



Multifunctional polyamides containing pyrrole unit with different triarylamine units owning electrochromic, electrofluorochromic and photoelectron conversion properties



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ABSTRACT

Four kinds of novel polyamides (PAs) containing pyrrole core with different triarylamine (TAA) groups were designed and synthesized. These PAs exhibit good solubility in various organic solvents and excellent thermal stability. The two PAs prepared from cyclohexane-1,4-dicarboxylic acid exhibit fluorescence maximum at 475–476 nm with quantum yields up to 39.0% and 57.3% in *N,N*-dimethylacetamide (DMAc) solution. Furthermore, the polymer films show reversible electrochemical redox with color changing from yellowish to khaki to dark blue. Especially, the films have high coloration efficiency (up to 143 cm² C⁻¹ at 750 nm) and after over 1000 s the films still exhibit continuous cyclic stability of electrochromism. What's more, these PAs could be used as the photoelectric conversion material owing to their excellent optoelectronic properties.

1. Introduction

An electrochromic (EC) material, which can reversibly regulate its optical transmittance by different external potential, shows applications in smart window, antiglare rear-view mirrors, earth tone chameleon materials, and high contrast displays [1–7]. In recent years, bi-functional and multi-functional electrochromic materials have gained much attention. Compared with the simplex electrochromic materials, bi-functional electrochromic materials expand the range of applications. For example, Xu designed and synthesized a novel polymer, ProDOT-TPE, with aggregation-enhanced fluorescent emission and excellent electrochromic properties [8]. The phenomenon present both of its color and fluorescent state could be synchronously switched by different potential. Meanwhile, they found that a WO₃ film mixed with Eu ions exhibited the bi-functionality of electrochromic switching and red emission, which showed a potential application in preparation of illuminable “smart windows” [9]. Liou's group fabricated the electrofluorochromism devices by using the combination of aggregation-enhanced emission and electrochromic properties [10]. Wei's group designed a smart covalently crosslinked polymer, which can respond to six different stimuli and perform multifarious functions, such as pH-induced shape memory, light manipulated activities, metal ion enhanced light controlled activation [11].

PAs are well known as high performance polymeric materials for their excellent properties. But most of them also have some shortcomings, such as excessive melting points, softening temperatures or low optical transparency and are insoluble in most organic solvents, which limiting their applications. In order to solve these problems, many efforts have been done. Zhao's group introduced fluorene-based triphenylamine unit into the PA backbone, which improves the solubility of the polymers and lead to interesting electroswitchable-fluorescence and electrochromic properties [12]. Zhang's group designed and synthesized a new series of diamine compounds containing a planar and electron-rich pyrrole core with different side groups, which enhance the charge-transporting capacity of the polymer [13]. In addition, Hsiao's group introduced O(TPA)₂ group into the polymer backbone, which reduced the intervalence charge-transfer absorptions and the polymer showed a multi-colored electrochromic behavior [14].

From previous report, TAA derivatives are well known for their electroactive and electrochromic properties [15], meanwhile, propeller-like TAA units would avoid the chain packing and crystallinity of the polymer without destroying the solubility and processibility. Therefore, incorporating TAA group is a better choice to improve the properties and applications of the PA. Furthermore, the introducing of the planar and electron-rich pyrrole moiety into the PA backbone is expected to enhance the electron donating property and the charge-

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transporting capacity along the polymer backbone for device application.

Thus, in this paper, we designed and synthesized two novel kinds of diamine compounds, 4,4'-(1-(4-(bis(4-(tert-butyl)phenyl)amino)phenyl)-1H-pyrrole-2,5-diyl)dianiline and 4,4'-(1-(4-(diphenylamino)phenyl)-1H-pyrrole-2,5-diyl)dianiline, containing a pyrrole core with different TAA units, and the derived electroactive PAs. The goal of our research work is to enlarge the applications of the PAs, and fabricate the multi-functional materials with electrochromic, photogenerated and electrofluorochromic properties. Meanwhile, the discussion of the structure–property relationship is beneficial to design new functional PAs for high-performance polymer devices.

