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COMMUNICATION

One-pot efficient synthesis of dimeric, trimeric, and tetrameric BODIPY dyes for panchromatic absorption†

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One-pot Knoevenagel self-condensation reaction of β-formyl BODIPY dye bearing a formyl group at 2-position offered dimeric, trimeric and tetrameric BODIPY dyes containing a formyl capping end group, exhibiting panchromatic absorption.

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) dyes have received an upsurge of interest because they possess a variety of distinctive and desirable properties such as high absorption coefficients, narrow absorption and emission bands, good stability, excellent emission quantum yields, and have promising applications in supramolecular fluorescent gels, solar cells, sensing and imaging.[1] A series of BODIPY-based oligomers, polymers and dendrimers have been reported.[2–8] These oligomeric and polymeric BODIPY dyes display significant red shifts in absorption and emission, and possess broad absorption bands compared with their monomeric forms.[2–6] Polymeric BODIPY dyes have been shown to have promising applications in solar cells.[2] However, in most previous reports, multistep organic reactions were required, employing several protecting groups and reactive intermediates, in order to prepare oligomeric and polymeric BODIPY dyes.[2–4,8] These tedious procedures limit practical use of these new BODIPY dyes. It is highly desirable to develop a facile, efficient and cost-effective method to prepare oligomeric BODIPY dyes for potential solar cell and other applications.

In this communication, we report efficient synthesis of dimeric, trimeric and tetrameric BODIPY dyes with a formyl capping end group through a one-pot Knoevenagel self-condensation reaction of β-formyl BODIPY dye (Scheme 1). The formyl capping end group of these new BODIPY dyes can be further functionalized with a variety of groups, *e.g.* a cyanoacrylic acid electron acceptor group, through the Knoevenagel reaction. These BODIPY dyes display panchromatic absorption from visible to partial near-infrared regions.

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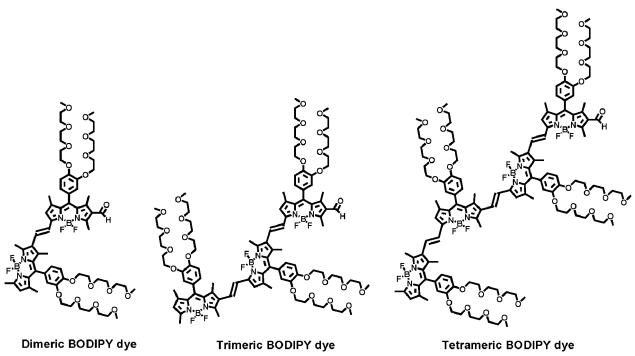
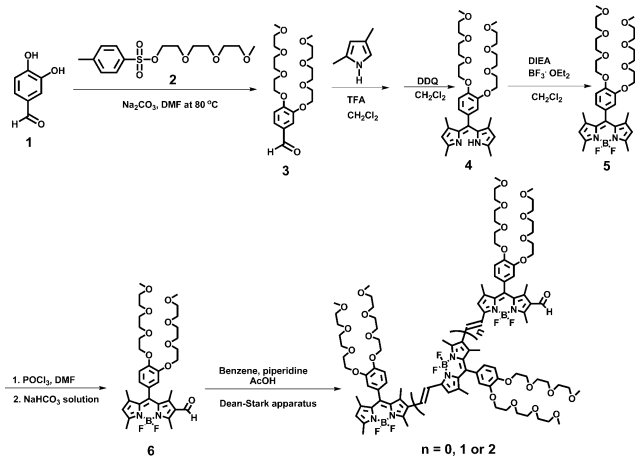
A variety of aryl groups can be introduced to BODIPY monomers at the *meso*-position to enhance solubility of dimeric, trimeric and tetrameric BODIPY dyes in organic solvents (Scheme 2). We employed tri(ethylene glycol)methyl ether side chains instead of *n*-alkyl chains to facilitate separation of dimeric, trimeric and tetrameric compounds. Meso-aryl-substituted BODIPY dye (**5**) was prepared by reacting the formyl benzene derivatives (**3**) with an excess of 2,4-dimethylpyrrole under acid catalysis, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and treatment with BF_3-etherate in the presence of *N*,*N*-diisopropylethylamine (DIEA) (Scheme 2).[3] β-Formyl BODIPY dye (**6**) was prepared from BODIPY dye **5** *via* the Vilsmeier–Haack reaction. Self-condensation of β-formyl BODIPY dye **6** for 3 h afforded dimeric, trimeric and tetrameric BODIPY dyes (Scheme 2). Prolonged reaction times beyond 3 h resulted in formation of oligomeric and polymeric BODIPY dyes with higher molecular weights.

