CHEMPHYSCHEM

DOI: 10.1002/cphc.201100052

Photochromism and Metal Complexation of a Macrocyclic Styryl Naphthopyran

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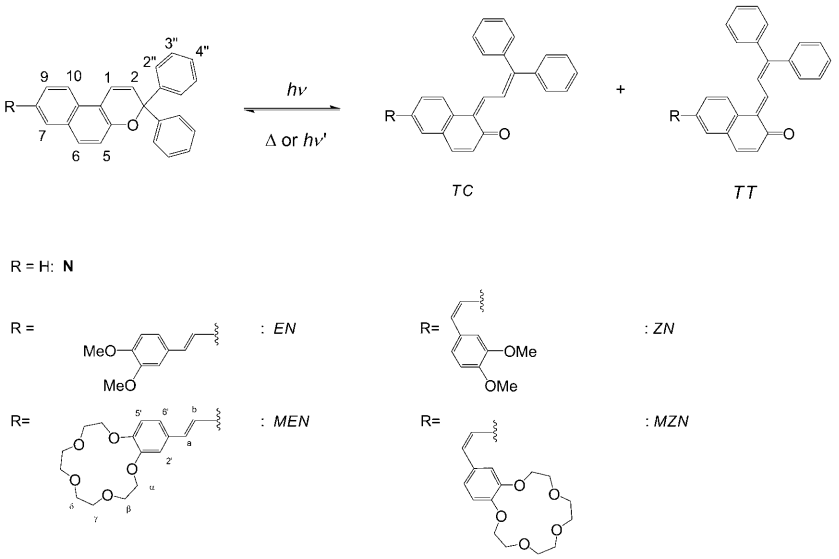
A macrocyclic benzo-15-crown-5 ether unit tethered to a photochromic naphthopyran by a styryl spacer (**MEN**) is shown to form a 1:1 complex with magnesium(II). The structure and dynamics of the specific host–metal interactions were investigated by PFG-NMR analysis. A combination of UV/Vis and variable temperature multi-dimensional ^{1}H NMR photokinetic analysis of the crown-containing styryl naphthopyran and its metal complex was used to probe the effect of metal complexation on the photochromism.

1. Introduction

In the last few years, naphthopyrans have evolved as an interesting family of photochromic molecules because of their synthetic availability, ease of modification, durable persistency and addressable bleaching kinetics.[1] They are commercially used as sun-protective ophthalmic lenses, optical filters and smart windows. In addition, they promise to be the basis of intelligent materials for temporary or permanent memories.[2,3] Diphenyl-naphthopyran, **N**, first reported by Michl and Becker[4a] is known to generate two open isomers upon irradiation, namely the *transoid–cis*, *TC* and the *transoid–trans*, *TT* (Scheme 1).[4b] When it is substituted with an ethylenic bridge in position 8 as in compound **EN**, four photoisomers (*ETC, ETT, ZTC* and *ZTT*) are expected to be found as the result of *E/Z* isomerization and ring-opening.[4c] Finally, introduction of a macrocycle **M** gives rise to the hybrid biphotochromic system **MEN**, which allows one to combine photochromic properties with metal coordination. In these conditions, due to the species multiplication effects, much more versatile hybrid systems can be obtained.[3f,4] For instance, a strong stabilization of a metastable state through metal–ligand interactions could be expected, improving its thermal durability.[5] In other applications, the possible sequential control of the electronic properties could find potential applications in gated-photochromism.[4,6]

A full understanding of the photochemical pathways and the identification of stable intermediates is critical for learning



Scheme 1. Structures of the three generic naphthopyrans **N**, **EN** and **MEN**. Each specific isomer is indicated in italics.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cphc.201100052.

how to construct and manipulate these synthetic hybrid bi-photochromic systems.[7] The purpose of this manuscript is to analyse the complexation and the photochromic behaviour of the macrocyclic styryl naphthopyran compound **MEN** and its model compounds **N** and **EN**. The first part is dedicated to the structural characterisation of naphthopyrans **N**, **EN**, **MEN** and its metal complex with magnesium(II) cation by UV/visible and NMR spectroscopy. The second part deals with the dynamics of the response under irradiation of the various compounds, looking especially at the effect of magnesium(II) cation complexation on the photochromic properties of the **MEN** compound.

