Supporting Information for

Copper and silver nanoparticles stabilized by bis-triazole-based dendritic amphiphile micelles for reduction of 4-nitrophenol

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Experimental Section

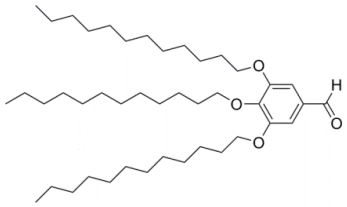
Synthesis and characterization

First and second generation dendron alcohols (**1** and **2**) were synthesized starting from 3,4,5-trihydroxy benzoic acid and 3,5-dihydroxy benzoic acid by following reported procedure.[1]

Dendron-aldehyde (3, 4)

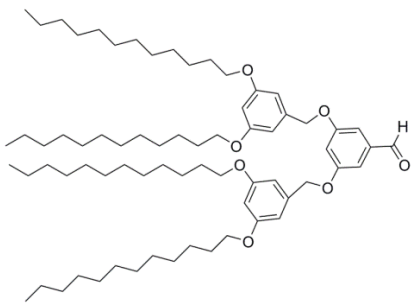
In a 100 mL round bottom flask PCC (1.5 eq.) was suspended in 7 mL of dichloromethane and a solution of dendron alcohol (**1** or **2)** (1 eq.) in 20 mL DCM was added rapidly by syringe at room temperature. The reaction mixture was stirred for 3 h. Then reaction mixture was diluted five times by diethyl ether, the solvent was decanted and the residue was washed twice with diethyl ether. Solvents were evaporated and residue obtained was purified by column chromatography on silica gel using ethyl acetate: pet ether (1:9) mixture as eluant.

3,4,5 G1-aldehyde (3)



Yield 84%. ^{1}H NMR (200 MHz, $CDCl_3$), δ ppm 9.84 (s, 1 H, -CHO), 7.09 (s, 2 H, Ar H), 4.04 (m, 6 H, OCH_2), 1.80 (m, 6H, CH_2), 1.08-1.61 (m, 54H, CH_2), 0.89 (t, 9 H, J = 7 Hz, –CH_3). ^{13}C NMR (50MHz, $CDCl_3$, δ): 191.23 (CHO), 153.52(Ar C-O), 143.93(Ar **C**-CHO), 131.46(Ar C-O), 107.92(Ar CH), 73.63(OCH_2), 69.26(OCH_2), 31.92(CH_2), 29.68(CH_2), 29.62(CH_2), 29.36(CH_2), 29.26(CH_2), 26.06(CH_2), 22.68(CH_2), 14.07(CH_3). MALDI-TOF MS *m/z* $[M+Na]^+$ Calcd. for $C_{43}H_{78}O_4$ 682.09, Found: 681.44.

3,5 G2-aldehyde (4)

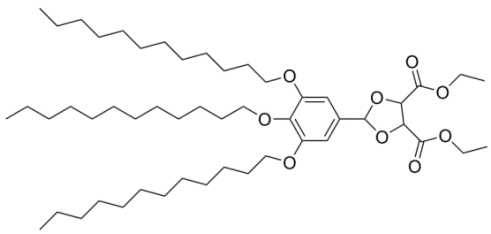


Yield 78%. ^{1}H NMR (200 MHz, $CDCl_3$), δ ppm 9.90 (s, 1 H, -CHO), 7.10 (d, 2 H, J = 2.3Hz; Ar H), 6.86 (t, 1H; Ar H), 6.55 (d, 4H, J= 2.3Hz; Ar H), 6.42 (t, 2H, J = 2.2Hz; Ar H), 5.01 (s, 4H; OCH_2Ar), 3.95 (t, 8H; J = 6.5Hz, OCH_2), 1.78 (m, 8H; CH_2), 1.20 - 1.52 (m, 72H; CH_2), 0.89 (t, 12H, J = 7Hz; CH_3). ^{13}C NMR (50 MHz, $CDCl_3$), δ ppm, 191.72(CHO), 160.60(Ar C-O), 160.39(Ar C-O), 138.36(Ar C), 108.70(Ar C), 108.30(Ar C), 105.74(Ar C), 100.97(Ar C), 70.41(OCH_2), 68.11(OCH_2), 31.91, 29.62, 29.34, 29.26, 26.06, 22.68, 14.09(CH_3). MALDI-TOF MS *m/z* $[M+Na]^+$ Calcd. for $C_{69}H_{114}O_7Na$ 1078.65, found: 1078.76.

Dendron-acetal-diester (5, 6)

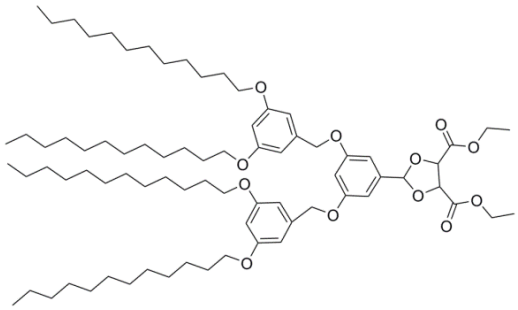
A mixture of *D,L*-diethyl tartrate (10 eq.), dendron-aldehyde (**3** or **4**) (1 eq.) and p-toluene sulfonic acid monohydrate (0.08 eq.) in 60 mL of dry toluene was heated at reflux under N_2 atmosphere using a Dean-Stark apparatus for 12 h. The reaction mixture was transferred to a separating funnel and washed twice with $NaHCO_3$ solution followed by brine solution and water. The organic layer was dried over anhydrous Na_2SO_4. Solvent was removed to get crude product, which was purified on silica gel column (treated with triethyl amine) eluting with ethyl acetate : pet ether (0.2:10). Triethyl amine (0.3 mL) was added per 100 mL of mobile phase.

3,4,5G1-Diester (5)



Yield 70%. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm 6.81(d, 2H, Ar H), 6.06(s, 1H, OCH), 5.3-4.6(m, 2H, OCH), 4.23-4.37(m, 4H, OCH_2), 3.9-4.05(m, 6H, OCH_2), 1.68-1.87(m, 6H, CH_2), 1.46(m, 6H, J=7Hz; CH_2), 1.2-1.4(m, 54H, CH_2), 0.88(t, 9H, J=7Hz; CH_3). ^{13}C NMR (125MHz, $CDCl_3$), δ ppm 169.63(C=O), 169.05(C=O), 153.14(Ar C-O), 139.30(Ar C-O), 130.16(Ar C-O), 107.77, 106.82, 105.45, 77.45, 73.34, 69.01, 62.05, 62.00, 61.91, 61.86, 33.56, 31.91, 30.27, 29.73, 29.69, 29.6, 29.39, 29.35, 26.08, 22.67, 14.10. MALDI-TOF MS *m/z* $[M+Na]^+$ Calcd. for $C_{51}H_{90}O_9Na$ 870.26, found: 868.53.

