# Reaction of Amines with 8-MethylthioBODIPY: Dramatic Optical and Laser Response to Amine Substitution\*\*

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Abstract: A thorough study of the photophysical and laser properties of 8aminoboron dipyrromethene dyes was undertaken to determine the role of amine substitution and spatial disposition on the properties of the dyes. It was found that the fluorescent and laser response varied significantly. Although primary amines give rise to highly fluorescent products at the blue edge of the visible region, secondary amines yield nonfluorescent analogues in polar media. The crystal structures of two analogues are reported and described. Steric hindrance and the higher electron-releasing ability of the amine favor the formation of a quenching intramolecular charge-transfer state. Accordingly, boron dipyrromethene derivatives with primary amines exhibited laser emission with efficien-

**Keywords:** charge transfer • dyes/ pigments • fluorescence • heterocycles • laser chemistry cies of up to 44%. Besides, the more efficient derivative was also the most photostable, leading to a significant improvement in the lasing performance with regard to previously reported 8aminoboron dipyrromethene derivatives. An increase in the solvent polarity, and mainly the presence of tertiary cyclic amines, led to a dramatic decrease or even the loss of the laser action.

# Introduction

Boron dipyrromethene (BODIPY)-related reports continue to grow in the chemical literature mainly for two reasons: 1) synthetic chemists are developing new methods to tailor the properties of the BODIPY core (1) by introducing several functional groups around its periphery,<sup>[1]</sup> and 2) new

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- [\*\*] BODIPY=boron dipyrromethene.
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and exciting applications derive from these novel analogues.<sup>[2]</sup>

The most common way to build the BODIPY fragment into the substrate of interest is based upon the well-known Lindsey method.<sup>[3]</sup> This method relies upon the acid-catalyzed condensation of pyrrole, or its alkylated derivatives, with a formyl group previously attached to the molecule of interest. Oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and BF<sub>3</sub>•OEt<sub>2</sub> coordination yield the final product (Scheme 1).



Scheme 1. Typical Lindsey method to build the BODIPY core into a substrate molecule. TEA = triethylamine.

Despite its practicality, this method is not suitable for complex molecules that posses functional groups that are sensitive to acids, oxidation, or

Lewis acids. Our groups have demonstrated the usefulness of methylthioBODIPY (2)<sup>[4]</sup>. A host



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of different boronic acids react under neutral conditions with **2** in a palladium-catalyzed, copper(I)-mediated reaction (the Liebeskind–Srogl cross-coupling reaction<sup>[5]</sup>).<sup>[6]</sup> In addition to being an excellent partner in cross-coupling reactions, the methylthio group can be displaced in a  $S_NAr$ -like process by amines to give highly emitting dyes that fluoresce at the blue edge of the visible spectrum; a property unknown for BODIPY dyes until recently.<sup>[7]</sup> These new findings provide new opportunities for functionalization of complex molecules. Two new strategies are conceptually possible (Scheme 2). In one, a boronate ester may be introduced into



Scheme 2. Two new conceptually protocols for the fluorescent tagging of complex molecules.

the target molecule by using Hartwig chemistry.<sup>[8]</sup> The boronate ester would then be oxidatively hydrolyzed to yield the target, suitably functionalized molecule for fluorescent tagging. In the other, more straightforward, strategy, if the target molecule has an amine (either primary or secondary, see below), it would react directly with **2** to give the desired product. This approach is of particular importance owing to large number of natural (and non-natural) products containing one or more amino groups that are particularly suitable for labeling.

Being aware of the potential for the quick tagging of complex molecules through an amino group, we decided to extend the study of our previous reports to a larger number of amines with different substitution patterns (Scheme 3).

An additional and important motivation for this contribution lies in the fact that the development of highly efficient and stable blue-emitting dyes, to overcome some of the most important shortcomings of available chromophores, is of great technological importance for modern optical, analytical, electronic, and biological applications. In fact, many organic dyes with emission in the blue spectral region suffer from low efficiency and rapid chemical photobleaching,<sup>[9]</sup> which has impaired the practical implementation of blueemitting lasers based on dyes. On the other hand, certain BODIPY dyes are excellent laser dyes in the yellow–green (and even red, after proper structural modifications) spectral region to the point of currently being considered as the benchmark against which to compare the lasing performance of organic dyes in that spectral region. Thus, the



Scheme 3. Structures of the 8-aminoBODIPY dyes studied herein.

question arises as to whether it would be possible to extend the operation of these dyes towards the blue region of the spectrum, while retaining their excellent lasing performance.

