

## Synthesis and Fluorescence Emission Properties of a Bis-anthracenyl Macrotricyclic Ditopic Receptor. Crystal Structure of its Dinuclear Rubidium Cryptate

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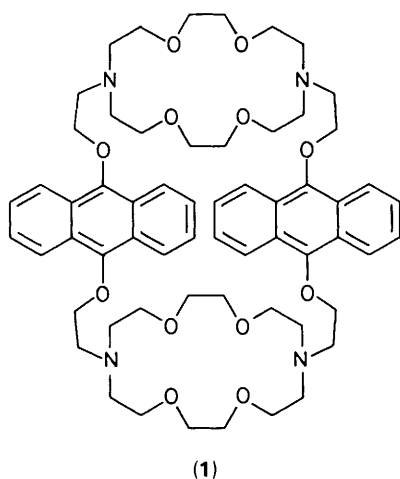
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The new macrotricyclic ditopic bis-anthracenyl receptor (**1**) displays remarkable fluorescence properties (dual emission: 'monomer' and excimer type) which are strongly and selectively modified by binding RbClO<sub>4</sub> and 1,7-diaminoheptane dihydrochloride.

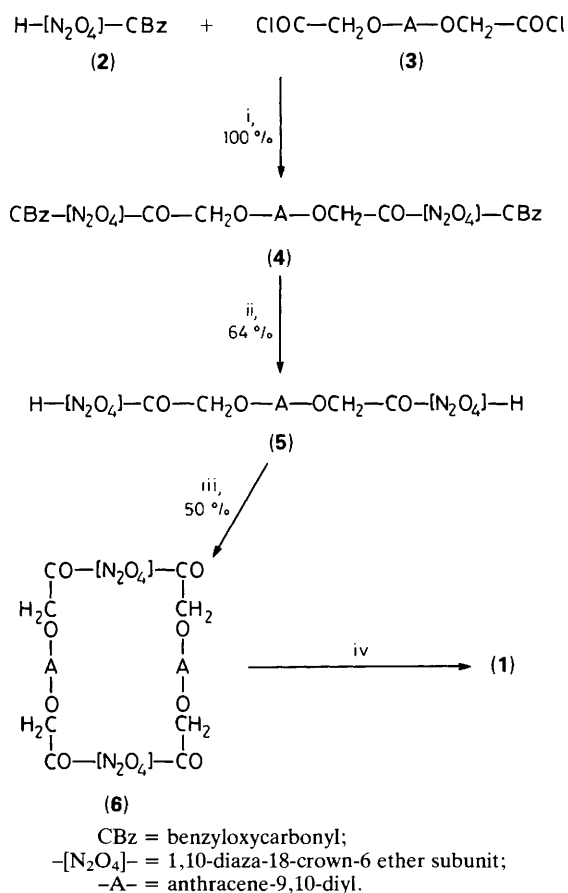
Molecular systems which combine binding ability and photochemical and/or photophysical properties are of great interest for designing molecular devices displaying photoactivity features.<sup>1</sup> In that connection, fluorescent probes for cation detection have been developed recently.<sup>2</sup> These sensors

involve complexation of spherical guest species and generally present only hydrophilic cavities; consequently they are not suited for selective optical detections of molecular ionic substrates.

The fluorescent macrotricyclic ditopic receptor (**1**), incor-



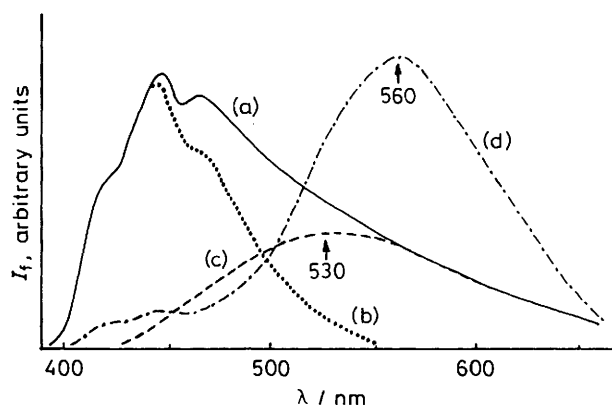
Bis-anthracenyl macrotricyclic ditopic receptor (1).



