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Synthesis and second-order nonlinear optical properties of push-pull BODIPY derivatives

Wen-Jing Shi [a], Pui-Chi Lo [a], Anu Singh [b], Isabelle Ledoux-Rak [b], Dennis K.P. Ng [a,*]

[a] Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China
[b] Laboratoire de Photonique Quantique et Moléculaire UMR CNRS 8537, Institut d'Alembert, ENS Cachan, 61 Aveneue du Président Wilson, 94235 Cachan, France

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ABSTRACT

A series of boron dipyrromethene derivatives bearing an electron-donating 4-(dimethylamino)phenylethynyl group and an electron-withdrawing 4-nitrophenylethynyl group in the opposite 2- and 6-positions have been synthesized by Knoevenagel condensation followed by sequential Sonogashira coupling reactions. The compounds have been fully characterized with various spectroscopic methods. Their electrochemical properties have also been studied by cyclic voltammetry in CH_2Cl_2. It has been found that expansion of the π systems by introduction of the 4-dodecyloxystyryl or 4-(dimethylamino) phenylethynyl group results in lowering of the first oxidation potential, while the first reduction potential remains relatively unaffected. The second-order nonlinear optical properties of these compounds have also been studied by electric-field-induced second-harmonic generation method in $CHCl_3$. The values of the dot product $\mu\cdot\beta$ are in the range from 94×10^{-48} to 330×10^{-48} esu at 1907 nm, depending the substituents at the 3- and 5-positions.

1. Introduction

Since the optical second-harmonic generation was first observed in the early 1960s, nonlinear optics has become a vibrant field of research.[1] The development was particularly rapid in the late 1970s when various tools were developed to accurately measure and calculate hyperpolarizabilities, and a better understanding was achieved on the origin of nonlinear optical (NLO) phenomena and the structure–property relationships of NLO chromophores.[2] Organic NLO materials, which can be modulated and processed readily, are of much contemporary interest because of their potential applications in modulation of optical signals, microfabrication and imaging, laser technology, data storage, telecommunication, etc.[2,3] To achieve second-order NLO effects, the chromophores generally contain a conjugated π system with strong electron-donor and -acceptor groups preferably at the opposite ends, thereby creating a large dipole in the molecule.[4] Octupolar molecules are a well-known exception, which exhibit nonzero molecular first hyperpolarizabilities (β) despite being nonpolar.[5] Solid thin films with highly ordered molecular assemblies can also exhibit enhanced NLO susceptibility.[6] A number of conjugated frameworks, such as merocyanines,[7] porphyrins,[8] phthalocyanines,[9] and graphenes[10] have been employed to construct push–pull systems as second-order NLO materials. Boron dipyrromethene (BODIPY) derivatives, which can be regarded as half-porphyrins, represent another versatile class of functional dyes.[11] As part of our continued interest in these compounds as sensors for metal ions,[12] photosensitizers for photodynamic therapy,[13] and components for artificial photosynthetic models,[14] we believed that these compounds, by having strong electron-donor and -acceptor groups at the opposite 2- and 6-positions, can also serve as second-order NLO materials. The π-skeleton can be further modulated by introducing the substituents at the 3- and 5-positions. To our knowledge, only a few push–pull BODIPY derivatives have been reported, focusing on their spectroscopic and electrochemical properties, but their second-order NLO response has not been studied so far.[15] We report herein the preparation of a series of BODIPY derivatives bearing an electron-donating 4-(dimethylamino)phenylethynyl group and an electron-withdrawing 4-nitrophenylethynyl group in the opposite 2- and 6-positions. The second-order NLO properties of these push–pull BODIPY derivatives are also reported for the first time.

2. Results and discussion

The preparation of these compounds is shown in Scheme 1. Knoevenagel condensation of BODIPY **1**[16] with 1 equiv of benzaldehyde **2**[17] gave the monostyryl BODIPY **3** in 27% yield, while the use of 4 equiv of **2** led to the isolation of the distyryl BODIPY **4** in

* Corresponding author. E-mail address: dkpn@cuhk.edu.hk (D.K.P. Ng).

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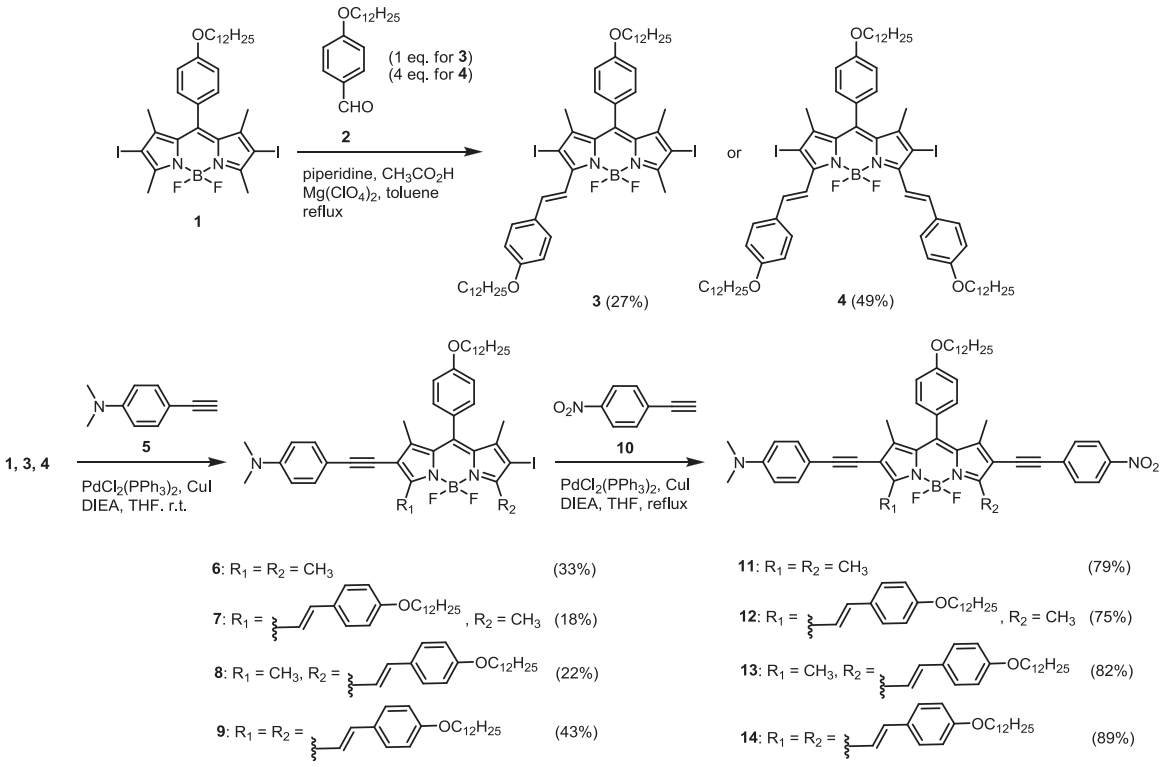

Scheme 1. Synthesis of push–pull BODIPY derivatives **11**–**14**.

