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SUPPORTING INFORMATION

Fluorescent Strategy for Direct Quantification of Arm Component in Mikto-Arm Star Copolymers

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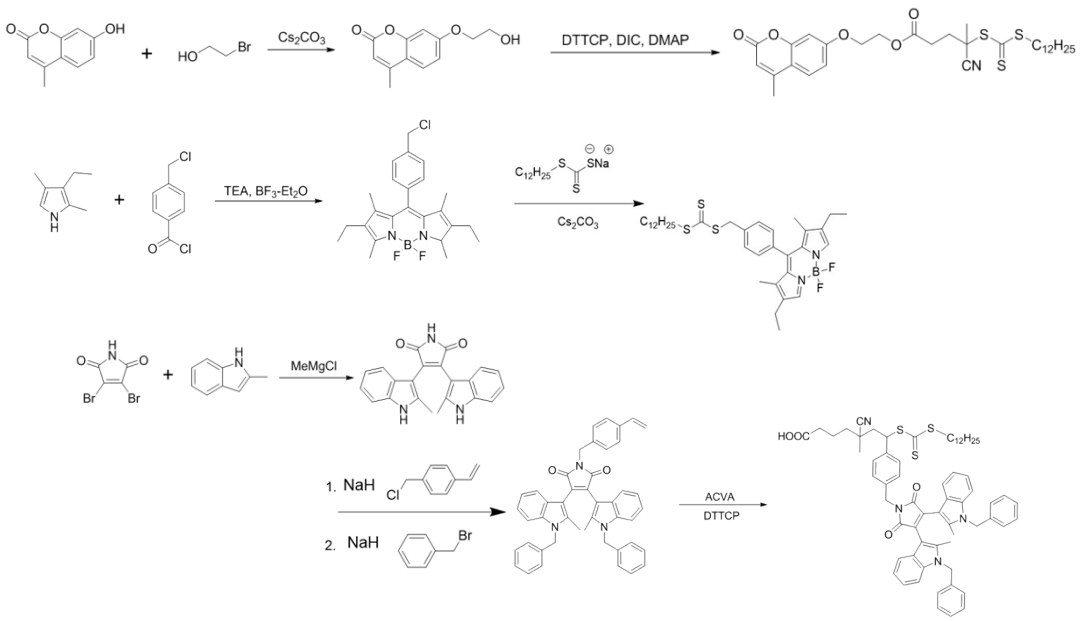

Figure S1 Synthetic routes of Fluorescent RAFT agents.

