Supporting Information

Impact of Cyclic Topology: Odd-Even Glass Transition Temperatures and Fluorescence Quantum Yields in Molecularly-Defined Macrocycles

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Materials.

Zinc dust (99.99% metals basis, 600 mesh, Aladdin), 4-hydroxylbenzophenone (98%, Energy Chemical), titanium tetrachloride ($TiCl_4$, AR, Enox), 2-bromoethanol (≥96%, Adamas), diethyl azodicarboxylate (DEAD, > 98%, Energy Chemical), sodium azide (≥99.5%, Aldrich), 3-bromo-1-(triisopropylsilyl)-1-propyne and tetrabutylammonium fluoride (TBAF, 1.0 mol. L^{-1} in tetrahydrofuran (THF), Energy Chemical) were used as received. Copper (I) bromide (CuBr, chemical pure) was purified by washing with acetic acid, water and ethanol, and dried in vacuum. *N, N, N', N", N"*-Pentamethyldiethylenetriamine (PMDETA, 98%, J&K) was dried with 4 Å molecular sieves and then distilled under vacuum. Tetrahydrofuran (THF, AR) was refluxed with sodium and a little bit of benzophenone and distilled prior to use. Unless otherwise noted, the chemicals were all purchased from Shanghai Chemical Reagent Co. Ltd., Shanghai, China and used without purification.

Instruments and Characterization

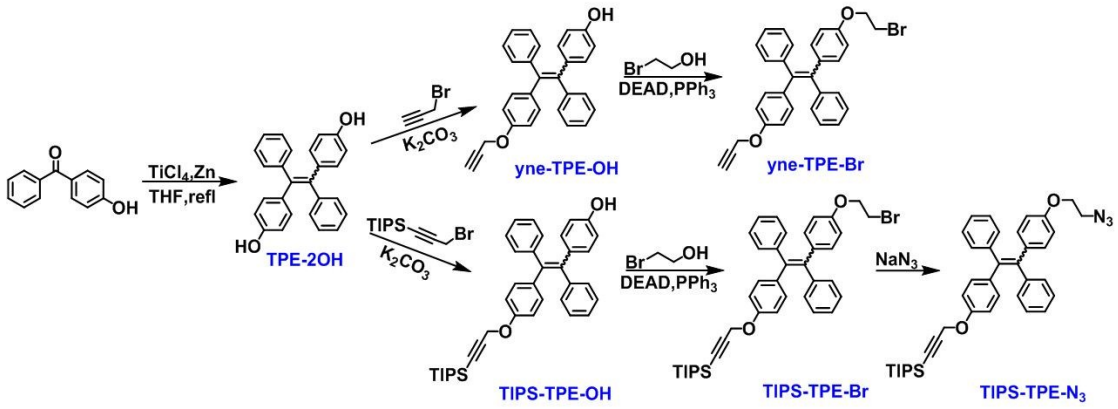
Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as the solvent, and tetramethylsilane (TMS) as the internal standard. The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the obtained oligomers were determined using a TOSOH HLC-8320 gel permeation chromatograph (GPC) equipped with refractive-index and UV detectors, using two TSKgel Super Mutipore HZ-N (3 μm beads size) columns arranged in series with a molecular weight range of 500-190,000 Daltons, calibrated with narrow-distributed polystyrene standard samples. THF was utilized as the eluent at a flow rate of 0.35 mL min^{-1} operated at 40 °C. An Agilent PL-50 preparative GPC system equipped with a manual injector was used to purify the crude oligomers. The eluent was THF at a flow rate of 3 mL min^{-1}. Separations were obtained using a PLgel 10 μm MIXED-D, 300 × 25 mm preparative GPC column maintained at 40 °C. Each composition was determined by the TOSOH HLC-8320 GPC column as described above. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker TENSOR-27 FT-IR spectrometer using the KBr disc technique. The UltrafleXtreme MALDI-TOF mass spectrometer equipped with a 1 kHz smart beam-II laser was employed to obtain the mass spectroscopy. The instrument was previously calibrated with specific molecular weight PMMA. *Trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (matrix, DCTB, Aldrich, >98%) was dissolved at a concentration of 20 mg mL^{-1} in $CHCl_3$. The sample concentration was 10 mg mL^{-1} in $CHCl_3$. The sodium trifluoroacetate prepared in ethanol at a concentration of 10 mg/mL was used as cationizing agent. All samples were dissolved in THF at a concentration of about 10 mg/mL. All of the spectra were measured in positive reflection mode. The fluorescence emission spectra in the aggregate state were obtained on a HITACHI F-4600 fluorescence spectrophotometer at room temperature. Differential scanning calorimetry (DSC) was performed using a TA instrument DSC2010 under the protection of nitrogen with a heating/cooling rate of 10 ^oC min^{-1}. The DSC2010

instrument was calibrated by pure indium for temperature and enthalpy changes. The obtained dried samples (4-5 mg) were directly crimped into standard aluminum pans. The data of second traces were taken and the glass transition temperature (T_g) was taken at the midpoint of the heat capacity jump. Modulated differential scanning calorimetry（MDSC） was performed using a TA Instruments DSC Q200. Each sample was kept at 200 °C for 10 min, and then cooled at 10°C/min to 30°C. After that, it was measured with modulation temperature amplitude of 0.21°C and modulation period of 40 s and ramped at 2 °C/min to 200 °C. The dried samples of 3-5 mg were put into sealed aluminum pans. All the tests were taken under a dry nitrogen purge. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer Pyris 1 instruments with a heating rate of 10 °C /min from the 40 °C to 800 °C under the nitrogen atmosphere. WAXD was measured with a X'Pert-Pro MPD device using Cu K_α-radiation. Samples were prepared in powder on standard single-crystal Si supports. The X-ray intensity was measured in the range from 2θ=5° to 90°. ^{13}C CPMAS spectra was recorded on a Bruker AVANCE III HD 500 MHz superconducting high-resolution nuclear magnetic resonance spectrometer. The fluorescence spectra of sample in solid powder was obtained on a HITACHI F-4600 fluorescence spectrophotometer and Orient KOJI QY-2000 integrating sphere fluorescence spectrometer.

Synthesis

Synthesis of α-alkyne-ω-bromine unimer yne-TPE-Br and TIPS-protected α-alkyne-ω-azide unimer TIPS-TPE-N_3.

The synthetic routes of α-alkyne-ω-bromine unimer yne-TPE-Br and TIPS-protected α-alkyne-ω-azide unimer TIPS-TPE-N_3 were outlined in Scheme S1, and detailed synthetic process was as follows.



Scheme S1. Synthesis routes of α-alkyne-ω-bromine unimer yne-TPE-Br and TIPS-protected α-alkyne-ω-azide unimer TIPS-TPE-N_3.

(a) Synthesis of 1, 2-bis (4-hydroxyphenyl)-1, 2-diphenylethene (TPE-2OH).

The TPE-2OH was synthesized according to McMurry coupling reaction described in the literature.[S1] The purified product was light yellow solid. Yield: 92.8 %.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.16-6.95 (m, 10H, Ar H), 6.83-6.64 (m, 4H, Ar H), 6.65-6.50 (m, 4H, Ar H), 4.54-4.78 (d, 2H, -OH).

(b) Synthesis of yne-TPE-OH and TIPS-TPE-OH.

Into a 500 mL three-necked round-bottom flask was added a mixture of TPE-2OH (26.00 g, 71.42 mmol) and anhydrous K_2CO_3 (11.0 g, 79.72 mmol) in 300 mL acetone. 3-bromo-1-propyne (6.34 g, 52.36 mmol) dissolved in 25 mL acetone was then added into the flask dropwise within 0.5 h under reflux. After reacting another 1 hour, the reacting mixture was cooled to room temperature and filtered. After concentrated in vacuo, the residue was purified with silica gel column chromatography using petroleum ether: ethyl acetate (10:1 by volume) as eluent to give the desired product: light yellow solid. Yield: 48.4 %.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.18-6.47 (m, 18H, Ar H), 4.74-4.46 (m, 3H, -OCH_2- and -OH), 2.55-2.44 (s, 1H, -C≡CH).

TIPS-TPE-OH was obtained from TPE-2OH and 1-bromo-3-(triisopropylsilyl)-2-propyne using the same procedure as yne-TPE-OH. The purified product was light yellow solid. Yield: 58.7%. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.14-6.48 (m, 18H, Ar H), 4.70-4.60 (m, 3H, -CH_2- and -OH), 1.10-0.94 (d, 21H, -Si (CH $(CH_3)_2)_3$).

(c) Synthesis of yne-TPE-Br and TIPS-TPE-Br.

