New molecular systems for functional dye-based molecular switching of luminescence

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Abstract. Three types of molecular switching processes involving luminescence are reported. The first section deals with photochemical induced switching. The bisarylene-substituted dihydroazulene/vinylheptafulvene (DHA-PA/VHF-PA) couple containing a photoswitchable substructure (photochemical forward and thermal reverse reaction) shows on/off switching of luminescence arising from the fluorescent DHA-PA and the non-fluorescent VHF-PA. The second part pertains to electrochemically induced switching. Benzodifurane quinone BFQ-A can reversibly be reduced to the hydroquinone dianion BFQ-A^{2-} in a two-step process via quinone radical anion BFQ-A$^{.-}$. BFQ-A and BFQ-A$^{.-}$ are non-fluorescent or weakly fluorescent respectively, whereas reduction to BFQ-A^{2-} leads to a significant fluorescence. In the third part the generation of electrochemiluminescence (ECL) by the stilbene-like compounds SN-A, QN-A and QS-A is described. Electrochemical and optical properties were investigated by cyclic voltammetry and spectroelectrochemical methods.

INTRODUCTION

The interaction of functional dyes with electrons and photons provides the molecular basis for the photochemical/photophysical or electrochemical/electrophysical switching processes which can be of multi-mode type (1). For this reason those dyes are well suited for use as probes for analytical and sensor chemistry (2) and as building blocks for the fabrication of optoelectronic devices (3).

To accomplish target-oriented applications molecular and supramolecular substrates, as described in Scheme 1, have to be synthesized. The general structure includes antenna and emitter subunits which are chemically linked. An external perturbation originating from chemical or physical interaction has to be transduced into a response signal of the emitter. What are sought are new dye compounds with an unique combination of molecular functionalities (4).
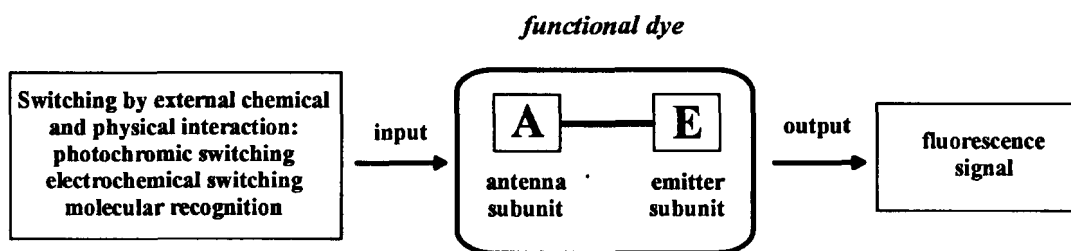
functional dye

Scheme 1: Schematic view of a functional dye by which an external interaction is transformed into an on/ off-output of a fluorescence signal.

In recent studies we and others have investigated molecular switching of light-sensitive and electron transfer-active dye compounds based on their photochromic and electrochromic behavior and the mutual participation of them to generate photochemically driven redox switching (5). This report describes present studies dealing with the development of multifunctional dye systems which are used to transform an external stimulation into an emerging fluorescence signal (Scheme 1). Since optical emission is a powerful, highly sensitive and selective probe which can either be used in frequency, intensity or time-resolved mode (6), it is expected to have impact on such different fields as the analytics of chemical and biochemical systems or in the fabrication of devices for optical data storage and signal amplification, for example light-emitting devices (LEDs).

