

# Electronic energy transfer in adducts of aromatic crown ethers with protonated 9-methylaminomethylanthracene

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In CH<sub>2</sub>Cl<sub>2</sub> solution the protonated form of 9-methylaminomethylanthracene gives adducts with aromatic crown ethers; absorption, emission and excitation spectra show that adduct formation causes the quenching of the crown ether fluorescence and the sensitization of fluorescence of the anthracene moiety.

It has long been known that crown ethers can form adducts with organic ammonium ions.<sup>1</sup> More recently it has been realized that suitable 'wire-type' ammonium ions can thread crown ethers to give pseudorotaxane structures.<sup>2,3</sup> Our interest in the development of photochemical molecular devices<sup>4</sup> has led us to explore whether this type of hydrogen bonding interaction can be exploited to design systems of photochemical and photo-physical interest. We have therefore chosen a fluorescent aromatic ammonium ion and fluorescent aromatic crown ethers and studied the photoinduced processes that take place in their adducts.

All the experiments were carried out in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature with equipment and procedures previously described.<sup>5</sup> The compounds used were purified commercial products.

The absorption and fluorescence spectra of 9-methylaminomethyl anthracene **1** is shown in Fig. 1. The fluorescence of the anthracene moiety is partly quenched by intramolecular electron transfer involving the lone pair of the amino group. Addition of trifluoroacetic acid (AH) causes the protonation of the lone pair and prevents the quenching process, with a consequent increase in the fluorescence intensity.<sup>6-8</sup> The crown ether dibenzo-24-crown-8 **2** shows an absorption band with  $\lambda_{\max}$  284 nm and a fluorescence band with  $\lambda_{\max}$  310 nm, which are largely unaffected by addition of trifluoroacetic acid.

The absorption and fluorescence spectra of a CH<sub>2</sub>Cl<sub>2</sub> solution containing  $1.0 \times 10^{-4}$  M **1** and **2** are exactly those expected in the absence of any interaction between the two species. More specifically, excitation at 350 nm, where only **1** absorbs, causes

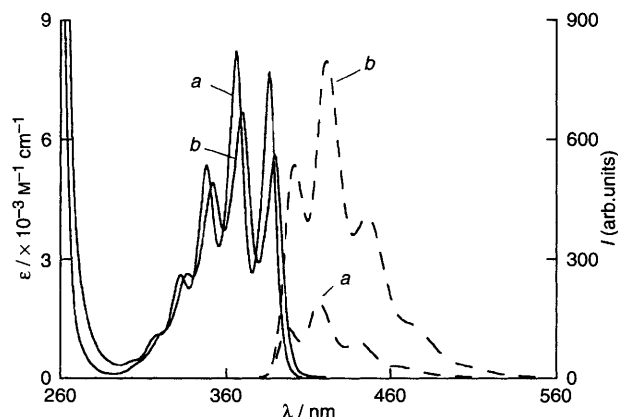


Fig. 1 Absorption (—) and fluorescence (---) spectra of a  $1.0 \times 10^{-4}$  M of **1** in CH<sub>2</sub>Cl<sub>2</sub> solution (a) before and (b) after addition of  $1.0 \times 10^{-3}$  M of CF<sub>3</sub>CO<sub>2</sub>H

the anthracene fluorescence ( $\lambda_{\max}$  417 nm), whereas excitation at 284 nm, where both **1** and **2** absorb, causes the fluorescence of both **1** ( $\lambda_{\max}$  417 nm) and **2** ( $\lambda_{\max}$  310 nm), with relative intensities proportional to the quantum yields of the two components and the fraction of absorbed light.

When the solution containing **1** and **2** is titrated with CF<sub>3</sub>CO<sub>2</sub>H, small changes in the absorption spectrum are observed, as expected for acid addition to the anthracene-based component alone (Fig. 1). The fluorescence spectrum of the solution, however, undergoes profound changes, as shown in Fig. 2. For 350 nm excitation, which corresponds to an isosbestic point of **1** and **1H**<sup>+</sup>, the addition of acid causes a strong increase in the fluorescence intensity of **1**, almost coincident with that observed for **1** alone [Fig. 2(a)]. For 284 nm excitation, where both **1** and **2** absorb, one can observe that: (i) the fluorescence intensity of **2** with a maximum at 310 nm remains almost unchanged until addition of one acid equivalent

