

Supporting Information

Synthesis, Characterization and Electrochromic Property of Novel Redox Triarylamine-based Aromatic Polyethers with Methoxy Protecting Groups

Jung-Tsu Wu,[‡] Yang-Ze Fan[‡] and Guey-Sheng Liou*

Experimental Section

Materials

Tri-*tert*-butylphosphine, acetone nitrile, toluene and *N*-methyl-2-pyrrolidone (NMP) were stored in the glove box; cesium fluoride, sodium *tert*-butoxide, sodium tetrafluoroborate and tetra-*n*-butylammonium bromide were stored in the auto dry box. 4-Bromophenoxy-*tert*-butyldimethylsilane (**Br-Si**), 4-amino-4',4''-dimethoxy-triphenylamine (**TPA-NH₂**), 4,4'-dibromo-4''-methoxytriphenylamine (**TPA-2Br**) and 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole¹ were synthesized follow the previous literature. Tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) was acquired by the following process: Excess saturated sodium tetrafluoroborate aqueous solution was added into a saturated tetra-*n*-butylammonium bromide aqueous solution, the white precipitate was then filtered and recrystallized by ethyl acetate. The other reagents were received from commercial source and used without further purification.

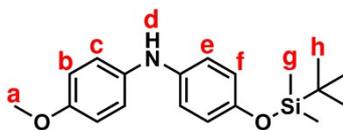
Measurements

Melting point was mainly detected by OptiMelt-Automated Melting Point System at the scan rate of 5°C/min or DSC at the scan rate of 5 °C/min if mentioned. ¹H NMR (500MHz) and ¹³C NMR (125 MHz) spectra were recorded on Bruker AVIII-500MHz FT-NMR. The definition of splitting pattern is carried out as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Fourier transform infrared (FT-IR) spectra were obtained by PerkinElmer Spectrum 100 Model FT-IR spectrometer. Elemental analysis (EA) was run in elemental vario EL cube (for NCSH & O). Electrochemistry was executed with CH Instrument 611B Electrochemical Analyzer or CH Instrument 612C Electrochemical Analyzer. Ultraviolet-visible (UV-Vis) spectra were carried out by Agilent 8453 UV-visible Spectroscopy System. CIELAB data were collected from JASCO V-650 UV-VIS spectrophotometer. Cyclic voltammetry was conducted by using a conventional liquid cell in which measured electrodes (working area about 30 mm×0.7 mm) was used as a working electrode and a platinum wire as an auxiliary electrode against a Ag/AgCl as reference electrode in anhydrous acetonitrile containing 0.1 M of TBABF₄ as supporting electrolyte in nitrogen atmosphere at the scan rate of 50 mV/s. Spectroelectrochemistry was conducted with the same system at the range of 300 and 1100 nm.

Monomer Synthesis

4-(tert-Butyldimethylsilyl-oxy)-N-(4-methoxyphenyl)aniline (DPA-Si):

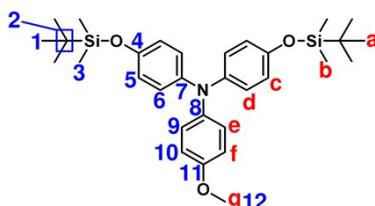
Tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$, 0.37 g, 0.40 mmol) and tri-*tert*-butylphosphine ($\text{P}(t\text{Bu})_3$, 0.20 mL, 0.80 mmol) were added into a 250 mL three-necked round-bottom flask containing 100 mL anhydrous toluene in the glove box. After stirring at room temperature under nitrogen atmosphere for 10 minutes to undergo ligand exchanging, *p*-anisidine (13.06 g, 0.10 mol) was added to the flask sequentially and stirred at 50°C till the *p*-anisidine dissolved completely. **Br-Si** (23.4 g, 80.0 mmol) and sodium *tert*-butoxide (NaOtBu , 11.00 g, 0.11 mol) were then added into the solution and the mixture was stirred at 90°C for 17 hours. After cooling to room temperature, the mixture was extracted with ethyl acetate and water till the water layer was cleared. The organic layer was dried over MgSO_4 and rotary evaporator. The residual was purified by flash column and recrystallized from hexane to obtain 18.3 g of pale orange crystal (69% yield), mp 67°C. FT-IR (KBr, cm^{-1}): $\nu=3375, 3000, 2956, 2928, 2856, 1609, 1506, 1253, 1030, 927, 827$. ^1H NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 7.53 (s, 1 H, H_d), 6.93 (d, $J=9.0$ Hz, 2 H, H_b), 6.85 (d, $J=8.8$ Hz, 2 H, H_f), 6.81 (d, $J=8.9$ Hz, 2 H, H_c), 6.69 (d, $J=8.9$ Hz, 2 H, H_e), 3.69 (s, 3 H, H_a), 0.94 (s, 9 H, H_h), and 0.15 (s, 6 H, H_g).



4,4'-Bis(tert-butyl(dimethyl)silyloxy)-4''-methoxytriphenylamine (TPA-2Si):

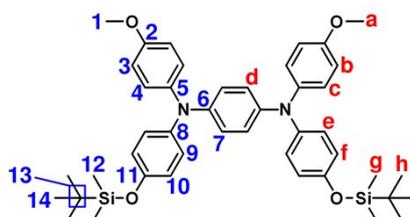
Tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$, 0.88 g, 0.96 mmol) and tri-*tert*-butylphosphine ($\text{P}(t\text{Bu})_3$, 0.390 g, 1.93 mmol) were added into 500 mL three-necked round-bottom flask containing 200 mL anhydrous toluene in the glove box. After stirring at room temperature under nitrogen atmosphere for 10 minutes to undergo ligand exchanging, **Br-Si** (55.3 g, 193 mmol) was added into the solution and stirred

for 15 minutes. *p*-Anisidine (10.7 g, 87.5 mmol) and sodium *tert*-butoxide (12.6 g, 131 mmol) were successively added into the reactor. The solution was then under reflux for 2 hours. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate and washed with brine. The extracted organic layer was dried over MgSO₄ and rotary evaporator to obtain the orange oil. The final product was recrystallized by methanol to give white needle crystal (53% yield), mp 71.3-73.0°C. FT-IR (KBr, cm⁻¹): ν =2927, 2854, 1500, 1250, 1040, 919, 829. ¹H NMR (500 MHz, THF-*d*₈, δ , ppm): 6.92 (d, *J*=7.2 Hz, 2 H, H_f), 6.85 (d, *J*=7.1 Hz, 4 H, H_c), 6.78 (d, *J*=7.2 Hz, 2 H, H_e), 6.69 (d, *J*=7.1 Hz, 4 H, H_d), 3.72 (s, 3 H, H_g), 0.99 (s, 18 H, H_a), 0.19 (s, 12H, H_b). ¹³C NMR (125 MHz, THF-*d*₈, δ , ppm): 156.7 (C₁₁), 151.7 (C₄), 143.7 (C₇), 142.9 (C₈), 126.4 (C₉), 125.4 (C₆), 121.3 (C₅), 115.5 (C₁₀), 55.7 (C₁₂), 26.3 (C₁), 19.0 (C₂), -4.2 (C₃).



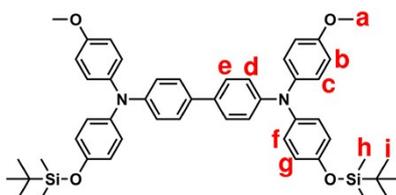
N,N'-Bis(4-*tert*-butyldimethylsilyl-phenoxy)-*N,N'*-bis(4-methoxyphenyl)-1,4-phenylenediamine (TPPA-2Si): Palladium(II) acetate (Pd(OAc)₂, 90 mg, 0.40 mmol) and tri-*tert*-butylphosphine (P(*t*Bu)₃, 0.090 mL, 0.33 mmol) were added into a 50 mL round-bottom flask containing 20 mL anhydrous toluene in the glove box. After stirring at room temperature under nitrogen atmosphere for 30 minutes to undergo the ligand exchange, **DPA-Si** (6.87 g, 20.8 mmol), 1,4-bromobenzene (2.36 g, 10.0 mmol) and sodium *tert*-butoxide (NaOtBu, 2.40 g, 25.0 mmol) were added into the container sequentially and then the solution was refluxed for 4 hours. After cooling to room temperature, the mixture was extracted with water and dichloromethane till the

water phase was cleared. The organic layer was dried over MgSO₄ and poured into methanol and recrystallized by ethyl acetate/methanol to obtain 4.83 g of yellow schist crystal (66% yield), mp 190-191°C (measure by DSC with the scan rate of 5°C/min). FT-IR (KBr, cm⁻¹): ν =2953, 2859, 1602, 1499, 1241, 1038, 915, 826. ¹H NMR (500 MHz, THF-*d*₈, δ , ppm): 6.97 (d, *J*=9.0 Hz, 4 H, H_b), 6.90 (d, *J*=8.8 Hz, 4 H, H_f), 6.80-6.78 (m, 8 H, H_{d+c}), 6.71 (d, *J*=8.9 Hz, 4 H, H_e), 3.73 (s, 6 H, H_a), 0.99 (s, 18 H, H_h), 0.20 (s, 12 H, H_g). ¹³C NMR (125 MHz, THF-*d*₈, δ , ppm): 156.9 (C₂), 151.9 (C₁₁), 143.9 (C₆), 143.4 (C₈), 142.5 (C₅), 126.8 (C₃), 125.8 (C₁₀), 124.2 (C₇), 121.4 (C₉), 115.5 (C₄), 55.7 (C₁), 26.3 (C₁₄), 19.0 (C₁₃), -4.2 (C₁₂). Anal. calcd for C₄₄H₅₆N₂O₄Si₂ (733.10): C 72.09, H 7.70, N 3.82; found: C 71.79, H 7.62, N 3.84.



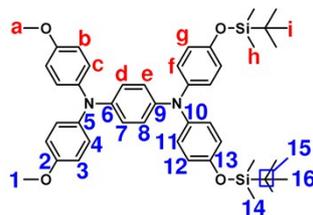
N,N'-Bis(4-*tert*-butyldimethylsilyl-phenoxy)-*N,N'*-bis(4-methoxyphenyl)-1,1'-biphenyl-4,4'-diamine (TPB-2Si): Palladium(II) acetate (Pd(OAc)₂, 90 mg, 0.40 mmol) and tri-*tert*-butylphosphine (P(*t*Bu)₃, 0.09 mL, 0.33 mmol) were added into a 50 mL round-bottom flask containing 20 mL anhydrous toluene in the glove box. After stirring at room temperature under nitrogen atmosphere for 30 minutes to undergo the ligand exchange, **DPA-Si** (6.87 g, 20.8 mmol), 4,4'-dibromo-1,1'-biphenyl (3.13 g, 10.0 mmol) and sodium *tert*-butoxide (NaO*t*Bu, 2.40 g, 25.0 mmol) were added into the container sequentially and then the solution was refluxed for 4 hours. After cooling to room temperature, the mixture was extracted with water and dichloromethane till the water phase was cleared. The organic layer was dried over MgSO₄ and poured into hot methanol and recrystallized by ethyl acetate/methanol to obtain 5.74 g of pale

yellow powder (71% yield), mp 144-146°C. FT-IR (KBr, cm^{-1}): $\nu=2928, 2856, 1605, 1501, 1241, 1038, 914, 822$. ^1H NMR (500 MHz, THF- d_8 , δ , ppm) 7.36 (d, $J=8.7$ Hz, 4 H, H_e), 7.02 (d, $J=8.9$ Hz, 4 H, H_b), 6.96 (d, $J=8.8$ Hz, 4 H, H_g), 6.92 (d, $J=8.6$ Hz, 4 H, H_d), 6.83 (d, $J=8.9$ Hz, 4 H, H_c), 6.76 (d, $J=8.8$ Hz, 4 H, H_f), 3.75 (s, 6 H, H_a), 1.00 (s, 18 H, H_i), 0.21 (s, 12 H, H_h).



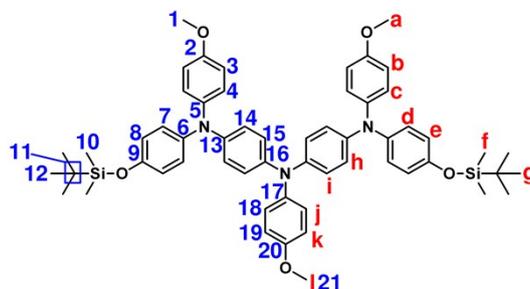
N,N-Bis(4-*tert*-butyldimethylsilyl-phenoxy)-*N',N'*-bis(4-methoxyphenyl)-1,4-phenylenediamine (STPPA-2Si): Tris(dibenzylideneacetone)dipalladium(0) ($\text{Pd}_2(\text{dba})_3$, 0.093 g, 0.10 mmol) and tri-*tert*-butylphosphine ($\text{P}(t\text{Bu})_3$, 0.05 mL, 0.20 mmol) were added into a 50 mL round-bottom flask containing 20 mL anhydrous toluene in the glove box. After stirring at room temperature under nitrogen atmosphere for 10 minutes to undergo the ligand exchange, **TPA-NH₂** (0.74 g, 2.3 mol), **Br-Si** (1.4 g, 5.0 mol) and sodium *tert*-butoxide (NaOtBu , 1.4 g, 14.0 mol) were then added into the solution. The mixture was stirred at reflux temperature for 12 hours and then extracted with ethyl acetate and water till the water layer was cleared. The organic layer was dried over MgSO_4 and rotary evaporator. The residual was purified by flash column and precipitated from methanol to obtain 1.1 g of pale orange powder (64% yield), mp 150-152°C. FT-IR (KBr, cm^{-1}): $\nu=2926, 2854, 1633, 1499, 1243, 911, 825$. ^1H NMR (500 MHz, THF- d_8 , δ , ppm): 6.96 (d, $J=7.2$ Hz, 4 H, H_b), 6.90 (d, $J=7.1$ Hz, 4 H, H_g), 6.80-6.78 (m, 8 H, H_{d+e+c}), 6.71 (d, $J=7.1$ Hz, 2 H, H_f), 3.72 (s, 6 H, H_a), 0.99 (s, 18 H, H_i), 0.19 (s, 12 H, H_h). ^{13}C NMR (125 MHz, THF- d_8 , δ , ppm): 156.8 (C₂), 152.0 (C₁₃), 144.4 (C₆), 143.5 (C₉), 143.3 (C₅), 142.6

(C₁₀), 126.6 (C₃), 126.0 (C₁₂), 124.7 (C₇), 123.7 (C₈), 121.4 (C₁₁), 115.5 (C₄), 55.7 (C₁), 26.3 (C₁₆), 19.0 (C₁₅), -4.2 (C₁₄). Anal. calcd for C₄₄H₅₆N₂O₄Si₂ (733.10): C 72.09, H 7.70, N 3.82; found: C 72.02, H 7.75, N 3.86.



N,N'-Bis(4-*tert*-butyldimethylsilyl-phenoxy)-*N,N'*-bis(4-methoxyphenyl)-4-methoxytriphenylamine (BDATPA-2Si): Palladium(II) acetate (Pd(OAc)₂, 0.01 g, 0.06 mmol) and tri-*tert*-butylphosphine (P(*t*Bu)₃, 0.02 g, 0.1 mmol) were added into a 250 mL round-bottom flask containing 100 mL anhydrous toluene in the glove box and stir at room temperature for 30 minutes to undergo ligand exchange. Then, the **TPA-2Br** (10.8 g, 25.0 mmol) was added into the reaction and stirred for 15 minutes. **DPA-Si** (18.1 g, 55.0 mmol) and sodium *tert*-butoxide (NaOtBu, 7.9 g, 82.5 mmol) were successively added into the reactor. The solution was stirred at reflux temperature for 15 hours. After cooling to room temperature, the reaction mixture was diluted with chloroform and washed with brine, and the solvent was removed few amount under reduced pressure. After that the solution precipitated into methanol. The ethyl acetate was used as the recrystallization solvent and 1.8 g of final product was obtained as pale yellow crystals (79% yield), mp 268-270°C. FT-IR (KBr, cm⁻¹): ν =2933, 2857, 1502, 1242, 1040, 922, 830. ¹H NMR (500 MHz, THF-*d*₈, δ , ppm): 7.01 (d, *J*=8.9 Hz, 2 H, H_k), 6.97 (d, *J*=9.0 Hz, 4 H, H_b), 6.90 (d, *J*=8.9 Hz, 4 H, H_e), 7.84 (d, *J*=9.0 Hz, 4 H, H_i), 6.81-6.78 (m, 10 H, H_{c+h+j}), 6.71 (d, *J*=8.9 Hz, 4 H, H_d), 3.72 (s+s, *J*=1.3 Hz, 9 H, H_{a+l}), 0.99 (s, 18 H, H_g), 0.19 (s, 12 H, H_f). ¹³C NMR (125 MHz, THF-*d*₈, δ , ppm): 157.1 (C₂₀), 157.0 (C₂), 152.0 (C₉), 144.2 (C₆), 143.5 (C₁₃), 143.4 (C₁₆), 142.5 (C₅),

142.3 (C₁₇), 127.0 (C₁₉), 126.8 (C₃), 125.9 (C₈), 124.7 (C₁₅), 124.0 (C₁₄), 121.4 (C₇), 115.5 (C₄₊₁₈), 157.1 (C₂₀), 55.7 (C₁₊₂₁), 26.3 (C₁₂), 19.0 (C₁₁), -4.2 (C₁₀). Anal. calcd for C₅₇H₆₇N₃O₅Si₂ (930.33): C 73.59, H 7.26, N 4.52; found: C 73.79, H 7.31, N 4.49.



