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Photostabilisation of Photochromic Materials: Contribution of Amphoteric Counter-Ions on the Photostability of Spiropyrans and Related Compounds

Hironori Oda

Department of Chemistry, Nagoya Women's University,
1302, Takamiya, Tenpaku-ku, Nagoya 468, Japan

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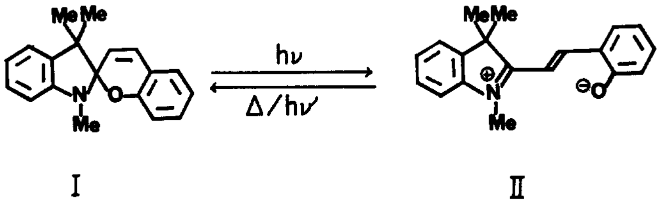
ABSTRACT

Photochromic spiropyrans are receiving considerable attention as functional dyes for reversible image recording medium. Metal complexes of hydroxycarboxylic acids or dicarboxylic acids were prepared to prolong the life of coloured species. The protecting effect of these compounds towards the photofading or dark decay reaction of photocoloured species was examined on cellulose. It was found that zinc salts of 1-hydroxy-2-naphthoic acid and its derivatives are very effective for stabilising the coloured form of spiropyran and related compound.

1 INTRODUCTION

The chemistry of spiropyrans has recently become of importance, particularly in connection with the rapid development of information recording system.[1–5] The ordinary photochromism of spiropyrans is known to involve the conversion of a stable colourless state **I** into a coloured metastable state **II** with ultraviolet light. The colourless modification is transformed from the coloured one either spontaneously when the solution is stored in the dark, or by irradiation with visible light. State **II** is called the photomerocyanine, state, since it is similar in structure to merocyanine dyes. The process which takes place in the photochromic system is presented in Scheme 1.

Use of the photochemical system in data storage requires that states **I** and



Scheme 1

II should be reasonably stable at ordinary temperatures in the absence of provoking illumination, and that the photochemical interconversion of states I and II should also be possible at ordinary temperatures. Many kinds of spiropyrans which are photochemically active at room temperature and above have been developed, but until recently the thermal instability of state II included their use in practical data storage devices.[6,7]

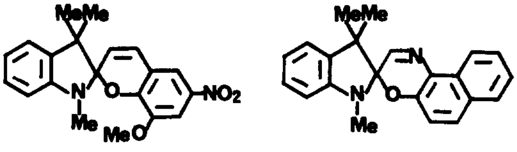
In a previous paper,[8] metal complexes capable of the contribution of amphoteric counter-ion on the photostability of the colour formers were prepared, and the protecting effect of these compounds towards the photofading of colour materials derived from colour formers was examined on cellulose. It was found that nickel or zinc salts of 2-hydroxybenzoic acid and its derivatives provided more marked improvements in the lightfastness properties of colour formers than conventional stabilisers in solar radiation. These metal carboxylates were also observed to improve the image stability of the indicator dyes.

Therefore, it could be anticipated that the contribution of amphoteric counter-ions may be also involved in the stability of the photocoloured state of spiropyrans. The influence of amphoteric counter-ions on the photochromic behaviour of spiropyrans has been investigated in the solid state, and a new approach for improving the photostability of colourants for imaging and data recording systems is now reported.

2 EXPERIMENTAL

2.1 Materials

6-Nitro-8-methoxy-1′,3′,3′-trimethylspiro(1H-1-benzopiran-2,2′-indoline) (**1**) and 1,3,3-trimethylspiro(indoline-2,3′-(3H)naphth(2,1-b)(1,4)oxazine) (**2**) were obtained from a commercial source. Their chemical structures are shown in Fig. 1. Nickel dimethyldithiocarbamate (NMC) was a commercial reagent (Tokyo Kasei Co. Ltd). Metal carboxylates were synthesised and recrystallised according to the procedures described in the literature.[9]



1 2

Fig. 1. Photochromic materials used in this study.

