

Synthesis and Characterization of Polyimides Based on Twisted Non-coplanar Backbone Containing Indolocarbazole^①

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ABSTRACT A diamine monomer (4,4'-(((5,11-dihydroindolo[3,2-b]carbazole-6,12-diyl)bis(4,1-phenylene))bis(oxy))dianiline) containing a rigid conjugated indolocarbazole was designed and synthesized through a three-step reaction. A series of high-performance functional polyimides were prepared through simple condensation polymerization of the monomer with different industrial dianhydrides 6FDA, BTDA and ODP, respectively, which exhibit superior thermal stability, good solubility in polar organic solvents and good mechanical properties. The glass transition temperature (T_g) is above 334 °C, and the 5% weight loss temperature ($T_{d5\%}$) of polyimides under nitrogen atmosphere falls in the range of 502~526 °C. The tensile strength and tensile modulus are 49.45~60.08 MPa and 1.4~1.6 GPa, respectively. In addition, the maximum fluorescence emission wavelength of polyimides in the NMP solution (0.02 mg/mL) are around 448 nm with blue light emission and 451 nm as film without significant red shift, which indicates the prepared polyimides possess a certain application potential in high-performance flexible polymer optoelectronic devices.

Keywords: polyimides, indolocarbazole, thermal stability; DOI: 10.14102/j.cnki.0254-5861.2011-3212

1 INTRODUCTION

In recent years, high-performance functional aromatic polyimides and their applications have attracted widespread research attention, such as in flexible photovoltaic devices^[1], high-performance interlayer media^[2], and the fifth-generation mobile communication technology (5G technology) and other fields. Compared with other polymer materials, polyimide not only has the advantages of excellent stability, including thermal stability, chemical stability, dimensional stability, etc., but also owns better mechanical properties as well as various processability^[3]. Conventional polyimides such as Kapton, produced by Du Pont in 1965, have been widely applied in many high-tech fields such as

aerospace applications in the past decades. However, these polyimides generally exhibit poor solubility in organic solvents and low optical transparency simultaneously^[4]. In response to this problem, many efforts have been done on the modification of the polyimide backbone structure^[5-7], for example, by introducing flexible bonds^[8], fluorine-containing substituents^[9], asymmetric units^[10] or twisted groups^[11] into the molecular chain to functionalize polyimides. Moreover, attention has been focused on introducing aromatic heterocycle into the polyimide backbone^[12-14] in recent years, such as perylene^[15], pyridine^[16], phenanthroline and so on.

The carbazole is considered as a potential blue light emission material for light-emitting devices due to its rigid

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planar structure, excellent chemical stability and hole transport function. Moreover, the 2, 3, 6, 7, and 9 positions of carbazole are easy to be chemically modified and then linked into polymeric chains to adjust the photoelectric properties of the material^[17, 18]. Unfortunately, the thermal and morphological stability of small molecular weight materials is a challenge. Most importantly, these kinds of small organic molecule light-emitting devices are fabricated by vacuum sublimation technique. Polymer light-emitting diodes have captured lots of interests for their high thermal stability, simple structure of devices, mechanical process performance, easy chemical modification and low cost. Therefore, polymers based on carbazole groups have always been the hot spots of research. Huang *et al.*^[19, 20] reported that the solubility and optical properties of synthesized polyimides were enhanced by introducing unsymmetrical and noncoplanar carbazole. Kim *et al.* synthesized carbazole dendrimers which showed stable electrochemical properties and high T_g simultaneously^[21]. Furthermore, indolocarbazole is an important derivative of carbazole with a larger planar structure and higher mobility. Wang's group^[22] synthesized indolo[3,2-*b*]carbazole derivatives (DPDT-ICZ and DNDT-ICZ) that displayed deep-blue emissions with CIE(0.15, 0.08), but two compounds exhibited rather low glass transition temperature at about 124 °C. Moreover, most materials tend to modify the N-H group instead of remaining its characteristics^[23]. Thus, based on the advantages of polyimides and the carbazole group, designing a new polyimide material with indolocarbazole in the main chain to prepare functionalized high-performance polyimides is worthy of further exploration.

