

# Red-edge-wavelength finely-tunable laser action from new BODIPY dyes†

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New BODIPY dyes with two 4-formylphenyl, 4-(2,2-dimethoxycarbonylvinyl)phenyl and 4-(2,2-dicyanovinyl)phenyl groups at the 3- and 5-positions have been successfully designed and synthesized *via* palladium-catalyzed coupling reaction or Knoevenagel-type condensations. Structural modification of the BODIPY core *via* conjugation-extending residues significantly affects the spectroscopy and photophysical properties of the BODIPY fluorophore. These substituents cause the largest bathochromic shift in both absorption and emission spectra, which are shifted toward the red compared to its 4-phenylsubstituted analogue. Additionally, the fluorescence quantum yields and the Stokes shifts are also significantly higher than the corresponding phenyl-substituted dye. New BODIPY dyes have a high laser photostability, superior to that of commercial dyes with laser emission in the same spectral region, such as Perylene Red and Rhodamine 640. The substitution introduced in these derivatives allows to obtain tunable laser emission with a bandwidth of 0.15 cm<sup>-1</sup> and a tuning range of up to 50 nm. So with these three dyes it is possible to cover the spectral range 590–680 nm in a continuous way and with stable laser emission and small linewidth.

## 1. Introduction

The development of new fluorescent BODIPY dyes has become a booming area of research due to the potential applications of these dyes, for their use as sensors in biology and in clinical diagnosis, photosensitizers for photodynamic therapy, laser generators, waveguides, manufacture of light emitting diodes (OLED), photovoltaic cells and electroluminescent devices including also the usual conventional applications of organic dyes.<sup>1</sup> All these and other emerging applications are conditioned by the emission wavelength, quantum yield and stability of the dyes under the working conditions required for each specific application.

In particular, BODIPYs are one of the most used laser dyes family as active media of tunable dye lasers in the green–yellow visible region of the electromagnetic spectrum due to their high lasing efficiency and photostability, high fluorescence quantum yield, low rate constant of intersystem crossing and large molar absorption coefficient.<sup>1a,c</sup>

The photophysical properties of these dyes can be modulated to some extent incorporating the adequate substitution in the molecular structure of the parent BODIPY chromophore. Thus, the design of long-wavelength BODIPY dyes has especially attracted attention in the last years. Red-shifts of the optical spectra can be realized by substitution with aryl, vinyl, styryl, ethynylphenyl, fused aryl groups at the core or inserting heteroatoms at different positions of the chromophore (aza-BODIPY).<sup>1a,c,2</sup>

Recently, the synthesis of 3,5-dichloro-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-s-indacene (**1**) has been described.<sup>3</sup> In the present work, we have carried out the synthesis, photophysical and lasing characterization of new 8-tolyl-substituted boradiazaindacenes (**2–4**) with absorption and emission spectra shifted towards longer wavelengths by extending the conjugation of the BODIPY core at the 3,5-positions (see Fig. 1).

The photophysical properties of these compounds have been compared with other 8-tolyl-substituted BODIPYs, and in addition, the behaviour of commercial dyes with laser emission in the same spectral region, such as Rhodamine

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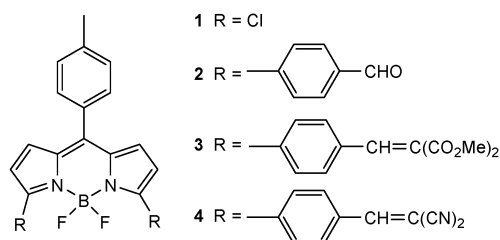


Fig. 1 Chemical structures of the BODIPY dyes 1–4.

640 and Perylene Red was analyzed under the same pumping conditions. The present results suggest that the inclusion of *para* substituted phenyl groups at 3 and 5 positions of the 8-tolyl-BODIPY gives rise to an extended red emission, characterized by higher fluorescence capacity and a larger Stokes shift than other red-sensitive dyes. All these factors contribute to the laser behaviour of these new red emitting BODIPY, which lase with good efficiency and higher photostability than other commercial dyes lasing in the same spectral region.

## 2. Experimental

### 2.1 Materials

Starting materials and reagents used in the preparation of BODIPY dyes **1–4** are commercially available unless the synthesis is described. The solvents were dried and distilled, before use.

The commercial laser dye Rhodamine 640 (laser grade, Exciton) was used as received with a purity >99% (checked by spectroscopic and chromatographic methods). Perylene Red (BASF Lumogen Red 305) was first used as received with a purity of only 90% (checked by spectroscopic and chromatographic methods). Then, the dye purity was improved up to 99% through flash column chromatography based on silica with hexane–ethyl acetate 95/5 v/v proportion as eluent, to remove the *N*-methyl-2-pyrrolidone, identified by <sup>1</sup>H-NMR as the principal impurity. Solvents for laser studies were of spectroscopic grade (Merck, Aldrich or Sigma) and were used without purification.