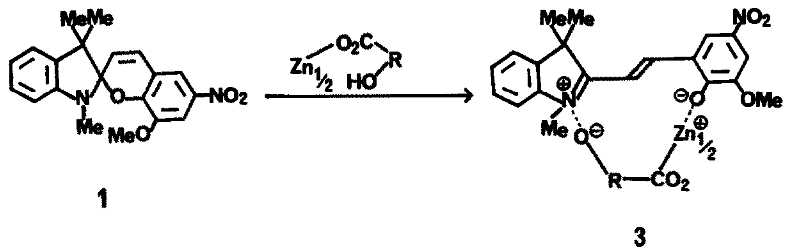
2.2 Photochromism of spiropyran and related compound on cellulose

A solution of 1 (8×10^{-3} mol dm^{-3}) in ethanol or dimethylsulphoxide (10 cm^3) with or without an additive (4×10^{-2} mol dm^{-3}) such as metal carboxylates or NMC was prepared. Portions of the solutions (1×10^{-2} cm^3) were spotted on cellulose TLC plates using a microsyringe, and dried. The plates were irradiated at 25°C with an external 500 W mercury lamp (Ushio Electric Inc., UI-501). Undesirable wavelengths were excluded using filters (Toshiba, Number UV-D36C, O-54). The changes of colour developed on irradiation with ultraviolet light were monitored with a Shimazu thin-layer chromatoscanner (CS-920 type). The percentage conversion was calculated by comparison with irradiated colour for 1 min. The coloured spots faded back to their original state in the dark. The dark decay reaction was also monitored in the same manner as above. A similar procedure was also used for spirooxazine 2. The percentage conversion was calculated by comparison with irradiated colour for 30 s.

3 RESULTS AND DISCUSSION

3.1 Effect of various zinc complexes on the photostability of spiropyran

The spiropyran 1 is known to undergo reversible change between colourless and coloured form with application of either light or heat. The colourless 'closed' form has the structure of a spiropyran, I, and the coloured 'open' form has the structural feature of merocyanine dye, II, as shown in Scheme 1.[6] In a preliminary study,[8] the effect of various counter-ions on the photofading of colour materials derived from colour formers was investigated. It was found that amphoteric counter-ion effect plays a very important role in the photostability of colour formers. It was therefore of interest to prepare a stabiliser, i.e. metal carboxylate, capable of the contribution of amphoteric counter-ion such as 3 on the photostability of the spiropyran, since this could provide a more positive effect on the



Scheme 2

stabilisation of the photomerocyanine (see Scheme 2). The quantitative determination of spectro-kinetic or photochemical parameters is generally achieved in solution, but many applications require the use of plastic or other solid supports such as paper, films, semi-conductors or polymeric materials.[6,7] In this work, the effect of various additives on the photostability of the photomerocyanine derived from spiropyran **1** was examined on cellulose plate. The influence of some additives on the photofading of **1** on cellulose was investigated in air on exposure to filtered radiation ($\lambda = 365$ nm) from a 500 W high-pressure mercury lamp, and it was found that the zinc complex affords an excellent suppressing effect on that fading. These results are shown in Fig. 2. Spiropyran **1** on cellulose develops colour upon irradiation with ultraviolet light, but the colour gradually fades upon continued irradiation. The photofading behaviour was determined by comparison with the concentration on ultraviolet irradiation of **1** for 1 min. The addition of the zinc complex of 2-hydroxybenzoic acid in the photofading system afforded a considerable protection against fading. Particularly the use of the zinc salt of 1-hydroxy-2-naphthoic acid completely

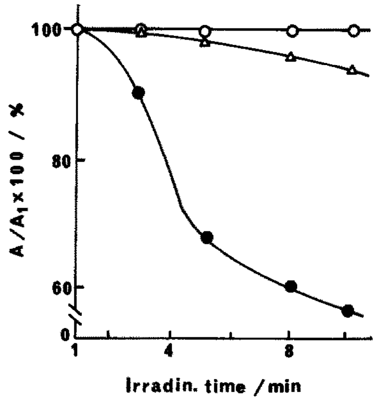


Fig. 2. Effect of additives on the photofading of **1** on cellulose. Initial concentrations: (**1**) 8×10^{-3} mol dm^{-3}; additive 4×10^{-2} mol dm^{-3}. ●, No additive; △, 2-hydroxybenzoic acid zinc salt; ○, 1-hydroxy-2-naphthoic acid zinc salt.

