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## Ultrafast Energy Transfer in Triptycene-Grafted Bodipy Scaffoldings\*\*

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Abstract: A series of new compounds in which various Bodipy dyes are grafted logically on triptycene rigid structures are synthesized and characterized, and their absorption spectra and photophysical properties are studied, also by pump-probe transient absorption spectroscopy. The studied compounds are: the mono-Bodipy species TA, TB, and TC (where A, B, and C identify different Bodipy subunits absorbing and emitting at different wavelengths), the multichromophore species TA<sub>3</sub>, which bears three identical A subunits, and the three multichromophoric species TAB, TBC, and TABC, all of them containing at least two different types of Bodipy subunits. The triptycene moiety plays the role of a rigid scaffold, keeping the various dyes at predetermined distances and allowing

#### Introduction

Multichromophoric species have been extensively investigated in the last decades.<sup>[1]</sup> These species are interesting for solar energy conversion purposes, because suitably designed multichromophore assemblies can play the role of light-harvesting antenna components for artificial photosynthesis (i.e., direct solar fuels production),<sup>[2]</sup> and in dye-sensitized solar cells (i.e., for conversion of solar light into electricity).<sup>[3]</sup> Moreover, multichromophoric species featuring photoinduced energy transfer between donor and acceptor sub-

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- [\*\*] Bodipy = difluoroborondipyrromethene.
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for a three-dimensional structural arrangement of the multichromophoric species. The absorption spectra of the multichromophoric Bodipy species are essentially additive, indicating that negligible inter-chromophoric interaction takes place at the ground state. Luminescence properties and transient absorption spectroscopy indicate that a very fast (on the picosecond time scale) and efficient photoinduced energy transfer occurs in all the multi-Bodipy species, with the lower-energy Bodipy subunits of each multi-Bodipy compounds playing the role of an electronic energy collector. In TAB, an

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energy transfer from the A-type Bodipy subunit to the B-type one takes place with a rate constant of  $1.6 \times$  $10^{10} \text{ s}^{-1}$ , whereas in TBC an energy transfer from the B-type Bodipy subunit to the C-type subunit is bi-exponential, exhibiting rate constants of  $1.7 \times 10^{11}$  and  $1.9 \times 10^{10} \text{ s}^{-1}$ ; the possible presence of different conformers with different donor-acceptor distances in this bichromophoric species is proposed to cause the bi-exponential energy-transfer process. Interpretation of the intricate energy-transfer pathways occurring in TABC is made with the help of the processes identified in the bichromophoric compounds. In all cases, the measured energy-transfer rate constants agree with a Förster mechanism for the energy-transfer processes.

units are of interest for the design of luminescence sensors in biological systems when a large wavelength separation between the exciting light pulse and the analyzing light signal is required.<sup>[4]</sup>

Recently, Bodipy dyes (i.e., difluoroborondipyrromethene species, also named bora-indacene) have emerged as efficient and tunable light-absorption and luminescent species.<sup>[5-9]</sup> As a consequence, multi-Bodipy systems have been prepared and extensively investigated.<sup>[10-12]</sup> In particular, these studies have provided useful information on various aspects of intercomponent energy transfer in multichromophoric assemblies, such as external modulation of energy transfer processes<sup>[13]</sup> and the effect of appropriate alignment of transition dipole moment vectors on the energy transfer efficiency,<sup>[14]</sup> and have uncovered limitations of simplified Förster theories in predicting energy transfer rate constants for fixed geometries<sup>[15]</sup> and visualizing nanomechanical properties of molecular-scale bridges.[16]

Various pre-organized platforms have been scrutinized for the connection of Bodipy dyes. Direct linkage of Bodipy dyes or linking through an unsaturated spacer form basically 1D systems.<sup>[11,13]</sup> Two-dimensional systems are more planar and are constructed around soluble truxene scaffoldings<sup>[10]</sup> or flat Bodipy as the central core.<sup>[17]</sup> The use of 3D plat-

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**Abstract in French:** Une nouvelle séries de sondes Bodipy ont été construites sur une plateforme triptycene T préalablement fonctionnalisée. L'approche synthétique a consistée à construire d'abord un triptycene modifié avec trois Bodipy identiques TA<sub>3</sub> et à sélectivement transformer les unités existantes en des composés ayant des couleurs différentes (A, B, et C). De nombreux composés modèles ont ainsi pu être préparés tels que TA, TB, TC, TAB, TBC. La molécule cible TABC possède un ensemble de chromophores capable de transférer leur énergie sur la sonde de plus basse énergie et ses processus en cascade permettent de concentrer les photons sur un émetteur unique localisé à basse énergie. Le spectre d'absorption individuelle des quatre modules démontrant une faible interaction dans l'état fondamental. Les transferts d'énergie sont extrêmement rapides (picoseconde) et ont été étudiés par absorption transitoire. Plus précisément dans

démontrant une faible interaction dans l'état fondamental. Les transferts d'énergie sont extrêmement rapides (picoseconde) et ont été étudiés par absorption transitoire. Plus précisément dans le modèle TAB le transfert d'énergie de A vers B a lieu en 60 ps tandis que le transfert de B vers C dans TBC se fait en 6 et 50 ps. La présence de différents conformères a été invoquée pour expliquer le déclin bi-exponentiel. L'interprétation des phénomènes de transfert d'énergie dans TABC a été faite à l'aide des composés modèles et donne une image réaliste de l'ensemble des processus impliqués lors d'une irradiation. L'ensemble de ces données sont en accord avec un transfert d'énergie par résonnance lié à une superposition spectrale de l'émission du donneur et de l'absorption de l'accepteur (théorie de Förster). Ces résultats montrent les progrès réalisables dans la concentration de photons et la monochromatisation de la lumière dans des molécules tridimensionnelles.

