A Versatile Synthesis of Long-Wavelength-Excitable BODIPY Dyes from Readily Modifiable Cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes

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Abstract: Knoevenagel condensation of a simple methylated borondipyrromethene (Bodipy) with 4,4′-dihexyl-4*H*-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophenes functionalized at one end by a triphenylamine residue and at the other by a carbaldehyde fragment leads to novel dye species. These bisvinylic derivatives exhibit pronounced absorption in the visible range extending above 850 nm. Addition of other Bodipy units by coupling to a central iodophenyl entity enables filling of the gaps in absorption of the pivotal starting material. Efficient cascade energy transfer between the Bodipys is facilitated by spectral overlap between the energy donor and the energy acceptor. All photons between 350 nm and 750 nm are channeled to the distyryl centers which emit at 864 nm.

Key words: BODIPY, dithiophene, pyrene, energy transfer, panchromatic dyes

The programmed synthesis of sophisticated multichromophoric dyes is challenging but has blossomed during the last few years due to the demand for energy conversion devices.[1–3] Red/near-infrared radiation (NIR, 650–1000 nm) accounts for approximately 33% of the solar energy arriving at the surface of the Earth, while visible radiation (350–650 nm) accounts for about 40%.[4,5] The key issue toward achieving efficient organic solar cells is the development of red and NIR absorbing dyes to harvest a larger fraction of the solar spectrum. We have been interested in borondipyrromethene[6] and diketopyrrolopyrrole[7] dyes as their performance can be fine-tuned by architectural alternations and molecular engineering. In this regard, various tools have been used, such as: i) the introduction of strong electron-donating subunits; ii) the increase of the conjugation pathway by construction of unsaturated vinylic or acetylenic side arms; iii) the introduction of auxiliary energy or electron acceptors in the vicinity of the central absorbing core. Many specific synthetic approaches have been found fruitful for the construction of dye molecules with strong absorption in the red or near-infra red spectral windows.[8,9] In many cases, however, the solubility of these dyes is hampered by the presence of a flat aromatic core, a situation highly favorable for undesirable aggregation process which limits their utilization in solution-processed device fabrication and biomedical applications. Thus, many structural modifications have been designed to encumber the dyes with bulky three-dimensional units. We have developed a synthetic protocol based on the 'chemistry at boron' of several borondipyrromethene (Bodipy) dyes in order to solve the problems of solubility, stability and aggregation.[10] In the present contribution, we disclose the synthesis of highly colored Bodipy dyes absorbing over a large window into the NIR and in some cases exploit the chemistry at boron to import steric bulkiness and additional energy absorbing units capable of engendering cascade energy transfer.[11] Our earlier studies have shown that the use of thiophene or bisthiophene in the construction of delocalized BODIPY dyes can provide: i) green absorbing dyes; ii) material capable of transporting equally electrons and holes (ambipolar behavior) in condensed phases, and iii) efficient solar cells build from bulk heterojunctions.[12]

The fused bisthiophene platform of 4,4′-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene is particularly useful in the design of new Bodipy derivatives because of the possibility of its orthogonal functionalization at the *ortho* positions of the thiophene and at the central cyclopentadienyl ring. A diphenylaminophenyl unit attached to one thiophene can enhance the electron density at a carbaldehyde attached to the other and so give a very reactive site for Knoevenagel reactions giving highly colored Bodipy dyes.[13] Solubilizing chains linked to the cyclopentadienyl ring can be modified at will, ensuring both solubility as well as steric bulkiness at the center to avoid aggregation of the dyes. A phenyliodo residue attached to the pseudo-*meso* position can be exploited to graft additional photoactive modules absorbing at higher energy and providing input energy for intramolecular cascade energy transfer (ICET) and excitonic energy concentration. Finally, many additional synthetic possibilities exist to link additional useful items at the boron centers.

Thus, we describe herein a synthetic approach to the fabrication of the next generation of Bodipy dyes capable of absorbing light over a broad wavelength range. The objective was to provide two different Bodipy moieties with different energy absorbing levels linked together in a covalent manner. A pivotal molecule was the orthogonally functionalized 1-formyl-7-triphenylamine-4,4′-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**11**) which was prepared in ten steps from 3-bromothiophene and 3-formylthiophene (Scheme 1) according to references 14 and 15.

The fused bisthiophene derivative **5** was prepared according to a literature procedure[14] by lithiation of **1** followed by reaction with 3-carbaldehydethiophene. The intermediate 3-thienylmethanols were not isolated but further lithiated at low temperature and then reacted with iodine, leading to compound **3** which was separated from side products and purified. Oxidation of the alcohol to the ketone was achieved with pyridinium chlorochromate (PCC) and ring closure was ensured by an Ullman reaction. Reduction of the ketone was performed with hydrazine under basic conditions.[15] Then, a Vilsmeier–Haack reaction followed by electrophilic bromination with NBS afforded derivative **9** in good yields. Suzuki cross-coupling between **9** and **10** provided **11** in acceptable yields.

