Electronic supplementary information

Conjugation of Cationic poly(p-phenylene ethynylene) with Dendritic Polyethylene Enables live-cell imaging

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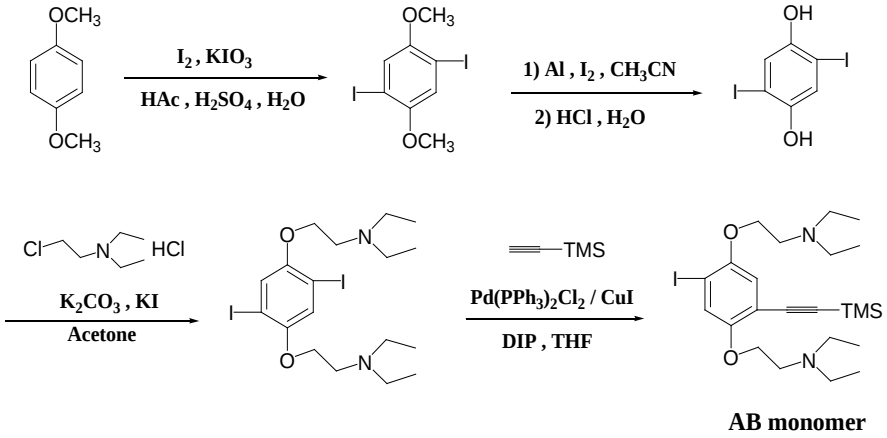
1 Synthesis of 1,4-Bis[3-(*N*,*N*-diethylamino)-1-oxapropyl]-2-iodo-5-[(trimethylsilyl)ethynyl] benzene (AB monomer)



AB monomer

Scheme S1. Synthesis of AB monomer.

1.1 Synthesis of 2,5-Diiodo-1,4-dimethoxybenzene

2,5-Diiodo-1,4-dimethoxybenzene was synthesized, as reported in the literature.[1] ^{1}H NMR ($CDCl_3$) δ 7.19 (s, 2 H, Ph-*H*), 3.83 (s, 6 H, OC*H*$_3$); ^{13}C NMR ($CDCl_3$) δ 153.25, 121.63, 85.57, 57.33.

1.2 Synthesis of 2,5-Diiodo-1,4-hydroquinone

2,5-Diiodo-1,4-hydroquinone was synthesized, as reported in the literature.[2] ^{1}H NMR (acetone-d6) δ 8.55 (s, br, 2H, Ph-O*H*), 7.15 (s, 2H, Ph-*H*); ^{13}C NMR (acetone-d6) δ 150.98, 124.38, 84.07.

1.3 Synthesis of 1,4-Bis[3-(*N*,*N*-diethylamino)-1-oxapropyl]-2,5-diiodobenzene [3]

A 250 mL round-bottom flask with magnetic stirring bar was charged with anhydrous potassium carbonate (16.59g, 0.12mol, 6.0eq.), 2,5-diiodo-1,4-hydroquinone (7.24 g, 0.02 mol, 1.0eq.), KI (0.332g, 0.002mol, 0.1eq.) and 200 mL of acetone. The stirred mixture was sparged with nitrogen for 15 min and

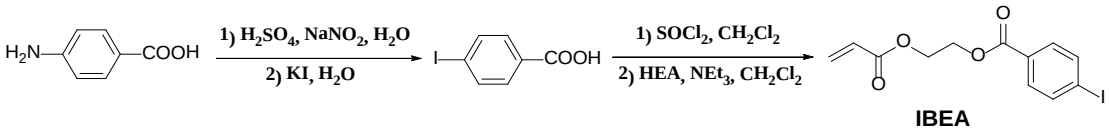
then refluxed for about 30 min. After 30 min of refluxing, 2-chlorotriethylamine hydrochloride (8.61 g, 0.05 mol, 2.5eq.) was added into the round-bottom flask and the mixture was then refluxed at 72°C in the dark for 3 days. The precipitate mixture was filtered away, and the filtrate was rotary evaporated. The residue was poured into water and extracted with ether five times, and the combined organic layers were concentrated to appropriate volume, followed by rinsing with 10% aqueous NaOH twice, water twice, and brine once. The ether layer was separated and was dried over $MgSO_4$, filtered and the solvent was removed *in vacuo* to yield dark brown solid. The crude product was recrystallized with hexane to afford light yellow needle crystals (7.75g, yield 68%). ^{1}H NMR ($CDCl_3$) δ 7.21 (s, 2 H, Ph-*H*) 4.01 (t, *J* = 6.2 Hz, 4 H, OC*H*$_2$), 2.92 (t, *J* = 6.2 Hz, 4 H, OCH_2CH_2N), 2.66 (q, *J* = 7.1 Hz, 8 H, $N(CH_2CH_3)_2$), 1.10 (t, *J* = 7.1 Hz, 12 H, $N(CH_2CH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 152.77, 122.84, 86.12, 69.33, 51.63, 48.07, 12.35; EI-MS: m/z = 560.7.

