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Surface-Functionalization of Oleate-Capped Nano-Emitters for Stable Dispersion in 3D-Printable Polymers

Akhilesh Kumar Pathak, Sachin Prashant Kulkarni, Rachel R. Chan, Chad A. Mirkin, Koray Aydin,* and Sridhar Krishnaswamy*

Two-photon polymerization 3D-printing is a well-known technique for fabricating passive micro/nanoscale structures, such as microlenses and inversely designed polarization splitters. The integration of light emitting nanoparticle (NP) dopants, such as quantum dots (QDs) and rare-earth doped nanoparticles (RENPs), into a polymer resist would enable 3D printing of active polymer micro-photonic devices, including sensors, lasers, and solid-state displays. Many NPs contain oleic acid ligands to prevent degradation, but oleate-capped NPs (oc-NPs) tend to agglomerate in nonpolar media despite the hydrophobicity of the ligand. This results in an uneven nanoparticle distribution and increased optical extinction. In this work, a general approach is proposed for dispersing oc-NPs in commercial 3D printable polymers. Controlled growth of small carbon chains around the oc-NPs is achieved by functionalizing them with methyl-methacrylate monomers. The proposed approach is validated on RENPs (≈ 65 nm) and CdSe/ZnS quantum dots (≈ 12 nm) using commercial polymer resists (IP-Dip and IP-Visio). Dispersions of functionalized NPs (f-NPs) have improved the NP density by an order of magnitude and are shown to be stable for several weeks with minimal impact on printing quality. The approach is generalizable to other oc-NPs, enabling synthesis of functional resins for high-quality polymer-based optical and electronic devices.

1. Introduction

Nanotechnology has revolutionized the development of active photonic devices,^[1] light-emitting diodes,^[2] optical amplifiers,^[3] bioimaging techniques,^[4] and solid-state displays.^[5] Functional nanoparticles (NPs), in particular, have proven extremely useful for realizing classical and quantum devices due to their tunable morphologies and electronic properties.^[6] Among the various types of NPs, rare-earth nanoparticles (RENPs) are known to display highly desirable optical properties, such as a large Stokes shift, resistance to photobleaching, and sharp emission bands.^[7] Synthesizing these NPs through thermal decomposition requires oleates or acetates in boiling organic solvents, resulting in NP surfaces covered with hydrophobic ligands (e.g., oleic acid).^[8,9] The oleic acid (OA) ligand contains a long alkyl chain along with a terminal carboxyl group and plays a crucial role in the controlled growth of NPs.

The integration of NPs into dielectric media enables fabrication of micro-photonic

devices that surpass conventional semiconductor processes. For example, NPs with electrical, magnetic, or optical properties mixed into a 3D-printable matrix can be harnessed for displays, sensors, and actuators.^[10,11] To achieve a high-quality nanocomposite, it is important to maximize the loading (density) of NPs in the 3D-printable polymer matrix while minimizing changes to the photoresist's intrinsic properties. However, maximizing the loading of NPs in a polymer matrix is challenging and often leads to immediate agglomeration despite the hydrophobicity of the oleate capping. In a nonpolar matrix, agglomeration can occur via depletion forces induced by the oligomeric components in the photoresin, leading to attractive forces between larger dopant NPs (Figure 1a).^[12,13] Large clusters formed by agglomeration result in incident light scattering and modified absorption profiles due to coupling of electronic bands between NPs.^[14] Larger clusters also quickly settle to the bottom of the resin matrix, making it difficult to extract an evenly dispersed volume of resin.

