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ARTICLE TYPE

Synthesis of Indole-Based Functional Polymers with Well-Defined Structures via Catalyst-free C-N Coupling Reaction

Guanjun Chang,*[a] Li Yang,[a] Shenye Liu,[b] Xuan Luo,[b] Runxiong Lin,[c] Lin Zhang[b]

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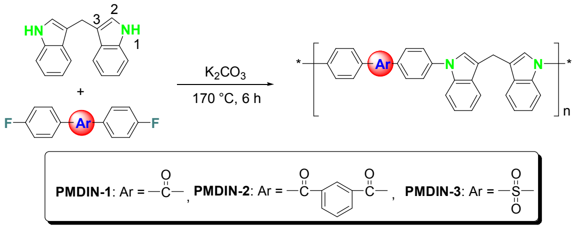
Poly(*N*-arylene diindolylmethane)s (**PMDINs**) with precise structures and high molecular weights (M_w up to 389200) in high yields (up to 95%) were synthesized by the catalyst-free nucleophilic substitution polycondensation of 3,3'-diindolylmethane with different activated difluoro monomers via C-N coupling reaction process. Model reaction was carried out to assist in the optimal reaction conditions for the polymerization and to elucidate the chemical structures of the polymers. The resulting polymers exhibited good thermal stability with high decomposition temperature ($T_{5\%} \geq 377$ °C). Fluorescent spectral studies indicated that all these **PMDINs** had strong solid-state fluorescence. Especially, the polymer **PMDIN-3** carrying sulfonyl units was a good blue-light emitter with high quantum yields (21.6%, determined against quinine sulfate). The results obtained by cyclic voltammetry suggested that **PMDINs** possessed good electroactivity. In addition, owing to the electrochemically active of indole rings at the 2- position, **PMDIN-3** was readily cross-linked by electrochemical oxidation and the cross-linking film was characterized by scanning electron microscopy. High molecular weights and good comprehensive performance of the indole-based polymers suggested that the catalyst-free C-N coupling reaction of indole derivatives with difluoro monomers could be considered as an effective polymerization route for the synthesis of new functional polymers with well-defined structures.

Introduction

Indole is ubiquitous in biological and biochemical structure, and has attracted extensive interest in the construction of pharmaceuticals, fragrances, agrochemicals, dyes and materials in past decades due to its unique electrical, chemical, and optical properties.[1,2] There are multiple reactive sites in the indole group e.g. 1-hydrogen position, 2-position, 3-position, etc. (see numbering of indole nucleus in Scheme 1), which can be used to design numerous significant bioactive natural products and chemical intermediates through C-N[3-5] or C-C[6,7] bond-forming reactions. The reactive sites in indole group could also be used to construct indole-based polymers for the applications in electronics, electrocatalysis, anode materials, anticorrosion coatings and biological areas, such as polyindole, which is usually obtained by polymerization of indole on its 2,3-position through the synthetic strategy of chemical oxidation or electrochemical polymerization.[8-10] Despite considerable efforts, the availability of such polymers is limited to a certain extent for a variety of reasons, including molecular weights, solubility in common organic solvents like $CHCl_3$, mechanical strength and thermal stability, etc.[8d,11] Therefore, the development of a new strategy for construction of soluble, heat-resistant and functional polyindoles with high molecular weights through chemical polymerisation still remains an attractive and promising goal.

In recent years, the catalytic *N*-arylation of indole using transition-metal[3-5] has become an important synthetic procedure for series of indole-based compounds. In view of some drawbacks in industrial applications of these transition-metal catalysts, such as expensive, oxygen sensitive, difficult to remove after the reaction and apt to leave toxic trace metal contaminants. Therefore, the development of a mild and efficient method for constructing *N*-arylindole motifs from indoles is highly desirable. In this study, we explore a facile and easier controlled polymerization technique for the synthesis of novel poly(*N*-arylene diindolylmethane)s (**PMDINs**) with structural regularity by a catalyst-free C-N coupling polycondensation reaction. 3,3'-diindolylmethane with two functional groups is rationally designed to react with activated difluoro monomers, which could proceed smoothly under milder nucleophilic substitution polycondensation reaction conditions compared with our previous reports[12] and successfully lead to chain propagation to give high molecular weight polymers (Scheme 1). Since the new indole-based polymers possess indole rings in the mainchain, they are expected to be endowed with high thermal stability, outstanding photoluminescence and good electroactivity, which would warrant their potential of applications for advanced high-performance materials.



Scheme 1 Synthesis of poly(*N*-arylene diindolylmethane)s (**PMDINs**) via C-N coupling reaction.

Experimental Section

Materials

1,3-bis(4'-fluorobenzoyl) benzene and indole were purchased from Sigma-Aldrich Chemicals and used without further purification. 4,4'-difluorobenzophenone and 4,4'-difluorodiphenyl sulphone were purchased from J & K Technology Co., Ltd., and were purified by recrystallization from alcohol twice before use. 3,3'-Diindolylmethane was synthesized according to the procedures reported by Pool et al.[13] The rest of materials and reagents were obtained from different commercial sources and used without further purification.