### 2.2 Synthesis of BODIPY 1-4

BODIPYs **2–4** were synthesized from 3,5-dichloro-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (**1**).<sup>3</sup> Compound **1** was synthesized by a method previously described.<sup>3</sup> Their spectroscopic data are in agreement with those previously described (<sup>1</sup>H NMR spectra is shown in the ESI, page 5).<sup>†</sup>

### 2.3 Characterization of the new dyes

Spectral data of the known compounds were in accordance with the literature data. Flash column chromatography was performed using silica gel Merck 60 (230–400 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance-DPX-300 spectrometer (300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C) and a Bruker Avance-AV-500 spectrometer (500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C). All spectra were recorded in CDCl<sub>3</sub>. <sup>1</sup>H chemical shifts are reported in ppm relative to tetramethylsilane ( $\delta = 0.00$  ppm), using the residual solvent signal as internal reference. <sup>13</sup>C chemical shifts are reported in ppm with CDCl<sub>3</sub> ( $\delta = 77.67$  ppm) as the internal standard. Chemical shift multiplicities are reported as *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet and *m* = multiplet. IR spectra (in cm<sup>-1</sup>) were recorded in a Bruker Tensor-27-FTIR spectrophotometer. Melting points were determined in open capillaries and are uncorrected. Mass spectra were registered by electron impact at 70 eV in a VG12-250 spectrometer. High resolution mass spectra were determined by electro spray ionization in the positive mode (ESI<sup>+</sup>) in a Accurate-Mass Q-TOF LC/MS 6520 (Agilent Technologies). Combustion analyses (C, H, N)

were obtained on a LECO CHNS-932 apparatus at the Universidad Complutense de Madrid analysis services and were within 0.4% of the theoretical values.

### 2.4 Photophysical properties

The photophysical properties were registered in  $3 \times 10^{-6}$  M solutions in different solvents, prepared by adding the corresponding solvent to the residue from the adequate amount of a *ca.*  $10^{-3}$  M stock solution in acetone, after vacuum evaporation of the solvent. UV-Vis absorption and fluorescence spectra were recorded on a Cary 4E spectrophotometer and on a SPEX Fluorolog 3–22 spectrofluorimeter, respectively. Fluorescence quantum yields ( $\phi$ ) were evaluated from corrected spectra, using a *ca.*  $10^{-6}$  M solution of the commercial PM650 dye in ethanol ( $\phi = 0.10$ )<sup>4</sup> as reference. Radiative decay curves were registered by the time correlated single-photon counting technique (Edinburgh Instruments, model FL920). Fluorescence emission was monitored at the maximum emission wavelength after excitation at 470 nm by means of a diode laser (PicoQuant, model LDH470) 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 rate constant of radiative ( $k_{\text{r}}$ ) and non-radiative ( $k_{\text{nr}}$ ) deactivations were calculated by means of:  $k_{\text{r}} = \phi/\tau$  and  $k_{\text{nr}} = (1-\phi)/\tau$ .

The ground state geometry was optimized using the B3LYP method and the double valence basis set (6-31G) implemented in the Gaussian 03 software. The energy minimization process was performed without any geometrical restrictions, and was considered to be adequately concluded when the analysis of the vibrational frequencies did not give any negative frequency.

### 2.5 Laser experiments

Liquid solutions of dyes were contained in 1 cm optical-path quartz cells that were carefully sealed to avoid solvent evaporation during experiments. The liquid cells of the newly synthesized red-edge dyes were transversely pumped at 532 nm, with 5 mJ pulse<sup>-1</sup>, 6 ns FWHM pulses from a frequency-doubled Q-switched Nd:YAG laser (Monocrom OPL-10) at a repetition rate of up to 10 Hz, and at 568 nm, with 5 mJ, 10 ns FWHM pulses from a Nd-YAG-pumped dye laser (Spectron SL800 with an ethyl acetate solution of PM567). The exciting pulses were line-focused onto the lateral flat surface of the solid samples, providing pump fluences on the active medium of 180 mJ cm<sup>-2</sup>. The oscillation cavity (2 cm length) consisted of a 90% reflectivity aluminium mirror, with the end face of the sample as output coupler.

For pumping at 532 nm, the concentrations of new BODIPY **2**, **3** and **4** were  $9 \times 10^{-4}$  M,  $8 \times 10^{-4}$  M and  $3 \times 10^{-3}$  M, respectively, leading to solutions with an optical density of *ca.* 16. For pumping at 568 nm, the concentrations of **2**, **3** and **4** dyes were  $9 \times 10^{-4}$  M,  $4 \times 10^{-4}$  M and  $2 \times 10^{-3}$  M, respectively, matching the optical density selected for irradiation at 532 nm.