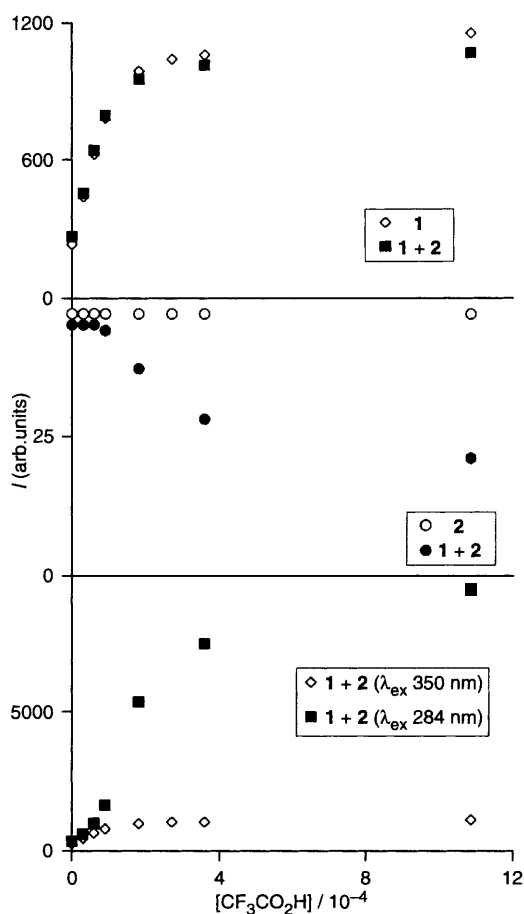
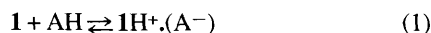


Fig. 2 Changes in the fluorescence intensity of a CH<sub>2</sub>Cl<sub>2</sub> solution containing  $1.0 \times 10^{-4}$  M **1** and/or **2**; (a)  $\lambda_{\text{exc}}$  350 nm;  $\lambda_{\text{em}}$  420 nm; (b)  $\lambda_{\text{exc}}$  284 nm;  $\lambda_{\text{em}}$  310 nm; (c)  $\lambda_{\text{exc}}$  284 nm;  $\lambda_{\text{em}}$  420 nm

and then decreases strongly, whereas it remained unchanged in the case of **2** alone [Fig. 2(b)]; (ii) the anthracene fluorescence intensity ( $\lambda$  417 nm) increases as it does for anthracene alone until one acid equivalent is added, but upon further addition of acid the increase becomes steeper [Fig. 2(c)]. It can also be seen that all the changes level off for a strong excess of added acid.

The above results show that the first effect caused by acid addition to the 1 : 1 mixture of **1** and **2** is the protonation of **1** exactly as it occurs in a solution of **1** alone, and that the interaction between **1** and **2** begins only after addition of more than one equivalent of acid.

These results can be explained as follows. At the beginning of the titration the anion of the added acid keeps the ammonium ion engaged in an ion pair [eqn. (1)]. From the



first part of the titration curve, a value of the order of  $10^6 \text{ M}^{-1}$  can be estimated for the equilibrium in eqn. (1). Under these conditions, association of  $\mathbf{1}\text{H}^+$  with the crown ether is prevented. On further addition of acid, however, the  $\text{A}^-$  counter ion can be engaged in hydrogen bonds with another AH species [eqn. (2)], thereby leaving  $\mathbf{1}\text{H}^+$  available for association with **2** [eqn. (3)]. When  $\text{CF}_3\text{COOH}$  is replaced

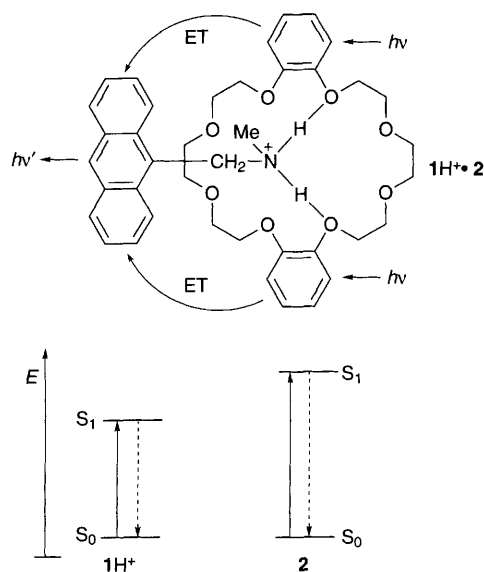
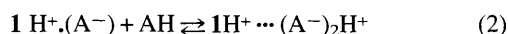


Fig. 3 Schematic representation of the energy transfer process

by the stronger  $\text{CF}_3\text{SO}_3\text{H}$  acid, protonation of the amine leads directly to its association with the crown ether.

As one can see from Fig. 2(b) and (c) association between  $\mathbf{1}\text{H}^+$  and **2** causes the quenching of the fluorescence of **2** and the parallel sensitization of the fluorescence of **1**. This means that the fluorescent excited state of **2** is deactivated by energy transfer to the lower lying fluorescent excited state of  $\mathbf{1}\text{H}^+$  (Fig. 3). Analysis of the data shown in Fig. 2 allowed us to estimate values of *ca.* 2000 and  $40\,000 \text{ M}^{-1}$  for the association constant of eqn. (2) and eqn. (3), respectively. A comparison between the absorption and excitation spectra of the adduct shows that in the adduct, energy transfer from the crown ether to the anthracene moiety is 100% efficient.

Preliminary investigations have shown that electronic interaction between the components of adducts formed by fluorescent ammonium ions and aromatic crown ethers is a general phenomenon. Results similar to those described above have been obtained with dibenzo-30-crown-10, whereas in the case of dinaphtho-30-crown-10 the interaction leads to the disappearance of the structured anthracene fluorescence and the appearance of a broad emission in the same spectral region that can be assigned to a luminescent exciplex.

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