# Fluorescent properties of an azacrown-containing styryl derivative of naphthopyran: ion-binding response and photochemical switching off†

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The fluorescent properties of a recently synthesized photochromic naphthopyran containing a 1-aza-15-crown-5 moiety (**1b**) and its crownless analogue (**1a**) were studied. **1b** emits fluorescence with a maximum at 528 nm, quantum yield 0.1 and characteristic lifetime 2.4 ns (in acetonitrile at room temperature). Its luminescence could be switched off photochemically in two ways using two parallel photochemical reactions characteristic for this type of naphthopyran. The first way is the irreversible *trans–cis* photoisomerization of a closed form ("stilbene-like reaction"). The second way is the thermally reversible reaction of closed form transition to the open form ("chromene-like reaction"). The fluorescence of **1b** is quenched by alkali earth metal cations by the mechanism of static quenching. Stability constants for 1 : 1 complexes of **1b** with $Mg^{2+}$ and $Ba^{2+}$ determined from Stern–Volmer plots are in agreement with that obtained by UV spectroscopy.

## 1 Introduction

Macroscopic properties of materials can be modulated by light through switching between the two stable states of a photochromic system.[1–4] In particular, photochemical transformations associated with photochromic compounds can be exploited to switch the luminescence of molecules under the action of light.[5–11] Compounds with photocontrolled fluorescence are of interest for 3D optical memory,[12–15] imaging technologies, visualizing sensors,[16] and characterization of diffusion in polymers and biological systems.[17]

According to estimations, the information capacity of 3D optical memory could be more than 1 Tbyte.[18] Luminescent readout is considered to be one of the most promising approaches in optical information technologies.[19] Light-sensitive materials can exhibit fluorescence either in their initial state (negative photoluminescent media) or in the photo-induced form (positive luminescent media). For negative media, fluorescence disappears upon recording, while for positive media it emerges upon irradiation.

Light-modulated luminescence was reported for diarylethenes,[7,20–23] fulgides,[8,24–26] spiropyrans,[5,6,17,27] spirooxazines,[28–33] chromenes[11,32–40] and proteins.[41–44] In the case of chromenes the fluorescence of the closed form was observed in ref. 32–40. In several cases, both closed and open forms are fluorescent.[11,34,35,39]

Incorporation of a crown-ether fragment into the structure of a photochromic compound opens the possibility to control its properties *via* complexation with metal cations.[1,45–47] In particular, control of fluorescence is possible.[45,46,48–50] Addition of alkali earth cations to azacrown styryl dyes was found to result in both enhancement and quenching of fluorescence.[45,48] A number of fluorogenic crown-ether based chemosensors for different metal cations are described in ref. 49 and references therein. Addition of alkali earth metal cations to naphthalimide derivatives bearing an *N*-benzocrown ether fragment was reported to significantly enhance the luminescence.[50]

Recently we described the synthesis and properties of several crown-containing naphthopyrans and their crownless analogues (Scheme 1).[51] These compounds were found to demonstrate two types of photochemical reactions. One of them was *trans–cis* isomerisation of a closed form ("stilbene-like" reaction, Scheme 2a), and the second reaction was the spiro-bond cleavage that resulted in the occurrence of an open form ("chromene-like" reaction, Scheme 2b). Geometrical

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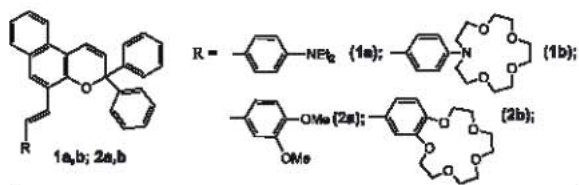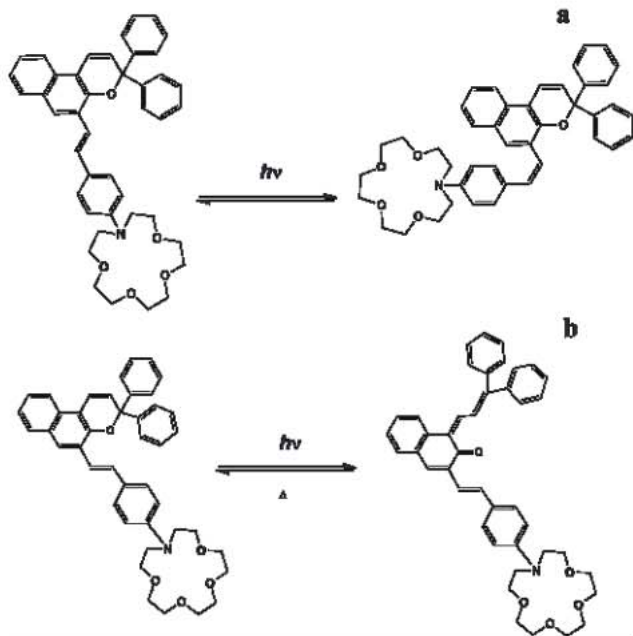[b]*Novosibirsk State University, 2 Pirogova str., 630090 Novosibirsk, Russia*
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**Scheme 1**



**Scheme 2**

isomerization of the closed form (Scheme 2a) is irreversible.[51,52] The electrocyclic reaction (Scheme 2b) is thermally reversible. Stilbene-like and chromene-like reactions were found to be parallel photochemical processes.[51]

Among the chromenes shown in Scheme 1, only compounds **1a** and **1b** were found to be fluorescent in closed *trans*-form. This paper describes the effect of irradiation and complexation with metal cations on the fluorescent properties.

