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Electronic supplementary information for:

Conjugated Copolymer-Photosensitizer Molecular Hybrids with Broadband Visible Light Absorption for Efficient Light-Harvesting and Enhanced Singlet Oxygen Generation

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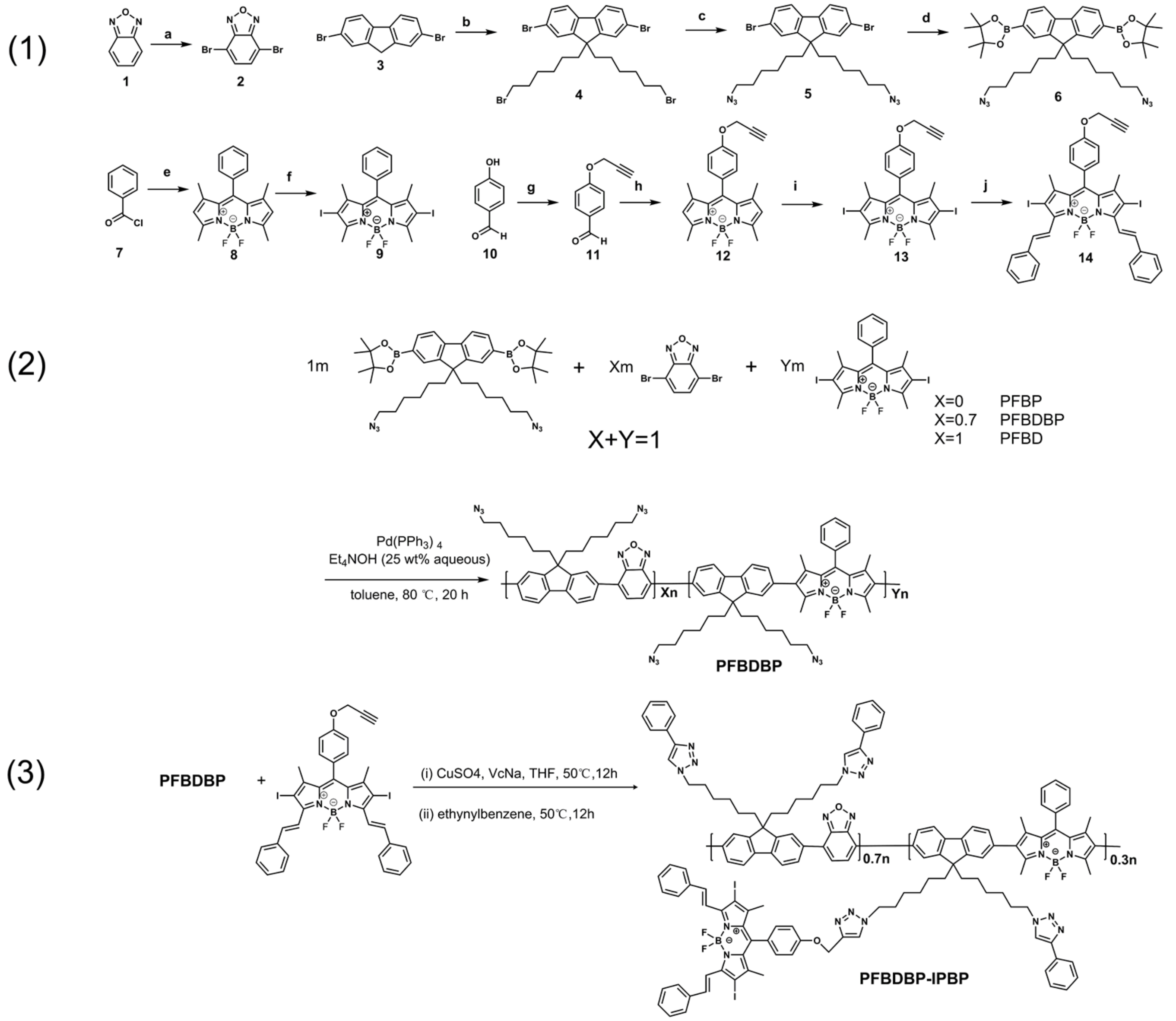

Scheme 1 (1) Preparation of small molecules: (a) Fe, Br_2, 90 °C, 2 h; (b) 1,6-dibromohexane, KOH, TBAB, 75 °C,4 h; (c) NaN_3, DMSO, 60 °C, 2h; (d) $Pd(dppf)_2Cl_2$, CH_3COOK, bis(pinacolato)diboron, anhydrous dioxane, 85 °C, 24 h; (e) 2,4-dimethylpyrrole, CH_2Cl_2, rt ,overnight; Et_3N, BF_3•Et_2O, ice-cold, 2h; (f) CH_2Cl_2, NIS, rt, 4h; (g) K_2CO_3, acetone, propargylbromide, refluxed, 2h; (h) 2,4-dimethylpyrrole, TFA, CH_2Cl_2, rt, overnight; DDQ, rt, 1h; Et_3N, BF_3•Et_2O, ice-cold, 2 h; (i) $CHCl_3$, NIS, rt, 8 h; (j) benzaldehyde, piperidine, acetic acid, toluene, refluxed, 12 h. (2) Preparation of **PFBDBP**. (3) Preparation of **PFBDBP-IPBP**.

Experimental section

General methods. All reagents used in synthesis are analytical pure and were used as received. UV-Vis absorption spectra and fluorescence spectra were recorded on a Hitachi U-3900 ultraviolet-visible spectrophotometer and a Hitachi F-7400 fluorophotometer, respectively. Fluorescence lifetimes were measured on a FluoroMax-4 TCSPC (Horiba Jobin Yvon) spectrofluorometer, using a pulsed pulsed 457 nm and 566 nm diode laser (IBH NanoLED) as the excitation source for **PFBDBP** and **PFBDBP-IPBP**, respectively. Decay data analysis was performed using the DAS6 software (Horiba Jobin Yvon IBH), the average lifetimes were calculated using the equation:

$$\bar{\tau} = \frac{\sum_{i=1}^{n} \alpha_i {\tau_i}^2}{\sum_{i=1}^{n} \alpha_i \tau_i}$$

where τ_i is the fluorescence decay time and α_i the normalized pre-exponential factor. Absolute quantum yields were measured using the integrating sphere approach on a FluoroMax-4 spectrofluorometer equipped with an F-3018 integrating sphere accessory (Horiba Jobin Yvon). Gel permeation chromatography (GPC) data were calibrated against polystyrene standards and collected on a Waters 1515 equipped with a Waters 2414 Refractive Index Detector using THF as eluent. ^{1}H NMR spectra were recorded on a 500 MHz Brucker Advance 500 Ⅲ spectrometer at 25 °C. FTIR spectra was collected on a Nicolet Avatar 330 (Thermo Electron Corporation, USA).

Photooxidation. Photooxidation of DHN**:** The photosensitizers (2.0×10^{-6} M, in IPBP units)) and DHN (2.0×10^{-4} M) were in CH_2Cl_2/MeOH mixed solvent (9:1, 10 mL), then air was bubbled through the solution for 15 min. The solution was then irradiated using a 150 W xenon arc lamp (CHF-XM-150W, Beijing Trusttech). $NaNO_2$ solution (50 g/L) was set between the lamp and the photoreactor to block the <385 nm UV light and IR light. UV-Vis absorption spectra were recorded at intervals of 2-5 min. The consumption of DHN was monitored at intervals of the UV absorption at 301 nm, and the concentration of DHN was calculated based on its molar extinction coefficient ($\varepsilon = 7664\ M^{-1}\ cm^{-1}$). Photooxidation of DPBF: Air saturated DCM was obtained by bubbling air for 15 min. The absorbance of DPBF was adjusted around 1.0 in air saturated DCM. Then, the photosensitizer was added to cuvette and the concentration of photosensitizer is 2.5×10^{-6} M (in IPBP units). The cuvette was irradiated with monochromatic light at 445 nm and 545 nm for 10 s. Absorbance was measured after each irradiation. The slope of plots of absorbance of DPBF at 414 nm vs irradiation time for each photosensitizer was calculated.