49% yield. These compounds could be purified readily by column chromatography followed by size exclusion chromatography with Bio-Beads S-X1 beads. The dodecyl chains were introduced to enhance the solubility of these compounds. Without these chains, purification of the subsequent products was found to be difficult. Compounds **1**, **3**, and **4** then underwent palladium-catalyzed Sonogashira cross-coupling reaction with 4-(dimethylamino)-phenylethyne (**5**) using diisopropylethylamine (DIEA) as the base to give the corresponding BODIPY derivatives. As expected, treatment of the unsymmetrical BODIPY **3** with **5** gave two products (**7** and **8**), which fortunately could be separated by column chromatography. The two compounds could be distinguished by comparing their ^{1}H NMR spectra. As shown in Fig. 1, the two doublets for the vinylic protons (labeled as a and b) of **7** are significantly downfield-shifted compared with those for **8**, which are almost identical with those of the parent compound **3**. The downfield shift could be attributed to the deshielding effect by the neighboring alkynyl group. A further cross-coupling reaction of **6**–**9** with 4-nitrophenylethyne (**10**) afforded the respective push–pull BODIPY derivatives **11**–**14** in good yield. In contrast to the first coupling reactions, which

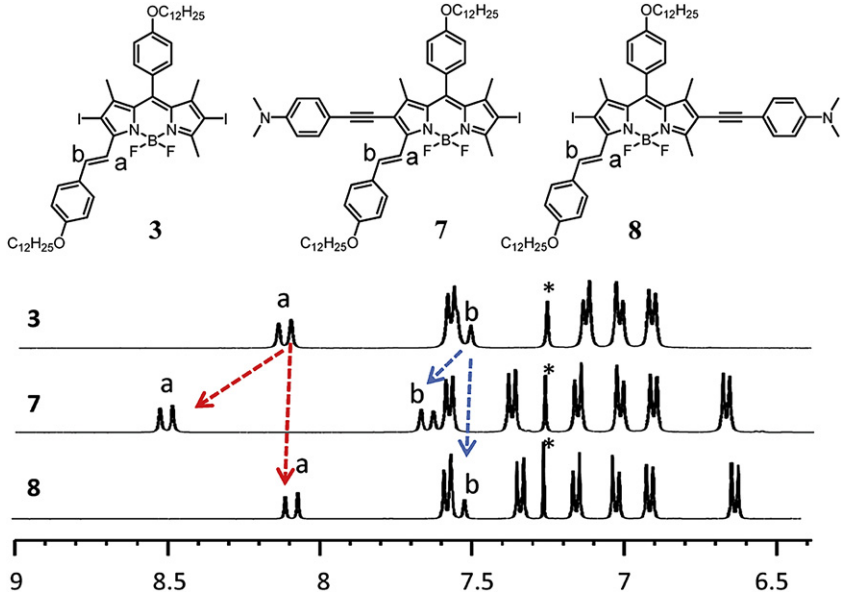

Fig. 1. ^{1}H NMR spectra of **3**, **7**, and **8** in $CDCl_3$.

proceeded smoothly at room temperature, the second coupling reactions required a refluxing condition, which is probably due to the lower reactivity of alkyne **10** compared with **5**. All the new compounds were characterized with various spectroscopic methods.

The electronic absorption and fluorescence data of all these compounds were measured in CH_2Cl_2 and are compiled in Table 1. Fig. 2a shows the absorption spectra of the push–pull BODIPY derivatives **11**–**14**. Compound **11** exhibited a broad Q band at 574 nm, which was significantly red-shifted compared with that of **6** (555 nm) and **1** (533 nm) (Figs. S1 and S2 in Supplementary data), showing the effect of stepwise expansion of the π system. The monostyryl and distyryl BODIPY derivatives also followed the same trend. For the monostyryl analogues **7** and **8**, their Q bands appeared at the same position (619 nm). However, after the introduction of the 4-nitrophenylethynyl group, the Q band of **12** was more intense and red-shifted than that of **13** [638 nm (log ε=4.90) vs 626 nm (log ε=4.84)]. This observation indicated that introduction of this strong electron-acceptor on the opposite side of the styryl group exerts larger perturbation to the π system. This can be rationalized by examining the structure of **12**, which contains the electron-donating 4-(dimethylamino)phenylethynyl and 4-dodecyloxystyryl groups on one side and the electron-withdrawing 4-nitrophenylethynyl group on the other side, thereby imparting a greater intramolecular charge-transfer character to **12**. Fig. 2b shows the steady-state fluorescence spectra of **11**–**14** in CH_2Cl_2. The emission position followed the trend of the Q-band position: **14** (699 nm)>**12** (640 nm)≅**13** (633 nm)>**11** (587 nm), and the fluorescence quantum yield (Φ_F) generally decreased upon conjugation with the alkynyl moieties (Table 1). In addition, the mono-alkynyl compounds **7**–**9** and dialkynyl analogues **12**–**14** showed a relatively small Stokes shift (2–7 nm) compared with the other less π-expanded derivatives (12–19 nm) as shown in Table 1.