Several methods have been considered to improve the dispersity of NPs in polymer nanocomposites. Ingrosso et al. developed a nanocomposite composed of an epoxy photoresist and oleate-capped CdSe/ZnS quantum dots (QDs) using various liquid organic solvents to reduce the resin viscosity.^[15]

A. K. Pathak, S. Krishnaswamy
Department of Mechanical Engineering
Center for Smart Structures and Materials
Northwestern University
Evanston, IL 60208, USA
E-mail: sridhar.krishnaswamy@northwestern.edu
S. P. Kulkarni, K. Aydin
Department of Electrical and Computer Engineering
Northwestern University
Evanston, IL 60208, USA
E-mail: aydin@northwestern.edu
R. R. Chan, C. A. Mirkin
Department of Chemistry
Northwestern University
Evanston, IL 60208, USA



The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adfm.202412064>

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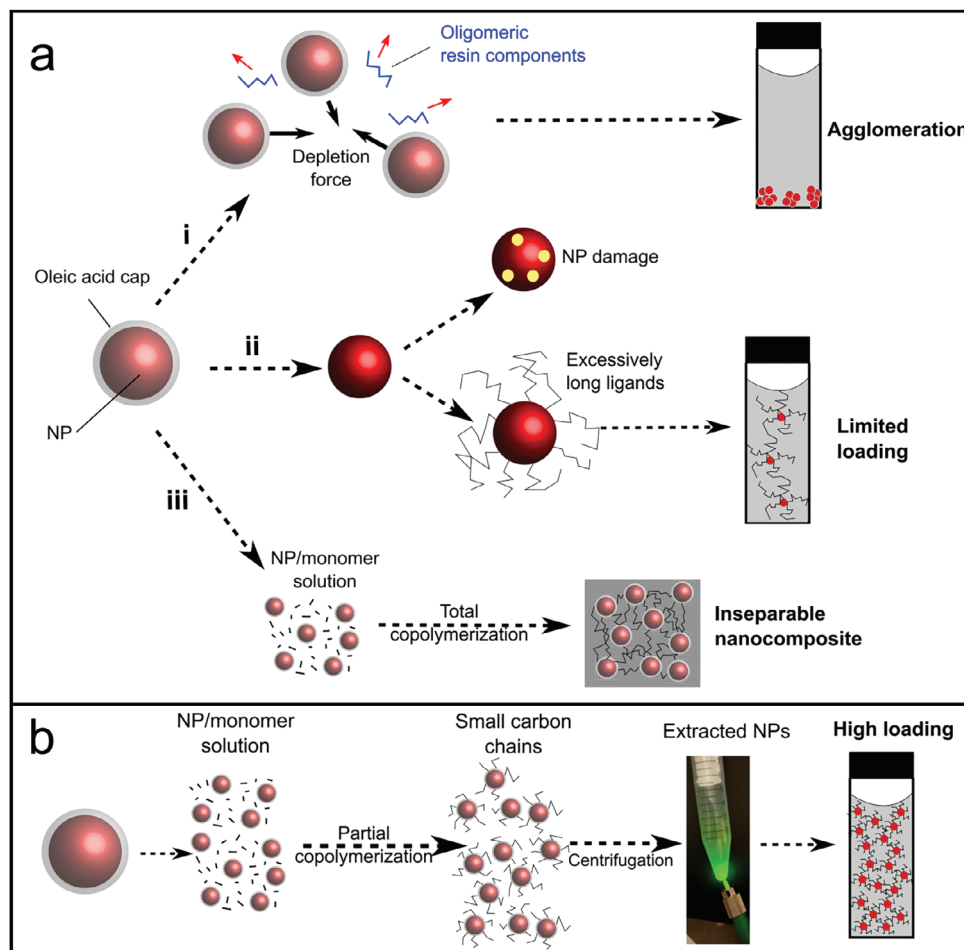


Figure 1. a) Consequences of various dispersion methods explored in existing literature, such as (i) direct dispersion of oc-NPs, (ii) ligand exchange, and (iii) nanocomposite formation. b) a schematic of our new procedure that enables NP functionalization and dispersion in other resins.

