A novel crown ether–cryptand photoswitch

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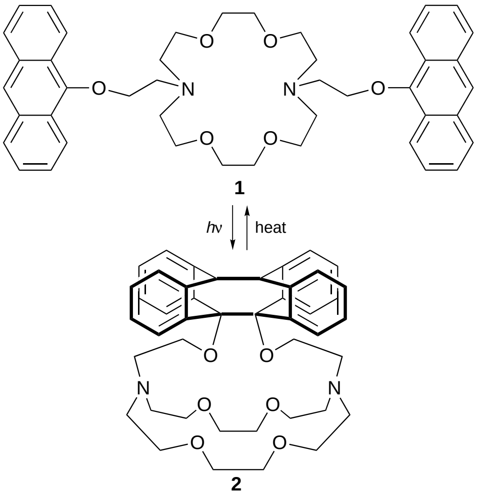
A new photoactive bis-anthracenyl crown undergoes a reversible photocyclisation to form a cryptand, with the efficiency of the forward reaction and the rate of the thermal reverse reaction strongly affected by the presence of cation substrates.

Photoresponsive molecular devices are of current interest due to their relevance to semiochemistry, substrate transport and sensor technology.[1] A number of supramolecular systems incorporating the photoactive anthracene moiety have previously been studied,[1f,2] including iono-photoswitches, where light is used to affect the ion binding properties of a system.[3] Here we report a new bis-9-anthracenyl crown ether **1** (Scheme 1) and give preliminary results on its unusual spectroscopic properties and photoreactivity in the absence and presence of guest substrates.

Compound **1** can be synthesised from diaza-18-crown-6 *via* two different routes; either directly from the reaction with 9-bromoethyloxyanthracene[4] or with 9-anthracenyloxyacetyl chloride,‡ followed by reduction using a method described previously.[5] An X-ray crystallographic study fully confirms the structure of **1** with the two pendant arms *trans* to one another.[6]

Complex formation with H^+, Na^+, K^+, Cs^+ and Rb^+ is evidenced by changes to the ^1H NMR spectrum of **1** (300 MHz) in $CDCl_3$–CD_3OD (1 : 1; 0.04 M). Addition of aliquots of Group 1 cations to **1** confirms the 1 : 1 stoichiometry of each complex, which can, in principle, adopt either a *cis* or *trans* geometry (Fig. 1). The observation of only one set of signals throughout each titration indicates that cation exchange between free ligand and complex, as well as any interconversion between the two isomers, is fast on the NMR timescale.

Previous crystallographic studies on Group 1 complexes of a closely related diaza-crown ether derivative[7] suggest that a *cis* orientation is favoured for larger ions, with the cation situated



Scheme 1

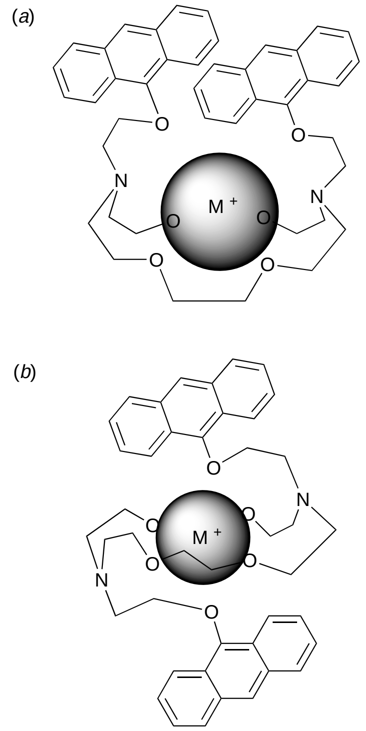


Fig. 1 The complex **1** : M^+ with the anthracenyl groups depicted (*a*) *cis* and (*b*) *trans* to one another

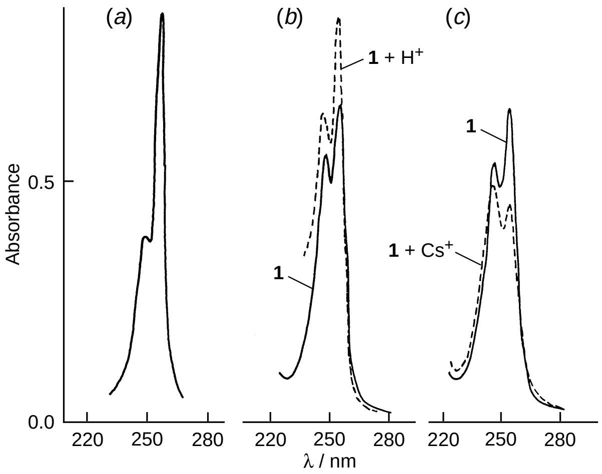


Fig. 2 UV spectra in CH_3OH (conc *ca.* 5 × 10^{-5} M, room temp.) of (*a*) 1-(9-anthryloxy)-3,6,9-trioxadecane, as the monochromophoric reference compound; (*b*) compound **1** (—); **1** + CF_3COOH (*ca.* 10^{-2} M) (----); (*c*) compound **1** (—); **1** + $CsClO_4$ (*ca.* 10^{-2} M) (----)

above the plane or the ring [Fig. 1(*a*)], whereas a *trans* orientation is prefered for complexes of smaller ions, with the cation symmetrically located in the plane of the macrocycle [Fig. 1(*b*)]. For this system, the addition of either Rb^+ or Cs^+ to **1** produce NMR spectra markedly different from those found with other guests. In particular, large upfield shifts for all five anthracene signals are observed upon the addition of Rb^+ and Cs^+ (and to a lesser extent with K^+) which is indicative of a strong π-π interaction.[8] Such an interaction is consistent with the *cis* conformation being favoured as the size of the guest increases.