Abstract in Italian: E' stata sintetizzata e caratterizzata una nuova famiglia di antenne costituite da diversi frammenti cromoforici Bodipy ancorati su un core tripticenico. Sono stati studiati i loro spettri di assorbimento e le loro proprietà fotofisiche, anche tramite spettroscopia pump-probe di assorbimento transiente. Oltre ai sistemi multicromoforici TAB, TBC, e TABC (A, B, e C identificano differenti subunità Bodipy, che assorbono ed emettono a diversa energia) sono state preparate e studiate sia le specie modello monocromoforiche TA, TB e TC sia la specie multicromoforica TA<sub>3</sub>, contenente tre Bodipy identici. Il frammento tripticenico ha il ruolo fondamentale di permettere un arrangiamento topologicamente controllato e rigido, nelle tre dimensioni, dei diversi cromofori. Gli spettri di assorbimento delle specie multicromoforiche sono essenzialmente additivi, indicando che allo stato fondamentale l'interazione intercromoforica è trascurabile. Le proprietà di luminescenza e la spettroscopia di assorbimento transiente hanno messo in evidenza che in tutti i sistemi multicromoforici investigati si verificano processi di trasferimento di energia elettronica fotoindotti, particolamente efficenti e veloci (nella scala temporale dei ps) verso la subunità a più bassa energia (trappola di energia) di ciascun sistema multi-Bodipy. In particolare, nel sistema TAB il trasferimento di energia dalla subunità di tipo A a quella di tipo B avviene con una costante di velocità pari a  $1.6 \times 10^{10} \, \text{s}^{-1}$ , mentre in TBC il trasferimento da B a C è biesponenziale, con costanti di velocità pari a  $1.7 \times 10^{11}$  e  $1.9 \times 10^{10}$  s<sup>-1</sup>. Tale comportamento potrebbe essere razionalizzato grazie alla presenza, per tale specie, di diversi conformeri con differenti distanze donatore accettore. I risultati ottenuti per i sistemi bicromoforici hanno permesso di interpretare le complesse dinamiche di decadimento degli stati eccitati caratteristiche della specie multicromoforica TABC. Per tutte le specie investigate, i risultati ottenuti sperimentalmente sono in accordo con un meccanismo di trasferimento energetico fotoindotto di tipo Förster.



forms is less common and some examples are focused on dendrimers<sup>[18]</sup> and fullerenes.<sup>[19]</sup> This is the reason why triptycene, a 3D rigid structure, caught our attention. Triptycene belongs to the family of iptycene and consists of three phenyl rings separated by a saturated [2.2.2]biclyclooctatriene bridgehead framework.<sup>[20]</sup> This 3D-shape-persistent structure has several interesting applications in the field of: 1) molecular machines (e.g., gyroscopes, compasses,<sup>[21]</sup> brakes,<sup>[22]</sup> or ratchets<sup>[23]</sup>), due to restricted rotation of the molecule preventing interdigitation; 2) molecular balances<sup>[24]</sup> for evaluation of  $\pi$ - $\pi$  and other non-covalent interactions; 3) material sciences, such as polymers and liquid crystals for large internal free volumes providing large porosity for gas absorption;<sup>[25]</sup> and 4) crystal engineering in host-guest supramolecular chemistry.<sup>[26]</sup> The rigid triptycene core also has applications in coordination chemistry, catalysis for stabilizing highly reactive intermediates<sup>[27]</sup> and sterically bent complexes,<sup>[28]</sup> and electrophosphorescence.<sup>[29]</sup> Furthermore, electron and energy transfer in rigid triptycene-bipyridine metal complexes<sup>[30]</sup> and in porphyrin-based dyads and triads for charge separation<sup>[31]</sup> has also been investigated. Studies on triptycene-bridged donors/acceptors have demonstrated that electronic interactions occur through the  $\sigma$ -bridged system,<sup>[32]</sup> and that no homoconjugation effect is present in the  $\pi$ -conjugated oligomers.<sup>[33]</sup>

Herein, we report the synthesis, characterization, and study of the absorption spectra and photophysical properties (including pump-probe transient absorption spectroscopy) of a new series of compounds in which various Bodipy dyes are grafted on a preorganized triptycene rigid structure. The triptycene moiety plays the role of a rigid scaffold, keeping the various dyes at predetermined distances. The compounds whose spectroscopic and photophysical properties have been investigated are: the mono-Bodipy species TA, TB, and TC (for simplicity, the Bodipy subunits contained are named A, B, and C, respectively, in descending order based on their excited-state energy), the multichromophoric species TA<sub>3</sub>, which contains three identical A subunits, and the three multichromophoric species TAB, TBC, and TABC, all of which contain at least two different types of Bodipy subunits (see Schemes 1-3 for their structural formulas). The results indicate that very fast and efficient energy transfer takes place in all the multi-Bodipy species studied here. Comparison of the energy-transfer rate constants with those reported in the literature for some selected multi-Bodipy species have also been made.

## **Results and Discussion**

**Synthesis:** The pivotal compound 2,6,14-triiodotriptycene (T), was synthesized in three steps from commercially available triptycene according to a procedure previously described by Zhang and Chen (Scheme S1 in the Supporting Information).<sup>[34]</sup> First, triptycene was reacted with nitric acid while heating at reflux to give 2,6,14- and 2,7,14-trinitrotriptycene (64 and 21% yield, respectively). These two re-

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Scheme 1. Preparation of the Bodipy subunits A, B, and C. i) [Pd(PPh\_3)<sub>2</sub>Cl<sub>2</sub>], CuI, trimethylsilylacetylene Et<sub>3</sub>N, C<sub>6</sub>H<sub>6</sub>, 50 °C, 18 h; ii) MeOH, K<sub>2</sub>CO<sub>3</sub>, RT.

gioisomers were separated by column chromatography on silica gel with an appropriate solvent and were unambiguously characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Indeed, the <sup>13</sup>C NMR spectrum of the symmetrical isomer 2,7,14-trinitrotriptycene shows only six signals for the aromatic carbon atoms (as expected for a C3 symmetry), whereas the derivative 2,6,14-trinitrotriptycene exhibits eleven signals, as found for T. Reduction of the trinitro derivative by using Pd(10%)/C and  $H_2$  gave the corresponding triaminotriptycene in 90% yield. Finally, a Sandmeyer reaction under standard conditions provided the 2,6,14-triiodotriptycene (T) in 55% yield. The three different modules A, B, and C were prepared as shown in Scheme 1.

