

Stilbazolium salts as fluorescence probes for monitoring local viscosity and pH of solutions

Agnieszka BAJOREK, Ilona WRZEŚNIEWSKA, Marek PIETRZAK - Faculty of Chemical Technology and Engineering, University of Technology and Life Sciences, Bydgoszcz

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1. Introduction

The first well-defined molecule fluorophore was the natural product quinine, an important compound for organic chemistry and medicine [1]. The visible emission from an aqueous quinine solution was reported by Herschel in 1845 [2]. A few years later Stokes showed that this phenomenon was due to the absorption and the emission of light by quinine and coined the term "fluorescence" to describe this process. The fluorescence process begins when a molecule absorbs a photon of suitable energy. This promotes an electron to higher energy orbital. Back to the electronic ground state can occur with photon emission (fluorescence) or in a non-radiative fashion.

In the recent years dyes are widely used as fluorescence probes which are spectroscopic tools used in chemistry, biology and physics for monitoring specific properties of the medium in which they are incorporated. It is possible because their fluorescence is sensitive to changes in temperature, polarity, viscosity, pH or rigidity of the environment [3 ÷ 6]. Therefore, one can use them to estimate polarity and viscosity of medium by measuring the changes in their emission intensity or value of the emission maximum shift. Essentially there are four different kinds of fluorescent probes: (1) excimer forming, (2) twisted intramolecular charge-transfer (TICT) probes, (3) charge-transfer probes, and (4) fluorescent organic salts. The last group of probes is organic salts of the $D-\pi-A^+ X^-$ type. It includes substituted stilbazolium salts that exhibit a very strong temperature effect. Although structurally $D-\pi-A^+ X^-$ type probes are similar to the charge-transfer probes, their photo-physical properties are different. The photo-physics and spectroscopic behaviour of this class of compounds has been described by Fromherz's [7] and Rettig's [8] research groups. Stilbazolium salts were applied as fluorescence probes for measuring the progress of photo-polymerization of methacrylates [9, 10].

In this report, we describe the relationship between the changes in the emission spectra of a series of structurally different stilbazolium salts in solutions:

- including water and polyethylene glycol with different molecular weights, and thus solutions of very different local viscosity
- aqueous solutions of different pH values.

2. Experimental

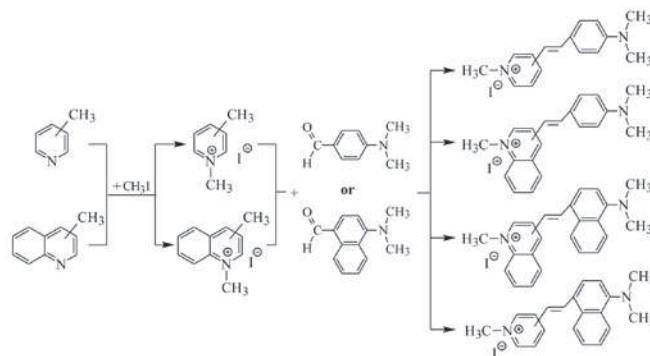
2.1. Spectral measurements

The UV-Vis absorption spectra were recorded at room temperature using a Shimadzu UV-Vis Multispec-1501 spectrophotometer, and fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter.

2.2. Synthesis

A general route for the synthesis of the tested dyes is shown in Scheme 1. Dimethylpyridinium and dimethylquinolinium iodides were obtained in 90% yield by refluxing the mixture of appropriate methylpyridine or methylquinoline (0.05 mol) and methyl iodide (0.05 mol) in acetone for 2 h. The precipitated crystals were filtered off, dried under vacuum, and used directly in the next step. The condensation of 4-(*N,N*-dimethylamino)benzaldehyde and 4-dimethylamino-1-naphthaldehyde with *N*-substituted picolines and methylqui-

nolinium iodides occurs during refluxing these compounds in methanol (3-4 h), in the presence of a few drops of piperidine. The precipitate formed after cooling down the reaction mixture was filtered and dried. The structure and purity of the prepared compounds were confirmed by NMR spectroscopy and thin layer chromatography.



Scheme 1. General route for synthesis of styrylpyridinium and styrylquinolinium iodides

3. Results and discussions

All probes under the study are well soluble in water. The structures of the tested stilbazolium salts, their basic spectroscopic properties and abbreviations are summarised in Table 1.