Our next target became the attachment of carbaldehyde **11** to BODIPY **12**. To reach the goal, we made use of a Knoevenagel reaction under the experimental conditions we have previously described.[16]

The use of forcing conditions allowed the selective formation of the bisvinyl derivative at the expense of the mono derivative (green compound). The final deep-red-brown dye **13** was isolated pure by flash silica column chromatography in 98% isolated yield (Scheme 2).[17]

Our design opens up the possibility of engineering sophisticated hybrid dyes bearing additional fluorophores with complementary absorption features. From cross-linking of such modules in substitution position 8, we anticipated a significant enhancement of the panchromatic features of the final dye. We also expected that this would be an ideal situation for cascade energy transfer processes controlled by the additional chromophore.[18] In some cases, polyaromatic residues could be grafted to the boron center to augment the absorption features. To access such interesting hybrid structures, we envisaged coupling of the known dyes **14**[19] and **15**[20] (Figure 1) to the module **13**.

The cross-linking between the iodo dye **13** and the alkyne-substituted dyes **14** and **15** was straightforward using palladium catalysts, e.g. [Pd(PPh$_3$)$_4$], under mild reaction conditions. The highly colored mixed dyes **16**[21] and **17**[22] are soluble and stable, and they are easily purified by flash column chromatography and were isolated in 73% and 88% yields, respectively (Figure 2).

The ^{1}H NMR spectra reflect the complexity of molecules **16** and **17** (see the Supporting Information and references 21 and 22). Diagnostic signals for the β-pyrrolic proton are found at δ = 6.10, 6.82, 6.87 ppm (in acetone-d_6) for
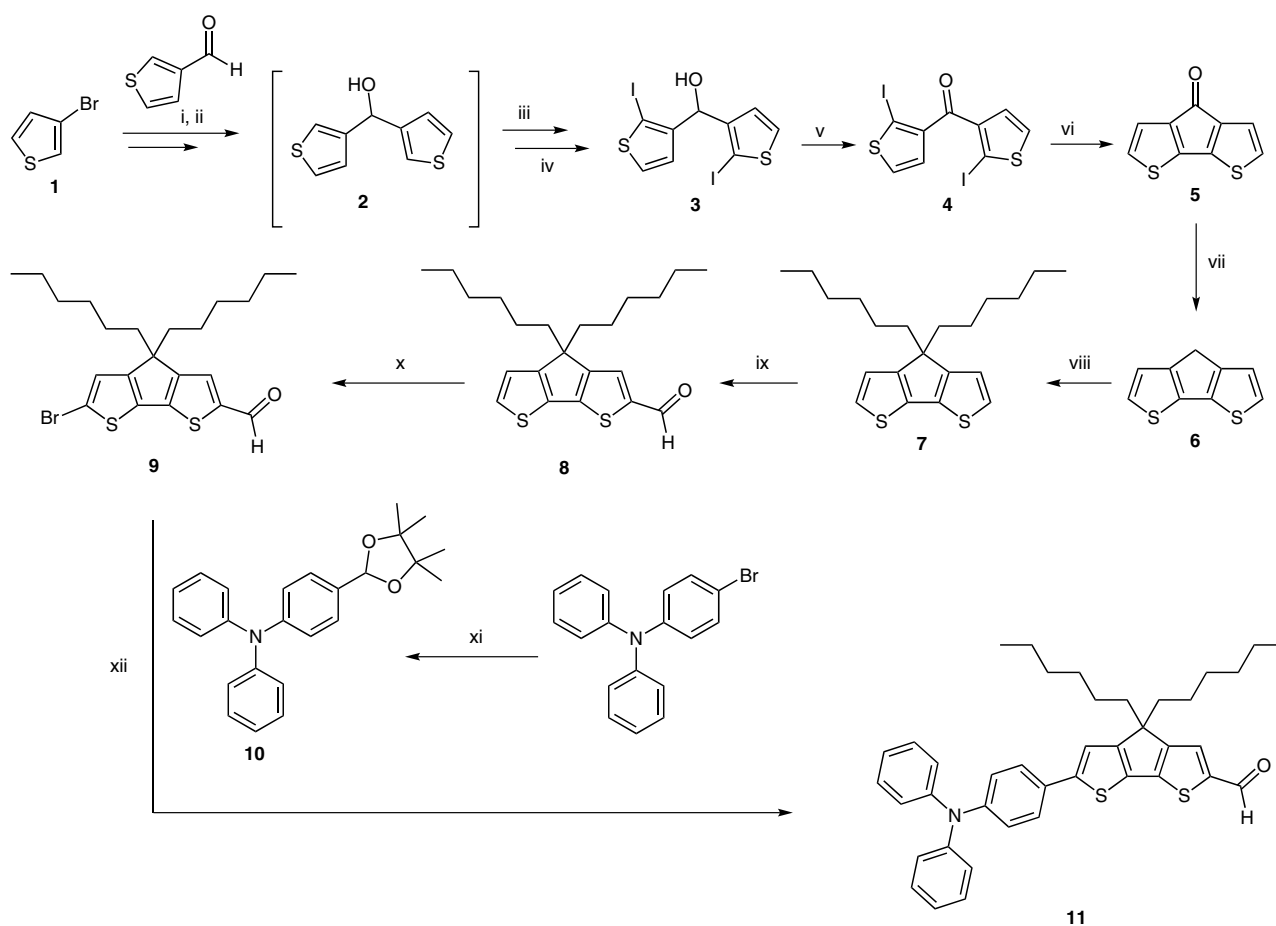

