Photochromic Properties of a Spirooxazine and a Spiropyran in Alcoholic Solutions of Zirconium and Aluminium Alkoxides: Influence of the Ethyl Acetoacetate Chelating Agent on the Optical Properties

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The photochromism of two spiro compounds, a spiropyran and a spirooxazine, dissolved in alcoholic solutions of metal alkoxides M(OR)$_n$ (M = Zr, Al) has been studied. In the case of the aluminium alkoxide Al(O*s*Bu)$_3$, special photochromic behaviour is observed characteristic of complexation between the coloured form of the dyes and the aluminium. This chemical interaction induces a considerable shift in the absorption spectra and a significant retardation rate in the dark. Addition of ethyl acetoacetate, a bidentate chelate of aluminium, leads to the disappearance of this particular photochromic behaviour.

Introduction

Photochromism involving changes in the visible absorption spectrum has drawn much attention over the last decades because of the variety of practical applications of photochromic systems.[1] In particular, the synthesis of solid photochromic materials using the sol-gel process has been studied extensively.[2−18] Little is known, however, about the dye−matrix interaction. The photochromic properties of spiro compounds are well known. Spiropyrans have been widely studied in the past[1,19−21] and, more recently, spirooxazines have been investigated.[1,22,23] Interest in these compounds is in part explained by their high durability with respect to photoexcitation.

The photochromism of these molecules is due to photocleavage of the spiro bond under UV irradiation, creating an open merocyanine structure (photomerocyanine) which absorbs in the visible region. The reverse reaction proceeds thermally or under irradiation with visible light. Two spiro compounds (Figure 1) have been used in this study: a spiropyran denoted **SP** (1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline]) and a spirooxazine denoted **SO** (1,3,3-trimethylspiro[indoline-2,3′-3′*H*-naphtho[2,1-*b*][1,4]-oxazine]). The photochromism of these two dyes in different solvents is well documented,[24,25] and is very sensitive to the chemical environment of the molecule. In particular, the photochromic band of merocyanine in the visible region is known to be solvatochromic. This absorption band shifts as a function of the polarity of the solvent and the colour changes. **SP** presents a negative solvatochromism characteristic of a prevalent zwitterionic coloured form, whereas **SO** presents a positive solvatochromism characteristic of a prevalent quinonic coloured form. In this paper, we report the photochromic properties (absorption properties and kinetics of thermal bleaching of the coloured form) of **SO** and **SP** in several alcoholic solutions of metal alkoxides M(OR)$_n$ (M = Zr, Al).

Usually such alkoxides are used for the synthesis of sol-gel materials in which **SO** and **SP** can be doped. The physicochemical properties of these materials depend on the chemical nature of the alkoxide(s) and especially on their possible complexation by a chelating agent. Since in solid media photochromism is directly linked to the local envir-

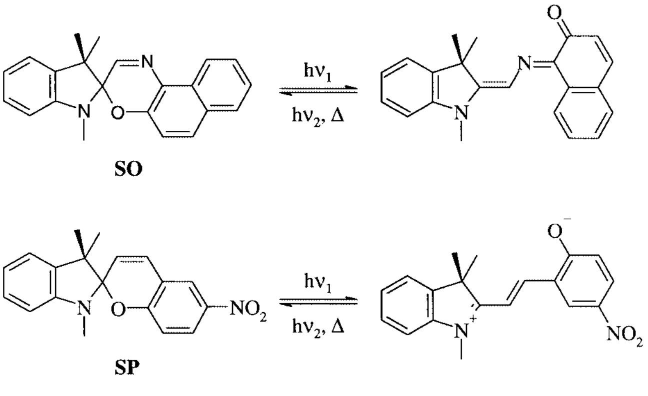

Figure 1. Molecular structures of **SO** and **SP** photochromic dyes

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onment of the organic doped dye, it is important to determine the possible chemical interaction likely to occur with corresponding molecular precursor(s). Thus, we have studied the photochromic behaviour of **SO** and **SP** in these alkoxides modified or not by a chelating agent. This study will help us in future work on solid media using **SO** and **SP** as local probes of their environment and for understanding their photochromic behaviour in terms of physicochemical dye−matrix interactions.

In the case of the aluminium alkoxide $Al(OsBu)_3$ we observed a significant modification of the photochromic behaviour of **SO** and **SP**, which can be attributed to a complexation of the photomerocyanine by aluminium. Addition of the aluminium chelating agent ethyl acetoacetate (EtacH) to the alkoxide $Al(OsBu)_3$ leads to the superposition of both the complexed and the normal photochromisms for **SP** as well as the sudden disappearance of the complexed photochromism for **SO**.

Results

Characterisation of Metal Alkoxides

Metal alkoxides $M(OR)_n$ in alcoholic solutions can exist as a variety of oligomeric species,[26,27] especially if the charge on the metal ion is less than its usual coordination number. The principal oligomeric structures proposed in the literature[28−34] for the three commercial alkoxides used in this study $Zr(OnPr)_4$, $Al(OsBu)_3$ and $[Al(OsBu)_2(Etac)]$ are shown in Figure 2. For $Zr(OnPr)_4$ the oligomeric structures contain solvent molecules.