## 2   Experimental

Synthesis, physical properties and NMR-spectra of **1a** (4-[2-(3,3-diphenyl-3*H*-benzo[*f*]chromen-5-yl)ethenyl]-*N*,*N*-4-[2-(3,3-diphenyl-3*H*-benzo[*f*]chromen-5-yl)ethenyl]-*N*,*N*-diethylaniline) and **1b** were reported in ref. 51. Naphthopyran **1b** was a mixture of *cis*- and *trans*-isomers with a ratio of 1 : 5, respectively[51] (Scheme 2a). We failed to separate the individual isomers. Compound **1a** exists as only the *trans*-isomer of the closed form. Mg(ClO$_4$)$_2$ and Ba(ClO$_4$)$_2$ (Aldrich) were used as the sources of Mg$^{2+}$ and Ba$^{2+}$ cations. Spectrophotometric grade acetonitrile was used as solvent. When necessary, solutions were deoxidized by bubbling with argon. UV absorption spectra were recorded using Agilent HP-8453 and Cary 50

spectrophotometers. Stationary luminescence spectra at ambient and lower temperatures were recorded on a Hitachi MPF-4 spectrofluorimeter. Quantum yield of luminescence was measured using quinine bisulfate as a reference. Quantum yield of the open form formation was determined from the kinetic data by means of the method described elsewhere.[53,54] Time-resolved luminescence was recorded using the FLSP-920 spectrofluorimeter (Edinburgh Instruments). In these experiments luminescence was excited by the irradiation of the Xe-900 xenon lamp or the EPLED-280 laser diode ($\lambda_{ex}$ = 280 nm, pulse duration 600 ps). Stationary photolysis was performed using a high pressure mercury lamp with sets of glass filters to select light with the necessary wavelengths.

*Trans–cis* photoisomerization and formation of the open form are parallel processes. In order to distinguish their inputs in the absorption and emission changes we used the following procedure: between the sample irradiation and measurements we were waiting until the complete disappearance of the open form in the course of the thermal reaction. When studying the input of open form formation we have neglected the *trans–cis* isomerisation because this reaction proceeds with a quantum yield that is 40 times smaller than the ring opening.

## 3   Results and discussion

### 3.1   UV spectrum of 1b

The electronic absorption spectra of the naphthopyrans studied are temperature-dependent. Fig. 1 demonstrates the changes in the absorption of **1b** in closed form. In the case of a closed form in acetonitrile solution (Fig. 1) two isosbestic points (at 343 and 354 nm) are conserved upon the change of temperature. This fact gives an indication of transitions between two isomeric forms. These forms are not *trans*- and *cis*-isomers of **1b** closed form (Scheme 1a), because the fingerprint of *trans–cis* isomerization of **1b** is the conservation of a single isosbestic point in the region of 292 nm (see Fig. 2a).
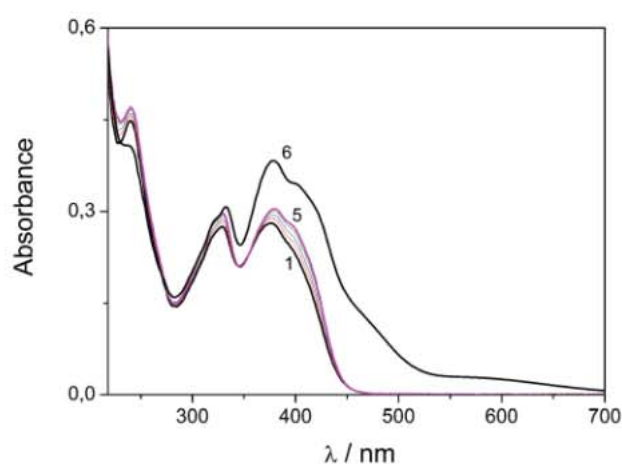


**Fig. 1** UV spectra of closed form **1b** at 20, 0, −15, −30, −40 °C (curves 1–5, correspondingly) and open form (curve 6) at −40 °C (3.1 × 10$^{-5}$ M in a 1 cm cell) in acetonitrile.
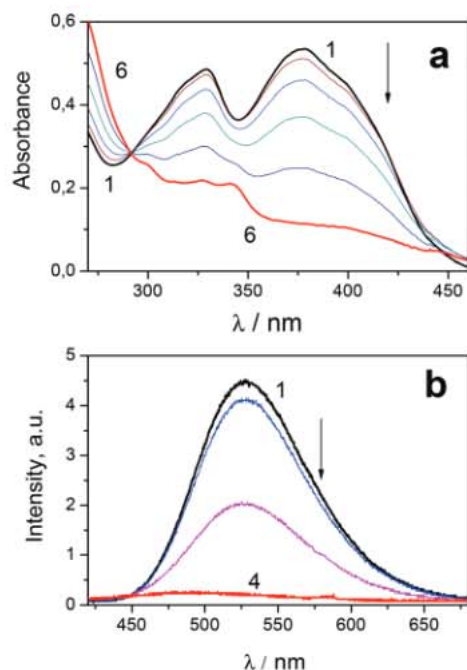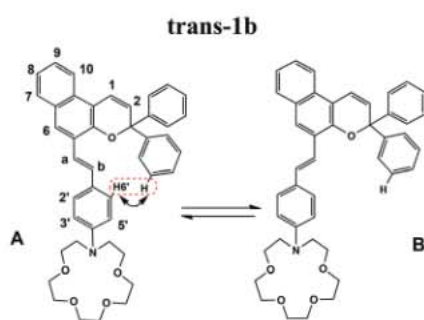
**Fig. 2** Spectral evolution in the course of *E–Z* photoisomerization of **1b** (313 nm). 2.5 × 10⁻⁵ M of chromene in CH₃CN, 1 cm cell, 295 K. (a) Changes in the UV spectra in the course of photolysis. Curves 1–6 correspond to 0, 0.5, 2, 5, 10, and 15 min of irradiation. (b) Changes in the emission spectrum (excitation at 291 nm). Curves 1–4 correspond to 0, 0.5, 5, and 15 min of irradiation.



