

Electronic Supplementary Information

Supramolecular polymerization induced self-assembly into micelle and vesicle *via* acid-base controlled formation of fluorescence responsive supramolecular hyperbranched polymers

Lijie Li, Xiaorui Zheng, Bingran Yu, Lipeng He, Jing Zhang, Haomin Liu, Yong Cong and Weifeng Bu*

Key Laboratory of Nonferrous Metals Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou City, Gansu Province, China, E-mail: buwf@lzu.edu.cn

Instruments and Materials

¹H and ¹³C NMR spectra were recorded on a JNM-ECS400 spectrometer or Varian 600 NMR in CD₂Cl₂ and/or CDCl₃ with TMS as an internal standard. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were obtained on a Bruker APEX II FT-MS mass spectrometer. Luminescence measurements were made on a Hitachi F-7000 spectrofluorimeter with a xenon lamp as the excitation source. Dynamic light scattering (DLS) measurements were performed on a Brookhaven BI-200SM spectrometer. TEM images were obtained with JEM-2100 operating at 200 kV. All measurements were carried out at room temperature. All reaction operations were performed under an anhydrous Ar atmosphere. Anhydrous tetrahydrofuran (THF) were distilled over Na and benzophenone. Dichloromethane and *i*-Pr₂NH was dried over CaH₂.

Synthetic procedures:

Compounds **3**^{s1} and 1,3,5-Triethynylbenzene^{s2} were synthesized according to the procedures in the related literatures and showed identical ¹H NMR spectra to those reported therein.

Compound 4: 1,3,5-triethynylbenzene (0.20 g, 1.33 mmol), **3** (3.50 g, 5.99 mmol), CuI (0.10 g, 0.53 mmol) and Pd(PPh₃)₄ (0.31 g, 0.27 mmol) were added to a

mixture solvent of THF (49 mL) and *i*-Pr₂NH (49 mL) in an oven dried Schlenk flask under an argon atmosphere. The resulting mixture was stirred at 65 °C for 10 h. After removing the solvents, the crude product was extracted by dichloromethane (3 × 50 mL) and dried over anhydrous MgSO₄. Further purification was achieved by column chromatography (SiO₂) using petroleum ether as eluent to afford **4** as a yellow oil (1.7 g, 89% yield). ¹H NMR (400 MHz, CDCl₃, ppm), δ: 7.60 (s, 3H, Ar), 6.97-6.96 (d, 6H, Ar), 3.94-3.83 (m, 12H, OCH₂), 1.81-1.76 (m, 6H, CH), 1.63-1.28 (m, 48H, CH₂), 1.01-0.86 (m, 36H, CH₃), 0.28 (s, 27H, SiMe₃). ¹³C NMR (100 MHz, CDCl₃, ppm), δ: 154.63, 154.04, 134.12, 124.54, 117.29, 116.76, 114.27, 113.96, 101.42, 100.43, 93.45, 87.43, 77.68, 77.36, 77.04, 72.38, 71.99, 39.95, 39.87, 31.00, 30.84, 29.48, 29.44, 23.43, 23.42, 14.46, 14.43, 11.61.

Compound 5: 4 (1.00 g, 0.70 mmol) and K₂CO₃ (1.15 g, 8.33 mmol) were added to a THF/MeOH mixture solvent (56 mL, volume ratio, 1/1) in a round bottom flask. The resulting mixture was stirred at room temperature for 5 h and then the solvent was removed. The crude product was extracted by dichloromethane (3 × 50 mL) and dried with anhydrous Na₂SO₄. Further purification was achieved by column chromatography (SiO₂, petroleum ether as eluent). The product **5** was isolated as a yellow oil. (0.82 g, 96% yield). ¹H NMR (400 MHz, CDCl₃, ppm), δ: 7.53 (s, 3H, Ar), 6.91-6.90 (d, 6H, Ar), 3.82-3.80 (m, 12H, OCH₂), 3.26 (s, 3H, ≡CH), 1.74-1.69 (m, 6H, CH), 1.52-1.18 (m, 48H, CH₂), 0.92-0.77 (m, 36H, CH₃). ¹³C NMR (100 MHz, CDCl₃, ppm), δ: 154.67, 154.65, 154.06, 134.18, 124.50, 117.75, 117.06, 114.30, 113.33, 113.31, 93.43, 87.26, 82.77, 80.23, 77.68, 77.36, 77.04, 72.40, 72.36, 39.83, 39.66, 30.80, 29.46, 29.35, 24.20, 23.42, 23.37, 14.41, 11.60, 11.45.

Compound 6a and 6b: 5 (1.04 g, 0.85 mmol), 4-iodobenzaldehyde (197 mg, 0.68 mmol), CuI (5.72 mg, 0.03 mmol) and Pd(PPh₃)₄ (46.2 mg, 0.04 mmol) were added to a mixture solvent of THF (54 mL) and *i*-Pr₂NH (54 mL) in an oven dried Schlenk flask under an argon atmosphere. The mixture was stirred at 20 °C for 6 h. The solvent was removed and then the crude product was extracted by dichloromethane (3 × 25 mL). The organic layers were merged and dried over anhydrous MgSO₄. Further purification was achieved by column chromatography (SiO₂) using petroleum

ether/dichloromethane (10/1) as eluent. The product **6a** (124 mg, 11% yield) and **6b** (146 mg, 12% yield) were isolated as a yellow oil, respectively.

6a: ^1H NMR (400 MHz, CDCl_3 , ppm), δ : 10.03 (s, 1H, CHO), 7.89-7.87 (d, 2H, Ar), 7.68-7.66 (d, 2H, Ar), 7.61 (s, 3H, Ar), 7.04 (s, 1H, Ar), 7.02 (s, 1H, Ar), 6.99 (s, 2H, Ar), 6.98 (s, 2H, Ar), 3.95-3.88 (m, 12H, OCH_2), 3.35 (s, 2H, $\equiv\text{CH}$), 1.84-1.77 (m, 6H, CH), 1.63-1.34 (m, 48H, CH_2), 1.01-0.87 (m, 36H, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ : 191.76, 154.72, 154.41, 154.23, 154.10, 135.69, 134.22, 132.23, 130.18, 129.95, 124.55, 124.48, 117.83, 117.14, 114.70, 114.38, 113.36, 93.90, 93.45, 90.60, 87.36, 87.30, 82.76, 80.27, 77.68, 77.56, 77.36, 77.04, 72.53, 72.49, 72.46, 39.95, 39.90, 39.71, 29.49, 24.37, 23.45, 23.40, 14.45, 11.65, 11.63, 11.49.

6b: ^1H NMR (400 MHz, CDCl_3 , ppm), δ : 9.96 (s, 2H, CHO), 7.82-7.80 (d, 4H, Ar), 7.61-7.59 (d, 4H, Ar), 7.55 (s, 3H, Ar), 6.97 (s, 2H, Ar), 6.95 (s, 2H, Ar), 6.92 (s, 1H, Ar), 6.91 (s, 1H, Ar), 3.87-3.81 (m, 12H, OCH_2), 3.28 (s, 1H, $\equiv\text{CH}$), 1.75-1.74 (m, 6H, CH), 1.54-1.27 (m, 48H, CH_2), 0.93-0.81 (m, 36H, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ : 191.77, 154.39, 154.21, 135.67, 132.30, 129.95, 124.53, 116.96, 116.87, 114.61, 113.65, 94.35, 93.84, 90.55, 87.42, 77.68, 77.36, 77.04, 72.48, 72.23, 39.92, 39.87, 31.01, 29.48, 23.46, 23.43, 14.41, 14.44, 11.65, 11.62.

Compound 8a: **6a** (0.24 g, 0.17 mmol), **7** (0.25 g, 0.44 mmol), CuI (7.62 mg, 0.04 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (20.1 mg, 0.02 mmol) were added to a mixture solvent of THF (12 mL) and *i*-Pr₂NH (6 mL) in an oven dried Schlenk flask under an argon atmosphere. The mixture was stirred at 65 °C for 4 d. The solvent was removed and then the crude product was extracted by dichloromethane (3 × 25 mL). The organic layers were merged and dried over anhydrous MgSO_4 . Further purification was achieved by column chromatography (SiO_2) using dichloromethane/acetone (10/1) as eluent. The product **8a** was isolated as a yellow oil (50.0 mg, 13% yield). ^1H NMR (400 MHz, CD_2Cl_2 , ppm), δ : 9.94 (s, 1H, CHO), 7.81-7.79 (d, 2H, Ar), 7.61-7.59 (d, 2H, Ar), 7.55 (s, 3H, Ar), 7.27-7.20 (m, 4H, Ar), 7.04-6.97 (m, 16H, Ar), 4.30-4.26 (m, 16H, OCH_2), 3.88-3.87 (m, 12H, OCH_2), 3.77-3.70 (m, 16H, OCH_2), 1.57-1.54 (m, 16H, OCH_2), 1.74-1.60 (m, 6H, CH), 1.55-1.42 (m, 48H, CH_2), 0.93-0.80 (m, 36H, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2 , ppm), δ : 191.27, 153.99, 153.71, 148.82, 148.34,

147.99, 147.79, 135.55, 133.67, 131.90, 129.45, 124.34, 123.52, 119.79, 116.57, 114.05, 113.27, 110.00, 93.91, 92.94, 89.93, 87.27, 77.62, 74.15, 72.11, 71.90, 69.27, 69.18, 68.88, 68.72, 68.56, 68.40, 67.45, 53.76, 53.58, 53.40, 53.22, 53.04, 52.80, 47.81, 44.40, 39.60, 30.65, 30.08, 29.66, 29.14, 29.11, 26.16, 24.03, 23.11, 23.07, 22.67, 18.62, 13.90, 11.10, 11.02.

Compound AB₂-1: 8a (88.7 mg, 0.04 mmol) and benzylamine (4.30 mg, 0.04 mmol) were dissolved in anhydrous dichloromethane (8 mL) in an oven dried Schlenk flask (25 mL) under an argon atmosphere. The resulting solution was stirred at 35 °C for 1d. The in-situ ¹H NMR spectrum revealed that 98% of **8a** converted into a Schiff-base form. Subsequently sodium triacetoxyborohydride (29.7 mg, 0.14 mmol) was added under an argon atmosphere. The resulting mixture was stirred at room temperature for another day. The solvent was removed and then the crude product was purified by recrystallization in a chloroform/methanol mixture solvent (1/3). The final product **AB₂-1** was isolated as a claybank solid (57.0 mg, 63% yield). ¹H NMR (400 MHz, CD₂Cl₂, ppm), δ : 7.54 (s, 3H, k, Ar), 7.42-7.41 (d, 2H, o, Ar), 7.30-7.23 (m, 6H, x, t, n, Ar), 7.18-7.17 (d, 1H, w, Ar), 7.04-7.02 (d, 2H, q, Ar), 6.97-6.95 (m, 7H, i, j, l, m, p, Ar), 6.80 (s, 8H, s, Ar), 6.78-6.76 (d, 2H, r, Ar), 4.05-4.03 (m, 16H, α , OCH₂), 3.86-3.85 (m, 28H, β , a, OCH₂), 3.74 (s, 2H, θ , NH₂), 3.72 (s, 2H, v, NH₂), 3.69-3.67 (m, 16H, γ , OCH₂), 1.76-1.71 (m, 6H, b, CH), 1.52-1.27 (m, 48H, c, d, e, g, CH₂), 0.94-0.79 (m, 36H, f, h, CH₃). ¹³C NMR (100 MHz, CD₂Cl₂, ppm), δ : 154.08, 153.84, 153.70, 149.71, 149.12, 148.67, 133.71, 131.55, 128.44, 125.27, 124.47, 121.46, 116.67, 116.49, 115.98, 114.68, 114.33, 113.58, 113.23, 112.93, 95.14, 92.90, 87.43, 84.66, 72.20, 71.99, 71.15, 69.94, 69.76, 69.33, 53.88, 53.70, 53.52, 53.34, 53.16, 39.72, 30.76, 30.73, 29.78, 29.25, 13.99, 11.20. HR-ESI-MS (m/z), [C₂₉₂H₃₇₄N₂O₄₄ + H₂]²⁺ calculated: 2308.8674; found: 2308.8711.