Measurements

FT-IR spectra were recorded on a Nicolet 6700 FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker AMX600 MHz NMR spectrometers in CDCl$_3$ or DMSO-d_6, depending on the solubility of the material being analyzed. The elemental analysis characterization technique was performed using a Vario EL III apparatus. The molecular weights and molecular weight distributions were estimated by gel permeation chromatography (GPC) on a Wyatt DAWN HELEOS using *N,N*-dimethylformamide (DMF) as an eluent, testing temperature 50 °C. Thermogravimetric analysis (TGA) was performed on a Setarma TG-92 at a heating rate of 10 °C/min under air and nitrogen atmosphere. Absorption spectra were detected on a SHIMADZU UV-3150 uv-vis-NIR sprectrophotometer. Fluorescent emission spectra were collected on a PerkinElmer LS-55 fluorescence spectrometer. The cyclic voltammograms were recorded with a Zennium IM6 electrochemical workstation (Zahner, Germany) using a normal three-electrode cell with a Pt working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode in 1.0 M H$_2$SO$_4$ at a scan rate of 20 mV/s. Electrochemical oxidation and deposition of polymers on stainless steel substrate were carried out using PARSTAT 2273 potentiostat controlled by powersuite software (Princeton Applied Research, USA) with polymer solution (30 mM in *N*-methylpyrrolidinone) with tetrabutylammonium chloride as supporting electrolyte (80 mM). Scanning electron microscopy (SEM) measurements were taken using a ZEISS EVO18 instrument.

General synthetic procedure for model compounds (3-5)

A typical synthetic procedure for model compound **3** is illustrated as an example. An oven-dried resealable Schlenk flask was evacuated and backfilled with argon. The flask was charged with indole (2.2 mmol), 4,4'-difluorobenzophenone (1.0 mmol), K$_2$CO$_3$ (2 mmol), and *N*-methylpyrrolidinone (NMP) (5 mL). The reaction mixture was evacuated and flushed with high-purity argon. This procedure was repeated three times. The flask was immersed with continuous stirring in a 160 °C oil bath for 4 h. The resulting solution was allowed to slowly cool to room temperature and subsequently poured into cold water, filtered through Celite, and dried. The crude material was purified by flash chromatography on silica gel and recrystallized from *N,N*-dimethylacetamide (DMAc) to afford **3** as light yellow crystals (0.41 g, yield 98%). Syntheses of **4** and **5** were carried out in the same manner with yields all above 95%.

3: Yield: 98%; M.p. 204 ºC; FT-IR spectrum (KBr pellet, cm^{-1}): 3042, 1652, 1600, 1510, 1455, 1335, 755; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.80 (d, J = 1.8 Hz, 2H), 7.18 (t, J = 7.8 Hz, 7.2 Hz, 2H), 7.26 (t, J = 7.8 Hz, 7.2 Hz, 2H), 7.69 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 3.0 Hz, 2H), 7.85 (d, J = 8.4 Hz, 4H), 8.02 (d, J = 8.4 Hz, 4H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 104.9, 110.7 120.9, 121.2, 122.8, 123.0, 128.2, 129.6, 131.6, 134.2, 134.8, 142.6, 193.6 ppm; Anal. Calcd for C$_{29}$H$_{20}$N$_2$O: C, 84.44; H, 4.89; N, 6.79; Found: C, 84.16; H, 4.92; N, 6.70.

4: Yield: 95%; M.p. 133 ºC; FT-IR spectrum (KBr pellet, cm^{-1}): 3052, 1658, 1599, 1516, 1455, 1338, 743; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.78 (d, J = 2.4 Hz, 2H), 7.16 (t, J = 4.2 Hz, 3.6 Hz, 4H), 7.68 (m, 4H), 7.78 (d, J = 2.4 Hz, 2H), 7.83 (m, 5H), 8.03 (d, J = 8.4 Hz, 4H), 8.13 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 105.0, 110.7, 120.9, 121.2, 122.8, 123.0, 128.2, 129.3, 129.6, 130.5, 131.8, 133.3, 133.6, 134.7, 137.2, 142.9, 194.0 ppm; Anal. Calcd for C$_{36}$H$_{24}$N$_2$O$_2$: C, 83.70; H, 4.68; N, 5.42; Found: C, 83.36; H, 4.70; N, 5.38.

5: Yield: 97%; M.p. 198 ºC; FT-IR spectrum (KBr pellet, cm^{-1}): 3048, 1592, 1520, 1453, 1336, 763; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 6.78 (d, J = 3.0 Hz, 2H), 7.16 (t, J = 7.2 Hz, 2H), 7.23 (t, J = 7.8 Hz, 7.2 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 3.0 Hz, 2H), 7.90 (d, J = 8.4 Hz, 4H), 8.19 (d, J = 8.4 Hz, 4H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 105.3, 110.7, 121.1, 121.2, 123.0, 124.0, 128.2, 129.4, 129.7, 134.6, 137.8, 134.3 ppm; Anal. Calcd for C$_{28}$H$_{20}$N$_2$O$_2$S: C, 74.98; H, 4.49; N, 6.25; Found: C, 74.73; H, 4.52; N, 6.19.

