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Supporting Information

Oxidation-Induced Fluorescence Turn-on Approach for Non-Luminescence Flexible Polyimide Films

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Experimental section

Materials: Phthalic anhydride, 4,4'-sulfonyldianiline (DDS), 1,4-dibromobenzene, and 4-aminothiophenol were purchased from Aladdin and used as received. 1,4-Dibromocyclohexane was obtained from Zhengzhou Zhongwei Bio-tech Co., Ltd, and used as received. 4,4'-Thiodianiline (SDA) was purchased from TCI and recrystallized from ethanol. *N*,*N*-Dimethylformamide (DMF) purchased from Aladdin was dried over calcium hydride for 12 h and distilled under reduced pressure. 4,4-Oxydiphthalic anhydride (ODPA) was purchased from J&K Chemical Ltd., and recrystallized from acetic anhydride. All other reagents were analytical grade from commercial sources and used as received, unless otherwise mentioned.

Instrumentation:

^{1}H NMR were recorded on a Varian Mercury-plus 300 spectrometer, and ^{13}C NMR spectra were performed on a Varian Unity Inova 500 NB spectrometer. Elemental analysis was conducted with CHNS elemental analyzer. Mass spectra were analyzed by Thermo EI mass spectrometer (DSQ II). Infrared spectra (IR) were obtained by a BRUKER TENSOR 27 Fourier-transform infrared (FT-IR) spectrometer. X-ray diffraction (XRD) measurements were performed on Rigaku SmartLab X-ray diffractometer at a scanning rate of 10 ^{o}/min. The inherent viscosities (η_{inh}) of the polymers were measured at a solid content of 0.5 wt% in DMF at 30 °C with an Ostwald viscometer. Ultraviolet-visible (UV-vis) absorption and transmittance spectra were obtained on Hitachi UV-Vis spectrophotometer (U-3900). The fluorescence spectra were recorded using Shimadzu RF-5301PC spectrometer. The excitation spectra were obtained by detecting the fluorescence intensities at the peak wavelength of the emission spectra, and the emission spectra were obtained with excitation at the peak wavelength of the corresponding excitation spectra. The photoluminescence quantum yield (Φ_{PL}) and lifetime were calculated by using a calibrated integrating sphere coupled to an Edinburgh Instrument Ltd. FLS980 spectrometer. Samples were excited at the wavelength of corresponding excitation peak. Differential scanning calorimetry (DSC) curves were obtained with a PekinElmer DSC-4000 thermal analyzer at a heating rate of 10 ^{o}C/min under a nitrogen flow. Thermogravimetric analyses (TGA) were carried out on a TA thermal analyzer (Q50) under a nitrogen atmosphere at a heating rate of 20 °C/min. Thermomechanical analyses (TMA) were conducted with a TA TMA Q400 analyzer at a preload force of 0.05 N and a heating rate of 10 °C/min. Tensile test was conducted by a SANS Model CMT6103 instrument.

Molecular simulation and analysis were carried out with the Gaussian 09 program package. The molecular geometry and the molecular orbitals of the model unit in the polyimide molecular structure were calculated and optimized by means of the density functional theory (DFT), using the Becke's three-parameter hybrid density functional method in conjunction with Lee-Yang-Parr's correction functional (B3LYP) method, and the 6-31+G(*d*) basic set. For all simulations, vibration frequencies were calculated analytically to ensure the minimum total energy of the optimized molecular geometry.

Synthesis and Preparation

Synthesis of diamine monomers

The diamine 4,4'-(1,4-phenylenebis(sulfanediyl))dianiline (diSDA) and 4,4'-(cyclohexane-1,4-diylbis (sulfanediyl))dianiline (diSCHDA) shared a similar synthetic procedure as follow: To a solution of dibromo-compound (20 mmol) and 4-aminobenzenethiol (5.26 g, 42 mmol) in *N*-methyl-2-pyrrolidone (NMP) (80 mL), potassium carbonate (4.98 g, 36 mmol) and toluene (15 mL) were added. The mixture was rigorously stirred at 70 °C for 1 hour, 150 °C for 2 hours, and 210 °C for 1 hour under argon. After cooling to room temperature, the resulting mixture was poured into ice water (300 mL). The crude product was filtered off and recrystallized from ethanol to afford the diamine compound.

