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Novel Fluorescence Probes Based on 2,6-Donor−Acceptor-Substituted Anthracene Derivatives

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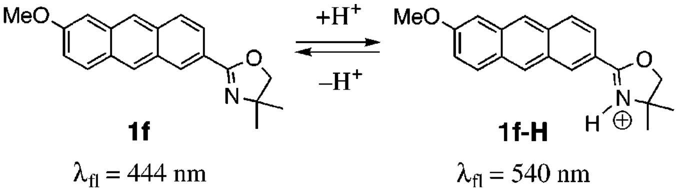
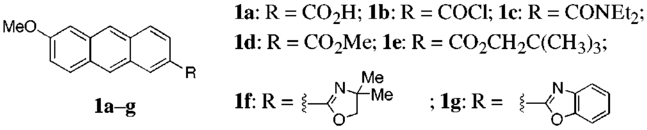
ABSTRACT



The fluorescence properties of selected derivatives of 6-methoxyanthracene-2-carboxylic acid were studied. The corresponding ester and oxazoline derivatives exhibit a moderate solvatochromism, which is caused by the donor–acceptor interplay. The fluorescence band shift and intensity of oxazoline 1f may be reversibly modulated by protonation or complexation with silver ions; thus, the oxazoline heterocycle serves as a useful substituent with switchable acceptor strength.

Fluorescent organic molecules exhibit a high potential as sensors for organic and inorganic analytes and as probes and markers in biological or supramolecular systems.[1] Among the most frequently used fluorophores in this area are anthracene derivatives, because they exhibit good emission properties with moderate to high quantum yields.[2] During our studies of donor−acceptor-substituted fluorescent probes, we synthesized for the first time the 2,6-donor−acceptor-substituted anthracene **1a**, which possesses interesting photophysical and photochemical properties.[3] Along with a moderate solvatochromism, the emission properties of the fluorophore could be significantly changed on acidification. In search for efficient fluorescent probes, whose emission properties may be modulated by their environment, we prepared further derivatives of the carboxylic acid **1a**, i.e., the amide **1c**, the esters **1d** and **1e**, the oxazoline **1f**, and the benzoxazole **1g**. Herein, we report the photophysical properties of these novel fluorescent anthracene derivatives and demonstrate that the acceptor strength of the oxazoline functionality in anthracene **1f** may be efficiently and reversibly modulated through protonation and silver-ion complexation.

The anthracene derivatives **1c−g** (Figure 1) were obtained



1a: R = CO_2H; **1b**: R = COCl; **1c**: R = $CONEt_2$;
1d: R = CO_2Me; **1e**: R = $CO_2CH_2C(CH_3)_3$;
1f: R = ; **1g**: R =

Figure 1. Donor−acceptor-substituted anthracene derivatives **1a−g**.

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† Undergraduate research participant, Spring 1999.

[1] (a) *Chemosensors of Ion and Molecular Recognition*; Desvergne J.-P., Czarnik, A. W., Eds.; Kluwer Academic Press: Dordrecht, The Netherlands, 1997; Vol. 492. (b) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515. (c) *Fluorescent Chemosensors for Ion and Molecule Recognition*; *ACS Symp. Ser. 538*; Czarnik, A. W., Ed; American Chemical Society: Washington D. C., 1993. (d) Valeur, B. In *Topics in Fluorescence Spectroscopy*; Lakowics, J. R., Ed.; Plenum Press: New York, 1994, Vol. 4; Chapter 2.

[2] For recent examples, see (a) Ishikawa, J.; Sakamoto, H.; Nakao, S.; Wada, H. *J. Org. Chem.* **1999**, *64*, 1913. (b) Wang, W.; Gao, S.; Wang, B. *Org. Lett.* **1999**, *1*, 1209. (c) Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M. T.; Marquis, D.; Pérez-García, L.; Stoddart, J. F. *Eur. J. Org. Chem.* **1998**, 81. (d) Hashimoto, K.; Kawaguchi, H.; Okuno, T.; Shirahama, H. *Synlett* **1997**, 1202. (e) Daub, J.; Beck, M.; Knorr, A.; Spreitzer, H. *Pure Appl. Chem.* **1996**, *68*, 1399. (f) Vollmer, M. S.; Würthner, F.; Effenberger, F.; Emele, P.; Meyer, D. U.; Stümpfig, T.; Port, H.; Wolf, H. C. *Chem. Eur. J.* **1998**, *4*, 260.

