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Photoinduced control of cation binding ability of non-conjugated bichromophoric receptors

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Abstract

Several receptors based on nonconjugated bichromophores displaying phototunable cation binding properties have been designed and studied. Some of these systems undergo a reversible photocyclisation to produce a crown ether or a cryptand; the photoswitching induces *significant changes on a long time scale* (hours to months after illumination) of the complexing ability of the material. Other bitopic receptors display a *sudden and transitory change* of cation concentration only during the singlet excited state lifetime.

Keywords: Coronands; Photocontrol of cation binding; Photoswitches; Supramolecular photochemistry

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1. Introduction

Supramolecular systems incorporating a photoactive centre associated with a cation complexing subunit are of interest in the design of molecular switching devices [1], for the photocontrol of the cation transport flux, and for the light-triggered delivery of an ionic species in a given medium.

As recently reported by us and others [2,3], the photoswitching efficiency is fundamentally dependent on the nature of the photosensitive centre which drives the chemical event following the light exposure. Among the molecular systems explored, several exhibit a light-tunable binding ability. In a reciprocal fashion, luminescence and/or photochemical properties of a photoactive supramolecular system can be affected by the guest bound to the complexing subunit. These effects are used for the construction of luminescent and photoresponsive sensors for metal ions and other species [3,4].

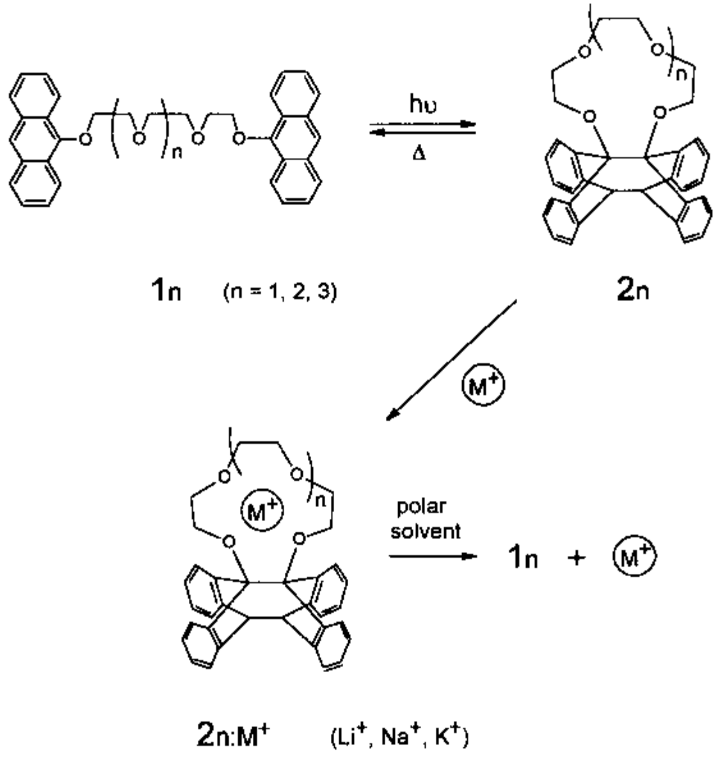
In the present contribution, typical examples of molecular photoswitches designed and developed in our group are reported. Emphasis is placed on the role played by the bound cationic species on the photophysics of the receptor and the influence of the photochemistry on complexation. These systems are constituted of coronands incorporating paradioxyaryl chromophores directly tethered to the complexing subunits represented by polyoxaalkane chains. Aromatic hydrocarbons were chosen as chromophores because they are usually characterized by a strong and often dual fluorescence (resulting from excimer formation) which may be combined with photoreactivity [5]. Anthracene and benzene were selected for their complementary optical response from the UV to the visible range accompanied with a clean and clear-cut photophysical and photochemical behaviour.

