Photochromism, anomalous multi-banded fluorescence and laser properties of some amino- and tosyl-derivative of oxadiazole

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Abstract

The multi-banded fluorescence and laser properties of 11 new amino- and tosylamino-derivatives of 2,5-diphenyl-1,3,4-oxadiazole and oxadiazole in various solvents at 293 K are reported. All the compounds investigated possess intramolecular hydrogen quasi-bond (HQB) of 4.6–5.2 kcal mol\textsuperscript{-1} in the ground state. In the excited state they can undergo protolytic dissociation or intra-molecular proton-initiated transfer of proton and reveal anomalous fluorescence which cannot be explained within the framework of the Kasha and Kasha–Vavilov rules. Depending upon the excitation wavelength, solvent, concentration and pH of the medium, the compounds studied show a single, double, triple or even a four-banded fluorescence, which has not been reported earlier. The nature of multi-banded fluorescence is explained in terms of the possible photophysical processes in excited states. Quantum yields and decay times of the different fluorescence bands are reported. Anomalies dependence of quantum yield upon concentration of the solvents is observed. Laser properties of the compounds studied are carefully tested. Laser action based on the fluorescence of the so-called bi-radical molecules is reported. Various possible arrangements of singlet and triplet levels of compounds investigated are discussed.

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1. Introduction

A number of molecules containing donor (D) and acceptor (A) groups show multiple fluorescence. In dual fluorescence compounds, the two fluorescence bands are separated by a single bond, the two fluorescence bands often originate from a "locally excited" (LE) state and an intra-molecular charge transfer (CT) state. The most well-known examples are p-(dimethylaminobenzonitrile (DMABN)\textsuperscript{1} [1]. In this molecule, charge transfer leads to a configurational change, the nature of which has been the subject of much discussion in the literature [2–6]. DMABN displays two fluorescence emission bands, which are strongly dependent on both the polarity of the solvent and the temperature [1,7]. In non-polar solvents only the LE type band is observed while an additional longer wavelength band appears in polar solvents. Since the discovery of dual fluorescence in DMABN, it has been found to be common in other flexible D–A type molecules. Several amino derivatives of DMABN display this phenomenon. Cyano-substituted N-phenylpyrrole show interesting changes in their dual fluorescence under different conditions. N-Phenylpyrrole itself shows dual fluorescence in the polar solvents ethanol and acetonitrile with the CT component increasing with decreasing temperature [5]. The presence of the electron-accepting cyano group at the 4-position leads to a strong increase of the CT component. In many cases while dual fluorescence is observed in n-hexane in polar solvents only the CT component is obtained [8–12]. Some compounds even exhibit triple fluorescence. p-(N,N-Dimethylamino)benzene displays dual fluorescence in cetyl trimethylammonium micelles, with an excimer emission being dominant [13,14]. Upon aggregation in a water–dioxane mixture, this compound shows triple fluorescence. This phenomenon is also exhibited by p-(dialkylamino)salicylic acids and their esters. Here, an intra-molecular proton transfer is thought to be responsible for one of the emission bands [15–17]. A similar process is responsible for one of the bands in the double
and triple fluorescence exhibited by molecules containing the tosylamino group with a chelated cycle in the S0 state [18–20]. In molecules containing the tosylamino group in which an intramolecular proton transfer is possible, one fluorescence band is formed by the mono- or di-basic molecules, and the other one is due to protolytic dissociation [20]. The multi-band fluorescence of such molecules has nothing to do with the fluorescent excimer or exciplex molecules [20,21]. Firstly, the absorption spectra of such compounds do not depend on the concentration of solution either in inert or in polar solvents. Secondly, analogous multi-band fluorescence is observed in inert and in polar solvents. Thus, there are many compounds that exhibit double or even triple fluorescence. However, in many cases, the quantum yields and fluorescence decay times of the various bands have not been measured and the possibility of laser action in these compounds has not been tested.

