

Syntheses and Characterizations of Carbazole-Based Conjugated Polymers for Blue-light Emitting and Photovoltaic Applications

(青色発光と太陽電池への応用を目的とするカルバゾール構造を有する共役系高分子の合成と性質)

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1. Background

Conjugated organic polymers are basically long chain macromolecules that have alternating carbon-carbon single and multiple bonds (might have cumulative double bonds) along the backbone. Electrons delocalized along the  $\pi$ -conjugated backbone contribute electrical conductivity of the polymers. Shirakawa, MacDiarmid, and Heeger have discovered electrical conductivity of a polyacetylene film upon chemically doping with bromine in 1977 [1, 2]. For the last few decades, conjugated polymers have attracted considerable interest around the world and considerable developments have been made. Many different conjugated polymers have been extensively studied, such as polythiophenes and polypyrroles, among others, as shown in Figure 1-1 [3-9].

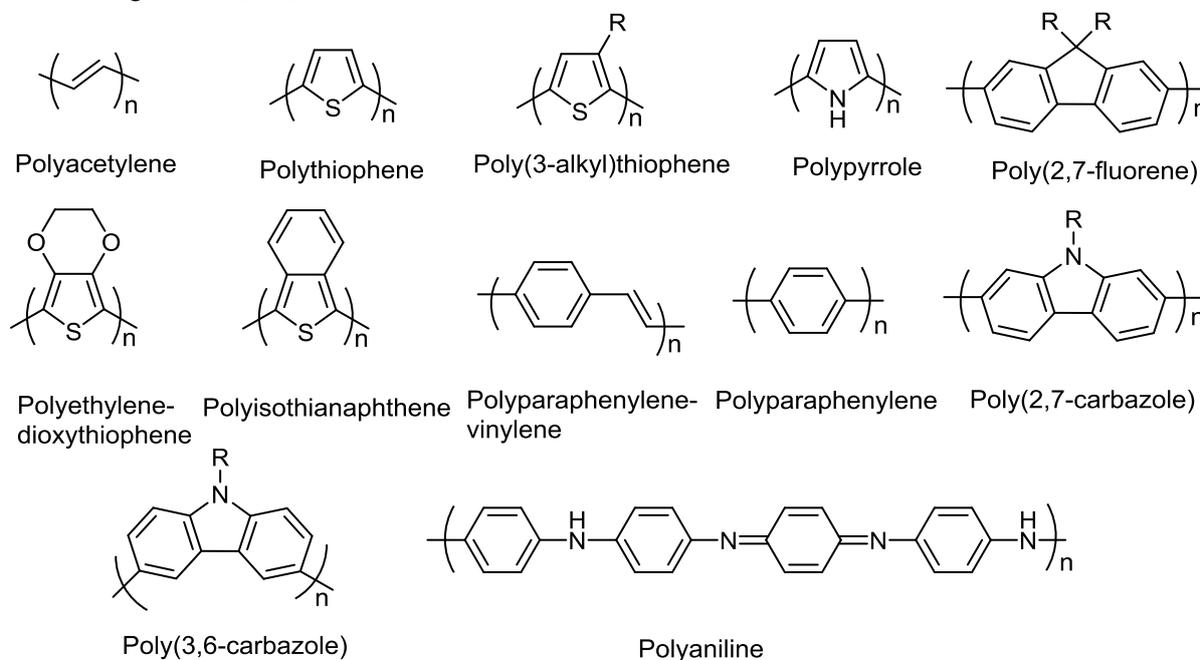
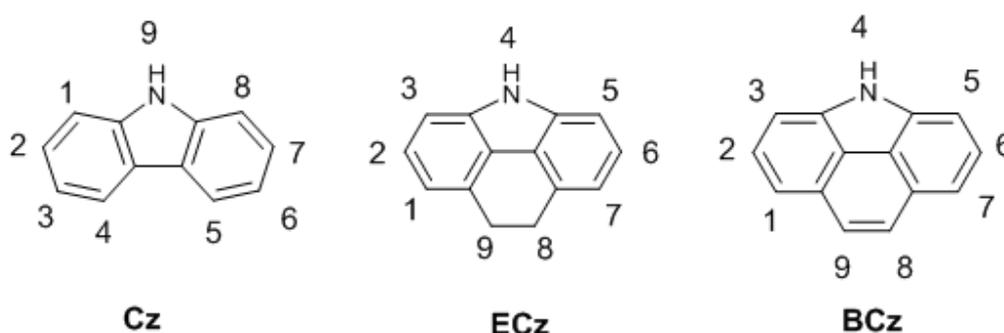


Figure 1-1. Chemical structures of some commonly used conjugated polymers

Originally it was thought these types of polymer systems would serve as substitution for highly conductive metals, such as copper and aluminum. However, the conjugated polymers were chemically unstable in atmospheric conditions. In 1990, the first polymer light-emitting diodes (PLEDs) was reported by

Burroughes and co-workers [10], which was a demonstration of practical applications in the field of conjugated polymers. Subsequently, conjugated polymers have been successfully used in a wide range of applications including thin film transistors [11], chemical sensors for massive analyses [12, 13], light emitting electrochemical cells (LECs) [14-16] and organic photovoltaic cells (OPV) [17, 18]. Electronic devices, such as organic light-emitting devices and photovoltaic cells are currently under development for practical uses. These are not only unique materials for basic researches on organic semiconductors but also promising materials for industrial applications, since they can be easier to make devices for energy conservation and energy generation than alternative materials. These electroactive and photoactive conjugated polymers have an advantage of easy tuning their properties through simple chemical modifications [19, 20].

