Dyes and Pigments 89 (2011) 324-329



Contents lists available at ScienceDirect

Dyes and Pigments



journal homepage: www.elsevier.com/locate/dyepig

Kinetic modelling of the photochromism and metal complexation of a spiropyran dye: Application to the Co(II) – Spiroindolinediphenyloxazolebenzopyran system

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ARTICLE INFO

Article history: Received 29 January 2010 Received in revised form 23 April 2010 Accepted 16 June 2010 Available online 26 June 2010

Keywords: Spiropyran Photochromism Metal—ion complexation kinetics

ABSTRACT

A spirobenzopyran containing 6-chloro and 8-diphenyloxazole substituents has been investigated in acetonitrile solution by nanosecond laser photolysis at room temperature. In degassed solution, a short-lived transient (5 μ s) has been identified as the triplet state of the closed spiro form. The ratio between the singlet and triplet pathways of ring opening has been determined from oxygen quenching measurements. In the presence of Co(II), UV irradiation is needed to induce the complexation. The fast second order rate constant for the 1:1 complex formation has been determined. It is suggested that such kinetic parameter could be used to characterise the properties of metallochromic spiropyrans.

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1. Introduction

The design and synthesis of functional dye molecules that could serve as molecular devices for sensors, photo-switching, and signal transduction is an area of intense activity. Among the compounds that could be used for such purpose are the photochromic spiropyrans [1] (Scheme 1).

Spiropyrans belong to a group of photo-switchable organic molecules which photochromism involves UV light induced cleavage of the C–O bond of the neutral spirocyclic form SP producing a strongly coloured merocyanine open form MC. The latter slowly decaying through a thermal process back to the SP form, this allows reversible switching between a colourless closed form SP and conjugated zwitterionic form MC. Spiropyrans have been extensively studied due to their potential applications in optical switching, high density optical storage, image processing etc.

From a more fundamental point of view, they are of considerable interest since these molecules are key-compounds for fast time-resolved studies in organic photochemistry. The main result of femtosecond transient investigations [2] is that the ring opening occurs in a sequential way involving at least three intermediate states in the following stages. The first step is assigned to the formation of an electronic upper excited state which evolves during a radiationless transition towards the reactive excited state. The lifetime of this transition is about 40–100 fs. Then, there is a vibrational relaxation to an intermediate state where the C–O bond of the pyranic cycle is broken. This cisoïd zwitterionic state which is often called "X" evolves during 200-350 fs. Then, radiationless transition from X leads to the formation of the colored merocyanine form MC after appropriate isomerizing bond rotations. The duration of this last stage lies between 1 and 10 ps depending on the structure of the spiropyran under investigation and the reaction medium [3]. Since the pioneering work of Fischer [4], all time-resolved experiments point to the very fast formation of the relaxed merocyanine open form under the transoïd-transoïd-cis configuration (TTC).

Depending on the donor—acceptor character of the substituents and the polarities of the solvents, the triplet excited-state channel can also play a role in the dynamics of MC formation [5]. Knowledge of the relative importance of the triplet pathway is of interest since

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^{0143-7208/\$ –} see front matter @ 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2010.06.005



Scheme 1. Photochromism of the spiroindoline-diphenyloxazolebenzopyran.

diffusion-controlled quenching of the longer lived SP triplet state could occur if no special precaution to eliminate oxygen from the sample is taken.

Another interesting property of photochromic spiropyrans is the possibility to form complexes with metal ions in solvents of medium polarity such as acetonitrile [6]. The complexation is due to the possibility of electrostatic interactions between the metal cation and the phenate anion of the merocyanine form. Moreover, substituting the original structure by a suitably placed appropriate heterocyclic moiety has been used to increase the metal ion binding capabilities of these systems [7]. Such features require further studies to elucidate the mechanism of complexation.