2. From α,ω-bis (9-anthryl) polyoxaalkanes to crown ethers

2.1. The photoextraction of cations

Linking two 9-anthryl groups with a polyoxyethylene chain gives the fluorescent podands **1n** [6] in which the chain is the complexing subunit and the anthracenes the light absorbing moieties. Upon UV irradiation these linear flexible bichromophoric compounds were found to efficiently cycloisomerize to produce crown ethers **2n,** dubbed *photocrowns* because they were the first coronands to be prepared photochemically. The high cyclisation quantum yields ranging from 0.27 ($n = 1$) to 0.20 ($n = 4$) underline the great flexibility of the polyoxaalkane sequence due to the presence of oxygen atoms in the chain [5]. These *photocrowns* **2n** cannot be isolated since they are thermally cleaved to the starting materials **1n**, at room temperature. Addition of a metal cation (alkali and alkaline-earth perchlorate) to a fluid solution of **1n** (diethyl ether, acetonitrile…) was found to modify neither the fluorescence emission spectrum nor the photocycloaddition quantum yield; besides, no modifications were observed on their UV spectra. These facts indicate that podands **1n** do not significantly coordinate the cations tested and cannot be used as fluorescent sensors for their detection (Scheme 1).

Nevertheless, UV irradiation of $\mathbf{1}_1$ in $LiClO_4$ saturated diethyl ether produced a stable white precipitate corresponding to the 1:1 complex [$\mathbf{2}_1$: $LiClO_4$]. Although no X-ray structure of the complex was available, it was proposed that the stability of the photoproduct is augmented by Li^+ coordinated to the four oxygens forming a 12-crown-4 derivative, thus locking the photoproduct $\mathbf{2}_1$. Therefore, extraction of



Scheme 1.

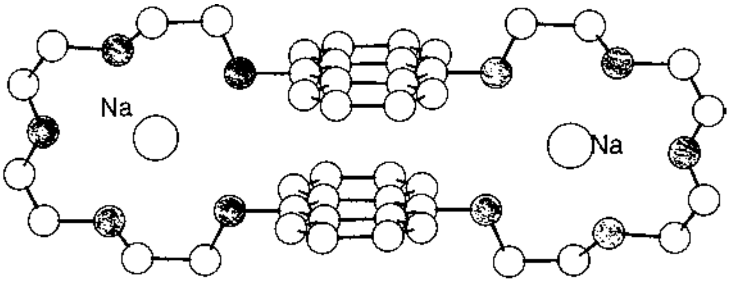


Fig. 1. Molecular conformation of the binuclear complex $2Na^+ \subset \mathbf{3}$ in the crystal [8].

Li^+ could be *photochemically controlled* with $\mathbf{1}_1$. Polar solvents, such as acetonitrile or methanol in excess, successfully compete with $\mathbf{2}_1$ for the solvation of Li^+, i.e. extract Li^+ from [$\mathbf{2}_1$: $LiClO_4$] with the result that the crown is *unlocked* and readily reverts to the starting material $\mathbf{1}_1$; the latter could be consequently used for a further extraction step. Efficient photoextraction of larger cations requires longer polyoxaalkane chains. In the case of Na^+, K^+ or Ba^{2+}, links incorporating five and six oxygens, respectively, are preferred in order to form a complexing cavity of a suitable size for the relevant cation. Podands **1n** are thus phototunable receptors *capable*, during a long period of time after irradiation, to *significantly decrease the cation concentration in a fluid solution*. Other podands investigated in the series were found to display similar properties [7].

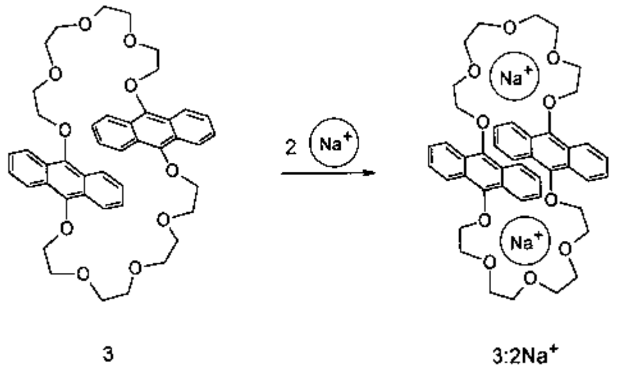
3. Anthraceno coronands

3.1. The photomodulation of cation concentration; increased binding in the excited state

Bitopic coronand **3** [8] was designed in order to improve the binding ability and the fluorescence response of the photoactive receptor towards cations. With respect to podands **1n**, anthracenophane **3** has the potential to form loops able to accommodate up to two cations before irradiation (Fig. 1, Scheme 2).