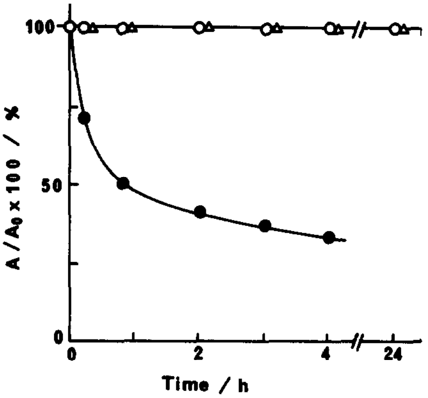


Fig. 3. Effect of additives on the dark decay reaction of 1 on cellulose (for key see Fig. 2).

suppressed that fading. A similar suppressing effect by the zinc complex was also observed in the case of the dark decay reaction of **1**. The results are shown in Fig. 3. The coloured form generated by illumination with ultraviolet light decayed to the colourless form readily on storage in the dark. However, the addition of zinc complex of 2-hydroxybenzoic acid or of 1-hydroxy-2-naphthoic acid in this system completely stopped the dark decay reaction. Moreover, this coloured state was stable even after 24 h. These results suggest that the zinc complex of hydroxycarboxylic acids have a very useful protecting effect towards the photofading or dark decay reaction of photocoloured species of spiropyrans.

3.2 Influences of various metal carboxylates on the photochemical stability of spironaphthoxazine

Photochromic spironaphthoxazines have recently received attention as functional dyes for reversible image recording medium on account of their high fatigue resistance in the reversible reaction of colouring and decolouring.[7] In such a case, it is important to control the stability of the photocoloured state. Compound **2** on cellulose plate is colourless and becomes intensely blue upon exposure to ultraviolet light. The intense blue colour disappears rapidly when ultraviolet irradiation ceases. This reversible colour change is explained, as in the case of spiropyrans, by the transformation of the 'closed' spiro structure to the 'open' merocyanine dye structure.[7] Metal complexes of hydroxycarboxylic acids were prepared to prolong the life of coloured species. The protecting effect of these compounds towards the dark decay reaction of photocoloured species of **2** was examined on cellulose. As shown in Fig. 4, the coloured form generated by illumination with ultraviolet light decayed thermally to the colourless form readily at ambient

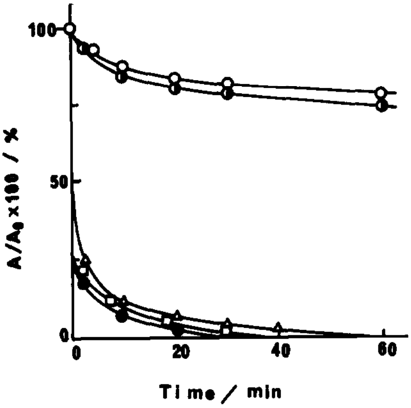


Fig. 4. Effect of additives on the dark decay reaction of **2** on cellulose. Initial concentrations: (**2**) 8×10^{-3} mol dm^{-3}; additive 4×10^{-2} mol dm^{-3}. ●, No additive; □, 2-hydroxyphenylacetic acid zinc salt; △, 2-hydroxybenzoic acid zinc salt; ◑, 2-hydroxy-1-naphthoic acid zinc salt; ○, 1-hydroxy-2-naphthoic acid zinc salt.

temperature. Zinc complexes of 2-hydroxyphenylacetic acid or of 2-hydroxybenzoic acid had the effect of stabilising the coloured form, but to a lesser degree. However, the zinc complexes of 1-hydroxy-2-naphthoic acid or of 2-hydroxy-1-naphthoic acid remarkably decreased the decolouration rate. A similar stabilising effect by these zinc salts was also observed on the photofading behaviour in ultraviolet light. As shown in Fig. 5, the spot of **2** faded drastically in air on exposure to filtered radiation ($\lambda = 365$ nm) from a high-pressure mercury lamp source. The addition of the zinc complex of 2-hydroxyphenylacetic acid of of 2-hydroxybenzoic acid in the photofading system afforded little protection against fading. However, the rate of photofading was appreciably retarded by adding the zinc complex of 1-

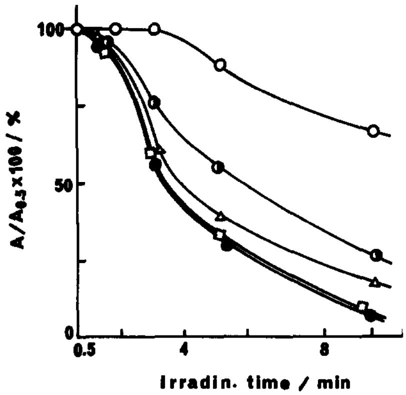


Fig. 5. Effect of additives on the photofading of **2** on cellulose (for key see Fig. 4).