Scheme 1 *Reagents and conditions*: (i) *n*-BuLi, Et$_2$O, −78 °C; (ii) 3-carbaldehydethiophene, Et$_2$O, −78 °C to r.t.; (iii) *n*-BuLi, Et$_2$O, −23 °C to r.t.; (iv) I$_2$, Et$_2$O, −23 °C to r.t., 63% to 69%; (v) PCC, 1,2-dichloroethane, 80 °C, 72%; (vi) Cu, DMF, reflux, 85% to 99%; (vii) N$_2$H$_4$·H$_2$O, KOH, ethyleneglycol, 180 °C, 89%; (viii) 1-bromohexane, KI, KOH, DMSO, r.t., 68% to 74%; (ix) POCl$_3$, DMF, 1,2-dichloroethane, 0 °C, 96%; (x) NBS, THF, r.t., quant.; (xi) [Pd(dppf)Cl$_2$], KOAc, dioxane, 85 °C, 87%; (xii) [Pd(PPh$_3$)$_4$], K$_2$CO$_3$, THF, reflux, 94%.
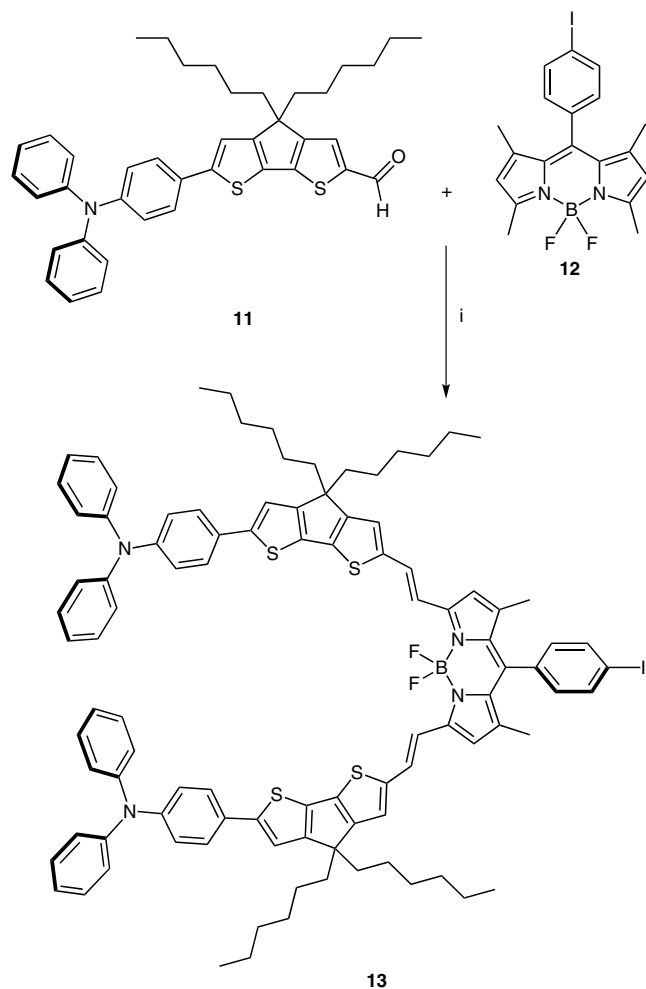
Scheme 2 *Reagents and conditions*: (i) compound **11** (3 equiv), compound **12** (1 equiv), toluene, piperidine, *p*-TsOH trace amounts, dryness, 98%.