The fluorescence emission spectrum of **3** is dual, with a strong intramolecular excimer contribution. In acetonitrile, the excimer band which culminates at ≈ 520 nm indicates a partial (non sandwich) overlap of the anthracenes. Contrary to **1n**, addition of metal cations induces spectral modifications, and very strong effects were registered with $NaClO_4$ (Fig. 2). With an excess of salt, the fluorescence emission spectrum essentially displayed a nonstructured red-shifted band peaking at ≈ 570 nm characteristic of a quasi-sandwich excimer [9].

Thus **3** acts as a fluorescence probe for sodium cations (the UV spectra sensitive to addition of Na^+, also supports a symmetrical approach of the two chromophores). In the complex [**3**: $2Na^+$], as revealed by X-ray analysis, the parallel and slightly shifted aromatics are separated by ca. 3.4 Å. In the crystal, the two complexing loops delineate a cavity size matching the diameter of the cation with a geometry reminiscent of complexes formed by 15-crown-5 derivatives and Na^+ [10]. Here, the coordination of the cation (coordination number 7) is assured



Scheme 2.

by the 5 oxygens of the bridge and those belonging to the two counteranions ClO_4^- (the Na^+...oxygens separation is slightly higher than the sum of Van der Waals distances ca. 2.5 Å, and the distance between the two Na^+ is 9.0 Å). Analysis of the titration data in solution revealed, as expected, a 1:2 stoichiometry (from UV or fluorescence emission data), but the determination of the stepwise binding constants led to unexpected results. Indeed, a *positive cooperative effect* was found in methanol and acetonitrile ($4K_{12} \gg K_{11}$, see Table 1 for definition). If such a positive cooperative effect is usually observed in biological systems and self-assembling substrates [11], it is much less common for cations and crown ethers [12]. In the

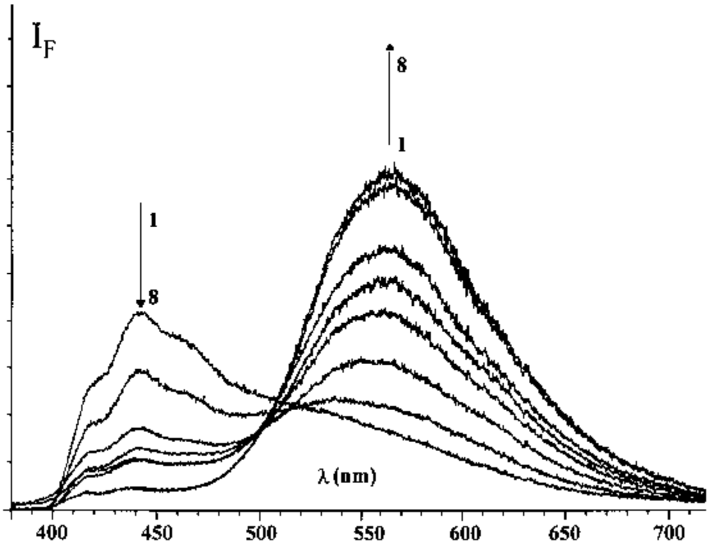


Fig. 2. Fluorescence titration of **3**, in degassed acetonitrile ((5×10^{-6}M) with $NaClO_4$ at ambient temperature ($\lambda_{exc.} = 360$ nm): 1 (**0**), 2 (**1**), 3 (**2**), 4 (**3**), 5 (**4**), 6 (**5**), 7 (**50**), 8 (**100**); the Na^+ concentrations in parentheses are given in 10^{-3} M.

