



**HAL**  
open science

# Synthesis, Characterization and Cation-Induced Isomerization of Photochromic Calix[4](aza)crown-Indolospiropyran Conjugates

Istvan Bitter, Alajos Grün, Peter Kerekes

► **To cite this version:**

Istvan Bitter, Alajos Grün, Peter Kerekes. Synthesis, Characterization and Cation-Induced Isomerization of Photochromic Calix[4](aza)crown-Indolospiropyran Conjugates. *Supramolecular Chemistry*, 2008, 20 (03), pp.255-263. 10.1080/10610270601186091 . hal-00513503

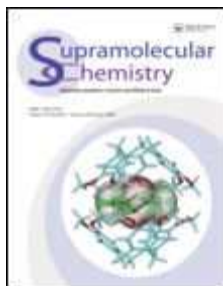
**HAL Id: hal-00513503**

**<https://hal.science/hal-00513503>**

Submitted on 1 Sep 2010

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

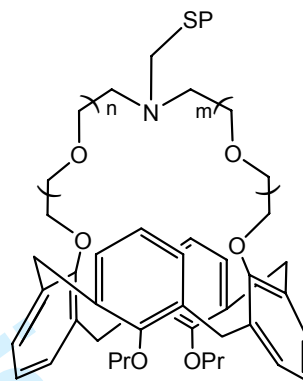
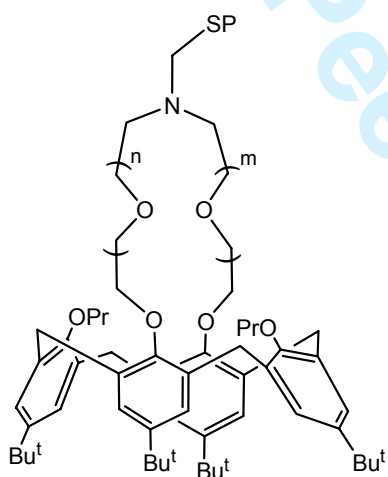
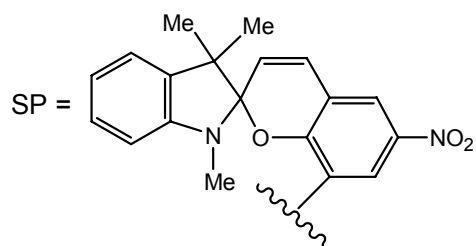
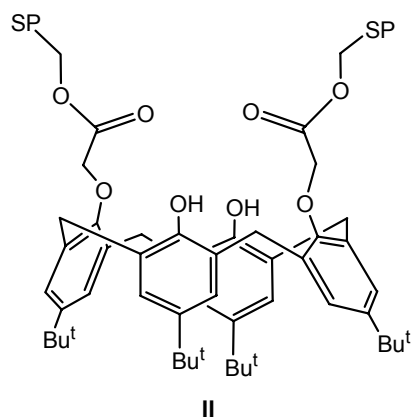
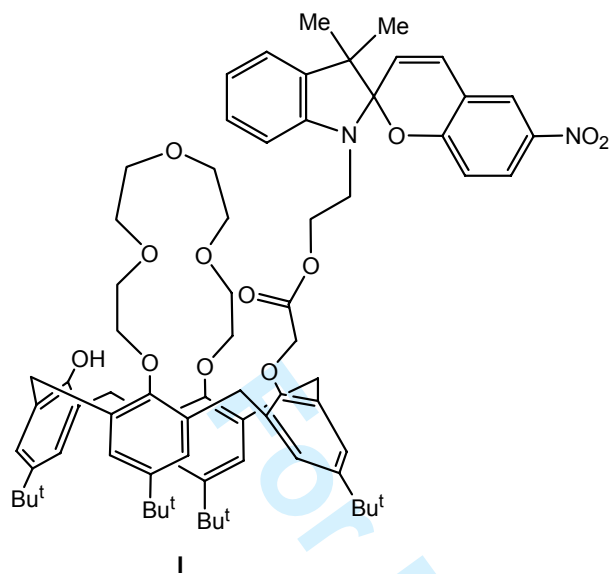
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

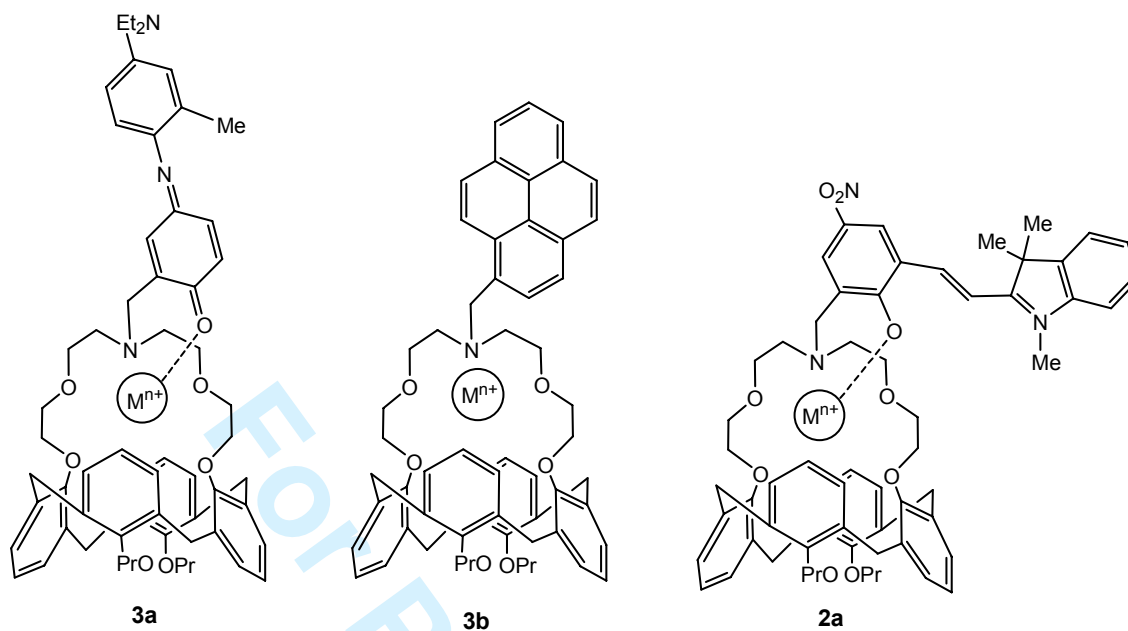


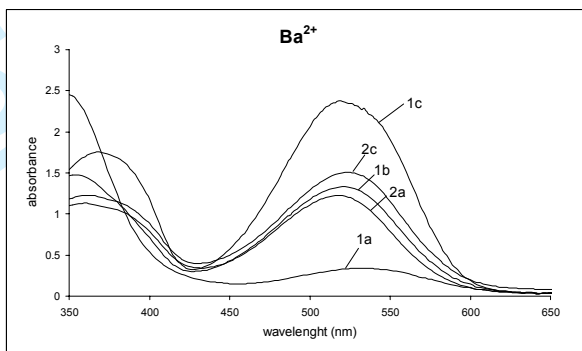
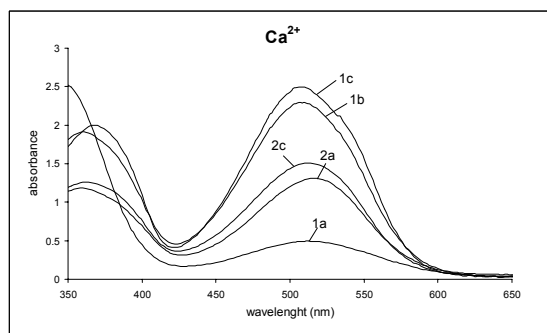
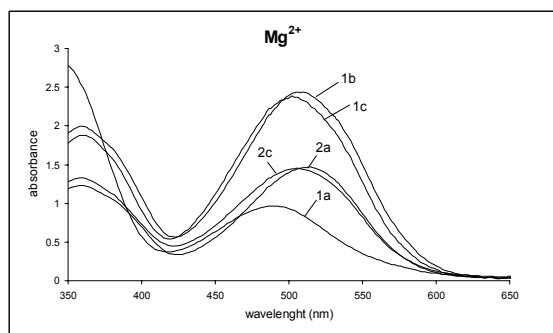
**Synthesis, Characterization and Cation-Induced  
Isomerization of Photochromic Calix[4](aza)crown-  
Indolospiropyran Conjugates**