Compound 8b: 6b (100 mg, 0.07 mmol), **7** (45.9 mg, 0.08 mmol), CuI (1.34 mg, 0.007 mmol) and Pd(PPh₃)₄ (16.19 mg, 0.014 mmol) were dissolved to a mixture solvent of THF (6 mL) and *i*-Pr₂NH (3 mL) in an oven dried Schlenk flask under an argon atmosphere. The mixture was stirred at 65 °C for 3d. The solvent was removed and then the crude product was extracted by dichloromethane (3 × 25 mL). The

organic layers were merged and dried over anhydrous MgSO_4 . Further purification was achieved by column chromatography (SiO_2) using dichloromethane/acetone (10/1) as eluent. The product **8b** was isolated as a yellow oil (24.9 mg, 19% yield). ^1H NMR (400 MHz, CDCl_3 , ppm), δ PPM: 9.95 (s, 2H, CHO), 7.82-7.79 (d, 4H, Ar), 7.61-7.59 (d, 4H, Ar), 7.55 (s, 3H, Ar), 7.05-7.03 (d, 2H, Ar), 6.97-6.92 (m, 7H, Ar), 6.82 (s, 5H, Ar), 6.76-6.74 (d, 1H, Ar), 4.09-4.07 (m, 8H, OCH_2), 3.87-3.86 (m, 20H, OCH_2), 3.78 (s, 8H, OCH_2), 1.77-1.74 (m, 6H, CH), 1.48-1.28 (m, 48H, CH_2), 0.94-0.80 (m, 36H, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , ppm), δ : 191.74, 154.36, 154.26, 154.18, 153.95, 135.64, 134.23, 132.28, 130.12, 129.93, 124.67, 124.45, 116.94, 116.86, 114.64, 113.59, 94.30, 93.89, 93.29, 90.55, 87.33, 77.68, 77.57, 77.36, 77.04, 72.47, 70.23, 69.73, 39.90, 39.85, 30.99, 29.47, 23.44, 23.41, 14.45, 14.42, 11.63, 11.60.

Compound AB₂-2: 8b (120 mg, 0.064 mmol), benzylamine (13.7 mg, 0.128 mmol) were dissolved in anhydrous dichloromethane (12 mL) in an oven dried Schlenk flask under an argon atmosphere. The resulting mixture was allowed to stir at 35 °C for 1 d. The in-situ ^1H NMR spectrum revealed that 98% of **8b** converted into a Schiff-base form. Subsequently sodium triacetoxyborohydride (108.5 mg, 0.512 mmol) was added under the argon atmosphere. The resulting solution was stirred at room temperature for another day. The solvent was removed and then the crude product was purified by recrystallization in a chloroform/methanol mixture solvent (1/3). The final product **AB₂-2** was isolated as a claybank solid (98.0 mg, 76% yield). ^1H NMR (400 MHz, CD_2Cl_2 , ppm), δ : 7.54 (s, 3H, k, Ar), 7.43-7.41 (d, 4H, o, Ar), 7.30-7.24 (m, 12H, x, t, n, Ar), 7.19-7.17 (d, 2H, w, Ar), 7.04-7.02 (d, 1H, q, Ar), 6.98-6.96 (m, 7H, i, j, l, m, p, Ar), 6.81 (s, 4H, s, Ar), 6.78-6.76 (d, 1H, r, Ar), 4.05-4.03 (m, 8H, α , OCH_2), 3.86-3.79 (m, 8H, β , OCH_2), 3.75 (s, 4H, θ , NH_2), 3.72 (s, 4H, ν , NH_2), 3.70 (s, 8H, γ , OCH_2), 1.76-1.70 (m, 6H, b, CH), 1.59-1.28 (m, 48H, c, d, e, g, CH_2), 0.94-0.81 (m, 36H, f, h, CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2 , ppm), δ : 154.07, 153.83, 153.70, 149.73, 149.14, 148.69, 141.38, 140.63, 133.72, 131.51, 128.39, 128.26, 128.20, 126.95, 125.26, 124.45, 121.86, 121.44, 116.70, 114.49, 114.32, 95.04, 92.98, 87.40, 85.75, 72.20, 72.04, 71.25, 71.16, 69.96, 69.79, 69.35, 53.88, 53.70, 53.52, 53.34, 53.16, 39.76, 39.72, 30.77, 30.74, 29.25, 23.24, 14.01,

13.98, 11.21, 11.14. HR-ESI-MS (m/z), [C₁₃₆H₁₇₀N₂O₁₄ + H]⁺ calculated: 2058.2881, found: 2058.2847.

¹H and ¹³C NMR spectra:

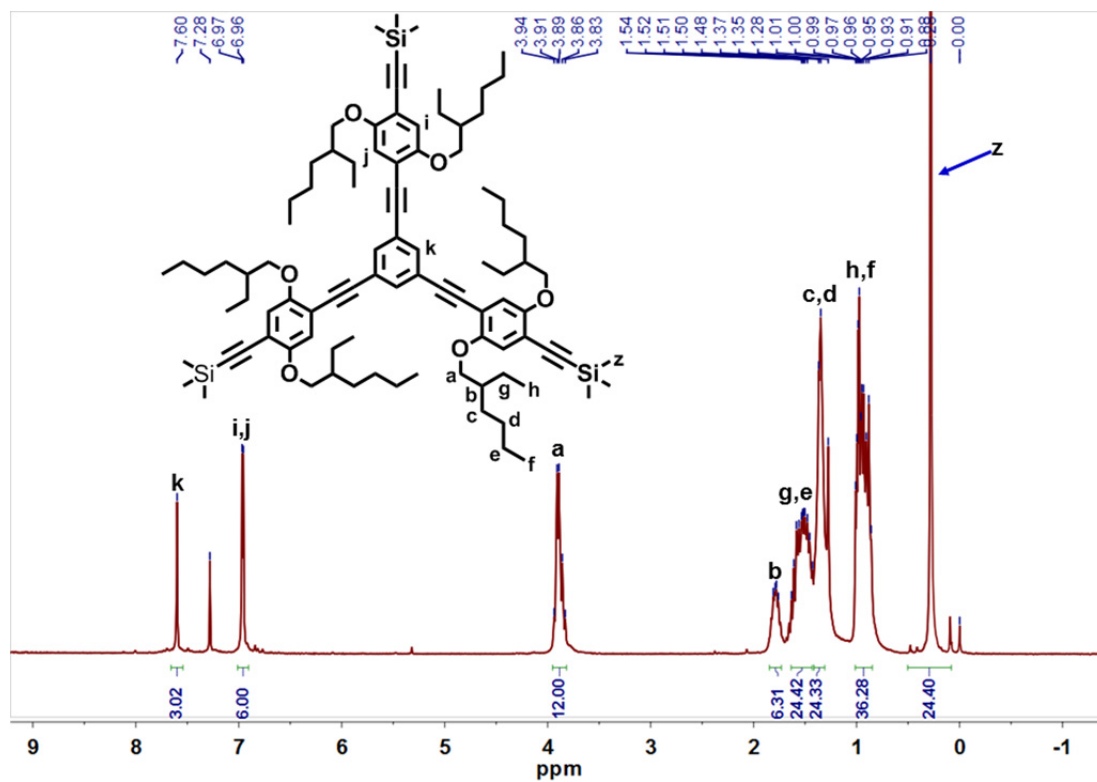


Fig. S1 ¹H NMR spectrum of 4.

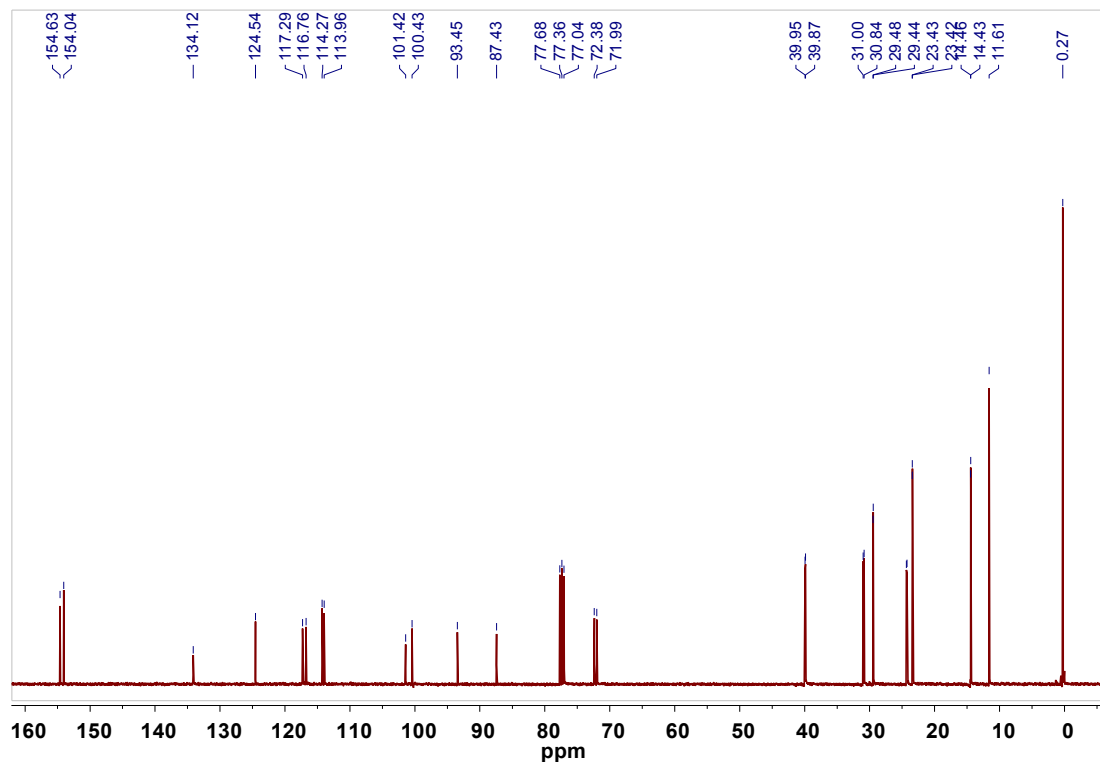


Fig. S2 ^{13}C NMR spectrum of 4.

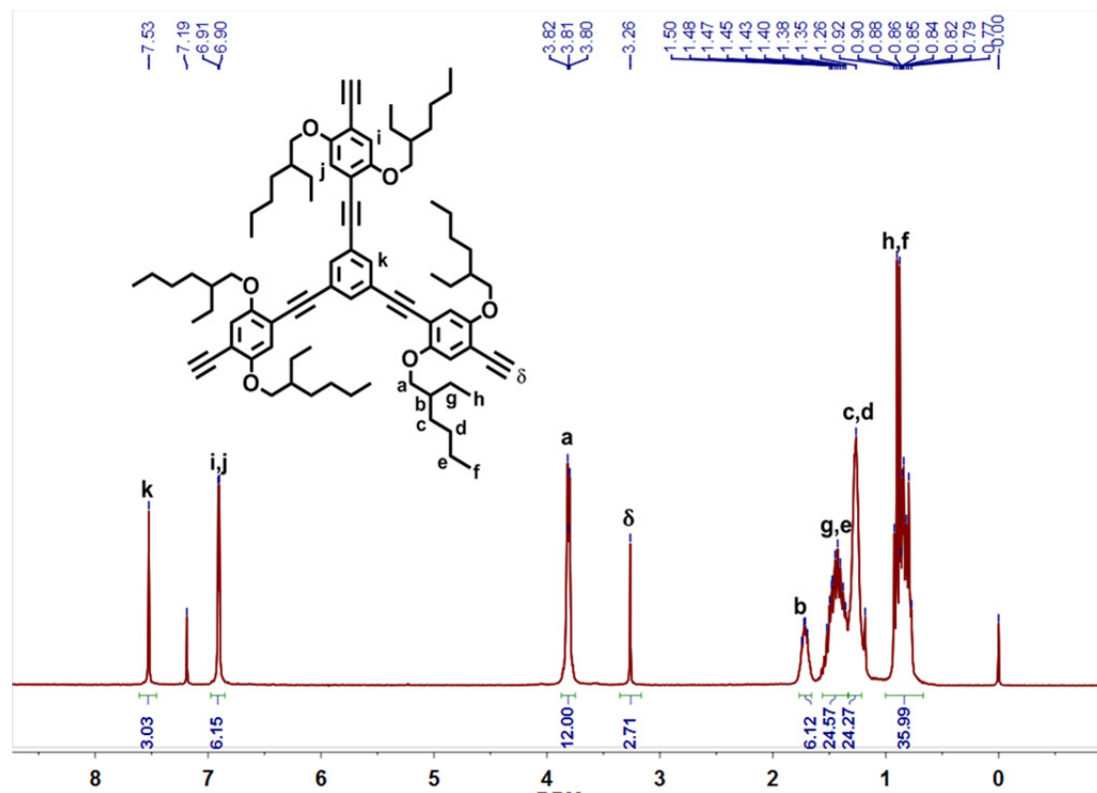


Fig. S3 ^1H NMR spectrum of 5.