Table 1
Stepwise association constants for the 1:1 (K_{11}) and 1:2 (K_{12}) complexes of coronands **3-8** in CH_3CN at room temperature, determined from the UV absorption spectra using the LETAGROP programme [21][a]

	3 (Na^+)	**4** (Na^+)	**5** (Na^+)	**5** (Sr^{2+})	**6** (Ba^{2+})	**7** (Ba^{2+})	**8** (Ba^{2+})
β/M^{-2}	37 000 (100 000)	15 000	14 454	44 670	1.8×10^{10} (1.29×10^9)		
K_{11}/M^{-1}	178 (200)	300	645	1820	56 200 (28 180)	12 000 (10 000)	98 (100)
K_{12}/M^{-1}	236 (500)	50	22	25	323 600 (45 900)		

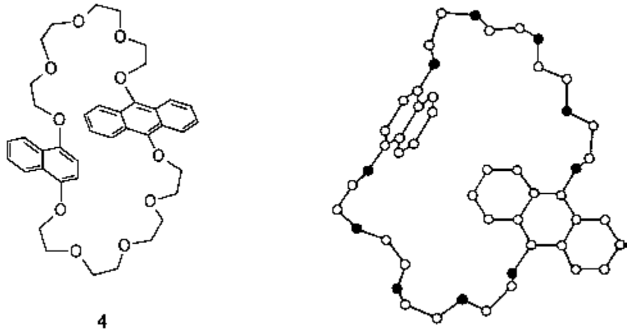
[a] The data in parentheses refer to the excited state [8].

present situation, the complexation of the first cation probably induces the preorganization of the second binding site favourable for the complexation. Moreover, the *repulsive interaction* between the two cations in the coronate is, at least in part, balanced by the electronic shielding brought about by the two parallel and closely separated (ca. 3.4 Å) anthracene rings.

A second surprise emerged from the results of the titration experiments from the fluorescence data, which provide information of the complexing ability of the singlet excited state. A positive cooperative effect was also observed and the global binding constant ($\beta = K_{11}K_{12}$) was found to be significantly higher (ca. 3 fold); inspection of the stepwise constants showed that K_{12} is appreciably increased (in contrast to K_{11} which remains practically unaffected). This effect could be explained by the contribution to the stability of the complex of long-lived excimers (a set of excimers of lifetimes (35–200 ns was indeed identified). It may be argued that the enhancement of the stability constant K_{12} in the excimer comes from the interring attraction.

Results obtained using coronand **4** [13] (where one anthracene is replaced by a naphthalene substituted in the 1,4 positions) (Fig. 3) supports the preceding conclusions: the compound is able to bind a series of light metal cations but does not emit excimer fluorescence and displays an anticooperative effect (note that the anticooperative effect is relatively moderate, probably owing to the intercalation of the two electron rich aromatic rings between the two metal cations, Table 1). Moreover, the binding properties of **4** were not found to be light-sensitive.

Finally, compound **3**, which can be used as a probe for sodium cation detection, is also remarkable for its phototunable complexing properties. *During light exposure, the concentration of free Na*$^+$ *in the solution decreases*; consequently, **3** belongs to a new class of photoswitches for *triggering a sudden and transitory decrease of metal cation concentration* in a solution.



4

Fig. 3. Molecular structure (right) of **4** in the crystal (the two aromatic rings are perpendicular, oxygen atoms are shaded and hydrogen atoms are omitted for clarity).

4. Benzeno coronands

4.1. The photomodulation of cation concentration; transitory decrease of cation binding ability

Benzeno coronand **5**, the parent compound of **3**, was anticipated to display similar binding properties and spectral sensitivity towards cations but in a different wavelength range. As expected, addition of alkali and alkaline-earth elements induced important hypsochromic shifts of the UV spectra [14]. The strongest effects were observed with Na^+, Ca^{2+}, Sr^{2+} and Ba^{2+} (cation radii: 0.95–1.35 Å), whereas Li^+ and Mg^{2+} induced very weak or no spectral changes (cation radii: 0.65–0.70 Å) (Fig. 4).

As demonstrated by the X-ray structure of [**5**:$2Sr^{2+}$], complexation of cations involves the phenolic oxygens which consequently raises the energy of the electronic transition. Two identical Sr^{2+} (ca. 8.8 Å intramolecular separation) are coordinated to five oxygens of the bridge and four additional molecules of water for a total coordination number of nine (see Fig. 5).

