Electronic Supplementary Information

Tuning fluorescence of aggregates for end-functionalized polymers through varying polymer chains with different polarities

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Contents

Figure S16 Typical fluorescence decay curves associated with lamp profile for TPP-NI in DMF/water mixture and PS-NI in DMF/ethanol mixture. Excitation wavelength is constant at 371 nm.

Figure S17 Typical fluorescence decay curves associated with lamp profile for PNIPAM-NI in THF/water mixture (left) and THF/hexane mixture (right). Excitation wavelength is constant at 371 nm.

Figure S18 Absorption spectra of TPP-A (left) and TPP-NI (right) with the composition of the DMF/water mixture (Concentration: 25 μM).

Figure S19 Normalized absorption and emission spectra of PS-A in different solvents ($\lambda_{ex} = \lambda_{abs}$, respectively, Concentration: 5 μM).

Figure S20 Normalized absorption and emission spectra of PS-NI in different solvents ($\lambda_{ex} = \lambda_{abs}$, respectively, Concentration: 5 μM).

Figure S21 Absorption spectra of PS-A (left) and PS-NI (right) with the composition of the DMF/ethanol mixture (Concentration: 5 μM).

Figure S22 Normalized absorption and emission spectra of PNIPAM-A in different solvents ($\lambda_{ex} = \lambda_{abs}$, respectively, Concentration: 5 μM).

Figure S23 Normalized absorption and emission spectra of PNIPAM-NI in different solvents ($\lambda_{ex} = \lambda_{abs}$, respectively, Concentration: 5 μM).

Figure S24 Absorption spectra of PNIPAM-A (left) and PNIPAM-NI (right) with the composition of the THF/hexane mixture (Concentration: 5 μM).

Figure S25 Change in QYs of TPP-A (left) and TPP-NI (right) in the DMF/water mixture (Concentration: 5 μM).

Figure S26 Change in QYs of PS-A (left) and PS-NI (right) in the DMF/ethanol mixture (Concentration: 5 μM).

Figure S27 Change in QYs of PNIPAM-A (left) and PNIPAM-NI (right) in the THF/hexane mixture (Concentration: 5 μM).

Figure S28 Change in QYs of PNIPAM-A (left) and PNIPAM-NI (right) in the THF/water mixture (Concentration: 5 μM).

Figure S29 Calibration curve for determining the percentage of TPP-A or TPP-NI in polymers, using TPP-A or TPP-NI as standard.

Figure S30 Absorption (left) and normalized emission (right) spectra of TPP-A (the dye concentration: 2.5 μM) in different solvents (DMF/water = 1:9 by volume).

Figure S31 Absorption (left) and normalized emission (right) spectra of TPP-NI (the dye concentration: 2.0 μM) in different solvents (DMF/water = 1:9 by volume).

Figure S32 Absorption (left) and normalized emission (right) spectra of PS-A (the dye concentration: 2.5 μM) in different solvents (DMF/ethanol = 1:9 by volume).

Figure S33 Absorption (left) and normalized emission (right) spectra of PS-NI (the dye concentration: 2.0 μM) in different solvents (DMF/ethanol = 1:9 by volume).

Figure S34 Absorption (left) and normalized emission (right) spectra of PNIPAM-A (the dye concentration: 2.5 μM) in different solvents (THF/water or THF/hexane = 1:9 by volume).

Figure S35 Absorption (left) and normalized emission (right) spectra of PNIPAM-NI (the dye concentration: 2.0 μM) in different solvents (THF/water or THF/hexane = 1:9 by volume).

General Information

The fluorescent quantum yields (QYs) in the solution were determined using quinine bisulfate (Φ_F = 0.54 in 0.1 mol L^{-1} H_2SO_4) or fluorescein (Φ_F = 0.79 in 0.1 mol L^{-1} NaOH) using the equation:

$$\phi_s = \frac{F_s}{F_r}\frac{{n_s}^2}{{n_r}^2}\frac{A_r}{A_s}\phi_r \qquad (1)$$

In this equation, subscripts s and r represent the sample and reference, respectively. F is the integral area of the fluorescence spectra, n is the refractive index of the solution, A is the absorbance, ϕ is the fluorescence quantum yield.

Experimental

Synthesis of 4-(5-(4-(dimethylamino)phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)phenyl 2-bromo-2-methylpropanoate (**TPP-A**)

3-(4-(dimethylamino)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (**PhAO**) was prepared according to the relevant published literature.[1] 4-(5-(4-(dimethylamino)phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)phenol (TPP-AO) was synthesized by reacting phenylhydrazine with chalcone PhAO, as follows. A mixture of phenylhydrazine (10 mmol) and chalcone PhAO (10 mmol) in ethanol (50 mL), and 37 % HCl (5 mL), was refluxed for 24 hr under N_2. The resulting mixture was cooled, and the precipitate filtered to afford the crude products, which were recrystallized from ethanol/water with 75 % yield. 4-(5-(4-(dimethylamino)phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)phenyl 2-bromo-2-methylpropanoate (TPP-A) was synthesized by reacting TPP-AO with 2-bromopropionyl bromide, as follows. A mixture of TPP-AO (1.0 mmol) and triethylamine (3.0 mmol) in THF (100 mL) was cooled to 0 ^oC in an ice/water bath. Then, 2-bromopropionyl bromide (2.0 mmol) in THF (40 mL) was added to a 50 mL pressure equalizing addition funnel fitted to the flask under N_2 (g). After being added dropwise, the reaction mixture was stirring overnight and allowed to warm to room temperature. The solution was then filtered and poured into a large amount of water; the precipitate was filtered to afford the crude products, which were recrystallized from ethanol with 86 % yield.

4-(5-(4-(dimethylamino)phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)phenol (TPP-AO)

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.75 (s, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.10 (s, 4H), 6.97 (d, J = 7.6 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 6.66 (d, J = 8.1 Hz, 3H), 5.24 (s, 1H), 3.87 – 3.67 (m, 1H), 2.97 (d, J = 17.3 Hz, 1H), 2.84 (s, 6H).

^{13}C NMR (400 MHz, DMSO-d_6) δ 158.66, 150.10, 147.96, 145.31, 130.46, 129.16, 127.76, 127.05, 124.02, 118.31, 115.95, 113.25, 113.17, 63.18, 43.85.

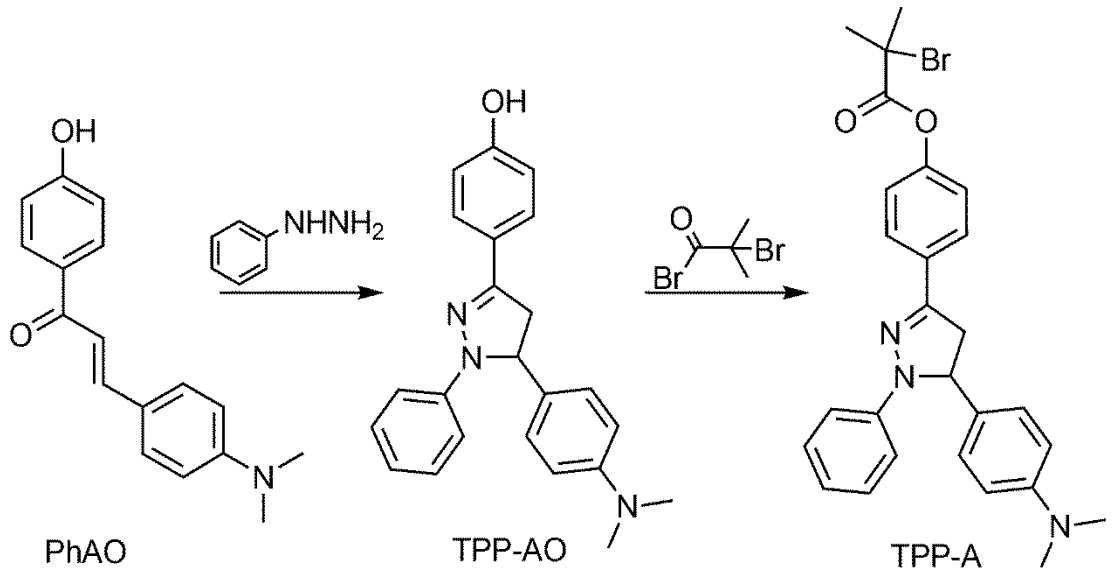
HR-MS (m/z): $[M+H]^+$ Ion Formula: $C_{23}H_{24}N_3O$, Calcd for, 358.1914; Found, 358.1926.

4-(5-(4-(dimethylamino)phenyl)-1-phenyl-4,5-dihydro-1H-pyrazol-3-yl)phenyl 2-bromo-2-methylpropanoate (TPP-A)

^{1}H NMR (400 MHz, DMSO) δ 7.86 – 7.80 (m, 2H), 7.27 – 7.21 (m, 2H), 7.14 (dd, J = 15.1, 7.9 Hz, 4H), 7.03 (dd, J = 6.3, 2.4 Hz, 2H), 6.71 (t, J = 7.2 Hz, 3H), 5.38 (dd, J = 12.1, 6.4 Hz, 1H), 3.87 (dd, J = 17.4, 12.1 Hz, 1H), 3.08 (dd, J = 17.4, 6.3 Hz, 1H), 2.86 (s, 6H), 2.07 (s, 6H).

