

Synthesis and Physical Properties of the Conjugated Dendrons Bearing Twisted Acenes Used in Solution Processing of Organic Light-Emitting Diodes

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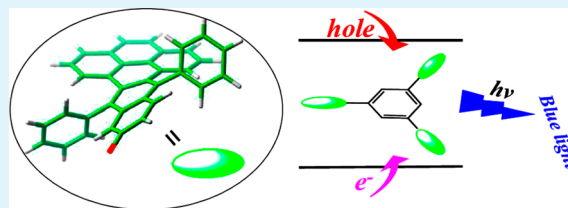
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Supporting Information

ABSTRACT: Five novel organic conjugated derivatives containing multifraction twisted acene units have been synthesized and characterized. These compounds and the model molecule 2-methyl-5,12-diphenyl-6:7,10:11-bisbenzotetracene emit strong blue light in diluted solution with quantum yields of 0.21–0.67, while in the solid state, except for the 1,2,3,4,5,6-hexa(2-(5,12-diphenyl-6:7,10:11-bis(4'-*tert*-butylbenzo)tetracene))benzene, green luminance is seen. The experimental results also indicate that the multifraction structure leads to a significant fluorescence enhancement (over two times) compared to the monomer, which might be attributed to the formation of delocalized excited state in multibranch structures. The quantum-chemical calculation implies that only two branches are involved in formation of the delocalized system for the multibranch derivatives. Furthermore, the organic light-emitting diode (OLED) devices using compounds 1,4-di(2-(5,12-diphenyl-6:7,10:11-bis(4'-*tert*-butylbenzo)tetracene))benzene, 1,3-di(2-(5,12-diphenyl-6:7,10:11-bis(4'-*tert*-butylbenzo)tetracene))benzene, and 1,3,5-tri(2-(5,12-diphenyl-6:7,10:11-bis(4'-*tert*-butylbenzo)tetracene))benzene as emitters exhibit good electroluminescent performance. Our systematic studies might provide more chances to challenge the rational design and synthesis of new- and high-generation branched dendrimers.

KEYWORDS: synthesis, emitter, physical property, acene, twisted structure, OLED



1. INTRODUCTION

Driven by the extensive exploitation in the next-generation electronics, organic small molecules and conjugated polymers have attracted a growing amount of research interest during the past decade. The electrical and electronic devices based on the organic conjugated compounds could exhibit excellent performance, and some of them became commercially available including light-emitting diodes (LED), field effect transistors (FETs), solar cells, and biosensors.^{1–10} Among them, organic LEDs attracted researchers' attention because of their potential use in novel display devices. Until now, as the primary-color-emitting organic materials, the green and red light materials have been extensively exploited in the large-area flat panel displays and can meet the technological standard in industry.^{11–13} However, the blue light counterparts obviously lagged behind owing to various reasons such as the color purity, stability, and lifetime.^{14–17} Thus, efforts have been made to develop the high-performance blue-emitting materials.

It is well-known that the fluorescence of organic luminophores is usually quenched in the solid state compared with in diluted solution, which impedes the practical application

in organic photoelectronics.¹⁸ However, the quenching effect could be solved by aggregation-induced emission (AIE) discovered by Tang and co-workers.^{19–21} On the other hand, it has been found that the bulky substituents decorated on the π -conjugated skeleton could effectively suppress the aggregation in the solid state.^{22–33} On the basis of this idea, a molecule with twisted structure, which has been demonstrated to be effective in inhibiting π -stacking, was utilized here as a building block to construct a conjugated structure with tunable physical properties through proper molecular design.