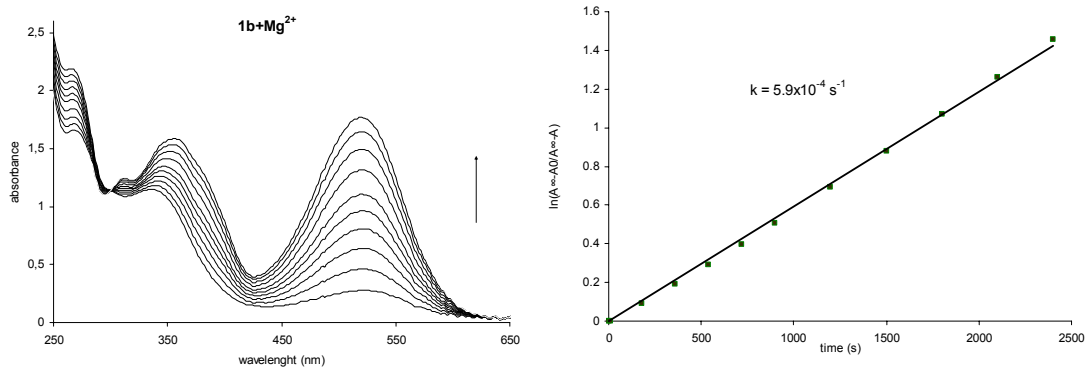
Journal:	<i>Supramolecular Chemistry</i>
Manuscript ID:	GSCH-2006-0119.R1
Manuscript Type:	Full Paper
Date Submitted by the Author:	19-Dec-2006
Complete List of Authors:	Bitter, Istvan; Budapest University of Technology and Economics, Organic Chemical Technology Grün, Alajos; Budapest University of Technology and Economics, Organic Chemical Technology Kerekes, Peter; Budapest University of Technology and Economics, Organic Chemical Technology
Keywords:	Calix[4]crowns, Indolospiropyrans, Isomerization, Cation recognition, UV-vis spectroscopy
<p>Note: The following files were submitted by the author for peer review, but cannot be converted to PDF. You must view these files (e.g. movies) online.</p>	
scheme1.cdx	

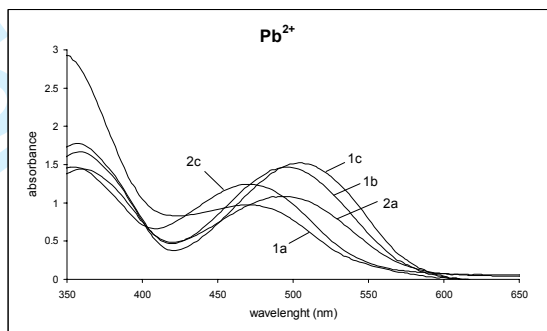
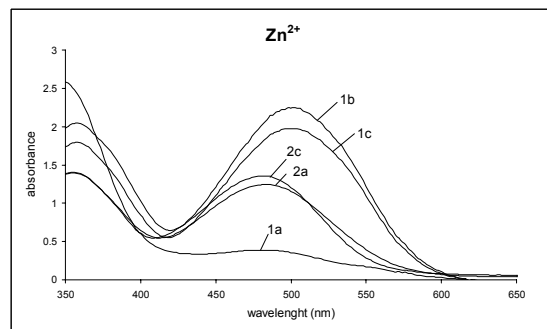
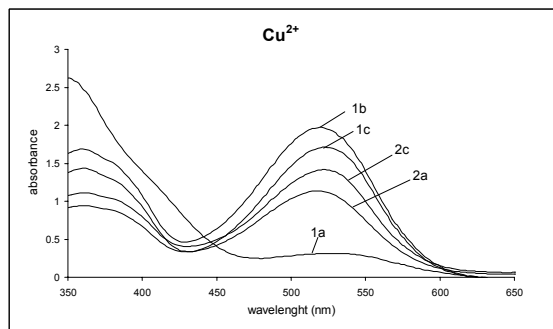












$M^{n+}$	Ionic radius <sup>a</sup> (r, Å)	Charge density <sup>b</sup>
Li	0.76	1.32
Na	1.02	0.98
K	1.38	0.73
Cs	1.70	0.59
Mg	0.72	5.55
Ca	1.00	4.00
Ba	1.36	2.95

<sup>a</sup>for 6 coordination number [20] <sup>b</sup>expressed as  $n^2/r^{n+}$ , the so-called ionic index [21]

For Peer Review Only



<b>L</b>	$k \cdot 10^4 \text{ (s}^{-1}\text{)}^a / \lambda_{\text{max}} \text{ (nm)}$		
	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{Ba}^{2+}$
<b>1a</b>	2.9 (490)	-	-
<b>1b</b>	5.9 (518)	7.1 (520)	8.0 (526)
<b>1c</b>	2.0 (504)	4.1 (512)	1.9 (526)
<b>2a</b>	1.7 (512)	2.3 (516)	2.3 (518)

[L]/[M<sup>2+</sup>] = 1:1 (10<sup>-4</sup> M, MeCN, 25°C); <sup>a</sup>reproducibility ±7%

For Peer Review Only

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25

## Synthesis, Characterization and Cation-Induced Isomerization of Photochromic Calix[4](aza)crown-Indolospiropyran Conjugates

Alajos Grün, Péter Kerekes and István Bitter\*

*Department of Organic Chemical Technology, Budapest University of Technology and  
Economics, H-1521, Budapest, Hungary*

---

**Abstract**— Calix[4](aza)crown-5, -6 and -7 ionophores in cone and 1,3-alt conformation carrying photochromic indolospirobenzopyran (**SP**) signalling group were synthesized and their cation-induced isomerization to the colored merocyanine (**Mc**) form was studied by UV/vis spectroscopy in the presence of mono- and divalent metal ions. Under dark conditions the **SP-Mc** equilibrium was remarkably shifted to the colored **Mc** form by cations of high positive charge density (alkaline earth metal ions), and it was affected by some transition metal ions ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ ) as well. Generally, the extent of isomerization of the cone conformers was larger than that of the 1,3-alt counterparts. The chelation-induced reaction was evaluated by calculating the rate constants of the coloration process.

---

Abbreviated title for running headlines: Photochromic calix[4]azacrown ethers

Keywords: Calix[4](aza)crowns, Indolospiropyrans, Isomerization, Cation recognition

### INTRODUCTION

Photochromic materials have attracted much attention in the last decades because of their potential applications as optical fibers, switches, optical memories and other

---

\* Corresponding author. Tel: 36-1-4631379, fax: 36-1-463-3648; e-mail: ibitter@mail.bme.hu

1  
2  
3  
4 molecular devices [1,2]. Photochromism is defined as a reversible transformation of a  
5  
6 chemical species between two forms with different absorption spectra, shifted in one or  
7  
8 both directions by absorption of electromagnetic radiations [3]. The photochromic  
9  
10 behaviour of spirobenzopyrans (**SP**) was discovered in 1952 and in the course of time  
11  
12 these molecules have become one of the most extensively studied groups of  
13  
14 photochromic materials [4]. Upon UV irradiation, the colorless spiropyran is  
15  
16 transformed to the colored merocyanine (**Mc**) by cleavage of the C-O bond. The process  
17  
18 is reversed either thermally or by irradiation with visible light. The stability of the  
19  
20 merocyanine form depends primarily on the substituents attached to the aromatic  
21  
22 nucleus of the benzopyran moiety and the nitrogen atom of the indoline ring,  
23  
24 respectively. Numerous **SP** dyes linked with crown ethers have been synthesized and  
25  
26 their photoresponsive behaviour toward metal cations was investigated by spectroscopic  
27  
28 methods. These ligands were reported to isomerize to the colored open form upon  
29  
30 complexation of some alkali-and alkaline earth metal ions even under dark conditions  
31  
32 [5-14]. Consequently, the crowned **SP** molecules are regarded as special chromogenic  
33  
34 receptors of dual character. Their crown ether parts behave as ionophores, meanwhile  
35  
36 the photochromic moieties not only act as indicators, but their colored form can  
37  
38 influence the selectivity pattern of the binding site by contribution of the phenolate  
39  
40 group to the stabilization of the complexed cation, thereby resulting in different  
41  
42 photoresponsive effects under dark condition or after UV irradiation.