Polymer Synthesis

To a 50 mL round-bottom flask was added CsF (2.3 mmol) and dried at 150°C for 3 hours under the vacuum system. After cooling to the room temperature, different disilyl ether monomer (1.0 mmol) and 15 wt% anhydrous NMP were added into the flask and the temperature was increased to 120°C for 3 hours. Then, bis(4-fluorophenyl)sulfone or 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (1.0 mmol) was added into the mixture, respectively, the temperature was further raised to 180°C for 12 hours with stirring. The obtained polymer solution was cooled to room temperature and slowly poured into methanol, then the precipitate polymer was further purified by using Soxhlet extractor for 24 hours and dried over vacuum system at 150°C.

TPA-PES: FT-IR (KBr, cm⁻¹): ν =3062, 1607, 1492, 1226, 845, 745, 639, 511. ¹H NMR (500 MHz, THF-*d*₈, δ , ppm): 7.84 (d, J =4.1 Hz, 4 H), 7.06-6.85 (m, 16 H), 3.73 (s, 3 H).

TPPA-PES: FT-IR (KBr, cm⁻¹): ν =3038, 2834, 1586, 1497, 1241, 1152, 1107, 1034, 831, 580. ¹H NMR (500 MHz, THF-*d*₈, δ , ppm): 7.83 (d, J =3.6 Hz, 4 H), 7.03-6.83 (m, 24 H), 3.72 (s, 6 H).

STPPA-PES: FT-IR (KBr, cm^{-1}): $\nu=3038, 2926, 2834, 1587, 1498, 1239, 1151, 1107, 1035, 829, 580$. ^1H NMR (500 MHz, THF- d_8 , δ , ppm): 7.84 (d, $J=4.3$ Hz, 4 H), 7.08-6.79 (m, 24 H), 3.71 (s, 6 H).

TPB-PES: FT-IR (KBr, cm^{-1}): $\nu=3037, 2926, 2835, 1586, 1488, 1239, 1150, 1106, 829, 578$. ^1H NMR (500 MHz, THF- d_8 , δ , ppm): 7.85 (d, $J=4.3$ Hz, 4 H), 7.40 (d, $J=3.8$ Hz, 4 H), 7.07-6.85 (m, 24 H), 3.73 (s, 6 H).

BDATPA-PES: FT-IR (KBr, cm^{-1}): $\nu=3037, 2931, 2833, 1586, 1499, 1240, 1150, 1106, 1035, 827, 576$. ^1H NMR (500 MHz, THF- d_8 , δ , ppm): 7.82 (d, $J=4.4$ Hz, 4 H), 7.04-6.79 (m, 32 H), 3.71 (s, 9 H).

TPA-PEOX: FT-IR (KBr, cm^{-1}): $\nu=3032, 2831, 1611, 1487, 1405, 1237, 1169, 880, 840$. ^1H NMR (500 MHz, THF- d_8 , δ , ppm): 8.07 (d, $J=3.7$ Hz, 4 H), 7.13-6.87 (m, 16 H), 3.75 (s, 3 H).

TPPA-PEOX: FT-IR (KBr, cm^{-1}): $\nu=3039, 2924, 2834, 1613, 1487, 1240, 1036, 830, 541$. ^1H NMR (500 MHz, THF- d_8 , δ , ppm): 8.05 (s, 4 H), 7.11-6.86 (m, 24 H), 3.74 (s, 6 H).

TPB-PEOX: FT-IR (KBr, cm^{-1}): $\nu=3037, 2928, 2834, 1610, 1489, 1241, 1036, 824, 747, 586, 520$. ^1H NMR (500 MHz, THF- d_8 , δ , ppm): 8.08 (s, 4 H), 7.44 (s, 4 H), 7.13-6.88 (m, 24 H), 3.75 (s, 6 H).

BDATPA-PES: FT-IR (KBr, cm^{-1}): $\nu=3036, 2929, 2834, 1612, 1500, 1240, 1035, 827, 542$. ^1H NMR (500 MHz, THF- d_8 , δ , ppm): 8.04 (s, 4 H), 7.05-6.69 (m, 32 H), 3.773 (s, 9 H).

Preparation of the Films

Polyether films: The solutions of **PESs** and **PEOXs** in CHCl_3 were casted onto the glass substrates, respectively, and dried at room temperature for 12 hours with a controlled vacuum degree and then 120°C for 8 hours under a high vacuum degree. The obtained films were used for further measurements.

Electrochromic films: 400 μL solutions of these polyethers in *o*-dichlorobenzene (2 mg/1 c.c.) were casted onto the ITO-coated glass substrates ($4\times 3\text{ cm}^2$) and dried at 100°C in nitrogen atmosphere for 8 hours and then 150°C for 5 hours under vacuum. The obtained glass was then cut into a size of $4\times 1\text{ cm}^2$.

Result and Discussion

First, for **TPA-PEOX**, the colour changed from colourless to a cyan colour when the applied potentials increased positively from 0.00 to 0.95 V, and the absorption peak at 752 nm grew up intensely as shown in Fig. S36a and S36e. **TPPA-PEOX** revealed two colour changes related to the oxidation states. When the applied potentials increased positively from 0.00 to 0.75 V, the peak of the characteristic absorption at 337 nm decreased gradually while three new peaks grew up at 415, 568, and 955 nm with the colour change from colourless to yellowish green. Then, the peaks at 415 and 955 nm decreased gradually while a broad peak grew up at 772 nm as potential was adjusted to 1.00 V, corresponding to the second oxidation state, became a blue colour depicted in Fig. S36b and S36f. For **TPB-PEOX**, the peak of the characteristic absorption at 349 nm decreased gradually while two new peaks grew up at 482 and 710 nm during the first oxidation stage when the applied potential increased positively from 0.00 to 0.80 V, and the colour change from colourless to light orange. As the

potential was adjusted to 1.00 V, corresponding to the second oxidation state, enhanced absorption over the visible light region and a broad band with peak at 878 nm could be observed, and the colour changed into a blue colour as illustrated in Fig. S36c and 36g. Finally, **BDATPA-PEOX** exhibited a three stage colour changes. The peak of the characteristic absorption at 332 nm decreased gradually while four new peaks grew up at 438, 539, 808 nm, and a IV-CT broad band in the near-infrared (NIR) region during the first oxidation stage when the applied potentials increased positively from 0.00 to 0.65 V with the colour change from colourless to a yellowish green. Then, peak at 438 nm decreased meanwhile the absorption at peak 539 nm and IV-CT band grew up with a shifting to 559 and 1050 nm, and colour-changing to purple, respectively, as potential was adjusted to 0.90 V related to the second oxidation state. Afterwards, colour changed to deep blue colour with a broad absorption band peak at 805 nm in the final oxidation state as shown in Fig. S36d and S36h.

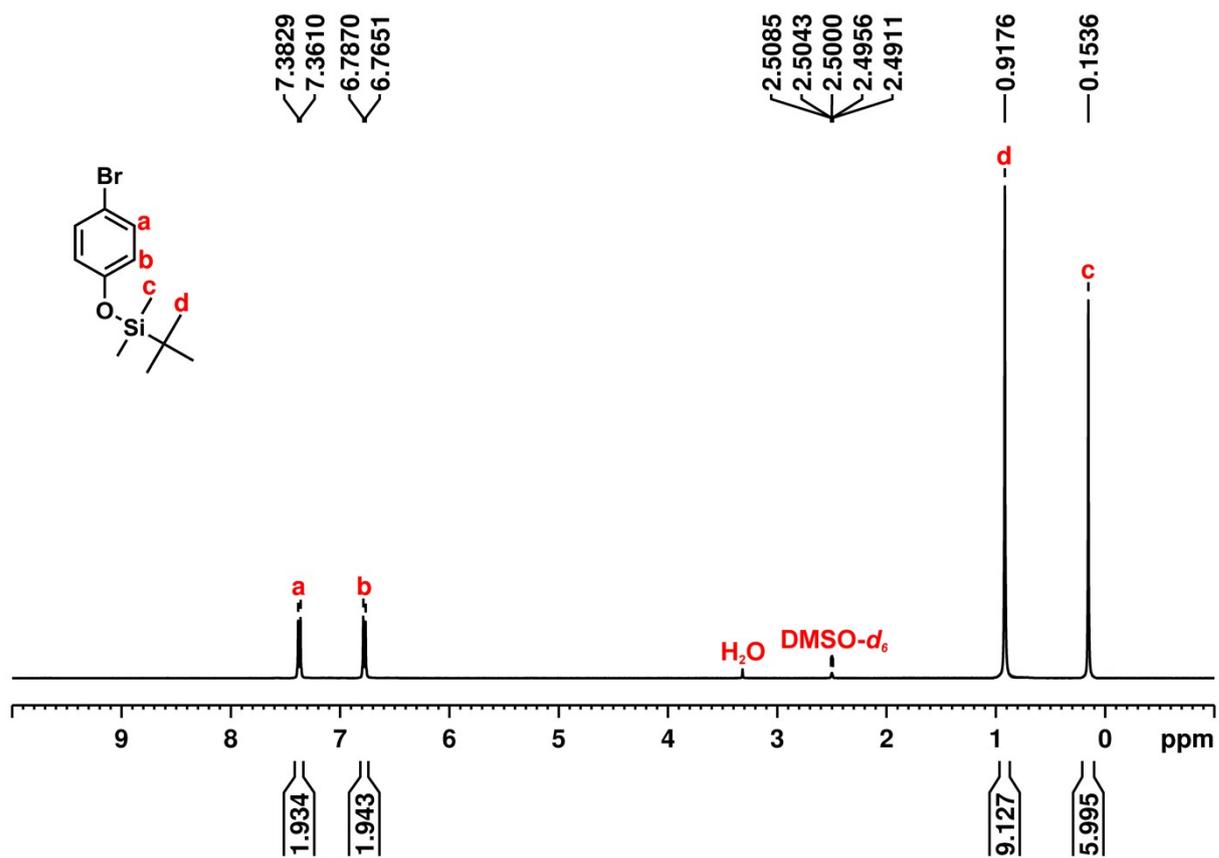


Fig. S1. ^1H NMR spectrum of **Br-Si** in $\text{DMSO-}d_6$.

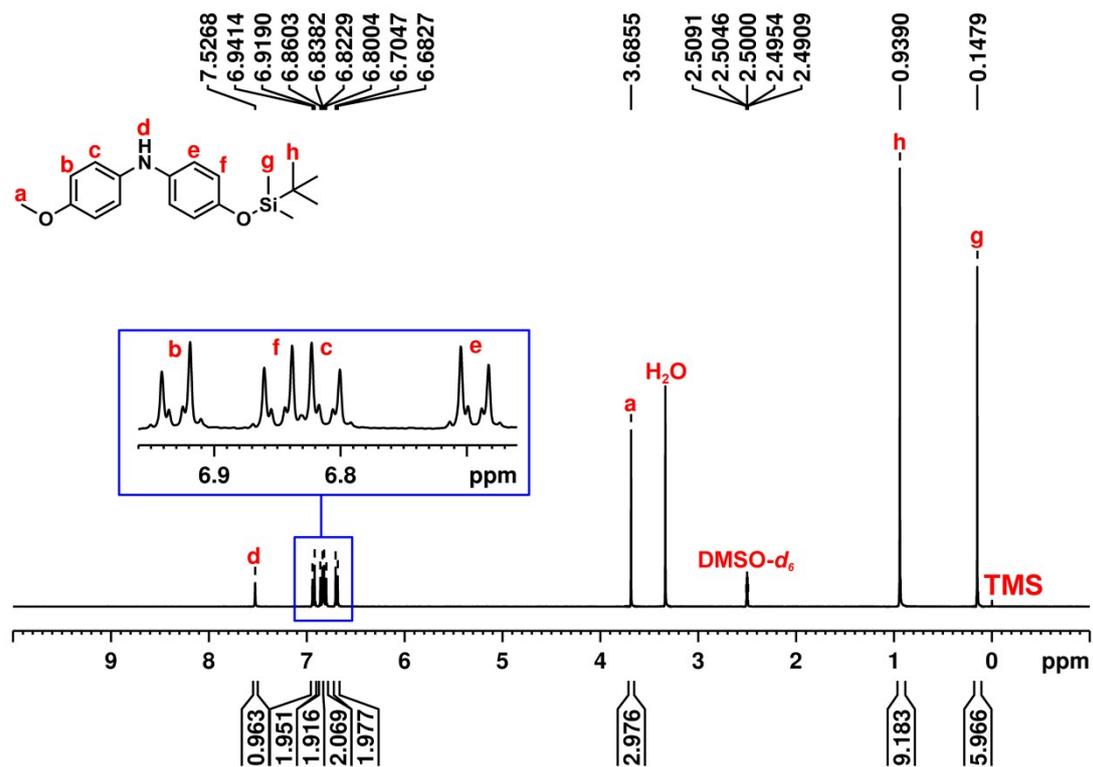


Fig. S2. ¹H NMR spectrum of DPA-Si in DMSO-*d*₆.

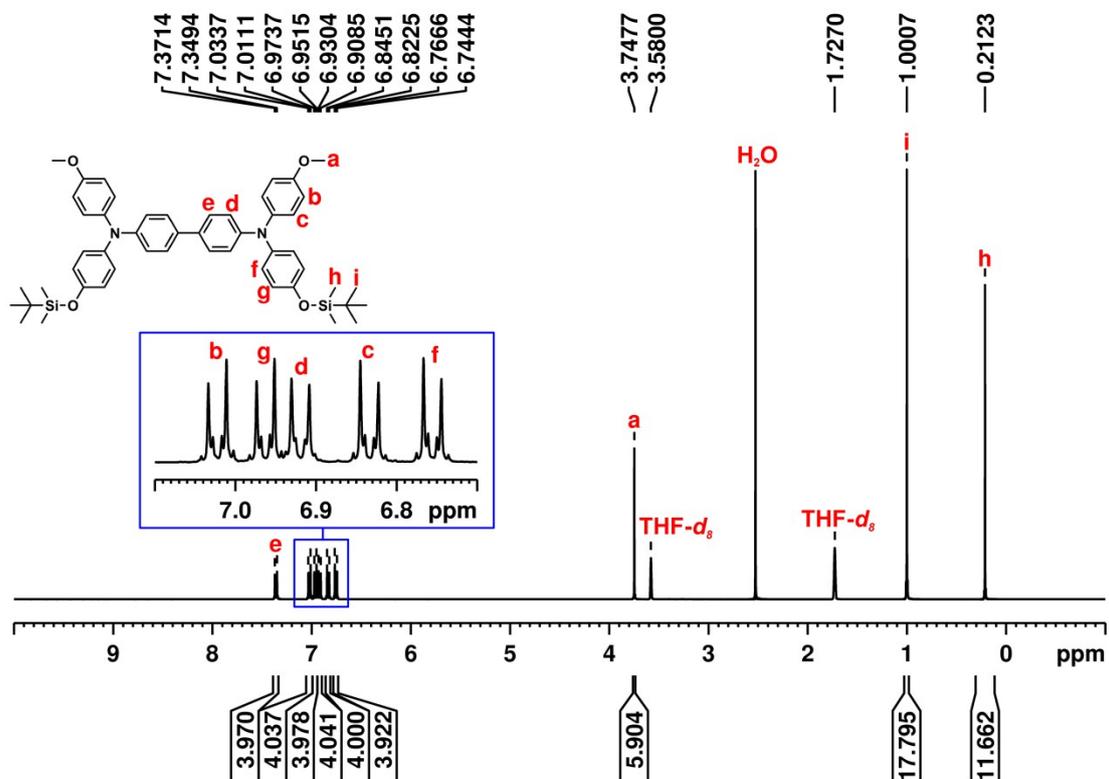


Fig. S3. ¹H NMR spectrum of TPB-2Si in THF-*d*₈.

