# Novel azacrown ether-containing spiro[indoline-2,3′-naphthoxazines]: design, synthesis and cation-dependent photochromism

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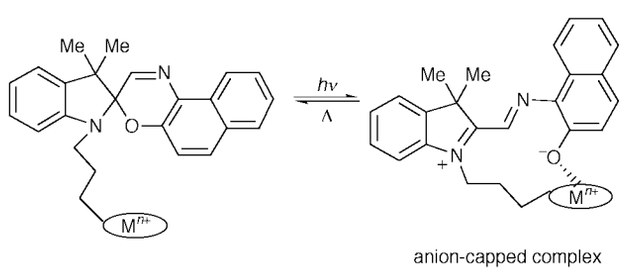
Novel spironaphthoxazine compounds with an aza-15-crown-5 ether fragment at position 5′ or 9′ of the naphthalene ring were synthesised. Spectrokinetic measurements showed the occurrence of two competing formation processes for complexation with alkaline earth or rare earth metal cations. A comparative study of the prepared compounds demonstrated the role of molecular design and the metal cation nature in the cation-dependent photoinduced transformation of spiro[indoline-naphthoxazines].

## Introduction

Crown-containing dyes are able to bind selectively with metal cations and also to absorb light in the visible region of the spectrum.[1–3] These compounds have been used, for example, as reagents for calorimetric or luminescence determination of metal cations and as fragments of photoswitchable molecular devices.[4–6] We have reported previously[7] that the introduction of a crown-ether fragment into a styryl dye molecule gives compounds capable of changing their spectral and photochemical properties upon complex formation. Compounds of this type are promising in the construction of chemical sensors, in molecular electronics and in systems of information imaging and storage. Other examples of photochromic crown ethers known to date[8–11] are crown ether-containing spiropyrans and spironaphthoxazines. For spiro compounds in which the crown ether is a part of an *N*-substituent, the formation of an additional coordination bond between the oxygen atom of the merocyanine form and the metal ion in the crown ether cavity (anion-capped complex) was observed (Scheme 1).[8,11]




**Scheme 1**

The stability of an anion-capped complex depends appreciably on the structure and position of the crown ether fragment. Thus, for spiro[indoline-2,3′-naphthoxazine] linked to a benzo-15(18)-crown-5(6) fragment,[12] it was found that the rigid spacer structure prevents the formation of an anion-capped complex and, therefore, the addition of metal ions to a solution of such a compound does not affect essentially its photochromic properties. It is worth mentioning that in all the papers cited,[8–12] the complex formation was analysed without taking into account the fact that the oxygen atom of the merocyanine form (MF) can interact with free metal cations occurring in the solution. This process competes with the formation of the anion-capped complex and can affect strongly the optical properties of the molecule. This work deals with the synthesis and spectroscopic study of novel spironaphthoxazine derivatives bearing an aza-15-crown-5 ether moiety at positions 5′ and 9′ of the naphthalene ring. The diversity of the crown ether position and the length of spacer in the spiro molecule make it possible to study in detail the complex formation and its influence on the optical properties of spironaphthoxazine.

## Results and discussion

### Syntheses

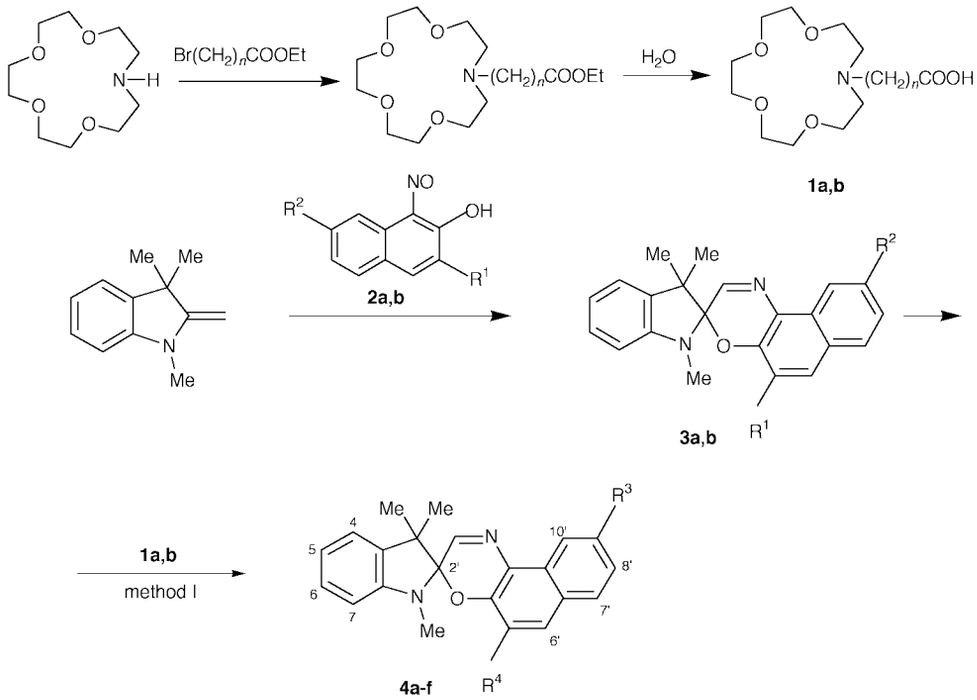
Crown-containing spironaphthoxazines (CSN) **4b**,**c**,**e**,**f** and reference compounds **4a**,**d** containing no crown ether fragments were synthesised (see Scheme 2).

1-Nitroso-2,3-dihydroxynaphthalene[13] **2a** and 1-nitroso-2,7-dihydroxynaphthalene[14] **2b** were prepared in almost quantitative yields as described previously. Spiro[indoline-2,3′-naphthoxazines] **3a**,**b** were obtained by condensation of 1,3,3-trimethyl-2-methyleneindoline with **2a**,**b** in dry ethanol.[12]

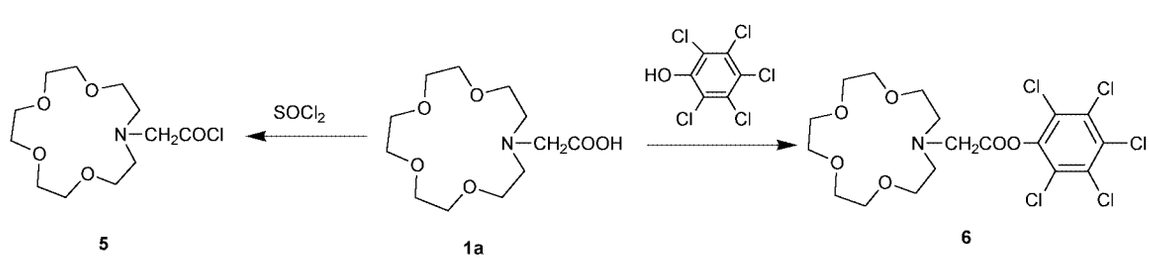
The crown-containing amino acids **1a**,**b** (unknown previously) were obtained by a two-step procedure. The alkylation of aza-15-crown-5 ether by ethyl bromoalkanoates in the presence of $Na_2CO_3$ or $Et_3N$ gave the corresponding crown-containing esters, which were hydrolysed in water without isolation.

