Support information

A robust platform to construct molecular patchy particles with pentiptycene skeleton toward controlled mesoscale structures

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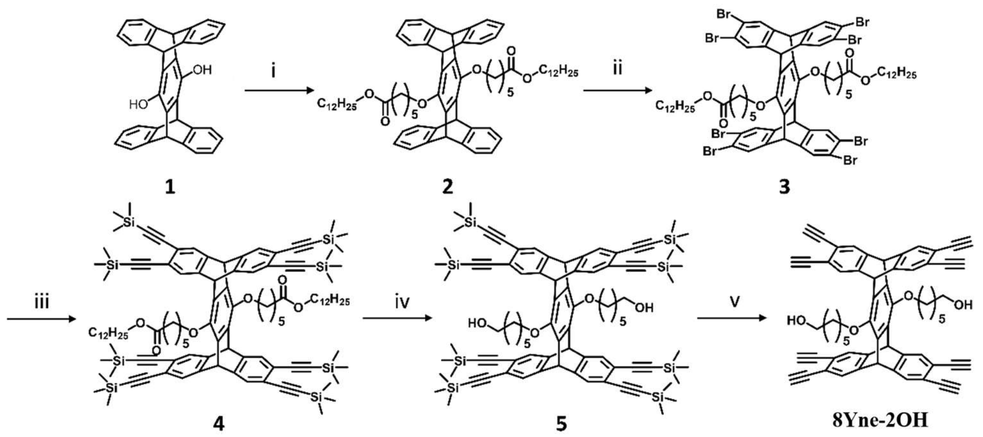
1. Synthesis section



Scheme S1. i) K_2CO_3, Acetone (85%); ii) Br_2, Fe, $CHCl_3$(60%); iii) $Pd(Ph_3P)_4$, CuI, THF, TEA (50%); iv) $LiAlH_4$, THF (80%); v) TBAF, THF (75%).

Experimental

Chemicals and solvents. Anthracene (99%, Adamas), p-benzoquinone (99%, Adamas), tetrachloro-1,4-benzoquinone (97%, Adamas), 6-bromohexanoic acid (99%, Adamas), 1-dodecanol (99%, Adamas), p-touenesulfonic acid monohydrate (99%, Adamas), bromine (99%, xxx), iron powder (98%, Adamas), ethynyltrimethylsilane (98%, Adamas), palladium (98%, Adamas), triphenylphosphine (99%, Adamas), hydrazinium hydroxide (80% in water, Adamas), lithium aluminum hydride (97%, Adamas), tetrabutylammonium fluoride (1 M in THF, containing ca. 5% water), N,N-dicyclohexylcarbodiimide (99%, Adamas), 4-pentynoic acid (98%, Adamas), tetrahydrofuran (THF, >99%, Greagent), 1H,1H,2H,2H-erfluoro-1-iodo-n-octane (97%, TCI), 3-hydroxymethyl-3-methyloxetane (98%, Sigma-Aldrich), methylene dichloride (DCM, 99.5%, Adamas)， petroleum ether (60-90 °C, Greagent), ethylacetate (EA, >99.5, Greagent), Silica gel (Adamas, 300 mesh) was activated by heating to 110 °C for 12 h. Pentiptycene-diol[1] was synthesized according to the literature.

Characterization.

All ^1H and ^{13}C spectra were achieved in $CDCl_3$ or $(CD_3)_2SO$ at 30 °C using a Varian 400 or 500 MHz spectrometer. The ^1H NMR spectra were referenced to the residual proton impurities in the $CDCl_3$ at δ 7.27ppm. The ^{13}C NMR spectra were referenced to $CDCl_3$ at δ 77.00 ppm.

Size Exclusion Chromatography (SEC). SEC analyses for the synthesized giant molecules were performed on a Waters instrument equipped with three gel columns and a triple detector system. THF was used as the eluent with a flow rate of 1.0 mL/min at 25 °C.

Matrix-asswasted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) Mass Spectroscopy. MALDI-TOF mass spectroscopy (MS) were acquired on an UltrafleXtreme MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) equipped with an Nd:YAG smart beam-II laser with 355-nm wavelength and 200 Hz firing rate. For high-resolution mass analyswas, the instrument was operated in the reflector mode.

Transmission electron microscope (TEM). Bright field images of the thin-slice samples were recorded on a JEM-1400 flash with an accelerating voltage of 120 kV on a digital CCD camera. Data processing was completed with the accessory digital imaging system.

Small-angle X-ray scattering (SAXS). SAXS experiments were performed on a Xenocs instrument (France) equipped with a two-dimensional (2D) multiwire area detector and a microfocus sealed copper tube. The working x-ray source is from MetalJet-D2 (Excillum) with the wavelength of 0.134 nm. The scattering vector (q) was calibrated using standard of silver behenate with the primary reflection peak at ($q = 1.067\ nm^{-1}$). The recording time for each sample was 15−30 s, depending on the scattering intensity. The data analysis was done with Igor software. Before testing by the small-angle X-ray scattering (SAXS) experiment, samples were annealed at 140 ℃ for 12 hours to induce phase separation.

Differential Scanning Calorimetry (DSC). Thermal properties of the samples were characterized utilizing TA Instruments DSC 2500. For each run of the experiments, the initial mass of the samples used was about 2-10 mg. The samples were weighed and sealed in aluminum pans, and heated to specific temperature with a heating rate of 5, 10 and 20 °C/min respectively.

FT-IR spectra were recorded on a Nicolet 6700 spectrometer. Samples were ground with KBr pellet under IR lamp and pressed into a wafer.

Preparation of 8Yne -2OH

8H -2C$_{12}$. To a 500-mL round bottom flask, molecule 1 (10.0 g, 21.6 mmol, 1.0 equiv.) and dodecyl 6-bromohexanoate (19.6 g, 53.8 mmol, 2.5 equiv.) were added with 250 mL acetone, potassium carbonate (11.9 g, 86.4 mmol, 4.0 equiv.) was added under nitrogen atmosphere, then the reaction was allowed to reflux for another 24h. After filtration of the salt, acetone was removed using rotatory evaporator then the crude product was purified with flash column with DCM:PE= 1:6 to 1:2 to give product as white solid 18.2 g. yield: 82%. ^1H NMR ($CDCl_3$, 400

MHz, ppm): 7.3 (m, 8H), 6.94 (m, 8H), 5.62 (s, 4H), 4.12 (t, 4H), 3.89 (t, 4H), 2.47 (t, 4H), 2.02 (m, 4H), 1.87 (m, 4H), 1.71 (m, 4H), 1.66 (m, 4H), 1.4-1.2 (m, 36H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$, 400 MHz, ppm): 173.75, 146.02, 145.30, 125.13, 123.53, 75.78, 64.65, 48.40, 34.40, 31.93, 30.29, 29.77, 29.65, 29.60, 29.55, 29.29, 28.72, 26.05, 25.98, 25.03, 22.70, 14.14.