43  
44  
45 Similar conjugates in the calixcrown series have not been preceded, and to the best  
46  
47 of our knowledge, only two calixarenes carrying photochromic group **I** and **II** have  
48  
49 been described until now [15,16]. One of them refers to our early attempt, when a  
50  
51 calix[4]crown-5 ether was combined with a spiropyran moiety through an adjacent ester  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 group (**I**), but the spiropyran-merocyanine equilibrium was not affected by  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

group (**I**), but the spiropyran-merocyanine equilibrium was not affected by  
complexation of alkali-and alkaline earth metal cations, probably due to the large  
intramolecular distance between the crown ether binding site and the signalling unit  
[15]. Calixarene diester **II** was disclosed to respond to lanthanide ions as photo-  
switchable molecular device [16] (Fig. 1).

#### FIGURE 1

Recently, we have developed a facile method to synthesize distally bridged  
calix[4](aza)crowns of various ring size [17] that provide an easy access to cone  
calixcrown-indolospiryran conjugates **1a-c**. As the binding properties of calixcrowns  
significantly depends on the skeletal conformation, 1,3-alt **2a,c** were also planned to  
prepare. Several calix[4](aza)crown chromo/fluoroionophores comprised of the same  
binding site as **2a,c** were reported to respond to alkali cations (primarily  $K^+$  and  $Rb^+$ )  
and/or divalent cations (alkaline earth- and transition metal ions) depending on the  
nature of the chromo/fluorogenic pendant side arms [18,19]. The indoaniline  
counterpart **3a** (Fig. 2) was claimed to exhibit a cation sensitivity order of  
 $Zn^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+} > Na^+ > Rb^+ > K^+ = Cs^+$  based on the bathochromic shifts of the  
indoaniline chromophore [19c]. When a pyrenylmethyl fluorophore group was  
introduced in **3b**, a  $Cu^{2+} \approx Pb^{2+} > Rb^+ > K^+ > Ag^+ > Cs^+ > Zn^{2+} > Na^+ \approx Sr^{2+} > Ca^{2+} > Mg^{2+}$   
selectivity order was observed according to the chelation-enhanced fluorescence effect  
[19b].

#### FIGURE 2.

1  
2  
3  
4 Herein, we report on the synthesis and spectroscopic investigation of photochromic  
5 calixcrowns **1** and **2** focusing on the spiropyran-merocyanine isomerization induced by  
6  
7 a wide choice of cations under dark conditions.  
8  
9

## 10 11 12 RESULTS AND DISCUSSION

### 13 14 15 Synthesis of Photochromic Calix[4]azacrowns **1** and **2**

16  
17 The synthesis of the target compounds was based on our recent method developed for  
18 the preparation of cone N-tosyl-calix[4](aza)crowns **3a-c** [17] followed by cone-  
19 selective alkylation with PrBr under PTC conditions to give **4a-c**. The respective 1,3-alt  
20 **6a,c** was prepared following literature method [18]. After detosylation effected by  
21 LiAlH<sub>4</sub>, deprotected azacrowns **5a-c** and **7a,c** were obtained which were then  
22 condensed with chloromethylspiropyrans **8** [9,11] according to literature analogy  
23 to give photochromic molecules **1** and **2** (Scheme 1).  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33

34  
35 SCHEME 1.

### 36 37 38 Optical Responses of Crowned Spiropyrans cone **1a-c** and 1,3-alt **2a,c** to 39 40 41 Metal Ions under Dark Conditions

42  
43 The cation-induced isomerization of crowned SP hosts **1**, **2** to their merocyanine form  
44 was studied in MeCN solutions containing equimolar amount of host and alkali or  
45 alkaline earth metal perchlorate (10<sup>-4</sup> M), and the UV/vis spectra of samples were  
46 recorded after overnight staying in the dark to achieve equilibrium. The spectra of the  
47 metal free hosts displayed a band around 346-350 nm characteristic of the  
48 nitrobenzoxazine absorption and a weak if any absorption in the visible region. Upon  
49 chelation, the absorbances of the new bands appeared in the range 490-530 nm and  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 attributable to the merocyanine form were scarcely increased further, when twofold  
5  
6 excess of metal salts were added, indicating a 1:1 complex stoichiometry.  
7  
8

### 9 10 *Alkali and Alkaline Earth Metal Ion-Induced Isomerization*

11  
12  
13 The isomerization of **1a-c** to the merocyanine form was inefficiently promoted by Na<sup>+</sup>,  
14  
15 K<sup>+</sup> and Cs<sup>+</sup> giving rise to weak coloration. It means, even if these cations are included in  
16  
17 the calixcrown rings of **1a-c**, the low positive charge densities (the measure of the  
18  
19 electrostatic attraction in the complex) of Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup> (Table 1) are not sufficient to  
20  
21 induce the C-O cleavage of the **SP** form. The moderate effect of Li<sup>+</sup> observed only for  
22  
23 **1b** can be ascribed to the relatively high charge density of cation associated with a weak  
24  
25 complexation.  
26  
27  
28  
29

30  
31 Table 1.  
32

33  
34 FIGURE 3.  
35

36  
37 As seen in Fig 3, alkaline earth metal ions Mg<sup>2+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup> possessing high charge  
38  
39 densities, on the other hand, induce significant change in the absorption spectrum of  
40  
41 each host, due to complexation followed by strong ionic interaction of bound cation  
42  
43 with the phenolate anion of the zwitter-ionic **Mc** form. Furthermore, remarkable  
44  
45 differences can be observed in respect of absorbance (**A**) and absorption maximum  
46  
47 ( $\lambda_{\max}$ ) values of the **Mc** form as well. The smallest and rigid crown-5 host **1a** displays a  
48  
49 moderate but distinct absorbance for only Mg<sup>2+</sup> that can be ascribed to its strong affinity  
50  
51 to the nitrogen donor atom of the crown. By increasing ring size of hosts, the **A** values  
52  
53 (the extent of isomerization) are remarkably enhanced in accord with the coordination  
54  
55 requirement and ionic radius of cations (**1b**: Mg<sup>2+</sup> ≈ Ca<sup>2+</sup> >> Ba<sup>2+</sup>, **1c**: Mg<sup>2+</sup> ≈ Ca<sup>2+</sup> ≈ Ba<sup>2+</sup>).  
56  
57  
58  
59  
60

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

In addition, the complexation was generally accompanied by considerable decrease of the  $\lambda_{\max}$  values with decreasing ionic radius (increasing charge density) from  $\text{Ba}^{2+}$  to  $\text{Mg}^{2+}$ . The blue-shift of the absorption maxima reflects the extent of solvation of the phenolate moiety in the merocyanine form [22], and indicative of the strength of interaction between the complexed cation and the **Mc**-phenolate anion. Our observations, in accord with the results of other crowned spirobenzopyrans, revealed that the **SP-Mc** equilibrium can be affected alike by the binding ability of the crown rings and the strength of ionic interaction in the complex. While the latter could induce photoisomerization, the former may not always cause any change in photoisomerization behaviour. We assume, the marked effect of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  on the thermal isomerisation of **1a-c** is attributable to both interactions, although in different proportions. The superior isomerization efficiency of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  for hosts **1b,c** and  $\text{Ba}^{2+}$  for **1c** can be due to both effects, namely to the high charge density of cations associated with appropriate binding ability of the chelating site. In the calixcrown series, being different from the classical crown ethers in respect of ring size and conformational mobility, straightforward relationship between the number of donor atoms and the coordination parameters of cations is not always expected. The binding selectivities, therefore, can be evaluated carefully, in particular if the complexation is monitored by a photochromic group. In this case we do not have direct information on the binding capacity of the crown site, only the final stage of a three-component equilibrium ( $\text{SP}+\text{M}^+\leftrightarrow\text{SP}-\text{M}^+\leftrightarrow\text{Mc}-\text{M}^+$ ) is detected that, in turn, is primarily charge-controlled and the fitting requirements are of less important. For example, the ionic radius and coordination number of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  are comparable with those of  $\text{Mg}^{2+}$ ,