Into a 250 mL round-bottom flask were placed yne-TPE-OH (8.52 g, 21.14 mmol) and triphenylphosphine (16.53 g, 63.03 mmol) in 100 mL tetrahydrofuran. A mixture of 2-bromoethanol (10.65 g, 84.53 mmol) and diethyl azodicarboxylate (11.08 g, 63.03 mmol) was added into the flask dropwise within 1 h at 20 °C. Refluxing for 24 h and then evaporating the solvent, the residue was poured into 80 mL water and the mixture was extracted with 200 mL dichloromethane three times followed by washing by brine twice. Drying over anhydrous sodium sulfate for 4h, the crude product was then purified with silica gel column chromatography using petroleum ether: ethyl acetate (20:1 by volume) as eluent to give the desired product as light green viscous liquid. Yield: 81.3 %.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.21-6.47 (m, 18H, Ar H), 4.77-4.51 (q, 2H, -OC$\underline{H_2}$-C≡CH), 4.34-4.06(q, 2H, -CH_2Br), 3.74-3.41(q, 2H, -OC$\underline{H_2}CH_2$Br), 2.58-2.44 (s, 1H, -C≡CH).

TIPS-TPE-Br was generated from TIPS-TPE-OH using the same procedure as yne-TPE-Br. The purified product was light green viscous liquid. Yield: 76.4%. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.18-6.63 (m, 18H, Ar H), 4.70-4.62 (q, 2H, -OC$\underline{H_2}$-C≡C-), 4.28-4.16 (q, 2H, -CH_2Br), 3.65-3.57(q, 2H, -OC$\underline{H_2}CH_2$Br), 1.12-0.94 (d, 21H, -Si (CH $(CH_3)_2)_3$).

(d) Synthesis of TIPS-TPE-N_3.

TIPS-TPE-Br (10.70 g, 16.00 mmol) in 30 mL DMF was placed into a 50 mL round-bottom flask. Then sodium azide (1.3 g, 20.0 mmol) was added at 25 °C. After stirring overnight, 40 mL water was added and the mixture

was extracted by 200 mL dichloromethane three times. The organic solution was washed by brine twice and then dried over anhydrous sodium sulfate for 4 h. Upon removing the organic solvent, light green viscous liquid was obtained. Yield: 97 %.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.18-6.63 (m, 18H, Ar H), 4.72-4.63 (q, 2H, -OC$\underline{H_2}$-C≡C-), 4.13-4.03(q, 2H, -CH_2N_3), 3.63-3.51(q, 2H, -OC$\underline{H_2}CH_2N_3$), 1.12-0.94 (d, 21H, -Si (CH $(CH_3)_2)_3$).

Synthesis of molecularly defined macrocycles *cyclic*-TPE$_{n+1}$(n=1-6) and corresponding *linear*-TPE$_{n+1}$.

The synthetic routes of *linear*-TPE$_{n+1}$ and *cyclic*-TPE$_{n+1}$were shown in Figure 1. *Linear*-TPE$_{n+1}$ and *cyclic*-TPE$_{n+1}$with n=1were chosen as typical samples prepared by the "click" stepwise chain-growth reaction, and the detailed synthetic procedure was as follows. The synthetic process and characterization of other *linear*-TPE$_{n+1}$ and *cyclic*-TPE$_{n+1}$ (n=2-6) as well as correlative products were similar to *linear*-TPE$_{n+1}$ and *cyclic*-TPE$_{n+1}$ with n=1 and described below.

Synthesis of TIPS-TPE$_{n+1}$-Br with n=1 (linear-TPE$_{n+1}$-Br).

Into a 100 mL three-necked round-bottom flask was added a mixture of yne-TPE-Br (5.32 g,10.51 mmol) and TIPS-TPE$_n$-N_3 with n=1 (6.35 g, 10.02 mmol) in 30 mL DMFunder N_2. Stirring for 2 h, CuBr (71.60 mg, 0.50 mmol) and PMDETA (173.3 mg, 1.00 mmol) were then introduced. After another 2 h, 40 mL water was added and the mixture was extracted by 150 mL ethyl acetate three times. The obtained solution was then washed by brine twice and dried over anhydrous sodium sulfate for 4 h. After concentrated in vacuo, the crude product was purified on a silica-gel column using petroleum ether: ethyl acetate (2:1 by volume) as eluent. The obtained product was light yellow powder. Yield: 93.2 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 1H, -N-CH=C-N=), 7.18-6.63 (m, 36H, Ar H), 5.25-5.02 (m, 2H, -OCH_2-C=C-), 4.83-4.68(t, 2H, -O-$CH_2C\underline{H_2}$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 2H, -O-C$\underline{H_2}CH_2$N-C-), 4.24-4.15(q, 2H,-CH_2Br), 3.63-3.45(q, 2H, -C$\underline{H_2}CH_2$Br), 1.12-0.94 (m, 21H, -Si (CH $(CH_3)_2)_3$).

Synthesis of TIPS-TPE$_{n+1}$-N_3 and yne-TPE$_{n+1}$-N_3 with n=1.

TIPS-TPE$_{n+1}$-Br with n=1 (10.00 g, 8.80 mmol) in 25 mL DMF was placed into a 50 mL round-bottom flask. Then sodium azide (0.70 g, 11.39 mmol) was added at 35 ^{o}C and stirred overnight, and then 40 mL water was added and the mixture was extracted by 200 mL dichloromethane three times. The organic solution was washed by brine twice and then dried over anhydrous sodium sulfate for 4 h. The obtained product TIPS-TPE$_{n+1}$-N_3 with n=1was light yellow solid. Yield: 98.0 %.^{1}H NMR (300 MHz, CDCl3, δ, ppm): 7.85-7.68 (t, 1H, -N-CH=C-N=), 7.18-6.63 (m, 36H, Ar H), 5.25-5.02 (m, 2H, -OCH_2-C=C-), 4.83-4.68(t, 2H, -O-$CH_2C\underline{H_2}$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 2H, -O-C$\underline{H_2}CH_2$N-C-), 4.16-3.96(q, 2H, -CH_2N_3), 3.63-3.45(q, 2H, -C$\underline{H_2}CH_2N_3$), 1.12-0.94 (m, 21H, -Si (CH $(CH_3)_2)_3$).

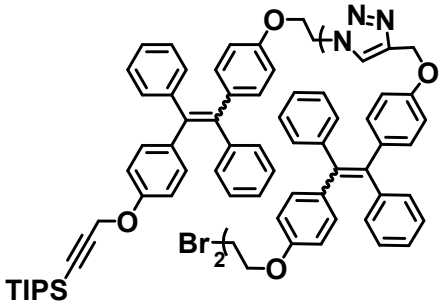
Then TIPS-TPE$_{n+1}$-N_3 with n=1(1.30 g, 1.21 mmol) was placed into a 25mL round-bottom flask with 10 mL THF followed by the addition of TBAF (1.40 mL, 1.40 mmol). After stirring for another 20 minutes, the organic

solution was poured into 50 mL water and the mixture was extracted by ethyl acetate three times. The organic solution was washed by brine twice and then dried over anhydrous sodium sulfate for 4 h. After evaporating the organic solvent, light yellow powder was obtained. Yield: 95.6 %.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 1H, -N-CH=C-N=), 7.18-6.63 (m, 36H, Ar H), 5.25-5.02(m, 2H, -OCH_2-C=C-), 4.83-4.68(t, 2H, -O-$CH_2C\underline{H}_2$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 2H, -O-$C\underline{H}_2CH_2$N-C-), 4.16-3.96(q,2H,-CH_2N_3), 3.63-3.45(q, 2H, -$C\underline{H}_2CH_2N_3$), 2.58-2.44 (s, 1H, -C≡CH).

Synthesis of *cyclic*-TPE_{n+1} with n=1.

