JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

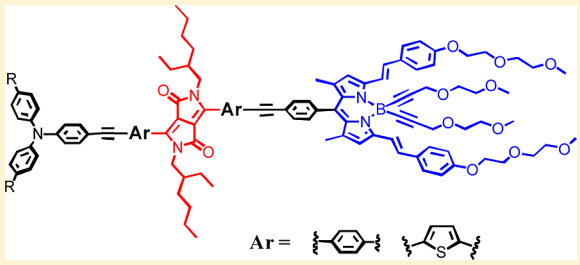
Step-by-Step Synthesis of Multimodule Assemblies Engineered from BODIPY, DPP, and Triphenylamine Moieties

Elodie Heyer and Raymond Ziessel*

Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), Laboratoire de Chimie Organique et Spectroscopies Avancées (LCOSA), Université de Strasbourg/CNRS (UMR 7515), École Européenne de Chimie, Polymères et Matériaux (ECPM), 25 rue Becquerel, 67087 Strasbourg, France

Supporting Information

ABSTRACT: In the present account we describe unsymmetrical triads constructed from extended borondipyrromethene (BODIPY) dyes, diketopyrrolopyrrole (DPP) dyes, and electron donor fragments based on triarylamine. The assemblages are such that each module maintains its individual optical and redox properties. The use of phenyl-alkyne-phenyl or phenyl-alkyne-thienyl spacer units is favorable for weak electronic interaction between the modules. The step-by-step linking of each module using palladium-catalyzed cross-coupling reactions provides both mono- and disubstituted derivatives, the latter obtained by passing in particular through a pivotal monosubstituted DPP building block with a reactive bromo substituent. Thus, grafting of a second dye occurs in a controlled manner, providing the target triads in good yields. This protocol allows also the synthesis of key intermediates and dyads, which appear useful for the understanding of the electrochemical and spectroscopic properties. All the dyes exhibit redox and optical properties suitable for cascade energy transfer and photoinduced electron transfer processes in appropriate solvents.



INTRODUCTION

Natural photosynthesis is a fantastic machinery responsible for life developments on earth and capable of incredible chemical transformations.[1] Paramount among the multiple steps associated with natural photosynthesis is the collection of sunlight by light-harvesting complexes (LHC), the pigments being arranged in extremely well organized and efficient networks that act in a cooperative fashion.[1,2] For example, the LHC of the purple bacterium *Rhodopseudomonas acidophila*[3] has pigments arranged into rings of discrete size, with individual molecules being held in place by the protein scaffold. The availability of high-quality crystal structures has facilitated comprehensive studies into the mechanisms by which rapid EET (EET = excitation energy transfer) occurs within these natural ensembles. Much is known about the structure/function activity of natural LHCs and the theory of EET so that, in principle, it should be possible to construct effective artificial analogues incorporating multiple, linked chromophores capable of giving rise to a cascade EET event. Indeed, systems suitable for artificial photosynthesis have been widely explored,[4] and a major effort has been devoted, for example, to the synthesis of wheel-like porphyrin arrays.[4,5] Other examples include a light-harvesting array of metalated porphyrins in which the excitation energy is transferred rapidly to a C_{60} reaction center so that the porphyrin-fullerene charge-separated state $P^{+\bullet}$-$C_{60}^{-\bullet}$ is formed with a quantum yield of 70%.[6] Self-assembled monolayers of linear ferrocene-porphyrin-fullerene molecular triads and linear boron-dipyrrin dyes have been studied in order to examine both energy and electron transfer in the artificial reaction center (C_{60}).[7]

There are many reviews dedicated to the design of linear and cyclic porphyrin arrays as models for photosynthetic units.[8] Single-molecule spectroscopy has been used to probe energy migration in cyclic porphyrin arrays.[9] A rigid antenna-based system has been designed to include three types of light-absorbing chromophores, organized in a wheel-like fashion, including bis(phenylethynyl)anthracene (λ_{abs} 450 nm), a boron dipyrromethene dye (λ_{abs} 513 nm) and a Zn-tetraarylporphyrin (λ_{abs} 418 and 598 nm). Quantitative EET and 95% quantum efficiency for formation of the P^{+}-C_{60}^{-} charge-separated state have been found for this system.[10] Other attractive and highly informative systems developed by many different research groups are known.[11] In particular, multichromophoric assemblages have been engineered and studied with the aims of extending the spectral absorption window[12] and promoting very efficient charge separation with appended fullerene acceptor reservoirs.[13]

Along these lines borondipyrromethene (BODIPY)[14] and diketopyrrolopyrrole (DPP)[15] dyes appear very promising for the construction of multichromophoric scaffoldings. These dyes have features that combine high molar extinction coefficients and high fluorescence quantum yields, strong chemical and photochemical stability in solution and in the solid state, and remarkable electron and/or transfer properties. Furthermore,

Received: April 23, 2015
Published: June 16, 2015

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

their optical properties are very sensitive to modification of the pyrrole core (BODIPY cases) and of the bis-lactam fused system (DPP core). The well-defined molecular structure of both families of dyes makes it easier to establish firm structure–property relationships.[14b,16]

Herein we describe multichromophoric dyes constructed from diketopyrrolopyrrole (DPP) and borondipyrromethene (BODIPY) fragments linked in a covalent manner by a tolane spacer (here phenyl-alkyne-phenyl or thienyl-alkyne-phenyl) and end-capped by a triarylamine module. The choice of a BODIPY unit is based on the following: (i) its divinyl derivative has appropriate absorption and emission windows to complement those of the DPP module; (ii) its ready functionalization with short polyethylene glycol chains facilitates the purification of the materials by column chromatography; (iii) it can be rendered insensitive to substitution at boron and is compatible with most metal catalyzed cross-coupling reactions; finally (iv) substitution at boron can be used to enhance the photostability of the dyes and their solubility in most common solvents.

RESULTS AND DISCUSSION

Synthesis. Construction of the molecular dyads and triads requires the preparation of the key building blocks depicted in Figure 1. We have used previously described procedures or adapted synthetic procedures, and checked the purity of these starting materials by NMR spectroscopy. In all cases, column chromatography allows purification of the desired compounds and a single crystallization using THF as solvent and diffusion of pentane as counter-solvent provides the analytically pure dyads and triads.

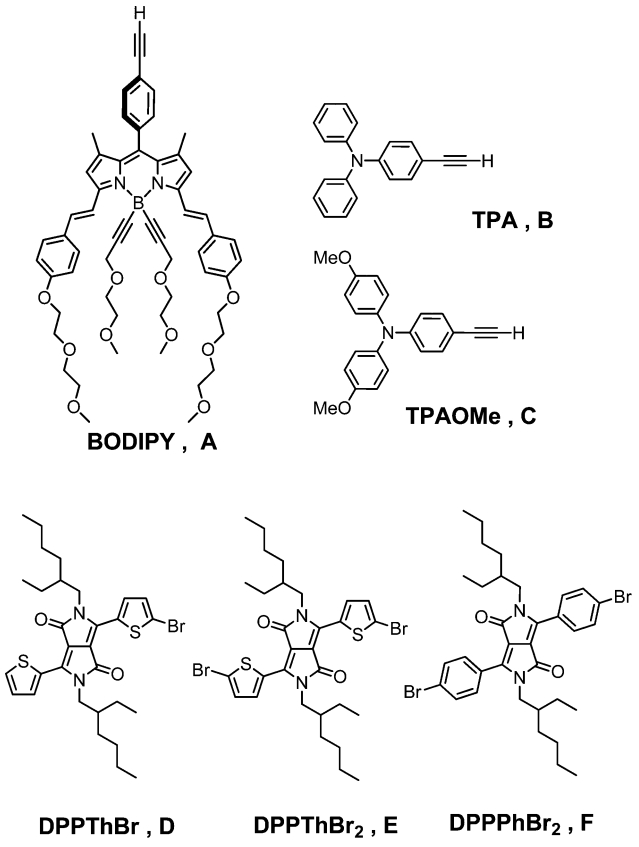


Figure 1. Key building blocks requested for the synthesis of the dyads and triads.

Dyads of BODIPY/triphenylamine or BODIPY/DPP were first elaborated as spectroscopic and electrochemical reference compounds as well as to optimize the synthetic protocols for the cross-linking reactions. Sonogashira–Hagihara cross-coupling reactions were catalyzed by Pd(0) species either generated in situ from Pd(II) complexes and Cu(I) or provided as air sensitive Pd(0) complexes.[17]

The best experimental conditions found for the cross-coupling reaction between BODIPY **1** and triphenylamines are given in Scheme 1, using $[Pd(PPh_3)_2Cl_2]$ (6 mol %) and CuI (6 mol %) under mild condition. Triethylamine was preferred from a range of several secondary and tertiary amines investigated. The good isolated yields 89 and 70% are reproducible, and purification by column chromatography is straightforward in the absence of an excess of the polar BODIPY derivative **A**. All attempts to prepare the dyad **2** the other way around [BODIPY **A** and 4-bromotriphenylamine (BrTPA)] failed due to the lack of reactivity of BrTPA under mild experimental conditions (Scheme 1).

The ^{1}H NMR spectrum of dyad **2** exhibits a deshielded doublet at 8.20 ppm (integration 2 protons) with a coupling constant of 16.3 Hz assigned to the vinylic protons in a *trans* configuration (Figure S1). Globally, no significant shifts were observed in the peaks assigned to the component units, consistent with weak electronic coupling between the building blocks. Observations on the dyad **3** containing the $TPA(OMe)_2$ moiety were similar, with a deshielded doublet at 8.08 ppm (2H, ^3J = 16.2 Hz)[18] and no significant shift of the signals. The methoxy substituents on the para position of the phenyl rings, giving a singlet at 3.80 ppm (6H), simplify the aromatic region resonances and facilitate the assignments there.

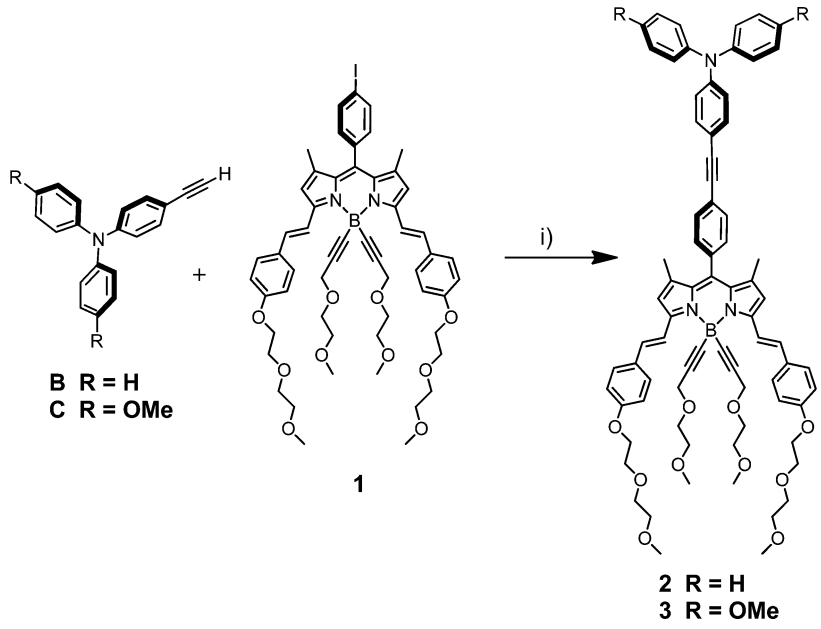
The reactivity of the alkyne-BODIPY **A** was examined in the presence of the monobromo (**D**) and dibromo (**E**) derivatives of DPPTh[19] under similar conditions and according to Scheme 2. We found that these cross-coupling reactions were more effective in the absence of copper salt. The use of $[Pd(PPh_3)_4]$ (10 mol %) allowed the preparation of compound **4** in 64% yield (Scheme 2). When two reactive bromide functions were present on the DPPTh starting material **E**, the monosubstituted derivative **5** was isolated in 43% yield using substoichiometric amounts of the BODIPY derivative **A**. The side product (bis coupled derivative) could not be isolated pure due to the presence of various other unidentified products.

The proton NMR spectra of dyads **4** and **5** showed peaks readily assigned to the different modules, and integration of the *β*-pyrrolic protons (2 and 6 in Scheme 2), as a singlet at 6.63 ppm (2H) and thienyl doublets at 6.89 ppm (1H, ^3J = 4.1 Hz) and at 8.93 ppm (1H, ^3J = 4.1 Hz) confirmed the linking of both the BODIPY and DPPTh fragments (Figure S2). For compound **5**, the most deshielded proton signal, a doublet at 8.91 ppm (1H, ^3J = 4.1 Hz) was assigned to the bridging-thienyl five membered ring, while the fact that the vinylic protons resonated as doublets at 7.13 and 8.10 ppm with a coupling constant of 16.2 Hz is characteristic of a *trans* configuration of the double bonds.

To further investigate the scope of this methodology, we examined the cross-coupling reaction of triphenylamine-alkyne derivatives with the same mono- and disubstituted DPPTh derivatives **D** and **E** (Scheme 3). Very good yields for the monosubstituted compounds were obtained (93% for **6** and 87% for **7**). The statistical cross-coupling reaction, under dilute conditions, using **E** and substoichiometric amounts of **B** or **C** afforded the monoderivative **10** and **11** in respectively 42 and

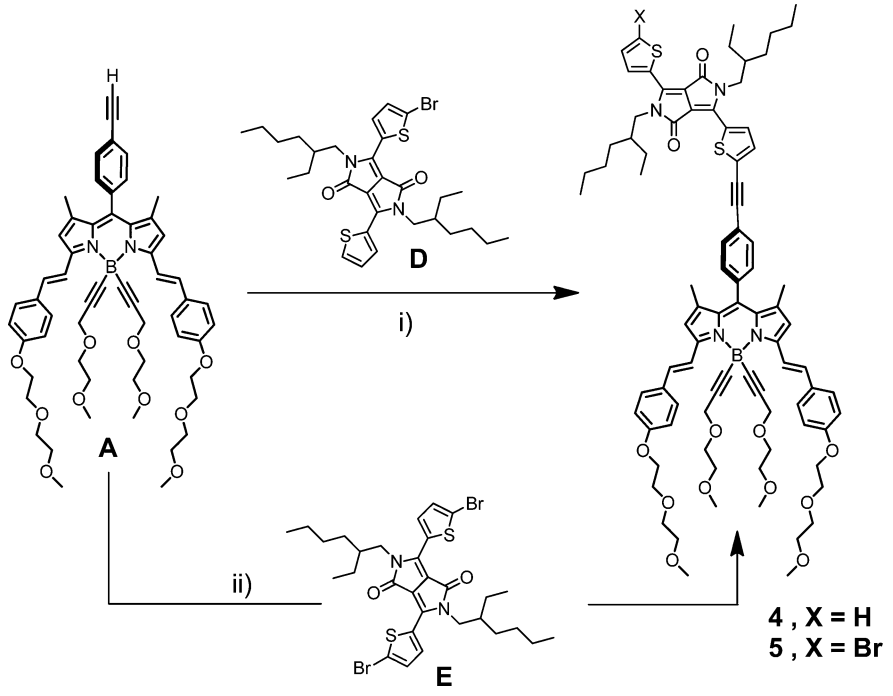
DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737–6753

Scheme 1[a]



[a]Reagents and conditions: (i) $[Pd(PPh_3)_2Cl_2]$ (6 mol %) and CuI (6 mol %), benzene, Et_3N, 65 °C, 89%, 72 h for **2** and 70%, 15 h for **3**.

Scheme 2[a]



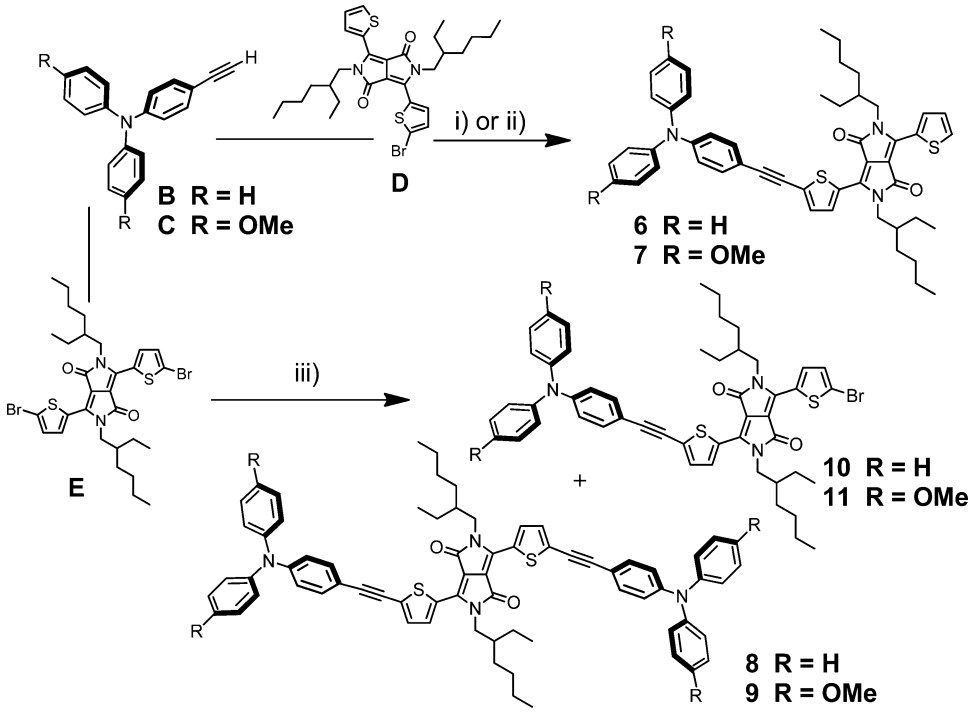
[a]Reagents and conditions: (i) $[Pd(PPh_3)_4]$ (10 mol %) benzene, Et_3N, 60 °C, 48 h, 64% yield for **4**; (ii) $[Pd(PPh_3)_4]$ (5 mol %) benzene, Et_3N, 60 °C, 72 h, 43% yield for **5**.

