Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Cyanotriphenylamine-based Polyimidothioethers as Multifunctional Materials for Ambipolar Electrochromic, Electrofluorochromic Devices, and Fluorescent Electrospun Fibers

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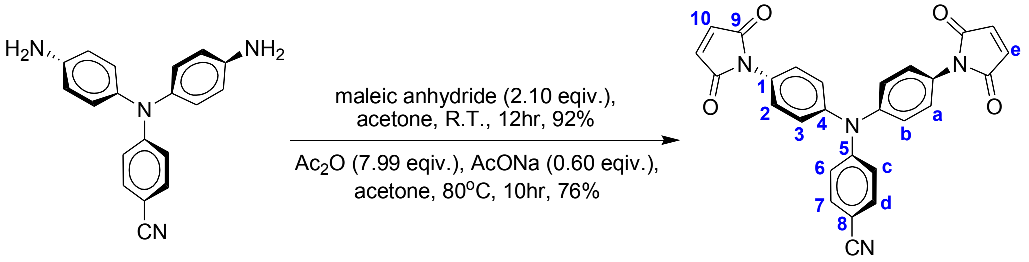
Experimental Section

Materials.

4,4'-Diamino-4''-cyanotriphenylamine (**1**) was prepared according to the reported literature.[S1] Commercially available monomers such as 1,2-ethanedithiol (**DT-C$_2$**) and 4,4'-thiobisbenzenethiol (**DT-S**) were used as received. Maleic anhydride (SHOWA) was purified by vacuum sublimation. TBAP (Acros) was recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

Monomer synthesis



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CN-BMI

4,4'-Bismaleimido-4''-cyanotriphenylamine (CN-BMI)

A solution of maleic anhydride (2.06 g, 20.98 mmol) in 20 mL of acetone was charged into a 100-mL three-necked round-bottomed flask equipped with a feed tube under nitrogen atmosphere. Then, a solution of compound **1** (3.00 g, 9.99 mmol) dissolved in 70 mL of acetone was dropped into the flask slowly through the feed tube. The mixture was stirred at -5 ^{o}C for 12 hr. The insoluble solid was collected by filtration and washed with acetone to obtain 4.55 g (92 % in yield) of orange solid as diamic acid compound. FT-IR (KBr): 2212 cm^{-1} (C≡N stretch), 3286 cm^{-1} (N-H stretch), 2800-3600 (-OH stretch), 1714 (C=O stretch). ^{1}H and ^{13}C NMR spectra can refer to Figure S4 in page *SI-7*.

A solution of diamic acid compound (4.46 g, 8.99 mmol) in 35 mL of acetone and anhydrous sodium acetate (0.44 g, 5.40 mmol) were charged into a 100-mL three-necked round-bottomed flask equipped with a stirring bar under nitrogen atmosphere. Acetic anhydride (6.75 mL, 71.91 mmol) was added dropwise as the mixture was heated to 80 ^{o}C slowly. After the solution was stirred at reflux temperature for 10 h, the mixture was poured into water, and the precipitated yellow powder was collected by filtration and recrystallized by acetone. The product was filtered to afford 3.15 g (76 % in yield) of yellow crystal with a mp of 242-244 ^{o}C (by DSC). FT-IR (KBr): 2220 cm^{-1} (C≡N stretch), 1714 (C=O stretch), 1596 (C=C stretch), and 1146 cm^{-1} (imide ring deformation). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 6.96 (d, *J* = 8.1 Hz, 2H), 7.19 (s, 4H), 7.28 (d, *J* = 8.7 Hz, 4H), 7.37 (d, *J* = 8.7 Hz, 4H), 7.66 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 102.48, 119.51 (-C≡N), 120.10, 126.45, 128.48, 128.63, 133.89, 134.93, 144.68, 151.07, 170.06. Anal. Calcd (%) for $C_{27}H_{16}N_4O_4$ (460.44): C, 70.43; H, 3.50; N, 12.17. Found: C, 70.14; H, 3.63; N, 12.10.