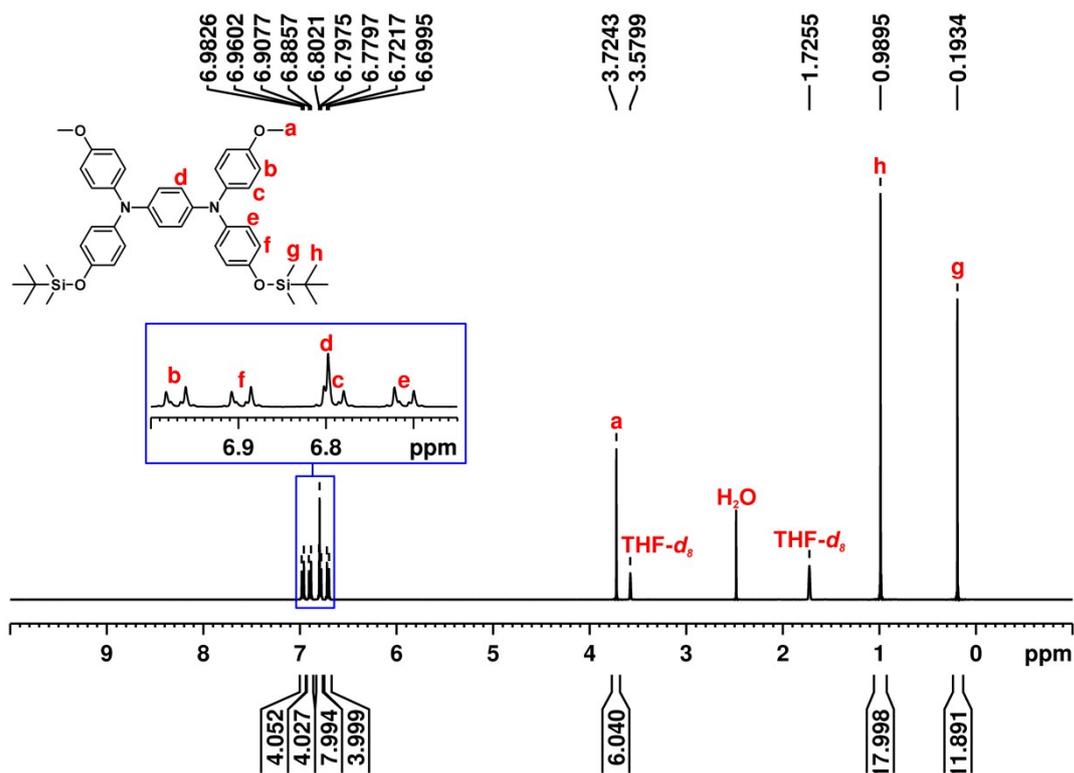


Fig. S4. ¹H NMR spectrum of TPPA-2Si in THF-*d*₈.

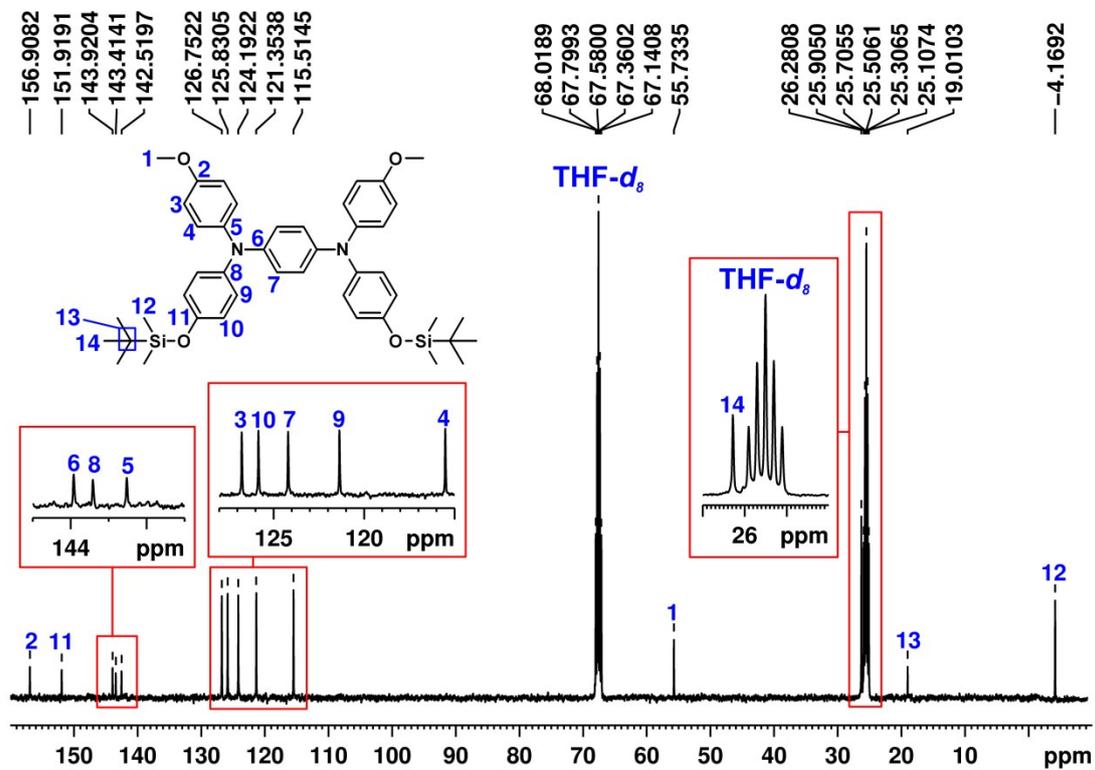


Fig. S5. ¹³C NMR spectrum of TPPA-2Si in THF-*d*₈.

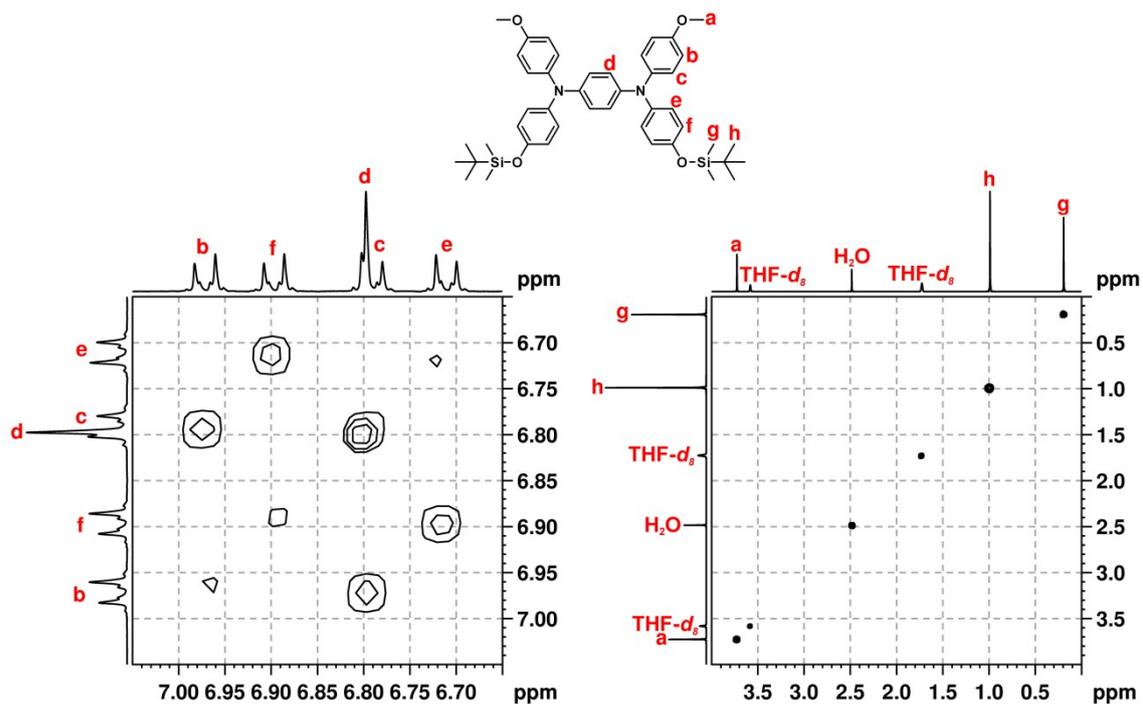


Fig. S6. H-H COSY spectrum of TPPA-2Si in THF-*d*₈.

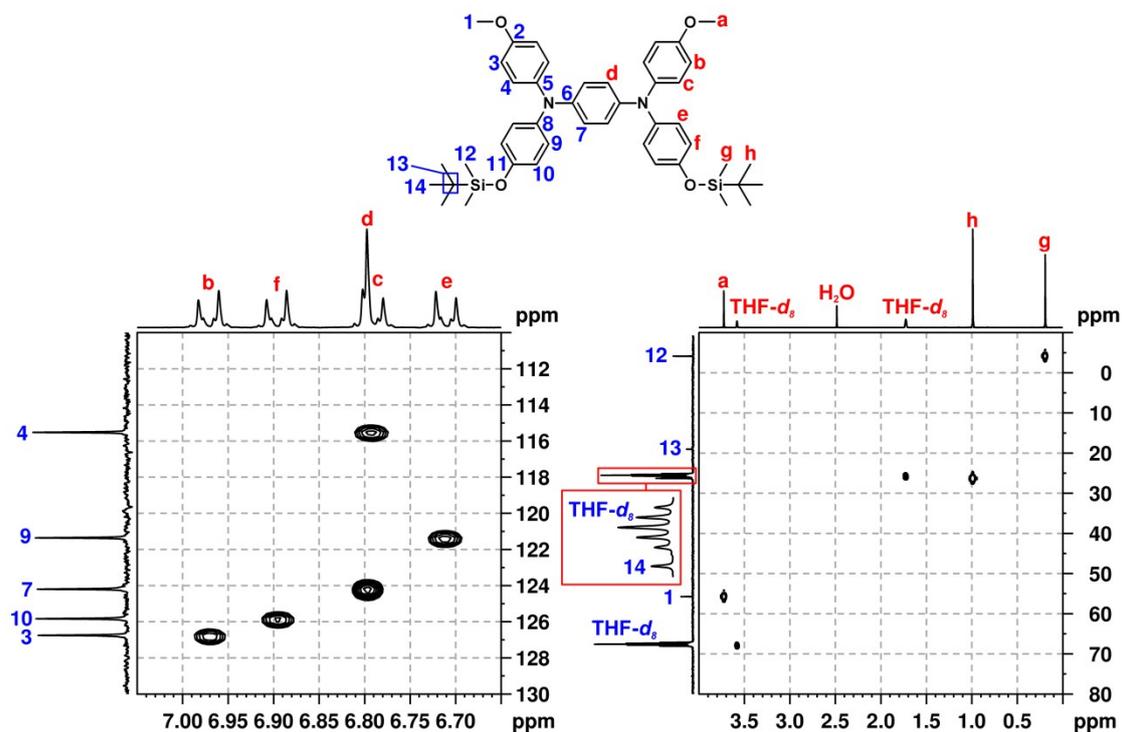


Fig. S7. C-H HSQC spectra of TPPA-2Si in THF-*d*₈.

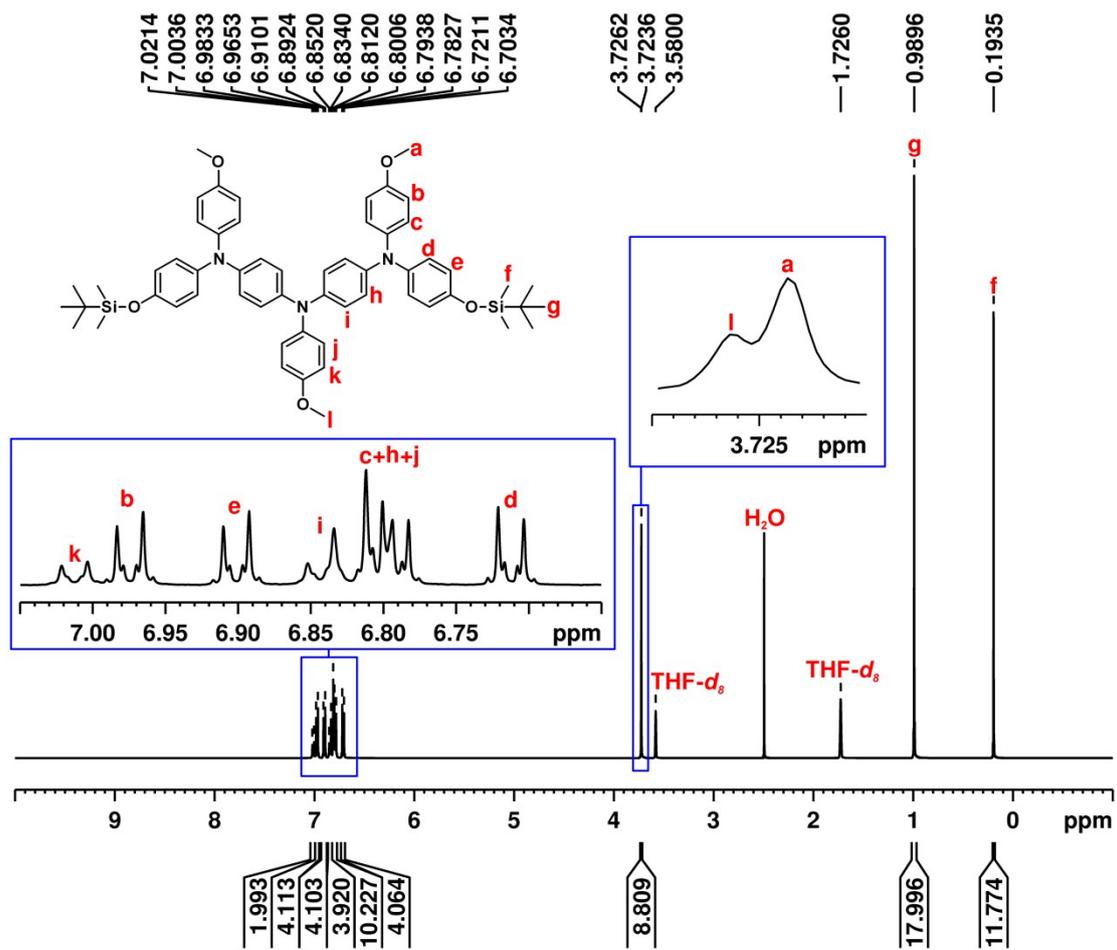


Fig. S8. ^1H NMR spectrum of BDATPA-2Si in $\text{THF-}d_8$.

