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1,1′-Binaphtho(aza)crowns Carrying Photochromic Signalling Unit, I: Synthesis, Characterization and Cation Recognition Properties

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(*S*)-1,1′-Binaphtho(monoaza)crown-5,-6 and-7 ionophores carrying photochromic indolospirobenzopyran (SP), naphthoxazine (NO) and naphthopyran (NP) signalling groups were synthesized and their cation-induced isomerisation to the colored merocyanine or quinone forms was studied by UV/Vis spectroscopy in the presence of alkali and alkaline earth metal ions. Under dark conditions the equilibrium of SP and NO dyes were remarkably shifted to the colored form by cations of high positive charge density (Li^+ and alkaline earth metal ions). The same effects were observed with crowned NPs after UV irradiation. The stability of some merocyanine-cation complexes were evaluated by calculating the kinetic parameters of the coloration process.

Keywords: Binaphthocrowns; Indolospiropyran; Naphthoxazine; Naphthopyran; Photochromism; Cation recognition

INTRODUCTION

Photochromic materials have attracted much attention in recent 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 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 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 to the nitrogen atom of the indoline ring, respectively. Numerous spirobenzopyrans linked with crown ethers have been synthesized and their photoresponsive behavior towards metal cations was investigated by spectroscopic methods [7–15]. Extraction and transport studies were reported on the interaction of simple merocyanines with the zwitterionic amino acids [16,17]. These results prompted Tsubaki *et al.* [18] to synthesize the chiral binaphthylspiropyran (R)-**1**, the merocyanine form of which was claimed to discriminate between the enantiomers of a series of amino acids by forming diastereomeric complexes (Scheme 1).

The enantiomeric differentiations were expressed by the half-life ($t_{1/2}$) values for the decoloration of the merocyanine-D or L-amino acid complexes measured by UV/Vis spectrophotometry after irradiation of the sample mixture with UV light [18]. To the best of our knowledge, chiral crown-spiropyran conjugates have not been reported until now, although after Cram's pioneering work [19] chiral crown ethers have attracted great interest as excellent chiral selectors for ammonium salts and amino acid derivatives [20].

As part of our ongoing research we have synthesized 1,1′-binaphthyl-appended chromogenic

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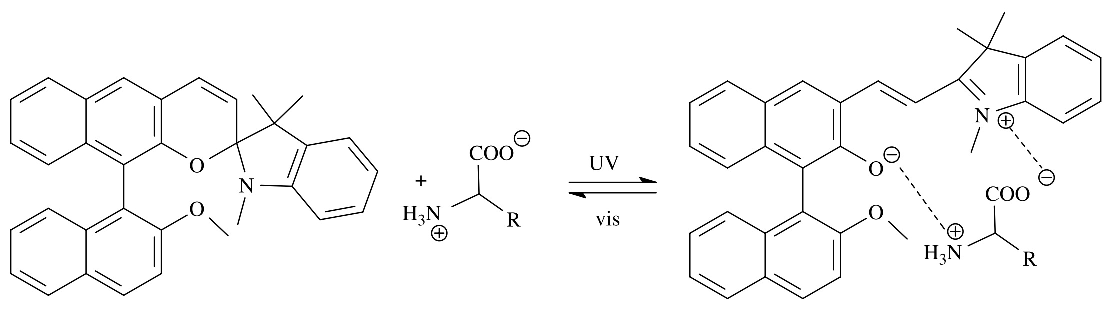


(*R*)-**1** spiropyran

(*R*)-**1** merocyanine

SCHEME 1 Interaction of chiral 1,1′-binaphtyl-spiropyran (*R*)-1 with amino acids.

calix[4]crowns for the optical recognition of chiral amines [21]. In addition, recently we have also reported the preparation of a calix[4]crown-spirobenzopyran conjugate [22].

These preliminaries prompted us to utilize our previous experiences in the synthesis of (*S*)-1,1′-binaphthol-derived azacrown hosts (*S*)-**2–4** bearing different photochromic moieties. (Fig. 1) Due to the easy light fatigue of spirobenzopyrans (**SP**) [23], our studies were extended to spironaphthoxazines (**NO**) [8,23] and naphthopyrans (chromens, **NP**) [24,25] because of their greater resistence to photodegradation. The UV light induced ring opening of the colorless **NO** and **NP** photochromes is similar to that of **SP** (C–O cleveage), but here quinoidal and not zwitterionic structure of the open forms is responsible for the coloration [26,27] (Fig. 1). The crowned **SP** and **NO** dyes

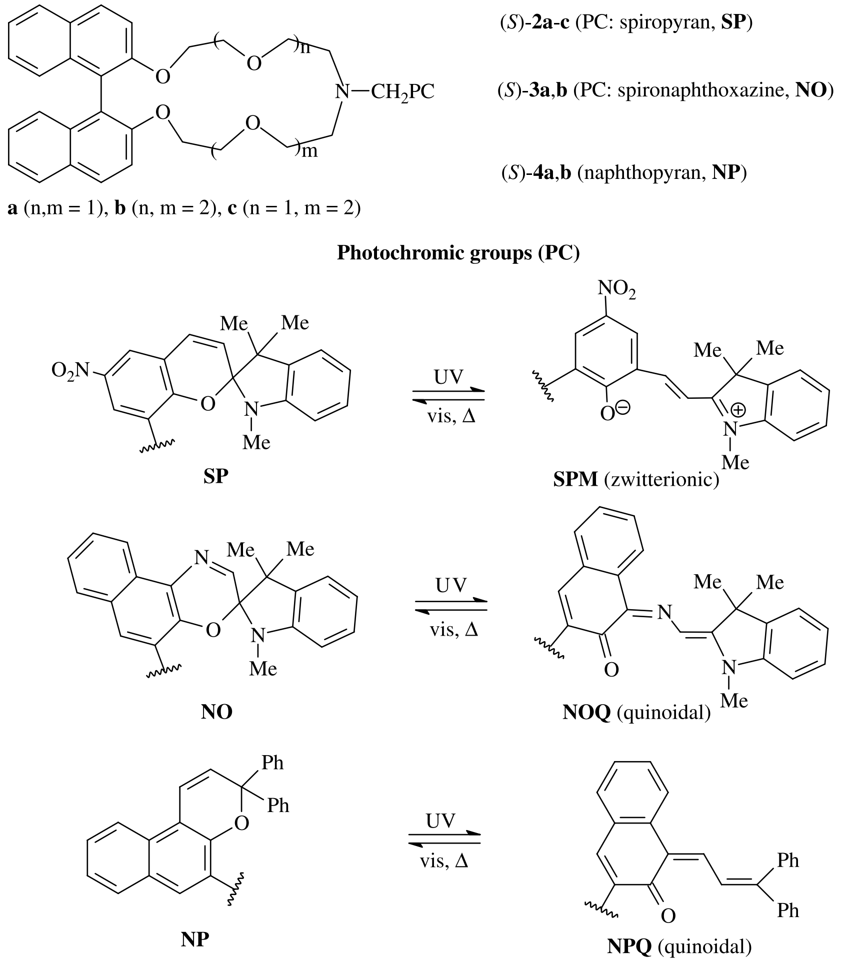


FIGURE 1 Synthesized 1,1′-binaphthoazacrowns **2–4** bearing photochromic moieties.

