Supporting Information

Triphenylamine-Based Luminogens and Fluorescent Polyimides: Effects of Functional Group and Substituent on Photophyscial Behaviors

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Experimental Section

Materials

N,N-Bis(*N*'-methyl-4-phthalimide)aniline **(1a)**, *N,N*-bis(4-phthalic acid)aniline **(2a),** *N,N*-bis(4-phthalic anhydride)aniline **(3a)**, (4-bromophenyl)diphenylamine **(4b)**, (4-cyanophenyl)diphenylamine **(4d),** and 4-(1,3-dioxoalan-2-yl)aniline were prepared according to the previously reported procedures.[1] Commercially available 4,4'-oxydianiline **(5a)** and 2,2-bis(4-aminophenyl)hexafluoropropane **(5b)** were purified by vacuum sublimation. 9,9-Bis(4-aminophenyl)fluorene **(5c)** and bis(4-aminocyclohexyl)methane **(5d)** were recrystallized by methanol and hexane respectively. Triphenylamine **(4a)**, 4-(*N,N*-diphenylamino)benzaldehyde **(4c)**, and all other reagent grade chemicals were used as received from commercial sources.

Monomer Synthesis

N,N-bis(N'-methyl-4-phthalimide)-4-bromoaniline (1b)

A solution of *N*-bromosuccinimide (1.96 g, 11 mmol) in 10 ml DMF was added to a solution of *N,N*-bis(*N'*-methyl-4-phthalimide)aniline **(1a) (**4.11 g, 10 mol) in 40 ml chloroform, then reacted at 80 °C for 1day. After reaction, the mixture was poured into methanol, and the precipitate was washed thoroughly with methanol and dried in vacuo at 80 °C to afford 4.66 g (95% in yield) of green powder with mp of 260-261 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.71-7.69 (d, 2H), 7.50-7.48 (d, 2H), 7.44 (s, 2H), 7.30-7.28 (d, 2H), 7.01-6.99 (d, 2H), 3.13 (s, 6H). 13C NMR (100 MHz, $CDCl_3$, δ, ppm): 167.60, 167.51, 151.52, 144.19, 134.51, 133.59, 127.95, 127.14, 126.19, 124.81, 119.82, 117.29, 23.96. FTIR (KBr): 2976-2941 cm^{-1} (CH_3 stretch), 1768 and 1712 cm^{-1} (asym. and sym. imide C=O stretch). Elemental Analysis (%) Calcd for $C_{24}H_{16}BrN_3O_4$: C, 58.79 %; H, 3.29 %; N, 8.57 %. Found: C, 58.93 %; H, 3.46 %; N, 8.54 %.

N,N-bis(N'-methyl-4-phthalimide)-4-(1,3-dioxoalan-2-yl)aniline (1c')

In a 250 ml three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 0.067 g of $Pd(OAc)_2$ (0.3 mmol), 0.30 g of *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (*rac*-BINAP) (0.45 mmol), 7.82 g of Cs_2CO_3 (24 mmol) were dispersed in 30 ml of anhydrous toluene. After pre-catalyzing at 90 °C for 1 h, 6.24 g of *N*-methyl-4-bromorophthalimide (26.0 mmol), 1.65 g of 4-(1,3-dioxoalan-2-yl)aniline (10 mmol) were added to the mixture. After heating under stirring at 110 °C for 3 days, the mixture was concentrated and washed with water and methanol. The precipitate was then washed thoroughly with methanol and dried in vacuo at 80 °C to afford 3.48 g (72 % in yield) of yellow powders with mp of 134-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.89-7.87 (d, 2H), 7.50-7.48 (d, 2H), 7.45 (d, 2H), 7.30-7.28 (dd, 2H), 7.13-7.11 (d, 2H), 7.79 (s, 1H), 4.15-4.02 (m, 4H), 3.12 (s, 6H). 13C NMR (100 MHz, $CDCl_3$, δ, ppm): 167.68, 167.62, 151.78, 145.84, 136.24, 134.42, 128.60, 127.26, 126.27, 125.99, 124.71, 117.32, 102.86, 65.33, 23.93. FTIR (KBr): 2953-2887 cm^{-1} (CH_3 stretch), 1769 and 1709 cm^{-1} (asym. and sym. imide C=O stretch). Elemental Analysis (%) Calcd for $C_{27}H_{21}N_3O_6$: C, 67.08 %; H, 4.38 %; N, 8.69 %. Found: C, 65.93 %; H, 4.68 %; N, 8.56 %.

N,N-bis(N'-methyl-4-phthalimide)-4-formylaniline (1c)

0.48 g of **1c'** (1 mmol), 9 mg of TsOH (5 mol%), and acetone/water 1:1 co-solvent were added into three-neck round-bottomed flask under nitrogen atomosphere, then stirred at reflux for 6 hours. After reaction, the mixture was poured into methanol, and the precipitate was washed thoroughly with methanol and dried in vacuo at 80 °C to afford 0.42 g (95% in yield) of yellow powder with mp of 235-237 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 9.93 (s, 1H), 7.85-7.83 (d, 2H), 7.77-7.75 (d, 2H), 7.50(d, 2H), 7.38-7.36 (dd, 2H), 7.20-7.19 (d, 2H), 3.15 (s, 6H). 13C NMR (100 MHz, $CDCl_3$, δ, ppm): 190.22, 167.40, 167.35, 151.11, 150.64, 134.64, 133.02, 131.70, 128.71, 127.35, 125.00, 124.43, 118.70, 24.03. FTIR (KBr): 2957-2851 cm^{-1} (CH_3 stretch), 1770 and 1710 cm^{-1} (asym. and sym. imide C=O stretch). Elemental Analysis (%) Calcd for $C_{25}H_{17}N_3O_5$: C, 68.33 %; H, 3.90 %; N, 9.56 %. Found: C, 68.77 %; H, 4.59 %; N, 8.91 %.

N,N-bis(N'-methyl-4-phthalimide)-4-cyanoaniline (1d)

This compound was prepared from *N*-methyl-4-bromorophthalimide and 4-cyanoaniline using the same procedure as **(1c')**. Yield= 80%; mp= 261-262 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.77-7.75 (d, 2H), 7.60-7.59 (d, 2H), 7.47 (d, 2H), 7.36-7.33 (dd, 2H), 7.15-7.13 (d, 2H), 3.13 (s, 6H). 13C NMR (100 MHz, $CDCl_3$, δ, ppm): 167.30, 167.26, 150.84, 149.25, 134.67, 134.09, 128.76, 127.55, 125.07, 124.50, 118.69, 118.10, 108.25, 24.04. FTIR (KBr): 2946-2886 cm^{-1} (CH_3 stretch), 2233 cm^{-1} (CN stretch), 1769 and 1705 cm^{-1} (asym. and sym. imide C=O stretch). Elemental Analysis (%) Calcd for $C_{25}H_{16}N_4O_4$: C, 68.80 %; H, 3.70 %; N, 12.84 %. Found: C, 68.37 %; H, 3.85 %; N, 12.83 %.

N,N-bis(4-phthalic acid)-4-bromoaniline (2b)

(2b) was chosen as an example to illustrate the general synthetic route used to produce the tetracarboxylic acid compounds. To a solution of 15% NaOH aqueous solution (90 mL) was added 9.8 g of compound **(1b)** (20 mmol). The resulting mixture was refluxed for 48 h under a nitrogen atmosphere after the solid was completely dissolved. After cooling to room temperature, the solution was adjusted to pH = 1.0 with 6 N HCl. Extracted by EA and the yellow precipitate was collected to afford 9.5 g (95% in yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 13.07 (b, 4H), 7.70-7.68 (d, 2H), 7.60-7.58 (d, 2H), 7.18-7.16 (dd, 2H), 7.14 (s, 2H), 7.11 (d, 2H). 13C NMR (100 MHz, DMSO-d_6, δ, ppm): 168.94, 167.89, 148.60, 144.98, 136.23, 133.44, 131.25, 128.43, 126.32, 124.44, 122.16, 118.12. FTIR (KBr): 3450-2520 cm^{-1} (OH stretch), 1703 cm^{-1} (C=O stretch).

N,N-bis(4-phthalic acid)-4-formylaniline (2c)

Yield= 98%. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 13.14 (-COOH), 9.90 (s, 1H), 7.88-7.86 (d, 2H), 7.73-7.71 (d, 2H), 7.31-7.26 (m, 4H), 7.21-7.19 (d, 2H). FTIR (KBr): 3450-2520 cm^{-1} (OH stretch), 1703 cm^{-1} (C=O stretch).

N,N-bis(4-phthalic acid)-4-cyanoaniline (2d)

2.25 g of triflic acid (15 mmol) was added to a well-stirred solution of 2.25 g of **2c** (5 mmol), 0.49 g sodium azide (7.5 mmol) in CH_3CN (10 mL), and the mixture was stirred at room temperature for 30 min. After removal of the solvent under reduced pressure, the residue was extracted with EtOAc, and the yellow precipitate was collected to afford 1.59 g (71% in yield). ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 13.14 (-COOH), 7.78-7.76 (d, 2H), 7.74-7.72 (d, 2H), 7.30-7.27 (dd, 2H), 7.26 (s, 2H), 7.16-7.14 (d, 2H). 13C NMR (100 MHz, DMSO-d_6, δ, ppm): 168.61, 167.97, 150.02, 147.74, 136.06, 134.36, 131.30, 128.21, 126.62, 124.24, 123.58, 119.21, 105.55. FTIR (KBr): 3450-2520 cm^{-1} (OH stretch), 2227 (CN stretch), 1703 cm^{-1} (C=O stretch).

N,N-bis(4-phthalic anhydride)-4-bromoaniline (3b)

(3b) was chosen as an example to illustrate the general synthetic route used to produce the dianhydride compounds. 5.0 g of tetracarboxylic acid **(2b)** was dissolved in acetic acid (5 mL) and acetic anhydride (5 mL), and the mixture was heated to reflux for 3h. The solution was filtered without cooling and recrystallized to afford 3.5 g (75% in yield) yellow crystal with a mp of 262-263 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$, δ, ppm): 8.03-8.01 (d, 2H), 7.73-7.71 (d, 2H), 7.80 (s, 2H), 7.56-7.54 (dd, 2H), 7.29-7.27 (d, 2H). 13C NMR (100 MHz, DMSO-d$_6$, δ, ppm): 163.19. 162.75, 152.75, 143.96, 134.08, 134.02, 129.85, 129.76, 127.76, 125.20, 120.37, 118.42. FTIR (KBr): 1846 and 1776 cm^{-1} (asym. and sym. imide C=O stretch). Elemental Analysis (%) Calcd for $C_{22}H_{10}BrNO_6$: C, 56.92 %; H, 2.17 %; N, 3.02 %. Found: C, 56.53 %; H, 2.26 %; N, 2.93 %.

N,N-bis(4-phthalic anhydride)-4-formylaniline (3c)

Yield: 68%. mp: 245-248 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$, δ, ppm): 9.98 (s, 1H), 8.09-8.07 (d, 2H), 8.00-7.98 (d, 2H), 7.67 (s, 2H), 7.66-7.63 (dd, 2H), 7.40-7.38 (d, 2H). 13C NMR (100 MHz, DMSO-d$_6$, δ, ppm): 192.07, 163.07, 162.72, 152.49, 150.19, 134.15, 133.81, 132.07, 131.32, 127.84, 126.22, 125.92, 120.06. FTIR (KBr): 1843 and 1777 cm^{-1} (asym. and sym. imide C=O stretch). Elemental Analysis (%) Calcd for $C_{23}H_{11}NO_7$: C, 66.83 %; H, 2.68 %; N, 3.39 %. Found: C, 66.14 %; H, 3.17 %; N, 3.42 %.

N,N-bis(4-phthalic anhydride)-4-cyanoaniline (3d)

Yield: 65%. mp: 285-288 °C. ^{1}H NMR (400 MHz, DMSO-d$_6$, δ, ppm): 8.08-8.06 (d, 2H), 7.93-7.91 (d, 2H), 7.69-7.68 (d, 2H), 7.65-7.62 (dd, 2H), 7.36-7.34 (d, 2H). 13C NMR (100 MHz, DMSO-d$_6$, δ, ppm): 163.04, 162.72, 152.31, 149.10, 134.84, 134.16, 131.43, 127.84, 126.39, 126.09, 120.23, 118.86, 108.27. FTIR (KBr): 1843 and 1772 cm^{-1} (asym. and sym. imide C=O stretch). Elemental Analysis (%) Calcd for $C_{23}H_{10}N_2O_6$: C, 67.32 %; H, 2.46 %; N, 6.83 %. Found: C, 67.08 %; H, 3.10 %; N, 6.41 %.