In this study, we have successfully designed and synthesized a new diamine monomer 4,4'-(((5,11-dihydroindolo[3,2-*b*]carbazole-6,12-diyl)bis(4,1-phenylene))-bis(oxy))dianiline (DCPN) and a series of polyimides (PIs) with three dianhydrides via a two-step method. By introducing the rigid indolocarbazole unit into the main chains of the PIs, the polymers exhibit high thermal decomposition temperature, high glass transition temperature, and better solubility in organic solvents. Moreover, the introduction of ether bonds can increase the flexibility of polymer chains and reduce the molecular chain packing, thus increasing solubility without affecting the glass transition temperature^[24]. Photoluminescence properties were also evaluated due to the carbazole structure. The resultant polymers exhibit similar UV absorption spectrum at about

277 nm and emission spectra around 448 nm in NMP solution (0.02 mg/mL). Moreover, three polyimides exhibit certain optical properties as film without significant red shift, which is worthy of further exploration on optoelectronic devices.

2 EXPERIMENTAL

2.1 Materials

Acetonitrile (AR), N,N-dimethylformamide (DMF, AR), N-methyl-2-pyrrolidone (NMP, AR), dimethyl sulfoxide (DMSO, AR), dimethylacetamide (DMAc, AR) and methanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, 99%), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic anhydride (ODPA) and palladium on activated charcoal (10% Pd, containing 40~60% H₂O) were obtained from Aladdin. 1-Fluoro-4-nitrobenzene (98%) was obtained from Damas-beta and hydrazine monohydrate (98%) was from Alfa Aesar. Commercially, NMP was purified by distillation under reduced pressure and dehydrated with 4 Å molecular sieves. 6FDA, BTDA and ODPA were purified in a sublimation device at 300 °C prior to use. Compound A (4,4'-(5,11-dihydroindolo[3,2-*b*]carbazole-6,12-diyl)diphenol) was synthesized as our previous work^[25] (Fig. S1).

2.2 Measurements

¹H NMR spectrum was measured on a Bruker AVANCE III 400 MHz. Fourier transform infrared (FTIR) spectra were recorded via a VERTEX70 FT-IR spectrometer. Differential scanning calorimetry (DSC) was obtained using a Q20 under an atmosphere of nitrogen at a heating rate of 10 °C/min. A thermogravimetric analyzer of STA449C analyzer (Netzsch, Germany) was used to analyze the oxidation stability of the samples. Mechanical property was measured with a universal tensile test machine (SHIMADZU, AUTOGRAPH AG-X plus) at a tensile rate of 0.5 mm/min. The effective part of the stretched spline has a size of 5mm × 40mm and an average thickness of 35 μm. The morphologies of membranes were observed via a field-emission scanning electron microscope (SU8010, Hitachi). X-ray diffraction (MiniFlex, Rigaku) with CuKα radiation was measured to investigate the aggregation state and molecular chain spacing of polymers. UV-visible absorption spectra were obtained using a Perkin Elmer Lambda35 spectrometer. Fluorescence spectra were recorded using a Cary Eclipse

Fluorescence Spectrometer.

2.3 Synthesis of monomers

Compound A (3 mmol, 1.32 g), dried potassium carbonate (7 mmol, 0.97 g) and DMF (30 mL) were added to a 50 mL three-necked flask under a nitrogen atmosphere. The reaction mixture was heated to 100 °C, followed by adding 0.99 g (7 mmol) of 1-fluoro-4-nitrobenzene. After 12 h, the yellow precipitation was collected by filtration and washed with water thoroughly, then dried in vacuo for 24 hours to obtain compound B as an orange solid.

In a 250 mL round-bottomed flask, compound B (2.46 g, 3 mmol) and 0.70 g of 10% Pd/C were suspended in 100 mL the mixture of ethanol and NMP (1:1). The reaction mixture was heated to reflux under nitrogen, and then 6 mL of hydrazine monohydrate was added very slowly to the mixture drop by drop. After that the mixture was maintained at the reflux temperature. The solution was hot filtered to remove Pd/C after further reaction for 48 h, and the clear solution was concentrated to 2 mL and then poured into 100 mL the mixture of deionized water and ethanol (7:3). Then the precipitate was obtained by filtration. Monomer DCPN

was obtained as a pale-yellow solid without further purification.

¹H NMR (400 MHz, DMSO-*d*₆) δ 10.50 (s, 2H), 7.77~7.51 (m, 4H), 7.44 (d, 2H), 7.26 (t, 2H), 7.22~7.09 (m, 6H), 7.01~6.91 (m, 4H), 6.86 (t, 2H), 6.75~6.63 (m, 4H), 5.06 (s, 4H).

