Synthesis and complexation properties of photochromic benzochromenes containing aza- and diaza-18-crown-6-ether fragments

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Complex formation of Mg^{2+} , Ba^{2+} , and Pb^{2+} perchlorates with 3,3-diphenyl-3*H*-benzo[*f*]chromenes containing aza- and diaza-18-crown-6-ether or morpholine fragments was studied. The strong influence of the metal cations on the spectral characteristics of these organic ligands and on the kinetic of photochromic transformations was found. The results obtained were explained by the formation of carbonyl-"capped" complexes of various structures.

Key words: aza-18-crown-6 ethers, 3,3-diphenyl-3H-benzo[f]chromenes, complex formation, photoinduced transformations, carbonyl-"capped" complex, magnesium complexes, barium complexes, lead complexes.

Photochromic compounds attract attention due to a possibility of using them as photochromic coatings, lenses, films, optical memory elements, and photoswitches. $^{1-5}$ To improve their characteristics, chemical modification is used through introduction of diverse substituents differing in nature into the molecule skeleton.⁶⁻⁸ An alternative method for changing the photochromic properties of the compounds is the introduction of ionophoric fragments capable of binding to metal cations. Complex formation often affects substantially the characteristics of photochromic compounds.^{9–15} However, the synthesis and properties of benzochromenes containing ionophoric fragments are poorly studied: only several crown-containing benzochromenes were described.¹⁶⁻¹⁸ The synthesis of benzochromenes with ionophoric fragments is not only of theoretical interest but can induce the preparation of new optical sensors for metal cations, photoswitchable extracting complexones, and metal cation carriers through membranes.

In the present work, we synthesized benzochromenes **1a,b** containing morpholine and aza-18-crown-6-ether fragments as substituents and diaza-18-crown-6 ether **1c** with two benzochromene substituents. A known procedure of three-step synthesis^{18,19} (Scheme 1) was used to synthesize these compounds. Since aza- and diazacrown ethers can bind with a wide range of metal cations differing in nature, it seemed reasonable to analyze the types of complexes formed from metal cations with ligands 1a-c and the influence of complex formation on the photochemical and spectral properties of the latter.

Complex formation of the closed form of benzochromenes 1a—c. Compounds 1a—c in acetonitrile have similar UV spectra. The addition of metal cations (Li⁺, Na⁺, Mg²⁺, Sr²⁺, Ba²⁺, Ag⁺, Cd²⁺, Pb²⁺) to solutions of benzochromenes induce slight shifts (to 5 nm) of the absorption band (Table 1). Since the crown-ether fragment is not conjugated with the chromophoric moiety of the molecule, metal cation binding with the ionophoric fragment induces only slight shifts in the position of the long-wavelength absorption band for the closed form.

The changes in the position of signals for protons in the ¹H NMR spectra of benzochromenes 1a-c upon the addition of perchloric acid or Ca²⁺, Ba²⁺, and Pb²⁺ perchlorates are shown in Table 2. In the presence of the alkaline-earth metal cations, the NMR spectrum of compound 1a exhibits insignificant changes. When lead perchlorate is added to a solution of ligand 1a, almost all signals for protons undergo downfield shift similarly to the shift occurred upon the addition of perchloric acid to a solution of ligand 1b. The nitrogen atom of the crownether fragment of 1b is protonated under acidic conditions; the quaternized N atom becomes a withdrawing substituent. Lead cations are capable, most likely, of coordinating at the nitrogen atom of the morpholine residue, which shifts signals for protons in the spectrum. The

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Scheme 1

addition of the metal salts to crown-containing benzochromenes **1b,c** induces metal cation binding to the crown-ether fragment (Scheme 2), which reflects in the shape of the ¹H NMR spectrum. However, the character of the changes observed differs substantially from that found for benzochromene **1a**, as well as for benzochromene **1b** in the presence of perchloric acid in the solution (see Table 2).

