

New Fluorene-Based Polyquinoxalines with Ether-Linkage in The Main Chain: Synthesis and Light-Emitting Properties

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Abstract

We synthesized and characterized new fluorene-based polyquinoxalines with ether-linkage in the main chain, which have luminescent properties. Cyclic voltammetry reveals that these polymers have a low-lying LUMO and HOMO energy levels. Therefore, the polymers would be attractive candidates for electron-transporting or hole-blocking materials in LEDs.

1. Introduction

Since the first report on electroluminescence (EL) from poly(*p*-phenylenevinylene) (PPV),¹ many advances have been made in developing light-emitting diodes (LEDs) of various colors, device efficiency and stability from many π -conjugated polymers. It is established that EL device efficiency can be obtained by achieving both efficient charge injection and balanced mobility of both charge carriers inside the EL materials. In general, most *p*-type polymer EL materials have been known as very good hole-injection but very poor electron injection properties due to their inherent richness of π -electrons. Thus, synthesis of new luminescent polymers with efficient electron injection and transporting properties is needed to further improve device performance. Therefore, n-type conjugated polymers such as polyquinoxaline,² oxadiazole,³ triazole⁴ and polyquinoline⁵ have recently been introduced as electron transport (ET) layer and EL material in LEDs.

Poly(phenylquinoxalines) (PPQx) were first polymerized by a condensation reaction between aromatic bis(*o*-diamines) and bis(1,2-dicarbonyls) for use as heat-and chemical-resistant materials.⁶ Recently, poly(*p*-phenylene) (PPP) type

polyquinoxalines have been synthesized by dehalogenation polycondensation using nickel complexes.⁷ Also, PPV-type polymers with quinoxaline moieties in the polymer backbone were reported by Andersson et al.⁸ Furthermore, Jenekhe group reported a thiophene-linked polyquinoxaline as an excellent electron transport (ET) material for polymer LEDs.² As shown in Figure 1, in our preceding paper, synthesis and luminescent properties of new polyquinoxalines (PFQx I, PFQx II) with fluorene unit in the main chain were reported.⁹

In this study, synthesis and characterization of novel fluorene-based polyquinoxalines with ether-linkage in the main chain are described and their optical, electrochemical, and light-emitting properties are also investigated.