8Br -2C$_{12}$. To 500-mL two neck round bottom flask, C_{12}-(H)P-C_{12} (10 g, 9.1 mmol, 1.0 equiv.) was dissolved in 300 mL chloroform, iron powder (100 mg, 1.8 mmol, 0.2 equiv.) was added as the catalyst, then Br_2 (8.3 mL, 156 mmol, 16 equiv.) was added slowly at room temperature, the reaction mixture was refluxed for another 10 h. After cooling to room temperature, the reaction solution was poured into ice water with extra care, then $NaSO_3$ was added slowly to remove excess bromine, the organic phase was collected and washed twice with water, then Na_2SO_4 was added to removed water. The organic phase was concentrated and then precipitated into methanol, the precipitate was collected with filtration and dried under vacuum condition to give product as pale-yellow powder 12.9 g. Yield: 80%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.57 (s, 8H), 5.53 (s, 4H), 4.15 (t, 4H), 3.86 (t, 4H), 2.50 (t, 4H), 2.01 (m, 4H), 1.90 (m, 4H), 1.71 (m, 4H), 1.66 (m, 4H), 1.4-1.2 (m, 36H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 173.63, 146.21, 144.88, 135.42, 128.82, 121.36, 76.10, 64.76, 34.16, 31.93, 30.23, 29.64, 28.74, 25.98, 24.81, 22.71, 14.15.

8TMSYne -2OH. To a 500-mL Schlenk bottle, C_{12}-(Br)Pentiptycene-C_{12} (10.0 g, 6.0 mmol, 1.0 equiv.) was dissolved in 150 mL THF and 150 mL TEA, ethynyltrimethylsilane (9.4 g, 96 mmol, 16 equiv.) was further added to the solution, CuI and $Pd(Ph_3P)_4$ was added under argon atmosphere as the catalysts. Then the solution was stirred at 80 °C for another 12 h. When the reaction finished, solvent was removed using the rotatory evaporator, the crude product was purified by flash column. The crude product was then reduced by $LiAlH_4$ in anhydrous THF at 0 °C. The reaction was monitored by the thin layer chromatography (TLC), after the fully reduction of the ester group, water (5.0 mL) was added slowly to quench the reaction. And further purified with flash column with DCM: PE= 1:1 to pure DCM to afford product as white solid 4.32 g. Yield: 50%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.35 (s, 8H), 5.48 (s, 4H), 3.85 (t, 4H), 3.76 (t, 4H), 1.95 (t, 4H), 1.70 (m, 8H), 1.6 (m, 4H) , 0.21 (m, 72H) ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 146.10, 144.27, 135.35, 127.38, 123.35, 103.49, 98.03, 77.36, 76.34, 63.01, 47.57, 32.84, 30.51, 26.26, 25.89, 0.17.

8Yne-2OH: To a 500 mL round bottom flask, HO-(TMSYne)Pentiptycene-OH (2.0 g, 1.4 mmol, 1.0 equiv.) was dissolved in 300 mL DCM, then TBAF (13.4 mmol, 13.4 mL, 9.4 equiv.) was added dropwise under nitrogen atmosphere, TLC was used to monitor the reaction process. Upon the fully deprotection of trimethylsilyl group, the crude product was purified by a flash column using EA and DCM as the eluent to give pure product as white solid 0.83 g. Yield: 70%. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz, ppm): 7.57 (s, 8H), 5.86 (s, 4H), 3.88 (t, 4H), 3.49 (t, 4H), 1.89 (t, 4H), 1.56 (m, 8H), 1.48 (m, 4H). ^{13}C NMR ($(CD_3)_2SO$, 500 MHz, ppm): 145.88, 144.75, 135.00, 127.51, 121.82, 84.17, 81.57, 76.11, 60.71, 46.00, 32.52, 32.84, 29.80, 25.55, 25.45. MS (MALDI-TOF, Da.), Calcd. for [M•Na$^+$]: 877.3; Found: 877.4.

General procedure for the copper catalyzed azide-alkyne cycloaddition (CuAAC) "click" reaction. All the "click" reactions were conducted in a glovebox under argon atmosphere. To a 20-mL vial HO-(Yne)Pentiptycene-OH (100 mg, 0.117 mmol, 1 equiv.) was added with a stir bar, then corresponding azido ligands (9.6 equiv. per molecule or 1.2 equiv. per alkyne group), then 10 mL THF was added as solvent, trifluoromethyl benzene was used for the synthesis of perfluoro-pentiptycene considering the solubility of the product. Then CuBr (2 mg, 0.014 mmol, 0.12 equiv.) and PMDETA (4.8 mg, 0.028 mmol, 0.24 equiv.) was added as the catalyst. The reaction solution was stirred for another 12 h. The crude products were purified using flash column with MeOH: DCM= 1: 30 to give pure product.

8pH-2OH. 5-(azidomethyl)-2,2,5-trimethyl-1,3-dioxane (207 mg, 1.122 mmol) and 10 mL THF were used. The product was collected as white solid (259 mg, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.75 (s, 8H), 7.27 (s, 8H), 5.85 (s, 4H), 4.45 (s, 16H), 4.04 (t, 4H), 3.66 (t, 4H), 3.62 (m, 16H), 3.38 (m, 16H), 2.02 (m, 4H), 1.66 (m, 8H), 1.41-1.38 (m, 48H), 0.74 (s, 24H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 146.43, 145.60, 136.17, 126.75, 125.84, 124.74, 98.78, 62.88, 53.89, 48.13, 35.09, 33.10, 30.10, 28.87, 26.12, 23.10, 19.42, 18.27.

8F-2OH. 6-azido-1,1,1,2,2,3,3,4,4-nonafluorohexane (324 mg, 1.122 mmol) and 10 mL trifluoromethyl benzene were used. The product was collected as white solid (340 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.74 (s, 8H), 7.29 (s, 8H), 5.87 (s, 4H), 4.56 (s, 16H), 4.04 (t, 4H), 3.65 (t, 4H), 2.82 (m, 16H), 2.03 (t, 4H), 1.68 (m, 8H), 1.56 (m, 4H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 146.39, 145.21, 126.07, 125.43, 123.10, 100.10, 62.38, 47.59, 41.99, 32.59, 31.10, 30.07, 25.557.

8BPOSS -2OH. BPOSS-N_3 (324 mg, 1.122 mmol) and 10 mL THF were used. The product was collected as white solid (340 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.72 (s, 8H), 7.30 (s, 8H), 5.84 (t, 8H), 5.80 (s, 4H), 4.28 (s, 16H), 4.04 (t, 4H), 3.64 (t, 4H), 3.21 (s, 16H), 2.48 (m, 16H) 2.16 (m, 16H), 1.85 (m, 56H), 1.59 (m, 48H), 1.59 (m, 4H), 0.96 (m, 336H), 0.59 (m, 112H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 171.73, 16.26, 145.01, 135.69, 126.42, 125.30, 122.53, 69.00, 64.75, 49.72, 47.58, 41.78, 35.31, 33.27, 30.44, 29.62, 28.50, 25.59, 23.73, 22.89, 22.30, 14.29, 9.39.

General procedure for the esterification. All the esterification reactions were conducted in the following steps, in a 100-mL round bottom flask, 8X-2OH was dissolved in DCM and catalytic amount of DMAP was added with 4.0 equiv. of TEA, then alkyne anhydrous anhydride was added dropwise which was freshly prepared by adding 1.2 equiv. of DCC into 2.4 equiv. 4-pentnoic acid. The crude products were purified with flash column with MeOH: DCM= 1: 30.

