

Two Stage Colour Modulation of Triarylmethine Dyes Derived from a Photochromic Naphthopyran

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Dedicated to Professor John D. Hepworth on the occasion of his 70th birthday

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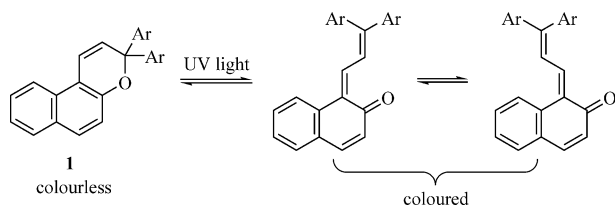
The synthesis of the unsymmetrical triarylmethine dyes **4** derived from a lithiated naphthopyran and diaryl ketones is reported. In toluene solution **4** display a typical reversible photochromic response becoming coloured upon irradiation with UV light and fading upon cessation of irradiation. At low pH an intensely coloured dye cation is generated and

UV irradiation of this solution results in a further colour change as a consequence of photochromic cycling of the naphthopyran unit.

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Introduction

The phenomenon of photochromism is well documented.^[1] One class of organic photochromes that has attracted considerable attention over the last decade are the naphthopyrans, e.g. 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyran (**1**), which exhibit photochromism through a reversible electrocyclic ring-opening–ring-closing sequence (Scheme 1).^[2]



Scheme 1. Photochromic response of a 3*H*-naphtho[2,1-*b*]pyran.

Current interest in naphthopyrans has focussed on the mechanism of colour generation,^[3] spectroscopic characterisation of the coloured species^[4] and control over the hue and persistence of the photo-generated colour.^[5] The influence of the matrix,^[6] metal-ion concentration,^[7] solvent polarity^[8] and pH^[9] on the photochromism of variously substituted naphthopyrans has also been reported. Additionally, linking of two photochromic naphthopyrans together^[10] or linking a naphthopyran with a spiro[indoline-

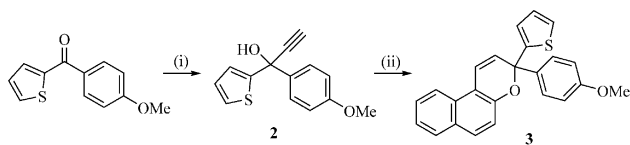
naphthoxazine]^[11] has been investigated. However, the union of a naphthopyran to a traditional dye chromophore has, to the best of our knowledge, not been studied. In this report we describe our initial investigations on the synthesis and spectroscopic properties of some 3*H*-naphtho[2,1-*b*]pyrans that contain a triarylmethanol unit.

Results and Discussion

A variety of triarylmethine dyes have been conveniently accessed by the addition of an aryllithium or -magnesium reagent, derived from an aryl iodide or bromide, to a benzophenone.^[12] Furthermore, a lithiated heterocycle, obtained by a facile heteroatom-directed lithiation sequence, has been reacted with a benzophenone to obtain heteroaryl diarylmethine dyes.^[13] Adopting this latter simple methodology requires access to a naphthopyran containing a suitable heterocyclic moiety. The 3,3-diaryl-3*H*-naphtho[2,1-*b*]pyrans can be obtained with a wide variety of substituents in the *geminal* aryl units through the acid-catalysed reaction between 2-naphthol and a 1,1-diarylprop-2-yn-1-ol.^[2,14] This procedure is also appropriate for the synthesis of 3-aryl-3-heteroaryl-substituted naphthopyrans.^[15,16] Thus heating 2-naphthol with 1-(4-methoxyphenyl)-1-(2-thienyl)-prop-2-yn-1-ol (**2**), derived from the addition of lithium trimethylsilylacetate to 2-(4-methoxybenzoyl)thiophene with subsequent base-promoted unmasking of the terminal acetylene function, gave the naphthopyran **3** in 65% yield after recrystallisation from a mixture of EtOAc and hexane (Scheme 2). The ¹H NMR spectrum of **3** displayed the typical doublet for 2-H at ca. δ = 6.2 ppm with J = 9.9 Hz and a low field doublet at δ = 7.9 for 10-H.^[15]

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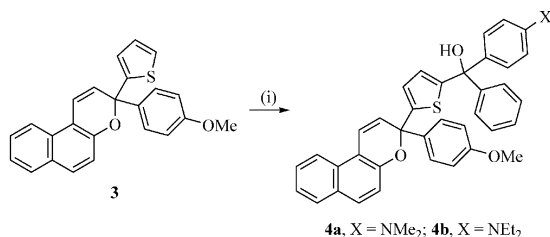
Supporting information for this article is available on the WWW under <http://www.eurjoc.org> or from the author.