In previous papers,<sup>[7]</sup> we demonstrated that, by attaching different amino groups at the 8-position of a fully unsubstituted BODIPY (1), blue-emitting BODIPY dyes are obtained, some of which exhibited very high fluorescence quantum yields and large Stokes shifts, leading to highly efficient laser emission with photostabilities much higher than those exhibited by current dyes with emission in the same spectral region. The present work hopes to provide a deeper insight into the role of amino substitution (electron-releasing ability and spatial disposition) on the photophysical and lasing properties of BODIPY dyes. To this end, we looked for the best structural modifications to enhance the photonic performance at the blue region or to make the fluorescence sensitive to a certain solvent property (i.e., polarity/acidity).

# **Results and Discussion**

# Synthesis

The synthesis of 8-aminoBODIPY dyes was carried out as previously reported.<sup>[7]</sup> Thus, derivative **2** was treated with a variety of amines to give the desired products (Table 1).

The synthesis was very efficient and straightforward, as well as being a spot-to-spot procedure, which facilitated the purification process. The reduced nucleophilicity of aniline was reflected in the lower yield and longer reaction time of the formation of  $\mathbf{8}$ .<sup>[4]</sup> Both primary and secondary amines reacted within a few minutes with high yields. Tertiary amines did not react.

#### Photophysical Properties in Solution

A number of BODIPY dyes were prepared with different amino groups at the 8-position with different substitution patterns (Scheme 3).

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[a] Yield of isolated product.

# Secondary 8-AminoBODIPY Derivatives (Compounds 3, 8, 9, and 10)

The presence of the electron-donating amine group at the *meso* position resulted in a significant blueshift of the spectral bands; this was more important for absorption (Figure 1). As a result, these derivatives are characterized by a large Stokes shift (up to  $2500-3000 \text{ cm}^{-1}$ ). These tendencies are in agreement with the results obtained for derivatives with monoalkylated amines.<sup>[7b]</sup> Such displacement of the spectral bands towards higher energies was rationalized



Figure 1. Absorption (A) and fluorescence (B) spectra of reference compound 1 and its derivatives with secondary amines (3, 8, 9 and 10) in *c*hexane. Inset: the 8-amino-induced resonant hemicyanine structure from the cyanine one.

in terms of an increase in the LUMO energy (Figure S1 in the Supporting Information), owing to electron-releasing ability of the amine, and the formation of a hemicyaninelike  $\pi$  system (Figure 1), owing to electronic coupling with the chromophoric core. Those BODIPY derivatives with the most electron-donating amines (methylaryl or methylbenzyl substituents) exhibit greater instability of the LUMO. Moreover, in spite of the presence of the aryl rings, the optimized geometries indicate that the amine is coplanar to the chromophore (Figure S2 in the Supporting Information), which enables the formation of the hemicyanine, the delocalized system of which is shorter than the normal cyclic cyanine in BODIPY. The presence of this mesomeric form was confirmed by previously reported NMR spectra.<sup>[7]</sup>

The electrochemical properties of a selected representative derivative of secondary amines (compound 3) were analyzed by cyclic voltammetry. Reference compound 1 showed an irreversible oxidation at 1.72 V and a quasi-reversible reduction at -0.71 V (Figure 2). Whereas the oxidation wave



Figure 2. Cyclic voltammograms (scan rate of  $0.1 \text{ Vs}^{-1}$  in the negative direction) of compound **1** (A, 1 mM) and compounds **3** and **5** (B; 0.5 mM, only the reduction potential) in acetonitrile with tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte.

remained almost unaltered in the presence of the amine, the reduction peak was shifted towards more negative values for compound 3 (-1.67 V). Thus, amination implies that the compound is more difficult to reduce because its electron-donating ability causes instability in the corresponding radical anion. Such behavior supports strong electronic coupling between both entities and the theoretical increase in the

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Table 2. Photophysical data of the parent BODIPY dye and the secondary 8-aminoBODIPY derivatives in *c*-hexane and methanol.<sup>[a]</sup>

