Dyes and Pigments **26** (1994) 229–235
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0143-7208/94/$7.00

New Near Infrared Absorbing Acidochromic Dyes and Their Application in Sensor Techniques

Heike Lindauer,[a] Peter Czerney,[a] Gerhard J. Mohr[b] & Ulrich-W. Grummt*[a]

[a] Institute of Physical Chemistry, Friedrich-Schiller-University,
07743 Jena, Germany
[b] Institute of Organic Chemistry, Karl-Franzens-University,
8010 Graz, Austria

(Received 18 May 1994; accepted 23 June 1994)

ABSTRACT

Two new acidochromic styrylcyanines **1** *and* **2** *and one new benzopyrylotrimethinium dye* **3** *have been synthesized. Their VIS and NIR absorption spectra have been recorded as a function of pH in fluid solution and embedded in polymer layers. The layers proved to be useful as pH sensors.*

1 INTRODUCTION

Acidochromic dyes absorbing in the 600–900 nm region are of importance, for instance, in sensor techniques and medical diagnostics. The absorbance of most materials to be probed, e.g. biological samples, is minimal in this region and hence does not interfere with the absorbance of a NIR chromophore. Furthermore, scattering losses are also minimized. With their absorption wavelength matched to the emission wavelength of suitable laser diodes, these dyes are particularly useful for the design of optrodes.

An acidochromic dye must contain a pH-sensitive functional group that produces a considerable change of the π-system of the indicator molecule on protonation or deprotonation, resulting in a spectral change.

Indicators absorbing above 600 nm are very scarce, cf. Ref. 1. There are no commercially available pH-indicators absorbing in the NIR.

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* To whom correspondence should be addressed.

Although a number of new IR absorbing dye systems have been prepared in the last decade,[2–4] particularly for use in dye laser technology, to the best of our knowledge there is no stable NIR indicator dye. Patonay[2,3] has reported the synthesis of a NIR absorbing pH-sensitive carbocyanine. However, the very large spectral changes observed with this dye cannot be explained in terms of a protolytic equilibrium.

In this paper we describe three new NIR dyes belonging to two different structural types which are very useful for pH determination.

2 EXPERIMENTAL

2.1 Reagents and instruments

The indicator dyes investigated were synthesized as described in other publications from our laboratory.[5,6]

Polyvinylchloride (PVC, high molecular), potassium tetrakis(4-chlorophenyl)borate (PTCB) and tetrahydrofuran (THF) were obtained from Fluka (Buchs, Switzerland). The plasticizer, tris(2-ethylhexyl)phosphate (TOP) was supplied by Aldrich (Steinheim, Germany). Polyester membrane (Mylar), with a thickness of 175 μm, was from Du Pont de Nemours and Co. (USA). For the determination of the pH dependence of the membranes, a buffer that covered a wide pH range was selected; this was obtained by dissolving a mixture of 2·4 ml of concentrated acetic acid, 2·7 ml of concentrated phosphoric acid (85%) and 2·47 g crystalline boric acid in water and making up to 1 litre. The desired pH (between 2 and 12) was adjusted with 2 M sodium hydroxide. All aqueous samples and buffer solutions were prepared with distilled water.

2.2 Preparation of PVC membrane

The dyes were immobilized in a PVC membrane by the following procedure.

A batch of 120 mg PVC, 3·8 mg PTCB, 240 mg TOP and 2 mg of indicator dye was dissolved in 1·5 ml freshly distilled THF. Using a home-made coating jig, 0·1 ml of this highly viscous polymer solution was spread onto a dust-free Mylar foil. After being left in a desiccator in a THF-saturated atmosphere for 3 h, the foil was exposed to air for 15 min for further drying. The thickness of the PVC coating was about 1·5 μm, as estimated from the coated area and the volume and concentration of the PVC solution.

