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ORIGINAL PAPER

Synthesis of regiocontrolled triarylamine-based polymer with a naphthol unit

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Abstract

Redox-active polytriarylamine with hydroxyl groups is a useful material for optoelectronic applications, especially in the solution-processable multilayer devices. A novel regiocontrolled triarylamine-based polymer, poly(di-5-naphthyl-2-ol)phenylamine, with 2-naphthol units was synthesized via oxidative coupling polymerization. Polymerization in tetrahydrofuran using a Cu-amine complex oxidant under O_2 atmosphere produced polymers with number-averaged molecular weights as high as 11,300 g mol^{-1}. The structure of the polymer was characterized by ^1H and ^{13}C NMR spectroscopy, showing that the oxidative coupling polymerization occurred at the outer *ortho* position of the 2-naphthols, preserving the hydroxyl groups. The polymer exhibited good solubility in polar aprotic solvents, with a high thermal stability of 446 °C that corresponded to 5% weight loss. The UV–vis absorption of the polymer was similar to that of DNPA, indicating that the kinked-structured polymer hindered the formation of charge-transfer complexes. These results suggest promising applications of the developed polymer in optoelectronic devices.

Keywords Oxidative coupling polymerization · 2-Naphthol · Triarylamine · Regiocontrolled polymer

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Introduction

Aromatic polymers, including polyphenylene, polyaniline, polypyrrole, and polythiophene, have attracted significant interest due to their optoelectrical, thermal, and mechanical properties [1–4]. Typically, two polymerization methods are used in the synthesis of aromatic polymers: The first is a transition metal-catalyzed coupling polymerization of aryl dihalides [5–7], and the other involves oxidative coupling polymerization via electrochemical or chemical methods [8–11]. While the former strategy requires auxiliary functional groups for polymerization, such as dihalides, oxidative coupling polymerization can form carbon–carbon bonds from simple monomer structures [12]. Therefore, oxidative coupling polymerization provides a more practical route for the synthesis of aromatic polymers.

Hydroxyl-modified aromatic polymers have been applied for primer coating [13, 14], positive-type photosensitive polymer [15–18], and semiconductor manufacturing as both protection and insulation layers [19–21]. The reactive hydroxyl groups allow simple functionalization of the polymer, facilitating their usefulness for several applications [22–26]. However, oxidative coupling of phenolic hydroxyl groups generally involves C–O bond formation [27–29]. Therefore, a naphthol alternative has been used for oxidative coupling polymerization. Particularly, oxidative coupling of 2-naphthol using a catalytic amount of a Cu-amine complex showed good regioselectivity with excellent yields [30] suitable for polymer synthesis with a regioregular structure and preservation of its hydroxyl groups. Successful synthesis of hydroxyl-modified regioregular aromatic polymers has been reported, and extensive applications have been demonstrated [31–35].

The electron-rich and redox-active properties of triarylamine derivatives are useful for optoelectronic devices [36–38]. In addition, their bulky and propeller-shaped structure provides a porous aromatic framework for mesoporous materials with a high surface area that is suitable for use in proton membranes [39–42]. Triarylamine derivatives in polymers have advantages in terms of mechanical properties and easy processability compared to monomeric and oligomeric analogues [43–45]; especially, the oxidative coupling polymerization of triarylamine derivatives provides a straightforward method for preparing polymeric triarylamine and has been used for the successful synthesis of triarylamine polymers [46].

Herein, we report the synthesis of regiocontrolled poly(di-5-naphthyl-2-ol)phenylamine (PDNPA) by oxidative coupling polymerization of the triarylamine monomer containing two naphthol units. A novel triarylamine monomer was prepared by replacing phenyl rings with 2-naphthol units. Introduction of the naphthalene rings can lead to steric repulsion, which is advantageous in preventing a close packing of polymer chains due to its large dihedral angle and suppressing the formation of charge-transfer complex [47]. In addition, the hydroxyl group on naphthalene ring imparts a good adhesion and site that can introduce cross-linkable group for multilayer optoelectronic devices [48–50]. The synthesized polymer has BINOL structures in the main chain as a result of the oxidative coupling reaction of 2-napthol and can also be used as a soluble polymer-supported BINOL for various catalytic applications [51–55].

