Available online at www.sciencedirect.com
ScienceDirect
Analytica Chimica Acta 581 (2007) 202–207
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

Luminescent sensing of organophosphates using europium(III) containing imprinted polymers prepared by RAFT polymerization

Glen E. Southard, Kelly A. Van Houten *, Edward W. Ott Jr., George M. Murray

The Johns Hopkins University Applied Physics Laboratory, Laurel, MD 20723, United States

Received 8 August 2006; received in revised form 15 August 2006; accepted 16 August 2006
Available online 22 August 2006

Abstract

Molecularly imprinted polymers capable of sensing organophosphorous compounds by luminescence have been prepared by reversible addition fragmentation chain transfer (RAFT) polymerization. The polymer contained a dithiobenzoate substituted tris(β-diketonate) europium(III) complex which served as a polymerization substrate and as a luminescent binding site for pinacolyl methylphosphonate (PMP), the hydrolysis product of the nerve agent Soman. The resultant polymer allowed quantitation of PMP in the low ppb range with minimal interference from similar compounds. Polymers were characterized by luminescence spectroscopy and scanning electron microscopy.

Keywords: Molecular imprinting; Luminescence; Organophosphates; Controlled polymerization

1. Introduction

Molecular imprinting is a useful technique for making a chemically selective binding site [1]. The method involves building a synthetic polymeric scaffold of molecular complements containing the target molecule and subsequent removal of the target to leave a cavity with a structural "memory" of the target. Molecularly imprinted polymers can be employed as selective adsorbents of specific molecules or molecular functional groups. Sensors for specific molecules can be made using optical transduction through chromophores residing in the imprinted site. The use of metal ions as chromophores can improve selectivity due to selective complex formation. The combination of molecular imprinting and spectroscopic selectivity can result in sensors that are highly sensitive and nearly immune to interferences [2].

Lanthanide ions are useful as intrinsic and extrinsic chromophores. Complexation by certain organic ligands enhances the luminescence intensity of the tripositive lanthanide, Ln(III) ions. The enhancement of luminescence has been explained by a ligand to metal energy transfer mechanism [3]. A large number of organic ligands have been used to enhance lanthanide luminescence intensity [4]. When making an imprinted polymer sensor, the ligands must be chosen with sufficient affinity for the lanthanide, so as to coordinatively bind the ion in the polymer as well as provide intense luminescence. β-Diketones are well known as good sensitizers for lanthanide luminescence. Model systems employing β-diketone lanthanide complexes show luminescence enhancement with the addition of a variety of organophosphates.

β-Diketones with fluorinated substituents were particularly effective. The inclusion of β-diketones with aromatic rings was especially useful to shift absorbance from the UV to more easily accessible excitation wavelengths. However, in order to apply molecular imprinting as a selectivity enhancement, the ligand must be polymerizable. When β-diketones were functionalized with vinyl substituents, their ability to complex a lanthanide ion was often compromised. The ligands either failed to complex the lanthanide or were readily displaced whenever syntheses of an imprinting complex with an organophosphate adduct was attempted. Only 4-vinylbenzoylmethane and 3-vinylbenzoylmethane readily formed tris complexes with europium(III). Other vinyl-substituted β-diketones simply would not form stable complexes with europium(III) or would be easily decomposed by addition of water.

* Corresponding author. Tel.: +1 443 778 2094; fax: +1 443 778 6914.
E-mail address: Kelly.van.houten@jhuapl.edu (K.A. Van Houten).

0003-2670/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.aca.2006.08.027

In this work we used a thioester-substituted β-diketone ligand for polymerization [5]. β-Diketones are well known as good sensitizers for lanthanide luminescence. Dithioesters have proven themselves through reversible addition fragmentation chain transfer (RAFT) methods to be excellent inifterers in many other organic polymerizations [6,7]. The preparation and evaluation of bulk RAFT polymers containing a dithiobenzoate substituted tris(β-diketonate) europium(III) complex are described. The europium(III) complex serves as a polymerization substrate and as a binding site for pinacolyl methylphosphonate (PMP), the hydrolysis product of the nerve agent Soman. The combination of molecular imprinting and luminescent detection provides great sensitivity and selectivity.

2. Experimental

2.1. Reagents

Unless otherwise indicated, chemicals were obtained Aldrich (Milwaukee, WI) or Fisher Scientific (Pittsburgh, PA) and used without further purification, except for monomers which were cleansed of inhibitors by filtration through alumina (Brockman Grade I). Analytical reagent grade chemicals were used along with deionized water (Barnstead Easypure UV water purification system) to prepare solutions. Wako V-65 was purchased from Wako Specialty Chemicals (Richmond, VA). The preparation of dithiobenzoic acid, **1**, 4-vinylnaphthoyltrifluoroacetone and **2**, 3-vinyldibenzoylmethane (3-VBDM) are discussed elsewhere [5,8].