Reagents and conditions: (i) TMS-acetylene, *n*-BuLi, anhyd. THF, N₂, –78 °C to r.t. then KOH, MeOH 0 °C to r.t.; (ii) 2-naphthol, PhMe, acidic alumina, reflux.

Scheme 2. Preparation of 3*H*-naphtho[2,1-*b*]pyran **3**.

The heteroatom-directed lithiation of **3** with *n*-butyllithium in THF under N₂ at –78 °C for 1 h followed by quenching the mixture with 4-(dimethylamino)benzophenone resulted in a clean reaction mixture after aqueous work-up that contained a new product (TLC) together with unreacted **3** and the benzophenone (Scheme 3). Column chromatography (50% EtOAc in hexane) gave the triaryl-methanol **4a** in 50% yield.^[17] The ¹H NMR spectrum of **4a** displayed the expected doublet for 2-H at δ = 6.24 ppm (J = 9.9 Hz) and a singlet at δ = 2.79 attributed to the hydroxy proton. The thiophene ring protons appeared as an AB system with a doublet at δ = 6.50 and at δ = 6.70 with J = 3.7 Hz, the magnitude of this coupling constant is typical for $J_{3,4}$ of a 2,5-disubstituted thiophene ring.^[18] Repeating the low temperature metallation protocol provided access to **4b** from 4-(diethylamino)benzophenone in 31% yield^[19] (Scheme 3). Interestingly, compounds **4a,b** were formed as a mixture of diastereoisomers indicated by the presence of an additional doublet at ca. δ = 6.70 ppm. Recording the ¹H NMR spectrum of **4b** in [D₆]benzene enabled additional signals for the diastereoisomers to be observed.



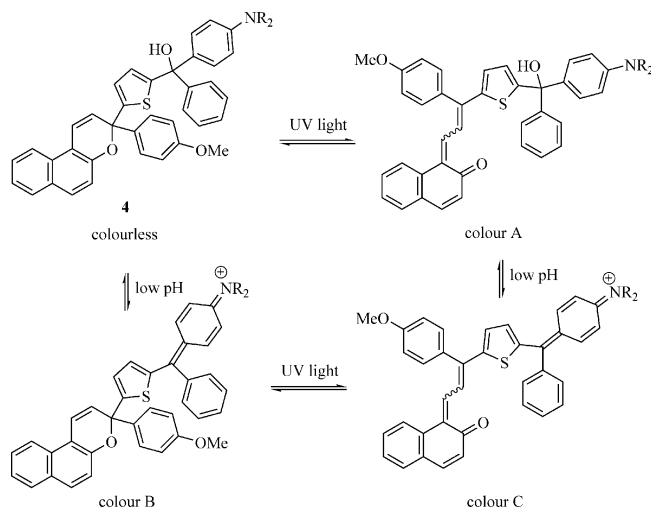
Reagents and conditions: (i) *n*-BuLi, anhyd. THF, N₂, –78 °C then diaryl ketone, –78 °C to r.t.

Scheme 3. Preparation of 3*H*-naphtho[2,1-*b*]pyrans **4**.

It is noteworthy that initial attempts to obtain an accurate mass determination of **4** by electron impact HRMS were inconclusive. However, more extensive investigation using softer ionising techniques (MALDI and electrospray) revealed the expected molecular ions. The low intensity of the ion in electrospray ionisation confirms the labile nature of **4** arising from the resonance stabilisation of the cation by the dialkylaminophenyl group.

The photophysical properties of **3** and **4** merit some comment. With the exception of precursor **3** the naphthopyrans are expected to exhibit both photochromism, under irradiation with UV light, due to reversible pyran ring-opening and also display absorption properties typical of a triaryl-methine unit when dissolved in an acidic medium (low pH). Perhaps of greatest interest are the spectroscopic properties

of these compounds in an acidic medium under UV irradiation where combined behaviour may be expected. Scheme 4 depicts the structural and colour changes that the molecules are predicted to undergo upon UV irradiation in neutral (toluene) and acidic solutions.



Scheme 4. Structural reorganisations of 3*H*-naphtho[2,1-*b*]pyrans **4** under UV irradiation and at low pH.

The photochromic response of toluene solutions of **3** and the series of diarylmethanol-substituted compounds **4** were recorded. Irradiation with UV light (365 nm, 8 Watt) to a steady state effected the ring-opening of the original colourless naphthopyran unit in each case to generate the orange-red coloured species which upon cessation of irradiation readily reverted to their original colourless state (Figure 1). From these data (Table 1) it is evident that the incorporation of the diarylmethanol unit induces an approximately 12 nm bathochromic shift in λ_{max} of these compounds with **4** absorbing at ca. 486 nm and **3** at 474 nm. Similar reversible photochromic behaviour was noted for acetone solutions of **3** and **4**.