Experimental

Materials

Tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$], tri-*tert*-butylphosphine [$(t\mathrm{Bu})_3P$], sodium *tert*-butoxide (NaO*t*Bu), toluene, anhydrous tetrahydrofuran (THF, 99.9%), anhydrous *N,N*-dimethylformamide (DMF, 99.8%), tetramethylenediamine (TMEDA) tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), and anhydrous acetonitrile (99.8%) were purchased from Sigma-Aldrich. Aniline, methyl iodide (MeI), di-μ-hydroxo-bis[(*N,N,N′.N′*-tetramethylethylenediamine)copper(II)] chloride [CuCl(OH)TMEDA], and potassium carbonate (K_2CO_3) were purchased from TCI. Hydrobromic acid (HBr, 48% solution), acetic acid (99%), and sodium bicarbonate ($NaHCO_3$) were purchased from Junsei. Ethyl acetate (EA, 99%), hexane (95%), and magnesium sulfate ($MgSO_4$) were purchased from Daejung. 5-Iodo-2-naphthol was prepared according to a previously described method [56].

Material characterization

The ^{1}H and ^{13}C NMR spectra of the synthesized materials were recorded using a Bruker Fourier Transform AC 400 (400 MHz) spectrometer. Chemical shifts were expressed in parts per million (ppm) with reference to the residual peaks of DMSO for ^{1}H (2.49 ppm) and ^{13}C (39.52 ppm). Mass spectra were obtained using a microTOF-Q, and elemental analysis was recorded using a FLASH 200 series instrument. Polymer molecular weights and distributions were measured via size exclusion chromatography (SEC). The SEC traces were obtained using a Viscotek TDA302 instrument equipped with a RI detector and packing column (three PLgel 10 µm MIXED-B) using tetrahydrofuran (THF) as the eluent at 35 °C. The number and weight average molecular weights of the polymers were calculated relative to linear polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted using TA Instruments TGA Q500 and DSC Q100 instruments, respectively. The TGA and DSC measurements were performed under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The T_g values were determined from the second heating scan of the DSC thermograms after cooling to 0 °C from 200 °C. Wide-angle X-ray diffraction (WAXD) pattern was obtained with a Rigaku D/MAX-2500 X-ray diffractometer. Cu K alpha (1.5418 Å) was used as a light source. UV–vis spectra were measured on a JASCO V-530 spectrometer. The electrochemical experiments were performed using a CH instrument CHI 617B potentiostat equipped with a three-electrode system. Pt wire was used as the counter electrode, silver/silver nitrate ($Ag/AgNO_3$) as the reference electrode, and a 2-mm-diameter platinum disk as the working electrode.

Preparation of 6-(2-methoxy)-1-iodonaphthalene (1) 5-Iodo-2-naphthol (8.65 g, 32.03 mmol), anhydrous K_2CO_3 (22.110 g, 160 mmol), and MeI (22.71 g, 160 mmol) were dissolved in anhydrous DMF (100 mL). The solution was then heated at 70 °C and stirred for 16 h under a nitrogen atmosphere. The reaction mixture was subsequently poured into water and extracted with ethyl acetate. The organic layer was successively washed with water and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the remaining residue was purified via column chromatography on silica gel with ethyl acetate/hexane (1/4, v/v) as the eluent to yield an orange viscous liquid (9.01 g, 99%). ^1H and ^{13}C NMR spectra are shown in Figs. S1, S2.

^1H NMR (DMSO-d_6, 400 MHz, ppm): 7.94 (dd, 1H, $J=7.2$, 1.2 Hz), 7.89 (*d*, 1H, $J=7.6$ Hz), 7.87 (*d*, 1H, $J=6.8$ Hz), 7.35 (1H, *d*, $J=2.4$ Hz), 7.28 (dd, 1H, $J=9.2$ Hz), 7.20 (1H, *t*, $J=8$ Hz), 3.89 (3H, *s*). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 157.75, 134.96, 134.84, 132.88, 129.06, 127.91, 127.66, 120.36, 106.69, 99.15, 55.44.

