Supporting Information

High-Efficiency Fluorescent Polyimides Based on Locally Excited Triarylamine-containing Dianhydride Moieties

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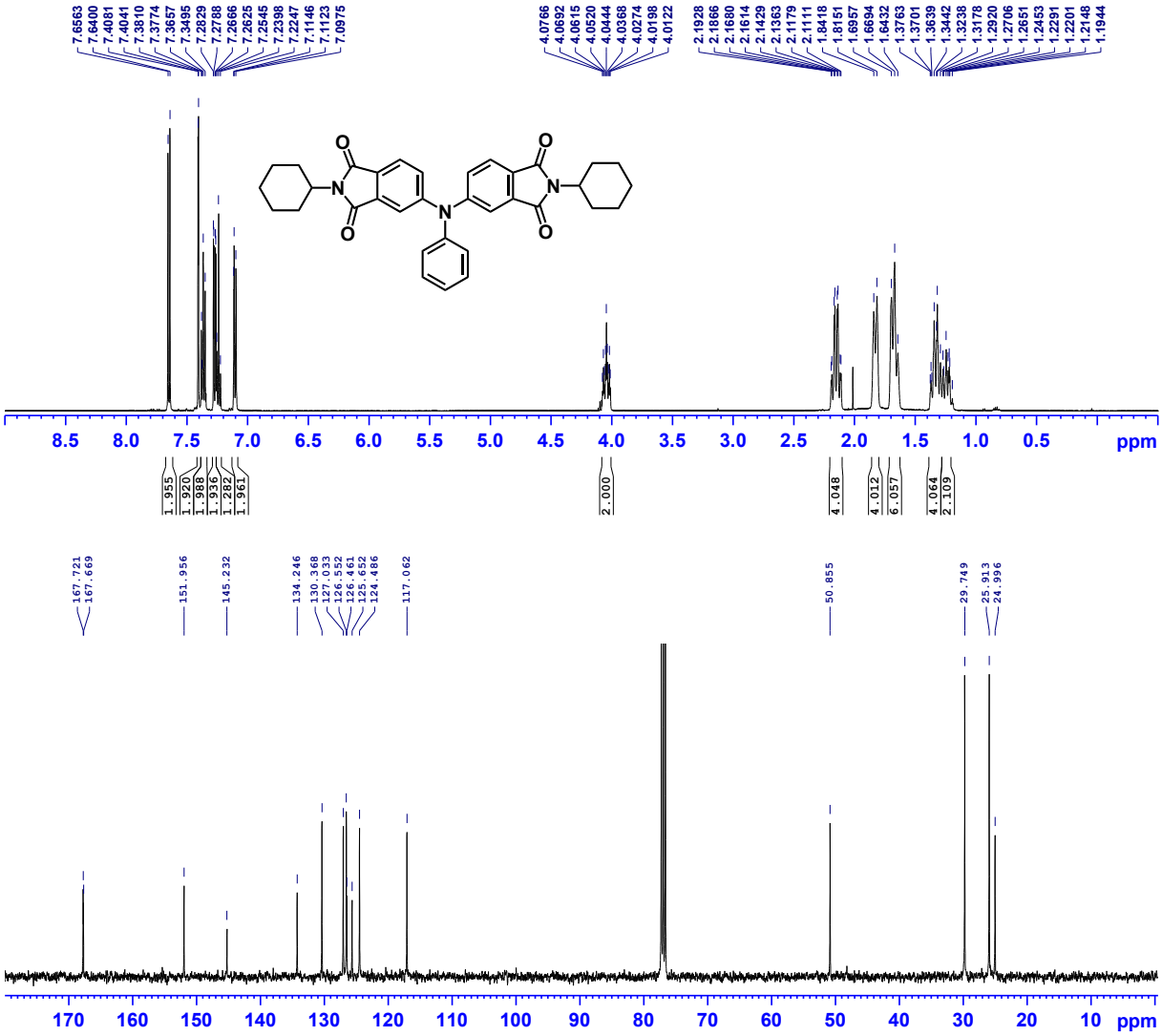

Scheme S1. NMR spectra of **M-Ph** in $CDCl_3$.

