Supporting information for

Photoresponsive assemblies of linear-dendritic copolymers containing azobenzene in the dendron interior: Effect of dendron structure on dye encapsulation and release

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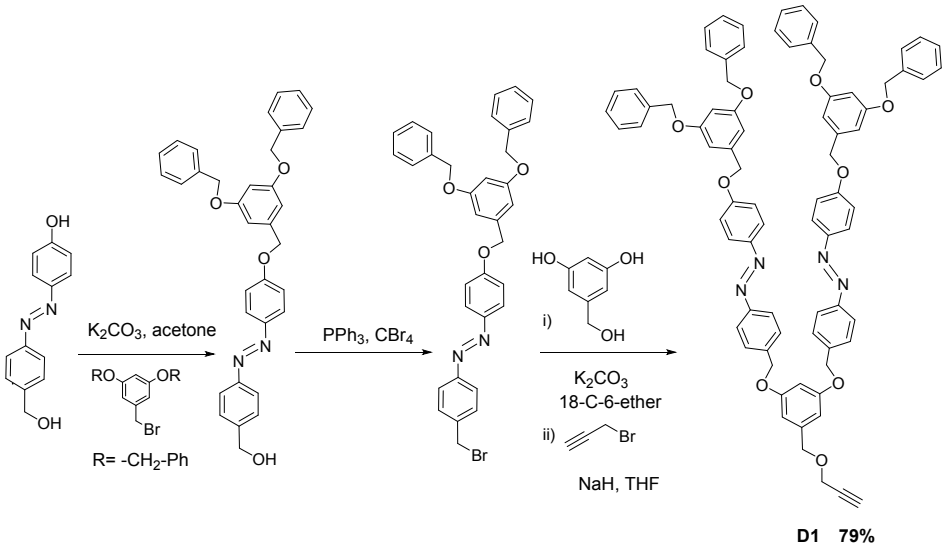
Synthesis:

Precursors to dendron with benzyl ether on periphery were synthesized by reported procedure.[1] Procedures and data for compounds with dodecyloxy group are given below. 3,5-didodecyloxybenzyl alcohol was synthesized using reported procedure.[2]

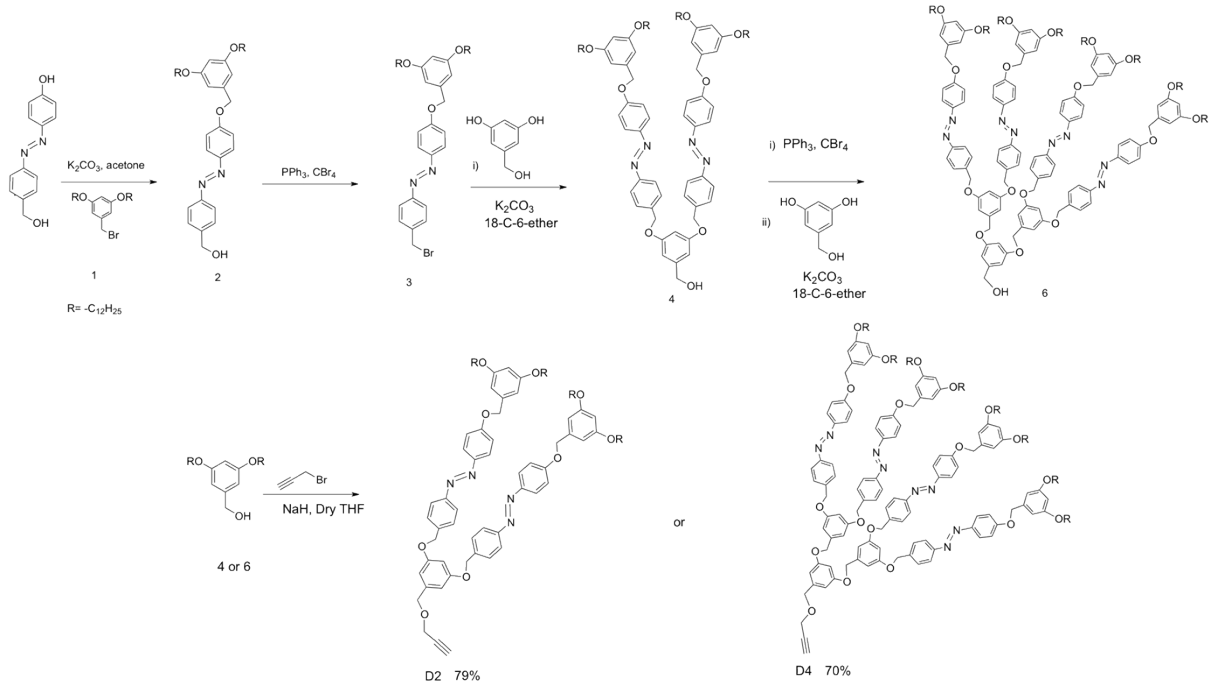


Scheme S1. Synthesis of dendron **D1**.

Compound 1: 3,5-didodecyloxy benzyl alcohol (1g, 2.1 mmol) was dissolved in dry THF and triphenyl phosphine (0.82g, 3.1 mmol), CBr_4 (1.04g, 3.1 mmol) was added and stirred at 0˚C for 30 min. The reaction was monitored by the TLC. After completion of the reaction, evaporated the solvent under reduced pressure washed with water and extracted with dichloromethane and dried over anhydrous sodium sulphate. Solvent was evaporated on rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography by eluting with 10% ethyl acetate and pet ether. This compound was further used for the next step. Yield:80 %.

Compound 2: 4-(4'-hydroxy phenylazo) benzyl alcohol (2.67g, 11.7 mmol) and Compound **1** (5.4g, 14 mmol) were dissolved in 50 mL dry acetone, added the K_2CO_3 (3.74g, 28 mmol) and 18-Crown-6 ether (0.6g, 2.3 mmol) reflux for 24 h. After completion of the reaction solvent was removed under the reduced pressure and extract the product in ethyl acetate. Organic layer was dried over sodium sulphate and solvent was evaporated under reduced pressure. The crude product was purified by column chromatography in 20% ethyl acetate and pet ether. Yield 80%. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 0.89(s, 6H,-CH_2), 1.27(s, 36H, -CH_2), 1.77(m, 4H), 3.95(t, 4H, J=6Hz), 4.78(d, 2H, J=2Hz), 5.08(s, 2H), 6.43(s, 1H), 6.58(s, 2H), 7.06(d, 2H, J=10Hz), 7.53-(d, 2H, J=10Hz), 7.87-7.94(t, 4H, J=6Hz) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 14.16, 22.73, 26.08, 29.64, 31.96, 64.98, 68.13, 70.31, 100.87, 105.67, 115.16, 122.82, 124.76, 127.47, 138.61, 143.19, 147.13, 152.25, 160.61, 161.23 ppm.

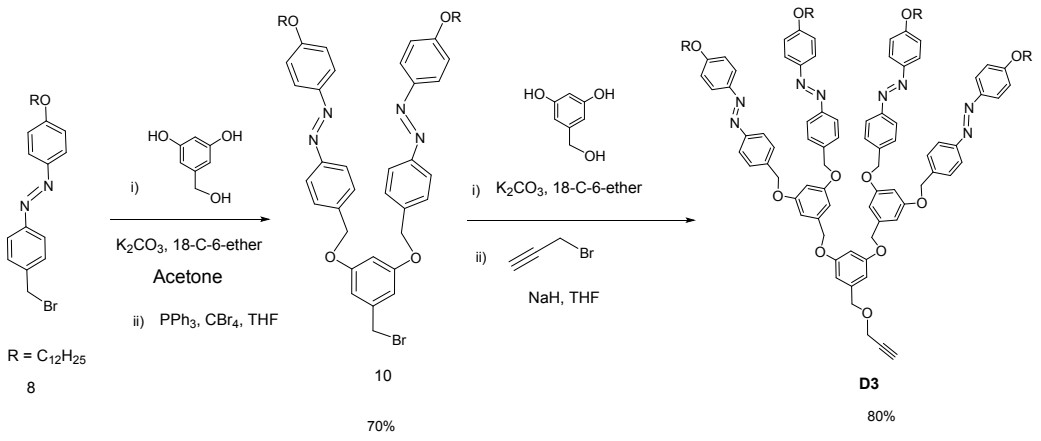
Compound 3: Compound **2** (5g, 7.2 mmol) was dissolved in dry THF and triphenyl phosphine (2.86g, 10.9 mmol), CBr_4 (3.61g, 10.9 mmol) was added and stirred at 0˚C for 30 min. The reaction was monitored by the TLC. After completion of the reaction, evaporated the solvent under reduced pressure washed with water and extracted with dichloromethane and dried over anhydrous sodium sulphate. Solvent was evaporated on rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography by eluting with 20% ethyl acetate and pet ether. This compound was further used for the next step. Yield 70 %.



Scheme S2. Synthesis of dendrons **D2** and **D4**.

Compound 4: Compound **3** (3.7g, 1.6 mmol), 3,5 dihydroxy benzyl alcohol (0.314g, 0.6 mmol) were dissolved in 50 mL of dry acetone-THF (1:1) mixture, K_2CO_3 (1.24g, 2.7 mmol) and 18-crown-6 ether (0.118g, 0.2 mmol) were added and refluxed for 24 h. After completion of the reaction solvent was removed under reduced pressure and the product was extracted in dichloromethane. Organic layer was dried over sodium sulphate and solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography in 20% ethyl acetate and pet ether. Yield 75%. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 0.89(s, 12H, -CH_2), 1.27(s, 72H, -CH_2), 1.75(m, 8H), 3.95(t, 8H, J=6Hz), 4.64(d, 2H, J=8Hz), 5.08(m, 8H), 6.43(s, 2H), 6.59-6.66(m, 7H, Ar-H), 7.06(d, 4H, J=10Hz), 7.53(d, 4H, J=10Hz), 7.88-7.94(m, 8H) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz) δ: 14.17, 22.74, 26.09, 29.68, 31.96, 68.13, 70.32, 100.88, 101.42, 105.67, 115.16, 122.85, 124.81, 127.97, 138.60, 147.13, 152.44, 160.04, 160.61, 161.29 ppm.

Compound 6: Compound **5** (2.5g, 4.9 mmol), 3,5 dihydroxy benzyl alcohol (0.095g, 2.2 mmol) were dissolved in 50 mL of dry acetone-THF (1:1) mixture, K_2CO_3 (0.36g, 2.7 mmol) and 18-Crown-6 ether (0.071g, 0.2 mmol) were added and refluxed for 24 h. After completion of the reaction solvent was removed under reduced pressure and the product was extracted in dichloromethane. Organic layer was dried over sodium sulphate and solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography in 20% ethyl acetate and pet ether. Yield 65%.^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 0.89(t, 24H, J=6Hz), 1.27(bs, 144H), 1.78(m, 16H), 3.95(t, 16H, J=6Hz), 4.57(d, 2H, J=6Hz), 4.99- 5.11(m, 20H), 6.43-6.68(m, 21H), 7.06(d, 8H, J=8Hz), 7.51(d, 8H, J=8Hz), 7.85-7.94(t, 16H, J=8Hz) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz):14.15, 22.72, 26.08, 29.28, 29.38, 29.66, 31.95, 65.23, 68.12, 70.32, 100.90, 105.69, 106.32, 115.16, 122.83, 124.81, 127.97, 138.60, 139.12, 139.54, 147.12, 152.40, 160.03, 160.62, 161.30.



Scheme S3. Synthesis of dendron **D3**

Compound 7: 4-(4'-hydroxy phenylazo) benzyl alcohol (2g, 8.7 mmol), dodecyl bromide (2.61g, 10.5 mmol) were dissolved in 50 mL of dry acetone:THF mixture (1:1), K_2CO_3 (4.8g, 28 mmol) and catalytic amount of KI were added and refluxed for 24 h. After completion of the reaction solvent was removed under reduced pressure, product was extracted in ethyl acetate. Organic layer was dried over sodium sulphate and solvent was evaporated under reduced pressure. The crude product was purified by column chromatography in 10% ethyl acetate and pet ether. Yield 80%. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 0.89(s, 3H,-CH2), 1.28(m, 18H, -CH_2), 1.78(m, 4H), 4.05(t, 2H, J=6Hz), 4.77(d, 2H, J=2Hz), 6.99(d, 2H, J=8Hz), 7.48(d, 2H, J=8Hz), 7.86(t, 4H, J=8Hz) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 14.12, 22.68, 26.00, 29.63, 31.9, 64.95, 68.36, 114.69, 122.74, 124.73, 127.43, 143.02, 146.8, 152.25, 161.73 ppm.

Compound 8: Compound **8** (1.8 g, 4.5 mmol) was dissolved in dry THF and triphenyl phosphine (1.78 g, 6.6 mmol), CBr_4 (2.2 g, 6.6 mmol) was added and stirred at 0˚C for 30 min. After completion of the reaction as indicated by TLC, solvent was evaporated under reduced pressure, crude product was washed with water and extracted with dichloromethane. Organic layer was dried over anhydrous sodium sulphate. Solvent was evaporated on rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography by eluting with 20% ethyl acetate and pet ether. This compound was further used for the next step. Yield 70 %.

Compound 9: Compound **9** (1.5 g, 3.2 mmol), 3,5 dihydroxy benzyl alcohol (0.207 g, 1.4 mmol) were dissolved in 40 mL dry acetone:THF mixture (1:1). K_2CO_3 (0.82 g, 5.8 mmol) and 18-Crown-6ether (0.072 g, 0.2 mmol) were added and refluxed for 24 h. solvent was removed under reduced pressure and product was extracted in dichloromethane. Organic layer was dried over sodium sulphate and solvent was evaporated on rotary evaporator. Crude product was purified by flash column chromatography in 20% ethyl acetate and pet ether. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: : 0.89(s, 6H,-CH2), 1.28(bs, 36H, -CH_2), 1.83(m, 4H), 4.05(t, 4H, J=6Hz), 4.67(d, 2H, J=4Hz), 5.13(s, 4H), 6.57(s, 1H), 6.66(d, 2H, J=2Hz), 6.99(d, 4H, J=8Hz), 7.53(d, 4H, J=8Hz), 7.88-7.94(m, 8H) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 14.15, 22.72, 26.04, 29.67, 31.95, 64.61, 68.41, 69.68, 105.92, 114.73, 122.80, 124.81, 127.96, 143.59, 146.85, 152.49, 160.04, 161.82 ppm. Yield 75%.

Compound 10: Synthesis was carried out by following same procedure as for compound **8**. Yield 65%.

Compound 11: Compound **8** (2 g, 2.08 mmol), 3,5 dihydroxy benzyl alcohol (0.132g, 0.9 mmol) were dissolved in 60 mL of dry acetone:THF mixture (1:1), K_2CO_3 (0.527g, 3.7 mmol) and 18-Crown-6 ether (0.049g, 0.18mmol) were added reflux for 24 h. ^{1}H NMR (200.13 MHz, $CDCl_3$) δ: 0.89(t, 12H, J=6Hz), 1.28(bs, 72H, -CH_2), 1.82(m, 8H), 4.03(t, 8H, J=6Hz), 4.58(d, 2H, J=4Hz), 4.98(s, 4H), 5.11(s, 8H), 6.53-6.67(m, 9H), 6.97(d, 2H, J=2Hz), 6.99(d, 8H, J=8Hz), 7.50(d, 8H,

J=8Hz), 7.88-7.93(t, 16H, J=8Hz) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 14.15, 22.72, 26.04, 29.67, 31.95, 61.9, 63.36, 65.27, 68.41, 69.69, 101.78, 105.93 114.73, 122.80, 124.81, 127.96, 143.59, 146.85, 152.49, 160.04, 161.82 ppm. Yield 79%.

General procedure for synthesis of Gn-Azo-alkyne dendrons

In a dry three-necked round bottom flask NaH (1.2mol, 60% suspension in mineral oil) was taken and washed with hexanes under argon. Dry THF followed by dendron with benzyl alcohol at the focal point (1 mol) were added and stirred for 10 min followed by addition of propargyl bromide (1.1mol). The reaction mixture was stirred for 12h and poured in water and extracted with dichloromethane, organic layer was washed with water, brine and dried over anhydrous sodium sulphate before concentrating on rotary evaporator. The crude product was purified by precipitating it in cold diethyl ether.

Dendron D1: ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.48(t, 1H, J=2Hz), 4.1(d, 2H, J=4Hz), 4.58(s, 2H, -CH_2), 5.06-5.14(m, 16H, -CH_2), 6.61-6.71(m, 9H, Ar H), 7.05(d, 4H, J=8Hz), 7.36-7.42(m, 20H, Ar H), 7.54(d, 4H, J=8Hz), 7.89-7.93(m, 8H, Ar H) ppm. ^{13}C NMR (CDCl3, 50.32 MHz) : 57.17, 69.71, 70.20, 71.41, 74.78, 101.77, 106.41, 107.14, 115.20, 122.85, 124.83, 127.57, 128.64, 136.78, 138.94, 139.22, 147.23, 152.48, 159.99, 160.29, 161.19 ppm. MALDI-TOF MS: Calcd. 1203.41 Found 1203.39 for [M^+]. Yield 80%.