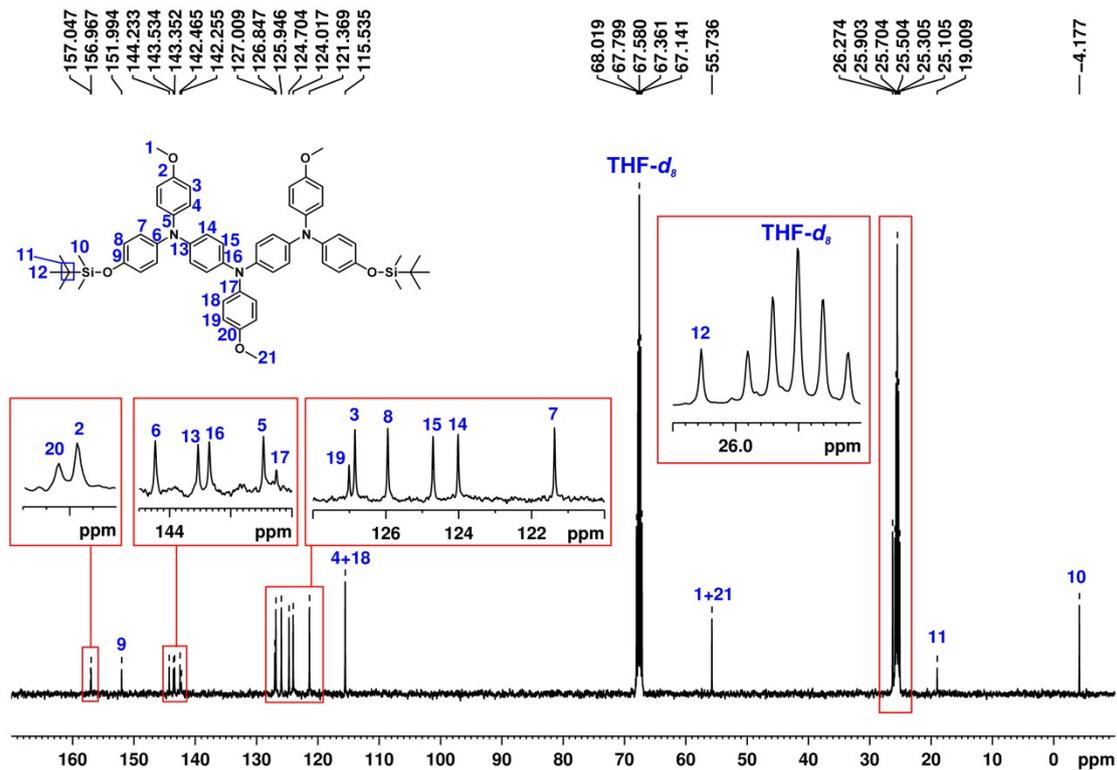


Fig. S9. ^{13}C NMR spectrum of **BDATPA-2Si** in $\text{THF-}d_8$.

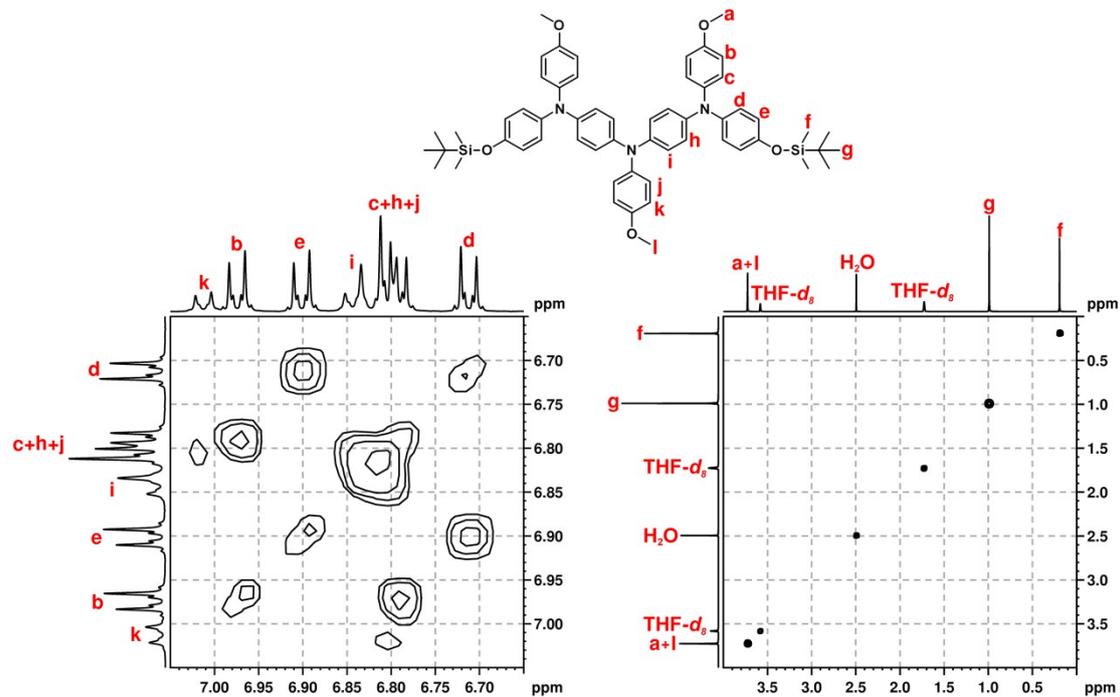


Fig. S10. H-H COSY spectrum of **BDATPA-2Si** in $\text{THF-}d_8$.

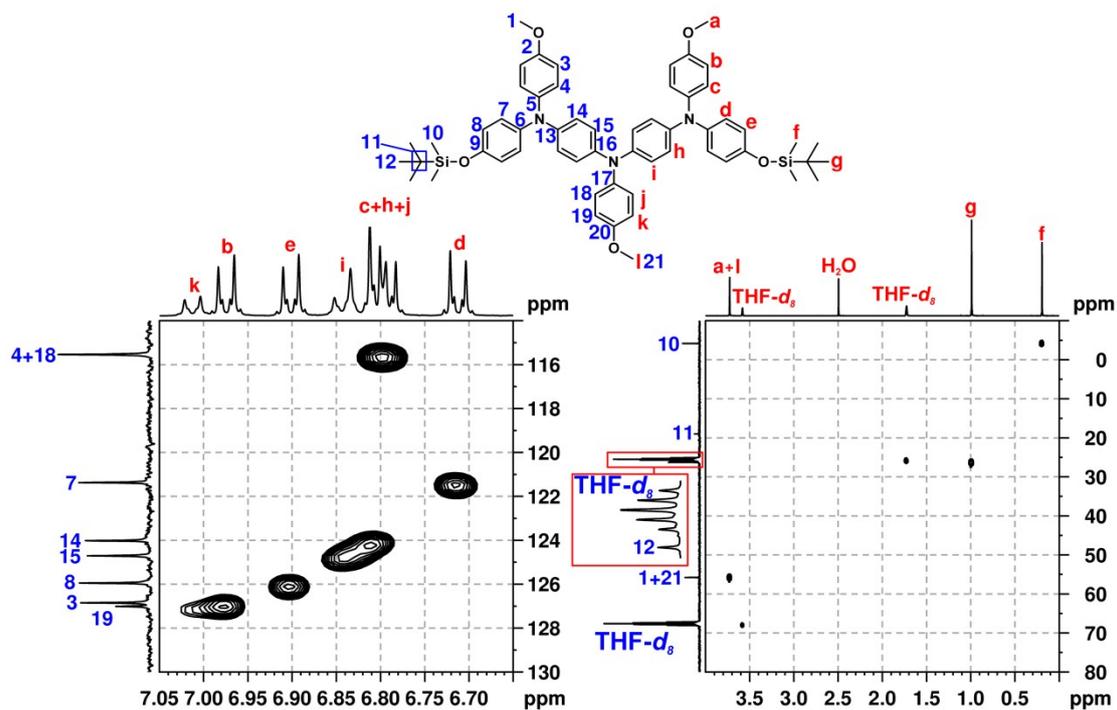


Fig. S11. C-H HSQC spectra of BDATPA-2Si in THF- d_8 .

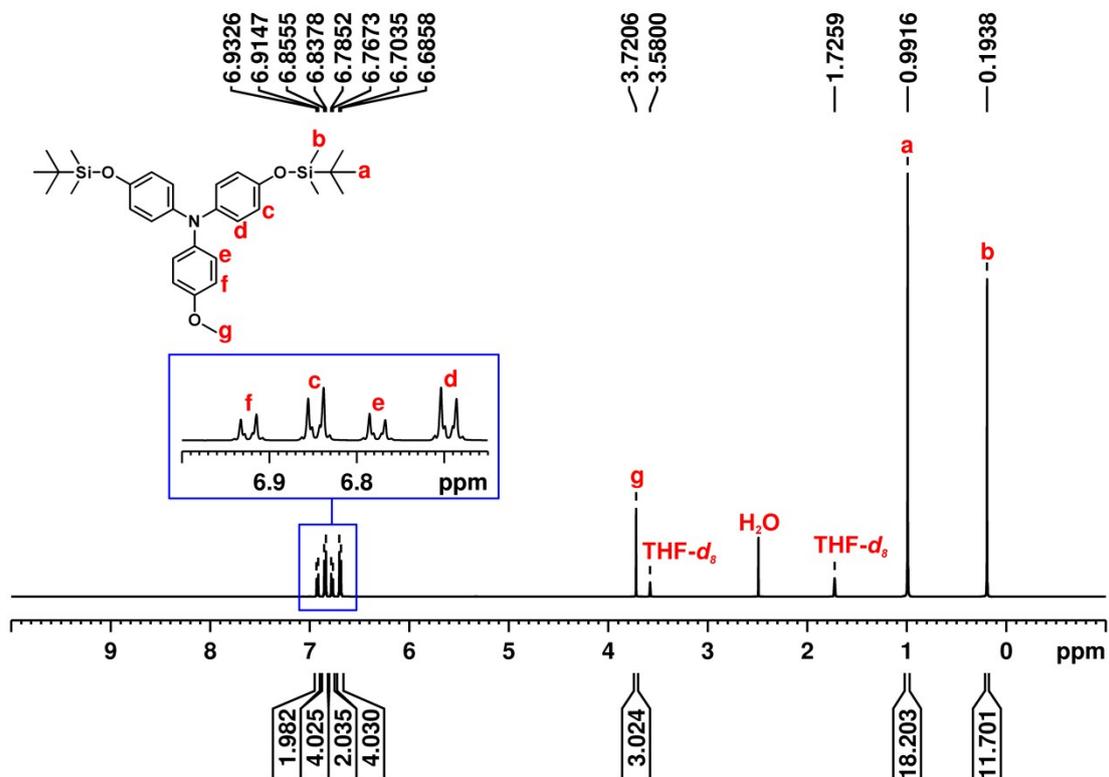


Fig. S12. ^1H NMR spectrum of TPA-2Si in THF- d_8 .

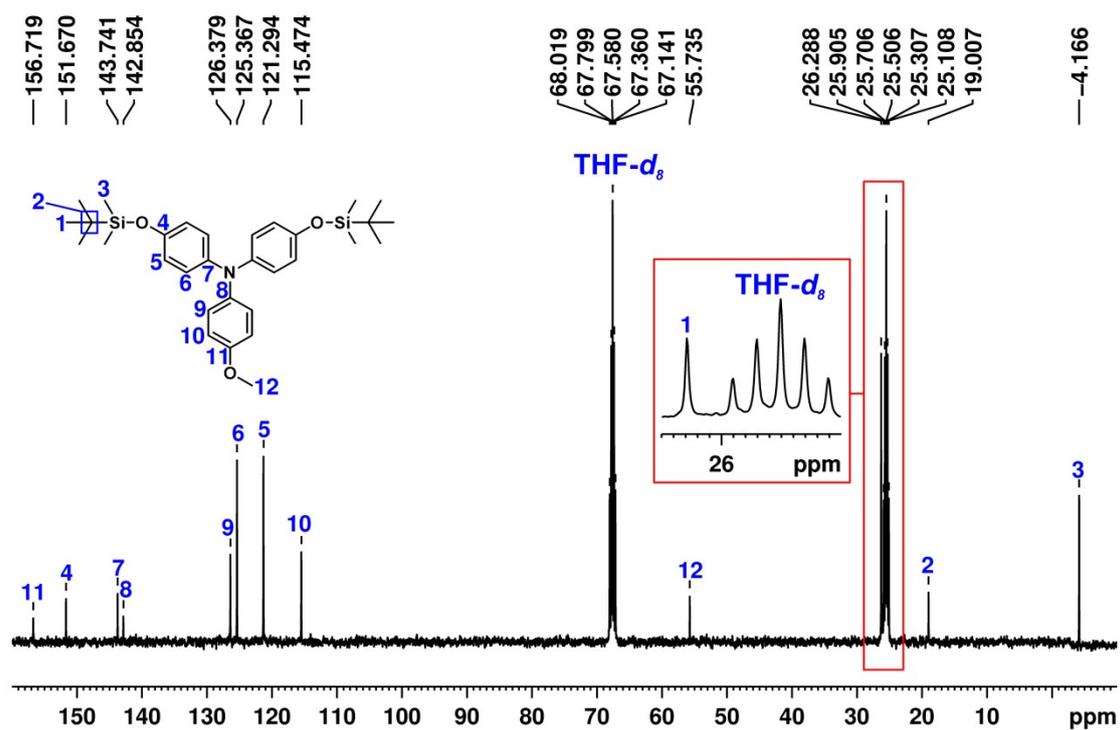


Fig. S13. ^{13}C NMR spectrum of TPA-2Si in THF- d_8 .

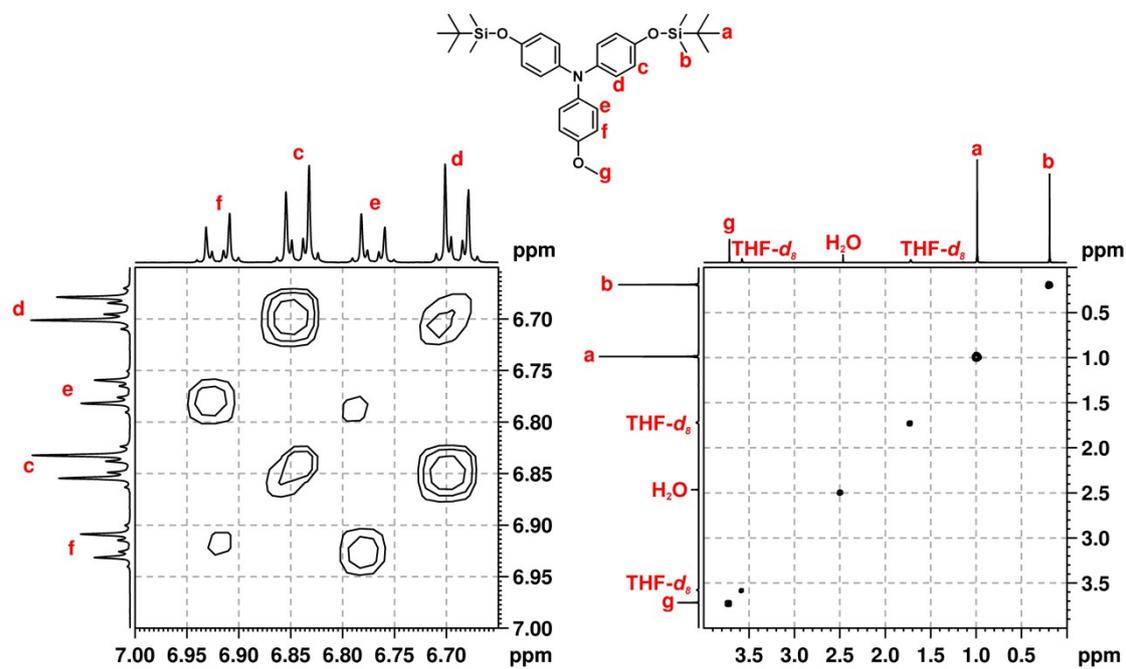


Fig. S14. H-H COSY spectrum of TPA-2Si in THF- d_8 .

