A Controlled Post-Loading Method for Incorporating Luminescent Probes into Polymer Particles for Responsive Materials

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Introduction

We developed a systematic post-loading strategy to incorporate $[Ru(bpy)_3]^{2+}$ into amphiphilic polymer nanoparticles as a model system for future lanthanide-based chemical sensors[1,2]. By simply mixing $[Ru(bpy)_3]^{2+}$ with pre-formed nanoparticles, we investigated how the core-to-shell ratio affects probe loading efficiency and retention, particularly within responsive hydrogel environments.

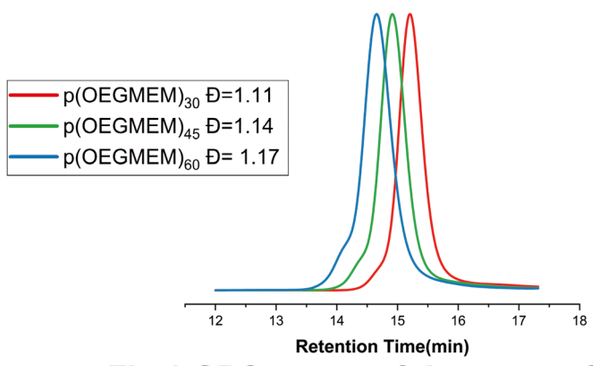

Fig 1 GPC traces of the macro-CTAs

Amphiphilic polymer nanoparticles synthesised via two-step RAFT polymerisation. P(OEGMEM) macro-CTAs with controlled DP was prepared(**Fig 1**), followed by emulsion polymerisation with MMA and EGDMA crosslinker(**Fig 2**).