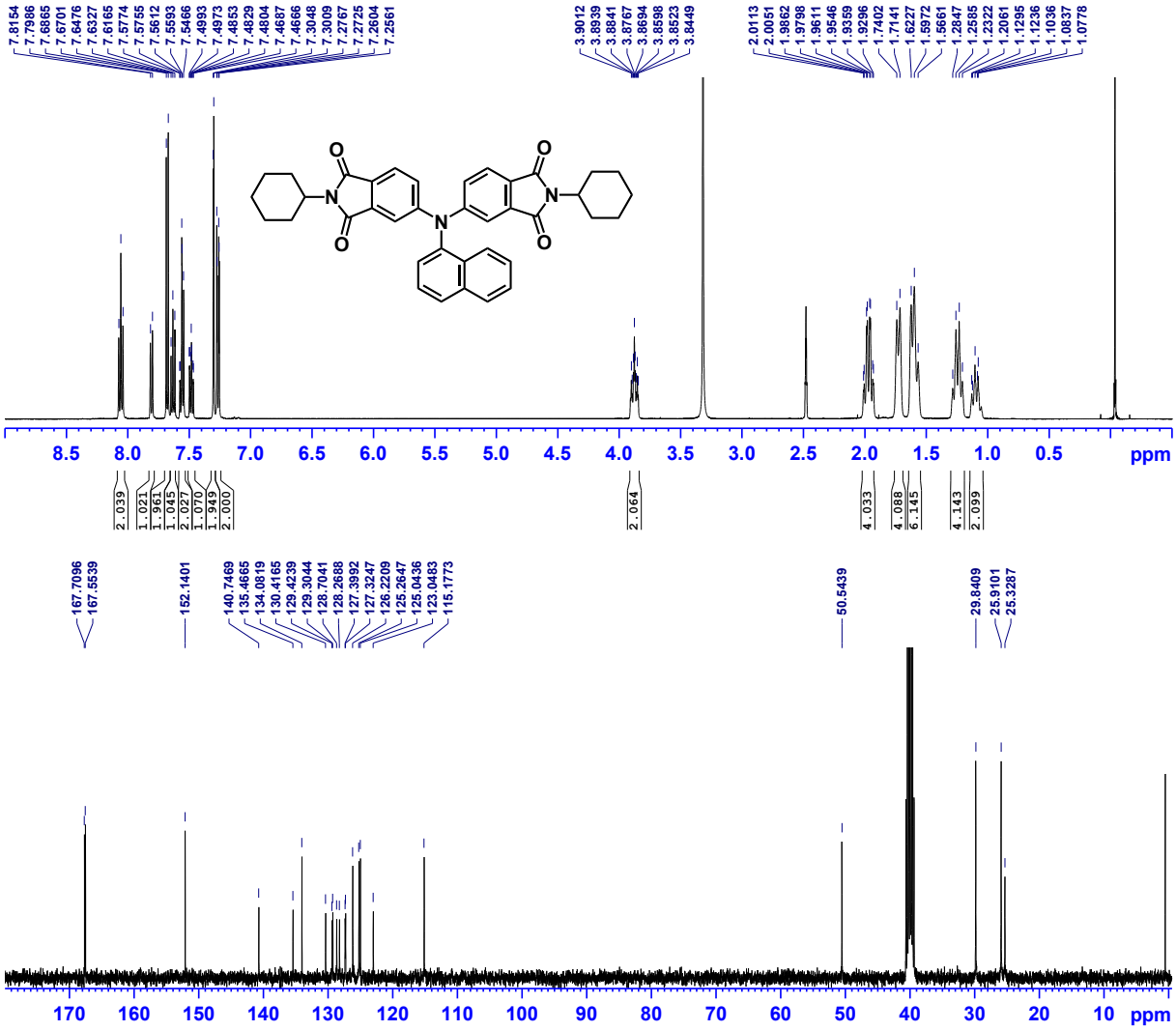

Figure S1. NMR spectra of **M-Np** in $CDCl_3$.

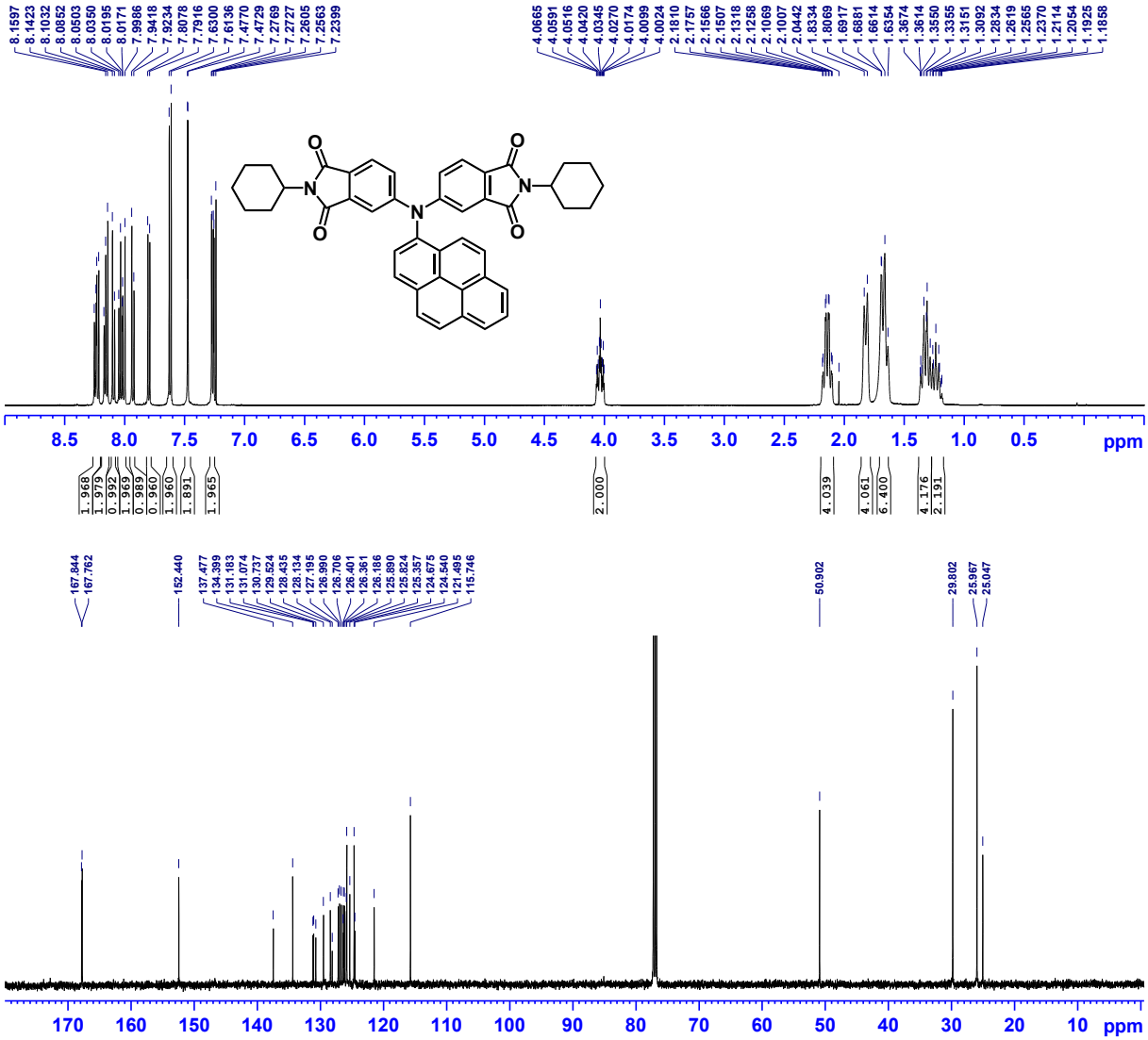

Figure S3. NMR spectra of **M-Py** in $CDCl_3$.

