

Novel Multicolor Electrochromic Aromatic Polyamides with 4-dimethylamino substituted Tetraphenyl-*p*-phenylenediamine: Synthesis and Electrochromic properties.

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Abstract A new diamine monomer, *N,N'*-Bis(4-aminophenyl)-*N,N'*-di(4-dimethylamino)-1,4-phenylenediamine, was successfully synthesized through three steps. Then the derived polyamides were prepared via polycondensation reactions with our synthesized diamine monomer with various diacid compounds. The polyamide films displayed four reversible electrochemical redox with the changes of four colors, which also exhibited good stability.

Keywords: polyamides; electrochromic materials; triphenylamine

1. Introduction

Electrochromic material is known as the reversible change in transmittance of light when applying different external potentials [1]. It has attracted scientists' interest because of their excellent properties and potential applications [2-4]. At present, this fascinating species is widely used in many fields such as smart windows, automatic anti-glazing mirrors and displays [5]. To date, a vast number of electrochromic materials have been developed, which can be divided into two classes: inorganic and organic materials. Triphenylamine with propeller structure exhibits high oxidizability combined with high stability of the corresponding radical cations and its derivatives have been widely used as hole injecting or hole transporting materials in optoelectronic devices. In the present article, the diamine monomer, *N,N'*-Bis(4-aminophenyl)-*N,N'*-di(4-dimethylamino)-1,4-phenylenediamine (**3**) and its derived various aromatic polyamides were synthesized. The characterizations of structure and property were carried out by means of common characterization methods such as FT-IR and NMR.

2. Experimental

2.1 Materials

N-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and *o*-dichlorobenzene were dried over 4 Å molecular sieves before use. Commercial dicarboxylic acid monomers such as 4,4'-oxidibenzoic acid (TCI) and 2,2'-bis(4-carboxyphenyl)hexafluoropropane (TCI) were directly used after purchased. All other reagents were used as received from commercial sources.

2.2 Monomer Synthesis

4-dimethylamino-4'-nitrodiphenylamine (**1**)

A mixture of 13.62 g (100 mmol) of *N,N*-dimethyl-*p*-phenylenediamine, 7.06 g (50 mmol) of 4-fluoronitrobenzene and 5.06 g (50 mmol) of triethylamine with 70 mL of DMSO as solvent was heated to 90 °C for 20 h under nitrogen atmosphere. The resultant solution was cooled to room temperature and then poured into 500 mL cold water. The precipitation was recrystallized from ethanol and DMF and dried under vacuum at 90 °C to obtain 11 g pure compound **1**. IR (KBr): 3330 cm⁻¹ (N-H); 1598, 1293 cm⁻¹ (NO₂). ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm): 9.02 (s, 1H), 8.03 (d, J = 9.3 Hz, 2H), 7.09 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 9.3 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 2.90 (s, 6H).

N,N'-Bis(4-nitrophenyl)-N,N'-di(4-dimethylamino)-1,4-phenylenediamine (2)

To a 100 mL three-necked flask, 4.94 g (19.2 mmol) of compound 1, 2.63 g (8 mmol) of 1,4-diiodobenzene, 1.23 g (19.2 mmol) of copper, 2.65 g (19.2 mmol) of anhydrous potassium carbonate and 0.42 g (1.6 mmol) of 18-crown-6-ether were added. Then 15 mL of *o*-dichlorobenzene was poured into the flask. The mixture was heated to 170 °C for 18 h under nitrogen and filtrated to remove the undissolved solids. The compound 2 was precipitated by adding ethanol to the filtrate and dried under vacuum at 90 °C to gain 3.8 g of compound 2. IR (KBr): 1585, 1294 cm⁻¹ (NO₂). ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm): 8.04 (d, *J* = 9.4 Hz, 2H), 7.29 (s, 2H), 7.13 (d, *J* = 9.0 Hz, 2H), 6.79 (m, 4H), 2.93 (s, 6H).

