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

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

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**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 ($Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$) 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.**

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

Similar conjugates in the calixcrown series have not been precedented, and to the best of our knowledge, only two calixarenes carrying photochromic group **I** and **II** have been described until now [17–19]. One of them refers to our early attempt, when a calix[4]crown-5 ether was combined with a spiropyran moiety through an adjacent ester 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 [17].

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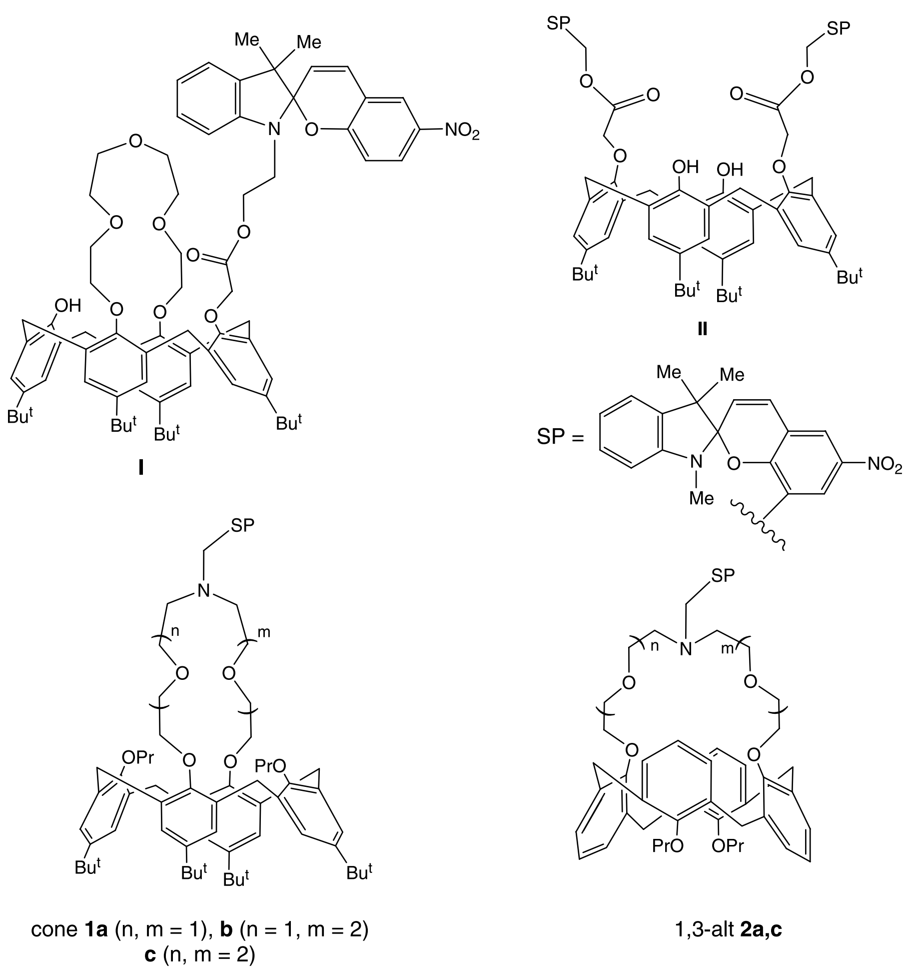


FIGURE 1 Calix[4]arene-indolospiropyran conjugates; literature preliminaries (I, II) and target molecules 1,2.

Calixarene diester **II** was disclosed to respond to lanthanide ions as photo-switchable molecular device [18,19] (Fig. 1).

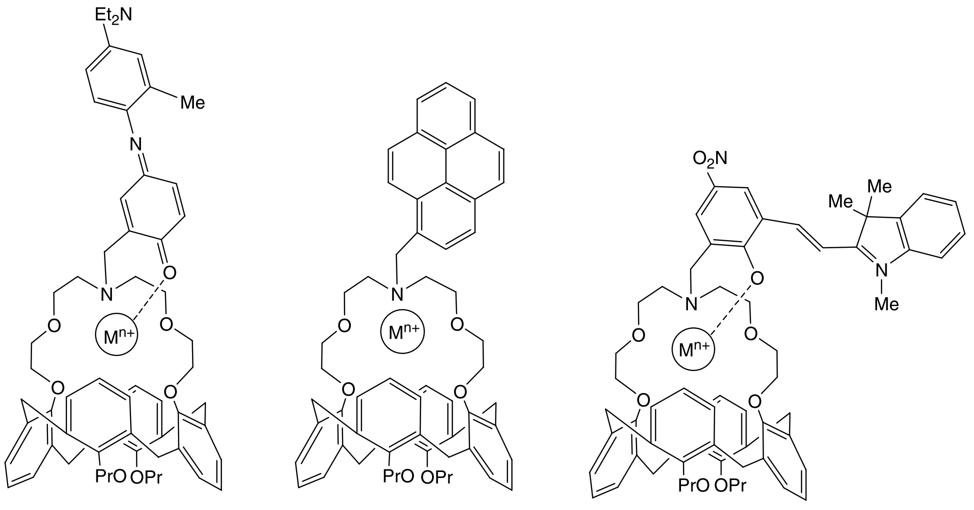
Recently, we have developed a facile method to synthesize distally bridged calix[4](aza)crowns of various ring size [20] that provide an easy access to cone calixcrown-indolospiropyran conjugates **1a–c**. As the binding properties of calixcrowns significantly depends on the skeletal conformation, 1,3-alt **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 [21–24]. 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 [24]. 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 [23].

Herein, we report on the synthesis and spectroscopic investigation of photochromic calixcrowns **1** and **2** focusing on the spiropyran–merocyanine isomerization induced by a wide choice of cations under dark conditions.