Scheme 2



M^{z+} = Li⁺, Na⁺, Mg²⁺, Sr²⁺, Ba²⁺, Ag⁺, Cd²⁺, Pb²⁺

Substantial shifts of signals for the protons of the methylene groups in the crown-ether fragment were revealed. Their analysis suggests the structures of the complexes. For example, the Ca^{2+} cations are relatively small for the cavity of the 18-crown-6-ether fragment. The character of shifts of the signals shows the strongest coordination with the oxygen atoms and, hence, the greatest shifts were observed for the H_{δ} , H_{ω} , and H_{σ} protons. The size of the Ba^{2+} cations corresponds to the cavity of the 18-crown-6-ether fragment, which allows them to coordinate with all heteroatoms. Coordination of the lead cations with the oxygen atoms of the crown-ether ring is weaker than that of the alkaline-earth metal cations.

Interestingly, the signal of the H(6) proton of the naphthalene fragment of crown-containing benzochromenes **1b,c** (δ 7.89) exhibits a downfield shift compared to a similar signal for the proton of morpholine derivative 1a (δ 7.75). Since the electronic effects of the morpholine and azacrown-ether substituents should be close, the differences observed in the ¹H NMR spectra are caused, most likely, by other factors. Another unusual fact found for this proton is related to the upfield shift of the signal from the H(6) proton (see Table 2) induced by the addition of the metal cations to crown-containing compounds **1b,c**, while the signals for other protons of the naphthalene ring undergo downfield shifts. Perhaps, this effect is due to the conformational rearrangement of the compound, which occurs during complex formation at the crown-ether fragment.

The shift of the signal for the H(8) proton of the naphthalene ring for the complexes under study is always slightly greater than those for other naphthalene protons. The fact observed agrees with the known data¹⁹ that the donor and acceptor effects of substituents are especially pronounced when the substituents occupy position 8 of the naphthalene ring.

Table 1. Spectral parameters (λ_{max}) of the initial forms of chromenes **1a**—**c**, photoinduced merocyanine forms **2a**—**c**, and their complexes with different metal cations; absorption of the merocyanine form (A_2^{max}) in the photostationary state and the rate constants of thermal relaxation of the colored form (k_{2-1}) $(C_1/C_M = 1:100, \text{ MeCN}, 25 \,^{\circ}\text{C})$

Initial	Cation	λ_1	λ_2	A_2^{\max}	k_{2-1}
chromene		n	m		/\$ 1
1a	_	355	422	0.52	0.50
	Li ⁺	355	430	0.38	0.17
	Na ⁺	355	430	0.33	0.13
	Mg^{2+}	360	460	0.22	0.024
	Sr ²⁺	355	420	0.34	0.16
	Ba ²⁺	355	420	0.36	0.15
	Ag^+	365	462	0.82	0.39
	Cd^{2+}	360	467	0.72	0.30
	Pb ²⁺	365	465	0.21	0.67
1b	_	355	420	0.42	0.09
	Li ⁺	360	450	0.63	0.008
	Na ⁺	360	440	0.65	0.013
	Mg^{2+}	365	470	0.34	0.16
	Sr ²⁺	360	470	0.70	0.002
	Ba ²⁺	360	460	0.68	0.006
	Ag^+	365	460	0.48	0.26
	Cd^{2+}	365	495	0.68	0.004
	Pb ²⁺	360	500	0.70	0.011
1c	_	360	405	0.31	0.08
	Li ⁺	360	440	0.42	0.042
	Na ⁺	360	430	0.55	0.015
	Mg ²⁺	360	470	0.45	0.13
	Sr ²⁺	360	465	0.43	0.004
	Ba ²⁺	360	450	0.53	0.005
	Ag^+	355	460	0.20	0.13
	Cd^{2+}	360	490	0.53	_
	Pb ²⁺	360	490	0.58	0.006

Complex formation of the open form of benzochromenes 1a-c. When chromenes **1a,b** are irradiated with the light at the 365-nm wavelength, the conversion to the corresponding merocyanine forms **2a,b** in the photostationary state is rather high (>80%) (Scheme 3). Under the same photoexcitation conditions, the conversion of chromene **1c** to merocyanine form **2c** does not exceed 50%. It is most likely that in the molecule of **1c** two chromene

Scheme 3



residues are rather rigidly bonded through the crownether fragment resulting in steric hindrance on going from the compact closed form to the longer open form of benzochromene. The long-wavelength absorption bands of merocyanine colored forms **2a,b** lie at 420 nm, while for **2c** these bands are observed at 405 nm.

