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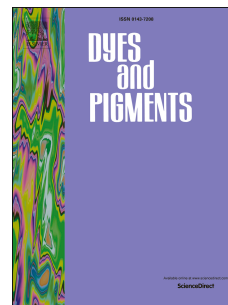
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# Accepted Manuscript

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# Negatively Photochromic Organic Compounds: Exploring the Dark Side

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**Abstract:** The last few years have seen an explosion of interest in traditional photochromic systems not only for their applications in variable transmission devices, which continues to attract commercial interest, but also for the ability of these molecules to undergo structural and electronic reorganisation which has been seized upon by materials scientists for the development of switches, logic gates, photoinduced molecular motions such as rotors and fibrils, and photoregulation of drug availability. This comprehensive review examines, for the first time, the ‘dark side of photochromism’; negatively photochromic systems which are coloured in their ground state and reversibly photobleach upon exposure to electromagnetic radiation with a wavelength over ca. 400 nm i.e. visible light responsive systems. This review is organised by structural class and examines their synthesis, structure, key spectroscopic data for coloured and bleached species, structure – switching relationships and applications. The usefulness of these negatively photochromic systems is only gradually coming to the fore with the advantages of low energy activation c.f. conventional UV-activated switches, enabling the modulation of a plethora of useful optical and physical properties and the design of new materials with broad ranging applications.

**Keywords:** photochromism, negative photochromism, spirobenzopyran, naphthoxazine, thioindigoid, dithienylethene, dihydropyrene, switches, logic gates.

## 1.0 Introduction

The phenomenon of photochromism may be simply defined as:

‘a light-induced reversible transformation of a chemical species between two states having different absorption spectra’,

and was first noted in 1866 by J. Fritzsche who observed the reversible photodimerisation of anthracene.<sup>1</sup> Brown compiled the first major review of photochromism, in *Techniques of Chemistry*, volume III, entitled 'Photochromism' in 1971.<sup>2</sup> Normal or positive photochromism is exemplified by the reversible development of an intense colour upon irradiation, typically with UV light, of the photochromic molecule. Colour fading, associated with return of the photogenerated species to its original state, either occurs thermally upon cessation of irradiation (T-type photochromism) or upon irradiation with an alternative wavelength of light (P-Type photochromism). Here the authors note that the originally conceived distinction between T- and P- type photochromic systems is somewhat fuzzy since many photochromic systems originally described as T-type do indeed show some component of P-type behaviour with the reverse reaction responding to some extent to irradiation as well as temperature.<sup>3</sup> Studies on P-type photochromic systems are almost entirely dominated by switching applications of diarylethenes. T-Type photochromic behaviour is a common occurrence for wearers of ophthalmic sunlenses where the lens appears coloured in normal sunlight and fades upon being placed in the shade. To date photochromic sunlenses remain the major commercial application of photochromism and sunlenses invariably utilize combinations of naphtho-<sup>4</sup> and indeno-<sup>5</sup> pyrans and spiroindolinonaphthoxazines.<sup>6</sup> The absorption spectra of a simple T-Type photochromic dye, pre- and post- irradiation, are presented in Figure 1.

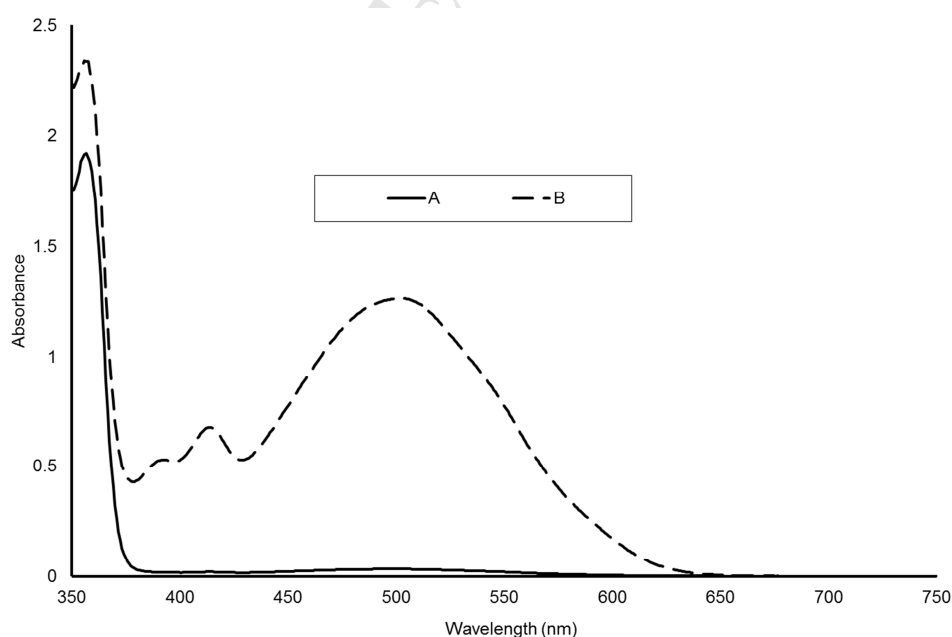


Figure 1. Response of a typical T-type positive photochromic dye solution (A pre-irradiated, B immediately after cessation of irradiation)

Conversely, negative photochromism (sometimes referred to as reverse or inverse photochromism) is observed when the colour of a dye reversibly fades on exposure to electromagnetic radiation such as visible light or sunlight but the intensity of the colour recovers in the absence of visible light i.e. the intense colour of the dye develops in the dark. The term negative photochromism has also been extended to systems wherein the intensity of the long wavelength absorption band of a dye has decreased (hypochromism) upon irradiation with the emergence of a new band at shorter wavelength in the visible region of the electromagnetic spectrum.

There have been several academic reviews concerning photochromism and photochromic systems following on from the initial comprehensive volume edited by Brown.<sup>2</sup> In 1998 a two volume set in the series Topics in Applied Chemistry was edited by Crano and Guglielmetti; volume 1 dealt with the synthesis and properties of the ‘Main Photochromic Families’<sup>7</sup> and volume 2 with ‘Physicochemical Studies, Biological Applications and Thermochromism’.<sup>8</sup> Irie edited a complete issue of Chemical Reviews dedicated to the application of photochromism in memories and switches, though much valuable general information on photochromic systems was included.<sup>9</sup> Perhaps as a consequence of the appearance of the latter two reviews and a general increase in interest in the subject Dürr and Bouas-Laurent revised their original book, ‘Photochromism Molecules and Systems’,<sup>10</sup> and included much more material in the 2003 revision.<sup>11</sup> The most recent addition to major works on photochromism entitled ‘Photochromic Materials’ was edited by Tian and Zhang in 2016.<sup>12</sup> An English translation of a more obscure multi-authored Russian work entitled ‘Organic Photochromes’ edited by El’tsov appeared in 1990.<sup>13</sup> Whilst many of the foregoing reviews focus on more academic aspects of photochromism one major work, edited by McArdle in 1992, ‘Applied Photochromic Polymer Systems’, is devoted to the behaviour and application of photochromic polymers,<sup>14</sup> though due to the relatively recent activity in the area of photochromic polymer systems, see for example work by Evans *et al.*,<sup>15-17</sup> ‘McArdle’ is probably due an update.

Other general reports and reviews featuring photochromism have appeared<sup>18-22</sup> and more specific reviews dedicated to individual photochromic systems have been published, noteworthy amongst these are those on diaryl benzo- and naphtho- pyrans,<sup>23</sup> diarylethenes,<sup>24-28</sup> spiropyrans,<sup>29-31</sup> spiropyran-based materials,<sup>32</sup> spiroindolinonaphthoxazines,<sup>33,34</sup> photochromic compounds as ligands,<sup>35</sup> photoswitching transition metal complexes,<sup>36,37</sup> photochromic systems containing crown ether units<sup>38,39</sup> and azobenzenes.<sup>40-42</sup> A notable

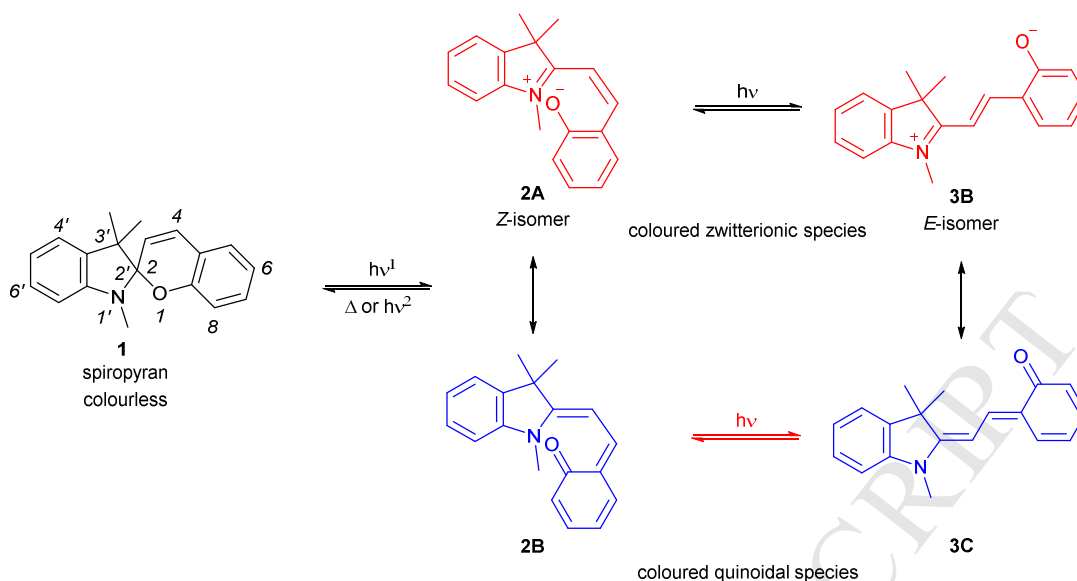
recent review by Jacquemin *et al.*, examines highly functional materials which contain more than one photochromic switching moiety.<sup>43</sup> Photochromic systems also feature in reviews concerned with the control of molecular architecture,<sup>44</sup> molecular switches,<sup>45,46</sup> devices and machines,<sup>47</sup> photoswitchable bio-materials and bio-molecules<sup>48</sup> and in reversible optical data storage devices.<sup>49</sup> Special issues of Molecular Crystals, Liquid Crystals<sup>50-56</sup>, Dyes & Pigments<sup>57</sup> and also Advanced Optical materials<sup>58</sup> containing papers and abstracts from the International Symposia on Photochromism (ISOP) have appeared. In spite of such activity on positive or normal photochromic systems there remain relatively few articles concerning negative photochromism, indeed the phenomenon was summarised in only a few lines by Brown.<sup>59</sup> A short account of the reverse photochromism of spiropyrans was authored by Barachevsky in the Russian language in 1997.<sup>60</sup>

Of the many photochromic systems described in the foregoing reviews very few exhibit negative photochromism. This review primarily divides the phenomenon of negative photochromism into T- and P- type systems and thence subdivisions based on the molecular system and where there are sufficient examples further division into substituent and matrix effects.

## 2.0 Systems that Exhibit Predominantly T-Type Negative Photochromism

### 2.1 Spirobenzopyrans (spiro[2*H*-[1]-benzopyran-2,2'-indolines])

The spirobenzopyran system is perhaps historically the best known positive photochromic system. UV irradiation of the colourless pyran (1',3',3'-trimethylspiro[2*H*-[1]-benzopyran-2,2'-indolines]) **1** results in cleavage of the 1' – 2' (O – *spiro*-C) bond to afford the zwitterionic (*Z*)-2-(2-(1,3,3-trimethyl-3*H*-indol-1-ium-2-yl)vinyl)phenolate **2A** which isomerises to the (*E*)-2-(2-(1,3,3-trimethyl-3*H*-indol-1-ium-2-yl)vinyl)phenolate **3B** (Scheme 1). It is generally accepted that quinoidal forms of **2B** and **3B** may also be present and the ratio between these and the zwitterions is dependent upon substituents and the nature of the matrix.<sup>61,62</sup> Additionally the possibility of various rotamers of **2** and **3** should be noted.

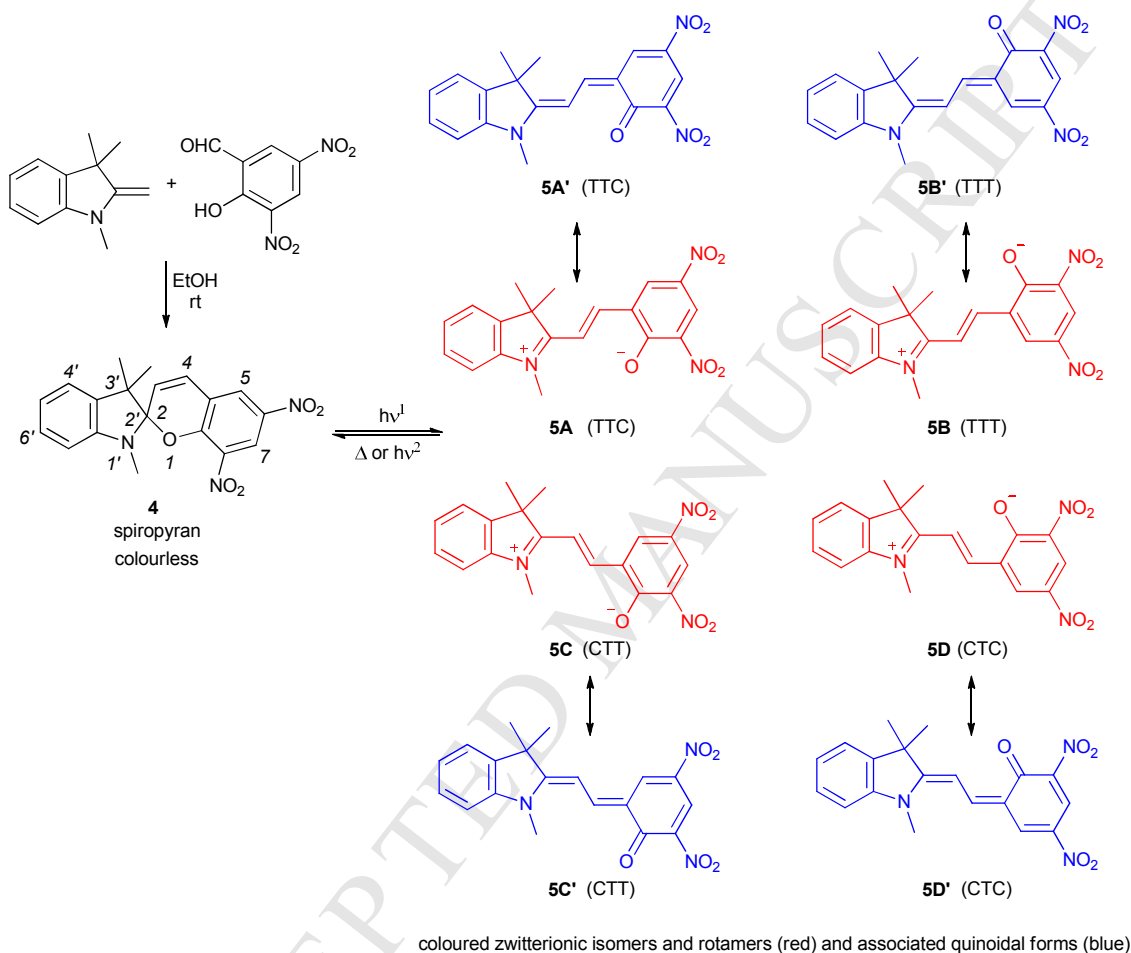


Scheme 1. Relationship between the ring-opened forms of spiropyran **1**

However, there are several examples of ‘spiropyran’ bearing unique combinations of substituents which result in a negative photochromic response from the spiropyran system. That is to say that the photomerocyanine, a 2-(2-(3*H*-indol-1-ium-2-yl)vinyl)phenolate, is the thermodynamically stable species which upon irradiation with a suitable wavelength of light reversibly cyclises to the spiropyran. Stabilisation of the 2-(2-(3*H*-indol-1-ium-2-yl)vinyl)phenolate species is most commonly accomplished through the presence of electron withdrawing substituents in the benzopyran / phenolate unit which can delocalise the negative charge associated with the oxygen atom in the phenolate form. Thus most studies of negatively photochromic spiropyran involve the 1',3',3'-trimethyl-6,8-dinitrospiro[2*H*-[1]-benzopyran-2,2'-indoline] **4** and the derived zwitterionic species **5A – D**. It should be noted that the historical convention adopted throughout the scientific literature is to refer to the spiropyran **4** rather than the zwitterionic form **5** despite the fact that the spiropyran is often only observed transiently. Given that the majority of readers are those familiar with this historic convention and that literature searches afford a greater number of pertinent returns when the spiropyran search term is employed this convention will be used in the present review.

The earliest account of the synthesis of **4** appeared in 1952 and involved the condensation of 3,5-dinitrosalicylaldehyde with 1,3,3-trimethyl-2-methyleneindoline in EtOH at room temperature for a number of days (Scheme 2). The product was reported to be isolated as dark green crystals in good yield.<sup>63</sup> A dramatic reduction in reaction time from days to 15

min and a yield of 87 % of **4** has been claimed when the reaction mixture was irradiated with ultrasound (55 Watt).<sup>64</sup> The use of tetramethyl-3*H*-indolium iodide in conjunction with piperidine under an Ar atmosphere in anhydrous EtOH to generate 1,3,3-trimethyl-2-methyleneindoline *in situ* with subsequent addition of 3,5-dinitrosalicylaldehyde and a 3 h reflux affords **4** in 79 % yield.<sup>65</sup>



Scheme 2. Various ring-opened species of spiropyran **4**

Crystals of **4** grown from an acetone solution were shown, by X-ray crystallography (Cambridge Crystallographic Data Centre file CCDC111968), to be the near planar **5B** which was termed the *trans, trans, trans* (TTT) isomer (Figure 2).<sup>66</sup> Key bondlengths of **5B** are presented in Table 1 and the alternating bondlengths of the four carbon unit  $C^1 - C^4$  affirm the zwitterionic rather than a quinodal structure in the solid state. The  $N^1 - C^1$  bondlength of 132.6 pm in **5B** is suggestive of double bond character and the geometry about the  $N^1$  atom is consistent with  $sp^2$  hybridisation.



There have been extensive spectroscopic investigations of **4** in solution. In either D<sub>6</sub>-acetone or D<sub>6</sub>-DMSO solution the prevailing forms of **4** are the TTT **5B** (minor) and *trans, trans, cis* (TTC) **5A** (major) rotamers established by 2D NMR experiments. The spiropyran form **4** is present in an appreciable amount, *ca.* 35 mol %, in CDCl<sub>3</sub> solution.<sup>66</sup>

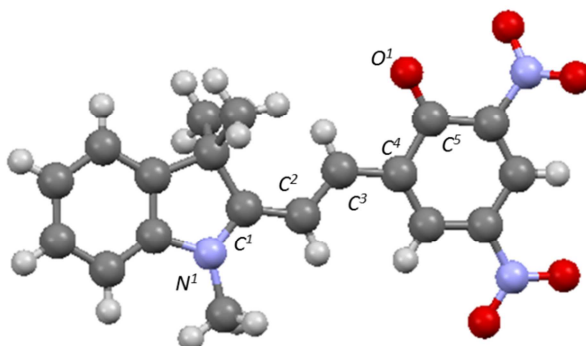


Figure 2. Crystal structure representation of zwitterion **5B**

Bondlength pm		Bondlength pm	
$N^1 - C^1$	132.6	$C^3 - C^4$	142.4
$C^1 - C^2$	140.6	$C^4 - C^5$	145.5
$C^2 - C^3$	134.9	$C^5 - O^1$	124.9

Table 1. Selected bondlengths for zwitterion **5B**

Key <sup>1</sup>H NMR signals in for **5A** and **4** are presented in Figure 3. The central alkene protons of **5A** show mutual coupling of 16 Hz typical for a *trans*- substituted alkene unit.<sup>66</sup> For the spiropyran the alkene proton coupling constant is 10.5 Hz confirming the *cis*- arrangement.<sup>67</sup> The protons of the *N*-Me unit in **4** resonate at *ca.* δ 2.8 (D<sub>6</sub>-acetone) but are shifted downfield to *ca.* δ 4.0 in accord with the localised +ve charge on the indolinium *N*-atom in **5A**.<sup>66,68</sup>

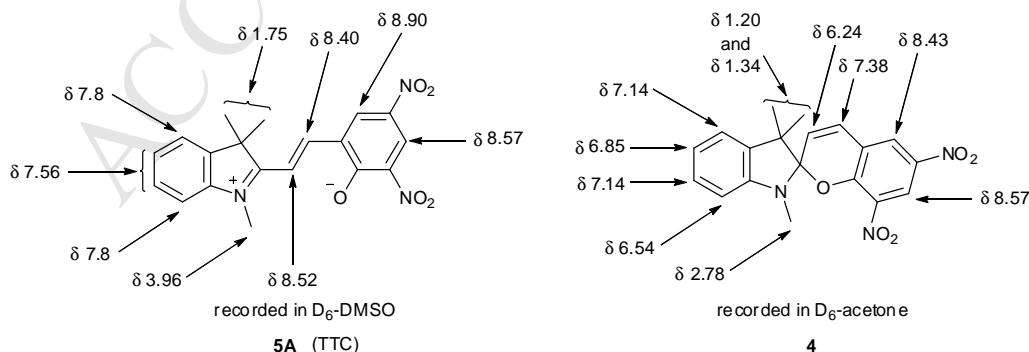


Figure 3. Selected <sup>1</sup>H NMR chemical shifts for **5A** and **4**

In a further interesting aspect concerning the NMR experiments performed on **4** / **5A** the alkene proton which resonates at  $\delta$  8.52 (**5A**, Figure 3) was demonstrated to undergo facile deuterium exchange in  $D_6$ -DMSO upon addition of  $D_2O$ .<sup>66</sup> The observation of the foregoing deuterium exchange enabled isotopic shifts to be explored by  $^{13}C$  NMR spectroscopy. For C-3 deuterated **5A**, isotope shifts can be observed over a distance of 5 bonds, but for the C-3 deuterated spiroopyran 1',3',3'-trimethyl-6-nitrospiro[2*H*-[1]-benzopyran-2,2'-indoline] **6** isotope shifts are observed only over 3 bonds.<sup>69</sup> This latter study provided detailed assignments of the  $^{13}C$  NMR resonances of **5A** and **6** (Figure 4).