Photostability. The photostability of **PFBDBP-IPBP** and IPBP was examined by recoding the absorption spectra as a function of time with 150 W xenon arc lamp (CHF-XM-150W, Beijing Trusttech), which the solution 20 cm distance from the lamp. The concentration of **PFBDBP-IPBP** (in IPBP unit) and IPBP were 1.0×10^{-5} M, UV-Vis absorption spectra were recorded at intervals of 10 min.

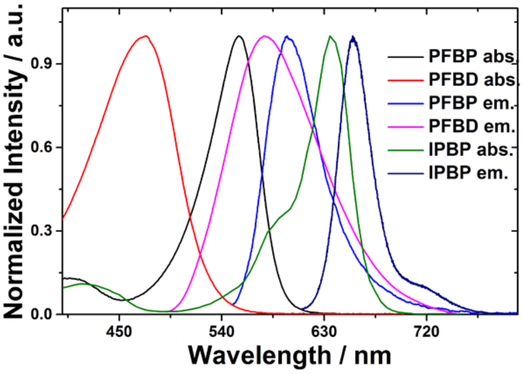

Figure S1. Normalized UV-Vis absorption and fluorescence emission spectra of **PFBD** (λ_{ex} = 470 nm), **PFBP** (λ_{ex} =540 nm) and **IPBP** (λ_{ex} =600 nm) (For recording UV-Vis absorption, concentration of **PFBDBP** and **IPBP** is 2.0 × 10^{-6} M; for recording fluorescence spectra, the concentration of **PFBDBP** and **IPBP** is 1.0 × 10^{-7} M). Solvent: DCM.

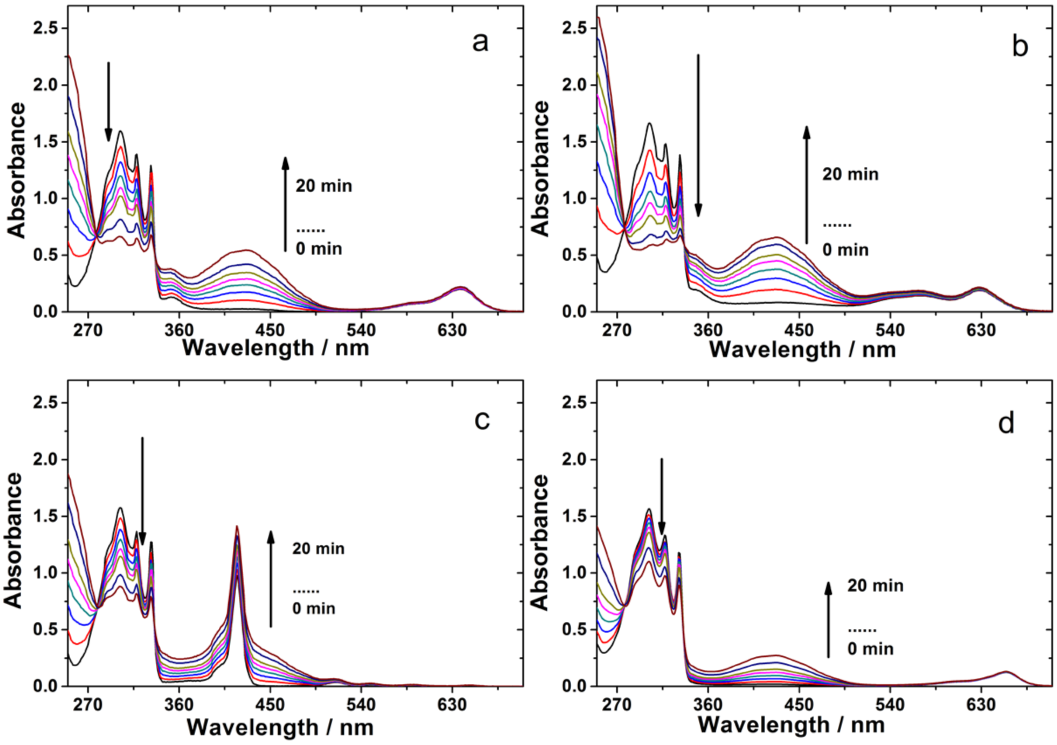

Figure S2. UV-Vis absorption spectra showing photooxidation of DHN with a) **IPBP**, b) **PFBDBP-IPBP**, c) TPP and d) MB (In DCM/MeOH, 9 : 1, v/v), [Photosensitizers] = 2.0 × 10^{-6} M (**PFBDBP-IPBP** is in **IPBP** units), [DHN] = 1.0 × 10^{-4} M, 20 °C.

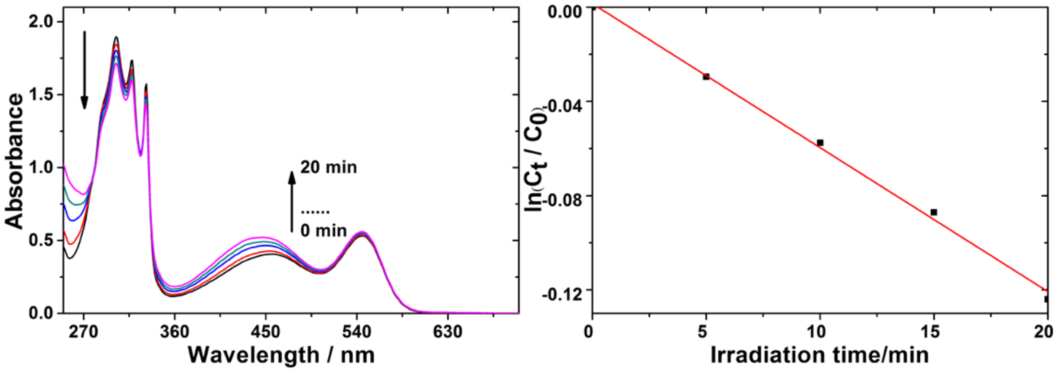

Figure S3. a) UV-Vis absorption spectra showing photooxidation of DHN with **PFBDBP**. b) Plots of ln (C_t/C_0) vs irradiation time for **PFBDBP**. [Photosensitizers] = 2.0 × 10^{-6} M (in polymer backbone unit), and [DHN] = 1.0 × 10^{-4} M, 20°C.

Table 1 Photophysical parameters of the conjugated polymers

polymer	F/BD/BP[a]	M_n g mol^{-1}	M_w g mol^{-1}	PDI M_w/M_n	number of azide group	$\lambda_{abs\ max}$[b] nm	ε_{max} × 10^{-5} cm^{-1} M^{-1}	λ_{em}[c] nm	Φ[d] %
PFBP	1/0/1	20035	43685	2.18	54	555	2.41	597	28.8
PFBDBP	1/0.7/0.3	23766	46190	1.94	80	545	2.64	594	37.1[e], 40.7[f]
PFBD	1/1/0	26928	52792	1.96	101	473	1.06	577	47.0

[a] The ratio of F, BD, BP in polymer molecular, determined by ^{1}H NMR. [b] In DCM (2.0 × 10^{-6} M). [c] In DCM (1.0 × 10^{-7} M). [d] Absolute photoluminescence quantum yield of **PFBD** and **PFBP** excited at 470 nm and 540 nm, respectively. In DCM. [e] Excited at 545 nm. In DCM. [f] Excited at 445 nm. In DCM.

Synthesis and molecular structure characterization data

4,7-Dibromo-2,1,3-benzoxadiazole (BD) (2).[1] The mixture of 2,1,3-benzoxadiazole (2.50 g, 20.84 mmol) and iron (0.25 g, 4.46 mmol) was heated to 90 °C. Then bromine (3.2 mL, 61.40 mmol) was added dropwise. The mixture was stirred at 90 °C for additional 2 h, cooled to room temperature and poured into 125 mL of water. The resulting solid was filtered, removed to 150 mL saturated $NaHCO_3$, stirred for 60 min to ensure completed neutralize the excess bromine and filtered. The crude product was further purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to give compound **2** (4.53 g, yield: 80 %). ^{1}HNMR (500 MHz, $CDCl_3$, ppm) δ: 7.51 (s, 2 H).

