Electronic Supplementary Information

FRET supramolecular polymers constructed by a BODIPY-bridged pillar[5]arene dimer with BODIPY guests for mimicking light-harvesting system of natural photosynthesis

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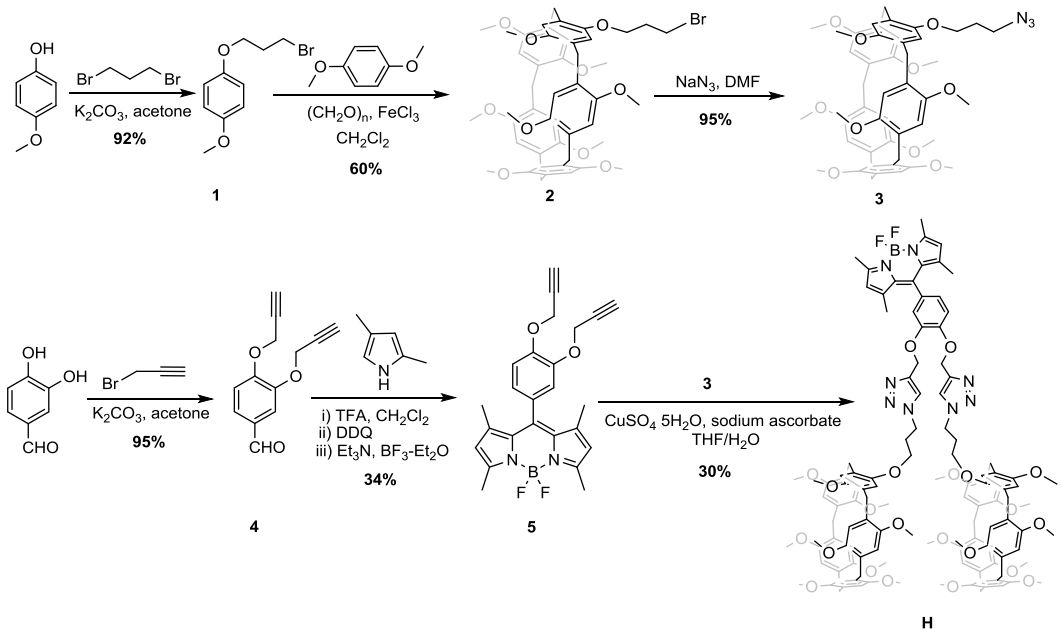
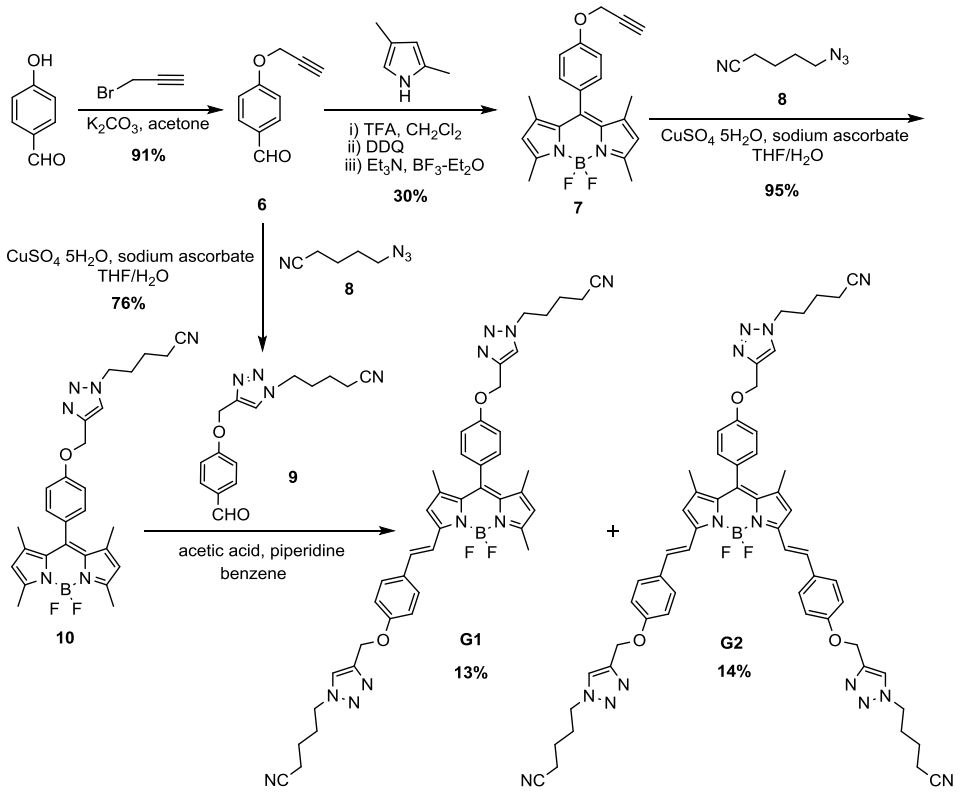
1. Materials and methods

All reactions were performed in atmosphere unless otherwise stated. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. Column chromatography was performed with silica gel (200-300 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). All yields were given as isolated yields. Melting points (M.p.) were determined using a Focus X-4 apparatus (made in China) and were not corrected. NMR spectra were recorded on a Bruker DPX 300 MHz or 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts (δ) were expressed in ppm and *J* values were given in Hz. 2D NOESY and 2D DOSY experiments were performed on a Bruker DPX 400 MHz spectrometer. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan MatTSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion. The UV-Vis absorption spectrum was measured on a Perkin Elmer Lambda 35 UV-Vis Spectrometer. The excitation and emission spectra were recorded on a Hitachi F-7000 Fluorescence Spectrometer. Scanning electron microscopy (SEM) investigations were carried out on a Shimadzu SSX-550 instrument.

2. Synthesis of H, G1, and G2



Scheme S1 Synthetic route of host **H**.

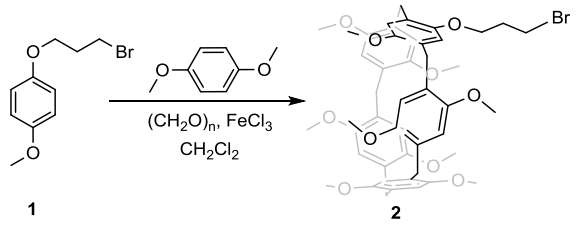


Scheme S2 Synthetic route of guests **G1** and **G2**.

Compounds **1**,[S1] **4**,[S2] **6**,[S3] 7[S4] and **8**[S5] were prepared according to previous literatures

and other synthetic procedures were described as follows:

Compound 2[S6]



To a solution of compound **1** (0.37 g, 1.5 mmol) and 1, 4-dimethoxybenzene (3.32 g, 24 mmol) in DCM (500 mL), paraformaldehyde (2.16 g, 72 mmol) was added in a nitrogen atmosphere. Then anhydrous ferric chloride (0.62 g, 3.84 mmol) was added to the solution and the mixture was stirred at room temperature for 2 h. H_2O (100 mL) was added and the product was extracted with DCM (3 × 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by column chromatograph (silica gel, DCM/hexane=1/1, v/v) to give compound **2** as a white solid (0.77 g, 60%). M.p. 99–101 ^oC. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ (ppm) 6.78-6.65 (m, 10H, ArH), 3.92 (t, J = 5.9 Hz, 2H, CH_2), 3.78 (s, 10H, CH_2), 3.71-3.57 (m, 27H, CH_3), 3.49 (t, J = 6.5 Hz, 2H, CH_2), 2.20-2.11 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) 151.3, 150.9, 149.7, 128.4, 128.4, 128.2, 128.2, 115.1, 114.2, 114.1, 114.1, 66.1, 55.8, 32.6, 30.3, 29.8, 29.7. ESI-MS: m/z 874.3 $[M + NH_4]^+$ (100%). HR-ESI-MS: calcd for $C_{47}H_{57}BrNO_{10}$ $[M + NH_4]^+$ 874.3160, found 874.3162.

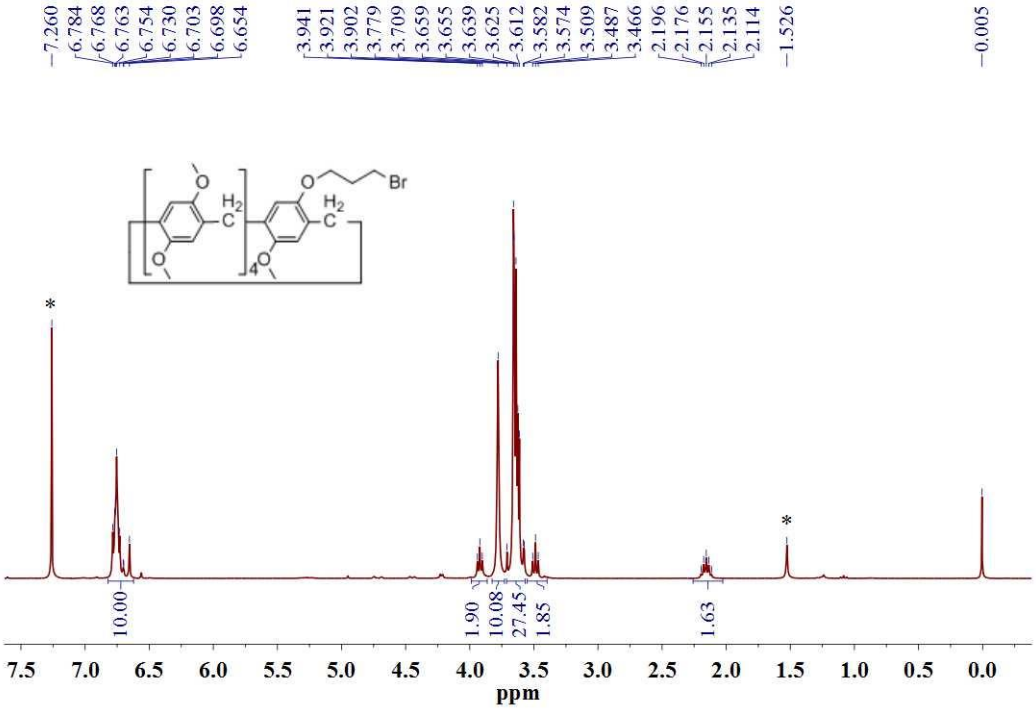


Fig. **S1** ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound **2** (solvent peaks are marked with asterisks).