The ethynyl function was grafted on the iodophenyl derivative by a cross-coupling reaction with trimethylsillylacetylene and promoted by in situ prepared Pd<sup>0</sup> precursors. Afterwards, the trimethylsilyl (TMS) group was deprotected by using K<sub>2</sub>CO<sub>3</sub> in methanol to afford the desired module with excellent yields in each case (Scheme 1). Cross-coupling of these modules to the preorganized platform T provided the reference dyes TA, TB, and TC in expected yields for a statistical cross-coupling reaction with three reactive functions (Scheme 2). The side products of double and triple crosscoupling reactions were not isolated.

Likewise, cross-coupling between TB and A, or TC and B gave the TAB and TBC dyads in 37 and 20% yield, respectively. Again, the side products TA2B and TB2C were not isolated. Unfortunately, the final compound TABC could not be isolated by reacting TBA or TBC with dyes C or A, respectively, due to the presence of an intractable mixture of compounds.

After some trials, the best way to prepare the target TABC started from the triply substituted dye TA<sub>3</sub> by using regioselective Knoevenagel reactions. The first condensation between  $TA_3$ and paramethoxyeth-

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#### oxyethoxybenzaldehyde

(1 equiv) gave compound  $TA_2B$ in a respectable yield of 24%. Here the polarity and solubility imported by the ethyleneglycol chain facilitated the purification process. This was clearly observed by the color of the reaction mixture, which turned magenta rather than deep-blue, as would be expected by formation of a double vinyl function on the same Bodipy core.<sup>[35]</sup> This was further confirmed by proton NMR spectroscopy, in which a new singlet at  $\delta =$ 6.84 ppm (1 H) for the  $\beta$ -pyrrolic proton (labeled e; see Scheme 3 for the proton assignment) is in close proximity to

the vinyl function, compared to the singlet at  $\delta = 6.13$  ppm (5H) for the other  $\beta$ -pyrrolic protons.<sup>[36]</sup> Note that for TA<sub>3</sub> a single signal is found at  $\delta = 6.13$  ppm (protons b, 6H; Figure 1A). Confirmation of the single substitution was obtained by dissymmetrization of the singlets at  $\delta = 1.45$  and 2.50 ppm (for  $TA_3$ ), which were assigned to the methyl groups a, c and d (Figure 1B). All other signals for the ethyleneglycol chain and the phenyl rings are in keeping with this statement.

Finally, the condensation of TA<sub>2</sub>B with the bis-bipyridine aldehyde 8 allowed the preparation of the multichromophoric target dye TABC in 19% yield (Scheme 3); again, the condensation was regioselective, causing monovinyl derivatization on a second tetramethyl-Bodipy side. This serendipitous discovery is likely due to the stronger acidity of the methyl groups of the tetramethyl-Bodipy group with respect to a monovinyl methyl group. It is not excluded that steric congestion might also be part of the reason for selective monocondensation on each site. Proton NMR spectroscopy was again used for the characterization of the final structure. In particular, two additional singlets are observed at  $\delta =$ 6.80 ppm (1 H), assigned to the  $\beta$ -pyrrolic proton (g), and at  $\delta = 6.07$  ppm (1 H), assigned to the  $\beta$ -pyrrolic proton (b"; Figure 1 C). In parallel, the methyl signals are split according to the multiplicity expected by the dissymmetrization of the structure (inset in Figure 1C). The de-shielded bipyridine proton and ethyleneglycol proton signals are in keeping with the step-by-step monofunctionalization. Interestingly, the C-H bridgehead protons 9 and 10 are weakly split ( $\delta =$ 5.88 and 5.89 ppm) in case of TABC, whereas they resonate as singlets at  $\delta = 5.87$  ppm in the model compounds TA<sub>2</sub>B and TA<sub>3</sub> (Figure 1C).

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Scheme 2. Preparation of the multichromophoric species TAB and TBC. i)  $[Pd(PPh_3)_4]$ , diisopropylamine (DIPA),  $C_6H_6$ , 70 °C 18 h; ii) toluene, piperidine, *p*-TsOH (Ts=tosyl), 140 °C.

**Absorption spectra**: The absorption spectra of the studied compounds in the solvents used (acetonitrile (AN) and 1,2-dichloroethane (DCE)) are dominated by the absorption of the Bodipy subunits, as expected, because the triptycene moieties do not absorb significantly in the visible region and their UV absorption is not comparable with the molar absorption of the Bodipy unit. All the absorption spectra data are collected in Table 1, and Figures 2 and 3 show the absorption spectra of representative compounds in DCE. The absorption spectra of representative compounds in AN are shown in the Supporting Information (Figure S25 in the Supporting Information).

For the mono-Bodipy species, the absorption spectrum of TA, essentially due to the absorption of its Bodipy subunit A, is at a maximum at about  $\lambda = 500$  nm, the absorption spectrum of TB, essentially due to its Bodipy subunit B, peaks at about  $\lambda = 580$  nm, and the absorption spectrum of TC, mainly due to the Bodipy chromophore C, is at a maximum at about  $\lambda = 605$  nm. In all cases, the visible absorption of the compounds is assigned to Bodipy-centered spin-al-

lowed  $\pi$ - $\pi$ \* transitions; however, a significant charge-transfer (CT) character is expected to be present in the lowerenergy band of TC.<sup>[5,10,13]</sup>

The absorption spectra of the multiple Bodipy-decorated, triptycene-based compounds are essentially the superposition of the absorption of the individual chromophoric subunits, indicating the supramolecular nature of the multiple-Bodipy species (i.e., multicomponent species made of electronically weakly coupled units). Each chromophore maintains its individual absorption properties in the multicomponent assemblies. This is exemplified by the comparison between the absorption spectra of TA and TA<sub>3</sub>, which essentially differ by three times more intense visible bands of the latter, due to the presence of multiple A-type chromophores (Table 1). It can be noted that because of the complementarity of the absorption spectrum of the individual dyes, compound TABC efficiently absorbs over a broad part of the whole visible spectrum ( $\lambda = 380-680$  nm).





Figure 1. Proton NMR spectra of a)  $TA_3$ , b)  $TA_2B$ , and c) TABC in  $[D_6]$  actone. For the sake of clarity, the spectra have been cut below  $\delta = 3.2$  ppm. The insets in dashed lines are expansions of the methyl region.