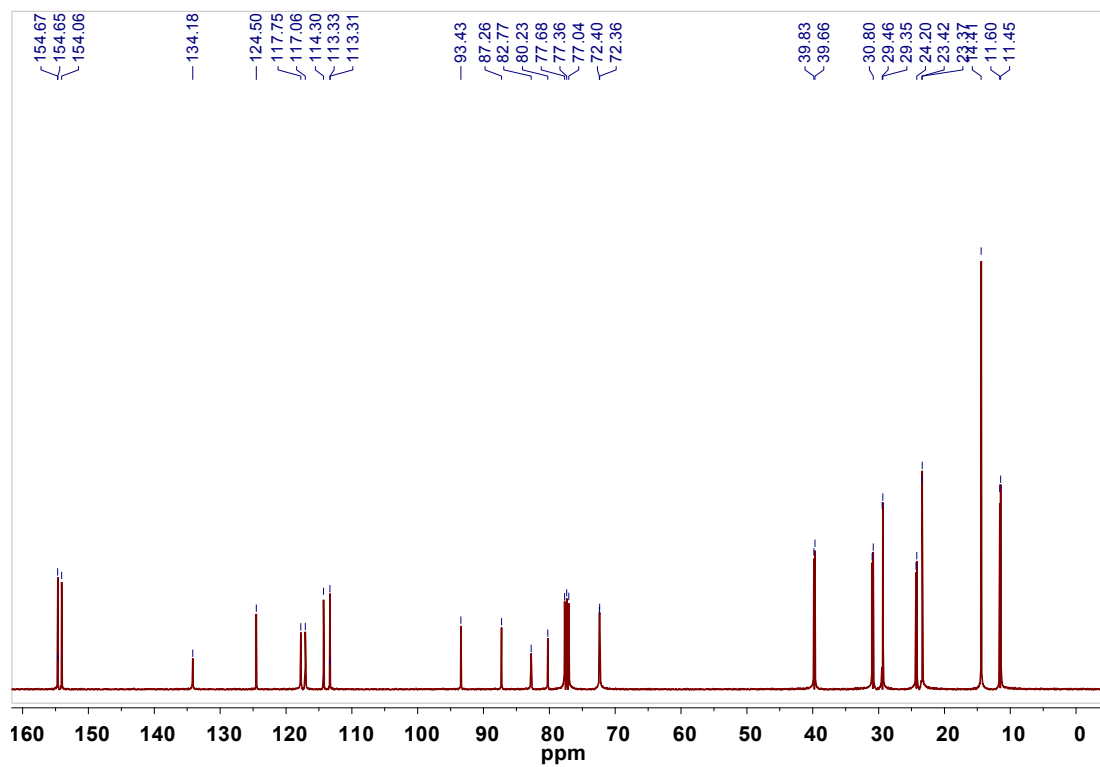


Fig. S4 ^{13}C NMR spectrum of **5**.

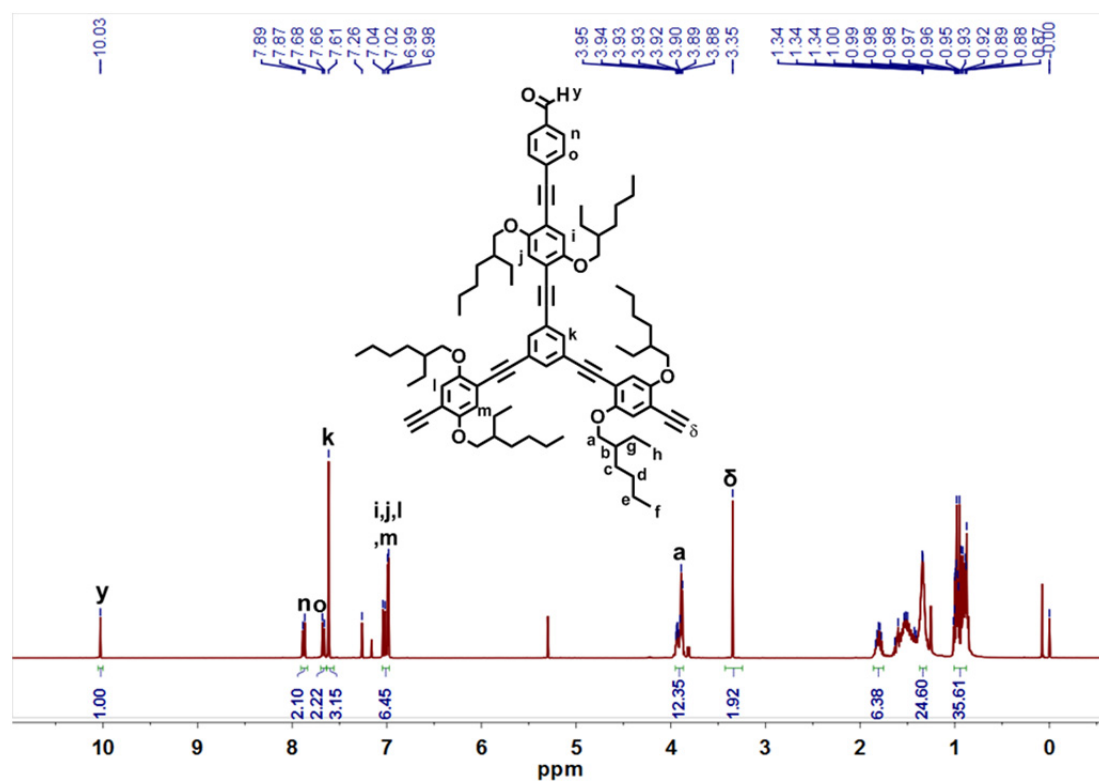


Fig. S5 ^1H NMR spectrum of **6a**.

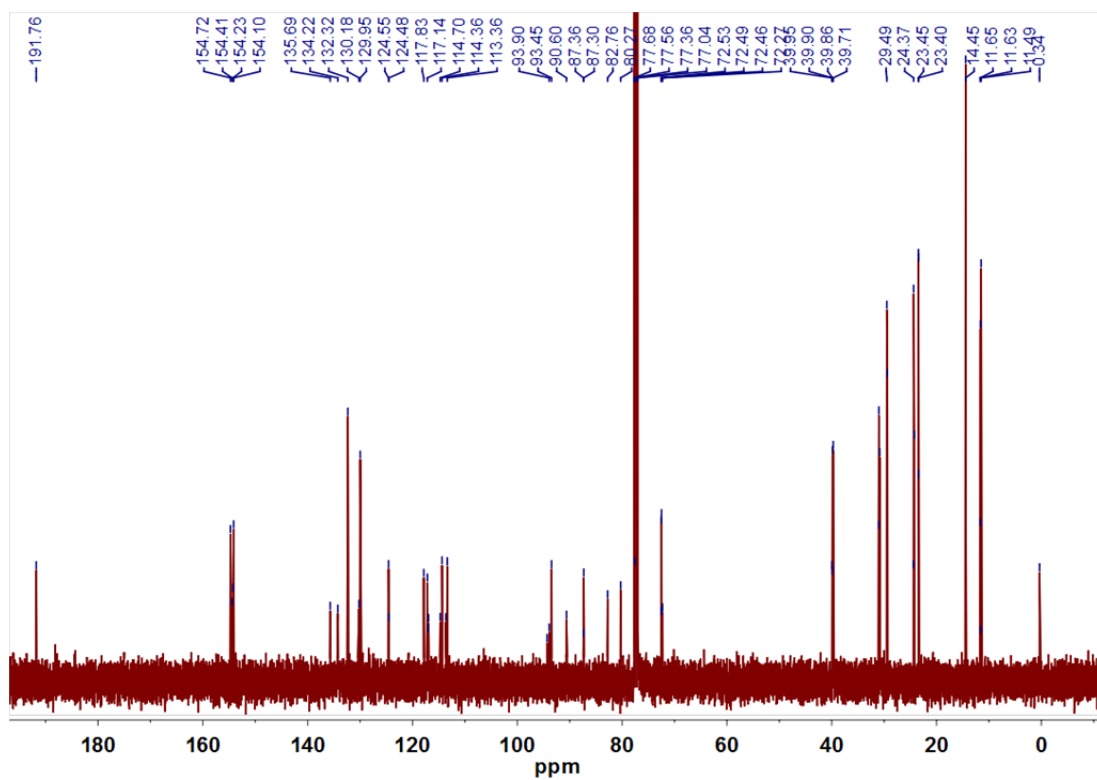


Fig. S6 ^{13}C NMR spectrum of **6a**.

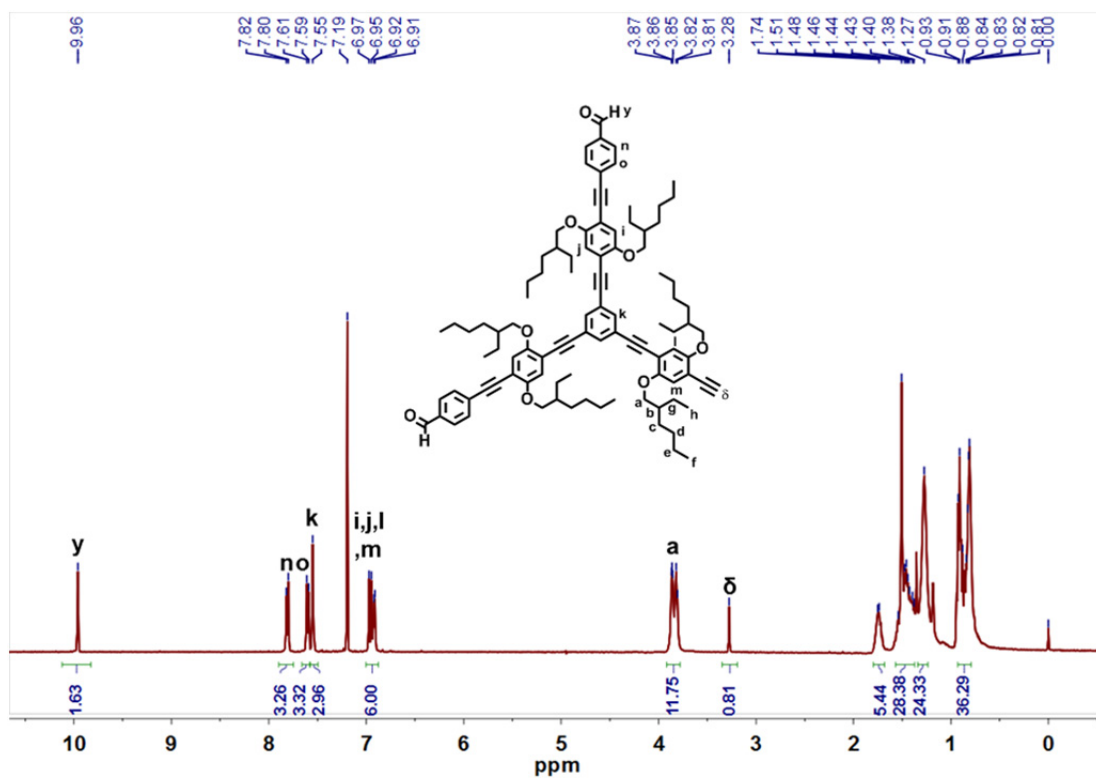


Fig. S7 ^1H NMR spectrum of **6b**.