Monomer diSDA: white needle crystal (4.22 g, 65%). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 7.14–7.12 (d, 4H), 6.94 (s, 4H), 6.60–6.58 (d, 4H), 5.49 (s, –NH$_2$, 4H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 115.25, 115.61, 127.74, 136.39, 137.13 and 150.29. Anal. calcd for $C_{18}H_{16}N_2S_2$: C, 66.63; H, 4.97; N, 8.63, S, 19.76. Found: C, 66.30; H, 5.08; N, 8.83; S, 19.66. MS (EI, m/z): [M]$^+$ calcd for $C_{18}H_{16}N_2S_2$: 324.08. Found: 324. IR (KBr, ν, cm^{-1}): 3405, 3320, 1591, 1493, 1476 and 1287.

Monomer diSCHDA: white crystalline solid (1.78 g, 27 %). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 7.07–7.05 (d, 4H), 6.51–6.48 (d, 4H), 5.28 (s, –NH$_2$, 4H), 2.68 (s, 2H), 1.87–1.85 (m, 4H), 1.25–1.17 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 33.11, 46.70, 114.62, 117.18, 136.25 and 149.39. Anal. calcd for $C_{18}H_{22}N_2S_2$: C, 65.41; H, 6.71; N, 8.48, S, 19.40. Found: C, 65.27; H, 6.98; N, 8.58; S, 19.46. MS (EI, m/z): [M]$^+$ calcd for $C_{18}H_{22}N_2S_2$: 330.12. Found: 330. IR (KBr, ν, cm^{-1}): 3380, 3312, 2930, 2853, 1597, 1491 and 1277.

Synthesis of model compound 2,2'-(thiobis(4,1-phenylene))bis(isoindoline-1,3-dione) (M1)

SDA (1.30 g, 6.0 mmol) and phthalic anhydride (5.33 g, 36 mmol) were mixed and dissolved in acetic acid (40 mL). The solution was stirred at 120 °C under argon for 6 h. After cooling to room temperature, the resulting precipitate was filtered and washed by ethanol to give a grey powder (1.91 g, 67%). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.00–7.98 (m, 4H), 7.93–7.91 (m, 4H), 7.57–7.51 (m, 8H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 123.97, 128.83, 131.63, 131.75, 132.02, 134.80, 135.25 and 167.31. Anal. calcd for $C_{28}H_{16}N_2O_4S$: C, 70.58; H, 3.38; N, 5.88, S, 6.73. Found: C, 70.41; H, 3.46; N, 6.05; S, 6.75. MS (EI, m/z): [M]$^+$ calcd for $C_{28}H_{16}N_2O_4S$: 476.08. Found: 476. IR (KBr, ν, cm^{-1}): 1713, 1495 and 1377.

Synthesis of model compound 2,2'-(sulfonylbis(4,1-phenylene))bis(isoindoline-1,3-dione) (M2)

M2 was synthesized by the reaction between DDS and phthalic anhydride using a similar procedure as M1 to give a white solid (yield: 54%). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.21–8.19 (d, 4H), 8.02–7.99 (m, 4H), 7.96–7.92 (m, 4H), 7.79–7.77 (d, 4H). ^{13}C NMR (125 MHz, DMSO-d_6, δ, ppm): 124.14, 128.41, 128.73, 131.92, 135.44, 137.15, 140.13 and 166.90. Anal. calcd for $C_{28}H_{16}N_2O_6S$: C, 66.14; H, 3.17; N, 5.51, S, 6.30. Found: C, 66.02; H, 3.14; N, 5.53; S, 6.28. MS (EI, m/z): [M]$^+$ calcd for $C_{28}H_{16}N_2O_6S$: 508.07. Found: 508. IR (KBr, ν, cm^{-1}): 1716, 1497, 1377, 1321 and 1153.