2.4 Synthesis of polymers

Two-step method was applied to the synthesis of polymer membranes. The equivalent moles of 6FDA were added to a solution of DCPN dissolving in NMP under a nitrogen atmosphere, 6FDA dissolved gradually and the solid contents of the mixture solution were 15 wt%. Then the reaction mixture was stirred for 24 h at 0~5 °C to yield a viscous PAA solution. The obtained solution was poured onto a glass plate in a vacuum oven for thermal imidization with a four-step temperature programmed: 60 °C for 1 h, 150 °C for 1 h, 200 °C for 1 h, and 250 °C for 1 h, obtaining the polyimide membrane (denoted by DCPN-6FDA) (Fig. 1). DCPN-BTDA and DCPN-ODPA membranes (Fig. S1) were prepared in a similar way.

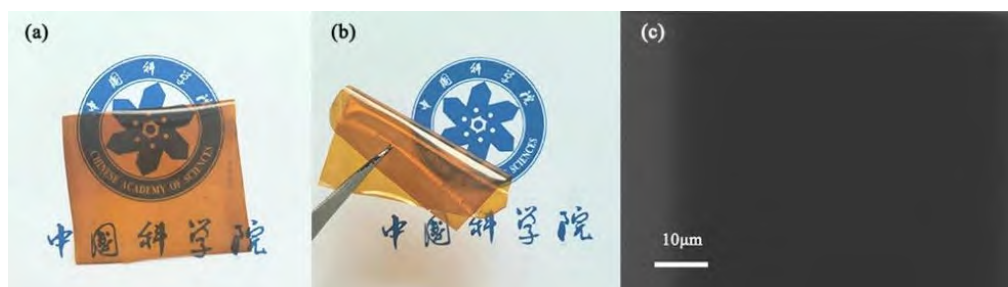


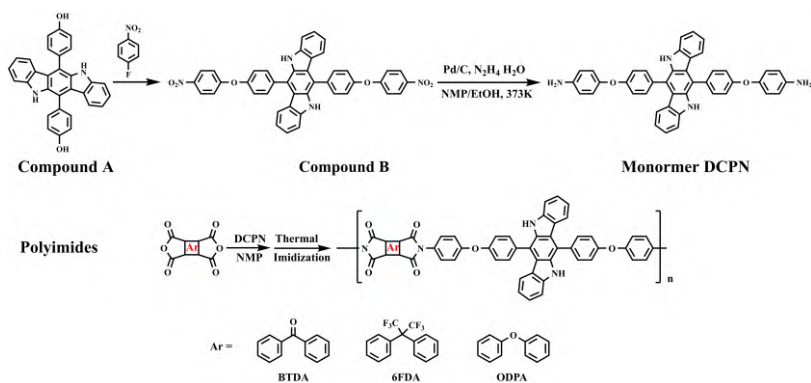
Fig. 1. Images of DCPN-6FDA (a, b) and SEM image of DCPN-6FDA surface (c)

