Electronic Supplementary Information

Novel High-efficiency PL Polyimide Nanofiber Containing Aggregation-Induced Emission (AIE)-active Cyanotriphenylamine Luminogen

By *Hung-Ju Yen, Chih-Jung Chen, and Guey-Sheng Liou**

Functional Polymeric Materials Laboratory, Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan

Tel: +886-2-336-5315; Fax: +886-2-336-5237; E-mail: gsliou@ntu.edu.tw

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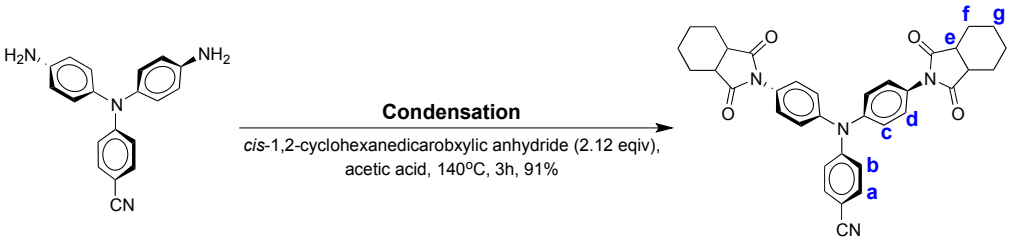
Experimental Section

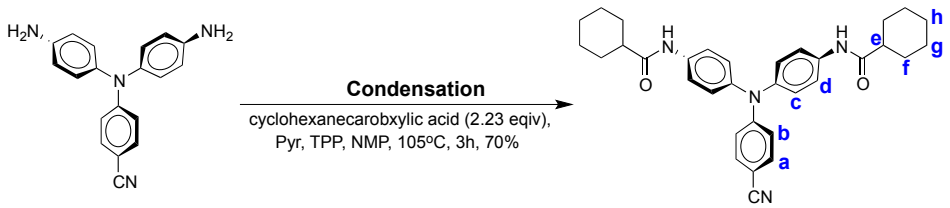
Materials.

4,4'-Diamino-4''-cyanotriphenylamine (**1**) was prepared according to a previously reported procedure.[S1] Synthesis and characterization results of model compounds, 4,4'-di(1,2-cyclohexanedicarboxyimido)-4''-cyanotriphenylamine (**M-PI**) and 4,4'-di(cyclohexylamido)-4''-cyanotriphenylamine (**M-PA**), are included in the Supporting Information. *trans*-1,4-Cyclohexanedicarboxylic acid (**CHDA**) was purchased from Tokyo Chemical Industry (TCI) Co. and used as received. 1,2,4,5-Cyclohexanetetracarboxylic dianhydride (**HPMDA**) was dried under vacuum at 150 °C for 12 h before use. Commercially obtained anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 180 °C for 8 h. All other reagents were used as received from commercial sources.



4,4'-Di(1,2-cyclohexanedicarboxyimido)-4''-cyanotriphenylamine (**M-PI**).

A 50 mL round-bottom flask equipped with a magnetic stirrer was charged with 0.403 g (1.34 mmol) of diamine **1**, 0.437 g (2.84 mmol) of *cis*-1,2-cyclohexanedicarobxylic anhydride, and 6.7 mL of acetic acid. The reaction mixture was heated with stirring at 140 °C for 3 h. The resulting reaction solution was poured into 30 mL of stirring methanol giving rise to white precipitate that was collected by filtration, washed thoroughly with methanol, and dried. Yield = 0.703 g (91%); mp = 239-240 °C. IR (KBr): 2927-2850 cm^{-1} (Cyclohexyl C-H stretch), 2215 cm^{-1} (C≡N stretch), 1778 (asym. imide C=O stretch), and 1711 cm^{-1} (sym. imide C=O stretch). ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.39 (m, 8H, H_g), 1.75 (m, 8H, H_f), 3.10 (t, 4H, H_e), 6.95 (d, J = 8.9 Hz, 2H, H_b), 7.25 (d, J = 8.9 Hz, 4H, H_c), 7.31 (d, J = 8.9 Hz, 4H, H_d), 7.66 (d, J = 8.9 Hz, 2H, H_a).



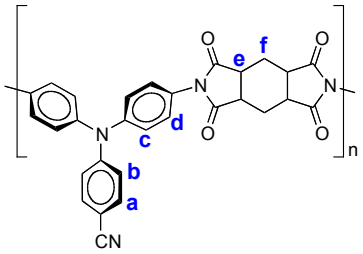
4,4'-Di(cyclohexylamido)-4''-cyanotriphenylamine (**M-PA**).

A mixture of 0.416 g (1.36 mmol) of diamine **1**, 0.388 g (3.03 mmol) of

cyclohexanecarobxylic acid, 1.4 mL of triphenyl phosphite, 0.7 mL of pyridine, and 1.4 mL of *N*-methyl-2-pyrrolidinone (NMP) was heated with stirring at 105 °C for 3 h. The mixture was poured slowly into 50 mL of stirring methano/water, then was collected by filtration and purified by acetone/acetonitrile, and dried. Yield = 70%; mp = 217-218 °C. IR (KBr): 3284 cm^{-1} (N-H stretch), 2927-2853 cm^{-1} (Cyclohexyl C-H stretch), 2220 cm^{-1} (C≡N stretch), 1656 cm^{-1} (amide carbonyl). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.11-1.61 (m, 12H, H_g+H_h), 1.72 (m, 8H, H_f), 2.26 (t, 2H, H_e), 6.70 (d, J = 8.6 Hz, 2H, H_b), 7.06 (d, J = 8.6 Hz, 4H, H_c), 7.48 (d, J = 8.6 Hz, 2H, H_a), 7.59 (d, J = 8.6 Hz, 4H, H_d), 9.82 (s, 2H, amide-NH).

