Copper-Mediated Stepwise Polymerization of Benzynes: Construction of Amphiphilic Block Copolymers and their Self-Assembly in Water

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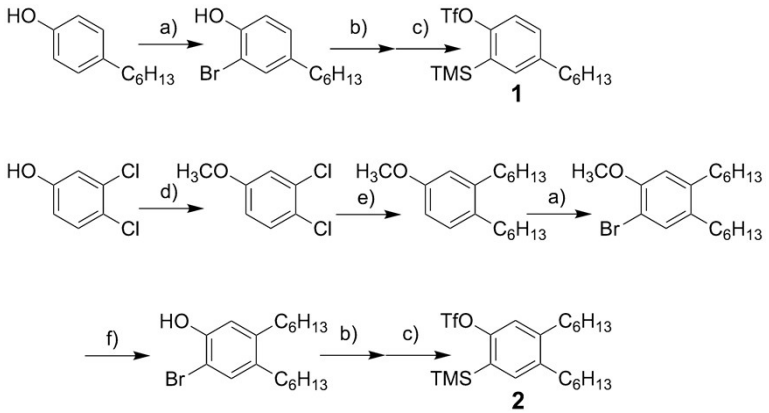
Supporting Information

General

All chemicals were purchased from commercial supplies used without further purification. NMR spectra were recorded on a Bruker AVANCE NEO400 OneBay NMR spectrometer at 400.13 and 100.62 MHz for ^{1}H and ^{13}C in $CDCl_3$ solutions. Chemical shifts are reported relative to internal TMS. UV-Vis absorption and fluorescence spectra were measured on a SHIMAZU UV2600 and a JASCO FP-8050. High-resolution time-of-flight mass spectra with atmospheric pressure chemical ionization (HR-APCI-TOF-MS) and matrix-assisted laser desorption/ionization time-of flight mass spectra were obtained by a Bruker Daltonics micrOTOF II and a Bruker microflex LRF. Gel permeation chromatography was performed at 303 K on a Shodex GPC KF-804L column with a JASCO UV-1575 UV detector and a JASCO RI-930 RI detector using THF as an eluent at a flow rate of 1 mL/min. Field-emission scanning electron microscope (FE-SEM) images recorded in a Hitachi S-5000 FE-SEM (Hitachi, Tokyo, Japan) with Pt sputter coating. Dynamic light scattering (DLS) profiles were obtained by a Malvern Panalytical Zetasizer nano. For quantitative measurements such as dynamic light scattering (DLS), experiments were performed in five independent replicates, and the results are presented as the mean ± standard deviation (SD). Statistical analyses for the level of significance and mean separation methods were not applicable to the physicochemical characterizations conducted in this study.

Synthesis of block copolymer 7: CsF (76 mg, 0.48 mmol), CuCN (1.1 mg, 13 μmol), and 18-crown-6 (0.25 g, 0.96 mmol) were dissolved in dry THF (1.4 mL) and stirred at room temperature for 10 min under an Ar atmosphere. A solution of **1** (92 mg, 0.24 mmol) in THF (0.7 mL) was added to the reaction mixture and stirred for 1 hr under an Ar atmosphere. After 1 hr, a solution of **3** (100 mg, 0.24 mmol) in THF (0.7 mL) was added to the reaction mixture and stirred for 24 hr. The reaction mixture was quenched by the addition of an aqueous solution of NH_4Cl and extracted with $CHCl_3$. The combined organic phases were dried over Mg_2SO_4, and the solvent was evaporated. The crude product was purified by size exclusion chromatography (BioRad Bio-Beads S-X1, eluent: THF) to obtain **7**. Yield 120mg.

Scheme S1. Synthesis of *o*-trimethylsilyl aryl triflates **1** and **2**[a]



[a] **Regents and conditions**: a) Br_2, CH_2Cl_2, 0°C; b) HMDS, THF, reflux; c) n-BuLi, Tf_2O, THF, -70°C; d) CH_3I, K_2CO_3, rt; e) Mg, $C_6H_{13}Br$, [1,2-Bis(diphenylphosphino)nickel (II)] dichloride, diethyl ether, reflux; f) BBr_3, CH_2Cl_2, -70°C.

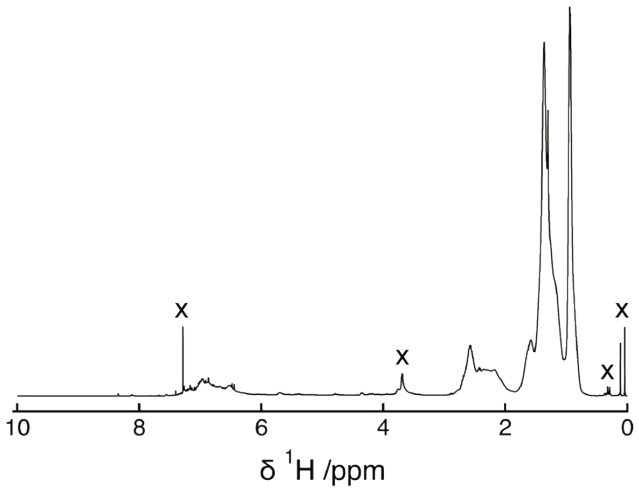


Fig.S1 ^{1}H NMR spectrum of **4** in $CDCl_3$ at 25°C (X: solvents and impurities).