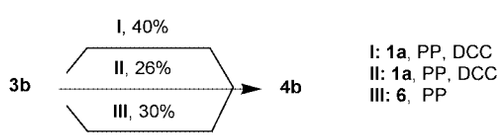
We devised several pathways to the CSN using **4b** as an example (see Scheme 3).

The preparation of the ester **4b** has been achieved from the condensation of the spiro[indoline-2,3′-naphthoxazine] **3b** with the acid **1a**. Among the numerous methods reported in the literature, esterification[14] using dicyclohexylcarbodiimide (DCC) and a catalytic amount of 4-pyrrolidinopyridine (PP) seems to be the most convenient procedure. Indeed, the reaction of **1a** with **3b** in the presence of PP and DCC is performed under mild conditions with a relatively good yield (40%) (method **I**), though even short-term heating to 40 °C led to resinification of the reaction mixture. It was also shown that **4b**




**Scheme 2**




**Scheme 3**

is highly susceptible for hydrolysis, the initial compound **3b** being recovered when **4b** is purified by column chromatography on silica gel. We tentatively performed two other methods for the preparation of **4b**, using the esterification reaction from the acid chloride **5** or the transesterification reaction from the activated ester **6**. Unfortunately, the hydroxynaphthoxazine **3b** does not react with the acid chloride of *N*-carboxymethyl-aza-15-crown-5 ether **5** in the presence of dimethylaniline at ambient temperature. On the other hand, the pentachlorophenyl ester **6** was obtained in 53% yield in THF, starting from pentachlorophenol, acid **1a**, and an equimolar amount of PP in the presence of DCC. We showed that ester **6** can be used without isolation and purification to perform the transesterification reaction with **3b** in the presence of PP. Compound **4b** has been prepared in 26% yield without isolation of the ester **6** (method **II**) and 30% yield from isolated ester **6** (method **III**).

Finally, method **I** was retained to prepare the spirooxazines **4a**,**c**–**f** with yields up to 90%. The structures of **1a**,**b**, **3a**,

**4a**–**f**, and **6** were established by $^1$H NMR spectroscopy and mass spectrometry and confirmed by elemental analysis (see Experimental section).

The MS (EI technique) of the *N*-carboxyalkyl derivative of aza-15-crown-5 ether **1b** (see Experimental section) shows the peak of the [M] − OH ion. The most intense peak with *m*/*z* 232 in the mass-spectrum of **1a** is due to the cleavage of the β-C–C bond relative to the nitrogen atom, which is typical of amino acids.

The suggested structures of **4b**,**d**,**f** were confirmed by the presence of the corresponding molecular ion peak. The mass spectra of **4c** contains no molecular ion peak, but has intense peaks with *m*/*z* 344 due to the loss of the substituted aza-15-crown-5 ether fragment. Further fragmentation involves elimination of the dihydroxynaphthalene skeleton (*m*/*z* 185) and the indole skeleton (*m*/*z* 158).

### Molecular simulation of CSN complexes

CSN complexes with alkaline earth and rare earth metal cations were calculated with the help of GenMol[15] according to the following procedure. In the first step, the free molecule was constructed and the geometry was optimised (particularly, the conformation corresponding to the minimum energy was chosen). The cation was introduced by a docking technique, by forcing interaction between the cation and the O atoms of the ligand (the crown, ester, carbonyl, and oxazine O atoms) and the crown nitrogen atom. Finally, the geometry and the conformation of the complex were optimised without constraint. If the cation remained bonded after the energy optimization (molecule relaxation), this meant that the interaction energy of the cation with ligand was high enough to balance the molecular strain corresponding to the geometry deformation necessary to keep the cation linked to the oxygen atoms. These considerations allowed us to take the energy of interaction ($E_i$) between the cation and the free ligand as a measurement of the stability of the complex at the enthalpy level.[16] This energy is the sum of non-bonded interactions (in our case, the van der Waals and Coulombic interactions). The complex stability is related to the $E_i$ value, which is proportional to the association constant.

In these calculations, corresponding to a gas state model, solvation and anion effects can be considered as equivalent in the homogeneous series of compounds studied. On the other hand, for experiments being performed at constant temperature, the entropy effects are of the same order of magnitude and have minor influence on the predictions of the structure of the most stable complexes.

**Complexation with $Mg^{2+}$.** According to the calculations the most stable complexes could be readily formed respectively for crown-ether on the 5′ and 9′ positions with CSN **4b** and **4f**. Indeed, $E_i$ is −134, −125, −136 and −142 kcal mol$^{-1}$ respectively for **4b**, **4c**, **4e** and **4f**. Unfortunately, the oxazine O atom is not involved in the interaction.

**Complexation with $Zn^{2+}$ or $Eu^{3+}$.** Our idea was to obtain complexes of these ligands with bulkier cations. Some interesting results have been obtained for 5′-crown ether-substituted spiroxazine and $Zn^{2+}$ and $Eu^{3+}$ cations. It seemed of interest to consider the role of different alkyl chains ranging from $(CH_2)_5$ to $(CH_2)_{15}$ in the formation of anion-capped complexes. In the case of $Zn^{2+}$, if $n < 15$, the O atom of the open form cannot form a coordination bond with the metal cation located in the crown ether cavity, due to the specific structure of the complex. In the case of $Eu^{3+}$, it is possible to obtain an anion-capped complex even for $(CH_2)_5$ (Fig. 1). For *n* ranging from 6 to 10, the structure of the open form becomes such that formation of the anion-capped type complex is disfavoured; this complex formation could arise when the spacer corresponds to $n = 12$ or 15.

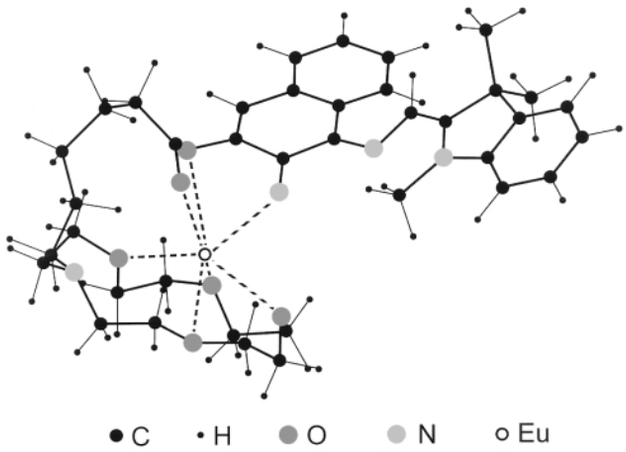



**Fig. 1** Calculated spatial structure of the complex (**4f**·$Eu^{3+}$).

### Spectrokinetic studies of the photoinduced interconversions of CSN and their complexes

Irradiation of compounds **4a**–**f** induces a reversible coloration–decoloration reaction. The presence of the crown ether fragment at position 9′ of the naphthalene ring does not affect the absorption spectra of the initial and coloured forms of **4b**,**c** and the thermodynamic equilibrium between these forms (see Table 1). However, the thermal fading rate constant ($k_f$) of the coloured form of **4b**,**c** was found to increase, due to the steric influence of the large substituent on the conformation interconversion, which accompanies the photoreaction.

