

Microwave-assisted synthesis of polymer nanoparticles with physically entrapped fluorophores

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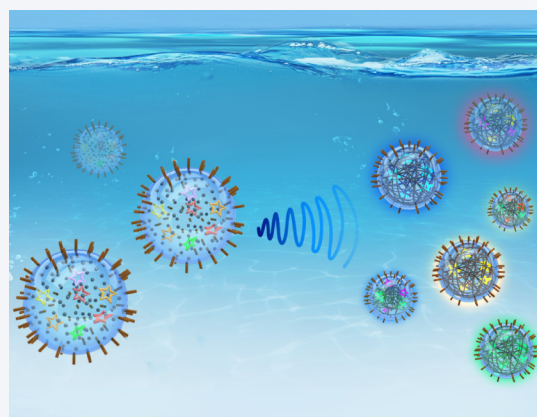
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 Cite this article: Nano Research, 2026, 19, 94908583. <https://doi.org/10.26599/NR.2026.94908583>

ABSTRACT: Microwave irradiation has emerged as a highly advantageous alternative to conventional heating methods, with well-documented merits in the synthesis of diverse nanomaterials, including fluorescent nanomaterials. However, its potential for enabling the rational fabrication of fluorescent polymer nanoparticles (FPNs) with precisely tunable size, fluorescence wavelength, and brightness, a critical requirement for their broad practical applications, remains underexplored. Here, we present a microwave-assisted strategy for the rapid preparation of FPNs incorporating physically entrapped fluorophores, using monomer emulsions pre-doped with dye molecules as precursors. By systematically modulating the concentrations of salt and surfactant, the type and loading of fluorophores, and the monomers prior to polymerization, we achieve precise control over dye–dye interactions, energy transfer processes, and the local microenvironment within the FPNs. This approach enables fine-tuning of FPN size, emission wavelength, and fluorescence brightness while endowing the nanoparticles with thermoresponsive properties. We anticipate that this facile and efficient FPNs fabrication protocol will facilitate the large-scale production and practical deployment of these functional fluorescent nanomaterials.

KEYWORDS: fluorescent polymer nanoparticles, microwave-assisted synthesis, aggregation-induced emission, dye–dye interaction, energy transfer



1 Introduction

Fluorescent polymer nanoparticles (FPNs) have emerged as versatile nanomaterials with unique physicochemical properties, enabling transformative applications across bioimaging, coating, sensing, photonics, and electronics [1–6]. The burgeoning interest

in FPNs has catalyzed significant innovations in synthetic strategies aimed at precisely regulating their structural and optical characteristics for tailored functionalities [1, 2].

Among various fabrication approaches, the most straightforward methodology involves direct incorporation of commercially available fluorescent components, such as organic dyes, rare-earth complexes, conjugated polymers, and fluorescent proteins, into monomer emulsions, followed by heterogeneous thermally initiated polymerization to yield solid particles [1, 2, 7]. This strategy leverages fluorophores with well-defined molecular structures and predictable emission properties, circumventing the tedious synthesis of fluorophore-functionalized monomers or custom-designed polymers [8–11], and facilitates facile preparation of FPNs

Received: December 26, 2025; **Revised:** February 8, 2026

Accepted: February 15, 2026

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spanning the full visible spectrum with sizes ranging from tens of nanometers to several micrometers [1–3]. However, existing protocols suffer from several critical limitations: They are often time-consuming, lack operational reproducibility, and frequently exhibit poor control over particle size distribution [2]. These deficiencies stem primarily from mass and heat transfer heterogeneities during conventional polymerization processes, which impair both reproducibility and scalability for practical applications.

In stark contrast to conventional heating methodologies, microwave irradiation excites polar chemical species, compelling them to continuously realign with the oscillating electric field and thereby generating heat internally throughout the reaction medium [12–14]. Although initially pioneered by Percy Spencer for food heating applications in the 1940s, microwave technology has evolved into a formidable tool for diverse chemical syntheses since the 1980s [12, 14–18]. The superiority of microwave heating over conventional thermal methods manifests not only in enhanced reaction rates, improved product yields, and superior purity, but also in excellent reproducibility and expanded reaction scope [12, 14]. For instance, our group previously reported the microwave-assisted ultrafast synthesis of phase change nanocapsules exhibiting an impressive latent heat storage capacity of approximately 114.9 J/g [19].

Microwave technology has also been extensively employed in the synthesis of various fluorescent nanomaterials [11, 20–25]. However, the majority of reported studies predominantly focus on carbon dots, which possess ill-defined fluorophores and demonstrate limited tunability in both size and fluorescence properties [20–22]. The remaining examples typically involve fluorophores covalently bound to polymer matrices, including our previous works on microwave-mediated multicomponent polycondensation of fluorescent monomers yielding FPNs for bioimaging applications [23–25]. To our knowledge, the microwave-assisted synthesis of polymer nanoparticles with physically encapsulated fluorescent dyes has not been documented in the literature, thus representing a significant untapped area in FPN synthesis methodology.

