Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Novel Lanthanide-Polymer Complexes: Dye-Free Dual Modal Probes for MRI and Fluorescence Imaging

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NMR characterization of 4-(3-oxo-3-phenylpropanoyl)phenyl methacrylate (DKMA)

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS δ in ppm) δ = 16.87 (s, 1H -CH=C-O*H*), 8.04 (d, *J* = 8.8 Hz, 2H ArH), 7.99 (d, *J* = 6.8 Hz, 2H ArH), 7.58–7.54 (m, 1H ArH), 7.51–7.47 (m, 2H ArH), 7.27 (d, *J* = 6.8 Hz, 2H ArH), 6.84 (s, 1H -C*H*=C-OH), 6.39 (t, *J* = 1.2 Hz, 1H CH_2=C), 5.80 (t, *J* = 1.2 Hz, 1H CH_2=C), 2.08 (s, 3H CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$,25 °C, TMS δ in ppm) δ = 185.6, 185.2, 165.5, 154.4, 135.7, 135.5, 133.2, 132.6, 128.8, 128.8, 128.0, 127.3, 122.1, 93.2, 18.5 ppm; HRMS (ESI): calculated for $C_{19}H_{16}O_4$ [M] 308.1049, found 308.1048.

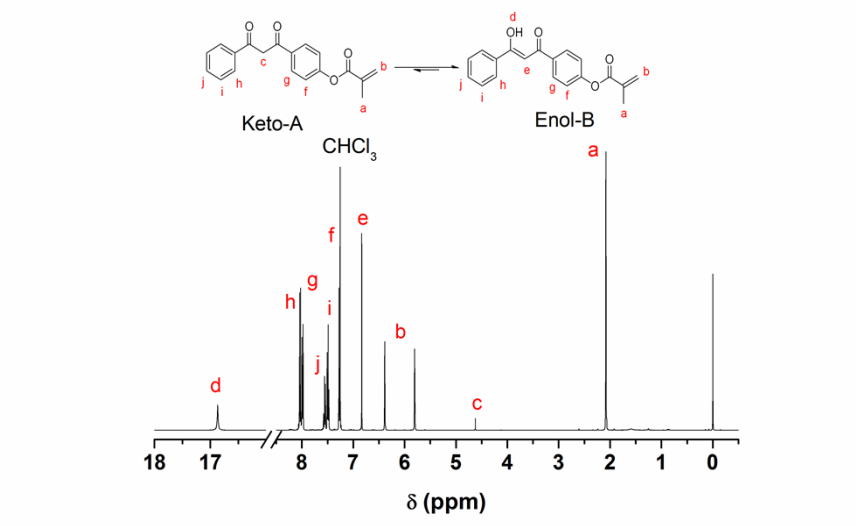


Figure S1. ^{1}H NMR spectrum of DKMA monomer.

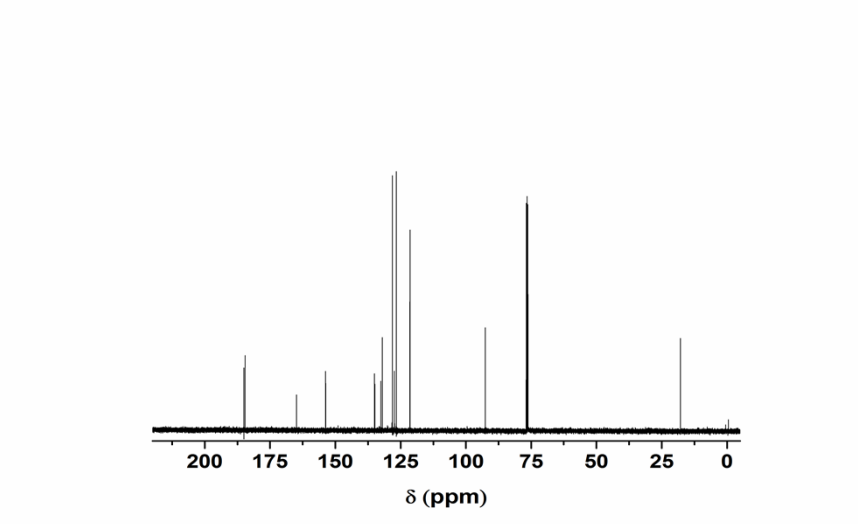


Figure S2. ^{13}C NMR spectrum of DKMA monomer.

