

Efficient Synthesis of Panchromatic Dyes for Energy Concentration

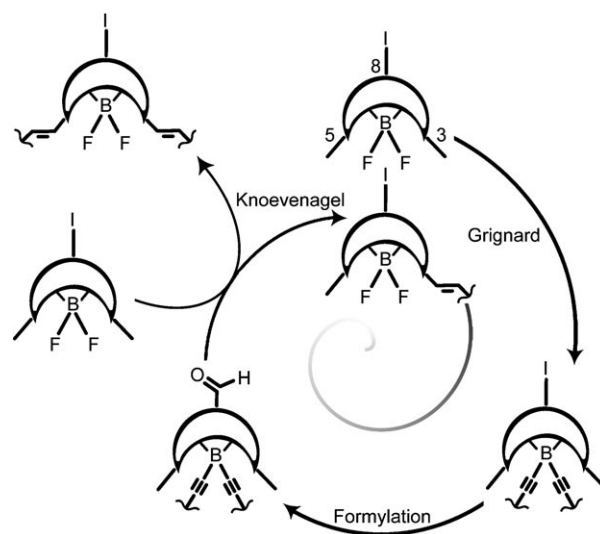
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Energy collection and migration are fundamental aspects of the functioning of both photosynthetic organisms and artificial solar concentrators.^[1,2] In the past decade, many systems based on mimicry of energy concentration in natural systems have been scrutinized.^[3,4] In most cases, their development required tedious multistep synthetic procedures involving masked functionalities, protecting groups, highly reactive intermediates, and toxic residues, which hampered their application.

The synthetic advantages of 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene (Bodipy) rigid cyanine dyes derive from the possibility of controlling the reactivity at the central core (dipyrrromethene) and at the boron atom.^[5] The upsurge of interest in such dyes stems from their pronounced stability, high absorption coefficients, narrow emission profiles, and outstanding emission quantum yields, which reach unity in the best cases.^[6] The numerous applications of Bodipy dyes were recently reviewed.^[5,7]

Herein, we report a novel strategy for the creation of covalently linked dyes in an iterative fashion, whereby each cycle provides an additional module capable of energy transfer. The strategy involves (Scheme 1): 1) substitution at the boron atom of a Bodipy dye with a Grignard reagent; 2) formylation of a phenyliodo residue; 3) a Knoevenagel reaction between methyl groups of another Bodipy unit and the formyl group to provide both divinyl and monovinyl derivatives, which could be used in another sequence of reactions to produce higher oligomers in a controlled fashion. The essence of the strategy is that substitution at boron can be used to control the accessibility of the two methyl groups in the 3,5-positions nearest to the boron center (see compound **1** in Scheme 2).^[8] This strategy avoids self-condensation of the carbaldehyde in the 8-meso position and the methyl residues in the 3,5-positions on the same molecule.

The pivotal formyl dye **3** was prepared by a carboformylation reaction^[9] catalyzed by Pd⁰ with sodium formate as the reductant and a flow of CO under mild conditions (Scheme 2). Under these conditions, no alkyne reduction was observed. This approach appears to be very useful for the



Scheme 1. Iterative approach to the synthesis of multichromophoric dyes.

production of aldehydes without side reactions, even in the presence of vinyl groups (see below).

As anticipated, the reaction of dye **3** with dye **1** provided a mixture of the monovinyl derivative **4a** (magenta) and the bisvinyl derivative **4b** (blue) in good yields (Scheme 2).^[10,11] The ratio of mono- to bisvinyl products can be controlled routinely by the amount of aldehyde **3** used.