[3] Ihmels, H. *Eur. J. Org. Chem.* **1999**, 1595.

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by routine transformations of the carboxylic acid functionality from the acid chloride **1b** and characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis or high-resolution mass spectrometry (cf. Supporting Information).

Except for the amide **1c**, which emits at $\lambda = 448$ nm in methanol, acetonitrile, and benzene, anthracene derivatives **1d**−**g** exhibit a moderate solvatochromism in their emission spectra, exemplified by the benzoxazole-substituted anthracene **1g** (Table 1). Generally, the emission maximum of derivatives **1d**−**g** is red-shifted with increasing solvent polarity. Moreover, a broad band with one maximum was observed in polar solvents such as methanol and acetonitrile, whereas in the nonpolar benzene and cyclohexane solutions, additional local maxima and/or shoulders appear, as shown for methyl ester **1d** (Figure 2). The absorption maxima of the anthracene derivatives **1c**−**g** only showed small shift differences in the various solvents (Table 1).

Table 1. Solvent Dependent Absorption and Emission Maxima of Anthracene **1g**

solvent	$\lambda_{abs}{}^{a,b}$	log ϵ	$\lambda_{fl}{}^{a,c}$	$\phi_{fl}{}^{d}$
cyclohexane	404	4.05	433	0.49
benzene	407	3.99	442	0.43
CH_2Cl_2	406	3.97	452	0.44
n-BuCN	405	3.97	453	0.48
CH_3CN	404	3.95	456	0.45
DMF	407	3.97	458	0.45
DMSO	409	3.97	461	0.43
MeOH	403	4.01	462	0.43

[a] In nm. [b] Maximum with highest wavelength; absorption spectra were recorded in 10^{-4} M solutions. [c] Emission spectra were recorded in 10^{-5} M solutions, $\lambda_{ex} = 390$ nm. [d] Determined relative to quinine sulfate in 1 N H_2SO_4 (cf. Supporting Information).

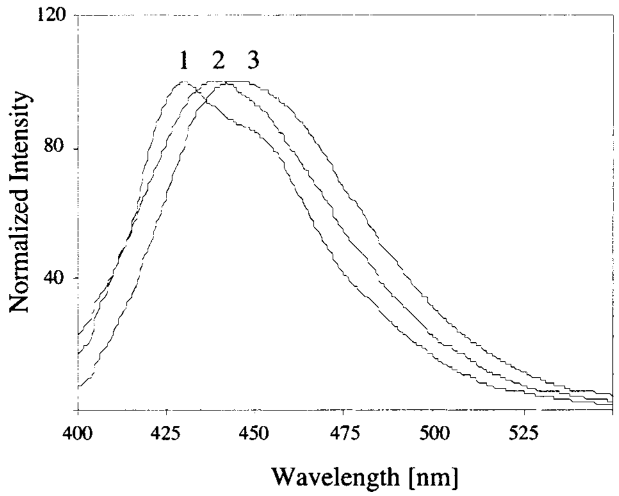

Figure 2. Normalized fluorescence spectra of methyl anthracenecarboxylate **1d** in benzene (1), acetonitrile (2), and methanol (3); $\lambda_{ex} = 380$ nm.

The most remarkable emission properties were observed for the oxazoline **1f**. On slight acidification (pH = 3) of a methanol solution of anthracene **1f**, the emission maximum at $\lambda = 444$ nm was significantly quenched (90%), and a new maximum appeared at $\lambda = 540$ nm (Figure 3). Further acidification led to the total disappearance of the short-wavelength fluorescence; however, on neutralization of the solution, the initial emission spectrum of anthracene **1f** was regained. A similar effect was observed in the presence of silver cations, i.e., titration of an aqueous silver nitrate solution to anthracene **1f** led to a significant red-shift of the emission band to $\lambda = 462$ nm (Figure 3). Significant is the fact that the fluorescence intensity decreased only slighty (<5%) during the titration. The original oxazoline fluorescence was regained by addition of equimolar EDTA solution. Whereas the addition of cadmium salts to oxazoline **1f** did not influence its emission properties, titration with mercury acetate resulted in a significant quenching of the fluorescence intensity without a band shift (Figure 4).

