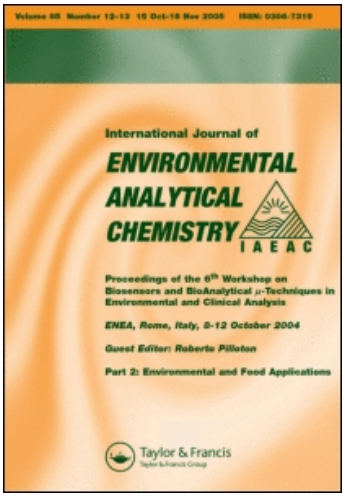

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Karina Schönefeld[a]; Anne Barann[a]; Kerstin Vogel[a]; Karl-Heinz Feller[a]; Denise Kunze[a]; Petra Müller[b]; Edwin Weber[b]
[a] University of Applied Sciences Jena, Faculty of Medical Engineering, D-07745 Jena, Germany [b] Freiberg University of Mining and Technology, Institute of Organic Chemistry, D-09596 Freiberg, Germany

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Fluorescence studies of crown ether complexes – solvent effects regarding the inclusion properties of host–guest sensor complexes

KARINA SCHÖNEFELD†, ANNE BARANN†, KERSTIN VOGEL†, KARL-HEINZ FELLER*†, DENISE KUNZE†, PETRA MÜLLER‡ and EDWIN WEBER‡

†University of Applied Sciences Jena, Faculty of Medical Engineering, Carl-Zeiss-Promenade 2, D-07745 Jena, Germany
‡Freiberg University of Mining and Technology, Institute of Organic Chemistry, Leipziger Strasse 29, D-09596 Freiberg, Germany

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Absorption and fluorescence of a crown ether complex, benzo-15-crown-5 coupled with a fluorescent anthracene unit (AEB), was studied in dependence on the solvent polarity and pH value. Whereas the absorption spectrum is only very weak solvent dependent, the fluorescence spectra are very dependent upon the polarity and the pH of the solvent with spectral changes of about 60 nm. Additional strong fluorescence quenching of the crown ether–anthracene complex in comparison to the pure anthracene was found. The results are discussed in the framework of the dual luminescence concept of Visser and Varma.

Keywords: Crown ether complexes; Fluorescence

1. Introduction

During the last decades, extensive studies have been carried out to investigate host–guest molecular systems with both high sensitivity and selectivity concerning the attracted guest molecule in low concentration range [1–3]. One of the main goals is to mimic the sensory receptors of plants and animals (insects) with respect to the odour profile of the attracting flower or plant in nature. There already exist many systems, especially in the field of ion detection [4–11] and low molecular weight molecules [12–17], where the recognition of the guest molecule of a special kind is neither a general nor a problem of selectivity even at extreme low concentration.

*Corresponding author. Fax: +49-3641-205 622. Email: Feller@FH-Jena.de

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Having very effective host–guest interacting systems, the main problem is the kind of signals produced to enable the detection of the interacting complex. Two main pathways have been used extensively in the past. The first one is the attachment of the guest molecule on the host complex adsorbed on the surface of an acoustical vibrator [16–21]. In this case the tuning of the resonance frequency due to the higher weight of the interaction complex is measured. A second pathway is the change of the corresponding fluorescence signals used as the detection principle. In cases when the guest molecule has auto-fluorescence or is made fluorescent by fluorescence markers attached to the analyte molecule, fluorescence quenching or even fluorescence enhancement is used as an analytical tool [22–24]. The guest molecule, usually, does not fluoresce. Here the fluorescence labeling of the host molecule complex gives a good tool to detect the attachment of the analyte at the host molecule [10, 14, 25–27]. This is even more the case when the fluorescence marker is sterically hindered by the attached guest molecule. Under such conditions the fluorescence properties, and not only the fluorescence intensity but the spectral parameters in general, can be changed dramatically [28, 29]. We have investigated a crown ether complex labeled with anthracene with respect to its spectral properties in dependence on the environment and the attachment of ions to account for the sensory ability in the field of low molecular weight molecule detection from the gas as well as from the liquid phase.