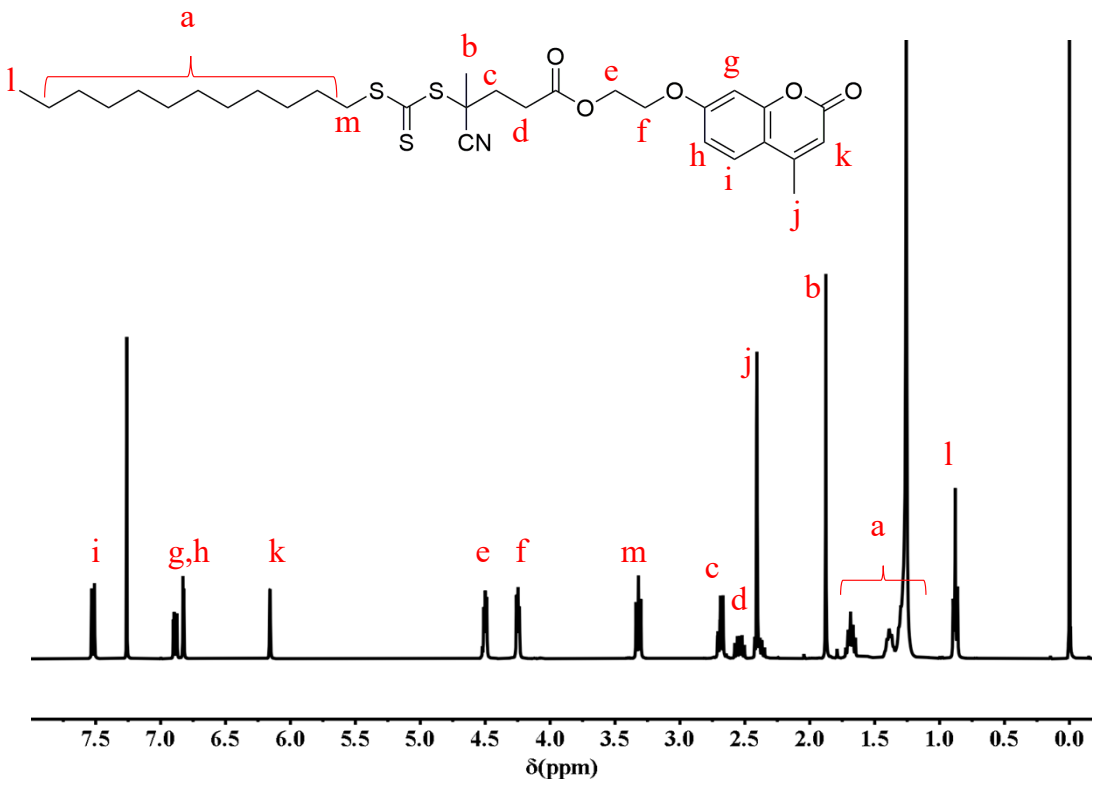

Figure S2 ^{1}H NMR spectrum of Coumarin-CTA RAFT agent (solvent: C*D*Cl$_3$).

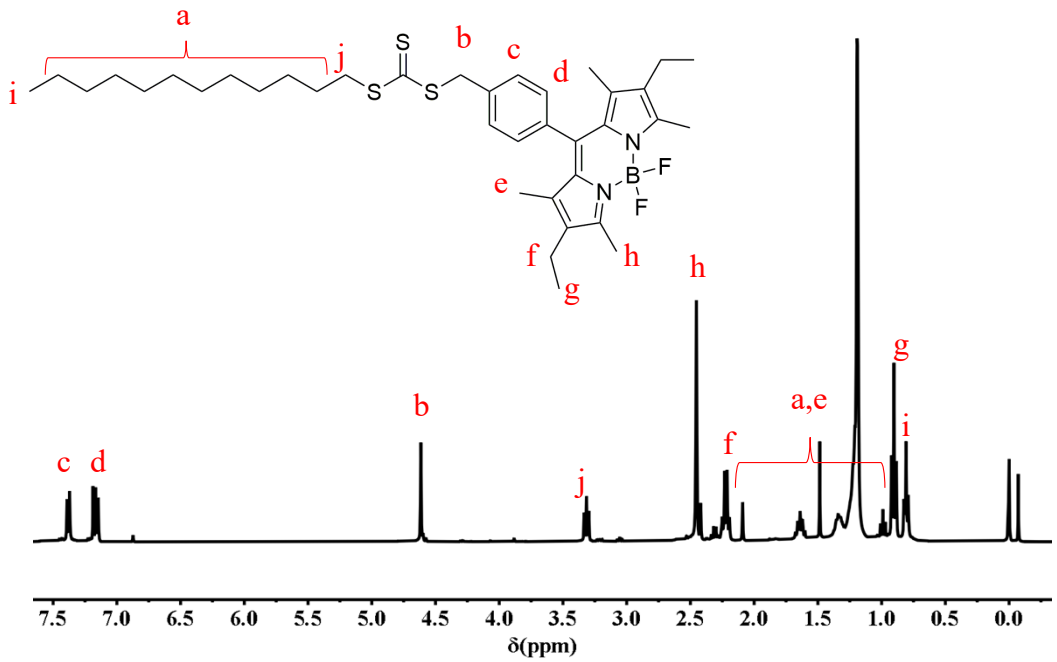

Figure S3 ^{1}H NMR spectrum of BODIPY-CTA RAFT agent (solvent: C*D*Cl$_3$).

