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



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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

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.

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(**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 $\left(E_{red}\right)$ and oxidation (Eox) 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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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 sulforphthalein 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][PF₆]) 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 $^{\circ}$ C, 30 min) reagents. All dye

solutions were made to a concentration of 0.5 mmol L^{-1} in acetonitrile with 50 mmol L^{-1} [TBA][PF6] as the supporting electrolyte.

Cyclic voltammetry was performed using a high surface area titanium mesh [30,31] as the counter electrode and platinum wire as both reference and working electrodes. Data was acquired under a nitrogen atmosphere in a glove box at a scan rate of 20 mV s⁻¹. A ferrocene/ferrocenium (Fc/Fc⁺) couple was used as an internal reference. [32].

The solutions used in the electrochemical study were then further diluted in acetonitrile to a concentration of 30 µmol L⁻¹ and used for UV–Vis spectroscopy. Spectra were acquired between 190 and 1000 nm using quartz cuvettes. The wavelength of the maximum absorption in the visible region was assigned $\lambda_{abs.}$ Fluorescence spectra of 10 µmol L⁻¹ dye solutions in acetonitrile were acquired using $\lambda_{abs.}$ as the excitation wavelength and the resulting emission peak recorded as λ_{em} . For particularly noisy or low fluorescing dyes, the concentration was gradually increased from 10 µmol L⁻¹ until a clear fluorescence emission peak λ_{em} was obtained.

Thermodynamic cycles were used to calculate the free energy changes for the oxidation and reduction of the ground state; where oxidised and reduced state were defined as the removal and addition of an electron from the ground state respectively. Calculations were done using a similar level of theory as was used by Speelman et al., see ESI[†] for further details. Briefly, the geometry of all species were optimised at the B3LYP/6-31 + G* [33–40] level of Kohn-Sham density functional theory while solvent effects were approximated using the COnductor-like Screening Model [41,42] (COSMO) with a solvent radius of 2.16 Å and dielectric constant of 36.64. Enthalpy and entropy values were determined via vibrational calculations on the optimised structure. Thermodynamic parameters from these normal mode analyses were used to calculate the reduction and oxidation potentials using a thermochemical cycle. The tabulated computational data can be found in the ESI⁺, Table S2. All computations were carried out using NWChem 6.4 [43], and managed by ECCE 7.0 [44].

The electrochemical, spectroscopic and computational data are tabulated in Table 1. Full cyclic voltammograms of the dyes before and after the addition of Fc/Fc⁺ (Figures S1–S9) and optical spectra (Figures S10–S18) are available in the ESI[†]. All dyes, owing to their similar chemical structures, showed reduction, oxidation and optical activity in similar ranges.

3. Results and discussion

3.1. Electrochemical characterisation

There were a few principal challenges in characterising some of the dyes by cyclic voltammetry. These included weak redox reactions that led to broad or indistinct peaks (see Fig. 2B) as well as the presence of multiple redox processes which made it difficult to assign peaks to a specific process. Furthermore, some of the redox processes were irreversible and prevented the calculation of $E_{1/2}$. In these cases, E_{ox} and E_{red} were defined as the potential corresponding to the oxidation and reduction peak respectively (E_{peak}). As the peak potential is an overestimation of $E_{1/2}$, an empirically determined correction factor of 0.3 V has been included for positions determined using E_{peak} and can be observed in Fig. 4C. Typically, nitrogen based dyes such as Ethyl Violet 1b, showed strong reversible redox processes (Fig. 2A) while oxygen based dyes such as Cresol Red 4b (Fig. 2B) were more problematic and exhibited many of the aforementioned issues

3.2. Optical spectroscopy characterisation

The combination of UV–Vis and fluorescence spectra was used to calculate ΔE_{opt} (Fig. 3) [28,45,46]. ΔE_{opt} was determined as the lowest energy intersect (λ_{int}) of the emission/excitation spectra. The variability in concentration between absorbance and fluorescence is assumed to affect λ_{int} with an empirically approximated symmetrical error of 0.04 eV.