3,5 G2-Diester (6)



Yield 80% .^{1}H NMR (400 MHz, THF-d8), δ ppm 6.87(d, 2H, Ar H), 6.65(t, 1H, Ar H), 6.57(d, 4H, Ar H), 6.38(bs, 2H, Ar H), 6.02(s, 1H, O-CH), 4.97(s, 4H), 4.91(d, 1H, J = 4.1Hz, O-CH), 4.79(d 1H, J = 4.1Hz, O-CH), 4.15-4.30(m, 4H), 3.93(t, 8H, J = 6.4Hz, OCH_2), 1.65-1.87(m, 8H, CH_2), 1.2-1.55(m, 78H, CH_2), 0.89(t, 12H, J = 6.6Hz, CH_3). ^{13}C NMR (100 MHz, THF-d_8), δ ppm 170.36(C=O), 161.66(Ar C-O), 161.10(Ar C-O), 140.45, 107.43, 107.16, 106.49, 104.03, 101.47, 78.78, 78.40, 70.91, 68.68, 62.31, 33.05, 30.78, 30.49, 27.23, 23.74, 14.61. MALDI-TOF MS *m/z* $[M+Na]^+$ Calcd. for $C_{77}H_{126}O_{12}Na$ 1266.83, found: 1266.94.

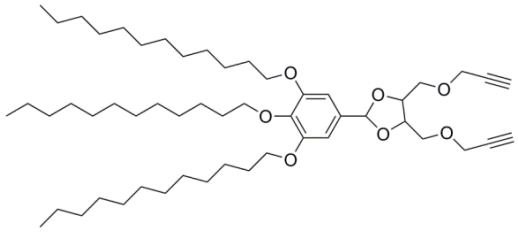
Dendron-acetal-dialkyne (9, 10)

In a three-neck flask $LiAlH_4$ (2.5 eq.) was suspended in dry THF (10 mL) at 0 ˚C and a solution of dendron-acetal-diester (**5** or **6**) (1 eq.) in dry THF was slowly added. The reaction mixture was stirred for 6 h at room temperature. Excess of $LiAlH_4$ was quenched by adding ethyl acetate at 0 °C, the solution was filtered and residue was washed three times with 100 mL of THF. Filtrate was concentrated and residue was dissolved in DCM. Organic layer was washed with water, dried over Na_2SO_4 and evaporated to get dendron-acetal-diol (**7** or **8**). Compounds **7** and **8** were found to adhere strongly to silica gel during column chromatography and hence were used without purification.

In a two-neck flask NaH was taken, washed with dry pet ether three times, dried under flow of argon and suspended in 5 mL of THF. Compound **7** or **8** dissolved in THF (10 mL) was added dropwise at 0 °C. After 30 min propargyl bromide was added and allowed to stir at room temperature for 12 h. Reaction mixture was poured in water and extracted with DCM. Organic layer was washed with water, dried over sodium sulfate and concentrated under

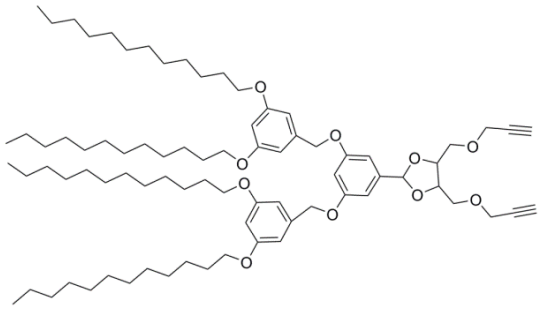
vacuum. Crude product was purified by column chromatography using ethyl acetate: pet ether (2:10) as eluant. Triethyl amine (0.3 mL) was added per 100 mL of mobile phase.

3,4,5G1-Dialkyne (9)



Yield 80%. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm 6.70(s, 1H, Ar H), 5.88(s, 1H, O-CH), 4.25(d, 4H, OCH_2), 4.22(m, 2H; OCH), 3.86-4.05(two t, 6H, OCH_2), 3.77(t, 4H, J= 4.4 Hz, OCH_2), 2.45 (s, 1H, alkyne-CH), 2.47(s, 1H, alkyne-CH), 1.65-1.85(m, 6H, CH_2), 1.15-1.50(m, 54 H, CH_2), 0.89(t, J = 7 Hz, 9 H CH_3). ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm 153.11(Ar C-O), 138.93, 132.07, 104.98, 104.19(O-C-O), 79.24, 77.81, 74.94(-C alkyne), 74.86(-C alkyne), 73.32, 69.89(CH alkyne), 69.80(CH alkyne), 69.01, 58.71, 31.92, 30.29, 29.74, 29.69, 29.65, 29.38, 29.36, 26.09, 22.68, 14.10. MALDI-TOF MS *m/z* $[M+Na]^+$ Calcd. for $C_{43}H_{78}O_4$ Na 862.30, found: 862.10.

3,5G2-Dialkyne (10)



Yield 84%. ^{1}H NMR (500 MHz, $CDCl_3$), δ ppm 6.79(d, 2H, J = 1.8Hz, Ar H), 6.62(bs, 1H, Ar H), 6.57(d, 4H, J = 1.5Hz, Ar H), 6.42(s, 2H, Ar H), 5.94(s, 1H, O-CH), 4.97(s, 4H, OCH_2), 4.33-4.18(m, 6H, OCH_2, OCH), 3.96(t,8H, J=6.6Hz, OCH_2), 3.73-3.82(m, 4H, OCH_2), 2.49 and 2.46(m, 2H, Alkyne CH), 1.79(m, 8H, CH_2), 1.47(m, 8H, CH_2), 1.29(m, 64H, CH_2), 0.91(t, 12H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$), δ ppm 160.46(Ar C-O), 159.92, 139.73, 138.90, 105.70, 105.60, 103.86, 103.09, 100.79, 77.85, 77.42, 74.94(-C alkyne), 70.15(CH alkyne), 69.92, 69.69, 68.05, 58.71, 31.91, 29.66, 29.63, 29.60, 29.58, 29.40,

29.35, 29.25, 26.05, 22.68, 14.12. MALDI-TOF MS $[M+Na]^+$ Calcd. for $C_{79}H_{126}O_{10}Na$ 1258.86, found: 1258.93.

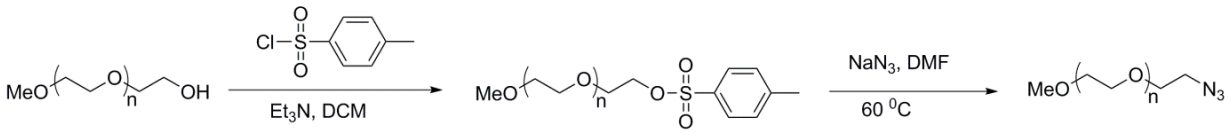
OEG-N_3

Into a 250 mL two necked round-bottom flask equipped with a dropping funnel were charged, MeO-OEG-OH (1 eq.) and triethylamine (0.95 eq.) in 70 mL DCM. The solution was stirred for 30 min, cooled to 0 ˚C, and p-toluenesulfonyl chloride (0.95 eq.) was added over a period of 1 h. The reaction mixture was further stirred at 0 ˚C for 1 h and at room temperature for 4 h. After completion of reaction, the mixture was filtered, the filtrate was washed with water and passed through short plug of silica using DCM as eluent. The solvents were evaporated to get MeO-OEG-OTs as yellowish oil.