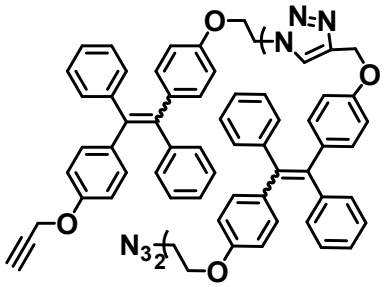
A typical synthetic procedure is as follows: 800 mL Toluene was added into a 1000 mL three-necked round-bottomed flask with a dynamoelectric stirrer and degassed by bubbling with N_2 for 5h, and then CuBr (143.0mg, 1.00 mmol) and PMDETA (0.26 g,1.50mmol) were introduced. Yne-TPE_{n+1}-N_3 with n=1 (0.19 g, 0.20 mmol) in 20 mL toluene was then added to the flask at 70 °C via a syringe pump at a rate of 0.8 mL/h under the protection of argon. After the addition was completed, the reaction was allowed to proceed for an additional24 h. The mixture was then cooled to room temperature, and the cuprous bromide was removed by flash chromatography using THF as solvent and the filtrate was concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography using petroleum ether: ethyl acetate (1:2 by volume) as eluent to give the desired product as light yellow powder. Yield: 86.3 %.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.96-7.47 (m, 2H, -N-CH=C-N=), 7.18-6.38 (m, 36H, Ar H), 5.44-4.83 (m, 4H, -OCH_2-C=C-), 4.83-4.42(m, 4H, -O-$CH_2C\underline{H}_2$N-C-), 4.25-4.03(q,4H, -O-$C\underline{H}_2CH_2$N-C-).

Synthesis of TIPS-TPE_3-Br.



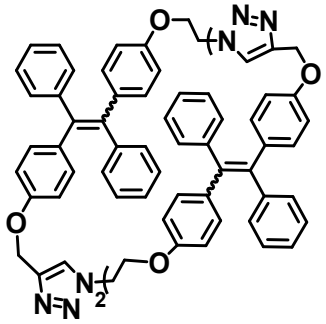
Azidation of TIPS-TPE_2-Br is referred to the synthesis of *linear*-TPE_2 and the following synthetic procedure is similar to that of TIPS-TPE_2-Br described above. White solid was obtained. Yield:79.8 %.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 2H, -N-CH=C-N=), 7.18-6.63 (m, 54H, Ar H), 5.25-5.02 (m, 4H, -OCH_2-C=C-), 4.83-4.68(t, 4H, -O-$CH_2C\underline{H}_2$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 4H, -O-$C\underline{H}_2CH_2$N-C-), 4.24-4.15(q, 2H, -CH_2Br), 3.63-3.45(q, 2H, -$C\underline{H}_2CH_2$Br), 1.12-0.94 (m, 21H, -Si (CH $(CH_3)_2)_3$).

Synthesis of *linear*-TPE_3**.**



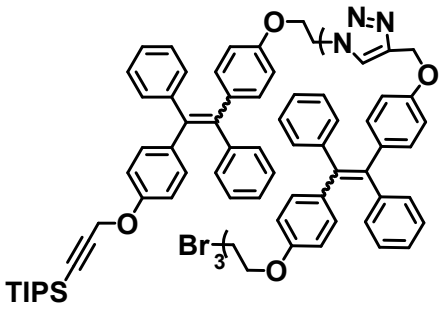
linear-$TPE_3$was generated from TIPS-TPE_3-Brusing the same procedure for preparation of *linear*-TPE_2 as white solid. Yield: 91.3 %.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 2H, -N-CH=C-N=), 7.18-6.63 (m, 54 H, Ar H), 5.25-5.02(m, 4H, -OCH_2-C=C-), 4.83-4.68(t, 4H, -O-$CH_2C\underline{H}_2$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 4H, -O-$C\underline{H}_2CH_2$N-C-), 4.16-3.96(q,2H,-CH_2N_3), 3.63-3.45(q, 2H, -$C\underline{H}_2CH_2N_3$), 2.58-2.44 (s, 1H, -C≡CH).

Synthesis of *cyclic*-TPE_3**.**



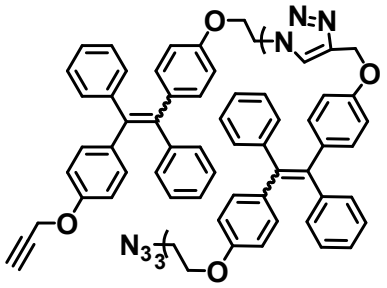
Using the same procedure for preparation of *cyclic*-TPE_2, *cyclic*-TPE_3 was obtained from *linear*-TPE_3 as white solid. Yield: 82.9%. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.60 (m, 3H, -N-CH=C-N=), 7.18-6.38 (m, 54H, Ar H), 5.28-4.92 (m, 6H, -OCH_2-C=C-), 4.83-4.50 (m, 6H, -O-$CH_2C\underline{H}_2$N-C-), 4.38-4.08 (q, 6H, -O-$C\underline{H}_2CH_2$N-C-).

Synthesis of TIPS-TPE_4-Br.



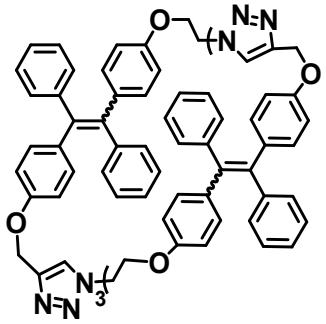
Azidation of TIPS-TPE_3-Br is referred to the synthesis of *linear*-TPE_2 and the following synthetic procedure is similar to that of TIPS-TPE_2-Br described above. White solid was obtained. Yield: 75.2 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 3H, -N-CH=C-N=), 7.18-6.63 (m, 72H, Ar H), 5.25-5.02 (m, 6H, -OCH_2-C=C-), 4.83-4.68(t, 6H, -O-$CH_2C\underline{H}_2$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 6H, -O-$C\underline{H}_2CH_2$N-C-), 4.24-4.15(q, 2H, -CH_2Br), 3.63-3.45(q, 2H, -$C\underline{H}_2CH_2$Br), 1.12-0.94 (m, 21H, -Si (CH $(CH_3)_2)_3$).

Synthesis of *linear*-TPE_4.



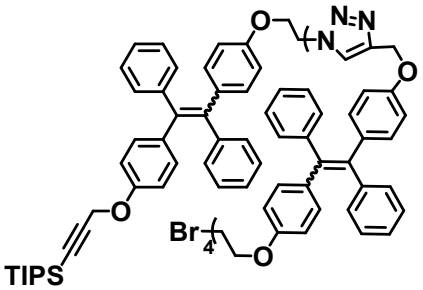
linear-TPE_4 was generated from TIPS-TPE_4-Brusing the same procedure for preparation of *linear*-TPE_2 as white solid. Yield: 92.8%. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 3H, -N-CH=C-N=), 7.18-6.63 (m, 54H, Ar H), 5.25-5.02 (m, 6H, -OCH_2-C=C-), 4.83-4.68(t, 6H, -O-$CH_2C\underline{H}_2$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 6H, -O-$C\underline{H}_2CH_2$N-C-), 4.16-3.96(q, 2H, -CH_2N_3), 3.63-3.45(q, 2H, -$C\underline{H}_2CH_2N_3$), 2.58-2.44 (s, 1H, -C≡CH).

Synthesis of *cyclic*-TPE_4.



Using the same procedure for preparation of *cyclic*-TPE_2, *cyclic*-TPE_4 was obtained from *linear*-TPE_3 as white solid. Yield: 72.6 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.60 (m, 4H, -N-CH=C-N=), 7.18-6.38 (m, 54H, Ar H), 5.28-4.92 (m, 8H, -OCH_2-C=C-),4.83-4.50 (m, 8H, -O-$CH_2C\underline{H}_2$N-C-), 4.38-4.08 (q, 8H, -O-$C\underline{H}_2CH_2$N-C-).

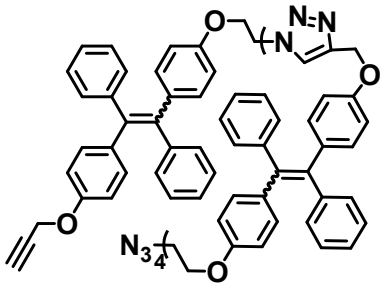
Synthesis of TIPS-TPE_5-Br**.**



Azidation of TIPS-TPE_4-Br is referred to the synthesis of *linear*-TPE_2 and the following synthetic procedure is similar to that of TIPS-TPE_2-Br described above. White solid was obtained. Yield: 70.6 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 4H, -N-CH=C-N=), 7.18-6.63 (m, 90H, Ar H), 5.25-5.02 (m, 8H, -OCH_2-C=C-), 4.83-

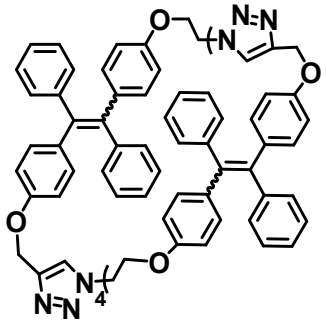
4.68(t, 8H, -O-CH_2C$\underline{H}_2$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 8H, -O-C$\underline{H}_2CH_2$N-C-), 4.24-4.15(q, 2H, -CH_2Br), 3.63-3.45(q, 2H, -C$\underline{H}_2CH_2$Br), 1.12-0.94 (m, 21H, -Si (CH $(CH_3)_2)_3$).