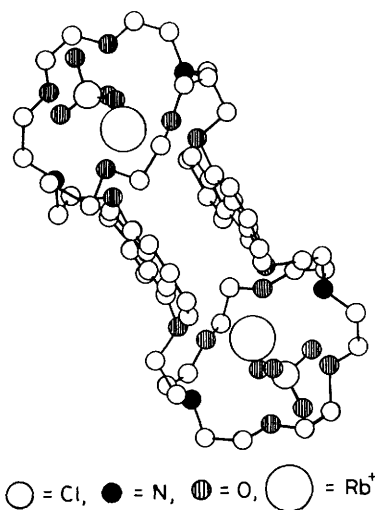
**Scheme 1.** Reagents and conditions: i,  $\text{Et}_3\text{N}$ ,  $\text{C}_6\text{H}_6$ ; ii,  $\text{HBr}$ , 30%  $\text{AcOH}$ ; iii, (3),  $\text{Et}_3\text{N}$ ,  $\text{C}_6\text{H}_6$ , high dilution; iv,  $\text{B}_2\text{H}_6$ , THF, then  $\text{CF}_3\text{CO}_2\text{H}$ , THF, then  $\text{LiOH}$ .

porating two anthracene units (delimiting a hydrophobic site) and two [18]- $\text{N}_2\text{O}_4$  subunits (hydrophilic parts) has been designed in view of its potential capacities to:

(i) display 'monomeric' and intramolecular excimer fluorescence sensitive to structural factors<sup>3</sup> (in contrast to naphthalenes, for instance, anthracenes are recognized to be able



**Figure 1.** Corrected fluorescence emission spectra of (1) in freeze-and-thaw degassed methanol (20 °C; conc.  $\leq 10^{-5}$  M): (a) free receptor (1), (b) DMO, (c) excited complex ('excimer'), (d) (1) and  $\text{RbClO}_4$ . The spectra of free (1) and DMO are normalized to the first vibronic band. The spectra are not drawn to scale.

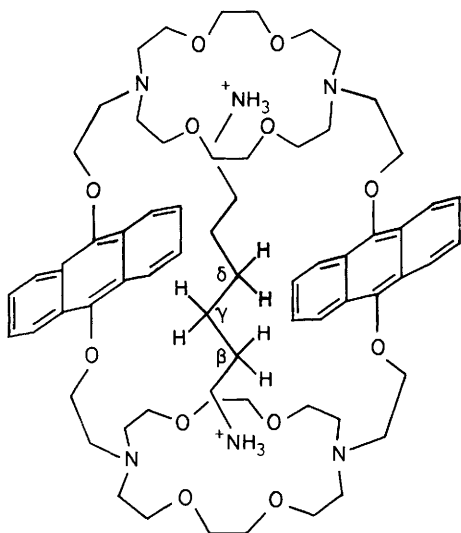


**Figure 2.** Crystal structure of the molecular cryptate formed by the receptor (1) and  $\text{RbClO}_4$ .

to generate, *in the visible region*, a set of optically well distinguishable excimers<sup>4</sup> differing by the degree of overlap between the two aromatic moieties); (ii) complex simultaneously two cationic species accompanied with specific host modification (interfering intramolecularly with the orientation of the aromatic rings); (iii) encapsulate selectively terminal diammonium cations  $\text{H}_3\text{N}^+[\text{CH}_2]_n\text{N}^+\text{H}_3$  of compatible length<sup>5</sup> which are expected to hinder the formation of an intramolecular excimer and favour the 'monomeric' emission.

We report here the synthesis, the photophysical properties in the absence and in the presence of salts, and the X-ray structure of the binuclear rubidium inclusion complex of the cylindrical receptor (1).

