



A molecular imprinting-based multifunctional chemosensor for phthalate esters



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ABSTRACT

This paper reports a molecular imprinting-based fluorescent and solvatochromic multifunctional chemosensor for phthalate esters (PAEs). The multifunctional chemosensor was fabricated through precipitation polymerization using 4-[(1E)-4-(2-hydroxyphenyl) ethenyl]-1-allylpyridinium bromide (HPEAPB) as the functional monomer and phthalamide-4,4'-dibutyl dimethyl ester (PDDB) as the mimic template. The molecular imprinting-based chemosensor shows specific affinity toward PDDB and dibutyl phthalate (DBP) in ethanol. Of note is that the molecular imprinting-based chemosensor shows turn-off fluorescent response toward PAEs in an ethanol solution with a limit of detection of $2.0 \times 10^{-6} \text{ mol L}^{-1}$ (0.7 ppm) when HPEAPB is in the protonated form (chemosensor 1), and shows solvatochromic properties, fluorescent enhancement and a colorimetric (from orange to bright yellow) response toward PAEs in an ethanol solution with a limit of detection of $4.0 \times 10^{-5} \text{ mol L}^{-1}$ by the naked eye when HPEAPB is in the deprotonated form (chemosensor 2). This multifunctional chemosensor is promising for the simple, accurate and low-cost detection of trace PAEs.

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1. Introduction

In recent years, food safety concerns have been raised on the occurrence of phthalic acid diesters (PAEs). PAEs are extensively used in poly(vinyl chloride) and other plastics as a plasticizer to impart flexibility and durability [1–3]. They are also used as industry additives or solvents in wall coverings, automotive applications, buildings and construction, cables and wires, flooring, food containers, food packaging, medical devices, blood bags, perfumes, cosmetics, shampoo, adhesive, clothing, insect repellent, and medication coating because of their low volatility, low price and other superior characteristics [4–12]. The extensive use of PAEs results in their presence in food, drinking water, beverages, distilled spirits, and other environmental samples [13]. Human exposure to high doses of PAEs results in adverse effects on the reproductive

system [14–20], a reduction of intelligence in children [21,22], an increase of oxidative stress and inflammation [23,24], and metabolic abnormalities such as abdominal obesity and insulin resistance in men [25]. Therefore, a simple, rapid, and selective analytical method for PAEs in diverse environmental matrices is highly desired.

To date, a number of detection strategies such as gas chromatography (GC) [26,27], liquid chromatography (LC) [28], gas chromatography coupled with mass spectrometry (GC–MS) [29–31] and electrochemical methods [32,33] have been developed for PAEs detection. Although sensitive, these methods are time consuming, expensive, require skilled operators, numerous sample preparation steps including solvent extraction, liquid–liquid extraction, and column chromatographic clean-up [7].

In recent years, colorimetric and fluorescent chemosensors have become particularly attractive because of their simplicity, high sensitivity, applicability to real-time and visual detection, and low cost [34,35]. However, to the best of our knowledge, no such sensors for PAEs have been reported. The main challenges in developing sensors for PAEs are that they are electroneutral molecules

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and they do not contain active sites or groups, and therefore the interaction between the sensor and the PAE is weaker than that with cationic or anionic ions [36–39]. Some fluorescence immunoassays have been developed for detection of PAEs by conjugation of fluorescein with an antibody [40–42]. However, the preparation of a PAE antibody is time consuming and requires animals, a process that cannot be realized in general chemical labs.

Molecular imprinting generates specific recognition sites with memory of the shape, size, and functionality of the template [43,44]. 4-[(1*E*)-4-(2-Hydroxyphenyl) ethenyl]-1-allylpyridinium bromide (HPEAPB, Fig. 1) is reported to be a colorimetric material [36], and after copolymerization with ethylene glycol dimethacrylate, the as-prepared polymer displayed both colorimetric and fluorescent properties [34]. In this work, to obtain both colorimetric and fluorescent responses toward electroneutral PAEs with good specificity, we harnessed the specificity of molecular imprinting toward the template and the colorimetric and fluorescent properties of HPEAPB. The chemosensor was prepared by a molecular imprinting technique using HPEAPB as the functional monomer, and phthalamide-4,4'-dibutyl dimethyl ester (PDDB) (Fig. 1) as the mimic template [43,45–47]. The as-prepared molecularly imprinted polymer (MIP) displays a turn-off fluorescent response toward PAEs when HPEAPB is in the protonated form (chemosensor 1). When HPEAPB is in the deprotonated form, the MIP displays solvatochromic properties, and colorimetric and fluorescent-enhancing responses toward PAEs (chemosensor 2).