Preparation of di(1-(6-(2-methoxy)naphthyl))phenylamine (2) The synthesis of compound **2** was performed based on a similar procedure that was described previously [57]. To a two-necked round-bottomed flask (RBF) equipped with a reflux condenser, **1** (8.93 g, 31.43 mmol), aniline (1.32 g, 14.19 mmol), $Pd_2(dba)_3$ (0.288 g, 0.31 mmol), $(tBu)_3P$ (0.25 g, 1.24 mmol), NaO*t*Bu (4.23 g, 44 mmol), and anhydrous toluene (80 mL) were added and stirred at 90 °C for 24 h under a nitrogen atmosphere. The mixture was poured into water and extracted with ethyl acetate. After drying over anhydrous $MgSO_4$, the solvent was evaporated. The residue was purified via column chromatography on silica gel with dichloromethane/hexane (1/1, v/v) as the eluent to yield a white solid (4.017 g, 86%). ^1H and ^{13}C NMR spectra are shown in Figs. S3, S4.

^1H NMR (DMSO-d_6, 400 MHz, ppm): 7.80 (2H, *d*, $J=9.2$ Hz), 7.67 (2H, *d*, $J=8.4$ Hz), 7.37 (4H, *m*), 7.12 (2H, *t*, $J=8$ Hz), 7.04 (2H, dd, $J=9.2$, 2.8 Hz), 6.96 (2H, dd, $J=7.4$, 1.2 Hz), 6.84 (1H, *t*, $J=7.2$ Hz), 6.56 (2H, dd, $J=8.6$, 1.2 Hz), 3.85 (6H, *s*). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): 157.25, 149.96, 144.17, 136.28, 129.04, 126.83, 125.09, 124.70, 124.55, 122.15, 120.60, 119.75, 118.68, 106.84, 55.16. Anal. Calcd. for $C_{28}H_{23}NO_2$: C, 82.94; H, 5.72; N, 3.45; O, 7.89. Found: C, 83.01; H, 5.70; N, 2.90. ESI–MS: *m/z* 406.17 for $[M+H]^+$ (Calcd for [M]: *m/z* 405.17).

Preparation of di(1-(6-(2-hydroxy)naphthyl))phenylamine (DNPA) To an RBF equipped with a reflux condenser, **2** (5.51 g, 13.59 mmol), HBr (17.1 mL, 48% solution), and acetic acid (70 mL) were added and stirred at 130 °C for 12 h. The mixture was subsequently poured into water and extracted with ethyl acetate. The organic layer was repeatedly washed with a basic solution (0.1 M $NaHCO_3$ aqueous solution). After drying over anhydrous $MgSO_4$, the solvent was removed under pressure. The residue was purified via column chromatography on silica gel with ethyl acetate/hexane (1/1, v/v) as the eluent. The resulting product was dissolved in toluene and precipitated in heptane to yield a gray solid (3.95 g, 77%).

^1H NMR (DMSO-d_6, 400 MHz, ppm): 9.79 (2H, *s*), 7.78 (2H, *d*, $J=9.2$ Hz), 7.53 (2H, *d*, $J=8.4$ Hz), 7.28 (2H, *t*, $J=8$ Hz), 7.17 (2H, *d*, $J=2.4$ Hz), 7.09 (2H, *t*, $J=7.8$ Hz), 6.95 (2H, dd, $J=9.2$, 2.4 Hz), 6.90 (2H, dd, $J=7.4$, 1.2 Hz), 6.80 (1H, *t*, $J=7.2$ Hz), 6.54 (2H, dd, $J=8.6$, 1.2 Hz). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm):

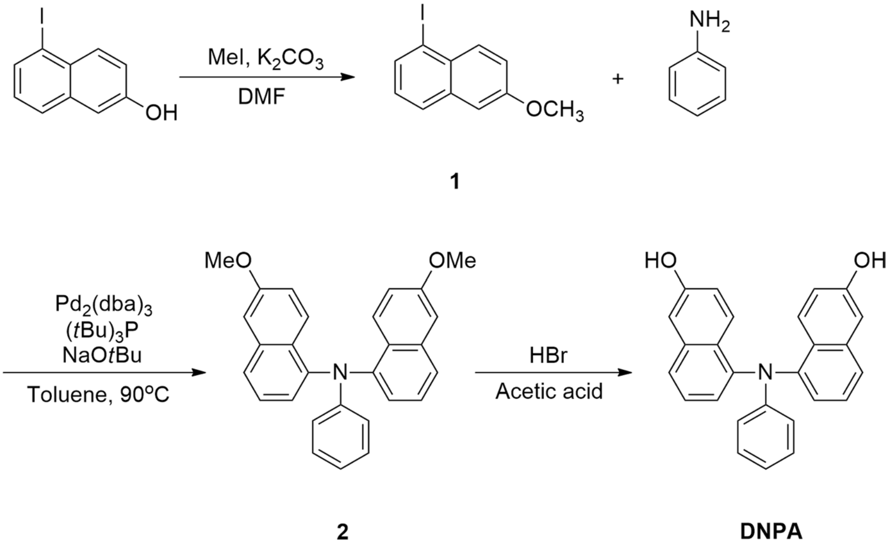
155.42, 150.08, 144.22, 136.57, 128.96, 126.54, 125.31, 124.04, 123.97, 121.43, 120.30, 119.54, 118.82, 109.43. Anal. Calcd. for $C_{26}H_{19}NO_2$: C, 82.74; H, 5.07; N, 3.71; O, 8.48. Found: C, 81.75; H, 5.18; N, 3.02. ESI–MS: *m/z* 378.14 for $[M+H]^+$ (Calcd for [M]: *m/z* 377.14).

