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Nonlinear optical properties of a porphyrin derivative incorporated in Nafion polymer

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Abstract

A solid state nonlinear optical medium is obtained by the incorporation of the metalloporphyrin, Zinc Tetra Phenyl Porphyrin (ZnTPP) in Nafion polymer membrane. The nonlinear refractive index of this membrane is measured at 632.8 nm by the z-scan technique and found to be on par with that exhibited by ZnTPP in the solution form. Photodegradation effects seen in the porphyrin solution appear to be inhibited due to its incorporation in the membrane. The material is found to exhibit optical limiting effects based on nonlinear refraction and its behaviour is investigated in comparison with that of ZnTPP in solution form. The nonlinearity appears to be of thermal origin.

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1. Introduction

Porphyrins and their derivatives are known to be interesting photonic materials in view of their large third-order optical nonlinearity and optical limiting properties, though not many studies have been made on the use of these materials as media for optical device applications [1,2]. Two major reasons for this are probably the difficulty of handling the materials in liquid form and the possibility of degradation of the medium with exposure to light [3]. This suggests the use of appropriate solid matrices to incorporate the porphyrin compounds [4], where both these difficulties can often be remedied while retaining the large nonlinear optical response.

Nafion (117) from Du Pont, a stable and inert ion-exchange polymer mainly used in fuel cell applications, has recently been used successfully as a matrix for nonlinear optical applications [5,6]. Zhao et al. [7] have studied the linear optical properties such as optical absorption and fluorescence of Nafion films incorporated with Zinc Tetra Phenyl Porphyrin (ZnTPP).

In the present work, we examine how the nonlinear optical response of ZnTPP gets modified due to incorporation in the Nafion membrane. The nonlinear optical refractive index (n_2) is determined with a low power continuous wave source by the well-known *z*-scan technique developed by Sheik-Bahae et al. [8]. Optical limiting behaviour based on aperture-controlled nonlinear refraction in porphyrin–Nafion–TPP membrane is investigated in the low power regime and the results are compared with those using ZnTPP solution.

2. Experimental

ZnTPP is synthesized and purified according to procedures reported in literature [9,10]. It is dissolved in

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spectroscopic grade toluene and the concentration of the solution is maintained at $\sim 10^{-4}$ M. Square sheets ($1\,\text{cm} \times 1\,\text{cm}$) of Nafion membrane of thickness 0.18 mm are cleaned thoroughly by boiling in concentrated nitric acid. These sheets are then immersed in fresh ZnTPP solution and kept in the dark till they attain equilibrium with the solution. The membrane is then removed from the solution and the solvent is evaporated at room temperature. The initially transparent membranes are found to turn green in color after a few hours of dipping in the ZnTPP solution. The actual amount of porphyrin that goes into the membrane is found to increase with the concentration of the starting solution, till saturation is reached at about a solution concentration of 10^{-3} M. The molar concentration of ZnTPP in solution form used for spectroscopic studies is about 3×10^{-4} mol/l and the concentration of ZnTPP when incorporated in Nafion is about 1.0 mol/m^3.

Optical absorption spectra of ZnTPP solution and ZnTPP incorporated in the Nafion membrane (Nafion–TPP) are recorded at room temperature using a Hitachi U-3400 spectro-photometer. Fluorescence spectra are recorded using an Amico–Bowman spectrofluorometer. The nonlinear refractive index (n_2) of both ZnTPP solution and Nafion–TPP is determined by the z-scan technique using the standard set up [8]. In the closed z-scan experiment, a helium–neon laser beam of wavelength 632.8 nm and of 20 mW maximum power is focused to a spot of radius 20 μm by a lens of focal length 75 mm and a photodetector fitted with an aperture of radius 0.6 mm is used to collect the output from the exit plane of the sample. The thicknesses of the samples are kept well within the Rayleigh limit of the lens. The sample is moved along the beam direction in the focal region in 80-micron steps with the help of a microcontrolled stepper motor. The output of the photodetector is fed to a computer.