Polymer Synthesis

The synthesis of PITE **CN-S** was used as an example to illustrate the general synthetic route used to produce the PITEs. First, the dithiol **DT-S** (545.7 mg; 2.14 mmol) was added to the solution of bismaleimide **CN-BMI** (983.4 mg; 2.14 mmol) dissolved in 5.3 mL of *m*-cresol and stirred for 10 min. Then, 10.7 μL of triethylamine were added slowly and the polymerization proceeded at room temperature for 4 hours. During the polymerization, the solution viscosity increased gradually, and the obtained polymer solution was then poured slowly into 300 mL acidified methanol giving rise to a white fiber-like precipitate which was collected by filtration, washed thoroughly with methanol, and dried under vacuum at 100 °C. Precipitations from DMAc into methanol were carried out twice for further purification. The inherent viscosity of the obtained PITE **CN-S** was 0.34 dL/g (measured at a concentration of 0.5 g/dL in DMAc at 30 °C). FT-IR (KBr): 2221 cm^{-1} (C≡N stretch), 1714 (C=O stretch), 1596 (C=C stretch), and 1180 cm^{-1} (C-S-C stretch). ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 7.65 (d, *J* = 4.98 Hz, 2H), 7.50 (d, *J* = 4.89 Hz, 4H), 7.29 (d, *J* = 4.89 Hz, 4H), 7.22 (d, *J* = 5.13 Hz, 4H), 7.17 (d, *J* = 5.13 Hz, 4H), 6.97 (d, *J* = 4.98 Hz, 2H), 4.57-4.54 (m, 2H), 3.44-3.39 (m, 2H), 2.82-2.78 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 36.08, 43.39, 102.84, 119.09 (-C≡N), 120.64, 125.75, 128.30, 128.59, 131.18, 131.30, 131.33, 131.48, 133.21, 133.59, 134.61, 145.10, 150.57, 169.49, 173.75, 174.72. Anal. Calcd. (%) For $(C_{39}H_{26}N_4O_4S_3)_n$ $(710.84)_n$: C, 65.90; H, 3.69; N, 7.88. Found: C, 65.63; H, 4.01; N, 7.98. The other PITE **CN-C$_2$** was prepared from bismaleimide **CN-BMI** and dithiol **DT-C$_2$** by the similar procedure as described above.

Preparation of the PITE Films

A solution of polymer was made by dissolving about 0.4 g of the PITE sample in 9 mL of DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven for 5 h to remove most of the solvent; then the semidried film was further dried *in vacuo* at 150 °C for 8 h. The obtained films were about 20–35 μm in thickness and were used for solubility tests and thermal analyses.

Fabrication of Electrospun Fibers

The polymer solutions with the concentration of 30 wt% in DMAc were used to produce the electrospun (ES) fibers. The ES fibers were prepared using a single-capillary spinneret. First, the solution was fed into the syringe pumps (KD Scientific model 100) connected to the metallic needle, with the feed rate of 0.05 mL/h. The metallic needle was connected to a high-voltage power supply (YSTC), and a piece of aluminum foil was placed 6 cm below the tip of the needle to collect the nanofibers. The spinning voltage was set at 15 kV. All experiments were carried out at room temperature.

Measurements

Elemental analyses were run in a Heraeus VarioEL-III CHNS elemental analyzer. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-AL 300 MHz NMR spectrometer in DMSO-d_6, using tetramethylsilane as an internal reference, and peak multiplicity was reported as follows: d, doublet; m, multiplet. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 ^{o}C. Gel permeation chromatographic (GPC) analysis was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5 μm Styragel HR-2 and HR-4 columns (7.8 mm I. D. × 300 mm) were connected in series with 50nM LiCl in DMAc as the eluent at a flow rate of 0.6 mL/min at 40 ^{o}C and were calibrated with polystyrene standards. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6-8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm^3/min) at a heating rate of 20 ^{o}C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 10 ^{o}C/min in flowing nitrogen (20 cm^3/min). Ultraviolet-visible (UV-Vis) spectra of the polymer films were recorded on a Hewlett-Packard 8453 UV-Visible diode array spectrometer. Photoluminescence (PL) spectra and CIE 1931 coordinates were measured with Fluorolog-3 spectrofluorometer. PL quantum yields (Φ_{PL}) of the samples in different solvents were measured by using quinine sulfate dissolved in 1 N sulfuric acid as a reference standard (Φ_{PL} = 0.546).[S2] The Photoluminescence quantum yields (PLQYs) of polymer thin films were determined using a calibrated integrating sphere by using Fluorolog-3 spectrofluorometer. All spectra were obtained by averaging five scans. Electrochemistry was performed with a CH Instruments 612C electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.5 cm x 1.1 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. Spectroelectrochemical experiments were carried out in a cell built from a 1 cm commercial UV-visible cuvette using Hewlett-Packard 8453 UV-Visible diode array spectrophotometer. The ITO-coated glass slide was used as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl cell as the reference electrode.

