

Synthesis

1. Synthesis of 4-aminopentadecylphenol (1a):

3-Pentadecylphenol (5 g, 0.016 mol) was added to potassium hydroxide (4.6 g, 0.082 mol) dissolved in ethanol (70 mL) in a 500mL RB and stirred for 15 minutes in ice cold conditions. The suphanilic acid (3.9 g, 0.023 mol) was converted to sodium salt by reacting with sodium carbonate under ice cold condition and to that, ice-cold solution of sodium nitrite was added. Later, concentrated HCl is added drop by drop at 0°C. The thick yellow precipitate thus obtained was added to the RB at ice cold condition. The colour of mixture turns to reddish brown due to the formation of azo dye and allowed to stir for 3 to 4 hours in ice cold condition. After that sodium dithionate (8.58 g) solution is added and refluxed for 1hour at 75 °C, during this step colour changes from reddish brown to yellow. To this, glacial acetic acid (55 mL) was added and again refluxed for about 1 hour at 80°C. The resulting reaction mixture is poured into 500 mL of distilled water and stirred properly; the precipitate is filtered, washed and then dried. Yield = 3.91 g (95%) ¹H NMR (CDCl₃, 400MHz) δ (ppm): 6.57 (m, 3H, aromatic protons) 2.44 (t, 2H, Ar-CH₂-), 1.59-1.26 (m, 26 H) 0.88 (m, 3H, CH₃)

Synthesis of Fmoc-(4-Aminopentadecyl Phenol) (Fmoc-PDP-OH) (2a):

Fmoc-Cl (2.0 g, 0.0078 mol) was taken in a 100 mL RB and dissolved in 10 mL of dioxane. To this add 10% NaHCO₃ solution (20mL). The reaction mixture was stirred for 15 minutes at 0°C. After 15 minutes solution of 4-amino-PDP (2 g) in dioxane (10 mL) is added drop by drop. And was stirred for 2 hours at 0 °C and then followed by room temperature for 24 hours. The dioxane was removed by rotor evaporator and added water to the mixture. This mixture is acidified with 6N HCl in ice cold condition. The product is extracted with ethylacetate and then concentrated. The product is purified using silica gel column chromatography (100-200 mesh) and eluted using 12 v/v% of ethyl acetate (ethyl acetate: PET ether). Yield=30% (2.6 g) ¹H NMR (CDCl₃, 400MHz) δ (ppm): 7.78-7.30 (m, 9H, Fmoc Ar protons), 6.62 (m, 2H, PDP Ar protons) 4.26 (d, 2H, Fmoc- CH₂-) 4.07(m, 1H, Fmoc-CH-), 2.49 (t, 2H, Ar-CH₂-) 1.57-1.27 (m, 26H) 0.88 (m, 3H, CH₃)

Synthesis of DiFmoc-(4-Aminopentadecyl Phenol) (Fmoc-PDP-Fmoc) (2b):

Fmoc-Cl (2.0 g, 0.0078 mol) was taken in a 100 mL RB and dissolved in 10 mL of dioxane. To this add 10% NaHCO₃ solution (20mL). The reaction mixture was stirred for 15 minutes at 0°C. After 15 minutes solution of 4-amino-PDP (1 g) in dioxane (5 mL) is added drop by drop. And was stirred for 2 hours at 0 °C and then followed by room temperature for 24 hours. The dioxane was removed by rotor evaporator and added water to the mixture. This mixture is acidified with 6N HCl in ice cold condition. The product is extracted with ethylacetate and then concentrated. The product is purified using silica gel column chromatography (100-200 mesh) and eluted using 20 v/v% of ethyl acetate

(ethyl acetate: PET ether). Yield=40% (2.9 g) ^1H NMR (CDCl_3 , 400MHz) δ (ppm): 7.81-7.02 (m, 17H, Fmoc Ar protons), 7.03 (m, 2H, PDP Ar protons) 4.52 (d, 2H, Fmoc-CH₂) 4.34 (m, 1H, Fmoc-CH-), 2.56 (t, 2H, Ar-CH₂-) 1.57-1.26 (m, 26H) 0.88 (m, 3H, CH₃)