Synthesis of model compound MO

In a suspension of M1 (0.40 g, 8.4 mmol) in acetic acid (5 mL) was added H_2O_2 (2 mL, 30 wt%), and the mixture was heated to reflux for 3 h. The resulting precipitate was filtered off to afford MO as a white solid (0.40 g).

Preparation of polyimides

The synthesis of polyimide SPI is used as an example for the general synthetic route of sulfide-based polyimides and DDSPI. To a solution of diamine SDA (0.3081 g, 1.424 mmol) in 5 mL of anhydrous DMF, was added dianhydride ODPA (0.4419 g, 1.424 mmol) in one portion. After stirring at room temperature under argon for 8 h, the resulting poly(amic acid) solution was subsequently coated on a clean glass plate, followed by thermal imidization in a vacuum oven at 100 ^{o}C/1 h, 200 ^{o}C/1 h, and 300 ^{o}C/1 h. After cooling to room temperature, the plate was soaked in warm water and the polyimide film was peeled off automatically. For diSCHPI, a precursor PAA film was achieved after the solvent was evaporated at 100 ^{o}C/2 h. The imidization was conducted by soaking the PAA film into a mixed solution of acetic anhydride/pyridine (v/v=2/1) for 24 h to afford a transparent PI film.

H_2O_2 incubation

The sulfide-based polyimide films were immersed in 5 wt% H_2O_2 in acetic acid solution (made up by mixing 30 wt% H_2O_2 aqueous solution and acetic acid) at 60 ^oC for 24 h, to result in tough and flexible sulfone-based polyimide films. Milder conditions of 1 wt% and 0.5 wt% acidic H_2O_2 at room temperature for 12 h were attempted for diSCHPI to evaluate the emission turn-on sensitivity. The film patterning was conducted by dropping the mixed solution onto the fillister carved on the wax-coated film, followed by incubating overnight at room temperature and wax-unwrapping.

