

Pyridone based binary and ternary monomethine dyes derived from 2-amino-4-chloro-5-formylthiophene-3-carbonitrile



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ABSTRACT

New monomethine dyes have been prepared by a simple and highly efficient method in acetic anhydride, in which the common pyridine-2,6-dione moiety and thiophene derivatives occupy each side of the methine unit. Among them, the ternary monomethine-azo dyes were first obtained by the particularly useful post-modification synthetic strategy, in order to further adjust the π -conjugated system and electronic spectra of 2-amino-3-cyano-4-chloro-5-formylthiophene based heterocyclic hydrazone/azo dyes. UV–Vis spectral analyses reveal that the synthesized heterocyclic dyes exhibit a large color gamut because of the extension of the conjugation length of the chromophore, where the maximum absorption wavelength (λ_{\max}) is significantly red-shifted up to 181 nm from binary monomethine to ternary monomethine-azo dyes.

1. Introduction

In recent years, merocyanine dyes have received increasing research interest due to their multiplicity of uses and applications in fields of biology and medicine [1,2], nonlinear optics and photorefractive materials [3,4], organic solar cells [5] and field-effect transistors [6–8]. It is well known that merocyanine dyes consist of a donor (D) and an acceptor (A) bearing a mono- or polymethine bridge. Because of the delocalization of π -electrons over D, A, and the mono/poly-methine bridge, some of these dyes exhibit brilliant magenta hues which are suited for applications in digital photography and color copying [9].

Post-modification is considered as a powerful tool in synthetic chemistry for implanting and tuning precursors with various architectures and functionalities owing to its versatile applications, for example in metal-organic frameworks [10], assembling of oligosaccharides [11], functionalized DNA molecules [12] and polymers [13]. For example, Tang et al. reported the synthesis of a series of defined 'PDSAs' with high polar functionalities through post-polymerization modification routes in 2015 [14]. As described previously by our group, the post-modification synthetic strategy has been introduced to explore how the post-modified terminal aldehyde group of some S-containing heterocyclic azo dyes affects the shade and color strength of the final products [15,16].

The current work was triggered by the fact that the monomethine pyridone dyes with large molar absorptivities could exhibit brilliant hues [17–19] if suitable heterocyclic moieties are correlated with pyridine-2,6-dione through the monomethine bridge. So 2-amino-4-chloro-5-formylthiophene-3-carbonitrile was first selected to react with pyridine-2,6-dione to prepare four binary monomethine pyridone dyes 1–4. Following the post-modification strategy, four ternary monomethine-azo dyes 9–12 were prepared via the condensation of pyridone with 5-formylthiophene based hydrazone dye (5) and 5-formylthiophene based azo dyes (6–8) (Scheme 1). It is gratifying that the ternary monomethine-azo dyes 9–12, having longer D– π –A structure with the common unmodified pyridine-2,6-dione heterocyclic acceptor, give a continuous shift to longer wavelength up to $\lambda_{\max} = 691$ nm (dye 12) in CHCl₃. Accordingly, the resultant monomethine-azo dyes with extended ternary skeleton are suggested to be good candidates for near-infrared dyes.