The obtained OEG-tosylate was dissolved in DMF and sodium azide (10 eq.) was added. The reaction mixture was stirred at 60 ˚C for 24 h, DMF was distilled at reduced pressure. The residue was dissolved in water, extracted with CH_2Cl_2 and dried over anhydrous Na_2SO_4. Solvent was evaporated on rotary evaporator and dried under vacuum at room temperature to get viscous yellowish oil. Yield 75%.

a) OEG_{550}-N_3 ^{1}H NMR (200MHz, $CDCl_3$), δ ppm 3.65 (m, 46H, OCH_2), 3.39 (m, 5H, OCH_3, -CH_2N_3). IR (KBr), ν = 2862, 2106, 1456, 1350, 1297, 1251, 1092, 946, 846 cm^{-1}.

b) OEG_{750}-N_3 ^{1}H NMR (200MHz, $CDCl_3$), δ ppm 3.65 (m, 70H, OCH_2), 3.39 (m, 5H, OCH_3, -CH_2N_3). IR (KBr), ν = 2862, 2106, 1456, 1350, 1297, 1251, 1092, 946, 846 cm^{-1}.



Scheme S1. Synthesis of OEG-azide

Encapsulation of pyrene

A solution of pyrene in acetone (10 µL, 5x 10^{-7} M) was taken in a vial. To this, 10 mL of 0.1 wt% amphiphile solution was added and stirred for 6 h. It was used for determination of CMC and micellar disassembly studies. For dye encapsulation study a stock solution was

prepared by adding pyrene (2 mg) into 0.1 wt% amphiphile solution (2 mL) followed by stirring overnight and filtering through 0.45 µm filter.

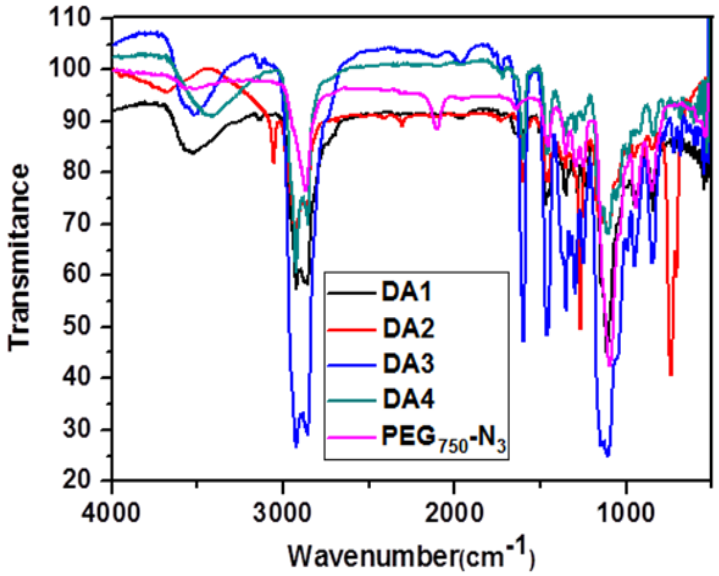


Fig. S1 FTIR spectra overlay for dendritic amphiphiles and OEG_{750}-N_3.