Synthesis of Polyimide by One-Step Method. The polyimide **CN-PI** was synthesized from diamine monomer **1** and dianhydride **HPMDA**. To a solution of 771.8 mg (2.57 mmol) of diamine **1** in 5.0 mL of co-solvent (GBL and DMAc), 576.0 mg (2.57 mmol) of **HPMDA** was added in one portion. After stirring for 2h, the catalyst (isoquinoline) was mixed with the above solution at 180 °C for 15 h. The obtained polymer solution was poured slowly into 300 mL of stirred methanol giving rise to a brownish fibrous precipitate that was collected by filtration, washed thoroughly with methanol, and dried under vacuum at 100 °C. Reprecipitations of the polymer by DMAc/methanol were carried out twice for further purification.

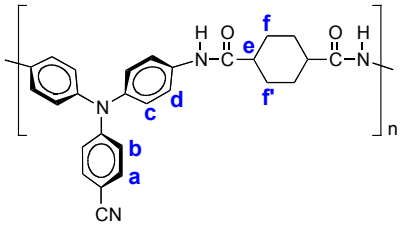
The inherent viscosity, weight-average molecular weights (M_w), and polydispersity index (PDI) of the obtained polyimide **CN-PI** were 0.49 dL/g (measured at a concentration of 0.5 g/dL in DMAc at 30 °C), 160,900 daltons, and 1.72, respectively. The FT-IR spectrum of **CN-PI** (film) exhibited characteristic imide absorption bands at around 1779 (symmetrical C=O) and 1709 (symmetrical C=O) with nitrile characteristic band at around 2221 cm^{-1} (C≡N stretching). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 2.15 (m, 4H, H_f), 3.12 (m, 4H, H_e), 6.95 (d, J = 8.7 Hz, 2H, H_b), 7.25 (d, J = 8.7 Hz, 4H, H_c), 7.32 (d, J = 8.7 Hz, 4H, H_d), 7.64 (d, J = 8.7 Hz, 2H, H_a).



Synthesis of Polyamide. The polyamide **CN-PA** was synthesized from diamine monomer **1** and diacid **CHDA**. A mixture of 1.502 g (5.00 mmol) of the diamine monomer **1**, 0.861 mg

(5.00 mmol) of **CHDA**, 0.60 g of calcium chloride, 4.0 mL of triphenyl phosphite, 2.5 mL of pyridine, and 4.0 mL of NMP was heated with stirring at 105 °C for 3 h. The obtained polymer solution was poured slowly into 300 mL of stirred methanol giving rise to a stringy, fiberlike precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried under vacuum at 100 °C. Reprecipitations of the polymer by DMAc/methanol were carried out twice for further purification.

The inherent viscosity, M_w, and PDI of the obtained polyamide **CN-PA** were 1.38 dL/g (measured at a concentration of 0.5 g/dL in DMAc at 30 °C), 78,300 daltons, and 1.91, respectively. The FT-IR spectrum of **CN-PA** (film) exhibited characteristic amide absorption bands at 3314 cm^{-1} (N-H stretch) and 1667 cm^{-1} (amide carbonyl), 2932-2863 cm^{-1} (cyclohexyl C-H stretch), and 2218 cm^{-1} (C≡N stretch). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 1.46 (m, 4H, H_f), 1.88 (m, 4H, H_f), 2.32 (m, 2H, H_e), 6.72 (d, J = 8.8 Hz, 2H, H_b), 7.10 (d, J = 8.6 Hz, 4H, H_c), 7.51 (d, J = 8.8 Hz, 2H, H_a), 7.62 (d, J = 8.6 Hz, 4H, H_d), 9.93 (s, 2H, amide-NH).



Preparation of the Polymer Films. A solution of polymer was made by dissolving about 1.2 g of the polymer sample in 15 mL of DMAc. The homogeneous solution was poured into a 12-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 160 °C for 8 h. The obtained films were about 60 μm in thickness as shown in Scheme 1, and were used for solubility tests and thermal analyses.

Fabrication of Electrospun Fibers. The polymer solutions with the concentration of 25 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 0.1 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. Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. NMR spectra were measured on a Bruker AVANCE-400 FT-NMR spectrometer using tetramethylsilane as an internal reference, and peak multiplicity was reported as follows: s, singlet; d, doublet. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 ^{o}C. 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. Thermal mechanical analyzer (TMA) experiments were conducted by a TA instrument TMA Q400 from 40 to 400 ^{o}C at a scan rate of 10 ^{o}C /min with a film/fiber probe under an applied constant load of 5mN. 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] and the Φ_{PL} of polymer thin films was determined by using a calibrated integrating sphere. All spectra were obtained by averaging five scans. The morphologies of ES fibers were characterized by field-emission scanning electron microscope (JEOL JSM-6330F). These samples were sputtered with Au/Pt and images were taken using a microscope operated at an accelerating voltage of 15 kV. Dynamic light scatting (DLS) experiments were carried out with ALV5000 Laser Light Scattering Instrument.

References

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

S2. H. J. Yen, G. S. Liou, *J. Polym. Sci. Part A: Polym. Chem.* 2008, **46**, 7354.

Results and Discussion

Synthesis and Characterization

The model compounds **M-PI** and **M-PA** were synthesized from the condensation of the CN-TPA containing diamine **1** with two equivalents of *cis*-1,2-cyclohexanedicarboxylic anhydride and cyclohexanecarboxylic acid, respectively. FT-IR and ^{1}H NMR spectroscopic techniques were used to identify the structures of these two model compounds as shown in Fig. S1 and Fig. S2, respectively. The results of all the spectroscopic analyses suggest the successful preparation of the target model compounds.

