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Synthesis and Cation Complexing Properties of a New Dissymmetrical Fluorescent Coronand

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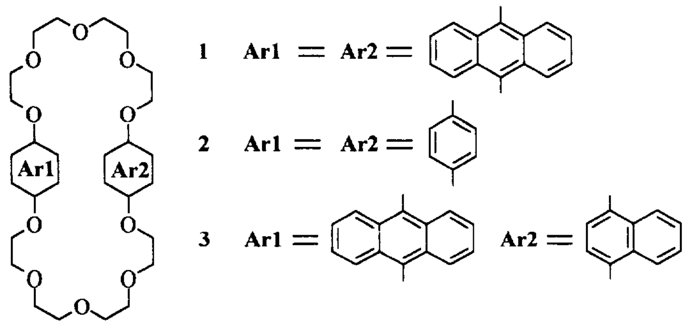
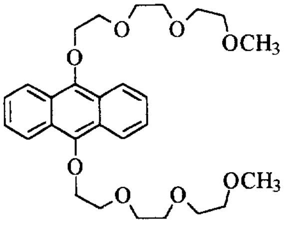
Abstract: A dissymetrical coronand containing two different subunits (i.e. anthracene and naphthalene) has been synthesized and the crystalline structure established. **3** forms a 2:1 complex with Na^+ and a 1:1 complex with K^+. A negative cooperativity has been revealed with Na^+. Some spectroscopic properties of **3** are described. Copyright © 1996 Elsevier Science Ltd

The design of fluorescing probes for cation detection is essential to the development of nanoscale devices applicable to biological sensing[1] (e.g. of Na^+, K^+, Ca^{++}) as well as to pollution treatment[2] (e.g. Cs^+, Sr^{++}, Ba^{++}). It has already been shown that **1** and **2** display specific optical responses towards alkaline and alkaline-earth metal cations[3,4]. The inclusion complexes formed are accompanied by a large conformational reorganization of the receptor producing a change in the latter's spectroscopic properties. In addition to their potential applications to cation sensing, these ditopic receptors could also be used to create tunable interactions between aromatics. Thus **1** accomodates two Na^+ ions and generates a green fluorescent complex in which the two anthracenes are in a near 'sandwich' geometry, in contrast to the free ligand characterized by a blue shifted emission[5] in agreement with a partial overlap between the chromophores. **2** behaves similarly with Sr^{++}, i.e. in the complex the benzene rings are parallel and maintained in a close proximity leading to a perturbation of the photophysical properties of the aromatics[4].





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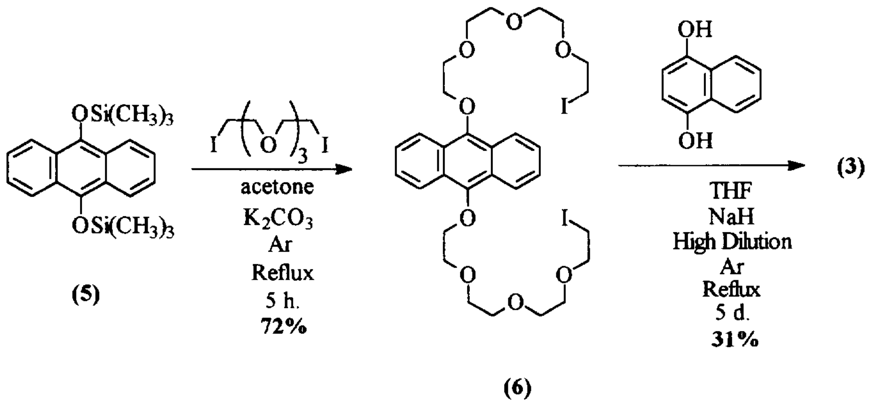
In the present letter, we report the synthesis, the structural, photophysical and complexation properties of the dissymetrical coronand **3** which is composed of two different photoactive chromophores. Compound **3** is expected to bring an insight into the photophysics of the anthracene-naphthalene pair and the influence of the dissymetrical aromatic couple on the complexing abilities of the receptor.