^{13}C NMR (400 MHz, DMSO-d_6) δ 170.09, 150.88, 146.74, 144.71, 131.16, 129.25, 127.35, 127.13, 121.98, 118.97, 113.53, 63.44, 57.49, 43.48, 30.50.

HR-MS (m/z): $[M+H]^+$ Ion Formula: $C_{27}H_{29}BrN_3O_2$, Calcd for, 506.1364; Found, 506.1437.



Scheme S1 Synthetic routines for TPP-A.

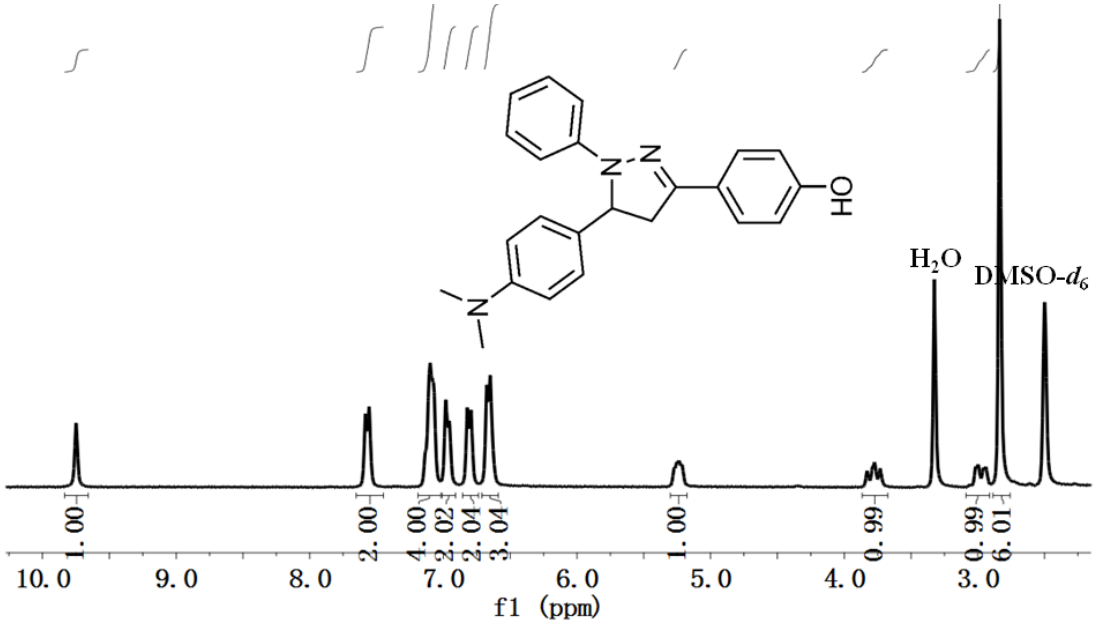


Figure S1 [1]H NMR spectrum of TPP-AO in DMSO-d_6.

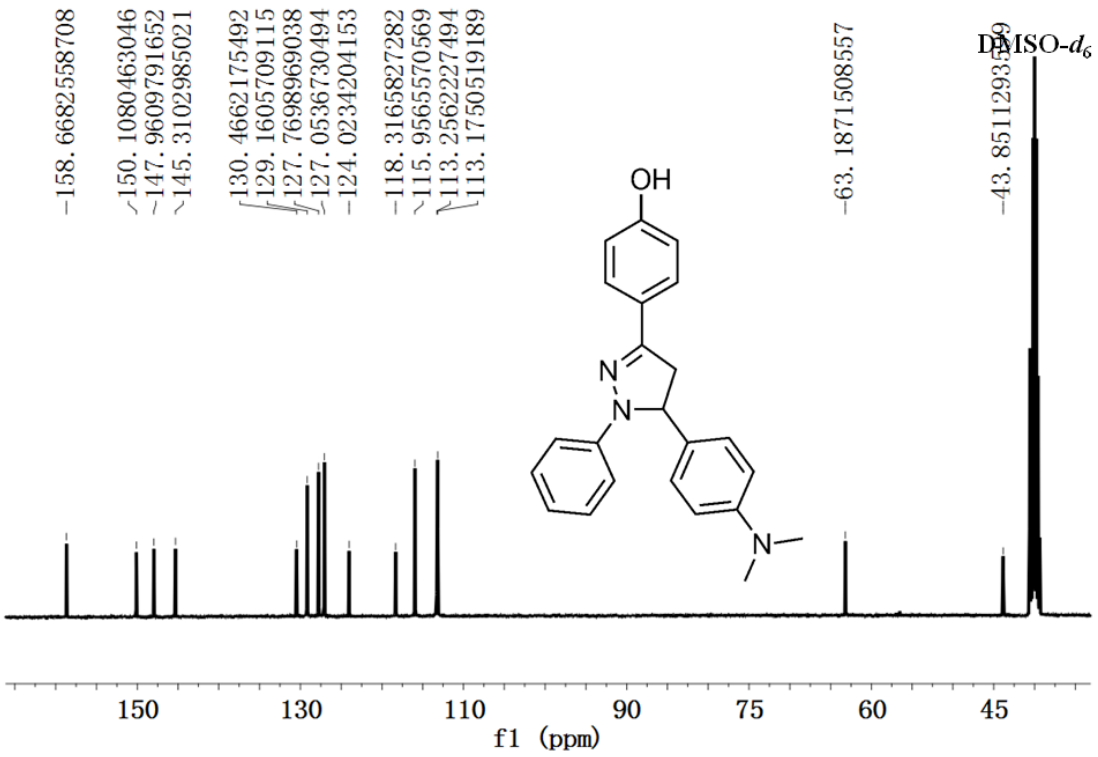


Figure S2 [13]C NMR spectrum of TPP-AO in DMSO-d_6.

