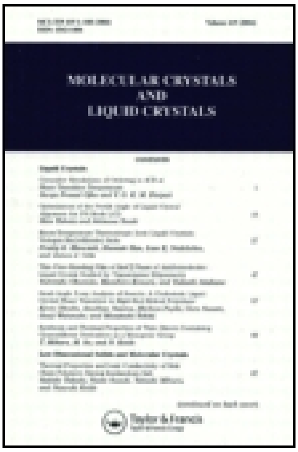

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Synthesis and Characterization of Di-hexyl-fluorene and Triphenylamine Based Copolymers Containing 1,3,4-Oxadiazole Pendants

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Synthesis and Characterization of Di-hexylfluorene and Triphenylamine Based Copolymers Containing 1,3,4-Oxadiazole Pendants

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*π-Conjugated polymers, poly(N-(4-(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)-phenyl)-4-(9,9-dihexyl-9*H*-fluoren-2-yl)-*N*-phenyl-benzenamine (TPAOXDPF) and poly(N-(4-butylphenyl)-4-(9,9-dihexyl-9*H*-fluoren-2-yl)-*N*-phenylbenzenamine) (TPAPF), were synthesized for light emitting diode application. The electron transporting unit, conjugated 1,3,4-oxadiazole, is attached on the main chain as a pendant. The copolymers were thermally stable up to 393°C. The electroluminescent (EL) device based on TPAOXDPF (ITO/TPAOXDPF/Al) has an efficiency of 0.018 cd/A, which is significantly higher than that of the device based on TPAPF (ITO/TPAPF/Al) (0.008 cd/A). This is due to that 1,3,4-oxadiazole pendants improve the electron transporting properties in the emissive layer.*

Keywords Dihexylfluorene; 1,3,4-oxadiazole; polymer light emitting diode; triphenylamine

Introduction

Polymer light emitting diodes (PLEDs) have made dramatic progress in comparison to LEDs based on inorganic materials over the past years [1]. The electroluminescent (EL) device has the potential to provide an innovative low cost technology for backlight, illumination, and display application [2–6]. For the device efficiency point of view, balanced charge injection and transport are essential to get high external quantum efficiency (EQE) in PLED. Small molecules or polymers containing triphenylamine (TPA) units are one of the most widely used hole-transport materials because they are easily oxidized to form stable radical cation and relatively high-lying ionization potential [7]. 1,3,4-Oxadiazole (OXD) was aroused special interest in recent years due to its high electron affinity and good thermal stability. It has

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been successfully incorporated into polymers to apply as the electron-transport materials in multilayer PLEDs. The attempts to simultaneously incorporate TPA and OXD into small molecules have been proven to be an effective way to obtain materials with high luminescent efficiency [8–13]. This study reports the preparation and characterization of a series of polyfluorene (PF) derivatives with TPA segment in polymers backbones and OXD group as a pendant to polymer main chain. The OXD moieties were linked to the phenyl rings of TPA so that the electron affinity of the polymer would be improved. Therefore, improvement of electron affinity helps recombination in the emissive layer. We also synthesized poly[(N-(4-butylphenyl)-4-(9,9-dihexyl-9H-fluoren-2-yl)-*N*-phenylbenzen-amine)] (TPAPF) to compare the optical, electrochemical, and electroluminescent properties with TPAOXDPF. We investigated the fundamental optical, electrochemical and electroluminescent properties as well as the role of OXD in the improvement of EL efficiency of the polymer.

Experimental

Materials

All chemicals were purchased from Aldrich Chemical Co. or Tokyo Chemical Industry (TCI) Chemical and used as received. Tetrahydrofuran (THF) and dichloromethane (DCM) were distilled from sodium hydride.