The preparation of the polyimide **CN-PI** was carried out by a one-pot, high-temperature solution polycondensation method. In this procedure, the dianhydride **HPMDA** and the diamine **1** were polymerized in *N,N*-dimethylacetamide (DMAc) and γ-butyrolactone (GBL) at 180 ^{o}C in the presence of isoquinoline as catalyst.[14] On the other hand, polyamide **CN-PA** was synthesized from the diamine **1** and dicarboxylic acid **CHDA** according to the phosphorylation technique using triphenyl phosphite and pyridine as condensing agents described by Yamazaki[15] (Scheme 1). Under these conditions, polymerization reactions proceeded homogenously and led to the formation of highly viscous polymer solutions, then could be precipitated into tough fiber-like form when slowly pouring the resulting polymer solutions into methanol. The inherent viscosities and molecular weight of these polymers are summarized in Table S1. All these high molecular weights polymers could afford transparent and tough films via solution casting. IR and NMR spectroscopic techniques were used to identify structures of the prepared polymers, where the spectra agree well with the proposed molecular structures (Fig. S3 and Fig. S4).

Polymer Properties

Solubility and Film Property

The solubility behavior of these resulting polymers was investigated qualitatively, and the results are also listed in Table S2. All of the polymers were readily soluble in polar aprotic organic solvents such as NMP, DMAc, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and *m*-cresol. Thus, the excellent solubility makes these polymers as potential candidates for practical applications by spin-coating or inkjet-printing processes to afford high performance thin films for optoelectronic devices. As shown in Scheme 1 and Fig. 1a, the polymers could be solution cast into flexible, transparent, and tough films with pale yellowish color. The enhanced solubility can be attributed to the incorporation of bulky and propeller-like nonplanar conformation CN-TPA moiety along the polymer backbone, which

results in a high steric hindrance to prevent close packing, and thus reduces the crystallization tendency.

Thermal Properties

The thermal properties of polymers were examined by TGA and TMA, and the thermal behavior data are summarized in Table S3. TGA curves of these resulting polymers in both air and nitrogen atmospheres are shown in Fig. S5. All the prepared polymers exhibited good thermal stability with insignificant weight loss up to 400 ^{o}C under nitrogen or air atmosphere, and the carbonized residue (char yield) of these polymers in a nitrogen atmosphere was more than 49 % at 800 ^{o}C. The glass-transition temperatures (T_g) could be easily measured in the TMA thermograms (as shown in Figure S5). In Table S3, polyimide **CN-PI** revealed a much higher T_g (426 ^{o}C) than the corresponding polyamide **CN-PA** (366 ^{o}C), indicating the polyimide **CN-PI** with more chain stiffness as compared with the molecular structure of polyamide **CN-PA**. In addition, these polymers revealed a remarkably increased T_g as a result of the presence of rigid TPA aromatic units and the high polarity of nitrile groups.

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

Polymer	η_{inh} (dL/g)	M_w	M_n	PDI[c]	DP[d]
CN-PI	0.49	160,900	93,500	1.72	191
CN-PA	1.38	78,300	41,000	1.91	94

[a] Measured at a polymer concentration of 0.5 g/dL in DMAc at 30 °C.
[b] Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 mL/min at 40 °C.
[c] Polydispersity Index = M_w/M_n.
[d] Degree of Polymerization.

Table S2 Solubility Behavior of Polymers

Code	Solubility in various Solvent[a]						
	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	$CHCl_3$
CN-PI	＋＋	＋＋	＋＋	＋＋	＋＋	－	－
CN-PA	＋＋	＋＋	＋＋	＋＋	＋＋	＋－	－

[a] The solubility was determined with a 10 mg sample in 1 mL of a solvent. ＋＋, soluble at room temperature; ＋－, partially soluble or swelling; －, insoluble even on heating. NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; $CHCl_3$: chloroform.

Table S3 Thermal Properties of Polymers

Polymer[a]	T_g (°C)[b]	CTE (ppm/K)[c]	T_d^5 (°C)[d]		T_d^{10} (°C)[d]		R_{w800} (%)[e]
			N_2	Air	N_2	Air	
CN-PI	426	63	415	410	465	455	49
CN-PA	366	65	470	465	500	505	58

[a] The polymer film samples were heated at 300 °C for 1 h prior to all the thermal analyses.
[b] Glass transition temperature measured by TMA with a constant applied load of 5 mN at a heating rate of 10 °C/min by film/fiber probe in nitrogen.
[c] The CTE data was determined over a 50-250 °C range by expansion mode.
[d] 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.
[e] Residual weight percentages at 800 °C under nitrogen flow.

Table S4 Photophysical properties of **M-PI** in different solvents (10 μM)

Solvent	ε[a]	λ_{abs} (nm)	λ_{em} (nm)	Φ_{PL} (%)[b]	CIE 1931 coordinates	
					x	*y*
Cyclohexane	2.0	315	385	58.8	0.1623	0.0202
$CHCl_3$	4.8	318	423	47.1	0.1541	0.0513
THF	7.6	313	426	39.2	0.1537	0.0534
CH_2Cl_2	8.9	316	433	35.4	0.1517	0.0685
NMP	32.0	312	448	35.0	0.1493	0.1060
MeCN	37.5	312	451	28.9	0.1496	0.1172
DMSO	46.7	315	454	22.9	0.1494	0.1309

[a] Dielectric constant of the solvent.

[b] The quantum yield was measured by using quinine sulfate (dissolved in 1 N H_2SO_4 with a concentration of 10 μM, assuming photoluminescence quantum efficiency of 0.546) as a standard at 24-25 °C.

