



Visible and near-infrared electrochromic properties of polymers based on triphenylamine derivatives with acceptor groups

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ABSTRACT

A series of triphenylamine derivatives containing acceptor groups, including TPA-CHO, TPA-E2CN, TPA-2T-CHO, TPA-2T-E2CN, TPA-2EDOT-CHO, and TPA-2EDOT-E2CN, was synthesized, and their corresponding polymers were prepared. The polymer films exhibited reversible color changes upon electrochemical doping and dedoping. Among them, P(TPA-2T-CHO) and P(TPA-2EDOT-CHO) films showed reversible color changes from yellow to black and from green to blue, respectively. These polymer films had moderate optical contrasts in visible region and high optical contrasts in the near-infrared region. The optical contrasts of P(TPA-2T-CHO) and P(TPA-2EDOT-E2CN) films were 42.8% and 37.7% at 647 nm, and reached 81.8% and 75.6% at 1000 nm, respectively. Furthermore, these polymer films showed reasonable response times and redox stabilities upon electrochemical doping and dedoping.

1. Introduction

The materials that change color upon electrochemical doping and dedoping are said to be electrochromic materials [1]. In recent decades, electrochromic materials have received considerable attention due to their promising applications in smart windows, antiglare rearview mirrors, and displays, etc [2–4]. Furthermore, the electrochromic smart windows are considered to be able to reduce energy consumption and provide indoor comfort in buildings [5]. The electrochromic materials are classified as inorganic systems, mainly transition metal oxides [6] and organic systems, including organic conjugated small molecules [7], organometallic complexes [8], and conjugated polymers [9]. In our previous work, we have synthesized a series of conjugated line-shaped and star-shaped oligothiophene derivatives and studied their electrochromic properties [10–12]. As solid films, these conjugated oligothiophene derivatives show reversible and clear color changes upon electrochemical doping and dedoping. The organic conjugated compounds are considered to have greater potential as electrochromic materials because of their shorter response time and a broader color palette compared with inorganic electrochromic materials [13–15].

Organic conjugated compounds based on triphenylamine and its derivatives have been widely used in organic field effect transistors (OFETs) [16], organic light-emitting diodes (OLEDs) [17], and organic solar cells (OSCs) [18] because of their good photo and electroactive properties. Triphenylamine and its derivatives can be easily oxidized to

form stable radical cations accompanied by significant color changes. Thus, many triphenylamine and its derivatives have been applied to electrochromic devices (ECDs) [19–21]. The electrochromic materials based on triphenylamine and its derivatives exhibited good electrochromic properties, such as high optical contrast, rapid switch time [22], and multicolor [23]. However, in previous reports about the electrochromic materials based on triphenylamine and its derivatives, few alternating copolymers of aromatic rings and triphenylamines containing acceptor groups have been used as electrochromic materials. Xu *et al.* reported alternating copolymers of benzo[1,2-b:3,4-b']-dithiophene (BDT) derivative and triphenylamine [24], which exhibited reversible electrochromic performance. Therefore, the synthesis of triphenylamine derivatives containing dicyanovinyl or aldehyde groups still attract considerable attention due to their promising applications in optoelectrochemical devices.

Synthesizing electrochromic polymers showing black-to-clear transitions is interesting due to their straightforward use into several relevant applications as e-readers or privacy windows, where this color transition is demanded [25]. In recent years, the black electrochromic materials have been prepared by copolymerizing two or more monomers, and blending or stacking several polymer films [26,27]. However, the reported black electrochromic materials were usually random copolymers or physical mixture, which could result in batch to batch problem, due to the poor reproducibility. Thus, it is necessary to prepare a homopolymer to use as the black electrochromic material. In

