

Synthesis and Properties of a Solution-Processable Truxene Derivative for OLED Devices

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A soluble truxene derivative (**TR1**) attached with triphenylamine at the peripheral position was designed and synthesized. The structure and purity of **TR1** were carefully characterized by ¹H NMR, UV/vis and photoluminescent spectroscopy, mass spectroscopy, and thermal analyses. It exhibited good solubility in common organic solvents and good film forming properties. The maximum absorption and emission peaks in THF solution were shown at 358 nm and 415 nm, respectively. Bright blue emission was observed in both solution and solid states under UV excitation. The fluorescent quantum efficiency was 0.46. The best luminous efficiency was found to be 3.65 cd/A with CIE coordinates of (0.163, 0.260) in electroluminescence devices.

Keywords: Truxene, Blue Emitter, Solution Processed OLEDs, Electroluminescence, Brightness.

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1. INTRODUCTION

The development of economically viable large-area flat panel displays depends largely on the technologies that would replace the traditional vacuum deposition techniques which are now the industry standard for fabrication of such devices. The past decade has seen many researches on solution-processable devices as possible ways to substitute traditional techniques.^{1–3} Solution processability is an old concept in organic devices and its reemergence owes largely to the development of bilayer devices and the developments there after. In recent years there have been a number of studies aimed at investigating the structureproperty relationship regarding truxene derivatives.^{4–7}

This could be regarded as a logical extension of the studies that were carried out in fluorenes and their derivatives owing to efficient blue emitting properties.^{8–10}

Fluorene and its derivatives are among the most promising candidates for blue electroluminescent (EL) materials because of their high photoluminescence efficiency, good charge transport and easy tailorability of properties. Truxene and its derivatives provide properties similar to fluorene molecules on the two dimensional domain and show many interesting attributes from their own properties. For example, the two dimensional structure of the truxene derivatives enables them to have a good arene stacking behavior leading to amorphous nature, which is much desirable in thin film devices. It has also been reported that trialkylated truxenes show self association property which could be useful for device applications.¹¹

The optical properties of blue truxene derivatives can be tuned by incorporating oligothiophene and polyphenylene motifs to their peripheral position.^{8, 12} Fluorene-functionalized truxene derivatives were found to be thermally and electro-chemically stable towards both p and n doping.⁹ These excellent characteristics for truxene-type molecules make them good candidates for blue organic light emitting materials.

In this paper, we report the detailed synthetic method, characterization and optical properties including EL efficiency of new type of truxene derivative as a promising candidate for blue-light emitting devices.

2. EXPERIMENTAL DETAILS

2.1. Materials

All the starting materials were purchased from Aldrich Co., LTD. and used without further purification unless otherwise noted. 2,7,12-Tribromo-5,5',10,10',15,15'-hexahexyl-truxene (1) and triphenylamine boronic acid (2) were prepared according to literature procedures.^{13,14}

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2.1.1. Tr1

Compound 1 (6.0 g, 5.5 mmol), compound 2 (9.2 g, 25.0 mmol) and Pd(PPh₃)₄ (1.2 g, 1.1 mmol) were taken in a flask, degassed and added anhydrous toluene (200 mL). The mixture was stirred at room temperature under N_2 for 30 min. 2 M Na₂CO₃ aqueous solution was added and stirred at 80 °C for 96 hrs. The mixture was cooled and extracted with CH₂Cl₂ and aqueous ammonium chloride. The organic extracts were dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The mixture was purified by column chromatography on silica gel with petroleum ether: CH_2Cl_2 (3:1) to afford Tr1 (3.1 g, 36%). ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.41 (d, 1H, J = 8.1 Hz), 7.62 (d, 2H, J = 6.0 Hz), 7.31–7.02 (m, 14H), 3.05-2.95 (m, 2H), 2.18-2.09 (m, 2H), 0.93-0.87 (m, 14H), 0.70–0.44 (m, 10H); MALDI-TOF m/z: 1577.3 (M⁺), 1493.1 ([M-C₆H₁₃]); Anal. Calcd. for C₁₁₇H₁₂₉N₃ (1577.3): C, 89.09; H, 8.24; N, 2.66. Found: C, 89.09; H, 8.24; N, 2.66.

