the three compounds in dichloromethane solution were measured by using 9,10-diphenylanthracene ($\Phi_f \sim 0.90$) as a calibration

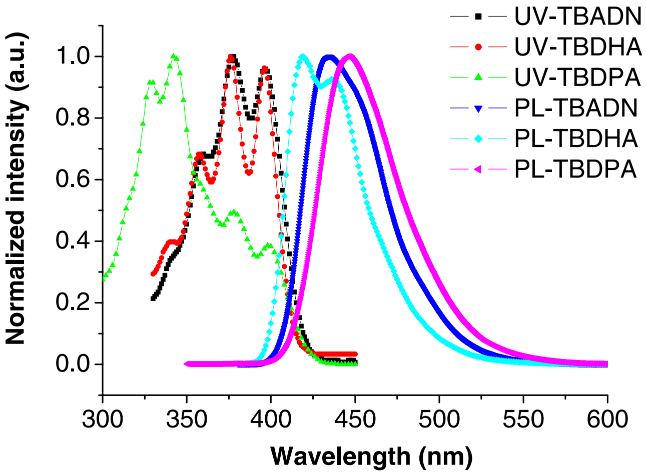


Fig. 3. UV–Vis absorption and PL spectra of anthracene derivatives.

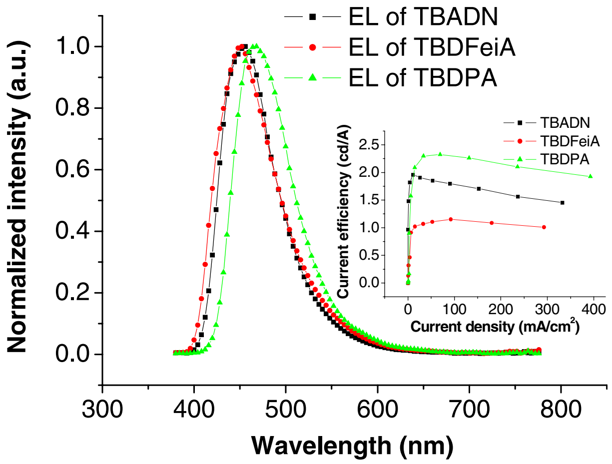


Fig. 4. EL spectra of the anthracene derivatives based devices, inset is current efficiency vs. current density of the anthracene derivatives based devices.

standard [14]. All of the three compounds give bright blue fluorescence with high quantum yields ($\Phi_f = 0.71–0.85$).

3.3. Electroluminescent devices

OLEDs using these three compounds as blue host emitters were fabricated with a configuration of ITO/copper phthalocyanine (CuPc) (15 nm)/ 4,4′-bis[N-(1-naphthyl)-N-phenyl amino] biphenyl (NPB) (50 nm)/host emitter (30 nm)/tris (8-quinolinolato) aluminum (Alq$_3$) (50 nm)/ Mg:Ag (200 nm). In these devices, ITO (indium tin oxide) and Mg:Ag are the anode and cathode, respectively; CuPc is the hole injection material; NPB is the material for the hole transporting layer (HTL); and Alq$_3$ is the material for the electron transporting layer (ETL).

Fig. 4 shows EL spectra of the OLEDs based on these three compounds. EL spectra of the devices based on TBADN, TBDHA, and TBDPA are peaked at 456 nm, 452 nm, and 468 nm, respectively. The similarity of the PL and EL spectra indicates that the EL can be attributed to emission from the radiation decay of singlet-excited state of the three compounds. The current efficiency versus current density characteristics for the three devices is illustrated in the inset of Fig. 4. TBADN based device exhibit a maximum current efficiency of 2.0 cd/A, which is comparable to that of the device based on ADN [19]. TBADN based device exhibits bright blue emission with a purer blue CIE coordinates of $x = 0.16$; $y = 0.14$ as compared to $x = 0.20$; $y = 0.26$ for ADN based device, which is blue green emission [19]. The maximum efficiency of TBDPA based device is higher than that of ADN based device. This increase in efficiency may be attributed to the higher fluorescence quantum efficiency and longer wavelength of emission. EL performances of the three OLEDs are list in Table 2.