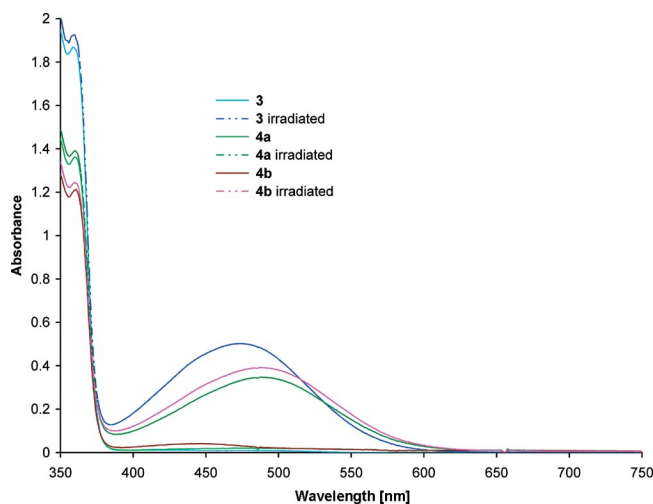
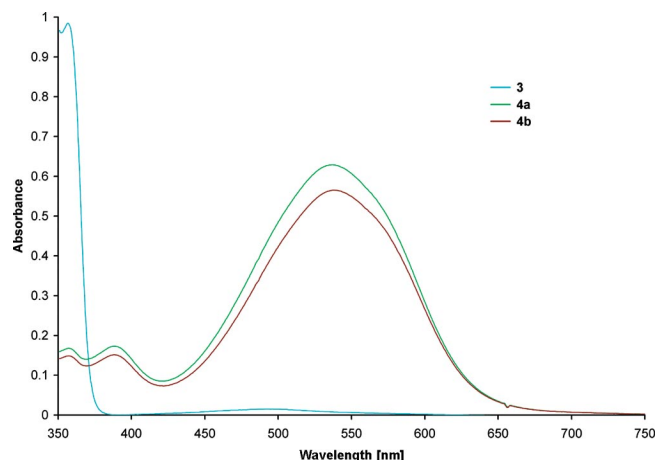


Figure 1. Visible spectra of the photochromic dyes **3** and **4** in PhMe recorded prior to and immediately after UV irradiation.

Table 1. Spectroscopic data for naphthopyrans **3** and **4** for solutions at room temperature.

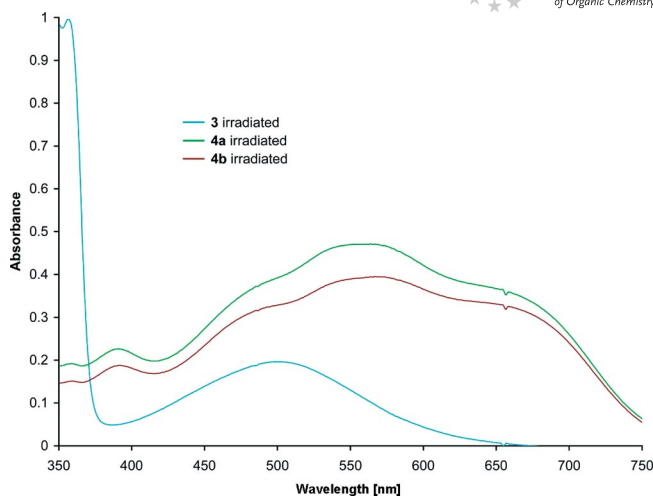
	AcOH (no UV)		AcOH (with UV)	PhMe (with UV)
	$\lambda_{\max}$ [nm]	$\epsilon_{\max}$ [mol ⁻¹ dm ³ cm ⁻¹]	$\lambda_{\max}$ [nm]	$\lambda_{\max}$ [nm]
3	—	—	500	474
4a	536	41100	564 (br)	486
4b	538	42900	566 (br)	485

The colour properties of the cationic dyes derived by protonation and facile elimination of water from **4** were next studied. In accord with traditional $\lambda_{\max}$ measurements of triarylmethine dyes^[12] solutions of **3** and **4a, b** in 98% aqueous acetic acid were examined (Table 1). The spectra of the photochromic dyes **3** and **4** are presented in Figure 2. The dyes **4** afford an intensely coloured cation with $\lambda_{\max}$ ca. 537 nm and extinction coefficients of ca. 41000 mol⁻¹ dm³ cm⁻¹ whereas **3** remains essentially colourless.