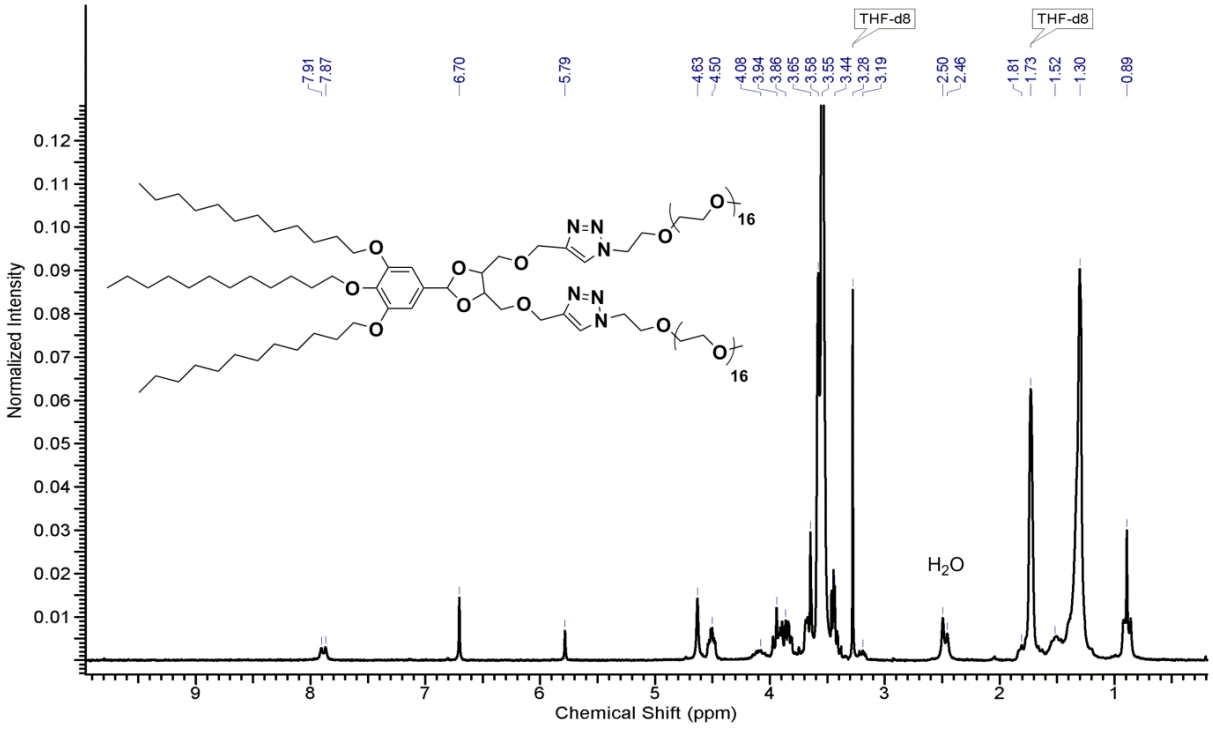


Fig. S2 200 MHz 1H NMR spectrum of DA1 in THF-d_8

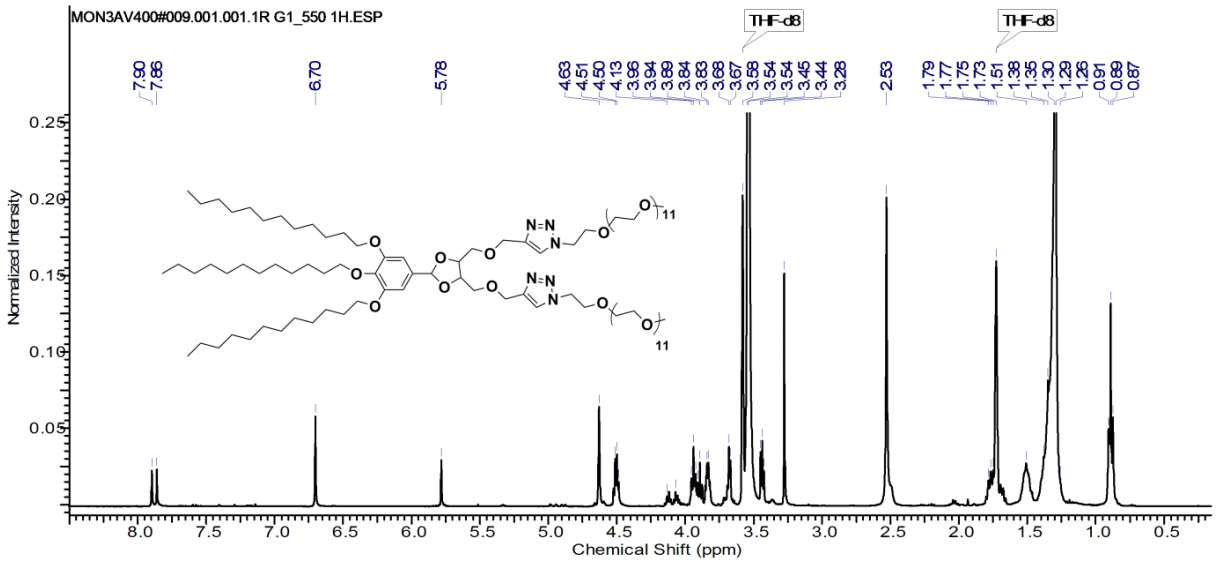


Fig. S3 400 MHz ^{1}H NMR spectrum of DA2 in THF-d_8

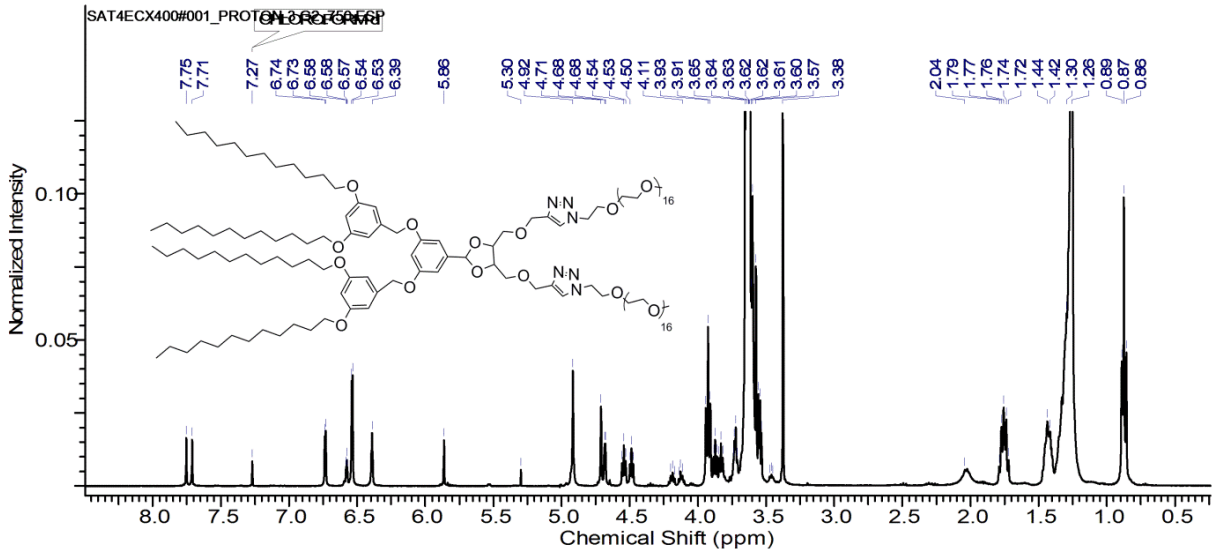


Fig. S4 200 MHz 1H NMR spectrum of DA3 in $CDCl_3$

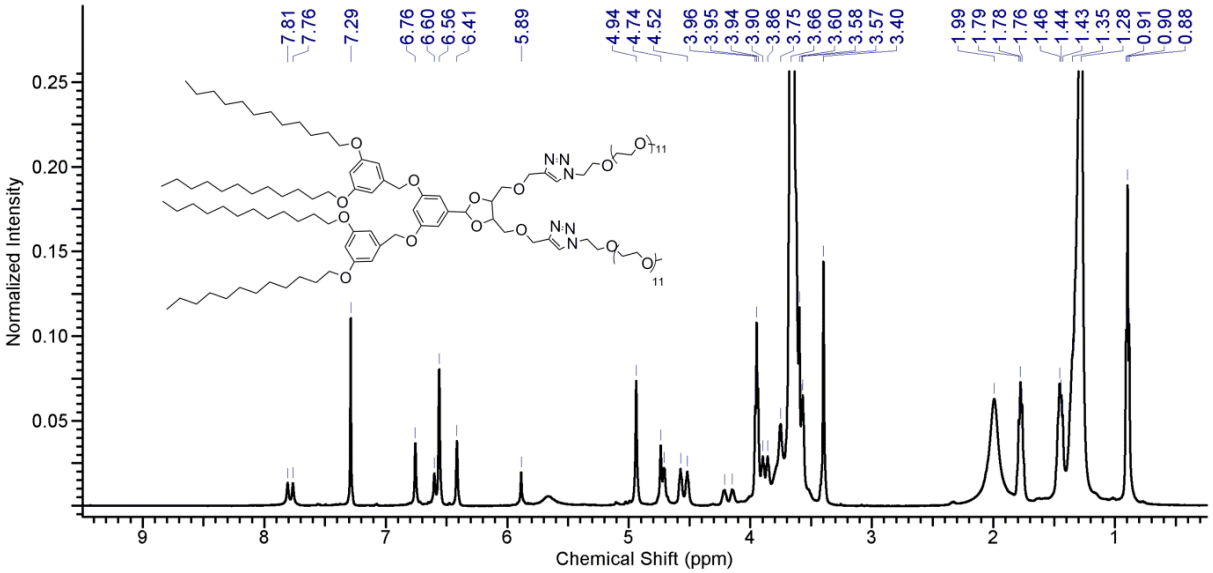


Fig. S5 500 MHz ^{1}H NMR spectrum of DA4 in $CDCl_3$

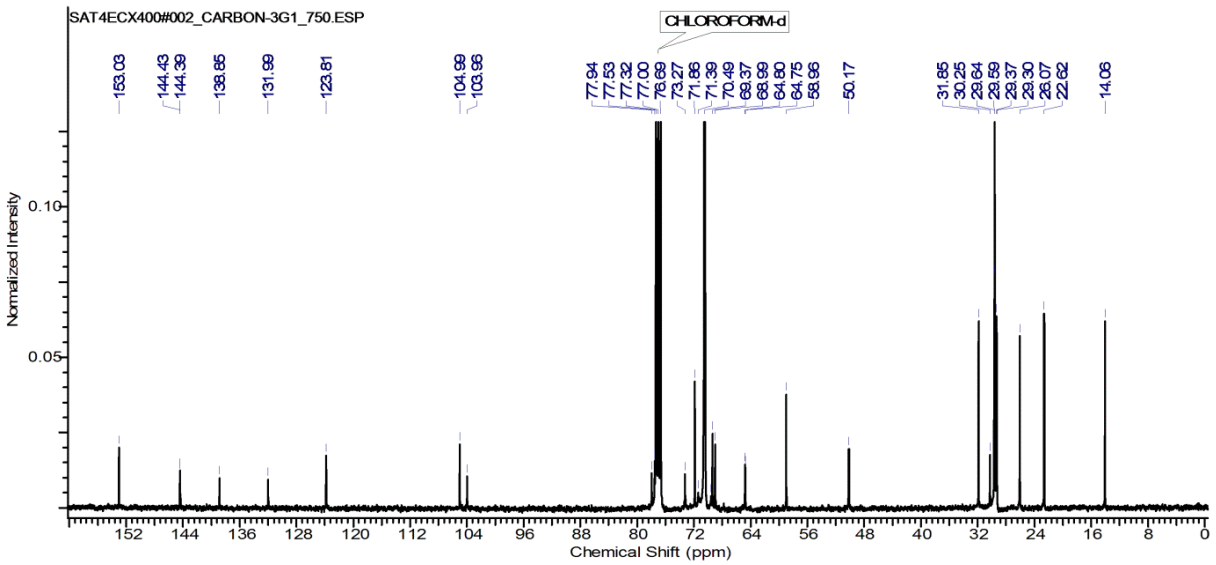