3 RESULTS AND DISCUSSION

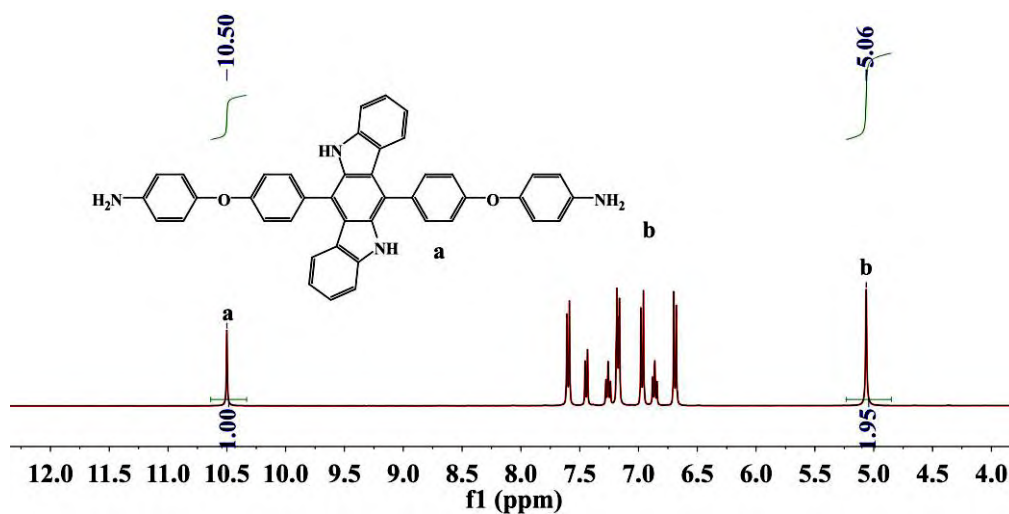
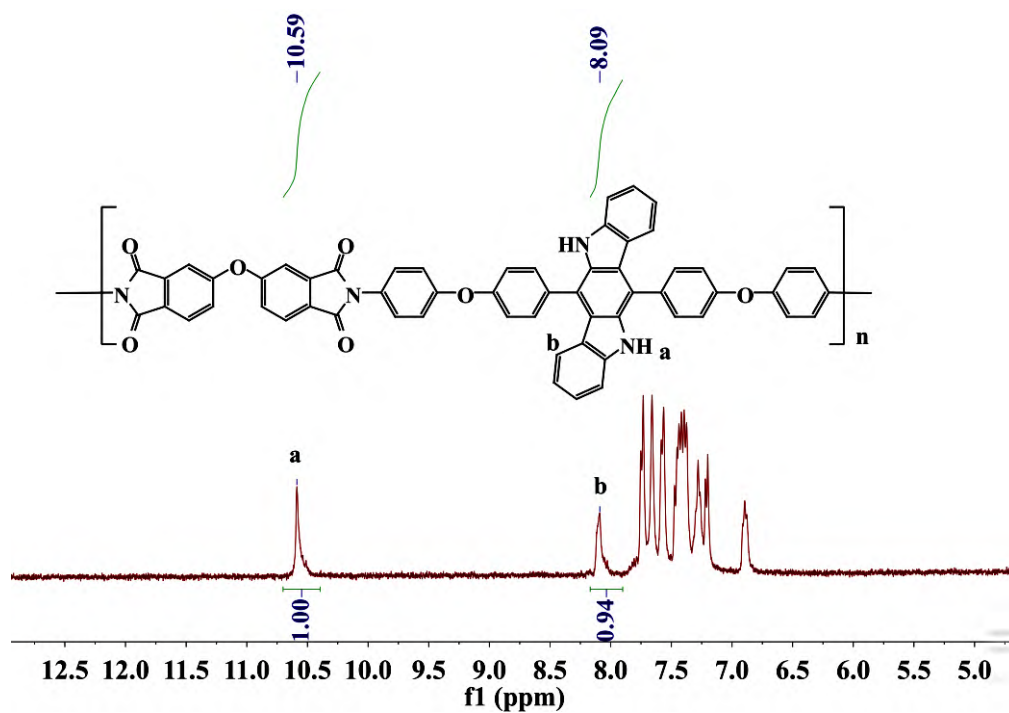
3.1 Synthesis chemistry of monomer and polyimides

A diamine (DCPN) containing rigid indolocarbazole backbone was designed and synthesized through three steps of reactions, as shown in Scheme 1. Then the diamine monomer DCPN was polymerized with three dianhydrides BTDA, ODPA and 6FDA respectively to obtain PAA solution, and then three kinds of flexible transparent PI films were prepared by thermal imidization process. NMR and IR were used to identify the structures

of the synthesized polyimides and intermediates. In the ¹H NMR spectrum of DCPN in Fig. 2, a singlet at 5.06 ppm was attributed to the four amino protons. The peak area of NH₂ is twice larger than that of N-H group of the benzocarbazole, which indicates the monomer DCPN is synthesized successfully. Fig. 3 shows NMR spectrum of DCPN-ODPA, and spectra of DCPN-6FDA and DCPN-BTDA are shown in the supporting information. The NH₂ peak disappeared after polycondensation and the peak of COOH was not observed, thus confirming the complete conversion of nitro groups into amino groups.