2.2. Instrumentation

An in-house detection system was employed for screening lanthanide complexes that included: an Ar Ion Laser, Model 543 Head and Model 170 Power Supply (Omnichrome, Chino, CA) and an f/4, 0.5 m monochromator (Chromex, Albuquerque, NM) equipped with a Model ST-6 CCD detector (Santa Barbara Instrument Group, Inc., Santa Barbara, CA). KestrelSpec software (Rhea Corp. Wilmington, DE) was used to operate the CCD and record the compound luminescence. A Cary 50 UV/VIS spectrophotometer (Varian, Walnut Creek, CA) was used to obtain absorbance spectra. The luminescence titrations were obtained using a Model QM-2 Fluorimeter/Phosphorimeter (Photon Technologies International, Monmouth, NJ) using an excitation wavelength of 360 nm with monochrometer excitation and emission slits of 2 nm. A triangular cell using 1.5 mL aliquots was employed. Thermogravimetry was performed using a Model SDT 2960 Simultaneous DSC-TGA (TA Instruments, New Castle, DE). A Hewlett-Packard Model 5400 ICP-MS (Yokogawa Analytical Systems, Tokyo, Japan) was used to verify metal concentrations in all sample solutions. NMR was performed using a Model EFT 90 MHz spectrometer (Anasazi Instruments, Indianapolis, IN). The purity of synthesized organics was established using a Model QP 5050A GC/MS (Shimadzu, Columbia, MD). Microanalyses were performed by Desert Analytics, Inc. (Tuscon, AZ).

2.3. Synthesis

2.3.1. Compound 3

Compound **1** (1.54 g, 10 mmol), compound **2** (2.92 g, 10 mmol), and carbon tetrachloride (6 mL) were place together into a 15 mL round bottomed flask equipped with a reflux condenser under an argon atmosphere. The reaction was heated at 70 °C for 16 h when a second aliquot of **1** (0.77 g, 5 mmol) was added and the reaction was continued for another 4 h. The solvent was removed by vacuum and the final product was isolated by column chromatography using silica gel with 60/40 hexanes/chloroform as eluent to give a viscous red oil (2.2 g, 50% yield).

^{1}H NMR δ 8.48 (m, 1 H), 8.06–7.35 (m, 10 H), 6.44 (s, 1 H), 5.27–5.19 (q, $J = 6.9$ Hz, 1 H), 1.95 (d, $J = 6.9$ Hz, 3H). Anal.: Calc. for $C_{23}H_{17}F_3O_2S_2$: C, 61.87; H, 3.81. Found: C, 60.84; H, 3.37.

2.3.2. Compound 4

Compound **3** (1.0 g, 2.24 mmol) was dissolved in THF (5 mL) in a 15 mL round bottomed flask and 1.0 M sodium hydroxide (2.46 mL) was added, dropwise. A solution of europium chloride hexahydrate (0.274 g, 0.75 mmol) in water (2 mL) was added and the flask was equipped with a reflux condenser. The reaction was heated to reflux for 3 h before excess methanol was added to end the reaction. The precipitate were removed by filtration, dried, dissolved in ether, filtered again, and precipitated into hexanes. The precipitate was isolated by filtration, which gave a red solid (750 mg, 66% yield). Anal.: Calc. $C_{69}H_{54}EuF_9O_6S_6$: C, 53.73; H, 3.53. Found: C, 53.55; H, 3.56.

2.4. General procedure for conventional free radical polymerization

Divinylbenzene (2.86 g, 22 mmol), styrene (1.14 g, 11 mmol), Wako V-65 (8 mg, 0.032 mmol), PMP (5.22 mg, 0.029 mmol), and toluene (4 mL) were placed into a disposable glass reaction flask equipped with a stir bar. The flask also contained $Eu(NTFA)_3$ (40 mg, 0.040 mmol) or $Eu(3\text{-VDBM})(NTFA)_2$ (40 mg, 0.039 mmol). The solution was subjected to three freeze/pump/thaw cycles with argon backfill. The solution was placed into an oil bath heated to 60 °C for 18 h before the solvent and unreacted monomer were removed by heating to 60 °C while under vacuum (0.5 Torr) for 4 h. The polymer was ground with a freezer mill to a fine powder.

2.5. General procedure for RAFT polymerizations with methacrylics

Ethylene glycol dimethacryate (3.17 g, 16 mmol), methyl methacrylate (0.8 g, 8 mmol), toluene (4 mL), Wako V-65 (11 mg, 0.044 mmol), PMP (5.22 mg, 0.029 mmol), and **4** (40 mg, 0.029 mmol) were placed into a disposable glass reaction flask equipped with a stir bar. The solution was subjected to three freeze/pump/thaw cycles with argon backfill. The solution was placed into an oil bath heated to 60 °C for 18 h before the solvent and unreacted monomer were removed by heating to