2. Results and Discussion

2.1. Spectral Characterization of the Naphthopyrans N, EN, MEN and the MEN Magnesium(II) Complex

2.1.1. Steady-State Absorption Measurements

The spectral characteristics of the model compounds **N**, **EN**, free and complexed **MEN** are summarized in Table 1. In their closed forms, the three molecules exhibit roughly the same absorption bands. However, the **MEN** spectrum shows a structureless absorption band at 322 nm corresponding mainly to a transition induced by the stilbene group (Figure 1 a). The same effect is also observed for **EN** (not shown). This band is likely to overlap the lowest-energy naphthopyran transition peaking at 360 nm (see the spectrum of the model compound **N**).[8,9] As expected, conjugation induces a strong bathochromic shift for the **EN** and **MEN** open forms.

Table 1. Spectral characteristics of naphthopyrans **N**, **EN** and **MEN** with its magnesium (II) complex in CH_3CN at 295 K.

Compound	λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]	λ_{max} [nm] open form
N[a]	357, 343, 315		425
EN	354, 340, 322	4.34×10^4 (at 354 nm)	494
MEN	354, 340, 322	4.31×10^4 (at 354 nm)	495
MgMEN	351, 337, 315	4.81×10^4 (at 315 nm)	485

[a] Data extracted from ref. [8].

The UV/Vis monitoring of the **MEN** host titration with magnesium(II) exhibits a nice isosbestic point in the UV/Vis spectra at 324 nm (Figure 1 b). Due to its presence, it has been assumed that the complexation with magnesium(II) can be described by the simple equilibrium displayed in Scheme 2 with the binding constant K_{11}. The small ionic diameter of the Mg^{II} cation (1.56 Å) fits well with the size of the internal cavity of the benzo-15-crown-5 ether unit and is expected to be inserted into the cavity thus surrounded by the oxygen atoms. The value of the binding constant ($\log K_{11} = 4.5 \pm 0.1$) obtained from UV/Vis titration by Specfit calculations are in good agreement with our previously reported data for the benzo-15-crown-5-containing styryl dyes.[5b]

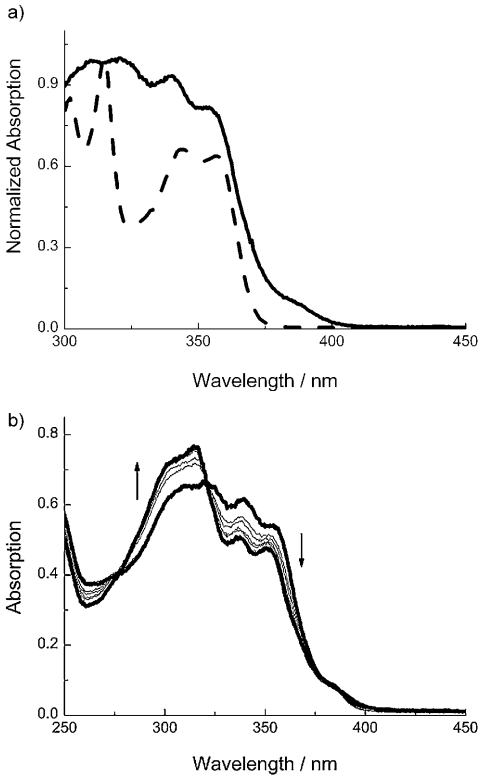
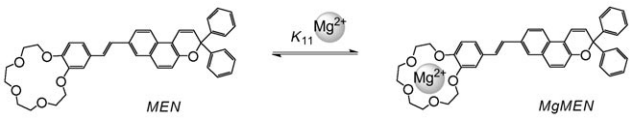


Figure 1. a) Normalized absorption spectra of **N** (-----) and **MEN** (——), b) spectrophotometric titration of **MEN** $C_L = 1.3\times10^{-5}$ M with $Mg(ClO_4)_2$ ($0 \le x_{M/L} \le 80$) in acetonitrile.



Scheme 2.

2.1.2. Structural Analysis of the Model Styryl Naphthopyran EN by NMR Spectroscopy

The styryl naphthopyran **EN** exist as *E* and *Z* isomers. Both isomers were obtained by chromatographic separation. In the ^1H NMR spectra, the resonances of *ZN* are shifted upfield (Figure 2). Particularly, the vinyl protons H-*a* and H-*b* ($^3J = 12.4$ Hz) are shifted to $\Delta\delta = -0.60$ ppm compared to the vinyl protons in *EN* ($^3J = 16.5$ Hz).

Dipolar correlations in 2D-ROESY are observed between H-*a* and H-2′, H-*b* and H-7 in *EN*, and between H-*b* and H-9, H-*b* and H-7, H-7 and H-2′, 5′, 6′ in *ZN*, thus indicating that only one average of several conformers resulting from free rotation around C_b–C_8 and C_a–$C_{1'}$ is present in both cases.