Table 1
Absorption and fluorescence data for the BODIPY derivatives in CH_2Cl_2

Comp.	λ_{max}/nm (log ε)	λ_{em}/nm	Stokes shift/nm	Φ_F
1	385 (4.00), 533 (4.89)	548	15	0.08[a]
3	347 (4.38), 597 (4.96)	614	17	1[b]
4	380 (4.52), 663 (4.82)	682	19	0.20[c]
6	309 (4.48), 382 (4.09), 455 (4.08), 555 (4.64)	567	12	0.04[a]
7	373 (4.53), 333 (4.52), 500 (3.96), 619 (4.78)	624	5	0.02[b]
8	315 (4.55), 497 (4.09), 619 (4.76)	623	4	0.01[b]
9	393 (4.64), 687 (4.85)	689	2	0.006[c]
11	310 (4.58), 397 (4.31), 468 (4.13), 574 (4.76)	587	13	0.03[a]
12	374 (4.59), 512 (4.03), 638 (4.90)	640	2	0.007[b]
13	333 (4.59), 333 (4.59), 501 (4.10), 626 (4.84)	633	7	0.04[b]
14	329 (4.55), 388 (4.68), 696 (4.98)	699	3	0.005[c]

[a] With reference to rhodamine B in ethanol (Φ_F=0.49).[18]
[b] Due to the very different emission positions of these compounds, it was difficult to find an appropriate reference. Hence, the relative fluorescence intensities are reported.
[c] With reference to zinc(II) phthalocyanine in DMF (Φ_F=0.28).[19]

The electrochemical properties of these compounds were also studied by cyclic voltammetry in CH_2Cl_2 and the data are compiled in Table 2. BODIPY **1** showed a quasi-reversible oxidation and a quasi-reversible reduction at +1.25 V and −1.10 V, respectively, relative to the saturated calomel electrode (SCE). Introduction of the 4-dodecyloxystyryl group (in compounds **3** and **4**) facilitated both processes, particularly the oxidation as shown by the gradual

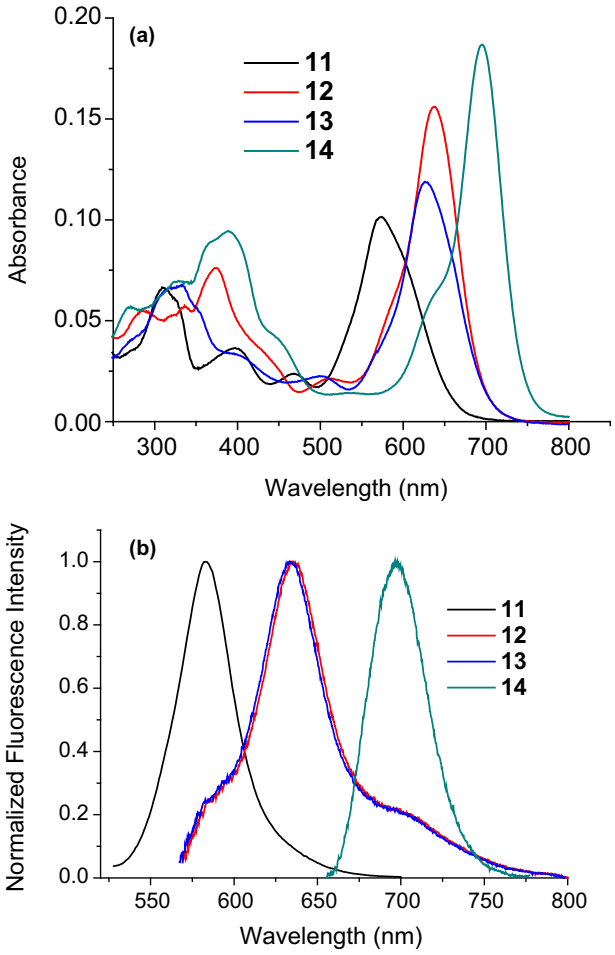

Fig. 2. (a) Electronic absorption (all in 2 μM) and (b) normalized fluorescence spectra of **11**–**14** in CH_2Cl_2.

Table 2
Electrochemical data for the BODIPY derivatives[a]

Compound	E_{ox}/V	E_{red}/V
1	+1.25[b]	−1.10[b]
3	+0.98[b]	−1.05[b]
4	+0.87[b]	−0.91[b]
6	+0.80[c]	−1.15[b]
7	+0.77[c]	−1.05[b]
8	+0.73[c]	−1.04[b]
9	+0.73[c]	−0.94[b]
11	+0.79[c]	−1.16[b]
12	+0.77[c]	−1.01,[b] −1.18[b]
13	+0.72[c]	−1.00,[b] −1.14[b]
14	+0.72[c]	−0.95,[b] −1.16[b]

[a] Recorded with $[Bu_4N][PF_6]$ as the electrolyte in CH_2Cl_2 (0.1 M) at ambient temperature with a scan rate of 50 mV s^{-1}. Potentials are expressed as the half-wave potentials ($E_{1/2}$) (for quasi-reversible couples) or the cathodic or anodic potentials (E_{pc} or E_{pa}) (for irreversible processes) in volts vs SCE using ferrocene as an internal reference [$E_{1/2}$ (Fc/Fc^+)=+0.38 V vs SCE].
[b] Quasi-reversible.
[c] Irreversible.

and significant decrease in the potential to +0.98 V (for **3**) and +0.87 V (for **4**). Introduction of the electron-donating 4-(dimethylamino)phenylethynyl group (in compounds **6**–**9**) greatly reduced the first oxidation potential of these compounds to +(0.73–0.80) V, while the first reduction potential was not significantly affected. However, a further introduction of the electron-withdrawing 4-nitrophenylethynyl group (in compounds **11**–**14**) did not exert a significant influence on both processes. Fig. 3, which

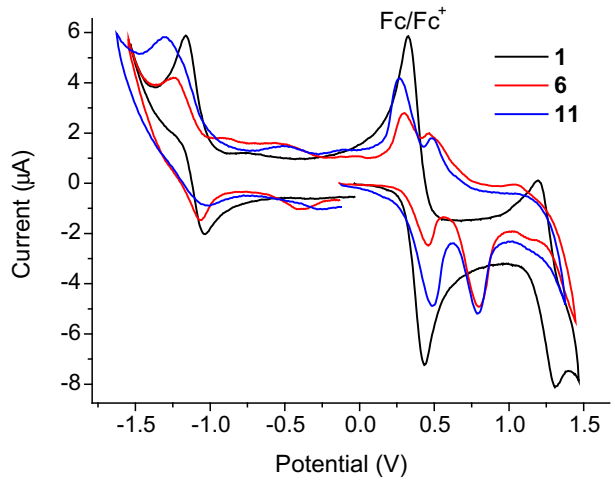

Fig. 3. Cyclic voltammograms of **1**, **6**, and **11** in CH_2Cl_2 containing 0.1 M $[Bu_4N][PF_6]$ with a scan rate of 50 mV s^{-1}. Ferrocene (Fc) was added as an internal reference.

shows the voltammograms of **1**, **6**, and **11**, is given as an example to illustrate the effects of these substituents.