The compounds given in Scheme 2 are designed to contribute to the following three topics: (i) Photo-chemically induced on/off-switching of luminescence by the photochromic dihydroazulene (DHA-PA)/vinylheptafulvene (VHF-PA) system. (ii) Electrochemically induced on/off- switching of luminescence by the anthracenyl substituted benzodifurane quinone (BFQ-A). (iii) Generation of luminescence by electrochemical activation of the donor/acceptor substituted stilbene-like compounds NN-A, SN-A, ON-A, OS-A and Me-OS-A.
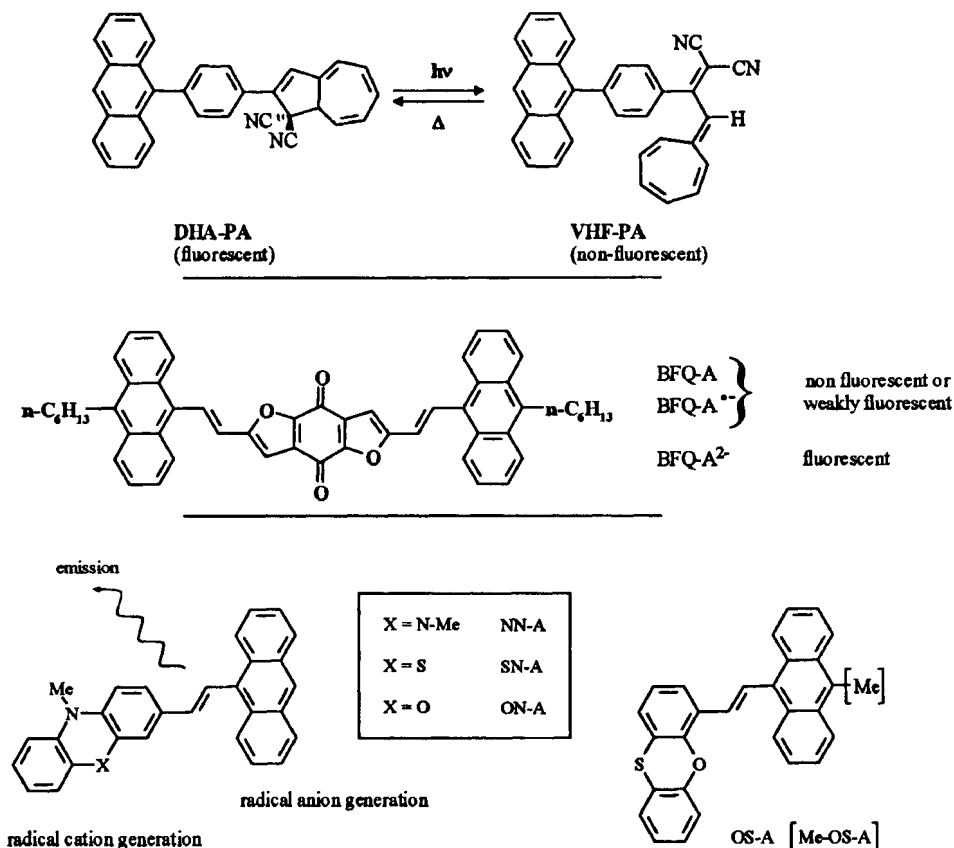
Scheme 2: Compounds used in this study. Systems for on/off switching of luminescence by external photochemical or electrochemical stimulation.

EXPERIMENTAL

The compounds included in this study were synthesized by methods described in three doctoral theses (7). The electrochemical and optoelectronic properties of these systems are studied by cyclic voltammetry [Amel 5000 electrochemical system, undivided cell, three-electrode configuration, platinum disc as working electrode, platinum plate as counter electrode, AgCl coated silver wire as "pseudo" reference electrode]. All potentials are referenced against ferrocene/ferrocenium (FOC) as internal standard. Tetra-n-butylammoniumhexafluorophosphate (TBAHFP) was used as supporting electrolyte. Solvents were used as indicated. UV/VIS/NIR-spectroelectrochemistry [Perkin-Elmer Lambda 9 spectrophotometer, potential adjustment by an AMEL 550 potentiostat, thin-layer cell (8)] and spectroelectrochemistry in emission [Amel 5000 electrochemical system, three-compartment cell with the compartements separated by membranes, platinum disc as working electrode, glassy carbon as counter electrode, AgCl coated silver wire as "pseudo" reference electrode; Hitachi F-4500 fluorescence spectrometer (9)].

Photochemical induced on/off switching of luminescence by DHA-PA/VHF-PA

Photochromic fluorescent switches are suitable species for being incorporated in optical computing devices based on molecular architecture (10). The „write" information can be given by the photochromic switching and the fluorescent signal may serve as „read" information. In addition fluorescent switches may be utilizes to examine supramolecular systems since photochromic switching, in general, is accompanied by a change of size and therefore on/off switching depends on the molecular environment (11).

