

Synthesis of New Multibranch Chromophores with Strong Light-emitting in Solution and in PMMA Film

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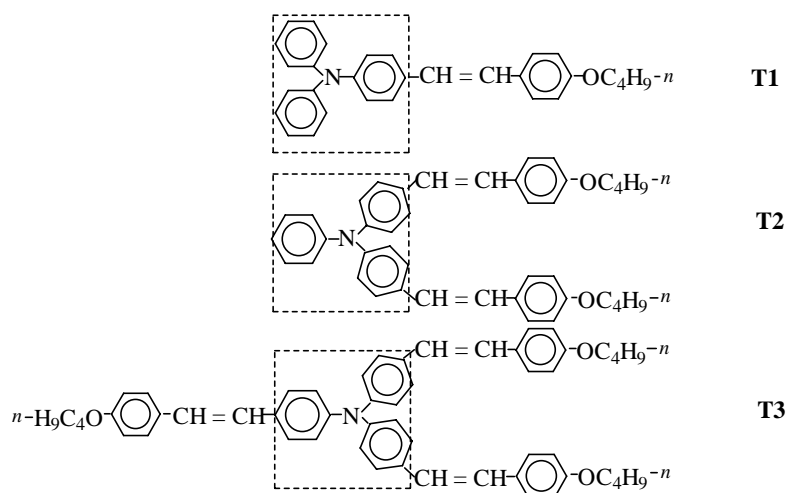
Abstract: Three new chromophores with triphenylamine as molecular focal point bearing one, two, or three 4-(*n*-butyloxy styryl) group(s) at the periphery respectively, (named as **T1**, **T2**, and **T3**) have been synthesized and characterized. It is interesting to find that the fluorescence quantum yield increases from **T1** (0.489), to **T3** (0.535), and to **T2** (0.628) in cyclohexane, meanwhile the lifetime for **T3** is shorter than **T1** and **T2**, which is an important characteristic for applications in light emitting diode. Also PMMA (polymethyl methacrylate) film doped with **T3** gives stronger fluorescence than **T1**, and **T2**. Cyclic voltammetry showed that **T3** exhibited lowest oxidation potential of -0.52 V vs SCE, suggesting its better hole-transport property.

Keywords: *Trans*-4-(4'-*n*-butyloxy-styryl) triphenylamine, *trans*-4,4-di (4'-*n*- butyloxy- styryl)-triphenylamine, *trans*-4,4,4-tris(4'-*n*-butyloxy styryl)triphenylamine, photo- luminescence, film.

Light emitting diode (LED) based on small molecules or polymer is currently the object of wide interest from a scientific and technological points of view. Generally, EL efficiencies (η_{EL}) are related to PL efficiencies (η_{PL}) by the relationship: $\eta_{EL} \leq 0.75\eta_{PL}$. And it is much lower than this upper limit, because of problems inherent to device fabrication, such as unmatched charge injection and inefficient luminescence film of the materials, *etc.* Thus, the requirement for electroluminescent devices to display light EL efficiencies is to synthesize materials with high PL quantum yield and suitable electroactive property.

In this letter, the synthesis and photoluminescence properties of new multibranch chromophore based on triphenylamine as molecular focal point bearing 4- (*n*-butyloxy styryl)group(s) at the periphery, that is, monosubstituted triphenylamine (abbreviated as **T1**), disubstituted triphenylamine (abbreviated as **T2**), and trisubstituted triphenylamine abbreviated as **T3**) have been reported. The results obtained have shown that triphenylamine with three conjugated substituents reduces the fluorescence lifetime of the chromophore but the fluorescence quantum yield remains high. Meanwhile, labelled chromophore exhibits suitable electroactive property. The newly synthesized molecular structures are shown as follows:

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Experimental

IR spectra, nuclear magnetic resonance spectra, mass spectra and element analysis were measured on a Nicolet FT-IR 5DX, GCT-TOF, INOVA400 and Perkin 2400 (II) instruments, respectively. Absorption spectra in cyclohexane with $d_0 = 1.0 \times 10^{-5}$ mol/L have been measured in quartz cuvettes of 1 cm path on UV-Vis TU-1800 recording spectrophotometer. Photoluminescence spectra of combined fluorescence lifetime & steady state spectrometer (Edinburgh FLS920) in different solvents and in PMMA film were recorded. The slits are 0.5 mm for solutions and 1 mm for the film. Cyclic voltammetry (CV) were recorded at a scanning of 100 mV/s and performed in 0.10 mol/L solution of tetrabutylammonium chloride (Bu_4NCl) in deoxygenated DMF.