Table S5 Photophysical properties of **M-PA** in different solvents (10 μM)

Solvent	ε[a]	λ_{abs} (nm)	λ_{em} (nm)	Φ_{PL} (%)[b]	CIE 1931 coordinates	
					x	*y*
Cyclohexane	2.0	313	415	36.9	0.1565	0.0390
$CHCl_3$	4.8	318	472	36.4	0.1536	0.2162
THF	7.6	307	477	30.8	0.1515	0.2226
CH_2Cl_2	8.9	315	484	25.7	0.1614	0.2720
NMP	32.0	306	500	17.3	0.1908	0.4009
MeCN	37.5	308	505	7.9	0.2077	0.4322
DMSO	46.7	308	508	6.1	0.2192	0.4646

[a] Dielectric constant of the solvent.

[b] The quantum yield was measured by using quinine sulfate (dissolved in 1 N H_2SO_4 with a concentration of 10 μM, assuming photoluminescence quantum efficiency of 0.546) as a standard at 24-25 °C.

Table S6 Optical properties of polyamide **CN-PA** in water-NMP with different water fraction (f_w; 10 μM)

f_w (v %)	λ_{abs} (nm)	λ_{em} (nm)	Φ_{PL} (%)[a]	CIE 1931 coordinates	
				x	*y*
0	308	497	13.5	0.1870	0.3887
30	322	477	17.6	0.1583	0.2356
50	324	477	19.2	0.1563	0.2311
70	324	475	20.0	0.1580	0.2335
90	326	475	20.8	0.1559	0.2233
Film	313	472	45.6[b]	0.1534	0.2052

[a] The quantum yield was measured by using quinine sulfate (dissolved in 1 N H_2SO_4 with a concentration of 10 μM, assuming photoluminescence quantum efficiency of 0.546) as a standard at 24-25 °C.

[b] PL quantum yields in solid states were determined using a calibrated integrating sphere.

Table S7 Optical Properties of Polymers

Index	CIE 1931 coordinates					
	NMP (10 μM) solution		Solid Film		ES Fiber	
	x	*y*	*x*	*y*	*x*	*y*
CN-PI	0.1499	0.0930	0.1726	0.1618	0.1834	0.1905
CN-PA	0.1870	0.3887	0.1534	0.2052	0.1558	0.2273

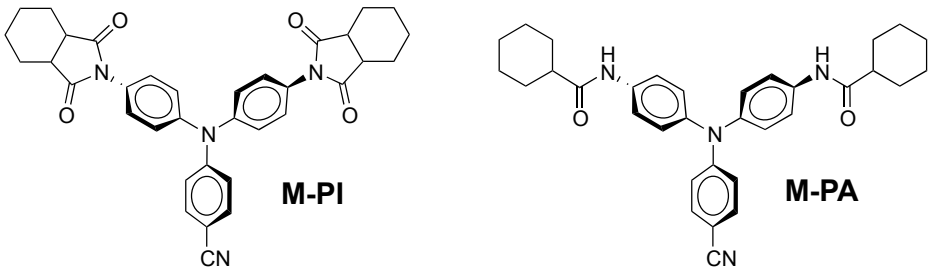


Chart 1 Structures of model compounds **M-PI** and **M-PA**.

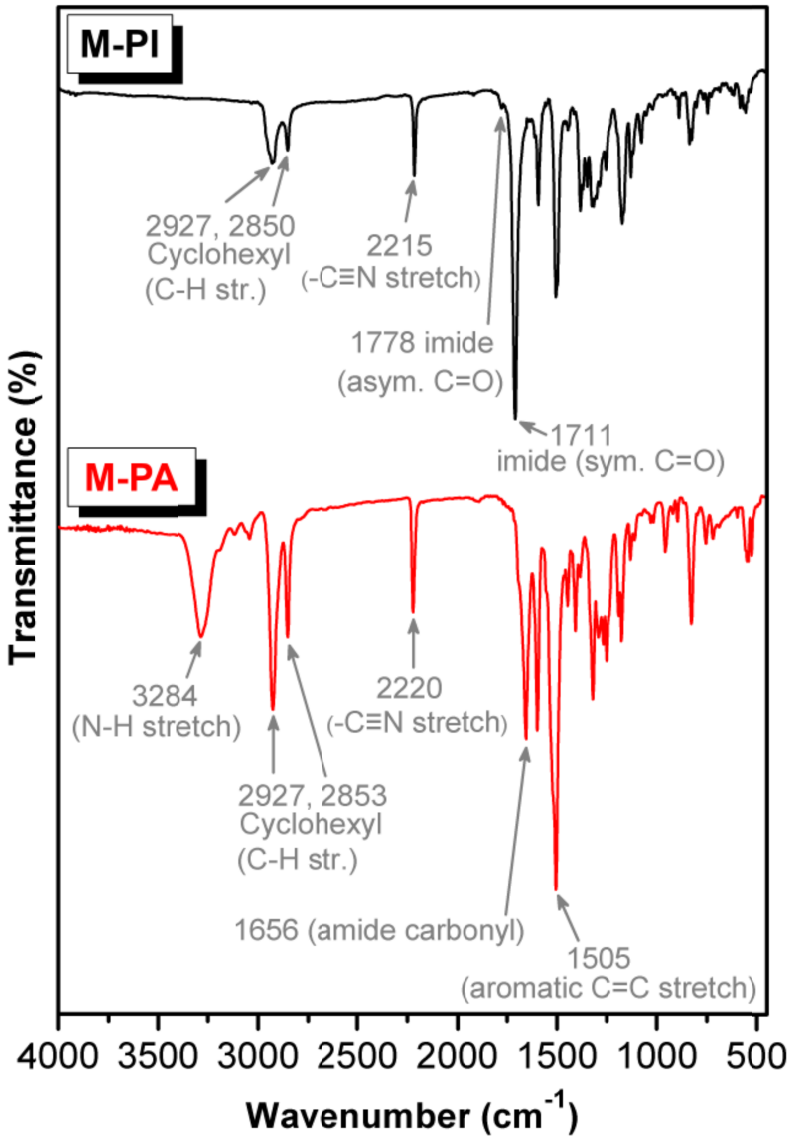


Fig. S1 IR spectra of model compounds (a) **M-PI** and (b) **M-PA**.