Figure S1 – ^1H NMR Spectrum of Fmoc-PDP-OH (2a)

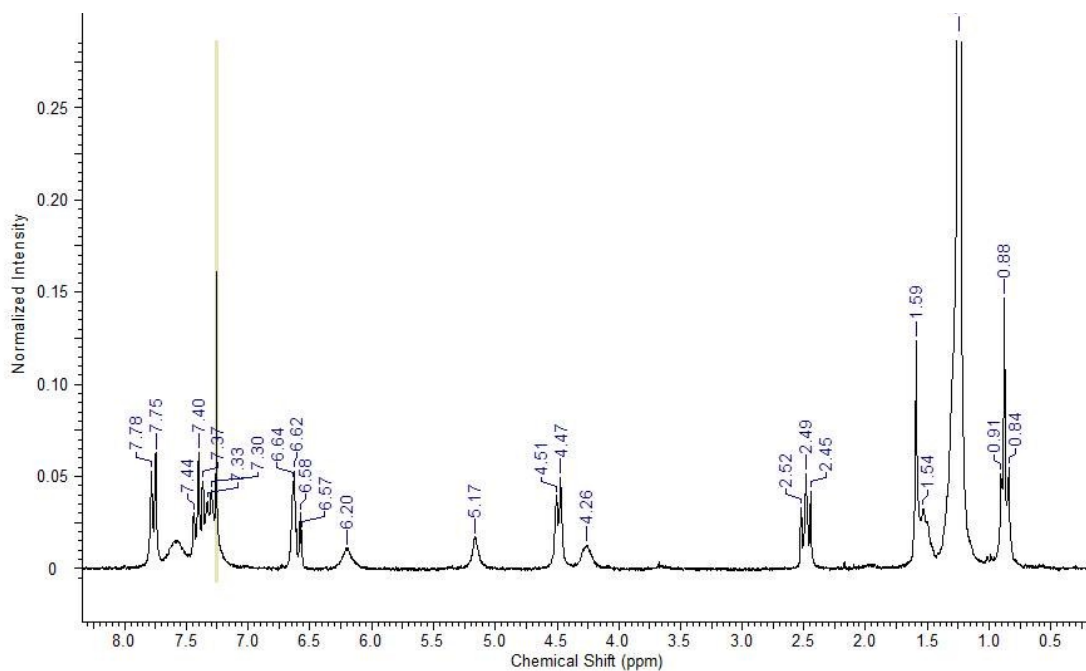


Figure S2 - ^1H NMR Spectrum of Fmoc-PDP-Fmoc (2b)