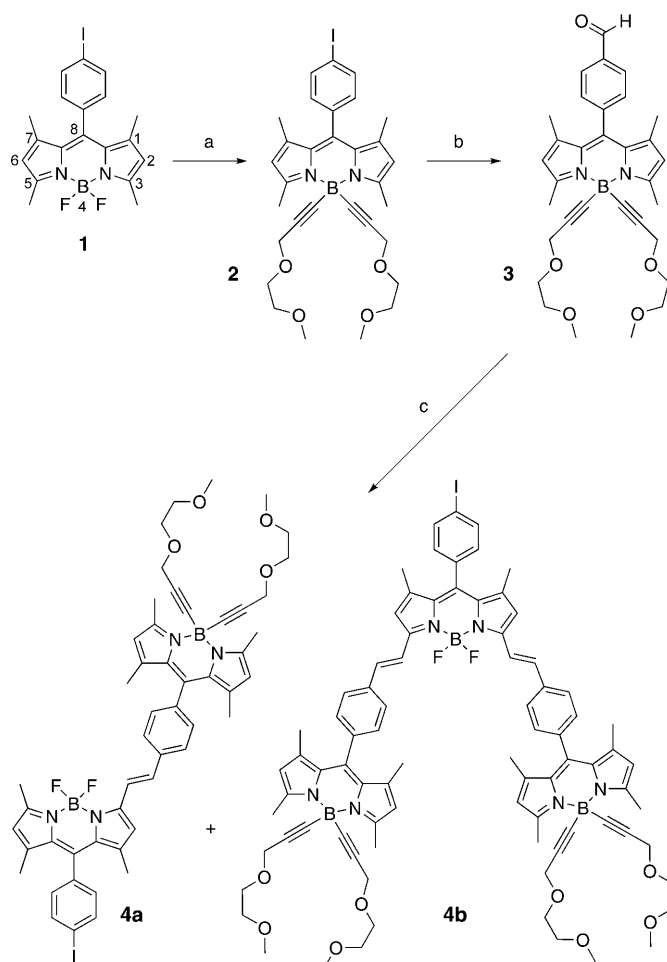
In both cases, the observed proton–proton coupling constant of 16.4 Hz for the vinyl group is in keeping with an *E* conformation of the double bonds, as expected for this type of condensation. Interestingly, there was no evidence for the self-condensation of **3**. The inertness of the methyl groups in this compound for a Knoevenagel condensation is possibly due to the steric crowding caused by the substituents on the boron atom.

Our next objective was the substitution of the iodo group in compound **4a** by a formyl group to repeat the synthesis of vinyl derivatives for the next generation of multichromophoric dyes. Compound **4a** was transformed into compound **6** in a straightforward manner in two steps (Scheme 3). Remarkably, formylation occurred without reduction of the alkene functionality. We prepared compounds **7a** and **7b**, in which three and five colored subunits, respectively, are linked through conjugated bridges, by similar procedures (Scheme 3). Use of an excess of the formyl derivative **6** drove the reaction toward the bisvinyl derivative **7b** preferentially. Under these conditions, **7b** was obtained in up to 75% yield.

The level of Bodipy substitution can be monitored readily on the basis of the ¹H NMR chemical shifts of the β -pyrrolic hydrogen atoms, which resonate at δ = 6.17 ppm in the

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Scheme 2. a) EtMgBr , $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{C}\equiv\text{CH}$, THF, 60°C , 2 h; then **1**, 60°C overnight, 90%; b) $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, DMF, HCOONa (1.1 equiv), CO (1 atm), 90°C , 3 h, 70%; c) **1** (1 equiv), **3** (1.5 equiv), piperidine, toluene, *p*-TsOH (trace amount), 140°C ; **4a**: 33%, **4b**: 66%. DMF = *N,N*-dimethylformamide.

tetramethyl-substituted dye and at $\delta = 6.24$ and 6.91 ppm in the trimethyl-substituted dye (see compound **6** in Scheme 3), and the integration of these signals. The most deshielded hydrogen atom is assigned as that nearest to the vinyl bond. These chemical shifts are similar for **7a** and **7b**. An additional singlet appears at $\delta = 6.99$ ppm for the two β -pyrrolic hydrogen atoms of the dimethyl-substituted Bodipy unit in **7b**.

The X-ray crystal structures of the two compounds **3** and **4a** were determined (Figure 1). In both, the sterically congested boron center adopts an almost tetrahedral geometry, with an N-B-N angle of about 106° and a C-B-C angle of about 112° . The B-C bond lengths range from 1.56 (for **4a**) to 1.59 Å (for **3**), and the ethynyl tethers retain bond lengths typical of triple bonds (ca. 1.19 Å). The bond lengths within each indacene moiety remain characteristic of fully delocalized cyanine units. Deviations from the mean ligand plane (17 atoms including methyl-substituent carbon atoms and the aromatic carbon atom directly attached to the heterocyclic core) range from 0.037 to 0.072 Å, with the usual deviation