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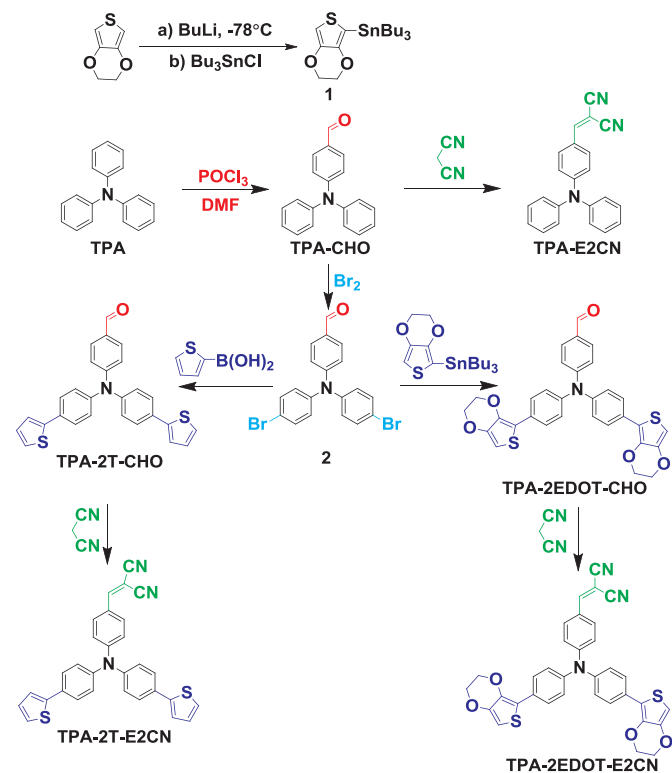
In addition, it is very important and difficult to prepare green electrochromic materials in the field of electrochromism because the green is one of the three primary colors (RGB) and the green electrochromic materials need to exhibit dual-band absorptions in both the red and blue regions [28]. The green electrochromic materials have been prepared through constructing donor-acceptor (D-A) polymers [29,30]. In previous reports about the green polymers, several groups (e.g., 5,7-di(thien-2-yl)thieno[3,4-b]pyrazine (DTP), Benzo[*c*][1,2,5]thiadiazole (BTD)) have been used as acceptor units, the thiophene derivatives have been used as donor units. But the triphenylamine derivatives containing aldehyde group have almost not been used to prepare the green electrochromic materials. Therefore, the synthesis of homopolymers of triphenylamine derivatives containing aldehyde may constitute an interesting new route to obtain green or black electrochromic materials.

In this paper, a series of triphenylamine derivatives, namely 4-(di-phenylamino)benzaldehyde (TPA-CHO), 4-(2,2-dicyanovinyl)-phenyl (diphenyl) amine (TPA-E2CN), 4-[bis(4-thiophen-2-yl-phenyl)amino]benzaldehyde (TPA-2T-CHO), 4-(2,2-dicyanovinyl)phenyl[4-bis(4-thiophene-2-yl-phenyl)amino] (TPA-2T-E2CN), 4-[bis[4-(3',4'-ethylenedioxythien-2'-yl)-phenyl]amino]benzaldehyde (TPA-2EDOT-CHO), and 4-(2,2-dicyanovinyl)phenyl[4-bis[4-(3',4'-ethylenedioxythien-2'-yl)-phenyl]amino] (TPA-2EDOT-E2CN) (Scheme 1), were synthesized, and their optoelectrochemical properties were investigated. Furthermore, their corresponding polymers were prepared by electropolymerization, and their electrochromic properties were also investigated.

2. Experimental section

2.1. Materials

All solvents were purified and dried using standard methods. 2-Thienylboronic acid, triphenylamine (TPA), *trans*-dichlorobis(triphenylphosphine)palladium(II) (Pd(PPh₃)₂Cl₂), and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) were purchased from Sigma-Aldrich



Scheme 1. Synthetic routes for the triphenylamine derivatives.

Co., Ltd. *n*-Butyllithium (2.2 M in hexane), 3,4-ethylenedioxythiophene (EDOT), bromine (Br₂), phosphorous oxychloride (POCl₃), tri-*n*-butyltin chloride (TBTC), and malonodinitrile were purchased from Alfa Aesar Chemical Co., Ltd. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Aladdin Chemical Co., Ltd. Dichloromethane (DCM), petroleum, acetonitrile (ACN), dimethylformamide (DMF), 1,2-dichloroethane, toluene, ammonium chloride (NH₄Cl), tetrahydrofuran, anhydrous potassium carbonate (K₂CO₃), potassium hydroxide (KOH), sodium hydroxide (NaOH), and anhydrous sodium sulfate (Na₂SO₄) were obtained from Sinopharm Chemical Reagent Co., Ltd. All reagents were commercially available and used without further purification.

2.2. Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE-600 NMR spectrometer. Mass spectra were carried out on Bruker Agilent 1290 mass spectrometer. Electronic absorption spectra were measured using a Thermo Helios-γ spectrometer. Electrochemical properties were measured using a CHI750A electrochemical workstation (Zhenhua Apparatus Co., Ltd Shanghai) and an electrochromic cycling tester (Zhuhai Kaivo Optoelectronic Technology Co., Ltd.)

