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Synthesis and optoelectronic properties of new polyarylates with 2-naphthyldiphenylamine units

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ABSTRACT

Herein, five kinds of soluble electrochromic polyarylates were synthesized from the reaction of N,N'-bis(4-carboxyphenyl)-N,N'-di-2-naphthyl-1,4-phenylenediamine with five bisphenols via direct polycondensation process, respectively. These new materials showed no significant decomposition below 400 °C in nitrogen atmosphere. The maximum UV–vis absorption bands of these polyarylates located at 328–348 nm and 327–353 nm for solid films and DMSO solution, respectively. The polyarylate **6a**, as an example, exhibited not only aggregation-induced emission (AIE) effect in different fraction tetrahydrofuran/water solution, but also solvatochromism in various polar solvents, markedly. Two reversible pairs of distinct redox peaks were associated with noticeable color changed from original colorless to yellowish orange and green for polymeric film could be observed in the cyclic voltammetry (CV) test. New absorption peaks emerged in near–infrared (NIR) region with increasing voltage in the UV–vis spectra, which indicates these polyarylates can be used as NIR electrochromic materials. These polyarylates performed high contrast of optical transmittance change around 42–53% with the highest coloration efficiency up to 236 cm^2C^{-1}.

1. Introduction

Electrochromic materials can change color reversibly to reach significant goals of energy saving, safety and camouflage by means of sufficient electrochemical potential or redox process [1–3]. So far, the family of electrochromic materials has become more and more abundant [4]. Among them, conducting polymer possesses some great advantages providing the chance to various chemical design and modifications, which make a significant impact on processing properties and performance, such that some excellent properties what we desire, easier machining process, multicolor change, high contrast and rapid response [5–7]. Thus, conducting polymer is one important part of electrochromic materials. In addition to the outstanding representatives of polyaniline, polypyrrole, polythiophene and their derivatives, the other high–performance polymers as electrochromic materials, such as poly–schiff base, polyamide (PA), polyimide (PI), and polyarylate have being developed [8–13].

However, the vast majority of aromatic PA, PI and polyarylate are difficult to commercialize due to the poor solubility in common organic solvent and excessively high melting temperature, in the early days. In terms of polyarylate, these drawbacks are intractable and make them hard to process that limits its market promotion and applications. One of the effective methods to overcome these problems is to incorporate long flexible chain, which can only meet less demanding applications in thermal stability. Introduction three-dimensional and bulky group into the polymeric side or main chain, which can make the chains separate and the chain packing lower to obtain bigger free volume of polymer so that the processibility and solubility would increase greatly without deteriorating its own excellent properties, is a better choice to solve this issue [14,15].

Considered from these perspectives, nonplanar triarylamine structure is consistent with the above requirements. The twisty triarylamine units would avoid the chain packing and crystallinity for the polymer to gain better solubility and processibility. The most important thing is that triarylamine is a typical base of electrochromic architecture for our investigation. Therefore, the introduction of triarylamine is fully staffed. Moreover, besides linear polymers, triarylamine-containing dendritic aromatics are also

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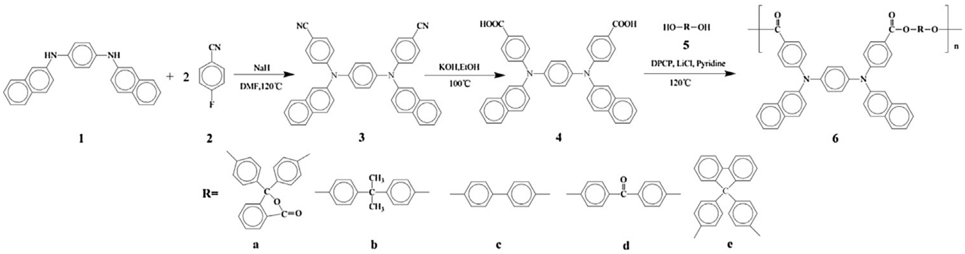

Scheme 1. Process of preparing polyarylates **6a–6e**.

demonstrated in the organic light emitting diodes (OLEDs) and solar cell devices as hole-transporting materials (HTMs) in the optoelectronic fields because of the high charge-carrier mobility [16–19]. For example, Abate and co-workers have reported Si-OMeTPA (PEH-2) perovskite-based solar cells (PSCs) devices with a long half-life of 6000 h and power conversion efficiency (PCE) of 13.5% [20].

Liou and Hsiao have reported a large number of triarylamine-based PA and PI electrochromic materials, but less polyarylates [21,22]. Although this work concerning structurally related PAs and PIs [23,24], to the best of our knowledge, there is no literature reporting the structures and properties of polyarylates derived from dicarboxylic monomer, N,N’-bis(4-carboxyphenyl)-N,N’-di-2-naphthyl-1,4-phenylenediamine, with five bisphenols. So, in this work, the synthesis and characterization of monomers and polymers are reported, and the solubility, thermal stability, electrochemical, electrochromic and fluorescence properties of these polyarylates are also described herein.

2. Experimental

2.1. Materials

N,N’-di-2-naphthyl-1,4-phenylenediamine was purchased from Aladdin Co.; phenolphthalein, 4,4′-isopropylidenediphenol and tetrabutylammonium perchlorate (Bu_4NClO_4) were purchased from Sinopharm Chemical Reagent Co. LTD; diphenylchlorophosphate (DPCP), 4,4′-dihydroxybiphenyl and 4,4′-dihydroxy benzophenone, 9,9-bis(4-hydroxyphenyl) fluorene were purchased from TCI Co.; N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co. LTD. DMF was dried and distilled over calcium hydride under insert atmosphere. The other organic reagents are supplied from commercial source.

