Towards Efficient and Photostable Red-Emitting Photonic Materials Based on Symmetric all-BODIPY-Triads, -Pentads, and -Hexads

Edurne Avellanal-Zaballa,^[a] Juan Ventura,^[b] Leire Gartzia-Rivero,^[a] Jorge Bañuelos,^{*,[a]} Inmaculada García-Moreno,^[c] Clara Uriel,^[b] Ana M. Gómez,^{*,[b]} and J. Cristobal Lopez,^{*,[b]}

Abstract: The development of efficient and stable red and near-IR emitting materials under hard radiation doses and/or prolonged times is a sought-after task due to their widespread applications in optoelectronic and bio-photonic. To this aim, novel symmetric all-BODIPY-triads, -pentads, and -hexads have been designed and synthesized as light-harvesting arrays. These photonic materials are spectrally active in the 655-730 nm region and display high molar absorption across UV-visible region. Furthermore, they provide, to the best of our knowledge, the highest lasing efficiency (up to 68%) and the highest photostability (tolerance >1300 GJ.mol⁻¹) in the near-IR spectral region ever recorded under drastic pumping conditions. Additionally, the modular synthetic strategy to access the cassettes allows the systematic study of their photonic behavior related to structural factors. Collectively, the outstanding behavior of these multichromophoric photonic materials provides keystones for engineering multifunctional systems to expedite the next generation of effective red optical materials.

Introduction

Red and near-infrared (NIR) fluorescent dyes are required in relevant technological fields ranging from laser, information storage, or solar power conversion to labeling and photosensing.^[1] To boost these advanced applications, fluorophores with high absorption over a broad spectral window and bright red-fluorescent emission are required. Even so, the keystone promoting its workability is surely a high resistance

against photodegradation especially under strong conditions, such as hard radiation laser doses and/or prolonged times.^[2] In spite of the effort of the modern chemistry in synthesizing highly efficient and stable fluorophores with emission deeply shifted towards the red edge of the visible spectral region, they still present some important drawbacks: low absorption at standard laser wavelength, poor stability under intense irradiation, and/or limited chemical versatility for post-functionalization.^[3]

In the last years, photonic materials based on the difluoroboron dipyrromethene (BODIPY) chromophore have surfaced as chromophores of choice,^[4] since their unique spectroscopic and photophysical properties can be easily fine-tuned by synthetic post-modifications on its skeleton to meet all the above pointed requirements (Figure 1).^[5] In fact, the real power of the BODIPYs is closely related to their ability to undergo a wavelength shift upon selective chemical or biological functionalization of the diaza-indacene core. Thereby, different synthetic postmodifications^[6,7] have been applied to bathochromically shift the absorption and emission wavelength from the parent BODIPYs, e.g. **1**,^[8] **2**^[4a] ($\approx$ 500 nm) up to the red spectral region (> 650 nm), for instance, extension of the π -system through incorporation of peripheral alkynyl or distyryl substituents (e.g. **3**,^[9] **4**,^[10] **5**^[11] in Figure 1),^[12] and/or fusion of aromatic rings.^[13] In this context, compounds **3b** and **4** had already shown a remarkable behavior, in terms of efficiency and photostability, as laser dyes.^[14]

An additional approach to photonic materials, also based on the chemical versatility of the dipyrroin core, has focused on the design of multichromophoric systems enabling effective excitation energy transfer (EET) through covalently linked BODIPY building blocks acting as either energy-donor and/or energy-acceptor units.^[15] This last strategy is very appealing since such multichromophoric organic architectures allow a more versatile selection of the excitation source and energy, ensure a better exploitation of the incoming light and avoid photodegradation since the final emitting chromophoric subunit is not directly pumped but indirectly through EET from the donor units yielding in this way long-lasting and glow emission.^[16]

[a] Miss E. Avellanal-Zaballa, Dr. L. Gartzia-Rivero, Dr. J. Bañuelos
Dpto. Química Física
Universidad del País Vasco (UPV/EHU),
Aptdo. 644, 48080 Bilbao, Spain
E-mail: jorge.banuelos@ehu.es

[b] Dr. J. Ventura, Dra. C. Uriel, Dr. A. M. Gómez, Prof. J. C. López
Instituto de Química Orgánica General (IQOG-CSIC)
Juan de la Cierva 3, 28006 Madrid, Spain 2
E-mail: ana.gomez@csic.es; jc.lopez@csic.es

[c] Prof. I. García-Moreno
Instituto Química-Física "Rocasolano" (IQFR-CSIC)
Serrano 119, 28006 Madrid, Spain

Figure 1. BODIPY (1), 1,3,5,7-tetramethyl-8-phenyl BODIPY (2), 2,6-dialkynyl BODIPY (3) and 3,5-distyryl BODIPY (4), superimposed onto a portion of the visible light spectrum. λ_{ab} = absorption maximum (nm), λ_{em} = emission maximum (nm), ϕ = fluorescence quantum yield.

Nowadays, even though many supramolecular cassettes based on BODIPY scaffolds have been described, light-harvesting systems with effective emission in the red-edge of the spectral region are still scarce.^[15,16] Actually, most of these assembled architectures, rather than involving a long-wavelength BODIPY as energy acceptor, incorporate less efficient and/or photostable chromophoric skeletons such as perylene-diimides,^[16c] porphyrins^[17] and also aza-BODIPYs,^[18] among others.^[19] Furthermore, to the best of our knowledge, the photonic behavior of these structures under strong irradiation-regime, as well as their dependence on the number and position of fluorophores acting as donor and acceptor units have never been described. In an attempt to simultaneously address all these challenges and searching for the development of highly efficient and stable red-emitting photonic materials, in this manuscript we disclose the synthesis, the photophysical signatures (aided by computational simulations), and the laser characterization of novel multichromophoric all-BODIPY materials,^[15a,15b,15h,20] i.e., BODIPY-triads **6**, **7**, and **8**; BODIPY-pentad **9** and BODIPY-hexad **10** (Figure 2). The acceptor unit(s) in these multichromophores (highlighted in red in Figure 2) is a BODIPY whose absorption and emission has been bathochromically shifted up to the red-edge spectral region by extension of its π -conjugation through the combination of styryl substituents at C-3 and C-5, and either alkynyl substituents or, previously unexplored, triazolyl units at C-2 and C-6. Thus, acceptor- and peripheral-donor-BODIPYs were connected through *ortho*-aryl C-8 substituents by way of: *i*) styryl moieties, e.g. **6**, **7**; *ii*) triazole residues, e.g. **8**, or *iii*) through both, in the case of BODIPY pentad **9** (Figure 2). The presence of the *ortho*-C8 aryl-substituent combined with the presence of the C-1 and C-7 methyl groups was key to ensure the required orthogonal orientation (by rotational restriction) between the C-8 aromatic residue and the BODIPY core, thus avoiding resonant electronic interactions. These set of derivatives differ in the number of donor and acceptor BODIPY subunits as well as in their linkage

positions. Accordingly, *i*) two donors and one acceptor are present in triads **6–8**, with multichromophores **7** and **8** differing in the attachment points of the BODIPY donor elements; *ii*) four donors and one acceptor in BODIPY pentad **9**, and finally *iii*) four donors and two acceptors in bis-urea dimer **10**.

Figure 2. All-BODIPY multichromophores **6–10**, studied in this work. Single BODIPY starting material (**11**). Key retrosynthetic disconnections: (A) Knoevenagel condensation; (B) copper azido alkyne cycloaddition (CuAAC) reaction; (C) bis-urea dimerization.

FULL PAPER

In this way, the new ensemble of all-BODIPY multichromophores becomes the first example of: a) a straightforward synthetic strategy for all-BODIPY cassettes using one single BODIPY progenitor, i.e., **11** (Figure 2), which makes use of copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) reactions,^[21–23] chemoselective Knoevenagel condensations of 2,6-dialkynyl BODIPYs,^[24] and an efficient ureation protocol recently described by us (synthetic disconnections **A**, **B**, **C**, respectively, Figure 2);^[25] b) a systematic analysis of the photonic behavior of red-emitting cassettes based on structural factors such as the number of donor and acceptor units, and the position and the spacers connecting the building blocks; and c) remarkable red-emitting laser cassettes endowed with an effective absorption in the UV-visible spectral region, and, particularly one of the highest emission efficiency and photostability described so far, key parameters to guarantee long-lasting emission in any advanced applications.

Results and Discussion

Synthesis and characterization

As previously mentioned, our approach to multichromophores **6–10**, started from a single precursor, 8-phenyl *ortho*-hydroxymethyl BODIPY **11**, readily available by a one-pot protocol previously described in our laboratory.^[26] In this context, synthetic transformations on the hydroxymethyl moiety of **11** paved the way to azidomethyl and formyl BODIPYs **12** and **13**, respectively.^[26] Subsequent synthetic postmodifications on the dipyrromethene core of **11** allowed access to differently 2,6-disubstituted derivatives **14**,^[26] **15a**, **15b**^[26] and **16** (Figure 3). Compounds **15** and **16**, with π -extended conjugation, displayed red-shifted absorption and emission in agreement with literature precedents.^[7b]

Next, we carried out investigations on the chemoselective Knoevenagel condensation of aldehyde **13** with BODIPYs **15** and **16** (rather than self-condensation of **13**). These studies emanated from the observation by Akkaya's group^[12a,27] that electron-withdrawing substituents (at C-2 and C-6) in 1,3,5,7-tetramethyl BODIPYs experienced a clear enhancement on the acidity of the methyl groups compared to the parent unsubstituted derivatives. They, indeed had taken advantage of this finding for the preparation of 1,3,5,7-tetrasteryl-BODIPY dyes.^[12a] However, to the best of our knowledge, this reactivity difference had not been used to date in eliciting chemoselective Knoevenagel condensations involving formyl BODIPYs^[28] (see Supporting Information for details).