51% yields. The bis-derivatives **8** and **9** were also isolated here in respectively 26 and 9% yields. This reaction is in marked contrast with the BODIPY cross-coupling reaction where the DPPTh/bis-BODIPY derivatives could not be isolated pure (vide supra). The insertion of triphenylamine modules was obvious in the ^1H NMR spectra, where multiple signals appeared around 7 ppm, corresponding to protons of the phenyl rings. Insertion of one triphenylamine module in cmpd **E** resulted in splitting of the signal of the β-thienyl protons around 9 ppm (see Supporting Information), illustrating the lower symmetry of compounds **10** and **11**. With a second triphenylamine moiety as in **8** and **9**, one signal was observed for 2H at 8.91 ppm for the β-thienyl protons, consistent with recovery of the 2-fold symmetry.

For the synthesis of triads **12** and **13**, mild conditions were used but with longer reaction times and substoichiometric amounts of the BODIPY **A** (about 0.9 equiv). This strategy enabled the easy purification of the target triads without

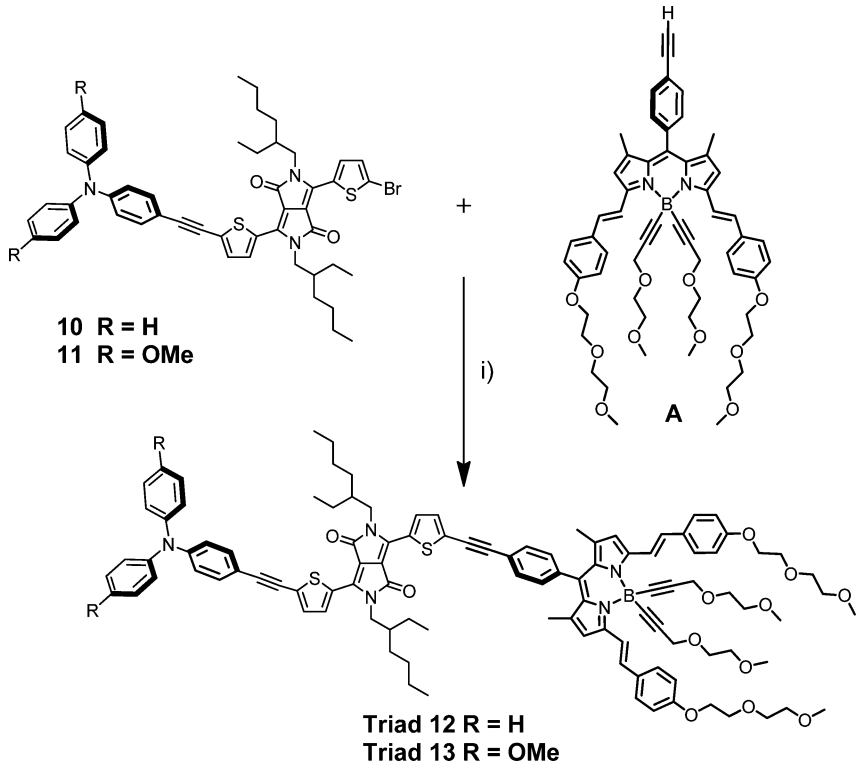
DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

Scheme 3[a]



[a]Reagents and conditions: (i) [$Pd(PPh_3)_4$] (6 mol %), benzene, Et_3N, 60 °C, 15 h, 93% yield for **6**. (ii) [$Pd(PPh_3)_2Cl_2$] (6 mol %) and CuI (6 mol %), benzene, Et_3N, 60 °C, 4 h, 87% yield for **7**. (iii) [$Pd(PPh_3)_4$] (11 mol %) benzene, Et_3N, 70 °C, 35 h, 42% yield for **10**, 51% for **11**, 26% for **8** and 9% for **9**.

Scheme 4[a]

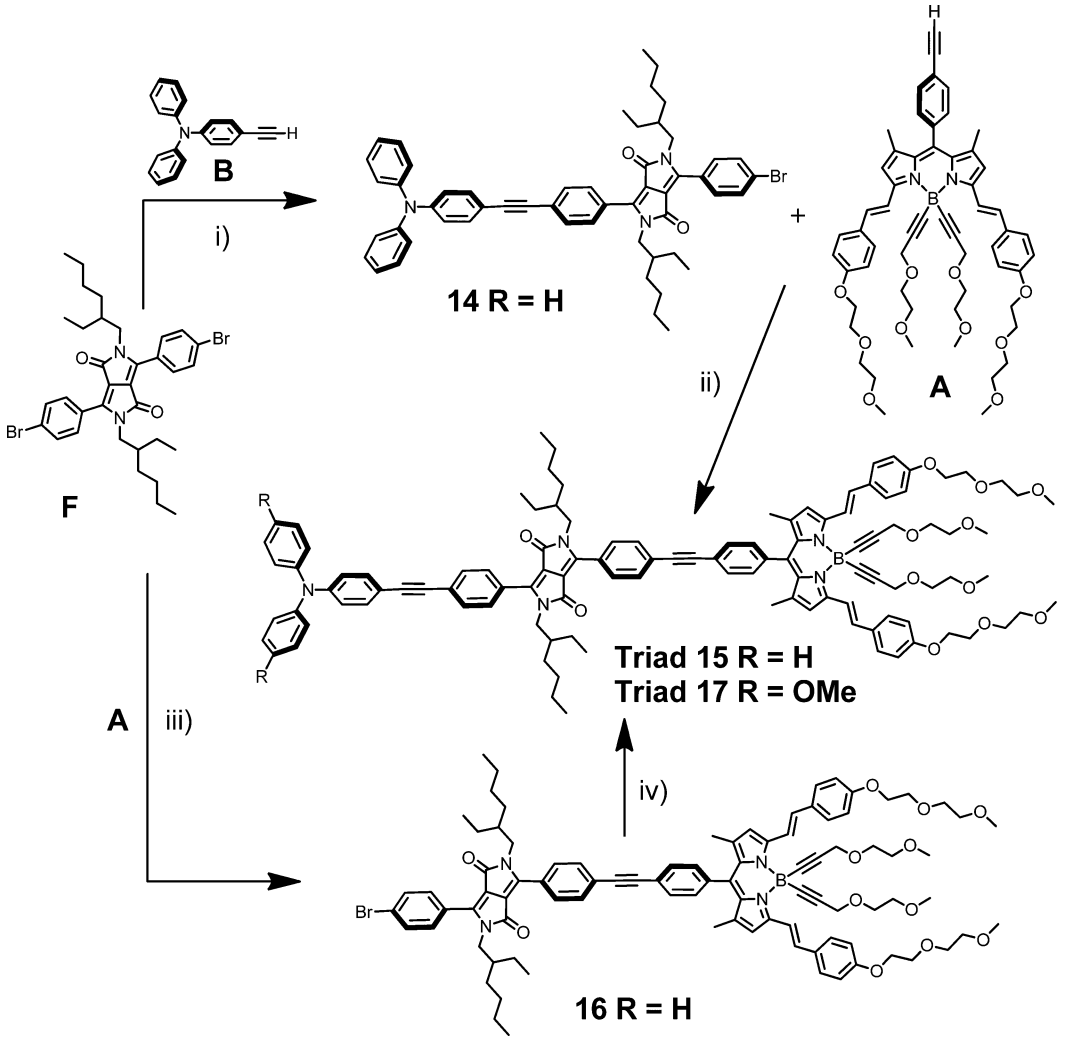


[a]Reagents and conditions: (i) for triad **12** [Pd(PPh3)4] (7 mol %), benzene, Et_3N, 70 °C, 48 h, 66% yield; for triad **13** [$Pd(PPh_3)_4$] (9 mol %), toluene, Et_3N, 100 °C, 16 h, 54% yield.

contamination with the polar starting BODIPY material **A** which has similar polarity to the final compounds. Acceptable yields of 66 and 54% were obtained for dyes **12** and **13** respectively (Scheme 4).

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

Scheme 5[a]



[a]Reagents and conditions: (i) $[Pd(PPh_3)_4]$ (5 mol %), benzene, Et_3N, 70 °C, 15 h, 68% yield for **14**; (ii) $[Pd(PPh_3)_4]$ (8 mol %), benzene, Et_3N, 60 °C, 20 h, 97% yield for **15**; (iii) $[Pd(PPh_3)_4]$ (7 mol %), benzene, Et_3N, 50 °C, 60 h, 54% yield for **16**; (iv) $[Pd(PPh_3)_4]$ (7 mol %), benzene, Et_3N, 60 °C, 72 h, 65% yield for **17**.

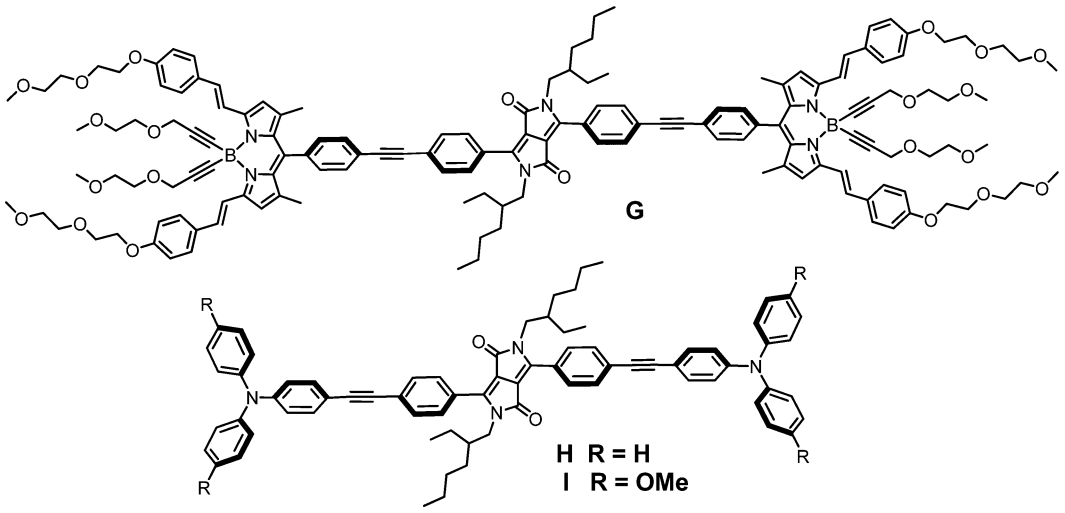


Figure 2. Molecular structures of the side products obtained during the synthesis of compounds **14** and **16**.

The ^1H NMR spectra of triads **12** and **13** are shown in Figure S3. In both cases the deshielded signal at about 9 ppm (2H with ^3J = 4.7 Hz), was assigned to one part of the AB quartet of the bridged thienyl unit. The well-defined doublet at

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

Table 1. Electrochemical Data for Triads 12 and 15 and Associated Reference Compounds[a]

cmpds	E_{ox} (V), ΔE (mV)	E_{red} (V), ΔE (mV)	E_{HOMO} (eV)[b]	E_{LUMO} (eV)[b]
2	+0.65 (60); +0.93 (90); +0.98 (irr)	−1.17 (70)	−5.43	−3.61
4	+0.68 (60); +0.89 (60); +1.22 (80)	−1.13 (60); −1.19 (60); −1.71 (irr)	−5.46	−3.65
5	+0.67 (60); +0.92 (60); +1.23 (80)	−1.16* (80); −1.78 (irr)	−5.45	−3.62
6	+0.81 (60); +0.97 (60); +1.37 (70)	−1.19 (60)	−5.59	−3.59
8	+0.82* (100); +1.15 (60); +1.41 (70)	−1.08 (70)	−5.60	−3.70
10	+0.85 (60); +0.99 (60); +1.39 (irr)	−1.10 (80); −1.76 (irr)	−5.63	−3.68
12	+0.67 (60); +0.83 (60); +0.97 (60); +1.22 (60); +1.39 (irr)	−1.08 (60); −1.17 (60); −1.72 (irr)	−5.45	−3.70
14	+0.94 (60); +1.15 (60)	−1.23 (80); −1.86 (irr)	−5.72	−3.55
15	+0.66 (60); +0.92 (70); +1.16 (60)	−1.20* (irr)	−5.44	−3.58
16	+0.67 (60); +1.09 (irr)	−1.15 (90); −1.25 (60)	−5.45	−3.63
G	+0.66 (60); +1.10 (irr); +1.27 (irr)	−1.14* (110)	−5.44	−3.64
H	+0.93* (80); +1.16 (60)	−1.24 (70)	−5.71	−3.54

[a]All potentials were measured in CH_2Cl_2; 20 °C; Pt; Bu_4NPF_6 0.1 M; Fc/Fc^+ (+0.38 V vs SCE); *assigned as a two-electron process; peak potentials (E_{ap} or E_{cp}) were used for irreversible processes. [b]Calculated assuming that ferrocene (Fc) has an ionization potential of −4.78 eV for the Fc/Fc^+ redox system below the vacuum level.[20]

Table 2. Electrochemical Data for Triads 13 and 17 and Associated Reference Compounds[a]

cmpds	E_{ox} (V), ΔE (mV)	E_{red} (V), ΔE (mV)	E_{HOMO} (eV)[b]	E_{LUMO} (eV)[b]
3	+0.66* (80); +1.06 (80); +1.20 (80); +1.35* (80); +1.50 (irr) (60)	−1.18 (irr)	−5.44	−3.60
4	+0.68 (60); +0.89 (60); +1.22 (80)	−1.13 (60); −1.19 (60) −1.71 (irr)	−5.46	−3.65
5	+0.67 (60); +0.92 (60); +1.23 (80)	−1.16* (80); −1.78 (irr)	−5.45	−3.62
9	+0.67* (70); +0.93 (60); +1.28 (60); +1.40* (60)	−1.12 (80); −1.77 (irr)	−5.45	−3.66
11	+0.68 (60); +0.94 (60); +1.28 (60); +1.42 (irr)	−1.14 (60)	−5.46	−3.64
13	+0.67* (60); +0.92 (60); 1.07 (60); +1.23* (100); +1.41 (80)	−1.07 (60); −1.16 (60); −1.68 (irr)	−5.45	−3.71
16	+0.67 (60); +1.09 (irr)	−1.15 (90); −1.25 (60)	−5.45	−3.63
17	+0.64* (60); +1.19 (irr); +1.36 (70); +1.50 (irr)	−1.14 (60); −1.23 (60) −1.75 (irr)	−5.42	−3.64
G	+0.66 (60); +1.10 (irr); +1.27 (irr)	−1.14* (110)	−5.44	−3.64
I	+0.65* (60); +1.13 (80); +1.34* (90)	−1.25 (irr)	−5.43	−3.53

[a]All potentials were measured in CH_2Cl_2; at rt; Pt; Bu_4NPF_6 0.1 M; Fc/Fc^+ (+0.38 V vs SCE); *assigned as a two-electron process; peak potentials (E_{ap} or E_{cp}) were used for irreversible processes. [b]Calculated assuming that ferrocene (Fc) has an ionization potential of −4.78 eV below the vacuum level.[20]

8.1 ppm (2H with ^3J = 16.2 Hz for **12** and 16.1 Hz for **13**), was assigned to the vinylic protons in a *trans* conformation. Interestingly, despite the complexity of these assemblies (**12** and **13**) with respectively 116H and 120H, the variety of the substituents of each building block allowed a relatively easy assignment of the signals.

We were pleased to find that the protocols described above could be adapted to the DPP-phenyl (DPPPh) series. Cross-coupling **F** with the ethynyl-TPA **B** provided the monosubstituted derivative **14** in respectable yield (68%) (Scheme 5). The bis-coupled side product **H** could also be isolated in 14% yield (Figure 2). Cross-coupling of **14** with **A** in stoichiometric amounts provided triad **15** in 97% yield. Unfortunately, with methoxy substituents on the triphenylamine platform, the monosubstituted BrDPPPh-TPA$(OMe)_2$ could not be isolated but the disubstituted derivative **I** was isolated in 69% yield (Figure 2). Triad **17** was prepared the other way around by first linking the BODIPY dye to the DPP, providing compound **16** in 54% yield (the bis-coupled compound **G** was isolated in 18% yield). The monosubstituted compound was cross-coupled with the TPA$(OMe)_2$ alkyne (cmpd **C**) to provide the desired triad **17** in 65% yield.

Proton NMR spectra of triads **15** and **17** based on DPPPh are depicted in Figure S4. The signals were similar to those observed for DPPTh based triads (**12** and **13**), especially those between 5.0 and 0.5 ppm, characteristic of alkyl groups and polyoxyethylene chains. In the aromatic region, typical signals of the BODIPY moiety were observed at 6.64 ppm (s, 2H), at 8.11 (d, 2H, ^3J = 16.2 Hz) and 8.10 (d, 2H, ^3J = 16.1 Hz), corresponding to the β-pyrrolic protons and the vinylic protons in *trans* configuration, respectively. Here again, despite the relative complexity of the systems, all the 120 and 124 protons of triads **15** and **17** could be separately assigned.