Synthesis of *linear*-TPE_5**.**



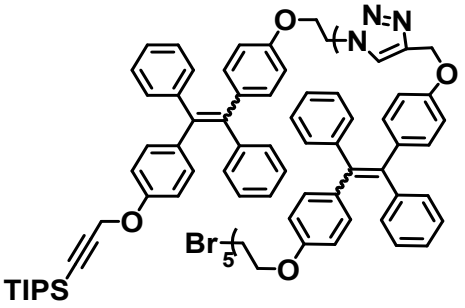
linear-TPE_5 was generated from TIPS-TPE_5-Br using the same procedure for preparation of *linear*-TPE_2 as white solid. Yield: 90.5 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 4H, -N-CH=C-N=), 7.18-6.63 (m, 90H, Ar H), 5.25-5.02 (m, 8H, -OCH_2-C=C-), 4.83-4.68(t, 8H, -O-CH_2C$\underline{H}_2$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 8H, -O-C$\underline{H}_2CH_2$N-C-), 4.16-3.96(q, 2H, -CH_2N_3), 3.63-3.45(q, 2H, -C$\underline{H}_2CH_2N_3$), 2.58-2.44 (s, 1H, -C≡CH).

Synthesis of *cyclic*-TPE_5**.**



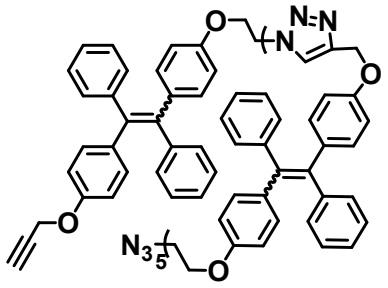
Using the same procedure for preparation of *cyclic*-TPE_2, *cyclic*-TPE_5 was obtained from *linear*-TPE_5 as white solid. Yield: 73.5 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.60 (m, 5H, -N-CH=C-N=), 7.18-6.38 (m, 90H, Ar H), 5.28-4.92 (m, 10H, -OCH_2-C=C-), 4.83-4.50 (m, 10H, -O-CH_2C$\underline{H}_2$N-C-), 4.38-4.08 (q, 10H, -O-C$\underline{H}_2CH_2$N-C-).

Synthesis of TIPS-TPE_6-Br**.**



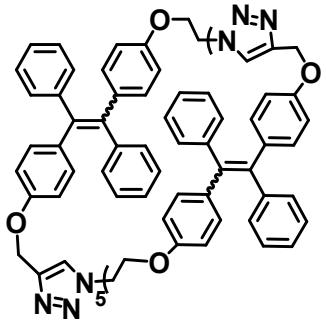
Azidation of TIPS-TPE_5-Br is referred to the synthesis of *linear*-TPE_2 and the following synthetic procedure is similar to that of TIPS-TPE_2-Br described above. White solid was obtained. Yield: 76.3%.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 5H, -N-CH=C-N=), 7.18-6.63 (m, 108H, Ar H), 5.25-5.02 (m, 10H, -OCH_2-C=C-), 4.83-4.68 (t, 10H, -O-$CH_2C\underline{H}_2$N-C-), 4.67-4.53 (q, 2H, -OCH_2-C≡C), 4.37-4.18 (m, 10H, -O-$C\underline{H}_2CH_2$N-C-), 4.24-4.15 (q, 2H, -CH_2Br), 3.63-3.45 (q, 2H, -$C\underline{H}_2CH_2$Br), 1.12-0.94 (m, 21H, -Si (CH $(CH_3)_2)_3$).

Synthesis of *linear*-TPE_6**.**



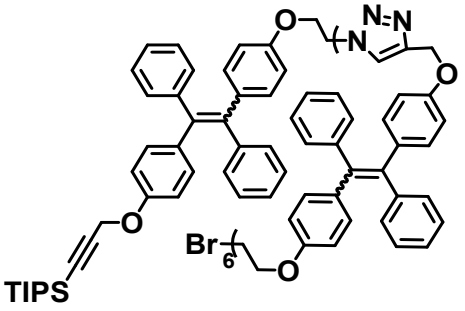
linear-TPE_6 was generated from TIPS-TPE_6-Br using the same procedure for preparation of *linear*-TPE_2 as white solid. Yield: 93.2 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 5H, -N-CH=C-N=), 7.18-6.63 (m, 108H, Ar H), 5.25-5.02 (m, 10H, -OCH_2-C=C-), 4.83-4.68(t, 10H, -O-$CH_2C\underline{H}_2$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 10H, -O-$C\underline{H}_2CH_2$N-C-), 4.16-3.96 (q, 2H, -CH_2N_3), 3.63-3.45 (q, 2H, -$C\underline{H}_2CH_2N_3$), 2.58-2.44 (s, 1H, -C≡CH).

Synthesis of *cyclic*-TPE_6.



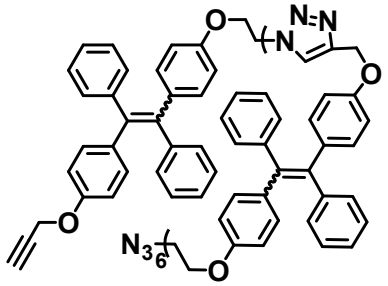
Using the same procedure for preparation of *cyclic*-TPE_2, *cyclic*-$TPE_6$was obtained from *linear*-TPE_6 as white solid. Yield: 68.7%.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.60 (m, 6H, -N-CH=C-N=), 7.18-6.38 (m, 108H, Ar H), 5.28-4.92 (m, 12H, -OCH_2-C=C-), 4.83-4.50 (m, 12H, -O-$CH_2C\underline{H}_2$N-C-), 4.38-4.08 (q, 12H, -O-$C\underline{H}_2CH_2$N-C-).

Synthesis of TIPS-TPE_7-Br.



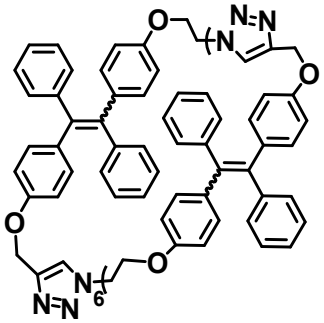
Azidation of TIPS-TPE_6-Br is referred to the synthesis of *linear*-TPE_2 and the following synthetic procedure is similar to that of TIPS-TPE_2-Br described above. White solid was obtained. Yield: 69.8 %.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 6H, -N-CH=C-N=), 7.18-6.63 (m, 126H, Ar H), 5.25-5.02 (m, 12H, -OCH_2-C=C-), 4.83-4.68(t, 12H, -O-$CH_2C\underline{H}_2$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 12H, -O-$C\underline{H}_2CH_2$N-C-), 4.24-4.15(q, 2H, -CH_2Br), 3.63-3.45 (q, 2H, -$C\underline{H}_2CH_2$Br), 1.12-0.94 (m, 21H, -Si (CH $(CH_3)_2)_3$).

Synthesis of *linear*-TPE_7.



linear-TPE_7 was generated from TIPS-TPE_7-Br using the same procedure for preparation of *linear*-TPE_2 as white solid. Yield: 91.2 %. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.68 (t, 6H, -N-CH=C-N=), 7.18-6.63 (m, 126H, Ar H), 5.25-5.02 (m, 12H, -OCH_2-C=C-), 4.83-4.68(t, 12H, -O-$CH_2C\underline{H}_2$N-C-), 4.67-4.53(q, 2H, -OCH_2-C≡C), 4.37-4.18(m, 12H, -O-$C\underline{H}_2CH_2$N-C-), 4.16-3.96 (q, 2H, -CH_2N_3), 3.63-3.45 (q, 2H, -$C\underline{H}_2CH_2N_3$), 2.58-2.44 (s, 1H, -C≡CH).

Synthesis of *cyclic*-TPE_7.



Using the same procedure for preparation of *cyclic*-TPE_2, *cyclic*-TPE_7 was obtained from *linear*-TPE_7 as white solid. Yield: 66.8%.^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-7.60 (m, 7H, -N-CH=C-N=), 7.18-6.38 (m, 126H, Ar H), 5.28-4.92 (m, 14H, -OCH_2-C=C-), 4.83-4.50 (m, 14H, -O-$CH_2C\underline{H}_2$N-C-), 4.38-4.08 (q, 14H, -O-$C\underline{H}_2CH_2$N-C-).