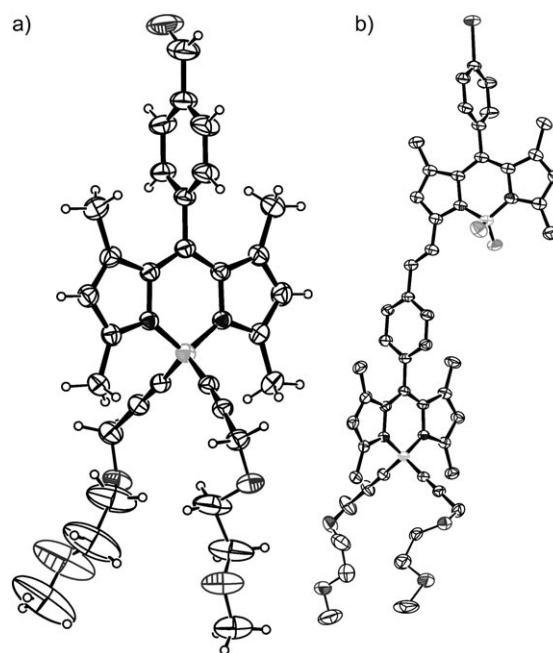
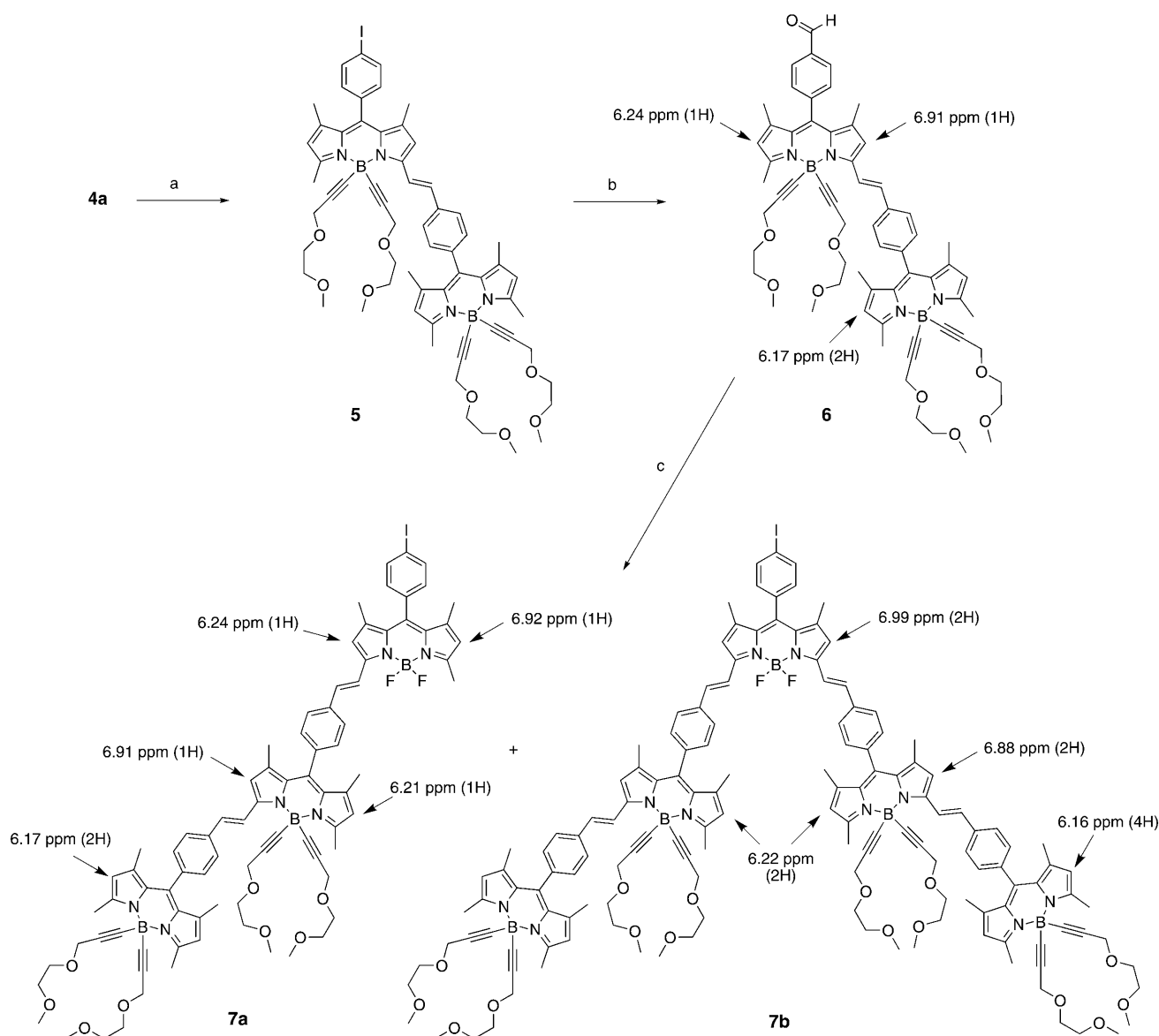