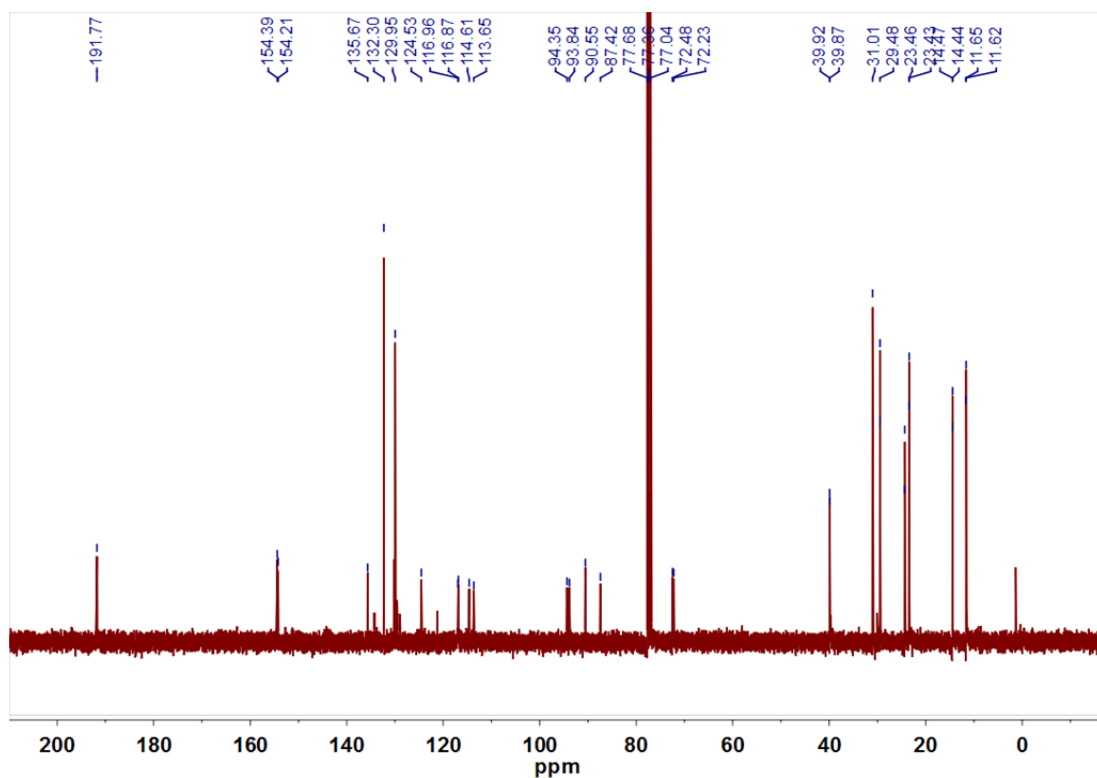


Fig. S8 ^{13}C NMR Spectrum of **6b**.

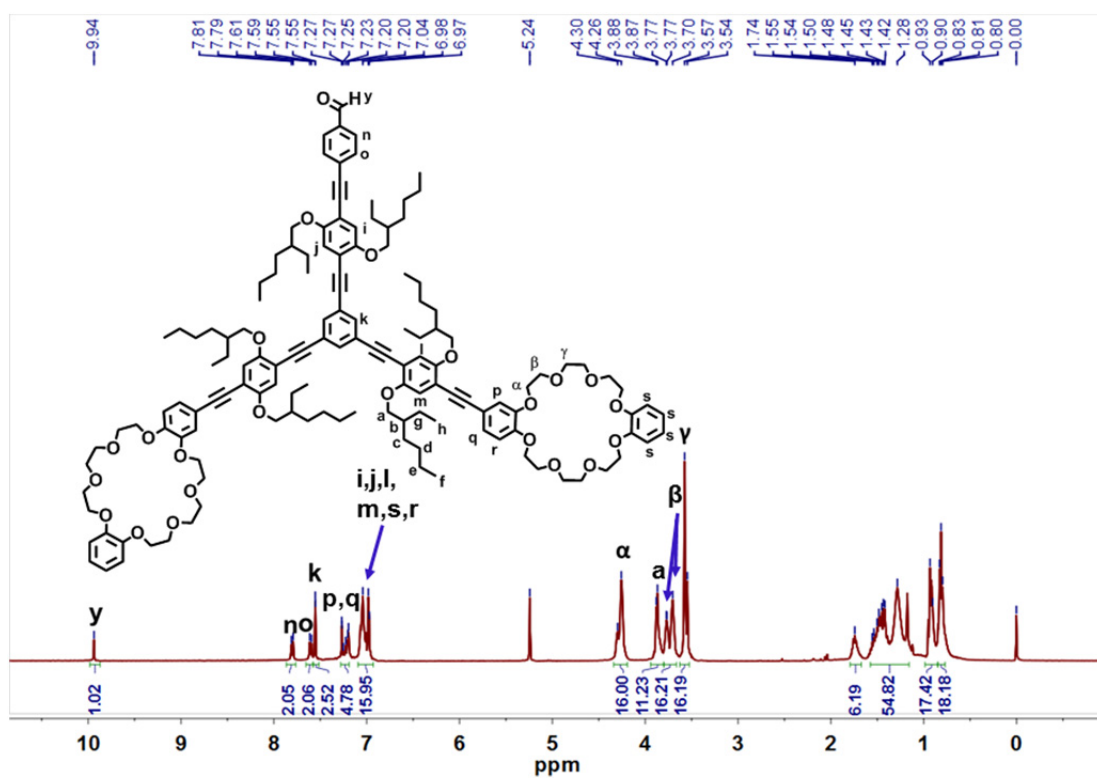


Fig. S9 ^1H NMR Spectrum of **8a**.

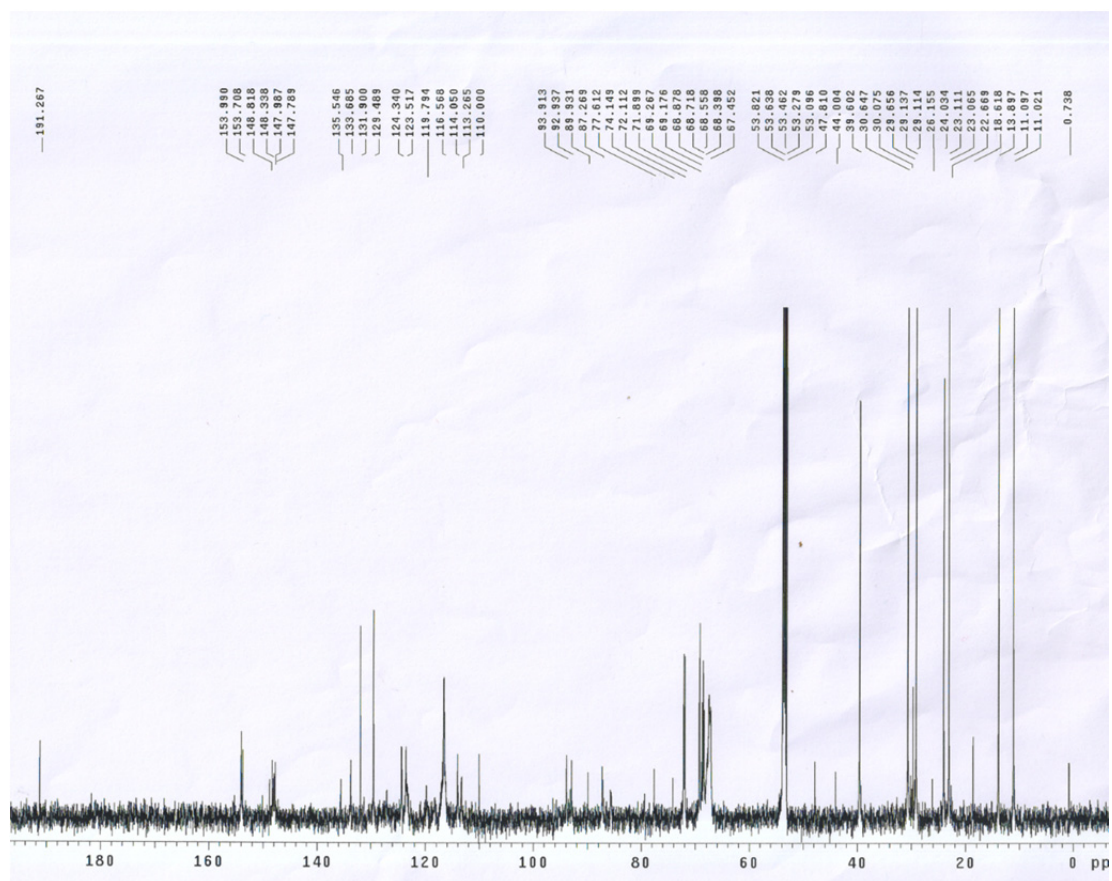


Fig. S10 ^{13}C NMR Spectrum of **8a**.

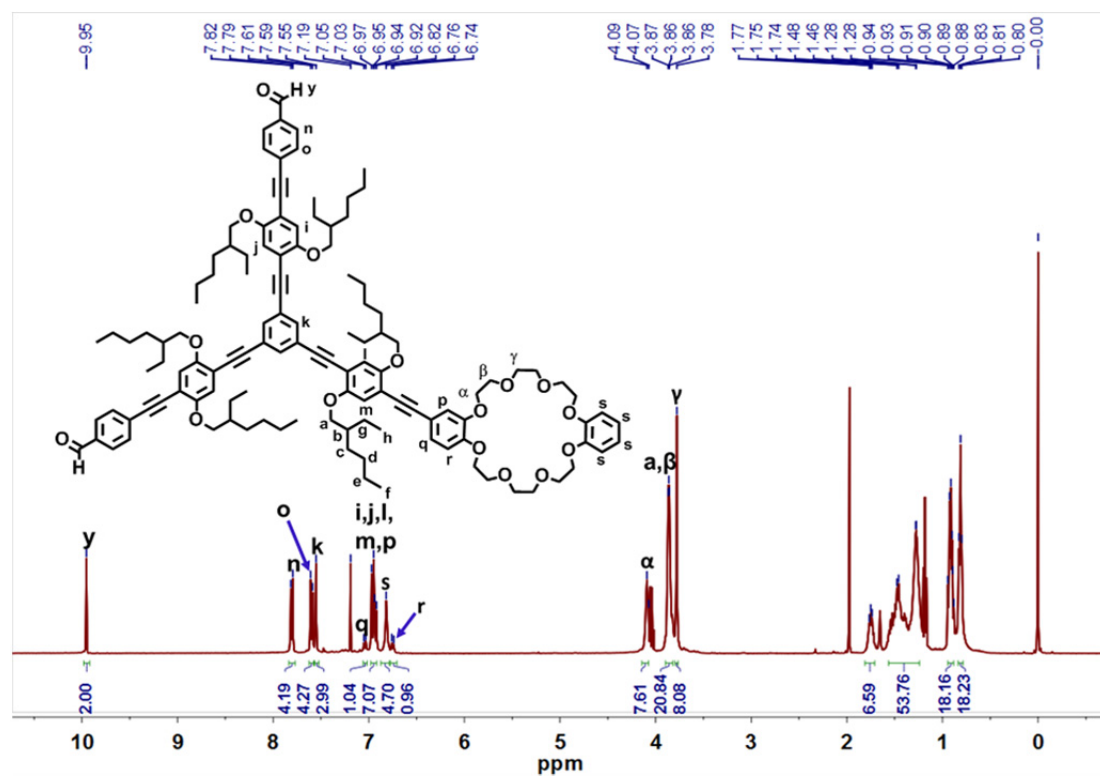


Fig. S11 ^1H NMR Spectrum of **8b**.

