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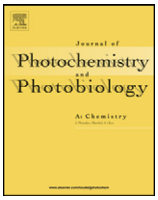

Structural and photochemical aspect of metal-ion-binding to a photochromic chromene annulated by crown-ether moiety

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ABSTRACT

Complexation between a benzopyran entity annulated with a 15-crown-5 ether unit and three metal cations, Mg^{2+}, Ba^{2+}, and Pb^{2+} has been investigated by UV–vis and NMR spectroscopy. The complexes composition, the stability constants and the structural arrangements have been determined. The photochemical and thermal properties of the photochromic benzopyran derivative in absence and in the presence of metals have been studied. The metal-ion-binding ability of the fused macrocyclic entity drastically modifies photochromism by decreasing the thermal stability of photomerocyanines, whereas the metal cations are partially ejected from crown-ether cavity when benzopyran is in open configuration.

1. Introduction

Photochromism is defined as the reversible photoinduced transformation of a photosensitive compound into another isomer exhibiting a different absorption spectrum [1–4]. These properties have been the subject of a great number of investigations due to the potential applications, such as optical variable-transmission materials, optical switches and memories [5–7]. Spiropyrans, spirooxazines, benzo- and naphthopyrans (also called chromenes) are well-known photochromic families, also called T-photochromes, as the return to the initial state when irradiation is stopped is mainly thermal [1–4]. Among them, the photochromic properties of benzopyrans were firstly reported by Becker and Michl in 1966 [8], paving the way for extensive investigations of this family as the result of their excellent photochromism: fast and intense photocoloration, fast thermal relaxation and high resistance to photodegradation. Irradiation with UV light leads to the cleavage of the C– bond, resulting in distribution of isomeric open forms named photomerocyanines, which are thermally reversible [4,9,10].

The development of photochromic systems aims at improving the photostability, obtaining a higher sensitivity, a wide choice of operating wavelengths and amplification capability [11–14]. It is possible to control different features by supramolecular mode. Incorporation of a crown-ether moiety, able to bind metal ions, into the molecule skeleton can be exploited to tune the photochromic properties by complex formation. The approach has been found to be effective for different kinds of photochromic compounds [14–24]. Among these, the synthesis and investigation of benzochromenes joined through different spacers to ionophoric groups or bearing a crown-ether moiety conjugated with the chromophore system have been reported. Due to the conjugation between ionophoric and photochromic parts, the complex formation substantially modifies the spectral and kinetic characteristics of the chromophore part, whereas the photochromic transformation changes the binding ability of the ligand remarkably [25–28]. We therefore report in the present paper on the structural aspect of complexes between a benzopyran annulated by 15-crown-5 ether moiety, **1** (Scheme 1) in closed and photoinduced merocyanine forms with three metal cations (Mg^{2+}, Ba^{2+} and Pb^{2+}) investigated by UV–vis and NMR spectroscopy.

2. Experimental

2.1. Materials

16,16-Diphenyl-2,3,5,6,8,9,11,12-octahydro-2H-[1,4,7,10,13]pentaoxacyclopentadeca[2,3-]chromene **1** [29] was prepared

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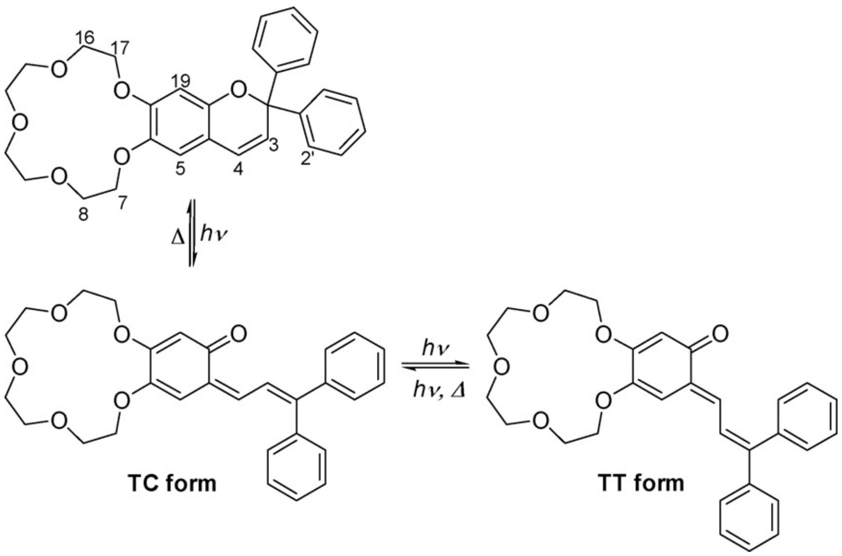


Scheme 1. Photochromic equilibrium of benzopyran **1**.

according the described procedure [30] from 2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecin-15-ol (4-hydroxybenzo-15-crown-5 ether) (0.57 g, 2 mmol) and β-phenylcinnamaldehyde (0.42 g, 2 mmol) as a white powder (0.19 g, 20%); found: C, 73.2; H, 6.3. $C_{29}H_{30}O_6$ requires C, 73.0; H, 6.4%; ^{1}H NMR (300 MHz; CD_3CN): δ ppm 3.58–3.70 (8 H, m, 5-H, 6-H, 8-H, 9-H), 3.72–3.83 (4 H, m, 3-H, 11-H), 3.96–4.02 (2 H, m, 2-H), 4.04–4.12 (2 H, m, 12-H), 6.25 (1 H, d, J 9.8, 17-H), 6.48–6.63 (2 H, m, 18-H, 14-H), 6.69 (1 H, s, 19-H), 7.22–7.65 (10 H, m, ArH); ^{13}C NMR (75 MHz; CD_3CN): δ ppm 68.5 (t), 68.8 (t), 69.2 (t), 69.7 (t), 69.8 (t), 70.1 (t), 70.4 (t), 70.5 (t), 82.0 (s, 16-C), 102.8 (d), 112.9 (d), 113.8 (s), 123.3 (d), 126.5 (4 × d), 126.8 (d), 127.5 (2 × d), 128.2 (4 × d), 143.4 (s), 145.3 (2 × s), 147.2 (s), 150.4 (s).

2.2. Preparation of complexes

Anhydrous CH_3CN, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, and $Pb(ClO_4)_2{\cdot}3H_2O$ were used without additional purification.

2.3. UV–vis spectroscopy measurements

UV/vis absorption spectra were recorded with Varian Cary 50 spectrometer. The absorption spectra of merocyanine isomers were measured upon steady-state irradiation of solutions with 250 W Xe-lamp equipped with monochromator or high pressure Hg lamp 120 W equipped with optical filters ($\lambda_{max} = 313$ nm).

