



## 2-Amino-4-chloro-5-formylthiophene-3-carbonitrile derived azo dyes



Jiao Geng<sup>a</sup>, Yuan Dai<sup>a</sup>, Hui-Fen Qian<sup>b</sup>, Na Wang<sup>a</sup>, Wei Huang<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu Province, 210093, PR China

<sup>b</sup> College of Sciences, Nanjing Tech University, Nanjing, Jiangsu Province, 210009, PR China

### ARTICLE INFO

#### Article history:

Received 15 December 2014

Received in revised form

5 February 2015

Accepted 7 February 2015

Available online 20 February 2015

#### Keywords:

Thiophene based heterocyclic dye

UV–Vis spectrum

Solvatochromism

Acid-base discoloration

Crystal structure

Azo dye

### ABSTRACT

Six azo dyes derived from the common 2-amino-4-chloro-5-formylthiophene-3-carbonitrile unit and different aniline based couplers were synthesized by the traditional diazotization-coupling strategy. Solvatochromism has been studied for this family of donor– $\pi$ –acceptor heterocyclic azo dyes. Furthermore, UV–Vis spectral comparisons (maximum absorption wavelength, molar extinction coefficient and full width at half maximum) have been made between the six new azo dyes reported in this work and four previously reported 4-nitro-4'-amino-azobenzene disperse dyes. In addition, X-ray single-crystal structure of one representative azo dye has been included, which constitutes the first structural report on azo dyes containing the 2-amino-4-chloro-5-formylthiophene-3-carbonitrile diazo component.

© 2015 Elsevier Ltd. All rights reserved.

### 1. Introduction

Azo dyes are one of the most important categories of synthetic dyes because they are easily synthesized and have broad color spectrum [1]. In general, they can be classified into monoazo dyes, disazo dyes, trisazo dyes and polyazo dyes, but the monoazo compounds account for the great majority of them. Azo dyes also have versatile applications in many fields such as optical data storage, non-linear optics, dye-sensitized solar cells, ink jet printers and metallochromic indicators [2–8]. Even though some azo dyes have been reported poisonous, many additional dyes can be used in drugs and food [9]. Among them the azo dyes containing azobenzene skeleton have been widely reported in literature [10–14].

Heterocyclic derived dyes have been used in disperse dye chemistry for many years due to their excellent brightness of shade [15,16]. Excellent reviews exist to discuss the developments of preparation and application of azo dyes containing heterocyclic moieties because they have shown advantages such as color-deepening effects and excellent sublimation fastness on the dyed fibers [17,18]. We have previously reported several nitrogen-containing disperse dyes, such as 'dyes containing units such as

pyridine-2,4-dione, quinoline 2,4-dione and pyrazolone; all of these dyes crystallize in the hydrazone tautomer in the solid state [19–21]. In addition, we have studied some sulfur-containing azo dyes having a benzothiazole/benzisothiazole based skeleton [22,23].

To date, the commercialized sulfur-containing dyes can be mainly sorted into four categories, namely, benzothiazoles, benzisothiazoles, thiazoles and thiophenes. Among them, thiophene based disperse azo dyes only became commercially available in the past few decades and the color of these dyes is mainly involved in red, orange and green since the thiophene ring in these dyes is generally electron rich. It is known that the introduction of electron-withdrawing groups into the thiophene ring can bring obvious bathochromic shifts in UV–Vis spectra and display hyperchromic effects on fibers [24]. The first marketed thienylazo dye, i.e. C.I. Disperse Green 9, was derived from 2-amino-3,5-dinitrothiophene.

In comparison with disperse red and yellow dyes, the design and development of primary disperse blue dyes with the narrow full width at half maximum (FWHM) and high molar extinction coefficient ( $\epsilon$ ) are very challenging mainly owing to the restriction of a low molecular weight, which will not allow for a large delocalized  $\pi$  system. In this sense, increasing the discrepancy of electron-donating and electron-withdrawing abilities of donor and acceptor units for a  $\pi$ -system molecule is suggested to be the practical synthetic strategy for preparing blue disperse dyes. In this work, we intend to use a new 2-aminothiophene derivative bearing

\* Corresponding author. Tel.: +86 25 83686526; fax: +86 25 83314502.