The macrotricyclic compound (1) was synthesized by the following procedure (see Scheme 1). Condensation of the monoprotected [18]- $\text{N}_2\text{O}_4$  macrocycle<sup>6</sup> (2) with the diacid chloride<sup>7</sup> (3) gave the diamide (4) (oil; quantitative yield), which afforded, after treatment with 30% hydrogen bromide in acetic acid, the bis-macrocycle (5) (oil; 61% yield).



Hypothetical structure, by analogy with the dinaphthyl receptor,<sup>5</sup> of the inclusion complex (X) between 1,7-diaminoheptane dihydrochloride and (1).

Condensation under high-dilution conditions of (5) with the dichloride (3) gave the macrotricyclic carboxamide (6) (m.p. 195–250 °C; 50% yield). This tetra-amide was reduced by diborane in tetrahydrofuran (THF) at reflux for about 10 h. Standard treatment of the crude amine borane adduct (6 M HCl; reflux) failed to afford the tetra-amine (1) cleanly but trifluoroacetic acid in THF (1 h reflux) was found to be effective, with limited anthraquinone formation [(1), m.p. 212 °C; 20% yield from (6)].<sup>†</sup>

The fluorescence emission spectrum of (1) is dual (Figure 1) and relatively weak in intensity compared with that of the reference monochromophoric compound 9,10-dimethoxyanthracene (DMO) (the fluorescence emission quantum yields,  $\Phi_{FT}$ , in degassed methanol being 0.06 and 0.48, respectively). By comparison with the spectrum of DMO two emissions can be characterized: e.g., a structured 'monomer' region with  $\Phi_{FM}$  0.03 (similar in shape to DMO emission) and a broad red-shifted band peaking at 530 nm ( $\Phi_{FE}$  0.03) ascribable to the formation of an intramolecular complex ('excimer') involving one anthracene unit in the singlet excited state and the other chromophore in the ground state.<sup>8</sup> Addition of salts to the fluid solution of (1) was found to affect the emission spectrum selectively. We emphasize here the results obtained with  $RbClO_4$  and 1,7-diaminoheptane dihydrochloride with which large and specific spectral modifications were observed.

Addition of anhydrous rubidium perchlorate to a methanolic solution of (1) generates a new and intense red-shifted emission centred at 560 nm ( $\Phi_{FE}$  0.22) at the expense of the 'monomer'-like (structured) emission ( $\Phi_{FM}$  0.02) (Figure 1). This behaviour appears to be specific to  $Rb^+$ ; other alkali metals or metal salts do not show such a clear and large effect. The typical fluorescence emission spectrum recorded with  $Rb^+$  is consistent with the formation of a quasi-sandwich excimer (slightly staggered) as already described<sup>3a</sup> with a bis-anthraceno-crown ether and  $Na^+$ , originating in the

complexation of two  $Rb^+$  cations which brings the aromatic moieties close together. That  $Rb^+$  modifies the mutual orientation of the aromatic parts is supported by UV<sup>‡</sup> and NMR spectroscopy in the ground state. Indeed, in the presence of  $Rb^+$ , the aromatic protons display remarkable high-field shifts ( $\Delta\delta$  -1.05 and -0.42 ppm for protons on the 1 and 2 vertices, respectively) underlining the close and quasi-parallel alignment of the anthracene rings. This statement is borne out by the X-ray structure analysis<sup>§</sup> of the crystalline complex [(1)·2 $RbClO_4$ ] (obtained from the slow evaporation of a chloroform-methanol solution) which shows the complexation of two rubidium cations by the 'hydrophilic' parts inducing a slightly staggered sandwich interaction between the aromatic units (interplanar separation  $\leq 3.5$  Å  $\approx$  van der Waals distance), see Figure 2.