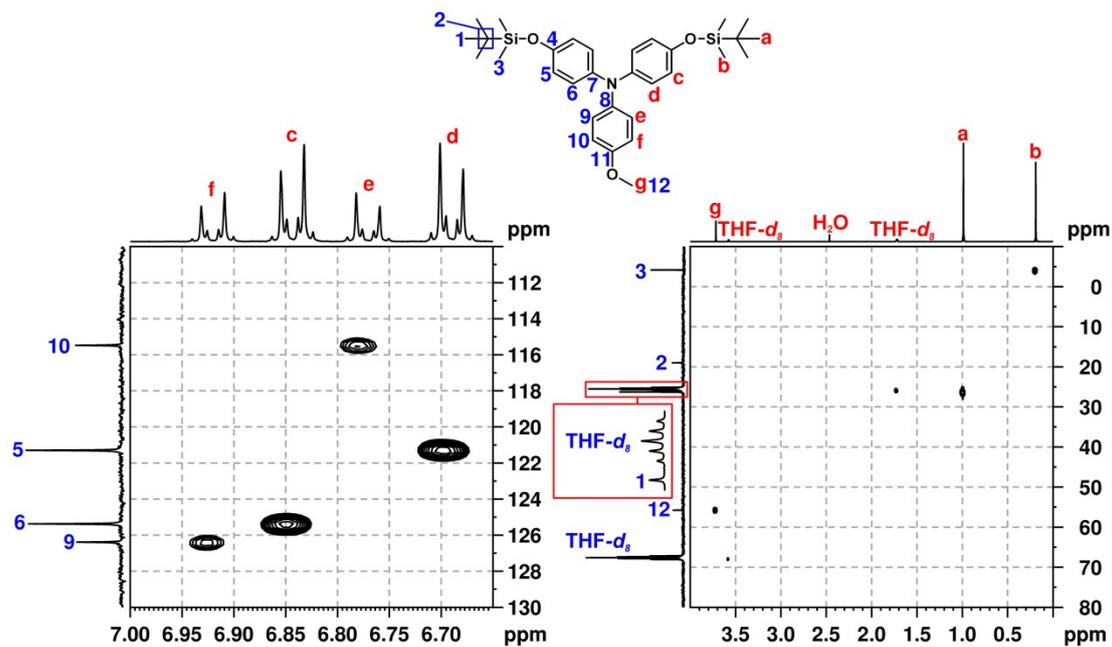


Fig. S15. C-H HSQC spectrum of TPA-2Si in THF- d_8 .

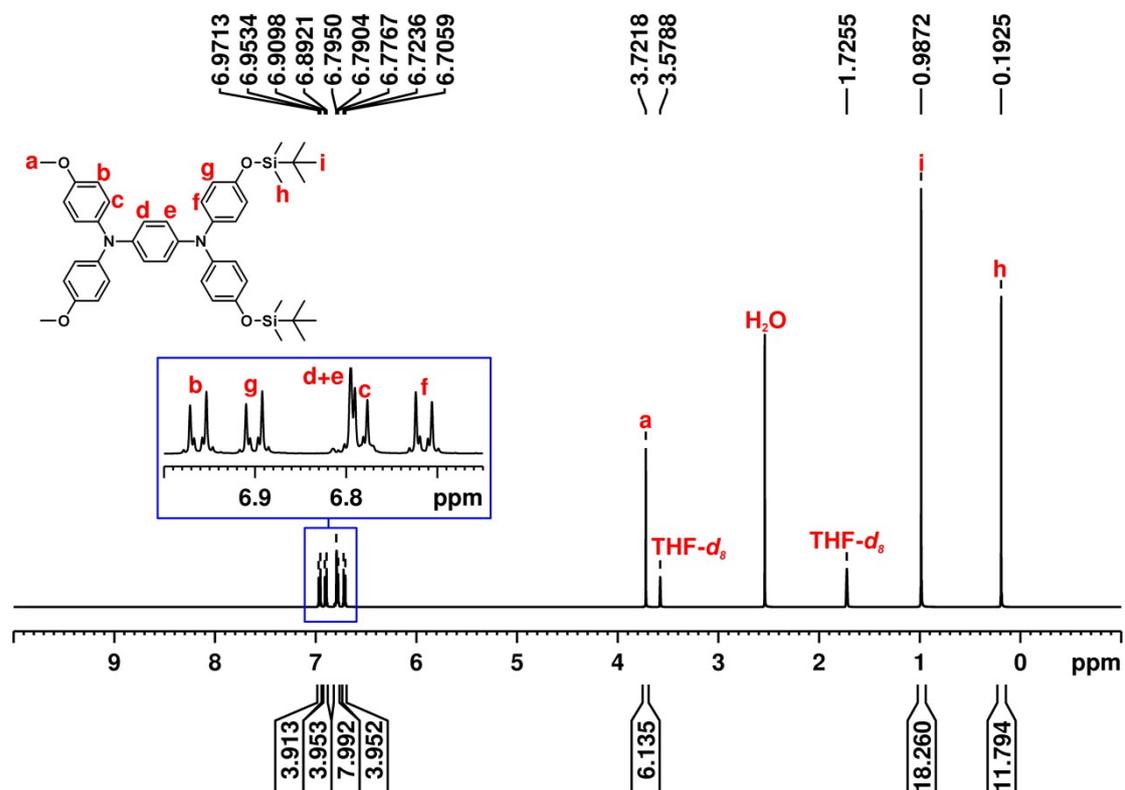


Fig. S16. ^1H NMR spectrum of STPPA-2Si in THF- d_8 .

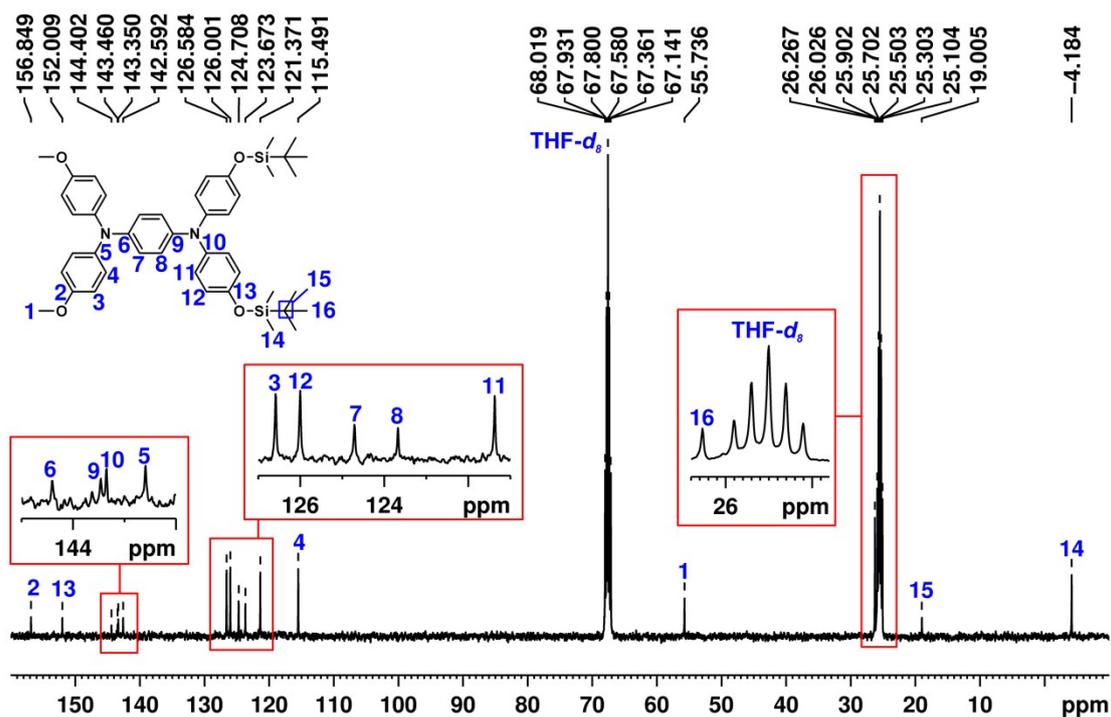


Fig. S17. ¹³C NMR spectrum of STPPA-2Si in THF-*d*₈.

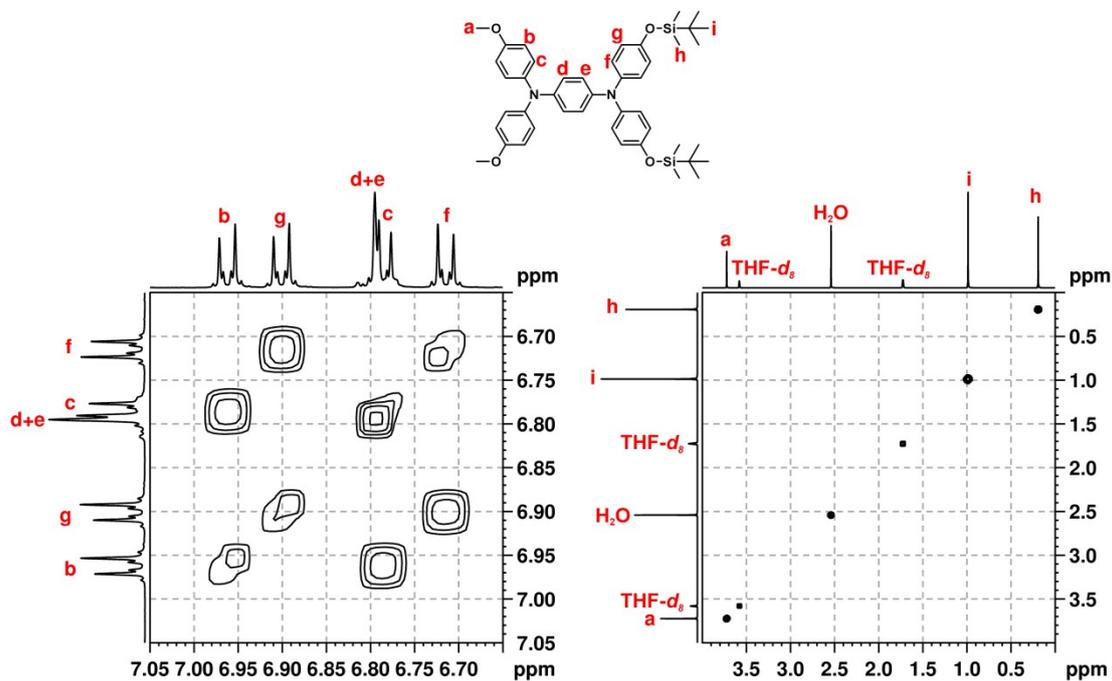


Fig. S18. H-H COSY spectrum of STPPA-2Si in THF-*d*₈.

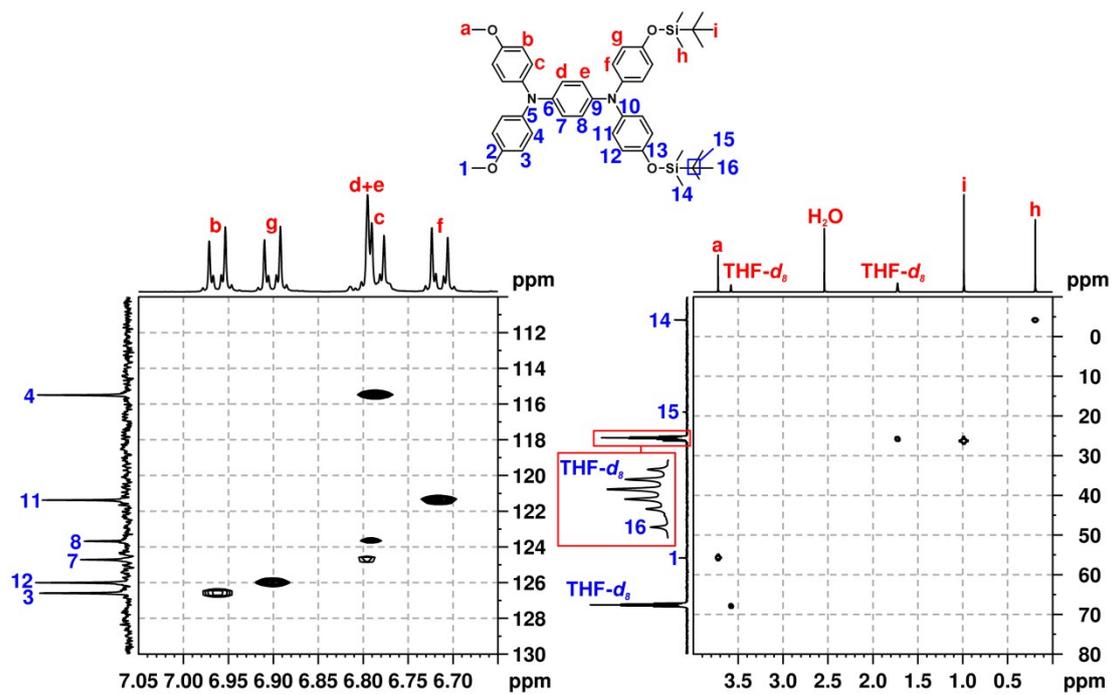


Fig. S19. C-H HSQC spectrum of STPPA-2Si in THF-*d*₈.

Table S1. Inherent viscosity and GPC data of polyethers

Polymer	η^a (dL/g)	GPC data ^c		
		M_n	M_w	PDI ^d
TPA-PES	0.25	31000	94500	3.05
TPPA-PES	0.42	45000	176000	3.91
STPPA-PES	0.24	31000	68000	2.19
TPB-PES	0.40	61500	151500	2.46
BDATPA-PES	0.33	30070	97500	3.24
<hr style="border-top: 1px dashed black;"/>				
TPA-PEOX	0.22	16500	34500	2.09
TPPA-PEOX	0.27	26500	101500	3.83
TPB-PEOX	0.53 ^b	46000	91000	1.98
BDATPA-PEOX	0.24	25500	63000	2.47

^a Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.

^b Measured at a polymer concentration of 0.5 g/dL in CHCl₃ at 30 °C

^c Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 1 mL/min at 40 °C.

^d Polydispersity Index (M_w/M_n).

Table S2. Solubility tests of polyethers

Polymer	Solubility in various solvent ^a					
	NMP	DMAc	DMF	DMSO	THF	CHCl ₃
TPA-PES	++	++	++	++	+-	+-
TPPA-PES	++	++	++	+-	++	++
STPPA-PES	++	++	++	+	++	++
TPB-PES	++	++	+-	+-	++	++
BDATPA-PES	++	++	++	+-	++	++
<hr style="border-top: 1px dashed black;"/>						
TPA-PEOX	++	++	++	++	++	++
TPPA-PEOX	++	++	+-	+-	++	++
TPB-PEOX	++	++	+-	+-	+	++
BDATPA-PEOX	++	++	++	+-	++	++

^a The solubility tests were carried out by using 5 mg of sample in 1 mL of solvent. ++: soluble at r.t.; +: soluble under heat; + -: partial soluble or swelling under heat; -: insoluble even under heat.

Table S3 Thermal properties of polyethers

Polymer	T _g (°C) ^a	T _d ⁵ (°C) ^b		T _d ¹⁰ (°C) ^b		R _{w800} (%) ^c
		N ₂	Air	N ₂	Air	
TPA-PES	205	450	440	460	470	52
TPPA-PES	202	435	435	450	460	60
STPPA-PES	198	440	445	455	465	63
TPB-PES	217	460	455	475	485	54
BDATPA-PES	205	440	450	460	470	62
<hr style="border-top: 1px dashed black;"/>						
TPA-PEOX	202	450	440	460	480	47
TPPA-PEOX	200	440	420	455	450	61
TPB-PEOX	225	460	450	475	485	55
BDATPA-PEOX	200	440	420	470	450	57

^a Glass transition temperature was measured by DSC with a heating rate of 20 °C/min in nitrogen.

^b Temperature at which 5% and 10% weight loss occurred, respectively, recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 30 m³/min.

^c Residual weight percentages at 800 °C under nitrogen flow.