References

S1. L. Li, R. Kikuchi, M. A. Kakimoto, M. Jikei, A. Takahashi, *High Perform. Polym.* 2005, **17**, 135.

S2. (*a*) H. J. Yen, G. S. Liou, *J. Polym. Sci. Part A: Polym. Chem.* 2008, **46**, 7354; (*b*) H. J. Yen, J. H. Wu, W. C. Wang, G. S. Liou *Adv. Opt. Mater.* 2013, **1**, 668-676

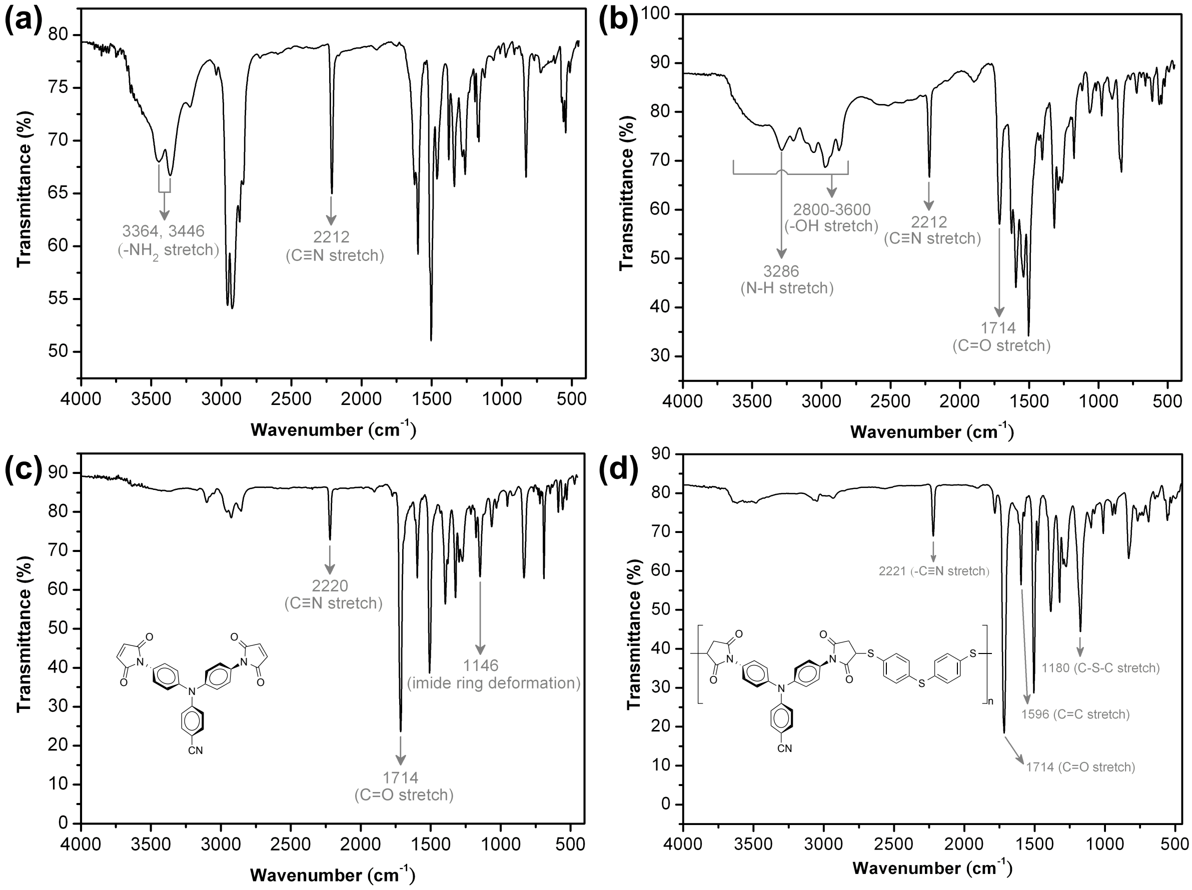

Figure S1. FT-IR spectra of (a) diamino compound **1**, (b) diamic acid compound, (c) **CN-BMI**, and (d) PITE **CN-S**.