Electrochemical Properties. The triads exhibit interesting redox properties analyzable in terms of those of the individual modules and the associated dyads. Principal results are gathered in Table 1 and Table 2 and illustrated in Figures 3 and 4. As expected from the redox activity of the individual building blocks, the triads displayed several reversible redox processes.

For triad **12**, five distinguishable oxidation processes could be extracted from the cyclovoltamogramm (Figure 3a) and the three first reversible processes at +0.67, +0.83 and +0.97 V were assigned by reference to the corresponding model compounds (Table 1) to the reversible formation of the radical cations of respectively the BODIPY,[21] DPPTh[16a] and triphenylamine fragments.[22] Clearly, the highest occupied molecular orbital (HOMO) of the triad is located on the BODIPY part of the triad (−5.45 eV). The anodic part of the cyclovoltamogramm revealed two reversible processes at −1.08 and −1.17 V and an irreversible process at −1.72 V. By comparison with non-substituted BODIPY and DPPTh dyes, the first reduction potential was taken to be localized on the DPPTh fragment of the triad, enabling assignment of the energy of the lowest unoccupied molecular orbital (LUMO) as −3.70 eV. An in

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

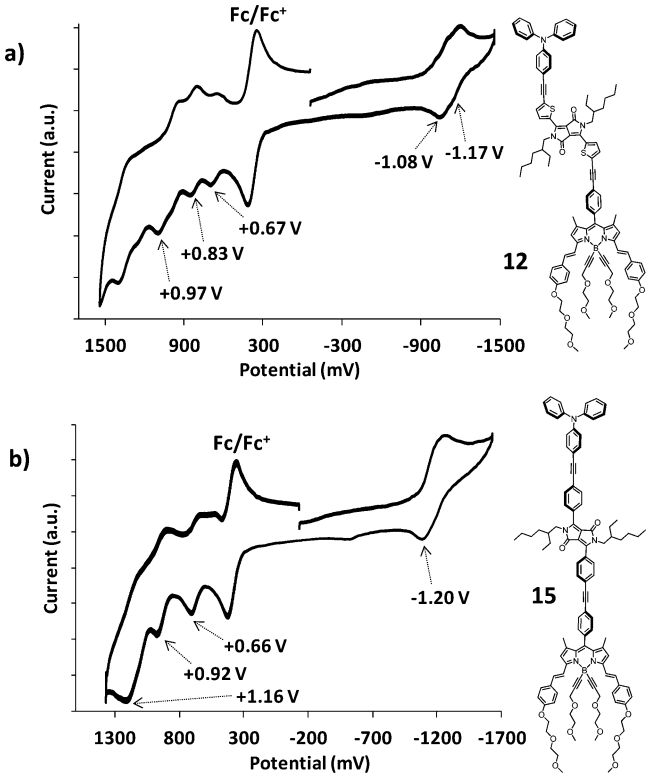


Figure 3. Cyclic voltammograms of triad **12** (a) and of triad **15** (b), measured in CH_2Cl_2; at rt, using Bu_4NPF_6 as supporting electrolyte ≈0.1 M; ferrocene Fc/Fc^+ was used as internal reference and calibrated versus the saturated calomel electrode (SCE). An additional irreversible reduction for **12** (top panel) has been suppressed for the sake of clarity.

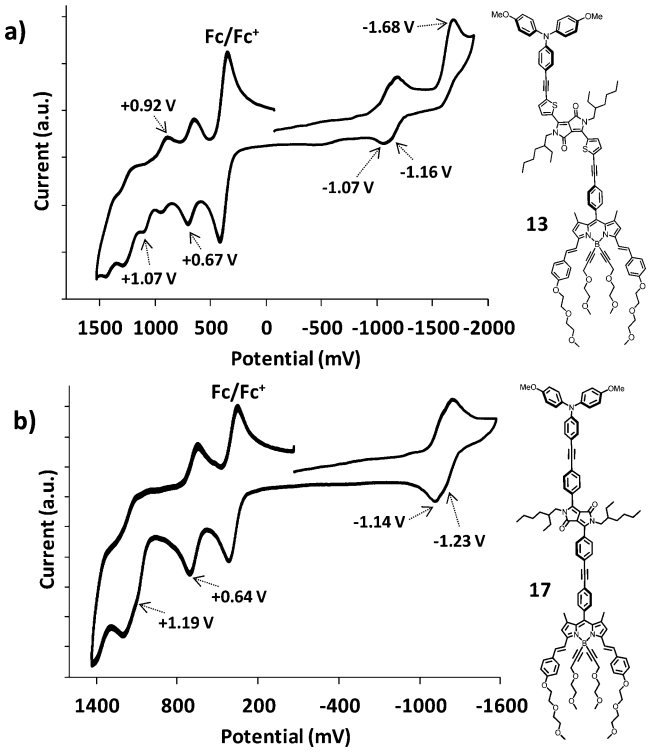


Figure 4. Cyclic voltammograms of triads **13** (a) and **17** (b), measured in CH_2Cl_2; at rt, using Bu_4NPF_6 as supporting electrolyte 0.1 M; ferrocene Fc/Fc^+ was used as internal reference and calibrated versus the saturated calomel electrode (SCE).

depth analysis of triad **12** and related model compounds using spectroelectrochemical techniques has recently been published by our co-workers.[23]

For the triad **15**, only three reversible redox processes were observed at +0.66, +0.92 and +1.16 V (Figure 3b and Table 1) and were assigned by comparison with the individual modules to the radical cations of BODIPY, DPPPh and TPA. In the anodic regime, a single but broad signal was observed at −1.20 V and its integration suggested the presence of two overlapping reversible processes assigned to the radical anions of the DPPPh and BODIPY subunits. In triad **15** we concluded that the HOMO and LUMO frontier orbitals at −5.44 and −3.48 eV are most likely located on the BODIPY moiety.

The situation differs on substitution of the TPA unit with methoxy donor fragments in triads **13** and **17** (Figure 4 and Table 2).

For triad **13**, two reversible anodic processes were observed at −1.07 and −1.16 V and an irreversible wave at −1.68 V. These processes correspond respectively to the radical anions of the DPPTh and BODIPY fragments. As expected, several oxidation processes were observed and the first oxidation at +0.67 V was a two-electron process assigned to the isopotential oxidation of both the BODIPY and $TPA(OMe)_2$ fragments. For triad **17**, the CV exhibited (Figure 4b) two close but distinct processes at −1.14 and −1.23 V, assigned by reference to the model compounds to formation of the radical anions of the BODIPY and DPPPh fragments, respectively. In oxidation, four reversible processes were observed at +0.64, +1.19, +1.36, +1.50 V. The first oxidation has a double intensity due to two overlapping redox processes, as previously observed for triad **13** and corresponds to the simultaneous oxidation of the BODIPY and $TPA(OMe)_2$ modules. Because of the overlapping of the redox processes, the assignment of the HOMO/LUMO frontier orbitals is uncertain in triads **13** and **17** bearing the $TPA(OMe)_2$ module.

Spectroscopic Properties. *Triphenylamine/BODIPY Dyads.* The spectroscopic properties of the dyads and triads were again analyzed by reference to those of the model compounds. Principal results are gathered in Tables 3−5, and illustrated in Figures 5−7. The BODIPY/Triphenylamine dyads **2** and **3** exhibit absorption spectra similar to that of the free BODIPY dye **A**. The most intense transition around 643 nm was assigned to the $S_0 \rightarrow S_1$ of the BODIPY unit, with a vibronic sequence of 1300 cm^{-1} on the high energy side typical of the dipyrromethene framework.[24] The second intense absorption band at higher energy appeared to involve overlap between the $S_0 \rightarrow S_2$ of the BODIPY unit and the absorption of the BODIPY unit and triphenylamine subunit.[25] Negligible shift of this transition was observed by substitution the *para*-position of the TPA unit with a methoxy group (Figure 5b) attesting to the absence of significant electronic interaction between the TPA and BODIPY modules. This effect is expected based on the twisting of the phenyl rings along the tolane spacing unit.[26]

Interestingly, irradiation of the dyads in the less energetic absorption band resulted in strong structured fluorescence, mirroring the absorption spectra, an observation indicative of a singlet emitter (Figure 5). The lifetimes of the excited state are in the nanosecond range (respectively 6.2 ns for cmpd **2** and 4.3 ns for dyad **3**, Table 3). The weak Stokes shifts (<400 cm^{-1}) are in keeping with little reorganization in the excited states and are typical of a singlet emission.[27] The excitation

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

Table 3. Spectroscopic Data for Dyads 2 and 3[a]

cmpds	λ_{abs} (nm)	fwhm (cm^{-1})	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Δss (cm^{-1})	Φ_f	τ (ns)	solvent
2	375/595/649	720	146 000	664/725	350	0.59	6.3	Toluene
	371/593/643	760	132 000	660/719	400	0.44	6.2	THF
3	376/596/649	740	139 000	662/725	300	0.66	4.5	Toluene
	374/593/645	730	138 000	658/720	310	0.61	4.3	THF

[a]BODIPY TetraOMe (Φ_f = 0.49 in CH_2Cl_2, excitation λ_{ex} = 650 nm)[28] used as reference.

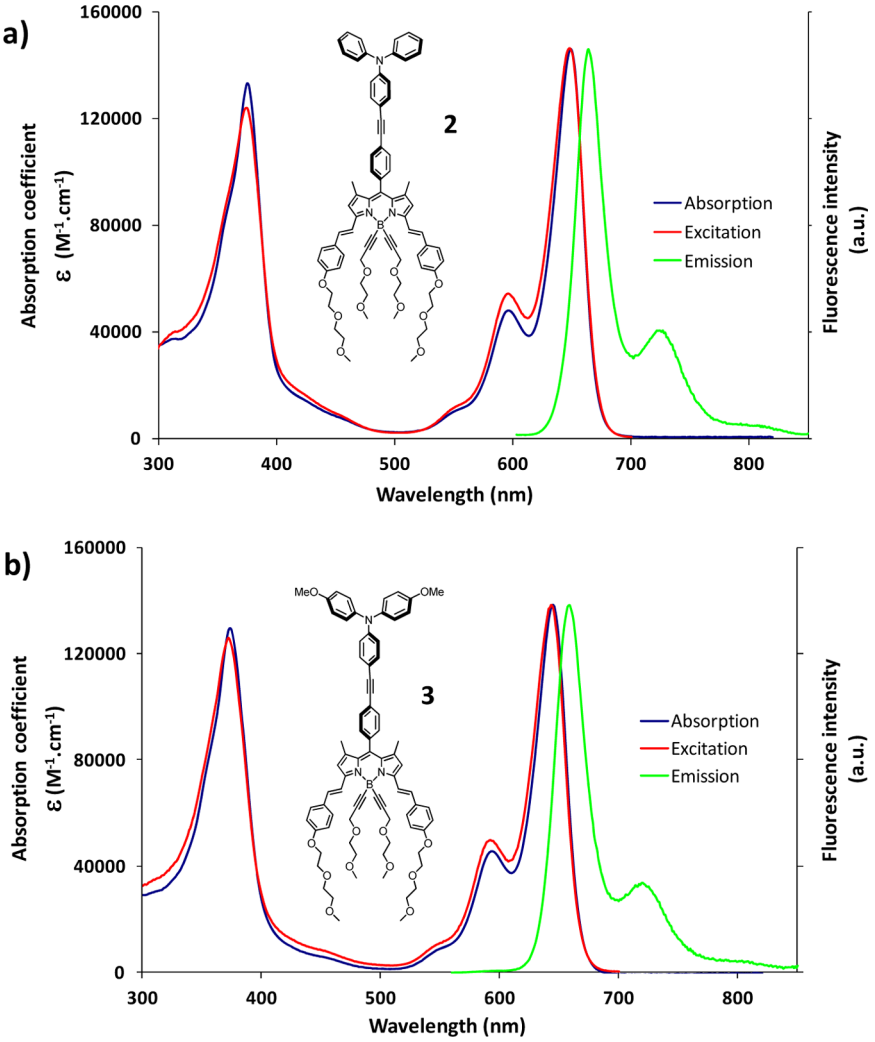


Figure 5. Absorption (blue line), emission (green line) and excitation spectra (red line, λ_{em} = 725 nm for **2**, 720 nm for **3**) of dyad **2** (a) and dyad **3** (b) at rt in THF.

spectra measured with an emission at 720 nm perfectly overlaps the absorption spectra and thus excluded formation of aggregates and the presence of impurities. The fluorescence quantum yields were high in both dyads and not solvent dependent. No electron transfer from the triarylamine to the excited state of the BODIPY seemed to be effective under these conditions. This result is in keeping with the absence of fluorescence quenching when compared to the fluorescence of the isolated BODIPY dye under the same conditions [Φ_f = 48% and τ = 4.7 ns and in THF for derivative **A**].

DPP/BODIPY Dyads. In contrast with the previous dyads based on triphenylamine, dyad **16** exhibited three main absorption bands at 372, 489, and 645 nm (Figure 6). The shape and wavelengths of these bands were similar to the absorption of the isolated modules and reflect the absence of major electronic interactions. Indeed the global absorption spectrum was an almost linear combination of the absorption of the respective modules. Selective irradiation of the DPPPh absorption at 489 nm did not produce any residual emission at 568 nm but exclusively emission at 659 nm with a QY of 53%. This was the result of almost quantitative energy transfer from the DPPPh module to the BODIPY moiety, as confirmed by the excitation spectrum which overlapped perfectly with the absorption spectra and proved that the DPPPh contributed to the emission at 659 nm. This result is in keeping with previous observations made with similar linked systems.[29] The QY and lifetime of the excited state were not influenced by the proximity of the bromine atom at the para position of the external phenyl ring. The efficiency of this energy transfer is probably due to a favorable spectral overlap between the

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

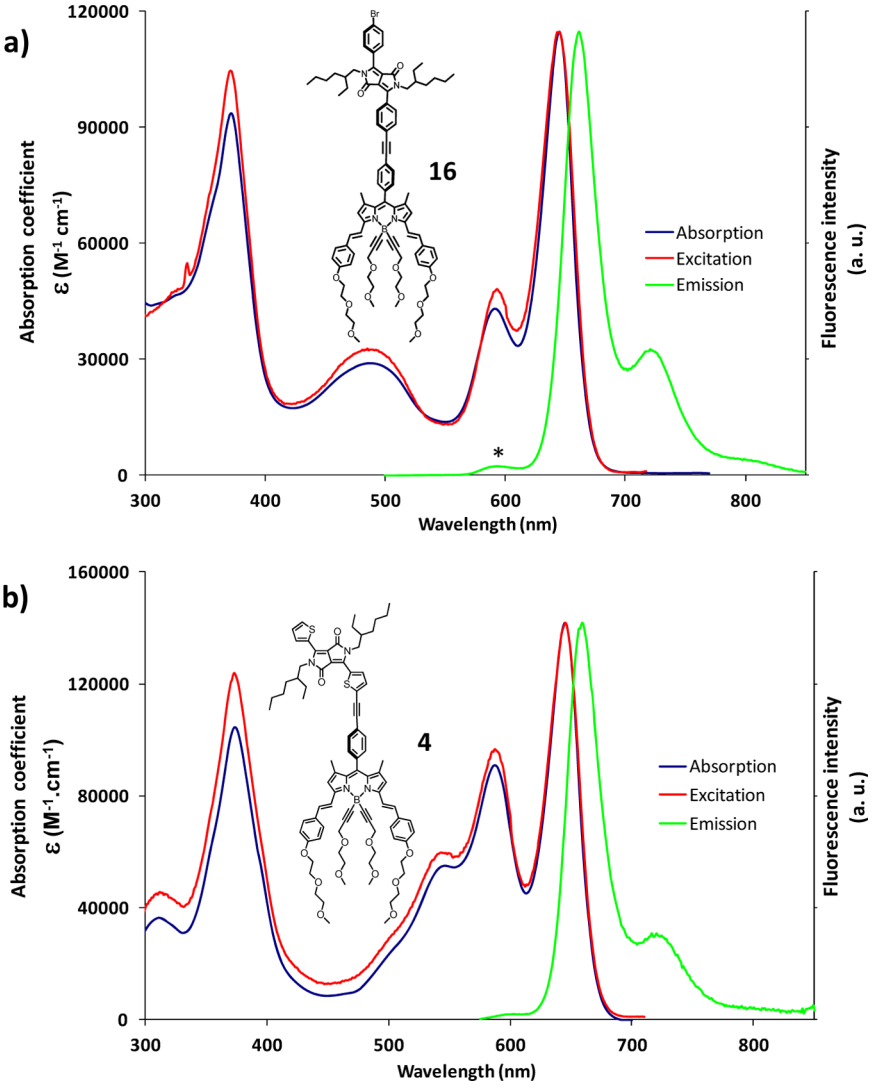


Figure 6. Absorption (blue line), emission (green line) and excitation spectra (red line, λ_{em} = 669 nm for **16**, 667 nm for **4**) of dyad **16** (a) and dyad **4** (b) at rt in THF. *Emission of traces of a side product assigned to the monovinyl BODIPY derivative.