2. Experimental

Benzo-15-crown-5 coupled with a fluorescent anthracene unit (AEB, figure 1) was synthesized according to standard procedures [30]. Anthracene was commercially available from Merck. All solvents (Merck, UV-spectroscopy grade) were used as purchased.

The AEB stock solution (0.1 mM) was prepared in acetone. The coupled system of anthracene and crown ether required a comparison of absorption and fluorescence spectra of AEB with single anthracene. Therefore solutions of AEB (10 μM) and anthracene (10 μM) dissolved in acetone were prepared.

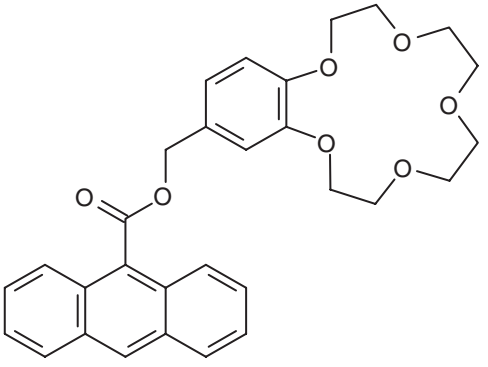

Figure 1. Structure of the used compound (benzo-15-crown-5-ether coupled with anthracene via carboxyl group, abbreviated AEB).

To check the AEB behaviour in polar and nonpolar environments, working solutions (10 μM) are prepared by dissolving stock solutions in different solvents, such as cyclohexane, toluene, chloroform, dichloromethane, acetone, acetonitrile and water. AEB was tested under aqueous conditions due to fulfilling requirements for sensor application. So it was necessary to examine AEB detailed under aqueous conditions. The working solutions were prepared by mixing acetone stock solution of AEB with water (1 : 10). The emission spectra were recorded in a time range of 24 h to investigate the stability of AEB. All further experiments with AEB in aqueous environment have been done for this reason 24 h after preparation.

The actual state of the crown ether–anthracene molecule (AEB) aged for 24 h was examined by a liquid–liquid extraction in a non-polar solution such as dichloromethane. Therefore a mixture of an aqueous solution of AEB aged for 24 h and dichloromethane in equal ratio was produced and shaken for 5 min. The fluorescence of both resulting phases, polar water phase and the non-polar dichloromethane phase, were investigated after 30 min.

Investigations of AEB in alkaline and acidic environments were done with an aqueous AEB solution aged for 24 h. The extreme alkaline and acidic conditions were reached by 1 M NaOH-solution and 1 M HCl-solution in 10 μM AEB.

Measurements of absorption spectra were done by a Perkin-Elmer UV-Vis spectrometer Lambda 2 in the range of 320–420 nm. Fluorescence spectra were recorded on a Perkin-Elmer spectrofluorimeter LS-50B in the range of 370–550 nm. An excitation wavelength of 360 nm was selected.

3. Results

The chromophore system of the crown ether complex is the anthracene molecule deviated by the linking ester chain with the dominant carbonyl group. This is very well reflected in the absorption spectrum as seen in figure 2. The figure shows the anthracene absorption spectrum (2) in comparison to the absorption spectrum of the