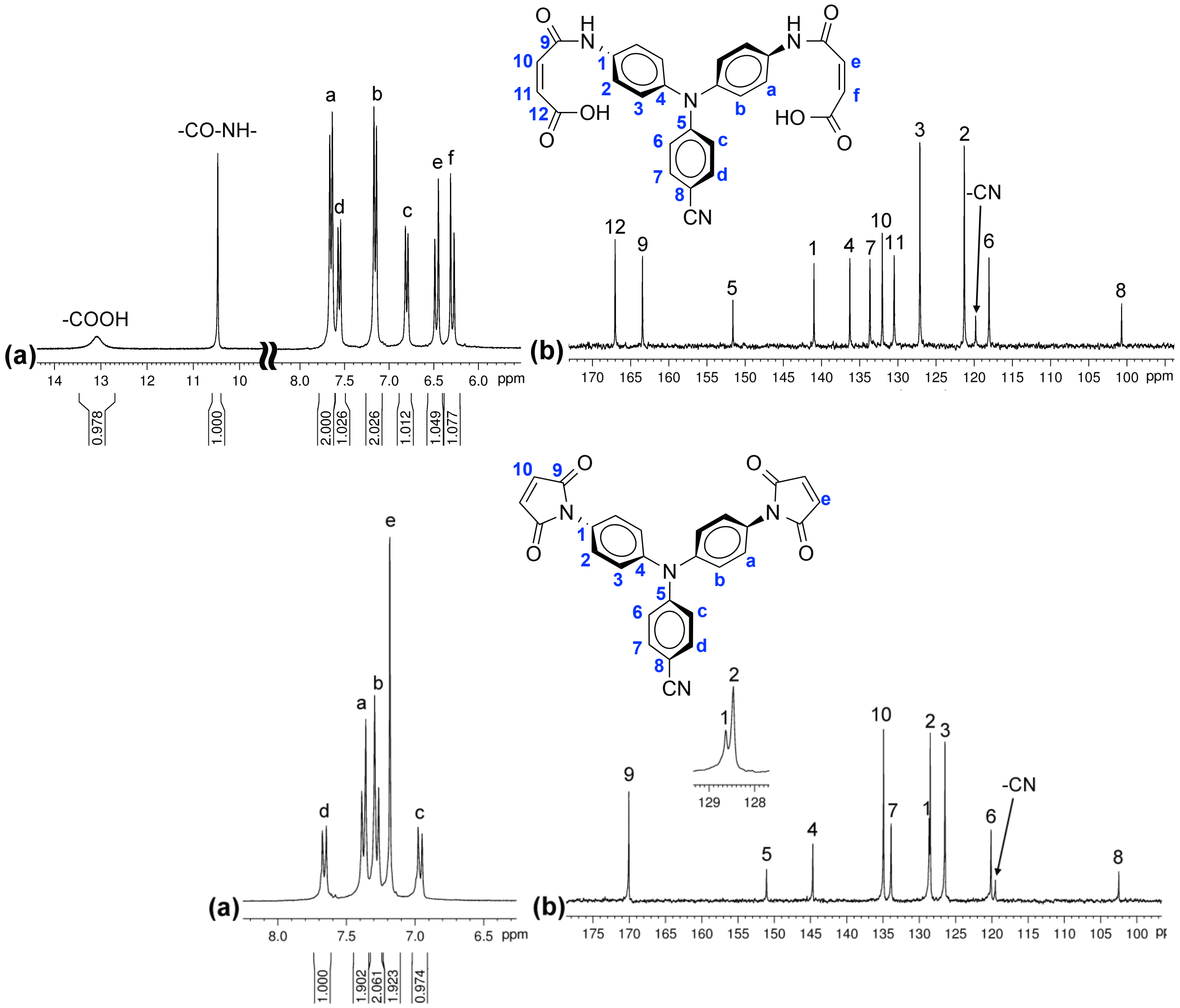

Figure S2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of diamic acid compound and **CN-BMI** in DMSO-d_6.