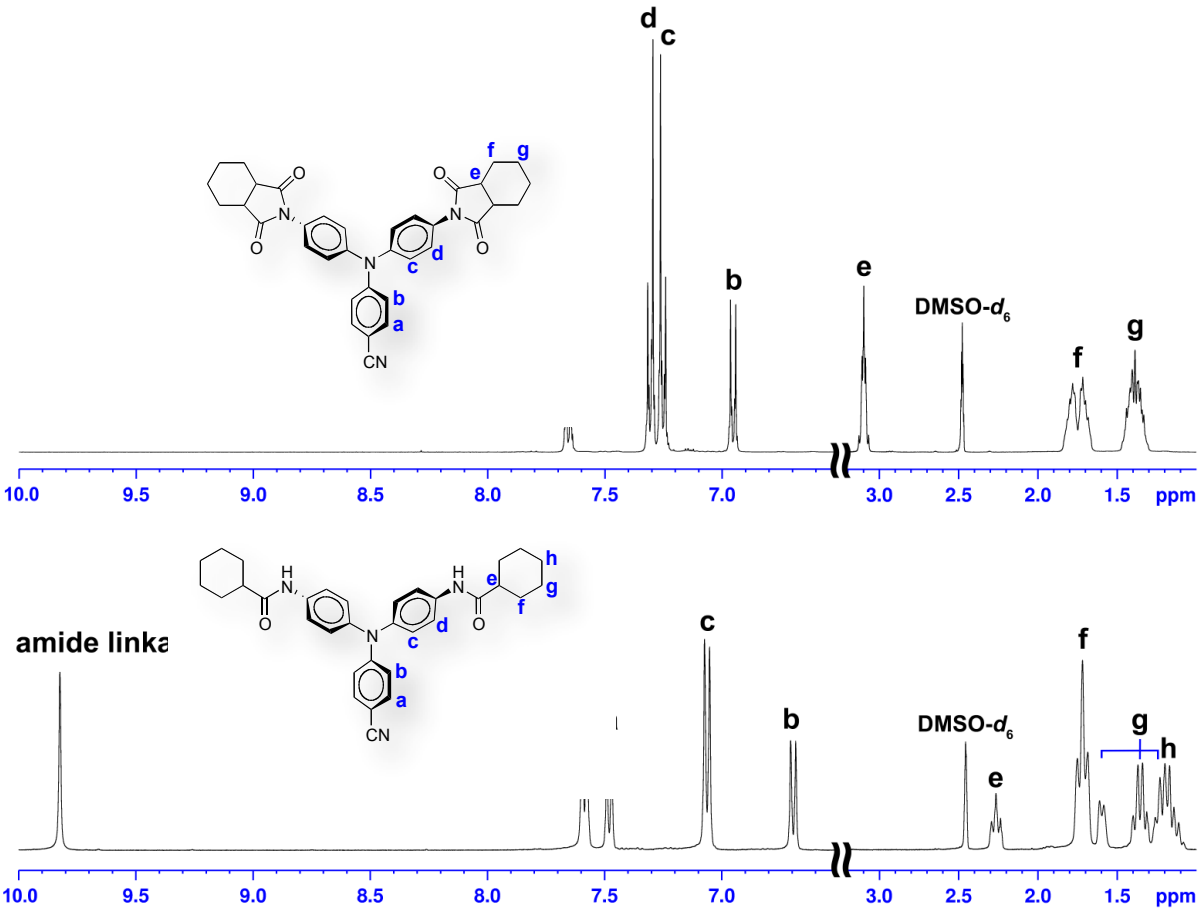


Fig. S2 ^{1}H NMR spectra of model compound (a) **M-PI** and (b) **M-PA** in DMSO-d_6.