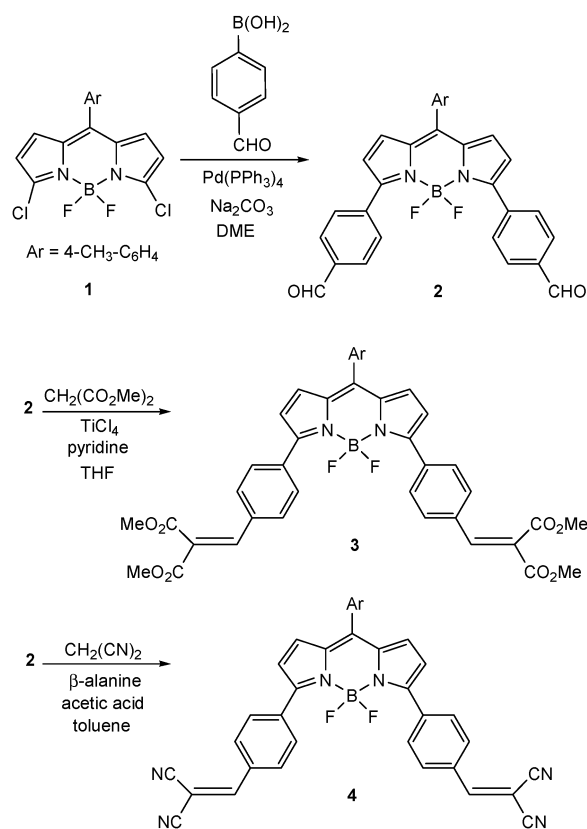
The photostability of each dye was evaluated by irradiating under lasing conditions at 532 nm 10  $\mu$ L of a solution in ethyl acetate. The solutions were contained in a cylindrical Pyrex tube (1-cm height, 1-mm internal diameter) carefully sealed to avoid solvent evaporation during the experiments. Monitoring of sample photolysis was carried out by recording the laser-induced fluorescence emission, excited transversally to the capillary with the same pump pulses from the Nd:YAG laser used for producing dye laser emission, as a function of the pump pulses at 10 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 experience was repeated at least three times. The estimated error of the energy measurements was 10% and the experimental error in the photostability measurements was estimated to be on the order of 7%. Details of the experimental setup can be found elsewhere.<sup>5,6</sup>

Narrow-linewidth laser emission and tuning ranges of dye solutions were obtained by placing the samples in a homemade Shoshan-type oscillator<sup>7</sup> consisting of full-reflecting aluminium back and tuning mirrors, and a 2400 lines  $\text{mm}^{-1}$  holographic grating in grazing incidence, with outcoupling *via* the grating zero order. Wavelength tuning was accomplished by rotation of the tuning mirror. Tuning mirror and grating (both from Optometrics) were 5 cm wide and the angle of incidence on the grating was 88.5°. Laser linewidth was measured with a Fabry-Perot etalon (IC Optical Systems) with a free spectral range of 15.9 GHz.

### 3. Results and discussion

#### 3.1 Synthesis

BODIPY fluorophore can be easily functionalized at the 3- and 5-positions with two 4-formylphenyl groups by palladium-catalyzed coupling reaction of the 3,5-dichloro-4,4-difluoro-8-(4-tolyl)-4-bora-3a,4a-diaza-*s*-indacene (**1**)<sup>3</sup> using the Suzuki reaction. In these conditions, BODIPY derivative **2** was obtained (see Scheme 1). Compound **2** was transformed in the dimethoxycarbonylvinyl and dicyanovinyl-substituted fluorophores **3** and **4**, respectively, by Knoevenagel condensation (see Scheme 1). Suzuki coupling for the formation of aryl-substituted dye **2** was carried out under microwave or ultrasonic irradiation. Thus, **1** was treated with 2.5 equivalents of 4-formylphenylboronic acid under microwave irradiation for 30 min at 150 °C with a power of 200 W affording the diarylated derivative **2** (46%). When the reaction was run under ultrasonic irradiation at 75 °C with a power of 720 W, longer time (15 h) and 6 equivalents of boronic acid were required, affording **2** in 50% yield. Subsequently, BODIPY **3** was obtained with a 47% yield, from diaryl-substituted dye **2** with dimethyl malonate in the presence of  $\text{TiCl}_4$ . Similarly, the Knoevenagel reaction of compound **2** and malononitrile in the



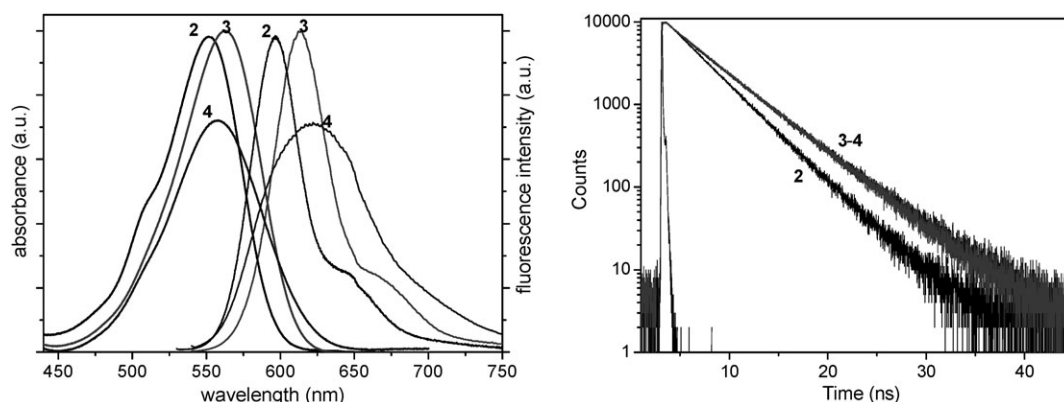
Scheme 1 Synthetic routes of derivatives **2–4** from **1**.

presence of  $\beta$ -alanine and acetic acid led to the formation of **4** (21%).