Dendron D2: ^{1}H NMR (200 MHz, $CDCl_3$) δ:0.89(t, 12H, J=6Hz),1.27(bs, 72H), 1.78(m, 8H), 2.48(t, 1H, J=2Hz), 3.95(t, 8H, J=6Hz) 4.19(t, 2H, J=2Hz),4.58(s, 2H), 5.08-5.13(m, 8H, -ArCH_2), 6.43(s, 2H, Ar H), 6.59-6.65(m, 7H), 7.06(d, 4H, J=10Hz), 7.54(d, 4H, J=8Hz), 7.88-7.92(m, 8H, Ar H) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): 14.17, 22.74, 26.09, 29.29, 29.64, 31.96, 57.14, 62.96, 68.15, 70.34, 74.78, 100.91, 105.69, 107.09, 115.18, 122.85, 124.82, 128.03, 138.63, 138.63, 139.17, 147.16, 152.46, 159.98, 160.63, 161.30 ppm. MALDI-TOF MS: Calcd. 1516.20 Found 1538.85 for [M^++ Na^+]. Yield 78%.

Dendron D3: ^{1}H NMR (200 MHz, $CDCl_3$) δ:0.89(t, 12H, J=6Hz),1.27(bs, 72H), 1.78(m, 8H), 2.46(t, 1H, J=2Hz), 4.04(t, 8H, J=6Hz) 4.16(d, 2H, J=2Hz),4.55(s, 2H), 4.99(s, 4H), 5.12(s, 8H, -ArCH_2), 6.60-6.70(m, 9H), 6.98(d, 8H, J=8Hz), 7.52(d, 8H, J=8Hz), 7.87-7.93(m, 16H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$, 125.76 MHz): 14.51, 23.09, 26.43, 29.61, 30.07, 32.33, 57.52, 68.80, 70.31, 71.82, 75.11, 80.02, 102.18, 106.90, 107.43, 111.53, 115.12, 123.18, 125.19, 128.36, 139.41, 139.88, 147.27, 152.87, 160.44, 162.19 ppm. MALDI-TOF MS: Calcd. 1936.11 Found 1958.92 for [M^++ Na^+]. Yield 82%.

Dendron D4: ^{1}H NMR (500.13 MHz, $CDCl_3$) δ: 0.90(t, 24H, J=10Hz), 1.28(bs, 144H), 1.78(m, 16H), 3.95(t, 16H, J=5Hz), 4.17(d, 2H, J=5Hz), 4.56(s, 2H), 5.00- 5.12 (m, 20H), 6.43(s,4H), 6.58-6.71(m, 17H), 7.07(d, 8H, J=10Hz), 7.52(t, 8H, J=10Hz), 7.87-7.93(t, 16H, J=8Hz) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz):14.15, 22.71, 26.07, 29.37, 29.62, 29.66, 31.93, 57.11, 68.10, 70.30, 100.88, 105.66, 106.48, 115.13, 122.83, 124.80, 127.99, 138.58, 139.09, 147.12, 152.42, 160.02, 160.60, 161.26. MALDI-TOF MS: Calcd. 3098.46 Found 3097.55 for [M^+]. Yield 65%.

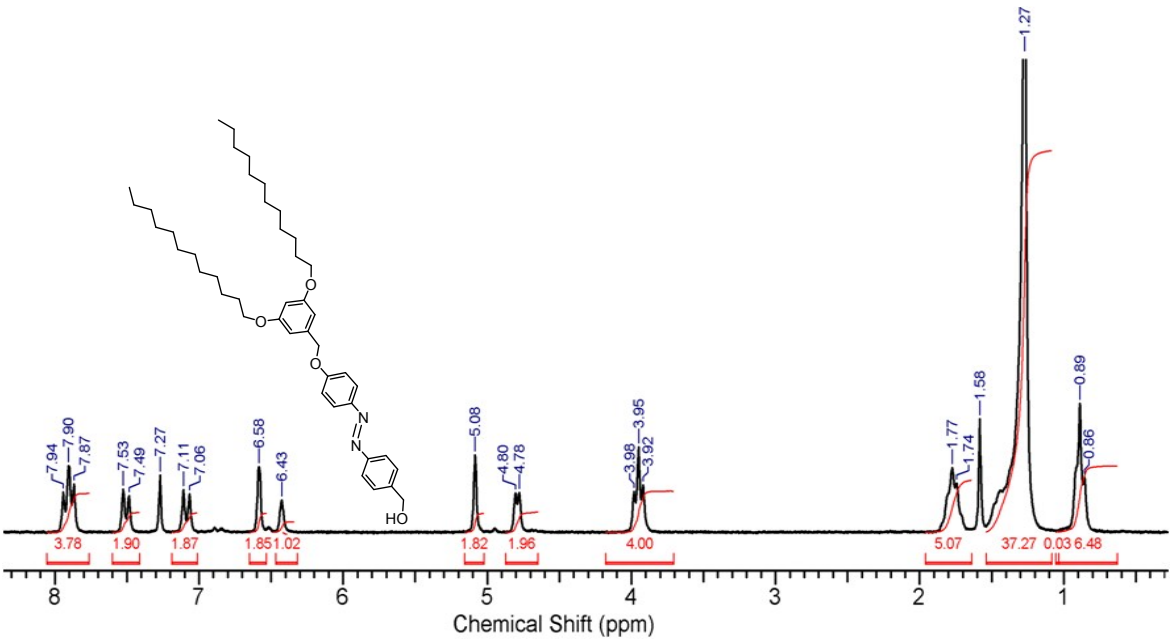


Fig. S1. 200 MHz ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

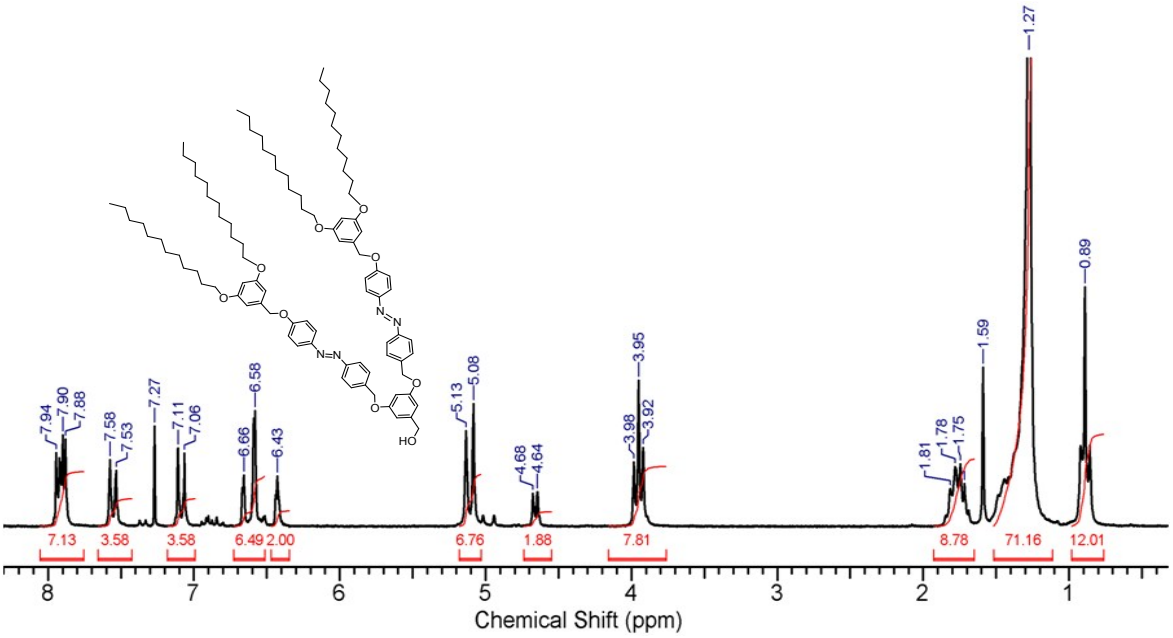


Fig. S2. 200 MHz ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

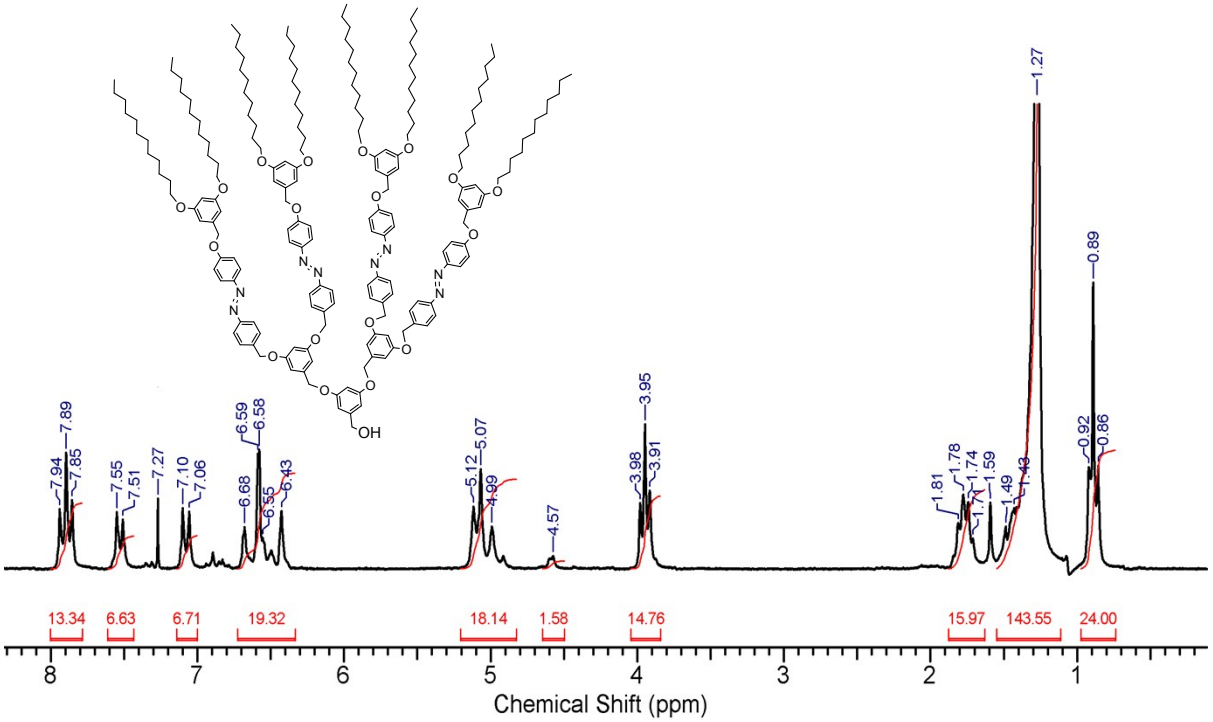


Fig. S3. 200 MHz ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

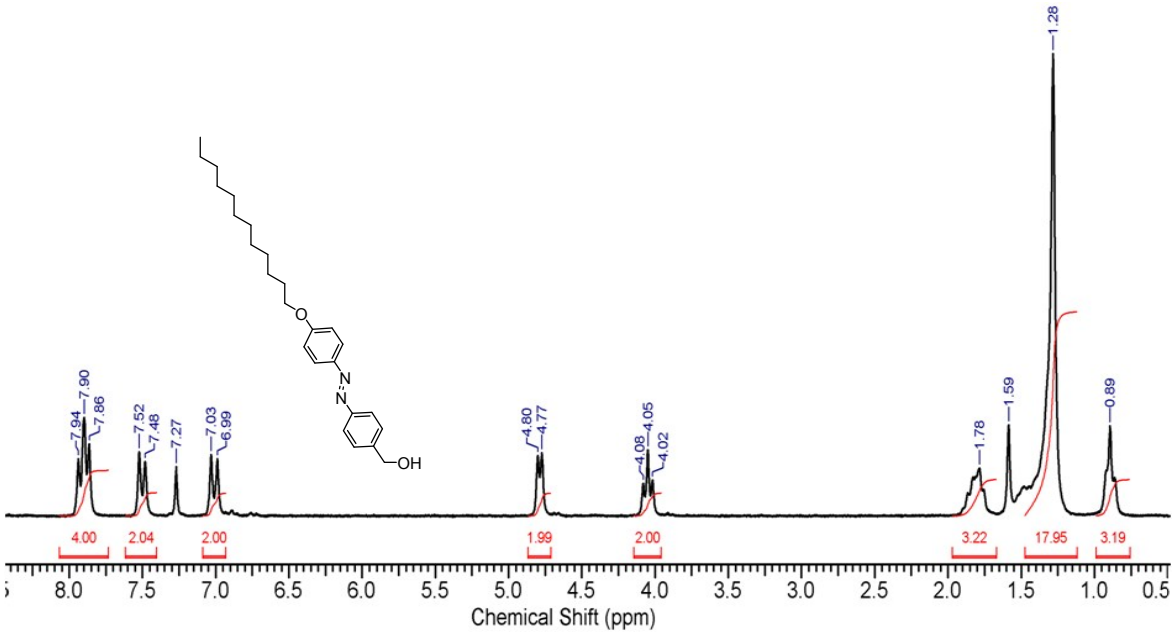


Fig. S4 200 MHz ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

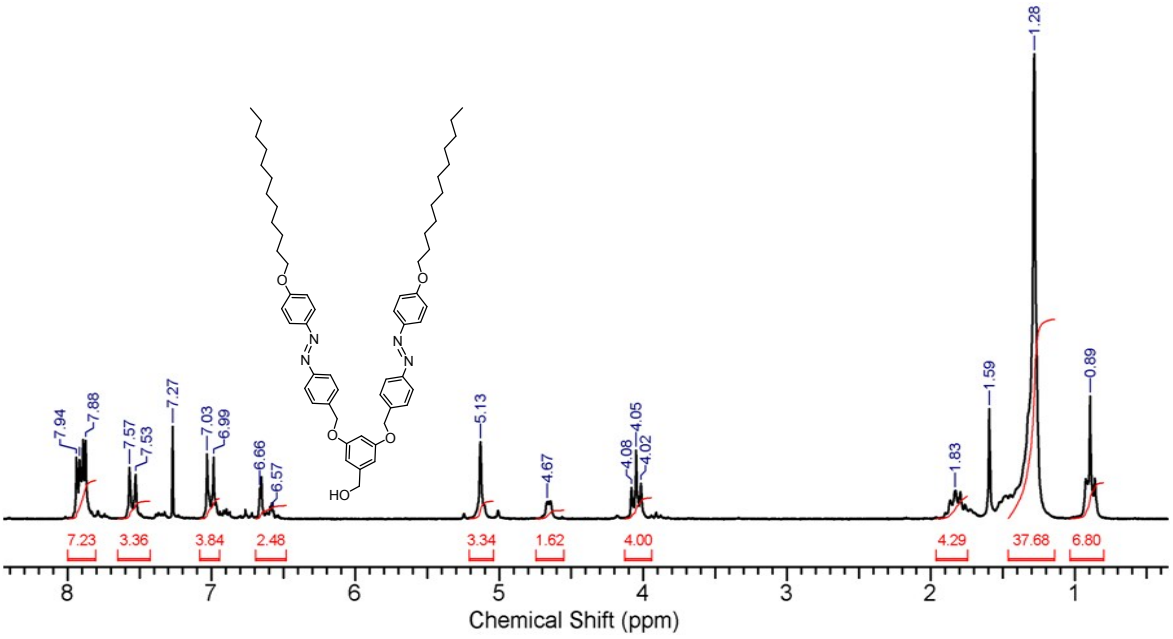


Fig. S5 200 MHz ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

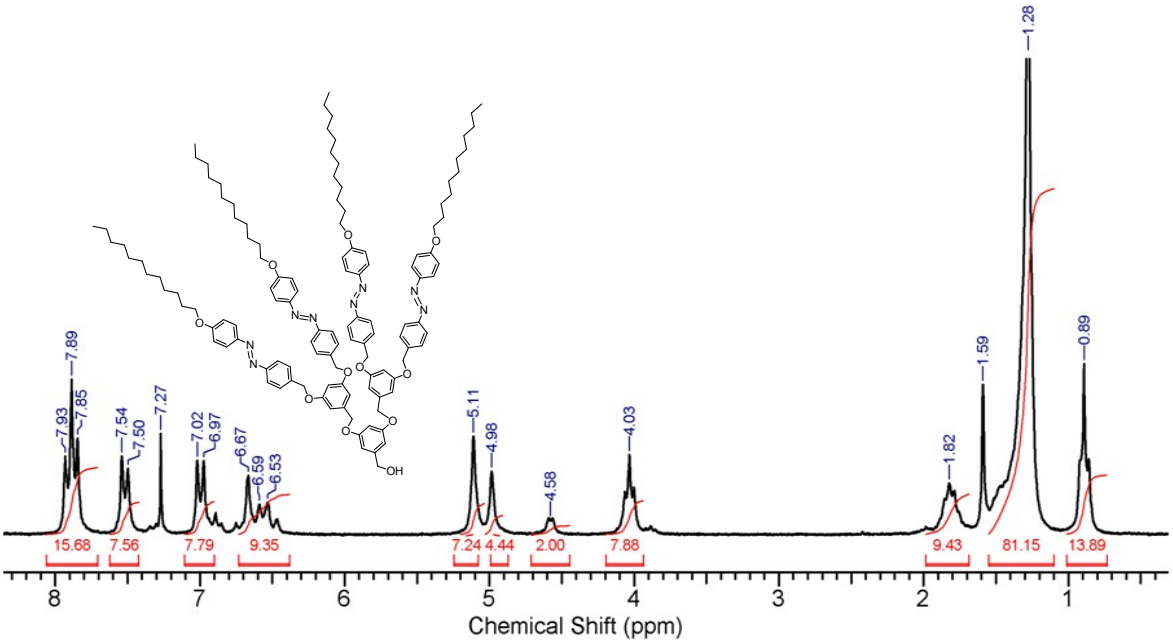


Fig. S6. 200 MHz ^{1}H NMR spectrum of compound **9** in $CDCl_3$.