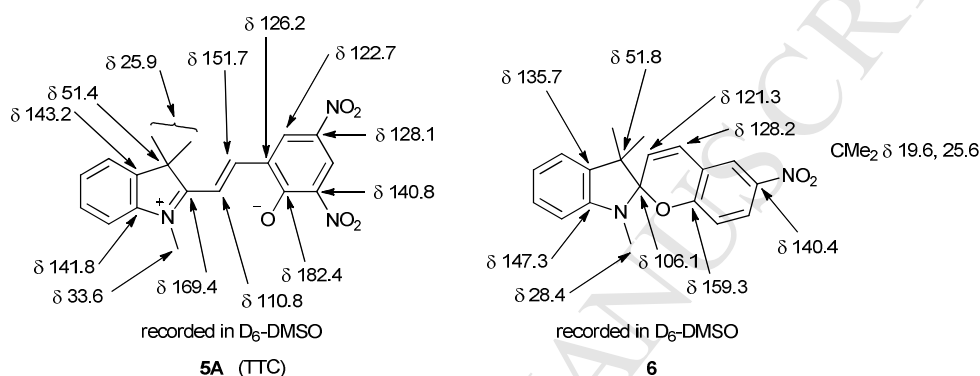


Figure 4. Selected  $^{13}C$  NMR signals for **5A** and **6**

The influence of temperature on the thermal recolouration of a visible light bleached film of **5A** has been studied.<sup>70</sup> As the temperature of the film was raised the rate of formation of the coloured isomer **5A** increased. A series of UV-visible absorption spectra of 1'-isobutyl-3',3'-trimethyl-6,8-dinitrospiro[2*H*-[1]-benzopyran-2,2'-indoline] **7** (Figure 6) are presented in Figure 5.<sup>71</sup> The molar extinction coefficient of **7** was determined as  $37.3 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ , which compares favourably with that for the *N*-Me analogue **4**<sup>66</sup> of  $\sim 40 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  with  $\lambda_{\text{max}}$  at 541 nm together with a second less intense band, maxima at 382 nm, which tails into the visible region. A freshly prepared solution of **7**, protected from daylight, in spectroscopic grade acetone appears deep red - orange but after bleaching with white light ( $\lambda > 400 \text{ nm}$  for 30 seconds) fades to almost colourless at 20 °C (Figure 5).

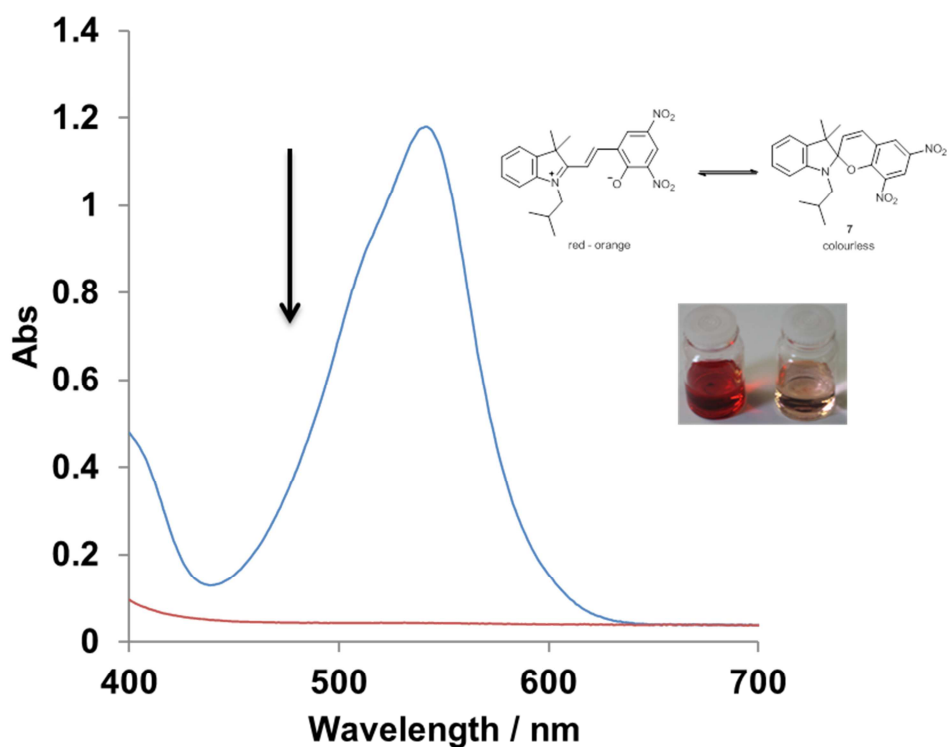
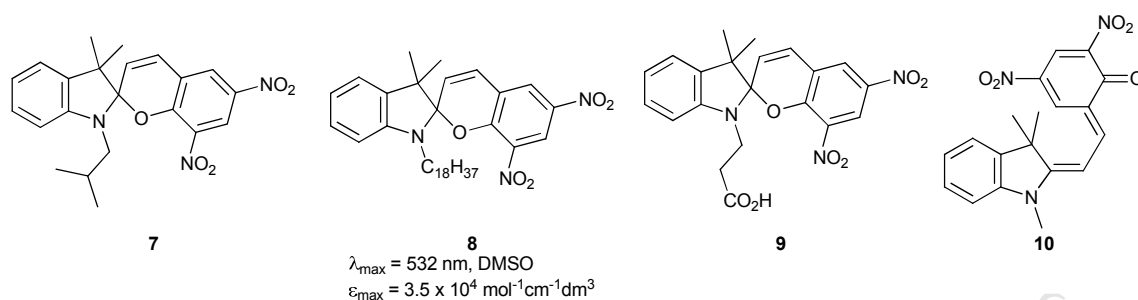


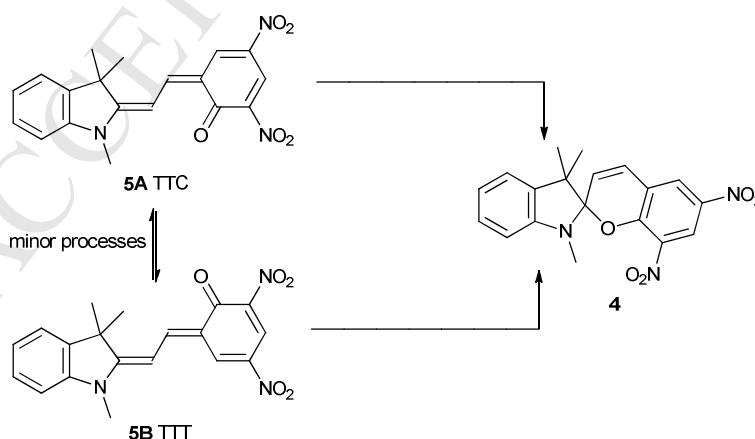
Figure 5. Visible absorption spectra of **7** before and after irradiation

The dynamic behaviour of the interconversion between **5** and **4** and related *N*-alkyl derivatives has been studied by transient absorption spectroscopy. In the nanosecond time domain an initial study of the *N*-octadecyl substituted spiropyran **8** revealed that the zwitterion bleaching (ring-closing reaction) involved three components at <25 ns, 240 ns and 3.4  $\mu$ s and that the recovery of the colour involved two components (620 ns and 3 – 4  $\mu$ s). The inference was made that the transient species in this time domain were consistent with a triplet pathway;<sup>72</sup> both singlet and triplet pathways have been inferred for the colouration of positively photochromic nitrospiropyrans.<sup>73,74</sup> The negative photochromism of **8** (Figure 6) has also been examined in a Langmuir-Blodgett film where atomic force microscopy recorded changes in the surface of the film upon cycling **8** with visible light irradiation.<sup>75</sup>

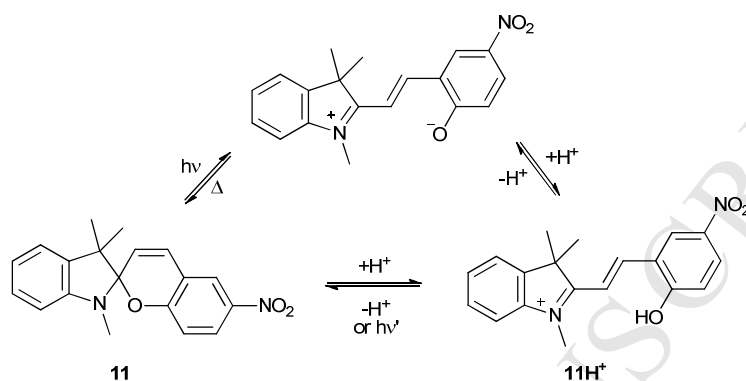
The sub-picosecond – nanosecond timescale of the reversible ring closure of **5** and **9** has also been investigated and a purely singlet state manifold was proposed for the mechanism for the reaction which was complete in ca. 400 ps. In the latter ultrafast photodynamic study a metastable intermediate was postulated that was either a quinoidal *cis*-merocyanine **10** (Figure 6) or a zwitterionic species twisted about the central methine bond.<sup>76</sup>

Figure 6. Structures of dinitrospiropyrans **7** – **10**

More recent studies of the interconversion between the assumed quinoidal forms of **5** and spiropyran **4** in chloroform solution on the femtosecond timescale using ultraviolet / visible pumping with visible / mid IR probing revealed that both ring – closing and ring – opening could be accomplished photochemically. Interestingly, the ring-closing – ring-opening cycle could be accomplished in under 6 ps whereas the ring-opening – ring-closing cycle was complete in ca. 40 ps leading to the summary that **4** behaves as an ultrafast bidirectional switch.<sup>65</sup> In a further femtosecond laser spectroscopy study of **5** it was shown that the TTC ( $\lambda_{\max} = 560 \text{ nm}$ , major) and TTT ( $\lambda_{\max} = 600 \text{ nm}$ , minor) quinoidal isomers absorb at different wavelengths respectively in chloroform solution and that each isomer could be closed to the spiropyran by a  $6\pi$ -electrocyclic reaction (Figure 7).<sup>77</sup> Coherent two-dimensional electronic spectroscopy has been proved of value in the study of photoreactive species. Application of this technique to the quinoidal TTC and TTT forms of **5** reveals that geometrical isomerisation of these two forms does not play a major role in the reversible photochemical ring-opening – ring-closing process on the ultrafast fast timescale.<sup>78</sup>

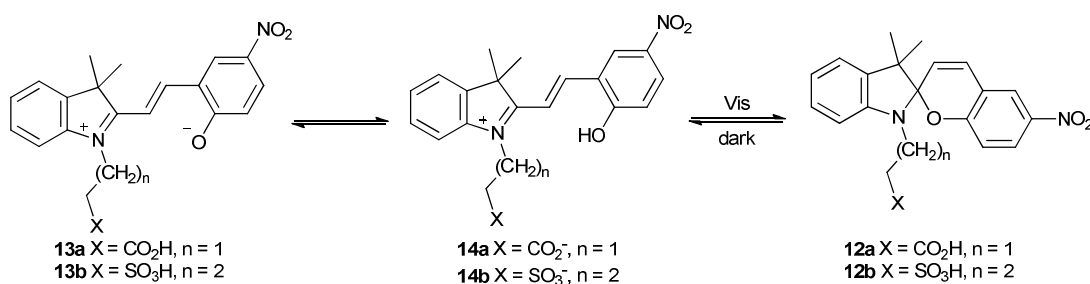
Figure 7. Interconversion of quinoidal forms of ring-opened spiropyran **4**

The response and stability of the dinitrospiropyran **4**  $\leftrightarrow$  merocyanine **5** system towards solvent polarity and pH has been investigated.<sup>79</sup> Interestingly, treatment of an acetone solution of the mononitrospiropyran **11** with malonic acid gave the protonated merocyanine **11H<sup>+</sup>** which exhibited negative photochromism i.e. the malonate salt could be reversibly bleached by irradiation with visible light (Scheme 3).<sup>80,81</sup>



Scheme 3. Photochemical and pH induced switching of nitrospiropyran **11**

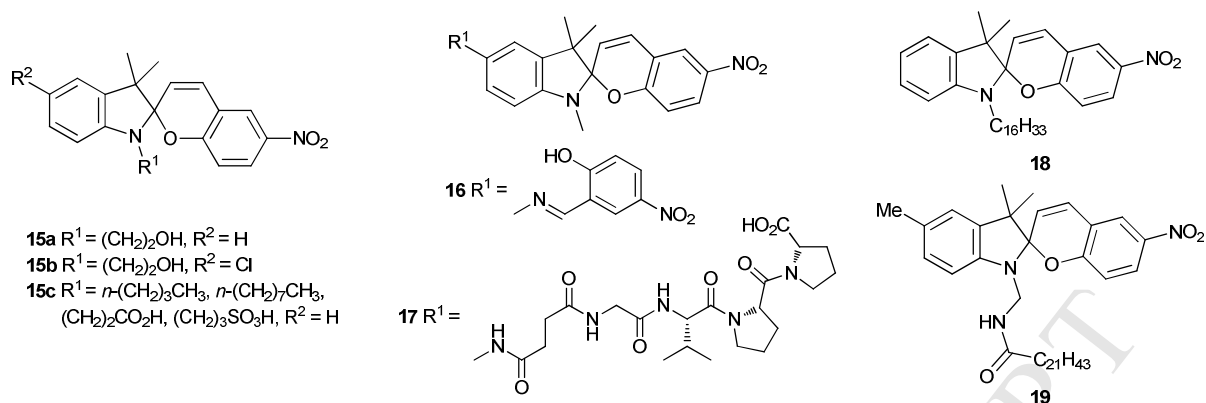
Incorporation of acidic functions ( $-\text{CO}_2\text{H}$ ,  $-\text{SO}_3\text{H}$ ) into the indoline *N*-alkyl substituent led to some interesting observations regarding the role of the solvent on the performance of the systems **12a**, **b** under irradiation. When in dioxane solution positive photochromism was observed for **12a** but the addition of water resulted in stabilisation of the merocyanine **13a**, the visible light irradiation of which led to bleaching of the absorption maximum at 528 nm. The intensity of the absorbance at 528 nm recovered upon standing in the dark (Scheme 4).<sup>82</sup> Visible light irradiation of **14b** results in ring-closure to afford **12b** with loss of colour and generation of  $\text{H}^+$ . The proton dissociated state (spiropyran) has a half-life of ca. 70 s and results in a change of pH of the medium of ca. 2.2 units. The relatively long-lived photo-acid has been employed to catalyse an esterification and manipulate the volume of a pH-sensitive polymer.<sup>83</sup> A photo-acid generating spiropyran has been used to manipulate the colour of a pH sensitive dithienylethene derivative, leading to an all optical four-state colour switching system.<sup>84</sup>



Scheme 4. Prototropy and photochromism of nitrospiropyrans **12a, b**

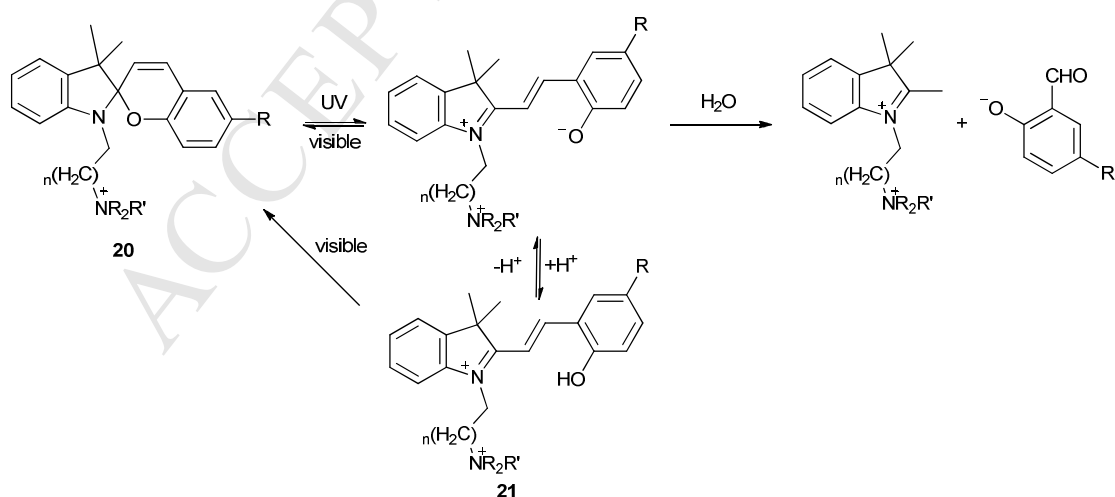
Further evidence of the influence of the matrix on the photochromic response was evident from the behaviour of the mononitrospiropyran **15a** which upon standing in aq. MeOH solution (1:1) at 45 °C in the dark gradually established an equilibrium mixture over ca. 50 min with an appreciable content of the merocyanine form as evidenced by the appearance of a pink solution ( $\lambda_{\text{max}}$  515 nm). Storage of either MeCN, CHCl<sub>3</sub>, PhH or THF solutions of **15a** under similar conditions resulted in no pink coloration; the stabilisation of the merocyanine form by H-bonding with water molecules was deemed responsible for this behaviour.<sup>85</sup> The merocyanine form of **15a** has also been generated and stabilised in perhydropolysilazane which had been treated with water; hydrogen bonding with Si-OH functions was responsible for the stabilising effect.<sup>86</sup> Poly(vinyl alcohol) films of **15b** were magenta ( $\lambda_{\text{max}} = 534$  nm) and could be bleached with ‘UV free’ visible light.<sup>87</sup> Temperature gated switching between negative and positive photochromism of microencapsulated samples of **15a** and **11** in fatty acid matrices has recently been described.<sup>88</sup>

Switching between negative and positive photochromism has also been noted for the mononitrospiropyrans **15c** in room temperature ionic liquids (Figure 8). In contrast to **14** in the foregoing study, **15c** substituted with either R<sup>1</sup> = *N*-alkyl carboxylic acid or R<sup>1</sup> = *N*-alkane sulfonic acid groups positive photochromism was observed in a broad range of ionic liquids. However, for **15c** R<sup>1</sup> = alkyl, R<sup>2</sup> = H solutions in *N*-hydroxyalkyl-imidazolium salts, with a strong acid anion such as bistriflimide ion, deep red - purple coloured solutions of **15c** R<sup>1</sup> = alkyl, R<sup>2</sup> = H resulted at room temperature which could be reversibly bleached upon UV-irradiation. Whereas positive photochromism was noted for all **15c** in various *N*-butylimidazolium carboxylates.<sup>89</sup> Solvent dependent negative photochromism was also noted for mononitrospiropyrans derived from 5-amino Fischer’s base with the mononitrospiropyran – Schiff base dyad **16**<sup>90</sup> and supramolecular hydrogels based on mononitrospiropyran – peptide conjugates **17** (Figure 8).<sup>91</sup> The matrix also has a significant impact on the routine photochromic switching of the parent spiropyran **1** which can be modified to exhibit negative photochromism when it is entrapped in the rigid channels of a zinc ion-rich metal organic framework<sup>92</sup> and covalent linking of 6-hydroxyspiropyran to the polymer backbone of an acrylate copolymer stabilised the coloured zwitterionic form which could be reversibly bleached upon irradiation.<sup>93</sup>

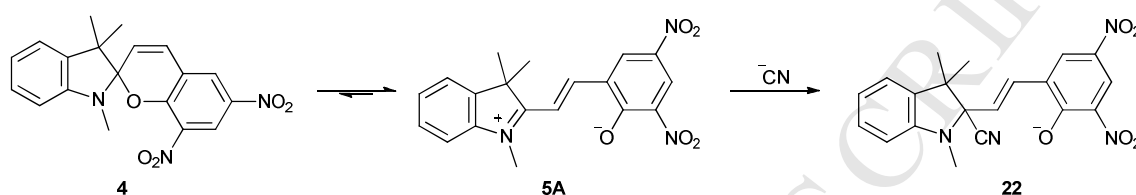
Figure 8. Structures of nitrospiropyrans **15** - **19**