1  
2  
3  
4 Ca<sup>2+</sup> and Ba<sup>2+</sup> (Table 1), the former group of ions still cannot or hardly induce  
5  
6 isomerization with any of hosts tested.  
7  
8

9  
10 Unexpectedly, the optical behaviour of 1,3-alt **2a,c** (Fig. 3) was similar to that of cone  
11  
12 **1a-c**, as far as the insufficient isomerization with alkali cations is concerned. Alkaline  
13  
14 earth metal salts, however, induced more pronounced isomerization of **2a** vs. **1a** in the  
15  
16 order of Mg<sup>2+</sup> (512 nm) ≈ Ca<sup>2+</sup> (516 nm) > Ba<sup>2+</sup> (518 nm) (Fig. 3). The enhanced binding  
17  
18 capacity of **2a** can be due to the additional contribution of the *anti* phenyl rings to  
19  
20 binding by π-cation interaction. The alkaline earth metal cation preference of **2a** is  
21  
22 comparable to that of indoaniline dye **3a**, as the complexed cations are stabilized in both  
23  
24 cases by the pendant side arms via ionic or ion-dipole interaction. Increasing the crown  
25  
26 ring size from **2a** to **2c** caused some enhancement of absorbances (Ba<sup>2+</sup> > Ca<sup>2+</sup> ≈ Mg<sup>2+</sup>),  
27  
28 but the extent of isomerization still falls behind that of cone **1c**, and it was scarcely  
29  
30 influenced by the quality of cations.  
31  
32  
33  
34

#### 35 36 37 ***Kinetics of Mg<sup>2+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup> -Induced Coloration of cone 1a-c and 1,3-alt 2a***

38  
39  
40 For studying the kinetics of isomerization, the spectra of **1a-c** and **2a**-cation complexes,  
41  
42 after decoloration by irradiation with visible light, were taken at room temperature. The  
43  
44 absorbances measured at the λ<sub>max</sub> values of **Mc** were recorded in response to time **Mc**  
45  
46 (see illustration in Fig. 4) and the first-order rate constants of coloration, i.e. the  
47  
48 conversion of the colorless spirobenzopyran to the merocyanine form, were calculated  
49  
50  
51  
52 (Table 2).  
53

54  
55  
56 FIGURE 4.

57  
58  
59 Table 2.  
60



Obviously, the evaluation of the reverse decoloration process, i.e. the decay of the spectra of ligand- $M^+$  systems after UV light irradiation, could provide reliable information on the stability of merocyanine complexes. However, in this way we failed to obtain reproducible results due to photodegradation. Nevertheless, some conclusions on the binding characteristics can be drawn if the coloration rate constants are compared only. Starting from the equilibrium of the colorless  $SP-M^{2+}$  system, its transformation to the colored  $Mc-M^{2+}$  complex takes place ca. 2-4-fold faster with host **1b** vs. **1c** and **2a** depending on the cations. The highest isomerization rate of **1b** suggests that the crown-6 ring of medium size basically adopts each cation providing the highest kinetic stability for the  $Mc-M^{2+}$  complexes. In this case the order of rates ( $Ba^{2+} > Ca^{2+} > Mg^{2+}$ ) reflects some selectivity in respect of the cation radii, unlike the larger crown-7 **1c** ( $Ca^{2+} > Mg^{2+} \approx Ba^{2+}$ ). The low isomerization rates of the 1,3-alt crown-5 **2a**, which are more or less irrespective of the size of cations, may be due to strong  $SP-M^{2+}$  complexes, where the cation is located in the calixarene cavity relatively far from the nitrogen atom, thereby resulting in slower isomerization.

#### *Heavy and Transition-Metal-Induced Isomerization*

As transition and heavy metal ions were claimed to exhibit unusually strong affinities to 1,3-alt calix(aza)crowns [19b,c], the effect of  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Ag^+$  on the isomerisation of **2a,c** was also tested. As the relevant ion-selectivities of the analogous cone calixazacrowns have not been available, for comparison, **1a-c** were also involved in studies (Fig. 5).

FIGURE 5.

1  
2  
3  
4  
5 Ag<sup>+</sup> ion, just like the other monovalent cations, did not affect notably the spectra of any  
6  
7 ligands being either cone or 1,3-alt conformation. However, 1,3-alt **2a,c** exhibited  
8  
9 significant chelation-induced effect (**2c**>**2a**) in the order of Zn<sup>2+</sup> (486 nm)≈Cu<sup>2+</sup> (520  
10  
11 nm)>Pb<sup>2+</sup> (494 nm). Interestingly, the isomerization efficiency of Zn<sup>2+</sup> and Cu<sup>2+</sup> for  
12  
13 cone **1a,c** was also remarkable approaching to that of alkaline earth metal ions, due to  
14  
15 the strong affinity of these ions to the amino group. Again **1b** and **1c** show larger extent  
16  
17 of isomerization than **2a,c**, displaying comparable absorbances effected by the same  
18  
19 order of cations (Fig. 5) and the λ<sub>max</sub> values follow somewhat different band-shift  
20  
21 tendency: Zn<sup>2+</sup> (500-502 nm, **1b,c**), Cu<sup>2+</sup> (520-522 nm, **1b,c**), Pb<sup>2+</sup> (496 nm, **1b** and 502  
22  
23 nm, **1c**). Ligand **1a** responds moderately only to Pb<sup>2+</sup> (474 nm) with the largest blue-  
24  
25 shift.  
26  
27  
28  
29  
30

31  
32 These preliminary results allow to conclude that the cation-induced coloration of  
33  
34 calix[4](aza)crown-indolospiropyran conjugates can also be effected by transition and  
35  
36 heavy metal ions and the **SP-MC** isomerization susceptibility of cone calixcrown hosts  
37  
38 toward a wide choice of cations exceeds that of the 1,3-alt conformers.  
39  
40  
41  
42

## 43 CONCLUSIONS

44  
45  
46 A series of calix[4](aza)crowns bearing indolospiropyran photochromic signalling unit  
47  
48 were synthesized and the **SP** (colorless)-**Mc** (colored) isomerization was investigated in  
49  
50 the presence of various mono- and divalent cations under dark conditions. On the basis  
51  
52 of UV/vis spectroscopic and kinetic measurements the effect of cations on the extent of  
53  
54 isomerization was evaluated. We found more efficient coloration of cone dyes **1**  
55  
56 induced by alkaline earth metal cations (Mg<sup>2+</sup>, Ca<sup>2+</sup> and Ba<sup>2+</sup>), transition- and heavy  
57  
58  
59  
60

metal ions ( $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Pb^{+}$ ) than that of 1,3-alt **2a,c**. Some cation selectivities depending on the ring size of the crown ether binding site were observed.

## EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded in  $CDCl_3$  at 500/125 MHz on a Bruker Avance DRX-500 spectrometer. FAB mass spectra were taken on a Finnigan MAT 8430 spectrometer (ion source temperature: 25°C, matrix: *m*-nitrobenzyl alcohol, gas: xenon, accelerating voltage: 9 kV). UV/VIS spectra were recorded on a HP 8452A spectrophotometer. Precoated silica gel plates (Merck 60 F<sub>254</sub>) were used for analytical TLC and Kieselgel 60 for column chromatography. All chemicals were reagent grade and used without further purification. N-tosyl-calix[4](aza)crowns **3a-c** [16] and **6a,c** [19a], and photochromic precursors **8** [11] were prepared as described in the literature.