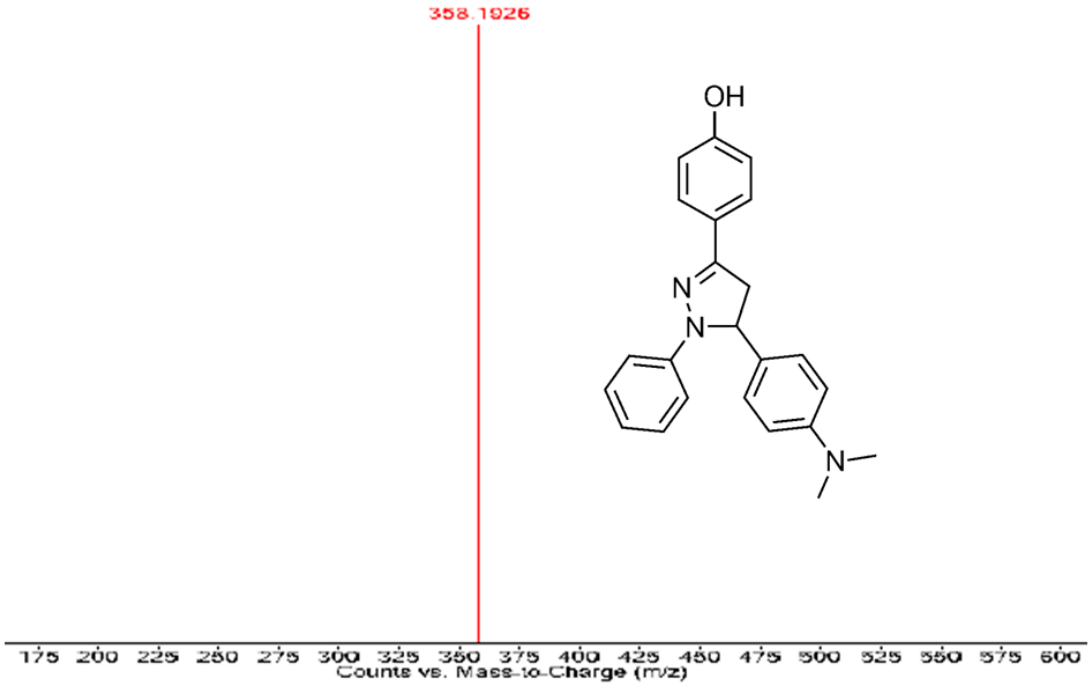


Figure S3 HR-MS spectrum of TPP-AO

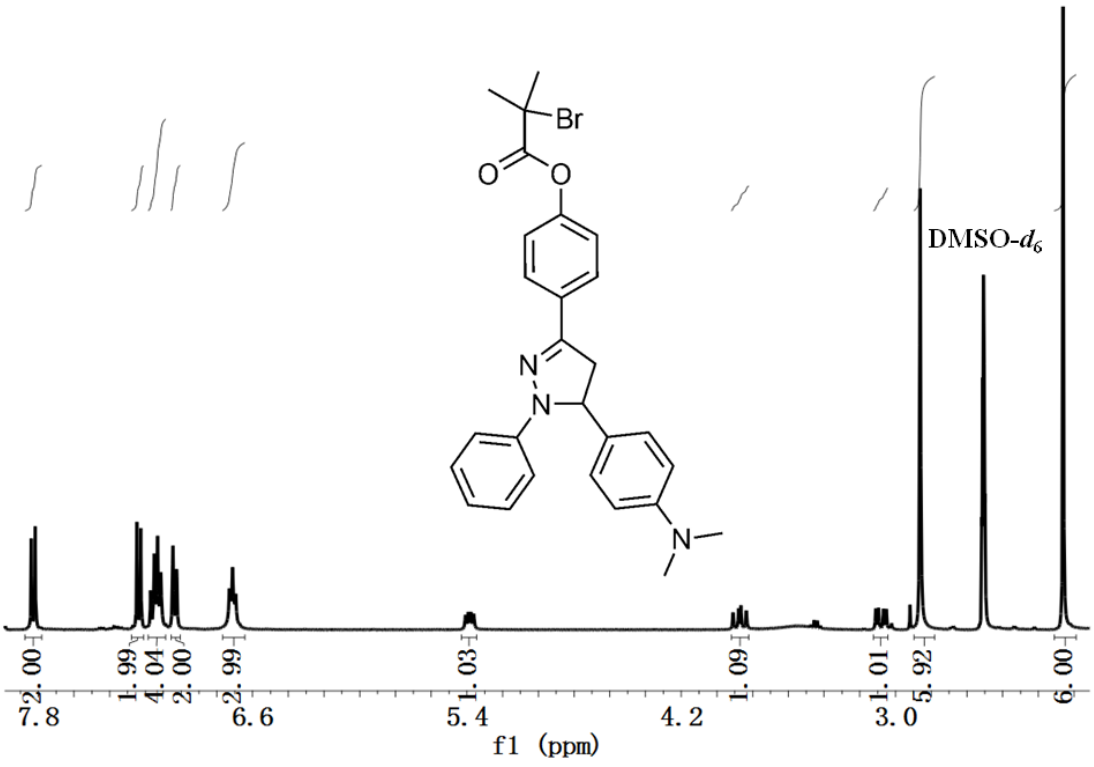


Figure S4 ^{1}H NMR spectrum of TPP-A in DMSO-d_6.

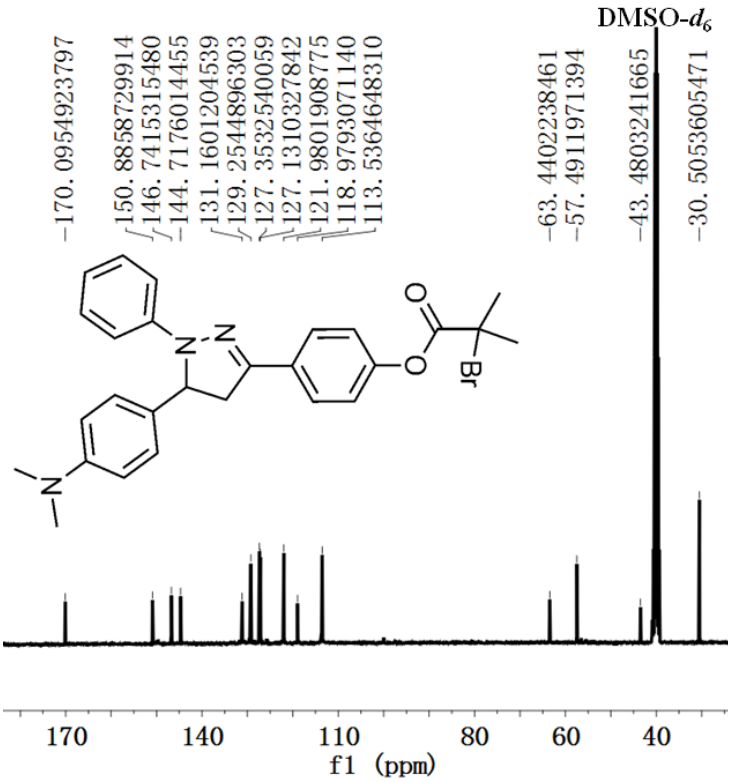


Figure S5 ^{13}C NMR spectrum of TPP-A in DMSO-d_6.

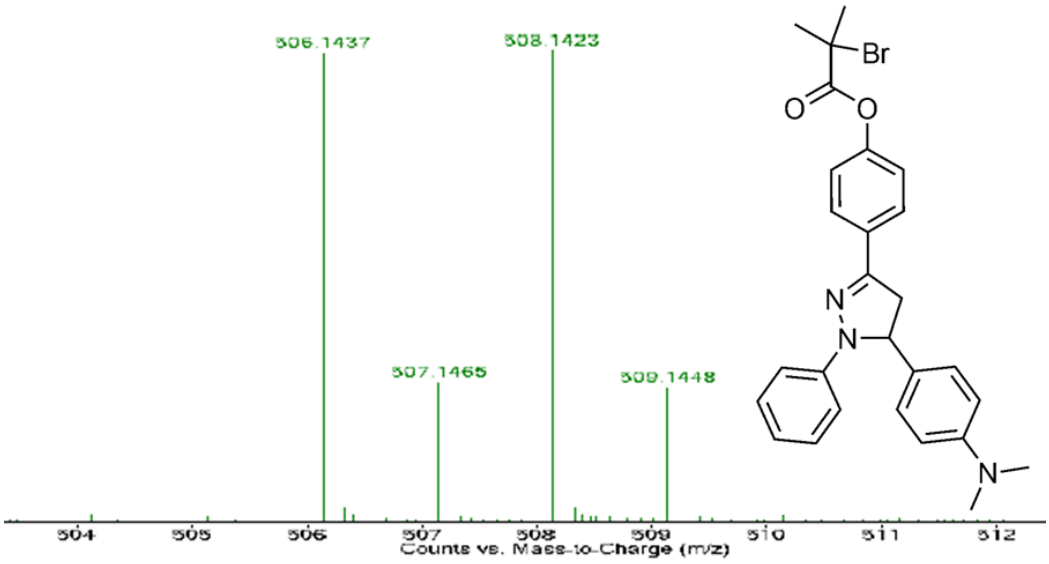


Figure S6 HR-MS spectrum of TPP-A

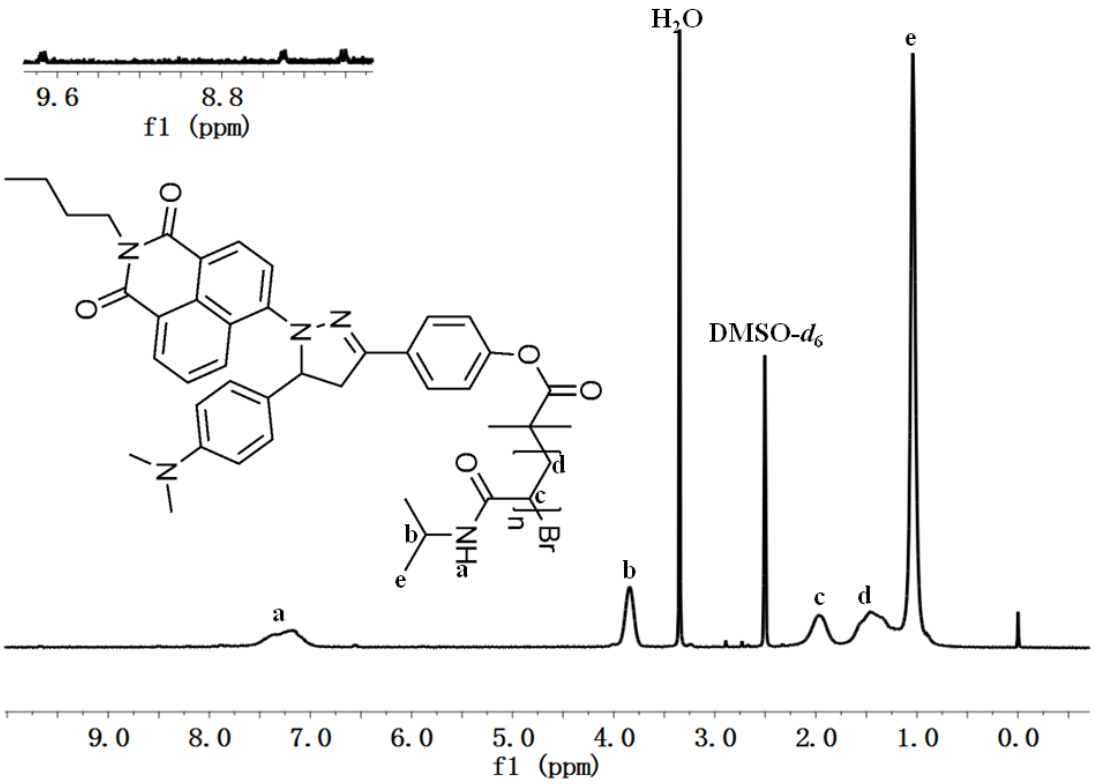


Figure S7 ^{1}H NMR spectrum of PNIPAM-NI in DMSO-d_6.

