Supplementary Information

Luminescent supramolecular polymer based on stiff-stilbene bridged pillar[5]arene as an Pd^{2+}-responsive smart material

Jing Wu, [a] Chuanyun Liang, [a] Jianyi Zhao, [a] H. Zuilhof,[a, b] Hongxia Zhao*[a]

a. Tianjin Key Laboratory for Modern Drug Delivery & High-Efficiency, School of Pharmaceutical Science and Technology, Faculty of Medicine, Tianjin University.

b. Laboratory of Organic Chemistry, Wageningen University Stippeneng 4, 6708WE Wageningen (The Netherlands)

* **Corresponding E-mail addresses**

zhaohongxia@tju.edu.cn

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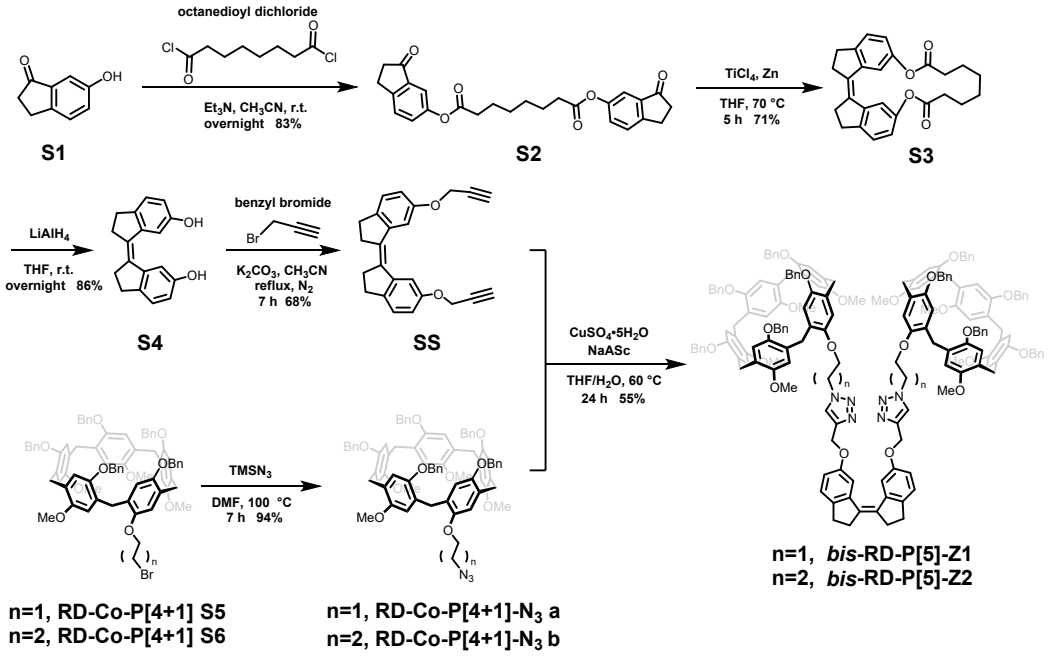
1. General information

The reagents that were commercially available were used as they were provided, without further purification. Detailed reaction conditions and yields were provided. NMR spectroscopy was conducted on a Bruker Avance III 400 MHz spectrometer, maintaining ambient temperature. Chemical shifts (δ) were reported in parts per million (ppm), relative to the solvent peak, and scalar coupling constants (J) were measured in units of hertz (Hz). For NMR interpretation, the following abbreviations were used: s = singlet; d = doublet; t = triplet; q = quartet; and m = multiplet. Matrix Assisted Laser Desorption Ionization (MALDI) mass spectra were acquired using a Daltonics UltrafleXtreme time of flight (TOF) equipment (Bruker, German). UV-vis absorption spectra were measured with a Hitachi UV-vis Spectrophotometer. The excitation and emission spectra were recorded on a FL360 Fluorescence Spectrometer (Gangdong, China), and an EnSpire Multilabel Reader (PerkinElmer, USA). Dynamic light scattering (DLS) measurements were performed on a Zetasizer Nano ZS Tester (Malvern, UK). Transmission Electron Microscope (TEM) observations were conducted on a Sigma 500 instrument (Zeiss, Germany).

2. Synthesis procedures



Scheme S1. Synthetic route for compounds ***bis*-RD-P[5]-*Z***.

Synthesis of compound **S2**: To a solution of **S1 (**6-methyl-1-indanone) (1.30 g, 8.77 mmol) and Et_3N (1.4 mL, 9.90 mmol) in CH_3CN (20.0 mL) was added octanedioyl dichloride (1.0 g, 4.74 mmol), and the mixture was stirred overnight. Subsequently, the solvent was removed using a vacuum evaporator, and the remaining residue was treated with H_2O (65 mL). The resulting mixture was filtered and the solid residue was dried in an oven at 55°C. The dried solid was further purified by column chromatography, employing EtOAc/PE (v/v = 1:4) as the eluent to give **S2** as a white solid (1.70 g, 82.9%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.48 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 2.4 Hz, 2H), 7.30 (dd, J = 8.2, 2.5 Hz, 2H), 3.14 (t, J = 5.9 Hz, 4H), 2.74 (t, J = 6.6 Hz, 4H), 2.60 (t, J = 7.5 Hz, 4H), 1.80 (s, 4H), 1.50 (s, 4H). NMR data were in accordance with literature.[1]

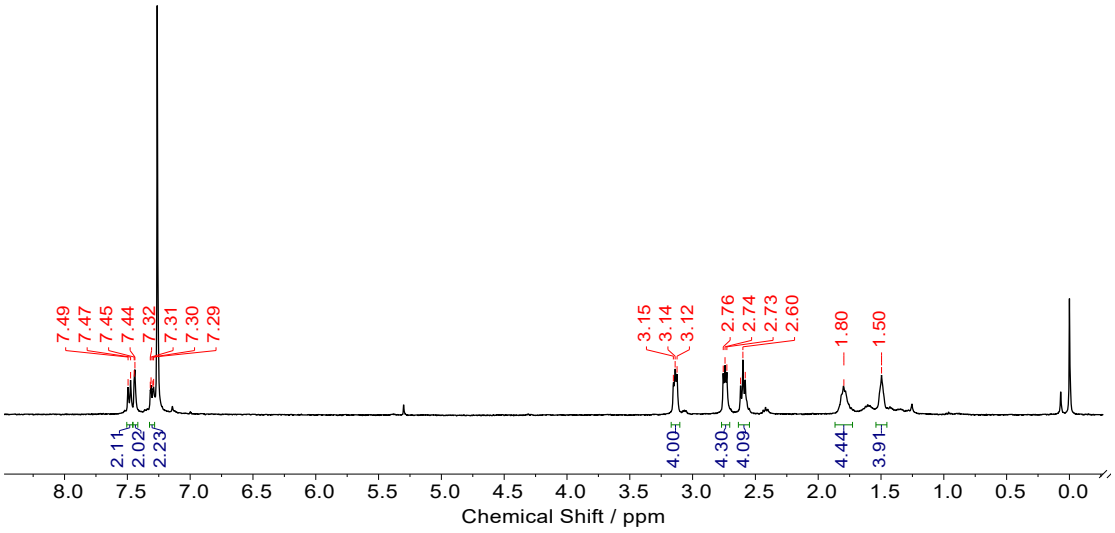


Fig. S1. ^{1}H NMR (400 MHz) spectrum of **S2** ($CDCl_3$, 298 K).

Synthesis of compound **S3**: $TiCl_4$ (1.3 mL) was gradually added dropwise to a stirred suspension of Zn powder (3.00 g, 4.60 mmol) in anhydrous tetrahydrofuran (THF) (60 mL) at 0 ℃. The mixture was then refluxed for 2 hours to activate the reaction system. Subsequently, compound **S2** (1.00g, 2.30mmol) dissolved in dry THF was added to the refluxing mixture over a period of 3 hours, divided into six separate portions using a syringe and introduced into the sealed system. The mixture was further refluxed for an additional hour. After cooling to room temperature, the reaction was treated with saturated ammonium chloride solution followed by extraction with ethyl acetate (3×500 mL). The combined organic fractions were dried over magnesium sulfate, filtered, and concentrated using vacuum evaporator. The resulting residue was purified through column chromatography, employing a mixture of ethyl acetate and petroleum ether (EtOAc/PE, V/V=1:15) as the eluent to give **S3** as a yellow solid (420 mg, 70.6%). ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 7.51 (d, J = 2.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 6.95 (dd, J = 8.1, 2.1 Hz, 2H), 2.95 (t, J = 8.4 Hz, 4H), 2.83 (t, J = 6.2 Hz, 4H), 2.65 – 2.58 (m, 4H), 1.71 – 1.64 (m, 4H), 1.36 (q, J = 3.6, 3.0 Hz, 4H). NMR data were in accordance with literature.[1]

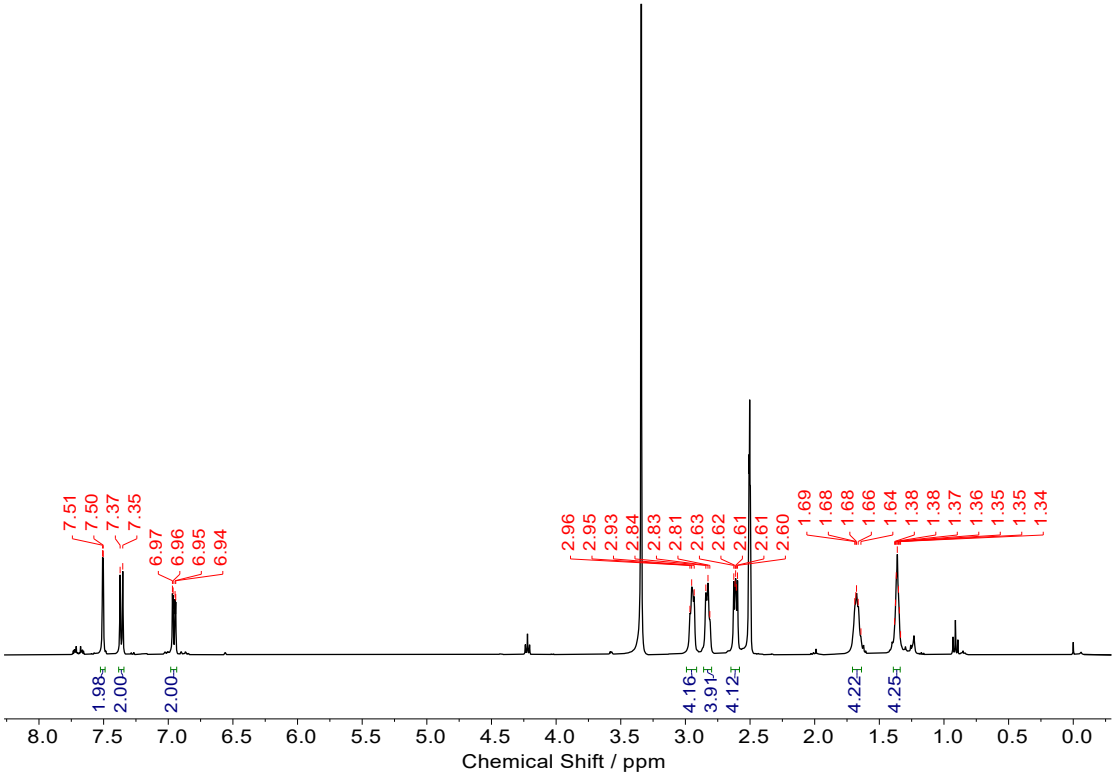


Fig. S2. ^{1}H NMR (400 MHz) spectrum of **S3** (DMSO-d6, 298 K).

Synthesis of compound **S4**: Compound **S3** (300 mg, 0.72 mmol) was dissolved in anhydrous tetrahydrofuran (THF) and added dropwise to a suspension of lithium aluminum hydride (550 mg, 1.44 mmol) in dry THF under a nitrogen atmosphere at 0 °C. The resulting mixture was gradually warmed to room temperature and stirred for 24 hours. Subsequently, water was cautiously added dropwise to the reaction mixture, and the resulting solid precipitate was filtered and washed with dichloromethane three times. The combined organic fractions were dried over magnesium sulfate and evaporated. The residual material was further purified using column chromatography, employing a mixture of ethyl acetate and petroleum ether (v/v, 1:4) as the eluent, to afford **S4** as white solid (160 mg, 86.2%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.69 (d, J = 2.3 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 6.71 (dd, J = 8.2, 2.4 Hz, 2H), 2.89 (t, J = 6.6 Hz, 4H), 2.79 (t, J = 6.3 Hz, 4H). NMR data were in accordance with literature.[1]

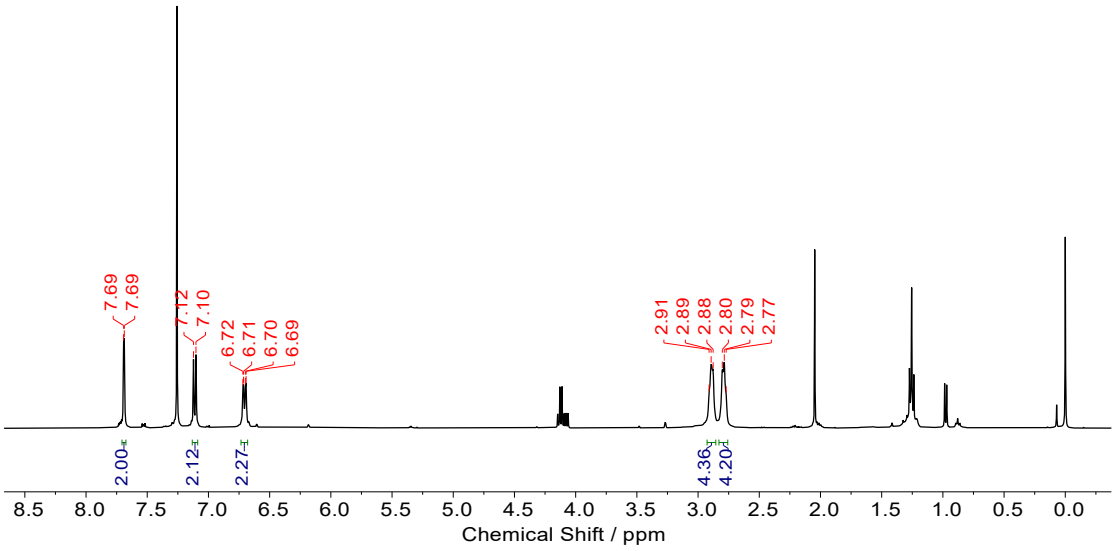


Fig. S3. ^{1}H NMR (400 MHz) spectrum of **S4** ($CDCl_3$, 298 K).