Scheme 1. Synthetic routes of the monomer DCPN and polyimides

Fig. 2. ^1H NMR spectrum ($\text{DMSO}-d_6$) of monomer DCPNFig. 3. ^1H NMR spectrum ($\text{DMSO}-d_6$) of DCPN-ODPA

FT-IR analysis spectra of the three polymers are given in Fig. 4. The doublet peaks near 1775 and 1714 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of the carbonyl group of the imide group, respectively, which represent that polyimides have been formed. The peak at 1368 cm^{-1} belongs to the C–N.

According to different dianhydride structures, the peak at 1663 cm^{-1} attributes to the C=O of BTDA and those at 1233 and 962 cm^{-1} are from C–F of 6FDA. Moreover, the peaks of DCPN-BTDA at 2923 and 2853 cm^{-1} indicate the formation of hydrogen bond between N–H of carbazole and C=O of BTDA.

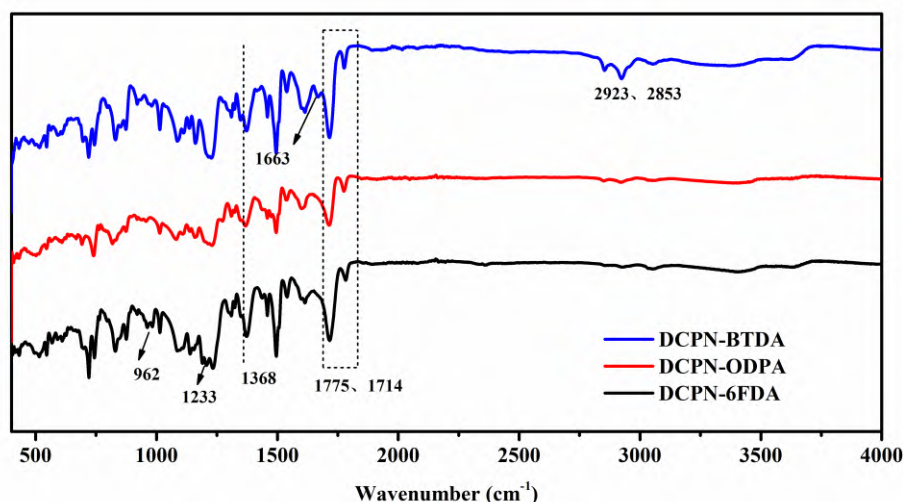


Fig. 4. IR spectra of DCPN-6FDA, DCPN-ODPA and DCPN-BTDA

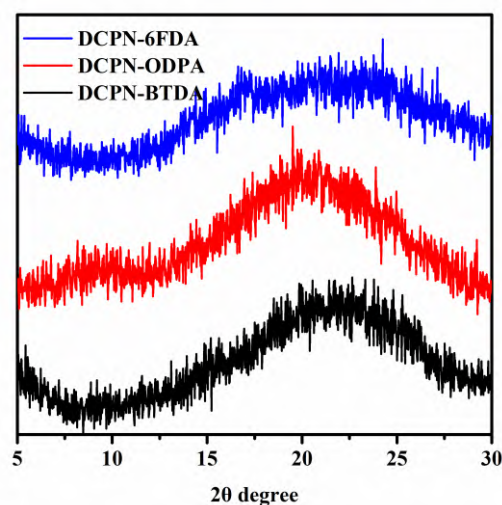


Fig. 5. XRD of DCPN-6FDA, DCPN-ODPA and DCPN-BTDA

To determine the aggregate state and inter-chain spacing of mixed matrix membranes, XRD analysis was performed and the spectra are shown in Fig. 5. A dispersion diffraction peak is observed for all the films, which indicates all membranes are amorphous state. It can be seen that DCPN-6FDA shows a relatively broader diffraction peak, suggesting that the bridge structure of $(\text{CF}_3)_2$ separates the molecular chains more effectively.

3.2 Solubility of the polyimides

The solubility of all polymers was determined by 5% solid content at room temperature or upon heating. Due to the rigid backbone of the polyimides, the solubility of the synthesized polymers in non-polar solvent is poor. Table 1 shows the solubility of the resulting polyimides in several polar solvents. The better solubility of DCPN-6FDA should result from the polarizability of $-(\text{CF}_3)_2-$ bridge structure.