However, the dispersibility was limited by the polarity mismatch between the oleate ligands and the various solvents, and long-term stability was not reported. Zhao et al. synthesized a nanocomposite using RENPs dispersed in a hydrolyzed polyhedral oligomeric silsesquioxane-graft poly-methyl methacrylate (H-POSS-PMMA) matrix.^[16] The resulting nanocomposite exhibited nearly single nanoparticle dispersion at a high solid loading of 10 vol% along with excellent thermal stability and optical properties, but the added processing time and chemicals significantly increased the method's feasibility and fabrication footprint. Zhao et al. documented that full polymerization of RENPs in a methyl methacrylate (MMA) solvent generated nanocomposites with uniform and stable NP dispersions due to the unsaturated OA bonds that could copolymerize with MMA monomers (Figure 1a).^[17,18] This procedure was relatively simple and cost-effective, but the total polymerization of the mixture prevented the extraction of the NPs for use in any other polymer matrix, limiting the fabrication of photonic devices to spin-coating-based methods centered around PMMA. Soon after, Momper et al. utilized a ligand exchange approach to remove the oleate capping from the CdSe/ZnS QDs and attach thiol-terminated poly-methyl methacrylate (PMMA-SH) chains with greater compatibility to

commercial 3D-printable resins (Figure 1a).^[19] The ligand exchange process could potentially damage the NP surface as the protective ligand is removed and a new ligand is added, making it a risky approach for highly sensitive quantum emitters.^[20] The process is also limited to NPs composed of materials with a high affinity for thiol bonds (plasmonic NPs, sulfide QDs, etc.), effectively excluding NaYF₄-based RENPs.

A simple procedure that does not remove the native ligand in conjunction with the ability to transfer the processed NPs into other resins would be highly desirable for 3D-printing of active photonic devices. We hypothesize that by intentionally terminating the polymerization of an NP/MMA mixture before completion, NPs can be functionalized with PMMA chains over the oleic acid ligand, allowing extraction and re-suspension of NPs into various 3D-printable polymers with more uniform and stable dispersion compared to unmodified NPs (Figure 1b). While unmodified NPs require mechanical dispersion and begin to settle almost immediately, our functionalized NPs exhibit great dispersibility and long-term stability for several weeks. Our approach has been validated for various sizes and types of photoluminescent NPs, with oleic acid ligands (QDs and RENPs). The improved dispersibility, long-term stability, and generalizability

of this process makes it possible to synthesize uniform polymer nanocomposites for 3D printing of optical devices.

2. Results and Discussion

2.1. Functionalization and Process Optimization

The dispersibility of the oc-NPs depends on the compatibility of the ligand covering the NPs with a polymer matrix. Both oleate-capped RENPs (Er,Yb:NaYF₄) and quantum dots (CdSe/ZnS, 620 nm emission) are considered as candidates for surface modification. Core/shell RENPs were synthesized according to standard procedures reported in the literature (Section S1, Supporting Information). The synthesized RENPs are hexagonal in shape with sizes ranging from 50 to 65 nm (Section S2, Supporting Information). Commercially available QDs are spherical with particle sizes ranging from 8 to 12 nm (Section S2, Supporting Information).

For attaching MMA to the OA ligand, our process is derived from the procedure described in Yang et al. However, the reaction time and temperature are adjusted to control the extent of MMA polymerization (See Methods section). The mixture fully polymerizes and solidifies after 2 h, so the reaction is studied within this timeframe. To observe the degree of agglomeration during the reaction, a small amount of the mixture is extracted periodically and drop-cast onto a glass slide for fluorescence imaging. The fluorescence images from the samples extracted at 0 and 2 h of processing (Figure 2a,b) are shown with the corresponding emission spectra measured from various locations within the area (Figure 2c,d). The variability in emission decreases in the sample processed for 2 h, whereas the unfunctionalized sample generates micron-scale clusters with extremely strong emissions from these sites and weaker emissions from the other regions. The energy-dispersive x-ray (EDX) spectra of oc-RENPs and functionalized-RENPs (f-RENPs) are shown in Figure 2e,f. The spectra, obtained from the locations indicated in the inset TEM images, reveal expected peaks corresponding to the RENP constituent elements: sodium (Na), yttrium (Y), fluorine (F), ytterbium (Yb), and erbium (Er). However, the observed increase in carbon and oxygen peaks for the functionalized RENP sample validates the growth of carbon chains on f-RENPs.