Temporary negative photochromism was imparted into two long chain substituted mononitrospiropyrans **18** and **19**, in thin films, upon protonation with HCl. Infrared spectroscopy was used to monitor the cycling between the spiropyran and the *trans*-merocyanine form, with the band at  $1610\text{ cm}^{-1}$  being assigned to the *trans* C=C bond (Figure 8).<sup>94</sup>

Water has been demonstrated to attack the conjugated system of the merocyanines of **20**  $R = \text{NO}_2$ , CHO, CN at neutral pH resulting in formation of the indolinium salt and the nitrosalicylaldehyde, presumably via a retro-aldol process. However, at low pH the protonated merocyanine form **21**, which could be cyclised to the spiropyran by irradiation with visible light in accord with observations for simple *N*-alkyl substituted systems, was shown to be stable to hydrolytic degradation (Scheme 5).<sup>95</sup>

Scheme 5. Photochromism and hydrolysis of spiropyran **20**

The zwitterion **5A** is susceptible to attack by strong nucleophiles such as cyanide ion and thiols. The former results in disruption of the donor –  $\pi$  – acceptor system with an attendant hypsochromic shift in  $\lambda_{\max}$  from ca. 525 to 400 nm (aq. MeCN) (Scheme 6). The site of cyanide ion attack was established by  $^1\text{H}$  NMR spectroscopy which resulted in an upfield shift of the NMe signal from  $\delta$  3.97 **5A** (merocyanine) to  $\delta$  2.69 **22** (CN adduct). The change in absorption spectrum was shown to be selective for cyanide ion amongst 12 other anions and the system offers potential as a cyanide ion sensor.<sup>96</sup>



Scheme 6. Behaviour of zwitterion **5A** towards cyanide ion

The spiropyran **4** and the 4'- and 6'- hydroxymethyl analogues **23** and **24** have been used as sensors for thiol-containing amino acids<sup>97,98</sup> and the *N*-alkylthio derivative **25**, when bound to a gold surface, has been employed as a reusable sensor for antibodies (Figure 9).<sup>99</sup> In the presence of serum albumins the thermal ring opening of the 6,8-dinitrospiropyrans **4** to the zwitterion **5A** was accelerated.<sup>100</sup> The response of the dithiolane appended 6-nitrospiropyran **26** was modulated from positive photochromism in 1,2-dichloroethane solution to negative photochromism when anchored to cadmium sulphide nanoparticles treated with 1-decanethiol (Figure 9). The transition from positive to negative photochromism was thought to occur due to stabilising electrostatic interactions between the zwitterionic species and the surface of the nanoparticles.<sup>101</sup>

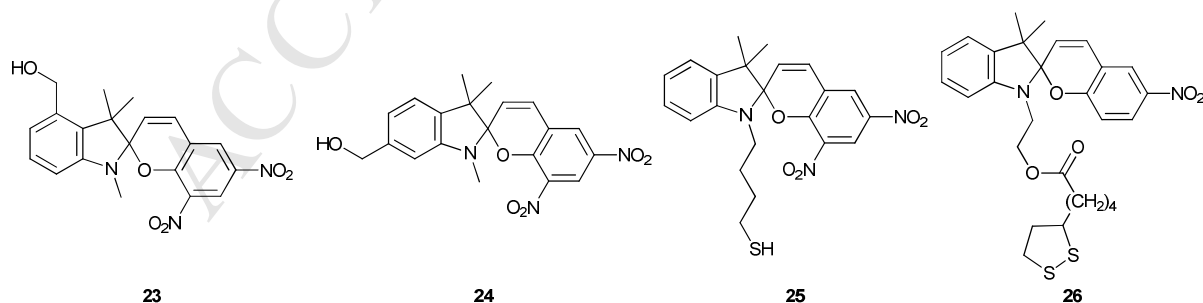


Figure 9. Structures of nitrospiropyrans **23** – **26**

A series of new negatively photochromic spirobenzopyrans derived from 3,5-dinitrosalicylaldehyde and variously substituted 1,3,3-trimethyl-2-methyleneindolines were



synthesised by Minami *et al.*,<sup>102</sup> using the general synthetic procedure reported by Gruda *et al.*, for the preparation of simple spirobenzopyrans, namely heating a salicylaldehyde with a 1,3,3-trimethyl-2-methyleneindoline in ethanol under reflux for ca. 6 hours.<sup>103</sup> Variation of the 5'-substituent had only a marginal influence on  $\lambda_{\max}$  of the coloured forms of **27a – d** relative to that of **4** (Figure 10) However, of particular note was the observation that for **28** normal (positive) photochromism was observed in  $\text{CHCl}_3$  and in acetone solution; only in DMSO solution was negative photochromic behaviour observed indicating the significant influence of the polar matrix upon the stability of the ring-opened species. The influence of benzannelation *viz.* **29** was also negligible. The alternate benzo-fused isomer **30** has been reported but its photochromic response was not elaborated (Figure 10).<sup>104</sup>

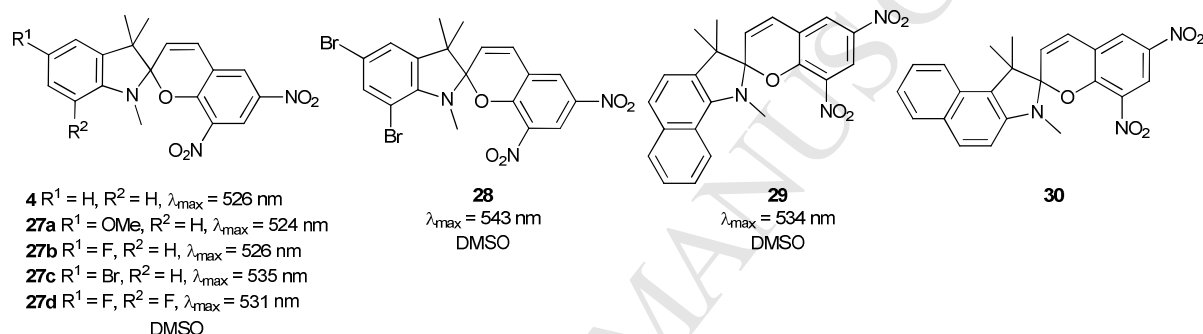
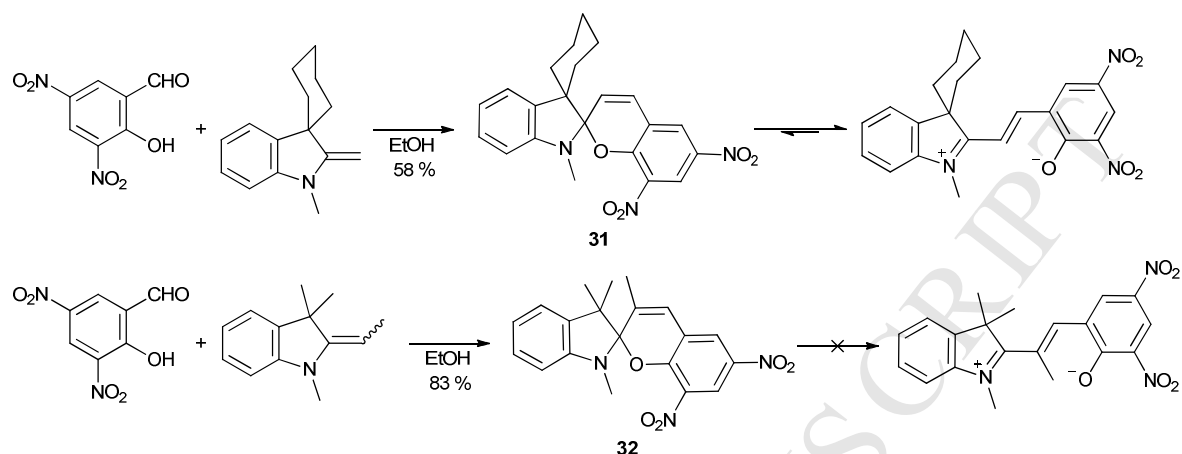


Figure 10. Dinitrospiropyran structures **4** and **27 – 30**

The influence of structural variation at the 3 and the 3' positions upon the spiropyran  $\leftrightarrow$  2-(2-(3*H*-indol-1-ium-2-yl)vinyl)phenolate equilibrium has been described in two papers reported by Roxburgh *et al.*<sup>105,106</sup> Compounds **31** and **32** were obtained by isolation of the appropriately substituted Fischer's base from the indoleninium triflate with 40 % aq. NaOH and  $\text{Et}_2\text{O}$  extraction prior to routine spiropyran formation by heating 3,5-dinitrosalicylaldehyde and the liberated Fischer base in EtOH for 24 h (Scheme 7). The introduction of the 3'-spirocyclohexane group resulted in the presence of a mixture of the spiropyran (minor) **9** and the ring-opened form (major) in  $\text{DMSO-d}_6$  solution at 298 K as evidenced by the presence of olefinic signals in the  $^1\text{H}$  NMR spectrum ( $\delta$  8.3, d,  $J = 15 \text{ Hz}$  and  $\delta$  5.9, d,  $J = 10 \text{ Hz}$ ) and  $\text{N}^+\text{-Me}$  and  $\text{N-Me}$  signals at  $\delta$  3.8 and  $\delta$  2.8, respectively. Increasing the temperature in ca. 20 K increments up to 410 K resulted in increasing the amount of spiropyran. No such equilibrium mixture was detected in  $\text{DMSO-d}_6$  solution in the temperature range 298 – 410 K by  $^1\text{H}$  NMR spectroscopy for the 3-Me analogue **16**; substitution at the 3-position favouring the exclusive presence of the spiropyran form. In

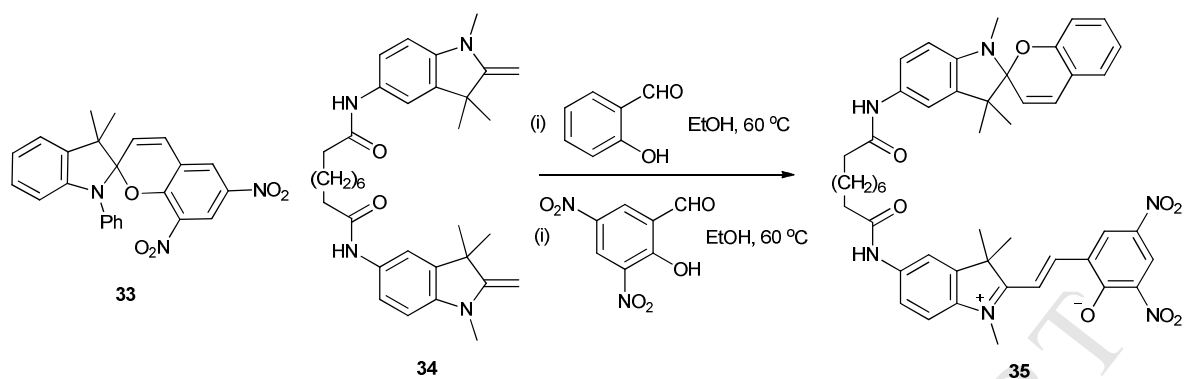
contrast with ultrafast spectroscopic studies of **4** / **5A** where no appreciable isomerism between the quinoidal forms **5A** and **5B** was noted, slow isomerism between the TCC and TTC isomers of **15** was proposed.



Scheme 7. Preparation of spiroopyrans **31** and **32**

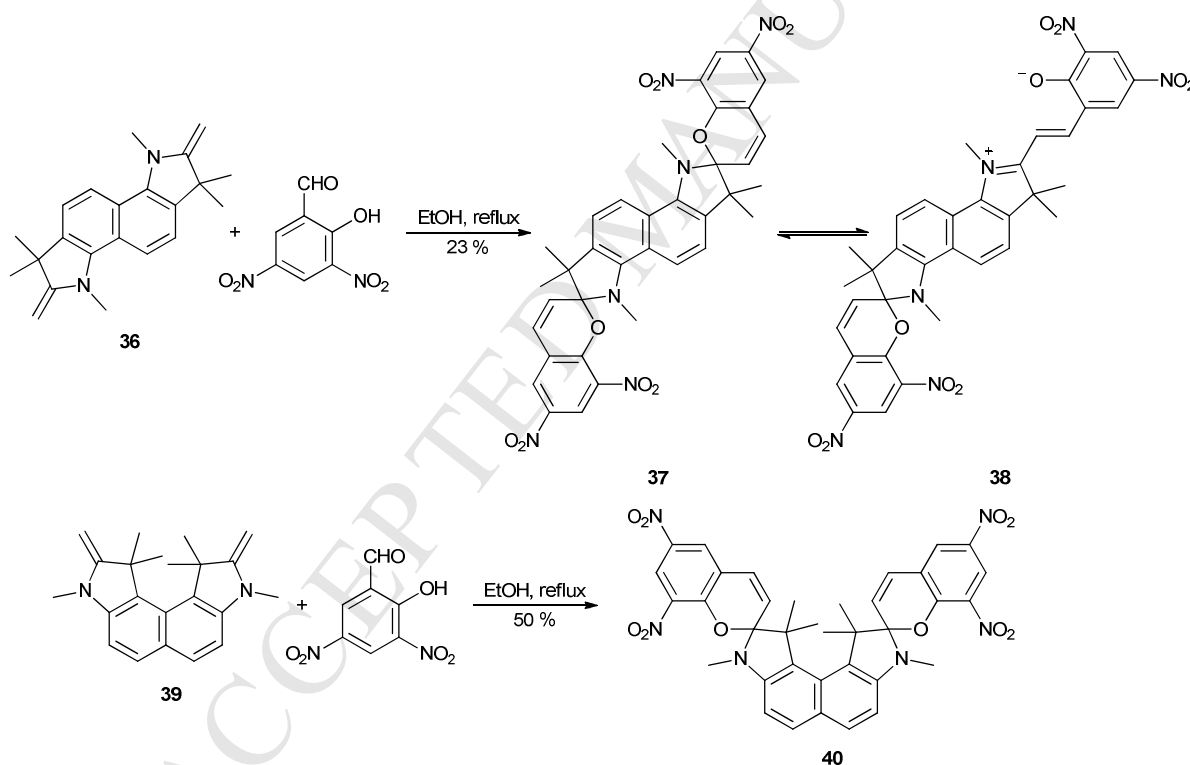
A variety of substituents have been introduced by standard synthetic procedures at the indoline *N*-atom including branched alkyl groups e.g. **7**,<sup>71</sup> and long chain alkyl groups **8**<sup>75,79</sup> and functional alkyl groups e.g. **9**<sup>107</sup> leading to compounds which retain negative photochromic behaviour. The *N*-phenyl analogue **33** was first reported in 1961<sup>108</sup> and its negatively photochromic behaviour commented upon in a more recent patent.<sup>109</sup>

Unsymmetrical bis-indolinospiroopyran **35** has been synthesised by sequential reaction of the bis-Fischer's base **34**, derived from reaction of an excess of 5-amino-1,3,3-trimethyl-2-methyleneindoline with sebacyl chloride, with salicylaldehyde and the resulting mono spiroopyran condensed with 3,5-dinitrosalicylaldehyde to afford the product (Scheme 8).<sup>110</sup> <sup>1</sup>H NMR spectroscopy of a solution of **35** in CDCl<sub>3</sub> indicated the presence of a 1:1 mixture of a spiroopyran unit ( $\delta_{\text{NMe}}$  2.70, and  $\delta_{3\text{-H}}$  5.82) and a ring – opened unit ( $\delta_{\text{NMe}}$  4.05, and  $\delta_{3\text{-H}}$  6.54) and irradiation of a DMSO solution resulted in reversible bleaching of the initially present colour. Two 6-nitrospiroopyran units linked through their indoline *N*-atoms by a peptide unit displayed red luminescence in aqueous solution which could be significantly, reversibly diminished upon irradiation with visible light due to ring closure of the merocyanine species.<sup>111</sup>



Scheme 8. Structure of *N*-Phenylspiropyran **33** and linked spiropyran **35**

The isomeric bis-Fischer's bases **36** and **39** have been condensed with 3,5-dinitrosalicylaldehyde under standard conditions to afford the bis-indolinospiroyrans **37** and **38** in moderate yields (Scheme 9).<sup>112</sup>



Scheme 9. Preparation of isomeric bis-indolinospiroyrans **37** and **40**

The UV-visible absorption spectrum of **37** in EtOH displayed an absorption maximum at 553 nm in the visible region which was indicative of the presence of a ring opened spiropyran unit. Whereas the spectrum of **40** exhibited a longest wavelength absorption band at 417 nm. These data were supported by <sup>1</sup>H NMR studies (DMSO-d<sub>6</sub>) which revealed the presence of two sets of signals, of unequal intensity, for **37**. The major set of signals were attributed to the

symmetrical bis-indolinospiropyran **37** (alkene coupling constant  $J_{cis} = 10.5$  Hz) and the minor set of signals to **38** in which one of the spiropyran rings is present as the zwitterionic unit (alkene coupling constants  $J_{cis} = 10.3$  Hz and  $J_{trans} = 14.3$  Hz). The  $^1\text{H}$  NMR spectrum of **40** displayed only one set of signals which were in accord with the symmetrical bis-spiropyran structure. Interestingly, the  $^1\text{H}$  NMR spectra of the analogous bis-indolinospiropyrans **41** and **42** (Figure 11), derived from **36** and **39** with 3,5-dibromosalicylaldehyde, each showed the presence of some ring – opened species.<sup>112,113</sup> Unfortunately, a detailed study of the photochromic response of **37**, **38**, **40** – **42** was not provided. However on the spectroscopic evidence provided for the presence of the ring – opened species and by analogy with simple monomeric spiropyrans substituted with two electron withdrawing functions negative photochromic behaviour would be expected.

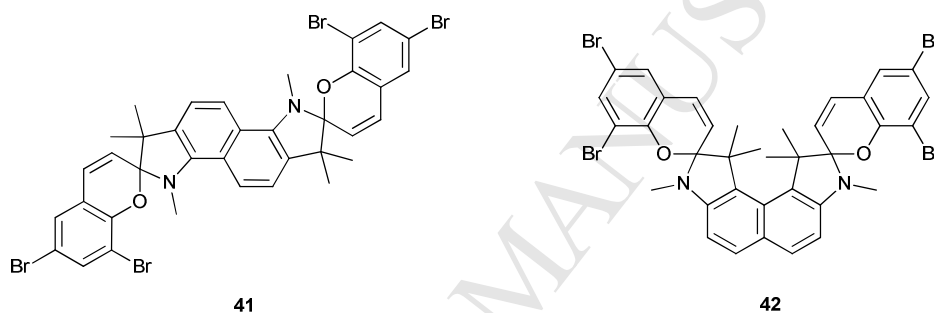


Figure 11. Structures of bis-indolinospiropyrans **41** and **42**

Replacement of the 8-nitro substituent with halogens e.g. Br, **43**<sup>114,115</sup> results in an equilibrium mixture of ring – opened and ring – closed forms in DMSO- $d_6$  solution in which the zwitterionic form was indicated to be present in about 60% by  $^1\text{H}$  NMR spectroscopy. At 155 °C the amount of the ring – opened species of **43** present in DMSO- $d_6$  solution was decreased to ca. 5% and reflects the thermal dependence of the equilibrium.<sup>116</sup> Spectroscopic studies of **43** and the ester derivative **44** R = Me (Figure 12) in a series of solvents of different polarity revealed equilibrium mixtures of ring – opened and ring – closed forms with ring – opened form favoured by polar solvents such as ethanol and acetonitrile. Interestingly, in this study the photocoloration was proposed to operate via a triplet manifold.<sup>117</sup> An earlier report concerning the synthesis of a series of **44** with varying R groups indicated that positive photochromism was observed for these compounds.<sup>118</sup> A study of the  $^1\text{H}$  NMR spectra of **44** and **45** R = Me revealed that each isomer was present with their ring – opened form in ca. 40 and 70 %, respectively. Increasing the temperature of the DMSO- $d_6$  solution resulted in a decrease of the amount of ring – opened species present.<sup>116</sup>

In this same NMR study examination of the  $^1\text{H}$  NMR spectra of the isomeric carboxylic acid derivatives **43** and **44**  $\text{R} = \text{H}$  indicated that each of these carboxylic acids were present with very appreciable amounts of their ring – opened species. The presence of intramolecular H-bonding between the 8-carboxylic acid function and the adjacent oxide unit was invoked to rationalise the very high proportion (95 %) of the ring – opened form of **44**  $\text{R} = \text{H}$  at room temperature.