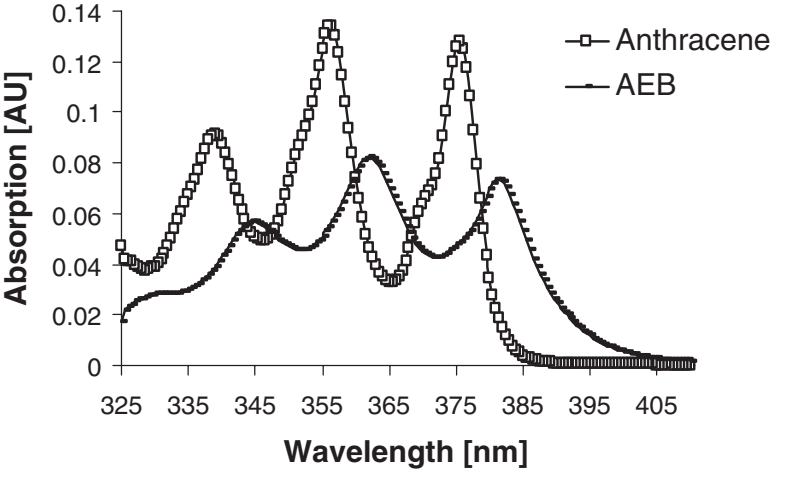

Figure 2. Comparison between the absorption spectrum of AEB and anthracene in acetone.

crown ether complex as depicted in figure 1. The crown ether complex has a red-shifted anthracene-like absorption with less pronounced vibrational structure due to the ester link. The absorption spectrum is nearly independent on the solvent polarity and pH value (figure 2).

No concentration dependence of the absorption spectra was found which excludes any dimer contribution to the absorption spectrum. The fluorescence spectra strongly depend very much on the nature of the solvent, the pH value and time, even in some cases indicating very slow changes of the structure of the investigated chromophore complex. Beside an anthracene-like spectrum in most cases the fluorescence spectrum of the solution in different solvents shows an unstructured maximum around 460 nm. This is shown for the case of acetone solution in figure 3. In dependence on the solvent the unstructured fluorescence band was shifted between 440–470 nm (figure 4).

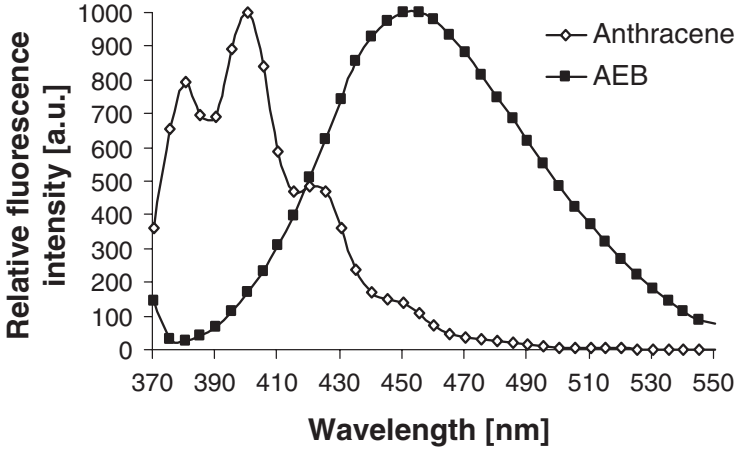

Figure 3. Comparison between emission spectrum of AEB and anthracene in acetone.

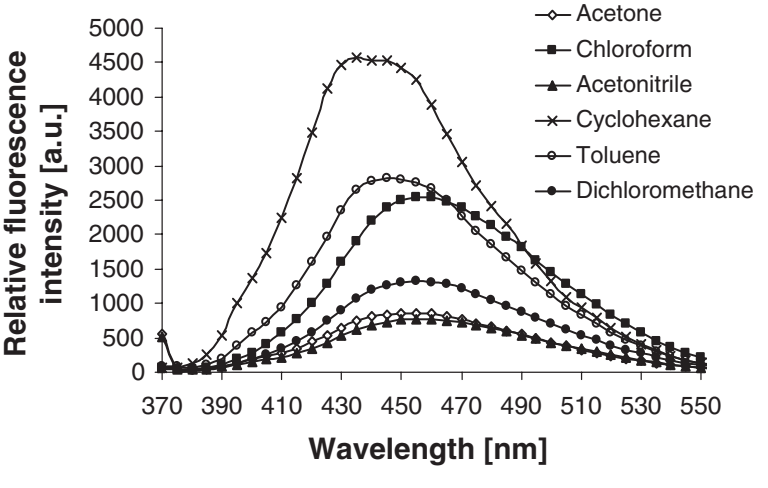

Figure 4. Solvent dependence of the fluorescence spectra of AEB.