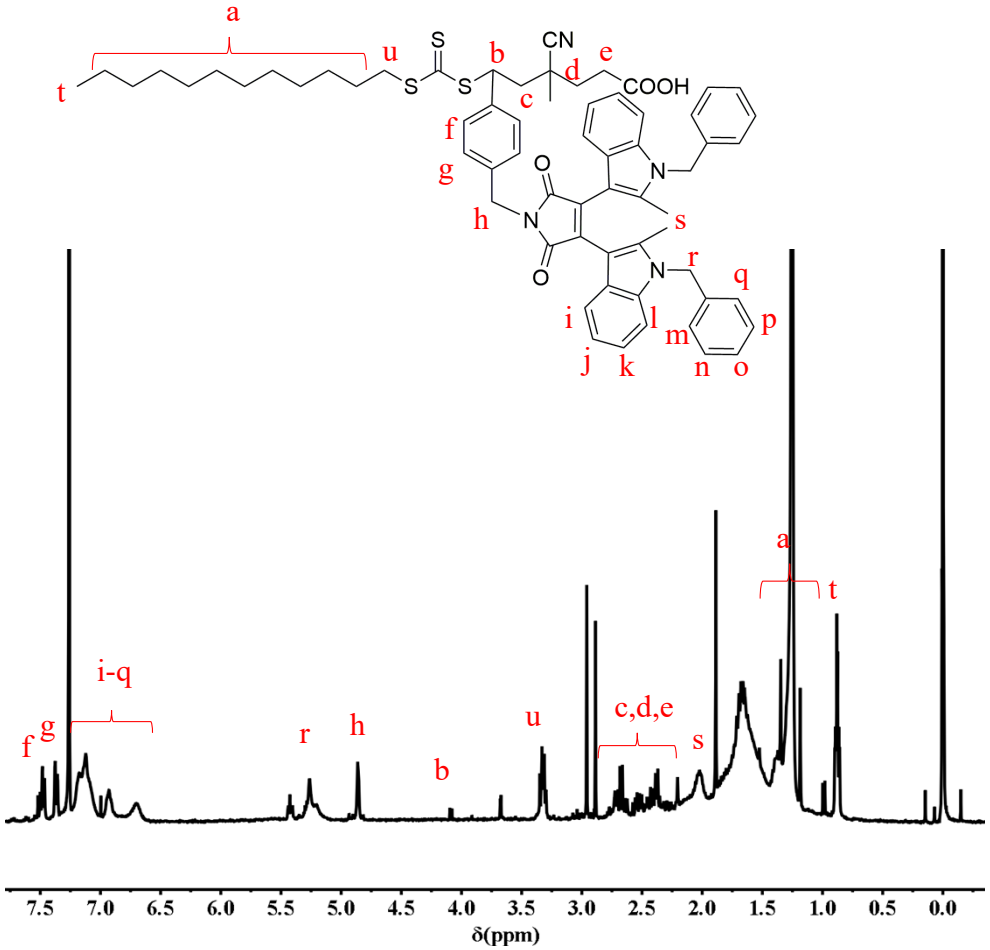

Figure S4 ^{1}H NMR spectrum of BIM-CTA RAFT agent (solvent: C*D*Cl$_3$).

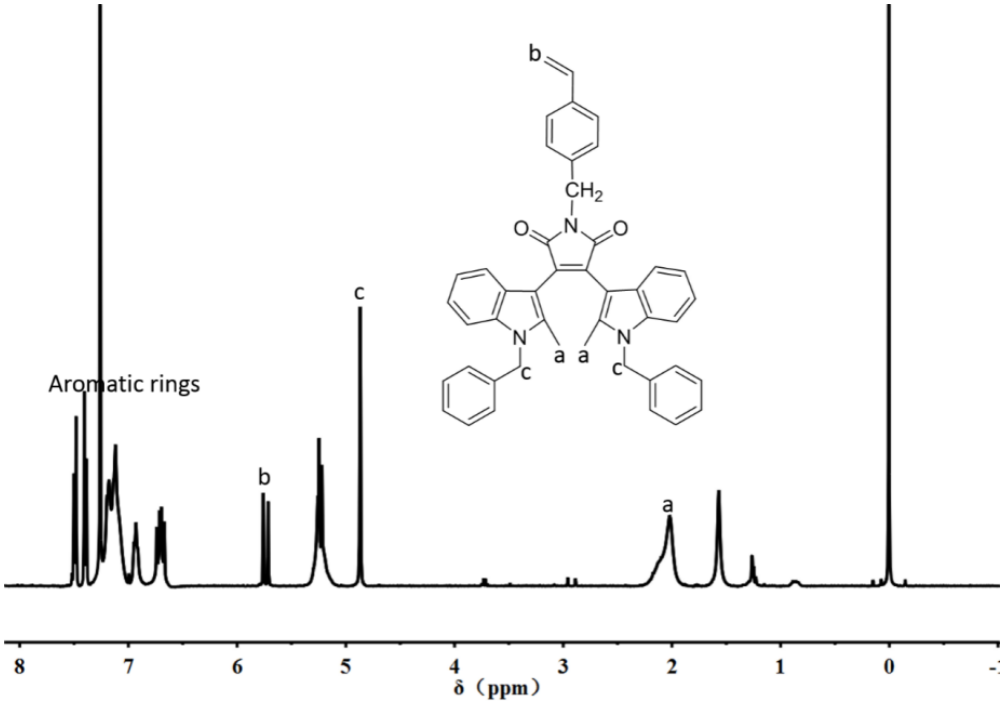

Figure S5 ^{1}H NMR of the spectrum of bisindolylmaleimide functionalized monomer (solvent: C*D*Cl$_3$).