Synthesis of Polyimides by One-Step Method

The synthesis of **IIa** was used as an example to illustrate the general synthetic route used to produce the series of PIs, **I**, **II**, and **IV**. Into a 50 mL round-bottom flask were added 0.464 g (1.00 mmol) of dianhydride **(3b)**, 0.200 g (1.00 mmol) of 4,4'-oxydianiline, 0.24 ml isoquinoline, and 2.7 ml *m*-cresol. The reaction mixture was stirred at 50°C under nitrogen atmosphere for 5 h. Then, the reaction temperature was increased to 200 °C for 15 h. Then, the mixture was cooled to room temperature, and the viscous polymer solution was then poured slowly into 300 ml of stirred methanol giving rise to a yellow fibrous precipitate. Reprecipitation of the polymer by DMAc/methanol was carried out twice for further purification.

Synthesis of Polyimides by Two-Step Method

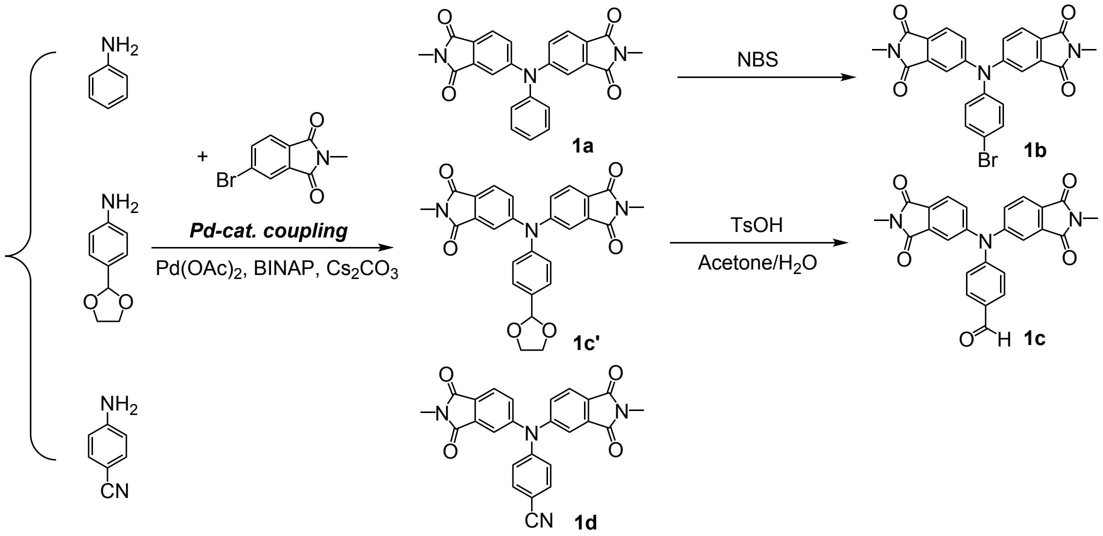
The synthesis of polyimide **IIIa** was used as an example to illustrate the general synthetic route used to produce the III series of polyimides (**IIIa**−**IIId**). The solution of 0.200 g (1.0 mmol) of diamine **(5a)** in 5.5 mL of NMP was mechanically stirred at room temperature. Until the diamine monomer dissolved completely, using liquid nitrogen with acetone bath to freeze the solution. And then, 0.413 g (1.0 mmol) of dianhydride (**3c**) was added in one portion (10 wt % solid content). The mixture was mechanically stirred and kept at low temperature (ca. −10 °C) for about 3 h to yield a viscous poly(amic acid) solution. The poly(amic acid) was subsequently converted to polyimide **IIIa** via a chemical imidization process by addition of pyridine 0.48 mL (6.0 mmol) and acetic anhydride 0.56 mL (6.0 mmol), and the mixture was heated at 100 °C for 3 h to effect complete imidization. The resulting polymer solution was poured into 200 mL of methanol, giving a yellowish green precipitate, which was washed thoroughly with methanol, and collected by filtration.

Measurements

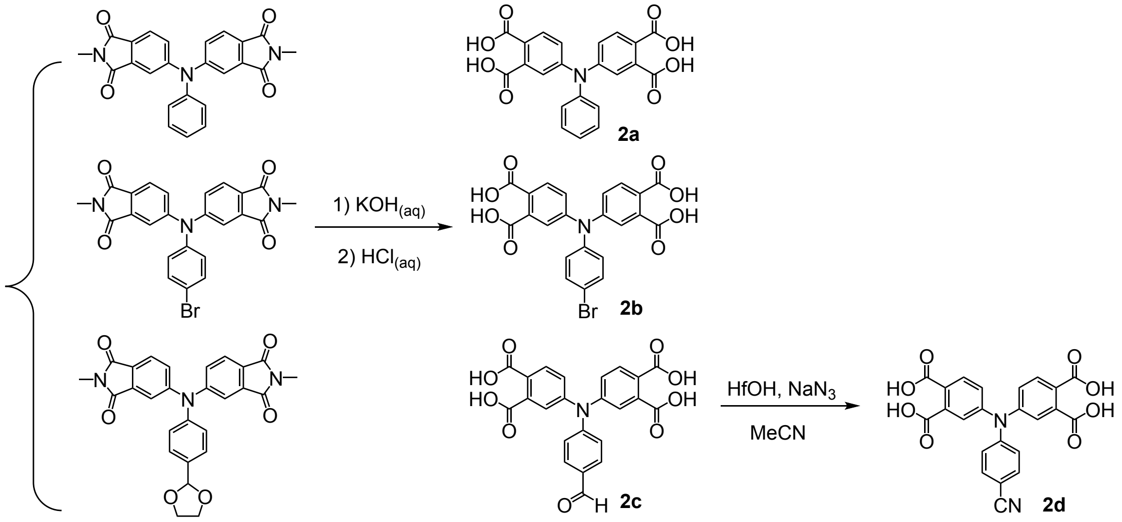
Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. Elemental analyses were run in a Heraeus VarioEL-III CHNS elemental analyzer. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400MHz FT-NMR, and peak multiplicity was reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a TA Instruments Q50 in flowing nitrogen or air (flow rate = 60 cm^3/min) at a heating rate of 20 °C/min. Differential Scanning Calorimetry (DSC) was conducted with a TA instrument DSC Q20 in flowing nitrogen (50 cm^3/min) at a heating rate of 10 °C/min. Ultraviolet-visible (UV-Vis) spectra were recorded on Hitachi U-4100 spectrometer. Photoluminescence (PL) spectra were measured with HORIBA Fluorolog-3 spectrofluorometer. PL quantum yield (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), and the Φ_{PL} of molecules and polymers in solid state was determined by using a calibrated integrating sphere. All spectra were obtained by averaging three scans.

Quantum Chemical Calculation

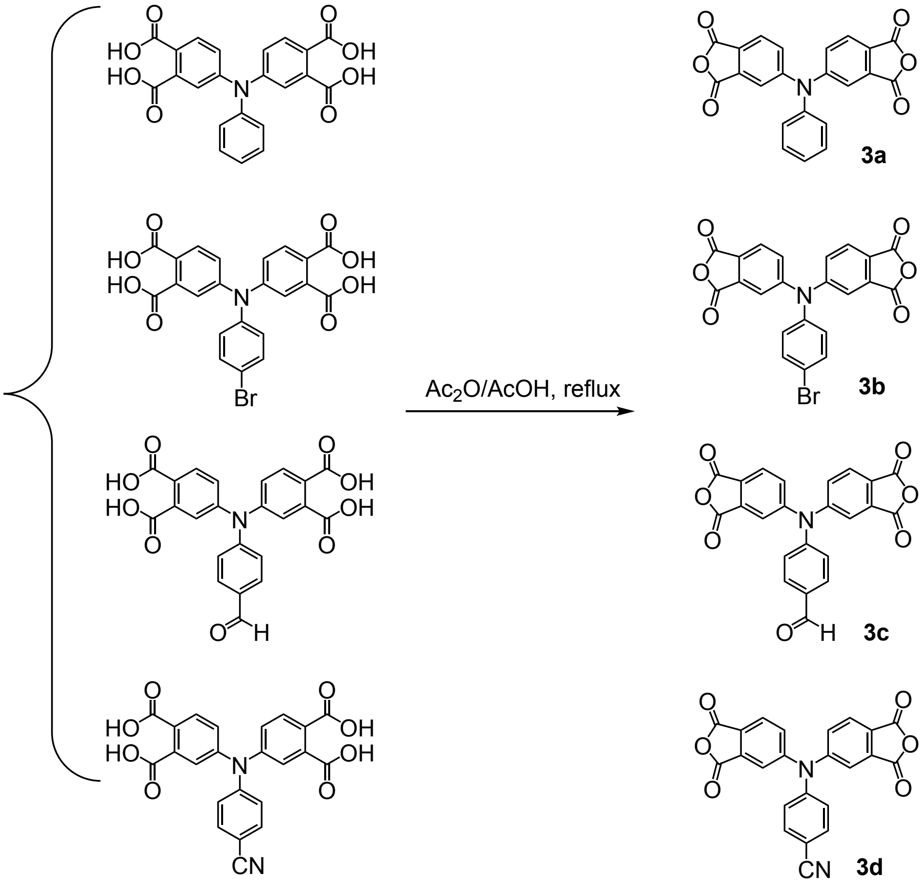
The Molecular simulation in this study was performed by Gaussian 09 program package, which implements analytical gradients at the time-dependent density functional theory (TD-DFT). The DFT method at the Becker style three-parameter density functional theory using the Lee-Yang-Parr correlation functional level of theory (B3LYP) with the 6-31G (d) basic set was adopted for calculating electronic structures and spectroscopic properties of the model compounds.



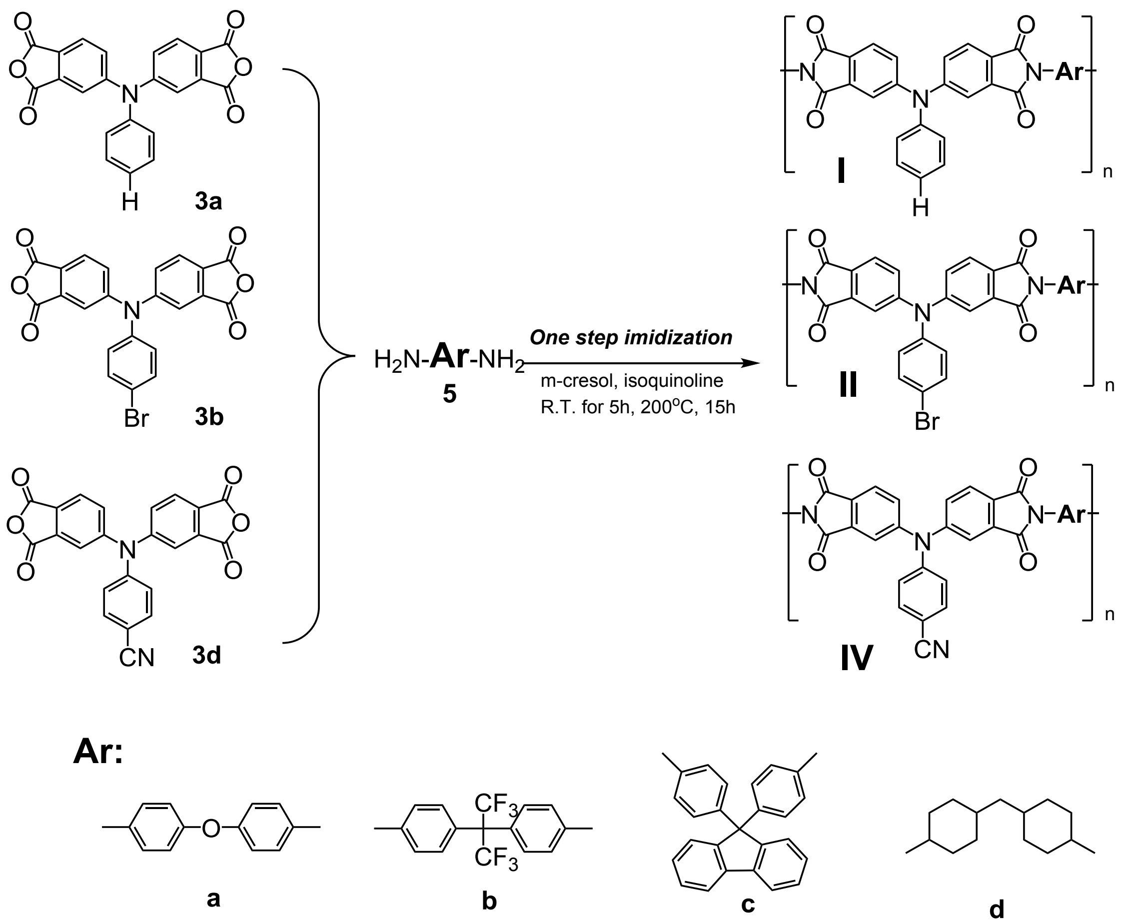
Scheme S1. Synthetic route of triphenylamine-based diimides.