	$\lambda_{ab}$ [nm]	$\varepsilon_{\rm max} (f) [10^4 \ {\rm m}^{-1} { m cm}^{-1}]$	$\lambda_{\rm fl}$ [nm]	$\phi$	τ [ns]	$k_{ m fl}  [10^8  { m s}^{-1}]$	$k_{\rm nr}  [10^8  { m s}^{-1}]$
c-hexane							
1	503.5	7.6 (0.38)	510.5	0.96	6.47	1.48	0.06
8	423.0	4.3 (0.38)	480.0	1.00	5.25	1.90	0.00
9	422.0	2.8 (0.25)	472.0	1.00	4.92	2.03	0.00
10	424.0	4.2 (0.35)	475.0	1.00	5.02	1.99	0.00
3	423.0	4.1 (0.35)	478.5	0.98	5.24	1.87	0.04
methanol							
1	497.0	5.8 (0.39)	507.0	0.87	7.33	1.18	0.18
8	403.5	4.1 (0.45)	461.0	0.16	$0.92^{[b]}$	1.74	9.13
9	403.0	2.3 (0.23)	453.5	0.09	$0.49^{[b]}$	1.84	18.6
10	404.5	3.1 (0.33)	460.5	0.05	$0.32^{[b]}$	_	_
3	403.0	3.4 (0.36)	464.0	0.15	0.94 <sup>[b]</sup>	1.60	9.04

[a] Photophysical data: absorption  $(\lambda_{ab})$  and fluorescence wavelength  $(\lambda_{fl})$ , molar absorption  $(\varepsilon_{max})$ , oscillator strength (f), fluorescence quantum yield  $(\phi)$ , lifetime  $(\tau)$ , and radiative  $(k_{fl})$  and nonradiative  $(k_{nr})$  deactivation rate constants. The full photophysical data in other solvents are listed in Table S1 in the Supporting Information. [b] Main component of the decay curve; the corresponding rate constants are calculated from this lifetime only when its contribution to the decay curve is higher than 98%.

LUMO energy suggested above as reasons for the enhancement in the energy gap.

The main photophysical data for the novel BODIPY derivatives with monofunctionalized amines are listed in Table 2. The results obtained exhibit the same tendencies as those previously reported for the derivative with the 8-methvlamino moiety.<sup>[7b]</sup> Indeed, the fluorescence capacity showed a marked dependence on the nature of the solvent. Thus, the new BODIPYs are highly fluorescent in apolar media, such as c-hexane (up to 100%), but in polar media both the fluorescence quantum yields (down to 10%) and lifetimes (around hundreds of picoseconds) drastically decline. In polar media, the fluorescence decay curves were analyzed as biexponentials, with the main decay (which is the one listed in Table 2) characterized by a short lifetime, and the minor decay (with a much lower contribution) by a long lifetime  $(\approx 4 \text{ ns})$ , which is reminiscent of that of BODIPY. Such evolution is clearer in compounds 9 and 10, which contain the more electron-donating amines (benzylamine and methyl benzylamine).

These results suggest the presence of an extra deactivation process, in particular, a nonfluorescent (no new bands are detected) intramolecular charge-transfer state (ICT). The population of such state depends markedly on the polarity of the environment; thus, the quenching of the fluorescence emission from the locally excited state (LE) by the ICT is more efficient in polar media. The presence of this ICT state is supported by augmentation of the fluorescence capacity in protic media (such as  $F_3$ -ethanol) with respect to other polar solvents (Table S1 in the Supporting Information), because the electron pair of the amino group is more fixed, owing to specific interaction with these protic solvents, leading to a decrease in the electron-donating capacity of the amine and the ICT probability.

Accordingly, the short lifetime of the biexponential decay curve in polar media is attributed to deactivation of the LE through ICT and the long reminiscent lifetime is attributed to the relaxed LE. Such assignment is supported by the dependence of the contribution of the lifetimes to the multiexponential adjustment on the wavelength selected to monitor the deactivation curves. Thus, at wavelengths longer than the maximum of the emission (detection wavelength placed in a region closer to the possible ICT emission), the contribution of the short lifetime to the decay curve increases considerably (data not shown). In the next section, the conducting temperature-dependence measurements provide further evidence of the operative ICT state.

#### Tertiary 8-AminoBODIPY Derivatives (Compounds 4-7)

As expected, the spectral bands of these derivatives are blueshifted relative to reference compound 1 (Figure 3). However, the extension of such a hypsochromic shift was smaller (with the exception of derivative 7) than that recorded previously for secondary amines. Indeed, the reduction potential in compound 5 decreases (less negative, -1.17 V; Figure 2) with regard to counterpart 3, with secon-



Figure 3. Absorption (A) and fluorescence (B) spectra of reference BODIPY 1 and its derivatives 8-substituted by tertiary cyclic amines (4, 5, 6, and 7) in *c*-hexane.