Figure 1. ORTEP views of the X-ray crystal structures of compounds **3** and **4a**. Disordered components with a higher occupancy factor only are displayed. Ellipsoids are drawn at the 30% probability level, H atoms as small spheres of arbitrary radius.

(ca. 0.3 Å) of the boron atom from this plane found in F-Bodipy systems.

In **3**, which has approximate twofold rotational symmetry consistent with the static disorder of the aldehyde group, the indacene core is orthogonally substituted on both sides by the benzaldehyde and the ethyne tether ($\text{C3}'\text{-C2}'\text{-C1}'\text{-B-C1}''\text{-C2}''\text{-C3}''$) moieties (the respective dihedral angles are $87.5(2)$ and $88.5(2)^\circ$). The slight tilt between the mean plane of the phenyl substituent and that described by the ethynyl tethers is $10.1(2)^\circ$. For **4a**, the orthogonality with the core is similar ($84.3(2)$ and $89.7(2)^\circ$, with $5.7(2)^\circ$ between the phenyl and the ethynyl-tether planes). The additional iodophenyl-substituted F-Bodipy group [despite the near orthogonality (dihedral angle: $80.9(2)^\circ$) of its components and only a $9.6(4)^\circ$ tilt between the iodophenyl and F-B-F planes] breaks the apparent twofold symmetry of **3** and leads to a bending of the overall elongated (ca. 30 Å long) superstructure, as characterized by a dihedral angle between the two indacene cores of $64.1(1)^\circ$.

Intense bands in the UV/Vis region of the absorption spectra reflect the presence of the different residues in the final scaffolds: tetramethyl-substituted Bodipy, $\lambda_{\text{abs}} = 502$ nm (red);^[12] trimethyl-substituted Bodipy, $\lambda_{\text{abs}} = 569$ nm (magenta);^[13] and dimethyl-substituted Bodipy, $\lambda_{\text{abs}} = 639$ nm (blue)^[14] (Figures 2 and 3 and Table 1). Prototypical examples of the fluorescence behavior of these compounds are provided by structures **4a** and **4b**, which exhibit intense fluorescence at 578 and 650 nm, respectively, with the absence of residual fluorescence at 513 nm due to the tetramethyl-substituted Bodipy unit. These results demonstrate that the extent of energy transfer from the tetramethyl Bodipy subunit



Scheme 3. a) EtMgBr , $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{C}\equiv\text{CH}$, THF, 60°C , 2 h; then **4a**, 60°C overnight, 52%; b) $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$, DMF, HCOONa (1.1 equiv), CO (1 atm), 90°C , 3 h, 70%; c) **1** (1 equiv), **6** (2 equiv), piperidine, toluene, $p\text{-TsOH}$ (tr), 140°C ; **7a**: 10%, **7b**: 75%. The ^1H NMR chemical shifts of the β -pyrrolic hydrogen atoms are given for compounds **6**, **7a**, and **7b** in $[\text{D}_6]\text{acetone}$.

to the tri- or dimethyl Bodipy is greater than 99%. Energy transfer is promoted by a favorable spectral overlap between the energy donor (tetramethyl-substituted Bodipy) and the energy acceptor (tri- or dimethyl-substituted Bodipy).^[15] The rate of electronic energy transfer (EET) is expected to be very fast: more than $2 \times 10^{10} \text{ s}^{-1}$, as estimated from our resolution limits.

The situation is even more interesting in the next generation of multichromophoric dyes, **7a** and **7b**. In both cases, the absorption corresponds to a linear combination of the three and five modules in **7a** and **7b**, respectively. For **7a** and **7b**, one and two intense intramolecular-charge-transfer bands (ICTB), respectively, were observed around 340 nm (Figure 3). One ICTB band, at 336 nm, corresponds to the two individual styryl moieties of compound **7a** (Figure 3a), the less energetic ICTB band, at 359 nm, to the presence of

the bisstyryl fragment in compound **7b** (Figure 3b). Three well-defined absorption bands corresponding to the singlet absorption of each type of Bodipy moiety were deciphered. Upon excitation at 480 nm, no residual emission of the tetramethyl-substituted Bodipy moiety was detected (also in the case of **4a**, **4b**, **5**, and **6**), whereas a weak emission, which could be assigned unambiguously to residual fluorescence of the trimethyl-substituted Bodipy moiety, was observed at 583 nm.