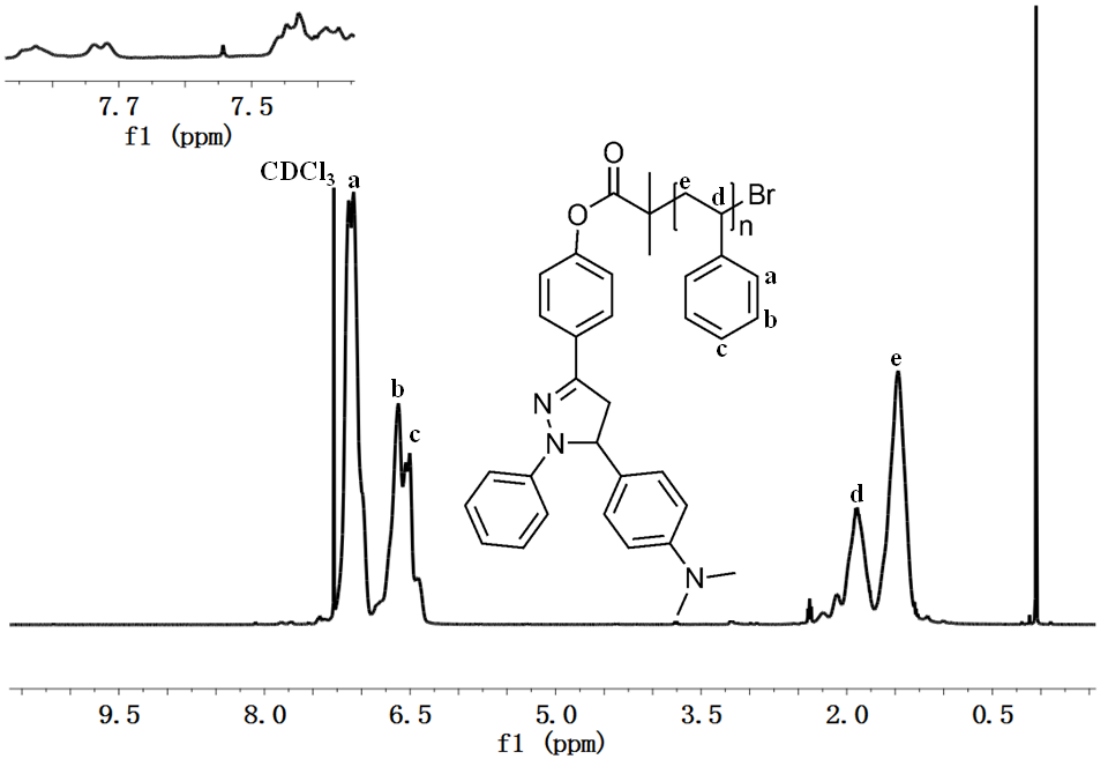


Figure S8 ^{1}H NMR spectrum of PS-A in $CDCl_3$.

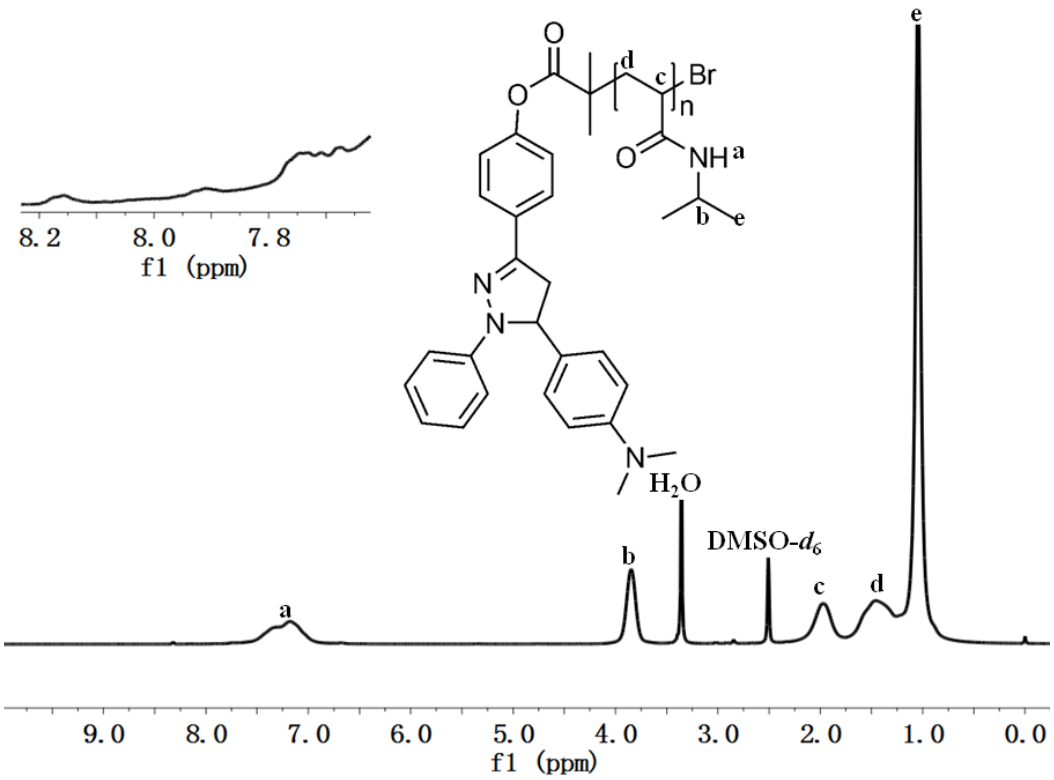


Figure S9 ^{1}H NMR spectrum of PNIPAM-A in DMSO-d_6.

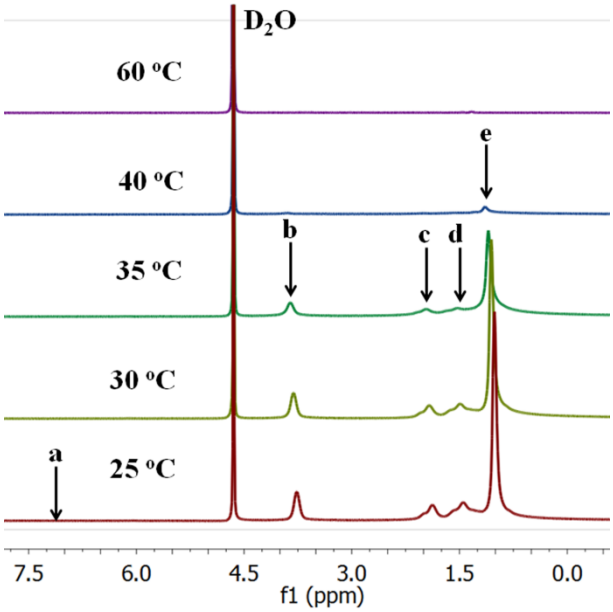


Figure S10 ^{1}H NMR spectra of PNIPAM-NI were taken in D_2O at various temperatures.

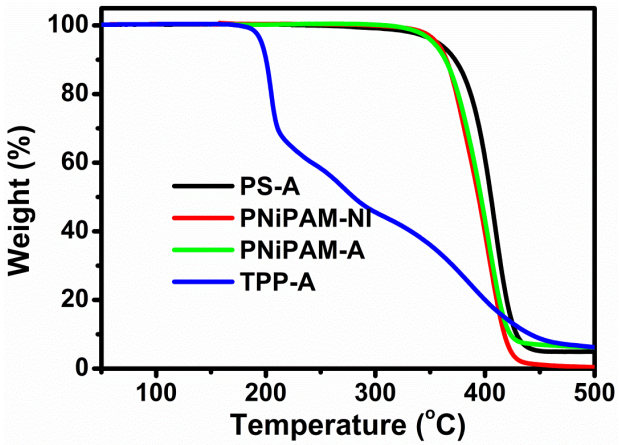


Figure S11 TGA thermograms of initiator and their polymers, recorded under N_2 at a heating rate of 20 ^oC min^{-1}.

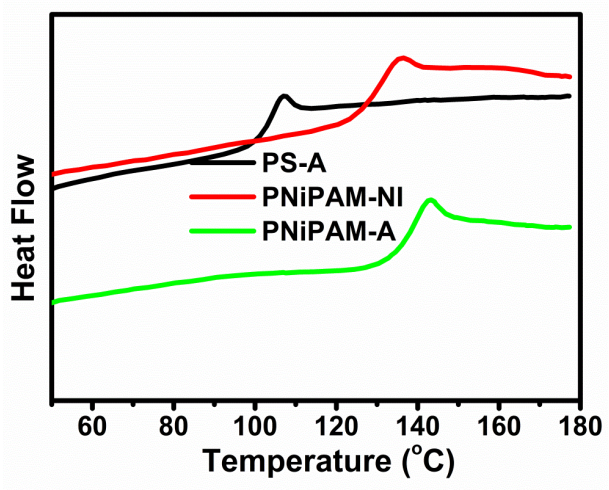


Figure S12 DSC thermograms of polymers, recorded under N_2 at a heating rate of 10 ^oC min^{-1}.

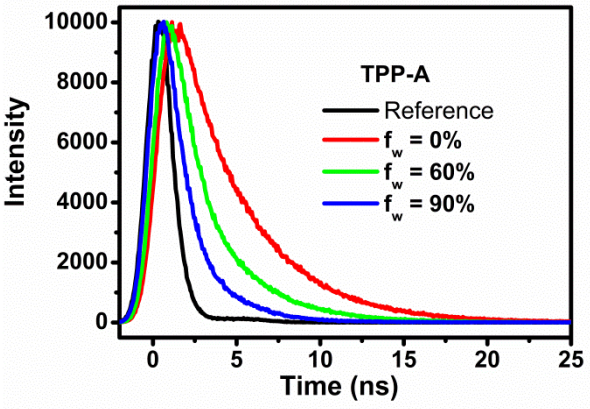


Figure S13 Typical fluorescence decay curves associated with lamp profile for TPP-A in DMF/water mixture. Excitation wavelength is constant at 371 nm.

