



Electrochromic properties of novel chalcones containing triphenylamine moiety



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ARTICLE INFO

Article history:

Received 28 November 2013

Received in revised form

27 January 2014

Accepted 17 February 2014

Available online 3 March 2014

Keywords:

Quantum chemical calculation

Triphenylamine

Chalcone

Electrochemistry

Electrochromism

Spectroelectrochemical

ABSTRACT

A series of novel electrochromic chalcones containing triphenylamine units were synthesized by Aldol reaction and characterized by NMR, IR and MS. Their optical, electrochemical properties were investigated using UV–vis, photoluminescence spectra and cyclic voltammetry. The molecular orbital energy levels and excitation energies were calculated by quantum chemical calculation. It was found that the fluorescence intensity is decreasing with formation of charge-transfer state. The existence of electron donating group on triphenylamine unites caused a significant bathochromic shift of the UV absorption maximum and increased E_{HOMO} and E_{LUMO} . The electrochromic property of the synthesized compounds was studied by spectroelectrochemical experiments. The results showed that the chalcones containing triphenylamine moiety presented good electrochromic stability, with a color change from yellow to blue as applied potentials ranging from 0.0 to 2.8 V. The coloring and bleaching time was in the range of 2.9–4.2 s and 1.7–3.3 s, respectively.

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1. Introduction

In recent years, electrochromic materials have attracted a lot of attention because of their potential applications such as tunable windows [1], variable reflectance mirrors [2], and electrochromic displays [3]. Compared to widely used inorganic electrochromic materials [4–6], organic electrochromic materials, such as viologens [7] and conducting polymers [8], have aroused more and more interests due to their large-scale processability, fast response time, high coloration efficiency and easy color adjustment [9–11].

Triphenylamine (TPA) derivatives have been extensively investigated as hole-transport material [12–14] and photovoltaic materials [15–17] due to their well-known electron-rich property. In addition, TPA derivatives can also easily be oxidized to form cationic radicals accompanying with a noticeable change of coloration [18–21]. Liou and co-workers reported that TPA-containing polyimides show excellent electrochromic/electroactive stability [22–25]. However, acylamino groups of polyimides would occupy

two *para*-positions of TPA, where TPA could be modified by some function groups. Three new fluorophores containing TPA moiety were reported by Kim et al. [26]. But hydrogen atom at *p*-position of the TPA benzene ring lost during electrochromism, which resulted in the polymerization of TPA and low electrochromic stability.

In this paper, a series of novel chalcones with TPA moiety were designed and synthesized. Optical, electrochemical and electrochromic properties of these compounds were studied in detail. The detailed electronic transitions of neutral and radical absorptions were investigated by quantum chemical calculations. Furthermore, electrochromic devices based on TPA-chalcones were fabricated to study the electrochromic property of the synthesized compounds.

2. Experimental section

2.1. Materials and methods

All the chemical reagents and solvents, unless otherwise stated, were used as received from commercial sources without further purification. *N,N*-dimethylformamide (DMF) and phosphorus oxychloride (POCl_3) were redistilled before use. Dichloromethane (CH_2Cl_2) was used after drying by calcium chloride. NMR spectra (^1H at 400 MHz, ^{13}C at 100 MHz) were obtained in CDCl_3 using an

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AVANCE III spectrometer with tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on an LCQ Deca XP MAX mass spectrometer. Infrared and UV–vis spectra were recorded on a Thermo Nicolet 380 spectrometer and a PE LAMBDA35 spectrometer, respectively. Cyclic voltammetry (CV) experiment was performed on a CHI660E electrochemistry workstation. Fluorescence spectra were measured using F-7000 spectrometer.

2.2. Synthesis

The synthesis route of compounds **1a–1f** is given in Scheme 1. Firstly, 2-Methylthiophene (**2**) was formylated by Vilsmeier reagent at room temperature to afford 5-methylthiophene-2-carbaldehyde (**3**). Then, 2,5-dimethylthiophene (**4**) was obtained through the Kishner–Wolff–Huang reduction reaction. 3-Acetyl-2,5-dimethylthiophene (**5**) was prepared by Friedel–Crafts reaction in good yield. TPA derivatives **7a–7f** were synthesized via corresponding TPA **6a–6f** and Vilsmeier reagent [27].