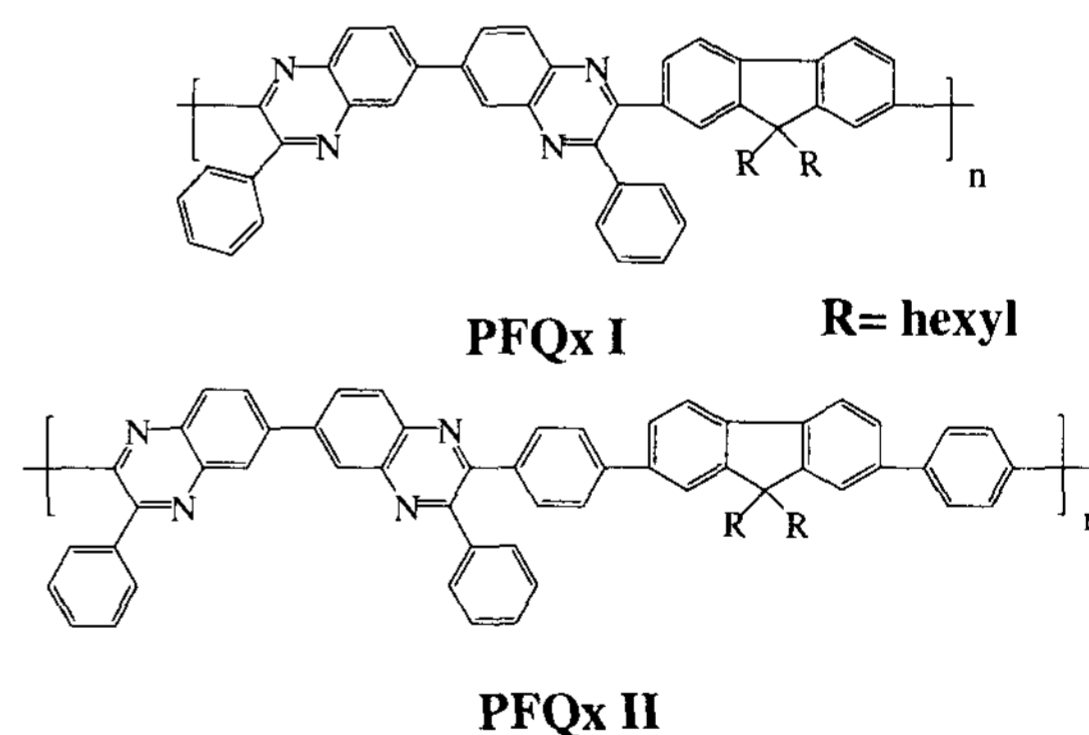


Figure 1 Chemical structures of the PFQx I and PFQx II.

2. Experimental

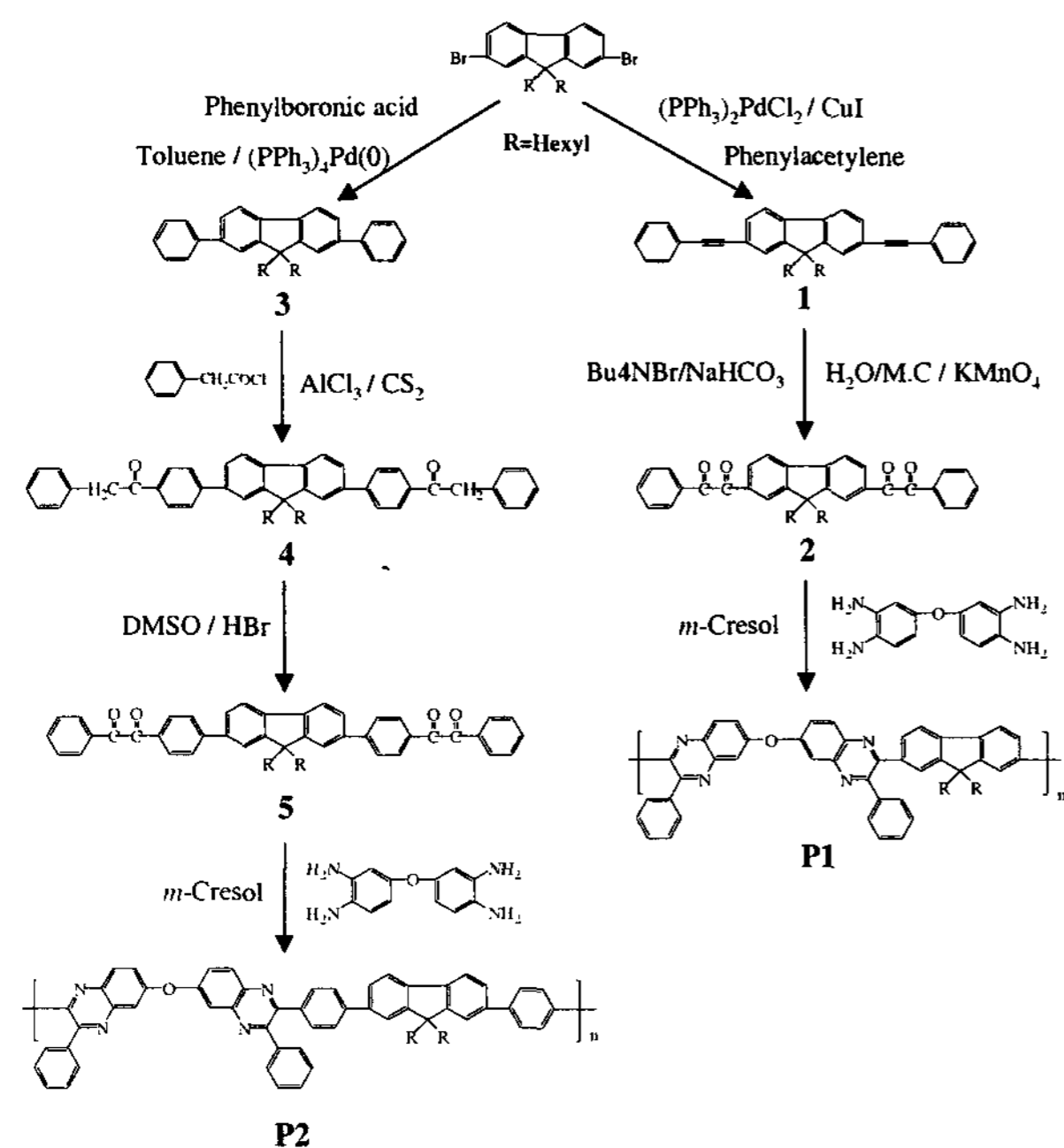
P1: Equimolar amounts of compound 2 (1.0 g, 1.67 mmol) and 3,3',4,4'-tetraaminodiphenyl ether (384