were reported to isomerize to the colored open form upon complexation of some alkali- and alkaline earth metal ions even under dark conditions [7–15]. In contrast, crowned **NP** molecules were published to resist to alkali cation-facilitated thermal isomerization, while Ca^{2+} and Mg^{2+} induce moderate coloration. Upon UV irradiation, however, the opening of the pyran ring of **NP** dyes was markedly facilitated by alkali-and alkaline earth metal cations as well [23,24]. Consequently, the crowned **SP**, **NO** and **NP** molecules are regarded as special chromogenic receptors of dual character. Their crown ether parts behave as ionophores, meanwhile the photochomic moieties not only act as indicators, but their colored form can influence the selectivity pattern of the binding site by contribution of the phenolate or quinone carbonyl group to the stabilization of the complexed cation, thereby resulting in different photoresponsive effects under dark condition or after UV irradiation. Our main goal with the synthesis of chiral **2–4** ligands was to extend the number of the unique chiral photochrom molecules and later on to study their optical recognition ability towards properly chosen chiral guests by measuring the rates of the coloration/decoloration process. Herein we report on the synthesis and optical behavior of compounds **2–4** to characterize their fundamental photoresponsive properties in the presence of alkali- and alkaline earth metal salts under dark conditions and, where it was possible, after UV irradiation.

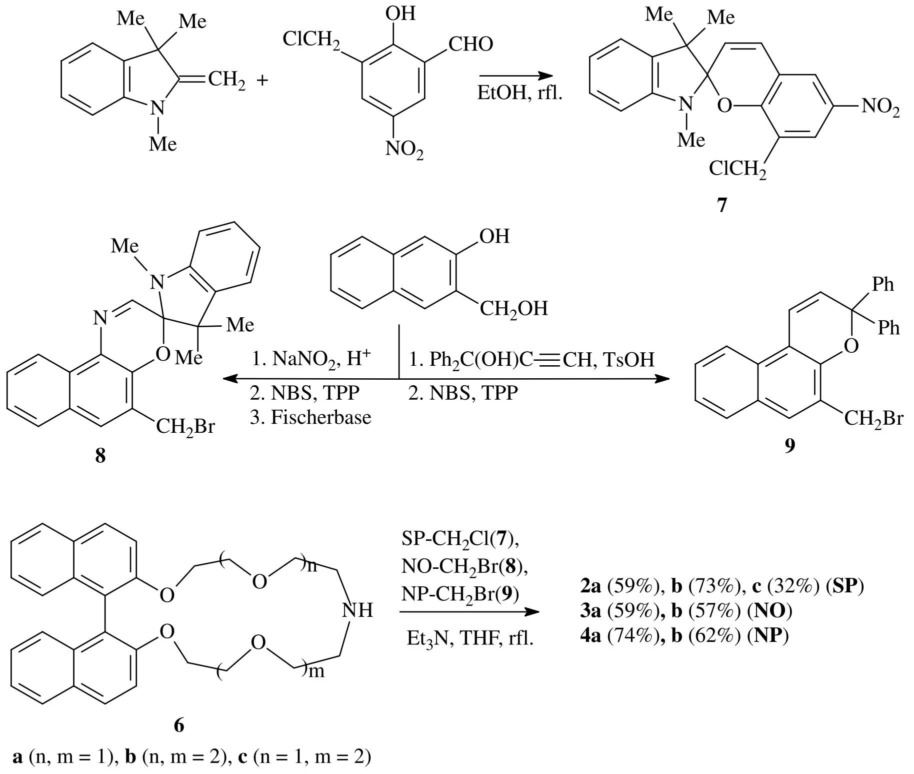
RESULTS AND DISCUSSION

Synthesis of Photochromic Binaphtho(azacrowns) 2–4

The synthesis of the target compounds was based on our recent method developed for the preparation of *N*-tosyl-binaphtho(azacrowns) **5a–c** [28]. After detosylation effected by Na/Hg, deprotected azacrowns **6a**,**b**,**c** were obtained which were condensed with chloromethyl-spirobenzopyran **7** [11,13], 3-bromomethyl-1-nitroso-2-naphthol **8** [29] and bromomethylchromene **9** [29], respectively, according to literature analogy to give photochromic molecules **2–4** (Scheme 2).

Optical Responses of Crowned Spirobenzopyrans 2a–c to Metal Ions

First, the cation-induced isomerization of crowned **SP** hosts **2a–c** 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 the equilibrium. The spectra of the metal free hosts (except for **2c**) displayed scarcely discernible



SCHEME 2 Synthesis of photochromic 1,1′-binaphtho(azacrown-5, 6-and 7) **2–4**.

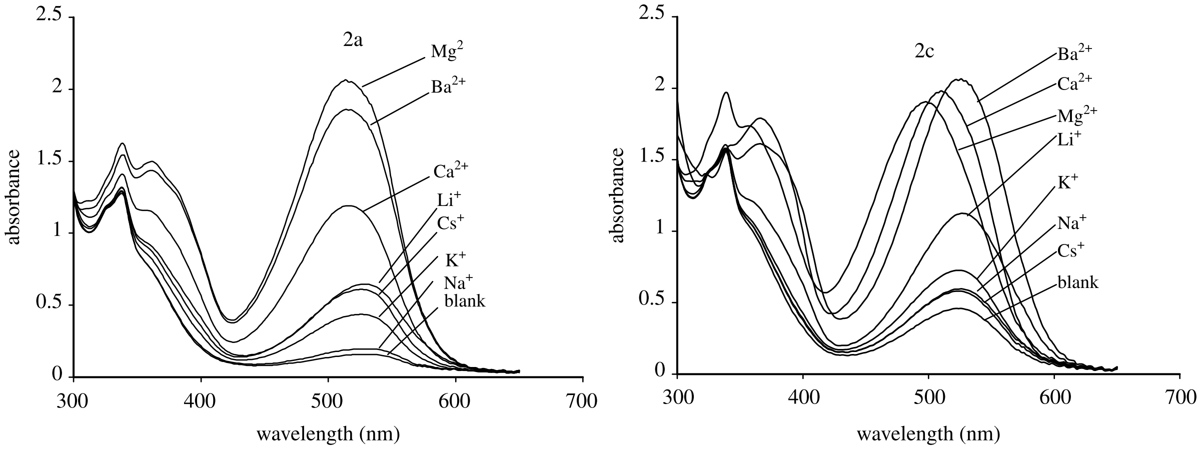


FIGURE 2 Spectral changes of **2a,c** upon addition of equimolar metal salts.

absorption in the visible region assignable to the merocyanine form (Figs. 2 and 3).