Polymerization

PDNPA (run 8) To an RBF, DNPA (0.132 g, 0.35 mmol), CuCl(OH)TMEDA (8.13 mg, 0.0175 mmol), and THF (1 mL) were added and stirred at 30 °C under oxygen. After polymerization for 16 h, the reaction mixture was poured into methanol containing a small amount of hydrochloric acid and subsequently filtered. The precipitate was washed in a Soxhlet apparatus with methanol and collected with THF, which was then condensed and precipitated in methanol. The final product was obtained after drying in vacuo at 60 °C, yielding a green powder (0.104 g, 78.6%).

Results and discussion

Synthesis of DNPA The synthetic routes for DNPA are shown in Scheme 1. The hydroxyl groups of 5-iodo-2-naphthol were protected before the palladium-catalyzed amination reaction. Compound **1** was reacted with 0.45 equiv. of aniline, and after deprotection of the methyl protecting groups, DNPA was afforded. DNPA was purified via column chromatography followed by reprecipitation of the toluene solution into heptane to yield a pale brown powder. The chemical structure of DNPA was verified by ^{1}H-NMR and C-H correlated spectroscopy (COSY). Figure 1 shows the ^{1}H-NMR spectrum of the prepared DNPA, consisting multiplets at 6.54–7.78 ppm



Scheme 1 Synthetic routes of DNPA

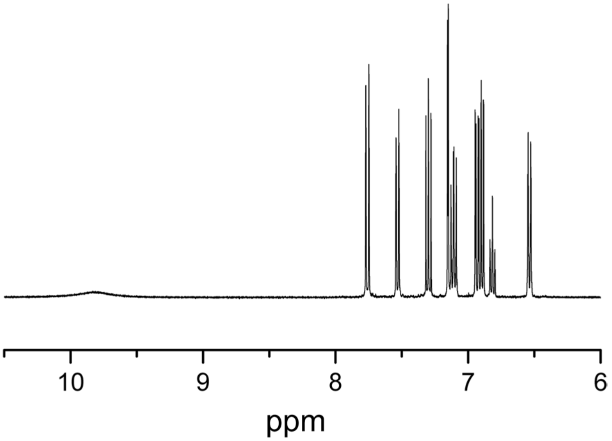


Fig. 1 ^{1}H-NMR spectrum of the obtained DNPA (400 MHz, DMSO-d_6)

and a broad peak at 9.79 ppm, which were assigned to the aromatic and hydroxyl protons, respectively. Figure 2 shows the C-H COSY spectrum for aromatic region of DNPA with corresponding peak assignments.

Cyclic voltammogram The oxidative coupling reaction includes a radical coupling step, in which the radical species generated by one-electron oxidation are involved in the coupling process [58]. Therefore, it is important to measure the