mg, 1.67 mmol) were dissolved in 7 mL of *m*-cresol in a 50 mL glass reactor fitted with a mechanical stirrer. The reaction mixture was stirred under argon purge at 100°C for 48 h during which progressive increase of the solution viscosity was observed. The reaction mixture was poured into 600 mL methanol, precipitating a yellow polymer, which was collected by filtration and dissolved in chloroform. The solution was filtered through a micro filter to remove residual particles and precipitated in methanol. The obtained polymer was dried in a vacuum oven at 40°C for 2 days. 1.1 g (87.3%).

P2: P2 was synthesized in the same manner as P1 using 1.0 g (1.33 mmole) of compound 5 and 306 mg (1.33 mmole) of 3,3', 4,4'-tetraaminodiphenyl ether, to give 1.1 g (90.9%) P2.

3. Results and discussion

We used different synthetic methods to prepare tetraketone compounds, which is showed in Scheme 1.



Scheme 1 Synthetic route to the polymers

The 2,7-dibromo-9,9-di-*n*-hexylfluorene were cross-coupled with phenylacetylene in a palladium-catalyzed Heck reaction to compound 1. The compound 1 could easily be oxidized to the tetraketone compound 2 with KMnO_4 in CH_2Cl_2

according to the procedure for the oxidation of 2,5-bis(phenylethynyl)thiophene described by Jenekhe et al.² The 2,7-bis(4-benzil)-9,9-di-*n*-hexylfluorene (5) was usually prepared by HBr (48% solution) oxidation of 2,7-bis(4-phenacetylphenyl)-9,9-di-*n*-hexylfluorene (4) which is obtained by Friedel-Crafts acylation. As shown in Scheme 1, new fluorene-based polyquinoxalines with ether-linkage in the main chain were synthesized by polycondensation reaction between tetraketone monomers and 3,3', 4,4'-tetraaminodiphenyl ether.

The UV-vis and photoluminescence (PL) spectra of P1 and P2 in the thin films are shown in Figure 2. The UV-vis absorption maxima of P1 and P2 in thin film appear at 393 and 385 nm, respectively. The PL spectrum of the P1 exhibits a maximum at 432 nm. Also, the P2 showed blue emission at 440 nm in the thin film with a shoulder peak at 530 nm.