8pH -2Yne. The product was collected as white solid (yield: 90%)^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.76 (s, 8H), 7.26 (s, 8H), 5.81 (s, 4H), 4.45 (s, 16H), 4.15 (t, 4H), 3.98 (t, 4H), 3.59 (t, 4H), 3.34 (m, 16H), 2.56 (m, 8H), 2.02 (m, 4H), 1.66 (m, 8H), 1.41-1.38 (m, 48H), 0.75 (s, 24H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 171.75, 146.13, 145.82, 145.08, 135.68, 125.31, 124.26, 98.25, 82.59, 68.89, 66.59, 64.76, 53.42, 47.63, 34.58, 33.29, 30.81, 28.53, 25.97, 18.97, 17.76, 14.30. MS (MALDI-TOF, Da.), Calcd. for [M•Na^+]: 2518.3; Found: 2518.8.

8F-2Yne. The product was collected as white solid (yield: 92%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.74 (s, 8H), 7.29 (s, 8H), 5.87 (s, 4H), 4.56 (s, 16H), 4.04 (t, 4H), 3.65 (t, 4H), 2.82 (m, 16H), 2.03 (t, 4H), 1.68 (m, 8H), 1.56 (m, 4H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 171.78, 146.33, 145.10, 135.67, 126.13, 125.36, 123.02, 82.38, 68.78, 64.53, 47.58, 41.99, 31.26, 30.32, 28.37, 25.73. MS (MALDI-TOF, Da.), Calcd. for [M•Na^+]: 3349.6; Found: 3349.1.

8BPOSS -2Yne. The product was collected as white solid (340 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.72 (s, 8H), 7.26 (s, 8H), 5.81 (t, 8H), 5.79 (s, 4H), 4.28 (s, 16H), 4.11 (t, 4H), 3.96 (t, 4H), 3.19 (s, 16H), 2.57-2.48 (m, 16H) 2.17 (m, 16H), 1.84 (m, 56H), 1.73 (m, 48H), 1.59 (m, 4H), 0.96 (m, 336H), 0.59 (m, 112H).^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 171.73, 146.26, 145.01, 135.69, 126.42, 125.30, 122.53, 82.51, 69.00, 64.75, 49.72, 47.58, 41.78, 35.31, 33.27, 30.44, 29.62, 28.50, 25.59, 23.73, 22.89, 22.30, 14.29, 9.39. MS (MALDI-TOF, Da.), Calcd. for [M•Na$^+$]: 9035.93; Found: 9039.7.

General procedure for functionalized pentiptycene conjugated with polymer using CuAAC "click" reaction.

The "click" reactions were performed following the same procedure as depicted previously for the decoration of alkyne functionalized pentiptycene. Polystyrene (PS) end-capped with azido group was selected as the model polymer. The polystyrene end-capped with azido group was synthesized as reported[2]. The PS prepared by ATRP was narrowed by fractional precipitation several times to ensure the *Đ* < 1.1. The polymerization degree of the PS-N_3 is determined by ^{1}H NMR. The final product was purified by flash column.

8pH-2PS$_{28}$. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): 7.73 (m, 8H),7.45 (s, 2H), 7.26 (s, 8H), 7.30-6.28 (m, 282H), 5.80 (s, 4H), 5.05 (m, 2H), 4.46 (s, 16H), 4.09 (m, 4H), 3.96 (m, 4H), 3.59 (m, 16H), 3.36 (m, 16H), 2.63 (m, 8H), 2.15-1.29 (m, 168H), 1.43-1.33 (m, 48H), 0.94 (m, 12H), 0.61 (m, 24H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 177.87, 173.16, 146.61-145.52, 136.18, 129.18-124.70, 98.74, 77.62, 67.07, 66.99, 65.11, 60.30, 53.85, 48.09, 41.97, 40.72, 35.06, 31.01, 29.00, 28.86, 26.74, 26.47, 19.44, 18.26, 14.29. FT-IR (cm^{-1}): 3084, 3062, 3030, 2932, 2852, 2106, 1944, 1870, 1803, 1729, 1685, 1603, 1495, 1457, 1368, 1184, 1133, 1052, 1030, 908, 765, 706, 700. SEC (THF, RI detector): Mn = 8160 g·mol^{-1}, *Đ* = 1.02.

8F-2PS$_{28}$. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.72 (s, 8H), 7.32 (s, 8H), 7.30-6.28 (m, 282H), 5.80 (s, 4H), 5.04 (m, 2H), 4.55 (s, 16H), 4.02 (m, 4H), 3.95 (m, 4H), 3.60 (m, 4H), 2.78 (m, 16H), 2.82-2.45 (m, 8H), 2.15-1.29 (m, 184H), 0.90 (m, 18H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 177.31, 173.07, 146.34, 145.11, 135.68, 128.78, 123.08, 64.83, 59.75, 47.58-39.20, 31.22, 30.35, 29.33, 28.39, 13.78, 13.60. FT-IR (cm^{-1}): 3085, 3063, 3029, 3003, 2931, 2854, 1944, 1870, 1803, 1732 (C=O), 1603, 1495, 1455, 1359, 1240, 1137, 1029, 909, 760, 701. SEC (THF, RI detector): Mn = 7990 g·mol^{-1}, *Đ* = 1.01.

8BPOSS-2PS$_{28}$. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.67 (s, 8H), 7.55 (s, 8H), 7.30-6.28 (m, 282H), 5.80 (s, 4H), 5.17 (m, 2H), 4.32 (s, 16H), 4.02 (m, 4H), 3.95 (m, 4H), 3.65 (m, 4H), 3.21 (m, 4H), 2.82-2.45 (m, 8H), 2.15-1.29 (m, 168H), 1.88 (m, 64H), 0.96 (m, 384H), 0.90 (m, 12H), 0.6 (m, 128H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 171.73, 144.94, 128.67-122.49, 99.84, 64.56, 59.79, 49.67, 47.57, 41.78, 40.37, 35.28, 31.39, 29.61, 25.59, 23.73, 22.89, 22.30, 13.82, 9.40. FT-IR (cm^{-1}): 3442, 3370, 3083, 3061, 3028, 3002, 2955, 2927, 1943, 1869, 1802, 1732 (C=O), 1679, 1602, 1494, 1454, 1366, 1332, 1230, 1131, 1030, 907, 757, 700, 540, 485. SEC (THF, RI detector): Mn = 9600 g·mol^{-1}, *Đ* = 1.01.

8F-2PS$_{17}$. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): 7.73 (s, 8H), 7.32 (s, 8H), 7.30-6.28 (m, 172H), 5.80 (s, 4H), 5.05 (m, 2H), 4.55 (s, 16H), 4.01 (m, 4H), 3.95 (m, 4H), 3.59 (m, 4H), 2.78 (m, 16H), 2.82-2.45 (m, 8H), 2.15-1.29 (m, 118H), 0.90 (m, 18H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 177.31, 173.09, 146.34, 145.11, 135.69, 128.78, 123.08, 64.89, 59.75, 47.58-39.20, 31.22, 30.35, 29.33, 28.39, 13.73, 13.60. FT-IR (cm^{-1}): 3085, 3063, 3029, 3003, 2931, 2854, 1945, 1870, 1803, 1732 (C=O), 1603, 1495, 1455, 1359, 1240, 1137, 1029, 909, 760, 700. SEC (THF, RI detector): Mn = 5460 g.mol^{-1}, *Đ* = 1.01.