**Scheme 3**

The possible explanation of the observed spectral changes is the equilibrium between two conformers of *trans*-**1b** closed form (A and B in Scheme 3). Conformer B is energetically more favorable than conformer A due to the interaction of H(6′) and H(Ph) protons. A decrease in temperature results in the shift of equilibrium. The similar equilibrium between two conformers of *trans*-**1b** closed form supported by NOESY spectrum was described in ref. 51. For the open form, the influence of the thermal reaction did not allow us to measure correctly the temperature dependencies of the UV-spectrum.

### 3.2 Fluorescence of 1b

Emission, excitation and absorption spectra of naphthopyran **1b** are shown in Fig. 3. The emission spectrum consists of one band with a maximum at 528 nm (curve 3 in Fig. 3). The
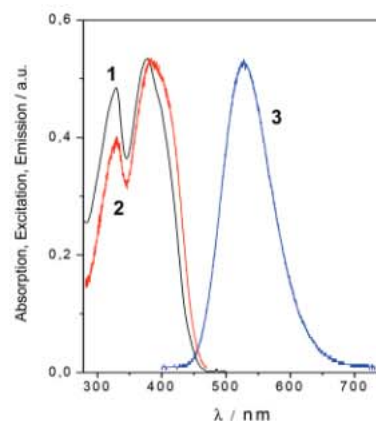


**Fig. 3** Absorption (curve 1), excitation (curve 2) and emission (curve 3) spectra of **1b** (*trans*-closed form) in acetonitrile solutions. Arbitrary units.

excitation spectrum almost coincides with the absorption spectrum of the *trans*-closed form of **1b** (Scheme 2a). The quantum yield of luminescence in acetonitrile solutions was measured to be 0.10 ± 0.01 (297 K). The kinetic curves of luminescence decay in deaerated acetonitrile solutions were monoexponential with a lifetime of 2.4 ± 0.1 ns.

Fig. 2 demonstrates the changes in the UV absorption spectrum (Fig. 2a) and emission spectrum (Fig. 2b) caused by the irradiation of naphthopyran **1b** in acetonitrile at room temperature. Absorption and emission spectra were recorded using the same sample. The changes in the UV absorption spectrum correspond to *trans–cis* isomerization of the closed form.[51,52] This process leads to the complete disappearance of fluorescence. The process of *trans–cis* isomerization is not reversible, therefore, the fluorescence could only be switched off in this manner, but switching on is not possible. The quantum yield of this reaction in acetonitrile at room temperature is 0.013 ± 0.001 for compound **1a** and 0.007 ± 0.001 for **1b**.

Chromene-like reaction of **1b** results in a significant decrease of the emission band due to the transition to the open form (Fig. 4). The quantum yield of this reaction in acetonitrile at room temperature is 0.28 ± 0.05 (the same for both **1a** and **1b**). The occurrence of the open form could be monitored at lower temperatures. Backward reaction of the open form transition to the closed form results in complete restoration of luminescence. The fluorescence could be restored by heating the sample (the rate constant of the open form transition to the closed form at ambient temperature is 0.08 s⁻¹, and the activation energy is 15 kcal mol⁻¹;[51] therefore, at 233 K the characteristic time of this reaction is about 3 h). Therefore, naphthopyran **1b** at lower temperatures acts as a thermally reversible photoluminescent media. The photochemical reactions' quantum yields and fluorescence parameters are collected in Table 1.

### 3.3. Effect of metal cations on 1b fluorescence

Naphthopyran **1b** forms 1 : 1 complexes with Mg²⁺ and Ba²⁺ cations.[52] The Mg²⁺ cation has an ionic radius of 0.72 Å.[55] This is smaller than the radius of the cavity in aza-15-crown-5-ether

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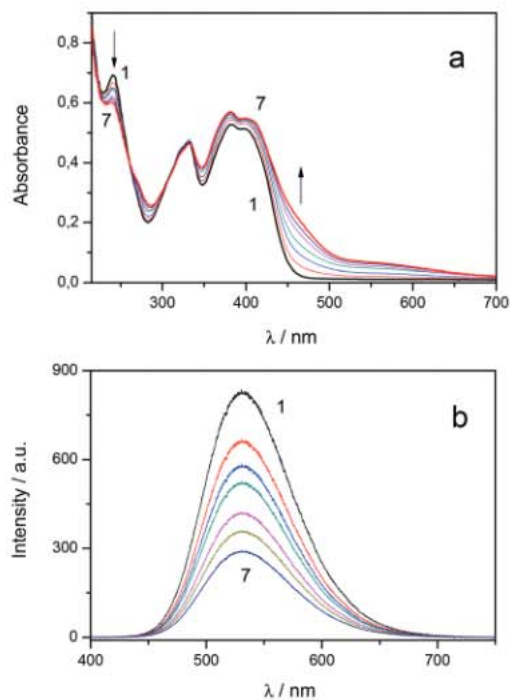*Photochem. Photobiol. Sci.*, 2013, **12**, 1803 1810 | **1805**

**Fig. 4** Spectral evolution of **1b** (2.3 × 10⁻⁵ M in acetonitrile, 1 cm cell) in the course of the open form formation (a and b depict changes in absorption and ⊡uorescence, correspondingly). Temperature −40 °C. Curves 1–7 correspond to 0, 10, 20, 30, 60, 90 and 150 s of irradiation (313 nm). After 150 seconds of irradiation, the sample reaches a photostationary state; further irradiation leads to the irreversible changes caused by *cis⊡trans* photoisomerisation. The excitation spectrum of the solution does not change during the experiment.