16 and at δ = 6.38, 6.89 ppm (in acetone-d_6) for **17**, confirming the number of styryl functions present in the molecules.[23] For the starting material **13**, the β-pyrrolic proton signal appears at δ = 6.64 ppm (in CDCl$_3$) whereas for **14** there is a singlet at δ = 6.32 ppm and for **15** two singlets at δ = 5.97 and 6.70 pm (in CDCl$_3$). Furthermore, for **17** a characteristic deshielded doublet is found at δ = 8.82 ppm (J = 8.0 Hz) for the proton localized in the α-position of the alkyne function of the pyrene units. In the case of **16**, an isolated doublet of an AB quartet belonging to the vinylic protons and confirming the *E* conformation of the double bonds is evident at δ = 7.69 ppm (J = 16.2 Hz), a result in keeping with the kind of reaction employed. The NMR spectra also confirm that there is little electronic interaction between the two fragments of the molecules in **16** and **17**, a situation expected based on the nature of the tolane linking unit and the presence of the methyl groups present in the 1,7-substitution positions of the Bodipy cores. For steric reasons, the aryl groups at the 8-position are taken to be tilted orthogonally, as seen in several X-ray crystallographic studies on single crystals.[24]
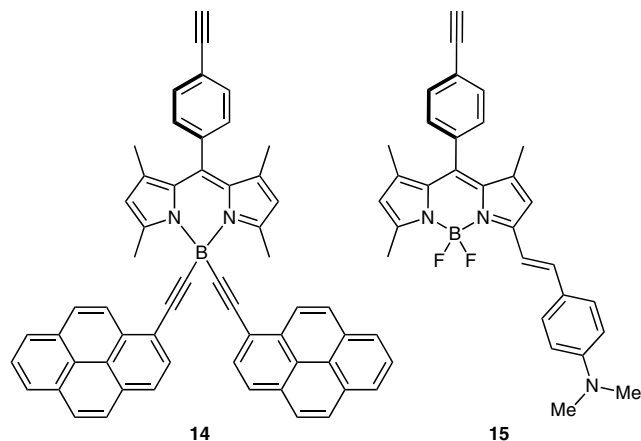
Figure 1 Structural representations of the terminal alkyne Bodipys **14** and **15** used for coupling to a central iodophenyl unit

The electronic spectra (absorption and emission) of the key precursors **13**, **14**, **15** and the protonated species [**15** + H$^+$] are shown in Figure 3. In all cases, the absorption spectra show an intense peak at different wavelengths reflecting the degree of electronic delocalization along the Bodipy framework. For **13**, **14**, **15** and [**15** + H$^+$] an intense peak at 800, 502, 605 and 561 nm, respectively, corresponds to the lowest energy S$_0$→S$_1$ transition of the Bodipy core.[25] The shoulder at higher energy of this most intense absorption reflects the vibronic structure of this excitation within the dipyrromethene framework. For **14**, the linked pyrene fragments exhibit intense absorption patterns below 380 nm reflecting the presence of several S-type excited states.[26] Additional transitions are observed below 300 nm (not shown in Figure 1b). For **13**, absorption at 512 nm is due to both vinyl linkers and largely overlaps the S$_0$→S$_2$ electronic transition of the Bodipy core. Note that this transition is more intense than S$_0$→S$_1$, with ε values reaching about 100,000 M^{-1}cm^{-1} (Figure 3a). Fluorescence is observed at about 864, 515, 689 and 576 nm, respectively, for **13**, **14**, **15** and [**15** + H$^+$] and is independent of the excitation wavelength. As expected, protonation of **15** results in a hypsochromic shift of 44 nm in absorption (113 nm in emission), an interesting feature in regard to fine-tuning of the spectral properties of the dyes.

For **14** and [**15** + H$^+$], the emission profile is the mirror image of the absorption, and the weak Stokes shift and short excited state lifetime (a few nanoseconds) are typical of a singlet excited state. However, for **13** and **15** the absorption and emission profiles are broader and the Stokes shifts are larger indicating that pronounced charge transfer from the donor (fused-thiophene cycle or NMe$_2$ fragments) is effective and perturbs the optical transitions.

Linking dye **13** to the modules **14** or **15** results in absorption spectra which clearly reflect the separate contributions of the respective modules [λ$_{abs}$ at 502 nm and 605 nm for **14** and **15**]. The final molecules **16** and **17** display a very broad absorption manifold between 300 nm and 850 nm (panchromatic behavior, Figures 4 and 5). Interesting-

ly, for **16** irradiation at 430 nm in the monodimethylamino styryl fragment gives an intense emission at 864 nm and insignificant emission at 689 nm, the wavelength at which the isolated dye **15** usually fluoresces (Figure 4). This is a good indication that almost quantitative excitonic energy transfer is occurring from one module to the other as a result of favorable spectral overlap between the emission of the energy donor (dimethylaminostyryl Bodipy) and the absorption of the energy acceptor (the distyryl dithienyl Bodipy). The result is that there is a virtual Stokes shift of 11,700 cm^{-1}. For the second system, **17**, the situation is a little different because the Bodipy bispyrene chromophore absorbs at higher energy and the spectral overlap is less favorable in this case because the acceptor is less absorbing around 520 nm (Figure 5). Nevertheless, irradiation of **17** at 320 nm generates no pyrene emission due to cascade energy transfer to the tetramethyl Bodipy unit (picoseconds time scale).[27] This result is in keeping with the observation made for compound **14** (Figure 1b). The excitonic energy of the tetramethyl Bodipy is transferred to

the final energy acceptor (the bis-styryl dye) which relaxes to the ground state by emitting light at 864 nm as in the previous case. Note that in this case some residual fluorescence is found at 515 nm with a quantum yield of 0.2% (see Figure 5). The quantum yield of dye **14** measured under the same conditions is 86%. This means that 99% of the excitonic energy is transferred to the distyryl energy-accepting centre. Double cascade energy transfer from the pyrene to the tetramethyl Bodipy and from this to the distyryl unit is indeed very effective (>98%). A similar situation is found for protonation of dye **16**, where the protonation causes a hypsochromic shift from 605 nm to 561 nm, disfavoring the energy transfer to some extent due to a poorer spectral overlap and leading to some residual emission at 576 nm (Figure 2b).