NMR characterization of Poly[4-(3-oxo-3-phenylpropanoyl)phenyl methacrylate] (PDKMA) with Di□erent Lengths.

PD2 for example, **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS δ in ppm) δ = 16.87 (s, -CH=C-O*H*), 7.86–7.18 (m, ArH), 6.84 (s, -C*H*=C-OH), 4.50 (s, CO-C*H*$_2$-CO), 2.44 (s, -CH_2-) 1.43 (s, -CH_3) ppm

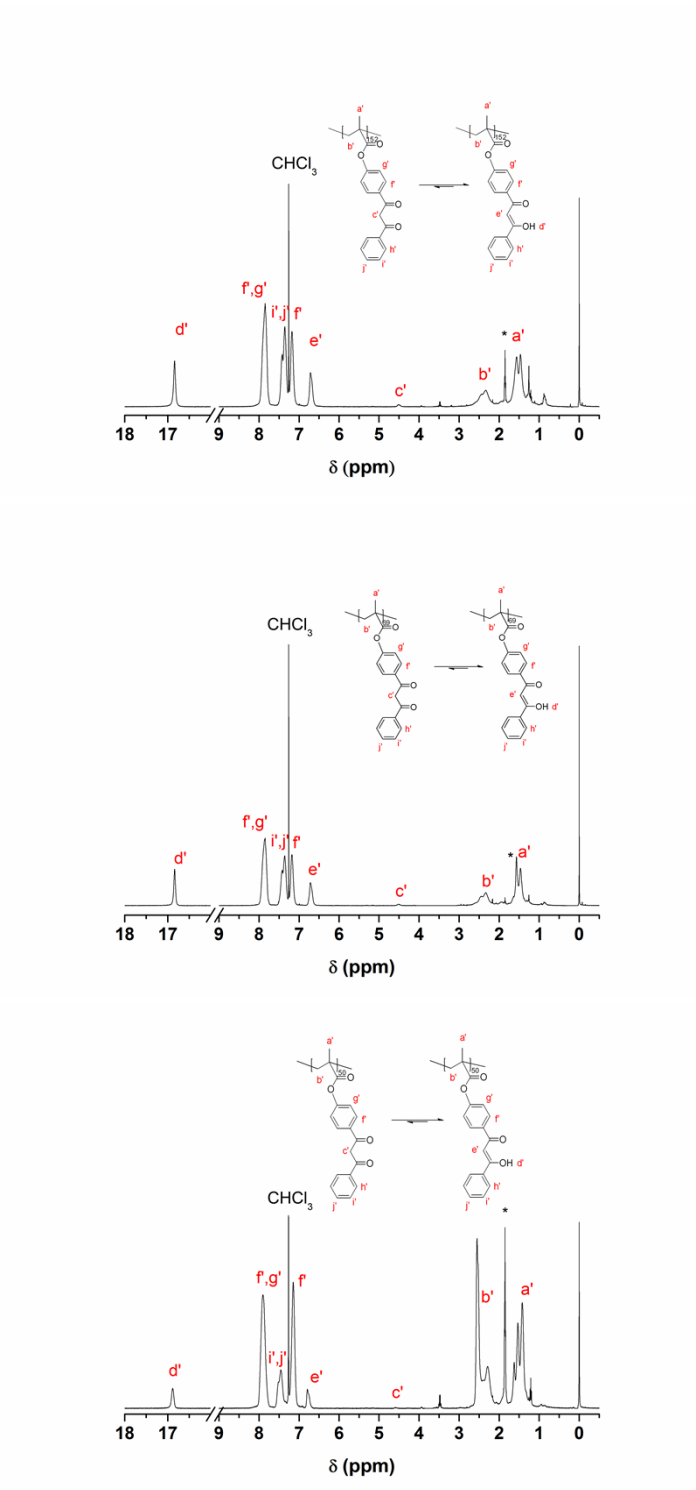


Figure S3. ^{1}H NMR spectrum of homo-polymer PDKMAs as macro-CTA.*: water.

NMR characterization of Poly[4-(3-oxo-3-phenylpropanoyl)phenyl methacrylate]-b-Ploy[Oligo(ethylene glycol) methyl ether methacrylate] (PDKMA-b-POEGMA) Diblock Copolymers.