As a result of our studies, we found that chemoselective Knoevenagel condensation of formyl-BODIPY **13** with "activated" BODIPYs **15a,b** takes place at room temperature in DMF, in the presence of piperidine and AcOH, to give distyryl derivatives **6a** and **6b**, in fairly acceptable yields, without traces of self-condensation products arising from **13** (Scheme 1a). Compound **7**, was then easily accessed from **6a** by CuAAC reaction with benzyl azide. On the other hand, access to BODIPY triad **8**, involved Knoevenagel condensation of dialkynyl derivative **15a** with benzaldehyde (AcOH, piperidine, DMF, 24 h, room temperature) followed by CuAAC reaction of the ensuing distyryl BODIPY **20a** with azidomethyl BODIPY **12** (Scheme 1c). Final access to BODIPY-pentad **9**, and -hexad **10** was straightforward from BODIPY trimer **6a**. Thus, CuAAC reaction of dialkynyl BODIPY **6a** with azidomethyl BODIPY **12**^[23] (Scheme 2) led to pentameric BODIPY **9**. Conversely, dimerization of azidomethyl BODIPY trimer **22**,^[25] obtained from **6a** upon treatment with 2-azido-1,3-dimethylimidazolinium hexafluorophosphate (ADMP) in the presence of DBU,^[29] yielded dimeric bis-urea trimer **10**.

Figure 3. Differently 2,6-disubstituted 1,3,5,7-tetramethyl 8-phenyl *ortho*-hydroxymethyl BODIPYs **14–16**, and their Knoevenagel-condensation products with benzaldehyde **17–21**. Dye concentration: 2 mM. Absorption (λ_{ab}) and fluorescence emission maxima (λ_{em}) wavelengths (nm); fluorescence quantum yield (ϕ). Values measured in EtOAc.

Scheme 1. Chemoselective Knoevenagel condensation of 2,6-dialkynyl BODIPYs **15a,b** with BODIPY aldehyde **13** (a). CuAAC Reaction of **6a** with benzyl azide leading to BODIPY-triad **7** (b). Synthesis of bis-triazolyl BODIPY **8** (c).

Scheme 2. Synthetic routes to multichromophores **9** and **10**, from BODIPY-triad **6a**.

Photophysical properties

The absorption profile of the molecular cassettes **6–10** featured three well-resolved bands (Figure 4). The long wavelength absorption was assigned to the π -extended central BODIPY subunit matching the spectrum recorded for the isolated dye **21**. This band became bathochromically shifted up to 655 nm when the triazol group grafted at position C-2 and C-6 of the BODIPY in dyes **7**, **8** and **9** was replaced by an acetylene group (in **6a** and **10**) or by an acetylenophenyl group (**6b**). With respect to the

triazol functionalization, these latter groups allowed a stronger electronic coupling to the central BODIPY unit inducing the red-shifted of the corresponding absorption band.

Figure 4. Absorption spectra of the all-BODIPY-based cassettes **6–10** in diluted solutions of diethyl ether. The corresponding spectrum of the isolated red-emitting dye **21** is also included for comparison.

A strong and dominating absorption band was registered at the green-yellow region (around 505 nm) and attributed to the absorption of the peripheral tetramethylated BODIPYs. The molar absorption coefficient of the new dyes in the green-red spectral region increased progressively with the number of BODIPY units covalently linked (Figure 4). Thus, an extinction coefficient at the red-edge maximum wavelength reached up to $170000 \text{ M}^{-1} \text{ cm}^{-1}$ for compound **10**, bearing two π -extended central BODIPYs, whereas this absorption coefficient at the green-yellow maximum wavelength became even higher than $200000 \text{ M}^{-1} \text{ cm}^{-1}$ for dyes **9** and **10**, bearing four pendant peripheral BODIPYs (Figure 4). Finally, an absorption band placed at the ultraviolet edge (360 nm in Figures 4) was recorded and was attributed to the interaction of the styryl arm at positions C-3 and C-5 with the pyrrole groups of the central BODIPY.^[12f] In addition, the peripheral BODIPYs should also be contributing to increase the absorption in this spectral region even though they weakly absorbed at this UV-wavelength, but owing to the number of chromophoric units linked this contribution was no longer residual and became significant. The computational simulation of the absorption spectra supported this assignment (see simulated spectra for the triads in Figure S3 in the Supporting Information). The molecular orbitals involved in the long-wavelength transition (HOMO $\rightarrow$ LUMO) were placed exclusively into the central BODIPY (see the molecular orbitals for the cassettes in Figures S4-S8 in the Supporting Information). The molecular orbitals responsible of the absorption in the green spectral region involved electronic configurations energetically close (for example HOMO-2 $\rightarrow$ LUMO+1 and HOMO-1 $\rightarrow$ LUMO+2 in trimeric **6b**, Figure S4 in the Supporting Information) and were located just at each peripheral BODIPY (Figures S4-S8 in the Supporting Information). The UV transition resulted from the

simultaneous contribution of multiple electronic configurations involving molecular orbitals placed at the peripheral BODIPYs and mainly at the central BODIPY with the electronic density mostly located at the C-3 and C-5 styryl groups. Therefore, the molecular design and the imposed geometrical hindrance were suitable to span the electronic delocalization through the aromatic functionalization without reaching the peripheral BODIPYs. As a result, each chromophoric subunit retained its molecular identity after the covalent linkage, contributing almost additively to the whole absorption spectrum.

On the other hand, the fluorescence spectra of the new cassettes, regardless of the excitation wavelength, featured mainly an unique band shifted to the red-edge, around 650–680 nm depending on the aromatic group grafted at positions C-2 and C-6 (Figure 5 and S1–S2 in the Supporting Information). Moreover, the excitation spectra monitored at such red emission matched nicely the absorption profile (Figures S1–S2 in the Supporting Information). These trends supported that these cassettes underwent highly efficient intramolecular EET (intra-EET) from the peripheral BODIPY donors to the central p-extended BODIPY acting as acceptor unit. Indeed, the emission from the donor units (placed at around 510–515 nm) was drastically quenched (being almost residual, see Figure 5, with a fluorescence efficiency lower than 1%) promoting the growth of the predominant red emission (fluorescence efficiency up to 68% in apolar media, Table 1).

Figure 5. Absorption (solid line) and fluorescence (dashed, under selective excitation at 475 nm) of the representative cassettes **9** (black) and **10** (red) in diluted solutions of diethyl ether. The corresponding spectra of cassettes **6–8** are collected in Figures S1–S2 in the Supporting Information.

Based on the decline of the fluorescence quantum yield of the donor upon binding to the acceptor, an intra-EET efficiency higher than 98% in all the media and cassettes was estimated. This high efficiency is related to the short donor-acceptor distance and the high spectral overlap between the donor fluorescence and the acceptor absorption. Both factors enhance and allow the required dipole-dipole coupling to undergo through-space EET via Förster mechanism. Moreover, the π -system of the central acceptor BODIPY, extended through the aromatic substituents at positions

3 and 5, as well as through the functional groups grafted at positions 2 and 6, could also enable a through-bond mediated EET^[20c] since the donors were directly and adequately connected to such moieties allowing the required electronic superexchange mechanism. As consequence of the viability and simultaneous contribution of both mechanisms, the transfer of excitation energy from the donor moieties to the central energy-trap is almost absolute.

The multichromophoric systems bearing a donor BODIPY grafted at *ortho* position of the 3,5-styryl groups (**6**, **7**, **9** and **10**) exhibited a fluorescent efficiency strongly dependent on the solvent polarity. In apolar media, they were characterized by a bright red emission peaked at 650–680 nm, with an efficiency ranging from 55% to 70%, and a monoexponential decay curve leading to a lifetime around 4.5 ns regardless of the excitation wavelength (Table 1). An increase of the solvent polarity led to a drastic reduction of the emission efficiency and a shortening of the lifetime (Figures 6 and 7, and Table 1). Indeed, the fluorescence decay curves acquired a bi-exponential character with a main and fast component of few hundreds picoseconds (Figure 7). Moreover, in the most polar media such as methanol and acetonitrile the emission was almost negligible revealing that the solvent polarity switched on in these molecular assemblies an effective non-radiative deactivation channel (Figure 6). This sensitivity of the fluorescent capacity on the solvent polarity is usually related to a non-emissive intramolecular charge transfer (ICT) process.^[22] As the polarity of the solvent increases the charge separation inherent to this ICT becomes more stabilized, strongly quenching the fluorescence from the locally excited (LE) state, regardless of its excitation pathway (direct absorption and/or via EET).