2.4. Stability constant measurements

Complex formation of **1** with $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, $Pb(ClO_4)_2$ in CH_3CN at $20 \pm 0.1\,^{\circ}C$ was studied by spectrophotometric titration. The ratio of $Mg(ClO_4)_2$ or $Ba(ClO_4)_2$ or $Pb(ClO_4)_2$ to **1** was varied in range 1/0 to 1/10 by adding aliquots of a corresponding salt solution of certain concentration to a solution of **1** alone (in range 1/0–1/2 with step 0.1 and in range 1/2–1/10 with step 2, 4, and 2, respectively). The absorption spectrum of each solution was recorded and the stability constants of the complexes were determined by applying the SPECFIT/32 [31] software to experimental data. Two equilibria were studied:

$$\mathrm{L} + \mathrm{M} \overset{\beta_{11}}{\rightleftharpoons} \mathrm{LM} \qquad \beta_{11} = \frac{[\mathrm{LM}]}{[\mathrm{L}][\mathrm{M}]}$$

$$2\mathrm{L} + \mathrm{M} \overset{\beta_{21}}{\rightleftharpoons} \mathrm{L_2M} \qquad \beta_{21} = \frac{[\mathrm{L_2M}]}{[\mathrm{L}]^2[\mathrm{M}]}$$

where L stands for ligand **1** and M stands for metal ion.

2.5. NMR spectroscopy

NMR spectra were recorded on Bruker 300 MHz and 500 MHz spectrometers (QNP, BBI, and TXI probes). Solutions in CD_3CN were investigated. Concentration $\sim 10^{-3}$ M. Sample volume 0.5 ml. Experiments with irradiation were performed using 1000 W Xe–Hg lamp equipped with (1) optical filter Schott 011FG09 ($259 < \lambda < 388$ nm, $\lambda_{max} = 330$ nm, $T = 79\%$ and (2) interferential optical filter with $\lambda_{max} = 313$ nm ($300 < \lambda < 335$ nm, $T = 7\%$).

3. Results and discussion

3.1. Complex formation of the chromene with metals ions

Complexation of the closed form **1** in acetonitrile was firstly examined by UV–vis spectroscopy. The electronic absorption spectra of **1** show small blue shift up to 5–8 nm of the longest wavelength absorption band upon addition of Mg^{2+}, Ba^{2+} and Pb^{2+} (Fig. 1) indicating that the metal cation is bound by the macrocyclic unit. No band characterizing the thermal opening of chromene induced by metal complexation (ionochromism) was observed, unlike that detected for some photochromic spirobenzopyrans [32,33]. Analysis of spectra recorded at various concentrations of Mg^{2+}, Ba^{2+} and Pb^{2+} perchlorates provided evidence for 1:1 (for the three cations) and 2:1 (for barium and lead ions only) complexation and the stability constants have been estimated (Table 1).

The Mg^{2+} ion, having the smallest ionic radius (0.72 Å) fits well the 15-crown-5 ether cavity (0.86–0.92 Å, $r_{ion}/r_{crown} \approx 0.8$) [35] resulting in an inclusive 1:1 complex when an ion is inside the crown-ether unit. The values of the stability constants for the three 1:1 complexes are similar, although an increase is observed with barium and especially with lead cations. As the sizes of Ba^{2+} and Pb^{2+} are greater than the crown-ether cavity ($r_{ion}/r_{crown} > 1$), the

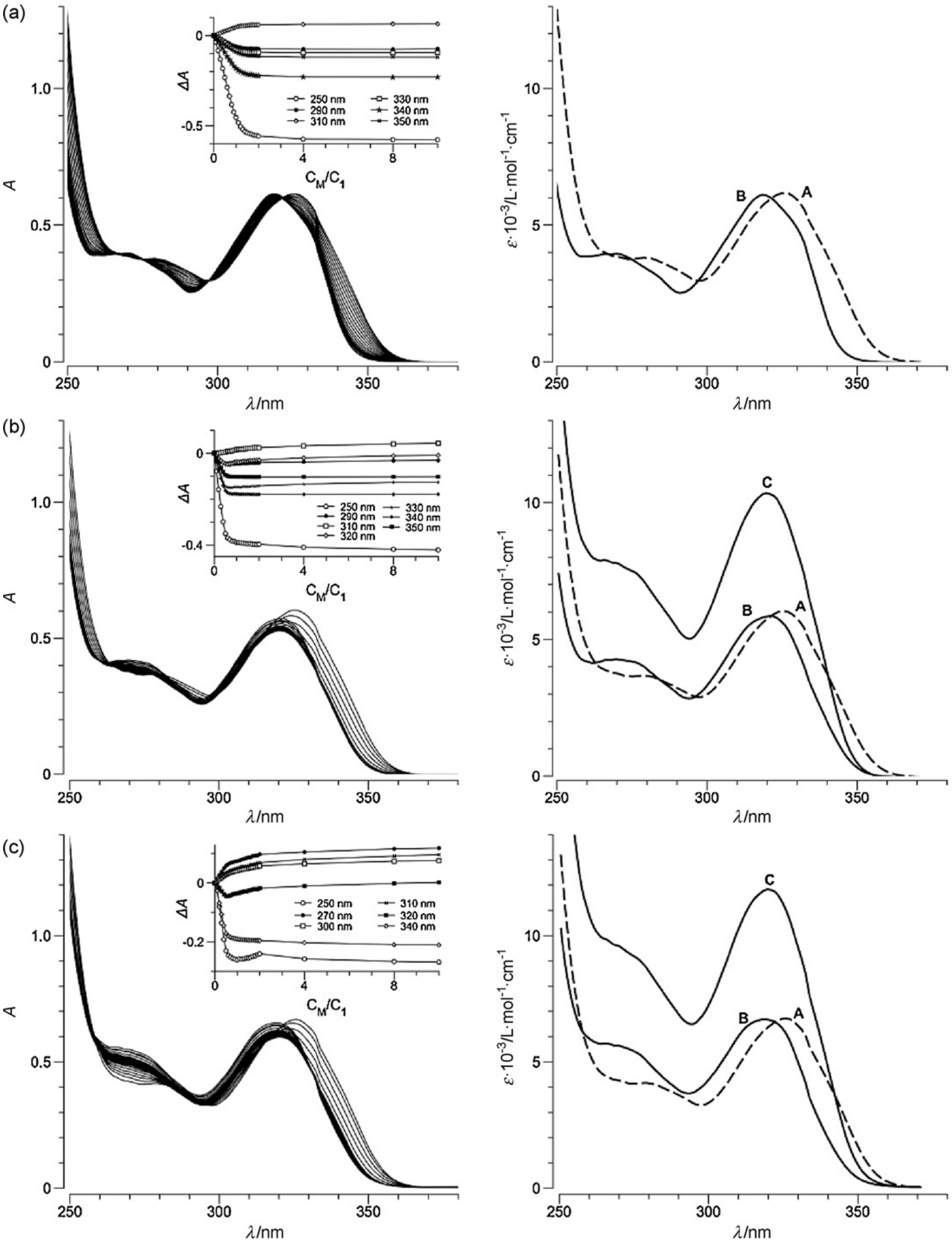


Fig. 1. UV spectral changes produced by changes in relative concentrations of **1** in acetonitrile with (a) $Mg(ClO_4)_2$, (b) $Ba(ClO_4)_2$ and (c) $Pb(ClO_4)_2$: experimental data are presented on the left plots, inset showing absorbance changes on specified wavelengths; initial electronic spectrum of chromene **1** (A) and determined spectra of complexes $\mathbf{1}{\cdot}M^{2+}$ (B) and $\mathbf{1}_2M^{2+}$ (C) are shown on the right plots.