Carbazole is a heterocyclic aromatic organic compound having a dibenzopyrrole structure. The structure and numbering of positions in carbazole (**Cz**) is shown in Figure 1-2. Carbazole is a conjugated unit that has interesting optical and electronic properties such as photoconductivity and photorefractivity [21, 22]. A number of carbazole derivatives have been synthesized and electrochemical and spectroscopic properties of them have been extensively investigated [23-25]. Carbazole has been widely used as a functional building unit of conjugated polymers for light-emitting layers in PLEDs and LECs devices and also utilized as active layer components for OPV. The optical and electrical properties of polymers based on carbazole can be easily tuned by substitution on the 2-, 3-, 6-, 7- and 9H-positions.



**Figure 1-2.** The structures and numbering system of **Cz**, **ECz** and **BCz**

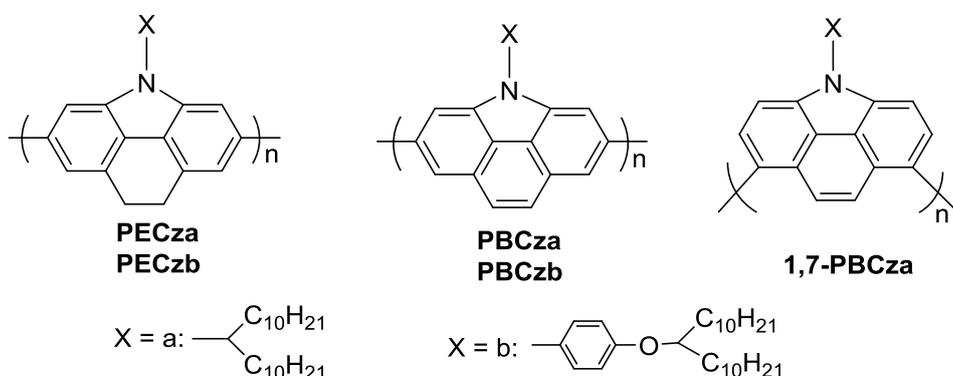
In this thesis, two different research issues in the field of organic electronics were studied. New materials based on carbazole for blue-light emitting and photovoltaic applications are developed and their basic properties and prospect in applications are described.

## **2. Syntheses and characterizations blue-light emitting $\pi$ -conjugated polymers.**

Blue light-emitting materials are of great significance for their unique applications in flat-panel displays and high-density information storage. Especially in full-color displays, the short-wavelength emission can serve as an excitation source for emission over the whole visible range [26]. Therefore, development of high-efficiency blue emitting materials is important. However, to develop stable pure blue polymeric emitters for PLEDs and LECs with their color coordinates in the Commission Internationale de L'Eclairage (CIE) chromaticity diagram within the standard blue (CIE:  $x < 0.15$ ;  $y < 0.1$ ) are still rare, It is also difficult to achieve high efficiency and a good charge balance due to the large energy bandgap ( $E_g$ ) of these materials [27]. In chapter 2, the design, syntheses and properties of new blue-light emitting  $\pi$ -conjugated materials are discussed.