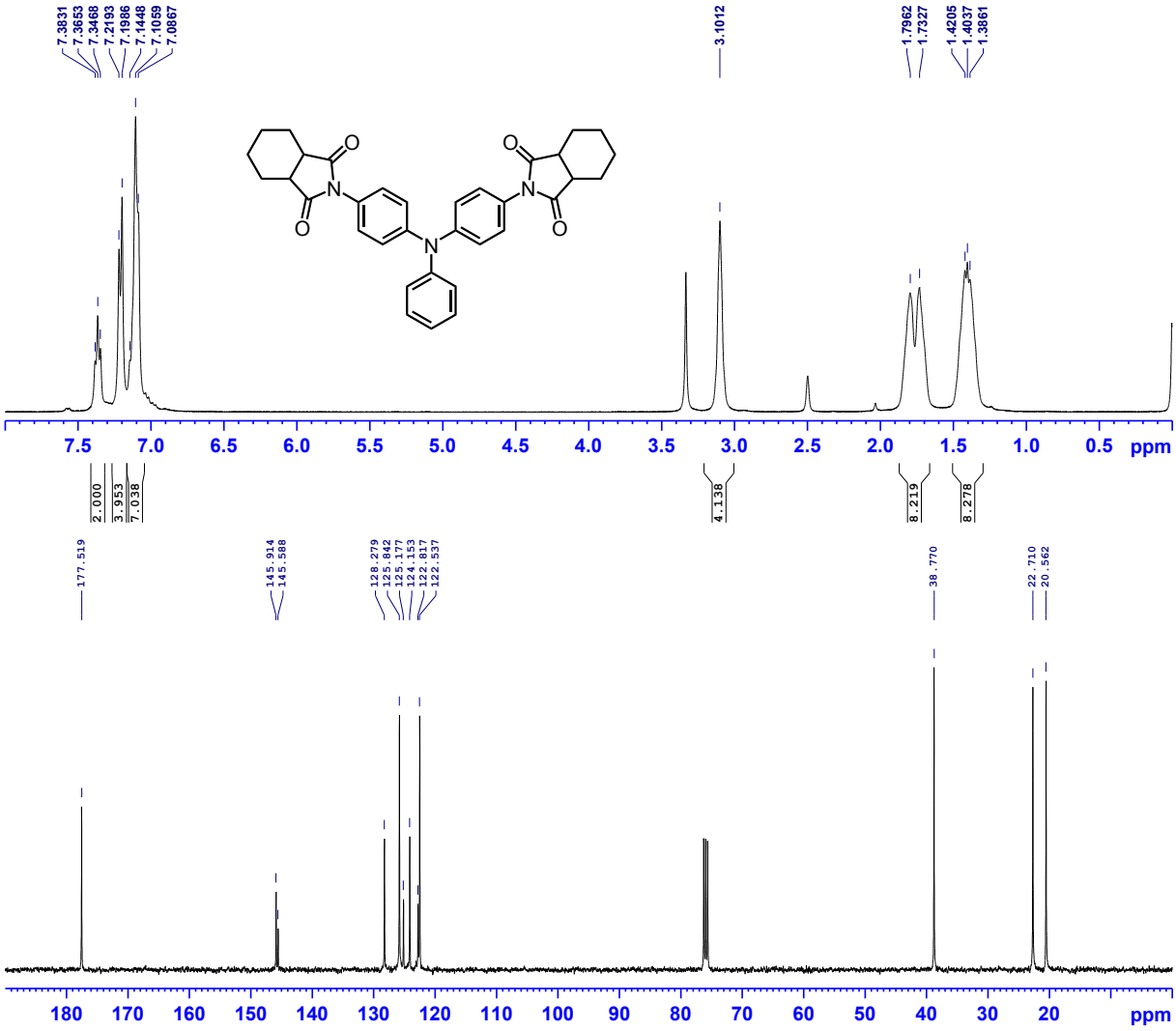

Figure S4. NMR spectra of **M-Ph'** in $CDCl_3$.

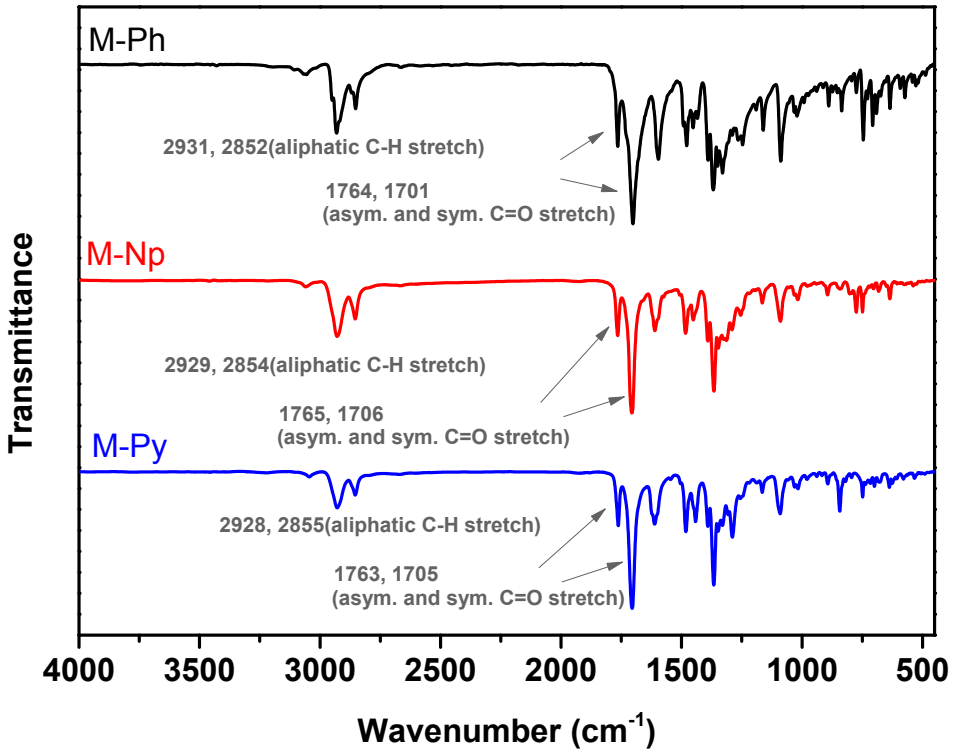

Figure S5. FTIR spectra of the model compounds.