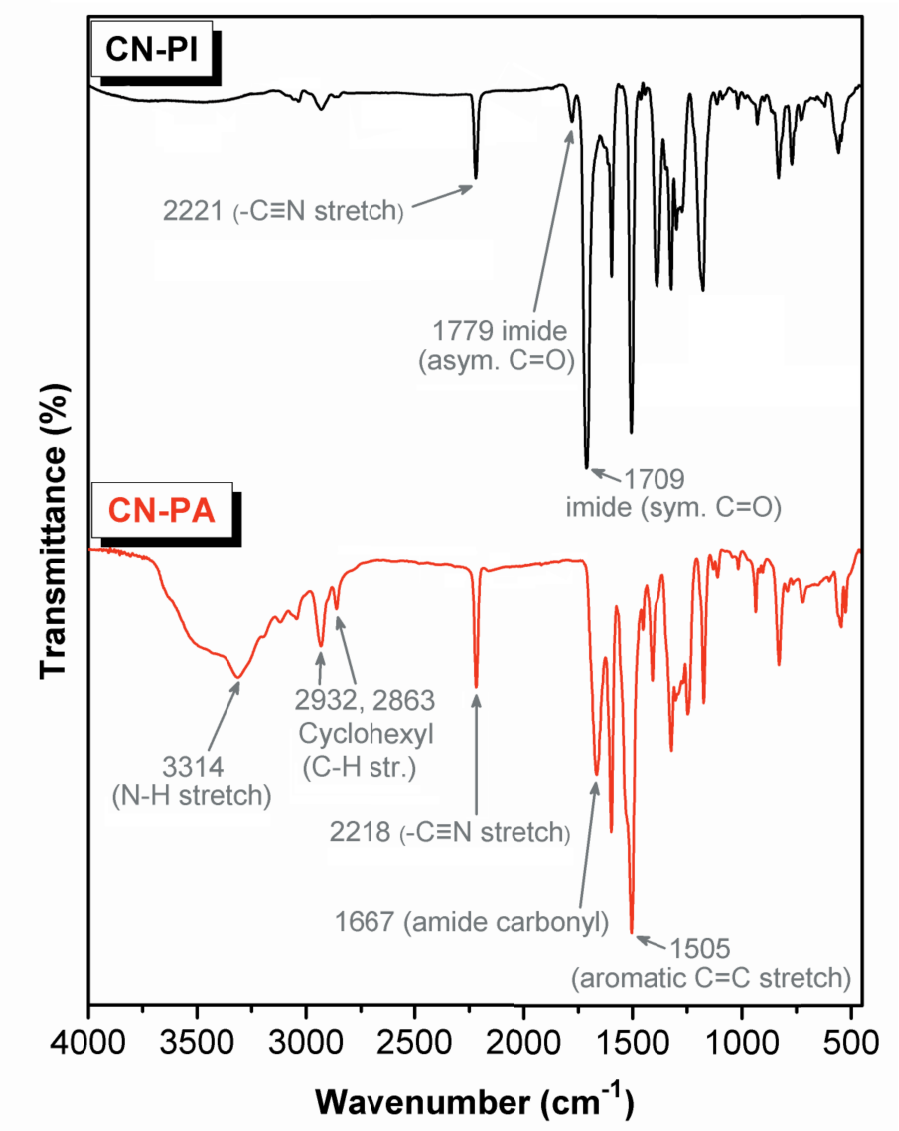


Fig. S3 IR spectrum of (a) **CN-PI** and (b) **CN-PA** films.

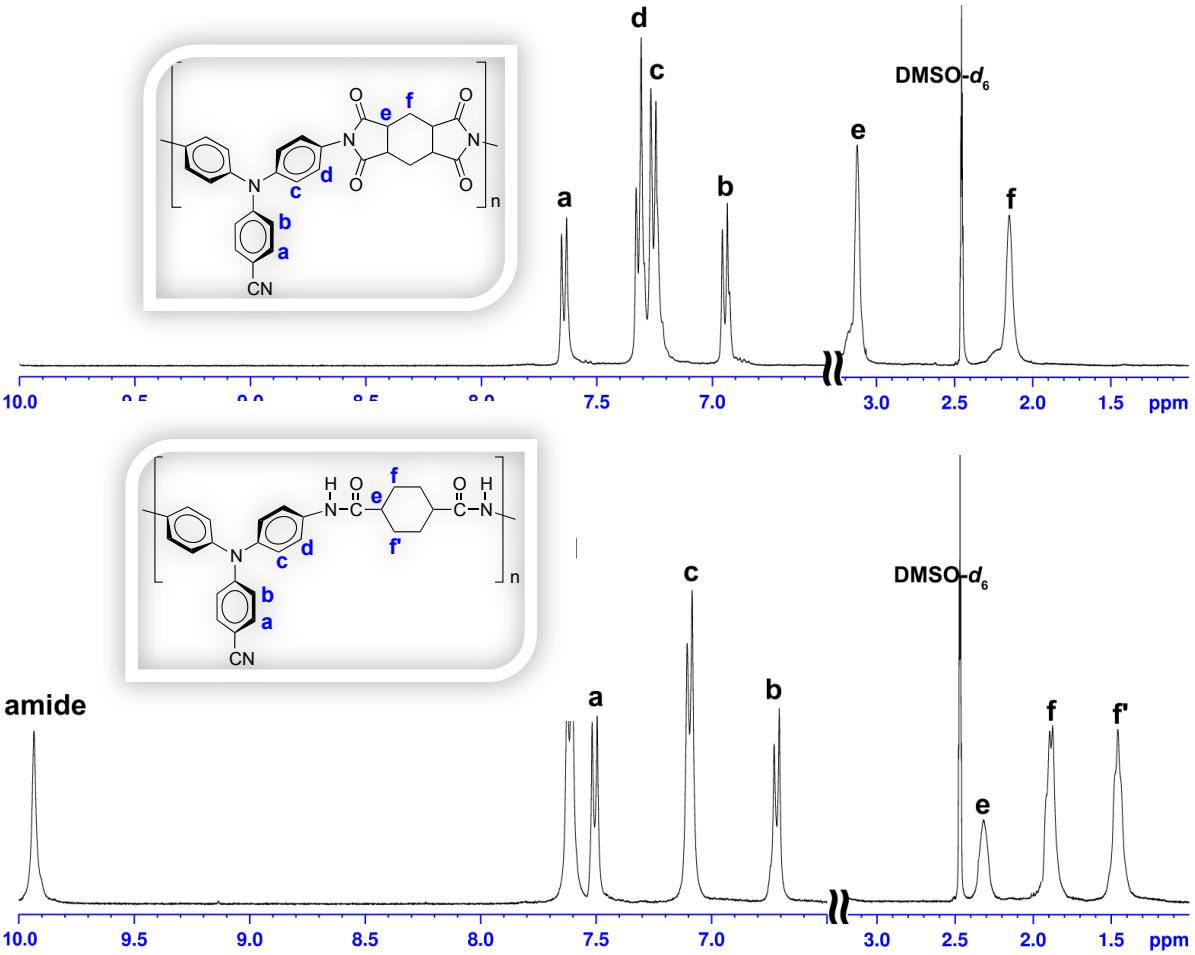


Fig. S4 ^{1}H NMR spectra of polymers (a) **CN-PI** and (b) **CN-PA** in DMSO-d_6.

