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A new distyrylbenzene derivative with Weinreb amide functionality: An efficient laser dye and nonlinear optical material

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ABSTRACT

We report here the synthesis of a distyrylbenzene derivative with end substituent as Weinreb amide. This Weinreb amide-based distyrylbenzene (WADSB) gives indications of highly efficient laser dye as well as a nonlinear optical medium. The photophysical parameters of the dye are given here. The lasing spectra of the dye have been measured in a cuvette configuration. The third-order nonlinear susceptibility has been measured by laser-induced transient grating technique (LITG). A comparison with the existing standard molecules shows that it is a comparably an efficient lasing material as well as an efficient nonlinear optical material at the pump wavelength of 355 nm.

1. Introduction

End-substituted distyrylbenzene and their derivatives have been widely used for electro-optic and solar applications [1]. End-substituted distyrylbenzene have appeared as potential energy transporters in one-dimensional channel and modifications in the nature of terminal substituents have been found to be useful in this aspect [1,2]. Generally (π)-conjugated organic materials of well-defined chain length exhibit efficient lasing property at various wavelengths, as well as nonlinear optical property for photonic application, light-emitting diodes, field-effect transistors or sensors devices in electro optics [3–6]. To the best of our knowledge, the use of Weinreb amide (WA) functionality [7] as one of the terminal substituents has never been made. The proposed distyrylbenzene derivative (DSB) containing Weinreb amide functionality is compound (**1**) and is abbreviated hereafter as Weinreb amide-based distyrylbenzene (WADSB) (Scheme 1). The synthesis of WADSB is envisaged through a Julia reaction between sulfone (**2**) [8] and commercially available terephthaladehyde (**3**).

In dye lasers the laser wavelengths are easily tunable within the broad bandwidth of the gain medium. The ability to quickly change the dyes to achieve a wide tuning range keeps dye lasers as an economic option even today. A vast literature is available on organic dyes [9]. In photonics, there is a continuous effort to look for new materials with large optical nonlinearity. Laser-induced transient grating (LITG) is one of the techniques to measure the nonlinear optical parameters of organic dyes and semiconductors [10,11]. In this paper, besides the synthesis of the new distyrylbenzene derivative WADSB and its photophysical parameters, we report its efficient lasing property and third-order optical nonlinearity. It is found that WADSB is more efficient laser dye than a standard dye POPOP at the pump wavelength of 355 nm. Its third-order optical nonlinearity is as large as the standard reference molecule carbon disulphide.

2. Experimental

2.1. Material synthesis and chemical characterization

Compound (**1**), (WADSB) whose systematic name is 4,4′-(1*E*, 1′*E*)-2,2′-(1,4-phenylene)bis(ethene-2,1-diyl)bis(*N*-methoxy-*N*-methyl benzamide) was prepared as follows. The requisite sulfone (**2**) is prepared by a method reported earlier [8]. It involves facile benzylic bromination of 4-methyl-*N*-methoxy-*N*-methyl benzamide with NBS, followed by nucleophilic substitution with 2-mercaptobenzothiazole and finally oxidation with $Na_2WO_4 \cdot 2H_2O$ and 30% H_2O_2.

Preparation procedure: a mixture of sulfone (**2**) (0.2 g, 0.53 mmol), terephthalaldehyde (**3**) (0.034 g, 0.25 mmol) and anhydrous K_2CO_3 (0.441 g, 3.18 mmol) was added to dry DMF (9 mL/mmol of sulfone (**2**)) and heated at 70 °C under N_2 atmosphere. The reaction course was monitored by TLC (4:6;

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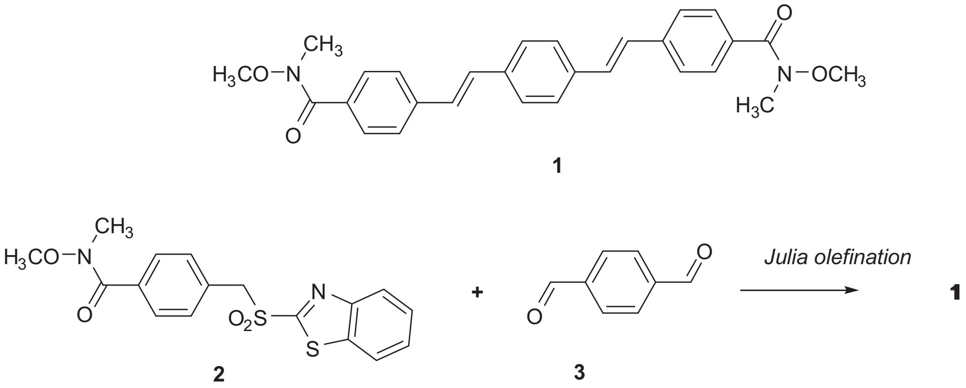

Scheme 1. Reaction equation of synthesis of WADSB.