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Under the dark conditions, forms $2\mathbf{a}-\mathbf{c}$ of the chromenes under study return rather slowly to their initial states $1\mathbf{a}-\mathbf{c}$, being the lowest in energy, which is caused by the presence of the morpholine or crown-ether fragments in their structures. The rate of this process is much slower for chromene **1c** than for **1b** (see Table 1).

The introduction of the alkaline metal salts into solutions of chromene **1a** exerts virtually no effect on the position of the long-wavelength absorption band of the merocyanine form of this compound (see Table 1). In the case of crown-containing chromenes **1b,c**, the presence of lithium in solutions of perchlorates shifts this band to the long-wavelength region by 30 and 20 nm, respectively, and the conversion to the merocyanine colored form for these compounds reaches nearly 100%. A similar behavior is observed when the Na⁺ salts are introduced into the solutions, but the observed shifts of the longwavelength absorption bands of the complexes of the merocyanine form of crown-containing chromenes are smaller than those in the case when the Li⁺ cations are introduced.

In the case of the alkaline-earth metals, the complex formation of merocyanine form **2a**, as follows from an analysis of the absorption spectra (see Table 1), is pronounced only for the Mg²⁺ cations (λ_{max} shifts to 40 nm) at rather high concentrations of the salts introduced into the solutions. This compound forms virtually no complexes with the Sr²⁺ and Ba²⁺ cations, whereas the spectra of forms **2b**,**c** in the presence of these ions exhibit considerable shifts (more pronounced for the Sr²⁺ cations as compared to the Ba²⁺ cations and greater for compound **2b** than for **2c**) (Fig. 1; see also Table 1).

The introduction of the alkaline and alkaline-earth metal salts into the solutions decreases the rate constant of thermal relaxation of merocyanine form 2a, which is more substantial for the Mg²⁺ cation. This agrees with a considerable influence of this cation on the spectral characteristics of merocyanine form 2a for complex formation.

The rate constant of thermal relaxation for merocyanine forms **2b,c** of crown-containing chromenes **1b,c** (k_{2-1}) , unlike the constant for chromene **1a**, are characterized by a more pronounced dependence of the nature of the metal involved in complex formation. As follows from the results presented in Table 1, the most stable complexes are formed with the Sr²⁺ cations, somewhat less stable complexes are characteristic of the Ba²⁺ cations, and the least stable complexes are formed with the Mg²⁺ cations.

Table 2.	2. Chemical shifts of signals for protons of benzochromenes $1a-c$ (δ) and their complexes with the Ca ²⁺ , Ba ²⁺ , and Pb ²⁺ cations in the ¹ H NMR s
CD ₃ CN	N (the changes in chemical shifts of signals for protons ($\Delta\delta$) upon complex formation of benzochromenes $1a-c$ with the cations are given in par
$(\Delta \delta = \delta)$	6(complex) – 6(ligand)))

