Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Luminescence 113 (2005) 33–44
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Pressure-sensitive paint (PSP): concentration quenching of platinum and magnesium porphyrin dyes in polymeric films

Severin Grenoble, Martin Gouterman, Gamal Khalil*, James Callis, Larry Dalton

Department of Chemistry, University of Washington, Seattle 98195, USA

Received 21 August 2004
Available online 24 November 2004

Abstract

We report the effect of dye concentration on luminescence quenching and decay lifetime for metallo-porphyrin dye molecules in polymeric film. In particular we report on films containing platinum tetra(pentafluorophenyl)porphine (PtTFPP), platinum octaethylporphine (PtOEP), and magnesium tetra(pentafluorophenyl)porphine (MgTFPP) in three polymers, two non-fluorinated (MAX and polycarbonate) and one fluorinated (FIB). We found: (i) the emission intensity for PtTFPP, PtOEP, and MgTFPP decreased at higher film concentrations, an effect much more pronounced for PtOEP than for PtTFPP; (ii) the absorption, emission, and excitation spectra for PtTFPP films were relatively unchanged with concentration, while with increased concentration MgTFPP films demonstrated clear absorption, emission, and excitation spectral changes; (iii) Stern–Volmer plots (I_{atm}/I versus P/P_{atm}) for PtTFPP and PtOEP at different film concentrations overlap at dilute concentrations but separate at higher concentrations; (iv) temperature coefficient values (intensity versus temperature plots) for MgTFPP films range from 0.15%/C to 0.08%/C, whereas for PtTFPP films they range from 1.81%/C to 1.25%/C from the lowest to highest film concentrations studied; (v) lifetimes for PtTFPP, PtOEP, and MgTFPP decrease at higher film concentrations; (vi) the singlet luminescence decay of MgTFPP fits a mono-exponential at all concentrations examined at 1 atm; (vii) the triplet luminescence decay of PtTFPP and PtOEP films is mono-exponential only at dilute dye concentration and in vacuum; (viii) response times for oxygen diffusion into PtTFPP films are faster at higher concentrations of PtTFPP. Concentration effects on spectra and lifetimes are clearly observed at concentration greater than 1.0 g of porphyrin per 60 g of polymer.

PACS: 07.07.Df; 33.50.−j; 78.40.Me

Keywords: Oxygen quenching; Concentration effects; Phosphorescence; Pressure-sensitive paint (PSP)

*Corresponding author. Tel.: +206-543-5579; fax: +206-616-6250.
E-mail address: gkhalil@u.washington.edu (G. Khalil).

0022-2313/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jlumin.2004.08.049

1. Introduction

From early studies on pressure-sensitive paint (PSP) [1,2], it has been presumed that too high a concentration of the metallo-porphyrin dye sensor [3] would lead to quenching of luminescence. Also, scattered observations in our laboratory suggested that tetra(pentafluorophenyl)porphyrins (TFPP) show significantly less concentration quenching than other common porphyrins such as octaethylporphyrins (OEP) [4,5]. The purpose of this paper is to present systematic studies on the effect of porphyrin concentration on luminescence intensity and lifetime for three metallo-porphyrins in three different polymers that are useful for pressure sensitive paint (PSP). In particular, we studied platinum tetra(pentafluorophenyl)porphine (PtTFPP) and platinum octaethylporphine (PtOEP). Their emission at 650 nm is phosphorescence (i.e., from the lowest excited triplet state) and is quenched by oxygen. We also studied magnesium tetra(pentafluorophenyl)porphine (MgTFPP), whose emission is a fluorescence (i.e., from the lowest excited singlet state) and is also at ~650 nm, and is unaffected by oxygen, so it can serve as an intensity reference luminescence. We used three different polymers, mutually exclusive, in our films. We studied 2 non-fluorinated polymers: (i) dimethylsiloxane-bisphenol A-polycarbonate, which is a block co-polymer that we refer to as 'MAX' and which has good adhesion to icy surfaces, and (ii) poly(bisphenol A-carbonate) polymer, that we refer to as 'polycarbonate'. We also studied (iii) a fluoroacrylic polymer that we refer to as 'FIB' [6,7]. An important objective of this paper is determination of the weight ratio of polymer:porphyrin above which concentration quenching effects are *not* observed. We found that at ~60 g (or higher) of polymer per gram of porphyrin, concentration quenching effects on luminescence are negligible.

This paper's contents are divided as follows: (i) a literature review regarding this topic; (ii) a description of how the PtTFPP, PtOEP, and MgTFPP films were prepared; (iii) a presentation of our data including a description of how the experimental measurements were carried out for the various spectra [absorption, emission, and excitation], for Stern–Volmer pressure sensitivity plots, for temperature coefficient plots, for lifetime decay curves, for response times, and for activation energy; (iv) then a plausible mechanism and model for understanding concentration quenching effects will be presented in terms of excitation energy transfer (also called *exciton* transfer).

Further literature review uncovers several important points. First, the extent of dye aggregation in polymeric films depends upon the initial dye concentration in the liquid solution and upon the choice of solvent used to prepare liquid paints [8]. For example, we have found that dye films prepared from dichloromethane (DCM) solution have different Stern–Volmer plots from dye films of the same concentration prepared from α,α,α-trifluorotoluene (TFT). Secondly, while dye concentration in polymeric films has a large effect on emission intensity and lifetime decay processes, the effect on Stern–Volmer pressure sensitivity is less [9]. Lastly, porphyrin concentration quenching of luminescence may be reduced by incorporating the following dye modifications: (i) fluorination of the dye [10], (ii) construction of multi-layered, ordered films [11], and (iii) covalent linkage or bridges between dye molecules to reduce aggregate formation and energy-sink interaction [12,13].

2. Experimental

2.1. Materials

Three metallo-porphyrin dyes were used: PtTFPP, PtOEP, and MgTFPP. All three were made by standard porphyrin metallation procedures by Frontier Scientific (formerly Porphyrin Products), Logan, UT, USA.

Three polymers were used: MAX was purchased from General Electric LR 3320, NJ, USA. Poly(bisphenol A-carbonate) polymer was purchased from Aldrich Chemical Company, Milwaukee, WI, USA. Fluoroacrylic polymer (FIB) was purchased from ISSI, Dayton, OH, USA. Two solvents were used: DCM CAS # 75-09-2 was purchased from Fisher Scientific Chemicals, New Jersey, USA, and TFT CAS # 98-08-8 was purchased from Acros Chemicals, NJ, USA.