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LETTERS

Synthesis and cation complexing properties of a new type of photoactive coronands. Towards photocontrol of Na^+ complexation

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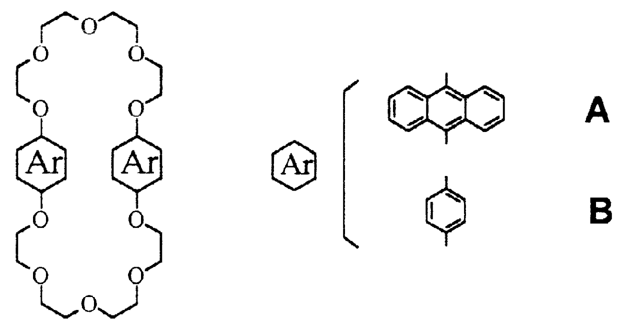
Abstract: The coronands isomers **1** and **2** have been synthesized and their respective cation affinities shown to be light tunable.

The design of nanoscale devices capable of converting a simple external physical stimulus into a measurable chemical event through a triggered structural or electronic perturbation raises a considerable interest.[1] In this field, the conception of tunable ion-capture, ion-transport and ion-release molecular systems is of special importance owing to their potential applications as molecular switching and memory storage devices.[1,2] In these systems, light can be used to trigger a reversible geometrical or chemical modification and consequently induces a drastic change of their complexing properties.[3,4] As part of a study of various ditopic receptors, we have recently reported a transitory enhancement of Na^+ cation affinity of anthracenocoronand **A** *upon light irradiation*;[5] the sudden and *provisional* decrease of free Na^+ concentration in the medium has been ascribed to the formation of an intramolecular excimer which stabilizes the bicomplex. In contrast, decomplexation *upon light irradiation* was observed in other systems, resulting in a *fast increase* of the free cation concentration;[6] this effect has been demonstrated for the benzenocoronand **B**, for which the conjugation of the cation coordinating lone pairs of the heteroatoms with the aromatic chromophore prevails in the excited state.[6c] Besides, photoisomerization of azobenzene, styryl dyes or other kind of chromophores linked to a crown ether subunit have been shown to modify the affinity of the complexing centre *on a longer time scale*.[7]



In the present letter, we wish to describe the synthesis and some spectroscopic properties of a new type of cation ditopic receptors (compounds **1** and **2**) for which Na^+ complexation can be directed by light: the process rests on the *cis-trans* isomerization of the double bond leading to *thermally stable* photoisomers displaying different cationic affinities.