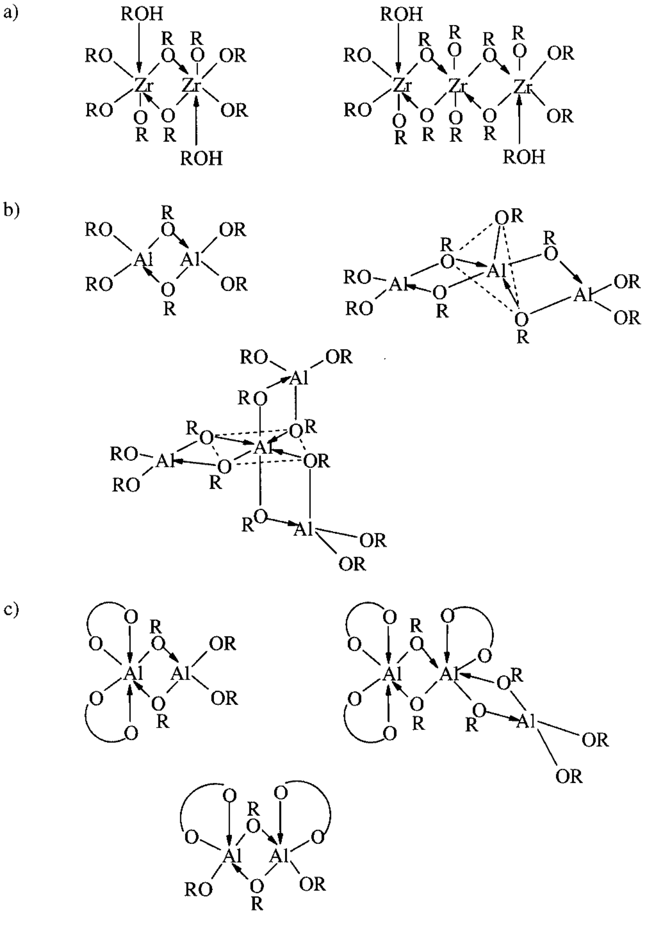

Figure 2. Prevalent oligomeric structures proposed for the metal alkoxides: (a) $Zr(OnPr)_4$; (b) $Al(OsBu)_3$; (c) $[Al(OsBu)_2(Etac)]$

To follow the influence of EtacH on $[Al(OsBu)_2(Etac)]$ we synthesised intermediate alkoxides denoted $[Al(OsBu)_{3-x}(Etac)_x]$, by mixing $Al(OsBu)_3$ with ethyl acetoacetate in molar ratios x = EtacH/Al with x = 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1. The reaction was exothermic.

The complexation between the bidentate chelate EtacH and aluminium was monitored by FTIR spectroscopy (Figure 3). The characteristic bands for EtacH are between 1745−1720 cm^{-1} and 1650−1630 cm^{-1} due to the stretching vibrations ν_{C-O} of the ketonic and enolic forms, respectively. In pure EtacH the ketonic isomer predominates[35] (Figure 4). There is no band due to the ketonic form of the Etac groups in the spectrum of $Al(OsBu)_{3-x}(Etac)_x$ or $Al(OsBu)_2(Etac)$. Only the bands characteristic of the enolic form appear between 1630−1610 cm^{-1} and 1525 cm^{-1} (ν_{C-O} and ν_{C-C}, respectively). This suggests that Equation (1) occurs.

$$Al(OsBu)_3 + x\ EtacH \rightarrow Al(OsBu)_{3-x}(Etac)_x + x\ sBuOH \qquad (1)$$

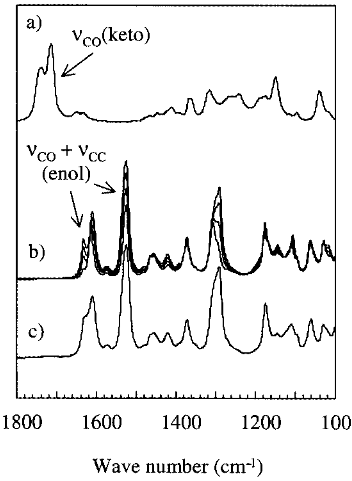

Figure 3. Infrared spectra of a) EtacH, b) $Al(OsBu)_{3-x}(Etac)_x$, c) $[Al(OsBu)_2(Etac)]$

We used ^{13}C NMR spectroscopy to look for free EtacH in the alkoxides $Al(OsBu)_{3-x}(Etac)_x$. The spectra of $Al(OsBu)_{2.7}(Etac)_{0.3}$ and $Al(OsBu)_2(Etac)_1$ (Figure 5) display two broad bands at $\delta \approx 175.6$ and 188.7 ppm. These two bands are characteristic of carbon atoms C-4 and C-2 of the Etac ligand chelated to the aluminium atom, and they confirm that the Etac groups are bonded to the aluminium centres in an enolic form (Figure 4). In comparison, the peaks indicating free EtacH are at δ = 173.5 and 176.7 ppm for the enolic form and at δ = 167.9 and 200.9 ppm for the diketonic form. Thus, the prevalent ketonic isomer of free Et-