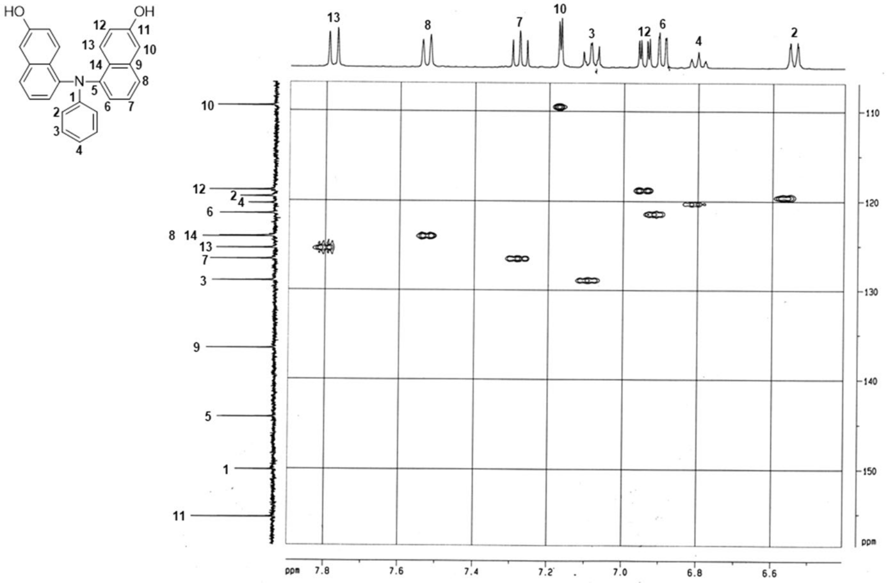


Fig. 2 C-H COSY spectrum of the obtained DNPA (400 MHz, DMSO-d_6)

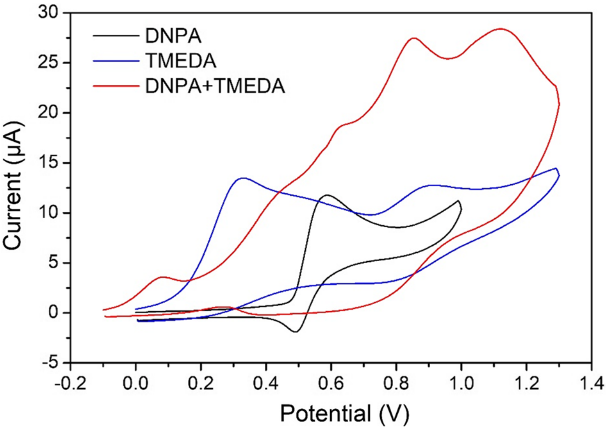
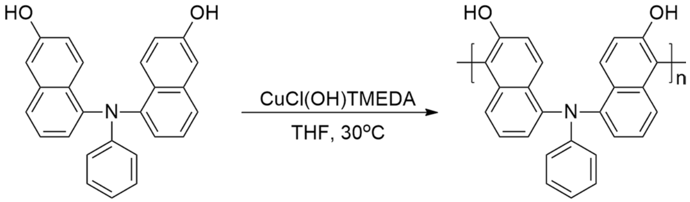


Fig. 3 Cyclic voltammograms of 1 mM DNPA (black line), 2 mM TMEDA (blue line), and 1 mM DNPA + 2 mM TMEDA (red line) in acetonitrile containing 100 mM Bu_4NBF_4 at a scan rate of 50 mV/s (color figure online)



Scheme 2 Oxidative coupling polymerization of DNPA

oxidation–reduction potentials of DNPA to select the proper oxidant. The oxidation potential of the first one-electron transfer from DNPA was estimated using cyclic voltammetry (CV) with Bu_4NBF_4 (0.1 M in acetonitrile) at a scan rate of 50 mV s^{-1} under a nitrogen atmosphere. It should be noted that the effect of TMEDA on the oxidation of DNPA was confirmed by comparing the oxidation and onset potentials of DNPA, TMEDA, and DNPA + TMEDA mixed solution. As shown in Fig. 3, first electrochemical oxidation peaks of DNPA and TMEDA were measured at 0.590 and 0.330 V, respectively, and the onset potentials of DNPA and TMEDA were 0.488 and 0.160 V, respectively. For the DNPA + TMEDA mixture (Fig. 3, red line), it is clear that a new oxidation peak and onset potential appeared at 0.068 and − 0.024 V, respectively, which were observed only in the mixed solution. The cyclovoltametric results indicate that DNPA can be affected by TMEDA, and its electrochemical oxidation shifted to a lower oxidation potential (even lower than the TMEDA oxidation potential). According to these results, CuCl(OH)TMEDA was selected as the oxidant for use in the oxidative coupling polymerization of DNPA.

