

Supporting information

From gas separation to ion transport in cavity of the hyperbranched polyamides based on triptycene aimed to electrochromic and memory device

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Materials

O-dichlorobenzene, pyridine, anhydrous sodium sulfate, 4-methoxyaniline, 4-fluoronitrobenzene, triethylamine, copper powder, potassium carbonate, 18-crown-6-ether, triphenyl phosphite, calcium chloride, sodium nitrite, potassium iodide, Reney-Ni, triptycene, calcium hydride (CaH_2) were bought from Aladdin. 1,4-cyclohexane dicarboxylic acid (CA, TCI), 2,2-bis(4-carboxyphenyl) hexafluoropropan (6F), 4,4'-oxybis(benzoic acid)(OA) were brought from TCI Co. Hydrazine hydrate, concentrated hydrochloric acid and concentrated nitric acid were bought from Sinopharm Chemical Reagent Company. Dichloromethane, petroleum ether was used as received, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), N-methyl pyrrolidone (NMP) were bought from Tianjin Fuyu fine Company. DMF and NMP were dried on CaH_2 for 12 h, then the solvents were distilled under reduced pressure and collected in an airproof brown bottle with 4 Å molecular sieves. THF was dried over Na wire and distilled before being used.

Instruments and Measurements

FT-IR spectra were obtained and recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. ^1H NMR, ^{13}C NMR, and C-H HSQC spectra were measured by a Bruker AC-400 MHz and AC-100 MHz spectrometer with tetramethylsilane as an internal reference. Gel permeation chromatography (GPC) analysis was performed on a Malvern Viscotek TDA305max multi-detector gel permeation chromatography containing refractive index (RI) detector, laser light angle scattering (LALS) detector,

and viscosity (IV-DP) detector manufactured by Malvern, UK, calibrated with polystyrene standards in 20mM LiBr solution with DMF as solvent at 45 °C. Mass spectrometer (MS) spectra were obtained on a Finnigan LC-MS/MS system (Thermo Electron, San Jose, CA, USA). Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 6 TGA. The sample was dried in a vacuum oven at 180 °C for 24 h, and the experiments were carried out by keeping about 10 mg powder samples heated at a heating rate of 10°C min⁻¹ and flowing nitrogen rate of 20 cm³ min⁻¹. Polyamide dissolved by DMF solution with a concentration of 1 mg/ml was drop coated to adhere to indium tin oxide (ITO) and dried in a vacuum drying oven at 80°C for 4 h. Then it was glued to the aluminum plate with conductive adhesive and then sputtered gold by vacuum, and the surface morphology of the films was observed by scanning electron microscopy (SEM, Zeiss, Gemini SEM 300, Germany). The surface morphology of the films was observed by scanning with an atomic force microscope (AFM, Agilent, SPM 5100) with SPM 5100 probe. The solution of HBPA in DMF at a concentration of 1 mg/ml was coated on silicon wafer and dried for 4 h at 80 °C in a vacuum drying oven. UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer (Kyoto, Japan) and the photoluminescence (PL) solution spectra were determined by a Jasco FP-6200 spectrometer with the light source of Xenon lamp. The cyclic voltammetry (CV) measurements were conducted on a CH Instruments (660A electrochemical analyzer) by using polyamide as the working electrode, a Pt flake as the counter electrode, an Ag/AgCl electrode as the quasi-reference electrode at a scan rate of 50 mV s⁻¹ in 0.1 M LiClO₄/ACN under a nitrogen atmosphere. The

Electrochemical Impedance Spectroscopy (EIS) curves were obtained from a CH instrument (660e electrochemical analyzer) with a polymer-coated ITO as the working electrode, a platinum sheet as the counter electrode, and a silver/silver chloride electrode as the quasi reference electrode, respectively, at an amplitude of 0.01V. The Nyquist curves were fitted by Zview software. Quantum chemical calculations were performed by using the Gaussian 03W program based on B3LYP/6-31G (d, p) basis set to investigate their ground and excited states. By converting the λ of the UV-Vis absorption plot to $1240/\lambda(\text{nm}) = \text{forbidden band width } (E)$, then convert the absorbance to $\alpha\lambda v^2$, and plot the two as a Tauc Plot, where α is absorption coefficient = 2.303, λ is the wavelength (nm), and v is the forbidden band width (eV). The linear part is made as a tangent line, and its intersection with the X-axis is the forbidden band width. Memory devices were fabricated with HBPA as an interlayer in which the top electrode was an Al electrode, and the bottom electrode was an ITO/glass. Al electrode was deposited by vacuum evaporation. Keithley 2636B system sourcemeter was used to test the memory performance.

Experimental part

Synthesis of 2, 6, 14-trinitrotritycene

Triptycene (4.0 g, 15.75 mmol) was added to a 500 mL three-necked round bottom flask followed by adding 150 mL concentrated nitric acid as solvent at the protection of N_2 atmosphere. Then, the mixture was heated to 80 °C under stirring and kept for 24 h.¹ The reaction was monitored by thin layer chromatography (TLC) until the starting

material disappeared. After the reaction, the solution was cooled to room temperature and then poured into 1 L of ice water while stirring slowly to make the product precipitate completely. Finally, the product was filtered with suction, washed with water to neutrality and dried under vacuum at 50 °C. The crude product was purified by silica gel chromatography (eluent: dichloromethane: petroleum ether = 3:2) and a light yellow product was obtained. Yield: 65%; mp: 175–178 °C; FTIR (KBr, cm^{-1}): 1320, 1595 ($\nu_{\text{N-O}}$), 1261 ($\nu_{\text{C-N}}$).

Synthesis of 2, 6, 14-triaminotriptycene (2)

2, 6, 14-trinitrotriptycene (4.2 g, 14.00 mmol) and Reney-Ni (1.0 g) were added into a 250 mL three-necked round bottom flask with 120 mL of dehydrated THF as solvent. Under an N_2 atmosphere, hydrazine hydrate (16 mL) was added dropwise. The reaction was heated to 65 °C and kept for 12 h.¹ The reaction was monitored by TLC until the starting raw material point disappeared. After the reaction, the solution was cooled to room temperature, Reney-Ni was removed by filtration, and the filtrate was dried under reduced pressure to obtain a red product. Yield: 70%, mp: 293–295 °C; FTIR (KBr, cm^{-1}): 3345, 3381 ($\nu_{\text{N-H}}$), 1246 ($\nu_{\text{C-N}}$).

Synthesis of 2, 6, 14-triiodotriptycene (3)

Compound 2 (3.0 g, 10.02 mmol) was put into a 250 mL three-necked round bottom flask with 54 mL water/HCl mixture (5:4 v/v) as the solvent. Then, 20 ml of NaNO_2 aqueous solution (2.67 g, 38.70 mmol) was added dropwise to the above system and stirred until the solution was clear at 0–5°C. After that, 25 mL KI aqueous solution

(12.7 g, 76.35 mmol) was added to the above mixed solution until the reaction solution turned brown. Then, the reaction system was heated to 80 °C and kept for 30 h.¹ The reaction was monitored by TLC until the starting raw material point disappeared. After the reaction, the solution was cooled to room temperature, followed by being washed with saturated NaHSO₃ solution, then being extracted with CH₂Cl₂ sequentially, and the organic phase was dried with anhydrous Na₂SO₄. The solvent was removed by rotary evaporation to obtain a crude product, which was purified by silica gel chromatography column (eluent: dichloromethane: petroleum ether = 1:3) to obtain white product 3. Yield: 50%; mp: 162–165 °C; ¹H NMR (400 MHz, CDCl₃); δ=7.71 (s, 3H, H₅), 7.37–7.35 (d, J= 8.0Hz, 3H, H₄), 7.12–7.10 (d, J= 8.0Hz, 3H, H₃), 5.26 (s, 1H, H₂), 5.25 (s, 1H, H₁) (Fig.S1).