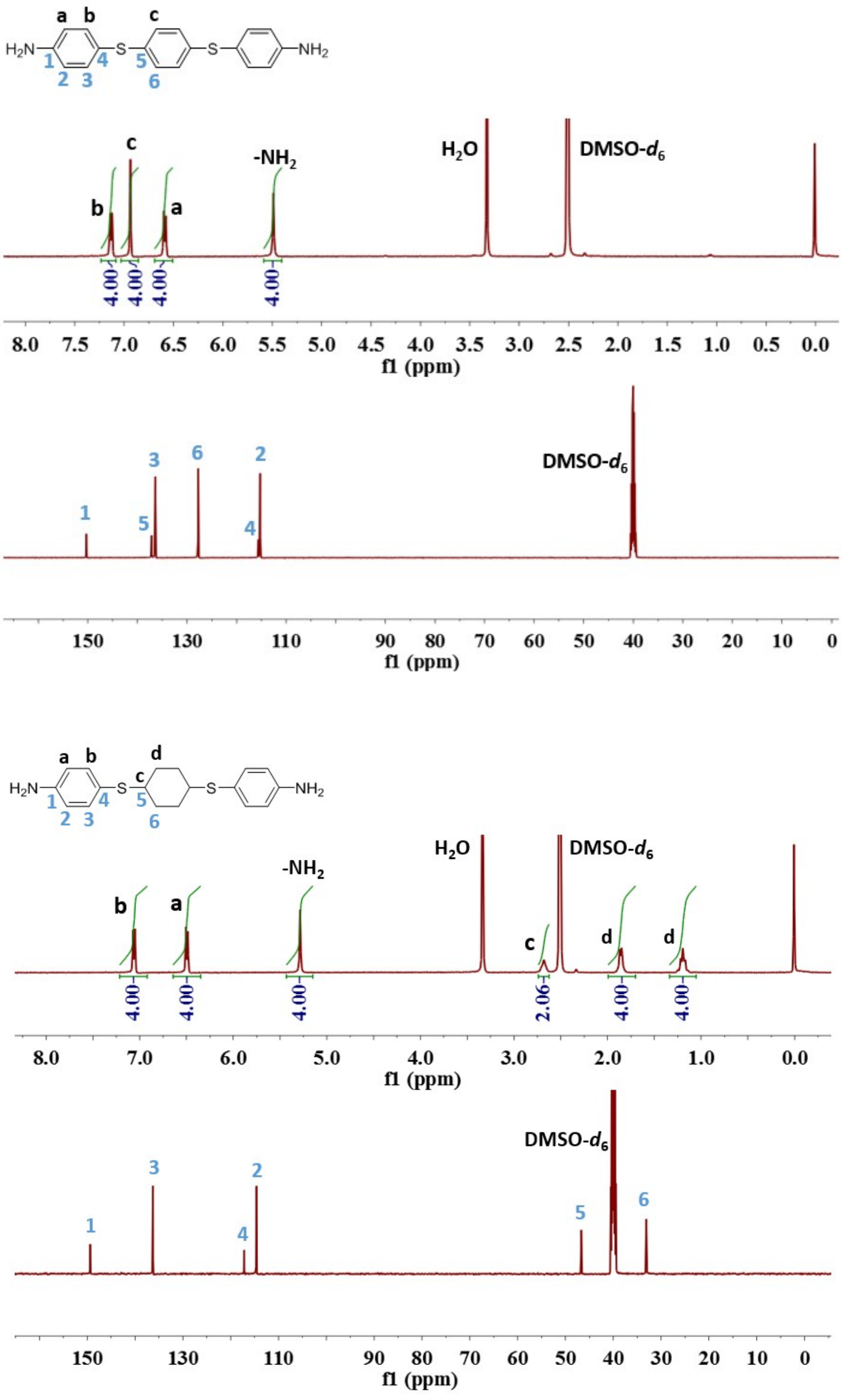

Fig. S1 ^{1}H NMR and ^{13}C NMR spectra of diamine monomers diSDA and diSCHDA.