Table S1 Fluorescence decays of excited states of the TPP-A in DMF/water mixture.

Solvent	TPP-A			
DMF/water	$A_1/A_2/A_3$ (%)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
f_w = 0%	4.18/5.73/90.09	0.26	1.93	3.99
f_w = 60%	16.29/31.22/52.49	0.10	1.18	3.36
f_w = 90%	49.82/47.44/2.75	0.09	1.64	7.18

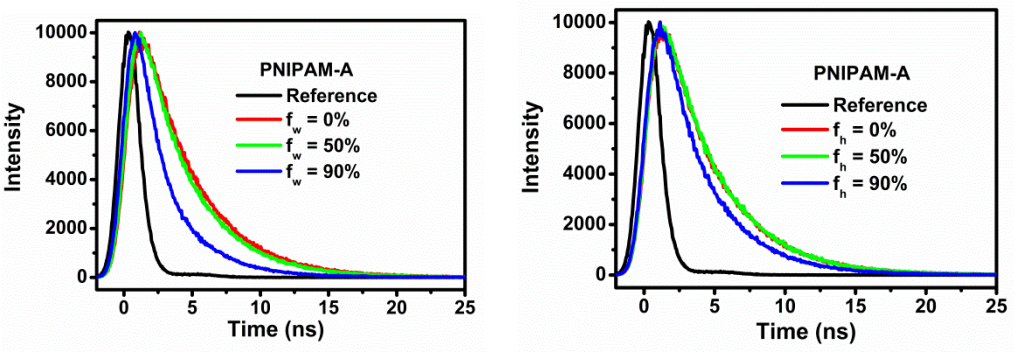


Figure S14 Typical fluorescence decay curves associated with lamp profile for PNIPAM-A in THF/water mixture (left) and THF/hexane mixture (right). Excitation wavelength is constant at 371 nm.

Table S2 Fluorescence decays of excited states of the PNIPAM-A in THF/water mixture.

Solvent	PNIPAM-A			
THF/water	$A_1/A_2/A_3$ (%)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
f_w = 0%	7.73/92.27/0	0.08	3.71	0
f_w = 50%	15.15/84.85/0	1.64	3.75	0
f_w = 90%	25.27/38.18/36.55	0.07	1.55	3.59

Table S3 Fluorescence decays of excited states of the PNIPAM-A in THF/hexane mixture.

Solvent	PNIPAM-A			
THF/hexane	$A_1/A_2/A_3$ (%)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
f_h = 0%	7.73/92.27/0	0.08	3.71	0
f_h = 50%	7.48/92.52/0	1.77	3.82	0
f_h = 90%	13.69/86.31/0	1.36	4.23	0

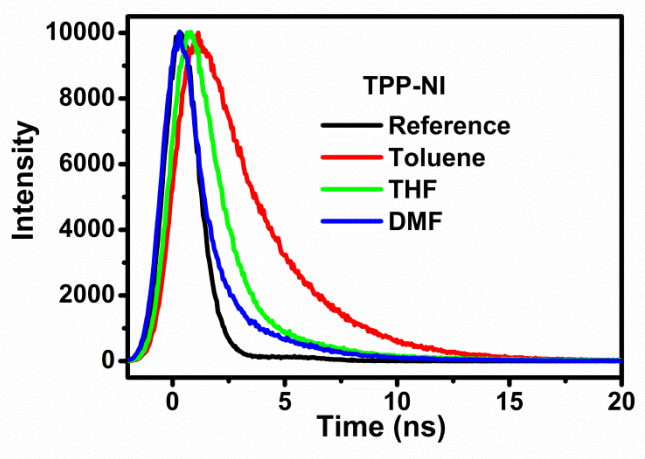


Figure S15 Typical fluorescence decay curves associated with lamp profile for TPP-NI in different solvents. Excitation wavelength is constant at 371 nm.

Table S4 Fluorescence decays of excited states of the TPP-NI in different solvents.

Solvent	TPP-NI			
	$A_1/A_2/A_3$ (%)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
Toluene	17.03/82.13/0.84	0.04	2.84	5.30
THF	37.48/51.94/10.59	0.06	1.19	5.43
DMF	70.08/24.72/5.20	0.07	1.93	5.49

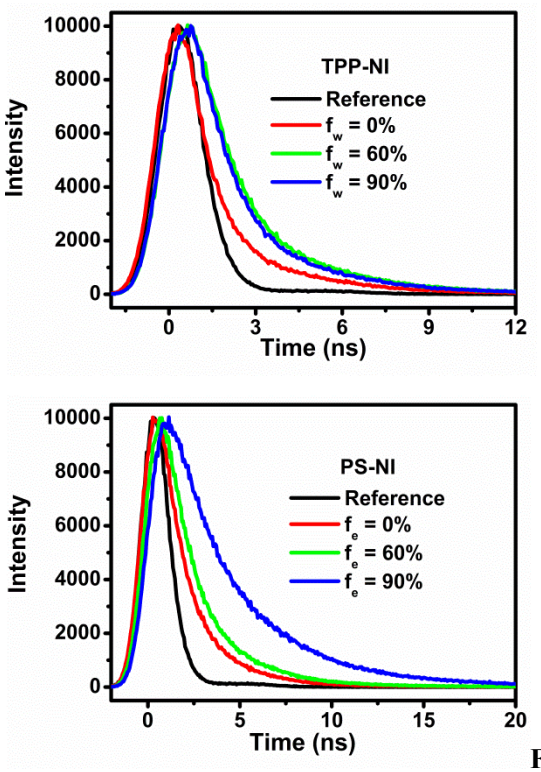


Figure S16 Typical fluorescence decay curves associated with lamp profile for TPP-NI in DMF/water mixture and PS-NI in DMF/ethanol mixture. Excitation wavelength is constant at 371 nm.

Table S5 Fluorescence decays of excited states of the TPP-NI in DMF/water mixture.

Solvent	TPP-NI			
DMF/water	$A_1/A_2/A_3$ (%)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
f_w = 0%	70.08/24.72/5.20	0.07	1.93	5.49
f_w = 60%	44.72/38.61/16.67	0.07	1.58	3.88
f_w = 90%	48.69/38.48/12.83	0.07	1.60	4.34

Table S6 Fluorescence decays of excited states of the PS-NI in DMF/ethanol mixture.

Solvent	PS-NI			
DMF/ethanol	$A_1/A_2/A_3$ (%)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
f_e = 0%	53.18/43.41/3.40	0.06	1.69	8.15

f_e = 60%	50.49/41.09/8.42	0.04	1.75	4.78
f_e = 90%	13.03/76.54/10.42	0.77	3.53	9.09

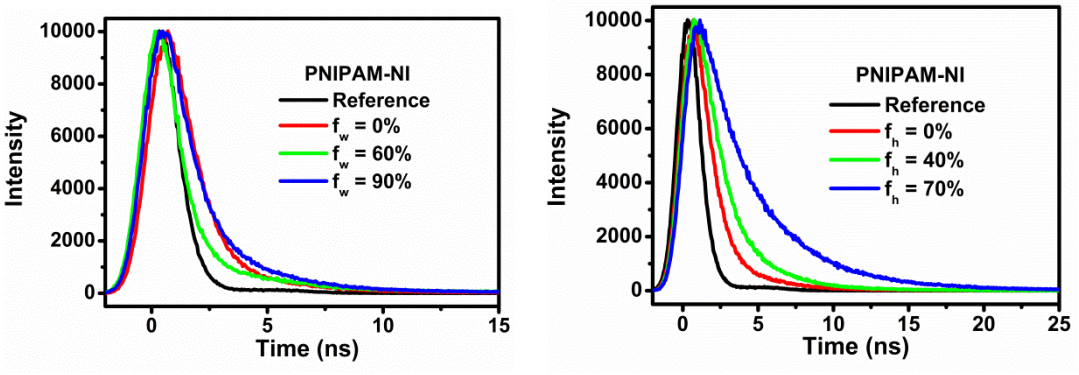


Figure S17 Typical fluorescence decay curves associated with lamp profile for PNIPAM-NI in THF/water mixture (left) and THF/hexane mixture (right). Excitation wavelength is constant at 371 nm.

Table S7 Fluorescence decays of excited states of the PNIPAM-NI in THF/water mixture.

Solvent	PNIPAM-NI			
THF/water	$A_1/A_2/A_3$ (%)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
f_w = 0%	37.88/54.51/7.61	0.09	1.06	4.88
f_w = 60%	72.59/21.68/5.72	0.18	2.84	27.5
f_w = 90%	52.91/42.95/4.14	0.47	2.27	22

Table S8 Fluorescence decays of excited states of the PNIPAM-NI in THF/hexane mixture.

