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

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A B S T R A C T

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 [12]. 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 terephthalaldehyde (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’-(1E, 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 Na2WO4. 2H2O and 30% H2O2.

Preparation procedure: a mixture of sulfone (2) (0.2 g, 0.53 mmol), terephthalaldehyde (3) (0.034 g, 0.25 mmol) and anhydrous K2CO3 (0.441 g, 3.18 mmol) was added to dry DMF (9 mL/mmol of sulfone (2)) and heated at 70°C under N2 atmosphere. The reaction course was monitored by TLC (4:6;
Isolated yield of the product (1H), 7.54 (d, 4H, traces of p-language by using standard numerical methods[12].

The pulse energy was calculated from the average power measured with the help of a photodiode (Becker and Hickle, PDI-400). The pulse energy was obtained from 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.

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 ($\chi^2$) 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].

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 $6.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ 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 fluorescence lifetime does not change with a hundred fold increase in concentration.
The fluorescence quantum yield (Q) is the ratio of the number of photons emitted to the number of photons absorbed by the sample. The natural radiative lifetime (τ₀) and the fluorescence lifetime (τ) are related with the quantum yield as [14]

\[
Q = \frac{\tau}{\tau_0}
\]  

The fluorescence lifetime is related with the rate constants of radiative (Kᵣ) and the nonradiative (Kₙᵣ) process as

\[
\frac{1}{\tau} = K_r + K_{nᵣ}
\]

The refractive index (n) of the medium surrounding a fluorophore is known to influence the value of Kᵣ. The Einstein A and B coefficients for absorption and spontaneous emission, respectively, can be used to derive a relation between the natural radiative lifetime and the absorption and emission spectra of a fluorophore by the Strickler–Berg formula [15]

\[
\frac{1}{\tau_0} = K_r = 2.88 \times 10^{-9} \times n^2 \times \frac{\int F(v)dv}{\int (F(v)/n^2)dv} \times \int \frac{c(v)}{\tau} dv
\]

here F is the fluorescence emission, c is the extinction coefficient and ν is frequency in wavenumber. The value of Kᵣ obtained using this formula is 0.95 ± 0.02 ns⁻¹ which gives the value of τ₀ as 1.05 ± 0.02 ns. This value is close to that obtained from the direct measurement (Fig. 2(B)). From these values, the quantum yield is comes out to be 0.93 ± 0.02. The high value of the quantum yield together with a constant value of the fluorescence lifetime with concentration indicates that this molecule can also be used as a fluorescent standard in spectroscopy.

3.3. Lasing property

The characterization of amplified spontaneous emission (ASE) is useful to identify laser materials. The semitransparent walls of the quartz cuvette also contribute to the partial lasing. As a result, highly directional laser spots were observed on both sides of the cuvette. The spectra of the observed spots for different concentrations of WADSB (in benzene) and POPOP (in cyclohexane) were recorded at the pump energy of 2.5 mJ/cm². At 10⁻³ M, both POPOP and WADSB exhibit lasing. However at 10⁻⁴ M there was no lasing observed for POPOP in contrast to that for WADSB (Fig. 3). This observation indicates that the new molecule is more efficient lasing material than POPOP. The stability of the dye molecule was confirmed by constant irradiation at the pump wavelength. First-order rate equation analysis [16] of gain was also made. It was found that the value of the gain for the WADSB is more than two times higher than that of the POPOP at 10⁻³ M.

3.4. Measurement of diffraction efficiency

The self-diffraction of two laser beams was obtained by using the setup described in the Panel B of Fig. 1. The intensity of one of the transmitted beams was measured by blocking the other beam to give the value of I₀. The measured intensity of the first-order self-diffracted beam gave the value of I₁. The ratio of the diffracted intensity to that of transmitted intensity gives the value of efficiency of first-order diffraction. Table 1 gives different photophysical parameters for WADSB in benzene, and POPOP in cyclohexane. The third-order nonlinear susceptibility (χ(3)) values obtained using Eq. (4) are also given in Table 1

\[
|\chi(3)| = \sqrt{\frac{100n^2r_0^2}{9z^2dWk^2m^2}}^{1/2}
\]

where d is sample thickness, W is peak energy of the excitation pulses, τ₀ is pulse width of the laser, k is wavevector, Z₀ is impedance of the free space and m is visibility of the interference fringes. Carbon disulphide (CS₂) was used as a standard for the calibration of the setup. The measured value of χ(3) for CS₂ (see Table 1) was found to be close to that reported in the literature [17].