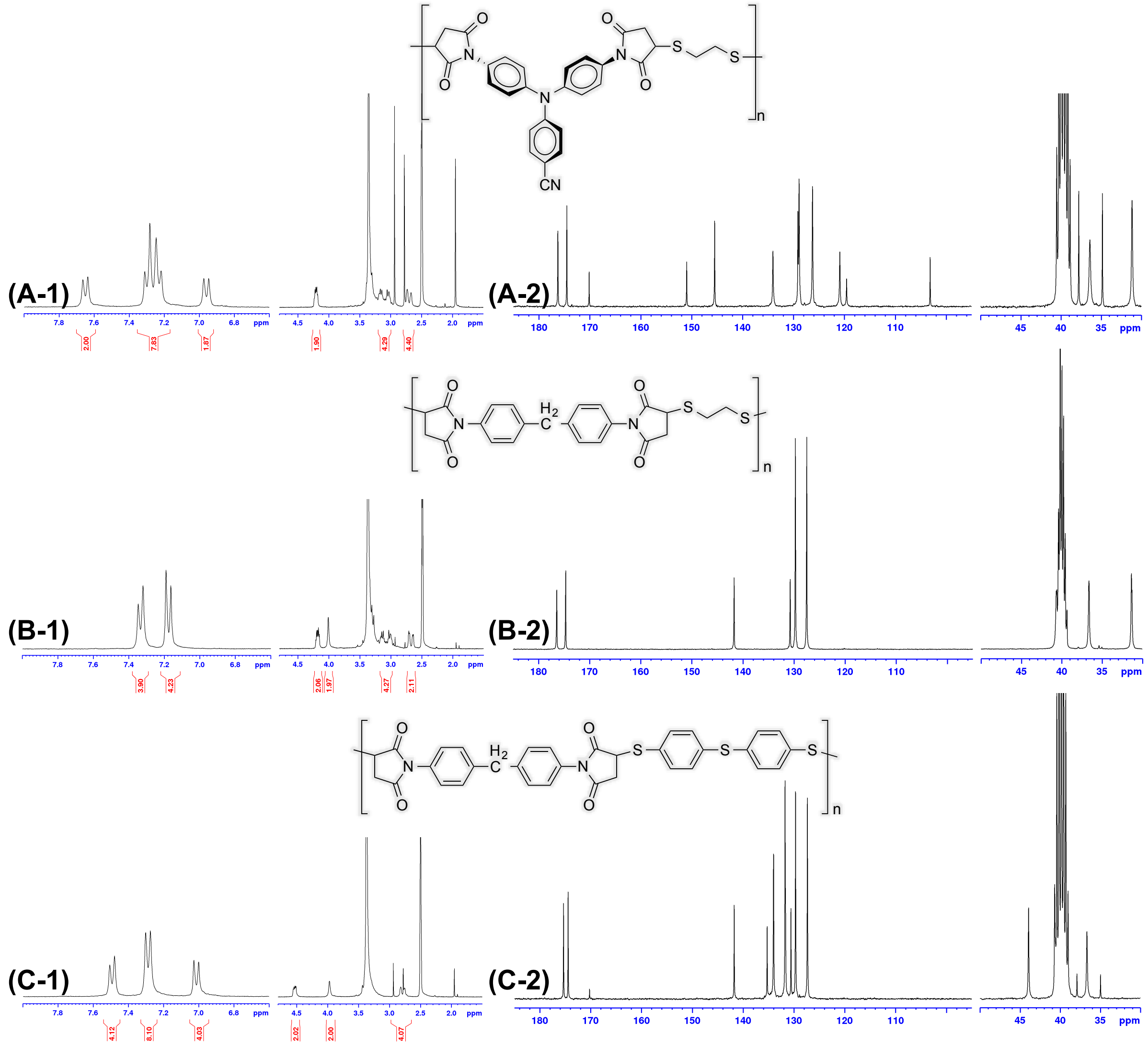

Figure S3. ^{1}H (left) and ^{13}C (right) NMR spectra of PITEs (A) **CN-C$_2$** (B) **CH$_2$-C$_2$**, and (C) **CH$_2$-S** in DMSO-d_6.