8F-2PS$_{75}$. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.74 (s, 8H), 7.32 (s, 8H), 7.30-6.28 (m, 752H), 5.80 (s, 4H), 5.04 (m, 2H), 4.55 (s, 16H), 4.03 (m, 4H), 3.95 (m, 4H), 3.60 (m, 4H), 2.78 (m, 16H), 2.82-2.45 (m, 8H), 2.15-1.29 (m, 466H), 0.91 (m, 18H). ^{13}C NMR (CDCl$_3$, 500 MHz, ppm): 177.39, 173.07, 146.34, 145.11, 135.68, 128.80, 123.08, 64.83, 59.75, 47.58-39.20, 31.22, 30.35, 29.33, 28.42, 13.78, 13.60. FT-IR (cm^{-1}): 3084, 3063, 3029, 3003, 2930, 2854, 1944, 1870, 1802, 1734 (C=O), 1603, 1496, 1455, 1359, 1239, 1136, 1030, 909, 760, 699. SEC (THF, RI detector): Mn = 18200 g.mol^{-1}, *Đ* = 1.01.

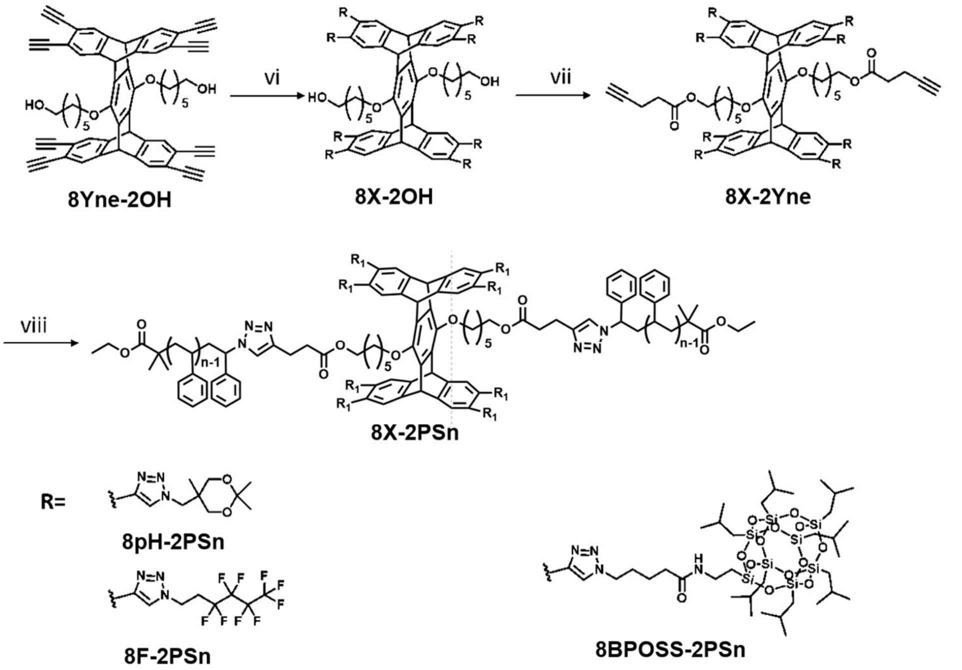
8F-2PS$_{63}$. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.71 (s, 8H), 7.32 (s, 8H), 7.30-6.28 (m, 632H), 5.80 (s, 4H), 5.04 (m, 2H), 4.55 (s, 16H), 4.02 (m, 4H), 3.94 (m, 4H), 3.60 (m, 4H), 2.78 (m, 16H), 2.82-2.45 (m, 8H), 2.15-1.29 (m, 394H), 0.89 (m, 18H). ^{13}C NMR (CDCl$_3$, 500 MHz, ppm): 177.35, 173.07, 146.34, 145.11, 135.68, 128.75, 123.08, 64.83, 59.75, 47.58-39.20, 31.22, 30.35, 29.35, 28.39, 13.78, 13.60. FT-IR (cm^{-1}): 3084, 3063, 3029, 3003, 2929, 2854, 1944, 1870, 1802, 1734 (C=O), 1603, 1495, 1455, 1359, 1239, 1136, 1030, 909, 760, 700. SEC (THF, RI detector): Mn = 16100 g.mol^{-1}, *Đ* = 1.01.

8F-2PS$_{40}$. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.72 (s, 8H), 7.30 (s, 8H), 7.30-6.28 (m, 402H), 5.80 (s, 4H), 5.04 (m, 2H), 4.53 (s, 16H), 4.02 (m, 4H), 3.95 (m, 4H), 3.60 (m, 4H), 2.79 (m, 16H), 2.82-2.45 (m, 8H), 2.15-1.29 (m, 256H), 0.90 (m, 18H). ^{13}C NMR (CDCl$_3$, 500 MHz, ppm): 177.31, 173.07, 146.32, 145.11, 135.68, 128.78, 123.08, 64.83, 59.77, 47.58-39.20, 31.22, 30.35, 29.33, 28.37, 13.78, 13.60. FT-IR (cm^{-1}): 3085, 3062, 3028, 3001, 2929, 2853, 1946, 1873, 1804, 1728 (C=O), 1602, 1496, 1454, 1358, 1238, 1136, 1029, 909, 758, 701. SEC (THF, RI detector): Mn = 11100 g.mol^{-1}, *Đ* = 1.01.

8F-2PS$_{37}$. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.72 (s, 8H), 7.32 (s, 8H), 7.30-6.28 (m, 372H), 5.83 (s, 4H), 5.04 (m, 2H), 4.55 (s, 16H), 4.02 (m, 4H), 3.99 (m, 4H), 3.60 (m, 4H), 2.78 (m, 16H), 2.82-2.45 (m, 8H), 2.15-1.29 (m, 238H), 0.88 (m, 18H). ^{13}C NMR (CDCl$_3$, 500 MHz, ppm): 177.33, 173.07, 146.34, 145.11, 135.68, 128.78, 123.10, 64.83, 59.75, 47.58-39.20, 31.22, 30.35, 29.33, 28.42, 13.78, 13.60.). FT-IR (cm^{-1}): 3083, 3062, 3029, 3002, 2929, 2852, 1945, 1873, 1805, 1729 (C=O), 1602, 1494, 1454, 1358, 1240, 1136, 1029, 908, 758, 700. SEC (THF, RI detector): Mn = 9600 g.mol^{-1}, *Đ* = 1.01.

8F-2PS$_{31}$. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.72 (s, 8H), 7.32 (s, 8H), 7.30-6.28 (m, 311H), 5.83 (s, 4H), 5.04 (m, 2H), 4.55 (s, 16H), 4.02 (m, 4H), 3.99 (m, 4H), 3.60 (m, 4H), 2.78 (m, 16H), 2.82-2.45 (m, 8H), 2.15-1.29 (m, 201H), 0.88 (m, 18H). ^{13}C NMR (CDCl$_3$, 500 MHz, ppm): 177.33, 173.07, 146.34, 145.11, 135.68, 128.78, 123.10, 64.83, 59.75, 47.58-39.20, 31.22, 30.35, 29.33, 28.42, 13.78, 13.60.). FT-IR (cm^{-1}): 3085, 3062, 3028, 3001, 2929, 2853, 1945, 1873, 1806, 1728 (C=O), 1602, 1495, 1454, 1358, 1241, 1136, 1029, 908, 758, 701. SEC (THF, RI detector): Mn = 8500 g.mol^{-1}, *Đ* = 1.01.