PDO1 for example, **^{1}H NMR** (400 MHz, $CDCl_3$, 25 °C, TMS δ in ppm) δ = 16.90 (s, -CH=C-O*H*), 7.89–6.74 (m, ArH), 6.84 (s, -C*H*=C-OH), 4.08 (s, O-$C\underline{H_2}C\underline{H_2}OCH_3$), 3.65 (s, O-$C\underline{H_2}C\underline{H_2}$-O), 3.38 (s, -$OCH_3$), 2.55 (s, C-$CH_3$), 0.88 (s, C-$CH_3$) ppm.

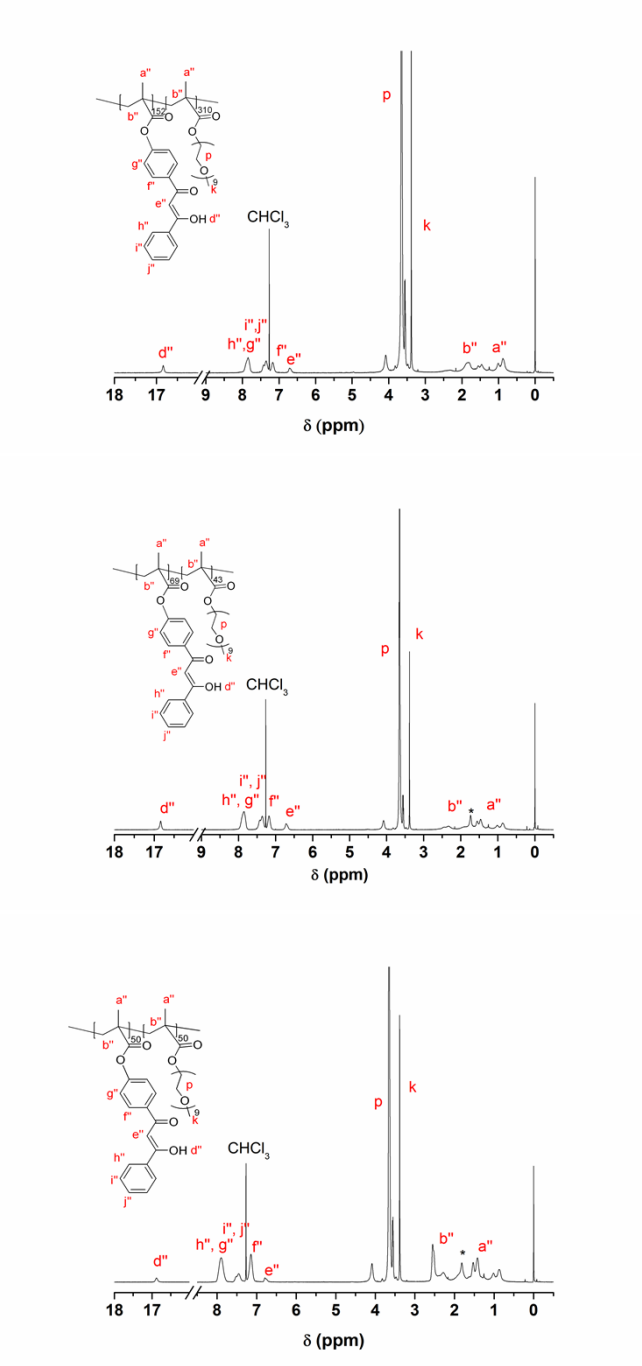


Figure S4. ^{1}H NMR spectrum of diblock polymer of PDKMA-*b*-POEGMAs. *: water.

Size exclusion chromatography (SEC) of PDKMAs using differential refractometer and multi-angle laser light scattering detector (MALLS)

MWs were determined by SEC on Triple-detection Size Exclusion Chromatography, A known molecular weight sample ($PDKMA_{69}$) was detected by SEC with differential refractometer and multi-angle laser light scattering detector (MALLS) and data analysis software to get the dn/dc = 0.2666 of homo-polymer (PDKMA), then the molecular weight of the unknown sample could be acquired by this dn/dc. Using this method, we got the molecular weight of PD1 (M_n = 47.1 DKa) as shown in Table 1.