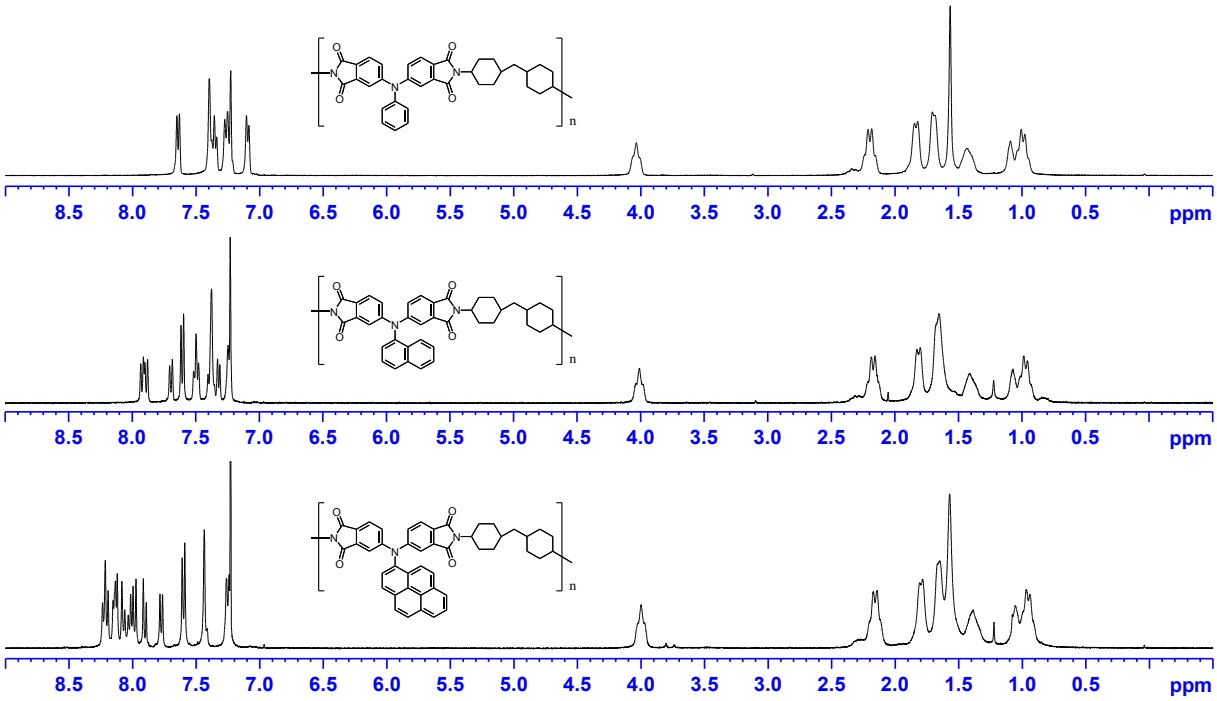

Figure S6. ^{1}H-NMR spectra of the polyimides in $CDCl_3$.

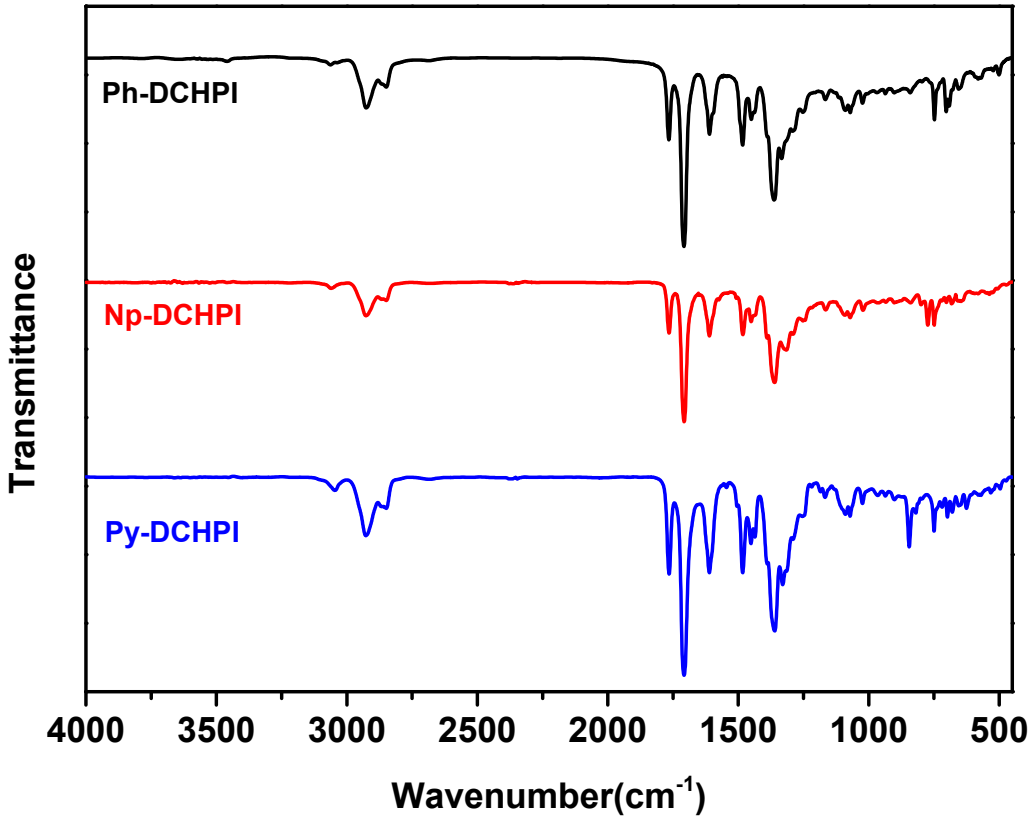

Figure S7. FTIR spectra of the polyimides.