Synthesis of compound **SS**: To a stirred suspension containing compound **S4** (100 mg, 0.37 mmol) and potassium carbonate (K_2CO_3) (156 mg, 1.13 mmol) in acetonitrile (CH_3CN, 10 mL), propargyl bromide (112 μL, 1.29 mmol) was added. The reaction mixture was subsequently sealed and refluxed for 10 hours under a nitrogen atmosphere. After cooling to room temperature, the insoluble solids were filtered and washed thoroughly with dichloromethane (CH_2Cl_2). The solvent was then removed under reduced pressure, and the residual material was purified by column chromatography, employing a mixture of ethyl acetate and petroleum ether (EtOAc/PE, v/v, 1:10) as the eluent, to give **SS** as a yellow oil (85 mg, 68.2%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.67 (d, J = 2.4 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 6.82 (dd, J = 8.3, 2.4 Hz, 2H), 4.64 (d, J = 2.4 Hz, 4H), 2.92 (t, J = 6.6 Hz, 4H), 2.81 (t, J = 6.4 Hz, 4H), 2.55 (t, J = 2.4 Hz, 2H). NMR data were in accordance with literature.[2]

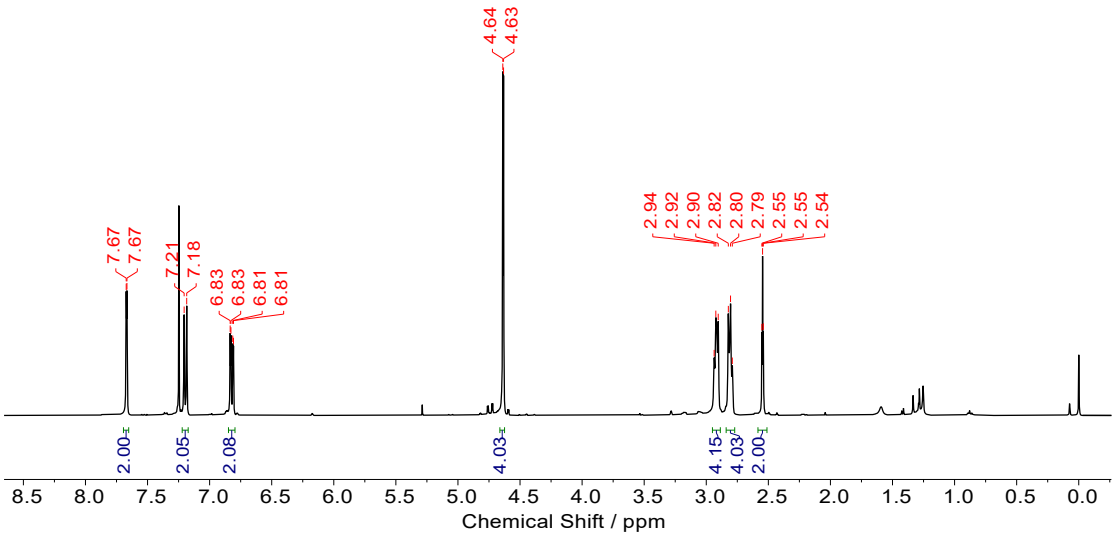


Fig. S4. ^{1}H NMR (400 MHz) spectrum of **SS** ($CDCl_3$, 298 K).

Synthesis of **RD-Co-P[4+1]-N_3 a**: To a solution of **RD-Co-P[4+1] S5**[3] (200 mg, 0.16 mmol) in DMF (2 mL) was added $TMSN_3$ (93 mg, 0.81 mmol), and mixture stirred for 8 h at 100 ℃. After cooling to room temperature, TMSN3 was removed by filtration, and the remaining residue was dissolved in water (30 mL), which was then extracted with CH_2Cl_2 (3×30 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under a vacuum to give a crude product. The crude product was washed by MeOH to obtain **RD-Co-P[4+1]-N_3 a** as a colorless solid (178 mg, 94.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32 – 7.26 (m, 5H), 7.25 – 7.17 (m, 20H), 6.83 (m, 10H), 4.46 (d, J = 2.9 Hz, 10H), 3.97 (t, J = 5.0 Hz, 2H), 3.89 – 3.78 (m, 10H), 3.78 – 3.68 (m, 12H), 3.53 (t, J = 5.0 Hz, 2H).

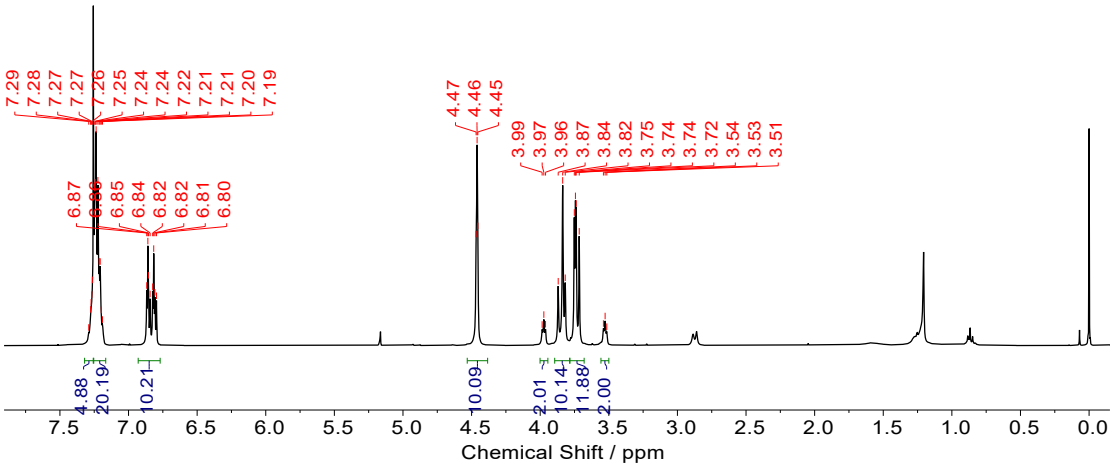


Fig. S5. ^{1}H NMR (400 MHz) spectrum of **RD-Co-P[4+1]-N_3 a** ($CDCl_3$, 298 K).

Synthesis of **RD-Co-P[4+1]-N_3 b**: To a solution of **RD-Co-P[4+1] S6** (500 mg, 0.40 mmol) in DMF (2 mL) was added $TMSN_3$ (190 mg, 2.04 mmol), and mixture stirred for 8 h at 100 ℃. After cooling to room temperature, $TMSN_3$ was removed by filtration, and the remaining residue was dissolved in water (75 mL), which was then extracted with CH_2Cl_2 (3×75 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under a vacuum to give a crude product. The crude product was washed by MeOH to obtain **RD-Co-P[4+1]-N_3 b** as a colorless solid (432 mg, 89.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.27 – 7.18 (m, 25H), 6.86 – 6.76 (m, 10H), 4.47 (t, J = 3.2 Hz, 10H), 3.95 (t, J = 6.0 Hz, 2H), 3.83 (d, J = 3.6 Hz, 10H), 3.72 (dd, J = 10.5, 3.0 Hz, 12H), 3.45 (t, J = 6.8 Hz, 2H), 1.98 (m, 2H).

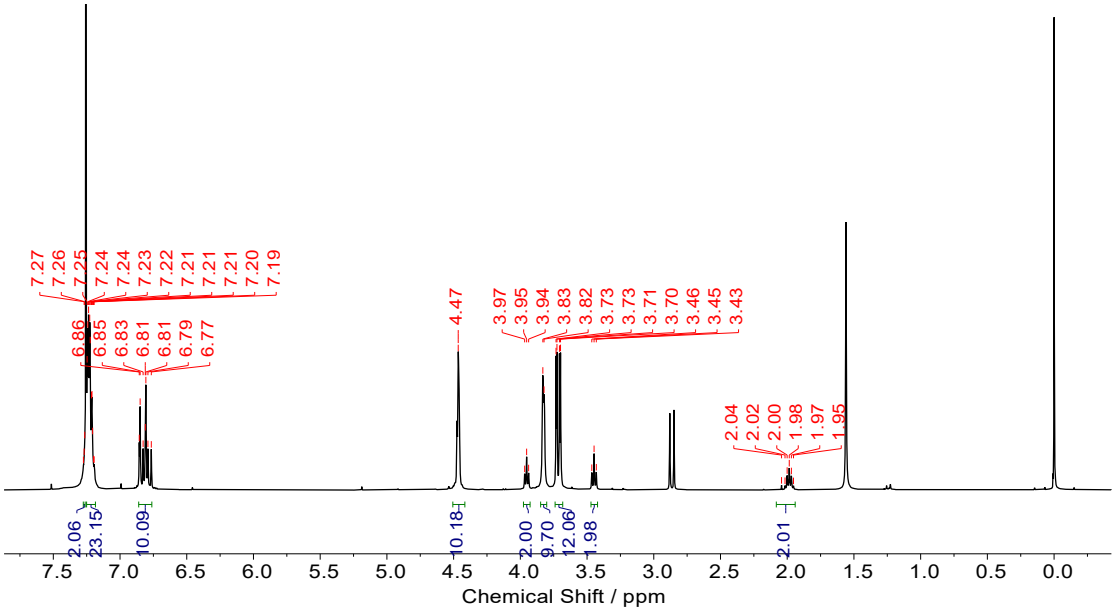
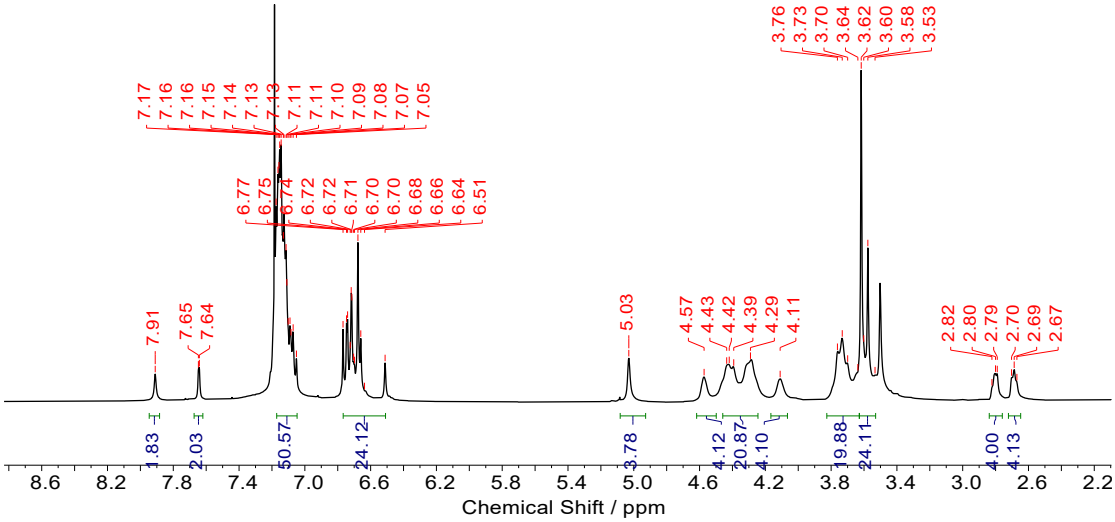


Fig. S6. ^{1}H NMR (400 MHz) spectrum of **RD-Co-P[4+1]-N3 b** ($CDCl_3$, 298 K).