This behaviour is even more pronounced in aqueous solution (prepared from the acetone stock solution), where the fluorescence spectrum of an aqueous solution immediately after preparation exhibits the unstructured red-shifted spectrum with very slow transformation into the anthracene-like fluorescence spectrum with a maximum at 400 nm after 3 h (final spectrum is reached within 24 h). The spectral changes are depicted in figure 5 in the time scale up to 3 h.

The behaviour is more obvious at different pH values. In acidic solution the fluorescence spectrum shows the normal unspecific shape with maximum at 490 nm, whereas with increasing pH-value the spectrum is blue-shifted. At neutral and alkaline pH values AEB shows the anthracene like spectrum which is also the case at all alkaline pH values (figure 6).

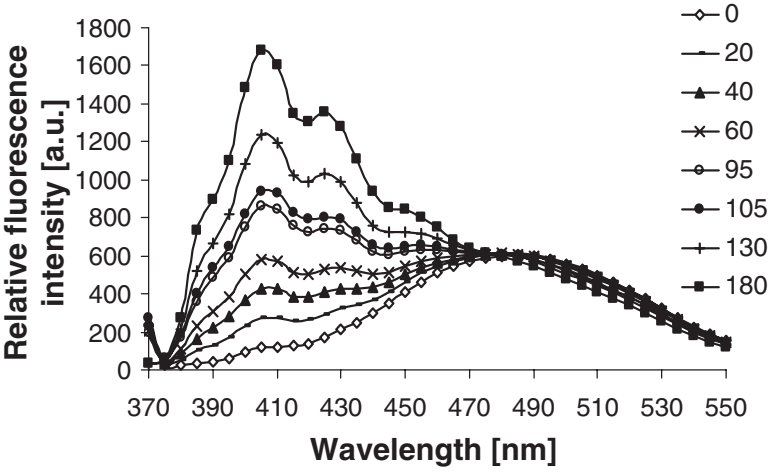

Figure 5. Fluorescence behavior of AEB in aqueous surrounding up to 3 h after preparation from acetone stock solution (0 min up to 180 min).

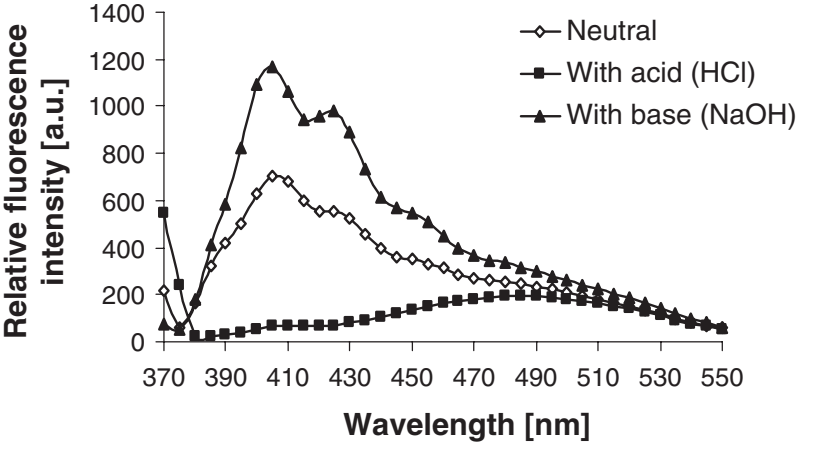

Figure 6. pH dependence of the fluorescence spectrum of AEB: (a) alkaline solution of AEB, pH = 12; (b) neutral solution of EAB, pH = 6; (c) acidic solution of AEB, pH = 1.