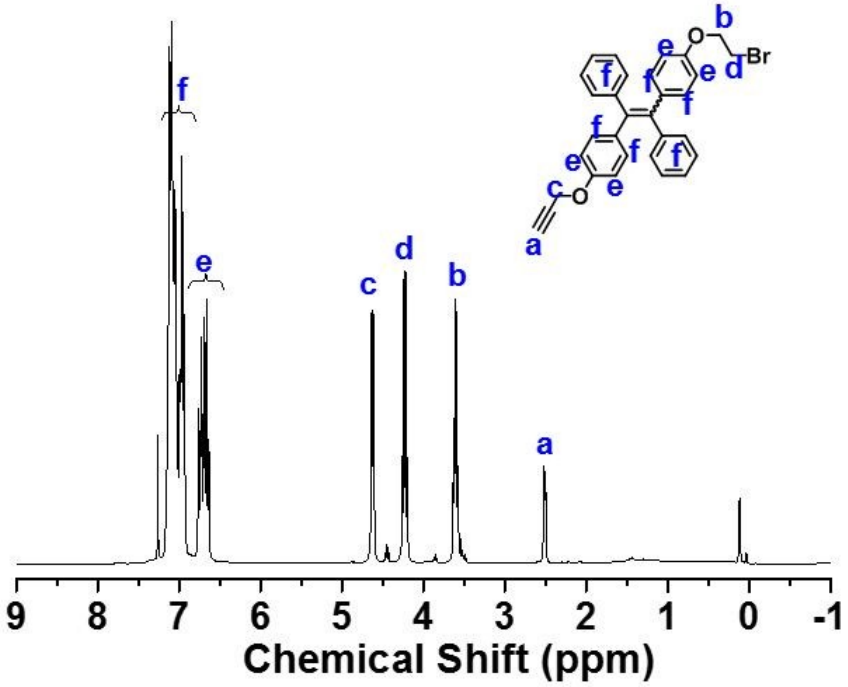


Figure S1. ^{1}H NMR spectra of the monoprotected ω-alkyne unimer yne-TPE-Br in $CDCl_3$.

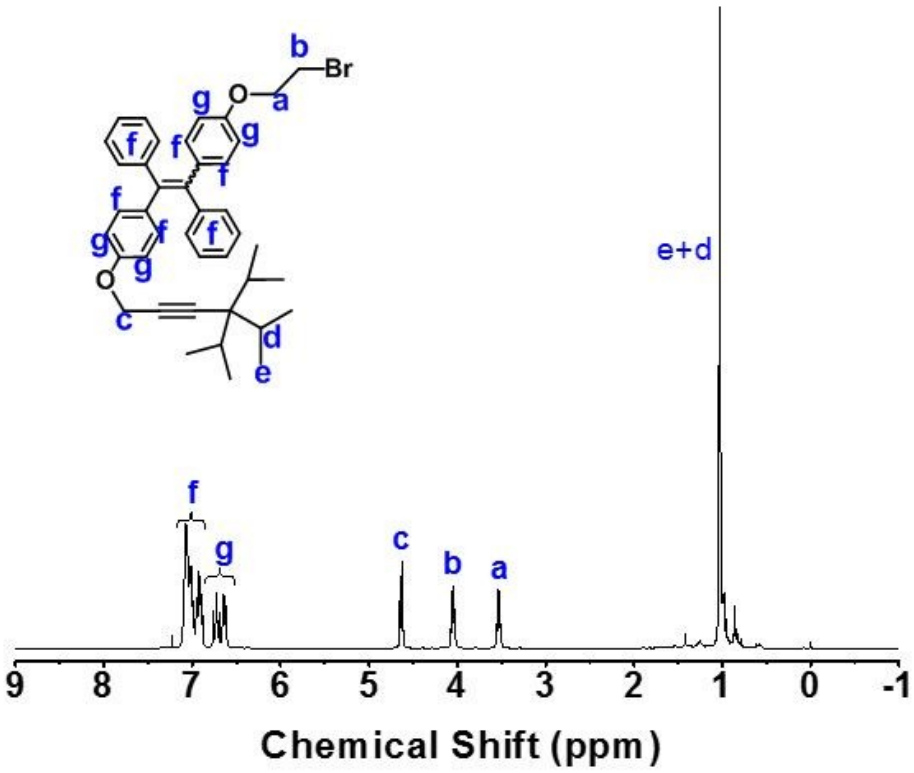


Figure S2. ^{1}H NMR spectrum of the α-azide unimer TIPS-TPE-N_3 in $CDCl_3$.

The preliminary cyclic products with n≥3 were further purified by the preparative-GPC to get rid of the small amounts of linear precursors, dimers or polycondensates of higher molecular weight. The GPC traces before and after pre-GPC were plotted in Figure S3.

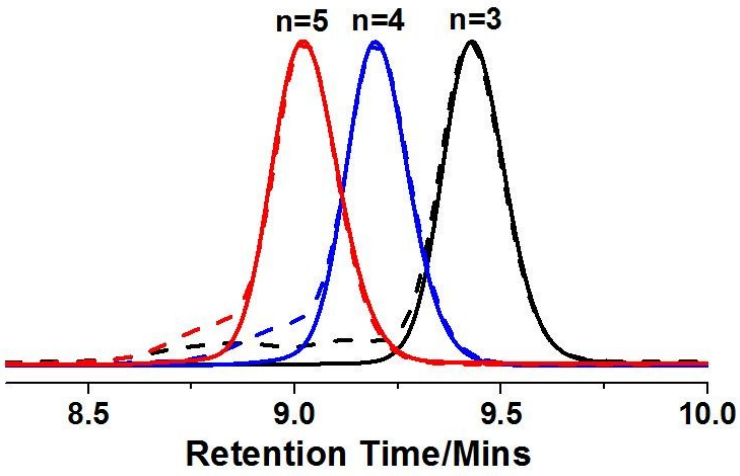
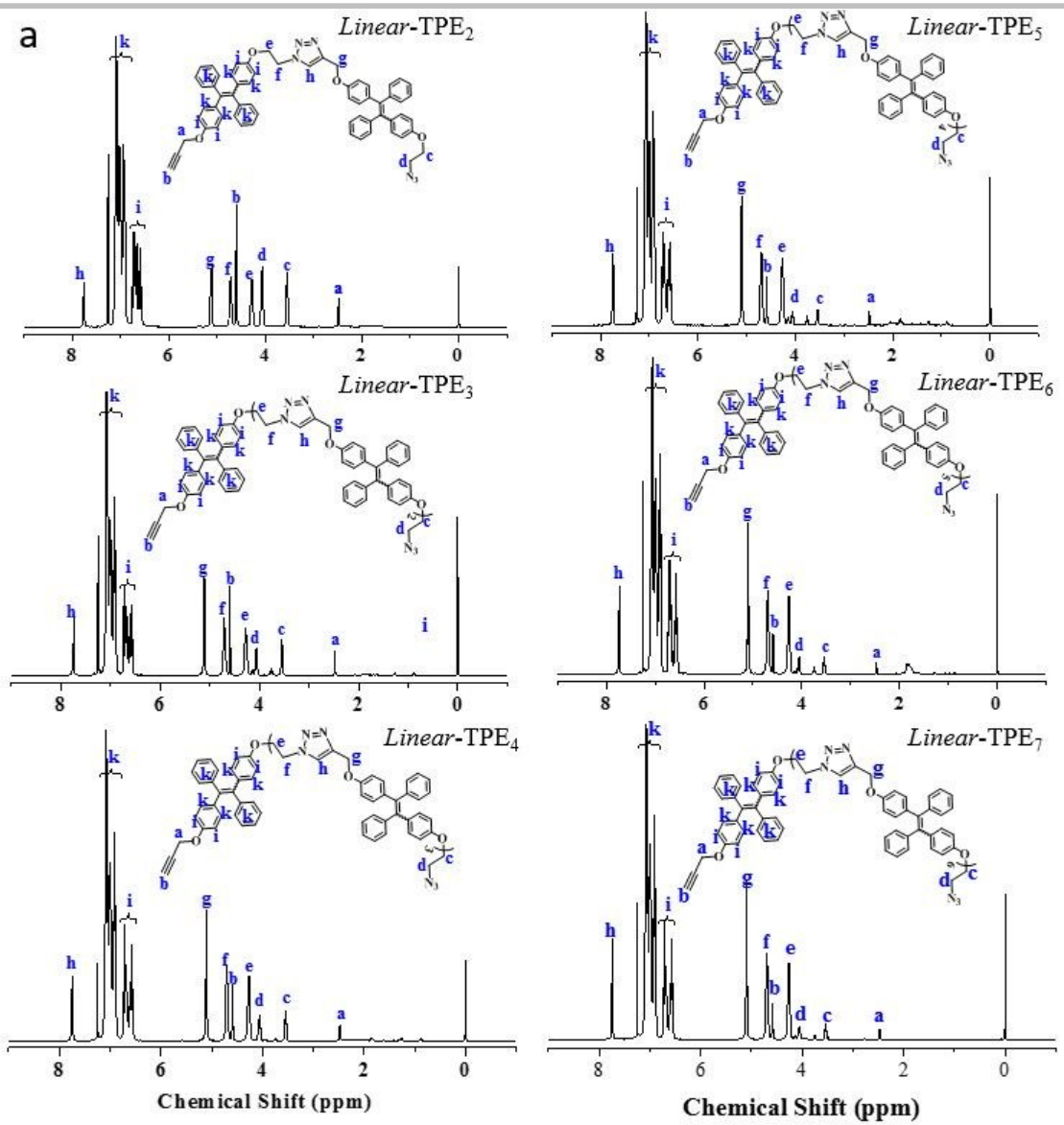