Synthesis of 4-Diphenylamino-benzonitrile (1)

A portion of 1.99 g (82.8 mmol) of NaH in 80 mL of anhydrous *N,N*-dimethylformamide (DMF) was stirred for 30 min at 0°C. A portion of 12.74 g (75.3 mmol) of diphenylamine and 10.03 g (82.8 mmol) of 4-fluorobenzonitrile was slowly added into a slurry of NaH in DMF under nitrogen gas atmosphere. After completion of addition of diphenylamine and 4-fluorobenzonitrile, the reaction mixture was stirred at 170°C for 15 hours. The reaction mixture cooled down to room temperature, 100 mL of water was added into the reaction mixture then extracted with 100 mL of DCM three times. The combined organic layer was dried over anhydrous magnesium sulfate then the solvent was removed using a rotary evaporator under reduced pressure. The crude product was purified by flash chromatography using *n*-hexane:ethyl actate (EA) (4:1). The white solid product was 14.5 g (64.1%). MS [M^+], m/z 300. mp: 157~159°C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.91 (d, 2H), 7.42 (d, 4H), 7.15 (m, 4H), 7.12 (d, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 151.81, 146.18, 133.35, 129.97, 126.36, 125.33, 119.91, 119.81, 102,77. Anal. Calcd. for $C_{15}H_{14}N_2$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.76; H, 5.02; N, 10.28.

Synthesis of Diphenyl-[4-(2H-tetrazol-5-yl)-phenyl]-amine (2)

A portion of 10.0 g (37.0 mmol) of compound **1**, 2.89 g (44.4 mmol) of NaN_3 and 2.37 g (44.4 mmol) of NH_4Cl was added into a 50 mL of DMF. The reaction mixture was stirred at 120°C for 24 hours. The reaction mixture cooled down to room temperature then neutralized with 5% HCl. The reaction mixture poured to 1000 mL of water then the precipitate was filtered. The crude precipitate was purified by recrystallization from methanol. The white solid product yield was 8.12 g (76.3%). MS: [M^+], m/z 319. mp: 221~224°C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.36 (d, 2H), 7.14 (t, 4H), 6.86 (m, 2H), 6.73 (d, 4H), 6.64 (d, 2H). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): δ 161.75, 146.25, 129.79, 128.15, 125.25, 124.33, 121.04. Anal. Calcd. for $C_{19}H_{15}N5$ S: C, 72.83; H, 4.82; N, 22.35; S. Found: C, 72.65; H, 4.55; N, 22.23.

Synthesis of {4-[5-(4-tert-Butyl-benzyl)-[1,3,4]oxadiazol-2-ylmethyl]-phenyl}-diphenylamine (3)

A mixture of 10.00 g (31.91 mmol) and compound **2**, 7.53 g (38.29 mmol) of 4-tert-butylbenzoyl chloride of pyridine was stirred for 5 hours at room temperature. A portion of 100 mL of water was added into the reaction mixture then the precipitate was filtered. The crude precipitate was purified by recrystallization from methanol. The white product yield was 14.0 g (82.1%). MS: [M^+], m/z 493. mp: 313–315°C. ^{1}H-NMR (400 MHz, DMSO-d_6, ppm): δ 7.27 (d, 2H), 7.03 (m, 6H), 6.91 (d, 2H), 6.82 (t, 2H), 6.52 (d, 4H), 6.47 (d, 2H), 1.49 (s, 9H). ^{13}C-NMR (100 MHz, DMSO-d_6, ppm): δ 164.59, 164.29, 155.24, 151.08, 146.91, 129.78, 128.18, 126.84, 126.18, 125.84, 124.55, 121.55, 121.40, 116.49, 35.25, 31.33. Anal. Calcd. for $C_{30}H_{27}N_3O$: C, 81.15; H, 6.60; N, 8.87; O, 3.38. Found: C, 80.98; H, 6.58; N, 8.49; O, 3.16.

Synthesis of Bis-(4-bromo-phenyl)-{4-[5-(4-tert-Butyl-benzyl)-[1,3,4]oxadiazol-2-yl]-phenyl}-amine (4)

A solution of 2.25 g (12.62 mmol) of NBS in 10 mL of DMF was added dropwise to a solution of 2.49 g (5.26 mmol) of compound **3** in 30 mL of DMF under nitrogen atmosphere at 5°C for a period of 30 min. After being stirred for 6 hours at room temperature, a portion of 100 mL of water was added into a reaction mixture then extracted with 100 mL of EA three times. The combined organic layer was washed with aqueous sodium bisulfite (10 wt.%) and then dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by column chromatography on silica gel using EA/DCM (1:4). The yield of light yellow solid was 0.86 g (18.1%). MS [M^+], m/z 633. mp: 252–254°C. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.31 (m, 8H), 7.01 (d, 2H), 6.61 (m, 2H), 6.47 (d, 4H), 1.48 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 164.62, 163.31, 155.32, 151.15, 146.93, 129.82, 128.23, 126.88, 126.22, 125.89, 124.59, 121.53, 121.41, 116.43, 35.29, 31.35. Anal. Calcd. for $C_{30}H_{25}Br_2N_3O$: C, 60.31; H, 4.41; Br, 25.89; N, 6.81. Found: C, 60.12; H, 4.19; N, 6.36.