4. Discussion

4.1 *Solvent dependence and behaviour in aqueous solution*

In polar solution, the AEB fluorescence is red-shifted with a maximum around 480 nm whereas with decreasing solvent polarity the fluorescence spectrum becomes more blue-shifted. The corresponding correlation between Reichardt's solvent parameter E_T and the fluorescence maxima is not overwhelming good but still shows a dominant tendency (figure 7).

The fluorescence spectrum in aqueous solution (prepared from acetone stock solution by dilution in water) was found to be transformed from the unstructured spectrum (being typical for the non-polar solutions) to the anthracene-like spectrum within 3 h. The reason for the extreme slow structural changes of emission spectrum (figure 5) from 480 nm to 410 nm is not yet clear. Investigations have shown that a degradation (or decomposition) of the AEB molecule, one possible reason of this effect, can be excluded. The result is shown in figure 8. Beside the general transformation it is seen that after a liquid–liquid extraction from aqueous solution the solution in a non-polar solvent like dichloromethane shows the same spectral features with respect to the band structure and the fluorescence intensity as the stock solution having the same concentration.

The main feature of the fluorescence spectra is the dual luminescence occurring in dependence on the pH solvent. In acid solution the compound shows a red-shifted fluorescence with a maximum around 480 nm. In a neutral and alkaline environment, the red-shifted fluorescence disappears totally connected with a fluorescence band around the non-bonded anthracene band (around 400 nm).

It can be concluded that there should exist at least two different spectroscopic states in the excited state leading to different luminescent deactivation channels. This general phenomenon is well known in the literature from the investigations of Visser and Varma [30] of the anomalous fluorescence from solutions of diaminobenzonitrile. The scheme of solvent-assisted intramolecular charge transfer is presented in figure 9.

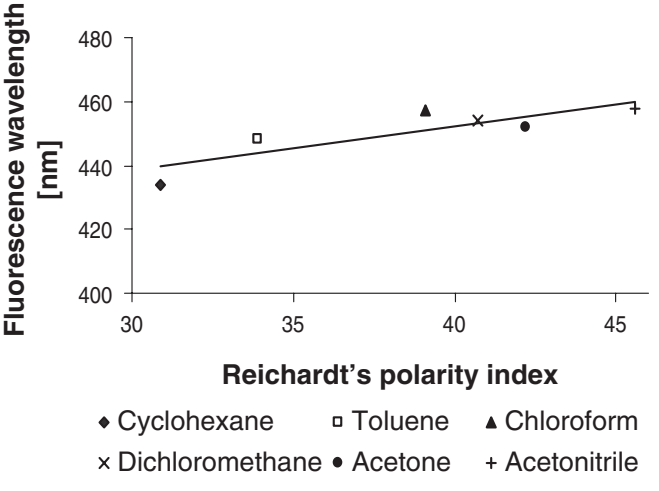

Figure 7. Correlation between the fluorescence maxima and the Reichardt's E_T values of the used solvents.

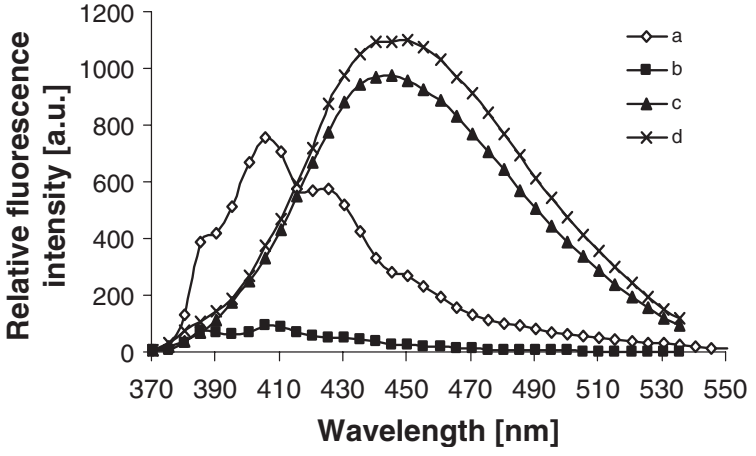

Figure 8. Comparison of the fluorescence spectra of AEB: (a) before extraction in aqueous solution (after 24 h); (b) after extraction in aqueous solution; (c) before extraction in dichloromethane; (d) after extraction in dichloromethane.