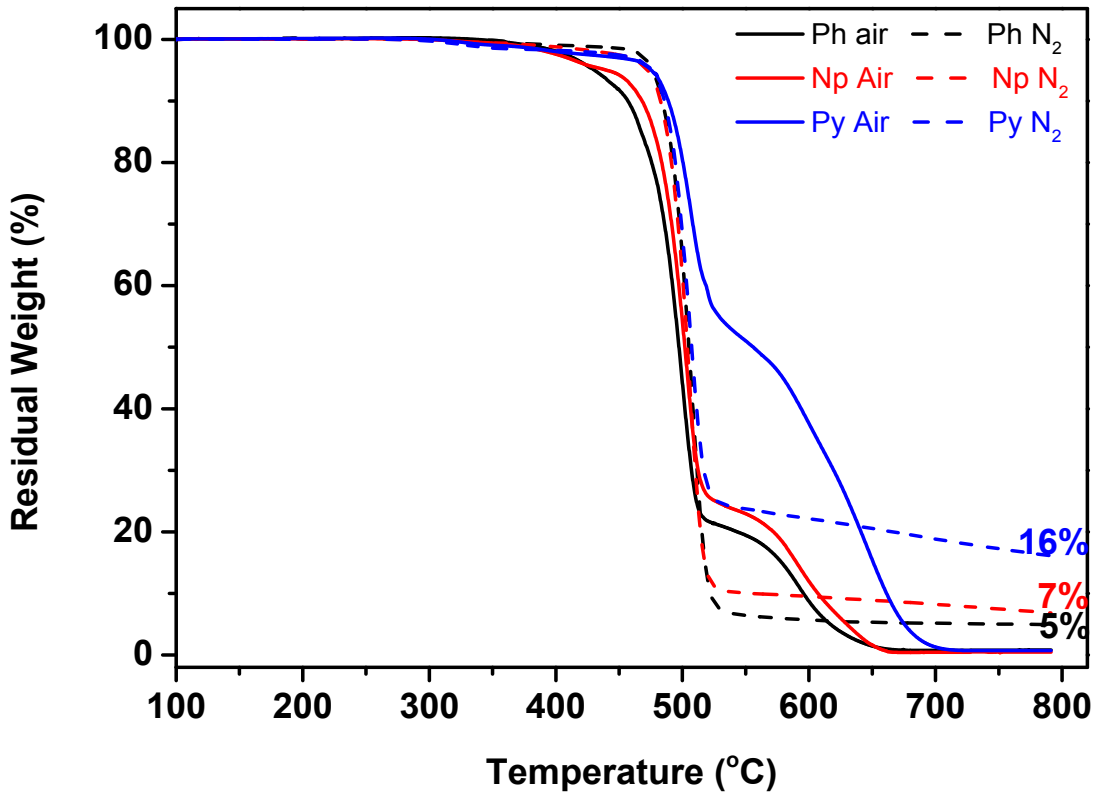

Figure S8. TGA thermograms of the polyimides.

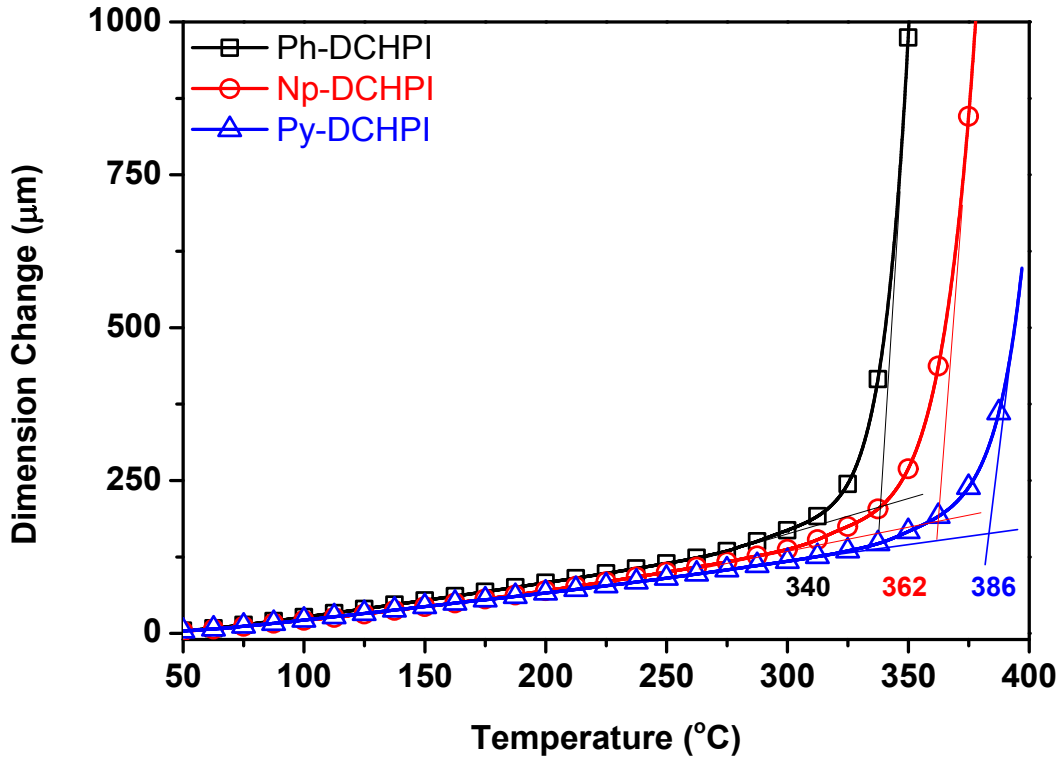

Figure S9. TMA thermograms of the polyimides.