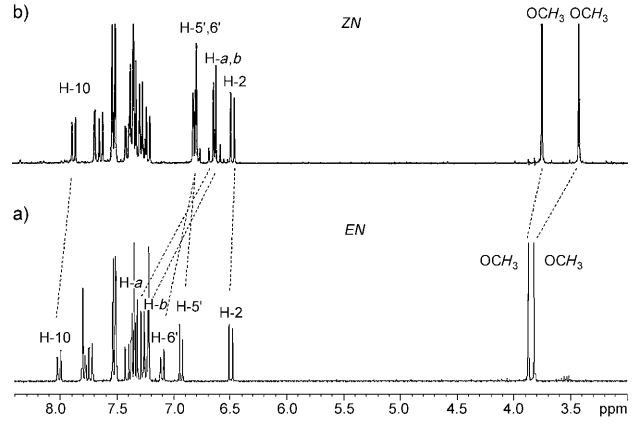


Figure 2. ^{1}H NMR spectra of isomers a) *EN* and b) *ZN* measured at 295 K in CD_3CN.

2.1.3. Conformational Analysis of Benzo-Crown-Styryl-Naphthopyran MEN and its Magnesium(II) Complex

Due to similar retention time values, the two isomers *MZN* and *MEN* could not be isolated by HPLC facilities. Therefore, ^{1}H NMR spectrum of the benzo-15-crown-5-styryl-naphthopyran indicates that the mixture contains 23% *MZN* and 77% *MEN* (Figure 3). However, the *MEN* isomer (97% purity) could

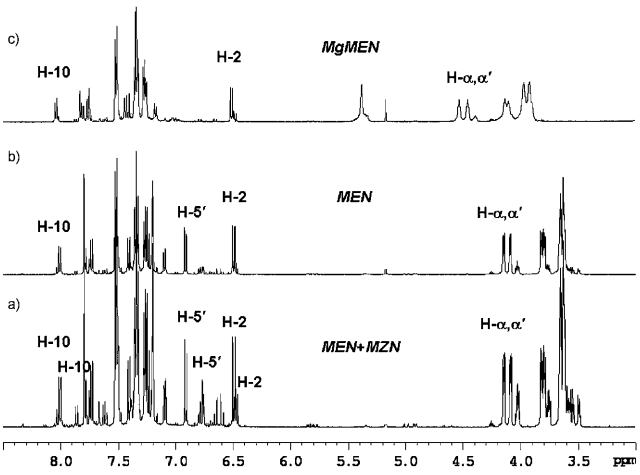


Figure 3. ^{1}H NMR spectra of initial mixture of a) *MEN* and *MZN*, b) *MEN* host obtained after irradiation (97% purity), c) *MgMEN* measured at 295 K in CD_3CN.

be obtained by photochemical methods after irradiation of the mixture with 313 nm light in acetonitrile at 295 K (Figure 3b).

The analysis of the binding process of *MEN* (97% purity) with magnesium(II) was done through ^{1}H NMR titrations. Subsequently, upon successive addition of magnesium perchlorate (0 to 1 equiv) to a solution of *MEN* in acetonitrile, the most pronounced changes in the proton spectra could be observed in the proximity of the methylene protons of the crown ether unit located more closely to the complexed cation. The ^{1}H NMR signals during the titration of *MEN* with magnesium in ratio of 1:1 are displayed in Figure 3c.

The thermodynamic parameters for the complex formation of *MEN* with magnesium(II) in acetonitrile were determined by measuring the temperature dependence of the binding constants by NMR spectroscopy. The separation of host–complex resonances, obtained by spectral deconvolution analysis, pointed to a sizable kinetic barrier for the exchange process and allowed the determination of the values of the binding constant ($\log K_{11} = 4.3 \pm 0.2$ for *MgMEN* at 295 K) in complete agreement with data deduced from UV/Vis spectroscopy. The measurements were repeated six times in the range 233–293 K. A van't Hoff plot of $\ln K$ versus T^{-1} (see the Supporting Information) afforded the reaction enthalpy and entropy for the complex formation ($\Delta H^0 = 2.9 \pm 0.1$ kJ mol^{-1} and $\Delta S^0 = 93.1 \pm 0.4$ J mol^{-1} K^{-1}). As a consequence of the cation and ligand desolvation, the binding process is entropically favored.

2.1.4. NMR DOSY Analysis of the Naphthopyrans N, MEN and the MgMEN Complex

To extract further information about the structure and dynamics of the host–metal interactions in solution, the translation diffusion coefficients (*D*) for each compound were measured using the pulsed-gradient spin-echo technique (PGSE) in CD_3CN at 295 K (Table 2) to determine their molecular

Table 2. Diffusion coefficients and values of hydrodynamic radii calculated for **EN**, **MEN** and its magnesium(II) complex in CD_3CN at 295 K.

