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Post-modification of 2-formylthiophene based heterocyclic azo dyes

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ABSTRACT

In order to further adjust the π-conjugated system, solubility and electronic spectrum of 2-amino-3-cyano-4-chloro-5-formylthiophene based blue colored heterocyclic blue azo dyes, a post-modification strategy has been used to extend their terminal aldehyde radical into either an imine, acetal or α,β-unsaturated cyanoacetic ester group. The resultant azo-azomethine dyes exhibit slight bathochromic shifts in their UV–Vis spectra with the increase of the π-conjugated system. In contrast, acetal terminated products display good solubility in organic solvents but hypsochromic shifts in their UV–Vis spectra. It is worth mentioning that the α,β-unsaturated cyanoacetic ester derivatives show significant bathochromic shifts and improvement of solubility simultaneously originating from the presence of increased π-conjugated system as well as the terminal cyano and ester groups. It is believed that the current study could provide a practical post-modification strategy for decorating and improving the dyeing performance of certain dyes with functional end groups.

1. Introduction

Investigations on the functionalized *N*- and *S*-containing heterocyclic azo dyes, based on heterocycles such as thiophene [1], thiazole [2–5], thiadiazole [6], benzothiazole [7] and benzoisothiazole [8], have made significant progresses on dye chemistry in recent years. To date, these heterocyclic azo dyes have shown many advantages in the aspects of brightness of shade, sublimation fastness, color-deepening effects and brilliant dyeing properties in comparison with conventional azobenzene based dyes [9–11]. Specifically, thiophene based monoazo disperse dyes bearing different electron-withdrawing groups (eg, CN, NO_2, COMe, CO_2Et, CO_2Bu) and electron-donating substituted groups (eg, Me, NR_2, NHCOR) have been previously studied, and they are believed to be possible replacements for blue anthraquinone colorants with limitations of poor dischargeability and sensitivity to oxides of nitrogen [12–15].

In chemistry research, post-modification is considered as a powerful strategy for implanting and tuning precursors with various architectures and functionalities because of its extensive applications in cyclic functional polymers [16], functionalizing DNA molecules [17], metal-organic frameworks [18], dye sensitized solar cells [19], assembling of oligosaccharides [20] and biosensors [21]. Regard to azo dyes with multifunctional groups, post-modification strategies could be directly applied for further extension when they have at least one terminal functional group. For example, Bello and Griffiths have carried out some studies on the formyl substituted phenyl azo dyes and thiazole based azo dyes, and subsequent introduction of dicyanovinyl groups into the dye backbones in the 1980's and 1990's [4,5,22]. We have first reported a series of 2-amino-4-chloro-5-formylthiophene-3-carbonitrile based blue azo dyes having different aniline couplers, where a terminal aldehyde group is present for every dye molecule [23]. With the purpose of tuning the shade and coloring strength for this family of blue azo dyes, we have introduced the post-modification strategy to explore how post-modification of the terminal aldehyde group affects the performance of these *S*-containing heterocyclic azo dyes.

There have been some reports on azo-azomethine dyes up till now, but most of them are based upon salicylaldehyde derivatives because of their high reaction activity [24–27]. As for studies on aromatic heterocyclic azo-azomethine dyes, only two reports have been found on 3-amino-1,2,4-triazole and 2-formylthiophene involved examples [28,29]. Considering the Schiff bases can be conventionally formed by treating certain amines with our 2-formylthiophene based blue azo dyes, azo-azomethine

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compounds **1**, **2** and **5** have been prepared successfully in this work. On the other hand, the terminated aldehyde groups can be easily reacted with alcohols and cyanoacetic ester to form corresponding acetals and α,β-unsaturated cyanomethylenes, respectively, from the viewpoints of organic functional group transformation. As a result, compounds **3**–**4** and **6**–**9** have been obtained in high yields. It is found that the acetal terminated products display good solubility and hypsochromic shifts in the UV–Vis spectra, and vice versa for azo-azomethine dyes. In contrast, the α,β-unsaturated cyanoacetic ester derivatives show both advantages of good solubility and dramatic bathochromic shifts.