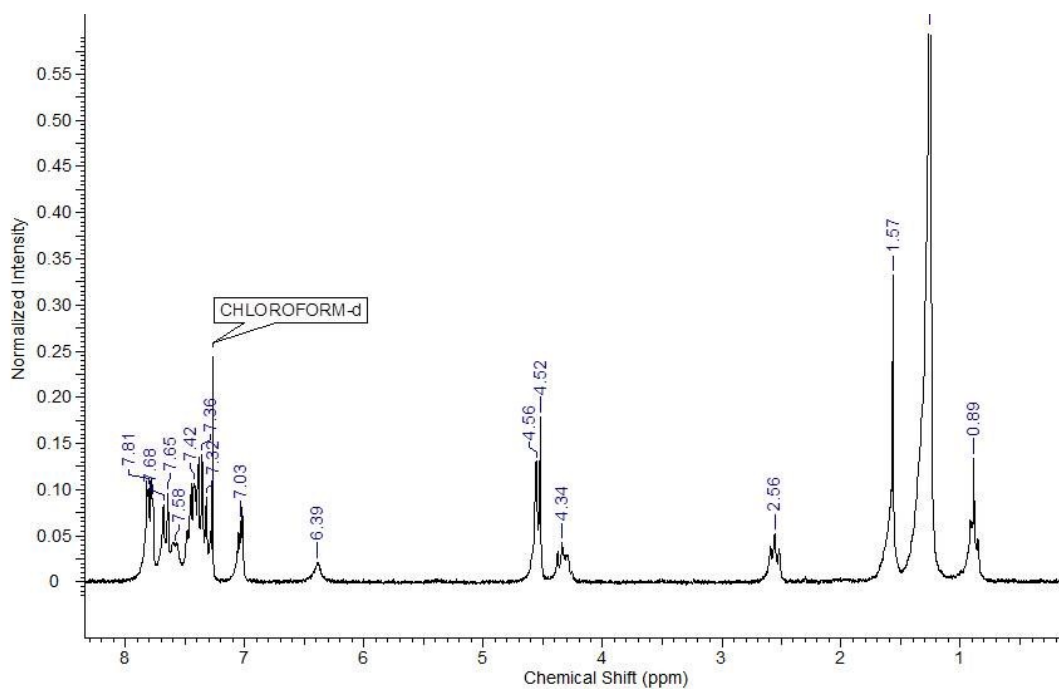


Figure S3 - IR spectra of Fmoc-PDP-OH and Fmoc-PDP-Fmoc

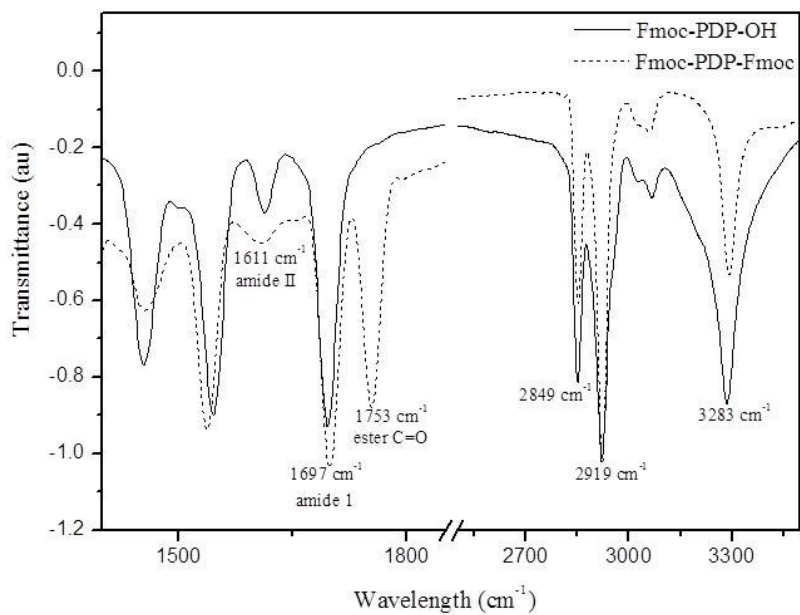


Figure S4- MALDI-TOF mass spectra of Fmoc-PDP-OH