The second-order NLO properties of the push–pull BODIPY derivatives **11**–**14** were measured by EFISH in $CHCl_3$ at 1907 nm and their dipole moments (μ) were calculated using the PM3 semi-empirical code included in the MOPAC2009 package.[20] The values of the dot product $\mu\cdot\beta$ and μ_{calcd}, as well as β derived from these data are listed in Table 3. Disperse Red 1, a common benchmark for NLO chromophores,[21] was used as the reference, which has a $\mu\cdot\beta$ value of 363×10^{-48} esu under the same experimental conditions. The β values were not corrected for resonance enhancement because the second-harmonic signal (954 nm) lies far from the electronic absorptions. Related push–pull porphyrins have been reported,[22] but a direct comparison of the β values is difficult because of different experimental conditions. Qualitatively, these BODIPY derivatives have lower hyperpolarizabilities. The values depend on the nature and position of the substituents at the 3- and 5-positions. Compound **12**, which has the electron-donating 4-(dimethylamino)phenylethynyl and 4-dodecyloxystyryl groups on the same side, shows the largest $\mu\cdot\beta$ value (330×10^{-48} esu). As expected, its calculated dipole moment is also the largest (10.9 D). By contrast, compound **13**, in which these two substituents are on the opposite side, exhibits the smallest $\mu\cdot\beta$ and β values. These observations suggest that charge transfer is an important factor for the second-order NLO properties, which is governed by the position of these substituents.

Table 3
Dipole moments and hyperpolarizabilities of **11**–**14**

Comp.	**11**	**12**	**13**	**14**
μ_{calcd}[a] (D)	9.2	10.9	7.8	10.3
$\mu\cdot\beta$[b] ($\times10^{-48}$ esu)	233	330	94	308
β[c] ($\times10^{-30}$ esu)	25	30	12	30

[a] Calculated by the MOPAC2009 package.
[b] With reference to Disperse Red 1 ($\mu\cdot\beta$=363×10^{-48} esu).
[c] Calculated by dividing $\mu\cdot\beta$ with μ_{calcd}.

3. Conclusion

In summary, a series of novel push–pull BODIPY derivatives have been synthesized by Knoevenagel condensation followed by sequential Sonogashira coupling reactions. Expansion of the π system by these two reactions results in significant red-shift of the absorption and fluorescence bands. The fluorescence quantum yield generally decreases upon conjugation with the alkynyl moieties. Electrochemical studies have shown that introduction of the electron-donating 4-dodecyloxystyryl and 4-(dimethylamino) phenylethynyl groups facilitates the first oxidation of these compounds, but their first reduction is not significantly affected. These compounds exhibit moderate $\mu\cdot\beta$ values [$(94–330)\times10^{-48}$ esu] as determined by EFISH at 1907 nm, which can be modulated by the peripheral substituents. Generally, by putting the electron-donating and electron-withdrawing groups on the opposite side of BODIPY core, this can promote the charge-transfer character of these compounds and enhance their second-order NLO properties. This structure–property relationship would be useful in further studies of BODIPY-based NLO materials.

4. Experimental

4.1. General

All the reactions were performed under an atmosphere of nitrogen. Tetrahydrofuran (THF), toluene, and CH_2Cl_2 were distilled from sodium benzophenone ketyl, sodium, and calcium hydride, respectively. Chromatographic purifications were performed on silica gel (Macherey-Nagel 230–400 mesh) columns with the indicated eluents. Size exclusion chromatography was carried out on Bio-Beads S-X1 beads (200–400 mesh) with THF as the eluent. All other solvents and reagents were of reagent grade and used as received. Compounds **1**[16] and **2**[17] were prepared as described.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer (^1H, 400; ^{13}C, 100.6 MHz) in $CDCl_3$. Spectra were referenced internally using the residual solvent (^1H: δ 7.26) or solvent (^{13}C: δ 77.2) resonances relative to $SiMe_4$. Electrospray ionization (ESI) mass spectra were recorded on a Thermo Finnigan MAT 95 XL mass spectrometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China. UV–vis and steady-state fluorescence spectra were taken on a Cary 5G UV–vis-NIR spectrophotometer and a Hitachi F-4500 spectrofluorometer, respectively. The fluorescence quantum yields of the samples [$\Phi_{F(sample)}$] were determined by the equation: $\Phi_{F(sample)} = (F_{sample}/F_{ref})(A_{ref}/A_{sample})(n^2_{sample}/n^2_{ref})\Phi_{F(ref)}$,[23] where F, A, and n are the measured fluorescence (area under the emission peak), the absorbance at the excitation position, and the refractive index of the solvent, respectively. Rhodamine B in ethanol was used as the reference [$\Phi_{F(ref)}$=0.49] for compounds **1**, **6**, and **11**.[18] The unsubstituted zinc(II) phthalocyanine in DMF was used as the reference [$\Phi_{F(ref)}$=0.28] for compounds **4**, **9**, and **14**.[19]

Electrochemical measurements were carried out on a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a platinum-sphere working electrode, a platinum-wire counter electrode, and a silver-wire pseudo-reference electrode. All measurements were carried out in deoxygenated CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ as the supporting electrolyte with a scan rate of 50 mV s^{-1}. Ferrocene was added as an internal standard, of which the $E_{1/2}$ value was set as +0.38 V vs SCE.