Table 1
Stability constants of complexes of **1** with Mg^{2+}, Ba^{2+}, and Pb^{2+} measured by spectrophotometric method in CH_3CN, 20 °C. Ionic radii (r_{ion}) of cations and mean ratios of the radii to 15-crown-5 ether cavity size are also reported.

Cation	$\lg \beta_{11}$	$\lg \beta_{21}$	Ionic radius [34], r_{ion} (Å)	Mean radii ratio, r_{ion}/r_{crown}
Mg^{2+}	5.26 ± 0.04	–	0.72	0.8
Ba^{2+}	5.39 ± 0.03	11.21 ± 0.06	1.35	1.5
Pb^{2+}	6.7 ± 0.3	13.7 ± 0.4	1.19	1.3

ions can form an exclusive type of 1:1 complexes when an ion is situated outside the macrocyclic entity. With the three metal ions, the interaction with the oxygen heteroatoms is essentially electrostatic in nature and, therefore, the charge density of the cations is dominant. The metal-ion Pb^{2+} is potentially softer and should, in principle, lead to less stable complexes with oxygen donor sites. However, its high polarisation and the covalent character of the interactions that it can establish may justify the highest stability of its complexes. This higher value for the association constant with Pb^{2+} when compared to that with Ba^{2+} was also reported in literature [34–37].

As for the 2:1 complexes, the size of Ba^{2+} and Pb^{2+} being larger (1.35 and 1.19 Å, respectively) than the size of Mg^{2+}, these can

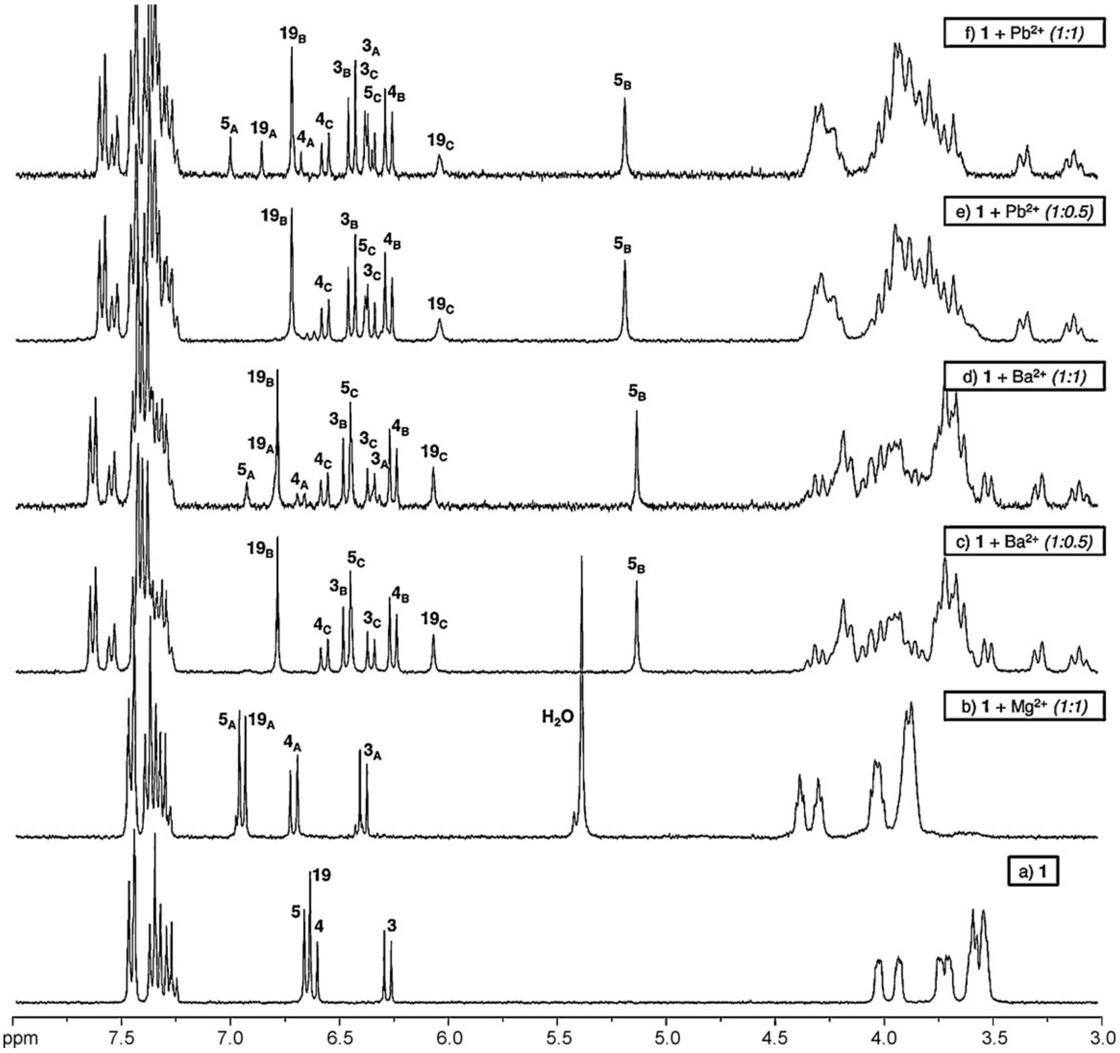


Fig. 2. (a–f) ^{1}H NMR spectra of free chromene **1** and in the presence of metal cations (CD_3CN, −45 °C).

form the sandwich complex with two benzo-15-crown-5 ether moieties. The larger binding constants β_{21} (logarithms of the constants for the corresponding steps are 5.82 and 7.0 for Ba^{2+} and Pb^{2+} respectively which are slightly larger than $\lg \beta_{11}$) suggest that the formation of 2:1 complexes is preferred. To gain insight into the structures of the complexes formed, the ^{1}H NMR spectra of **1** free and in the presence of metal cations have been recorded in CD_3CN and at low temperature (−45 °C) to increase the spectral resolution upon complex formation (Fig. 2).

The equimolar addition of $Mg(ClO_4)_2$ to **1** in CD_3CN leads to a downfield shift of all proton signals evidencing the coordination of cation with crown-ether moiety (Fig. 2(b)). More particularly, the crown-ether methylene proton resonances are in the region 3.8–4.4 ppm with Mg^{2+} while 3.5–4.1 ppm in the absence of the cation. The four protons H-3, H-4, H-5 and H-19 are also deshielded (from 0.1 to 0.3 ppm). Only one type of NMR signals (here labelled A) is observed thus confirming the formation of only one complex $1{\cdot}Mg^{2+}$.

As revealed in Fig. 2(c), upon addition of Ba^{2+} to benzopyran, with ratio 1:0.5 ($\mathbf{1}_2Ba^{2+}$), two groups of NMR signals with various peak intensities (labelled B and C) can be observed, suggesting the formation of two different complexes. In contrast to the previously observed variations in chemical shifts, some signals characterizing crown-ether methylene or H-5 protons are now upfield, whereas protons H-2′ in the phenyl groups are deshielded.