The absorbances of the new bands in the range 490–530 nm attributable to the merocyanine form were not increased further when twofold excess of metal salts were added, indicating 1:1 complex stoichiometry (Fig. 3). Figures 2 and 3 clearly show that the isomerization of **2a–c** to the merocyanine form was inefficiently promoted by Na^+, K^+ and Cs^+ (except for crown-7 host **2b**, which displays significant spectral change upon addition of K^+). Generally, Li^+ enhanced the isomerization more strongly than the other alkali ions. In the presence of alkaline earth metal ions possessing higher charge density than alkali ions on the other hand, the absorption spectra of each host changed significantly, due to the stronger ionic interaction with the phenolate anion. The absorbances decreased in the order of Mg^{2+}(510 nm) $>$ Ba^{2+}(522 nm) $\geqslant$ Ca^{2+}(512 nm) for crown-5 **2a**, Ba^{2+}, K^+(530 nm) $>$ Ca^{2+}(506 nm) $>$ Mg^{2+}(494 nm) for crown-7 **2b** and Ba^{2+}(526 nm) $>$ Ca^{2+}(510 nm) $>$ Mg^{2+}(500 nm) for crown-6 **2c**, respectively. As seen, in the latter two cases the complexation was accompanied by remarkable blue-shifts with decreasing ionic radius (increasing charge density) from Ba^{2+} (K^+) to Mg^{2+}. In contrast, the absorption maxima of **2a** did not show a similar tendency, although a large degree of metal ion-induced isomerization illustrated by the peak intensities of the merocyanine form is observed. The blue-shift of the absorption maxima reflects the extent of solvation of the phenolate moiety in the merocyanine forms [30], and indicative of the strength of interaction between the complexed cation and the phenolate anion. Our observations, in accord with the results of other crowned spirobenzopyrans, revealed that the spiropyran-merocyanine equilibrium can be affected both by the binding ability of the crown rings and by the strength of ionic interactions between the merocyanine phenolate anion and the metal cation. While the latter could induce photoisomerization, the former may not always cause change in photoisomerization behavior.

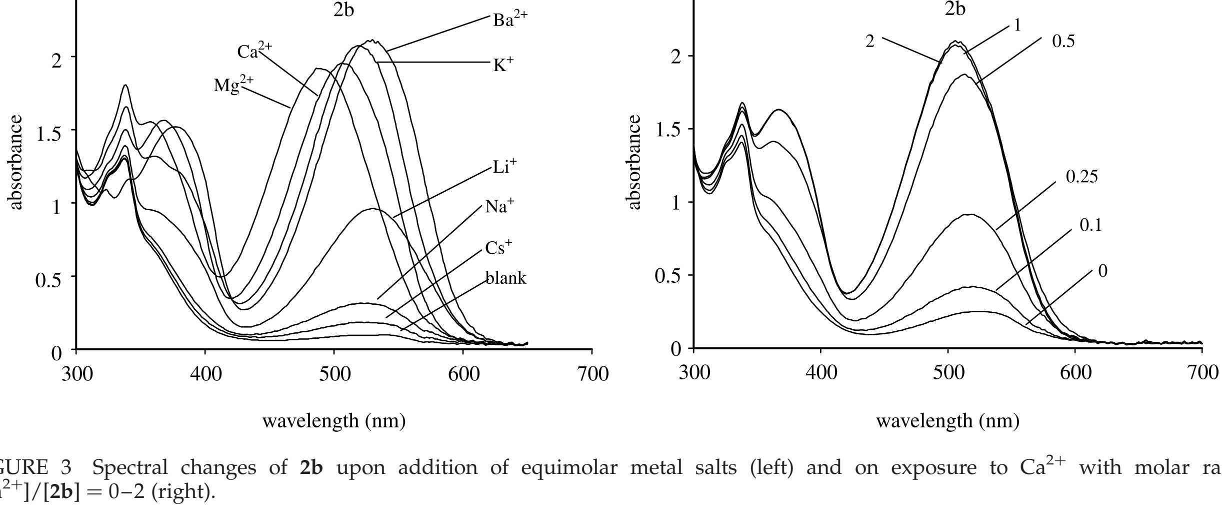


FIGURE 3 Spectral changes of **2b** upon addition of equimolar metal salts (left) and on exposure to Ca^{2+} with molar ratios $[Ca^{2+}]/[\mathbf{2b}] = 0–2$ (right).

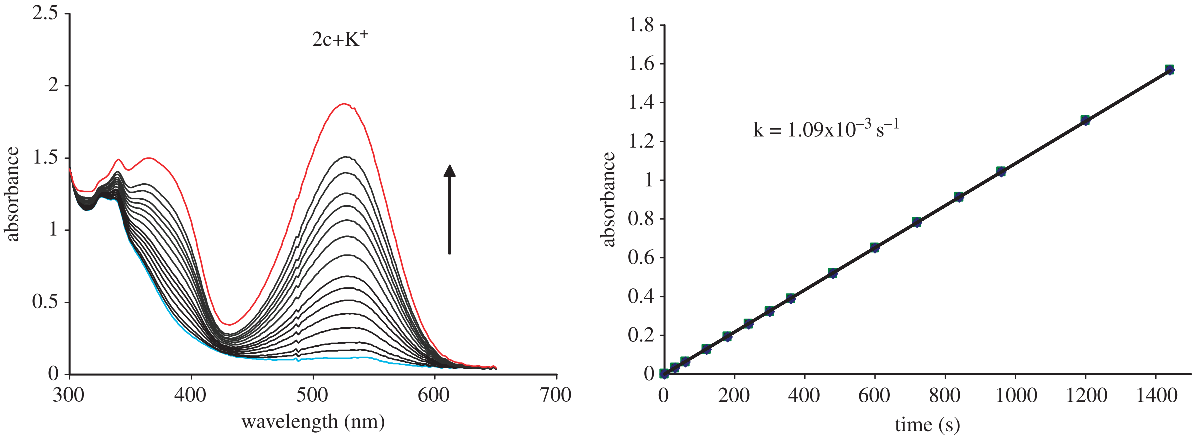


FIGURE 4 Coloration kinetics of $[\mathbf{2c}]/[\mathrm{K}^+] = 1{:}1$ system ($[\mathbf{2c}] = 10^{-4}$ M in MeCN, $\lambda_{\max} = 526$ nm) (left); $\log [A_\infty] - [A_0]/[A_\infty] - [A_t]$ values (A_∞: red line, A_0: blue line) plotted against time (right).

