

Synthesis and characterisation of azobenzene-bridged cationic–cationic and neutral–cationic electrochromic materials



Cheng-bin Gong, Li-hua He, Jun-fei Long, Lan-Tao Liu, Song Liu, Qian Tang*, Xiang-kai Fu

The Key Laboratory of Applied Chemistry of Chongqing Municipality, College of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, China

ARTICLE INFO

Article history:

Received 30 March 2016
Received in revised form 30 May 2016
Accepted 9 June 2016
Available online 22 June 2016

Keywords:

Electrochromic materials
Electrochromic devices
Azobenzene
Aromatic esters
Pyridinium salts

ABSTRACT

Azobenzene-bridged cationic–neutral and cationic–cationic were synthesized, characterized and compared with azobenzene-bridged neutral–neutral materials. Azobenzene-bridged cationic–cationic and neutral–neutral materials exhibited well-defined and reversible redox couples during redox processes, good electrochromic behavior, and appropriate contrast ratios in the visible regions. However, azobenzene-bridged cationic–neutral materials exhibited a quasi-reversible electrochemical process. The electrochromic stability of these compounds is in the order: azobenzene-bridged neutral–neutral materials > azobenzene-bridged cationic–cationic materials > azobenzene-bridged cationic–neutral materials. Electrochromic devices based on azobenzene-bridged neutral–neutral materials achieved maximum optical contrast, fast response time, and high coloration efficiency. The substituents of azobenzene-bridged cationic–cationic materials and the anions of azobenzene-bridged cationic–neutral materials did not significantly influence their electrochemical properties and response time, but slightly affected the maximum optical contrast, change in optical density, and coloration efficiency.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Electrochromic materials (ECMs) refer to materials that undergo optical changes due to electrochemical reaction [1,2]. Electrochromic devices (ECDs), which are based on ECMs, have potential applications in smart windows [3–6], electrochromic displays [7,8], ink-jet printers [9], earth-tone chameleon materials [10,11], and anti-glare rear-view mirrors for cars [12,13]. Consequently, ECMs have attracted extensive research attention from researchers since Platt [14] reported the electrochromic phenomenon in dyes. ECMs include inorganic materials, such as metal oxides [15–18], and organic materials, such as phenothiazine [19–24], anthraquinone [25–32], viologen [33–36], thiophene [37–40], polythiophene [41–47], polyaniline [48–50], polypyrrole [51–54], and polyimide [55]. Compared with inorganic ECMs, organic ECMs exhibit the unique advantages of high optical contrast, fast switching speed, flexible device fabrication, and a multitude of achievable colors via chemical structure variation.

Azobenzene and its derivatives comprise a dominant class of synthetic colorants that demonstrate the advantages of bright colors, good stability, low flammability, and reversible

photoisomerization [56,57]. Aromatic esters have been reported to display electrochromic properties through the formation of anionic radicals via electrochemical reduction [58–62]. Dicationic pyridinium salts, such as the viologens, are extensively used in electrochromic applications by reducing bleached dicationic pyridinium salts into colored monocationic pyridinium salts, and subsequently, into a neutral state [63,64]. Azobenzene-bridged neutral–neutral materials are reported to display good electrochromic properties [60,61]. In this work, azobenzene-bridged cationic–neutral materials (compounds **1a–d**) and cationic–cationic materials (compounds **2a–c**) (Scheme 1) were synthesised, and their electrochromic and photoresponsive properties were investigated and compared with azobenzene-bridged neutral–neutral materials. The influences of the substituents of compounds **1a–d** and the anions of compounds **2a–c** were also studied.

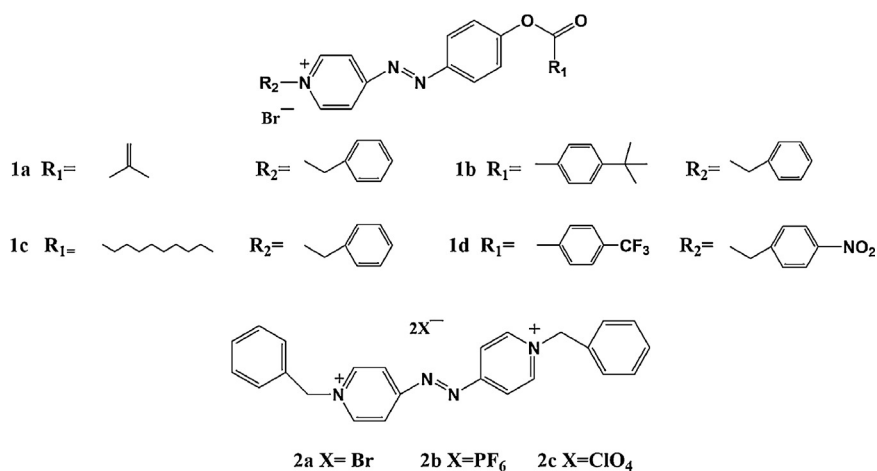
2. Experimental

2.1. Materials and instrumentation

All chemical reagents were purchased from Aladdin Co., Shanghai, China, and used as received. All solvents were of

* Corresponding author.

E-mail address: qiantang@swu.edu.cn (Q. Tang).



Scheme 1. Chemical structures of compounds **1a–d** and **2a–c**.

analytical-reagent grade, commercially available, and used without further purification.