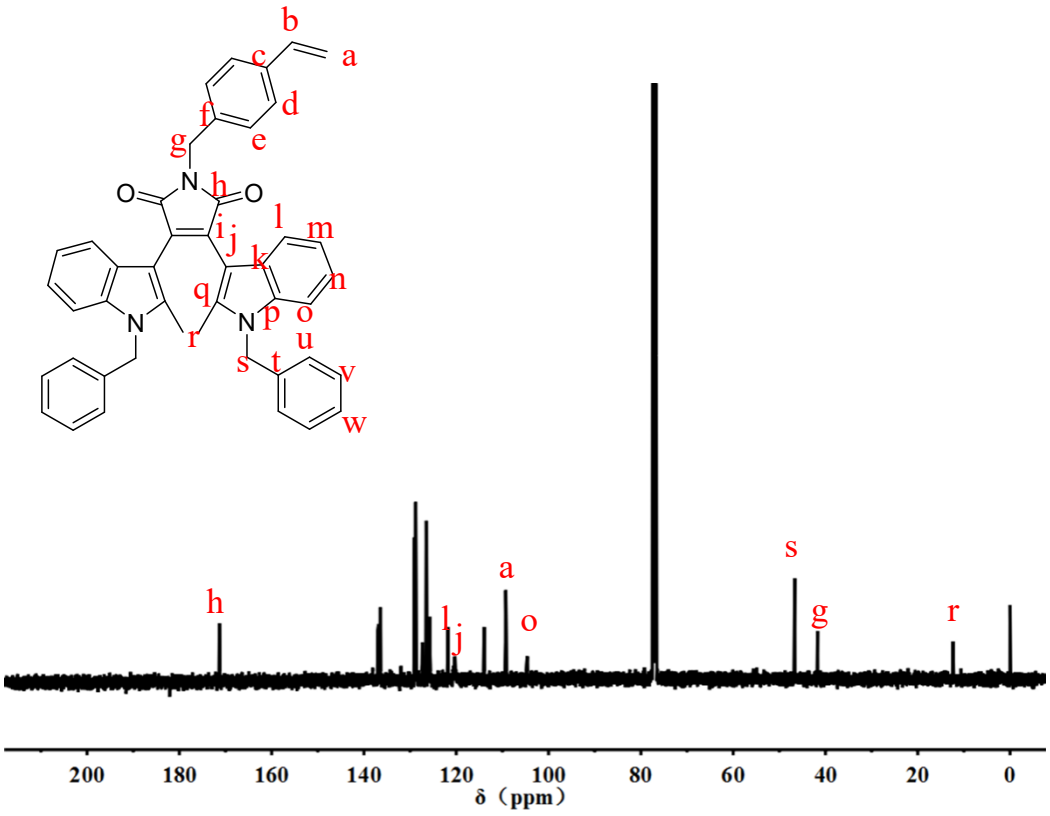

Figure S6 ^{13}C NMR spectrum of bisindolylmaleimide functionalized monomer (solvent: C*D*Cl$_3$).