#### 3.2 Photophysical properties

The new BODIPYs **2–4** present absorption and fluorescence bands at around  $\lambda_{\text{ab}} \approx 550\text{--}575$  nm and  $\lambda_{\text{fl}} \approx 595\text{--}625$  nm (see Fig. 2), shifted toward the red spectral region with respect to other alkyl-substituted BODIPY dyes with absorption and fluorescence bands at the green/yellow spectral region.<sup>8</sup> The absorption and fluorescence bands of the new dyes are well separated from each other, leading to a relatively large Stokes shift ( $\Delta\nu_{\text{St}} \approx 1200\text{--}1800$   $\text{cm}^{-1}$ ), about 3 times higher than that of typical alkyl-BODIPY derivatives. Fluorescent dyes with large Stokes shifts are of special interest in photonics because the loss of emission intensity by reabsorption effects, one of the main factors contributing to the losses in the resonator cavity of a dye laser, is reduced. The new dyes are also characterized by broad spectral bands, mainly for dye **4** (fwhm  $\approx 2200$   $\text{cm}^{-1}$ ).

Quantum mechanical calculations predict that the  $S_0\text{--}S_1$  transition of these new BODIPYs, responsible for these Vis absorption and emission bands, involves the HOMO and LUMO molecular orbitals. The electronic density of these orbitals is illustrated in Fig. 3 for the specific case of **4** (see ESI page 12 for similar electronic clouds obtained to compound **2** and **3**).<sup>†</sup> As can be observed, the electronic  $\pi$ -system is not only localized in the BODIPY core but is also extended through the aromatic ring of the substituents at the 3- and 5-position, mainly in the excited state. This high delocalization

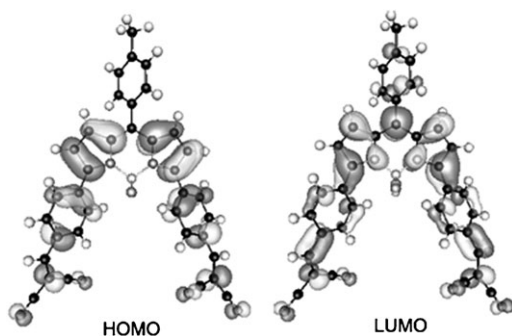


**Fig. 2** Absorption (normalized to emission spectrum), fluorescence spectra (scaled by their fluorescence quantum yield), and fluorescence decay curves of dyes **2**, **3** and **4** in trifluoroethanol.

in the electronic  $\pi$ -system should be responsible for the large spectral red shifts observed for these dyes.

Many of the reported red-emitting BODIPYs are achieved by the incorporation of delocalized substituents, bearing sometimes electron donor groups, usually at 3 and 5 positions of the chromophoric core.<sup>9</sup> The resonant interaction between such functional groups and the  $\pi$ -system of the BODIPY core provides a merocyanine like chromophore where electronic density could be shifted from the donor substituent to the BODIPY core leading to the formation of a charge transfer state, which quenches efficiently the fluorescent emission mainly in polar media.<sup>10</sup> In our case, the presence of electron acceptor groups at 3 and 5 positions causes a strong red shift, however such charge transfer states are not formed. In fact, and as discussed below, both the fluorescence quantum yield and the lifetime of dyes **2**, **3**, and **4** are nearly solvent independent. Therefore, the cyanine like delocalization typical of BODIPY is kept, as shown in Fig. 3, where the electronic density is extended through the whole molecule.

The optimized geometry in the ground state shows a nearly planar BODIPY core, with the phenyl unit at the *meso* 8-position twisted 51° and the aromatic rings at 3,5 positions twisted around 30°, with respect to the dipyrromethene plane. Upon excitation, the electronic distribution is extended to the vinyl group at *para* position of the phenyl substituents at 3 and 5 positions. Consequently the fluorescence band is more extended into the red, explaining the above commented large Stokes shift of these compounds. These red displacements are



**Fig. 3** Electronic density maps of the HOMO and LUMO orbitals for dye **4**.

more prominent for dyes **3** and **4** than for dye **2** (see Fig. 2), probably because of the presence of vinyl groups in the former dyes and stronger electron withdrawing units at the *para*-phenyl position (methoxycarbonyl or cyano *versus* formaldehyde).

Fluorescence decay curves of **2–4** are analyzed as mono-exponential decays (see Fig. 2), and the fluorescence lifetimes are evaluated from the corresponding slopes. The photophysical parameters of BODIPYs **2–4** in several solvents are summarized in Table 1. The fluorescence quantum yield and lifetime ( $\phi \approx 0.40$ – $0.65$ , and  $\tau \approx 3.5$ – $5.0$  ns, respectively) of these compounds are relatively high, in spite of the red emission of these dyes. In fact, systems with low  $S_1$ – $S_0$  energy have low fluorescence capacities because the non-radiative deactivation processes are favoured *via* a rapid internal conversion mechanism.<sup>11</sup> The increase in the internal conversion is probably the most critical issue to develop successfully efficient red emitting dyes. However, present red-emitting BODIPY dyes are characterized by a relative low non-radiative rate constant ( $k_{nr} < 1.5 \times 10^8$  s<sup>-1</sup>) and a relative high fluorescence rate constant ( $k_f \approx 1.3 \times 10^8$  s<sup>-1</sup>, in spite of the low absorption probability, molar absorption  $\epsilon_{max} \approx 1$ – $3 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>). Moreover, it has previously been probed that these dyes with a pendant phenyl group at the *meso* 8-position can enhance the internal conversion process *via* a rotational motion of the phenyl group, reducing the fluorescence efficiency.<sup>2b,12</sup> In the present cases, such a mechanism seems to have a minor effect, probably due to the high delocalization of the chromophoric  $\pi$ -system through the aromatic substituents at 3 and 5 positions.