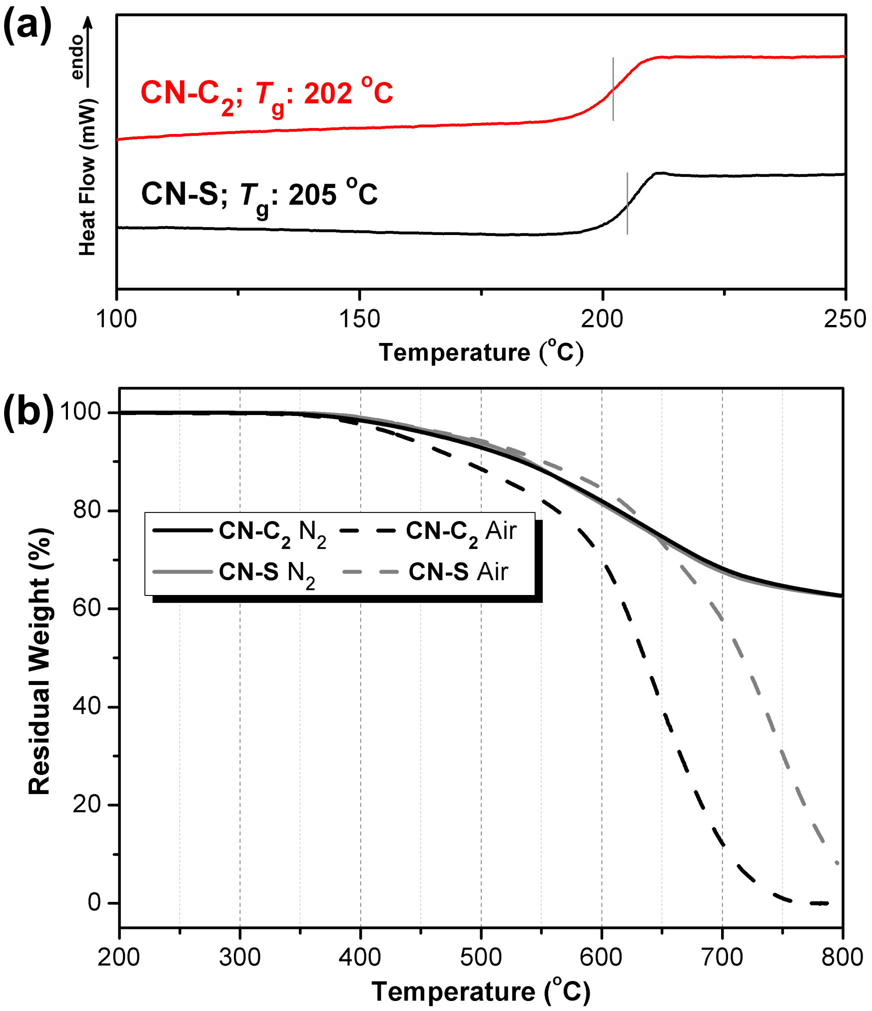

Figure S4. (a) DSC curves and (b) TGA thermograms of PITEs at a scan rate of 20 °C/min.

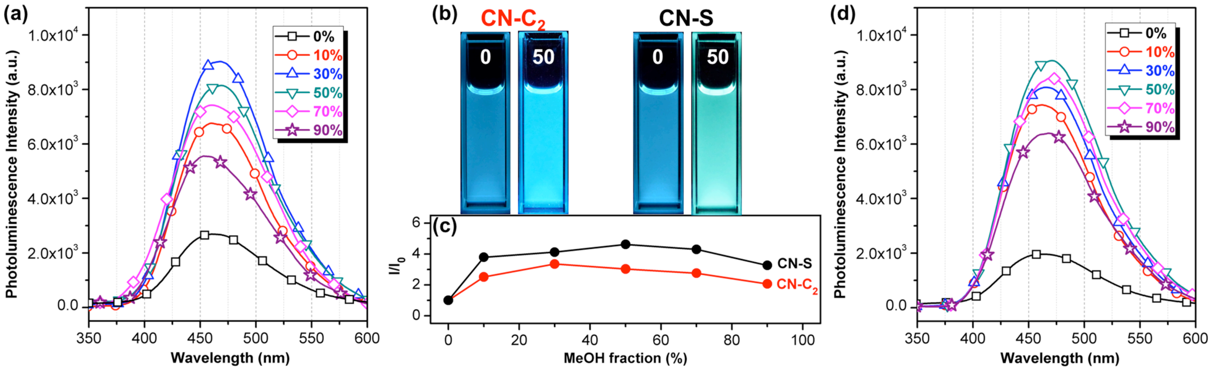

Figure S5. PL spectra of (a) **CN-C$_2$** and (d) **CN-S** in NMP-methanol with different methanol fraction (f_w/vol. %) (solution concentration is 10 µM and excited with each λ_max). (b) Photographs were taken under illumination of a 365 nm UV light. (c) Variation in PL intensity of PITEs in NMP-methanol with different methanol fraction.

