Nonlinear optical properties of pyrrolic organic dyes

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Abstract—Synthesizing materials with enhanced third order nonlinear optical parameters has been of great interest in view of many practical applications. We have developed a series of pyrrolic compounds based on BODIPY chromophores and studied their nonlinear optical properties using the z-scan technique. Results show that the new compound – MeO₂BODIPY has a greater nonlinear absorption coefficient compared to a standard pyrrolic dye material such as zinc-phthalocyanine.

Keywords—BODIPY, Nonlinear Optical material, z-scan, Nonlinear absorption

I. INTRODUCTION

Organic nonlinear optical materials have been attracting major attention in view of their potential applications in signal/image processing, optical power limiting, switching, data storage etc [1-6]. A number of materials such as porphyrins, phthalocyanines, azobenzenes etc., have been synthesized and characterizing in the recent past towards this goal. 4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) is an established class of pyrrolic chromophore with unique and attractive photophysical properties such as high extinction coefficient and fluorescence quantum yield. Often it is regarded as “porphyrin’s little sister” due to the similarity of their structure [7]. However, BODIPY possesses a high fluorescence quantum yield which is typically not a good quality when identifying nonlinear optical materials. The BODIPY unit has a major absorption peak (S₀→S₁ transition) near 500 nm. However, extension of the π-system by introduction of the organic p-methoxy styrylbenzene substituents gives rise to a 140 nm red-shift in the electronic absorption maximum from 500 (ε = 5.45 x 10⁵ M⁻¹ cm⁻¹) to 640 nm (ε = 4.34 x 10⁵ M⁻¹ cm⁻¹) with a slight increase in molar extinction coefficient for this lowest energy π→π* electronic transition. Furthermore, as discussed below, this structural modification also serves to enhance the multiphoton absorption properties of BODIPY competing directly with its typical radiative decay.

II. EXPERIMENT, RESULTS AND DISCUSSION

The nonlinear optical response of the compounds 3,5-dimethyl-BODIPY (BODIPY), 3,5-bis(methoxy-4-styrylbenzene)-BODIPY (MeO₂BODIPY) and Zn(II) phthalocyanine (ZnPc) have been investigated using the conventional optical z-scan technique [8]. The output of a frequency doubled Nd:YAG nanosecond laser is focused on to the sample using a 20 cm focal length lens. The sample is mounted on an automated translation stage and moved along the z direction through the focal point of the beam. At the focal point, the sample experiences optimum pump intensity, which decreases gradually on either side of the focus. As the incident intensity of the light changes, the transmittance varies according to the sample’s nonlinear properties. Although the original BODIPY system depicts a saturable absorber (not shown in the Figure 1), the newly synthesized MeO₂BODIPY shows a strong reverse saturable absorption behavior, likely due to two-photon absorption processes involving a BODIPY S₁→S₂ electronic excitation (Figure 1). In contrast, the nonlinear absorption behavior of the well-studied ZnPc molecule is relatively less compared to that of MeO₂BODIPY.

Figure 1: z-scan studies of MeO₂BODIPY and ZnPc.

REFERENCES