Synthesis of ***bis*-RD-P[5]-Z1**: To a 50 mL round-bottomed flask, **S5** (59 mg, 0.17 mmol), **RD-Co-P[4+1] N_3-a** (450 mg, 0.37 mmol), sodium ascorbate (35 mg,0.17 mmol) and $CuSO_4 \cdot 5H_2O$ (9 mg, 0.03 mmol), THF (4 mL) and H_2O (0.8 mL) were added. Then the resulting mixture was vigorously stirred for 12 hours at 66 ℃ under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was filtered to remove the precipitate and the solvent was removed under reduced pressure. Then the residue was extracted by CH_2Cl_2 (3×100 mL), The combined organic phase was washed with saturated ammonium chloride solution, dried over anhydrous Na_2SO_4, filtered, and concentrated under a vacuum to give a crude product, which was further purified using column chromatography, employing a mixture of EtOAc/PE/CH_2Cl_2 (v/v/v, 4:1:1) as the eluent to give ***bis*-RD-P[5]-Z1** as a white powdered solid (256 mg, 54.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (s, 2H), 7.64 (d, J = 2.3 Hz, 2H), 7.17 – 7.05 (m, 50H), 6.77 – 6.51 (m, 24H), 5.03 (s, 4H), 4.57 (s, 4H), 4.46 – 4.24 (m, 20H), 4.11 (s, 4H), 3.63 – 3.86 (m, 20H), 3.60 (d, J = 16.1 Hz, 24H), 2.84 – 2.76 (m, 4H), 2.69 (t, J = 6.5 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 156.65, 150.95, 150.92, 150.88, 150.74, 150.49, 149.72, 149.63, 148.98, 144.47, 141.67, 141.24, 138.03, 137.97, 137.92, 137.81, 135.52, 128.78, 128.57, 128.53, 128.38, 128.30, 128.29, 128.14, 128.04, 127.80, 127.60, 127.55, 127.28, 127.26, 127.23, 127.19, 125.72, 123.87, 115.66, 115.05, 114.96, 114.76, 114.44, 114.18, 114.05, 113.92, 109.80, 69.82, 69.76, 69.72, 69.64, 67.22, 62.33, 55.98, 55.90, 55.86, 55.79, 50.02, 35.29, 29.87, 29.80, 29.56. MALDI-TOF-MS m/z: calcd for $C_{176}H_{163}N_6O_{22}$ $[M + H]^+$ 2712.174, found: 2712.019.

(a)



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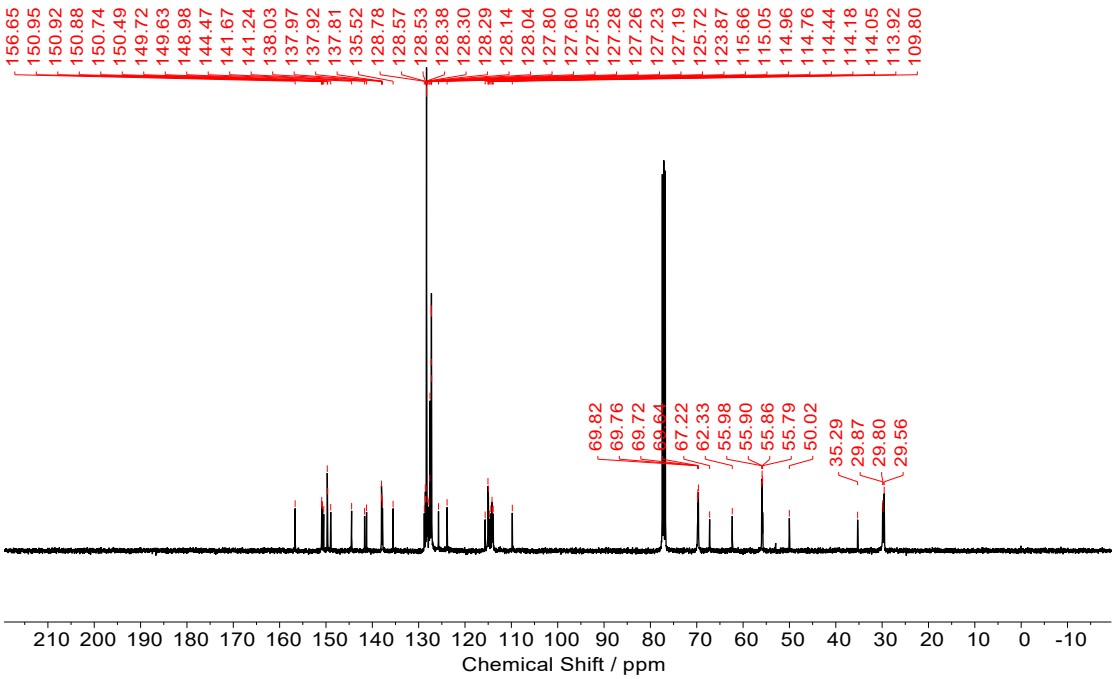


Fig. S7. (a) ^{1}H NMR (400 MHz) spectrum of ***bis*-RD-P[5]-Z1** ($CDCl_3$, 298 K). (b) ^{13}C NMR (101 MHz) spectrum of ***bis*-RD-P[5]-Z1** ($CDCl_3$, 298 K).

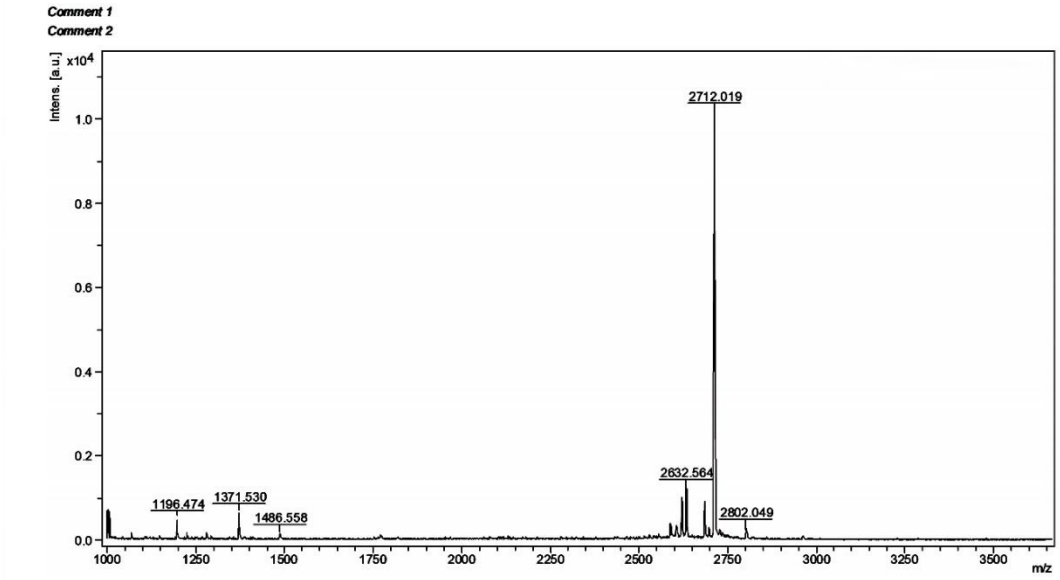
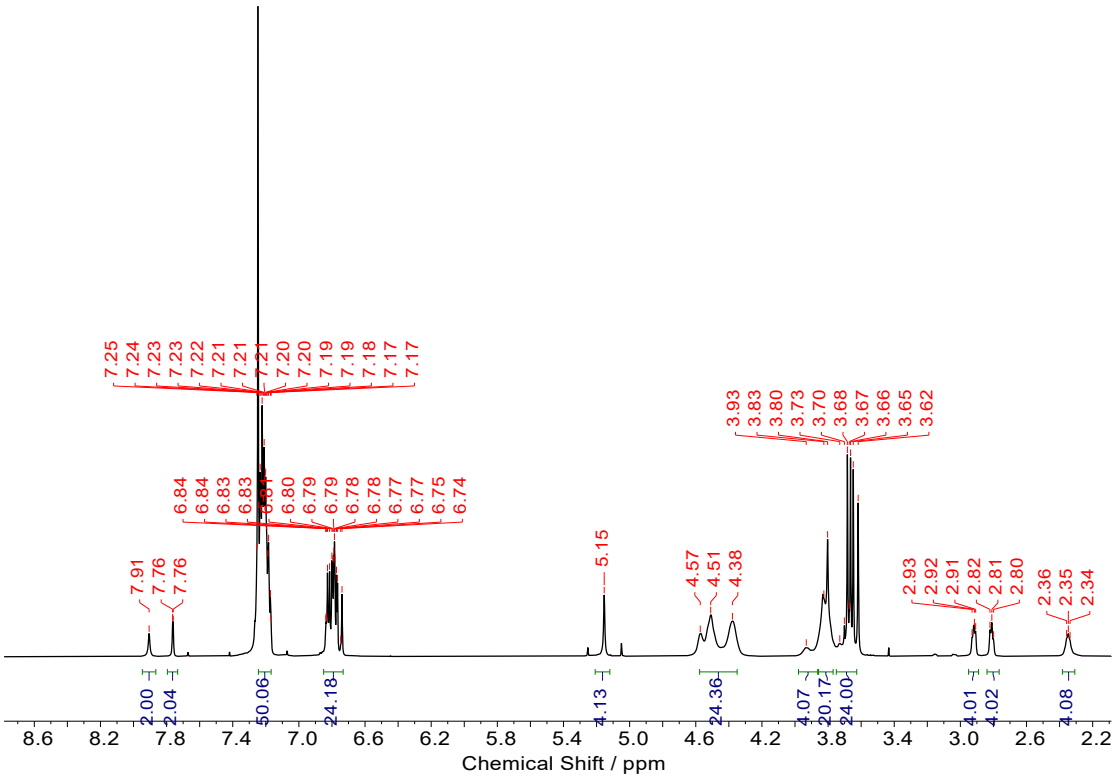


Fig. S8. MALDI-TOF-MS spectrum of ***bis*-RD-P[5]-Z1**.

Synthesis of ***bis*-RD-P[5]-Z2**: To a 25 mL round-bottomed flask, **S6** (50 mg, 0.15 mmol), **RD-Co-P[4+1] N_3-b** (388 mg, 0.32 mmol), sodium ascorbate (30 mg, 0.14 mmol) and $CuSO_4 \cdot 5H_2O$ (8 mg, 0.03 mmol), THF (4 mL) and H_2O (0.8 mL) were added. Then the resulting mixture was vigorously stirred for 12 hours at 66 ℃ under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was filtered to remove the precipitate and the solvent was removed under reduced pressure. Then the residue was extracted by CH_2Cl_2 (3×100 mL), The combined organic phase was washed with saturated ammonium chloride solution, dried over anhydrous Na_2SO_4, filtered, and concentrated under a vacuum to give a crude product, which was further purified using column chromatography, employing a mixture of EtOAc/PE/CH_2Cl_2 (v/v/v, 4:3:1) as the eluent to give ***bis*-RD-P[5]-Z2** as a white powdered solid (177 mg, 44.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.91 (s, 2H), 7.76 (d, J = 2.3 Hz, 2H), 7.24 – 7.17 (m, 50H), 6.85 – 6.73 (m, 24H), 5.15 (s, 4H), 4.58 – 4.35 (m, 24H), 3.93 (s, 4H), 3.77 – 3.85 (m, 20H), 3.75 – 3.63 (m, 24H), 2.95 – 2.89 (m, 4H), 2.81 (t, J = 6.6 Hz, 4H), 2.38 – 2.31 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 155.55, 149.72, 149.70, 149.68, 149.59, 148.89, 148.60, 148.57, 148.48, 148.31, 143.18, 140.61, 140.24, 136.91, 136.88, 136.82, 136.79, 134.44, 127.31, 127.28, 127.18, 127.11, 127.05, 126.98, 126.94, 126.83, 126.44, 126.12, 126.09, 126.05, 124.70, 122.47, 113.89, 113.80, 113.75, 113.62, 113.37, 112.97, 112.79, 108.54, 68.54, 68.52, 68.49, 68.42, 63.84, 61.34, 54.90, 54.73, 54.68, 46.52, 34.23, 29.45, 28.83, 28.64, 28.49, 28.40. MALDI-TOF-MS m/z: calcd for $C_{178}H_{167}N_6O_{22}$ $[M + H]^+$ 2740.206, found: 2740.301.

(a)



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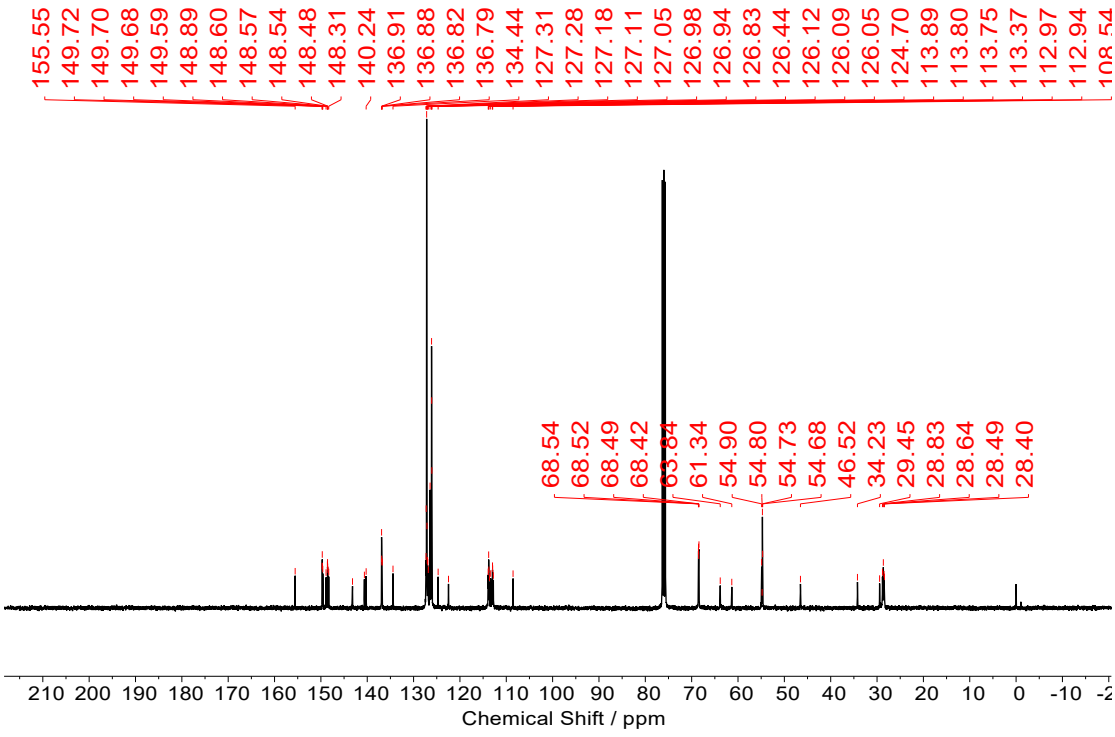


Fig. S9. (a) ^{1}H NMR (400 MHz) spectrum of ***bis*-RD-P[5]-Z2** ($CDCl_3$, 298 K). (b) ^{13}C NMR (101 MHz) spectrum of ***bis*-RD-P[5]-Z2** ($CDCl_3$, 298 K).

