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Substituent effects in twisted dibenzotetracene derivatives: Blue emitting materials for organic light-emitting diodes



PIĞMËNTS

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1. Introduction

During the past decade, a growing number of researchers have paid intense attention to the preparation of small, conjugated organic molecules with favorable properties including high fluorescence quantum yield in solution and/or solid-state, photochemical, chemical and thermal stability, good packing model, processability and tunability of color because these derivatives can be potentially employed in many aspects such as artificial light harvesting systems, organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), solar cells, biosensors and lasers [1–19]. In general, most of the synthesized molecules with high fluorescent quantum yield in solution exhibit weak or no fluorescence in high concentration solution and solid-state due to molecular aggregation [20]. Two approaches were used to alleviate the high-concentration/solid-state quenching: decorating with bulky and nonplanar molecular structures, for example, Würthner and coworkers synthesized 2,6-

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ABSTRACT

A series of dibenzotetracene derivatives containing different substituents at the 11-,12-positions have been successfully synthesized and characterized. Single crystal X-ray analysis indicates that the new molecules have a twisted structure, which can effectively decrease the intermolecular aggregation in the solid-state. The effect of both substituent and packing on the corresponding physical properties was also investigated. In addition, organic light-emitting diodes doped with 11,12-difluoro-9,14-diphenyl-dibenzo [de,qr]tetracene into the emitter 9,9'-(1,3-phenylene)bis-9*H*-carbazole were fabricated and exhibit good performance.

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diphenylphenoxy substituted perylene bisimide derivative which exhibited strong solid-state fluorescence [21]. Shimizu reported a series of 1,4-bis-(alkenyl)-2,5-dipiperidinobenzenes and their color could be tuned using different substituents at the alkenyl moieties [22]. Moreover, some other bulky groups were introduced into the conjugated frameworks, resulting in suppression of the aggregation in the solid-state [23–26].

Currently, acene and its derivatives are still the major subjects of extensive investigations owing to their high charge-carrier mobilities, interesting opto-electrical properties and potential applications [27–34]. However, some detracting features such as easy oxidation under ambient conditions, high photosensitivity, ease of dimerization and extensive purification hamper their application in organic electronics. Therefore much effort has been directed towards overcome those limitations including random synthesis [35–37] and step-by-step synthesis [27,38,39]. For example, phenyl, triisopropylsilylethynyl (TIPS) and arylthio substituents are utilized to produce persistent acene derivatives [40,41]; phenanthrene and pyrene units can be grafted into acene building blocks, which not only increases their stability and solubility in common organic solvents but also makes them twist to effectively decrease the

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molecular packing in the solid-state. In addition the twisted derivatives can be employed as emitters in organic electronics [42–52].

Until now it has generally been accepted that organic blue emitting material lagged behind the green and red emitters, and thus pursuing high electroluminacent performance blue materials is still a hot topic of the emitting material research.

In this manuscript, a series of dibenzotetracene derivatives (3a-3f) were synthesized and fully characterized (Scheme 1). X-ray diffraction analysis showed these compounds have twisted structures. Here we are more interested in the substituent effects in the conjugated skeletons on the physical properties. Therefore, the electro-optical and thermal properties of these compounds were investigated in detail. In addition a good performing light-emitting device was fabricated, based on compound **3c**, through a vacuum deposition method.

2. Experimental

2.1. Materials and instruments

All chemicals were purchased from J&K, TCI and Acros corporations and used without any purification. Column chromatography was performed on silica gel (200–300 mesh). ¹H NMR and ¹³C NMR spectra were recorded on Bruker 600 MHz spectrometer. MALDI-TOF mass spectra were performed on Bruker Biflex III MALDI-TOF. FT-IR spectra were carried out on a HE-3100 spectrometer. Melting points were recorded on a TX-4 hot-stage apparatus.