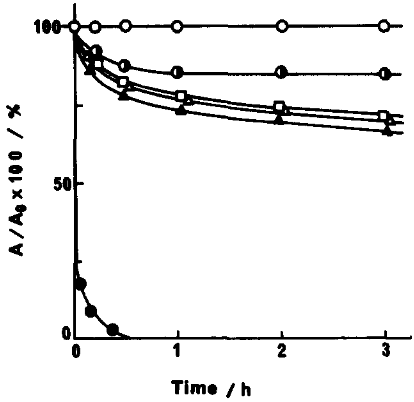


Fig. 6. Effect of the concentration of additives on the dark decay reaction of **2** on cellulose. Additive (initial concentration): ●, no additive; 2-hydroxy-1-naphthoic acid zinc salt (▲, 4×10^{-2} mol dm^{-3}; △, 8×10^{-2} mol dm^{-3}); 1-hydroxy-2-naphthoic acid zinc salt (□, 4×10^{-2} mol dm^{-3}; ◐, 8×10^{-2} mol dm^{-3}; ○, $1{\cdot}6 \times 10^{-1}$ mol dm^{-3}).

hydroxy-2-naphthoic acid or of 2-hydroxy-1-naphthoic acid. The suppressing effect of the zinc salt of 1-hydroxy-2-naphthoic acid zinc salt was especially excellent. Thes observations suggest that the zinc complexes of hydroxynaphthoic acid derivates may play a very important role in the stabilisation of the photomerocyanine. On the basis of these results, zinc complexes of 1-hydroxy-2-naphthoic acid and 2-hydroxy-1-naphthoic acid were chosen as the representative compounds, and the effect of concentration of the additives on the dark decay reaction of photocoloured species was examined on cellulose. As shown in Fig. 6, the decolouration rate in darkness was decreased remarkably with increasing concentration of additives. The suppressing effect provided by 1-hydroxy-2-naphthoic acid zinc salt was superior to that of 2-hydroxy-1-naphthoic acid zinc salt. The effect of the 2-hydroxy-1-naphthoic acid zinc salt could be achieved by using half the corresponding amount of 1-hydroxy-2-naphthoic acid zinc salt. Furthermore, it is noteworthy that the decolouration can be completely stopped by adding 1-hydroxy-2-naphthoic acid zinc salt 20-fold over the amount of **2**. A similar stabilising effect by these zinc salts was also observed on the photofading. The rate of photofading of **2** was completely retarded in the presence of 20-fold amount of 1-hydroxy-2-naphthoic acid zinc salt (see Fig. 7). Accordingly, the influence of some zinc complexes of hydroxycarboxylic acids on the stability of the photocoloured species of **2** was examined at this concentration. As shown in Fig. 8, the decolouration rate in darkness was scarcely supressed by the addition of 2-hydroxybenzoic acid zinc salt. However, the use of 1-hydroxy-2-naphthoic acid zinc salt or of 2-hydroxy-3-naphthoic acid zinc salt totally stopped that decolouration, and the coloured

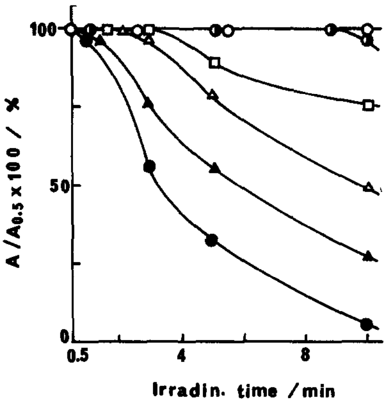


Fig. 7. Effect of the concentration of additives on the photofading of 2 on cellulose (for key see Fig. 6).

form was stable even after 25 h. Additionally, these zinc salts also completely retarded the rate of photofading of 2 when using the 365 nm Hg line for illumination (see Fig. 9). These results indicate that the zinc complexes of 1-hydroxy-2-naphthoic acid and of 2-hydroxy-3-naphthoic acid are very effective in stabilising the coloured form of spirooxazines. These zinc complexes may permit the use of spiropyrans or spirooxazines for practical photochromic materials.