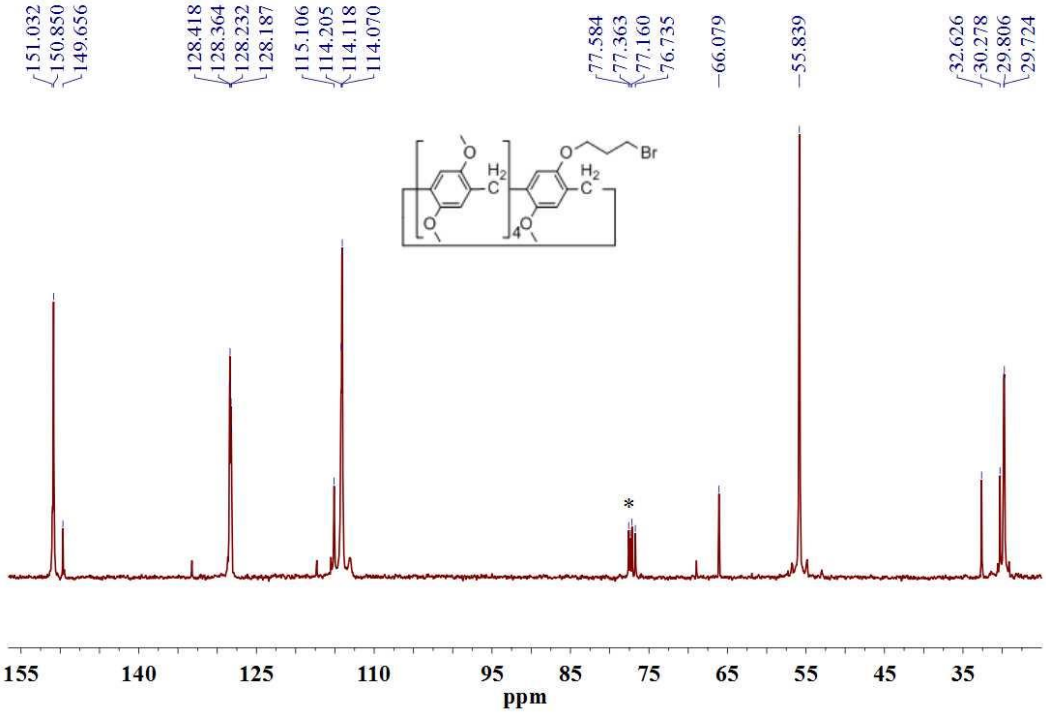
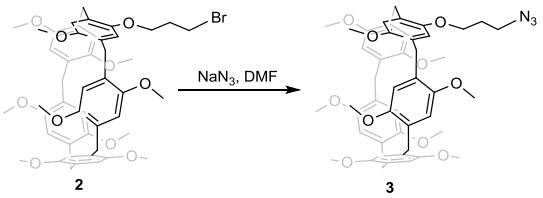


Fig. **S2** ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of compound **2** (solvent peaks are marked with asterisks).

Compound 3[S7]



Sodium azide (0.09 g, 1.38 mmol) was added to a solution of compound **2** (0.60 g, 0.69 mmol) in DMF (20 mL). The resulting mixture was heated up to 80 ^{o}C and stirred overnight. The mixture was then poured into H_2O (100 mL) and a white precipitate formed immediately. The precipitate was collected by filtration and evaporated to dryness to afford compound **3** as a white solid (0.54 g, 95%). M.p. 144–145 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ (ppm) 6.79-6.65 (m, 10H, ArH), 3.88 (t, J = 5.7 Hz, 2H, CH_2), 3.77 (s, 10H, CH_2), 3.71-3.58 (m, 27H, CH_3), 3.38 (t, J = 6.5 Hz, 2H, CH_2), 1.93-1.89 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) 151.1, 150.9, 149.7, 128.5, 128.4, 128.3, 128.2, 115.1, 114.4, 114.3, 114.2, 65.2, 48.5, 29.9, 29.8, 29.1. ESI-MS: m/z 837.2 $[M + NH_4]^+$ (100%). HR-ESI-MS: calcd for $C_{47}H_{53}N_3NaO_{10}$ $[M + Na]^+$ 842.3623, found 842.3625.

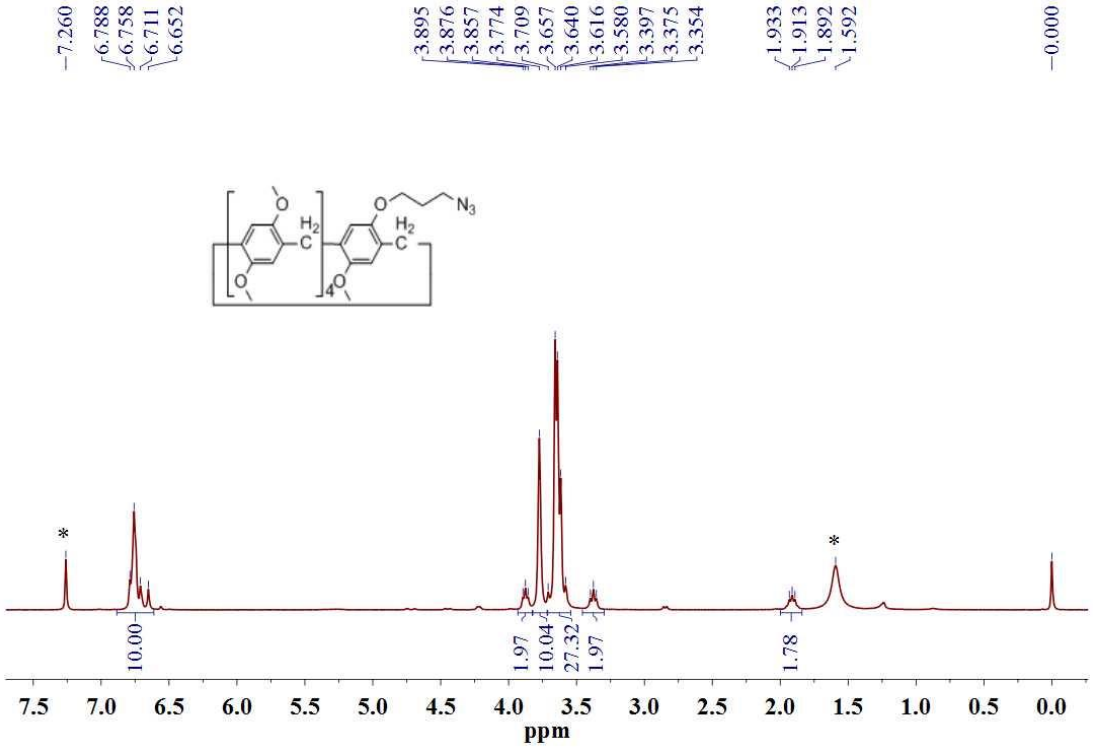


Fig. **S3** ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound **3** (solvent peaks are marked with asterisks).

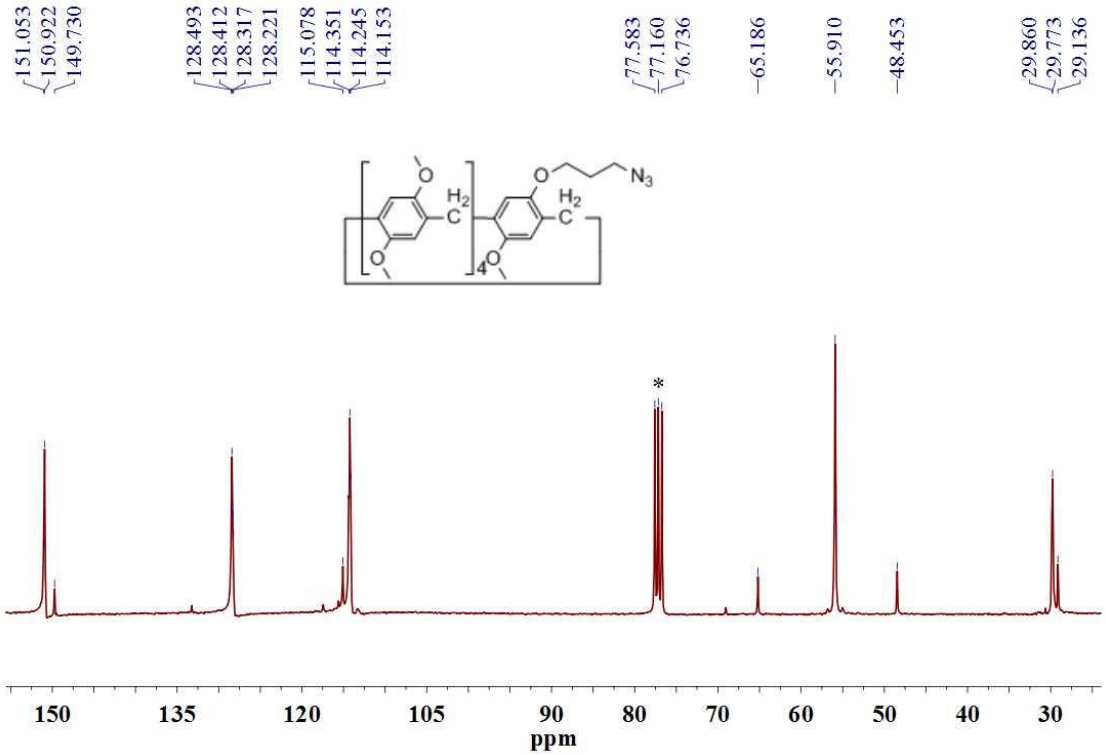
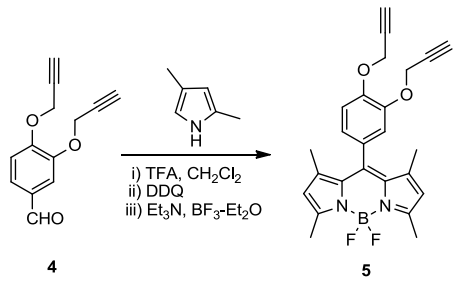


Fig. S4 ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of compound **3** (solvent peaks are marked with asterisks).

Compound 5[S8]



2, 4-Dimethylpyrrole (0.62 g, 6.6 mmol) and compound **4** (0.64 g, 3 mmol) were dissolved in dry DCM (200 mL) under nitrogen. Three drops of trifluoroacetic acid (TFA) were added, and the solution was stirred for 8 h at room temperature in the dark. Then 2, 3-Dichloro-5, 6-dicyanoquinone (DDQ, 0.68 g, 3 mmol) was added, and the mixture was stirred for an additional 2 h. The reaction mixture was then treated with triethylamine (5 mL) for 15 min. Boron trifluoride etherate (6 mL) was added dropwise to the mixture which was cooled in an ice-water bath and stirred for another 3 h at room temperature, and the dark-brown solution was washed with H_2O (2 × 20 mL) and brine (30 mL), dried over anhydrous Na_2SO_4, and concentrated under

reduced pressure. The crude product was purified by column chromatography (silica gel, DCM/hexane=1/1, v/v) to give compound **5** as an orange-red solid (0.44 g, 34%). M.p. 158–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ (ppm) 7.16 (dd, J = 8.1, 2.7 Hz, 1H, ArH), 6.99 (br, 1H, ArH), 6.89 (d, J = 8.1Hz, 1H, ArH), 5.99 (s, 2H, pyrrole-H), 4.83 (br, 2H, CH_2), 4.77 (br, 2H, CH_2), 2.56 (s, 6H, CH_3), 2.46-2.44 (m, 2H, C≡CH), 1.49 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) 155.7, 148.2, 143.3, 141.1, 131.8, 128.6, 121.7, 121.3, 115.5, 114.7, 57.2, 56.3, 32.1, 31.6, 30.3, 29.8, 29.5, 22.8, 14.7, 14.6, 14.3. ESI-MS: m/z 433.2 $[M + H]^+$ (100%). HR-ESI-MS (ESI): calcd for $C_{25}H_{24}BF_2N_2O_2$ $[M + H]^+$ 433.1893, found 433.1896.