Chemical structures of the new monomeric, dimeric, trimeric and tetrameric BODIPY dyes were confirmed by NMR spectra, and high-resolution mass spectroscopy.‡ The ^{1}H NMR spectrum of monomeric BODIPY dye shows four different singlet peaks at 2.79, 2.56, 1.72 and 1.50 ppm corresponding to four different methyl protons at 5,3,7,1-positions, respectively, and one single peak at 6.13 ppm corresponding to the proton at 2-position (Fig. 1). After the one-pot Knoevenagel self-condensation reaction of monomeric BODIPY dye, the singlet peak corresponding to the proton at the 2-position of the dimeric BODIPY dye shifts downfield from



Scheme 1 Chemical structures of BODIPY dyes.



Scheme 2 Synthetic route to dimeric, trimeric and tetrameric BODIPY dyes.

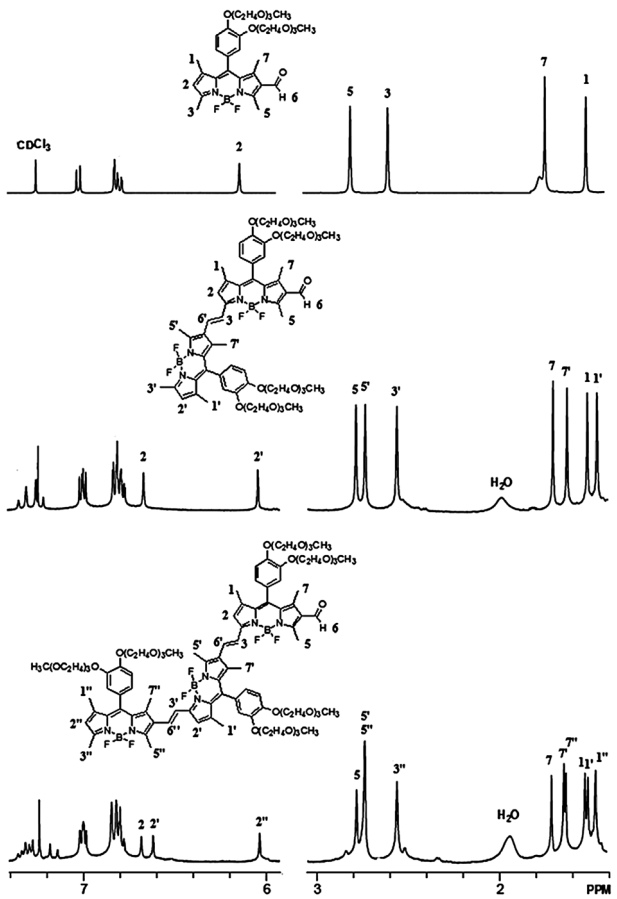


Fig. 1 ^{1}H NMR spectra of monomeric, dimeric and trimeric BODIPY in $CDCl_3$ solution.

