Dyes and Pigments 141 (2017) 356–362

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Aggregation-enhanced emission (AEE)-active polyamides with methylsulfonyltriphenylamine units for electrofluorochromic applications

Ningwei Sun [a, 1], Ziwei Zhou [b, 1], Shiyao Meng [a], Danming Chao [a], Xiaojing Chu [c], Xiaogang Zhao [a, *], Daming Wang [a], Hongwei Zhou [a], Chunhai Chen [a]

[a] Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, PR China
[b] State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, PR China
[c] Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Science, Yantai 264100, PR China

ARTICLE INFO

Article history:
Received 16 December 2016
Received in revised form
22 January 2017
Accepted 23 January 2017
Available online 24 February 2017

Keywords:
Triphenylamine
Sulfone
Polyamide
Electrochromism
Electrofluorochromism

ABSTRACT

In this work, a series of AEE-active polyamides containing methylsulfonyltriphenylamine units were prepared from a newly synthesized diamine "4,4′-diamine-4″-methylsulfonyltriphenylamine" and three dicarboxylic acids, which were highly soluble in various organic solvents and exhibited outstanding thermostability. The resulting polymer films showed one reversible redox couple along with apparent color changing from colorless to purple. The polymer solutions revealed relatively weak fluorescence with quantum yields in the range of 2.2–26.2%, which could be enhanced by induced aggregation in poor solvents. Furthermore, the bright fluorescence of the solid polymer film could be reversibly tuned by direct electrochemical redox of triphenylamine with a high contrast ratio (I_{off}/I_{on}) of 234. Overall, this comprehensive investigation of their interesting electrochromic and electrofluorochromic bifunctional properties not only supplies a deep understanding of the optical essence upon electrical stimuli but also paves the way for their future intelligent applications.

1. Introduction

Recently, stimuli-responsive fluorescent materials have attracted intense interest due to their potential applications in sensors and displays [1–4]. In particular, a promising approach to achieve reversible fluorescence switching is based on the conversion of the redox states driven by electrical stimuli, which is known as electrofluorochromism [5–7]. In view of the fascinating advantages and wide application foreground, several efforts have been made to exploit various electrofluorochromic materials, mainly including dyads and electroactive fluorophores [8–13]. Specially, the latter ones behave more attractive since their fluorescence could be switched by electrochemical modulation directly and readily. To further meet the requirement of commercial application, some parameters such as rapid response time, high contrast ratio and long term stability are crucial for high performance electrofluorochromic materials. However, most of the existing materials could not achieve all these demands at the same time, especially lack of high contrast due to their poor fluorescence essence. To better satisfy the future optoelectronic applications, more versatile materials are urgent to be further exploited.

Triphenylamine (TPA) with special starburst structure has been widely applied in various optoelectronic materials such as organic light emitting diodes (OLEDs), dye-sensitized solar cells (DSSCs) and polymer memory devices, owing to its strong electron-donating and transporting capability [14–19]. Moreover, the TPA derivatives always yield obvious changes in color during the oxidation process, and thus have been developed as attractive anodic electrochromic materials [20–25]. In addition, *para*-protective TPA has also been demonstrated an ideal electro-switching modulator for its stable electroactivity by effectively preventing coupling reaction [26,27]; several reported fluorescent TPA derivatives exhibited interesting electrochemical fluorescence switching behaviors [28–30]. However, the aggregation-caused quenching (ACQ) essence of most of these materials resulted in

* Corresponding author.
E-mail address: xiaogang@jlu.edu.cn (X. Zhao).
[1] N.W. Sun and Z.W. Zhou contributed to this work equally.