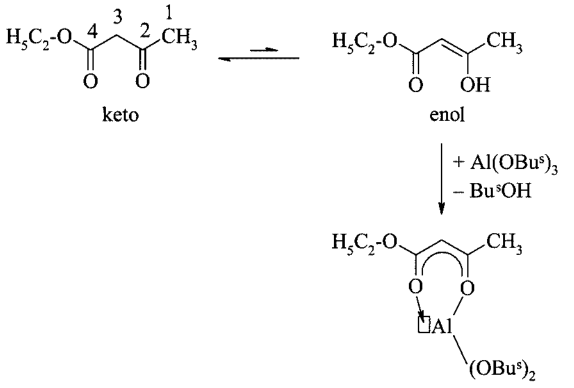

Figure 4. Keto-enol equilibrium of ethyl acetoacetate (EtacH), and schematic representation of the complexation of Al(O*s*Bu)$_3$ with the enol form of EtacH

acH is not present in the alkoxide Al(O*s*Bu)$_{3-x}$(Etac)$_x$: ^{13}C NMR spectroscopy suggests that the reaction in Equation (1) is quantitative in agreement with the reported behaviour of the reactions between metal alkoxides and chelating agents.[26]

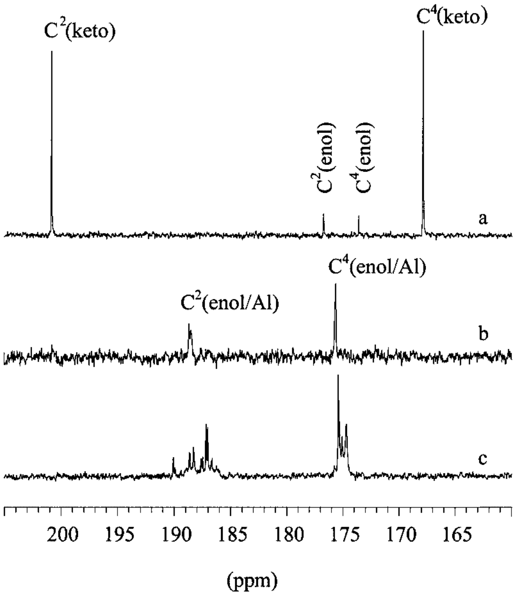

Figure 5. ^{13}C NMR spectra of (a) EtacH, (b) Al(O*s*Bu)$_{2.7}$(Etac)$_{0.3}$, (c) Al(O*s*Bu)$_2$(Etac)$_1$

^{27}Al NMR spectroscopy is very sensitive to the coordination number of aluminium.[33,34,36] The experimental and simulated ^{27}Al NMR spectra of the alkoxides Al(O*s*Bu)$_3$, Al(O*s*Bu)$_2$(Etac) (commercial) and Al(O*s*Bu)$_2$(Etac)$_1$ (prepared by mixing Al(O*s*Bu)$_3$ and EtacH at a molar ratio Etac/Al = 1) are presented in Figure 6. In Al(O*s*Bu)$_3$, the aluminium centres are mainly in tetracoordinate and pentacoordinate sites. The spectrum of Al(O*s*Bu)$_2$(Etac) is clearly different, however, with an observed increase in the coordination number of the aluminium atoms, with evidence for pentacoordinate and hexacoordinate sites. The spectra of Al(O*s*Bu)$_2$(Etac) and Al(O*s*Bu)$_2$(Etac)$_1$ are quite similar and indicate mainly hexacoordinate sites. The ^{27}Al NMR spectra of the alkoxides Al(O*s*Bu)$_{3-x}$(Etac)$_x$ (Figure 7) and their simulations (Table 1) reveal the direct influence of the bidentate ligand on the increase in aluminium's coordination number leading to a decrease of the Lewis acidity of the aluminium atom as *x* increases.