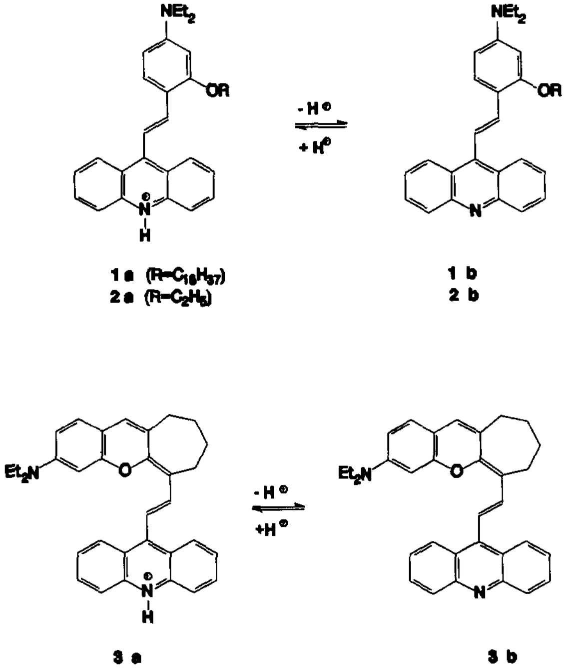
2.3 Apparatus and measurements

Absorption measurements were run on a Shimadzu 2101 UV–VIS spectrophotometer controlled by a 386B/25 PC. Measurements of the membranes were carried out in a flow-through cell described elsewhere.[7]

Essentially, solutions of known analyte concentration were pumped at a rate of 1·5 ml per min through a flow-through cell one wall of which was the sensing membrane, and optical changes in absorption of this membrane were continuously recorded. The pH of all buffer solutions was checked with a Metrohm 632 digital pH meter, calibrated at 21°C to standard buffers of pH 4·00 and 10·00.

3 RESULTS

Scheme 1 shows the dyes investigated. The longest wavelength absorption band of compound **1a** and **2a** is due to the styrylcyanine chromophore whereas **3a** represents an unsymmetric trimethinium dye. If the proton is removed from the acridine moiety, the compounds lose the polymethine character, giving rise to a strong blue shift.



Scheme 1.

Figure 1 shows some absorption spectra of **1** immobilized in a PVC membrane at different pH values. The absorption maxima of **1a** and **1b** are observed at 680 and 460 nm, respectively. The pK_a was 7·8. The octadecyloxy substituent in **1** ensures stability against leaching of the cationic dye **1a** from the polymer layer. After treating **1** embedded in a PVC membrane for 11 h in a flow-through cell with an acid buffer solution there was no detectable absorption loss of **1a**.

The occurrence of an isosbestic point in the spectra (Fig. 1) indicates that there are no absorbing species other than the acid and base forms of **1**. This underlines the observed reversibility shown in Fig. 2.

The spectral behaviour of **2a** and **2b** is similar to that of **1a** and **1b**. The longest wavelength absorption is hypsochromically shifted by 40 nm with respect to **1a**, and the pK_a is 6·6.

The unsymmetric trimethinium dye **3** absorbs at considerably longer wavelengths as compared to **1** and **2**, absorption maxima being at 850 and 536 nm for **3a** and **3b**, respectively; the pK_a was 8·6. A second absorption band at 450 nm in the visible region arises from the acid form as shown in Fig. 3.

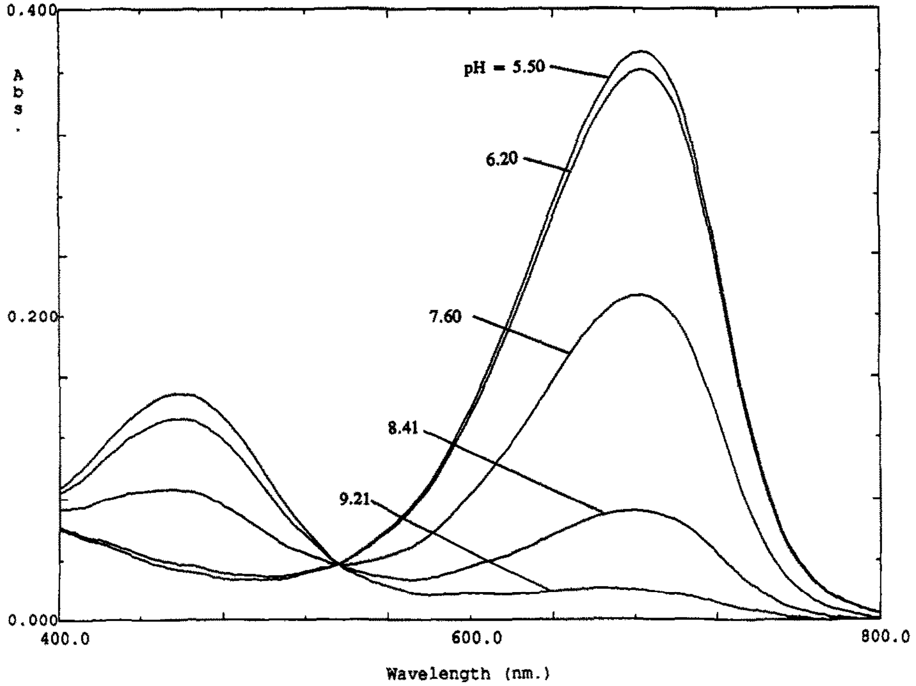


Fig. 1. Absorption spectra of **1** embedded in a PVC layer with variable pH (pK_a = 7·8).