Figure 6. Comparative evolution of the fluorescence quantum yields of all the cassettes on the solvent polarity. Full data are collected in Table S1 in the Supporting Information.

Table 1. Photophysical properties of the energy transfer cassettes in diluted solutions (2 mM) of apolar (diethyl ether, Et₂O) and polar (methanol, MeOH) solvents. Full photophysical data in different solvents are listed in Table S1 in the Supporting Information.

		$\lambda_{ab}^{[a]}$ (nm)	$\varepsilon_{max}^{[b]}$ (10 ⁴ M ⁻¹ ·cm ⁻¹)	$\lambda_{fl}^{[c]}$ (nm)	$\phi^{[d]*}$	$\tau^{[e]*}$ (ns)
6a	Et ₂ O	652.0	10.4	662.5	0.65	4.72
		501.5	10.6			
		361.5	5.3			
	MeOH	649.5	8.4	660.5	0.016	0.14 (97%) - 0.47 (3%)
		500.5	9.3			
		360.5	4.9			
6b	Et ₂ O	655.0	8.8	676.5	0.65	4.50
		504.0	10.2			
		361.5	4.0			
	MeOH	657.5	8.1	682.0	0.030	0.26 (99%) - 1.81 (1%)
		503.5	9.7			
		361.5	4.0			
7	Et ₂ O	632.5	7.2	654.5	0.54	4.39
		503.0	10.2			
		350.5	5.4			
	MeOH	629.0	7.0	651.0	0.024	0.22 (90%) - 0.92 (10%)
		502.5	10.2			
		350.5	6.1			
8	Et ₂ O	627.0	8.6	652.0	0.68	4.32
		502.5	13.6			
		349.5	6.8			
	MeOH	624.5	8.7	649.5	0.45	2.78
		502.0	12.8			
		347.5	7.2			
9	Et ₂ O	633.5	9.0	657.5	0.69	4.25
		502.0	20.2			
		352.0	6.2			
	MeOH	631.0	9.5	655.5	0.042	0.44 (91%) - 1.13 (9%)
		501.0	19.6			
		349.0	7.1			
10	Et ₂ O	651.5	17.4	664.5	0.65	4.56
		503.0	20.6			
		362.0	10.0			
	MeOH	650.5	15.4	666.0	0.018	0.12 (77%) - 0.48 (23%)
		501.5	20.0			
		362.0	8.8			

[a] Absorption wavelength, [b] molar absorption coefficient, [c] fluorescence wavelength, [d] fluorescence quantum yield, [e] fluorescence lifetime. *The fluorescence lifetimes and quantum yields are independent on the excitation wavelength

Figure 7. Evolution of the fluorescence decay curve with the solvent polarity for the representative pentad **9**. Full data are collected in Table S1 in the Supporting Information.

The only exception to this behavior was the photophysical signatures of cassette **8**, which showed a lower dependence on

the solvent polarity. Comparison of the photophysical properties of the structurally related trimers **7** and **8** allowed establishing the influence of the molecular design on the effectiveness of this ICT process. In fact, these cassettes just differ in the linkage position of the donor BODIPY units, which were grafted at the 3,5-styryl groups in **7** while they were linked at the 2,6-phenyl groups in **8** (Figure 2). Thus, whereas the emission from **7** clearly dropped as the solvent polarity increased, the fluorescent efficiency of **8** remained as high as 45% even in the most polar solvent (Figure 6). This finding unambiguously backs up the ability of the BODIPY grafted to 3,5-styryl groups to induce effective ICT processes. Furthermore, in the cassette **10** the urea spacer linking the acceptor BODIPYs was itself able to induce an effective ICT owing to its electron donor ability, as was reported previously in symmetric bis-BODIPYs.^[25] The viability of two pathways to induce effective ICT processes in **10** led to the lowest fluorescent quantum yield and the shortest lifetime in polar media among the cassettes herein synthesized (Table 1). These results highlight the complex excited state dynamics of these multichromophoric

systems in polar solvents where, besides of the ongoing intra-EET, ICT processes were also ruling their emission response.

Therefore, the molecular design of these multichromophoric dyes fulfilled all the desirable features of an optimal photonic cassette. It ensures broad and extremely efficient light harvesting, large "pseudo" Stokes shift, and competitive excitation energy transport to the final emitting trap, which displayed glow emission in all the tested media regardless of the pumping spectral region. Moreover, the high synthetic versatility of these multichromophoric systems allowed us to modulate and understand the influence of the molecular structure (number of donor and acceptor subunits, as well as the donor-acceptor linkage positions) into the photophysical signatures of the final cassettes.

Laser properties

According to the absorption properties of the new BODIPYs their lasing properties were studied under transversal pumping at standard laser wavelengths such as 355 nm and 532 nm. Since the new multichromophoric systems were designed to behave as highly efficient and photostable photonic materials, to properly assess their long-term stability as well as the dependence of their lasing properties on the number and position of the linked BODIPY units, we selected strong pumping conditions such as 8 mJ/pulse and 15 Hz, as pumping energy and repetition rate, respectively. Highlight that these pumping conditions are more drastic than those we usually selected for the laser characterization of BODIPY dyes (i.e. 5 mJ/pulse and 5 or 10 Hz repetition rate).^[30] The concentration that optimized the laser efficiency in ethyl acetate solution, understood as the ratio of the output and input (pump) energies, depended on both the given dye and the pumping wavelength, and were ranging from 0.09 to 2 mM. The lasing properties of the new monomeric and multichromophoric BODIPYs analyzed under these experimental conditions are reported in Table 2.

Table 2. Lasing properties of the monomeric and multichromophoric dyes in ethyl acetate solution pumped at both wavelengths, 355 and 532 nm.

Dye	532 nm			355 nm		
	%Eff ^[a]	λ_{la} ^[b] (nm)	E_{dose} ^[c] (GJ/mol)	%Eff	λ_{la} (nm)	E_{dose} (GJ/mol)
6a	52	720	308	49	716	265
6b	47	710	342	50	704	294
7	51	703	388	52	700	327
8	62	705	524	58	699	445
9	68	715	993	65	710	843
10	57	730	1137	56	722	938
15a	33	580	51			
15b	35	622	35			
16	36	610	58			
21				30	690	55

[a] Lasing wavelength, [b] lasing efficiency, [c] photostability, defined as the amount of pumping energy absorbed by the dye to retain 50% of its initial emission

The monomeric BODIPYs **15a**, **15b** and **16** were only pumped at 532 nm due to its low absorption at 355 nm and rendered broad-band laser emission peaked at 580 nm, 622 nm and 610 nm, respectively, with a pump energy threshold of 0.9 mJ, and lasing efficiencies up to 35%. On the other hand, the dye **21** was only pumped at 355 nm due to its low absorption at 532 nm, rendering

red-edge laser emission peaked at 690 nm with an efficiency of 30%.

In terms of traceability and feasibility of photonic materials, efficiency is not the only crucial variable to be considered. A further important parameter is the photostability of the emission over long operation times. Ideally, a high resistance to active medium photodegradation under repeated pumping is sought after. A reasonable evaluation of the photostability of laser materials can be obtained by irradiating a small amount of solution with exactly the same pumping energy and geometry as used in the laser experiments, and monitoring the evaluation of the laser-induced fluorescence intensity with respect to the number of pump pulses (see Experimental Section). To properly compare the intrinsic photodegradation rate of the active media irrespective of the cavity configuration/parameters and sample concentrations used, we introduced a normalized photostability parameter such as the accumulated pump energy absorbed by the system, per mole of dye, before the output energy falls to a 50% its initial value (E_{dose} in GJ mol⁻¹). The monomeric BODIPYs (**15a**, **15b** and **16**) exhibited good photostability (Table 2) particularly considering that they have been pumped at high repetition rate (15 Hz). It is well-established that the accumulation of heat into the active medium increased significantly with the pumping repetition rate resulting in a rapid decrease of the lasing photostability.

More interesting became the laser behavior of the new multichromophoric systems, which significantly improved those exhibited individually by the corresponding donor and acceptor components. The photophysical behavior of **6–10** dyes as effective EET cassettes allowed them to lase efficiently in the red spectral region when they were transversally pumped at 355 nm as well as at 532 nm. In fact, the covalent linkage of BODIPY units into the cassettes **6–10** led to a significant increase of the absorption at both pumping wavelengths compared to those exhibited individually by the related monomeric parent dyes. This is a key factor from the point of view of the laser action, since it allows reducing significantly the required gain-media concentrations, avoiding consequently dye-solubility problems, or emission quenching and/or aggregation processes, all of them with detrimental effects on laser action.