4.2. Monostyryl BODIPY 3

A mixture of dodecyloxy substituted BODIPY **1** (200 mg, 0.26 mmol), benzaldehyde **2** (76.4 mg, 0.26 mmol), piperidine (1.2 mL), acetic acid (1.0 mL), and a small amount of $Mg(ClO_4)_2$ in toluene (50 mL) was refluxed for 50 min. The water formed during the reaction was removed azeotropically with a Dean–Stark apparatus. The volatiles were removed under reduced pressure. The residue was purified by column chromatography using CH_2Cl_2/hexane (1:1, v/v) as the eluent followed by size exclusion chromatography with THF as the eluent. The desired product **3** was obtained as a brown solid (73.2 mg, 27%). ^1H NMR: δ 8.12 (d,

J=16.8 Hz, 1H, CH=CH), 7.57 (d, J=8.4 Hz, 2H, ArH), 7.53 (d, J=16.8 Hz, 1H, CH=CH), 7.13 (d, J=8.4 Hz, 2H, ArH), 7.02 (d, J=8.4 Hz, 2H, ArH), 6.91 (d, J=8.4 Hz, 2H, ArH), 3.98–4.04 (m, 4H, CH_2), 2.68 (s, 3H, CH_3), 1.76–1.86 (m, 4H, CH_2), 1.50 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.46–1.50 (m, 4H, CH_2), 1.28 (br s, 32H, CH_2), 0.87–0.90 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR: δ 160.5, 160.3, 156.5, 150.7, 146.4, 145.0, 140.4, 139.2, 132.8, 132.4, 129.4, 129.3, 126.9, 116.6, 115.5, 115.0, 86.0, 82.3, 68.4, 68.3, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.9, 17.8, 17.3, 16.3, 14.3 (some of the signals are overlapped). MS (ESI): m/z 1032 (100%, $[M]^+$). HRMS (ESI): m/z calcd for $C_{50}H_{69}BF_2I_2N_2O_2$ $[M]^+$: 1032.3512, found 1032.3511. Anal. Calcd for $C_{50}H_{69}BF_2I_2N_2O_2$: C, 58.15; H, 6.73; N, 2.71. Found: C, 58.13; H, 6.73; N, 2.27.

4.3. Distyryl BODIPY 4

According to the above procedure, BODIPY **1** (100 mg, 0.13 mmol) was treated with benzaldehyde **2** (153 mg, 0.53 mmol), piperidine (1.2 mL), acetic acid (1.0 mL), and a small amount of $Mg(ClO_4)_2$ in refluxing toluene (40 mL) for 1.5 h to give **4**, which was purified by column chromatography with CH_2Cl_2/hexane (2:3, v/v) as the eluent followed by size exclusion chromatography with THF as the eluent (83.7 mg, 49%). ^1H NMR: δ 8.13 (d, J=16.8 Hz, 2H, CH=CH), 7.60 (d, J=8.8 Hz, 4H, ArH), 7.59 (d, J=16.8 Hz, 2H, CH=CH), 7.15 (d, J=8.8 Hz, 2H, ArH), 7.03 (d, J=8.8 Hz, 2H, ArH), 6.94 (d, J=8.8 Hz, 4H, ArH), 3.99–4.05 (m, 6H, CH_2), 1.77–1.86 (m, 6H, CH_2), 1.55 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.42–1.51 (m, 6H, CH_2), 1.28 (br s, 48H, CH_2), 0.87–0.90 (m, 9H, CH_3). $^{13}C\{^1H\}$ NMR: δ 160.5 160.3, 150.5, 145.8, 139.2, 138.8, 133.4, 129.7, 129.6, 129.4, 127.2, 116.8, 115.5, 115.0, 82.7, 68.4, 68.3, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.9, 17.9, 14.3 (some of the signals are overlapped). MS (ESI): m/z 1305 (100%, $[M]^+$). HRMS (ESI): m/z calcd for $C_{69}H_{97}BF_2I_2N_2O_3$ $[M]^+$: 1304.5644, found 1304.5642.

4.4. BODIPY 6

A mixture of BODIPY **1** (301 mg, 0.40 mmol), $PdCl_2(PPh_3)_2$ (14.4 mg, 20.5 μmol), CuI (7.6 mg, 40 μmol), 4-(dimethylamino) phenylethyne (**5**) (63.4 mg, 0.44 mmol), and DIEA (5 mL) in THF (10 mL) was stirred at room temperature for 12 h. The volatiles were removed in vacuo, then the dark purple residue was subjected to column chromatography using CH_2Cl_2/hexane (1:1 to 3:2, v/v) as the eluent. The product was collected as a dark purple solid (102 mg, 33%). ^1H NMR: δ 7.33 (d, J=8.8 Hz, 2H, ArH), 7.13 (d, J=8.8 Hz, 2H, ArH), 7.02 (d, J=8.8 Hz, 2H, ArH), 6.63 (d, J=8.8 Hz, 2H, ArH), 4.02 (t, J=6.8 Hz, 2H, CH_2), 2.98 (s, 6H, CH_3), 2.70 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 1.84 (quintet, J=6.8 Hz, 2H, CH_2), 1.56 (s, 3H, CH_3), 1.44–1.54 (m, 2H, CH_2), 1.46 (s, 3H, CH_3), 1.28 (br s, 16H, CH_2), 0.87–0.90 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR: δ 160.2, 159.2, 155.4, 150.2, 144.3, 144.1, 142.0, 132.6, 132.2, 131.5, 129.3 126.6, 117.6, 115.4, 112.0, 110.3, 97.9, 84.8, 79.3, 68.4, 40.4, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.8, 17.1, 16.0, 14.3, 13.9 (some of the signals are overlapped). MS (ESI): m/z 778 (100%, $[M+H]^+$). HRMS (ESI): m/z calcd for $C_{41}H_{52}BF_2IN_3O$ $[M+H]^+$ 778.3218, found 778.3224. Anal. Calcd for $C_{41}H_{51}BF_2IN_3O$: C, 63.33; H, 6.61; N, 5.40. Found: C, 63.04; H, 6.67; N, 5.13.