## 2.1 N-substituted poly(4*H*-benzo[*def*]carbazole)s for blue photoluminescence

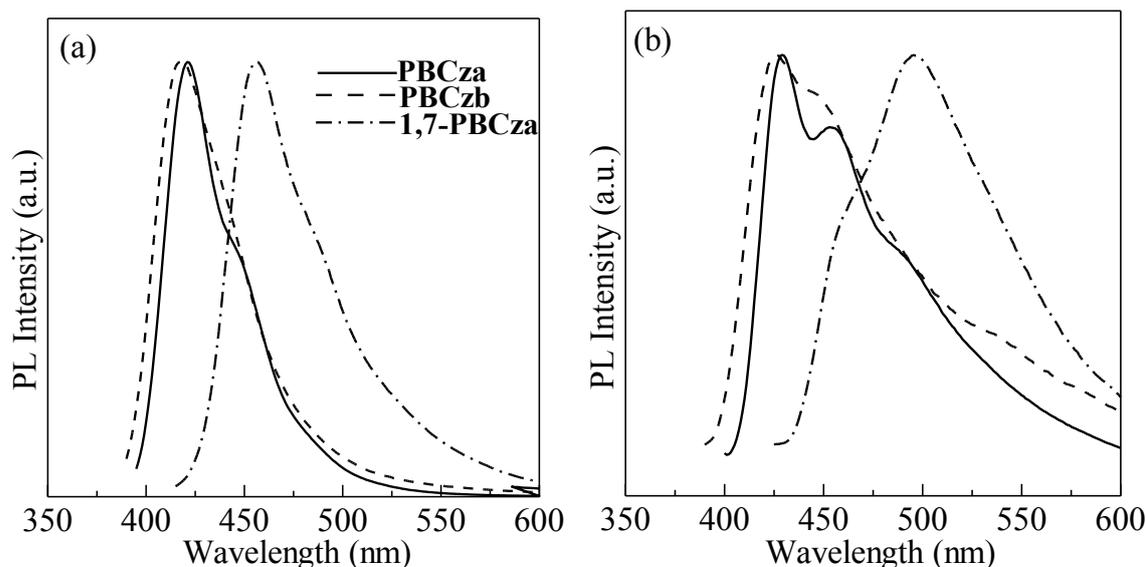
Since the first report on blue PLEDs device fabricated with poly(*p*-phenylene) (PPP) in 1992 [28], a large number of blue-light-emitting materials have been developed. Among the vast kinds of blue-light-emitting polymers, fluorene-based conjugated polymers have been recognized as a promising class of them, because of their good processability for making thin film devices and high fluorescent performances in the solid state [29]. Unfortunately, polyfluorenes have usually emitted impure blue colors due to emissions from contaminants such as excimers and keto-defects in addition to principal emission from  $\beta$ -phase, when they are applied as emitting layer materials in PLEDs [30]. Since early in this century, poly(2,7-carbazole)s regarded as a strained planner poly(4,4'-biphenylene) with an imino-bridge have been considered as a new candidate for blue light emitting materials comparable to the fluorene-based polymers, because they have band gaps appropriate for blue light emissions and smaller ionization potentials compared to polyfluorenes [25].



**Figure 2-1.** The structures of **PECza**, **PECzb**, **PBCza**, **PBCzb** and **1,7-PBCza**

In this section, a new series of N-alkyl and N-phenyl substituted poly(carbazole)s having a 4,5-ethylenylene bridge, poly(4*H*-benzo[*def*]carbazole)s (**PBCza**, **PBCzb** and **1,7-PBCza**) (Figure 2-1), were synthesized. Derivatives of 4,5-ethylene bridged poly(carbazole) (**PECza** and **PECzb**) were also synthesized for comparison. Basic properties of these polymers were compared with those of poly(2,7-carbazole)s and poly(3,6-carbazole)s.

This new series of carbazole-based homopolymers, had enough high molecular weights, good solubility in common organic solvents, amorphous nature in the film state and good thermal stability showing about 400 °C of temperature at 5 wt% loss in TGA. The band gaps of these polymers were in the range of 2.77-3.15 eV that were appropriate for bluish light emissions. The fluorescence maxima of these polymers in  $\text{CHCl}_3$  and in film state were in the ranges of 419-456 and 426-495 nm, respectively (Figure 2-2). The CIE(x, y) values of **PECza**, **PECzb**, **PBCza** and **PBCzb** in  $\text{CHCl}_3$  were almost identical to (0.15, 0.05) in the region of deep blue. In film state, CIE values for **PECz** (0.16, 0.15) were in the region of blue, while CIE values for **PBCz** (0.19, 0.21) shifted toward greenish blue but in the region of blue. The shift of the PL color is ascribed to the stronger intermolecular interaction between the larger planar units of **PBCz** as suggested in the XRD results. Poly(2,6-benzocarbazole)s (**PBCza** and **PBCzb**) showed unexpectedly blue-shifted absorption bands, the shallower  $E_{\text{HOMO}}$ , and the wider  $E_{\text{g}}$  compared with those of poly(2,7-carbazole) regardless of having the larger  $\pi$ -conjugation in the monomer unit. It is considered that **PECz** and **PBCz** have potential to be applied in PLEDs as blue-light emitting materials.