Table 4. Spectroscopic Data for Selected Compounds and Triads 4 and 16

cmpds	λ_{abs} (nm)	fwhm (cm^{-1})	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Δ_{ss} (cm^{-1})	Φ_f	τ (ns)	solvent
4	311/374/546/587/645	780	142 000	660/721[d]	420	0.43[a]	4.2	THF
5	315/373/551/592/645	750	133 000	663/722[d]	420	0.08[a]	1.2/4.0	THF
6	300/346/423/550/582	3000	52 000	617/664	980	0.30[b]	2.6	THF
7	301/352/556/585	3100	55 900	642/678/816	1520	aggegates	n.d.	THF
	302/356/560/589	3000	54 800	624/677	950	0.29[b]	2.7	Toluene
8	350/446/584/623	3000	83 500	660/717	900	0.32[a]	2.4	THF
9	353/461/592/633	3000	96 000	671/729	900	0.02[a]	n.d.	THF
10	307/339/432/558/591	3000	53 400	624/675	900	0.11[b]	2.4	THF
11	310/355/563/595	3000	64 500	–	–	–	–	THF
	311/360/565/600	2900	61 000	632/688	840	0.40[b]	2.7	Toluene
14	287/324/491	3900[c]	49 000	568	2800	0.27[b]	3.3	THF
16	372/489/592/645	750	115 000	659/721[d]	330	0.53[a]	4.6	THF
H	300/331/407/505	4000[c]	52 000	587	2800	0.47[b]	2.9	THF
I	337/427/512	4200[c]	51 200	–	–	–	–	THF
	340/434/513	4200	53 000	594/645	2700	0.86[b]	2.6	Toluene

[a]Quantum yields were determined using BODIPY TetraOMe (Φ_f = 0.49 in CH_2Cl_2, excitation λ_{ex} = 650 nm) as reference.[27] [b]Quantum yields were determined using cresyl violet (Φ_f = 0.51 in EtOH, excitation λ_{ex} = 578 nm) as reference.[32] [c]Estimated using an approximation on the absorption band on the high energy side. [d]Emission of the monostyryl BODIPY observed.

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737–6753

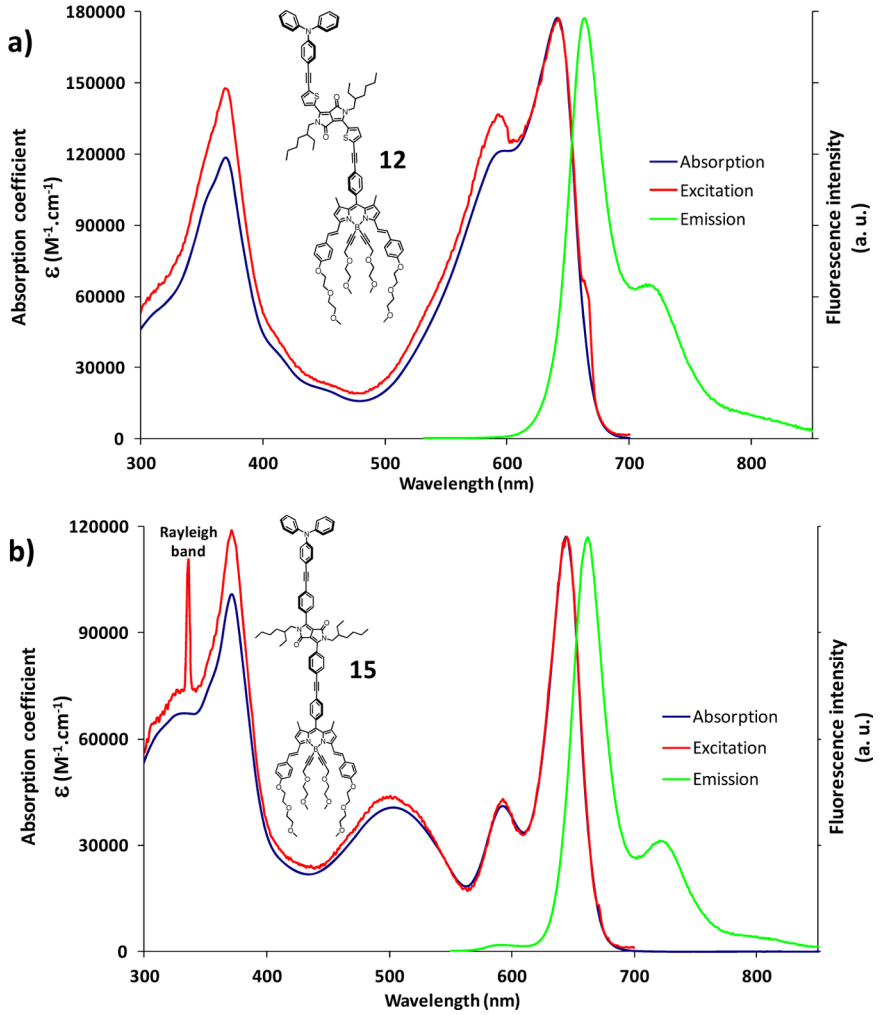


Figure 7. Absorption (blue line), emission (green line) and excitation spectra (red line, λ_{em} = 665 nm for **12**, 671 nm for **15**) of triads **12** (a) and **15** (b) at rt in THF.

emission of the DPPPh module and the absorption of the BODIPY.[30]

In the second dyad (cmpd **4**), the situation was different due to the fact that the DPPTh derivatives are bathochromically shifted by ca. 60 nm and partially overlaps with the absorption of the BODIPY core (Figure 6b). By irradiation in the DPPTh fragment around 510 nm exclusive fluorescence of the BODIPY is observed with a quantum yield of 43% in THF (Table 4). This fluorescence band was observed no matter what the excitation wavelength and the excitation spectrum confirmed that all the modules contributed to the emission of the BODIPY subunit. Unlike the DPPPh bearing a bromide atom, substitution of the external thienyl unit by a bromo function severely quenched the fluorescence (from 43% to 8%), likely due to intersystem crossing (ISC) favoring the triplet of the DPPTh due to an heavy atom effect.[26] The efficiency of the energy transfer reflected the strong spectral overlap between the energy donor (DPPTh) and the energy acceptor (BODIPY).[31]

Triphenylamine/DPP/BODIPY Triads. The spectral profiles of the TPA/DPPTh/BODIPY **12** and TPA/DPPPh/BODIPY **15** are shown in Figure 7, whereas the dimethoxy analogues (**13** and **17**) are shown in Figure 8. Selected data are gathered in Table 5.

The absorption spectrum of the thienyl based triad **12** exhibits two major absorption bands between 300 and 440 nm and 500−700 nm. The higher-energy absorption band involves an overlap of the absorption of the TPA[33] and $S_0 \rightarrow S_2$ transition of the BODIPY[34] fragments whereas the broad absorption at lower energy corresponds to an overlap between the absorption of the DPPTh[35] and the first excited state of the BODIPY.[36] Compared to the dyad DPPTh/BODIPY **4** a significant bathochromic shift of 50 nm of the DPPTh fragment in the triad was observed (Figure 7 and Table 4 and Table 5). The emission band at 662 nm in THF was structured but the QY dropped to 6% when compared to toluene (49%), a result observed regardless of the excitation wavelength. Recent results using ultrafast spectroscopy have revealed that electron transfer from the TPA to the DPPTh and BODIPY occurs within 52 ps.[37] Interestingly, when increasing the solvent polarity from toluene to THF, no significant bathochromic shift linked with a charge transfer process was observed on the BODIPY absorption. This observation could suggest that the charge transfer process would be more pronounced between the triphenylamine and the DPP module. The occurrence of a photoinduced electron transfer (PET) was estimated using the Rehm−Weller equation[38] and models (for instance **2** and **8**), which provided values of ΔG = −0.23 eV and ΔG = −0.13 eV for PET occurring respectively between TPA and BODIPY*

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

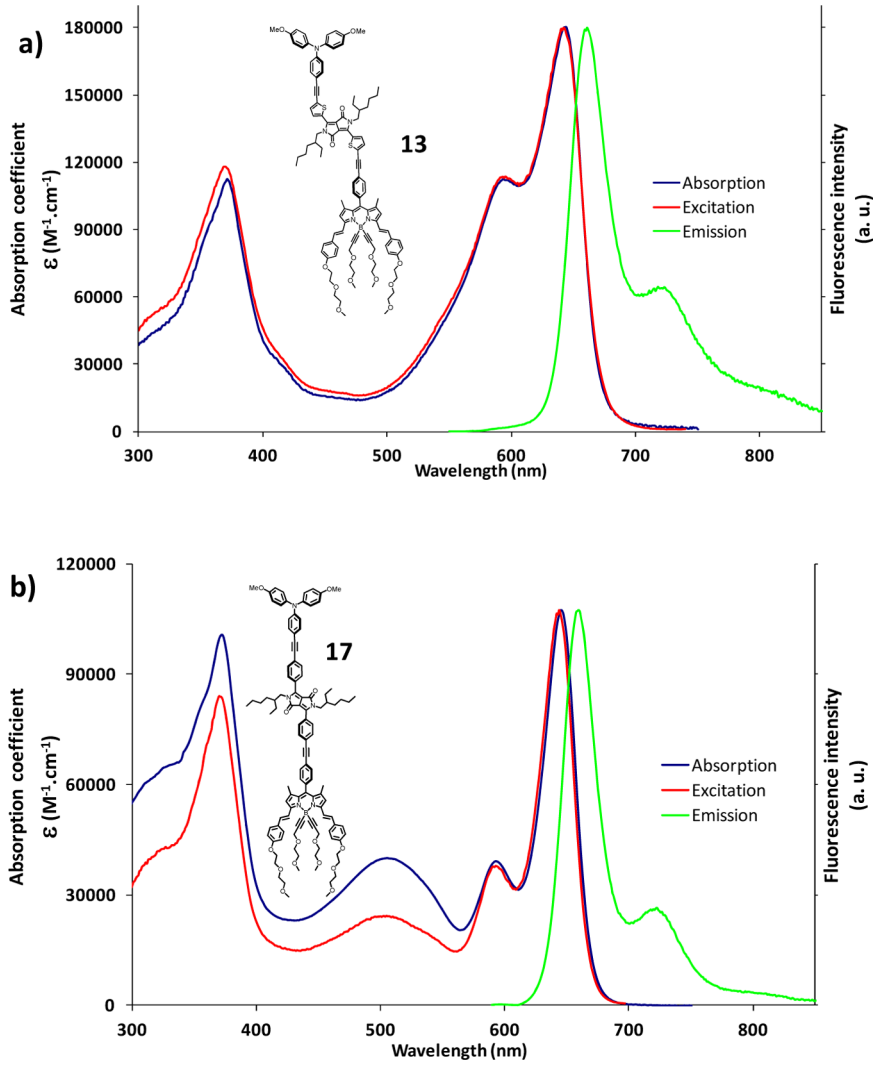


Figure 8. Absorption (blue line), emission (green line) and excitation spectra (red line, λ_{em} = 760 nm for **13**, 720 nm for **17**) of triads **13** (a) and **17** (b) at rt in THF.

Table 5. Spectroscopic Data for the Triads

cmpds	λ_{abs} (nm)	fwhm (cm^{-1})	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Δ_{ss} (cm^{-1})	Φ_f[a]	τ (ns)	solvent
12	370/599/648	2285	157 000	666/724	420	0.49	4.2	Toluene
	369/593/641	2420	177 000	662/719	500	0.06	0.8/3.6	THF
13	374/596/647	2135	181 000	663/723	370	0.47	3.7	Toluene
	371/593/644	2160	180 000	661/723	400	0.02	0.9/4.2	THF
15	323/375/504/598/650	720	139 000	665/727[b]	350	0.66	5.9	Toluene
	334/372/503/594/645	780	117 000	660/721[b]	350	0.34	4.8	THF
17	375/508/596/650	770	93 000	662/726	280	0.44	4.9	Toluene
	372/507/593/645	750	107 000	660/723	350	0.39	4.5	THF

[a]Quantum yields were determined using BODIPY TetraOMe (Φ_f = 0.49 in CH_2Cl_2, excitation λ_{ex} = 650 nm) as reference.[27] [b]Emission of residual monostyryl BODIPY derivative.

and TPA and DPPTh* (for details of calculations see Supporting Information paragraph 7).

As would be expected based on the fact that $TPA(OMe)_2$ is a better electron donor than TPA (see Electrochemical Properties section described above), the same decrease of quantum yield (from 47% in toluene to 2% in THF) was observed for **13** (Table 5). Concerning the DPPPh based triads, a decrease of the QY was also observed for **15** when increasing the dipolar moment of the solvent from toluene to THF (66−34%), while for triad **17** including the $TPA(OMe)_2$ moiety, no notable influence of the solvent polarity was observed (44−39%). Unlike those for for triad **12**, calculated free energies associated with PET in other triads had mostly positive values for a PET between the triphenylamine unit and BODIPY*, therefore indicating that no relation could be established between the decrease of QY and a potential PET process which is clearly unfavorable for triad **15**.

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

For the DPPPh triads, the decrease of quantum yield by increasing the dipole moment of the solvent was less spectacular (decrease of 48% in triad **15** compared to a decrease of 88% in triad **12** and a decrease of 11% in **17** compared to a decrease of 96% in **13**).

CONCLUSION

We succeeded in the development of an efficient strategy for the controlled synthesis of four electro- and photoactive dyads and four triads based on dedicated cross-coupling reactions promoted by palladium(0) precursors. Separation and purification of the target assemblage was facilitated by the increased polarity of the incoming module. In some cases statistical C−C bond formation reached values as high as 51% for monofunctionalization (DPPThio case) or 68% for the DPPPh case. This key monofunctionalization process allows the preparation of the dedicated triads in good yields. As expected from their design, the electroactivities of the dyads and triads could be analyzed in terms of the properties of the constituent modules, showing that there is no strong interaction of these units within the dyads and triads. Further support for this conclusion was provided in the absorption and emission spectra of the multichromophoric systems in dilute solutions. Examination of the respective QYs showed that some deactivation channels (e.g., photoinduced electron transfer) are effective in the triads incorporating the DPPTh backbone. These triads display very strong (panchromatic) absorption in the visible part of the electromagnetic spectrum (300−700 nm in the best cases), indicating possible applications in organic photovoltaics (solar cells, transistors, electronic tongues and noses) and research along these lines is currently in progress.

EXPERIMENTAL PROCEDURES

$[Pd(PPh_3)_4]$[39] and $[PdCl_2(PPh_3)_2]$[40] were synthesized according to the indicated literature procedures. Purifications of *N*-bromosuccinimide (NBS), Bu_4NPF_6, 2-(2-methoxyethoxy)ethanol were performed according to the reported literature.[41] All other reagents were used directly as obtained commercially.

General Procedure Number 1. Sonogashira cross coupling reactions were performed in Schlenk flasks under argon or nitrogen atmosphere. All the reagents/reactants were solubilized in the indicated solvent and base system and degassed for 30 min, before $[Pd(PPh_3)_4]$ was added in one portion. Temperature and time indications are given in the synthetic procedures.

General Procedure Number 2. Sonogashira cross coupling reactions were performed in Schlenk flasks under argon or nitrogen atmosphere. Reagents/reactants were solubilized in the indicated solvent and base system, including the catalyst ($[PdCl_2(PPh_3)_2]$]) and degassed for 30 min, before CuI was added in one portion. Temperature and time indications are given in the synthetic procedures. Please note that volatile reagents (e.g., ethynyltrimethylsilane) were added at the last minute.

BODIPY **A** was synthesized in two steps from compound **1**. First, the alkyne linker was introduced, followed by its deprotection.

BODIPY **1** was synthesized according to the literature procedure.[42] Metallic red solid, 1.142 g, 83%, ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.46 (s, 6H), 3.15−3.18 (m, 4H), 3.19 (s, 6H), 3.41 (s, 6H), 3.50−3.53 (m, 4H), 3.58−3.61 (m, 4H), 3.73−3.76 (m, 4H), 3.88−3.91 (m, 4H), 4.15 (s, 4H), 4.17−4.21 (m, 4H), 6.62 (s, 2H), 6.97 (d, 4H, ^3J = 8.8 Hz), 7.11 (d, 2H, ^3J = 8.3 Hz), 7.12 (d, 2H, ^3J = 16.2 Hz), 7.58 (d, 4H, ^3J = 8.8 Hz), 7.84 (d, 2H, ^3J = 8.3 Hz), 8.09 (d, 2H, ^3J = 16.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) =15.2, 58.9, 59.2, 59.5, 67.7, 68.3, 69.8, 70.9, 71.6, 72.1, 91.7, 94.6, 115.2, 118.2, 119.2, 128.9, 130.3, 130.8, 131.4, 134.2, 135.4, 136.8, 138.3, 140.1, 152.3, 159.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = −13.0 (s).