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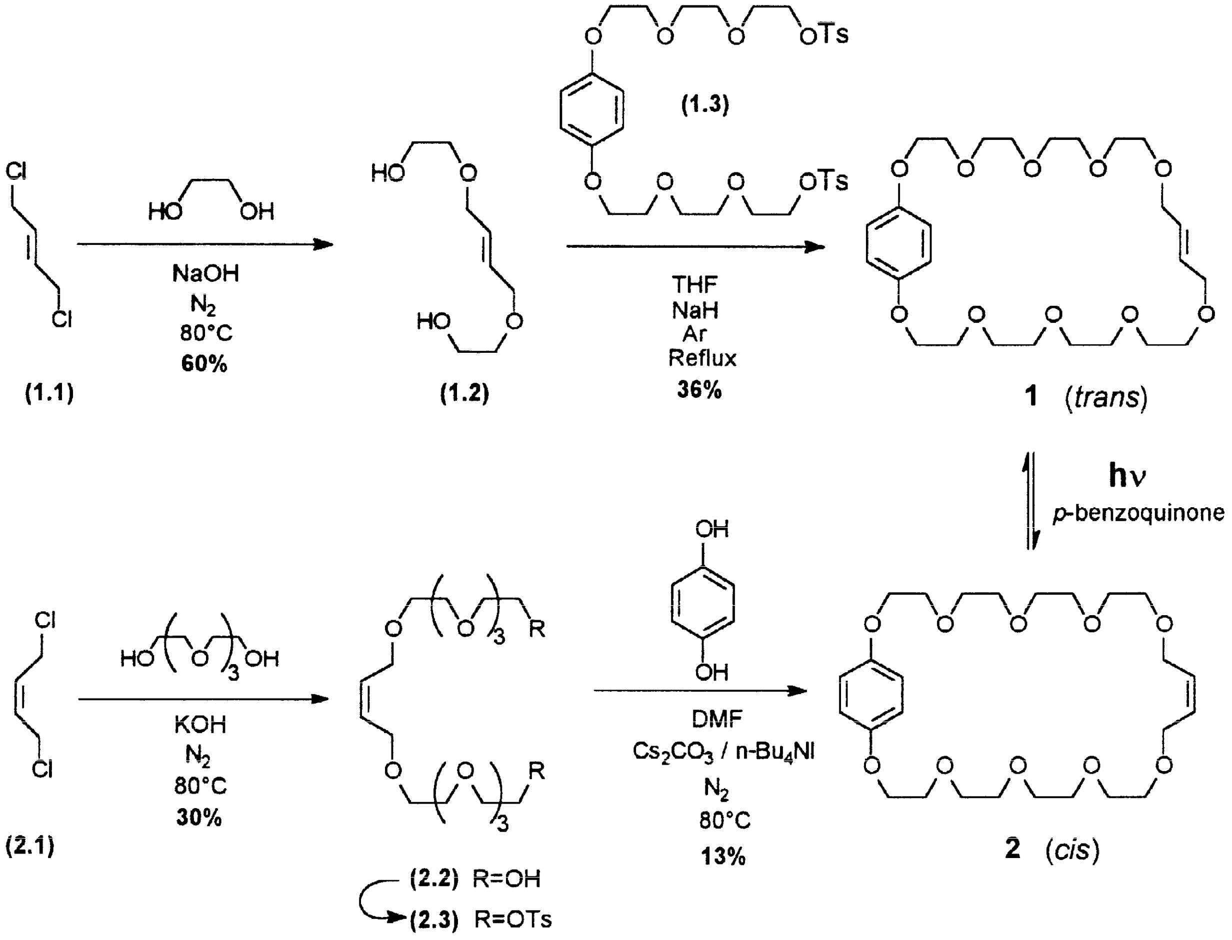
Results and discussion

The syntheses of **1** and **2** were achieved, from commercial *trans* and *cis*-1,4-dichlorobutenes, using two different reaction pathways in order to compare their respective efficiencies (scheme). Diol **1.2** was reacted in the presence of NaH with ditosylate **1.3** in THF, to afford **1** in 36% yield. The overall yield (22%) is similar to that already reported for other receptors.[5,6c,8] Ditosylate **2.3** (the 'crab' intermediate) was obtained from the *cis* olefin **2.1**. The cyclization of **2.3** with hydroquinone in the presence of Cs_2CO_3,[9] is poorly efficient (13% yield, 4% overall yield). Compounds **1** and **2** have been fully characterized by the usual methods.[10]



Contrary to 1,4-bis(1-methoxy-3,6,9-trioxaundecyloxy)benzene (a reference compound[6c] without any complexing cavity), the spectroscopic properties (electronic absorption and fluorescence emission spectra) of **1** and **2** are very sensitive to the presence of alkaline and alkaline-earth cations. Addition of perchlorate salts produces important hypo- and hypsochromic shifts of the absorption bands. These effects were ascribed, as demonstrated for other coronands,[6c] to the formation of inclusion complexes between the cations and the receptors. The complexation must involve the 'phenolic' oxygens which are thus no longer conjugated[6c] with the aromatics. The phenomenon is particularly noticeable for Na^+(Fig.1) which was consequently further investigated.

The stoichiometries of the complexes and the binding constants towards $NaClO_4$ in acetonitrile solutions have been determined using UV titration experiments (Letagrop-Spefo program[11]). As established for similar macrocycles,[6c,8] two stoichiometries 1:1 and 2:1 (metal:ligand) are calculated from the titration curves (Fig. 1). The ratio of theses two species, which demonstrates a negative cooperative effect, evolves in favour of the bicomplex as the concentration of salt increases. Worthy of note is that the complexation of $NaClO_4$ in acetonitrile is more efficient with **1** (*trans* isomer) than with **2** (*cis* isomer) ($K_{11}(t)/K_{11}(c) \approx 2$ and $K_{12}(t)/K_{12}(c) \approx 9$, leading to a global ratio of $\beta(t)/\beta(c) \approx 18$) (see Table 1).