4.5. Monostyryl BODIPY 7 and 8

According to the procedure described for **6**, monostyryl BODIPY **3** (200 mg, 0.19 mmol) was treated with $PdCl_2(PPh_3)_2$ (6.8 mg, 9.7 μmol), CuI (3.7 mg, 19.4 μmol), alkyne **5** (28.2 mg, 0.19 mmol), and DIEA (5 mL) in THF (10 mL) at room temperature for 12 h. The crude product was purified by column chromatography using CH_2Cl_2/hexane (1:1 to 3:2, v/v) as the eluent. The first two blue bands were collected to give **7** (37.2 mg, 18%) and **8** (45.3 mg, 22%), respectively. Compound **7**: ^1H NMR: δ 8.50 (d, J=16.4 Hz, 1H, CH=CH), 7.65 (d, J=16.4 Hz, 1H, CH=CH), 7.58 (d, J=8.4 Hz, 2H, ArH), 7.37 (d, J=8.8 Hz, 2H, ArH), 7.15 (d, J=8.8 Hz, 2H, ArH), 7.01 (d, J=8.8 Hz, 2H, ArH), 6.90 (d, J=8.4 Hz, 2H, ArH), 6.67 (d, J=8.8 Hz, 2H, ArH), 3.98–4.04 (m, 4H, CH_2), 3.00 (s, 6H, CH_3), 2.69 (s, 3H, CH_3), 1.76–1.87 (m, 4H, CH_2), 1.60 (s, 3H, CH_3), 1.42–1.54 (m, 7H, CH_2 and CH_3), 1.28 (br s, 32H, CH_2), 0.87–0.91 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR: δ 160.5, 160.1, 154.8, 153.3, 150.3, 145.6, 143.3, 140.2, 139.6, 132.5, 132.3, 129.7, 129.5, 129.4, 126.9, 116.7, 115.3, 115.0, 112.1, 110.3, 99.7, 85.0, 81.7, 68.4, 68.3, 40.4, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.8, 17.1, 16.1, 14.3, 13.7 (some of the signals are overlapped). MS (ESI): m/z 1051 (100%, $[M+H]^+$). HRMS (ESI): m/z calcd for $C_{60}H_{80}BF_2IN_3O_2$ $[M+H]^+$: 1050.5351, found 1050.5351. Anal. Calcd for $C_{60}H_{79}BF_2IN_3O_2$: C, 68.63; H, 7.58; N, 4.00. Found: C, 68.57; H, 7.81; N, 3.72. Compound **8**: ^1H NMR: δ 8.08 (d, J=16.4 Hz, 1H, CH=CH), 7.58 (d, J=8.8 Hz, 2H ArH), 7.54 (d, J=16.4 Hz, 1H, CH=CH), 7.34 (d, J=8.8 Hz, 2H, ArH), 7.15 (d, J=8.4 Hz, 2H, ArH), 7.02 (d, J=8.4 Hz, 2H, ArH), 6.91 (d, J=8.8 Hz, 2H, ArH), 6.63 (d, J=8.8 Hz, 2H, ArH), 3.98–4.04 (m, 4H, CH_2), 2.98 (s, 6H, CH_3), 2.74 (s, 3H, CH_3), 1.76–1.87 (m, 4H, CH_2), 1.56 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.42–1.49 (m, 4H, CH_2), 1.28 (br s, 32H, CH_2), 0.87–0.91 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR: δ 160.3, 160.1, 159.2, 150.2, 150.1, 149.8, 145.0, 143.7, 140.6, 138.3, 133.1, 132.6, 132.1, 129.6, 129.5, 129.2, 126.9, 117.9, 116.7, 115.4, 114.9, 112.1, 112.0, 110.4. 110.3, 98.1, 81.6, 79.5, 79.4, 68.4, 68.3, 40.4, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.9, 17.6, 14.3, 14.1, 13.9 (some of the signals are overlapped). MS (ESI): m/z 1051 (100%, $[M+H]^+$). HRMS (ESI): m/z calcd for $C_{60}H_{80}BF_2IN_3O_2$ $[M+H]^+$: 1050.5351, found 1050.5362. Anal. Calcd for $C_{60}H_{79}BF_2IN_3O_2$: C, 68.63; H, 7.58; N, 4.00. Found: C, 67.85; H, 7.60; N, 3.99.

4.6. Distyryl BODIPY 9

According to the procedure described for **6**, distyryl BODIPY **4** (201 mg, 0.15 mmol) was treated with $PdCl_2(PPh_3)_2$ (5.2 mg, 7.4 μmol), CuI (3.0 mg, 15.8 μmol), alkyne **5** (33.4 mg, 0.23 mmol), and DIEA (4 mL) in THF (10 mL) at room temperature for 12 h to give **9**, which was purified by column chromatography using CH_2Cl_2/hexane (1:1 to 3:1, v/v) as the eluent (87.3 mg, 43%). ^1H NMR: δ 8.53 (d, J=16.4 Hz, 1H, CH=CH), 8.09 (d, J=16.4 Hz, 1H, CH=CH), 7.71 (d, J=16.4 Hz, 1H, CH=CH), 7.58–7.63 (m, 5H, ArH and CH=CH), 7.37 (d, J=8.8 Hz, 2H, ArH), 7.17 (d, J=8.4 Hz, 2H, ArH), 7.02 (d, J=8.8 Hz, 2H, ArH), 6.95 (d, J=8.8 Hz, 2H, ArH), 6.92 (d, J=8.4 Hz, 2H, ArH), 6.67 (d, J=8.8 Hz, 2H, ArH), 3.99–4.04 (m, 6H, CH_2), 3.00 (s, 6H, CH_3), 1.77–1.88 (m, 6H, CH_2), 1.60 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 1.42–1.50 (m, 6H, CH_2), 1.28 (br s, 48H, CH_2), 0.87–0.90 (m, 9H, CH_3). $^{13}C\{^1H\}$ NMR: δ 160.5, 160.2, 160.1, 153.3, 150.2, 149.2, 145.1, 144.2, 139.7, 138.6, 138.0, 133.5, 133.2, 132.3, 129.8, 129.5, 129.2, 127.2, 117.0, 115.3, 115.0, 114.9, 112.1, 110.4, 99.9, 81.8, 68.4, 68.3, 40.3, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.8, 17.6, 14.3, 13.7 (some of the signals are overlapped). MS (ESI): m/z 1323 (100%, $[M+H]^+$). HRMS (ESI): m/z calcd for $C_{79}H_{108}BF_2IN_3O_3$ $[M+H]^+$: 1322.7491, found 1322.7496. Anal. Calcd for $C_{79}H_{107}BF_2IN_3O_3$: C, 71.75; H, 8.16; N, 3.18. Found: C, 71.49; H, 8.12; N, 2.92.