BODIPY 1-TMS. To a degassed solution of compound **1** (1.116g, 1.06 mmol) and $[PdCl_2(PPh_3)]$ (6 mol %) in benzene (50 mL) and triethylamine (12 mL) was added CuI (6 mol %) and ethynyltrimethylsilane (0.3 mL, 2.12 mmol, 2 equiv). The reaction medium was stirred at 70 °C overnight. The solution was then evaporated, taken up in CH_2Cl_2, washed with water twice, with brine and dried over Na_2SO_4. Purification on column chromatography (SiO_2) using EtOAc/CH_2Cl_2 as eluent (gradient from 90/10 to 100/0) afforded the desired product in 94% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.28 (s, 9H), 1.43 (s, 6H), 3.15−3.16 (m, 4H), 3.19 (s, 6H), 3.40 (s, 6H), 3.50−3.52 (m, 4H), 3.58−3.60 (m, 4H), 3.73−3.75 (m, 4H), 3.88−3.90 (m, 4H), 4.15 (s, 4H), 4.18−4.20 (m, 4H), 6.61 (s, 2H), 6.97 (d, 4H, ^3J = 8.8 Hz), 7.11 (d, 2H, ^3J = 16.4 Hz), 7.30 (d, 2H, ^3J = 8.2 Hz), 7.57 (d, 4H, ^3J = 8.8 Hz), 7.60 (d, 2H, ^3J = 8.4 Hz), 8.09 (d, 2H, ^3J = 16.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 0.0, 15.2, 58.9, 59.2, 59.5, 67.6, 68.3, 69.8, 70.9, 71.6, 72.1, 91.6, 95.7, 104.5, 115.2, 118.1, 119.2, 123.8, 128.9, 130.3, 131.3, 132.6, 134.0, 136.1, 137.5, 140.1, 152.2, 159.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = −13.0 (s). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 645 (145 500), 594 (48 300), 371 (90 700), 320 (25 100). ESI-MS (*m*/*z*, relative intensity) theoretical mass 1020.51 (100); found 1021.3 (100). Anal. Calcd for $C_{60}H_{73}BN_2O_{10}Si$ (M_r = 1020.51): C, 70.57; H, 7.21, N, 2.74. Anal. found: C, 70.38; H, 6.98; N, 2.52.

BODIPY A. A solution of BODIPY **1**-TMS (981.7 mg, 0.961 mmol) and K_2CO_3 (2.799 g, 20.25 mmol, 21 equiv) in THF/MeOH was stirred at rt overnight. The reaction medium was extracted with EtOAc, washed with water and brine, dried over Na_2SO_4. Purification on column chromatography (SiO_2) using EtOAc/CH_2Cl_2 (90/10) as eluent, followed by recrystallization in THF/*n*-pentane afforded metallic red needles (889.7 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.44 (s, 6H), 3.15−3.17 (m, 4H), 3.18 (s, 1H), 3.20 (s, 6H), 3.41 (s, 6H), 3.50−3.53 (m, 4H), 3.58−3.61 (m, 4H), 3.73−3.76 (m, 4H), 3.88−3.91 (m, 4H), 4.16 (s, 4H), 4.18−4.21 (m, 4H), 6.62 (s, 2H), 6.98 (d, 4H, ^3J = 8.8 Hz), 7.12 (d, 2H, ^3J = 16.2 Hz), 7.34 (d, 2H, ^3J = 8.1 Hz), 7.58 (d, 4H, ^3J = 8.8 Hz), 7.63 (d, 2H, ^3J = 8.1 Hz), 8.09 (d, 2H, ^3J = 16.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 15.2, 58.9, 59.2, 59.5, 67.7, 68.3, 69.8, 70.9, 71.7, 72.1, 78.5, 83.2, 91.7, 115.2, 118.1, 119.2, 122.8, 128.9, 129.1, 130.3, 131.4, 132.8, 134.1, 136.5, 137.4, 140.1, 152.3, 159.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = −13.0 (s). ESI-MS (*m*/*z*, relative intensity) theoretical mass 948.9 (100); found 949.3 (100). Anal. Calcd for $C_{57}H_{65}BN_2O_{10}$ (M_r = 948.47): C, 72.14; H, 6.90, N, 2.95. Anal. found: C, 71.90; H, 6.62; N, 2.77.

TPA (cmpd **B**) was synthesized in two steps according to the reported procedure.[43] (Yellowish oil, 470.5 mg, 59% over two steps, ^{1}H NMR (200 MHz, $(CD_3)_2CO$) δ (ppm) = 3.53 (s, 1H), 6.94 (d, 2H, ^3J = 8.8 Hz), 7.08−7.15 (m, 3 + 3H), 7.30−7.38 (m, 2 + 4H).

TPA(OMe)$_2$Br.[44] The Ullmann type condensation reaction was performed under an argon atmosphere, in a large round-bottom flask (250 mL) equipped with a condenser protected from light. *p*-Bromoaniline (4.9 g, 28.6 mmol, 1 equiv), CuCl (280.1 mg, 10 mol %), 1,10-phenanthroline·H_2O (557.0 mg, 10 mol %) and KOH (8.0 g, 143.0 mmol, 2.5 equiv) were successively added to a degassed solution of *p*-iodoanisole (16.0 g, 68.4 mmol, 2.4 equiv) in *p*-xylene (75 mL). The reaction medium was stirred at 160 °C for 40 h. Water was then added at rt and a solution of concentrated HCl was used to neutralize the black reaction medium. Extractions with CH_2Cl_2 were performed. The organic layers were combined and washed with water, dried with brine and over Na_2SO_4. Purification on an alumina column chromatography using PE/CH_2Cl_2 (90/10) as eluent afforded a brownish ochre solid (8.6 g, 78%). ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm) = 3.79 (s, 6H), 6.76 (d, 2H, ^3J = 8.9 Hz), 6.92 (d, 4H, ^3J = 9.1 Hz), 7.07 (d, 4H, ^3J = 9.1 Hz), 7.30 (d, 2H, ^3J = 8.9 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ (ppm) = 55.7, 112.2, 115.8, 122.0, 127.9, 132.5, 141.1, 149.3, 157.5. EI-MS (*m*/*z*, relative intensity) theoretical mass 383.05 (100), 385.05 (97.4); found 385.0 (100), 387.0 (100). Anal. Calcd for $C_{20}H_{18}BrNO_2$ (M_r = 384.27): C, 62.51; H, 4.72, N, 3.65. Anal. found: C, 62.35; H, 4.44; N, 3.48.

TPA(OMe)$_2$TMS.[39] $[PdCl_2(dppf)]$ (61.4 mg, 6 mol %) and ethynyltrimethylsilane (0.60 mL, 4.246 mmol, 3 equiv) were added

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

at rt to a degassed solution of TPA(OMe)$_2$Br (538.6 mg, 1.401 mmol), KI (173.7 mg, 75 mol %) and CuI (16.4 mg, 6 mol %) in THF (8 mL) and Et$_3$N (8 mL). The solution was stirred in a closed Schlenk tube at 90 °C for 60 h in the dark. The reaction medium was filtered on Celite, then extracted with CH_2Cl_2, washed with water and dried with brine and over Na_2SO_4. Filtration on a silica pad using a gradient of CH_2Cl_2/PE (40/60 to 50/50) gave yellow oil (506.6 mg, 90%). ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm) = 0.20 (s, 9H), 3.80 (s, 6H), 6.72 (d, 2H, ^3J = 9.0 Hz), 6.94 (d, 4H, ^3J = 9.0 Hz), 7.09 (d, 4H, ^3J = 9.0 Hz), 7.23 (d, 2H, ^3J = 9.0 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ (ppm) = 0.2, 55.8, 92.3, 106.9, 114.2, 115.8, 118.9, 128.4, 133.5, 140.7, 150.3, 157.8.

TPA(OMe)$_2$ (cmpd C).[39] K_2CO_3 (962.9 mg, 6.970 mmol, 5.5 equiv) was added to a solution of TPA(OMe)$_2$TMS (506.6 mg, 1.262 mmol) in THF (30 mL)/MeOH (20 mL)/H_2O (3 mL). The reaction was protected from light and stirred at rt for 15 h, then extracted with CH_2Cl_2, washed with water and dried with brine and over Na_2SO_4. Purification on a silica column chromatography, using a gradient of toluene/PE (50/50 to 80/20) afforded a yellow oil (276.5 mg, 67%). ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm) = 3.45 (s, 1H), 3.80 (s, 6H), 6.74 (d, 2H, ^3J = 8.8 Hz), 6.93 (d, 4H, (d, 2H, ^3J = 9.0 Hz), 7.09 (d, 4H, (d, 2H, ^3J = 9.0 Hz), 7.26 (d, 2H, (d, 2H, ^3J = 8.8 Hz). ^{13}C NMR (100 MHz, acetone-d_6) δ (ppm) = 55.7, 77.3, 84.8, 113.4, 115.8, 119.0, 128.4, 133.6, 140.7, 150.3, 157.8. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 322 (21 500), 295 (20 200).

DPPThBr (cmpd **D**) and DPPThBr$_2$ (cmpd **E**) were synthesized according to the reported procedures.[45,46] Cmpd **D**: fushia purple amorphous solid, 338.5 mg, 53%, ^{1}H NMR (300 MHz, CDCl3) δ (ppm) = 0.83−0.92 (m, 12H), 1.16−1.39 (m, 16H), 1.76−1.90 (m, 2H), 3.92−4.04 (m, 4H), 7.22 (d, ^3J = 4.2 Hz, 1H), 7.25−7.29 (m, 1H), 7.63−7.66 (m, 1H), 8.64 (d, ^3J = 4.2 Hz, 1H), 8.90−8.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.2, 14.2, 23.2, 23.7, 28.5, 30.3, 39.2, 39.3, 46.1, 107.9, 108.3, 118.8, 128.6, 129.9, 131.0, 131.4, 131.5, 135.2, 135.7, 139.1, 141.0, 161.6, 162.0, 219.3. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 557 (33 3000), 518 (27 800), 347 (13 100), 294 (23 500). EI-MS (*m*/*z*, relative intensity) theoretical mass 604.16 (100), 602.16 (93.8); found 602.1 (100), 604.1 (98). Anal. Calcd for $C_{30}H_{39}BrN_2O_2S_2$ (M_r = 603.68): C, 59.69; H, 6.51, N, 4.64. Anal. found: C, 59.52; H, 6.38; N, 4.32. Cmpd **E**: deep purple amorphous solid, 815.1 mg, 73%, ^{1}H NMR (300 MHz, CDCl3) δ (ppm) = 0.86−0.90 (m, 12H), 1.23−1.39 (m, 16H), 1.76−1.87 (m, 2H), 3.85−3.97 (m, 4H), 7.21 (d, 2H, ^3J = 4.1 Hz), 8.63 (d, 2H, ^3J = 4.1 Hz)). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.1, 23.2, 23.7, 28.5, 29.8, 30.3, 39.2, 46.2, 108.1, 119.1, 131.3, 131.6, 135.5, 139.5, 161.5. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 566 (36 100), 526 (30 400), 355 (13 900), 302 (25 200). EI-MS (*m*/*z*, relative intensity) theoretical mass 682.07 (100), 684.07 (56), 680.07 (49.1); found 682.0 (100), 684.0 (56), 680.0 (50). Anal. Calcd for $C_{30}H_{38}Br_2N_2O_2S_2$ (M_r = 682.57): C, 52.79; H, 5.61; N, 4.10. Anal. found: C, 52.54; H, 5.37; N, 3.72.

DPPPhBr$_2$ (cmpd **F**) was synthesized according to the reported procedure.[47] (Yellowish-orange solid, 376.9 mg, 25%, ^{1}H NMR (300 MHz, CDCl3) δ (ppm) = 0.69 (t, 6H, ^3J = 7.4 Hz), 0.78 (t, 6H, ^3J = 7.1 Hz), 1.06−1.18 (m, 16H), 1.35−1.44 (m, 2H), 3.67 (d, 4H, ^3J = 7.3 Hz), 7.58 (sl, 8H)). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.7, 14.3, 23.2, 24.1, 28.6, 30.7, 38.8, 45.2, 110.0, 125.9, 127.5, 130.4, 132.4, 148.0, 162.7. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 476 (17 400), 274 (26 900).

Compound **2**. According to general procedure number 2, compound **1** (179.5 mg, 0.170 mmol, 1 equiv), 4-ethynyl-*N*,*N*-diphenylaniline (cmpd **B**) (70.3 mg, 0.261 mmol, 1.5 equiv), [$PdCl_2(PPh_3)_2$] (6 mol %) and CuI (6 mol %) were stirred at 65 °C for 72 h in a solution of benzene (13 mL) and Et$_3$N (9 mL). Solvents were removed under a vacuum and the residue was taken up in EtOAc, washed twice with water and brine, dried over Na_2SO_4. Purification on silica gel using EtOAc as eluent followed by recrystallizzation from THF/*n*-pentane gave a greenish-blue powder (161.8 mg, 89%). ^{1}H NMR (300 MHz, acetone-d_6) δ (ppm) = 1.43 (s, 6H), 3.10 (s, 6H), 3.17−3.20 (m, 4H), 3.27 (s, 6H), 3.46−3.51 (m, 8H), 3.61−3.64 (m, 4H), 3.78−3.81 (m, 4H), 4.03 (s, 4H), 4.14−4.17 (m, 4H), 6.76 (s, 2H), 6.94 (d, 2H, ^3J = 8.8 Hz), 7.02 (d, 4H, ^3J = 8.8 Hz), 7.06−7.10 (m, 6H), 7.28−7.33 (m, 8H), 7.40 (d, 2H, ^3J = 8.6 Hz), 7.60−7.66 (m, 6H), 8.20 (d, 2H, ^3J = 16.3 Hz). ^{13}C NMR (75 MHz, acetone-d_6) δ (ppm) = 15.3, 58.7, 58.8, 59.6, 68.5, 69.1, 70.2, 71.3, 72.3, 72.7, 88.9, 91.8, 92.9, 116.0, 116.2, 119.0, 119.8, 122.5, 124.8, 125.1, 126.0, 129.7, 130.0, 130.5, 131.0, 132.0, 132.8, 133.5, 135.2, 136.1, 138.6, 140.8, 147.9, 149.2, 153.1, 160.8. ^{11}B NMR (128 MHz, acetone-d_6) δ (ppm) = −12,9. UV−vis (toluene) λ nm (ε, M^{-1} cm^{-1}) 649 (146 000), 569 (15 500), 375 (133 100). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 643 (132 200), 593 (43 900), 372 (119 800). EI-MS (*m*/*z*, relative intensity) theoretical mass 1191.58 (100); found 1191.3 (100). Anal. Calcd for $C_{75}H_{78}BN_3O_{10}$ (M_r = 1192.25): C, 75.56; H, 6.59; N, 3.52. Anal. found: C, 75.27; H, 6.37; N, 3.22.

Compound **3**. According to general procedure number 2, compound **1** (73.2 mg, 0.070 mmol), TPA(OMe)$_2$ (**C**) (33.5 mg, 0.102 mmol, 1.5 equiv), [$PdCl_2(PPh_3)_2$] (5 mol %) and CuI (cat.) were stirred in a solution of benzene (10 mL) and Et$_3$N (6 mL), at 65 °C for 15 h. The reaction medium was extracted with CH_2Cl_2, washed with H_2O, dried with brine and over Na_2SO_4. Purification on an alumina column chromatography, using EtOAc/Et$_3$N (99/1), afforded compound **3** in 82% yield. Recrystallization from THF/*n*-pentane gave red metallic needles (61.5 mg, 70%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm) = 1.52 (s, 6H), 3.17 (s, 6H), 3.17−3.20 (m, 4H), 3.36 (s, 6H), 3.46−3.48 (m, 4H), 3.54−3.56 (m, 4H), 3.67−3.70 (m, 4H), 3.80 (s, 6H), 3.83−3.86 (m, 4H), 4.11 (s, 4H), 4.16−4.19 (m, 4H), 6.70 (s, 2H), 6.83 (d, 2H, ^3J = 8.8 Hz, $\Delta\nu_{AB\ syst}$ = 193.3 Hz), 6.88 (d, 4H, ^3J = 9.0 Hz, $\Delta\nu_{AB\ syst}$ = 88.5 Hz), 6.99 (d, 4H, ^3J = 8.7 Hz, $\Delta\nu_{AB\ syst}$ = 246.0 Hz), 7.10 (d, 4H, ^3J = 8.9 Hz, $\Delta\nu_{AB\ syst}$ = 88.5 Hz), 7.20 (d, 2H, ^3J = 16.2 Hz), 7.34 (d, 2H, ^3J = 8.8 Hz, $\Delta\nu_{AB\ syst}$ = 193.3 Hz), 7.36 (d, 2H, ^3J = 8.1 Hz, $\Delta\nu_{AB\ syst}$ = 112.4 Hz), 7.60 (d, 4H, ^3J = 8.8 Hz, $\Delta\nu_{AB\ syst}$ = 246.0 Hz), 7.64 (d, 2H, ^3J = 8.2 Hz, $\Delta\nu_{AB\ syst}$ = 112.4 Hz), 8.08 (d, 2H, ^3J = 16.2 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) = 15.4, 56.0, 59.0, 59.2, 59.7, 68.2, 68.9, 70.1, 71.2, 72.1, 72.5, 88.0, 91.8, 92.5, 113.6, 115.3, 115.4, 115.5, 118.4, 119.1, 119.4, 125.1, 127.9, 129.4, 129.5, 130.7, 131.8, 132.4, 132.9, 134.8, 135.4, 138.6, 140.5, 141.2, 149.8, 152.6, 157.2, 160.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = −13.2 (s). UV−vis (toluene) λ nm (ε, M^{-1} cm^{-1}) 649 (138 800), 596 (46 000), 376 (129 100). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 645 (138 000), 593 (45 700), 374 (128 300). EI-MS (*m*/*z*, relative intensity) theoretical mass 1251.60 (100); found 1251.4 (100). Anal. Calcd for $C_{77}H_{82}BN_3O_{12}$ (M_r = 1251.60): C, 73.85; H, 6.60; N, 3.36. Anal. found: C, 73.62; H, 6.32; N, 3.04.