^1H NMR and ^{13}C NMR spectra were measured with a Bruker AV 600 (600 MHz) spectrometer at 298 K using tetramethylsilane as the internal standard. Ultraviolet–visible (UV–vis) spectra were obtained with a UV-4802 spectrophotometer [UNICO (Shanghai) Instruments Co. Ltd., China]. Cyclic voltammetry (CV) was performed on a CHI 650B electrochemical workstation using a three-electrode system. Ag/AgCl was used as the reference electrode. High performance liquid chromatography–Mass spectra were performed on a Bruker Esquire 2000 HCT LC/MS system. Melting points were measured on a SGWX-4 melting point apparatus (Shanghai Yidianwuliguangxue Instrument Co., Ltd.). Elemental analysis was performed by an Elementar Vario Micro Select (Germany). Fourier transform infrared spectra (FT-IR, 400–4000 cm^{-1}) were recorded on a Perkin-Elmer Model GX spectrometer (USA) via the KBr pellet method.

2.2. General synthesis of cationic–neutral materials (compounds **1a–d**)

The synthetic route of compounds **1a–d** is depicted in **Scheme 2**.

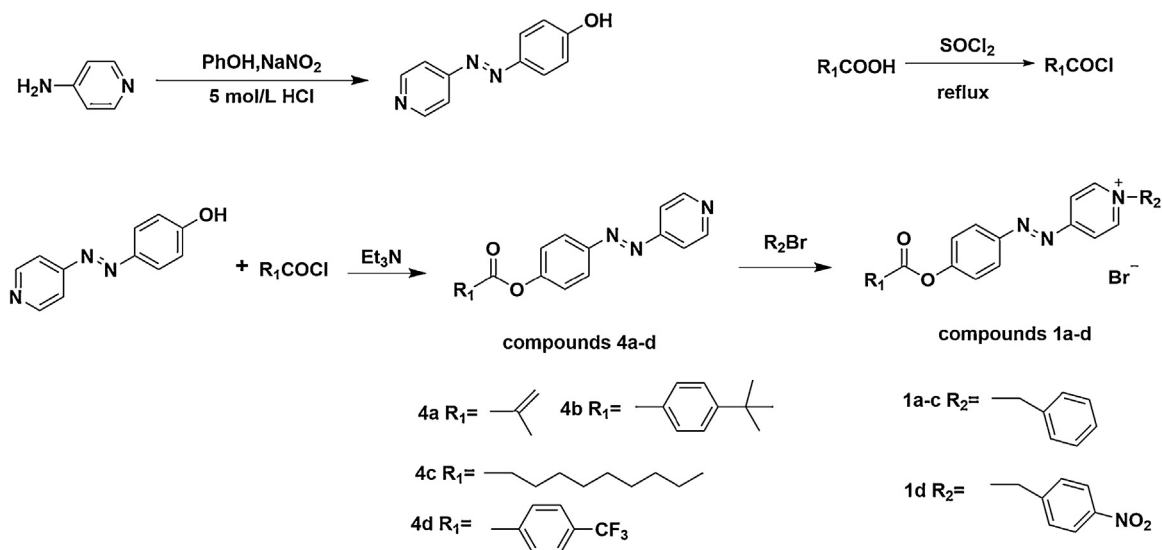
4-(4-Hydroxyphenylazo)pyridine was synthesized according to the method reported by Lu et al. [65]. ^1H NMR (600 MHz, DMSO- d_6)

δ (ppm): 8.72 (s, 2H, $J=6.0$ Hz), 7.92 (d, 2H, $J=8.4$ Hz), 7.77 (d, 2H, $J=3.6\sim 6.0$ Hz), 6.97 (d, 2H, $J=9.0$ Hz), 4.87 (s, 1H).

R_1COCl was synthesized by refluxing R_1COOH (126.0 mmol) in thionyl chloride (20 mL, 0.27 mol) for 6 h, which yielded a clear yellow solution. Removal of excess thionyl chloride via distillation yielded the crude product of R_1COCl , which was used directly for the next reaction without further purification.

4-(4-Hydroxyphenylazo)pyridine (5.0 mmol) was dissolved in dry dichloromethane (10 mL). Triethylamine (2.0 mL, 14.0 mmol) was added and the mixture cooled in an ice bath, and an ice-cooled (0 °C) solution of R_1COCl (8.0 mmol) in dichloromethane (20 mL) was added dropwise. The resulting solution was mechanically stirred overnight at room temperature. The solvent was removed by rotary evaporation. (*E*)-4-(Pyridin-4-yl diazenyl)phenyl 4-substituted benzoate (compounds **4a–d**) was obtained by recrystallising from methanol.

(*E*)-4-(Pyridin-4-yl diazenyl)phenyl methacrylate (Compound **4a**): orange solid (0.80 g) yielded 59.7%. Mp: 144.0–145.0 °C. MS (ESI): (CH_2Cl_2 , positive mode) m/z : 268.2 (mass = 267.15 g mol^{-1}). ^1H NMR (600 MHz, DMSO- d_6) δ (ppm): 8.82 (d, 2H, $J=6.0$ Hz), 8.03 (d, 2H, $J=8.4$ Hz), 7.73 (d, 2H, $J=6.0$ Hz), 7.34 (d, 2H, $J=9.0$ Hz), 6.40 (s, 1H), 5.83 (s, 1H), 2.09 (s, 3H). ^{13}C NMR (150 MHz, DMSO- d_6) δ (ppm): 165.34, 157.40, 154.24, 150.96, 149.95, 135.63, 127.88, 124.81, 122.55, 116.41, 18.34. Elemental analysis calculated (%) for



Scheme 2. Synthetic route for compounds **1a–d**.

Download English Version:

<https://daneshyari.com/en/article/1440076>

Download Persian Version:

<https://daneshyari.com/article/1440076>

[Daneshyari.com](https://daneshyari.com)