Herein, we report a microwave-mediated method for synthesizing functional nanoparticles with precisely tunable dimensions and continuously editable fluorescence spectra. This synthesis is achieved by dissolving fluorescent dyes in monomers and forming stable emulsions in saline solution with the aid of surfactants, followed by rapid polymerization under microwave irradiation (Fig. 1). We demonstrate our concept using a model system composed of styrene, tetramethoxy tetraphenylethylene (TMTPE), sodium dodecyl sulfate (SDS), and sodium chloride aqueous solution. We show that this approach exhibits high robustness and scalability, yielding FPNs with widely tunable sizes. Subsequently, we systematically vary the type and concentration of dyes to regulate fluorescence emission wavelengths and expand the scope of our methodology. Furthermore, by doping mixtures of TMTPE and Nile red at various concentrations and ratios, we achieve continuous editing of FPN fluorescence wavelengths from 480 to 661 nm. Finally, we demonstrate that our approach can be utilized for synthesizing functional FPNs by replacing styrene with benzyl methacrylate, yielding thermally-responsive FPNs for advanced applications.

2 Experimental

The polymerization system consisted of an oil phase and an

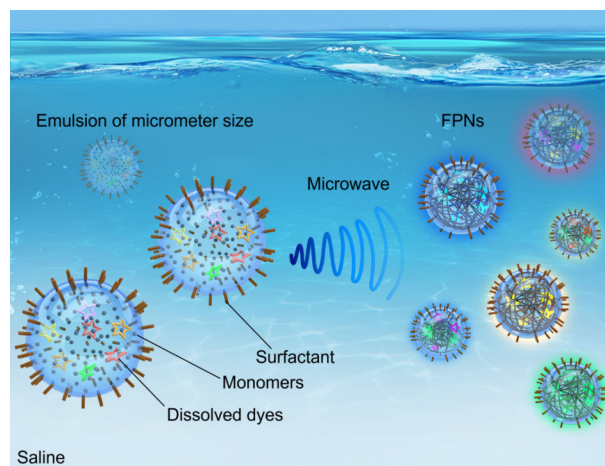


Figure 1 The idea of physically entrapping fluorescent molecules by *in-situ* formed polymer chains during the microwave-mediated conversion of monomer emulsions into FPNs.

aqueous phase. For preparing the aqueous phase, 1.0 g of the emulsifier SDS was dissolved in 100 g of deionized water, followed by the addition of 2.0 g of NaCl (2.0 wt.% relative to water), which was placed in a 250 mL plastic beaker. For the oil phase, 5.0 g of monomer (styrene or benzyl methacrylate), 50 mg of fluorescent dye (corresponding to a concentration of 1 wt.% in the resulting nanoparticle), and 0.35 g of the initiator azobisisobutyronitrile were mixed and dissolved under stirring. The resulting oil phase was then added to the aforementioned aqueous phase. Mechanical emulsification was performed at a stirring speed of 8000 rpm for 10 min to form a stable oil-in-water (O/W) emulsion. The obtained emulsion was transferred into a 250 mL round-bottom flask, and microwave-assisted polymerization was carried out at 70 °C and 600 W for 35 min to yield a nanoparticle suspension (for the controlled experiment initiated by thermal heating, the mechanically emulsified O/W emulsion was heated in a 250 mL round-bottom flask at 70 °C for 12 h). Finally, the resulting nanoparticle suspension was demulsified with ethanol and subjected to vacuum filtration. The collected particles were alternately washed several times with hot ethanol and hot water to remove SDS and NaCl, followed by drying at room temperature for 48 h to obtain the fluorescent polymer nanoparticle as a fine powdery substance.

3 Results and discussion

The reaction system described herein comprises four essential components: (i) a saline solution serving as a microwave-absorbing medium that efficiently converts electromagnetic energy into molecular kinetic energy, thereby inducing localized thermal effects [12, 14]; (ii) polymerization constituents, including monomers amenable to thermally initiated free radical polymerization (dispersed as emulsions in the aqueous phase) supplemented with small amounts of the thermal initiator azobisisobutyronitrile; (iii) structurally well-defined organic fluorescent dyes molecularly dissolved in the dispersed droplets; and (iv) surfactants that maintain colloidal stability of the emulsions and simultaneously promote interfacial accumulation of counterions at elevated concentrations to enhance microwave energy absorption and conversion [19].

For our model system, NaCl was selected as the salt, styrene as

the monomer, TMTPE as the model fluorescent molecule, and SDS as the surfactant (Fig. 2(a)). In initial experiments, SDS, NaCl, and monomer were formulated at 1 wt.%, 2 wt.%, and 5 wt.% (relative to water), respectively, with 1 wt.% TMTPE dissolved in styrene (relative to styrene). Following homogenization, the resulting mixture formed relatively uniform micrometer-scale droplets (Fig. S1 in the Electronic Supplementary Material (ESM)). Prior to polymerization, negligible fluorescence excitation and emission spectra were detected in the emulsion (Fig. 2(b) and Fig. S2 in the ESM). This is attributed to the complete dissolution of TMTPE in styrene. As a classic aggregation-induced emission (AIE) luminogen, TMTPE dissipates excited-state energy via intramolecular rotation rather than fluorescence emission when fully dissolved [26, 27]. As styrene gradually polymerizes into polystyrene chains, intramolecular rotation of TMTPE becomes increasingly restricted, manifested by a rapid enhancement in

fluorescence excitation and emission intensities (Figs. 2(b) and 2(c), and Fig. S2 in the ESM) [26–28].