Compound	MW[a]	D [nm^2 s^{-1}]	DOSY hydrodynamic radius [Å] and dimensions[b] [diameter × height]
EN	496.6	0.99	6.3 (19.6 × 5.8)
MEN	626.7	0.90	6.9 (22.2 × 5.8)
MgMEN	651.0	0.89	7.0 (22.2 × 5.9)

[a] Molecular weights of uncharged molecules in case of **EN** and **MEN,** and of the cation in case of **MgMEN** correspond to the exact formula of the unsolvated compounds; [b] the dimensions for oblate ellipsoid shape were obtained by AM1 calculation.

volume.[10] The DOSY (Diffusion Order SpectroscopY) technique is increasingly being used in conjunction with NOE to investigate aggregation and encapsulation phenomena, intermolecular or interionic interactions.[11,12] For instance, it was demonstrated that the diffusion coefficients of the various free crown ethers were sensitive to both conformational changes and changes in molecular size upon complexation.[13] The ^{1}H DOSY spectra were recorded first for the **EN** and **MEN** molecules and for the **MgMEN** complex. The values for the free **MEN** host and the **MgMEN** complex do not differ significantly, revealing that the complex formed by the **MEN** host with magnesium(II) at a 1:1 ratio should be of similar size as the free **MEN** host, which is actually in compliance with the fact that the molecular weights of MEN and the **MgMEN** complex do not differ substantially. The hydrodynamic radii r_H of the spherical particles in a solvent of viscosity η could be calculated from the translational diffusion coefficients by using the Stokes–Einstein–Debye formula [Eq. (1)]:[15a,b]

$$D = \frac{k_B T}{f_T} = \frac{k_B T}{6\pi\eta r_H} \quad (1)$$

where k_B is the Bolzmann constant, T is the absolute temperature, and f_T is the friction factor. To enable a fit with the real shape of the particle in solution, all molecules were considered as oblate ellipsoidal objects. Relative to the spherical model, the ellipsoidal model imposes a shape factor to extract molecular dimensions from the translation diffusion coefficients obtained by NMR.[15b] For the sake of comparison, compound **EN** was investigated in the same conditions. At room temperature its translational diffusion coefficient about 0.99 $nm2\,s^{-1}$ corresponds to a hydrodynamic radius of 6.3 Å. The AM1 calculation used to fit this value with an oblate ellipsoidal object leads to dimensions of 19.6×5.8 $Å^2$. Furthermore, the introduction of the bulky crown-ether substituent in **MEN** increases the diameter up to 22.2 Å. Its hydrodynamic radius is not drastically altered upon binding of the magnesium(II) cation.

2.2. Photochromism

2.2.1. Investigations at 295 K by UV/Vis Spectroscopy

UV-irradiation of the *trans*-isomers of **MEN** and **EN** at 365 nm in acetonitrile at ambient temperature gives rise to the formation of the thermally reversible merocyanines. The newly formed absorption at 494–495 nm is strongly red-shifted relative to the 425 nm maximum of the corresponding ring-opened form of the parent naphthopyran **N** (Figure 4 a).[8a,d] This result is in agreement with an important π-conjugation between the naphthopyran and the stilbene moiety in the ring-opened forms. In addition, a distinct hypsochromic shift of the absorption band at 495 nm of the opened merocyanine **MEN** form up to 15 nm was observed for the **MgMEN** complex (Figure 4 b).

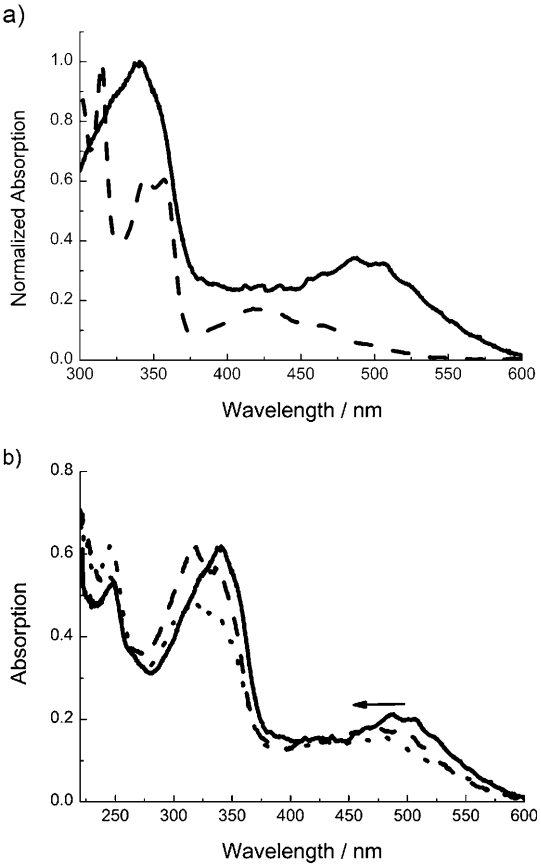


Figure 4. a) Normalized absorption spectra of naphthopyrans **MEN** (——) and **N** (-----) obtained after 10 s irradiation at 365 nm; b) absorption spectra of **MEN** (——) and its complex **MgMEN** (-----) obtained after 10 s irradiation at 365 nm ($C = 1.3 \times 10^{-5}$ M, 295 K).