Although the association constants of the parent binaphthocrown-5, 6, 7 molecules with the cations tested have not been determined, we assume the marked effect of Mg^{2+}, Ca^{2+}, Ba^{2+} and K^+ on the thermal isomerisation is attributable to both interactions, although in different proportions. In this respect the moderate effect of Li^+ to the coloration of hosts **2b**,**c** possessing large crown ring is confusing. We suppose that a part of the twisted crown rings can provide a binding site for the small Li^+ ion but in a relatively remote position from the merocyanine phenolate, therby resulting in a weaker ionic interaction as expected, causing no discernible blue shifts in the spectra.

For studying the photoresponsive properties of spiropyrans **2a–c**, the kinetic measurement of the metal ion-induced coloration with the most effective cations provides a fast method to evaluate the fundamental optical characteristics (the K_{ass} values were not determined, as these molecules were prepared to investigate their responses to chiral guests). Therefore, the spectra of **2**-cation complexes after decoloration by irradiation with visible light were taken at room temperature by recording the **SPM** absorbances at the $\lambda_{\max}$ values in response to time, and the first-order rate constants of coloration were calculated (see illustration for **2c**-K^+ in Fig. 4).

The kinetic data along with the the blank rate constants of metal free experiments are summarized in Table I.

TABLE I Coloration rate constants for **2a–c** (with wavelength of maximal absorptions) on exposure to different metal ions

		$k \times 10^3\ (\mathrm{s}^{-1})^a/\lambda_{\max}$ (nm)			
L	Blank	Mg^{2+}	Ca^{2+}	Ba^{2+}	K^+
2a	0.86 (543)	0.15 (510)	0.38 (512)	0.21 (522)	0.27 (522)
2b	0.78 (525)	0.25 (494)	1.30 (506)	5.20 (530)	5.10 (530)
2c	0.20 (540)	0.26 (500)	4.56 (510)	0.86 (526)	1.09 (526)

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

Unfortunately, the reverse decoloration process, i.e. the decay of the spectra of ligand-M^+ systems after UV light irradiation, could not be evaluated due to insufficient reproducibility caused by photodegradation under our irradiation conditions. Although the simultaneous evaluation of the kinetic data of both processes could provide reliable information on the dual metal interaction influencing the isomerization, some conclusions on the binding characteristics can be drawn if only the coloration rate constants are compared. The *k* values of **2a** measured with all cations and those of **2a**,**b** with Mg^{2+} are smaller than the respective blank values, that is the rate of isomerization of spiropyran is suppressed in these cases, which may originate from the high kinetic stability of the respective **SP**-M^+ complexes. If this supposition is true, upon UV irradiation the merocyanine form should be converted to the original spiropyran form, that is to say, a negative photochromism should appear. To prove this phenomenon observed by Kimura with other crowned spiropyrans towards Li^+ and alkaline earth metal cations [12], UV irradiation measurements under thoroughly controlled conditions are in progress.

Obviously, the binding characteristics of binaphthocrowns cannot be compared with that of the classical crown ethers; some selectivities, however, are observable with the enlargement of the crown ether rings: the 20-crown-6 ligand **2c** strongly binds with Ca^{2+}, while 23-crown-7 **2b** prefers the larger K^+ and Ba^{2+} exhibiting the highest isomerization rates, in accord with the increasing ring size and the number of donor atoms.

In a preliminary experiment the spectrum of **2b** (10^{-4} M in MeCN) was recorded upon addition of excess of (*R*)-and (*S*)-phenylglycine (PG) to check if some enantiomer-dependent optical responses occur under dark conditions. Although weak complexation-induced coloration took place, distinct differences were found in the absorption maxima and the

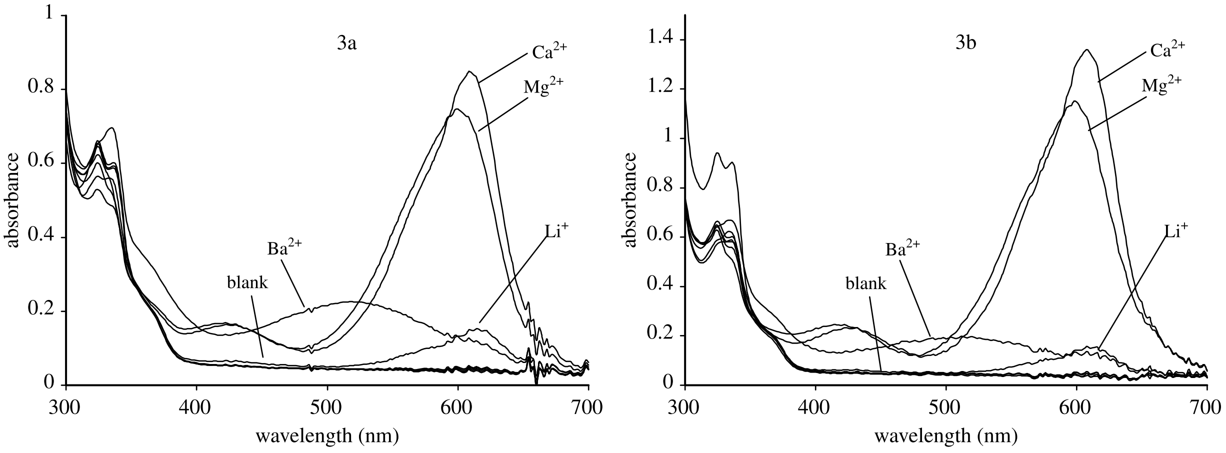


FIGURE 5 Spectral changes of **3a**,**b** on addition of equimolar metal salts.

absorbances: at 520 nm $A = 0.1524$ for (*R*)-PG and at 528 nm $A = 0.2818$ for (*S*)-PG indicating that (*S*)-phenylglycine facilitates more effectively the thermal isomerization to the merocyanine form than the (*R*)-enantiomer. The investigation of this kind of chiral recognition with other amino acid derivatives and ammonium salts is in progress in our laboratory and will be reported in due course.

Optical Responses of Crowned Spironaphthoxazines 3a,b to Metal Ions

The analogous dark experiments with **NO** dyes **3a**,**b** revealed that only Ca^{2+} and Mg^{2+} induced significant opening of naphthoxazine ring affording more intense absorbance with Ca^{2+}(610 nm) than with Mg^{2+}(608 nm) in the case of both ligands. Notably, both cations effected a higher degree of isomerization with the larger crown **3b**. Li^{+} and Ba^{2+} exhibited weak effects with a great widening of the spectrum in the latter case (Fig. 5).