In Fig. 2(d), a third type of resonance, with the lowest intensity (labelled A) is detected. As these signals present the same chemical shifts than those of the previously assigned signals in complex $1{\cdot}Mg^{2+}$, they have been straightforwardly attributed to the 1:1 complex $1{\cdot}Ba^{2+}$. This assignment is confirmed by increasing the concentration of Ba^{2+} from 1:0.5 up to 1:1, resulting in the appearance of the A signals (Fig. 2(d)). In contrast, the two other groups of resonances B and C remain present and have their intensity decreased. This is in agreement with the existence of two $\mathbf{1}_2Ba^{2+}$ complexes (B, major and C, minor).

Finally, addition of Pb^{2+} to **1** generates the observation of the three groups (A–C) of signals (Fig. 2(e) and (f)). Increasing the concentration of Pb^{2+} is associated with the appearance of complex A, while the signals associated to complexes B and C are still observable (Fig. 2(f)).

Two-dimensional NMR spectroscopy has been applied to elucidate the assignment of signals and more particularly, ^{1}H–^{1}H scalar (COSY) and dipolar (NOESY), and ^{1}H–^{13}C direct (HSQC) and long-range (HMBC) correlations have been acquired. Whereas COSY NMR spectroscopy involves the through bond correlation of neighbouring protons in the same molecule, exchange spectroscopy visualizes the magnetization transfer pathway between protons on two or more unique molecular species in chemical exchange with one another. Thus, when the chemical exchange (in this case between two geometrical isomers) is slow enough on the NMR time

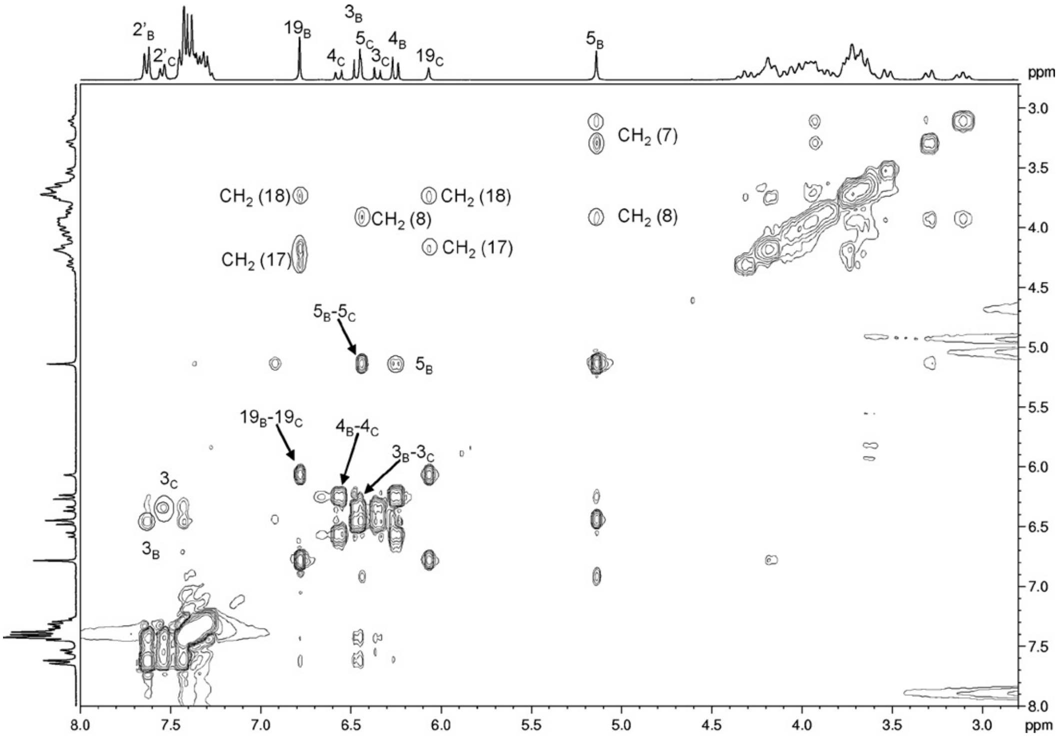


Fig. 3. 2D-NOESY of complexes $\mathbf{1}_2Ba^{2+}$. Spots with circles denote dipolar correlations. Spots indicated by arrows characterize exchange contacts.

Table 2
Shifts in proton signal positions ($\Delta\delta = \delta_{complex} - \delta_{\mathbf{1}}$) upon complex formation of **1** with Mg^{2+}, Ba^{2+}, and Pb^{2+} in CD_3CN at −45 °C.

	Mg^{2+}	Ba^{2+}			Pb^{2+}		
	A 1:1	A 1:1	B 2:1	C 2:1	A 1:1	B 2:1	C 2:1
H-3	+0.11	+0.05	+0.19	+0.05	+0.09	+0.17	+0.08
H-4	+0.09	+0.06	−0.36	+0.06	+0.08	−0.34	+0.06
H-5	+0.29	+0.27	−1.52	−0.21	+0.34	−1.46	−0.27
H-19	+0.29	+0.16	+0.15	−0.58	+0.16	+0.09	−0.59

scale, off diagonal exchange cross-peaks will be observed between protons originating from different species. The pulse sequence used to obtain an EXSY NMR spectrum is identical to the 2D NMR technique used to obtain nOe data (NOESY) [38], which gives information about through space correlations. In this case not only does the technique map the magnetization transfer between the two isomers via exchange spectroscopy, but it also supplies through space correlations essential to the assignment. The diagonals of 2D-NOESY spectra are, by convention, phased negatively. Relatively small molecules with fast tumbling times produce nOe cross-peaks opposite in sign to the diagonal (i.e. nOes are positive). In contrast, EXSY cross-peaks appear as the same sign as the diagonal,

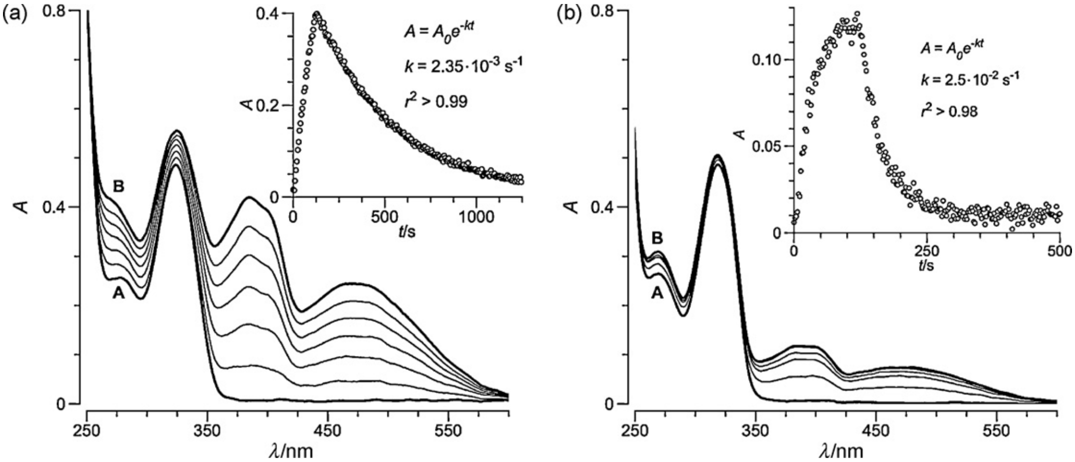


Fig. 4. UV–vis spectra of (a) **1** (7.1×10^{-5} M) and (b) **1** $+Mg^{2+}$ (7.1×10^{-5} M + 7.2×10^{-5} M) in CH_3CN at 25 °C. Spectra labelled (A) were recorded before irradiation. Spectra labelled (B) were recorded after 2 min of irradiation (λ = 313 nm). The inset represents the spectrum evolution in time at 400 nm. The mono-exponential fit results are noted.