Synthesis of poly(*N*-arylene diindolylmethane)s (PMDINs)

A typical synthetic procedure for polymer **PMDIN-1** is illustrated as an example. To a three-necked flask (25 mL) equipped with magnetic stirrer, an argon outlet, inlet, and water-cooled condenser, 3,3'-diindolylmethane (4.0 mmol), 4,4'-difluorobenzophenone (4.0 mmol), K$_2$CO$_3$ (8 mmol), and NMP (10.0 mL) were added. The reaction mixture was evacuated and flushed with high-purity argon. This procedure was repeated three times. The reaction mixture was heated to 170 ºC and maintained at this temperature for 6h. The resulting polymer solution was allowed to slowly cool to room temperature, and subsequently poured into cold water, filtered, washed with water and methanol, and then dried at 100 °C under vacuum (1.645 g, yield 97%). Syntheses of other **PMDINs** were carried out in the same manner with yields all above 95%.

PMDIN-1: Yield: 97%; FT-IR spectrum (KBr pellet, cm^{-1}): 3044, 2916, 1659, 1598, 1512, 1454, 1249, 745; ^{1}H NMR (600 MHz, CDCl$_3$): δ = 4.32 (s, 2H), 7.20 (s, 6H), 7.52 (m, 4H), 7.66 (m, 4H), 7.91 (m, 4H) ppm; Anal. Calcd for (C$_{30}$H$_{20}$N$_2$O)$_n$ (424.49)$_n$: C, 84.88; H, 4.75; N, 6.60; Found: C, 82.76; H, 4.83;

N, 6.48.

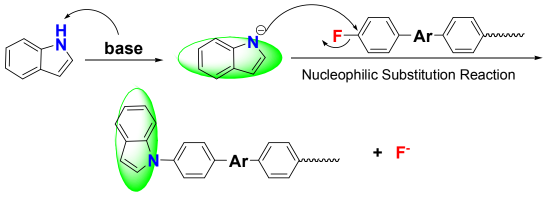
PMDIN-2: Yield: 95%; FT-IR spectrum (KBr pellet, cm^{-1}): 3047, 2900, 1677, 1591, 1499, 1454, 1307, 1152, 747; ^1H NMR (600 MHz, $CDCl_3$): δ = 4.30 (s, 2H), 7.14 (m, 6H), 7.54 (d, *J* = 12.0 Hz, 4H), 7.61 (m, 5H), 7.91 (d, *J* = 12.0 Hz, 4H), 7.99 (d, *J* = 10.8 Hz, 2H), 8.21 (s, 1H) ppm; Anal. Calcd for $(C_{37}H_{24}N_2O_2)_n$ $(528.60)_n$: C, 84.07; H, 4.58; N, 5.30; Found: C, 83.66; H, 4.62; N, 5.13.

PMDIN-3: Yield: 96%; FT-IR spectrum (KBr pellet, cm^{-1}): 3055, 2918, 1655, 1594, 1511, 1456, 1270, 930, 743; ^1H NMR was not recorded due to the poor solubility of the polymer in DMSO-d_6 and $CDCl_3$ at room temperature; Anal. Calcd for $(C_{29}H_{20}N_2O_2S)_n$ $(460.55)_n$: C, 75.63; H, 4.38; N, 6.08; Found: C, 73.96; H, 4.40; N, 6.00.

Results and Discussion

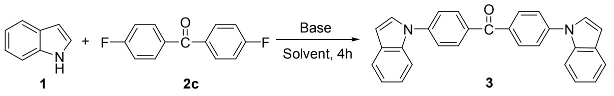
Model reaction

To confirm the activity of the NH group in the nucleus of indole and gain insights into the chemical structures of the polymers, we performed the *N*-arylation of indole with electron-deficient fluorobenzene as a model reaction. In this work, we here describe a simple, highly efficient catalyst-free *N*-arylation in which fluorines of fluorobenzene derivatives having additional electron-withdrawing groups like carbonyl and sulfonyl is substituted for indoles. This was determined during a preliminary survey of reaction conditions with use of highly electron-deficient 4,4'-difluorobenzophenone and indole as model arylating agents shown in Table 1. To identify the optimized reaction conditions for the reaction, a series of different organic solvents, bases and reaction temperatures were examined. At low temperature, no or trace amount of product was obtained (Table 1, entries 1 and 2). At the higher temperatures, the yields increased dramatically (compare entries 3-4). In addtion, we found that the choices of base and solvent were also crucial to the outcome of the reaction. Among the solvents tested, NMP was clearly the best choice, while DMF, DMAc and sulfolane provided slightly low yields (compare entries 4-8), this may be related to the dissolution properties of the products. Of the bases tested, potassium carbonate or cesium carbonate was most effective and efficient for product formation (compare entries 4 and 9-14), and this indicated that indole moiety with negative charge (nucleophile) could be easily formed with potassium carbonate or cesium carbonate being used as the base (Scheme 2).



Scheme 2 *N*-arylation of indole with electron-deficient fluorobenzene.