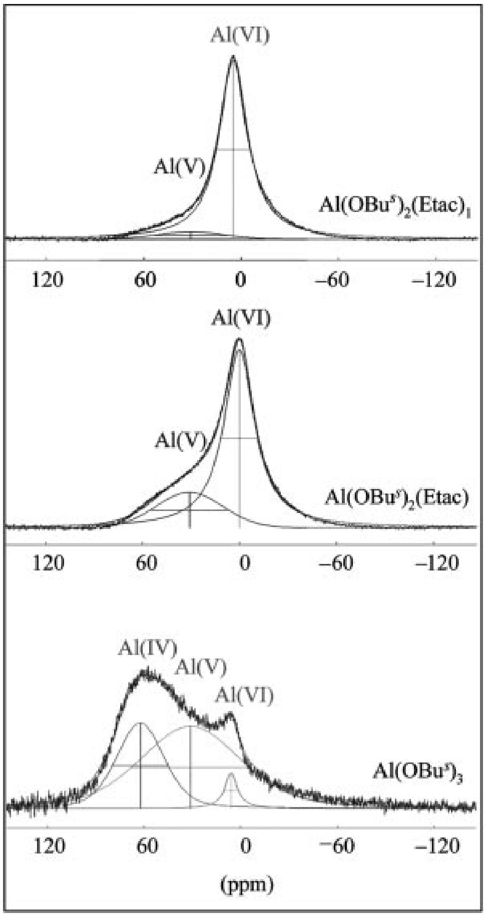

Figure 6. ^{27}Al NMR spectra of Al(O*s*Bu)$_3$, Al(O*s*Bu)$_2$(Etac)$_1$ and Al(O*s*Bu)$_2$(Etac) and their simulations

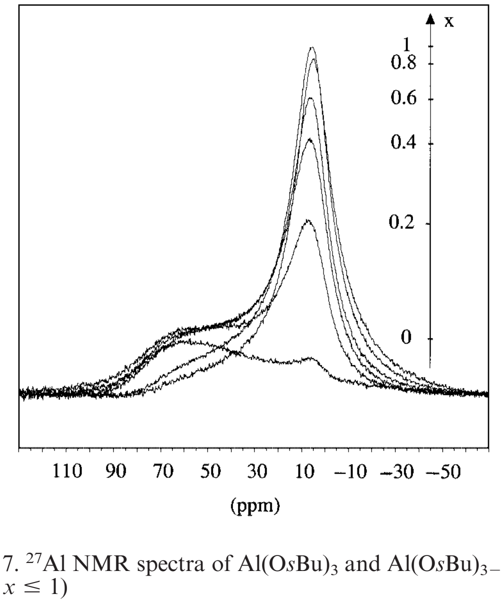

Figure 7. ^{27}Al NMR spectra of Al(O*s*Bu)$_3$ and Al(O*s*Bu)$_{3-x}$(Etac)$_x$ ($0.2 \le x \le 1$)

Table 1. Percentage of tetracoordinate, pentacoordinate and hexacoordinate aluminium in the alkoxides $Al(OsBu)_3$ 75%, $Al(OsBu)_{3-x}(Etac)_x$ and $Al(OsBu)_2(Etac)$

Alkoxide	Al^{IV} (%)	Al^{V} (%)	Al^{VI} (%)
$Al(OsBu)_3$ 75%	32	63	5
$Al(OsBu)_{2.8}(Etac)_{0.2}$	28	29	43
$Al(OsBu)_{2.6}(Etac)_{0.4}$	10	39	51
$Al(OsBu)_{2.4}(Etac)_{0.6}$	4	42	54
$Al(OsBu)_{2.2}(Etac)_{0.8}$	1	16	83
$Al(OsBu)_2(Etac)_1$	0	6	94
$Al(OsBu)_2(Etac)$	0	23	77

The oligomeric structures of the alkoxides $Al(OsBu)_{3-x}(Etac)_x$ can therefore be considered as intermediates between the oligomers of $Al(OsBu)_3$ and $Al(OsBu)_2(Etac)$ (see b and c in Figure 2).

Absorption Spectra

The absorption properties of the coloured forms of **SO** and **SP** in alcoholic solutions of zirconium and aluminium alkoxides were compared with those obtained in the corresponding solvent of the alkoxide (PrOH or *s*BuOH) or in the chelating agent EtacH (Table 2). Several metal alkoxides noted as $M(OR)_n$ x% (M = Zr, Al) were used at different percentage x by weight in the corresponding alcohol ROH.

Table 2. Absorption maxima [nm] of **SO** and **SP** in metal alkoxides $M(OR)_n$ [$M(OR)_n$ at a concentration c in ROH]

		SO $\lambda_{B,max}$ [nm]	SP $\lambda_{B,max}$ [nm]	
Solvent:				
PrOH		611	541	
*s*BuOH		611	551	
EtacH		600	567	

	$c[M(OR)n]$ [$mol\cdot L^{-1}$]	$\lambda_{B,max}$ [nm]	$\lambda_{B1,max}$ [nm]	$\lambda_{B2,max}$ [nm]
Alkoxide:				
$Zr(OnPr)_4$ 70%	2.1	610	496	–
$Zr(OnPr)_4$ 7%	0.17	611	530	–
$Al(OsBu)_3$ 75%	2.8	595	464	–
$Al(OsBu)_3$ 10%	0.33	593	457	–
$Al(OsBu)_{2.8}(Etac)_{0.2}$	2.5	594	463	–
$Al(OsBu)_{2.7}(Etac)_{0.3}$	2.5	605	462	550
$Al(OsBu)_{2.6}(Etac)_{0.4}$	2.5	–	461	555
$Al(OsBu)_{2.4}(Etac)_{0.6}$	2.3	–	466	555
$Al(OsBu)_{2.2}(Etac)_{0.8}$	2.2	–	469	555
$Al(OsBu)_2(Etac)_1$	2.1	609	469	555
$Al(OsBu)_2(Etac)$	2.2	610	460	557

The absorption spectrum of **SO** in the alkoxide $Zr(OnPr)_4$ in PrOH at 70% by weight is similar to that obtained in PrOH. For **SP**, the maximum absorption wavelength measured in $Zr(OnPr)_4$ shows a hypsochromic shift of 45 nm relative to **SP** in PrOH, which suggests a weak stabilizing interaction between the coloured form of **SP** and zirconium (see a in Figure 8). This shift is reduced to 11 nm with a dilution of $Zr(OnPr)_4$ in PrOH at 7% by weight.