Of note, the two parallel aromatic rings do not overlap as in [**3**:$2Na^+$]. Smaller cations, such as Mg^{2+}, are probably not strongly bound to the receptor and have no effect on the UV spectrum. A crystal structure of **5** and $Mg(ClO_4)_2$ shows that the metal ions are not directly associated to **5**, but coordinated to six water molecules, which are themselves connected through hydrogen bonds to the macrocycle and perchlorate counteranions. With larger metal cations, titration experiments (UV spectra) revealed, under our experimental conditions, the occurrence of a mixture of a 1:1 and 1:2 complexes (ligand/cation), the binuclear complex being predominant for high cation concentrations (Fig. 6). The overall binding constants (β) listed in Table 1 are in the range of those already published for related

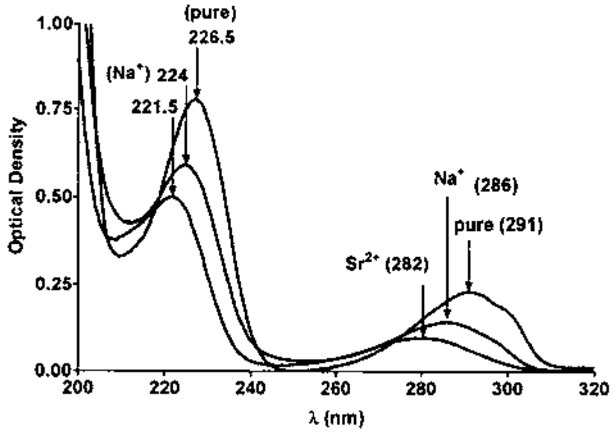


Fig. 4. UV absorption spectra of **5** in the absence and in the presence of a large excess of metal cations (perchlorate) in acetonitrile, at 20°C.

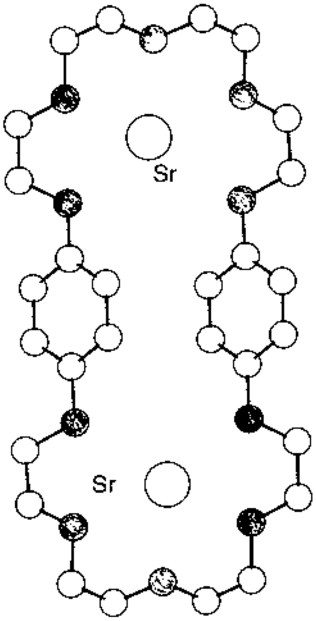


Fig. 5. Molecular conformation of the binuclear complex $2Sr^{2+} \subset \mathbf{5}$ in the crystal.

molecules [15]. However, in contrast to anthracenocoronand **3**, the data display a negative cooperative effect ($4K_{12} \ll K_{11}$); this is presumably because of intramolecular electrostatic repulsions between the two cations (8.8 Å separation) which are not balanced (vide supra) by sufficient shielding from the aromatic rings (which do not overlap).

Fluorescence emission spectrum of single crystals of **5**, [**5**:Mg^{2+}] and [**5**:$2Sr^{2+}$], typical of 1,4-dialkoxybenzenes, displayed structureless bands and shifts related as

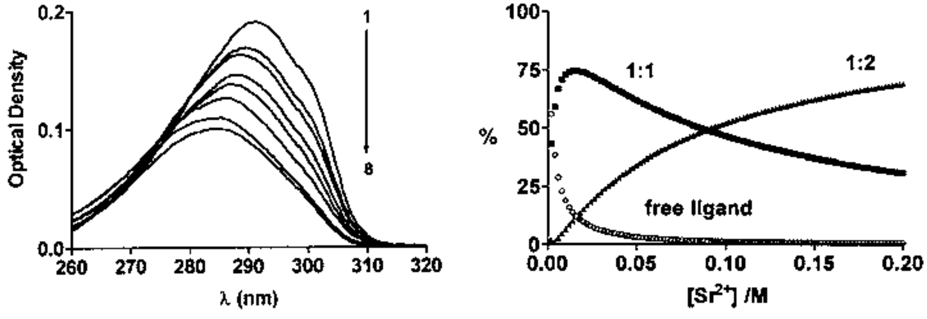


Fig. 6. (Left) Titration in CH_3CN at 20°C of a solution of **5** (ca. 2×10^{-5} M) by $Sr(ClO_4)_2$ *curve* 1 (**0**), 2 (**4**), 3 (**10**), 4 (**20**), 5 (**40**), 6 (**80**), 7 (**100**), 8 (**120**), the Sr^{2+} concentrations in parentheses are given in 10^{-3}M. (Right) Computed distribution diagram of free ligand, 1:1 and 2:1 complexes as a function of salt concentration.