2.2.2. Identification of the Merocyanines of MEN and MgMEN by NMR Spectroscopy

The photochemical behavior of the macrocyclic styryl naphthopyran **MEN** and its Mg^{II} complex was monitored by NMR spectroscopy using step-wise 313 or 365 nm irradiation in CD_3CN at ambient and low temperatures. At 295 K, only the *Z*/*E* photoisomerization is observed as the photomerocyanines are not sufficiently stable to be detected by NMR spectroscopy.

On the other hand, at a lower temperature (233 K), UV irradiation with 313 or 365 nm leads to both the opening of the naphthopyrans and the *E*/*Z* isomerisation of the ethylenic junction. The formation of photomerocyanines occurs in the *TC* and *TT* isomers (Scheme 1). For instance, the *transoid–cis* isomer can be evidenced easily by considering the most deshielded proton, H-2, around 8.5 ppm and the proton H-5 at 6.4 ppm while the *transoid–trans* isomer is well recognized from its H-5 proton at 6.3 ppm (Figure 5 a). The identification can also be

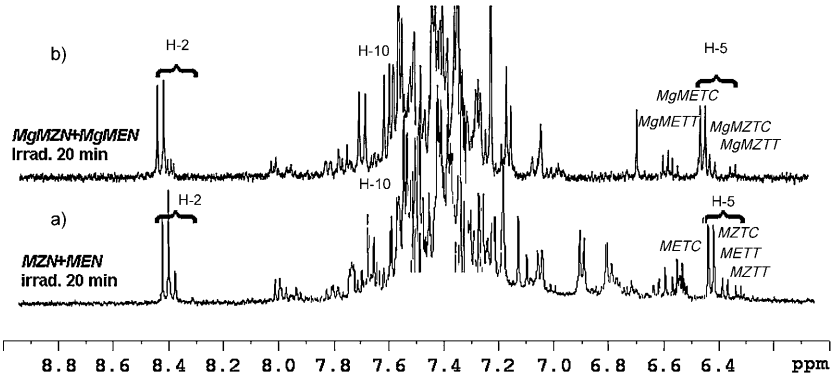


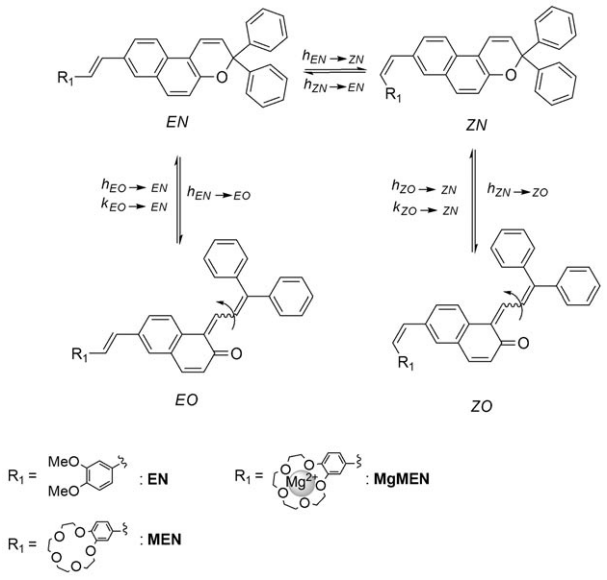
Figure 5. ^{1}H NMR spectra (aromatic region) measured at 233 K in CD_3CN: a) mixture of *MEN* and *MZN* after 20 min irradiation at 365 nm; b) *MgMEN* and *MgMZN* complexes after 20 min irradiation at 365 nm. Note the specific signals attributed to the isomeric forms *METC*, *MZTC*, *METT* and *MZTT* in spectrum (a) and the various complexes *MgMETT*, *MgMETC*, *MgMZTC* and *MgMZTT* in spectrum (b).

performed on the basis of the signal intensities and their thermal stability. It is well-known that the *TC* isomers are usually formed in higher concentrations upon irradiation than the *TT* isomers, and during the thermal relaxation process, they undergo a faster reclosing.[4b] One week later, NMR spectra revealed that the open forms fully disappeared and we could observe the characteristic resonances of the *E* and *Z* isomers of initial compounds with naphthopyran in the closed configuration.