3.3. Computational results

Computationally derived oxidation and reduction potentials were in most cases of the same order of magnitude as the experimentally derived electrochemical data (Fig. 4). This is particularly satisfying given that a relatively small basis set had to be used to yield manageable computational times owing to the large size of the organic molecules in this study. The large size of the dyes also rules out the use of more accurate post-Hartree-Fock methods *e.g.* Moeller-Plesset perturbation theory or coupled-cluster approaches. A significant weakness was also the inherent poor accuracy of implicit solvation models, which precludes the attainment of chemical accuracy.

Fable 1	
Tabulated data from electrochemical, computational and spectroscopic experiments.	

Dye	Cyclic voltammetry			Computational (B3LYP/6-31 + G*)			Optical spectroscopy			
	$E_{ox} (eV)^{a}$	$E_{red} (eV)^a$	$\Delta E_{CV} (eV)^{b}$	E _{ox} (eV) ^c	$E_{red} (eV)^{c}$	$\Delta E_{calc} (eV)$	$\lambda_{abs} \ (nm)^d$	λ _{em} (nm) ^e	$\lambda_{int} (nm)$	$\Delta E_{opt} \left(eV \right)^{f}$
1a	-5.70	-3.79	1.91	-5.42	-3.35	2.07	588	638	612	2.03
1b	-5.67	-3.78	1.88	-5.64	-3.35	2.28	592	639	616	2.02
2a	-5.66	-4.04	1.61	-5.68	-3.63	2.05	618	669	643	1.93
2b	-5.65	-4.06	1.60	-5.78	-3.62	2.16	626	678	648	1.92
3	-5.53	-4.01	1.51	-5.64	-3.16	2.47	420	547	500	2.48
4a	-5.63	-4.14	1.49	-6.89	-3.87	3.02	390	516	461	2.69
4b	-5.53	-4.07	1.46	-5.00	-2.84	2.16	394	553	465	2.67
4c	-5.56	-4.19	1.37	-5.48	-3.13	2.35	388	534	461	2.69
4d	-6.08	-4 18	1.90	-5.75	-3 56	219	420	544	472	2.63

^a Assigned as the first clearly identifiable redox couple ($E_{1/2}$) on the respective oxidation and reduction sides. Converted to absolute energies by the relationship: eV = $E_{Fc/Fc}^+ - E_{ox/red}$, where $E_{Fc/Fc}^+ = -4.988$ eV [53].

^b The difference between E_{ox} and E_{red} .

 c ΔG is obtained from the calculations and converted to a potential ($E_{ox/red}$) via the relationship: $\Delta G = -nFE$, full details in ESI[†].

 $^{d}~\lambda_{\text{max}}$ from UV–Vis absorbance spectrum.

 e λ_{max} from fluorescence emission spectrum.

^f The intersect between the UV–Vis and fluorescence spectra.



Fig. 2. Cyclic voltammograms of 0.5 mmol L^{-1} solutions of Ethyl violet (**A**) and Cresol Red (**B**) in acetonitrile with 50 mmol L^{-1} [TBA][PF₆] at a scan rate of 20 mV/s. Computed reduction and oxidation potentials are indicated in blue and red, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Normalised UV–Vis absorbance (black) and fluorescence emission (red) spectra of Ethyl Violet in acetonitrile (30 μ M and 10 μ M, respectively). The $\lambda_{intersect}$ that corresponds to ΔE_{opt} is shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. Comparison between characterisation techniques

There was overall poor correlation between either the electrochemical and spectroscopic data, or the electrochemical and computational data. A detailed analysis shows that while the computational method quite accurately predicts the oxidation potential for some dyes, and fails spectacularly for others, it systematically overestimates the reduction potential, leading to the overall poor correlation between ΔE_{CV} and ΔE_{calc} (Fig. 4B). There were some notable exceptions, however, and these include Ethyl Violet and other members of the nitrogen based dyes (dyes **1a-b** and **2a-b**) which underwent reversible redox reactions. In either case the magnitude of non-systematic errors and the limited data range precluded the establishment of a simple linear correlation between the computed and experimentally determined data such as that described by Speelman et al. to better link computational and experimental data.