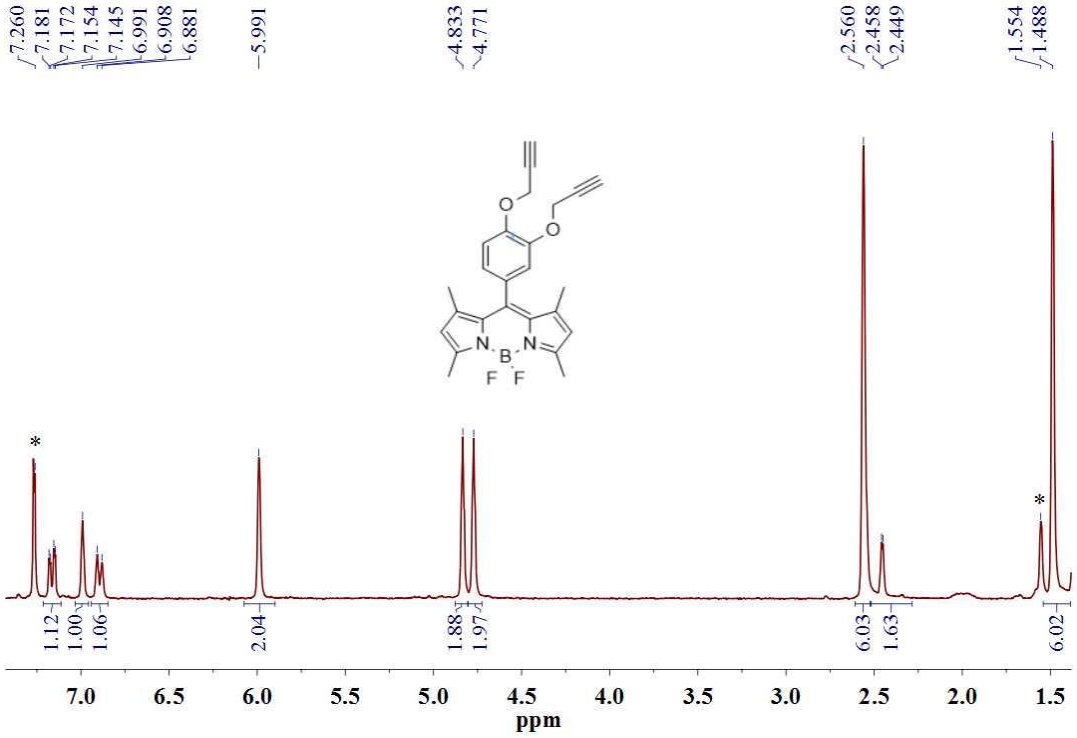


Fig. **S5** ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound **5** (solvent peaks are marked with asterisks).

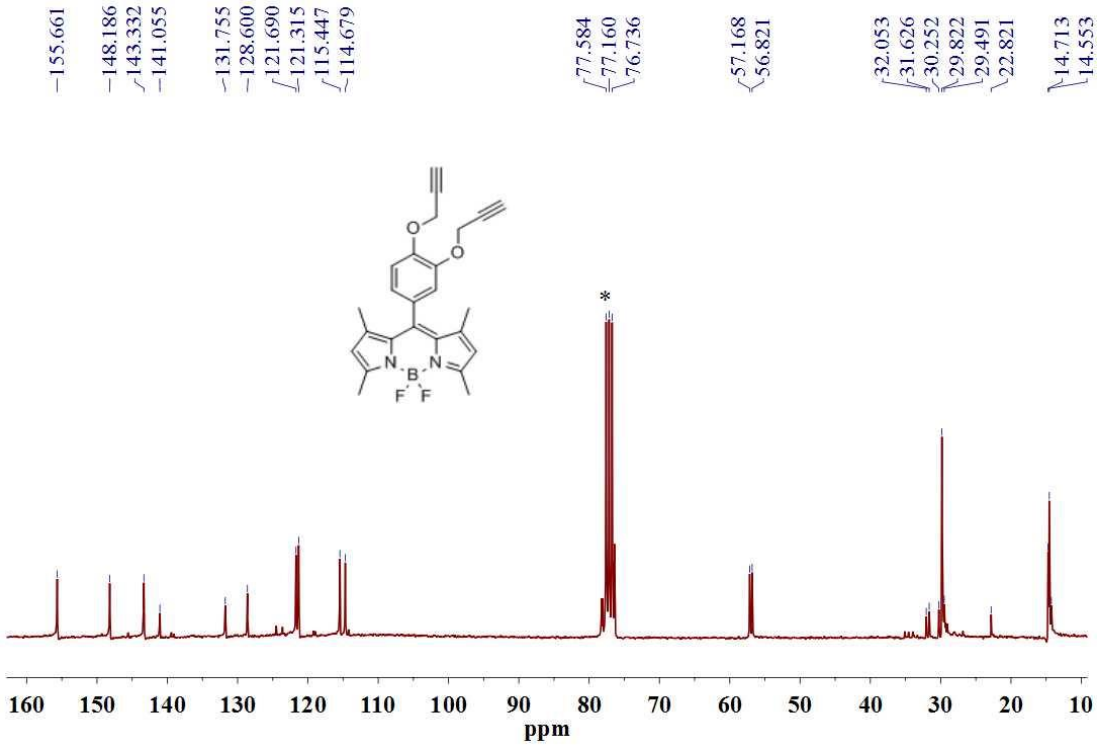
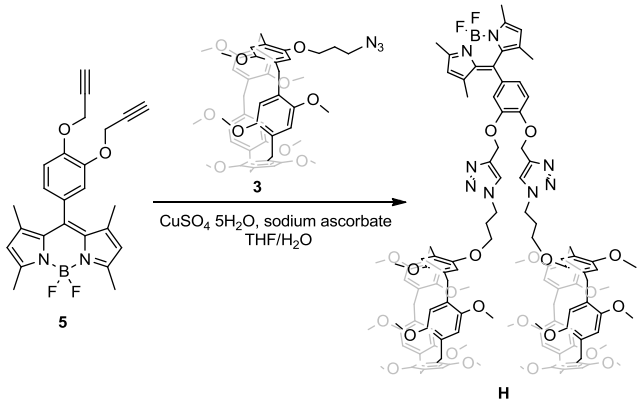


Fig. S6 ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of compound **5** (solvent peaks are marked with asterisks).

Compound H[S7]



Compound **5** (86 mg, 0.20 mmol) and compound **3** (328 mg, 0.40 mmol) were dissolved in a mixture of THF (8 mL) and water (2 mL). Then $CuSO_4$ $5H_2O$ (20 mg, 0.08 mmol) and sodium ascorbate (32 mg, 0.16 mmol) were added and the mixture was stirred at room temperature for 24 h. Then the mixture was diluted with water (5 mL) and extracted by DCM (3 × 10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM/methanol=100/1, v/v) to

give compound **H** as an orange-red solid (124 mg, 30%). M.p. 139–141 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ (ppm) 7.78 (s, 1H, triazole-H), 7.72 (s, 1H, triazole-H), 7.16 (d, J = 8.4 Hz, 1H, ArH), 6.96 (br, 1H, ArH), 6.85 (d, J = 8.4 Hz, 1H, ArH), 6.77-6.61 (m, 20H, ArH), 5.95 (s, 2H, pyrrole-H), 5.31 (s, 2H, CH_2), 5.21 (s, 2H, CH_2), 4.47-4.40 (m, 4H, CH_2), 3.77 (s, 20H, CH_2), 3.64-3.54 (m, 58H, CH_3 and CH_2), 2.54 (s, 6H, CH_3), 2.25-2.22 (m, 4H, CH_2), 1.40 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) 155.6, 151.3, 151.0, 150.9, 149.5, 149.2, 143.5, 143.1, 141.1, 131.7, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 123.8, 121.9, 121.3, 115.7, 115.3, 115.1, 114.5, 114.3, 114.2, 64.8, 63.5, 56.2, 56.0, 55.9, 47.5, 30.3, 30.0, 29.9, 14.7, 14.5. HR-ESI-MS: calcd for $C_{119}H_{129}BF_2N_8O_{22}Na$ $[M + Na]^+$ 2093.9175, found 2093.9159.

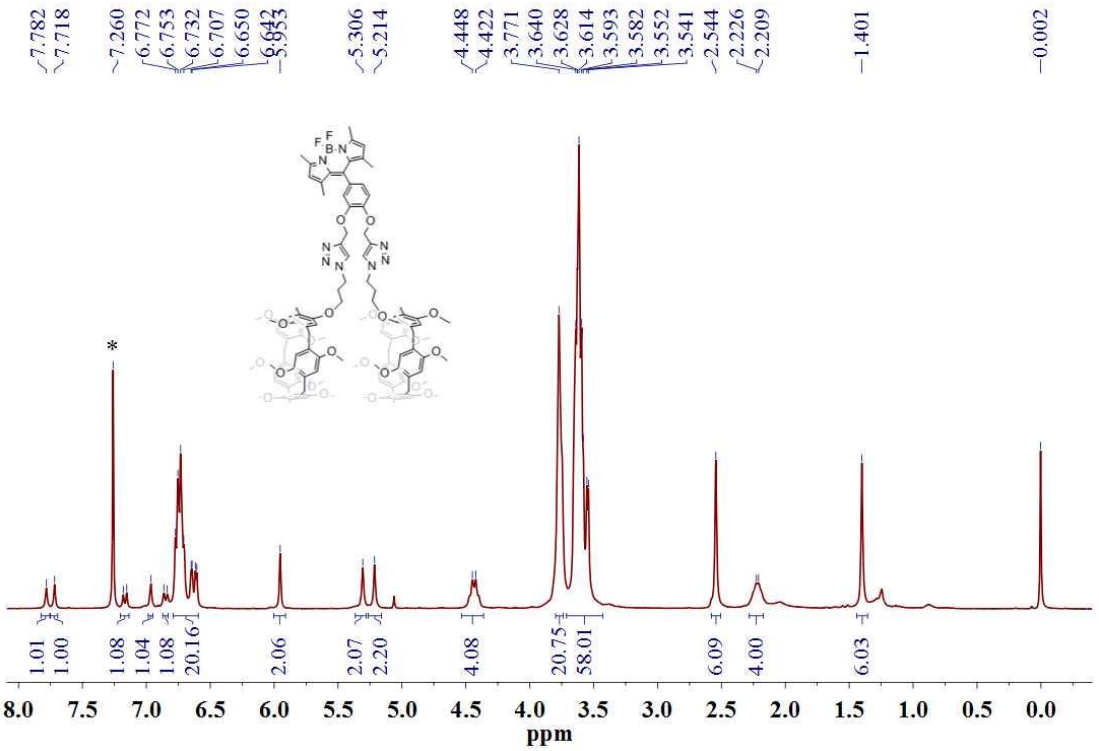


Fig. **S7** ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound **H** (solvent peaks are marked with asterisks).

