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New Nonlinear Optical Crystal of Rhodamine 590 Acid Phthalate

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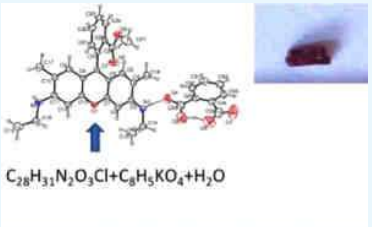
ABSTRACT: The synthesis and crystal structure of rhodamine 590 acid phthalate (RhAP) have been reported. This novel solid-state rhodamine derivative not only has a longer fluorescence lifetime compared to rhodamine solid-state matrixes where emission is quenched but also possesses strong nonlinear optical characteristics. The static and dynamic first- and second-order hyperpolarizabilities were calculated using the time-dependent density functional theory at the B3LYP/6-31+G* level. The computed static values of β and γ of RhAP by the X-ray diffraction (XRD) structure were 31.9×10^{-30} and 199.0×10^{-36} esu, respectively. These values were about 62 times larger than the corresponding values in urea, an already well-known nonlinear optical material. The second-order hyperpolarizability of the compound was determined experimentally by measuring the two-photon absorption cross section using intensity-modulated light fields. The reported compound, excitable at near-infrared, exhibited frequency upconversion with the two-photon absorption coefficient enhanced by two orders of magnitude compared to that of the dye solution. Hosting the dye in the solid, at high concentrations, exploits the nonlinearity of the dye itself as well as results in significant excitonic effects including formation of broad exciton band and superradiance.



Static hyperpolarizability (esu)

Gas phase	RhAP	Urea
$\beta_{\|\|}(0;0,0)$	21.5362D-30	0.314415D-30
$\gamma_{\|\|}(0;0,0,0)$	147.402D-36	3.22137D-36

1. INTRODUCTION

Organic molecular crystals with strong nonlinear optical (NLO) response have received much attention owing to their potential applications in optoelectronics. Applications in optical storage devices and frequency doublers,[1−8] X-ray monochromators, and X-ray analyzers[9−14] have been reported. Large molecular hyperpolarizability is one of the basic requirements for NLO applications. Organic dyes have applications in different fields due to their wide spectral range in the visible region.[15] These dyes can be used in solid, liquid, or gas phases, where their concentration and hence their absorption and gain can be readily controlled. Solid matrixes containing organic laser dyes have been developed with the goal of fabricating practical solid-state dye lasers offering direct access to the visible spectrum at a lower cost. Different solid-state materials like polymers, organic semiconductors, zeolites, sol−gel, and NLO crystals have been used as host media for organic laser dyes. These studies are aimed at the fabrication of dye-doped single-crystal microlasers.[16−29]

Nonlinear organic optical crystals doped with luminescent laser dyes can combine their nonlinear optical property with broadband tunability of the dye.[23−25] Quantum chemical studies have indicated that conjugated heteroaromatic ring systems with extended delocalization of π-electrons exhibit large hyperpolarizability.[30−38] Moreover, the electronic nature and location of heterocyclic rings play a subtle role in the NLO properties of π-conjugated donor−acceptor compounds.[39−42] Although a vast number of nonlinear crystals have been reported in the literature, synthesis of dye-doped crystals has been constrained due to the requirements of transparency, phase-matching, high optical quality, nonlinearity, mechanical stability, photostability, and availability in the bulk form.

Recently, dye-doped metal-free phthalate has been the subject of nonlinear optical studies.[43] The nonlinear optical response in this system arises from the influence of electron clouds of the π-bonds and also from the hyperpolarizability of hydrogen bonds.[44,45] Furthermore, as phthalate belongs to the family of esters, it has been used as a plasticizer for polymers to modify their physical characteristics. Hayden et al. have used esters as a linkage for the preparation of coumarin dye-attached copolymers.[46] Such polymers containing a nonlinear dye moiety can be used in designing a broad set of optical devices like modulators, parametric converters, directional couplers, switches, and lasers. However, it should be noted that hosting the dye in the solid at high concentrations allows us to exploit the nonlinearity of the dye itself. Hence, in this paper, we present the synthesis and properties of a new laser dye crystal, rhodamine 590 acid phthalate. Although different materials

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