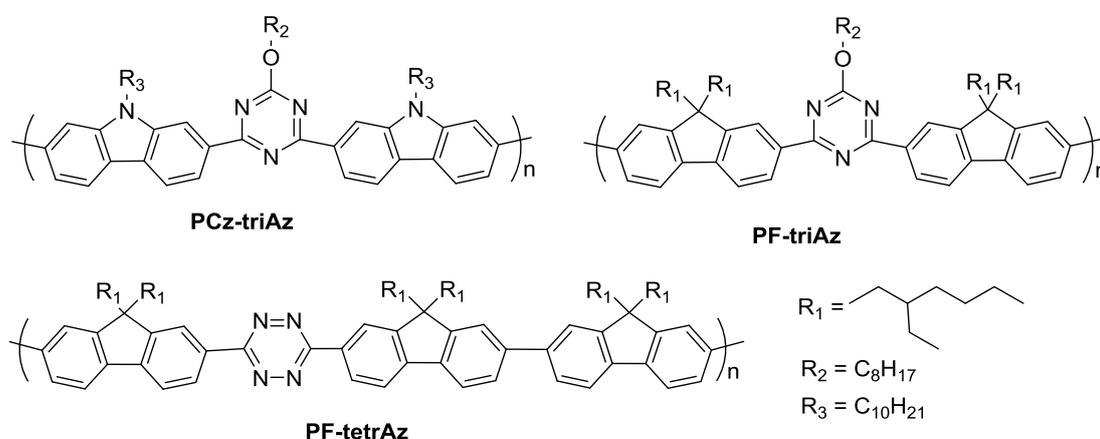


**Figure 2-2.** PL spectra of **PBCza**, **PBCzb** and **1,7-PBCza** in CHCl<sub>3</sub> (a) and flim state (b).

On the other hand, **1,7-PBCz** is found to have unique properties that the absorption and emission bands were observed in considerable longer region in wavelength with moderate  $\phi_{\text{fl}}$ , which were quite different from those of poly(3,6-carbazole)s. **1,7-PBCza** showed the shallow  $E_{\text{HOMO}}$  and narrow  $E_{\text{g}}$  fluorescing in blue green color (CIE (0.20, 0.33)) in the film state. Therefore, the **1,7-BCz** unit would rather be applied in a donor component of donor-acceptor-type narrow band gap polymers for organic solar cells.

## 2.2 Synthesis and characterization of D-A-polymers having azine unit for blue light emission.

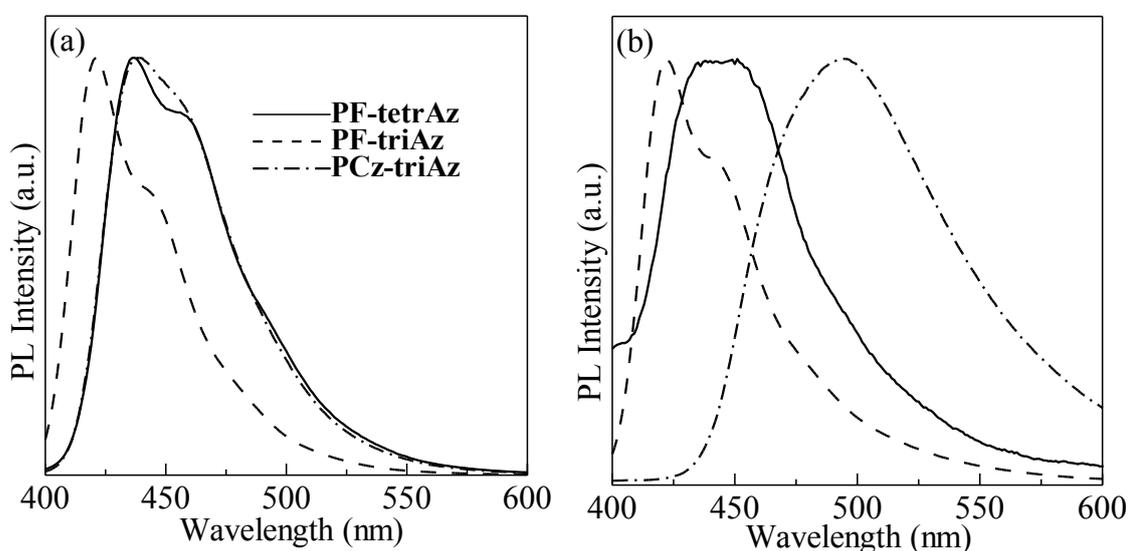
In this part, the rational design of p-type conjugated polymers by incorporating electron-withdrawing groups, such as azine unit, seems to be a straightforward strategy to tune carrier injection and transporting properties of known materials. A new D-A system has been designed, which is expected to lower both the energy level of the  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ , giving rise to a series of intriguing properties such as improved resistance to oxidation, facilitated electron injection, and ambipolar characteristics, which could simplify device fabrication and operation.



**Figure 2-3.** The structures of **PCz-triAz**, **PF-tetraAz** and **PF-triAz**

The synthesis, characterization and photoluminescence properties of these polymers, **PCz-triAz**, **PF-tetrAz** and **PF-triAz**, shown in Figure 2-3 were investigated. Herein, the carbazole/fluorene sequences were selected as D for the reason of good thermal and electrochemical stability, high fluorescence yield and facile chemical functionalization, while 1,2,4,5-tetrazine (**tetrAz**) and 1,3,5-triazine (**triAz**) were chosen as A for their electron deficiency.