Ultimate proof of the occurrence of the cascade process is evident in the excitation spectra for both hybrid dyes **16** and **17** (Figures 4 and 5), which fairly well match the absorption spectra and thus prove the contribution of each module to the energy transfer events. By extending the

16

17
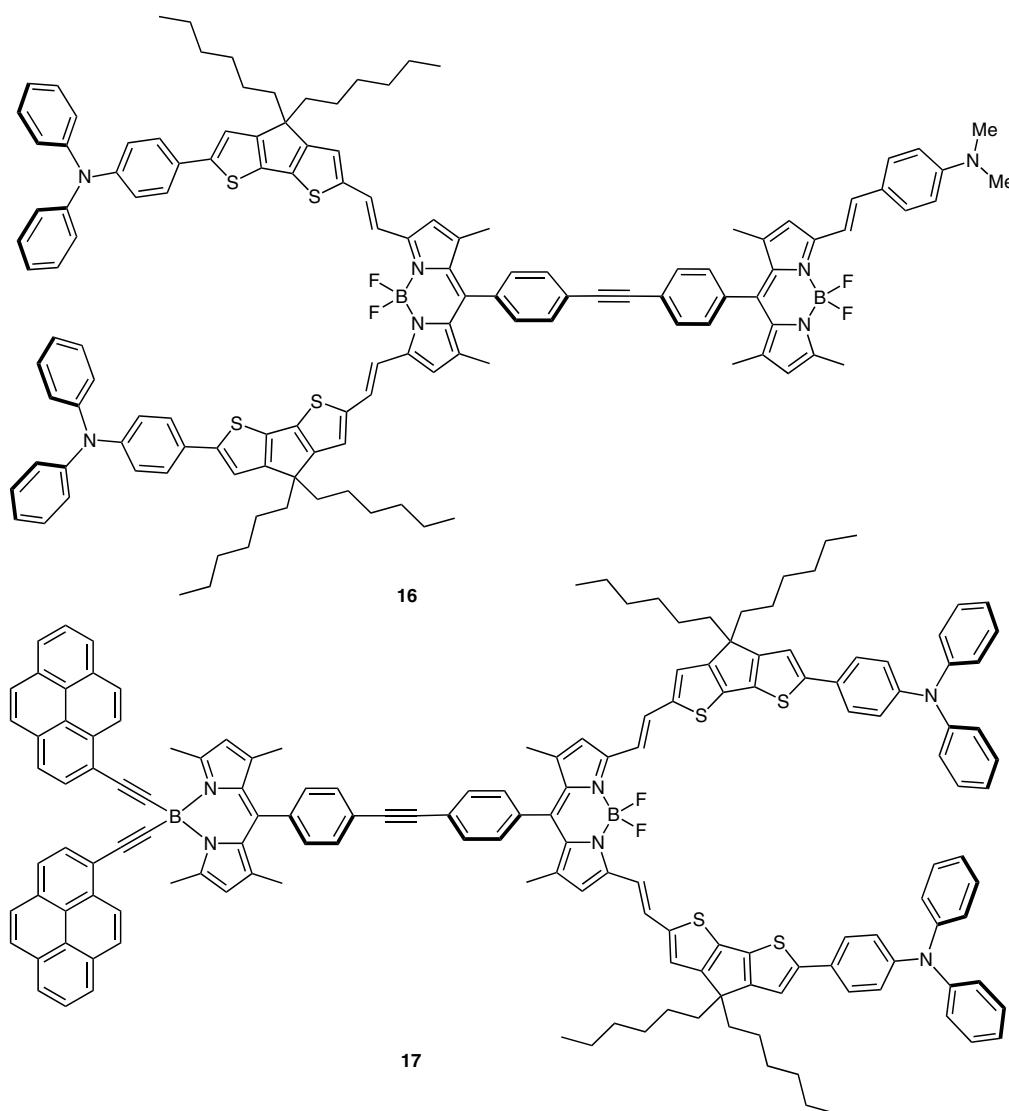
Figure 2 Chemical formulas of the hybrid dyes
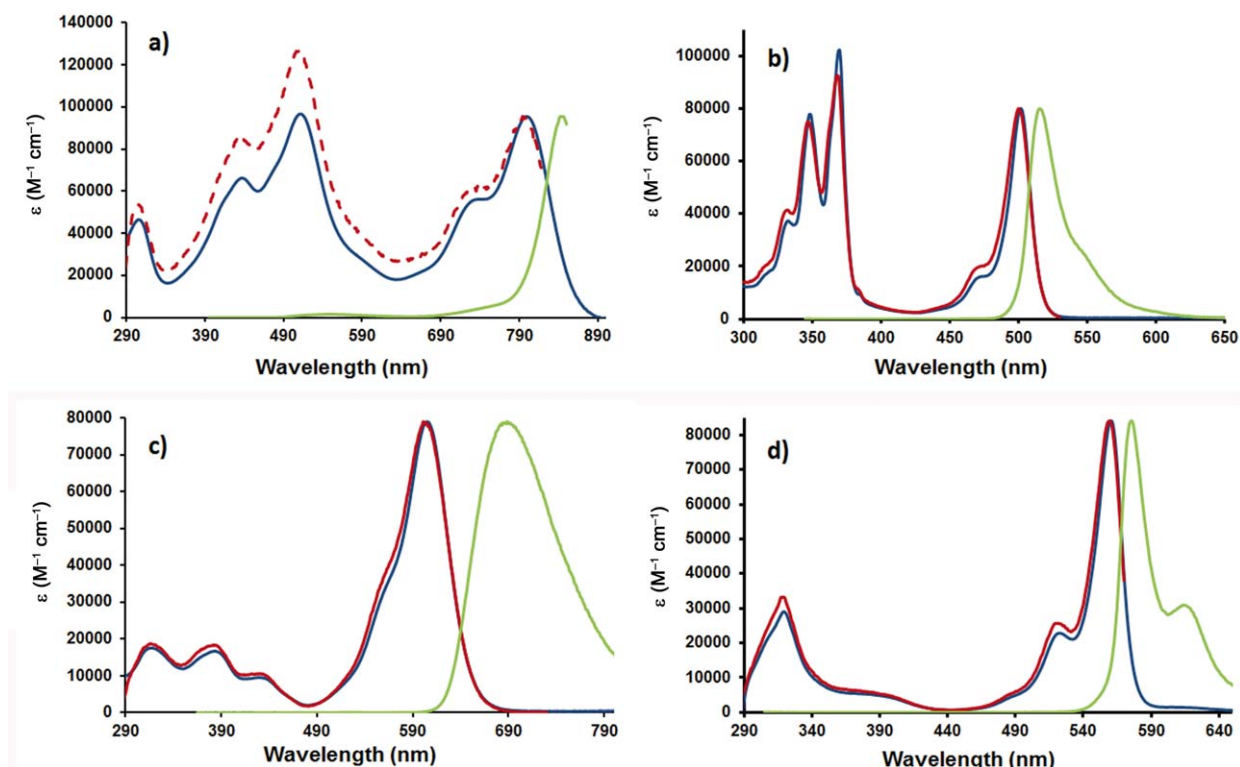
Figure 3 Absorption (blue trace), emission (green trace), and excitation (dashed red line) spectra in THF at r.t.: (a) for **13**, (b) for **14**, (c) for **15** and (d) for [**15** + **H**$^+$] formed by addition of excess H_3PO_4.
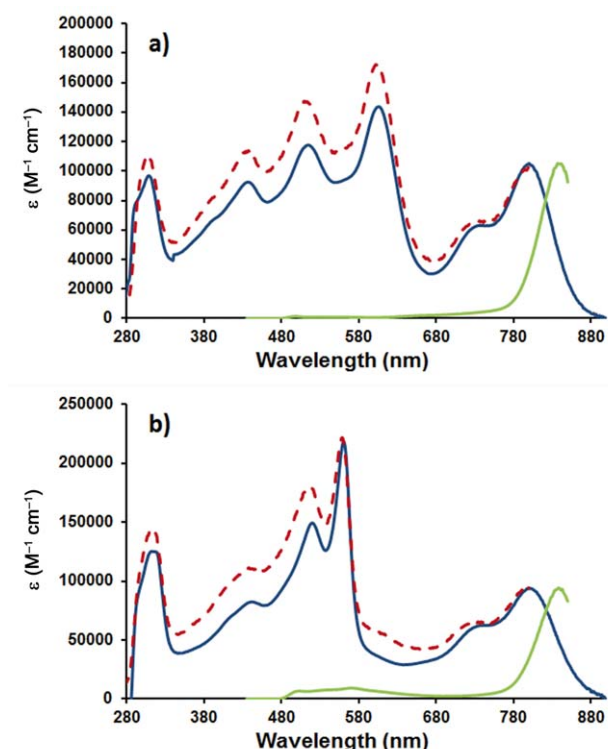