SYNTHESIS

The synthesis of **3** has been achieved (22% overall yield) using an improved procedure[6] outlined in Scheme 1.



Scheme 1

In acetone, under basic conditions (K_2CO_3), the protected 9,10-dihydroxyanthracene **5** and the polyoxalkane chain gave **6** (72% yield)[6]. **6** was then condensed with 1,4-dihydroxy-naphthalene under high dilution conditions to produce **3** (31% yield). Compound **3** has been fully characterized by the usual spectroscopic methods, elemental analysis and X-ray structure[7] determination.

In the crystal (Figure 1), the naphthalene moiety is perpendicular to the anthracene ring ('herringbone' fashion[8]), in contrast to **1** where the two anthracenes lie parallel[9] to each other. As a result, in the solid, the two aromatics in **3** display no significant π-overlap.

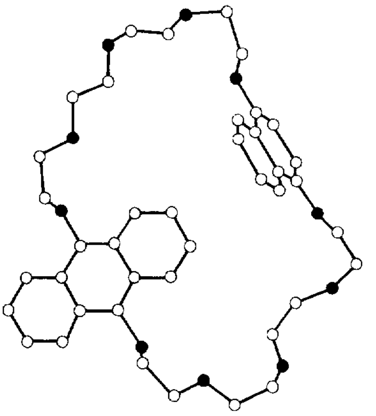


Fig. 1 Structure of **3** in the crystal. The two aromatic rings are perpendicular. A contact between the anthryl H atoms and π cloud of the naphthalene ring is to be noticed.

PHOTOPHYSICAL PROPERTIES

In the absence of cation. Whilst the reference compound **4** presents a well structured fluorescence emission spectrum[6], under the same conditions (10^{-5}M), **3** exhibits a poorly structured band suggesting the occurrence of a weakly stabilized intramolecular excimer between the naphthalene and the anthracene subunits[10]. The formation of such an excimer is supported by the relative fluorescence quenching of **3** (as compared to **4**, Table 1) and by the fluorescence biexponential decay which demonstrates the presence of at least two kinetically distinguishable excited species (the fluorescence decay of **4** is monoexponential) (Table 1).

In the crystal, the fluorescence emission spectrum displays sharp vibronic bands characteristic of a nonperturbed anthracene as is expected in a medium of high viscosity where the dynamical effects are reduced.

Table 1. Fluorescence Quantum Yields Φ_F and Fluorescence Decays $1/\lambda_n$ (λ_{exc}=415nm) of **3** and **4** in Several Degassed Solvents at +20°C.

Compound	Solvent	Φ_F	$1/\lambda_1$ (ns)	$1/\lambda_2$ (ns)
4	MeOH MCH MeCN	0.65 0.71 0.69	14.1 14.5 15.0	— — —
3	MeOH MCH MeCN	0.04 0.08 0.06	2.0 2.1 1.9	5.8 19.3 8.4
3+CH_3COOK **3**+CH_3COOK	MeOH MeCN	0.03 0.06	2.0 2.0	8.5 7.7
3+$NaClO_4$ **3**+$NaClO_4$	MeOH MeCN	0.06 0.09	3.8 3.9	15.8 23.5

In the presence of cations. Unlike **4**, the UV spectrum (Figure 2) and fluorescence emission properties (Table 1) of **3** are very sensitive to the addition of Na^+ or K^+ ions. The spectral changes are attributed to a conformational reorganization of the host (as demonstrated for parent molecules[6]), as a result of cation complexation by the polyoxalkane loops. The UV intensity redistribution of the high energy transition band (250nm) suggests that in the complex, the chromophores are probably in close proximity to each other as already shown for **1** and **2**. The stoichiometry of the complexes and the associated binding constants were determined (LETAGROP-SPEFO program[11]) in methanol and acetonitrile (Table 2).