An estimated rate constant of $1.6 \times 10^8 \text{ s}^{-1}$ was calculated on the basis of the quantum yields for energy transfer from the internal trimethyl-substituted Bodipy moieties in **7b** to the blue dimethyl-substituted Bodipy moieties at the termini with an efficiency of 82% ($k_{\text{EET}} = [(\phi_0/\phi) - 1]/\tau_2$; ϕ_0 is the quantum yield of the unquenched compound **5**, ϕ is the quantum yield of the fragment equivalent to **5** (quenched) in

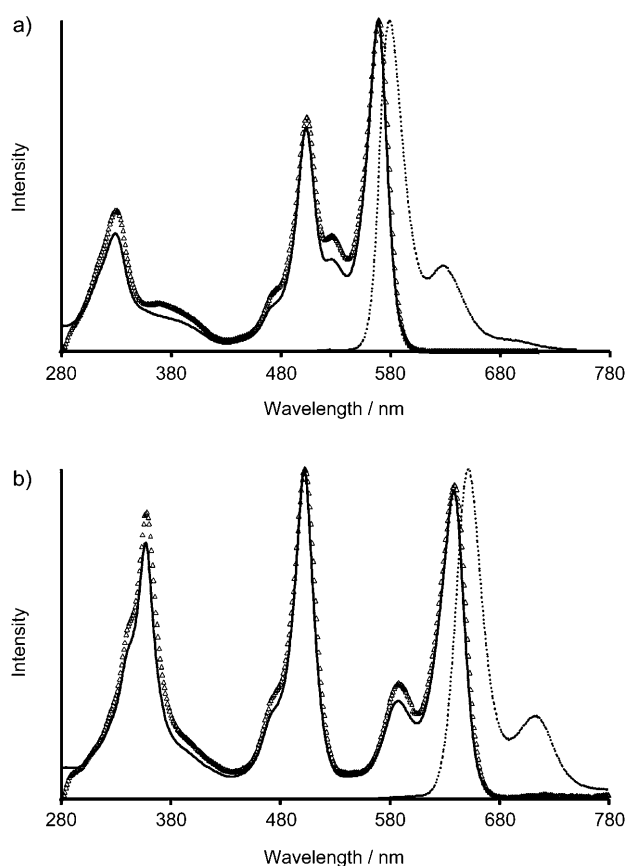


Figure 2. a) Absorption (solid line), emission (dotted line), and excitation spectra (triangles) of a) **4a** and b) **4b**.

molecule **7b**, and τ_2 is the lifetime of the unquenched compound **5**). A similar rate constant of $1.0 \times 10^8 \text{ s}^{-1}$ was calculated on the basis of lifetimes ($k_{\text{EET}} = 1/\tau_2 - 1/\tau_2^*$; τ_2^* is the lifetime of the fragment equivalent to **5** (quenched) in molecule **7b**, and τ_2 is the lifetime of the unquenched compound **5**). As confirmed by the excitation spectra for emission at 652 nm, all the modules participated in the energy-transfer process (Figure 3b). Furthermore, virtual Stokes shifts of about 5500 cm^{-1} were calculated. Thus, multicascade energy transfer from the tetramethyl Bodipy to the trimethyl Bodipy, and finally to the dimethyl Bodipy is very efficient within these linked dyes, and the input energy is efficiently concentrated on a single emitting dye, as observed in bacteria and higher plants.^[17]

In short, we have described a facile and straightforward route to panchromatic fluorescent materials. The key step is the introduction of an aromatic aldehyde group by a smooth and selective carbopalladation reaction with CO and NaHCOO. This carbaldehyde functionality is essential for linking the modules and creating a gradient of energy levels along each lateral arm. The presence of a phenyl fragment in the middle of the starting Bodipy moiety ensures that each linked Bodipy subunit remains electronically isolated. By the excitation of each module, a cascade energy transfer is effective with photons channeled to the dyes localized at the termini. Further chemical modifications at the terminal iodophenyl group can be foreseen. For example, anionic