Three types of D-A copolymers were designed and synthesized by combination of an electron donor unit of carbazole/fluorene sequences and an electron acceptor azine unit such as 1,2,4,5-tetrazine and 1,3,5-triazine. They have good thermal stability showing about at 360 °C with 5 wt% loss in TGA. Three copolymers exhibited intense blue photoluminescence with emission peak maxima at 438, 437 and 421 nm in CHCl<sub>3</sub>, respectively (Figure 2-4). In the film state, the emission peak of **PCz-triAz** was observed at 495 nm, while the emission peak maxima at 451 nm for **PF-tetrAz** and 422 nm for **PF-triAz**. The CIE values for **PF-tetrAz** (0.16, 0.12) and **PF-triAz** (0.16, 0.07) were in the region of blue, while CIE values for **PCz-triAz** (0.2, 0.32) shifted toward blush green. These polymers exhibited good fluorescence quantum efficiencies in CHCl<sub>3</sub> ( $\phi_{\text{fl}} = 0.62, 0.63, 0.97$ ).



**Figure 2-4.** PL spectra of **PCz-triAz**, **PF-tetrAz** and **PF-triAz** in CHCl<sub>3</sub> (a) and film state (b).

Compared to **PCz-triAz** ( $E_{\text{HOMO}} = -5.47\text{eV}$ ,  $E_{\text{g}} = 2.77\text{ eV}$ ), **PF-tetrAz** and **PF-triAz** showed acceptable  $E_{\text{HOMO}}$  ( $-5.83, -6.0\text{ eV}$ ) for hole transport and proper  $E_{\text{g}}$  (2.96, 3.12 eV) for blue emission. According to above results, these D-A copolymers have a great potential to be applied in PLEDs as the blue-light emitting materials.

### 2.3 Efficient blue luminescence D- $\pi$ -A type copolymers having sulfone/phosphine oxide unit

Donor- $\pi$ -acceptor (D- $\pi$ -A) type copolymers have aroused much interest because they show high fluorescent quantum yields and good charge carrier transport properties for using as hole- and electron-transporting moieties [31]. It has been proved that use of D- $\pi$ -A type molecules can enhance the electroluminescence efficiencies of PLEDs [32, 33]. However, the D- $\pi$ -A structure can enlarge  $\pi$  conjugation and lead the intramolecular charge transfer trend to remarkable fluorescence red shifts [34]. In this work, to design high-efficiency pure blue electroluminescence materials, it is important to suitably control the

enlargement of  $\pi$ -conjugation and trend of the intramolecular charge-transfer inside the molecules.

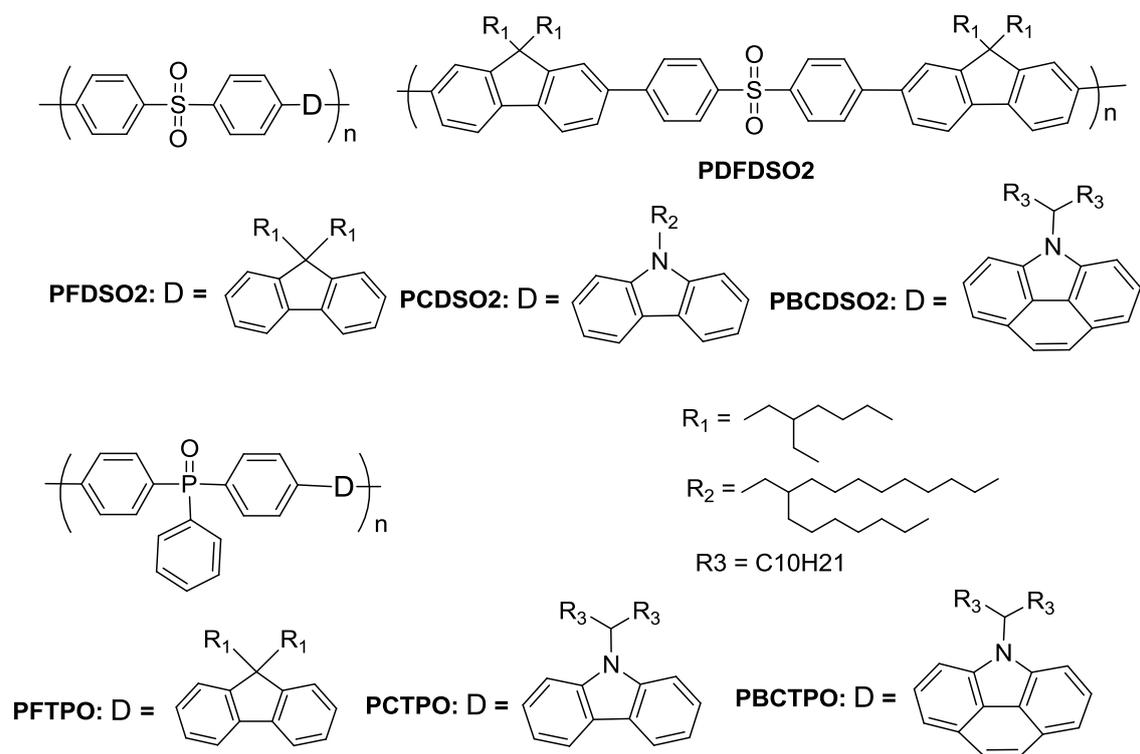


Figure 2-5. The structures of **PFDSO2**, **PCDSO2**, **PBCDSO2**, **PDFDSO2**, **PFPTPO**, **PCTPO** and **PBCTPO**