N,N'-Bis(4-aminophenyl)-N,N'-di(4-dimethylamino)-1,4-phenylenediamine (3)

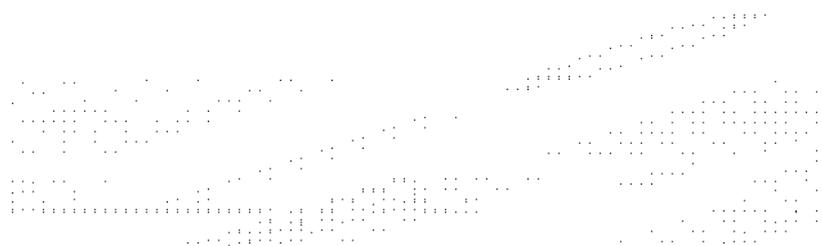
A solution of 2 g (3.4 mmol) of compound 2 and 7.66 g (34 mmol) of stannous chloride dihydrate in 20 mL of hydrochloric acid (37%) and 15 mL of DMF was heated to reflux for 18 h. The pH of the resultant solution was adjusted to near 13 by 15% of sodium hydroxide solution after the resultant solution was cooled to room temperature. The precipitation was filtrated and purified by DMF and water and dried under vacuum at 90 °C to gain 1.2 g. IR (KBr): 3449, 3360 cm⁻¹ (N-H). ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm): 6.83 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 9.1 Hz, 2H), 6.61 (s, 2H), 6.49 (d, *J* = 8.7 Hz, 2H), 4.87 (s, 2H), 2.82 (s, 6H).



Scheme 1. Synthetic route of monomer 3.

2.3 Polymer Synthesis

The synthesis of polymer 4b was taken as an example to illustrate the synthesis of all polymers. A mixture of 0.5287 g (1 mmol) of diamine monomer 3, 0.3923 g (1 mmol) of 2,2'-bis(4-carboxyphenyl)hexafluoropropane, 0.1 g of calcium chloride, 1 mL of triphenyl phosphite, 0.5 mL of pyridine and 2 mL of NMP was heated to 110 °C for 3 h under nitrogen. When cooled to room temperature, the solution was poured slowly into 200 mL of ethanol to give rise to yellowish fibrous precipitation. The precipitated polymer was filtrated and washed with hot water and ethanol to gain 0.7876 g of polymer 4b. IR (KBr): 3310 cm⁻¹ (N-H), 1662 cm⁻¹ (C=O). ¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm): 10.30 (s, 1H), 8.01 (d, *J* = 7.1 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 6.5 Hz, 2H), 7.04 – 6.51 (m, 8H), 2.85 (s, 6H).



Scheme 2. Synthetic route of polyamides.

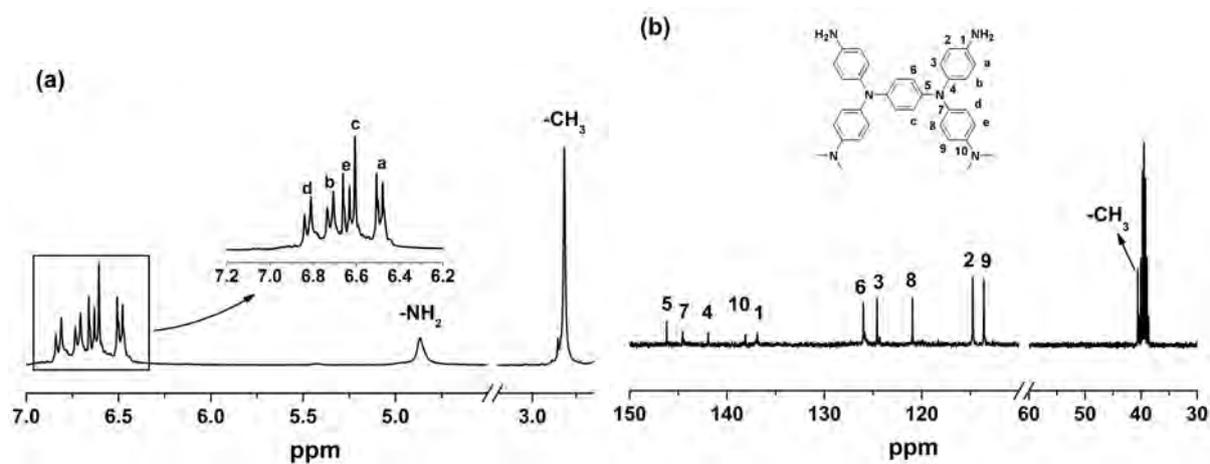


Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectra of compound **3** in $\text{DMSO-}d_6$.

2.4 Characterization

FTIR spectrum was performed with a Bruker Vector 22 spectrometer at a resolution of 4 cm^{-1} in the range of $400\text{--}4000\text{ cm}^{-1}$. Nuclear magnetic resonance (NMR) spectra was conducted with a BRUKER-300 spectrometer at 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR in deuterated dimethyl sulfoxide. Electrochemistry was performed with a CH Instruments 660e electrochemical analyzer. Ultraviolet-visible (UV-vis) spectra of the polymer films were measured using a PerkinElmer Lambda 950 spectrophotometer.