Synthesis of 4-methoxy-4'-nitrodiphenylamine (4)

4-methoxy-4'-nitrodiphenylamine was prepared according to the literature.² 4-methoxyaniline (25.0 g, 203.13 mmol) and triethylamine (20.8 g, 203.12 mmol) were sequentially added to a 500 mL three-necked round bottom flask with 150 mL of dry DMSO (dimethyl sulfoxide) as the solvent. Then, 4-fluoronitrobenzene (22.0 g, 156.0 mmol) was added dropwise under nitrogen atmosphere, reacted at 90°C for 36 h.² After the reaction, the solution was cooled to room temperature and was poured into ice water to precipitate orange powder. Then the crude product was recrystallized by DMSO/ethanol (1:3) to obtain orange needle-like crystals. Yield: 82%; mp: 158–160 °C; ¹H NMR (400 MHz, DMSO- d₆): δ= 9.08 (s, 1H), 8.04–8.02 (d, J = 8 Hz, 2H), 7.15(s, 2H), 6.97–6.95(d, J = 8 Hz, 2H), 6.88–6.85 (d, J = 12 Hz, 2H), 3.75 (s, 3H).

Synthesis of model compound 1

Model compound 1 was synthesized according to the general route. T3TPA (0.2 g, 0.22 mmol), benzoic acid (0.027 g, 0.22 mmol), 1.2 mL pyridine, 3 mL triphenyl phosphite (TPP) were added in a 25 mL three-necked round-bottomed flask with 3 mL NMP containing 0.25 g CaCl₂ as solvent. The reaction mixture was magnetically stirred at room temperature for 10 minutes under a nitrogen atmosphere. Then the reaction temperature was increased to 130 °C and reacted for 3 h. After the reaction, the reaction solution was poured into 100 mL of methanol, and the fibrous solid product was precipitated. It was dried at 50 °C for 24 h using the vacuum drying oven. FTIR (KBr, cm⁻¹): 3512 (ν_{N-H}), 2924 (ν_{C-H}), 1625 (ν_{C=O}), 1587 (β_{N-H}) ; ¹H NMR (400 MHz, CDCl₃): δ= 7.89 (d, *J*= 8.0Hz, 2H at position a), 7.34–7.19 (m, *J*= 8.0Hz, 2H at position b), 6.87–6.78 (d, *J*= 12.0Hz, 4H at position d), 6.53–6.38 (m, *J*= 4.0Hz, 4H at position c), 3.68 (s, 4H, NH₂).

Synthesis of model compound 2

Model compound 2 was synthesized according to the general route. T3TPA (0.2 g, 0.22 mmol), benzoic acid (0.054 g, 0.44 mmol), 1.2 mL pyridine, 3 mL triphenyl phosphite (TPP) were added in a 25 mL three-necked round-bottomed flask with 3 mL NMP containing 0.25 g CaCl₂ as solvent. The reaction mixture was magnetically stirred at room temperature for 10 minutes under a nitrogen atmosphere. Then the reaction temperature was increased to 130 °C and reacted for 3 h. After the reaction, the reaction solution was poured into 100 mL of methanol, and the fibrous solid product was precipitated. It was dried at 50 °C for 24 h using the vacuum drying oven. FTIR (KBr,

cm⁻¹): 3434 ($\nu_{\text{N-H}}$), 2913 ($\nu_{\text{C-H}}$), 1656 ($\nu_{\text{C=O}}$), 1594 ($\beta_{\text{N-H}}$) ; ¹H NMR (400 MHz, CDCl₃): δ = 7.89 (d, J = 8.0Hz, 4H at position a), 7.39–7.23 (m, J = 4.0Hz, 4H at position b), 6.88–6.82 (m, J = 12.0Hz, 4H at position d), 6.59–6.52 (m, J = 4.0Hz, 4H at position c), 3.69 (s, 4H, NH₂).

Synthesis of model compound 3

Model compound 3 was synthesized according to the general route. T3TPA (0.2 g, 0.22 mmol), benzoic acid (0.081 g, 0.66 mmol), 1.2 mL pyridine, 3 mL triphenyl phosphite (TPP) were added in a 25 mL three-necked round-bottomed flask with 3 mL NMP containing 0.25 g CaCl₂ as solvent. The reaction mixture was magnetically stirred at room temperature for 10 minutes under a nitrogen atmosphere. Then the reaction temperature was increased to 130 °C and reacted for 3 h. After the reaction, the solution was poured into 100 mL of methanol, and the fibrous solid product was precipitated. It was dried at 50 °C for 24 h using the vacuum drying oven. FTIR (KBr, cm⁻¹): 3376 ($\nu_{\text{N-H}}$), 2922 ($\nu_{\text{C-H}}$), 1667 ($\nu_{\text{C=O}}$), 1582 ($\beta_{\text{N-H}}$); ¹H NMR (400 MHz, CDCl₃): δ = 7.87 (d, J = 8.0Hz, 4H at position a), 7.43–7.23 (m, J = 4.0Hz, 4H at position b).

Reference

- 1 C. Zhang, C. Chen, *J. Org. Chem.*, 2006, **71**, 6626-6629.
- 2 T. Stalin, N. Rajendiran, *J. Photoch. Phoyobio. A.*, 2006, **182(2)**, 137-150.

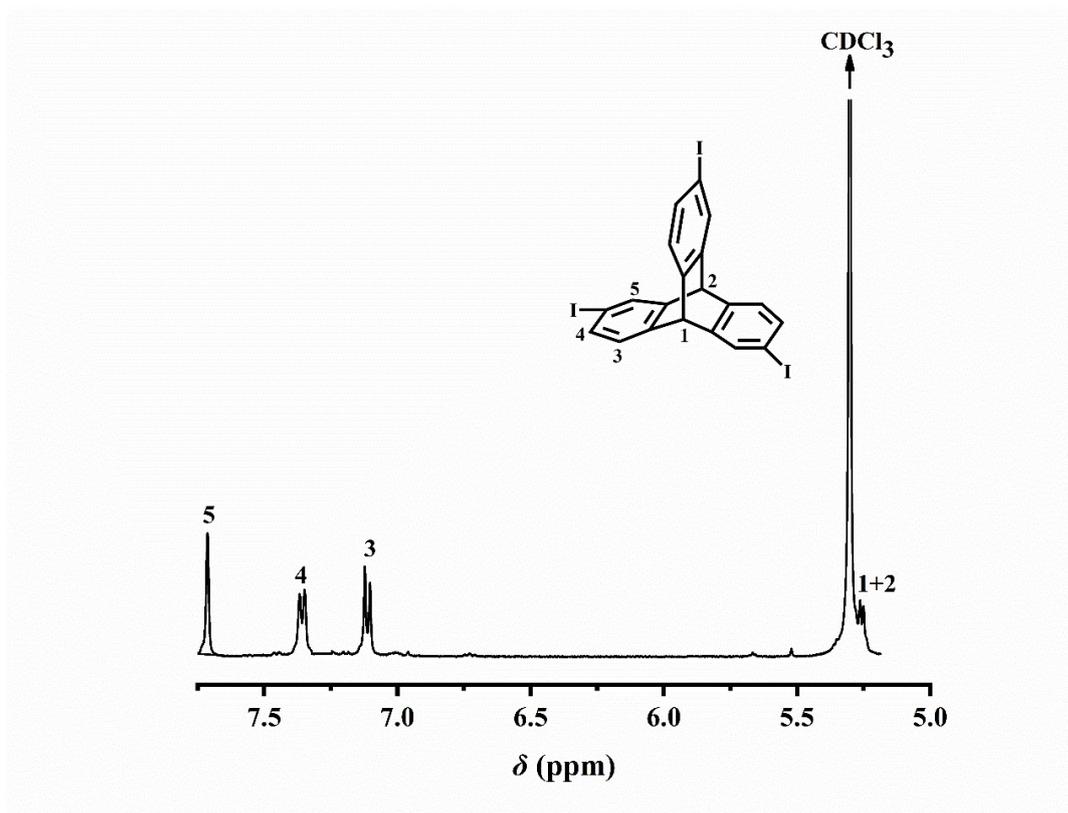


Fig. S1. ^1H NMR spectrum of **3** in CDCl_3 .