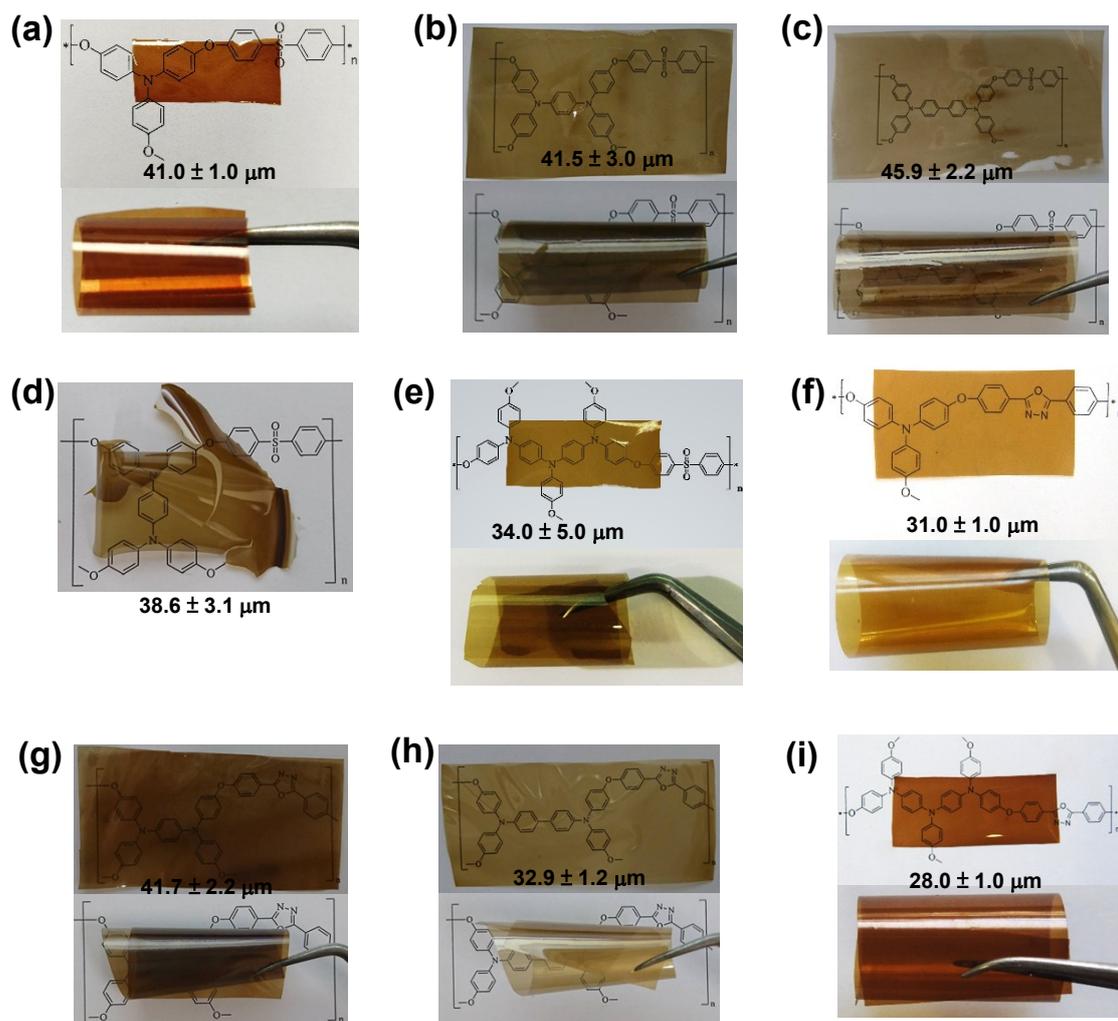


Fig. S20. The photographs of polyether films (a) TPA-PES, (b) TPPA-PES, (c) TPB-PES, (d) STPPA-PES, (e) BDATPA-PES, (f) TPA-PEOX, (g) TPPA-PEOX, (h) TPB-PEOX and (i) BDATPA-PEOX.

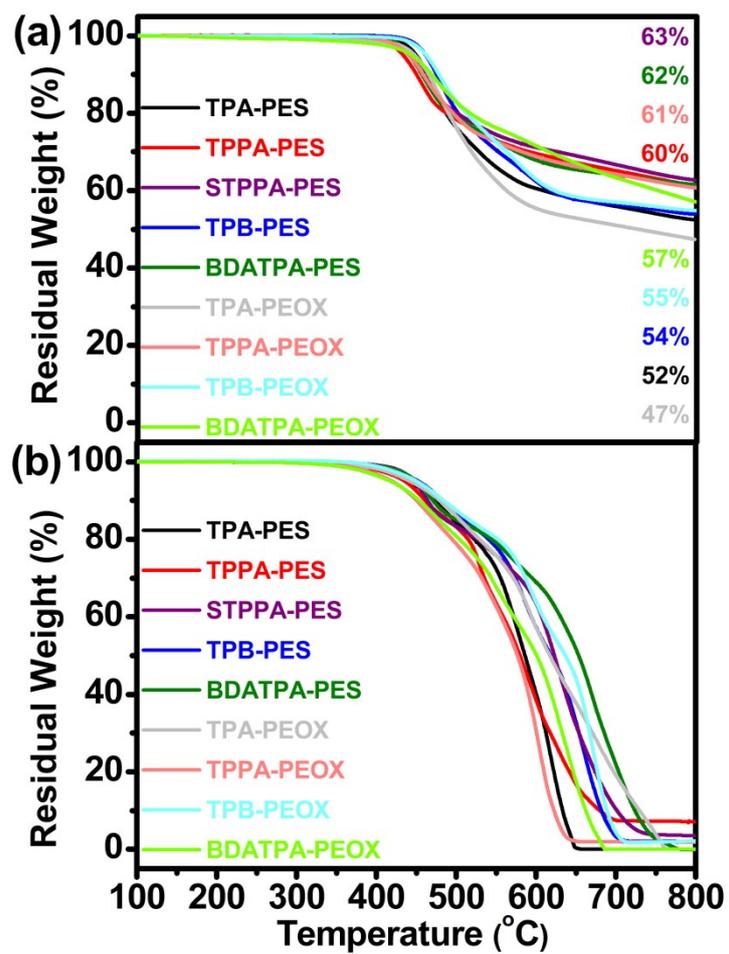


Fig. S21. TGA thermograms of polyethers under (a) N₂ and (b) air at a heating rate of 20 °C/min.

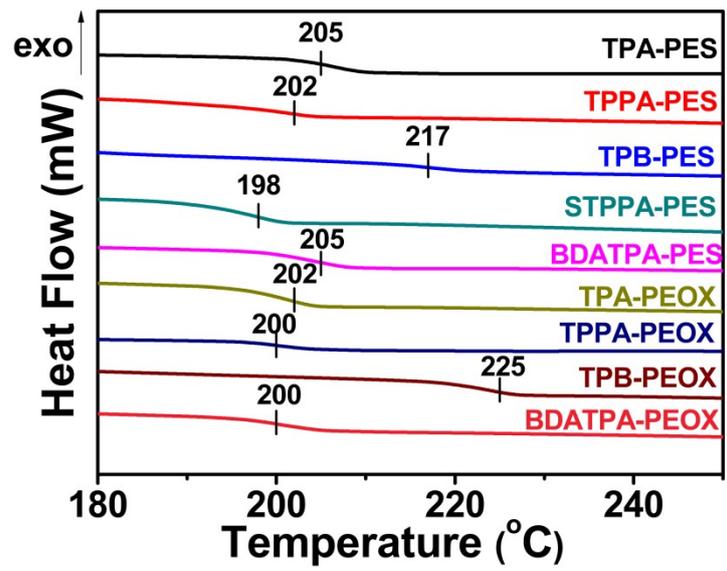


Fig. S22. DSC traces of the polyethers under N₂ at a heating rate of 20 °C/min.

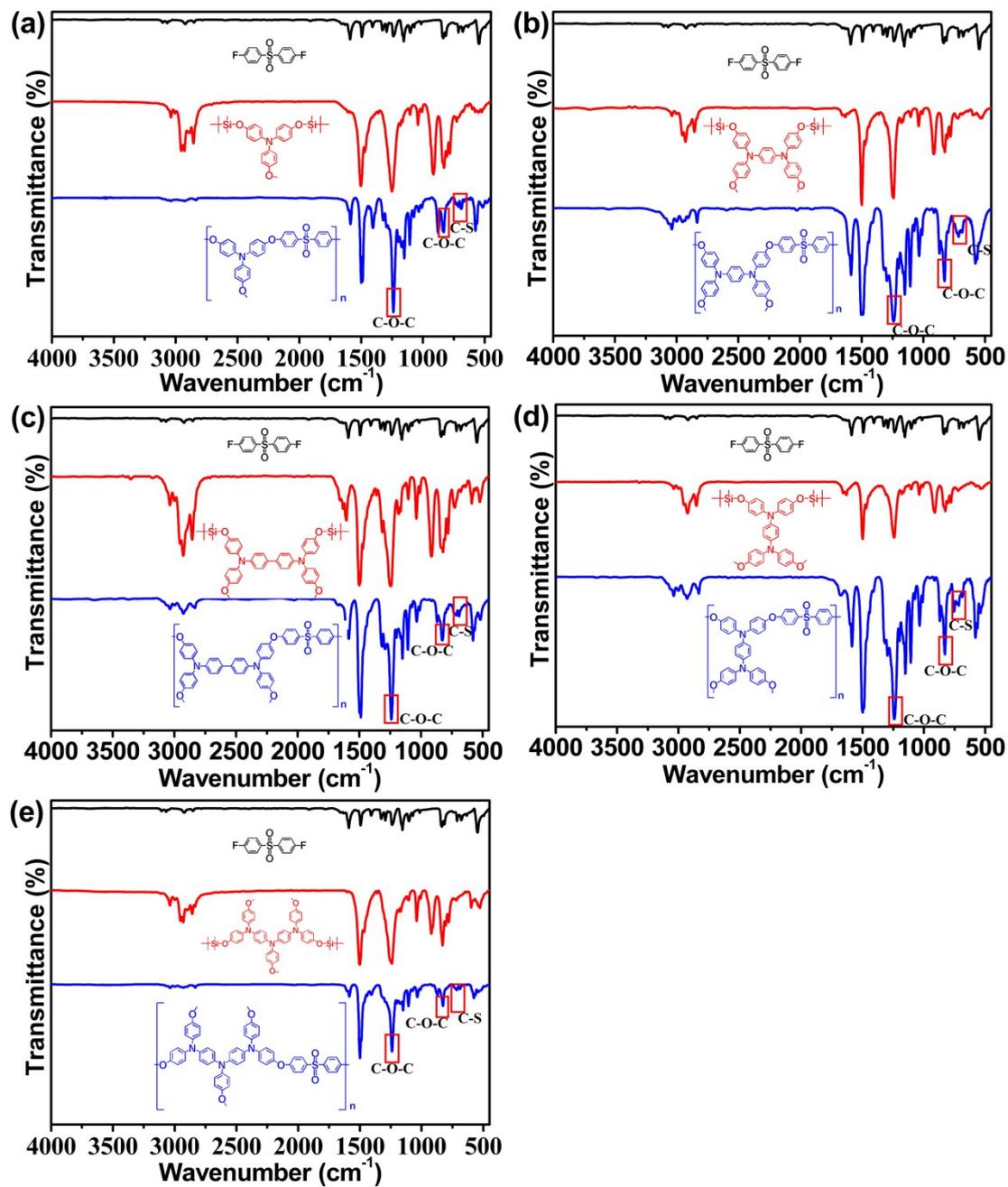


Fig. S23. FT-IR spectra of (a) TPA-PES, (b) TPPA-PES (c) TPB-PES, (d) STPPA-PES, and (e) BDATPA-PES.

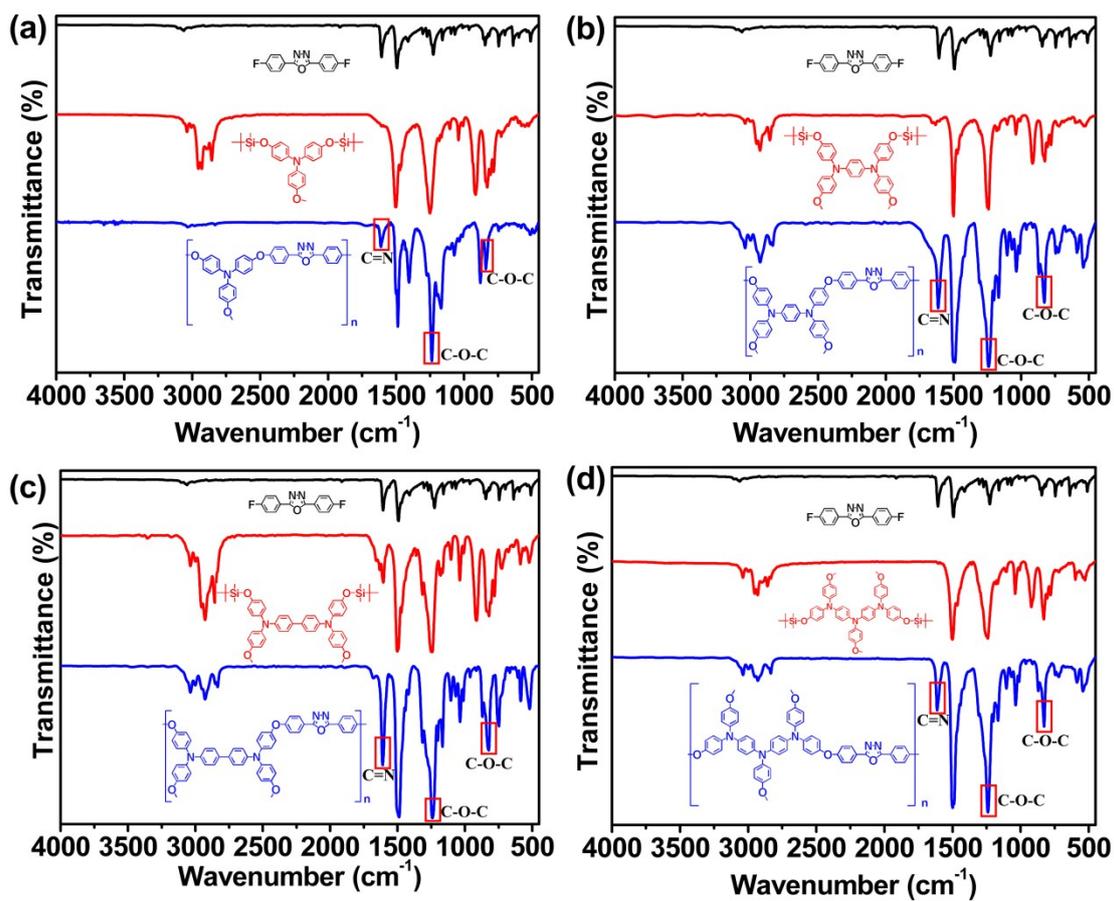


Fig. S24. FT-IR spectra of (a) TPA-PEOX, (b) TPPA-PEOX, (c) TPB-PEOX, and (d) BDATPA-PEOX.

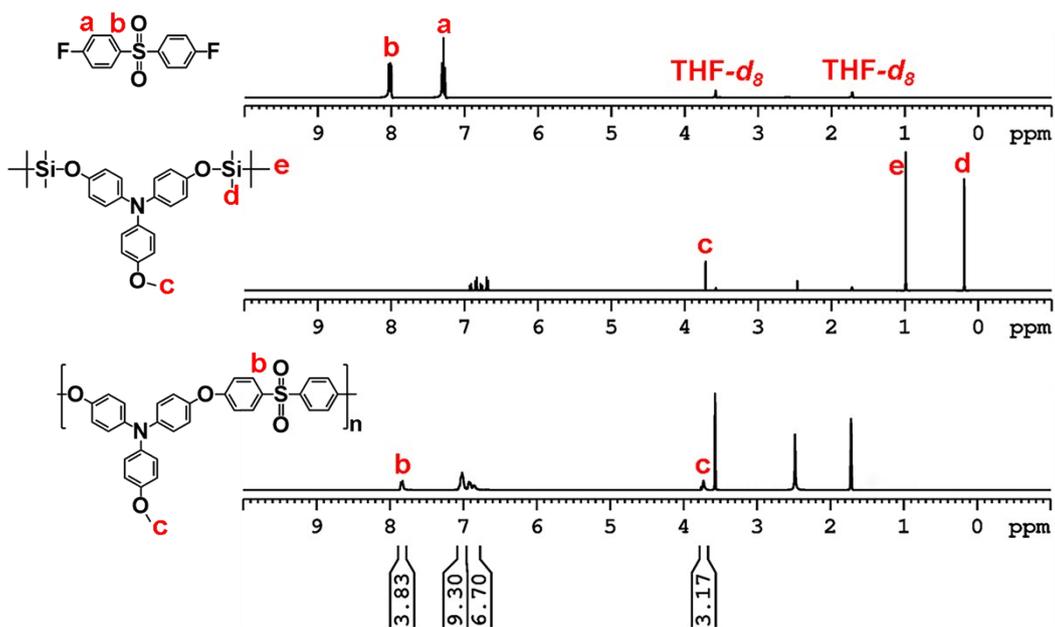


Fig. S25. ^1H NMR spectra of the bis(4-fluorophenyl)sulfone, TPA-2Si, and TPA-PES.