## RESULTS AND DISCUSSION

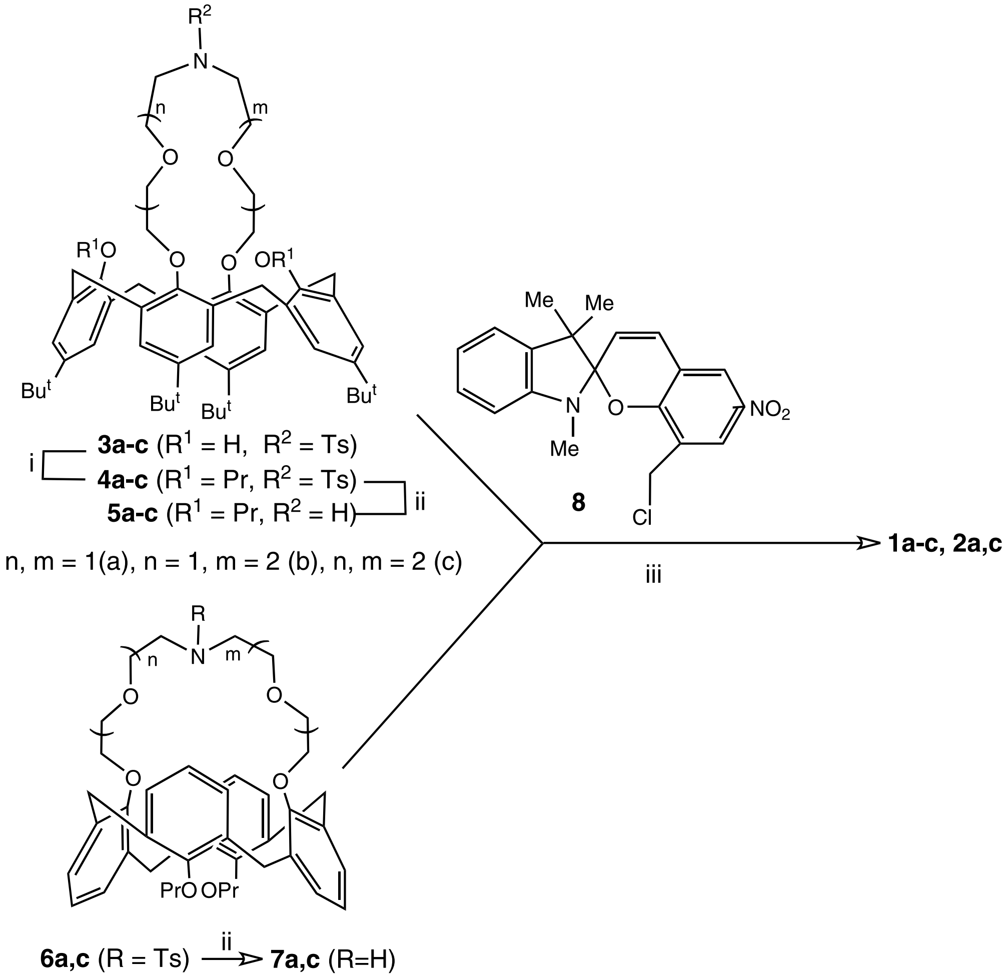
### Synthesis of Photochromic Calix[4]azacrowns 1 and 2

The synthesis of the target compounds was based on our recent method developed for the preparation of cone N-tosyl-calix[4](aza)crowns **3a–c** [20] followed by cone-selective alkylation with PrBr under PTC conditions to give **4a–c**. The respective 1,3-alt **6a,c** was prepared following literature method [21]. After detosylation effected by $LiAlH_4$, deprotected azacrowns **5a–c** and **7a,c** were obtained which were then condensed with chloromethylspirobenzopyran **8** [11,13] according to literature analogy to give photochromic molecules **1** and **2** (Scheme 1).



**3a** **3b** **2a**

FIGURE 2 The schematic representation of chromo/fluorogenic 1,3-alt calix[4]azacrown-cation complexes **3a**, **b** vs **2a**.



SCHEME 1 Synthesis of photochronic calix[4]azacrowns 1 and 2. Reagents and conditions (i) PrBr, toluene, 50% aq. NaOH, $Bu_4NBr$, 100°C; (ii) $LiAlH_4$, THF, Δ; (iii) $Et_3N$, ThF, Δ.

TABLE I Ionic radii and change densities of cations tested

| $M^{n+}$ | Ionic radius† (r, Å) | Charge density‡ |
|---|---|---|
| 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 |

† For 6 coordination number [25]; ‡ Expressed as $n^2/r^{n+}$, the so-called ionic index [26].

## Optical Responses of Crowned Spirobenzopyrans Cone 1a–c and 1,3-alt 2a,c to Metal Ions Under Dark Conditions

The cation–induced isomerization of crowned **SP** hosts **1**, **2** to their merocyanine form was studied in MeCN solutions containing equimolar amount of host and alkali or alkaline earth metal perchlorate ($10^{-4}$ M), and the UV/vis spectra of samples were recorded after overnight staying in the dark to achieve equilibrium. The spectra of the metal free hosts displayed a band around 346–350 nm characteristic of the nitrobenzoxazine absorption and a weak if any absorption in the visible region. Upon chelation, the absorbances of the new bands appeared in the range 490–530 nm and attributable to the merocyanine form were scarcely increased further, when twofold excess of metal salts were added, indicating a 1:1 complex stoichiometry.