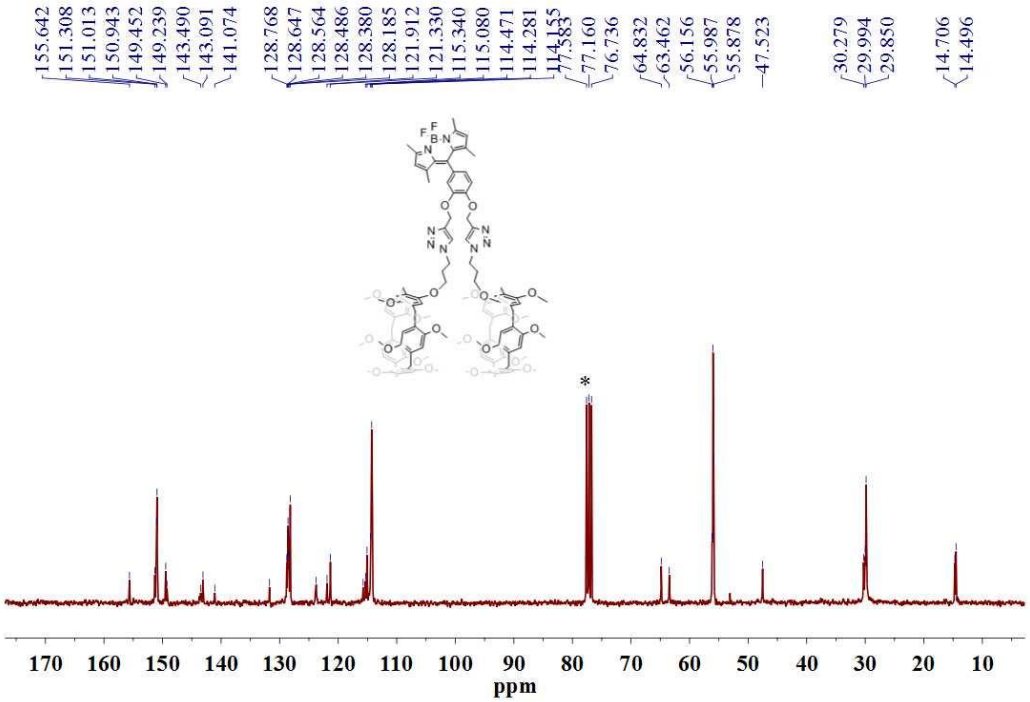
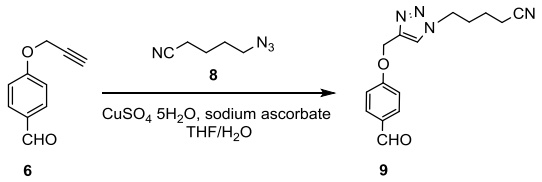


Fig. **S8** ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of compound **H** (solvent peaks are marked with asterisks).

Compound 9[S7]



Compound **6** (0.55 g, 3.46 mmol) and compound **8** (0.43 g, 3.46 mmol) were dissolved in a mixture of THF (20 mL) and water (5 mL). Then $CuSO_4$ 5 H_2O (0.17 g, 0.69 mmol) and sodium ascorbate (0.27 g, 1.38 mmol) were added and the mixture was stirred at room temperature for 24 h. Then the mixture was diluted with H_2O (10 mL) and extracted by DCM (3 × 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, AcOEt/hexane=1/1, v/v) to give compound **9** a white solid (0.75 g, 76%). M.p. 102–103 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ (ppm) 9.89 (s, 1H, O=CH), 7.84 (d, J = 8.8 Hz, 2H, ArH), 7.66 (s, 1H, triazole-H), 7.10 (d, J = 8.8 Hz, 2H, ArH), 5.29 (s, 2H, CH_2), 4.45 (t, J = 6.8 Hz, 2H, CH_2), 2.41 (t, J = 6.8 Hz, 2H, CH_2), 2.13-2.07 (m, 2H, CH_2), 1.74-1.66 (m, 2H,

CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) 190.9, 163.1, 143.4, 132.0, 130.3, 123.1, 119.0, 115.1, 62.0, 49.4, 29.0, 22.3, 16.7. ESI-MS: *m*/*z* 285.1 $[M + H]^+$ (100%). HR-ESI-MS: calcd for $C_{15}H_{16}N_4NaO_2$ $[M + Na]^+$ 307.1165, found 307.1168.

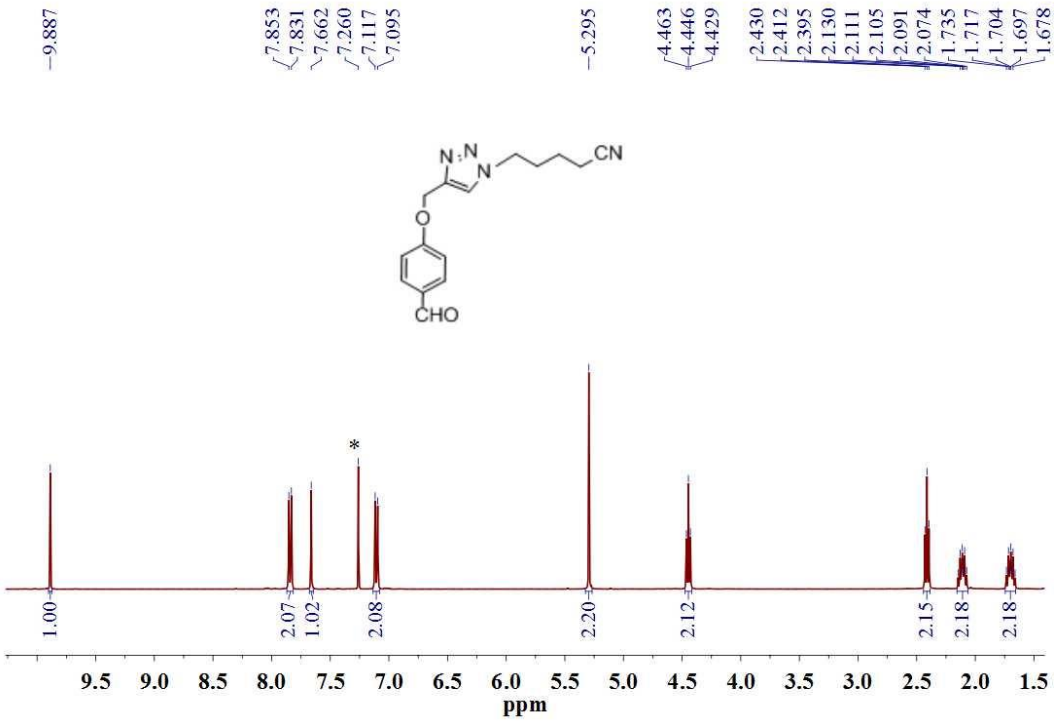


Fig. **S9** ^1H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **9** (solvent peaks are marked with asterisks).

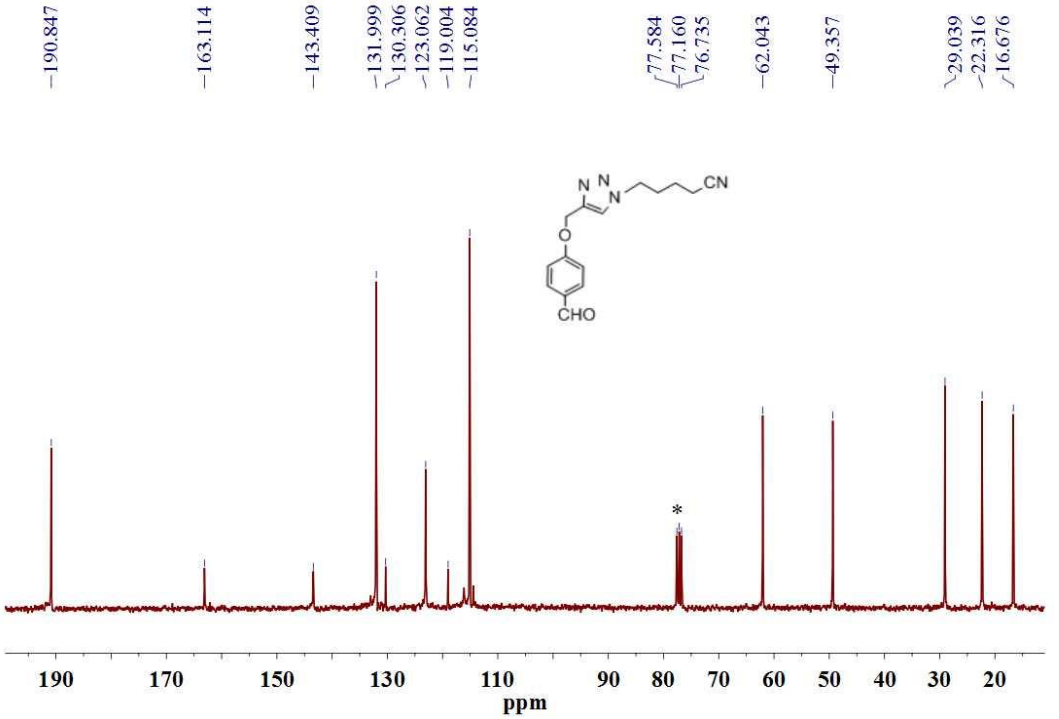
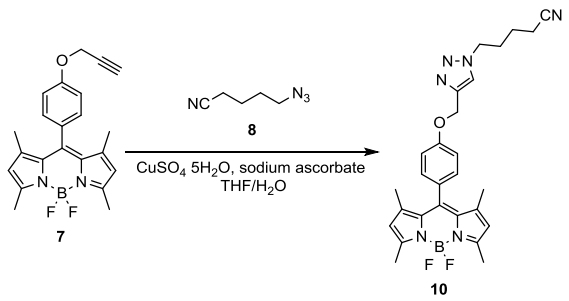


Fig. **S10** ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of compound **9** (solvent peaks are marked with asterisks).