Trans-4-(4'-*n*-butyloxystyryl) triphenylamine (**T1**): A flask fitted with magnetic stirrer and condenser was charged with 12.0 g (0.05 mol) 4-butyloxybenzyl bromide, then 13.0 g (0.05 mol) of triphenylphosphine in the presence of fresh distilled toluene were added. The reaction was refluxed for 2 hours, then cooled to room temperature and filtered. The white powder was recrystallized from ethanol in high yield to give colorless crystals 4-butyloxybenzyl (triphenyl)phosphonium bromide **1**.

Under anhydrous and oxygen-free conditions, a solution of 1.2 g (0.01 mol) of potassium *tert*-butoxide in *tert*-butyl alcohol was added by a dropping funnel into a flask in the presence of 2.2 g (0.008 mol) diphenylamino benzaldehyde¹ and 4.1 g (0.008 mol) of **1** in dry THF solution at room temperature. After finishing the addition, the mixture was refluxed for 40 hours. Cooled to room temperature and poured into warm water, neutralized with dilute hydrochloric acid, extracted with chloroform, and dried over anhydrous magnesium sulfate, then removed the solvent by evaporation, and purified through column chromatography. 1.77 g pale yellow needle crystals (**T1**) were obtained, yield 52.8 % mp 132-134 °C. ν (KBr)/ cm^{-1} 3030.00, 2956.83, 2868.33, 1604.38, 1588.53, 1511.06, 1492.55, 1281.83, 1247.89, 1173.04, 966.24 (*trans*-CH=CH). Mass spectrum: m/z 419.88 (M^+), 362.95, 346.95, 324.08, 268.13, 212.18. ^1H NMR (CDCl_3 , ppm) : δ 0.964-0.999 (t, 3H, $J=7.0$ Hz, CH_3), 1.453-1.527 (m, 2H, $J=7.0$ Hz, CH_2), 1.740-1.810

(m, 2H, $J=7.0$ Hz, CH₂), 3.965-3.997 (t, 2H, $J=6.6$ Hz, OCH₂), 6.870-6.891 (d, 2H, $J=8.4$ Hz, Ar-H), 6.930-6.951 (d, 2H, $J=8.4$ Hz, Ar-H), 6.983-7.118 (m, 10H, C₆H₅), 7.235-7.274 (d, 2H, $J=15.6$ Hz, *trans*-CH=CH), 7.325-7.373 (d, 2H, $J=8.4$ Hz, Ar-H), 7.405-7.426 (d, 2H, $J=8.4$ Hz, Ar-H). Element analysis (%): Calcd. C, 85.74; H, 6.91; N, 3.33. Found C, 85.39; H, 7.03; N, 3.32.

Trans-4,4'-bis(4-*n*-butyloxystyryl)triphenylamine (**T2**): Following the similar method of our previous work¹ to get 4, 4-triphenylamine dialdehyde. **T2** can be synthesized according to the same method as **T1**, just 4, 4-triphenylamine dialdehyde was added instead of diphenylamino benzaldehyde. Yellow crystals of **T2** were obtained. Yield 45% and m.p.:148-152°C. ν (KBr)/cm⁻¹ 3026.11, 2952.64, 2868.83, 1607.03, 1510.65, 1311.17, 1254.76, 1176.69, 965.00 (*trans*-CH=CH). Mass spectrum: m/z 593.33 (M⁺), 536.26, 480.20, 432.22, 240.60. ¹H NMR (CDCl₃, ppm): δ 0.965-1.001 (t, 6H, $J=7.2$ Hz, CH₃), 1.473-1.526 (m, 4H, $J=7.4$ Hz, CH₂), 1.741-1.811 (m, 4H, $J=7.4$ Hz, CH₂), 3.967-3.998 (t, 4H, $J=6.2$ Hz, OCH₂), 6.873-6.894 (d, 4H, $J=8.4$ Hz, Ar-H), 6.937-6.953 (d, 4H, $J=6.4$ Hz, Ar-H), 6.994-7.173 (m, 5H, C₆H₅), 7.235-7.274 (d, 2H, $J=15.6$ Hz, *trans*-CH=CH), 7.365-7.386 (d, 4H, $J=8.4$ Hz, Ar-H), 7.411-7.432 (d, 4H, $J=8.4$ Hz, Ar-H). Element analysis (%): Calcd. C, 84.99; H, 7.25; N, 2.36. Found C, 85.40; H, 7.56; N, 2.34.