As is known, polycyclic aromatic hydrocarbons (PAHs) played an important role in organic optical materials. Under the umbrella of PAHs, linear polyacenes have been studied widely both in theory^{34–36} and in experiments.^{37–46} For example, they could serve as active semiconducting surrogates in thin-film transistors.^{47,48} More importantly, the introduction of a single terminal pyrene unit in the oligoacene results in a twisting

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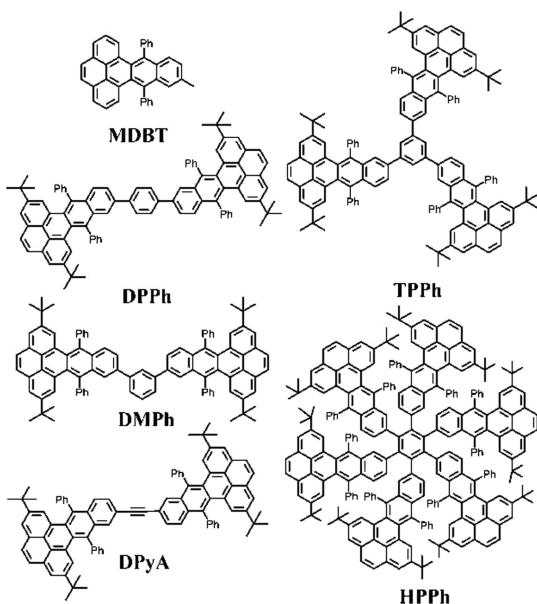
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structure, which improves not only the photoluminescence efficiency but also the thermal stability.^{49–56} For these reasons the twisted structure could be used in design of the emitting material in organic LEDs.

In addition, the well-defined branched conjugated dendrimers usually have the advantages of small molecules and polymers in three-dimensional space, and they might exhibit fascinating physical and chemical properties, which can be useful for various applications in electronic devices. In the present work, we are more interested in the introduction of twisted acenes into the conjugated cores to form a series of dendrons. This synthetic strategy not only decreases the intramolecular and intermolecular interactions but also inhibits electron cyclotron in 3D architecture and promotes the charge separation and transport, which might improve the performance of organic materials in application for OLED devices.

Herein, five novel dendrimer derivatives, **DPPh**, **DMPH**, **TPPh**, **DPyA**, and **HPPh**, were synthesized and characterized (Scheme 1). The synthetic process of the model twisted

Scheme 1. Chemical Structures of MDBT–HPPh

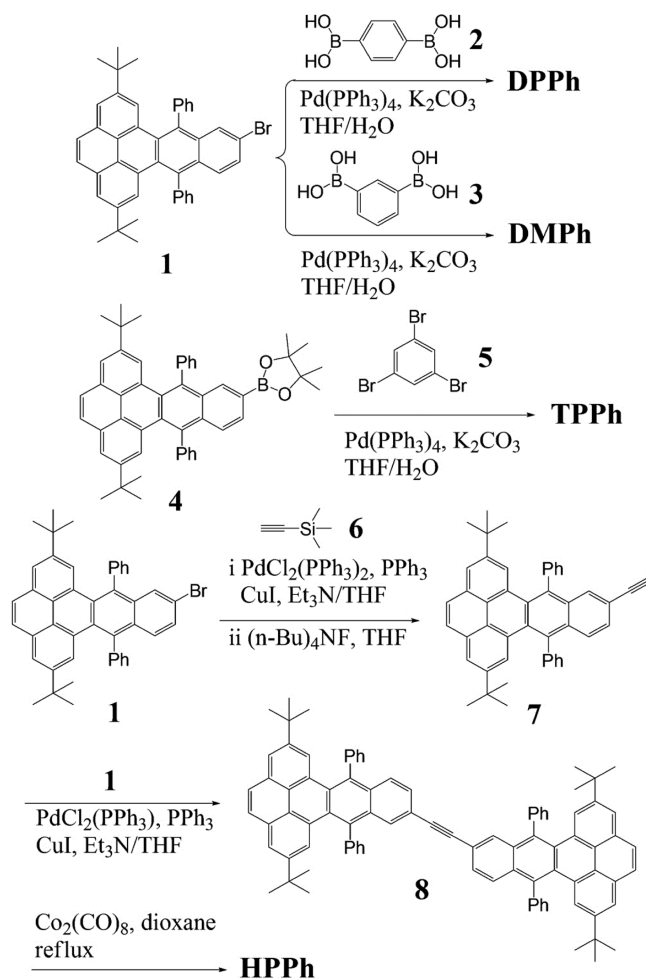


molecule **MDBT** has been reported elsewhere. In the present paper, the photophysical, electrochemical, and thermal properties were also investigated in detail. The results show that these derivatives emit blue light in diluted solution and display good thermal stability. The 3D structures rendered the as-formed molecules easily soluble in organic solvents. Thus, solution-processed OLED devices based on **DPPh**, **DMPH**, and **TPPh** were fabricated, and the results indicate that they are all promising candidates as the emitters.

