Supporting Informations

Supramolecular Reactor from Self-Assembly of Rod-Coil Molecule in Aqueous Environment

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Scheme 1. Synthesis of rod-coil triblock molecule **1**.

Experimental section

Materials

p-Toluene-sulfonyl chloride (98 %) from Tokyo Kasei was used as received. Poly(ethylene glycol) methyl ether ($M_w = 750$), tetrakis(triphenylphosphine) palladium (0) (99%), 1-iodo-4-nitrobenzene, 1-bromo-4-nitrobenzene, 1-chloro-4-nitrobenzene, 4-iodoanisole, 4-bromoanisole, 4-chloroanisole, iodobenzene, bromobenzene, chlorobenzene and palladium (II) acetate (98 %) (all from Aldrich) and the conventional reagents were used as received. Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Lancaster, TCI, etc.). All atmosphere sensitive reactions were done under nitrogen. Flash column chromatography was carried out with Silica Gel 60 (230-400 mesh) from EM Science.

Techniques

^1H - and ^{13}C -NMR spectra were recorded from CDCl_3 and DMSO solutions on a Bruker AM 250 spectrometer. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60). Microanalysis was performed with a Perkin Elmer 240 elemental analyzer at Organic Chemistry Research Center, Sogang University, Korea. Molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) with a Waters R401 instrument equipped with Stragel HR 3, 4 and 4E columns, M7725i manual injector, column heating chamber and 2010 Millennium data station. Measurements were made by using an UV detector, CHCl_3 as a solvent (1.0 ml min^{-1}). Dynamic light scattering measurements were performed using an ALV / CGS-3 Compact Goniometer System. The scanning electron microscopy (SEM) was recorded on a Jeol JSM-6500F at an acceleration voltage of 12kV. The transmission electron microscope (TEM) was performed at 120 kV using JEOL-JEM 2010. Optical absorption spectra were obtained from a Shimadzu 1601 UV spectrophotometer. The steady-state fluorescence spectra were obtained from a Hitachi F-4500 fluorescence spectrophotometer.

Synthesis of compound 2.

Poly (ethylene glycol) methyl ether ($M_w = 750$) (7.5 g, 10 mmol) and p-toluenesulfonyl chloride (7.5 g, 40 mmol) were dissolved of dry methylene chloride. Pyridine (2 ml, 20 mmol) was added under nitrogen. The reaction mixture was stirred at 25°C under nitrogen for 5h. The resulting solution was extracted with methylene chloride and 1M HCl and water. The methylene chloride solution dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and

the crude product was purified by column chromatography (silica gel) using ethyl acetate : methanol (4:1 v/v) as eluent to yield of colorless liquid. yield 67.6 % ; ^1H -NMR (250 MHz, CDCl_3 , ppm) : δ = 7.79 (d, 2Ar-*H*; *o* to SO_3 , J = 8.2 Hz), 7.34 (d, 2Ar-*H*; *m* to SO_3 , J = 8.0 Hz), 4.15 (t, 2H, $-\text{CH}_2\text{OS}$, J = 5.1 Hz), 3.51-3.68 (m, 66H, $-\text{CH}_2\text{O}$), 3.36 (s, 3H, $-\text{CH}_3\text{O}$), 2.43 (s, 3H, $-\text{CH}_3\text{phenyl}$).

Synthesis of compound 3.

Compound **2** (3 g, 3.33 mmol), 4'-bromo-[1,1'-biphenyl]-4-ol (0.83 g, 3.33 mmol) and excess K_2CO_3 were dissolved in 100 ml of anhydrous acetonitrile. The mixture was heated at reflux for 24 h. The resulting solution was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using ethyl acetate : methanol (4:1 v/v) as eluent to yield 3.1 g (95.3 %) of a waxy solid. yield 95.3% ; ^1H -NMR (250 MHz, CDCl_3 , ppm) : δ = 7.54-7.39 (m, 6Ar-*H*), 6.99 (d, 2Ar-*H* ; *o* to ArBr, J = 6.8 Hz), 4.15 (t, 2 CH_2O ; *o* to ArO, J = 5.1 Hz), 3.51-3.68 (m, 66H, $-\text{CH}_2\text{O}$), 3.38 (s, 3H, CH_3O).

Synthesis of compound 1.