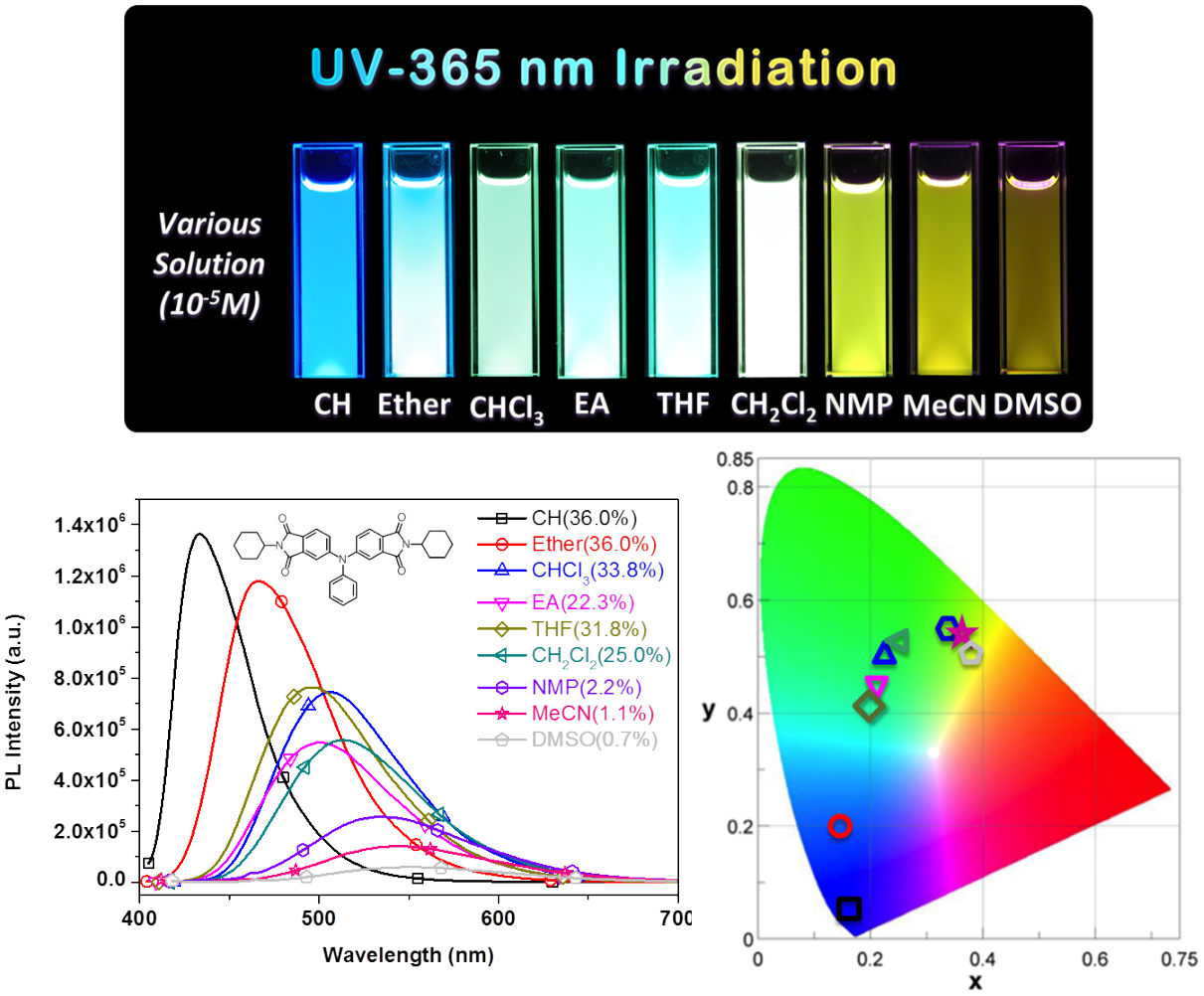

Figure S10. PL spectra and quantum efficiency of the model compound **M-Ph** in different solvents excited at abs_{max} (solution concentration 10 μM). Photographs were taken under illumination at 365 nm.