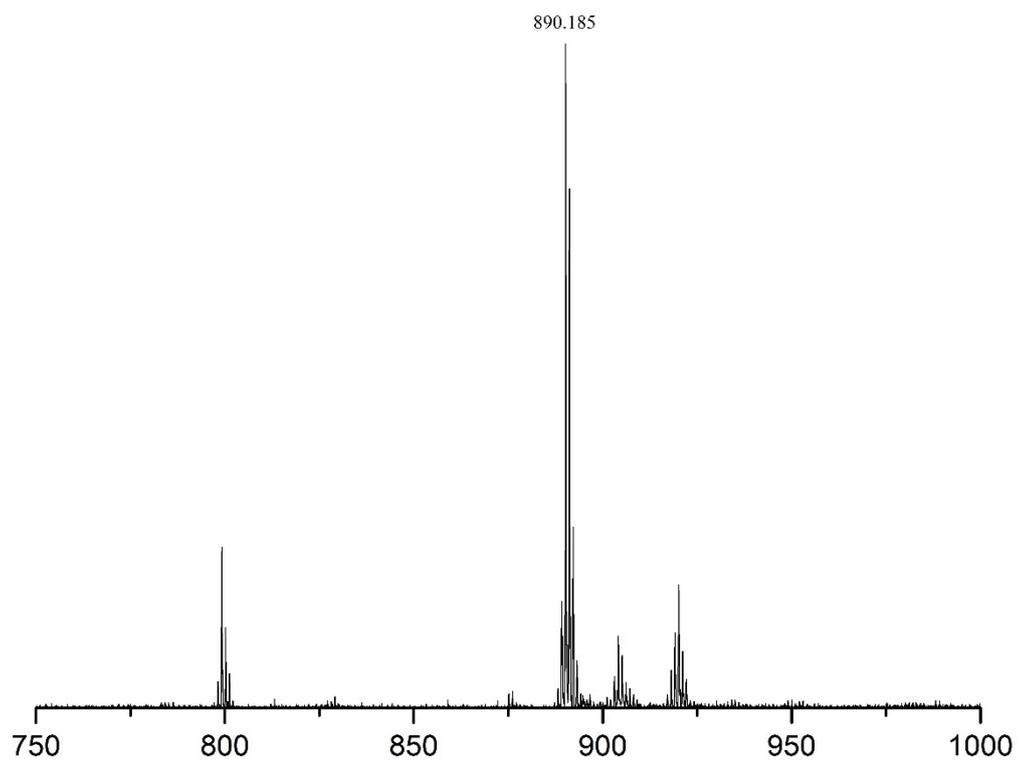
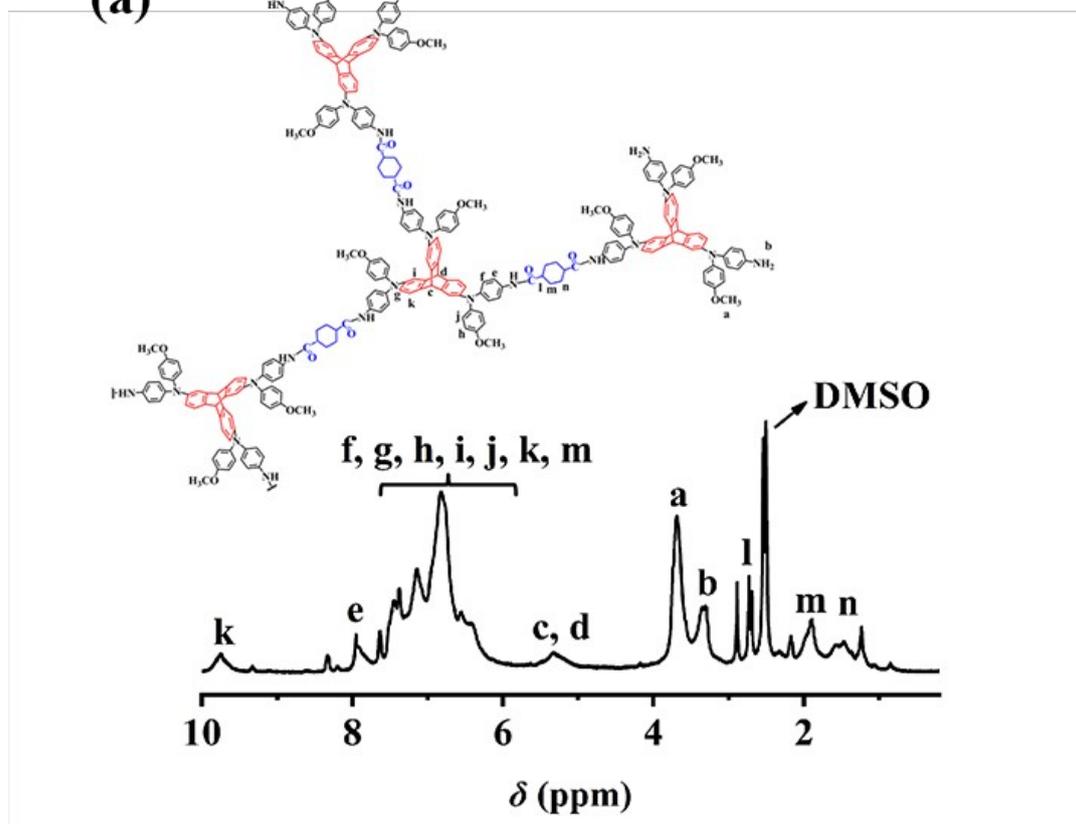
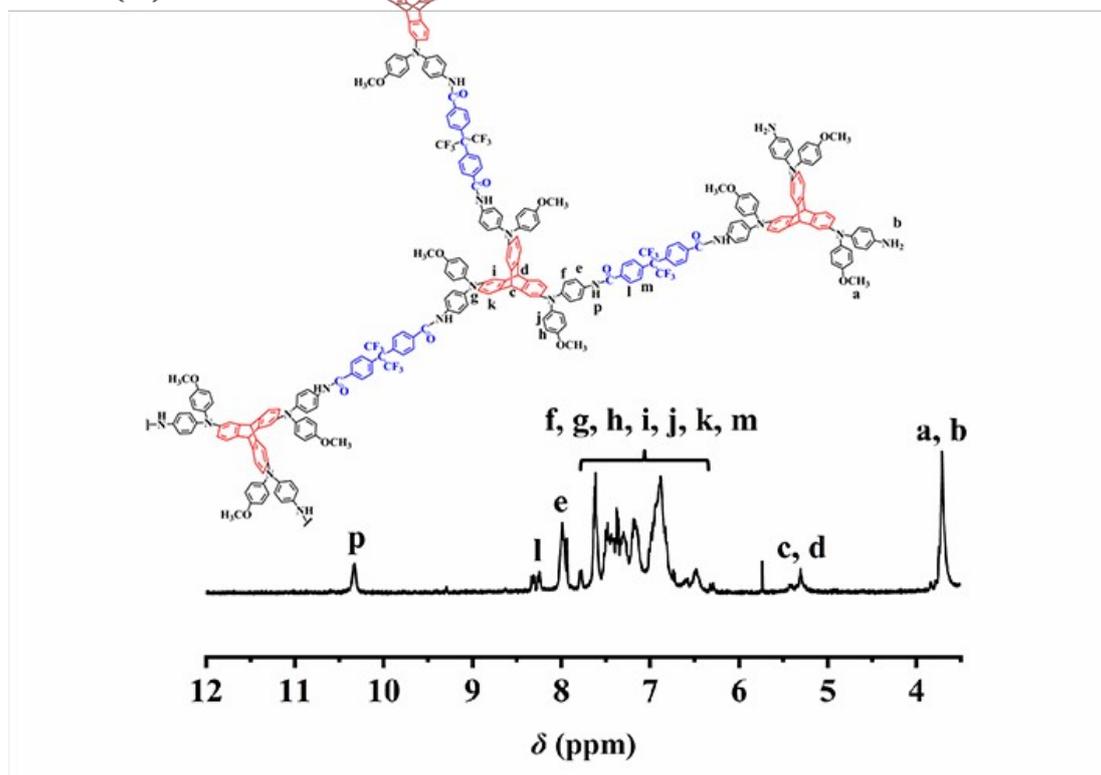


Fig. S3. HRMS (ESI-MS) spectrum of T3TPA.