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dary amines (-1.67); this is indicative of a reduced energy gap. Although tertiary amines have a higher electron-donating character, they take part in the ring, which implies steric hindrance with adjacent positions of the core. Indeed, the optimized geometries (Figure S2 in the Supporting Information) indicate that cyclic amines are twisted around 26° and are out of the indacene plane (the secondary counterparts were around 10° and almost coplanar). As result of accommodation of the cyclic amine, the planarity of the chromophore is distorted (up to 20° along the transverse axis). Therefore, the coplanar arrangement between the amine and BODIPY is hindered, which reduces the probability of the formation of the hemicyanine, and consequently, lowering of the magnitude of the spectral blueshift (Figure 3). Further evidence is provided by compound 7, which contains the smallest cycle (pyrrolidine). In this case, steric hindrance should be lower and enable a coplanar disposition of the amine, leading to a greater contribution from the hemicyanine form. Compound 7 shows the largest blueshift of all compounds studied herein.

Table 3 collects the main photophysical data of the tertiary 8-aminoBODIPYs in *c*-hexane and methanol. A com-

Table 3. Photophysical data of the parent BODIPY dye and its tertiary 8-amino derivatives in the *meso* position in c-hexane and methanol. Full photophysical data are reported in Table S2 in the Supporting Information.

	$\lambda_{ab} [nm]$	$\varepsilon_{\rm max}~(f)~[10^4~{\rm m}^{-1}{\rm cm}^{-1}]$	$\lambda_{\rm fl}  [\rm nm]$	$\phi$	τ [ns]	$k_{ m fl} \ [10^8 \ { m s}^{-1}]$	$k_{\rm nr}  [10^8  { m s}^{-1}]$
c-hexane							
1	503.5	7.6 (0.38)	510.5	0.96	6.47	1.48	0.06
7	409.5	2.9 (0.26)	472.5	0.05	$0.04^{[a]}$	12.5	237
6	440.0	2.9 (0.44)	498.0	0.49	1.93	2.54	2.64
5	439.5	4.2 (0.36)	496.0	0.27	$1.94^{[a]}$	1.39	3.76
4	435.0	3.9 (0.41)	492.0	0.07	1.23 <sup>[a]</sup>	0.56	7.57
methanol							
1	497.0	5.8 (0.39)	507.0	0.87	7.33	1.18	0.18
7	391.5	2.4 (0.26)	454.5	0.004	-	1.90	474
6	419.5	2.4 (0.41)	445.5	0.006	-	-	-
5	419.5	2.6 (0.38)	452.0	0.006	-	-	-
4	413.0	3.1 (0.43)	437.5	0.001	-	-	-

[a] Main component of the decay curve; the corresponding rate constants are calculated from this lifetime only when its contribution to the decay curve is higher than 98%. The fluorescence lifetimes of compounds **4**–**7** in methanol were below the temporal resolution of our picosecond photon counter (around 30–40 ps).

parison of the results in Tables 2 and 3 shows clearly an important decrease in both the fluorescence capacity (which is negligible in polar media) and the lifetimes in the derivatives with cyclic amines, even in apolar solvents, such as *c*-hexane. This decrease is particularly noticeable if there are no other heteroatoms in the cyclic amines. It is likely that the presence of heteroatoms (O and N) in the ring (**5** and **6**) removes electron density from the amine, and hence, decreases the probability of the formation of the ICT state. Steric hindrance (discussed above) could not only decrease the probability of the formation of the hemicyanine form, but also cause the electron-donating amino group to be positioned such that it is more orthogonal to the BODIPY chromophore to alleviate the steric hindrance; thus favoring the formation of an ICT state (probably a twisted intramolecu-

lar charge-transfer state (TICT)). Moreover, theoretical calculations confirm twisting of the amine and reveal a loss of planarity in the chomophore, owing to accommodation of the bulky cyclic amine. Such geometrical distortion is usually related to an enhancement of the internal conversion processes. Consequently, even in apolar media, in which the ICT state is less favored, derivatives **5** and **6** have a lower fluorescence capacity than the secondary 8-aminoBODIPY dyes. In polar media, the fluorescence emission was almost negligible for all disubstituted cyclic amines. The dynamics of the ICT process in these solvents should be very fast (tens of picoseconds, under the temporal resolution of the photon counter), indicating that such a processes is highly favored.<sup>[10]</sup>