2.2. Monomer synthesis

Monomer **3** and **4** were prepared according to the reported method [25].

N,N’-bis(4-cyanophenyl)- N,N’-di-2-naphthyl-1,4-phenylenediamine (**3**)

In a 250 mL three-neck round-bottom flask, 0.36 g (15.0 mmol) of sodium hydride was added into the 110 mL anhydrous DMF and stirred for 0.5 h at room temperature. Then, 1.80 g (5.0 mmol) of N,N’-di-2-naphthyl-1,4-phenylenediamine and 1.45 g (12.0 mmol) of 4-fluorobenzonitrile were dissolved in the mixed solution. The mixture was heated at 120 °C for 24 h under N_2 atmosphere. The cold resulting solution was poured into the 700 mL water/methanol (1:1) to precipitate the crude product that was recrystallized from acetic acid/water to afford 43% in yield of light yellow powder. HR-MS calcd for compound **3** [$C_{40}H_{26}N_4$]: 563.221, found 563.033. FTIR (KBr, cm^{-1}): 2220 (C≡N stretch). ^1H NMR (400 MHz, DMSO–d_6, δ, ppm): 7.00–7.02 (d, 4H, H_b), 7.24 (s, 4H, H_j), 7.34–7.37 (dd, 2H, H_f), 7.47–7.52 (m, 4H, $H_c + H_i$), 7.63–7.65 (d, 4H, H_a), 7.74 (d, 2H, H_d), 7.84–7.86 (t, 2H, H_e), 7.90–7.93 (t, 2H, H_h), 7.97–7.99 (d, 2H, H_g). The IR and ^1H NMR spectra of monomer **3** are shown in Fig. S1 and S2 .

N,N’-bis(4-carboxyphenyl)- N,N’-di-2-naphthyl-1,4-phenylenediamine (**4**)

In a 250 mL three-neck round-bottom flask, a mixture of 2.25 g (4.0 mmol) of compound **3** and 8.19 g (146 mmol) of potassium hydroxide in 5 mL of distilled water and 18 mL ethanol were stirred at 100 °C until no further ammonia was generated. Then, the reaction solution was cooled, and the dilute hydrochloric acid was added to make the pH value near 3. The crude product was collected by filtration and washed with water, and recrystallized from acetic acid/water to give 57% in yield of powder. HR-MS calcd for compound **4** [$C_{40}H_{28}N_2O_4$]: 600.668, found 600.965. FTIR (KBr, cm^{-1}): 1681 (C═O stretch), 2500–3300 (O—H stretch). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.04–7.07 (d, 4H, H_c), 7.14 (s, 4H, H_k), 7.29–7.31 (dd, 2H, H_g), 7.43–7.49 (m, 8H, $H_j + H_d + H_b$), 7.59–7.60 (d, 2H, H_e), 7.69–7.72 (t, 2H, H_f), 7.81–7.85 (q, 4H, $H_h + H_i$), 12.05 (br, s, 2H, H_a). ^{13}C NMR (100 Hz, $CDCl_3$, δ, ppm): 103.2 (C^2), 120.2 (C^4), 123.6 (C^9), 125.0 (C^{11}), 125.8 (C^7), 126.7 (C^{15}), 126.9 (C^{17}), 127.3 (C^{10}), 127.7 (C^{12}), 131.2 (C^{14}), 133.3 (C^3), 134.2 (C^8), 134.1 (C^{17}), 142.6 (C^{16}), 143.1 (C^6), 151.3 (C^5), 167.5 (C^1).

2.3. Polymer synthesis

The process of preparing polyarylates **6a–6e** was according to the early literature, which was described in Scheme 1 [20,21]. Herein, the synthesis of polyarylate **6d** is used to be an example to illustrate the general synthetic process of polyarylates.

The 4 mL of pyridine solution containing 0.08 g of LiCl and 0.69 g of DPCP were stirred at room temperature for 0.5 h, and then added dropwise for 15 min at 120 °C to a 2 mL pyridine solution containing 0.11 g (0.5 mmol) of 4,4′-dihydroxy benzophenone and 0.30 g (0.5 mol) of N,N’-bis(4-carboxyphenyl)-N,N’-di-2-naphthyl-1,4-phenylenediamine (**4**). The mixture was heated at 120 °C for 3 h. And then the cooled solution was poured slowly into 300 mL water to precipitate crude product, which was recrystallized from THF/methanol. FTIR (KBr, cm^{-1}): 1739 (ester carbonyl, C═O). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 7.02–7.04 (d, H_d), 7.18 (s, H_l), 7.33–7.37 (m, H_h), 7.44–7.52 (m, $H_g + H_k + H_b$), 7.74 (s, H_e), 7.82–7.84 (d, $H_c + H_f$), 7.86–7.99 (m, $H_i + H_a + H_j$).

2.4. Measurements

Infrared spectra were recorded on a PerkinElmer Spectrum 100 Model Fourier transform infrared spectrometer (FTIR). ^1H and ^{13}C NMR spectra were marked down by a Bruker AC–400 MHz spectrometer with tetramethylsilane as an internal reference. The weight–average molecular weight ($\bar{M}_w$) and number–average molecular weight ($\bar{M}_n$) were performed by Gel permeation chromatography (GPC) analysis on Malvern instrument calibrated with polystyrene standards in DMF solution at 35 °C. Thermogravimetric analysis (TGA) was conducted by a PerkinElmer Pyris 6 TGA car-

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