**Table 1** Quantum yields of the photochemical reactions and the ⊡uorescence parameters of compounds investigated

| Compound | $\phi^{open}$ | $\phi^{trans\,cis}$ | $\lambda_{max.}^{fluor}$ (nm) | $\phi^{fluor}$ | $\tau$ (ns) |
|---|---|---|---|---|---|
| **1a** | 0.28 ± 0.05 | 0.013 ± 0.001 | 440 | 0.10 | 2.4 |
| **1b** | 0.28 ± 0.05 | 0.007 ± 0.001 | 505 | 0.11 | 2.4 |

(0.85–1.1 Å).⁵⁶ Therefore, Mg²⁺ is situated inside the cavity, and the formation of the 1 : 1 complex is essential. The Ba²⁺ cation with an ionic radius of 1.36 Å⁵⁵ is situated outside the cavity. In this case, one could expect the formation of [Ba²⁺] : [chromene] = 1 : 2 sandwich complexes. These complexes are formed for crown-containing naphthopyran **2b**,⁵² but not for azacrown-containing naphthopyran **1b**. The formation of sandwich complexes is not characteristic for azacrown ethers, probably due to the steric hindrances caused by the nonplanar structure of the molecules.⁴⁶

The formation of complexes between metal cation and crown-containing naphthopyran affects the UV spectra of the compounds. The spectral changes of **1b** caused by complexation with Mg²⁺ are shown in Fig. 5a. Formation of a complex results in the quenching of **1b** fluorescence (Fig. 5b). Fig. 6 demonstrates changes in UV absorption and fluorescence spectra caused by the addition of Ba²⁺ cations to **1b**. To obtain the quantitative results, the excitation of fluorescence was
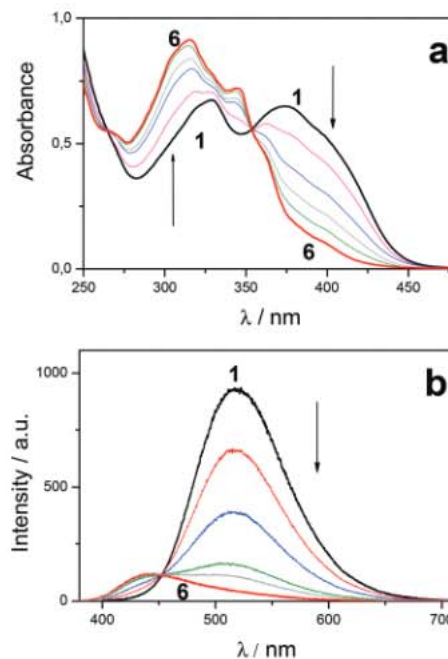


**Fig. 5** E⊡ect of complexation with Mg²⁺ on the UV absorption (panel a) and ⊡uorescence (panel b) of naphthopyran **1b**. 2.9 × 10⁻⁵ M of **1b** in CH₃CN, 1 cm cell, 295 K. Excitation of luminescence at 354 nm. Curves 1–6 on both panels correspond to 0, 3.5 × 10⁻⁴, 2.7 × 10⁻³, 6.6 × 10⁻³, 1.1 × 10⁻², and 4.3 × 10⁻² M of Mg(ClO₄)₂.
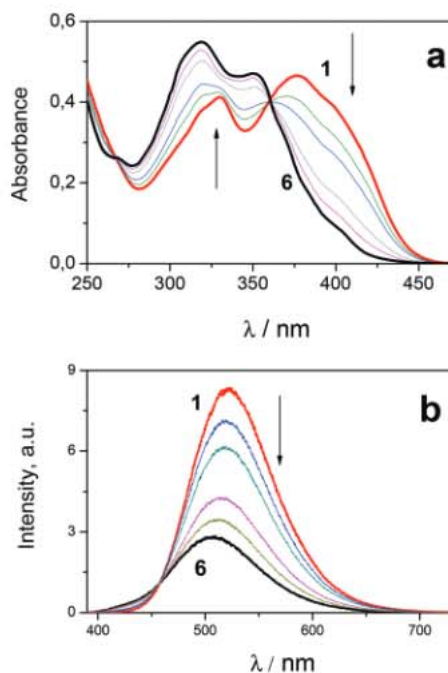


**Fig. 6** E⊡ect of complexation with Ba²⁺ on the UV absorption (panel a) and ⊡uorescence (panel b) of naphthopyran **1b**. 2.0 × 10⁻⁵ M of **1b** in CH₃CN, 1 cm cell, 295 K. Excitation of ⊡uorescence at 360 nm. Curves 1–6 on both panels correspond to 0, 4.6 × 10⁻⁵, 9.2 × 10⁻⁵, 3.5 × 10⁻⁴, 7.8 × 10⁻⁴, and 2.0 × 10⁻³ M of Ba(ClO₄)₂.

performed in the region of the isosbestic point corresponding to the equilibrium between chromene and its complex with