In general, compound **4**, bearing cyano groups, presents the lowest fluorescent efficiency while dyes **2** and **3** show the highest  $\phi$  value. The presence of electron withdrawing cyano groups induces a decrease in the  $k_f$  value, which is correlated with a lower absorption probability in BODIPY **4**. A more proper assignation of a decrease in the fluorescence probability should be made on the basis of the  $k_f/\nu$ ,<sup>3</sup> since the Einstein spontaneous emission is proportional to the fluorescence frequency. Again, it is confirmed that dye **4** bearing a cyano group has a lower fluorescence emission probability. Although this reduction in the fluorescence ability will reduce the lasing efficiency of this compound, its high Stokes shift would decrease the losses in the resonator cavity favouring its laser action.

**Table 1** Photophysical properties of dyes **2**, **3** and **4** in apolar (c-hexane), polar (acetone and ethyl acetate) and polar/protic solvents (ethanol, methanol and F<sub>3</sub>-ethanol); absorption ( $\lambda_{\text{ab}}$ ) and fluorescence ( $\lambda_{\text{fl}}$ ) wavelength ( $\pm 0.5$  nm), molar absorption ( $\epsilon_{\text{max}}$ ,  $\pm 0.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ), fluorescence quantum yield ( $\phi \pm 0.05$ ) and lifetime ( $\tau$ ,  $\pm 0.05$  ns), radiative ( $k_{\text{fl}}$ ,  $10^8 \text{ s}^{-1}$ ) and non-radiative ( $k_{\text{nr}}$ ,  $10^8 \text{ s}^{-1}$ ) rate constants, and Stokes shift ( $\Delta\nu_{\text{St}}$ ,  $\text{cm}^{-1}$ )

| Solvent                 | $\lambda_{\text{ab}}$ | $\epsilon_{\text{max}}$ | $\lambda_{\text{fl}}$ | $\phi$ | $\tau$ | $k_{\text{fl}}$ | $k_{\text{nr}}$ | $\Delta\nu_{\text{St}}$ |
|-------------------------|-----------------------|-------------------------|-----------------------|--------|--------|-----------------|-----------------|-------------------------|
| <b>Dye 2</b>            |                       |                         |                       |        |        |                 |                 |                         |
| F <sub>3</sub> -ethanol | 551.5                 | 3.0                     | 595.5                 | 0.58   | 4.54   | 1.28            | 0.92            | 1365                    |
| Methanol                | 557.0                 | 3.1                     | 598.0                 | 0.46   | 3.65   | 1.26            | 1.48            | 1225                    |
| Ethanol                 | 559.0                 | 3.1                     | 600.5                 | 0.53   | 3.91   | 1.35            | 1.20            | 1250                    |
| Acetone                 | 558.5                 | 3.1                     | 599.5                 | 0.51   | 3.48   | 1.46            | 1.41            | 1225                    |
| Ethyl acetate           | 558.0                 | 3.0                     | 599.0                 | 0.57   | 3.67   | 1.55            | 1.17            | 1240                    |
| c-Hexane <sup>a</sup>   | 561.0                 | 3.3                     | 597.5                 | 0.54   | 3.68   | 1.46            | 1.25            | 1080                    |
| <b>Dye 3</b>            |                       |                         |                       |        |        |                 |                 |                         |
| F <sub>3</sub> -ethanol | 562.5                 | 1.8                     | 613.5                 | 0.59   | 4.98   | 1.18            | 0.82            | 1470                    |
| Methanol                | 570.0                 | 1.9                     | 618.5                 | 0.60   | 4.56   | 1.31            | 0.88            | 1380                    |
| Ethanol                 | 573.5                 | 1.9                     | 621.0                 | 0.62   | 4.67   | 1.33            | 0.81            | 1330                    |
| Acetone                 | 572.5                 | 1.9                     | 620.0                 | 0.61   | 4.61   | 1.32            | 0.84            | 1345                    |
| Ethyl acetate           | 572.0                 | 1.9                     | 620.0                 | 0.64   | 4.56   | 1.40            | 0.79            | 1355                    |
| c-Hexane <sup>a</sup>   | 575.5                 | 1.8                     | 618.0                 | 0.56   | 4.39   | 1.27            | 1.00            | 1190                    |
| <b>Dye 4</b>            |                       |                         |                       |        |        |                 |                 |                         |
| F <sub>3</sub> -ethanol | 558.0                 | 0.6                     | 622.0                 | 0.42   | 4.80   | 0.87            | 1.21            | 1845                    |
| Methanol                | 564.0                 | 0.7                     | 623.0                 | 0.41   | 4.53   | 0.90            | 1.30            | 1675                    |
| Ethanol                 | 566.0                 | 0.6                     | 625.0                 | 0.47   | 4.59   | 1.02            | 1.15            | 1665                    |
| Acetone                 | 565.5                 | 0.6                     | 625.0                 | 0.44   | 4.80   | 0.92            | 1.16            | 1690                    |
| Ethyl acetate           | 563.0                 | 0.6                     | 617.5                 | 0.54   | 4.66   | 1.16            | 0.98            | 1570                    |
| c-Hexane <sup>a</sup>   | 572.0                 | 0.4                     | 622.5                 | 0.53   | 4.63   | 1.14            | 1.01            | 1420                    |

<sup>a</sup> Not fully soluble.