http://dx.doi.org/10.1016/j.dyepig.2017.01.078
0143-7208/

weak fluorescence in the solid states, which greatly decreased the fluorescence "on/off" sensitivity. To address this problem, the opposite of ACQ, aggregation-induced emission (AIE) effect which was first reported by Tang [31] paves a facile way for the design and synthesis of efficient solid-state materials. Remarkably, sulfone-containing materials are receiving increasing attention due to their effectively enhanced photoluminescence quantum yields [32,33]. Adachi and coworkers have reported amount of TPA-sulfone derivatives with interesting thermal activated delayed fluorescence (TADF) properties, ascribed to the small energy gap between the lowest single (S_1) and the lowest triplet (T_1) states resulting in strong reverse intersystem crossing (RISC) process [34–37]. Lee et al. reported several donor-acceptor molecules with high-efficiency blue light-emitting based on sulfone as acceptor [38,39]. In view of the propeller-like structure and electron-donating characteristic of TPA as well as the enhanced fluorescence and electron-withdrawing properties of sulfone unit, TPA-sulfone derivatives may readily act as electro and AIE-active modulators in electro-switching system, which will greatly promote the development of electrochromic and electrofluorochromic materials.

In this work, we herein report the synthesis of a new diamine monomer, "4,4'-diamine-4"-methylsulfonyltriphenylamine", and its derived electroactive polyamides. Their properties such as organic solubility, thermal stability, AEE fluorescence, redox, electrochromic and electrofluorochromic performances are also disclosed and investigated in detail.

2. Experimental section

2.1. Materials

4-Methylsulfonylaniline (TCI), 4-fluoronitrobenzene (Acros), cesium fluoride (CsF, Acros), 10% palladium on charcoal (Pd/C, TCI), hydrazine monohydrate (TCI), triphenyl phosphite (TPP, Acros) were used as received. The model compound with aliphatic structure was synthesized and characterized as described in the supporting information. Calcium chloride was dried under vacuum at 180 °C for 20 h prior to use. *N*-methyl-2-pyrrolidinone (NMP) and dimethyl sulfoxide (DMSO) were dried using 4 Å molecular sieves prior to use. Tetrabutylammonium perchlorate (TBAP, Acros) was recrystallized twice from ethanol under nitrogen atmosphere and then dried under vacuum at 40 °C before use. Commercially available dicarboxylic acids that include *trans*-1,4-Cyclohexanedicarboxylic acid (3a, TCI), 4,4′-dicarboxydiphenylether (3b, TCI) and 2,2-bis(4-carboxy-phenyl)hexafluoropropane (3c, TCI) were dried under vacuum at 100 °C prior to use. Other commercially available chemicals and solvents were used without further purification.

2.2. Synthesis of 4,4′-dinitro-4″-methylsulfonyltriphenylamine

In a 250 mL round-bottom flask equipped with a stirring bar, a mixture of 12.0 g (70.2 mmol) of 4-Methylfulfonylaniline, 20.8 g (147.4 mmol) of 4-fluoronitrobenzene and 22.4 g (147.4 mmol) of CsF in 130 mL of DMSO was heated under nitrogen atmosphere at 165 °C for 24 h. After cooling to room temperature, the reaction solution was poured into 500 mL of ethanol to form yellow crude which was subsequently washed thoroughly by hot water and ethanol. Then the crude was recrystallized from DMF/ethanol, yielding 24.1 g of the desired dinitro compound in 83.1% with a melting point of 271 °C. FT-IR (KBr): 1307 cm^{-1}, 1578 cm^{-1} ($-NO_2$ stretch). ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.24 (d, J = 9.2 Hz, 4H), 7.97 (d, J = 8.9 Hz, 2H), 7.43 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 9.2 Hz, 4H), 3.27 (s, 3H).