This paper presents a careful study of the multi-band fluorescence and laser properties of aminotosylamino derivatives of 2,5-diphenyl-1,3,4-oxidiazole (PDD). The compounds studied are: (1) PDD, (2) 2-(aminomethyl)-1-phenyl-1,3,4-oxidiazole, (3) 2,5-diphenyl-1,3,4-oxidiazole, (4) 2-phenyl-5-(tosylaminomethyl)-1,3,4-oxidiazole, (5) 2,5-di(tosylaminomethyl)-1,3,4-oxidiazole, (6) 2-phenyl-5-tosylamino-4-methylphenyl-1,3,4-oxidiazole, (7) 2-(4-biphenyl)-5-phenylamino-1,3,4-oxidiazole, (8) 2-(4-naphthyl)-2-(4-phenylamino)-1,3,4-oxidiazole, (9) 2-(4-dimethylaminophenyl)-1,3,4-oxidiazole, (10) 2-phenyl-4-(tosylaminomethyl)-1,3,4-oxidiazole, (11) 2-(4-naphthyl)-2-(2-tosylaminophenyl)-5-(2,4-dioxadiophenyl)-1,3,4-oxidiazole, (12) 1-styrenyl-2-(4-phenylamino)-5-(2,4-dioxadiophenyl)-1,3,4-oxidiazole. The molecular structures of these compounds are shown schematically in Fig. 1.

2. Experimental methods

The compounds shown in Fig. 1 were re-crystallized, sublimed and purity-controlled using chromatography. Ultraviolet absorption spectra were recorded using a SPECORD M40 spectrophotometer with spectrograde heptane, toluene or ethanol as solvents. A Hitachi MPF-4 spectrophotofluorimeter was used to record the fluorescence spectra with the spectral bandwidths of the excitation monochromator chosen to be not greater than 0.5 nm in each case. The emission slit-width was chosen depending on the fluorescence intensity, but always sufficiently narrow to avoid distortion of the fluorescence spectrum. The quantum yields of fluorescence were measured using the method described [22] and explained previously [23]. A dilute solution of 9,10-diphenylanthracene in ethanol was used as the standard, with its quantum yield taken as 0.95 [24]. The standard refractive index correction was performed according to [24]. The decay times of fluorescence, τf, were measured using a SLM-4800S phase fluorimeter. The error limits were 10% for quantum yields of fluorescence and 5–10% for decay times.

Optical pumping during the testing of the laser properties was carried out using either a XeCl or a N2 laser, whose frequencies are 32,456 and 20,679 cm⁻¹, respectively. In all cases, transverse pumping was employed. A B-doped cell with a bore of two millimetres in a prism was used [25]. A qualitative test for laser action was done in the broad-band mode [26]. A plane-parallel resonator without telescope or Fabry-Perot Etalons was used.

The tuning range was found with the help of a grating, instead of a blazed mirror. The concentration of each solution was chosen to get the maximum laser effect and depended on the compound studied.

3. Results and discussion

PDD consists of the oxidazole ring and two phenyl rings which are joined to the oxidazole ring at positions 2 and 5. The PDD molecule is distorted slightly from planarity in the ground state. The S0 → S1 transition is accompanied by π-electron density transfer from the oxidazole ring to the phenyl rings and has an oscillator strength of 1.59. It displays normal single-band molecular fluorescence (denoted in the following as M-fluorescence), with the quantum yield and the decay time in cyclohexane of 0.20 and 3.53 ns, respectively [27]. In heptane the quantum yield and decay time are the same as in cyclohexane, altering to 0.81 and 1.50 ns in ethanol. PDD shows laser activity in ethanol with λmax at 348 nm (see Table 1), obtained using the NeCl laser for pumping.

Compounds (2) and (3) are ethyl amino derivatives of PDD possessing chelated cycles in the ground state, due to the internal hydrogen bond (IHB). Pariser-Parr-Pople (PPP) [28,29] semiempirical quantum chemical calculations show that in contrast to PDD, the S0 → S1 transition (which is of λ → π* nature) of compounds (2) and (3) is accompanied by π-electron density transfer from the NH2 group(s) and peripheral rings to the oxidazole ring. During this transition the IHB strengthens. The second, S0 → S2 transition in these molecules is of A → 1A1 nature and hence forbidden. The third, S0 → S3 transition is accompanied by π-electron density transfer from the oxidazole ring to the peripheral rings and NH2 group(s) leading to a weakening of the IHB. Hence, the S0 → S3 transition in compounds (2) and (3) has the same nature as the S0 → S1 transition in PDD. The absorption and fluorescence spectra of compound (2) is given in Fig. 2. The absorption spectra of these compounds are very structured, especially that of compound (3). This can be explained in terms of the geometry of molecules (2) and (3).

