

Supporting Information

***In situ* visualizable self-assembly, aggregation induced emission and circularly polarized luminescence of tetraphenylethene and alanine based chiral polytriazole**

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Experimental Section

Materials

All chemicals and reagents were used as received unless stated otherwise. Sodium azide, *p*-toluenesulfonyl chloride, 4-bromobenzophenone, 1,2-bis(4-bromophenyl)-1,2-diphenylethene, 3,5-dibromobenzoic acid, thionyl chloride, triphenylphosphine, trimethylsilylacetylene and alanine methyl ester hydrochloride were purchased from Sigma-Aldrich, J&K Scientific or Energy Chemical. DCM, DMF, MeOH, Et₃N, ethanol, zinc, TiCl₄, Pd₂(dba)₃, CuI, Cu(PPh₃)₃Br and other chemicals were ordered from Energy Chemical or Aladdin. THF was distilled from sodium benzophenone ketyl

under nitrogen and normal pressure immediately before use. DMF and Et₃N were stirred with CaH₂, and DMF was distilled under reduced pressure, while Et₃N was under normal pressure.

Characterizations

¹H and ¹³C NMR spectra were measured on a VNMRs 400 (Varian, USA) NMR spectrometer in CDCl₃ or DMSO-*d*₆ using tetramethylsilane (TMS; δ = 0) as internal reference. High-resolution mass spectra (HRMS) were measured on a GCT Premier CAB 048 mass spectrometer in an electron-ionization or a MALDI-TOF mode. Weight-average molecular weights (*M*_w) and polydispersity indices (*M*_w/*M*_n) of the polymers were estimated on a Waters gel permeation chromatography (GPC) system equipped with RI detector and calibrated by using a set of standard linear polystyrenes. DMF with 0.01 M LiBr was used as an eluent at a flow rate of 1.0 mL min⁻¹. TGA and DSC analyses were carried out on a TA TGA Q5000 and a TA Instruments DSC Q1000, respectively, at a heating rate of 10 °C min⁻¹ under nitrogen. UV spectra were recorded using a UV-2600 spectrometer (Shimadzu, Japan). Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Morphological structures of the aggregates were investigated by a Bruker Multimode VIII atom force microscopy (AFM) instrument, FEI Tecnai G² F30 transmission electron microscopy (TEM) and HITACHI-SU8010 scanning electron microscope (SEM) at accelerating voltages of 200 and 5 kV, respectively. Fluorescence images were captured using the fluorescence microscope DHG-9070A (Olympus, Japan). Fluorescence quantum yields were measured using a Hamamatsu absolute photoluminescence quantum yield spectrometer C11347 Quantaaurus-QY. CD spectra were recorded using a Chirascan spectrometer (Applied Photophysics, England). CPL spectra were recorded using a CPL-200 instrument (JASCO, Japan) at room temperature. Polymer thin films were fabricated on silicon wafers from the THF solutions (~10 mg mL⁻¹) *via* spin-coating process (1000 rpm; 1 min). Silicon wafers were fully cleaned by sequential treatments with dichloromethane, THF, ethanol, deionized water, and acetone in an ultrasonic bath before use. The obtained polymer films were dried overnight in a vacuum oven at room temperature. Refractive indices of the polymer films were determined on a Woollam ellipsometer with a model of Alpha-SE and a wavelength tunability from 390 to 890 nm. The photopattern was generated by the UV irradiation of its thin film through a copper photomask for 20 min in air at room temperature. The photo-irradiation process was conducted using 365 nm light from a Spectroline ENF-280C/F UV lamp at a distance of 3 cm as the light source. The incident light intensity was ~18.5 mW cm⁻². The photomask used herein was a grid pattern, where the square areas were coated with copper and the grid lines were transparent glass substrates. The fluorescent photopattern was obtained on a fluorescence optical microscope (Olympus BX 41) under a UV light

source (330–385 nm).

Preparation of 4-Methylbenzenesulfonyl azide: Into a 500 mL round-bottom flask was added sodium azide (1.43 g, 22 mmol) and a mixture of ethanol/water (57 mL/10 mL). After the solid was completely dissolved, *p*-toluenesulfonyl chloride (3.81 g, 20 mmol) dissolved in 100 mL acetone was added into the flask. The mixture was stirred at room temperature overnight with a large amount of white precipitate appeared. After filtration and solvent evaporation, the organic layer was diluted with DCM, washed with water three times, and then dried over MgSO₄ for an hour. The filtrate was concentrated by a rotary evaporator and the product was dried in a vacuum oven at 30 °C to a constant weight. Colorless liquid of 4-Methylbenzenesulfonyl azide was obtained in 91.8% yield (3.67 g).

Preparation of 1,2-bis(4-bromophenyl)-1,2-diphenylethene (TPE-2Br): Into a 500 mL two-necked round-bottom equipped with a reflux condenser was placed 4-bromobenzophenone (10.444 g, 0.04 mol) and zinc dust (7.925 g, 0.12 mol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. After THF (200 mL) was added, the mixture was cooled down to 0 °C, into which TiCl₄ (11.44 g, 6.63 mL, 0.06 mol) was added dropwise, then warmed slowly to room temperature and refluxed overnight. Afterward, the reaction mixture was cooled to room temperature. After most of the solvent was evaporated, the filtrate was poured into 1 M HCl solution (100 mL), and extracted by DCM three times. The organic layer was combined and washed with brine and water, and then dried over MgSO₄. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using petroleum ether as eluent. A white solid of TPE-2Br was obtained in 91.9% yield (8.42 g).