Polymerization of N-(4-(5-(4-tert-Butylphenyl)-1,3,4-oxadiazol-2-yl)phenyl)-n-(4-(9,9-dihexyl-2-methyl-9H-fluoren-7-yl)phenyl)-4-methylbenzenamine (TPAOXD-PF)

A portion of 0.39 g (0.5 mmol) of compound **4**, 0.2511 g (0.5 mmol) of 2-(2-(1,3,2-dioxaborinan-2-yl)-9,9-dihexyl-9H-fluoren-7-yl)-1,3,2dioxaborinane, tetrakis-(triphenylphosphine palladium) ($Pd(PPh_3)_4$) (0.01 mmol), several drops of surfactant (aliquat 336) were dissolved in a mixture of 3 mL of degassed toluene and 2 mL of degassed K_2CO_3 (2 M aq). The mixture was stirred at 80°C for 2 days under argon atmosphere. At the end of polymerization, 0.1 mL of 1-bromo-4-tertbutylbenzene was added as a monofunctional end-capping reagent. After being stirred the mixture for 12 hours, 60 mg of phenyl boronic acid was added and stirred for 12 hours. After cooling to room temperature, the reaction mixture was poured into 250 mL of methanol. The precipitate was filtered and dissolved in 40 mL of chloroform, extracted with 100 mL of deionized water three times. The organic layer dried over anhydrous $MgSO_4$ and the solvent was removed by evaporation under reduced pressure. The polymer was dissolved in small amount of DCM and poured into a stirred methanol. The polymer was collected by filtration and dried under vacuum for 12 hours. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.09–8.01 (br, Ar-*H*), 7.89–7.83 (br, Ar-*H*), 7.71–7.68 (br, Ar-*H*), 7.48–7.46 (br, Ar-*H*), 7.35–7.34 (br, Ar-*H*), 6.92–6.91 (br, Ar-*H*), 6.61–6.60 (br, Ar-*H*), 6.41–6.39 (br, Ar-*H*), 2.01–1.99 (br, -CH_2CH_2-), 1.41–1.40 (br, -C(CH_2)$_4$), 0.98–0.97 (br, -CH_3).

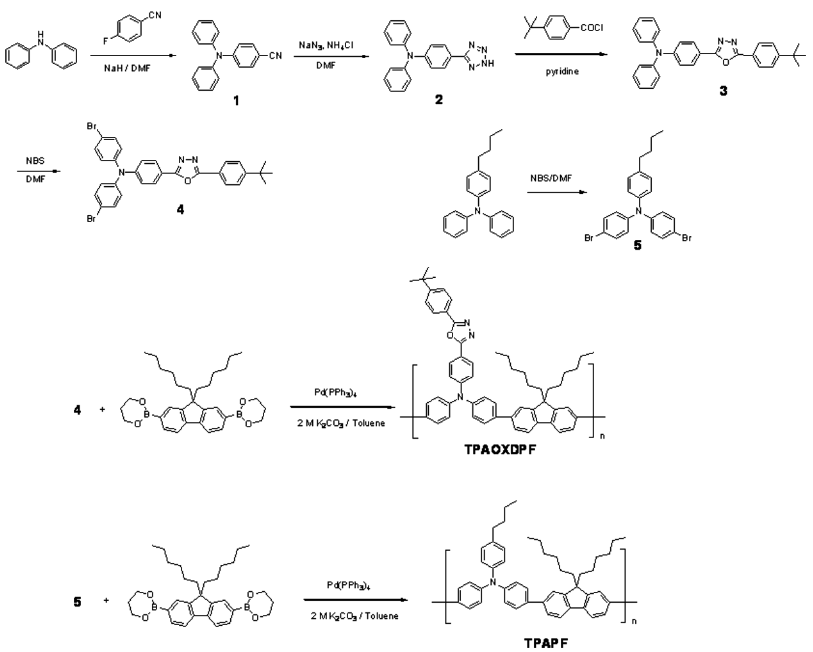
Polymerization of N-(4-Butylphenyl)-n-(4-(9,9-dihexyl-2-methyl-9H-fluoren-7-yl)phenyl)-4-methylbenzenamine (TPAPF)