Luminescence properties: All the compounds exhibit intense Bodipy-based emissions, which, in the multi-Bodipy species, mainly involves the singlet  $\pi - \pi^*$  excited state of the Bodipy unit with its excited state at the lowest energy. However, less-intense emission bands at higher energies also appear in all multi-Bodipy compounds except TA<sub>3</sub>, for which excitation is performed at wavelengths corresponding to the absorption of the high-energy Bodipy components. Table 1 shows the luminescence data of the compounds at room temperature in acetonitrile and DCE. Figures 4 and 5 display the emission spectra of most of the compounds in DCE. Emission spectra of other representative compounds are reported in the Supporting Information (Figure S26 in the Supporting Information).

Let us start our discussion from the species containing only one type of Bodipy dye. From the data in Table 1, it is clear that for the species containing the A and B Bodipy chromophores-that is, TA, TA<sub>3</sub>, and TB-passing from acetonitrile to DCE solution only has a small effect on the absorption and emission band energies; this agrees with the essentially pure  $\pi$ - $\pi$ \* nature of the corresponding transitions. Also, the emission quantum yields and lifetimes are

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essentially solvent-independent for TA, TA<sub>3</sub>, and TB within experimental uncertainty. On the contrary, for TC, which contains the Bodipy dye C, the lowestenergy absorption band is weakly solvent dependent but the emission spectrum is significantly blue-shifted on passing from acetonitrile to DCE; in fact, the emission maximum (Table 1) moves from  $\lambda =$ 705 nm (acetonitrile) to  $\lambda =$ 665 nm (DCE). This agrees with the already-mentioned significant CT character of the corresponding electronic transition, with the N,N'-bis(bipyridyl)-aminophenyl group playing the role of the electron-donor subunit and the Bodipy moiety acting as the electron acceptor, as is already known for this and similar subunits in analogous species.<sup>[5,10-13]</sup> Because acetonitrile is a more polar solvent than DCE, the CT excited state is more stabilized in acetonitrile and therefore the emission spectrum is significantly sensitive to the solvent polarity. The large red-shift of the emission in acetonitrile also suggests the presence of noticeable nuclear reorganization in the CT state

in polar solvents before emission. The nature of the solvent also affects the emission lifetime of TC (Table 1), which is reduced in acetonitrile in comparison to DCE; because the emission quantum yield is essentially constant on moving from acetonitrile to DCE, it can be concluded that both the non-radiative and the radiative decay rate constant are larger in acetonitrile than in DCE for this compound.

Let us move to the multichromophoric species containing different types of Bodipy dyes. For the compounds TAB and TBC, in both acetonitrile and DCE solutions the dominant emission band (at about  $\lambda = 585$  nm for TAB and at  $\lambda = 705$ or 665 nm for TBC depending on the solvent, see the discussion above for TC) is clearly due to the excited state of the lowest-energy Bodipy subunit (see Figures 4 and 5) at any excitation wavelength.<sup>1</sup>The wavelength of the minor emission components at higher energy (namely, at  $\lambda = 510$  nm for TAB and at about  $\lambda = 590$  nm for TBC), whose lifetimes are close to the detection limit of our equipment (140 ps), indi-

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<sup>&</sup>lt;sup>1</sup> For any excitation wavelengths here—as well as in other parts of this paper-we refer to excitation performed at wavelengths corresponding to the absorption bands of the various Bodipy components on multi-Bodipy species.



Scheme 3. Preparation of the multichromophoric species TABC. i) Toluene, piperidine, p-TsOH, 140°C.

cate that such high-energy emission corresponds to the emission of the higher-energy Bodipy units in each multichromophoric species (Table 1). These are assigned to partially quenched higher-energy Bodipy chromophores present in the multi-Bodipy species.

As far as TABC is concerned, the emission spectrum of this compound (Figure 5 c) in both acetonitrile and DCE solutions is dominated by the emission of the C-based chromophore at any excitation wavelength. However, upon excitation at wavelengths shorter than  $\lambda = 500$  nm, the emission spectrum also shows a small component at  $\lambda = 510$  nm, corresponding to the partially quenched excited state of the A-type subunit, with an apparent lifetime (e.g., 140 ps in acetonitrile) coincident with the experimental limit. A non-negligible emission from the B-type dye is also present at  $\lambda = 580$  nm, but its lifetime cannot be recorded with our apparatus.

Similarly to what is reported in the literature for other multi-Bodipy species,<sup>[5,10-15]</sup> quenching of the higher-energy Bodipy subunits in TAB, TBC, and TABC is attributed to an energy transfer to the lower-energy Bodipy subunits. Excitation spectra confirm this attribution. As an example, the

excitation spectrum of TABC is shown in the inset of Figure 5 c; it is clear that emission at  $\lambda = 680$  nm, mainly involving the lower-lying C subunit, is also contributed from excitation centered in the A and B chromophores.

Because the lifetimes of the partially quenched emission components in the multicomponent species are less reliable (in all cases they are too close to our equipment limit), calculations of the energy-transfer rate constants cannot be made on the basis of the emission data. Comments on interchromophore energy transfer rate constants are therefore demanded to transient absorption spectroscopy results (see later).

**Pump-probe transient absorption spectroscopy**: The transient absorption spectra of the mono-Bodipy species TA, TB, and TC and of the multi-Bodipy compounds TAB, TBC, and TABC have been investigated in 1,2-dichloroethane at room temperature by using  $\lambda = 400$  nm as the excitation wavelength. All the spectra were investigated after 600 fs from the laser pulse. It was not possible to perform analogous experiments in acetonitrile, because some of the compounds were not stable under laser light in this medium. For

technical problems, excitation at different wavelengths than  $\lambda = 400$  nm was also not available.