Preparation of 1,2-bis(4-azidophenyl)-1,2-diphenylethene (TPE-2N₃, 1): Into a 250 mL round-bottom flask was placed 1,2-bis(4-bromophenyl)-1,2-diphenylethene (3.677 g, 7.5 mmol). The flask was evacuated under vacuum and flushed with dry nitrogen three times. After THF (80 mL) was added, the solution was cooled down to –78 °C, into which *n*-BuLi (11.25 mL, 18 mmol, 1.6 M in hexane) was added dropwise. The mixture was kept at –78 °C for 2 h and then 3.550 g (18 mmol) of 4-methylbenzenesulfonyl azide dissolved in 20 mL of THF was added into the flask dropwise. After reacting at –78 °C for 1 h, the mixture was warmed slowly to room temperature and stirred overnight. Afterward, saturated NH₄Cl solution (100 mL) was added to quench the reaction, and THF was evaporated. Then, DCM was added to extract the product three times. The organic layer was combined and washed with water and brine and dried over MgSO₄. After filtration and solvent evaporation, the crude

product was purified by a silica gel column chromatography using petroleum ether as eluent. Pale yellow solid of TPE-2N₃ was obtained.

Preparation of 3,5-dibromobenzoic acid methyl ester: A solution of 8 g of 3,5-dibromobenzoic acid (28.0 mmol) in 150 mL of anhydrous methanol was refluxed and to this mixture 8 ml of thionyl chloride was added dropwise. Heating was continued for 2 h and the solvent was evaporated. The residue was purified by column chromatography on silica gel, using dichloromethane as eluent. After solvent evaporation the product was obtained as white crystals.

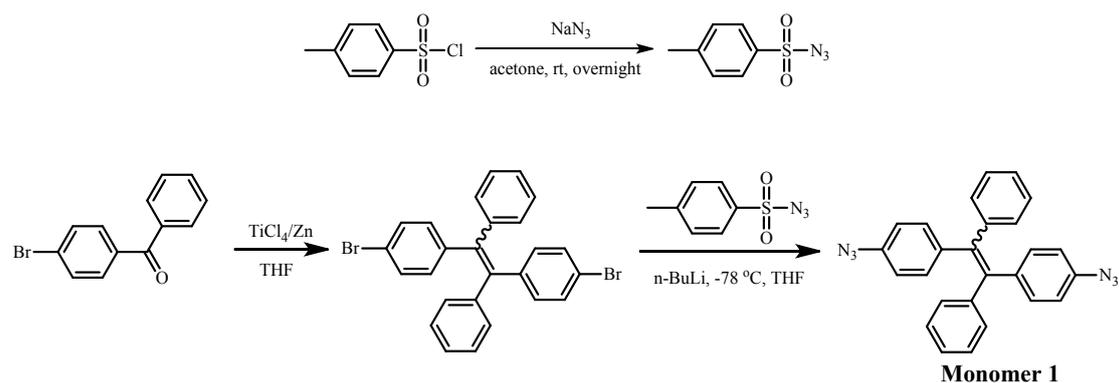
Preparation of methyl 3,5-bis(trimethylsilylethynyl) benzoate: A solution of 4.00 g of 3,5-dibromobenzoic acid methyl ester (13.34 mmol) in dry triethylamine (TEA, 50 mL) was deoxygenated with argon and then 366 mg of Pd₂(dba)₃, 102 mg of CuI and 70 mg of triphenylphosphine was added. After the mixture was heated up to 70 °C, 7.54 mL of trimethylsilylacetylene (0.053 mol) was charged. The solution was allowed to react over 24 h at this temperature, then the solvent was evaporated and the solid, brownish-black residue was extracted with chloroform (2 × 100 ml). The combined organic solutions were evaporated with silica gel (20 g) and then the adsorbed product was loaded onto chromatographic column. The product was eluted with hexane-ether (98 : 2, v/v). After solvent evaporation, methyl 3,5-bis(trimethylsilylethynyl) benzoate was obtained as yellow oil which tends to crystallize into yellowish needles.

Preparation of 3,5-diethynylbenzoic acid: Methyl 3,5-bis(trimethylsilylethynyl) benzoate was (2.00 g, 6.05 mmol, 1.0 equiv) was solved in MeOH (25 mL). After addition of NaOH (0.97 g, 24.2 mmol, 4.0 equiv.), the mixture was stirred for 1 h at room temperature. The resulting white precipitate was dissolved by adding small amounts of HCl. The reaction mixture was extracted with DCM (4 × 20 mL) and dried over MgSO₄. After removing the solvent under reduced pressure the desired product was afforded as a white solid in 81.4% yield (0.84 g).

Preparation of 3,5-diethynylbenzoyl-D-Alanine methyl ester (Monomer 2): 3,5-Diethynylbenzoic acid was added to dry THF with two drops of dimethylformamide (DMF). The mixture was cooled with an ice bath, to which 2 mL of SOCl₂ was added dropwise. The mixture was then refluxed for 1.5 h. Afterward, the solution was concentrated by a rotary evaporator to give an orange solid of 3,5-diethynylbenzoyl chloride. Into a 100 mL round-bottom flask were added 1.02 g (6.1 mmol) of alanine methyl ester hydrochloride, 3 mL of pyridine, and 10 mL of DCM under nitrogen. The contents were mixed by stirring and cooled with an ice bath. A solution of 3,5-diethynylbenzoyl chloride (1.00 g, 6.1 mmol) in 10 mL of DCM was then slowly

injected into the flask. The reaction mixture was gradually warmed to room temperature and stirred overnight. The mixture was then diluted with 100 mL of DCM, and the resultant solution was washed twice with dilute HCl solution and once with water. The organic layer was dried over 5 g of magnesium sulfate. After filtration of the solid and removal of the solvent, the crude product was purified on a silica gel column using a mixture of CH₂Cl₂/acetone (15:1 by volume) as eluent.