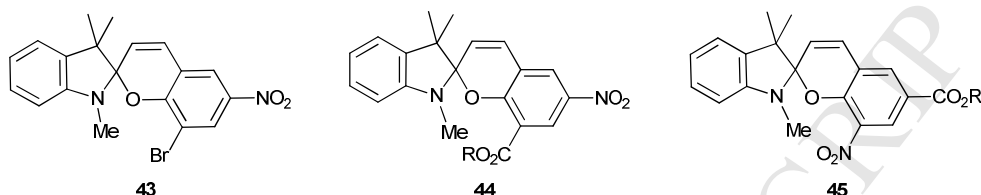
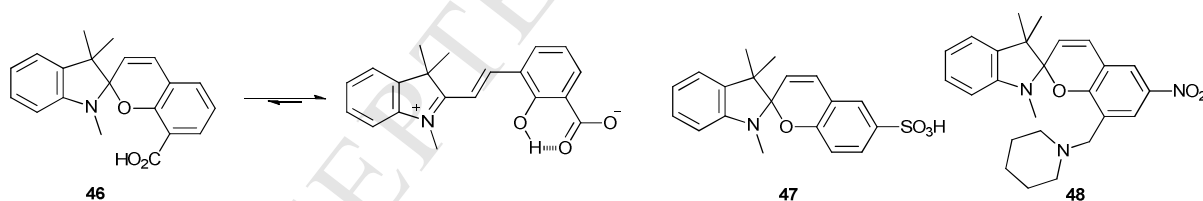


Figure 12. Nitrospiropyrans **43** – **45**

The presence of the 8-carboxylic acid unit alone (**46**) in the benzopyran unit is sufficient to stabilise, by intramolecular H-bonding, the ring – opened species which then exhibits negative photochromism (Scheme 10).<sup>119,120</sup> Placement of the carboxylic acid group at C-6 resulted in no photochromic response unless the mixture was acidified with malonic acid. In contrast to these foregoing observations the 6-sulfonic acid derivative **47** (Figure 13) displayed negative photochromism in a selection of polar protic solvents and in reversed micelles.<sup>121</sup>



Scheme 10. Ring-opening and stabilisation of spiropyran **46**

Figure 13. Structures of spiropyrans **47** and **48**

In addition to the presence of carboxylic acids at C-8 stabilising the phenoxide unit, much use has been made of substituents at C-8 which, in conjunction with the phenoxide unit, can in this position behave as bidentate ligands for various metal cations. The resulting complexes offer a stabilising influence for the merocyanine form and include the piperidinomethyl compound **48** (Figure 13).<sup>122</sup> The usefulness of the 8-chloromethyl-6-nitrospiropyran moiety **49** is exemplified by its conversion to negatively photochromic ammonium salts upon reaction with various tertiary amines and pyridine<sup>123</sup> and to crown ether systems **50**,<sup>124</sup> **51**<sup>125</sup>

and **52** (Figure 14).<sup>126</sup> The foregoing photoactive crown ethers **50** – **52** have been used to complex various metal ions. The addition of alkaline-earth metal ions to a solution of **50**  $n = 1$  unexpectedly resulted in intense colour generation with a maximum absorption at ca. 540 nm as a consequence of the cooperative capture of the metal ion by the crown and phenoxide units. Irradiation of the solution of the metal – crown species resulted in a very significant reduction of the colour presumably as a consequence of reformation of the spiropyran ring leaving the metal held by the crown unit alone. A similar spectroscopic response was noted upon complexation of **51** with  $Mg^{2+}$  ions.

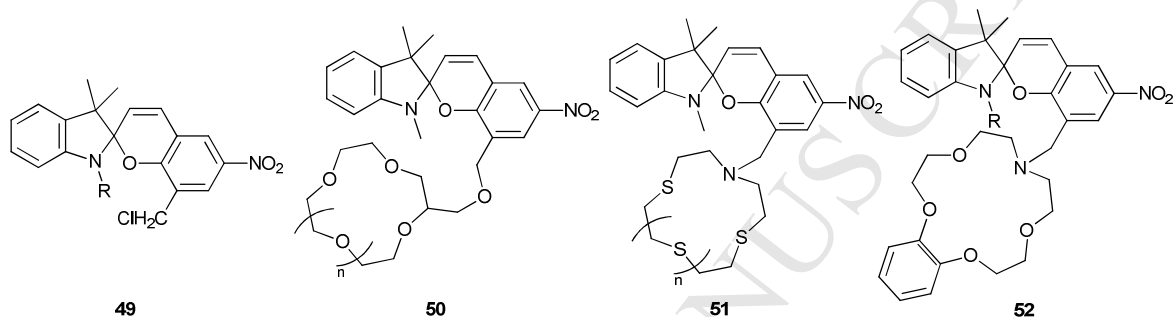
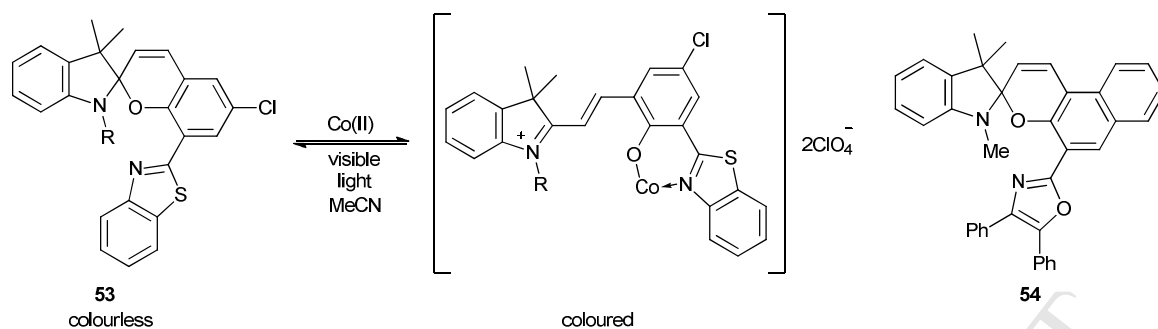


Figure 14. Macrocycle substituted spiropyrans (**50** – **52**) and their precursor **49**

The location of an ‘electron deficient’ azole unit adjacent to the pyran oxygen atom also facilitates ring – opening of the spiropyran unit in the presence of metal ions, the resulting metal ion – zwitterion complexes exhibit negative photochromism. In the absence of metal ions a normal photochromic response is recorded.<sup>127</sup> Thus the 2-benzothiazolyl substituted spiropyran **53** instantaneously forms an intensely coloured 1:1 complex with Co(II) and a 1:2 complex with Ni(II) ions in MeCN solution (Scheme 11). The strength of the complex was dependent upon the size of the *N*-alkyl substituent and irradiation of the complexes with white light resulted in release of the metal ion and regeneration of the inactive spiropyran.<sup>128</sup> Similar complex forming ability and thermally reversible photodecolouration with visible light was noted for the 4,5-diphenyloxazol-2-yl substituted spironaphthopyran **54** with Zn(II), Mn(II) and Cd(II) ions (Figure 15).<sup>129</sup>



Scheme 11. Transition metal assisted stabilisation of the zwitterionic form of spirocyanine **53**.

Figure 15. Spirocyanine **54**

During a study of the preparation of 6-styryl substituted spirocyanines the 6-formyl intermediate **55** (Figure 16) was prepared as dark violet crystals, an ethanolic solution of which, with  $\lambda_{\text{max}}$  at 530 nm, reversibly bleached upon irradiation with visible light. Replacement of the formyl group by a styryl unit (**56**) resulted in positive photochromism and led to the inference that two electron withdrawing groups conjugated to the oxide anion in the ring – opened form were essential for negative photochromism to be observed.<sup>130</sup> The closely related 8-formyl compound **57** (Figure 16) was described in an early patent,<sup>131</sup> however detailed examination of the properties of this compound was not made though the general text in the patent infers normal photochromic behaviour; a further study of the properties of this compound is warranted. Whilst negative photochromism was not discussed for the 6-benzoyl-8-nitrospirocyanine **58** (Figure 16) it was noted that this compound required more energy to ring close than a model compound.<sup>132</sup>

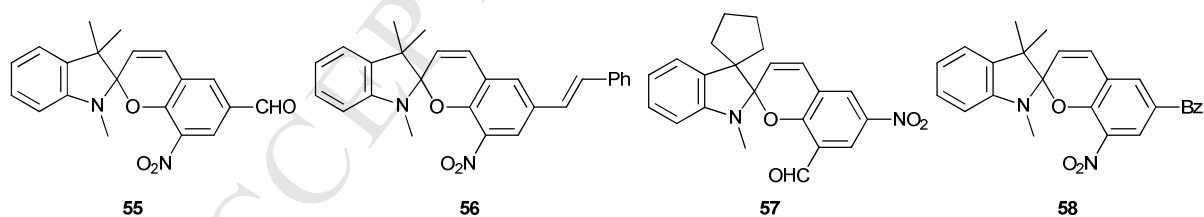
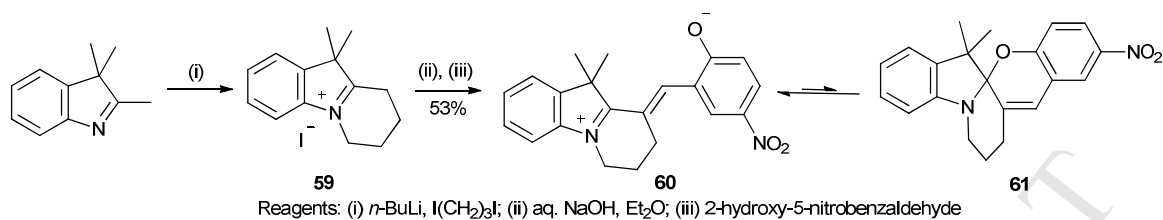


Figure 16. Substituted mononitrospirocyanines **55** – **58**

Quenching the anion derived from the action of *n*-butyllithium on 2,3,3-trimethyl-3*H*-indole with 1,3-diiodopropane gave the tricyclic indolinium iodide **59**. Liberation of the 10,10-dimethyl-6,7,8,10-tetrahydropyrido[1,2-*a*]indole (a novel Fischer base) and subsequent condensation with 2-hydroxy-5-nitrobenzaldehyde gave the zwitterion **60** as an amorphous purple solid. Solutions of **60** in polar protic (EtOH, MeOH) and polar aprotic (DMSO, MeCN) solvents were intensely coloured and could be bleached to spirocyanine **61** upon

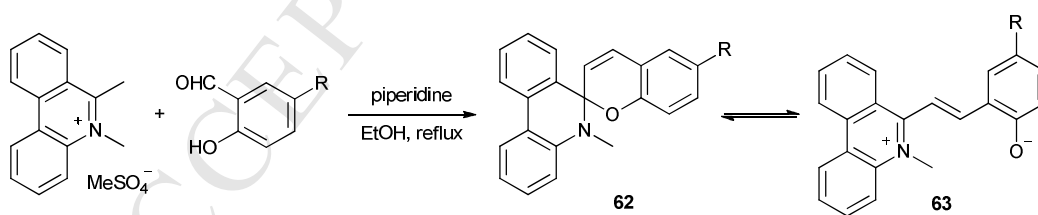
irradiation with visible light. The initial intense colour gradually recovered when the irradiation was ceased (Scheme 12).<sup>133</sup>



Scheme 12. Preparation of bridged nitrospiropyran **61**

The photochromism of various spiropyrans in which the traditional indoline unit has been replaced by either a ring expanded variant or by replacement of the *geminal* methyl unit with a chalcogen<sup>134</sup> has been explored and some of these systems exhibit negative photochromism.

The presence of an electron withdrawing nitro group was crucial for the isolation of the merocyanine derived from the condensation of 5,6-dimethylphenanthridin-5-ium methylsulfate with salicylaldehydes. When R = H the colourless spiropyran **62** prevailed, however when R = NO<sub>2</sub> the zwitterion **63** was isolated as red brown crystals (Scheme 13).<sup>135</sup> Through careful choice of solvent interconversion between the spiropyran and merocyanine for R = NO<sub>2</sub> could be accomplished. Thus refluxing a suspension of **63** R = NO<sub>2</sub> in *o*-dichlorobenzene resulted in the isolation of the pale yellow spiropyran **62** R = NO<sub>2</sub>. Dissolution of **62** R = NO<sub>2</sub> in refluxing ethanol resulted in isolation of the original zwitterion **63**.



Scheme 13. Preparation and reversible ring opening of **62**

Replacement of the *geminal* methyl group of the indolenine unit of spiropyran **1** with either S or Se, by base-catalysed condensation of a salicylaldehyde with either a 2-methylbenzothiazolium or a 2-methylbenzoselenazolium salt to afford either 3-methyl-3*H*-spiro[benzo[*d*]thiazole-2,2'-chromenes] **64** R = H or 3-methyl-3*H*-spiro[benzo[*d*][1,3]selenazole-2,2'-chromenes] **65** respectively (Figure 17), has been examined. Vandewyer *et al.*, noted the high stability of the ring-opened form of **64** R = H but



that introduction of a 3'-Me group (**64** R = Me), which destabilised the merocyanine system through steric interactions, resulted in photochromic properties.<sup>136</sup> In this report the influence of solvent polarity and presence and location of substituents on the kinetics of the decolouration reaction were delineated. Polar solvents and the presence of electron withdrawing substituents decrease the rate of decolouration.

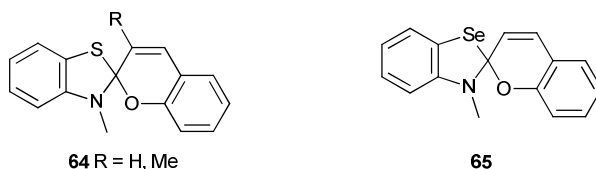
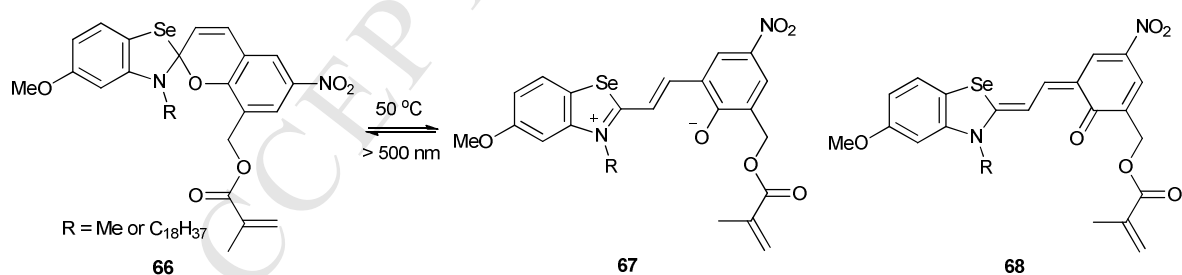


Figure 17. Thia and seleno substituted spiropyrans

Good negative photochromism has been demonstrated for the 6'-, 8'- disubstituted 3*H*-spiro[benzo[*d*][1,3]selenazole-2,2'-chromenes] **66** R = Me, C<sub>18</sub>H<sub>37</sub> with irradiation of DMSO solution with visible light ( $\lambda > 500$  nm) resulting in almost complete loss of the original absorption band at ca. 550 nm due to ring-closure of the zwitterion **67**. Complete recovery of the original purple colour was assisted by warming the solution to ca. 50 °C. The solvatochromic behaviour of **67** and <sup>1</sup>H NMR spectroscopy was used to affirm the zwitterionic rather than quinoidal form **68** (Scheme 14).<sup>137,138</sup> Co-polymerisation of **66** with methyl methacrylate afforded polymer systems which retained the negative photochromic behaviour though warming to 80 °C was required to fully recover the initial colour of a polymer thin film.<sup>139</sup>



Scheme 14. Thermal and photochemical behaviour of 3*H*-spiro[benzo[*d*][1,3]selenazole-2,2'-chromenes] **66**

In the absence of an 8'-substituent negative photochromism is still observed for the *N*-octadecyl derivative **69**.<sup>140</sup> Incorporation of a fluorescent *N*-pyrenylmethyl substituent in the benzologue **70** resulted in a dyad which exhibited negative photochromism on irradiation

with visible light of ca. 700 nm; irradiation with light of ca. 600 nm afforded no change in the absorption spectrum.<sup>141</sup>

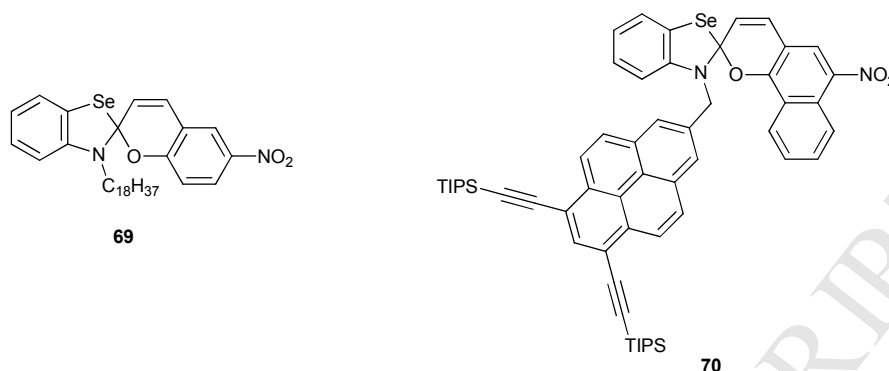
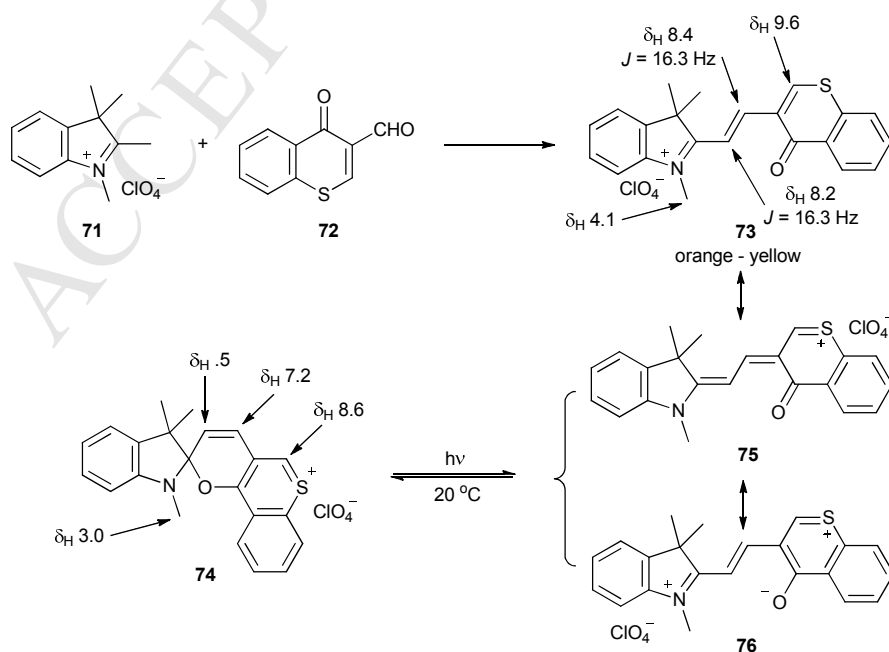


Figure 18. Spiro[benzo[*d*][1,3]selenazole-2,2'-chromenes] **69** and **70**

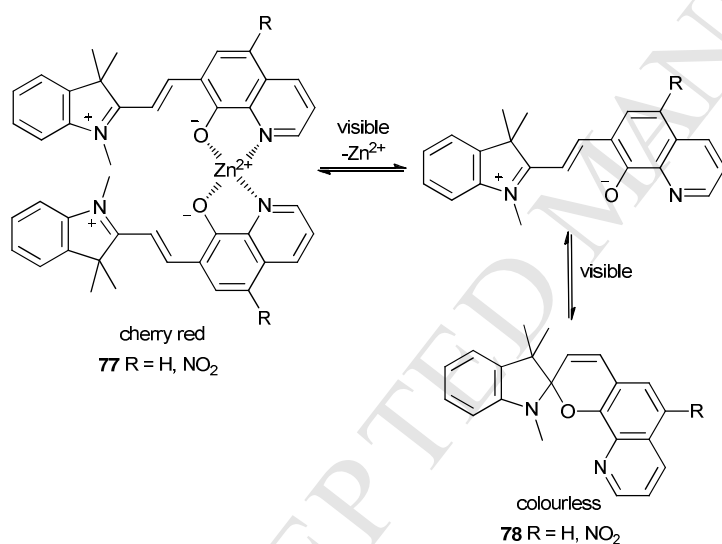
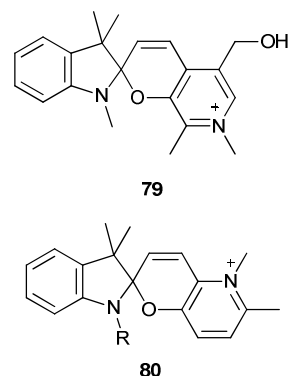
## 2.2 Heterofused Spiropyrans

Condensation of the indolinium salt **71** with 3-formyl-4*H*[1]-benzothiopyra-4-one **72** gave the orange – yellow ( $\lambda_{\max}$  456 nm,  $\epsilon_{\max}$   $34.7 \times 10^3 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$ , 1,2-DCE) merocyanine **73**. Irradiation of a solution of **73** with visible light ( $\lambda > 390 \text{ nm}$ ) for 60 s bleached the initial orange-yellow solution as the colourless spiropyran **74** formed. Recovery of the initial colour and intensity was accomplished within 125 min at 20 °C. The cyclisation of **73** may operate via the isomerisation and electrocyclicisation of the dienone **75** or via isomerisation and a subsequent polar nucleophilic addition process driven by the sulfur heteroatom via the thiopyrylium-4-olate **76** (Scheme 15).<sup>142</sup>



Scheme 15. Synthesis and photochromism of merocyanine **73**

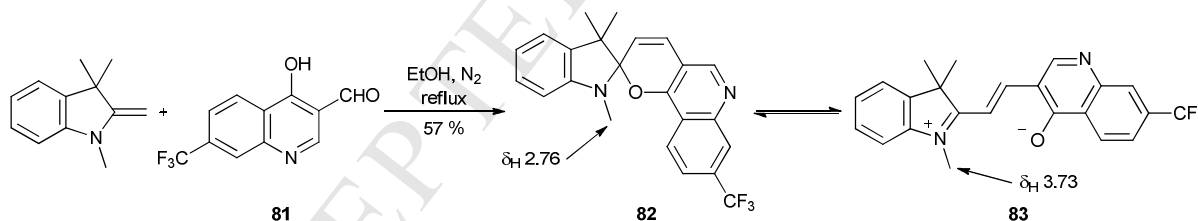
Incorporation of the 8-hydroxyquinoline moiety into a spiropyran unit as in **77** R = H has enabled fluorescent cation sensing with parts per billion sensitivity.<sup>143</sup> In an extension of this pioneering study the reversible photoinduced switching of metal complexation in an aqueous medium was described for the zinc(II) complex **77** R = H (Scheme 16).<sup>144</sup> Complex **77** R = NO<sub>2</sub> exhibits photoreversible decomplexation with loss of the associated intense red colour only in solvents of low dielectric constant, with solvent which are more polar than THF, e.g. MeCN, then the zwitterionic species is more efficiently stabilised and no photochromism is observed. Exposure of a solution of **77** R = H in MeCN to visible light results in the temporary ejection of the complexed Zn(II) ion with a concomitant loss of the cherry red colour ( $\lambda_{\text{max}}$  564 nm) in ca. 8 s as the metal free species cyclise to the colourless spiropyran **78**. Upon cessation of irradiation the Zn(II) ion is recaptured and the colour is returned.

