



Original article

A novel fluorescent epoxy resin for organophosphate pesticide detection

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ABSTRACT

In this work, a novel bisbenzimidazolylpyridine-functionalized fluorescent epoxy resin was synthesized for organophosphate pesticide detection. The epoxy resin was characterized by Fourier-transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance spectroscopy (¹H NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and fluorescence spectroscopy. After loading with Eu(III) ions, the epoxy resin showed a strong fluorescence emission. The fluorescence emission was observed to be instantaneously quenched when exposed to trace amount of diethyl chlorophosphate in solution. The Stern–Volmer quenching constants K_{sv} for quenching at 617 nm was determined to be 0.377×10^3 L/mol. This sensitive emission-quenching function and easy processing nature of the polymeric support enable the resin to be a promising chemosensor candidate for the detection of organophosphates.

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1. Introduction

Organophosphate pesticides as harmful contaminants and toxic substances often exist in agriculture products and environment. The severe fatal damage to the human health as well as threat to the safety of poultry and domestic animals are caused by their harmful effect to inhibit the normal function of acetylcholinesterase, which is a critical enzyme in nervous system [1,2]. Considerable concerns about the amount of organophosphate residue in environment and their threat to biological systems have stimulated intensive researches to develop sensitive and selective methods for detection of these compounds [3,4]. Huge research effort has been devoted to develop various organophosphate detection methods. Most well-known methods include gas chromatography–mass spectrometry [5], surface acoustic wave [6], surface-enhanced Raman spectroscopy [7], fiber optics [8], colorimetric [9–11] and fluorimetric method [12–15].

Fluorescent detection is generally considered as one of the best options owing to its high selectivity, sensitivity, portability and operational simplicity [16,17]. Recently, the emission properties of

macromolecules containing tridentate aromatic scaffolds 2,2':6',2''-terpyridine (terpy) or 2,6-bis-(1'-methyl-benzimidazolyl)pyridine (MeBIP) complexing with trivalent lanthanides Eu(III) have been explored [18–21]. These previous researches show that the systems are very sensitive to the organophosphates. The sensitivity and sub-second response of these metal–ligand functionalized polymers make them to be suitable candidates for organophosphates detection.

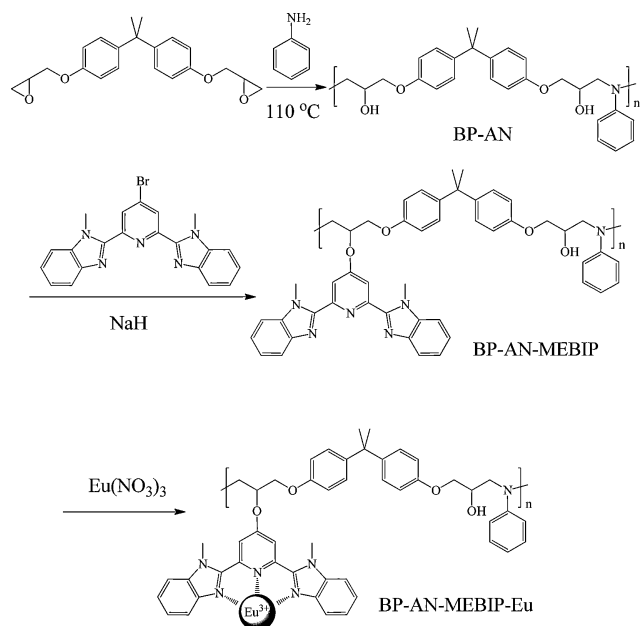
As a continuation of our previous investigations, this study concentrates on the synthesis and characterization of a novel bisbenzimidazolylpyridine-functionalized fluorescent epoxy resin/Eu(III) complex, which is designed to be used as chemosensor for organophosphates detection.

2. Experimental

Aniline, bisphenol-A diglycidyl ether, diethyl chlorophosphate (DCP) and Eu(NO₃)₃·6H₂O were purchased from Alfa Aesar. Sodium hydride (60 wt% dispersion in mineral oil) was purchased from Sigma–Aldrich. 4-Bromo-2,6-bis-(1'-methyl-benzimidazolyl)pyridine (Br-MeBIP) was prepared according to literature procedures [22]. Tetrahydrofuran (THF) was purified by distillation with sodium and benzophenone. Deionized water (resistivity >18 MΩ cm) was provide by a Milli-Q water purification system. All other reagents and solvents were purchased commercially and

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Scheme 1. The synthetic route of the fluorescent polymer BP-AN-MeBIP-Eu.

used without further purification. ^1H NMR spectroscopy was performed on a JEOL JNM-ECA300 NMR spectrometer with dimethyl- d_6 sulfoxide as solvent and tetramethylsilane (TMS) as the internal standard. FT-IR spectra were collected on a Nicolet 560-IR spectrometer: the samples were mixed with KBr and then pressed into thin transparent disks. Fluorescence spectra were measured at room temperature on an F-4500 spectrophotometer equipped with a Xenon lamp excitation source. The molecular weights and molecular weight distributions were evaluated by a gel permeation chromatographic (GPC) instrument equipped with a PLgel 5 μm mixed-D column and a refractive index (RI) detector (Wyatt Optilab rEX). The measurement was carried out at 35 $^\circ\text{C}$ with polystyrene as the standards and THF as the eluent under a flow rate was 1.0 mL/min. Thermal analyses of the compounds were carried out using TA Instruments Q2000 system at a heating rate of ± 10 $^\circ\text{C}/\text{min}$ under a nitrogen purge.