2. RESULTS AND DISCUSSION

The synthetic procedure of compound **DPPh–HPPh** is outlined in Scheme 2, and the detailed synthesis is summarized in the Supporting Information. Meanwhile, **MDBT**, **1**, and **4** were synthesized elsewhere. The commercially available starting compounds 1,4-benzenediboronic acid (**2**) and 1,3-benzenediboronic acid (**3**) were reacted with compound **1** in the presence of $\text{Pd}(\text{PPh}_3)_4$ and K_2CO_3 in THF/ H_2O solution to afford the target compounds **DPPh** (28% yield) and **DMPH** (44% yield) through the classic Suzuki reaction, respectively.

Scheme 2. Synthetic Procedure of DPPh–HPPh



TPPh was synthesized in the analogous coupling reaction between the single boronic ester **4** and 1,3,5-tribromobenzene (**5**) in moderate yield (64%). It should be noted that the reaction between compound **4** and 1,2,4,5-tetrabromobenzene (**9**) did not produce the tetrasubstituted derivatives (**10**, Figure S1, Supporting Information), which might be mainly due to the steric resistance and inactivation of more bromine atoms in the benzene ring. Thus, we predict that **HPPh** might not be obtained through the Suzuki coupling reaction between **4** and perbromobenzene, and so **HPPh** was synthesized with a modified procedure¹⁷ shown as follows. The Sonogashira coupling reaction of aryl bromide **1** and trimethylsilylacetylene **6** using $\text{PdCl}_2(\text{PPh}_3)_2$, PPh_3 , and CuI as the catalyst in dry THF/ Et_3N solution was performed, and then the as-obtained intermediate was directly treated with $(n\text{-Bu})_4\text{NF}$ to produce **7**. The repeated coupling of **7** and **1** can yield precursor **DPyA** (**8**) in medium yield. **HPPh** was finally produced via $\text{Co}_2(\text{CO})_8$ -catalyzed cyclotrimerization of precursor **DPyA** in a low yield (9%), which might be ascribed to the strong steric hindrance. The as-formed molecules can dissolve in organic solvents such as methylene chloride, chloroform, toluene, 1,2-dichlorobenzene (ODCB), and THF, which were fully characterized by ^1H NMR and ^{13}C NMR spectroscopy and mass spectrometry. We note that until now **HPPh** was only characterized by MALDI-TOF. Although **HPPh** is easily dissolved in deuterated chloroform, further characterization of **HPPh** through NMR spectroscopy could not be carried out,

and the broad peaks were only obtained without obvious splitting.

The absorption and fluorescence spectra of the compounds were investigated in methylene chloride solution (1×10^{-5} M) and solid state at room temperature as shown in Figure 1, and

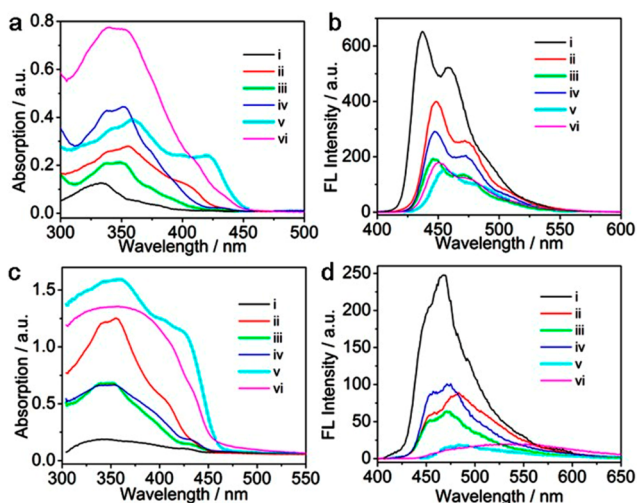


Figure 1. (a) UV-vis absorption, (b) fluorescence spectra in methylene chloride ($c = 1 \times 10^{-5}$ M), (c) solid-state absorption, and (d) solid-state fluorescence spectra of compounds **MDBT** (i, black line), **DPPh** (ii, red line), **DMPH** (iii, green line), **TPPh** (iv, blue line), **DPyA** (v, cyan line), and **HPPh** (vi, magenta line).