4.7. BODIPY 11

A mixture of compound **6** (50.0 mg, 64.3 μmol), $PdCl_2(PPh_3)_2$ (2.3 mg, 3.3 μmol), CuI (1.4 mg, 7.4 μmol), 4-nitrophenylethyne (**10**) (18.9 mg, 0.13 mmol), and DIEA (2 mL) in THF (4 mL) was refluxed for 12 h. The volatiles were removed in vacuo, then the dark blue residue was chromatographed using CH_2Cl_2/hexane (3:2 to 2:1, v/v) as the eluent. The product was collected as a dark blue solid (40.4 mg, 79%). ^1H NMR: δ 8.18 (d, J=8.8 Hz, 2H, ArH), 7.55 (d, J=8.8 Hz, 2H, ArH), 7.33 (d, J=8.8 Hz, 2H, ArH), 7.17 (d, J=8.8 Hz, 2H, ArH), 7.04 (d, J=8.8 Hz, 2H, ArH), 6.63 (d, J=8.8 Hz, 2H, ArH), 4.03 (t, J=6.4 Hz, 2H, OCH_2), 2.98 (s, 6H, CH_3), 2.72 (s, 3H, CH_3), 2.71 (s, 3H, CH_3), 1.84 (quintet, J=6.4 Hz, 2H, CH_2), 1.58 (s, 6H, CH_3), 1.46–1.54 (m, 2H, CH_2), 1.33–1.43 (m, 2H, CH_2), 1.28 (br s, 14H, CH_2),

0.87–0.90 (m, 3H, CH_3). $^{13}C\{^1H\}$ NMR: δ 160.3, 160.2, 156.8, 150.3, 146.7, 144.6, 143.4, 142.8, 132.6, 131.8, 131.3, 130.8, 129.2, 126.2, 123.8, 118.2, 115.4, 114.1, 111.9, 110.0, 98.4, 94.7, 88.4, 79.1, 68.4, 40.4, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.8, 14.3, 13.9, 13.7. MS (ESI): m/z 797 (100%, $[M+H]^+$). HRMS (ESI): m/z calcd for $C_{49}H_{56}BF_2N_4O_3$ $[M+H]^+$: 797.4416, found 797.4425. Anal. Calcd for $C_{49}H_{55}BF_2N_4O_3$: C, 73.86; H, 6.96; N, 7.03. Found: C, 73.55; H, 7.02; N, 6.80.

4.8. Monostyryl BODIPY 12

According to the procedure described for **11**, monostyryl BODIPY **7** (37.1 mg, 35.3 μmol) was treated with $PdCl_2(PPh_3)_2$ (1.2 mg, 1.7 μmol), CuI (0.7 mg, 3.7 μmol), alkyne **10** (15.5 mg, 0.11 mmol), and DIEA (3 mL) in THF (6 mL) to give **12**, which was purified by column chromatography using CH_2Cl_2/hexane (1:2 to 2:1, v/v) as the eluent (28.3 mg, 75%). ^1H NMR: δ 8.53 (d, J=16.4 Hz, 1H, CH=CH), 8.16 (d, J=8.8 Hz, 2H, ArH), 7.65 (d, J=16.4 Hz, 1H, CH=CH), 7.59 (d, J=8.8 Hz, 2H, ArH), 7.53 (d, J=8.8 Hz, 2H, ArH), 7.36 (d, J=8.8 Hz, 2H, ArH), 7.19 (d, J=8.8 Hz, 2H, ArH), 7.02 (d, J=8.8 Hz, 2H, ArH), 6.92 (d, J=8.8 Hz, 2H, ArH), 6.66 (d, J=8.8 Hz, 2H, ArH), 3.98–4.03 (m, 4H, CH_2), 2.99 (s, 6H, CH_3), 2.74 (s, 3H, CH_3), 1.77–1.86 (m, 4H, CH_2), 1.59 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.45–1.52 (m, 4H, CH_2), 1.28 (br s, 32H, CH_2), 0.87–0.91 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR: δ 160.7, 160.2, 156.2, 154.1, 150.3, 146.6, 145.8, 142.4, 140.8, 140.3, 133.6, 132.3, 131.7, 130.9, 129.6, 129.5, 126.6, 123.8, 116.5, 115.5, 115.3, 115.0, 114.0, 112.0, 110.2, 100.1, 94.9, 88.8, 81.5, 68.4, 68.3, 40.3, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 26.2, 22.8, 14.3, 13.9, 13.7, 13.6 (some of the signals are overlapped). MS (ESI): m/z 1069 (100%, $[M]^+$). HRMS (ESI): m/z calcd for $C_{68}H_{83}BF_2N_4O_4$ $[M]^+$: 1068.6470, found 1068.6462. Anal. Calcd for $C_{68}H_{83}BF_2N_4O_4$: C, 76.39; H, 7.82; N, 5.24. Found: C, 75.65; H, 7.86; N, 4.94.

