Electronic Supplementary Information for

Dendritic Molecular Brushes: Synthesis via Sequential RAFT Polymerization and Cage Effect for Fluorophores

Sipei Li, Chao Gao*

MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, 38 Zheda Road, Hangzhou 310027, P. R. China.

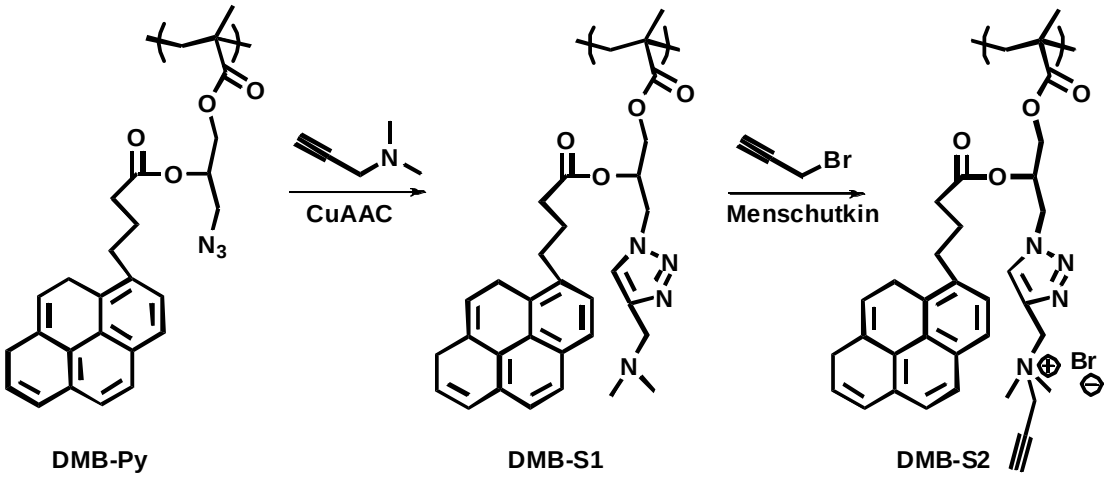
*To whom correspondence should be addressed. E-mail: chaogao@zju.edu.cn

Experimental Section

Synthesis of DMB-S1. Into a 10 mL Schlenck flask equipped with a stirring bar and 0.3 mL DMF, were dissolved 9 mg DMB-Py (1 equiv), 5 mg N,N-dimethylpropargyamine (3 equiv) and 6 μL PMDETA (1 equiv). After 15 min of deoxygenation, 2.84 mg CuBr (1 equiv) was instantly added under nitrogen protection. After reacting for 24 h at room temperature, the solution was poured into 10-fold excess of diethyl ether and centrifuged. The obtained products were dried in vacuo and subjected to FTIR and ^{1}H NMR analyses. The disappearing of peak at ~2100 cm^{-1} indicates the consumption of the azido groups of DMB-Py (Figure S2). The peak at 2.2 ppm in the ^{1}H NMR spectrum (Figure S3), corresponding to the the N,N-dimethyl groups, indicates successful conjugation of N,N-dimethylpropargyamine.

Synthesis of DMB-S2. In a 10 mL round bottom flask equipped with a strring bar, 15 mg DMB-S1 (1 equiv) were dissolved in 0.3 mL DMF. After 20 min of deoxygenation, 10 mg propargyl bromide (3 equiv) were added dropwise via syringe. After reacting for 24 h, the solution was poured into 10-fold excess of diethyl ether and centrifuged. The obtained products were dried in vacuo and subjected to FTIR and ^{1} H NMR analyses. The disappearing of the peak at 2.2 ppm in the ^{1}H NMR spectrum of DMB-S2 indicates the complete conversion of the Menschutkin reaction (Figure S4). The typical peak at ~2100 cm^{-1} of the FTIR spectrum of DMB-S2 indicates the attachment of propargyl functional groups.

Scheme S1 Sequential functionalization of DMB-Py.



DMB-Py DMB-S1 DMB-S2

Fig. S1 TEM images of DMB-Py (a) and DMB-TPE (b). The scale bar corresponds to 1 μm (large picture) and 200 nm (inset picture) respectively. Samples concentration: 1×10^{-5} mg/mL.

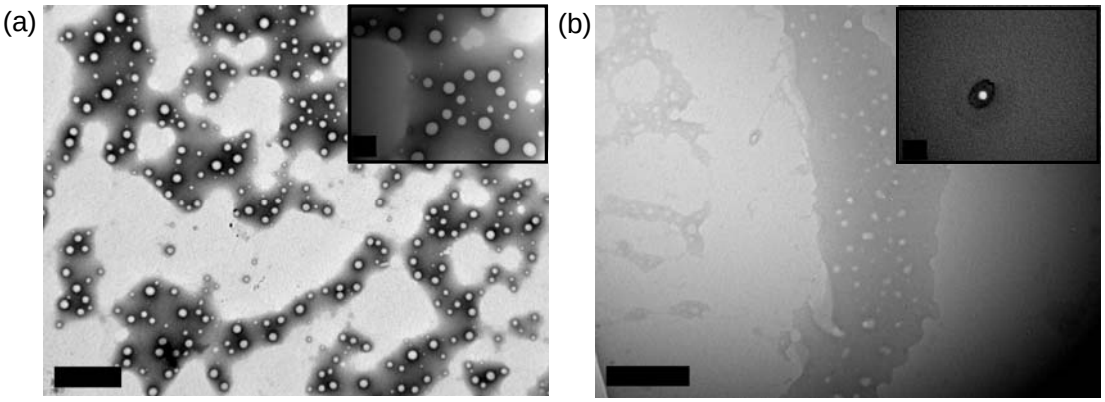


Fig. S2 FTIR spectra of DMB-2, DMB-S1 and DMB-S2.