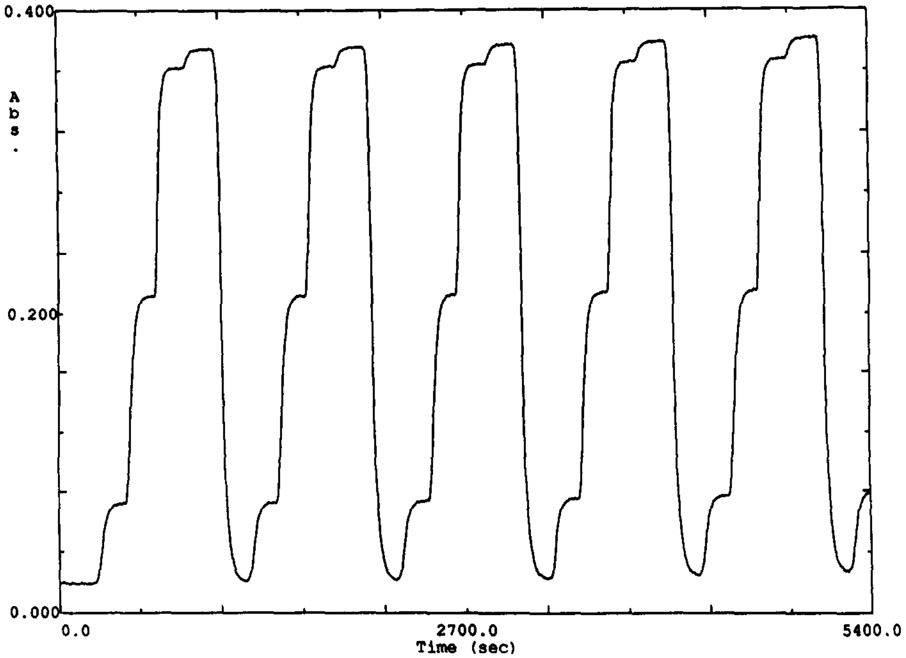


Fig. 2. Reversible colour change of **1** recorded at 680 nm for the same pH values as given in Fig. 1.

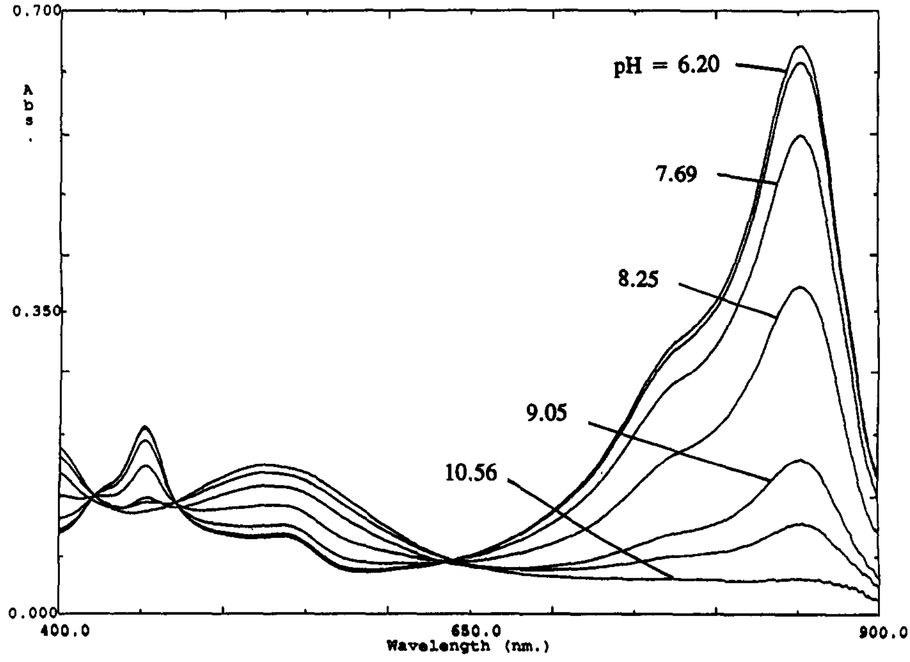


Fig. 3. Absorption spectra of **3** embedded in a PVC layer with variable pH ($pK_a = 8{\cdot}6$).