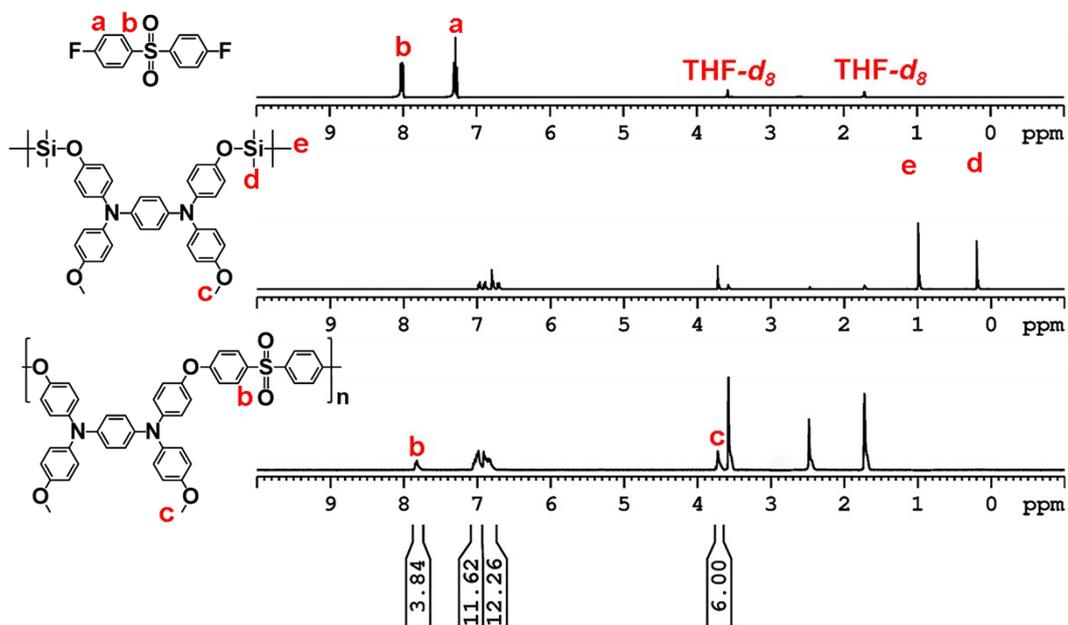


Fig. S26. ^1H NMR spectra of bis(4-fluorophenyl)sulfone, TPPA-2Si, and TPPA-PES.

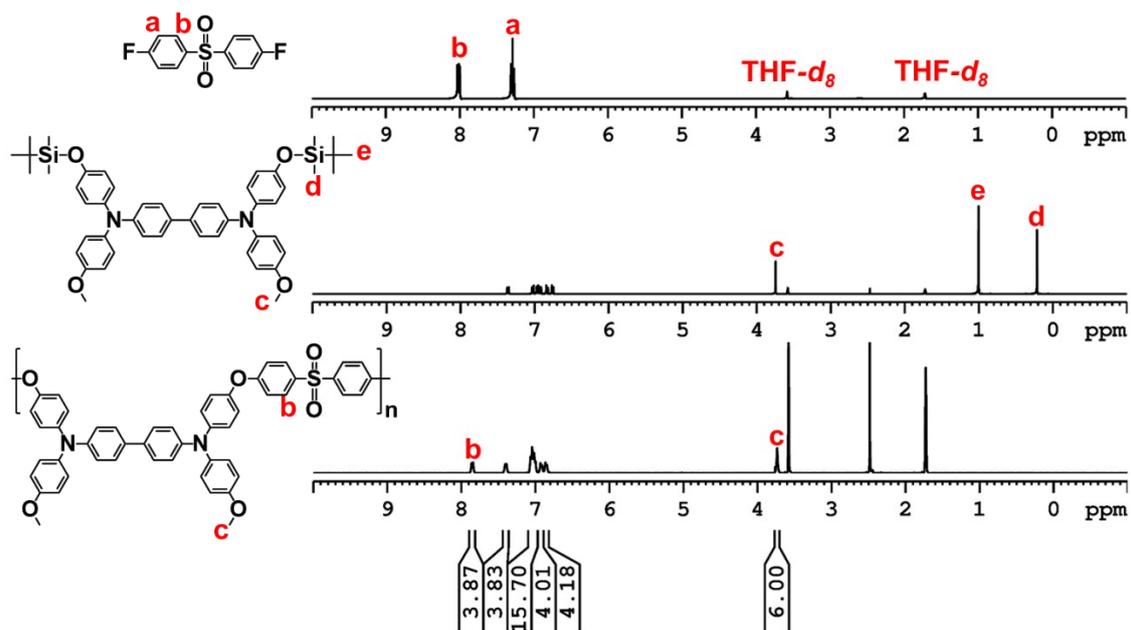


Fig. S27. ^1H NMR spectra of bis(4-fluorophenyl)sulfone, TPB-2Si, and TPB-PES.

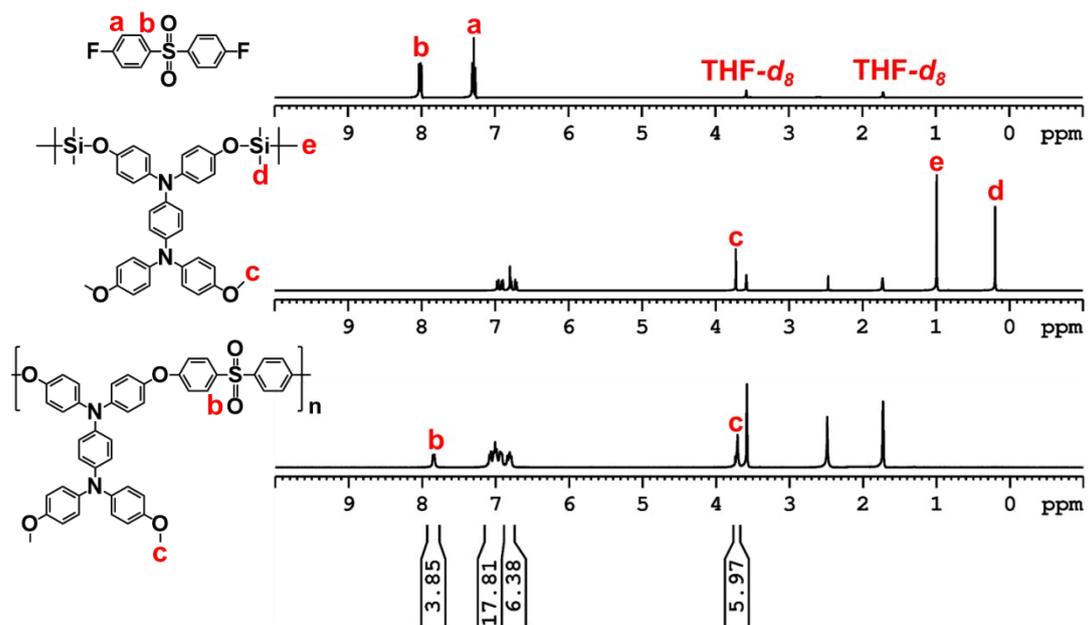


Fig. S28. ^1H NMR spectra of bis(4-fluorophenyl)sulfone, STPPA-2Si, and STPPA-PES.

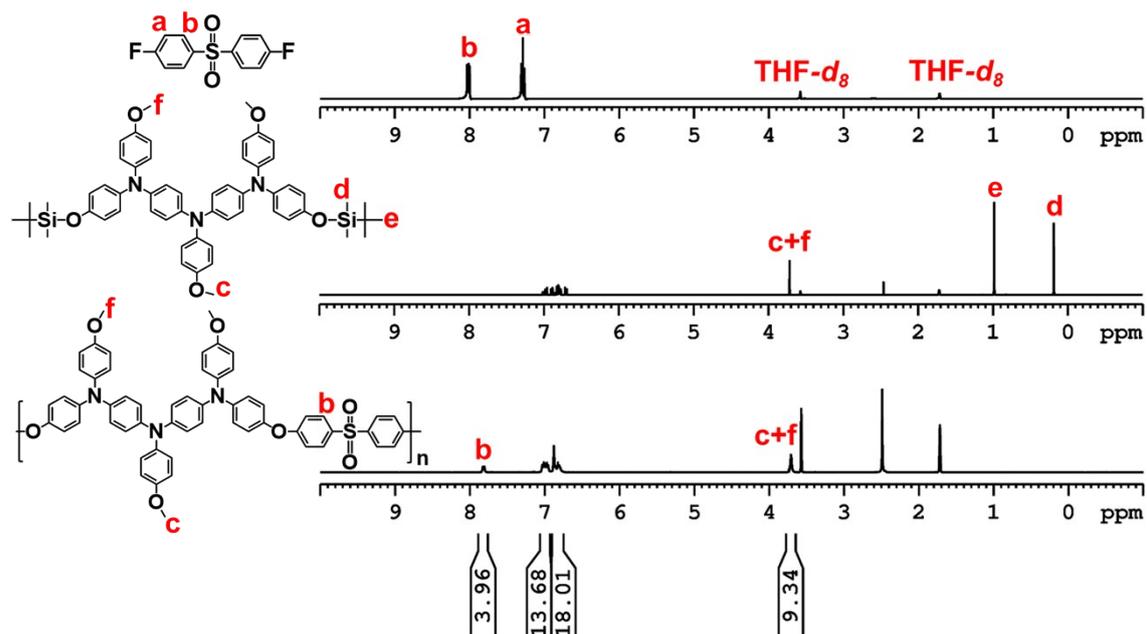


Fig. S29. ^1H NMR spectra of bis(4-fluorophenyl)sulfone, **BDATPA-2Si**, and **BDATPA-PES**.

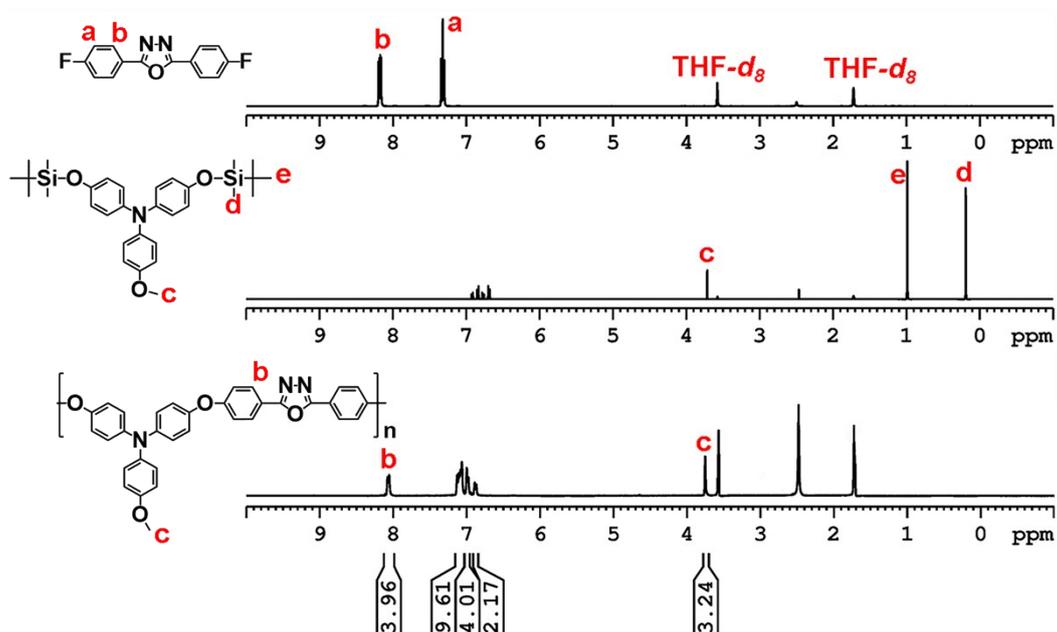


Fig. S30. ^1H NMR spectra of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole, **TPA-2Si**, and **TPA-PEOX**.

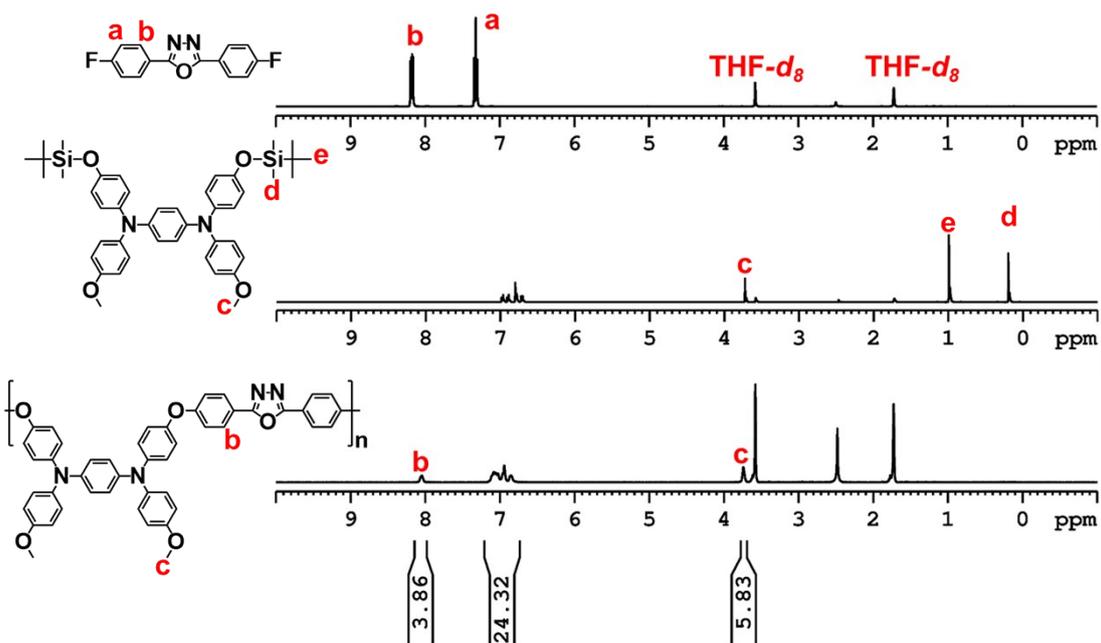


Fig. S31. ^1H NMR spectra of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole, TPPA-2Si, and TPPA-PEOX.

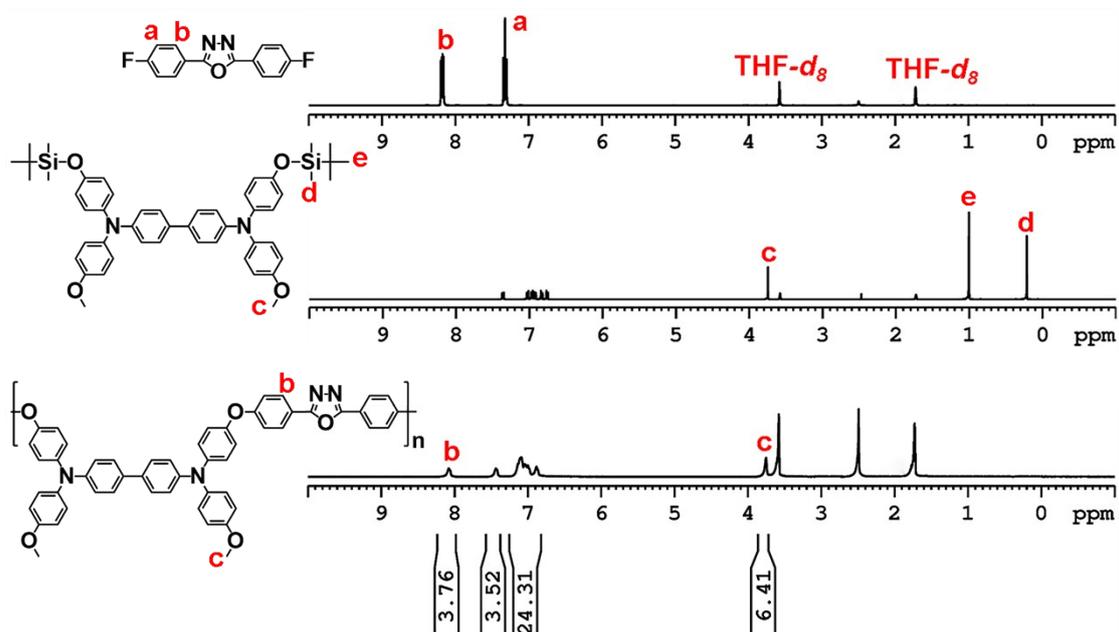


Fig. S32. ^1H NMR spectra of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole, TPB-2Si, and TPB-PEOX.