2,7-Dibromo-9,9-bis(6-bromohexyl)-fluorene (4).[2] 2,7-dibromofluorene (6.48 g, 20.00 mmol) and tetra-butyl-ammoniumbromide (TBAB) (0.64 g, 2.00 mmol) were dissolved in 100 mL of 1,6-dibromohexane and 50 mL of a 50 % KOH solution was then injected. The solution was stirred at 75 °C for 4 h. Then the mixture was cooled to room temperature and extraction with CH_2Cl_2, the combined organic layers were washed successively with water, aqueous HCl (1 M), again water, and brine and then dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the excess 1,6-dibromohexane was removed through vacuum distillation. The residue was further purified by silica gel column chromatography (petroleum ether / ethyl acetate = 10 : 1) to give compound **4** (10.53 g, yield: 81 %). ^{1}H MNR (500 MHz, $CDCl_3$, ppm), δ: 7.43-7.54 (m, 6 H), 3.28-3.31 (t, 4 H), 1.90-1.95 (m, 4 H), 1.65-1.69 (m, 4 H), 1.08-1.20 (m, 8 H), 0.55-0.63 (m, 4 H).

2,7-Dibromo-9,9-bis(6-azidohexyl)fluorene (5).[3] A solution of 2,7-dibromo-9,9-bis(6-bromohexyl)fluorene (6.50 g, 10.00 mmol) and sodium azide (1.96 g, 30.00 mmol) in 100 mL DMSO was stirred at 60 °C for 2 h. The mixture was poured into 250 mL water, and extracted with dichloromethane. The organic layer was washed with water, brine and dried over anhydrous $MgSO_4$. After removal of dichloromethane under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether \ dichloromethane = 8 : 2) to afford **5** (5.26 g, yield: 92%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 7.43–7.53 (m, 6 H), 3.13-3.16 (t, 4 H), 1.91-1.94 (t, 4 H), 1.38-1.42 (m, 4 H), 1.05-1.17 (m, 8 H), 0.56-0.62 (m, 4 H).

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(6-azidohexyl)fluorene (F) (6).[3] To a flask of compound **5** (2.86 g, 5.00 mmol), potassium acetate (3.38 g, 35.00 mmol), bis(pinacolato)diboron (3.18 g, 12.50 mmol), $Pd(dppf)_2Cl_2$ (0.20 g, 0.25 mmol) added anhydrous 40 mL dioxane. The system was degassed by applying three freeze–pump–thaw cycles to replace air with argon. The reaction mixture was kept at 85 °C for 24 h. After cooling down to room temperature, the mixture was diluted with dichloromethane, washed with water and brine several times and then dried over $MgSO_4$. After solvent removal under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether / dichloromethane = 1/1) to afford **6** (2.34 g, yield: 70%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 7.71-7.82(m, 6 H), 3.09-3.11 (t, 4 H), 1.99-2.02 (t, 4 H), 1.39 (s, 24 H), 1.33-1.39 (m, 4 H), 1.04-1.09 (m, 8 H), 0.52-0.58 (m, 4 H).

1,3,5,7-tetramethyl-8-phenyl-4, 4-difluoroboradiazaindacene (8).[4] Benzoylchloride (3.64 g, 25.00 mmol) and 2, 4-dimethylpyrrole (5 mL, 3.7 g, 50.00 mmol) were added to 150 ml anhydrous CH_2Cl_2 via syringe under nitrogen atmosphere. Then the mixture was stirred at room temperature overnight under dark condition. Then Et_3N (30 mL) and BF_3•Et_2O (30 mL) were added under ice-cold condition, and reaction mixture was stirred for additional 2 h. After the reaction, the mixture was poured into 300 mL water, the organic layer was collected and washed with water several times, dried over anhydrous $MgSO_4$. Then the CH_2Cl_2 was evaporated under reduced pressure. The crude product was further purified by silica gel column chromatography (petroleum ether / dichloromethane = 1/1) to give **8** (3.00 g, yield: 38%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47-7.49 (m, 3 H), 7.26-7.29 (m, 2 H), 5.98 (s, 2 H), 2.56 (s, 6 H), 1.37 (s, 6 H).

2,6-Diiodo-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene (BP) (9).[4] To a flask of compound **8** (1.58 g, 5.00 mmol), N-iodo-succinimid (NIS) (4.50 g, 20.00 mmol) added 100 mL CH_2Cl_2. The mixture was stirred at room temperature for about 4h. The reaction mixture was then concentrated under vacuum, and the crude product was purified by silica gel column chromatography (petroleum ether / dichloromethane = 2:1) to give **9** (2.56 g, yield: 90%). ^1H NMR (500 MHz, $CDCl_3$) δ: 7.51-7.53 (m, 3 H), 7.24-7.26 (m, 2 H), 2.65 (s, 6 H), 1.38 (s, 6 H).

4-(prop-2-ynyloxy)benzaldehyde (11).[5] 4-hydroxybenzaldehyde (6.12 g, 50.00 mmol) and propargyl bromide (11.90 g, 100.00 mmol) were dissolved in 250 mL acetone. K_2CO_3 (9.67 g, 70.00 mmol) was added. Then the mixture was refluxed for 2 h. After cooling down to room temperature, the solvent was evaporated in vacuum, extracted with water and $CHCl_3$. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether / chloroform =1:1) to give **9** (7.84 g, yield: 98%). ^1H NMR ($CDCl_3$, 500 MHz) δ: 9.91(s, 1 H), 7.85-7.87 (d, 2 H), 7.09-7.10 (d, 2 H), 4.78-4.79 (d, 2 H), 2.57 (s, 1 H).

1,3,5,7-Tetramethyl-8-(4-Propargyloxyphenyl)-4,4-difloroboradiazaindacene (12).[5] 500 mL CH_2Cl_2 was purged with nitrogen for 30 min. Compound **11** (2.98 g, 18.60 mmol) and 2,4-dimethylpyrrole (3.80 g, 40.00 mmol) were added. The color of the solution turned into red after the addition of 3 drops of trifluoroacetic acid. Then the mixture was stirred at room temperature overnight under dark condition. Then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (4.22 g, 18.60 mmol) was added and the reaction mixture was stirred at room temperature for 1 h. Then 30 mL Et_3N and 30 mL BF_3•Et_2O were added under ice-cold condition, and reaction mixture was stirred for additional 2 h, Then it was extracted with water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether / chloroform = 1:1) to give **12** (1.05 g, yield: 15 %). ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.19-7.21 (d, 2 H), 7.08-7.10 (d, 2 H), 5.97 (s, 2 H), 4.76 (d, 2 H), 2.55 (m, 7 H), 1.42 (s, 6 H).

2,6-diiodo-1,7-dimethyl-8-(4-propargyloxyphenyl)- 4, 4-difluoroboradiazaindacene (13).[5] To a flask of compound **12** (0.94 g, 2.50 mmol), N-iodo-succinimid (NIS) (2.25 g, 10.00 mmol) added 100 mL $CHCl_3$. The mixture was stirred at room temperature for about 8h. The reaction mixture was then concentrated under vacuum, and the crude product was purified by silica gel column chromatography (petroleum ether / chloroform = 1:1) to give **13** (1.15 g, yield: 73%). ^1H NMR ($CDCl_3$, 500 MHz) δ: 7.16-7.18 (d, 2 H), 7.11-7.13 (d, 2 H), 4.78 (s, 2 H), 2.64 (s, 6 H), 2.57 (s, 1 H), 1.44 (s, 6 H).

2,6-diiodo-1,7-dimethyl-3,5-diphenylethynyl-8-(4-propargyloxyphenyl)-4, 4difluoroboradiaz- aindacene (IPBP) (14).[5] Compound **13** (630 mg, 1.00 mmol) and benzaldehyde (318 mg, 3.00 mmol) were dissolved in toluene. 0.2 mL piperidine and 0.2 mL glacial acetic acid were added. The solution was refluxed using Dean-Stark apparatus for 12 h. Then, toluene was evaporated in vacuo. It was extracted with CHCl3 and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using (petroleum ether / chloroform = 2:1) to give **14** (258 mg, yield: 32%). ^1H NMR ($CDCl_3$, 500 MHz) δ: 8.13-8.17 (d, 2 H), 7.65-7.72 (m, 6 H), 7.33-7.44 (m, 6 H), 7.13-7.22 (m, 4 H), 4.80 (s, 2 H), 2.58 (s, 1 H), 1.52 (s, 6 H). MALDI: calculated for M+H 807.03, found 807.04.