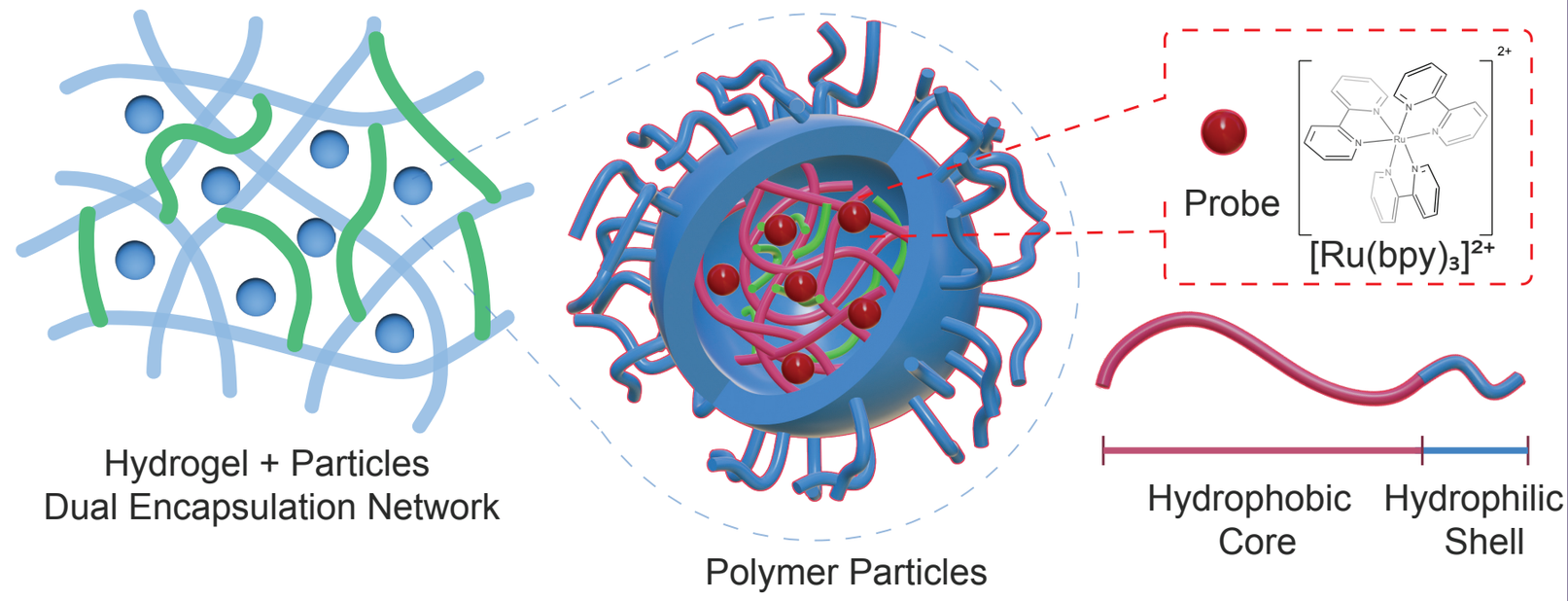

Fig 2 Synthesis of polymer particles using RAFT emulsion polymerisation

Result and Discussion

Particle Synthesis and Morphological Analysis

Eight particle compositions(**Table 1**) achieved high conversion rates (**82.4-98.9%**), high solid content (**20%**) and relative narrow size range (**27-38nm**), demonstrating robust synthetic protocols suitable for systematic structure-property studies.

Table 1 Particle size and polydispersity data for raw, Treated, and Control groups

Particles composition		Conversion	Raw Particles		Treated*		Control group	
Stabilising block	p(MMA) DP		Diameter/nm	PI	Diameter/nm	PI	Diameter/nm	PI
30	200	93.6%	27.06	0.07031	27.95	0.1857	25.39	0.1178
45	300	98.9%	24.72	0.08535	30.23	0.2346	24.21	0.1234
45	350	96.4%	37.16	0.1691	37.88	0.1746	36.40	0.1985
60	200	86.9%	29.81	0.1143	29.54	0.2218	24.95	0.1758
60	250	82.4%	35.88	0.05431	43.60	0.3455	29.40	0.1141
60	300	93.1%	30.71	0.09000	35.26	0.2512	25.12	0.1715
60	350	87.5%	36.67	0.1033	30.01	0.2975	31.45	0.1672
60	400	88.5%	38.44	0.04493	34.38	0.2284	31.69	0.1103

*MMA added during mixing with the the model probe.

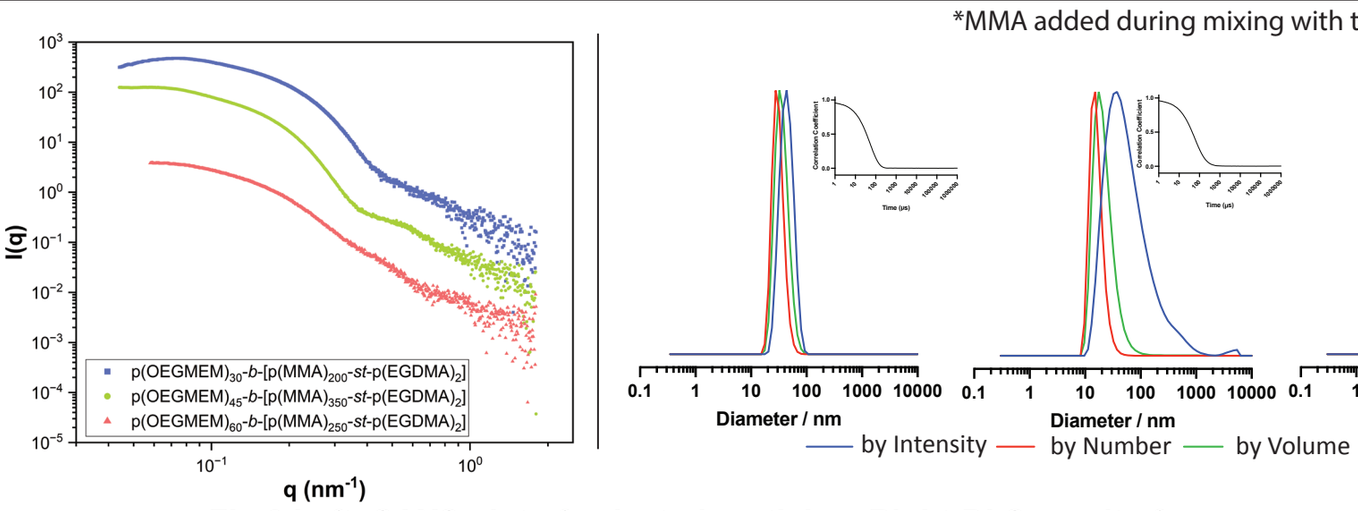

Fig 3 Left: SAXS plot of selected particles; Right:DLS result of p(OEGMEM)60-b-[p(MMA)250-st-p(EGDMA)2],Raw,T reated and control group after mixing with $[Ru(bpy)_3]^{2+}$(Left to right)

Enhanced Probe Incorporation through MMA

- **105% maximum loading increase** achieved across particle compositions (**Fig 4**) by simply adding MMA during mixing particles with $[Ru(bpy)_3]^{2+}$.
- **Particle Swelling:** diameters increased from **27-38nm** to **28-44 nm** post-swelling (**Table 2**).