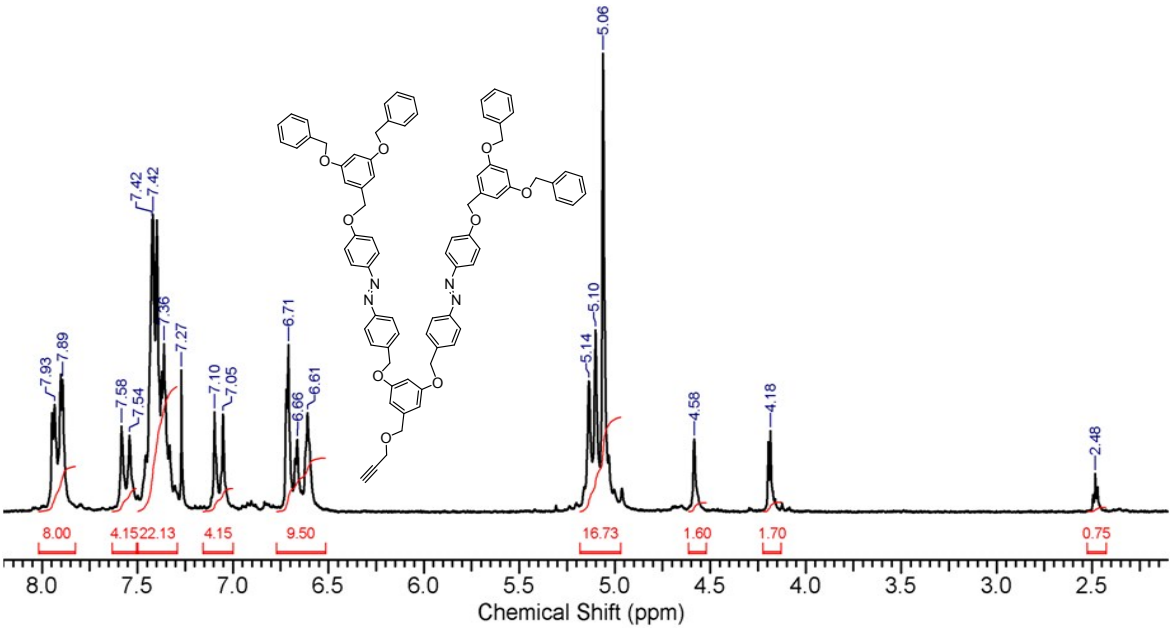


Fig. S7. 200 MHz ^{1}H NMR spectrum of **D1** in $CDCl_3$.

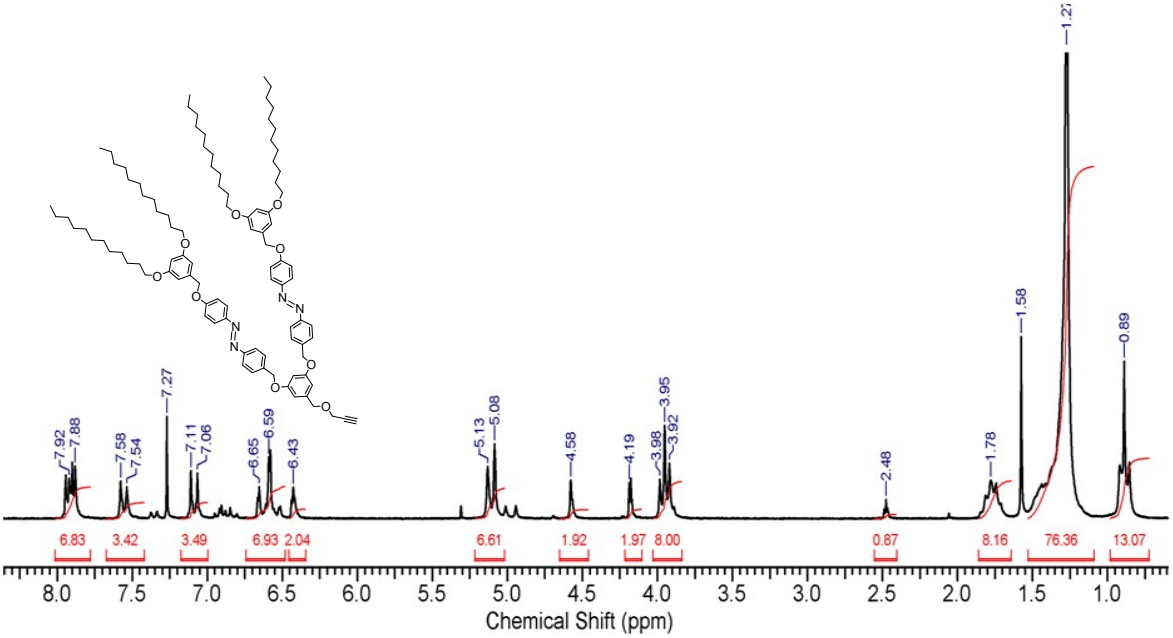


Fig. S8. 200 MHz ^{1}H NMR spectrum of **D2** in $CDCl_3$.

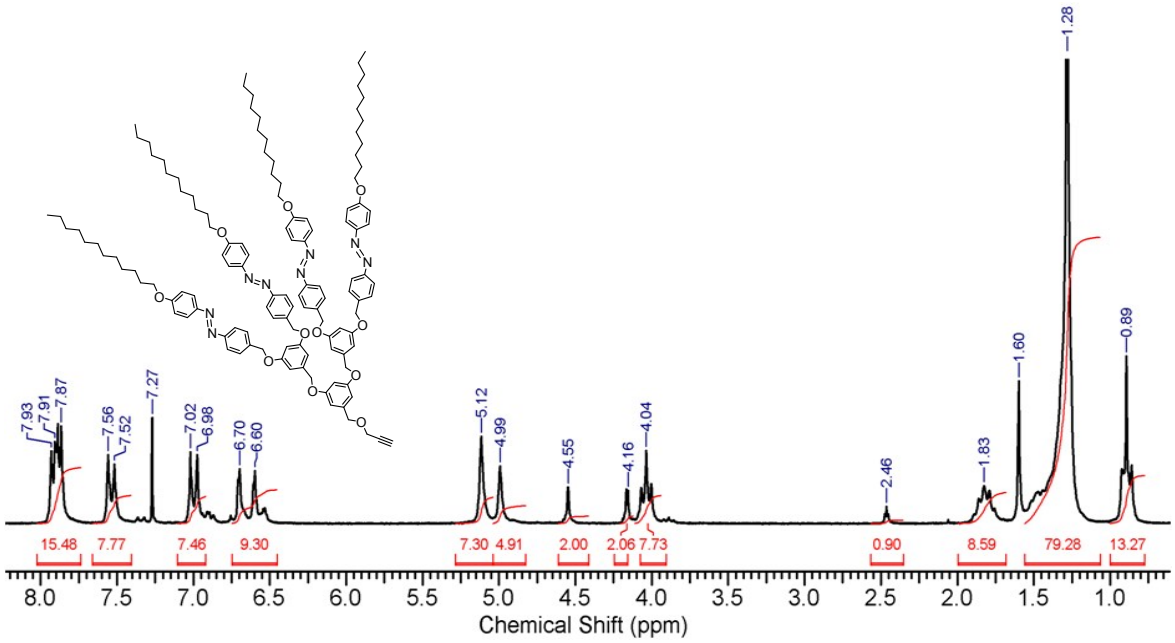


Fig. S9. 200 MHz ^{1}H NMR spectrum of **D3** in $CDCl_3$.

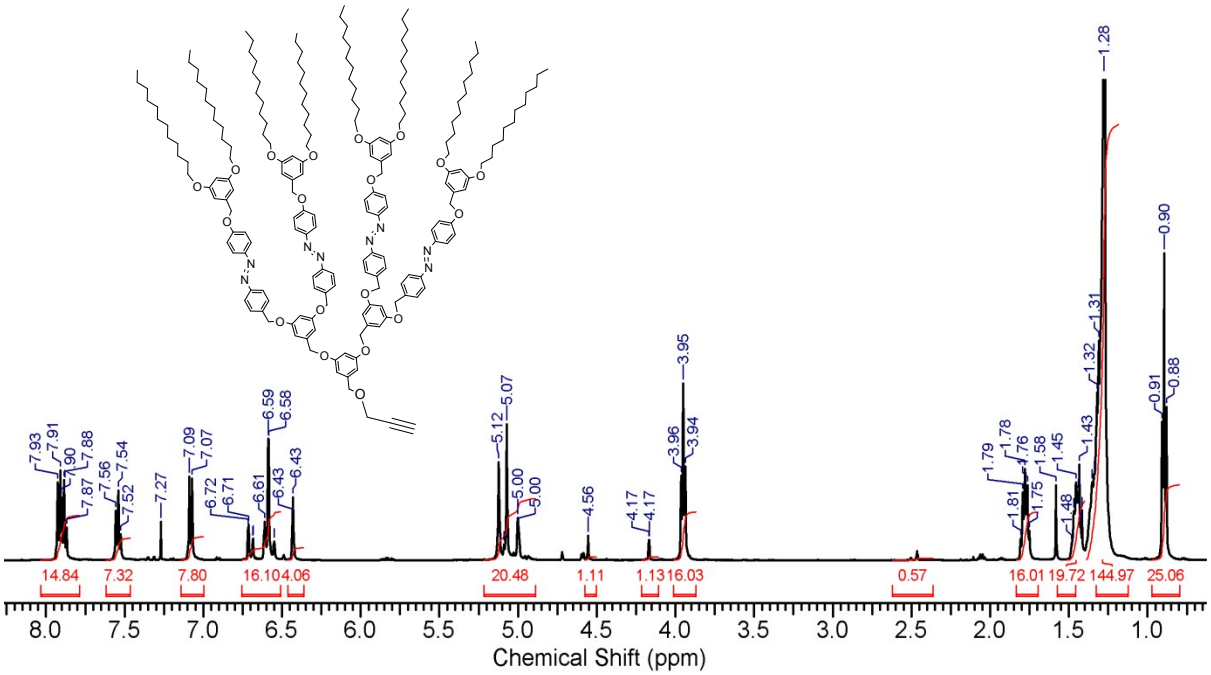


Fig. S10. 500 MHz ^{1}H NMR spectrum of **D4** in $CDCl_3$.

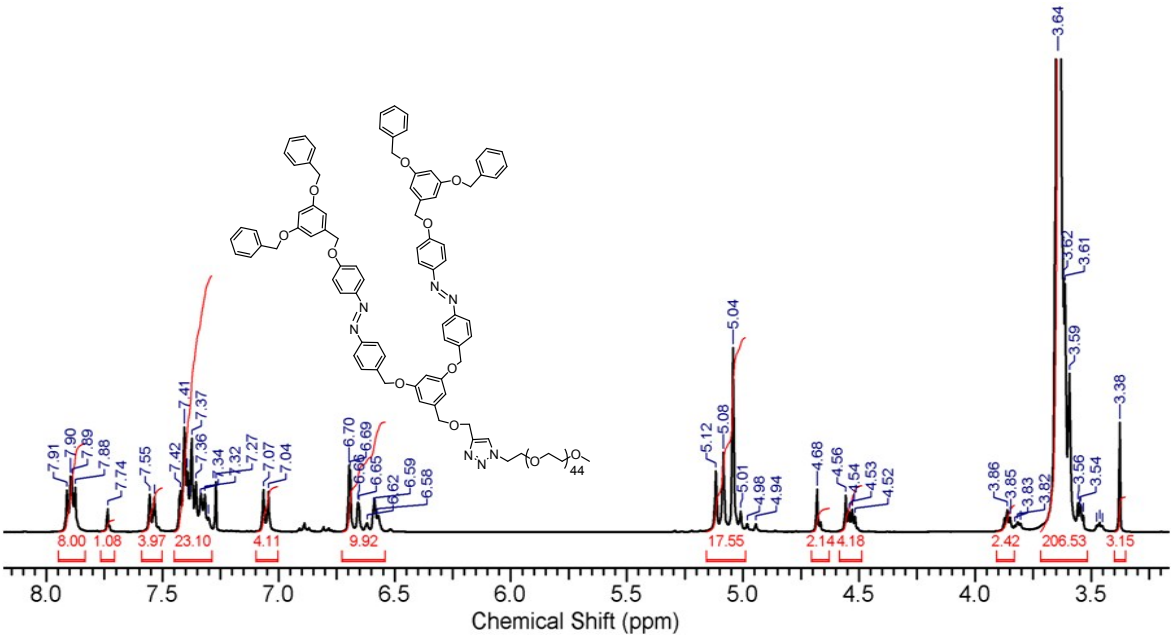


Fig. **S11**. 400 MHz ^{1}H NMR spectrum of **P1** in $CDCl_3$.

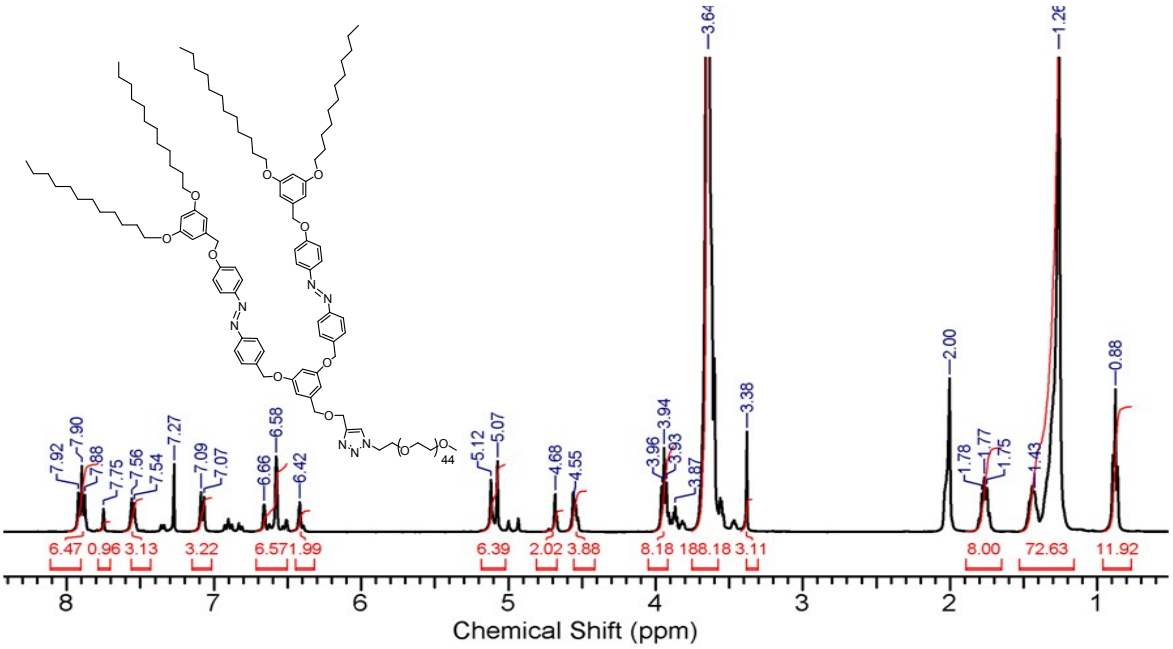


Fig. **S12**. 400 MHz ^{1}H NMR spectrum of **P2** in $CDCl_3$.

