Supporting Information for

Application of thermal azide-alkyne cycloaddition (TAAC) reaction as a low temperature cross-linking method in polymer gate dielectrics for organic field-effect transistors

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1.1. General information

Nuclear magnetic resonance (NMR) spectra were recorded on a Mercury plus 400 MHz instrument. All FT-IR spectra of the polymer films spin-coated onto a single-side polished silicon wafer were recorded in a transmission mode using a PerkinElmer Spectrum 100 Fourier transform infrared spectrometer. Thermogravimetric analyses (TGA) were carried out on a TA instrument Q5000TGA at a heating rate of 20 °C min\(^{-1}\) under nitrogen gas flow. Differential scanning calorimeter (DSC) studies were carried out with a TA instrument Q2000DSC under nitrogen flow. Sample (about 5.0 mg in weight) was heated up to 300 °C. Molecular weights and molecular weight distributions (M\(_w\)/M\(_n\)) of polymer were determined on a gel permeation chromatograph (GPC, Tosoh Corporation) using DMF as an eluent with polystyrenes as standards.

1.2. Materials

Chemicals were purchased from Internet Aladdin Reagent Database Inc. and Sinopharm Chemical Reagent Co. Azobisisobutyronitrile (AIBN) was recrystallized in ethanol before use. Styrene was washed with aqueous sodium hydroxide (5 wt. %) solution to remove inhibitor, was dried with over night and was distilled before use. 4-Hydroxystyrene was synthesized according to literature procedures\(^1\). Toluene was freshly distilled over sodium wire under a nitrogen atmosphere prior to use. Flash chromatography was carried out on silica gel (200-300 mesh).

1.3 Synthetic procedures

![Synthesis of 4-vinylbenzyl azide](image)

Synthesis of 4-vinylbenzyl azide. A mixture of 4-vinylbenzylchloride (3.00 g, 20.0 mmol) and sodium azide (6.50 g, 100.0 mmol) in of N, N-dimethylformamide (25 mL) was stirred at room temperature for 36 h. It was added to water (80 mL) and was extracted with diethyl ether (100 mL). The organic phase was separated and washed with water, dried with sodium sulfate anhydrous. The solvent was evaporated to provide 4-vinylbenzyl azide 3.05 g (94%) as a light yellow liquid. \(^1\)H NMR (\(\delta\), CDCl\(_3\)): 7.44 (d, J = 8.5 Hz, 2 H), 7.28 (d, J = 8.5 Hz 2 H), 6.72 (dd, J = 17.6, 11.6 Hz, 1 H), 5.78 (d, J = 17.6 Hz, 1 H, trans), 5.24 (d, J = 11.6 Hz, 1 H, cis), 4.32 (s, 2 H). \(^13\)C NMR (\(\delta\), CDCl\(_3\)): 173.85, 136.43, 135.00, 128.67, 126.96, 114.68, 54.75

![Synthesis of 4-propargyloxystyrene](image)

Synthesis of 4-propargyloxystyrene. Freshly prepared 4-hydroxystyrene (1.00 g, 7.6 mmol) was
dissolved in acetone (50 mL) under a nitrogen atmosphere. Then, potassium carbonate (3.15 g, 22.8 mmol) and tetrabutyl ammonium bromide (TBAB, 0.50 g, 1.5 mmol) were added. The mixture was heated to reflux and propargyl bromide (2.71 g, 22.8 mmol) was added dropwise. After 24 h water (50 mL) and CH₂Cl₂ (40 mL) were added to the mixture. The organic phase was separated, and the water phase was extracted with CH₂Cl₂ for three times. The organic layers were combined, dried over sodium sulfate anhydrous, and evaporated. The crude product was purified by flash chromatography using n-hexane as eluent to give a colourless oil (1.14 g, 95%). ¹H NMR (δ, CDCl₃): 7.36 (d, J = 8.5 Hz, 2 H), 6.94 (d, J = 8.5 Hz, 2 H), 6.67 (dd, J = 17.6, 11.6 Hz, 1 H), 5.63 (d, J = 17.6 Hz, 1 H, trans), 5.15 (d, J = 11.6 Hz, 1H, cis), 4.70 (d, J = 3.2 Hz, 2 H), 2.53 ppm (t, J = 3.2 Hz, 1 H). ¹³C NMR (δ, CDCl₃): 157.47, 136.30, 131.55, 127.60, 115.14, 112.33, 78.73, 75.80, 56.05