### General Procedure for the Cone-Selective Alkylation of **3a-c**

A mixture of **3** (1 mmol), PrBr (10 mmol) and  $Bu_4N^+Br^-$  catalyst (0.03 g) in toluene (20 ml) and 50% aq. NaOH (1 ml) was vigorously stirred at 100°C for 6 h. After cooling, water (10 ml) was added and the organic phase was separated, washed with dilute aq. HCl and water, subsequently. The toluene solution was dried then evaporated to dryness to give crude products purified by trituration with MeOH.

**Compound 4a:** yield: 80%, mp 232-233°C;  $^1H$  NMR  $\delta$  7.73 (d, 2H,  $J = 8.5$ , ArH), 7.32 (d, 2H,  $J = 8$ , ArH), 7.11 (s, 4H, ArH), 6.41 (s, 4H, ArH), 4.31 (d, 4H,  $J = 12.5$ , ArCH<sub>2</sub>Ar), 4.27 (m, 4H, OCH<sub>2</sub>), 4.16 (m, 4H, OCH<sub>2</sub>), 3.86 (t, 4H,  $J = 5.5$ , OCH<sub>2</sub>), 3.65 (t, 4H,  $J = 7$ , OCH<sub>2</sub>), 3.49 (t, 4H,  $J = 5.5$ , NCH<sub>2</sub>), 3.13 (d, 4H,  $J = 13$ , ArCH<sub>2</sub>Ar), 2.44

(s, 3H, CH<sub>3</sub>), 1.88 (m, 4H, CH<sub>2</sub>), 1.34 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.99 (t, 6H, *J* = 7.5, CH<sub>3</sub>), 0.80 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>); anal. calcd. for C<sub>65</sub>H<sub>89</sub>NO<sub>8</sub>S (1044.47): C, 74.75, H, 8.59; found: C, 74.52, H; 8.62%.

**Compound 4b:** yield: 98%, mp 92-94°C; <sup>1</sup>H NMR δ 7.77 (d, 2H, *J* = 8.5, ArH), 7.34 (d, 2H, *J* = 8, ArH), 7.15 (s, 4H, ArH), 6.46 (d, 4H, *J* = 1, ArH), 4.40-4.29 (m, 4+4H, ArCH<sub>2</sub>Ar, OCH<sub>2</sub>), 4.10 (m, 4H, OCH<sub>2</sub>), 3.96 (t, 2H, *J* = 7.5, OCH<sub>2</sub>), 3.80-3.65 (m, 10H, OCH<sub>2</sub>), 3.36 (m, 4H, NCH<sub>2</sub>), 3.16 (d, 2H, *J* = 13, ArCH<sub>2</sub>Ar), 3.15 (d, 2H, *J* = 12.5, ArCH<sub>2</sub>Ar), 2.46 (s, 3H, CH<sub>3</sub>), 1.98 (m, 4H, CH<sub>2</sub>), 1.38 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.07 (t, 6H, *J* = 7.5, CH<sub>3</sub>), 0.84 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>); anal. calcd. for C<sub>67</sub>H<sub>93</sub>NO<sub>9</sub>S (1088.52): C, 73.93, H, 8.61; found: C, 74.08, H; 8.58%.

**Compound 4c:** yield: 92%, mp 81-84°C; <sup>1</sup>H NMR δ 7.74 (d, 2H, *J* = 8, ArH), 7.33 (d, 2H, *J* = 8, ArH), 7.13 (s, 4H, ArH), 6.48 (s, 4H, ArH), 4.38 (d, 4H, *J* = 12.5, ArCH<sub>2</sub>Ar), 4.25-4.16 (m, 8H, OCH<sub>2</sub>), 3.78-3.69 (m, 16H, OCH<sub>2</sub>), 3.41 (t, 4H, *J* = 6, NCH<sub>2</sub>), 3.15 (d, 4H, *J* = 12.5, ArCH<sub>2</sub>Ar), 2.46 (s, 3H, CH<sub>3</sub>), 1.97 (m, 4H, CH<sub>2</sub>), 1.36 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.05 (t, 6H, *J* = 7.5, CH<sub>3</sub>), 0.85 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>); anal. calcd. for C<sub>69</sub>H<sub>97</sub>NO<sub>10</sub>S (1132.57): C, 73.17, H, 8.63; found: C, 73.31, H; 8.61%.

#### General Procedure for the Detosylation of Calix[4](aza)crowns 4 and 6

A mixture of **4a-c** or **6a,c** (1 mmol), LiAlH<sub>4</sub> (0.4 g, 10 mmol) in dry THF (20 ml) was stirred under reflux for 6 h. After cooling the excess of LiAlH<sub>4</sub> was decomposed by dropping water, evaporated to dryness and extracted with EtOAc (2x20 ml) and after standard workup **5a-c** or **7a,c** were obtained as white solids. The crude materials were essentially pure and used directly **in** the next reactions.

1  
2  
3  
4  
5 **Compound 5a:** yield: 35%, mp 257-259°C;  $^1\text{H}$  NMR  $\delta$  7.11 (s, 4H, ArH), 6.41 (s, 4H,  
6 ArH), 4.35 (m, 4+4H, ArCH<sub>2</sub>Ar, OCH<sub>2</sub>), 4.14 (m, 4H, OCH<sub>2</sub>), 3.78 (t, 4H,  $J = 5$ ,  
7 OCH<sub>2</sub>), 3.72 (t, 4H,  $J = 7$ , OCH<sub>2</sub>), 3.15 (d, 4H,  $J = 13$ , ArCH<sub>2</sub>Ar), 2.98 (t, 4H,  $J = 5$ ,  
8 NCH<sub>2</sub>), 1.91 (m, 4H, CH<sub>2</sub>), 1.34 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.03 (t, 6H,  $J = 7.5$ , CH<sub>3</sub>), 0.81 (s,  
9 18H, C(CH<sub>3</sub>)<sub>3</sub>);  $^{13}\text{C}$  NMR  $\delta$  155.3, 152.8, 145.2, 144.3, 135.5, 131.8, 125.9, 124.6 (Ar),  
10 77.9, 72.6, 69.4, 68.8 (OCH<sub>2</sub>), 46.9 (NCH<sub>2</sub>), 34.3, 33.8 (C(CH<sub>3</sub>)<sub>3</sub>), 31.9, 31.3 (CH<sub>3</sub>),  
11 31.5 (ArCH<sub>2</sub>Ar), 23.6 (CH<sub>2</sub>), 10.9 (CH<sub>3</sub>); FAB-MS  $m/z$  (%) 890.6 [M+H]<sup>+</sup> (11), anal.  
12 calcd. for C<sub>58</sub>H<sub>83</sub>NO<sub>6</sub> (890.28): C, 78.25, H, 9.40; found: C, 78.32, H; 9.38%.

13  
14 **Compound 5b:** yield: 42%, mp 252-256°C;  $^1\text{H}$  NMR  $\delta$  7.10 (s, 4H, ArH), 6.43 (s, 4H,  
15 ArH), 4.36 (d, 4H,  $J = 12.5$ , ArCH<sub>2</sub>Ar), 4.29-4.08 (m, 8H, OCH<sub>2</sub>), 3.73 (m, 8H, OCH<sub>2</sub>),  
16 3.13 (d, 4H,  $J = 12.5$ , ArCH<sub>2</sub>Ar), 2.87 (m, 4H, NCH<sub>2</sub>), 1.96 (m, 4H, CH<sub>2</sub>), 1.33 (s, 18H,  
17 C(CH<sub>3</sub>)<sub>3</sub>), 1.04 (t, 6H,  $J = 7$ , CH<sub>3</sub>), 0.81 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>);  $^{13}\text{C}$  NMR  $\delta$  154.8, 154.6,  
18 145.3, 144.2, 135.8, 132.0, 125.8, 124.6 (Ar), 77.9, 72.3, 72.2, 71.1, 70.6, 70.5, 70.2,  
19 69.3 (OCH<sub>2</sub>), 49.1 (NCH<sub>2</sub>), 34.3, 33.8 (C(CH<sub>3</sub>)<sub>3</sub>), 32.0, 31.4 (CH<sub>3</sub>), 31.3 (ArCH<sub>2</sub>Ar),  
20 23.7 (CH<sub>2</sub>), 10.9 (CH<sub>3</sub>); FAB-MS  $m/z$  (%) 932.6 [M+H]<sup>+</sup> (9), anal. calcd. for  
21 C<sub>60</sub>H<sub>87</sub>NO<sub>7</sub> (934.34): C, 77.13, H, 9.39; found: C, 77.32, H; 9.35%.