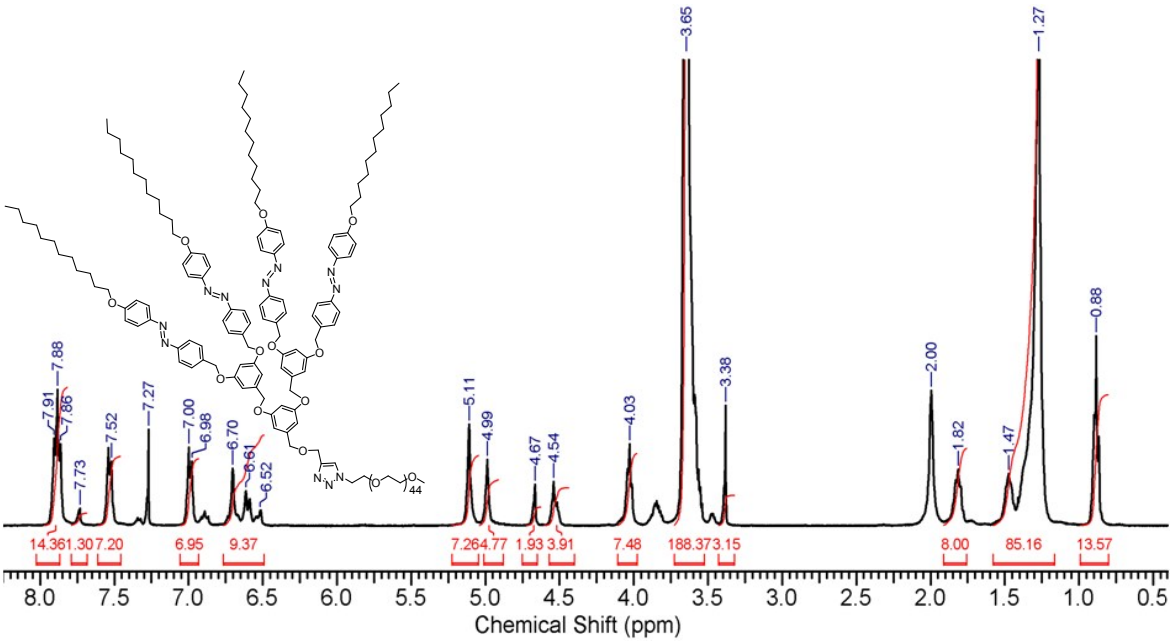


Fig. **S13**. 400 MHz ^{1}H NMR spectrum of **P3** in $CDCl_3$.

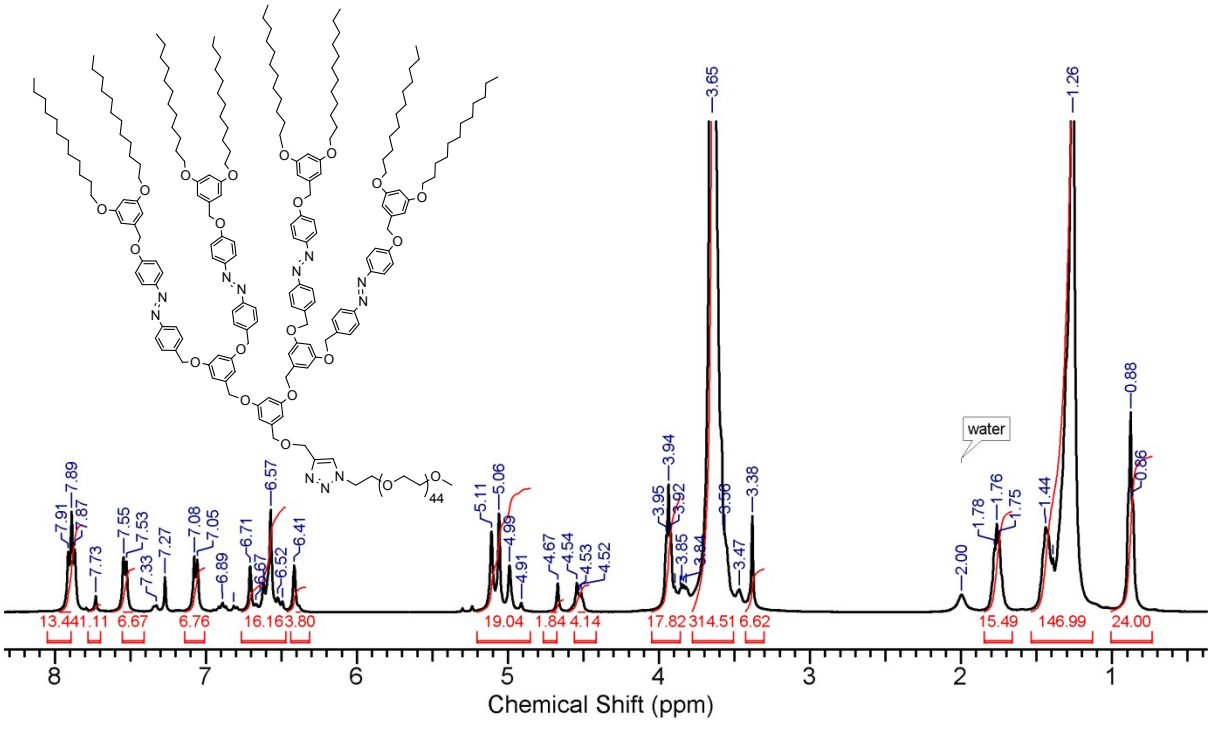


Fig. **S14**. 400 MHz ^{1}H NMR spectrum of **P4** in $CDCl_3$.

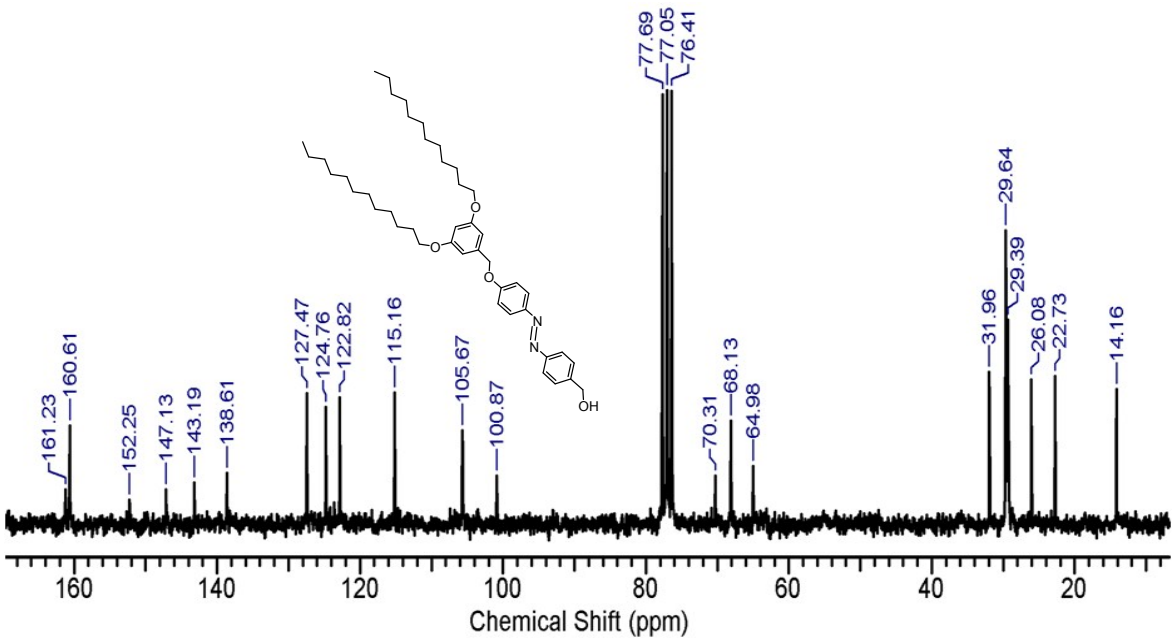


Fig. **S15**. 50 MHz ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

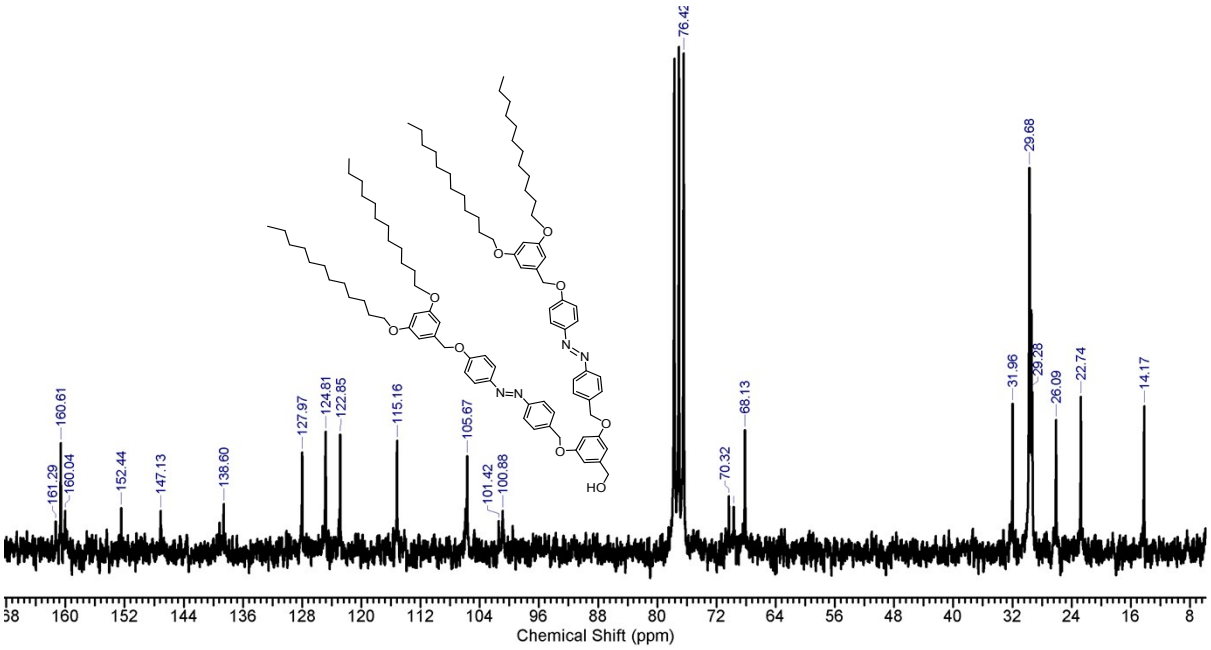


Fig. **S16**. 50 MHz ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

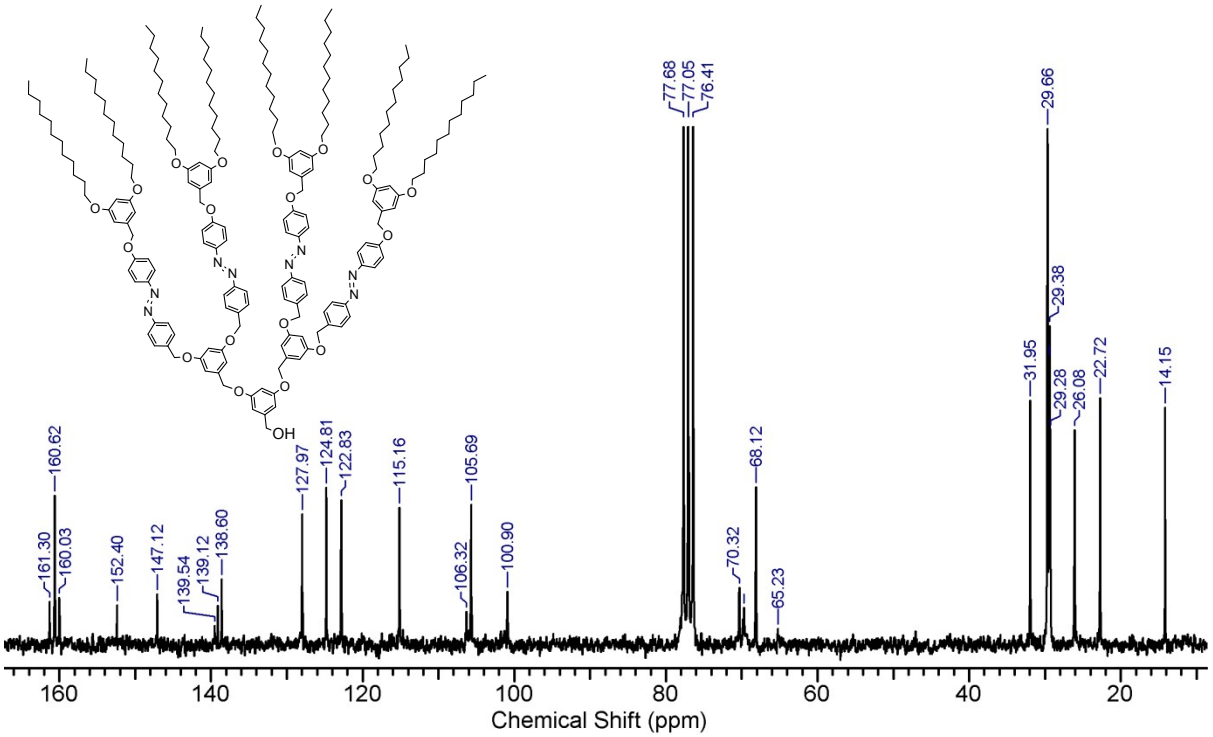


Fig. **S17**. 50 MHz ^{13}C NMR spectrum of compound **6** in $CDCl_3$.

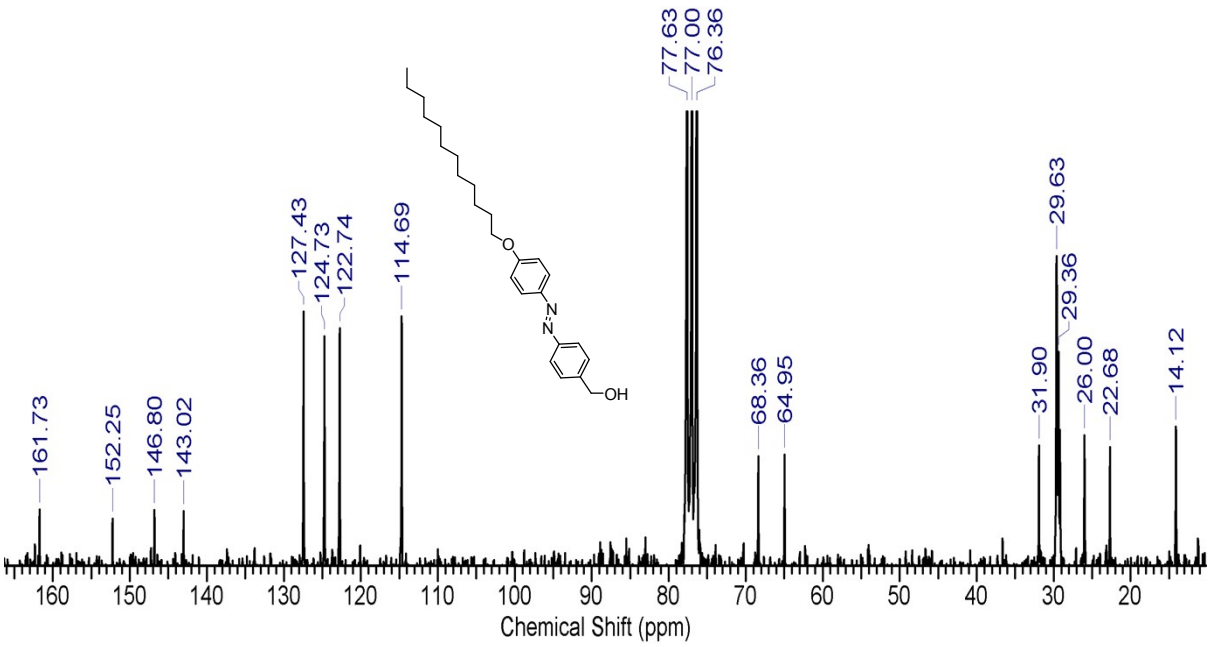


Fig. **S18**. 50 MHz ^{13}C NMR spectrum of compound **5** in $CDCl_3$.