Herein, a series of D- $\pi$ -A type copolymers were designed and synthesized (Figure 2-5). The widely used hole-transporting moiety, fluorene/carbazole, was selected as the electron-donor for its relatively mild electron-donating ability, sulfone/phosphine oxide unit as acceptor unit for these excellent electron injection properties. Moreover, the sulfone and phosphine oxide with two rotatable phenyl rings, serve as a breaker of  $\pi$ -conjugation, because of their conformations of tetrahedral (sulfone)/ trigonal-pyramidal (phosphine oxide), which could effectively confine the  $\pi$ -conjugation of the molecules. All of these copolymers were fabricated simple LECs devices with structure of ITO/ PEDOT:PSS (40 nm)/ emission layer + ionic liquid/ Al (100 nm). The electroluminescence properties of these materials were investigated.

A new series of D- $\pi$ -A type copolymers were designed and synthesized. They have good thermal stability showing at about 400 °C with 5 wt% loss in TGA. These copolymers exhibited intense blue photoluminescence with emission peak maxima at 380 ~ 447 nm in  $CHCl_3$ . In the film state, the emission peaks of polymers were observed at 404 ~ 449 nm. All the polymers exhibited good fluorescence quantum efficiencies in  $CHCl_3$ . The polymers basically have good molecular weights, good solubility in common organic solvents, shallow HOMO levels (5.58-6.05 eV) (Figure 2-6), a conjugated polymers that shows excellent fluorescence quantum efficiency, and proper bandgaps ( $E_g$ ) for blue emission. These polymers have been used as emitting layer materials of LECs devices that have a configuration of ITO/ PEDOT:PSS/ polymer+ionic liquid /Al. The LECs device embedded with **PDFDSO2** shows intense luminance of about 12 00  $cd\ m^{-2}$ , while the devices embedded with **PFDSO2** and **PCDSO2** show less luminance but retain the color purity of blue emission under a wide range of applied voltages.