The coloration process was too fast at room temperature, reliable rate constants, therefore, could not be determined. Nevertheless, the photoresponsive behavior of **NO** dyes **3a**,**b** compared with the respective **SP** dyes **2a**,**b** points to the different character of interaction of cations with **SPM** phenolate or with **NOQ** carbonyl groups: while the negative charge of the former can bind with cations of less charge density also, the electron pairs of the latter strongly coordinate only the ones of highest positive charge density.

Photochromism of Crowned Naphthopyrans 4a,b with Metal Ions

In contrast to **SP** and **NO** dyes, ligands **4a**,**b** did not show any significant isomerization associated with coloration upon addition of metal salts under dark conditions. After 1 min UV light irradiation (365–380 nm), however, the spectra drastically changed and new bands attributable to the **NPQ** form appeared in the range 420–490 nm (Fig. 6). The cation-facilitated isomerizations tooke place to different extents producing red-shift of the absorption maxima in all cases. Without metal salts the

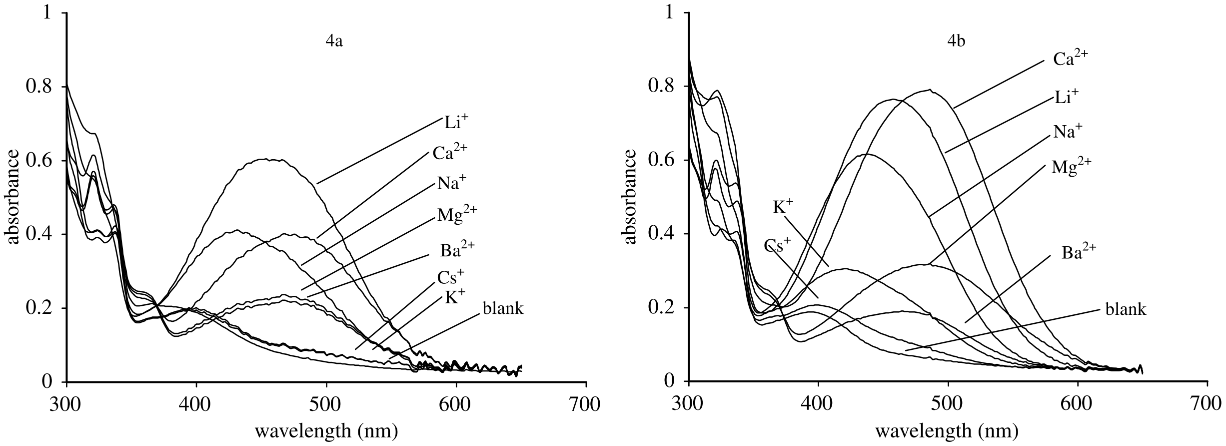


FIGURE 6 Spectral changes of **4a**,**b** after UV irradiation upon addition of metal salts.

NPQ bands of **4a**,**b** were assigned around 400 nm with weak absorbances.

For **4a** the highest degree of isomerization was induced by Li^+(460 nm), considerable effects were produced by Na^+(432 nm) and Ca^{2+}(484 nm), slight spectral change was caused by Mg^{2+} and Ba^{2+}(466 nm), while K^+ and Cs^+ did not affect the isomerization. In the case of **4b**, Ca^{2+}(486 nm) and Li^+(464 nm) induced the more drastic spectral change, considerable effect was achieved by Na^+(430 nm), moderate and slight effects were observed with K^+(422 nm), Mg^{2+}(484 nm) and Ba^{2+}(464 nm), respectively. As seen, straight ring size-dependent selectivity of the crown moieties was not observed, Li^+, Ca^{2+} and, to a less extent, Na^+ were preferred by both ligands. Other **NP** dyes containing 12-crown-4, 15-crown-5 and 18-crown-6 moieties were reported to show some size-dependent cation discrimination for Li^+ vs Na^+ with enlargement of the crown ring [24]. Our ligands, comprised of a 17-crown-5 (**4a**) and a 23-crown-7 (**4b**) binding site with twisted binaphthyl subunit, cannot provide ideal steric environment for complexation, therefore only part of the donor atoms can be involved in binding. Consequently, cations of the least coordination demand and of the highest charge density, such as Li^+ and Ca^{2+}, can effect notable complexation-induced photoisomerization with the contribution of the quinone carbonyl stabilizing the colored **NPQ**-M^+ complex (Fig. 7).

In accord with the literature results [24], our **NPQ** dyes also exhibit red-shifts upon metal ion complexation in contrast to crowned **SPM**s, where blue-shifts were observed. Both shifts can be due to solvation and the quinoidal form of chromenes actually show slight red-shifts in polar solvents [31]. The cation-induced red-shifts of **4a**,**b** decreased in the order of Ca^{2+}(84, 86 nm) > Li^+(60, 64 nm) > Na^+(32, 30 nm) reflecting the order of positive charge densities and the strength of interaction between the cations and the carbonyl group as well. The photostability of **4a**,**b** allows us to determine the decoloration rate constants, which is in progress. In preliminary experiments performed under non-thermostated conditions in the presence of Li^+ after UV irradiation, a ca. two-fold enhancement of the decoloration rate was measured with the ring enlargement from **4a** to **4b** supporting the expectation [24], that Li^+ stabilizes the colored form of crown-5 **4a** more efficiently than that of the larger crown-7 **4b**.

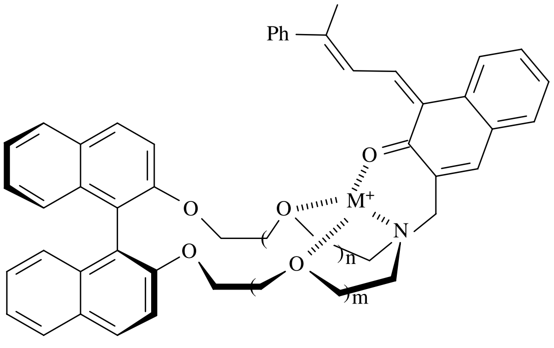


FIGURE 7 Interaction of the metal ion with the carbonyl group and the crown ether unit.