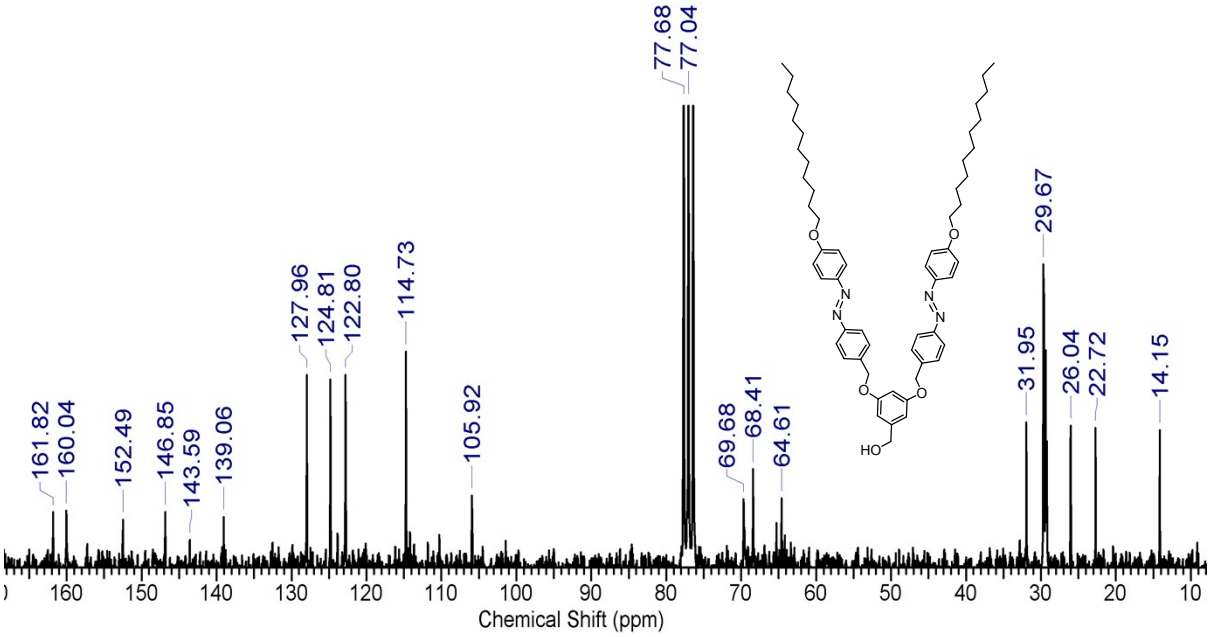


Fig. **S19**. 50 MHz ^{13}C NMR spectrum of compound **7** in $CDCl_3$.

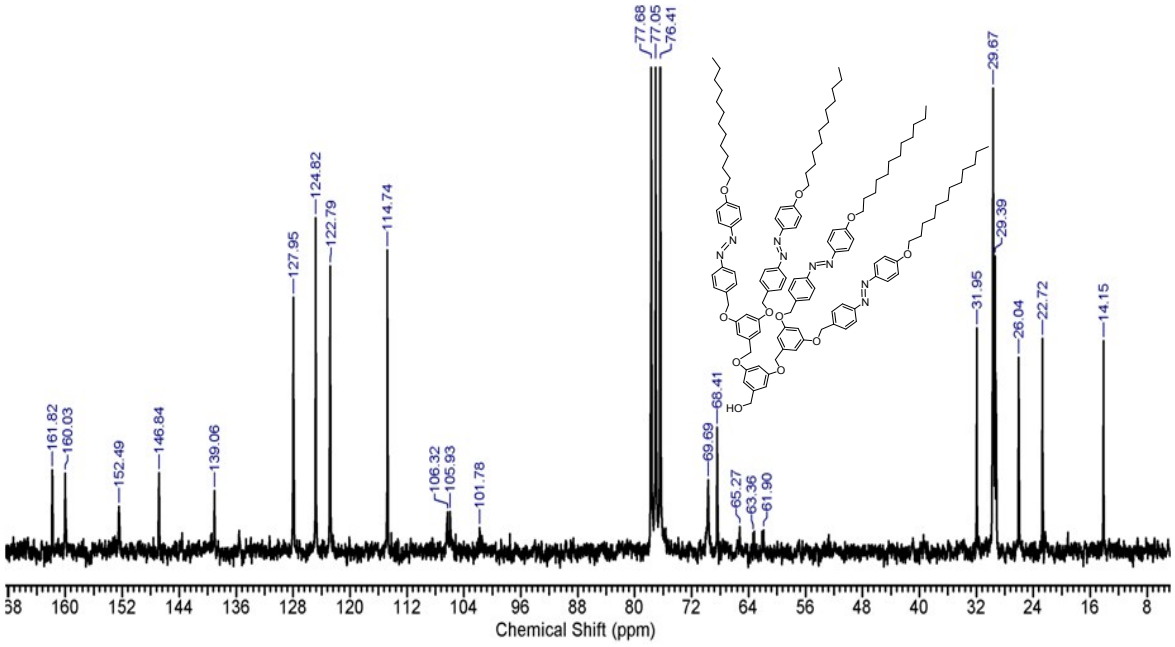


Fig. **S20**. 50 MHz ^{13}C NMR spectrum of compound **9** in $CDCl_3$.

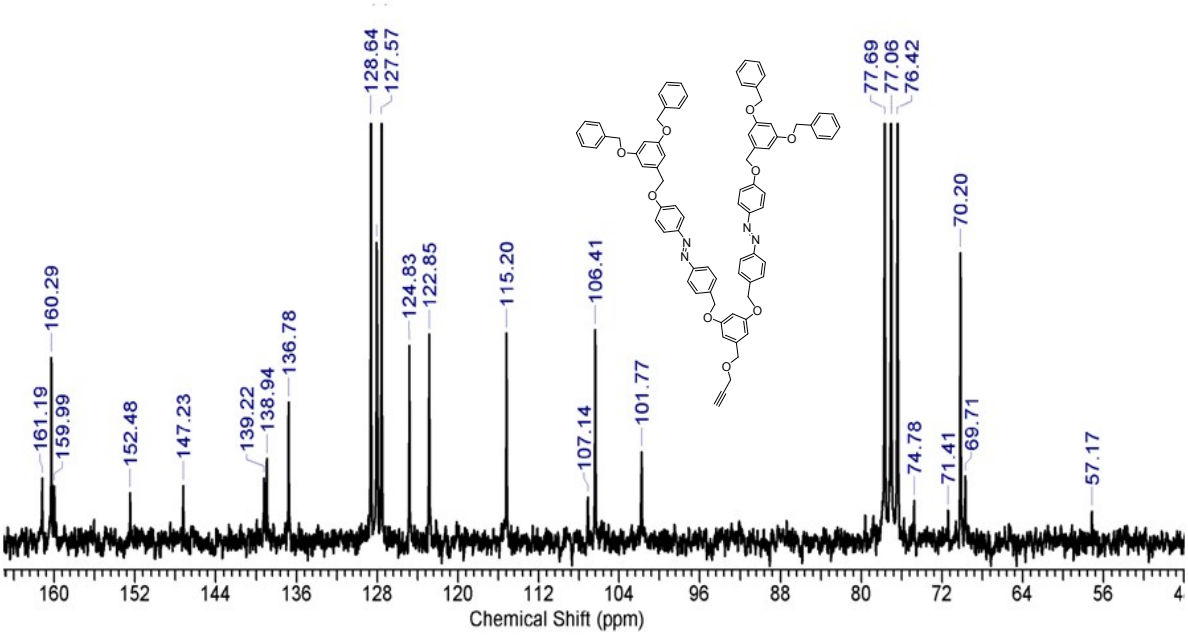


Fig. **S21**. 50 MHz ^{13}C NMR spectrum of **D1** in $CDCl_3$.

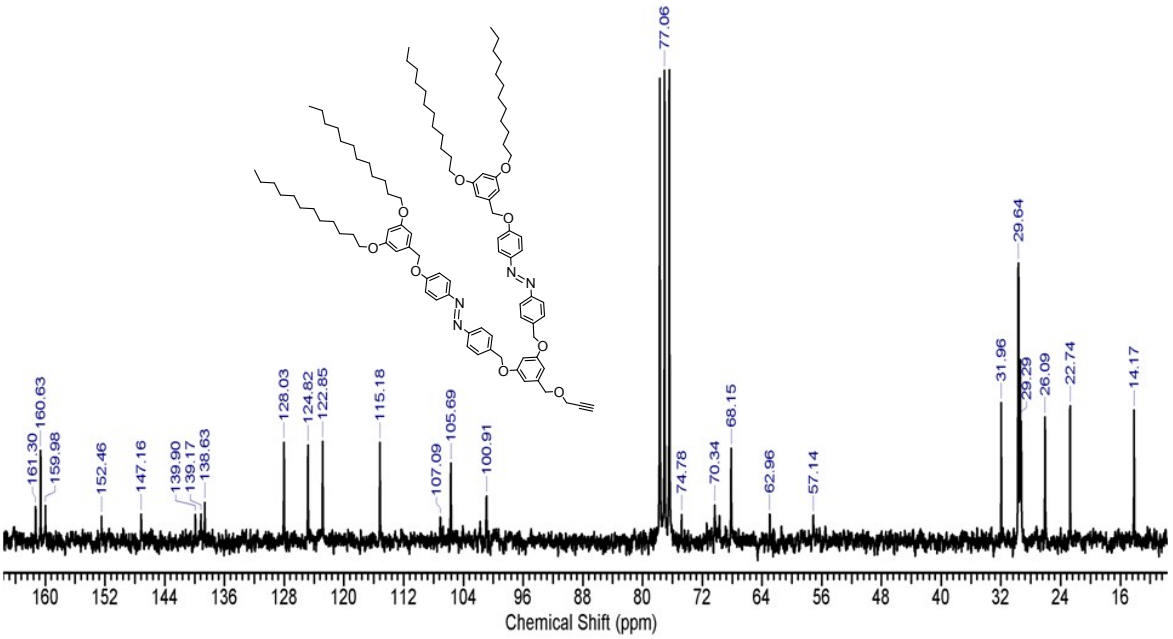


Fig. **S22**. 50 MHz ^{13}C NMR spectrum of **D2** in $CDCl_3$.

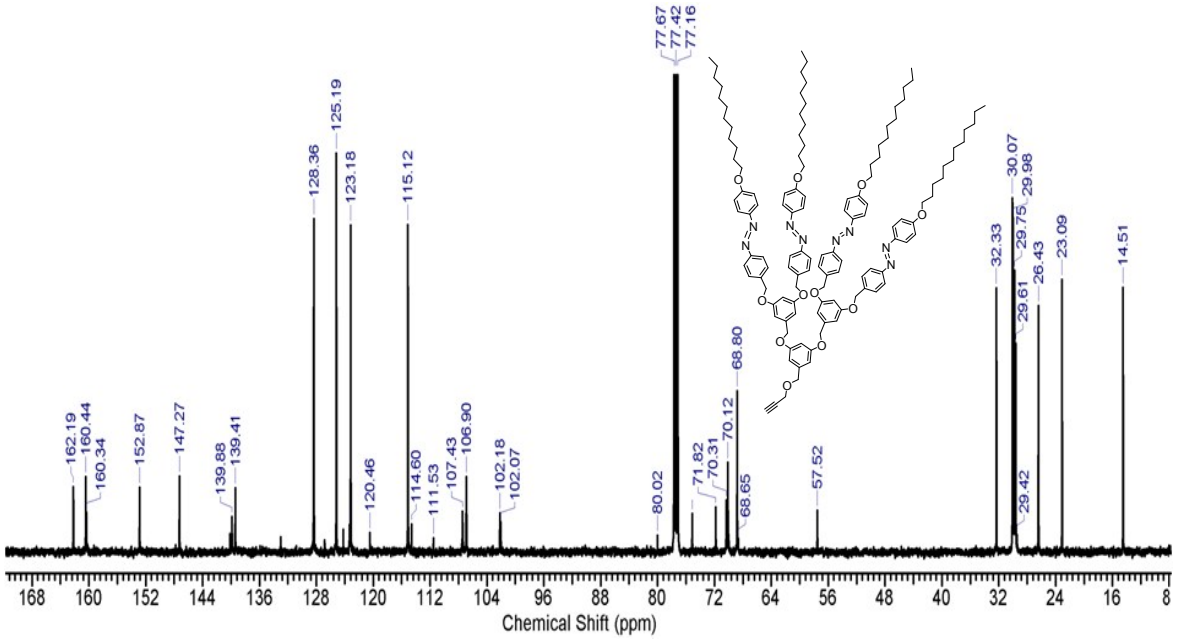


Fig. **S23**. 125 MHz ^{13}C NMR spectrum of **D3** in $CDCl_3$.

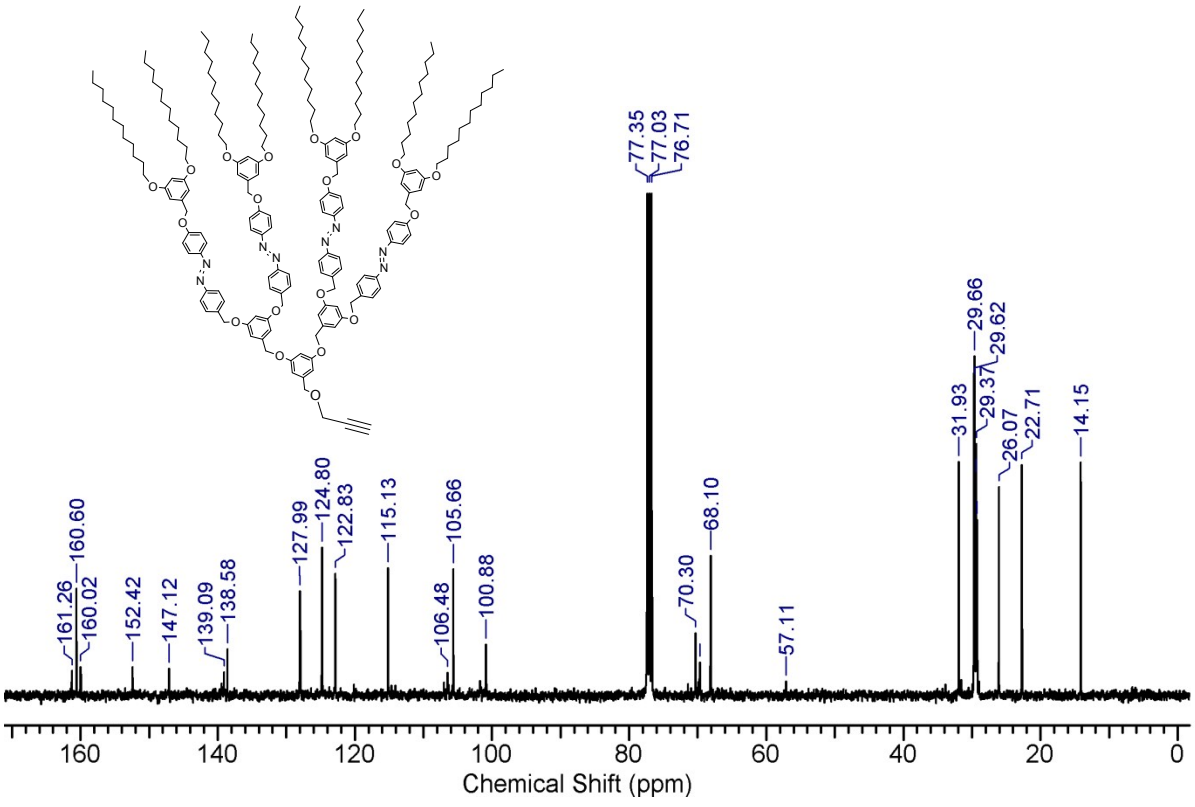


Fig. S24. 100 MHz ^{13}C NMR spectrum of D4 in $CDCl_3$.