2. Experiments

2.1. Materials

2-Bromo-1-(4-nitrophenyl)ethanone, hydroxymethanesulfonic acid monosodium salt dehydrate (rongalite), bis(4-(tert-butyl)phenyl)amine, diphenylamine, cyclohexane-1,4-dicarboxylic acid (ChDA) and terephthalic acid (PTA) were purchased from Aladdin and used as received. 10% palladium on charcoal (Pd/C, Acros), p-toluenesulfonic acid (PTSA, TCI) was used as received. 4-fluoronitrobenzene, calcium chloride (CaCl_2), pyridine, triphenyl phosphate (TPP) and 80% hydrazine hydrate were purchased from Sinopharm Chemical Reagent Co. Ltd. and the commercially obtained anhydrous CaCl_2 was dried under vacuum at 200 °C for 6 h. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF) and toluene purchased from Sinopharm Chemical Reagent Co. Ltd. were dried over calcium hydride for 24 h and distilled under reduced pressure. All the other reagents and solvents were analytical grade and without further purification. Flash column chromatography purification was carried out on silica gel (200–300 mesh).

2.2. Synthesis of monomers

The synthetic route of the monomers is shown in Scheme 1. The 1,4-bis(4-nitrophenyl)butane-1,4-dione (1) was synthesized by the coupling reaction of 2-bromo-1-(4-nitrophenyl)ethan-1-one with rongalite in dry DMF according to the reported method [16]. *N,N*-bis(4-(tert-butyl)phenyl)benzene-1,4-di-amine (2) and *N,N*-diphenylbenzene-1,4-diamine (2') were synthesized according to the method previously described in the literature [17].

2.2.1. Synthesis of 4-(2,5-bis(4-nitrophenyl)-1H-pyrrol-1-yl)-*N,N*-bis(4-(tert-butyl)phenyl)aniline (PyTDN)

In a 250 mL round-bottom flask equipped with a stirring bar, a nitrogen inlet and areflux condenser was charged with 1,4-bis(4-

nitrophenyl)butane-1,4-dione (1) (0.50 g, 1.52 mmol), *N,N*-bis(4-(tert-butyl)phenyl)benzene-1,4-di-amine (2) (0.57 g, 1.52 mmol), PTSA (0.20 g, 1.16 mmol) and 100 mL toluene. The mixture was stirred at 120 °C for 72 h. After being cooled to room temperature, the toluene was evaporated. The crude product was purified by silica-gel column chromatography using dichloromethane/petroleum ether ($v/v = 1/1$). IR (KBr, ν , cm^{-1}): 2956 (t-butyl C–H stretching), 1589 (C=N, stretching), 1507, 1342 ($-\text{NO}_2$ stretching). ^1H NMR (400 MHz, $\text{DMSO}-d_6, \delta$, ppm): 8.32–8.29(d, 4H), 8.13–8.11(d, 4H), 7.52(d, 2H), 7.36–7.33(d, 4H), 7.05(d, 2H), 7.02–7.00(d, 4H), 6.85(s, 2H), 1.25(s, 18H). MS (EI, m/z): $[\text{M}]^+$ calcd for $\text{C}_{42}\text{H}_{40}\text{N}_4\text{O}_4$:664.79. Found: 664.69.