(a)



(b)



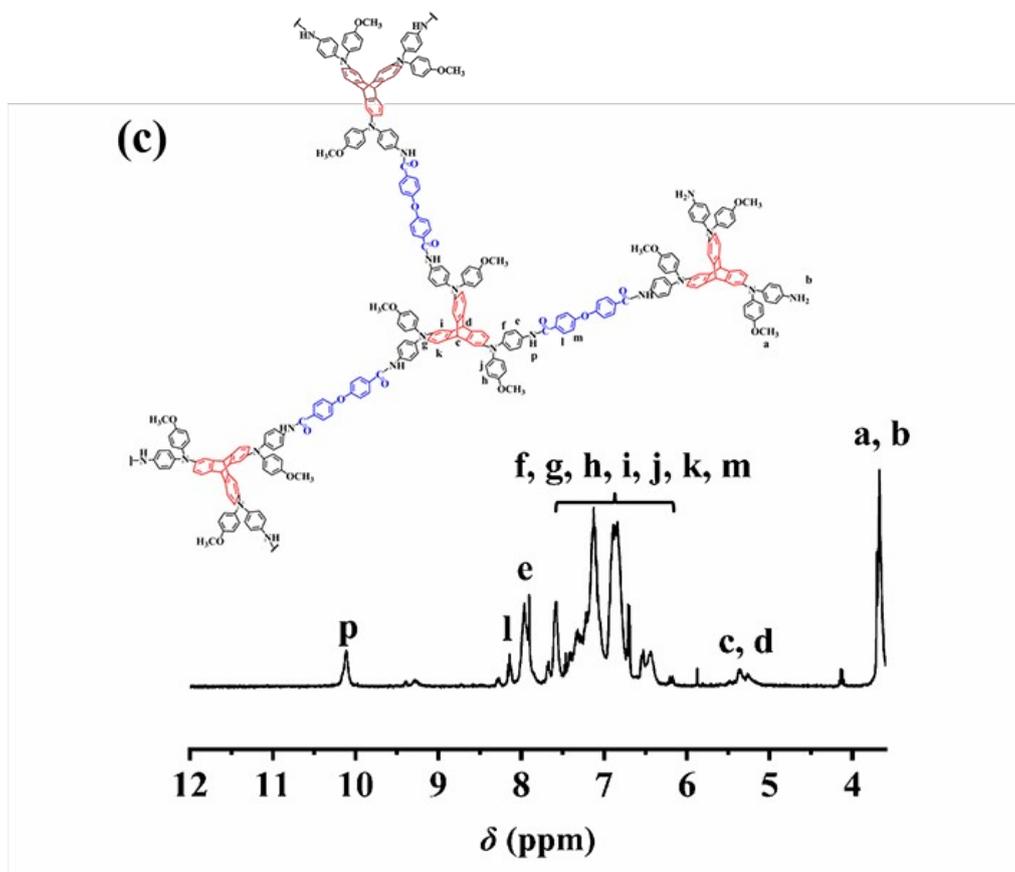
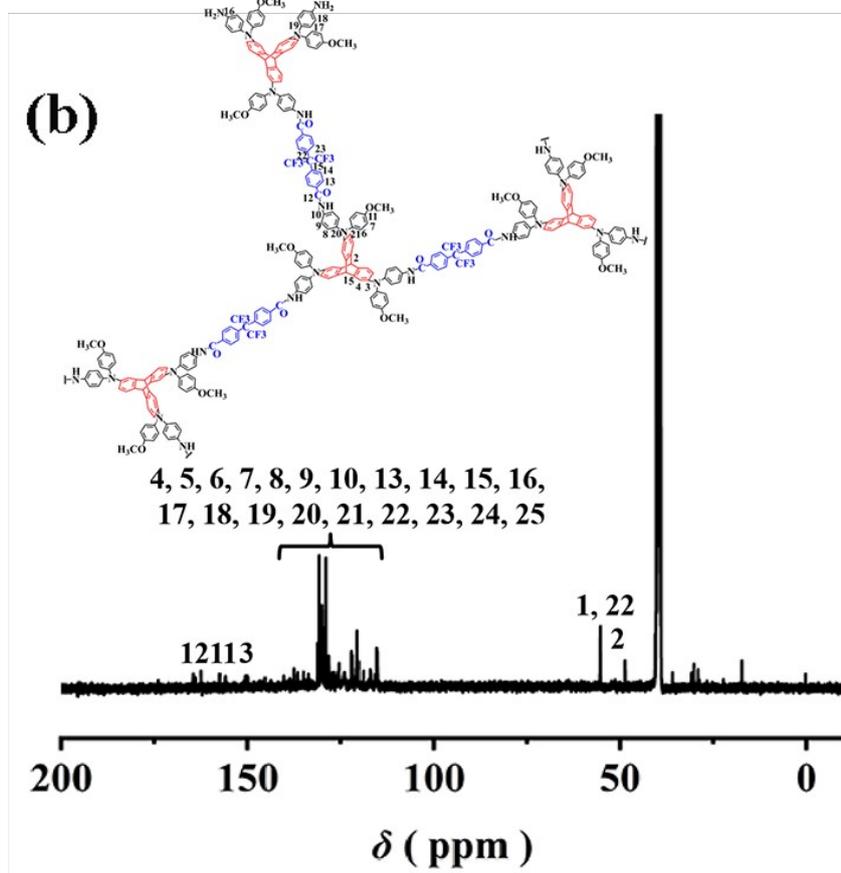
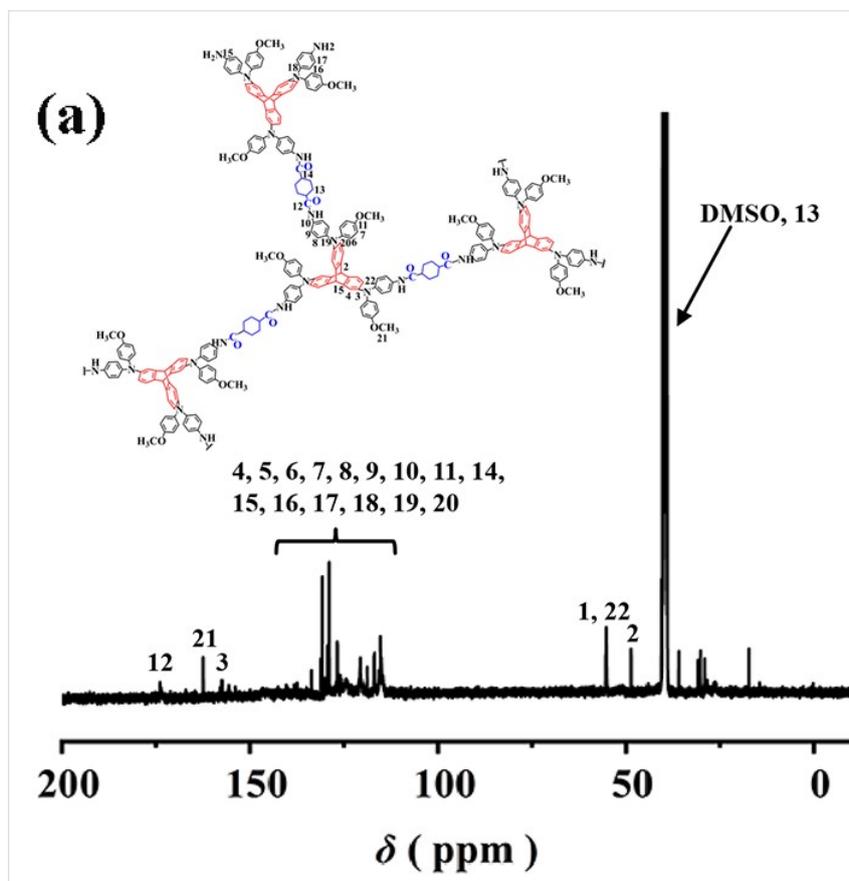


Fig. S4. ^1H NMR spectrum and structure of (a) T3TPA-CA (b) T3TPA-6F (c) T3TPA-OA in $\text{DMSO-}d_6$.