UV–Vis absorption and fluorescence spectra were carried out on Shimadzu UV-2550 and RF5300PC spectrometer, respectively. Cyclic voltammograms were measured on CHI 630 A electrochemical analyzer with Pt wire as the counter electrode, Ag/Ag⁺ electrode as the reference electrode and glassy carbon as the working electrode. Tetrabutylammonium hexafluorophosphate dissolved in anhydrous methylene chloride (0.1 M) was used as the supporting electrolyte. The scan rate is 0.1 V/s. X-ray crystallographic data were collected at 298 K with a graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å) on a Bruker APEX II CCD diffractometer.

2.2. Synthesis route

The typical synthetic procedures of **3a**–**3d** are shown as follows. Substituted 2-aminobenzoic acid (**2**) dispersed in degassed 1,2dichloroethane (DCE, 10 mL) solution and isoamyl nitrile (2 mL) were added alternately into a solution of 1,3-diphenylcyclopenta[*e*] pyrene-2-one (**1**) preheated at 90 °C in (DCE, 10 mL). The mixture was stirred overnight and then cooled to room temperature. Brine (60 mL) was added to the reaction mixture. The aqueous phase was further extracted with methylene chloride (30 mL × 3). The collected organic layers were dried with Na₂SO₄ and the solvent was removed under reduced pressure. The crude product was purified through silica gel column chromatography to afford target compound (**3**) as solids.

11-methyl-9,14-diphenyldibenzo[de,qr]tetracene (**3a**, yield, 25%). Mp: 259.4–260.3 °C. FT-IR (KBr): 3048, 2925, 1601, 1494, 1445, 829, 731, 702 cm⁻¹. ¹H NMR (600 MHz, CDCl₃, 298 k): δ = 7.87 (s, 2H), 7.85–7.80 (m, 5H), 7.69 (s, 1H), 7.54–7.52 (m, 10H),



Scheme 1. Chemical structures of compounds 3a-3f.

7.34–7.30 (m, 3H), 2.48 (s, 3H). ¹³C NMR (150 MHz, CDCl₃, 298 K): δ = 142.41, 136.43, 135.88, 135.53, 132.49, 132.39, 132.21, 130.73, 130.49, 130.47, 129.28, 129.08, 128.75, 128.55, 128.31, 128.20, 127.47, 127.45, 126.80, 125.92, 125.57, 125.53, 124.68, 124.63, 22.00. MS (EI): Calc. for C₃₇H₂₄: [M]⁺ 468.19, found: [M]⁺ 468. HRMS (*m*/*z*): calcd for C₃₇H₂₄, 468.1872, found 468.1872.

11.12-dimethoxyl-9.14-diphenyl-dibenzolde.grltetracene (**3b**. vield, 44%). Mp: 311.2-312.6 °C. FT-IR (KBr): 3053, 2926, 1616, 1567. 1498, 1430, 1254, 1205, 1136, 1029, 833, 708 cm⁻¹. ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.88 (s, 2H), 7.85 (d, I = 0.6 Hz, 1H), 7.84 (d, J = 1.2 Hz, 1H), 7.81 (d, J = 1.2 Hz, 1H), 7.80 (d, J = 0.6 Hz, 1H), 7.57–7.51 (m, 10H), 7.35–7.32 (m, 2H), 7.21 (s, 2H), 3.82 (s, 6H). ¹³C NMR (150 MHz, CDCl₃, 298 K): $\delta = 149.44$, 142.76, 132.14, 130.71, 130.42, 129.20, 128.35, 128.25, 127.75, 127.52, 126.83, 125.61, 125.28, 124.57, 105.30, 55.65. MS (MALDI-TOF): Calc. for C₃₈H₂₆O₂: [M]⁺ 514.19, found: $[M]^+$ 514.2. HRMS (m/z): calcd for C₃₈H₂₆O₂, 514.1927, found 514.1925. 11,12-difluoro-9,14-diphenyl-dibenzo [de,qr]tetracene (**3c**, yield, 13%). Mp: 337.1–337.8 °C. FT-IR (KBr): 3053, 1509, 1440, 1255, 883, 824, 736, 707 cm⁻¹. ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 7.89 (s, 2H), 7.88 (d, J = 1.2 Hz, 1H), 7.87 (d, J = 0.6 Hz, 1H), 7.82 (d, J = 0.6 Hz, 1H), 7.80 (d, J = 1.2 Hz, 1H), 7.68 (t, J = 10.2 Hz, 2H), 7.58–7.54 (m, 6H), 7.52–7.50 (m, 4H), 7.33 (t, J = 7.8 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃, 298 K): $\delta = 141.80, 135.95,$ 132.03, 130.76, 129.78, 129.60, 129.44, 128.62, 127.96, 126.88, 126.13, 125.84, 124.77, 112.89, 112.86, 112.80, 112.76. MS (MALDI-TOF): Calc. for C₃₆H₂₀F₂: [M] 490.15, found: [M] 490.1. HRMS (*m*/*z*): calcd for C₃₆H₂₀F₂, 490.1528, found 490.1526.