Consequently, irradiation of the free host **MEN** as well as of the magnesium(II) complex **MgMEN** at 233 K resulted in the formation of the four expected photomerocyanines, *TC* and *TT* with the *E* and *Z* isomeric forms of the ethylenic function (Figure 5).

2.2.3. Kinetic Analysis of the Photochemical and Thermal Processes

The peak-intensity measurements in ^{1}H NMR spectra recorded at regular time intervals during irradiation with 313 and 365 nm, and during the thermal evolution at 233 K allowed us to plot the time evolution of concentrations. To simplify, the concentrations of open photomerocyanines with the same *E*/*Z* isomeric forms were merged such that $ZTC+ZTT=ZO$ and $ETC+ETT=EO$. Therefore, the system can be described by a four-species model system as displayed in Scheme 3. This system was analyzed quantitatively by means of our self-developed kinetic-curve-fitting Sa software.[17] The estimated apparent photochemical rate constants (h_{ij}[18]) of the two isomerization processes *E* vs *Z* and of the ring opening vs ring closure, and the thermal rate constants, k_{ij}, of the relaxation monitored at 233 K are reported in Table 3.



Scheme 3. Four-species system showing *E* vs *Z* photoisomerisation, photochemical ring opening vs ring closure and thermal relaxation. *E*- and *Z*-(*TC*+*TT*) are merged into *E*-*O* and *Z*-*O* open isomers, respectively.

Table 3. Extracted apparent photochemical rate constants (*h*) under 313 and 365 nm irradiation at 295 and 233 K and thermal rate constants of relaxation (*k*) at 233 K.

		EN and *ZN*	*MEN* and *MZN*	*MgMEN* and *MgMZN*
$\lambda_{irr}=313$ nm	$h_{EN\rightarrow ZN}$	2.22×10^{-5}	1.43×10^{-5}	8.8×10^{-5}
$T=295$ K	$h_{ZN\rightarrow EN}$	1.31×10^{-4}	6.56×10^{-4}	6.1×10^{-4}
$\lambda_{irr}=365$ nm	$h_{EN\rightarrow ZN}$	2.28×10^{-4}	3.95×10^{-5}	3.38×10^{-4}
$T=295$ K	$h_{ZN\rightarrow EN}$	1.74×10^{-4}	4.09×10^{-4}	1.5×10^{-3}
	$h_{EN\rightarrow ZN}$	2.92×10^{-4}	6.09×10^{-4}	7.69×10^{-4}
	$h_{ZN\rightarrow EN}$	3.51×10^{-4}	2.14×10^{-3}	1.52×10^{-3}
$\lambda_{irr}=313$ nm	$h_{EN\rightarrow EO}$	2.22×10^{-3}	4.23×10^{-3}	2.26×10^{-3}
$T=233$ K	$h_{ZN\rightarrow ZO}$	2.02×10^{-4}	1.77×10^{-3}	3.15×10^{-3}
	$h_{EO\rightarrow EN}$	5.99×10^{-3}	6.55×10^{-4}	6.30×10^{-4}
	$h_{ZO\rightarrow ZN}$	1.05×10^{-3}	5.54×10^{-5}	8.89×10^{-4}
	$h_{EN\rightarrow ZN}$	7.11×10^{-4}	2.66×10^{-5}	1.65×10^{-3}
	$h_{ZN\rightarrow EN}$	6.72×10^{-4}	4.01×10^{-4}	3.92×10^{-3}
$\lambda_{irr}=365$ nm	$h_{EN\rightarrow EO}$	5.38×10^{-3}	4.24×10^{-3}	2.71×10^{-3}
$T=233$ K	$h_{ZN\rightarrow ZO}$	4.75×10^{-4}	1.73×10^{-3}	4.19×10^{-3}
	$h_{EO\rightarrow EN^*}$	3.46×10^{-3}	3.95×10^{-4}	4.52×10^{-4}
	$h_{ZO\rightarrow ZN^*}$	9.60×10^{-4}	1.29×10^{-3}	8.56×10^{-4}
$T=233$ K	$k_{EO\rightarrow EN}$	1.81×10^{-4}	1.42×10^{-4}	2.55×10^{-4}
	$k_{ZO\rightarrow ZN}$	1.70×10^{-4}	1.38×10^{-4}	1.43×10^{-4}

