

Triphenylamine-cored tetramethyl-BODIPY dyes: synthesis, photophysics and lasing properties in organic media†

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A series of tetramethyl BODIPY branched triphenylamine derivatives TPA-BDP1, TPA-BDP2 and TPA-BDP3 have been designed and synthesized. Their emissions are tunable from green to red by changing solvent polarity and exhibit highly efficient and stable amplified spontaneous emissions (ASE) in the green region, under transversal pumping at 355 nm.

Amplified spontaneous emission (ASE) phenomenon in organic matrices containing luminescent molecules has been widely studied in recent years.¹ Structures that give off ASE are sometimes referred to as “mirrorless lasers”, because they have most of the properties of a laser.² In recent years, a substantial number of research publications have focused on the light amplification and luminescence spectral narrowing of laser dyes doped on polymeric films as well as in solutions.^{3,4}

In particular, boron dipyrromethene (BODIPY) derivatives are widely used as the active media for tunable lasers⁵ due to their advantageous photophysical properties such as high fluorescence quantum yields, high photostability, and efficient laser emission in solution.⁶ Their laser action is better than that of rhodamine dyes, and thus are considered as the benchmark in laser performance.⁷ Moreover, their laser performance and photophysical properties can be finely tuned by introducing substituents at appropriate positions benefitting from recent developments in BODIPY chemistry. Recently, Boens *et al.*⁸ have done much work on the synthesis and reactivity of BODIPY derivatives.

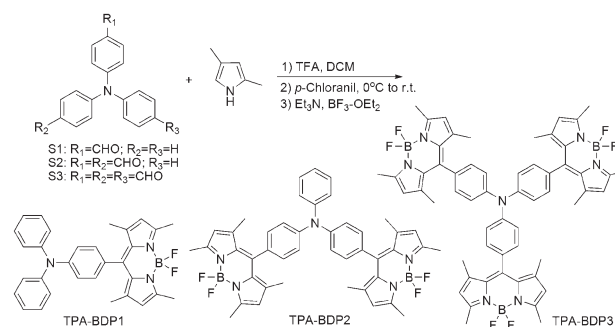
As a part of our interest in developing highly efficient laser materials,⁹ in this paper we have developed a series of triphenylamine cored starburst BODIPY dyes with a donor-acceptor (D-A) conjugated structure and further studied their

photophysical properties and laser actions in solutions (Scheme 1).

Formyl substituted triphenylamine S1–3 and BODIPY derivatives TPA-BDP1–3 were synthesized by following the literature procedure.^{10,11} All the intermediates and products were characterized by IR, NMR and mass spectroscopies with satisfactory results.

The absorption spectra of TPA-BDP1–3 change little in solvents with different polarities and exhibit a strong absorbance band at about 500 nm assigned to the S₀–S₁ transition.¹² The shoulder peak at about 470 nm is attributed to the S₀–S₁ vibrational transition. Finally, a second and higher energy absorption maximum peak is shown broadly at 350–400 nm assigned to the S₀–S₂ transition (see Fig. S2 in ESI†).¹³ The absorbance of the three dyes increases with the number of BODIPY units in solution, suggesting that the molar extinction coefficient has been increased by introducing more BODIPY units into the molecular structure. The fact that the absorption peaks of TPA-BDP1–3 show no particular trend as a function of solvent polarity suggests that the excited state of the dyes is immune to surrounding dipolar variations.

Although the absorption spectra of TPA-BDP1–3 are nearly solvent independent, the fluorescence spectra of the three dyes present a marked dependency on the nature of the solvent (Fig. 1). Besides the original emission of BODIPY core at 510 nm, which is strongly quenched, a new emission band appears at longer



Scheme 1 Synthesis of TPA-BDP1–3.