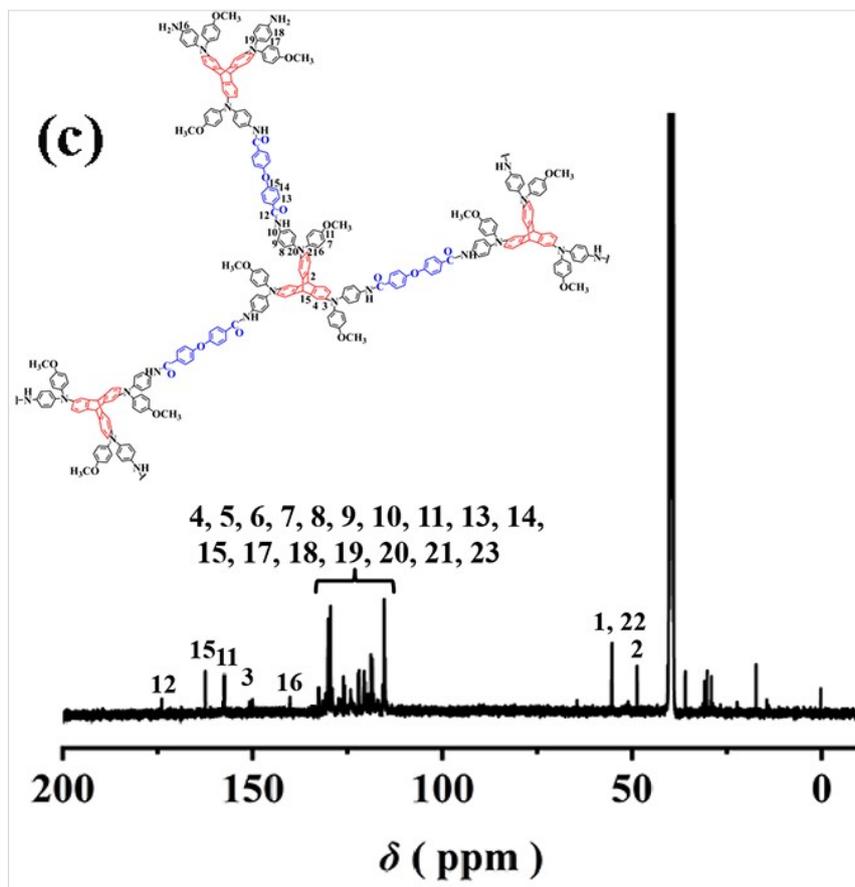


Fig. S5. ^{13}C NMR spectrum and structure of (a) T3TPA-CA (b) T3TPA-6F (c) T3TPA-OA in $\text{DMSO-}d_6$.

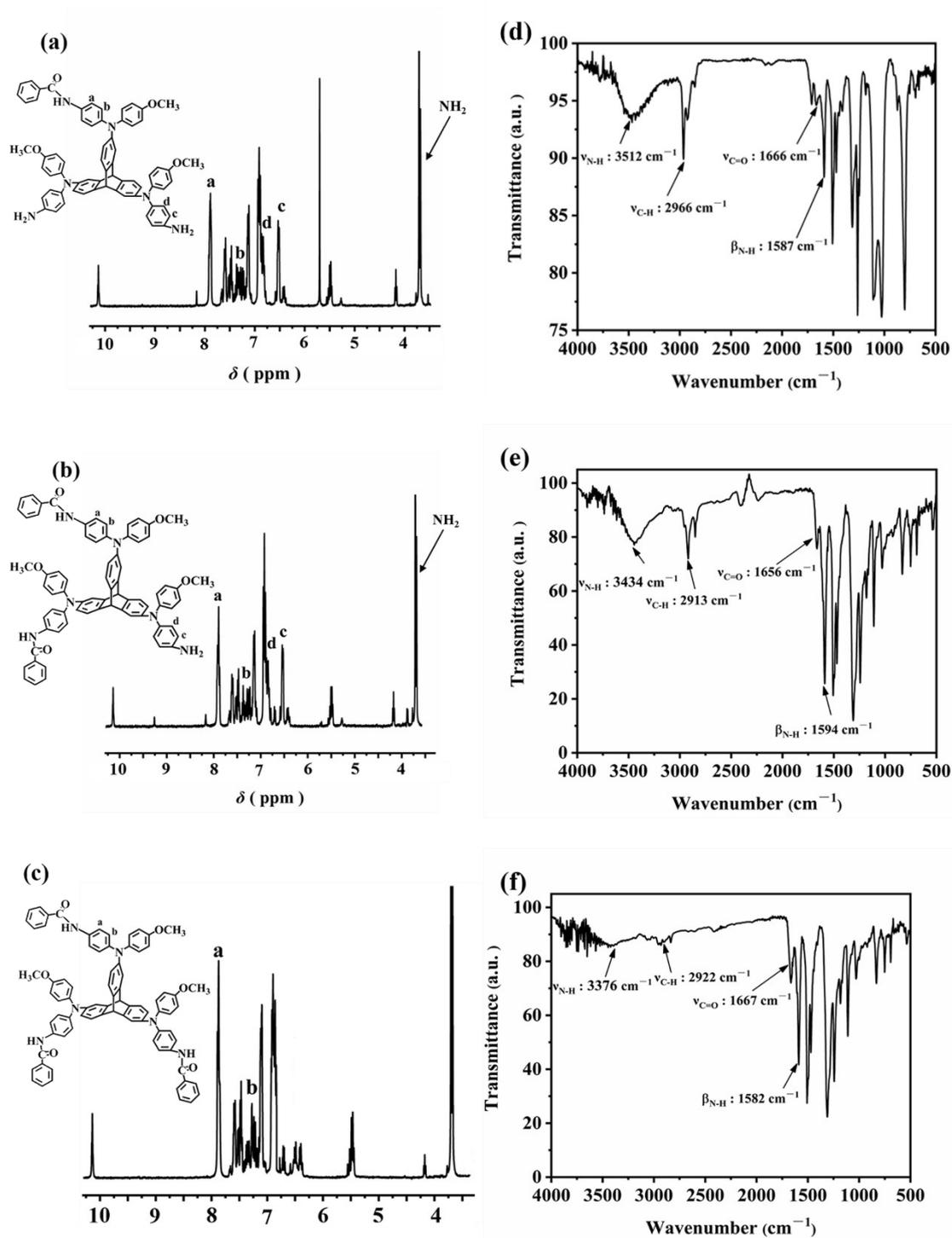


Fig. S6. (a) ^1H NMR spectrum of Model compound 1. (b) ^1H NMR spectrum of Model compound 2. (c) ^1H NMR spectrum of Model compound 3 in DMSO-*d*₆. (d) FTIR spectrum of compound 1. (e) FTIR spectrum of compound 2. (f) FTIR spectrum of compound 3.