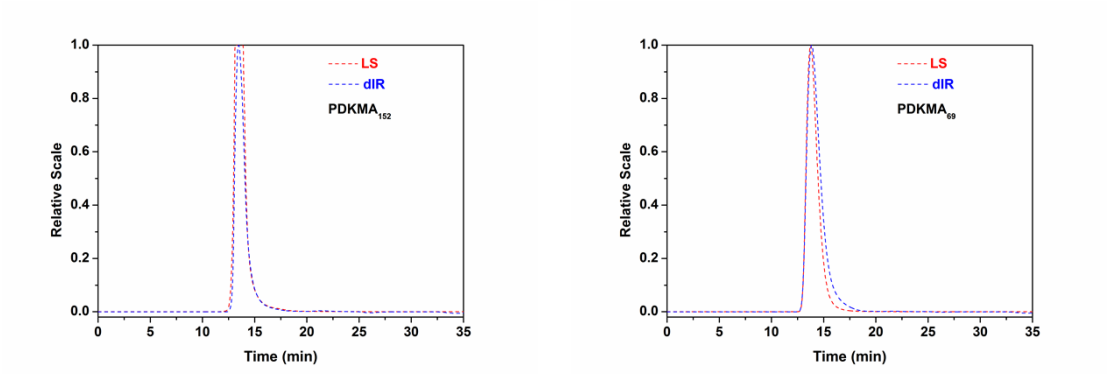


Figure S5. SEC traces of PDKMAs which were detected by differential refractometer and multi-angle Laser light scattering detector (MALLS)

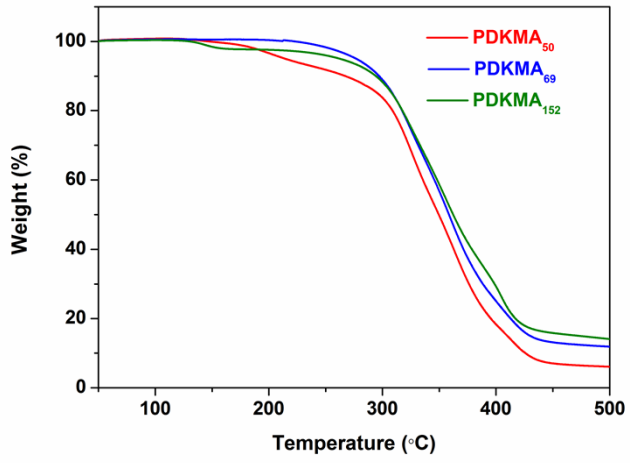
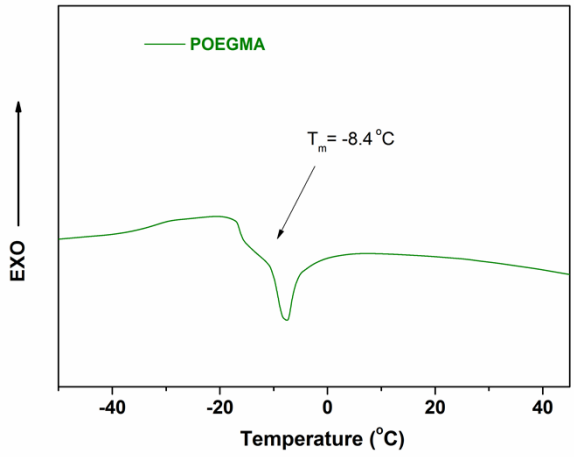
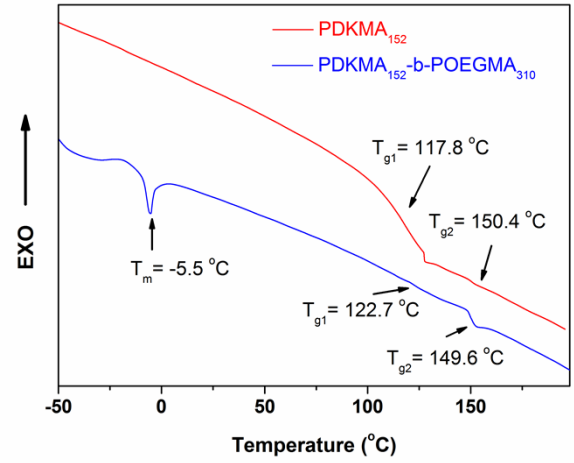
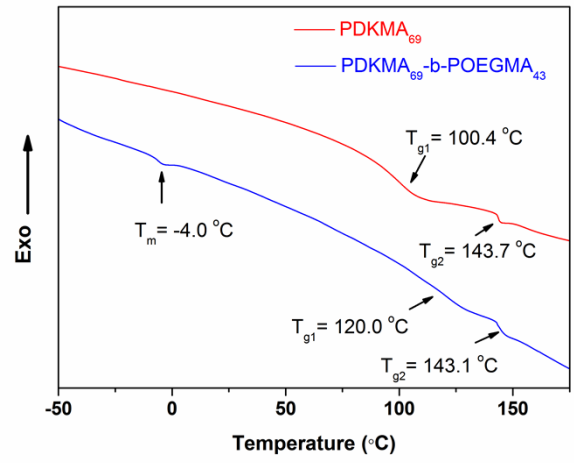


Figure S6. TGA plot of PDKMAs with a heating rate of 10 °C/min under the protection of nitrogen.