Preparation of P(TPE-Alanine): The polymerization reaction was carried out under nitrogen in Schlenk tube. Into a 15mL Schlenk tube were added 0.30 g (0.71 mmol) of (1), 0.18 g (0.71 mmol) of (2) and 0.013 g (0.014 mmol) of Cu(PPh₃)₃Br. Then 5.0 mL of anhydrous DMF was injected. After stirring at 60 °C for 6 h, the mixture was diluted with chloroform and added dropwise into 100mL of methanol. The precipitate was allowed to stand overnight, collected by filtration, and dried under vacuum at room temperature to a constant weight.



Scheme S1 Synthetic route to Monomer 1, TPE-2N₃.

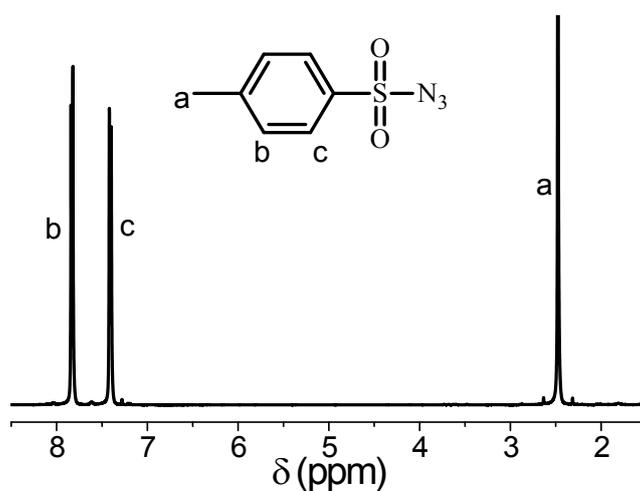


Fig. S1 ¹H NMR spectrum of TsN₃ in CDCl₃.

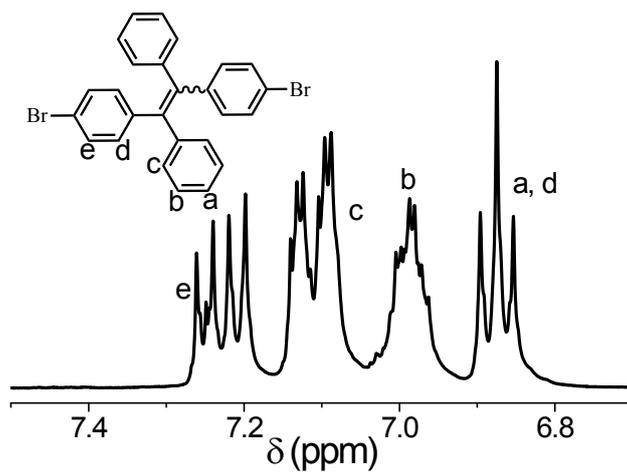


Fig. S2 ^1H NMR spectrum of TPE-2Br in CDCl_3 .

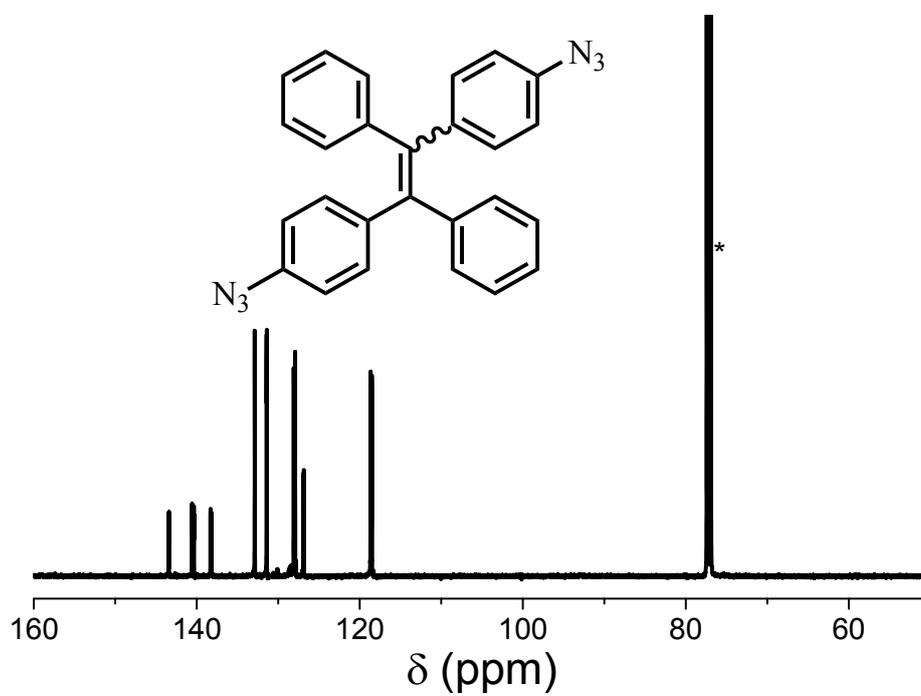
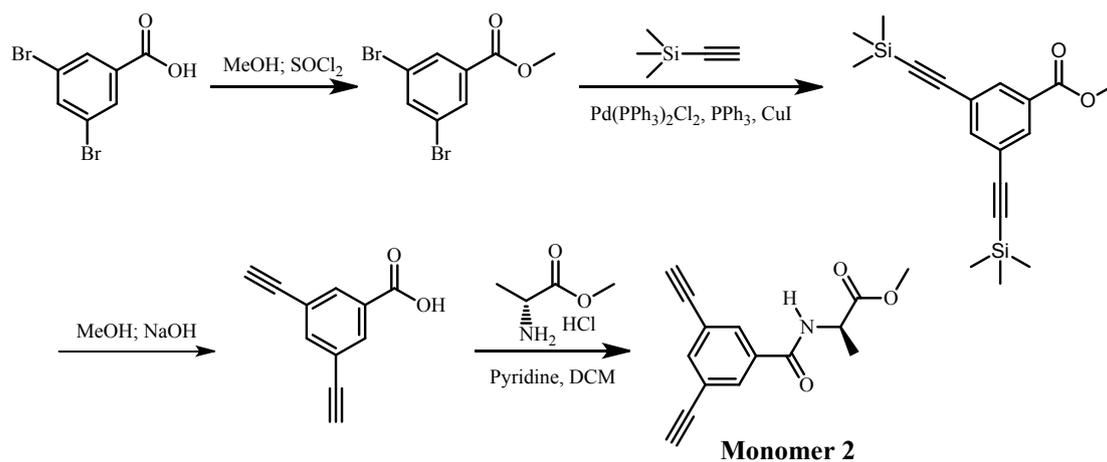