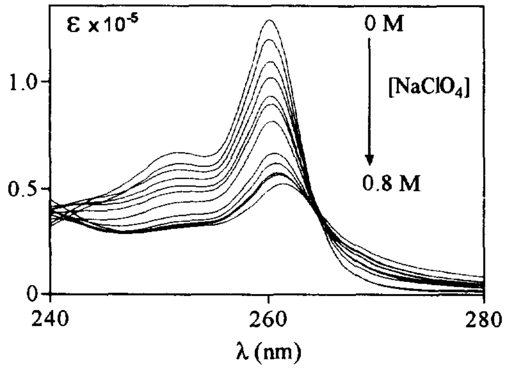


Fig. 2. UV titration of **3** with $NaClO_4$ in MeCN (the low energy transition band is weakly affected in the same conditions).

Table 2. Association constants of **3** determined from UV titration at +20°C.

3	$K_{11}{}^a$	$K_{12}{}^a$	β^b
MeCN / Na^+	300	50	15 000
MeOH / Na^+	30	3	90
MeOH / K^+	13	—	—

^{a} K_{11} and K_{12} in M^{-1}; ^{b} $\beta=K_{11}\times K_{12}$ in M^{-2}

A 2:1 and a 1:1 complex were revealed with Na^+ and K^+ respectively. These two different stoichiometries could be connected with the size of the cations (K^+ is too large to promote a 2:1 complex r_{iNa^+}=0.98Å, r_{iK^+}=1.33Å). Mass spectrometry (LSIMS, 70eV) experiments support the selectivity of **3** towards Na^+ and fully confirm the respective stoichiometries (Na^+ and K^+) established from UV titrations as shown elsewhere[12]. Indeed whilst [**3**+Na^+], [**3**+$2Na^+$] and [**3**+K^+] species were clearly revealed upon salt addition ($NaClO_4$ and CH_3COOK respectively), in no case was a signal corresponding to the [**3**+2K$^+$] species detected.

Worthy of note is that the overall binding constant is lower in methanol because this solvent can strongly compete with the host. Moreover, a negative cooperative effect was revealed for Na^+ as already mentioned for **2**[4]. Thus, **3** does not behave as **1** which exhibits a positive cooperativity with Na^+ under the same conditions, and this might indicate that the anthracene-naphthalene pair experiences a different geometry in the complex.

Experiments are currently under way to shed light on this interesting effect and the photochemistry and crystal structure of **3** will also be detailed in the full paper.

ACKNOWLEDGEMENTS

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7. **(3)** was obtained as follows: **(6)** (3.7g, 4.73mmol) and 1,4-dihydroxynaphthalene (0.76g, 4.73mmol) in dried THF (50mL) were added over 5h with a syringe under argon to NaH (0.76g, 1.9mmol) in dried THF (1.5L). The reaction mixture was refluxed for 5 days. The solvent was removed *in vacuo* and column chromatography [silica gel, ethyl acetate] gave a yellow solid which was recrystallised in acetone to yield **(3)** as yellow crystals (1.00g, 31%); m.p. 99-100°C; ^1H NMR ($CDCl_3$, 250MHz) δ 3.87-3.91 (16H, m); 3.98-4.04 (8H, m); 4.12-4.14 (4H, m); 4.28-4.32 (4H, m); 6.34 (2H, s); 7.28-7.37 (6H, m); 8.14-8.18 (2H, m); 8.33-8.37 (4H, m); ^{13}C NMR ($CDCl_3$, 250MHz) δ 68.3; 69.8; 70.6; 71.1; 74.8; 104.7; 121.7; 122.6; 125.0; 125.3; 125.6; 126.3; 147.0; 148.5; HRMS 686.3088 (M^+) calc: 686.3091; Elem. Anal. Calc:C 69.95%, H 6.75%, O 23.29% Found. C 69.88%, H 6.69%, O 23.17%. Crystal Data: triclinic, space group $P\bar{1}$, a=10.83(3), b=11.511(5), c=15.663(6)Å, α=93.81(2), β=109.77(3), γ=96.93(3)°, V=1812Å^3, Z=2, the structure being determined by direct methods using the Mithril package (C.J. Gilmore *J. Appl. Cryst.* 1984, *17*, 42-46). All hydrogen atoms were found by difference Fourier syntheses and introduced into the calculation. The final reliability factors are R=0.048 and R_w=0.05 for 4832 reflections. The highest residue on the final electronic density map was about 0.25/Å^3.
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