Addition of cadaverine dication ( $H_3N^+[CH_2]_5N^+H_3$  2 $Cl^-$ ) to compound (1) in methanol ( $10^{-5}$  M) did not significantly alter the fluorescence emission properties of the solution (dual emission,  $\Phi_{FM}$  0.04 and  $\Phi_{FE}$  0.03), but addition of the dication  $H_3N^+[CH_2]_7N^+H_3$  2 $Cl^-$  produced a strong enhancement (ca. ten-fold) of the 'monomer'-like emission ( $\Phi_{FM}$  0.32) accompanied by the total disappearance of the excimer part, the spectrum being similar in shape to that of DMO; compound (1) thus behaves as a single anthracene chromophore. These data are consistent with the formation of the mononuclear dihapto cryptate  $\{H_3N^+[CH_2]_7N^+H_3 \subset (1)\} 2Cl^-$  (X) in which the two anthracene rings are parted from each other by the lipophilic polymethylene chain hindering intramolecular formation of excited complexes and fluorescence quenching. This behaviour is only observed with the  $[CH_2]_7$  sequence whose length corresponds to the size of the intramolecular cavity of the receptor, as observed in earlier studies of linear recognition of diammonium substrates by a macrotricyclic receptor, and in agreement with space-filling Corey-Pauling-Koltun (CPK) molecular models; the  $[CH_2]_5$  substrate is probably too short to induce the intramolecular complexation of both ammonium end groups within the receptor (1). The inclusion complex of the diammonium substrate ( $n$  7) with receptor (1) has also been characterized by  $^1H$  NMR

<sup>‡</sup> Marked UV spectral modifications were observed on addition of  $RbClO_4$  to fluid solutions of (1) (methanol and other solvents); the changes in spectra compare well with those recorded with  $Na^+$  and another anthracenophane in which a quasi-sandwich overlap between the aromatic nuclei is observed.<sup>3a</sup>

<sup>§</sup> The crystals (transparent yellow needles; m.p. 210–220 °C (decomp.)) are platelets (from chloroform-methanol). *Crystal data:*  $C_{60}H_{80}N_4O_{12} \cdot 2RbClO_4$ ,  $M = 1417$ , space group  $P\bar{1}$ , No. 2, triclinic,  $a = 13.088$ ,  $b = 13.166$ ,  $c = 13.824$  Å,  $\alpha = 105.14$ ,  $\beta = 94.98$ ,  $\gamma = 126.96^\circ$ ,  $Z = 1$ ,  $U = 1742.8$  Å<sup>3</sup>,  $D_c = 1.352$  g cm<sup>-3</sup>,  $\mu = 31.4$  cm<sup>-1</sup>,  $F(000) = 736$ , Cu- $K_\alpha$  radiation (graphite monochromator,  $\lambda = 1.5405$  Å); the structure was solved by the Patterson method. Refinement was carried out using block-diagonal least-squares with anisotropic thermal parameters for non H-atoms, converging to a present  $R = 0.068$  for 5287 reflections. All hydrogen atoms were introduced at calculated positions and refined with isotropic thermal parameters. Fourier difference maps show residual densities ascribed to solvent in a probably non-stoichiometric arrangement. Disorder affected the O atoms of the  $ClO_4^-$  moiety. The characterization of included solvent is in progress. Present atomic co-ordinates and thermal parameters lead to bond lengths and angles in good agreement with usual values except for  $ClO_4^-$  in which the bonds appear too short owing to the high artificial thermal motion applied. Additional details will be published later. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

<sup>†</sup> The reactions were performed in degassed solvents, under inert atmosphere (nitrogen or argon) and in the dark. All new compounds described here gave analytical and spectral data in agreement with their structure.

spectroscopy (200 MHz;  $\text{CDCl}_3\text{-CD}_3\text{OD}$ , 1:1 v/v). Three upfield resonances at  $\delta$  0.38, -1.23, and -2.17 (from  $\text{SiMe}_4$ ) are recorded when an equimolar amount of the amine salt is added to the solution of the free host; these signals correspond to the  $\beta$ ,  $\gamma$ , and  $\delta$  protons of the guest respectively, the large upfield shifts being due to the magnetic effect of the anthracene ring and confirming the inclusion of the diammonium substrate into the molecular cavity.

These are the first examples of *selective optical detection* of  $\text{Rb}^+$  and of a linear  $\alpha$ ,  $\omega$ -diammonium alkane salt.

Received, 25th October 1989; Com. 9/04601A

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