2. Experimental

2.1. Materials and apparatus

4-Methylpyridine (AR, 98%), 4-hydroxybenzaldehyde (AR, 98%), acetic anhydride (AR, 98%), allyl bromide (AR, 98%), phthalic acid (AR, 98%), thionyl chloride, methyl 4-aminobutyrate hydrochloride (AR, 98%), sodium acrylamide (AR, 98%), trimethylolpropane-trimethacrylate (TRIM, AR, 98%), azobisisobutyronitrile (AIBN, AR, 98%), di-*n*-octyl phthalate (DNOP, AR, 98%), benzyl butyl phthalate

(BBP, AR, 98%), di-(2-ethylhexyl) phthalate (DEHP, AR, 98%), and dicyclohexyl phthalate (DCHP, AR, 98%), and DBP (AR, 98%) were purchased from Aladdin Co., Shanghai, China. Other reagents and solvents were supplied from commercial sources and used without further purification.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV 600 (600 MHz spectrometer (Karlsruhe, German)) at 298 K using tetramethylsilane as the internal standard. Ultraviolet–visible (UV–Vis) spectra were obtained on an UV-4802 spectrophotometer (UNICO [Shanghai] Instruments Co. Ltd., China). Mass spectra were collected using a Bruker Esquire 2000 HCT LC/MS system. Fluorescence measurements were taken on a F380 (Tianjin Gangdong Technology Co. Ltd., Tianjin, China). The morphological evaluation was recorded using a scanning electron microscope (SEM, Hitachi S-4800 FE-SEM, operating at 5 kV, Japan). Nitrogen adsorption-desorption analysis was measured on an Autosorb-1 apparatus (Quantachrome, USA) at 77 K. The specific surface areas and pore diameters were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) models, respectively. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin–Elmer model GX Spectrometer (Perkin–Elmer, Waltham, USA) using the KBr pellet method. Thermogravimetric analysis (TGA) was conducted on a SDT Q600 thermal analyzer (USA) at a heating rate of 10 °C min⁻¹ up to 650 °C under flowing N₂ (100 mL min⁻¹). The emission quantum yields were measured on a FLSP920 (Edinburgh Instruments, Beijing, China).

2.2. Synthesis of the functional monomer HPEAPB

HPEAPB was conveniently synthesized according to a previous method reported by Chen and coworkers [36].

2.3. Synthesis of the mimic template PDDB

PDDB was synthesized via acylation and ammonolysis reactions using phthalic acid and methyl 4-aminobutyrate hydrochloride as the starting materials (Fig. 2).

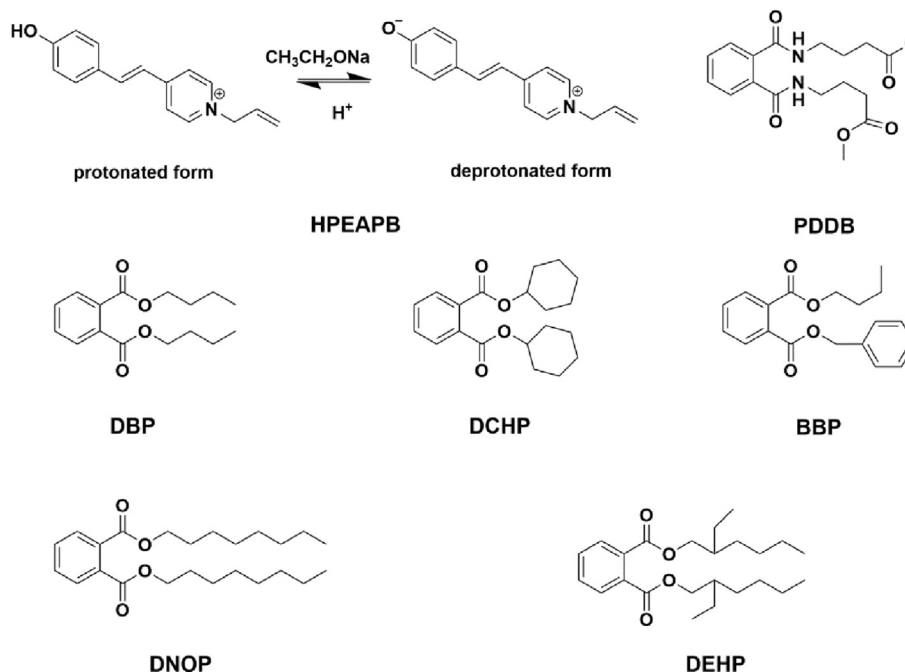


Fig. 1. Chemical structures of HPEAPB, PDDB, DBP, DCHP, BBP, DNOP, and DEHP.

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