the detailed data including the quantum yield, lifetime, and radiative and nonradiative rate constants were presented in Table S1 (Supporting Information). The model compound **MDBT** features the shortest wavelength absorption peak at 334 nm (Figure 1a), while **DPPh**, **DMPH**, **TPPh**, and **HPPh** displayed the analogous red-shifted absorption peaks with the maximum at ca. 337 and 350 nm. These lower energy absorptions are ascribed to the delocalization of the $\pi-\pi^*$ transition moment of the whole molecule. In contrast to the spectra of the other branched molecules using the phenyl unit as the bridge, **DPyA**, where two **MDBT** units are connected through acetylene, has a distinct shoulder peak at 420 nm, indicating a lower energy excited state arisen from the facilitated conjugation by an acetylene bridge. In addition, one could also notice that the relative intensity of absorption increased, and the bands became slightly broadened from **DMPH**, **TPPh**, to **HPPh**. The absorption enhancement might be assigned to the increased moiety number, and the broadened absorption profile might result from the branch–branch interaction according to previous literature.²⁷

To get more information about the properties of these compounds after excitation, quantum calculations were employed. All the calculations were performed in the framework of density functional theory (DFT) using the Gaussian 09 program package.⁵⁷ The structures of all the systems were optimized using the method of the B3LYP/6-31G model, and for the optimized structure the time-dependent DFT calculation was carried out at the same level (B3LYP/3-21G) to get the excited-state information. The excited-state properties were characterized with the three-dimensional (3D) representation of the charge difference density (CDD). The 3D CDD illustrates the electron density difference between the

excited state and ground state, i.e., the distribution of net change as a result of electronic transition.^{58,59}

Figure 2 portrayed the CDD between the first excited state and the ground state for all molecules studied. Here, a

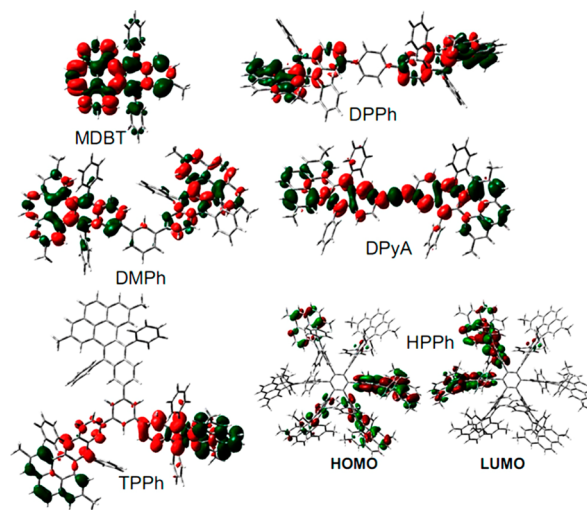


Figure 2. Difference of the electron density (CDD) between the excited state and the ground state of the molecules studied. The negative density (green) corresponds to hole and the positive (red) to electron. For **HPPh**, only the HOMO and LUMO states are shown.