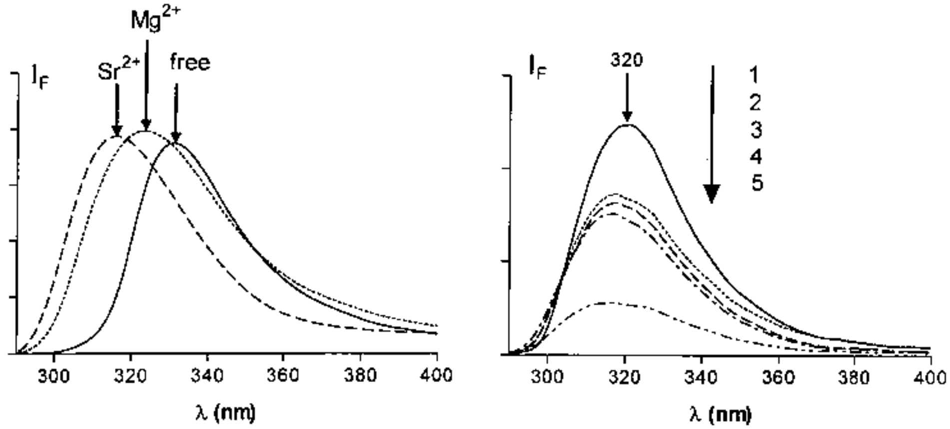
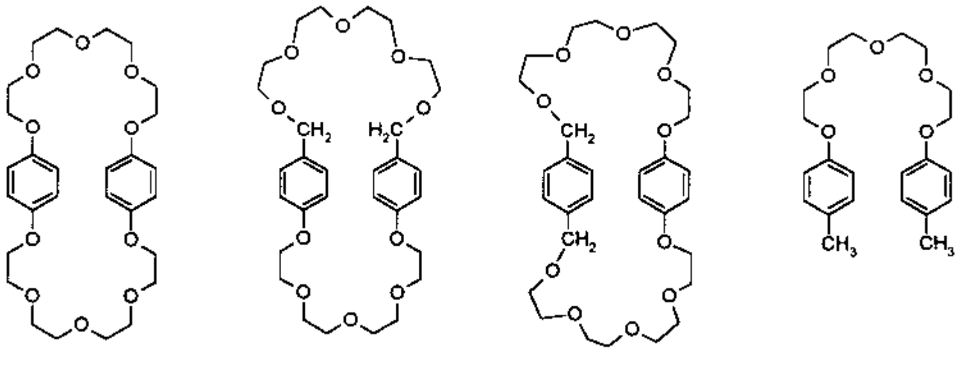


Fig. 7. (Left) Fluorescence spectra of crystals of **5** and its $Mg(ClO_4)_2$ and $Sr(ClO_4)_2$ complexes. (Right) Fluorescence spectra of the free ligand **5** (conc. $(2 \times 10^{-5}$ M, $\lambda_{exc.} = 280$ nm) (curve 1), and in the presence of a large excess (10 000 fold) of Ca^{2+} (2), Na^{+} (3), Sr^{2+} (4), Ba^{2+} (5).

expected to those registered for the UV spectra. However, in fluid solutions (CH_3CN), only a *negligible hypsochromic shift* was recorded in the presence of salts, together with some fluorescence quenching as observed in the presence of ion pairs [16] and enhanced by heavy-atom effect. The fact that the spectra resemble that of the free ligand **5** is compatible with the (at least partial) decomplexation in the singlet excited state [17] of the metal cation which consequently would explain the 'pure' host emission. Thus contrary to compound **3**, *irradiation of* ***5*** *should produce a sudden and transitory increase of the concentration of free cation* in the solution during the excited state lifetime (Fig. 7, Schemes 3 and 4).