Fig. S3 ^{13}C NMR spectrum of TPE-2N₃ in CDCl_3 .



Scheme S2 Synthetic route to Monomer 2, 3,5-diethynylbenzoyl-D-Alanine methyl ester.

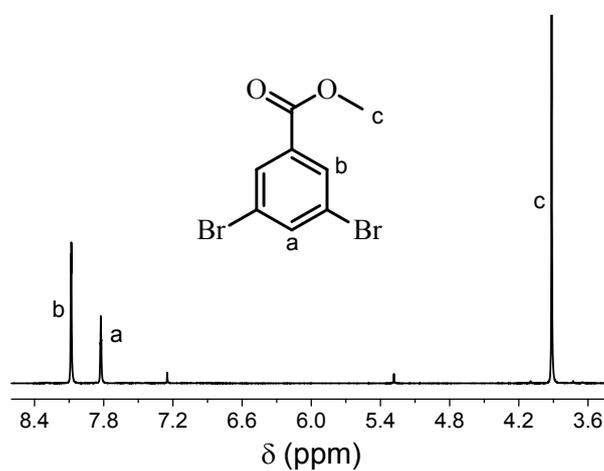


Fig. S4 ^1H NMR spectrum of dibromobenzoic acid methyl ester in CDCl_3 .

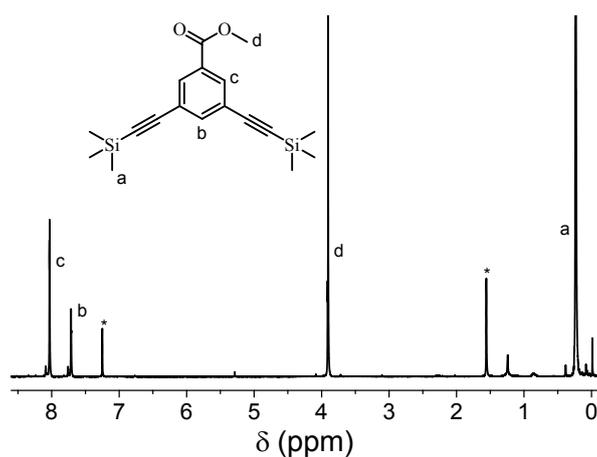


Fig. S5 ^1H NMR spectrum of methyl 3,5-bis(trimethylsilylethynyl) benzoate in CDCl_3 . The solvent peaks were marked with asterisks.

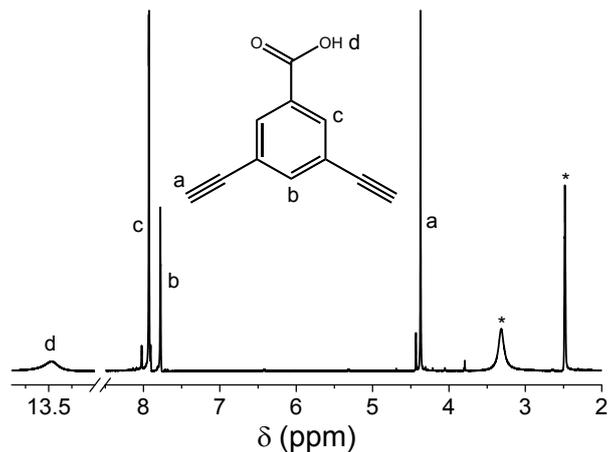


Fig. S6 ¹H NMR spectrum of 3,5-diethynylbenzoic acid in DMSO-*d*₆. The solvent and water peaks were marked with asterisks.