Fig. S6 100 MHz ^{13}C NMR spectrum of DA1 in $CDCl_3$

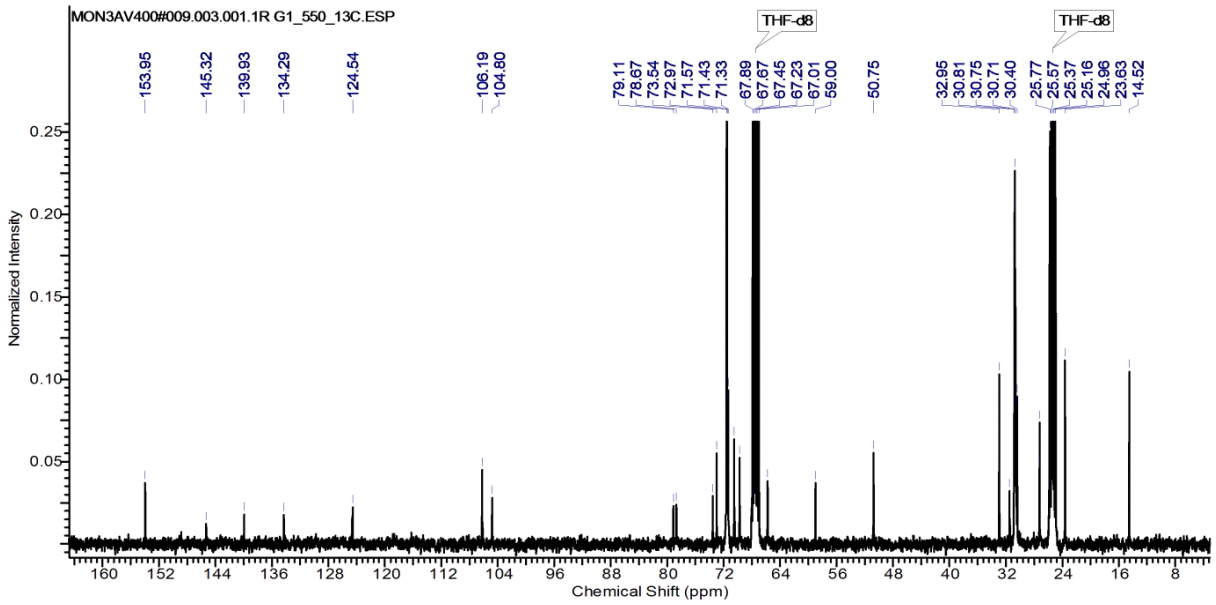


Fig. S7 100 MHz ^{13}C NMR spectrum of DA2 in THF-d_8

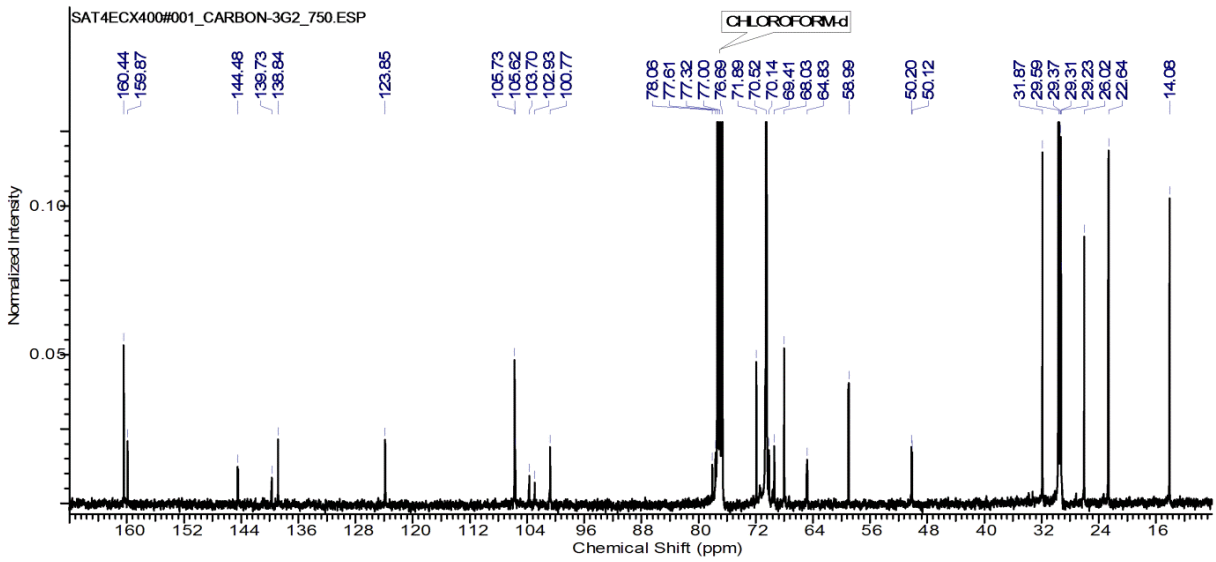


Fig. S8 100 MHz ^{13}C NMR spectrum of DA3 in $CDCl_3$

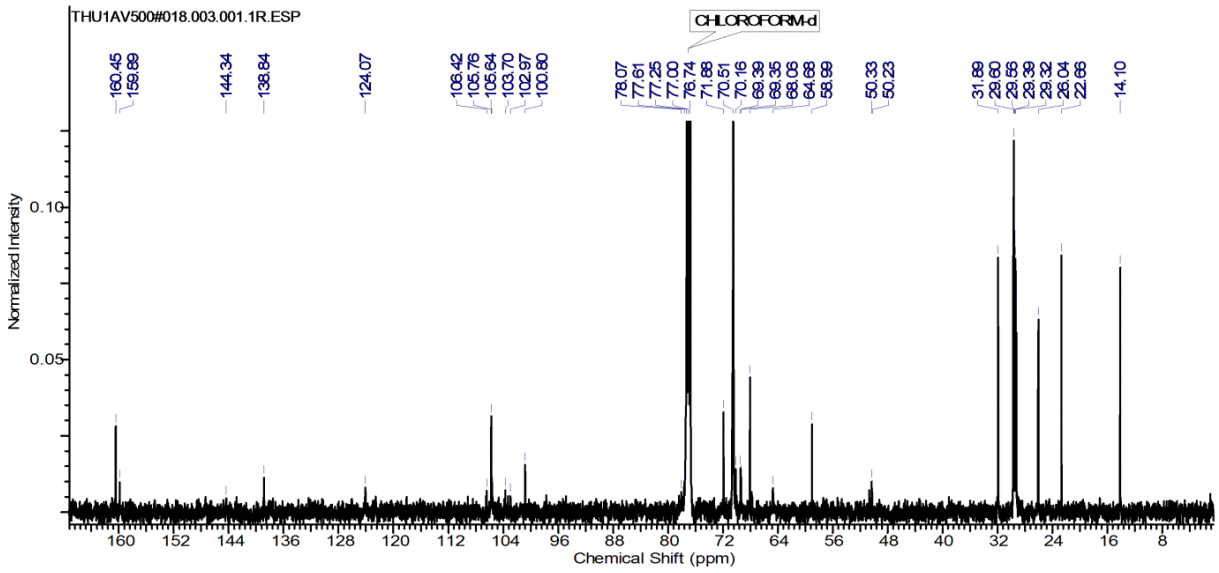


Fig. S9. 125 MHz ^{13}C NMR spectrum of DA4 in $CDCl_3$

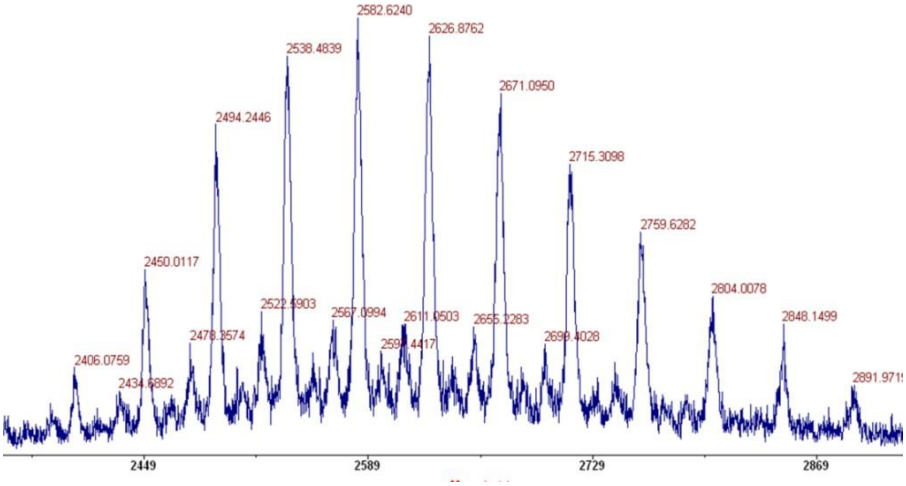