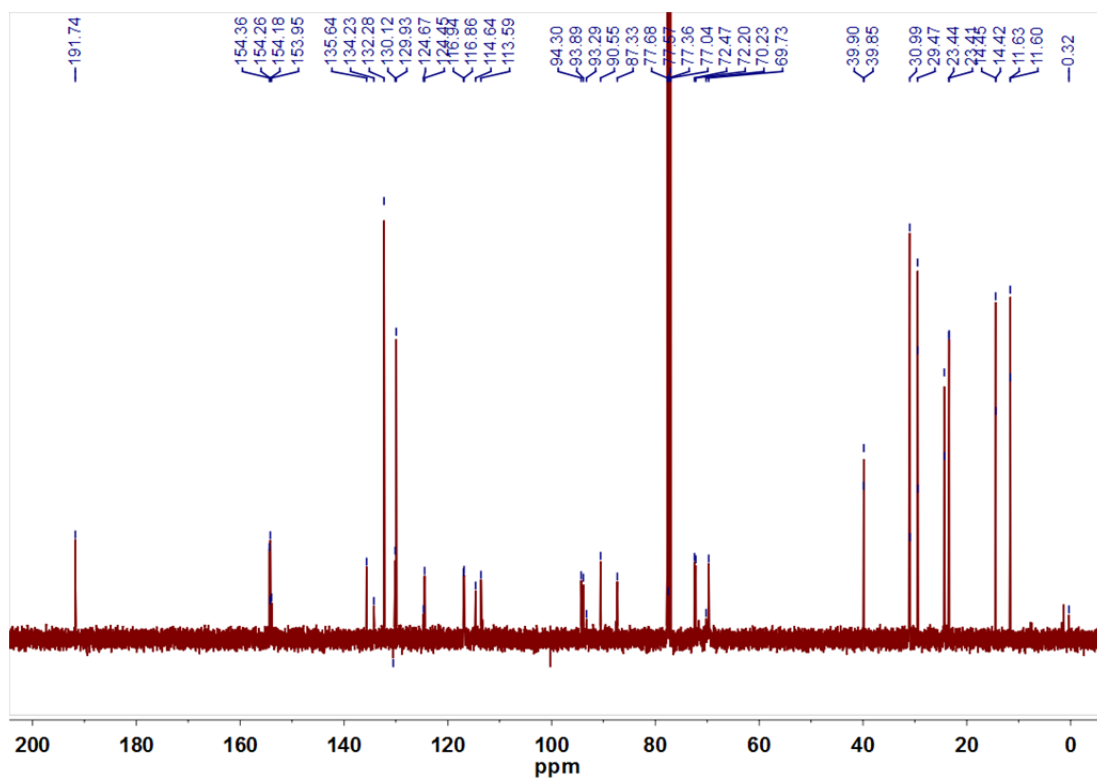


Fig. S12 ^{13}C NMR Spectrum of 8b.

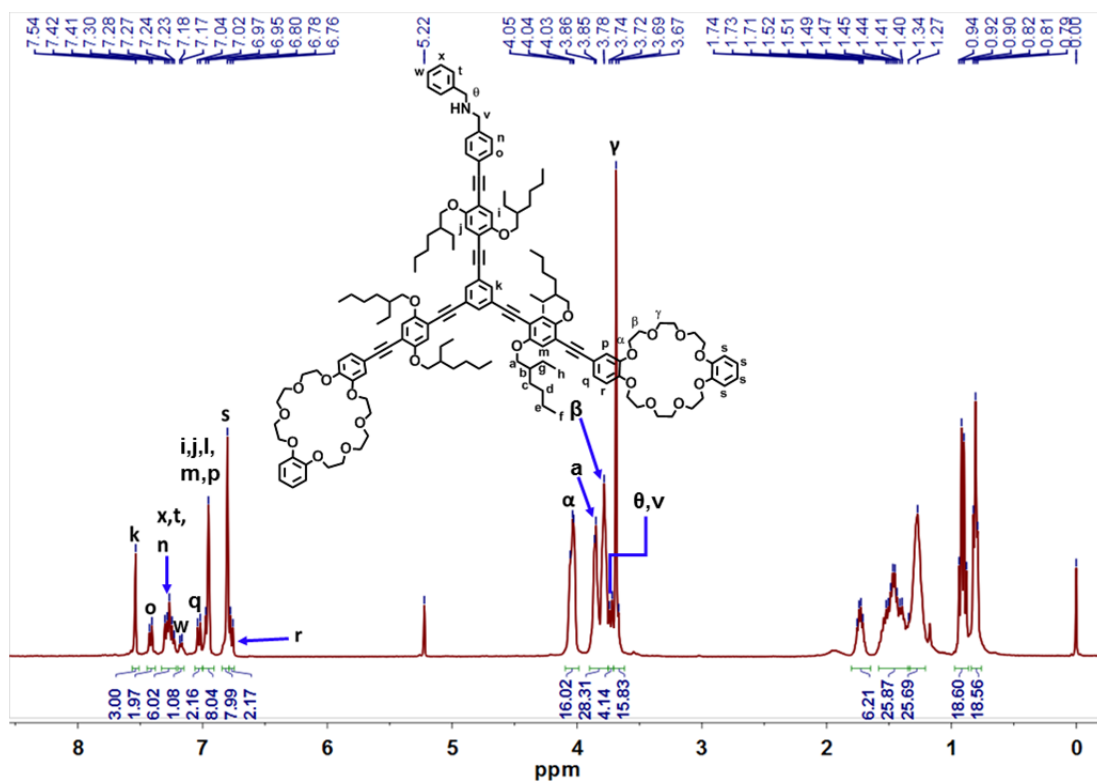


Fig. S13 ^1H NMR Spectrum of $\text{AB}_2\text{-1}$.

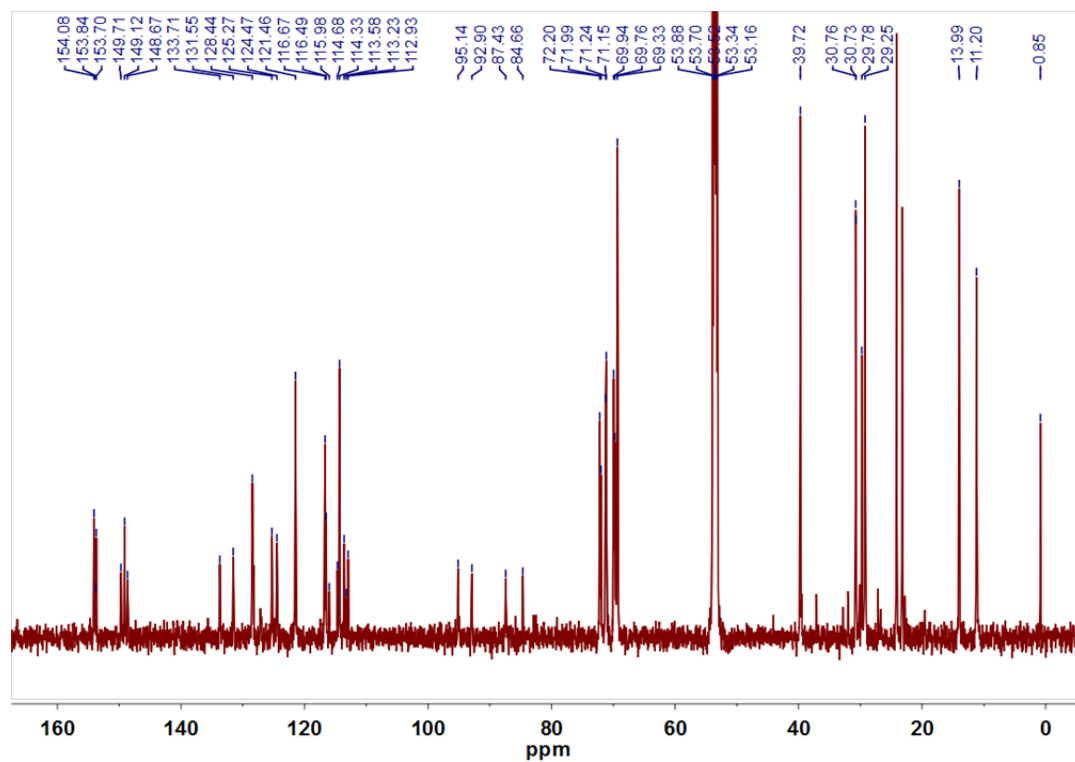


Fig. S14 ^{13}C NMR Spectrum of $\text{AB}_2\text{-1}$.

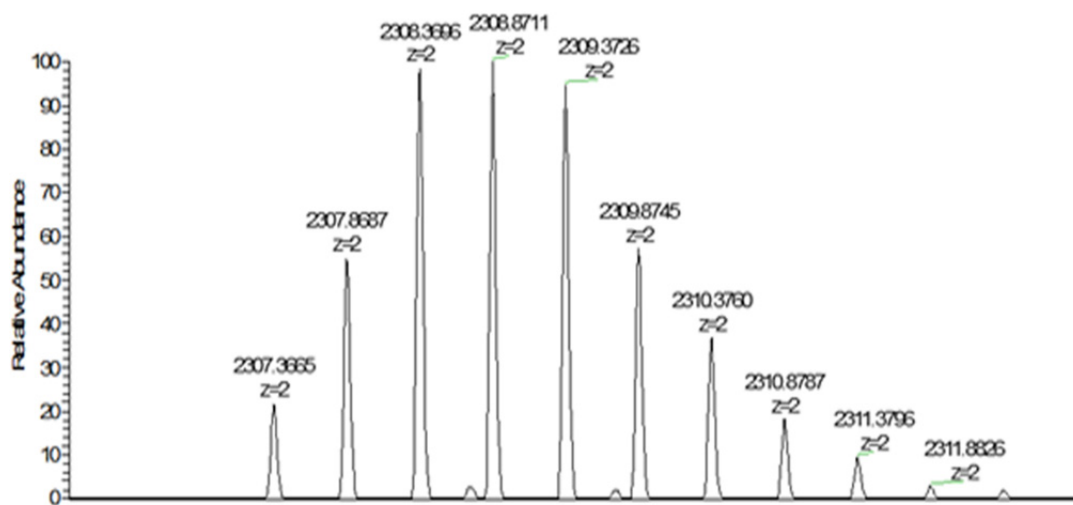


Fig. S15 HR-ESI-MS of $\text{AB}_2\text{-1}$, $[\text{C}_{292}\text{H}_{374}\text{N}_2\text{O}_{44} + \text{H}_2]^{2+}$, m/z, calculated: 2308.8674.

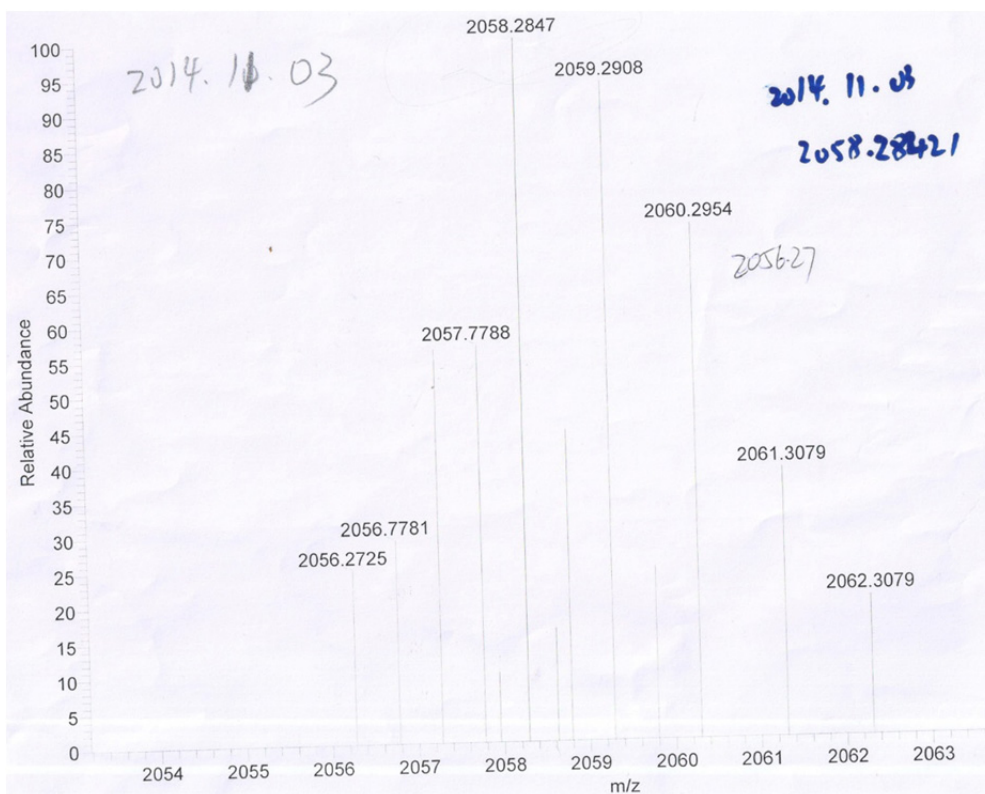


Fig. S18 HR-ESI-MS of **AB₂-2**, $[\text{C}_{136}\text{H}_{170}\text{N}_2\text{O}_{14} + \text{H}]^+$, m/z , calculated: 2058.2881.