pronounced $\pi-\pi^*$ transition was observed in the brick unit (**MDBT**) in spite of the absence of planar structure due to the steric hindrance of the pyrene unit and phenyl groups. For **DPPh**, **DMPH**, and **TPPh**, with two or three **MDBT** bondings on one phenyl group with a twisted conformation, their CDDs show a characteristic pattern where the CDD is localized and observed only in the wings, indicative of a limited conjugation. That is the cause of the observed absorption small red-shift (<20 nm) in the dendrimers with respect to the monomer. For **DPyA**, the good communication between both sides through the central bridge suggests that the replacement of phenyl by alkyne improves the conjugation effectively⁶⁰ and lowers the excited state energy, resulting in the absorption band at 420 nm. Of course, as mentioned above, the free rotation around alkyne leads to a faster energy relaxation, i.e., shorter excited-state lifetime⁶¹ (Table S1, Supporting Information). Unfortunately, we failed to get the TD-DFT result of **HPPh** due to the limited computation power of the computer. However, the frontier orbital profiles still reveal the conjugation through the adjacent branches as in the case of **TPPh**. It is clear that the significantly increased fluorescence yield for the dendrimers should be ascribed to the conjugation system. Calculated absorption spectra of the compounds match well with measured spectra, verifying the validity of the results (see the Supporting Information, Figure S2).

In addition, we notice that in comparison to the dimer structure of **DMPH**, **TPPh** containing three branches does not exhibit remarkable change of its physical properties as shown in Table S1, Supporting Information. In response, the CDD profile of **TPPh** could be observed on only two wings, and the third one does not participate in charge transfer and can be regarded as unexcited. Moreover, considering the fact that only parts of the wings take part in the frontier orbital formation in the hexamer **HPPh**, we assume that only two branches are recruited in the conjugation system in the present or other

similar multibranch structure, which might have a linear or V geometrical conformation, and more additional branches usually make limited or no contribution to the delocalized excited state.

The fluorescence measurement indicates that all compounds give strong blue emission in methylene chloride. When excited at 334 nm, the emission peaks at 437 and 458 nm are observed for **MDBT** (Figure 1b). For comparison, the fluorescence spectra of **DPPh**, **DMPH**, and **TPPh** show similar profiles but are red-shifted about 11 nm. It can be seen that the emission maxima is shifted to longer wavelengths as one moved to **DPyA** (455 nm, 481 nm). In addition, the vibrational structure diminishes to a certain degree when more **MDBT** units were grafted onto the benzene core from **MDBT**, **DPPh**, **DMPH**, **TPPh** to **HPPh**, which was consistent with the results observed in absorption spectra because of the interchromophore interaction in dendrimers.⁶² The quantum yields of these compounds in methylene chloride were also determined in the range of 0.21–0.67, using 9,10-diphenylanthracene ($\Phi_f = 0.95$ in ethanol)⁶³ as the standard.

The absorption and fluorescence spectra in films are shown in Figure 1c and 1d. The absorption peaks of **DPPh**, **DMPH**, **TPPh**, and **DPyA** exhibited profiles similar to the corresponding ones in organic solvents, which provided evidence that these dendrimer molecules containing a twisted topology structure could effectively suppress the π - π stacking interaction in the solid state.^{22–33} Nevertheless, the absorption bands in films of **MDBT** and **HPPh** became broad along with the obvious disappearance of the defined vibronic structures, which might be attributed to the stacking interaction in the densely packing film. Note that there are no fluorescence spectral shifts for **DPPh**, **DMPH**, and **TPPh** in films, but the solid-state emissions of **MDBT**, **DPyA**, and **HPPh** with the broad featureless characteristics are bathchromically shifted compared to those in diluted solutions.

The fluorescence decay curves of the as-investigated compounds in methylene chloride were measured using a time-correlated single-photon counting (TCSPC) spectrometer and can be fitted satisfactorily with a monoexponential model (Table S1 and Figure S3, Supporting Information). The lifetimes of **DPPh**, **DMPH**, and **TPPh** were close to that of **MDBT**, which inferred that the emitting light might mainly result from the **MDBT** unit. The faster decay of **HPPh** might be assigned to the strong intramolecular coupling interaction of side chromophores.⁶⁴ The free rotation of the acetylene bridge in **DPyA** could lead to the dissipation of energy in the excited state, which might account for the shortest lifetime. Overall, higher Φ_f and larger k_r of **DPyA** make it a promising candidate for OLED applications. However, the broadened emission spectrum with green component reduces its potential application as displaying material.