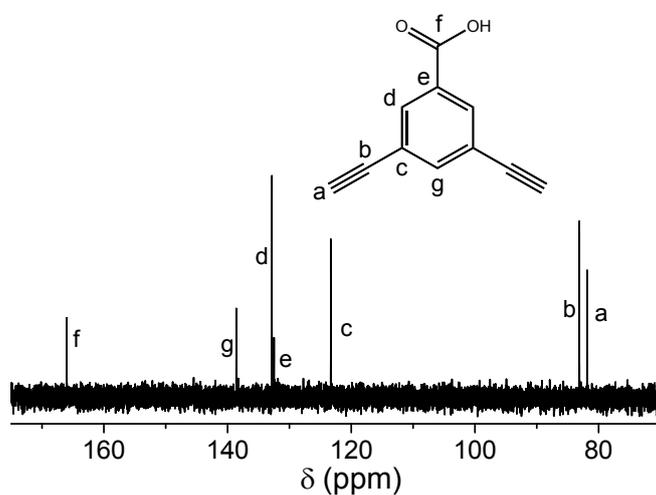


Fig. S7 ¹³C NMR spectrum of 3,5-diethynylbenzoic acid in DMSO-*d*₆.

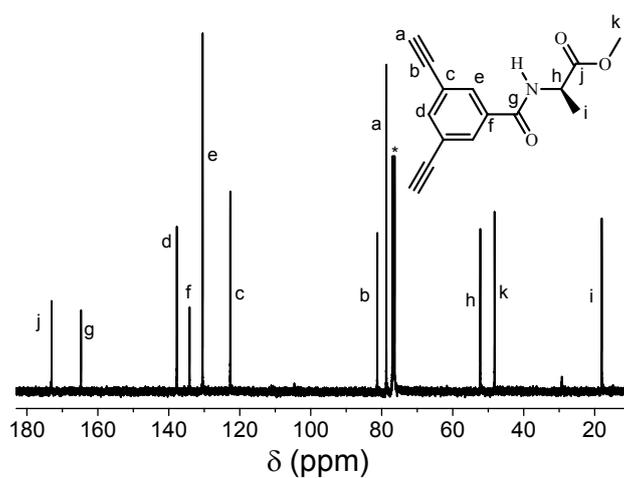


Fig. S8 ¹³C NMR spectrum of 3,5-diethynylbenzoyl-D-Alanine methyl ester in CDCl₃. The solvent peak was marked with asterisk.

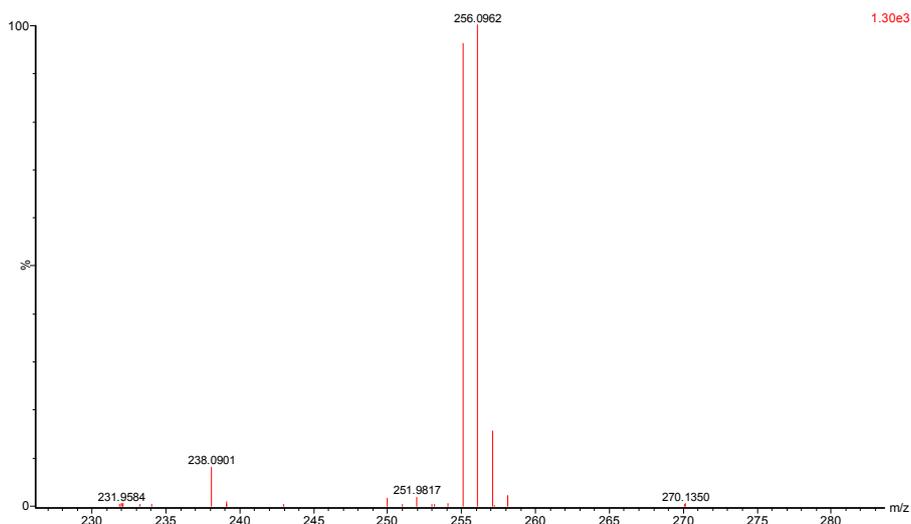


Fig. S9 HRMS spectrum of 3,5-diethynylbenzoyl-D-Alanine methyl ester.

In the IR spectrum, P(TPE-Alanine) shows no stretching vibration bands of $\equiv\text{C}-\text{H}$ at 3293 cm^{-1} and $\text{C}\equiv\text{C}$ and N_3 at 2122 cm^{-1} (Fig. S10C), revealing that almost all the acetylene and azide groups in Monomer 1 and Monomer 2 have been consumed by the click polymerization and transformed to triazole rings in P(TPE-Alanine). The absorption band of the carbonyl group shifts from 1743 cm^{-1} in Monomer 2 to 1724 cm^{-1} in P(TPE-Alanine) because of the forming of intramolecular hydrogen bond.

We performed the ^1H NMR and ^{13}C NMR analyses of all the monomers and polymer in CDCl_3 and $\text{DMSO}-d_6$. Fig. S11 shows the ^1H NMR spectra of P(TPE-Alanine) as well as its monomers in CDCl_3 . The $\text{CH}-$ protons on benzene ring adjacent to the azide group of monomer 1 resonated at δ 6.77 (peak 1), which disappeared in P(TPE-Alanine) (marked with red circle) after the click polymerization. The resonance of acetylene protons of monomer 2 at δ 3.14 (peak 6) also disappeared, further substantiating the conclusion drawn from the IR spectral analysis. The new peak at δ 8.25 (peak 18) was associated with the resonance of the protons in the triazole ring, while the other resonance peaks became broad in P(TPE-Alanine), in contrast to the sharp peak of Monomer 1 and Monomer 2.