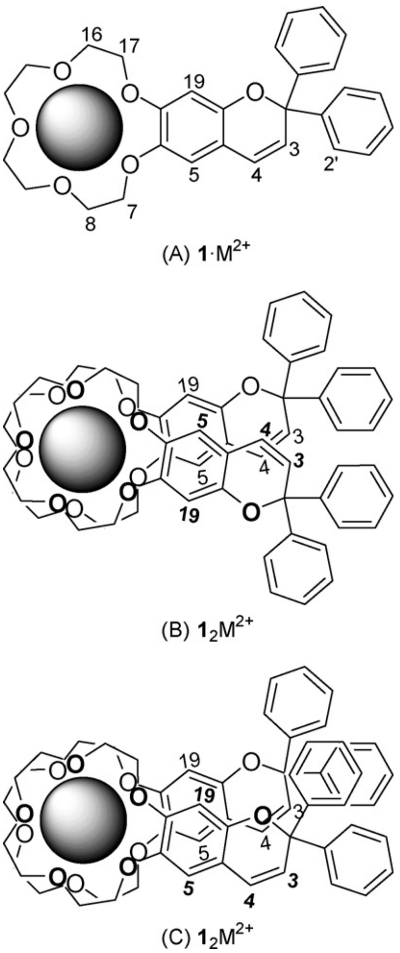
i.e. negative, therefore allowing the two types of cross-peaks to be distinguished. As illustrated in the NOESY map (Fig. 3) of the complex $\mathbf{1}_2Ba^{2+}$, circles have been added to underline these spots. Among them, one can observe dipolar correlations between protons at 7.65 (doublet, 8 Hz, 4H) and 6.45 (doublet, 9.8 Hz, 1H) ppm, and between 6.26 (doublet, 9.8 Hz, 1H) and 5.14 (singlet, 1H). Therefore, these two couples have been attributed to dipolar correlations between H-2′ and H-3 and between H-4 and H-5 in complex B.

In addition, cross-signals (here pointed with arrows) caused by chemical exchange, unlike the NOESY signals, and having the same phase as the diagonal peaks, are also observed. They underline the exchange phenomena between conformers, here between both complexes B and C [39]. Consequently, these spots can be nicely used as a help for assignment.

The set of ^{1}H chemical shifts deduced from all of the NMR experiments in the various complexes (**1** with Mg^{2+}, Ba^{2+}, and Pb^{2+}) has been compared to the data measured with the free benzopyran **1** and is reported in Table 2.

The complex A has been characterized as a 1:1 association between the 15-crown-5 ether cavity and the metal cation. As for the complexes resulting from an association between two benzopyrans and one cation, the formation of syn and anti complexes are expected. In the syn complex, the close disposition of aromatic rings should cause the anisotropic effect leading to upfield shifts of aromatic protons, whereas the anti complex should not modify greatly the chemical shifts.

Examination of data in Table 2 indicates that the complex B displays the strongest upfield shifts of H-4 and H-5 signals. Such a modification in the chemical shifts is associated with the mutual orientation of the chromene units in the syn sandwich-like complex, but in an asymmetrical arrangement. In this arrangement, the protons H-4 and H-5 of one molecule experience the shielding cone effect of the other one, thus accounting for their upfield shifts. As for the second complex 2:1 (C), the greatest variations of chemical shift concern H-19 and H-5 signals with again an upfield moving. A syn sandwich complex is therefore also proposed but with a symmetrical association of both benzopyrans (Scheme 2).



Scheme 2. The suggested complexes structures of 1 with metal ions: 1:1 complexes (A), 2:1 complexes of (B) and (C) syn-arrangement.

3.2. Photochromic properties of the chromene

Complexation of the open form of **1** free and with metal cations was firstly investigated by UV–vis spectroscopy. UV-irradiation of **1** resulted in the appearance of broad absorption band in visible region, which thermally faded with $k_\Delta = 2.35 \times 10^{-3}\,s^{-1}$ at 25 °C, after irradiation had been stopped (Fig. 4(a)). The same experiment was repeated with solution of **1** in presence of the metals leading to similar behaviour (Fig. 4(b)), namely the appearance of an absorption band in the visible range, but with a thermal rate constant of relaxation having a remarkable dependency on the amount of the metal added (Figs. 5 and 6).

The bleaching rate depends on the amount of the metal present in solution. Thus, the successive addition of the metal solution leads to rate increasing till the plateau when new portions of the metal do not result in rate changes. However an abrupt increase is observed when passing through the concentrations ratio close to 1 or 0.5 in case of Mg^{2+} or Ba^{2+} and Pb^{2+} respectively (Figs. 5 and 6), thus confirming the formation of 1:1 and 2:1 complexes with open forms. The large addition of Mg^{2+} or Ba^{2+} ($C_\mathbf{1}/C_{metal} > 2$ or 3) leads to the significant increase (up to two order of magnitude) of the bleaching rate, the constants being ca. $1 \times 10^{-1}\,s^{-1}$ and ca. $6 \times 10^{-2}\,s^{-1}$, respectively (compared to $2.35 \times 10^{-3}\,s^{-1}$ of the free **1**). In contrast, the thermal relaxation curve in the presence of Pb^{2+} has a clear biexponential pattern (Fig. 6). One of the exponential rate factor changes in the same manner as observed with Mg^{2+} and Ba^{2+}, namely the addition of the metal leads to the rate increase up to the plateau with $k \approx 8 \times 10^{-2}\,s^{-1}$. The other rate component changes significantly upon addition of excess metal ion. Apparently, the exhibited behavior may be the result of degradation of the photochromic chromene involving oxidation processes. For photochromic spironaphthoxazines there have been reported concerning the oxidative chemistry in presence of silver, gold and lead

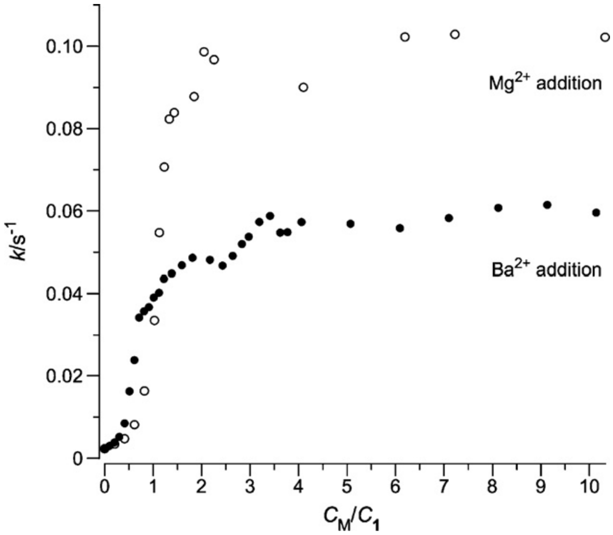


Fig. 5. Dependence of constants of thermal relaxation on the amount of the metal, Mg^{2+} or Ba^{2+}, added to the chromene solution at 25 °C.