Compound **4**. According to general procedure number 1, BODIPY **A** (63.1 mg, 0.067 mmol, 0.9 equiv), DPPThBr (cmpd **D**) (44.6 mg, 0.074 mmol, 1 equiv) and [$Pd(PPh_3)_4$] (10 mol %) were stirred in benzene (25 mL) and Et$_3$N (5 mL) at 60 °C for 48 h. The solvent was removed under a vacuum; the crude product was then extracted with CH_2Cl_2, washed with water, dried with brine and over Na_2SO_4. Purification on an alumina column chromatography using a gradient of CH_2Cl_2/petroleum ether (60/40 to 100/0 + 2% EtOH) followed by recrystallization in THF/*n*-pentane gave a blue/black powder (63.1 mg, 64%). mp = 141 °C (starts to melt before). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.86−0.94 (m, 12H), 1.25−1.42 (m, 16H), 1.48 (s, 6H), 1.84−1.96 (m, 2H), 3.15−3.18 (m, 4H), 3.20 (s, 6H), 3.41 (s, 6H), 3.51−3.54 (m, 4H), 3.59−3.62 (m, 4H), 3.73−3.76 (m, 4H), 3.88−3.91 (m, 4H), 4.02−4.06 (m, 4H), 4.17 (s, 4H), 4.18−4.21 (m, 4H), 6.63 (s, 2H), 6.98 (d, 4H, ^3J = 8.8 Hz), 7.13 (d, 2H, ^3J = 16.2 Hz), 7.28 (t, 1H, ^3J = 4.1 Hz), 7.40 (d, 2H, ^3J = 8.3 Hz), 7.43 (d, 1H, ^3J = 4.1 Hz), 7.59 (d, 4H, ^3J = 8.8 Hz), 7.69 (d, 2H, ^3J = 7.9 Hz), 8.09 (d, 2H, ^3J = 16.2 Hz), 8.90 (d, 1H, ^3J = 4.1 Hz), 8.93 (dd, 1H, ^3J = 4.0 Hz, ^4J = 1.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.2, 23.2, 23.7, 28.5, 28.5, 30.3, 30.4, 39.2, 46.1, 46.2, 81.9, 98.5, 108.6, 114.7, 121.8, 124.1, 125.5, 128.6, 129.3, 129.6, 130.0, 130.2, 130.8, 132.5, 132.7, 135.5, 135.6, 139.7, 140.5, 147.1, 148.8, 161.8, 161.8. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = −13.2. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 645 (141 700), 587 (90 800), 546 (54 900), 374 (104 300), 311 (36 300). EI-MS (*m*/*z*, relative intensity) theoretical mass 1470.7 (100), 1471.7 (99.5); found 1471.6 (95), 1470.3 (30). Anal. Calcd for $C_{87}H_{103}BN_4O_{12}S_2$ (M_r = 1471.71): C, 71.00; H, 7.05; N, 3.81. Anal. found: C, 70.84; H, 6.76; N, 3.61.

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

Compound **5**. According to general procedure number 1, $DPPThBr_2$ (cmpd **E**) (116.7 mg, 0.171 mmol, 1 equiv), BODIPY **A** (146.0 mg, 0.154 mmol, 0.9 equiv) and $[Pd(PPh_3)_4]$ (5 mol %) were stirred in benzene (60 mL) and Et_3N (10 mL) at 60 °C for 72 h. Purification on an alumina chromatographic column using a gradient of EtOAc/PE (40/60 to 100/0), followed by recrystallization from THF/*n*-pentane afforded the desired compound as a black bluish powder (103.0 mg, 43%). mp = 144 °C (starts to melt before). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.85−0.93 (m, 12H), 1.26−1.39 (m, 16H), 1.47 (s, 6H), 1.81−1.05 (m, 2H), 3.15−3.18 (m, 4H), 3.20 (s, 6H), 3.41 (s, 6H), 3.51−3.54 (m, 4H), 3.58−3.62 (m, 4H), 3.73−3.76 (m, 4H), 3.88−3.91 (m, 4H), 3.94−4.03 (m, 4H), 4.17 (s, 4H), 4.18−4.21 (m, 4H), 6.63 (s, 2H), 6.98 (d, 4H, ^3J = 8.8 Hz), 7.13 (d, 2H, ^3J = 16.2 Hz), 7.23 (d, 1H, ^3J = 4.1 Hz), 7.41 (d, 2H, ^3J = 8.6 Hz), 7.43 (d, 1H, ^3J = 4.3 Hz), 7.59 (d, 4H, ^3J = 8.8 Hz), 7.69 (d, 2H, ^3J = 8.3 Hz), 8.10 (d, 2H, ^3J = 16.2 Hz), 8.68 (d, 1H, ^3J = 4.3 Hz), 8.90 (d, 1H, ^3J = 4.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.2, 15.2, 23.2, 23.7, 28.4, 30.3, 30.3, 39.3, 46.2, 46.3, 58.9, 59.2, 59.6, 67.7, 68.3, 69.8, 71.0, 71.7, 72.1, 83.6, 91.7, 97.1, 108.4, 108.9, 115.2, 118.2, 119.2, 119.2, 123.0, 128.2, 128.9, 129.3, 130.3, 131.0, 131.3, 131.4, 131.6, 132.2, 133.4, 134.2, 135.6, 136.7, 137.2, 139.5, 139.8, 140.1, 152.3, 159.7, 161.6, 161.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = −12.8. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 645 (133 200), 592 (96 200), 551 (57 000), 373 (96 200), 315 (43 900). EI-MS (*m*/*z*, relative intensity) theoretical mass 1549.62 (100), 1550.62 (90.8); found 1548.2 (100), 1550.5 (95). Anal. Calcd for $C_{87}H_{102}BBrN_4O_{12}S_2$ (M_r = 1550.61): C, 67.39; H, 6.63; N, 3.61. Anal. found: C, 67.11; H, 6.47; N, 3.49.

Compound **6**. According to general procedure number 1, DPPThBr (cmpd **D**) (41.4 mg, 0.069 mmol, 0.9 equiv), *N*,*N*-diphenyl-4-ethynylaniline (cmpd **B**) (20.7 mg, 0.077 mmol, 1 equiv) and $[Pd(PPh_3)_4]$ (6 mol %) were stirred in Et_3N (2.5 mL) and benzene (5 mL) at 60 °C for 15 h. The reaction medium was evaporated, extracted with CH_2Cl_2, washed with water, dried with brine and over Na_2SO_4. Purification on alumina column chromatography using a gradient of CH_2Cl_2/PE (15/85 to 30/70) afforded the desired compound as a purple solid (50.6 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.83−0.92 (m, 12H), 1.23−1.41 (m, 16H), 1.83−1.93 (m, 2H), 3.99−4.05 (m, 4H), 7.01 (d, 2H, ^3J = 8.6 Hz), 7.07−7.14 (m, 6H), 7.27−7.37 (m, 6H), 7.39 (d, 2H, ^3J = 8.8 Hz), 7.63 (dd, 1H, ^3J = 5.1 Hz, ^4J = 1.2 Hz), 8.89 (d, 1H, ^3J = 4.3 Hz), 8.91 (dd, 1H, ^3J = 4.0 Hz, ^4J = 1.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.2, 23.2, 23.7, 28.5, 30.3, 30.4, 39.2, 46.1, 46.2, 81.9, 98.5, 108.6, 114.7, 121.8, 124.1, 125.5, 128.6, 129.3, 129.6, 130.0, 130.2, 130.8, 132.5, 132.7, 135.5, 135.6, 139.7, 140.5, 147.1, 148.8, 161.8, 161.8. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 582 (52 000), 550 (47 000), 423 (8 300), 346 (23 300), 300 (23 000). EI-MS (*m*/*z*, relative intensity) theoretical mass 791.4 (100); found 791.2 (100). Anal. Calcd for $C_{50}H_{53}N_3O_2S_2$ (M_r = 792.10): C, 75.82; H, 6.74; N, 5.30. Anal. found: C, 75.67; H, 6.55; N, 5.04.

Compound **7**. According to general procedure number 2, $TPA(OMe)_2$ (cmpd **C**) (50 mg, 0.152 mmol 1.3 equiv), DPPThBr (cmpd **D**) (72.1 mg, 0.119 mmol), $[PdCl_2(PPh_3)_2]$ (6 mol %) and CuI (6 mol %) were stirred in a solution of benzene (3 mL) and Et_3N (3 mL) at 60 °C for 4 h. The reaction medium was extracted with Et_2O, washed with H_2O, dried with brine and over Na_2SO_4. Purification on silica column chromatography using EtOAc/PE (10/90) afforded the desired compound (88.4 mg, 87%) as a black solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.83−0.93 (m, 12H), 1.14−1.40 (m, 16H), 1.83−1.95 (m, 2H), 3.81 (s, 6H), 3.99−4.05 (m, 4H), 6.83−6.85 (m, 2H), 6.87 (d, 4H, ^3J = 8.9 Hz), 7.10 (d, 4H; ^3J = 8.9 Hz),7.25−7.28 (m, 2H), 7.31 (d, 1H, ^3J = 6.8 Hz), 7.31 (d, 1H, ^3J = 6.3 Hz), 7.62 (dd, 1H, ^3J = 5.1 Hz, ^4J = 0.8 Hz), 8.90 (d, 1H, ^3J = 4.3 Hz), 8.91 (d, 1H, ^3J = 4.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.2, 23.2, 23.7, 28.5, 30.3, 30.4, 39.2, 46.1, 46.2, 55.6, 81.5, 99.1, 108.3, 108.5, 112.5, 115.0, 118.8, 127.5, 128.6, 129.6, 129.9, 130.0, 130.7, 132.2, 132.6, 135.5, 135.7, 139.8, 140.0, 140.3, 149.6, 156.7, 161.8, 161.9. UV−vis (toluene) λ nm (ε, M^{-1} cm^{-1}) 589 (54 800), 560 (49 700), 356 (31 500), 302 (33 400). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 585 (55 900), 556 (50 500), 352 (33 800), 301 (36 500). EI-MS (*m*/*z*, relative intensity) theoretical mass 851.4 (100); found 851.2 (100), 820.2 (15). Anal. Calcd for $C_{52}H_{57}N_3O_4S_2$ (M_r = 852.16): C, 73.29; H, 6,74; N, 4.93. Anal. found: C,73.04; H, 6.50; N, 4.72.

Compounds **8** *and* **10**. According to general procedure number 1, $DPPThBr_2$ (cmpd **E**) (282.4 mg, 0.414 mmol, 1 equiv), *N*,*N*-diphenyl-4-ethynylaniline (cmpd **B**) (101.2 mg, 0.376 mmol, 0.9 equiv) and $[Pd(PPh_3)_4]$ (11 mol %) were stirred in Et_3N (10 mL) and benzene (75 mL) at 70 °C for 35 h. The solution was evaporated, extracted with CH_2Cl_2, washed with water and dried with brine and over Na_2SO_4. Purification on column chromatography (alumina, eluent: CH_2Cl_2/PE, gradient from 20/80 to 50/50), followed by recrystallization in THF/MeOH or CH_2Cl_2/MeOH afforded the monocoupled product as a purple solid (138.5 mg, 42%) and the bis-coupled product as a blue solid (103.3 mg, 26%). Cmpd **10**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.84−0.92 (m, 12H), 1.21−1.40 (m, 16H), 1.80−1.93 (m, 2H), 3.93−4.01 (m, 4H), 7.01 (d, 2H, ^3J = 8.8 Hz), 7.09 (t, 2H, ^3J = 7.5 Hz), 7.13 (d, 4H, ^3J = 7.6 Hz), 7.22 (d, 1H, ^3J = 4.1 Hz), 7.30 (dd, 4H, ^3J = 7.5 Hz, ^3J = 7.6 Hz), 7.33 (d, 1H, ^3J = 4.3 Hz), 7.38 (d, 2H, ^3J = 8.8 Hz), 8.65 (d, 1H, ^3J = 4.1 Hz), 8.90 (d, 1H, ^3J = 4.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.2, 23.2, 23.7, 28.5, 30.3, 30.3, 39.2, 46.2, 46.2, 81.9, 98.8, 108.4, 114.5, 118.9, 121.7, 124.1, 125.5, 129.6, 130.0, 131.4, 131.6, 132.5, 132.7, 135.4, 136.0, 139.0, 140.1, 147.0, 148.8, 161.5, 161.7. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 591 (53 400), 558 (47 400), 432 (8 300), 339 (25 500), 300 (23 600). EI-MS (*m*/*z*, relative intensity) theoretical mass 869.27 (100), 871.27 (99.2); found 869.2 (100), 871.2 (98). Anal. Calcd for $C_{50}H_{52}BrN_3O_2S_2$ (M_r = 871.00): C, 68.95; H, 6.02; N, 4.82. Anal. found: C, 68.78; H, 5.84; N, 4.77. Cmpd **8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.85−0.93 (m, 12H), 1.23−1.44 (m, 16H), 1.87−1.96 (m, 2H), 4.02 (d, 2H, ^3J = 7.4 Hz), 4.03 (d, 2H, ^3J = 7.9 Hz), 7.01 (d, 4H, ^3J = 8.8 Hz), 7.09 (t, 4H, ^3J = 7.3 Hz), 7.13 (d, 8H, ^3J = 8.1 Hz), 7.30 (dd, 8H, ^3J = 7.3 Hz, ^3J = 8.1 Hz), 7.33 (d, 2H, ^3J = 4.1 Hz), 7.38 (d, 4H, ^3J = 8.6 Hz), 8.91 (d, 2H, ^3J = 4.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.2, 23.2, 23.7, 28.5, 30.3, 39.3, 46.3, 81.9, 98.7, 108.8, 114.6, 121.8, 124.1, 125.5, 129.4, 129.6, 130.2, 132.5, 132.7, 135.8, 139.6, 147.1, 148.8, 161.7. UV−vis (CH_2Cl_2) λ nm (ε, M^{-1} cm^{-1}) 625 (76 900), 588 (70 400), 451 (17 800), 351 (62 300). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 623 (83 500), 584 (74 800), 446 (19 800), 350 (65 700). EI-MS (*m*/*z*, relative intensity) theoretical mass 1058.46 (100), 1059.47 (76.5); found 1058.3 (100), 1059.3 (70). Anal. Calcd for $C_{70}H_{66}N_4O_2S_2$ (M_r = 1059.43): C, 79.36; H, 6.28; N, 5.29. Anal. found: C, 79.00; H, 5.84; N, 4.92.

Compounds **9** *and* **11**. According to general procedure number 1, $DPPThBr_2$ (cmpd **E**) (183.3 mg, 0.269 mmol, 1 equiv), $TPA(OMe)_2$ (cmpd **C**) (69.9 mg, 0.212 mmol, 0.8 equiv) and $[Pd(PPh_3)_4]$ (5 mol %) were stirred in a solution of toluene (50 mL) and Et_3N (10 mL), at 60 °C for 15 h. The reaction medium was evaporated to dryness, then purified on a silica column chromatography, using a gradient of AE/PE (10/90 to 30/70). Recrystallization from CH_2Cl_2/MeOH afforded the mono (**11**) and bis (**9**) coupled products, respectively in 51% (100.7 mg) and 9% (22.5 mg). Cmpd **11**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.85−0.93 (m, 12H), 1.24−1.38 (m, 16H), 1.82−1.92 (m, 2H), 3.81 (s, 6H), 3.93−4.01 (m, 4H), 6.83−6.87 (m, 6H), 7.09 (d, 4H, ^3J = 8.8 Hz), 7.22 (d, 1H, ^3J = 4.2 Hz), 7.30−7.32 (m, 3H), 8.64 (d, 1H, ^3J = 4.2 Hz), 8.91 (d, 2H, ^3J = 4.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.2, 23.2, 23.68, 23.71, 28.5, 30.28, 30.32, 39.2, 39.3, 46.17, 46.23, 56.6, 81.5, 99.4, 108.4, 108.5, 112.4, 115.0, 118.7, 118.8, 127.5, 129.8, 130.0, 131.4, 131.6, 132.3, 132.6, 135.3, 136.1, 138.8, 139.9, 140.3, 149.7, 156.7, 161.5, 161.8. UV−vis (toluene) λ nm (ε, M^{-1} cm^{-1}) 600 (60 900), 565 (53 000), 360 (30 900), 311 (32 600). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 595 (64 500), 563 (57 000), 355 (35 900), 310 (40 100). EI-MS (*m*/*z*, relative intensity) theoretical mass 931.29 (100), 929.29 (92); found 931.1 (100), 929.1 (100). Anal. Calcd for $C_{52}H_{56}BrN_3O_4S_2$ (M_r = 931.05): C, 67.08; H, 6.06; N, 4.51. Anal. found: C, 66.78; H, 5.67; N, 4.12. Cmpd **9**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.85−0.92 (m, 12H), 1.24−1.42 (m, 16H), 1.86−1.96 (m, 2H), 3.81 (s, 12H), 4.01 (d, 2H, ^3J = 7.4 Hz), 4.02 (d, 2H, ^3J = 7.8 Hz), 6.84 (d, 4H, ^3J = 8.0 Hz), 6.84−6.88 (m, 8H), 7.07−7.11 (m, 8H), 7.31 (d, 4H, ^3J = 8.4

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

Hz), 7.31 (d, 2H, ^3J = 4.1 Hz), 8.91 (d, 2H, ^3J = 4.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.2, 23.2, 23.7, 28.5, 30.3, 39.2, 46.2, 55.6, 81.5, 99.2, 108.7, 112.5, 115.0, 118.8, 127.5, 129.7, 129.9, 132.3, 132.6, 135.8, 139.5, 139.9, 149.6, 156.7, 161.7. UV−vis (toluene) λ nm (ε, M^{-1} cm^{-1}) 634 (101 200), 593 (86 000), 472 (19 700), 355 (71 300). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 633 (96 000), 592 (83 900), 461 (21 100), 353 (72 900). EI-MS (m/z, relative intensity) theoretical mass 1178.50 (100); found 1178.4 (100). Anal. Calcd for $C_{74}H_{74}N_4O_6S_2$ (M_r = 1179.53): C, 75.35; H, 6.32; N, 4.75. Anal. found: C, 75.17; H, 6.18; N, 4.52.