The inclusion of *p*-substituted-phenyl groups at 3,5 positions results in more polar BODIPY dyes reducing their solubility in apolar media (*i.e.* c-hexane). The solvent effect on the photophysics of these new dyes (see Table 1) is the typical one observed in many alkyl-BODIPY dyes,<sup>8</sup> for instance: hypsochromic shifts of the spectral bands with the solvent polarity/acidity; a nearly solvent independent fluorescence quantum yield, and a progressive increase of the fluorescence lifetime and Stokes shift with the solvent's acidity and polarity. These BODIPYs have low solubility in apolar media. Anyway, their photophysics in such media (c-hexane, dioxane, diethylether and THF) was also registered (data in c-hexane included in Table 1, data in the rest of solvents not shown) for comparison. The results are consistent with the above commented evolutions with the solvent properties, corroborating the absence of any quenching charge transfer state in polar media and the maintenance of the cyanine like electronic  $\pi$ -system delocalization, in spite of the incorporation of electron withdrawing groups (aldehyde, ester and cyano).

The photophysical behaviour of the new red emitting dyes **2**, **3** and **4** is compared with other structurally related 8-tolyl-BODIPYs found in the literature,<sup>13</sup> (see Fig. 4). The unsubstituted 8-tolyl-BODIPYs present a very low fluorescence quantum yield (see Fig. 4), attributed to an important internal conversion deactivation *via* the rotational motion of the pendant 8-aryl group.<sup>2b,12</sup> Besides, red-emitting dyes present low fluorescence capacity because the low S<sub>0</sub>-S<sub>1</sub> energy gap favours the internal conversion processes.<sup>11</sup> However, the incorporation of 3,5-phenyl groups in 8-tolyl-BODIPY not only leads to a large red shift, but also to a progressive enhancement of the fluorescence quantum yield (see Fig. 4). Experimental results suggest that the internal conversion of 8-tolyl-BODIPYs is drastically reduced when aryl groups are incorporated at 3 and

5 positions of BODIPY core. The  $\pi$ -electronic delocalization through these groups induces a double bond character to the linking BODIPY-phenyl bonds, reducing the rotational motion of these aryl groups. Moreover, this extended  $\pi$ -system also reduces the electronic density at the *meso* 8-carbon of the BODIPY-core, mainly in the excited state (see Fig. 3), decreasing the effect of the 8-aryl rotation on the internal conversion of these dyes. The fluorescence bands of the new dyes **2**, **3** and **4** are more extensively red-shifted with a higher fluorescence quantum yield because the presence of adequate *para*-substituents at the 3,5-phenyl groups favours the delocalization of the  $\pi$ -system through these moieties, increasing their fluorescence ability.

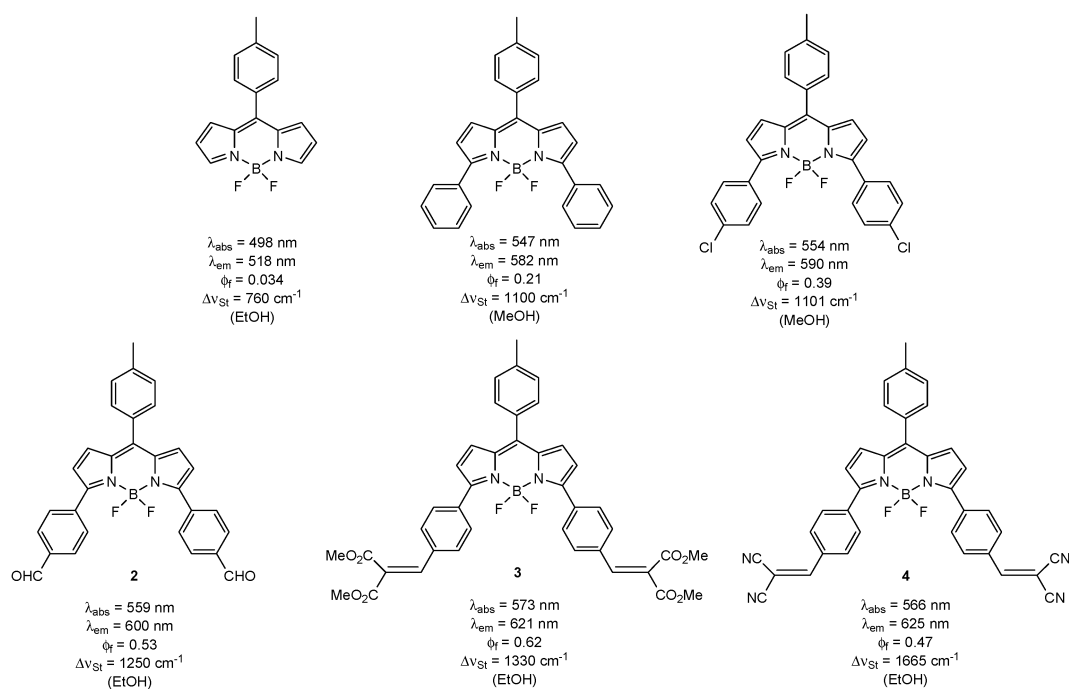
Therefore, the present red-emitting BODIPY dyes show an important fluorescence capacity in the red part of the visible region and are promising candidates to be used as active media for developing an efficient red-dye laser.