POEGMA
T_m = -8.4 °C
EXO
-40
-20
0
20
40
Temperature (°C)


PDKMA$_{152}$
PDKMA$_{152}$-b-POEGMA$_{310}$
T_{g1} = 117.8 °C
T_{g2} = 150.4 °C
T_m = -5.5 °C
T_{g1} = 122.7 °C
T_{g2} = 149.6 °C
EXO
-50
0
50
100
150
Temperature (°C)


PDKMA$_{69}$
PDKMA$_{69}$-b-POEGMA$_{43}$
T_{g1} = 100.4 °C
T_m = -4.0 °C
T_{g2} = 143.7 °C
T_{g1} = 120.0 °C
T_{g2} = 143.1 °C
Exo
-50
0
50
100
150
Temperature (°C)

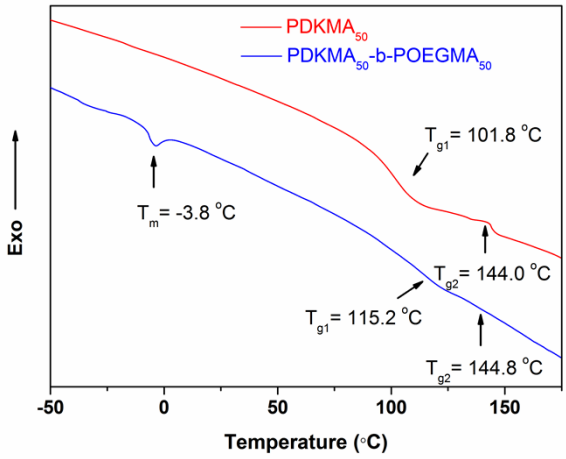


Figure S7. DSC plot of POEGMA, PDKMAs and PDKMA-*b*-POEGMAs with a second scan at a rate of 10 °C/min under the protection of nitrogen.

The critical micelle concentration (CMC) of the PDKMA-*b*-POEGMAs in Aqueous Media.

The critical micelle concentration (CMC) of PDKMA-*b*-POEGMAs were measured by the pyrene fluorescent probe method.[1, 2] 1mL pyrene (6×10^{-6} mol/L) in acetone was added to each of a series of 10.0 mL volumetric flasks and then acetone was evaporated. To each flask was then added a measured amount of PDKMA-*b*-POEGMA assemblies to obtain a series of different concentrations of PDKMA-*b*-POEGMA solutions. The solutions were then heated for 3 h at 60 °C to equilibrate the pyrene and the micelles and then cool to room temperature. The intensity ratio of the peaks at 333 nm and 338 nm from pyrene with excitation spectra at 390 nm was calculated. The results show that the CMC of PDO1, PDO2, and PDO3 were 2.63×10^{-2} mg/mL, 1.59×10^{-4} mg/mL and 1.67×10^{-4} mg/mL, respectively.