Poly(9,9-bis(6-azidohexyl)fluorene-alt-2,1,3-benzoxadiazole-alt-1,3,5,7-tetramethyl-8-phenyl-4,4-difluoroboradiazaindacene) (PFBDBP). The respective monomers for example for **PFBDBP**: compound **6** (200.4 mg, 0.30 mmol), compound **2** (58.4 mg, 0.21mmol), compound **9** (51.84 mg, 0.09 mmol), $Pd(PPh_3)_4$ (5.0 mg, 0.004mmol) were dissolved in 10 mL toluene. The solution was degassed with three freeze–pump–thaw cycles to remove air. After the mixture was heated to 80 °C, an aqueous Et_4NOH solution (25 wt %, 1 mL) was added to initiate the reaction. After

20 h, the reaction was stopped and cooled down to room temperature. The mixture was dropped slowly into 150 mL methanol to precipitate the brown polymer followed by centrifugation. The brown polymer was subsequently redissolved in 200 mL dichloromethane, washed with water several times, and dried over $MgSO_4$. After solvent removal, **PFBDBP** (112.8 mg, yield: 63%) was obtained as an brown solid by precipitation in methanol. ^1H NMR (500 MHz, $CDCl_3$) δ: 7.09-8.21 (br, 17.70 H), 3.14 (s, 8.00 H), 2.63 (s, 3.82 H), 2.17 (br, 8.16 H), 1.41 (br, 12.17 H), 1.21 (br, 16.08 H), 0.88 (br, 7.73 H).

PFBDBP-IPBP. PFBDBP (14.90 mg, 0.05mmol (in azide group unit) and 6 % molar equavalent **IPBP** (2.42 mg, 0.003 mmol) were dissolved in 50 mL THF. Then 5 molar equivalent $CuSO_4•5H_2O$ (62.42 mg, 0.25 mmol), 25 molar equivalent vitamin C sodium salt (VcNa) (247.63 mg, 1.25 mmol) were added. The reaction mixture was stirred at 50 °C for 24 h, then 2 molar equivalent ethynylbenzene (10.21 mg, 0.10 mmol) was injected and stirred at 50 °C for additional 18 h. After the solution cooled down to room temperature, the mixture was dropped slowly into 250 mL methanol/H_2O (7/3) to precipitate the polymer followed by centrifugation. The polymer was subsequently dissolved in dichloromethane (200 mL), washed with water several times, and dried over $MgSO_4$. After solvent removal, **PFBDBP-IPBP** (5.54 mg, yield: 32%) was obtained as a dark gray solid by precipitation in methanol.

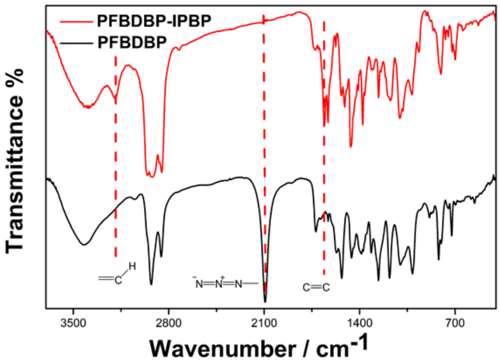

Figure S4. IR spectra of **PFBDBP-IPBP** and **PFBDBP**

NMR spectra

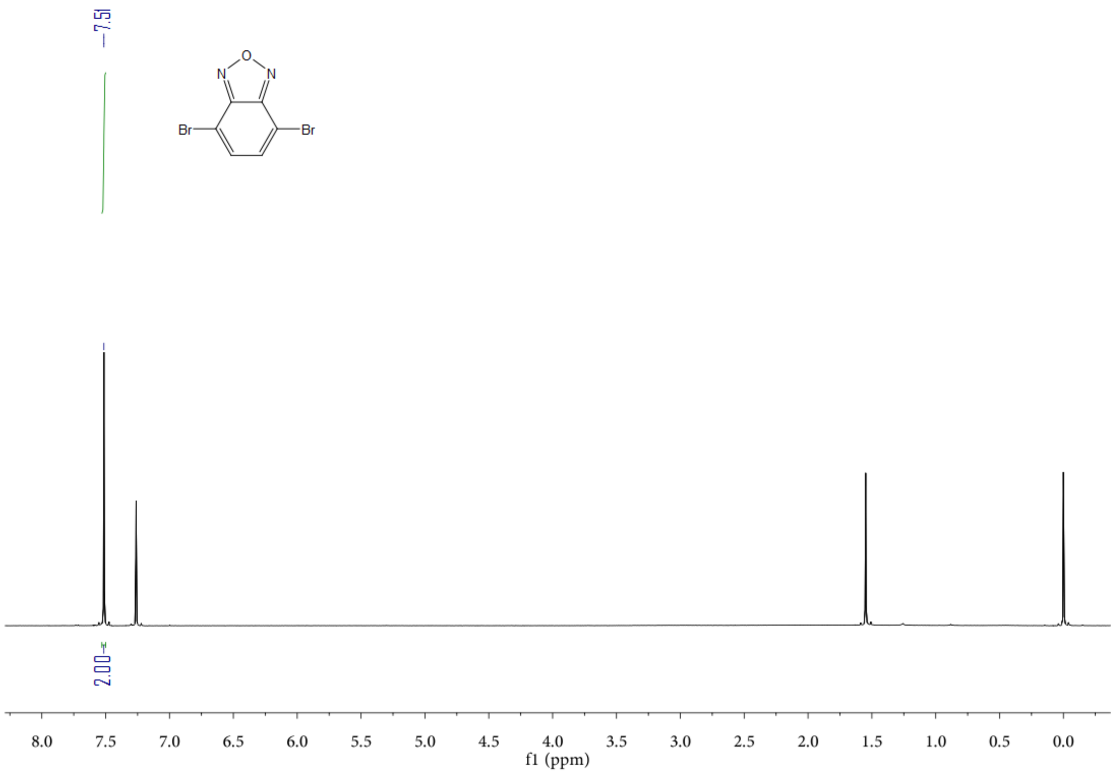

Figure S5. ^{1}H NMR of **2** (500 MHz, $CDCl_3$).

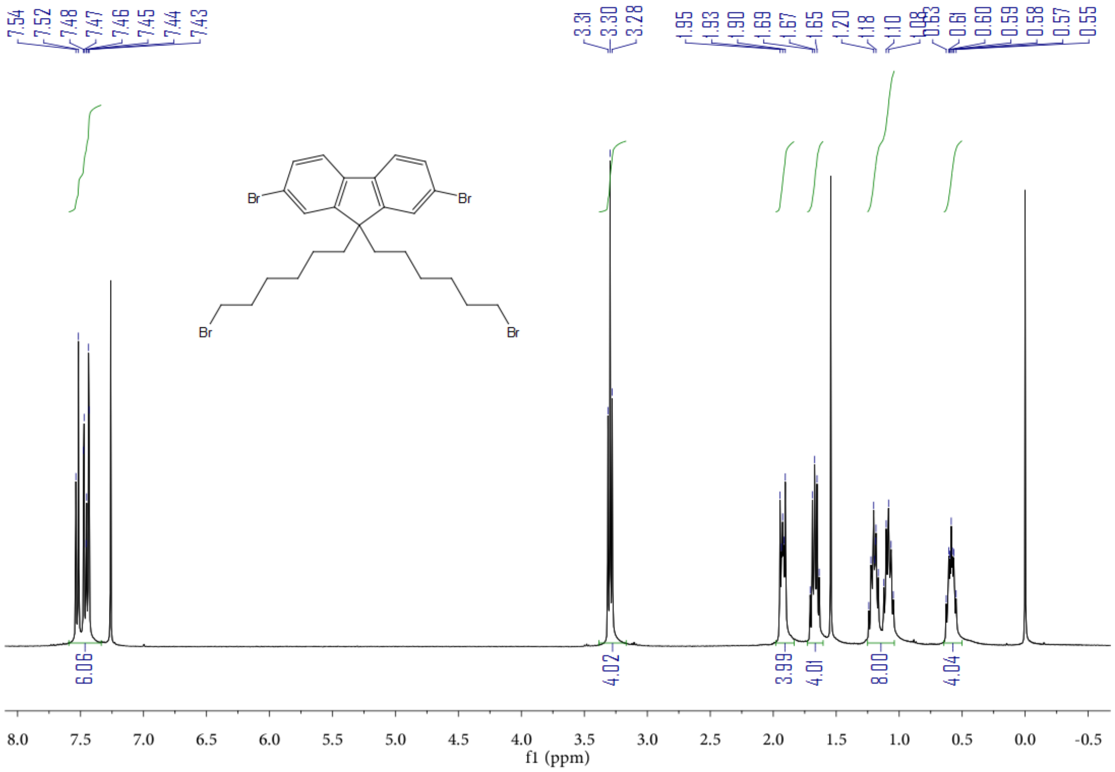

Figure S6. ^{1}H NMR of **4** (500 MHz, $CDCl_3$).