These molecules are planar and rigid in the ground state, because of the chelated cycles. The absorption bands due to the S0 → S1 and S0 → S2 transitions are indicated in Fig. 2. They are clearly well separated and easily distinguishable. The S0 → S2 absorption band of compound (2) resembles the S0 → S2 absorption band of PDD and occurs over a very similar spectral range. The same can be said about compound (3), although in this case the intensity of the S0 → S3 band is much lower. In fact, simulation predicts that the oscillator strength of the S0 → S3 transition in compound (3) is nearly 0.315. The decrease in the S0 → S3 band intensity between compounds (2) and (3) and relative to the corresponding band of PDD is explained by π-electron charge shifting towards the NH2 group(s) (which have donor nature) during the S0 → S3 transition.
Fig. 1. Structural formulae of the compounds investigated.
Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Solvent</th>
<th>3α → Sβ</th>
<th>Fluorescence bands (λmax (nm)) (δ, τ)</th>
<th>Mβ</th>
<th>Mα</th>
<th>Mα’</th>
<th>BR</th>
<th>λmax (nm)</th>
<th>Δλmax (nm)</th>
</tr>
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<td>1</td>
<td>Hexane</td>
<td>1.500</td>
<td>–</td>
<td>340 (0.80, 1.35)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>348</td>
<td>348–355</td>
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<tr>
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<td>Ether</td>
<td>1.400</td>
<td>–</td>
<td>340 (0.81, 1.36)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>348</td>
<td>348–355</td>
</tr>
<tr>
<td>2</td>
<td>Hexane</td>
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<td>310 (0.15, 0.00)</td>
<td>390 (0.30, 2.45)</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Ether</td>
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<td>330 (0.25, 0.00)</td>
<td>430 (0.38, 4.46)</td>
<td>–</td>
<td>–</td>
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</tr>
<tr>
<td>3</td>
<td>Hexane</td>
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<td>Weak</td>
<td>400 (0.36, 2.00)</td>
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<td>–</td>
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<td>–</td>
</tr>
<tr>
<td></td>
<td>Ether</td>
<td>1.000</td>
<td>Weak</td>
<td>400 (0.40, 2.00)</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
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<td>Toluene</td>
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<td>Very weak</td>
<td>440 (0.34, 1.50)</td>
<td>510 (0.00, 1.20)</td>
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<td>510–520</td>
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<td>320 (0.00, 1.60)</td>
<td>440 (0.34, 1.50)</td>
<td>510 (0.00, 1.20)</td>
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<td>Ether</td>
<td>0.375</td>
<td>Very weak</td>
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<td>510 (0.07, 1.10)</td>
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<td>510–520</td>
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<td></td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
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<td>Very weak</td>
<td>440 (0.08, 1.30)</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
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<td>Ether</td>
<td>0.300</td>
<td>Very weak</td>
<td>440 (0.08, 1.30)</td>
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<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>6</td>
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<td>Very weak</td>
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<td>–</td>
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<td>–</td>
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<tr>
<td></td>
<td>Ether</td>
<td>0.300</td>
<td>Very weak</td>
<td>420 (0.08, 1.30)</td>
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<td>7</td>
<td>Toluene</td>
<td>0.250</td>
<td>Very weak</td>
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<td>400 (0.08, 2.50)</td>
<td>415</td>
<td>415–450</td>
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<tr>
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<td>0.150</td>
<td>320 (0.01, 1.60)</td>
<td>390 (0.08, 1.50)</td>
<td>400 (0.08, 2.50)</td>
<td>415</td>
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<td>8</td>
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<td>–</td>
<td>370 (0.01, 2.30)</td>
<td>390 (0.02, 1.20)</td>
<td>390</td>
<td>390–410</td>
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<td>–</td>
<td>370 (0.01, 2.30)</td>
<td>390 (0.02, 1.20)</td>
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<tr>
<td>9</td>
<td>Toluene</td>
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<td>–</td>
<td>450 (0.17, 1.30)</td>
<td>–</td>
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<tr>
<td></td>
<td>Ether</td>
<td>0.150</td>
<td>–</td>
<td>450 (0.17, 1.30)</td>
<td>–</td>
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<td>10</td>
<td>Toluene</td>
<td>0.300</td>
<td>–</td>
<td>480 (0.08, 1.60)</td>
<td>–</td>
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<tr>
<td></td>
<td>Ether</td>
<td>0.200</td>
<td>–</td>
<td>480 (0.08, 1.60)</td>
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<td>–</td>
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<td>Toluene</td>
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<td>420 (0.70, 1.00)</td>
<td>430</td>
<td>430</td>
<td>430</td>
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<td>430–450</td>
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<tr>
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<td>0.200</td>
<td>–</td>
<td>420 (0.70, 1.00)</td>
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<td>430</td>
<td>430</td>
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<td>430–450</td>
</tr>
<tr>
<td>12</td>
<td>Toluene</td>
<td>0.250</td>
<td>–</td>
<td>380 (0.15, 0.85)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Ether</td>
<td>0.200</td>
<td>–</td>
<td>380 (0.15, 0.85)</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tbody>
</table>