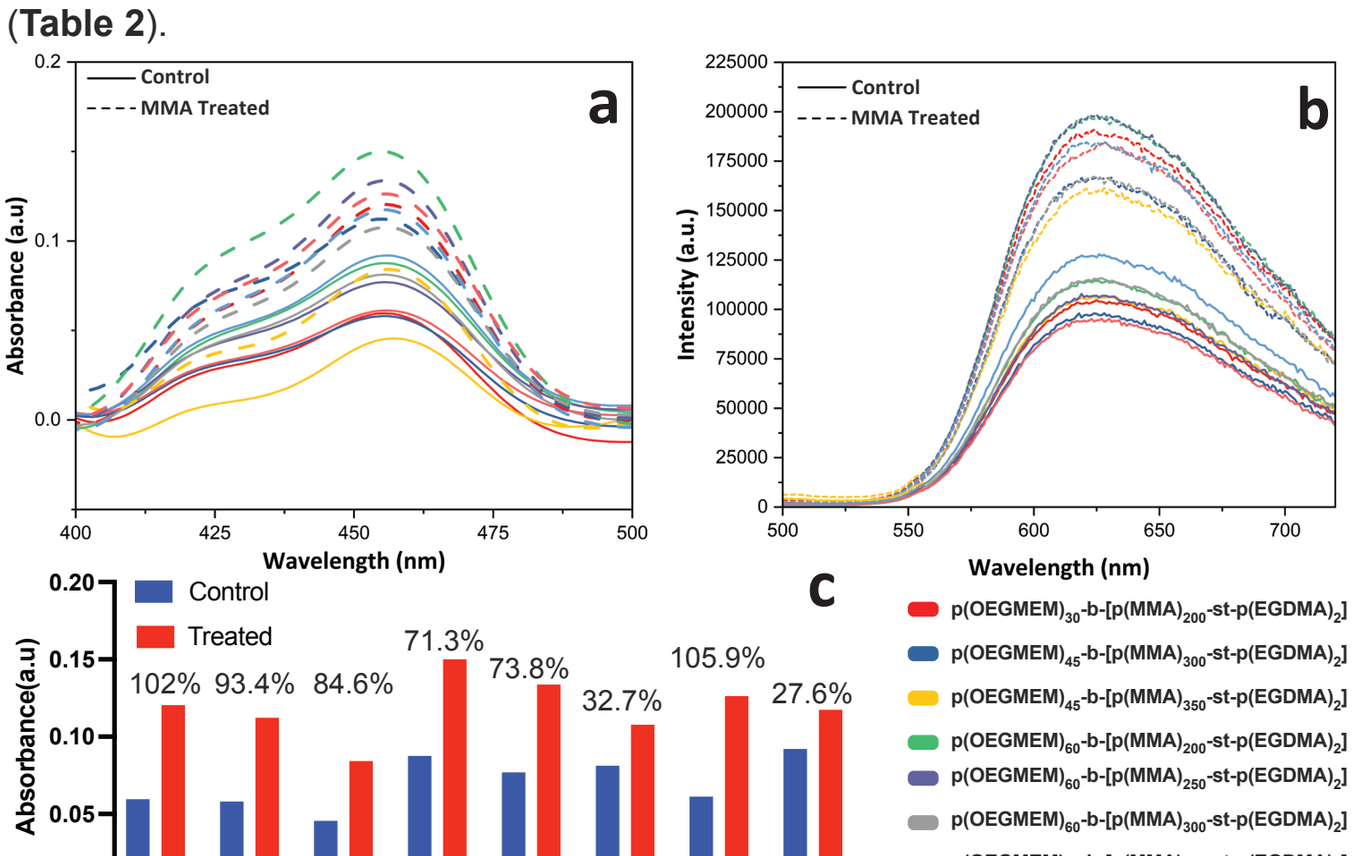

Fig 4 Characterisation and loading enhancement of $[Ru(bpy)_3]^{2+}$-loaded particles. (a) UV-vis absorptionspectra;(b) fluorescence emission spectra; (c) quantitative comparison of absorbance enhancement betweencontroland MMA-treated samples.