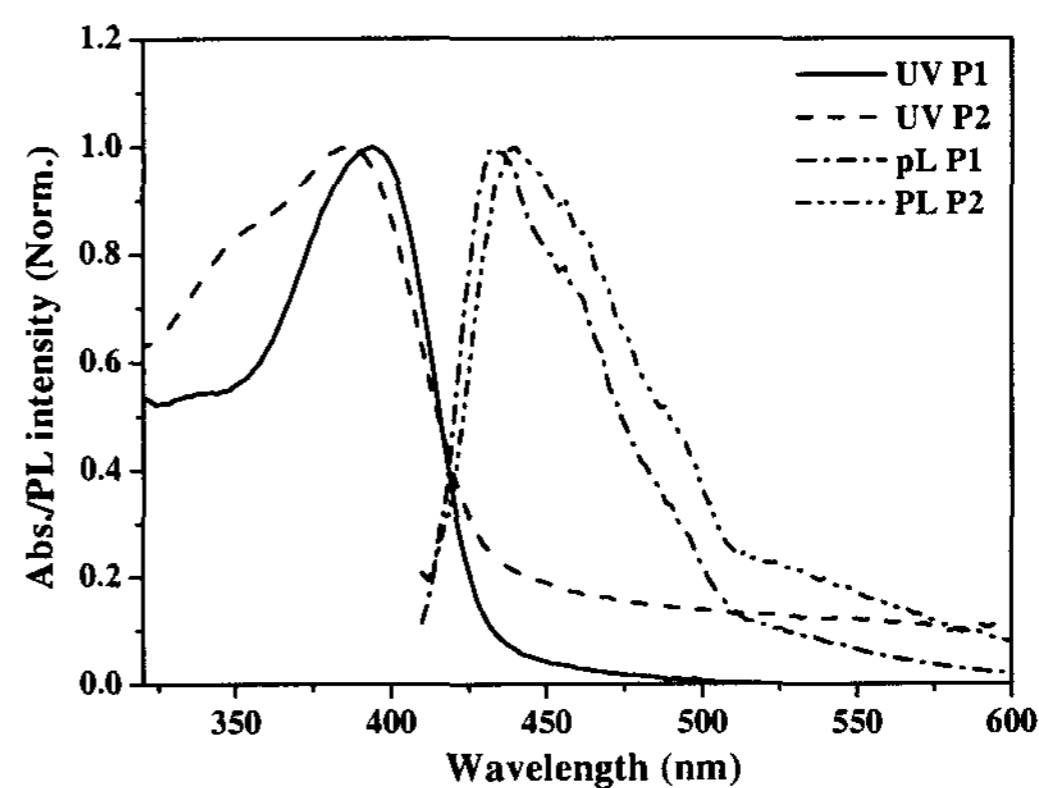


Figure 2 UV-vis and photoluminescence spectra of the polymers in thin film

Multi-layered light-emitting diodes with the device structure of ITO/PEDOT/polymer(P1 or P2):PVK blend (2:8)/LiF/Al were fabricated to investigate the electroluminescent properties and the current-voltage characteristic of P1 and P2. As shown in Figure 3, The EL spectra of P1 and P2 give highest peaks in the blue EL emissive band at 434 nm for P1 and 448 nm for P2. Figure 4 and 5 show the current-voltage and luminance-voltage characteristics of ITO/PEDOT/P1:PVK blend (2:8)/LiF/Al and ITO/PEDOT/P2:PVK blend (2:8)/LiF/Al devices. In forward bias, the turn-on voltages (determined from the onset of luminance in the plot for log light intensity versus voltage) of the diodes are 15 V for P1 and 18 V for P2. The maximum brightness of P1 was $0.56 \mu\text{W}/\text{cm}^2$ at 29 V

and the highest external quantum efficiency was 0.056%. P2 reached a brightness of $0.50 \mu\text{W}/\text{cm}^2$ at 34 V and has a relatively low external quantum efficiency of 0.015%.