6.13 to 6.67 ppm, due to the replacement of the methyl group by a vinyl group at the 3-position. The singlet peak at 2.56 ppm corresponding to the methyl protons at the 3-position of monomeric BODIPY dye also disappears with the formation of the vinyl bond. The singlet peaks at 2.78 and 1.71 ppm corresponding to methyl protons at 5,7-positions in dimeric BODIY dye shift very slightly to lower field, compared with the monomeric ones at 2.79 and 1.72 ppm. These 0.01 ppm shifts are slight because these methyl protons are relatively far away from the vinyl bond at the 3-position in dimeric BODIPY dye. Five additional singlet peaks appear in the ^{1}H spectrum of dimeric BODIPY dye at 6.05, 2.73, 2.56, 1.63 and 1.47 ppm corresponding to the proton at 2′-position and four different methyl protons at 5′,3′,7′,1′-positions. When trimeric BODIPY was formed, the two singlet peaks corresponding to the protons at 2,2′-positions in dimeric BODIPY dye move downfield from 6.67 and 6.05 ppm to 6.68 and 6.62 ppm, respectively. However, the change (0.57 ppm) of chemical shift of the proton at 2′-position is much more significant than that (0.01 ppm) at 2-position because it is closer to the newly formed vinyl bond in trimeric BODIPY dye. Four different singlet peaks corresponding to the methyl protons at 5′,7′,1′,1-positions in trimeric BODIPY dye slightly shift to low field by 0.01 or 0.02 ppm compared with those in dimeric BODIPY dye due to the electron withdrawing character of the second vinyl bond in trimeric BODIPY dye, while two singlet peaks corresponding to the methyl protons at 7,5-positions in the trimeric compound remain unchanged as they are far away from the second vinyl bond. Four additional singlet peaks at 6.03, 2.56, 1.63 and 1.47 ppm appear, corresponding to the proton at 2″-position and methyl protons at 3″,7″,1″-positions, while one additional singlet peak at 2.74 ppm corresponding to the methyl protons at 5″-position overlaps with the singlet peak of the methyl protons at 5′-position. The singlet peak at 2.56 ppm corresponding to the methyl protons at 3′-position of dimeric BODIPY dye also disappears with the formation of the second vinyl bond (Fig. 1). All oligomeric BODIPY dyes possess a singlet peak at 9.98 ppm corresponding to the proton from the formyl capping end group (see ^{1}H spectra of oligomeric BODIPY dyes in ESI†).

All these new BODIPY dyes are readily soluble in common solvents such as acetone, ethanol, dimethylformamide, dimethyl sulfoxide, ethyl acetate, tetrahydrofuran, methylene chloride and chloroform. The absorption properties of monomeric BODIPY dye in CH_2Cl_2 solution are characterized by a strong $S_0 \rightarrow S_1$ (π–π^*) transition at 497 nm with an absorption coefficient of 8.5×10^4 M^{-1} cm^{-1} and a weaker broad band around 350 nm attributed to the $S_0 \rightarrow S_2$ (π–π^*) transition (Table 1); it shows a fluorescent peak at 511 nm in CH_2Cl_2 solution. Compared with monomeric BODIPY dye, the dimeric BODIPY dye displays broader absorption with maximum absorption at 643 nm with slightly higher absorption coefficient of 9.0×10^4 M^{-1} cm^{-1}, and shoulder peak at 518 nm (Fig. 2). Trimeric BODIPY dye shows a much broader absorption ranging from 460 to 740 nm with four different absorption peaks at 512, 554, 680 and 727 nm. This broad absorption arises from the significantly extended π-conjugation in this trimeric compound, which considerably enhances its absorption coefficient to 1.3×10^5 M^{-1} cm^{-1} at 727 nm. Tetrameric BODIPY dye exhibits panchromatic absorption extending

Table 1 Absorption coefficients and maximum absorption wavelengths of the monomeric and oligomeric BODIPY dyes

BODIPY dye	Monomeric	Dimeric		Trimeric		Tetrameric	
λ_{abs}/nm	497	518	643	554	727	632	764
$10^{-5}\varepsilon/M^{-1}$ cm^{-1}	0.85	0.32	0.90	0.63	1.3	0.88	1.1

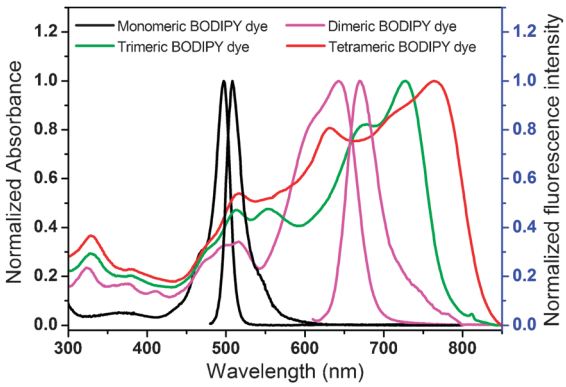


Fig. 2 Absorption spectra of monomeric, dimeric, trimeric and tetrameric BODIPY dyes, and fluorescence spectra of monomeric and dimeric BODIPY dyes in CH_2Cl_2 solution.

