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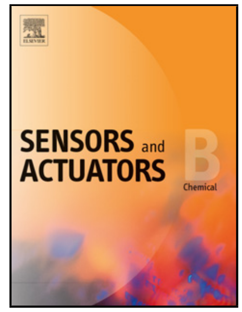

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Author: Gerhard J. Mohr

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Synthesis of naphthalimide-based indicator dyes with a 2-hydroxyethylsulfonyl function for covalent immobilisation to cellulose

Gerhard J. Mohr

JOANNEUM RESEARCH Forschungsgesellschaft mbH – Materials, Franz-Pichler-Straße 30, A-8160 Weiz, Austria, E-Mail: gerhard.mohr@joanneum.at

Abstract

A new approach for the synthesis of 2-hydroxyethylsulfonyl type indicator dyes has been introduced to the naphthalimide chemical structure. Thus, fluorescent indicator dyes can be obtained that can be covalently linked to cellulose used e.g. in optical sensor layers, textiles and wound dressings. The approach is tailored to be simple in synthesis and with a minimum number of steps required to obtain a highly functional and stable sensor material. Three different pH indicator dyes have been prepared and covalently immobilised to transparent cellulose layers. The pK_a values of the cellulose-immobilised dyes were found to be 3, 6 and 7, thus covering the physiologically relevant pH range. Using the 2-hydroxyethylsulfonyl group, covalent immobilisation of naphthalimides with various receptor functions may become possible.

Keywords: vinylsulfonyl dyes, optical sensors, chemosensors, pH detection, smart textiles

Introduction

Optical chemical sensors have received significantly increased attention by the industry in the last decade. For one part, optical sensors only need to consist of one biocompatible polymer and an indicator dye, being often much less toxic than electronic sensors that need electronics, battery and display to function properly. Accordingly, optical sensors for controlling food spoilage,[1] food packaging integrity[2] and wounds[3] are more easily implemented. Second, optical sensor modules have already been fully integrated into wearables to e.g. detect pulse frequency, and manufacturers naturally are looking for other applications of their technology in smartwatches and smartphones. The development of new indicator dyes and materials is impressive, with improvements in the field of operational stability,[4] long-wavelength absorption and emission of indicator dyes,[5] new luminescent lifetime probes,[6] up-converting nanoparticles,[7] fluorogenic mesoporous silica[8], and ultrafast nanofibers[9], just to name a few.

In the context of facile synthesis and easy structural modification, chemosensors and indicator dyes with a naphthalimide structure have received massive attention, and hundreds of selective indicator dyes and probes have been developed on the basis of this one specific structure. Since the ground-breaking work of A. P. de Silva,[10,11] it is synonymous for photo-induced energy transfer (PET), often showing strong fluorescence off-on mechanism upon analyte recognition which is preferred in optical detection. A major advantage of the naphthalimide dyes is their synthetic approach which allows step-wise introduction of functional groups. Typically first, in refluxing ethanol the functional group for solubility and/or immobilisation is introduced. Then, in the second step, using a higher boiling solvent such as methoxyethanol or *N,N*-dimethylformamide, the functional group for analyte recognition is attached. Based on this procedure, indicator dyes and probes for alkali,[12] earth alkaline[13] and heavy metal ions[14,15] have been introduced, also using ratiometric approaches[16,17] and excimer-monomer switching.[18] Furthermore, chemosensors for temperature,[19] water,[20] redox-reactions[21,22], hydrogen peroxide,[23] anions,[24,25] amino acids,[26] saccharides,[27,28] thiols,[29,30]