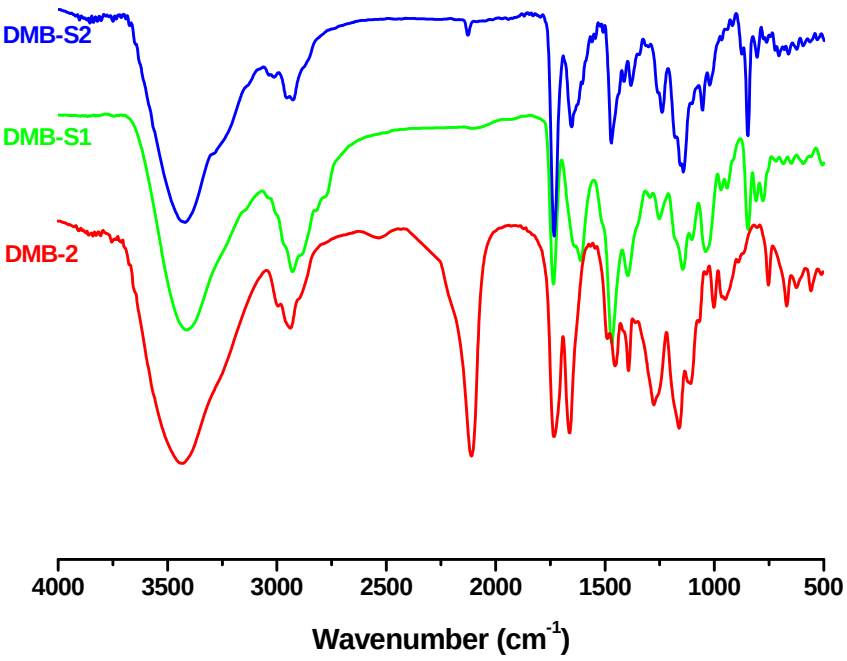


Fig. S3 ^{1}H NMR spectrum of DB-S1s.

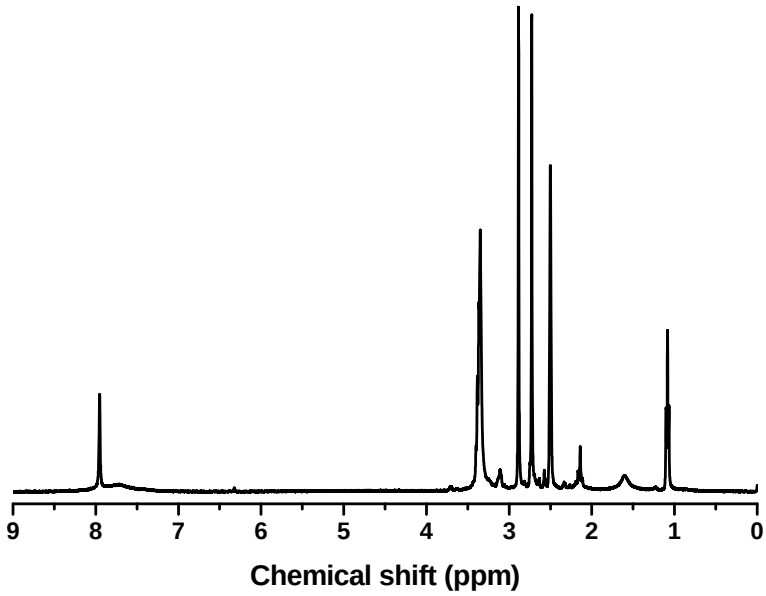


Fig. S4 ^{1}H NMR spectrum of DB-S2s.

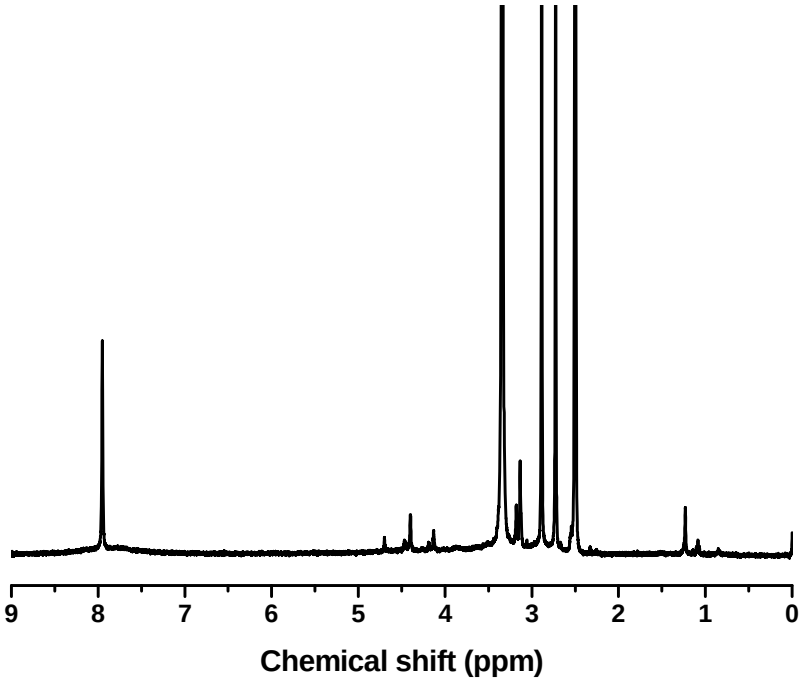


Fig. S5 ^{13}C NMR spectrum of alk-CTA.