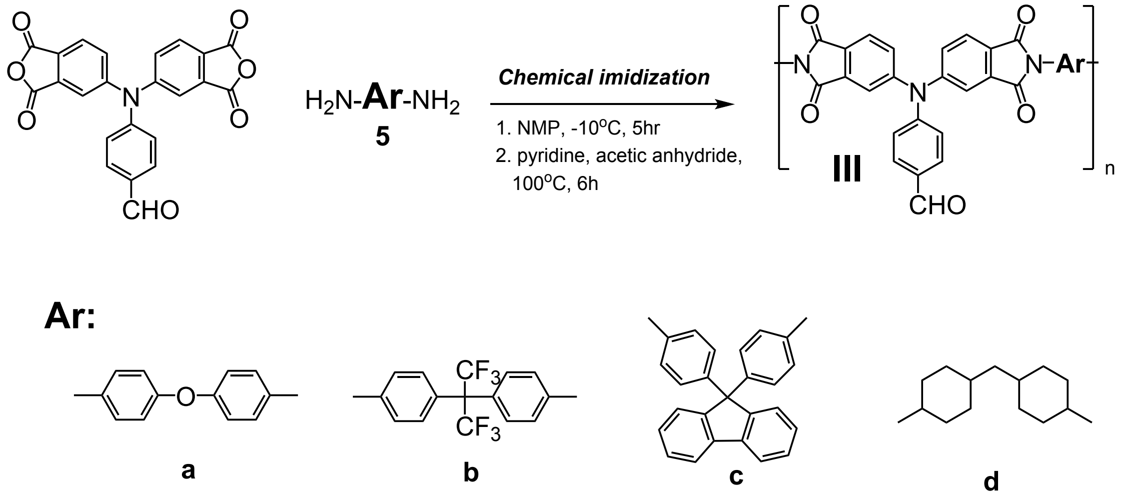
Scheme S2. Synthetic route of triphenylamine-based tetracarboxylic acids.



Scheme S3. Synthetic of triphenylamine-based dianhydride monomers.



Scheme S4. Synthesis of triphenylamine-based polyimides by one-step imidization.



Scheme S5. Synthesis of triphenylamine-based polyimides by chemical imidization.

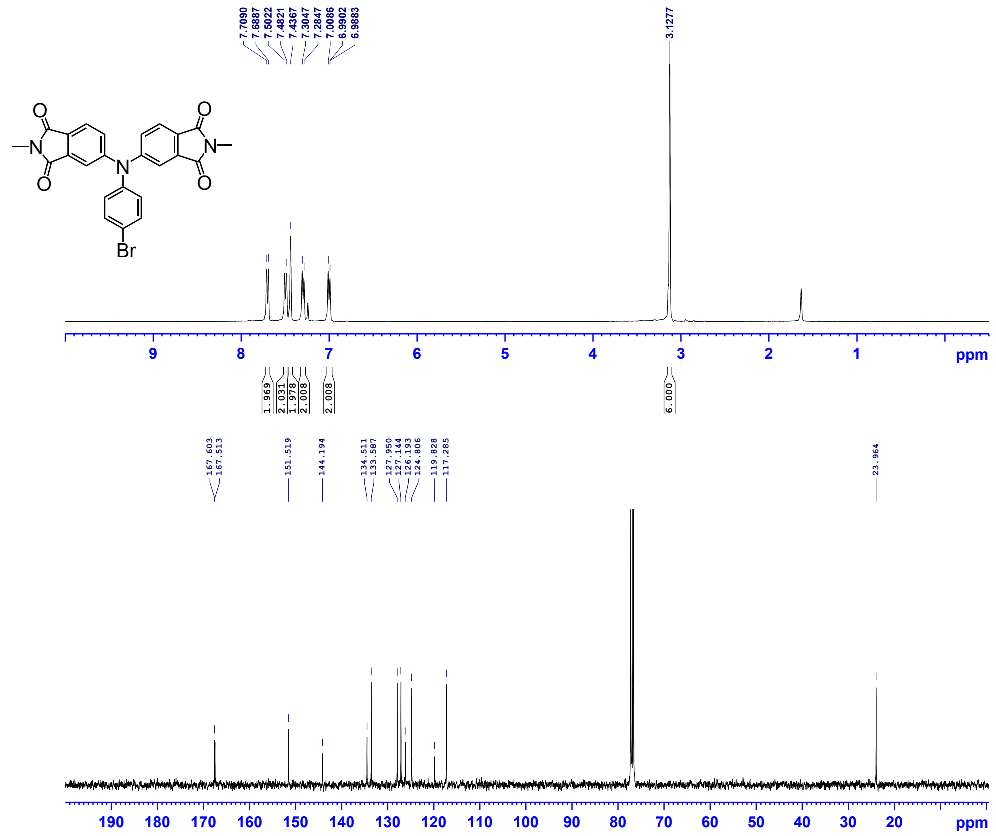


Figure S1. ^{1}H and ^{13}C NMR spectra of diimide **1b** in $CDCl_3$.

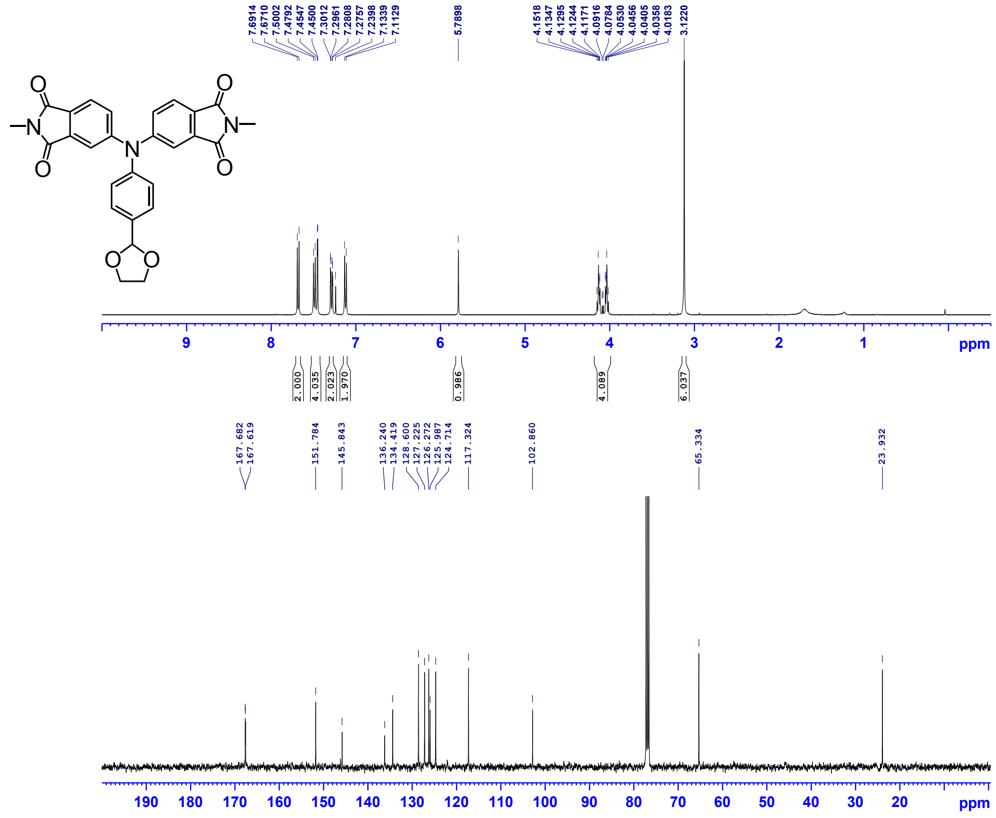


Figure S2. ^{1}H and ^{13}C NMR spectra of diimide **1c’** in $CDCl_3$.

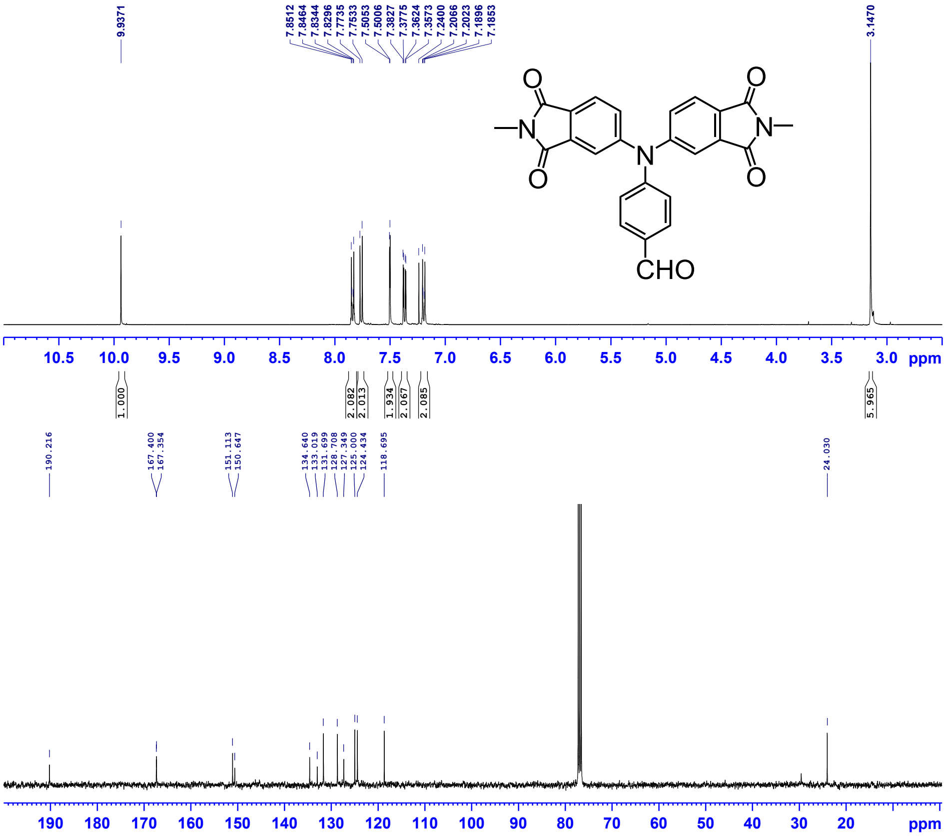


Figure S3. ^{1}H and ^{13}C NMR spectra of diimide **1c** in $CDCl_3$.

