Electronic Supplementary Information (ESI)

L-Valine methyl ester-containing tetraphenylethene: aggregation-induced emission, aggregation-induced circular dichroism, circularly polarized luminescence, and helical self-assembly

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Table of Contents

Experimental Section

General Information

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl in an atmosphere of nitrogen immediately prior to use. *N,N*-Dimethylformamide (DMF) and 1,2-dichloroethane (DCE) were used as received. $Cu(PPh_3)_3Br$ was prepared according to the literature method.[1]

The ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 NMR spectrometer in $CDCl_3$ 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. UV absorption spectra were taken on a Milton Ray Spectronic 3000 array spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Morphological structures of the aggregates were investigated by JEOL 2010 transmission electron microscopy (TEM) and JEOL-6700F scanning electron microscope (SEM) at accelerating voltages of 200 and 5 kV, respectively. CD spectra were taken on a JASCO J-810 spectropolarimeter in a 1 mm quartz cuvette using a step resolution of 0.1 nm, a scan speed of 100 nm/min, a sensitivity of 0.1 nm, and a response time of 0.5 s. Circular photoluminescence spectra (CPL) were recorded on a home-made CPL spectroscopy system.[2] The system is composed of a 325 nm He-Cd laser as the light source, a photo-elastic modulator (Hinds, PEM-90, 50 kHz), a broad-band Glan-laser polarizer (Special Optics) oriented at 45º to the PEM optical axis and a monochromator (SPEX 500 M) and a photomultiplier (PMT, Hamamatsu, R928). The sample was irradiated with the laser beam at the wavelength 325 nm from the same side of emission collection. A UV depolarizer was used on the excitation light to avoid non-nature CPL. The retardation of the emitted light was controlled by the quarter-wave 50 kHz modulator PEM-90 and detected by the photomultiplier tube after passing through the linear polarizer. The DC component of the PMT output was measured by a digital multimeter (Thurlby 1905a), while the AC component with frequency of 50 kHz was amplified by a pre-amplifer (Stanford Research Systems, SR560) and analyzed by a lock-in amplifier (Stanford Research

Systems, SR510). The CPL dissymmetry factor, $g_{em} = 2(I_L - I_R)/(I_L + I_R)$, was evaluated from the ratio of the AC signal to the DC signal.

Sample preparation for PL measurement

A stock THF solution of Val-TPE with a concentration of 2×10^{-4} M was prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, distilled water was added dropwise under vigorous stirring to afford 2×10^{-5} M solutions with different water fractions (0-95 vol%). The PL measurements of the resulting solutions were then conducted immediately.

**Fabrication of micropatterned Val-TPE using Teflon-based stamp**

The Teflon stamp was fabricated using the method developed by Wu's lab.[3] The obtained Teflon stamp was sealed onto a clean quartz substrate using clamps. 5 μL of Val-PTE solution (1 wt%) in DMF was added at one end of the Teflon stamp, and it filled the microchannels (10 μm wide and 10 μm deep) between the Teflon stamp and the quartz substrate spontaneously due to capillary effect. The whole assembly was put into a vacuum oven to evaporate DMF solvent inside the microchannels at various evaporation rates. Finally, the Teflon stamp was removed to leave the micropatterned Val-TPE fibers on the quartz substrate.

Synthesis

1-[4-(azidomethyl)phenyl]-1,2,2-triphenylethene (**1**) and *4-ethynylbenzoyl-L-valine methyl ester* (**2**) were synthesized according to our previous papers.[4,5]
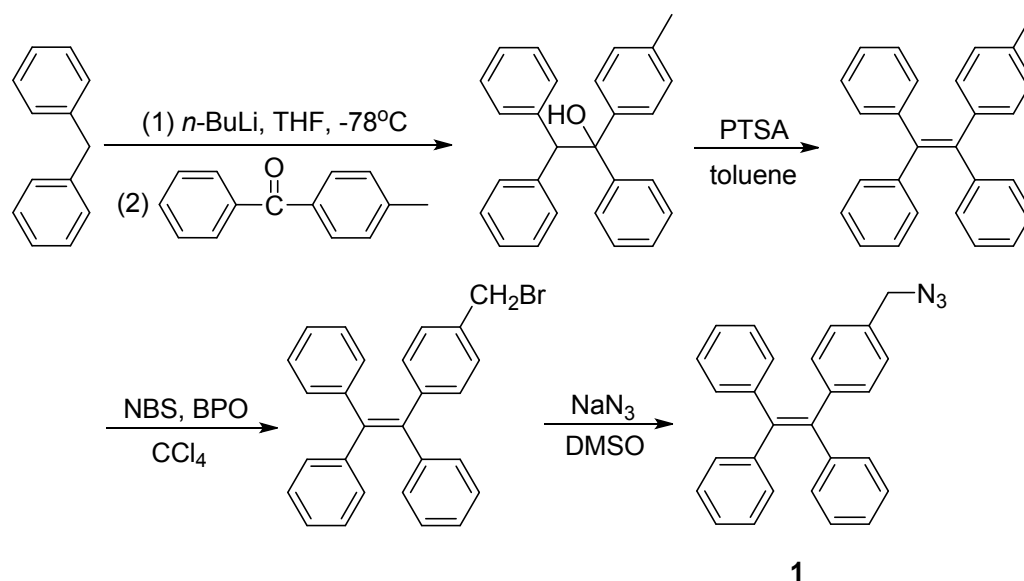
Scheme S1 Synthetic route to **1**.