The cyclic voltammetry measurement was conducted at room temperature in anhydrous methylene chloride having tetrabutylammonium hexafluorophosphate (**TBAPF₆**) as a supporting electrolyte using a three-electrode configuration containing a Pt counter electrode, acetonitrile **Ag/Ag⁺** as reference electrode, and a glass carbon as the working electrode (Figure 3 and Table S2, Supporting Information). The onset oxidation potentials of all compounds were measured as 0.92, 0.77, 0.86, 0.86, 0.81, and 0.79 V, respectively. On the basis of the equation $\text{HOMO} = -([E_{\text{onset}}]^{\text{ox}} + 4.4)$ eV,⁶⁵ the HOMO energy levels were calculated to be -5.32, -5.17, -5.26, -5.26, -5.31, and -5.29 eV for **MDBT**, **DPPh**, **DMPH**, **TPPh**, **DPyA**,

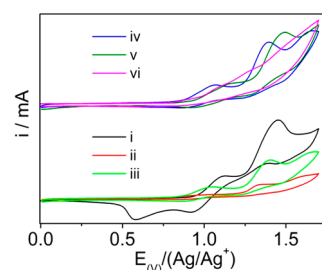


Figure 3. Cyclic voltammograms of compounds **MDBT** (i, black line), **DPPh** (ii, red line), **DMPH** (iii, green line), **TPPh** (iv, blue line), **DPyA** (v, olive line), and **HPPh** (vi, magenta line) in 0.1 M *n*-**TBAPF₆**/**CH₂Cl₂** at a scan rate of 0.1 V s⁻¹.

and **HPPh**, which is in good agreement with the quantum calculation results (Supporting Information Figure S4). Furthermore, thermal properties of **MDBT-HPPh** were studied through thermal gravimetric analysis (TGA) under a nitrogen atmosphere. As shown in Figure S5 and Table S2 (Supporting Information), the onset temperatures of 5% weight loss of these compounds were 370, 462, 241, 232, 444, and 277 °C, respectively, which demonstrates that these molecules have good thermal stability. It should be noted that the linear compounds (**MDBT**, **DPPh**, and **DPyA**) exhibited higher decomposition temperatures than the branched molecules (**DMPH**, **TPPh**, and **HPPh**) owing to the more rigid structures in the linear derivatives. Clearly, taking the photoluminescence, CV, and TGA results into consideration, the as-prepared materials might be exploited as luminescent emitters in OLEDs. Herein, **DPPh**, **DMPH**, and **TPPh** were selected and utilized as active layers in OLEDs.

To assess the electroluminescent behavior, multilayer devices were fabricated according to the sandwich structure using **DPPh**, **DMPH**, and **TPPh** as the emitters, and the results are depicted in Figure 4, Figure 5, and Table S3 (Supporting Information). The device configurations (inset in Figure 4c) are presented as follows: ITO/PEDOT:PSS(40 nm)/**DPPh** or **DMPH** or **TPPh** (50 nm)/TPBi (30 nm)/LiF (1 nm)/Al. The mixture of poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) was spin-coated onto the patterned ITO as a hole

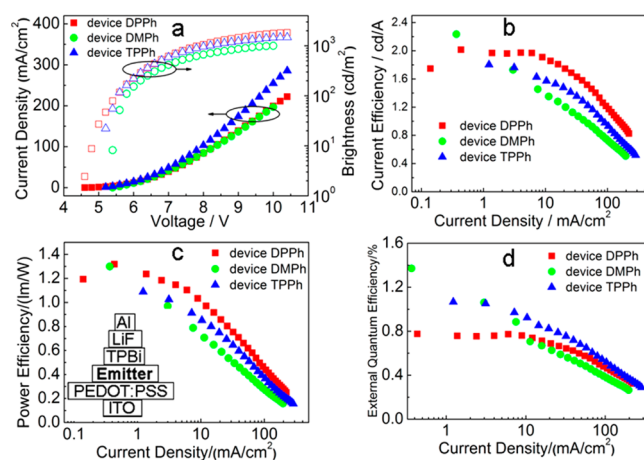


Figure 4. (a) Current density–voltage and brightness–voltage spectra of devices **DPPh**, **DMPH**, and **TPPh**. (b) Current efficiency versus current density of devices. (c) Power efficiency versus current density of devices. (d) External quantum efficiency versus current density of devices.