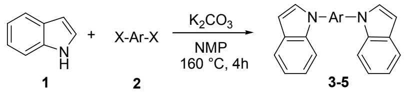
Table 1 Some representative results from the screening of reaction conditions for the *N*-arylation of indole with 4,4'-difluorobenzophenone[a]

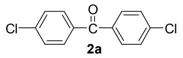
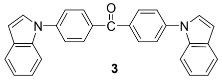
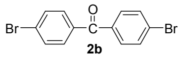
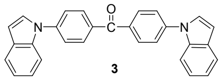
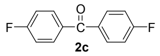
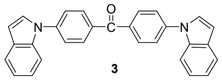
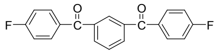
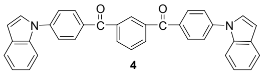
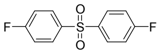
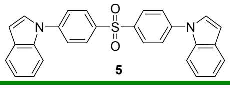


Entry	Solvent	Temp (°C)	Base	Yield [b] (%)
1	NMP	100	K_2CO_3	*c*
2	NMP	120	K_2CO_3	<8
3	NMP	140	K_2CO_3	55
4	NMP	160	K_2CO_3	98
5	DMF	160	K_2CO_3	92
6	DMA	160	K_2CO_3	93
7	DMSO	160	K_2CO_3	80
8	sulfolane	160	K_2CO_3	84
9	NMP	160	K_3PO_4	95
10	NMP	160	KF	21
11	NMP	160	Li_2CO_3	*c*
12	NMP	160	Na_2CO_3	13
13	NMP	160	Cs_2CO_3	99
14	NMP	160	NaO*t*Bu	26

[a] Reaction conditions: indole (2.2 mmol), 4,4'-difluorobenzophenone (1.0 mmol), and base (2.0 equiv) in 5.0 mL of solvent under an argon atmosphere for 4h. [b] Isolated yields (average of two runs). [c] Little coupling product was determined. NMP = *N*-methylpyrrolidone, DMF = *N*,*N*'-dimethylformamide, DMAc = *N*,*N*'-dimethylacetamide, DMSO = dimethylsulfoxide.

Table 2 *N*-arylation of indoles with electron-deficient halobenzenes[a]



Entry	Electron-deficient halobenzenes	Product	Yield[b] (%)
1	 **2a**	 **3**	58
2	 **2b**	 **3**	26
3	 **2c**	 **3**	98
4	 **2d**	 **4**	95
5	 **2e**	 **5**	97

[a] Reaction conditions: indole (2.2 mmol), **2** (1.0 mmol), and 2.0 mmol of K_2CO_3 in 5 mL of NMP at 160 ºC under an argon atmosphere for 4h. [b] Isolated yields (average of two runs) based on **2**.

With optimized conditions now in hand, we explored the scope of the *N*-arylation reactions of a series of other electron-deficient halobenzenes with indole in the presence of 2.0 equiv of K_2CO_3 in NMP at 160 ºC under an argon atmosphere, and the results are summarized in Table 2. Gratifyingly, each replacement of fluorine reacted under the optimized reaction conditions to give the corresponding *N*-arylated indole derivatives in good to excellent yields (up to 98%) (entries 3-5), although chlorobenzene or bromobenzene showed poorer reactive activity and gave lower yield. The model compounds **3-5** were characterized by standard spectroscopic techniques from which satisfactory analysis data corresponding to their expected molecular structures were obtained (see Experimental Section for details). Therefore, we envisaged that the present methodology might be a clue for constructing new *N*-arylindoles as well as various indole-based functional polymer materials.

Polymerization reaction

To explore the catalyst-free C-N coupling reaction of NH group with activated difluoride into a useful tool for the preparation of sequentially well-defined indole-based polymers, we rationally designed a bifunctional monomer 3,3'-diindolylmethane, and the synthesis of it was carried out as depicted in Supporting Information for details. The polymerization reaction of 3,3'-diindolylmethane with different aromatic difluoro monomers was performed in NMP, and a series of novel poly(*N*-arylene diindolylmethane)s (**PMDINs**) with high molecular weights were obtained in high yields (Scheme 1).

To search for optimum conditions for the polymerization, we first studied temperature effect on the polymerization in NMP. Taking **PMDIN-1** as an example, as exhibited in Table 3, the temperature exerted strong effect on the reaction. Upon increasing the temperature from 140 to 170 °C, M_w increased from 10600 to 141700 and the resulting polymer was obtained in high yield (97%). Clearly, the polymerization proceeded only when sufficient energy was provided.

Table 3 Temperature effect on the polymerization of 4,4'-difluorobenzophenone with 3,3'-diindolylmethane to form **PMDIN-1**[a]

Entry	Temp (°C)	M_n[b]	M_w[b]	M_w/M_n[b]	Yield (%)
1	140	5100	10600	2.08	52
2	150	21300	47300	2.22	78
3	160	45000	98700	2.19	90
4	170	65600	141700	2.16	97

[a] Carried out under an argon atmosphere in NMP for 6 h. Concentrations of monomers were 0.4 mol/L. [b] Determined by GPC in DMF on the basis of a polystyrene calibration.

We then investigated the concentration effect on the molecular weights. As shown in Table 4, neither lower (0.3 mol/L) nor higher (0.5 mol/L) concentrations of monomers were good for the polymerization. The reaction rates are slower with a lower concentration, and higher concentration promote by-product formation. Instead, a concentration of 0.4 mol/L is enough to give a soluble polymer with a high molecular weight in a high yield.