Scheme 16. Zn(II) complexation of irradiated **78**Figure 19. Pyridinium fused spiropyrans **79** and **80**

Interestingly normal photochromism was observed in chloroform solution and in the solid-state for the pyridinium fused spiropyrans **79** and **80** (R = Me) (Figure 19), with the pale yellow colour of the spiro form becoming intense red upon UV irradiation leading to the ring opened form. The absence of an isosbestic point in the decay profile of **79** suggested a more complex equilibrium and allowed the inference that the presence of the CH<sub>2</sub>OH group facilitated dimer formation via H-bonding between molecules of the closed and open ring forms leading to an equilibrium with more than two components.<sup>145</sup> However, embedding

analogues of **80** R = Me, Ph, *n*-hexyl, hydroxyethyl, in silica gel prepared by gelation of tetramethyloxysilane revealed competition between negative and normal photochromism.<sup>146</sup>

Reimer-Tiemann formylation of 4-hydroxy-7-trifluoromethylquinoline gave the salicylaldehyde analogue **81** in 16 % yield. Subsequent condensation of **81** with Fischer's base in refluxing EtOH gave a purple crystalline solid on recrystallization from EtOH (Scheme 17). The <sup>1</sup>H NMR spectrum of this material recorded in CDCl<sub>3</sub> solution revealed a mixture of the spiroopyran **82** ( $\delta_{\text{NMe}}$  2.76) and the zwitterion **83** ( $\delta_{\text{NMe}}$  3.73), in which **82** was present in ca. 40%.<sup>147</sup> The <sup>1</sup>H NMR spectrum recorded in DMSO-d<sub>6</sub> only showed signals attributable to **83** in accord with previous reports of highly polar solvents favouring the zwitterionic species in the equilibrium.<sup>66</sup> X-ray crystallography revealed that the purple solid was the zwitterion **83**, which was stabilised by a head-to-tail (H-type aggregation) crystal packing with intermolecular dipole interactions between the layers. Negative photochromic behaviour was observed only for solutions of **83** stored below -30 °C, though the bleaching process could be accelerated by irradiation with visible light. Protonation of **83** with MeSO<sub>3</sub>H resulted in the loss of the purple colour ( $\lambda_{\text{max}}$  543 nm) with the concomitant emergence of a new band at 450 nm (yellow-orange solution); this hypsochromic shift of the absorption maxima of the zwitterion upon protonation has been observed for other negatively photochromic spiroopyrans.<sup>79,95</sup>

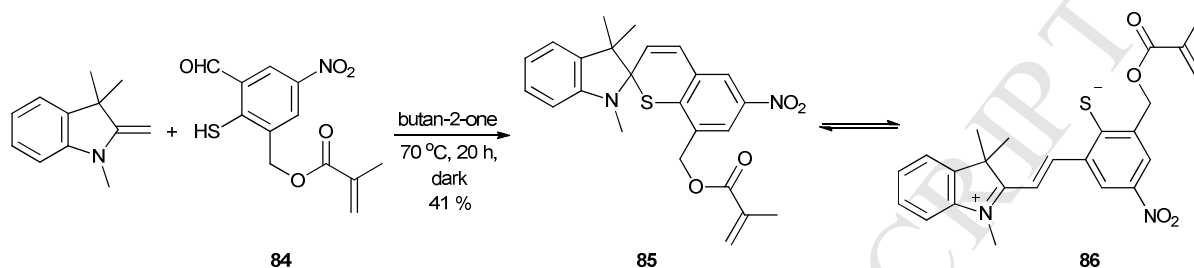


Scheme 17. Synthesis and photochromism of quinoline fused spiroopyran **82**

### 2.3 Spirobenzothiopyrans (spiro[2*H*-[1]-benzothiopyran-2,2'-indolines])

There are considerably fewer examples of spirothiopyrans than the oxygen isosteres, presumably as a consequence of either the lack of availability of commercial starting materials or the reluctance of chemists to synthesise such precursors which involves the handling of malodorous sulfur compounds. There would appear to be no reported examples of spirobenzothiopyrans which exhibit negative photochromism. However, the acrylate derivative **85**, obtained from the condensation of 1,3,3-trimethyl-2-methyleneindoline with the thiosalicylaldehyde **84** (Scheme 18), displays some interesting solvent dependent

properties.<sup>148,149</sup> Irradiation of a methanol solution of **85** for 3 h with 365 nm light results in the development of a blue-green solution from which deep blue needles of the photomerocyanine **86** could be isolated (5.4 % yield) and examined by X-ray crystallography revealing a zwitterion structure. Others have commented upon the highly zwitterionic nature of the ring-opened forms of spirobenzothiopyrans.<sup>150</sup>



Scheme 18. Synthesis and reversible ring-opening of spirothiopyran **85**

The  $^1\text{H}$  NMR spectrum of **86** has been examined in acetone- $d_6$  and in DMSO- $d_6$  (Figure 20). Irradiation of the acetone- $d_6$  solution with visible light (500 W,  $\lambda > 500$  nm) resulted in photobleaching of the deep blue - green solution to afford a yellow solution, the  $^1\text{H}$  NMR spectrum of which was in complete agreement with the signals for **85**.<sup>151</sup>

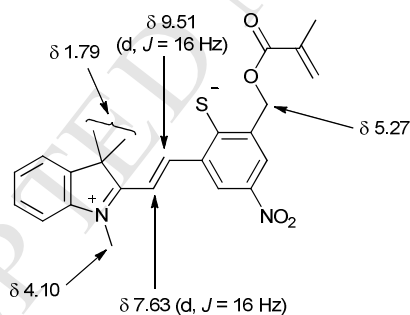
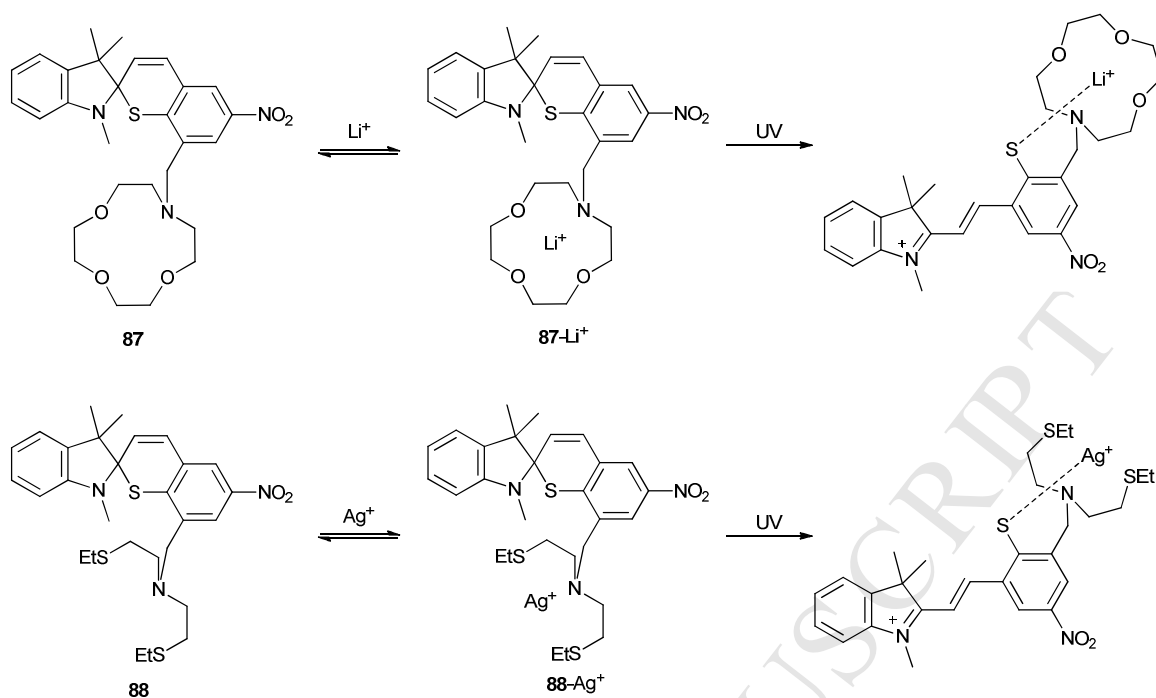


Figure 20. Selected  $^1\text{H}$  NMR signals of zwitterion **86** ( $D_6$ -DMSO)

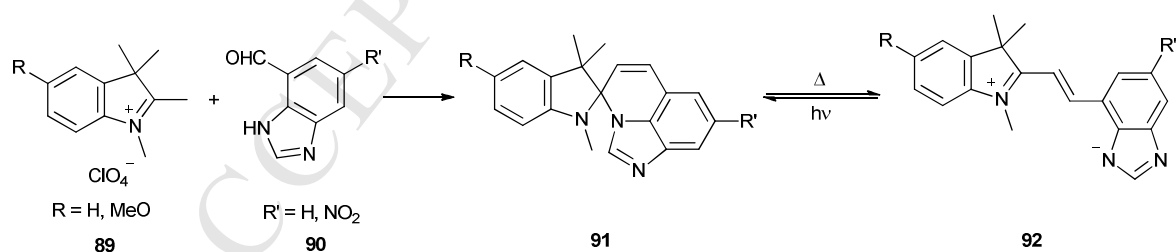
Spirobenzothiopyrans decorated with either an 8-(1,4,7-trioxa-10-azacyclododecane) crown ether unit, **87**,<sup>152</sup> or an 8-(bis(2-(ethylthio)ethyl)amino) ligating unit, **88**,<sup>125</sup> do not spontaneously ring open upon addition of a solution of a metal ion salt, unlike their structurally related spirobenzopyran counterparts e.g. **50**.<sup>124</sup> Photoirradiation of the pale coloured solutions of either **87**- $\text{Li}^+$  or **88**- $\text{Ag}^+$  complexes induces ring-opening to the respective stabilised, intensely coloured zwitterionic complexes (Scheme 19).



Scheme 19. Metal complexing behaviour of spirothiopyrans **87** and **88**

## 2.4 1',3',3'-Trimethylspiro[imidazo[4,5,1-*ij*]quinoline-4,2'-indolines]

The base promoted condensation between the indolinium salts **89** and the formylbenzimidazoles **90** affords the spiro[imidazo[4,5,1-*ij*]quinoline-4,2'-indoline] **91** which equilibrates in methanol to afford the orange zwitterion **92**. Exposure to light of 464 nm for 3 minutes resulted in almost complete bleaching of the colour which was recovered upon standing for 2 days (Scheme 20).<sup>153-155</sup>

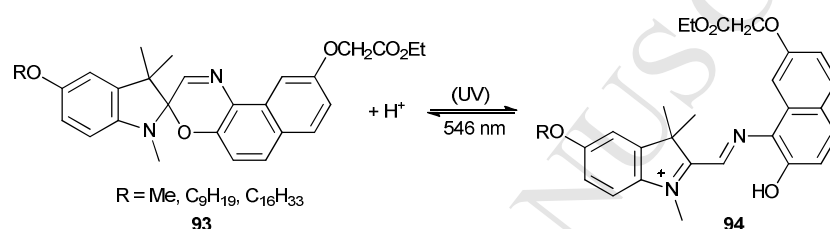


Scheme 20. Preparation of spiro[imidazo[4,5,1-*ij*]quinoline-4,2'-indoline] **91**

## 2.5 Spiroindolinonaphthoxazines

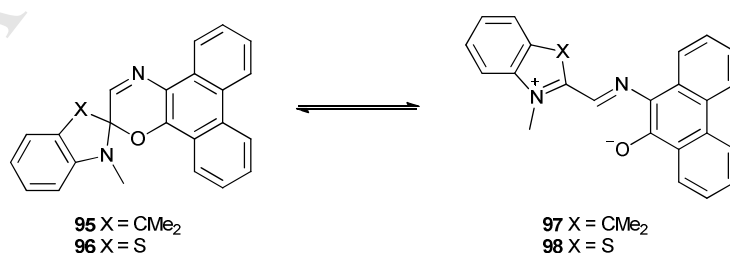
The positive photochromic response of spiroindoline-2,3'-naphtho[2,1-*b*][1,4]oxazines is well known and such molecules have been widely studied in the context of their application in ophthalmic sun lenses where they are typically employed to generate blue, purple and green shades.<sup>156-159</sup>

There appears to be no reports of simple spiroindoline-2,3'-naphtho[2,1-*b*][1,4]oxazines exhibiting negative photochromism though negative photochromic behaviour has been observed for a protonated oxazine. The addition of HCl to a colourless ethanolic solution of the oxazines **93** results in the gradual evolution of a purple colour with an intense absorption band at 532 nm due to the protonated zwitterionic forms **94**. Similarly, acidification of a freshly irradiated solution of **93**, which displayed the typical absorption maximum at 621 nm with a shoulder at ca. 580 nm, resulted in the evolution of the band at 532 nm with concomitant loss in intensity at 621 nm. Under visible light irradiation ( $\lambda = 546$  nm) the intense purple colour rapidly faded to near colourless but recovered the purple hue upon storage of the solution in the dark (Scheme 21).<sup>160</sup>



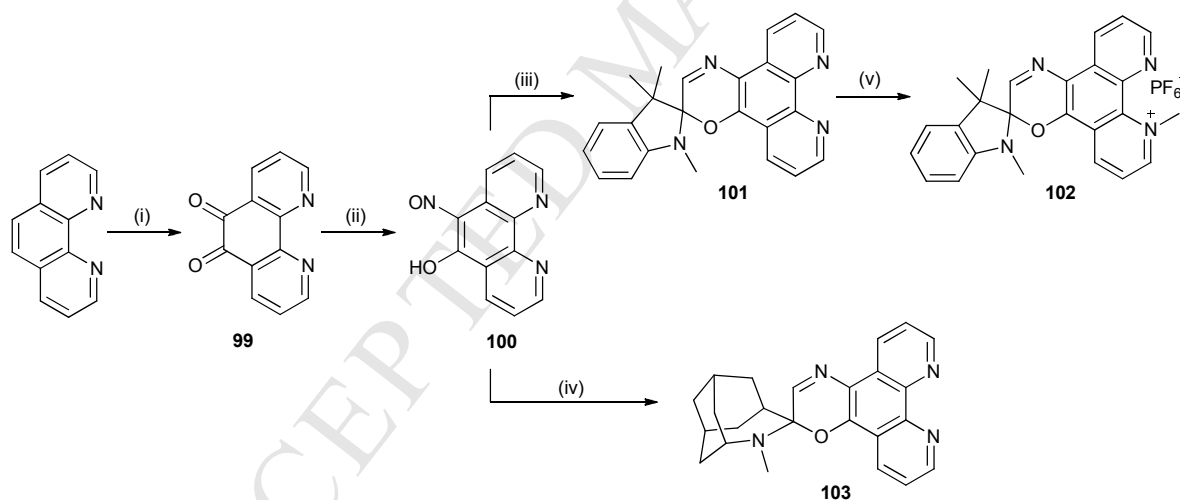
Scheme 21. Reversibility of protonated spirooxazine **93**

The 1,3,3-trimethylspiro[indoline-2,2'-phenanthro[9,10-*b*][1,4]oxazine] **95** X = CMe<sub>2</sub> and the 3-methyl-3*H*-spiro[benzo[*d*]thiazole-2,2'-phenanthro[9,10-*b*][1,4]oxazine] **96** X = S were obtained from the condensation between 10-nitrosophenanthren-9-ol and either Fisher's base or 3-methyl-2-methylene-2,3-dihydrobenzothiazole, respectively. Whilst **95** X = CMe<sub>2</sub> exists as an equilibrium mixture of the spirooxazine and zwitterion **97** in which the spirooxazine dominates, UV irradiation generated an intense blue coloured solution with  $\lambda_{\text{max}} = 592$  nm. However, the sulfur-containing analogue **96** X = S could be crystallised in the zwitterionic form **98** and toluene solutions showed negative photochromism with the turquoise solution ( $\lambda_{\text{max}} = 613$  nm) fading (Scheme 22).<sup>161,162</sup>



Scheme 22. Spirooxazine – zwitterion interconversion

The positive photochromism of the spiro[indoline-2,2'-[1,4]oxazino[2,3-*f*][1,10]phenanthroline] **101** in non-polar and polar solvents has been reported on several occasions.<sup>163-166</sup> The synthesis of **101** commences with the oxidation of commercially available phenanthroline with either KBr or NaBr in a mixture of c. H<sub>2</sub>SO<sub>4</sub> and c. HNO<sub>3</sub> at reflux<sup>167-173</sup> or under milder conditions using KBrO<sub>3</sub> 60% aq. H<sub>2</sub>SO<sub>4</sub> at rt to afford the quinone **99**.<sup>174</sup> Oximation of the quinone affords the 6-nitroso-1,10-phenanthrolin-5-ol **100** which, depending upon reaction conditions, may be isolated as either the hydrochloride salt or the free base (Scheme 23).<sup>166,175,176</sup> Here the authors would add a note of caution as **100** is a severe nasal mucus membrane irritant inducing sneezing episodes and as such must only be manipulated in an efficient fume cupboard. An alternative strategy to **100** relies upon the nitrosation (NaNO<sub>2</sub>, aq. HCl) of 5-hydroxy-1,10-phenanthroline.<sup>177</sup> Routine condensation of either 1,2,3,3-tetramethyl-3*H*-indol-1-ium iodide in *i*-PrOH containing piperidine<sup>178</sup> or Fisher's base in toluene<sup>166</sup> with **100** affords the target oxazine **101** in moderate yield. Monomethylation of **101** with an excess of methyl iodide at rt reportedly occurs regioselectively to afford the 9-methylated isomer **102** in excellent yield.<sup>179</sup>



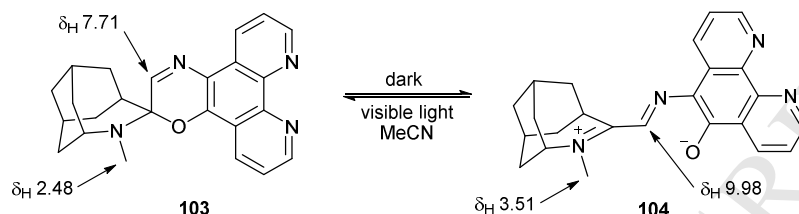
Reagents: (i) either KBr, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> or KBrO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, (ii) NH<sub>2</sub>OH.HCl, aq. EtOH; (iii) either 1,3,3-trimethyl-2-methyleneindoline, PhMe (25 %) or 1,2,3,3-tetramethyl-3*H*-indol-1-ium iodide, piperidine, *i*-PrOH (38 %); (iv) 4,5-dimethyl-4-azahomoadamant-4-enium iodide, Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, mol. sieve (32 %); (v) MeI, then chromatography AcMe, 10% NH<sub>4</sub>PF<sub>6</sub> (94 %)

#### Scheme 23. Construction of spiro[azacycle-2,2'-[1,4]oxazino[2,3-*f*][1,10]phenanthrolines]

The azahomoadamantyl analogue **103** was prepared by liberation of the 4-methyl-5-methylene-4-azahomoadamantane from the 4,5-dimethyl-4-azahomoadamant-4-enium iodide with Et<sub>3</sub>N and subsequent condensation with 6-nitroso-1,10-phenanthrolin-5-ol **101** (Scheme 23).<sup>166</sup> In marked contrast to the behaviour of **101** in polar solvents such as MeCN or MeOH the thermal equilibrium for **103** lies towards the oxazine ring-open form **104**. Visible light



irradiation of a purple solution of **104** results in reversible photobleaching of the colour (Scheme 24). Crystallisation of **104** from EtOAc afforded two pseudo polymorphs; the trihydrate form of which was shown to have strong H-bonds with water molecules and possessed bondlengths for the chromophore unit which were more closely aligned with a zwitterionic structure.