5 **6** **7** **8**

Scheme 3.

Related compounds **6**, **7** and **8** were designed in order to modulate the complexing properties of the system in enlarging the series essentially by intercalation of CH_2 groups between the phenyl ring and the phenoxy oxygens. This was anticipated to enhance the binding ability and improve the cooperativity. These receptors were found to behave similarly (Table 1) to **5**. Upon addition of metal cations (alkali and alkaline-earth elements), the UV spectra were blue-shifted in agreement with complexation of the metal by the polyoxaalkane loop and the phenoxy groups (vide supra). Titrations indicated a mixture of 1:1 and 1:2 stoichiometry for **6** and **7** with a negative cooperative effect for **7** (see Table 1 for Ba^{2+}), and an important positive effect for **6** ($K_{12}/K_{11} \approx 1.6$).

This latter effect could originate from a larger separation of the two Ba^{2+} (diminishing the repulsive potential), accompanied by the presence of an insulating hydrocarbon area (attempts to grow crystals of the complexes for supporting this point have not been successful), as well as the fact that in **6** each benzene *holds only one coordinating oxygen*. Thus the complexation should not strongly influence the basicity of the oxygens of the second loop. In that connection, one can remark that the binding abilities of **6** and **7** are improved compared to **5** where 4 phenolic oxygens were involved in the coordination. Molecular modelling of the $2Ba^{2+}$ (**6** complex using an MM2 Force Field (PC Model) indicates an inter-cation distance of ca 9.8 Å (Fig. 8).

The spectroscopic properties of the reference compound **8** were also found to be cation dependent with spectral changes comparable to those recorded on benzeno-

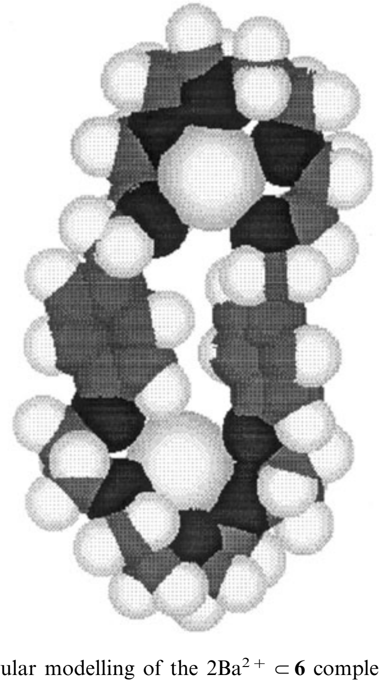
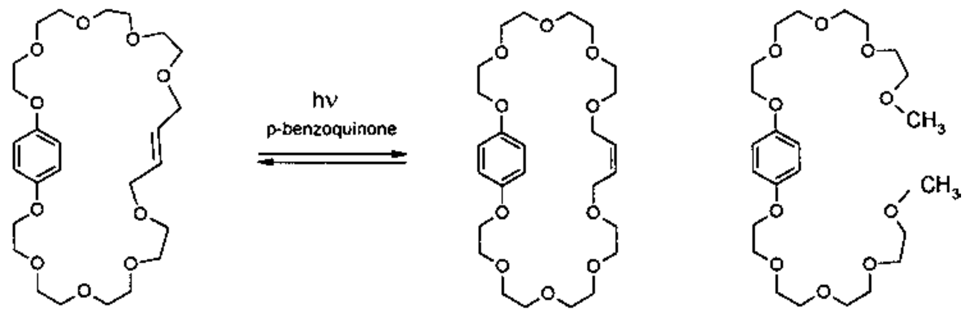


Fig. 8. Molecular modelling of the $2Ba^{2+} \subset$ **6** complex using PC Model.



9t **9c** **10**

Scheme 4.

complex [**8**:Ba^{2+}], the five nearly coplanar oxygens of the bridge are wrapped around the cation (Fig. 9) with an average Ba^{2+}-oxygen distance of 2.8–2.9 Å. The cation is also bound to five oxygens of two perchlorate counteranions with a coordination number of 10, value usually encountered for this element [19]. The two non parallel benzenes are not mutually shifted (compared to [**5**:2Sr^{2+}]) and experience some attractive interaction via 2 hydrogens of one ring and the cloud of the other ring. This weak interaction probably participates to the stabilization of the complex [20].