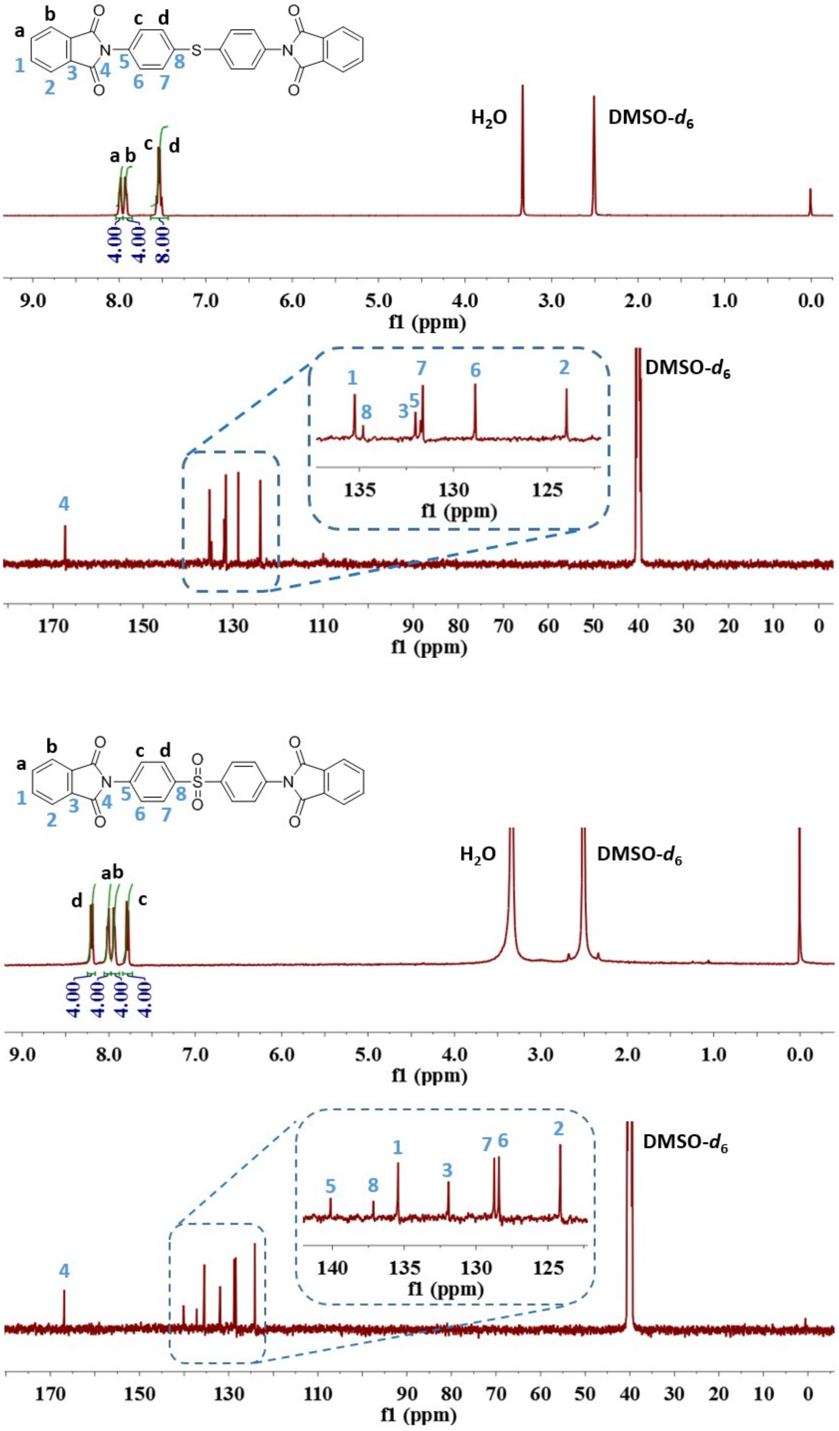

Fig. S2 ^{1}H NMR and ^{13}C NMR spectra of the model compounds M1 and M2.

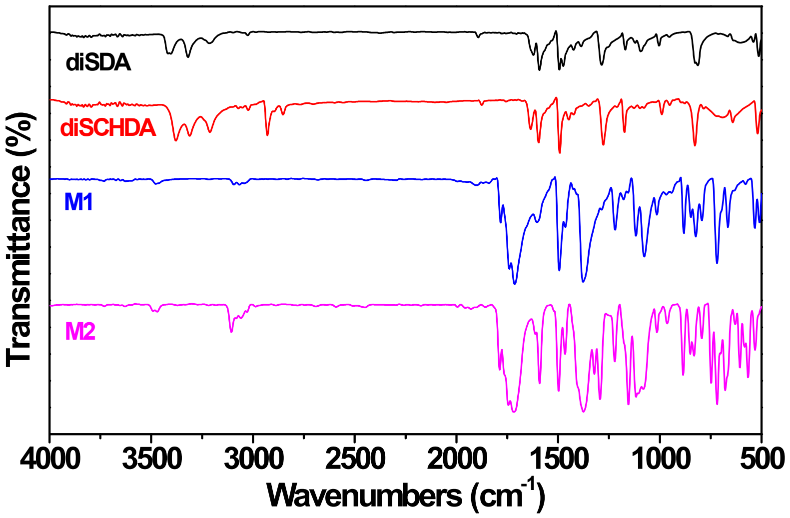

Fig. S3 FTIR spectra of diSDA, diSCHDA, M1 and M2.