Consistent with our previous findings [19], microwave polymerization was conducted for 35 min. Interestingly, the fluorescence intensity peaked at ~ 15 min. Analogous trends were observed when the TMTPE loading was adjusted from 1 wt.% to 0.1 wt.% or 10 wt.% (Fig. 2(c), and Figs. S3 and S4 in the ESM). We further measured the fluorescence quantum yield (QY) of FPNs at various polymerization stages (Fig. S5 in the ESM). The QY of FPNs peaked at 10 or 15 min, consistent with the fluorescence intensity data (Fig. 2(c)). Notably, the QY of all FPNs exceeded that of pristine TMTPE (41%), indicating that microwave-generated *in-situ* polymer chains effectively suppress non-radiative energy loss.

To understand the unexpected observation, a series of experiments were conducted. First, microwave-assisted polymerization was analyzed by ultraviolet-visible (UV-Vis)

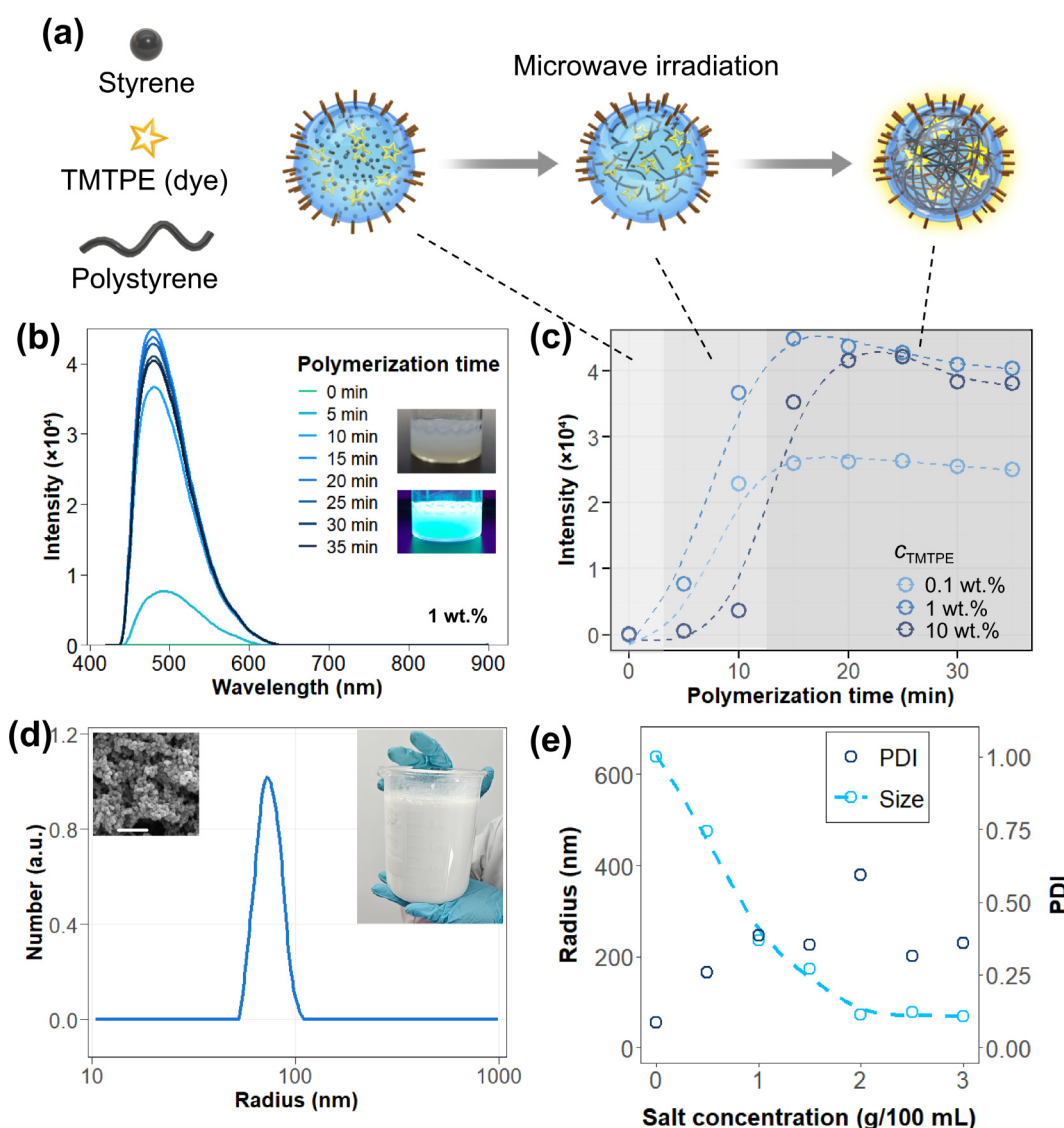


Figure 2 Conceptual illustration of microwave-assisted FPN synthesis in a model system. (a) Schematic illustration of the conversion from non-fluorescent monomer emulsion to fluorescent polymer nanoparticles with physically entrapped dye molecules. (b) Fluorescence evolution during microwave reaction in the model system containing 1 wt.% TMTPE. (c) Fluorescence intensity experiences a rapid increase followed by a slight decrease during microwave-assisted polymerization of the monomer emulsion, independent of TMTPE concentration. (d) Size and size distribution of FPNs characterized by DLS and SEM, and optical image of a 1 L-scale FPN sample prepared via continuous-flow synthesis. (e) Size tuning of FPNs via variation of saline concentration.