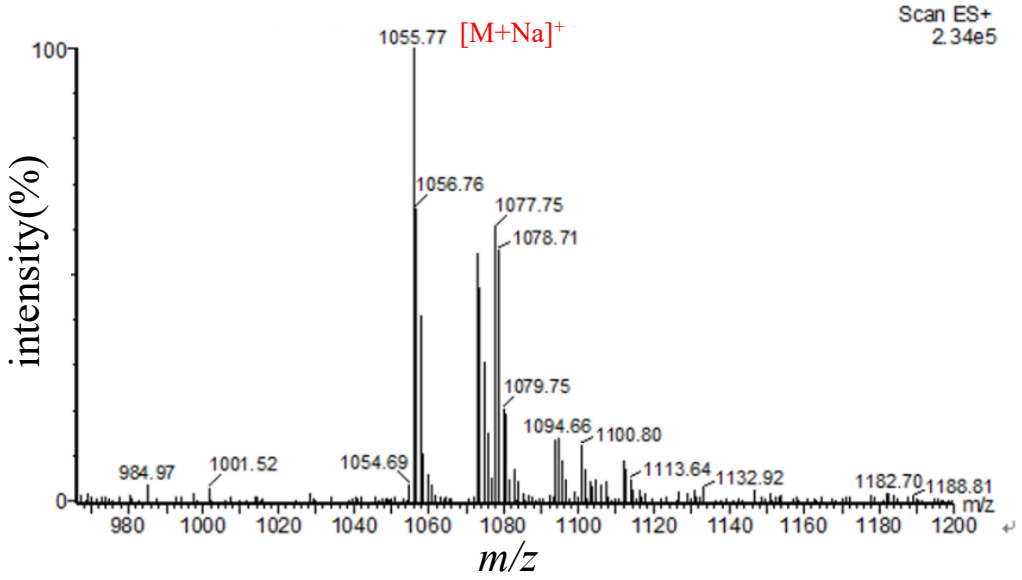

Figure S7 ESI-MS spectrum of bisindolylmaleimide functionalized RAFT agent in positive ion mode in acetonitrile. MS [M + Na^+] calcd as 1055.47; found as 1055.77.

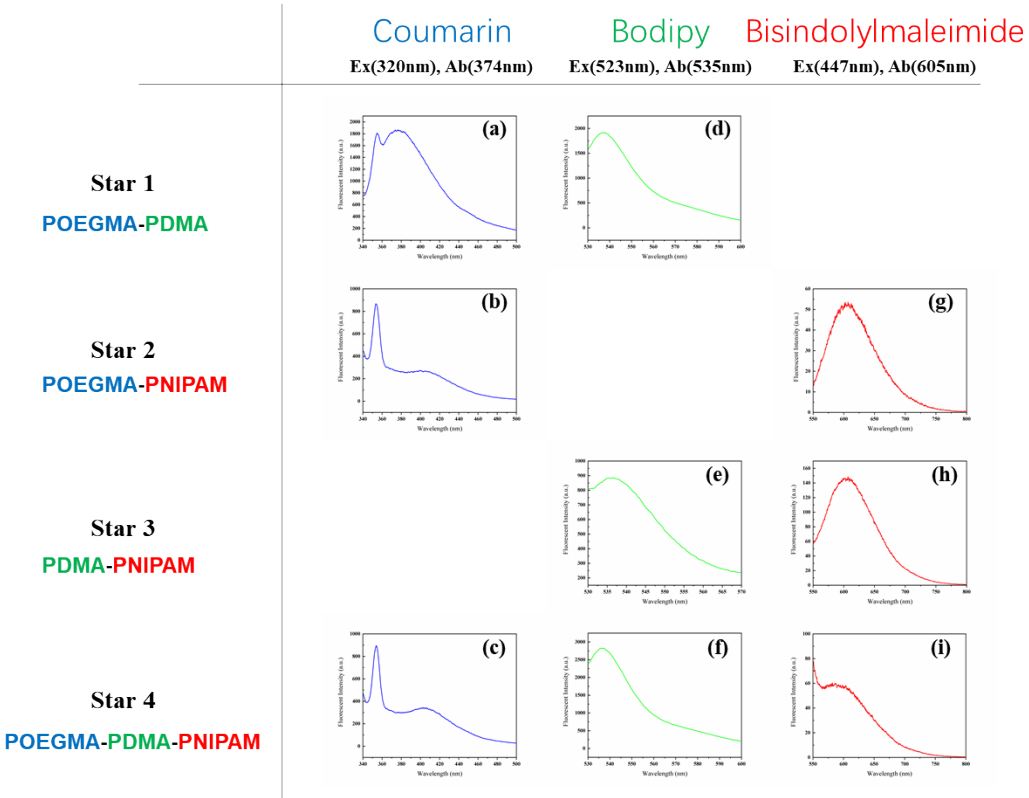

Figure S8 Fluorescence emission spectra and peak fluorescent absorption intensity of the mikto-arm star polymers. The stars were treated with the given excitation wavelength and monitored the specific absoption wavelength with respect to the arm components. (a), (b), (c) Coumarin labeled in POEGMA (excited at 320 nm, show peaks at 374 nm). (d), (e), (f) Bodipy labeled PDMA (excited at 523 nm, show peaks at 535 nm). (g), (h), (i) Bisindolylmaleimide labeled PNIPAM (excited at 447 nm, show peaks at 605 nm).

