Dyes and Pigments 115 (2015) 96–101

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Characterisation of a series of triarylmethane dyes as light harvesters for photo-electrochemical systems

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ARTICLE INFO

Article history:
Received 17 October 2014
Received in revised form
28 November 2014
Accepted 16 December 2014
Available online 24 December 2014

Keywords:
Triarylmethane dye
Characterization
Electrochemistry
Computational chemistry
Optical spectroscopy
Commercial dyes

ABSTRACT

A series of commercially available dyes were characterised by electrochemical, spectroscopic and computational methods. Several dyes, including Fuchsin Basic and Malachite Green were found to have properties that make them potential candidates for use in photo-electrochemical systems. The risks of combining different characterisation methods are also highlighted, namely the combination of thermodynamic reactions (electrochemical redox reactions), electronic transitions (optical spectroscopy) and the use of computational techniques to describe them.

1. Introduction

The role of dyes as a functional component in electrochemical systems is a rapidly expanding field of which dye sensitised solar cells (DSSC) is perhaps the most prominent example [1–4]. Many of these devices utilise metal-based dyes that require expensive or toxic rare-earth elements [5], or custom synthesis of donor-acceptor type organic dyes [6], There are however, several low cost and commercially available dye families – such as those based on the *azo* and triarylmethane functionalities – that may show potential in these applications, many of which are non-toxic and produced annually on a large industrial scale [7,8].

Of particular interest to our research is the use of dyes in electrochemical systems as light harvesters [9], catalysts [10], and as substrate materials [11,12]. These applications take advantage of the inherent ability of the dye to absorb light and its electrochemical properties in order to create a photosensitive system. For the efficient design of a device it is thus imperative for a proper characterisation of both the photo- and electro-chemical properties [13–15].

We here investigate a series of triarylmethane dyes (Fig. 1) that are used as staining agents in microscopy (**1c**), pH indicators (**4a, 4b**), anti-microbial agents (**2a, 2b**) as well as for colouring (**1b**) [16–18]. More importantly, triaryl dyes are known to be compatible with intrinsically conducting polymers [19], and present unique opportunities for developing novel organic dye sensitised systems. Yet, despite their advantages and commercial availability, the use of triaryl dyes as low-cost light harvesters in photo-electrochemical systems has thus far been limited.

To analyse these dyes, we explore several methods of characterisation. One of the most common is the use of cyclic voltammetry (CV) for the determination of the reduction (E_{red}) and oxidation (E_{ox}) potentials [20,21]. This method allows for the determination of the absolute energy levels, as opposed to relative energy levels, and is important in the understanding of the overall electron flow in the system. Another common technique is the combination of UV–Vis and fluorescence spectroscopy to identify the optical electronic transition energy (ΔE_{opt}) between the HOMO and LUMO energy levels [22,23]. Supplemented by CV data, ΔE_{opt} can be used to approximate the gap between reduction and oxidation potentials [24,25]. Additionally, computational methods are used to predict thermodynamic reduction and oxidation potentials. This last technique offers the possibility of exploring the properties of arbitrary dye structures, but requires a precise knowledge of the structures of the reactants and products. Here we are inspired by the DFT-based method of Speelman et al. [26,27] which are computationally affordable even in cases where access to high performance computing facilities is limited.