The qualitative correlation between the computational (ΔE_{calc}) and spectroscopic (ΔE_{opt}) data was somewhat better. According to the Franck-Condon principle, optical excitation is rapid and generally not accompanied by structural or chemical changes and instead constitutes a vertical electronic excitation. This was an implicit assumption present in the computational method - in that no chemical changes were accounted for - and may explain the relatively good correlation between ΔE_{calc} and ΔE_{opt} (Fig. 4A). However, this isn't necessarily the case for thermodynamic processes such as electrochemical reduction and oxidation where the species can undergo subsequent reactions, ranging from protonation/deprotonation and reorganisation [47-49]. The generally poor agreement between ΔE_{opt} and ΔE_{CV} (Fig. 4D) and much better agreement between ΔE_{opt} and ΔE_{calc} suggests that most of the dyes undergo at least some structural rearrangement. This is further supported by the observation where dyes that underwent reversible redox processes and exhibited clear redox waves -e.g.nitrogen based dyes - showed a closer agreement between the different methods. The reversibility indicates that they underwent minimal rearrangement, while dyes that were irreversibly reduced or oxidised, or showed diffuse peaks in the CV spectrum - such as the oxygen based dyes - showed a much poorer agreement, most likely due to redox induced structural and chemical changes. These irreversible processes strongly indicate that they can no longer be represented by a simple single electron addition/removal from the conjugated π system as is done in the computational method, and similarly, are not suitable targets for optical spectroscopy approximations that rely on vertical HOMO-LUMO transitions.

This is an important point to note due to the prevalence in the current literature that makes use of such approximations i.e., the determination of the LUMO (reduction) position by the addition of an optically determined band gap to an electrochemically determined HOMO (oxidation) level [50–52]. While the simplicity of this process is attractive, the present work is a strong reminder that not all species conform to this approximation; in particular, species that undergo conformational or chemical changes (*i.e.* pH dependent species). The lack of structural relaxation in the case of electronic transitions, as determined by the optical methods, means that these methods should yield a larger ΔE than the electrochemical method, which is a thermodynamic process.

Though the combination of optical and electrochemical methods is not empirically incorrect, it is important to be aware of the fundamental issues associated with combining a slow thermodynamic process (redox reactions) with a rapid electronic process (optical transitions) without proper consideration of the system.



Fig. 4. Comparison between the different data sets. Values that lie on or close to the dotted line is indicative of good correlation between the methods.

4. Conclusions

We have compared electrochemical, spectroscopic and computational techniques as probes for the selection of triarylmethane dyes as low-cost light harvesters in electrochemical systems. We find that while there is some correlation between the methods for narrow classes of dyes, overall neither the optical or computational methods can predict the suitability of a dye for inclusion in photo-electrochemical devices as they do not reflect the presence of irreversible redox processes, nor do they provide a good quantitative indication of where these processes will occur.

The nitrogen based dyes (**1a-b**, **2a-b**) showed promising features such as redox reversibility and strong light absorbance making them potential candidates for inclusion in photo-electrochemical systems. In contrast, the oxygen based dyes (**3**, **4a-d**) revealed chemically unstable redox states and weak light absorption and as such, are unlikely candidates for light harvesters. However, these characteristics may lend themselves to applications as sensors.

Because the correlation between the different methods explored was low, the findings highlight the potential issues with characterisation methods currently employed for functional dyes: restricting the characterisation to a single or partial method is insufficient in providing a full and accurate picture of the dye's behaviour in photo-electrochemical systems.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2014.12.016.

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