Some authors have reported the influence of the ring size of amine-containing cycles in the photophysical properties of chromophores (i.e., rosamine and naphthalimides).<sup>[11]</sup> They concluded that charge transfer was more feasible in the bigger cycles; N-atom inversion is hindered in the smaller rings. Surprisingly, a new, weak fluorescence band appeared at around 600 nm, after the emission from the LE state, only for compound **7** (which has the smallest ring),

when dissolved in apolar *c*-hexane (Figure 4). This band could be attributed to emission from the ICT state. Furthermore, some authors have claimed that the ICT state can eventually evolve into an exciplex-like state upon coulombic interactions (harpooning effect).<sup>[12]</sup> Such an entity causes a weak and redshifted emission and has even been reported for some BODIPYs if ICT takes part.<sup>[13]</sup>

Such a new band was no longer detected upon changing the solvent to a more polar one, although the decrease in the fluorescence emission was also very clear and drastic (Figure 4). Thus, further stabili-



Figure 4. Normalized fluorescence spectra of dilute solutions of 7 in (2  $\mu$ M) of *c*-hexane (a) and methanol (b).

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zation of the ICT (by more electron-donating amines or more polar solvents) suppresses its fluorescence emission. This apparent mismatch can be rationalized when considering that the stabilization of the ICT does not imply a stronger emission, rather the opposite, because the ICT state is energetically close to the ground state. The closer the proximity of the electronic state, the highest the probability of internal conversion, in terms of the energy gap law. Moreover, heating a solution of compound 7 in c-hexane led to a concomitant decrease in the ICT fluorescence band, because vibrational coupling is enhanced (Figure S3 in the Supporting Information). Furthermore, ICT stabilization by solvent polarization could give rise to a nonfluorescent charge-separation (CS) state that hampers detection of the ICT fluorescence. Similar trends were claimed for a BODIPY derivative with 8-aniline forced to be perpendicular through steric hindrance.<sup>[14]</sup>

Summing up, the feasibility of ICT formation should control not only the fluorescence behavior, but also laser performance. Therefore, we conducted temperature-dependence fluorescence measurements to unambiguously assign fluorescence quenching to ICT. The cooling of compound **5** down to 77 K led to a large increase in the fluorescence signal (Figure 5). Usually, a temperature decrease enhances fluorescence efficiency because the vibrational motion is



Figure 5. Fluorescence spectra of compound  $\mathbf{5}$  in ethanol from 290 to 77 K.

hindered, and hence, internal conversion is reduced. However, in the present case, the huge improvement of the fluorescence emission after freezing the sample indicates that the quenching process present at room temperature is no longer taking place. Similar results were also obtained for compound **3**, which contains a secondary amine (data not shown). Considering that ICT is an activated process, at low enough temperatures its population is avoided; thus confirming the key role of such a process in the photophysical properties of mono- and disubstituted cyclic 8-aminoBODI-PYs.

Finally, a careful comparison of the optical properties of the 8-aminoBODIPYs prepared so far (primary, secondary, and tertiary amines) shows that there is an evident trend in the fluorescent response of the product, according to the nature of the amino groups. Indeed, if the dyes are irradiated at  $\lambda = 366$  nm (Figure 6), primary amines and ammonia yield highly fluorescent dyes, whereas secondary and aromatic amines give nonemissive products (ICT stabilization), thereby providing a basis for their utilization as an amine chemodosimeter.

#### Solid-State Emission

Solid-state quantum yields ( $\Phi_{F,S}$ ) for compounds **3–6** and **9** were measured by means of a calibrated integrating sphere. Relatively high  $\Phi_{F,S}$  values were deduced from measurements of the secondary aminoBODIPYs. For example, the  $\Phi_{F,S}$  values of **9** and **3** were 33.8 and 12.7%, respectively. Meanwhile, tertiary aminoBODIPY derivatives **4** and **6** have low  $\Phi_{F,S}$  value of 0.08 and 2.2%, respectively (Scheme 4).



Scheme 4. Quantum yield of selected aminoBODIPYs in the solid state.

#### X-ray Study

Single-crystal structures of secondary aminoBODIPY 9 and tertiary aminoBODIPY 5 were obtained to gain detailed information about the solid-state molecular structures (Figure 7). The BODIPY core is almost coplanar and the nitrogen atom substituted on the 8-position of BODIPY lies on the same plane in both 9 and 5, whereas the phenyl ring in compound 9 is twisted out of the plane. The packing modes of these two compounds are different. In the singlecrystal structure of 9 (Figure 7C), the plane-to-plane distance of two closest BODIPY moieties is 3.700 Å and the two BODIPY moieties are staggered. A distance of 2.286 Å was observed between the amino proton and one fluorine atom; this indicates hydrogen-bonding interactions. Such hydrogen bonding connects molecules through the parallel direction of the BODIPY plane. Different from 9, the singlecrystal structure of 5 adopts a head-to-tail packing mode (Figure 7D). The plane-to-plane distance of the closest BODIPY moieties is 3.776 Å and the BODIPY cores were