Firstly, the cassettes **6–10** were transversely pumped at 532 nm, wavelength at which only absorbed the BODIPYs acting as donor units. Under these experimental conditions, they exhibited lasing emission peaked in the red-edge of the visible spectrum, ranging from 705 nm to 730 nm, with a pump energy threshold as low as 0.04 mJ, an efficiency up to 68% and a very high photostability since up to 1300 GJ.mol⁻¹ were required for a 50% decrease of its initial emission (Table 2). The enhancement of the photonic behavior on going from the monomeric dyes to the multichromophoric cassettes strongly depended on the molecular design following the rule: the highest the number of peripheral BODIPYs acting as donor units the lowest became the pump energy threshold, and the highest the lasing efficiency and photostability. In this regard, the lasing emission of the new multichromophoric cassettes **9** and **10** stand out by a pump energy threshold up to 22-fold lower, and an efficiency and photostability up to 2- and 20-fold higher than those recorded from the corresponding monomeric BODIPY **21** acting as acceptor unit

FULL PAPER

(Table 2 and Figure 8). The outstanding laser behavior of **6–10** has to be related to its molecular design, which led to: a) high “pseudo” Stokes Shifts (up to 5100 cm^{-1}), which reduced re-absorption/re-emission processes and, thus, their deleterious effect in the laser action; b) high dipole moments allowing the molecular alignment with respect to the polarization of the exciting laser beam to enhance the emission efficiency of the media;^[30] and c) an effective EET from the peripheral BODIPYs to the central red-emitting BODIPY, which significantly reduced the rate and extension of the photodegradation processes.

Figure 8. Lasing efficiency and photostability (10^{10} J/mol) of the cassettes **6–10** under pumping at 355 nm with respect to the isolated red-emitting energy acceptor dye **21**.

Another additional advantage of the molecular design of these cassettes that increases its photonic applicability is the versatility to be also pumped in the UV region. In fact, under laser pumping at 355 nm, cassettes **6–10** exhibited also red laser emission with a threshold and efficiency similar to those recorded at 532 nm (Table 2 and Figure 8). It should be noted that at 355 nm the BODIPY acting as acceptor absorbed partially the pumping radiation although with a coefficient lower than the multiple BODIPYs acting as donor units. The direct excitation of the acceptor could reduce the photostability of the final system. However, this deleterious effect in the cassettes **6–10** became balanced by a “pseudo” Stokes shift that increased up to 14470 cm^{-1} thus ensuring long operation times regardless of the laser excitation wavelength. These outstanding results point out the rational design of multichromophoric BODIPY cassettes as a smart skeleton on developing highly efficient and photostable photonic materials with emission in the red-edge region of the visible spectrum.

Conclusions

Hitherto the photonic performance and resistance under intense irradiation of red-emitting optical materials were either too limited or unreported or at least not well documented. Herein we

described a concise entry to symmetric all-BODIPY-triads, -pentads, and -hexads as artificial light-harvesting systems in which up to four energy donors are surrounding and covalently linked to one or two central red-emitting energy acceptors. The design and characterization of these multichromophoric systems entailed major achievements in widespread knowledge fields spanning from organic synthesis, computer-assisted photophysics to photonics.

From a synthetic viewpoint a novel, one-pot, efficient synthetic protocol was designed to develop all multichromophoric systems herein studied. The new synthetic approach makes use of *one single BODIPY progenitor 11*, and takes advantage of the acidity enhancement of the 3,5-methyl groups in 1,3,5,7-tetramethyl BODIPYs bearing electron-withdrawing substituents (at C-2 and C-6) in eliciting chemoselective Knoevenagel condensations. Additionally, we have demonstrated the effectiveness of dimerization as a synthetic short-cut in the generation of valuable light-harvesting derivatives. Thus, the generation of multichromophore **10**, by dimerization of BODIPY-triad **22** (Scheme 2) compares well in terms of synthetic efficiency with the preparation of BODIPY-pentad **9** from **6a** (Scheme 2). Multichromophores **9** and **10**, comprising four BODIPY donor units each, although differing in the number of acceptor elements (one and two, respectively) displayed comparable lasing properties (see Figure 8).

From the standpoint of computational-aided photophysical characterization, the new BODIPY cassettes showed efficient light-harvesting properties across the ultraviolet-visible spectral region owing to the orthogonal donor-acceptor disposition, which assured the required sterical hindrance to avoid both resonant electronic interactions as well as supramolecular aggregation by π - π stacking interactions, with deleterious effect on the emission efficiency. Regardless of the excitation wavelength, the new multichromophoric BODIPYs exhibited bright fluorescence mainly in the red-edge spectral region due to the ongoing effective intramolecular EET process. The high synthetic versatility of the multichromophoric BODIPYs allowed the first systematic and in-depth study of the photophysical behavior of red-emitting cassettes on the solvent polarity as well as on structural factors such as number of donor and acceptor units, and position and spacers connecting the corresponding building blocks.

From the photonic viewpoint, the new BODIPY cassettes lased beyond 700 nm with, to the best of our knowledge, the highest lasing efficiency and photostability and “pseudo” Stokes shift ever recorded under strong pumping conditions such as hard radiation laser doses and prolonged times mimicking those applied in the most advanced photonic and bio-photonic applications. In these materials, the enhancement of its photonic behavior strongly depended on the molecular design following the rule: the highest the number of peripheral BODIPYs acting as donor units the lowest became the pump energy threshold, and the highest the lasing efficiency and photostability. In this way, the new cassettes make it possible to achieve near-IR lasing emission with efficiencies as high as 68%, pump energy thresholds as low as 0.04 mJ, and most crucially, outstanding photostabilities requiring pump energy doses as high as $1300\text{ GJ}\cdot\text{mol}^{-1}$ to drop just 50% its initial emission. Collectively, the improved understanding of the

processes governing the synthesis and the outstanding photonic behavior of the new library of BODIPYs related to its structure should facilitate and speed up the rational design of advanced red-emitting optical materials.

Experimental Section

General experimental methods. All solvents and reagents were obtained commercially and used as received unless stated otherwise. Residual water was removed from starting compounds by repeated coevaporation with toluene. Reactions were executed at ambient temperatures unless stated otherwise. All moisture-sensitive reactions were performed in dry flasks fitted with glass stoppers or rubber septa under a positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred by syringe or stainless steel cannula. Anhydrous MgSO_4 or Na_2SO_4 were used to dry organic solutions during workup, and evaporation of the solvents was performed under reduced pressure using a rotary evaporator. Flash column chromatography was performed using 230–400 mesh silica gel. Thin-layer chromatography was conducted on Kieselgel 60 F254. Spots were observed under UV irradiation (254 nm). ^1H - and ^{13}C -NMR spectra were recorded in CDCl_3 at 300, 400 or 500 MHz and 75, 101 or 126 MHz, respectively. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane with the residual protium (CHCl_3 : δ 7.25 ppm) and carbon (CDCl_3 : δ 77.0 ppm) solvent resonances as internal references. Coupling constants (J) are given in Hz. All presented ^{13}C NMR spectra are proton-decoupled. Mass spectra were recorded by direct injection with an Accurate Mass Q-TOF LC/MS spectrometer equipped with an electrospray ion source in positive mode. BODIPY monomers **11**, **12**, **13**, **14**, **15b**, **17** and **18** were prepared according to previously reported methods.^[26]

General Procedures.

General method for Knoevenagel reaction. a) **At 80 °C under microwave (MW) irradiation.** To a solution of the corresponding BODIPY 14–16 (0.1 mmol) and the aromatic aldehyde (4 equiv) in dry DMF (25 mL/mmol) were added piperidine (0.1 mL) and acetic acid (0.1 mL). The condensation reaction was performed under MW irradiation for 2 h at 80 °C. The resulting crude mixture was then partitioned between CH_2Cl_2 and water, and the aqueous layer was re-extracted. The organic phase was dried over MgSO_4 , concentrated and purified on a silica gel column. b) **At room temperature.** To a solution of the corresponding BODIPY (0.1 mmol) and the appropriate aldehyde (2–4 equiv) in dry DMF (25 mL/mmol) were added piperidine (0.1 mL) and acetic acid (0.1 mL) at room temperature (usually 24 h). The resulting crude mixture was then partitioned between CH_2Cl_2 and water, and the aqueous layer was re-extracted. The organic phase was dried over MgSO_4 , concentrated and purified on a silica gel column.

General method for Copper(I)-catalyzed alkyne-azide cycloaddition reaction (CuAAC). The corresponding azide (2 equiv.), sodium ascorbate (3 equiv.), and CuSO_4 (1.5 equiv.) were added to a solution of the appropriate alkyne-BODIPY (50 mg, 0.1 mmol) in $\text{EtOH}/\text{H}_2\text{O}$ (1:1, v/v, 50 mL/mmol). The solution was subjected to MW irradiation at 80 °C until no starting materials were left. The reaction mixture was then concentrated under reduced pressure and the residue was purified by silica gel column chromatography.

General method for ureation reaction. The appropriate azidomethylphenyl-BODIPY (0.1 mmol) was added to a mixture of 1M triethylammonium hydrogen carbonate buffer (2.6 equiv.) and 1,4-dioxane (60 mL/mmol). Triphenylphosphine (1.3 equiv.) was added, and the reaction was monitored by TLC. After disappearance of the starting material, the solvent was evaporated in vacuo to dryness. The obtained BODIPY dimer was purified by flash chromatography on silica gel.

Spectroscopic data of multichromophoric all-BODIPY materials.