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

The isomerization of **1a–c** to the merocyanine form was inefficiently promoted by $Na^+$, $K^+$ and $Cs^+$ giving rise to weak coloration. It means, even if these cations are included in the calixcrown rings of **1a–c**, the low positive charge densities (the measure of the electrostatic attraction in the complex) of $Na^+$, $K^+$ and $Cs^+$ (Table I) are not sufficient to induce the C—O cleavage of the **SP** form. The moderate effect of $Li^+$ observed only for **1b** can be ascribed to the relatively high charge density of cation associated with a weak complexation.

As seen in Fig. 3, alkaline earth metal ions $Mg^{2+}$, $Ca^{2+}$ and $Ba^{2+}$ possessing high charge densities, on the other hand, induce significant change in the absorption spectrum of each host, due to complexation followed by strong ionic interaction of bound cation with the phenolate anion of the zwitter-ionic **Mc** form. Furthermore, remarkable differences can be observed in respect of absorbance (A) and absorption maximum ($\lambda_{max}$) values of the Mc form as well. The smallest and rigid crown-5 host **1a** displays a moderate but distinct absorbance for only $Mg^{2+}$ that can be ascribed to its strong affinity to the nitrogen donor atom of the crown. By increasing ring size of hosts, the **A** values (the extent of isomerization) are remarkably enhanced in accord with the coordination requirement and ionic radius of cations (**1b**: $Mg^{2+} \approx Ca^{2+} >> Ba^{2+}$, **1c**: $Mg^{2+} \approx Ca^{2+} \approx Ba^{2+}$). In addition, the complexation was generally

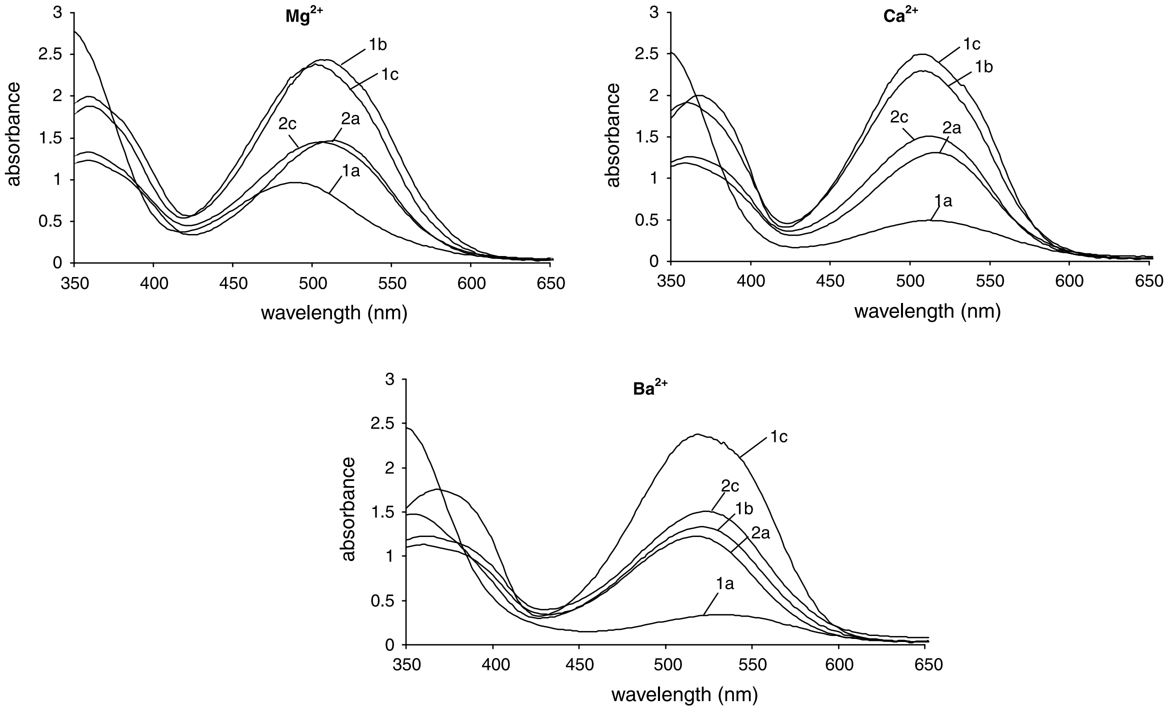


FIGURE 3 Spectral changes of **1a-c** and **2a,c** in response to $Mg^{2+}$, $Ca^{2+}$ and $Ba^{2+}$.

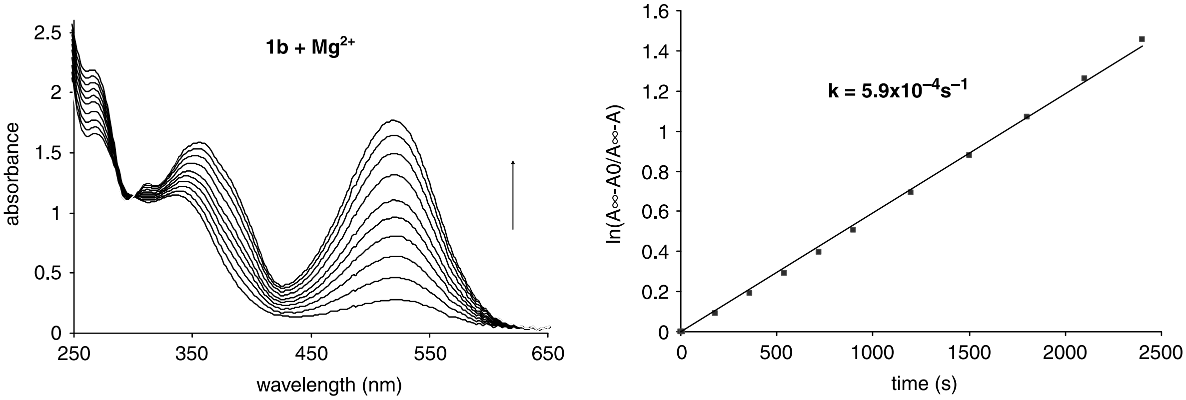


FIGURE 4 (left) Coloration kinetics of **1b**-Mg$^{2+}$(1:1) system in MeCN at 25°C, (right) calculation of the first-order rate constant.