Table 1. Solubility Data of the Three Polyimides

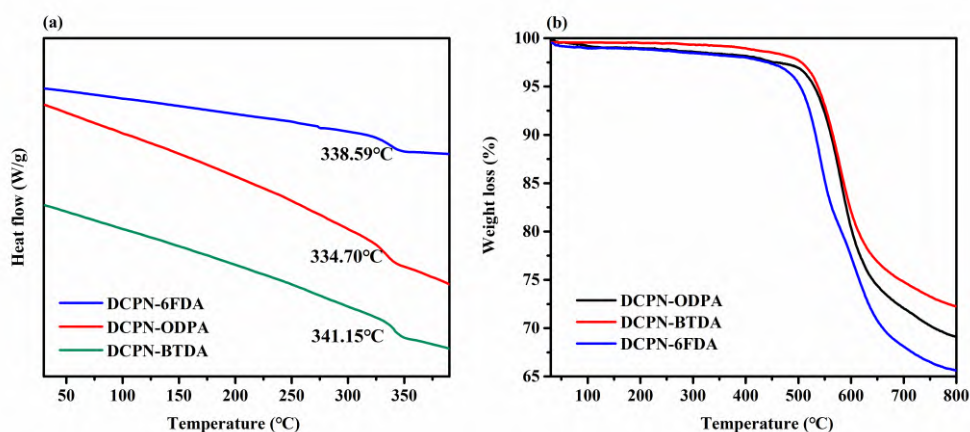
Polyimides	Solvents				
	NMP	DMAc	DMF	DMSO	THF
DCPN-BTDA	+	+	+ -	+ -	-
DCPN-ODPA	+	+	+	+ -	+ -
DCPN-6FDA	++	++	+	+	+ -

++: soluble at room temperature; +: soluble on heating; + -: partially soluble on heating; -: insoluble at heating

3.3 Thermal properties

The thermal properties of the polyimides are evaluated via DSC and TGA, and the curves of the three polyimides are shown in Fig. 6. The analysis data are summarized in Table 2. The glass transition temperature is the upper limit temperature used for polymer materials. The glass transition temperature of the three polymers is all above 330 °C ,

showing extremely high thermal stability because the main chain structure is a rigid indolocarbazole structure. The slight difference between the three polymers is mainly due to the dianhydride structure. Among them, BABP-ODPA exhibits the lowest T_g due to the existence of an extra flexible ether linkage of ODPA.

**Fig. 6. (a) DSC curves of polyimides and (b) TGA curves****Table 2. Thermal Properties of Three Polyimides**

Polyimides	T_g (°C)	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	Char residue (%)
DCPN-ODPA	334.70	526.60	560.60	68.71
DCPN-BTDA	341.15	522.28	558.28	70.75
DCPN-6FDA	338.59	502.45	532.45	65.62

Meanwhile, TGA curves were recorded in the range of 30~800 °C . The three polyimides show high 5% weight loss temperature ($T_{d5\%}$) above 500 °C and high carbon residue level (Rc) above 65% at 800 °C under nitrogen atmosphere because of their high aromatic content. Soluble polyimides with excellent thermal stability were rarely reported in the previous literature.

3.4 Mechanical characteristic

The polyimide films also showed good mechanical properties (Table 3). Due to the twisted rigid structure in the polymer main chain, the orderly arrangement of the

molecular chain is destroyed, thereby reducing the tensile properties of the polyimide. DCPN-6FDA shows the lower Young's modulus compared with DCPN-ODPA and DCPN-BTDA.

By introducing aromatic rigid non-planar indolocarbazole structure and flexible ether bond in the PI main chains, the resulting polyimides exhibit good solubility, excellent thermal stability, and good mechanical properties. Furthermore, based on the optical property of indolocarbazole, the polyimides are expected to explore the application on optoelectronics industry.

Table 3. Mechanical Properties of the Three Polyimides

Polyimides	Tensile strength (MPa)	Young modulus (GPa)	Elongation at break (%)
DCPN-ODPA	58.06	1.4	8.85
DCPN-BTDA	60.08	1.6	8.00
DCPN-6FDA	49.45	1.4	9.23

3.5 Photoluminescence properties

The DFT calculations were carried out to gain insight into the electronic structure of monomer DCPN, with the results shown in Fig. 7. HOMO and LUMO are both predominantly distributed along the indolocarbazole unit, showing a

perpendicular arrangement. The estimated HOMO and LUMO energy levels are -4.33 and -1.82 eV, respectively. Energy level difference (E_g) between HOMO and LUMO was 2.51 eV, which indicates DCPN can be used as a stable hole carrying material.