1-[4-(azidomethyl)phenyl]-1,2,2-triphenylethene (**1**): White solid; ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.09 (m, 9H), 7.04 (m, 10H), 4.24 (s, 2H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 143.9, 143.5, 143.4, 141.4, 140.2, 133.2, 131.7, 131.3, 127.7, 127.6, 126.5, 54.5.
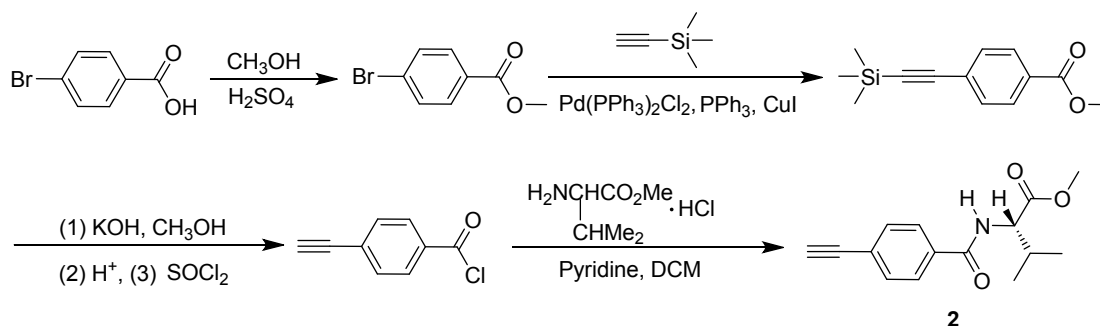
Scheme S2 Synthetic route to **2**.

4-ethynylbenzoyl-L-valine methyl ester (**2**). White solid; ^{1}H NMR (400 MHz, CDCl$_3$), δ (TMS, ppm): 7.76 (d, 2H), 7.56 (d, 2H), 6.63 (d, 1H), 4.78 (m, 1H), 3.77 (s, 3H), 3.19 (s, 1H), 2.27 (m, 1H), 1.00 (m, 6H). ^{13}C NMR (100 MHz, CDCl$_3$), δ (TMS, ppm): 172.5, 166.3, 133.9, 132.2, 126.9, 125.5, 82.6, 79.5, 57.4, 52.2, 31.5, 18.9, 17.9.

4-{1-[4-(1,2,2-triphenylvinyl)benzyl]triazoyl}benzoyl-L-valine methyl ester (**Val-TPE**).

