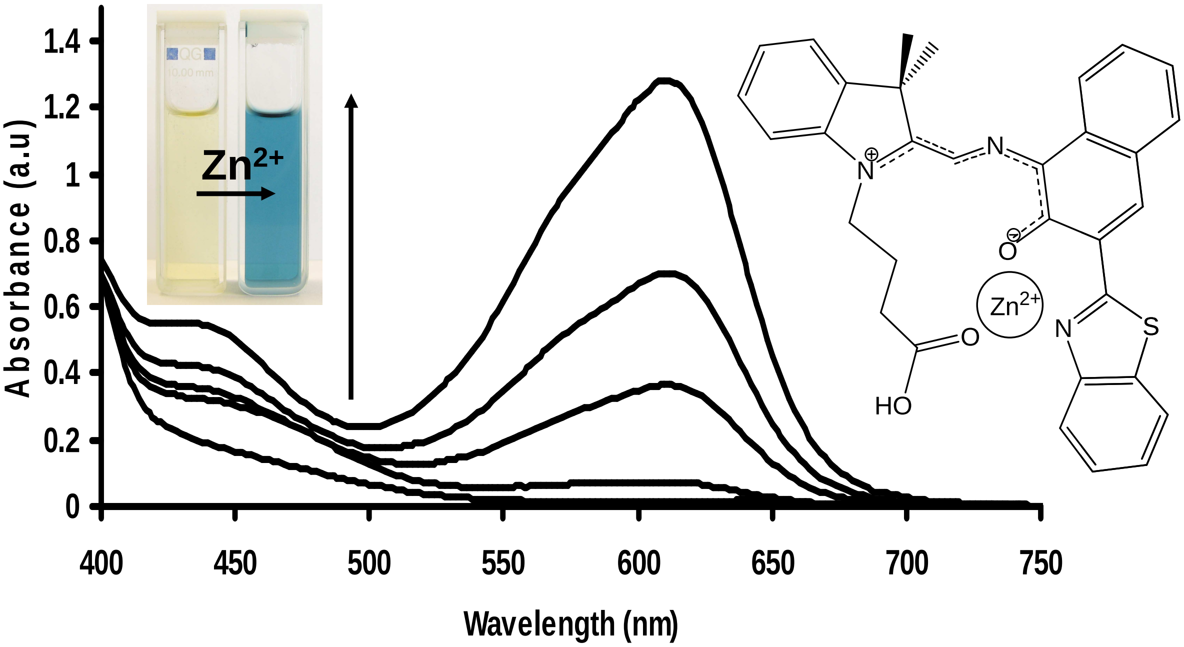
Graphical Abstract



Novel synthesis and characterisation of 3,3-dimethyl-5′-(2-benzothiazolyl)-spironaphth(indoline-2,3′-[3*H*]naphth[2,1-*b*] [1, 4]oxazine) derivatives.

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Abstract

Novel modified spirooxazines (SO) with additional chelating groups were synthesised and the crystal structure of one of these was determined. UV-vis spectroscopic characterization of the photoisomerization of the SO derivatives shows that the photochromic behaviour is altered with Zn^{2+} coordination. In particular, addition of a carboxylic acid (**5**) to the indole section of the SO increases the lifetime of the merocyanine Zn^{2+} complex by 20-fold compared to the methylated indole (**6**).

Spirooxazines are a particularly interesting family of photochromic molecules,[1,2] due to their remarkable properties, such as photo-fatigue resistance, strong photocoloration and fast thermal relaxation.[3-6] These properties give spirooxazines the ability to be applied in a wide range of applications such as memory devices, optical switches, displays, and chemical sensors.[7a-k] The photochromic reaction of these compounds is due to photo isomerization, reversible heterolytic cleavage and rebinding of the C_{spiro}-O atom. Upon UV irradiation through the formation of the highly coloured merocyanine **MC** (open zwitterionic form) and vice versa upon visible-light irradiation or heating, reformation of the spirooxazine **SO** (closed uncharged form) occurs which is colourless or pale yellow, see Scheme 1. Furthermore, the **MC** isomer has a phenolate anion site through which certain (d- and f-element) metal ions can bind, giving rise to a new absorption band in the visible spectrum.[8]

Scheme 1.

The creation of surfaces in the immobilised photoswitchable ligands is an attractive strategy due to the possible control of the recognition site by photons. For example, these materials could play an important role in many applications, including biological[9,10] and environmental separation techniques.[11] There have been numerous studies on the modification of spiropyrans for enhanced ion complexation via the photomerocyanine isomers[12-23] but not so many for spirooxazines.[24-26]

Herein, we report the synthesis and characterization of novel spirooxazines **4** and **5** with additional chelating sites at the nitrogen atom of the indoline group. Furthermore, we present the crystal structure of compound **4**.

The synthesis of spirooxazine compounds **4** and **5** was carried out in a four to five step sequence as depicted in Scheme 2. The preparation of target compound **4** started with the *N*-alkylation of indole compound **1** with methyl bromobutyrate, to obtain the indolium bromide salt **2**.[27] Subsequently, compound **2** was condensed with **3**, as reported previously,[7i] to form the initial spirooxazine target compound. This compound was isolated by recrystallization from ethanol in a 35% yield. The resulting pure compound **4** was then hydrolysed with sodium hydroxide to afford the second spirooxazine target compound **5** in a 15% yield. Crystals of **4** suitable for X-ray crystallography were grown by slow evaporation from ethanol solution. Compounds **6** and **7** were synthesised according to our previously reported methods and are included for comparative studies.[7i]

Scheme 2.