Compound 10[S7]



Compound **7** (0.30 g, 0.80 mmol) and compound **8** (0.10 g, 0.80 mmol) were dissolved in a mixture of THF (20 mL) and water (5 mL). Then $CuSO_4$ 5 H_2O (40 mg, 0.16 mmol) and sodium ascorbate (63 mg, 0.32 mmol) were added, and the mixture was stirred at room temperature for 24 h. Then the mixture was diluted with H_2O (10 mL) and extracted by DCM (3 × 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, AcOEt/hexane=1/1, v/v) to give compound **10** as an orange-red solid (0.38 g, 95%). M.p. 183–184 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ (ppm) 7.69 (s, 1H, triazole-H), 7.20 (d, J = 8.7 Hz, 2H, ArH), 7.11 (d, J = 8.7 Hz, 2H, ArH), 5.98 (s, 2H, pyrrole-H), 5.26 (s, 2H, CH_2), 4.47 (t, J = 6.8 Hz, 2H, CH_2), 2.55 (s, 6H, CH_3), 2.43 (t, J = 6.8 Hz, 2H, CH_2), 2.19-2.09 (m, 2H, CH_2), 1.77-1.68 (m, 2H, CH_2), 1.42 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) 158.8, 155.2, 143.8, 143.1, 141.6, 131.7, 129.2, 127.5, 122.9, 121.2, 119.0, 115.4, 61.9, 49.3, 29.1, 22.3, 16.6, 14.5. ESI-MS: m/z 503.2 $[M + H]^+$ (100%). HR-ESI-MS: calcd for $C_{27}H_{30}BF_2N_6O$ $[M + H]^+$ 503.2537, found 503.2539.

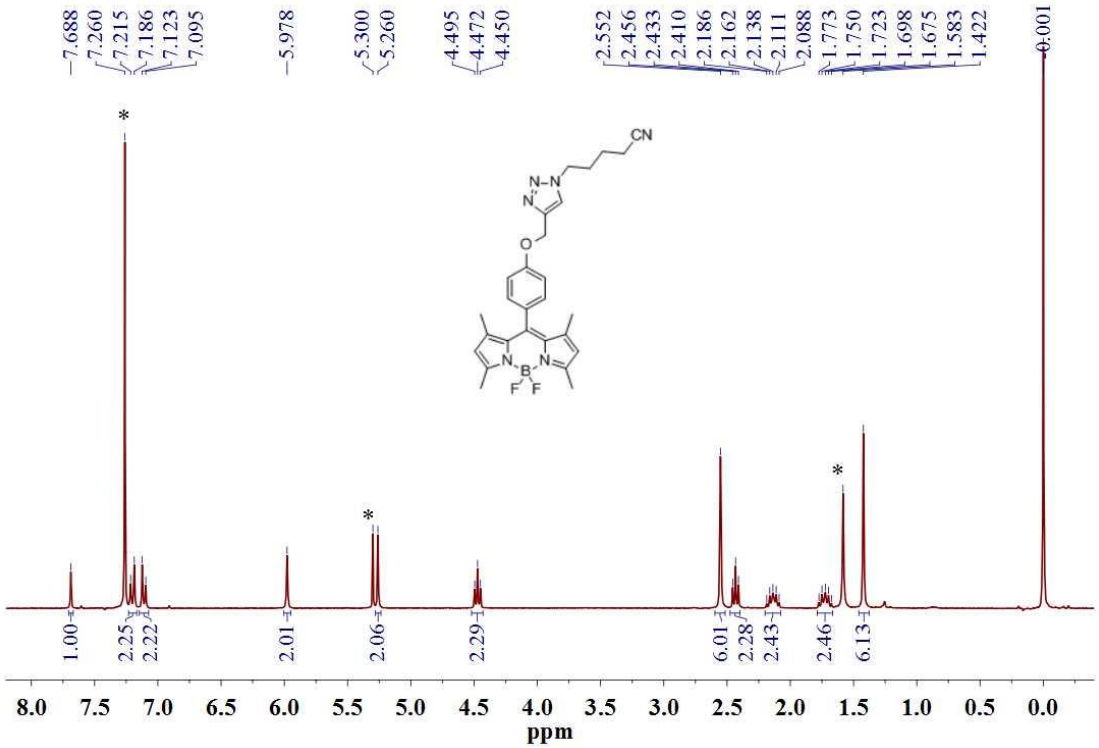


Fig. **S11** ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound **10** (solvent peaks are marked with asterisks).

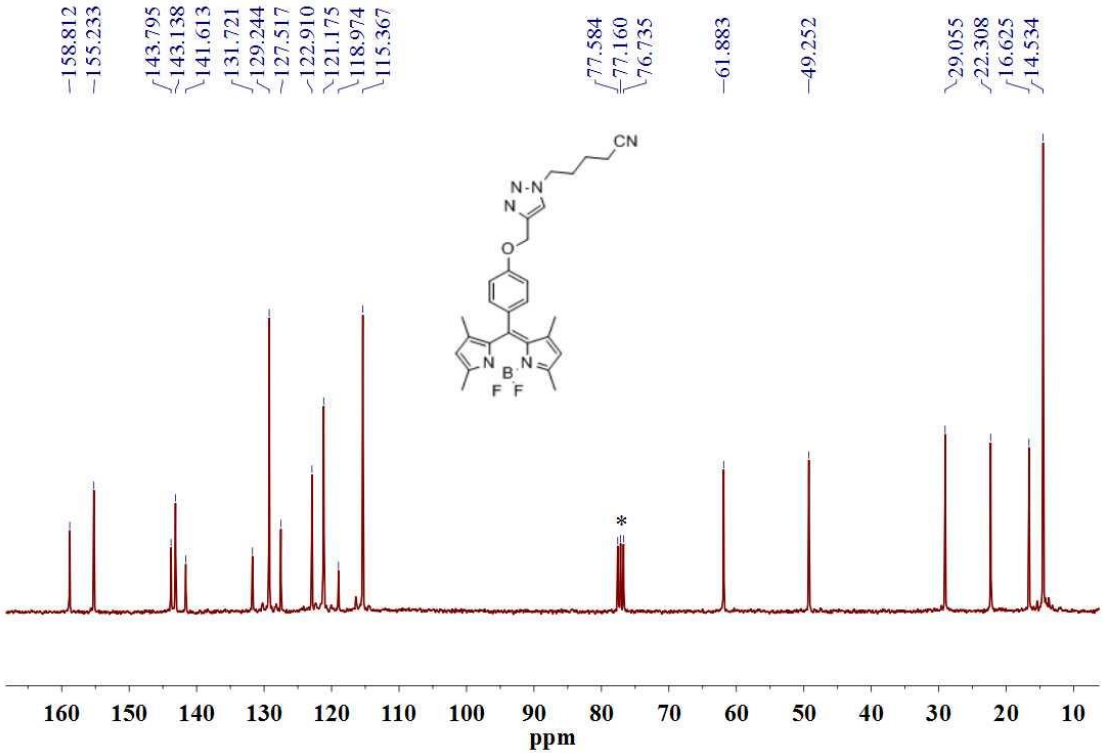
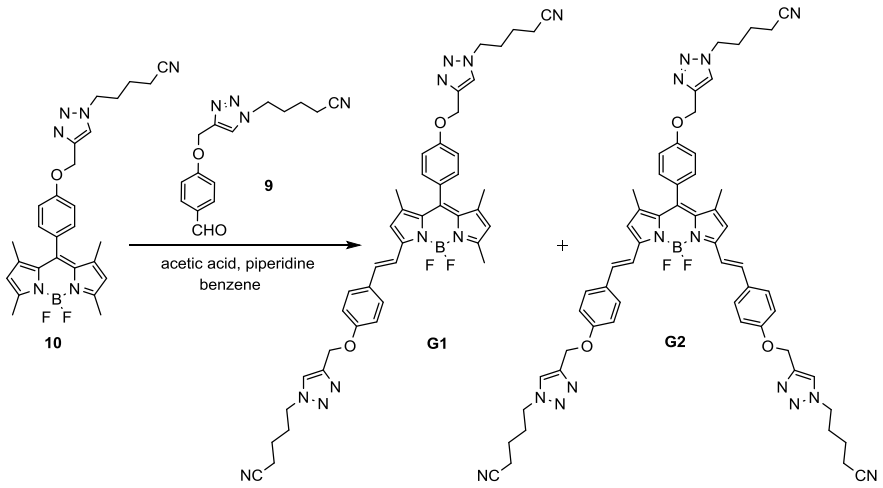


Fig. **S12** ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of compound **10** (solvent peaks are marked with asterisks).

Compound G1 and G2[S9]



Compound **10** (0.40 g, 0.80 mmol) and compound **9** (0.30 g, 1.04 mmol) were dissolved in benzene (20 mL). Glacial acetic acid (0.8 mL, 14 mmol) and piperidine (1.0 mL, 10 mmol) were added. The resulting mixture was refluxed using Dean-Stark apparatus for 20 h. Then the solvent was evaporated under reduced pressure, and the residual was diluted with H_2O (20 mL) and extracted by DCM (3 × 30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM/methanol=100/1, v/v). The pink-color band was collected to give compound **G1** as a purple solid (70 mg, 13%) while the blue-color band to give compound **G2** as a blue solid (110 mg, 14%). **G1**: M.p. 96–98 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ (ppm) 7.70 (s, 1H, triazole-H), 7.63 (s, 1H, triazole-H), 7.57-7.52 (m, 3H, C=CH and ArH), 7.24-7.10 (m, 5H, C=CH and ArH), 6.99-6.97 (m, 2H, ArH), 6.58 (s, 1H, pyrrole-H), 6.00 (s, 1H, pyrrole-H), 5.26 (s, 4H, CH_2), 4.50-4.42 (m, 4H, CH_2), 2.59 (s, 3H, CH_3), 2.46-2.39 (m, 4H, CH_2), 2.19-2.06 (m, 4H, CH_2), 1.75-1.67 (m, 4H, CH_2), 1.47 (s, 3H, CH_3), 1.44 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) 159.0, 154.9, 153.0, 144.2, 142.6, 140.1, 135.8, 133.2, 132.2, 130.0, 129.6, 129.1, 127.8, 123.0, 121.3, 119.0, 117.5, 116.3, 116.1, 115.4, 115.2, 62.1, 49.37, 29.1, 22.4, 16.8, 14.9, 14.8, 14.7. ESI-MS: *m*/*z* 769.2 $[M + H]^+$ (100%). HR-ESI-MS: calcd for $C_{42}H_{44}BF_2N_{10}O_2$ $[M + H]^+$ 769.3704, found 769.3709. **G2**: M.p. 97–99 ^{o}C. ^{1}H NMR (300 M, $CDCl_3$, 298 K): δ (ppm) 7.70 (s, 1H, triazole-H), 7.65-7.56 (m, 8H,

triazole-H, C=CH and ArH), 7.22-7.10 (m, 6H, C=CH and ArH), 7.01 (d, J = 8.4 Hz, 4H, ArH), 6.61 (s, 2H, pyrrole-H), 5.28 (s, 6H, CH_2), 4.50-4.42 (m, 6H, CH_2), 2.46-2.39 (m, 6H, CH_2), 2.16-2.07 (m, 6H, CH_2), 1.75-1.70 (m, 6H, CH_2), 1.48 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ (ppm) 159.0, 158.9, 152.5, 144.1, 143.9, 142.1, 138.3, 135.7, 133.6, 130.1, 129.8, 129.1, 127.8, 123.0, 119.1, 117.7, 117.5, 116.3, 115.4, 115.3, 62.0, 49.3, 29.1, 22.4, 16.7, 14.9. ESI-MS: m/z 1035.3 $[M + H]^+$ (100%). HR-ESI-MS: calcd for $C_{57}H_{57}BF_2N_{14}NaO_3$ $[M + Na]^+$ 1057.4691, found 1057.4695.