Fig. S10 MALDI-TOF spectrum of DA1

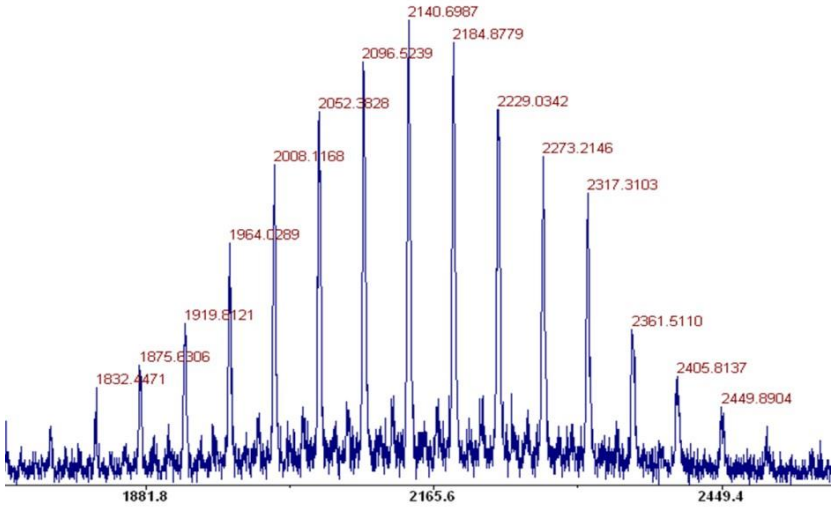


Fig. S11 MALDI-TOF spectrum of DA2

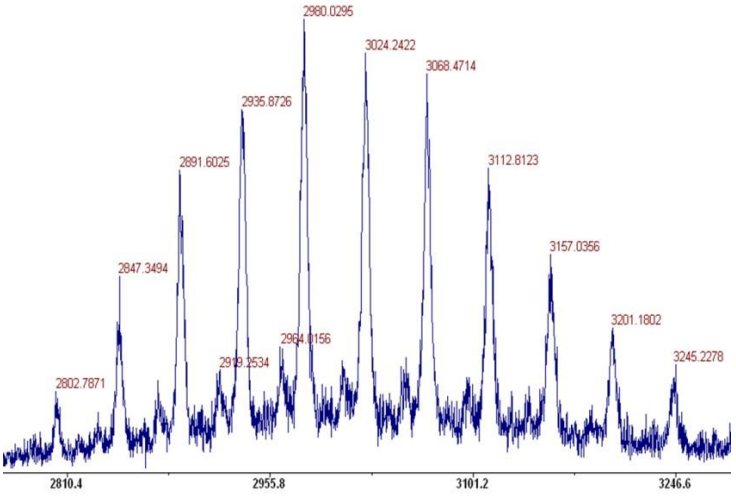


Fig. S12 MALDI-TOF spectrum of DA3

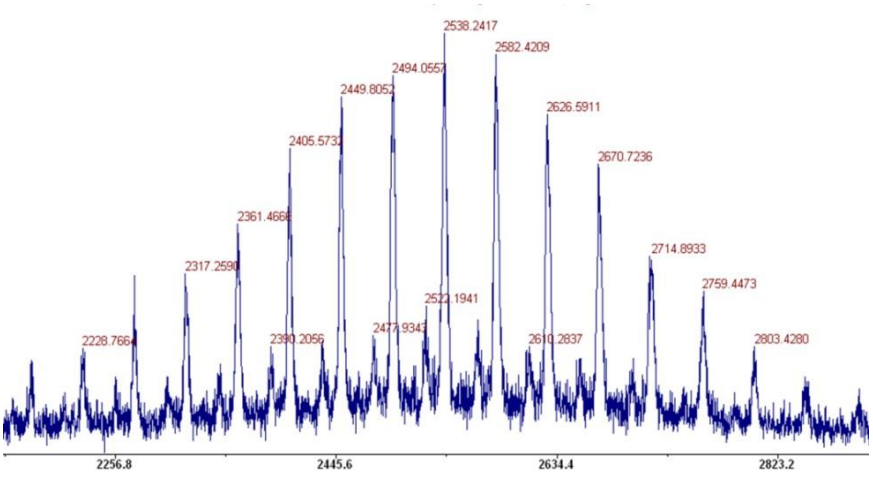


Fig. S13 MALDI-TOF spectrum of DA4

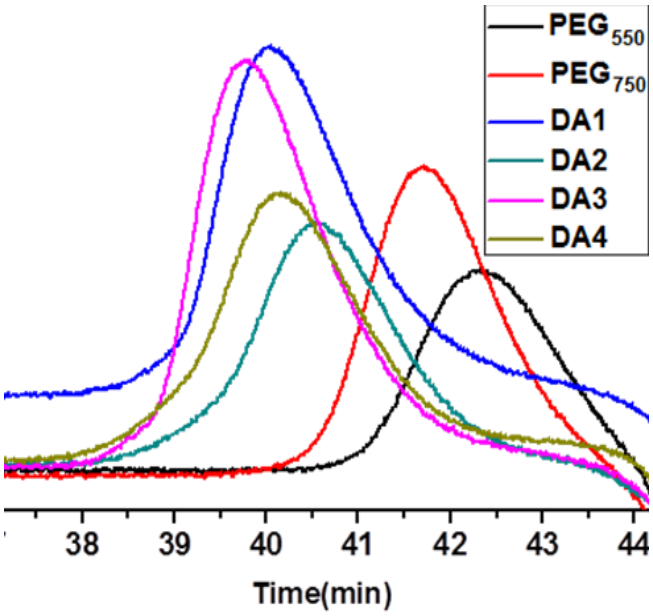


Fig. S14 GPC chromatograms for **DA1**-**DA4** and **OEG-N_3** with THF as eluant.