accompanied by considerable decrease of the $\lambda_{max}$ values with decreasing ionic radius (increasing charge density) from Ba$^{2+}$ to Mg$^{2+}$. The blue-shift of the absorption maxima reflects the extent of solvation of the phenolate moiety in the merocyanine form [27], 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 Mg$^{2+}$, Ca$^{2+}$ and Ba$^{2+}$ on the thermal isomerisation of **1a–c** is attributable to both interactions, although in different proportions. The superior isomerization efficiency of Mg$^{2+}$ and Ca$^{2+}$ for hosts 1b,c and 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 (**SP** + M$^{+}$ ↔ **SP**–M$^{+}$ ↔ **Mc**–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 Li$^{+}$, Na$^{+}$ and K$^{+}$ are comparable with those of Mg$^{2+}$, Ca$^{2+}$and Ba$^{2+}$ (Table I), the former group of ions still cannot or hardly induce isomerization with any of hosts tested.

TABLE II Coloration rate constants for **1a-c** and **2(a)** (measured at $\lambda_{max}$) on exposure to alkaline

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

[L]/[M$^{2+}$] = 1:1 ($10^{-4}$ M, MeCN, 25°C); $^{\dagger}$reproducibility ± 7%

Unexpectedly, the optical behaviour of 1,3-alt **2a,c** (Fig. 3) was similar to that of cone **1a–c**, as far as the insufficient isomerization with alkali cations is concerned. Alkaline earth metal salts, however, induced more pronounced isomerization of **2a** vs. **1a** in the order of Mg$^{2+}$(512 nm) ≈ Ca$^{2+}$(516 nm) > Ba$^{2+}$(518 nm) (Fig. 3). The enhanced binding capacity of **2a** can be due to the additional contribution of the *anti* phenyl rings to binding by π-cation interaction. The alkaline earth metal cation preference of **2a** is comparable to that of indoaniline dye **3a**, as the complexed cations are stabilized in both cases by the pendant side arms via ionic or ion–dipole interaction. Increasing the crown ring size from **2a** to **2c** caused some enhancement of absorbances (Ba$^{2+}$ > Ca$^{2+}$ ≈ Mg$^{2+}$), but the extent of isomerization still fells behind that of cone **1c**, and it was scarcely influenced by the quality of cations.

## Kinetics of Mg$^{2+}$, Ca$^{2+}$and Ba$^{2+}$ -induced Coloration of Cone 1a–c and 1,3-alt 2a

For studying the kinetics of isomerization, the spectra of **1a–c** and **2a**-cation complexes, after decoloration by irradiation with visible light, were taken at room temperature. The absorbances measured at the $\lambda_{max}$ values of **Mc** were recorded in response to time **Mc** (see illustration in Fig. 4) and the first-order rate constants of coloration, i.e. the conversion of the colorless spirobenzopyran to the merocyanine form, were calculated (Table II).

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 [23,24], 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).

$Ag^{+}$ ion, just like the other monovalent cations, did not affect notably the spectra of any ligands being either cone or 1,3-alt conformation. However, 1,3-alt **2a**,**c** exhibited significant chelation-induced effect (**2c** > **2a**) in the order of $Zn^{2+}$(486 nm) ≈ $Cu^{2+}$(520 nm) > $Pb^{2+}$(494 nm). Interestingly, the isomerization efficiency of $Zn^{2+}$ and $Cu^{2+}$ for cone **1a,c** was also remarkable approaching to that of alkaline earth metal ions, due to the strong affinity of these ions to the amino group. Again **1b** and **1c** show larger extent of isomerization than **2a**,**c**, displaying comparable absorbances effected by the same order of cations (Fig. 5) and the $\lambda_{max}$ values follow somewhat different band-shift tendency: $Zn^{2+}$(500–502 nm, **1b**,**c**), $Cu^{2+}$(520–522 nm, **1b**,**c**), $Pb^{2+}$(496 nm, **1b** and 502 nm, **1c**). Ligand **1a** responds moderately only to $Pb^{2+}$(474 nm) with the largest blue-shift.

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

## CONCLUSIONS

A series of calix[4](aza)crowns bearing indolospiropyran photochromic signalling unit were synthesized and the **SP** (colorless)–**Mc** (colored) isomerization was investigated in the presence of various mono-and divalent cations under dark