absorption spectroscopy and gel permeation chromatography (GPC). UV-Vis results showed that monomers were completely consumed at approximately 30 min (Fig. S6 in the ESM), while GPC indicated that the molecular weight reached 170 kDa in the early polymerization stage and remained almost constant thereafter (Fig. S7 in the ESM), suggesting rapid reaction between radical and monomer. Second, replacing styrene with methyl methacrylate (MMA) as the monomer in microwave polymerization also yielded a similar phenomenon (Fig. S8 in the ESM), confirming that this behavior is not specific to styrene. Third, reducing AIBN dosage delayed the appearance of the maximum and reduced the post-maximum fluorescence decline (Fig. S9 in the ESM). Therefore, we hypothesized that the observation might be attributed to reaction between radical and TMTPE at the late-stage of microwave-induced polymerization where monomers are exhausted, although no direct evidence for TMTPE-free radical reaction products was obtained via ^1H nuclear magnetic resonance (NMR, Figs. S10 and S11 in the ESM).

To evaluate the stability of FPNs prepared via this non-covalent entrapment strategy, the as-obtained products were dispersed in ethanol. Following 14 days of dialysis against water and ethanol, the fluorescence intensity of FPNs decreased by 5% and 11%, respectively (Fig. S12 in the ESM). Furthermore, we also evaluated the environmental stability of FPNs under two different acid-base conditions (pH = 3 and pH = 12, Fig. S13 in the ESM) and two different temperature conditions (30 and 70 °C, Fig. S14 in the ESM). After 7 days of exposure under these four conditions, the fluorescence intensity of FPNs decreased by approximately 6% in each case. This confirms that polymer chains can encapsulate the majority of fluorescent molecules, preventing their leaching from the nanoparticles. Nevertheless, practical applications of FPNs in fields such as textiles and construction demand enhanced stability, which could be further improved by incorporating cross-linkers during synthesis or introducing stronger interactions (e.g., electrostatic and quadrupole interactions) [29, 30].

As a control experiment, TMTPE that entrapped in the FPNs in non-covalent way was replaced with vinyl tetraphenylethylene (VTPE), an AIE luminogen capable of incorporating into the polymer chain during polymerization. The observed phenomena were largely consistent with those of TMTPE, including a slight fluorescence decrease upon prolonged polymerization (Figs. S15–17 in the ESM). These results not only confirm that encapsulating AIE molecules physically during microwave polymerization enables fabrication of highly robust FPNs but also suggest that AIE molecules can serve as probes to monitor the microscopic processes of microwave reactions. Although recent advances in instrumentation and probe materials have enabled visualization of localized hotspots in microwave reactions, the spatiotemporal resolution of current studies remains to be improved [31, 32]. We propose that AIE probes hold significant potential for imaging microwave absorption and heat transfer with superior spatiotemporal resolution, analogous to their successful applications in monitoring diverse physicochemical processes (e.g., phase transition of polymer materials, charge-discharge dynamics of solid-electrolyte interphases, and interfacial catalysis) [28, 33–35].

Subsequently, the size and size distribution of FPNs were characterized via dynamic light scattering (DLS) and scanning electron microscopy (SEM) (Fig. 2(d)). DLS measurements revealed a hydrated particle size of 73 nm with a relatively narrow size distribution (polydispersity index (PDI) = 0.59). SEM images

demonstrated a uniform particle size distribution with an average diameter of ~ 30 nm. Given that DLS measures hydrated particle size, these two sets of data are in good agreement. To exam the reproducibility of our method, 50 batches of FPN samples with 1 wt.% TMTPE doping were synthesized. The fluorescence intensity of FPNs was determined to be 40476 ± 355 , with a fluorescence emission wavelength of 484.8 ± 0.7 nm. The high stability of the fluorescence properties of FPNs is due to the fact that their fluorescence is mainly determined by the dye molecules encapsulated inside, which is less affected by the polymerization process. The statistical result of the hydrated radius was 65.25 ± 12.65 nm; despite the observed fluctuations, the particle size distribution remains narrow (Fig. S18 in the ESM). We further performed a correlation analysis of four key parameters (hydrated radius, PDI, fluorescence intensity, and emission wavelength), and the results revealed extremely weak correlations among all these parameters (Table S1 and Fig. S19 in the ESM). Furthermore, a 1 L-scale sample (Fig. 2(d), corresponding to ~ 50 g of FPN product) was prepared via a continuous-flow approach, with well-preserved particle size and luminescent properties (Fig. S20 in the ESM). In contrast, conventional thermal polymerization of the same emulsion for FPN preparation required 12 h to complete and yielded FPNs with a DLS particle size exceeding 1100 nm (Fig. S21 in the ESM). Overall, the advantage of the microwave-assisted FPNs synthesis over conventional heating method lies in its significant improvement in efficiency and the capability to obtain nanoparticles of smaller size under the same feed conditions. This is consistent with the conclusions reported in traditional studies on microwave-assisted nanomaterial synthesis [18, 19, 36, 37]. Compared with the preparation of FPNs by methods such as anti-solvent precipitation using solution of polymers and fluorescent dyes, the advantages of this method lie in eliminating the need for polymer purification and redissolution processes, as well as its feasibility to access crosslinked structures [2]. In addition, this method avoids the synthesis of dye-appended monomers required for covalent bonding to dyes to polymers [9, 10, 24, 25].