Compound TA: The transient spectrum of TA shows a bleach in the region  $\lambda = 460-600$  nm, corresponding to the

Table 1. Absorption and emission data recorded at room temperature.<sup>[a]</sup>

	Absorption	Luminescence		
	$\lambda_{\max} [nm] (\epsilon [M^{-1}cm^{-1}])$	$\lambda_{em}$ [nm]	$\Phi$	τ [ns]
TA	500 (75000)	510	0.55	2.4
	505 (79000)	515	0.60	2.7
TA <sub>3</sub>	500 (225 000)	510		
	505 (235 000)	515	0.59	2.8
TC	602 (75000)	705	0.26	2.0
	609 (99000)	665	0.24	3.8
ТВ	568 (92000)	580	0.99	3.8
	577 (118000)	590	0.99	3.9
TAB	500 (82000)	580, 510	0.99	$3.7^{[b]}$
	568 (92000)			
	505 (91600)	590, 515	0.99	4.1 <sup>[c]</sup>
	577 (118000)			
TBC	568 (128000)	705, 580	0.26	$2.0^{[d]}$
	602 (76000)			
	577 (170000)	665, 590	0.25	3.9 <sup>[e]</sup>
	609 (102 000)			
TABC	501 (87600)	705, 580, 510	0.26	$2.0^{[f]}$
	568 (125700)			
	602 (77400)			
	505 (97000)	665, 599, 515	0.23	3.9 <sup>[g]</sup>
	577 (170 000)			
	609 (102 000)			

[a] For each species, the data in the first row, in italics, are in acetonitrile and the data in the second row, in plain text, refer to 1,2-dichloroethane; compounds are labeled as given in Schemes 2 and 3; excitation was performed at  $\lambda = 408$  nm. [b] A shorter lifetime component was recorded at  $\lambda = 510 \text{ nm}$  (A-based quenched emission). Its apparent value (0.2 ns) is close to the limit of the equipment, so it cannot be considered the real residual lifetime of the A subunit. [c] A shorter lifetime component (0.25 ns) was recorded at  $\lambda = 520$  nm, see also footnote [b]. [d] A shorter lifetime component was recorded at  $\lambda = 580$  nm (B-based quenched emission), see footnote [b]. [e] The reported lifetime was recorded at  $\lambda =$ 640 nm. The lifetime of the emission at  $\lambda = 590$  nm could not be recorded with our equipment. [f] A shorter lifetime component (140 ps) was recorded at 510 nm (A-based quenched emission), see footnote [b]. It was not possible to record a short emission lifetime component at  $\lambda = 580$  nm. [g] This lifetime refers to the  $\lambda = 609$  nm emission. The lifetimes of the emission contributions at  $\lambda = 592$  and 520 nm were under the detection limit of our equipment.



Figure 2. Absorption spectra of TA (-----), TB (-----), and TC (-----) in DCE.



Figure 3. Absorption spectra of TAB (----), TBC (----), and TABC (----) in DCE.



Figure 4. Luminescence spectra of TA (----), TB (----), and TC (----) in DCE at room temperature.



Figure 5. Luminescence spectra of a) TAB, b) TBC, and c) TABC in DCE. Excitation wavelength in all the cases was  $\lambda = 408$  nm. The inset in panel c is the excitation spectrum of TABC, emission wavelength  $\lambda = 680$  nm; its comparison with the absorption spectrum of TABC (Figure 3) confirms an efficient inter-Bodipy energy transfer.

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ground-state absorption at lowest energy (see Figure 6). The transient spectrum seems to directly decay mono-exponentially to the ground state in the time window explored; however, the lifetime of the excited state cannot be measured



Figure 6. Transient absorption spectra of TA.

with care by transient absorption data, as expected, because the upper time limit of our experimental setup (3.2 ns) is comparable to the excited-state lifetime measured by luminescence decay (2.7 ns in DCE).

Compound TB: The transient spectrum of TB exhibits a bleach in the  $\lambda = 550-660$  nm range, with a maximum at about  $\lambda = 575$  nm and transient absorption bands at wavelengths shorter than  $\lambda = 550$  nm and longer than  $\lambda = 670$  nm (Figure 7). Similarly to what was found for TA, even the transient spectrum of TB directly decays to the ground state with an apparent mono-exponential process on a longer



Figure 7. Transient absorption spectra of TB.

time scale than the experimentally investigated window, which is in agreement with the emission lifetime of TB (3.9 ns in DCE).

Compound TC: The initial transient spectrum of TC exhibits a bleach in the region  $\lambda = 580-720$  nm and a transient at  $\lambda < 550$  nm. Contrary to the spectra of TA and TB, the transient spectrum of TC does not decay directly to the ground state, but undergoes a series of successive processes (see Figures 8–10). In the time frame 0.6–2 ps (Figure 8), the bleach at about  $\lambda = 610$  nm is partially recovered and the bleach at wavelengths longer than  $\lambda = 650$  nm increases, suggesting the presence of a transient absorption in the  $\lambda = 600-750$  nm region—partially obscured by the strong bleaching—which is modified in this time range. Isosbestic points at about  $\lambda = 650$  and 575 nm hold during this process, the time constant ( $\tau$ , the reciprocal of the rate constant) of which is about 1 ps, calculated both at  $\lambda = 610$  and at



Figure 8. Transient absorption spectra of TC, shorter time range (see text).



Figure 9. Transient absorption spectra of TC, intermediate time range (see text).



Figure 10. Transient absorption spectra of TC, longer time range (see text).

680 nm. This process, because of the relatively small spectral changes and time regime, is assigned to vibrational relaxation of the initially prepared Franck-Condon state. Successively, within the time range 2-500 ps (Figure 9), the bleach in the region  $\lambda = 630-720$  nm tended to disappear, until a transient peak at about  $\lambda = 650$  nm was clearly formed. For time delays longer than 800 ps from the laser pulse (Figure 10), the transient spectrum decayed mono-exponentially within the available time range without any further spectral change, which is in fair agreement with emission data. The nature of the processes occurring in the time frame 2-500 ps in the excited-state decay of TC was not investigated here; however, it seems likely that the excitedstate decay process of TC deals with some structural rearrangement involving the polypyridine moiety, because the transient absorption spectra of analogous Bodipy species containing the amino group but missing the polypyridine fragments do not exhibit such complex behavior. The intrinsic excited-state decay of TC has to be taken into account when discussing the intercomponent energy transfer processes in the multichromophoric species containing this type of subunit.





Figure 11. Transient absorption spectra of TAB. The inset shows the kinetics of the bleach recovery at  $\lambda = 505$  nm ( $\odot$ ) and the bleach increase at  $\lambda = 578$  nm ( $\diamond$ ). For details, see text.