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**Fig. 7** Stern–Volmer plots for the quenching of **1b** fluorescence in acetonitrile by alkali earth metal cations. Experimental curves and fits obtained by means of eqn (1) with parameters listed in Table 2. Treatment of the data in Fig. 5b and 6b. Integral intensity of luminescence is used for plotting. Panel a: system (**1b**–$Mg^{2+}$), $2.9 \times 10^{-5}$ M of chromene; panel b: system (**1b**–$Ba^{2+}$), $2.0 \times 10^{-5}$ M of chromene.
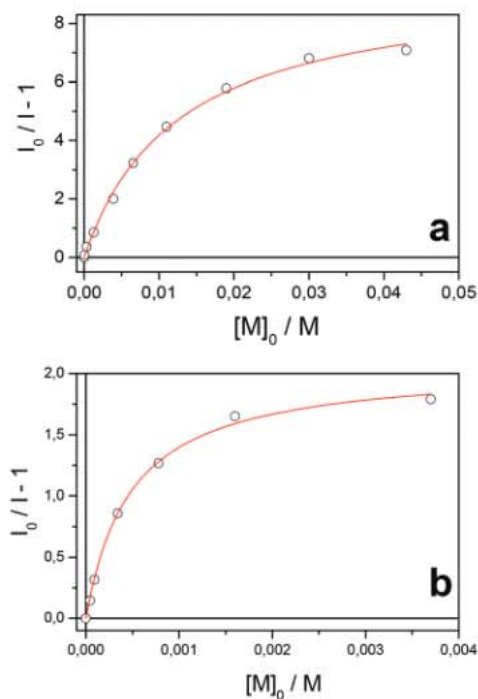
**Table 2** Stability constants ($K$) and fluorescence parameters for L–M complexes

| System | $\lg K$,[a] absorption ($M^{-1}$) | $\lg K$, fluorescence ($M^{-1}$) | $\phi_{comp}^{fluor}$ | $\lambda_{max.}^{fluor}$ (nm) |
|---|---|---|---|---|
| **1b**-Mg | $2.78 \pm 0.05$ | $2.85 \pm 0.05$ | $0.012 \pm 0.001$ | 440 |
| **1b**-Ba | $3.87 \pm 0.05^{a}$ | $3.85 \pm 0.05$ | $0.035 \pm 0.003$ | 505 |

[a] Measured in ref. 52.

$$\frac{[LM]}{[L]_0} = 1 - \frac{[L]}{[L]_0} \quad (3)$$

$$\frac{I_0}{I} - 1 =$$
$$\frac{2K[L]_0 \phi_r}{1 + K[L]_0 + K[M]_0 - \sqrt{\left(1 + K[L]_0 + K[M]_0\right)^2 - 4K^2[L]_0[M]_0}} \left[1 - \phi_r\right] + 2K I_{LM}[L]_0 \quad (4)$$

Since $I_0 = I_L$, substituting eqn (2) and (3) into (1) and following the use of eqn (1) in $I_0/I - 1$ gives the final 1 : 1 binding isotherm (4). Eqn (4) satisfactorily describes the Stern–Volmer plot for both (**1b**–$Mg^{2+}$) and (**1b**–$Ba^{2+}$) systems (Fig. 7). The results of the experimental curve fitting are shown in Table 2.

The stability constants obtained by the Stern–Volmer plots (1) were compared with the values calculated from the data obtained from UV spectroscopy (Fig. 5a and 6a). The UV data were analyzed by a numerical method described previously[57] (consult ESI† for details). The obtained values are shown in Table 2. The values of the stability constants obtained from the quenching of fluorescence are in fair agreement with those obtained from the UV absorption spectra. Note that in ref. 51 we have reported the overestimate value of $K_1$ for the (**1b**–$Mg^{2+}$) complex. Now we report the corrected values based on the application of two independent methods.

An interesting point is that the value of $K_1$ for the $Mg^{2+}$ cation which is situated inside the crown-ether cavity is smaller than that for the outside $Ba^{2+}$ cation. The low value of $K_1$ for $Mg^{2+}$ could be explained by the steric hindrances caused by the nonplanar structure of the azacrown-containing chromene.

the metal cation (354 and 360 nm for the cases of (**1b**–$Mg^{2+}$) and (**1b**–$Ba^+$) systems, correspondingly). At high concentrations of $Mg^{2+}$, weak residual fluorescence with a maximum in the region of 440 nm is observed (curve 6 in Fig. 5b). Addition of $Ba^{2+}$ also results in the quenching of **1b** fluorescence.

Fig. 7 shows the Stern–Volmer plots for (**1b**–$Mg^{2+}$) and (**1b**–$Ba^+$) systems. Integral intensity obtained by numerical integration of the fluorescence spectra was used to construct these plots. In both cases, no linearity typical for simple dynamic or static quenching was observed. Experimental Stern–Volmer plots were analyzed in the framework of static quenching in which both free ligands (L) and complexes (LM) are fluorescent with different quantum yields. Under the experimental conditions, the observed intensity can be described by eqn (1), where $I_L$ and $I_{LM}$ corresponds to the intensity of solutions with $[L] = [L]_0$ and $[LM] = [L]_0$, correspondingly.

$$I = \frac{I_L[L] + I_{LM}[LM]}{[L]_0} \quad (1)$$

For the formation of the 1 : 1 complex, eqn (2) and (3) express the dependencies of [L] and [LM], correspondingly ($K$ = stability constant for the LM complex).[57]

$$[L] = \frac{-\left(1 + K[L]_0 + K[M]_0\right) + \sqrt{\left(1 + K[L]_0 + K[M]_0\right)^2 + 4K[L]_0}}{2K} \quad (2)$$

## 4  Conclusions

The present work describes the fluorescent properties of an azacrown-containing chromene (naphthopyran) **1b**. This chromene exhibits two parallel photochemical reactions: irreversible *trans–cis* isomerization of a closed form and the thermally reversible transition to an open form. Among the different isomers of **1b**, only the *trans*-isomer of the closed form is fluorescent. Its fluorescence could be switched off either irreversibly by means of *trans–cis* isomerization of the closed form or by a thermally reversible transition to the open form. Fluorescence is quenched by alkali earth metal cations *via* the mechanism of static quenching.