Headers from left to right are: compound number, λmax (nm) (maximum of the absorption band formed by the Sα → Sβ transition), δ (oscillator strength), λmax (nm) (maximum of the fluorescence band), τ (fluorescence quantum yield measured at C = 5 x 10⁻⁶ mol/L), BR (brilliance), Mα (molar absorption coefficient), Mα’ (molar absorption coefficient), Mβ (molar absorption coefficient), Δλmax (maximum of excitation range), Δλmax (maximum of emission range).

Depending on the excitation wavelength, compound (2) can exhibit either normal single-photon fluorescence (the long-wavelength band) or dual fluorescence. Normal M-fluorescence is exhibited if the excitation occurs within the range of the long wavelength absorption band. For example, when the excitation wavelength is 345 nm the hexane solution of compound (2) reveals normal M-fluorescence (shown by the longest wavelength solid line in Fig. 2). However, if the excitation wavelength is situated in the range of the Sα → Sβ absorption band then dual fluorescence is pronounced (Fig. 2, dashed-dot curve). The position and form of the short wavelength fluorescence band (hereafter referred to as M’ fluorescence) of compound (2) resembles the fluorescence of PPD itself. Due to the aforementioned shift of the π-electron density to the NH2 group, during the Sα → Sβ transition, when the NH2 group loses its donor properties, the chelated ring can be broken by inter-molecular collisions. As a consequence, the conjugation between the NH2 group and the rest of the molecule is also broken. Hence, the short wavelength M’-band of the dual fluorescence of compound (2) originates from molecules with broken HBB. Compound (3) can also display single and dual fluorescence, depending on the excitation wavelength, in the same manner as compound (2). Furthermore, compound (3) shows laser activity when dissolved in ether.
It is clearly seen that the absorption spectrum of this compound consists of two bands. The long wavelength absorption band is situated in the range 28,000–33,000 cm⁻¹. PPP calculation reveals that this band belongs to excitation localized on the chromophore labelled A in Fig. 3, and is formed by the $S_0 \rightarrow S_1$ transition. During this transition the $\pi$-electron density is transferred from the tosylamino group to the oxadiazole ring.

The short wavelength absorption band is situated in the range 33,000–38,000 cm⁻¹, with the maximum situated at approximately 35,500 cm⁻¹. This band originates on chromophore B, and results from the $S_0 \rightarrow S_2$ transition during which $\pi$-electron density is transferred from the oxadiazole ring to the peripheral rings and onto the tosylamino group. The fluorescence properties of this compound are very complicated. Depending on the conditions, it can display single, double, or even triple fluorescence.

The shape of the fluorescence bands and the fluorescence parameters are strongly dependent upon the solvent, concentration, and excitation wavelength (Fig. 4). For example, in ethanol with an excitation wavelength of 337 nm, compound (4) displays dual fluorescence with the band maxima at 24,000 and 20,000 cm⁻¹ (see Fig. 3).