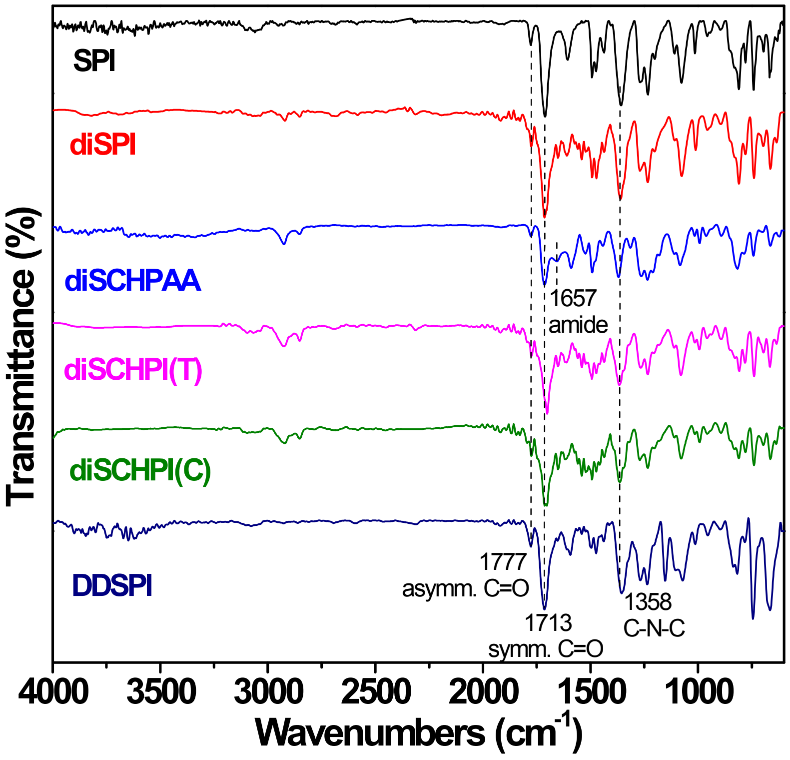

Fig. S4 FTIR spectra of polymer films SPI, diSPI, diSCHPAA, diSCHPI(T), diSCHPI(C), and DDSPI.

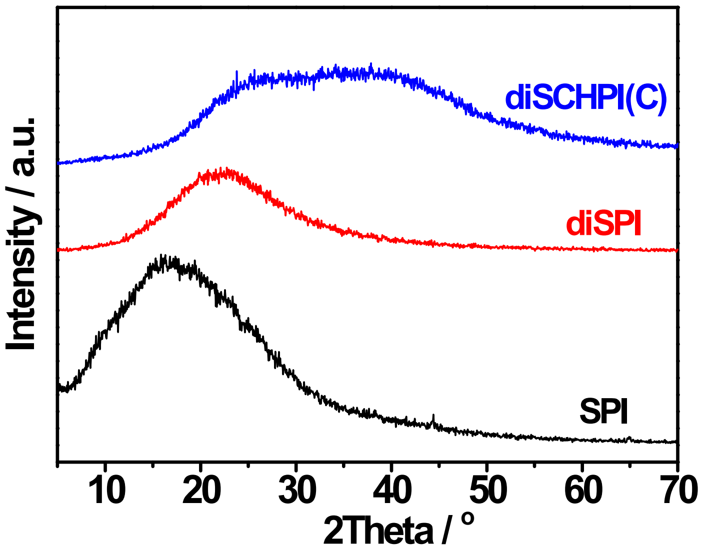

Fig. S5 XRD patterns of SPI, diSPI and diSCHPI(C).