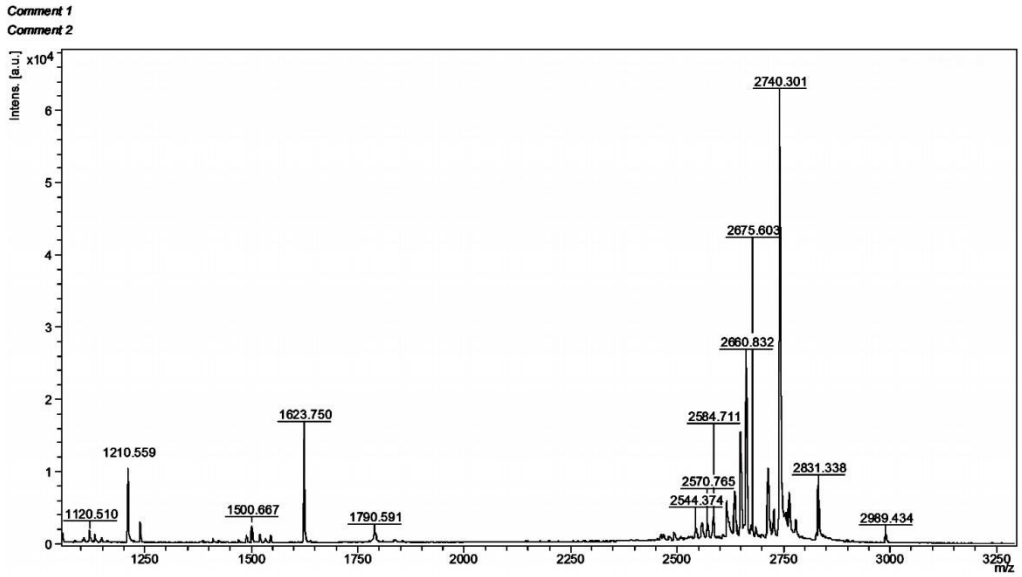
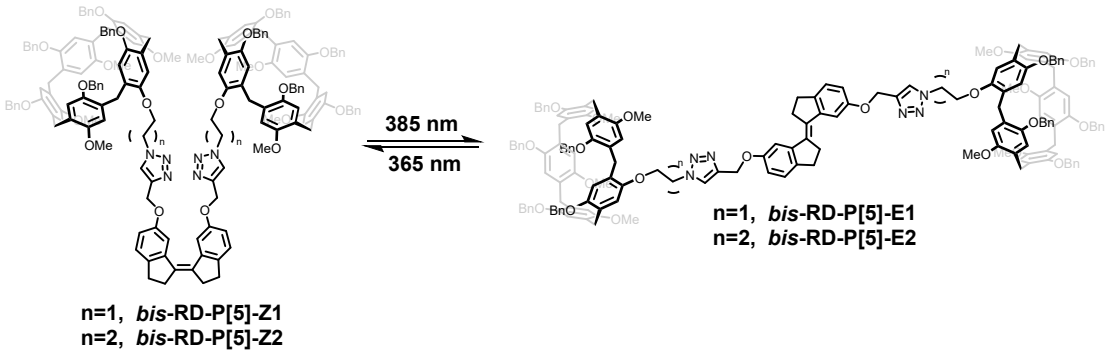


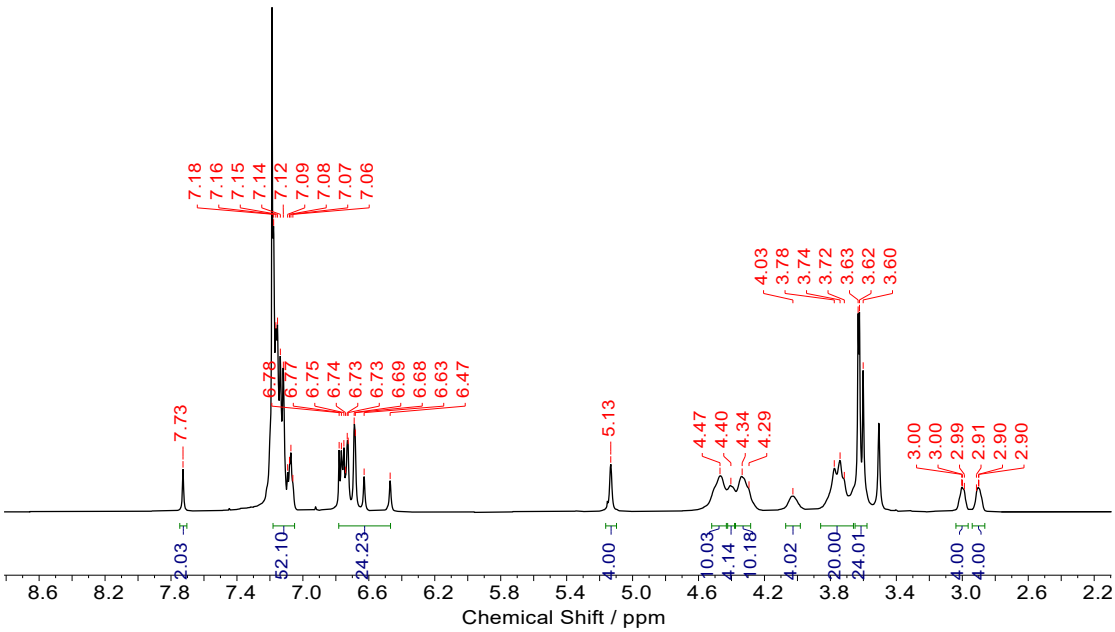
Fig. S10. MALDI-TOF-MS spectrum of ***bis*-RD-P[5]-Z2**.



Scheme S2. Photoisomerization process between ***bis*-RD-P[5]-Z** and ***bis*-RD-P[5]-E**.

Synthesis of ***bis*-RD-P[5]-E1**: ***Bis*-RD-P[5]-Z1** (100 mg, 0.0369 mol) was dissolved in 10 mL mixed solvent of EtOAc and CH_3CN with the volume ratio of 1:1. The solution was exposed to UV light with a wavelength of 385 nm for 20 min. The solvent was then removed under reduced pressure, and the residual material was purified by column chromatography, employing a mixture of EtOAc/PE/CH_2Cl_2 (v/v/v, 4:1:1) as the eluent to give ***bis*-RD-P[5]-E1** as a white powdered solid (85 mg, 85.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.73 (s, 2H), 7.18 – 7.05 (m, 52H), 6.78 – 6.47 (m, 24H), 5.13 (s, 4H), 4.47 (s, 10H), 4.40 (s, 4H), 4.31 (d, J = 16.6 Hz, 10H), 4.03 (s, 4H), 3.86 – 3.66 (m, 20H), 3.65 – 3.58 (m, 24H), 3.04 – 2.96 (m, 4H), 2.94 – 2.86 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 157.24, 150.95, 150.93, 150.90, 150.74, 150.55, 149.77, 149.70, 148.93, 144.65, 144.48, 140.11, 138.00, 137.96, 137.92, 137.81, 137.75, 135.83, 128.75, 128.70, 128.60, 128.55, 128.36, 128.31, 128.28, 128.23, 128.19, 128.01, 127.78, 127.62, 127.59, 127.56, 127.31, 127.27, 127.24, 127.21, 127.16, 125.30, 123.62, 115.53, 115.12, 115.06, 114.80, 114.20, 114.07, 113.93, 113.73, 111.22, 69.90, 69.85, 69.75, 69.67, 67.15, 62.38, 56.03, 55.94, 55.89, 55.83, 50.00, 32.43, 30.25, 29.94, 29.84, 29.72, 29.60. MALDI-TOF-MS m/z: calcd for $C_{176}H_{164}N_6O_{22}$ $[M + 2H]^+$ 2713.174, found: 2713.241.

(a)



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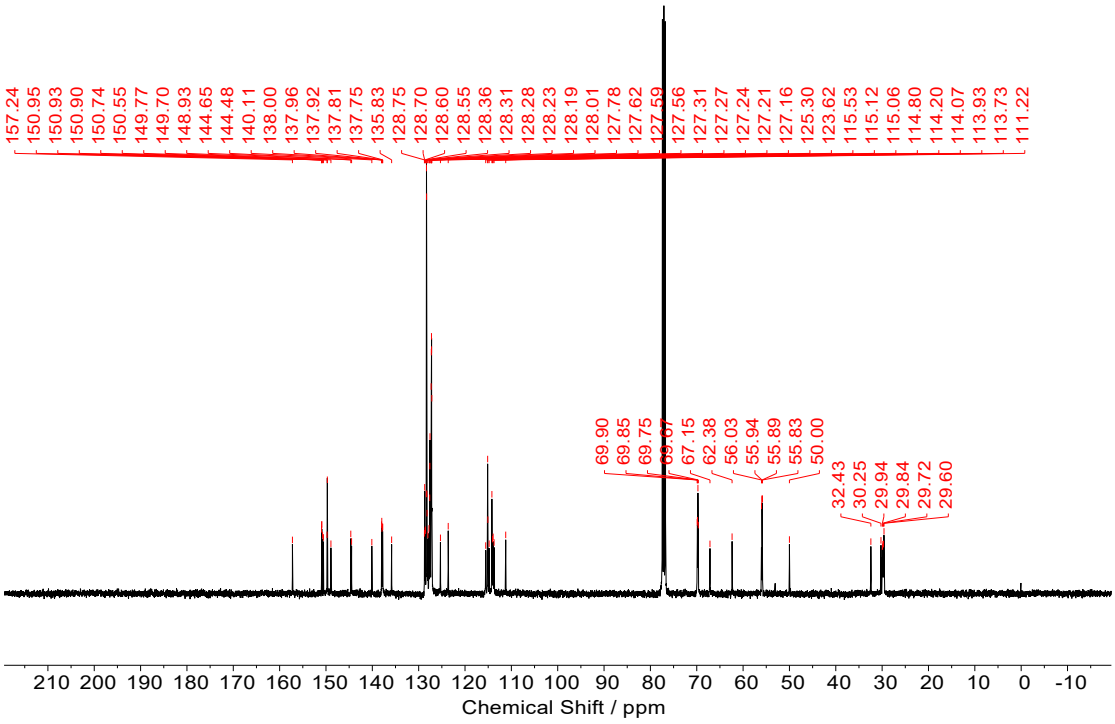


Fig. S11. (a) ^{1}H NMR (400 MHz) spectrum of ***bis*-RD-P[5]-E1** ($CDCl_3$, 298 K). (b) ^{13}C NMR (101 MHz) spectrum of ***bis*-RD-P[5]-E1** ($CDCl_3$, 298 K).

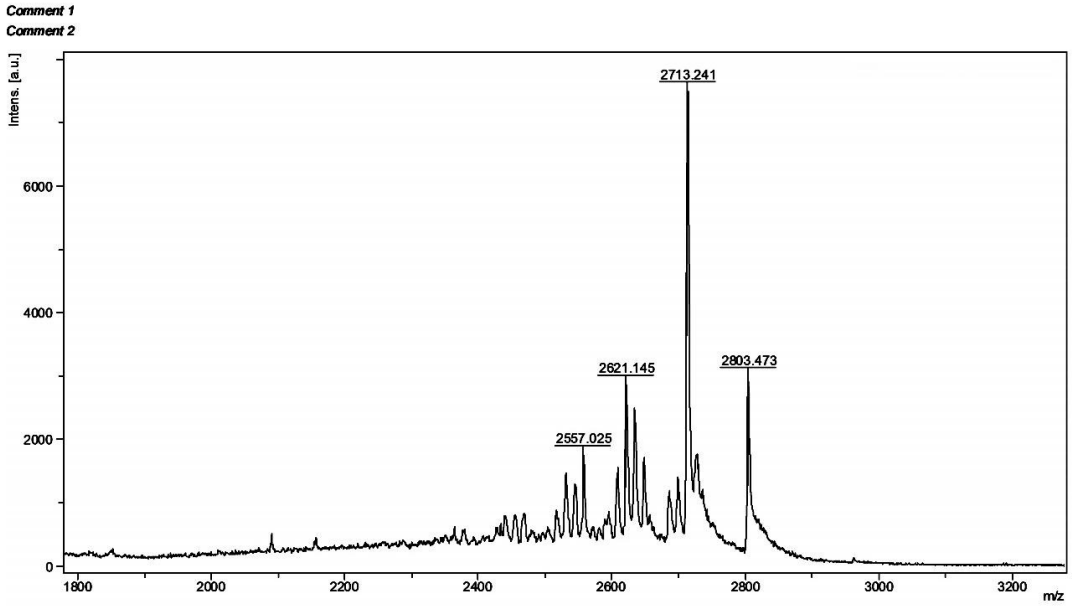
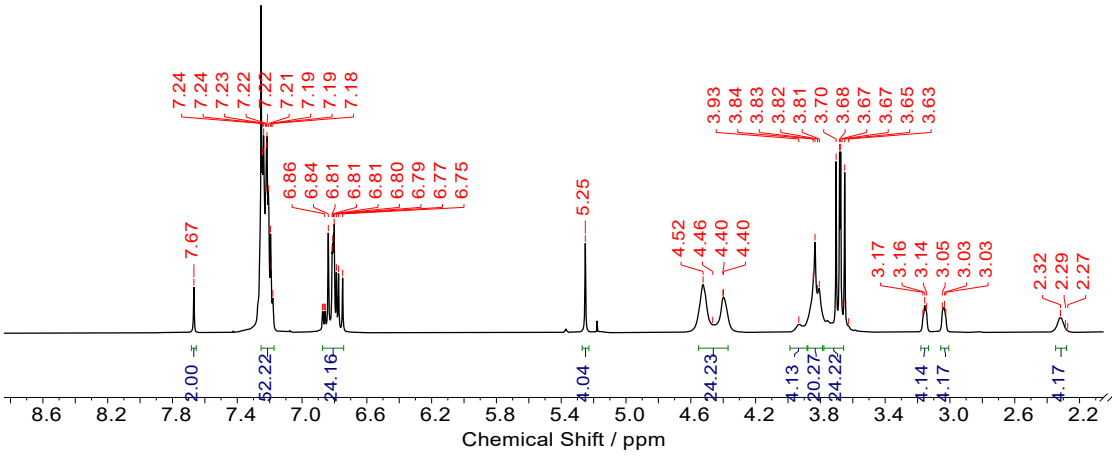


Fig. S12. MALDI-TOF-MS of ***bis*-RD-P[5]-E1**.