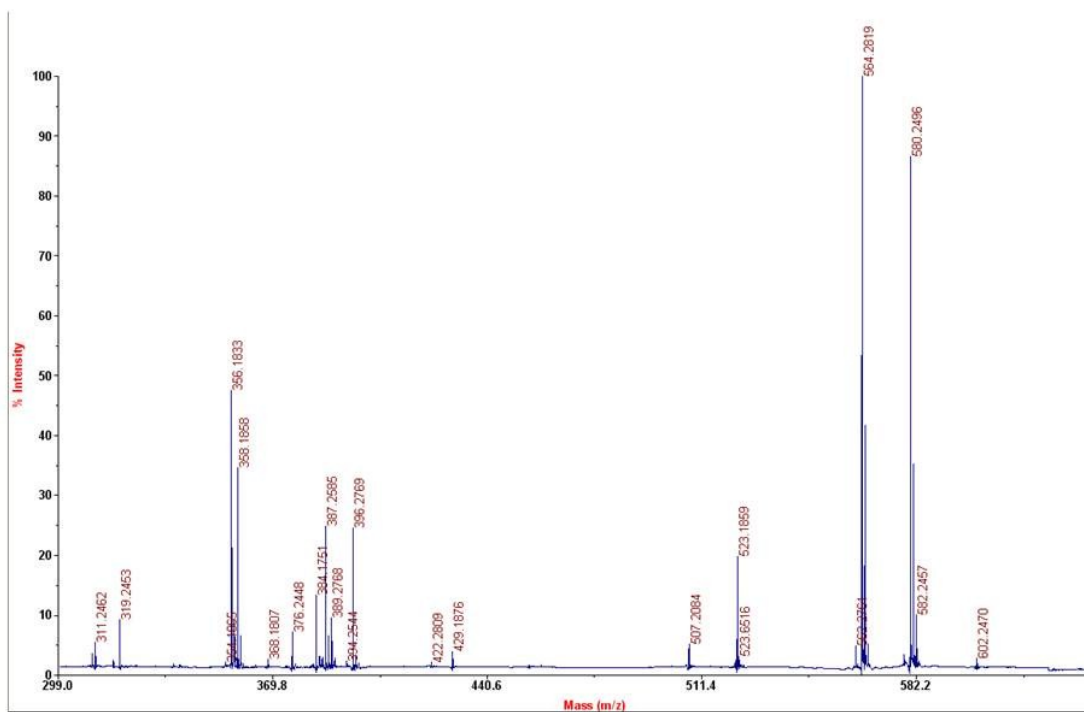


Figure S5 – MALDI-TOF mass spectrum of Fmoc-PDP-Fmoc

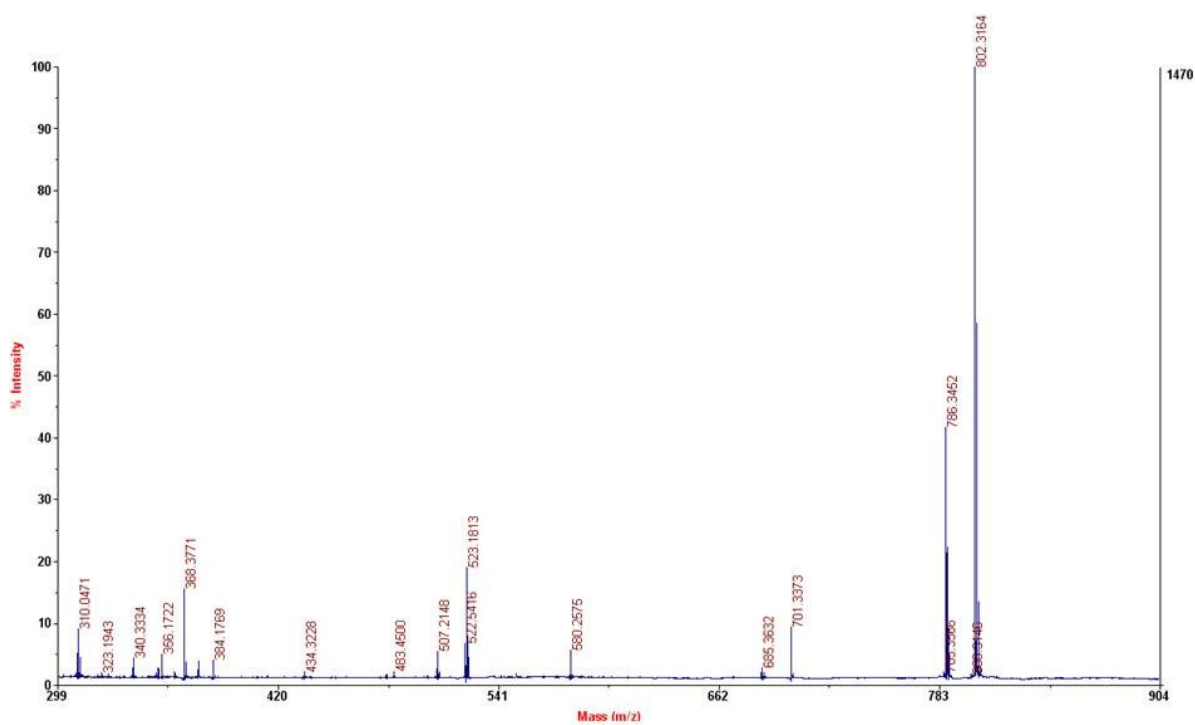
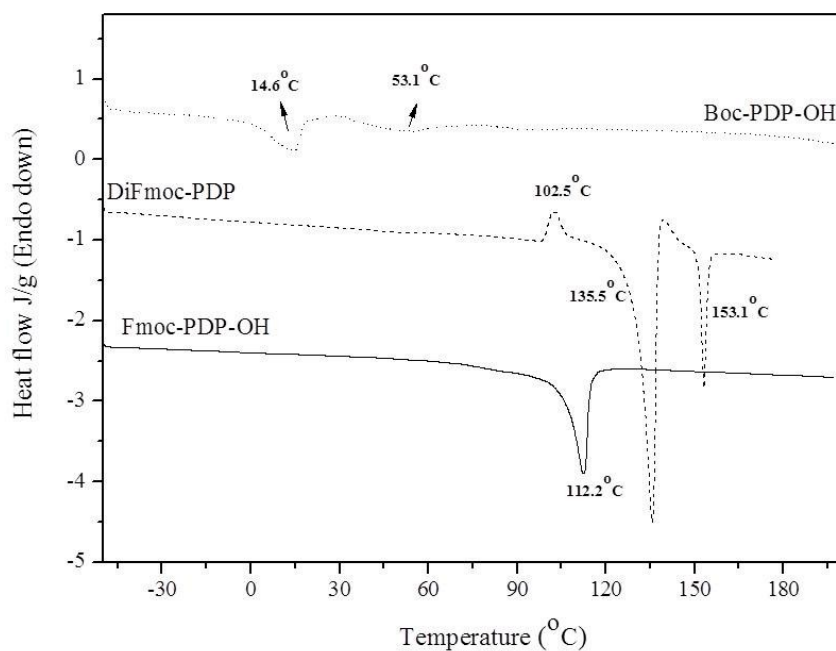