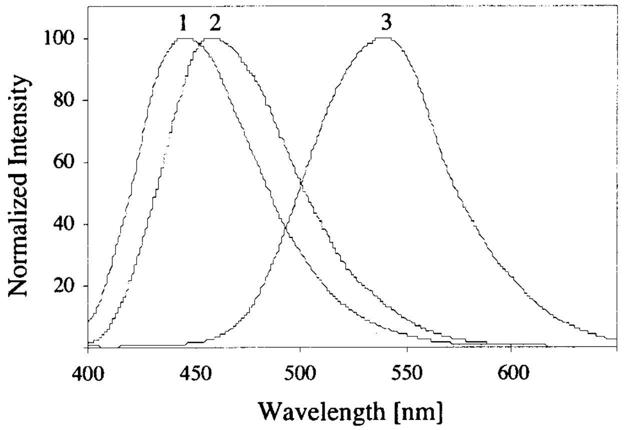

Figure 3. Normalized fluorescence spectra of oxazoline **1f** (10^{-5} M) in methanol (1), 7 × 10^{-3} M $AgNO_3$ in methanol (2), and 0.5 M HCl in methanol (3); $\lambda_{ex} = 390$ nm.

The acid and silver-ion titration also influenced the absorption spectra of oxazoline **1f**. On addition of acid to the anthracene **1f**, which exhibits a long-wavelength maximum at $\lambda = 402$ nm, a new, unstructured, and red-shifted absorption band at $\lambda = 440$ nm appeared. Although, oxazole **1g** did not display a red-shift of the absorption and emission bands on acidification, a bathochromic shift was observed from $\lambda = 462$ nm to $\lambda = 474$ nm along with a steady quenching of the fluorescence intensity on addition of aqueous silver nitrate solution.

The anthracene derivatives **1d**−**g** exhibit moderate solvatochromism.[4] It may be assumed that the first excited-state S_1 has a larger dipole moment than the ground state due to an photoinduced internal charge transfer from the donor to the acceptor functionality.[1d,5] Consequently, polar

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(4) Suppan, P.; Ghoneim, N. *Solvatochromism*; The Royal Society of Chemistry: London, 1997; Chapter 4.

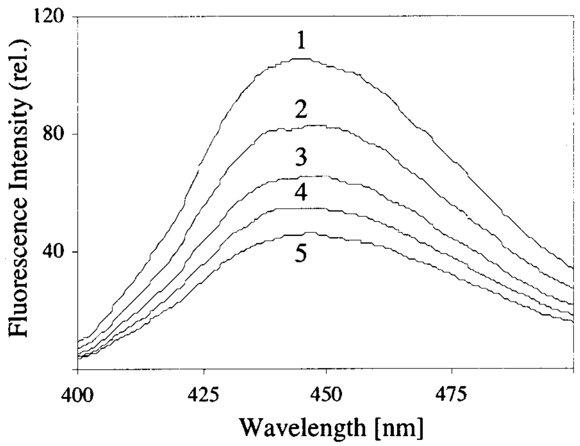
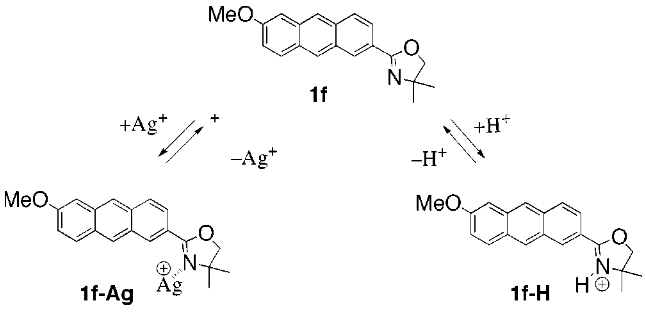