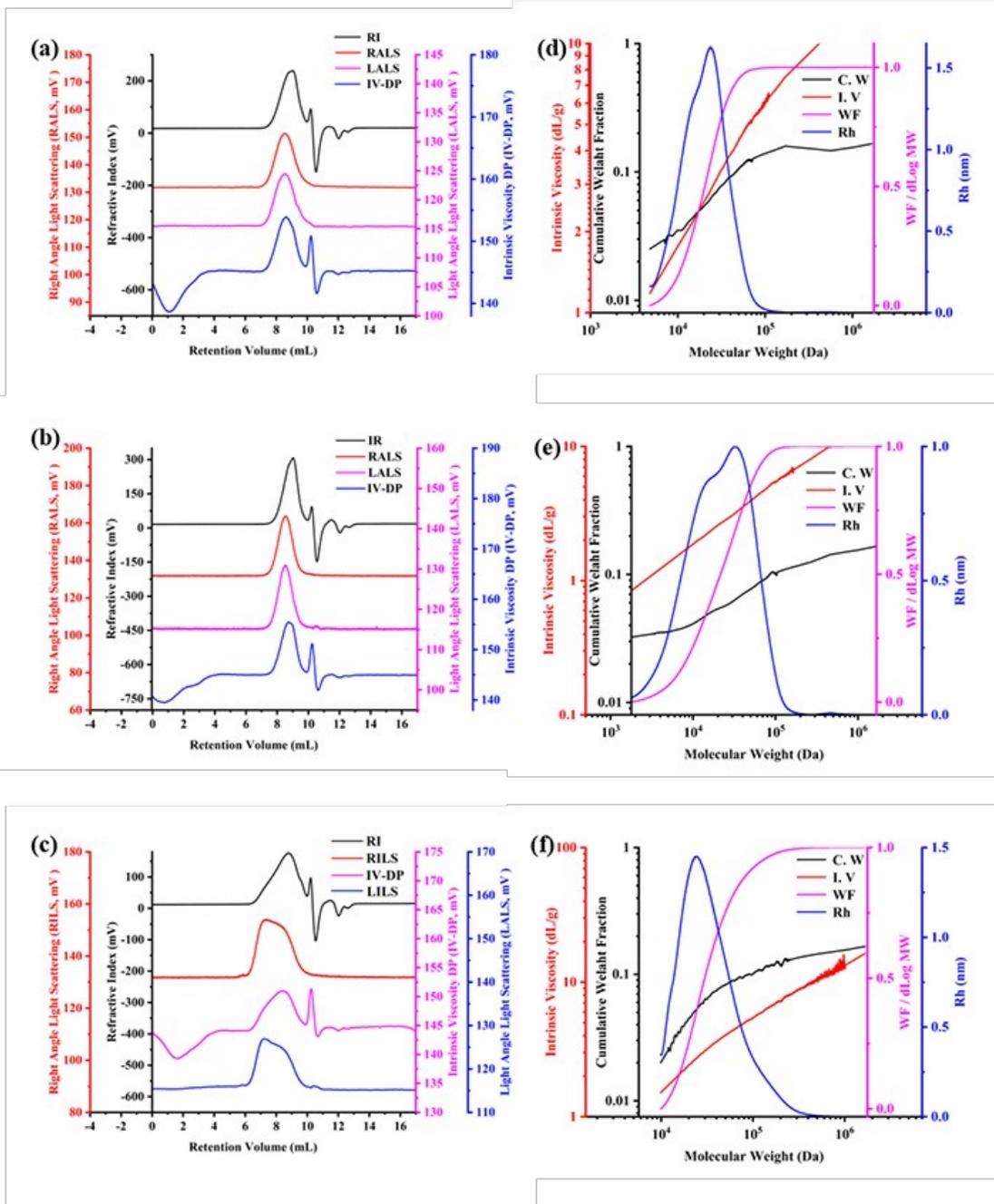


Fig. S7. Results of GPC analysis of (a)(d) T3TPA-CA (b)(e) T3TPA-6F (c)(f) T3TPA-OA solutions at 45 °C with 20mM LiBr in DMF solution as eluent. RI is the refractive index signal, RALS is the right-angle light scattering signal, LALS is the small-angle light scattering signal, and IV-DP is the intrinsic viscous number pressure differential signal.

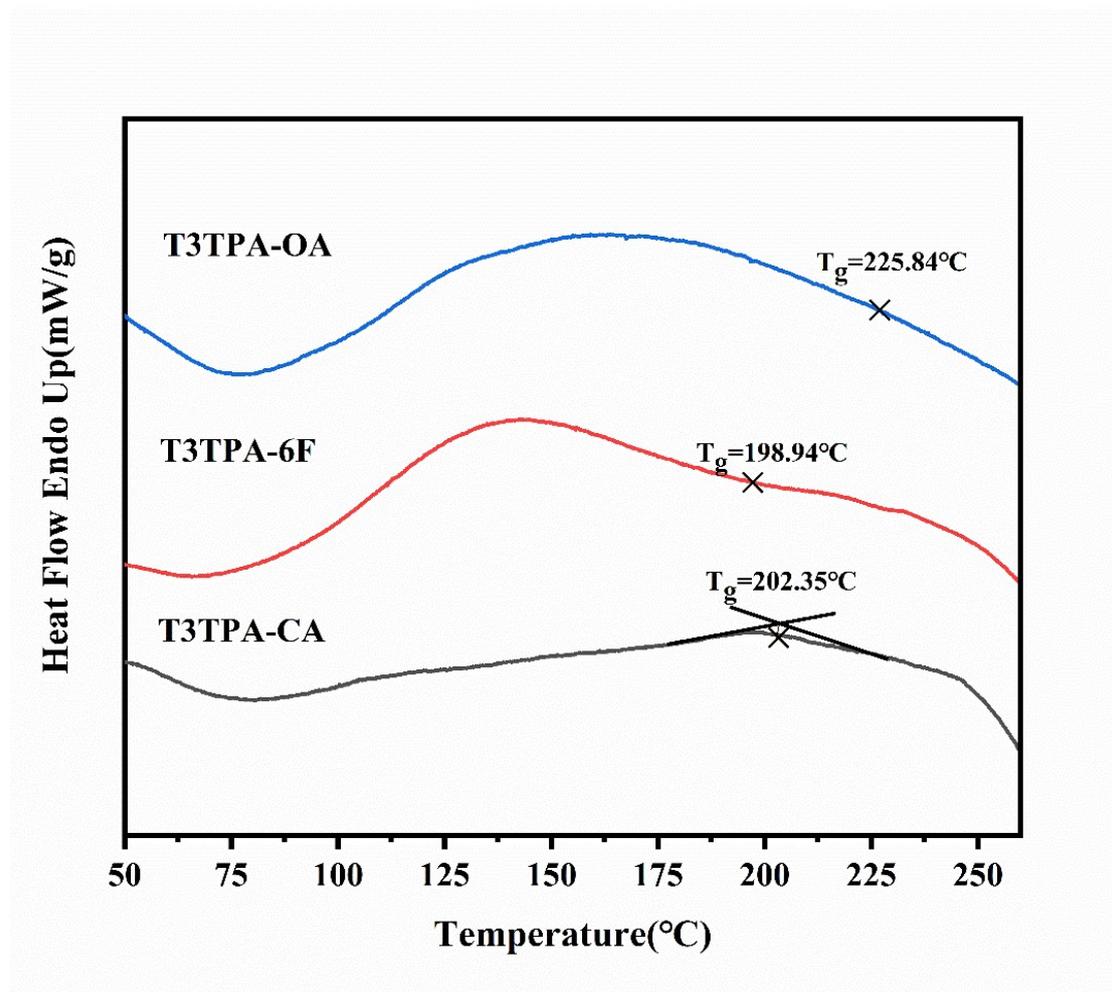


Fig. S8. DSC curves of the HBPAs.