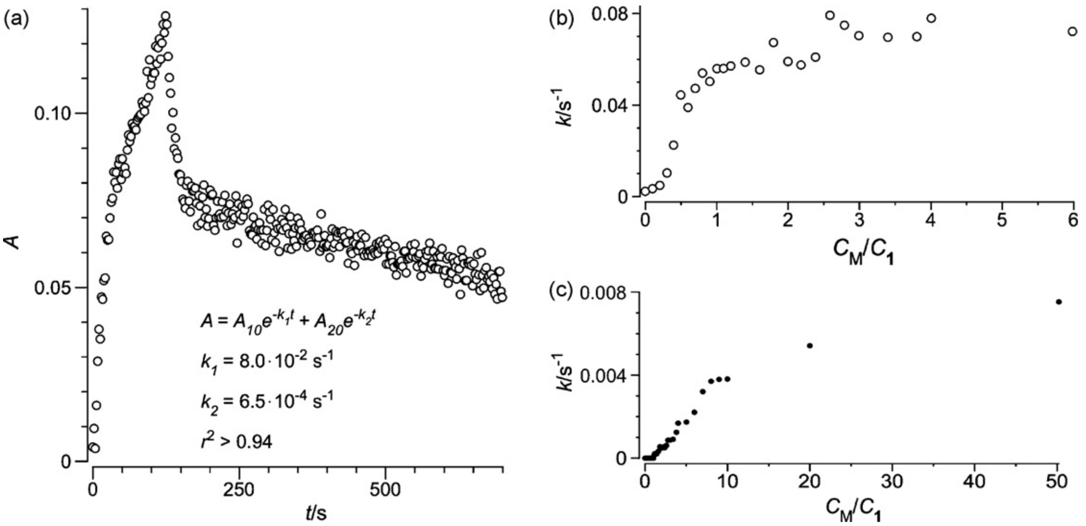


Fig. 6. (a) Kinetic curve of the relaxation process in presence of Pb^{2+}. (b and c) Dependencies of the rate constants of thermal relaxation (k_1 and k_2) on concentrations ratio at 25 °C.

ions yielding non-photochromic alkoxy derivatives [40–42]. The analogue processes have not been yet described for photochromic benzopyran molecules but could be suggested.

^{1}H NMR spectrum at −45 °C recorded after irradiation with UV light (λ = 313 nm) highlighted the conversion of free benzopyran **1** into the two expected photomerocyanines **TC** and **TT** (Fig. 7(b)). More particularly, the formation of **TC** isomer is well characterized by the downfield doublet at 8.56 ppm with the coupling constant ^3J = 12.2 Hz, whereas the presence of **TT** is identified by the doublet at 7.2 ppm with ^3J = 12.7 Hz [43]. The two photomerocyanines are thermally stable at −45 °C. Thermal evolution was observed by increasing the temperature. At 0 °C, **TC** form transformed into initial species with rate constant $k = 7 \times 10^{-5}$ s^{-1}, while **TT** form was quite stable, but disappeared at room temperature. This behaviour is typical of the photochromism of benzopyrans with the breaking of the C-O bond upon irradiation and the thermal reversion into the initial closed form when irradiation is stopped (Scheme 1) [1–4].

Irradiation of a 1:1 mixture of **1** and Mg^{2+} led to the appearance of new signals in NMR spectrum. As displayed in Fig. 7(d), the characteristic doublet signal at 8.56 ppm evidences the formation of **TC** photomerocyanine. 2D scalar correlations underlined correlations with two doublet resonances at 7.08 ppm (less concentrated)

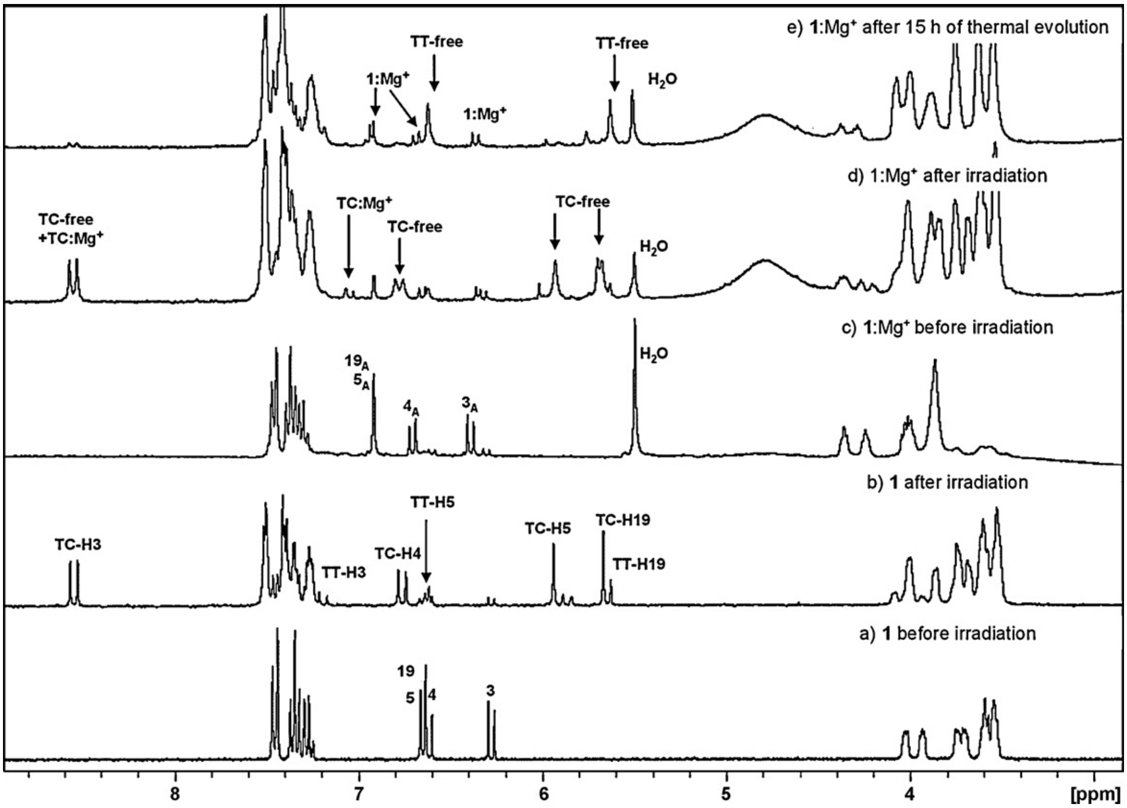
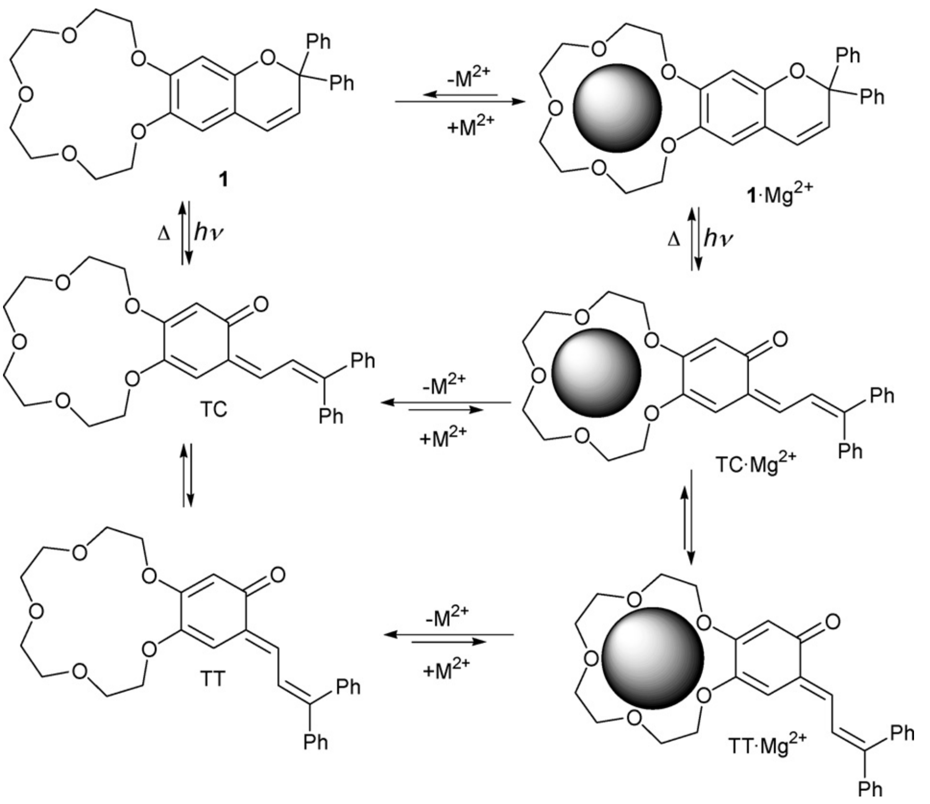