Table 1

Structures and spectroscopic properties of the tested dyes in *N,N*-dimethylformamide (DMF), acetonitrile (MeCN) and tetrahydrofuran (THF)

| Ab. | Structure | Solv. | Absorption $\lambda_{\text{max}}^{\text{abs}} [\text{nm}]$ | Molar abs. coefficient ϵ [$\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$] | Fluorescence $\lambda_{\text{max}}^{\text{fl}} [\text{nm}]$ / Stokes shift $\tilde{\nu} [\text{cm}^{-1}]$ |
|-------|-----------|-------|---------------------------------------------------------------|---------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
| A1Ch1 | | DMF | 470 | 35.0×10^3 | 629 / 5379 |
| | | MeCN | 471 | 45.5×10^3 | 621 / 5128 |
| | | THF | 475 | | 615 / 4793 |
| A1Ch2 | | DMF | 459 | 39.0×10^3 | 605 / 5257 |
| | | MeCN | 456 | 43.5×10^3 | 603 / 5346 |
| | | THF | 461 | | 597 / 4942 |
| A1Ch3 | | DMF | 541 | 40.2×10^3 | 705 / 4300 |
| | | MeCN | 538 | $700 / 4301$ | |
| | | THF | 553 | 41.1×10^3 | 690 / 3590 |
| A1Ch4 | | DMF | 523 | 52.3×10^3 | 663 / 4037 |
| | | MeCN | 520 | $666 / 4216$ | |
| | | THF | 535 | 55.5×10^3 | 697 / 4345 |
| A2Ch1 | | DMF | 443 | 24.4×10^3 | 662 / 7467 |
| | | MeCN | 449 | $662 / 7166$ | |
| | | THF | 365 | 25.0×10^3 | 651 / 12036 |
| A2Ch2 | | DMF | 432 | 18.8×10^3 | 637 / 7449 |
| | | MeCN | 432 | $634 / 7375$ | |
| | | THF | 375 | 21.2×10^3 | 620 / 10538 |
| A2Ch4 | | DMF | 488 | 23.8×10^3 | 690 / 5999 |
| | | MeCN | 489 | $690 / 5957$ | |
| | | THF | 574 | 24.7×10^3 | 721 / 3552 |

The absorption spectra for selected dyes under the study in DMF are presented in Figure 1.

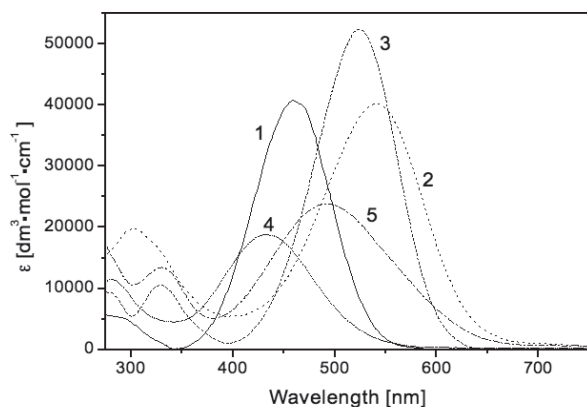


Fig. 1. Illustrative electronic absorption spectra of tested dyes in DMF: 1 - A1Ch2; 2 - A1Ch3; 3 - A1Ch4; 4 - A2Ch2; 5 - A2Ch4

All electronic absorption spectra clearly present two bands whose maxima are located at about 300 and 450-550 nm regions. The shortest wavelength bands are attributed to the $\pi \rightarrow \pi^*$ transitions whereas the long wavelength bands, generally characterized by higher molar absorption coefficients, are attributed to an intramolecular charge transfer ($S^0 \rightarrow CT$) involving the electron lone pair of the amino nitrogen and the cationic pyridinium or quinolinium nitrogen terminal [11]. Inspection of the absorption spectra, presented in Figure 1, and the analysis of the spectral data collected in Table I shows that the position and intensity of CT absorption band depends on the dye molecule structure.

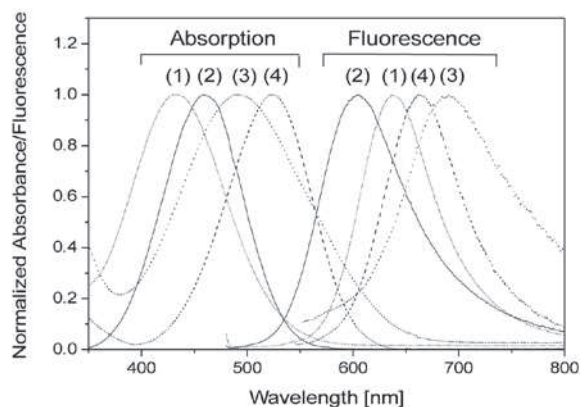


Fig. 2. Normalized absorption and fluorescence emission spectra of the dyes: (1) - A2Ch2; (2) - A1Ch2; (3) - A2Ch4; (4) - A1Ch4. Spectra recorded in DMF