8F-2PS$_{22}$. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): 7.74 (s, 8H), 7.32 (s, 8H), 7.30-6.28 (m, 222H), 5.80 (s, 4H), 5.05 (m, 2H), 4.55 (s, 16H), 4.02 (m, 4H), 3.96 (m, 4H), 3.60 (m, 4H), 2.81 (m, 16H), 2.82-2.45 (m, 8H), 2.15-1.29 (m, 148H), 0.90 (m, 18H). ^{13}C NMR ($CDCl_3$, 500 MHz, ppm): 177.31, 173.07, 146.34, 145.14, 135.68, 128.78, 123.08, 64.83, 59.76, 47.58-39.20, 31.22, 30.35, 29.35, 28.39, 13.78, 13.60. FT-IR (cm^{-1}): 3084, 3062, 3028, 3002, 2929, 2853, 1945, 1873, 1805, 1728 (C=O), 1602, 1495, 1454, 1358, 1239, 1136, 1029, 908, 758, 701. SEC (THF, RI detector): Mn = 6800 g·mol^{-1}, $Đ$ = 1.01.



Scheme S2. vi) CuBr, PMDETA, THF (95%); vii) DMAP, TEA (90%); viii) CuBr, PMDETA, PS-N_3 (85%); ix) TFA, CH_2Cl_2 (90%).

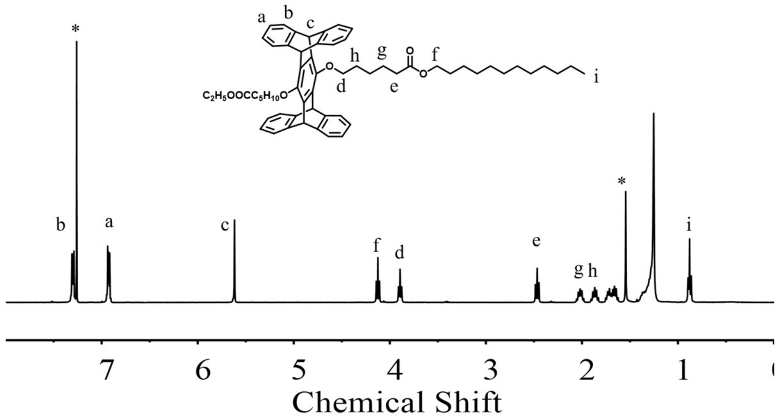


Figure S1. ^{1}H NMR of Molecule 8H-2C_{12}.

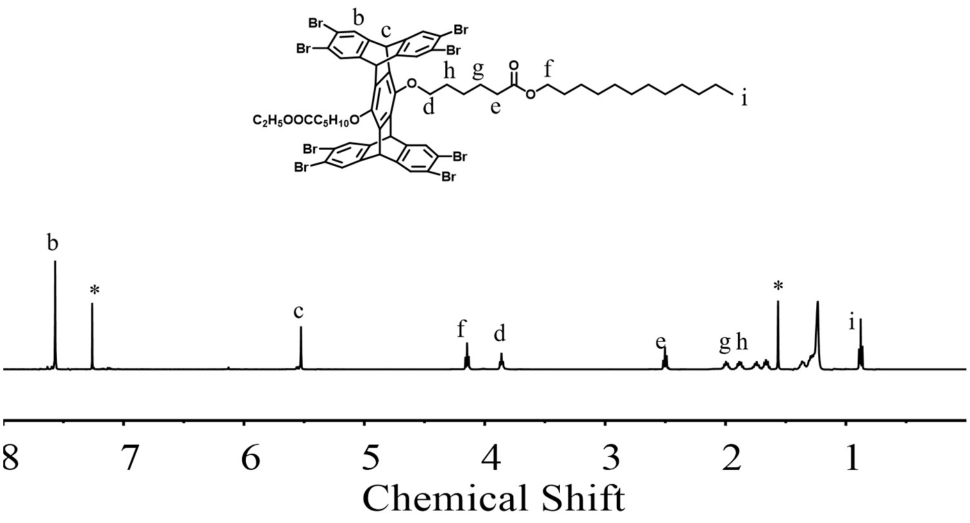


Figure S2. ^{1}H NMR of Molecule 8Br-2C_{12}.

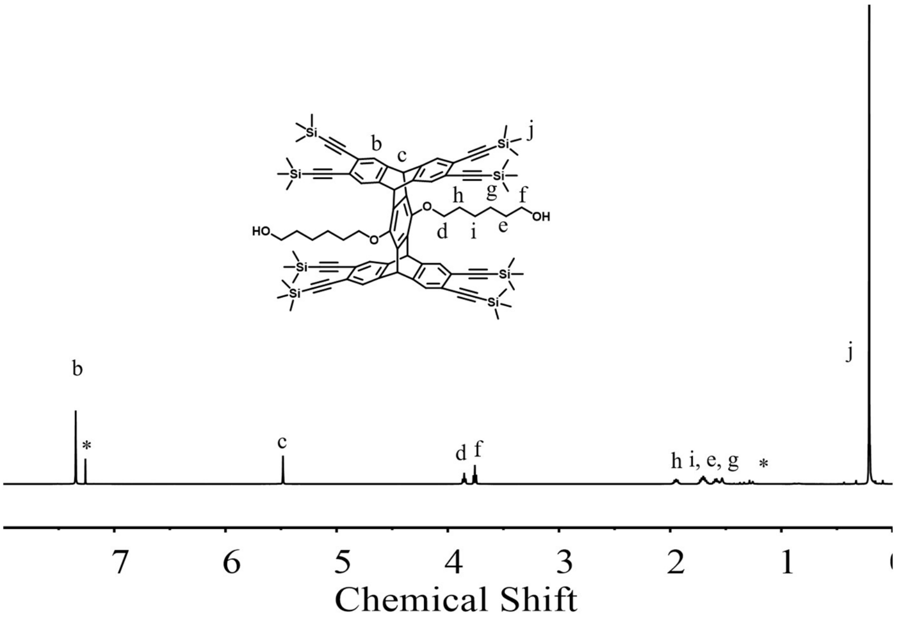


Figure S3. ^{1}H NMR of Molecule 8TMS-2C_{12}.