Figure S3. The GPC traces of cyclic-TPE_n with n≥3 before and after pre-GPC using THF as the eluent (n = 3-5).


a
Linear-TPE2
Linear-TPE5
Linear-TPE3
Linear-TPE6
Linear-TPE4
Linear-TPE7
Chemical Shift (ppm)
Chemical Shift (ppm)

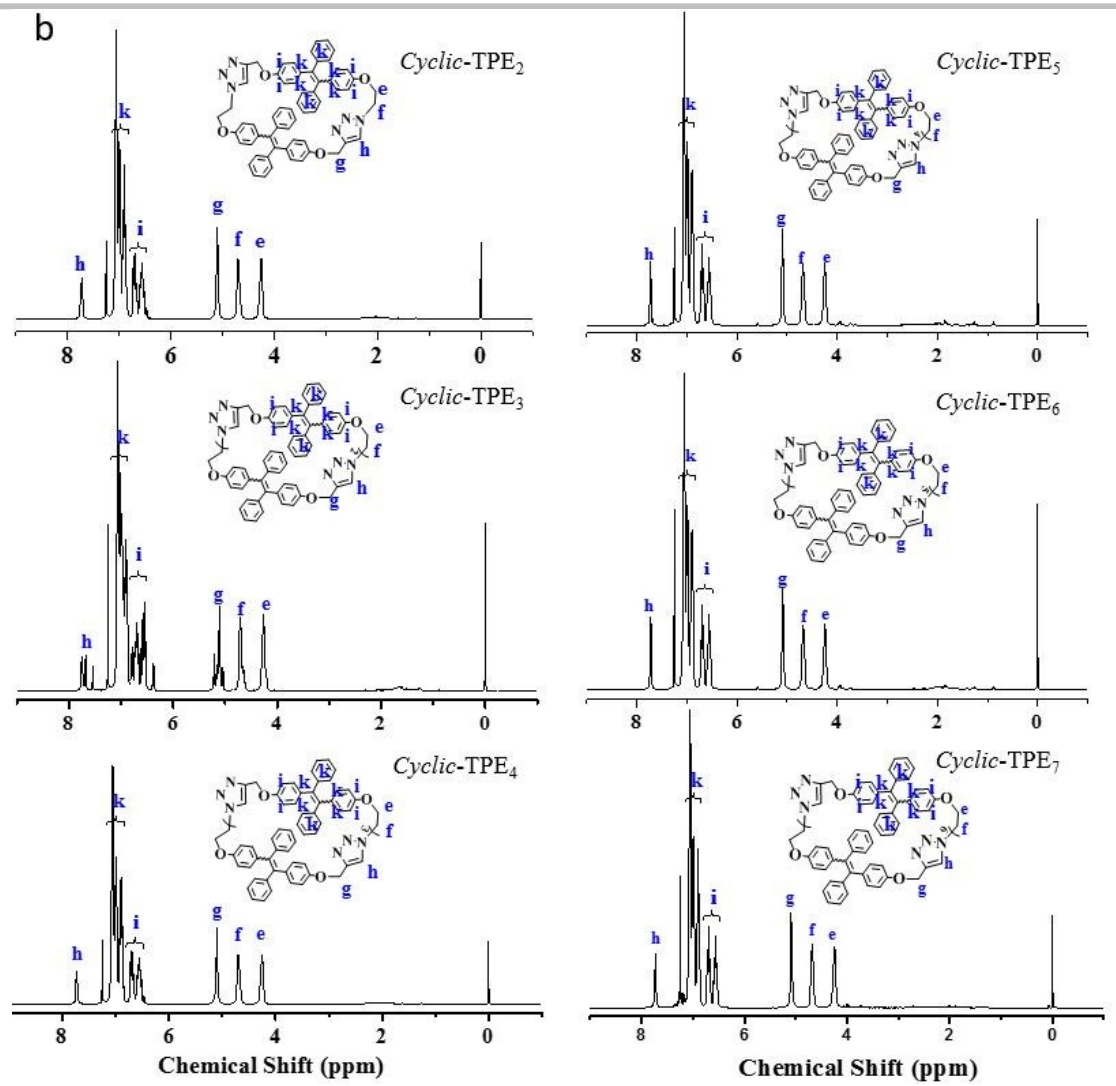


Figure S4. ^{1}H NMR spectra of the *linear*-TPE$_{n+1}$ and *cyclic*-TPE$_{n+1}$(n=1-6) in $CDCl_3$. **a,** *linear*-TPE$_{n+1;}$ **b,** *cyclic*-TPE$_{n+1}$.

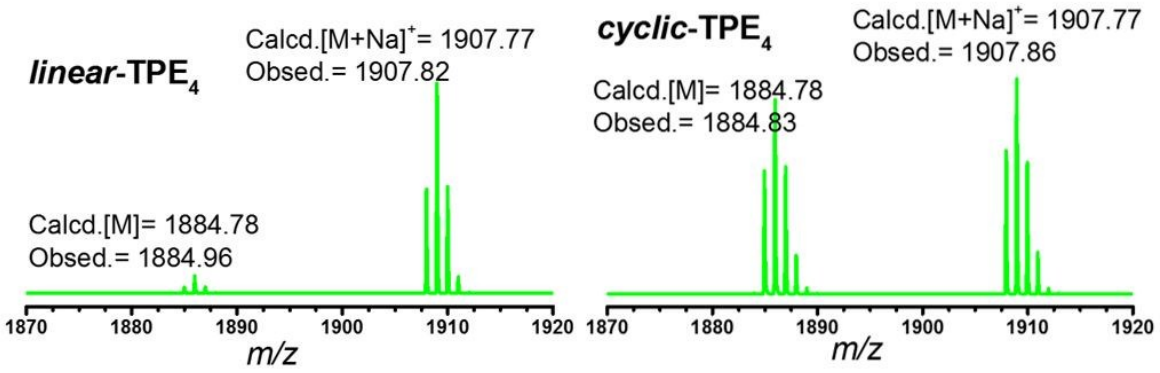


Figure S5. Local images magnified by MALDI-TOF mass spectra of the *linear*-TPE$_4$and *cyclic*-TPE$_4$ (Theor. M_W=1884.78 Da).

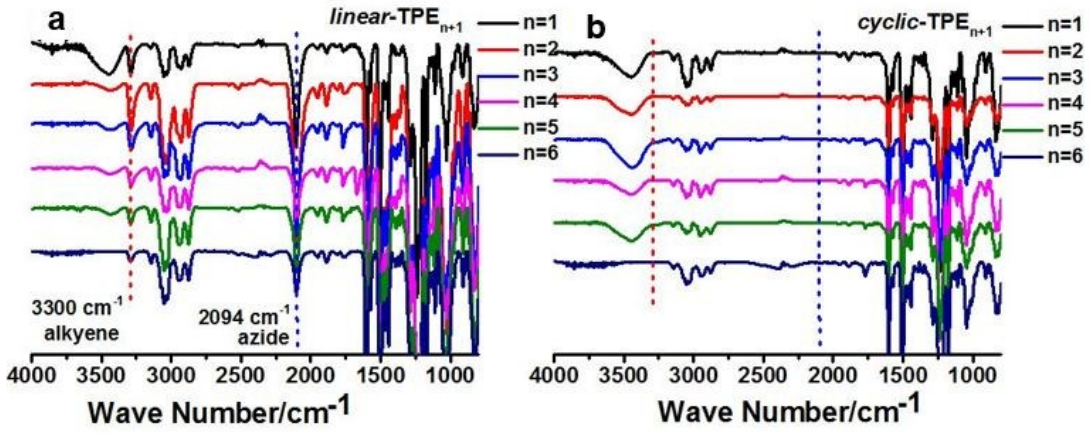


Figure S6. The FT-IR spectra of the *linear*-TPE$_{n+1}$ **a** and *cyclic*-TPE$_{n+1}$ **b**.