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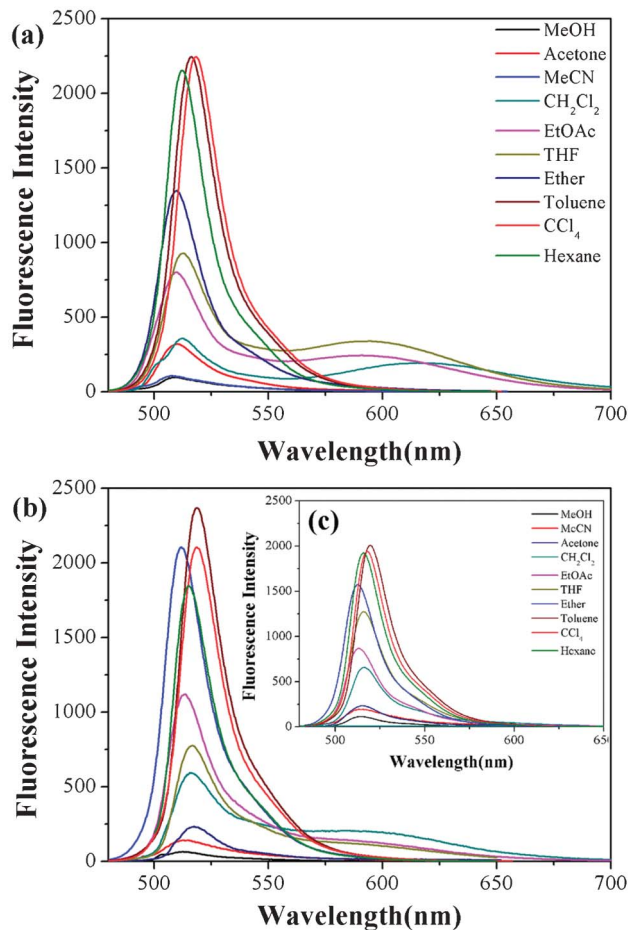


Fig. 1 Overlapped fluorescence spectra of (a) TPA-BDP1, (b) TPA-BDP2 and (c) TPA-BDP3 in different solvents.

wavelengths around 600 nm. The intensity and position of the new band depends on the solvent polarity. The new red band becomes less intense in polar and protic solvents. Moreover, the fluorescence quantum yield (Φ_F) varies between 0.02 and 0.95 and drops precipitously in most polar solvents. The Φ_F of TPA-BDP1-3 in medium and nonpolar solvents are considerably high, but the fluorescence yields for TPA-BDP1 and 2 decrease more than tenfold upon changing the solvent from ethyl acetate to dichloromethane (Table 1). For TPA-BDP3, this effect is slightly decreased upon increasing solvent polarity (about 6 fold). The fluorescence quenching in polar solvents and lower values of Φ_F are often attributed to the formation of a nonemissive charge-transfer state that entails some symmetry breaking since the cores of those dyes are identical.¹⁴

The fluorescence behavior of TPA-BDP1-3 under UV excitation (365 nm) also strongly varies upon different solvents (see Fig. S3 in ESI†). In nonpolar ones, the BODIPY fluorophore emits intense green light. However, the dyes TPA-BDP1 and TPA-BDP2 show two fluorescence bands when the solvent polarity increases, the whole spectrum moves to red region in relatively nonpolar solvents such as dichloromethane, with a concomitant decrease in emission intensity. The origin of the dual fluorescence bands may be

Table 1 Photophysical properties of TPA-BDP1-3 in various solvents

Solvent	$E_T(30)^a$	TPA-BDP1			TPA-BDP2			TPA-BDP3 ^b		
		λ_{abs}	λ_{em}	Φ_F	λ_{abs}	λ_{em}	Φ_F	λ_{abs}	λ_{em}	Φ_F
Hexane	31.0	501	512	69.1%	501	515	69.2%	501	515	60.9%
CCl ₄	32.4	503	518	95.1%	504	518	74.4%	504	521	64.3%
Toluene	33.9	503	516	93.1%	504	519	94.6%	504	519	95.4%
Ether	34.5	499	510	47.9%	499	512	70.1%	499	512	76.3%
THF	37.4	500	512	2.3%	500	518	15%	500	516	56.2%
EtOAc	38.1	499	510	2.6%	498	517	11%	498	513	40.7%
CH ₂ Cl ₂	40.7	501	513	0.17%	501	516	1%	501	517	6.6%
Acetone	42.2	498	512	0.14%	499	516	0.17%	498	515	0.73%
MeCN	45.6	497	511	0.05%	497	511	0.08%	497	513	0.2%
MeOH	55.4	498	512	0.02%	498	513	0.06%	498	513	0.2%