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Figure 6. Fluorescent response of the 8-aminoBODIPY dyes to the nature of the amino group (solutions in ethyl acetate, under excitation at  $\lambda = 366$  nm).

highly overlapped along the perpendicular axis. A distance of 2.303 Å was observed between the oxygen atom on the morpholine ring and the proton on the 3-position of BODIPY, indicating intramolecular interactions along the parallel axis of the BODIPY plane. Taking these intermolecular interactions and steric hindrance into account, molecules of **5** packed in a closer manner in the crystal state than that of **9**, which may quench the solid-state emission. Hence, it has a smaller  $\Phi_{\rm FS}$  value compared with **9**.

#### Lasing Properties

The lasing properties of representative examples of the new BODIPY derivatives were studied under pumping at  $\lambda = 355$  nm, which is the usual pump wavelength for dyes emitting in the blue spectral region. Under our experimental conditions (transversal excitation and strong focusing of the incoming pump radiation, see the Experimental Section), the concentration of the dyes in different solvents should be in the millimolar range to ensure total absorption of the pump radiation within the first millimeter at most of the solution, to obtain an emitted beam with near-circular cross-section, and to optimize the lasing efficiency (ratio between the energy of the dye laser output and the pump energy incident on the sample surface). Although in all cases the highest fluorescence quantum yields of the new derivatives

were obtained in *c*-hexane, none of the dyes could be dissolved in this solvent at the concentrations required to obtain laser emission. The BODIPY derivatives with primary amines did exhibit laser emission in ethyl acetate, acetone,  $F_3$ -ethanol, and ethanol (Figure 8), with efficiencies correlated with their photophysical properties in dilute solutions (Table S1 in the Supporting Information): the higher the fluorescence quantum yield and the lower the nonradiative rate constant, the higher the lasing efficiency.

None of the derivatives with secondary amines exhibited laser action, even at the highest possible concentrations, as expected on account of their very low quantum yields and high nonradiative rate constants (Table S2 in the Supporting Information). Therefore, such correlation indicates that the lasing efficiency is controlled by the influence of the ICT state on the photophysics of the dye.

As shown in Figure 8, the highest lasing efficiencies were obtained in ethyl acetate, which is the more apolar solvent after c-hexane among the solvents used in this work, that is, in media where the probability of fluorescence quenching through ICT processes is reduced. The dependence of the laser action of BODIPY derivatives **8**, **9**, **10** and **3** on the corresponding dye concentrations was analyzed in ethyl acetate, which was the solvent in which the dyes exhibited the highest fluorescence quantum yield, together with the lowest nonradiative rate constant. It was found that, in all

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Figure 7. Single-crystal structures and crystal packing modes of **9** (A and C) and **5** (B and D).



Figure 8. Lasing efficiencies of the new BODIPYs derivatives (3: grey, 8: white, 9: striped, and 10: black) in different solvents under  $\lambda = 355$  nm pumping.

cases, the optimum concentration was  $4 \times 10^{-3}$  M (Figure 9), with lasing efficiencies ranging from 14 (10) up to 44% (8).

An important parameter for any practical application of the dye lasers is their lasing photostability under repeated pumping. We studied the lasing photostability of the new BODIPY derivatives in ethanol because, in this solvent, the nonradiative constants of the dyes studied exhibit significant variations that correlate well with the photostability. Figure 10 depicts the actual evolution of the laser-induced



Figure 9. Dependence of the lasing efficiency of the new BODIPY derivatives (3: grey, 8: white, 9: striped, and 10: black) on their concentration in ethyl acetate under 355 nm pumping.



Figure 10. Normalized laser-induced fluorescence emission as a function of the number of pump pulses at a 5 Hz repetition rate for solutions of dyes 8 ( $\blacksquare$ ), 9 ( $\bigcirc$ ) and 10 ( $\blacktriangle$ ) in ethyl acetate under transversal pumping at  $\lambda = 355$  nm.

fluorescence emission of dyes 8, 9, and 10 with the number of pump pulses at a 5 Hz repetition rate. There is an excellent correlation between the values of the nonradiative constants and the photostability: the lower the nonradiative rate constant, the higher the photostability. Figure 10 does not show the photostability of dye 3 because it is almost identical to that of 8, which is in agreement with both dyes having the same value of nonradiative decay constant.