5. Photoisomerizable benzeno-coronand

5.1. Photoswitchable allosteric receptors

Photoconvertible and thermally stable cation ditopic receptors **9t** and **9c** were designed in order to *tune the cation complexation ability of the host on a long time scale*. Due to steric factors, it was anticipated that the two isomers (*trans* and *cis* olefins) would present different metal cation affinities.

In contrast to reference compound **10**, which did not show significant complexing properties, the spectroscopic properties (UV and fluorescence) of **9t** and **9c** were found to be very sensitive to the presence of alkali metal cations and similar to those recorded on **5** [22]. These effects were ascribed, as demonstrated for the coronands **3**–**7**, to the formation of inclusion complexes where the ‘phenolic’ oxygens participate to the coordination of the metal. This effect is particularly marked for Na$^+$. As for coronands **3**–**7** (vide supra), two stoichiometries (1:1 and 1:2 complexes) are present in the range of cation concentration investigated, even for a large excess of cation ([Na$^+$]/[receptor] > 500). The two receptors show a *negative cooperative effect* ($K_{12}/K_{11} \approx 0.05$ for **9t** and 0.01 for **9c**, respectively) and

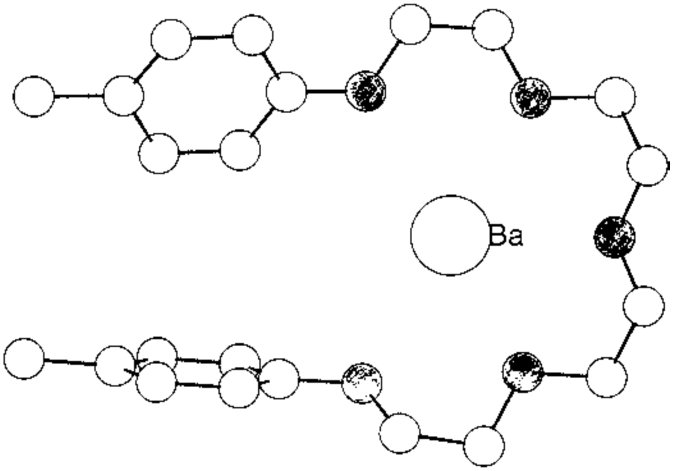


Fig. 9. Molecular conformation of the complex $Ba^{2+} \subset$ **8** in the crystal.

the complexation of $NaClO_4$ (acetonitrile) is more efficient with **9t** (β**9t**/β**9c** ≈ 18). The fact that the overall stability constant *increases* 18-fold on going from the *cis* to the corresponding *trans* isomer was attributed to geometrical factors in the complex. Contrary to **9t**, the aromatic subunit and the complexing loops in **9c** should be in the same plane thus increasing *repulsive interactions* with the olefin bridge. UV irradiation promotes the triplet sensitized isomerization of the olefinic part and a photostationary state is reached (**9c**/**9t** $\approx 2/3$) (Scheme 4). Under these conditions, pure **9t** or **9c** could not be isolated after illumination. However, a decrease of the binding properties of a solution of pure **9t** could be observed upon irradiation as the concentration of the *trans* isomer is diminishing; whereas the opposite effect was registered starting with pure **9c**. As a consequence, receptors **9c** and **9t** could be used for a *selective and durable photoadjustment of* Na^+ *cation concentration* [23].

6. Conclusion

Several photoswitchable cation binding receptors incorporating a complexing subunit (polyoxaalkane sequence or coronand) and two non conjugated chromophores have been described. The specific properties of these systems rest on the photoactive moieties, as the switching antennae, for an enhanced or decreased cation binding. It was shown that the switching can produce either a sudden and transitory jump of cation concentration during the photochemical event or a complexing change on longer time scales. Some of the systems reported could be of interest for the design of devices for photochemical extraction of cation and fine tuning of the cationic flux in solutions.

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