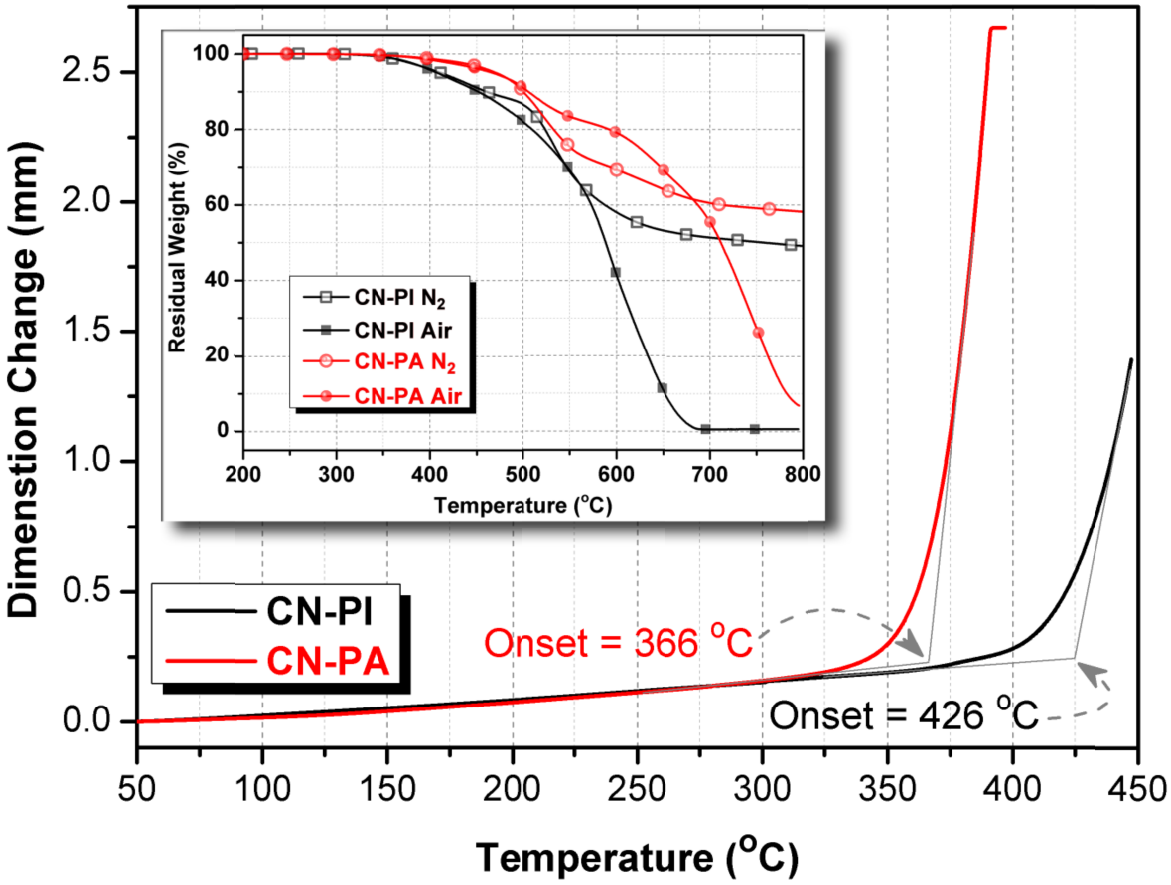


Fig. S5 TMA and TGA traces of polymers **CN-PI** and **CN-PA**.

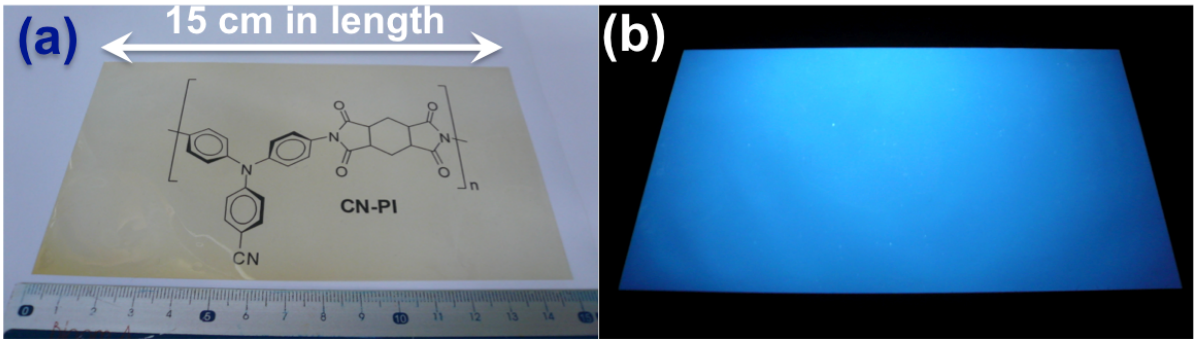


Fig. S6 (a) The photograph of self-standing and flexible **CN-PI** film with *ca.* 35 μm thickness. (b) The PL photograph of **CN-PI** was taken under illumination of a 365 nm UV light.