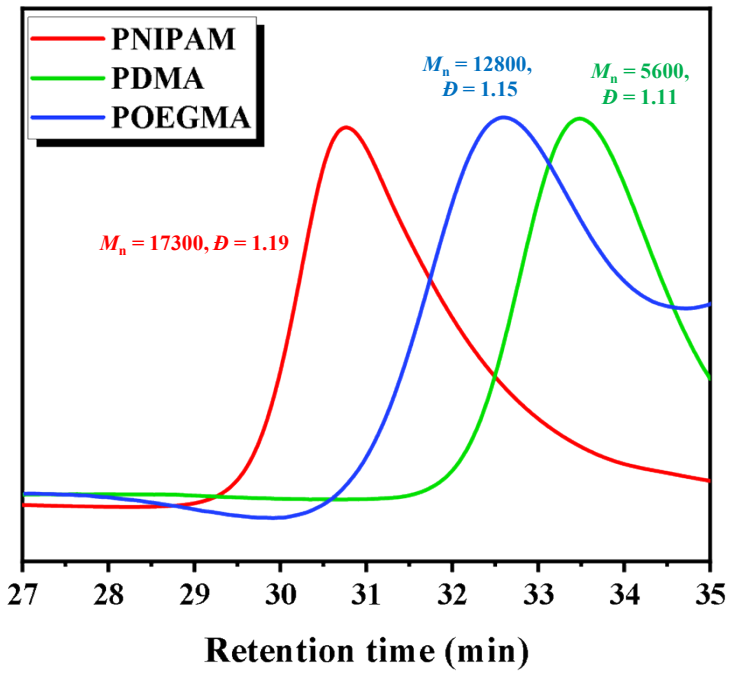

Figure S9 SEC traces with refractive index detection for POEGMA (M_n = 12800, $Đ$ = 1.15) (blue line), PDMA (M_n = 5600, $Đ$ = 1.11) (green line) and PNIPAM (M_n = 17300, $Đ$ = 1.19).

Table S1 The molar amounts of components in polymerization mixtures used for mikto-arm copolymers syntheses.

Entry	Total DMF/mL	POEGMA (10^{-6}mol)	OEGMA (10^{-6} mol)	PDMA (10^{-6} mol)	DMA (10^{-6} mol)	PNIPAM (10^{-6} mol)	NIPAM (10^{-6} mol)	PEGD (10^{-6} mol)	ACCN (10^{-6} mol)
Star 1	0.6	3	18	3	18	0	0	72	2
Star 2	0.6	3	18	0	0	3	18	72	2
Star 3	0.6	0	0	3	18	3	18	72	2
Star 4	0.6	3	18	3	18	3	18	108	3

Table S2 Concentration of components in polymerization mixtures used for mikto-arm copolymers syntheses.

Entry	Total DMF/ml	POEGMA (mmol/L)	OEGMA (mmol/L)	PDMA (mmol/L)	DMA (mmol/L)	PNIPAM (mmol/L)	NIPAM (mmol/L)	PEGD (mmol/L)	ACCN (mmol/L)
Star 1	0.6	5	30	5	30	0	0	120	3.3
Star 2	0.6	5	30	0	0	5	30	120	3.3
Star 3	0.6	0	0	5	30	5	30	120	3.3
Star 4	0.6	5	30	5	30	5	30	180	5.0

As mentioned before, multiple peaks of one polymer were used in case for overlapping.

Table S3 Quantification reference via ^{1}H NMR. **I** stands for the integration for corresponding peaks. **r** is the calculation criterion.

Entry	ref.	POEGMA δ 4.11, s, 2H	POEGMA δ 3.61-3.80, m, 16H	δ 3.58, s, 3H	PDMA δ 3.22-2.79, m, 6H	PNIPAM δ 1.17, s, 6H
Star1	I	4.04			12.75	
	r	0.052345167			0.040291998	
Star2	I		56.82			66.49
	r		0.092360208			0.073877778
Star3	I				0.93	5.36
	r				0.002938946	0.005955556
Star4	I			3.18	14.31	80.62
	r			0.027468256	0.045221843	0.089577778

$$r = \frac{I}{n_H \times DP}$$

DP is the polymerization degree of the polymer, n_H is the number of hydrogen at the corresponding peak location. Ratio of **r** stands for the ratio of polymer. Calculated DP for POEGMA, PDMA, PNIPAM are 38.59, 52.74 and 150 (via ^{1}H NMR) respectively.