Solvent	PNIPAM-NI				
THF/hexane	$A_1/A_2/A_3/A_4$ (%)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)
f_h = 0%	37.88/54.51/7.61/0	0.09	1.06	4.88	0
f_h = 40%	30.20/54.71/14.32/0.77	0.05	1.46	3.74	12.03

f_h = 70%	39.60/60.40/0/0	1.93	4.78	0	0

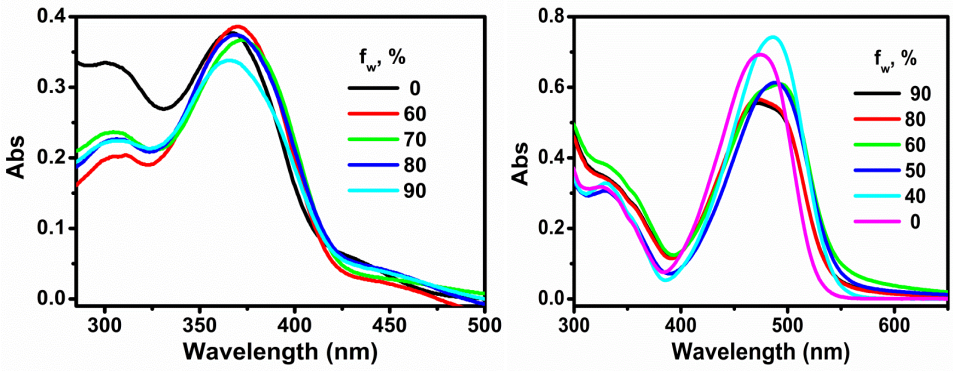


Figure S18 Absorption spectra of TPP-A (left) and TPP-NI (right) with the composition of the DMF/water mixture (Concentration: 25 μM).

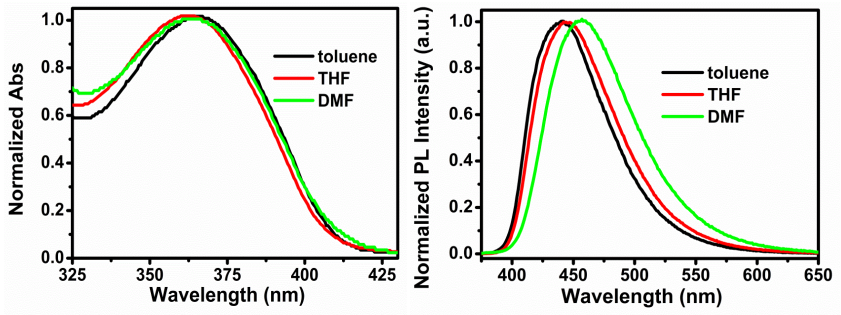


Figure S19 Normalized absorption and emission spectra of PS-A in different solvents ($\lambda_{ex} = \lambda_{abs}$, respectively, Concentration: 5 μM).

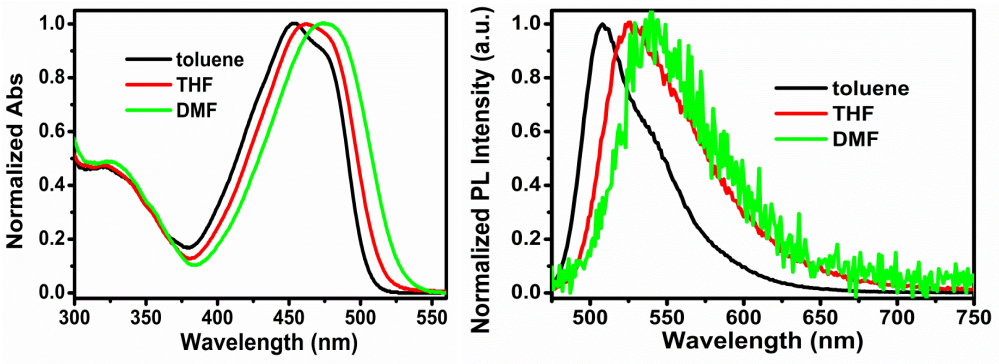


Figure S20 Normalized absorption and emission spectra of PS-NI in different solvents ($\lambda_{ex} = \lambda_{abs}$, respectively, Concentration: 5 μM).

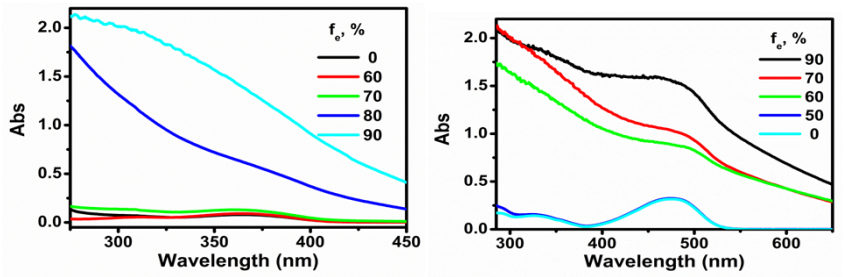


Figure S21 Absorption spectra of PS-A (left) and PS-NI (right) with the composition of the DMF/ethanol mixture (Concentration: 5 μM).

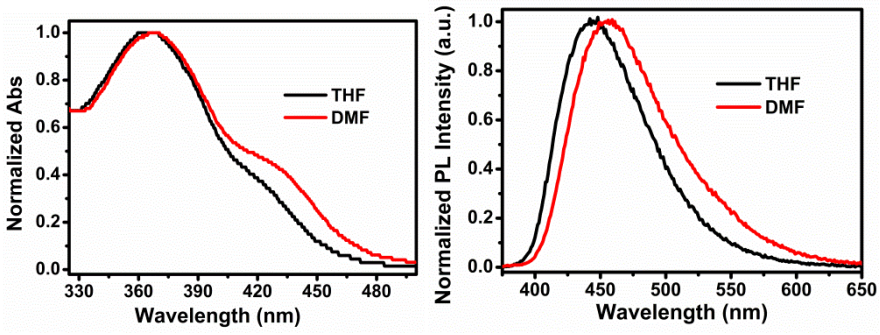


Figure S22 Normalized absorption and emission spectra of PNIPAM-A in different solvents (λ_{ex} = λ_{abs}, respectively, Concentration: 5 μM).

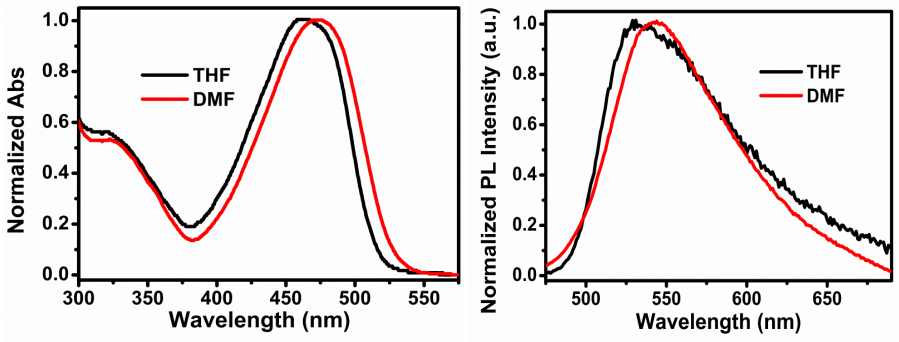


Figure S23 Normalized absorption and emission spectra of PNIPAM-NI in different solvents (λ_{ex} = λ_{abs}, respectively, Concentration: 5 μM).

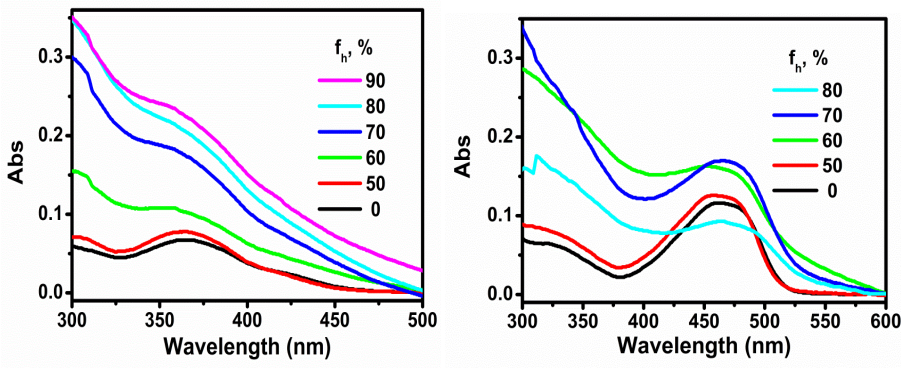


Figure S24 Absorption spectra of PNIPAM-A (left) and PNIPAM-NI (right) with the composition of the THF/hexane mixture (Concentration: 5 μM).