22  
23 **Compound 5c:** yield: 41%, mp 210-213°C;  $^1\text{H}$  NMR  $\delta$  7.08 (s, 4H, ArH), 6.46 (s, 4H,  
24 ArH), 4.37 (d, 4H,  $J = 12.5$ , ArCH<sub>2</sub>Ar), 4.25-4.15 (m, 8H, OCH<sub>2</sub>), 3.75-3.64 (m, 16H,  
25 OCH<sub>2</sub>), 3.12 (d, 4H,  $J = 12.5$ , ArCH<sub>2</sub>Ar), 2.82 (t, 4H,  $J = 4.5$ , NCH<sub>2</sub>), 1.96 (m, 4H,  
26 CH<sub>2</sub>), 1.32 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.04 (t, 6H,  $J = 7.5$ , CH<sub>3</sub>), 0.82 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>);  $^{13}\text{C}$   
27 NMR  $\delta$  154.4, 152.4, 145.0, 144.0, 135.5, 131.9, 125.4, 124.5 (Ar), 77.9, 72.1, 71.0,  
28 70.5, 70.3, 70.1 (OCH<sub>2</sub>), 48.7 (NCH<sub>2</sub>), 34.1, 33.6 (C(CH<sub>3</sub>)<sub>3</sub>), 31.9, 31.4 (CH<sub>3</sub>), 31.1  
29 (ArCH<sub>2</sub>Ar), 23.7 (CH<sub>2</sub>), 10.7 (CH<sub>3</sub>); FAB-MS  $m/z$  (%) 978.7 [M+H]<sup>+</sup> (33), anal. calcd.  
30 for C<sub>62</sub>H<sub>91</sub>NO<sub>8</sub> (978.39): C, 76.11, H, 9.37; found: C, 75.89, H; 9.40%.

**Compound 7a:** yield. 92%,  $^1\text{H NMR}$   $\delta$  7.11 (d, 4H,  $J = 7.5$ , ArH), 7.04 (d, 4H,  $J = 7.5$ , ArH), 6.83 (t, 2H,  $J = 7.5$ , ArH), 6.77 (t, 2H,  $J = 7.5$ , ArH), 3.74 (s, 8H, ArCH<sub>2</sub>Ar), 3.50-3.43 (m, 16H, OCH<sub>2</sub>), 2.77 (m, NCH<sub>2</sub>), 1.47 (m, 4H, CH<sub>2</sub>), 0.80 (t, 6H,  $J = 7.5$ , CH<sub>3</sub>);  $^{13}\text{C NMR}$   $\delta$  157.0, 156.5, 134.1, 130.6, 122.1, 121.9 (Ar), 72.5, 71.1, 70.3, 70.1 (OCH<sub>2</sub>), 48.6 (NCH<sub>2</sub>), 38.0 (ArCH<sub>2</sub>Ar), 22.9 (CH<sub>2</sub>), 10.1 (CH<sub>3</sub>); anal. calcd. for C<sub>42</sub>H<sub>51</sub>NO<sub>6</sub> (665.86): C, 75.76, H, 7.72; found: C, 75.88, H; 7.70%.

**Compound 7c:** yield 93%,  $^1\text{H NMR}$   $\delta$  7.12 (d, 4H,  $J = 7.5$ , ArH), 7.01 (d, 4H,  $J = 7.5$ , ArH), 6.76 (m, 4H, ArH), 3.71 (s, 8H, ArCH<sub>2</sub>Ar), 3.68-3.59 (m, 16H, OCH<sub>2</sub>), 3.45 (t, 4H,  $J = 7.5$ , OCH<sub>2</sub>), 3.40 (t, 4H,  $J = 5$ , OCH<sub>2</sub>), 2.83 (t, 4H,  $J = 5$ , NCH<sub>2</sub>), 1.43 (m, 4H, CH<sub>2</sub>), 0.80 (t, 6H,  $J = 7.5$ , CH<sub>3</sub>);  $^{13}\text{C NMR}$   $\delta$  156.7, 156.0, 133.8, 133.6, 130.0, 129.8, 122.1, 121.8 (Ar), 72.8, 70.8, 70.6, 70.4, 70.3, 69.8 (OCH<sub>2</sub>), 49.1 (NCH<sub>2</sub>), 37.2 (ArCH<sub>2</sub>Ar), 23.1 (CH<sub>2</sub>), 10.3 (CH<sub>3</sub>); anal. calcd. for C<sub>46</sub>H<sub>59</sub>NO<sub>8</sub> (753.96): C, 73.28, H, 7.89; found: C, 73.42, H; 7.86%.

### General Procedure for the Synthesis of Calix[4](aza)crown Photochroms **1** and **2**

To the mixture of **8** (0.5 mmol) and triethylamine (1.5 mmol, 0.2 ml) in dry THF (5 ml) was added **5a-c** or **7a,c** (0.5 mmol) dissolved in 10 ml dry THF. The solution was then refluxed overnight under argon atmosphere in the dark. After cooling, the solvent was evaporated and the residue was chromatographed on silica (eluent: hexane-ethyl acetate = 8:2) to give **1a-c**, **2a,c** as purple greasy solids.

**Ligand 1a:** yield 32%;  $^1\text{H NMR}$ :  $\delta$  8.27 (s, 1H, ArH), 7.97 (s, 1H, ArH), 7.22 (t, 1H,  $J = 7.5$ , ArH), 7.16 (s, 4H, ArH), 7.12 (d, 1H,  $J = 7$ , ArH), 6.97 (d, 1H,  $J = 10$ , CH=), 6.91 (t, 1H,  $J = 7.5$ , ArH), 6.58 (d, 1H,  $J = 7.5$ , ArH), 6.45 (s, 4H, ArH), 5.90 (d, 1H,  $J = 10.5$ , CH=), 4.38 (d, 4H,  $J = 12.5$ , ArCH<sub>2</sub>Ar), 4.30 (m, 4H, OCH<sub>2</sub>), 4.19 (m, 4H,

OCH<sub>2</sub>), 3.72 (t, 4H, *J* = 7, OCH<sub>2</sub>), 3.62 (bs, 4H, OCH<sub>2</sub>), 3.52 (m, 2H, NCH<sub>2</sub>), 3.18 (d, 4H, *J* = 12.5, ArCH<sub>2</sub>Ar), 2.82-2.73 (m, 3+4H, NCH<sub>3</sub>, NCH<sub>2</sub>), 1.96 (m, 4H, CH<sub>2</sub>), 1.38 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.33 (s, 3H, CH<sub>3</sub>), 1.24 (s, 3H, CH<sub>3</sub>), 1.07 (t, 6H, *J* = 7, CH<sub>3</sub>), 0.84 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR δ 157.5, 155.1, 152.5, 147.7, 145.0, 144.0, 140.7, 136.2, 135.4, 131.7, 127.8, 127.2, 126.2, 125.6, 124.5, 121.5, 121.4, 119.8, 118.5, 107.1 (Ar), 128.6, 121.2 (C=) 106.7 (spiro C), 77.9, 72.6, , 71.0, 69.3, (OCH<sub>2</sub>), 53.6, 53.2, (NCH<sub>2</sub>), 52.1 (C(CH<sub>3</sub>)<sub>2</sub>), 34.2, 33.6 (C(CH<sub>3</sub>)<sub>3</sub>), 31.8, 31.2 (CH<sub>3</sub>), 31.1 (ArCH<sub>2</sub>Ar), 29.0 (NCH<sub>3</sub>), 25.9, 20.1 (CH<sub>3</sub>) 23.6 (CH<sub>2</sub>), 10.9 (CH<sub>3</sub>); anal. calcd. for C<sub>78</sub>H<sub>101</sub>N<sub>3</sub>O<sub>9</sub> (1224.65): C 76.50, H 8.31, found C 76.31, H 8.35%