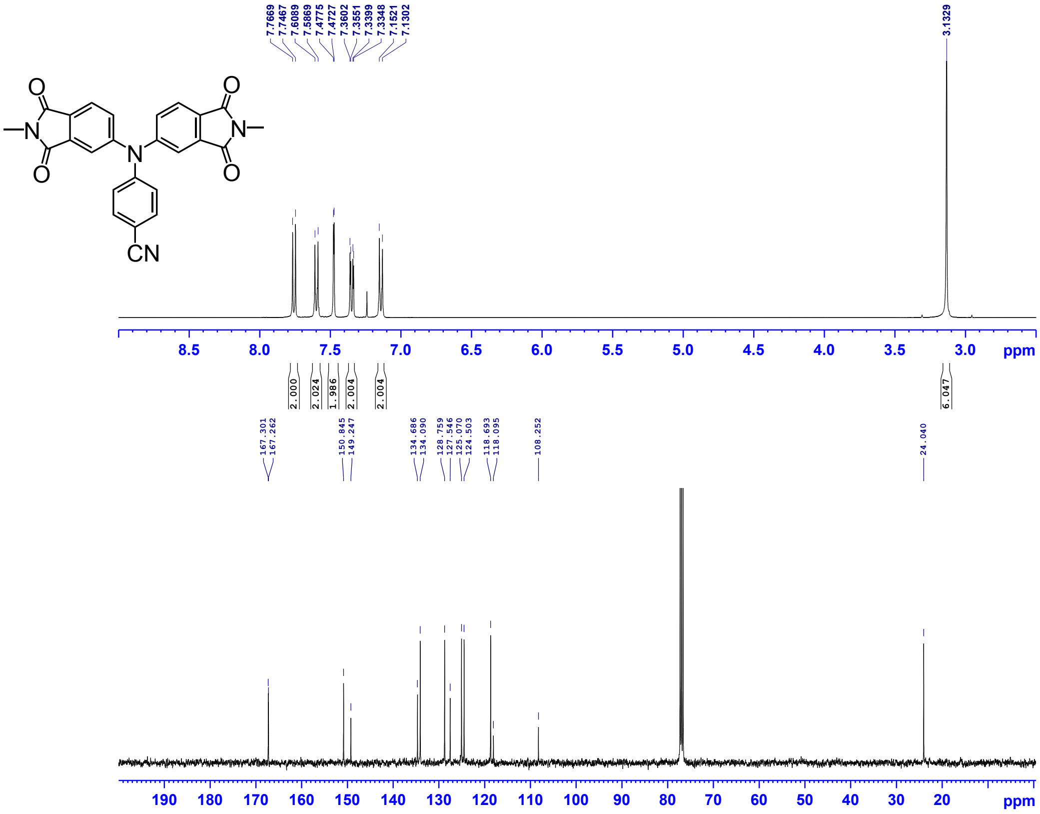


Figure S4. ^{1}H and ^{13}C NMR spectra of diimide **1d** in $CDCl_3$.

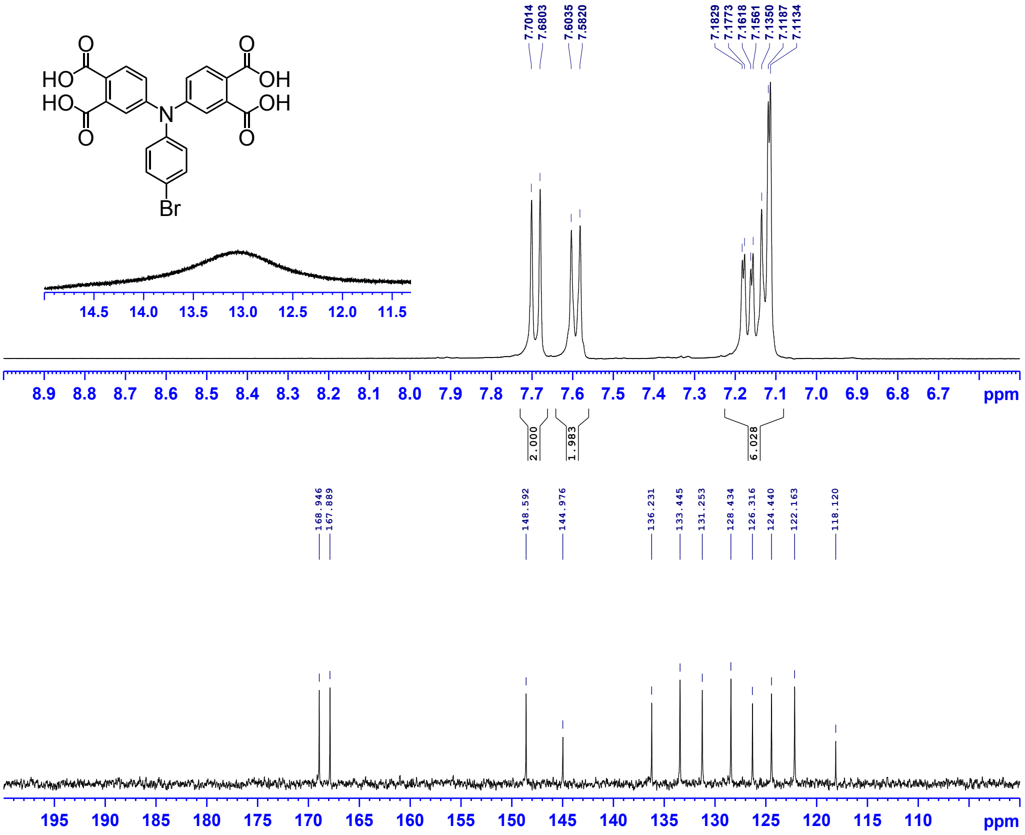


Figure S5. ^{1}H and ^{13}C NMR spectra of tetracarboxylic acid **2b** in DMSO-D$_6$.

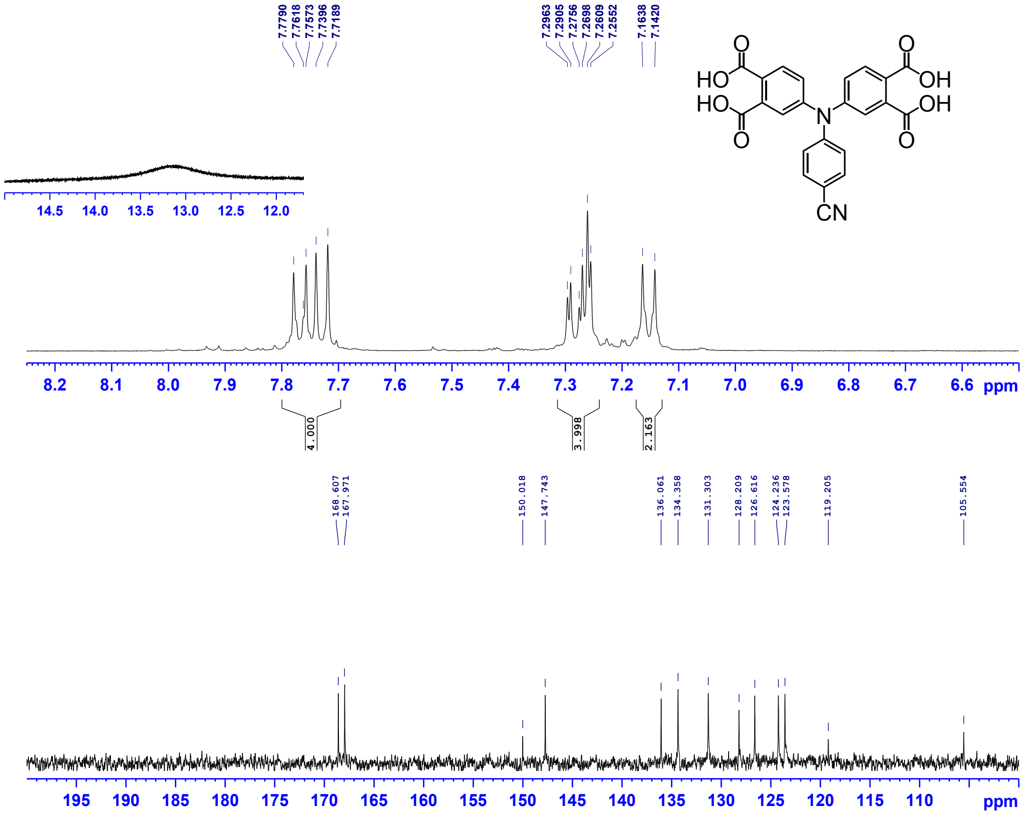


Figure S6. ^{1}H and ^{13}C NMR spectra of tetracarboxylic acid **2d** in DMSO-D$_6$.

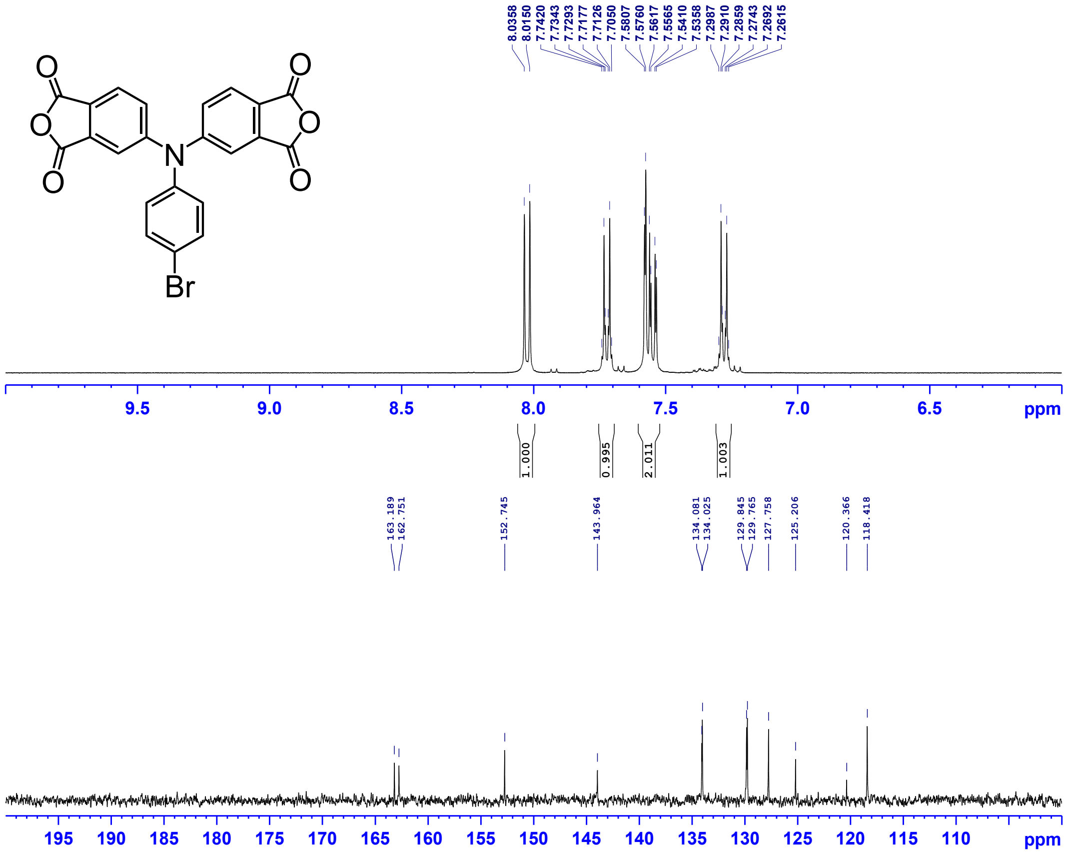


Figure S7. ^{1}H and ^{13}C NMR spectra of dianhydride **3b** in DMSO-D$_6$.

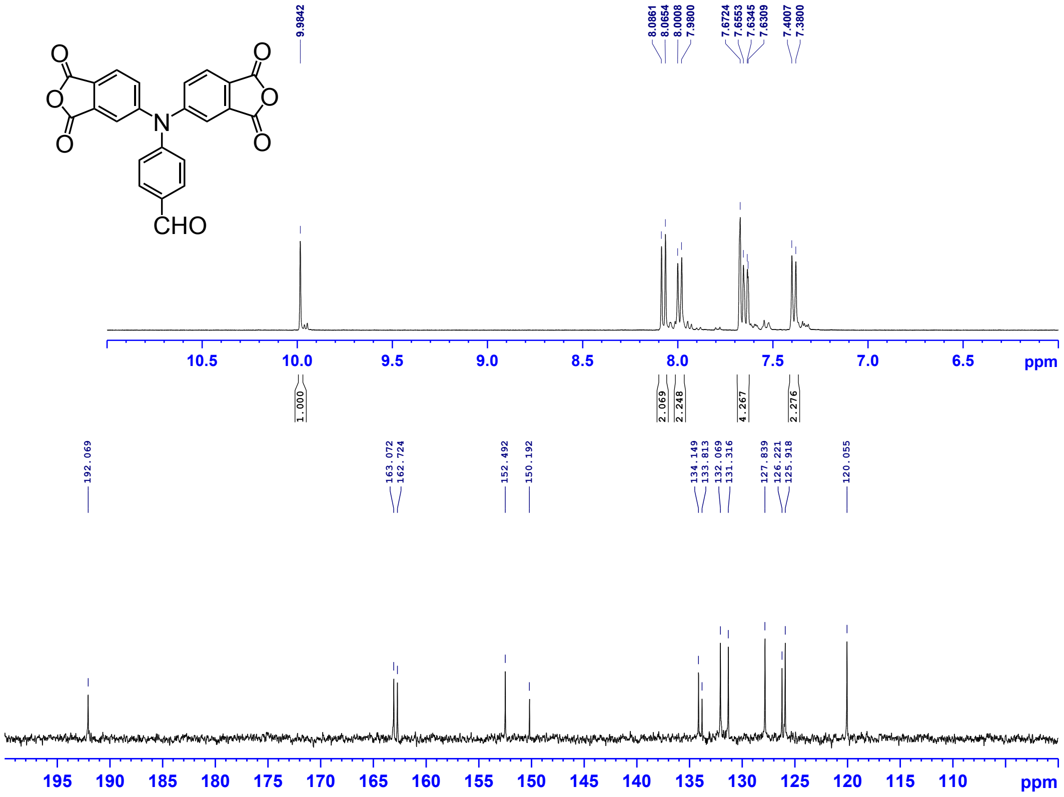


Figure S8. ^{1}H and ^{13}C NMR spectra of dianhydirde **3c** in DMSO-D$_6$.