By contrast, the visible spectra of 5′-substituted compounds **4d**–**f** exhibit a weak absorption band, corresponding to the MF, which may be due to the stabilisation of the MF through interaction with the carbonyl group[17] (Scheme 5, complex **C**).

The addition of Mg, Ca or Ba perchlorates to solutions of **4a**–**c** in MeCN with the ratio $C_L/C_M = 1:1$ ($C_L$ is the ligand concentration and $C_M$ is the salt concentration) does not change substantially the spectral or kinetic parameters. An increase in salt concentration to $C_L/C_M = 1:100$ causes a slight bathochromic shift of the long-wave band ($\Delta\lambda$) in the absorption spectra of the MF, which is up to 5 nm for **4c** and up to 15 nm for **4b** (see Table 1).

When $Mg^{2+}$, $Ca^{2+}$ or $Ba^{2+}$ cations are added to acetonitrile solutions of **4a**–**c**, the $k_f$ values decrease (Table 1). For spiro compounds **4a**,**c**, these effects are slight, whereas for **4b** the effect was found to be more pronounced (Table 1). To explain these results, we propose the following complex formation scheme (Scheme 4).

The formation of type **A** complex has been observed previously[18] for compounds containing no crown ether fragments. In the case of spironaphthoxazine **4a**, the formation of complex **A** upon the addition of metal ions should decrease the ground state energy of the MF, and, therefore, it should increase the potential barrier to the thermal relaxation process.

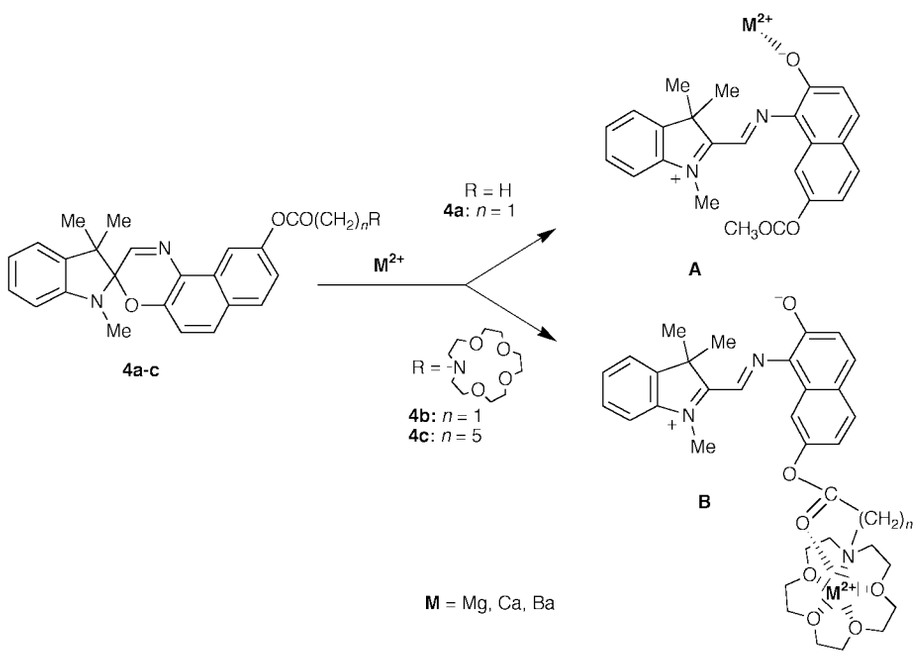
When alkaline earth metal ions are added to acetonitrile solutions of CSN **4b**,**c** (crown-ether on the 9′-position), the metal ions are bound by the crown ether fragment (type **B** complex formation, Scheme 5), which can be monitored by electronic spectroscopy (Table 1) and confirmed by the results of computer simulation (see 'Molecular simulation of CSN' section). The involvement of the carbonyl oxygen in the formation of type **B** complex causes redistribution of the π-electron density in the conjugation chain of the MF chromophore, leading to additional stabilisation of this form. The most substantial effect of the complex formation on the fading rate constant $k_f$ was found for CSN **4b**, which is in good agreement with the calculation results, indicating that the most stable complex is formed by CSN **4b**.

The effect of the metal cation on the equilibrium between the open and closed forms for compounds **4d**–**f** (crown-ether on the

**Table 1** Spectrokinetic characteristics of compounds **4a**–**f** and their complexes with $Mg^{2+}$, $Ca^{2+}$ and $Ba^{2+}$ in MeCN

| Compound (L) | Cation (M) | [L]:[M] | $\lambda_L$/nm | $\Delta\lambda$/nm | $\varepsilon_o/10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$ | $\varepsilon/\varepsilon_o$ | $k_f$/s$^{-1}$ | $k_f/k_f^o$ |
|---|---|---|---|---|---|---|---|---|
| **4a** | — | | 597 | | 0 | | 0.53 | 1 |
| | $Mg^{2+}$ | 1:100 | 596 | −1 | 0 | | 0.10 | 0.19 |
| | $Ca^{2+}$ | 1:100 | 597 | 0 | 0 | | 0.13 | 0.24 |
| | $Ba^{2+}$ | 1:100 | 598 | +1 | 0 | | 0.38 | 0.72 |
| **4b** | — | | 595 | | 0 | | 1.10 | 1 |
| | $Mg^{2+}$ | 1:100 | 607 | +12 | 0 | | 0.060 | 0.055 |
| | $Ca^{2+}$ | 1:100 | 607 | +12 | 0 | | 0.040 | 0.036 |
| | $Ba^{2+}$ | 1:100 | 610 | +15 | 0 | | 0.20 | 0.18 |
| **4c** | — | | 595 | | 0 | | 0.96 | 1 |
| | $Mg^{2+}$ | 1:100 | 597 | +2 | 0 | | 0.20 | 0.21 |
| | $Ca^{2+}$ | 1:100 | 598 | +3 | 0 | | 0.24 | 0.25 |
| | $Ba^{2+}$ | 1:100 | 599 | +4 | 0 | | 0.66 | 0.69 |
| **4d** | — | | 595 | | 0.05 | 1 | 0.35 | 1 |
| | $Mg^{2+}$ | 1:1 | 594 | −1 | 0.13 | 2.5 | 0.10 | 0.29 |
| | $Mg^{2+}$ | 1:10 | 592 | −3 | 0.30 | 6 | 0.04 | 0.11 |
| **4e** | — | | 597 | | 0.02 | 1 | 0.46 | 1 |
| | $Mg^{2+}$ | 1:1 | 597 | 0 | 0.11 | 6 | 0.12 | 0.26 |
| | $Mg^{2+}$ | 1:10 | 597 | 0 | 0.18 | 9 | 0.045 | 0.10 |
| **4f** | — | | 595 | | 0.02 | 1 | 0.45 | 1 |
| | $Mg^{2+}$ | 1:1 | 575 | −20 | 0.39 | 20 | 0.35 | 0.78 |
| | $Mg^{2+}$ | 1:10 | 587 | −8 | 0.3 | 15 | 0.15 | 0.33 |
| | $Mg^{2+}$ | 1:100 | 590 | −5 | 0.5 | 25 | 0.06 | 0.13 |

[a] ($\Delta\lambda = \lambda_{ML} - \lambda_L$ is the shift of the long-wave band in the absorption spectra upon the complex formation; $\lambda_{ML}$ is the long-wave band of the complex; $\lambda_L$ is the long-wave band of the free MF; $\varepsilon/\varepsilon_0$ is the ratio of the extinction coefficients of the MF bound in the complex and free; $k_f$ is the fading rate constant; $k_f/k_f^o$ is the ratio of the fading rate constants of the complex and the free ligand).