Scheme 24.  $^1\text{H}$  NMR chemical shift data for azahomoadamantyl analogue **103**

The ability of the azahomoadamantyl unit to stabilise the zwitterionic species leading to a negative photochromic response in **103** has been harnessed in the modulation of short wavelength fluorescence in the dyads **105** and **106** through visible light cycling of the oxazine unit (Figure 21).<sup>180</sup> The application of the negative photochromic behaviour of **107** has been employed for the photoswitching of polymer nanoparticle fluorescence (Figure 21).<sup>181</sup>

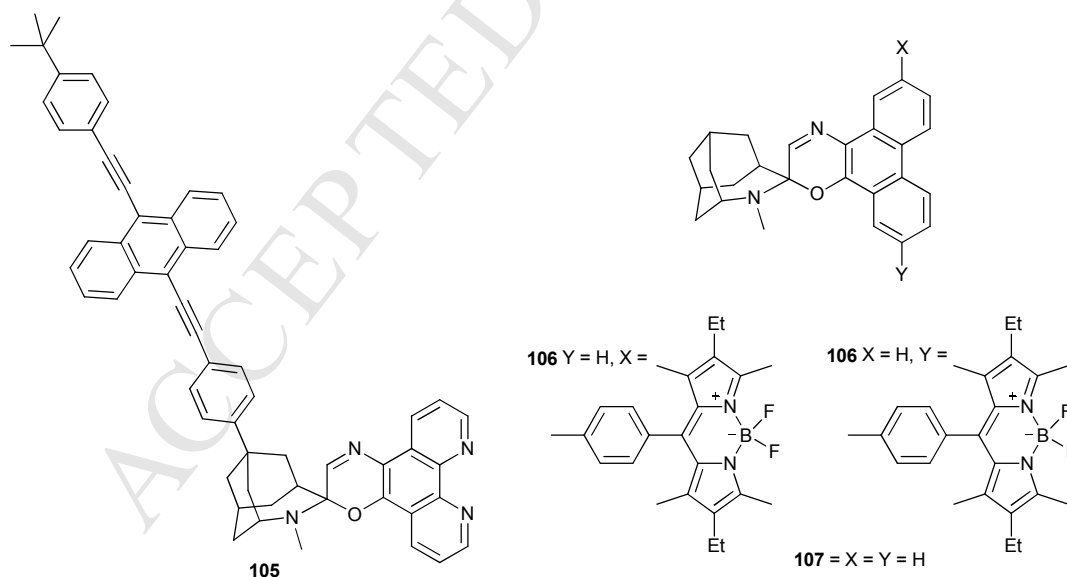
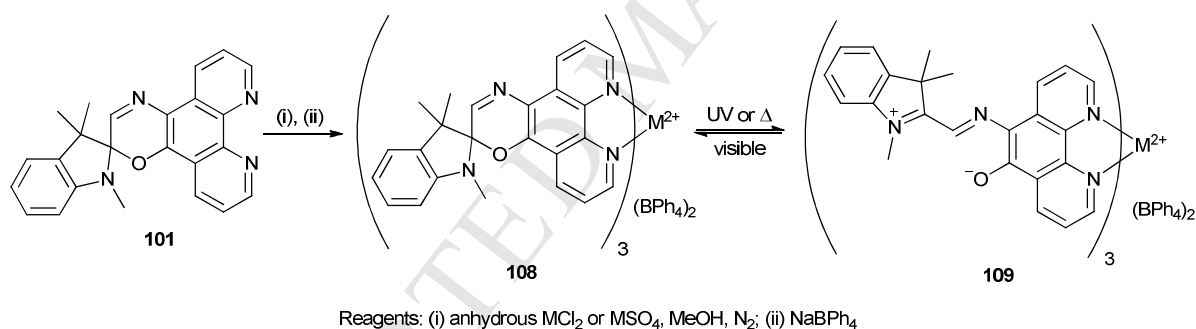


Figure 21. Structures of spirooxazines **105** – **107**

Unsurprisingly the phenanthroline unit in the spiro[indoline-2,2'-[1,4]oxazino[2,3-f][1,10]phenanthroline] **101** serves as an excellent bidentate ligand and has been used to obtain a variety of transition metal complexes of the type **108** where the metal cation  $\text{M}^{2+}$  was

selected from Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) in the original studies by Frank *et al.*, (Scheme 25).<sup>182,183</sup> Further examples of related metal complexes have been obtained from variants of **101** derived from 5-substituted Fischer bases<sup>176,184,185</sup> interestingly the influence of the *N*-substituent of the Fischer's base upon the photochromic response has not been examined. Metal complex formation results in the formation of deep blue solutions from which the complexes, with tetraphenylborate counterions, were isolated as blue solids. The transition metal complexes **108** afford an intense blue solution in MeCN, the precise absorption maxima of which varies over the range 591 nm [Co(II)] to 605 nm [Fe(II)]. The blue solutions contain an equilibrium mixture of **108** and **109** which can be readily reversibly bleached upon irradiation with visible light of a wavelength > 600 nm; the blue colour, attributed to **109**, recovers upon storage in the dark at rt (Figure 22 illustrates the thermal recovery of **109** (MeOH solution) after bleaching with white light). Variable temperature magnetic susceptibility measurements suggested deviations from cubic symmetry associated with desymmetrization induced by a dependence of the ligand field strength on the open / closed state of the oxazine ring.



Scheme 25. Metal complexation behaviour of spiro[indoline-2,2'-[1,4]oxazino[2,3-*f*][1,10]phenanthroline] **101**

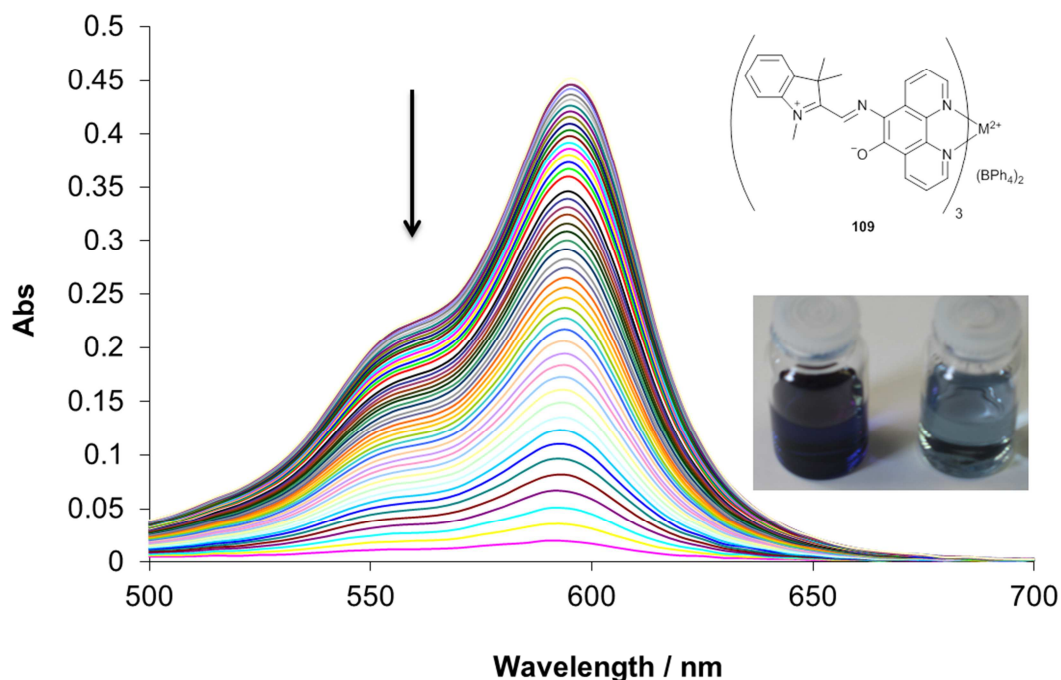
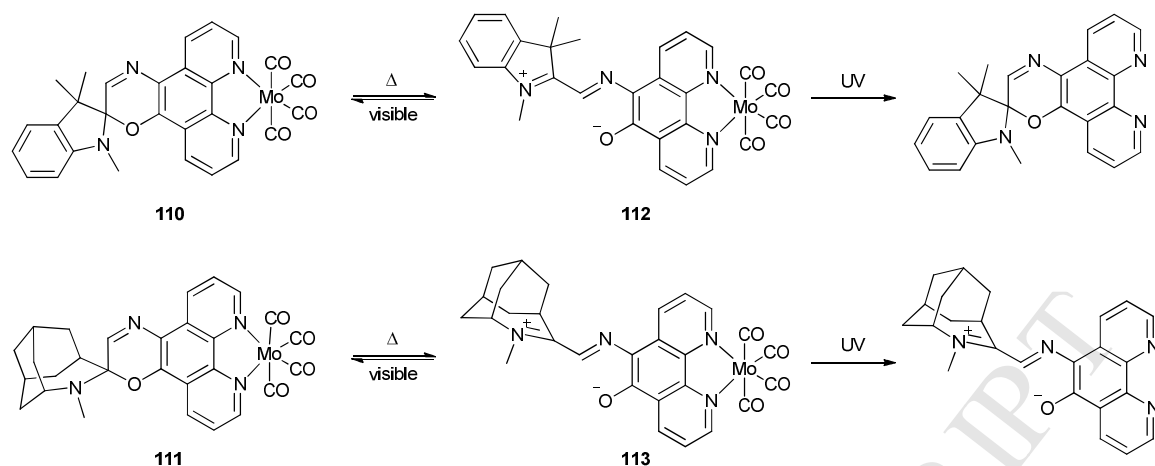


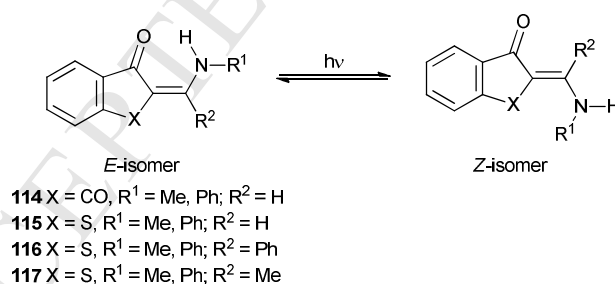
Figure 22. Thermal recovery of **109** (MeOH solution) after bleaching with white light

The thermal equilibrium constants for the molybdenum tetracarbonyl complexes **110** and **111**, derived from **101** and **103** respectively, obtained from their  $^1\text{H}$  NMR spectra by comparison of the relative integrals of the azomethine signals for the ring-closed ( $\sim \delta$  8) and ring-opened isomers ( $\sim \delta$  10) revealed that the oxazine form **110** was more prevalent in solution for the indolyl substituted compound but the zwitterion form **113** was more dominant for the azahomoadamantyl derivative.<sup>186</sup> Steady-state irradiation of solutions of **110/112** and **111/113** with visible light ( $\lambda = 568$  nm) resulted in a decrease of the intensity of the purple ( $\lambda_{\text{max}} \sim 570$  nm) solutions. Upon cessation of the irradiation the solutions recovered their initial equilibrium intensity. Conversely, UV irradiation resulted in an increase of the intensity of the maximum absorption band at ca. 570 nm with a concomitant decrease in the intensity of the weaker metal-to-ligand charge transfer (MLCT) band at ca. 490 nm as the residual oxazine in the equilibrium solution undergoes ring-opening to the photo-zwitterion. Upon cessation of irradiation however, the intensity of the MLCT band at ca. 490 nm is not recovered as UV-induced decomplexation had occurred and the absorption maximum of the decomplexed zwitterion / oxazine had been shifted to lower wavelength. Prolonged cycles of UV irradiation and thermal relaxation eventually led to degradation of the oxazine structures (Scheme 26).

Scheme 26. Photochemical and thermal behaviour of **110** and **111**

## 2.6 2-(Alkylidene)benzo[*b*]thiophen-3(2*H*)-ones

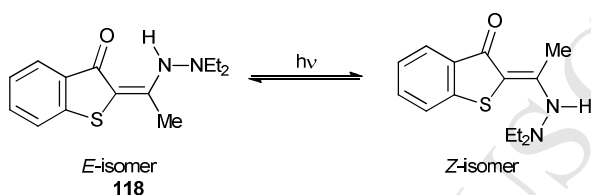
Dubonosov *et al.*, have summarised the studies on negative photochromism undertaken at the Institute of Physical and Organic Chemistry (Rostov State University) on hetero- and carbocyclic systems containing an enaminone (ketoenamine) unit.<sup>187</sup> Irradiation of a solution of either of the enaminones **114** or **115**, which were shown to be present in solution as an unequal mixture of the *E*- and *Z*- isomers, resulted in their interconversion (Scheme 27). The small, 3 – 4 nm, difference between  $\lambda_{\max}$  of the major and minor geometrical isomers enabled the claim of negative photochromism to be made.

Scheme 27. Photochemical interconversion of *E*- and *Z*- isomers of enaminones **114** – **117**

Introduction of a phenyl substituent on the exocyclic methylene unit stabilised the *E*-isomer **116** and prevented photochromism irrespective of the nitrogen substituent (R<sup>1</sup>). However, for **117** with R<sup>1</sup> = Ph, R<sup>2</sup> = Me negative photochromism was observed. Thus irradiation of an initial equilibrium mixture of the *Z*- and *E*- isomers of **117** at the long wavelength absorption maxima of ca. 436 nm resulted in the decrease of the intensity of this long wavelength absorption band with a concomitant increase in the absorption maxima at ca. 420 – 425 nm

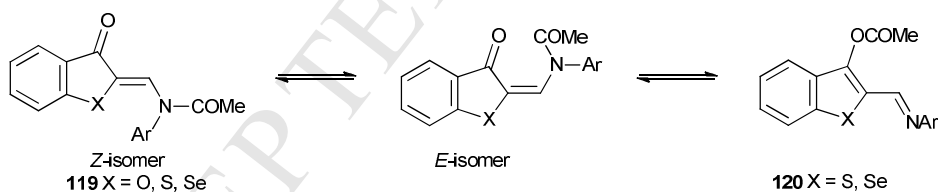
(Scheme 27). It was noted that for systems of type **114** – **117** the likelihood of photoinduced geometrical isomerism is a balance between the strength of the intramolecular H-bond and steric interactions.

Negative photochromism with greatly improved band separation  $\Delta\lambda_{\max} \sim 80$  nm was observed for the hydrazinoethylidenebenzo[*b*]thiophen-3(2*H*)-one **118**. The *E*-isomer appears orange – yellow and bleaches completely in ca. 12 minutes upon irradiation at 436 nm. The thermal reversion *Z*  $\rightarrow$  *E* is markedly temperature dependent and at 233 K the *Z*-isomer persists for 3 h (Scheme 28).



Scheme 28. Photochromism of hydrazinoethylidenebenzo[*b*]thiophen-3(2*H*)-one **118**

The *N*-acylated benzo[*b*]furan derivative **119**, X = O displays reversible *Z* / *E* photoisomerism whereas the benzo[*b*]- thiophene **119**, X = S and selenophene **119**, X = Se exhibit a thermal acyl group migration in the *E*-isomer to afford the *O*-acyl derivatives **120** (Scheme 29).



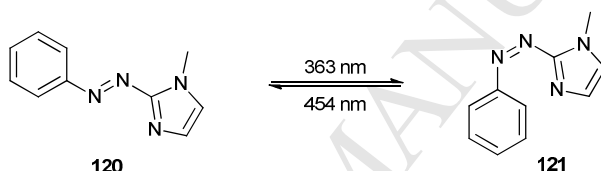
Scheme 29. Photochemical isomerisation of chalcogens **119**

## 2.7 Azobenzenes

Azo dyes and pigments have been extensively commercialised due to the broad range of intense colours and typically good lightfastness when appropriately substituted.<sup>188-191</sup> The *E*  $\leftrightarrow$  *Z* photoisomerisation of azobenzenes has attracted considerable attention over the last 40 or so years principally as a means of switching between two orientations or inducing motion in host systems.<sup>192-199</sup> Very recently there has been a resurgence in interest in azobenzene isomerisation with several tetra *ortho*-substituted azobenzenes being employed as in vivo

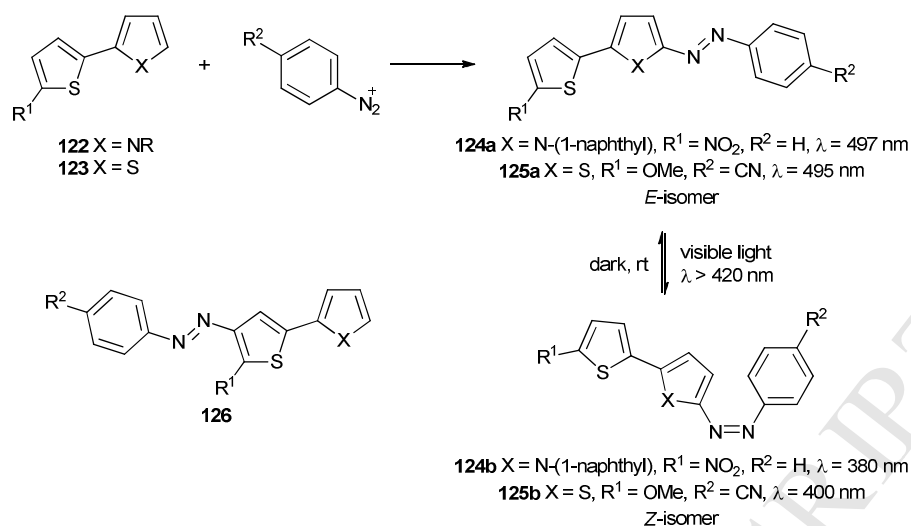
photoswitches.<sup>200,201</sup> For tetra *ortho*-fluoro substituted azobenzenes visible light irradiation ( $\lambda > 500$  nm) induced *E*- to *Z*- isomerisation which afforded appreciable amounts of long-lived *Z*-isomers with  $\lambda_{\text{max}}$  hypsochromically shifted relative to their *E*-precursors.<sup>202,203</sup> In contrast to these reports focussing on enhanced switching performance and switching – motion inducing behaviour relatively little attention has been focussed on the colour switching, photochromism, of these systems.