^a $E_T(30)$ is the solvent polarity parameter, high values corresponding to high solvent polarity. ^b Low solubility in hexane.

attributed to a different conformer for the excited state, or from a charge transfer (CT) state (sensitivity to the solvent polarity), causing a bathochromic shift in the emission color and also a dramatic decrease in emission efficiency.¹⁵

The dependence of laser action of the TPA-BDP1-3 on the dye concentration is analyzed in toluene by varying the optical density while keeping all the other experimental parameters constant (Fig. 2). As expected, the new dyes exhibited good ASE conversion efficiencies (the ratio between the laser and pump energies); the highest value (9%) is achieved by the 10 mM solution. Further increases in the dye concentration compromise the ASE efficiency. This trend can be related to the increase in reabsorption/re-emission processes with a deleterious effect in the laser action.¹⁶ A similar photophysical property and ASE behavior have also been observed for TPA-BDP2 and 3, with ASE efficiencies of 7.4% and

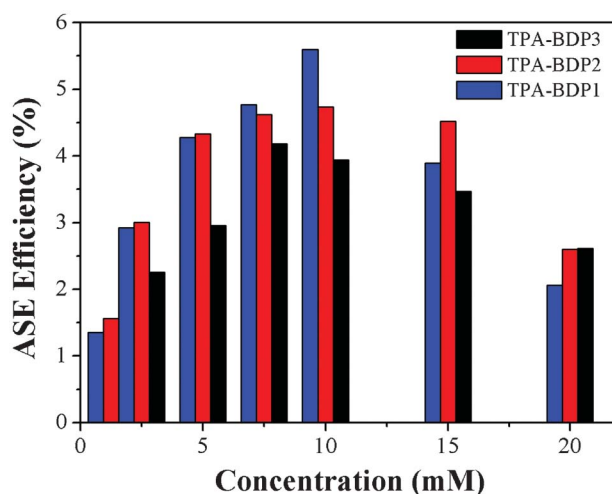


Fig. 2 ASE efficiency of the dyes TPA-BDP1 (blue), TPA-BDP2 (red) and TPA-BDP3 (black) as a function of the dye concentration in toluene solution.

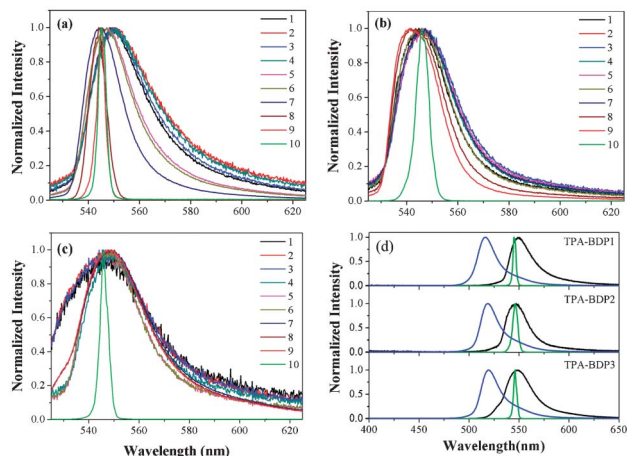


Fig. 3 Normalized emission spectra of the dyes (a) TPA-BDP1, (b) TPA-BDP2 and (c) TPA-BDP3 in toluene with increasing pump energy (1–10) and (d) fluorescence spectra (blue), spontaneous emission spectra (black) and ASE spectra (green).

7% (10 mM and 7.5 mM), respectively and center wavelength of 545 nm.