*Compound TAB*: The bleaches present at about  $\lambda = 505$  and 580 nm in the transient absorption spectrum of TAB are indicative of the simultaneous excitation of the A and B Bodipy dyes, respectively, in TAB (see Figure 11). In the time frame 1-90 ps, the transient absorption spectrum evolves, with the recovery of the bleach at  $\lambda = 505$  nm and a (slight) increase and red-shift of the bleach at about  $\lambda =$ 580 nm. The recovery of the bleach at  $\lambda = 505$  nm indicates the decay of the A-centered excited state, whereas the concomitant changes in the  $\lambda = 580$  nm bleach suggest further production of the B-centered excited state. Isosbestic points remain at about  $\lambda = 660$  and 570 nm. The time constants measured for the spectral changes at  $\lambda = 505$  [(63±10) ps] and 578 nm  $[(62\pm22) \text{ ps}]$  are nearly identical (Figure 11, inset), signaling an energy transfer from the excited state of the A subunit to the excited state of the B subunit of TAB (i.e., T(\*A)B-to-TA(\*B) energy transfer). Then, the produced transient spectrum decays to the ground state with an apparent mono-exponential process, the time domain of which is out of the explored window.

Compound TBC: The initial bleaching at about  $\lambda = 575$  nm and that in the  $\lambda = 600-700$  nm range are taken as signatures of the T(\*B)C and TB(\*C) states, respectively (see Figure 12, compared with Figures 7 and 8). In the time range 330 fs-1.30 ps, the bleaching in the range  $\lambda = 560-640$  nm is partially recovered, whereas the bleaching at



Figure 12. Transient absorption spectra of TBC.

longer wavelengths increases with an isosbestic point kept at  $\lambda = 642$  nm. This process, which occurs with  $\tau = (700 \pm 90)$  fs, appears to be qualitatively similar to the fast decay process

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of TC (see Figure 8), so it is assigned to vibrational relaxation within the C subunit. The successive process involves recovery of the bleach at  $\lambda = 575$  nm coupled with a bleach at a slightly higher wavelength than  $\lambda = 610$  nm (Figure 12, transient absorption spectra between 1.29 and 187 ps). Several isosbestic points hold during this time range, for example at  $\lambda = 702$  nm. This process is biphasic, with a faster component having a time constant of  $(5.8\pm1)$  ps and a slower component having a time constant of  $(52\pm7)$  ps, As the decay of the C-based subunit exhibits components in this time range (see Figure 9), one tends to attribute at least one of these decay components of TBC to an intrinsic decay of the C subunit. However, the spectral changes at  $\lambda = 575$  nm, which are monotonic within the overall 1.3-187 ps range, suggest that decay of the B subunit predominates (note that a B-to-C energy transfer would impose recovery of the bleaching, whereas an intrinsic decay within C would led to an increase of the bleach in this time range, see Figure 9), and the simultaneous increase of the bleach at  $\lambda = 610$  nm supports the attribution of both components to an energy transfer from the excited state of the B subunit to the excited state of the C subunit. The possible presence of two conformers in which the B and C dyes have different inter-chromophoric separation could justify the bi-exponential nature of the energy-transfer process. Once produced, TB(\*C) decays with a complex behavior, analogously to that of T(\*C).

Compound TABC: In the initially formed transient absorption spectrum of this compound (Figure 13), the bleachings at  $\lambda = 505$ , at 575, and in the  $\lambda = 600-700$  nm range can be assumed as signatures for the presence of T(\*A)BC, TA(\*B)C, and TAB(\*C), respectively. To investigate the possible intercomponent energy-transfer processes, it is convenient to analyze the fate of the bleachings at  $\lambda = 575$  and



Figure 13. Transient absorption spectra and normalized kinetic decays of TABC (inset), shorter time range. The focus here is on the energy transfer from the B-centered to the C-centered excited states (see text).

at 505 nm separately. After an initial spectral evolution in the fs time scale (not shown), which appears to be almost at an end after 1 ps  $[(\tau = 720 \pm 100)$  fs] and recalls the fast process occurring in TC and TBC (thus is assigned to vibrational relaxation within the C-based unit), the bleaching at  $\lambda =$ 575 nm, typical of a B-based excited state, is recovered by a

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biphasic process (Figure 13). The faster component has a rate constant of  $(3.3\pm0.2)\times10^{11}$  s<sup>-1</sup> [time constant,  $(3\pm0.4)$  ps]. This process is simultaneous to an increased bleach at  $\lambda = 610$  nm, having the same rate constant (Figure 13, inset). The slower component of the  $\lambda = 575$  nm bleach recovery takes place with a time constant of  $(56\pm6)$  ps (see Figure 14).<sup>2</sup>These processes are very similar, both from a



Figure 14. Transient absorption spectra and normalized kinetic decays of TABC (inset), longer time range. The focus here is on the energy transfer from the B-centered to the C-centered excited states (see text).

spectral viewpoint and as far as time constants are concerned, to the first two processes exhibited by TBC and can be assigned to an energy transfer from TA(\*B)C to TAB(\*C). Bleach recovery at  $\lambda = 505$  nm takes place with a time constant of  $(34\pm4)$  ps and is accompanied by a small increase of the bleach at  $\lambda = 610$  nm (Figure 15). On longer



Figure 15. Transient absorption spectra and normalized kinetic decays of TABC (inset), intermediate time range. The focus here is here on the disappearance of the A-based excited state (see text).

time scales, the prepared TAB(\*C) decays to the ground state with the typical processes already evidenced for TC (spectra not shown).