The particle size of FPNs can be tuned from 73 to 640 nm by varying the salt concentration or adjusting the SDS concentration (Fig. 2(e), and Figs. S22 and S23 in the ESM), demonstrating excellent particle size tunability. FPN particle size decreased monotonically as the salt concentration increased from 0 to 3 g/100 mL, then remained constant thereafter, which is consistent with our previous work [19]. Notably, as the SDS concentration in the saline solution increased, FPN particle size first decreased and then increased, reaching a minimum at 0.5 g/100 mL. We hypothesize that excess SDS forms monomer-free micelles in the aqueous phase, which compete with monomer droplets for microwave energy [12]. This attenuates the advantages of microwave-assisted polymerization, leading to an unexpected increase in FPN particle size at high SDS concentrations [19].

Our FPN synthesis strategy was anticipated to exhibit high generality. In principle, any fluorophores soluble in the monomer phase and compatible with free radical polymerization can be fabricated into FPNs via this strategy [1, 38, 39]. To verify this, we first extended the aforementioned protocol to a commonly used aggregation-caused quenching (ACQ) dye, Solvent Green 5 (SG5) (Fig. 3(a), and Fig. S24 and Table S2 in the ESM). In contrast to TMTPE, the SG5-doped monomer emulsion exhibited strong fluorescence emission even prior to polymerization initiation [40]. As the SG5 doping level in the emulsions increased from 0.01 wt.%

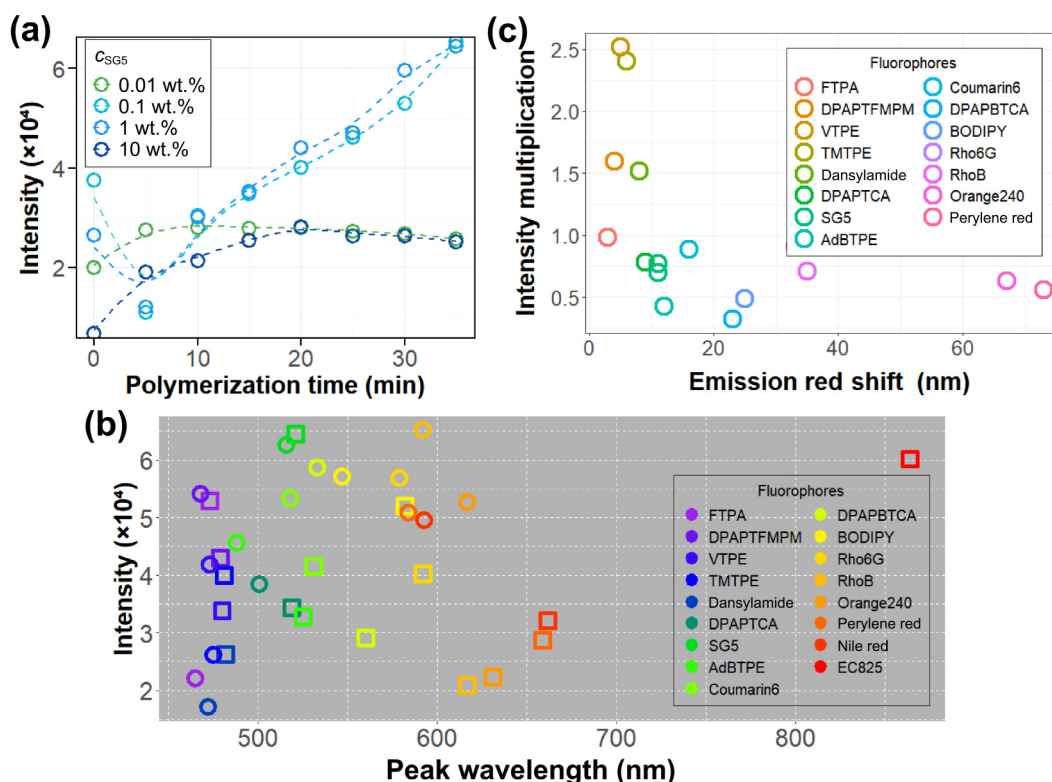


Figure 3 Tailoring emission wavelength and brightness via tuning dye type and concentration in emulsions during microwave-assisted FPN synthesis. (a) Fluorescence evolution during microwave-assisted polymerization of monomer emulsions containing various concentrations of SG5. (b) Summary of fluorescence spectral peak wavelengths and intensities for FPNs doped with different dyes at concentrations of 0.1 wt.% (square) and 1 wt.% (circle). (c) Summary of peak wavelength redshift and peak intensity fold enhancement when dye concentration is increased from 0.1 wt.% to 1 wt.%.

to 0.1 wt.% and 1 wt.%, and ultimately to 10 wt.%, the fluorescence intensity initially increased and subsequently decreased, confirming the occurrence of ACQ for SG5 when its concentration rose from 0.1 wt.% to 10 wt.%. During polymerization, the fluorescence intensity of emulsions with 0.01 wt.% and 10 wt.% SG5 remained nearly unchanged, suggesting no change in the status of SG5 molecules happens during the polymerization. Whereas that of emulsions with 0.1 wt.% and 1 wt.% SG5 gradually increased, suggesting that *in-situ* formed polymer chains segregate dye molecules, thereby inhibiting their aggregation [26, 38]. However, the fluorescence intensity of FPNs with 1 wt.% SG5 did not exceed that of FPNs with 0.1 wt.% SG5, presumably because the average distance between adjacent SG5 is estimated to be 2 nm (Table S3 in the ESM).