Polymer synthesis and thermal properties The polymerization of DNPA was performed in the presence of CuCl(OH)TMEDA (5 mol% per monomer fed) in THF at

Table 1 Oxidative coupling polymerization of DNPA

Run	Time (h)	Yield (%)	M_n^a (kg mol^{-1})	M_w^a(kg mol^{-1})	PDI^a
1	2	2.0	4.6	5.5	1.20
2	4	36.6	4.6	6.1	1.33
3	6	48.8	5.2	7.5	1.44
4	8	54.7	5.4	8.4	1.56
5	10	61.6	5.9	10.1	1.71
6	12	71.5	6.9	15.9	2.30
7	14	73.7	7.8	20.2	2.59
8	16	78.6	9.2	31.1	3.38
9^b	18	80.8	11.3	54.2	4.80

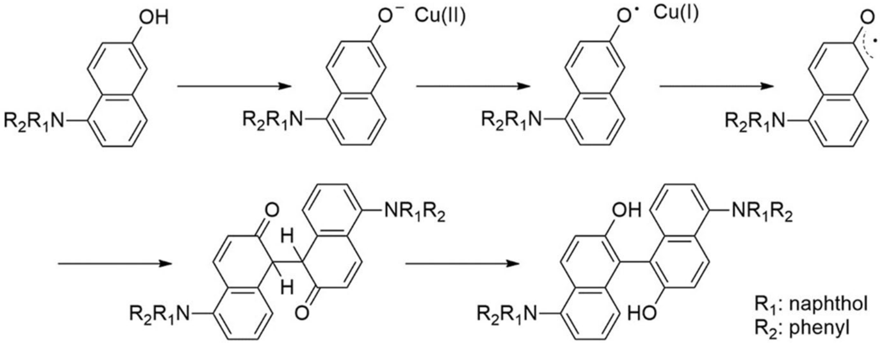
Polymerization was performed using CuCl(OH)TMEDA as an oxidant in THF at 30 °C under O_2 atmosphere

[a] Determined by THF-SEC based on linear polystyrene standards

[b] Run 9 contained approximately 25% insoluble polymer

30 °C (Scheme 2), and the results are summarized in Table 1. After polymerization, the resulting polymers were purified by repeated precipitation with methanol containing a small amount of HCl and Soxhlet extraction with methanol to remove any remaining catalyst. With increasing reaction time, the molecular weights of polymers increased. The polymers obtained from run 1–8 were soluble in THF, but run 9 contained approximately 25% insoluble polymer. The polymer was soluble in polar organic solvents such as THF, DMF, and DMSO at room temperature (20 °C) but was only partly soluble even under heating in chloroform, methylene chloride, and acetone.

As shown in Scheme 3, the mechanism of oxidative coupling reaction could be explained by the redox process accompanying a single electron transfer between 2-naphthalate and Cu(II) ion [10]. The resulting 2-naphthoxy radical is stabilized by delocalization, and carbon–carbon coupling reaction is occurred on C−1 position with the highest electron spin density. The monomers undergo successive oxidation and coupling reaction giving the high molecular weight polymer.



Scheme 3 Mechanism of oxidative coupling reaction of the naphthol monomer

During polymerization, the Cu(II) is recovered by oxidation of the Cu(I) under oxygen.

The structure of PDNPA (run 8) was determined by NMR spectroscopy. The ^{1}H NMR spectrum of PDNPA hardly showed clear peak splitting (Fig. 4) due to the restricted conformations induced by the repulsion between bulky naphthalene rings. Consequently, the structure of PDNPA was estimated using ^{13}C NMR and distortionless enhancement by polarization transfer (DEPT) spectroscopy. The aromatic region of the ^{13}C and DEPT45 spectra and assignment of DNPA are described in Fig. 5. After oxidative polymerization, the outer *ortho* position (C-10 peak) of the 2-naphthols of DNPA shifted down field and subsequently disappeared in the DEPT45 spectrum. This clearly indicated that coupling occurred selectively at the C-10 position. For better assignment, ^{13}C NMR and DEPT45 analysis of the low molecular weight polymer (run 4) was also conducted (Fig. S5). Unlike the high molecular weight polymer, it showed a sharp spectrum and provided useful information for analysis of the polymer structure.