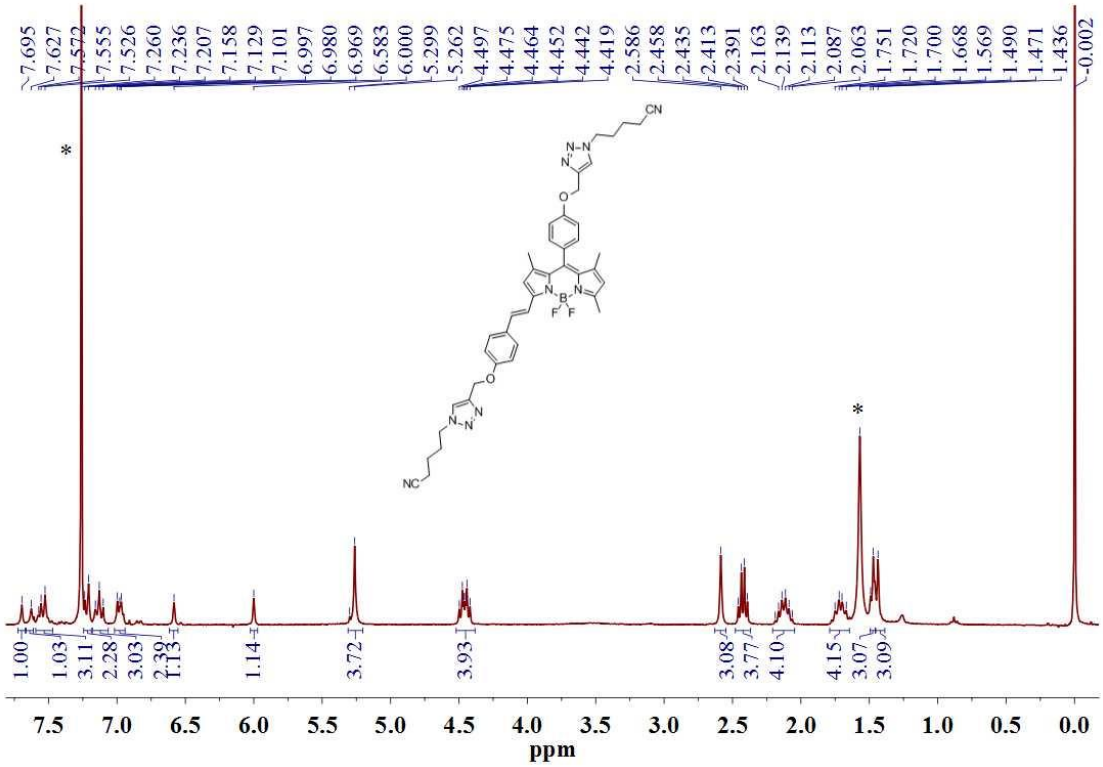


Fig. **S13** ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound **G1** (solvent peaks are marked with asterisks).

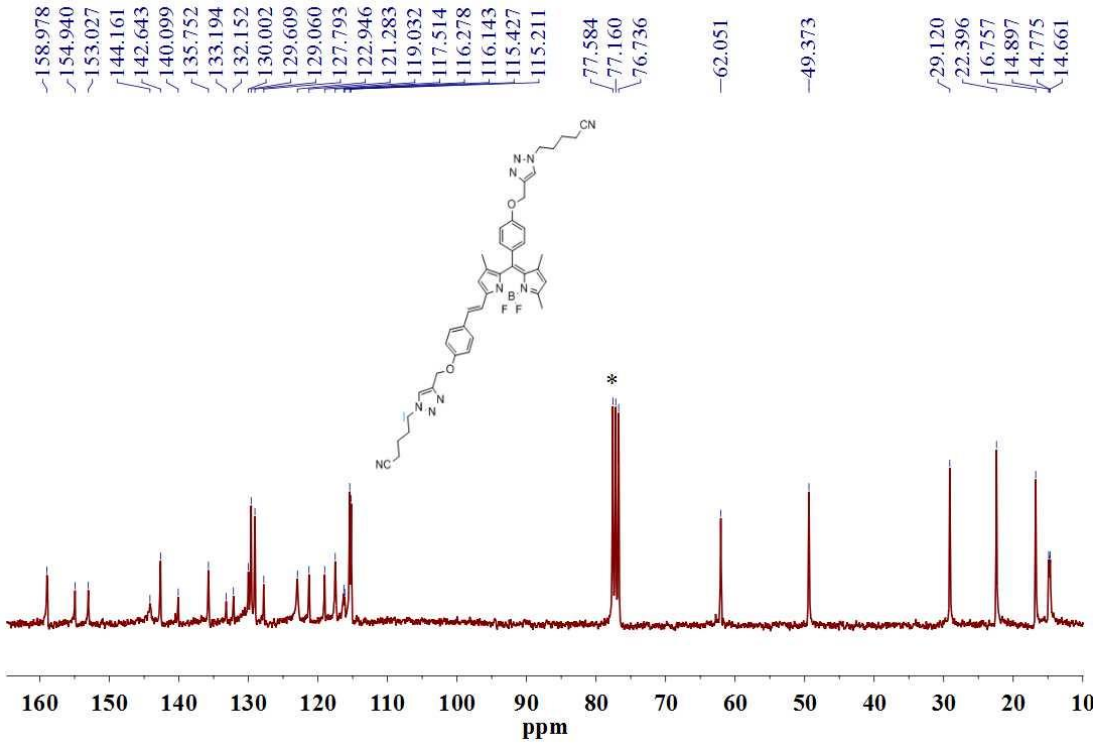


Fig. **S14** ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of compound **G1** (solvent peaks are marked with asterisks).

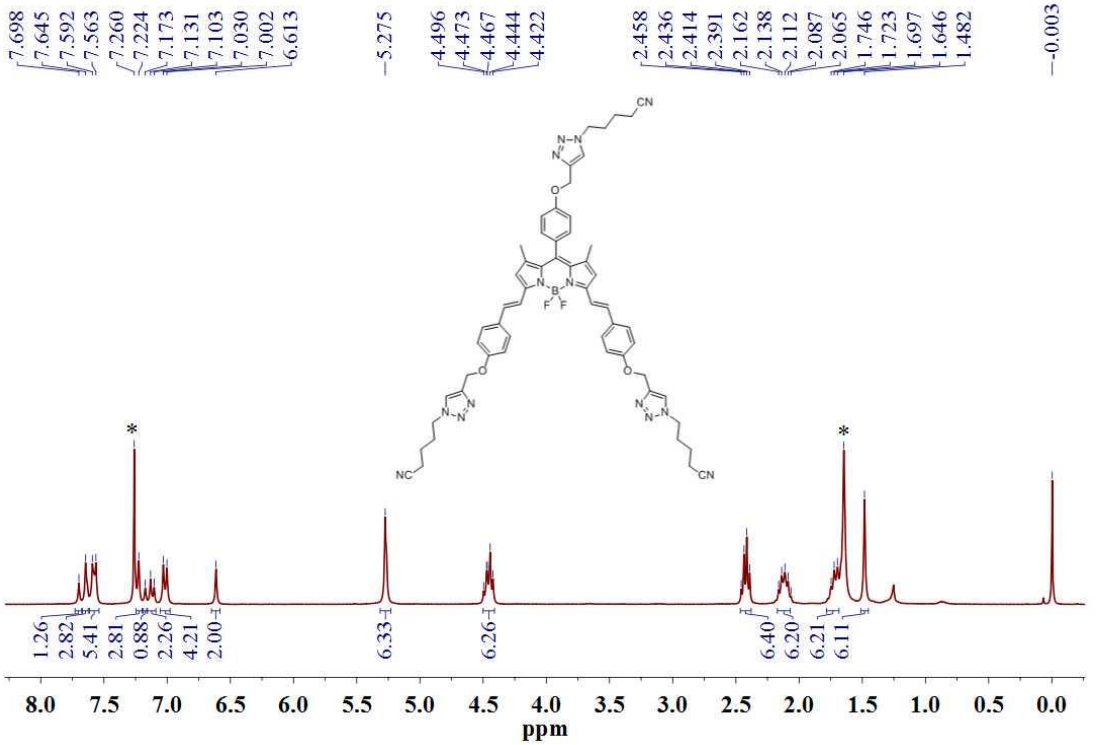


Fig. **S15** ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 298 K) of compound **G2** (solvent peaks are marked with asterisks).