11,12-dibromo-9,14-diphenyl-dibenzo[de,qr]tetracene (**3d**, yield, 28%). Mp: 329.2–330.4 °C. FT-IR (KBr): 3053, 1606, 1576, 1488, 1440, 1312, 1110, 970, 882, 824, 706 cm⁻¹. ¹H NMR (600 MHz, CDCl₃, 298 K): δ = 8.18 (s, 2H), 7.88 (s, 3H), 7.87 (s, 1H), 7.77 (d, J = 6.0 Hz, 2H), 7.56–7.55 (m, 6H), 7.51–7.50 (m, 4H), 7.35 (t, J = 7.8 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃, 298 K): 141.10, 135.47, 132.18, 131.77, 131.26, 130.76, 130.50, 129.71, 129.44, 128.80, 128.08, 126.89, 126.35, 125.92, 124.82, 122.31. MS (MALDI-TOF): Calc. for C₃₆H₂₀Br₂: [M]⁺ 612.35, found: [M]⁺ 612.0. HRMS (*m/z*): calcd for C₃₆H₂₀Br₂, 609.9926, found 609.9933.

Synthesis of 11,12-dinonylthio-9,14-diphenyl-dibenzo[de,qr] tetracene (3e). Triflic acid (25 µL) was added to a mixture of 11,12dimethoxyl-9,14-dipheny-dibenzo[de,qr]tetracene (3b, 200 mg, 0.39 mmol) and 1-nonanethiol (144 mg, 0.90 mmol) in toluene which was preheated at 110 °C under a nitrogen atmosphere. After stirring for 12 h, the reaction solution was cooled to room temperature. Methylene chloride (30 mL) was added. The solution was then washed with 5% aqueous solution of NaOH (50 mL \times 3) and brine (50 mL \times 3). After the solvents were removed under reduced pressure, the yellow residue was further purified by column chromatography on silica gel with methylene chloride/petroleum ether (3:40, v/v) to afford **3e** as a vellow solid (132 mg, 46%). Mp: 129.1-129.6 °C. FT-IR (KBr): 3053, 2926, 2858, 1597, 1577, 1440, 1118, 1000, 834, 727 cm⁻¹. ¹H NMR (600 MHz, CDCl₃, 298 K): 7.88 (s, 2H), 7.86-7.83 (m, 4H), 7.67 (s, 2H), 7.54-7.53 (m, 10H), 7.35 (t, J = 7.8 Hz, 2H), 2.81 (t, J = 7.8 Hz, 4H), 1.63–1.60 (m, 4H), 1.31–1.26 (m, 24H), 0.90 (t, J = 6.0 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃, 298 K): 142.20, 135.66, 135.27, 132.16, 130.77, 130.49, 130.26, 129.14, 128.95, 128.54, 127.59, 126.82, 125.84, 125.73, 124.66, 124.33, 33.12, 31.87, 29.49, 29.27, 29.21, 29.01, 28.85, 22.64, 14.04. MS (MALDI-TOF): Calc. for $C_{54}H_{58}S_2$: $[M]^+$ 770.40, found: $[M]^+$ 770.3. HRMS (*m/z*): calcd for C₅₄H₅₈S₂, 770.3974, found 770.3971.