The molecular process responsible for the fluorescence bands of compound (4) are as follows. During the $S_0 \rightarrow S_1$ transition, the $\pi$-electron density is transferred from the tosylamino group to the oxadiazole ring. As a result of this process a proton can be transferred along the IHB from the amino group to the N-atoms of the oxadiazole group so that a bi-radical (BR) molecule is produced. This bi-radical molecule is responsible for the long wavelength fluorescence band. The process can be expressed as...
follows:

\[ M_0 + h\nu_{abs} \rightarrow M^* \rightarrow BR^* \rightarrow h\nu_B + BR_0 \rightarrow M_0 \]

or, as a result of inter-molecular collisions the following process can occur (protolytic dissociation).

\[ M_0 + h\nu_{abs} \rightarrow M^* \rightarrow (M^-)^* + H^* \rightarrow h\nu_B + M_0^- + H^* \rightarrow M_0 \]

Hence, one of the two bands of fluorescence results from the formation of excited BR\(^*\) molecules. In other words, the longest wavelength fluorescence band is formed due to the intramolecular proton transfer (IPT) process. The other fluorescence band is caused by the excited \((M^-)^*\) molecules, formed by protolytic dissociation. At an excitation wavelength of 280 nm, compound (4) exhibits triple fluorescence in ethanol solution (pH 7). The shortest fluorescence band belongs to excited molecules with a broken E2E, \(M^-\) fluorescence, as described earlier. This process can be represented by the following scheme:

\[ M_0 + h\nu_{abs} \rightarrow M^{**} \rightarrow (M^-)^* \rightarrow h\nu_B + M_0^- \rightarrow M_0 \]

At low temperature (77 K) compound (4) exhibits only one fluorescence band, which is attributed to intramolecular proton transfer (BR\(^*\) fluorescence). At low temperature protolytic dissociation becomes almost impossible and only intramolecular proton transfer can occur.

In Fig. 4(d) and (b), the shorter wavelength band is attributed to excited anion, and the longer wavelength band is formed by the emission from excited biradical. At pH \(\geq 11\) only one fluorescence band is formed, and the excited \((M^-)^*\) molecules (due to protolytic dissociation) is to be expected, since the protolytic dissociation is likely to be the predominant mechanism in basic solutions. In solid film only the BR fluorescence band is exhibited since intramolecular proton transfer is the preferred process. Only one fluorescence band is seen in \(\text{H}_2\text{SO}_4\) solution, although the nature of this band is not clear. It may arise due to some complex molecular formation, perhaps between molecules of \(\text{H}_2\text{SO}_4\) and compound (4).

The quantum yield of the \((\text{BR})^*\) fluorescence band anomalously depends on the concentration of the solution (see Fig. 4(c)). Increasing the concentration of the solution from \(C = 1 \times 10^{-5}\) mol l\(^{-1}\) to \(C = 1 \times 10^{-4}\) mol l\(^{-1}\) results in an eight-fold increase in the \((\text{BR})^*\) fluorescence quantum yield, while the quantum yield of \((M^-)^*\) fluorescence is slightly decreased. Such behaviour can be explained as follows. With the increase of concentration the following three processes can contribute to the \((\text{BR})^*\) fluorescence:

\[ M_0 + h\nu_{abs} \rightarrow M^* \rightarrow (M^-)^* + H^* \rightarrow BR^* \rightarrow h\nu_B + BR_0 \rightarrow M_0 \]

\[ M_0^* + h\nu_{abs} \rightarrow (M^-)^* + H^* \rightarrow BR^* \rightarrow h\nu_B + BR_0 \rightarrow M_0 \]

\[ BR_0 + h\nu_{abs} \rightarrow BR^* \rightarrow h\nu_B + BR_0 \rightarrow M_0 \]

In the first process, an excited neutral molecule initially losses a proton, becoming an excited anion which then gains a proton from the medium onto the oxadiazole ring, forming the excited biradical. The second process is initiated through ground state anion absorption before following a similar path to the first. The third possibility involves a ground state biradical as the starting point. All these three processes become more probable with increasing concentration.

Compound (4) shows very interesting laser properties. Laser excitation of this compound is based on the \((\text{BR})^*\) fluorescence band. Such laser excitation becomes possible at \(C > 10^{-7}\) mol l\(^{-1}\). To the best of the authors' knowledge, this is the first report of laser activity in a compound capable of showing multi-banded fluorescence. The absorption and fluorescence of compound (5) are shown in Fig. 5. The fluorescence properties of this compound are very similar to those of compound (4). Depending on the excitation wavelength, it can also show diode or triple fluorescence and shows laser activity based on the \((\text{BR})^*\) fluorescence band. The intensity of the \((\text{BR})^*\) fluorescence band is greater than in compound (4). For both compounds (4) and (5), the Stokes shift of the fluorescence bands is large: 10,000–12,000 cm\(^{-1}\) for \((\text{BR})^*\) band and 6000–8000 cm\(^{-1}\) for the \((M^-)^*\) band.