Trimer 6a. ^1H NMR (500 MHz, CDCl_3) δ 8.48 (d, J = 16.3 Hz, 2H), 8.16 (d, J = 8 Hz, 2H), 7.89 (d, J = 16.3 Hz, 2H), 7.68 – 7.48 (m, 6H), 7.29 – 7.25 (m, 3H), 7.10–7.07 (m, 1H), 5.98 (s, 4H), 4.48 (s, 2H), 3.47 (s, 2H), 2.55 (s, 12H), 1.40 (s, 12H), 1.38 (s, 6H) δ ^{13}C NMR (125 MHz, CDCl_3) δ 155.6, 152.5, 146.3, 143.4, 139.9, 138.7, 138.1, 135.4, 135.2, 135.1, 132.3, 132.2, 131.6, 130.2, 129.6, 128.8, 128.7, 128.5, 128.0, 125.5, 121.4, 119.8, 113.8, 88.6, 88.5, 68.0, 62.3, 14.6, 14.0, 12.5; ^{19}F NMR (376 MHz, CDCl_3) δ -138.97 (m), -145.34 (m), -146.88 (m). HRMS (ESI-TOF): m/z calc for $\text{C}_{64}\text{H}_{55}\text{N}_6\text{O}_3\text{F}_6$ $[\text{M}+\text{NH}_4]^+$; 1093.45403; found 1093.45519.

Trimer 6b. ^1H NMR (500 MHz, CDCl_3) δ 8.04 (d, J = 16.0 Hz, 2H), 7.93 (d, J = 7.8 Hz, 2H), 7.71 – 7.38 (m, 12H), 7.31 – 7.06 (m, 10H), 5.70 (s, 2H), 5.66 (s, 2H), 4.59 (s, 2H), 2.43 (s, 6H), 2.42 (s, 6H), 1.45 (s, 6H), 1.36 (s, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.7, 155.6, 152.2, 145.8, 142.9, 139.6, 139.2, 138.3, 136.9, 136.2, 134.4, 132.7, 132.6, 131.6, 131.5, 131.0, 130.2, 129.8, 129.0, 128.9, 128.7, 128.5, 128.2, 128.1, 127.0, 123.0, 122.3, 121.5, 114.8, 98.3, 82.0, 68.3, 62.5, 14.8, 14.0, 13.0. ^{19}F NMR (376 MHz, CDCl_3) δ -140.12 (m), -146.94 (m), -147.99 (m). HRMS (ESI-TOF): calc for $\text{C}_{76}\text{H}_{67}\text{B}_3\text{F}_6\text{N}_7\text{O}$ $[\text{M}+\text{NH}_4]^+$; 1240.55942; found 1240.56160.

Trimer 7. ^1H NMR (500 MHz, CDCl_3) δ 8.00 (dd, J = 8.1, 1.2 Hz, 2H), 7.80 (d, J = 16.4 Hz, 2H), 7.65 – 7.52 (m, 3H), 7.43 (tdd, J = 7.6, 5.0, 1.3 Hz, 3H), 7.38 – 7.21 (m, 10H), 7.16 – 7.03 (m, 7H), 6.71 (d, J = 16.4 Hz, 2H), 6.04 (s, 2H), 6.02 (s, 2H), 5.33 (s, 4H), 4.57 (s, 2H), 2.62 (s, 6H), 2.61 (s, 6H), 1.38 (s, 6H), 1.37 (s, 6H), 1.26 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 155.3, 151.0, 143.8, 142.2, 140.1, 139.8, 139.0, 138.2, 135.8, 135.4, 134.4, 134.0, 132.8, 132.6, 131.5, 130.9, 129.8, 129.6, 129.0, 128.7, 128.4, 128.0, 127.5, 126.1, 123.0, 122.5, 121.4, 121.3, 62.3, 53.6, 14.8, 14.0, 13.9. HRMS (ESI-TOF) m/z calcd for $\text{C}_{78}\text{H}_{69}\text{B}_3\text{F}_6\text{N}_{12}\text{NaO}$ $[\text{M}+\text{Na}]^+$; 1359.58244, found: 1359.57729.

Trimer 8. ^1H NMR (500 MHz, CDCl_3) δ 7.80 – 7.66 (m, 3H), 7.61 – 7.19 (m, 31H), 7.04 (d, J = 16.5 Hz, 2H), 5.97 (s, 2H), 5.93 (s, 2H), 5.47 (s, 4H), 4.70 (s, 2H), 2.54 (s, 6H), 2.51 (s, 6H), 1.27 – 1.22 (m, 18H); ^{13}C NMR (125 MHz, CDCl_3) δ : 156.8, 156.5, 151.7, 142.7, 142.4, 142.1, 140.8, 138.8, 138.7, 137.8, 136.6, 133.6, 132.8, 132.7, 132.6, 130.9, 130.6, 130.2, 129.9, 129.4, 128.9, 128.7, 128.6, 128.4, 127.6, 124.4, 122.1, 121.8, 118.6, 62.2, 51.2, 14.7, 14.0, 12.4. HRMS (ESI-TOF) m/z calcd for $\text{C}_{78}\text{H}_{70}\text{B}_3\text{F}_6\text{N}_{12}\text{O}$ $[\text{M}+\text{H}]^+$; 1337.60050, found: 1337.60301.

Pentamer 9. ^1H NMR (500 MHz, CDCl_3) δ 7.96 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 16.4 Hz, 2H), 7.70 – 7.60 (m, 1H), 7.51 (dtd, J = 10.6, 7.7, 1.6 Hz, 4H), 7.45 – 7.30 (m, 8H), 7.26 (s, 10H), 7.21 – 7.15 (m, 1H), 7.10 (s, 2H), 7.06 (dd, J = 7.6, 1.4 Hz, 2H), 7.00 – 6.94 (m, 2H), 6.65 (s, 1H), 6.62 (s, 1H), 5.99 (s, 2H), 5.96 (s, 2H), 5.83 (d, J = 2.3 Hz, 4H), 5.17 (d, J = 4.3 Hz, 4H), 4.64 (s, 2H), 2.55 (s, 12H), 2.36 (s, 12H), 1.23 – 1.27 (m, 30H). ^{13}C NMR (125 MHz, CDCl_3) δ : 156.5, 156.4, 155.4, 151.1, 143.4, 143.0, 142.8, 141.9, 139.7, 139.4, 138.4, 138.2, 135.5, 134.6, 134.1, 133.5, 132.9, 132.5, 131.3, 130.9, 130.0, 129.9, 129.6, 129.5, 129.2, 128.7, 128.6, 128.5, 128.1, 125.9, 123.7, 122.3, 121.7, 121.2, 121.1, 62.3, 50.4, 14.6, 14.3, 13.9, 13.8, 13.7, 12.2. HRMS (ESI-TOF) m/z calcd for $\text{C}_{104}\text{H}_{95}\text{B}_5\text{F}_{10}\text{N}_{16}\text{NaO}$ $[\text{M}+\text{Na}]^+$; 1851.81289, found: 1851.81945.

Hexamer 10. ^1H NMR (400 MHz, CDCl_3) δ 8.47 (d, J = 16.3 Hz, 4H), 8.16 (d, J = 8.0 Hz, 4H), 7.88 (d, J = 16.3 Hz, 5H), 7.63 (m, 4H), 7.57 – 7.46 (m, 4H), 7.47 – 7.37 (m, 3H), 7.12 – 6.97 (m, 2H), 5.97 (s, 4H), 5.95 (s, 4H), 4.37 (t, J = 6.0 Hz, 2H), 4.05–4.12 (m, 4H), 3.46 (s, 2H), 3.45 (s, 2H), 2.55 (s, 12H), 2.53 (m, 12H), 1.40–1.35 (m, 36H) ^{13}C NMR (125 MHz, CDCl_3) δ : 166.2, 155.7, 152.4, 149.3, 149.0, 146.2, 143.3, 139.8, 135.6, 135.3, 132.1, 131.5, 130.2, 129.6, 128.8, 125.5, 121.4, 119.7, 113.8, 110.0, 88.8, 81.4, 58.8, 41.7, 14.6, 14.0, 12.5. HRMS (ESI-TOF) m/z calcd for $\text{C}_{129}\text{H}_{110}\text{B}_6\text{F}_{12}\text{N}_{14}\text{O}$ $[\text{M}+\text{H}]^+$; 2164.95073, found: 2164.95431

Photophysical properties. Spectroscopic properties were registered in diluted solutions (around 2×10^{-6} M), prepared by adding the corresponding solvent (spectroscopic grade) to the residue from the adequate amount of a concentrated stock solution in acetone, after vacuum evaporation of this solvent. UV-Vis absorption spectra were recorded on a Varian model CARY 4E spectrophotometer, whereas the fluorescence and excitation spectra, as well as the decay curves were registered in an Edinburgh Instruments spectrofluorimeter (model FLSP 920). Fluorescence quantum yields (ϕ) were obtained using as reference commercial cresyl violet ($\phi^r = 0.54$ in methanol), for the long-wavelength emission of the energy acceptor, and commercial PM546 ($\phi^r = 0.81$ in methanol) to account for the green, and quenched emission owing to energy transfer, of the energy donor subunit. The values were corrected by the refractive index of the solvent. Radiative decay curves were registered with the time correlated single-photon counting technique using a multichannel plate detector with picosecond time-resolution. Fluorescence emission was monitored at the maximum emission wavelength after excitation by means of a wavelength-tunable Fianium Supercontinuum laser. The fluorescence lifetime (τ) was obtained after the deconvolution of the instrumental response signal from the recorded decay curves by means of an iterative method. The decay curve was essentially the same regardless of the excited visible absorption band. The goodness of the exponential fit was controlled by statistical parameters (χ^2 -square and the analysis of the residuals). The radiative (k_r) and non-radiative (k_{nr}) rate constants were calculated from the fluorescence quantum yield and lifetime; $k_{fl} = \phi/\tau$ and $k_{nr} = (1-\phi)/\tau$.