**Scheme 4**

5′-position) depends on the salt concentration (see Figs. 2, 3, Table 1). Up to the ratio $C_L/C_M = 1:1$, the addition of $Mg^{2+}$ to solutions of CSN **4e**,**f** causes a much more pronounced increase in the intensity of the MF band in the visible spectrum than that in the case of **4d**, devoid of the crown ether fragment (*cf.* Fig. 2 and Fig. 3, Table 1). Taking into account the data of electronic spectroscopy, the molecular simulation (see 'Molecular simulation of CSN' section) and published data,[8–11,17] we propose a scheme of complex formation for spiro compounds **4d**–**f** and alkaline earth metal cations (see Scheme 5).

The observed shift of the equilibrium towards the MF in the case of CSN **4e**,**f** at $C_L/C_M = 1:1$ can be attributed to the formation of anion-capped complex **D**. It can be seen from experimental and molecular simulation results that the magnitude of this effect depends on the length of the polymethylene spacer between the photochromic and ionophoric parts of the molecule. Thus, CSN **4e**,**f**, containing crown ether fragments of the same size but alkyl spacers of different lengths showed different colouring efficiency in the presence of $Mg^{2+}$ cations, because the more rationally designed open form of **4f** allows the interaction of the crowned $Mg^{2+}$ cation with the oxygen atom of the MF. As can be seen from the absorption spectra, the formation of complexes **C** has no significant effect on the longwave band position in UV-spectrum (see Table 1 for **4d**). The changes of the absorption bands upon the formation of complex **D** of CSN **4f** with $Mg^{2+}$ and complex **B** of **4b** with $Mg^{2+}$ made it possible to find out, using the spectrophotometric titration method,[18] that the stability constant for complex **D** is more than two orders of magnitude higher than that of complex **B**.

When the $C_M/C_L$ ratio becomes more than 1, complex **E** is formed through the interaction of the MF with free $Mg^{2+}$ cations. This conclusion is supported by the change in the shape of the MF absorption band (Fig. 2).

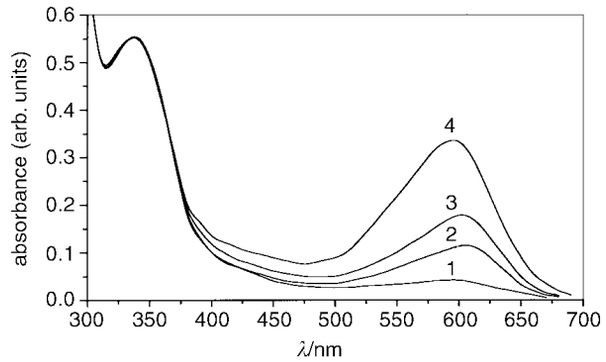



**Fig. 2** Absorption spectra of MF **4d** (1) and its complexes with $Mg^{2+}$ in MeCN. $C_L = 5 \times 10^{-4}$ mol $l^{-1}$; [L]/[M] = 1 : 1 (2), 1 : 10 (3), 1 : 100 (4).

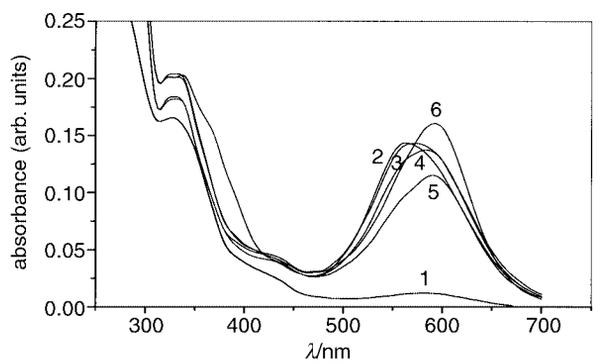



**Fig. 3** Absorption spectra of MF **4f** (1) and its complexes with $Mg^{2+}$ in MeCN. $C_L = 5 \times 10^{-4}$ mol $l^{-1}$; [L]/[M] = 1 : 0.5 (2), 1 : 2 (3), 1 : 5 (4), 1 : 20 (5), 1 : 50 (6).

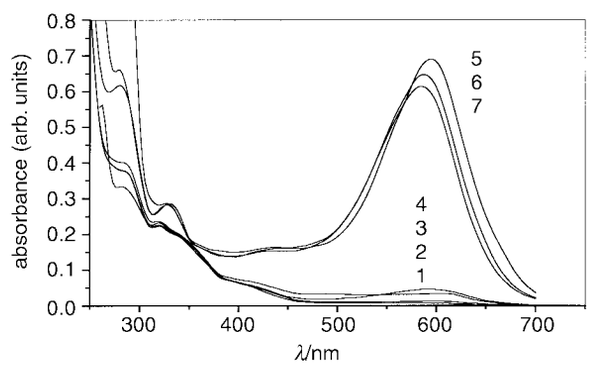
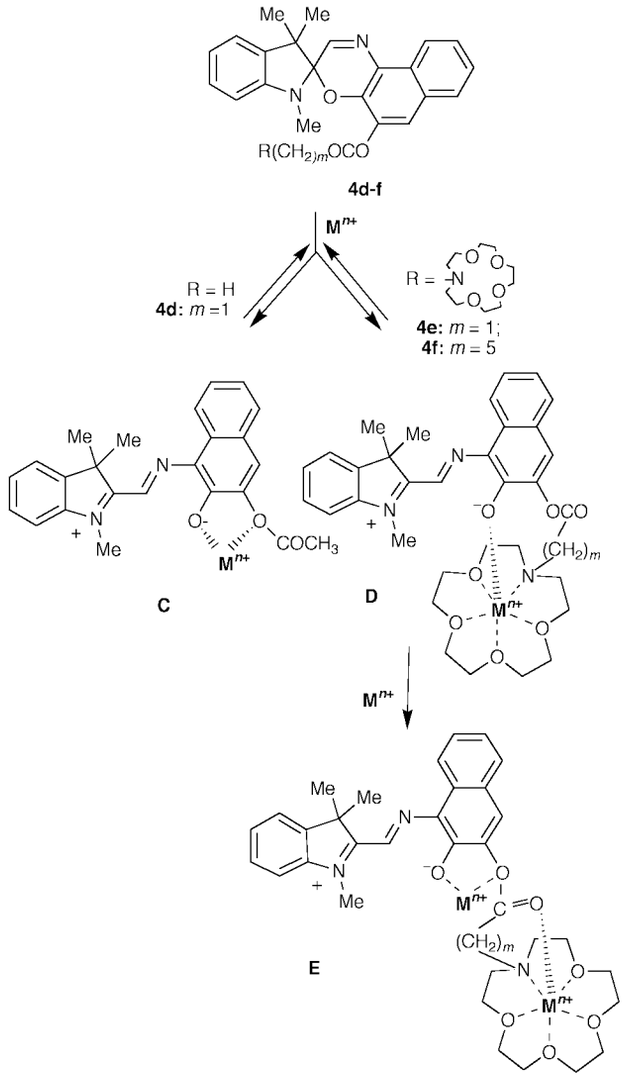



**Fig. 4** Absorption spectra of MF **4d** (1) and its complexes with $Mg^{2+}$ (4), $Ca^{2+}$ (3), $Ba^{2+}$ (2), $La^{3+}$ (5), $Eu^{3+}$ (6) and $Tb^{3+}$ (7) in MeCN. $C_L = 2 \times 10^{-4}$ mol $l^{-1}$; [L]/[M] = 1 : 100.