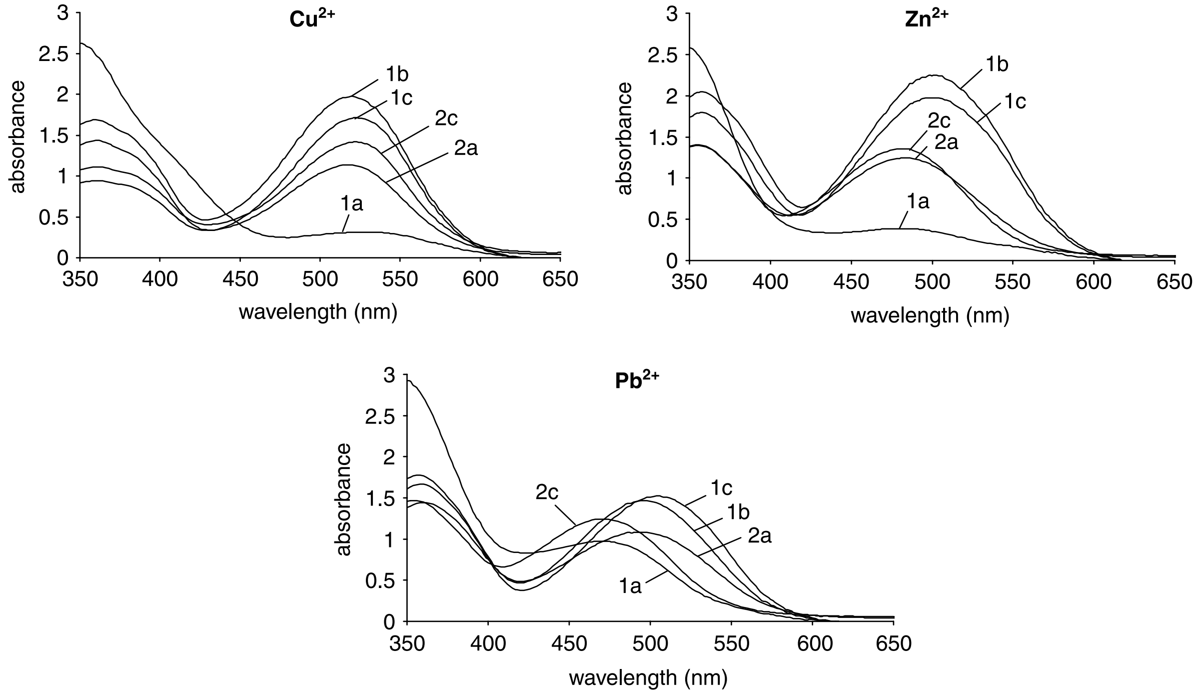


FIGURE 5 Spectral changes of **1a-c** and **2a,c** upon addition of equimolar amount of transition and heavy metal salts.

conditions. On the basis of UV/vis spectroscopic and kinetic measurements the effect of cations on the extent of isomerization was evaluated. We found more efficient coloration of cone dyes **1** induced by alkaline earth metal cations ($Mg^{2+}$, $Ca^{2+}$ and $Ba^{2+}$), transition- and heavy 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 $F_{254}$) 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** [18,19] and **6a,c** [22], and photochromic precursors **8** [13] 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; $^1$H NMR δ 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, $ArCH_2Ar$), 4.27 (m, 4H, $OCH_2$), 4.16 (m, 4H, $OCH_2$), 3.86 (t, 4H, J = 5.5, $OCH_2$), 3.65 (t, 4H, J = 7, $OCH_2$), 3.49 (t, 4H, J = 5.5, $NCH_2$), 3.13 (d, 4H, J = 13, $ArCH_2Ar$), 2.44 (s, 3H, $CH_3$), 1.88 (m, 4H, $CH_2$), 1.34 (s, 18H, $C(CH_3)_3$), 0.99 (t, 6H, J = 7.5, $CH_3$), 0.80 (s, 18H, $C(CH_3)_3$); anal. calcd. for $C_{65}H_{89}NO_8S$ (1044.47): C, 74.75; H, 8.59; found: C, 74.52; H, 8.62%.

### *Compound 4b*

Yield: 98%, mp 92–94 °C; $^1$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, $ArCH_2Ar$, $OCH_2$), 4.10 (m, 4H, $OCH_2$), 3.96 (t, 2H, J = 7.5, $OCH_2$), 3.80–3.65 (m, 10H, $OCH_2$), 3.36 (m, 4H, $NCH_2$), 3.16 (d, 2H, J = 13, $ArCH_2Ar$), 3.15 (d, 2H, J = 12.5, $ArCH_2Ar$), 2.46 (s, 3H, $CH_3$), 1.98 (m, 4H, $CH_2$), 1.38 (s, 18H, $C(CH_3)_3$), 1.07 (t, 6H, J = 7.5, $CH_3$), 0.84 (s, 18H, $C(CH_3)_3$); anal. calcd. for $C_{67}H_{93}NO_9S$ (1088.52): C, 73.93; H, 8.61; found: C, 74.08; H, 8.58%.

### *Compound 4c*

Yield: 92%, mp 81–84 °C; $^1$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, $ArCH_2Ar$), 4.25–4.16 (m, 8H, $OCH_2$), 3.78–3.69 (m, 16H, $OCH_2$), 3.41 (t, 4H, J = 6, $NCH_2$), 3.15 (d, 4H, J = 12.5, $ArCH_2Ar$), 2.46 (s, 3H, $CH_3$), 1.97 (m, 4H, $CH_2$), 1.36 (s, 18H, $C(CH_3)_3$), 1.05 (t, 6H, J = 7.5, $CH_3$), 0.85 (s, 18H, $C(CH_3)_3$); anal. calcd. for $C_{69}H_{97}NO_{10}S$ (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 4and 6

A mixture of **4a–c** or **6a,c** (1 mmol), $LiAlH_4$ (0.4 g, 10 mmol) in dry THF (20 ml) was stirred under reflux for 6 h. After cooling the excess of $LiAlH_4$ 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.