The DHA/VHF photochromism shows two-state switching between isomers which differ strongly in their electronic properties (12). At room temperature dihydroazulene (DHA) and vinylheptafulvene (VHF) are weakly fluorescent and non-fluorescent respectively (13). In the DHA form the fluorescence competes with photochemical deactivation and it is likely that in VHF radiation-less deactivation dominates. Therefore, we prepared DHA-PA in which the anthracenylphenylene group, which is covalently attached at C-2, provides an additional fluorescent label.
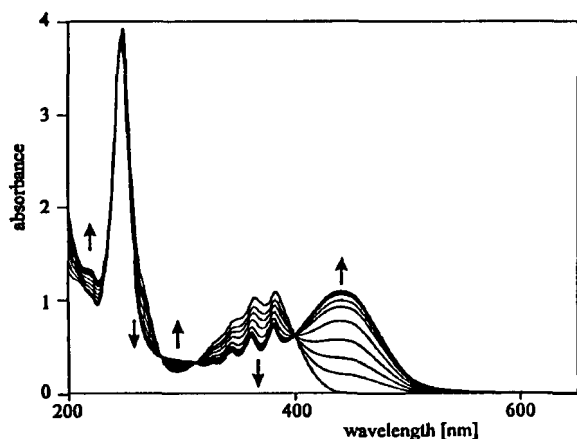

Fig. 1: Photochromism by interconversion of DHA-PA/VHF-PA in cyclohexane. Irradiation of DHA-PA in the range of 290 to 400 nm. Reverse reaction under thermal conditions.

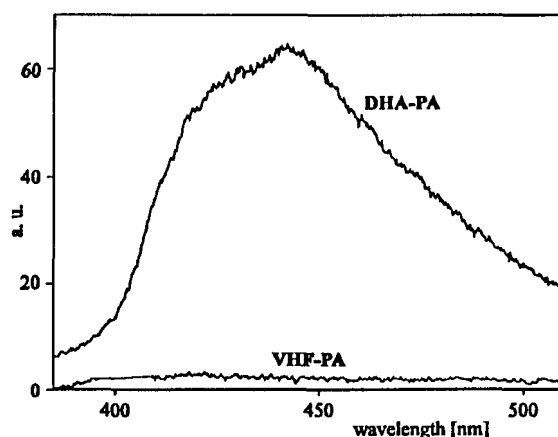**Fig. 2**: Dual-mode on/off switching of luminescence of DHA-PA/VHF-PA system.

Figure 1 displays the photochromic switching of the DHA-PA/VHF-PA system in cyclohexane. On irradiating the long-wavelength absorption of DHA-PA (λ_{max}=383 nm), which consists of the overlapping bands of the anthracene and the dihydroazulene substructures, decreases and a new absorption assigned to the vinylheptafulvene chromophore appears at λ_{max}= 440 nm. The fluorescence spectra depending on the shifting of the DHA-PA/VHF-PA equilibrium were determined in cyclohexane at room temperature. The results are given in Fig. 2. The DHA-PA form shows fluorescence after excitation at 366 nm whereas the VHF-PA form is non-fluorescent (excitation wavelength 361 nm). Investigations in order to evaluate the fluorescence quantum yields quantitatively and to study the fluorescent response on irradiating the DHA-PA/VHF-PA in a supramolecular environment are in progress.

Electrochemically induced on/off- switching of luminescence by BFQ-A

Charge (electron)-transfer is quite often responsible for the quenching of fluorescence (14). It is also known that radical anions are non-fluorescent (15). To investigate the effect of the redox state on the emission signal we selected benzodifurane quinone BFQ-A as a model compound. In BFQ-A, which by the condensed furan rings is likely to be a highly transmissive central unit (16), the electron transfer active quinone is symmetrically linked to two fluorophoric anthracenes. The reduction of the quinone to the hydroquinone dianion in THF occurs in a reversible two step process at $E_{1/2}$ = -1223 V and $E_{1/2}$ = -1913 V, as indicated by the cyclic voltammogram (Fig. 3). The spectra obtained for the radical anion and dianion forms by UV/VIS/NIR spectroelectrochemistry are in agreement with the quinone substructure illustrating
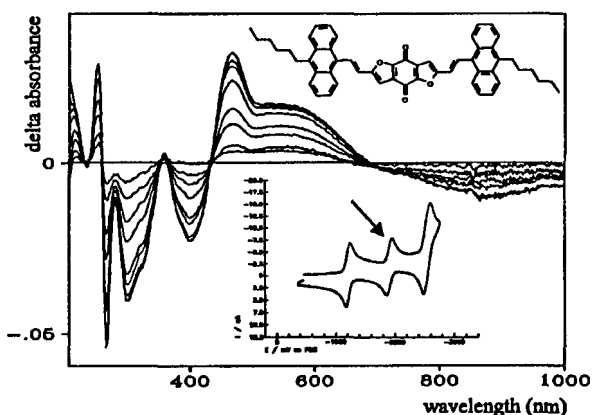