Several remarkable features are gathered in the Table 3. The consequences of the magnesium(II) cation addition to the initial host ligand can be estimated by comparing the apparent photochemical rate constants in the **MEN** and **MgMEN** columns. In all the cases, the apparent photochemical rate constant of the $E\rightarrow Z$ isomerisation is increased in the complexed host ligand. Moreover, addition of magnesium(II) also induces a higher rate of the reverse $Z\rightarrow E$ isomerisation under 365 nm. The effect is, however, almost negligible at an irradiation wavelength of 313 nm. On the other hand, the effect of the presence of a free macrocycle can be seen by comparing the **EN** and **MEN** columns. Under 365 nm irradiation, there is a clear-cut decrease in the $E\rightarrow Z$ photochemical rate, while this effect is not significant under 313 nm. On other hand, the general trend for the reverse $Z\rightarrow E$ isomerisation is to increase in the presence of the free macrocyclic unit. It is also interesting to consider the apparent rate constants obtained at 233 K in order to compare the reactivity of each isomer (*E* and *Z*) toward ring opening as opposed to the *E* vs *Z* photoisomerization, under 313 and 365 nm irradiation. The relative reactivity is obtained by dividing the two apparent photochemical rates (see Table 4). For instance, under 313 nm irradiation for **EN**, we have $h_{EN\rightarrow ZN}/h_{EN\rightarrow EO}=2.22e{-}3/2.92e{-}4=7.6\approx8$.

The results show that this ratio, which characterizes the intimate reactivity of the excited state is sensitive both to the structure and wavelength of irradiation. In **EN** and **MEN**, it appears that whatever the irradiation wavelength is, the ring opening is much more efficient in the case of the *E* isomer. The tendency mentioned above is less pronounced for the magnesium(II) complex of host macrocyclic ligand.

Table 4. Relative photochemical reactivities (ring-opening vs *E,Z* isomerisation) of the various isomers at 233 K under 313 and 365 nm irradiation.

Relative Reactivity	EN	MEN	MgMEN
EN→*EO* vs *EN*→*ZN* (313 nm)	8	7	3
EN→*EO* vs *EN*→*ZN* (365 nm)	8	160	1.6
ZN→*ZO* vs *ZN*→*EN* (313 nm)	0.6	0.8	2
ZN→*ZO* vs *ZN*→*EN* (365 nm)	0.7	4	1

From the recorded [*E*]:[*Z*] photosteady-state concentration ratio (from NMR spectral analysis) and the measured values of the molar extinction coefficients (from absorption spectra analysis), the quantum yield ratios for the two reversible processes Φ_Z/Φ_E can be estimated from Φ_Z/Φ_E (at λ_{irr}) = ($\varepsilon_E/\varepsilon_Z$) (at λ_{irr}) × ([*E*]/[*Z*]) (final at λ_{irr}, Table 5).

Table 5. Analysis of the *E* vs *Z* photoisomerisation at 295 K, under 313 and 365 nm irradiation.

	EN:ZN	*MEN:MZN*	*MgMEN:MgMZN*
[*E*]:[*Z*] initial	5:95	77:23	76:24
[*E*]:[*Z*] (final at 313 nm)	86:14	97:3	86:14
[*E*]:[*Z*] (final at 365 nm)	39:61	90:10	82:18
ε_E (313 nm)	49000	49000	48000
ε_Z (313 nm)	22500	22000	21500
$\varepsilon_E/\varepsilon_Z$ (313 nm)	2.18	2.23	2.23
ε_E (365 nm)	25500	25000	15500
ε_Z (365 nm)	5700	5400	6700
$\varepsilon_E/\varepsilon_Z$ (365 nm)	4.47	4.63	2.31
Φ_Z/Φ_E (313 nm)	≈15	≈70	≈15
Φ_Z/Φ_E (365 nm)	≈3	≈40	≈10

These ratios are always higher than one, thus indicating that *Z*→*E* photoisomerisation is always favored with respect to the *E*→*Z* reverse reaction. Comparison between **MEN** and **MgMEN** shows that, both at 313 and 365 nm irradiation, the quantum yields ratio Φ_Z/Φ_E is reduced significantly by about a factor of 4 after metal cation addition. Moreover, this ratio is within the same order of magnitude for **EN** and **MgMEN**. The effect of the macrocyclic ring's existence is annulled when it is Mg^{II}-filled.

3. Conclusions

In summary, we investigated a hybrid biphotochromic molecule **MEN** based on a thermally reversible naphthopyran and an alkaline-earth cation binding benzo-15-crown-5 macrocycle linked by a photochemically bistable stilbene moiety. This ligand forms a 1:1 complex with magnesium(II) cation. Additionally, the thermodynamic parameters of the complexation, the diffusion coefficients and the hydrodynamic radius of the various free and complexed species have been determined.