3. Result and Discussion

3.1 Monomer Synthesis

As shown in scheme 1, the target diamine monomer **3** was successfully synthesized via three synthetic steps. The intermediate compound **1** resulted from the nucleophilic substitution reaction of *N,N*-dimethyl-*p*-phenylenediamine with 4-fluoronitrobenzene under the catalyzing of triethylamine. The diamine monomer **3** was synthesized by stannous chloride-catalyzed reduction of the dinitro compound **2** obtained by the Ullmann reaction of the compound **1** with 1,4-diiodobenzene. FT-IR, NMR spectral methods were used to identified structures of our synthesized monomers. As shown in Figure 1, ^1H and ^{13}C spectra of monomer **3** exhibited that all peaks agreed well with the proposed structure.

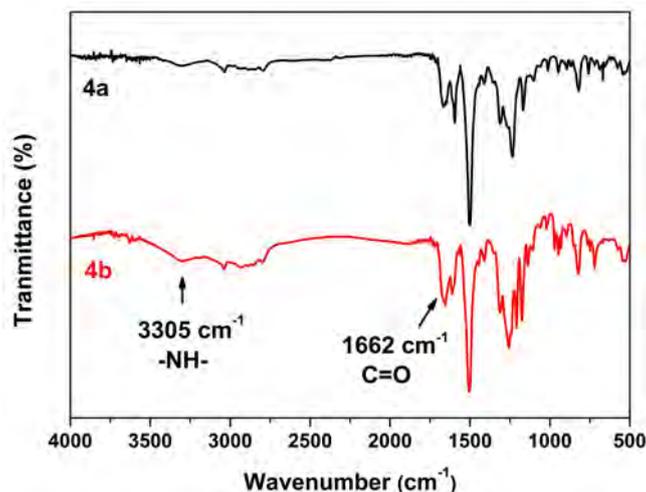


Figure 2. IR spectra of polyamides.

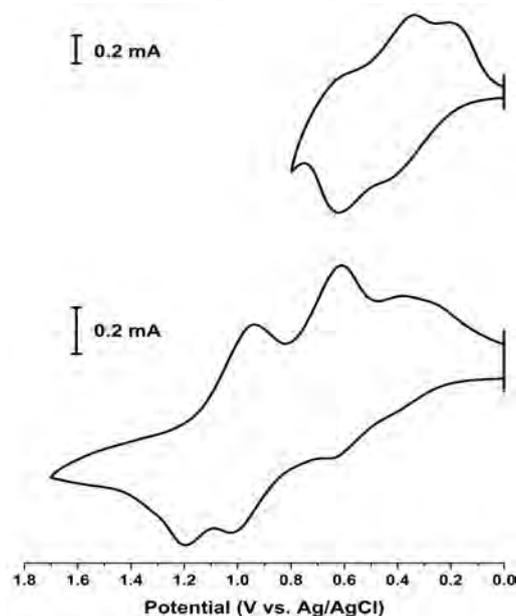


Figure 3. Cyclic voltammetric diagrams of **4a**.

3.2 Polymer Synthesis

Scheme 2 listed the synthetic routes of all polyamides. The polyamides were prepared by the polycondensation reactions of the diamine monomer **3** with various diacid compounds. All polycondensation reactions proceeded smoothly and homogeneously. The resultant solution could precipitate into fibriform solid when poured slowly in ethanol. The structure characteristics of polymers were identified through IR and ^1H NMR spectroscopic means. The IR spectrum of all polyamides shown in Figure 2 exhibited characteristic amide group absorption at around 3310 cm^{-1} (N-H stretching) and 1662 cm^{-1} (amide carbonyl).

3.3 Electrochemical Properties

The electrochemical behaviors of polyamides were investigated by cyclic voltammetry, and the typical cyclic voltammetric diagram of polyamide **4a** was described in Figure 3. The polyamide **4a** showed four reversible redox waves at half-wave of 0.30 V, 0.48 V, 0.82 V and 1.07 V. The first and second redox process occurred on the pendent dimethylamino group and the third and fourth redox occurred on the nitrogen at the main chain.

4. Conclusions

A new diamine monomer, N,N'-Bis(4-aminophenyl)-N,N'-di(4-dimethylamino)-1,4-phenylene diamine, was successfully synthesized from available reagents. Then a series of novel polyamides were readily prepared from the newly synthesized diamine monomer and various aromatic diacids by direct phosphorylation polycondensation. The polyamides revealed good stability of electrochromic characteristics. Therefore, these characteristics suggest that the new polyamides have great potential in the development of optoelectronics applications.

References

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