The thermal properties of PDNPA were investigated with TGA and DSC. PDNPA showed good thermal stability, with a polymer weight loss of < 5% at 446 °C (T_{d5}) under a nitrogen atmosphere. In addition, PDNPA exhibited high char yields of 73% at 800 °C. In the derivative thermogravimetry (DTG) curve, the major degradation peak appeared at 687 °C and the second degradation peak appeared at 438 °C (Fig. 6). The DSC trace exhibited no endothermic peaks or baseline shift indicating a melting point or glass transition, respectively. The crystalline structure of the polymer film was further studied with the WAXD. The polymer film was prepared by spin coating the polymer solution (THF) on a silicon wafer. As shown in Fig. 7, the WAXD pattern of polymer indicated that the polymer was amorphous.

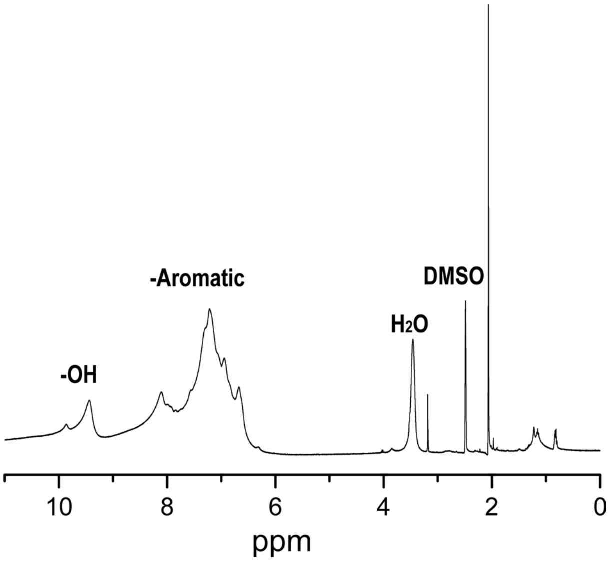


Fig. 4 ^{1}H-NMR spectrum of PDNPA (run 8; 400 MHz, DMSO-d_6)

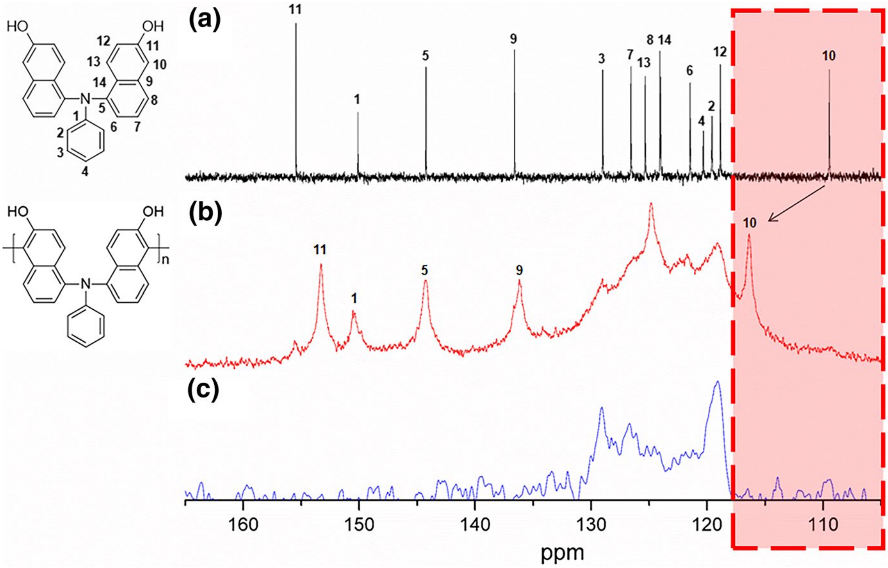


Fig. 5 Aromatic regions in the NMR spectra of DNPA and PDNPA (run 8); **a** ^{13}C NMR spectrum of DNPA; **b** ^{13}C NMR spectrum of PDNPA; **c** DEPT45 spectrum of PDNPA (100 MHz, DMSO-d_6)