Subsequently, we expanded the scope of fluorescent dyes to include both classic fluorophores (e.g., dansylamide, perylene, and rhodamines) and triphenylamine-based AIE luminogens (Figs. S25–28 in the ESM). This not only validates the excellent functional group tolerance of our strategy but also enables the fluorescence spectra of FPNs to span the visible to near-infrared (NIR) region. We selected two molecules representative of AIE and ACQ dyes, namely AdBTPE and Rhodamine B (RhoB), and determined the changes in their fluorescence intensity during the fabrication of FPNs (Fig. S29 in the ESM). Both of them also exhibited a maximum value similar to that of TMTPE. Unlike SG5, both of these two dyes possess reactive functional groups, indicating that the specific molecular structures of dyes exert an influence on their compatibility with the method reported in this study. We systematically synthesized 14 types of FPNs with different physically encapsulated dyes at concentrations of 0.1 wt.% and 1 wt.%,

respectively, and their fluorescence spectra are presented in Fig. 3(b), and Figs. S30–S43 and Table S2 in the ESM. When the dye concentration in FPNs was increased from 0.1 wt.% to 1 wt.%, all FPNs exhibited spectral red shifts of varying magnitudes (Fig. 3(c)), characteristic of the transition in emission behavior from individual dye molecules to dye ensembles [41–44]. Among these dyes, perylene red showed the largest red shift (up to 73 nm, Fig. 3(c)), presumably due to its large planar conjugated structure that favors J-aggregate formation [43, 44]. The increased dye concentration also altered the excitation spectra of these FPNs (Fig. S44 in the ESM). While most spectra underwent red shifts, some exhibited significant blue shifts (e.g., FPNs containing Orange 240), indicating the formation of H-aggregates in these FPNs that elevate the energy level of the excited state [41].

For most conventional ACQ dyes, increasing their concentration in FPNs from 0.1 wt. to 1 wt.% resulted in decreased fluorescence intensity. This is attributed to the reduction in the average distance between adjacent dye molecules from approximately 10 to below 5 nm (Table S3 in the ESM), which substantially enhances energy transfer pathways that compete with fluorescence emission [26, 45]. Unexpectedly, for several AIE luminogens (e.g., AdBTPE), FPNs with 0.1 wt.% doping exhibited stronger fluorescence than those with 1 wt.% doping (Fig. S44(b) in the ESM). We propose that the restriction of intramolecular rotation of dye molecules by polymer chains is more effective than the restriction induced by aggregation between certain AIEgens [27].

The above results suggest that the approach reported herein can serve as a promising platform for regulating dye–dye interactions, motivating us to introduce two distinct fluorophores during the microwave-assisted synthesis of FPNs. Previous studies have shown

that assembling multiple types of dyes or encapsulating them into polymer/inorganic nanoparticles enables fine-tuning of their fluorescence properties by regulating charge transfer between different dyes [1, 2, 39, 46–49]. The diversity of fluorescent dyes and their combinatorial complexity provide a vast exploration space, which demands more efficient synthetic methods. We envision that the rapid and efficient synthesis of FPNs via microwave-assisted approaches can accelerate the exploration of this chemical space.

As a proof-of-concept, we added mixtures of TMTPE and Nile red to styrene droplets at a series of ratios while maintaining their total concentration at 1 wt.% prior to microwave-initiated polymerization (Fig. 4). It should be noted that although all the aforementioned dyes have been encapsulated in polymer nanoparticles via *in-situ* polymerization, the encapsulation efficiency of different dyes is not necessarily consistent. To precisely regulate the contents of the two dyes in FPNs in subsequent experiments, we evaluated the encapsulation efficiencies of TMTPE and Nile red by UV–Vis absorption spectroscopy (Fig. S45 in the ESM). The results showed that the encapsulation efficiencies of TMTPE and Nile red were 94.55% and 91.33%, respectively. Given that the two values are relatively close and generally high, the concentrations discussed in the subsequent work still refer to the mass fraction in the feed. By precisely controlling the amounts of the two dyes in FPNs, we achieved continuous tuning of the emission peak from 480 to 659 nm (Fig. 4(a) and Fig. S46 in the ESM). These two dyes were selected for demonstration due to their distinct emission spectra. Nevertheless, since the excitation spectrum of Nile red overlaps with the emission spectrum of TMTPE, the emission spectra of these FPNs were predominantly dominated by Nile red when its concentration reached 0.05 wt.%. Similarly, the excitation spectra of the FPNs were dominated by Nile red when its concentration reached 0.03 wt.% (Fig. 4(a)). Plotting the excitation spectrum peak of FPNs against dye concentration revealed an intermediate phase between the TMTPE-dominated and Nile red-dominated regions (Fig. S47 in the ESM), suggesting a transition state governed by energy transfer [41, 42].

This transition state was further supported by the emission spectra when the total dye concentration was reduced to 0.1 wt.% (Fig. 4(b) and Fig. S48 in the ESM). In addition to the continuous tuning of emission wavelengths, as the Nile red concentration increased from 0.0 wt.% to 0.01 wt.%, a red shift of the main peak

was accompanied by the emergence of a longer-wavelength shoulder peak (Fig. 4(b)). Further increases in Nile red concentration led to the intensification of the shoulder peak, which eventually became the main peak. We attribute the appearance and shift of this shoulder peak to significant energy transfer within the FPNs [41, 42, 45].