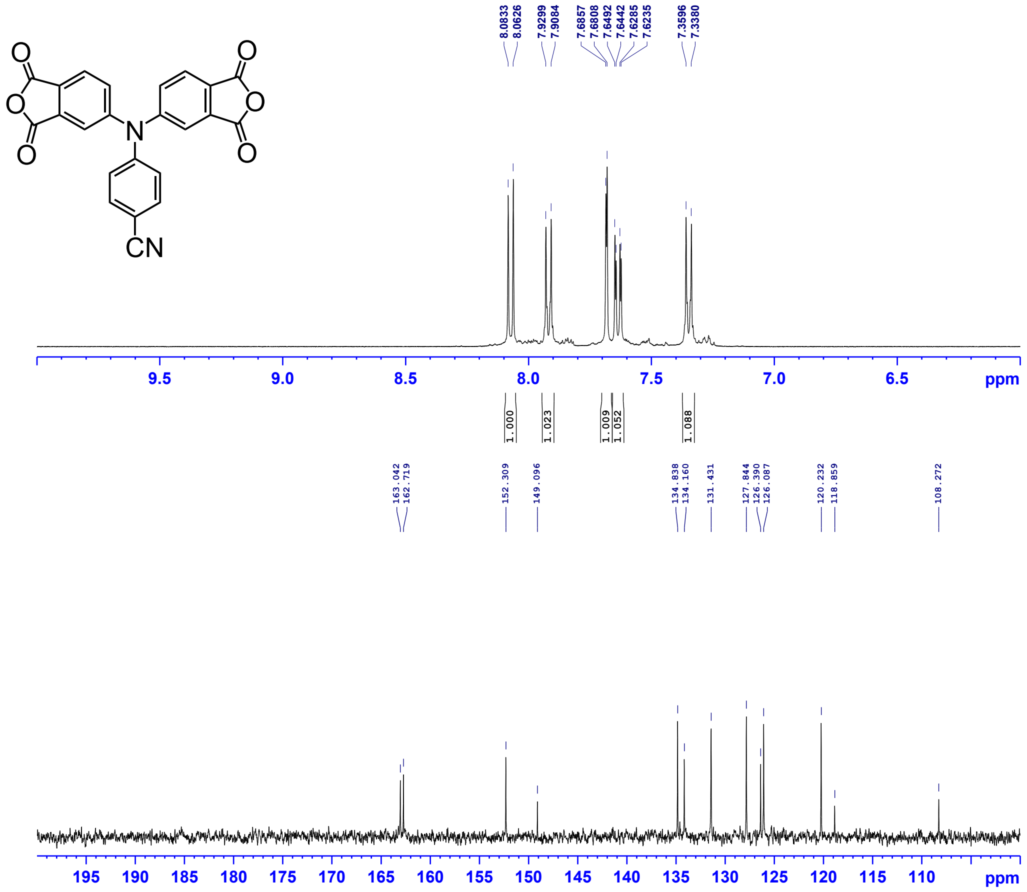


Figure S9. ^{1}H and ^{13}C NMR spectra of dianhydride **3d** in DMSO-D$_6$.

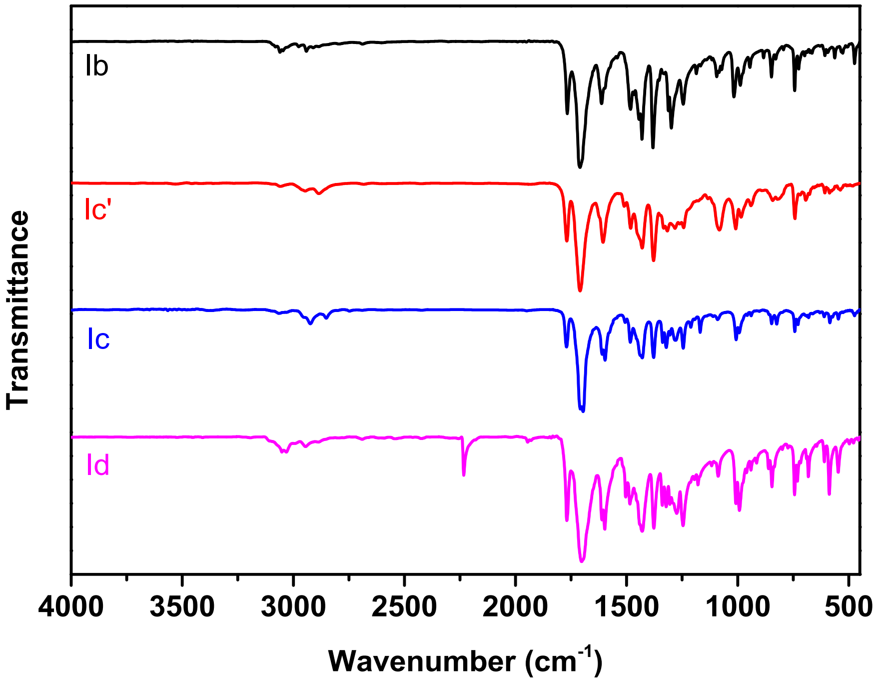


Figure S10. FT-IR spectra of diamine compounds.

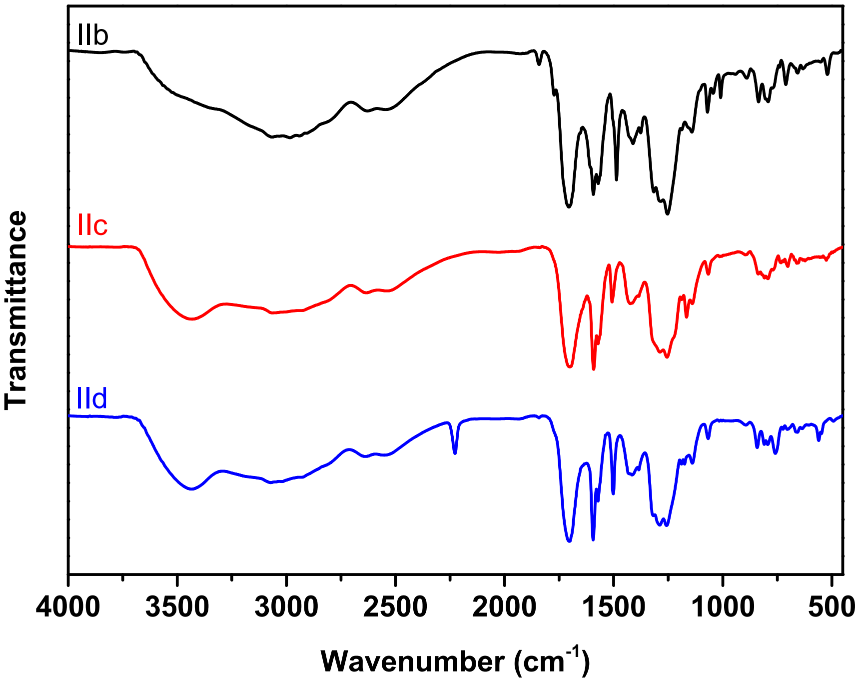


Figure S11. FT-IR spectra of tetracarboxylic acid compounds.

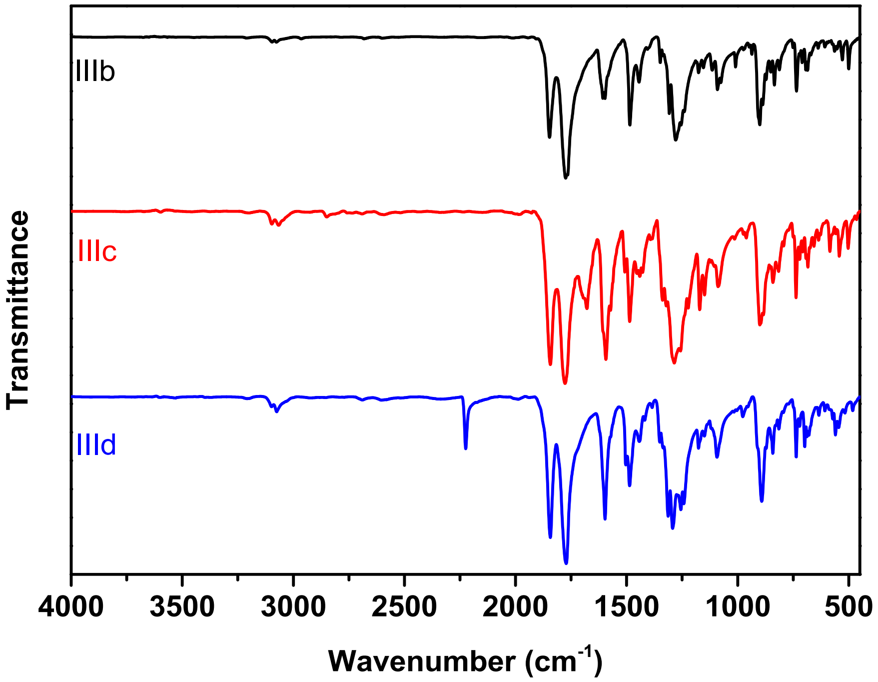


Figure S12. FT-IR spectra of dianhydride compounds.

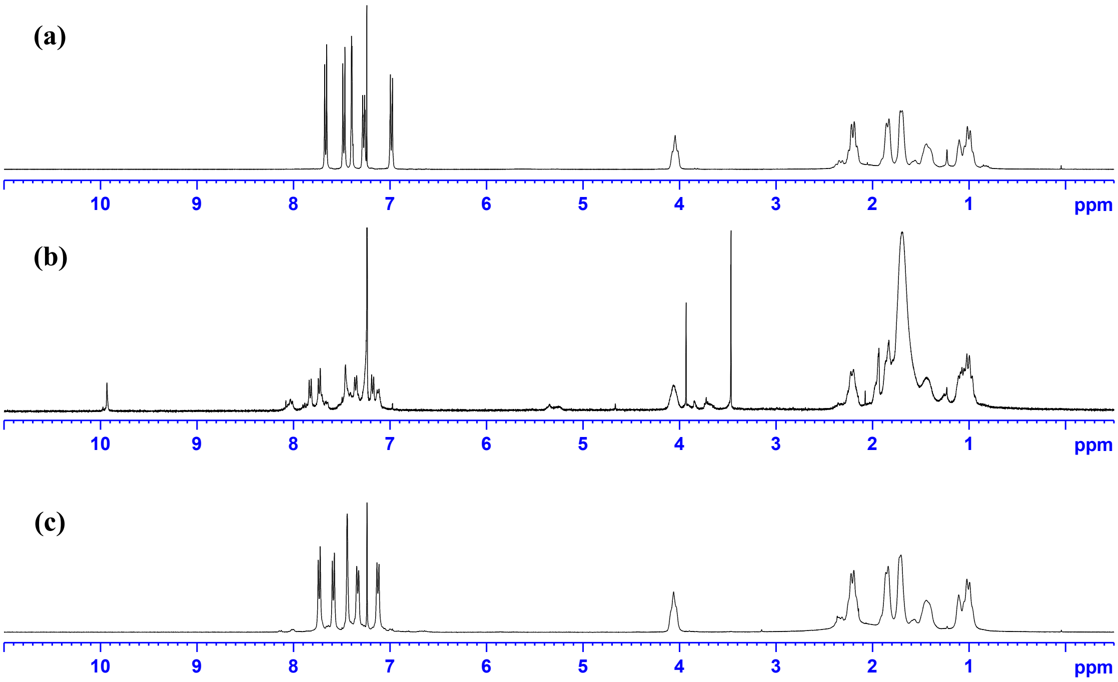


Figure S13. ^{1}H NMR spectra of polyimides (a) **IId**, (b) **IIId**, and (c) **IVd** in $CDCl_3$.