Optical limiting property of both ZnTPP solution and Nafion–TPP is studied by an experimental set-up where the intensity of the input laser beam incident on the sample is varied continuously using a polarizer-analyzer combination and the whole beam output is captured by a large aperture ($\sim$25) mm photodetector kept at 10 cm distance from the nonlinear sample. The sample is placed at a point beyond the focal point of the lens where maximum defocusing of the beam occurs. The output power transmitted by the sample is measured as a function of the input power in this experiment.

3. Results and discussion

Fig. 1 shows the optical absorption spectra of fresh ZnTPP in toluene solvent with a concentration of 10^{-4} M and of the Nafion–TPP membrane. The Soret band and Q band are found to get redshifted due to incorporation of the porphyrin in Nafion. The Soret band shifted from 422 nm to 432 nm and the Q (1, 0) band from 547 nm to 650 nm. The host material, Nafion polymer membrane, is transparent in the wavelength region of interest. The fluorescence emission peak at 650 nm of the ZnTPP solution is also found to get redshifted to 670 nm in the case of Nafion–TPP. This is in agreement with the results of Zhao et al. [7], who have attributed the redshift of the Soret and Q band to the replacement of Zn ion in ZnTPP complex by two protons to form freebase porphyrin H_2TPP and further protonation to give $[H_4TPP]^{2+}$ in the Nafion matrix. The absorbance value of the Nafion–TPP membrane at 632.8 nm is higher than that of ZnTPP solution at the same wavelength. This is due to the red shift in the Q band as well as the larger concentration of ZnTPP in the membrane.

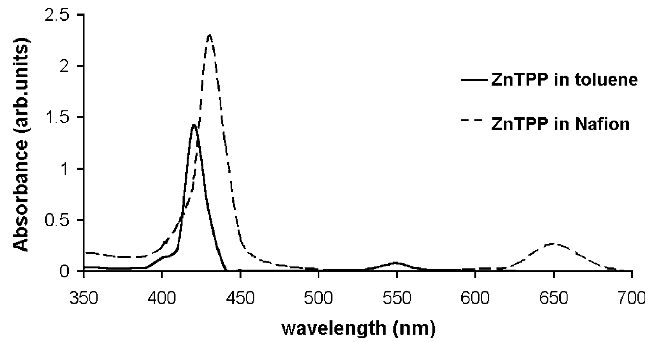

Fig. 1. Optical absorption spectra of ZnTPP in toluene of conc. 10^{-4} M (—) and Nafion–TPP membrane (- - -).

ZnTPP in the solution form is known to undergo photodegradation when exposed to light [3]. In the present work, the intensity ratio of the Soret band to the Q band was originally 0.26 for the solution and remained at that value even after 25 h of exposure to ambient light. Further exposure for 75 h increased this ratio to 0.28, after which, the increase appeared to be much smaller, maintaining the ratio near 0.28 even after 200 h of exposure. On the other hand, the intensity ratio of the Soret band to the Q band in the Nafion–TPP membrane was about 0.13, which is found to be unchanged even after 200 h of exposure. In fact the ratio remains at the same value even after exposure to ambient light for several months. The optical absorption spectrum of the Nafion–TPP membrane remained unaffected indicating that the Nafion–TPP membrane is stable against photodegradation.

Nonlinear optical response of ZnTPP is studied in solution form and also after incorporation in Nafion. Fig. 2 shows the purely refractive z-scan traces for ZnTPP solution (curve *a*) and Nafion–TPP (curve *b*). The solid lines are generated theoretically using the z-scan theory [8] for a nonlinear phase shift less than π.