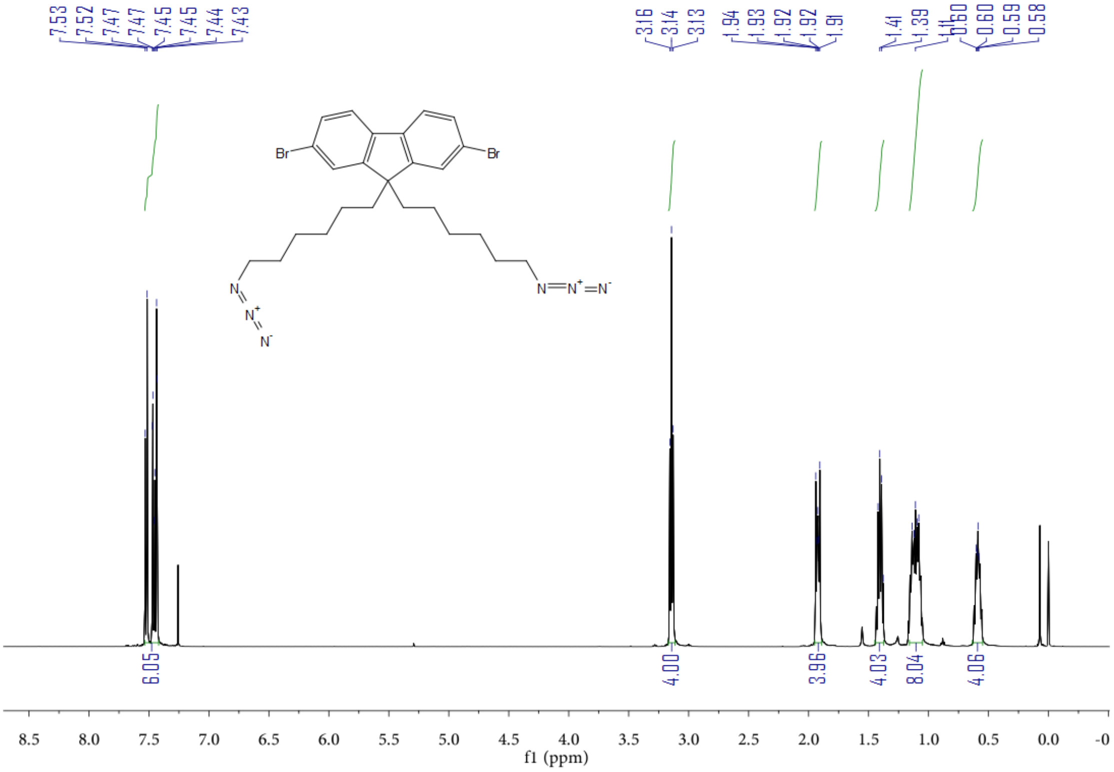

Figure S7. ^{1}H NMR of **5** (500 MHz, $CDCl_3$).

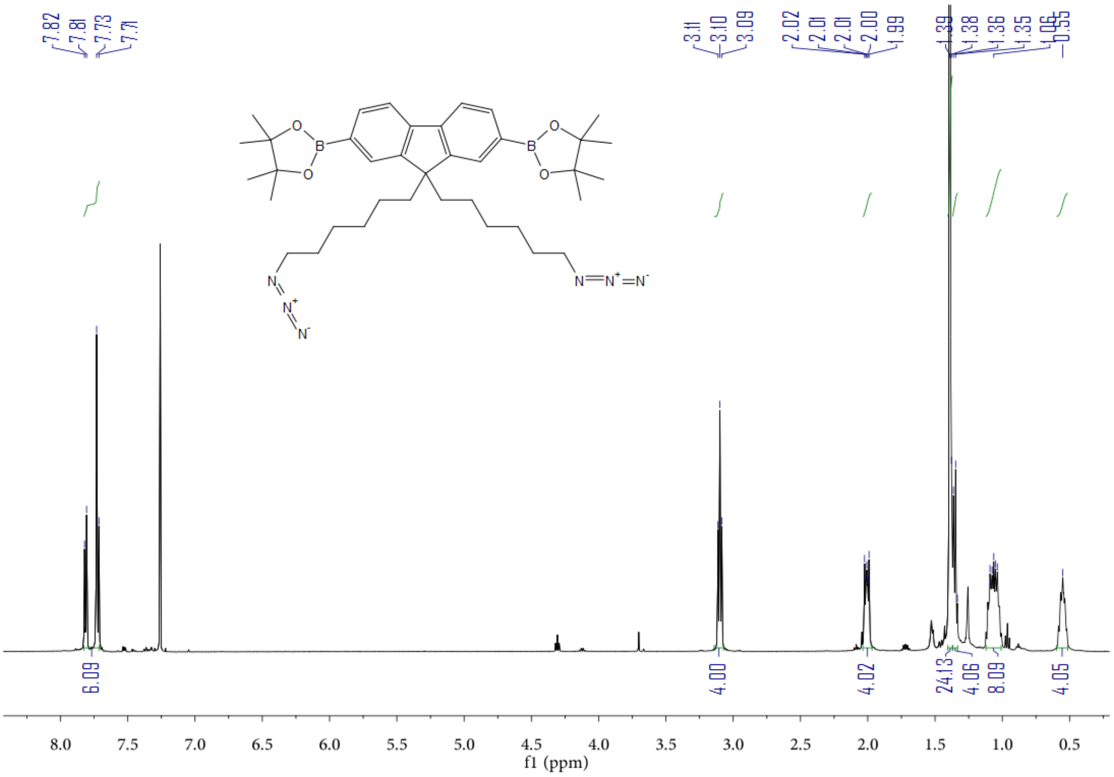

Figure S8. ^{1}H NMR of **6** (500 MHz, $CDCl_3$).