Dye **8** leads to improved efficiency and photostability over that previously obtained with 8-aminoBODIPY derivatives,<sup>[7b]</sup> which in turn leads to significantly improved lasing performance compared with that of commercial coumarin dyes pumped under identical experimental conditions.<sup>[7a,b]</sup> This fact highlights the potential of these dyes to act as laser emitters in the blue spectral region.

### Conclusion

Eight new 8-aminoBODIPY dyes were efficiently prepared and an in-depth study was performed to understand the role of amine spatial disposition on the photophysical and lasing properties of BODIPY. Crystal structures of derivatives **9** and **5** were obtained. In both cases, the BODIPY core remained nearly planar, although the packing mode of **9** and **5** 

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differed from each other. In 9 the BODIPY moieties were staggered, whereas in 5 they adopted a head-to-tail arrangement.

These dyes were characterized by their emission at the blue edge of the visible region, owing to their hemicyaninelike delocalized  $\pi$  system. Whereas the attachment of aryl rings to the amine gave rise to improved fluorescence and lasing efficiencies in apolar media, the inclusion of the amine in a cycle resulted in a drastic decline in the fluorescence efficiency and the derivatives no longer lased. In the former monosubstituted amines, high fluorescence quantum yields (approaching the 100%) were achieved in apolar media and superseded commercial blue-emitting dyes in terms of their lasing performance. However, in polar media, a quenching ICT state was populated, which reduced their lasing ability. The quenching effect was even more apparent after attaching cyclic amines to the core. The induced steric hindrance twisted the amine and hampered electronic coupling with the chromophore. Consequently, the statistical weight of the hemicyanine resonant structure was reduced, leading to a lower blueshift of the spectral bands and fluorescence quenching by the ICT (reinforced by the higher electron donor ability of the tertiary amine) was more marked and caused the completely loss of the fluorescence signal in polar media. Therefore, the stabilization of the ICT process, which in turns depended on the substitution pattern of the amino group and the environment, determined the laser performance of these BODIPY derivatives working at the blue part of the visible spectrum.

# **Experimental Section**

#### Materials

Solvents for laser and photophysical studies were of spectroscopic grade (Merck, Aldrich, or Sigma) and were used without purification; those used in synthetic work were purified by standard methods. Other reagents were from commercial sources and used as received. BODIPY **8** was prepared according to a literature procedure.<sup>[4]</sup>

#### Photophysical, Electrochemical, and Quantum Mechanical Properties

The photophysical properties were recorded in dilute solutions (around  $2 \times 10^{-6}$  M), which were prepared by adding the corresponding solvent to the residue from an adequate amount of a concentrated stock solution in acetone after vacuum evaporation of this solvent. UV/Vis absorption and fluorescence spectra were recorded on a Varian model CARY 4E spectrophotometer and a SPEX Fluorolog 3-22 spectrofluorimeter, respectively. Fluorescence quantum yield ( $\Phi$ ) was obtained by using a solution of coumarin 1 in ethanol as a reference ( $\Phi^r = 0.75$ ). Temperature-dependence measurements were performed by using a liquid-hydrogen-cooled cryostat (Oxford) and an external electronic temperature controller device for heating. Radiative decay curves were obtained with the timecorrelated single-photon-counting technique (Edinburgh Instruments, model FL920, with picosecond time resolution). Fluorescence emission was monitored at the maximum emission wavelength after excitation at  $\lambda = 370$  nm by means of a diode laser (PicoQuant, model LDH370) with 150 ps FWHM pulses. The fluorescence lifetime ( $\tau$ ) was obtained after the deconvolution of the instrumental response signal from the recorded decay curves by means of an iterative method. The goodness of the exponential fit was controlled by statistical parameters (chi-square, Durbin-Watson and the analysis of the residuals). The radiative  $(k_{f})$  and nonradiative  $(k_{nr})$  rate constants were calculated from the fluorescence quantum yield and lifetime:  $k_{\rm fl} = \varphi/\tau$  and  $k_{\rm nr} = (1-\varphi)/\tau$ . The solid-state fluorescence quantum yields were determined on an integrating sphere, according to the method described by de Mello et al.<sup>[15]</sup> A  $\lambda = 325$  nm continuous-wave (CW) light from a He–Cd laser was used for optical pumping. The studied sample was placed inside the integrating sphere, in which light emission was redistributed isotropically over the interior surface of the sphere. An optical fiber collected light from the sphere and directed it to an Ocean Optics (Ocean Optics, Inc.) USB2000 miniature fiber optics spectrometer. The number of emitted photons was obtained by integrating the measured photoluminescence (PL) signal over the emission wavelengths. The response of the fiber and spectrometer detector system was normalized by using a calibrated light source.