TPAPF was synthesized by the Suzuki coupling reaction between bis-(4-bromophenyl)-(4-butyl-phenyl)-amine and 2-(2-(1,3,2-dioxa-borinan-2-yl)-9,9-dihexyl-9H-fluoren-7-yl)-1,3,2-dioxaborinane. Similar conditions were used as in the polymerization of TPAOXDPF. ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 8.02–7.97 (br, Ar-*H*), 7.77–7.62 (br, Ar-2*H*), 7.60–7.37 (br, Ar-2H), 7.28–6.84 (br, Ar-8H), 6.63–6.45 (br, Ar-6H), 2.68–2.64 (br, -CH_2), 1.98–1.68 (br, -CH_2- -CH_2-), 1.39–1.34 (br, (CH_2)$_9$), 1.03–0.97 (br, -CH_3).

Results and Discussion

The synthetic routes to the monomers and polymers are shown in Scheme 1. All the compounds were characterized by ^{1}H-NMR, ^{13}C-NMR and MASS. The polymerization was conducted by the well known Suzuki coupling reaction. The chemical structure of TPAOXDPF and TPAPF were confirmed by the ^{1}H-NMR. The number average molecular weights of TPAPF and TPAOXDPF measured by GPC were 11,300 and 8,200 with polydispersity index (PDI) 1.98 and 1.83, respectively. As shown in Figure 1, the degradation temperature (T_d, the point of 5% weight loss of polymer) of TPAPF and TPAOXDPF appeared at 346 and 393°C, respectively, in the TGA thermogram. TPAOXDPF exhibited higher T_d than that of TPAPF because of OXD side chain on the polymer backbone.

As shown in Figure 2, TPAPF solution in chloroform and film show the absorption maximum (UV_{max}) at 386 and 388 nm, respectively. The PL maximum (PL_{max}) wavelength of TPAPF solution and film are appeared at 432 and 435 nm, respectively. TPAOXDPF solution in chloroform and film show UV_{max} at 374 and 376 nm, respectively (Fig. 3). The PL_{max} of TPAOXDPF solution and film are appeared at 451 and 478 nm (Fig. 3), respectively. The band gap energies figured out from the UV-Vis spectrum of TPAOXDPF and TPAPF films are 2.87 and



Scheme 1. Synthesis of monomer and polymer.

2.90 eV, respectively. This indicates that the OXD pendant in TPAOXDPF does not affect the band gap energy significantly.

The HOMO energy level estimated from the oxidation onset potential of TPAPF is −5.28 eV, which is slightly lower than that of TPAOXDPF (−5.13 eV).

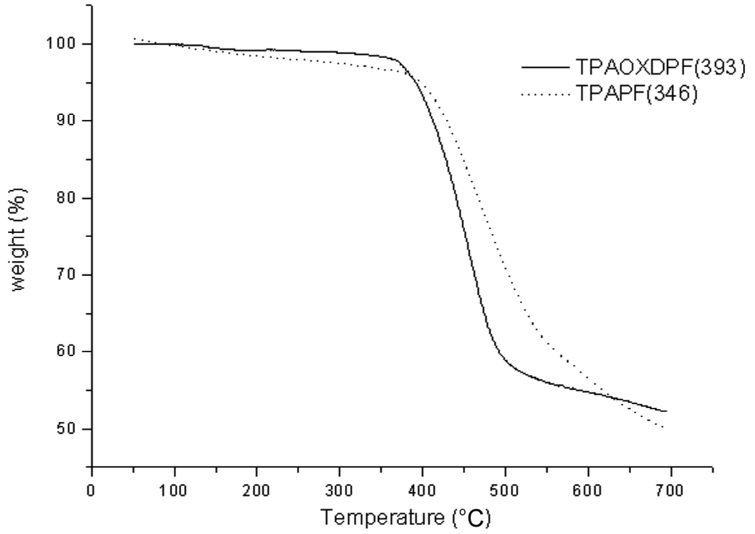


Figure 1. TGA thermograms of the copolymers. (Conditions: N_2 flow, heat from 50°C to 700°C at 10°C/min).