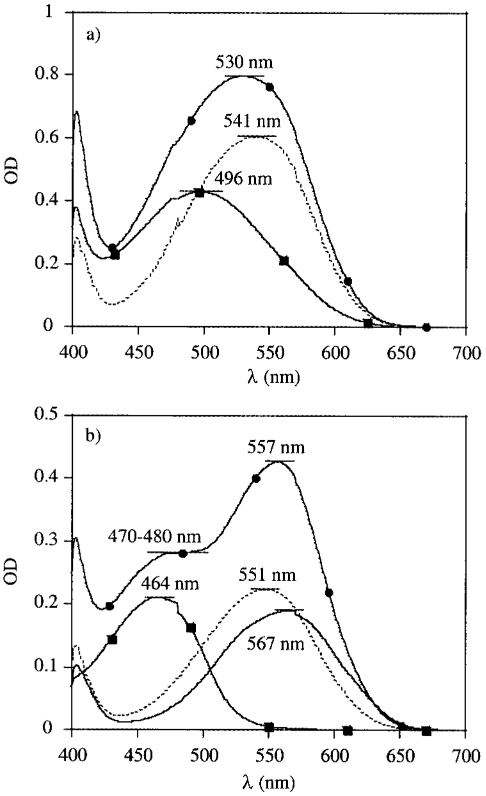

Figure 8. Visible absorption spectra of **SP** under UV irradiation in: (a) $Zr(OnPr)_4$ 70% (squares), $Zr(OnPr)_4$ 7% (dots) and PrOH (···); (b) $Al(OsBu)_3$ 75% (squares), $Al(OsBu)_2(Etac)$ (dots), *s*BuOH (···) and EtacH (—)

A drastic change in the absorption spectra of the coloured form of these dyes is observed in $Al(OsBu)_3$. The absorptions of the photomerocyanine isomers that exist before irradiation are shifted hypsochromically by 20 and 90 nm for **SO** and **SP**, respectively, relative to the values observed in *s*BuOH. This reveals a strong interaction between the photomerocyanine of the dyes and the aluminium alkoxide. This specific photochromic behaviour does not disappear with dilution of $Al(OsBu)_3$ in *s*BuOH by up to 10% by weight.

In the alkoxide $Al(OsBu)_2(Etac)$, **SO** exhibits classic photochromism whereas **SP** presents an absorption spectrum with two bands: one at 460 nm characteristic of a complexed photomerocyanine and the other at 555 nm close to the value obtained in EtacH (Figure 8, part b) revealing the direct influence of Etac on the photochromic behaviour. The absorption spectra of **SP** in the alkoxides $Al(OsBu)_{3-x}(Etac)_x$ before and during UV irradiation (Figure 9) confirm the direct link between the molar ratio x and the behaviour of the complexed dyes. Two distinct situations are observed: (a) only when x is less than 0.3 do **SO** and **SP** show photochromism whose characteristic features correspond to a complexed dye, and (b) when x is greater than or equal to 0.3 **SO** displays its usual photochromic response whereas **SP** shows a superposition of free and complexed photochromic dyes. This suggests competition between the chelation of aluminium by the ligand EtacH and its chemical interaction with the photomerocyanine of the dye.