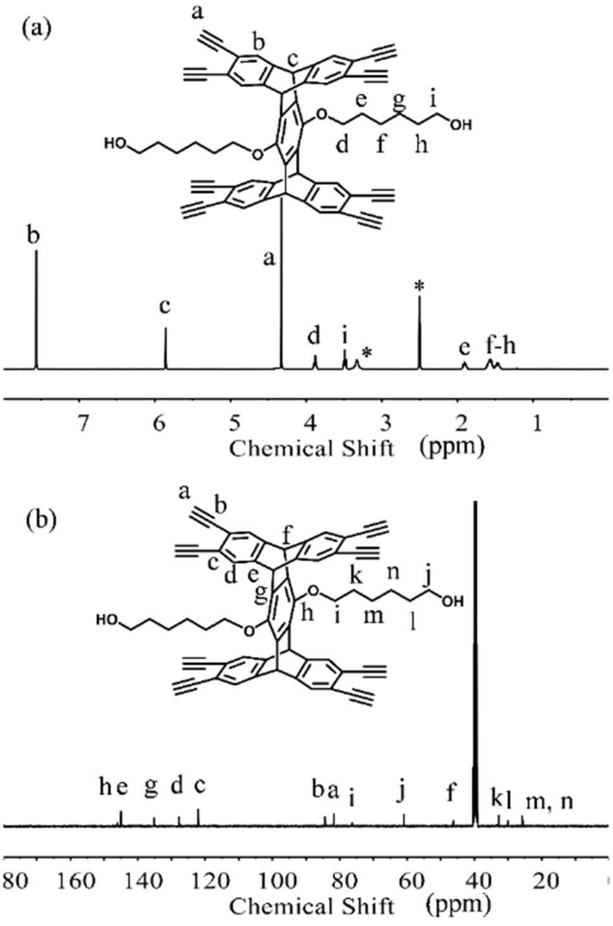


Figure S4. (a)^{1}H and (b)^{13}C NMR spectra of 8Yne-2OH.

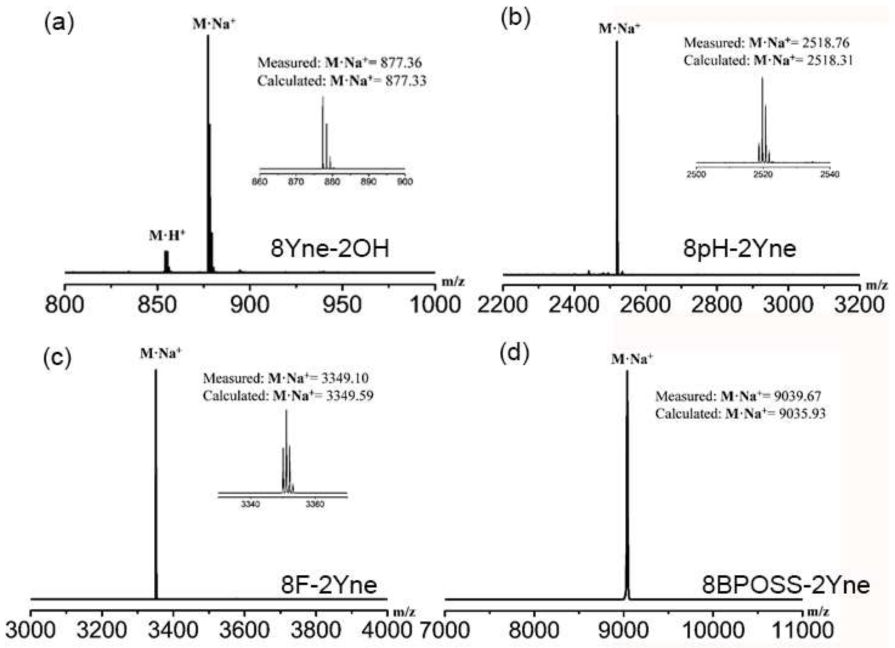


Figure S5. MALDI-TOF spectra of (a) 8Yne-2OH, (b) 8pH-2Yne, (c) 8F-2Yne and (d)

8BPOSS-2Yne.

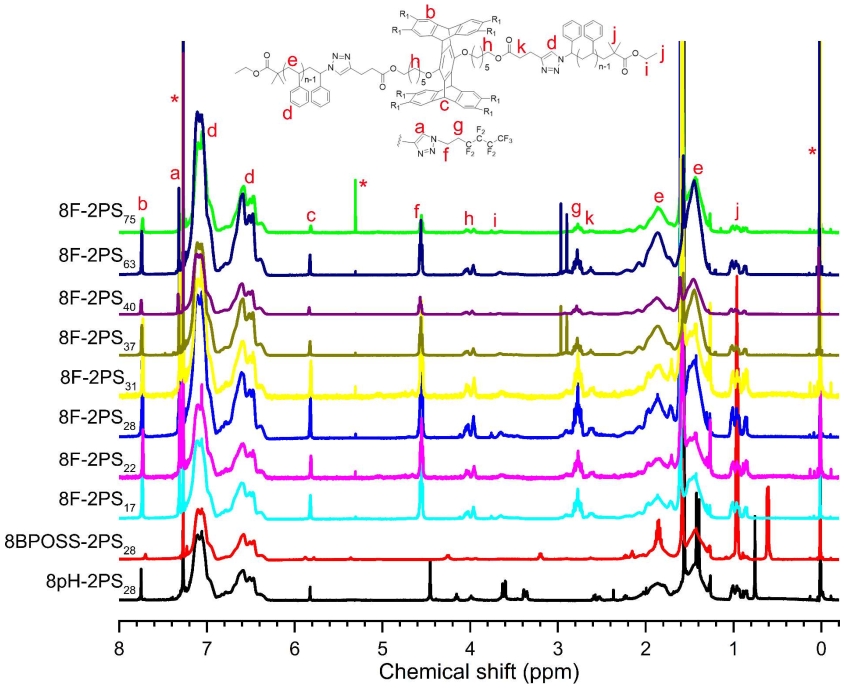


Figure S6. ^{1}H NMR spectra of the molecular patchy particles.

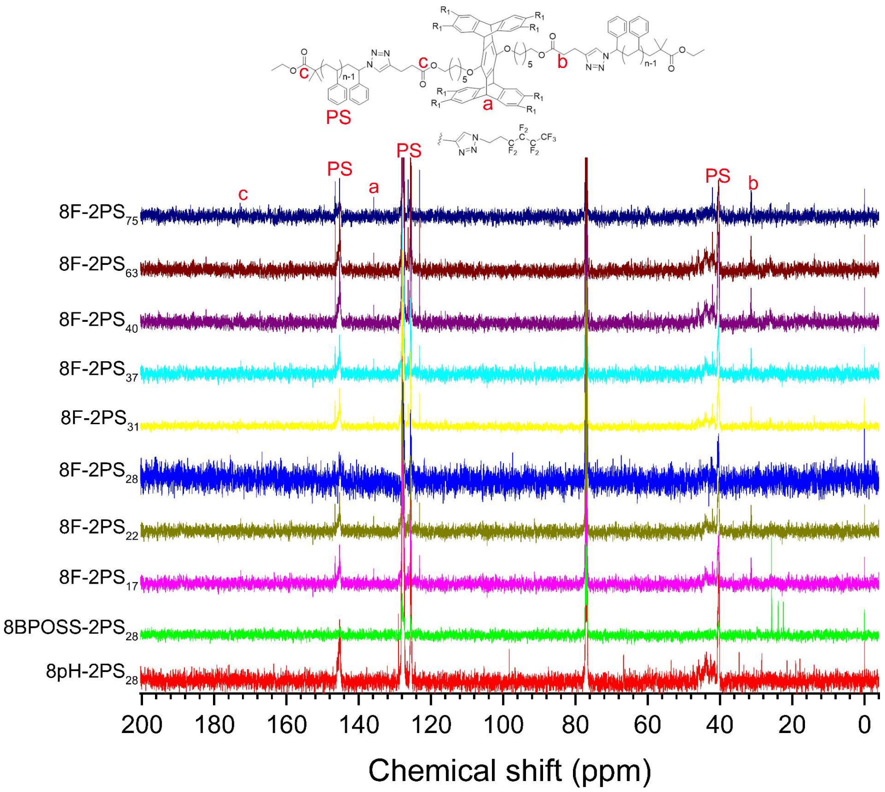


Figure S7. ^{13}C NMR spectra of the molecular patchy particles.