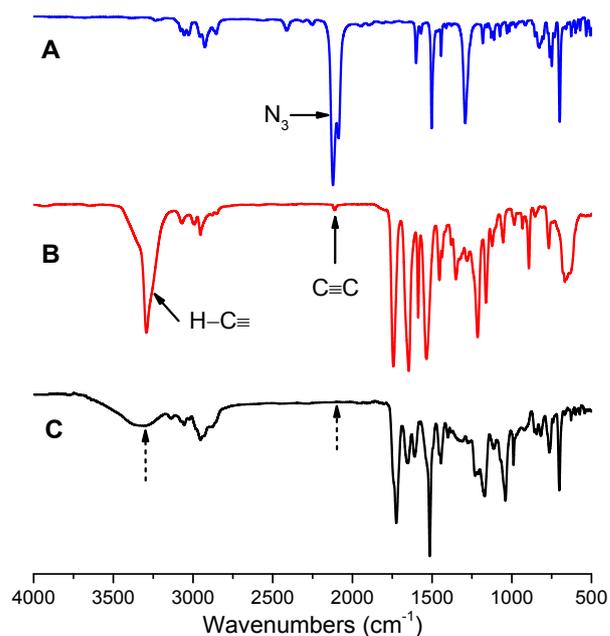


Fig. S10 IR spectra of (A) TPE-2N₃ (Monomer 1), (B) 3,5-diethynylbenzoyl-alanine methyl ester (Monomer 2), and (C) polymer P(TPE-Alanine).

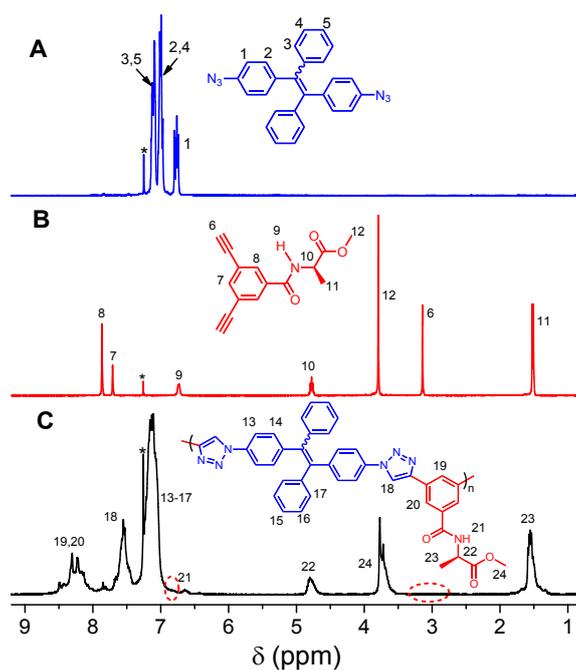


Fig. S11 ¹H NMR spectra of (A) TPE-2N₃ (Monomer 1), (B) 3,5-diethynylbenzoyl-alanine methyl ester (Monomer 2), and (C) P(TPE-Alanine) measured in CDCl₃ at room temperature. The solvent peaks are marked with asterisks.

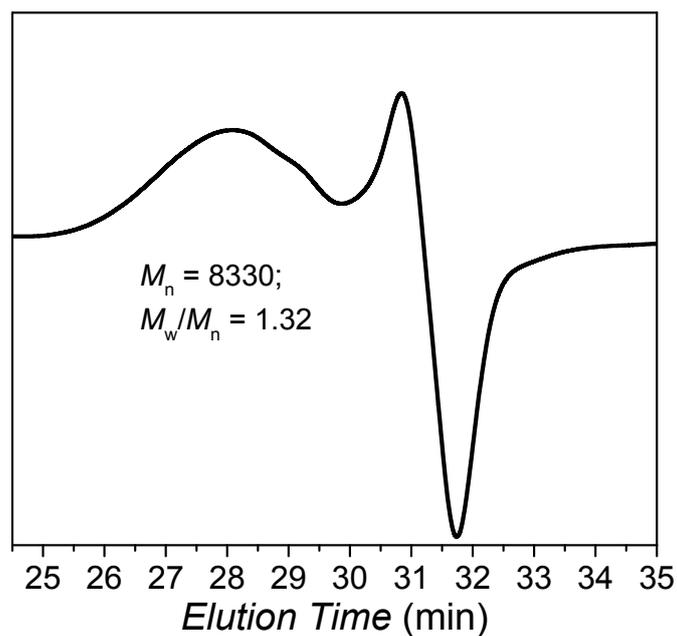


Fig. S12 Full GPC trace of P(TPE-Alanine) in DMF on the basis of a linear PMMA calibration.

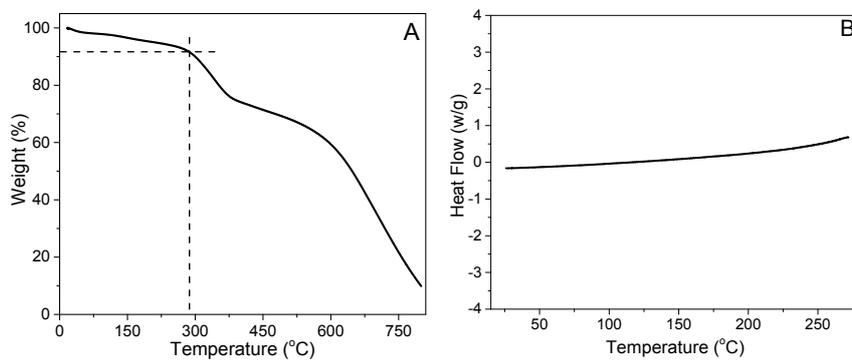


Fig. S13 (A) Thermo gravimetric (TGA) and (B) differential scanning calorimetry (DSC) analysis traces of P(TPE-Alanine) recorded under at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