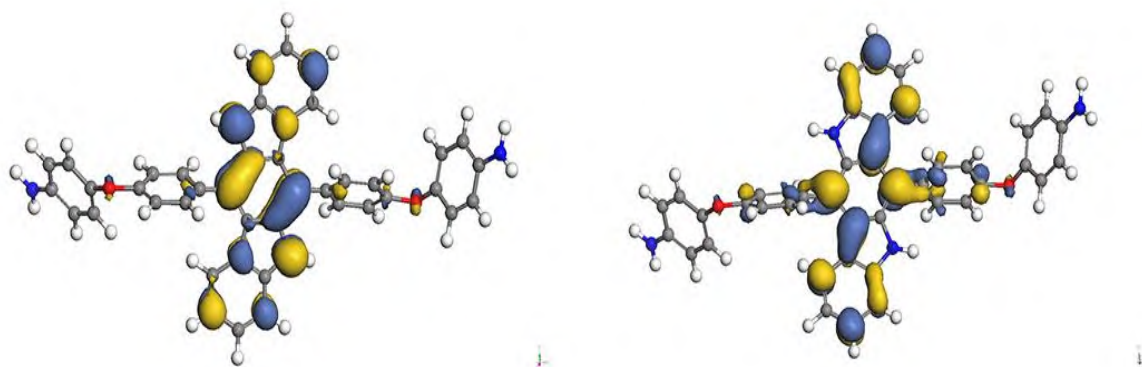
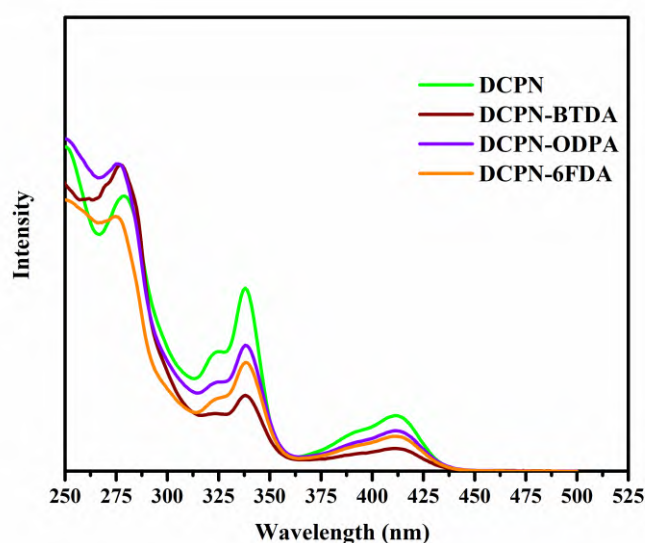


Fig. 7. HOMO (left) and LUMO (right) of the monomer DCPN

The absorption behavior of monomer and polyimides was analyzed by UV-vis spectroscopy at room temperature using NMP (0.02 mg/mL), as shown in Fig. 8. The respective shorter absorption maxima (λ_{\max}) at about 277 nm for DCPN

and DCPN serials polymers are due to the absorption of indolocarbazole groups. The additional absorption peaks at about 338 and 410 nm are attributed to the π - π^* transition associated with the conjugated polymer backbone.

Fig. 8. UV-Vis spectra of monomer DCPN and polymers in NMP solution (0.02 mg/mL)

The PL spectra are shown in Fig. 9 and PL data of synthesized PIs in NMP (0.02 mg/mL), NMP (1 mg/mL) and film are summarized in Table 4. The PL spectral data of PIs are found similar with the indolocarbazole monomer, which indicates that the structure of dianhydride has little effect on fluorescence, and monomeric indolocarbazole is the main color group. However, the strength of the three polymers has been weakened, indicating the formation of electron transfer complex (CTC) between the segments^[4]. The intensity of BTDA is smaller than that of 6FDA and ODPA, which reveals the introduction of flexible aliphatic segments and greater free volume of 6FDA can hinder the formation of CTC on a certain degree, and thus decrease the optical loss and improve the optical properties (light color, high

transparency, etc.)^[26]. The aggregation of molecules has a significant impact on the light-emitting behavior of the polymer. As the concentration increases to 1 mg/mL, there may be intermolecular charge transfer between the indolocarbazole molecule and the polyimide backbone, which will affect the photoluminescence performance of polyimides in the aggregate state, leading to slight red shift. In film state, the fluorescence of polyimides still maintains certain photoluminescence performance with maximum emission wavelength at about 451 nm but fluorescence is quenched dramatically. In addition, the intensity of DCPN-6FDA is higher than that of DCPN-ODPA as film because of the higher transparency and lighter color of DCPN-6FDA.