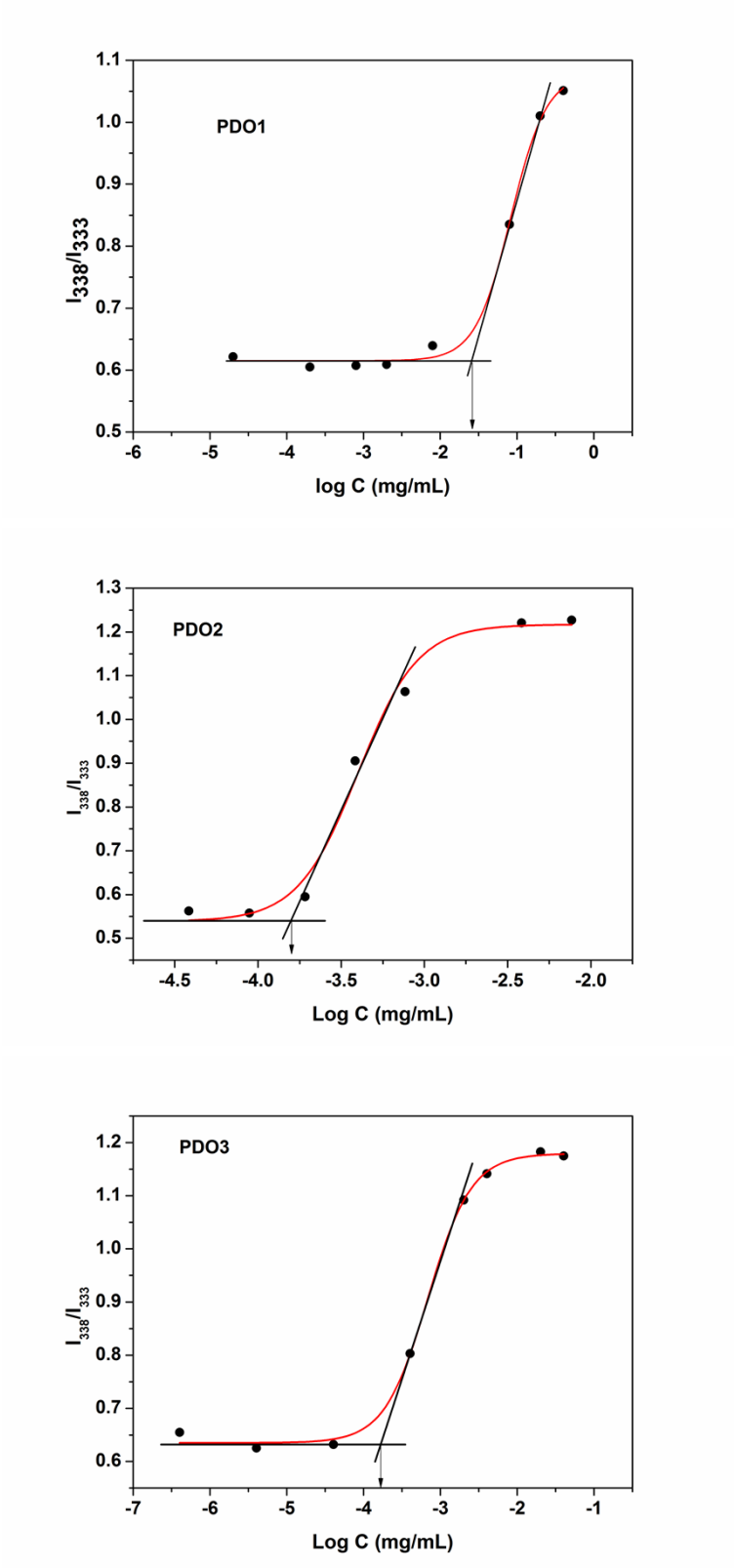


Figure S8. Determination of CMC for the block copolymer PDKMA-*b*-POEGMAs using the fluorescent method with pyrene as a probe.

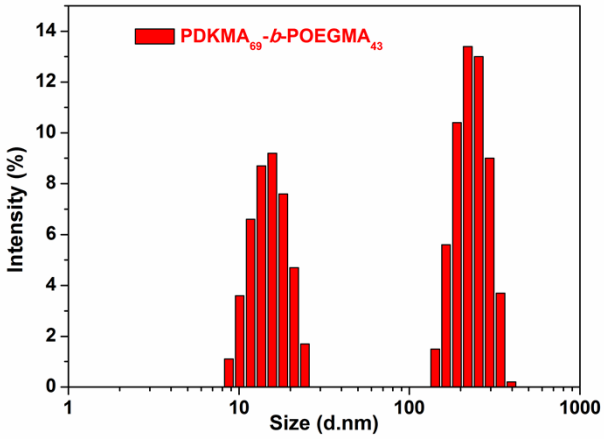


Figure S9. DLS data of NPDO2 in water.