Since many years, an intense effort has been devoted to the synthesis and the structural determination of the various chelating spiropyrans and their metal complexes [8]. However, only few quantitative characterisations of their complexation behaviour have been attempted. A possible explanation of this lack of quantitative results could lie in the relatively cumbersome data collection and analysis necessary for extracting association constants between the various metal-ions and the spiropyrans under investigation [9,10]. Although these thermodynamic parameters could be useful to direct the synthetic efforts towards the best adapted structures for a given application, only very few experimental values can be found in the literature. This is why we want to present a kinetic approach that could be used to obtain quantitative information about both reaction mechanism and structure-properties relationships, namely the analysis of fast Absorbance vs time traces recorded during photochromism and metal-ion complexation processes.

The aim of this manuscript is to analyse the kinetics of the early step of the Co(II) complexation of a newly synthesized spiroindoline-diphenyloxazolebenzopyrane able to produce a chelating merocyanine isomer using a short-lived light pulse. The incorporation of a chelating substituent into a spiropyran molecule in the vicinity of the phenate leads to a chelating bidentate ligand. The nitrogen containing 4,5-diphenyl-1,3-oxazol-2-yl substituent has been selected as it is well known that oxazole derivatives, especially those containing aromatic rings in positions 2 and 5, are good fluorophores [11,12]. Such substituent makes the compound more versatile as metal-induced fluorescence modulation could be used for analytical purposes.

2. Experimental

2.1. Products

The synthesis of compound **1** ($C_{36}H_{31}N_2O_2Cl$, FW = 558.5) has been already published [13]. UV spectrum is displayed on Fig. 1.

Cobalt perchlorate hexahydrate, Co(ClO₄)₂, 6H₂O; FW = 366.74; (99.999% pure) was purchased from Alfa Aesar and used without further purification. Acetonitrile was of HPLC grade with T% >82 at 197 nm.



Fig. 1. UV spectrum of **1** in acetonitrile solution. Lack of absorbance in the visible range (not shown) indicates the absence of traces of open merocyanine form.

2.2. Laser flash photolysis

Nano-microsecond transient absorption experiments were performed using a laser flash photolysis apparatus. Excitation pulses at 355 nm (7–8 ns, 1 mJ) were provided by a 20-Hz Nd:YAG laser (DIVA II, Thales laser). The probe light was provided by a Xe lamp (XBO 150 W/CR OFR, OSRAM). Acetonitrile solutions of **1** were contained in a quartz cell (10 × 10 mm² section). The total number of photons was around 1.8 × 10⁺⁵ photons/pulse. Within the laser beam, the total irradiated volume was about 100 µL where the total number of molecules was around 4.6 × 10⁺⁵ for a concentration of 7.7 × 10⁻⁵ mol L⁻¹ giving an absorbance of 1 at 355 nm. Degassed solutions were obtained by bubbling Argon. The transmitted light was analyzed by a spectrometer equipped with a photomultiplier (R1477-06, Hamamatsu) coupled to a digitalized oscilloscope (TDS 540, Tektronix).

2.3. NMR and UV-visible measurements under irradiation

Compound **1** was dissolved in CD₃CN ($C = 2.8.10^{-4}$ M). ¹H NMR spectra were recorded at 233 K on a 500 MHz NMR spectrometer equipped with a TXI probe. UV–visible spectra were recorded using a micro-volume optical fibre probe (optical path = 2 mm) inserted into the NMR tube (diameter = 5 mm) and connected to a Cary 50 UV–visible spectrophotometer in order to measure simultaneously the absorbance and the extent of photoisomerization.

Photoirradiation was carried out directly into the NMR tube using a thermostated home-built apparatus with a 1000 W high-pressure Hg–Xe lamp and a filter (Schott 11FG09: $259 < \lambda < 388$ nm with $\lambda_{max} = 330$ nm, T = 79%).