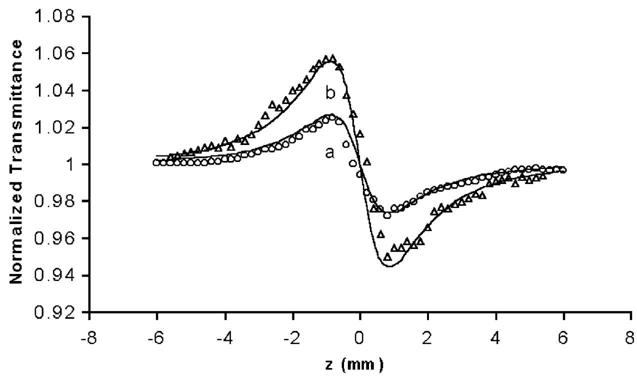

Fig. 2. Close z-scan traces of (a) ZnTPP in toluene (○) and (b) ZnTPP in Nafion (△) and the respective theoretical fits (—).

The results show that the porphyrin-incorporated membrane also shows a large negative nonlinearity similar to that of the solution. The value of n_2 for the membrane is estimated to be 2.05×10^{-8} cm^2/W, whereas the corresponding value is 1.26×10^{-8} cm^2/W for the ZnTPP solution. The slight increase in the n_2 value of the Nafion–TPP could be due to the fact that in the Nafion–TPP membrane possesses a larger value of linear absorption coefficient at 632.8 nm as compared to ZnTPP solution. The host material Nafion membrane does not show any z-scan behaviour of its own.

Since the source used to probe the nonlinear material is a low power continuous wave laser, the optical nonlinearity in both ZnTPP solution and Nafion–TPP membrane observed here is likely to be of thermal origin, arising from the temperature dependence of refractive index. The response time of the material as recorded by an oscilloscope is found to be in millisecond regime, which is to be expected in the case of such nonlinearity.

Fig. 3 shows the optical limiting curves obtained with a He–Ne laser input of wavelength 632.8 nm for both ZnTPP solution (curve *a*) and Nafion–TPP membrane (curve *b*). Both the samples show very good optical limiting behaviour arising from nonlinear refraction. The output power rises initially with increase in input power, but after a certain threshold value the samples start defocusing the beam resulting in a greater part of the beam cross-section being cut off by the aperture. Thus the transmittance recorded by the photodetector remained reasonably constant showing a plateau region. The threshold power value at which the limiting occurs for ZnTPP solution and Nafion–TPP membrane are found to be 0.48 mW and 0.12 mW, respectively. In the case of Nafion–TPP, the output power remains clamped at below 0.2 mW even at an input power of more than 5 mW. Separate optical limiting experiments are performed on pure Nafion polymer membrane and it is found to have no contribution to optical limiting in the power range of the laser used.

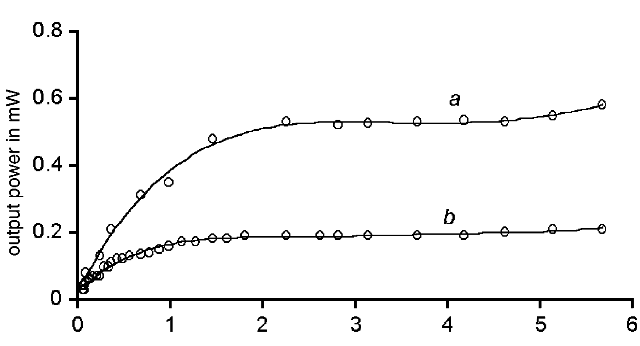

Fig. 3. Output power as a function of input power showing optical limiting in ZnTPP solution (curve *a*) and Nafion–TPP (curve *b*).

Since the open z-scan traces of both the samples returned no evidence of nonlinear absorption, the optical limiting of the beam by the nonlinear samples in the aperture-limited geometry is attributed to nonlinear refraction arising from the dependence of refractive index on the local temperature.

4. Conclusion

Incorporation of ZnTPP in Nafion membrane is found to inhibit photodegradation effects rendering the porphyrin in the form of a convenient solid membrane for linear and nonlinear optical applications. The nonlinear response of the membrane is compared with that of the porphyrin solution and is found to be similar in nature. Nonlinear refraction in the membrane is used to obtain optical limiting behaviour in an aperture-limited geometry. The origin of optical nonlinearity observed in the CW regime is attributed to the thermal variation of local refractive index in the medium.

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