Hydrogel Integration and Leach-out Studies

- **Trimmed samples:** Leaching observed with water changes at 7, 14, and 30 days for UV-vis analysis (**Fig 5**), indicating end of leaching after 30 days, **with fluorescence retained**(**Fig** 6).
- **Intact hydrogels: No detectable leaching** after 24-hour soaking.
- **SEM analysis:** Uniform particle distribution with discrete spherical nanoparticles embedded throughout matrix(**Fig 7**).

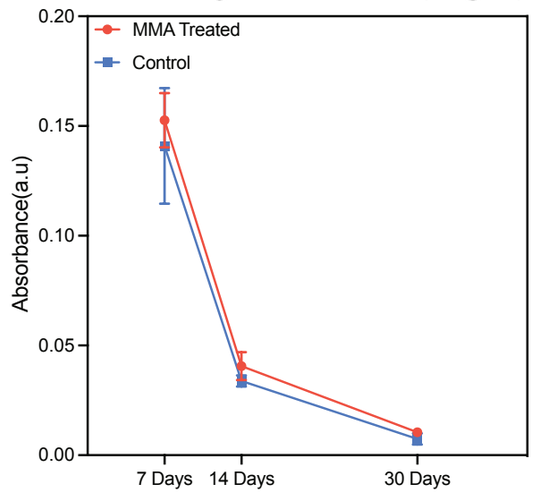

Fig 5 Leaching behaviour of trimmed hydrogel samples over time.

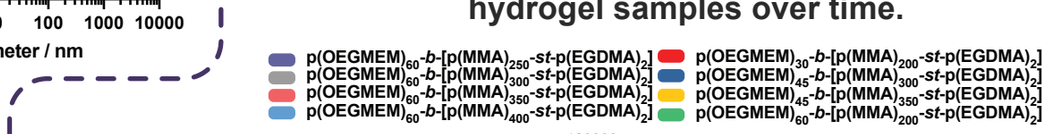

Fig 6 Steady state emission of trimmed samples.` Left: 0 Days;Right: 30 Days.

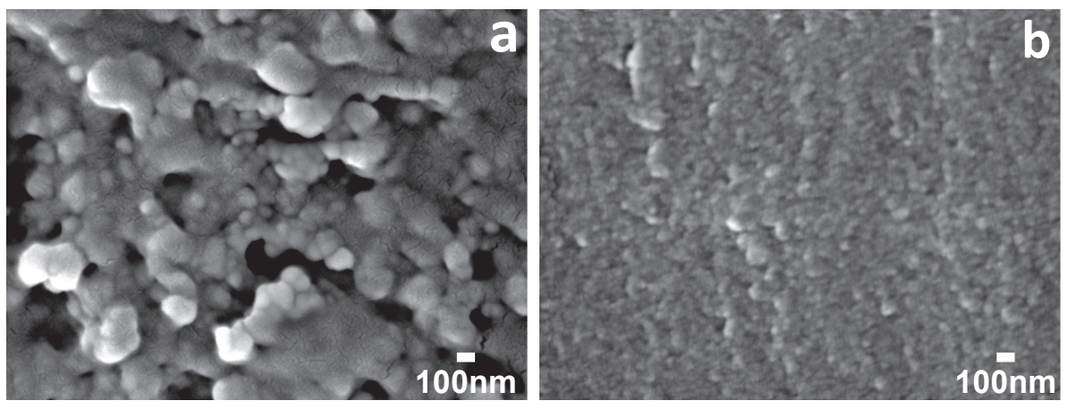

Fig 7 SEM characterisation of hydrogel surfaces. (a) Particle-embedded hydrogel (b) Blank hydrogel control.

Conclusion

- **Stable dual encapsulation** for varying particle sizes
- **MMA swelling** achieved 105% loading enhancement.
- **Leaching characterised:** trimmed samples stabilised after 30 days, intact matrices retained probes.
- **Platform validated** for future sensing or other potential applications.

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