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# The Synthesis and Characterisation of Thiol-Bearing C. I. Disperse Red 1

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## Abstract

C. I. Disperse Red 1 (DR1) was chemically modified by a facile, one-step, Steglich esterification to yield the thiol-bearing analogue. The dye produced possesses the appropriate functionality to be readily incorporated into appropriate materials by highly effective thiol-ene ‘click’ chemistry reactions. This method of dye modification greatly widens the application range of hydroxyl-bearing reactive dyes for various materials, enabling the facile production of coloured materials by using the thiol groups added.

## 1. Introduction

The covalent incorporation of dye molecules into the molecular structure of materials offers an effective method to impart a desired colour to the particular substrate. Forming a covalent bond between the colourant and a substrate improves the stability of the dye molecules, and has been utilised for the permanent binding of reactive dyes that possess reactive groups including a 1, 3, 5-triazine ring with at least one chlorine substituent [1] and vinylsulfone [2]. These reactive groups can react with nucleophilic groups present on natural and synthetic fibres, for example the hydroxyl groups on cellulose fibre, to form covalent bonds. Contemporary examples of the covalent conjugation of dye molecules to various substrates include the conjugation of a ruthenium-based dye to zinc oxide nanoparticles for use as a dye-sensitised solar cell [3]. The strong covalent bond formed enables the dyes to be homogeneously distributed on substrates, preventing dye diffusion and segregation, while enabling the substrates to remain stable. Producing materials that contain covalently-bound dye molecules in a cost-effective manner, with minimal side products generated,

therefore remains a significant challenge, both commercially and environmentally.

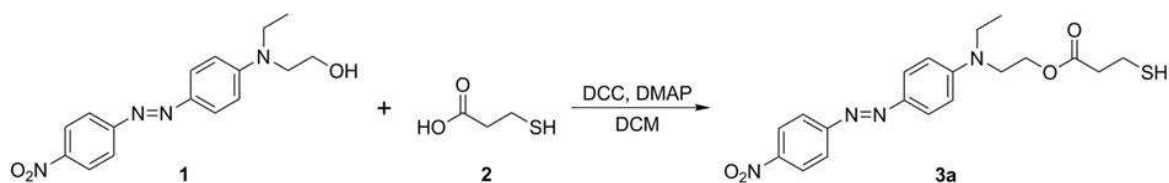
The reaction between a thiol group and an alkene is termed a 'thiol-ene' click (TEC) reaction [4, 5], and is one of the 'click' chemistry reactions that are defined by proceeding with high efficiency, versatility, and selectivity [6]. The unique reaction mechanism by which the thiol (SH) group and carbon-carbon double bond (C=C) combine with each other, in the presence of UV light or heat, has many attractive features such as a simple reaction mechanism to produce product at high yield, no hindrance by oxygen or water, and a lack of undesirable side products. Furthermore, the reaction is unproblematic to execute under standard laboratory conditions. Consequently, thiol-ene reactions are widely used for the production of crosslinked systems, and for the functionalisation of biomaterials [5]. Thiol-functionalised dyes offer a chromophore that may be covalently bound to a substrate by chemically simplistic thiol-ene reactions. Thiol-containing dyes themselves are used for dyeing polyester fibre or hairs, and employed within dye-sensitised solar cells [3]. Consequently, a chemically-simplistic and cost-effective method that reproducibly produces thiol-containing commercial dyes at high yield is highly desirable. The dye with thiol functionality may be readily incorporated into materials containing (C=C) groups by highly effective TEC reactions, enhancing the prospect of efficient dye conjugation to an appropriate substrate. One application example is to incorporate the dyes into plant oils [7], enabling the production of highly durable coating materials.

In this paper we describe a chemically-simplistic and cost-effective method to create thiol-bearing C. I. Disperse Red 1 (DR1) to extremely high reproducibility. DR1 was selected as the dye to be investigated as it is a commercially-important dye molecule that possesses one reactive aliphatic alcohol (OH) group within its structure. This OH group can be converted into other functional groups such as alkoxy silane [8] depending on the materials the dye is intended to be incorporated within. Interestingly, DR1 exhibits a second-order nonlinear optical (NLO) effect, and has photoresponsive properties based on light-induced trans-cis isomerisation [9]. The research acts as a template for the covalent coupling of small thiol-containing molecules to the hydroxyl functional group that exists within many dye molecules, and consequently may be exploited for the creation of thiol-containing dye molecules. Optimum reaction conditions were found for the production of a dye molecule that is an excellent candidate for the dye modification of substrates by facile TEC reactions.