2.2.1. General procedure

To a mixture of 3-acetyl-2,5-dimethylthiophene (**5**) (1.54 g, 10 mmol), corresponding aldehyde (10 mmol) and ethanol (140 mL) was added aqueous solution of sodium hydroxide (13 M) (20 mL). The mixture was stirred at room temperature until corresponding aldehyde was consumed completely (monitored by thin-layer chromatography). The crude product was collected by filtration, followed by washing with water and recrystallization from ethanol to afford the products **1a–1f**.

2.2.2. 1-(2,5-Dimethylthiophen-3-yl)-3-(4-(N,N-diphenylamino)phenyl)prop-2-en-1-one (**1a**)

Yellow powder, yield 3.63 g (92%), m.p. 143.0–144.5 °C; MS (APCI): m/z calcd for $C_{27}H_{23}NOS$: 410.16 $[M+H]^+$; found: 410.35; 1H NMR (400 MHz, $CDCl_3$) δ : (ppm) 7.67 (d, $J = 15.6$ Hz, 1H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.32 (t, $J = 7.7$ Hz, 4H), 7.22–7.09 (m, 7H), 7.08–6.99 (m, 3H), 2.72 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : (ppm) 186.6, 150.0, 146.9, 146.4, 143.4, 137.1, 135.2, 129.5, 129.5, 128.1, 126.0, 125.4, 124.0, 122.6, 121.8, 15.8, 15.0; FT-IR (cm^{-1} , KBr): 700, 759, 1136, 1171.75, 1222, 1279, 1325, 1488, 1504, 1583, 1650.

2.2.3. 1-(2,5-Dimethylthiophen-3-yl)-3-(4-(N-phenyl-N-(4-methylphenyl)amino)phenyl)prop-2-en-1-one (**1b**)

Yellow powder, yield 3.58 g (85%), m.p. 153.5–154.5 °C; MS (APCI): m/z calcd for $C_{28}H_{25}NOS$: 424.17 $[M+H]^+$; found: 424.54; 1H NMR (400 MHz, $CDCl_3$) δ : (ppm) 7.67 (d, $J = 15.6$ Hz, 1H), 7.48 (d, $J = 8.5$ Hz, 2H), 7.32 (t, $J = 7.7$ Hz, 4H), 7.22–7.09 (m, 7H), 7.08–6.99

(m, 3H), 2.72 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : (ppm) 186.7, 150.2, 147.0, 146.3, 144.3, 143.5, 137.2, 135.2, 134.1, 130.2, 129.5, 129.4, 127.6, 126.1, 125.9, 125.1, 123.8, 122.4, 121.2, 21.0, 15.8, 15.0; FT-IR (cm^{-1} , KBr): 821, 976, 1171, 1221, 1265, 1295, 1319, 1483, 1504, 1580, 1648.

2.2.4. 3-(4-(N,N-Di(4-methylphenyl)amino)phenyl)-1-(2,5-dimethylthiophen-3-yl)prop-2-en-1-one (**1c**)

Yellow powder, yield 3.56 g (81%), m.p. 121.0–122.0 °C; MS (APCI): m/z calcd for $C_{29}H_{27}NOS$: 438.19 $[M+H]^+$; found: 438.34; 1H NMR (400 MHz, $CDCl_3$) δ : (ppm) 7.67 (d, $J = 15.6$ Hz, 1H), 7.44 (d, $J = 8.6$ Hz, 2H), 7.17–6.94 (m, 13H), 2.72 (s, 3H), 2.46 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : (ppm) 186.8, 150.4, 146.2, 144.3, 143.6, 137.2, 135.2, 133.9, 130.1, 129.5, 127.2, 126.1, 125.6, 122.1, 120.5, 20.9, 15.8, 15.0; FT-IR (cm^{-1} , KBr): 818, 978, 1134, 1174, 1220, 1265, 1294, 1321, 1503, 1582, 1650.