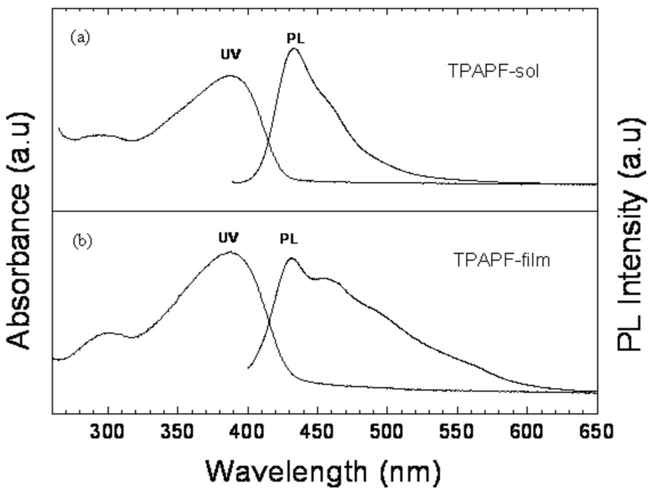


Figure 2. UV-Vis and PL spectra of TPAPF (a) solution and (b) film.

One can also noticed that the OXD pendant does not affect the HOMO level significantly. The LUMO energy level of TPAPF and TPAOXDPF are −2.38 and −2.26 eV, respectively. The optical and electrochemical properties of copolymers were summarized in Table 1.

In order to investigate EL properties, single layer light emitting diodes (ITO/polymer/Al) were fabricated based on copolymers. As shown in Figure 5, typical rectification characteristics are observed in the devices. The maximum brightness and efficiency of the device based on TPAOXDPF (167 cd/m^2 and 0.018 cd/A) are higher than those of TPAPF (42.1 cd/m^2 and 0.008 cd/A) based device, indicating that very strong electronegative OXD group in the side chain improved electron transporting property. The enhanced device performance is result of the more

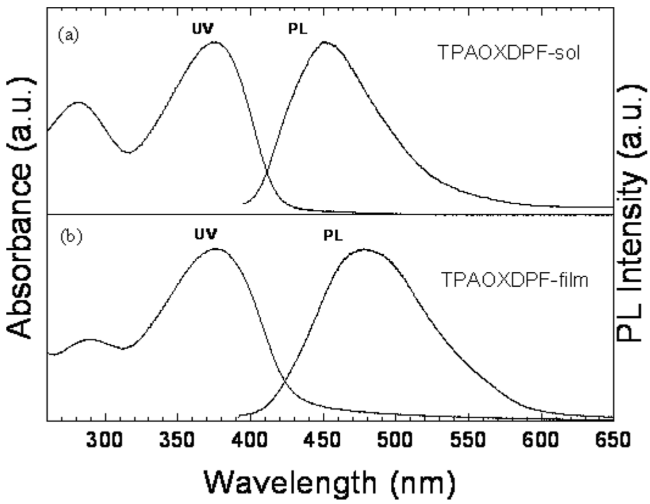


Figure 3. UV-Vis and PL spectra of TPAOXDPF (a) solution and (b) film.

Table 1. Summary of photophysical properties of the polymers

	$\lambda_{\text{max, solution}}$ (nm)		$\lambda_{\text{max, thin film}}$ (nm)		Energy levels		
	UV	PL	UV	PL	HOMO[a] (eV)	LUMO[b] (eV)	E_g[c] (eV)
TPAPF	386	432	388	435	−5.28	−2.38	2.90
TPAOXDPF	374	451	376	478	−5.13	−2.26	2.87

[a] Estimated from the onset oxidation potential in the cyclic voltammogram.
[b] Estimated from the HOMO and Egap.
[c] Figured out from the absorption edge from the UV-Vis spectrum.