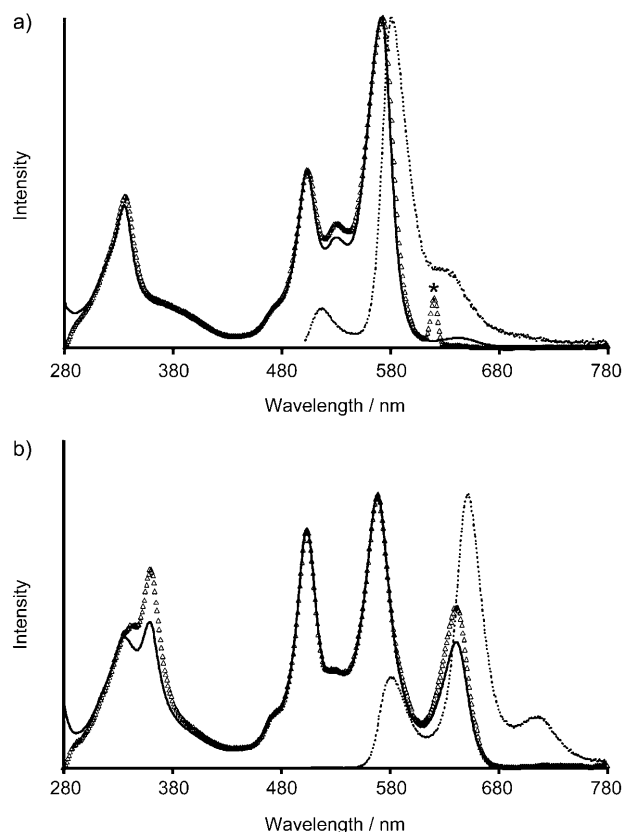


Figure 3. a) Absorption (solid line), emission (dotted line), and excitation spectra (triangles) of a) **7a** and b) **7b**. ★ Emission wavelength.

Table 1: Selected spectroscopic data.

Dye	λ_{abs} [nm]	ϵ [M cm ⁻¹]	λ_{F} [nm]	$\Phi_{\text{F}}^{[a]}$ (λ_{exc} [nm])	$\tau_1^{[b]}$ [ns]	$\tau_2^{[b]}$ [ns]	$\tau_3^{[b]}$ [ns]
2	502	74 000	513	0.55 (480)	5.28	—	—
3	504	80 500	518	0.42 (480)	3.11	—	—
4a	503	90 000	—	—	—	—	—
	569	115 000	578	0.66 (480) 0.68 (550)	—	6.43	—
4b	502	148 000	—	—	—	—	—
	639	137 500	650	0.52 (480) 0.53 (605)	—	—	5.70
5	502	84 000	—	—	—	—	—
	569	108 000	579	0.73 (480) 0.73 (550)	—	6.20	—
6	503	80 000	—	—	—	—	—
	570	104 000	581	0.72 (480) 0.73 (550)	5.54	—	—
7a	503	84 000	517	0.03 (480)	3.00	—	—
	571	157 000	581	0.36 (480) 0.37 (560)	—	3.66	—
7b	503	193 000	—	—	—	—	—
	568	221 000	583	0.10 (480) 0.08 (550)	—	3.83 ^[c]	—
	641	102 000	652	0.47 (480) 0.47 (550)	—	—	5.21
				0.57 (625)	—	—	—

[a] The fluorescence quantum yield was determined in toluene ($\epsilon \approx 1.10 \times 10^{-6} \text{ M}$) at 298 K with Rhodamine 6G as a reference ($\Phi_{\text{F}} = 0.78$ in water, $\lambda_{\text{exc}} = 488 \text{ nm}$).^[16] All Φ_{F} values are corrected for changes in the refractive index. [b] Lifetimes are denoted τ_1 for the tetramethyl-substituted subunit, τ_2 for the trimethyl-substituted subunit, and τ_3 for the dimethyl-substituted subunit. [c] This value corresponds to τ_2^* in the k_{EET} equation.

anchors (acetylacetonate, carboxylic or phosphonic acids) suitable for connecting the energy concentrators to semi-conducting surfaces or mesoporous matter could be grafted to the dyes at this position.^[18] Studies along these lines are in progress.