Trans-4,4',4''-tris(4-*n*-butyloxystyryl)triphenylamine (**T3**): 2.2 g (0.008 mol) of **T1**, 5.8 g (0.08 mol) of dimethyl formamide and 30 g (0.2 mol) of phosphorus oxychloride were mixed in the vessel under the ice bath. Then the mixture was refluxed for about one hour, poured into ice water, neutralized, filtered and purified through column chromatography on silica gel. The orange oil or very soft solid of *trans*-4-(4'-*n*-Butyloxystyryl) triphenylamine di-aldehyde **2** was got.

7.0 g (0.014 mol) of **1** and 2.85 g (0.006 mol) of **2** were mixed following the similar method to synthesize **T1**, then the crude product was purified through column chromatography for several times until one speckle to be shown on the thin-layer chromatography with different eluents. After removing the solvent, yellow needle crystals with m.p. 110-115°C (0.95 g) of **T3** were got in yield 20.75%. ν (KBr)/cm⁻¹ 3027.97, 2956.12, 2930.27, 2869.75, 1604.69, 1509.87, 1247.90, 1174.08, 963.87 (*trans*-CH=CH). Mass spectrum: m/z 767.963 (M⁺), 711.023, 654.087, 595.237. ¹H NMR (CDCl₃, ppm): δ 0.965-1.001 (t, 9H, $J=7.2$ Hz, CH₃), 1.454-1.511 (q, 6H, $J=7.6$ Hz, CH₂), 1.758-1.796 (m, 6H, $J=7.6$ Hz, CH₂), 3.966-3.998 (t, 6H, $J=6.4$ Hz, -OCH₂-), 6.874-6.894 (d, 4H, $J=8.0$ Hz, Ar-H), 6.947-6.963 (d, 4H, $J=6.4$ Hz, Ar-H), 7.013-7.034 (d, 4H, $J=8.4$ Hz, Ar-H), 7.058-7.079 (d, 4H, $J=8.4$ Hz, Ar-H), 7.234-7.324 (q, 6H, $J=12.0$ Hz, *trans*-CH=CH), 7.378-7.399 (d, 4H, $J=8.4$ Hz, Ar-H), 7.415-7.434 (d, 4H, $J=7.6$ Hz, Ar-H). Element analysis (%): Calcd. C, 84.45; H, 7.482; N, 1.825. Found C, 84.18; H, 7.556; N, 1.834.

Results and Discussion

Fluorescence quantum yields (referenced to quinine sulfate²) are 0.628 (**T2**) > 0.535 (**T3**) > 0.489 (**T1**) in cyclohexane (1×10⁻⁵ mol/L). Photoluminescence spectra of PMMA film (~2 μ m thick) doped **T1**, **T2**, and **T3**, respectively, coating on ITO glass exhibit (the spectra not shown here) that **T3** displays the strongest light-emitting while **T2** gives the

secondary and **T1** is the weakest. Solvents effect of photoluminescence shows that all chromophores are sensitive to the solvent polarity and give both red shift and gradually decreased fluorescence with an increase of solvent polarity. All of these suggest that the twisted intramolecular charge transfer (“TICT”) model³⁻⁴ mechanism may predominate during photophysical process of these chromophores. And the noncoplanarity of the molecules induced by three *n*-butyloxy-styryl groups likely hamper the “TICT” state that may go against fluorescence behavior⁵. Cyclic voltammetry (CV) curves have shown that all chromophores are quasi-reversible redox process and possess lower oxidation potential *vs* SCE, -0.46 V for **T1**, $+0.17$ V for **T2**, and -0.52 V for **T3**, respectively. Furthermore, **T3** exhibits two consecutive oxidation peak potentials, indicating two oxidation steps that may correspond to the successive formation of dications and the labelled chromophore tends to facilitate hole transport. Further investigations of these chromophores for OLED applications are in progress.

Acknowledgments

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