Fig. 7. (a–e) ^{1}H NMR spectra of **1** and **1**:Mg^{2+} before and after UV-irradiation (λ = 313 nm) in CD_3CN at −45 °C.



Scheme 3. Suggested behaviour for **1**·Mg^{2+} during the photochromic process.

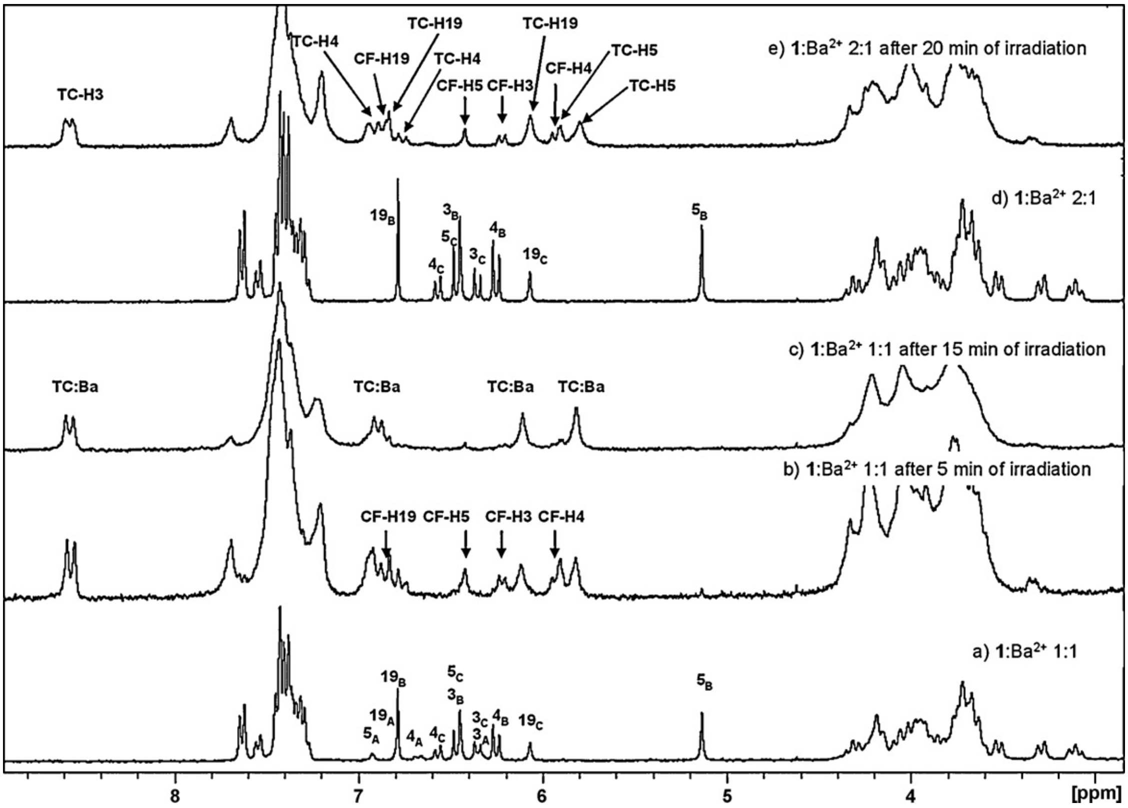


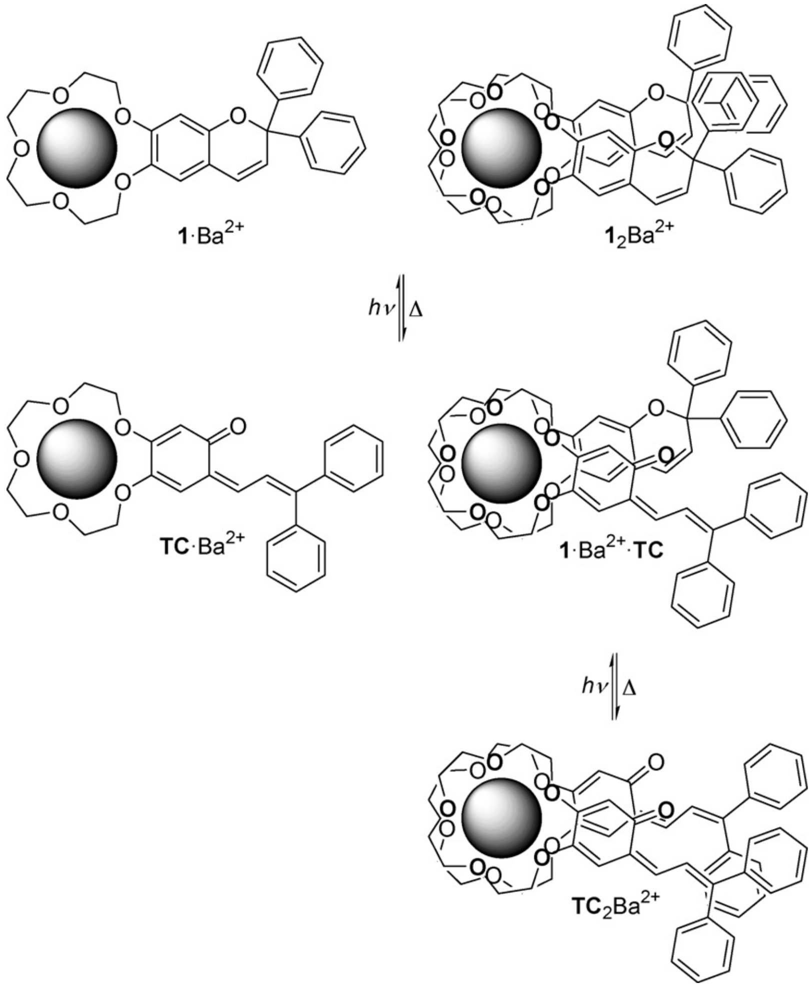
Fig. 8. (a–e) ^{1}H NMR spectra of **1** in presence of Ba^{2+} (1:1 and 2:1 molar ratios) before and after UV-irradiation (λ = 313 nm) in CD_3CN at −45 °C.