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- [1] R. E. Blankenship, *Molecular Mechanisms of Photosynthesis*, Blackwell, Oxford, **2002**.
- [2] a) Y. Nakamura, N. Aratani, A. Osuka, *Chem. Soc. Rev.* **2007**, 36, 831–845; b) N. Armaroli, V. Balzani, *Angew. Chem.* **2007**, 119, 52–67; *Angew. Chem. Int. Ed.* **2007**, 46, 52–66.
- [3] a) J. M. Serin, D. W. Brousmiche, J. M. J. Fréchet, *Chem. Commun.* **2002**, 2605–2607; b) T. Weil, E. Reuther, K. Müllen, *Angew. Chem.* **2002**, 114, 1980–1984; *Angew. Chem. Int. Ed.* **2002**, 41, 1900–1904; c) M. Cotlet, T. Vosch, S. Habichi, T. Weil, K. Müllen, J. Hofkens, F. De Schryver, *J. Am. Chem. Soc.* **2005**, 127, 9760–9768.
- [4] a) D. Holten, D. F. Bocian, J. S. Lindsey, *Acc. Chem. Res.* **2002**, 35, 57–69; b) A. Harriman, R. Ziessel in *Carbon-Rich Compounds* (Eds.: M. M. Haley, R. R. Tykwinski), Wiley-VCH, Weinheim, **2006**, pp. 26–89.
- [5] G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem.* **2008**, 120, 1202–1219; *Angew. Chem. Int. Ed.* **2008**, 47, 1184–1201.
- [6] R. P. Haughland, *Handbook of Fluorescent Probes and Research Products*, 9th ed., Molecular Probes, Eugene, **2002**, pp. 36–46.
- [7] A. Loudet, K. Burgess, *Chem. Rev.* **2007**, 107, 4891–4932; see also Ref. [6] for applications of Bodipy dyes.
- [8] a) G. Ulrich, C. Goze, M. Guardigli, A. Roda, R. Ziessel, *Angew. Chem.* **2005**, 117, 3760; *Angew. Chem. Int. Ed.* **2005**, 44, 3694–3698; b) C. Goze, G. Ulrich, R. Ziessel, *J. Org. Chem.* **2007**, 72, 313–322; c) C. Goze, G. Ulrich, R. Ziessel, *Org. Lett.* **2006**, 8, 4445–4448.
- [9] T. Okano, N. Harada, J. Kiji, *Bull. Chem. Soc. Jpn.* **1994**, 67, 2329–2332.
- [10] a) R. P. Haughland, H. C. Kang, US Patent 4,774,339, Sep. 27, **1988**; b) K. Rurack, M. J. Kollmannsberger, J. Daub, *New J. Chem.* **2001**, 25, 289–292; c) Z. Dost, S. Atilgan, E. U. Akkaya, *Tetrahedron* **2006**, 62, 8484–8488; d) S. Atilgan, Z. Ekmekci, A. L. Dogan, D. Guc, E. U. Akkaya, *Chem. Commun.* **2006**, 4398–4400.
- [11] R. Ziessel, G. Ulrich, A. Harriman, M. A. H. Alamiry, B. Stewart, P. Retailleau, *Chem. Eur. J.* **2009**, 15, 1359–1369.
- [12] R. Ziessel, *C. R. Chim.* **2007**, 10, 622–629.
- [13] D. Kumaresan, R. P. Thummel, T. Bura, G. Ulrich, R. Ziessel, *Chem. Eur. J.* **2009**, 15, 6335–6338.
- [14] R. Ziessel, M. A. H. Alamiry, K. J. Elliott, A. Harriman, *Angew. Chem.* **2009**, 121, 2810–2814; *Angew. Chem. Int. Ed.* **2009**, 48, 2772–2776.
- [15] a) S. Diring, F. Puntoriero, F. Nastasi, S. Campagna, R. Ziessel, *J. Am. Chem. Soc.* **2009**, 131, 6108–6110; b) A. Harriman, L. J. Mallon, K. J. Elliot, A. Haefele, G. Ulrich, R. Ziessel, *J. Am. Chem. Soc.* **2009**, 131, 13375–13386.
- [16] J. J. Olmsted, *J. Phys. Chem.* **1979**, 83, 2581–2591.
- [17] M. Y. Okamura, G. Feher, N. Nelson in *Photosynthesis: Energy Conversion by Plants and Bacteria, 1:195* (Ed.: I. Govindjee), Academic Press, New York, **1982**, pp. 799.
- [18] J.-H. Olivier, A. Haefele, P. Retailleau, R. Ziessel, *Org. Lett.* **2010**, 12, 408–411.