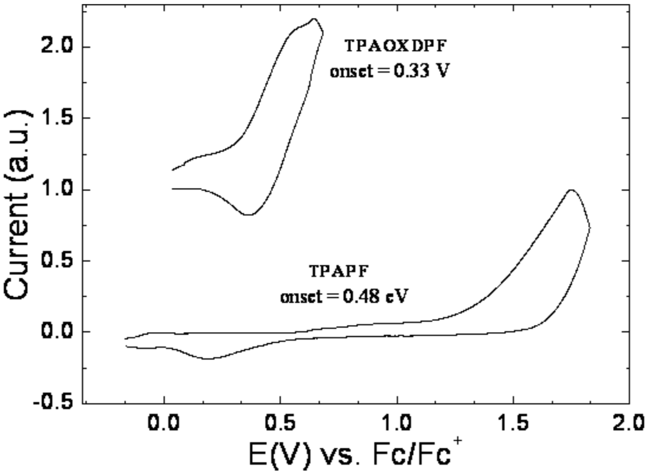


Figure 4. Cyclic voltammogram of TPAOXDPF and TPAPF. CVs were performed in polymer solution in 0.1 M Bu_4NPF_6 solution in DCM at a scan rate of 100 mV/s.

balanced injection rates of both carriers due to the simultaneous introduction of TPA and 1,3,4-oxadiazole pendant into polymer.

Conclusion

We synthesized new PF derivatives with TPA and OXD. These copolymers exhibited good solubility in common organic solvents and good thermal stability. The efficiency of the device based on TPAOXDPF was higher than that of the device based on TPAPF. It was suggested that the hole-electron recombination processes were facilitated in the emitting layer by of OXD pendants.

Acknowledgment

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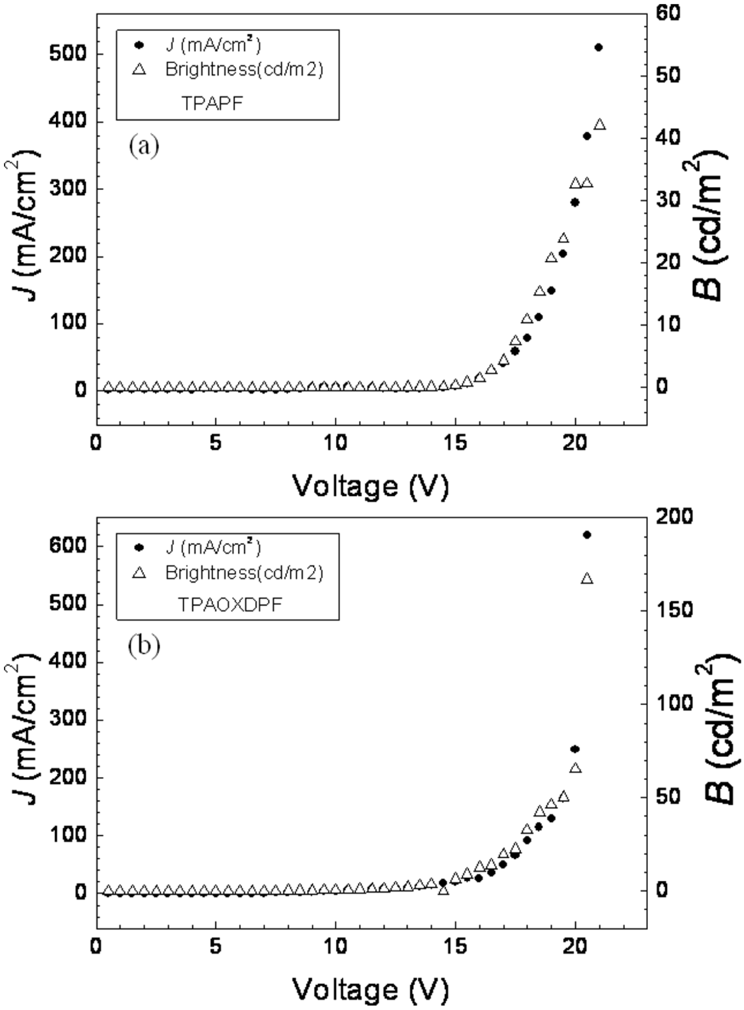

Figure 5. Current density – voltage – brightness curves of (a) ITO/TPAPF/Al and (b) ITO/TPAOXDPF/Al (filled circle: current density – voltage, triangle: brightness – voltage).

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