2.2.2. Synthesis of 4-(2,5-bis(4-nitrophenyl)-1H-pyrrol-1-yl)-*N,N*-diphenylaniline (PyHDN)

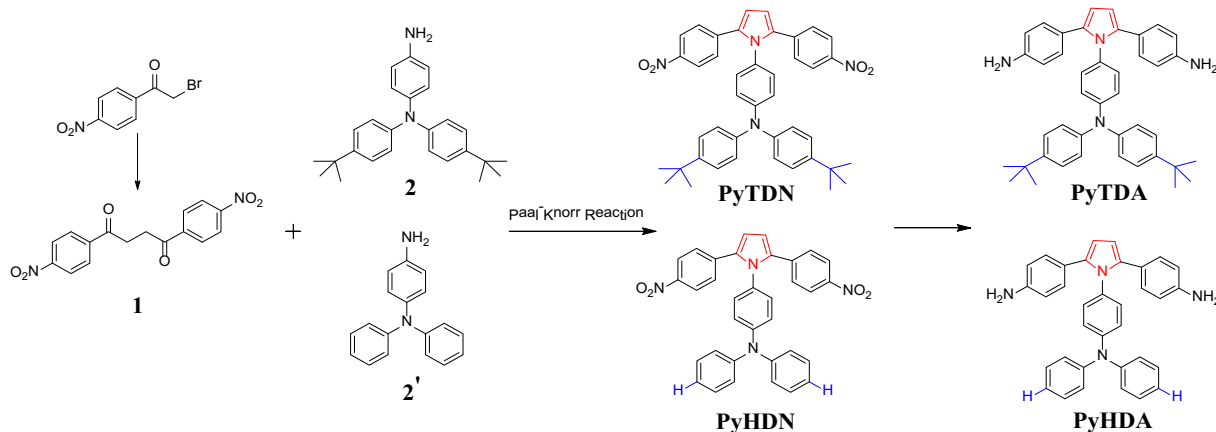
The PyHDN was prepared by an analogous procedure as PyTDN. IR (KBr, ν , cm^{-1}): 1589 (C=N, stretching), 1513, 1330 ($-\text{NO}_2$ stretching). ^1H NMR (400 MHz, $\text{DMSO}-d_6, \delta$, ppm): 8.32–8.30(d, 4H), 8.14–8.13(d, 4H), 7.54(d, 2H), 7.36–7.33(d, 4H), 7.09–7.06(d, 2H), 6.91–6.93(d, 2H), 6.85(s, 2H). MS (EI, m/z): $[\text{M}]^+$ calcd for $\text{C}_{34}\text{H}_{24}\text{N}_4\text{O}_4$:552.18. Found: 552.61.

2.2.3. Synthesis of 4,4'-(1-(4-(bis(4-(tert-butyl)phenyl)amino)phenyl)-1H-pyrrole-2,5-diyl)dianiline (PyTDA)

In a 250 mL three-neck round-bottom flask equipped with a stirring bar under nitrogen atmosphere, 3.00 g (4.51 mmol) of PyTDN and 1.00 g of 10% Pd/C were dissolved suspended in 100 mL of ethanol, 12 g of hydrazine monohydrate was added slowly to the mixture at room temperature. The suspension solution was heated at reflux temperature for about 24 h. The solution was filtered to remove Pd/C, and the filtrate poured into 500 mL distilled water to obtain white product. After standing for 12 h, the product was collected by filtration and dried in vacuum at 26 °C. IR (KBr, ν , cm^{-1}): 3462, 3379 (N–H, stretching), 2963 (t-butyl C–H stretching), 1615 (C=N, stretching). ^1H NMR (400 MHz, $\text{DMSO}-d_6, \delta$, ppm): 7.32–7.30(d, 4H), 6.90–6.89(d, 4H), 6.87(d, 2H), 6.81(d, 2H), 6.73–6.71(d, 4H), 6.41–6.39(d, 4H), 6.13(s, 2H), 5.03(s, 4H, NH_2), 1.26(s, 18H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6, \delta$, ppm): 147.47(C^1), 145.91(C^{13}), 144.98(C^{10}), 135.71(C^5), 133.94(C^7), 130.65(C^8), 129.44(C^{12}), 126.77(C^3), 123.98(C^2), 123.09(C^9), 121.37(C^4), 113.85(C^{11}), 107.62(C^6), 34.52(C^{14}), 31.67(C^{15}). MS (EI, m/z): $[\text{M}]^+$ calcd for $\text{C}_{42}\text{H}_{44}\text{N}_4$:604.36. Found: 604.59.

2.2.4. Synthesis of 4,4'-(1-(4-(diphenylamino)phenyl)-1H-pyrrol-2,5-diyl)dianiline (PyHDA)

The PyHDA was prepared by an analogous procedure as PyTDA. IR (KBr, ν , cm^{-1}): 3450, 3361 (N–H, stretching), 1615 (C=N, stretching). ^1H NMR (400 MHz, $\text{DMSO}-d_6, \delta$, ppm): 7.31–7.29(d, 4H), 7.03–7.00(d, 2H), 6.97–6.95(d, 4H), 6.90–6.89(d, 2H), 6.72–6.71(d, 2H),



Scheme 1. Synthesis routes of monomers.

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