Quantum mechanical calculations. Ground state geometries were optimized at the Density Functional Theory (DFT) using range-separated hybrid wB97XD method. The vertical Franck-Condon electronic transition was predicted by the Time Dependent (TD) method and the same functional. In both cases the double valence basis set with one polarization functions (6-31g*) was used owing to the large size of the computed multichromophoric molecules. The geometries were considered as energy minimum when the corresponding frequency analysis did not give any negative value. The solvent effect (cyclohexane) was considered in the conducted theoretical simulations by means of the Polarizable Continuum Model (PCM). All the calculations were performed using the Gaussian 16 software as implemented in the computational cluster "arina" of the UPV/EHU.

Laser properties. Laser efficiency was evaluated from concentrated solutions (milimolar) of dyes in ethyl acetate contained in 1-cm optical-path rectangular quartz cells carefully sealed to avoid solvent evaporation during experiments. The liquid solutions were transversely pumped with 8 mJ, 8 ns FWHM pulses from the third harmonic (355 nm) or the second harmonic (532 nm) of a Q-switched Nd:YAG laser (Lotis TII 2134) at a repetition rate of 1 Hz. The exciting pulses were line-focused onto the cell using a combination of positive and negative cylindrical lenses ($f = 15$ cm and $f = -15$ cm, respectively) perpendicularly arranged. The plane parallel oscillation cavity (2 cm length) consisted of a 90% reflectivity aluminium mirror acting as back reflector, and the lateral face of the cell acting as output coupler (4% reflectivity). The pump and output energies were detected by a GenTec powermeter. The photostability of the dyes in ethyl acetate solution was evaluated by using a pumping energy and geometry exactly equal to that of the laser experiments. We used spectroscopic quartz cuvettes with 0.1 cm optical to allow for the minimum solution volume ($V_s = 40 \mu\text{L}$) to be excited. The lateral faces were grounded, whereupon no laser oscillation was obtained. Information about photostability was obtained by monitoring the decrease in laser-induced fluorescence (LIF) intensity. In order to facilitate comparisons independently of the experimental conditions and sample, the photostability figure of merit was defined as the accumulated pump energy absorbed by the system (E_{dose}), per mole of dye, before the output energy

falls to a 50% its initial value. In terms of experimental parameters, this energy dose, in units of GJ mol^{-1} , can be expressed as:

$$E_{\text{dose}}^{50\%} (\text{GJ} \cdot \text{mol}^{-1}) = \frac{E_{\text{pump}} (\text{GJ}) \cdot (1 - 10^{-\epsilon CL}) \cdot \sum \frac{f}{\text{\#pulses}}}{CV_s} \quad (1)$$

where E_{pump} is the energy per pulse, C is the molar concentration, ϵ is the molar absorption coefficient in units of $\text{M}^{-1} \text{cm}^{-1}$, L is the depth of the cuvette expressed in cm, V_s is the solution volume, in litres, within the cuvette, and f is the ratio between the LIF intensity after #pulses and the LIF intensity in the first pulse. To speed up the experiment the pump repetition rate was increased up to 15 Hz. The fluorescence emission and laser spectra were monitored perpendicular to the exciting beam, collected by an optical fiber, and imaged onto a spectrometer (Acton Research corporation) and detected with a charge-coupled device (CCD) (SpectraMM: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. The estimated error in the energy and photostability measurements was 10%.Details.

Acknowledgements

We gratefully acknowledge the Spanish *Ministerio de Economía y Competitividad* for financial support (projects CTQ2015-66702-R, MAT2017-83856-C3-1-P and 3-P). We also thank the *Ministerio de Ciencia Innovación y Universidades* (project RTI2018-094862-B-I00) and the *Gobierno Vasco* for financial support (project IT912-16) and for a predoctoral fellowship to E. A.-Z. The authors thank SGiker of UPV/EHU for technical support with the computational calculations, which were carried out in the "arina" informatic cluster.

Keywords: Red-emitting materials • all-BODIPY multichromophores • photostability • lasers • energy transfer

- [1] a) M. Vendrell, D. Zhai, J. C. Er, Y. T. Chang, *Chem. Rev.* **2012**, *112*, 4391; b) S. van de Linde, M. Sauer, *Chem. Soc. Rev.* **2014**, *43*, 1076; c) A. J. C. Kuehne, M. C. Gather, *Chem. Rev.* **2016**, *116*, 12823; d) P. Murto, A. Minotto, A. Zampetti, X. Xu; M. R. Andersson, F. Cacialli, E. Wang, *Adv. Opt. Mater.* **2016**, *4*, 2068; e) Y. Zhang, S. Xia, M. Fang, W. Mazi, Y. Zeng, T. Johnston, A. Pap, R. L. Luck, H. Liu, *Chem. Commun.* **2018**, *54*, 7625; f) S. Zhu, Z. Rui, R. Tian, B. C. Yung, Q. Yang, S. Zhao, D. O. Kiesewetter, G. Niu, H. Sun, A. L. Antaris, X. Chen, *Adv. Mater.* **2018**, *30*, 1802546; g) E. Oliveira, E. Bértolo, C. Nuñez, V. Pilla, H. M. Santos, J. Fernandez-Lodeiro, A. Fernandez-Lodeiro, J. Djafari, J. L. Capelo, C. Lodeiro, *ChemistryOpen* **2018**, *7*, 9; h) C. Staudinger, J. Breininger, I. Klimant, S. M. Borisov, *Analyst* **2019**, *144*, 2393.
- [2] a) M. Grossi, M. Morgunova, S. Cheung, D. Scholz, E. Conroy, M. Terrile, A. Panarella, J. C. Simpson, W. M. Gallagher, D. F. O'Shea, *Nat. Commun.* **2016**, *7*, 10855; b) X. Wu, Y. Zhang, K. Takle, O. Bilsel, Z. Li, H. Lee, Z. Zhang, D. Li, W. Fan, C. Duan, E. M. Chan, C. Lois, Y. Xiang, G. Han, *ACS Nano*, **2016**, *10*, 1060; c) J. Liu, Y.-Q. Sun, H. Zhang, H. Shi, Y. Shi, W. Guo, *ACS Appl. Mater. Interfaces*, **2016**, *8*, 22953; d) Y. Zhang, S. A. Autry, L. E. McNamara, S. T. Nguyen, N. Le, P. Brogdon, D. L. Watkins, N. I. Hammer, J. H. Delcamp, *J. Org. Chem.* **2017**, *82*, 5597; e) D. Pfeifer, I. Klimant, S. M. Borisov, *Chem.-Eur. J.* **2018**, *24*, 10711; f) A. Adamow, L. Sznitko, E. Chrzumnicka, J. Stachera, A. Szukalski, T. Martynski, J. Mysliwiec, *Sci. Rep.* **2019**, *9*, 2143.