Firstly, the ¹H NMR and the UV—visible spectra of initial solution were recorded. Then, an irradiation for 3 min was applied leading to the appearance of a low intensity wide band at \approx 615 nm characterizing the formation of a small amount of the expected photomerocyanine. However, in NMR spectroscopy, the conversion was not sufficient to allow us to observe the corresponding signals of the merocyanine. Increasing the time of irradiation led to the formation of new absorption bands which were attributed to some photodegradation. Possible aggregation has been ruled-out since the amount of produced merocyanine remained always very low.



Fig. 2. Transient absorption spectra of compound 1 in deaerated (argon-purged) acetonitrile solution at 0.55, 2, 3, 5 and 9.3 μ s after the 355 nm pump excitation pulse.

3. Results and discussion

3.1. Irradiation of the free compound **1** in aerated and degassed solution

The purpose of this experiment was to check if triplet quenching by ambient oxygen could influence the dynamics of ring opening [14,15]. Time-resolved experiments have been performed using a 10 μ s time window.

Fig. 2 shows some typical transient absorption spectra recorded after 355 nm excitation of a degassed solution of compound **1** in acetonitrile. The spectrum recorded immediately after the laser pulse shows a weak and unresolved absorption around 510 nm and a strong band peaking at 640 nm. This last one can be attributed to the relaxed open merocyanine form. Then, during a 10 μ s time scale, the strong 640 nm band increases significantly whereas the weak absorbance at 510 nm decreases. An isosbestic point appears at 550 nm.



Fig. 3. Optical density changes recorded at 640 and 510 nm after the 355 nm laser pulse for a degassed solution (black traces) and an aerated solution (blue traces). The red lines are the best fits to the oxygen free data.

3.2. Analysis of kinetic traces

Fig. 3 shows two kinetic traces recorded on at 510 and 640 nm, *i.e.*, on both sides of the isosbestic point, for degassed (black traces) and aerated (blue traces) solutions. In both solutions, the transient responses at 510 and 640 nm evolve simultaneously and show an initial instantaneous rise and a subsequent slower decay (510 nm)/ rise (640 nm) component. In the degassed solution, a time constant of about 5 µs is measured for the slow component. In the presence of oxygen, this evolution occurs with a much shorter lifetime (around 0.25μ s). In addition, whereas the amplitude of the fast rising component at 640 nm is nearly similar to that observed in the degassed solution (a), the amplitude of the slow rising component is much weaker (c-a < b-a), which clearly indicates that the slow reaction of production of the open form is quenched by oxygen. These results demonstrate that the open merocyanine form of 1 is produced via two different ways, a fast process, kinetically unresolved at the time resolution of the experiment, and a slow oxygen-sensitive process. The fast reaction is likely arising at the excited singlet state. Within our time scale, this process appears as instantaneous as it is well known that the singlet state reaction pathway leads to the open form in few picoseconds or less [16]. The oxygen-sensitive process is likely involving the triplet state T₁, since triplet states are usually strongly quenched by oxygen. Accordingly, we assign with confidence the transient absorption band in the 450-550 nm domain (Fig. 2) to the lowest excited triplet state of the closed form of 1. The relative yield of ring opening from the singlet and triplet pathways can then be estimated from the amplitude ratio of the fast and slow rising contributions in the 640 nm kinetics on Fig. 3 (see below).

3.3. Kinetic modelling of the singlet vs triplet ring opening pathways

In order to check the validity of these assumptions, and to describe semi-quantitatively the singlet *vs* triplet ring opening processes, a global model [17] has been proposed. This model involves only four species: the closed form SP, its singlet S_1 and triplet T_1 states, and the open merocyanine form MC. For the sake of simplicity, all the intermediate short-lived transient species such as open forms of higher energies whatever their multiplicities, have been short-cut since they are too fast to be seen within the μ s time-scale kinetics. The processes under consideration are based on classical photochemistry laws such as deactivation or internal conversion, intersystem crossing and ring opening. The kinetic model is then described by a system of simple differential equations which can be integrated algebraically. The assumed kinetic model is listed on Table 1.