$CD_3CN (t)$ $(\Delta \delta = \delta(co)$	he chang mplex) –	es in chen 8(ligand))	nical shift	ts of signa	uls for pro	tons $(\Delta \delta)$	npon co.	mplex for	nation of	benzochr	omenes 1	, and rough a a-c with	the catio	ins are giv	en in par	entheses
Com- pound	H(1)	H(2)	H(6)	H(7)	H(8)	H(9)	H(10)	H(2 [°]), H(2 ["])	H(3'), H(3'')	H(4'), H(4")	CH_2	$\substack{H_{\alpha^{\prime}}}_{H_{\alpha^{\prime}}}$	$\substack{H_{\beta},\\H_{\beta^{\prime}}}$	$\begin{array}{c} H_{\gamma}, H_{\gamma'}; \\ H_{\delta}, H_{\delta'} \end{array}$	$\underset{H_{\sigma^{'}}}{H_{\sigma^{'}}}$	$\underset{H_{\omega,}}{H_{\omega,}}$
la	7.44	6.51	7.75	7.78	7.37	7.49	8.02	7.63	7.36	7.27	3.78	2.57	3.70	I	I	
1a · Ca ²⁺	7.49 (0.05)	6.44 (-0.07)	7.92 (0.17)	7.84 (0.06)	7.45 (0.08)	7.60 (0.11)	8.10 (0.08)	7.54 (-0.09)	7.39 (0.03)	7.32 (0.05)	4.37 (0.59)	3.07 (0.5)	3.74 (0.04)	Ι	Ι	I
la · Pb ²⁺	7.51 (0.07)	6.43 (-0.08)	7.98 (0.23)	7.87 (0.09)	7.48 (0.11)	7.64 (0.15)	8.14 (0.12)	7.52 (-0.11)	7.41 (0.05)	7.34 (0.07)	4.58 (0.80)	3.34 (0.77)	3.92 (0.22)	Ι	I	I
la ⋅ Ba ²⁺	7.42 (-0.02)	6.48 (-0.03)	7.74 (-0.01)	7.76 (-0.02)	7.35 (-0.02)	7.48 (-0.01)	8.00 (-0.02)	7.60 (-0.03)	7.34 (-0.02)	7.25 (-0.02)	3.81 (0.03)	2.59 (0.02)	3.68 (-0.02)	I	I	I
1b	7.42	6.43	7.89	7.79	7.34	7.45	7.98	7.56	7.34	7.25	3.94	2.82	3.56	3.56	3.47	3.56
1b. Ca ²⁺	7.46 (0.04)	6.45 (0.02)	7.73 (-0.16)	7.80 (0.01)	7.40 (0.06)	7.52 (0.07)	8.03 (0.05)	7.44 (-0.12)	7.39 (0.05)	7.33 (0.08)	4.28 (0.34)	2.66 (-0.16)	3.61 (0.05)	3.76 (0.20)	3.68 (0.21)	3.84 (0.28)
1b · Pb ²⁺	7.49 (0.07)	6.53 (0.10)	7.74 (-0.15)	7.84 (0.05)	7.43 (0.09)	7.55 (0.10)	8.06 (0.08)	7.48 (-0.08)	7.40 (0.06)	7.35 (0.10)	4.46 (0.52)	3.73 (0.91)	3.75 (0.19)	3.80 (0.24)	3.75 (0.28)	3.84 (0.28)
1b•Ba ²⁺	7.45 (0.03)	6.51 (0.08)	7.60 (-0.29)	7.80 (0.01)	7.38 (0.04)	7.51 (0.06)	8.01 (0.03)	7.45 (-0.11)	7.38 (0.04)	7.32 (0.07)	4.31 (0.37)	3.63 (0.81)	3.70 (0.14)	3.73 (0.17)	3.64 (0.17)	3.80 (0.24)
1b•H ⁺	8.09 (0.67)	7.05 (0.62)	8.58 (0.69)	8.44 (0.65)	8.05 (0.71)	8.20 (0.75)	8.67 (0.69)	8.06 (0.50)	7.97 (0.63)	7.91 (0.66)	5.24 (1.30)	3.82 (1.00)	4.19 (0.63)	4.17 (0.61)	4.15 (0.68)	4.26 (0.70)
1c	7.45	6.50	7.89	7.76	7.32	7.46	8.00	7.59	7.35	7.25	3.97	2.88	3.63	3.52	Ι	Ι
1c •Ca ²⁺	7.49 (0.04)	6.47 (-0.03)	7.77 (-0.12)	7.84 (0.08)	7.42 (0.10)	7.55 (0.09)	8.06 (0.06)	7.47 (-0.12)	7.42 (0.07)	7.37 (0.12)	4.37 (0.40)	2.82 (-0.06)	3.59 (-0.04)	3.68 (0.16)	I	Ι
lc∙Pb ²⁺	7.49 (0.04)	6.53 (0.03)	7.78 (-0.11)	7.87 (0.11)	7.42 (0.10)	7.54 (0.08)	8.06 (0.06)	7.42 (-0.17)	7.42 (0.07)	7.38 (0.13)	4.36 (0.39)	2.70 (-0.18)	3.56 (-0.07)	3.56 (0.04)	I	I
Note. $C_{\rm L} =$	$5 \cdot 10^{-3} \text{ m}$	nol L ⁻¹ , C_1	$M = 2.5 \cdot 1$	10 ⁻² mol 1	L ⁻¹ (for co	omplexes	1b • Pb ²⁺	and 1c · Pb	$C^{2+} C_{\rm M} = 0$	5 • 10 ⁻² mc	ol L ⁻¹ ; for	· 1b · H ⁺ C	$C_{\rm L} = C_{\rm M} =$	8.2 • 10 ⁻³	mol L ⁻¹)	