Table S1. Data corresponding to theoretical weights and observed molecular weights determined by MALDI-TOF MS and GPC (M_n, GPC) of *linear*-TPE$_{n+1}$ and *cyclic*-TPE$_{n+1}$ (n = 1-6).

Sample	Theor. [Da]	Obsed. [m/z]	$M_{n,GPC}$ [Da]
linear-TPE$_2$	942.39	942.21	790
cyclic-TPE$_2$		942.24	260
linear-TPE$_3$	1413.58	1413.77	1390
cyclic-TPE$_3$		1413.85	820
linear-TPE4	1907.78 (+Na$^+$)	1907.82	1990
cyclic-TPE$_4$		1907.80	1330
linear-TPE$_5$	2378.97(+Na$^+$)	2379.22	2420
cyclic-TPE$_5$		2379.27	1780
linear-TPE$_6$	2850.17(+Na$^+$)	2850.45	3040
cyclic-TPE$_6$		2850.52	2210
linear-TPE$_7$	3221.36 (+Na$^+$)	3321.57	3600
cyclic-TPE$_7$		3321.60	2500

Theor.: theoretical molecular weight (Da) of *linear*-TPE_{n+1} and *cyclic*-TPE_{n+1} (n = 1-6) with Na or without Na; Obsed.: molecular mass (m/z) of *linear*-TPE_{n+1} or *cyclic*-TPE_{n+1} (n =1-6) obtained from MALDI-TOF mass spectra.

Table S2. The decomposition temperature (T_d) and Glass transition temperature (T_g) of the *linear*-TPE_{n+1}-Br and *cyclic*-TPE_{n+1} (n=1-6).

Sample		T_d/°C [a)]	T_g [b)]/°C	ΔT_g/°C
n=1	*linear*-TPE_2-Br	290.3	71.1	97.4
	cyclic-TPE_2	353.0	168.5	
n=2	*linear*-TPE_3-Br	289.5	92.9	33.0
	cyclic-TPE_3	345.4	125.9	
n=3	*linear*-TPE_4-Br	294.3	103.3	44.2
	cyclic-TPE_4	346.0	147.5	
n=4	*linear*-TPE_5-Br	303.3	109.5	27.3
	cyclic-TPE_5	347.4	136.8	
n=5	*linear*-TPE_6-Br	310.3	119.2	23.9
	cyclic-TPE_6	346.8	143.1	
n=6	*linear*-TPE_7-Br	314.6	126.7	11.2
	cyclic-TPE_7	342.6	137.9	

[a)]: Determined by TGA. T_d: decomposition temperature, the temperatures for 5% weight loss of initial weight, averaging the values of three times. [b)]: Determined by DSC. T_g: glass transition temperature, averaging the values of three times; ΔT_g: the difference values of glass transition temperature between the *linear*-TPE_{n+1}-Br and *cyclic*-TPE_{n+1}.

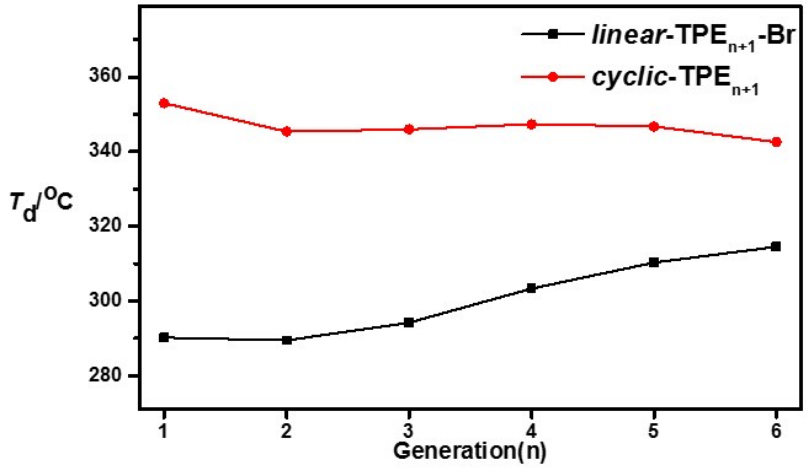


Figure S7. The dependence of decomposition temperature (Td) of the linear-TPE$_{n+1\text{-}Br}$ and cyclic-TPE$_{n+1}$ (n=1-6).

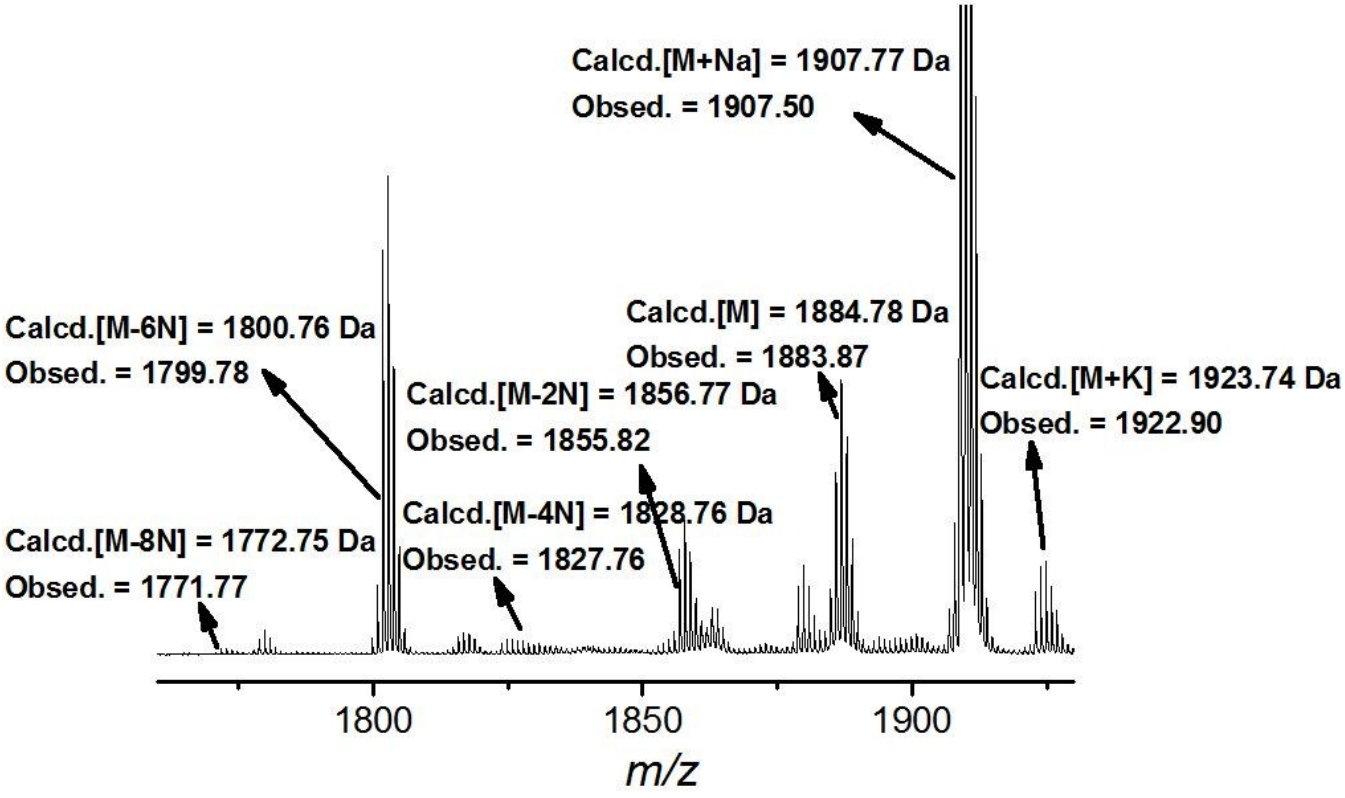


Figure S8. The MALDI-TOF mass spectra of *cyclic*-TPE$_4$ during the beginning decomposition in T_d testing (Theor. M_W=1884.78 Da) *.

*: The sample was firstly heated to a little below 290 °C (temperature of the starting weight loss) and held for ten minutes, and then the remains were dissolved in chloroform and analyzed by MALDI-TOF mass spectra. As shown in Figure S8, it could be found that the beginning decomposition values 1855.82, 1827.76, 1799.78 and 1772.75 were corresponding to the molecule weight of the cyclic oligomer that lost two, four, six and eight nitrogen atoms respectively, resulting from the destruction of triazole ring in the *cyclic*-TPE$_4$.