**Ligand 1b:** yield 50%; <sup>1</sup>H NMR: δ 8.29 (d, 1H, *J* = 2.5, ArH), 7.91 (d, 1H, *J* = 3, ArH), 7.16 (t, 1H, *J* = 7.5, ArH), 7.11 (s, 4H, ArH), 7.07 (d, 1H, *J* = 7, ArH), 6.92 (d, 1H, *J* = 10.5, CH=), 6.85 (t, 1H, *J* = 7.5, ArH), 6.53 (d, 1H, *J* = 7.5, ArH), 6.43 (s, 4H, ArH), 5.85 (d, 1H, *J* = 10.5 Hz, CH=), 4.32 (m, 4+2H, ArCH<sub>2</sub>Ar, OCH<sub>2</sub>), 4.15 (m, 6H, OCH<sub>2</sub>), 3.74-3.47 (m, 14H, OCH<sub>2</sub>, NCH<sub>2</sub>), 3.13 (d, 4H, *J* = 12.5, ArCH<sub>2</sub>Ar), 2.70 (m, 3+4H, NCH<sub>3</sub>, NCH<sub>2</sub>), 1.94 (m, 4H, CH<sub>2</sub>), 1.34 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.29 (s, 3H, CH<sub>3</sub>), 1.20 (s, 3H, CH<sub>3</sub>), 1.02 (t, 6H, *J* = 7, CH<sub>3</sub>), 0.81 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR δ 157.5, 154.8, 154.6, 152.6, 147.9, 145.4, 145.3, 144.2, 140.9, 136.4, 135.9, 135.8, 132.1, 131.9, 127.9, 127.7, 126.4, 125.6, 125.5, 124.7, 124.6, 121.7, 121.5, 119.9, 118.6, 107.2 (Ar), 128.8, 121.3 (C=), 106.7 (spiro C), 77.9, 72.4, 72.0, 71.6, 70.6, 70.3, 70.2, 69.8, 69.6 (OCH<sub>2</sub>), 55.0, 54.7, 53.6 (NCH<sub>2</sub>), 52.2 (C(CH<sub>3</sub>)<sub>2</sub>), 34.3, 33.8 (C(CH<sub>3</sub>)<sub>3</sub>), 32.0, 31.4 (CH<sub>3</sub>), 31.2, 31.1 (ArCH<sub>2</sub>Ar), 29.1 (NCH<sub>3</sub>), 26.1, 20.2 (CH<sub>3</sub>) 23.8 (CH<sub>2</sub>), 11.0 (CH<sub>3</sub>); anal. calcd. for C<sub>80</sub>H<sub>105</sub>N<sub>3</sub>O<sub>10</sub> (1268.70): C 75.74, H 8.34, found C 75.52, H 8.38%

**Ligand 1c:** yield 49%; <sup>1</sup>H NMR: δ 8.27 (d, 1H, *J* = 2, ArH), 7.91 (d, 1H, *J* = 2.5, ArH), 7.17 (t, 1H, *J* = 7.5, ArH), 7.09 (s, 4H, ArH), 7.07 (d, 1H, *J* = 8, ArH), 6.92 (d, 1H, *J* =



1  
2  
3  
4  
5 10,  $CH=$ ), 6.86 (t, 1H,  $J = 7.5$ , ArH), 6.53 (d, 1H,  $J = 7.5$ , ArH), 6.46 (s, 4H, ArH), 5.85  
6  
7 (d, 1H,  $J = 10.5$ ,  $CH=$ ), 4.36 (d, 4H,  $J = 12.5$ , ArCH<sub>2</sub>Ar), 4.24-4.13 (m, 8H, OCH<sub>2</sub>),  
8  
9 3.74-3.63 (m, 12H, OCH<sub>2</sub>), 3.47 (m, 4+2H, OCH<sub>2</sub>, NCH<sub>2</sub>), 3.12 (d, 4H,  $J = 12.5$ ,  
10  
11 ArCH<sub>2</sub>Ar), 2.68 (m, 3+4H, NCH<sub>3</sub>, NCH<sub>2</sub>), 1.96 (m, 4H, CH<sub>2</sub>), 1.32 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>),  
12  
13 1.28 (s, 3H, CH<sub>3</sub>), 1.20 (s, 3H, CH<sub>3</sub>), 1.03 (t, 6H,  $J = 7.5$ , CH<sub>3</sub>), 0.82 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>);  
14  
15 <sup>13</sup>C NMR  $\delta$  157.3, 154.4, 152.5, 147.7, 145.1, 144.0, 140.8, 136.2, 135.6, 132.0, 127.9,  
16  
17 127.8, 127.4, 126.3, 125.5, 124.5, 121.5, 121.3, 119.8, 118.4, 107.1 (Ar), 128.6, 121.1  
18  
19 (C=), 106.5 (spiro C), 77.8, 72.0, , 70.7, 70.3, 69.8, 69.6 (OCH<sub>2</sub>), 54.3, 52.9 (NCH<sub>2</sub>),  
20  
21 52.1 (C(CH<sub>3</sub>)<sub>2</sub>), 34.1, 33.6 (C(CH<sub>3</sub>)<sub>3</sub>), 31.8, 31.2 (CH<sub>3</sub>), 31.0 (ArCH<sub>2</sub>Ar), 28.9 (NCH<sub>3</sub>),  
22  
23 25.9, 20.1 (CH<sub>3</sub>) 23.6 (CH<sub>2</sub>), 10.8 (CH<sub>3</sub>); anal. calcd. for C<sub>82</sub>H<sub>109</sub>N<sub>3</sub>O<sub>11</sub> (1312.76): C  
24  
25 75.02, H 8.37, found C 74.88, H 8.40%

26  
27  
28  
29  
30 **Ligand 2a:** yield 30%; <sup>1</sup>H NMR:  $\delta$  8.31 (s, 1H, ArH), 7.96 (s, 1H, ArH), 7.23 (t, 1H,  $J =$   
31  
32 7, ArH), 7.14 (d, 1H,  $J = 7$ , ArH), 7.09 (m, 8H, ArH), 6.96 (d, 1H,  $J = 10.5$ ,  $CH=$ ), 6.92  
33  
34 (t, 1H,  $J = 7$ , ArH), 6.81 (t, 4H,  $J = 7.5$ , ArH), 6.60 (d, 1H,  $J = 7.5$ , ArH), 5.89 (d, 1H,  $J$   
35  
36 = 10.0,  $CH=$ ), 3.81 (s, 8H, ArCH<sub>2</sub>Ar), 3.53 (bs, 4H, OCH<sub>2</sub>), 3.42 (m, 4+2H, OCH<sub>2</sub>,  
37  
38 NCH<sub>2</sub>), 3.27 (bs, 4H, OCH<sub>2</sub>), 3.20 (bs, 4H, OCH<sub>2</sub>), 2.76 (s, 3H, NCH<sub>3</sub>), 2.54 (bs, 4H,  
39  
40 NCH<sub>2</sub>), 1.34 (s, 3H, CH<sub>3</sub>), 1.27 (m, 4H, CH<sub>2</sub>) 1.24 (s, 3H, CH<sub>3</sub>), 0.73 (t, 6H,  $J = 7.0$ ,  
41  
42 CH<sub>3</sub>), <sup>13</sup>C NMR  $\delta$  157.0, 156.7, 147.6, 140.7, 136.2, 134.0, 133.7, 129.8, 129.7, 129.6,  
43  
44 127.7, 122.2, 122.1, 121.5, 119.7, 118.6, 107.0 (Ar), 128.6, 121.1 (C=) 106.5 (spiro C),  
45  
46 72.0, 70.8, 69.8, 69.7, (OCH<sub>2</sub>), 53.3, 52.5, (NCH<sub>2</sub>), 52.0 (C(CH<sub>3</sub>)<sub>2</sub>), 38.1 (ArCH<sub>2</sub>Ar),  
47  
48 29.8 (NCH<sub>3</sub>), 25.9, 20.1 (CH<sub>3</sub>) 22.4 (CH<sub>2</sub>), 10.0 (CH<sub>3</sub>); anal. calcd. for C<sub>62</sub>H<sub>69</sub>N<sub>3</sub>O<sub>9</sub>  
49  
50 (1000.23): C 74.45, H 6.95, found C 74.64, H 6.92%