Figure 4 Absorption (blue trace), emission (green trace) and excitation (dashed red line) spectra in THF at r.t.: (a) for **16**; (b) for [**16** + **H**$^+$] formed by addition of excess H_3PO_4.

spectral analysis window to the NIR-IR using a photomultiplier tube (PMT) liquid-nitrogen-cooled near-infrared detector, well-defined steady state emission of dyes **13**, **16** and **17** was measured at very similar wavelengths (Figure 6). The fact that all photons between 250 nm to 830 nm are channeled to the dyes absorbing at the lower energy is auspicious for the engineering of solar energy concentrators.[28]
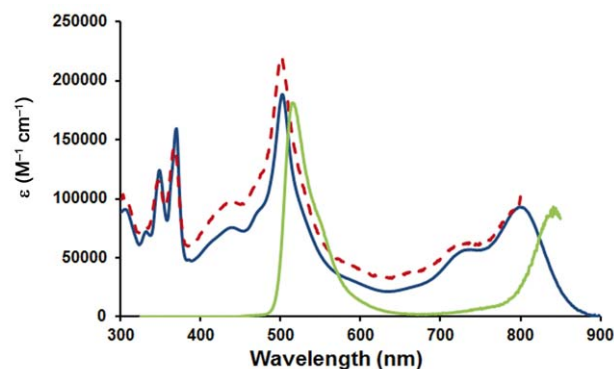
Figure 5 Absorption (blue trace), emission (green trace) and excitation (dashed red line) spectra for **17** in THF at r.t.