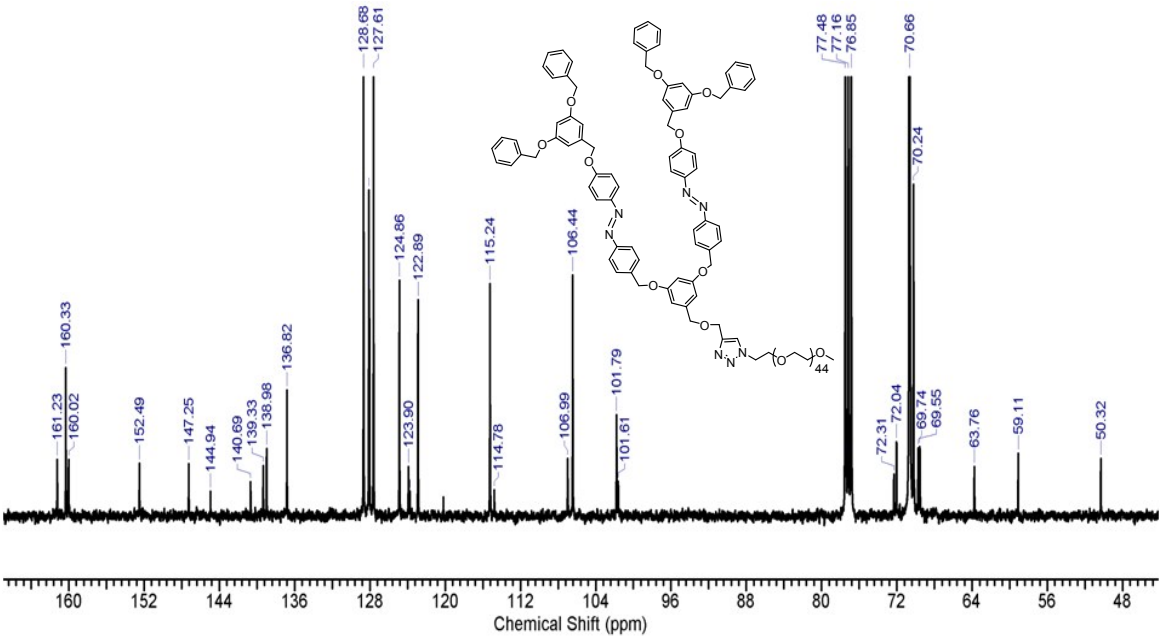


Fig. **S25.** 100 MHz ^{13}C NMR spectrum of **P1** in $CDCl_3$.

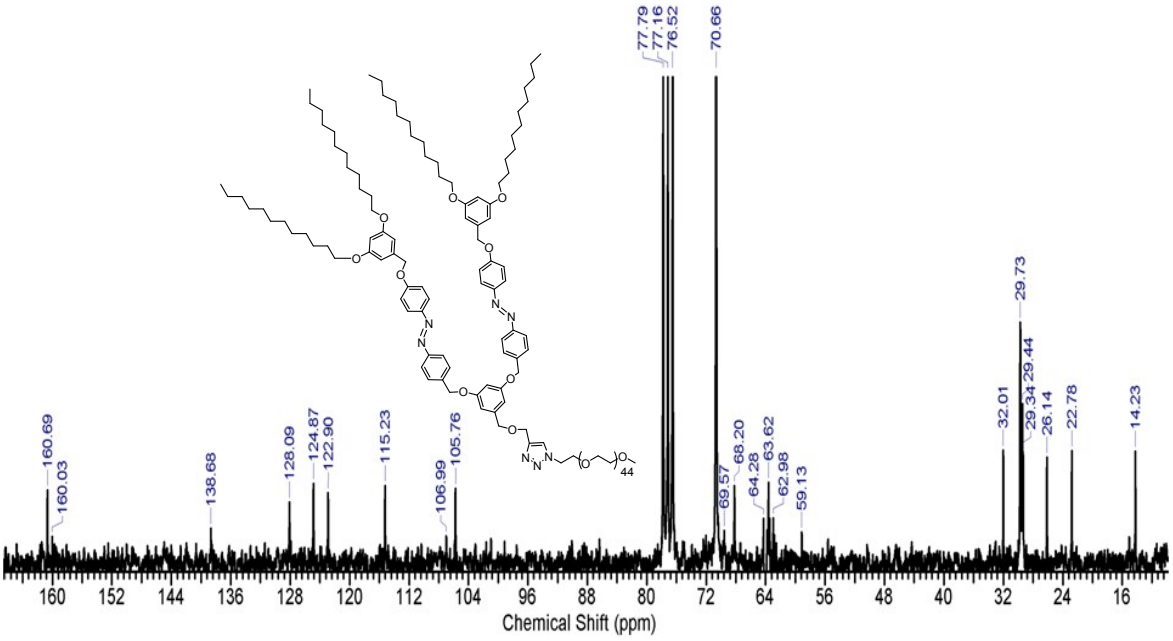


Fig. **S26**. 50 MHz ^{13}C NMR spectrum of **P2** in $CDCl_3$.

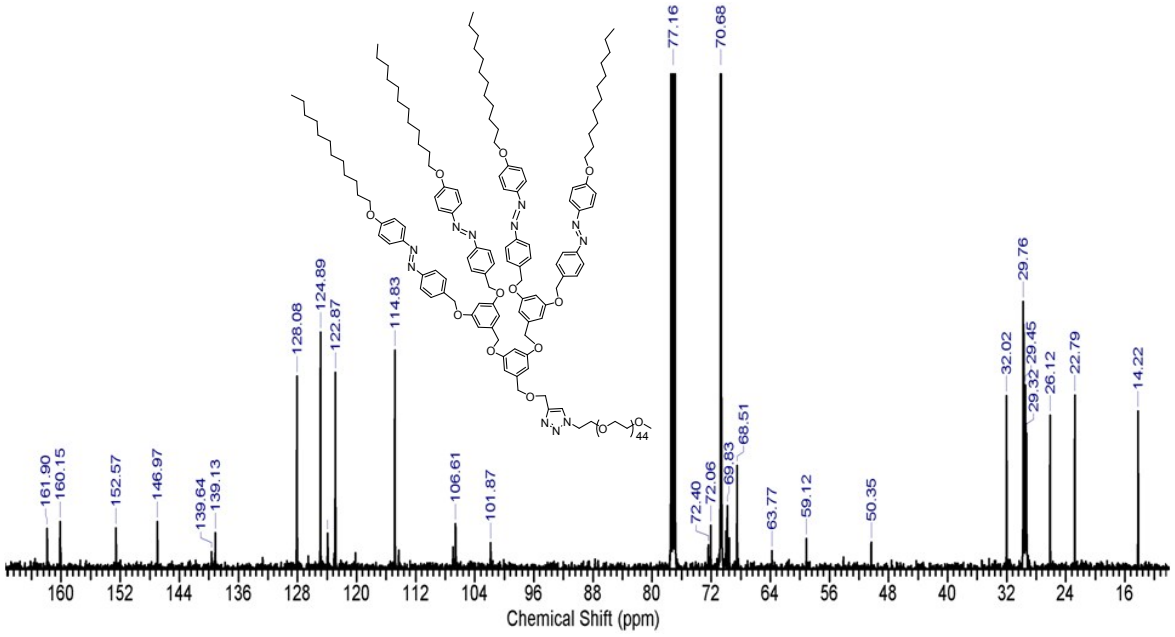


Fig. **S27**. 125 MHz ^{13}C NMR spectrum of **P3** in $CDCl_3$.

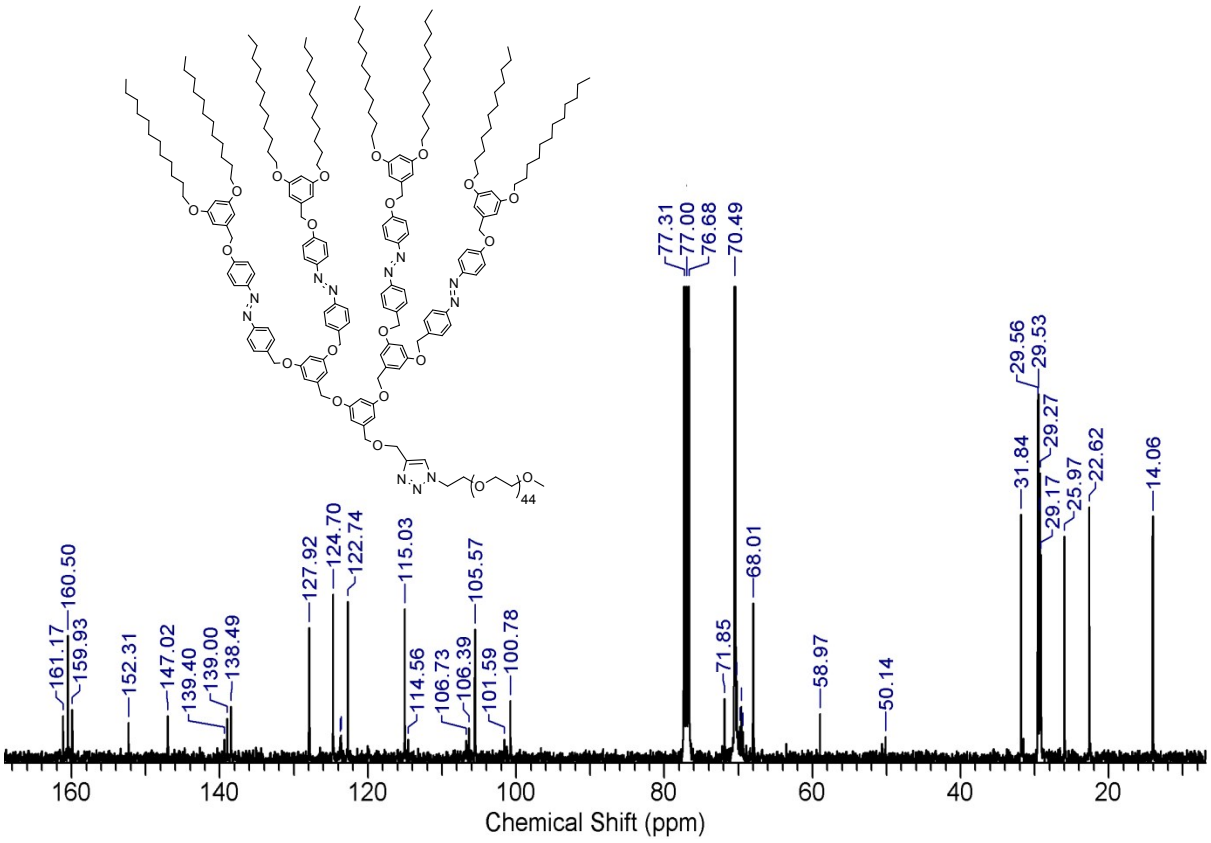


Fig. **S28**. 100 MHz ^{13}C NMR spectrum of **P4** in $CDCl_3$.

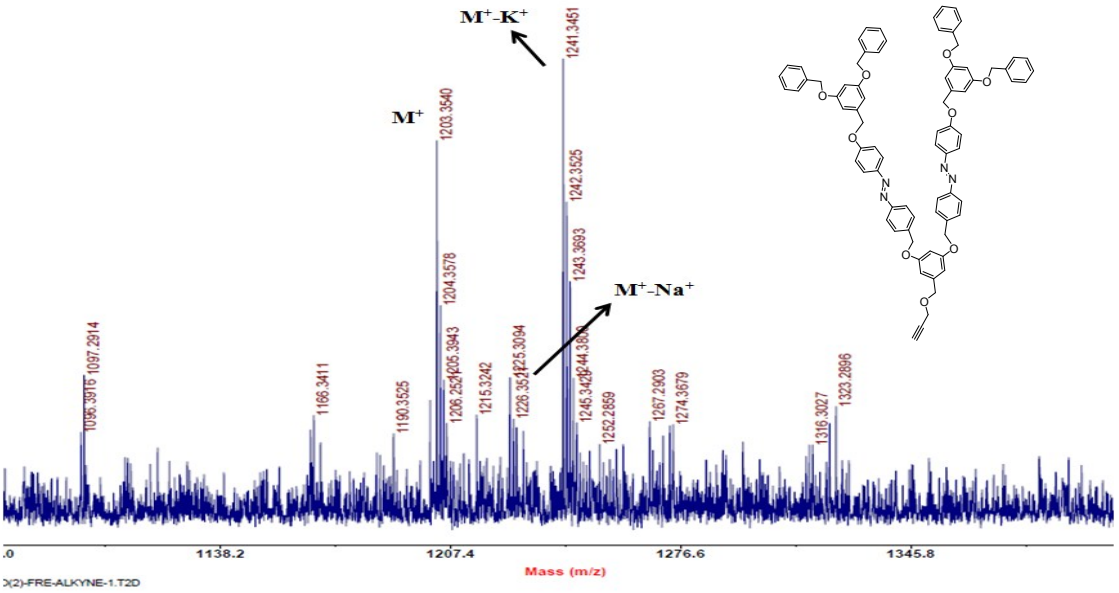


Fig. **S29**. MALDI-TOF spectrum of **D1**.

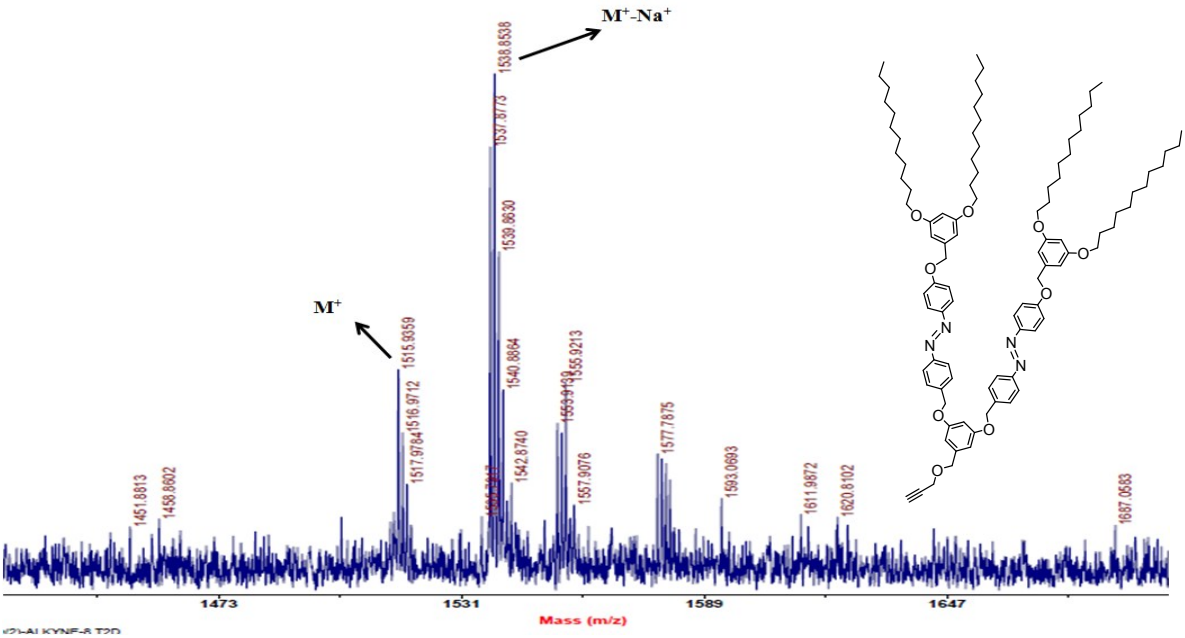


Fig. **S30**. MALDI-TOF spectrum of **D2**.

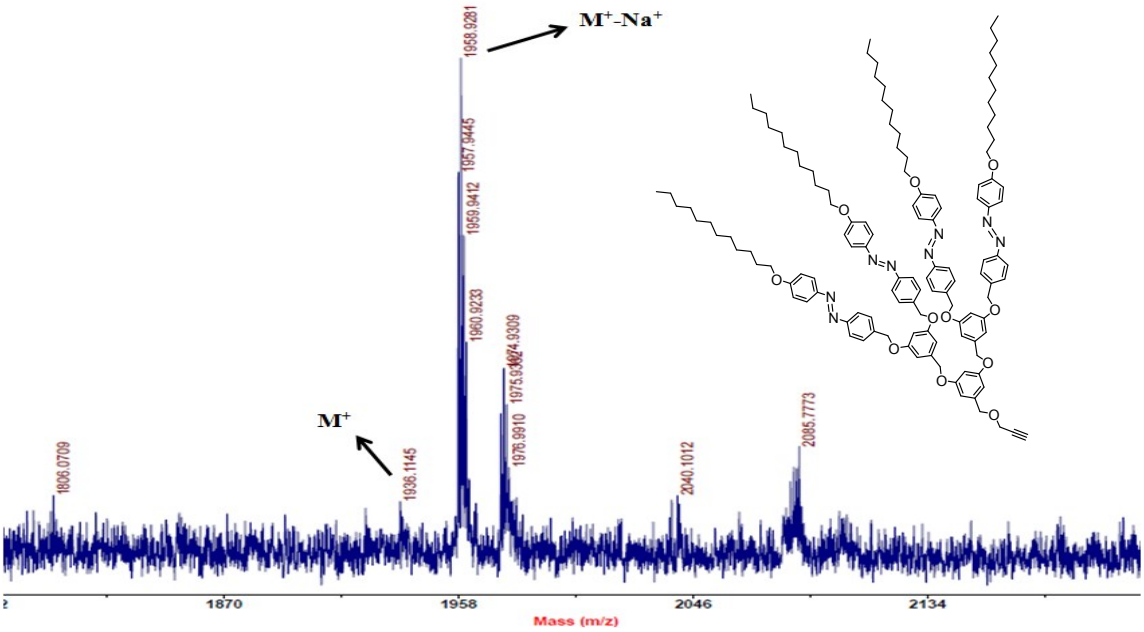


Fig. **S31**. MALDI-TOF spectrum of **D3**.