Compared with inorganic nanoparticles, polymer nanoparticles offer numerous opportunities to modulate fluorescent properties by tailoring the microenvironment [38, 47, 50]. Since the core of our approach lies in converting monomer emulsions into polymers via microwave heating, we can endow FPNs with additional functionalities by using functional monomers. To demonstrate this, we replaced styrene with benzyl methacrylate as the monomer for FPN synthesis. Given that poly(benzyl methacrylate) (PBzMA) has a glass transition temperature (T_g) of 54 °C [51], we anticipated the FPNs to exhibit thermoresponsive fluorescence. We found that FPNs with physically entrapped TMTPE and Nile red showed distinct temperature responses: FPNs doped with 1 wt.% TMTPE exhibited significantly lower fluorescence intensity below T_g (25 °C) than above T_g (70 °C), whereas the opposite trend was observed for FPNs doped with 1 wt.% Nile red (Fig. S49 in the ESM). Nevertheless, the responsiveness to temperature exhibit poor reversibility. In particular, for FPNs encapsulated with Nile red, the fluorescence intensity at 25 °C attenuates by approximately 60% after 5 temperature cycles (Fig. S49 in the ESM). We attribute this phenomenon to the poor compatibility between PBzMA and dye molecules, which leads to more severe irreversible aggregation of dye molecules during temperature cycles.

We hypothesized that the introduction of a crosslinking agent could inhibit the large-scale irreversible aggregation of dyes in FPNs. Therefore, we replaced 10 wt.% of benzyl methacrylate with a crosslinking agent during polymerization, which considerably improve the reversibility of FPNs during temperature cycles (Fig. 5). For Nile red-encapsulated FPNs with the crosslinking agent, the fluorescence intensity at 25 °C decreases by less than 20% after 5 temperature cycles. This represents a significant improvement compared with the non-crosslinked system (~ 60% decrease), although there remains a huge gap between this result and real application as nanoscale thermometer [32, 52]. We attribute this phenomenon to the glass transition of poly(benzyl methacrylate), which alters the aggregation state of the dyes, amplifying the AIE effect for TMTPE and the ACQ effect for Nile

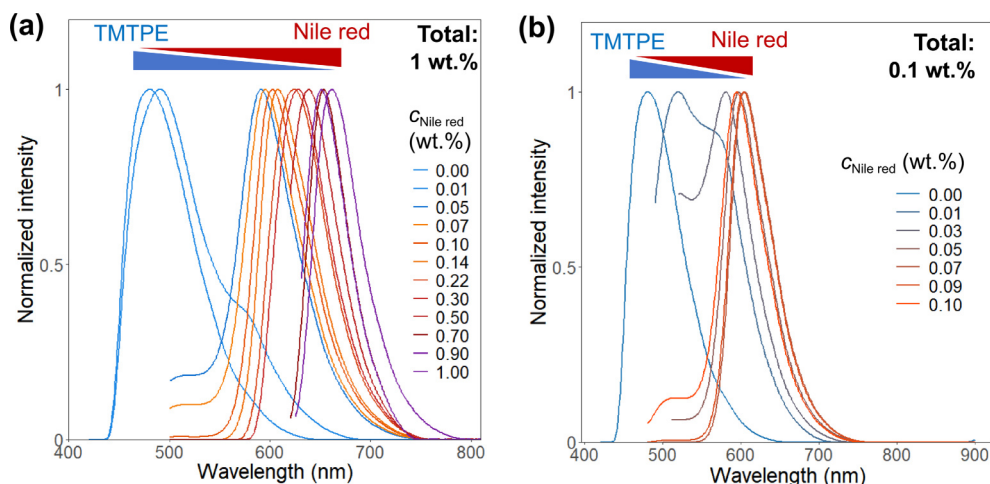


Figure 4 Modulating energy transfer in dual-fluorophore-doped FPNs. ((a) and (b)) FPNs with physically entrapped TMTPE and Nile red at total fluorophore concentrations of (a) 1 wt.% and (b) 0.1 wt.% exhibit a continuous red shift and the emergence of shoulder peak in their fluorescence emission spectra.