2.2. General Instrumentation

¹H NMR spectra were recorded on a Varian Oxford 300 NMR Spectroscopy. Chemical shifts were reported in ppm relative to trimethylsilane. Mass Spectra were carried out on a Voyager DE[™] STR Workstation/Mass Spectrometer. Elemental analysis was performed by SNU Basic Science Center. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 14 Spectrophotometer. PL spectra were recorded on an Edinburgh FS920 Steady-State Fluorometer with 450W Xe-lamp. Fluorescence quantum yields were measured by relative actinometry using quinine sulfate ($\Phi_f = 0.546$ in 0.05 M H₂SO₄) as an actinometer.¹⁵ Thermal properties were measured by TA Instruments DSC 2091 Analyzer and Shimadzu TGA 50 Thermogravimetric analyzer under N2 atmosphere at a heating rate of 10 °C/min. The onset degradation temperature (T_d) was measured where 5% weight loss occurs.

2.3. Fabrication of OLED Devices

Poly(3,4-ethylene dioxythiophene) (PEDOT) doped with polystyrene sulfonate (PSS) (Baytron P VP AI 4083, H. C. Starck GmbH.) was spin-coated onto indium-tinoxide (ITO: work function 4.9 eV) and baked at 200 °C in N₂ atmosphere for 5 min. **TR1** dissolved in a mixed solvent of toluene and cyclohexanone (8:2 v/v) as an active blue emitting layer was spin-coated on the top of a PEDOT/PSS layer. A blue emitting dopant, 4,4-bis(2,2diphenylvinyl)-1,1-biphenyl (DPAVBi), can be doped into **TR1** host.¹⁶ After baking of the film at 100 °C for 15 min, aluminum (III) bis(2-methyl-8-quninolinato)-4phenylphenolate (BAlq) was deposited as an electron transporting and hole blocking layer. 1 nm of LiF and 200 nm of Al cathode layers were then deposited on the emitting layer under vacuum below 5×10^{-7} torr. The OLED devices were encapsulated with a glass lid by using a UV curable epoxy resin. Current-voltage-luminescence (I-V-L) characteristics were obtained with a Keithley 238 source-measure unit and a PR650 spectrophotometer.

3. RESULTS AND DISCUSSION

The structure and synthetic route leading to TR1 are summarized in Scheme 1. The preparation of TR1 involves multistep synthesis including 3-fold Suzuki coupling reactions. Specifically, tribrominated truxene core 1 was coupled with 3 equiv. of boronic acid pinacol ester triphenvlamine 2 in the presence of Pd(0) and aqueous Na_2CO_3 to afford TR1. It is readily soluble in common organic solvents as desired. Triphenylamine-based truxene molecules with a stilbene linkage were reported by Xia et al.¹⁰ Although their photophysical properties indicated that the materials are good candidates for the OLED applications, they can be thermally unstable at high temperatures due to the degradation of double bonds. Thus, we designed the TR1 molecule without double bonds. Thermal properties of **TR1** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The DSC analysis did not yield the glass transition temperature (T_{o}) and the melting temperature (T_{m}) , showing that the material possesses amorphous nature. As we expected, the decomposition temperature (T_d) was found at 395 °C indicative of good thermal stability of the material.

The absorption and photoluminescence spectra were measured in THF solution (Fig. 1). The results are also reported in Table I. The absorption trace of **TR1** exhibits a main absorption band at wavelength maximum 358 nm.

The main absorption band arises due to $\pi - \pi^*$ transition from conjugated truxene backbones. Compared to the truxene part that absorbs at around 310 nm, the absorption band of **TR1** is significantly red-shifted indicating that the conjugation is very well localized throughout the molecule. The emission spectrum of **TR1** is dominated by a strong and broad fluorescence band centered at 415 nm. The fluorescence quantum efficiency is 0.46. The absorption and emission spectra in solid states are almost similar to those observed in solution. The absorption and emission



Scheme 1. Chemical structure and synthesis of TR1.