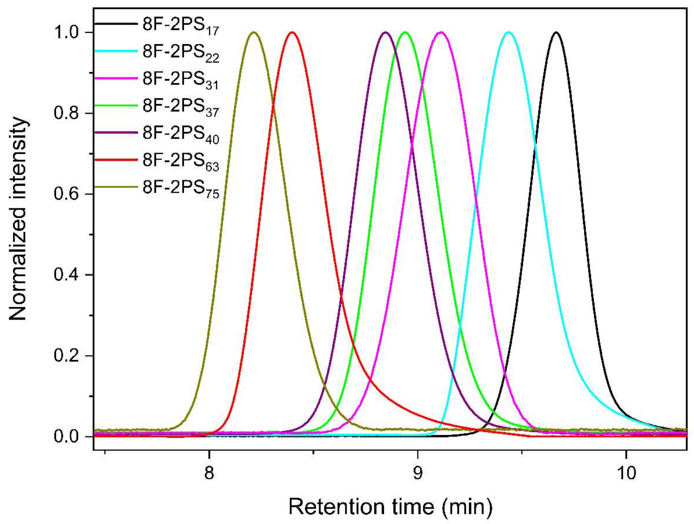


Figure S8. GPC traces of the molecular patchy particles.

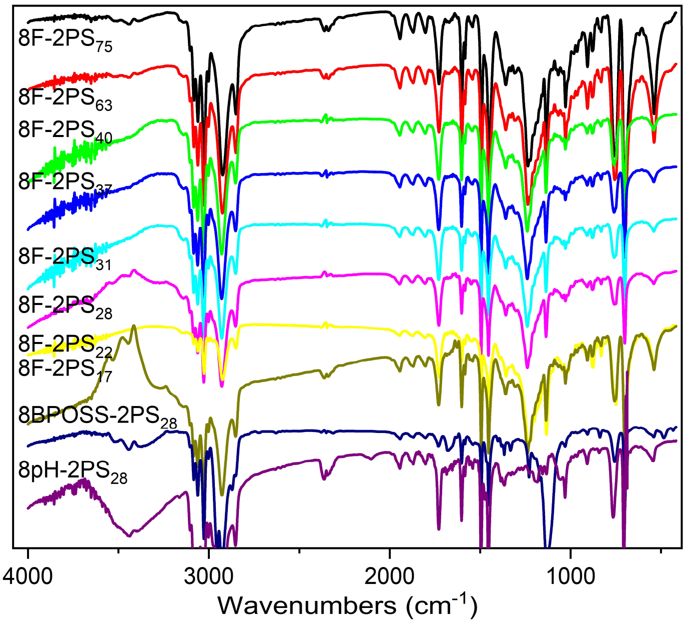


Figure S9. Infrared spectra of the molecular patchy particles.

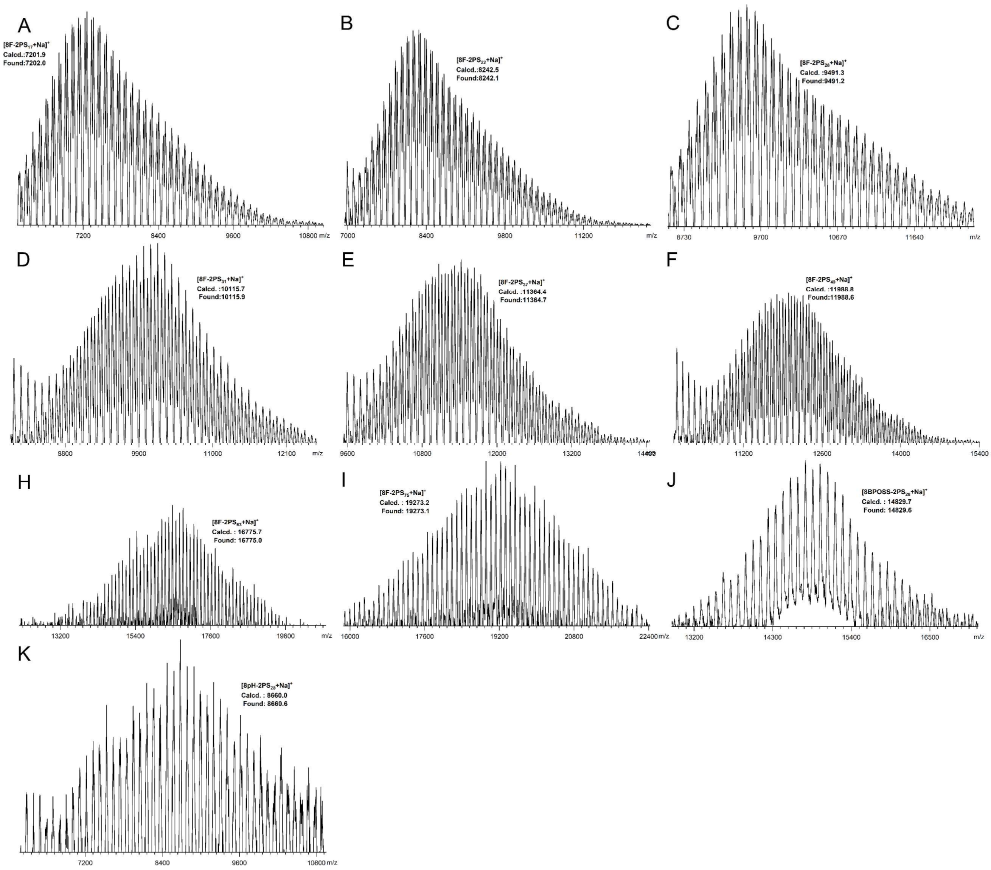


Figure S10. MALDI-TOF-MS spectra of the molecular patchy particles.

2. Structure analysis

Calculation of volume fraction

The volume fractions of PS could be calculated based on the molecular weight and density,

$f_{ps} = \dfrac{\frac{M_{PS}}{\rho_{PS}}}{(\frac{M_{PS}}{\rho_{PS}}+\frac{M_{MNP}}{\rho_{MNP}})}$ where the density of polystyrene is 1.052 g/cm^3, the density of pentiptycene functionalized with fluoride groups is 1.057 g/cm^3, and the molecular weight of fluoride pentiptycene here is 3.3k Da..

For HEX phase, the average number of molecules (μ) in one pentiptycene thickness can be calculated by: $\mu = \frac{\rho V N_A}{M} = \frac{2\rho {d_1}^2 h N_A}{\sqrt{3} M}$. Here the thickness of one fluorinated pentiptycene h is set as 1.2 nm. The fan-angle α can therefore be obtained from $\alpha = 2\pi/\mu$.