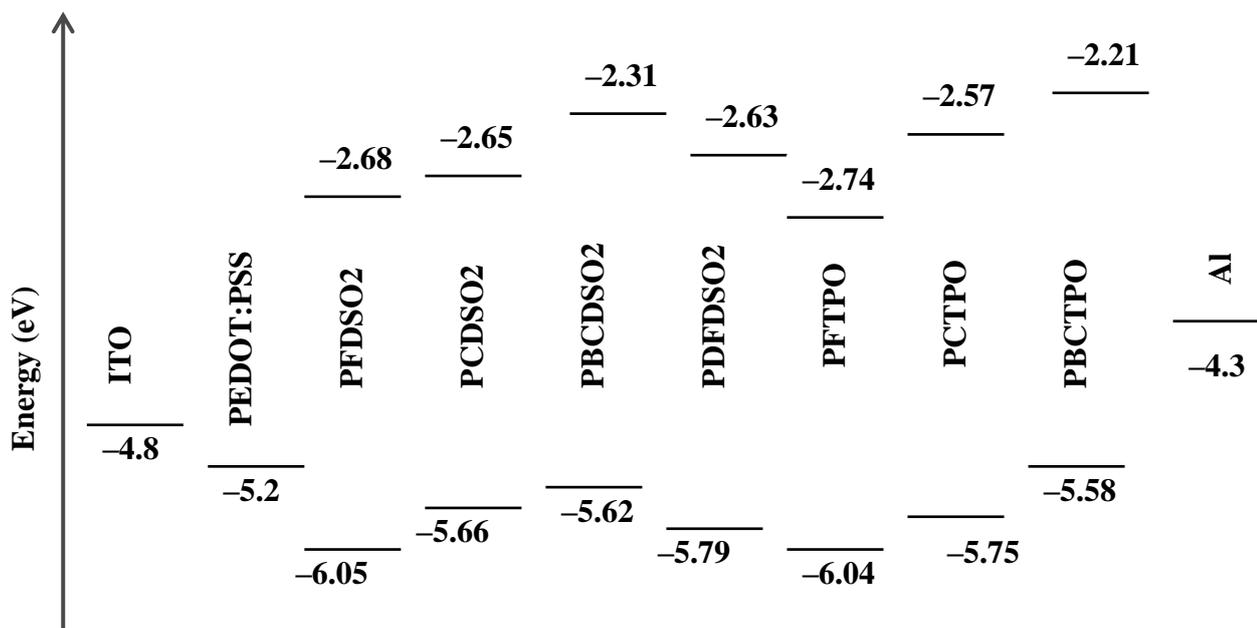


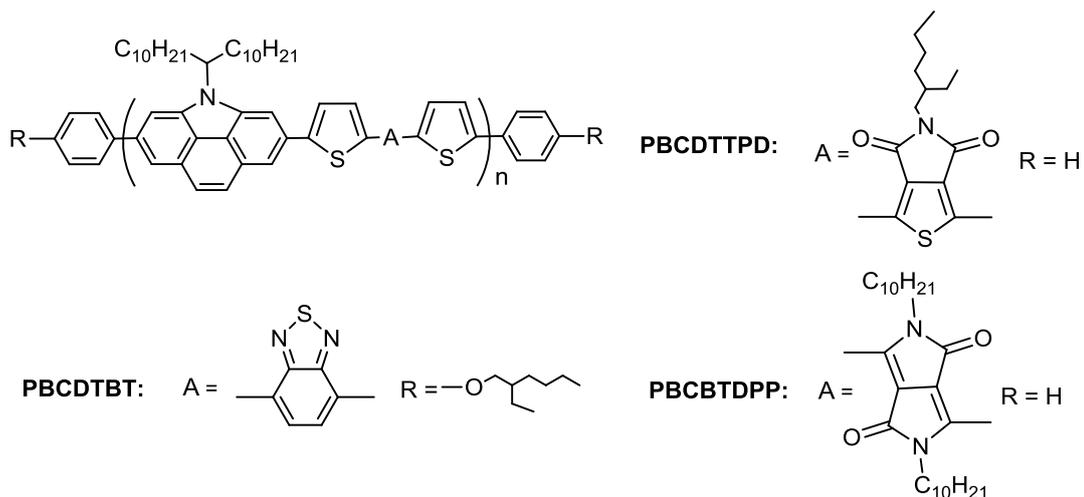
Figure 2-6. Energy band diagrams of the polymers.

### 3. Synthesis and photovoltaic performance of D-A-structure narrow bandgap copolymers based on benzo[def]carbazole

The bulk heterojunction (BHJ) OPV as renewable energy system has attracted much attention because of their many unique features such as low cost, easy fabrication, light weight and good flexibility [35, 36]. To obtain high-performance OPV, it is necessary to design and synthesize conjugated polymers with desired properties, such as (1) sufficient solubility to uniform thin film, (2) miscibility with an n-type material, (3) narrow band gap for matching the high photon flux region of the solar spectrum to ensure enough light harvesting and (4) high hole mobility for efficient charge transport [37, 38]. Narrow-bandgap  $\pi$ -conjugated polymers can harvest more sunlight and increase the exciton concentration in the active layers, leading to an increase of short-circuit current ( $J_{sc}$ ) [39]. Therefore, new polymers with proper properties of photoabsorption, semiconducting, energy levels, and stability have been attempted to be developed up to date.

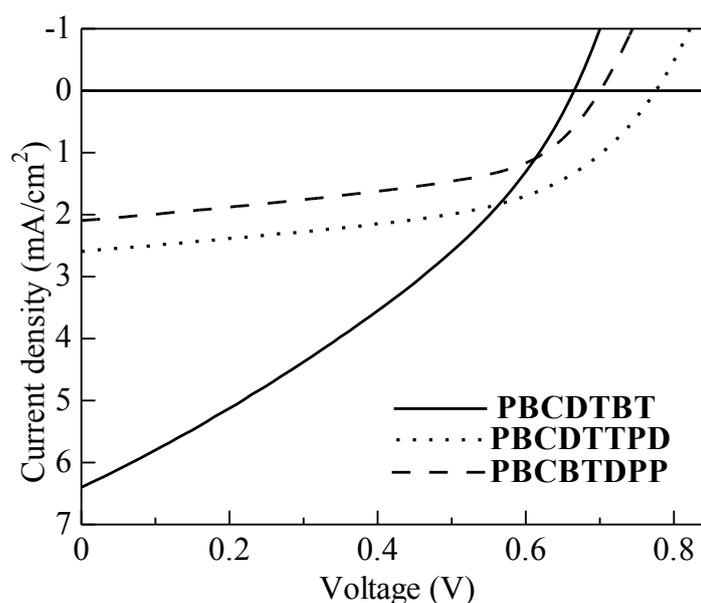
In this section, a simple strategy, synthesize D-A type narrow-bandgap copolymers was used. Benzo[def]carbazole is chosen as the donor unit for this new attempt for synthesis of the DA-type copolymers. Because this  $\pi$ -extended planar fused aromatic ring, benzo[def]carbazole, will be helpful for intensifying intermolecular  $\pi$  overlap and thus narrowing  $\pi$ - $\pi$  stacking, which can contribute to enhancing charge carrier mobility. Moreover, the bridging nitrogen-atom in benzo[def]carbazole offer a center for solubilizing functionality and tuning of energy levels of molecular orbitals by introducing appropriate substituents.