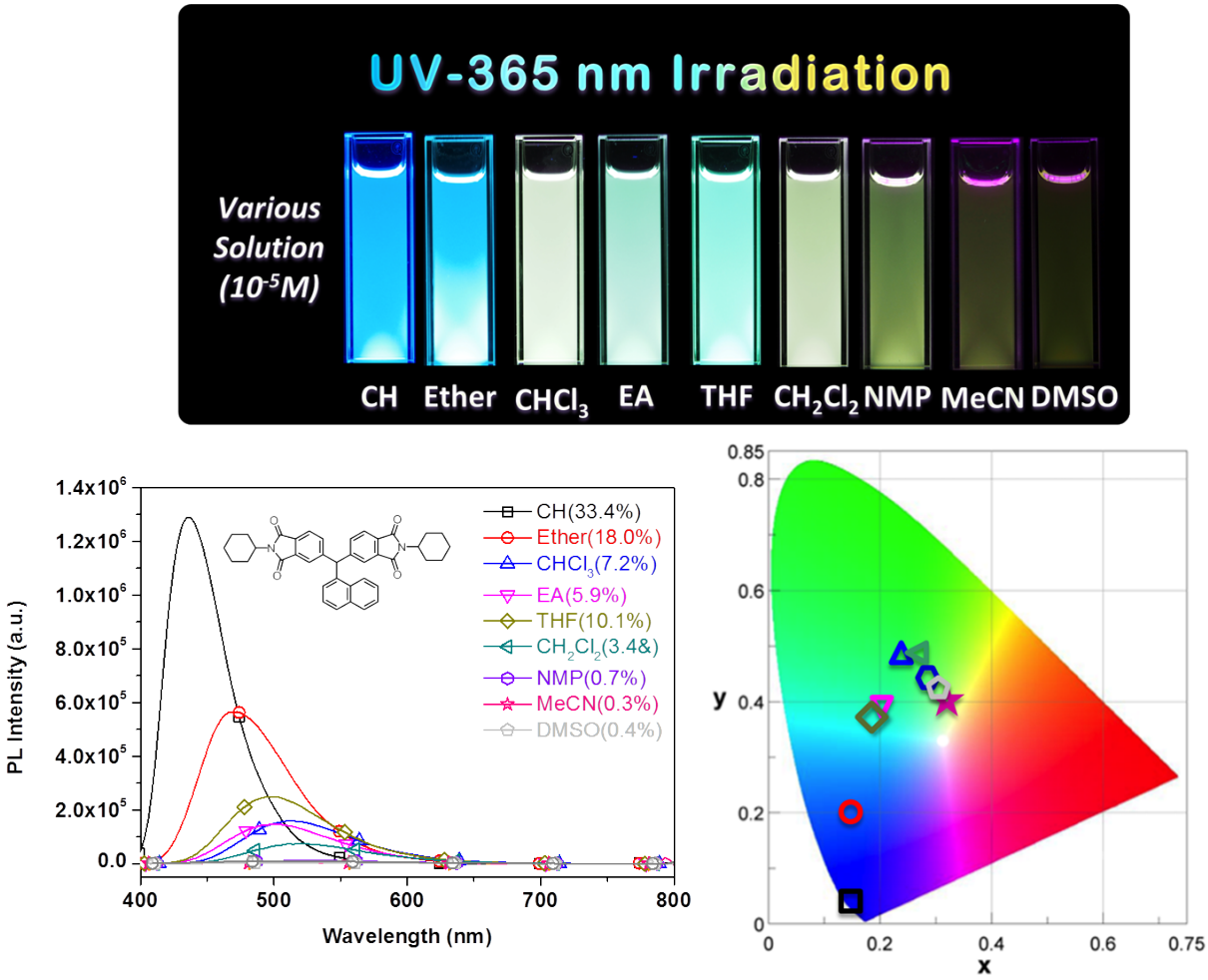

Figure S11. PL spectra and quantum efficiency of the model compound **M-Np** in different solvents excited at abs_{max} (solution concentration 10 μM). Photographs were taken under illumination at 365 nm.

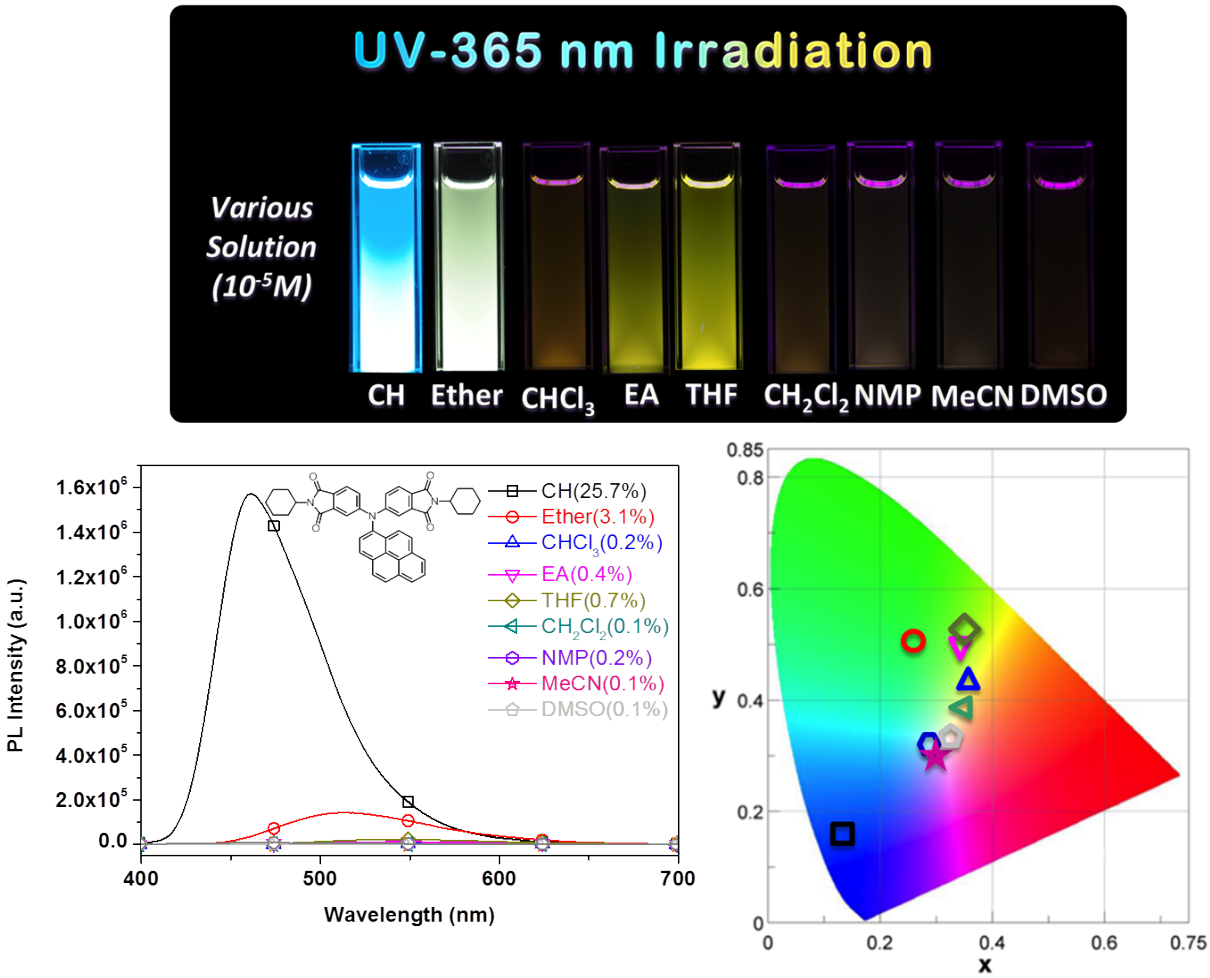

Figure S11. PL spectra and quantum efficiency of the model compound **M-Py** in different solvents excited at abs_{max} (solution concentration 10 μM). Photographs were taken under illumination at 365 nm.

Table S1. Inherent viscosity and molecular weight of the polyimides

Polymer	η_{inh} (dL/g)[a]	Mn[c]	Mw[c]	PDI[d]
Ph-DCHPI	1.53[b]	-	-	-
Np-DCHPI	1.17	67900	142200	2.09
Py-DCHPI	0.54	19900	45000	2.26

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

[b] η_{inh} (dL/g) measured at polymer concentration of 0.5 g/dL in H_2SO_4 at 30°C.