Synthesis of ***bis*-RD-P[5]-E2**: ***Bis*-RD-P[5]-Z2** (100 mg, 0.0365 mol) was dissolved in 10 mL mixed solvent of EtOAc and CH_3CN with the volume ratio of 1:1. The solution was exposed to UV light with a wavelength of 385 nm for 20 min. The solvent was then removed under reduced pressure, and the residual material was purified by column chromatography, employing a mixture of EtOAc/PE/CH_2Cl_2 (v/v/v, 4:3:1) as the eluent to give ***bis*-RD-P[5]-E1** as a white powdered solid (87 mg, 87.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.67 (s, 2H), 7.25 – 7.16 (m, 52H), 6.88 – 6.74 (m, 24H), 5.25 (s, 4H), 4.61 – 4.33(m, 24H), 3.91 (s, 4H), 3.88 – 3.78 (m, 20H), 3.68 (dd, J = 17.9, 13.9 Hz, 24H), 3.16 (t, J = 6.7 Hz, 4H), 3.08 – 3.00 (m, 4H), 2.36 – 2.27 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): ^{13}C NMR (101 MHz, Chloroform-*d*) δ (ppm): 157.30, 150.81, 150.71, 150.04, 149.83, 149.69, 149.61, 149.37, 144.50, 140.19, 138.00, 137.96, 137.86, 135.91, 128.59, 128.55, 128.44, 128.31, 128.21, 128.10, 128.01, 127.97, 127.58, 127.54, 127.24, 127.22, 127.18, 125.40, 123.16, 115.05, 114.92, 114.78, 114.26, 114.14, 114.07, 113.89, 113.72, 111.23, 69.65, 69.55, 64.77, 62.53, 56.15, 55.90, 55.87, 55.83, 47.58, 32.54, 30.36, 30.31, 29.86, 29.75, 29.65, 29.50. MALDI-TOF-MS m/z: calcd for $C_{178}H_{167}N_6O_{22}$ $[M + H]^+$ 2740.206, found: 2740.309.

(a)



(b)

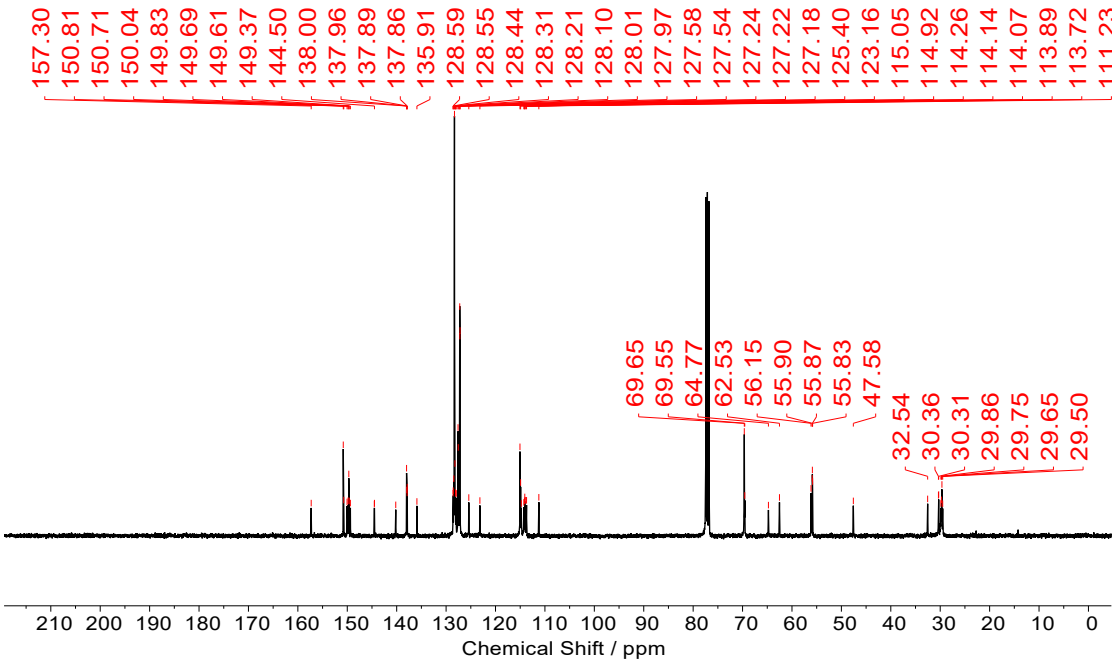


Fig. S13. (a) ^{1}H NMR (400 MHz) spectrum of ***bis*-RD-P[5]-E2** ($CDCl_3$, 298 K). (b) ^{13}C NMR (101 MHz) spectrum of ***bis*-RD-P[5]-E2** ($CDCl_3$, 298 K).

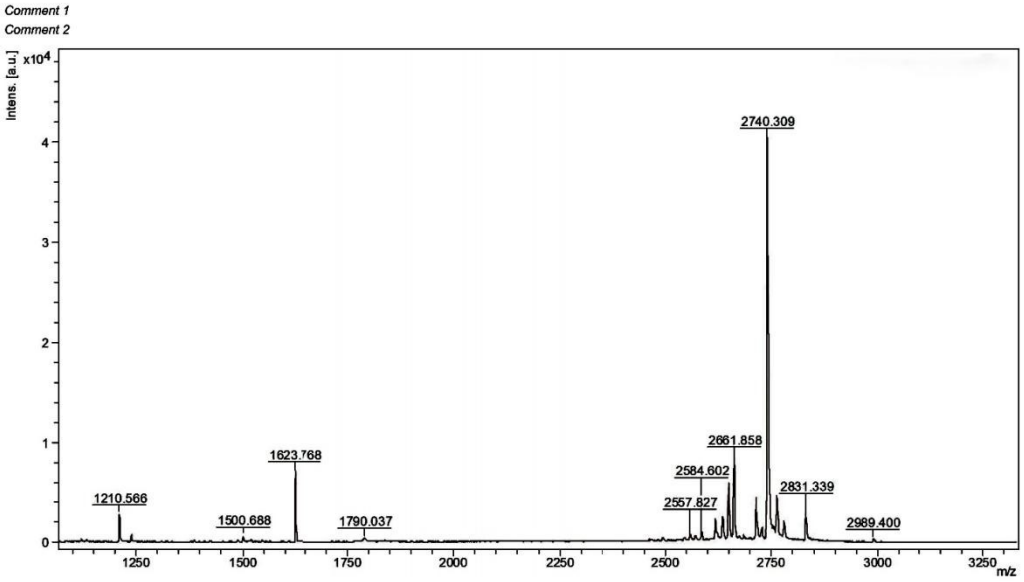
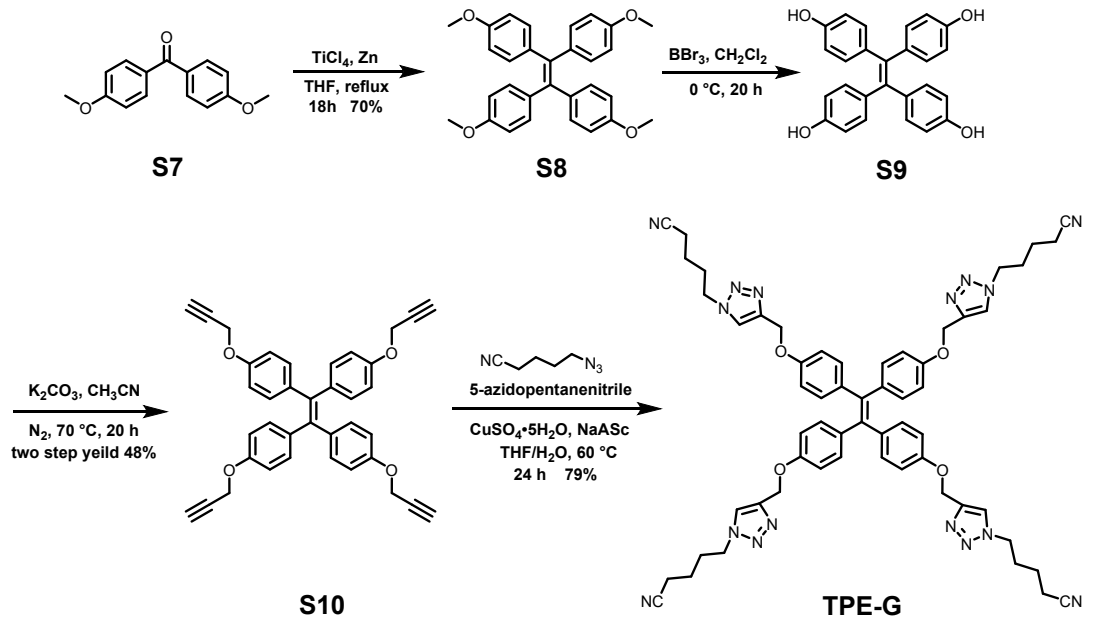


Fig. S14. MALDI-TOF-MS of ***bis*-RD-P[5]-E2**.



Scheme S3. Synthetic route for **TPE-G**.

Synthesis of compound **S8**: $TiCl_4$ (1.65 mL) was added to a stirred suspension of Zn powder (1.35 g, 20.64 mmol) in anhydrous THF (15 mL) at 0 ℃. After completion of the addition, the mixture was refluxed for 2 h. Then the **S7** (1.00 g, 4.13 mmol) was added into the above suspension and stirred under reflux overnight. After cooling to room temperature, the reaction mixture was filtered to remove the precipitate and the solvent was removed under reduced pressure. Then the residue was extracted by CH_2Cl_2 (3×200 mL). The combined organic phase was washed with saturated ammonium chloride solution, dried over anhydrous Na_2SO_4, filtered, and concentrated under a vacuum to give a crude product, which was further purified using column chromatography, employing a mixture of EtOAc/PE (v/v, 1:10) as the eluent to give **S8** as a white powdered solid (650 mg, 69.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.93 (d, J = 8.6 Hz, 8H), 6.64 (d, J = 8.6 Hz, 8H), 3.74 (s, 12H). NMR data were in accordance with literature.[4]

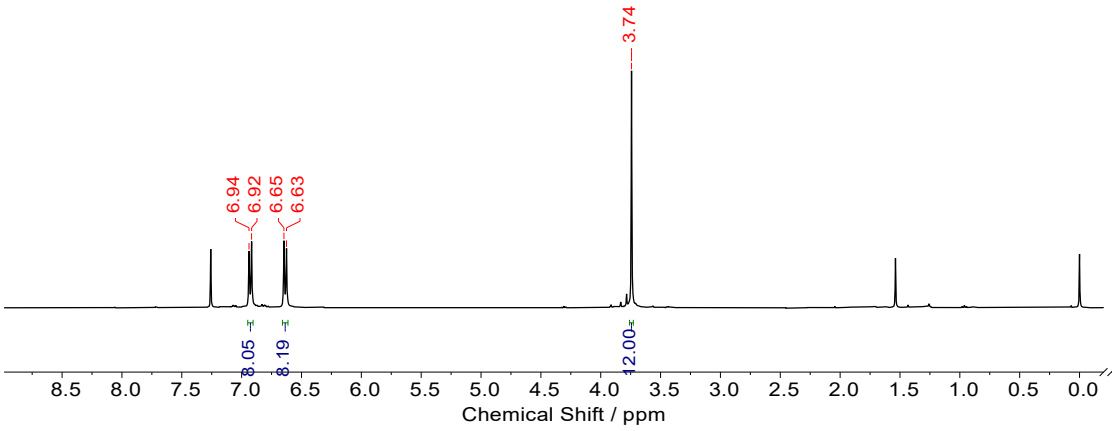


Fig. S15. ^{1}H NMR (400 MHz) spectrum of compound **S7** ($CDCl_3$, 298 K).