### *Compound 5a*

Yield: 35%, mp 257–259 °C; $^1$H NMR δ 7.11 (s, 4H, Ar*H*), 6.41 (s, 4H, Ar*H*), 4.35 (m, 4 + 4H, $ArCH_2Ar$, $OCH_2$), 4.14 (m, 4H, $OCH_2$), 3.78 (t, 4H, $J = 5$, $OCH_2$), 3.72 (t, 4H, $J = 7$, $OCH_2$), 3.15 (d, 4H, $J = 13$, $ArCH_2Ar$), 2.98 (t, 4H, $J = 5$, $NCH_2$), 1.91 (m, 4H, $CH_2$), 1.34 (s, 18H, $C(CH_3)_3$), 1.03 (t, 6H, $J = 7.5$, $CH_3$), 0.81 (s, 18H, $C(CH_3)_3$); $^{13}$C NMR δ 155.3, 152.8, 145.2, 144.3, 135.5, 131.8, 125.9, 124.6 (Ar), 77.9, 72.6, 69.4, 68.8 ($OCH_2$), 46.9 ($NCH_2$), 34.3, 33.8 ($C(CH_3)_3$), 31.9, 31.3 ($CH_3$), 31.5 ($ArCH_2Ar$), 23.6 ($CH_2$), 10.9 ($CH_3$); FAB-MS m/z (%) 890.6 $[M + H]^+$(11), anal. calcd. for $C_{58}H_{83}NO_6$ (890.28): C, 78.25; H, 9.40; found: C, 78.32; H, 9.38%.

### *Compound 5b*

Yield: 42%, mp 252–256 °C; $^1$H NMR δ 7.10 (s, 4H, ArH), 6.43 (s, 4H, ArH), 4.36 (d, 4H, J = 12.5, $ArCH_2Ar$), 4.29–4.08 (m, 8H, $OCH_2$), 3.73 (m, 8H, $OCH_2$), 3.13 (d, 4H, J = 12.5, $ArCH_2Ar$), 2.87 (m, 4H, $NCH_2$), 1.96 (m, 4H, $CH_2$), 1.33 (s, 18H, $C(CH_3)_3$), 1.04 (t, 6H, *J* = 7, CH$_3$), 0.81 (s, 18H, C(CH$_3$)$_3$); $^{13}$C NMR δ 154.8, 154.6, 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, 69.3 (OCH$_2$), 49.1 (N*C*H$_2$), 34.3, 33.8 (*C*(CH$_3$)$_3$), 32.0, 31.4 (*C*H$_3$), 31.3 (Ar*C*H$_2$Ar), 23.7 (*C*H$_2$), 10.9 (*C*H$_3$); FAB-MS m/z (%) 932.6 [M + H]$^+$(9), anal. calcd. for $C_{60}H_{87}NO_7$ (934.34): C, 77.13; H, 9.39; found: C, 77.32; H, 9.35%.

### *Compound 5c*

Yield: 41%, mp 210–213 °C; $^1$H NMR δ 7.08 (s, 4H, Ar*H*), 6.46 (s, 4H, Ar*H*), 4.37 (d, 4H, *J* = 12.5, ArC*H*$_2$Ar), 4.25–4.15 (m, 8H, OC*H*$_2$), 3.75–3.64 (m, 16H, OC*H*$_2$), 3.12 (d, 4H, *J* = 12.5, ArC*H*$_2$Ar), 2.82 (t, 4H, *J* = 4.5, NC*H*$_2$), 1.96 (m, 4H, C*H*$_2$), 1.32 (s, 18H, C(C*H*$_3$)$_3$), 1.04 (t, 6H, *J* = 7.5, C*H*$_3$), 0.82 (s, 18H, C(C*H*$_3$)$_3$); $^{13}$C NMR δ 154.4, 152.4, 145.0, 144.0, 135.5, 131.9, 125.4, 124.5 (Ar), 77.9, 72.1, 71.0, 70.5, 70.3, 70.1 (OCH$_2$), 48.7 (NCH$_2$), 34.1, 33.6 (C(CH$_3$)$_3$), 31.9, 31.4 (CH$_3$), 31.1 (ArCH$_2$Ar), 23.7 (CH$_2$), 10.7 (CH$_3$); FAB-MS m/z (%) 978.7 [M + H]$^+$(33), anal. calcd. for $C_{62}H_{91}NO_8$ (978.39): C, 76.11; H, 9.37; found: C, 75.89; H; 9.40%.

### *Compound 7a*

Yield: 92%, $^1$H NMR δ 7.11 (d, 4H, *J* = 7.5, Ar*H*), 7.04 (d, 4H, *J* = 7.5, Ar*H*), 6.83 (t, 2H, *J* = 7.5, Ar*H*), 6.77 (t, 2H, *J* = 7.5, Ar*H*), 3.74 (s, 8H, ArC*H*$_2$Ar), 3.50–3.43 (m, 16H, OC*H*$_2$), 2.77 (m, NC*H*$_2$), 1.47 (m, 4H, C*H*$_2$), 0.80 (t, 6H, *J* = 7.5, C*H*$_3$); $^{13}$C NMR δ 157.0, 156.5, 134.1, 130.6, 122.1, 121.9 (Ar), 72.5, 71.1, 70.3, 70.1 (O*C*H$_2$), 48.6 (N*C*H$_2$), 38.0 (Ar*C*H$_2$Ar), 22.9 (*C*H$_2$), 10.1 (*C*H$_3$); anal. calcd. for $C_{42}H_{51}NO_6$ (665.86): C, 75.76; H, 7.72; found: C, 75.88; H, 7.70%.