Irradiation of a toluene solution of the *trans*-2-(phenylazo)imidazole **121** resulted in efficient conversion to the *cis*-isomer **122** which absorbed at  $\sim 320$  nm, hypsochromically shifted by ca. 40 nm relative to the major absorption band of the *trans*-isomer **121**. <sup>1</sup>H NMR spectroscopy was employed to determine the *cis:trans* ratio of 98:2 at a stationary state achieved upon irradiation with light of 363 nm (Scheme 30). Whilst thermal reversion was not discussed, photochemical bleaching ( $\lambda = 454$  nm) was effective.<sup>204</sup>



Scheme 30. Photochemical geometrical isomer switching of 2-(phenylazo)imidazole **121**

Two series of heterocyclic azo dyes **124a** and **125a** derived from 5-(2-thienyl)pyrroles **122**<sup>205</sup> and 2,2'-bithiophenes **123**<sup>206</sup> respectively, have recently been described. Irradiation of a solution of either **124a** or **125a** with visible light ( $> 420$  nm) led to the rapid decrease in intensity of up to a maximum 50% intensity of the long wavelength absorption band with the concomitant emergence of a short wavelength absorption band at ca. 390 nm which was assigned to the *Z*-isomers (**124b**, **125b**). A photostationary state containing both the *E*- and *Z*-isomer was established in ca. 30 s but which remains appreciably coloured leading to moderate contrast between the two states. Upon cessation of irradiation the original intensity was gradually restored (Scheme 31). Interestingly, a further series of isomeric dyes **126**, also derived from **123**, only exhibited a very weak photochromic response but were moderately fluorescent.<sup>206</sup> It may be that the weak photochromic response results as a consequence of the fluorescence affording a more rapid and energetically favourable 'relaxation' process to the azo bond isomerism. The photochromic switching of an esoteric series of azobenzene bound bis(terpyridine) complexes of transition metals has been reviewed.<sup>207</sup>



Scheme 31. Synthesis, structure and photoisomerisation of heterocyclic azo dyes **124** – **126**

## 2.8 Imidazolyl Dimers

Whilst exploring the synthesis of further analogues of hexaarylbiimidazoles<sup>208</sup> in which the two imidazole cores are tethered together Abe *et al.*,<sup>209-211</sup> made the serendipitous discovery of a new biimidazole which exhibited negative photochromism. The synthetic strategy commences with lithium – halogen exchange of **127** to introduce the aldehyde functions into the 1,1'-binaphthyl unit and then classical construction of the imidazole nucleus, the oxidation of which proceeds anomalously to afford the orange species **128** which upon exposure to visible light bleaches (Scheme 32). The orange hue is returned in ca. 20 minutes in the dark at room temperature. The absorption spectra as a function of time recorded in toluene at room temperature immediately after the visible light bleaching of **128** are presented in Figure 23; and clearly show the recovery of the orange hue, with λ<sub>max</sub> at ca. 490 nm. The photodecolouration was shown to proceed via short-lived radical with a half-life of 9.4 μs.<sup>212</sup>



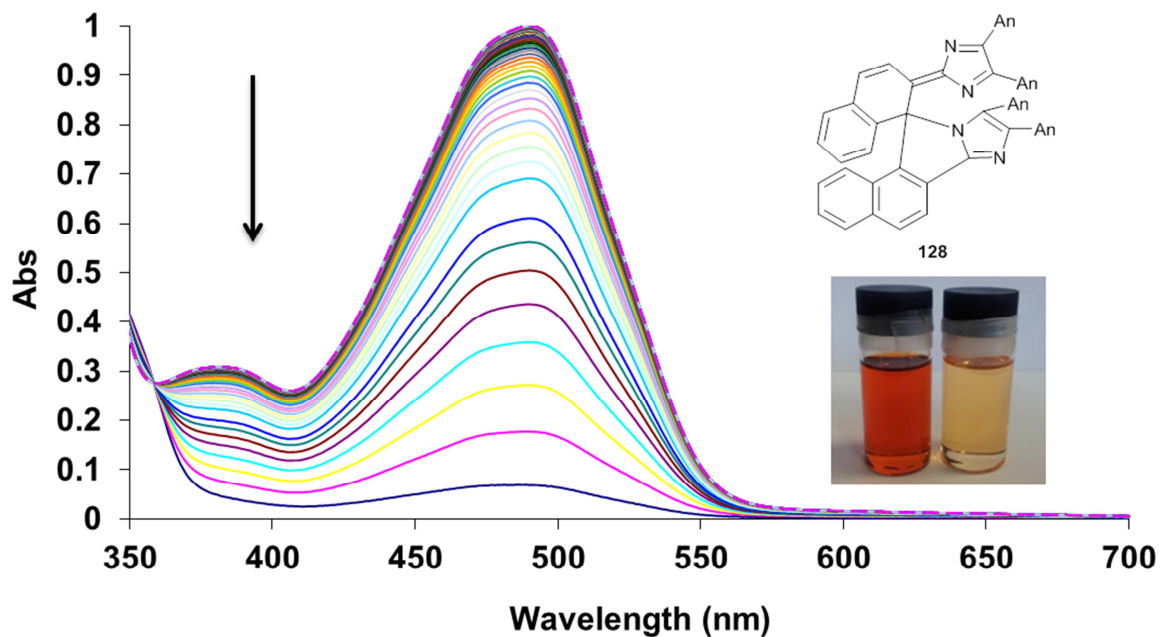
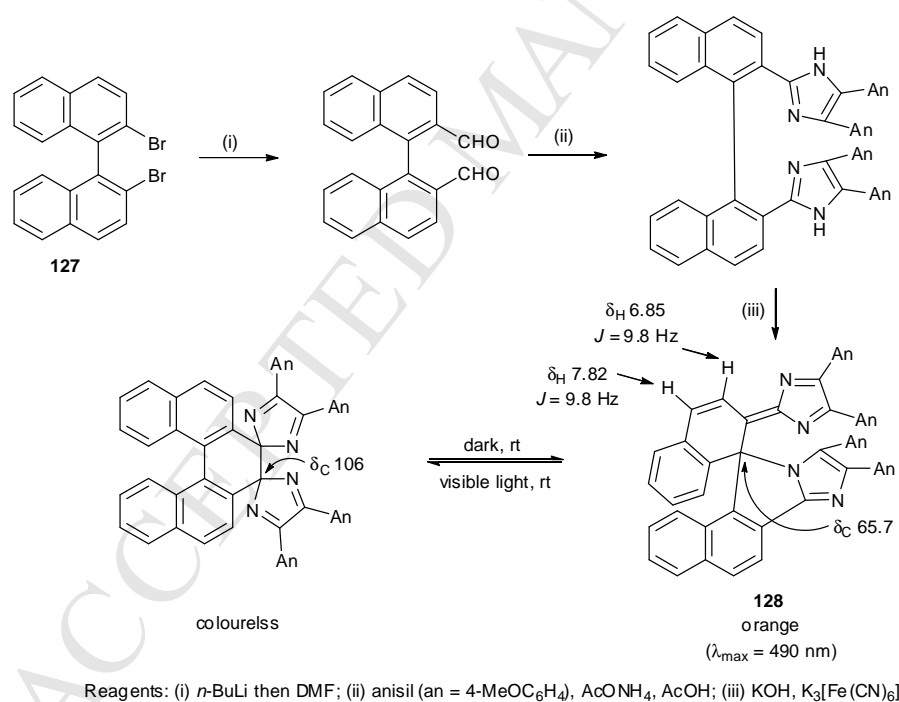


Figure 23. Photochromic response of Abe's complex biimidazole **128**

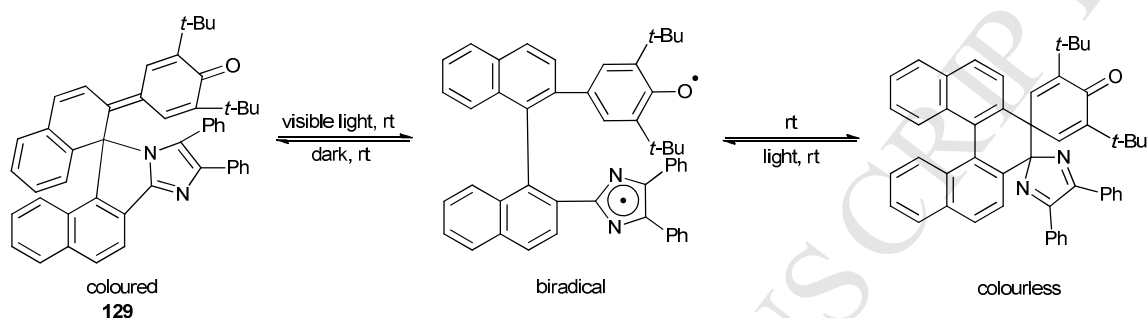


Scheme 32. Synthesis of complex biimidazole **128**

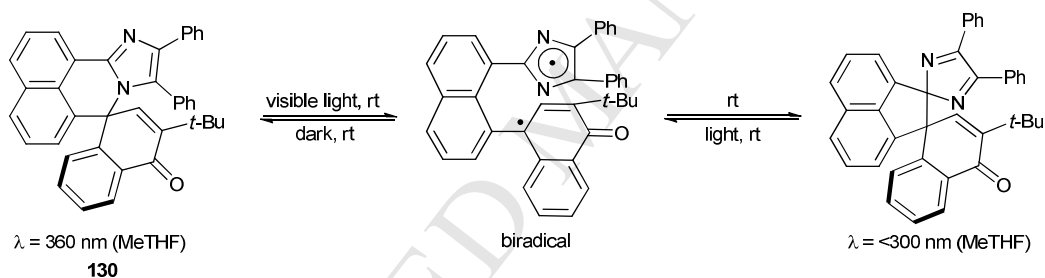
The negative photochromic properties of this new system have been tuned to afford the unsymmetrical analogues **129** and **130**. For **129** replacement of one imidazole unit by a 2,6-di-*t*-butylphenol unit results in instantaneous decolouration with thermal recovery of the initial orange – yellow colour in ca. 1.9 s (Scheme 33).<sup>213</sup> Greater structural variation was



accomplished using a 1,8-disubstituted naphthalene scaffold as in **130**. In this instance the long wavelength absorption band appears in the UV region at ca. 360 nm and is diminished in MeTHF at 153 K after irradiation with 365 nm light with a new band appearing at shorter wavelength. Thermal restoration of the original band was accomplished in ca. 175 ms at 298 K (Scheme 34). The presence of an asymmetric carbon in the structure makes fast chiroptical switching available.<sup>214</sup>



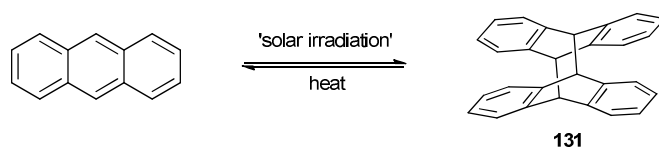
Scheme 33. Photochromism of fused imidazole **129**



Scheme 34. Photochromism of 1,8-disubstituted naphthalene derived photochrome **130**

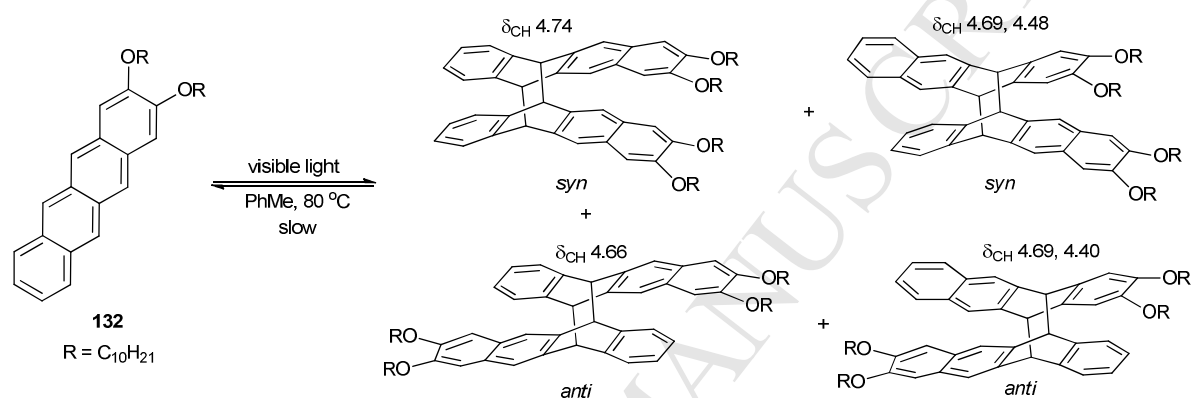
## 2.9 Acenes

The photodimerization of anthracene is one of the oldest established photochemical reactions and was reported in 1866.<sup>215</sup> The photocycloaddition of anthracene results in a reduction of the conjugation (Scheme 35) and thus the cycloadduct **131** does not absorb above 300 nm whereas anthracene itself absorbs relatively strongly in the range  $\sim 310 - 380 \text{ nm}$ . The cycloreversion, whilst very slow at rt, occurs readily at  $170 \text{ }^\circ\text{C}$ . The photodimerisation of anthracene and higher acenes has been extensively reviewed.<sup>216-218</sup>



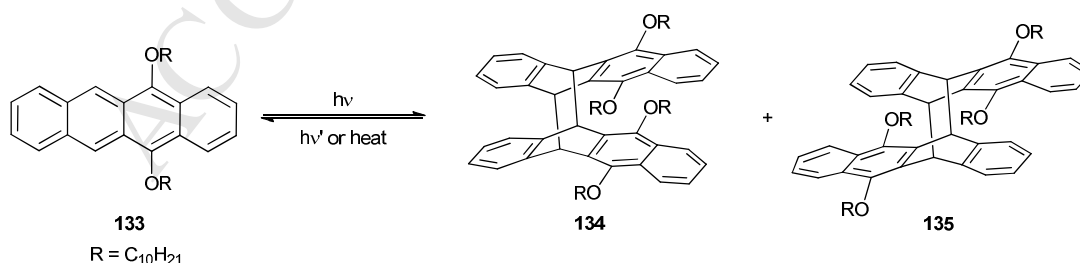
Scheme 35. Reversible photodimerization of anthracene

One problem noted in attempts to study the photochemistry of higher acenes is their poor solubility which arises as a consequence of their planar structure which facilitates aggregation ( $\pi$ -stacking). To enhance the solubility of tetracene both the 2,3-bis(decyloxy) **132** and 5,12-bis(decyloxy) **133** analogues have been synthesised and their photochromic response studied. Visible light irradiation of a cyclohexane solution of **132** resulted in bleaching of the yellow orange solution and afforded four isolable photostable dimers through cycloaddition involving the internal rings of the tetracene unit (Scheme 36). Cycloreversion was effected by heating at 80 °C in toluene for several hours.<sup>219</sup>



Scheme 36. Photodimerisation of tetracene **132** showing key  $^1\text{H}$  NMR chemical shift data

Two colourless photodimers ( $\lambda_{\text{max}}$  ca. 310 nm) were obtained in a 1:1 ratio from the irradiation of the red-orange solution of **133** (Scheme 37). Restoration of the monomer was accomplished by gentle heating or by UV irradiation.<sup>220</sup> In addition to the usual characterization techniques fluorescence spectroscopy was useful since naphthalene eximer fluorescence was noted for the dimer **134** whereas dimer **135** exhibits naphthalene monomer fluorescence.<sup>221</sup>

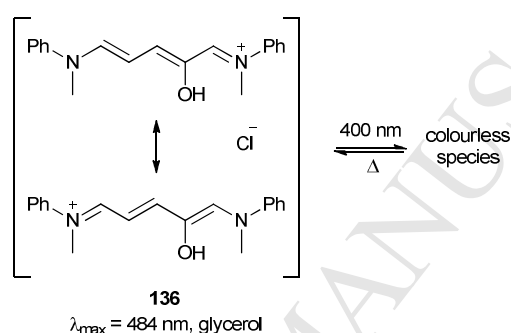


Scheme 37. Isomers resulting from the photodimerization of the dialkoxytetracene **133**

The photodimerization of acene derivatives has recently been employed in reversible gelation studies<sup>222,223</sup> and for the reversible photocapture of a [2]rotaxane.<sup>224</sup>

## 2.10 Miscellaneous systems

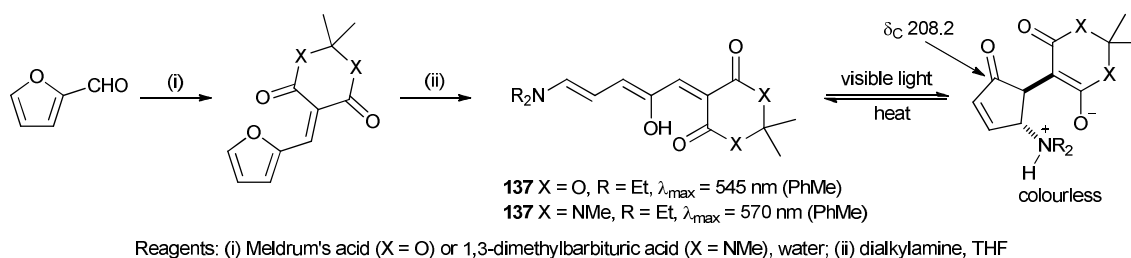
Intensely coloured solutions of Stenhouse salts **136**, hydroxyl substituted pentamethine dyes, in alcohols are reversibly bleached upon irradiation with light of ca. 400 nm (Scheme 38). Simple pentamethine dyes i.e. the foregoing Stenhouse salts with the enol function (hydroxyl group) absent, did not exhibit this phenomenon. The use of UV irradiation resulted in the gradual degradation of the substrate and thus limited the usefulness of these compounds. The mode of operation of the photochromism was unexplored though the authors noted that simple enol-keto tautomerism is unlikely to be responsible for the effect since the extended heptamethine analogues with an hydroxyl group did not exhibit this phenomenon.<sup>225</sup>



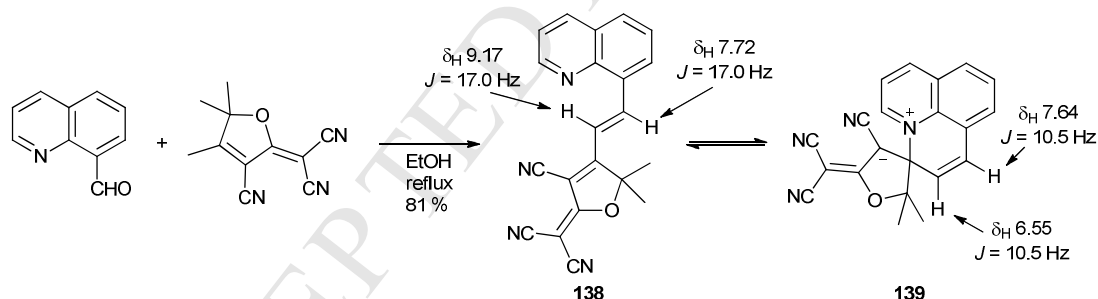
Scheme 38. Proposed photochromism of Stenhouse salt **136**

The negative photochromism of the merocyanines **137** (X = O, NMe), structurally related to **136**, has recently been investigated. Condensation of furfural with either Meldrum's acid or 1,3-dimethylbarbituric acid, respectively affords the 5-(furan-2-ylmethylene) derivatives which readily add the secondary amine with concomitant opening of the furan unit. The nature of the colourless species has been elucidated by NMR spectroscopy and crystallography (Scheme 39).<sup>226,227</sup> The mechanism of the photoswitching of such donor-acceptor Stenhouse adducts has been explored and has been shown to proceed by *Z* ↔ *E* isomerism followed by a thermal, conrotatory 4π-electrocyclisation.<sup>228</sup>

A TDDFT investigation of the photochromism of these new negatively photochromic merocyanines has recently been reported.<sup>229</sup> Initial reports detailing applications of this rediscovered photochromic system include spatiotemporal patterning of polycarbonate surfaces<sup>230</sup>, a temperature mapping molecular sensor for polyurethane elastomers<sup>231</sup> and a visible light responsive controlled drug release system.<sup>232</sup>

Scheme 39. Synthesis and photochromism of Stenhouse salt derivatives **137**

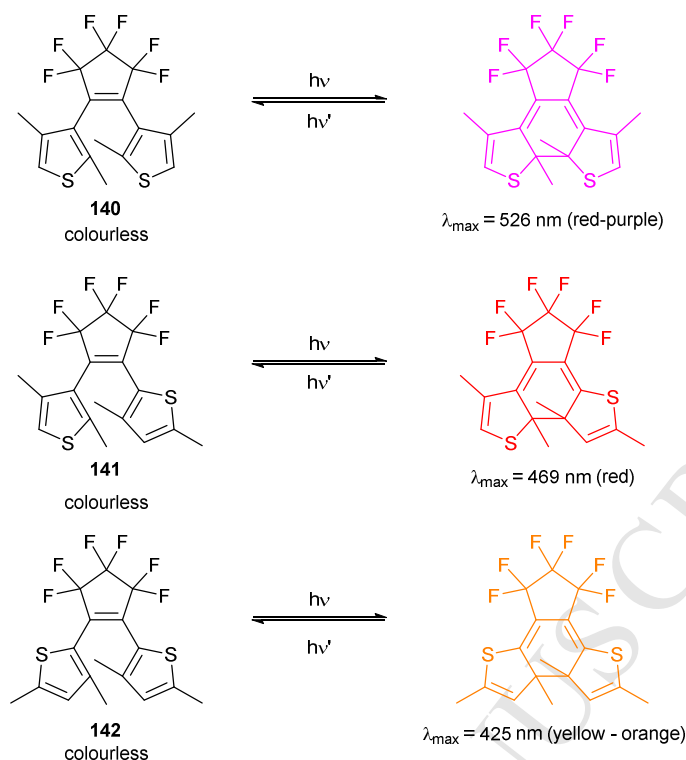
The extended conjugated system **138** with *E* geometry, as evidenced by a  $^1\text{H}$  NMR coupling constant for the alkene signals at  $\delta$  9.17 and  $\delta$  7.72 of 17 Hz, was constructed by a Knoevenagel type condensation between 8-formylquinoline and 2-(3-cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene)malononitrile. In DMSO solution **138** has a maximum absorption at 428 nm with a molar extinction coefficient of  $2.93 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ . Upon irradiation with visible light (LED, 470 nm) the orange-yellow solution reversibly bleached in under 1 s (estimated 92 % conversion) to afford the betaine **139** which contains a new cyclic alkene unit with protons resonating at  $\delta$  7.46 and  $\delta$  6.55 and  $J = 10.5$  Hz (Scheme 40).<sup>233</sup> The thermal reversion of **139**  $\rightarrow$  **138** can be effected slowly in the dark at room temperature ( $t_{1/2} = 102$  min) or more quickly photochemically by UV irradiation at 254 nm.