CONCLUSIONS

A series of (*S*)-1,1′-binaphthoazacrowns bearing photochromic signalling units (indolospiropyran, indolospironaphthoxazine, naphthopyran) were synthesized to extend the choice of the extremely rare and unique chiral photochrom molecules that may have potential in photoresponsive chiral recognitions. In this paper their optical behavior in the presence of alkali-and alkaline earth metal cations was explored. The cation-induced isomerization of the colorless forms to the colored merocyanine or quinone species was studied under dark conditions (spiropyrans and spironaphthoxazines) and after UV irradiation (naphthopyrans). On the basis of UV/Vis spectroscopic and kinetic measurements the effect of cations on the photoisomerization was evaluated. We found efficient thermal coloration of **SP** and **NO** dyes is primarily induced by cations of high positive charge density (alkaline earth metal cations and Li^+), while the isomerization of **NP** ligands was affected by the same cations only after UV irradiation. Some cation selectivities depending on the ring size of the crown ether binding site and the nature of the photochromic group were observed. Preliminary experiments performed with (*S*)-and (*R*)-phenylglycine evidenced a distinct chiral recognition of indolospiropyran **2b** towards the (*S*)-enatiomer, encouraging us to further investigate the utilization of our chiral crowned photochroms in optical recognition processes.

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 (frequently in the presence of a mixture of alkali picrates) 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 recored 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-1,1′-binaphtho(azacrowns) **5a–c** [28] and photochromic precursors

7 [13], **8**, **9** [29] were prepared as described in the literature.

General Procedure for the Detosylation of Binaphthocrowns (*S*)-5a–c to (*S*)-6a–c

A mixture of (S)-**5a–c** (1 mmol), freshly prepared Na/Hg (4%, 4.6 g) and dry Na_2HPO_4 (4 mmol, 0.57 g) in methanol (20 cm^3) was stirred under reflux for 24 h. After cooling the solution was decanted from the amalgam and evaporated to dryness. The residue was dissolved in $CHCl_3$ (20 cm^3), washed with 10% aqueous Na_2HPO_4 (2 × 20 cm^3), dried (Na_2SO_4) and after evaporation of the solvent, **6a–c** were obtained as yellow oils in almost quantitative yields. The crude materials were essentially pure and used directly for the next reactions.

(S)-1,1′-Binaphtho(17-azacrown-5) (6a)

98%, $[\alpha]_D^{20} = -129.6$ (c 1, $CHCl_3$); ^{1}H NMR: δ 7.92 (d, 2H, $J = 9$ Hz, Ar*H*), 7.84 (d, 2H, $J = 8$ Hz, Ar*H*), 7.49 (d, 2H, $J = 9$ Hz, Ar*H*), 7.30 (t, 2H, $J = 7$ Hz, Ar*H*), 7.19 (t, 2H, $J = 7$ Hz, Ar*H*), 7.12 (d, 2H, $J = 8.5$ Hz, Ar*H*), 4.26 (m, 2H, C*H*$_2$), 3.88 (m, 2H, C*H*$_2$), 3.57 (m 2H, C*H*$_2$), 3.51 (m 2H, C*H*$_2$), 3.41 (m 2H, C*H*$_2$), 3.27 (m 2H, C*H*$_2$), 2.63 (t, 4H, $J = 5.5$ Hz, NC*H*$_2$); ^{13}C NMR δ 154.7, 134.0, 129.4, 129.3, 127.9, 126.2, 125.3, 123.6, 120.4, 116.3, (Ar), 69.9, 69.5, 68.9, (O*C*H$_2$), 48.5 (N*C*H$_2$); FAB-MS m/z (%) 444.0 $[M + H]^+$(32), $C_{28}H_{29}NO_4$ (443.21).

(S)-1,1′-Binaphtho(23-azacrown-7) (6b)

94%, $[\alpha]_D^{20} = -65.8$ (c 1, $CHCl_3$); ^{1}H NMR: δ 7.92 (d, 2H, $J = 6.5$ Hz, Ar*H*), 7.85 (d, 2H, $J = 8$ Hz, Ar*H*), 7.46 (d, 2H, $J = 9$ Hz, Ar*H*), 7.31 (t, 2H, $J = 7$ Hz, Ar*H*), 7.20 (t, 2H, $J = 7$ Hz, Ar*H*), 7.15 (d, 2H, $J = 8.5$ Hz, Ar*H*), 4.15 (m, 2H, C*H*$_2$), 4.04 (m, 2H, C*H*$_2$), 3.61–3.20 (m 16H, C*H*$_2$), 2.78 (m 4H, NC*H*$_2$); ^{13}C NMR δ 154.5, 134.1, 129.5, 129.3, 127.8, 126.2, 125.5, 123.7, 120.9, 116.4, (Ar), 70.5, 70.4, 70.2, 70.0, 68.8 (O*C*H$_2$), 48.8 (N*C*H$_2$); FAB-MS m/z (%) 531.9 $[M + H]^+$(43), $C_{32}H_{37}NO_6$ (531.26).

(S)-1,1′-Binaphtho(20-azacrown-6) (6c)

97%, $[\alpha]_D^{20} = -54.3$ (c 1, $CHCl_3$); ^{1}H NMR: δ 7.93 (m, 2H, Ar*H*), 7.85 (m 2H, Ar*H*), 7.47 (m, 2H, Ar*H*), 7.32 (m, 2H, Ar*H*), 7.22–7.15 (m, 4H, Ar*H*), 4.15 (m, 2H, C*H*$_2$), 4.17–3.22 (m, 16H, C*H*$_2$), 2.73 (m 4H, NC*H*$_2$); ^{13}C NMR δ 154.3, 154.0, 133.9, 133.8, 130.1, 129.9, 129.7, 129.5, 128.1, 128.0, 126.4, 125.4, 124.9, 124.3, 123.8, 121.9, 119.8, 117.8, 115.9 (Ar), 70.7, 70.4, 70.2, 69.9, 69.6, 69.3, 66.3, 66.1 (O*C*H$_2$), 48.7, 48,6 (N*C*H$_2$); FAB-MS m/z (%) 487.9 $[M + H]^+$(55), $C_{30}H_{33}NO_5$ (487.23).

General Procedure for the Synthesis of Crowned Photochroms (S)-2–4

To the mixture of (S)-**6** (0.5 mmol) and triethylamine (1.5 mmol, 0.2 cm^3) in dry THF (5 cm^3) was added dropwise **7**, **8** or **9** (0.5 mmol) dissolved in 15 cm^3 dry THF. The solution was then refluxed overnight in the dark. After cooling the solvent was evaporated and the residue was chromatographed on silica (eluent: toluene-methanol = 95:5) to give **2a–c** (purple), **3a**,**b** (yellowish-green), **4a**,**b** (yellow) as greasy solids.