**Interchromophoric energy transfer in multi-Bodipy species**: From the above-reported transient absorption data, the following conclusions can be summarized and are collected in Table 2:

Table 2. Rate constants (calculated values from Equation (1) and experimental data from transient absorption spectroscopy measurements) of the intercomponent energy-transfer processes occurring in the multi-Bodipy species.<sup>[a]</sup>

	Energy-transfer (involved subunits)	$J_{\rm F}$ [cm <sup>6</sup> ]	$k_{ ext{en}} [ extsf{s}^{-1}]^{[ ext{b}]}$	$[\mathrm{s}^{-1}]^{[\mathrm{c}]}$
ГАВ	$A \rightarrow B$	$4.3 \times 10^{-13}$	$7.4 \times 10^{10}$	$1.6 \times 10^{10}$
ГВС	$B\!\rightarrow\! C^{[d]}$	$6.8 \times 10^{-13}$	$1.6 \times 10^{11}$	$1.7 \times 10^{11}$
				$1.9 \times 10^{10}$
ГАВС	$A \rightarrow B$	as for TAB	as for TAB	assumed as
				for TAB
	$B\!\rightarrow\!C^{[d]}$	as for TBC	as for TBC	$3.3 \times 10^{11}$
				$1.8 \times 10^{10}$
	$A \rightarrow C$	as for TAB	$5.5 \times 10^{10}$	$1.3 \times 10^{10[e]}$

[a] The solvent was 1,2-dichloroethane; for the parameters used in Equation (1), see text. [b] Calculated by using Equation (1). [c] Obtained from the transient absorption data. [d] The B-to-C energy-transfer process is experimentally biphasic, see main text. [e] This is an estimated value, obtained from the difference between the decay of the A-based excited state in TABC and the decay of the corresponding chromophore subunit in TAB, see text.

- 1) Energy transfer from A to B subunits in TAB takes place with  $\tau = 62$  ps (rate constant,  $k_{en} = 1.6 \times 10^{10} \text{ s}^{-1})^3$ .
- 2) Energy transfer from B to C subunits in TBC takes place bi-exponentially with time constants of about 6 and 52 ps (i.e.,  $k_{\rm en} = 1.7 \times 10^{11}$  and  $1.9 \times 10^{10}$  s<sup>-1</sup>, respectively); the possible presence of two conformers of TBC is likely responsible for this biphasic behavior.
- 3) In the multichromophoric TABC species, energy transfer from B to C is quite similar to the corresponding process in TBC, exhibiting time constants of about 3 ps ( $k_{en} = 3.3 \times 10^{11} \text{ s}^{-1}$ ) and 56 ps ( $k_{en} = 1.8 \times 10^{10} \text{ s}^{-1}$ ).
- 4) In TABC, the excited state of A can decay by energy transfer to both B and C. Assuming that the energy transfer from A to B in TABC is identical to that found in TAB—that is, it occurs with  $k_{en} = 1.6 \times 10^{10} \text{ s}^{-1}$ —this assumption must be taken with care because some (although small) kinetic difference between B-to-C energy-transfer processes in TBC and TABC is indeed present. The difference in the time constants for the disappearance of the A-based excited state in TAB (62 ps, see above) and TABC (34 ps) is attributed to a contribution from direct energy transfer from the A subunit to C. Direct energy transfer from A to C in TABC is therefore assumed to occur with a rate constant of about  $k_{en} = 1.3 \times 10^{10} \text{ s}^{-1.4}$  Note that the energy transfer from the A to the

<sup>4</sup> The time constant of 34 ps for the decay of the A-centered excited state in TABC, equivalent to a decay rate constant of  $2.9 \times 10^{10} \text{ s}^{-1}$ , would therefore be factorized into two energy-transfer components, that is, [ $k_{en}$ (A-to-B)+ $k_{en}$ (A-to-C)].

<sup>&</sup>lt;sup>2</sup> The expected concomitant increase of the bleach at  $\lambda = 610$  nm during this slower process is probably balanced by the intrinsic decay of the C-based subunit, which has components in the same time scale. As a consequence, the  $\lambda = 610$  nm bleach is almost constant in this time scale (see insets of Figures 14 and 15).

<sup>&</sup>lt;sup>3</sup> In principle, the rate constant of the energy-transfer process is not given by the reciprocal of the time constant of the decay, because the intrinsic decay of the chromophore also contributes to this later process. However, because the intrinsic decays of the A and B chromophores (i.e., the emission lifetimes of TA and TB) are negligible compared to the excited state decays of the A-based and B-based chromophores in multicomponent species, the rate constants of the intercomponent energy transfer are approximated to the reciprocal of the respective decay time constants for all the energy-transfer processes discussed here.

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B subunit in TABC should be followed by energy transfer from B to C. Because both the components of the energy-transfer process from B to C in TABC are faster than energy transfer from A to B, the intermediate TA(\*B)C in the two-step, cascade energy-transfer pathway from A to C cannot be experimentally proven.



Figure 16. Schematic of the excited states and decay (upon population of the excited state involving the highest-energy Bodipy subunit) of the multi-Bodipy compounds TAB, TBC, and TABC. The asterisk denotes where the excitation is localized in each level. Wavy, dashed lines indicate energy-transfer processes and solid lines indicate radiative decays; radiative decays from higher-energy Bodipy subunits are neglected, as well as radiationless decays to the ground state. Energy-transfer time constants are shown (time constants in the grey background are estimated, not measured, see text). The energy of the excited-state levels are not to scale.

The above discussion is summarized in Figure 16, which shows a schematic of the excited-state levels and decays of the multi-Bodipy species studied here.

In multi-Bodipy systems, inter-Bodipy energy transfer usually takes place through a Förster mechanism.<sup>[5,10–15]</sup> A simplified Förster equation is shown in Equation (1):

$$k_{\rm en}^{\rm F} = 8.8 \times 10^{-25} \frac{K^2 \Phi}{n^4 r_{\rm AB}^6 \tau} J_{\rm F} \tag{1}$$

In Equation (1),  $J_F$  is the Förster overall integral between the luminescence spectrum of the donor,  $F(\bar{V})$ , and the absorption spectrum of the acceptor,  $\varepsilon(\bar{V})$ , on an energy scale (in [cm<sup>-1</sup>]). The expression for  $J_F$  is given in Equation (2), and the  $J_F$  values calculated by this equation for energy transfer from A-to-B, A-to-C, and B-to-C subunits of the multicomponent species studied herein are reported in Table 2.

$$J_{\rm F} = \frac{\int F(\bar{\mathbf{V}})\varepsilon(\bar{\mathbf{V}})/\bar{\mathbf{V}}^4 \mathrm{d}\bar{\mathbf{V}}}{\int F(\bar{\mathbf{V}})\mathrm{d}\bar{\mathbf{V}}}$$
(2)