The addition of $Mg(ClO_4)_2$ to solutions of **4d–f** decreases the fading rate constant $k_f$ (see Table 1), showing that complexation with oxazine oxygen atom is responsible for this phenomenon. However, for CSN **4f** the decrease is lower than for **4d**, suggesting that the crown ether moiety might keep the complexed cation away from the quinoid part of the photomerocyanine.

Thus, the isomerization of the spiro compounds **4d–f** to the coloured merocyanine form is induced by the formation of complexes **C** (with the oxygen atom of the MF) or **D** (anion-capped complex) with metal cations. It is obvious that the type of the arising complex would depend on the nature of the metal cation. Figs. 4 and 5 show the visible spectra of acetonitrile solutions of crown ether-free **4d** and CSN **4f** in the presence of $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, $Ba(ClO_4)_2$, $Eu(NO_3)_3$, $La(NO_3)_3$ and $Tb(NO_3)_3$. The results of experiments with **4d**,**f** in acetonitrile demonstrated that the influence of the metal cation on the optical spectra did not depend on the type of anion.

The effect of the rare earth metal cation on the isomerisation of both compounds is remarkable (Figs. 4, 5). The intensity of




**Scheme 5**

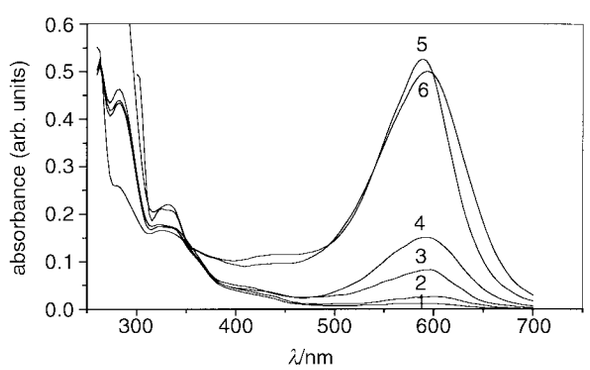



**Fig. 5** Absorption spectra of MF **4f** (1) and its complexes with $Mg^{2+}$ (4), $Ca^{2+}$ (3), $Ba^{2+}$ (2), $La^{3+}$ (5), $Eu^{3+}$ (6) in MeCN. $C_L = 2 \times 10^{-4}$ mol $l^{-1}$; [L]/[M] = 1 : 100.

the absorption bands observed does not depend noticeably on whether or not a crown ether fragment is present in the molecule. The results can be explained by assuming the formation of complexes possessing the same chelate fragments (complexes **C** for **4d** and **E** for **4f**, see Scheme 5). This hypothesis was also supported by studies of the absorption spectra of CSN **4f** at various concentrations of $Eu^{3+}$ in solution (Fig. 6). An increase in the metal concentration induced no shift of the long-wave absorption band, indicating a similar nature of the complexes formed at low and high metal concentrations. The high surface charge density on the rare earth metal cations[19] ensures their effective complexation with the MF oxygen.

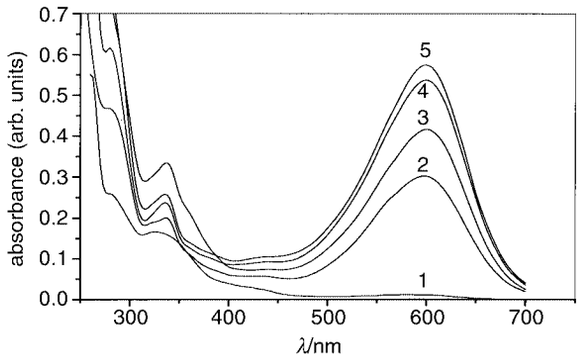



**Fig. 6** Absorption spectra of MF **4f** (1) and its complexes with $Eu^{3+}$ in MeCN. $C_L = 5 \times 10^{-4}$ mol $l^{-1}$; [L]/[M] = 1 : 0.5 (2), 1 : 2 (3), 1 : 5 (4), 1 : 20 (5).

## Conclusions

We devised a synthetic route to novel spironaphthoxazines with azacrown ether substituents at position 5′ or 9′ of the naphthalene ring. Comparative studies of the compounds synthesised demonstrated the role of molecular design and of the metal cation nature in the cation-dependent photochromic behaviour of spiro[indoline-2,3′-naphthoxazines]. The introduction of a flexible spacer containing 5 methylene groups at position 5′ between the spironaphthoxazine unit and the crown ether fragment allowed us to obtain a system with a particular influence on the complex formation attributed to the anion-capped complex. The intramolecular interaction of the phenoxide anion with a crowned metal cation in the anion-capped complex stabilises the MF of the spiro compound and promotes the bleaching process. Thus, incorporation of a crown ether moiety into the spironaphthoxazine skeleton affords novel spiro compounds whose photochromic properties can be modified by virtue of the complex formation process.

## Experimental

### Synthesis

The $^1$H NMR spectra were recorded on Bruker AC-200p (200 MHz) and Bruker AMX-400 (400 MHz) spectrometers in DMSO-$d_6$ or $CD_3CN$. Tetramethylsilane was used as an internal standard; the *J* values are given in Hz. Mass spectra were recorded on a Varian MAT311A spectrometer. Thin layer chromatography (TLC) was performed on DC-Alufolien plates with a 0.2 mm layer of Kieselgel 60F254 (Merck).

Ethyl bromoacetate, ethyl 6-bromohexanoate, 2,3- and 2,7-dihydroxynaphthalene, 4-pyrrolidinopyridine, dicyclohexylcarbodiimide, aza-15-crown-5 and pentachlorophenol were commercial preparations (Aldrich).

***N*-Carboxymethyl-1,4,7,10-tetraoxa-13-azacyclopentadecane (1a).** This was prepared according to a published procedure.[20] A mixture of aza-15-crown-5 ether (2.00 g, 9.13 mmol), ethyl bromoacetate (1.12 cm$^3$, 10.1 mmol), anhydrous $Na_2CO_3$ (1.09 g, 10.3 mmol) and dry MeCN (100 cm$^3$) was refluxed for 24 h. After cooling, the precipitate was filtered off and the filtrate was concentrated *in vacuo*. The residue was dissolved in $CHCl_3$ and washed with water, and the aqueous layer was additionally extracted with $CHCl_3$. The combined extracts were concentrated *in vacuo* and the residue was refluxed with water (40 cm$^3$) for 50 h. After cooling, the solution was extracted with benzene and the aqueous layer was concentrated *in vacuo* to give 2.3 g of **1a**, yield 88%; *m/z* 233 [M − $CH_2$-COOH]$^+$ (17%), 232 (100), 202 (35), 172 (11), 156 (16), 144 (54), 114 (52), 100 (36), 86 (15), 82 (44), 56 (28); $\delta_H$([$^2H_6$]-DMSO) 2.90 (4 H, m, 2 $CH_2N$); 3.37 (2 H, s, $CH_2N$); 3.54 (16 H, m, 8 $CH_2O$).