Synthesis of 11,12-dicyano-9,14-diphenyl-dibenzo[de,qr]tetracene (**3f**). Cuprous cyanide (90 mg, 1 mmol) was added to a solution of 11,12-dibromo-9,14-diphenyl-dibenzo[de,qr]tetracene (**3d**, 150 mg, 0.25 mmol) in dry NMP. The mixture was stirred under argon at 180 °C for 3 days. After the mixture was cooled to 60 °C, an aqueous solution of $[(NH_4)_2Fe(SO_4)_2]$ was added and stirred for 2 h. After cooling to room temperature, the reaction mixture was extracted with methylene chloride (30 mL × 3) and the combined solvents were removed under reduced pressure. The brown residue was further purified by column chromatography on silica gel with methylene chloride/petroleum ether (2:7, v/v) to afford **3f** as a yellow solid (80 mg, 64%). Mp: 368.8–369.3 °C. FT-IR (KBr): 3053, 2232, 1607, 1548, 1489, 1450, 1313, 912, 834, 707 cm⁻¹. ¹H NMR (600 MHz, CDCl₃, 298 K): 8.41 (s, 2H), 7.97 (d, J = 7.2 Hz, 2H), 7.93 (s, 2H), 7.85 (d, J = 7.2 Hz, 2H), 7.61–7.60 (m, 6H), 7.49–7.47 (m, 4H), 7.40 (t, J = 7.8 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃, 298 K): 139.92, 139.88, 137.15, 135.43, 135.38, 133.72, 132.00, 131.32, 130.91, 130.89, 129.84, 129.81, 129.21, 128.82, 128.80, 127.54, 127.52, 127.07, 127.05, 126.17, 126.15, 125.11, 125.05, 116.49, 116.41, 108.90, 108.82. MS (MALDI-TOF): Calc. for C₃₈H₂₀N₂: [M]⁺ 504.16, found: [M]⁺ 504.0, [M+Na]⁺ 527.0. HRMS (*m*/*z*): calcd for C₃₈H₂₀N₂, 504.1621, found 504.1621.

3. Results and discussion

3.1. Synthesis

As outlined in Scheme 2, compounds 3a-3d were synthesized in one-pot by a [4+2] cycloaddition reaction of dienophile 2 and diene 1 in the presence of isoamyl nitrile in anhydrous 1,2dichloroethane under nitrogen atmosphere. The intermediate 1 was obtained according to the literature [43]. Subsequently, compound 3b was converted to the sulfide 3e via *ipso*-substitution between aryl methyl ether 3b and 1-nonanethiol catalyzed by triflic acid in toluene solution [53]. When compound 3d was treated with 10 equiv of CuCN in *N*-methyl pyrrolidone (NMP) at 180 °C for three days, the substitution reaction was finished to give 3f in 64% yield [54]. The new molecules are light green solids and are readily soluble in common solvents such as methylene chloride, chloroform, toluene, 1,2-dichlorobene (ODCB) and THF. In addition, they are all unambiguously characterized by ¹H NMR, ¹³C NMR spectroscopy and MALDI-TOF mass spectrometry.

3.2. Single crystal structure

To obtain more information about their spatial arrangement, single crystal X-ray measurement were performed. The suitable single crystals for determination (**3a**, **3b** and **3c**) were obtained by slow evaporation of CH_2Cl_2/CH_3OH solutions. The crystal of **3c** is observed as thin needles, while the crystals of **3a** and **3b** are light



Scheme 2. Synthetic procedure of compounds 3a-3f.