Fig. 1. Absorption spectra of the initial chromene **1b** (*I*) and chromene **1b** in the presence of Mg(ClO₄)₂ (2), Ba(ClO₄)₂ (3), and Pb(ClO₄)₂ (4) in solution irradiated with the light at the 365-nm wavelength ($C_{\rm L} = 2 \cdot 10^{-4} \text{ mol L}^{-1}$, MeCN).

The presence of salts of transition (Ag^+, Cd^{2+}) and heavy (Pb^{2+}) metals in solutions of the compounds under study results in the efficient formation of complexes of the merocyanine form with cations of these metals, which follows from the character of the spectra. However, for solutions of these compounds, in the presence of the Ag⁺ ions, the positions of the absorption bands of the complexes virtually coincide, whereas in the presence of the Cd^{2+} and Pb^{2+} cations the observed spectral shifts for crown-containing forms **2b,c** are much greater than those for form **2a** containing the morpholine residue.

According to the rate constants of thermal relaxation of the merocyanine form (see Table 1), the Cd^{2+} and Pb^{2+} salts are characterized by a high degree of stabilization of the complexes of crowned chromenes, whereas the introduction of silver perchlorate destabilizes merocyanine colored forms **2b,c**.

It should be taken into account for an analysis of the observed spectral effects that the complex formation of merocyanine forms 2b,c can involve two coordination centers, namely, the crown-ether fragment and the carbonyl oxygen atom. The shifts of the absorption bands for compound 2a during complex formation depend mainly on the efficiency of interaction between the metal cation and the oxygen atom of the merocyanine form.

The Li⁺ and Na⁺ ions are much smaller than the cavity of aza-18-crown-6 ether and, hence, complexes of these cations with the ionophoric fragment are, most likely, very unstable. Therefore, for compounds 2a-c the main contribution to complex formation with the Li⁺ and Na⁺ ions is made by metal cation binding at the carbonyl oxygen atom (Scheme 4).

As a result of this complex formation, the absorption spectra are shifted to the long-wavelength region, because the carbonyl oxygen atom is a part of the chromophoric system of the molecule. In addition, the formation of the oxygen—metal coordination bond prevents, most likely,



Scheme 4

 $M^{+} = Li^{+}, Na^{+}$

ring closure, which is observed as the stabilization effect of the open merocyanine form (see Table 1).

The presence of the Sr^{2+} , Ba^{2+} , Ag^+ , Cd^{2+} , and Pb^{2+} cations in the photochromic transformations of chromene **1a** exerts a weak effect on the stabilization of the open form. Probably, the effect observed can be explained by the low charge density on the alkaline-earth metal cations and the low affinity of other cations to the carbonyl oxygen atom (see Table 1).

