Available online at www.sciencedirect.com
SCIENCE DIRECT®
Sensors and Actuators B 107 (2005) 32–39
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Study of a new evanescent wave optical fibre sensor for methane detection based on cryptophane molecules

M. Benounis [a], N. Jaffrezic-Renault [a,*], J.-P. Dutasta [b], K. Cherif [c], A. Abdelghani [c]

[a] *CEGELY, UMR CNRS 5005, Ecole Centrale de Lyon, B.P. 163, 69134 Ecully Cedex, France*
[b] *Laboratoire de Chimie de l'École Normale Supérieure de Lyon, UMR CNRS 5182, France*
[c] *Laboratoire de Physique des Semiconducteurs et Capteurs, IPEST, Tunis, Tunisia*

Received 7 April 2004; received in revised form 1 October 2004; accepted 18 October 2004
Available online 9 February 2005

Abstract

An evanescent fibre sensor for detection of methane was fabricated by the inclusion of two types of cryptophane molecules in a transparent polymeric cladding (polysiloxane), deposited on a PCS fibre. Synthesis of crytophanes A and E are described as well as the preparation of the specific polymeric cladding, its deposition on the uncladded part of the optical fibre, the optimal thickness being 5 μm and the optimal length of uncladded part being 5 cm. By modelling the curves $P(\alpha)$—normalised light power transmitted versus injection angle—it was shown that the specific absorption of methane in cryptophane A led to an increase of the refractive index of the specific cladding. Detection limit for methane is 2% (v/v) with cryptophane A and 6% (v/v) with cryptophane E. When alkane concentrations (methane, ethane, butane) are less than 8% (v/v), only methane leads to an optical response. For concentrations of alkanes higher than 15% (v/v), a strong effect of condensation of butane in the polymer itself is observed.

Keywords: Cryptophane; Alkanes; Optical fibre sensor; Methane

1. Introduction

It is well known that alkanes and specially methane, even at very low concentrations, are chemical compounds very dangerous for human safety and environment. Low-cost chemical sensors are then needed for monitoring methane leakages.

Several measuring techniques were previously used to develop methane sensors. Metal oxide thin films have been traditionally used as gas sensing materials. These sensors operate on the principle that the surface conduction of the semiconductor sensors varies in relation to the adsorption of the ambient gas [1–4]. In order to make them selective, the concept was based on the different catalytic activity of platinum and palladium towards the oxidation of methane, at around 400 °C. The detection limit attained is about 0.5% of methane [5]. Catalytic gas sensors were also developed for methane detection. They consist of narrow diameter Pt wire coils surrounded by a catalyst supported on an inert porous refractory material such as alumina. The detection limit of this type of sensor is 0.1% of methane [6].

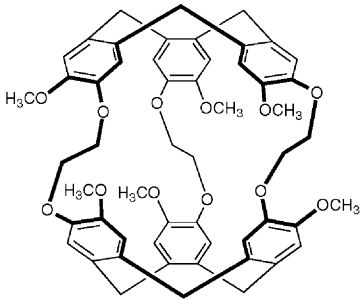
The characteristic NIR-absorption lines of methane and ethane are being acquired simultaneously and their concentrations are determined using a tunable DFB laser diode. One paper reports on the development of a hand-held and low-power sensor, based on direct absorption spectroscopy for leak detection (methane), natural gas identification and lower-explosion-limit (LEL) measurements (methane and ethane). The achievable detection limit is lower than 5 ppm [7].

To detect chemical species with optical fibre sensors, the strategy followed in our laboratory consists in covering the optical fibre core by a transparent polymer whose effective refraction index is modified during absorption of species to be detected. A simple evanescent wave (EW) optical

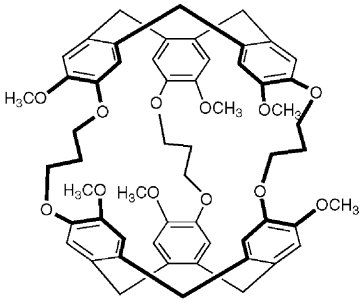
* Corresponding author. Tel.: +33 472186243; fax: +33 478433717.
E-mail address: Nicole.Jaffrezic@ec-lyon.fr (N. Jaffrezic-Renault).