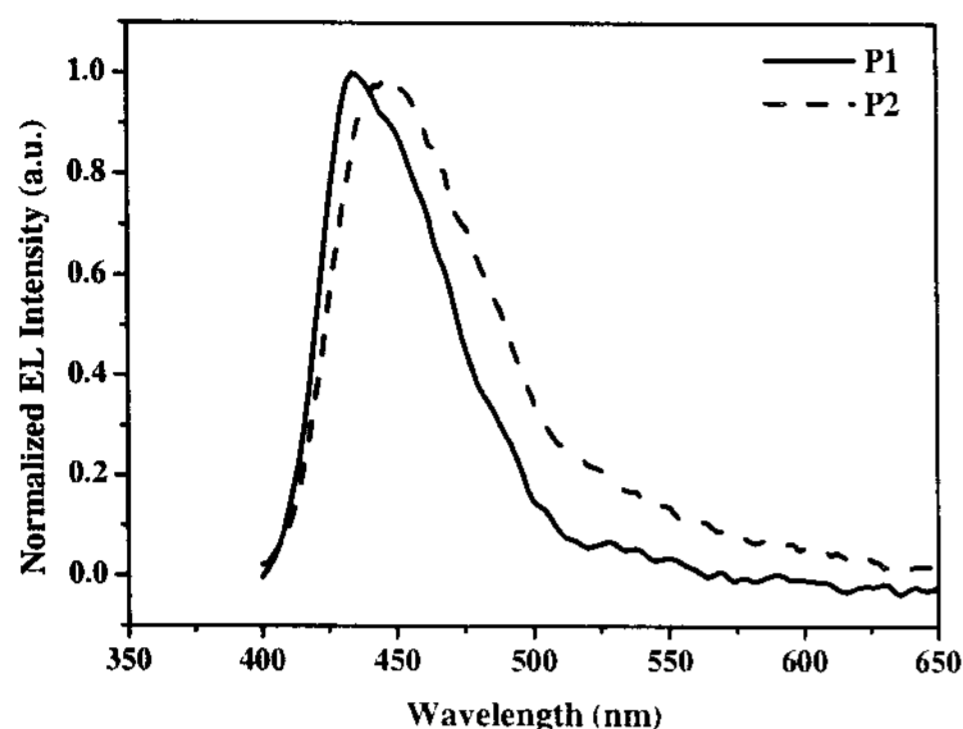


Figure 3 EL spectra of P1 and P2

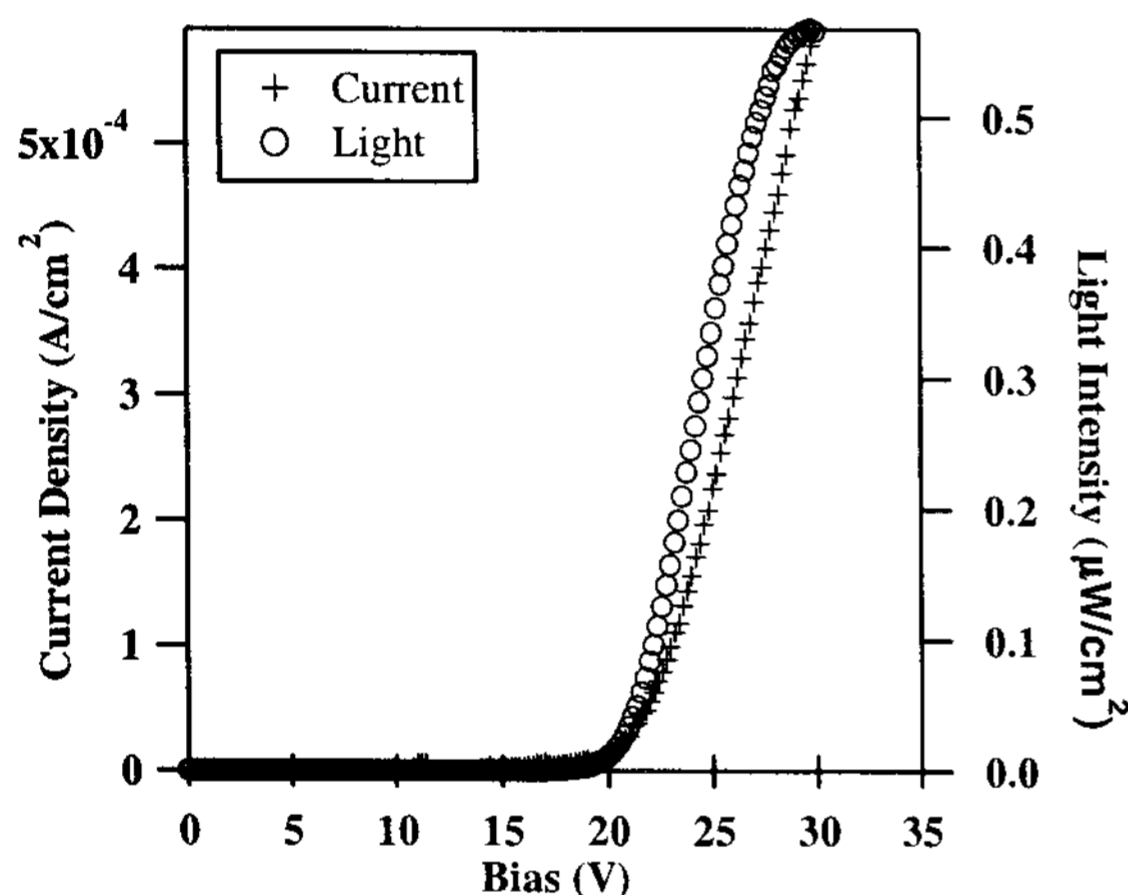


Figure 4 I-V-L curve of P1 in device of configuration ITO / PEDOT / P1:PVK blend(2:8) / LiF / Al