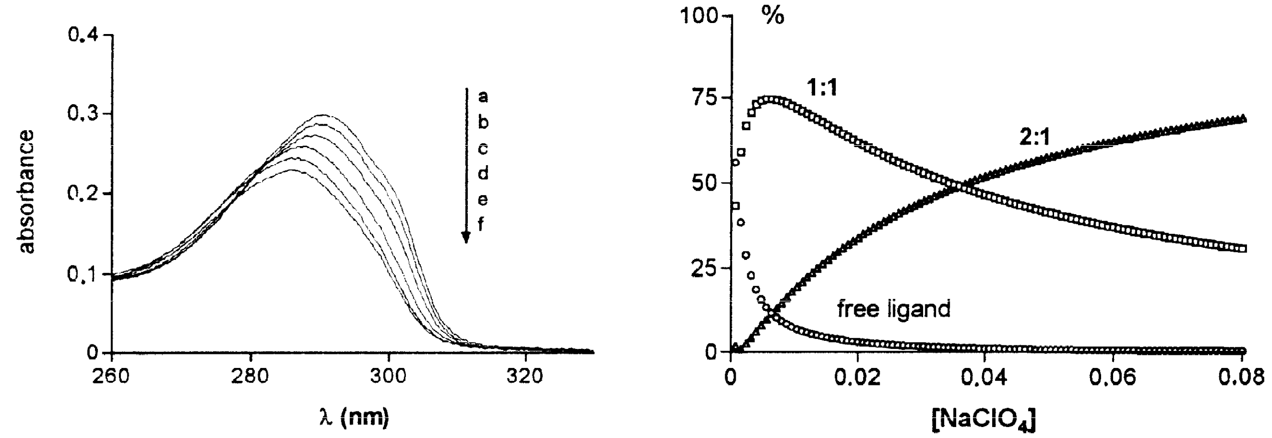


Figure 1: *Left*: UV titration of **2** in MeCN ($1.5x10^{-4}M$) with $NaClO_4$ (a:0, b:10^{-3}, c:$4x10^{-3}$, d:$2x10^{-2}$, e:$6x10^{-2}$, f:$8x10^{-2}M$) at 20°C. *Right*: Distribution diagram of **2** ($1.5x10^{-4}M$) and its 1:1 and 2:1 complexes in acetonitrile from the UV titration experiment as calculated by the Letagrop-Spefo program[11].

Table 1: Binding constants of compounds **1** and **2** at 20° C with $NaClO_4$ in acetonitrile solutions and their photoisomerization in benzene with *p*-benzoquinone as sensitizer (photodegradation of the receptors occurred upon direct irradiation).

	$\log K_{11}$*	$\log K_{12}$*	$\log\beta$*	% *cis* (after hν)	% *trans* (after hν)
1 (*trans*)	2.87 ±0.1	1.60 ±0.1	4.47 ±0.11	37	63
2 (*cis*)	2.54 ±0.1	0.67 ±0.1	3.21 ±0.14	40	60
B	2.81 ±0.1	1.35 ±0.02	4.16 ±0.12		

* as determined from UV titration experiments ($\beta=K_{11}xK_{12}$). The values are close to those of coronand **B**[6c]

No good crystals could be grown for X-ray structure analysis but a simplified molecular computed minimisation[12] of the structures of the complexes indicates that in compound **2** (*cis*), the geometry of the macrocycle would hinder the coordination of the cations in the two binding loops. Contrary to **1**, the benzenic moiety in **2** lies in the plane of the macrocycle and experiences increased repulsive interactions with the olefin.