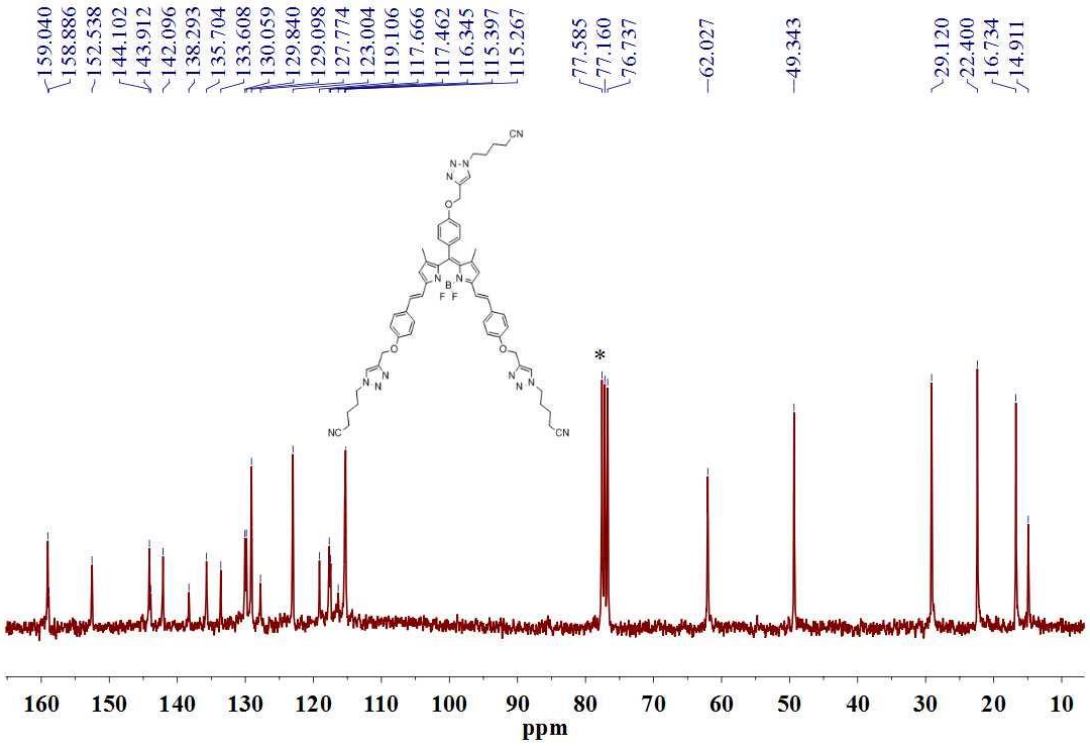


Fig. **S16** ^{13}C NMR spectrum (75 MHz, $CDCl_3$, 298 K) of compound **G2** (solvent peaks are marked with asterisks).

3. ^{1}H NMR complexation analysis of G2⊂H

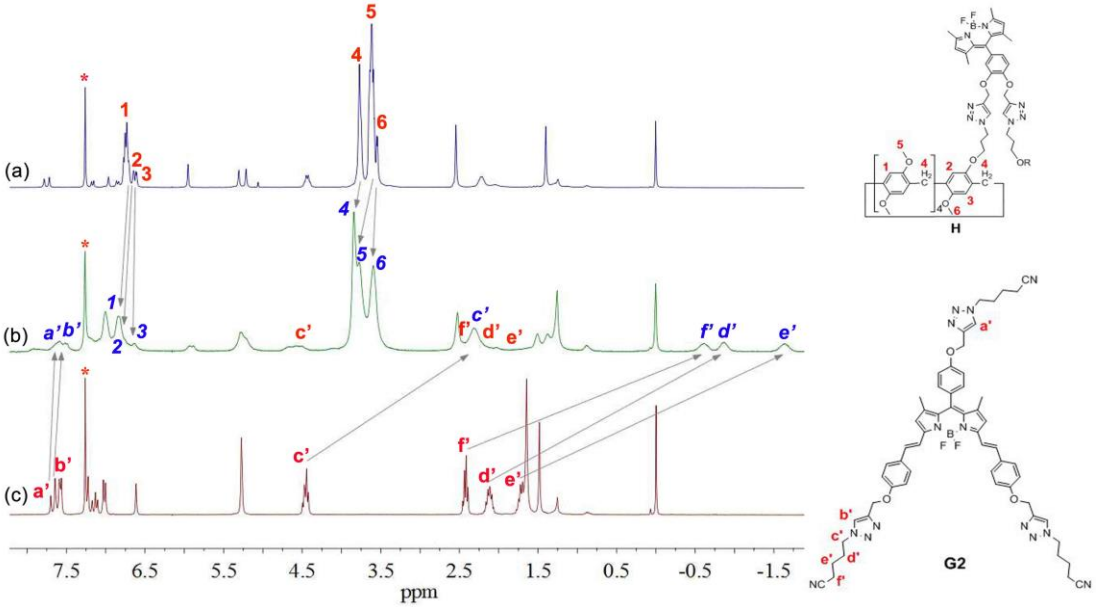


Fig. **S17** ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) spectra of (a) 4 mM **H**, (b) **G2⊂H** ([**G2**] = 2.6 mM, [**H**] = 4 mM, [**G2**]/[**H**] = 2:3) and (c) 2.6 mM **G2** (Blue italics represent complexed host and guest and the solvent peaks are marked with asterisks).

4. 2D NOESY analysis of G1⊂H

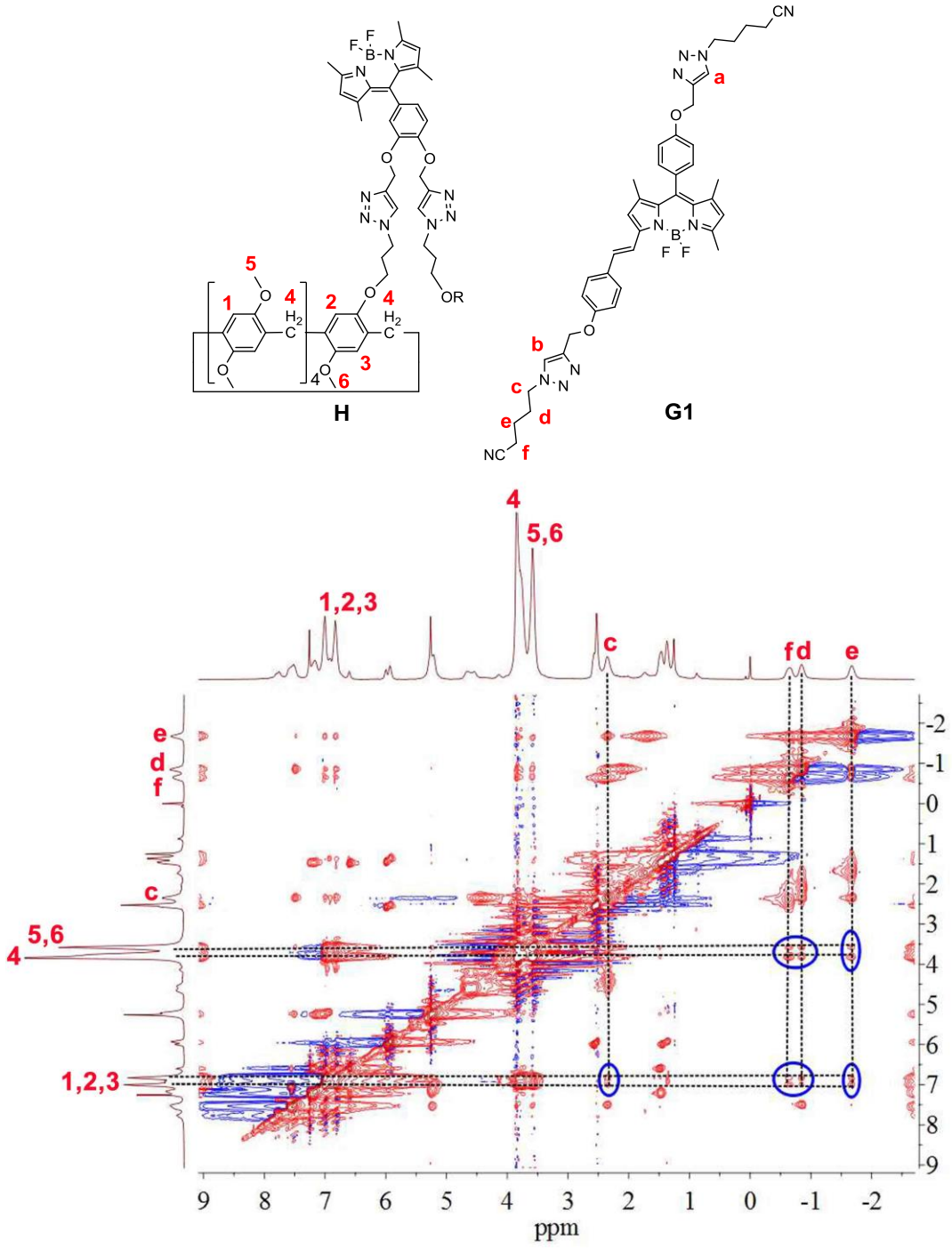


Fig. S18 2D NOESY (400 MHz, 298 K) analysis of **G1⊂H** ([**G1**] = [**H**] = 20 mM, [**G1**]/[**H**] = 1:1) in $CDCl_3$ with a mixing time of 300 ms (NOE correlation signals are marked with circles).

5. 2D NOESY analysis of G2⊂H

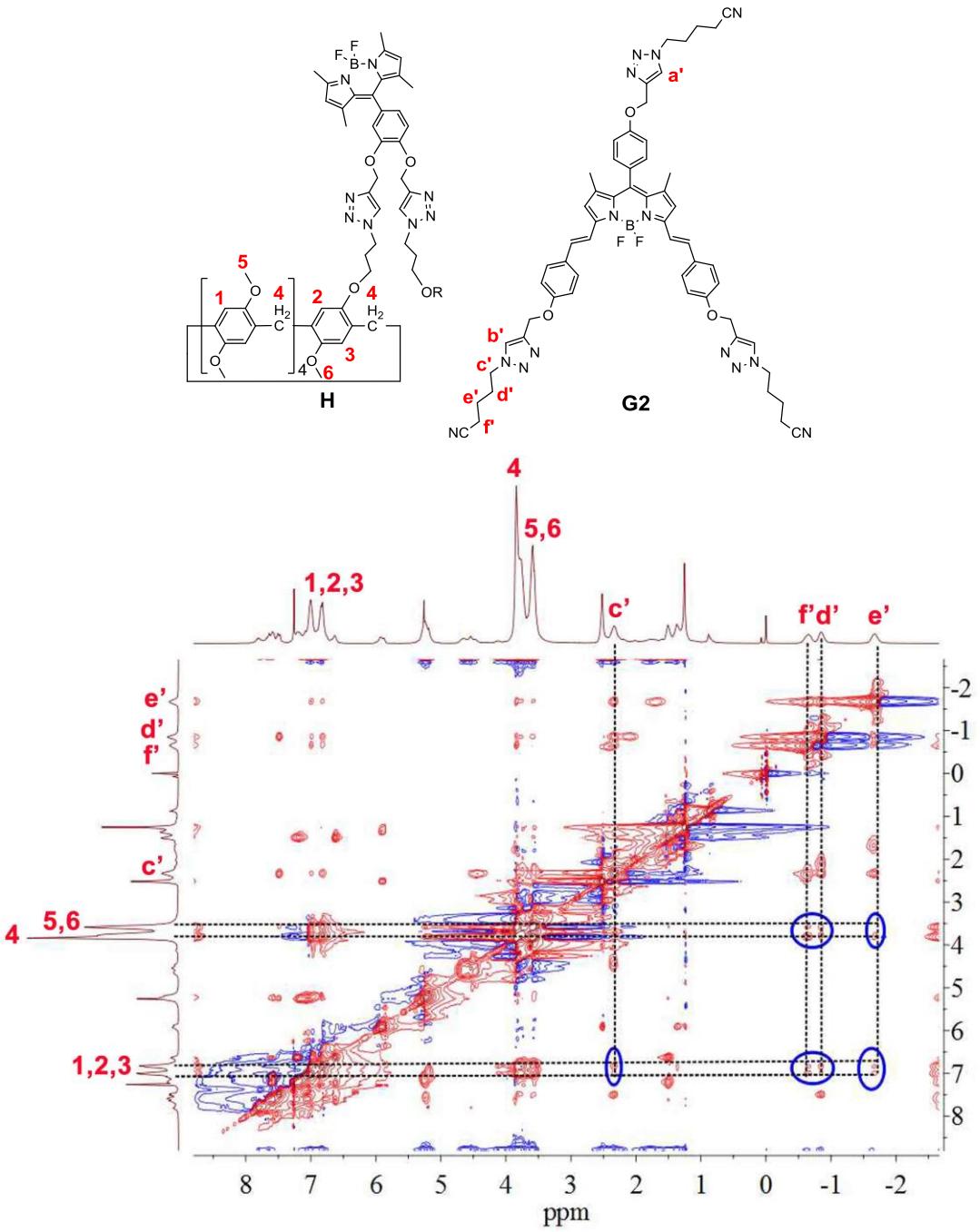


Fig. **S19** 2D NOESY (400 MHz, 298 K) analysis of **G2⊂H** ([**G2**] = 13.3 mM, [**H**] = 20 mM, [**G2**]/[**H**] = 2:3) in $CDCl_3$ with a mixing time of 300 ms (NOE correlation signals are marked with circles).