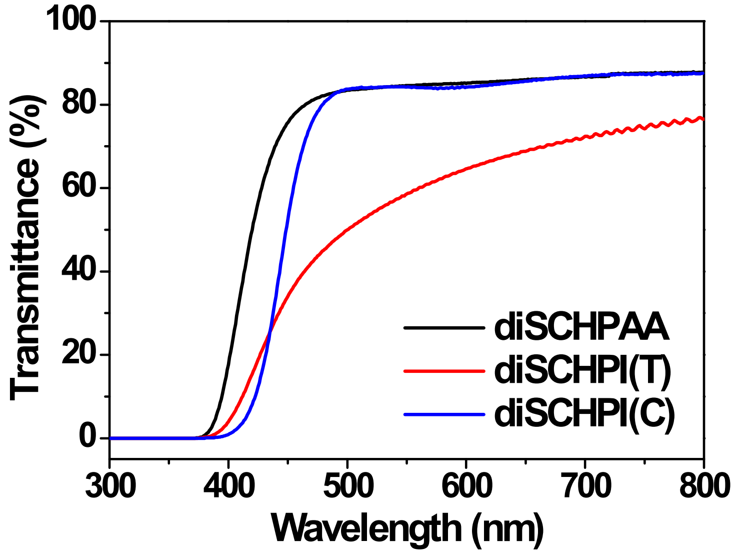

Fig. S6 Transmittance spectra of diSCHPAA, diSCHPI(T), and diSCHPI(C).

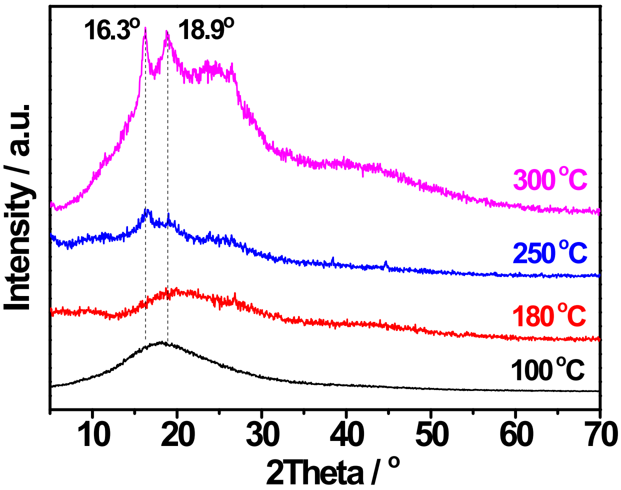

Fig. S7 XRD patterns of diSCHPAA after the treatment at varied temperature.

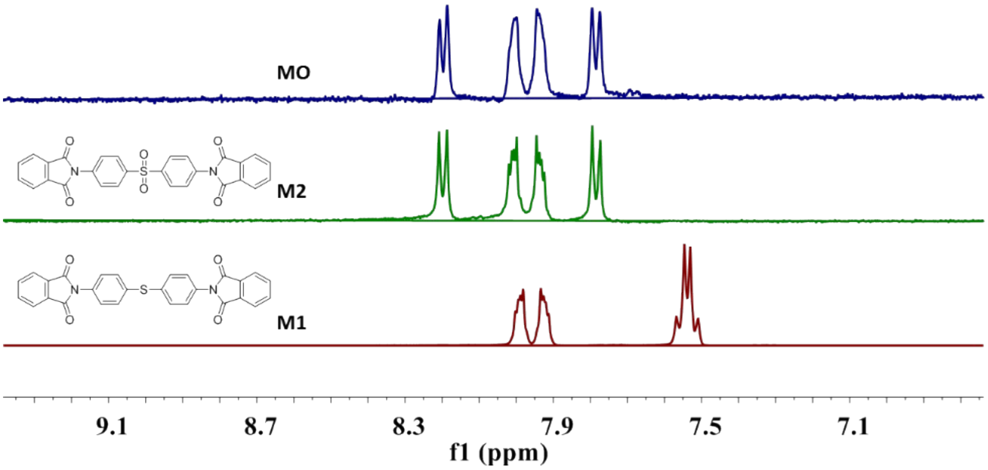

Fig. S8 ^{1}H NMR spectrum comparison of the model compounds M1, M2, and MO.