E-mail address: [whuang@nju.edu.cn](mailto:whuang@nju.edu.cn) (W. Huang).

three electron-withdrawing groups (cyano group, chlorine group, aldehyde group) as the diazo component, i.e. 2-amino-3-cyano-4-chloro-5-formylthiophene (**1**), to replace 2-amino-3,5-dinitrothiophene in order to produce a new family of blue disperse dyes for potential commercial applications with the help of fine tuning of different aniline based couplers. In addition, the aldehyde group in the thiophene backbone could be further prepared for Schiff-base derivatives with certain diamines. As a result, six new  $\pi$ -system thioenylazo disperse dyes **2–7** have been prepared and fully characterized, as shown in Scheme 1. X-ray single-crystal structures of one representative heterocyclic azo dye **2** and the diazo component **1** have been studied. To our knowledge, this is the first structural report on azo dyes derived from the 2-amino-3-cyano-4-chloro-5-formylthiophene diazo component.

## 2. Experimental

### 2.1. Materials and physical measurements

Elemental analyses (EA) for carbon, hydrogen and nitrogen were performed on a Perkin–Elmer 1400C analyzer. All melting points were measured without corrections. The reagents of analytical grade were purchased from commercial sources and used without any further purification. Infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded using a Nicolet FT–IR 170X spectrophotometer on KBr disks. Electrospray ionization mass spectra (ESI–MS) were recorded on a Finnigan MAT SSQ 710 mass spectrometer in a scan range of 200–2000 amu. Electroionization time-of-flight mass spectra (EI–TOF–MS, electron energy 70 eV) were recorded by a GCT TOF mass spectrometer (Micromass, Manchester, UK).  $^1\text{H}$  NMR spectra were measured with a Bruker DMX500 MHz NMR spectrometer at room temperature in  $\text{CDCl}_3$  with tetramethylsilane as the internal reference. UV–Vis spectra were recorded with a Shimadzu UV–3150 double-beam spectrophotometer using a quartz glass cell with a path length of 10 mm.

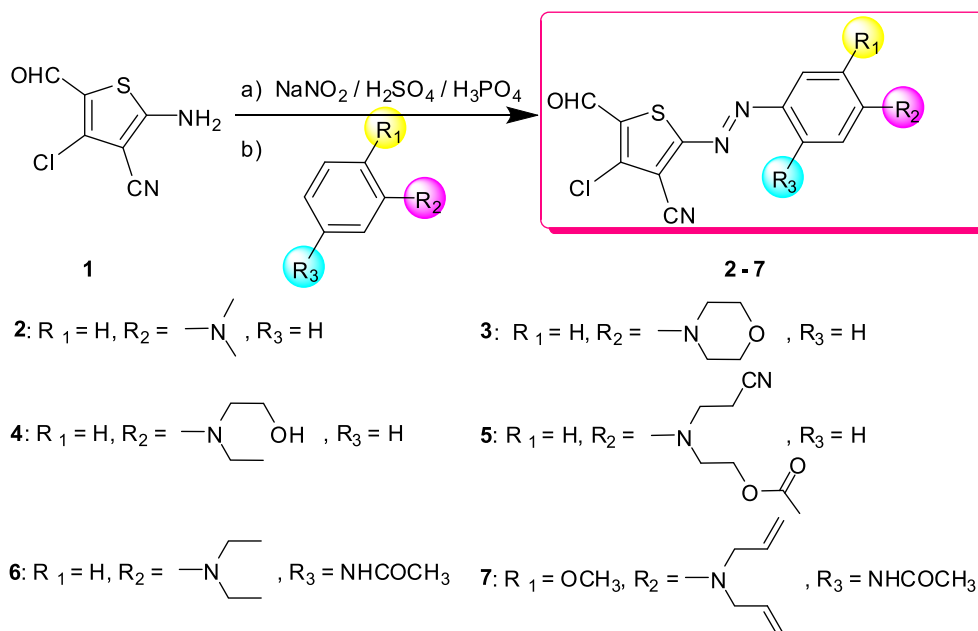
#### 2.1.1. Preparation of azo dye **2** ((*E*)-4-chloro-2-((4-(dimethylamino)phenyl)diazanyl)-5-formylthiophene-3-carbonitrile)

2-Amino-4-chloro-5-formylthiophene-3-carbonitrile (**1**) (1.87 g, 10.0 mmol) was dissolved in a mixture of concentrated sulfuric acid