(S)-1,1′-Binaphtho(17-azacrown-5)-SP (2a)

59%; ^{1}H NMR: δ 8.19 (s,1H, Ar*H*), 7.92(d, 2H, $J = 9$ Hz, Ar*H*), 7.89 (d, 1H, $J = 1.5$ Hz, Ar*H*), 7.84 (d, 2H, $J = 8$ Hz, Ar*H*), 7.47 (d, 2H, $J = 9$ Hz, Ar*H*), 7.31–7.02 (m, 8H, Ar*H*), 6.90 (d, 1H, $J = 10.5$ Hz, C*H*═), 6.84 (q, 1H, Ar*H*), 6.51 and 6.45 (d, 1H, $J = 8$ Hz, Ar*H*), 5.83 (d, 1H, $J = 10.5$ Hz, C*H*═), 4.25 (m, 2H, C*H*$_2$), 3.93 (m, 2H, C*H*$_2$), 3.53 (m, 2H, C*H*$_2$), 3.35 (m, 4H, C*H*$_2$), 3.19 (m, 2H, C*H*$_2$), 2.67 and 2.65 (s, 3H, NC*H*$_3$), 2.48 (m, 2H, NC*H*$_2$), 2.36 (m, 2H, NC*H*$_2$), 1.24 (s, 3H, C*H*$_3$), 1.18 (s, 3H, C*H*$_3$); ^{13}C NMR δ 157.3, 154.7, 147.8, 140.9, 136.4, 134.3, 129.6, 129.3, 128.8, 128.0, 127.9, 126.4, 125.6, 125.5, 123.7, 121.4, 121.3, 120.6, 119.9, 118.5, 116.4, 107.2 (Ar) 128.4, 121.7 (*C*═), 107.2 (spiro *C*) 70.2, 69.9, 69.8 (O*C*H$_2$), 54.1, 52.2 (N*C*H$_2$), 53.0 (*C*(CH$_3$)$_2$), 29.0 (N*C*H$_3$), 26.1, 20.2 (CH$_3$); FAB-MS m/z (%) 778.2 $[M + H]^+$(3); anal. calcd. for $C_{48}H_{47}N_3O_7$ (777.91): C 74.11, H 6.09, found C 74.47, H 6.15%.

(S)-1,1′-Binaphtho(23-azacrown-7)-SP (2b)

73%; ^{1}H NMR: δ 8.23 (s,1H, Ar*H*), 7.91(d, 2H, $J = 9$ Hz, Ar*H*), 7.89 (d, 1H, $J = 2$ Hz, Ar*H*), 7.84 (d, 2H, $J = 8$ Hz, Ar*H*), 7.45 (d, 2H, $J = 9$ Hz, Ar*H*), 7.32–7.04 (m, 8H, Ar*H*), 6.91 (d, 1H, $J = 10.5$ Hz, C*H*═), 6.84 (m, 1H, Ar*H*), 6.51 (m, 1H, Ar*H*), 5.83 (d, 1H, $J = 10.5$ Hz, C*H*═), 4.15 (m, 2H, C*H*$_2$), 4.01 (m, 2H, C*H*$_2$), 3.60 (m, 2H, C*H*$_2$), 3.50–3.28 (m, 12H, C*H*$_2$), 2.69 and 2.68 (s, 3H, NC*H*$_3$), 2.63 (m, 4H, NC*H*$_2$), 1.27 and 1.26 (s, 3H, C*H*$_3$), 1.19 (s, 3H, C*H*$_3$); ^{13}C NMR δ 157.3, 154.5, 147.6, 140.7, 136.2, 134.0, 129.4, 129.2, 129.0, 128.2, 127.8, 126.2, 125.4, 123.6, 121.2, 121.1, 120.7, 119.7, 118.3, 116.1, 107.0 (Ar), 128.5, 121.5 (*C*═), 106.4 (spiro *C*) 70.7, 70.4, 70.0, 69.8, 69.6 (O*C*H$_2$), 53.8, 52.0 (N*C*H$_2$), 52.4 (*C*(CH$_3$)$_2$), 28.8 (N*C*H$_3$), 25.9, 20.0 (CH$_3$); FAB-MS m/z (%) 904.5 $[M + K]^+$(7), 885.5 $[M + Na]^+$(7), 866.5 $[M + H]^+$(5); anal. calcd. for $C_{52}H_{55}N_3O_9$ (866.02): C 72.12, H 6.40, found C 71.63, H 6.52%.

(S)-1,1′-Binaphtho(20-azacrown-6)-SP (2c)

32%; ^{1}H NMR: δ 8.25 (s,1H, Ar*H*), 7.94–7.83(m, Ar*H*), 7.46 (m, 2H, Ar*H*), 7.32–7.02 (m, 8H, Ar*H*), 6.91

(d, 1H, $J = 10$ Hz, CH═), 6.82 (m, 1H, ArH), 6.48 (m, 1H, ArH), 5.83 (d, 1H, $J = 10$ Hz, CH═), 4.37 (m, 1H, CH_2), 4.18 (m, 2H, CH_2), 3.99 (m, 3H, CH_2), 3.73–3.06 (m, 12H, CH_2), 2.68 and 2.66 (s, 3H, NCH_3), 2.50 (m, 2H, NCH_2), 2.42 (m, 2H, NCH_2), 1.25 and 1.24 (s, 3H, CH_3), 1.18 (s, 3H, CH_3); ^{13}C NMR δ 157.2, 154.6, 154.0, 147.7, 140.8, 136.2, 134.3, 134.1, 129.5, 129.3, 129.2, 129.1, 128.9, 128.6, 127.9, 127.5, 126.2, 125.5, 125.4, 123.7, 123.6, 123.3, 121.2, 120.7, 119.7, 118.3, 116.1, 114.7, 107.0 (Ar), 128.3, 121.5 (C═), 106.4 (spiro C) 70.9, 70.8, 70.3, 70.1, 70.0, 69.8, 69.6 67.9 (OCH$_2$), 54.2, 54.0, 52.1 (NCH$_2$), 52.4 (C(CH$_3$)$_2$), 28.9 (NCH$_3$), 25.9, 20.1 (CH$_3$); FAB MS m/z (%) 860.5 [M + K]$^+$(4), 844.4 [M + Na]$^+$(5), 822.3 [M + H]$^+$(2); anal. calcd. for $C_{50}H_{51}N_3O_8$ (821.97): C 73.06, H 6.25, found C 73.48, H 6.32%.