51  
52  
53  
54  
55  
56 **Ligand 2c:** yield 17%; <sup>1</sup>H NMR:  $\delta$  8.31 (d, 1H,  $J = 2.0$ , ArH), 7.92 (d, 1H,  $J = 2.5$ ,  
57  
58 ArH), 7.19 (t, 1H,  $J = 6.5$ , ArH), 7.11 (d, 4H,  $J = 7.5$ , ArH), 7.07 (d, 1H,  $J = 7.5$ , ArH),  
59  
60



7.01 (d, 4H,  $J = 7.5$ , ArH), 6.93 (d, 1H,  $J = 10.5$ , CH=), 6.88 (t, 1H,  $J = 7.5$ , ArH), 6.76 (m, 4H, ArH), 6.54 (d, 1H,  $J = 7.5$ , ArH), 5.85 (d, 1H,  $J = 10.5$ , CH=), 3.72 (s, 8H, ArCH<sub>2</sub>Ar), 3.40 (t, 4H,  $J = 5.5$ , OCH<sub>2</sub>), 3.65-3.44 (m, 16+2H, OCH<sub>2</sub>, NCH<sub>2</sub>), 3.40 (t, 4H,  $J = 5.5$ , OCH<sub>2</sub>), 2.71 (m, 3+4H, NCH<sub>3</sub>, NCH<sub>2</sub>), 1.42 (m, 4H, CH<sub>2</sub>), 1.29 (s, 3H, CH<sub>3</sub>), 1.20 (s, 3H, CH<sub>3</sub>), 0.79 (t, 6H,  $J = 7.5$ , CH<sub>3</sub>), <sup>13</sup>C NMR  $\delta$  157.3, 156.7, 156.1, 147.6, 140.7, 136.2, 133.8, 133.7, 129.9, 129.8, 127.7, 127.3, 126.3, 122.1, 121.9, 121.5, 121.3, 119.7, 118.4, 107.0 (Ar), 128.5, 121.1 (C=) 106.5 (spiro C), 72.7, 70.7, 70.4, 70.0, 69.9, 69.8 (OCH<sub>2</sub>), 54.3, 52.7, (NCH<sub>2</sub>), 52.1 (C(CH<sub>3</sub>)<sub>2</sub>), 37.3 (ArCH<sub>2</sub>Ar), 28.9 (NCH<sub>3</sub>), 25.9, 20.0 (CH<sub>3</sub>) 23.0 (CH<sub>2</sub>), 10.2 (CH<sub>3</sub>); anal. calcd. for C<sub>66</sub>H<sub>77</sub>N<sub>3</sub>O<sub>11</sub> (1088.33): C 72.84, H 7.13, found C 72.55, H 7.16%

#### ACKNOWLEDGEMENTS

Financial support from the Hungarian Scientific Research Found (OTKA No. T 046055) is gratefully acknowledged. Dr. Gy. Parlagh and A. Makó are acknowledged for the FAB mass spectra.

#### REFERENCES

- [1] Dürr, H.; Bouas-Laurent, H., Eds.; *Photochromic Molecules and Systems*; Elsevier: Amsterdam, 1990, Chapter 8.
- [2] a) Crano, J. C.; Guglielmetti, R., Eds.; *Organic Photochromic and Thermochromic Compounds*; KluwerAcademic/Plenum: New York, 1998; Vol. 1. b) Crano, J. C.; Guglielmetti, R., Eds.; *Organic Photochromic and Thermochromic Compounds*; KluwerAcademic/Plenum: New York, 1999; Vol. 2.
- [3] Bouas-Laurent, H.; Dürr, H. *Pure Appl. Chem.* **2001**, *73*, 639.

- 1  
2  
3  
4 [4] For recent reviews: a) Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*,  
5 1741-1753. b) Inouye, M. *Coord. Chem. Rev.* **1996**, *148*, 265-283.  
6  
7  
8  
9 [5] Kimura, K.; Yamashita, T.; Yokoyama, M. *J. Chem. Soc. Perkin Trans. 2* **1992**, 613.  
10  
11 [6] Kimura, K.; Kaneshige, M.; Yamashita, T.; Yokoyama, M. *J. Org. Chem.* **1994**, *59*,  
12 1251-1256.  
13  
14  
15 [7] Inouye, M.; Noguchi, Y.; Isagawa, K. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1163-  
16 1166.  
17  
18  
19 [8] Inouye, M.; Akamatsu, K.; Nakazumi, H. *J. Am. Chem. Soc.* **1997**, *119*, 9160-9165.  
20  
21 [9] Kimura, K.; Teranishi, T.; Yokoyama, M.; Yajima, S.; Miyake, S.; Sakamoto, H.;  
22 Tanaka, M. *J. Chem. Soc. Perkin Trans. 2* **1999**, 199-204.  
23  
24 [10] Tanaka, M.; Nakamura, M.; Salhin, M. A. A.; Ikeda, T.; Kamada, K.; Ando, H.;  
25 Kitagaki, T.; Shibutani, Y.; Kimura, K. *J. Org. Chem.* **2001**, *66*, 1533-1537.  
26  
27 [11] Tanaka, M.; Kamada, K.; Ando, H.; Shibutani, Y.; Kimura, K. *J. Org. Chem.* **2000**,  
28 *65*, 4342-4347.  
29  
30 [12] Nakamura, M.; Fujioka, T.; Sakamoto, H.; Kimura, K. *New J. Chem.* **2002**, *26*,  
31 554-559.  
32  
33 [13] Ahmed, S. A.; Tanaka, M.; Ando, H.; Tawa, K.; Kimura, K. *Tetrahedron* **2004**, *60*,  
34 6029-6036.  
35  
36 [14] Kőszegi, É.; Grün, A.; Bitter, I. *Supramol. Chem.* **2006**, *18*, 66-76.  
37  
38 [15] Grün, A.; Kőszegi, É.; Balázs, B.; Tóth, G.; Bitter, I. *Supramol. Chem.* **2004**, *16*,  
39 239-246.  
40  
41 [16] (a) Liu, Z.-H.; Jiang, L.; Liang, Z.; Gao, Y.-H. *Tetrahedron Lett.* **2005**, *46*, 885-  
42 887. (b) Liu, Z.-H.; Jiang, L.; Liang, Z.; Gao, Y.-H. *J. Mol. Struct.* **2005**, *737*, 267-270  
43  
44 [17] Grün, A.; Kőszegi, É.; Bitter, I. *Tetrahedron* **2004**, *60*, 5041-5048.  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3  
4 [18] Kim, J. S.; Shon, O. J.; Ko, J. W.; Cho, M. H.; Yu, I. J.; Vicens, J. *J. Org. Chem.*  
5  
6 **2000**, *65*, 2386-2392.

7  
8  
9 [19] (a) Kim, J. S.; Shon, O. J.; Lee, J. K.; Lee, S. H.; Kim, J. Y.; Park, K.-M.; Lee, S.  
10  
11 *S. J. Org. Chem.* **2002**, *67*, 1372-1375. (b) Kim, J. S.; Shon, O. J.; Rim, J. A.; Kim, S.  
12  
13 K.; Yoon, Y. *J. Org. Chem.* **2002**, *67*, 2348-2351. (c) Kim, J. S.; Shon, O. J.; Yang, S.  
14  
15 H.; Kim, J. Y.; Kim, M. J. *J. Org. Chem.* **2002**, *67*, 6514-6518.

16  
17 [20] Shannon, R. D. *Acta Crystallogr.* **1976**, *32A*, 751-767.

18  
19 [21] Nieboer, E.; Richardson, D. H. S. *Environ. Pollut. Ser. B* **1980**, *1*, 3.

20  
21 [22] Salhin, A. M. A.; Tanaka, M.; Kamada, K.; Ando, H.; Ikeda, T.; Shibutani, Y.;  
22  
23 Yajima, S.; Nakamura, M.; Kimura, K. *Eur. J. Org. Chem.* **2002**, 655-662.  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60