For HEX structure, the distance of the centroids of column is equal to $\frac{2d_1}{\sqrt{3}}$.

For BCC phase, the average number of molecules (μ) in each unit cell can be calculated by:

$$\mu = \frac{\rho a^3 N_A}{M_W n}$$

in which a, b and c are the unit cell dimension, n is number of motifs in one unit cell. For BCC, $a = b = c$ and $n = 2$.

Therefore, the solid angle of the cone-shape molecules $\Omega = 4\pi/\mu$.

The corresponding cone angle α can be calculated from the equation:

$$\alpha = 2\arccos(1 - \frac{\Omega}{2\pi}).$$

Table S1 Summary of molecular phases and parameters

Sample	Struture	μ	Angle
8F-2PS$_{31}$	HEX	5	72°
8F-2PS$_{37}$	HEX	5	72°
8F-2PS$_{40}$	HEX	5	72°
8F-2PS$_{63}$	HEX	5	72°
8F-2PS$_{75}$	BCC	33	40°

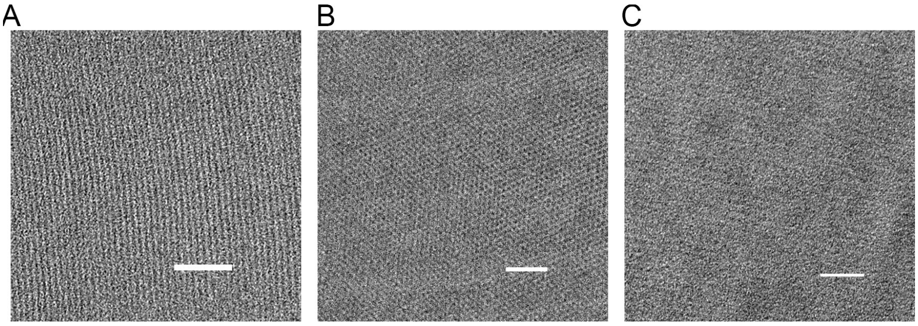


Figure S11. Bright-field TEM images of (A) 8F-2PS$_{17}$, (B) 8F-2PS$_{31}$ and (C) 8F-2PS$_{75}$. Scale bar: 50 nm.

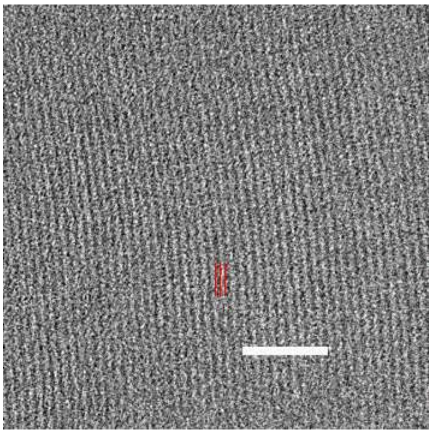


Figure S12. Bright-field TEM image of 8F-2PS$_{17}$. Scale bar: 50 nm. The d_0 is the d-spacing of the lamella structure which could also be calculated from SAXS data of 8F-2PS$_{17}$. d_1

here is the thickness of the black domain for fluoride pentiptycene, which is calculated as 2.64 nm. d_2 is the thickness of the grey domain for polystyrene. $d_0 = d_1 + d_2$. The red lines denote the boundaries of different phases.

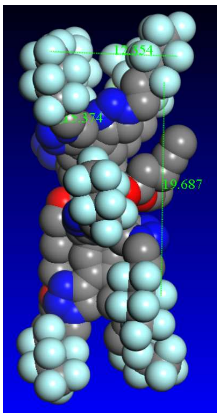


Figure S13. The molecular model of 8F-2Yne after geometry optimization of forcite calculation.

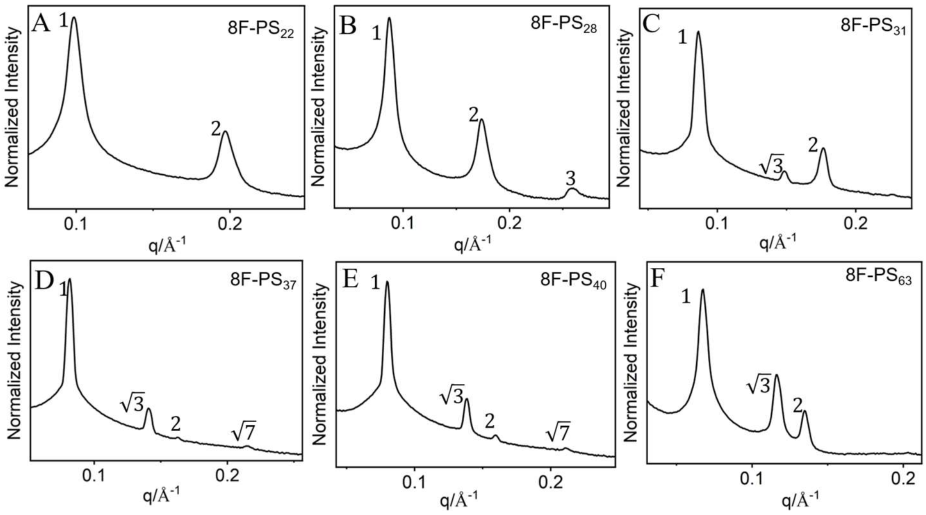


Figure S14. 1D SAXS of (A) 8F-2PS$_{22}$, (B) 8F-2PS$_{28}$, (C) 8F-2PS$_{31}$, (D) 8F-2PS$_{37}$, (E) 8F-2PS$_{40}$ and (F) 8F-2PS$_{63}$.

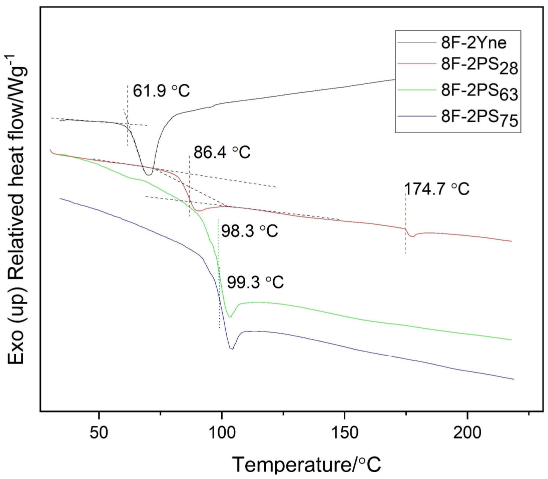


Figure S15. The DSC thermograms (heating process) of 8F-2Yne, 8F-2PS$_{28}$, 8F-2PS$_{63}$ and 8F-2PS$_{75}$.

1. Zhu, X.-Z.; Chen, C.-F., Iptycene Quinones: Synthesis and Structure. *The Journal of Organic Chemistry* **2005,** *70* (3), 917-924.
2. Ni, B.; Dong, X.-H.; Chen, Z.; Lin, Z.; Li, Y.; Huang, M.; Fu, Q.; Cheng, S. Z. D.; Zhang, W.-B., “Clicking” fluorinated polyhedral oligomeric silsesquioxane onto polymers: a modular approach toward shape amphiphiles with fluorous molecular clusters. *Polymer Chemistry* **2014,** *5* (11), 3588-3597.