from 460 to 800 nm and also shows a high absorption coefficient of 1.1×10^5 M^{-1} cm^{-1} at 764 nm in CH_2Cl_2 solution. This unusual panchromatic absorption spectrum may arise from a slight steric hindrance between a proton of each vinyl bond and its adjacent methyl proton, which slightly affects π-conjugation between each BODIPY unit, resulting in four different absorption peaks for tetrameric BODIPY species. Similar effects are also observed in the dimeric and trimeric BODIPY dyes. Dimeric BODIPY displays very weak fluorescence with maximum emission at 660 nm. Trimeric and tetrameric BODIPY dyes show no fluorescence in CH_2Cl_2 solution, although the monomeric BODIPY dye is highly fluorescent with a fluorescence quantum yield of 35.6%. Fluorescence quenching of these oligomeric BODIPY dyes may arise from the formyl group because initial introduction of the formyl group to the 2-position of BODIPY dye **5** (fluorescence quantum yield 92% in CH_2Cl_2 solution) to give the monomeric compound (**6**) significantly reduces its fluorescence (fluorescence quantum yield 35.6% in CH_2Cl_2 solution). However, the quenching mechanism of the oligomeric BODIPY dyes needs further investigation.

In conclusion, we have developed a facile, versatile and effective synthetic approach to prepare dimeric, trimeric and tetrameric BODIPY dyes containing a useful formyl capping end group through a one-pot Knoevenagel self-condensation reaction of β-formyl BODIPY dye. These BODIPY dyes display panchromatic absorption in the visible and partial near-infrared region, and possess higher absorption coefficients than the monomeric BODIPY dye.

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Notes and references

‡ Dimeric BODIPY, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.33 (d, J = 16.4 Hz, 1H), 7.24 (d, J = 16.4 Hz, 1H), 7.02–6.98 (m, 2H), 6.83–6.77 (m, 4H), 6.67 (s, 1H), 6.05 (s, 1H), 4.23–4.19 (m, 4H), 4.14–4.10 (m, 4H), 3.92–3.88 (m, 4H), 3.85–3.82 (m, 4H), 3.77–3.47 (m, 32H), 3.35 (s, 6H), 3.32 (s, 6H), 2.78 (s, 3H), 2.73 (s, 3H), 2.56 (s, 3H), 1.71 (s, 3H), 1.63 (s, 3H), 1.52 (s, 3H), 1.47 (s, 3H); HRMS (FAB) calc. for $C_{68}H_{92}N_4F_4B_2O_{17}$ $[M]^+$, 1334.6580; found, 1334.6578. Trimeric BODIPY, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.36–7.14 (m, 4H), 7.02–6.98 (m, 3H), 6.85–6.78 (m, 6H), 6.68 (s, 1H), 6.62 (s, 1H), 6.03 (s, 1H), 4.24–4.19 (m, 6H), 4.15–4.10 (m, 6H), 3.93–3.89 (m, 6H), 3.86–3.82 (m, 6H), 3.78–3.47 (m, 48H), 3.36 (s, 3H), 3.35 (s, 6H), 3.32 (s, 6H), 3.31 (s, 3H), 2.78 (s, 3H), 2.74 (s, 6H), 2.56 (s, 3H), 1.71 (s, 3H), 1.64 (s, 3H), 1.63 (s, 3H), 1.53 (s, 3H), 1.51 (s, 3H), 1.47 (s, 3H); HRMS (FAB) calc. for $C_{102}H_{137}N_6F_6B_3O_{25}$ $[M]^+$, 1992.9817; found, 1992.9843. Tetrameric BODIPY, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.35–7.13 (m, 6H), 7.03–6.99 (m, 4H), 6.86–6.79 (m, 8H), 6.69 (s, 1H), 6.64 (s, 1H), 6.61 (s, 1H), 6.03 (s, 1H), 4.24–4.20 (m, 8H), 4.15–4.11 (m, 8H), 3.93–3.89 (m, 8H), 3.87–3.83 (m, 8H), 3.70–3.46 (m, 64H), 3.37–3.36 (s × 4 CH_3, 12H), 3.33–3.32 (s × 4 CH_3, 12H), 2.79 (s, 3H), 2.75 (s, 6H), 2.74 (s, 3H), 2.56 (s, 3H), 1.71 (s, 3H), 1.65 (s, 6H), 1.63 (s, 3H), 1.53 (s, 3H), 1.52 (s, 6H), 1.47 (s, 3H); HRMS (MALDI) calc. for $C_{136}H_{183}N_8F_8B_4O_{33}$ $[M + H]^+$, 2652.3132; found, 2652.3159.

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