Synthesis of compound **S10**: To a cooled solution (0 °C) of compound **S8** (500 mg, 1.10 mmol) in CH_2Cl_2 (12 mL) was added dropwise of BBr_3 (4.4 mL, 8.84 mmol) in CH_2Cl_2 (8 mL) and the mixture was stirred for 15 minutes. Then the orange-red solution was allowed to warm up to room temperature overnight, followed by dropwise addition of water (25 mL). The mixture was then filtered and washed with water (100 mL), CH_2Cl_2 (100 mL), respectively. The crude product **S9** was dried and obtained as a grey solid, which was used for the next step without further purification. To a stirred suspension containing **S9** (400 mg, 1.00 mmol) and potassium carbonate (K_2CO_3) (1.52 g, 11.00 mmol) in acetonitrile (CH_3CN, 30 mL), 3-bromo-1-propyme (1.2 mL, 11.00 mmol) was added. The reaction mixture was subsequently sealed and refluxed for 12 hours under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was filtered to remove the precipitate and the solvent was removed under reduced pressure. The residue was further purified using column chromatography, employing a mixture of EtOAc/PE (v/v, 1:15) as the eluent to give **S10** as a white solid (262 mg, 48%). ^{1}H NMR (400 MHz, CDCl3) δ (ppm): 6.93 (d, J = 8.6 Hz, 8H), 6.70 (d, J = 8.6 Hz, 8H), 4.65 – 4.58 (m, 8H), 2.53 – 2.47 (m, 4H). NMR data were in accordance with literature.[5]

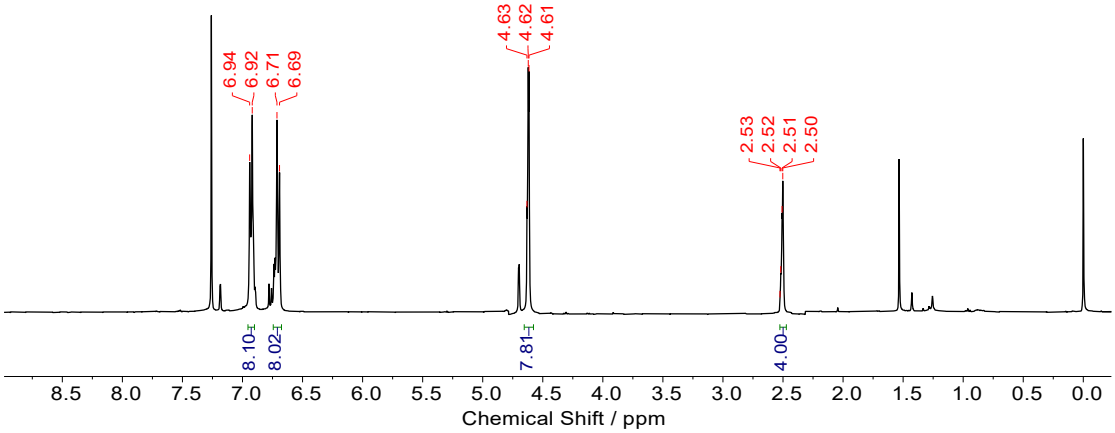


Fig. S16. ^{1}H NMR (400 MHz) spectrum of compound **S10** ($CDCl_3$, 298 K).

Synthesis of **TPE-G**: To a 25 mL round-bottomed flask, **S9** (200 mg, 0.36 mmol), 5-azidopentanenitrile (271 mg, 2.18 mmol), sodium ascorbate (15 mg, 0.07 mmol) and $CuSO_4 \cdot 5H_2O$ (19 mg, 0.07 mmol), THF (4 mL) and H_2O (0.8 mL) were added. Then the resulting mixture was vigorously stirred for 12 hours at 66 ℃ under a nitrogen atmosphere. After cooling to room temperature, the reaction mixture was filtered to remove the precipitate and the solvent was removed under reduced pressure. Then the residue was extracted by CH_2Cl_2 (3×100 mL), The combined organic phase was washed with saturated ammonium chloride solution, dried over anhydrous Na_2SO_4, filtered, and concentrated under a vacuum to give a crude product, which was further purified using column chromatography, employing a mixture of MeOH/EtOAc (v/v, 1:6) as the eluent to give **TPE-G** as a white powdered solid (300 mg, 78.9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.61 (s, 4H), 6.93 (d, J = 8.7 Hz, 8H), 6.72 (d, J = 8.8 Hz, 8H), 5.14 (s, 8H), 4.44 (t, J = 6.8 Hz, 8H), 2.41 (t, J = 7.0 Hz, 8H), 2.10 (dt, J = 14.8, 6.9 Hz, 8H), 1.70 (dt, J = 14.5, 7.2 Hz, 8H). NMR data were in accordance with literature.[5]

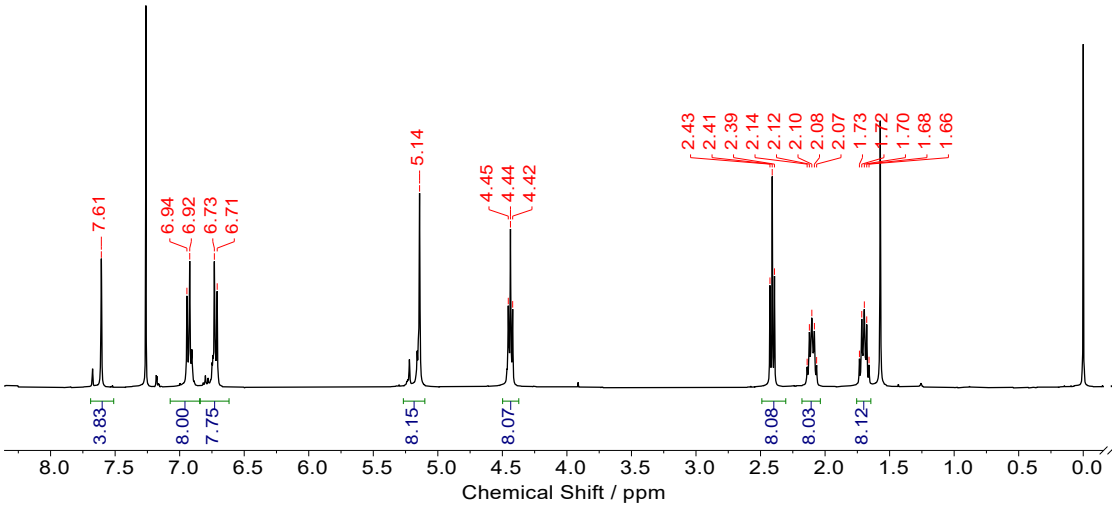


Fig. S17. ^{1}H NMR (400 MHz) spectrum of **TPE-G** ($CDCl_3$, 298 K).

3. Studies of photoisomerization of *bis*-RD-P[5]s

3.1 ^{1}H NMR spectra

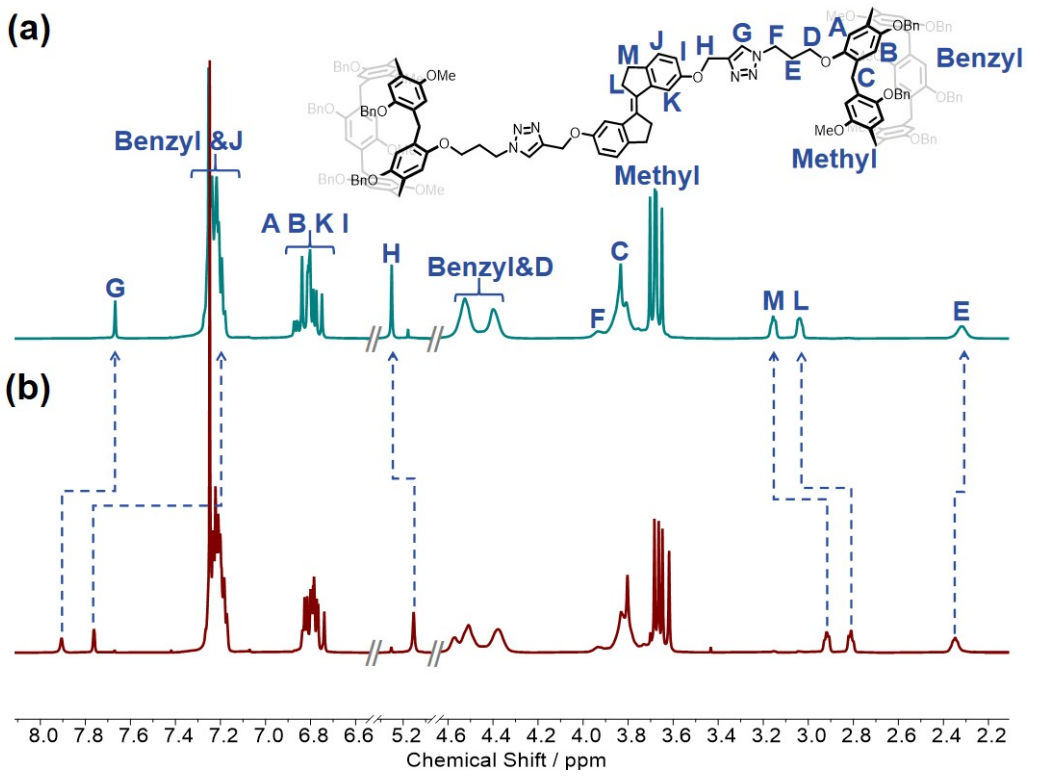


Fig. S18. Partial ^{1}H NMR spectra of ($CDCl_3$, 400 MHz, 298 K): (a) *bis*-RD-P[5]-**E2**; (b) ***bis*-RD-P[5]-Z2**.

3.2 Screening of solvents and concentrations of *bis*-RD-P[5]-E1

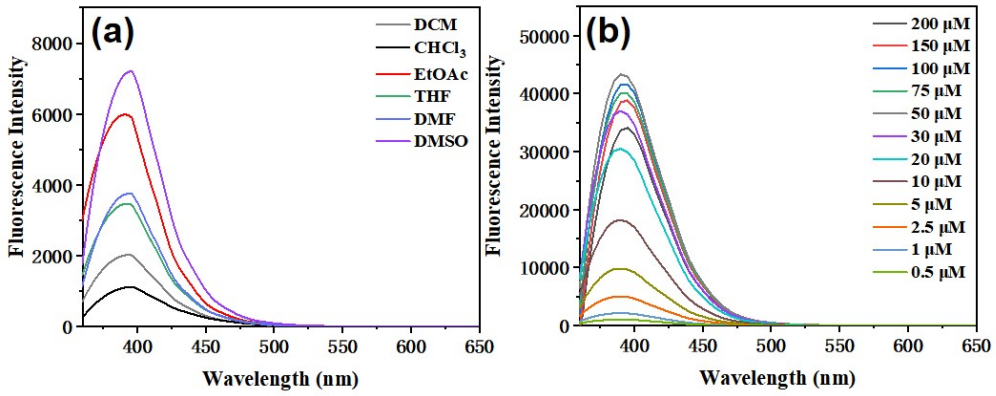


Fig. S19. Fluorescence spectra of *bis*-RD-P[5]-**E1** (a) in different solvent (b) under different concentration in EtOAc.

3.3 UV-vis spectra

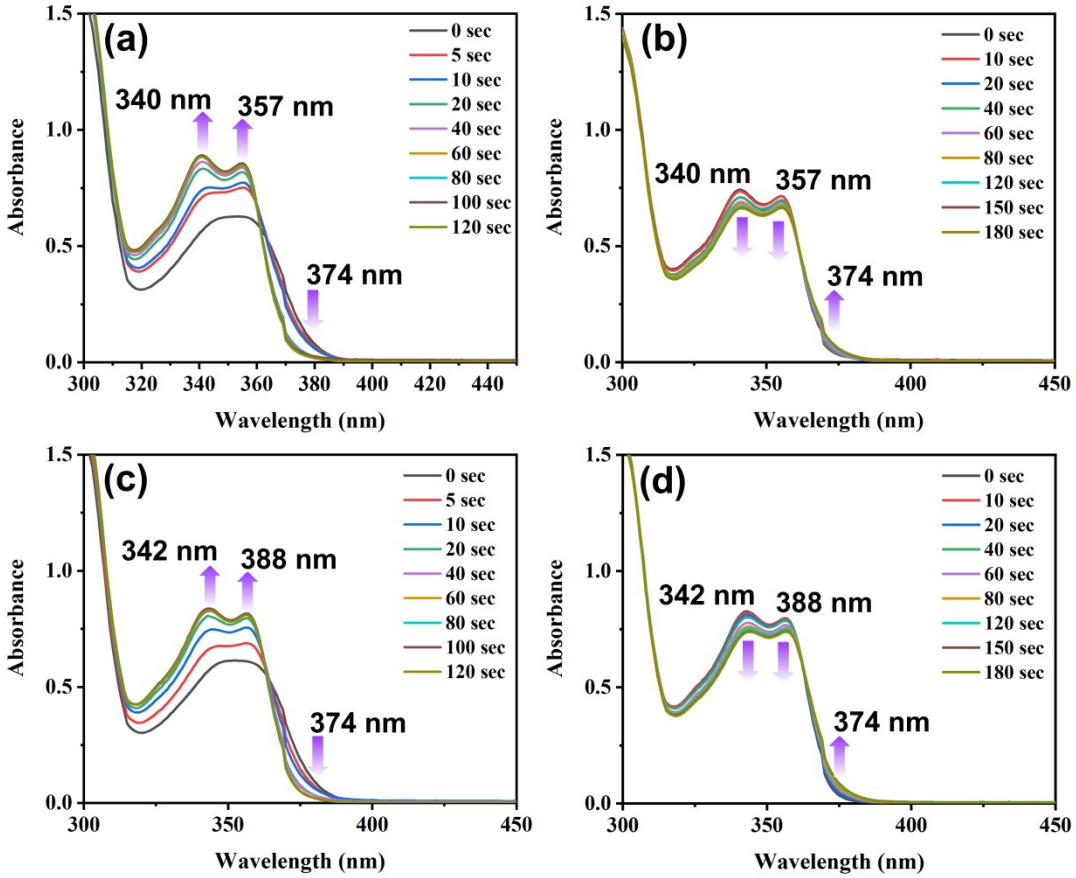


Fig. S20. UV absorbance spectra of *bis*-RD-P[5]s (c = 30 μM in EtOAc): (a) *bis*-RD-P[5]-**Z2**; (b) *bis*-RD-P[5]-**E2**; (c) *bis*-RD-P[5]-**Z1** (d) *bis*-RD-P[5]-**E1**, upon irradiation of (a), (c) at 385 nm and (b), (d) at 365 nm UV-light for different time periods.