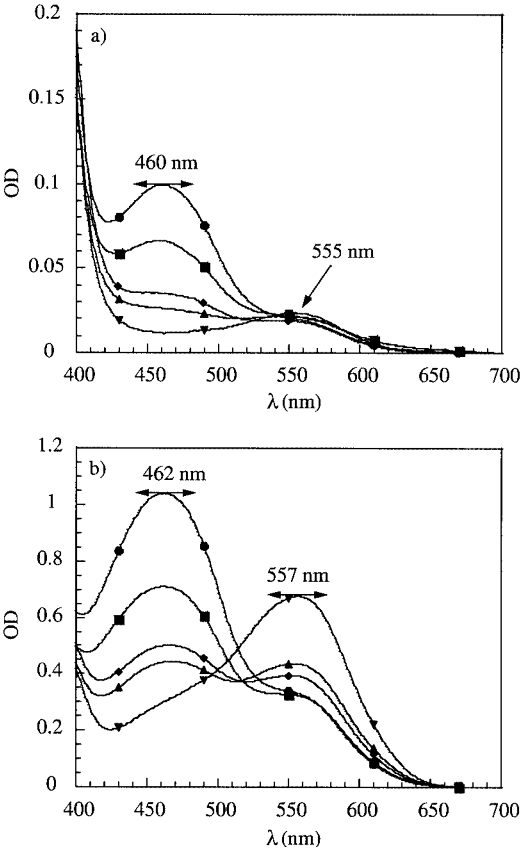

Figure 9. Visible absorption spectra of **SP** in $Al(OsBu)_{2.7}(Etac)_{0.3}$ (dots), $Al(OsBu)_{2.6}(Etac)_{0.4}$ (squares), $Al(OsBu)_{2.4}(Etac)_{0.6}$ (diamonds), $Al(OsBu)_{2.2}(Etac)_{0.8}$ (tringles, up), $Al(OsBu)_2(Etac)_1$ (triangles, down): (a) of initial coloured state and (b) under UV irradiation

Kinetics of Thermal Bleaching

The kinetics of thermal bleaching of photomerocyanines were investigated in solutions of aluminium alkoxides (Table 3) The kinetic fading rate constants k_Δ at the absorption maximum of **SO** and **SP** were obtained using a monoexponential simulation of the thermal fading versus time. When the dye exhibited superposition between a free and a complexed photochromism two kinetics of thermal bleaching $k_\Delta(\lambda_1)$ and $k_\Delta(\lambda_2)$ at each maximum of absorption λ_1 and λ_2 were observed. This suggests that no exchange between the two coloured photomerocyanines occurs during fading. To control the effect of viscosity on the fading rate we also report the relative viscosity of several aluminium alkoxides (Table 3).

Table 3. Relative viscosity η of aluminium alkoxides and thermal fading k_Δ of **SO** and **SP** in these media

		SO	**SP**	
		k_Δ [s^{-1}]	k_Δ [s^{-1}]	
Solvent:				
*s*BuOH		0.5	$2.6\ 10^{-3}$	
EtacH		1.1	$1.5\ 10^{-2}$	
	η [cP]	k_Δ [s^{-1}]	$k_\Delta(460)$ [s^{-1}]	$k_\Delta(555)$ [s^{-1}]
Alkoxide:				
$Al(OsBu)_3$ 75%	28	$2.6\ 10^{-2}$		–
$Al(OsBu)_3$ 10%	–	$5.6\ 10^{-2}$	$2.8\ 10^{-4}$	–
$Al(OsBu)_{2.8}(Etac)_{0.2}$	25	$5.4\ 10^{-2}$	$1.2\ 10^{-4}$	–
$Al(OsBu)_{2.7}(Etac)_{0.3}$	–	0.4	$3.6\ 10^{-4}$	$6\ 10^{-4}$
$Al(OsBu)_{2.6}(Etac)_{0.4}$	23	–	$7.3\ 10^{-4}$	$5.2\ 10^{-4}$
$Al(OsBu)_{2.4}(Etac)_{0.6}$	21	–	$1.1\ 10^{-3}$	10^{-3}
$Al(OsBu)_{2.2}(Etac)_{0.8}$	17	–	$1.4\ 10^{-3}$	$1.5\ 10^{-3}$
$Al(OsBu)_2(Etac)_1$	16	0.8	$2.7\ 10^{-3}$	$2.2\ 10^{-3}$
$Al(OsBu)_2(Etac)$	33	0.81	$8.8\ 10^{-4}$	$1.2\ 10^{-3}$

For **SO** when x is less than 0.3 the kinetics of thermal bleaching of the complexed coloured isomer are especially slow, indicating chemical stabilisation of the photomerocyanine by aluminium. For x greater than or equal to 0.3 the chemical interaction between **SO** and aluminium disappears but we still observe an increase in the fading rate with x. This might be due to the increase of the hydrophobic nature of the medium combined with the addition of Etac, for which the thermal fading k_Δ is especially fast: $k_\Delta(EtacH) \leq k_\Delta[Al(OsBu)_{3-x}(Etac)_x] \leq k_\Delta(sBuOH)$ for $x \geq 0.3$.

For **SP** when x is less than 0.3 the kinetics of thermal bleaching of the complexed isomer are slower than for the free isomer. This reveals a strong chemical stabilisation of the coloured photomerocyanine by aluminium. For x greater than 0.3 the thermal fading $k_\Delta(465)$ and $k_\Delta(555)$ are quite similar and become faster as x increases (Figure 10). These two values probably correspond to an average value $<k_\Delta>$ resulting from a fast chemical exchange of the metal/ligand type[37–39] between aluminium and the photomerocyanine of **SP**. The increase of this average value $<k_\Delta>$ with x could result from the decrease of the medium's viscosity and from the percentage of the complexed population of **SP**.