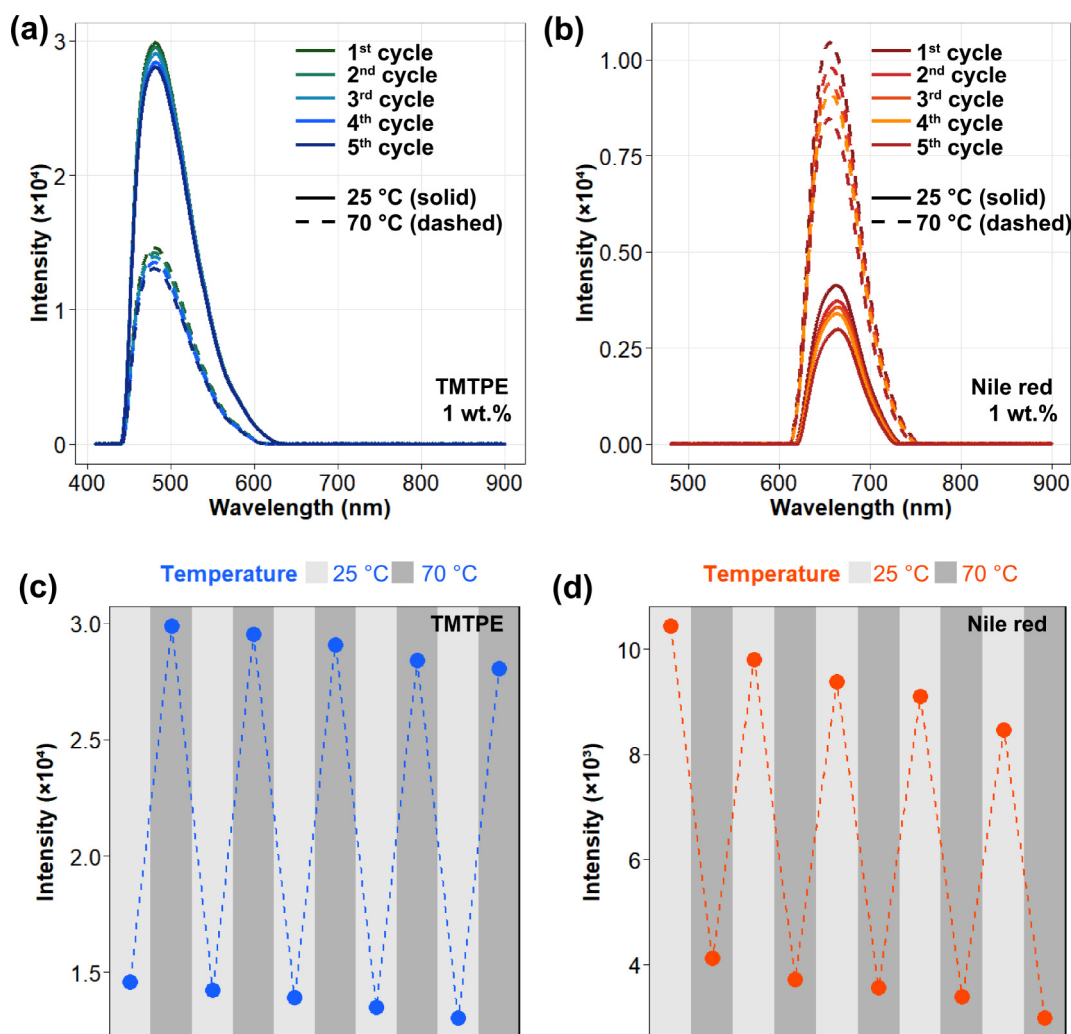


Figure 5 Thermal responsiveness of PBzMA-based FPNs with crosslinker. ((a) and (b)) Fluorescence spectra of (a) TMTPE-loaded FPNs and (b) Nile red-loaded FPNs during 5 cycles of variations in temperature. ((c) and (d)) The response of fluorescence intensity of (c) TMTPE-loaded FPNs and (d) Nile red-loaded FPNs to change in temperature were opposite.

red. This supports the proposed mechanism and further highlights the extensive tunability of fluorescence behavior in our FPNs.

4 Conclusions

We developed a simple, efficient, and scalable microwave-assisted method for preparing FPNs with precisely tunable size, continuously editable fluorescence wavelengths, and enhanced brightness using commercially available raw materials. The core innovation lies in the physical encapsulation of fluorescent dyes within *in-situ* formed polymer nanoparticles during microwave-induced thermal polymerization, achieving 24-fold acceleration compared to conventional heating. This platform enables precise regulation of dye-dye interactions and energy transfer processes, opening new avenues for custom-designed fluorescent nanomaterials.

This study also gives rise to several issues that merit further in-depth investigation. First and foremost, a key issue to be addressed is how to improve the compatibility between dye molecular structures and the polymerization process. Since no specific requirements were placed on the degree of polymerization and PDI, the influence of dye molecules on the free radical polymerization

process was not the focus of this work. However, free radicals may induce structural damage to dye molecules. In addition to optimizing experimental parameters (e.g., the type and feed dosage of initiators), an alternative strategy is to explore other polymerization techniques that exhibit higher compatibility with dye molecules. Second, from the perspective of practical applications, a crucial consideration is how to enhance the stability of FPNs through approaches such as the incorporation of crosslinking agents. Furthermore, another important aspect is how to modulate the luminescent behavior and particle size distribution of FPNs with higher precision and better controllability. Finally, a more fundamental question concerns why the size of nanoparticles synthesized via microwave polymerization is smaller than that prepared by conventional thermally initiated polymerization.

Electronic Supplementary Material: Supplementary material (details of experimental characterization, fluorescence spectra, DLS results, UV and GPC measurement for measuring the kinetics of polymerization, and synthetic details and NMR spectra of four dye molecules) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908583>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 22505207) and the Natural Science Foundation of Ningxia (No. 2025AAC030025). The authors acknowledge Assoc. Prof. Haijun Ma for providing some dyes used in this work. Dr. Jinzhao Ji and Dr. Dan Li received their Ph.D. from the Department of Chemistry, Tsinghua University.

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

D. L.: Experimental design, investigation. Y. D. W.: Investigation. S. Y. Y.: Investigation. G. C. H.: Writing manuscript. H. X. M.: Investigation. W. Q. S.: Funding acquisition. S. W. G.: Project administration, funding acquisition. Y. W.: Project administration, funding acquisition. J. Z. J.: Conceptualization, experimental design, data curation, writing manuscript. All the authors have approved the final manuscript.

Use of AI statement

During the preparation of this work, the authors used “Doubao” in order to translate some sentences. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication.

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