- [3] a) L. Yuan, W. Lin, K. Zheng, L. He, W. Huang, *Chem. Soc. Rev.* **2013**, 42, 622; b) Q. Zheng, M. F. Juette, S. Jockusch, M. R. Wassermann, Z. Zhou, R. B. Altman, S. C. Blanchard, *Chem. Soc. Rev.* **2014**, 43, 1044; c) Z. Yao, L. Yang, Y. Cai, C. Yan, M. Zhang, N. Cai, X. Dong, P. Wang, *J. Phys. Chem. C*, **2014**, 118, 2977; d) A. Dessi, M. Calamante, A. Mordini, M. Peruzzini, A. Sinicropi, R. Basosi, F. Fabrizi, M. Taddei, D. Colonna, A. Di Carlo, G. Reginato, L. Zani, *Chem. Commun.* **2014**, 50, 13952; e) T. Kowada, H. Maeda, K. Kikuci, *Chem. Soc. Rev.* **2015**, 44, 4953; f) D. Wu, A. C. Sedgwick, T. Gunnalaugsson, E. U. Akkaya, J. Yoon, T. D. James, *Chem. Soc. Rev.* **2017**, 46, 7105; g) Z. Gao, Y. Hao, M. Zheng, Y. Chen, *RSC Adv.* **2017**, 7, 7604; h) Z. Lei, X. Li, X. Luo, H. He, J. Zheng, X. Qian, Y. Yuag, *Angew. Chem. Int. Ed.* **2017**, 129, 3025; i) C. Schwechheimer, F. Röncke, U. Schepers, H. A. Wagenknecht, *Chem. Sci.* **2018**, 9, 6557; j) S. Basu, L. M. Needham, D. Lando, E. J. R. Taylor, K. J. Wohlfahrt, D. Shah, W. Boucher, Y. L. Tan, L. E. Bates, O. Takchenko, J. Cramard, B. C. Lagerholm, C. Eggeling, B. Hendrich, D. Klenerman, S. F. Lee, E. D. Laue, *Nat. Commun.* **2018**, 9, 2520.
- [4] a) A. Loudet, K. Burgess, *Chem. Rev.* **2007**, 107, 4891; b) G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem. Int. Ed.* **2008**, 47, 1184; c) R. Ziessel, G. Ulrich, A. Harriman, *New. J. Chem.* **2007**, 31, 496; d) A. Treibs, F.-H. Kreuzer, *Liebigs Ann. Chem.* **1968**, 718, 208–223.
- [5] a) A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y. Chung, K. Burgess, *Chem. Soc. Rev.* **2013**, 42, 77; b) J. Fan, M. Hu, P. Zhan, X. Peng, *Chem. Soc. Rev.* **2013**, 42, 29; c) A. Bessette, G. S. Hanan, *Chem. Soc. Rev.* **2014**, 43, 3342; d) J. Zhao, J. K. Xu, W. Yang, Z. Wang, F. Zhong, *Chem. Soc. Rev.* **2015**, 44, 8904; e) Y. Ge, D. F. O'Shea, *Chem. Soc. Rev.* **2016**, 45, 3846; g) J. Bañuelos, *Chem. Rec.* **2016**, 16, 355.
- [6] a) Y. Cakmak, E. U. Akkaya, *Org. Lett.* **2009**, 11, 85; b) V. Lakshmi, R. Rao, M. Ravikanth, *Org. Biomol. Chem.* **2015**, 13, 2501; c) N. Boens, B. Verbelen, W. Dehaen, *Eur. J. Org. Chem.* **2015**, 6577; d) C. F. A. Gomez-Duran, I. Esnal, I. Valois-Escamilla, A. Urias-Benavides, J. Bañuelos, I. Lopez Arbeloa, I. Garcia-Moreno, E. Peña-Cabrera, *Chem.–Eur. J.* **2016**, 22, 1048.
- [7] a) V. Lakshmi, R. Sharma, M. Ravikanth, *Rep. Org. Chem.* **2016**, 6, 1; b) H. Lu, J. Mack, Y. Yang, Z. Shen, *Chem. Soc. Rev.* **2014**, 43, 4778.
- [8] a) I. J. Arroyo, R. Hu, G. Merino, B. Z. Tanag, E. Peña-Cabrera, *J. Org. Chem.* **2009**, 74, 5719; b) K. Tram, H. Yan, H. A. Jenkins, S. Vassiliev, D. Bruce, *Dyes Pigm.* **2009**, 82, 392; A. Schmitt, B. Hinkeldey, M. Wild, G. Jung, *J. Fluoresc.* **2009**, 19, 755.
- [9] a) W. Wu, J. Zhao, H. Guo, J. Sun, S. Ji, Z. Wang, *Chem.–Eur. J.* **2012**, 18, 1961 (compound **3a**); D. Zhang, Y. Wang, Y. Xiao, S. Qian, X. Qian, *Tetrahedron* **2009**, 65, 8099 (compound **3b**).
- [10] L. Huang, X. Cui, B. Therrien, J. Zhao, *Chem.–Eur. J.* **2013**, 19, 14742.
- [11] W. Yang, A. Karatay, J. Zhao, J. Song, L. Zhao, Y. Xing, C. Zhang, C. He, H. G. Yaglioglu, M. Hayvali, A. Elmali, B. Küçüköz, *Inorg. Chem.* **2015**, 54, 7492.
- [12] a) O. Buyukcakil, O. A. Bozdemir, S. Kolenen, S. Erbas, E. U. Akkaya, *Org. Lett.* **2009**, 11, 4644; b) D. Frath, J. Massue, G. Ulrich, R. Ziessel, *Angew. Chem. Int. Ed.* **2014**, 53, 2290; c) L. Jiao, Y. Wu, S. Wang, X. Hu, P. Zhang, C. Yu, K. Cong, Q. Meng, E. Hao, M. G. H. Vicent, *J. Org. Chem.* **2014**, 79, 1830; d) N. L. Bill, J. M. Lim, C. M. Davis, S. Bähring, J. O. Jeppesen, D. Kim, J. L. Sessler, *Chem. Commun.* **2014**, 50, 6758; e) C. Cheng, N. Gao, C. Yu, Z. Wang, J. Wang, E. Hao, Y. Wei, X. Mu, Y. Tian, C. Ran, L. Jian, *Org. Lett.* **2015**, 17, 278; f) C. F. A. Gomez-Duran, I. Esnal, I. Valois-Escamilla, A. Urias-Benavides, J. Bañuelos, I. Lopez-Arbeloa, I. Garcia-Moreno, E. Peña-Cabrera, *Chem.–Eur. J.* **2016**, 22, 1048.
- [13] a) S. P. Singh, T. Gayathri, *Eur. J. Org. Chem.* **2014**, 22, 4689; b) L. Luo, D. Wu, W. Li, S. Zhang, Y. Ma, S. Yan, J. You, *Org. Lett.* **2014**, 16, 6080; c) C. Yu, L. Jiao, P. Zhang, Z. Feng, C. Cheng, Y. Wei, X. Mu, E. Hao, *Org. Lett.* **2014**, 16, 3048; d) C. Cheng, N. Gao, C. Yu, Z. Wang, J. Wang, E. Hao, Y. Wei, X. Mu, Y. Tian, C. Ran, L. Jiao, *Org. Lett.*, **2015**, 17, 278; e) S. Debnath, S. Singh, A. Bedi, K. Krishnamoorthy, S. S. Zade, *J. Phys. Chem. C* **2015**, 119, 15859; f) C. Maeda, T. Todaka, T. Ema, *Org. Lett.* **2015**, 17, 3090; g) S. Yamazawa, M. Nakashima, Y. Suda, R. Nishiyabu, Y. Kubo, *J. Org. Chem.* **2016**, 81, 1310; h) Z. Zhou, J. Zhou, L. Gai, A. Yuan, Z. Shen, *Chem. Commun.* **2017**, 53, 6621; i) A. Savoldelli, Q. Meng, R. Paolesse, F. R. Fronczek, K. M. Smith, M. G. H. Vicente, *J. Org. Chem.* **2018**, 83, 6498; j) Y. Li, Z. Qiao, T. Li, O. Zeika, K. Leo, *ChemPhotoChem* **2018**, 2, 1017; k) J. L. Belmonte-Vazquez, E. Avellanal-Zaballa, E. Enriquez-Palacios, L. Cerdan, I. Esnal, J. Bañuelos, C. Villegas-Gomez, I. Lopez-Arbeloa, E. Peña-Cabrera, *J. Org. Chem.* **2019**, 84, 2523.
- [14] I. Garcia-Moreno, D. Zhang, A. Costela, V. Martin, R. Sastre, Y. Xiao, *J. Appl. Physics* **2010**, 107, 073105.
- [15] a) T. Bura, P. Retailleau, R. Ziessel, *Angew. Chem., Int. Ed.* **2010**, 49, 6659; b) A. Bozdemir, S. Erbas-Cakmak, O. O. Ekiz, A. Dana, E. U. Akkaya, *Angew. Chem., Int. Ed.* **2011**, 50, 10907; c) R. Ziessel, G. Ulrich, A. Haefele, A. Harriman, *J. Am. Chem. Soc.* **2013**, 135, 11330; d) J. Fan, M. Hu, P. Zhan, X. Peng, *Chem. Soc. Rev.* **2013**, 42, 29; e) D. Su, J. Oh, S. C. Lee, J. M. Lim, S. Sahu, X. Yu, D. Kim, Y. T. Chang, *Chem. Sci.* **2014**, 5, 4812; f) M. A. H. Alamiry, A. Harriman, A. Haefele, R. Ziessel, *ChemPhysChem* **2015**, 16, 1867; g) A. Harriman, *Chem. Commun.* **2015**, 51, 11745; h) C. Azarias, R. Russo, L. Cupellini, B. Mennucci, D. Jacquemin, *Phys. Chem. Chem. Phys.* **2017**, 19, 6443; i) L. Lin, X. Lin, H. Guo, F. Yang, *Org. Biomol. Chem.* **2017**, 15, 6006; j) G. Reddy, N. Duvva, S. Seetharaman, F. D'Souza, L. Giribabu, *PhysChemChemPhys* **2018**, 20, 27418.
- [16] a) L. Cerdan, E. Enciso, V. Martin, J. Bañuelos, I. Lopez-Arbeloa, A. Costela, I. Garcia-Moreno, *Nat. Photonics* **2012**, 6, 621; b) G. Duran, A. R. Agarrabeitia, I. Garcia-Moreno, L. Gartzia, S. de la Moya, J. Bañuelos, I. Lopez Arbeloa, M. J. Ortiz, *Chem. Commun.* **2015**, 51, 11382; c) E. Avellanal-Zaballa, G. Duran-Sampedro, A. Prieto-Castañeda, A. R. Agarrabeitia, I. Garcia-Moreno, I. Lopez-Arbeloa, J. Bañuelos, M. J. Ortiz, *Phys. Chem. Chem. Phys.* **2017**, 19, 13210.
- [17] a) C. Y. Lee, O. K. Farha, B. J. Hong, A. A. Sarjeant, S. T. Nguyen, J. T. Hupp, *J. Am. Chem. Soc.* **2011**, 133, 15858; b) A. Meares, A. Satraitis, N. Santhanam, Z. Yu, M. Ptaszek, *J. Org. Chem.* **2015**, 80, 3858; c) G. Hu, R. Liu, E. J. Alexy, A. K. Mandal, D. F. Bocian, D. Holten, J. S. Lindsey, *New J. Chem.* **2016**, 40, 8032; d) M. D. Weber, V. Nikolaou, J. E. Wittmann, A. Nikolaou, P. A. Angaridis, G. Charalambidis, C. Stangel, A. Kahnt, A. G. Coutsolelos, R. D. Costa, *Chem. Commun.* **2016**, 52, 1602; e) A. N. Kursunlu, *RSC Adv.* **2014**, 4, 47960; f) H. R. A. Golf, A. M. Oltmanns, D. H. Trieu, H.-U. Reissig, A. Wiehe, *Eur. J. Org. Chem.* **2015**, 4224.
- [18] a) S. Guo, L. Ma, J. Zhao, B. Kucukoz, A. Karatay, M. Hayvali, H. G. Yaglioglu, A. Elmali, *Chem. Sci.* **2014**, 5, 489; b) V. Bandi, F. P. D'Souza, H. B. Gobeze, F. D'Souza, *Chem.–Eur. J.* **2015**, 21, 2669; c) S. Kumar, H. Gobeze, T. Chatterje, F. D'Souza, M. Ravikanth, *J. Phys. Chem. A*, **2015**, 119, 8338; d) S. Kumar, K. G. Thorat, M. Ravikanth, *J. Org. Chem.* **2017**, 82, 6568.
- [19] a) M. Galletta, F. Puntoriero, S. Campagna, C. Chiorboli, M. Quesada, S. Goeb, R. Ziessel, *J. Phys. Chem. A* **2006**, 110, 4348; b) J. Bañuelos, F. Lopez-Arbeloa, T. Arbeloa, S. Salleres, F. Amat-Guerri, M. Liras, I. Lopez-Arbeloa, *J. Phys. Chem. A* **2008**, 112, 10822; c) C. Dumas-Verdes, F. Miomandre, E. Lepicier, O. Galangau, T. T. Vu, G. Clavier, R. Meallet-Renault, P. Audebert, *Eur. J. Org. Chem.* **2010**, 2525; d) F. Puntoriero, F. Nastasi, S. Campagna, T. Bura, R. Ziessel, *Chem.–Eur. J.* **2010**, 16, 8832; e) M. T. Whited, P. I. Djurovich, S. T. Roberts, A. C. Durrell, C. W. Schlenker, S. E. Bradforth, M. E. Thompson, *J. Am. Chem. Soc.* **2011**, 133, 88; f) T. Lazarides, S. Kuhri, G. Charalambidis, M. K. Panda, D. M. Guldi, A. G. Coutsolelos, *Inorg. Chem.* **2012**, 51, 4193; g) Q. Hualme, E. Cece, A. Mirloup, R. Ziessel, *Tetrahedron Lett.* **2014**, 55, 4953; h) S. Diring, F. Puntoriero, F. Nastasi, S. Campagna, R. Ziessel, *J. Am. Chem. Soc.* **2009**, 131, 6108; i) J. Iehl, J.-F. Nierengarten, A. Harriman, T. Bura, R. Ziessel, *J. Am. Chem. Soc.* **2012**, 134, 988; j) T. Bura, F. Nastasi, F. Puntoriero, S. Campagna, R. Ziessel, *Chem.–Eur. J.* **2013**, 19, 8900; k) L. Huang, X. Cui, B. Therrien, J. Zhao, *Chem.–Eur. J.* **2013**, 19, 17472.
- [20] All-BODIPY based systems have been studied: a) X. Zhang, Y. Xiao, X. Qian, *Org. Lett.* **2008**, 10, 29; b) G. Barin, M. D. Yilmaz, E. U. Akkaya,