MEN hybrid biphotochromic naphthopyran gives rise to a complex reaction network and reacts upon photochemical stimulations according to two main pathways: the electrocyclic ring opening of the naphthopyran entity through cleavage of the C(sp^3)–O bond and the photoreversible *E,Z*-isomerization. At 295 K, the ring closure from the photomerocyanine to the naphthopyran moiety is sufficiently rapid to be without any effect on the *E*/*Z* isomerization. On the other hand, at 233 K, this ring closure reaction is slow and its contribution to the whole relaxation dynamics under irradiation can easily be subtracted. No [2π + 2π]-cycloaddition of the **MEN** stilbene unit was observed.

NMR photokinetic analysis of the photochromic behavior using numerical methods showed that in all cases, the quantum yield of the *Z*→*E* isomerization is higher than the reverse photochemical back reaction *E*→*Z*. At lower temperatures, in *EN* and *MEN*, the ring opening is much more efficient than the *E*→*Z* isomerization. The opposite effect was observed in the case of the *ZN* and *MZN* isomers. On the other hand, no clear-cut effect can be seen in **MgMEN** when the macrocycle is Mg-filled.

The knowledge of the photocoloration, photoisomerization and thermal bleaching parameters obtained for the hybrid biphotochromic molecule **MEN** could be helpful for the construction of more elaborate light and metal-sensitive systems exhibiting well-established gated-photochromism and photomodulation effects.

Experimental Section

General Information: The styryl naphthopyrans **EN** and **MEN** were synthesized by the Wittig method as based on an earlier report.[9] The *MEN* isomer (97% purity) isomer was obtained photochemically after irradiation of the *MZN* and *MEN* isomeric mixtures at 313 nm in CH_3CN and 295 K. Solvents and reagents were obtained from commercial suppliers and were used without further purification.

UV/Vis Absorption: Measurements were performed according to the procedure described in ref. [5b]. The binding constant and the stoichiometry were obtained from the titration curve by fitting these changes using the nonlinear regression analysis program SPECFIT32. Samples (1×10^{-5} M in CH_3CN) were irradiated in quartz cells (10 mm) at 295 K in an in-house-constructed apparatus attached to the UV/Vis spectrometer. The kinetic parameters of the ring closure reaction were determined at each temperature by monitoring the disappearance of the colored form at the wavelength of maximum absorbance after having removed the irradiating source.

NMR Experiments: All NMR experiments were recorded on a Bruker Avance DRX 500 MHz spectrometer using CD_3CN as internal reference in a TXI Bruker 5 mm probe.[20] Data acquisition and processing were performed with Topspin 2.1 software (Bruker). Aliquots of a metal perchlorate solution (0.01–0.1 M in CD_3CN) were added to a **MEN** solution (0.8–1.0 mM in CD_3CN) and ^1H NMR spectra were recorded after each addition. The quantities of the different species were calculated from the integrated areas of the NMR signals. The translational diffusion coefficients were determined by the PGSE-NMR technique by monitoring the ^1H signal. This method was first introduced by Stejskal and Tanner, and in our experiments, the BPP-STE-LED sequence combining constant time, stimulated echo,

bipolar pulse, and the longitudinal eddy current delay method was used.[21]

Irradiation in NMR Tubes: Samples (0.8–1.0 mM) in CD_3CN were irradiated in NMR tubes (5 mm) at 295 K in a home-made apparatus that has been described previously.[5b, 17a]

Fitting Procedure: Laboratory-developed software was used to perform kinetics curve fittings.[17d]

Acknowledgements

This work was supported by the Centre National de la Recherche Scientifique (CNRS) and Russian RFBR programs (09-03-00283, 10-03-93106). The 500 MHz NMR facilities were funded by the Région Nord-Pas de Calais (France), the Ministère de la Jeunesse de l'Education Nationale et de la Recherche (MJENR), and the Fonds Européens de Développement Régional (FEDER). Part of this collaborative work was realized within the framework of the International Research Group IRG CNRS 93 "Phenics" (Photoswitchable Organic Molecular Systems & Devices).

Keywords: alkaline earth metals · nmr spectroscopy · photochromism · structure elucidation · supramolecular chemistry

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[18] $h_{ij} = \Phi_{ij}\ \varepsilon_i\ l\ I_0\ F$ where Φ_{ij} is the quantum yield of the photoreaction from *i* to *j*, ε_i is the molar extinction coefficient of species *i*, *l* the optical path of irradiation, I_0 the irradiation photon flux and $F = (1-10^{-Abs'})/Abs'$, where Abs' is the total absorbance of the sample at the irradiation wavelength, *F* is the photokinetic factor assumed to be equal to 1.

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Received: January 21, 2011