The X-ray crystal structure analysis showed that compound **4** is comprised of two molecular components as described previously for spiro-compounds,[28a-i] an indoline group and a naphthooxazine ring which are linked through a C_{spiro} atom (C19) in orthogonal arrangement as defined by the interplanar angle (88.71), Figure 1. The C_{spiro} atom of the indoline group is out of plane and the indoline group is bent toward the oxygen atom of the oxazine ring. The C_{spiro}-O bond length is 1.468(2)Å, which is slightly longer than previously reported,[28d,i] and this has been shown to enhance photochromic C_{spiro}-O bond cleavage due to the anomeric effect.[29] The oxazine ring is not in a square-planar conformation, but it is folded toward the *gem*-methyl groups of the indoline group,[28e] whereas the benzothiazole group is in a planar conformation with the naphthooxazine group.

Figure 1.

The photoisomerization and subsequent physical behaviour of compounds **4-7** were investigated by UV-vis analysis. UV irradiation of compounds **4-7** in acetone yielded the photomerocyanine as expected (λ_{max} = 640 nm). The UV-vis analysis of the photoisomerization of compound **5** in acetone (1 x 10^{-4}M) is shown in Figure 2, negligible merocyanine absorption is seen in the dark (spectrum a); upon UV irradiation of the sample, a strong absorption band emerges within the visible region (spectrum b).

Figure 2.

The photomerocyanines of **4-7** have a phenolate anion site through which certain metal ions (e.g. d- and f-element) can bind, giving rise to a new absorption band in the visible spectrum. As reported previously,[8] addition of Ni^{2+}, Co^{2+} or Zn^{2+} to acetone solutions of **6** and **7** generates an [MC-M^{2+}] complex with a 1:1 stoichiometry and a new intense photo-reversible absorption band which is centered around 610 nm. The type of metal ion only slightly influences the spectral properties of the complexes, in contrast to the thermal relaxation which can differ by one order of magnitude. For this particular study, Zn^{2+} was chosen as the metal ion for complexation as it gives rise to the furthest blue shift of the three ions. Figure 3 demonstrates the effect of the addition 1 equiv. of $ZnCl_2$ on the visible spectrum of **5** over the time period 0-18 minutes, with kinetic analysis of complex formation at $\lambda_{complex}$ = 610 nm in the inset.

The photograph in Figure 3 shows the colour change in acetone solution of compound **5** that occurs upon addition of $ZnCl_2$.

Figure 3.

Kinetic measurements of the thermal relaxation of the photomerocyanine isomers of compounds **4-7** to the **SO** form were studied in acetone. Thermal relaxation of the photomerocyanine to the **SO** form follows first order kinetics as plots of $\ln A_0/A_t$ are linear and the slopes of the $\ln A_0/A_t$ lines give first order rate constants, k. In the absence of metal ions, the relaxation times of the photomerocyanines of **4-7** are between 12-20 seconds in acetone, see Table 1. It has been reported previously that the thermal relaxation of the photomerocyanine forms of **6** and **7** are unaffected on changing the *N*-alkyl group on the indoline fragment of the **SO** from a $–CH_3$ to $–C_4H_9$ group.[30] It can be clearly seen that upon ester hydrolysis of compound **4** → **5**, thermal relaxation rate constants decrease by more than 50%; this has been reported previously in similar experiments with spiropyran compounds and can be attributed to increased solvent stabilization of the merocyanine form of the carboxylic acid derivative (**5**) compared to the ester derivative (**4**).[31] In this case, the presence of a more polar substituent on the heterocyclic nitrogen in **5**, as compared to **4**, increases its solubility in polar solvents, rendering them soluble even in water.

Similar measurements of the thermal relaxation of compounds **4-7** were also studied in the presence of 1 equiv. of $ZnCl_2$, Figure 4. The rate constants of the thermal Zn^{2+} complexes decreased in the order **4** (2.3×10^{-2} s^{-1}), **6** (1.6×10^{-2} s^{-1}), **7** (1.0×10^{-2} s^{-1}) and **5** (0.27×10^{-2} s^{-1}), respectively. From Table 1, it can easily be seen that Zn^{2+} complexes increase the lifetimes of the photomerocyanine derivatives significantly. In particular, photomerocyanine lifetimes for compound **5** show a 20-fold increase in the presence of Zn^{2+}. This can be explained firstly by the increased solvent stabilization of the MC-Zn^{2+} complex and secondly by the mono-carboxylate ligand which is now available for ion-coordination. Carboxylates have previously been shown to act as strong chelating ligands for Zn^{2+}.[32] See supplementary information, Figures SI 1 and SI 2 for thermal relaxation of photomerocyanines **4** and **5** with and without $ZnCl_2$.

Figure 4.

In conclusion, we have successfully demonstrated an efficient route for the synthesis of both ester **4** and carboxylic acid **5** derivatives of 3,3-dimethyl-5′-(2-benzothiazolyl)-spironaphth(indoline-2,3′-[3*H*]naphtho[2,1-*b*][1,4]oxazine). X-ray diffraction analysis of **4** showed the benzothiazole group arranged in a planar position with respect to the oxazine ring. Compounds **4** and **5** exhibited photochromism upon UV irradiation. It was found that the choice of substituent groups on the heterocyclic nitrogen has a significant effect on the kinetics of **MC** → **SO** thermal relaxation, as the addition of a Zn^{2+} ion into an acetone solution of **4** and **5** enhanced their photostability by 3-fold and 20-fold, respectively. This indicates the importance in choosing the correct indole substituents when designing materials containing spirooxazine molecules for optical sensing of metal ions.

CCDC number 697506 contains the supplementary crystallographic data for compound **4**. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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