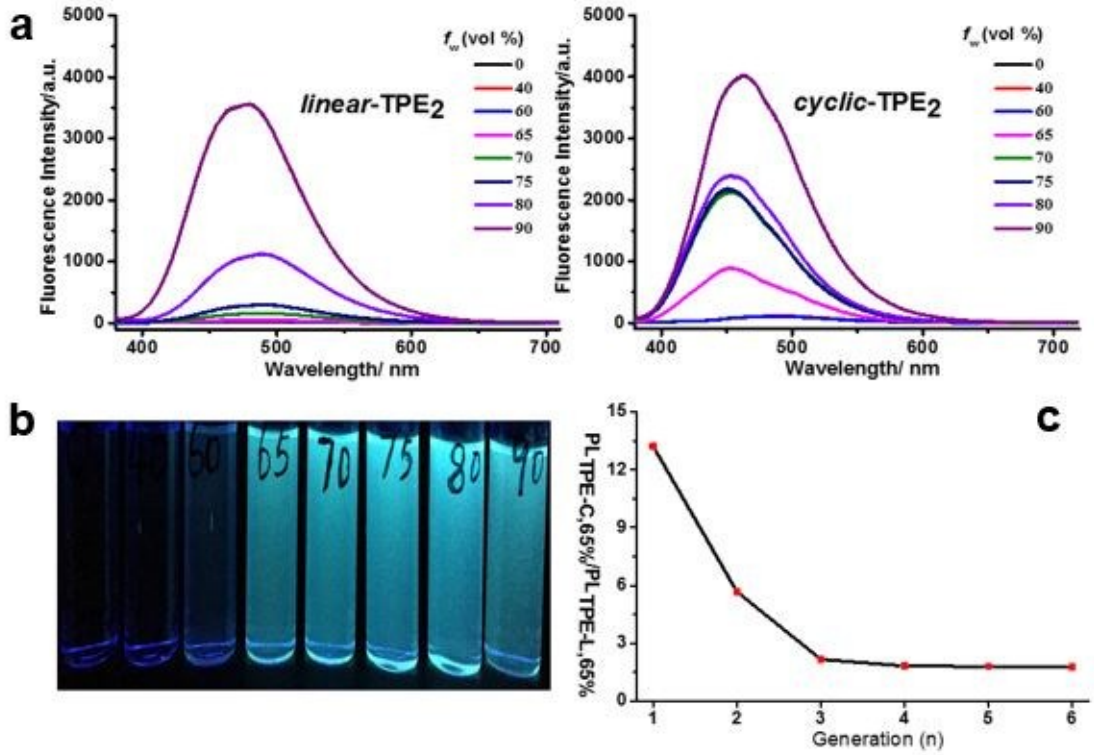


Figure S9. a, Fluorescence spectra of the *linear*-TPE_2 and *cyclic*-TPE_2 in THF/water mixture with the addition of water. Excitation wavelength: 369 nm. **b,** Photo of the *cyclic*-TPE_2 in THF/water mixture with the addition of water under UV lamp excitation. **c,** Ratios of fluorescence intensity of cyclic/linear oligomers at the water fraction of 65%.

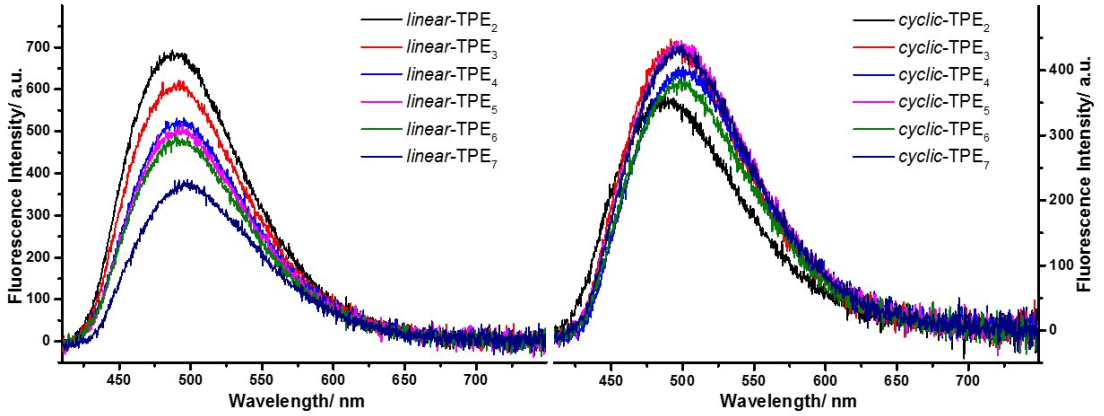


Figure S10. The fluorescence spectra of the *linear*-TPE_{n+1} and *cyclic*-TPE_{n+1} (n=1-6) in the solid powder.

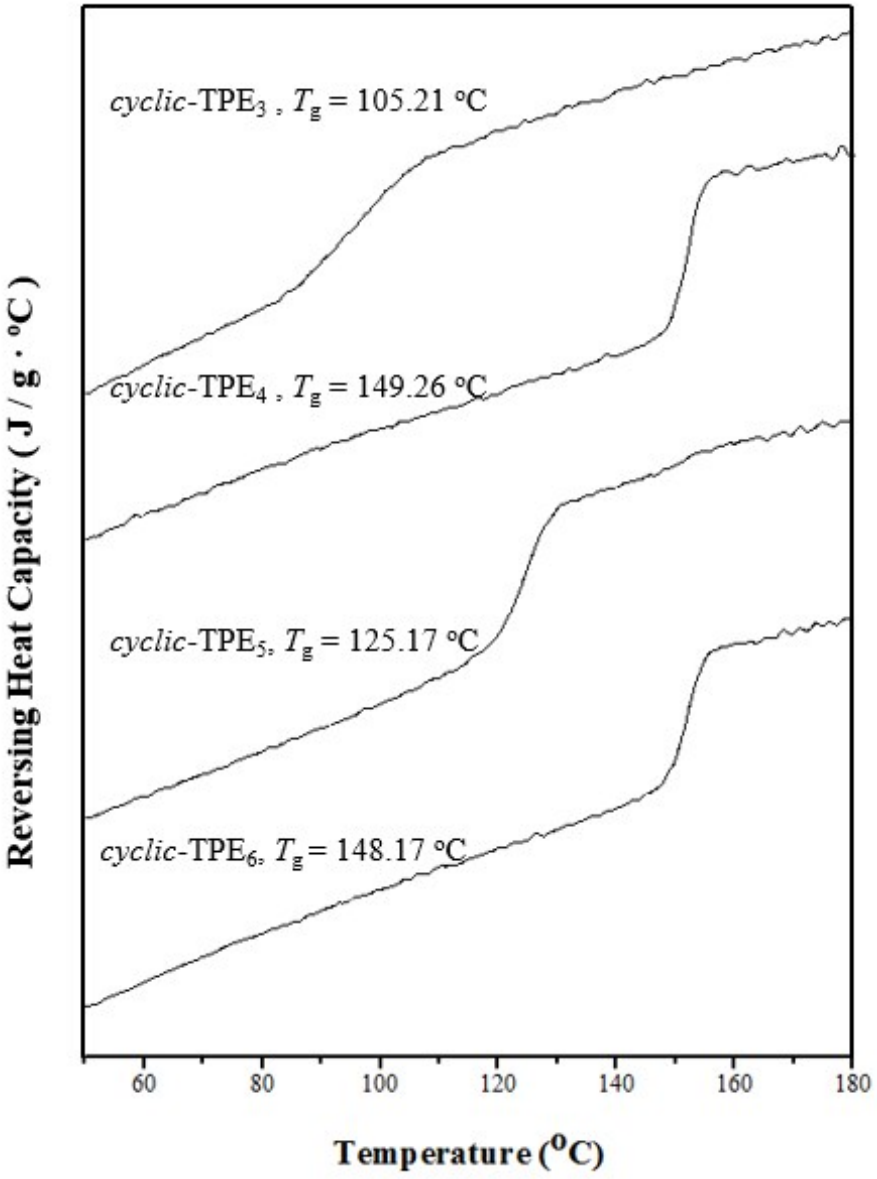


Figure S11. MDSC curves of the cyclic-TPE_3, cyclic-TPE_4, cyclic-TPE_5 and cyclic-TPE_6.

References

1. W. Z. Yuan, Z. Q. Yu, Y. Tang, J. W. Y. Lam, N. Xie, P. Lu, E. Q. Chen and B. Z. Tang, *Macromolecules*, 2011, **44**, 9618-9628.