Fig. 3: Difference spectra (referenced vs the spectrum of the radical anion BFQ-A⁻) showing the formation of the dianion BFQ-A²⁻ from BFQ-A⁻. The cyclic voltammogram is shown in the insert. The applied potential indicated by the arrow (solvent: 0.1 M TBAHFP in THF, three-electrode cell, gold mini-grid working electrode; Ag/AgCl quasi-reference electrode; gold plate as auxiliary electrode).
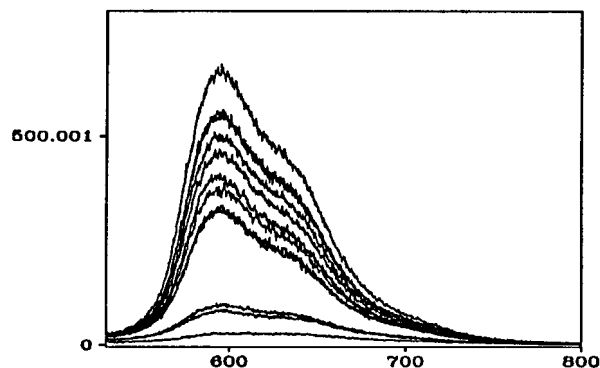
Fig. 4: Off/on switching of the luminescence during reduction of BFQ-A: Excitation wavelength at 520 nm, *detection* in the range of 530 to 800 nm.

that the two reversible redox processes are mainly localized at the benzodifuran unit. The reversible reduction of dianion BFQ^{2-} indicated by the third wave at $E_{1/2}$ = -2540 V is in agreement with an uptake of one or two extra electrons by the anthracene groups. The spectroelectrochemistry of the formation of BFQ-A^{2-} from the radical anion BFQ-$A^{\bullet-}$ is shown in Fig. 3. Fluorescence spectra were measured for electrolyzed solutions of BFQ-A in an electrochemical cell mounted within the fluorescence spectrometer. The results of these measurements are given in Fig. 4: At the beginning of the reduction process a weak fluorescence signal of the quinone BFQ-A appears. The successive formation of the hydroquinone form BFQ^{2-} is accompanied by a significant increase of the fluorescence signal.

Generation of luminescence by electrochemical switching

There is currently much research going on to develop organic light emitting diodes (LED's) based on polymer-embedded functional dyes which are responsible for the conversion of electrochemical energy into photonic energy (17). The prevailing technique to fabricate LEDs is based on making polymeric or oligomeric layer-structured systems. However, there also exist the idea of making light-emitting units using supramolecular architecture. This of course requires multifunctional dye compounds composed of „optoelectronic" substructures, which can be incorporated into supramolecular assemblies. We became interested in the stilbene-like compounds which (Scheme 2, bottom) contain electron donor as well as electron acceptor substructures (18). The preliminary goal is to evaluate their electrogenerated luminescence in solution. In the following the optoelectrochemical properties of these stilbene-like molecules are described.

The compounds NN-A, SN-A and ON-A give reversible waves for the formation of the radical cation and the radical anion as indicated by cyclic voltammetry. The formation of the radical ion of the phenoxathiine derivatives OS-A and Me-OS-A is an irreversible process. The reversibility of the formation of the radical cations follows also from UV/VIS/NIR spectroelectrochemistry. The long wavelength absorption bands of the radical cations of NN-A, SN-A and ON-A are given in Table 1.

Table 1: Long wavelength absorption bands of the radical cations of NN-A, SN-A and ON-A determined by spectroelectrochemical measurements in acetonitrile/TBAHFP.

	NN-A$^{\bullet+}$	SN-A$^{\bullet+}$	ON-A$^{\bullet+}$
absorption bands λ_{max}/ nm	724	846	1090