The laser pulse is assumed to be sufficiently short *vs* the duration of the observed phenomena. At the end of the laser pulse the produced singlet state S_1 evolves within a picosecond time scale according to three possible ways: (i) radiative or non radiative (internal conversion) deactivation to the ground state of SP (k_{sd}), (ii) ring opening pathway leading to the open form MC (k_{sr}), and (iii) intersystem crossing to the triplet state (k_{isc}). Therefore, the concentrations of the free merocyanine [MC]_p and triplet state [T]_p arising from S₁ are respectively:

$$[T_p] = k_{isc}[S_1]_0 / (k_{sd} + k_{sr} + k_{isc})$$

$$\tag{1}$$

and

$$[\mathsf{MC}_{\mathsf{p}}] = k_{\mathsf{sr}}[\mathsf{S}_1]_0 / (k_{\mathsf{sd}} + k_{\mathsf{sr}} + k_{\mathsf{isc}})$$
⁽²⁾

where $[S_1]_0$ is the total amount of S_1 produced by the pulse. The subscript "p" indicates that the concentrations of T and MC are to be considered just after the end of the laser pulse. The singlet state lifetime is then defined by $\tau_S = 1/(k_{sd} + k_{sr} + k_{isc})$. Then, during the

 Table 1

 List of processes used in the kinetic modeling of the singlet vs triplet ring opening of the spiropyran 1.

Processes	Rate constan	t Processes
$SP \rightarrow S_1$	laser pulse	excitation process
$S_1 \rightarrow SP$	k _{sd}	singlet state deactivation (radiative or not)
$S_1 \rightarrow MC$	k _{sr}	singlet state ring opening
$S_1 \rightarrow T_1$	k _{isc}	intersystem crossing
$T_1 \rightarrow MC$	$k_{\rm tr}$	triplet state ring opening
$T_1 + O_2 \rightarrow SP + O_2$	$k_q[O_2]$	triplet state quenching by dissolved oxygen
$T_1 \to SP$	$k_{\rm td}$	triplet state deactivation (radiative or not)

slow evolution occurring after the jump within the triplet time scale, [T] and [MC] obey respectively to the following differential equations:

$$d[T]/dt = -(k_{tr} + k_{td})[T]$$
(3)

and

$$d[MC]/dt = k_{tr}[T] \tag{4}$$

giving rise to mono-exponential kinetics:

 $[T] = [T]_{p} \exp(-t/\tau_{T})$ (5)

and

=

$$[MC] = [MC]_p + k_{tr}[T]_p \tau_T (1 - \exp(-t/\tau_T))$$
(6)

where $\tau_{\rm T}$ is the degassed triplet lifetime, $\tau_{\rm T} = 1/(k_{\rm tr} + k_{\rm td})$

When the experiment is performed in aerated solution, the triplet lifetime is reduced to: $\tau_{T(O_2)} = 1/(k_{tr} + k_{td} + k_q[O_2]) \approx 0.25 \ \mu$ s, therefore $k_q[O_2] = 1/\tau_{T(O_2)} - 1/\tau_T = ((1/0.25) - 1/5) \ \mu$ s⁻¹ = 3.8 × 10⁶ s⁻¹. Then, taking into account that in air saturated acetonitrile [18], the concentration of dissolved oxygen is about [O₂]_{diss} = 1.9 × 10⁻³ mol L⁻¹, a value of $k_q = 2 \times 10^9 \ M^{-1} \ s^{-1}$ is obtained, in agreement with the literature ($k_q = 1.9 \times 10^9 \ M^{-1} \ s^{-1}$) [19].