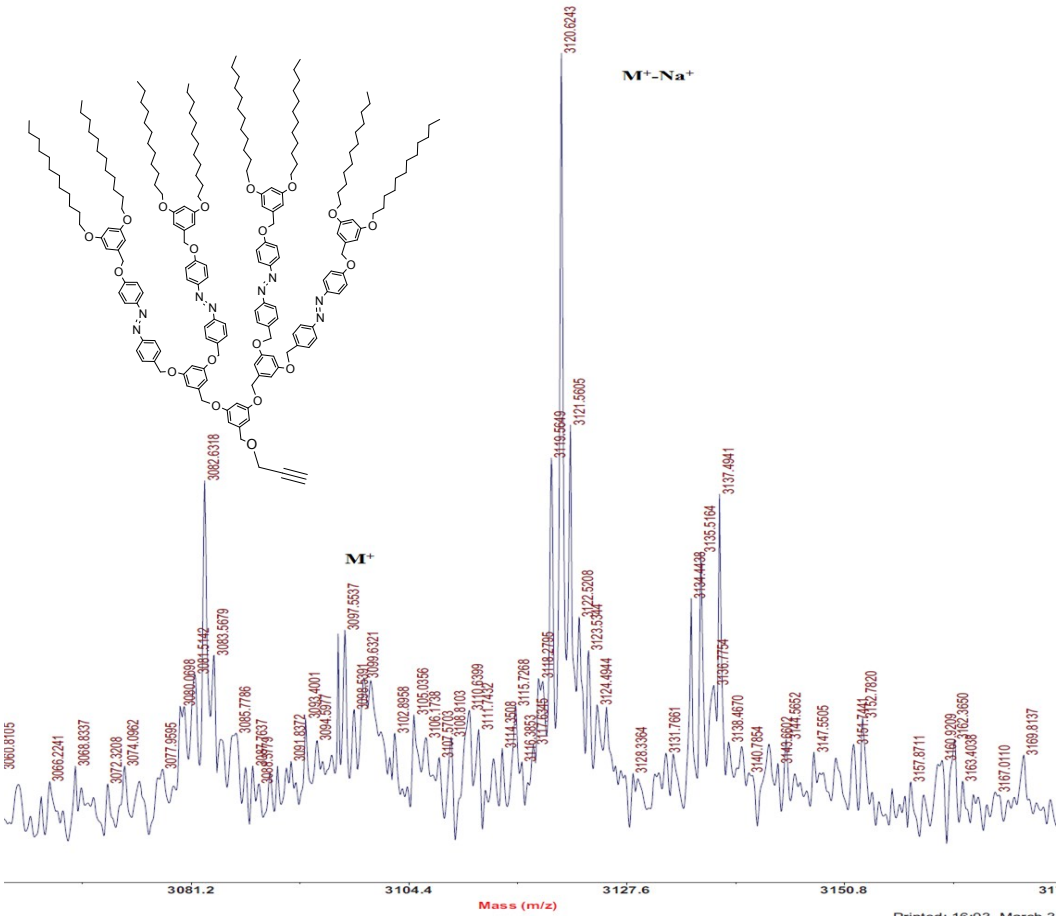


Fig. **S32**. MALDI-TOF spectrum of **D4**.

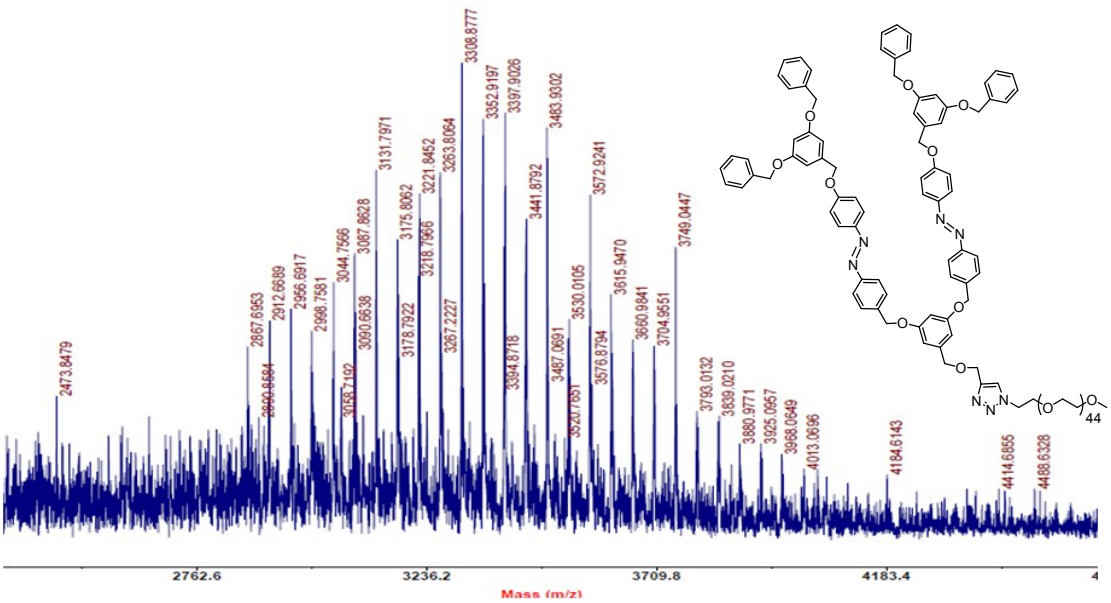


Fig. **S33**. MALDI-TOF spectrum of **P1**.

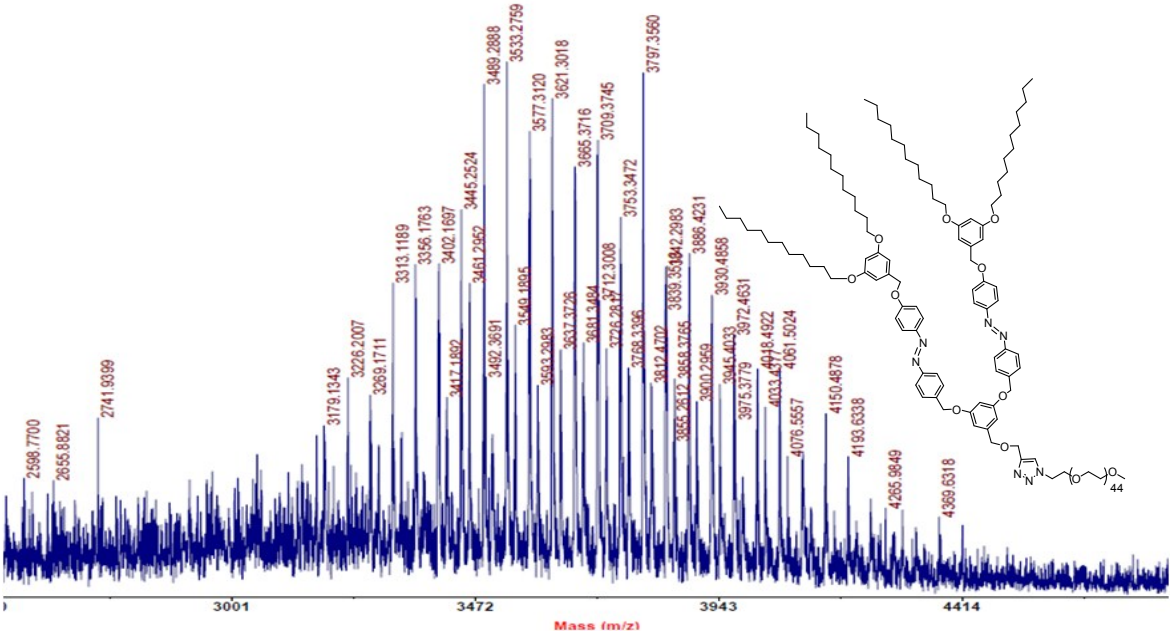


Fig. **S34**. MALDI-TOF spectrum of **P2**.

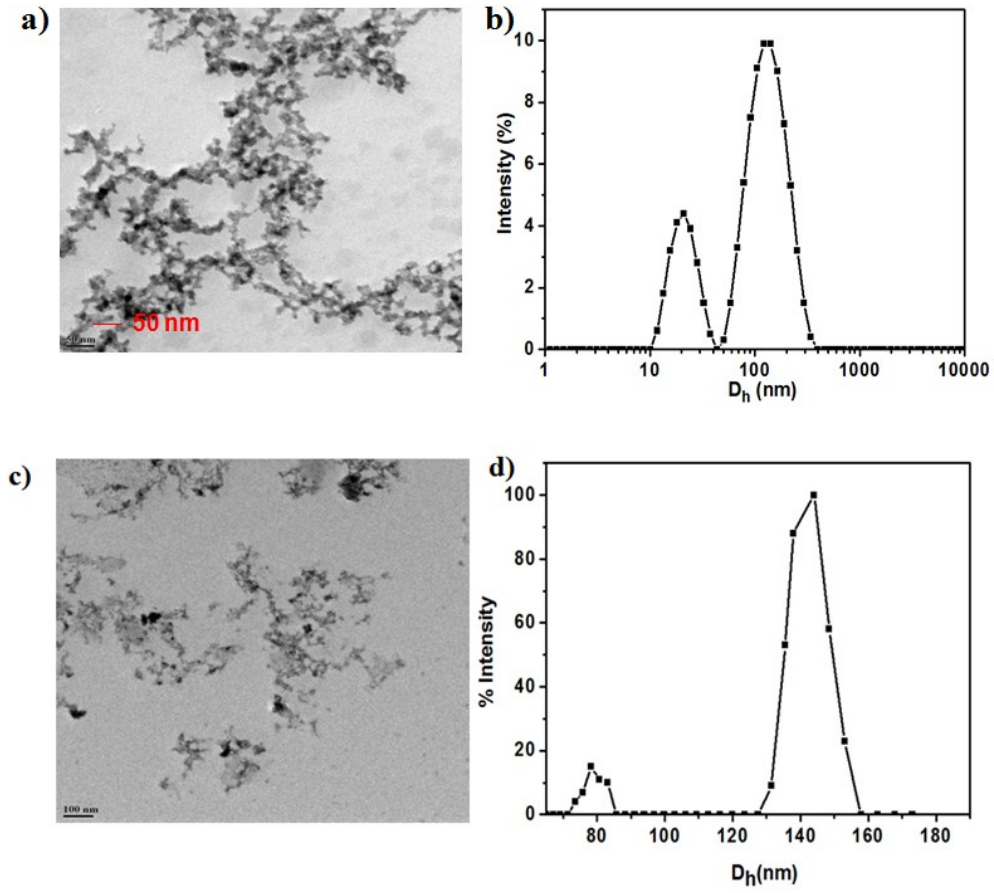


Fig. S35: a) TEM image and b) DLS size distribution curve for **P3** through dialysis of THF-H_2O solution.

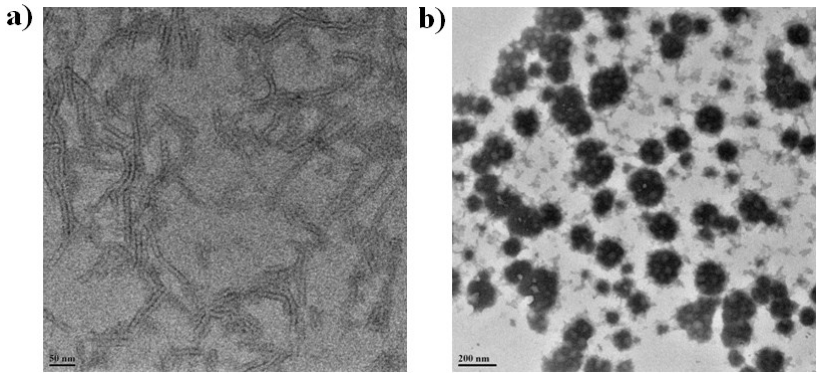


Fig. S36: TEM images of polymer **P3** (left) and **P4** through dialysis of DMF-H_2O solution.

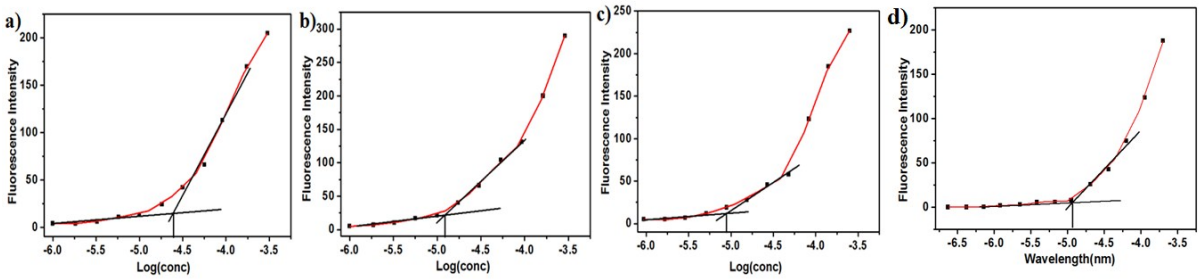


Fig. S37: Plots of fluorescence intensity vs. log (conc.) for polymers (a) **P1** (b) **P2** c) **P3** and (d) **P4**.

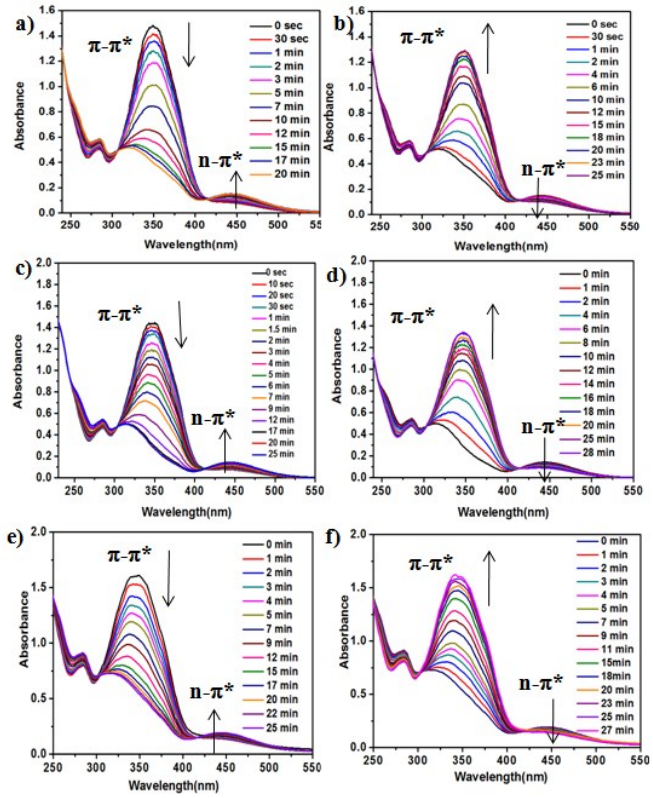


Fig. **S38**: UV-vis spectra for irradiation of 0.02 wt% aqueous solution of (a) **P1**, (c) **P2** (e) **P4** with 365 nm light and of (b) **P1**, (d) **P2 (e) P4** with 450 nm light.

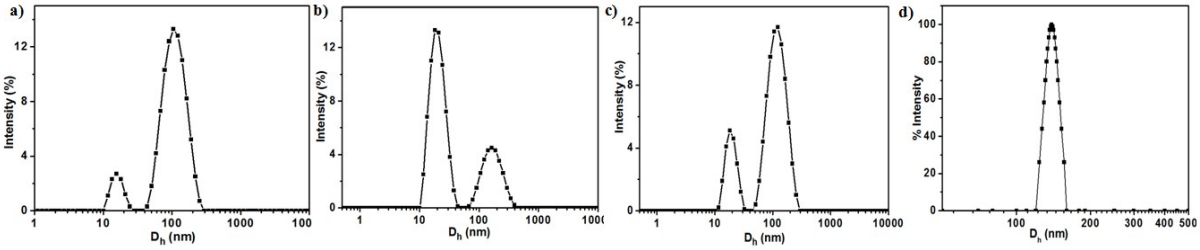


Fig. **S39**: Size distribution curves for aqueous solutions of (a) **P1** (b) **P2** (c) **P3** (d) **P4** after *trans-cis* isomerization. Average size (D_h) is 75 nm, 25 nm, 68 nm and 139 nm for **P1**, **P2**, **P3**, **P4** respectively.