For merocyanine forms 2b,c, one can propose the coordination of the metal cations (Mg²⁺, Sr²⁺, Ba²⁺, Ag⁺, Cd^{2+} , Pb^{2+}) primarily at the crown-ether fragment to form complexes of different structures. For instance, note a considerable stabilization effect of the merocyanine form for the Sr²⁺, Ba²⁺, Cd²⁺, and Pb²⁺ ions, which increases its lifetime by thousands times (see Table 1). It is clear that this effect can be due to the incorporation of the metal cation into the cavity of the crown-ether fragment. The crown-ether fragment is bonded to the chromene molecule through the methylene spacer, which is not a part of the chromophoric system of benzochromene and cannot significantly change the electron density distribution in the system of conjugated bonds and the ability to the closure reaction. This can occur only if the oxygen atom of the merocyanine form is involved in complex formation, *i.e.*, when a carbonyl-"capped" complex is formed (Scheme 5). The participation of the oxygen atom in the coordination of the metal cation bonded to the macrocycle substantially stabilizes the open form. This has been observed previously²⁰ for spironaphthooxazines containing the azacrown-ether fragment as a substituent.

Since the Ag^+ cation has a low charge density and a low oxygen affinity and the diameter of the Mg^{2+} cation is much smaller than the cavity of aza-18-crown-6 ether, the participation of these cations in the formation of carbonyl-"capped" complexes seems less probable. It can be assumed that the addition of silver and magnesium perchlorates induces the formation of a complex involving the macrocycle (see Scheme 5). In such a complex, probably, the electron density will be withdrawn to the metal cation, which would result in some decrease in the electron density on the carbonyl oxygen atom. As a result, the

Scheme 5



inverse transformation into the closed form of benzochromene would be accelerated. In fact, in the presence of the silver and magnesium cations, the rate constant of relaxation of merocyanine forms **2b,c** increases (see Table 1).

An interesting difference was observed for the influence of the Ba²⁺, Cd²⁺, and Pb²⁺ cations on the stabilization of the open form of chromene **2c** (Table 3). Experiments showed that equimolar additives of Cd²⁺ and Pb²⁺ to a solution of chromenes **2b,c** give similar values for the decrease in the rate constant of dark relaxation. In the presence of the Ba²⁺ cations, the decrease in k_{2-1} for bischromene **2c** is an order of magnitude higher than similar value for monochromene **2b**.

We believe that the above-described experimental facts are caused by the formation of carbonyl-"capped" complexes differing in structure, which appear in the presence of the Ba²⁺, Cd²⁺, and Pb²⁺ cations (Scheme 6). Close k_{2-1} values obtained for the complexes of crown-containing forms **2b,c** with the Cd²⁺ and Pb²⁺ cations indicate, probably, that the structures of the formed carbonyl-"capped" complexes are similar. It is most likely that compound **2c** with the Cd²⁺ and Pb²⁺ cations forms complexes involving the crown-ether fragment and the oxygen atom of one of merocyanines of benzochromene,

Table 3. Rate constants of thermal relaxation of colored forms **2a**-**c** of benzochromenes **1a**-**c** (k_{2-1}/s^{-1}) and their complexes with the Ba²⁺, Pb²⁺, and Cd²⁺ cations $(C_L/C_M = 1 : 1, MeCN, 25 °C)$

Com-		Cation				
pound	_	Ba ²⁺	Pb ²⁺	Cd ²⁺		
2a	0.11	0.18	0.12	0.36		
2b	0.11	0.0016	0.00035	0.0042		
2c	0.15	0.00034	0.00054	0.006		

which are similar to the carbonyl-"capped" complex formed by merocyanine form **2b**. The second fragment of benzochromene is not involved in the formation of the carbonyl-"capped" complex.