Within the framework of the model displayed on Table 1, the relative proportion of the merocyanine MC formed from singlet and triplet states can be calculated as:

% of MC arising from triplet = slow evolution/

(instantaneous + slow evolution)

(amplitude at
$$t \rightarrow \infty$$
 – amplitude at $t = 0$)/

amplitude at
$$t \to \infty = k_{\rm tr}[T]_{\rm p} \tau_{\rm T} / ([{\rm MC}]_{\rm p} + k_{\rm tr}[T]_{\rm p} \tau_{\rm T})$$

= $k_{\rm tr} k_{\rm isc} \tau_{\rm T} / (k_{\rm tr} k_{\rm isc} \tau_{\rm T} + k_{\rm sr})$ (7)

However, when the evolution is monitored through the absorbance, Beer's law applies:

$$Abs^{\lambda} = \left(\varepsilon_{MC}^{\lambda}[MC] + \varepsilon_{T}^{\lambda}[T]\ell\right)$$
(8)

$$Abs^{\lambda} = \left[\varepsilon_{MC}^{\lambda} (k_{tr} k_{isc} \tau_{T} + k_{sr}) + k_{isc} \left(\varepsilon_{T}^{\lambda} - \varepsilon_{MC}^{\lambda} k_{tr} \tau_{T} \right) \\ exp(-t/\tau_{T}) \right] \ell [S_{1}]_{0} \tau_{S}$$
(9)

where $\varepsilon_{MC}^{\lambda}$ and $\varepsilon_{T}^{\lambda}$ are respectively the molar absorption coefficients of open merocyanine MC and triplet state T at wavelength λ .

Then,
$$\operatorname{Abs}^{\lambda}(t \to \infty) = \varepsilon_{\operatorname{MC}}^{\lambda}(k_{\operatorname{tr}}k_{\operatorname{isc}}\tau_{\operatorname{T}} + k_{\operatorname{sr}})\mathfrak{Q}[S_1]_0\tau_{\operatorname{S}}$$
 (10)

and

$$Abs^{\lambda}(t = 0) = \left[\varepsilon_{MC}^{\lambda}(k_{tr}k_{isc}\tau_{T} + k_{sr}) + k_{isc}\left(\varepsilon_{T}^{\lambda} - \varepsilon_{MC}^{\lambda}k_{tr}\tau_{T}\right) \right]$$
$$\ell[S_{1}]_{0}\tau_{S}$$
(11)

which gives rise to the % of MC arising from triplet =

$$\left(\operatorname{Abs}^{\lambda}(t \to \infty) - \operatorname{Abs}^{\lambda}(t = 0) \right) / \operatorname{Abs}^{\lambda}(t \to \infty)$$

= $k_{\operatorname{isc}} \left(\varepsilon_{\operatorname{MC}}^{\lambda} k_{\operatorname{tr}} \tau_{\operatorname{T}} - \varepsilon_{\operatorname{T}}^{\lambda} \right) / \left[\varepsilon_{\operatorname{MC}}^{\lambda} (k_{\operatorname{tr}} k_{\operatorname{isc}} \tau_{\operatorname{T}} + k_{\operatorname{Sr}}) \right]$ (12)

At a wavelength where $\varepsilon_{\rm T}^{\lambda} \ll \varepsilon_{\rm MC}^{\lambda}$ the previous expression from eq. (7): $k_{\rm tr}k_{\rm isc}\tau_{\rm T}/(k_{\rm tr}k_{\rm isc}\tau_{\rm T} + k_{\rm sr})$ is recovered.

From the ratio of the triplet state lifetime in the degassed (0.25 µs) and aerated (5 µs) solutions, it appears that (5-0.25)/5 = 95% of the triplet state is quenched in the presence of oxygen and thus the yield of the open form arising from the triplet state is expected to be reduced by a factor of 20. According to an absorbance change = 0.021 (amplitude of the red curve at 640 nm = *b*-*a*) in the degassed solution (Fig. 3), it is thus expected that this amplitude was only 0.021/20 = 0.001 in the aerated solution. Such a value is close to the experimental value of $\Delta OD \approx 0.001$ (*c*-*a*). It is found that a/b = 62% of the ring opening originates from the singlet state S₁ and (b-a)/b = 38% from the triplet T₁. These results confirm that the mechanism shown in Table 1 is roughly sufficient to interpret the singlet *vs* triplet ring opening in spiropyran **1**. From these considerations, the following relationships between the various rate constants can be derived: $k_{sr}/(k_{tr}k_{isc}) = 8$ µs; $k_{tr} + k_{td} = 2 \times 10^{+5} \text{ s}^{-1}$ and $k_q = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