Table 4 Concentration effect on the polymerization of 4,4'-difluorobenzophenone with 3,3'-diindolylmethane to form **PMDIN-1**[a]

Entry	Concn of monomers (mol/L)	M_n[b]	M_w[b]	M_w/M_n[b]	Yield (%)
1	0.1	9500	19700	2.07	66
2	0.2	16700	35800	2.14	73
3	0.3	42200	88300	2.09	84
4[c]	0.4	65600	141700	2.16	97
5	0.5	46300	93600	2.02	89

[a] Carried out under an argon atmosphere in NMP at 170 °C for 6 h. [b] Determined by GPC in DMF on the basis of a polystyrene calibration. [c] Data taken from Table 3, entry 4.

The above investigation allowed us to polymerize other monomer combination under optimum conditions. The polymerization results are exhibited in Table 5. All the polymerizations proceed smoothly, affording polymers in high yields (95-97%) with high molecular weights (M_w = 109100-389200). Compared with that of traditional polyindole, the synthesis conditions of the acquired **PMDINs** are milder and the molecular weights and yields are much higher.[8d] The polymerization of 3,3'-diindolylmethane with 1,3-bis(4'-fluorobenzoyl) benzene gave much better results: the obtained polymer **PMDIN-2** with higher molecular weight up to 389200 was isolated in higher yield up to 95%. Furthermore, the synthesized polymers were characterized by FT-IR, ^{1}H NMR and elemental analyses. The satisfactory results were in good agreement with the proposed structures (see Experimental Section). The ^{1}H NMR spectrum of **PMDIN-2** is given in Fig. 1 (DMSO-d_6) as an example. There was no peak at δ 10.73 ppm, which was assigned to the resonance of the NH proton of 3,3'-diindolylmethane. It was suggestive of the occurrence of the polymerization. Moreover, the absorption peaks of **PMDIN-2** were much broader than those of monomers, indicative of its polymeric nature.

Table 5 Polymerization data for poly(*N*-arylene diindolylmethane)s (**PMDINs**)

Polymer Code	M_n[a]	M_w[a]	M_w/M_n[a]	Yield (%)
PMDIN-1	65600	141700	2.16	97
PMDIN-2	115800	389200	3.36	95
PMDIN-3	56100	119100	2.12	96

[a] Determined by GPC in DMF on the basis of a polystyrene calibration.

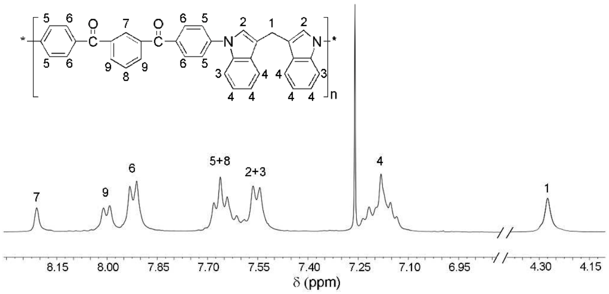


Fig. 1 ^{1}H NMR (600 MHz) spectrum of **PMDIN-2** recorded in $CDCl_3$.

Thermal stability

The thermal properties of **PMDIN**s were evaluated by thermogravimetric analysis (TGA). As depicted in Fig. 2, all the polymers enjoyed high thermal stability, exhibiting 5% weight loss at temperature (T_d) from 377 to 392 °C. They also carbonized in moderate yields up to *ca.* 42% when they were heated to 700 °C. The PMDINs showed higher decomposition temperatures in nitrogen than that in oxygen.

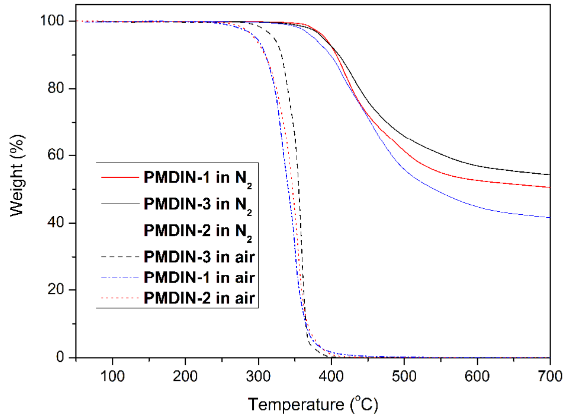


Fig. 2 TGA thermograms of **PMDINs** recorded under nitrogen.

Optical properties

According to our previous published paper,[12] we found that the prepared polyindoles were blue light-emitting polymers, in which there were undergone an intramolecular charge transfer from the electron donor (indole segment) to the acceptor (the electron-deficient group of sulfonyl or carbonyl portion) to result in luminescence. In this paper, our motivation was the introduction of more indole rings into the polymer main chains to construct some new efficient blue photoluminescence polyindoles promising for use in blue PLEDs. UV absorption and fluorescence spectra of dilute solutions of model comcounds **3-5** and **PMDINs** in NMP were recorded and the related photophysical data are summarized in Table 6. Fig. 3 shows the optical absorption and emission spectra of **PMDINs**. The polymers had two absorption peaks. Among the polymers, the absorption maxima of **PMDIN-3** containing the sulfonyl unit exhibited the blue-shifted absorption profile (278 and 338 nm), revealing that it possessed the lowest electronic conjugation (Fig. 3a and Table 6). In addition, model compounds **3-5** gave rise to similar UV absorption bands. **3** and **4** displayed almost the same electronic absorption energies, and the λ_{max} values were in the range of 288-341 nm. However, the long wavelength absorption maximum (327 nm) of **5** was obviously blue-shifted compared to that of **3** (341 nm) (Fig. S1). These results demonstrated a good agreement with those of **PMDINs**. Moreover, the absorption maximum of **PMDIN-3** solids was red-shifted by 14 nm compared with the maximum of it in solution. The red shift indicated enhanced intermolecular electronic interactions in the solid state.[14] In contrast, a blue shift of 27 nm observed for **PMDIN-2** was larger than that of **PMDIN-1** due to the lower polymer coplanarity in the solid state.