- Tetrahedron Lett.* **2009**, *50*, 1738; c) O. A. Bozdemir, Y. Cakmak, F. Sozmen, T. Odzemir, A. Siemiarczuk, E. U. Akkaya, *Chem.-Eur. J.* **2010**, *16*, 6346; d) Y. Xiao, D. Zhang, X. Qian, A. Costela, I. Garcia-Moreno, V. Martin, M. E. Perez-Ojeda, J. Bañuelos, L. Garztia, I. Lopez-Arbeloa, *Chem. Commun.* **2011**, *47*, 11513; d) P. Bonaccorsi, M. C. Aversa, A. Baratucci, T. Papalia, F. Puntoriero, S. Campagna, *Chem. Commun.* **2012**, *48*, 10550; e) T. M. Khan, M. S. Shaik, M. Ravikanth, *Dyes Pigments* **2012**, *94*, 66; f) R. Sharma, H. B. Gobeze, F. D'Souza, M. Ravikanth, *ChemPhysChem* **2016**, *17*, 2516.
- [21] a) S. K. Mamidyala, M. G. Finn, *Chem. Soc. Rev.* **2010**, *39*, 1252; b) M. Galibert, P. Dumy, D. Boturyn, *Angew. Chem. Int. Ed.* **2009**, *48*, 2576; M. Meldal, C. W. Tornøe, *Chem. Rev.* **2008**, *108*, 2952.
- [22] J. E. Moses, A. D. Moorhouse, *Chem. Soc. Rev.* **2007**, *36*, 1249.
- [23] a) M. R. Martinez-Gonzalez, A. Urias-Benavides, E. Alvarado-Martínez, J. C. Lopez, A. M. Gómez, M. del Rio, I. Garcia, A. Costela, J. Bañuelos, T. Arbeloa, I. Lopez Arbeloa, E. Peña-Cabrera, *Eur. J. Org. Chem.* **2014**, 5659; b) M. L. Lepage, A. Mirloup, M. Ripoll, F. Stauffert, A. Bodlener, R. Ziessel, P. Compain, *Beilstein J. Org. Chem.* **2015**, *11*, 659–667.
- [24] Styryl-BODIPY derivatives have proven to be remarkable near-IR emitting fluorophores.: for the first example of a monostyryl BODIPY, see: a) K. Kurack, M. Kollmannsberger, J. Daub, *Angew. Chem. Int. Ed.* **2001**, *40*, 385; for the first example of a distyryl BODIPY see: Z. Dost, S. Atilgan, E. U. Akkaya, *Tetrahedron* **2006**, *62*, 8484.
- [25] J. C. Lopez, M. del Rio, A. Oliden, J. Bañuelos, I. Lopez-Arbeloa, I. Garcia-Moreno, A. M. Gomez, *Chem.-Eur. J.* **2017**, *23*, 17511.
- [26] M. Del Rio, F. Lobo, J. C. Lopez, A. Oliden, J. Bañuelos, I. Lopez-Arbeloa, I. Garcia-Moreno, A. M. Gomez, *J. Org. Chem.* **2017**, *82*, 1240.
- [27] E. Deniz, G. C. Isbasar, O. A. Bozdemir, L. T. Yildirim, A. Siemiarczuk, E. U. Akkaya, *Org. Lett.* **2008**, *10*, 3401.
- [28] A seminal approach to all-BODIPY chromophores based on the chemoselective Knoevenagel condensation of a pivotal formyl 4,4'-dialkynylboron BODIPY dye with 8-aryl-1,3,5,7-tetramethyl BODIPY derivatives had been described by Ziessel's group. In this process, the selectivity of the "crossed" condensation over the "self-Knoevenagel condensation" had been ascribed to a reactivity-reduction of the C-3, C-5 methyl groups in the former, induced by the sterical congestion around the boron center, see reference 15a, and also: A. Mieloup, P. Retailleau, R. Ziessel, *Tetrahedron Lett.* **2013**, *54*, 4456.
- [29] M. Kitamura, T. Koga, M. Yano, T. Okauchi, *Synlett* **2012**, 1335.
- [30] L. Cerdán, A. Costela, I. García-Moreno, J. Bañuelos, I. López Arbeloa, *Laser Phys. Lett.* **2012**, *9*, 426

Entry for the Table of Contents

FULL PAPER

All-BODIPY based arrays provide red-emitting materials with one of the lowest threshold as well as the highest efficiency and photostability ever reported under strong pumping conditions. Our synthetic approach provide cornerstones paving the rational design of modern fluorophores for advanced (bio)-photonic applications.

Edurne Avellanal-Zaballa, Juan Ventura, Leire Gartzia-Rivero, Jorge Bañuelos*, Inmaculada García-Moreno, Clara Uriel, Ana M. Gómez* and J. Cristobal Lopez*

Page No. – Page No.

Towards Efficient and Photostable Red-Emitting Photonic Materials Based on Symmetric all-BODIPY-Triads, -Pentads, and -Hexads