Direct or sensitized isomerization reactions of olefins are well documented[13] and it has been shown that the triplet state of olefinic systems (similar to 2-butene) could be populated through an endothermic process[14]. Thus, ultraviolet irradiation (low mercury pressure lamp) of solutions of **1** or **2** ($4x10^{-2}$ M, E_T(*cis* or *trans*)>75-80 kcal. $mol.^{-1}$) in benzene (or acetonitrile) for 4 hours with *p*-benzoquinone as a sensitizer[15] ($4x10^{-2}M$, $E_T = 50$ kcal. $mol.^{-1}$) promoted the photoisomerization of the olefinic moiety. Chromatography coupled with spectral analyses of the oily residue recovered after irradiation indicated the simultaneous presence of both isomers with preservation of the macrocyclic structure. Thus, the ^1H NMR spectrum of the *cis* isomer **2** (or *trans* isomer **1**) displayed a redistribution of the olefinic signals to the benefit of new *trans* (or new *cis*) olefinic signals after irradiation. The spectroscopic data establish the mutual isomerization of the *cis* and the *trans* compounds. Integration of the olefinic signals (δ=5.58ppm for the *trans* isomer and δ =5.49ppm for the *cis* isomer) shows that the same photostationary state (*cis*/*trans* ≈ 2/3) is reached from **1** or **2** (Table 1), no pure *cis* or pure *trans* could be recovered. These triplet sensitized isomerizations are in line with those observed for other olefinic compounds[16-17]. Besides, irradiation of **1** or **2** in benzene, in the presence of *p*-benzoquinone, with $NaClO_4$ in a large excess (suspension) leads to very similar *cis/trans* ratios, and shows that the cation has no influence on the photoreaction in contrast to other systems.[5]

In summary, sensitized irradiation of acetonitrile solutions of **1** or **2** is followed by a change of the complexing properties of the medium, thus, the *overall binding constant of a solution of 1 decreases upon irradiation, whereas an increase is recorded under the same conditions for 2*. This type[18] of photoactive coronands could be of interest for the photocontrol of ion concentration.

Acknowledgements

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10. **1** was obtained as follows: (**1.2**) (0.59g, 3.37mmol) in dry THF (20mL) was added over 10min with a syringe to NaH (0.296g, 3.37mmol) in refluxed THF (500mL) under argon. After 1 hour of stirring, (**1.3**) (2.3g, 3.37mmol) in dry THF (200mL) was added over 1 hour. After 4 days residual NaH was quenched by water (2mL). The solvent was removed *in vacuo* and column chromatography [silica gel, ethyl acetate/ acetone (5:1)] afforded **1** as a colourless oil (630mg, 36%). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.33-3.52 (24H,m); 3.62-3.66 (4H,m); 3.77-3.80 (4H,m); 3.88-3.92 (4H,m); 5.58 (2H,m); 6.68 (4H,s). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 67.9; 69.1; 70.2; 70.4; 70.7; 115.3; 129.0;152.7. LSIMS m/z 514.2 [M^+]. HRMS Calc. 514.2777, Found 514.2777. **2** was obtained as follows: To a dry solution of Cs_2CO_3 (75g, 0.23mol) and n-Bu_4NI (1.1g, 2.98 mmol) in dry DMF (700mL) at 80°C was added hydroquinone (1.47g, 13.33mmol) in dry DMF (20mL) over 10min. After 1 hour, (**2.3**) (10g, 13.33mmol) in dry DMF (100mL) was added over 1 hour. After 5 days of stirring at 100°C, the solvent was removed *in vacuo* and the brown oil obtained was chromatographed [silica gel, ethyl acetate/acetone (5:1)] to afford **2** as a colourless oil (610mg, 13%). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.34-3.50 (24H,m); 3.62-3.66 (4H,m); 3.85-3.92 (8H,m); 5.49 (2H,m); 6.68 (4H,s). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 66.1; 67.6; 68.8; 69.8; 70.6; 115.0; 128.6; 152.4. LSIMS m/z 514.2 [M^+].HRMS Calc. 514.2777, Found 514.2786.
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18. see Fürstner, A.; Seidel, G.; Kopiscke, C.; Krüger, C.; Mynott, R. *Liebigs Ann*. **1996**, 655-662, for a recent paper on monotopic analogous systems for Ag^+.