3.4. Metal complexation

Metal complexation occurs from the negatively charged phenate substituent in the merocyanine MC open form. In the case of



Fig. 4. Variation of the absorbance at 630 and 530 nm for compound 1 in the presence of Co(II) ions in non-degassed acetonitrile at room temperature (left: $[Co] = 10^{-4} \text{ mol } L^{-1}$; right: $[Co] = 6.3 \times 10^{-4} \text{ mol } L^{-1}$) after 355 nm nanosecond laser pulse.

spiropyrans, in which an SP \leftrightarrow MC thermochromic equilibrium is present, there is always a small quantity of MC available for the complexation [20]. In these conditions, although it is assumed to be rapid, the rate of the metal complexation reaction (MC + **M** \rightarrow MC**M**) is limited by the SP \rightarrow MC ring opening process [21].

On the contrary, in the specific case of compound 1, the thermochromic equilibrium is not operative as there is no perceptible trace of merocyanine open form in the UV spectrum recorded in acetonitrile solution. UV irradiation is needed to provide the amount of merocyanine MC required to trigger the metal complexation. The fast relaxation of the MC + $\mathbf{M} \rightarrow MC\mathbf{M}$ (k_2) complexation reaction has been recorded in the merocyanine band at 630 and also at 530 nm after 355 nm nanosecond laser pulse. The 530 nm band is assigned to the 1:1 metal complex because within ionophoric spiropyrans, the recognition of a metal cation is accompanied by a strong hypsochromic shift of the absorption band of the merocyanine form. Since the formation of the relaxed open form occurs in the 10 µs time domain, it is expected that the complexation, whose relaxation time ranges on more than hundreds of µs, arises on the already relaxed open form. This assumption is confirmed by the absence of fast phase during the evolution of the complexation.

During the MC + $\mathbf{M} \rightarrow \text{MCM}(k_2)$ fast process we have: $\text{Abs}^{\lambda} = (\varepsilon^{\lambda}_{\text{MCM}}[\text{MC}] + \varepsilon^{\lambda}_{\text{MCM}}[\text{MCM}]) \ell$ with $\varepsilon^{630}_{\text{MC}} > \varepsilon^{630}_{\text{MCM}}$ and $\varepsilon^{530}_{\text{B}} < \varepsilon^{530}_{\text{MCM}}$. Hence, on Fig. 4 the decrease at 630 nm corresponds mainly to the consumption of the merocyanine while the increase at 530 nm characterizes the complex build-up. Numerical fitting of the relaxation kinetics recorded just after the laser flash shows a mono-exponential behaviour in accordance with the assumed process of formation of the 1:1 metal complex from the relaxed merocyanine [22]. The observed pseudo first-order rate constant is expressed as $k_{\text{obs}} = k_2 \times [\mathbf{M}]$ where $[\mathbf{M}]$ is the added metal concentration. This relationship allows the determination of $[\mathbf{M}]$ from the measurement of k_{obs} .