***N*-(5-Carboxypentyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (1b).** A solution of aza-15-crown-5 ether (1.095 g, 5.0 mmol), ethyl 6-bromohexanoate (0.89 cm$^3$, 5.0 mmol) and dry triethylamine (1.04 cm$^3$, 7.5 mmol) was kept at room temperature for 140 h. The precipitate formed was filtered, the filtrate was concentrated *in vacuo* and the residue was refluxed with water (20 cm$^3$) for 30 h. The water was removed *in vacuo* and the residue was extracted with hot hexane to give 1.6 g of **1b**, yield 95%; *m/z* 316 [M − OH]$^+$ (17%), 233 (13), 232 (100), 202 (19), 172 (21), 114 (18), 100 (21), 87 (14), 86 (15), 74 (13), 58 (15); $\delta_H$([$^2H_6$]DMSO) 1.25 (2 H, m, $CH_2$); 1.45 (4 H, m, 2 $CH_2$); 2.18 (2 H, m, $COCH_2$); 2.52 (2 H, m, $CH_2N$); 2.72 (4 H, m, 2 $CH_2N$); 3.55 (16 H, m, 8 $CH_2O$).

**1-Nitroso-2,3-dihydroxynaphthalene 2a.** This was prepared from 2,3-dihydroxynaphthalene as described previously.[14,21] The yield of **2a** was 80%.

**General procedure for the preparation of 1,3,3-trimethyl-5′(9′)-hydroxy-3′*H*-spiro[indoline-2,3′-naphtho[2,1-*b*][1,4]-oxazines] 3a,b.** A solution of 1,3,3-trimethyl-2-methyleneindoline (1.1 mmol) and nitrosodihydroxynaphthalene **2a**,**b** (1 mmol) in dry ethanol (5 cm$^3$) was refluxed for 2 h in an argon atmosphere. The solvent was removed *in vacuo*. For **3a**, the residue was purified by column chromatography on silica gel with a hexane–benzene (1 : 1) mixture as the eluent. For **3b**, the residue was purified by refluxing consecutively with ethanol, hexane and toluene.

*1,3,3-Trimethyl-5′-hydroxy-3′H-spiro[indoline-2,3′-naphtho-[2,1-b][1,4]oxazine]naphthoxazine **3a**.* Yield 16%; mp 103–107 °C; (Found: C, 75.11; H, 5.71; N, 6.18%. Calc. for $C_{22}H_{20}N_2O_2$·0.5 $H_2O$: C, 74.77; H, 5.99; N, 7.93%); $\delta_H$([$^2H_6$]DMSO) 1.24 (3 H, s, 3-Me); 1.26 (3 H, s, 3-Me); 2.72 (3 H, s, NMe); 6.66 (1 H, d, H(C-4) or H(C-7) in indoline, *J* 7.6); 6.82 (1 H, t, H(C-5) or H(C-6) in indoline, *J* 7.4); 7.10 (3 H, m, H(C-5) or H(C-6), H(C-4) or H(C-7) in indoline, H(C-6′) in naphthalene); 7.30 (2 H, m, H(C-8′), H(C-9′) in naphthalene); 7.62 (1 H, d, H(C-7′) in naphthalene, *J* 7.5); 7.85 (1 H, s, CH=N); 8.33 (1 H, d, H(C-10′) in naphthalene, *J* 8.8); 9.94 (1 H, br s, OH).

*1,3,3-Trimethyl-9′-hydroxy-3′H-spiro[indoline-2,3′-naphthol-[2,1-b][1,4]oxazine]naphthoxazine **3b**.* Yield 54%; mp 210–212 °C (decomp.); (Found: C, 76.27; H, 5.83; N, 8.13%. Calc. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 7.89%); $\delta_H$([$^2H_6$]DMSO) 1.15 (3 H, s, 3-Me); 1.17 (3 H, s, 3-Me); 2.69 (3 H, s, NMe); 6.63, 6.85 (2 H, 2d, H(C-4) and H(C-7) in indoline, *J* 7.7 and *J* 7.1); 6.81 (1H, d, H(C-7′) in naphthalene, *J* 8.8); 6.95 (1 H, dd, H(C-8′) in naphthalene, *J* 8.8 and *J* 2.3); 7.15 (2 H, m, H(C-5), H(C-6) in indoline); 7.63 (1H, d, H(C-6′) in naphthalene, *J* 9.3); 7.68 (1 H, d, H(C-5′) in naphthalene, *J* 9.3); 7.73 (1 H, d, H(C-10′) in naphthalene, *J* 2.3); 7.80 (1 H, s, CH=N); 9.92 (1 H, br s, OH).

**The pentachlorophenyl ester of *N*-(carboxymethyl)aza-15-crown-5 (6).** A solution of **1a** (0.332 g, 1.2 mmol), pentachlorophenol (0.399 g, 1.5 mmol) and PP (0.220 g, 1.5 mmol) in dry THF (4 cm$^3$) was cooled to 0 °C, and a solution of DCC (0.268 g, 1.3 mmol) in the same solvent (1 cm$^3$) was added. The resulting mixture was kept for 24 h at room temperature, the precipitate of dicyclohexylurea was filtered off, the filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel using benzene, benzene–ethyl acetate (1 : 1) and ethyl acetate as eluents. The yield was 0.33 g (53%); mp 88–90 °C; $\delta_H$([$^2H_6$]DMSO) 2.90 (4H, t, 2$CH_2N$, *J* 5.8), 3.56 (16H, m, 8$CH_2O$), 3.97 (2H, s, $COCH_2$).

**Azacrown ether-containing spiro[indoline-2,3′-naphthoxazines] 4a–f.** *Method I. The general procedure for the preparation of **4a–f**.* Acid **1a**,**b** (or glacial acetic acid for **4a**,**d**) (4.4–6.6 mmol), DCC (4.8 mmol) and PP (0.4 mmol) were added to a solution of **3a**,**b** (4.4 mmol) in $CH_2Cl_2$ (20 cm$^3$). The resulting

mixture was allowed to stand for 3 to 5 days in the dark at room temperature. The precipitate of dicyclohexylurea was filtered off and the filtrate was concentrated *in vacuo*. The residue was extracted with dry ether. For **4a**, the precipitate formed in the ether extract was filtered off and dried. For **4b**–**f**, the combined ether extracts were concentrated *in vacuo*. For **4b**, the residue was further purified by extraction with hot hexane and for **4d**, with cold hexane. The combined hexane extracts were concentrated *in vacuo*.