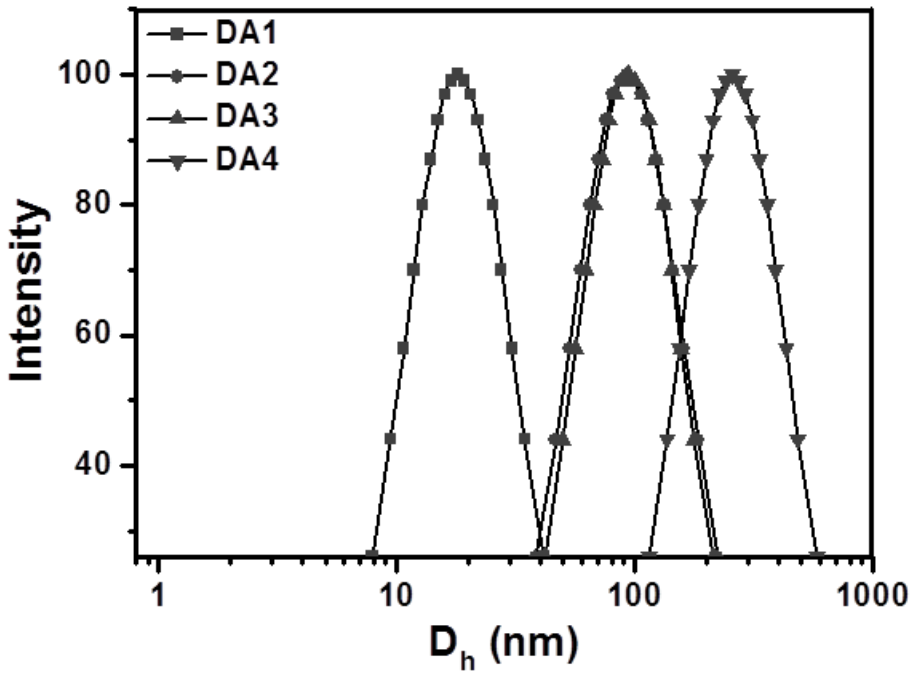


Fig. S15. DLS size distribution curves for **DA1**–**DA4** micelles

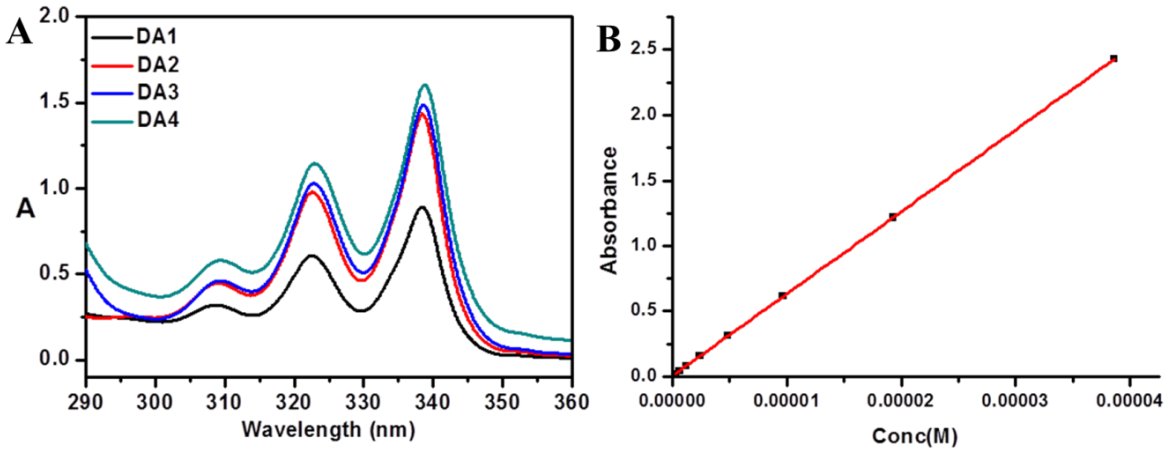


Fig. S16 A) UV-vis spectra of pyrene and B) Plot for determination of molar extinction coefficient of pyrene in chloroform.

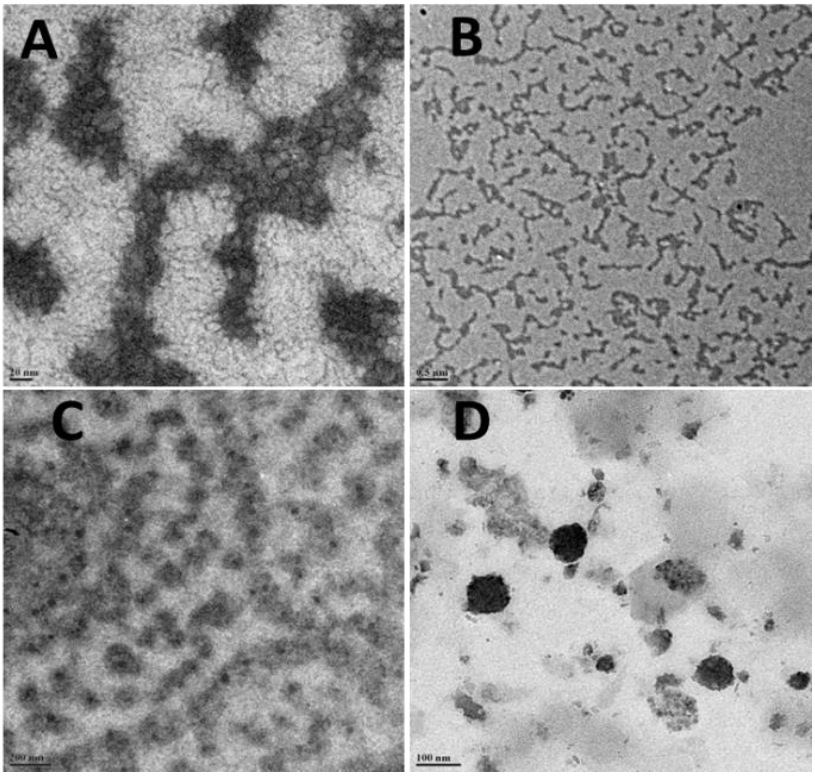


Fig. S17 TEM images for 0.1wt% aqueous solution of dendritic amphiphiles A) **DA1**, B) **DA2**, C) **DA3** and D) **DA4**. Scale bar: A) 20 nm, B) 500 nm, C) 200 nm, D) 100 nm.

