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Monodisperse Six-Armed Triazatruxenes: Microwave-Enhanced Synthesis and Highly Efficient Pure-Deep-Blue Electroluminescence

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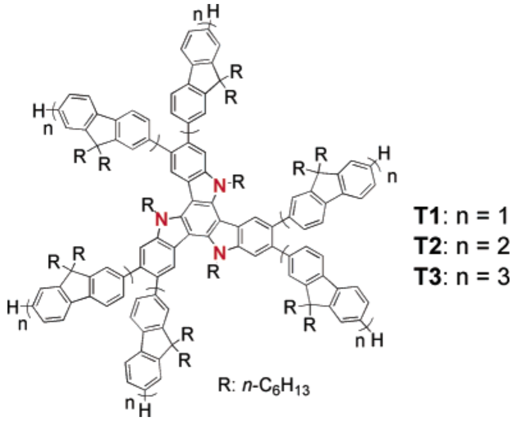
For large-area full-color displays, high-performance blue-light-emitting diodes (LEDs) are highly desired and yet still remain a materials challenge.[1] Fluorene-based oligomers and polymers (PFs) have proven so far the dominant candidates for their high quantum yields and good thermal stabilities;[2] however, a prime problem encountered is the formation of aggregates, excimers, or keto defects, which leads to reduced efficiency and additional green emission.[3] Efforts by us and others on incorporation of sterically hindered units to PFs and constructing cross-linked or hyperbranched PFs have been investigated to address the above problem.[4] The resulting materials are less prone to aggregation in the solid state due to their hindered structures and emit purer blue light, while the device efficiencies have not been much improved. Other efforts on introducing arylamine units (such as carbazole, triphenylamine, or triazole) into PFs have rendered promising results in improving device efficiency as well as color stability,[5] but the emissions are mainly light blue or sky blue, not saturated pure blue.[5c−e] Although deep-blue emission with improved color stability and efficiency has also been demonstrated by some of them, the device performance was found dependent on molecular weights (M_w), which are not readily controllable for polymers.[5b,f]

Scheme 1. General Structures of T1−T3



In these regards, luminescent monodisperse macromolecules with dendritic structures, such as dendrimers[6] and star-type oligomers,[7] which are characterized by well-defined and dendritic structures as well as superior chemical purity, are rather appealing and have recently attracted increasing interest. Highly branched and dendritic structures suppress aggregates and self-quenching and also make the materials form good quality amorphous films.[6a,b] These make them promising electroluminescent (EL) materials. Even so, highly efficient pure-blue LEDs based on this kind of materials have still remained thus far elusive.[6,7]

To obtain high-performance pure-blue LEDs, we herein propose a strategy to develop well-defined dendritic monodisperse macromolecules containing arylamine and fluorene units to improve color stability and purity as well as device efficiency. A family of monodisperse macromolecules with triazatruxene as a core and six oligofluorene arms as the branches has thus been designed as shown in Scheme 1. Triazatruxene, a novel arylamine derivative, is chosen as the core and expected to balance charge injection, transport, and combination for efficient EL.[5b,c] As far as we know, no reports have focused on the optoelectronic properties of its conjugated derivatives. Moreover, it provides multiple reactive sites to construct dendritic com-

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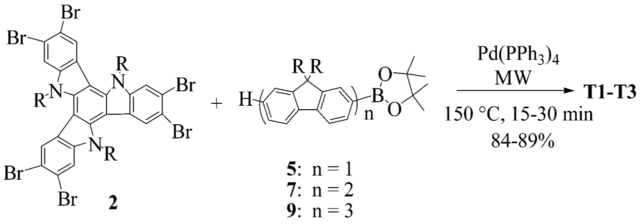
Scheme 2. Microwave-Enhanced Multiple Suzuki Couplings



pounds for suppressing aggregates and excimers. For efficient pure-blue EL, oligofluorenes with a certain length (from monofluorene to terfluorene)[5a] are chosen as the arms in terms of the high quantum yields of PFs.[2] To obtain the final multiarmed compounds conveniently with high purity, a critical parameter for the performance of LEDs,[2a] a powerful microwave (MW)-enhanced multiple coupling methodology has been developed, and desired compounds **T1−T3** (Scheme 1) were thus successfully constructed with high yield and purity. Finally, highly efficient and pure-deep-blue EL has been achieved.