Compound ***12***. According to general procedure number 1, cmpd **10** (96.7 mg, 0.111 mmol, 1.1 equiv), BODIPY **A** (95.0 mg, 0.100 mmol, 1 equiv) and $[Pd(PPh_3)_4]$ (7 mol %) were stirred in benzene (20 mL) and Et_3N (4 mL) at 70 °C for 48 h. The solution was evaporated, extracted with CH_2Cl_2, washed with water, dried with brine and Na_2SO_4. Purification on an alumina chromatographic column using CH_2Cl_2/PE (gradient from 80/20 to 100/0 + 1% MeOH) followed by recrystallization in THF/MeOH gave the desired product as iridescent blue/black powder (114.8 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.86−0.93 (m, 12H), 1.26−1.42 (m, 16H), 1.48 (s, 6H), 1.87−1.94 (m, 2H), 3.15−3.18 (m, 4H), 3.20 (s, 6H), 3.41 (s, 6H), 3.51−3.54 (m, 4H), 3.59−3.62 (m, 4H), 3.73−3.76 (m, 4H), 3.88−3.92 (m, 4H), 4.03 (d, 4H, ^3J = 6.8 Hz), 4.17 (s, 4H), 4.18−4.21 (m, 4H), 6.64 (s, 2H), 6.96−7.02 (m, 6H), 7.07−7.16 (m, 8H), 7.27−7.43 (m, 10H), 7.59 (d, 4H, ^3J = 8.8 Hz), 7.69 (d, 2H, ^3J = 8.3 Hz), 8.10 (d, 2H, ^3J = 16.2 Hz), 8.91 (d, 1H, ^3J = 4.3 Hz), 8.94 (d, 1H, ^3J = 4.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.2, 15.2, 23.2, 23.7, 28.5, 30.3, 39.3, 46.3, 58.9, 59.2, 59.6, 67.7, 68.3, 69.9, 71.0, 71.7, 72.1, 81.9, 83.7, 91.7, 97.0, 98.9, 108.7, 109.2, 114.5, 115.2, 118.2, 119.2, 121.7, 123.0, 124.1, 125.5, 128.0, 128.9, 129.3, 129.6, 129.7, 130.0, 130.3, 131.1, 131.4, 132.2, 132.6, 132.7, 133.4, 134.2, 135.5, 136.1, 136.7, 137.3, 139.2, 140.1, 147.0, 148.8, 152.3, 159.6, 161.6, 161.8. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = −12.8. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 641 (177 300), 593 (120 800), 369 (118 400). UV−vis (toluene) λ nm (ε, M^{-1} cm^{-1}) 648 (157 200), 599 (102 000), 374 (98 500). EI-MS (m/z, relative intensity) theoretical mass 1737.8 (100), 1738.8 (91.8); found 1738.5 (100), 1737.5 (80). Anal. Calcd for $C_{107}H_{116}BN_5O_{12}S_2$ (M_r = 1739.03): C, 73.90; H, 6.72; N, 4.03. Anal. found: C, 73.64; H, 6.52; N, 3.62.

Compound ***13***. According to general procedure number 1, dyad **11** (64.4 mg, 0.069 mmol, 1 equiv), BODIPY **A** (67.0 mg, 0.071 mmol, 1 equiv) and $[Pd(PPh_3)_4]$ (9 mol %) were stirred in a solution of toluene (10 mL) and Et_3N (4 mL) at 100 °C for 16 h. The reaction medium was evaporated to dryness, then purified on a basified silica column chromatography (0.2% Et_3N in the eluent EtOAc/CH_2Cl_2 (80/20)), using a gradient of EtOAc/CH_2Cl_2 (80/20 to 100/0). A black solid was obtained in 54% yield (67.7 mg). Recrystallization from THF/EtOH afforded a black powder (47.6 mg, 38%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm) = 0.86−0.93 (m, 12H), 1.23−1.42 (m, 16H), 1.52 (s, 6H), 1.86−1.94 (m, 2H), 3.18 (s, 6H), 3.18−3.21 (m, 4H), 3.37 (s, 6H), 3.47−3.49 (m, 4H), 3.54−3.57 (m, 4H), 3.68−3.70 (m, 4H), 3.80 (s, 6H), 3.84−3.86 (m, 4H), 3.99−4.04 (m, 4H), 4.12 (s, 4H), 4.17−4.19 (m, 4H), 6.71 (s, 2H), 6.82 (d, 2H, ^3J = 8.7 Hz), 6.89 (d, 4H, ^3J = 8.9 Hz), 6.99 (d, 4H, ^3J = 8.7 Hz), 7.10 (d, 4H, ^3J = 8.9 Hz), 7.21 (d, 2H, ^3J = 16.1 Hz), 7.31−7.34 (m, 3H), 7.43−7.50 (m, 3H), 7.55−7.67 (m, 4H), 7.72 (d, 2H, ^3J = 8.1 Hz), 8.09 (d, 2H, ^3J = 16.1 Hz), 8.89 (d, 1H, ^3J = 4.1 Hz), 8.93 (d, 1H, ^3J = 4.1 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) = 10.8, 14.4, 15.4, 23.6, 24.1, 28.9, 30.7, 39.75, 39.80, 46.5, 56.0, 59.0, 59.2, 59.7, 68.3, 69.0, 70.1, 71.3, 72.1, 72.5, 81.7, 83.9, 92.6, 97.3, 99.7, 109.2, 109.7, 112.5, 115.4, 115.6, 118.5, 118.7, 119.4, 123.6, 128.1, 129.0, 129.1, 129.4, 129.8, 130.2, 130.5, 130.7, 131.7, 131.8, 132.4, 132.5, 132.6, 132.7, 132.9, 133.8, 134.0, 134.9, 135.6, 136.3, 136.9, 138.1, 139.3, 140.2, 140.3, 141.1, 150.3, 152.7, 157.5, 160.3, 161.9, 162.0. ^{11}B NMR (128 MHz, CD_2Cl_2) δ (ppm) = −13.1. UV−vis (toluene) λ nm (ε, M^{-1} cm^{-1}) 647 (180 600), 596 (110 100), 374 (112 900). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 644 (179 900), 593 (112 200), 371 (112 300). EI-MS (m/z, relative intensity) theoretical mass 1798.84 (100), 1797.84 (85), 1799.84 (58); found 1799.2 (100), 1358.3 (35), 1005.4 (15). Anal. Calcd for $C_{109}H_{120}BN_5O_{14}S_2$ (M_r = 1799.09): C, 72.77; H, 6.72; N, 3.89. Anal. found: C, 72.93; H, 7.02; N, 4.08.

Compounds ***14*** *and* ***H***. According to general procedure number 1, $[Pd(PPh_3)_4]$ (5 mol %), *N*,*N*-diphenyl-4-ethynylaniline (cmpd **B**) (17.6 mg, 0.065 mmol, 0.9 equiv) and $DPPPhBr_2$ (cmpd **F**) (48.6 mg, 0.073 mmol, 1 equiv) were stirred in benzene (6 mL) and Et_3N (5 mL) at 70 °C for 15 h. The solution was concentrated, extracted with CH_2Cl_2, washed with water and brine, and dried over Na_2SO_4. Purification by column chromatography (SiO_2, EtOAc/petroleum ether: gradient from 4/96 to 20/80), followed by recrystallization in Et_2O/MeOH gave the desired mono coupled product (38.2 mg, 68%) as an orange-red powder. The bis coupled product was also obtained, recrystallized from CH_2Cl_2/MeOH to give a red powder (9.9 mg, 14%). Cmpd **14**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.72 (t, 6H, ^3J = 7.6 Hz), 0.80 (t, 6H, ^3J = 7.1 Hz), 1.09−1.24 (m, 16H), 1.48 (s_l, 2H),3.74 (t, 4H, ^3J = 8.1 Hz), 7.01 (d, 2H, ^3J = 8.8 Hz), 7.06−7.14 (m, 6H), 7.29 (t, 4H, ^3J = 8.4 Hz), 7.39 (d, 2H, ^3J = 8.8 Hz), 7.61 (d, 2H, ^3J = 8.4 Hz), 7.65 (s, 4H), 7.77 (d, 2H, ^3J = 8.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.1, 23.0, 23.9, 28.4, 30.5, 38.7, 38.7, 45.2, 45.3, 77.4, 89.0, 92.9, 110.1, 110.3, 115.5, 122.2, 123.9, 125.3, 125.6, 126.7, 127.5, 127.7, 128.7, 129.6, 130.2, 131.8, 132.3, 132.9, 147.2, 147.5, 148.5, 162.7, 162.8. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 491 (49 000), 324 (57 800), 287 (55 300). EI-MS (m/z, relative intensity) theoretical mass 857.4 (100), 859.4 (97.3); found 857.3 (100), 859.3 (98). Anal. Calcd for $C_{54}H_{56}BrN_3O_2$ (M_r = 858.95): C, 75.51; H, 6.57; N, 4.89. Anal. found: C, 75.37; H, 6.42; N, 4.52. Cmpd **H**: ^{1}H NMR ($CDCl_3$) δ (ppm) = 0.72 (t, 6H, ^3J = 7.4 Hz), 0.78−0.82 (m, 6H), 1.10−1.20 (m, 16H), 1.47−1.56 (m, 2H), 3.74−3.78 (m, 4H), 7.02 (d, 4H, ^3J = 8.8 Hz), 7.05−7.14 (m, 10 H), 7.26−7.32 (m, 10H), 7.40 (d, 4H, ^3J = 8.8 Hz), 7.63 (d, 4H, ^3J = 8.4 Hz), 7.79 (d, 4H, ^3J = 8.6 Hz). ^{13}C NMR ($CDCl_3$) δ (ppm) = 10.6, 14.1, 23.0, 23.9, 28.4, 30.5, 38.7, 45.3, 88.5, 92.9, 110.3, 115.5, 122.2, 123.7, 125.3, 126.6, 127.8, 128.7, 129.6, 131.8, 132.9, 147.2, 148.1, 148.5, 162.9. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 505 (51 900), 407 (32 700), 331 (77 400). EI-MS (m/z, relative intensity) theoretical mass 1046.55 (100), 1047.55 (81.6); found 1046.3 (100), 1047.3 (80). Anal. Calcd for $C_{74}H_{70}N_4O_2$ (M_r = 1047.37): C, 84.86; H, 6.74; N, 5.35. Anal. found: C, 84.57; H, 6.42; N, 5.17.

Compound ***15***. According to general procedure number 1, $[Pd(PPh_3)_4]$ (8 mol %), cmpd **14** (27.1 mg, 0.032 mmol) and BODIPY **A** (30.8 mg, 0.032 mmol) were stirred in benzene (3 mL) and Et_3N (2 mL) at 60 °C for 20 h. The reaction medium was evaporated to dryness and purified on an alumina column chromatography using a gradient of EtOAc/PE/EtOH (80/20/0 to 99/0/1), followed by recrystallization from THF/*n*-pentane afforded a black powder (53.7 mg, 97%). mp = 129−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.73 (t, 6H, ^3J = 7.4 Hz), 0.79−0.83 (m, 6H), 1.11−1.30 (m, 16H), 1.49 (s+m_l, 8H), 3.16−3.19 (m, 4H), 3.21 (s, 6H), 3.41 (s, 6H), 3.52−3.54 (m, 4H), 3.59−3.62 (m, 4H), 3.74−3.80 (m, 8H), 3.89−3.91 (m, 4H), 4.17 (s, 4H), 4.19−4.21 (m, 4H), 6.64 (s, 2H), 6.97−7.15 (m, 14H), 7.27−7.32 (m, 2H), 7.38−7.41 (m, 4H), 7.57−7.71 (m, 12H), 7.79−7.84 (m, 4H), 8.11 (d, 2H, ^3J = 16.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.1, 15.2, 23.0, 23.9, 28.4, 30.5, 39.0, 38.7, 45.3, 45.4, 58.9, 59.3, 59.6, 67.7, 68.3, 69.9, 71.0, 71.7, 72.1, 76.8, 77.1, 77.5, 77.9, 88.5, 90.3, 91.6, 91.7, 92.9, 110.3, 110.6, 115.3, 115.5, 118.2, 119.3, 122.2, 123.6, 123.9, 125.3, 125.7, 126.7, 127.7, 128.6, 128.8, 128.8, 128.9, 129.2, 129.6, 130.3, 131.4, 131.9, 132.1, 132.4, 132.9, 134.1, 136.3, 137.5, 140.2, 147.2, 147.8, 148.4, 148.5, 152.3, 159.7, 162.8, 162.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = −13.1. UV−vis (toluene) λ nm (ε, M^{-1} cm^{-1}) 650 (138 700), 598 (46 100), 504 (42 800), 375 (111 400), 323 (69 600). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 645 (116 900), 594 (41 000), 503 (40 600), 372 (100 700), 334 (67 2000). EI-MS (m/z, relative intensity) theoretical mass 1726.90 (100), 1725.90 (71.3); found 1727.0 (100), 1726.0 (80). Anal. Calcd for $C_{111}H_{120}BN_5O_{12}$ (M_r = 1726.98): C, 77.20; H, 7.00; N, 4.06. Anal. found: C, 76.89; H, 6.61; N, 3.89.

Compound ***16***. According to general procedure number 1, $DPPPhBr_2$ (cmpd **F**) (96.4 mg, 0.144 mmol), BODIPY **A** (121.1 mg, 0.128 mmol, 0.9 equiv) and $[Pd(PPh_3)_4]$ (7 mol %) were stirred

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

in benzene (50 mL) and Et_3N (6 mL) at 50 °C for 60 h. The reaction medium was evaporated to dryness and purified by column chromatography on silica gel using PE/EtOAc/EtOH (gradient from 10/90/0 to 0/96/4) as eluent. The desired monocoupled product was obtained in 54% yield (106.9 mg). Recrystallization from THF/*n*-pentane gave a dark green powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.69−0.74 (m, 6H), 0.78−0.83 (m, 6H), 1.09−1.29 (m, 16H), 1.48 (s_l+m, 6 + 2H), 3.15−3.18 (m, 4H), 3.20 (s, 6H), 3.41 (s, 6H), 3.51−3.54 (m, 4H), 3.58−3.62 (m, 4H), 3.71−3.76 (m, 8H), 3.88−3.91 (m, 4H), 4.17 (s, 4H), 4.18−4.21 (m, 4H), 6.63 (s, 2H), 6.98 (d, 4H, ^3J = 8.9 Hz), 7.13 (d, 2H, ^3J = 16.2 Hz), 7.39 (d, 2H, ^3J = 8.3 Hz), 7.58 (d, 4H, ^3J = 8.8 Hz), 7.65 (s, 4H), 7.67 (d, 2H, ^3J = 8.4 Hz), 7.70 (d, 2H, ^3J = 8.3 Hz), 7.81 (d, 2H, ^3J = 8.4 Hz), 8.10 (d, 2H, ^3J = 16.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.5, 10.6, 14.1, 15.2, 23.0, 23.8, 23.9, 28.4, 30.4, 38.7, 45.1, 45.2, 58.9, 59.2, 59.5, 67.7, 68.3, 69.8, 70.9, 71.6, 72.1, 90.2, 91.6, 110.2, 110.2, 115.2, 118.1, 119.2, 123.5, 125.7, 125.7, 127.4, 128.4, 128.8, 128.9, 129.2, 130.2, 130.3, 131.4, 132.1, 132.3, 132.4, 134.1, 136.3, 137.4, 140.1, 147.7, 148.2, 152.2, 159.6, 162.6, 162.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = −12.9. UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 645 (114 600), 592 (43 100), 489 (29 000), 372 (93 700). EI-MS (*m*/*z*, relative intensity) theoretical mass 1537.71 (100), 1538.71 (99.5); found 1536.3 (100), 1537.3 (98). Anal. Calcd for $C_{91}H_{106}BBrN_4O_{12}$ (M_r = 1538.55): C, 71.04; H, 6.94; N, 3.64. Anal. found: C, 70.71; H, 6.72; N, 3.38.