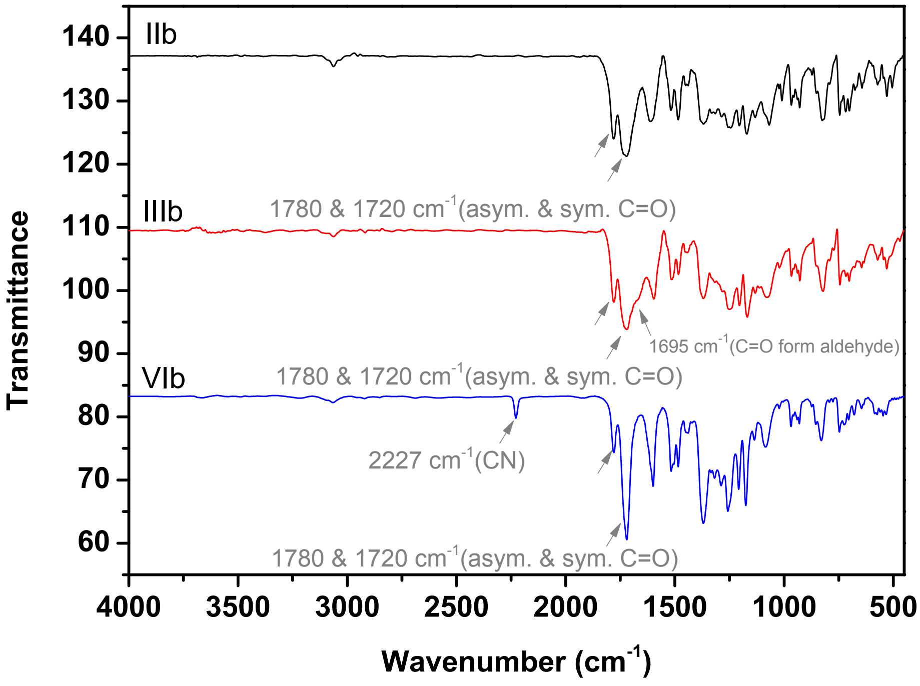


Figure S14. FT-IR spectra of polyimides.

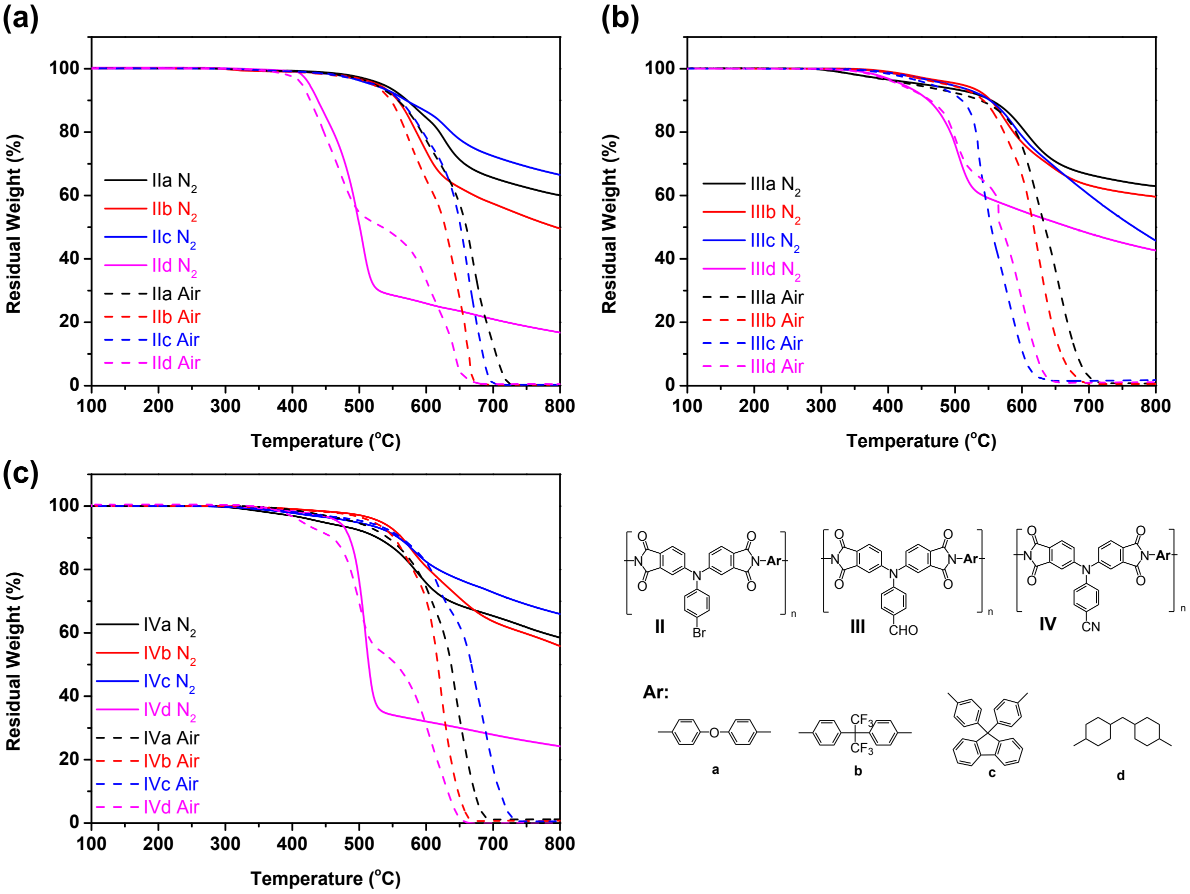


Figure S15. TGA traces of series of (a) **II**, (b) **III** and (c) **IV**.

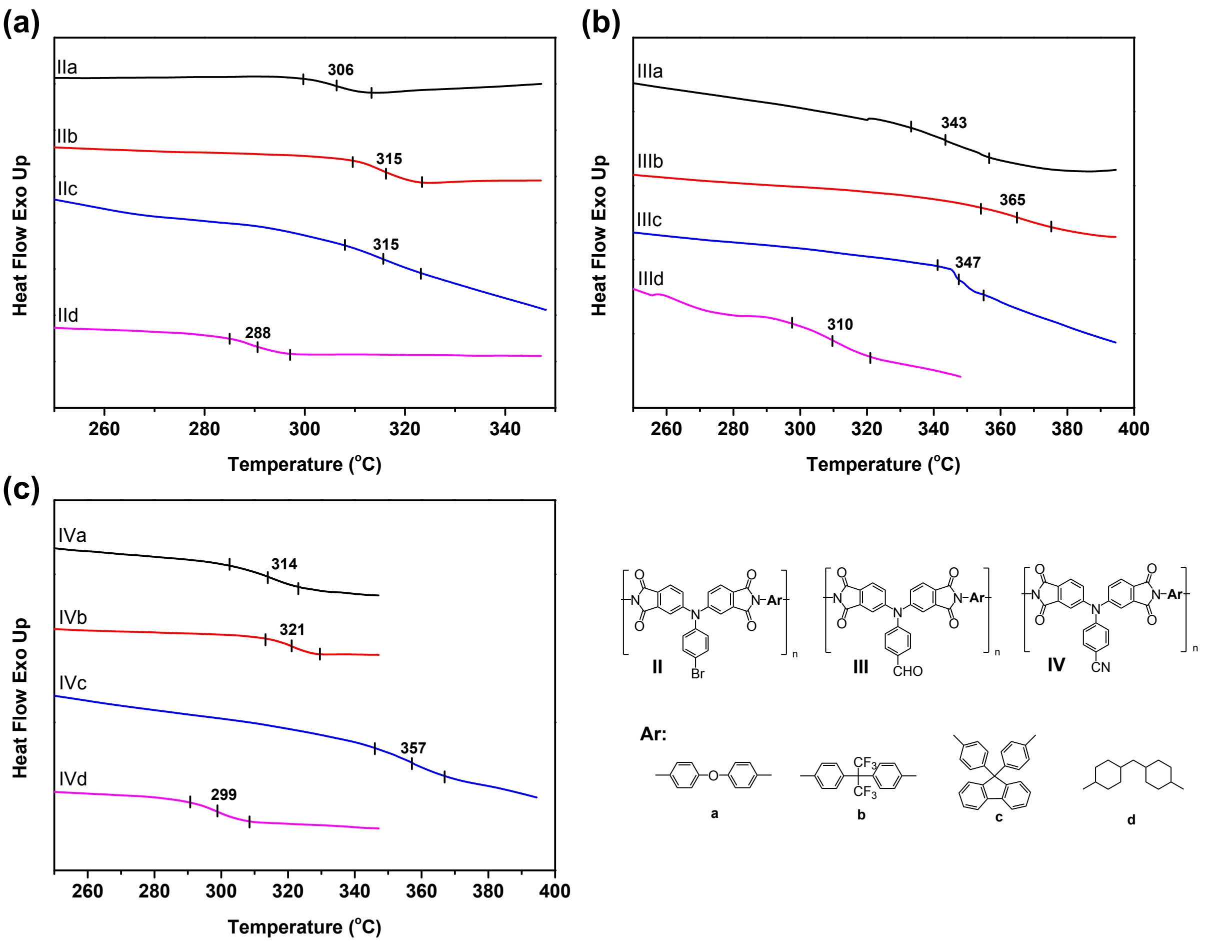


Figure S16. DSC traces of series of (a) **II**, (b) **III** and (c) **IV**.

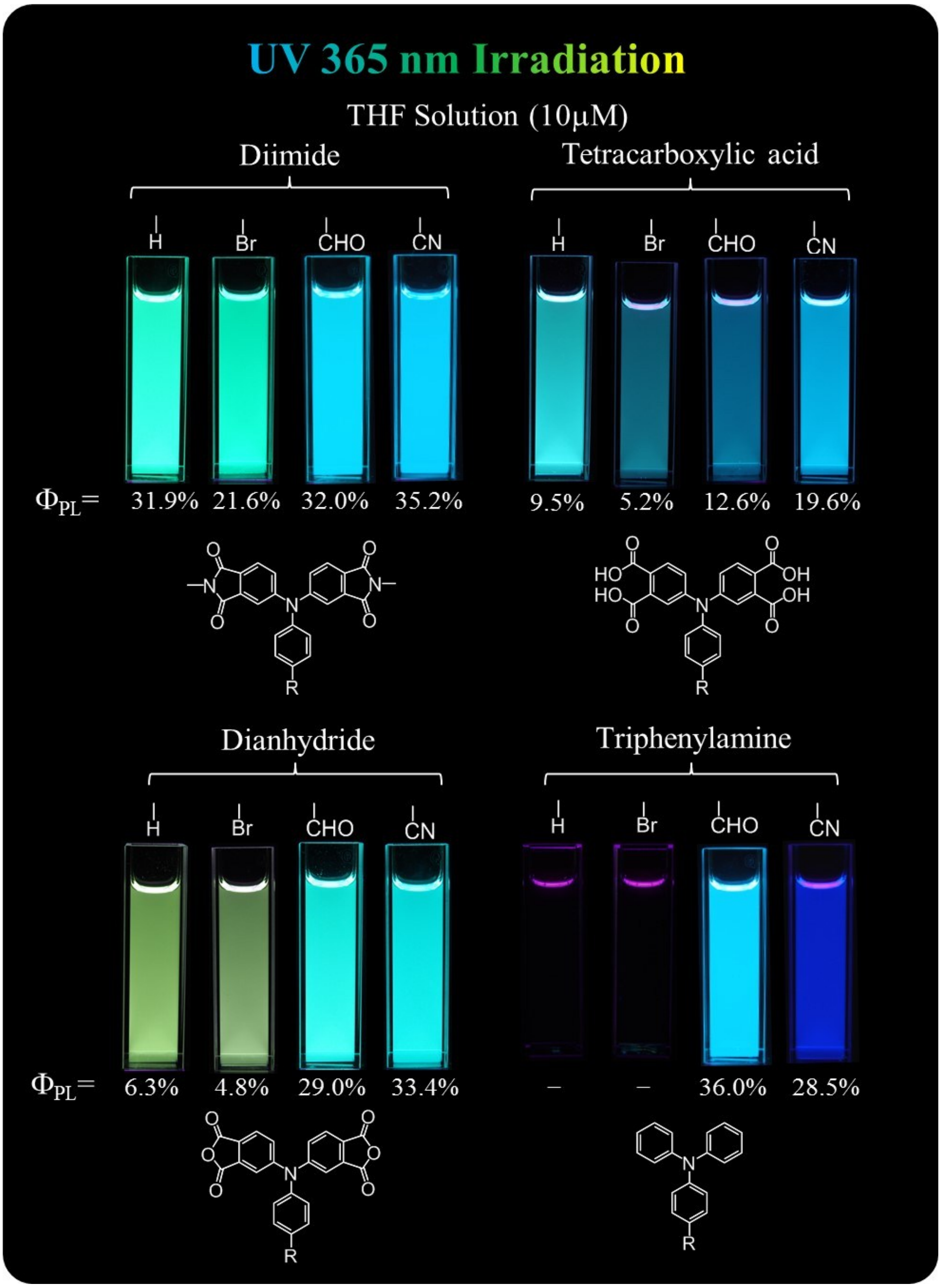


Figure S17. Photographs of molecules in 10 μM THF solution were taken under illumination of a 365 nm UV light.