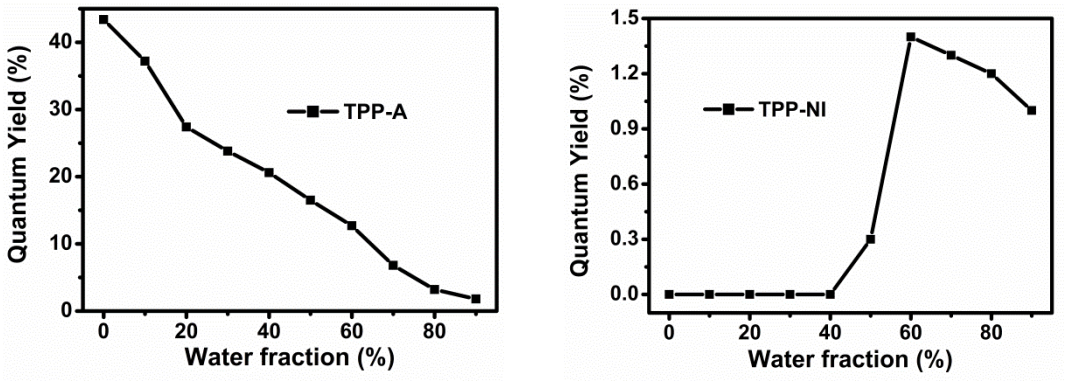


Figure S25 Change in QYs of TPP-A (left) and TPP-NI (right) in the DMF/water mixture (Concentration: 5 μM).

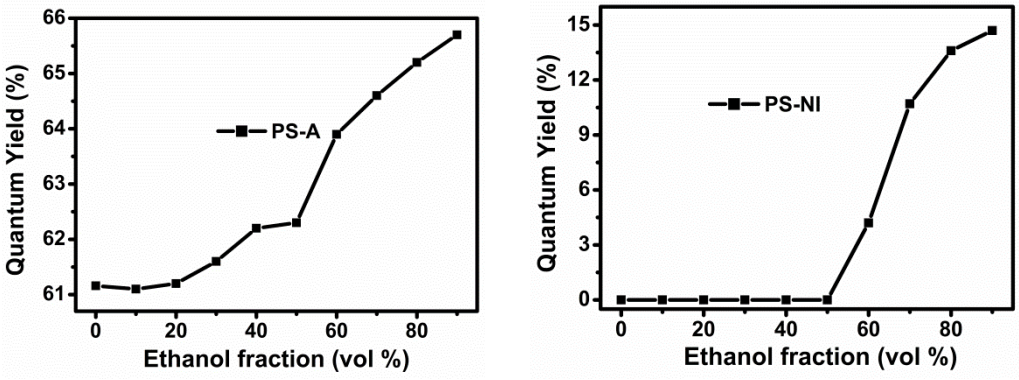


Figure S26 Change in QYs of PS-A (left) and PS-NI (right) in the DMF/ethanol mixture (Concentration: 5 μM).

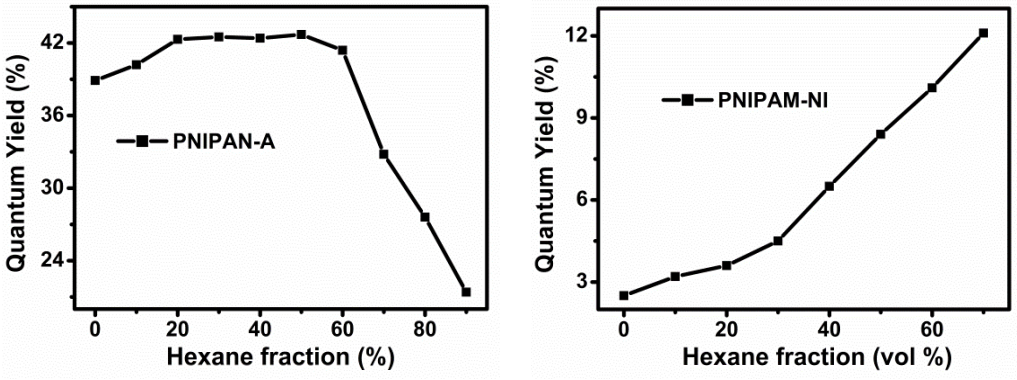


Figure S27 Change in QYs of PNIPAM-A (left) and PNIPAM-NI (right) in the THF/hexane mixture (Concentration: 5 μM).

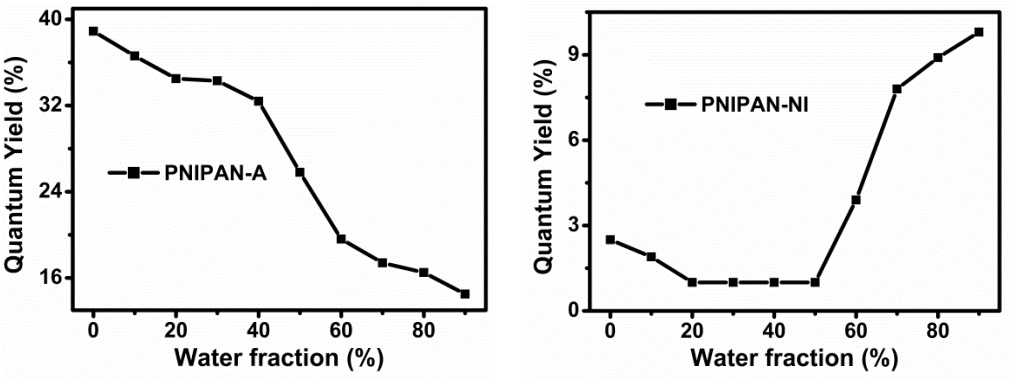


Figure S28 Change in QYs of PNIPAM-A (left) and PNIPAM-NI (right) in the THF/water mixture (Concentration: 5 μM).

Using the calibration curve drawn from the UV absorption data (Fig.ure S29), the degrees of labelling in PS-A, PNIPAM-A, PS-NI and PNIPAM-A are determined to be 1.29 wt%, 0.99 wt%, 4.14 wt% and 1.73 wt%, respectively.

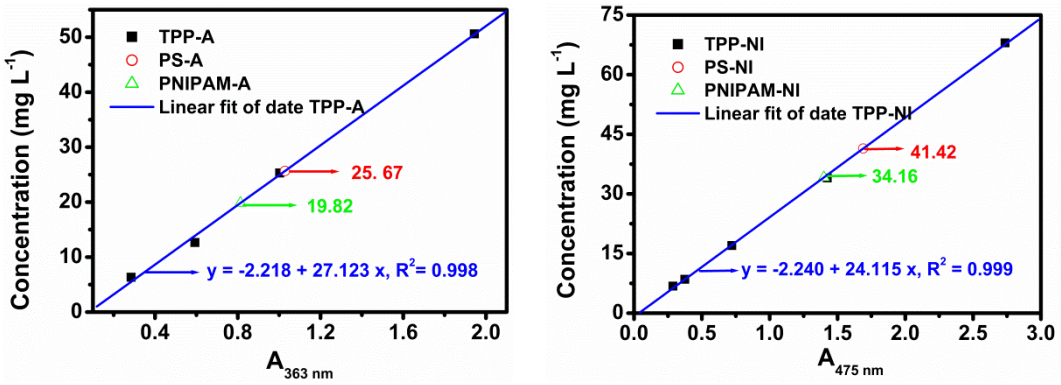


Figure S29 Calibration curve for determining the percentage of TPP-A or TPP-NI in polymers, using TPP-A or TPP-NI as standard.

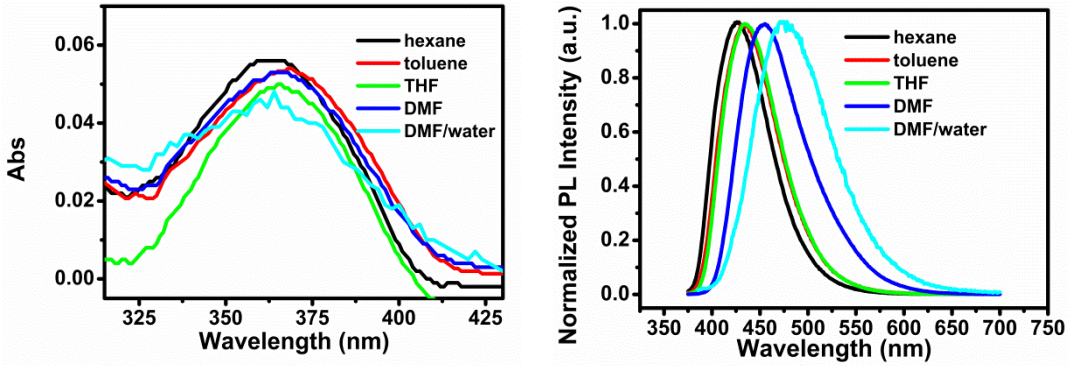


Figure S30 Absorption (left) and normalized emission (right) spectra of TPP-A (the dye concentration: 2.5 μM) in different solvents (DMF/water = 1:9 by volume).

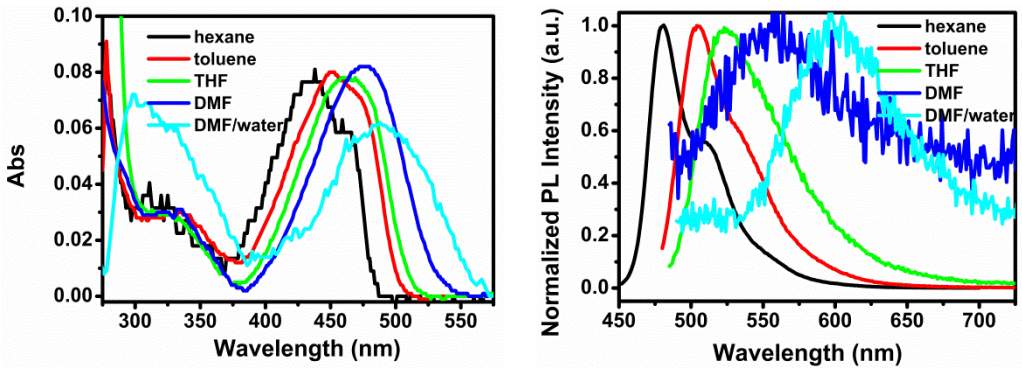


Figure S31 Absorption (left) and normalized emission (right) spectra of TPP-NI (the dye concentration: 2.0 μM) in different solvents (DMF/water = 1:9 by volume).