To study the EL properties of these three compounds as blue host materials, OLED using these three compounds as blue host and TBPe as blue dopant are fabricated. The device has the following structure of ITO/CuPc (15 nm)/ NPB (50 nm)/blue host: TBPe (30 nm)/Alq$_3$ (50 nm)/ Mg:Ag (200 nm). The blue host doped TBPe emission layer was produced by co-evaporation blue host materials and TBPe simultaneously and the ratio is controlled to be 0.5-wt%. Important electroluminescence performances data of the doped devices are list in Table 2. The current efficiency versus current density characteristic of TBDHA doped TBPe based device is shown in Fig. 5 and the EL spectrum of the doped device are shown in the inset of the figure. Maximum current efficiency of the device is 3.1 cd/A corresponding to 1.5 lm/W with a CIE coordinates of $x = 0.14$; $y = 0.23$. The emission spectrum of the doped device shows only narrow vibronic features that are characteristic of the TBPe dopant and this feature indicates that there is complete energy transfer from host material to dopant. Most important to note in this figure is that the efficiency of the device remains quite stable from a low current density to a higher current density. Doped devices with TBADN and TBDHA have better efficiency and maximum brightness as compared to its corresponding non-doped devices. The efficiency of TBADN doped device is comparable to that of the device based on ADN with a similar device structure, which is shown in Table 2. While doped device using TBDPA is comparable to its un-doped device. This result is partly due to incomplete energy transfer from host to dopant because of the poor overlap between the emission spectrum of host material and the absorption spectrum of dopant molecular.

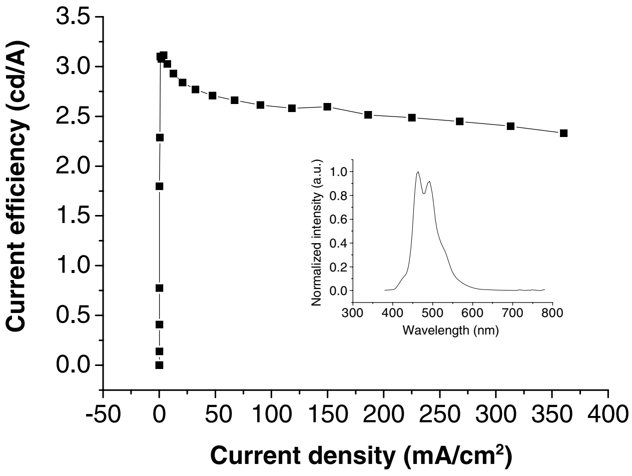


Fig. 5. Current efficiency vs. current density of TBDHA doped device, inset is the EL spectra of the device.

Table 2
Electroluminescence data for the devices based on anthracene derivatives

Compd.		ITO/CuPc(15 nm)/NPB(50 nm)/ Compd(30 nm):dopant/Alq$_3$ (50 nm)/ MgAg(200 nm)		
		Maximum current efficiency cd/A	CIE (x,y) at 20 mA/cm^2	ELλ_{max} (nm)
TBADN	0	2.0	0.16, 0.14	456
	0.5%	3.5	0.15, 0.19	456
TBDHA	0	1.3	0.16, 0.14	452
	0.5%	3.1	0.14, 0.23	464
TBDPA	0	2.3	0.16, 0.21	468
	0.5%	2.3	0.16, 0.24	464
ADN [19]	Non-doped	1.9	0.20, 0.26	460
	Doped	3.4	0.15, 0.23	465

4. Conclusion

In summary, a series of anthracene based blue host materials was synthesized for application in OLEDs. All three compounds reported have good thermal stability and film-forming property. Large aryl group substituted on anthracene moiety could improve the thermal properties. Introduction of *tert*-butyl in anthracene and using large aryl groups substituted anthracene could improve the film-forming properties. All of the anthracene derivatives are strongly blue fluorescent with high fluorescence quantum yields. Organic light emitting devices (OLEDs) fabricated with these three compounds as blue host emitter and using 0.5-wt% tetra (*t*-butyl) perylene (TBPe) doped emitting devices exhibit good light emitting performance with bright blue emission.

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