[c] Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 ml/min at 40 °C.

[d] Polydispersity Index (M_w/M_n).

Table S2. Solubility behavior of the polyimides.

Polymer	Solubility in various Solvent						
	NMP	DMAc	DMF	*m*-Cresol	THF	$CHCl_3$	Toluene
Ph-DCHPI	+ −	+ −	−	++	+	++	+ −
Np-DCHPI	++	+	+ −	++	++	++	+ −
Py-DCHPI	++	+ −	−	++	+	++	−

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	
Ph-DCHPI	340	475	430	485	445	5
Np-DCHPI	362	475	440	485	470	7
Py-DCHPI	386	475	475	485	490	16

[a] The polymer 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] 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. Transition wavelengths, oscillator strengths, and the assignment of $S_0 \rightarrow S_i$ transitions of the model compounds.

Code	State	Transition Wavelength (nm)	Oscillator Strength	Orbitls	Character of Transition	Contribution
M-Ph'	S1	329.2	0.5896	LE(π−π*)	HOMO→LUMO	0.99
	S2	318.1	0.0188	CT(π−π*)	HOMO→LUMO+1	0.08
				CT(π−π*)	HOMO→LUMO+2	0.06
				LE(π−π*)	HOMO→LUMO+4	0.82
	S3	312.9	0.3001	LE(π−π*)	HOMO→LUMO+3	0.97
M-Ph	S1	413.8	0.3038	LE(π−π*)	HOMO→LUMO	0.98
M-Np	S1	409.5	0.2341	LE(π−π*)	HOMO→LUMO	0.98
M-Py	S1	432.0	0.1489	LE(π−π*)	HOMO→LUMO	0.98
	S2	407.3	0.2911	LE(π−π*)	HOMO-1→LUMO+2	0.06
				LE(π−π*)	HOMO→LUMO+2	0.89
				LE(π−π*)	HOMO→LUMO+3	0.03

Table S5. Photophysical properties of model compound **M-Ph** in different solvents.

Solvent	ε^a	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)^b	Φ_{PL} (%)^c	CIE 1931 coordinates	
					x	*y*
Cyclohexane	2.0	395	433	36.0	0.1530	0.0463
Ethyl ether	4.3	394	466	36.0	0.1432	0.1852
$CHCl_3$	4.8	409	507	33.8	0.2138	0.4910
EA	6.0	399	500	22.3	0.2003	0.4357
THF	7.6	401	497	31.8	0.1823	0.4060
CH_2Cl_2	8.9	407	514	25.0	0.2448	0.5200
NMP	32.2	406	534	2.2	0.3274	0.5352
MeCN	37.5	402	544	1.1	0.3576	0.5274
DMSO	46.7	408	551	0.7	0.3691	0.4957

[a] Dielectic constant of the solvents.

[b] Excited at λ_{max}^{abs}.

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

Table S6. Photophysical properties of model compound **M-Np** in different solvents.

Solvent	ε[a]	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)[b]	Φ_{PL} (%)[c]	CIE 1931 coordinates	
					x	*y*
Cyclohexane	2.0	388	436	33.4	0.1523	0.0508
Ethyl ether	4.3	390	472	18.0	0.1513	0.2110
$CHCl_3$	4.8	403	511	7.2	0.2474	0.4974
EA	6.0	394	501	5.9	0.2092	0.4126
THF	7.6	393	498	10.1	0.1983	0.4011
CH_2Cl_2	8.9	400	520	3.4	0.2744	0.5109
NMP	32.2	402	526	0.7	0.2930	0.4560
MeCN	37.5	396	544	0.3	0.3260	0.4166
DMSO	46.7	401	547	0.4	0.3252	0.4279

[a] Dielectic constant of the solvents.

[b] Excited at λ_{max}^{abs}.

[c] 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.

Table S7. Photophysical properties of model compound **M-Py** in different solvents.

Solvent	ε^a	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)[b]	Φ_{PL} (%)[c]	CIE 1931 coordinates	
					x	*y*
Cyclohexane	2.0	378	461	25.7	0.1436	0.1593
Ethyl ether	4.3	374	512	3.1	0.2576	0.4984
$CHCl_3$	4.8	377	563	0.2	0.3609	0.4345
EA	6.0	377	544	0.4	0.347	0.4949
THF	7.6	379	541	0.7	0.352	0.5238
CH_2Cl_2	8.9	380	564	0.1	0.3462	0.3822
NMP	32.2	376	560	0.2	0.2934	0.3274
MeCN	37.5	375	566	0.1	0.3022	0.3031
DMSO	46.7	379	561	0.1	0.3204	0.3398

[a] Dielectic constant of the solvents.

[b] Excited at λ_{max}^{abs}.

[c] 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.

Table S8. Optical properties of the polyimides in NMP-MeOH with different methanol fraction.

Polymer	f_w [v%][a]	λ_{max}^{abs} [nm]	λ_{max}^{em} [nm]	Φ_{PL} [%]	CIE 1931 coordinates	
					x	y
Ph-DCHPI	0	407	527	5.2	0.2970	0.5226
	30	410	517	7.9	0.2733	0.5253
	50	408	520	5.9	0.2835	0.5288
	70	410	527	4.2	0.2997	0.5343
	90	406	531	3.1	0.3121	0.5361
Np-DCHPI	0	402	523	1.7	0.2874	0.4785
	30	402	512	5.9	0.2462	0.4778
	50	401	514	4.7	0.2572	0.4894
	70	401	517	3.5	0.2690	0.4974
	90	402	522	2.4	0.2827	0.4989
Py-DCHPI	0	378	553	0.3	0.3087	0.3587
	30	378	528	1.7	0.3248	0.5117
	50	377	526	1.3	0.3266	0.4946
	70	376	531	1.1	0.3351	0.4887
	90	378	545	0.8	0.3401	0.4710

[a] Polymer concentration is 10 μM with different MeOH fraction.