The substantial decrease in the k_{2-1} value for complex **2c** with the Ba²⁺ cation can be explained by the participation of the oxygen atom of the second merocyanine benzochromene in the formation of the carbonyl-"capped" complex. The additional coordination bond just leads to the further stabilization of a complex of the open form of bis(benzochromene) **2c**.

Thus, it is shown in the present work for crown-containing benzochromene **1b**, bis(benzochromene) **1c**, and model chromene **1a** having the morpholine residue instead of the crown-ether fragment how metal cations differing in nature and size affect the spectral and kinetic characteristics of the crown-containing photochromic compounds. Coordination of the metal cations can occur at the oxygen atom of the merocyanine form, which stabilizes the open form and shifts absorption maxima to the long-wavelength region. However, the strength of this coordination bond is low.¹⁷ Complex formation at the crown-ether fragment does not exert a substantial influence on the spectral and kinetic characteristics of the molecule, because this fragment is not conjugated with the skeleton of the photochromic molecule. The strongest binding of the metal cation and the most pronounced influence on the spectral and kinetic characteristics were observed for the carbonyl-"capped" complexes, whose formation simultaneously involved two coordination centers, namely, the crown-ether fragment and the oxygen atom of the merocyanine form. It is shown that carbonyl-"capped" complexes involving one or two benzochromene molecules can be formed in the case of bis(benzochromenes). Therefore, the barium, strontium, lead, and cadmium cations are most promising for binding the azaand diazacrown compounds containing one or two chromene residues. Cations of this type can provide efficient photocontrol of complex formation due to high distinctions in the spectral characteristics of the free and complexed ligands and substantial differences in stability of the complexes in the closed and open forms.

Experimental

¹H NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 MHz, 25 °C) using Me₄Si as the internal standard. Chemical shifts and spin-spin coupling constants were determined with an accuracy of 0.01 ppm and 0.1 Hz, respectively. Mass spectra were obtained on a Varian MAT 311A instrument (ionization energy 70 eV). The course of the reactions was monitored by TLC on 25 DC-Alufolien Kieselgel 60 F₂₅₄ and DC-Alufolien Aluminiumoxid 60 F₂₅₄ neutral (type E) plates (Merck). Silica gel 60 (0.063–0.200 mm) and aluminium oxide 150 (basic, type T, Merck) were used for column chromatography. 5-Bromomethyl-3,3-diphenyl-3*H*-benzo[*f*]chromene was synthesized according to a described procedure.^{21,22} Azacrown ethers, morpholine, and other reagents (Aldrich) were used as received.

Synthesis of chromenes 1a—c (general procedure). Azacrown ether or morpholine (0.2 mmol), 5-bromomethyl-3,3-diphenyl-3*H*-benzo[*f*]chromene (80 mg, 0.2 mmol; for diazacrown ether 160 mg, 0.4 mmol), triethylamine (60 mg, 0.6 mmol; for diazacrown ether 120 mg, 1.2 mmol), and anhydrous THF (25 mL) were placed in a three-necked flask under a nitrogen atmosphere. The reaction mixture was refluxed for 6 h. The solvent was evaporated, and the product was purified by column chromatography.

5-Morpholinomethyl-3,3-diphenyl-3*H***-benzo**[*f*]**chromene** (1a) was purified on SiO₂ (benzene—MeOH (10 : 1) mixture as eluent). The yield was 52 mg (57%), m.p. 150—152 °C (from hexane). Found (%): C, 83.18; H, 6.32; N, 3.19. $C_{30}H_{27}NO_2$. Calculated (%): C, 83.11; H, 6.28; N, 3.23. ¹H NMR (DMSO-d₆), δ : 3.30 (m, 4 H, NCH₂); 3.62 (m, 4 H, OCH₂); 3.74 (s, 2 H, PhCH₂); 6.61 (d, 1 H, H(2), J = 9.7 Hz); 7.24 (m, 2 H, H(4'), H(4'')); 7.34 (m, 5 H, H(8), 2 H(3'), 2 H(3'')); 7.47 (m, 2 H, H(1), H(9)); 7.60 (m, 4 H, 2 H(2'), 2 H(2'')); 7.75 (br.s, 1 H, H(6)); 7.80 (d, 1 H, H(7), J = 8.0 Hz); 8.06 (d, 1 H, H(10), J = 8.5 Hz). Mass spectrum, m/z (I_{rel} %)): 433 [M⁺] (22), 348 (37), 266 (100), 191 (33), 165 (23), 115 (22), 103 (26), 87 (65), 69 (51), 55 (67).