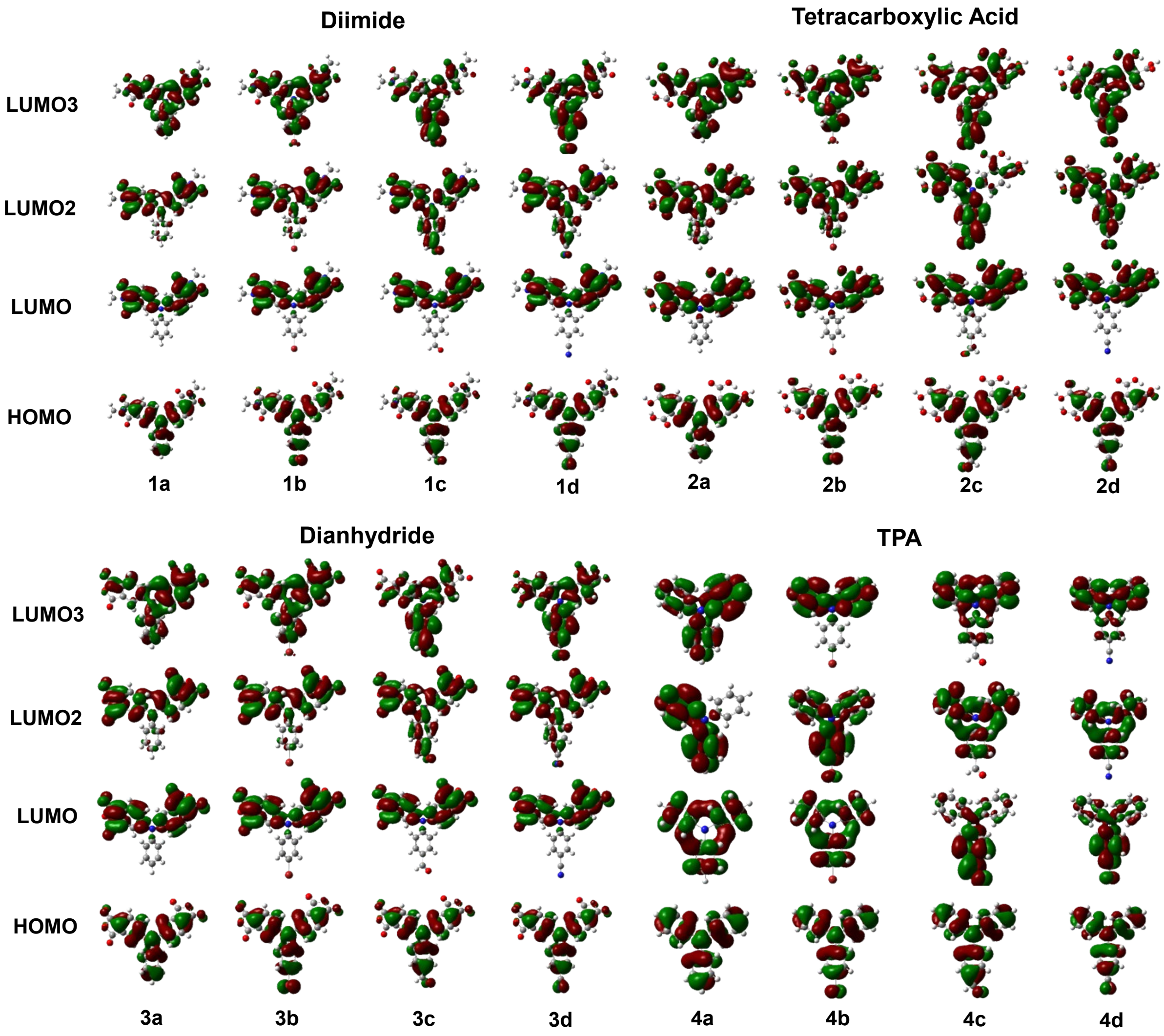


Figure S18. Calculated molecular orbitals of the model compounds (DFT method at B3LYP/6-31G(d)).

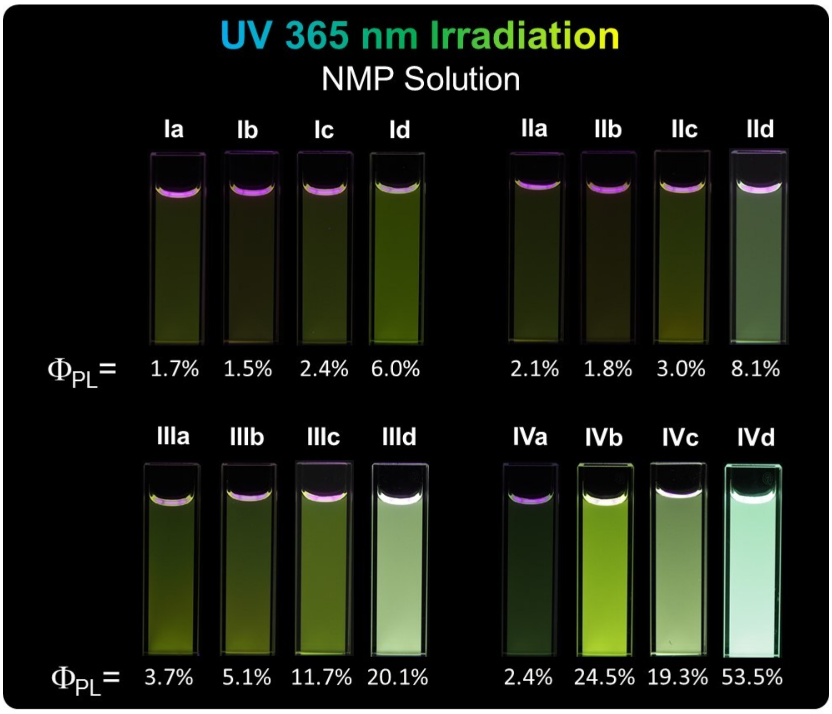


Figure S19. Photographs of polyimides in 10 μM NMP solution were taken under illumination of a 365 nm UV light.

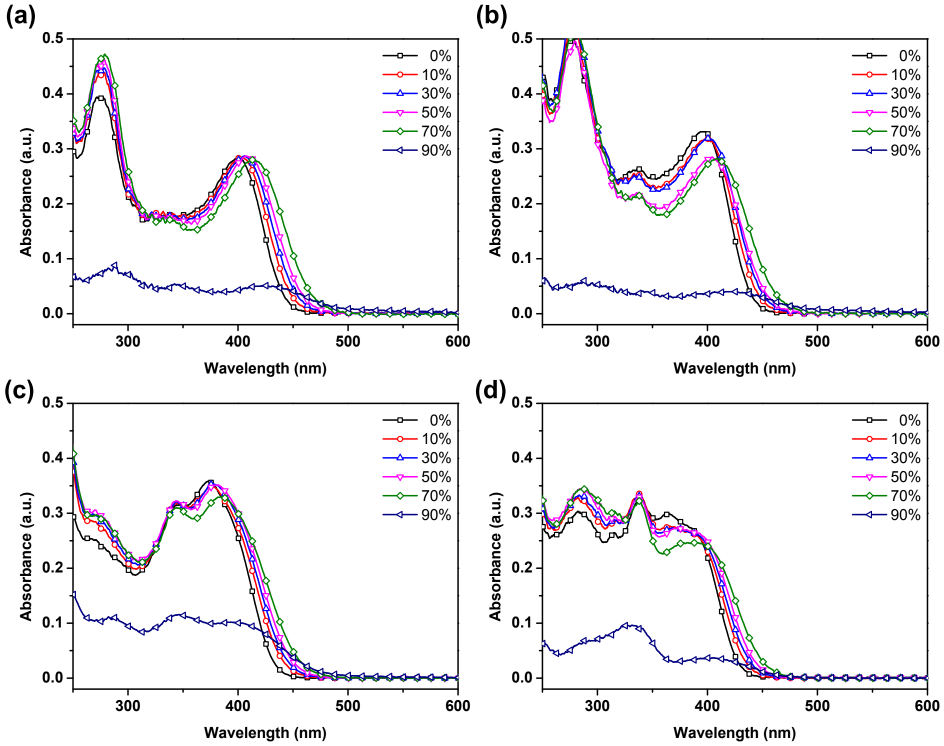


Figure S20. Absorption spectra of diimide compounds in different THF-water fraction. (a) **1a**, (b) **1b**, (c) **1c**, and (d) **1d**.