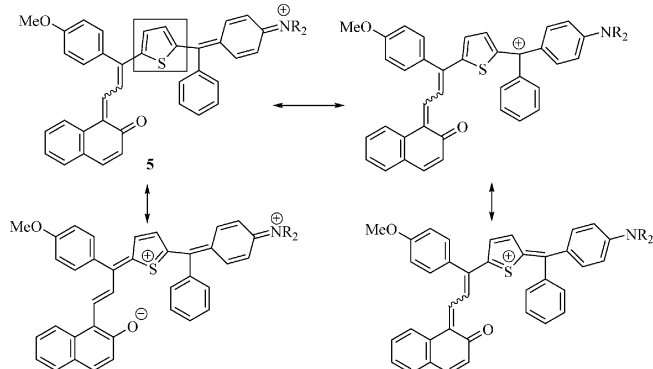
Figure 2. Visible spectra of photochromic dyes **3** and **4** in 98% aq. AcOH at room temperature.

Irradiation of an acetic acid solution of the naphthopyran **3** resulted in a bathochromic shift in $\lambda_{\max}$ of 26 nm relative to the value obtained for the toluene solution (Table 1 and Figure 3). This positive solvatochromism has been previously noted for simple naphthopyrans and confirms a quinone like rather than a zwitterionic structure for the ring-opened species.^[8]

Significant changes in the visible spectra of **4a** and **b** in AcOH were observed upon irradiation to a steady state with the initially developed violet shades ($\lambda_{\max}$ ca. 537 nm) reversibly affording dull purple – brown solutions with a complex line shape suggestive of three overlapping bands in the visible region (Figure 3 and Table 1). The maximum absorbance of this complex band appeared at ca. 565 nm with a peak width at half absorbance intensity of ca. 250 nm. We propose that these complex absorption spectra arise from the additive mixing of some of the remaining ring-closed naphthopyran cationic species together with a new coloured species that results when the naphthopyran unit of the cationic dye undergoes ring-opening. The new

Figure 3. Visible spectra of the dyes **3** and **4** in 98% aq. AcOH at room temperature immediately after UV irradiation.

species may be considered to be a resonance hybrid of **5** (Scheme 5) in which the bridging thiophene unit plays a unique role because it is integral to both the cationic and dienone chromophores (Scheme 5).

Scheme 5. Resonance stabilisation of cations derived from **4**.

To explore the reversibility of the combined UV irradiation and pH switching process a cold (ca. +10 °C) acetone solution of **4b** (Figure 4, far left image, prior to irradiation) was irradiated which resulted in the reversible development of an orange solution (Figure 4, left centre image). Once the orange colour had faded, two drops of MeSO₃H were added to the solution and the gradual development of a

Figure 4. Images of dye **4b** in acetone. Far left: solution prior to irradiation; left centre: solution immediately after UV irradiation; right centre: acidified solution; far right: UV irradiated acidified solution.

violet colour was noted (Figure 4, right centre image). This solution was then irradiated and the reversible evolution of a dull purple-brown shade was noted (Figure 4, far right image). Once this shade had faded the acidic solution was neutralised with aq. NaOH solution which resulted in the immediate formation of a virtually colourless solution, due to hydroxide ion interception of the cation. The complete irradiation, protonation, irradiation sequence was conducted for a second cycle, however when attempting to run the sequence for a third cycle the solution developed a slight haze, presumably due to salt formation upon acid neutralisation.

Conclusions

The naphthopyrans **4a** and **4b** containing pendant triarylmethanol units have been obtained by heteroatom-directed metallation of a naphthopyran bearing a 2-thienyl substituent and subsequent reaction with a benzophenone. These new naphthopyrans display typical reversible photochromism in toluene and also readily afford intense coloured solutions in acetic acid as a consequence of triarylmethine cation generation. Irradiation of these acidic solutions enables an additional coloured species to be generated as a consequence of interplay between the ring-opened naphthopyran unit and the cationic centre. The reversibility of the system has been demonstrated in acetone solution. Our studies on the modulation of the colour of traditional dyes through cycling of a photochromic unit are ongoing.

Experimental Section

Visible spectra were recorded using an Analytik Jena Specord S100 diode array spectrophotometer for solutions of the dyes in either spectroscopic grade toluene or acetic acid (98% aqueous) in the concentration range $1.1\text{--}2.8 \times 10^{-5}$ mol dm⁻³ in 1 cm quartz cells.

Supporting Information (see footnote on the first page of this article): A form of full experimental details for compounds **4a**, **b** is available.

Acknowledgments

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- [19] See Supporting Information for compound **4b**.

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