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Short communication

Electrochromic properties of new fluorophores containing triphenylamine moiety

Sung-Hoon Kim[a,*], Jang-Hyun Ryu[b], Heung-Jin Choi[c], Hong-Seok Kim[c]

[a]Department of Dyeing and Finishing, Kyungpook National University, Daegu 702-701, South Korea
[b]Department of Applied Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashiku, Fukuoka 812-8581, Japan
[c]Department of Industrial Chemistry, Kyungpook National University, Daegu 702-701, South Korea

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Abstract

New fluorophores (**5**–**7**) having triphenylamine were obtained by condensation between 2,3,3-trimethylindolenine **2**, 2-methylbenzoxazole **3**, quinaldine **4** and 4-diphenylamino-benzaldehyde **1** using a catalytic amount of benzyltriethylammonium chloride (BTEA) as a phase-transfer catalyst. The electrochromic properties of compounds **5**–**7** were studied by using a propylenecarbonate solution with Bu_4NClO_4 as supporting electrolyte. The electrochromic cells changed in colour to bluish-red or blue at an applied voltage of 2.2–2.5 V.

Keywords: Electrochromism; ITO glass; Fluorophore; Triphenylamine

1. Introduction

Electrochromism is a phenomenon of reversible change in colour produced electrochemically. Although inorganic systems are now in practical use, organic systems have advantages over inorganic systems in several ways, viz. operation at low voltage, colouration over a wide range, colour distinction, and multi-colouration, etc. A large number of organic compounds develop absorption bands in the visible region of the spectrum upon redox reaction and most compounds in this class exhibit electrochromic phenomena by reversible electrode deposition, e.g. viologens [1–4], pyridines [5], *ortho*-toluidines [6], and anthraquinones [7]. The colouration is achieved by an oxidation–reduction reaction, which can be a simple redox reaction or a redox reaction coupled with a chemical reaction to produce an insoluble coloured species. We have reported that the response improved electrochromic colour display using two kinds of viologen derivatives [3]. In this study, three kinds of new fluorophores containing triphenylamine moiety in the molecule have been synthesized, and exhibit distinct electrochromism in a comparatively low voltage region.

2. Synthesis

It is well known that the active methylene groups react with carbonyl groups, especially an aldehyde, to afford styryl dyes [8]. The fluorophores having triphenylamine were obtained by condensation between 2,3,3-trimethylindolenine **2**, 2-methylbenzoxazole **3**, quinaldine **4** and 4-diphenylamino-benzaldehyde **1** using a catalytic amount of benzyltriethylammonium chloride (BTEA) as a phase-transfer catalyst [9]. The general procedures to prepare the flurophores are shown in Scheme 1.

* Corresponding author. Tel.: +82 53 950 5641; fax: +82 53 950 6617.
E-mail address: shokim@knu.ac.kr (S.-H. Kim).

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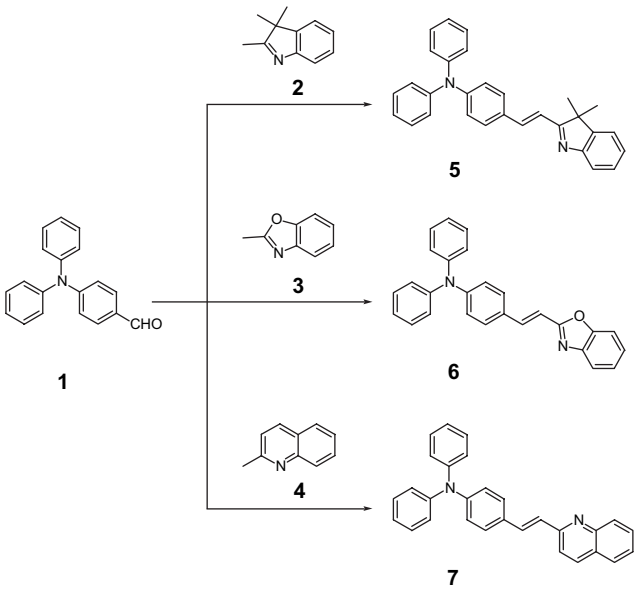

Scheme 1.

Compounds **5**–**7** were obtained using a previously described procedure [10]. 4-Diphenylamino-benzaldehyde **1** (0.01 mol, 2.73 g), 2,3,3-trimethylindolenine **2** (0.01 mol, 1.59 g) and BTEA (0.003 mol, 0.70 g) were mixed and stirred. Ten millilitres of 50% sodium hydroxide aqueous solution was added dropwise during 1 h. The mixture was stirred at 30–50 °C for 3 h. The reaction mixture was diluted with water and neutralized with hydrochloric acid (pH = 8–8.5). The product was filtered, washed with water, dried at 50 °C and crystallized from ethylacetate/*n*-hexane. Compounds **5**–**7** were obtained by a similar procedure using 2-methylbenzoxazole **3** and quinaldine **4**. These compounds were synthesized in 30–50% yield.

Compounds **5**–**7** absorb at 362–406 nm and emit at 506–508 nm in chloroform.