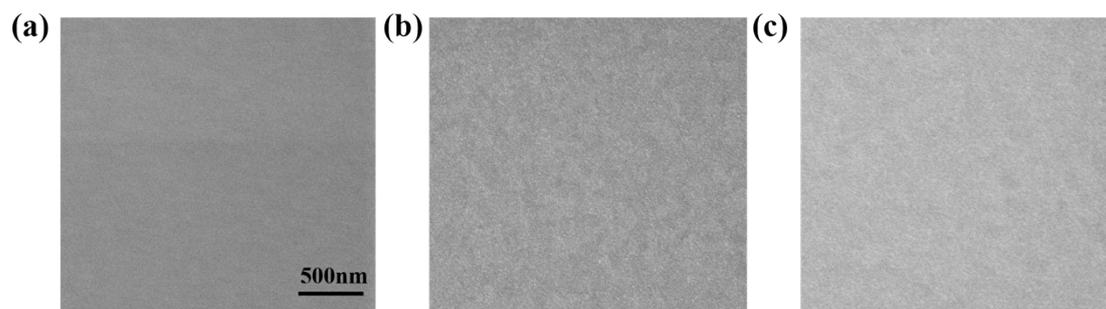


Fig. S9. Top-view SEM images of (a) T3TPA-CA (b) T3TPA-6F (c) and T3TPA-OA polymer films.

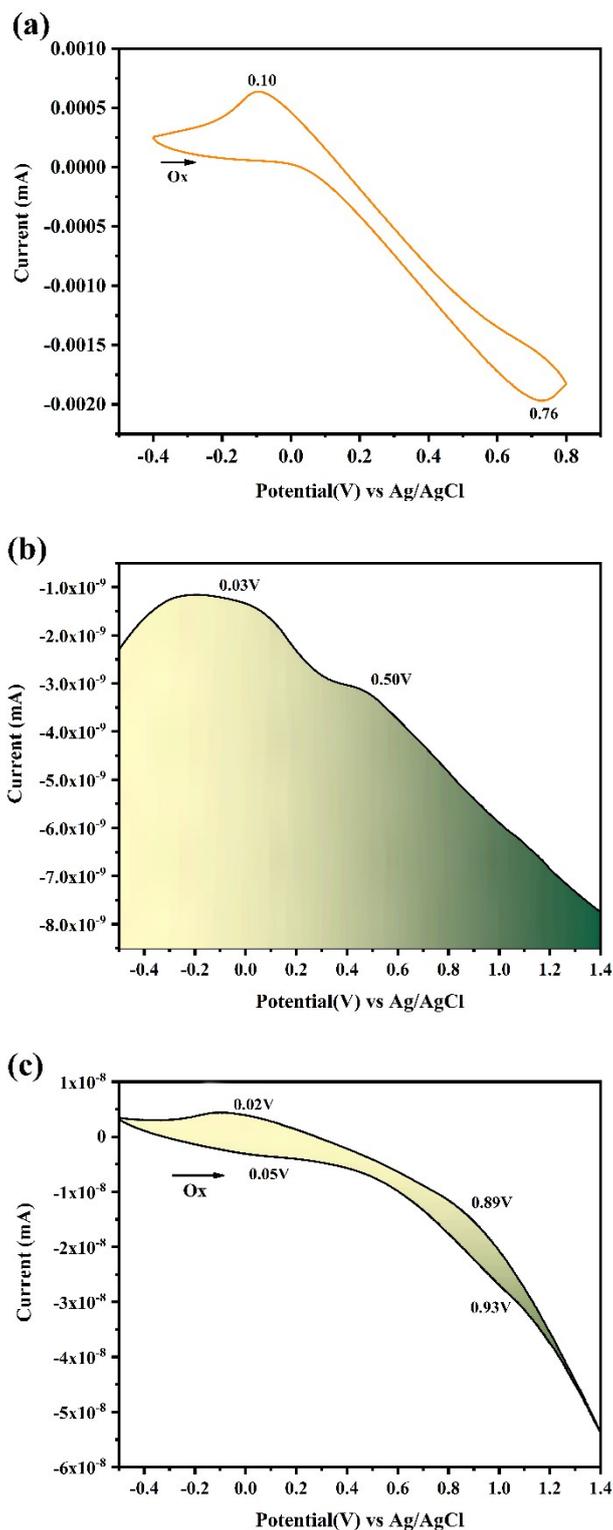


Fig. S10. CV curves of (a) ferrocene which was dissolved in 0.1M LiClO₄/ACN solution at a scan rate of 25 mv s⁻¹; (b) Differential pulse voltammogram curve of T3TPA in 0.1 M of LiClO₄/ACN with a platinum sheet, with a scan rate of 2 mV/s,

the pulse width of 25 ms, pulse period was 0.2 s, and pulse amplitude of 50 mV(c)
 CV curves of T3TPA in microelectrodes in 0.1 M LiClO₄/ACN solution at a scan rate
 of 25 mV s⁻¹.

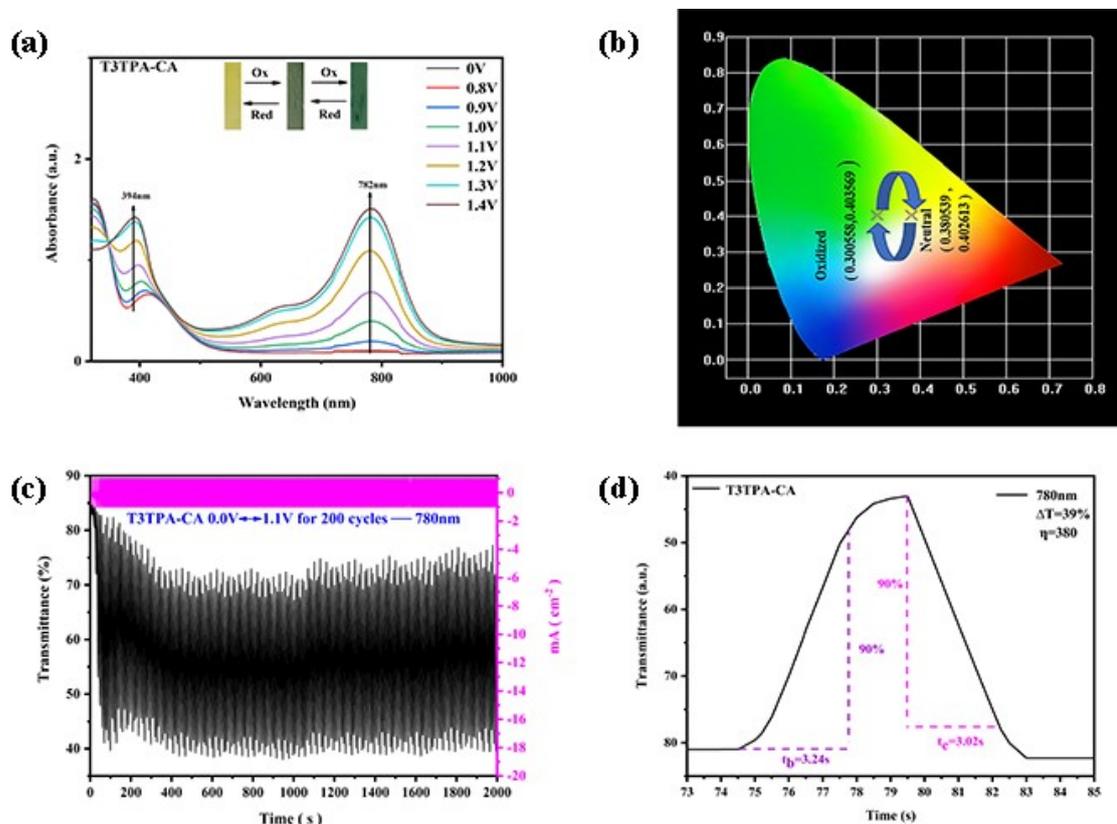


Fig. S11. Electronic absorption spectra (a) of T3TPA-CA thin film in LiClO₄ /ACN solution upon different voltages. (b) The CIE1931 coordinate (X, Y). (c) Dynamic changes of the transmittance and current. (d) Optical switching for T3TPA-CA.