Compound ***17***. According to general procedure number 1, dyad **16** (71.6 mg, 0.047 mmol, 1 equiv), $TPA(OMe)_2$ (cmpd **C**) (32.8 mg, 0.145 mmol, 2.1 equiv) and $[Pd(PPh_3)_4]$ (7 mol %) were stirred in a solution of benzene (10 mL) and Et_3N (5 mL), at 60 °C for 72 h. The reaction medium was evaporated to dryness, then purified on a silica column chromatography, using a gradient of EtOAc/EtOH (100/0 to 90/10) + 1% Et_3N (during the entire purification). The desired product **17** was obtained as a greenish-black solid (53.9 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.72 (t, 6H, ^3J = 7.4 Hz), 0.79−0.82 (m, 6H), 1.07−1.20 (m, 16H), 1.49 (s_l, 6H+2H), 3.15−3.17 (m, 4H), 3.20 (s, 6H), 3.41 (s, 6H), 3.51−3.53 (m, 4H), 3.59−3.61 (m, 4H), 3.73−3.81 (m, 4H+4H), 3.81 (s, 6H), 3.89−3.91 (m, 4H), 4.17 (s, 4H), 4.19−4.21 (m, 4H), 6.64 (s, 2H), 6.86 (d, 6H, ^3J = 8.9 Hz), 6.98 (d, 4H, ^3J = 8.6 Hz), 7.08 (d, 4H, ^3J = 8.8 Hz), 7.13 (d, 2H, ^3J = 16.1 Hz), 7.33 (d, 2H, ^3J = 8.7 Hz), 7.39 (d, 2H, ^3J = 8.1 Hz), 7.58−7.72 (m, 10H), 7.77−7.83 (m, 4H), 8.10 (d, 2H, ^3J = 16.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 10.5, 14.1, 15.3, 23.0, 23.8, 28.4, 30.4, 38.6, 38.7, 45.26, 45.33, 55.6, 58.9, 59.3, 59.6, 67.7, 68.3, 69.9, 71.0, 71.7, 72.1, 88.1, 90.3, 91.5, 91.7, 93.4, 110.2, 110.5, 113.3, 115.0, 115.2, 118.1, 119.0, 119.2, 123.6, 125.6, 126.9, 127.4, 127.5, 128.5, 128.7, 128.8, 128.9, 129.2, 130.3, 131.4, 131.7, 132.1, 132.4, 132.8, 134.1, 136.3, 137.5, 140.1, 140.2, 147.7, 148.5, 149.3, 152.3, 156.6, 159.6, 162.8, 162.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) = −12.7. UV−vis (toluene) λ nm (ε, M^{-1} cm^{-1}) 650 (93 400), 596 (35 600), 508 (37 800), 375 (92 000). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 645 (107 300), 593 (39 100), 508 (39 800), 372 (100 700). HRMS (EI-neat): theoretical 1785.9238, analyzed 1785.9212 for $C_{113}H_{124}BN_5O_{14}$.

Compound ***G***. Compound **G** was obtained as a side product from the synthesis of cmpd **16**, in 18% yield (54.5 mg) and recrystallized from THF/*n*-pentane. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 0.73 (t, 6H, ^3J = 7.4 Hz), 0.82 (t, 6H, ^3J = 6.8 Hz), 1.12−1.25 (m, 16H), 1.46−1.49 (s_l+m, 12H+2H), 3.15−3.18 (m, 8H), 3.20 (s, 12H), 3.51−3.54 (m, 8H), 3.59−3.62 (m, 8H), 3.73−3.81 (m, 8H+4H), 3.88−3.91 (m, 8H), 4.17−4.21 (s+m, 16H), 6.64 (s, 4H), 6.98 (d, 8H, ^3J = 8.6 Hz), 7.13 (d, 4H, ^3J = 16.0 Hz), 7.36−7.41 (m, 4H), 7.59 (d, 8H, ^3J = 8.6 Hz), 7.67−7.72 (m, 8H), 7.85 (d, 4H, ^3J = 8.3 Hz), 8.10 (d, 4H, ^3J = 16.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 10.4, 14.0, 15.1, 22.9, 23.7, 28.3, 30.3, 38.6, 45.2, 58.8, 59.1, 59.4, 67.6, 68.2, 69.7, 70.8, 71.5, 72.0, 90.1, 91.5, 110.4, 115.1, 118.0, 119.1, 123.4, 125.7, 128.3, 128.7, 128.8, 129.1, 130.2, 131.2, 131.3, 132.0, 132.3, 133.1, 134.0, 136.2, 137.3, 139.9, 140.0, 148.0, 152.1, 159.5, 162.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ (ppm) =- 12.7. UV−visible spectroscopy was not performed for this compound. EI-MS (*m*/*z*, relative intensity) theoretical mass 2393.25 (100), 2392.24 (97.4); found 2406.1 (100), 2407.1 (80). Anal. Calcd for $C_{147}H_{168}B_2N_6O_{22}$ (M_r = 2392.56): C, 73.79; H, 7.08; N, 3.51. Anal. found: C, 73.54; H, 6.77; N, 3.17.

Compound ***I***. According to general procedure number 1, $DPPPhBr_2$ (cmpd **F**) (33.4 mg, 0.0498 mmol, 1 equiv), $TPA(OMe)_2$ (cmpd **C**) (39.1 mg, 0.119 mmol, 2.4 equiv) and $[Pd(PPh_3)_4]$ (5 mol %) were stirred in benzene (7 mL) and Et_3N (4 mL), at 50 °C for 72 h. The reaction medium was extracted with CH_2Cl_2, washed with water, dried with brine and over Na_2SO_4. Purification on a silica column chromatography, using EtOAc/PE (25/75) + 1% Et_3N gave an orange solid. Precipitation from Et_2O afforded the desired compound as an orange powder (52.0 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.71 (t, 6H, ^3J = 7.4 Hz), 0.80 (t, 6H, ^3J = 7.1 Hz), 1.09−1.13 (m, 16H), 1.48−1.55 (m, 2H), 3.75−3.81 (m, 4H), 3.81 (s, 12H), 6.84−6.87 (m, 12H), 7.09 (d, 8H, ^3J = 6.6. Hz), 7.33 (d, 4H, ^3J = 8.7 Hz), 7.61 (d, 4H, ^3J = 8.4 Hz, $\Delta\nu_{AB\ syst}$ = 67.1 Hz), 7.78 (d, 4H, ^3J = 8.4 Hz, $\Delta\nu_{AB\ syst}$ = 67.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 10.6, 14.1, 23.0, 23.9, 28.4, 30.4, 38.6, 45.3, 55.6, 88.1, 93.3, 110.3, 113.4, 115.0, 119.1, 126.8, 127.3, 127.6, 128.7, 131.7, 132.8, 140.2, 148.1, 149.3, 156.6, 162.9. UV−vis (toluene) λ nm (ε, M^{-1} cm^{-1}) 513 (52 900), 434 (27 500), 340 (73 300). UV−vis (THF) λ nm (ε, M^{-1} cm^{-1}) 512 (51 200), 427 (23 800), 337 (65 600), 302 (48 300). EI-MS (*m*/*z*, relative intensity) theoretical mass 1166.59 (100); found 1166.3 (100). Anal. Calcd for $C_{78}H_{78}N_4O_6$ (M_r = 1167.48): C, 80.24; H, 6.73; N, 4.80. Anal. found: C, 79.97; H, 6.48; N, 4.54.

■ ASSOCIATED CONTENT

Supporting Information

List of the molecules, instrumentation, NMR traces for all compounds, spectroscopic data and PET energy calculations. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00917.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ziessel@unistra.fr. Fax: (+33) 3-68-85-27-61.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Région Alsace for a fellowship to Dr. Elodie Heyer and the Centre National de la Recherche Scientifique (CNRS) for financial support of this work. Dr. Thomas Roland, Li Liu, Dr. Adrian Ruff, Prof. Stefan Haacke and Prof. Sabine Ludwigs are warmly acknowledged for their contribution in previous published work on triad **12** and model compounds, using ultrafast spectroscopy and spectroelectrochemistry. Professor Jack Harrowfield (ISIS in Strasbourg) is warmly acknowledged for commenting on this manuscript prior to publication.

■ REFERENCES

(1) Blankenship, R. E. In *Molecular Mechanism of Photosynthesis*; Blackwell Science: Oxford, U.K., 2002.

(2) (a) Nakamura, Y.; Aratani, N.; Osuka, A. *Chem. Soc. Rev.* **2007**, *36*, 831. (b) Armaroli, N.; Balzani, V. *Angew. Chem., Int. Ed.* **2007**, *46*, 52.

(3) (a) Koepke, J.; Hu, X.; Muenke, C.; Schulten, K.; Michel, H. *Structure* **1996**, *4*, 581. (b) Roszak, A. W.; Howard, T. D.; Southall, J.; Gardiner, A. T.; Law, C. J.; Isaacs, N. W.; Cogdell, R. J. *Science* **2003**, *302*, 1969.

(4) (a) Wasielewski, M. R. *J. Org. Chem.* **2006**, *71*, 5051. (b) Imahori, H.; Sakata, Y. *Adv. Mater.* **1997**, *9*, 537. (c) Imahori, H. *Org. Biomol. Chem.* **2004**, *2*, 1425. (d) Campbell, W. M.; Burrell, A. K.; Officer, D. L.; Jolley, K. W. *Coord. Chem. Rev.* **2004**, *248*, 1363.

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753

(5) Kodis, G.; Terazono, Y.; Lidell, P. A.; Andréasson, J.; Garg, V.; Hambourger, M.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Am. Chem. Soc.* **2006**, *128*, 1818.
(6) Kuciauskas, D.; Liddell, P. A.; Lin, S.; Johnson, T. E.; Weghorn, S. L.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1999**, *121*, 8604.
(7) Imahori, H. *J. Phys. Chem. B* **2004**, *108*, 6130.
(8) (a) Sugiura, K. *Top Curr. Chem.* **2003**, *228*, 65. (b) Burrell, A. K.; Officer, D. L.; Pleiger, P. G.; Reid, D. C. W. *Chem. Rev.* **2001**, *101*, 2751. (c) Imamura, T.; Fukushima, K. *Coord. Chem. Rev.* **2000**, *198*, 133. (d) Wojaczynski, J.; Latos-Grazynski, L. *Coord. Chem. Rev.* **2000**, *204*, 113. (e) Würthner, F.; You, C.-C.; Saha-Möller, C. R. *Chem. Soc. Rev.* **2004**, *33*, 133.
(9) (a) Park, M.; Yoon, M.-C.; Yoon, Z. S.; Hori, T.; Peng, X.; Aratani, N.; Hotta, J. I.; Uji-I, H.; Sliwa, M.; Hofkens, J.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2007**, *129*, 3539. (b) Yang, J.; Park, M.; Yoon, Z. S.; Hori, T.; Peng, X.; Aratni, N.; Dedecker, P.; Hotta, J. I.; Uji-I, H.; Sliwa, M.; Hofkens, J.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2008**, *130*, 1879.
(10) Terazono, Y.; Kodi, G.; Liddell, P. A.; Garg, V.; Moore, V. T. A.; Moore, A. L.; Gust, D. *J. Phys. Chem. B* **2009**, *113*, 7147.
(11) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40; and *Acc. Chem. Res.* **2009**, *42*, 1890.
(12) Ziessel, R.; Harriman, A. *Chem. Commun.* **2011**, *47*, 611−631 and references cited therein.
(13) Kartsen, B. P.; Bouwer, R. K. M.; Hummelen, J. C.; Williams, R. M.; Janssen, R. A. J. *Photochem. Photobiol. Sci.* **2010**, *9*, 1055.
(14) (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891. (b) Ulrich, G.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 1202. (c) Boens, N.; Leen, V.; Dehaen, W. *Chem. Soc. Rev.* **2012**, *41*, 1130. (d) Benstead, M.; Mehl, G. H.; Boyle, R. W. *Tetrahedron* **2011**, *67*, 3573. (e) Lu, H.; Mack, J.; Yang, Y.; Shen, Z. *Chem. Soc. Rev.* **2014**, *43*, 4778. (f) Yuan, L.; Lin, W.; Zheng, K.; He, L.; Huang, W. *Chem. Soc. Rev.* **2013**, *42*, 622.
(15) (a) Hao, Z.; Iqbal, A. *Chem. Soc. Rev.* **1997**, *26*, 203. (b) Kaur, M.; Choi, D. H. *Chem. Soc. Rev.* **2015**, *44*, 58.
(16) (a) Hablot, D.; Retailleau, P.; Ziessel, R. *Chem.—Eur. J.* **2010**, *16*, 13346. (b) Hablot, D.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 7833.
(17) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467.
(18) (a) Yilmaz, M. D.; Bozdemir, O. A.; Akkaya, E. U. *Org. Lett.* **2006**, *8*, 2871. (b) Turfan, B.; Akkaya, E. U. *Org. Lett.* **2002**, *4*, 2857.
(19) Huo, L.; Hou, J.; Chen, H.-Y.; Zhang, S.; Jiang, Y.; Chen, T. L.; Yang, Y. *Macromolecules* **2009**, *42*, 6564.
(20) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
(21) Rousseau, T.; Cravino, A.; Bura, T.; Ulrich, G.; Ziessel, R.; Roncali, J. *Chem. Commun.* **2009**, 1673.
(22) Gomez Esteban, S.; de la Cruz, P.; Aljarilla, A.; Arellano, L. M.; Langa, F. *Org. Lett.* **2011**, *13*, 5362 and references cited therein.
(23) Ruff, A.; Heyer, E.; Roland, T.; Haacke, S.; Ziessel, R.; Ludwigs, S. *Electrochim. Acta* **2015**, DOI: 10.1016/j.electacta.2015.05.093.
(24) Bricks, J. L.; Kovalchuk, A.; Trieflinger, C.; Nofz, M.; Büschel, M.; Tolmachev, A. I.; Daub, J.; Rurack, K. *J. Am. Chem. Soc.* **2005**, *127*, 13522.
(25) Burghart, A.; Kim, H.; Wech, M. B.; Thorensen, L. H.; Reibenspies, J.; Burgess, K. *J. Org. Chem.* **1999**, *64*, 7813.
(26) Ziessel, R. *J. Chem. Educ.* **1997**, *74*, 673.
(27) Lakowicz, J. R. In *Principles of Fluorescence Spectroscopy*; Springer: Singapore, 2006.
(28) Ulrich, G.; Goeb, S.; De Nicola, A.; Retailleau, P.; Ziessel, R. *Synlett* **2007**, *10*, 1517.
(29) (a) Hablot, D.; Retailleau, P.; Ziessel, R. *Chem.—Eur. J.* **2010**, *16*, 13336. (b) Hablot, D.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 7833.
(30) Hablot, D.; Ziessel, R.; Alamiry, M.; Bahraidah, E.; Harriman, A. *Chem. Sci.* **2013**, *4*, 444.
(31) Scholes, G. D. *Annu. Rev. Phys. Chem.* **2003**, *54*, 57.
(32) Olmsted, J. *J. Phys. Chem.* **1979**, *83*, 2581.
(33) Shi, W.; Fan, S.; Huang, F.; Yang, W.; Liua, R.; Cao, Y. *J. Mater. Chem.* **2006**, *16*, 2387.
(34) Thoresen, L. H.; Kim, H.; Welch, M. B.; Burghart, A.; Burgess, K. *Synlett* **1998**, 1276.
(35) Bürckstümmer, H.; Weissenstein, A.; Bialas, D.; Würthner, F. *J. Org. Chem.* **2011**, *76*, 2426.
(36) Kollmannsberger, M.; Rurack, K.; Resch-Genger, U.; Daub, J. *J. Phys. Chem. A* **1998**, *102*, 10211.
(37) Roland, T.; Heyer, E.; Liu, L.; Ruff, A.; Ludwigs, S.; Ziessel, R.; Haacke, S. *J. Phys. Chem. C* **2014**, *118*, 24290.
(38) (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834.
(39) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(40) Dangles, O.; Guibe, F.; Balavoine, G.; Lavielle, S.; Manquet, A. *J. Org. Chem.* **1987**, *52*, 4984.
(41) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth Heinemann: Oxford, U.K., 2000.
(42) Ulrich, G.; Ziessel, R.; Niu, S.-l.; Haefele, A.; Bura, T. Int Patent WO2010/076516 A1, 2010.
(43) Teng, C.; Yang, X.; Yang, C.; Tian, H.; Li, S.; Wang, X.; Hagfeldt, A.; Sun, L. *J. Phys. Chem. C* **2010**, *114*, 11305.
(44) Mengel, A. K. C.; He, B.; Wenger, O. S. *J. Org. Chem.* **2012**, *77*, 6545.
(45) Loser, S.; Bruns, C. J.; Miyauchi, H.; Ponce Ortiz, R.; Facchetti, A.; Stupp, S. I.; Marks, T. J. *J. Am. Chem. Soc.* **2011**, *133*, 8142.
(46) Huo, L.; Hou, J.; Chen, H.-Y.; Zhang, S.; Jiang, Y.; Chen, T. L.; Yang, Y. *Macromolecules* **2009**, *42*, 6564.
(47) (a) Rabindranath, A. R.; Zhu, Y.; Heim, I.; Tieke, B. *Macromolecules* **2006**, *39*, 8250. (b) Pecher, J.; Huber, J.; Winterhalder, M.; Zumbusch, A.; Mecking, S. *Biomacromolecules* **2010**, *11*, 2776.

DOI: 10.1021/acs.joc.5b00917
J. Org. Chem. 2015, 80, 6737−6753