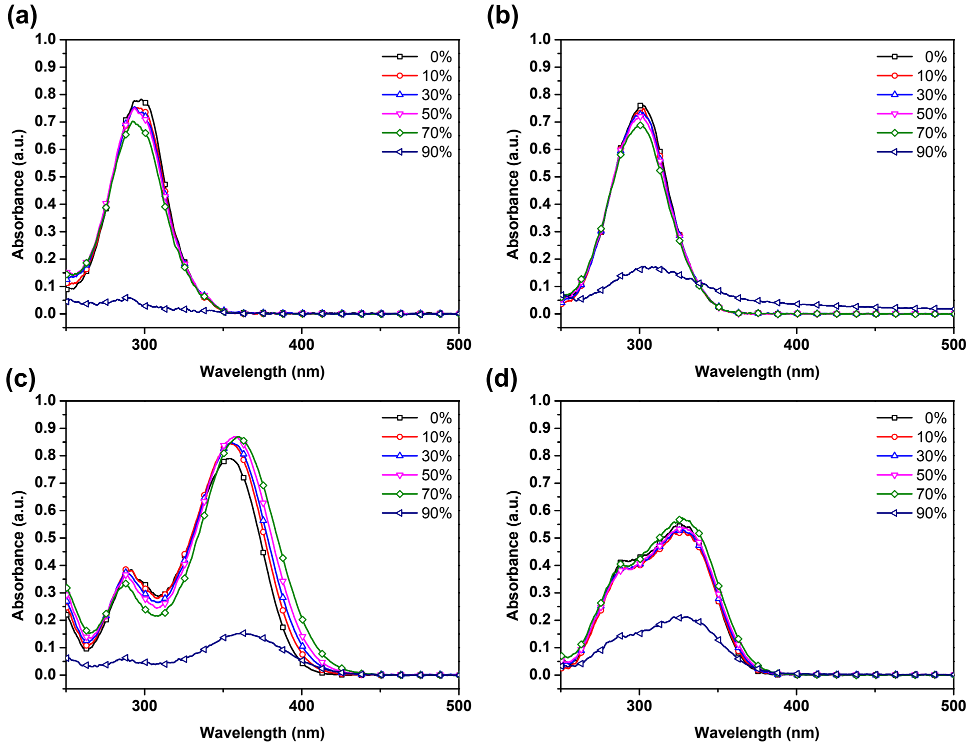
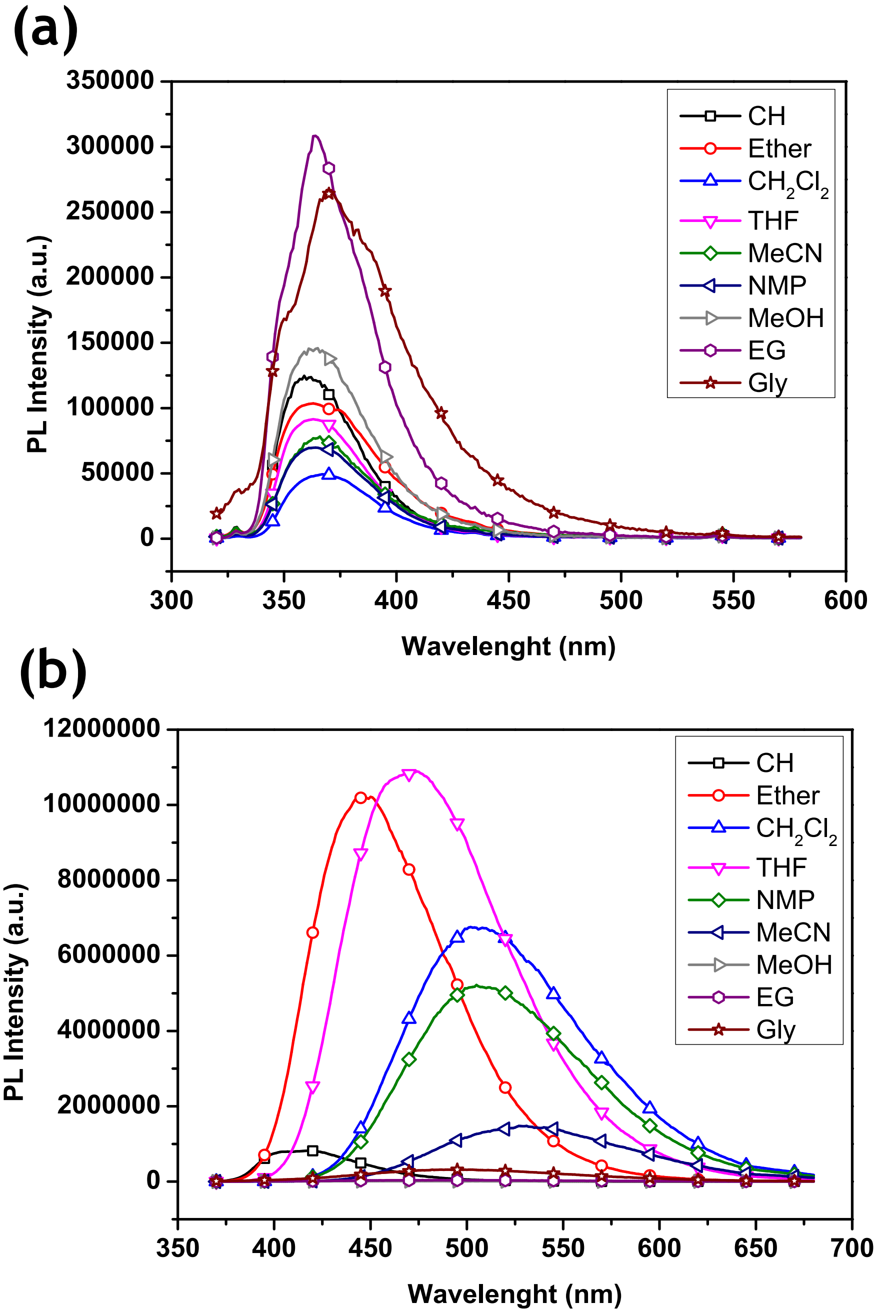


Figure S21. Absorption spectra of triphenylamine compounds in different THF-water fraction. (a) **4a**, (b) **4b**, (c) **4c**, and (d) **4d**.



Fugure S22. The PL spectra of (a) **4b** and (b) **4c** in various solvent (20μM). CH: cyclohexane; Ether: ethyl ether; NMP: *N*-methyl-2-pyrrolidone; EG: ethylene glycol; Gly: Glycerol.

Table S1 Inherent viscosity and molecular weight of the polyimides.

Polymer	η_{inh} [a]	Mn	Mw	PDI
IIa	-	33100	83700	2.53
IIb	0.40	36500	93800	2.57
IIc	0.50	40000	92800	2.32
IId	-	77500	205800	2.66
IIIa	0.21	7100	42500	5.98
IIIb	0.27	19000	103900	5.48
IIIc	0.29	19300	110700	5.73
IIId	0.37	18400	108600	5.91
IVa	0.24	14100	58900	4.18
IVb	0.29	19200	75500	3.93
IVc	0.35	18000	97100	5.38
IVd	0.61	26500	68800	2.69

[a] η_{inh} measured at polymer concentration of 0.5 g/dL in NMP at 30°C.

Table S2 Solubility behavior of the polyimides.

Polymer	Solubility in various Solvent					
	NMP	DMAc	DMF	*m*-Cresol	THF	$CHCl_3$
IIa	+ −	+ −	+ −	+ +	−	+ +
IIb	+ +	+ +	+ +	+ +	+ +	+ +
IIc	+ +	+ +	+ +	+ +	+ −	+ +
IId	+ −	−	−	+ +	+ −	+ +
IIIa	+ +	+ +	+ −	+ +	−	+ −
IIIb	+ +	+ −	+	+ +	+ −	+ −
IIIc	+ +	+ +	+ −	+ +	−	+ −
IIId	+ +	+ −	+ −	+ +	+ −	+ −
IVa	+ +	+ −	+ −	+ +	−	+
IVb	+ +	+ +	+ +	+ +	+ +	+ +
IVc	+ +	+ +	+ +	+ +	+ −	+
IVd	+ +	+ −	−	+ +	+ −	+ +

Qualitative solubility was tested with 5 mg of a sample in 1 mL of solvent. + +, soluble at room temperature; +, soluble on heating; + −, partially soluble or swelling; −, insoluble even on heating.

Table S3 Thermal properties of the polyimides.

Polymer[a]	T_g [°C][b]	T_d^5 [°C][c]		T_d^{10} [°C][c]		R_{w800} [%][d]
		N_2	Air	N_2	Air	
IIa	306	535	525	570	560	60
IIb	315	530	520	560	545	49
IIc	315	520	525	570	560	66
IId	288	425	415	440	425	17
IIIa	343	455	440	555	540	63
IIIb	365	510	490	555	540	60
IIIc	347	490	465	550	510	46
IIId	310	420	415	460	465	43
IVa	314	445	495	530	545	58
IVb	321	535	520	565	550	56
IVc	357	495	510	560	565	66
IVd	299	470	415	485	460	24

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

[b] Glass transition temperature measured by DSC at a heating rate of 10 °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 60 cm^3/min.

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

Table S4 Optical properties of fluorescent molecules.

Code	THF Solution				Solid Powder State			
	λ_{max}^{abs} [nm]	λ_{onset}^{abs} [nm]	λ_{max}^{em} [nm][a]	Φ_{PL} [%][b]	λ_{max}^{abs} [nm]	λ_{onset}^{abs} [nm]	λ_{max}^{em} [nm][a]	Φ_{PL} [%][c]
1a	397	449	506	31.9	436	493	509	24.6
1b	393	443	494	21.6	418	472	473	23.2
1c	371	432	477	32.0	409	483	504	27.8
1d	364	427	471	35.2	414	473	477	27.0
2a	340	388	443	9.5	366	480	511	13.5
2b	322	385	454	5.2	373	492	506	7.1
2c	343	384	439	12.6	363	550	457	0.7
2d	337	380	458	19.6	354	578	495	2.9
3a	388	436	518	6.3	407	478	491	39.4
3b	385	433	513	4.8	416	488	505	15.6
3c	382	425	490	29.0	400	520	519	17.5
3d	380	424	484	33.4	398	494	533	5.1
4a	296	331	361	–[d]	320	365	374	13.3
4b	301	340	364	–[d]	325	375	371	11.5
4c	353	393	465	36.0	380	437	451	65.1
4d	324	364	421	28.5	340	384	389	28.8

[a] Both of λ_{max}^{em} of solution and solid state were excited at λ_{max}^{abs}. [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 25°C. [c] PL quantum yields of molecules determined using a calibrated integrating sphere. [d] Not avalible.

Table S5 Optical properties of fluorescent polyimides.

Code	NMP Solution				Polymer film State			
	λ_{max}^{abs} [nm]	λ_{onset}^{abs} [nm]	λ_{max}^{em} [nm][a]	Φ_{PL} [%][b]	λ_{max}^{abs} [nm]	λ_{onset}^{abs} [nm]	λ_{max}^{em} [nm][a]	Φ_{PL} [%][c]
Ia	405	459	548	1.7	414	473	538	7.5
Ib	407	459	561	1.5	412	473	530	15.9
Ic	407	459	535	2.4	414	473	526	16.3
Id	406	454	532	6.0	403	460	512	32.0
IIa	402	456	540	2.1	409	475	522	8.3
IIb	405	456	549	1.8	409	474	536	13.6
IIc	403	457	541	3.0	410	473	527	11.2
IId	396	454	531	8.1	402	457	512	15.4
IIIa	394	458	538	3.7	410	478	538	6.2
IIIb	398	458	539	5.1	402	485	538	6.8
IIIc	396	458	529	11.7	400	491	545	6.4
IIId	392	456	518	20.1	387	459	532	8.5
IVa	391	448	521	2.4	413	474	513	3.4
IVb	393	448	529	24.5	395	459	514	9.5
IVc	393	451	520	19.3	401	470	516	4.8
IVd	387	444	512	53.5	374	442	510	17.1

[a] They were excited at λ_{max}^{abs}.

[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 25°C.

[c] PL quantum yields of polymer thin films determined using a calibrated integrating sphere.

Table S6 Quantum calculated results of small molecules (B3LYP/6-31G (d)).

Code	Dipole moment	Energy Level (eV)				Band gap		
		HOMO	LUMO	LUMO2	LUMO3	HOMO-LUMO	LUMO-LUMO2	LUMO2-LUMO3
1a	3.76	5.80	2.32	2.15	1.26	3.49	0.17	0.88
1b	2.06	5.90	2.42	2.26	1.43	3.48	0.16	0.82
1c	2.66	6.05	2.52	2.44	1.98	3.53	0.08	0.46
1d	3.13	6.14	2.58	2.48	1.84	3.56	0.11	0.63
2a	5.71	5.90	2.18	1.88	1.23	3.72	0.30	0.65
2b	4.80	5.99	2.28	2.00	1.39	3.71	0.28	0.61
2c	4.59	6.12	2.37	2.30	1.84	3.76	0.06	0.47
2d	5.20	6.21	2.43	2.28	1.78	3.78	0.15	0.50
3a	7.77	6.37	2.82	2.64	1.85	3.55	0.18	0.79
3b	6.24	6.44	2.92	2.74	1.99	3.53	0.17	0.75
3c	5.63	6.58	3.01	2.89	2.44	3.58	0.12	0.45
3d	4.21	6.68	3.08	2.95	2.36	3.60	0.13	0.59
4a	0.01	4.95	0.30	0.24	0.23	4.65	0.06	0.00
4b	2.32	5.11	0.54	0.54	0.39	4.57	0.00	0.14
4c	5.00	5.34	1.47	0.62	0.51	3.87	0.85	0.11
4d	6.40	5.43	1.22	0.75	0.60	4.21	0.47	0.15

References

1. (a) H. J. Yen, J. H. Wu, W. C. Wang and G. S. Liou, *Adv. Opt. Mater.*, 2013, **1**, 668; (b) J. H. Wu and G. S. Liou, *Adv. Funct. Mater.*, 2014, **24**, 6422; (c) B. V. Rokade and K. R. Prabhu, *J. Org. Chem.*, 2012, **77**, 5364; (d) J. A. Riddle, X. Jiang, J. Huffman and D. Lee, *Angew. Chem. Int. Ed.*, 2007, **46**, 7019.