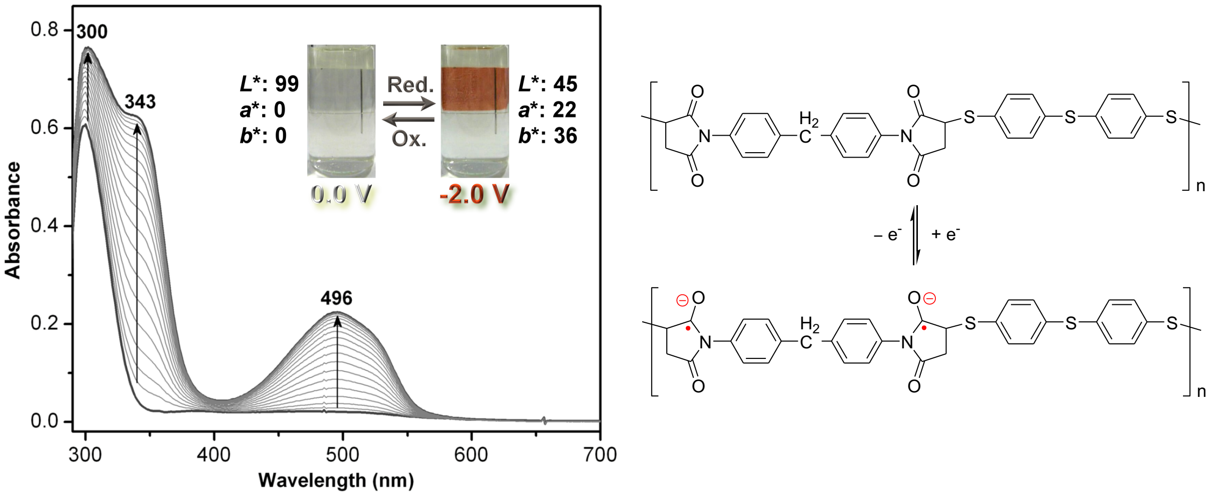

Figure S6. Electrochromic behavior and the postulated cathodic reduction pathway of PITE **CH_2-S** film.