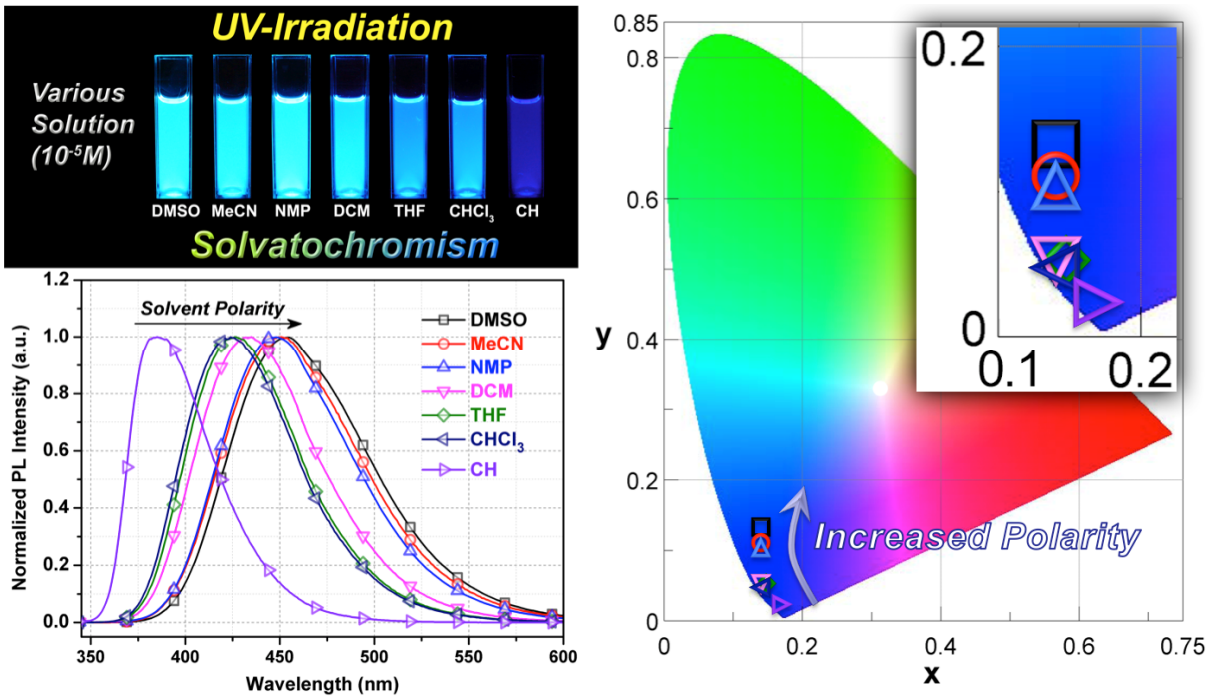


Fig. S7 Photoluminescence (PL) behavior of model compound **M-PI** in different solvents: DMSO: dimethyl sulfoxide; MeCN: acetonitrile; NMP: *N*-methyl-2-pyrrolidone; DCM: dichloromethane; THF: tetrahydrofuran; $CHCl_3$: chloroform; CH: cyclohexane (solution concentration is 10 μM and excited with abs_{max} respectively). Photographs were taken under illumination of a 365 nm UV light.

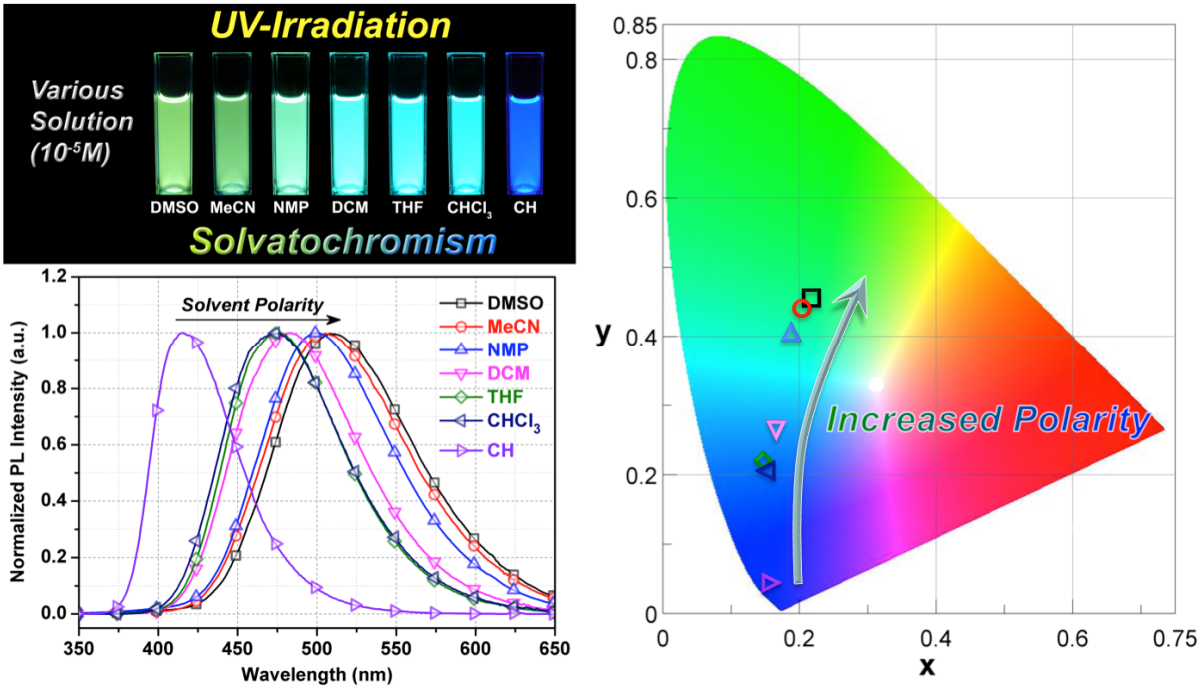


Fig. S8 Photoluminescence (PL) behavior of model compound **M-PA** in different solvents: DMSO: dimethyl sulfoxide; MeCN: acetonitrile; NMP: *N*-methyl-2-pyrrolidone; DCM: dichloromethane; THF: tetrahydrofuran; $CHCl_3$: chloroform; CH: cyclohexane (solution concentration is 10 μM and excited with abs_{max} respectively). Photographs were taken under illumination of a 365 nm UV light.