6. SEM micrographs

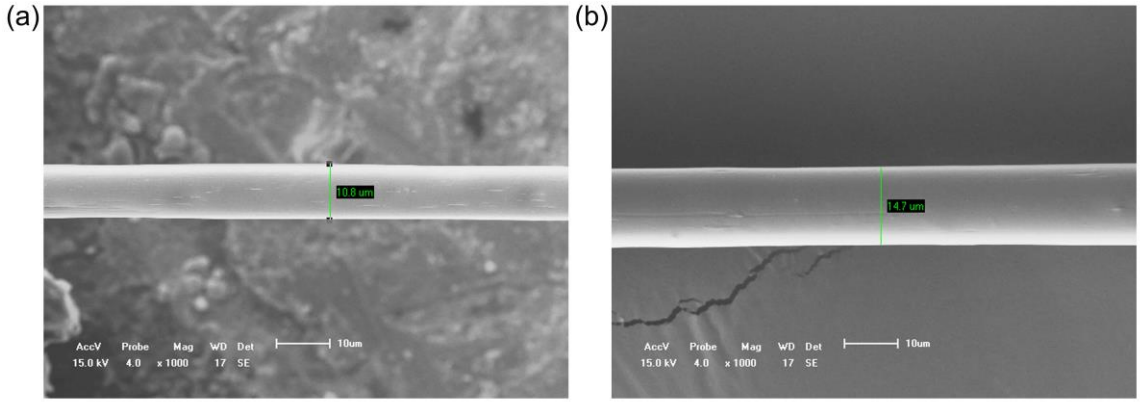


Fig. S20 SEM micrographs (gold coated) of a rodlike fiber drawn from a very concentrated solution of (a) **G1⊂H** (1:1 molar ratio) and (b) **G2⊂H** (2:3 molar ratio) in $CHCl_3$.

7. Normalized UV-Vis absorption and fluorescence excitation spectra

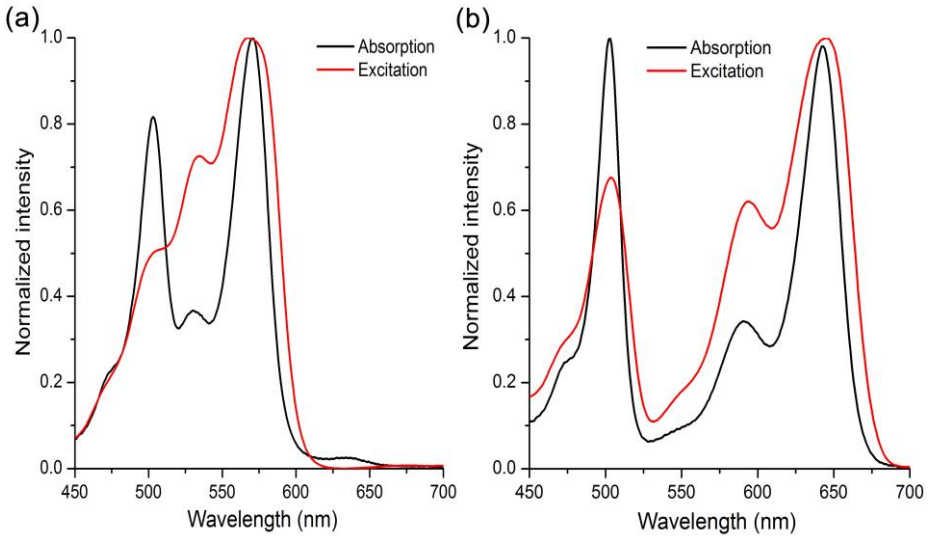


Fig. S21 Normalized UV-Vis absorption and fluorescence excitation spectra of (a) **G1⊂H** (1:1 molar ratio) and (b) **G2⊂H** (2:3 molar ratio) in $CHCl_3$.

8. Job plot for G1⊂H

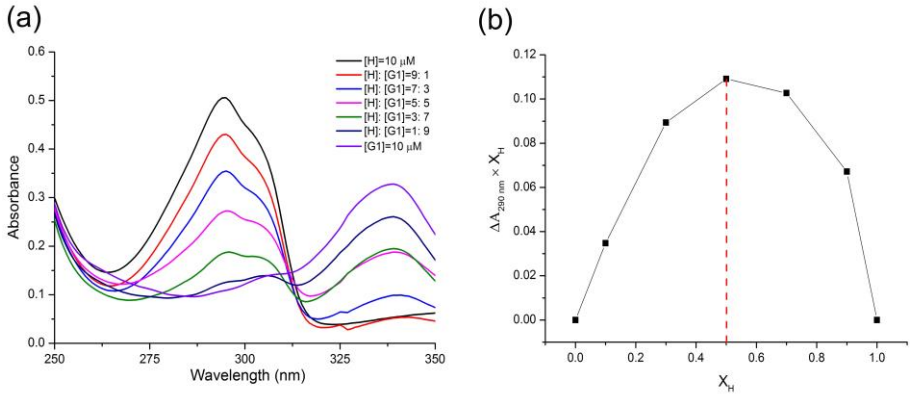


Fig. S22 (a) UV-Vis absorption spectra of complex **G1⊂H** with different molar ratios in chloroform while [**H**] + [**G1**] = 10 μM. (b) Job plot of complex **G1⊂H** showing a 1:1 stoichiometry between **G1** and **H** by plotting the absorbance difference at 290 nm (a characteristic absorption peak of **H**) against the mole fraction of **H**.

9. Job plot for G2⊂H

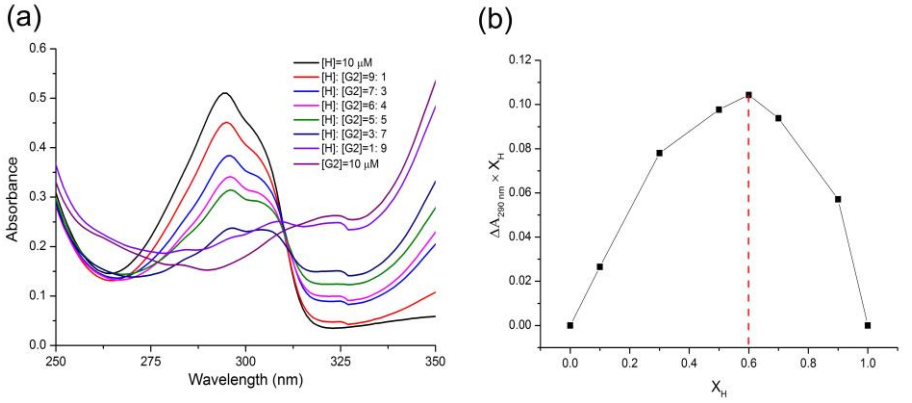


Fig. S23 (a) UV-Vis absorption spectra of complex **G2⊂H** with different molar ratios in chloroform while [**H**] + [**G2**] = 10 μM. (b) Job plot of complex **G2⊂H** showing a 2:3 stoichiometry between **G2** and **H** by plotting the absorbance difference at 290 nm (a characteristic absorption peak of **H**) against the mole fraction of **H**.

10. Specific viscosities of chloroform solutions of G1⊂H and G2⊂H

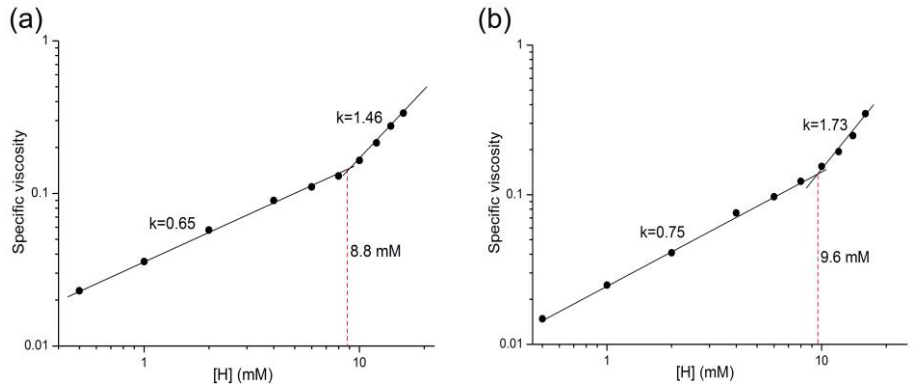


Fig. S24 Specific viscosities of the chloroform solutions of: (a) **G1⊂H** (1:1 molar ratio), and (b) **G2⊂H** (2:3 molar ratio) versus the concentration of **H** monomer (298 K). The critical polymerization concentration (CPC) values are 8.8 mM for **G1⊂H** and 9.6 mM for **G2⊂H**.

11. FRET efficiency calculation

The FRET efficiency *E* can be defined as the fraction of the donor de-excited via energy transfer to the acceptor. In our system, the efficiency *E* was calculated according to the following eqn (1):

$$E = 1 - I_{DA}/I_D \qquad (1)$$

where I_{DA} and I_D are the fluorescence intensities of the donor in the presence and absence of the acceptor, respectively.[S10] The I_{DA}, I_D values were measured as 2493, 5078 counts in the **G1⊂H** system and 2257, 6002 counts in the **G2⊂H** system. According to eqn (1), the efficiencies were calculated to be 51% for **G1⊂H** and 63% for **G2⊂H**, respectively.

12. References

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