3.5. Theoretical simulations for χ(3)

The wavelength dependence of χ(3) of WADSB was calculated theoretically and was compared with those obtained from the experiment (Table 1). Theoretically, the diffraction efficiency of a
The sample can be calculated as
\[ Z = \frac{9m^2}{25d^2} \left( \frac{\Delta \alpha^2}{4} + k^2 \Delta n^2 \right) \]  
(5)

where \( \Delta \alpha \) and \( \Delta n \) are the changes in absorption coefficient and the refractive index, respectively [11]. The calculated curve for diffraction efficiency and the \( \chi^{(3)} \) values as a function of the wavelength are shown in Fig. 4. It is can be seen that the contribution of the phase grating is more than that of the amplitude grating to the total efficiency. The efficiency of diffraction shows a maximum at 370 nm and vanishes below 280 nm and above 410 nm. Similarly the value of \( \chi^{(3)} \) also varies with the wavelength and shows a maximum at 370 nm. A comparison shows that the experimental values are larger at 355 nm than those obtained theoretically (Table 1). This

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solvent</th>
<th>( \lambda_{abs} ) (nm)</th>
<th>( \lambda_{em} ) (nm)</th>
<th>( \mid \chi^{(3)} \mid \times 10^{-21} ) (m²/V²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>WADSB</td>
<td>Benzene</td>
<td>368</td>
<td>434</td>
<td>(53 ± 6) \times 10^{-21}</td>
</tr>
<tr>
<td>POPOP</td>
<td>Cyclohexane</td>
<td>358</td>
<td>420</td>
<td>(24 ± 4) \times 10^{-21}</td>
</tr>
<tr>
<td>CS₂</td>
<td></td>
<td></td>
<td></td>
<td>(4.1 ± 0.4) \times 10^{-21}</td>
</tr>
</tbody>
</table>

\( a \) Wavelength of maximum absorption.
\( b \) Wavelength of emission maximum.
\( c \) At 355 nm.
\( d \) At \( \lambda = 532 \text{ nm} \) [17].

Fig. 3. Normalized fluorescence and lasing spectra for WADSB in benzene (Panel A) and POPOP in cyclohexane (Panel B). The pump wavelength is 355 nm.

Fig. 4. Plot of theoretically simulated diffraction efficiency vs. wavelength for WADSB (Panel A). The \( \chi^{(3)} \) values obtained from Eq. (4) are given in (Panel B). The parameters are \( d = 0.1 \text{ mm}, W_p = 8.7 \times 10^{-3} \text{ J/cm}^2 \) and \([\text{WADSB}] = 10^{-5} \text{ M}\).
observation suggests the presence of other contributions such as thermal or acoustic grating to the experimental data within the duration of the ps pulse [19]. Moreover, non-negligible susceptibility values of benzene [20,21] could also contribute to these values. Even though at the energy densities used in the work, we were unable to observe any visible self-diffraction from the pure benzene. It should be mentioned, however that we have not included the excited state absorption coefficients in the simulations as the values are not available at the present.

4. Conclusions

In conclusion, a new dye, WADSB with high quantum yield exhibiting lasing property is reported here. It is found that this dye is at least ten times more efficient than POPOP when pumped with the third harmonic of the Nd\(^3\):YAG laser. It is suggested that the dye will be useful at the other pump wavelength of excimer and nitrogen lasers as well. The \(\chi^{(3)}\) value of the WADSB is found to be of the order of the standards used in nonlinear optics [17].

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