The results of the kinetic traces analysis are gathered on Table 2. Careful examination of the data shows that the kinetic traces amplitudes are independent of the metal concentration. The differences $|Abs_0 - Abs_{\infty}|$ are of the same order of magnitude: 1.09×10^{-2} $vs 0.99 \times 10^{-2}$ at 530 nm and 2.93 $\times 10^{-2} vs 3.10 \times 10^{-2}$ at 630 nm for the 1.0 \times 10 $^{-4}$ and 6.3 \times 10 $^{-4}$ mol L^{-1} Co(II) concentrations, respectively. tively. Since the metal concentration is in excess in both cases, the amplitudes are only determined by the amount of merocyanine produced by the laser pulse. At the end of the evolution, all the merocyanine is complexed. The second-order complexation rate constant k_2 is around 1.5 \pm 0.9 \times 10⁺⁷ M⁻¹ s⁻¹. It is not easy to compare this value with literature data, because with the exception of the two pioneering papers by Görner and Chibisov [23] there are no more published studies. However, looking at Table 3, it is obvious that our value is more than one order of magnitude lower than those already published for Co(II) complexation of similar spiropyrans in acetonitrile solutions.

This difference can be interpreted by considering some structural features (see structure on Table 3): the presence of a chloro substituent instead of a nitro, the size of the nitrogen substituent of the indoline and the bulky DPO heterocycle limiting the access to

Table 2

Initial and final amplitudes and observed apparent rate constants of the monoexponential relaxation kinetic curves recorded in the merocyanine and metallic complex absorption bands.

	Curve	$[\mathbf{M}]$ (mol L ⁻¹)	Abs ₀	Abs $_{\infty}$	$k_{\rm obs}({\rm s}^{-1})$	k_2 (L mol ⁻¹ s ⁻¹)
Ī	530	10 ⁻⁴	$1.29 imes 10^{-2}$	$2.35 imes 10^{-2}$	$1.9 imes 10^3$	$1.9 \times 10^{+7}$
	630	10^{-4}	$5.03 imes 10^{-2}$	$2.1 imes 10^{-2}$	$2.6 imes 10^3$	$2.6 imes 10^{+7}$
	530	$6.3 imes 10^{-4}$	$1.25 imes 10^{-2}$	$\textbf{2.24}\times \textbf{10}^{-2}$	6.0×10^3	$9.5 imes 10^{+6}$
	630	$6.3 imes 10^{-4}$	3.42×10^{-2}	$\textbf{3.18}\times\textbf{10^{-3}}$	$\textbf{4.8}\times\textbf{10}^3$	$7.6 imes 10^{+6}$

Table 3

Effect of the structure of the spiropyran on the second order rate constant of Co(II) complexation. a, b: results from ref. 22b in non-degassed acetonitrile; 1: our result.



the phenate anion. From all these considerations, it appears that kinetic rate constants of metal complexation are very sensitive to the stereo-electronic effect of the various substituents. Therefore, in combination with complexation equilibrium constants they could profitably be used to characterize newly synthesized photochromic and metallochromic spiropyrans.

4. Conclusion

In this paper, we have analysed the photochromism and metallochromism of a DPO substituted spirobenzopyran. In this compound, as there is no thermal ring opening, UV irradiation in presence of the metal ion is necessary to trigger the complexation. In deaerated acetonitrile, about 38% of the ring opening proceeds from a triplet state exhibiting a lifetime around 5 µs. In presence of oxygen, the triplet lifetime is reduced to 0.25 μ s indicating a rapid quenching by oxygen ($k_q = 2 \times 10^{+9} \text{ M}^{-1} \text{ s}^{-1}$). In the 10 µs time scale open merocyanine accumulates. In presence of Co(II) ions, a fast complexation occurs leading to a hypsochromic shift. The second order rate constant of complexation has been determined at 1.5 \times 10⁺⁷ M⁻¹ s⁻¹. We propose to use the complexation kinetic rate constants for the quantitative characterisation of these dye molecules. Although, it necessitates time resolved absorbance measurements in the µs time scale, the main advantage of this approach is the possibility to consider new types of spiropyrans metal sensors [24] in which the metal complexation occurs only after photoisomerization.

Acknowledgements

MIZ thanks the France-Russia network of the "Ministère de l'Education Nationale, de l'Enseignement Supérieur et de la Recherche » for a grant. CC, JCM and MS gratefully acknowledge the French CNRS for financial support in the framework of the International Research Group n° 93 « PHENICS ».

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