Fig. 1. Single crystal structure and packing model of (a) (b) **3a**, (c) (d) **3b** and (e) (f) **3c**. Carbon, oxygen and fluoride atoms are colored in gray, red, green, respectively and hydrogen atoms are omitted for clarity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

green prisms. The crystal structures and packing models (3a-3c) are presented in Fig. 1 and the detailed crystallographic data are given in Table 1. Compounds 3a (CCDC number: 927068) and 3b (CCDC number: 991580) are observed to be triclinic crystal systems, space group P-1, but 3c (CCDC number: 991581) has monoclinic lattice and space group P21. The unit cell parameters of a = 10.6832(17) Å, b = 12.7735 (19) Å, c = 19.528 (3) Å, $\beta = 76.156(3)^{\circ}$ for **3a**, a = 15.657(2) Å, b = 16.770(3) Å, c = 23.094(3) Å, $\beta = 107.491(10)^{\circ}$ for **3b**, a = 12.5285(16) Å, b = 25.530 (3) Å, c = 7.5269 (10) Å, $\beta = 98.477(3)^{\circ}$ for **3c** are also observed. As depicted **3a**-**3c** unambiguously exhibit twisted structures owing to the strong interaction between benzo units in the pyrene unit and the proximal phenyl groups. The twisted angles between the pyrene moiety and naphthalene unit of **3a–3c** are 28.56°, 29.74° and 36.26°, respectively. These results clearly suggest that the different terminal substituents could influence the aggregation in the solid-state. In addition, the intermolecular distances are larger than the sum of van der Waals radii (3.83 Å), and the mismatch arrangements in the single crystals leads to significant decrease of the $\pi - \pi$ intermolecular interactions. Thus weak intermolecular interaction should be taken to account for the high fluorescent yield in the solid-state.

Table 1Crystal data of compounds 3a, 3b and 3c.

| | 3a | 3b | 3c |
|--------------------------|---------------------------------|--|--|
| Empirical formula | C ₃₇ H ₂₄ | C ₃₈ H ₂₆ O ₂ | C ₃₆ H ₂₀ F ₂ |
| Formula weight | 468.56 | 514.59 | 490.52 |
| Crystal system | Triclinic | Triclinic | Monoclinic |
| Space group | P-1 | P-1 | P21 |
| a [Å] | 10.6832(17) | 15.657(2) | 12.5285(16) |
| b [Å] | 12.7735(19) | 16.770(3) | 25.530(3) |
| c [Å] | 19.528(3) | 23.094(3) | 7.5269(10) |
| α | 74.376(3)° | 109.099(10)° | 90° |
| β | 76.156(3)° | 107.491(10)° | 98.477(3)° |
| γ | 87.626(3)° | 96.075(2)° | 90° |
| Volume [Å ³] | 2491.1(7) | 5322.9(15) | 2381.2(5) |
| Z | 4 | 8 | 4 |
| Density (calculated) | 1.249 Mg/m ³ | 1.284 Mg/m ³ | 1.368 Mg/m ³ |

3.3. Optical, electrochemical and thermal properties

The spectroscopic properties of all six dibenzotetracene derivatives were measured at room temperature both in methylene chloride and in solid-state. Clearly, the introduction of different substituents at the 11- and 12-positions brings about an obvious impact on the absorption spectra. Fig. 2a shows that compound **3a**. 3b and 3c have nearly identical absorption profile and maxima (λ_{max}) at 333 nm, 332 nm and 330 nm, respectively, which is ascribed to the $\pi - \pi^*$ transition of the conjugated building block. In comparison, bromo- and alkyl sulfanyl-substituted compounds 3d and 3e display the red-shifted absorption peaks (3d: 330 nm, 342 nm and shoulder peak at 367 nm, 3e: 332 nm, 345 nm). In the case of **3f**, the largest bathochromic shift of absorption maximum to 349 nm and 366 nm is observed. These phenomena can be ascribed to the increase of the conjugation length and the electron density with variation of substituents. The solid-state absorption spectra of compounds 3a-3f are presented in Fig. 2c. The solid-state absorption of compounds 3a-3c and 3f show a red-shift of about