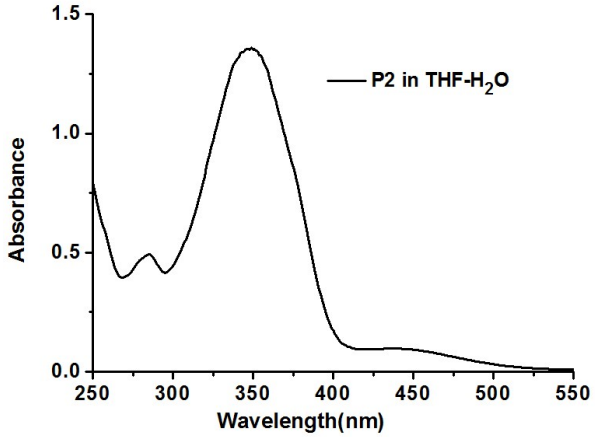


Fig. **S40:** UV-vis spectrum of 0.02 wt% solution of **P2** in THF:water (1:3 v/v).

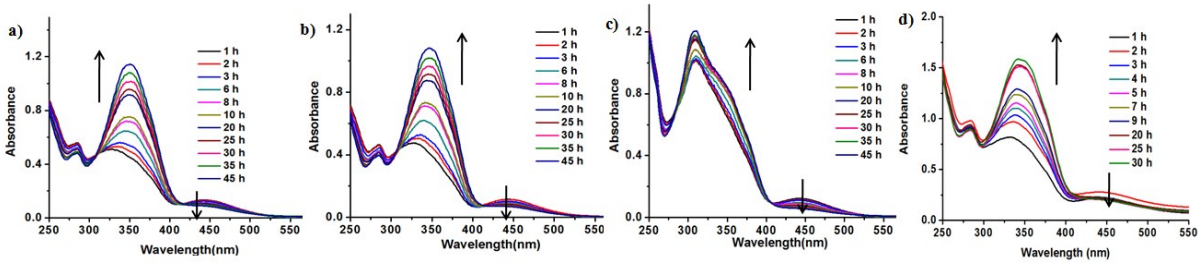


Fig. **S41**: UV-vis spectra for thermal cis-trans isomerization of azobenzene at different time intervals for 0.02 wt% aqueous solution of (a) **P1** (b) **P2** c) **P3** and (c) **P4**.

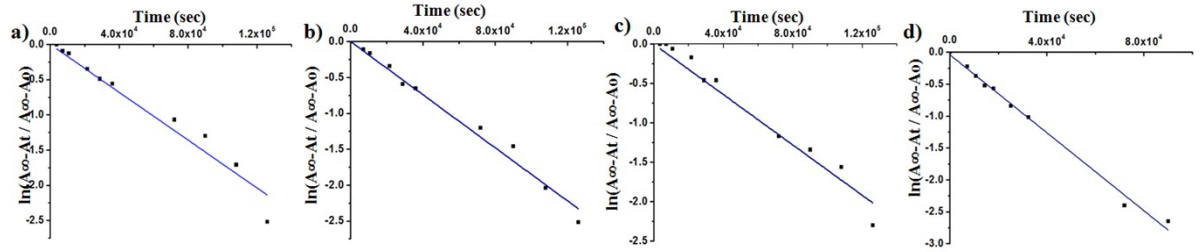


Fig. **S42**: Plots for calculation of first order rate constant of thermal *cis-trans* isomerisation for a) **P1** b) **P2** c) **P3** and d) **P4**

Nile red encapsulation capacity experiment

A thin film of the dye (0.5 mg) was prepared in each vial by solvent evaporation and vials were dried under vacuum for 5h. Then 0.5 wt% of aqueous solution of the polymer was added and stirred at room temperature for 12h. The insoluble dye was filtered through 0.45µm PVDF filter. From these solutions a known volume (0.5 mL) was taken into vials and lyophilized. The lyophilized samples were dissolved in methanol (4 mL) and absorption spectrum was recorded. The concentration of the dye was found by using reported value for molar extinction coefficient of the dye in methanol.

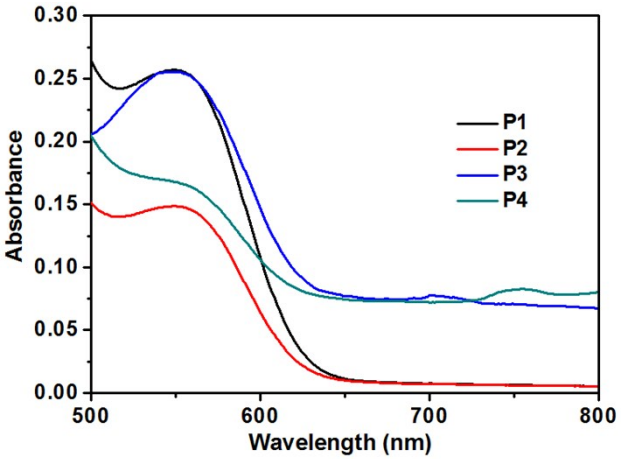


Fig. **S43:** UV-Vis spectra of Nile red in aqueous solution of **P1**, **P2, P3** and **P4** for calculation of encapsulation efficiency and encapsulation capacity.

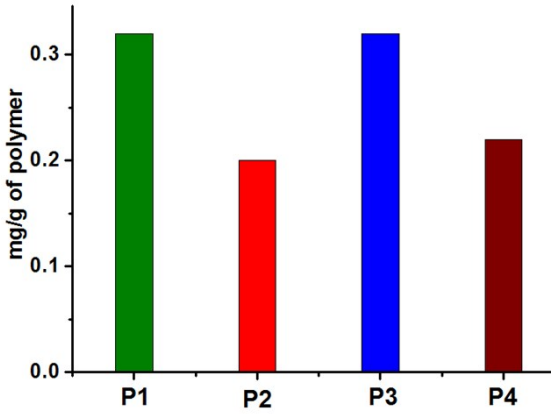


Fig. S44: Plot for encapsulation efficiency of aqueous solution of the copolymers (0.5 wt%) using Nile red.

Table S1. Dye encapsulation data for the copolymers

Polymer	**Encapsulation efficiency (mg/gof polymer)**	**Encapsulation capacity (mmol/mol of polymer)**
P1	0.32	3.2
P2	0.20	2.24
P3	0.32	3.98
P4	0.22	4.12

Dye encapsulation experiments were performed at 0.5 wt% aqueous solution of the polymers.

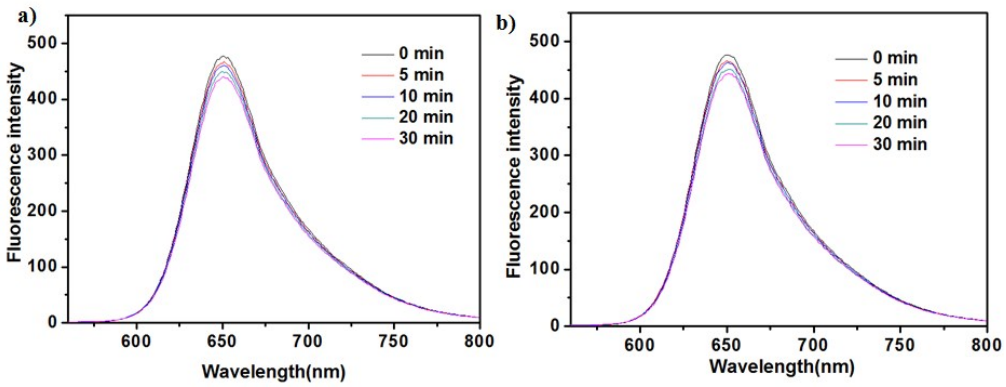


Fig. **S45**: Nile red emission spectra in MeOH: H2O (1:1) irradiating at a) 365 nm b) 450 nm.

Table S2. Data for dye release during photoisomerisation by two pathways.

Polymer	%decrease in fluorescence intensity (UV-dark)	%decrease in fluorescence intensity (UV –Vis)
P1	49	33
P2	12	39
P3	42	36
P4	41	49

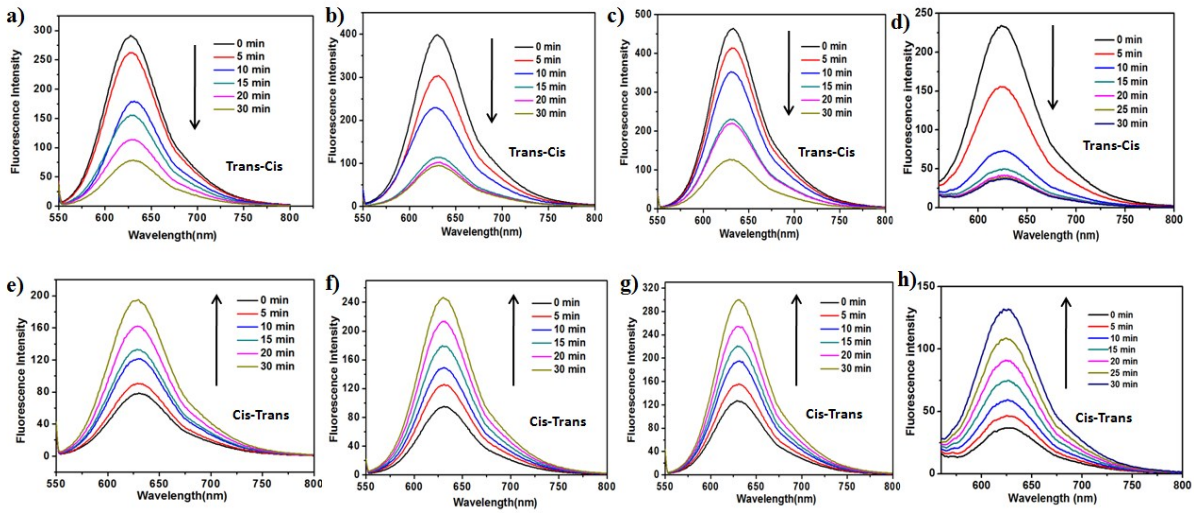


Fig. **S46**: Fluorescence emission spectra after irradiation at 365 nm for (a) **P1** (b) **P2** and (c) **P3** (d) **P4** followed by irradiation at 450 nm for (e) **P1** (f) **P2** and (g) **P3** (h) **P4** (first photocycle).

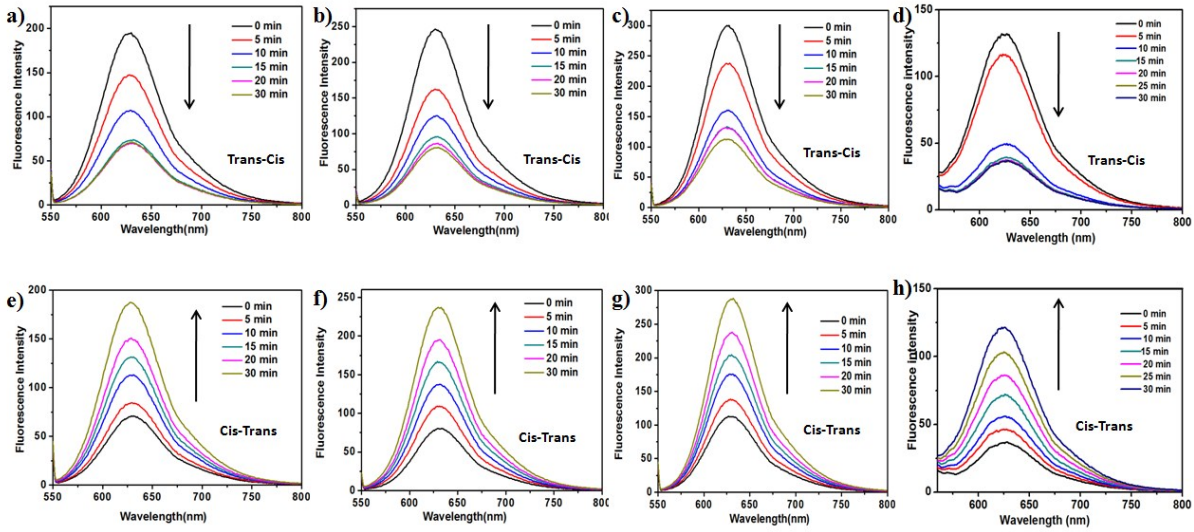


Fig. **S47**: Fluorescence emission spectra after irradiation at 365 nm for (a) P1 (b) P2 and (c) P3 (d) P4 followed by irradiation at 450 nm for (e) P1 (f) P2 and (g) P3 (h) P4 (second consecutive photocycle).

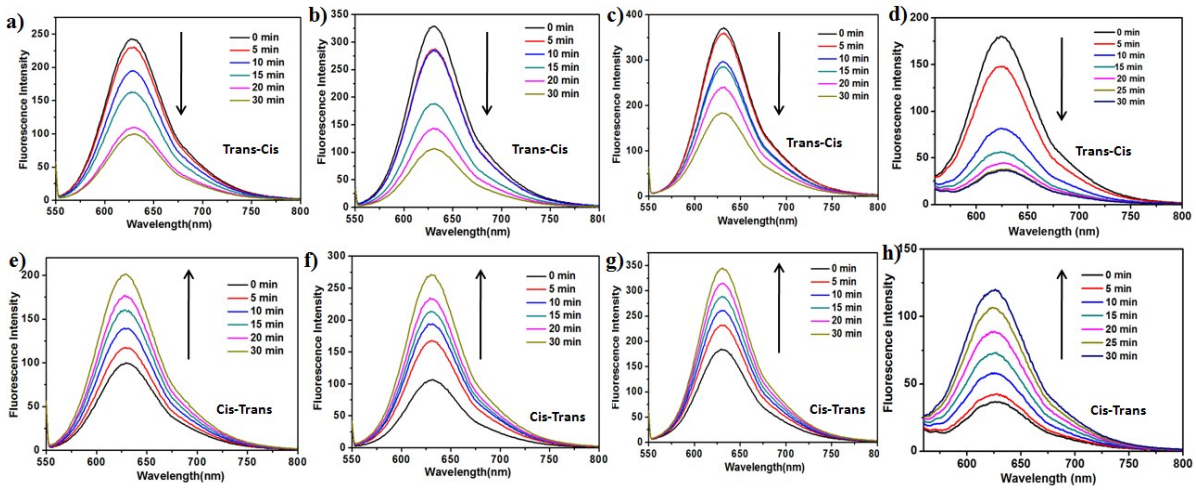


Fig. **S48**: Fluorescence emission spectra of Nile red after irradiation at (a)(b)(c) 365 nm and (d)(e)(f) 450 nm of aq. solution of **P1**, **P2**, **P3**, **P4** respectively after 12h thermal restoration (third photocycle).

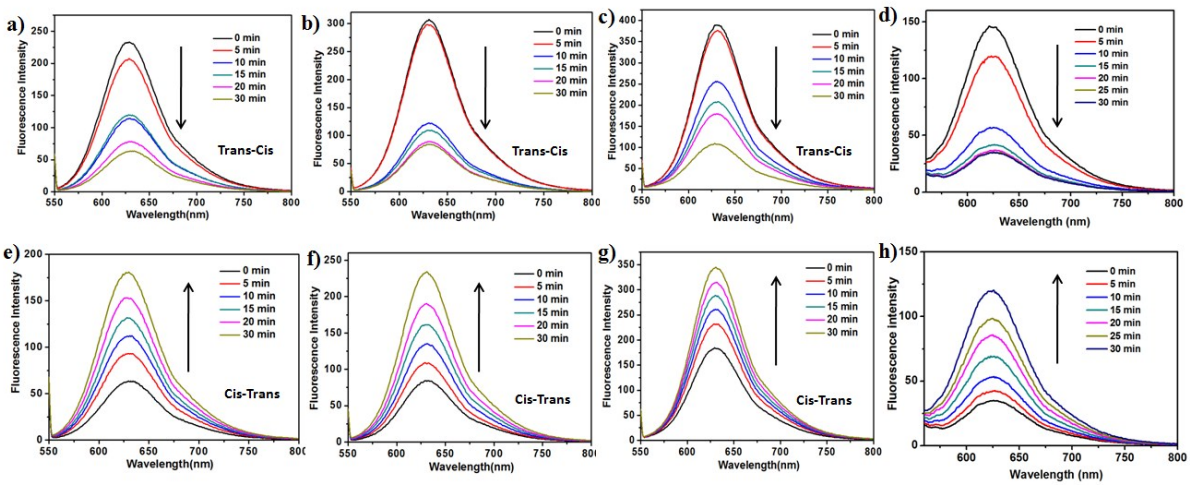


Fig. **S49**: Fluorescence emission spectra of Nile red after irradiation at (a)(b)(c)(d) 365 nm and (e)(f)(g)(h) 450 nm of aq. solution of **P1**, **P2**, **P3**, **P4** respectively after 4h thermal restoration (fourth photocycle).

References

1) L. X. Liao; D. M. Junge; D. V. McGrath *Macromolecules* **2002**, *35*, 319.

2) N. Kalva; V. K. Aswal; A. V. Ambade *Macromol. Chem. Phys*. **2014,** *215,* 1456.