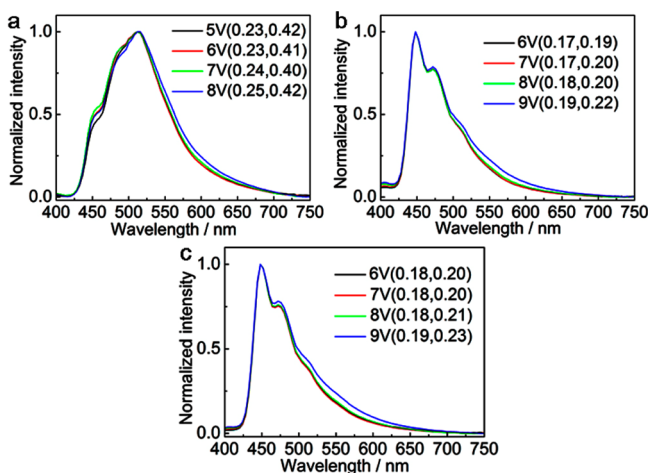


Figure 5. Normalized EL spectra of compounds DPPh (a), DMPPh (b), and TPPh (c) at the increasing applied voltage.

injection layer. Then the emissive layers (EMLs) were spin-coated on top of PEDOT:PSS from chlorobenzene and 1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene (TBPI), which is used as electron transport, and a hole-block layer was deposited by thermal evaporation.

Device DMPPh and device TPPh emitted strong blue electroluminances with the maximum brightness of 678 and 991 cd m^{-2} (bias voltage at 8 V), maximum current efficiency of 2.23 and 1.80 cd A^{-1} , and power efficiency of 1.30 and 1.09 lm W^{-1} , and maximum external quantum efficiency (EQE) of 1.06% and 1.07%, respectively. The corresponding Commission Internationale de L'Eclairage (CIE) coordinates are (0.19, 0.22) and (0.19, 0.23) at the brightness of 1000 cd m^{-2} . The electroluminant maximum bands of DMPPh and TPPh were centered at 447 and 448 nm, which was consistent with the fluorescence spectra in solid films. Meanwhile, the device maximum band at 512 nm of DPPh showed an obvious red-shift compared with its FL peak (481 nm). The maximum brightness of 1057 cd m^{-2} and maximum current efficiency of 2.02 cd A^{-1} were achieved with the CIE coordinate (0.25, 0.41) at the same driving voltage. Clearly, DPPh emitted an intense green light. These results indicate that the branched dendrons could have a lower impact on the emission than that of linear derivatives. In addition, the as-fabricated devices were stable. It can be seen that there were no obvious changes for spectral profiles upon increasing the applied voltages. The turn-on voltages of DPPh, DMPPh, and TPPh were 4.6, 5.4, and 5.2 V, respectively. At present, three materials give efficiency of 2.02, 2.23, and 1.80 cd A^{-1} , a high level for blue LEDs through the solution-processed method.^{66,67} The current density of device TPPh was slightly higher than those of device DPPh and DMPPh, which was indicative of higher charge-transport ability.

3. CONCLUSIONS

In summary, we have succeeded in the preparation of a series of novel linear and branched organic semiconductors containing a twisted structure and performed a systematic study on their optical, thermal, and electrochemical behaviors. The as-obtained compounds showed good thermal and chemical stability. The 3D architecture and molecular rigid tuning by introduction of the twisted acene units in different position could significantly affect their physical properties and spatial arrangement. DPPh, DMPPh, and TPPh were selected as

emitters in OLED devices through solution-processed methods that exhibited good performance. Further work on the fabrication of blue OLED devices based on MDBT and its derivatives through the vacuum evaporation method is on the way in our lab. Our results might provide more opportunities for the rational design and synthesis of the new and high-generation branched dendrimers for application in organic electronics.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, additional spectra, and structural characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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