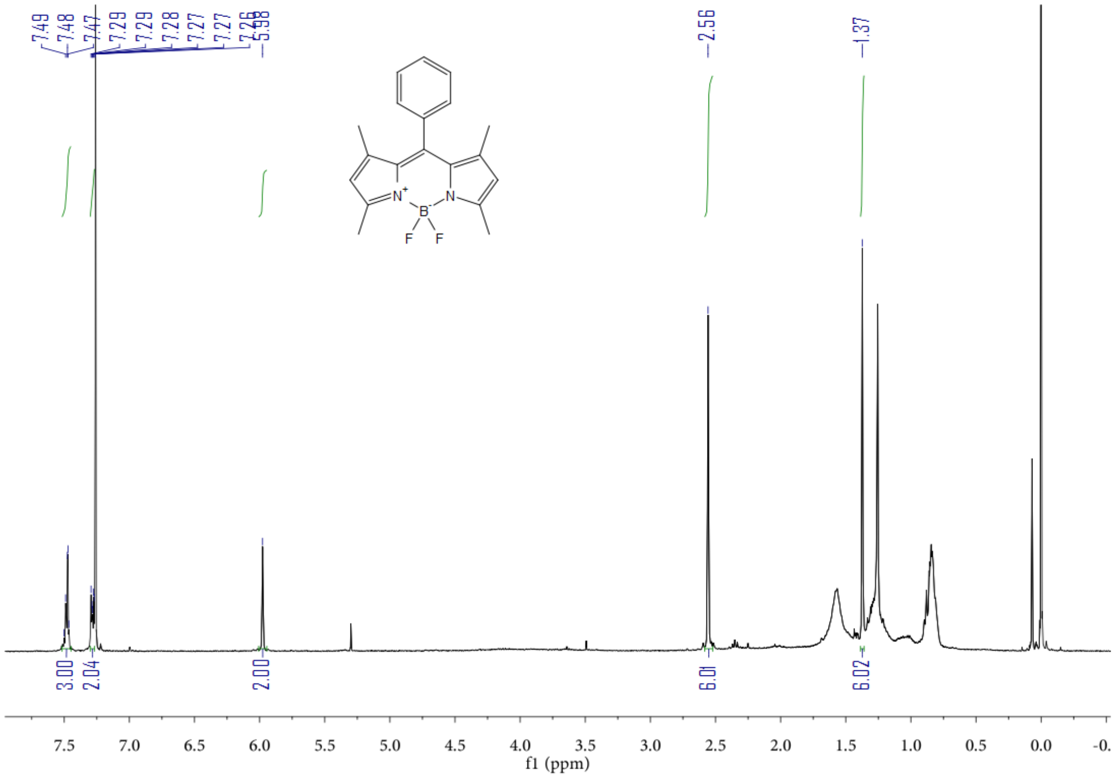

Figure S9. ^{1}H NMR of **8** (500 MHz, CDCl$_3$).

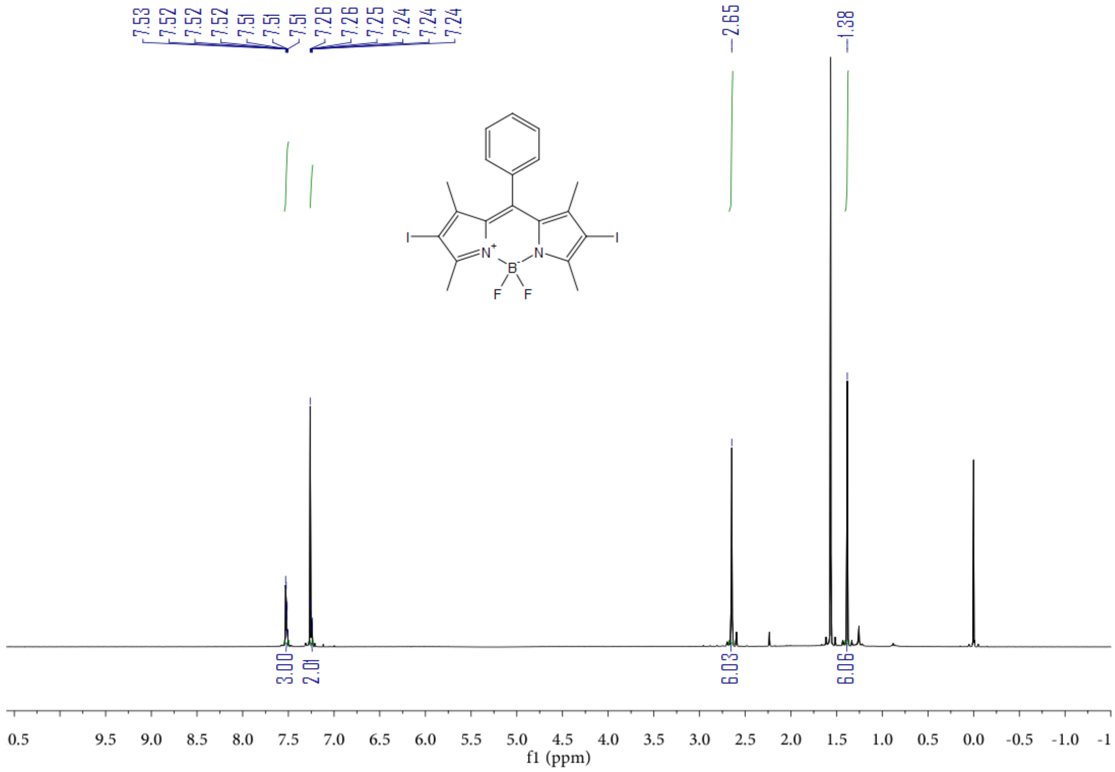

Figure S10. ^{1}H NMR of **9** (500 MHz, CDCl$_3$).

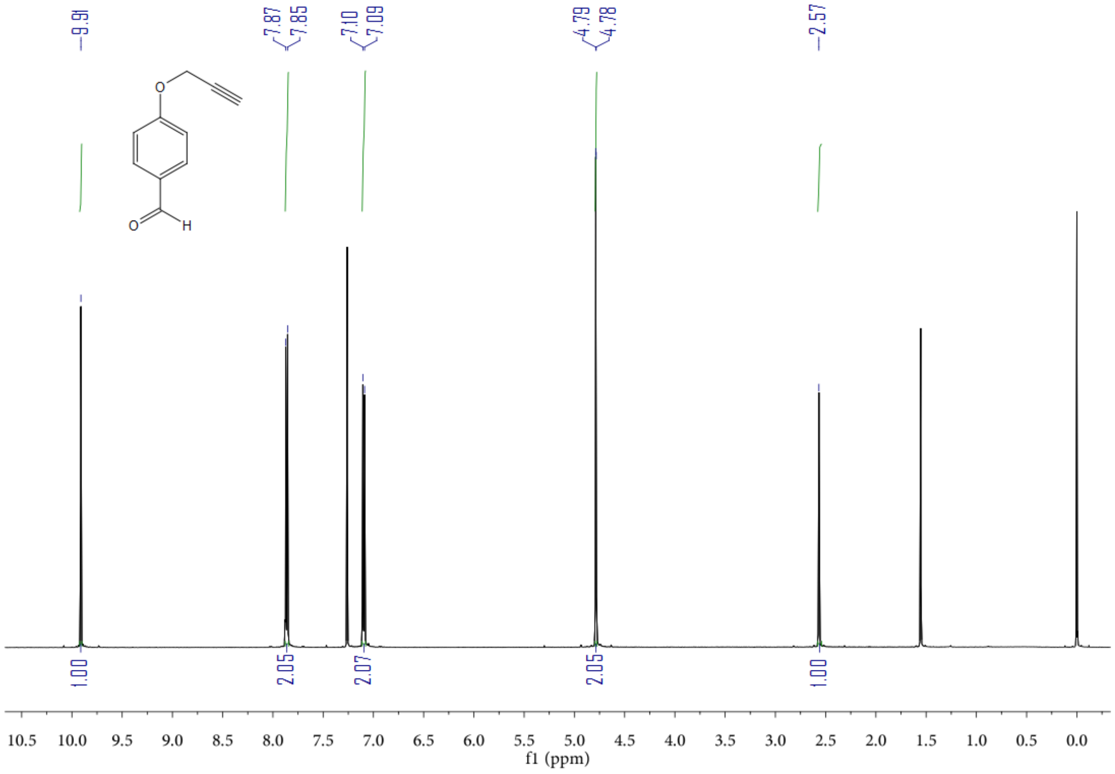

Figure S11. ^{1}H NMR of **11** (500 MHz, $CDCl_3$).