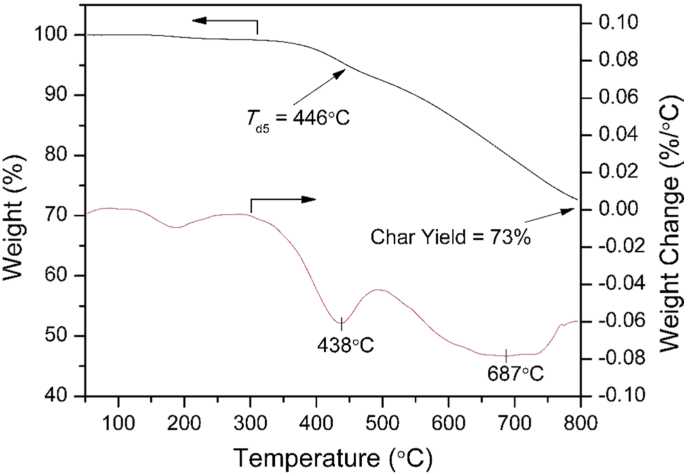
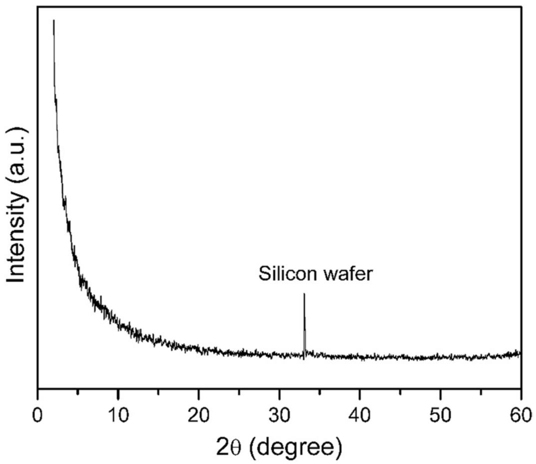


Fig. 6 TGA and DTG curves of PDNPA (run 8) under N_2

UV–vis absorption properties The normalized UV–vis absorption spectra of DNPA and PDNPA in THF are shown in Fig. 8. DNPA and PDNPA showed maximum absorptions at 344 and 356 nm, respectively. The UV–vis absorption onset of DNPA (381 nm) and PDNPA (388 nm) was similar, indicating a small extension of π-conjugation in PDNPA. This suggests that the steric repulsion of the naphthalene rings induced a large dihedral angle between neighboring naphthalene rings.

Fig. 7 WAXD pattern of the polymer film (run 8)



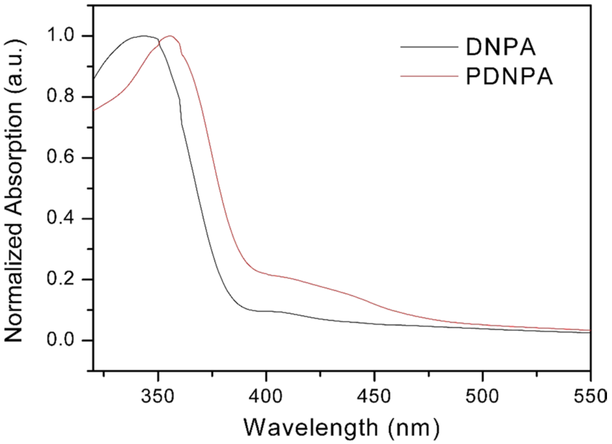


Fig. 8 UV-vis absorption spectra of DNPA and PDNPA (run 8) in THF

In addition, this kinked structure may prevent interchain interactions between polymer chains, hindering the formation of charge-transfer complexes, which results in reduced electroluminescence efficiency and an additional emission band in the long wavelength region when applied in optoelectronic devices [59, 60]. The optical band gap of PDNPA, as calculated from the onset absorption, was 3.19 eV.

Conclusions

Regiocontrolled PDNPA was prepared via oxidative coupling polymerization of DNPA using CuCl(OH)TMEDA as an oxidant. By increasing the polymerization time, the polymer molecular weight increased, but an insoluble portion was formed at times exceeding 16 h. The structure of PDNPA was characterized by ^{1}H and ^{13}C

NMR spectroscopy, indicating that the polymerization reaction selectively occurred at the outer *ortho* C-10 position of the 2-naphthol groups, leaving the hydroxyls unreacted. PDNPA exhibited good solubility in polar organic solvents and showed a high thermal stability of T_{d5} at 446 °C. Similar onset absorptions of DNPA and PDNPA in their UV–vis spectra revealed that the regioregularly kinked polymer structure prevented interchain interactions of the polymer chains. The hydroxyl groups of PDNPA allow for further modification for various purposes. In particular, this novel polymer could be applied in hole-transporting materials for solution-processable multilayer OLEDs through the introduction of cross-linkable groups.

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