4.9. Monostyryl BODIPY 13

According to the procedure described for **11**, monostyryl BODIPY **8** (45.0 mg, 42.9 μmol) was treated with $PdCl_2(PPh_3)_2$ (1.5 mg, 2.1 μmol), CuI (0.8 mg, 4.2 μmol), alkyne **10** (18.9 mg, 0.13 mmol), and DIEA (3 mL) in THF (6 mL) to give **13**, which was purified by column chromatography using CH_2Cl_2/hexane (1:1 to 2:1, v/v) as the eluent (37.2 mg, 82%). ^1H NMR: δ 8.22 (d, J=16.4 Hz, 2H, CH=CH), 8.20 (d, J=8.8 Hz, 2H, ArH), 7.62 (d, J=16.4 Hz, 1H, CH=CH), 7.57 (d, J=8.8 Hz, 2H, ArH), 7.56 (d, J=8.8 Hz, 2H, ArH), 7.33 (d, J=8.8 Hz, 2H, ArH), 7.18 (d, J=8.4 Hz, 2H, ArH), 7.00 (d, J=8.4 Hz, 2H, ArH), 6.93 (d, J=8.8 Hz, 2H, ArH), 6.63 (d, J=8.8 Hz, 2H, ArH), 4.01 (t, J=6.4 Hz, 4H, CH_2), 2.98 (s, 6H, CH_3), 2.75 (s, 3H, CH_3), 1.77–1.87 (m, 4H, CH_2), 1.60 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.42–1.54 (m, 4H, CH_2), 1.28 (br s, 32H, CH_2), 0.87–0.90 (m, 6H, CH_3). $^{13}C\{^1H\}$ NMR: δ 160.5, 160.2, 159.8, 152.0, 150.3, 146.8, 145.1, 143.8, 141.2, 138.3, 132.9, 132.6, 132.3, 131.5, 130.8, 129.5, 129.2, 126.5, 124.0, 118.1, 116.5, 115.4, 115.1, 112.0, 111.5, 110.1, 98.4, 96.1, 90.4, 79.3, 68.4, 40.4, 32.1, 29.8, 29.6, 29.5, 29.4, 26.2, 22.9, 14.3, 14.1, 13.9, 13.5 (some of the signals are overlapped). MS (ESI): m/z 1070 (100%, $[M+H]^+$). HRMS (ESI): m/z calcd for $C_{68}H_{84}BF_2N_4O_4$ $[M+H]^+$, 1069.6559, found 1069.6569.

4.10. Distyryl BODIPY 14

According to the procedure described for **11**, distyryl BODIPY **9** (50.0 mg, 37.8 μmol) was treated with $PdCl_2(PPh_3)_2$ (1.3 mg, 1.9 μmol), CuI (0.8 mg, 4.2 μmol), alkyne **10** (16.7 mg, 0.11 mmol), and DIEA (2 mL) in THF (4 mL) for 7 h to give **14**, which was purified by column chromatography using CH_2Cl_2/hexane (1:1 to 2:1, v/v) as the eluent (45.3 mg, 89%). ^1H NMR: δ 8.50 (d, J=16.4 Hz, 1H, CH=CH), 8.22 (d, J=16.4 Hz, 1H, CH=CH), 8.13 (d, J=8.8 Hz, 2H, ArH), 7.62–7.69 (m, 6H, CH=CH and ArH), 7.48 (d, J=8.8 Hz, 2H, ArH), 7.33 (d, J=8.4 Hz, 2H, ArH), 7.16 (d, J=8.4 Hz, 2H, ArH), 6.98 (d, J=8.8 Hz, 2H, ArH), 6.96 (d, J=8.8 Hz, 2H, ArH), 6.81 (d, J=8.8 Hz, 2H, ArH), 6.64 (d, J=8.8 Hz, 2H, ArH), 4.03 (t, J=6.4 Hz, 4H, CH_2), 3.87 (t, J=6.4 Hz, 2H, CH_2), 2.99 (s, 6H, CH_3), 1.78–1.85 (m, 6H, CH_2), 1.47–1.52 (m, 12H, CH_2 and CH_3), 1.29 (br s, 48H, CH_2), 0.87–0.91 (m, 9H, CH_3). $^{13}C\{^1H\}$ NMR: δ 160.7, 160.5, 160.0, 153.4, 151.2, 150.2, 146.5, 145.0, 144.4, 139.8, 139.1, 137.9, 133.9, 132.9, 132.3, 131.2, 130.7, 129.8, 129.7, 129.6, 129.2, 126.7, 123.8, 116.8, 115.4, 115.1, 112.0, 111.5, 110.3, 100.2, 96.3, 90.7, 81.7, 68.4, 68.3, 40.3, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 26.3, 26.2, 22.9, 14.3, 13.6, 13.4. MS (ESI): m/z 1342 (100%, $[M+H]^+$). HRMS (ESI): m/z calcd for $C_{87}H_{112}BF_2N_4O_5$ $[M+H]^+$: 1341.8688, found 1341.8679.

4.11. NLO measurements

The $\mu\cdot\beta$ values of **11**–**14** were measured in $CHCl_3$ by the EFISH method. The experimental set up is shown in Fig. S3 in Supplementary data. The measurements were made by using a commercial (SAGA from Thales Laser) Q-switched Nd^{3+}:YAG nanosecond laser operating at λ=1064 nm with a repetition rate of 10 Hz and pulse duration of 9 ns. The 1064 nm laser beam then entered into the 50 cm long hydrogen Raman cell with a high pressure (55 atm). The fundamental beam was shifted to λ=1910 nm (only the back scattered 1910 nm Raman emission was collected at a 45° incidence angle by the use of a dichroic mirror to eliminate most of the residual 1064 nm pump photons). A Schott RG 1000 filter was used to filter out the remaining visible light from the laser flash lamp. Suitable attenuators were used to control the power of the incident beam. The light was then focused into the EFISH cell with a lens with a focal length of 20 cm.

The measurements were carried out with a wedge-shaped cell (with a volume of 4 mL) comprised of two quartz windows, which were assembled with an appropriate angle on a stainless steel support. The inter-electrode distance was 2 mm, giving a static electric field. The whole cell was translated horizontally relative to the incident beam to produce a periodic second-harmonic generation signal. In this technique, the molecules in the solutions were aligned using a high-voltage DC pulse (5 kV with a pulse width of 200 μs and a delay of 1890 μs) synchronized with the laser pulse. The fundamental radiation (ω) was removed by filters, while the second-harmonic radiation (2ω) reached the photomultiplier, which was connected to a high-speed boxcar integrator card. The signals were processed by a home-made computer program to calculate the interfringe distance and the fringe amplitude. These data were then used to calculate the $\mu\cdot\beta$ values of the samples.

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Supplementary data

Electronic absorption and fluorescence spectra of **1**, **3**, **4**, and **6**–**9** in CH_2Cl_2, a schematic diagram showing the set up for EFISH measurements, and ^1H and $^{13}C\{^1H\}$ spectra of all the new compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.08.033.

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