In this work we have presented the phenomenological description of the fluorescent properties of **1b**. The detailed study of the mechanism (including solvent effects and time-resolved measurements) is in progress.

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## Notes and references

1 M. V. Alfimov, O. A. Fedorova and S. P. Gromov, Photoswitchable molecular receptors, *J. Photochem. Photobiol., A*, 2003, **158**, 183–198.

2 M. Sauer, Reversible molecular photoswitches: a key technology for nanoscience and fluorescence imaging, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 9433–9434.

3 M. L. Bossi and P. F. Aramendia, Photomodulation of macroscopic properties, *J. Photochem. Photobiol., C*, 2011, **12**, 154–166.

4 A. Bianco, S. Perissinotto, M. Garbugli, G. Lanzani and C. Bertarelli, Control of optical properties through photochromism: a promising approach to photonics, *Laser Photonics Rev.*, 2011, **5**, 711–736.

5 J. Cusido, E. Deniz and F. M. Raymo, Fluorescent switches based on photochromic compounds, *Eur. J. Org. Chem.*, 2009, 2031–2045.

6 T. Fukaminato, *J. Photochem. Photobiol., C*, 2011, **12**, 177.

7 M. Irie, Diarylethenes for memories and switches, *Chem. Rev.*, 2000, **100**, 1685–1716.

8 Y. Yokoyama, Fulgides for memories and switches, *Chem. Rev.*, 2000, **100**, 1717–1739.

9 F. M. Raymo and M. Tomasulo, Fluorescence modulation with photochromic switches, *J. Photochem. Photobiol., A*, 2005, **109**, 7343–7352.

10 G. Berkovic, V. Krongauz and V. Weiss, Spiropyrans and spirooxazines for memories and switches, *Chem. Rev.*, 2000, **100**, 1741–1753.

11 V. A. Barachevsky, Photofluorochromic spirocompounds and their application, *J. Fluoresc.*, 2000, **10**, 185–191.

12 D. A. Parthenopoulos and P. M. Rentzepis, 3-Dimensional optical storage memory, *Science*, 1989, **245**, 843–845.

13 S. Kawata and Y. Kawata, Three-dimensional optical data storage using photochromic materials, *Chem. Rev.*, 2000, **100**, 1777–1788.

14 V. A. Barachevsky, M. M. Krayushkin, V. V. Kyiko and E. P. Grebennikov, Light-sensitive organic recording media for 3D optical memory, *Phys. Status Solidi C*, 2011, **8**(9), 2841–2845.

15 T. Tsujioka, I. Onishi and D. Natsume, Photocurrent switching method based on photoisomerization of diarylethene layer for nondestructive readout of photochromic optical memory, *Appl. Opt.*, 2010, **49**, 3894–3899.

16 T. Takahashi, Y. Taniguchi, K. Umetani, H. Yokouchi, M. Hashimoto and T. Kano, *cis–trans* Photoisomerization of perinaphthothioindigo for use as a photo-imaging sensor using fluorescence under He–Ne-laser excitation, *Jpn. J. Appl. Phys.*, 1985, **24**, 173–176.

17 A. K. Chibisov and H. Gorner, Photoprocesses in spiropyran-derived merocyanines, *J. Phys. Chem. A*, 1997, **101**, 4305–4312.

18 V. A. Barachevsky, Y. P. Strokach, Y. A. Puankov, O. I. Kobeleva, T. M. Valova, K. S. Levchenko, V. N. Yaroshenko and M. M. Krayushkin, Light-sensitive heterocyclic compounds for information nanotechnologies, *ARKIVOC*, 2009, 70–95.

19 V. I. Skvortsov and M. V. Alfimov, Inhibited fluorescence at the deactivation of highly excited triplet-states, *Dokl. Akad. Nauk SSSR*, 1986, **291**, 1166–1169.

20 G. M. Tsivgoulis and J. M. Lehn, Photonic molecular devices – reversibly photoswitchable fluorophores for non-destructive readout for optical memory, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1119–1122.

21 G. M. Tsivgoulis and J. M. Lehn, Photoswitched and functionalized oligothiophenes: synthesis and photochemical and electrochemical properties, *Chem.□Eur. J.*, 1996, **2**, 1399–1406.

22 K. Kinashi, T. Kotake, Y. Ono, K. Ishida and Y. Ueda, Photoswitching of diarylethene using bisazomethine dye, *Opt. Mater.*, 2009, **31**, 1711–1714.

23 Y. Kutsunugi, C. Coudret, J. C. Micheau and T. Kawai, Photomodulation of the proton affinity and acid gated photochromism of a novel dimethylaminophenyl thiazole diarylethene, *Dyes Pigm.*, 2012, **92**, 838–846.

24 Y. C. Liang, A. S. Dvornikov and P. M. Rentzepis, Fluorescent photochromic fulgides, *Res. Chem. Intermed.*, 1998, **24**, 905–914.

25 Y. C. Liang, A. S. Dvornikov and P. M. Rentzepis, New near infrared-sensitive photochromic fluorescing molecules, *J. Mater. Chem.*, 2003, **13**, 286–290.

26 T. Inada, S. Uchida and Y. Yokoyama, Perfect on/off switching of emission of fluorescence by photochromic reaction of a binaphthol-condensed fulgide derivative, *Chem. Lett.*, 1997, 321–322.