3.4 Fluorescence intensity spectra

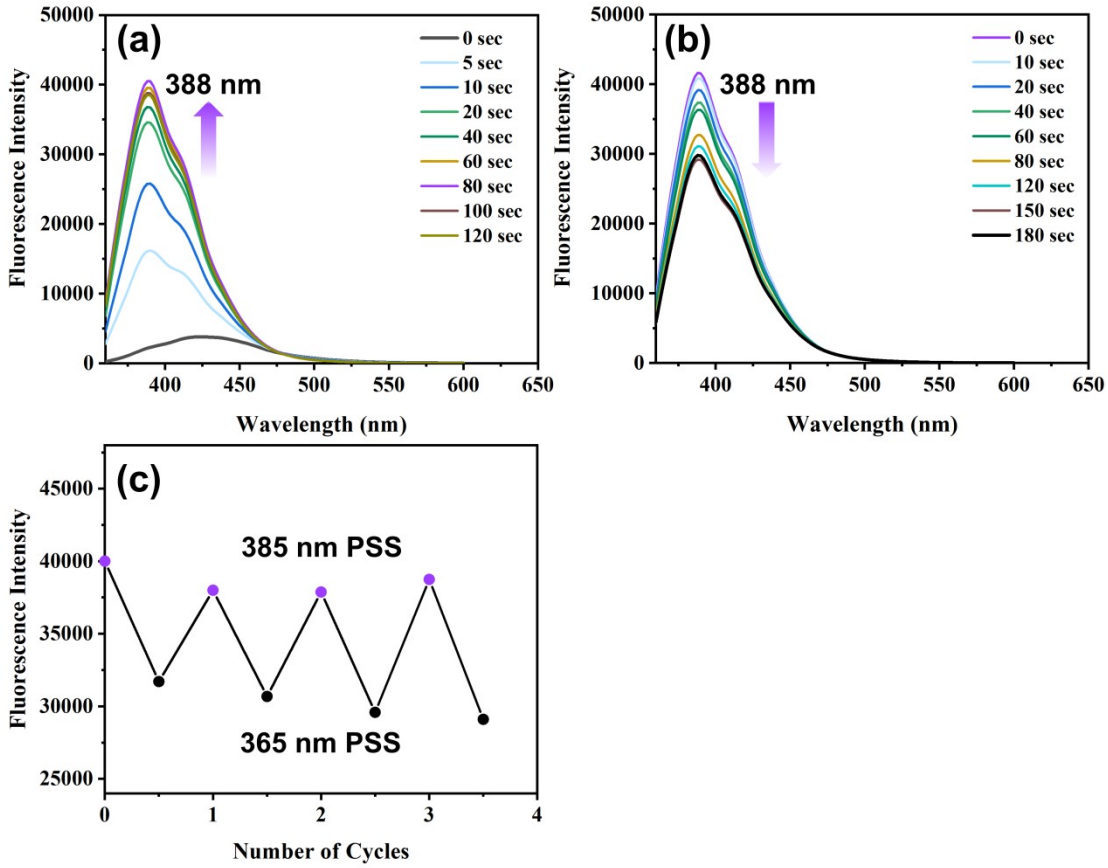


Fig. S21. Fluorescence spectra of *bis*-RD-P[5] **1** (c=30 μM in EtOAc) upon irradiation at UV-light (a) *bis*-RD-P[5]-**Z1** (λ_{ex} = 385 nm); (b) *bis*-RD-P[5]-**E1** (λ_{ex} = 365 nm) (c)Time-dependent fluorescence intensity changes.

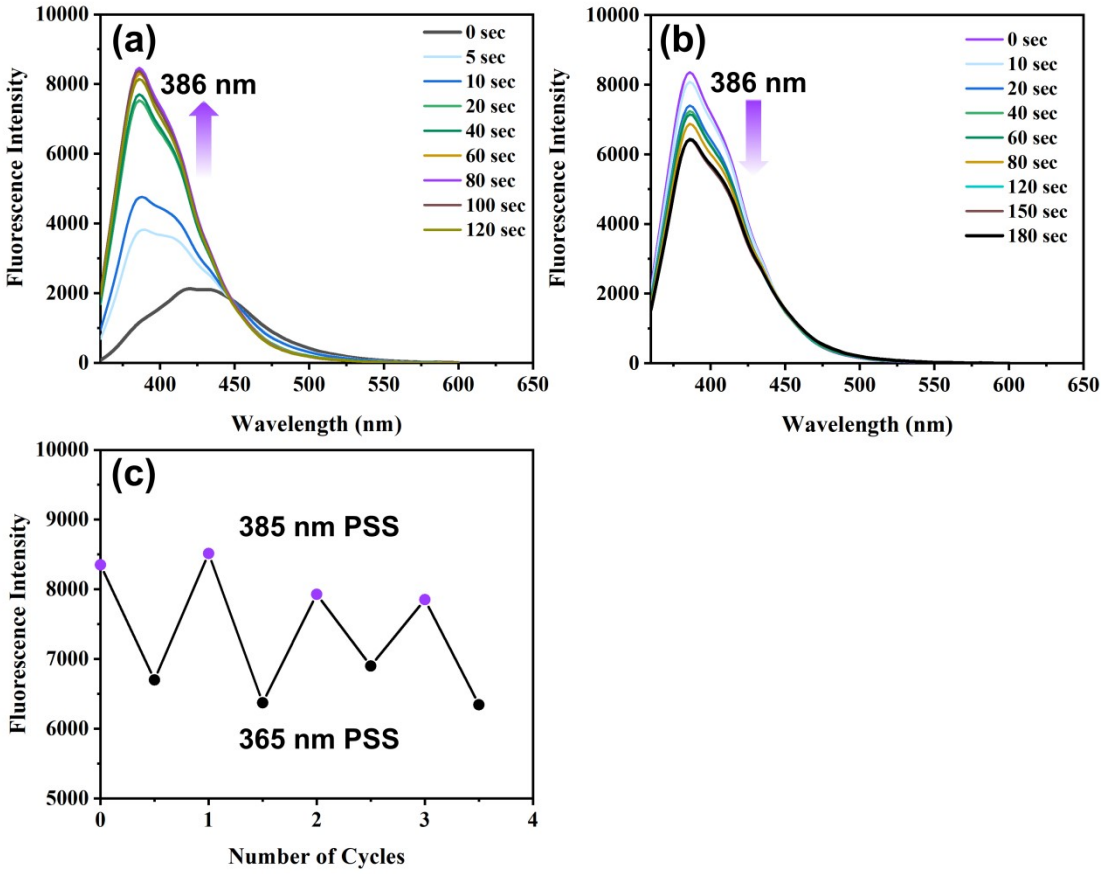


Fig. S22. Fluorescence spectra of *bis*-RD-P[5] **2** (c=30 μM in EtOAc) upon irradiation at UV-light (a) *bis*-RD-P[5]-**Z2** (λ_{ex} = 385 nm); (b) *bis*-RD-P[5]-**E2** (λ_{ex} = 365 nm) (c)Time-dependent fluorescence intensity changes.

4. UV-vis spectra of *bis*-RD-P[5]s

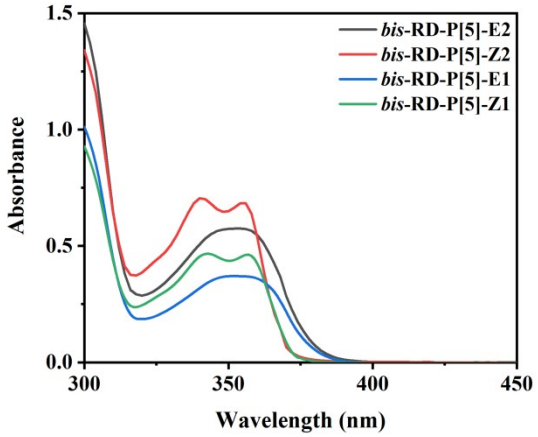


Fig. S23. Absorbance spectra of ***bis*-RD-P[5]s** (c = 30 μM in EtOAc).

5. Host–guest interaction between *bis*-RD-P[5]-E1 and TPE-G

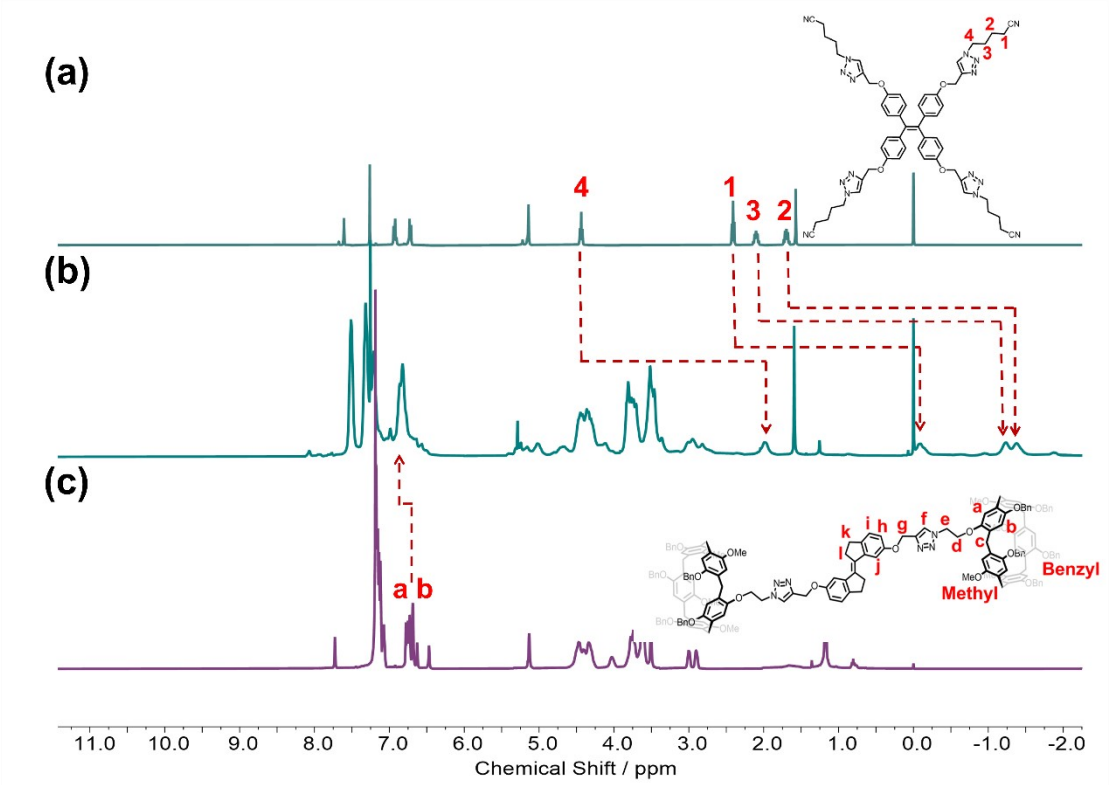


Fig. S24. Partial ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of (a) **TPE-G** (2.5 mM); (b) *bis*-RD-P[5]-**E1** (5 mM)⊃**TPE-G** (2.5 mM); (c) ***bis*-RD-P[5]-E2** (5 mM).