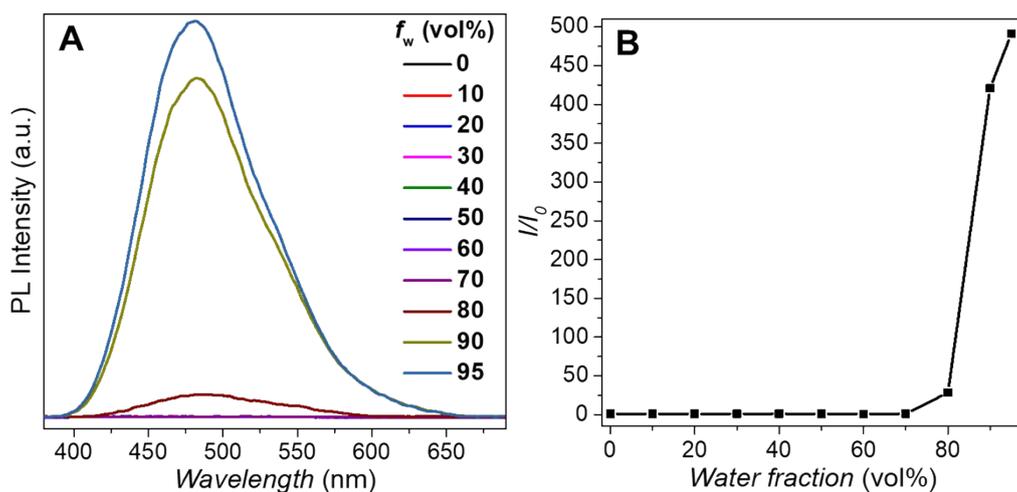


Fig. S14 (A) PL spectra of TPE-2Br in pure THF and THF/H₂O mixtures. Solution concentration: 10^{-5} M; excitation wavelength: 315 nm. (B) Plot of I/I_0 values versus the compositions of the solution.

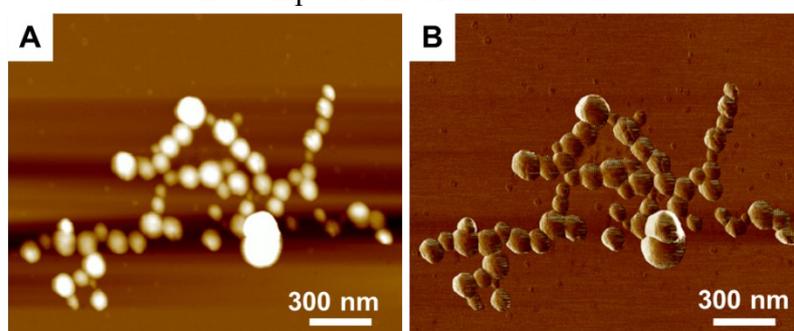


Fig. S15 AFM (A) height and (B) phase images of P(TPE-Alanine) obtained from THF/H₂O mixture at a volume ratio of 4 : 6. Solution concentration: 10^{-5} M.

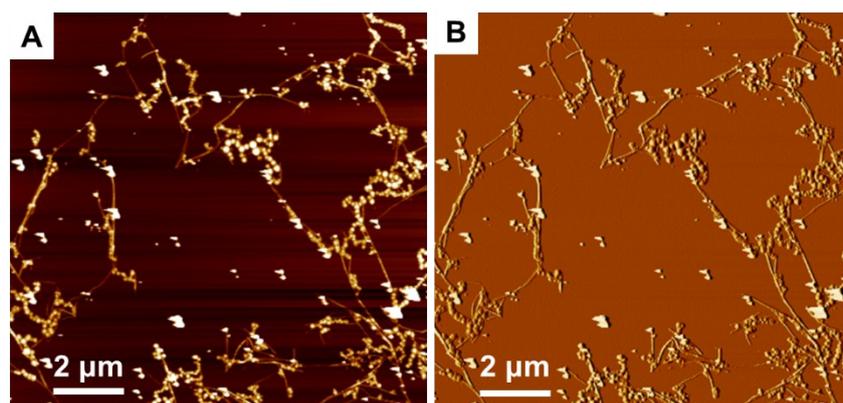


Fig. S16 AFM (A) height and (B) phase images of P(TPE-Alanine) obtained from THF/H₂O mixture at a water fraction of 80%. Solution concentration: 10^{-5} M.

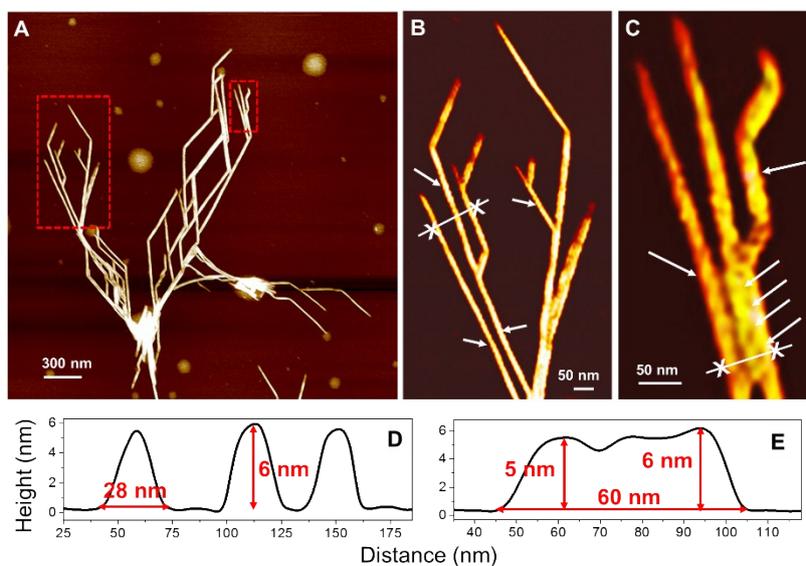


Fig. S17 (A) AFM image of P(TPE-Alanine) obtained from THF/H₂O mixture at a water fraction of 90%. (B, C) Zoomed-in images of the labeled areas in image A; (D, E) Height profiles of the labeled areas in images B and C, respectively.