2. Experimental section

2.1. Materials and apparatus

Unless otherwise stated, all reagents of analytical grade were purchased from commercial suppliers and used without any further purification. Two 2-amino-3-carbonitrile-4-chloro-5-formylthiophene based D–π–A heterocyclic azo dyes with different aniline couplers, i.e., (*E*)-2-((4-((4-chloro-3-cyano-5-formylthiophen- 2-yl)diazenyl)phenyl)(2-cyanoethyl)amino)ethyl acetate (**10**) and (*E*)-4-chloro-2-((4-(dimethylamino)phenyl)diazenyl)-5-formylthiophene-3-carbonitrile (**11**), were prepared according to our previously reported procedure [23]. Column chromatography was carried out on silica gel (200–300 mesh). All melting points were measured without corrections. Ultraviolet–Visible (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 at room temperature (25 °C). ^{1}H NMR spectral measurements were performed on a Bruker DMX300 MHz NMR or Bruker DMX400 MHz spectrometer, using chloroform-*d* ($CDCl_3$) as a solvent with tetramethylsilane (TMS) as the internal standard at room temperature (25 °C). Infrared spectra in the region of 4000–500 cm^{-1} were obtained using a Nicolet FT–IR 170X spectrophotometer on KBr disks. Electroionization time-of-flight mass spectra (EI–TOF–MS, electron energy 70 eV) were recorded by mass spectrometer. Elemental analyses (EA) for C, H and N were performed on a Perkin-Elmer 1400C analyzer.

2.2.1. Preparation of compound **1** (2-((4-((E)-(4-chloro-3-cyano-5-((E)-((2,3-dimethylphenyl)imino)methyl)thiophen-2-yl)diazenyl)phenyl)(2-cyanoethyl)amino)ethyl acetate)

Compound **10** (0.43 g, 1.00 mmol) was dissolved in hot acetonitrile (50 mL), and 2,3-dimethylaniline (0.30 g, 2.50 mmol) and 2 drops of acetic acid were added. The mixture was refluxed for 12 h and the solvent was removed by a rotatory evaporator under reduced pressure. The crude solid was subjected to column chromatography on silica gel (ethyl acetate/petroleum ether = 1:1), and compound **1** was obtained as purple powder in a yield of 0.41 g (77%). Mp: 103–105 °C. UV–Vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 550 nm/31300. Main FT–IR absorptions (KBr pellets, ν cm^{-1}): 2916 (w), 2351 (w), 2223 (w), 1740 (m), 1597 (s), 1515 (m), 1309 (m), 1227 (m) and 1140 (vs). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 8.55 (s, 1H), 7.98 (d, J = 9 Hz, 2H), 7.16 (m, 2H), 6.91 (m, 1H), 6.82 (d, J = 9 Hz, 2H), 4.35 (m, 2H), 3.91 (m, 4H), 2.75 (t, J = 6 Hz, 2H), 2.32 (d, J = 3 Hz, 6H) and 2.07 (s, 3H). EI–TOF–MS (*m/z*): Calcd for $[C_{27}H_{25}ClN_6O_2S]^+$: 532.1; Found: 532.0. *Anal.* Calcd. for $C_{27}H_{25}ClN_6O_2S$: C, 60.84; H, 4.73; N, 15.77%. Found: C, 60.68; H, 4.95; N, 15.62%. Single crystals for compound **1** suitable for X–ray diffraction measurement were obtained by slow evaporation of a mixture of CH_3Cl and methanol (v:v = 1:2) in air for one week.

2.2.2. Preparation of compound **2** (2-((4-((E)-(4-chloro-3-cyano-5-((E)-((4-nitrophenyl)imino)methyl)thiophen-2-yl)diazenyl)phenyl)(2-cyanoethyl)amino)ethyl acetate)

The synthetic procedure for compound **2** was analogous to that of described for compound **1** except that *p*-nitroaniline (0.35 g, 2.50 mmol) was used as the starting material to replace 2,3-dimethylaniline. Yield: 0.38 g (70%). Mp: 143–145 °C. UV–Vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 530 nm/38000. Main FT–IR absorptions (KBr pellets, ν cm^{-1}): 3440 (s), 2926 (w), 2361 (w), 2228 (w), 1736 (m), 1597 (s), 1509 (m), 1335 (s) and 1140 (vs). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 8.63 (s, 1H), 8.29 (d, J = 9 Hz, 2H), 7.97 (d, J = 9 Hz, 2H), 7.33 (d, J = 9 Hz, 2H), 6.84 (d, J = 9 Hz, 2H), 4.34 (t, J = 6 Hz, 2H), 3.92 (m, 4H), 2.76 (t, J = 6 Hz, 2H) and 2.07 (s, 3H). EI–TOF–MS (*m/z*): Calcd for $[C_{25}H_{20}ClN_7O_4S]^+$: 549.1; Found: 549.0. *Anal.* Calcd. For $C_{25}H_{20}ClN_7O_4S$: C, 54.60; H, 3.67; N, 17.83%. Found: C, 54.52; H, 3.78; N, 17.69%.