The general synthetic route toward the six-arm triazatruxenes **T1−T3** is shown in Scheme 2. Oligofluorene arms were obtained similarly as the procedures described in the literature.[7c] *N*-Alkylation of **1**[8] with 1-bromohexane in reflux tetrahydrofuran (THF) afforded **2** with good yield. With high temperature and pressure feasible in sealed vessels under MW conditions, where the energy was transferred directly to the reactants plus solvents,[9] the final 6-fold Suzuki couplings were performed successfully. The reactions of **2** with **5**, **7**, and **9** were found completed after holding for less than 30 min at an optimized temperature.[10] Desired products were isolated by column chromatography in ideal yields (>80%), while performing such complex transformations using traditional methods[7a,c] resulted in quite low yields and presented serious challenges to separate the desired products from partially substituted byproducts.

The structures and chemical purities of the final compounds were confirmed by NMR, MALDI-TOF mass spectroscopy (MS), elemental analysis, and gel permeation chromatography (GPC). The MALDI-TOF MS results fitted very well with the calculated values as shown in the Supporting Information (SI). GPC eluting curves of **T1−T3** exhibited a symmetrical narrow peak with a polydispersity of 1.01 (Figure S3), indicating a high purity.

Figure 1a presents the UV−vis absorption and emission spectra of **T1−T3** in dilute THF solution (10^{-6} M). **T1**, **T2**, and **T3** exhibit maximum absorptions at 348.5, 360.0, and 366.5 nm, respectively, and are gradually red-shifted with extending of oligofluorene arms. Photoluminescence (PL) spectra of **T2** and **T3** in THF peak nearly identically at 440 nm, with 11 nm red shifts relative to **T1** (429 nm). **T1−T3** exhibit efficient pure-blue emission both in solution (Φ_{PL} = 72−88%) and in the solid state (Φ_{PL} = 38−75%) (9,10-diphenylanthracene used as a standard, see SI). High PL efficiency, especially for **T3**, indicates that the intermolecular interactions of these starburst oligomers in the solid state are effectively suppressed due to the dendritic hindered structures. Thermal analysis of **T1−T3** by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) reveals that these starburst oligomers exhibit good thermal stability as well as PFs and possess amorphous properties.

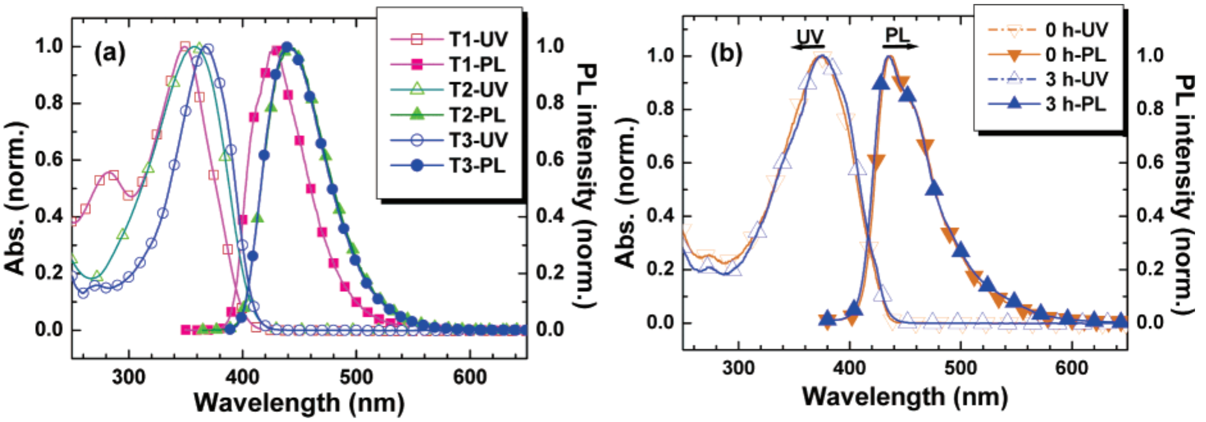


Figure 1. Absorption and PL spectra of (a) **T1−T3** in dilute THF solution and (b) spin-cast **T3** films, before and after annealing at 200 °C in air for 3 h.