Table S9 Photophysical data for TPP-A and TPP-NI

	TPP-A[a]			TPP-NI[f]		
State	λ_{abs}[b]	λ_{em}[c]	QY[d]	λ_{abs}	λ_{em}	QY
Hexane	363	428	26.4	437, 461	480, 510	54.6
Toluene	365	434	32.7	451	504	26.5
THF	363	434	30.1	460	523	6.2
DMF	363	453	43.9	475	557	0.28
DMF/water[e]	363	478	38.8	485	598	0.83

[a] The dye concentration is 2.5 uM. [b]The absorption wavelength (nm). [c] The emission wavelength (nm). [d] Fluorescence quantum yield (%). [e]DMF/water = 1: 9, by volume. [f] The dye concentration is 2 uM.

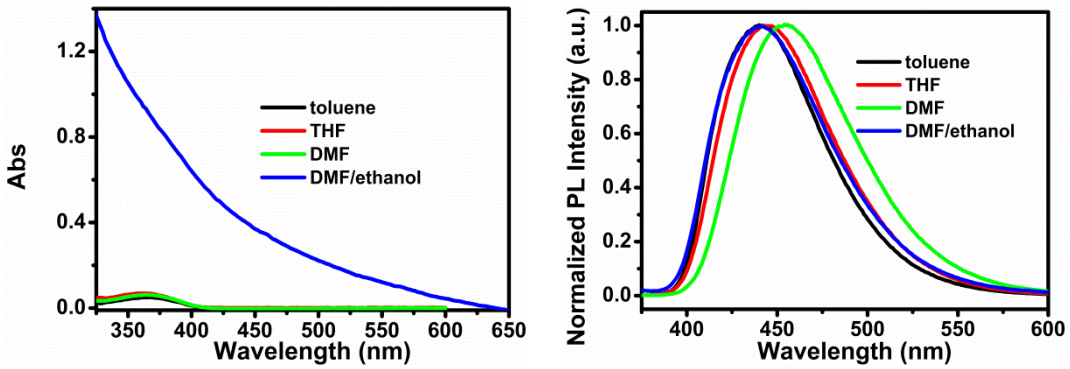


Figure S32 Absorption (left) and normalized emission (right) spectra of PS-A (the dye concentration: 2.5 μM) in different solvents (DMF/ethanol = 1:9 by volume).

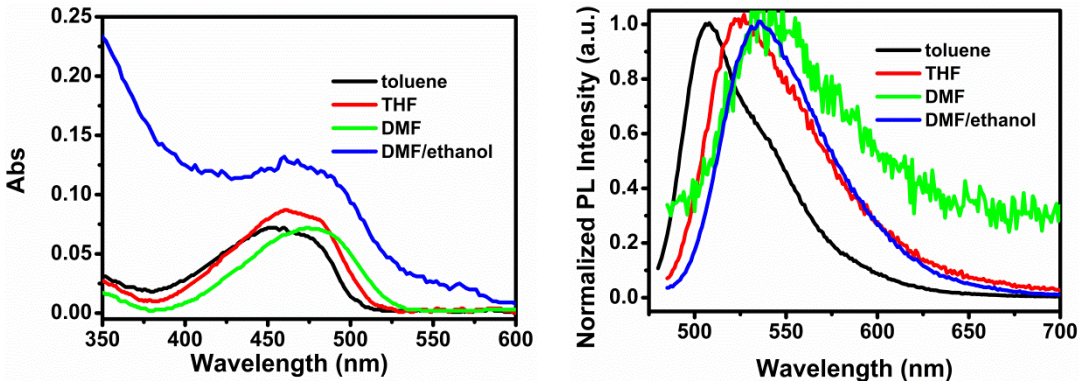


Figure S33 Absorption (left) and normalized emission (right) spectra of PS-NI (the dye concentration: 2.0 μM) in different solvents (DMF/ethanol = 1:9 by volume).

Table S10 Photophysical data for PS-A and PS-NI

	PS-A[a]			PS-NI[f]		
State	λ_{abs}[b]	λ_{em}[c]	QY[d]	λ_{abs}	λ_{em}	QY
Toluene	365	440	56.3	456	508	30.0
THF	365	442	59.7	463	526	5.0
DMF	365	457	63.4	475	539	0.6
DMF/ethanol[e]	369	440	72.1	477	537	15.7

[a] The dye concentration is 2.5 uM. [b]The absorption wavelength (nm). [c] The emission wavelength (nm). [d] Fluorescence quantum yield (%). [e] DMF/ethanol = 1: 9, by volume. [f] The dye concentration is 2 uM.

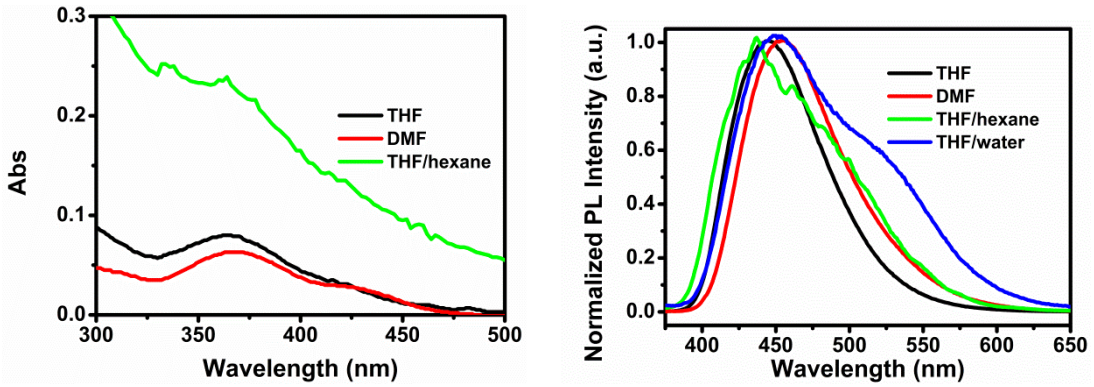


Figure S34 Absorption (left) and normalized emission (right) spectra of PNIPAM-A (the dye concentration: 2.5 μM) in different solvents (THF/water or THF/hexane = 1:9 by volume).

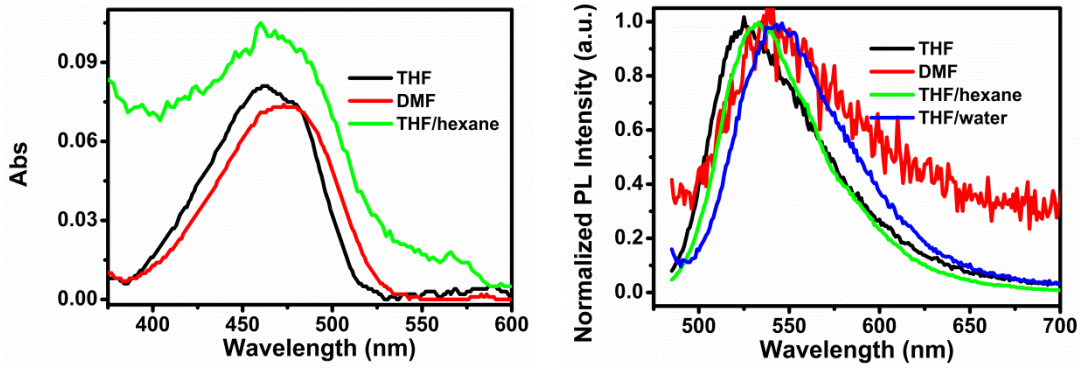


Figure S35 Absorption (left) and normalized emission (right) spectra of PNIPAM-NI (the dye concentration: 2.0 μM) in different solvents (THF/water or THF/hexane = 1:9 by volume).

Table S11 Photophysical data for PNIPAM-A and PNIPAM-NI

	PNIPAM-A[a]			PNIPAM-NI[g]		
State	λ_{abs}[b]	λ_{em}[c]	QY[d]	λ_{abs}	λ_{em}	QY
THF	365	444	39.8	466	529	4.6
DMF	366	455	57.8	471	544	0.5
THF/hexane[e]	366	437	24.3	463	533	18.4
THF/water[f]	367	450	15.3	465	546	5.4

[a] *The dye concentration is 2.5 uM.* [b] The absorption wavelength (nm). [c] The emission wavelength (nm).[d] Fluorescence quantum yield (%). [e] THF/hexane = 1: 9 by volume.[f] THF/water = 1: 9, by volume. [g] The dye concentration is 2 uM.

1 P. Y. Gu, C. J. Lu, F. L. Ye, J. F. Ge, Q. F. Xu, Z. J. Hu, N. J. Li and J. M. Lu, *Chem. Commun.*, 2012, **48**, 10234.