Previous UV studies on bis-anthracenes have shown that the shape of the second electronic transition band (^{1}Bb) is characteristic of the mutual interaction between the two aromatic (A) rings: For an isolated A ring [Fig. 2(*a*)], the 256 nm component largely predominates; conversely the 248 nm component intensity increases as a function of the degree of interring interaction.[3b] The UV spectrum of **1** [Fig. 2(*b*) and (*c*), solid line] in MeOH is thus indicative of a mixture of *cis* and *trans* isomers. Addition of excess CF_3CO_2H [Fig. 2(*b*), dotted line] induces a slight increase of the 256 nm component intensity, in keeping with an increase of the *trans*/*cis* ratio. With Cs^+ in excess, however, the intensity of the 248 nm band increases [Fig. 2(*c*), dotted line] which points to an increase of the *cis*/*trans* ratio. Similar results were obtained with K^+ and Rb^+ but no significant spectral modifications were displayed with Na^+.

The fluorescence emission spectrum of **1** is complex; it consists of a structured part (monomer emission) and a non-structured red-shifted band originating in exciplex (amine–anthracene) and excimer (anthracene–anthracene) species (Fig. 3). In the presence of a large excess of CF_3CO_2H, a strong increase of the fluorescence intensity and a clear decrease of the long wavelength contribution are observed. Among the metal cations investigated, Cs^+ gives the highest excimer/monomer ratio (Fig. 3), presumably because the 1:1 complex *cis* conformation, favoured in the ground state, displays the best geometry for excimer formation.

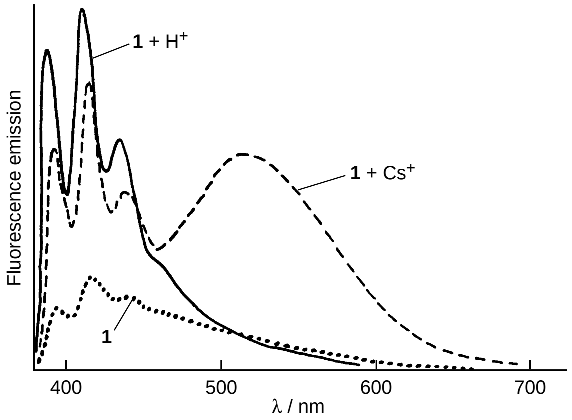


Fig. 3 Corrected fluorescence spectra (conc. *ca.* 5×10^{-5} M, λ_{exc} = 380 nm, room temp.) in degassed MeOH and fluorescence quantum yield (ϕ_F) of: **1** free ligand (●●●●) ϕ_F: 0.04; **1** + CF_3COOH (*ca.* 10^{-2} M) (—) ϕ_F: 0.16; **1** + $CsClO_4$ (*ca.* 10^{-2} M) (----) ϕ_F: 0.145. For comparison, 1-(9-anthryloxy)-3,6,9-trioxadecane has ϕ_F: 0.29.

Table 1 Intramolecular photocylcoaddition quantum yields (ϕ_R) for the formation of **2** from **1** (*ca.* 5×10^{-5} M) in the absence and in the presence of an excess of cations (*ca.* 10^{-2} M) in degassed MeOH (366 nm) and thermal dissociation rate constants for the reverse process at 25 °C

System	Φ_R (366 nm)	$k_{diss}/10^{-6}$ s^{-1}	$t_{1/2}$/h
1	0.10	5	38
1 + CF_3CO_2H	0.03	1.2	160
1 + $CsClO_4$	0.04	0.3	638

On irradiation of a methanol solution of **1** (*ca.* 5×10^{-5} M) at 366 nm, the photocycloadduct **2** is formed as evidenced by the disappearance of the ^{1}La UV absorption (300–400 nm) and the emergence of a new absorption (270–290 nm) characteristic of an *o*-xylene system. The reaction efficiency for this process (Φ_R = 0.10) is much greater than those found for analogous processes with more sterically hindered systems.[3b] Cryptand **2** reverts back to the crown **1** in the dark with a half life of 38 h. Preliminary photocyclisation studies have been carried out in the presence of H^+ and Cs^+ (*ca.* 1000-fold excess) with the relevant data displayed in Table 1. The closing and opening rates clearly depend upon the type of guest present; significantly, Cs^+ retards the rate of both the forward and reverse processes. It is likely that this substrate dependency is a result of increased steric hindrance for the forward process and an increased stabilisation of the cryptand geometry for the reverse process, as a consequence of the cation being enclosed within the cryptand cavity.

This is the first example of a molecular system that, upon the action of an external trigger, can switch *reversibly* between a crown and cryptand.[9] Preliminary studies indicate that the photocyclisation quantum yields and the rates of the thermal reverse reactions are clearly influenced by the nature of the bound substrate. Detailed studies of the cation binding ability of both **1** and **2** and also the transient kinetic analysis and electrochemical properties of **1** are currently underway.

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Footnotes

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‡ 9-Anthracenyloxyacetyl chloride is readily prepared from the acid, which is obtained by reacting anthrone with ethyl bromoacetate in the presence of base.

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