6. 2D COSY spectra of the *bis*-RD-P[5]-E1⊃TPE-G

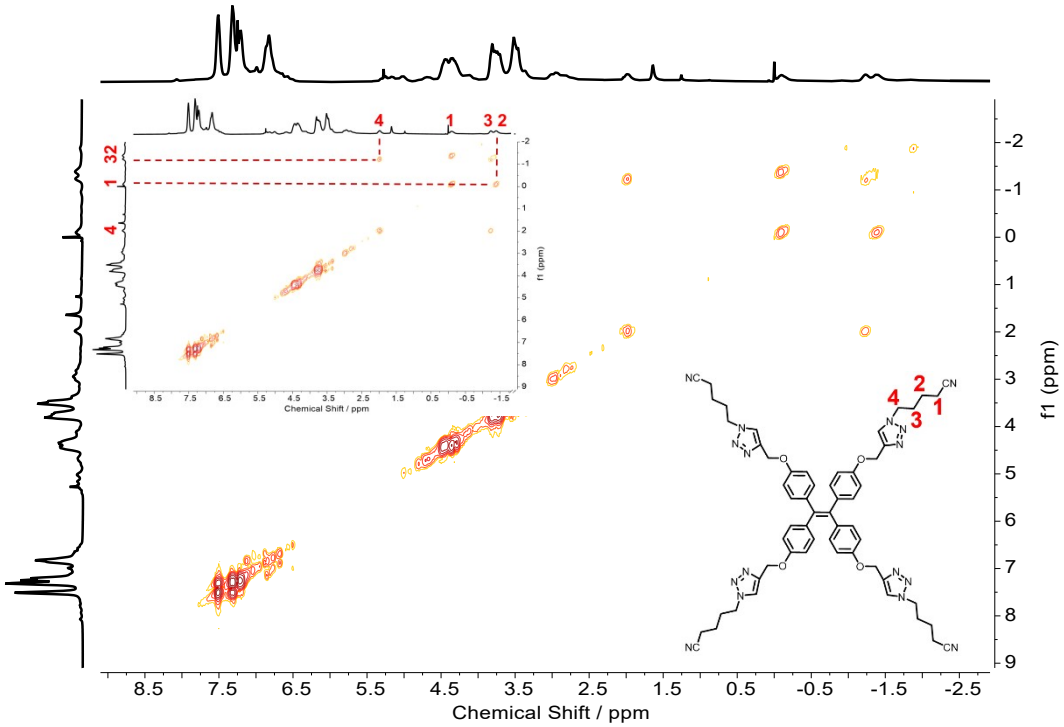


Fig. S25. COSY spectra (400 MHz) of *bis*-RD-P[5]-**E1** (20 mM)⊃**TPE-G** (10 mM) ($CDCl_3$, 298 K).

7. Job plot of *bis*-RD-P[5]-E1 with TPE-G

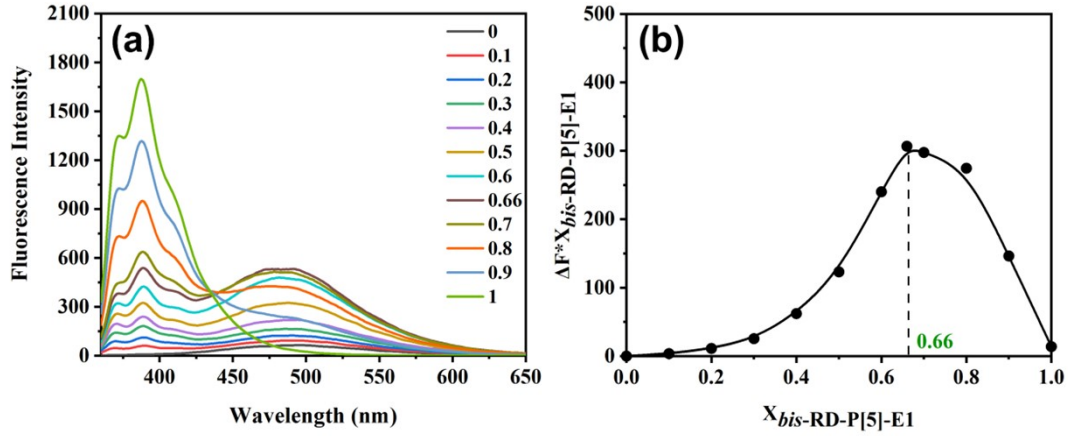


Fig. S26. (a) Fluorescence spectra of the ratio of *bis*-RD-P[5]-**E1** to **TPE-G** from 0 to 1; (b)Job's plot of *bis*-RD-P[5]-**E1** and **TPE-G** in $CHCl_3$, ([Host] + [Guest] = 20 μM); Result calculated by multiplying the changes in fluorescence intensity at 496 nm by the ratio of *bis*-RD-P[5]-**E1** to **TPE-G** from 0 to 1.

8. The limit of detection (LOD) of detecting Pd^{2+}

The sensing property of *bis*-RD-P[5]-**E1⊃TPE-G** (20 μM:7 μM) for Pd^{2+} was further investigated by fluorescence titration experiment in THF:H_2O (v/v, 6:4) co-solvent. As Fig. S28. shown, the fluorescence intensity decreased gradually with the increase of Pd^{2+} equivalent concentration. According to the LOD＝k*SD/slope (K= 3, SD was the standard deviation of the blank solution, and slope was the slope value of the regression line) equation, SD=103.83, slope= -611.48×10^{6} and LOD=5.09×10^{-7} mol/L.[6,7,8]

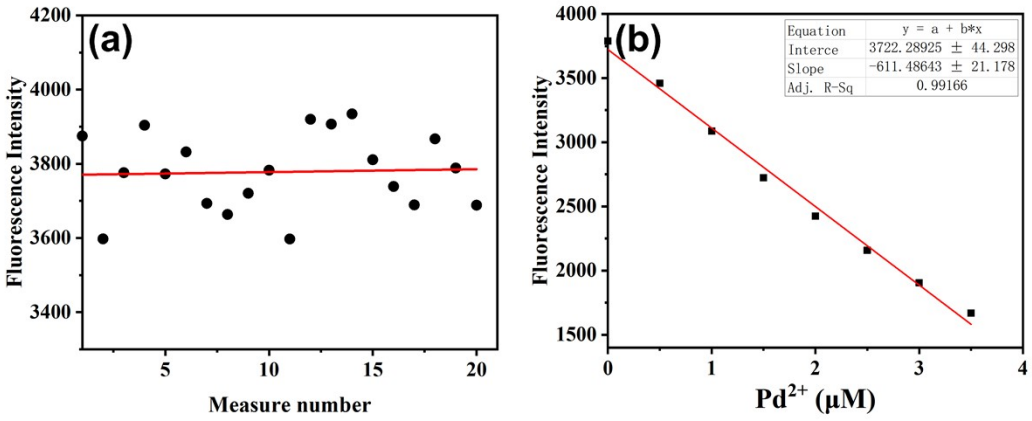


Fig. S27. (a) Twenty measurements of fluorescence intensity at 460 nm without added Pd^{2+} to *bis*-RD-P[5]-**E1⊃TPE-G** (20 μM:7 μM) in THF:H_2O (v/v, 6:4) co-solvent. (b) The fluorescence intensity at 460 nm with adding Pd^{2+} to *bis*-RD-P[5]-**E1⊃TPE-G** (20 μM:7 μM) in THF:H_2O (v/v, 6:4) co-solvent.

9. TEM and DLS results

TEM and DLS measurements were used to further study the size and morphology of the supramolecular aggregates formed by *bis*-RD-P[5]-**E1** and **TPE-G**. The steps are as follows: Firstly, we configured 8 mL solution 1 of *bis*-RD-P[5]-**E1** (20 μM)⊃**TPE-G** (3 μM) in THF:H_2O (v/v, 6:4) co-solvent, after which we sonicated solution 1 for 30 min, and left it for 5 min. Secondly, we took 4 mL of solution 1 and added 50 μM of Pd^{2+} to prepare solution 2, and at the step, the DLS tests were separately performed using 1 ml of solution 1 and solution 2. Lastly, we took 5 μL of each of the solutions respectively and added them dropwise on top of the copper grids, and then added another 5 μL dropwise after drying. Air-drying was carried out for 24 h, and then the TEM tests were carried out separately.

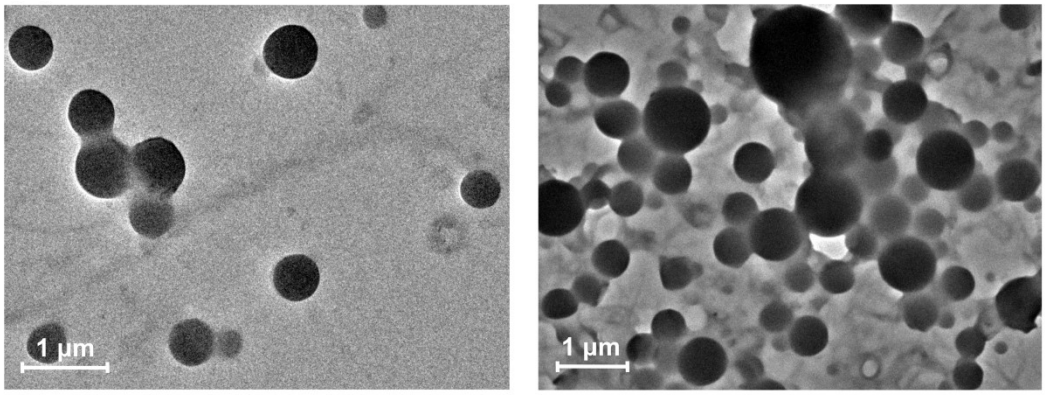


Fig. S28. TEM images of *bis*-RD-P[5]-**E1** (20 μM)⊃**TPE-G** (3 μM) in THF:H_2O (v/v, 6:4) co-solvent.

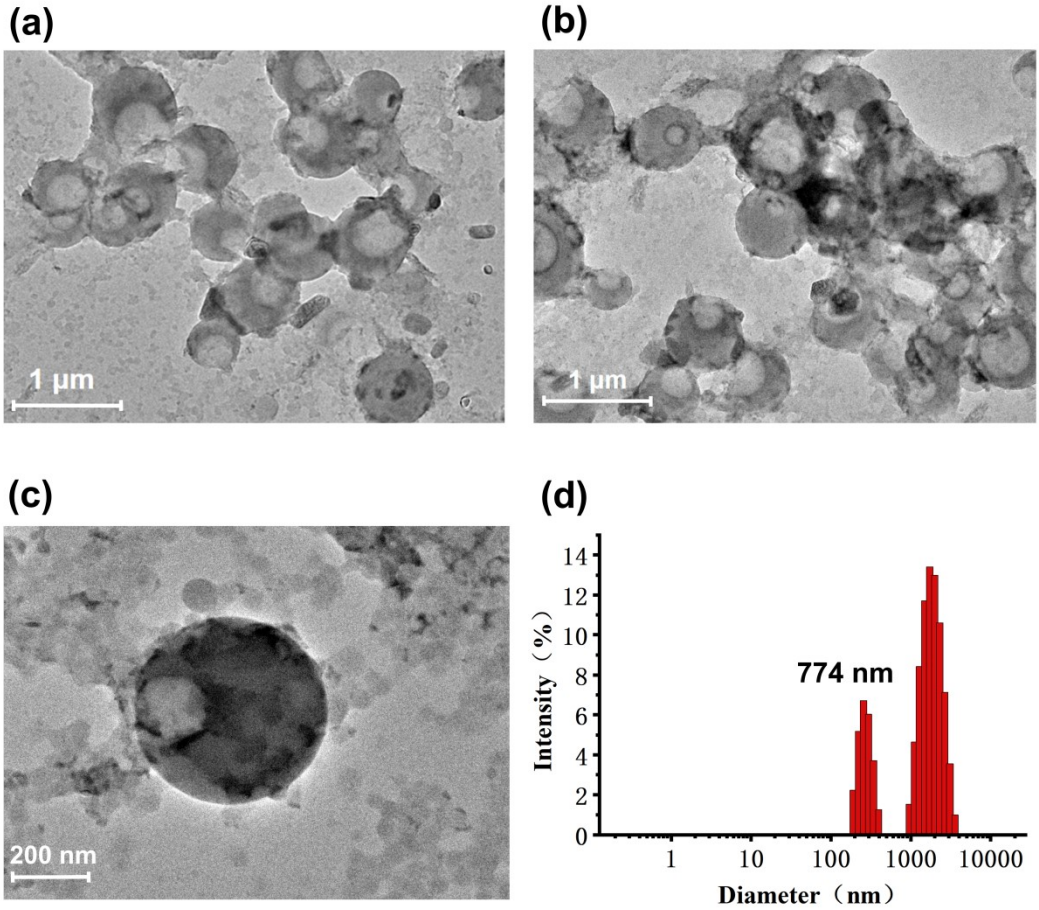


Fig. S29. *bis*-RD-P[5]-**E1** (20 μM)⊃**TPE-G** (3 μM) after adding Pd^{2+} in THF:H_2O (v/v, 6:4) co-solvent; (a), (b), (c) TEM images, (d) DLS result.

10. DOSY experiment

Two-dimensional diffusion-ordered ^{1}H NMR spectroscopy (DOSY) is a sensitive technique to study the self-assembly behavior of supramolecular polymers, since aggregates of different particle sizes exhibit different diffusion coefficients. DOSY experiment was carried out, which provided reliable information about the dimensions of the supramolecular aggregate systems. From Fig. S30., the measured weight average diffusion coefficient (D) of *bis*-RD-P[5]-**E1**⊃**TPE-G** decreased remarkably from 2.3×10^{-10} to 3.8×10^{-11} m^2/s, as the *bis*-RD-P[5]-**E1** concentration increased from 5.0 to 80 mM. The result revealed that the formation of high-molecular-weight polymeric species was intrinsically concentration dependent.

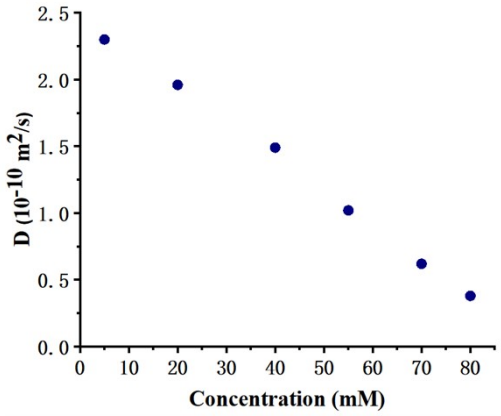


Fig. S30. Concentration dependence of diffusion coefficient D (from ^{1}H NMR spectroscopy; 400 MHz, $CDCl_3$, 293 K) of *bis*-RD-P[5]-**E1**⊃**TPE-G**.

11. References

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