(6 mL) and phosphoric acid (4.2 mL) at  $-5\text{ }^\circ\text{C}$  in an ice bath. Sodium nitrite (0.76 g, 11.0 mmol) was dissolved in cold water (10 mL) and added dropwise to the reaction mixture over 0.5 h under stirring. The diazonium salt was obtained and used for the next coupling reaction. *N,N*-dimethylaniline (1.21 g, 10.0 mmol) was added to a mixture of methanol/water (90 mL,  $v/v = 2:1$ ) solution in a three-necked flask immersed in an ice bath. The freshly prepared diazonium salt was added dropwise to the reaction mixture under vigorous mechanical stirring ( $0\text{--}5\text{ }^\circ\text{C}$ ). After that the mixture was stirred for 1 h. The precipitate was filtered and dried after thorough washing with distilled water. The crude product was obtained and the pure product was recrystallized from  $\text{CHCl}_3/\text{CH}_3\text{OH}$ . The microcrystals of dye **2** suitable for X-ray diffraction measurement were grown from  $\text{CH}_3\text{OH}$  by slow evaporation in air at room temperature for two weeks. Compound **2** (dark blue powder): Yield: 2.42 g (76%), Mp:  $243\text{--}245\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 10.04$  (s, 1H), 7.95 (d,  $J = 5$  Hz, 2H), 6.78 (d,  $J = 10$  Hz, 2H), 3.23 (s, 6H). Main FT–IR absorptions (KBr pellets,  $\text{cm}^{-1}$ ): 3456 (w), 2221 (w), 1650 (s), 1598 (vs), 1272 (vs) and 1153 (vs). Anal. Calcd. for  $\text{C}_{14}\text{H}_{11}\text{ClN}_4\text{OS}$ : C, 52.75; H, 3.48; N, 17.58%. Found: C, 52.62; H, 3.71; N, 17.49%. ESI–MS in methanol (negative):  $m/z = 318.17$  (100%),  $[\text{M}-\text{H}]^-$ . EI–TOF–MS ( $m/z$ ): 318.0 (100.0). UV–Vis in methanol,  $\lambda_{\text{max}}/\epsilon$  ( $\text{L mol}^{-1}\text{ cm}^{-1}$ ) = 571 nm/38213.

#### 2.1.2. Preparation of azo dyes **3** ((*E*)-4-chloro-2-((4-(morpholinoamino)phenyl)diazanyl)-5-formylthiophene-3-carbonitrile), **4** ((*E*)-4-chloro-2-((4-(ethyl(2-hydroxyethyl)amino)phenyl)diazanyl)-5-formylthiophene-3-carbonitrile), **5** (*E*)-2-((4-((4-chloro-3-cyano-5-formylthiophen-2-yl)diazanyl)phenyl)(2-cyanoethyl)amino)ethyl acetate, **6** (*E*)-*N*-(2-((4-chloro-3-cyano-5-formylthiophen-2-yl)diazanyl)-5-(diethylamino)phenyl)acetamide, **7** (*E*)-*N*-(2-((4-chloro-3-cyano-5-formylthiophen-2-yl)diazanyl)-5-(diallylamino)-4-methoxyphenyl)acetamide

The syntheses of azo dyes **3–7** were similar to that described for **2**. Dye **3** (violet powder): Yield: 2.67 g (74%), Mp:  $256\text{--}258\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta = 10.06$  (s, 1H), 7.98 (d,  $J = 10$  Hz, 2H), 6.95 (d,  $J = 10$  Hz, 2H), 3.89 (t,  $J = 5$  Hz, 2H), 3.52 (t,  $J = 5$  Hz, 2H). FT–IR absorptions (KBr pellets,  $\nu$ ,  $\text{cm}^{-1}$ ): 3438 (w), 2221 (w), 1654 (s), 1604 (vs), 1299 (s) and 1166 (vs). Anal. Calcd. for  $\text{C}_{16}\text{H}_{13}\text{ClN}_4\text{O}_2\text{S}$ : C, 53.26; H, 3.63; N, 15.53%. Found: C, 53.04; H,



Scheme 1. Schematic illustration for the preparation of aromatic heterocyclic azo dyes **2–7**.

Download English Version:

<https://daneshyari.com/en/article/175802>

Download Persian Version:

<https://daneshyari.com/article/175802>

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