Discussion

The observed changes in the photochromic properties of **SO** and **SP** obtained in $Al(OsBu)_3$ are characteristic of strong chemical interactions between the coloured forms of these dyes and the aluminium. For **SO** in $Al(OsBu)_3$ we observed a hypsochromic shift of 15 nm for the complexed photomerocyanine. This is surprising given that **SO** is known to show a positive solvatochromism associated with its prevalent quinonic structure. This shift could be ex-

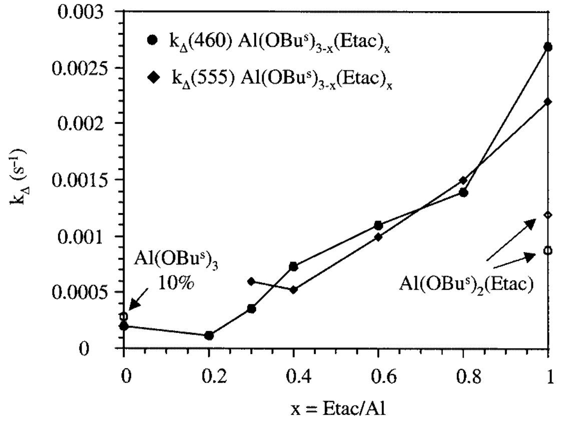

Figure 10. Evolution of the thermal fading of the free, $k_\Delta(555)$, and the complexed, $k_\Delta(460)$, photomerocyanines of **SP** with the molar ratio x = Etac/Al of the aluminium alkoxides

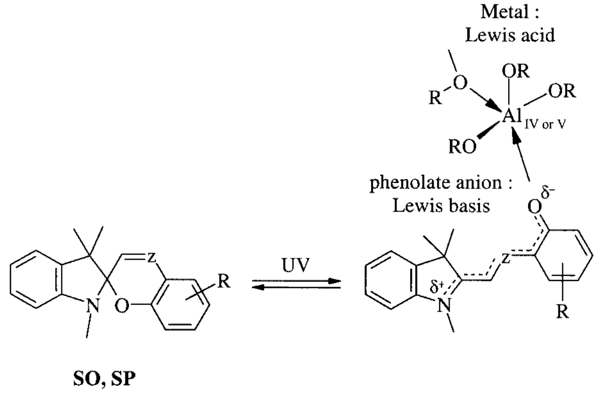

Figure 11. Schematic representation of the chemical interaction between the aluminium alkoxide and the photomerocyanine of **SO** and **SP** (Z = C or N); the depicted Al site is a representation of a trivalent aluminium cation with unsaturated coordination (tetra- or pentacoordinated)

plained by the stabilisation of the zwitterionic photomerocyanine of **SO** complexed with aluminium. The thermal fading of **SO** in 10% $Al(OsBu)_3$ of low viscosity is, surprisingly, ten times slower than the fading rate usually observed in butanol. This confirms the chemical stabilisation of the coloured form of **SO**. A similar, but more noticeable, result was observed for **SP**, with a hypsochromic shift of 90 nm and a fading rate ten times slower in 10% $Al(OsBu)_3$ than in butanol.

Addition of the chelating agent EtacH decreases the Lewis acidity of the aluminium atoms (its coordination increases), and this leads to the appearance of the free photochromic behaviour of the two dyes for x greater than or equal to 0.3. This result proves that the coloured form of the dye is sensitive to the low coordinate aluminium sites. Thus, we suggest that a monodentate Lewis acid/base interaction between the phenolate anion of the zwitterionic form of the photomerocyanine and the electronic lacuna of the tetracoordinate or pentacoordinate aluminium might be responsible for the changes in the photochromic properties (Figure 11). This interaction is monodentate since the photochromism of the **SP** complex still exists in the alkoxides $Al(OsBu)_2(Etac)_1$ and $Al(OsBu)_2(Etac)$ without tetracoordinate aluminium according to the ^{27}Al NMR simulations. This would explain the sudden and progressive disappearance of the photochromism of the complexed forms of **SO** and **SP** for x greater than or equal to 0.3 in $Al(OsBu)_{3-x}(Etac)_x$, since the complexation of the tetracoordinate or pentacoordinate aluminium by the chelating agent EtacH is in competition with the complexation of the coloured form of **SO** and **SP**.

In $Zr(OnPr)_4$, **SP** displays a weak stabilizing interaction with zirconium (small hypsochromic shift of 45 nm) whereas the photochromism of **SO** is similar to that in PrOH. The affinity of zirconium for alcohols has been discussed in the literature.[40,41] In particular it is well known that zirconium alkoxide solvates are quite stable. Indeed, the XRD structure of $[Zr(OiPr)_4,HOiPr]_2$ has been reported [42] but such affinity for alcohol ligands should be less effective for aluminium alkoxides. Besides, $Al(OsBu)_3$ is known to be a much stronger Lewis acid than $Zr(OnPr)_4$. This could explain both why the chemical complexation of the coloured forms of the dyes occurs more easily in $Al(OsBu)_3$ in *s*BuOH than in $Zr(OnPr)_4$ in PrOH, and the greater sensitivity of $Zr(OnPr)_4$ upon dilution in PrOH compared with $Al(OsBu)_3$ in *s*BuOH.