Table 6 Optical properties of model compounds, **PMDINs** in solution[a] and in solid-state

Model compound	$\lambda_{ab}{}^{b}$ (nm)		$\lambda_{em}{}^{c}$ (nm)	
	Soln		Soln ($\Phi_F{}^{d}$)	
3	288, 341		515 (0.53%)	
4	289, 337		518 (0.24%)	
5	288, 327		453 (15.8%)	
Polymer	$\lambda_{ab}{}^{b}$ (nm)		$\lambda_{em}{}^{c}$ (nm)	
	Soln	Solid	Soln ($\Phi_F{}^{d}$)	Solid
PMDIN-1	289, 357	348	513 (1.2%)	495
PMDIN-2	281, 353	326	463 (0.85%)	480
PMDIN-3	278, 338	352	460 (21.6%)	444

[a] In dilute NMP solution (10 μM). [b] Absorption maximum. [c] Emission maximum. [d] Φ_F = fluorescence quantum yield in NMP solution determined using quinine sulfate (Φ_F = 0.55 in 1 M H_2SO_4) as standard.

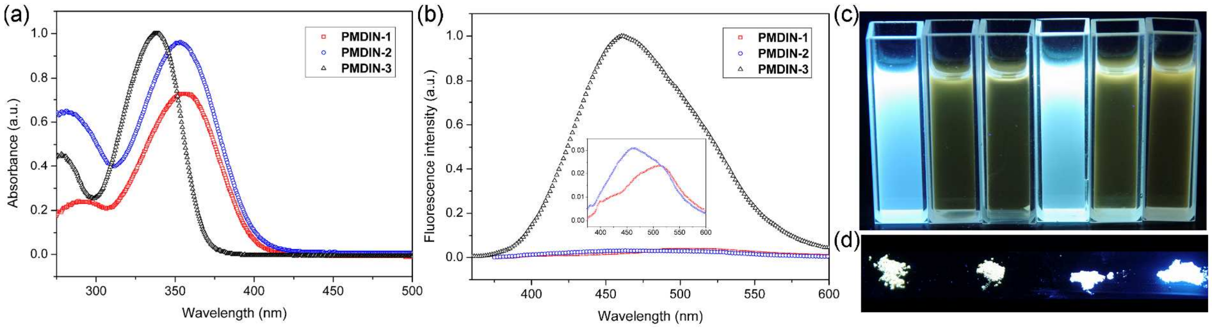


Fig. 3 (a) UV and (b) Fluorescence spectra of **PMDINs** in NMP solutions. Solution concentration: 10^{-5} M; excitation wavelength (nm): 355 (**PMDIN-1**), 353 (**PMDIN-2**), and 340 (**PMDIN-3**); excitation and emission slits (nm): 5.0 nm and 3.0 nm, respectively. (c) Fluorescence images of model compounds and **PMDINs** in NMP, irradiated at 365 nm; From left to right: **5**, **3**, **4**, **PMDIN-3**, **PMDIN-1**, and **PMDIN-2**. (d) Fluorescence images of **5** and **PMDINs** (powder, λ_{exc} = 365 nm). From left to right: **PMDIN-3**, **PMDIN-1**, **PMDIN-2**, and **5**.

Next, we investigate the photoluminescence properties of model compounds and **PMDINs**. The fluorescence curves in Fig. 3b show that the emission peaks of **PMDINs** in dilute NMP solutions at 10 μM were centered at 460-513 nm, whereas those of model comcounds **3-5** were observed at the slight shorter wavelengths of 453-518 nm (Fig. S2, Table 6). **3**, **4**, **PMDIN-1**, and **PMDIN-2** exhibited weak yellow fluorescent emissions. In contrast, **5** and **PMDIN-3** displayed blue-green fluorescent emissions (Fig. 3c). Notably, for **PMDIN-1** and **PMDIN-3**, the emission peaks were close to those of **3** and **5** as shown in Table 6. However, for **PMDIN-2**, the emission maximum was about a 55 nm blue shift relative to that of **4**. We have proposed that the drastic changes in the emission wavelength between polymers and model compounds mainly depended upon the dipole moment at an excited state.[15] It was inferred that the 1,3-bis-benzoyl groups in the polymer **PMDIN-2** chains were less suitable than the carbonyl groups or the sulfonyl groups for an perturbation of the dipole moment and electronic status at an excited state, which could give rise to dynamic changes in the emission wavelength. In addition, the fluorescence quantum yields (Φ_F) of **PMDINs** determined in NMP solutions using quinine sulfate (Φ_F = 0.55 in 1 M H_2SO_4) as standard[16] were 1.2%, 0.85% and 21.6%, respectively, whose values became much higher than those of model compounds (Φ_F = 0.53%, 0.24% and 15.8%, respectively).