It is also interesting to note that the fluorescence properties of newly prepared solutions of compounds (4) and (5) differ slightly from those that have been kept under illumination for some time. Older solutions show more intense \((M^-)^*\) and \((\text{BR})^*\) fluorescence (see Fig. 4(d)). This phenomenon is difficult to explain. It may be that following the illumination of solutions of compounds (4) and (5), the relative concentrations of the ground state anionic and biradical forms of the molecules increase. Excitation spectra for the fluorescence bands are different and very complicated. This is due to the presence of small quantities of ground state \(M_0\) and \(BR_0\) molecules. The excitation spectra of the \((M^-)^*\)-band (fluorescence of the molecule with broken chelated ring) look very much like the absorption spectra of PPD.

![Fig. 5. Absorption and fluorescence spectra of compound (5) in ethanol and heptane. Details as in Fig. 3.](image)
Absorption and fluorescence spectra of compound (6) are given in Fig. 6. Fluorescence properties of compound (6) are very similar to compound (4). It can also reveal double or triple fluorescence, only the M fluorescence is very weak and BR fluorescence is more intense. The increase in the intensity of BR fluorescence is explained by the fact that BR state is very similar to the triplet state.

Absorption and fluorescence spectra of compound (7) are given in Fig. 7. Depending on the excitation wavelength it can reveal double-handed or triple-handed or even four-handed fluorescence. Besides M fluorescence, [M] fluorescence and BR fluorescence, it can also show neutral M fluorescence. For example, if \( \lambda_{ex} = 320 \text{ nm} \) then ethanol solution of compound (7) shows double fluorescence (M fluorescence and BR fluorescence). If \( \lambda_{ex} = 345 \text{ nm} \) then it again shows double fluorescence, but of a different nature (M fluorescence and BR fluorescence), and if \( \lambda_{ex} = 300 \text{ nm} \) then compound (7) reveals four-handed fluorescence.