Conclusion

We have studied the photochromic properties of **SO** and **SP** in alcoholic solutions of zirconium and aluminium alkoxides. The photochromism of **SP** in $Zr(OnPr)_4$ reveals a weak stabilizing interaction with zirconium, whereas the photochromism of **SO** is not affected by this medium. In $Al(OsBu)_3$ both **SO** and **SP** show specific photochromism characteristic of a strong chemical interaction between the coloured form of the dyes and the aluminium (hypsochromic shift of the absorption maxima and decrease of the thermal fading). This complexed photochromism can be attributed to an acid/base Lewis interaction between the phenolate anion of the zwitterionic photomerocyanine and the electronic lacuna of the tetracoordinate or pentacoordinate aluminium centre. Addition of the chelating agent EtacH to $Al(OsBu)_3$ leads to the disappearance of the complexed photochromism from the molar ratio Etac/Al = 0.3. Thus, the Etac/Al ratio controls the photochromic behaviour of **SO** and **SP** in the alkoxides $Al(OsBu)_{3-x}(Etac)_x$ and the colour obtained under UV irradiation.

Finally this study provides useful data for a good understanding of the photochromism observed in solid materials obtained by the sol-gel process of these alkoxides.

Experimental Section

Synthesis: $Zr(OnPr)_4$ (70% in PrOH by weight), PrOH and *s*BuOH were purchased from Fluka. $Al(OsBu)_3$ (75% in *s*BuOH by weight) and $Al(OsBu)_2(Etac)$ (Etac = $C_6H_9O_3$) (95% in sBuOH by weight) were purchased from Gelest. Ethyl acetoacetate (EtacH), and the **SO** and **SP** dyes were purchased from Aldrich. $Zr(OnPr)_4$ was used at 70% and 7% by weight in PrOH, $Al(OsBu)_3$ was used at 75% and 10% by weight in sBuOH, $Al(OsBu)_2(Etac)$ was used at 70% by weight in sBuOH. $Al(OsBu)_{3-x}(Etac)_x$ alkoxides were synthesised by mixing $Al(OsBu)_3$ with ethyl acetoacetate at a molar ratio x = EtacH/Al with $x = 0.2$, 0.3, 0.4, 0.5, 0.6, 0.8 and 1. Solutions of **SO** and **SP** with these different metal alkoxides were prepared at a constant concentration of $5\ 10^{-3}$ mol·L^{-1}.

FTIR Spectroscopy: FTIR spectra were recorded with a 550 Magna Nicolet spectrometer using the ATR technique and a ZnSe crystal.

NMR Spectroscopy: ^{13}C NMR spectra were recorded in C_6D_6 with a Bruker AC 300 spectrometer in 5-mm tubes. Chemical shifts are given with respect to tetramethylsilane (TMS). ^{27}Al NMR spectra were recorded with a Bruker MSL 400 (104.26 MHz) spectrometer at room temperature. The reference ($\delta = 0$ ppm) was an acidic aqueous solution of aluminium nitrate. The sample was held in an 8-mm tube which was in turn placed in a 10-mm tube with C_6D_6 in the annulus as the lock solvent; 144 transients were accumulated for each sample with pulse widths of 10 μs and recycle delays of 10 s. A blank spectrum (including the probe signal) was recorded under the same experimental conditions and subtracted from each spectrum.

Viscosity Measurements: Relative viscosities were measured with a Carri-med CHR apparatus using a cylindrical geometry. Measurements were obtained under a constant pressure of 10 Pa, the equipment could not detect viscosity under 10^{-2} kg·m^{-1}·s^{-1}.

Optical Experiments: A schematic representation of the basic setup is given in Figure 12. UV light was filtered from a 400-W Xe lamp and used to activate the photocolouration of the photochromic samples. The light beam was then turned off to follow the dark fading for 10 min. The absorption spectra before and during UV irradiation, and kinetics of dark fading were recorded with a Uvikon 940 spectrophotometer in 1-mm thick quartz cells at room temperature. The kinetics of bleaching were studied by monitoring the fading of the absorbance at each wavelength of absorption maxima of the visible spectrum. The thermal bleachings were fitted ($R^2 > 0.95$) by using a mono-exponential equation: $A = B \exp(-k_{\Delta}t) + C$ (with C being the initial optical density before UV irradiation).

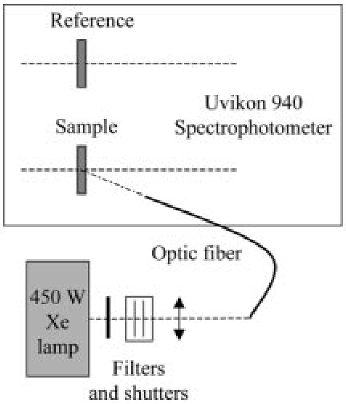

Figure 12. Schematic diagram of the apparatus used for the measurements of the photochromic samples during and after UV irradiation

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