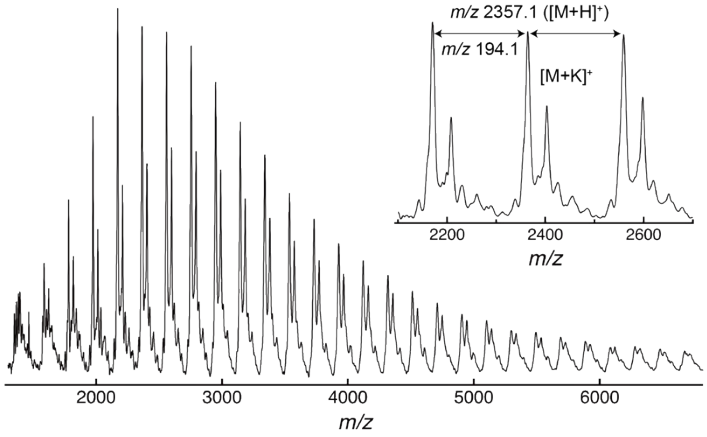


Fig.S2 MALDI-TOF-Ms spectrum of 6.

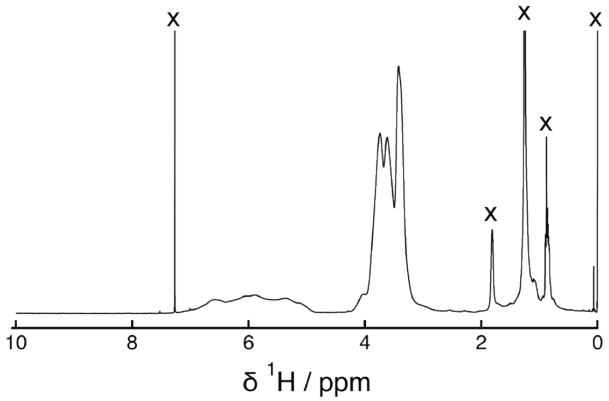


Fig.S3 ^{1}H NMR spectrum of **6** in $CDCl_3$ at 25℃ (X: solvents and impurities).

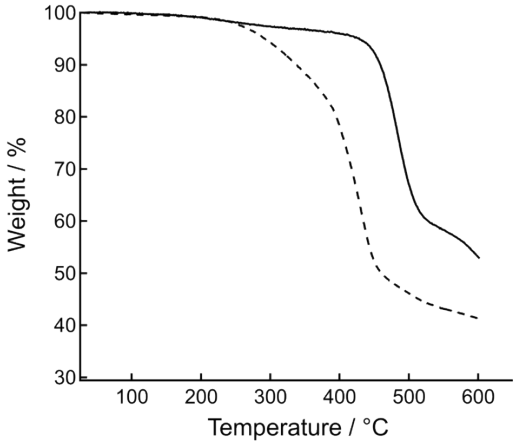


Fig. S4 TGA profiles of **4** (solid line) and **6** (dotted line) under N_2 atmosphere.

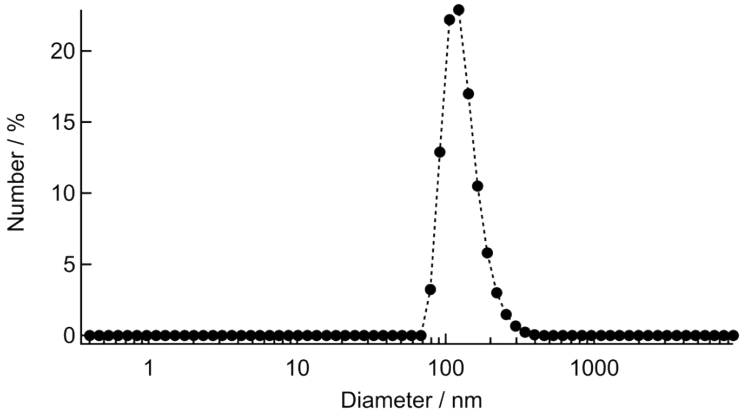


Fig. S5 DLS profile of aqueous dispersion of **7** at room temperature. The measurement was performed after dispersing a THF solution of **7** into water and allowing THF to evaporate under stirring for 2 hours at room temperature to ensure the system reached a stable equilibrium state. The data shown is a representative result from five independent replicates.

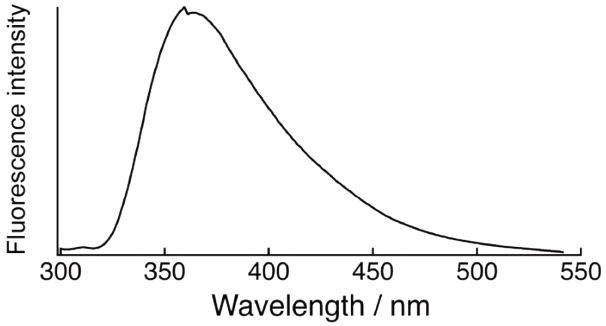


Fig. S6 Fluorescence spectra of aqueous dispersion of **7** (ex. = 260 nm).