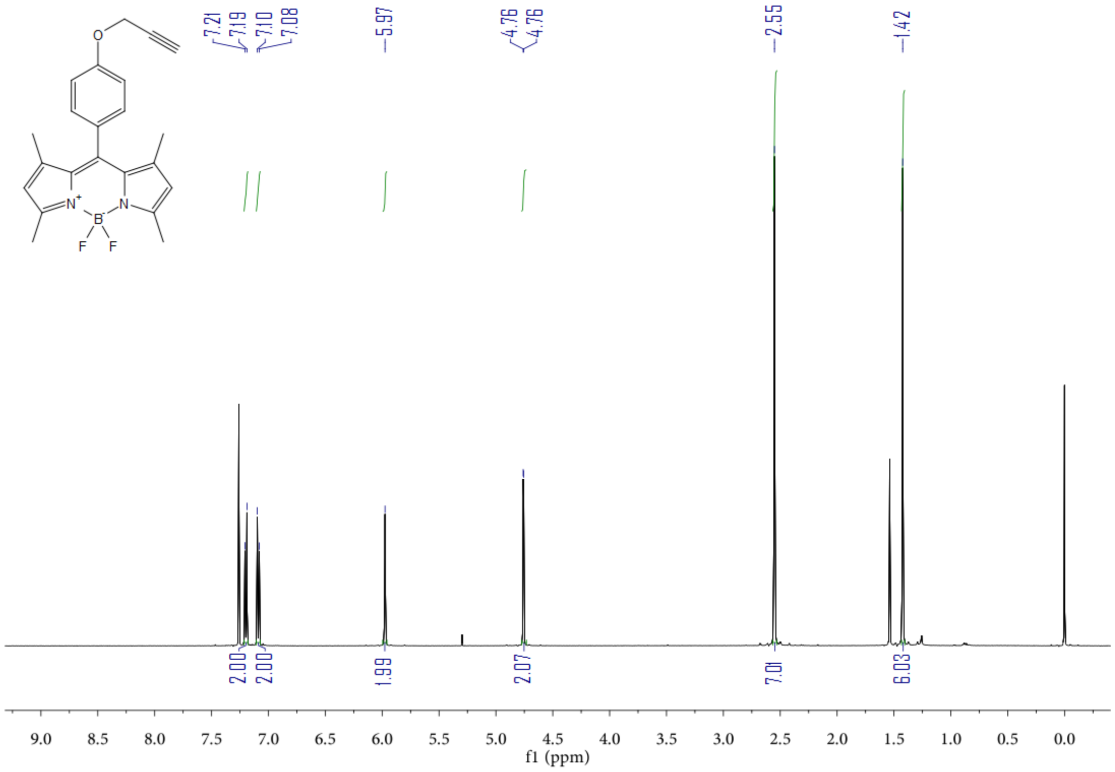

Figure S12. ^{1}H NMR of **12** (500 MHz, $CDCl_3$).

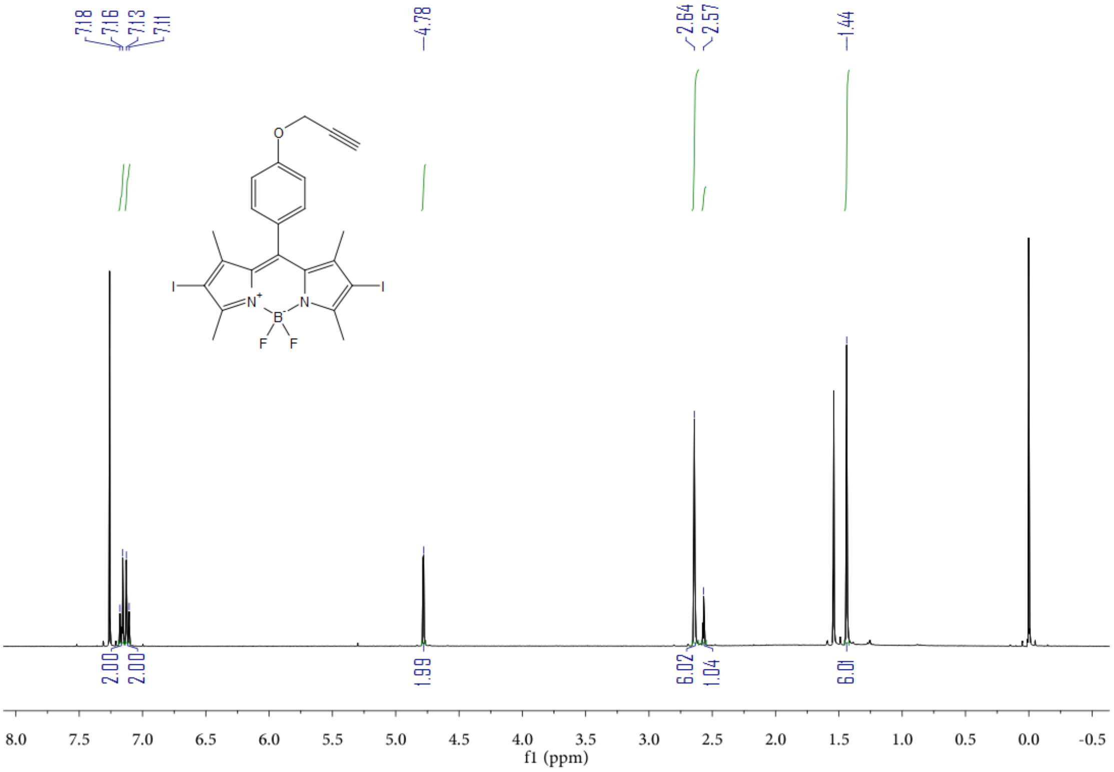

Figure S13. ^{1}H NMR of **13** (500 MHz, $CDCl_3$).

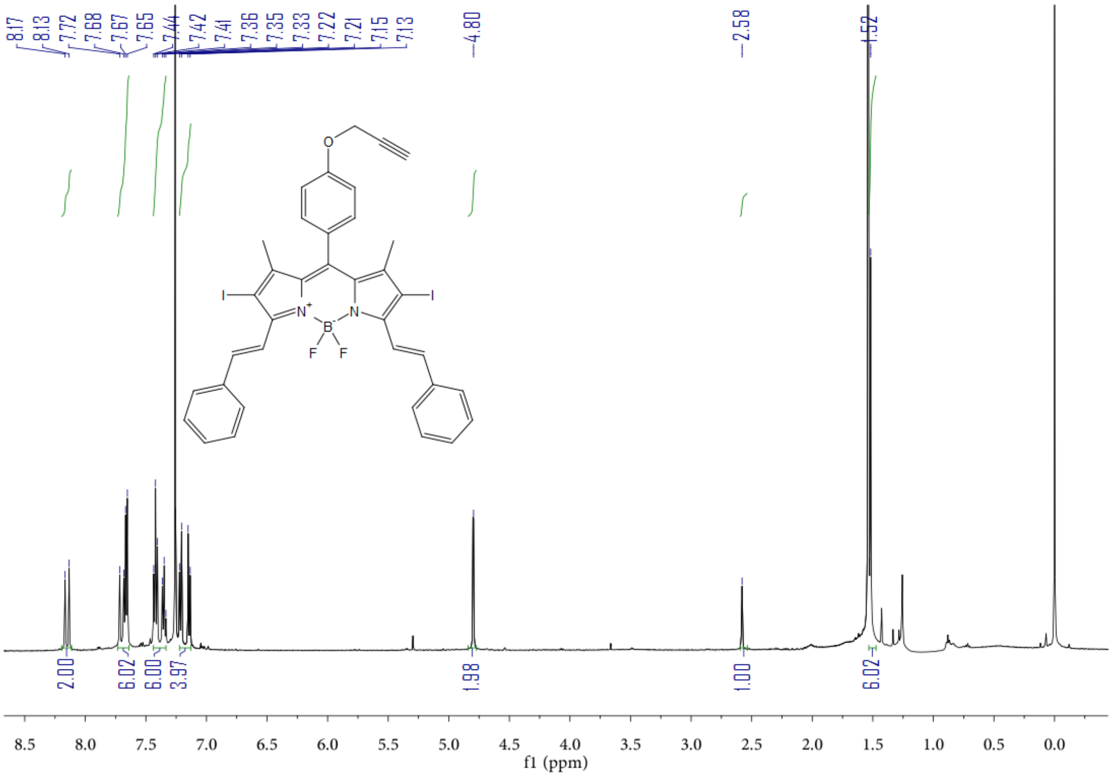

Figure S14. ^{1}H NMR of **14** (500 MHz, $CDCl_3$).