Fig. 1. Absorption (solid) and photoluminescence (dash) spectra of **TR1** in THF solution.

maximum value are about 370 nm and 465 nm, respectively. Electrochemical measurements were carried out to calculate the frontier orbital energies of **TR1**. The results are listed in Table I. The HOMO and LUMO levels of **TR1** are calculated to be -5.28 and -2.25 eV, respectively. Thus, the band gap is found to be 3.03.

A series of OLED devices were fabricated by varying the doping concentration. The emitting layer was prepared by solution-processing as described in the experimental section. A dopant DPAVBi was added into host **TR1** with 0, 1, and 3%. The DPAVBi is a well known material for blue emitting EML as well as a fluorescent dopant.^{17,18} In addition, BAlq was used for the electron transporting and hole blocking layer. Kwong et al. reported that it had excellent hole blocking characteristics in small molecule phosphorescent devices.¹⁸ As shown in Figure 2, the devices were constructed with ITO/PEDOT:PSS/**TR1**:DPAVBi (50 nm)/BAlq (20 nm)/LiF (1 nm)/Al (200 nm). The energy levels of the materials were well matched for OLED device operation.

Figure 3(a) displays the electroluminescence spectra obtained from **TR1** devices with 0, 1 and 3% of DPAVBi. In the neat **TR1**, a strong emission was observed at 482 nm. However in the presence of a dopant, the spectrum was shifted to blue wavelength with a sharper band which seems to increase at higher doping levels. The electroluminescence spectra clearly show that **TR1** is in the blue emitting region and addition of DPAVBi increases the blue properties. Figures 3(b) and (c) exhibit the I-V characteristics and brightness of the OLED devices,

Table I. Optical and electrochemical properties of TR1.

Sample	λ_{abs} (nm)	$oldsymbol{arepsilon}^b$	$\lambda_{ m PL}$ (nm)	$\Phi^c_{ m f}\(\%)$	HOMO (eV)	LUMO (eV)	Band gap (eV)
TR1 ^a	358	16.9	415	0.46	5.28	2.25	3.03

^{*a*}All the measurements were taken in THF solution. ^{*b*}Molar extinction coefficient (×10⁴ M⁻¹ cm⁻¹). ^{*c*}Fluorescence quantum yield measured relative to quinine sulfate ($\Phi_f = 0.546$ in 0.05 M H₂SO₄).



Fig. 2. An OLED device structure and HOMO and LUMO energy level diagram of the materials.

respectively. Turn-on voltage of all the devices was below 5 V. Among the series, the device with neat **TR1** showed best I-V response followed by 3% of DPVBi in the **TR1** system. Maximum current density from neat **TR1** was 167 mA/cm²(@10 V) with the turn on voltage of 4.0 V. 1% of DPVBi:**TR1** exhibited highest brightness over 6000 cd/m².

Figure 3(d) has the luminous efficiency versus applied voltage characteristics for the three optimized OLED



Fig. 3. (a) Electroluminescence spectra, (b) I-V curves, (c) L-V curves, and (d) luminance efficiency of OLED devices based on **TR1** with various dopant ratios.

Table II. Electroluminescence properties of TR1.

Host	Dopant	Turn on voltage (V)	CIE(x,y) @100nit	Max. efficiency (cd/A)
TR1	0% (neat)	4.0	(0.193, 0.312)	2.65
	1% DPAVBi	4.5	(0.169, 0.260)	3.44
	3% DPAVBi	4.0	(0.163, 0.260)	3.65

devices. The neat **TR1** device had a lower turn-on voltage for light emission, which is consistent with the current density characteristics. However, maximum efficiency of the **TR1** device showed 2.65 cd/A of the lower value than that of the 1% and 3% doped DPAVBi in the **TR1** host. Table II summarizes the I-V-L characteristics of the devices. The luminous efficiency of the devices varies depending on the doping concentration. The CIE coordinates of (0.163, 0.260) reveals that **TR1**:DPAVBi blending system can be used as blue emitting materials.