Scheme 40. Photochemical behaviour of **138** / **139**

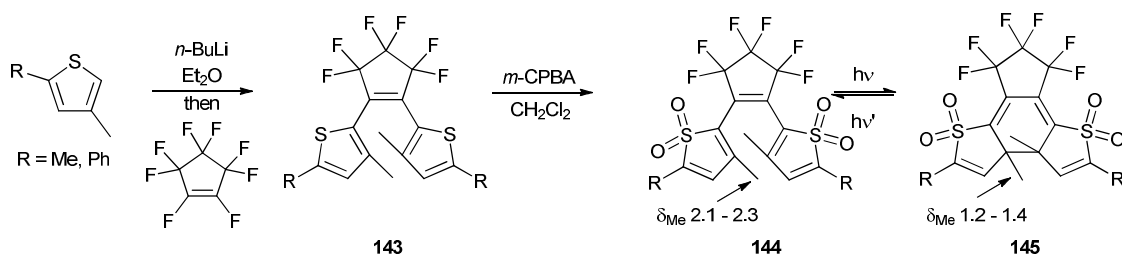
### 3.0 Systems that Exhibit Predominantly P-Type Negative Photochromism

#### 3.1 Diarylethenes

The class of diarylethenes are typified by the dithienylethene structures **140** – **142** which show positive photochromism in solution (Scheme 41).<sup>9,25-28</sup> The absorption maxima are markedly dependent upon the orientation of the thiophene rings, which dictates the length of the S-(CH=CH)<sub>n</sub>-S chromophore, and the electronic nature and location of substituents.

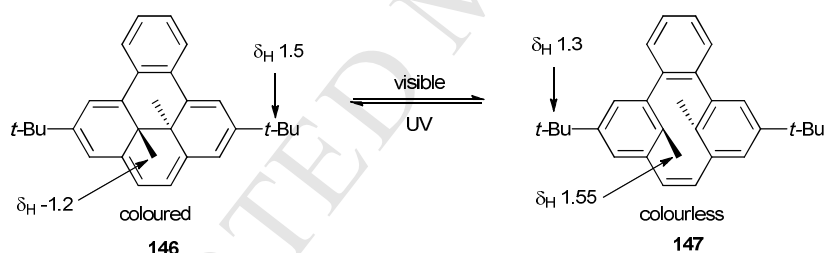
Scheme 41. Photocyclisation of isomeric diarylethenes **140** – **142**

Construction of the isomer **143**, where R = Me or phenyl, follows an established protocol which relies upon the metalation of a disubstituted thiophene unit with *n*-butyllithium followed by addition of octafluorocyclopentene. Oxidation of the sulfur heteroatoms of the substituted 2,2'-(perfluorocyclopent-1-ene-1,2-diyl)dithiophenes **143** with *m*-CPBA affords the tetra-oxide **144**.<sup>234,235</sup> Irradiation of a pale yellow 1,4-dioxane solution of **144** ( $\lambda_{\max} = 356$  nm) with light of wavelength  $> 430$  nm effected the electrocyclic ring closure to **145** ( $\lambda_{\max} = 260$  nm) with concomitant loss of the yellow colour; a process which was referred to as 'invisible photochromism'. Subsequent irradiation of **145** with light of  $\lambda = 313$  nm restored the original pale yellow colour (Scheme 42). Further evidence for the formation of the ring-closed isomer was obtained by  $^{13}\text{C}$  NMR spectroscopy which showed the evolution of a signal at ca. 45 ppm due to the  $\text{sp}^3$  hybridised 3*H*-thiophene ring carbon. The negative photochromic response of **144** has been examined by density functional theory calculations.<sup>236</sup>

Scheme 42. Construction and photochromic response of **144**

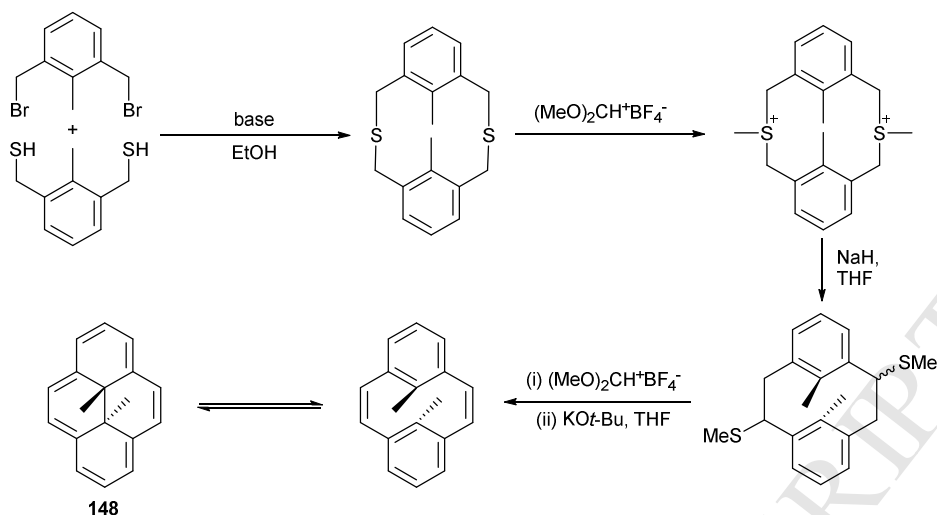
### 3.2 Dihydropyrenes

Dimethyldihydropyrenes represent an important but relatively little studied class of polyene system that exhibit predominantly negative photochromic behaviour.<sup>237</sup> Dimethyldihydrobenzo[*e*]pyrene **146**, undergoes a facile reversible interconversion, initiated by visible light, to the valence tautomer namely the annulene **147** (Scheme 43). The reverse reaction is typically effected by UV light or in some cases by heat or electrochemically. The thermally stable pyrenes are typically intensely purple coloured and fade upon irradiation as the electrocyclic ring-opening ensues. Interestingly **146** shows a clean (100%) conversion between the two photostates.<sup>238,239</sup>



Scheme 43. Dihydropyrene – annulene photointerconversion

The synthesis of such strained macrocycles is, unsurprisingly, difficult. Early work relied upon the transformation of sulfide linkages through a Stevens' rearrangement and a subsequent Hofmann elimination and is exemplified by the synthesis of dimethyldihydropyrene **148** (Scheme 44).<sup>240,241</sup> Some recent advances have reduced the number of steps in the sequence to four and obviate the use of sulfur reagents.<sup>242</sup> The generally lengthy synthetic protocols have resulted in only a limited number of analogues.

Scheme 44. Synthetic route to dihydropyrene **148**

Complexation of **146** with ruthenium(II) cyclopentadienyl to afford coloured complex **149** (Figure 24) results in slower visible light initiated ring-opening relative to the uncomplexed precursor **146** but with modified thermal ring-closure. Ring-closure with UV light is apparently unaffected.<sup>243</sup> Negative photochromism still operates for the tetrahydropyrene **150**, with a conversion from blue to very pale yellow being observed upon switching.<sup>244</sup> Dimethyldihydropyrene-appended metal complexes **151** (Figure 24) undergo visible light ( $\lambda > 630$  nm) induced ring-opening more efficiently when pyridinium, rather than phenylene bridges employed as connecting groups to the ligand unit; such complexes pave the way for multi-addressable photo- and redox- switches.<sup>245</sup>

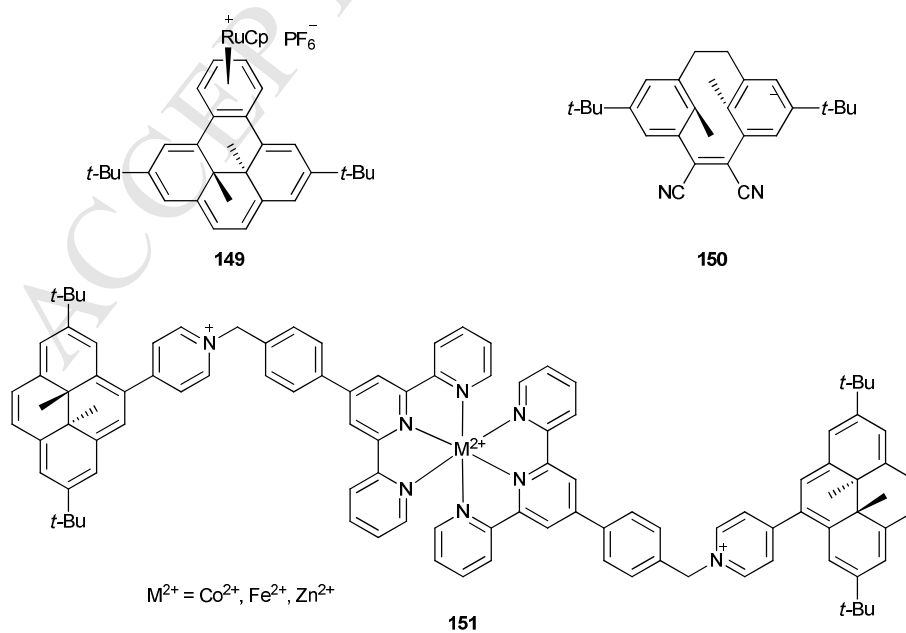
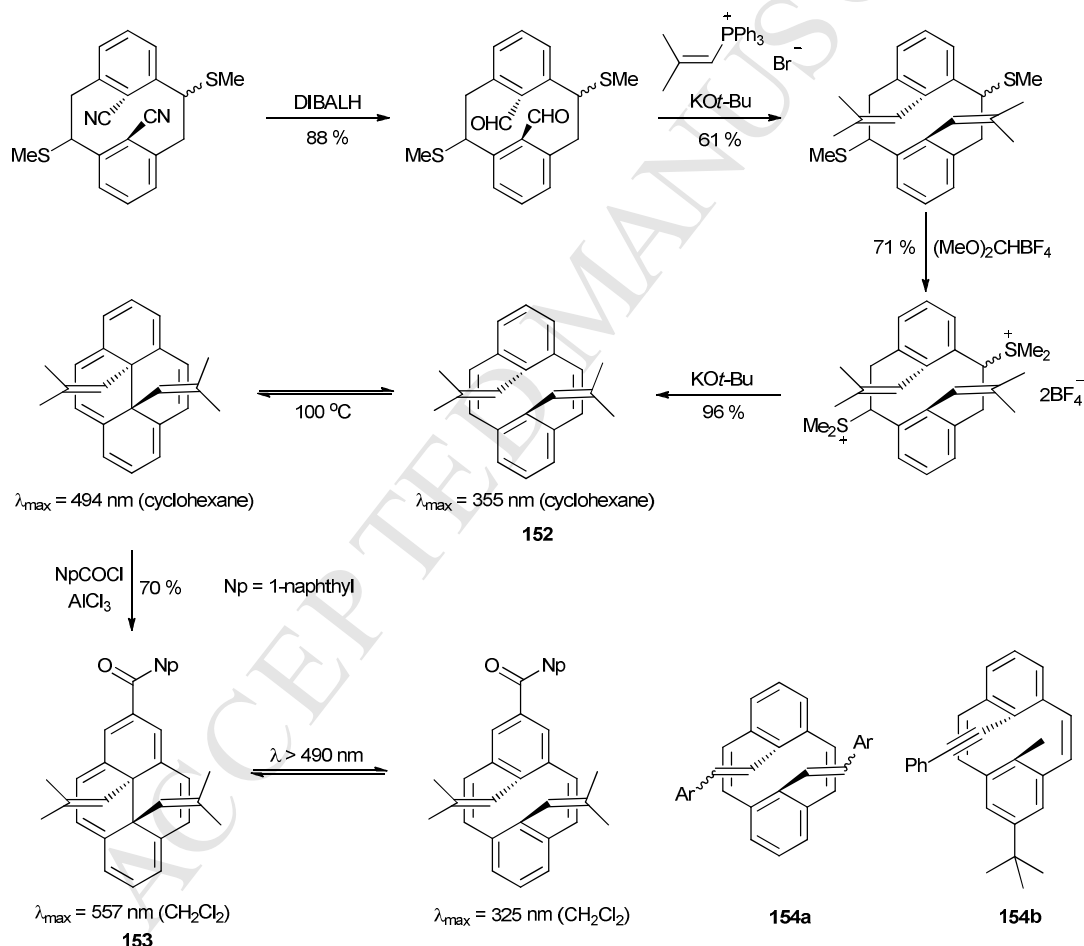


Figure 24. Structures of dihydropyrenes **149** – **151**

Mitchell and Bohne, leading exponents in the field of dihydropyrene photochromism, have substantially improved the photochromic response of dihydropyrenes through the use of DFT activation barrier calculations. Rather than employ central methyl groups central nitrile functions were introduced and efficiently manipulated (Scheme 45) to afford the bis(isobutenyl) substituted analogue **152**. Thermal isomerisation and Friedel-Crafts arylation afforded **153** which showed a remarkable ring-opening isomerisation quantum yield of ca. 0.66.<sup>246</sup> An extended series of alkenyl **154a** and alkynyl **154b** substituted dihydropyrenes have been synthesised by a similar strategy and their photo- and thermo-chemical properties explored.<sup>247</sup>



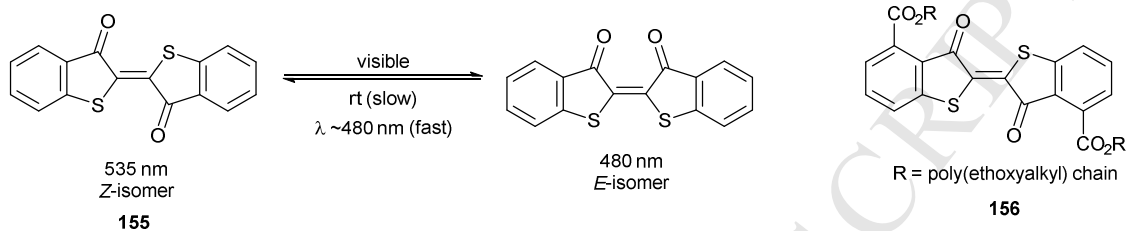
Scheme 45. Synthesis of alkenyl substituted dihydropyrenes

### 3.3 Thioindigoids and Hemithioindigoids

The photochromic response of indigoids and related compounds has been reviewed in the monograph edited by El'tsov.<sup>248</sup> Irradiation of a solution of *trans*-thioindigo **155** ( $\lambda_{\max}$  535



nm) with visible light results in the evolution of a new band at shorter wavelength (negative photochromism) due to interconversion to the *cis*-form ( $\lambda_{\text{max}}$  480 nm); under equilibrium conditions the solution contains a mixture of both isomers. The back reaction is relatively slow at room temperature but is markedly accelerated upon irradiation with light of ca.  $\lambda$  480 nm (Scheme 46).<sup>249,250</sup> Similar negative photochromic cycling was noted for substituted thioindigoid derivatives e.g. **156** (Figure 25), when adsorbed on silica gel.<sup>251</sup>



Scheme 46. Photoisomerisation of thioindigo **155**

Figure 25. Substituted thioindigoid **156**

#### 4.0 Conclusions and Outlook

Serendipity has played a major role in the discovery of negative photochromic systems, with only a few such systems resulting from truly targeted design. However, such fortune has been capitalised upon by chemists who have probed and examined this phenomenon over the years for a select group of molecules. Applications of negatively photochromic systems are becoming more common as they offer the advantage of relatively less destructive, lower energy switching, i.e. visible *versus* ultraviolet irradiation for the activation process, which may result in significantly increased numbers of switching cycles and improved device lifetimes. The alternative colour-bleaching / colour-recovery sequence to the traditional positive photochromic response offers the potential to open up new vistas in materials chemistry for the modulation of physical properties by molecular switching.

Of the negatively photochromic systems described to date the spiropyrans remain the most widely investigated and thus permit the formulation of some guidelines to ensure negative photochromic behaviour. Negative photochromic behaviour of spiropyrans should be assured through stabilisation of the ring – opened phenoxide ion when the 6- and 8- positions are substituted with strong electron withdrawing groups, with nitro groups being preferred. Replacement of the 8-nitro group with a halogen or ester function results in mixtures of the spiropyran and merocyanine (zwitterion) in which, by careful choice of polar solvent, negative photochromism can be observed. Negative photochromism can also be observed by

location of carboxylate groups at C-8 where H-bonding is inferred and also by sulfonic acid residues at C-6. The replacement of the benzene ring of the benzopyran unit with an electron deficient heterocyclic unit e.g. pyridine, also facilitates negative photochromism. The nature of the matrix is highly influential on the position of the spiropyran – zwitterion equilibrium with polar solvents favouring the zwitterion and, with appropriate functionality, e.g. ligating moieties and crown ether units, metal ions can be used to effect a negative photochromic response. Oxazine systems derived from a phenanthroline unit either require a bulky azahomoadamantyl unit or the presence of a ligated metal cation to appreciably stabilise the coloured zwitterionic species which can then exhibit negative photochromism. The isomerisation of an azo bond with pendant aryl and heteroaryl moieties enables switching between long and short wavelength absorbing coloured states and this switching behaviour has rekindled interest in azo systems for *in vivo* applications. The relatively recent discovery of negative photochromism for the hexaarylbiimidazole system offers opportunities to switch between red / orange and colourless states. Tetracenes, offering the same colour switching gamut, require relatively high temperatures to effect the back reaction, which when coupled with aggregation / solubility problems must be overcome to access their potential in devices. Somewhat surprisingly, the now ubiquitous diarylethene system scarcely features in the negative photochromism arena and P-type negative photochromism is championed by the relatively difficultly accessed dihydropyrenes, which offer good contrast between the two switching termini unlike the thioindigoids.

It is highly likely that the next decade will see sustained interest in molecular switches and low energy activated systems will claim the centre stage for the photoregulation of biological properties and structures such as membranes. Negatively photochromic systems will also offer materials scientists new tools with which to construct devices with complementary modes of operation to those of existing photochromic systems.

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(br), 1604, 1548, 1513, 1417, 1291, 1202, 1087, 1040, 974, 746  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  541 nm, 24,398  $\text{mol}^{-1}\text{dm}^3\text{cm}^{-1}$  (acetone),  $\delta_{\text{H}}$  (ring-opened, red)<sup>†</sup> 1.11 (6H, d,  $J = 7.0$  Hz,  $\text{CH}(\text{Me}_2)$ ), 1.84 (6H, s,  $\text{CMe}_2$ ), 2.45 (1H, septet,  $J = 7.0$  Hz,  $\text{CH}(\text{Me}_2)$ ), 4.17 (2H, d,  $J = 7.2$  Hz,  $\text{NCH}_2$ ), 7.38 (1H, m, Ar-H), 7.54 (3H, m, Ar-H), 8.15 (1H, d,  $J = 15.6$  Hz, alkene-H), 8.36 (1H, d,  $J = 3.1$  Hz, Ar-H), 8.82 (1H, d,  $J = 15.6$  Hz, alkene-H), 8.85 (1H, d,  $J = 3.1$  Hz, Ar-H),  $\delta_{\text{H}}$  (ring-closed) 0.91(6H, d,  $J = 6.9$  Hz,  $\text{CH}(\text{Me}_2)$ ), 1.23 (3H, s, CMe), 1.34 (3H, s, CMe), 2.02 (1H, m,  $\text{CH}(\text{Me}_2)$ ), 2.77 (1H, dd,  $J = 14.4, 9.3$  Hz, NCH), 3.02 (1H, dd,  $J = 14.4, 5.5$  Hz, NCH), 6.06 (1H, d,  $J = 10.7$  Hz, 3'-H), 6.58 (1H, d,  $J = 8.1$  Hz, 7-H), 6.89 (1H, m, 5-H), 6.98 (1H, d,  $J = 10.7$  Hz, 4'-H), 7.07 (1H, d,  $J = 7.9$  Hz, 4-H), 7.16 (1H, m, 6-H), 8.14 (1H, d,  $J = 2.7$  Hz, 7'-H), 8.59 (1H, d,  $J = 2.7$  Hz, 5'-H). Found  $[\text{M}+\text{H}]^+ = 410.4710$ ,  $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_5$  requires  $[\text{M}+\text{H}]^+ = 410.4716$ .  
<sup>†</sup>The  $^1\text{H}$  NMR spectrum indicated the presence of ethanol [(1.24 (3H, t,  $J = 7.0$  Hz,  $\text{CH}_3$ ), 3.71 (2H, q,  $J = 7.0$  Hz,  $\text{CH}_2$ )] even after prolonged drying at 40 °C, a feature which is suspected to be in the form of  $\frac{1}{2}$  mol of EtOH of crystallisation.

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## Negatively Photochromic Organic Compounds: Exploring the Dark Side

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### Highlights:

- The phenomenon of negative photochromism of organic compounds is reviewed
- T-Type negative photochromic systems are discussed
- P-Type negative Photochromic systems are discussed
- Spectroscopic data for negative photochromic organic compounds is presented.
- Applications of negative photochromic organic compounds have been identified