**Polymerization of azide-containing polymer (A).** 4-Vinylbenzyl azide (0.96 g, 6.0 mmol), styrene (0.63 g, 6.0 mmol), AIBN (0.048 g, 0.30 mmol), and toluene (15 mL) were combined in a 100 mL Schlenk flask equipped with a stir bar and argon was bubbled through the solution for 30 minutes. The solution was subsequently heated to 70 °C for 14 h. The reaction was cooled to room temperature and was precipitated into anhydrous methanol (250 mL). The mixture was filtered to give a pale yellow powder. The powder was dissolved into acetone (10 mL) and the solution was transferred into a dialysis tube (Mₙ cutoff 3500), which had been washed thoroughly with deionized water prior to use. The tubing was then closed and was placed in a beaker containing acetone (500 mL). After 2 days, the dialyzed solution was concentrated and was dried in vacuo to afford the product A as a pale yellow powder (0.76 g, 48% conversion, Mₙ = 12,538 g/mol, PDI = 1.5). ¹H NMR (δ, CDCl₃): 7.3-6.2 (m, 9H), 4.3-4.1 (m, 2H), 2.2-0.8 (m, 9H); FTIR 3063, 3022, 2931, 2857, 2095, 1598, 1491, 1450, 1260, 824, 758, 695 cm⁻¹.

**Polymerization of alkyne-containing polymer (B).** 4-Propargyloxystyrene (0.95 g, 6.0 mmol), styrene (0.63 g, 6.0 mmol), AIBN (0.048 g, 0.30 mmol), and toluene (15 mL) were combined in a 100 mL Schlenk flask equipped with a stir bar and argon was bubbled through the solution for 30 minutes. The solution was heated to 70 °C for 14 h. The reaction was cooled to room temperature and was precipitated into anhydrous methanol (250 mL). The mixture was filtered to give a white powder. The powder was dissolved into acetone (10 mL) and the solution was transferred into a dialysis tube (Mₙ cutoff 3500), which had been washed thoroughly with deionized water prior to
use. The tubing was then closed and placed in a beaker containing acetone (500 mL). After 2 days, the dialyzed solution was concentrated and was dried in vacuo to afford the product B as a white powder (0.92 g, 58% conversion, M_n = 12,356 g/mol, PDI = 1.2). ^1H NMR (δ, CDCl_3): 7.2-6.2 (m, 10H), 4.7-4.5 (m, 2H), 2.4-2.2 (m, 1H), 2.1-0.8 (m, 8H); FTIR 3290, 3063, 3030, 2923, 2849, 1729, 1606, 1507, 1450, 1367, 1219, 1162, 1029, 826, 701, 668 cm⁻¹.

![Fig. S1](image1.png)  
**Fig. S1** ^1H NMR spectrum of 4-vinylbenzyl azide.

![Fig. S2](image2.png)  
**Fig. S2** ^13C NMR spectrum of 4-vinylbenzyl azide.
Fig. S3 $^1$H NMR spectrum of 4-propargyloxystyrene.

Fig. S4 $^{13}$C NMR spectrum of 4-propargyloxystyrene.
Fig. S5 $^1$H NMR spectrum of azide-containing polymer (A).

Fig. S6 $^1$H NMR spectrum of alkyne-containing polymer (B).
Fig. S7 FTIR spectrum of azide-containing polymer (A).

Fig. S8 FTIR spectrum of alkyne-containing polymer (B).
Fig. S9 XRD patterns for TIPS-pentacene/PS film drop-casted on cross-linked styrenic polymer dielectric layer

Fig. S10 The top-view polarized optical micrograph of the device

2. OFETs Device Fabrication and Characterization

2.1. Device fabrication

A 40-nm aluminum metal layer was thermal evaporated with a shadow mask onto the cleaned glass substrate as the gate electrode. A/B blend dielectric was dissolved in chlorobenzene (A :B :Chlorobenzene = 20 mg: 20 mg: 1 mL) and spin-coated onto the sample at 3000 r/min for 1 min, followed by a cross-linking process at 100 °C for 1 h in an oven (150 nm). Then silver source/drain electrodes (60 nm) were evaporated on the dielectric, defining the channel width and length of 1200 and 60 μm, respectively. Subsequently, the electrodes were modified by immersing in a $5 \times 10^{-3}$ mol/L solution of perfluorobenzenethiol (PFBT) in ethanol for 2 min and then rinsed with ethanol. The semiconducting layer was finally drop-casted from a solution made by mixing 6,
13-bis(triisopropylsilylethynyl)-pentacene (TIPS-pentacene) and polystyrene (PS) at 10 mg/ml concentration of solids in chlorobenzene (3:1 ratio by volume). The devices were then annealed at 100 °C for 30 min in ambient environment.

2.2. Device Characterization

Electrical properties of the OTFT devices were characterized with a Keithley 4200 semiconductor characterization system. A WK6515B precision impedance analyzer was used to measure the capacitance. Film thickness was characterized by a KLA-Tencor D-120 profiler. The surface roughness was measured using a BioScope Veeco atomic force microscope.

References