*Method II.* A solution of **1a** (0.332 g, 1.2 mmol), pentachlorophenol (0.399 g, 1.5 mmol) and PP (0.220 g, 1.5 mmol) in dry THF (4 $cm^3$) was cooled to 0 °C and a solution of DCC (0.268 g, 1.3 mmol) in the same solvent (1 $cm^3$) was added. The resulting mixture was allowed to stand for 24 h at room temperature, the precipitate of dicyclohexylurea was filtered off and the filtrate was concentrated *in vacuo*. The residue was dissolved in dry THF (3 $cm^3$) and a solution of **3b** (0.120 g, 0.35 mmol) and PP (0.052 mg, 0.35 mmol) in the same solvent was added. The resulting mixture was allowed to stand for 24 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel with benzene, benzene–ethyl acetate (1 : 1) and ethyl acetate as eluents to give product 0.19 g of **4b** (26% yield).

*Method III.* A solution of **6** (0.269 g, 0.5 mmol), **3b** (0.172 g, 0.5 mmol) and PP (0.072 g, 0.5 mmol) in $CH_2Cl_2$ (5 $cm^3$) was allowed to stand for 24 h at room temperature. The solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel with benzene, benzene–ethyl acetate (1 : 1) and ethyl acetate as eluents to give product 0.09 g of **4b** (30% yield).

**9′-Acetoxy-1,1,3-trimethyl-3*H*-spiro[indoline-2,3′-naphtho-[2,1-*b*][1,4]oxazine] (4a).** Yield 28%; mp 180–182 °C (decomp.); (Found: C, 75.11; H, 6.09; N, 7.26%. Calc. for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.28%); $\delta_H$([$^2H_6$]DMSO) 1,26 (3 H, s, 3-Me); 1,28 (3 H, s, 3-Me); 2.34 (3 H, s, COMe); 2,69 (3 H, s, NMe); 6.66 (1 H, d, H(C-4) or H(C-7) in indoline, *J* 7.7); 6.84 (1H, t, H(C-5) or H(C-6) in indoline, *J* 7.3); 7.15 (4 H, m, H(C-4) or H(C-7), H(C-5) or H(C-6) in indoline, H(C-7′), H(C-8′) in naphthalene); 7.83 (1 H, d, H(C-5′) in naphthalene, *J* 9.1); 7.87 (1 H, s, CH=N); 7.92 (1 H, d, H(C-6′) in naphthalene, *J* 9.1); 8.14 (1 H, s, H(C-10′) in naphthalene).

**1,1,3-Trimethyl-5′-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)acetoxy-3*H*-spiro[indoline-2,3′-naphtho[2,1-*b*][1,4]-oxazine] (4b).** Yield 40%; *m*/*z* 603 $[M]^+$ (17%), 342 (16), 341 (61), 325 (46), 233 (13), 232 (100), 160 (19), 159 (61), 158 (25), 144 (25), 56 (9); $\delta_H$([$^2H_6$]DMSO) 1.28 (3 H, s, 3-Me); 1.29 (3 H, s, 3-Me); 2.72 (3 H, s, NMe); 2.95 (4 H, m, $2NCH_2$); 3.62 (16 H, m, 8 $CH_2O$); 3.81 (2 H, m, $COCH_2$); 6.66 (1 H, d, H(C-4) or H(C-7) in indoline, *J* 7.7); 6.83 (1 H, t, H(C-5) or H(C-6) in indoline, *J* 7.2); 7.13 (3 H, m, H(C-4) or H(C-7), H(C-5) or H(C-6) in indoline, H(C-7′) in naphthalene); 7.21 (1 H, dd, H(C-8′) in naphthalene, *J* 8.7 H *J* 2.4); 7.83 (1 H, d, H(C-5′) in naphthalene, *J* 9.0); 7.87 (1 H, s, CH=N); 7.92 (1 H, d, H(C-6′) in naphthalene, *J* 8.0); 8.14 (1 H, d, H(C-10′) in naphthalene, *J* 2.3).

**1,1,3-Trimethyl-9′-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)pentylcarboxy-3′*H*-spiro[indoline-2,3′-naphtho[2,1-*b*]-[1,4]oxazine] (4c).** Yield 89%; *m*/*z* 344 [M − $C_{10}H_{20}NO_4(CH_2)_5$-COOH]$^+$ (5%), 342 (9), 328 (37), 313 (20), 232 (7), 185 (76), 159 (63), 158 (100), 145 (16), 144 (51), 130 (22), 115 (17); $\delta_H$([$^2H_6$]DMSO) 1.47 (3 H, s, 3-Me); 1.49 (3 H, s, 3-Me); 1.50 (4H, m, 2 $CH_2$); 1.80 (2H, m, $CH_2$); 2.36 (2 H, m, $COCH_2$); 2.60 (2 H, m, $NCH_2$); 2.73 (4 H, t, 2 $NCH_2$, *J* 6.3); 2.80 (3 H, s, NMe); 3.60 (16 H, m, 8 $CH_2O$); 6.84 (1 H, d, H(C-4) or H(C-7) in indoline, *J* 7.8); 7.03 (1 H, t, H(C-5) or H(C-6) in indoline, *J* 7.0); 7.24 (3 H, m, H(C-7′) in naphthaline, H(C-4) or H(C-7), H(C-5) or H(C-6) in indoline); 7.30 (1 H, dd, H(C-8′) in naphthalene, *J* 8.7 and *J* 2.3); 7.90 (1 H, d, H(C-5′) in naphthalene, *J* 8.9); 7.95 (1 H, s, CH=N); 8.07 (1 H, d, H(C-6′) in naphthalene, *J* 8.9); 8.21 (1 H, d, H(C-10′) in naphthalene, *J* 2.3).

**5′-Acetoxy-1,1,3-trimethyl-3′*H*-spiro[indoline-2,3′-naphtho-[2,1-*b*][1,4]oxazine] (4d).** Yield 36%; *m*/*z* 386 $[M]^+$ (4%), 329 (13), 185 (39), 175 (78), 160 (91), 159 (73), 158 (74), 157 (60), 145 (70), 144 (71), 130 (69), 115 (66); $\delta_H$([$^2H_6$]DMSO) 1.32 (3 H, s, 3-Me); 1.38 (3 H, s, 3-Me); 1.98 (3 H, s, COMe); 2.66 (3 H, s, NMe); 6.60, 7.14 (2 H, 2d, H(C-4) and H(C-7) in indoline, *J* 7.7 and *J* 7.2); 6.90, 7.20 (2 H, 2t, H(C-5) and H(C-6) in indoline, *J* 7.2 and *J* 7.7); 7.47 (1 H, m, H(C-8′) in naphthalene); 7.53 (1 H, s, H(C-6′) in naphthalene); 7.60 (1 H, m, H(C-9′) in naphthalene); 7.81 (1 H, d, H(C-7′) in naphthalene, *J* 8.4); 7.88 (1 H, s, CH=N); 8.53 (1 H, d, H(C-10′) in naphthalene, *J* 8.4).