The present work has shown that the construction of electron-rich modules provides interesting dyes absorbing in the near-infrared. These dyes can be used to efficiently assemble multichromophoric (Bodipy) systems involving tetramethyl-, monovinyl- and bisvinyl Bodipy dyes. In
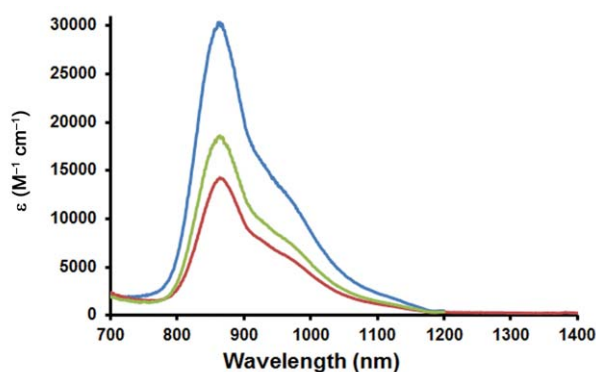
Figure 6 Steady state emission using a PMT liquid-nitrogen-cooled near-infrared detector for dyes: **13** (red trace), **16** (green trace) and **17** (blue trace).

one case, this new approach to the synthesis has provided a dye bearing polyaromatic modules on the boron center. Multiple cascade energy transfer events have been exploited to channel excitonic energy to a single emitting dye lying at low energy. This concept could certainly be extended to provide dyes emitting above 1000 nm. The present systems confirm that the construction of a module offering orthogonal functionalization is suitable to ensure regioselectivity during the cross-coupling or Knoevenagel reactions and that the introduction of paraffin chains engenders solubility in a wide variety of solvents. The legitimate prospect for the use of these new materials as luminescent molecular light concentrators in bulk heterojunctions for solar energy conversion is currently under development.[29,30]

Acknowledgment

Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/ 10.1055/s-00000083.

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(17) **Preparation of Compound 13**: To a solution of BODIPY **12** (207.9 mg, 0.46 mmol) in toluene (70 mL) were added 6-[4-(diphenylamino)phenyl]-4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2-carbaldehyde (**11**; 856.3 mg, 1.39 mmol), piperidine (1 mL) and *p*-toluenesulfonic acid (*p*-TsOH). The resulting mixture was stirred at reflux and the solvent was distilled to dryness using a Dean–Starck apparatus. Afterwards, the organic product was extracted with CH_2Cl_2, washed with H_2O and brine. The organic layer was dried over anhyd $MgSO_4$ and evaporated under vacuum. The crude product was purified by silica gel chromatography (from 80:20 → 50:50 petroleum ether–CH_2Cl_2) and recrystallized by evaporation in CH_2Cl_2–EtOH and washed with pentane to afford a deep-brown red compound (745.8 mg, 98%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.88 (d, [3]*J* = 8.1 Hz, 2 H), 7.52 (d, [3]*J* = 8.5 Hz, 4 H), 7.42 (s, 4 H), 7.29 (t, [3]*J* = 7.9 Hz, 8 H), 7.17 (d, [4]*J* = 4.0 Hz, 4 H), 7.15 (d, [3]*J* = 8.4 Hz, 2 H), 7.12 (d, [3]*J* = 7.7 Hz, 8 H), 7.02–7.08 (m, 8 H), 6.65 (s, 2 H), 1.88–1.96 (m, 8 H), 1.50 (s, 6 H), 1.13–1.24 (m, 24 H), 0.95–1.05 (m, 8 H), 0.81 (t, [3]*J* = 6.7 Hz, 12 H). ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 161.4, 159.5, 152.3, 148.0, 147.8, 146.9, 143.5, 141.8, 140.6, 138.8, 135.7, 135.5, 135.1, 134.1, 131.5, 130.4, 129.9, 129.6, 126.6, 125.1, 124.2, 123.8, 123.3, 118.5, 117.6, 116.2, 95.2, 38.6, 34.7, 32.2, 30.3, 25.1, 23.2, 22.9, 15.3, 14.4. MS (EI): *m/z* (%) = 1649.5 (100.0), 1629.5 (30). Anal. Calcd for $C_{99}H_{100}BF_2IN_4S_4$: C, 72.07; H, 6.11; N, 3.40. Found: C, 71.85; H, 5.80; N, 3.11.