The ECL experiments have been carried out in a conventional electrochemical cell by generating the reactants sequentially at a single electrode (19). In Figure 5 the formation of the chemiluminescence from the reaction between ON-A$^{\bullet-}$ and ON-A$^{\bullet+}$ is given. The phenazine derivative NN-A is found to be ECL-inactive in acetonitrile, which might be caused by the small difference of the half-wave potentials. The compounds SN-A, ON-A, OS-A and Me-OS-A are electrochemiluminescent (Table 2).
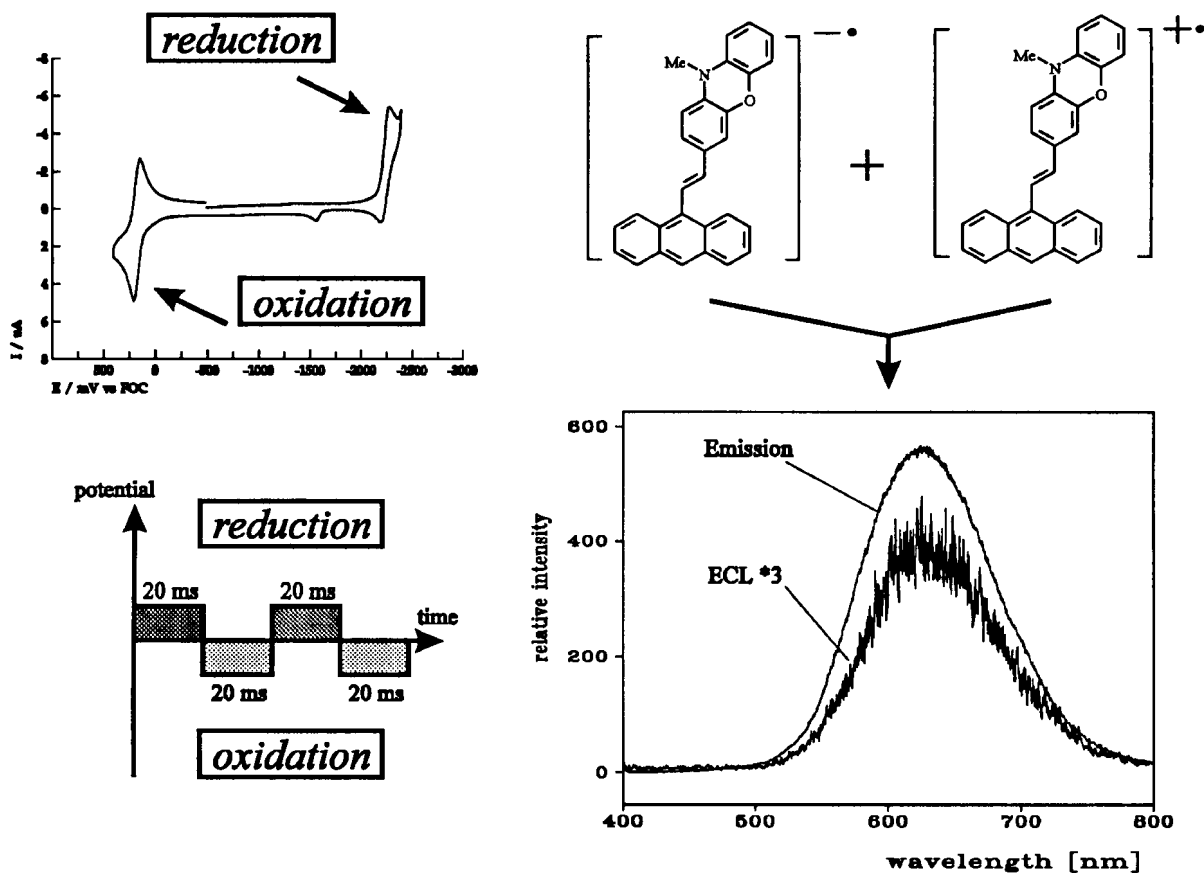
Fig. 5: ECL-experiment of QN-A (c = 10^{-4} M) in acetonitrile containing 0.1 M tetrabutylammonium-hexafluorophosphate as electrolyte in comparison with the conventional emission in acetonitrile by exitation at 398 nm. Sequential generation of radical cations and radical anions in 20 ms intervals at potential values as indicated in the cyclovoltammogram (cyclovoltammetry measurements according to the described data in the experimental part with 250 mV/sec).

Table 2: ECL- and photoemission of SN-A, QN-A, OS-A and Me-OS-A in comparison. Measurements in acetonitrile (ECL in acetonitrile/TBAHFP).

	SN-A	QN-A	OS-A	Me-OS-A
photoemission λ_{max}/ nm	625	625	483	510
ECL λ_{max}/ nm	630	630	~500	524

Despite their irreversible radical ion formation, the phenoxathiine derivative OS-A exhibits electrochemiluminescence which, however, is weakened because of film formation on the electrode. Modifying OS-A to Me-OS-A by appending a methyl group at the anthracene substructure has almost no effect on the cyclic voltammogram however it does lead to a stronger ECL-emission. Film formation on the electrode was not observed in this case.

ACKNOWLEDGEMENTS

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