Three DA-type benzo[def]carbazole-based copolymers, **PBCDTBT**, **PBCDTTPD** and **PBCBTDP**, shown in Figure 3-1 were synthesized and characterized. Herein, benzothiadiazole (**BT**), pyrrole-4,6-dione (**PD**) and 1,4-diketopyrrolopyrrole (**DPP**) were chosen as the typical A unit. The effects of the different a segments on the absorption spectra, energy levels, and the photovoltaic performances of the copolymers are also studied.



**Figure 3-1.** The structures of **PBCDTBT**, **PBCDTTPD** and **PBCBTDPP**

Three copolymers exhibited broad absorption bands in UV and visible regions from 350 to 700 nm with optical band gaps in the range of 1.68-2.11 eV, which overlapped with the major region of the solar spectrum. Cyclic voltammetry revealed that these copolymers showed energy levels of the highest occupied molecular orbital in the range of  $-5.22$  eV to  $-5.34$  eV, which could provide good air stability and high open circuit voltages in photovoltaic applications. The BHJ OPV using **PBCDTBT** exhibited the PCE value of 1.47% with  $J_{sc}$  of  $6.41 \text{ mA cm}^{-2}$ , FF of 0.33, and  $V_{oc}$  of 0.67 V (Figure 3-2), while those using **PBCDTTPD** and **PBCBTDPP** showed PCE of 1.03% (with  $J_{sc} = 2.52 \text{ mA cm}^{-2}$ , FF = 0.50,  $V_{oc} = 0.77$  V), and 0.78% (with  $J_{sc} = 2.10 \text{ mA cm}^{-2}$ , FF = 0.51,  $V_{oc} = 0.70$  V, respectively). The higher performance of **PBCDTBT**:PC<sub>70</sub>BM (1:3) than **PBCDTTPD**:PC<sub>70</sub>BM (1:3), and **PBCBTDPP**:PC<sub>70</sub>BM (1:4) was almost ascribed to the higher  $J_{sc}$  of the former device, because the blend films of **PBCDTBT**:PC<sub>70</sub>BM showed a rather smooth surface and more intimate mixing, which certainly increased the heterojunction interface area for exciton dissociation and consequently led to the higher  $J_{sc}$  of OPV.



**Figure 3-2**  $J$ - $V$  curves of BHJ solar cell of **PBCDTBT**:PC<sub>70</sub>BM (1:3), **PBCDTTPD**:PC<sub>70</sub>BM (1:3) and **PBCBTDPP**:PC<sub>70</sub>BM (1:4) under illumination of AM 1.5 G.

## 4. Conclusion

This thesis was the synthesis, characterization and the testing of new, environmentally stable materials based on carbazole for blue-light emitting and photovoltaic applications.

The chapter 2 in first part, new type of poly(carbazole)s for stable blue light emitting are succeeded to synthesize by bridging of 4,5-ethenylene to a carbazole unit to construct benzo[def]carbazole. These homopolymers exhibited high molecular weights, good solubility in common organic solvents, amorphous nature in the film state and good thermal stability. The CIE (x, y) values of them in film state were almost identified in the region of blue. The properties of poly(carbazole)s were studied to be applied in PLEDs as blue-light emitting materials. In second part, New D-A copolymers have been designed and synthesized with the electron donor unit of carbazole/fluorene sequences and an electron acceptor azine unit. These polymers showed intense blue photoluminescence with CIE values in the region of blue and showed good fluorescence quantum efficiencies in  $\text{CHCl}_3$ . Polyfluorenes having electron accepting azine units (**PF-tetrAz** and **PF-triAz**) showed shallow  $E_{\text{HOMO}}$  for hole transport and proper  $E_g$  for blue emission. These D-A copolymers will be applied in the blue-light emitting materials. In third part, a series of D- $\pi$ -A type copolymers were designed and synthesized. The sulfone/phosphine oxide with two rotatable phenyl rings served as a breaker of the  $\pi$ -conjugation to well-preserve blue emission. The polyfluorenes with electron accepting sulfone units (**PDFDSO2**) based LECs devices showed intense luminance of about  $12\ 00\ \text{cd m}^{-2}$ .

Chapter 3 presented synthesis, characterization and OPV study of a novel benzo[def]carbazole based polymers with the D-A architecture, with three different electron acceptors. These copolymers exhibited broad absorption bands in UV and visible regions and narrow optical band gaps, which overlapped with the major region of the solar spectrum. The BHJ OPV using poly(benzo[def]carbazole) having electron accepting benzothiadiazole units (**PBCDTBT**) exhibited the highest PCE, which ascribed to the higher  $J_{\text{sc}}$  of the device. The mixing morphology of film **PBCDTBT**:PC<sub>70</sub>BM showed a rather smooth surface and more intimate mixing led to the high  $J_{\text{sc}}$  of OPV. Benzo[def]carbazole is a kind of effective donor segment for the design of D-A type OPV according to initial performances of these copolymers.

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