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http://dx.doi.org/10.1016/j.dyepig.2014.12.016
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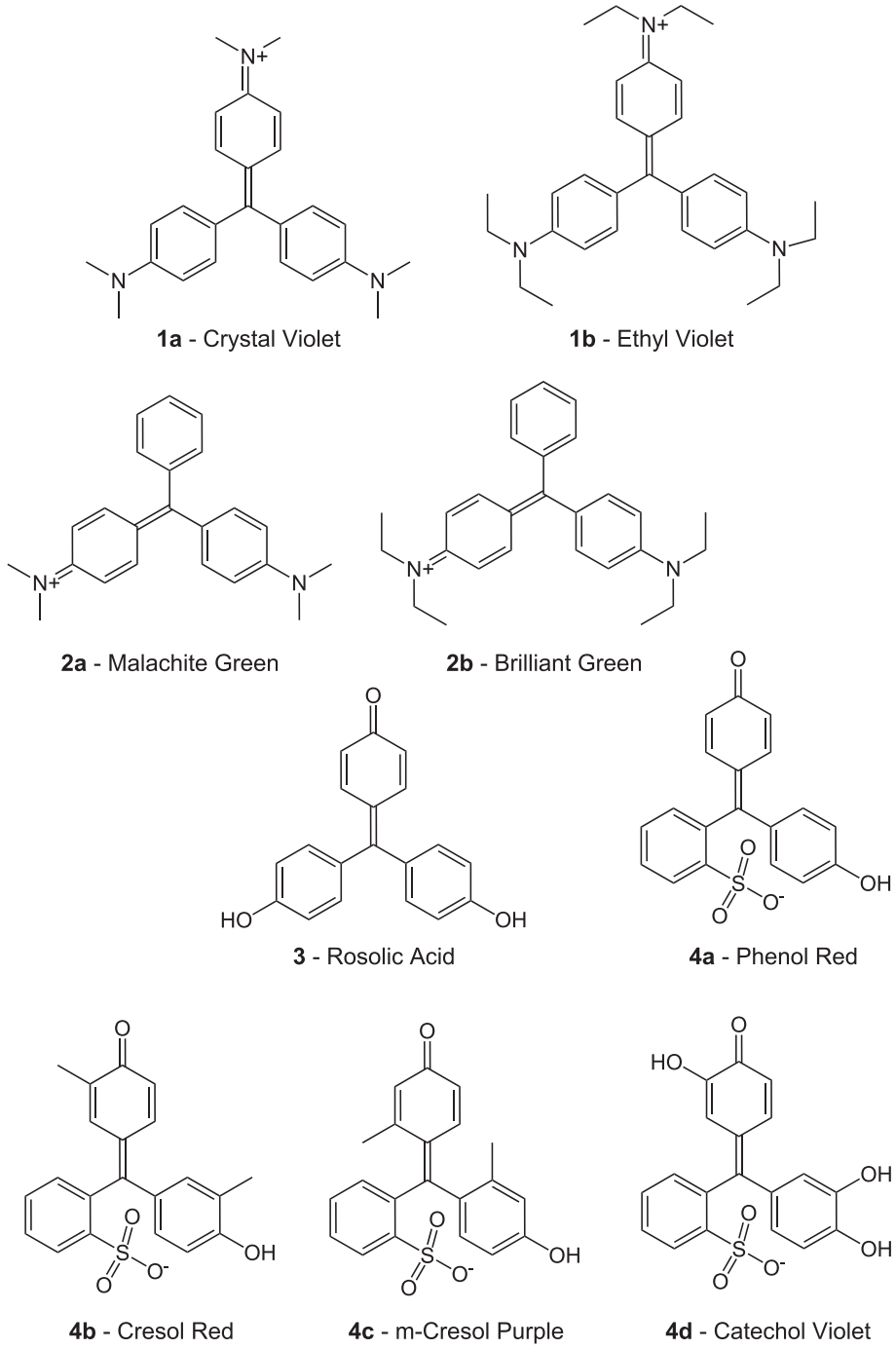

Fig. 1. Structures of the triarylmethane dyes in this study. Sub-groups 1 and 2 contain the nitrogen-based dyes: **1a**, **1b** for tri-amine dyes, **2a** and **2b** for di-amine dyes. Sub-groups 3–5 contain the oxygen based dyes which include the phenol type dyes **3** and the sulfonphthalein dyes **4a**, **4b**, **4c** and **4d**.

Importantly, by comparison and analysis of the varying techniques, the inherent short-comings of common literature methodologies are brought to light. These include, though is not limited to, the interchanging of the optically and electrochemically determined band gaps and the corresponding HOMO and LUMO energies. As this study and past studies support [28,29], significant deviations may result from its casual use.

2. Materials and methods

Ethyl Violet (**1b**), Malachite Green (**2a**), Brilliant Green (**2b**), p-Rosolic Acid (**3**), ferrocene (Fc) and tetrabutylammonium hexafluorophosphate ([TBA][PF_6]) were obtained from Sigma Aldrich. Crystal Violet (**1a**), Cresol Red (**4b**) and Catechol Violet (**4d**) were obtained from the British Drug House, m-Cresol Purple (**4c**) from May & Baker, and Phenol Red (**4a**) from Fluka AG. Anhydrous acetonitrile from Sigma Aldrich was dried over freshly prepared 4 Å molecular sieves and stored in a nitrogen atmosphere. All other chemicals were used as received and verified using UV–Vis spectroscopy and mass spectroscopy, see ESI† (Table S1 and Figures S19–S27). The dye structures are shown in Fig. 1.

Dye solutions were prepared under a nitrogen atmosphere in a glove box using oven-dried (70 °C, 30 min) reagents. All dye