2.2.3. Preparation of compound **3** ((E)-2-((4-((4-chloro-3-cyano-5-(dimethoxymethyl)thiophen-2-yl)diazenyl)phenyl)(2-cyanoethyl)amino)ethyl acetate)

A methanol solution (20 mL) of compound **10** (0.43 g, 1.00 mmol) and acetic acid (2 mL) were mixed and refluxed for 12 h and the solvent was removed by a rotatory evaporator under reduced pressure to get crude solid. The pure violet powder **3** was obtained by recrystallization from $CHCl_3/CH_3OH$ in a yield of 0.27 g (57%). Mp: 167–169 °C. UV–Vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 508 nm/38200. Main FT–IR absorptions (KBr pellets, ν cm^{-1}): 2957 (w), 2357 (w), 2223 (w), 1735 (m), 1596 (s), 1509 (w), 1376 (m), 1309 (m), 1227 (m), 1150 (vs), 1093 (s) and 1043 (s). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 7.93 (d, J = 9 Hz, 2H), 6.80 (d, J = 9 Hz, 2H), 5.64 (s, 1H), 4.32 (t, J = 6 Hz, 2H), 3.89 (m, 4H), 3.41 (s, 6H), 2.73 (t, J = 6 Hz, 2H) and 2.06 (s, 3H). EI–TOF–MS (*m/z*): Calcd for $[C_{21}H_{22}ClN_5O_4S]^+$: 475.1; Found: 475.0. *Anal.* Calcd. for $C_{21}H_{22}ClN_5O_4S$: C, 53.00; H, 4.66; N, 14.71%. Found: C, 55.52; H, 4.98; N, 14.65%.

2.2.4. Preparation of compound **4** (ethyl (E)-3-(5-((E)-(4-((2-acetoxyethyl)(2-cyanoethyl)amino)phenyl)diazenyl)-3-chloro-4-cyanothiophen-2-yl)-2-cyanoacrylate)

Ethyl cyanacetate (0.57 g, 5.00 mmol) was added to a solution of compound **10** (0.43 g, 1.00 mmol) in chloroform (50 mL) at 50 °C, and then two drops of piperidine was added. The reaction mixture was refluxed for 12 h and the solvent was removed by a rotatory evaporator under reduced pressure to get crude solid. Column chromatography was used to purify the crude solid on silica gel (ethyl acetate/petroleum ether = 1:1), and compound **4** was obtained as dark blue powder in a yield of 0.41 g (78%). Mp: 204–206 °C. UV–Vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 598 nm/39100. Main FT–IR absorptions (KBr pellets, ν cm^{-1}): 3445 (m), 2228 (w), 1734 (m), 1601 (s), 1523 (m), 1238 (vs) and 1140 (vs). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 8.49 (s, 1H), 8.04 (d, J = 8 Hz, 2H), 6.86 (d, J = 8 Hz, 2H), 4.44 (m, 2H), 4.37 (t, J = 4 Hz, 2H), 3.94 (m, 4H), 2.79 (t, J = 4 Hz, 2H), 2.08 (s, 3H) and 1.43 (t, J = 8 Hz, 3H). EI–TOF–MS (*m/z*): Calcd for $[C_{24}H_{21}ClN_6O_4S]^+$: 524.1; Found: 524.0. *Anal.* Calcd. for $C_{24}H_{21}ClN_6O_4S$: C, 54.91; H, 4.03; N, 16.01%. Found: C, 54.72; H, 4.26; N, 15.89%.

2.2.5. Preparation of compound **5** (4-chloro-2-((E)-(4-(dimethylamino)phenyl)diazenyl)-5-((E)-((2,3-dimethylphenyl)imino)methyl)thiophene-3-carbonitrile)

The synthetic procedure for compound **5** was analogous to that of described for compound **1** except that compound **11** (0.32 g, 1.00 mmol) was used as the starting material to replace compound **10**. Yield: 0.37 g (87%). Mp: >300 °C. UV–Vis in methanol, $\lambda_{max}/\varepsilon$ ($L\cdot mol^{-1}\cdot cm^{-1}$) = 572 nm/28300. Main FT–IR absorptions (KBr