Similar effectiveness was examined also using dicarboxylic acid zinc salts. These results are shown in Figs 10 and 11. These zinc salts retarded the rate of photofading, but may not be useful in controlling the decolouration rate in darkness. This behaviour suggests that zinc complex of dicarboxylic acid derivatives may not play a very important role in the stabilisation of

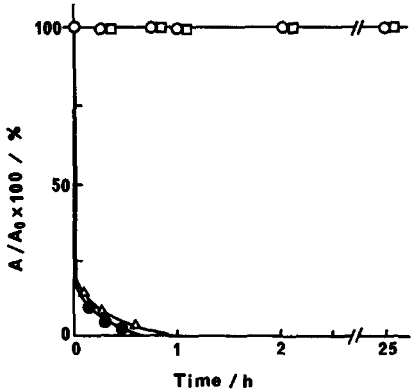


Fig. 8. Effect of additives on the dark decay reaction of 2 on cellulose. Initial concentrations: (2) 8×10^{-3} mol dm^{-3}, additive $1{\cdot}6 \times 10^{-1}$ mol dm^{-3}. ●, No additive; △, 2-hydroxybenzoic acid zinc salt; □, 1-hydroxy-2-naphthoic acid zinc salt; ○, 2-hydroxy-3-naphthoic acid zinc salt.

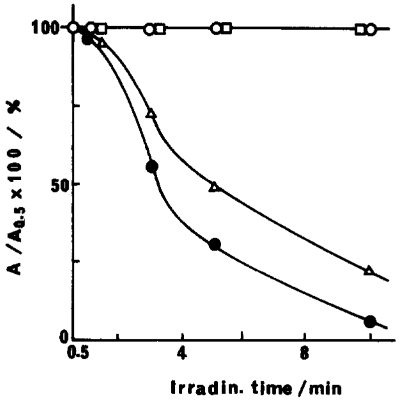


Fig. 9. Effect of additives on the photofading of **2** on cellulose (for key see Fig. 8).

the photomerocyanine. The effect of the nickel complex was also similarly examined. The nickel salt suppressed the rate of photofading significantly, but was not effective in darkness. Similar behaviour has also been observed on the addition of NMC, a good singlet oxygen quencher.[10,11] Therefore, this suppressing effect against the photofading may result from the singlet oxygen quenching ability by nickel salt.

3.3 Influence of zinc complex on the photochromism of spironaphthoxazine

From these results, the zinc salt of 1-hydroxy-2-naphthoic acid was chosen as representative compound, and the effect of additive on the photocolour-

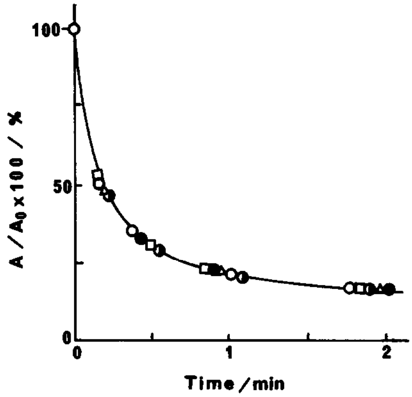


Fig. 10. Effect of additives on the dark decay reaction of **2** on cellulose. Initial concentrations: (**2**) 8×10^{-3} mol dm^{-3}, additive 8×10^{-2} mol dm^{-3}. ●, No additive; △, 1,2-benzenedicarboxylic acid zinc salt; □, 1,8-naphthalenedicarboxylic acid zinc salt; ◑, NMC; ○, 2-hydroxy-3-naphthoic acid nickel salt.

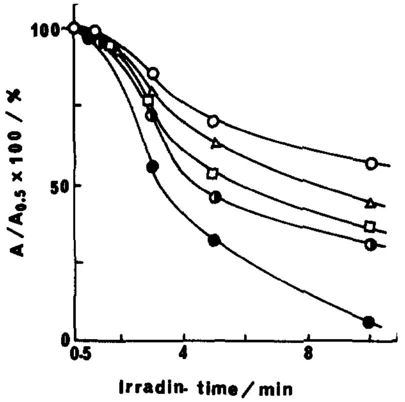


Fig. 11. Effect of additives on the photofading of **2** on cellulose (for key see Fig. 10).

ation and photobleaching process of **2** was examined on cellulose. The changes of **2** in the presence of 1-hydroxy-2-naphthoic acid zinc salt are shown in Fig. 12. The spot of **2** was colourless, and upon irradiation with ultraviolet light ($\lambda = 365\,\mathrm{nm}$) a deep blue colour was instantly formed. The coloured spot was not faded thermally, but decolourised by visible light ($\lambda > 540\,\mathrm{nm}$). The spot decolourised by visible light was recoloured upon