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(21) **Preparation of Compound 16**: To a degassed solution of **13** (63 mg, 0.038 mmol) and **15** (22 mg, 0.046 mmol) in benzene (10 mL) and Et_3N (2 mL) was added $[Pd(PPh_3)_4]$ (10 mg). The resulting mixture was stirred for 19 h at 70 °C and then cooled to r.t. After evaporation of the solvent under

vacuum, the organic product was extracted with CH_2Cl_2, washed with H_2O and brine. The organic layer was dried over anhyd Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel chromatography (from 50:50 → 40:60 petroleum ether–CH_2Cl_2) to obtain a brown compound (62 mg, 81%) and recrystallized by evaporation in THF–pentane and washed with pentane to afford a brown compound (54 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, ^3J = 8.1 Hz, 4 H), 7.47–7.56 (m, 8 H), 7.33–7.41 (m, 6 H), 7.20–7.31 (m, 12 H), 7.02–7.16 (m, 18 H), 6.69 (d, ^3J = 9.0 Hz, 2 H), 6.62 (s, 1 H), 6.61 (s, 2 H), 5.99 (s, 1 H), 3.04 (s, 6 H), 2.61 (s, 3 H), 1.82–1.95 (m, 8 H), 1.50 (s, 9 H), 1.45 (s, 3 H), 1.11–1.25 (m, 24 H), 0.94–1.07 (m, 8 H), 0.83 (t, J = 6.9 Hz, 12 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.5, 158.7, 155.2, 153.1, 151.9, 151.1, 147.4, 147.1, 146.2, 143.0, 142.6, 140.7, 140.4, 140.0, 138.2, 137.7, 135.9, 135.8, 135.3, 134.7, 133.6, 132.9, 132.2, 132.2, 130.9, 129.7, 129.3, 129.3, 129.2, 129.1, 128.8, 126.1, 124.6, 124.4, 123.9, 123.5, 123.5, 123.1, 122.4, 120.6, 117.9, 116.8, 116.1, 114.2, 112.0, 90.0, 68.0, 54.0, 53.4, 40.2, 38.0, 34.1, 31.6, 29.7, 25.6, 24.5, 22.7, 22.3, 14.9, 14.8, 14.6, 14.5, 14.0. MS (EI): m/z (%) = 2000.1 (100.0), 1981.1 (35), 1963.2 (15). Anal. Calcd for $C_{129}H_{127}B_2F_4N_7S_4$: C, 77.42; H, 6.40; N, 4.90. Found: C, 77.20; H, 6.09; N, 4.68.

(22) **Preparation of Compound 17**: To a degassed solution of **13** (92 mg, 0.056 mmol) and **14** (43 mg, 0.056 mmol) in benzene (20 mL) and Et_3N (2 mL) was added $[Pd(PPh_3)_4]$ (10 mg). The resulting mixture was stirred for 19 h at 80 °C and then cooled to r.t. After evaporation of the solvent under vacuum, the organic product was extracted with CH_2Cl_2, washed with H_2O and brine. The organic layer was dried over anhyd Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel chromatography (from 80:20 → 50:50 petroleum ether–CH_2Cl_2) to obtain a grey compound (119 mg, 93%) and recrystallized by evaporation in THF–pentane and washed with pentane to afford a brown compound (112 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, ^3J = 9.0 Hz, 2 H), 8.60 (d, ^3J = 9.2 Hz, 2 H), 7.96–8.29 (m, 18 H), 7.77 (d, ^3J = 7.9 Hz, 2 H), 7.66–7.74 (m, 2 H), 7.51 (d, ^3J = 7.9 Hz, 2 H), 7.39 (d, ^3J = 7.1 Hz, 2 H), 7.21–7.31 (m, 10 H), 6.99–7.17 (m, 24 H), 6.22 (s, 2 H), 3.18 (s, 6 H), 1.80–1.97 (m, 8 H), 1.56 (s, 6 H), 1.54 (s, 6 H), 1.11–1.31 (m, 24 H), 0.94–1.07 (m, 8 H), 0.82 (t, ^3J = 6.5 Hz, 12 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.7, 155.9, 147.4, 141.2, 132.5, 132.3, 132.2, 132.1, 131.6, 131.3, 131.2, 131.0, 130.5, 130.2, 129.7, 129.3, 128.7, 128.6, 128.5, 128.4, 127.9, 127.5, 127.3, 127.2, 126.3, 126.2, 126.0, 125.7, 125.7, 125.3, 125.2, 124.6, 124.4, 124.4, 124.4, 124.2, 123.9, 123.1, 122.4, 122.0, 120.3, 116.5, 82.7, 82.6, 38.0, 31.6, 29.7, 26.9, 24.5, 22.7, 16.6, 15.0, 14.9, 14.6, 14.1. MS (EI): m/z (%) = 2281.1 (100.0), 2262.1 (30) Anal. Calcd for $C_{156}H_{136}B_2F_2N_6S_4$: C, 82.08; H, 6.01; N, 3.68. Found: C, 81.74; H, 5.78; N, 3.51.

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