### 3.3 Lasing properties

An ethyl acetate solution of derivative **2** transversely pumped at 532 nm with 5 mJ pulse<sup>-1</sup> in a simple plane-plane non-tunable resonator emits broad-linewidth laser light at 615 nm, with an efficiency (Eff, percentage of the excitation energy converted into laser emission) of 14%. The extension of the conjugation at 3,5-BODIPY positions, red-shifts effectively the wavelength of the laser emission up to 37 nm, although with a significant decrease in the laser efficiency of dyes **3** and **4** (see Table 2). The laser-pump of the new dyes at a wavelength (568 nm) near their absorption maxima improves the laser efficiency which increases for a factor of up to 5 with respect to that registered under excitation at 532 nm (see Table 2).

The lasing characteristics observed in concentrated solutions of the new BODIPY dyes show good correlation with their photophysical properties in dilute solution. The presence of 3,5-dimethoxycarbonylvinyl- and dicyanovinyl substituents induced spectral red-shifts in the absorption and fluorescent bands similar to those observed in the lasing emission. A slight decrease in the  $k_{\text{fl}}$  value of dye **4** with respect to dye **2** (by a factor of ca 1.4) could suggest a diminution in the laser action, although not so significant reduction of the laser efficiency.

The actual effect of the solvent on the dye laser emissions was analyzed in solutions of apolar, polar nonprotic, and polar protic solvents at the dye concentrations that optimized the corresponding laser efficiency of each derivative. The results are summarized in Table 2. The low solubility of these new dyes in some common solvents prevents attaining the concentrated solutions required for laser experiments and, consequently, the correlation with the photophysical properties. However, some interesting tendencies can be derived from these experimental results: higher laser efficiencies of dye **2** are reached for polar aprotic solvents such as ethyl acetate and acetone. However, the very polar protic nature of the solvents (2,2,2-trifluoroethanol and methanol) improved the laser efficiencies of dyes **3** and **4** with respect to the values registered in apolar media. As previously discussed for commercial BODIPY dyes,<sup>14</sup> the behaviour of the new BODIPY derivatives in different solvents confirms the difficulty in understanding and predicting laser action on the basis of the



**Fig. 4** Chemical structures of 8-tolyl-BODIPYs substituted at 3 and 5 positions from the literature<sup>13</sup> and compounds **2–4** synthesized in this work.

**Table 2** Maximum wavelength of the laser emission ( $\lambda_1$ ) and lasing efficiency (Eff) of the new BODIPY dyes in several solvents under excitation at 532 nm and, within parentheses, at 568 nm

| Dye                  | Data                  | THF       | EtOAc     | Acetone   | CH <sub>2</sub> Cl <sub>2</sub> | F <sub>3</sub> -EtOH | MeOH      |
|----------------------|-----------------------|-----------|-----------|-----------|---------------------------------|----------------------|-----------|
| <b>2<sup>a</sup></b> | $\lambda_1/\text{nm}$ | 619 (620) | 615 (615) | 615 (613) | 617                             |                      |           |
|                      | Eff (%)               | 11 (16)   | 14 (20)   | 14 (20)   | 10                              |                      |           |
| <b>3<sup>b</sup></b> | $\lambda_1/\text{nm}$ | 636 (632) | 632 (628) |           |                                 | 625                  | 628 (626) |
|                      | Eff (%)               | 2 (8)     | 2 (10)    |           |                                 | 6                    | 11 (17)   |
| <b>4<sup>c</sup></b> | $\lambda_1/\text{nm}$ | 646 (659) | 648 (654) | 652       |                                 | 655 (657)            | 648       |
|                      | Eff (%)               | 2 (5)     | 4 (8)     | 3         |                                 | 5 (11)               | 3         |

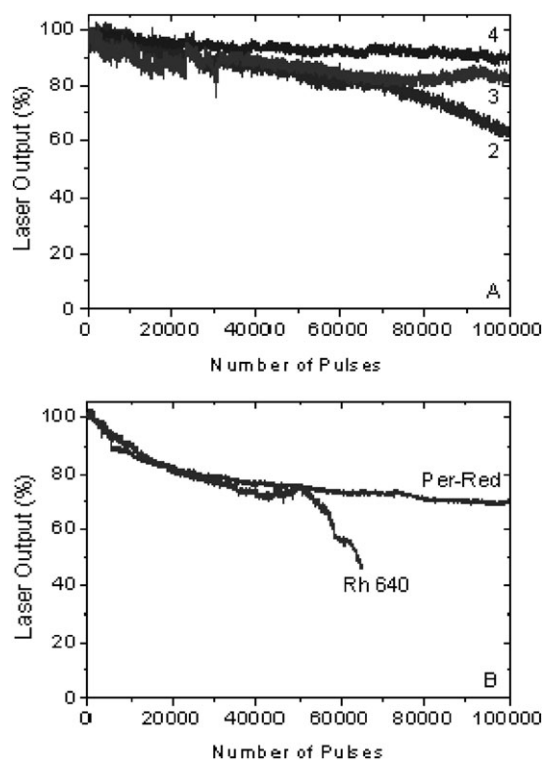
<sup>a</sup> Dye concentrations at 532 nm:  $9 \times 10^{-4}$  M and at 568 nm:  $9 \times 10^{-4}$  M. <sup>b</sup> Dye concentrations at 532 nm:  $8 \times 10^{-4}$  M and at 568 nm:  $4 \times 10^{-4}$  M. <sup>c</sup> Dye concentrations at 532 nm:  $3 \times 10^{-3}$  M and at 568 nm:  $2 \times 10^{-3}$  M.

polarity/polarizability or H-bond donor/acceptor ability or both liquid media, at least for dyes with a complex molecular structure.