2.3. Synthesis of 4,4′-diamino-4″-methylsulfonyltriphenylamine

In a 500 mL round-bottom flask, 15 g (8.8 mmol) of the dinitro compound 1 and 1.5 g of Pd/C were dispersed in 70 mL of ethanol. After heating the mixture to reflux, 8.4 g hydrazine monohydrate was added slowly into the react system. Then the mixture was stirred at the reflux temperature for 8 h. The Pd/C was removed by filtration and the resulting filtrate was cooled under a nitrogen flow to grow light-yellow crystals. Then the crystals were collected and dried under vaccum (11.0 g, 86.1% of yield, mp = 235 °C). ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 7.54 (d, J = 9.0 Hz, 2H, H_d), 6.93 (d, J = 8.6 Hz, 4H, H_b), 6.65–6.48 (m, 6H, $H_c + H_a$), 5.17 (s, 4H, $-NH_2$), 3.05 (s, 3H, $-CH_3$). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 153.58, 146.97, 133.86, 128.32, 128.08, 127.29, 114.90, 113.70, 44.35.

2.4. Synthesis of polyamides

A series of polyamides were prepared *via* polycondensation (as shown in Scheme 2) [40]. The prepared polyamides were abbreviated to 4a, 4b and 4c, respectively. In a typical procedure, a mixture of 0.353 g (1 mmol) of the diamine monomer 2, 0.172 g (1 mmol) of 3a, 0.12 g of calcium chloride, 1 mL of triphenyl phosphite, 0.5 mL of pyridine, and 2.5 mL of NMP was heated with stirring at 120 °C for 3 h. After cooling to room temperature, the obtained viscous polymer solution was poured slowly into 250 mL of methanol, producing a stringy, fiber-like precipitate. The resulting polymer was washed thoroughly with hot water and methanol, and then reprecipitated by DMAc/ethanol twice for further purification. The ^1H NMR data of these polyamides are listed as follows.

Polyamide 4a: ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 9.98 (s, 2H), 8.02–7.45 (m, 6H), 7.14 (d, J = 8.4 Hz, 4H), 6.83 (d, J = 8.6 Hz, 2H), 3.11 (s, 3H), 2.44–2.24 (m, 2H), 2.02–1.81 (m, 4H), 1.60–1.38 (m, 4H).

Polyamide 4b: ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 10.34 (s, 2H), 8.06 (d, J = 8.4 Hz, 4H), 7.84 (d, J = 8.7 Hz, 4H), 7.70 (d, J = 8.9 Hz, 2H), 7.31–7.12 (d, J = 8.4 Hz, 6H), 6.91 (d, J = 8.7 Hz, 2H), 3.12 (s, 3H).

Polyamide 4c: ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 10.53 (s, 2H), 8.05 (d, J = 8.4 Hz, 4H), 7.83 (d, J = 8.6 Hz, 4H), 7.70 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 7.9 Hz, 4H), 7.22 (d, J = 8.6 Hz, 4H), 6.92 (d, J = 8.8 Hz, 2H), 3.12 (s, 3H).

The polyamide films were prepared *via* solution casting. 0.3 g of sample was dissolved in 6 mL of DMAc to form the homogeneous solution, which was then poured into a 6 cm glass Petri dish and placed in the oven at 90 °C for 12 h to release the solvent slowly. After that, the damp-dry film was further dried at 160 °C for 12 h under vacuum. These as-prepared films were about 30–40 μm in thickness and were subsequently used for solubility tests and thermal analyses.

2.5. Measurements

Fourier transform infrared (FT-IR) spectra were recorded through a Bruker Vector 22 spectrometer at a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1}. Nuclear magnetic resonance (NMR) spectra were determined on a BRUKER-300 spectrometer at 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR in deuterated DMSO. Inherent viscosities (η_{inh}) were measured through an Ubbelohde viscometer with a 0.5 g/dL of DMAc solution at 25 °C. Weight-average molecular weight (M_w) and number-average molecular weights (M_n) were obtained *via* gel permeation chromatographic (GPC) analysis on the basis of polystyrene calibration on a PL-GPV 220 instrument with DMF as an eluent at a flow rate of 1.0 mL/min. Differential scanning calorimetric (DSC) analysis was