2.3. Synthesis of triphenylamine derivatives

The synthetic routes to the triphenylamine derivatives are shown in Scheme 1. The synthesis and characterization of compounds are shown in the experimental section of the Supporting Information.

TPA-CHO, ¹H NMR (CDCl₃, 600 MHz, ppm): δ 9.81 (s, 1H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 4H), 7.18–7.16 (m, *J* = 3.9 Hz, 6H), 7.02 (d, *J* = 8.7 Hz, 2H).

TPA-E2CN, ¹H NMR (CDCl₃, 600 MHz, ppm): δ 7.74 (d, *J* = 9.0 Hz, 2H), 7.51 (s, 1H), 7.39 (t, *J* = 7.8 Hz, 4H), 7.23 (t, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H).

2, ¹H NMR (CDCl₃, 600 MHz, ppm): δ 9.84 (s, 1H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 4H), 7.05 (d, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 4H).

TPA-2T-CHO, ¹H NMR (CDCl₃, 600 MHz, ppm): δ 9.84 (s, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 4H), 7.29 (t, *J* = 4.2 Hz, 4H), 7.19 (d, *J* = 8.6 Hz, 4H), 7.13 (d, *J* = 8.7 Hz, 2H), 7.09 (t, *J* = 3.6 Hz, 2H). ¹³C NMR (CDCl₃, 150 MHz, ppm): δ 190.39, 152.77, 145.24, 143.59, 131.35, 131.26, 129.82, 128.13, 127.21, 126.25, 124.84, 123.07, 120.33. HRMS (ESI): [C₂₇H₁₉NOS₂ + Na]⁺ 460.0803, calcd. for 460.0800.

TPA-2T-E2CN, ¹H NMR (CDCl₃, 600 MHz, ppm): δ 7.75 (d, *J* = 9.0 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 4H), 7.51 (s, 1H), 7.29 (d, *J* = 4.7 Hz, 2H), 7.28 (d, *J* = 5.1 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 4H), 7.09 (t, *J* = 3.6 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H). ¹³C NMR (CDCl₃, 150 MHz, ppm): δ 157.79, 152.86, 144.18, 143.28, 132.99, 132.55, 128.22, 127.37, 126.73, 125.19, 123.45, 123.39, 119.39, 119.39, 115.07, 113.95, 76.30. HRMS (ESI): [C₃₀H₁₉N₃S₂ + Na]⁺ 508.0911, calcd. for 508.0913.

TPA-2EDOT-CHO, ¹H NMR (CDCl₃, 600 MHz, ppm): δ 9.85 (s, 1H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 4H), 7.19 (d, *J* = 8.7 Hz, 4H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.33 (s, 2H), 4.35–4.33 (m, *J* = 2.4 Hz, 4H), 4.28–4.27 (m, *J* = 2.4 Hz, 4H). ¹³C NMR (CDCl₃, 150 MHz, ppm): δ 190.39, 152.92, 144.22, 142.29, 138.12, 131.31, 130.06, 129.48, 127.20, 126.12, 119.95, 116.83, 97.65, 64.83, 64.45. HRMS (ESI): [C₃₁H₂₃NO₅S₂ + Na]⁺ 576.0915, calcd. for 576.0910.

TPA-2EDOT-E2CN, ¹H NMR (CDCl₃, 600 MHz, ppm): δ 7.75 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 8.7 Hz, 4H), 7.52 (s, 1H), 7.18 (d, *J* = 8.7 Hz, 4H), 7.04 (d, *J* = 9.0 Hz, 2H), 6.32 (s, 2H), 4.33–4.31 (m, *J* = 2.1 Hz, 4H), 4.26–4.25 (m, *J* = 2.1 Hz, 4H). ¹³C NMR (CDCl₃, 150 MHz, ppm): δ 156.74, 151.99, 142.08, 141.30, 137.37, 131.95, 130.06, 126.30, 125.51, 122.13, 118.06, 115.50, 114.17, 113.03, 96.98, 74.72, 63.84, 63.42. HRMS (ESI): [C₃₄H₂₃N₃O₄S₂ + Na]⁺ 624.1023, calcd. for 624.1022.

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