2.2.5. 1-(2,5-Dimethylthiophen-3-yl)-3-(4-(N-phenyl-N-(4-methoxyphenyl)amino)phenyl)prop-2-en-1-one (**1d**)

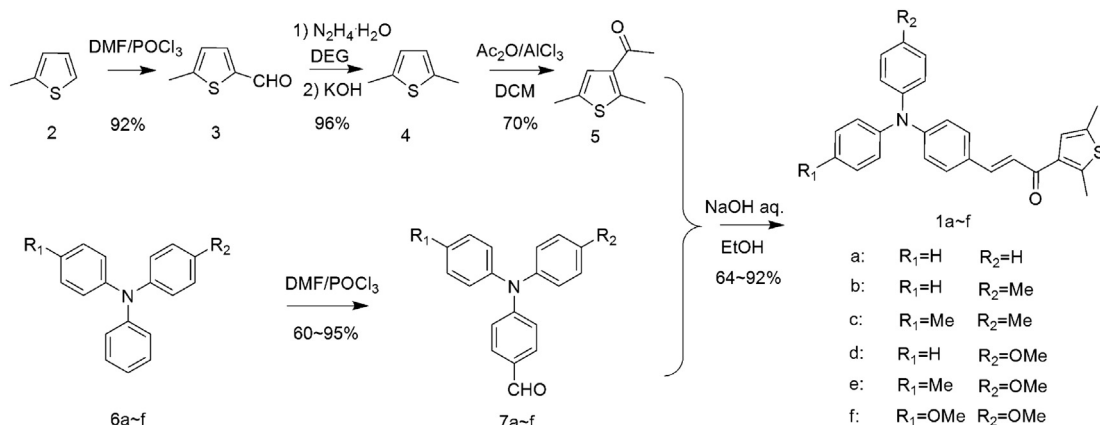
Yellow powder, yield 3.66 g (83%), m.p. 146.0–147.0 °C; MS (APCI): m/z calcd for $C_{28}H_{25}NO_2S$: 440.19 $[M+H]^+$; found: 440.22; 1H NMR (400 MHz, $CDCl_3$) δ : (ppm) 7.67 (d, $J = 15.6$ Hz, 1H), 7.45 (d, $J = 8.6$ Hz, 2H), 7.34–7.28 (m, 2H), 7.18–7.05 (m, 7H), 6.98 (d, $J = 8.6$ Hz, 2H), 6.90 (d, $J = 8.9$ Hz, 2H), 3.84 (s, 3H), 2.72 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : (ppm) 186.7, 156.9, 150.3, 147.0, 146.3, 143.6, 139.7, 137.2, 135.2, 129.6, 129.4, 128.0, 127.3, 126.1, 124.7, 123.6, 122.1, 120.4, 115.0, 55.5, 15.8, 15.0; FT-IR (cm^{-1} , KBr): 824, 999, 1135, 1186, 1224, 1244, 1289, 1326, 1437, 1505, 1567, 1644.

2.2.6. 1-(2,5-Dimethylthiophen-3-yl)-3-(4-(N-(4-methylphenyl)-N-(4-methoxyphenyl)amino)phenyl)prop-2-en-1-one (**1e**)

Yellow powder, yield 2.92 g (64%), m.p. 151.5–152.0 °C; MS (APCI): m/z calcd for $C_{29}H_{27}NO_2S$: 454.18 $[M+H]^+$; found: 454.30; 1H NMR (400 MHz, $CDCl_3$) δ : (ppm) 7.67 (d, $J = 15.5$ Hz, 1H), 7.43 (d, $J = 8.6$ Hz, 2H), 7.14–7.11 (m, 8H), 6.94 (d, $J = 8.6$ Hz, 2H), 6.89 (d, $J = 8.9$ Hz, 2H), 3.83 (s, 3H), 2.72 (s, 3H), 2.45 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : (ppm) 186.7, 156.8, 150.6, 146.2, 144.4, 143.7, 139.8, 137.2, 135.1, 133.7, 130.1, 129.6, 127.7, 126.7, 126.1, 125.3, 121.8, 119.7, 114.9, 55.5, 20.9, 15.8, 15.0; FT-IR (cm^{-1} , KBr): 823, 999, 1136, 1185, 1224, 1244, 1289, 1326, 1435, 1505, 1572, 1646.

2.2.7. 3-(4-(N,N-Di(4-methoxyphenyl)amino)phenyl)-1-(2,5-dimethylthiophen-3-yl)prop-2-en-1-one (**1f**)

Yellow powder, yield 4.13 g (88%), m.p. 166.0–168.0 °C; MS (APCI): m/z calcd for $C_{29}H_{27}NO_3S$: 470.18 $[M+H]^+$; found: 470.40;



Scheme 1. Synthesis routes of compounds **1a–1f**.

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