Compounds (8)-(12) have very simple absorption spectra but show different fluorescence properties. In most cases compound (8) shows double fluorescence: M fluorescence and BR fluorescence. Compound (10) in heptane and in toluene shows double fluorescence: M fluorescence and BR fluorescence, but in ethanol it shows only M fluorescence (see Fig. 8). Despite the presence of the tosylfluoroc group, compounds (9) and (11)-(12) show only ordinary single-handed fluorescence, that is M fluorescence. Laser action of compounds (9)-(12) is based on M fluorescence, while laser action of compounds (4)-(5) and compound (7) is based on BR fluorescence (see Table 1). The multi-form fluorescence properties of tosylamino derivatives of PFQ and oxadiazole can only be explained by the mutual transition of different singlet and triplet levels. The position of \( S_1^{\text{ex}} \) state, formed by the transition of \( n \)-electron from the oxygen of SO3 group to \( \pi^* \) orbitals of a molecule is extremely important, because due to such transitions oxygen becomes positively charged and pulls electron density from the \(-\text{NH} \) group, creating the possibility of protolytic dissociation and intra-molecular proton transfer. There could be several types of level arrangements. The most probable four of them are shown in Fig. 9. In the arrangement shown in Fig. 9(a), the lowest singlet level is formed by the electronic density transfer from a donor group ether or the tosylamino group, and \( S_2^{\text{ex}} \) (O and \( T_2^{\text{ex}} \) (O) levels are situated higher than \( S_1^{\text{ex}} \) (O) state. For example, in compound (9) the lowest singlet state is formed by the transfer of electron density from the dimethyloxide group to the oxadiazole ring and onto the toslylazino group. In this case the protolytic dissociation and intra-molecular proton transfer are possible. As a result of this only ordinary M fluorescence is possible, because the \( S_1^{\text{ex}} \) and \( T_2^{\text{ex}} \) degradation process is the most preferable. In another possible arrangement (Fig. 9(b)), the lowest singlet state is formed by the electronic density transfer from the toslylazino group to the oxadiazole ring, but the amount of electronic density transferred is not enough to create an opportunity for easy protolytic dissociation or for intra-molecular proton transfer.
Fig. 5. Four types of relative arrangements of singlet and triplet levels of pyrimidine derivatives of naphthalene. \( S_{1\text{exc}}(O) \) and \( T_{1\text{exc}}(O) \) are singlet and triplet states which are formed by \( n \rightarrow n' \) transition from the SO₂ group. \( S_{2\text{exc}}(C) \) and \( T_{2\text{exc}}(C) \) are singlet and triplet states formed by the electron density transfer from trypsinogen group to the pyrimidine ring.
In this case, M-fluorescence and Bc-fluorescence of low intensity are the only ones possible. In the levels arrangement shown in Fig. 9(c), the lowest singlet excited state is formed by the transfer of electronic density from tosylamino group to the oxadiazole ring. Here, S_{1}^{0}(O) and T_{1}^{0}(O) levels are situated below S_{2}^{0}(H) state. According to the classification of hetero-aromatic compounds [30], these molecules belong to class III and do not display π- or π-π' fluorescence. On being excited to S_{2}^{0}(H) state, they are degraded to T_{1}^{0}(O) state, from which they degrade to M−1 or BR2 states. That is why such molecules reveal either double- or triple-fluorescence depending on the excitation wavelength. In the last type of level arrangement (shown in Fig. 9(d)), the lowest singlet state is S_{1}^{0}(H), which is formed by a large transfer of electronic density from the tosylamino group to the oxadiazole ring, so that protolytic dissociation and intramolecular proton transfer processes become possible. Such molecules, as well as molecules of cases (a) and (b), belong to class IV as do molecules in case (a) and (b) and show π−π' fluorescence. S_{1}^{0}(O) and T_{1}^{0}(O) states, like in cases (a) and (b), do not play any role in energy degradation from the S_{2}^{0}(H) state. The dominant non-radiative processes in this case are S_{1}^{0}(H) → M−1, S_{2}^{0}(H) → BR2 or S_{2}^{0}(H) → T_{1}^{0}(H). Such molecules can reveal even single-banded fluorescence: M−1, M−2, (π−π') and BR fluorescence. Hence, tosylamino derivatives of oxadiazole can reveal normal single-banded (π−π') fluorescence or double-banded (M−1 and BR) fluorescence or triple-banded (M−1, BR) fluorescence or even four-banded (M−1, M−2, (π−π'), BR) fluorescence. Schematically, these possibilities are shown in Fig. 10.

4. Conclusions

Amino- and tosylamino-derivatives of PPD and oxadiazole may display single, dual, triple or even four-banded fluorescence. From the fluorescence and laser data presented and discussed in this paper, the following conclusion may be drawn. Amino- and tosylamino-derivatives of PPD display multi-banded fluorescence when the ground state structure includes a chelated cycle. The intensity of these bands and the quantum yields of the corresponding fluorescence depend upon the experimental conditions such as excitation wavelength, solvent, solution concentration and pH. In the case of the tosylamino derivatives, excitation within the absorption band formed by the S_0 → S_1 transition gives rise to the possibility of two fluorescence bands (which may be observed simultaneously under certain conditions). One of these bands is due to the anionic form of the molecules (resulting from protolytic dissociation) and the other one is due to emission from the so-called bi-radical molecules (resulting from an intra-molecular proton transfer process). Excitation of the tosylamino derivatives via the absorption band formed by the S_0 → S_1 transition (during which the π-electron density is transferred from the oxadiazole ring to the amino- or tosylamino group) results in the observation of a third fluorescence band. This latter band is due to emission from molecules with a broken chelated cycle. Such emission is also possible when the 6-amino derivatives are excited via the S_0 → S_2 transition. To the best of the authors’ knowledge this type of fluorescence has not been reported earlier. The 6-amino derivatives also display a second fluorescence band which arises from the S_2 excited state which contains an unbroken chelated cycle. If excitation of the 6-amino derivatives occurs within the S_0 → S_2 band, then this is the only fluorescence band observed. Investigation of laser properties of the compounds studied shows that ortho-tosylamino derivatives of PPD exhibit unusual laser oscillations. This results from the fluorescence of bi-radical molecules produced by the intra-molecular proton transfer process. This type of laser action is also observed for the first time.

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References