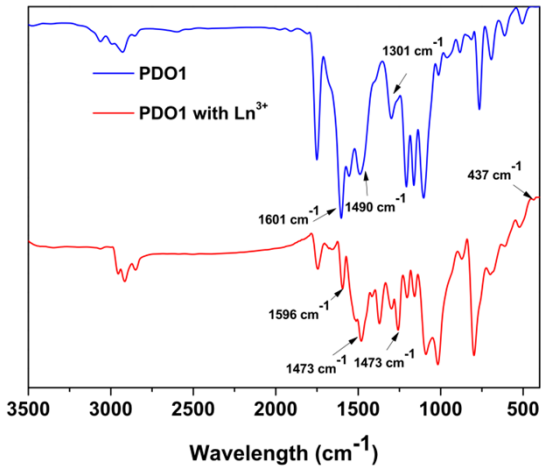


Figure S10. Comparison of FT-IR spectra (KBr) of Ln(III) complex and polymer (PDO1).

Table S1 The concentration of the Ln^{3+} in the NPs solution quantitatively analysis by ICP-OES.

Run	Eu (ppm)	Gd (ppm)	Gd-DTPA (ppm)
NPDO1	10.6	52.88	315.9
NPDO3	2	14.72	87.9
Dialysate of NPDO1[a]	-0.0433	0.0219	/
Dialysate of NPDO1[b]	-0.0425	0.2295	/

[a] at the start time of dialysis, [b] one week after dialysis.

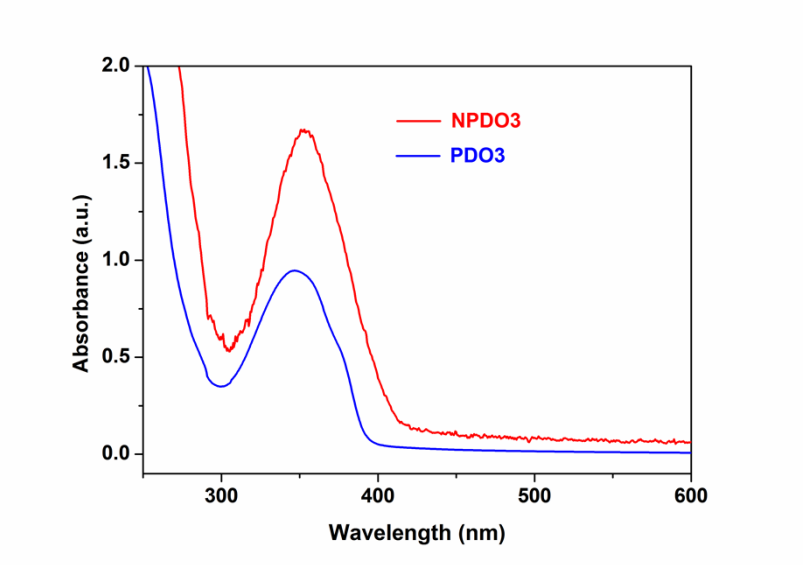


Figure S11. UV-Vis of 0.12 mg/mL NPDO3 and 0.0808 mg/mL PDO3.

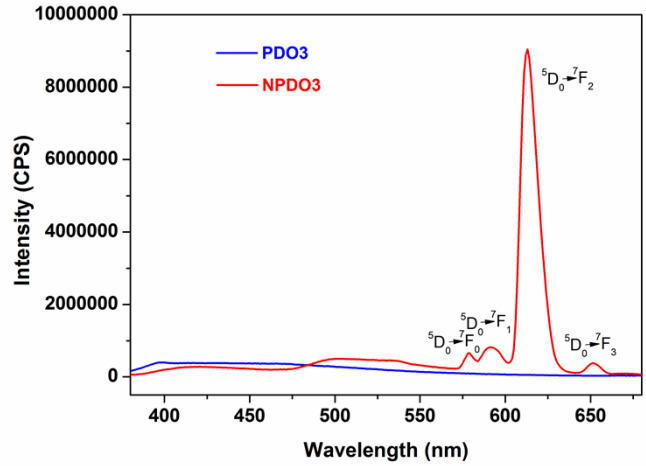


Figure S12. The emission spectra of Gd/Eu hybrid material NPDO3(1.47×10^{-3} mg/mL, $[Eu^{3+}]$ = 2 mg/L) and micelles of PDO3 (8.08×10^{-4} mg/mL) excited by ultraviolet light at 350 nm at 25 °C.

References

1. Z. Wang, M. Gao, J. Sun, D. Liang and X. Jia, *Macromolecules*, 2013, **46**, 1723-1731.
2. W. Wang, L. Chang, X. Li, Y. Wu, J. Xing, L. Deng and A. Dong, *Soft Matter*, 2012, **8**, 1575-1583.