## 2. Results and Discussion

### 2.1 Synthesis of Thiol-Bearing DR1

DR 1 (**1**) and 3-mercaptopropionic acid (**2**) were reacted by a Steglich esterification [10] (Scheme 1). To determine the conditions required to produce thiol-bearing DR1 to an optimal yield, the amounts of the starting materials, the reaction temperatures, and the reaction times were varied, and the product yields for each reaction determined (See Supplementary Information). The reaction conditions employed, and the results obtained from the performed reactions are shown in Table 1. Analysis of the reaction products by thin layer chromatography (TLC) revealed four clear spots other than the spot due to **1** on the TLC plate, in all cases. Among these four spots, the first and the second spots were more distinctive than the other spots and corresponded to products that possess lower polarity compared to **1**. Considering the addition of **2** decreases the polarity of **1**, the first product was considered to be **3a**, and the second product (**3b**) was considered to have the structure of a second molecule of **2** combined with **3a** through a thioester bond (Fig. SI 2). We separated these two compounds and their chemical structures were confirmed by FT-IR, <sup>1</sup>H NMR, mass spectrometry, and elemental analysis (Figures SI 1 and SI 2). Finally, the optimal reaction conditions were found to be those employed in reaction No. 6 where a 59.0% yield was obtained for the production of **3a**, and a 16.7% yield for **3b**.



**Scheme 1** Synthesis of thiol-bearing DR1.

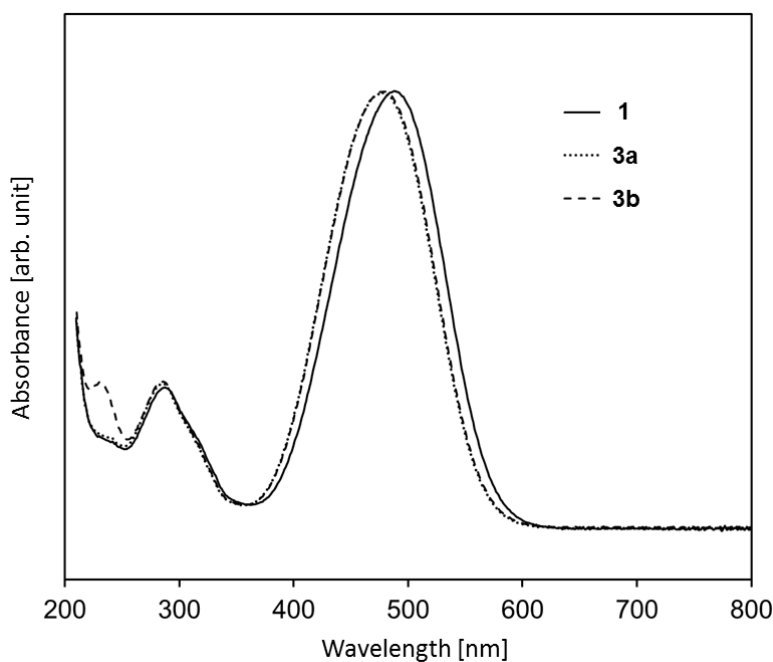
**Table 1** The reaction conditions and isolated yields of thiol-bearing dyes.

| No. | Molar ratio [eq.] | Temperature [°C] | Reaction Time [hour] | Isolated yield [%] |           |
|-----|-------------------|------------------|----------------------|--------------------|-----------|
|     |                   |                  |                      | <b>3a</b>          | <b>3b</b> |
|     | <b>1/2/DCC</b>    |                  |                      |                    |           |
| 1   | 1.0/0.9/1.1       | r. t.            | 2                    | 8.1                | 7.1       |
| 2   | 1.0/0.9/1.1       | r. t.            | 24                   | 7.4                | 6.1       |
| 3   | 1.0/3.0/3.0       | r. t.            | 2                    | 20.6               | 11.0      |
| 4   | 1.0/3.0/3.0       | 0                | 2                    | 32.3               | 12.4      |
| 5   | 1.0/5.0/5.0       | r. t.            | 2                    | 39.1               | 10.6      |
| 6   | 1.0/5.0/5.0       | 0                | 2                    | 59.0               | 16.7      |
| 7   | 1.0/5.0/5.0       | 0                | 3                    | 58.2               | 20.0      |

The amount of DMAP used was constant (0.01 eq.) in each case.

## 2.2 UV-Visible Spectroscopy

The UV-visible spectra of **1**, **3a** and **3b** in acetonitrile are shown in Fig. 1. The unmodified dye **1** has a maximum absorption at 488 nm, while **3a** and **3b** have a maximum absorption at 477 nm and 480 nm, respectively. These hypsochromic shifts in both **3a** and **3b** were also observed in previous research [8] and can be explained by the introduction of the chemical bond (-O-C=O) decreasing the electron-donating ability of the a donor unit [-N(CH<sub>2</sub>CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>OH)], while **1** has an acceptor unit (-NO<sub>2</sub>) at separated positions, decreasing the HOMO level of the dyes. As a result, the resonance absorption peak of both **3a** and **3b** shift to lower region.

**Fig. 1** UV-visible absorption spectra of **1**, **3a** and **3b**.

### 3. Conclusions

Thiol functionality was afforded to commercially available DR1 by the covalent conjugation of a small thiol-containing molecule (3-mercaptopropionic acid) to DR1 via one-step Steglich esterification. Reaction optimisation produced thiol-bearing dyes to relatively high yields. Although the side reaction of thioester formation was observed, each product obtained possessed both the chromophore and a thiol group, dictating that they can be utilised for colouration of substrates that possess C=C bonds via TEC reactions, thus enhancing the application range of conventional reactive dyes [7]. Furthermore, the thiol-modification method is applicable to other dyes which have aliphatic OH groups in their structures.

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