The synthetic route of the target fluorescent polymers is outlined in Scheme 1 which mainly contains three steps as follows. Firstly, an epoxy-based precursor polymers (BP-AN) was synthesized through the step polymerization between Bisphenol-A diglycidyl ether (BADGE) and aniline. Then, the polymeric ligand (BP-AN-MeBIP) was prepared through the Williamson coupling reaction between BP-AN and Br-MeBIP. Finally, the epoxy resin/Eu(III) complex (BP-AN-MeBIP-Eu) was obtained by the non-covalent binding reaction between BP-AN-MeBIP and Eu(III) ions in the THF solution. The synthetic details are described below.

2.1. BP-AN

The precursor polymer was prepared according to the literature method [23]. Bisphenol-A diglycidyl ether (18.81 g, 0.1 mol) and aniline (4.66 g, 0.05 mol) were homogeneously mixed and polymerized at 110 $^\circ\text{C}$ for 20 h. The crude product was dissolved in a $\text{CHCl}_3/\text{CH}_3\text{OH}$ solvent mixture (4:1, 200 mL) followed by precipitation in 800 mL of acetone. The polymer was collected by filtration and dried under vacuum for 24 h. IR (KBr, cm^{-1}): 3380 (O–H, s), 1600, 1510, 1463 (Benz. ring, s), 1250 (C–O, s). ^1H NMR ($\text{DMSO}-d_6$): δ 7.07 (d, 6H), 6.82 (d, 4H), 6.72 (d, 2H), 6.54 (m, 1H), 4.03 (m, 2H), 3.87 (s, 4H), 3.34–3.75 (m, 4H), 1.55 (s, 6H). GPC: $M_n = 44,620$, $M_w/M_n = 1.624$. DSC: $T_g = 89.9$ $^\circ\text{C}$.

2.2. BP-AN-MeBIP

Sodium hydride (0.28 g, 10 mmol), Br-MeBIP (0.05 g, 0.12 mmol) and BP-AN (1.0 g, 2.24×10^{-5} mol) were add into dried THF (40 mL) and reacted at room temperature for 24 h. The obtained mixture was dropped into plenty of petroleum ether, and the precipitate was collected by filtration. After washing with plenty of water for several times and drying, the crude product was dissolved in tetrahydrofuran and precipitated in petroleum ether again. The white solid product was obtained by filtration and dried in vacuum at 40 $^\circ\text{C}$ for 24 h. IR (KBr, cm^{-1}): 3366 (O–H, s), 2962, 2926, 2860 (C–H, s), 1663, (C=N, s), 1600, 1507, 1459 (Benz. ring, s), 1247 (C–O, s). ^1H NMR ($\text{DMSO}-d_6$): δ 8.54 (s, 2H), 7.75 (d, 2H), 7.68 (d, 2H), 7.36 (t, 2H), 7.30 (t, 2H), 7.08 (m), 6.84 (m), 6.72 (m), 6.54 (m), 5.37, 5.18 (m), 4.27 (s, 6H), 4.03 (m), 3.87 (m), 3.34–3.75 (m), 1.55 (m); GPC: $M_n = 46,760$, $M_w/M_n = 1.794$; DSC: $T_g = 94.3$ $^\circ\text{C}$.

2.3. BP-AN-MeBIP-Eu

BP-AN-MeBIP (100 mg) was dissolved in THF (15 mL) and then $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (45 mg, 0.1 mmol) was added into the solution. After stirring at room temperature for 6 h, the solvent was removed with rotary evaporator. The crude product was carefully washed with ethanol (3×15 mL) to remove the excess of unreacted Eu(III) ions. The product was dried in vacuum oven at 40 $^\circ\text{C}$ for 4 h to yield white solid material.

3. Results and discussion

The epoxy-based polymer (BP-AN) was synthesized through the step polymerization between bisphenol-A diglycidyl ether (BADGE) and aniline. The polymerization temperature was controlled to be 110 $^\circ\text{C}$ to avoid the possible side-reaction between the secondary hydroxyl groups generated by the ring-opening reaction and the unreacted epoxide rings. The abbreviation BP-AN denotes the polymer prepared by the reactions of BADGE with aniline. After the step polymerization, a large amount of hydroxyl groups is generated on the main-chain of BP-AN, which make it possible to be further modified to introduce the functional groups. The polymer shows good solubility in polar organic solvents such as tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMAc). All of these characteristics ensure BP-AN to be a perfect precursor polymer. The nucleophilic substitution reaction between BP-AN and Br-MeBIP was carried out in THF and catalyzed by NaH. Through this approach, the polymeric ligand (BP-AN-MeBIP) can be feasibly obtained. Finally, the fluorescent polymer BP-AN-MeBIP-Eu was obtained by the coordination between BP-AN-MeBIP and Eu(III) ions.

Fig. 1 shows the ^1H NMR spectra of the precursor polymer BP-AN and the polymer ligand BP-AN-MeBIP in $\text{DMSO}-d_6$.

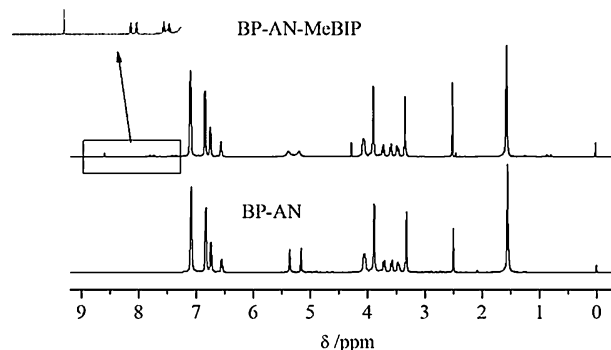


Fig. 1. ^1H NMR spectra (in $\text{DMSO}-d_6$) of BP-AN and BP-AN-MeBIP.

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