Table S1 Theoretical calculations of S_0 to S_1 transitions for the model units (MUs)

System	Transition Wavelength (nm)	Oscillator Strength	Orbitals	Contribution
S	324.40	0.0061	HOMO → LUMO	0.40
			HOMO → LUMO+1	0.33
S(O)	300.59	0.0459	HOMO → LUMO	0.54
			HOMO → LUMO+1	0.17
diS	326.47	0.0015	HOMO → LUMO+1	0.60
			HOMO → LUMO	0.15
diS(O)	300.54	0.0461	HOMO → LUMO	0.82
diSCH	308.80	0.0194	HOMO-2 → LUMO	0.29
			HOMO-1 → LUMO	0.18
			HOMO → LUMO	0.06
diSCH(O)	299.74	0.0459	HOMO → LUMO	0.85

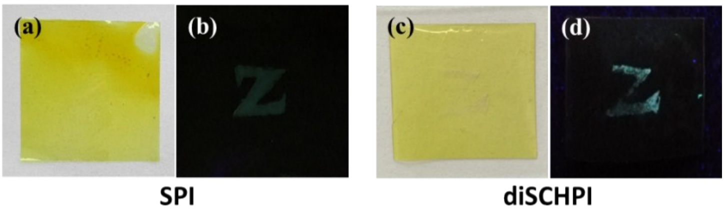

Fig. S9 The polyimide films SPI and diSCHPI(C) with H_2O_2-patterning under white light (a and c), and UV light (b and d).

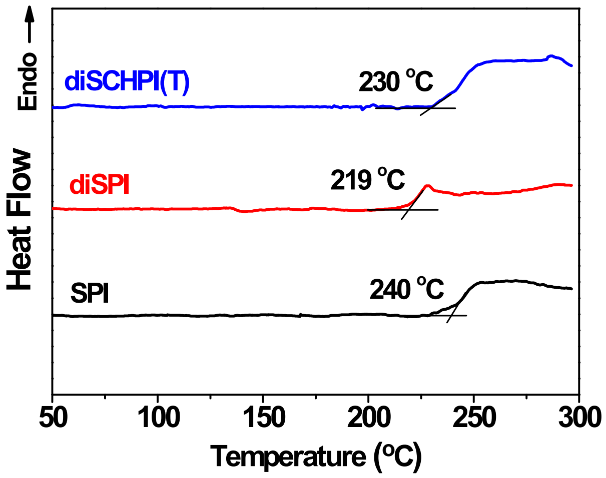

Fig. S10 DSC curves of the polyimide films.

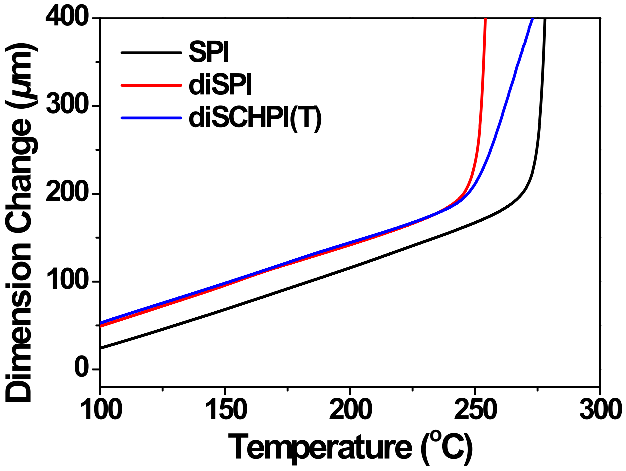

Fig. S11 TMA curves of the polyimide films.

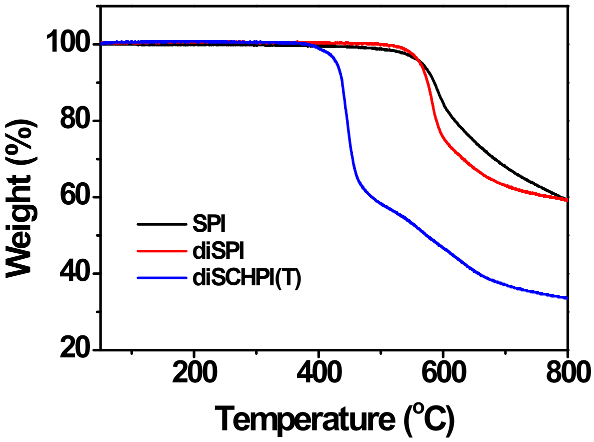

Fig. S12 TGA curves of the polyimide films.