Figure 4. Fluorescence spectra of oxazoline **1f** 10^{-5} M in methanol (1), upon addition of 5 μL (2), 10 μL (3), 15 μL (4), and 20 μL (5) of saturated aqueous $Hg(OAc)_2$ solution; $\lambda_{ex} = 390$ nm.

solvents stabilize the excited state more effectively than the ground state. Thus, a good correlation ($r^2 = 0.93$) of the red-shift of the emission band with the polarity parameter $E_T(30)$[6] of the aprotic solvents was found. Protic solvents such as methanol do not fit this correlation due to specific interactions by hydrogen bonding.[4] The anthracene derivative **1c** with the rather weak amide acceptor substituent does not exhibit solvatochromism such as the anthracene derivatives **1d**−**g**, which are substituted with comparably stronger electron-withdrawing groups. This observation confirms that the donor−acceptor interplay is the structural feature that determines the photophysical properties of the novel anthracene derivatives **1d**−**g**.

The significant red shift of the absorption and emission maxima of the oxazoline **1f** on acid or silver-ion titration results from the protonation or complexation of the oxazoline nitrogen atom (Scheme 1). The resulting "oxazolinium substituent" has a higher π-acceptor strength than the oxazoline, which promotes a stronger donor−acceptor interplay with the conjugating methoxy functionality, as manifested by the bathochromic shift of the absorption and emission bands. In control experiments it was shown, that the addition of silver nitrate to a methanol solution of 2-methoxy-6-methylanthracene[3] also yielded a slight decrease of the fluorescence intensity; however, no band shift was observed. These facts allow us to conclude that the emission band shift of the oxazoline **1f** on silver-cation addition is not due to cation−π interactions. Since an excess of silver nitrate is required for the emission band shift of the oxazoline **1f**, it may be concluded that the association between the oxazoline nitrogen atom and the silver cation is rather weak. Since the fluorescence intensity of oxazoline **1f** and oxazole **1g** is solely quenched without an accompanying band shift, the mercury cation is not complexed to the oxazoline nitrogen atom, as is the case for the silver cation. Presumably, the mercury cation tends to associate with the aromatic π system, which results in fluorescence quenching due to the heavy atom effect.[7] This assumption is confirmed by the observation that addition of mercury acetate solution to unsubstituted anthracene or 2-methoxy-6-methylanthracene[3] also results in the quenching of the emission intensity.

Scheme 1. Reversible Protonation and Complexation of Oxazoline **1f**



Since the protonation and complexation of oxazoline **1f** may be reversed by simple neutralization or decomplexation, the oxazoline heterocycle represents a substituent whose acceptor properties are, at will, reversibly modified. This chemical feature may be used for data storage and data processing by efficient switching of the fluorescence properties.[8] Moreover, it should be noted that the emission bands of the oxazoline **1f** and the protonated form **1f**−**H** do not overlap in the long- and short-wavelength regions of the emission spectrum, which is a prerequisite for the application in effective data processing.[9]

The concept to reversibly tune the donor or acceptor properties by attractive interactions with metal cations is known;[1d] however, there are only a few examples of acceptor modulation by this methodology.[10] Oxazoline **1f** represents a promising new feature which may be further explored to design and develop donor−acceptor-substituted chromophores with efficiently switchable emission properties.

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Supporting Information Available: Procedures for synthesis, characterization data, and selected absorption and emission spectra of compounds **1c**−**g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) PM3 calculations on the parent anthracene **1a** reveal that the excited state (4.4 D) has a higher dipole moment than the ground state (3.0 D).

(6) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

(7) Koziar, J. C.; Cowan, D. O. *Acc. Chem. Res.* **1978**, *11*, 334.

(8) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; McCoy, C. P.; Maxwell, P. R. S.; Rademacher, J. T.; Rice, T. E. *Pure Appl. Chem.* **1996**, *68*, 1443.

(9) However, a major drawback of the system is the instability of the protonated oxazoline **1f**−**H**, which decomposes slowly as was followed by the appearance of a new weak emission band after 24 h at room temperature. Experiments to design more stable protonated oxazolines are currently performed.

(10) (a) Bourson, J., Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552. b) Dix, J. P.; Vögtle, F. *Chem. Ber.* **1981**, *14*, 638.