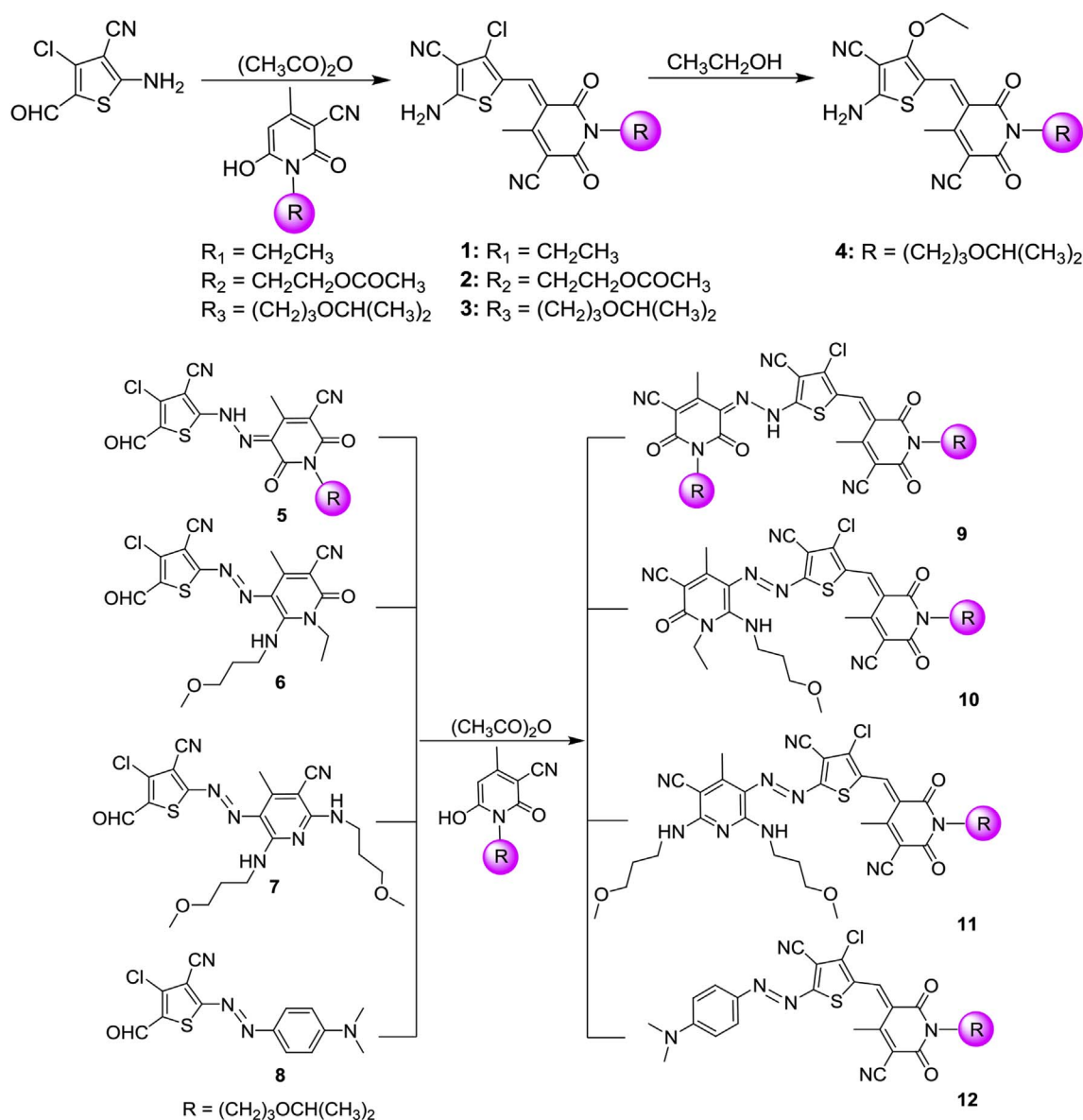
2. Experimental section

2.1. Materials and physical measurements

Analytical grade reagents were purchased from commercial suppliers Aladdin (AR) and Sigma-Aldrich (AR) and used without any

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Scheme 1. Synthetic route of binary and ternary monomethine dyes.

further purification unless otherwise stated. Compounds 5–8 were prepared according to the reported procedure [16,20,21]. 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 cell with a path length of 10 mm at room temperature (25 °C). ^1H NMR spectral measurements were performed on a Bruker DMX400 MHz or Bruker DMX500 MHz NMR spectrometer, using chloroform- d (CDCl_3) and dimethylsulphoxide- d_6 (DMSO) as the solvents at room temperature (25 °C). Infrared spectra in the region of 4000–500 cm^{-1} were obtained using a Nicolet FT-IR 170 \times spectrophotometer on KBr disks. Electrospray ionization mass spectra (ESI-MS) were recorded on a Finnigan MAT S5Q 710 mass spectrometer in a scan range of 50–500, 50–800 or 50–1000 amu. Elemental analyses (EA) for C, H and N were performed on a Perkin-Elmer 1400C analyzer.

2.1.1. Synthesis of dye 1 ((Z)-5-((5-amino-3-chloro-4-cyanothiophen-2-yl)methylene)-1-ethyl-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile)

A mixture of 2-amino-4-chloro-5-formylthiophene-3-carbonitrile

(0.93 g, 5.00 mmol) and 1-ethyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (0.89 g, 5.00 mmol) was dissolved in $(\text{CH}_3\text{CO})_2\text{O}$ (5 mL) and stirred at 90 °C for 2 h. The precipitate was filtered and dried after thorough washing with isopropanol, and the pure product was obtained in a yield of 1.35 g (78%). Mp: > 300 °C. UV-Vis in CHCl_3 , λ_{max} (nm)/ ϵ ($\times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) = 510/4.56. Main FT-IR absorptions (KBr pellets, $\nu \text{ cm}^{-1}$): 3307 (w), 3155 (m), 2222 (m), 1620 (s), 1550 (m), 1449 (vs), 1278 (s) and 1208 (s). ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ = 9.42 (s, 2H), 7.91 (s, 1H), 3.84 (m, 2H), 2.54 (s, 3H) and 1.09 (t, J = 7.0 Hz, 3H). Anal. Calcd. For $\text{C}_{15}\text{H}_{11}\text{ClN}_4\text{O}_2\text{S}$: C, 51.95; H, 3.20; N, 16.16%. Found: C, 51.82; H, 3.12; N, 16.31%. Negative ESI-MS in CH_3CN : m/z = 345.00 (100.0%), $[\text{M} - \text{H}]^-$.

2.1.2. Synthesis of dyes 2 ((Z)-2-(3-((5-amino-3-chloro-4-cyanothiophen-2-yl)methylene)-5-cyano-4-methyl-2,6-dioxo-3,6-dihydropyridin-1(2H)-yl) ethyl acetate) and 3 ((Z)-5-((5-amino-3-chloro-4-cyanothiophen-2-yl)methylene)-1-(3-isopropoxypropyl)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile)

The synthesis of dye 2 was analogous to that described for compound 1 except that 2-(3-cyano-6-hydroxy-4-methyl-2-oxopyridin-1(2H)-yl)ethyl acetate (1.18 g, 5.00 mmol) was used as the starting

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