It is a challenging project for the design and synthesis of polymers exhibiting highly efficient solid-state luminescence for the development of optoelectronic PLED devices. Conventional luminescent polymers often suffer from strong interstrand interaction in the aggregated state, which quenches and red-shifts their light emission.[17] However, in this work, it is remarkable that model compound **5** and **PMDINs** all exhibited strong solid-state fluorescence upon excitation with UV light (λ_{exc} = 365nm, Fig. 3d). The solid-state emission wavelengths of **PMDINs** were observed from 444 to 495 nm (Table 6). These results could be attributed to aggregation-induced emission (AIE).[18] We assumed that the indole units in **PMDINs** were linked together by methylene groups, which could rotate relatively freely in the solution state and the intramolecular rotation could serve as nonradiative pathways for the excitons to decay. In the aggregated state, such rotation was partially restricted, which blocked the relaxation channels and thus turned on the light emission of the luminophore.[19] These characteristics make these **PMDINs** potential candidates for polymer emitters and solid-state lighting devices.

Electrochemical properties

The energy levels of the HOMO and LUMO were determined by measuring the electrochemical properties of **PMDINs** using cyclic voltammetry (CV). A platinum (Pt) electrode was modified with a polymer film by means of dip-coating, and was used as the working electrode. A Pt wire was used as the counter electrode, and Ag/AgCl (4.0 M KCl) served as the reference electrode. The CV measurements were carried out in a 1.0 M H_2SO_4 electrolyte at room temperature at a scan rate of 20 mV/s. For all the polymers, a reversible oxidation process was observed (Fig. 4). The HOMO level of the polymers was deduced based on the oxidation onsets under the assumption that the energy level of ferrocene (Fc) was *ca.* -4.8 eV.[20] In the anodic scan, the onset of oxidation for **PMDIN-1**, **PMDIN-2**, and **PMDIN-3** occurred at 0.46, 0.48, and 0.45 V, respectively. We assumed that these peaks could be attributed to the oxidation of indole units which are still electrochemically active especially at the 2- positions.[9(a),12] The HOMO energy levels of **PMDIN-1-3** are -5.26, -5.28, and -5.25 eV, respectively. As expected from the structures of the polymers, **PMDINs** with identical backbone structures have similar HOMO energy values. The LUMO energy levels of the polymers were calculated using their HOMO energies and optical band gaps to be -2.60, -2.51, and -2.10 eV, respectively. The lower LUMO level of **PMDIN-3** indicated that sulfone moiety was a strong electron accepting building block. In addition, the very similar HOMO and LUMO levels measured for **PMDIN-1** and **PMDIN-2** demonstrated that the energy levels were mainly determined by their conjugated backbone. For this reason, we assumed that the electron-withdrawing sulfonyl group adopting the tetrahedron structure significantly affected the coplanar structure of the polymer and exerted an important effect on optical properties as well as electrochemical properties.

To further verify the electrochemically active of indole units at the 2- position, we also investigated the electrochemical deposition of the polymer **PMDIN-3**. The SEM images of a thin **PMDIN-3** film prepared in NMP were shown in Fig. 5. Macroscopically, the film that formed on a stainless steel anode was flat, compact and metallic black in color. Microscopically, the polymer film showed irregular growth of granules and resembled a growth of aggregates shaped as blossoms. It was expected that electrochemical oxidation of this polymer should result in coupling between 2-indolyl position, forming an extended three-dimensional cross-linked polymer network (Scheme 3). This confirmed the good redox activity of **PMDIN-3**. For comparison, the scanning electron micrograph of the dip coated linear **PMDIN-3** film was also tested (Fig. S10). Interestingly, the films formed by dip coated and electrodeposited had the different surface morphology. In order to further understanding the electrochemical activity of indole units at the 2- position, the IR spectrum of the electrodeposited film was carried out (Fig. S9). The peak located at 738 cm^{-1} can be assigned to the out-of-plane deformation of the C_2-H bond. It was obviously present for **PMDIN-3** and as lower for the electrodeposited film. This proved that the successful cross-linking of **PMDIN-3** occurred at the 2-position. Compared the CV of linear **PMDIN-3** with that of the electrodeposited film, the result further confirmed the cross-linking of **PMDIN-3**, but there still existed some unreactive 2-indolyl position in the film (inset in Fig. 5). All in all, the convenient and economical cross-linking method may be anticipated to construct an array of cross-linked polymer films with unique properties for high-technological applications, especially in advanced optoelectronic devices.

Table 7 Electrochemical data of polymers

Polymer	λ_{onset} (nm)	$E_g{}^a$ (eV)	E_{onset} (eV)	HOMO^b (eV)	LUMO^c (eV)
PMDIN-1	466	2.66	0.46	-5.26	-2.60
PMDIN-2	448	2.77	0.48	-5.28	-2.51
PMDIN-3	394	3.15	0.45	-5.25	-2.10

[a] Optical band gap calculated from the UV-Vis absorption onset. [b] The HOMO energy levels were determined from onset voltage of the first oxidation potential with reference to ferrocene at -4.8 eV. [c] LUMO levels of the polymers were estimated from the optical band gaps and the HOMO energies.