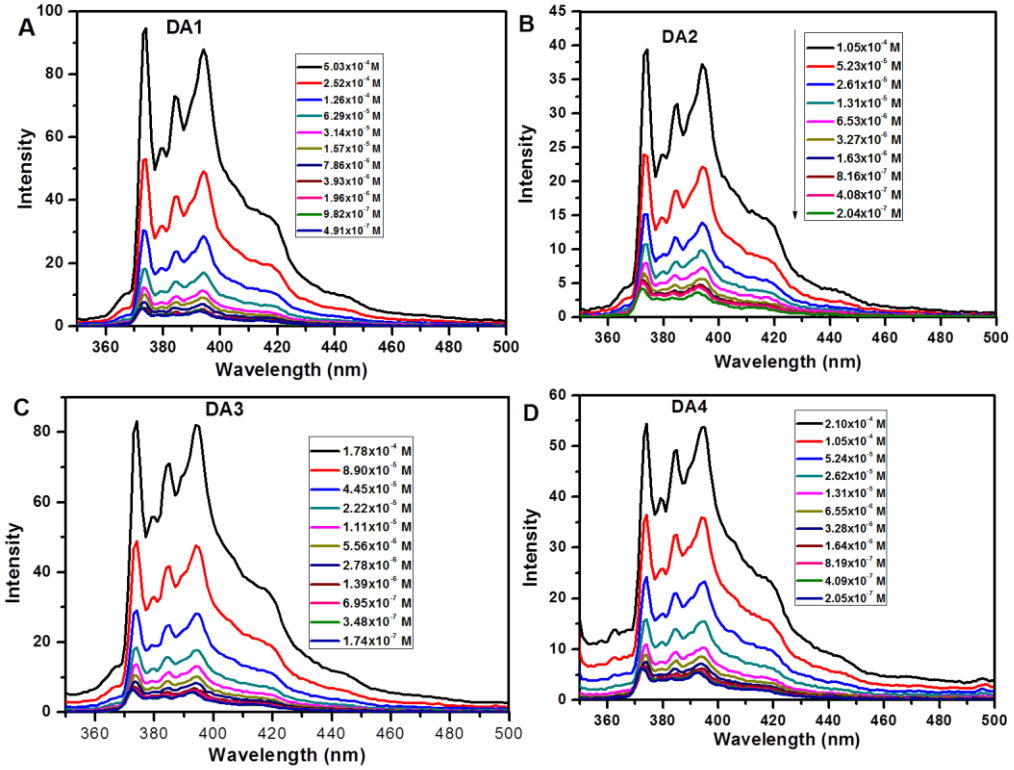


Fig. S18 Fluorescence emission spectra of pyrene in aqueous solution of A) DA1, B) DA2, C) DA3, D) DA4 for determination of cmc.

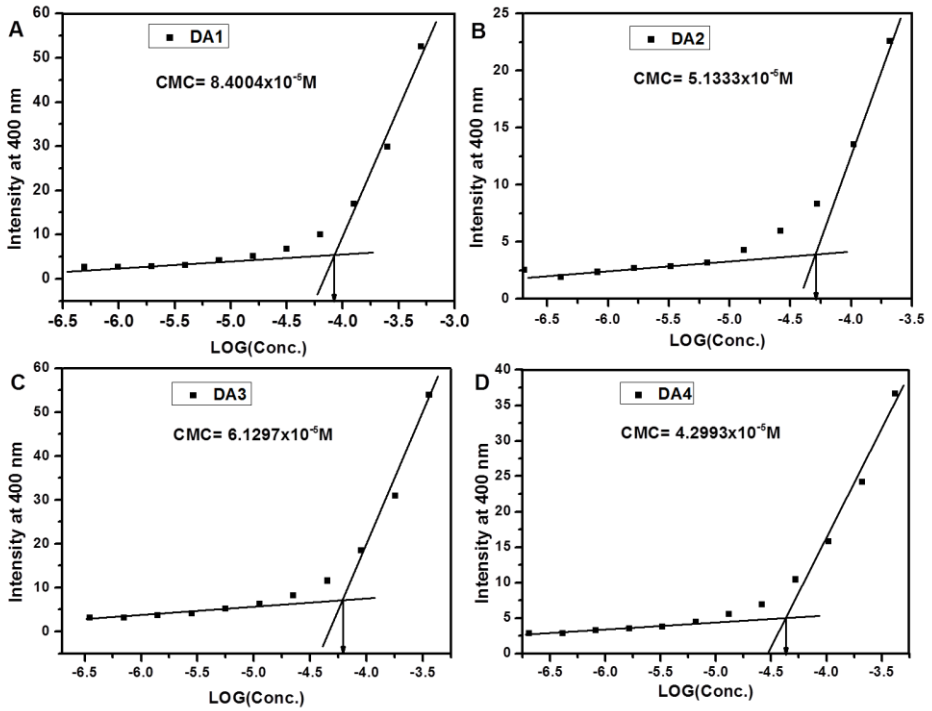


Fig. S19 Plots for cmc determination for A) **DA1**, B) **DA2**, C) **DA3** and D) **DA4**

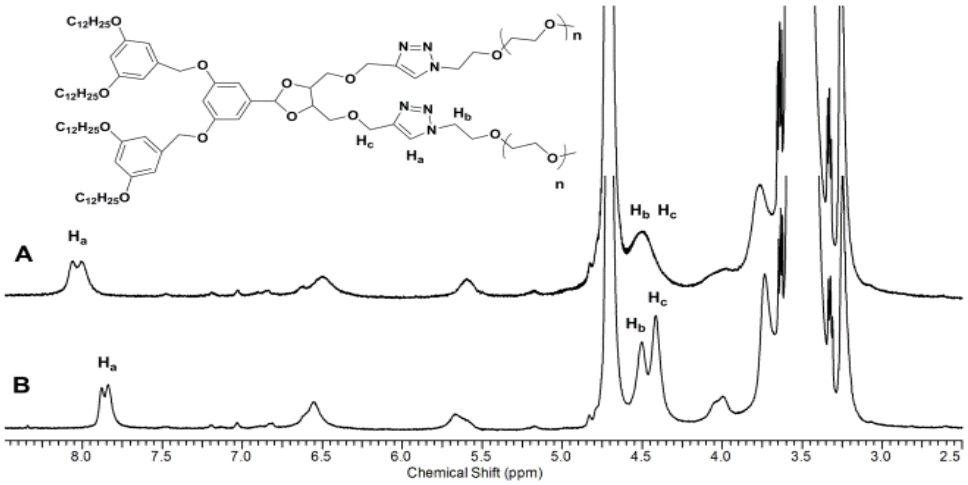


Fig. S20 ^{1}H NMR spectra of **DA4** A) with Ag^{+} ions and B) without Ag^{+} ions in D_2O.

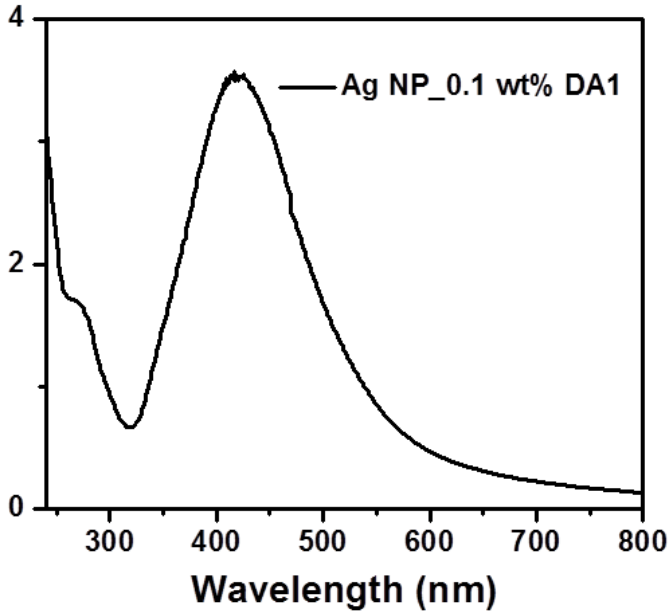


Fig. S21 UV-vis spectrum of 0.1 wt% aqueous solution of **DA1** with Ag NPs.

1. Kalva, N.; Aswal, V. K.; Ambade, A. V. *Macromol. Chem. Phys.* **2014**, *215*, 1456–1465.