The effect of various solvents on the dye laser action is analyzed in solutions at the optimized dye concentrations with the highest ASE conversion efficiency of each derivative (see Table S4 in ESI†). The low solubility of TPA-BDP2 and 3 in hexane prevented us from producing highly concentrated solutions that were required for the laser experiments under the pumping conditions selected in the present work. The ASE efficiency of TPA-BDP1 in ether was 0.62%, much lower than that in toluene. But in solvents with medium and high polarity such as ethyl acetate, chloroform and ethanol, no ASE phenomenon can be observed with TPA-BDP1–3, no matter how strong the pump intensity is. This is probably due to its low fluorescence quantum yield.¹⁷

The transition of TPA-BDP1–3 from normal fluorescence, through threshold, to complete ASE can be clearly seen in Fig. 3d. By increasing the excitation power above the threshold, the intensity of the ASE spectra is greatly increased, while the full width at half maximum (FWHM) of the spectra is further narrowed. At the pump energy of ~ 1 mJ, the FWHM of the ASE radiation is 5 nm centering at 545 nm. All the three dyes follow the same behavior, as seen in Fig. 3a–3c.

TPA-BDP1 shows a slightly better ASE conversion efficiency (9%) than the other two dyes of TPA-BDP2 (7.4%) and 3 (7%). The comparative ASE slope efficiencies of the BODIPY dyes clearly demonstrate an enhanced laser performance of dye 1 compared with 2 and 3, irrespective of the pump energy. The threshold pump energy values of the dye 1 (0.2 mJ) and 2 (0.32 mJ) are smaller than that of 3 (0.4 mJ). However, a comparable efficiency of dye 2 and 3 are achieved at a similar concentration to dye 1 but with a higher optical density at the pump energy values (Fig. 4). This indicates that varied number of BODIPY units has an obvious influence in ASE: the introduction of BODIPY forms D–A structure, which can decrease threshold pump energy and increase ASE conversion efficiency. However, excessive number will lead to

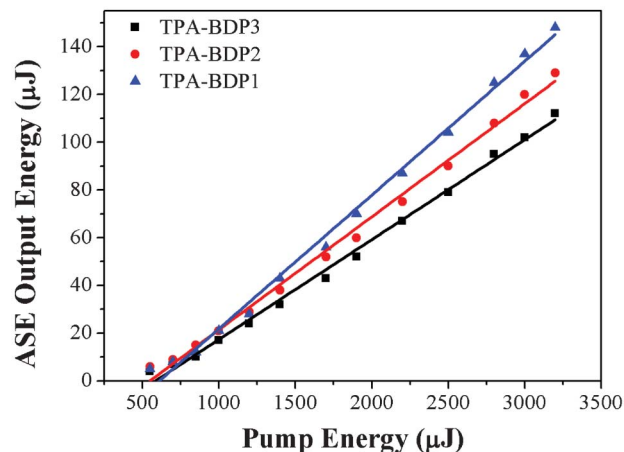


Fig. 4 ASE Laser output versus pump energy for the TPA-BDP1, 2 and 3 at the corresponding 10 mM in toluene determined by 355 nm irradiation with a Q-switched pulsed Nd:YAG laser.

opposite effect. This may be caused by electron-withdrawing effect of BODIPY and its enhanced symmetry.

In this work, we have synthesized a group of multi-branched TPA-BODIPY derivatives and studied their emission behavior in different solutions. Their emissions are tunable from green to red by changing solvent polarity. Under demanding transversal pumping conditions, the multi-branched BODIPYs exhibit enhanced laser actions (ASE) with good efficiency in toluene solution. The high ASE conversion efficiency of the BODIPYs could be related to their higher fluorescence quantum yields and to its lower nonradiative deactivation processes. Photophysical and lasing properties are correlated: the higher the fluorescence quantum yields are, the higher the ASE efficiencies can be measured. Considering the easy synthetic protocol and the wide variety of possible substituents, we are confident that this strategy could be successfully extended for the development of efficient green emitting materials and devices.

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