3.1. Spectral characteristic in polyethylene glycol – water mixtures

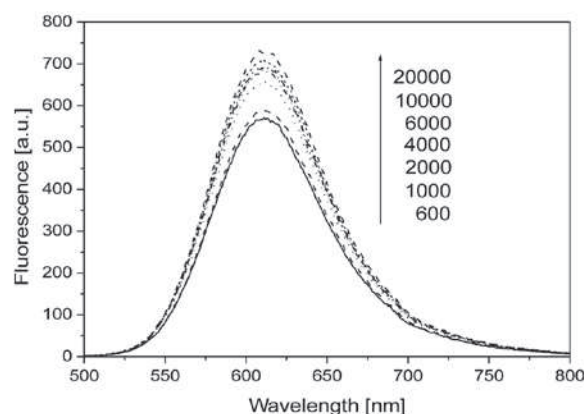


Fig. 3. Fluorescence spectra of A1ChI in solutions of polyethylene glycol-water : 1-2.6 (w/w). The molecular weights of polyethylene glycol are indicated in figure

The dependence of fluorescence properties of A1ChI in solutions of very different local viscosity is shown in Figure 3. As shown in Figure 3, the fluorescence intensity increases as the viscosity of the solution increases. However, it is necessary to emphasize that the changes are minor and do not have an analytical significance. This also applies to other dyes.

3.2. Spectral characteristic in solutions of varying acidity

Emission spectra of selected probes in solutions of varying acidity are presented in Figure 4. Interesting relations can be observed for the dyes derived of 4-dimethylamino-1-naphthaldehyde. Solutions of these compounds at low pH show a strong, depending on the pH, blue shift fluorescence. Such dependences are not observed for the derivatives of 4-(N,N-dimethylamino)benzaldehyde. Changes in the fluorescence for short- and long-wavelengths for selected dyes are shown in Figure 5.

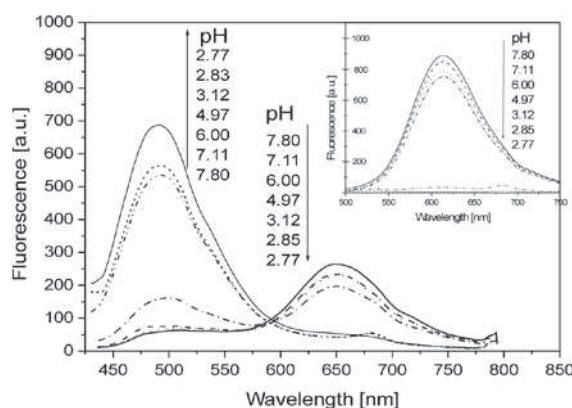


Fig. 4. pH dependent emission spectra of A2ChI in water (insert: A1ChI). The pH-values are indicated in figure

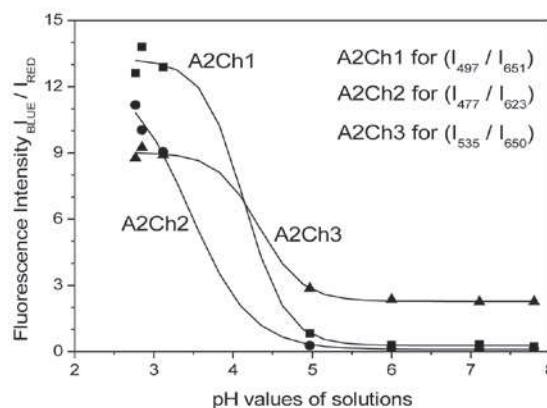


Fig. 5. Ratio of emission intensity at two selected wavelengths for A2Ch1, A2Ch2 and A2Ch3 probes versus pH of solutions

Presented results show, that studied compounds, derivatives of 4-dimethylamino-1-naphthaldehyde, can be used as spectroscopic probes monitoring the changes in pH.

Acknowledgment

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Translation into English by the Author

Agnieszka BAJOREK Ph.D.(Eng), is a graduate of the Faculty of Chemical Technology and Engineering, University of Technology and Agriculture in Bydgoszcz (1987). She obtained her Ph.D. degree at the Faculty of Chemistry, Nicolaus Copernicus University in Toruń (1999). Currently, she works at the Department of Physical Chemistry UTP in Bydgoszcz. Research interests: photochemistry of polymers, photo initiated polymerization, spectroscopic probes.

Ilona WRZEŚNIEWSKA M.Sc., is a graduate of the Faculty of Chemical Technology and Engineering, University of Technology and Life Sciences in Bydgoszcz (2010).

Marek PIETRZAK Ph.D.(Eng), is a graduate of the Faculty of Chemical Technology and Engineering, University of Technology and Agriculture in Bydgoszcz (1993). He obtained his Ph.D. degree at the Faculty of Chemistry, Adam Mickiewicz University in Poznań (2000). Currently, he works at the Department of Physical Chemistry UTP in Bydgoszcz. Research interests: photochemistry of polymers, photo initiated polymerization, organic synthesis, spectroscopic probes.

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