1.4 Synthesis of AB monomer.

1,4-Bis[3-(*N*,*N*-diethylamino)-1-oxapropyl]-2,5-diiodobenzene (5.60 g, 10mmol, 1.0eq.) , $Pd(PPh_3)_2Cl_2$ (0.140 g, 0.2 mmol, 0.02eq.), and CuI (0.095 g, 0.5 mmol, 0.05eq.) were added to dry and degassed diisopropylamine (DIPA) 20mL and THF 20mL in a flame dried 100 mL Schlenk flask, which was evacuated and refilled with nitrogen. Trimethylsilylacetylene (TMSA) (1.41mL, 0.982 g, 10mmol, 1.0eq.) was dissolved into the vigorously stirred solution at room temperature under nitrogen protection. The mixture was then subjected for three freeze-thaw cycle to remove any residue oxygen. After the flask was charged with dry nitrogen, cover it with aluminum foil and the reaction was allowed to stir at room temperature for 1d. Afterwards filtered, removal of the solvent in vacuo, followed by column chromatography (33% Ethylacetate/66% Petroleum ether/1%Triethylamine) over silica gel, afforded the desired product as yellow oil which may crystallize when stored in refrigerator (2.20 g, 41%). ^{1}H NMR ($CDCl_3$) δ 7.26 (s, 1 H, I-Ph-*H*), 6.85 (s, 1 H, C-Ph-*H*), 4.02 (t, *J* = 6.2 Hz, 4 H, OC*H*$_2$), 2.92 (t, *J* = 6.2 Hz, 4 H, OCH_2CH_2N), 2.67 (q, *J* = 7.1 Hz, 8 H, $N(CH_2CH_3)_2$), 1.09 (t, *J* = 7.1 Hz, 12 H, $N(CH_2CH_3)_2$), 0.26 (s, *J* = 7.0 Hz, 9 H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 154.52 (*Ph*-O), 151.67 (*Ph*-O),

123.72(*Ph*-H), 116.69(*Ph*-H), 113.31(*Ph*-C), 100.81(Ph-*C*≡C), 99.51(Ph-C≡*C*), 87.70 (*Ph*-I), 69.04(O*C*H_2), 68.67(O*C*H_2), 51.66(OCH_2*C*H_2), 48.10(*C*H_2CH$_3$), 12.37(*C*H_3), 0.21 (Si*Me*$_3$).

2 **Synthesis of polar comonomer 2-(4-Iodobenzoyloxy) ethyl acrylate (IBEA).**



Scheme S2. Synthesis of polar comonomer IBEA.

2.1 Synthesis of 4-Iodobenzoic acid

4-Iodobenzoic acid was synthesized via a Sandmeyer reaction, as reported in the literature.[4] ^{1}H NMR (CDCl$_3$) δ 7.86 (d, *J* = 8.7 Hz, 2 H), 7.77 (d, *J* = 8.7 Hz, 2 H).

2.2 Synthesis of IBEA

To a round-bottomed flask (250 mL) were added 4-iodobenzoic acid (12.41 g, 0.05 mol) and CH_2Cl_2 (150 mL) under the protection of N_2. Then $SOCl_2$ (3.63 g, 0.055 mol) was added at a slow rate. After addition, the mixture was stirred at 25°C overnight. An orange oil was obtained after removal of the solvent and unreacted $SOCl_2$ in vacuo. The mixture of CH_2Cl_2 (50mL) and NEt_3 (6.07g, 0.06mol) was then added to the orange oil, followed by dropwise addition of 2-hydroxyethyl acrylate (HEA) (5.52 g, 0.0475 mol) at 0°C. Then the ice bath was removed, and the reaction was kept under stirring at room temperature for overnight. Afterwards the precipitate mixture was filtered away, and the filtrate was washed by CH_2Cl_2 and H_2O, respectively. Dried over Na_2SO_4 and removal of the solvent in vacuo, followed by column chromatography over silica gel (EtOAc/Petroleum ether, 15:85), afforded the desired product as a clear yellow oil (13.50 g, 82%). ^{1}H NMR (CDCl$_3$) δ 7.82 (d, *J* = 8.4 Hz, 2 H, Ph-*H*),7.72 (d, *J* = 8.4 Hz, 2 H, Ph-*H*), 6.46 (d, *J* =17.1 Hz, 1 H, *H*CH=CH), 6.19 (dd, *J* = 9.2 Hz, 2H, CH_2=C*H*), 5.88 (d, *J* = 10.5Hz, 2 H, HC*H*=CH), 4.54 (mm, 4 H, OCH_2CH_2O); ^{13}C NMR (CDCl$_3$) δ 165.39, 165.33, 137.46, 131.18, 130.84, 128.99, 127.73, 100.89, 62.80, 62.00.

3 **Synthesis of dendritic polyethylene macromonomers terminated by iodine**

group (DPEI)

The classical chain walking Pd-diimine catalyst was synthesized according to the literature.[5] A prescribed amount of IBEA solution (C_M=0.3) in dichloromethane was transferred into the reactor. After thermal equilibration (35°C) for 10 min, 0.1 mmol palladium-diimine catalyst dissolved in 10 mL of dichloromethane was added into the reactor, and ethylene pressure (0.1atm) was controlled before starting the polymerization. After 48 h, the polymerization was terminated by venting the reactor and the solvent was subsequently evaporated to obtain the resultant oily polymer product. In order to remove catalyst residues, the polymer product was re-dissolved in petroleum ether and the solution was passed through a column packed with neutral alumina and silica gel until it became colorless. The polymer was finally precipitated out using methanol, and was dried under vacuum. ^{1}H NMR ($CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2 H, Ph-*H*), 7.72 (d, *J* = 8.4 Hz, 2 H, Ph-*H*), 4.51 (m, 4 H, OCH_2CH_2O), 2.33 (t, 2 H, CH_2COO), 1.35-0.8 (-CH_2, -C*H*, and -CH_3 of dendritic polyethylene backbone).

Reference:

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