Into a 50 mL round-bottom flask 0.426 g (1.1 mmol) of (**1**), 0.259 g (1.0 mmol) of (**2**) and $Cu(PPh_3)_3Br$ were added. 20 mL of anhydrous DMF was injected under N_2. The reaction mixture was stirred at 60 ^{o}C overnight. After cooled to room temperature, the reaction mixture was dissolved in 100 mL of water. The resulting solution was extracted with DCM. The organic phase was washed with brine and water, and then dried over Na_2SO_4 overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using hexane/ethyl acetate (1 : 1, v/v) mixture as eluent. A white solid of Val-TPE was obtained in 83.0% yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.89 (m, 4H), 7.67 (s, 1H), 7.10 (m, 9H), 7.06 (m, 4H), 7.03 (m, 6H), 6.65 (d, 1H), 5.50 (s, 2H), 4.81 (m, 1H), 3.80 (s, 3H), 2.30 (m, 1H), 1.02 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 172.8, 167.0, 147.1, 144.7, 143.6, 142.1, 140.2, 133.7, 132.2, 131.4, 128.0, 126.8, 126.0, 120.5, 57.5, 54.3, 52.4, 31.8, 19.1, 18.2. HRMS (MALDI-TOF), *m/z* 646.2945, (M$^+$, calcd 646.2944).
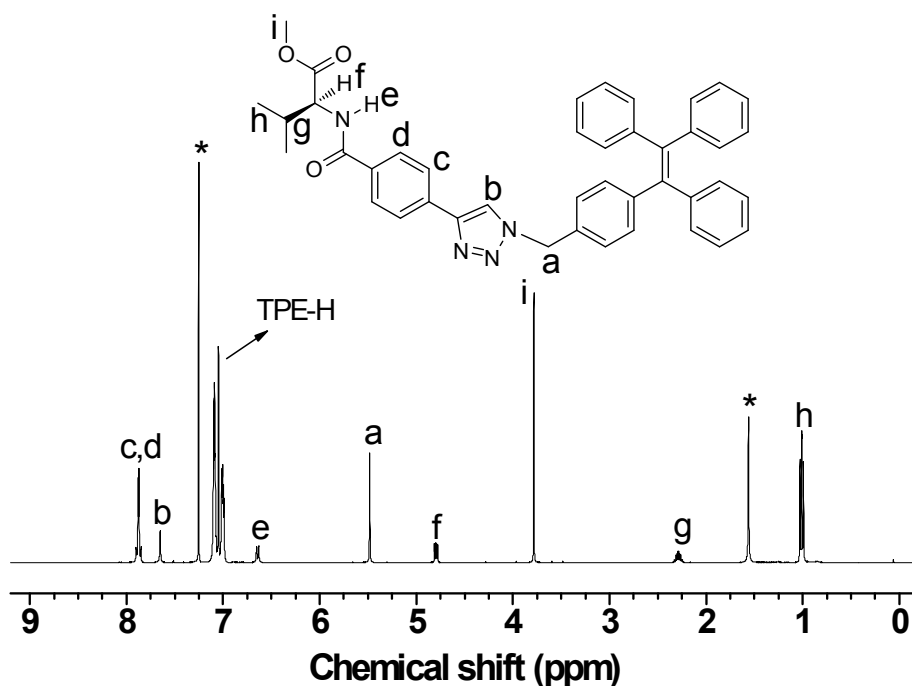

Fig. S1 ^{1}H NMR spectrum of Val-TPE in $CDCl_3$. The solvent and water peaks are marked with
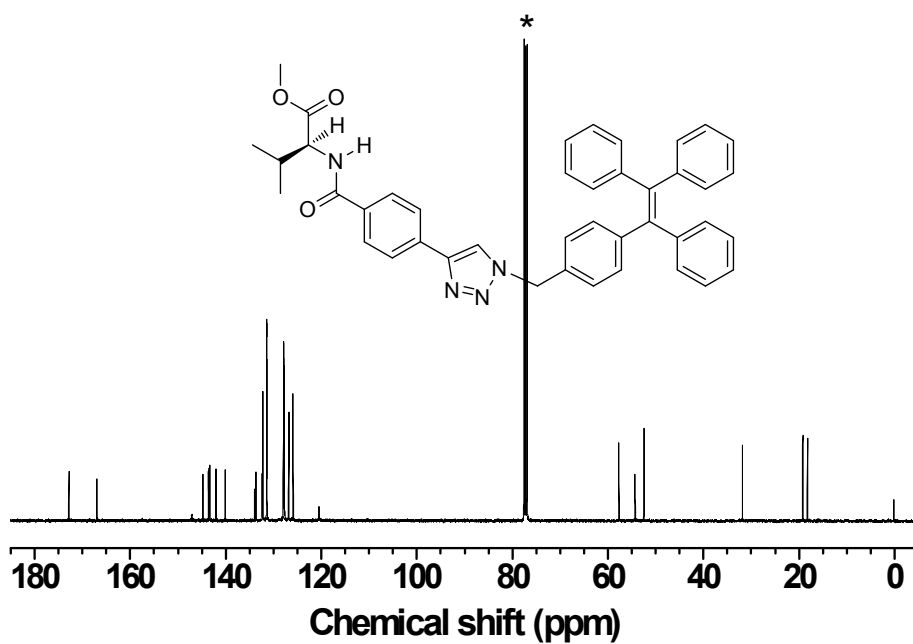
asterisks.