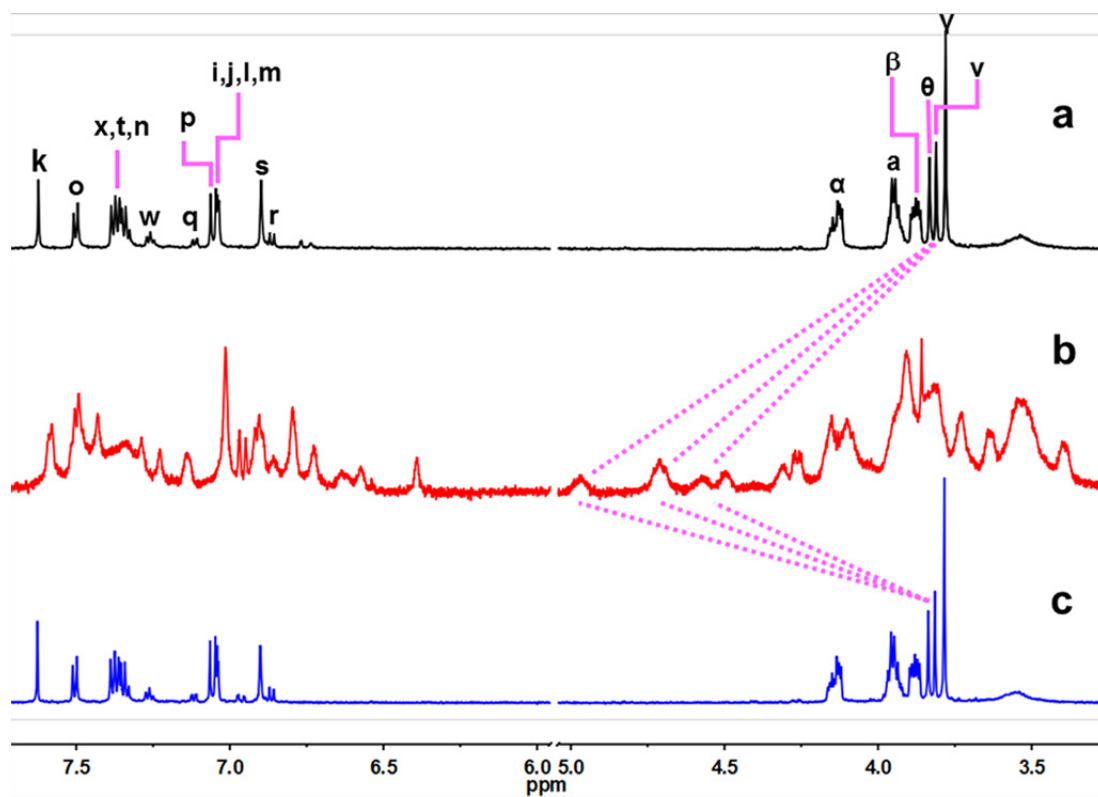
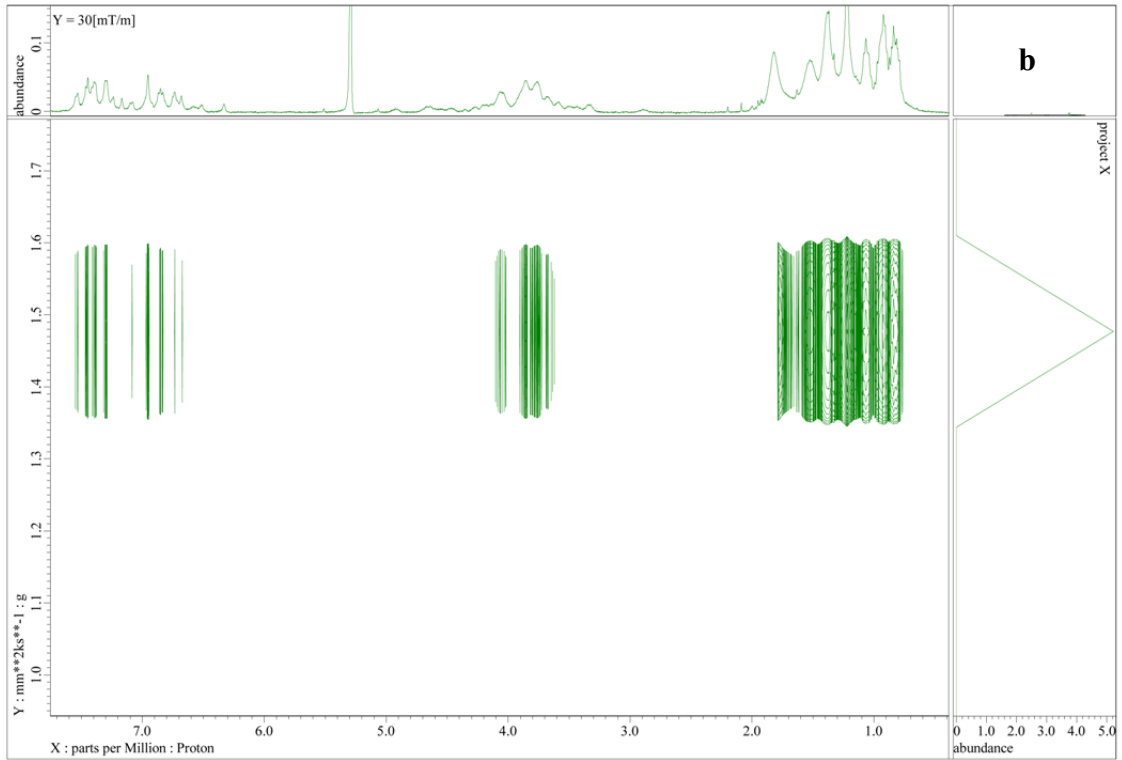
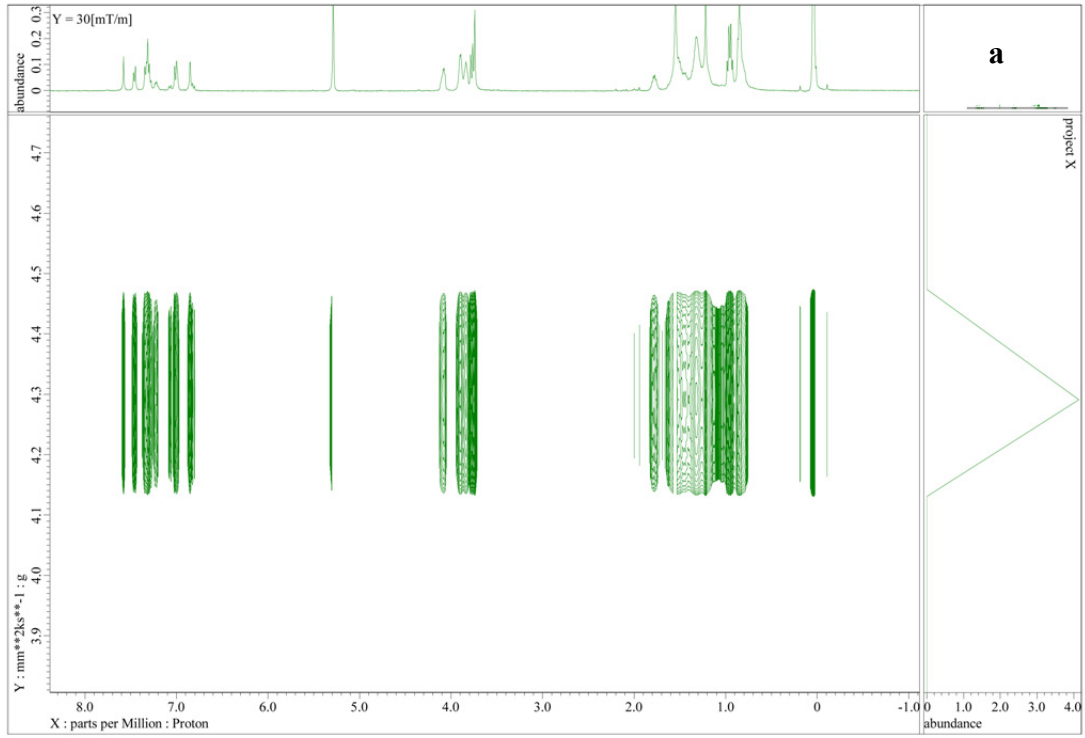


Fig. S19 Partial ^1H NMR spectra (400 MHz, CD_2Cl_2 , $2.14 \times 10^{-4} \text{ mol L}^{-1}$) of (a) **AB₂-2**, (b) **PAB₂-2** obtained by adding 2.4 equivalents of HFA to the solution of **AB₂-2**, (c) **AB₂-2** obtained by adding 2.8 equivalents of P_1 -*t*Bu to the solution of **PAB₂-2**.



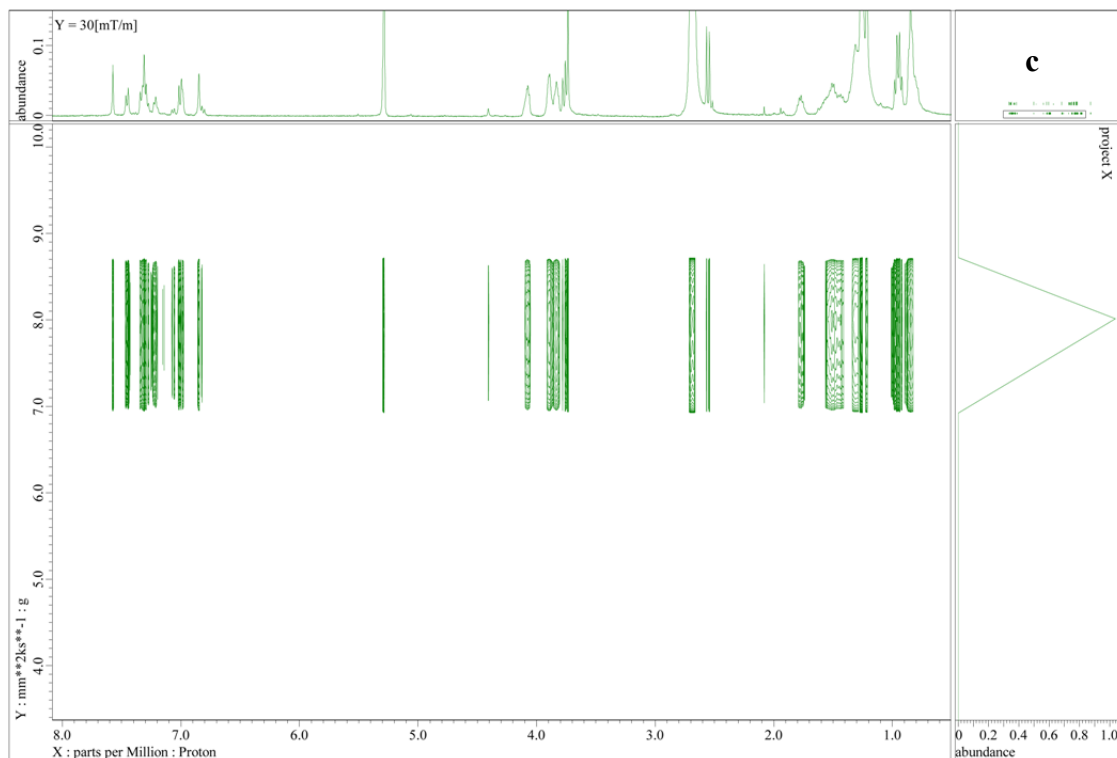


Fig. S20 Diffusion-ordered NMR spectroscopy (DOSY) of (a) **AB₂-2** (2.14×10^{-3} mol L⁻¹), (b) **PAB₂-2** obtained by adding 2.4 equivalents of HFA to the solution of **AB₂-2**, (c) **AB₂-2** obtained by adding 2.8 equivalents of P₁-*t*Bu to the solution of **PAB₂-2**.