The photostability (evolution of the emission with the number of pump pulses at 10 Hz) of each dye was evaluated by irradiating under lasing conditions 10  $\mu\text{L}$  of a solution in ethyl acetate contained in capillary tubes carefully sealed to avoid solvent evaporation during experiments. The concentrations of laser dyes were adjusted so that the laser action was optimum in all cases. Although the optical quality of the capillary prevents laser emission from the dyes, information about their photostabilities can be obtained by monitoring the decrease in laser-induced fluorescence intensity perpendicular to the exciting beam, under transversal excitation of the capillary, as a function of the number of pump pulses. The results obtained from the dyes are plotted in Fig. 5.

Under 532 nm pumping, the new derivatives **3** and **4** result in being highly photostable, with the emission dropping by less than 20 and 10%, respectively, with respect to the initial value after 100 000 pump pulses, while the derivative **2** experiences a faster photodegradation process, losing up to 40% of its fluorescence emission.

In order to put the present results in proper perspective, the lasing parameters of two well-known dyes lasing at the same wavelengths as the dyes studied herein were also measured in liquid solutions at 532 nm under similar conditions. Perylene Red, used as received, in ethyl acetate solution ( $5 \times 10^{-4}$  M) lases at 614 nm with an efficiency of 20%, while after purification the conversion efficiency of this dye increases to 26%. Rhodamine 640 ( $1 \times 10^{-3}$  M) lases in the same spectral region with higher efficiency (40%) but exhibiting a dual laser emission, at 620 and 650 nm, due to reabsorption/reemission phenomena and inhomogeneous spectral broadening.<sup>15</sup> For comparison, the lasing photostabilities obtained under the above described experimental conditions for commercial dyes Perylene Red and Rhodamine 640 are also included in Fig. 5. The commercial dyes exhibit lasing efficiencies higher than those obtained with the new BODIPY derivatives described here, although with lower photostabilities: the initial fluorescence emission of Rhodamine 640 drops to 45% of its initial value after 60 000 pump pulses while the purified Perylene Red maintains a 70% of its initial emission after 100 000 pump pulses.

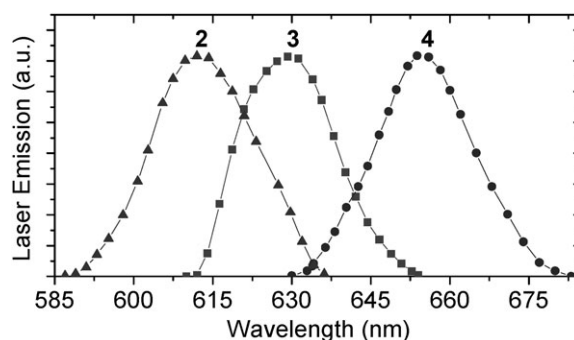


**Fig. 5** Normalized laser-induced fluorescence emission as a function of the number of pump pulses for the following dye solutions: (A) new BODIPY dyes **2**, **3** and **4** in ethyl acetate solution; and (B) **Per-Red** in ethyl acetate and **Rh640** in ethanol. Pump laser wavelength, energy and repetition rate: 532 nm, 5.5 mJ pulse<sup>-1</sup> and 10 Hz.

The tuning capability, one of the most important features of laser dyes, was determined for the new BODIPY dyes by placing their liquid solutions in the grazing-incidence grating tunable resonator. Tunable laser emission with a linewidth of the order of 0.15 cm<sup>-1</sup> and a tuning range of up to 50 nm was thus recorded, and the spectral region 590–680 nm can be continuously covered with narrow-linewidth and stable laser radiation by using the three dyes (see Fig. 6).

#### 4. Conclusions

We have successfully designed and synthesized new BODIPY dyes to achieve large spectral red-shifts with particularly useful photophysical properties. The position of the emission band can be modulated by the type of substituent attached to the BODIPY core. All the red emitting dyes presented in this work are characterized by a high fluorescence capacity since the coupling between the electronic clouds of the pyrromethene core and the 3,5-aryl groups reduces the rotational motion of the phenyl groups. Besides, the new dyes exhibit large Stokes shift, which could also improve their fluorescence ability from a technological point of view. The new BODIPY dyes lase with good efficiency and high photostability, allowing a wavelength finely tunable over a wide range (590–680 nm) with a narrow-linewidth. Considering the easy synthetic build-up, the wide variety of possible substituents and the large number of described BODIPY laser dyes, this powerful approach could



**Fig. 6** Laser tunability of new **2**, **3**, and **4** BODIPY dyes in ethyl acetate solutions. The solid lines in the tuning curves represent guidelines for the eyes.

be extended to other dyes of this family, with practical applications in optical and sensing fields.

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