3. Electrochromism

During the course of our investigation on the synthesis and optical properties of the fluorophores containing triphenylamine, we have found that compounds **5**–**7** exhibit electrochromic properties in solution. The electrochromic cell comprised two glass sheets (3 cm × 3 cm) separated by a 0.1 mm thickness spacer of PET film. The glass sheets were coated on one side with transparent conductive electrodes of indium-doped tin oxide (ITO), and these sides were placed so as to face each other on the inside of the cell, and the edges of the cell were sealed with insulating epoxide resin. Prior to the final sealing, the space between the electrodes was filled with a propylenecarbonate/methanol solution of 0.05 mmol fluorophore **5** and 1.5 mmol tetrabutyl ammonium perchlorate, Bu_4NClO_4, as electrolyte.

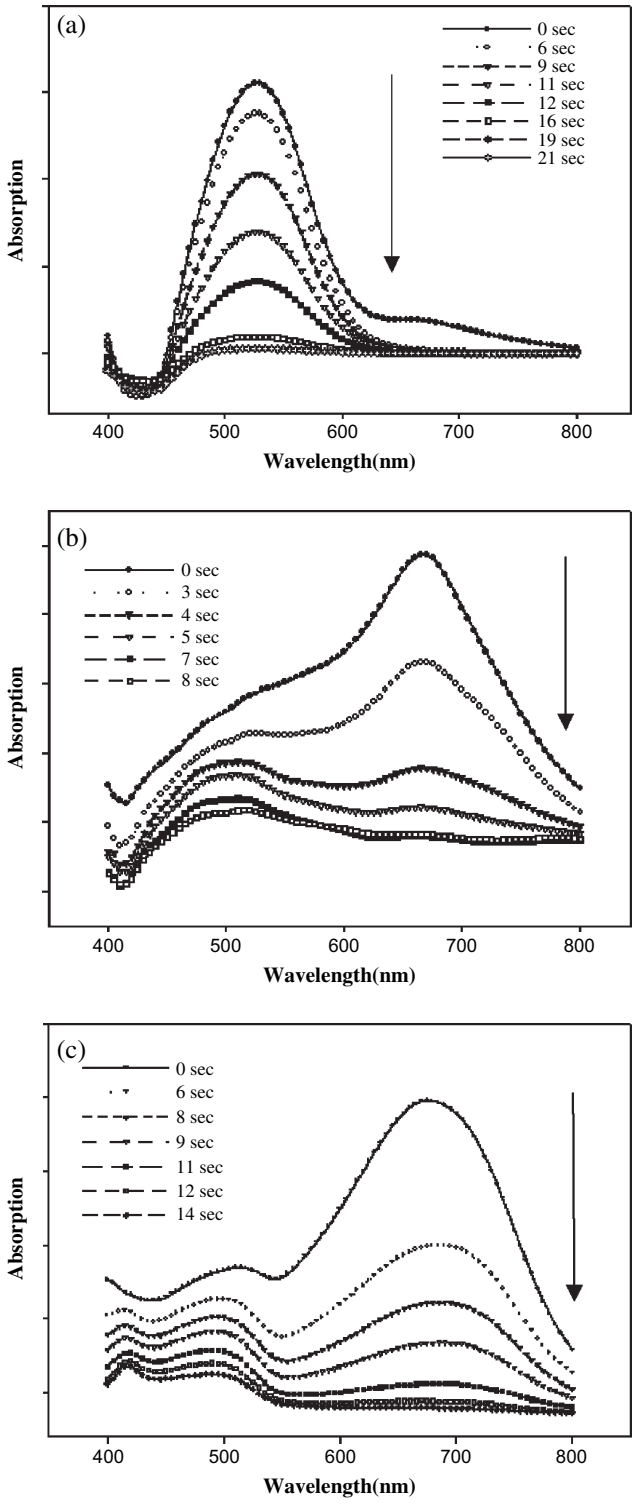

Fig. 1. Spontaneous bleaching of the absorption spectrum for compound **5** (a), **6** (b) and **7** (c) in open-circuit. Figures in the diagram denote bleaching time at 25 °C.

Viologen, bis-quarternary salts of bipyridine, undergoes a one-electron reduction to give a coloured radical cation. However, the absorption spectra of the coloured electrochromic cell were produced on the anode after

electrocolouration (Fig. 1a). The threshold voltages for the colouration are about 2.2 V for compound **5**. At an applied voltage of 2.2 V in the device, the absorption maximum was observed at around 530 nm and the colour was bluish-red, but in open-circuit condition rapidly bleached colourless. In the compound **6** and **7** system, the prominent peak appears at 670 nm and the colour is blue at 2.5 and 2.2 V, respectively, but changed to colourless in an open-circuit condition (Fig. 1b and c). The absorbance increases significantly depending on increment of the applied voltage. As can be seen in Fig. 1a–c, all of the electrochromic cell shows absorbance change within 20 s. Thus, the electrochemically grown compounds **5**–**7** are good candidates for electrochromic displays.

Acknowledgements

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[9] Analytical data agree with the proposed structure for **5**–**7**, (**5**) MP: 101–103 °C; anal. found: C, 88.66; H, 6.23; N, 6.61%. Calcd for $C_{30}H_{26}N_2$; mass (*m*/*z*) 414 (M^+), (**6**) MP: 133–135 °C; anal. found: C, 83.52; H, 5.64; N, 7.08%. Calcd for $C_{27}H_{20}N_2O$; mass (*m*/*z*) 388 (M^+), (**7**) MP: 120–122 °C; anal. found: C, 87.28; H, 5.37; N, 7.35%. Calcd for $C_{29}H_{22}N_2$; mass (*m*/*z*) 398 (M^+).
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