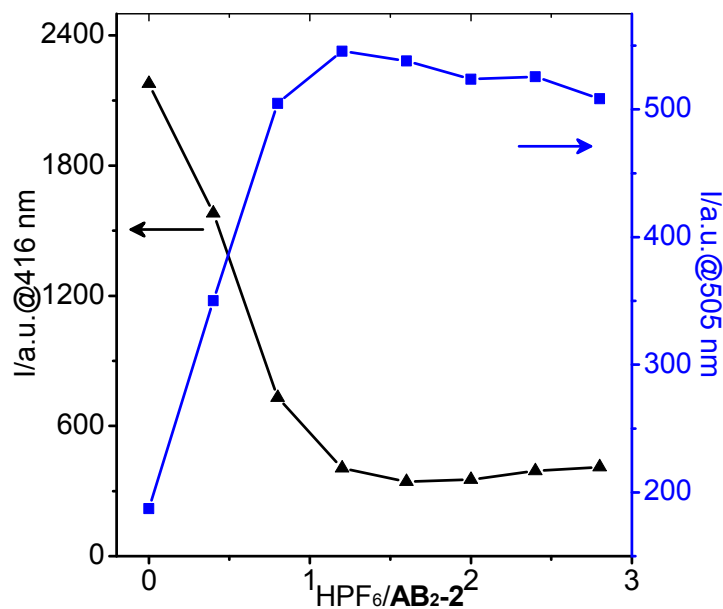


Fig. S21 Fluorescence intensity changes of **PAB₂-2** at 416 and 505 nm upon dropwise adding HPF₆.

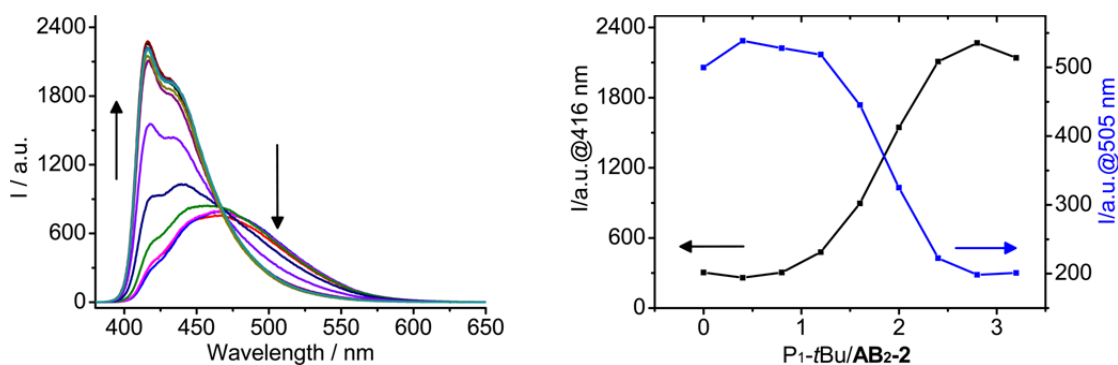


Fig. S22. (Left) Fluorescence spectra of **PAB₂-2** (1.57×10^{-5} mol L⁻¹) in dichloromethane upon titration with P₁-*t*Bu (P₁-*t*Bu/AB₂-2 = 0, 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2). (Right) Fluorescence intensity changes of **PAB₂-2** at 416 and 505 nm.

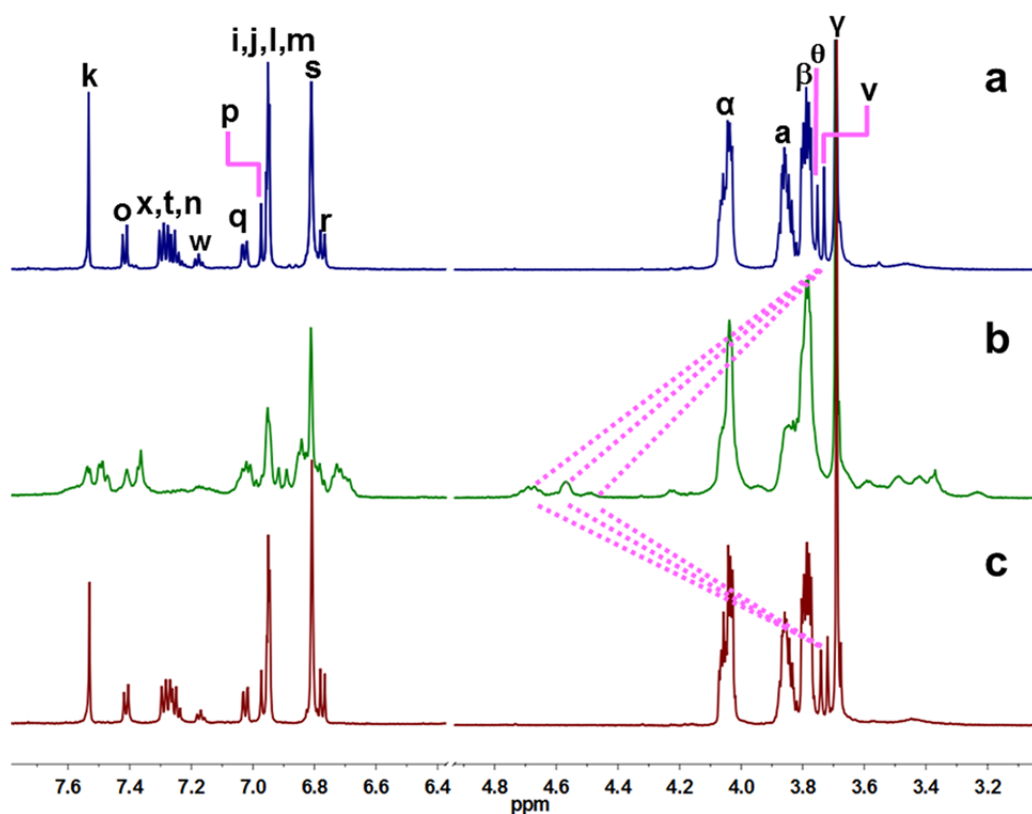
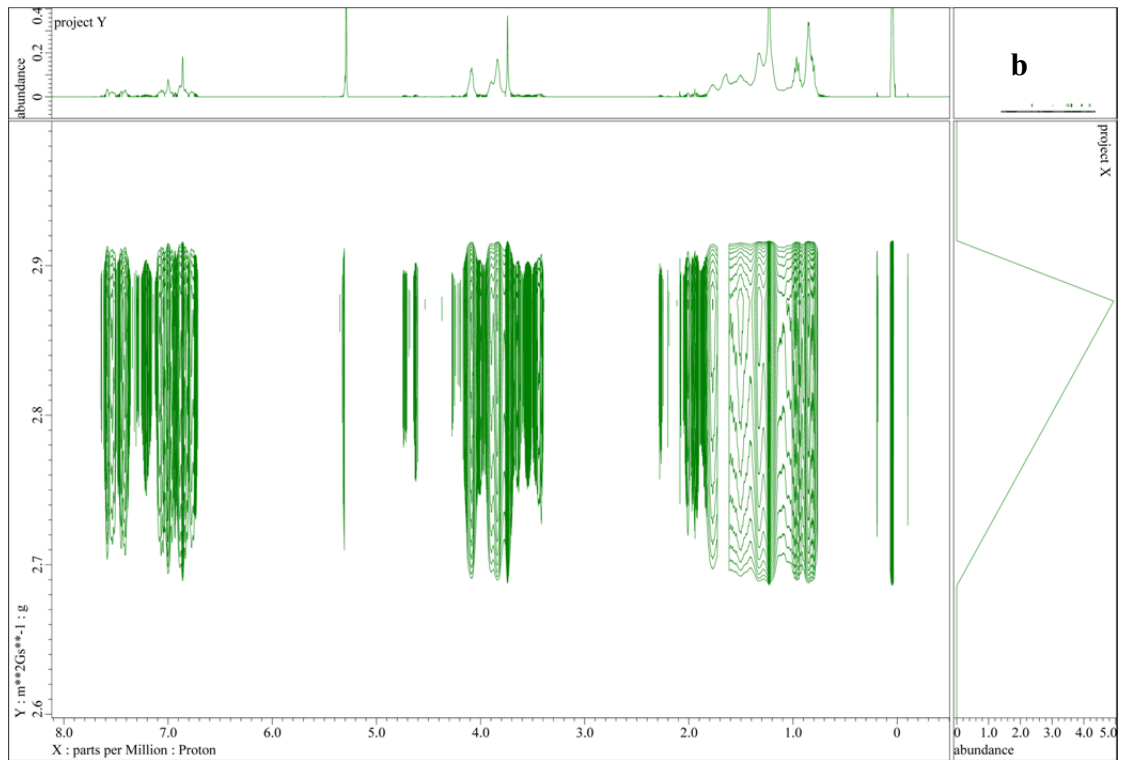
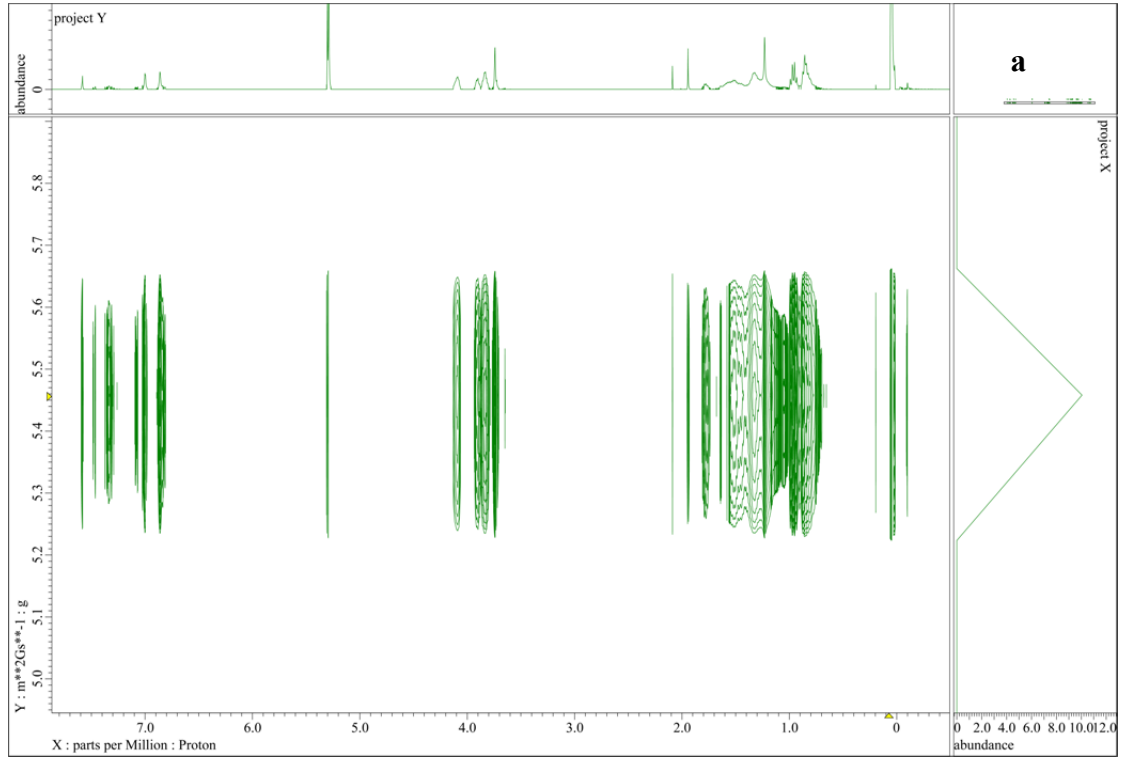


Fig. S23 Partial ¹H NMR spectra (400 MHz, CD₂Cl₂, 2.14×10^{-3} mol L⁻¹) of (a) **AB₂-1**, (b) **PAB₂-1** obtained by adding 1.2 equivalents of HFA to the solution of **AB₂-1**, (c) **AB₂-1** obtained by adding 1.4 equivalents of P₁-*t*Bu to the solution of **PAB₂-1**.