EA/hexane). After 16 h, the reaction mixture was quenched with water and extracted with chloroform thoroughly. The crude product was purified by silica-gel column chromatography. After isolation, the compound (**1**) was heated in a toluene solution with traces of *p*-toluenesulfonic acid to afford pure *E*, *E*-isomer [8]. Isolated yield of the product (**1**), *E*–*E* isomer was 57.3% (0.066 g). $R_f = 0.125$, (hexane–ethyl acetate, 6:4), yellow crystalline solid. M.P.: 222–226 °C; ^{1}H NMR [$CDCl_3$, 400 MHz]: $\delta = 3.37$ (s, 6H), 3.57 (s, 6H), 7.18 (d, 2H, $J = 16.4$ Hz), 7.13 (d, 2H, $J = 16.4$ Hz), 7.52 (s, 4H), 7.54 (d, 4H, $J = 8.4$ Hz), 7.71 (d, 4H, $J = 8.4$ Hz). ^{13}C NMR [$CDCl_3$, 100 MHz]: $\delta = 33.9$, 61.2, 126.2, 127.2, 128.0, 129.0, 129.9, 133.0, 136.8, 139.7, 169.6. IR (CH_2Cl_2): 1378, 1420, 1623 cm^{-1}.

2.2. Methods for investigation of optical properties

The steady-state absorption spectra were recorded using a UV–visible spectrometer (JASCO, V-570) in a quartz cell of 1 mm thickness. Absorption scans of the solvent alone were taken to ensure the absence of the impurities in the pump wavelength region. Fluorescence spectra were recorded by using a fluorescence spectrometer (JASCO, FL-6600) in a quartz cell of thickness 10 mm. Decay-time measurements were done with the time-correlated single-photon counting technique (TCSPC) [13] by keeping the samples in a glass capillary on excitation at 408 nm. The analysis of decay profiles was carried out by using, a commercial software (FAST, Edinburgh Instruments). The fitting of the decay curves was judged by the value of reduced chi square (χ^2) and weighed residuals.

The experimental geometries for measuring the lasing and diffraction efficiency are shown in Fig. 1. Briefly, the third harmonic of a picosecond cavity dumped Nd^{+3}:YAG laser (Quanta system, Himalaya series, 10 Hz, 2 mJ at 355 nm, pulse width of 60 ps) was used in the experiments. To observe the lasing spectra, the sample was taken in a 5 mm quartz cuvette. The laser beam was loosely focussed to a spot of 3 mm on the sample through a lens of focal length 1000 mm. The lasing spot was observed at the right-angle geometry (Panel A, Fig. 1). The spectra were measured with ocean optics spectrometer (HR 2000). For LITG measurements, the laser pulse was split into two by a beam splitter and the two beams were made to intersect in the sample through a convex lens of focal length 500 mm at an angle of 3° to form the grating. The intensity of the first-order diffraction was measured with the help of a photodiode (Becker and Hickle, PDI-400). The pulse energy was calculated from the average power measured by a power meter (Gentec-EO). The sample was kept in a 0.1 mm home made cells. Theoretical simulations for the diffraction efficiency were done by using a program written in C language by using standard numerical methods [12].

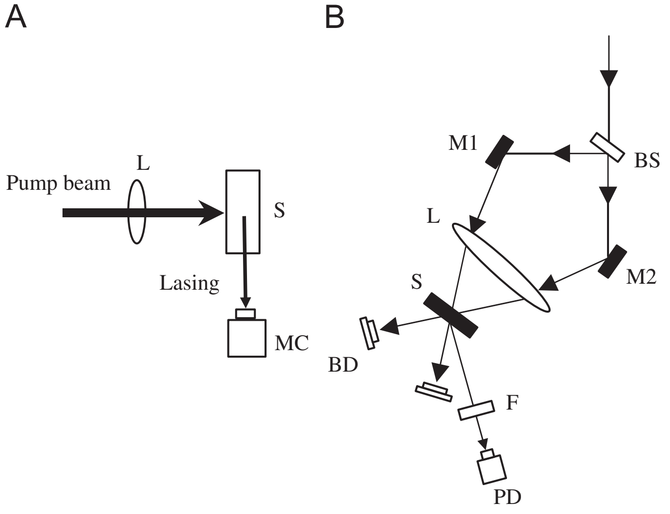

Fig. 1. The geometry used for recording the lasing spectra (Panel A): MC is the spectrometer. Experimental setup for the measurement of the self-diffraction of laser-induced transient grating (Panel B): M1, M2—mirrors, BS—beam splitter, BD—beam dump, PD—photodiode, L—focusing lens, F—filter and S—sample.

3. Results and discussion

3.1. Absorption and fluorescence spectra

Fig. 2 (Panel A) shows the absorption and fluorescence spectra of WADSB in benzene. A large value of extinction coefficient of $\sim 6.4 \times 10^6\ M^{-1}\ m^{-1}$ is obtained at the absorption maximum of the dye. It found that for the lower concentrations of the dye, the fluorescence shows a vibrational structure with a shoulder at 415 nm followed by the peak at 434 nm. With increase in the concentration, the vibrational spectrum diminishes with a subsequent shift of the peak by 5 nm towards the red. This kind of self-absorption induced behaviour is usually observed when the absorption spectra exhibit a tail extending near the emitting wavelengths.

3.2. Fluorescence lifetimes and quantum yield calculations

The fluorescence decay of WADSB (10^{-4} M) in benzene exhibits single exponential behaviour with a fluorescence lifetime of 0.98 ± 0.1 ns. Fig. 2 (Panel B) shows the fluorescent decay curves of WADSB. The decay profiles for various concentrations were also recorded. It was observed that the fluorescent lifetime does not change with a hundred fold increase in concentration.