### *Compound 7c*

Yield: 93%, $^1$H NMR δ 7.12 (d, 4H, *J* = 7.5, Ar*H*), 7.01 (d, 4H, *J* = 7.5, Ar*H*), 6.76 (m, 4H, Ar*H*), 3.71 (s, 8H, ArCH$_2$Ar), 3.68–3.59 (m, 16H, O*C*H$_2$), 3.45 (t, 4H, *J* = 7.5, OCH$_2$), 3.40 (t, 4H, J = 5, OCH$_2$), 2.83 (t, 4H, J = 5, NC*H*$_2$), 1.43 (m, 4H, C*H*$_2$), 0.80 (t, 6H, *J* = 7.5, C*H*$_3$); $^{13}$C NMR δ 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 (O*C*H$_2$), 49.1 (N*C*H$_2$), 37.2 (Ar*C*H$_2$Ar), 23.1 (*C*H$_2$), 10.3 (*C*H$_3$); anal. calcd. for $C_{46}H_{59}NO_8$ (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 Photochromes 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%; $^1$H NMR: δ 8.27 (s,1H, Ar*H*), 7.97 (s, 1H, Ar*H*), 7.22 (t, 1H, *J* = 7.5, Ar*H*), 7.16 (s, 4H, Ar*H*), 7.12 (d, 1H, *J* = 7, Ar*H*), 6.97 (d, 1H, *J* = 10, C*H* = ), 6.91 (t, 1H, *J* = 7.5, Ar*H*), 6.58 (d, 1H, *J* = 7.5, Ar*H*), 6.45 (s, 4H, Ar*H*), 5.90 (d, 1H, J = 10.5, C*H* = ), 4.38 (d, 4H, *J* = 12.5, ArC*H*$_2$Ar), 4.30 (m, 4H, OC*H*$_2$), 4.19 (m, 4H, OC*H*$_2$), 3.72 (t, 4H, *J* = 7, OC*H*$_2$), 3.62 (bs, 4H, OC*H*$_2$), 3.52 (m, 2H, NCH$_2$), 3.18 (d, 4H, *J* = 12.5, ArC*H*$_2$Ar), 2.82–2.73 (m, 3 + 4H, NC*H*$_3$, NC*H*$_2$), 1.96 (m, 4H, C*H*$_2$), 1.38 (s, 18H, C(C*H*$_3$)$_3$), 1.33 (s, 3H, C*H*$_3$), 1.24 (s, 3H, C*H*$_3$), 1.07 (t, 6H, *J* = 7, C*H*$_3$), 0.84 (s, 18H, C(C*H*$_3$)$_3$); $^{13}$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, (O*C*H$_2$), 53.6, 53.2, (N*C*H$_2$), 52.1 (*C*(CH$_3$)$_2$), 34.2, 33.6 (C(*C*H$_3$)$_3$), 31.8, 31.2 (*C*H$_3$), 31.1 (Ar*C*H$_2$Ar), 29.0 (N*C*H$_3$), 25.9, 20.1 (*C*H$_3$) 23.6 (*C*H$_2$), 10.9 (*C*H$_3$); anal. calcd. for $C_{78}H_{101}N_3O_9$ (1224.65): C, 76.50; H, 8.31, found: C, 76.31; H, 8.35%.

### *Ligand 1b*

Yield: 50%; $^1$H NMR: δ 8.29 (d,1H, *J* = 2.5, Ar*H*), 7.91 (d, 1H, *J* = 3, Ar*H*), 7.16 (t, 1H, *J* = 7.5, Ar*H*), 7.11 (s, 4H, Ar*H*), 7.07 (d, 1H, *J* = 7, Ar*H*), 6.92 (d, 1H, *J* = 10.5, C*H* = ), 6.85 (t, 1H, *J* = 7.5, Ar*H*), 6.53 (d, 1H, *J* = 7.5, Ar*H*), 6.43 (s, 4H, Ar*H*), 5.85 (d, 1H, J = 10.5 Hz, C*H* = ), 4.32 (m, 4 + 2H, ArC*H*$_2$Ar, OC*H*$_2$), 4.15 (m, 6H, OC*H*$_2$), 3.74–3.47 (m, 14H, OC*H*$_2$, NC*H*$_2$), 3.13 (d, 4H, *J* = 12.5, ArC*H*$_2$Ar), 2.70 (m, 3 + 4H, NC*H*$_3$, NC*H*$_2$), 1.94 (m, 4H, C*H*$_2$), 1.34 (s, 18H, C(C*H*$_3$)$_3$), 1.29 (s, 3H, C*H*$_3$), 1.20 (s, 3H, C*H*$_3$), 1.02 (t, 6H, *J* = 7, C*H*$_3$), 0.81 (s, 18H, C(C*H*$_3$)$_3$); $^{13}$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 (O*C*H$_2$), 55.0, 54.7, 53.6 (N*C*H$_2$), 52.2 (*C*(CH$_3$)$_2$), 34.3, 33.8 (C(*C*H$_3$)$_3$), 32.0, 31.4 (*C*H$_3$), 31.2, 31.1 (Ar*C*H$_2$Ar), 29.1 (N*C*H$_3$), 26.1, 20.2 (*C*H$_3$) 23.8 (*C*H$_2$), 11.0 (*C*H$_3$); anal. calcd. for $C_{80}H_{105}N_3O_{10}$ (1268.70): C, 75.74; H 8.34, found: C, 75.52; H, 8.38%.