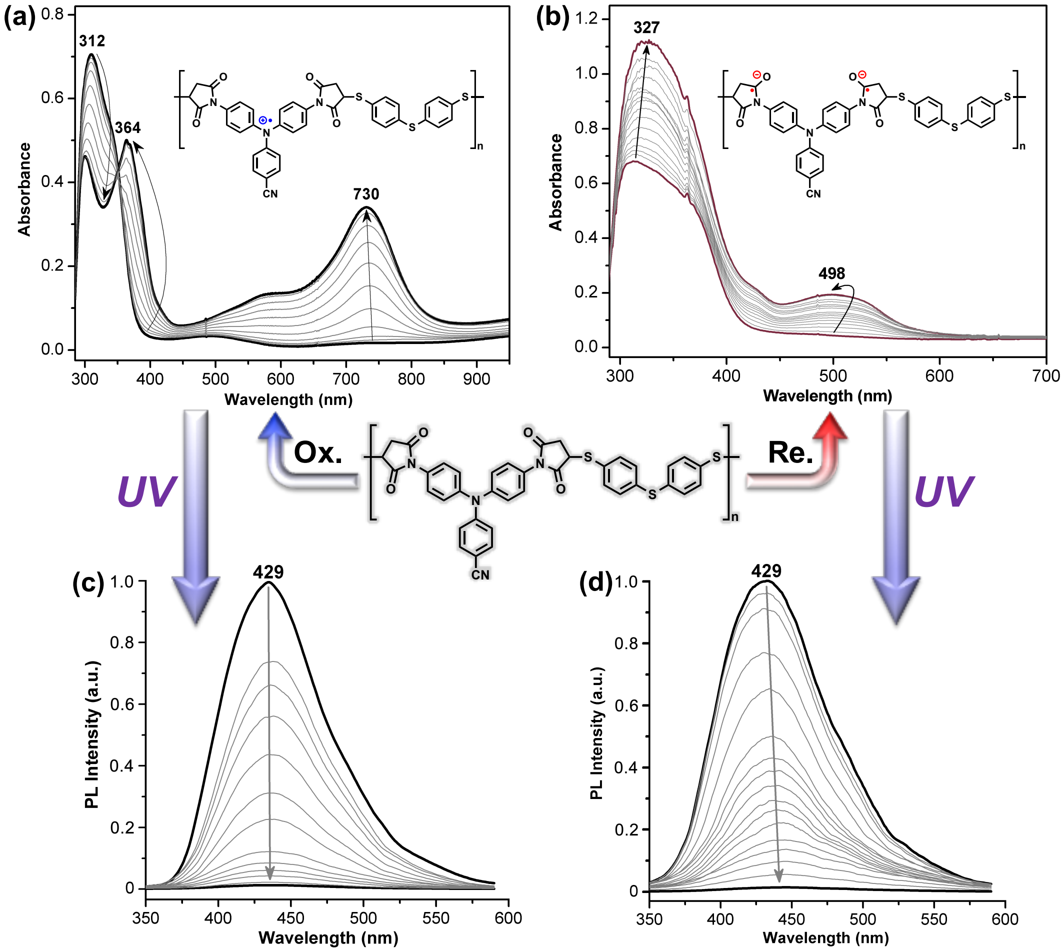

Figure S7. Spectroelectrochemistry of PITE **CN-S** thin film (~100 nm in thickness) by increasing and decreasing the applied voltage to (a) 1.70 and (b) -2.0 (V vs. Ag/AgCl), respectively. Fluorescence intensity changes of **CN-S** (~100 nm in thickness) by applying the electric voltage to (c) 1.70 and (d) -2.0 (V vs. Ag/AgCl), respectively.

Table S1. Inherent Viscosity[a] and Molecular Weights[b] of Polyimidothioethers

Polymer	η_{inh} (dL/g)	M_w	M_n	PDI[c]	DP[d]
$CN\text{-}C_2$	0.32	39,000	20,300	1.92	37
CN-S	0.34	42,900	21,200	2.02	31
$CH_2\text{-}C_2$	0.39	57,100	27,100	2.11	60
$CH_2\text{-}S$	0.48	73,100	35,500	2.06	58

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

[b] Calibrated with polystyrene standards, using DMAc with 50mM LiCl as the eluent at a constant flow rate of 0.6 mL/min at 40 °C.

[c] Polydispersity Index (M_w/M_n).

[d] Degree of Polymerization.

Table S2. Solubility Behavior of Polyimidothioethers

Code	Solubility in various Solvent						
	NMP	DMAc	DMF	*m*-Cresol	THF	$CHCl_3$	MeOH
$CN\text{-}C_2$	++	++	++	++	+−	+−	−
CN-S	++	++	++	++	+−	+−	−

The solubility was determined with a 50 mg sample in 1 mL of a solvent. ++, soluble at room temperature; +−, partially soluble or swelling; −, insoluble even on heating.

Table S3. Thermal Properties of Polyimidothioethers

Polymer[a]	T_g[b] (°C)	T_d^5 (°C)[c]		T_d^{10} (°C)[c]		ΔT (°C)[d]	R_{w800}[e] (%)
		N_2	Air	N_2	Air		
$CN\text{-}C_2$	202	470	435	535	485	268	62
CN-S	205	480	485	540	550	275	63

[a] The polymer film samples were heated at 300 °C for 1 h prior to all the thermal analyses.

[b] Midpoint temperature of baseline shift on the second DSC heating trace (rate: 20 °C /min) of the sample after quenching from 400 °C to 50 °C (rate: 200 °C /min) in nitrogen.

[c] 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 20 cm^3/min.

[d] The melting-process window (ΔT) was calculated as $\Delta T = T_d^5 - T_g$.

[e] Residual weight percentages at 800 °C under nitrogen flow.

Table S4. Redox Potentials and Energy Levels of Polyimidothioethers

Polymer	UV-vis absorption of the polymer films (nm)		Oxidation potential (V) (vs. Ag/AgCl in CH_3CN)		E_g[b] (eV)	HOMO[c] (eV)	LUMO (eV)
	λ_{max}	λ_{onset}	$E_{1/2}$[a]	E_{onset}			
CN-C_2	316	384	1.40	1.28	3.23	5.72	2.49
CN-S	312	391	1.40	1.29	3.17	5.73	2.56

[a] $E_{1/2}$ (Average potential of the redox couple peaks).

[b] The data were calculated from polymer films by the equation: $E_g = 1240/\lambda_{onset}$ (energy gap between HOMO and LUMO).

[c] The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV ; onset = 0.36V).