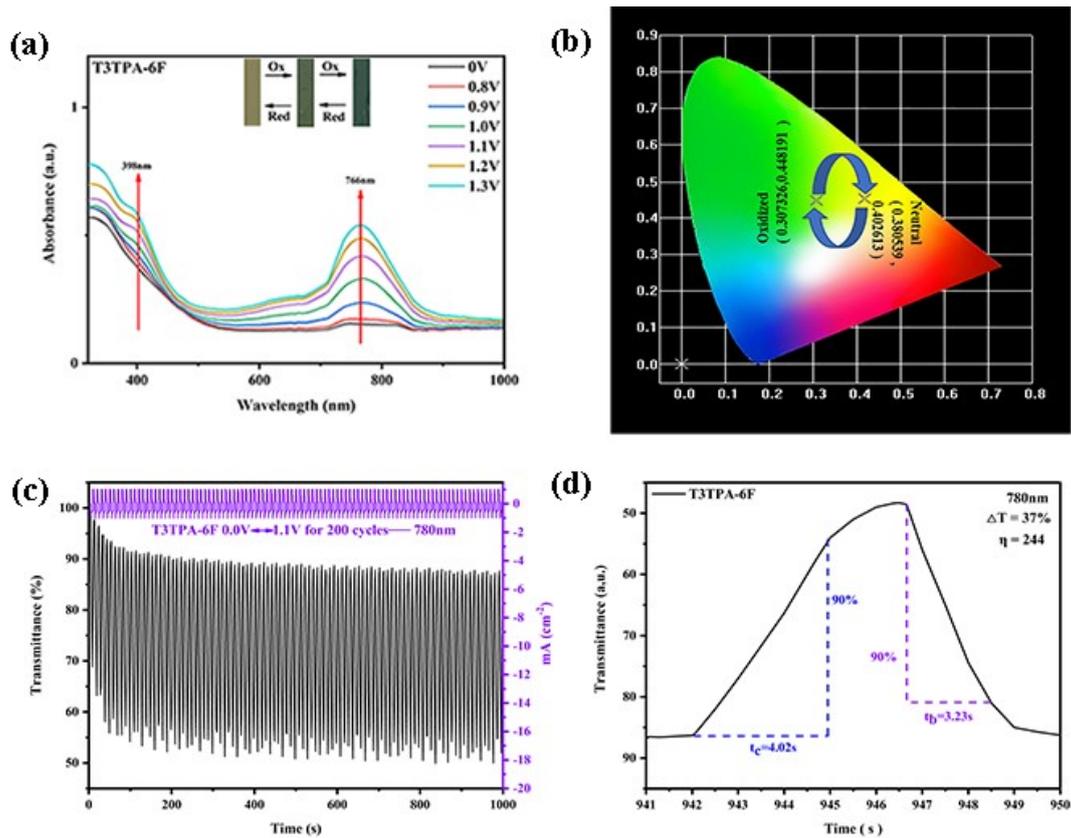


Fig. S12. Electronic absorption spectra (a) of T3TPA-6F thin film in LiClO₄ /ACN solution upon different voltages. (b) The CIE1931 coordinate (X, Y). (c) Dynamic changes of the transmittance and current. (d) Optical switching for T3TPA-6F.

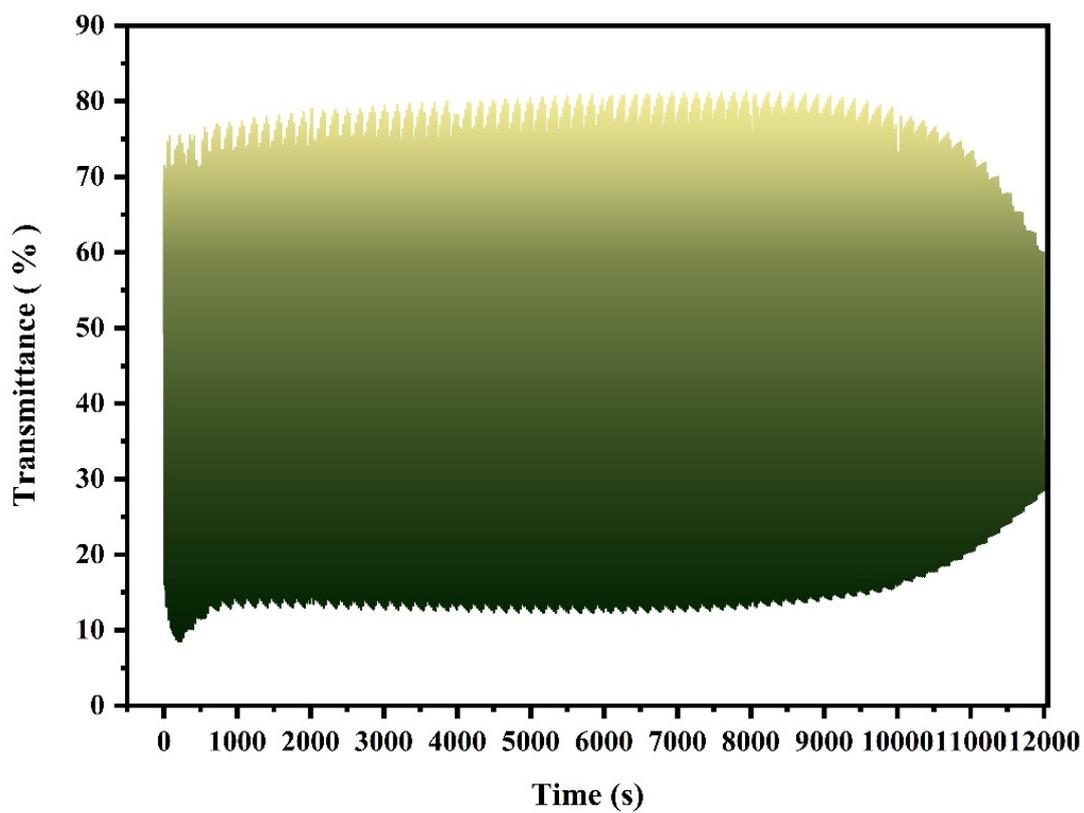


Fig. S13. The transmittance of T3TPA-OA was obtained with a pulse time of 10s, a voltage step between 0.0V-1.0V, and $\lambda_{\text{max}}=780$ nm for 12,000s continuously.

Table S1. Solubility of HBPA_s in different solvents.

HBPA _s Code	Solvent ^a						
	DMSO	DMF	NMP	THF	EAc	CH ₂ Cl ₃	Tol
T3TPA- CA	++	++	++	++	++	+-	+-
T3TPA-6F	++	++	++	+-	++	+-	+-
T3TPA- OA	++	++	++	++	++	+-	+-

^a ++: soluble at room temperature; +-: partially soluble at room temperature, fully soluble when heated to 80 °C; -: partially soluble when heated to 80 °C

Table S2. Photophysical properties of T3TPA-CA in different solvents.

Solvent	n ^a	ϵ^b	$\lambda_{\max}^{\text{abs}}$	$\lambda_{\max}^{\text{em}}$	CIE1931 coordinates	
			(nm) ^c	(nm) ^d	X	Y
Tol	1.5032	2.4	310, 411	578	0.4785	0.4506
DMAc	1.3689	4.4	307, 398	449	0.2339	0.2710
THF	1.4133	7.6	308, 401	520	0.2201	0.3636
NMP	1.4729	32.3	311, 406	442	0.2588	0.3885
DMF	1.3308	37.6	311, 410	451	0.2525	0.3721

^a Refractive index of solvent.

^b Dielectric constant of the solvents.

^c T3TPA-CA $\lambda_{\max}^{\text{abs}}$ for solution states.

^d T3TPA-CA $\lambda_{\max}^{\text{em}}$ for solution states.

Table S3. Summary of GPC results.

Sample name	Da	\overline{M}_n	\overline{M}_w	\overline{M}_z	\overline{M}_p	$\overline{M}_w/\overline{M}_n$	R_h^{\max}/nm
T3TPA-CA		1.68×10^4	2.32×10^4	3.16×10^4	1.57×10^4	1.3	0.9
T3TPA-6F		1.36×10^4	2.81×10^4	4.69×10^4	1.48×10^4	2.0	1.0
T3TPA-OA		2.69×10^4	4.41×10^4	9.59×10^4	2.42×10^4	1.6	1.4