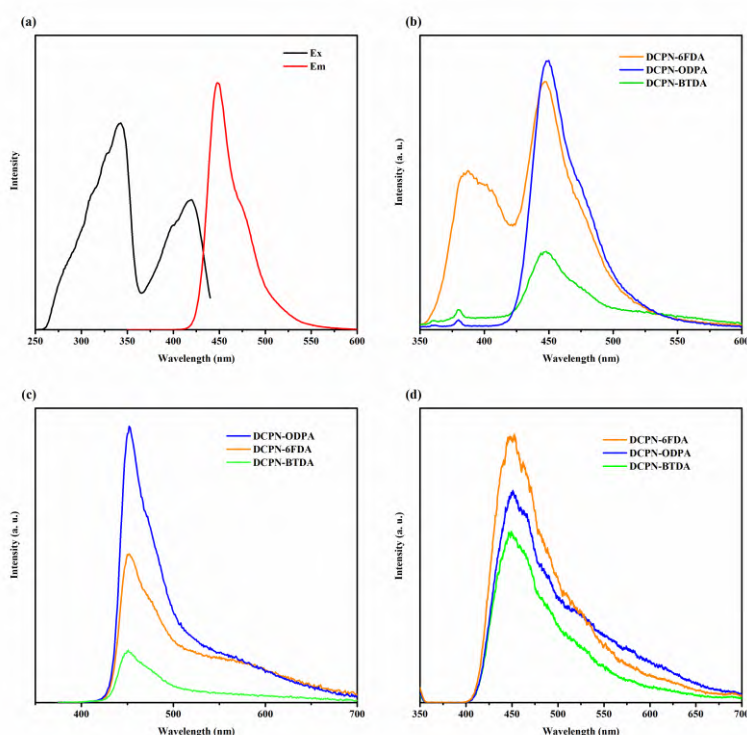


Fig. 9. (a) photoluminescence spectrum of monomer DCPN in NMP solution (0.02 mg/mL), (b) PL emission plots of polymers in NMP solution (0.02 mg/mL), (c) PL emission plots of polymers in NMP solution (1 mg/mL) and (d) PL emission plots of polymers as film spin-coated by 1 mg/mL NMP solution of polymers respectively

Table 4. Optical Properties of the Monomers and Polymers

Samples	0.02 mg/mL in NMP solution		1 mg/mL in NMP solution			Film
	λ_{\max} (UV)	λ_x (nm)	λ_m (nm)	λ_x (nm)	λ_m (nm)	λ_m (nm)
Monomer	279, 338, 412	343	448	/	/	/
DCPN-BTDA	277, 338, 410	339	448	377	451	449
DCPN-ODPA	275, 338, 411	346	450	371	452	451
DCPN-6FDA	275, 339, 411	338	447	375	450	453

The polyimide films exhibit high performance on thermal stability and mechanical property, organo-solubility in polar solvents and certain photoluminescence performance, which show great potential application in the field of optics and microelectronics.

4 CONCLUSION

A series of polyimides containing indolocarbazole in the main chain have been prepared from a new diamine monomer 4,4'-(((5,11-dihydroindolo[3,2-b]carbazole-6,12-diyl)bis(4,1-phenylene))bis(oxy))dianiline (DCPN) and different dianhydrides, which exhibit excellent film-forming

ability and high optical transparency. The properties of these polymers have been systematically researched. All polymers exhibit good solubility in polar solvents, high T_g above 334 °C and excellent thermal stability without significant weight loss under 500 °C. The DFT calculation indicates DCPN is a stable hole carrying materials with an energy level difference of 2.51 eV. The PL λ_{max} s of PIs are similar to that of the monomer without significant shift but optical loss. All polymers show the blue light in 0.02 mg/mL NMP solution and 1 mg/mL NMP, and exhibit certain photoluminescence performance as film state without any significant shift, which could be considered as newly processable and for optical uses in high performance polymer.

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