27 D. H. Hu, Z. Y. Tian, W. W. Wu, W. Wan and A. D. Q. Li, Photoswitchable nanoparticles enable high-resolution cell imaging: PULSAR microscopy, *J. Am. Chem. Soc.*, 2008, **130**, 15279.

28 V. G. Luchina, I. Y. Sychev, A. I. Shienok, N. L. Zaichenko and V. S. Marevtsev, Photochromism of spironaphthooxazines having electron-donor substituents, *J. Photochem. Photobiol., A*, 1996, **93**, 173–178.

29 W. F. Yuan, L. Sun, H. H. Tang, Y. Q. Wen, G. Jiang, W. Huang, L. Jiang, Y. L. Song, H. Tian and D. B. Zhu, A novel thermally stable spironaphthoxazine and its

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application in rewritable high density optical data storage, *Adv. Mater.*, 2005, **17**, 156.

30 A. V. Chernyshev, N. A. Voloshin, I. M. Raskita, A. V. Metelitsa and V. I. Minkin, Photo- and ionochromism of 5′-(4,5-diphenyl-1,3-oxazol-2-yl) substituted spiro indoline-naphthopyrans, *J. Photochem. Photobiol., A*, 2006, **184**, 289–297.

31 S. O. Besugliy, A. V. Metelitsa, V. Z. Shirinian, M. M. Krayushkin, D. M. Nikalin and V. I. Minkin, Novel photochromic spirocyclic compounds of thienopyrroline series: 2. Spirooxazines, *J. Photochem. Photobiol., A*, 2009, **206**, 116–123.

32 M. R. di Nunzio, P. L. Gentili, A. Romani and G. Favaro, Photochromic, thermochromic, and fluorescent spirooxazines and naphthopyrans: a spectrokinetic and thermodynamic study, *ChemPhysChem*, 2008, **9**, 768–775.

33 M. R. di Nunzio, E. O. Danilov, M. A. J. Rodgers and G. Favaro, Ultrafast excited-state dynamics in some spirooxazines and chromenes. Evidence for a dual relaxation pathway, *Photochem. Photobiol. Sci.*, 2010, **9**, 1391–1399.

34 S. Anguille, P. Brun, R. Guglielmetti, Y. P. Strokach, A. A. Ignatin, V. A. Barachevsky and M. V. Alfimov, Synthesis and photochromic properties of ferrocenyl-substituted benzo- and dibenzochromenes, *J. Chem. Soc., Perkin Trans. 2*, 2001, 639–644.

35 Y. P. Strokach, A. A. Ignatin, V. A. Barachevsky, M. V. Alfimov, S. Anguille, P. Brun and R. Guglielmetti, Photochromic properties of ferrocene substituted chromenes, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 2000, **344**, 119–124.

36 S. Coen, C. Moustrou, M. Frigoli, M. Julliard, A. Samat and R. Guglielmetti, Spectroscopic properties of thiophene linked 2*H*-chromenes, *J. Photochem. Photobiol., A*, 2001, **139**, 1–4.

37 F. Ortica, L. Bougdid, C. Moustrou, U. Mazzucato and G. Favaro, Structure effects on the photobehaviour of 2,2-diphenyl(2*H*)chromenes, *J. Photochem. Photobiol., A*, 2008, **200**, 287–293.

38 F. Ortica, P. Smimmo, G. Favaro, U. Mazzucato, S. Delbaere, D. Venec, G. Vermeersch, M. Frigoli, C. Moustrou and A. Samat, Effect of oligothiophene substituents on the photophysical and photochromic properties of a naphthopyran, *Photochem. Photobiol. Sci.*, 2004, **3**, 878–885.

39 S. Jockusch, N. J. Turro and F. R. Blackburn, Photochromism of 2*H*-naphtho-1,2-*b* pyrans: a spectroscopic investigation, *J. Phys. Chem. A*, 2002, **106**, 9236–9241.

40 L. W. Song, Y. H. Yang, Q. Zhang, H. Tian and W. H. Zhu, Synthesis and photochromism of naphthopyrans bearing naphthalimide chromophore: predominant thermal reversibility in color-fading and fluorescence switch, *J. Phys. Chem. B*, 2011, **115**, 14648–14658.

41 J. Lippincott-Schwartz and G. H. Patterson, Photoactivatable fluorescent proteins for diffraction-limited and super-resolution imaging, *Trends Cell Biol.*, 2009, **19**, 555–565.

42 D. M. Chudakov, M. V. Matz, S. Lukyanov and K. A. Lukyanov, Fluorescent proteins and their applications in imaging living cells and tissues, *Physiol. Rev.*, 2010, **90**, 1103–1163.

43 B. Wu, K. D. Piatkevich, T. Lionnet, R. H. Singer and V. V. Verkhusha, Modern fluorescent proteins and imaging technologies to study gene expression, nuclear localization, and dynamics, *Curr. Opin. Cell Biol.*, 2011, **23**, 310–317.

44 Y.-T. Kao, X. Zhu, F. Xu and W. Min, Focal switching of photochromic fluorescent proteins enables multiphoton microscopy with superior image contrast, *Biomed. Opt. Express*, 2012, **3**, 1955–1963.

45 E. N. Ushakov, S. P. Gromov, O. A. Fedorova and M. V. Alfimov, Crown-containing styryl dyes. 19. Complexation and cation-induced aggregation of chromogenic aza-15-crown-5-ethers, *Russ. Chem. Bull.*, 1997, **46**, 463–471.

46 E. N. Ushakov, M. V. Alfimov and S. P. Gromov, Design principles for optical molecular sensors and photocontrolled receptors based on crown ethers, *Russ. Chem. Rev.*, 2008, **77**, 39–59.