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In Equation (1), other relevant parameters beside  $J_{\rm F}$  are: n, the refraction index of the medium (for 1,2-dichloroethane, n = 1.4448), K, a statistical orientation factor, usually considered as 2/3 (this is the value we also assumed here, where free rotation of the dyes around the triple-bond axis connecting each dye to the triptycene scaffold is allowed, and some flexibility of the overall systems cannot be excluded),  $\Phi$  and  $\tau$ , the unquenched emission quantum yield and the lifetime of the donor (taken as the emission quantum yields and the lifetimes of the parent TA and TB species, reported in Table 1), and  $r_{AB}$ , the distance (in [Å]) between the donor and acceptor dipoles. The  $r_{AB}$  is probably one of the most difficult parameters to quantify for species in solution. For the multi-Bodipy species studied here, we approximated  $r_{AB}$  to the computed distance between the methene carbon atoms of different chromophores across the triptycene framework (22.9 Å). By using this approximate donoracceptor distance, the rate constants for the Förster energy transfer reported in Table 2 have been obtained. The calculated values have the same order of magnitude as the respective experimental values (for the B-to-C energy-transfer process, the calculated values are compared to the faster rate constant), so, considering the approximation used, Förster energy transfer is assumed to be an effective mechanism for the intercomponent energy-transfer processes in these compounds.

It should be noted that the energy-transfer rate constants measured for the present multi-Bodipy species are close to those obtained for star-shaped multi-Bodipy arrays made of similar Bodipy dyes arranged on a truxene core, also featuring comparable donor-acceptor distances.<sup>[10]</sup> This confirms the structural role of the triptycene scaffold and its "innocent" role-from an electronic point of view-for the inter-Bodipy energy-transfer mechanism (as well as for the truxene scaffold in the formerly studied species), according to the Förster theory. On the contrary, energy-transfer rate constants of one order of magnitude slower have been reported for inter-Bodipy dyes in roughly linear dichromophoric species containing a fluorene spacer, in spite of similar (or slightly smaller) donor-acceptor distances.<sup>[13]</sup> In this latter case, however, the Förster overlap integrals [Eq. (2)] between the donor emission and the acceptor absorption spectra were smaller and therefore probably responsible for the reduced energy-transfer rate constants.

Finally, the bi-exponential energy transfer from the B-centered subunit to the C-centered subunit in TBC and TABC, which is attributed to the existence of more than one conformer, warrants some further comment. We propose a tentative explanation based on the following discussion. Both B and C Bodipy dyes are asymmetric with respect to the main Bodipy framework because they have a single pyrrole ring substituted by a conjugate moiety (see Schemes 1–3). The lower-lying excited states of both B- and C-containing chromophore subunits—which are the excited states involved in the energy-transfer processes—are therefore expected to partially extend over these (conjugated) substituted fragments; this is also supported by the red shift of their absorp-

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tion and emission spectra with respect to those of TA.<sup>5</sup> This suggests that the donor-acceptor distance (and therefore the rate constant) for energy-transfer processes involving B- and C-containing chromophores also depends on the relative orientation of pyrrole-conjugate substituents. Whereas rotation of the A-type Bodipy subunit around the triple bond connecting it to the triptycene central moiety (or rotation of the Bodipy framework with respect to the phenyl ring linked to the triple bond) does not significantly modify the position of this chromophore with respect to the other chromophores in multi-Bodipy assemblies, rotation of the B-type and C-type chromophores around the triple bond connecting them with the triptycene moiety (or with respect to the phenyl ring linked to the triple bond) can substantially change the relative distance between their respective pyrrole substituents in multi-Bodipy species. This can strongly affect the effective donor-acceptor distance  $r_{AB}$ , leading to slower energy-transfer rate constant for TBC and TABC species having particularly distant B and C dyes and to conformers in which the effective through-space donor-acceptor distance-considering that the excited-state dipoles can involve the conjugate pyrrole substituents-can be smaller, so yielding different energy-transfer rate constants.

## Conclusion

A series of new compounds in which various Bodipy dyes are grafted on triptycene rigid structures have been synthesized and characterized, and their absorption spectra and photophysical properties have been investigated. The new compounds also include several multi-Bodipy species, most of them containing different chromophores. Step-by-step grafting of the Bodipy modules A, B, and/or C to the preorganized triptycene platform is feasible with two modules. For the linkage of three different Bodipy dyes leading to TABC, an original strategy was devised based on successive regioselective monosubstitution on a preformed homo-tris-Bodipy dye TA<sub>3</sub>. In the multi-Bodipy species studied here, the triptycene moiety plays the role of a rigid scaffold, keeping the various dyes at predetermined distances and allowing for a three-dimensional structural arrangement of the chromophores, guaranteeing the supramolecular nature of the arrays. The absorption spectra of the multichromophoric Bodipy species are essentially additive, indicating that negligible inter-chromophoric interaction takes place at the ground state, and are dominated by the absorption properties of the individual Bodipy dyes. Luminescence properties and transient absorption spectroscopy indicate that very fast (on the picosecond time scale) and efficient (>90%) photoinduced energy transfer occurs in all the multi-Bodipy species, with the lower-energy Bodipy subunits of each multi-Bodipy compound playing the role of the electronic energy collector. The interpretation of the intricate energy-transfer pathways occurring in the multicomponent TABC species is made with the help of the processes identified in TAB and TBC bichromophoric compounds. In all cases, the measured energy-transfer rate constants agree with a Förster mechanism for the energy-transfer processes.

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## CHEMISTRY

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#### **Bodipy Dyes -**

T. Bura, F. Nastasi, F. Puntoriero, S. Campagna,\* R. Ziessel\*.. **......** 

Ultrafast Energy Transfer in Triptycene-Grafted Bodipy Scaffoldings



Fast, faster, ultrafast: Grafting three identical Bodipy units on a triptycene core allowed regioselective transformation of a single Bodipy through a Knovenagel reaction. The use of two different aromatic aldehydes produced a triptycene platform modified by three different Bodipy dyes. Luminescence properties and transient absorption spectroscopy indicate a fast (ps) stepwise energy transfer from higher- to lower-energy Bodipy units (see figure).