16-[(3,3-Diphenyl-3*H*-benzo[*f*]chromen-5-yl)methyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (1b).¹⁸ Oil, purified on Al_2O_3 (CH₂Cl₂-MeOH (9 : 1) mixture as eluent). The yield was 43 mg (35%).

7,16-Bis[(3,3-diphenyl-3*H*-benzo[*f*]chromen-5-yl)methyl]-**1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (1c)** was purified on Al₂O₃ (CH₂Cl₂—MeOH (9 : 1) mixture as eluent). The yield was 69 mg (30%), m.p. 178—182 °C (from hexane). Found (%): C, 77.48; H, 6.55; N, 2.69. $C_{64}H_{62}N_2O_6 \cdot 2H_2O$. Calculated (%): C, 77.55; H, 6.71; N, 2.83. ¹H NMR (CDCl₃), δ : 2.95 (t, 8 H, NCH₂, *J* = 5.8 Hz); 3.58 (s, 8 H, OCH₂); 3.67 (t, 8 H, OCH₂, *J* = 5.8 Hz); 3.98 (s, 4 H, PhCH₂); 6.25 (d, 2 H, H(2), *J* = 10.1 Hz); 7.25 (m, 4 H, H(4'), H(4'')); 7.31–7.37 (m, 12 H, H(8), H(3'), H(3''), H(1)); 7.44 (m, 2 H, H(9)); 7.55 (m, 8 H, H(2'), H(2'')); 7.74 (d, 2 H, H(7), *J* = 7.8 Hz); 7.85 (br.s, 2 H, H(6)); 7.95 (d, 2 H, H(10), *J* = 8.4 Hz).

Study of complex formation by NMR spectroscopy. Complexes of **1a**—c with the Ca²⁺, Ba²⁺, and Pb²⁺ cations were prepared as follows. Calcium, barium, and lead perchlorates $(1.5 \cdot 10^{-5} \text{ mol})$; for complexes **1b** · Pb²⁺ and **1c** · Pb²⁺ 3 · 10⁻⁵ mol) and ligands **1a**—c (3 · 10⁻⁶ mol) were dissolved in CD₃CN (0.6 mL). The complex of **1b** with HClO₄ was synthesized according to the following procedure: compound **1b** and HClO₄ (4.92 · 10⁻⁶ mol) were dissolved in 0.6 mL of CD₃CN. The corresponding spectra are presented in Table 2.

Spectrophotometric and kinetic measurements. Spectrophotometric measurements were carried out in solutions of acetonitrile (Aldrich, water content 0.005%). Magnesium, barium, and lead perchlorates (reagent grade) were used for complex formation. The ratio of concentrations of the metal salts and ligands (C_M/C_L) was varied from 0.1 to 100 at $C_L = 2 \cdot 10^{-4}$ mol L⁻¹. Electronic absorption spectra of solutions were measured on a Cary 50 spectrophotometer in cells with the 0.2-cm optical path length at 25 °C. Photostationary absorption spectra were measured on a USB2000 fiber-optical spectrometer (Ocean Optics) with a continuous irradiation of the solutions with the light at the 365-nm wavelength from a DRSh-250 gas-discharge mercury lamp. Kinetic experiments were carried out using a laboratory setup providing measurements of the kinetics of photoprocesses in the time interval from 1 ms.

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