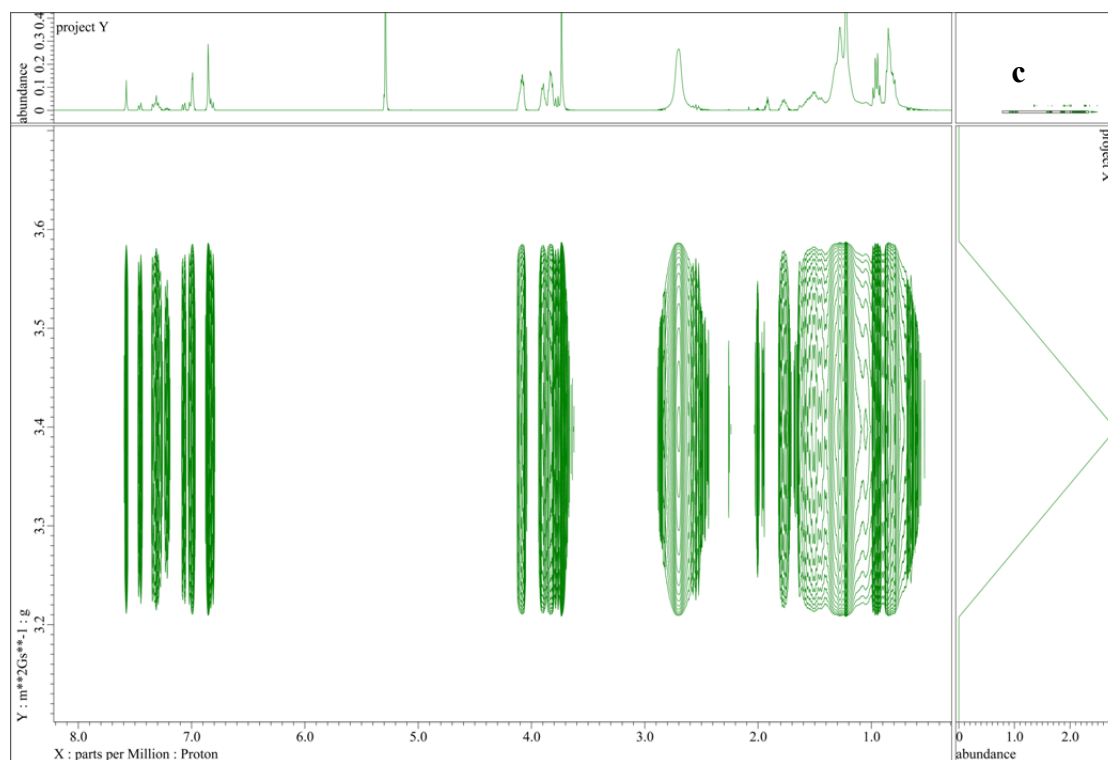


Fig. S24 Diffusion-ordered NMR spectroscopy (DOSY) of (a) **AB₂-1** (2.14×10^{-3} mol L⁻¹), (b) **PA₂B-1** obtained by adding 1.2 equivalents of HFA to the solution of **AB₂-1**, (c) **AB₂-1** obtained by adding 1.4 equivalents of P₁-*t*Bu to the solution of **PAB₂-1**.

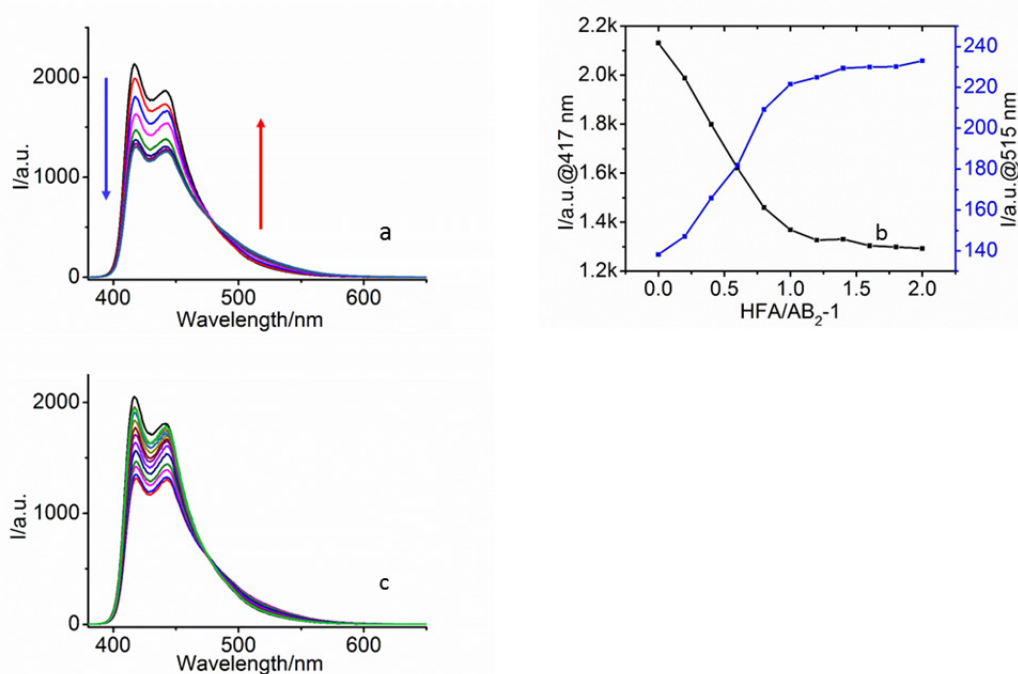


Fig. 25. (a) Fluorescence spectral change of **AB₂-1** (1.57×10^{-5}) in dichloromethane upon titration with HFA (HFA/**AB₂-1** = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0), (b) Fluorescence intensity changes of **A₂B-1** at 417 nm, (c) Fluorescence spectra of **PAB₂-1** in dichloromethane upon titration with P₁-*t*Bu.

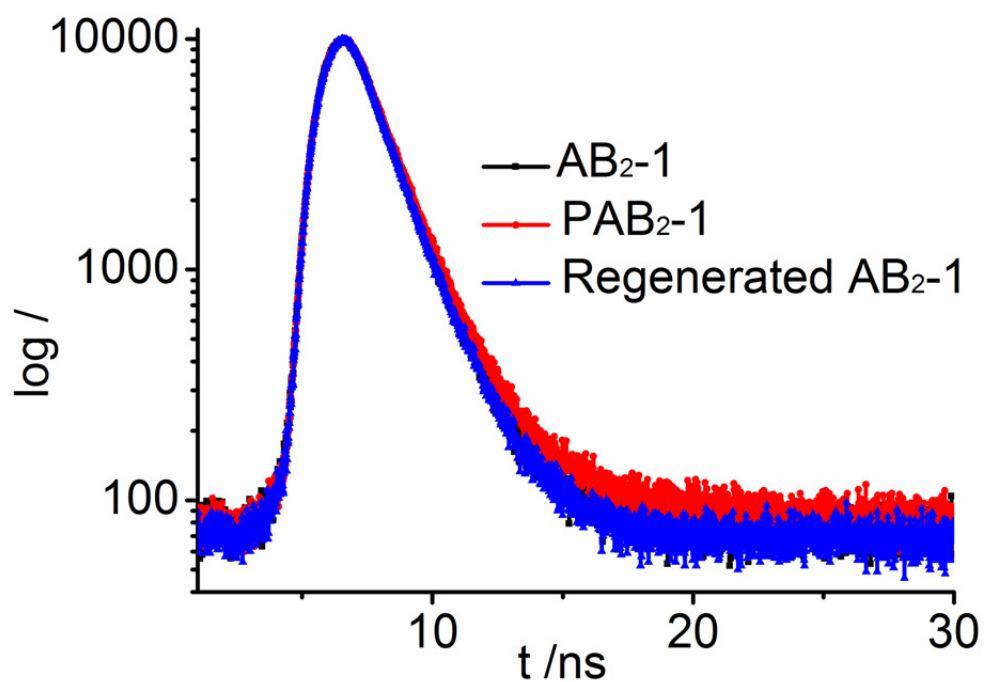


Fig. S26. Fluorescence decay profiles of **AB₂-1** (1.57×10^{-5} mol L⁻¹) in dichloromethane at 416 nm ($\lambda_{\text{ex}} = 370$ nm, a, black), (b, red) **PAB₂-1** obtained upon addition of 1.2 eq. of HFA, (c, blue) **AB₂-1** regenerated after addition of 1.4 eq. of P₁-*t*Bu.

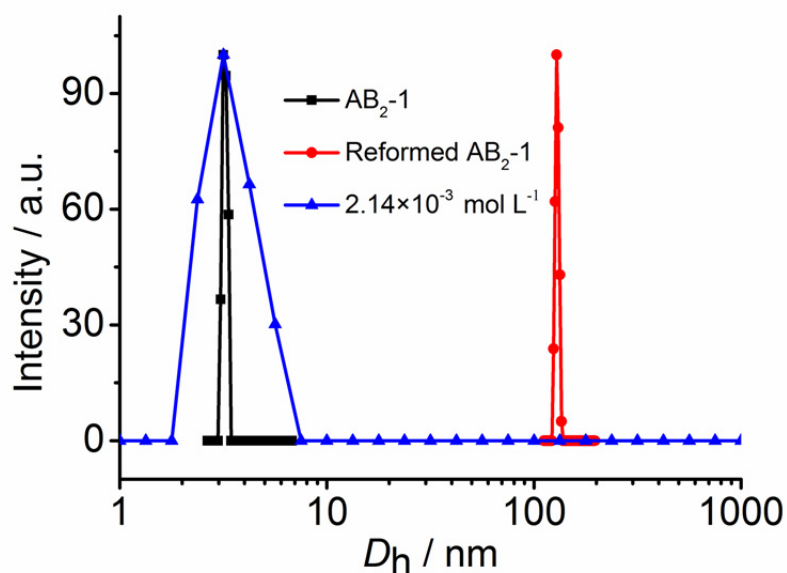


Fig. S27. (B) **AB₂-1** monomer, (L) AB-HFA 10^{-3} mol.L⁻¹, (f) obtained by PAB₂-1 with 2.8 equivalents of P₁-*t*Bu

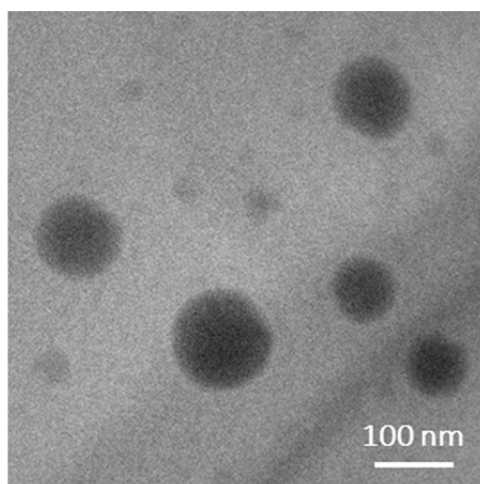


Fig. S28. TEM images **PAB₂-1** at a concentration of $2.14 \times 10^{-3} \text{ mol L}^{-1}$.

Table S1. Luminescence lifetime (τ_1 and τ_2) for **AB₂-2** and **PAB₂-2**.

Sample	τ_1 [ns]	RW %	τ_2 [ns]	RW %
[a]	1.33	100	–	–
[b]	1.47	44.92	12.46	55.08
[c]	1.32	100	–	–

[a] $1.57 \times 10^{-5} \text{ mol L}^{-1}$ (**AB₂-2**) solution in CH_2Cl_2 , [b] **PAB₂-2** obtained by adding 2.4 equivalents of HFA to the solution of **AB₂-2**, [c] **AB₂-2** obtained by adding 2.8 equivalent of P_1 -*t*Bu to the solution of **PAB₂-2**.

Table S2. Luminescence lifetime (τ_1 and τ_2) for **AB₂-1** and **PAB₂-1**.

Sample	τ_1 [ns]	RW %	τ_2 [ns]	RW %
[a]	1.30	100	–	–
[b]	1.32	96.32	3.88	3.68
[c]	1.28	100	–	–

[a] $1.57 \times 10^{-5} \text{ mol L}^{-1}$ (**AB₂-1**) solution in CH_2Cl_2 , [b] **PAB₂-1** obtained by adding 1.2 equivalents of HFA to the solution of **AB₂-1**, [c] **AB₂-2** obtained by adding 1.4 equivalents of P_1 -*t*Bu to the solution of **PAB₂-1**.

References

- S1 (a) F. Koch and W. Heitz, *Macromol. Chem. Phys.*, 1997, **198**, 1531; (b) Y. Shirai, Y. Zhao, L. Cheng and J. M. Tour, *Org. Lett.*, 2004, **6**, 2129.
 S2. S. Leininger, P. J. Stang and S. Huang, *Organometallics*, 1998, **17**, 3981.