Figure S6 - DSC thermograms of Fmoc-PDP-OH, DiFmoc-PDP and Boc-PDP (A) Heating cycle and (B) Cooling cycle

A) Heating Cycle



B) Cooling Cycle

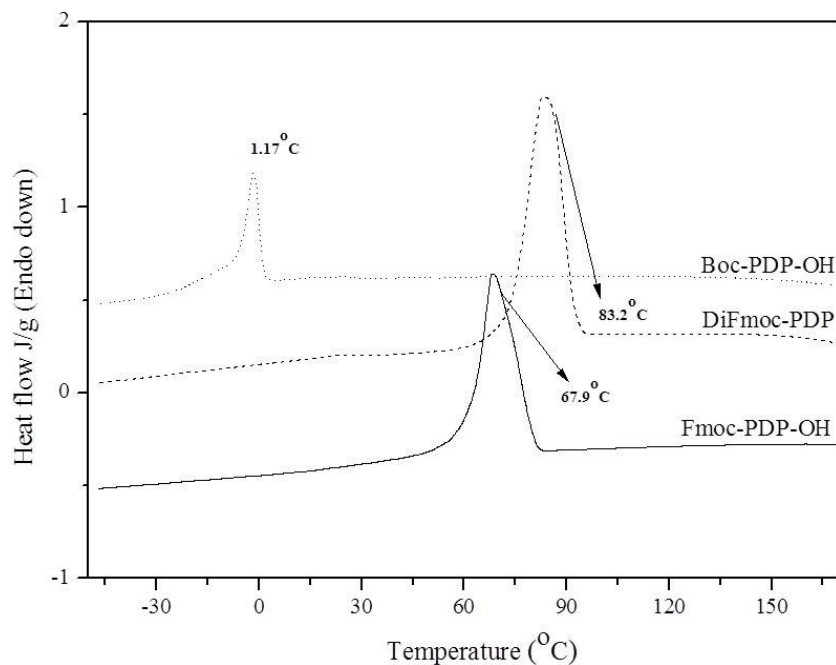


Figure S7- Powder XRD data of Fmoc-PDP-OH, DiFmoc-PDP and Boc-PDP-OH