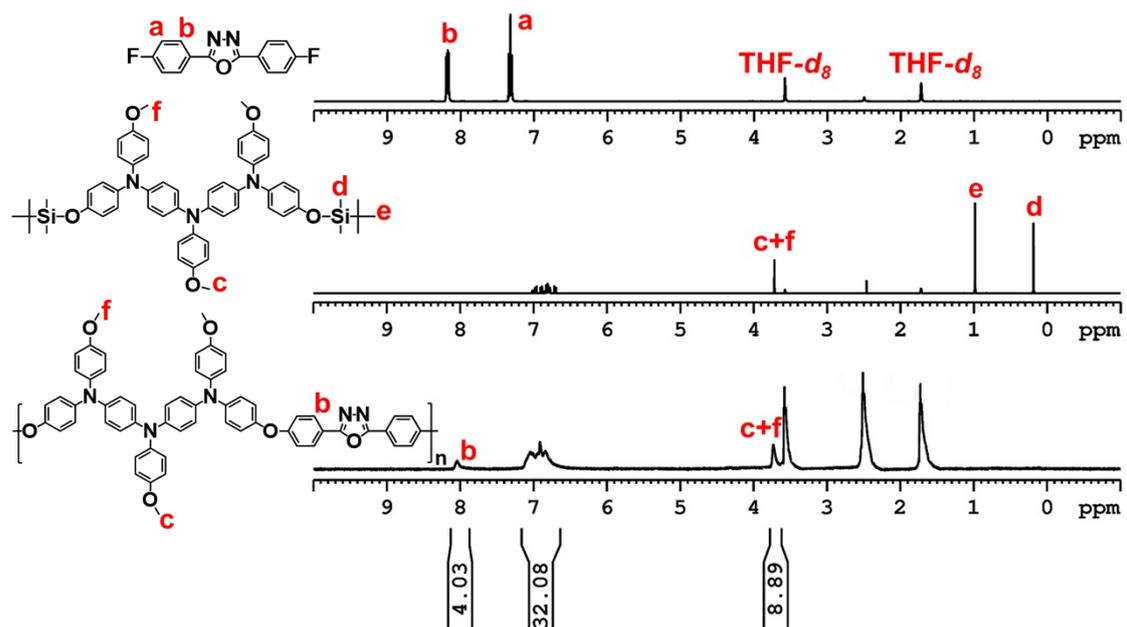


Fig. S33. ^1H NMR spectra of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole, **BDATPA-2Si**, and **BDATPA-PEOX**.

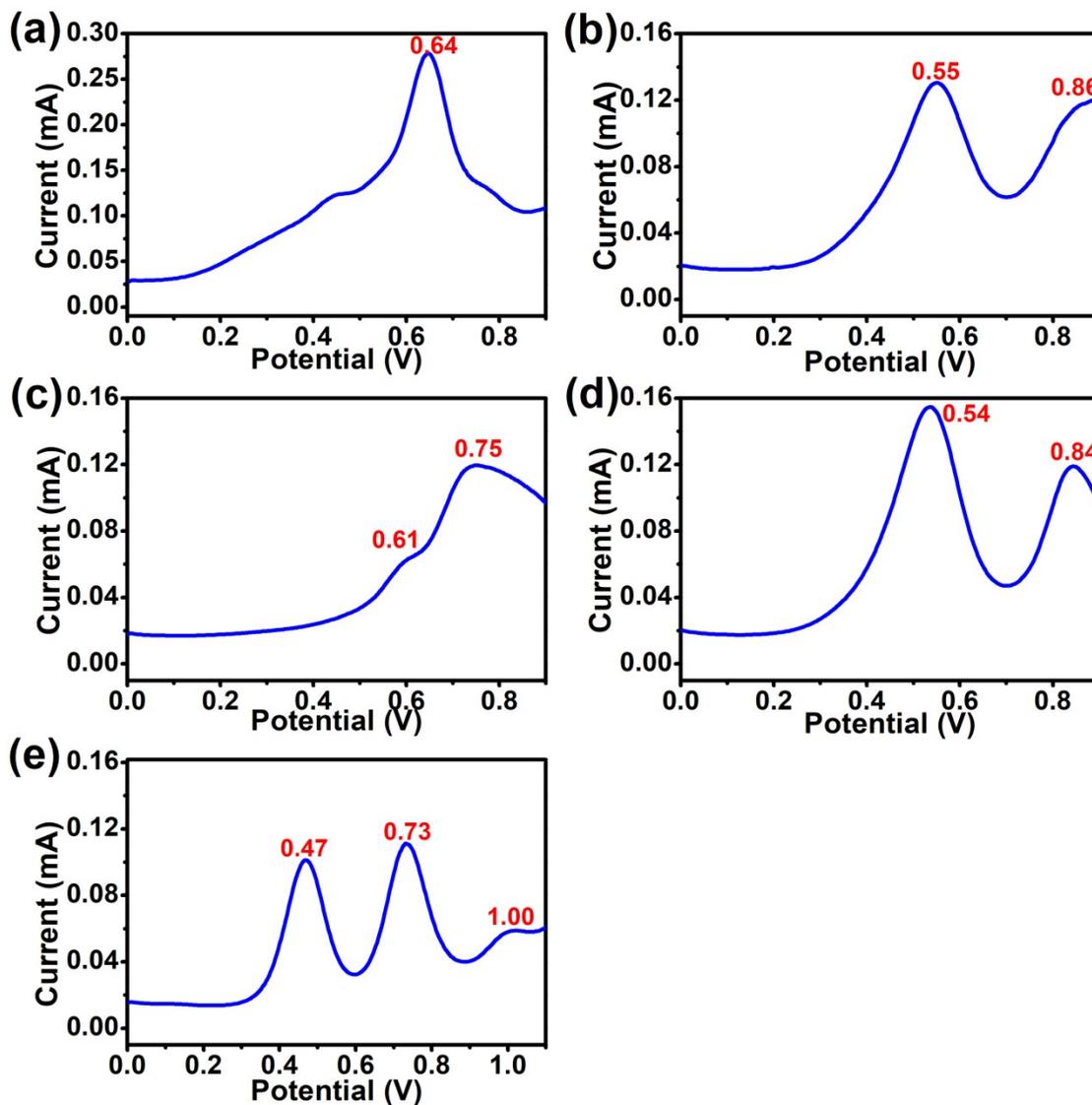


Fig. S34. Differential pulse voltammety diagrams of the 0.001 M (a) TPA-2Si in CH_3CN ; (b) TPPA-2Si, (c) TPB-2Si, (d) STPPA-2Si, and (e) BDATPA-2Si in NMP containing 0.1 M TBABF_4 . Scan rate: 2 mV/s; pulse amplitude: 50 mV; pulse width: 25 ms; pulse period: 0.2 s.

Table S4 Electrochemical properties of the polyethers.

Polymer	Oxidation potential (V) ^a			
	E _{onset}	E _{pa1} ^b	E _{pa2} ^b	E _{pa3} ^b
TPA-PES	0.76	1.07	-	-
TPPA-PES	0.49	0.82	1.15	-
STPPA-PES	0.53	0.68	0.98	-
TPB-PES	0.72	- ^c	1.11	-
BDATPA-PES	0.38	0.68	0.93	1.44
<hr style="border-top: 1px dashed black;"/>				
TPA-PEOX	0.81	1.12	-	-
TPPA-PEOX	0.49	0.83	1.14	-
TPB-PEOX	0.74	- ^c	1.12	-
BDATPA-PEOX	0.40	0.68	0.91	1.41

^a vs Ag/AgCl in CH₃CN.

^b E_{pa} (anodic peak potential).

^c No discernible signal was observed.

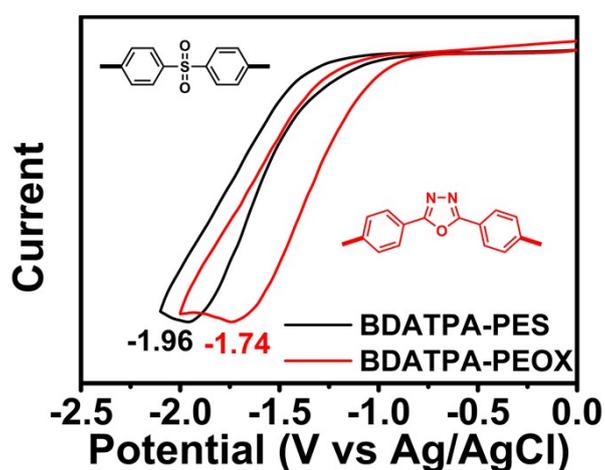


Fig. S35. Cyclic voltammograms of the **BDATPA-PES** and **BDATPA-PEOX** films on the ITO-coated glass substrates in CH₃CN containing 0.1 M TBABF₄ at the scan rate of 50 mV/s.

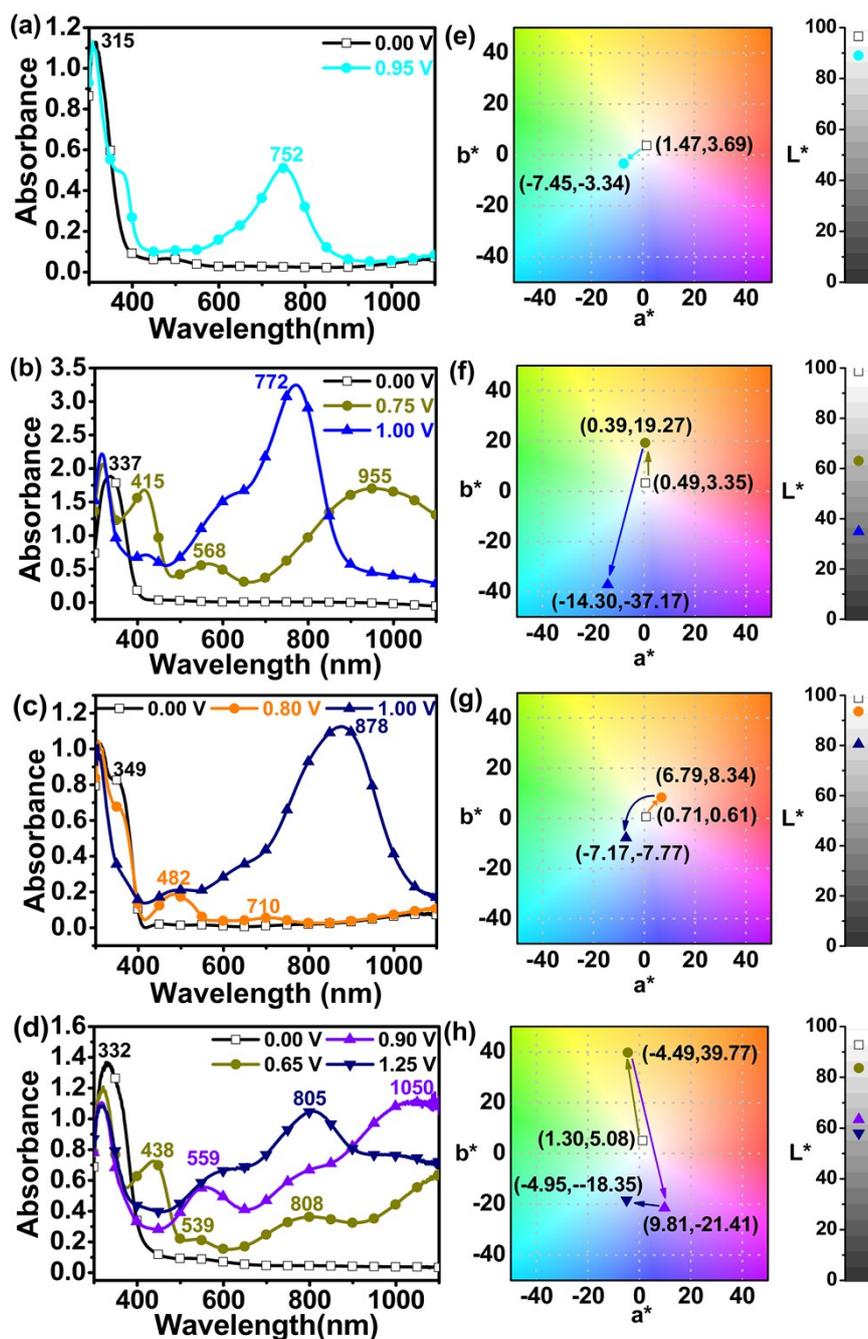


Fig. S36. Absorbance spectra and CIE $L^*a^*b^*$ data of (a, e) **TPA-PEOX** (250 ± 30 nm), (b, f) **TPPA-PEOX** (700 ± 50 nm), (c, g) **TPB-PEOX** (400 ± 30 nm) and (d, h) **BDATPA-PEOX** (500 ± 50 nm) films onto ITO-coated glass substrates in CH_3CN containing 0.1 M TBABF_4 at the applied potentials (V vs Ag/AgCl) related to the different oxidation states.

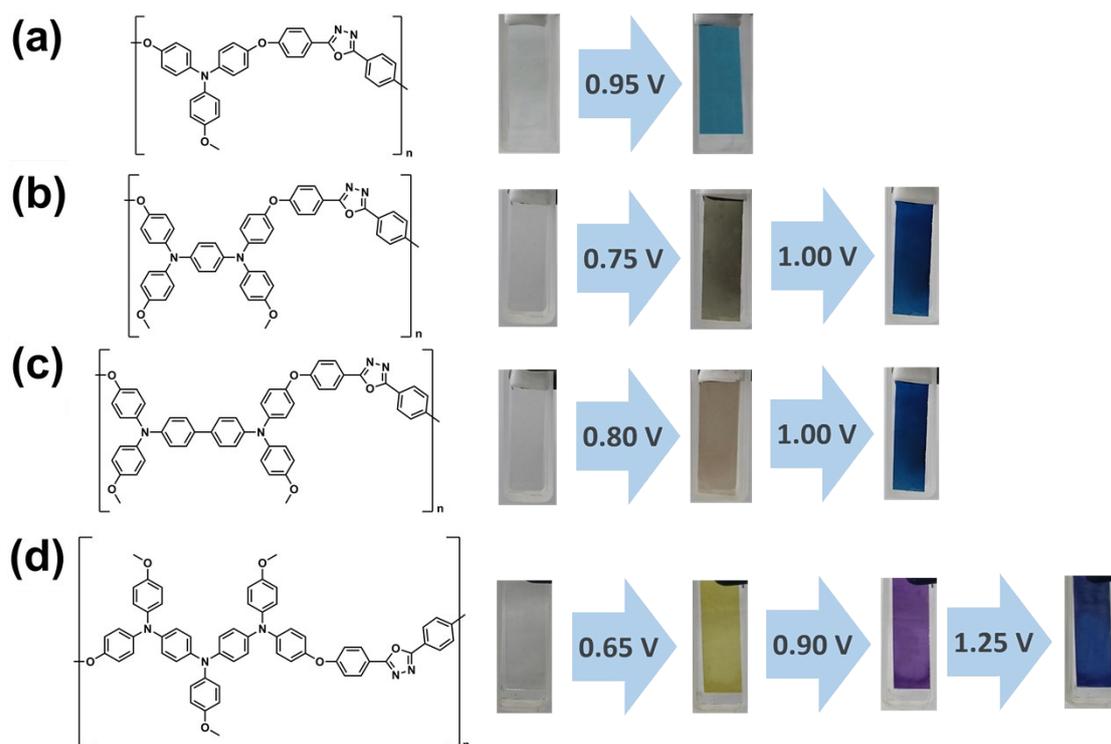


Fig. S37. Electrochromic behaviors of the oxadiazole-type polyether films with the thickness of (a) 650 ± 50 , (b) 700 ± 50 , (c) 700 ± 50 , and (d) 650 ± 50 nm on the ITO-coated glass in CH_3CN containing 0.1 M TBABF_4 at the applied potentials (V vs Ag/AgCl) related to different oxidation states.

Reference

1. J. L. Hedrick, R. Twieg, *Macromolecules*, 1992, **25**, 2021.