Single-crystal X-ray diffraction intensity data were collected at 100 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated  $Mo_{K\alpha}$  radiation. Processing of the intensity data was performed by using the SAINT and SADABS routines and the structures and refinements were achieved by using the SHELTL suite of X-ray programs (version 6.10).

CCDC 953705 (9) and CCDC 953706 (9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Electrochemical experiments (Metrohm Autolab) were performed by using a three-electrode setup with a platinum disk (diameter 3 mm) or layer (length 7,1 mm×width 8 mm) working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. A 0.1 m solution of TBAPF<sub>6</sub> in dry acetonitrile was used as the electrolyte solvent in which the compounds were dissolved to achieve a concentration of 0.5–1 mm. All redox potentials were reported versus ferrocene as an internal standard. The solutions were purged with argon and all measurements were performed under an inert atmosphere.

Ground- and excited-state geometries were optimized at the B3LYP and CIS theory level respectively, by using the double valence basis set (6-31g), as implemented in Gaussian 09. The geometries were considered as energy minima when the corresponding frequency analysis did not give any negative values.

#### Laser Experiments

Liquid solutions of dyes were contained in 1 cm optical-path quartz cells carefully sealed to avoid solvent evaporation during experiments. The solutions of the newly synthesized dyes were transversely pumped at  $\lambda$ = 355 nm, with 5 mJ/pulse, 8 ns full-width at half maximum (FWHM) pulses from the third-harmonic of Q-switched Nd:YAG laser (Spectron SL282G) and at a repetition rate of up to 5 Hz. The exciting pulses were line-focused onto the cell, providing pump fluences on the active medium of 110 mJ cm<sup>-2</sup>. The oscillation cavity (2 cm length) consisted of a 90% reflectivity aluminum mirror, with the lateral face of the cell as the output coupler.

The photostability of the dyes was evaluated by irradiating a solution (10 µL) in ethyl acetate under lasing conditions. The solutions were contained in a cylindrical Pyrex tube (1 cm height, 1 mm internal diameter) carefully sealed to avoid solvent evaporation during the experiments. Although the low optical quality of the capillary tube prevented laser emission from the dyes, information about photostabilities could be obtained by monitoring the decrease in laser-induced fluorescence intensity, excited transversally to the capillary tube, as a function of the number of pump pulses at a 5 Hz repetition rate. The fluorescence emission was monitored perpendicular to the exciting beam, collected by an optical fiber, and imaged onto the input slit of a monochromator (Acton Research corporation) and detected with a charge-coupled device (CCD) (SpectruMM:GS128B). The fluorescence emission was recorded by feeding the signal to the boxcar (Stanford Research, model 250) to be integrated before being digitized and processed by a computer. Each experiment was repeated at least three times. The estimated error in energy and photostability measurements was 10%.

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CHEMISTRY

# **AN ASIAN JOURNAL**

*Typical Procedure for the Aromatic Nucleophilic Substitution of 8methylthioBODIPY* **2** *with Primary and Secondary Amines* 

All reactions were initiated with 2 (20.0 mg, 0.08 mmol) as the limiting reagent and the amine (0.13 mmol). In a 5 mL flask, compound 2 was dissolved in acetonitrile (2 mL) and the amine was added in one portion and allowed to stir at 25 °C. The crude reaction mixture was dried in vacuo, the dry solid was transferred to a vial in which the solid was dissolved in dichloromethane and petroleum ether was added to carefully form two phases to promote crystallization of the solids.

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# **FULL PAPER**



**Blue glow**: 8-Monosubstituted aminoboron dipyrromethenes provide efficient blue fluorescence (even in the solid state) and laser emission, whereas those compounds with cyclic amines lead to poor fluorescence and negligible laser emission (see picture). In the latter case, the steric hindrance avoids the formation of the hemicyanine and promotes a quenching charge-transfer process.

# **Dyes/Pigments**

Ixone Esnal, Arlette Urías-Benavides, C. F. Azael Gómez-Durán, Carlos A. Osorio-Martínez, Inmaculada García-Moreno, Angel Costela, Jorge Bañuelos,\* Nerea Epelde, Iñigo López Arbeloa, Rongrong Hu, Ben Zhong Tang, Eduardo Peña-Cabrera\* \_\_\_

Reaction of Amines with 8-MethylthioBODIPY: Dramatic Optical and Laser Response to Amine Substitution