(S)-1,1′-Binaphtho(17-azacrown-5)-NO (3a)

59%; ^{1}H NMR: δ 8.51 (m,1H, ArH), 7.90 (m, 2H, ArH), 7.84 (d, 2H, $J = 8$ Hz, ArH), 7.71 (m, 2H, ArH), 7.45 (m, 2H, ArH), 7.32–7.00 (m, 9H, ArH, CH═), 6.83 (m, 1H, ArH), 6.52 and 6.42 (d, 1H, $J = 8$ Hz, ArH), 4.23 (m, 2H, CH_2), 3.92 (m, 2H, CH_2), 3.66–3.15 (m, 10H, CH_2), 2.71 and 2.65 (s, 3H, NCH_3), 2.58 (m, 2H, NCH_2),), 2.45 (m, 2H, NCH_2), 1.35 (s 3H, CH_3), 1.31 and 1.31 (s, 3H, CH_3); ^{13}C NMR δ 154.6, 150.3, 150.1, 147.7, 142.9, 136.1, 134.2, 129.4, 129.1, 128.6 128.2, 127.9, 127.7, 126.6, 126.2, 125.4, 124.2, 123.6, 122.7, 121.3, 120.5, 119.7, 116.2, 107.0 (Ar, C═), 98.6 (spiro C) 70.1, 69.7, 69.5 (OCH$_2$), 54.0, 50.9 (NCH$_2$), 51.6 (C(CH$_3$)$_2$), 29.6 (NCH$_3$), 25.5, 20.9 (CH$_3$); FAB-MS m/z (%) 784.6 [M + H]$^+$(11); anal. calcd. for $C_{51}H_{49}N_3O_5$ (783.96): C 78.14, H 6.30, found C 78.52, H 6.19%.

(S)-1,1′-Binaphtho(23-azacrown-7)-NO (3b)

57%; ^{1}H NMR: δ 8.52 (d, 1H, $J = 8.5$ Hz, ArH), 7.90 (d, 2H, $J = 9$ Hz, ArH), 7.83 (d, 2H, $J = 8$ Hz, ArH), 7.74 (m, 2H, ArH), 7.53 (t, 1H, $J = 7.5$ Hz, ArH), 7.43 (d, 2H, $J = 8$ Hz, ArH), 7.36 (t, 1H, $J = 7$ Hz ArH), 7.30 (t, 1H, $J = 7$ Hz ArH), 7.21–7.12 (m, 6H, ArH, CH═), 7.05 (t, 1H, $J = 6.5$ Hz ArH), 6.86 (m, 1H, ArH), 6.53 (m, 1H, ArH), 4.14 (m, 2H, CH_2), 4.02 (m, 2H, CH_2), 3.63–3.28 (m, 18H, CH_2), 2.86 (m, 2H, NCH_2), 2.72 and 2.71 (s, 3H, NCH_3), 2.68 (m, 2H, NCH_2),), 1.36 (s, 3H, CH_3), 1.34 (s, 3H, CH_3); ^{13}C NMR δ 154.6, 150.3, 150.1, 147.6, 142.9, 136.0, 134.2, 129.5, 129.3, 128.6 128.0, 127.9, 127.7, 126.7, 126.3, 125.6, 124.2, 123.7, 121.5, 121.4, 120.8, 119.8, 116.3, 107.1 (Ar, C═), 98.5 (spiro C) 70.8, 70.5, 70.1, 70.0 (OCH$_2$), 53.8, 51.7 (NCH$_2$), 51.7 (C(CH$_3$)$_2$), 29.7 (NCH$_3$), 25.6, 21.0 (CH$_3$); FAB-MS m/z (%) 910.4 [M + K]$^+$(4), 894.4 [M + Na]$^+$(3), 872.4 [M + H]$^+$(7);anal. calcd. for $C_{55}H_{57}N_3O_7$ (872.07): C 75.75, H 6.59, found C 75.28, H 6.41%.

(S)-1,1′-Binaphtho(17-azacrown-5)-NP (4a)

74%; ^{1}H NMR: δ 7.91 (d, 1H, $J = 6$ Hz, ArH), 7.89 (d, 2H, $J = 9$ Hz, ArH), 7.83 (d, 2H, $J = 8$ Hz, ArH), 7.73 (s, 1H, ArH), 7.53 (d, 1H, $J = 8$ Hz, ArH), 7.49–7.38 (m, 7H, ArH), 7.31–7.11 (m, 14H, ArH, CH═), 6.19 (d, 1H, $J = 10$ Hz CH═), 4.26 (m, 2H, CH_2), 3.94 (m, 2H, CH_2), 3.85 (q, 2H, NCH_2), 3.55 (m, 2H, NCH_2), 3.45–3.32 (m, 6H, CH_2), 2.75 (m, 2H, NCH_2), 2.58 (m, 2H, NCH_2); ^{13}C NMR δ 154.8, 149.4, 145.3, 145.1, 134.4, 130.0, 129.6, 129.3, 129.2, 129.0, 128.6 128.5, 128.4, 128.2, 128.1, 127.6, 127.2, 127.1, 126.4, 126.2, 125.6, 123.7, 121.2, 120.6, 120.2, 116.2, 113.9 (Ar), 82.8 (CPh$_2$) 70.4, 69.9, 69.6, (OCH$_2$), 54.8, 54.7 (NCH$_2$); FAB-MS m/z (%) 790.5 [M + H]$^+$(6); anal. calcd. for $C_{54}H_{47}NO_5$ (789.97): C 82.10, H 6.00, found C 81.89, H 6.09%.

(S)-1,1′-Binaphtho(23-azacrown-7)-NP (4b)

62%; ^{1}H NMR: δ 7.92 (d, 1H, $J = 9$ Hz, ArH), 7.89 (d, 2H, $J = 9$ Hz, ArH), 7.82 (d, 2H, $J = 8$ Hz, ArH), 7.80 (s, 1H, ArH), 7.68 (d, 1H, $J = 8$ Hz, ArH), 7.51–7.40 (m, 7H, ArH), 7.33–7.12 (m, 14H, ArH, CH═), 6.21 (d, 1H, $J = 10$ Hz CH═), 4.16 (m, 2H, CH_2), 4.03 (m, 2H, CH_2), 3.91 (q, 2H, NCH_2), 3.59–3.29 (m, 16H, CH_2), 2.84 (m, 4H, NCH_2); ^{13}C NMR δ 154.6, 149.3, 145.1, 134.2, 130.0, 129.8, 129.5, 129.3, 129.1, 129.0, 128.5 128.3, 128.1, 127.9, 127.5, 127.2, 127.1, 126.3, 126.2, 125.6, 123.7, 121.2, 120.8, 120.1, 116.3, 113.7 (Ar), 82.7 (CPh$_2$) 70.8, 70.6, 70.2, 70.1, 70.0 (OCH$_2$), 54.3 (NCH$_2$); FAB-MS m/z (%) 916.3 [M + K]$^+$(7), 900.3 [M + Na]$^+$(5), 878.4 [M + H]$^+$(10); anal. calcd. for $C_{58}H_{55}NO_7$ (878.07): C 79.34, H 6,31, found C 79.14, H 6.22%.

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