47 S. Shinkai, T. Nakaji, T. Ogawa, K. Shigematsu and O. Manabe, Photoresponsive crown ethers. 2. photocontrol of ion extraction and ion-transport by a bis(crown ether) with a butterfly-like motion, *J. Am. Chem. Soc.*, 1981, **103**, 111–115.

48 E. N. Ushakov, S. P. Gromov, O. A. Fedorova, Y. V. Pershina, M. V. Alfimov, F. Barigelletti, L. Flamigni and V. Balzani, Sandwich-type complexes of alkaline-earth metal cations with a bisstyryl dye containing two crown ether units, *J. Phys. Chem. A*, 1999, **103**, 11188–11193.

49 V. I. Minkin, A. D. Dubonosov, V. A. Bren and A. V. Tsukanov, Chemosensors with crown ether-based receptors, *ARKIVOC*, 2008, 90–102.

50 P. A. Panchenko, Y. V. Fedorov, V. P. Perevalov, G. Jonusauskas and O. A. Fedorova, Cation-dependent fluorescent properties of naphthalimide derivatives with *N*-benzocrown ether fragment, *J. Phys. Chem. A*, 2010, **114**, 4118–4122.

51 E. M. Glebov, A. B. Smolentsev, V. V. Korolev, V. F. Plyusnin, A. V. Chebunkova, S. V. Paramonov, O. A. Fedorova, V. Lokshin and A. Samat, Synthesis and photochromic properties of crown-containing styryl derivatives of naphthopyrans, *J. Phys. Org. Chem.*, 2009, **22**, 537–545.

52 A. B. Smolentsev, V. V. Korolev, E. M. Glebov, V. P. Grivin, V. F. Plyusnin, A. I. Kruppa, A. V. Chebun'kova, S. V. Paramonov, O. A. Fedorova, V. Lokshin and A. Samat, Crown-containing styryl derivatives of naphthopyrans: complexation with alkaline-earth metal cations and photochemistry, *Kinet. Catal.*, 2012, **53**, 54–64.

53 S. Delbaere, G. Vermeersch and J. C. Micheau, Quantitative analysis of the dynamic behaviour of photochromic systems, *J. Photochem. Photobiol., C*, 2011, **12**, 74–105.

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*Photochem. Photobiol. Sci.*, 2013, **12**, 1803 1810 | **1809**

54  M. Maafi and R. G. Brown, Photophysics and kinetics of naphthopyran derivatives, part 1: general analytical solutions for the kinetics of AB(k,phi) and ABC(k,phi) systems, *Int. J. Chem. Kinet.*, 2005, **37**, 162–174.

55  R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halidesand chalcogenides, *Acta Crystallogr., Sect. A: Cryst. Phys., Di□r., Theor. Gen. Crystallogr.*, 1976, **32**, 751–767.

56  K. J. Thomas, K. G. Thomas, T. K. Manojkumar, S. Das and M. V. George, Cation-binding and photophysical properties of a monoaza-15-crown-5-ether linked cyanine dye, *P. Indian AS □Chem. Sci.*, 1994, **106**, 1375–1382.

57  A. E. Hargrove, Z. L. Zhong, J. L. Sessler and E. V. Anslyn, Algorithms for the determination of binding constants and enantiomeric excess in complex host:guest equilibria using optical measurements, *New J. Chem.*, 2010, **34**, 348–354.

**Determination of stability constants from the UV data**

Spectrophotoelectric titration data and nonlinear regression analysis were used to determine the binding constants (K) of the complexes. This procedure was described in details elsewhere [53].

In the case of **1b** binding of $Mg^{2+}$ and $Ba^{2+}$ cations the scheme of complexation is
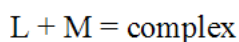
L + M = complex

Eqn (1) was used to determine the binding constant (K) and molar absorptivity of the complex ($\varepsilon_{comp}$). It was used as the input for a user-defined function in the nonlinear fitting function of Origin, which will then determine the values of K and $\varepsilon_{comp}$ from the best-fit curve. The procedure was carried out at 2 different wavelengths.

$$A = \frac{C_L}{2-(1-KC_M+KC_L)+\sqrt{4KC_M+(1-KC_M+KC_L)^2}} \times$$

$$\times (2\varepsilon_L + \varepsilon_{comp} \times (-(1-KC_M+KC_L)+\sqrt{4KC_M+(1-KC_M+KC_L)^2})) \quad (1)$$

where A – optical density (cuvette – 1 cm), $C_M$ and $C_L$ – $[M]_0$ and $[L]_0$ correspondingly.
Model Func_binding_11 (User)

Complexation **1b**-$Mg^{2+}$



| | | Func_binding_11 (User) | |
|---|---|---|---|
| Model | | | |
| Equation | | y = C0 / (2 - (1 - K*x + K*C0) + (4 *K*x + (1 - K*x + K*C0)^2)^0.5) * ( 2*E0 + E1*(- (1 - K*x + K*C0) + (4 *K*x + (1 - K*x + K*C0)^2)^0.5)) | |
| Reduced Chi-Sqr | | 1,2458E-4 | |
| Adj. R-Square | | 0,99579 | |
| | | Value | Standard Error |
| H | C0 | 2,9E-5 | 0 |
| H | E0 | 17685,86868 | 271,74567 |
| H | E1 | 2438,83511 | 259,9644 |
| H | K | 608,71898 | 63,60751 |

abs(400)
Func_binding_11 (User)Fit of H

Absorbance (400 nm) vs $C_{Mg(ClO_4)_2}$