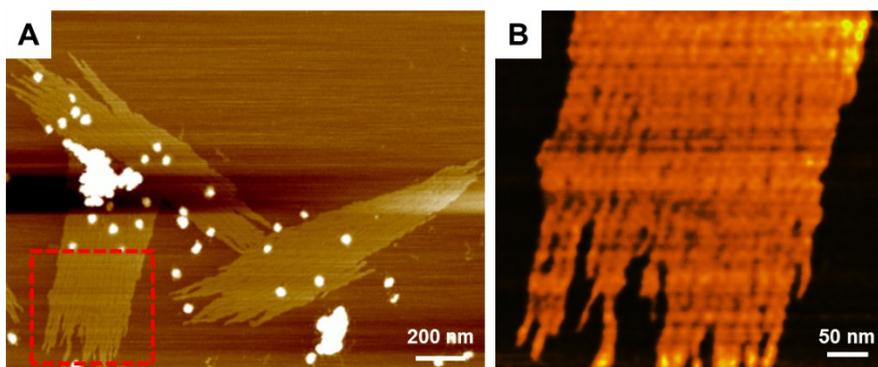


Fig. S18 (A) AFM image of P(TPE-Alanine) obtained from THF/H₂O mixture at a volume ratio of 1 : 9; (B) Zoomed-in image of the labeled areas in image A. Solution concentration: 10⁻⁵ M.

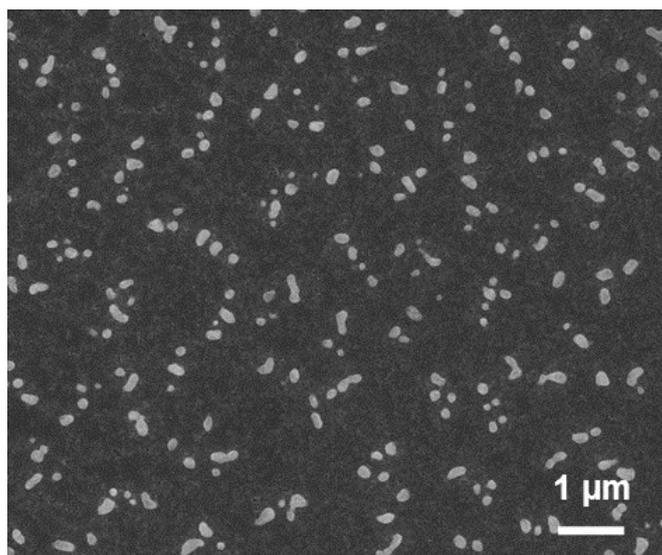


Fig. S19 SEM image of P(TPE-Alanine) obtained from THF/H₂O mixture at a volume ratio of 5 : 5. Solution concentration: 5×10^{-4} M.

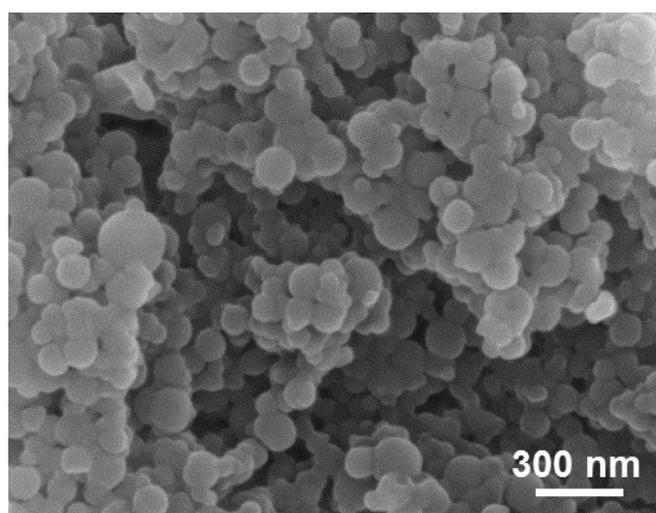


Fig. S20 Magnified SEM image of Fig. 5D.

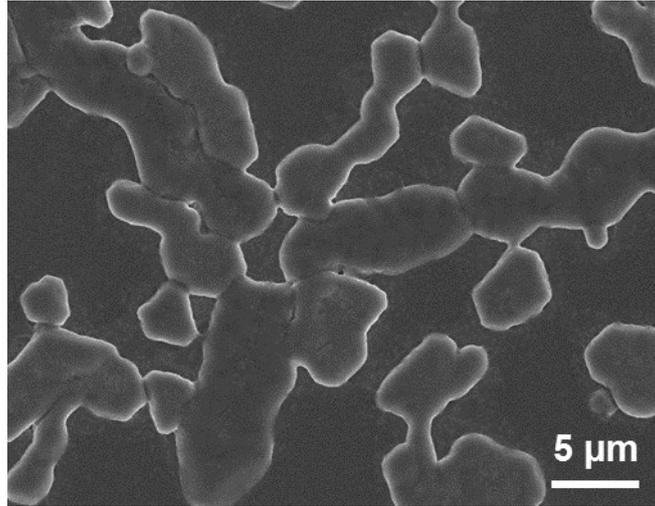


Fig. S21 Magnified SEM image of Fig. 6D.