Fig. S2 ^{13}C NMR spectrum of Val-TPE in CDCl$_3$. The solvent peaks are marked with asterisk.
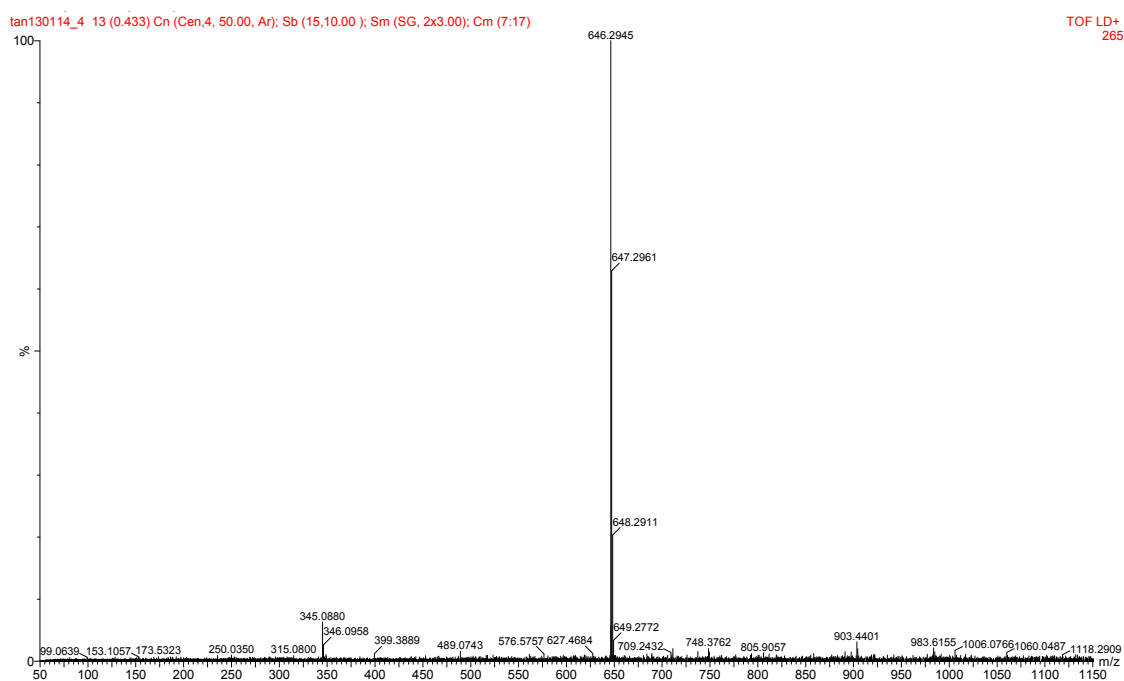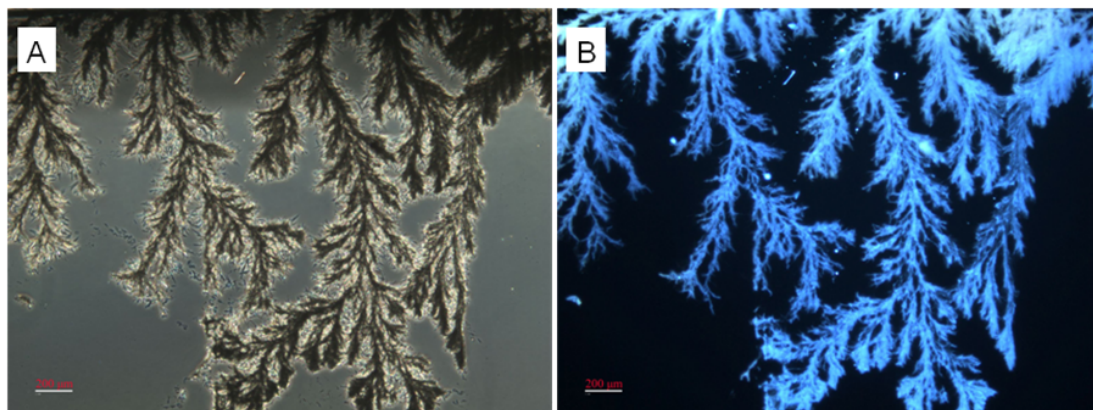

Fig. S3 HRMS spectrum of Val-TPE.

Fig. S4 Fluorescence microscope images under normal laboratory light (A) and UV excitation (B) of Val-TPE by evaporation of its DMF solution in microfluidic channels on quartz substrate.

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