The corresponding fluorescence spectra of these compounds in diluted solution and solid-state were recorded at room temperature. The normalized spectral shapes are shown in Fig. 2b. Compounds 3a-3e in methylene chloride emit blue light with the emission maxima bands at 437 nm, 432 nm, 434 nm 444 nm and 451 nm, respectively. In contrast, the fluorescence spectrum of 3f exhibits emission at 474 nm under the excitation at 349 nm. Note that compounds **3a-3e** have well-defined spectral shapes except for **3f** having a broad band. In addition, the Stokes shifts of all these compounds are over 100 nm, which might be ascribed to the formation of twisted structure that makes the ground and excited states distinct. The quantum yields (Φ_f) of **3a**–**3f** were measured in diluted methylene chloride using 9,10-diphenylanthracene (ethanol solution, $\Phi_{\rm f} = 0.95$) as the reference [56,57]. Compounds **3a–3c** and **3f** display strong fluorescence and the quantum yields are 0.25, 0.43, 0.47 and 0.33, respectively. However, **3d** ($\Phi_f = 0.03$) and **3e** ($\Phi_f = 0.07$) present weak fluorescence, which might be caused by the heavy atom effect, which results into the intersystem crossing to the nonradiative triplet state [58]. The fluorescence spectra of **3a-3f** in thin films are displayed in Fig. 2d. The solidstate emission spectra of compounds 3a and 3f with broad featureless profile are distinctly bathochromically shifted with respect to the case of solution. The emission maxima bands of 3b-3e correlate well with those in methylene chloride, and the intensity order of 3d and 3e is reversed.

The electrochemical behavior of the new molecules were conducted at room temperature in dry methylene chloride solution containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as a supporting electrolyte. As shown in Fig. 3, the



Fig. 2. UV–Vis (a: in methylene chloride, c: in thin film) and fluorescence spectra (b: in methylene chloride, d: in thin film) of compounds (i) 3a, (ii) 3b, (iii) 3c, (iv) 3d, (v) 3e, (vi) 3f.



 $\label{eq:Fig. 3. Cyclic voltammogram of compounds in $TBAPF_6/CH_2Cl_2$ solution. Scan rate = 0.1 V/s (i) 3a, (ii) 3b, (iii) 3c, (iv) 3d, (v) 3e, (vi) 3f.$

oxidation peaks of **3a–3f** are electrochemically irreversible. The first oxidation waves for compound **3a–3f** are observed at 0.92 V, 0.81 V, 1.07 V, 1.06 V, 0.80 V and 1.19 V, respectively. Dibenzotetracene derivatives 3b and 3e are about 0.11 V and 0.12 V, lower than the methyl substituted 3a, indicating of a better electrondonating ability, which is ascribed to the introduction of alkoxyl and alkyl sulfanyl groups. However, the first half-wave oxidation potentials of 3c, 3d and 3f are increased by about 0.15 V, 0.14 V and 0.27 V relative to **3a**, which provides a support of their strong electron-accepting ability. It should be pointed out that the electrochemical oxidations of compounds 3a, 3b and 3e containing electron-donating groups display two one-electron processes corresponding to the formation of dibenzotetracene monoanion and dianion. While only one oxidative wave is observed for **3c**, **3d** and **3f**. Taking the CV experimental results into consideration, one does believe that the obvious oxidation potentials of these derivatives (3a, 3b and 3e) containing electron-donating units arise from the oxidation of substituents (methyl, oxygen and sulfur) and the second redox processes belong to the oxidation of core building blocks. according In addition, to the empirical formula $E_{\text{HOMO}} = -[4.8 - E_{\text{FOC}} + E^{ox}_{\text{onset}}]$ eV, the HOMO energy levels of compounds **3a–3f** were estimated (onset potentials) to be -5.32 eV, -5.21 eV, -5.47 eV, -5.46 eV, -5.20 eV and -5.59 eV, respectively [59,60]. The thermal properties of the new molecules were also investigated through thermogravimetric analysis (TGA) in a nitrogen atmosphere. Their onset temperatures of the weight loss (5%) are ca. 362 °C (3a), 378 °C (3b), 341 °C (3c), 386 °C (3d), 363 °C (3e) and 403 °C (3f), suggesting that they exhibit good thermal stability (Fig. S1).