Compound **1** (3.1 g, 3.67 mmol) and 4,4'-biphenyldiboronic acid (0.51 g, 1.75 mmol) were dissolved in degassed THF (70 ml). Degassed 2M aqueous Na_2CO_3 (70 ml) was added to the solution and then tetrakis(triphenylphosphine) palladium (0) (22 mg, 0.018 mmol) was added. The mixture was heated at reflux for 48h with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, and the aqueous

layer was then washed twice with methylene chloride. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using methylene chloride : methanol (8:1 v/v) as eluent to yield 2.1 g (54.8 %) of a white solid. mp 216 °C ; Yield 54.8 % ; $^1\text{H-NMR}$ (250 MHz, CDCl_3 , ppm) : δ = 7.57-7.75 (m, 16Ar-*H*), 7.00 (d, 2Ar-*H*; *o* to ArO, J = 8.7Hz), 3.91 (t, 4H; Ar-OCH₂, J = 4.9Hz), 3.53-3.75(m, 132H; CH₂O), 3.36 (s, 6H, CH₃O) ; $^{13}\text{C-NMR}$ (250 MHz, CDCl_3 , ppm) : δ = 158.5, 139.8, 139.5, 128.0, 127.4, 127.3, 115.0, 77.6, 77.1, 76.6, 71.9, 70.8, 70.6, 69.7, 67.5, 59.0 ; M_n/M_w = 1.07 (GPC) ; Anal. Calcd for $\text{C}_{106}\text{H}_{166}\text{O}_{36}$: C, 63.14; H, 8.20. Found C, 63.14; H, 8.17.

Suzuki coupling reaction in water : Aryl halide (0.1 mmol), aryl boronic acid (0.12 mmol), NaOH (0.2 mmol), PPh_3 (0.001mmol, 1.0 mol %) and $\text{Pd}(\text{OAc})_2$ (0.0005mmol, 0.5 mol %) were added to the solution of **1** (50 mg) in water (10 ml). The reaction mixture was stirred at 25°C for 12h, and quenched with HCl. The product was extracted with methylene chloride, washed with brine and dried over anhydrous magnesium sulfate. The solvent was then removed in a rotary evaporator, and the residue was filtered by column chromatography (silica gel) using methylene chloride : hexane (1:1 v/v) as eluent. Yield of reaction was determined by GC-MASS analysis.

Dynamic laser light scattering : The dynamic laser light scattering experiments were performed with the aqueous solution of **1** (2×10^{-4} g/ml) at scattering angle of 90°.

Field-emission scanning electron microscopy (FE-SEM) : A drop of aqueous solution of **1** (2×10^{-4} g/ml) was put on glass, and dried under reduced pressure. The sample was then coated with gold in the ion coater for 30 sec.

Transmission electron microscope (TEM) : A drop of aqueous solution of **1** (2×10^{-4} g/ml) was placed onto a carbon-coated copper grid, and dried at room temperature.

Fluorescence : Aqueous solution of **1** (2×10^{-4} g/ml) was first prepared. Then phenyl boronic acid (0.4 mg) was added to the solution (5 ml) and sonicated for 10 minutes. The solution was pipetted into a quartz cuvette and the fluorescence spectrum was recorded at excitation wavelength of 333 nm. Also, each of fluorescence spectra for triphenyl phosphine and 1-bromo-4-nitrobenzene were recorded as the same methods.

UV/Vis spectroscopy : Aqueous solution of **1** (5×10^{-6} g/ml) and the solution of **1** (5×10^{-6} g/ml in methylene chloride) were pipetted into a quartz cuvette and the UV/Vis spectrum was recorded.

GC-MS analysis : Reference samples of the substrate, product, byproducts and xylene (internal standard) with known concentrations were injected to identify the retention time and response factor. Individual response factors [$\text{area}(\text{product}) \times \text{mg}(\text{standard}) / \text{area}(\text{standard}) \times \text{mg}(\text{product})$] were determined for all products by GC analysis. Determination of the ratio of the area of each product to the area of xylene obtained from GC run of the reaction mixture allowed calculation of the percent yields.

Temperature program: 100 °C for 3 min, then 30 °C/min to 280 °C. Apart from comparing the product and byproduct peaks to the standard (xylene) peaks under identical conditions, their authenticity was further confirmed by comparing their mass spectra with those of the actual compound in the spectral library.

Figure S1. The UV absorption spectra of **1**; (solid line) absorption in CH₂Cl₂ (5×10^{-6} g/ml); (dotted line) absorption of solid thin film; (dashed line) absorption in H₂O (5×10^{-6} g/ml).