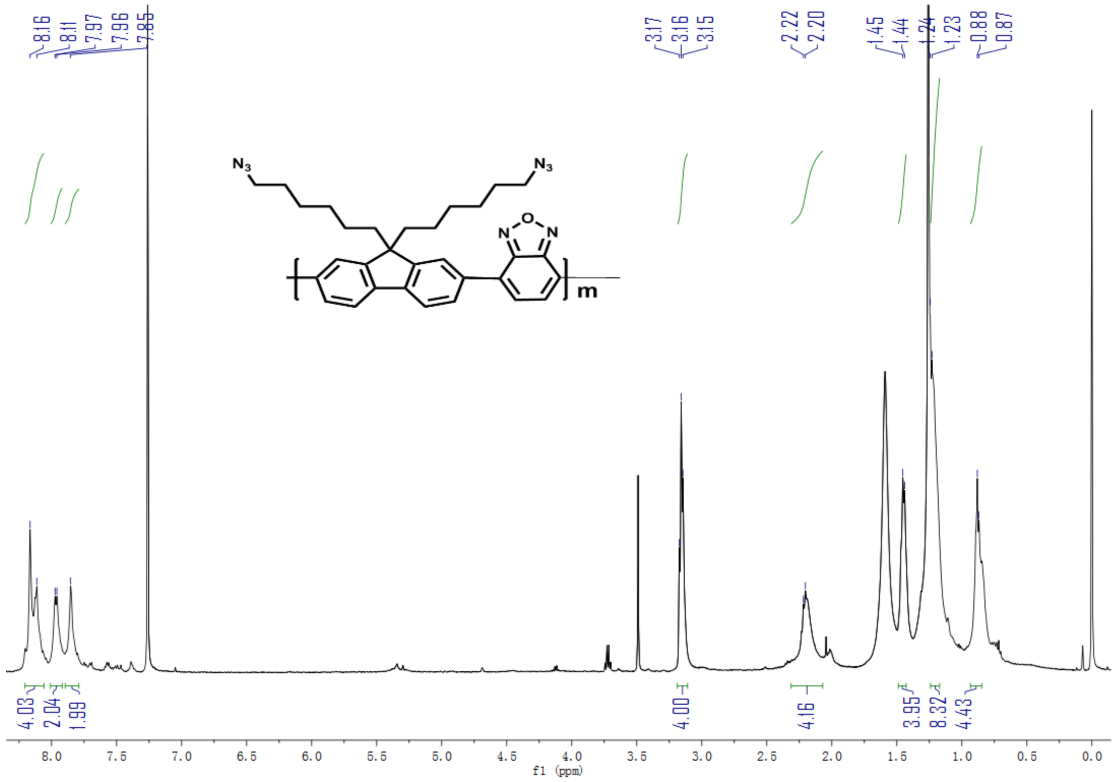

Figure S15. ^{1}H NMR of **PFBD** (500 MHz, $CDCl_3$).

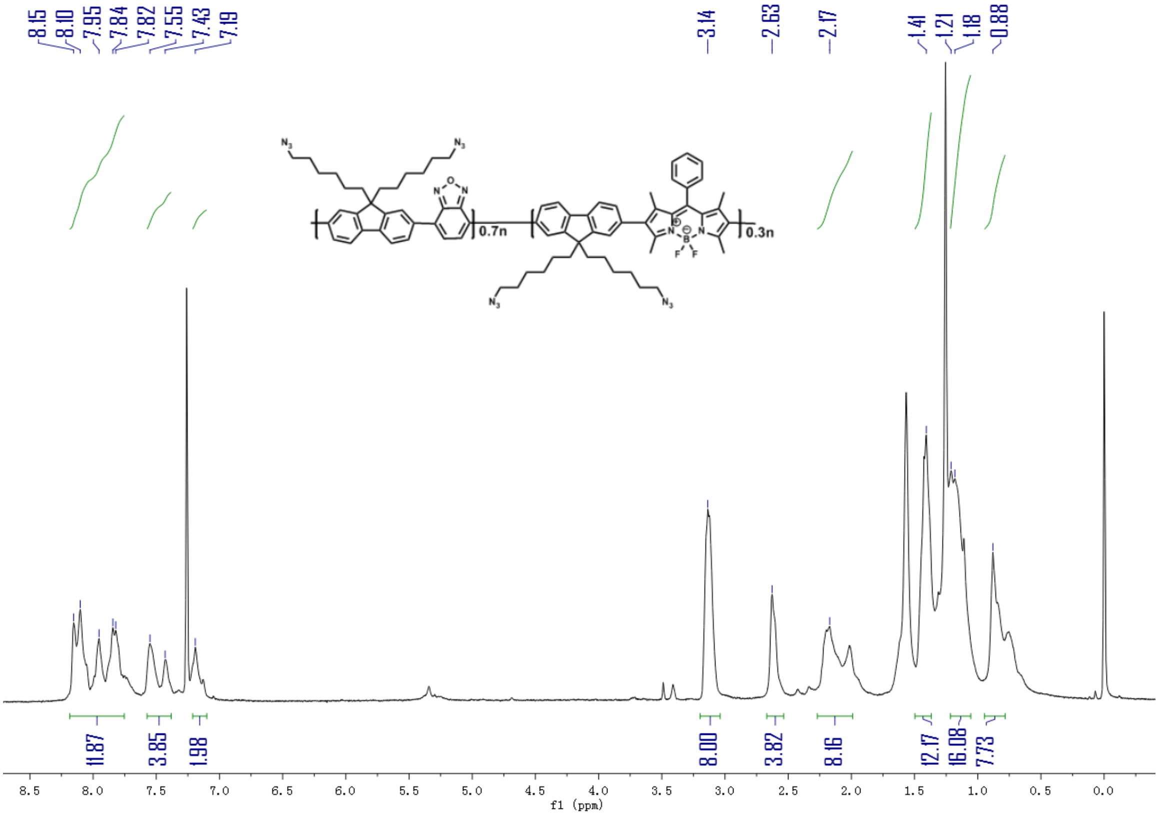

Figure S16. ^{1}H NMR of **PFBDBP-IPBP** (500 MHz, $CDCl_3$).

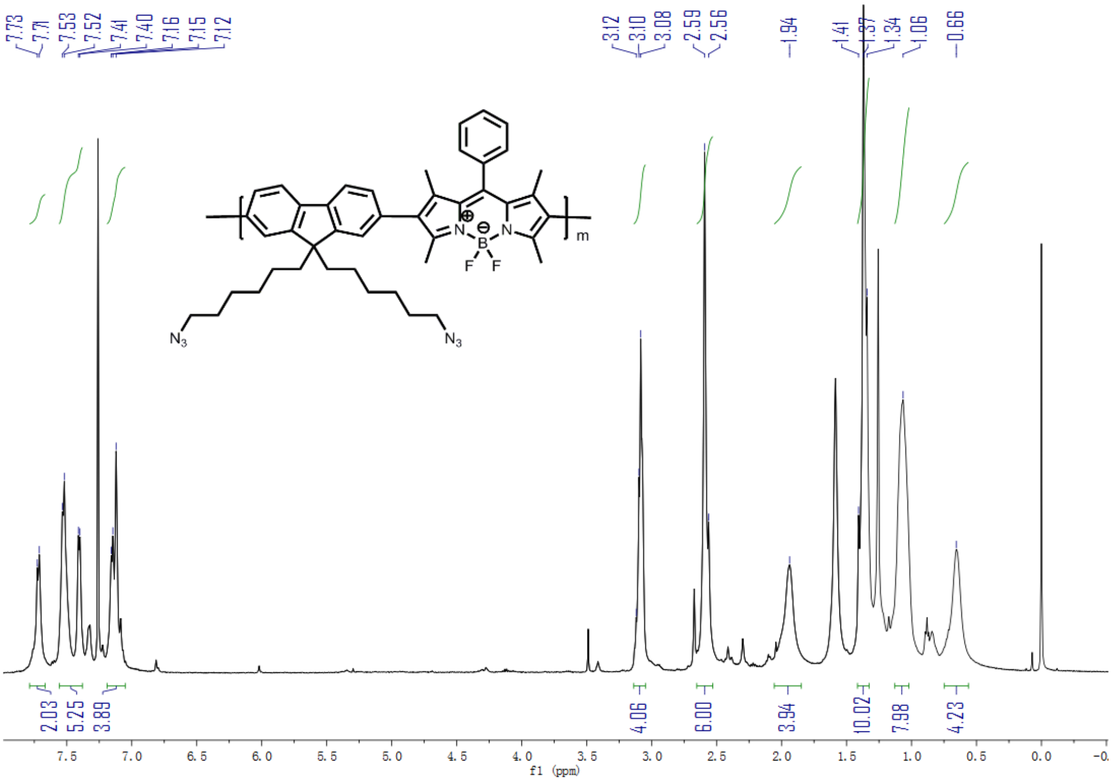

Figure S17. ^{1}H NMR of **PFBP** (500 MHz, $CDCl_3$).

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