Calculation references for fluorescent absorption is also given:
Calibration for Coumarin-labeled POEGMA:
$y = 698.69 + 7.00396E8x$
Calibration for BODIPY-labeled PDMA:
$y = 23.51 + 4.2619E9x$
Calibration for BIM-labeled PNIPAM:
$y = 25.305 + 1.97137E8x$
y is the fluorescent absorption intensity (a.u.), x is the concentration of the polymer (mol L^{-1}).

Table S4 Quantification reference via fluorescent spectrum.

Entry	POEGMA		PDMA		PNIPAM	
	x	***y***	***x***	***y***	***x***	***y***
Star1	1.67×10^{-6}	1866	4.44×10^{-7}	1915		
Star2	2.41×10^{-7}	867.6			1.43×10^{-7}	53.54
Star3			2.02×10^{-7}	885.4	6.26×10^{-7}	148.7
Star4	2.81×10^{-7}	895.7	6.57×10^{-7}	2823	1.64×10^{-7}	57.73

Table S5 Characteristics and calculation reference for mikto-arm star in Figure 5.

Entry	Polymer	Monomer Conv.[a] (%)	$M_{n,}$[a] (kDa)	$M_{n,}$[b] (kDa)	$Đ$[b]	Ex. Wavelength (nm)	Em. Peak (nm)	Fluorescent intensity (a.u.)	Concentration (mol L^{-1})	Arm distribution (%)
1	POEGMA-Coumarin	53	2.9	3.3	1.12	320	374	5376	5.86×10^{-6}	48.8
2	POEGMA-BODIPY	67	6.1	6.8	1.16	523	535	2763	3.73×10^{-6}	31.1
3	POEGMA-BIM	74	10.9	12.6	1.15	447	605	1704	2.41×10^{-6}	20.1

[a] Obtained by analysis of the ^{1}H NMR spectra. [b] Determined by SEC calibrated by PMMA.

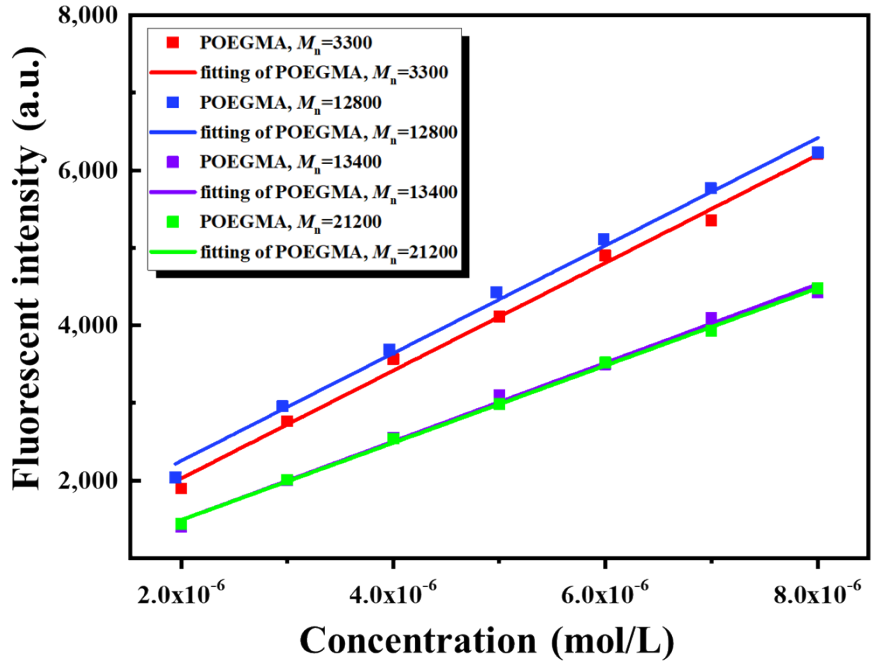

Figure S10 Linear fitting curve of polymer molar concentration and peek fluorescent absorption intensity for Coumarin-labeled POEGMA with different M_n. Fluorescent intensity vs concentration (squares) and fitting curve (solid line) were plotted for POEGMA, M_n=3300 (red); POEGMA, M_n=12800 (blue); POEGMA, M_n=13400 (purple); POEGMA, M_n=21200 (green).