**1,1,3-Trimethyl-5′-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)acetoxy-3′*H*-spiro[indoline-2,3′-naphtho[2,1-*b*][1,4]-oxazine (4e).** Yield 28%; mp 95–98 °C; (Found: C, 65.88; H, 7.03; N, 6.72%. Calc. for $C_{34}H_{41}N_3O_7 \cdot 1H_2O$: C, 65.68; H, 6.97; N, 6.76%); $\delta_H$([$^2H_6$]DMSO) 1.20 (6 H, m, 2 Me); 2.71 (3 H, s, NMe); 3.50 (22 H, m, $COCH_2$, 8 $CH_2O$, 2 $NCH_2$); 6.64 (1 H, d, H(C-4) or H(C-7) in indoline, *J* 8.0); 6.82 (1 H, t, H(C-5) or H(C-6) in indoline, *J* 6.8); 7.15 (2 H, m, H(C-4) or H(C-7), H(C-5) or H(C-6) in indoline); 7.46 (1 H, m, H(C-8′) in naphthalene); 7.60 (1 H, m, H(C-9′) in naphthalene); 7.69 (1 H, s, H(C-6′) in naphthalene); 7.84 (1 H, m, H(C-7′) in naphthalene); 7.95 (1 H, s, CH=N); 8.46 (1 H, d, H(C-10′) in naphthalene, *J* 8.6).

**1,1,3-Trimethyl-5′-(1,4,7,10-tetraoxa-13-aza-13-cyclopentadecyl)pentylcarboxy-3′*H*-spiro[indoline-2,3′-naphtho[2,1-*b*]-[1,4]oxazine] (4f).** Yield 90%; *m*/*z* 659 $[M]^+$ (<1%), 328 (36), 160 (26), 159 (69), 158 (100), 157 (31), 145 (24), 144 (73), 143 (23), 130 (21), 115 (24); $\delta_H$([$^2H_6$]DMSO) 1.25 (2 H, m, $CH_2$); 1.32 (3 H, s, 3-Me); 1.36 (3 H, s, 3-Me); 1.42 (2 H, m, $CH_2$); 1.57 (2 H, m, $CH_2$); 2.22 (2 H, t, $COCH_2$); 2.40 (2 H, m, $NCH_2$); 2.64 (7 H, m, NMe, 2 $NCH_2$); 3.56 (16 H, m, 8 $OCH_2$); 6.58, 7.12 (2 H, 2d, H(C-4′) in naphthalene and H(C-7) in indoline, *J* 7.7 and *J* 6.9); 6.87, 7.18 (2 H, 2t, H(C-5) and H(C-6) in indoline, *J* 7.4 and *J* 7.6); 7.46 (1 H, m, H(C-8′) in naphthalene); 7.51 (1 H, s, H(C-6′) in naphthalene); 7.79 (1 H, m, H(C-9′) in naphthalene); 7.29 (1 H, d, H(C-7′) in naphthalene, *J* 8.2); 7.86 (1 H, s, CH=N); 8.52 (1 H, d, H(C-10′) in naphthalene, *J* 8.4).

### Spectroscopy

UV–VIS absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in quartz cells of 1 cm pathlength at ambient temperature. The fading rate constants were measured on a kinetic apparatus in the time range 0.001–1000 seconds upon excitation of solutions by irradiation with a pulse Xe lamp. All the measurements were performed at 298 K in solutions with ligand concentration ($C_L$) $2 \times 10^{-4}$ mol $dm^{-3}$.

The spectra were measured in MeCN purchased from the Aldrich Chemical Company, water content 0.005%. $Mg(ClO_4)_2$, $Ca(ClO_4)_2$, $Ba(ClO_4)_2$, $Eu(NO_3)_3$, $La(NO_3)_3$, $Tb(NO_3)_3$ of the Aldrich Chemical Company were used as received.

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## References

1 M. Takagi, in *Cation Binding by Macrocycles. Complexation of Cationic Species by Crown Ethers*, eds. Y. Inoue and G. W. Gokel, Marcel Dekker, Inc., New York, 1990, ch. 11, pp. 465–495.

2 M. Pietraszkiewicz, in *Comprehensive Supramolecular Chemistry*, ed. D. N. Reinhoudt, Pergamon, Oxford, 1996, vol. 1, ch. 10, pp. 225–265.
3 A. P. De Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.
4 S. Shinkai, in *Cation Binding by Macrocycles. Complexation of Cationic Species by Crown Ethers*, eds. Y. Inoue and G. W. Gokel, Marcel Dekker, Inc., New York, 1990, ch. 9, pp. 397–428.
5 V. Balzani and F. Scandola, in *Comprehensive Supramolecular Chemistry*, ed. D. N. Reinhoudt, Pergamon, Oxford, 1996, vol. 10, ch. 23, pp. 687–746.
6 K. Kimura, *Coord. Chem. Rev.*, 1996, **148**, 41.
7 M. V. Alfimov and S. P. Gromov, in *Applied fluorescence in chemistry*, *biology and medicine*, eds. W. Rettig, B. Strehmel and S. Schrader, Springer-Verlag, Berlin, 1999, pp. 161–178.
8 M. Inouye, M. Uneo, K. Tsuchiya, N. Nakayama, T. Konishi and T. Kitao, *J. Org. Chem.*, 1992, **57**, 5377.
9 K. Kimura, M. Kaneshige, T. Yamashita and M. Yokoyama, *J. Org. Chem.*,1994, **59**, 1251.
10 M. Inouye, M. Ueno, T. Kitao and K. Tsuchiya, *J. Am. Chem. Soc.*, 1990, **112**, 8977.
11 K. Kimura, T. Yamashita and M. Yokoyama, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 613.
12 V. B. Nazarov, V. A. Soldatenkova, M. V. Alfimov, P. Lareginie, A. Samat and R. Guglielmetti, *Izv. Akad. Nauk, Ser. Khim.*, 1996, **9**, 2220 [*Russ. Chem. Bull.*, 1996, **45**, 611 (Engl. Transl.)].
13 A. P. Stankavichus and A. N. Kost, *Zh. Org. Chim.*, 1970, **6**, 1022.
14 M. El Malouli Bibout, P. Lareginie, L. Noussi, A. Samat and R. Guglielmetti, *Mol. Cryst. Liq. Cryst.*, 1994, **246**, 177.
15 G. Pepe and D. Siri, *Modeling of Molecular Structures and Properties*, ed. J. L. Rivail, Elsevier, Amsterdam, 1990, pp. 93–101.
16 Z. Asfari, J. P. Astier, C. Bressot, J. Estienne, G. Pèpe and J. Vicens, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 1994, **19**, 291.
17 *Photochromism: Molecules and Systems*, ed. H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990.
18 (*a*) E. N. Ushakov, S. P. Gromov, A. V. Buevich, I. I. Baskin, O. A. Fedorova, A. I. Vedernikov, M. V. Alfimov, B. Eliasson and U. Edlund, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 601; (*b*) O. B. Stanislavsky, E. N. Ushakov, O. A. Fedorova, S. P. Gromov and M. V. Alfimov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, **3**, 605 [*Russ. Chem. Bull.*, 1996, **45**, 564 (Engl. Transl.)].
19 N. M. Ditlov, V. Yu. Temkin and K. I. Popov, in *Metal complexes and complexones*, Chimia, Moscow, 1988.
20 F. R. Fronczek, V. J. Gatto, C. Mingani, R. A. Schultz, R. D. Gandour and G. W. Gokel, *J. Am. Chem. Soc.*, 1984, **106**, 7244.
21 V. V. Kozakov and Yu. P. Odinsov, *Zh. Prikl. Khim.*, 1944, **17**, 219.

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