and 6.78 ppm (more concentrated), thus characterizing the presence of two structures with the same **TC** isomery. 2D experiments enabled to assign the different resonances of the major photoproduct which are consistent with those of the **TC** photomerocyanine free (Fig. 7(b)). However, the thermal evolution (Fig. 7(e)) indicated the transformation of this open form **TC**-free into the second isomer of photomerocyanine, the **TT** form ($k = 2.5 \times 10^{-5}\ \mathrm{s}^{-1}$ at $-45\,^{\circ}$C and $k = 13.1 \times 10^{-5}\ \mathrm{s}^{-1}$ at $-35\,^{\circ}$C), whereas the **TC** form produced by irradiation of **1** alone is stable at low temperature.

In contrast, the thermal evolution of the less concentrated photoproduct showed its reversion into the initial complex closed form of benzopyran, **1**·Mg^{2+} ($k = 3.5 \times 10^{-5}\ \mathrm{s}^{-1}$ at $-45\,^{\circ}$C and $k = 9.9 \times 10^{-5}\ \mathrm{s}^{-1}$ at $-35\,^{\circ}$C). It was therefore attributed to the complexed **TC**·Mg^{2+} form. Surprisingly, the complete bleaching of the solution led to only the complex **1**·Mg^{2+}. The results are summarized in Scheme 3. Upon irradiation **1**·Mg^{2+} is transformed into **TC**·Mg^{2+}, the latter being less stable than the initial complex to give the mixture of the complexed and free **TC** forms observed in the NMR spectrum (Fig. 7(d)). After the irradiation is cut, the open forms slowly transform into initial closed species that quickly forms 1·Mg^{2+}. Apparently, *cis-trans* isomerisation of the complexed **TC** leads to the complexed **TT** forms that quickly eliminate the cation. Thus, the observed NMR spectrum after 15 h thermal evolution contains resonances of **1**·Mg^{2+} and free **TT** form (Fig. 7(e)).

Irradiation of a solution of **1** in presence of Ba^{2+} in the ratio 1:1 led to a poorly resolved ^{1}H NMR spectrum (Fig. 8(c)), where it is however possible to observe resonances at chemical shifts characteristic of **TC** opening ($\delta = 8.55$ ppm). To get more information about the process, irradiation with a shorter duration had been carried out (Fig. 8(b)) and evidenced the signals characterizing a closed form of benzopyran (CF), which is not the free molecule (**1** alone), nor the complex molecule (**1**·Ba^{2+} or **1**$_2$$Ba^{2+}$). Consequently, these signals which disappeared upon prolonged irradiation are attributed to an intermediate sandwich complex with one benzopyran in closed configuration and one benzopyran in open isomery. The same type of signals is observed when irradiating a solution with Ba^{2+} in 1:0.5 ratio. Besides, two types of different resonances (one with high intensity, the second with less intense signals) belonging to **TC** forms are also observed. Although an accurate measurement of peak intensities is not possible due to the low resolution, the signals with the lowest intensities follow the same evolution than the signals of the closed configuration (**CF**) (Fig. S18), thus underlining the pathway from initial **1**$_2$$Ba^{2+}$ complex towards **TC**$_2$$Ba^{2+}$ via the intermediate form **1**·Ba^{2+}·**TC** (Scheme 4). The thermal evolution has been followed at $-35\,^{\circ}$C leading to the return-back into the initial complexes of **1** with Ba^{2+}. As no signal underlying the formation of **TT** isomer was observed within the thermal evolution, no *cis-trans* isomerization between **TC** and **TT** could be evidenced.

Finally, the behaviour upon UV-irradiation of **1** in the presence of Pb^{2+} has been investigated. The NMR spectra of the complex are overcrowded what makes difficult for its proper interpretation. This is in agreement with data obtained by UV spectroscopy indicating the occurrence of simultaneous processes of phototransformation and oxidizing induced by lead ions.



Scheme 4. Suggested behaviour for complexes of **1** with Ba^{2+} during the photochromic process.

The whole set of results deduced from experiments realized upon irradiation underlines that the three metal cations Mg^{2+}, Ba^{2+} and Pb^{2+} accelerate the thermal relaxation of **TC** open forms towards initial closed state of **1**. Indeed, when no cation was added to initial solution, irradiation at −45 °C generated thermally stable photomerocyanines. Therefore, complexation with metal cations decreases the stability of photomerocyanines. Such a behaviour was already observed by Kumar et al. [44] when studying the thermal ring-closure of open form of a naphthopyran bearing an imidodiacetic acid substituent at position 5 in the presence of Mg^{2+} or by other authors [26–28] who reported that addition of divalent metal ions to a solution of crown-ether annulated to one phenyl group of naphthopyran resulted in binding in the dark, whereas photoisomerization with UV light dissociated the complex, that could be regenerated by photobleaching. In the present work, the destabilization observed for complexed open forms can reasonably suggest that the binding site is located in the crown-ether cavity, causing polarization of open forms. The ring-closure reaction is consequently accelerated in polar molecule.

4. Conclusions

The complexation between a benzopyran annulated by 15-crown-5 ether moiety and three metal cations (Mg^{2+}, Ba^{2+} and Pb^{2+}) has been investigated by UV–vis and NMR spectroscopy. Complexes with 1:1 ratio have been evidenced: Mg^{2+} is included within the cavity of the crown ether, while Ba^{2+} and Pb^{2+} lead to exclusive complexes, due to their large ionic radii. In addition to the stability constants deduced from UV-visible data that characterized the presence of 2:1 complexes $\mathbf{1}_2\mathrm{Ba}^{2+}$ and $\mathbf{1}_2\mathrm{Pb}^{2+}$, investigations by NMR spectroscopy enabled to propose structural insights of the association between two benzopyran entities and the metal cation. More particularly, two sandwich-complexes of syn-arrangement, symmetrical and asymmetrical, have been evidenced.

UV-irradiation of **1** and of **1** in presence of metals produced coloured photomerocyanine forms but it did not enhance the cation-binding abilities of the ligands through the creation of additional binding sites or geometry changes. Indeed, the investigation of the photochromic properties showed that both photochromism and complex formation influenced each other upon irradiation. The photomerocyanines appeared to have lower affinity to metal ions leading to partial destabilization of complexes. In parallel, complexation caused destabilization of the open forms resulting in a decrease of the coloured species lifetimes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.10.014.

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