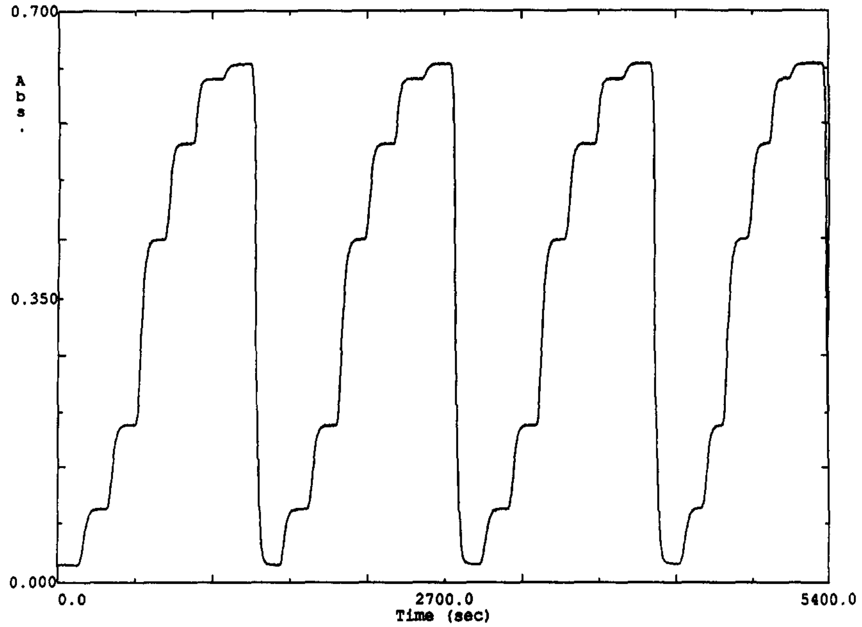


Fig. 4. Reversible colour change of **3** recorded at 850 nm for the same pH values as given in Fig. 3.

As expected for polymethine chromophores the molar absorptivity of **3a** is very large. As a consequence, the absorbance difference on changing the pH will also be large, and the accuracy of a pH measurement should therefore be optimal. Analogously, as shown in Fig. 2, we have also checked the reversibility of a layer containing dye 3; Fig. 4 shows the result.

The corresponding absorption maxima of the acidic and basic forms of dyes **1–3** and the pK_a values measured in an isopropanol/water mixture are listed in Table 1 for comparison.

TABLE 1
Absorption Maxima and pK_a Values of **1–3** in Isopropanol/Water (50/50 Vol.)

Dye	λ_{max} *a (nm)*	λ_{max} *b (nm)*	pK_a
1	664	465	5·30
2	645	452	5·65
3	840	532	6·35

4 ACKNOWLEDGEMENTS

We are indebted to Professor O. Wolfbeis, University of Graz, Austria, for providing chemicals and special equipment, and for encouraging discussions. The authors greatly acknowledge a grant by the Deutsche Forschungsgemeinschaft, under reference Di 481/1-1.

REFERENCES

1. Bishop, E., *Indicators*. Pergamon Press, Oxford, 1972.
2. Zeng J. M. & Patonay, G., *Anal. Chem.*, **63** (1991) 2934.
3. Boyer A. E., Devanathan, S., Hamilton, D. & Patonay, G., *Talanta*, **39** (1992) 505.
4. Nakatsuji, S., Nakazumi, H., Fukuma, H., Yahiro, T., Nakashima, K., Iyoda, M. & Akiyama, S., *J. Chem. Soc. Perkin Trans.* (1991) 1881.
5. Lindauer, H., Czerney, P. & Grummt, U.-W., *J. Prakt. Chem.*, **336** (1994) 521.
6. Lindauer, H., Czerney, P. & Grummt, U.-W., *J. Prakt. Chem.* (in press).
7. Wolfbeis, O.-S. & Schaffar, B.-P., *Anal. Chim. Acta* (1987) 198.