0925-4005/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2004.10.063

fibre sensor, based on intensity modulation is then obtained, using a simple laser diode ($\lambda = 670$ nm) as light source. The formulation of specific polymer is carried out while including in the polymeric matrix with the optical properties adapted (transparency, refraction index lower than that of the fibre core) molecules able to selectively trap the gaseous molecules. Cryptophanes are synthetic organic compounds with enforced cavity of suitable size for molecular guest encapsulation [8]. They are interesting and versatile molecular receptors, whose complexation properties have been widely studied in solution. For instance, cryptophane A is particularly adapted for the recognition of dichloromethane [9], xenon [10] or methane [11]. The selectivity essentially arises from size complementarity and efficient van der Waals interactions with the guest. Due to the selective inclusion of methane into cryptophane A in organic solution, this host was used as additive to the polymer. The larger cryptophane E (internal volume 121 $Å^3$ as compared to 95 $Å^3$ for cryptophane A) was also used in methane detection.



Cryptophane-A



Cryptophane-E

This paper describes the performances of the EW optical fibre sensor obtained by inclusion, in the specific polymeric cladding, of these both molecules that were not used in this configuration so far.

2. Experimental part

2.1. Synthesis of cryptophane molecules

Cryptophanes A and E were synthesised from vanillyl alcohol using a two-steps method according to a well-known procedure [12]. Starting from vanillin **1**, the bis-vanillin compounds **2** and **3** were prepared by reaction of **1** with 1/2 equivalent of dibromoethane or dibromopropane, respectively. The bis-aldehyde derivatives were then converted into the corresponding bis-vanillyl alcohol **4** and **5** by reacting with $NaBH_4$ in methanol. The ring closure reaction of benzylic alcohol **4** and **5** was performed in formic acid ($1.4–1.5 \times 10^{-3}$ M solutions) at 60 °C for 3 h. Cryptophanes A and E were obtained after purification of the reaction mixtures by column chromatography on silica gel in 4 and 14% yields, respectively (Scheme 1).

2.1.1. Description of synthesis of the intermediary products

*2.1.1.1. 1,2-Bis(4-formyl-2-methoxyphenoxy)ethane (**2**).* To a solution of vanillin **1** (30 g, 200 mmol) in ethanol (100 mL) was added a solution NaOH 10 M (20 mL) and 1,2-dibromoethane (9 mL, 100 mmol). The mixture was stirred at reflux temperature for 20 h. After cooling to room temperature, the solid compound was recovered by filtration to give 20 g of **1** as a beige powder (61% yield).

^{1}H NMR (DMSO-d_6) $\delta = 9.83$ (s, 2H, CHO), 7.54 (d, 2H, Ar), 7.39 (s, 2H, Ar), 7.24 (d, 2H, Ar), 4.45 (s, 4H, OCH_2), 3.80 (s, 6H, OCH_3).

*2.1.1.2. 1,3-Bis(4-formyl-2-methoxyphenoxy)propane (**3**).* 1,3-Bis(4-formyl-2-methoxyphenoxy)propane (**3**), was prepared as for **2** from **1** (30 g, 200 mmol) and 1,3-dibromopropane (10 mL, 100 mmol). Compound **3** was obtained as a beige powder (19.8 g, 58% yield).

^{1}H NMR ($CDCl_3$) $\delta = 9.86$ (s, 2H, CHO), 7.45 (d, 2H, Ar), 7.42 (s, 2H, Ar), 7.03 (d, 2H, Ar), 4.35 (t, 4H, OCH_2), 3.92 (s, 6H, OCH_3), 2.45 (qi, 2H, CH_2).

*2.1.1.3. 1,2-Bis(4-hydroxymethyl-2-methoxyphenoxy)ethane (**4**).* To a mixture of **2** (13 g, 39.8 mmol) in methanol (200 mL) was slowly added $NaBH_4$ (5 g, 131.6 mmol). The mixture is stirred for 15 h. After filtration the solid was washed with a methanol/water mixture (100 mL) and methanol (50 mL) to give 12.2 g of compound **4** as a white powder (93% yield).

^{1}H NMR (DMSO-d_6) $\delta = 6.86$ (m, 6H, Ar), 5.06 (t, 2H, OH), 4.39 (d, 4H, CH_2OH), 4.21 (s, 4H, OCH_2), 3.72 (s, 6H, OCH_3).

*2.1.1.4. 1,3-Bis(4-hydroxymethyl-2-methoxyphenoxy)propane (**5**).* 1,3-Bis(4-hydroxymethyl-2-methoxyphenoxy)propane (**5**), was prepared as for **4** from **3** (19.8 g, 58.1 mmol) and $NaBH_4$ (7 g, 184.5 mmol). Compound **5** was obtained as a white powder (19.8 g, 99% yield).

^{1}H NMR (DMSO-d_6) $\delta = 6.91$ (m, 6H, Ar), 5.02 (s, 2H, OH), 4.37 (s, 4H, CH_2OH), 4.06 (t, 4H, OCH_2), 3.71 (s, 6H, OCH_3), 2.08 (m, 2H, CH_2).