The HOMO/LUMO energy values of the polymers were $-6.16/-3.20$, $-5.92/-2.94$ and $-5.98/-3.00$ eV for P1, P2, and P3, respectively. These reduction potentials are lower than those of 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) (~ -2.4 eV), one of the most widely used electron-transporting/hole-blocking materials. It is believed that the low-lying LUMO levels of the polymers originate from the electron-deficient nature of the quinoxaline ring. Thus, the results suggest that the HOMO/LUMO positions of these polymers are sufficiently below those of conventional *p*-dope type

electroluminescent polymers (e.g. The HOMO/LUMO energy of PPV is $-5.7/-2.7$ eV). Such energy levels may provide a closer match to the work function of Al when they are used as electron-transporting/hole-blocking materials in polymer LEDs.

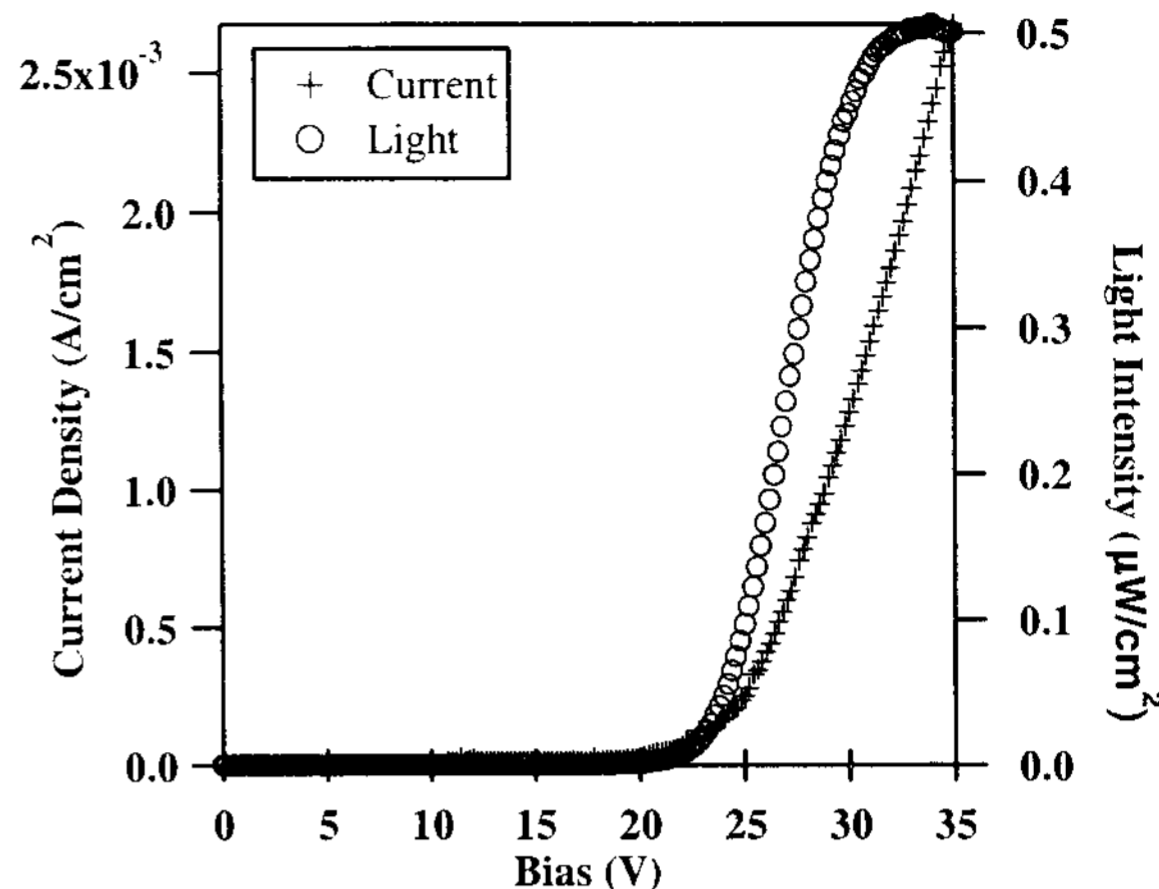


Figure 5 I-V-L curve of P2 in device of configuration ITO / PEDOT / P1:PVK blend(2:8) / LiF / Al

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