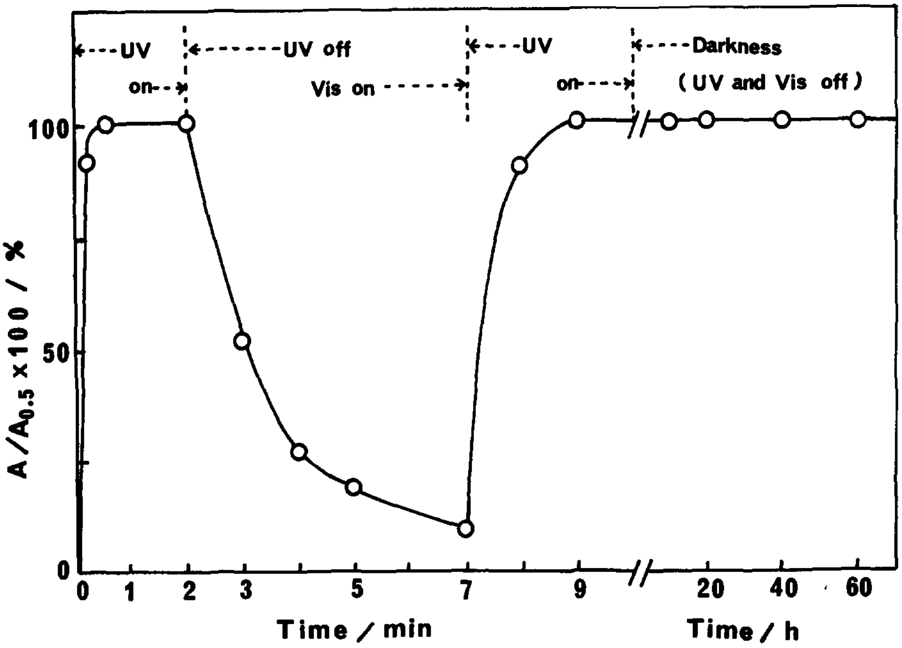
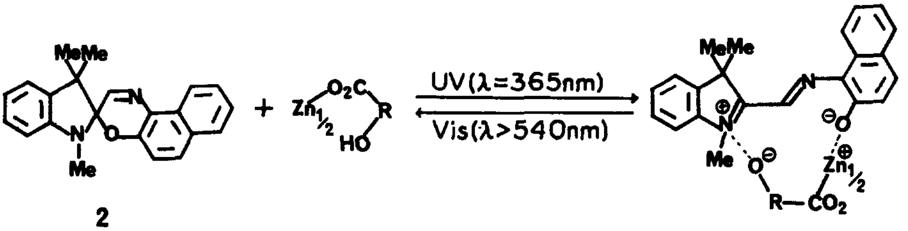


Fig. 12. Reversibility of the changes of **2** in the presence of 1-hydroxy-2-naphthoic acid zinc salt on cellulose. Initial concentrations: (**2**) $8 \times 10\,\mathrm{mol\,dm}^{-3}$, additive $1{\cdot}6 \times 10^{-1}\,\mathrm{mol\,dm}^{-3}$.



2

4

Scheme 3

ultraviolet irradiation. Even when this recoloured spot was retained for 60 h or more in darkness at room temperature, it was completely stable and maintained a deep blue colour. Such a photocolouration–photobleaching cycle could be repeated many times. These observations suggest that the influence of the amphoteric counter-ion on the photostability of the spironaphthoxazine could be as indicated in Scheme 3. The processes of formation of compound **4** are now being investigated and will be reported later.

4 CONCLUSION

Photochromic systems offer some interesting industrial applications including high-density optical memories.[1–5] It is important to control the stability of its photocoloured state. Whilst the contribution of counter-ions to the photofading of cationic dyes has been previously investigated by several workers,[12–15] there are few studies pertaining to the use of counter-ions as a means of improving the photostability of photochromic materials. In this paper, the influence of amphoteric counter-ions on the stability of photocoloured species of photochromic materials has been examined on the solid state. The results provide a novel approach for improving the photostability of functional dyes for reversible image recording medium. The metal complexes examined in this study may permit the use of spiropyrans and related compounds in practical data storage devices at ordinary temperatures.

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