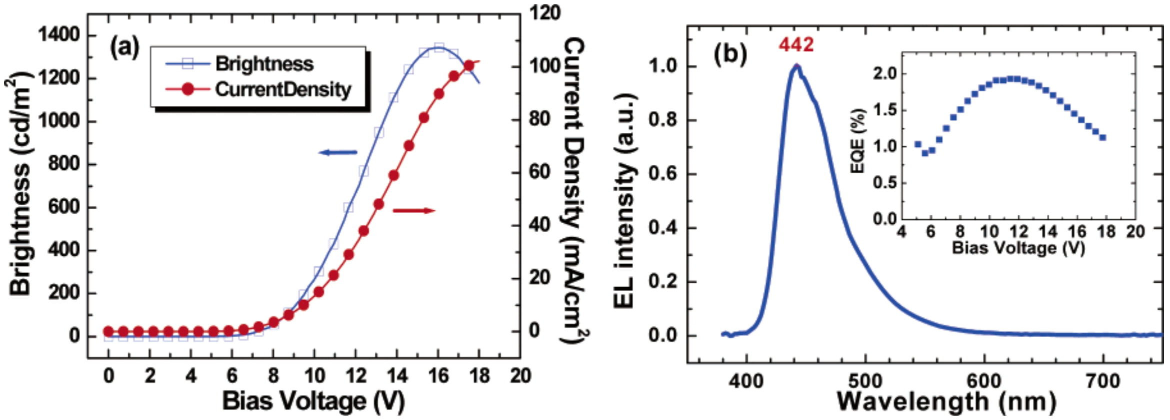


Figure 2. EL characteristics of **T3** with the configuration of ITO/PEDOT:PSS/**T3**/Ba/Al: (a) current density−voltage−brightness characteristics; (b) EL spectrum with the inset showing EQE−voltage characteristics.

The largest compound **T3** (ca. 6.5 nm) with highest thin-film PL efficiency has been selected to investigate thermal spectral stability and EL properties as an example. As shown in Figure 1b, **T3** maintains its color integrity even after annealing at 200 °C for 3 h in air. No additional emission in the range of 500−600 nm is observed, suggesting good thermal spectral stability.

A single-layer EL device based on **T3** is fabricated with the configuration of ITO/PEDOT:PSS/**T3** (spin-cast, 130 nm)/Ba/Al. Preliminary results are shown in Figure 2 and Figures S10 and S11 (SI). The device turns on at a voltage of 5.3 V (>1.0 cd/m^2). The peak brightness of 1343 cd/m^2 is achieved at a low current density of 90 mA/cm^2 (1.46 cd/A, ∼16 V) (Figure 2a). The emission of the device peaks at 442 nm (Figure 2b). The color is pure deep blue with C.I.E. 1931 color coordinates of (0.15, 0.09) (Figure S11), quite close to the National Television System Committee (NTSC) standard blue pixel coordinates of (0.15, 0.07). The maximum external quantum efficiency (EQE) and current efficiency achieve 2.0% and 2.07 cd/A, respectively, with a brightness of 602 cd/m^2 (29 mA/cm^2, ∼11.7 V). Furthermore, the color maintains deep blue, and no additional green emission (which commonly appears for PFs-based LEDs)[3] is observed during the device operation. To our best knowledge, such performance is significantly excellent for oligomer- or dendrimer-based blue LEDs and is comparable with or better than other PFs-based blue LEDs.[1,2,5] These excellent results might be attributed to the combined benefits derived from the design strategy, including that (a) six oligofluorene arms together with the core generate highly efficient pure-deep-blue emission; (b) the novel hindered six-arm architectures suppress the aggregation and self-quenching in the solid state; (c) the triazatruxene core facilitates the charge injection, transport, and combination inside the emissive layer[5b,c] and provides a possible “arylamine effect” for the improved spectral stability (possibly, their intrinsic features of arylamines should be responsible for this effect, such as easily forming relatively stable radical cations and possessing high thermal and photochemical stability, etc.); and (d) the powerful MW-enhanced synthesis provides high purity of the multiarmed compounds with diminished chain defects and impurities that may cause keto defects or quenching of excitons.[3]

To conclude, we have described an effective strategy to achieve highly efficient pure-blue EL via a novel series of six-arm monodisperse macromolecules based on the triazatruxene and fluorene units. MW heating has been found powerful in constructing these materials. The developed MW-enhanced multiple coupling methodology is fast, convenient, and powerful. It is believed to be applicable for the construction of other conjugated multibranched compounds. Highly efficient (2.07 cd/A, EQE 2.0%) and pure-deep-blue EL (C.I.E. $x = 0.15$, $y = 0.09$) with good color stability has been achieved. The exciting preliminary results suggest that this kind of material is considerably promising in achieving high-performance solution-processed blue LEDs. Further optimization of the devices and investigation of the relationships between their chemical structures and optoelectronic properties are in progress.

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Supporting Information Available: Experimental details, additional data, and all characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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