### *Ligand 1c*

Yield: 49%; $^1$H NMR: δ 8.27 (d,1H, *J* = 2, Ar*H*), 7.91 (d, 1H, *J* = 2.5, Ar*H*), 7.17 (t, 1H, *J* = 7.5, Ar*H*), 7.09 (s, 4H, Ar*H*), 7.07 (d, 1H, *J* = 8, Ar*H*), 6.92 (d, 1H, *J* = 10, C*H* = ), 6.86 (t, 1H, *J* = 7.5, Ar*H*), 6.53 (d, 1H, *J* = 7.5, Ar*H*), 6.46 (s, 4H, Ar*H*), 5.85 (d, 1H, J = 10.5, C*H* = ), 4.36 (d, 4H, $J = 12.5$, ArC$H_2$Ar), 4.24–4.13 (m, 8H, OC$H_2$), 3.74–3.63 (m, 12H, OC$H_2$), 3.47 (m, 4 + 2H, OC$H_2$, NC$H_2$), 3.12 (d, 4H, $J = 12.5$, ArC$H_2$Ar), 2.68 (m, 3 + 4H, NC$H_3$, NC$H_2$), 1.96 (m, 4H, C$H_2$), 1.32 (s, 18H, C(C$H_3$)$_3$), 1.28 (s, 3H, C$H_3$), 1.20 (s, 3H, C$H_3$), 1.03 (t, 6H, $J = 7.5$, C$H_3$), 0.82 (s, 18H, C(C$H_3$)$_3$); $^{13}$C NMR δ 157.3, 154.4, 152.5, 147.7, 145.1, 144.0, 140.8, 136.2, 135.6, 132.0, 127.9, 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 ($C$ = ), 106.5 (spiro $C$), 77.8, 72.0, 70.7, 70.3, 69.8, 69.6 (O$C$H$_2$), 54.3, 52.9 (N$C$H$_2$), 52.1 ($C$(CH$_3$)$_2$), 34.1, 33.6 ($C$(CH$_3$)$_3$), 31.8, 31.2 ($C$H$_3$), 31.0 (Ar$C$H$_2$Ar), 28.9 (N$C$H$_3$), 25.9, 20.1 ($C$H$_3$) 23.6 ($C$H$_2$), 10.8 ($C$H$_3$); anal. calcd. for $C_{82}H_{109}N_3O_{11}$ (1312.76): C, 75.02; H, 8.37, found: C, 74.88; H, 8.40%.

### *Ligand 2a*

Yield: 30%; $^1$H NMR: δ 8.31 (s,1H, Ar$H$), 7.96 (s, 1H, Ar$H$), 7,23 (t, 1H, $J = 7$, Ar$H$), 7.14 (d, 1H, $J = 7$, Ar$H$), 7.09 (m, 8H, Ar$H$), 6.96 (d, 1H, $J = 10.5$, C$H$ = ), 6.92 (t, 1H, $J = 7$, Ar$H$), 6.81 (t, 4H, $J = 7.5$, Ar$H$), 6.60 (d, 1H, $J = 7.5$, Ar$H$), 5.89 (d, 1H, $J = 10.0$, C$H$ = ), 3.81 (s, 8H, ArC$H_2$Ar), 3.53 (bs, 4H, OC$H_2$), 3.42 (m, 4 + 2H, OC$H_2$, NC$H_2$), 3.27 (bs, 4H, OC$H_2$), 3.20 (bs, 4H, OC$H_2$), 2.76 (s, 3H, NC$H_3$), 2.54 (bs, 4H, NC$H_2$), 1.34 (s, 3H, C$H_3$), 1.27 (m, 4H, C$H_2$) 1.24 (s, 3H, C$H_3$), 0.73 (t, 6H, $J = 7.0$, C$H_3$), $^{13}$C NMR δ 157.0, 156.7, 147.6, 140.7, 136.2, 134.0, 133.7, 129.8, 129.7, 129.6, 127.7, 122.2, 122.1, 121.5, 119.7, 118.6, 107.0 (Ar), 128.6, 121.1 ($C$ = ) 106.5 (spiro $C$), 72.0, 70.8, 69.8, 69.7, (O$C$H$_2$), 53.3, 52.5, (N$C$H$_2$), 52.0 ($C$(CH$_3$)$_2$), 38.1 (Ar$C$H$_2$Ar), 29.8 (N$C$H$_3$), 25.9, 20.1 (CH$_3$) 22.4 ($C$H$_2$), 10.0 ($C$H$_3$); anal. calcd. for $C_{62}H_{69}N_3O_9$ (1000.23): C, 74.45; H, 6.95, found: C, 74.64; H, 6.92%.

### *Ligand 2c*

Yield: 17%; $^1$H NMR: δ 8.31 (d,1H, $J = 2.0$, Ar$H$), 7.92 (d, 1H, $J = 2.5$, Ar$H$), 7.19 (t, 1H, $J = 6.5$, Ar$H$), 7.11 (d, 4H, $J = 7.5$, Ar$H$), 7.07 (d, 1H, $J = 7.5$, Ar$H$), 7.01 (d, 4H, $J = 7.5$, Ar$H$), 6.93 (d, 1H, $J = 10.5$, C$H$ = ), 6.88 (t, 1H, $J = 7.5$, Ar$H$), 6.76 (m, 4H, Ar$H$), 6.54 (d, 1H, $J = 7.5$, Ar$H$), 5.85 (d, 1H, J = 10.5, C$H$ = ), 3.72 (s, 8H, ArC$H_2$Ar), 3.40 (t, 4H, $J = 5.5$, OC$H_2$), 3.65–3.44 (m, 16 + 2H, OC$H_2$, NC$H_2$), 3.40 (t, 4H, $J = 5.5$, OC$H_2$), 2.71 (m, 3 + 4H, NC$H_3$, NC$H_2$), 1.42 (m, 4H, C$H_2$), 1.29 (s, 3H, C$H_3$), 1.20 (s, 3H, C$H_3$), 0.79 (t, 6H, $J = 7.5$, C$H_3$), $^{13}$C NMR δ 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 (O$C$H$_2$), 54.3, 52.7, (N$C$H$_2$), 52.1 ($C$(CH$_3$)$_2$), 37.3 (Ar$C$H$_2$Ar), 28.9 (N$C$H$_3$), 25.9, 20.0 (CH$_3$) 23.0 ($C$H$_2$), 10.2 ($C$H$_3$); anal. calcd. for $C_{66}H_{77}N_3O_{11}$ (1088.33): C, 72.84; H 7.13, found: C, 72.55; H, 7.16%.

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