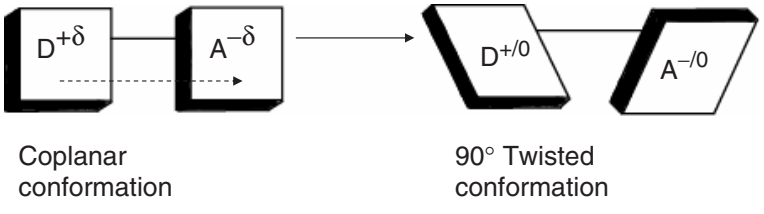

Figure 9. Scheme of coplanar and 90° twisted conformation of dimethylaminobenzonitrile explaining the solvent assisted dual luminescence behaviour after Visser and Varma [30].

Visser and Varma showed in a solute–solvent complex that the solvent induced wavelength shift is correlated to the dielectric properties of the medium. This behaviour is also well known as dual luminescence from the anthracene-9-carboxylic acid (9ACA) chromophore [31] which is, in our case, the fluorophore together with the linking group of the crown ether compound under investigation. It was shown by Ghoneim *et al.* [31] from concentration dependence measurements that both emissions are of molecular origin. In alkaline solution, the fluorescence is similar to that of anthracene, and this is explained by the authors as due to the wide energy gap between the anti-bonding orbitals of the aromatic ring and of the carbonyl group linked to the very strong donor O^- (figure 10).

It can be seen that the perpendicular conformation (charge separation) has strong fluorescence yield from the decoupled anthracene state with a fluorescence spectrum around the single anthracene spectrum. On the other hand, the twisted conformation in non-polar solvents tends to have a coupled fluorescence spectrum which is red-shifted due to the lower laying common ACOOH-state (figure 10) with strong fluorescence quenching (the fluorescence quantum yield of the coupled systems is around 4% of the uncoupled anthracene fluorescence quantum yield). Future work

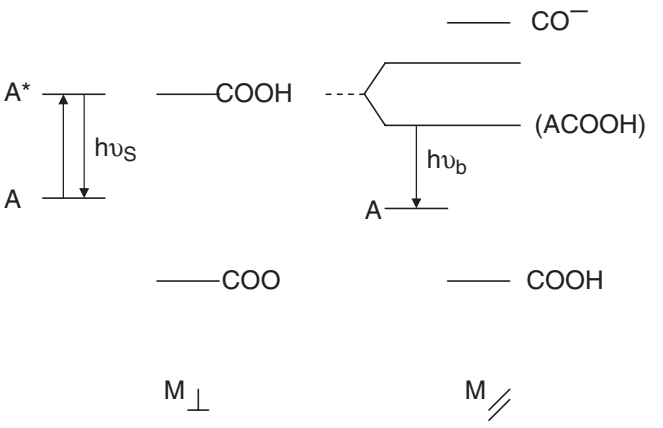

Figure 10. Energy level scheme of anthracene linked to carboxyl acid group (after Ghoneim *et al.* [31]).

will continue to investigate this very slow conformation process in more detail to understand finally the reason for the extremely low transformation speed [32].

5. Conclusion

A crown ether complex coupled with a fluorescent anthracene unit shows extraordinary solvent effects. Especially the results in aqueous environment pose a challenge to use such molecules for host–guest sensor complexes with strong wavelength shifts due to the polarity of the inclusion molecule. Direct control of the wavelength shift could possibly be used in sensor application.

Acknowledgement

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