4. CONCLUSION

A truxene derivative, **TR1**, having strong electron donating group at the periphery of the truxene core was synthesized as a promising candidate for blue emitting OLED devices. The UV-vis absorption and emission maxima for **TR1** were observed at 358 nm and 415 nm, respectively. It shows good solubility in common organic solvents, which enable solution casting of the material on OLED devices. The structure of the device was constructed with ITO/PEDOT:PSS/**TR1**:DPAVBi (50 nm)/BAlq (20 nm)/LiF (1 nm)/Al (200 nm). The EL band of **TR1** was observed at around 482 nm, exhibiting the blue emitting properties. The best EL efficiency of the devices obtained by **TR1** was found to be 3.65 cd/A. The CIE coordinates of the corresponding devices were (0.163, 0.260).

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References and Notes

- 1. C. W. Tang, S. A. Van Slyke, and C. H. Chen, *J. Appl. Phys.* 65, 3610 (1989).
- J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature* 347, 539 (1990).
- 3. Y. Yang and A. J. Heeger, Appl. Phys. Lett. 64, 1245 (1994).
- 4. X.-Y. Cao, X.-H. Zhou, H. Zi, and J. Pei, *Macromolecules* 37, 8874 (2004).
- 5. W.-B. Zheng, W.-H. Jin, X.-H. Zhou, and J. Pei, *Tetrahedron* 63, 2907 (2007).
- A. L. Kanibolotsky, R. Berridge, P. J. Skabara, I. F. Perepichka, D. D. C. Bradley, and M. Koeberg, J. Am. Chem. Soc. 126, 13695 (2004).
- Z. Yang, B. Xu, J. He, L. Xue, Q. Guo, H. Xia, and W. Tian, Org. Electron. 10, 954 (2009).
- Y. Geng, S. W. Culligan, A. Trajkovska, J. U. Wallace, and S. H. Chen, *Chem. Mater.* 15, 542 (2003).
- W. Wu, M. Inbasekaran, M. Hudack, D. Welsh, W. Yu, Y. Cheng, C. Wang, S. Kram, M. Tacey, M. Bernius, R. Fletcher, K. Kiszka, S. Munger, and J. O'Brien, *Microelectronics J.* 35, 343 (2004).
- H. Xia, J. He, B. Xu, S. Wen, Y. Li, and W. Tian, *Tetrahedron* 64, 5736 (2008).
- O. Frutos, T. Granier, B. Gomez-Lor, J. Jimenez-Barbero, A. Monge, E. Gutierrez-Puebla, and A. M. Echavarren, *Chem. Eur. J.* 8, 2879 (2002).
- J. Pei, J.-L. Wang, X.-Y. Cao, X.-H. Zhou, and W.-B. Zhang, J. Am. Chem. Soc. 125, 9944 (2003).
- X.-Y. Cao, H. Zi, W. Zhang, H. Lu, and J. Pei, J. Org. Chem. 70, 3645 (2005).
- 14. A. L. Kanibolotsky, R. Berridge, P. J. Skabara, I. F. Perepichka, D. D. C. Bradley, and M. Koeberg, J. Am. Chem. Soc. 126, 13695 (2004).
- 15. H. Du, R. A. Fuh, J. Li, A. Corkan, and J. S. Lindsey, *Photochem*.
 - & Photobio. 68, 141 (1998).
 - 16. K. O. Cheon and J. Shinar, Appl. Phys. Lett. 81, 1738 (2002).
 - 17. C. Hosokawa, M. Eida, M. Matsuura, K. Fukuoka, H. Nakamura, and T. Kusumoto, *Synth. Met.* 91, 3 (1997).
 - X.-Y. Jiang, Z.-L. Zhang, X.-Y. Zheng, Y.-Z. Wu, and S.-H. Xu, *Thin Solid Films* 401, 251 (2001).
 - C. Hosokawa, H. Higashi, H. Nakamura, and T. Kusumoto, *Appl. Phys. Lett.* 67, 3853 (1995).

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