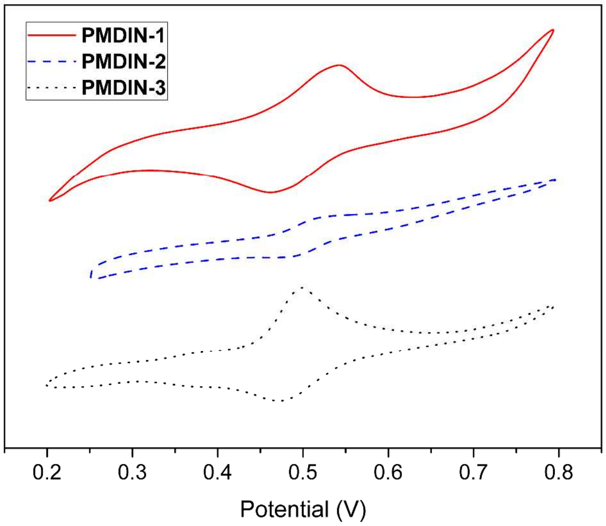


Fig. 4 Cyclic voltammograms of **PMDINs** conducted in aqueous H_2SO_4 (1.0 M) at a scan rate of 20 mV/s.

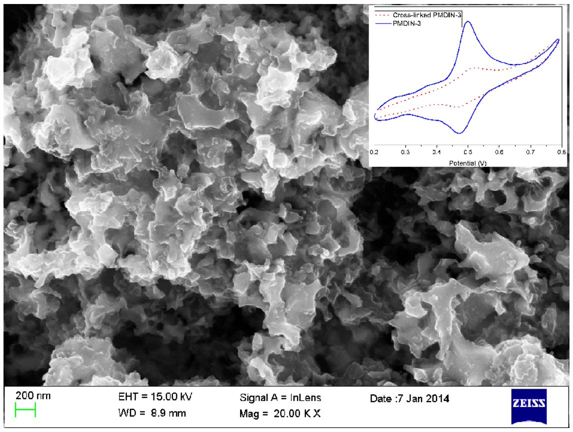


Fig. 5 Scanning electron micrograph of the electrodeposited **PMDIN-3**. Inset is the cyclic voltammograms of electrodeposited film.

Conclusions

In summary, we have demonstrated that nucleophilic substitution reactions with the NH group in the indole molecule as reactive groups gave novel **PMDINs**. The catalyst-free C-N polycouplings of 3,3'-diindolylmethane with different activated difluoro monomers proceed smoothly in NMP at 170 °C for 6 h, producing polymers **PMDIN-1-3** with high molecular weights in high yields. This provides a simple synthetic pathway that will allow the preparation of a great variety of indole-based polymers from commercially available aromatic compounds. Rational model reaction was performed to help elucidate the polymer structures. All these achieved polymers show good thermal stability with high decomposition temperatures (T_{d}s>370 $^{\mathrm{o}}$C). Due to the indole moieties in the main chains, these **PMDINs** are strong UV absorbers and display strong solid-state fluorescence. CV suggests that **PMDINs** have lower energy levels, particularly for **PMDIN-3**, which is promising as PLEDs materials. Moreover, owing to the good electroactivity, the polymers can be utilized as processable precursors to cross-linked films. This work does not only deepen our systemic understanding of catalyst-free nucleophilic substitution polycondensation but also provide new perspectives for generating indole-based polymers or cross-linked films with thermal stability and well optical properties. We expect that the present results will inspire research enthusiasm for creation of novel and high-performance polymers with new and/or enhanced functionalities and properties via this facile and easier synthetic strategy for high-technological applications in optoelectronics, automotive, aircraft, and spacecraft industry.

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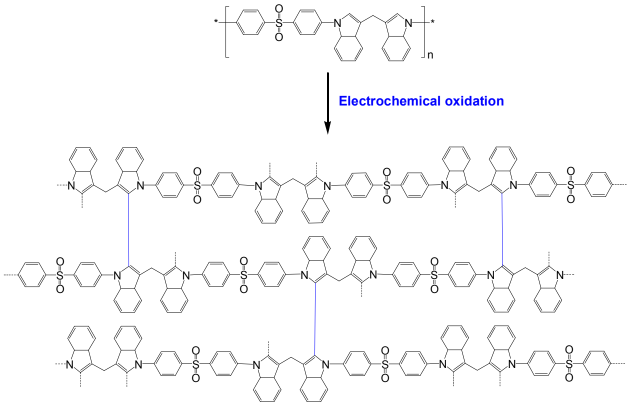

Scheme 3 A schematic representation of the formation of cross-linked polymer network.

Notes and references

[a] *State Key Laboratory Cultivation Base for Nonmetal Composite and Functional Materials & School of Material Science and Engineering, Southwest University of Science and Technology, Mianyang, 621010, People's Republic of China. Fax: +86-816-2419201; Tel: +86-13990158034; E-mail: gjchang@mail.ustc.edu.cn*
[b] *Research Center of Laser Fusion, China Academy of Engineering Physics, Mianyang, 621900, People's Republic of China.*
[c] *Engineering Research Center of High Performance Polymer and Molding Technology, Ministry of Education, Qingdao University of Science and Technology, Qingdao, 266042, People's Republic of China.*

† Electronic Supplementary Information (ESI) available: Optical properties, IR spectra for model compounds and **PMDINs**, copies of ^{1}H and ^{13}C NMR spectra. See DOI: 10.1039/b000000x/

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