3.4. Theoretical calculations

Density functional theory (DFT) at the B3LYP/6-31G level was used to optimize their geometry [61] and the plots of HOMOs and LUMOs are presented in Fig. 4. The HOMOs are different between compounds **3a**, **3b**, **3e** containing electron-donating groups and **3c**, 3d, 3f bearing electron-withdrawing units. The molecular orbitals of **3a**, **3b** and **3e** are mainly located on the benzo[*f*]tetraphene moiety and extended up to the methyl carbon, methoxyl oxygen, nonanethiol sulfur atoms, whereas those of 3b, 3c and 3f are delocalized on benzo[*e*]pyrene fragments and the substituents (-F, -Br, -CN) do not contribute to HOMOs. In contrast, the LUMOs of all the compounds are mainly on benzo[*f*]tetraphene segments. Obviously, both the electron-donating (-CH₃, -OCH₃, -SC₉H₁₉) and electron-withdrawing (-F, -Br, -CN) substituents participated in the LUMO orbitals. The HOMO energy levels are in the range of -5.13 to -5.81 eV, which matches well with the cyclic voltammetry data. These results also support the introduction of different substituents in the twisted dibenzotetracenes can effectively tune



Fig. 4. HOMO and LUMO molecular orbitals and energy levels (eV) of compounds 3a-3f calculated by DFT at B3LYP/6-31G.

the energy levels. The energy gap of these compounds were calculated to be -3.72 eV for **3a**, -3.75 eV for **3b**, -3.67 eV for **3c**, -3.62 eV for **3d**, -3.59 eV for **3f** and -3.40 eV for **3f**, which is close to the band gaps determined from the UV–Vis absorption and electrochemical experimental results.

3.5. OLED

Taking the high quantum yield of **3c** into consideration, a **3c**based multilayer OLED was fabricated with the following device structure: ITO/TAPC(20 nm)/mCP:**3c**(%1 or 3%)(30 nm)/TPBi (50 nm)/Liq(2 nm)/Al(150 nm). ITO refers to indium-tin-oxide, TAPC is 1,1-bis[4-[*N*,*N*-di(p-tolyl)amino]phenyl]cyclohexane (host material), mCP is 9,9'-(1,3-phenylene)bis-9*H*-carbazole and TPBi is 1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene (electron transporting material).

As shown in Fig. 5, the doping concentrations are 1% and 3% for **3c** in mCP. The devices emit strong blue light with CIE coordinate of (0.1582, 0.0868) for 1% doping and (0.164, 0.1116) for 3% dopant concentration, corresponding to the deep blue region. The turn on voltages with a brightness of 1.0 cd/m² for 1% and 3% doping **3c** were 4.5 V and 4.3 V, respectively. The devices could reach the same maximum brightness of 1850 cd/m² at 14 V, clearly implies that there is no obvious difference for the luminance with the increase of dopant concentration. In addition, the current efficiency of 3% doping is larger than that of 1% doping concentration of **3c** at the starting low bias (Fig. 5b), indicating a higher carrier injection and transport [62–64]. Evidently, the current efficiency is relatively low, and further optimization should be carried out in the feature.

The device exhibits the electroluminescence spectra at 435 nm and 458 nm, being consistent with the emission spectra in methylene chloride (434 nm and 457 nm) and solid-state (437 nm and



Fig. 5. (a) Luminance versus voltage curve. (b) Current efficiency versus voltage. (c) Normalized EL spectra of compound **3c** upon increasing applied voltage.

460 nm), which implies the emission resulted from the π -conjugated moiety (Fig. 5c). Note that the different applied voltages have negligible effect on the EL spectra from 8 V to 15 V.

4. Conclusions

In summary, we have synthesized a series of novel twisted dibenzotetracene derivatives (3a-3f) with different substituents of the terminal through a classical [4+2] cycloadditional reaction. Crystallographic analysis shows that 3a-3c can form a twisted conformation and stacks in a mismatch manner. The substituents of the terminal can affect the optoelectronic and electrochemical properties of the new molecules. An OLED device employing 3c as the emitter was prepared and good electroluminescent performance suggests they are fascinating blue-emitting materials. Taking the experimental and DFT results into consideration, one does believe that this study could be useful to fully determine the structure–property relationship and provide more chance to predict the rational design and functional property of organic molecular materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.07.007.

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