The progress of the polymerization reaction is quantified using Fourier Transform Infrared (FTIR) spectroscopy. To monitor the effect of the degree of polymerization, 1 mL of the polymerized mixture is extracted every 30 min. The FTIR spectra of pure MMA and RENPs functionalized with PMMA for 120 min are shown below (Figure 2g). The peak marked at 1610 cm⁻¹, corresponding to the stretching vibration of the C≡C in the spectra of pure MMA, implies the presence of the monomer.^[21] During polymerization, the C≡C bond is broken to form C—C bonds with neighboring monomers. Consequently, the peak corresponding to the C≡C stretching vibration at 1610 cm⁻¹ vanishes as copolymerization is allowed to progress, indicating the growth of a carbon chain. The complete FTIR analysis with all measurements from the intermediate time intervals is shown in Section S3 (Supporting Information). To confirm that the carbon chains are bound to the surface, the FTIR spectrum of the f-RENPs is obtained after the NPs are washed in cyclohexane and dried (Section S4, Supporting Information). The f-RENPs show distinct

absorption peaks that are also present in the MMA monomer solution, but not in the oc-RENPs. The localized polymerization around the oc-RENPs occurs due to the interaction between the oleic acid ligands on the surface of RENPs and the MMA monomers. The oleate ligands on the surface of RENPs and QDs contain unsaturated double bonds ≈1630–1695 cm⁻¹ (Section S4, Supporting Information) that play a crucial role in promoting localized copolymerization of MMA, which enables the carbon chains to remain attached even after multiple washings.

To further characterize the growth of the carbon chains, gas chromatography-mass spectrometry (GC-MS) is conducted on a partially polymerized MMA solution without any NPs added (Section S5, Supporting Information), as the binding of chains to the NP surface prevents volatilization of the polymer for measurement. All of the measured chains fall below 2000 Da, which corresponds to a maximum chain length of roughly 18 monomer units. We surmise that the carbon chains on the oc-NP will be similar in length. It is possible that the preferential binding sites on the oleate ligand could affect the polymerization rate, but the low viscosity of the final NP/MMA solution indicates that this effect is not so significant as to change the chain length substantially in the presence of NPs.

2.2. Dispersibility/Stability of Nanoparticles in 3D-Printable Resins

Once the polymerization reaction is optimized, the f-NP dispersibility needs to be validated in a liquid photorefin. Two types of functionalized oleate-capped photoluminescent nanoparticles (RENPs and commercial CdSe/ZnS QDs) were modified and redispersed in resins to assess dispersibility, stability, and functionality. The distribution of nanoparticles in a resin can be qualitatively gauged by the transparency of the mixture, which is essential for propagation of the pump laser in two-photon polymerization (2PP) printing. The oc-RENPs, f-RENPs, oc-QDs, and f-QDs and commercial CdSe/ZnS quantum dots were mechanically dispersed into proprietary photorefin (IP-Dip and IP-Visio, Nanoscribe GmbH). Different resins were used because IP-Dip naturally fluoresces under the laser used to pump the QDs, whereas IP-Visio is designed to have low autofluorescence. Changes in resin transparency are also documented before and after the addition of oc-NPs and f-NPs (Figure 3a). While the f-NPs maintain the transparency of the polymer, the oc-NPs scatter the ambient light to generate a cloudy translucent resin, which is most clearly observed in the oc-RENP mixture. In the case of the oc-QDs mixture, the agglomeration of particles is severe enough that individual clusters can be visibly observed in the resin even after sonication for more than 12 h. Despite having the same concentration, there is a stronger color imparted to the oc-QD mixture compared to the f-QDs mixture, likely due to the optical scattering properties of clusters comparable in size to visible light wavelengths.

Fluorescence imaging of the oc-QDs in photo resin shows non-uniform dispersion with bright clusters and dark regions in between (Figure 3b). However, with f-QDs, the fluorescence throughout the resin is more uniform with few discrete clusters and less emission contrast (Figure 3c). The dispersion is also gauged quantitatively by curing a drop of each mixture on a glass microscope slide using a UV lamp and measuring the emission

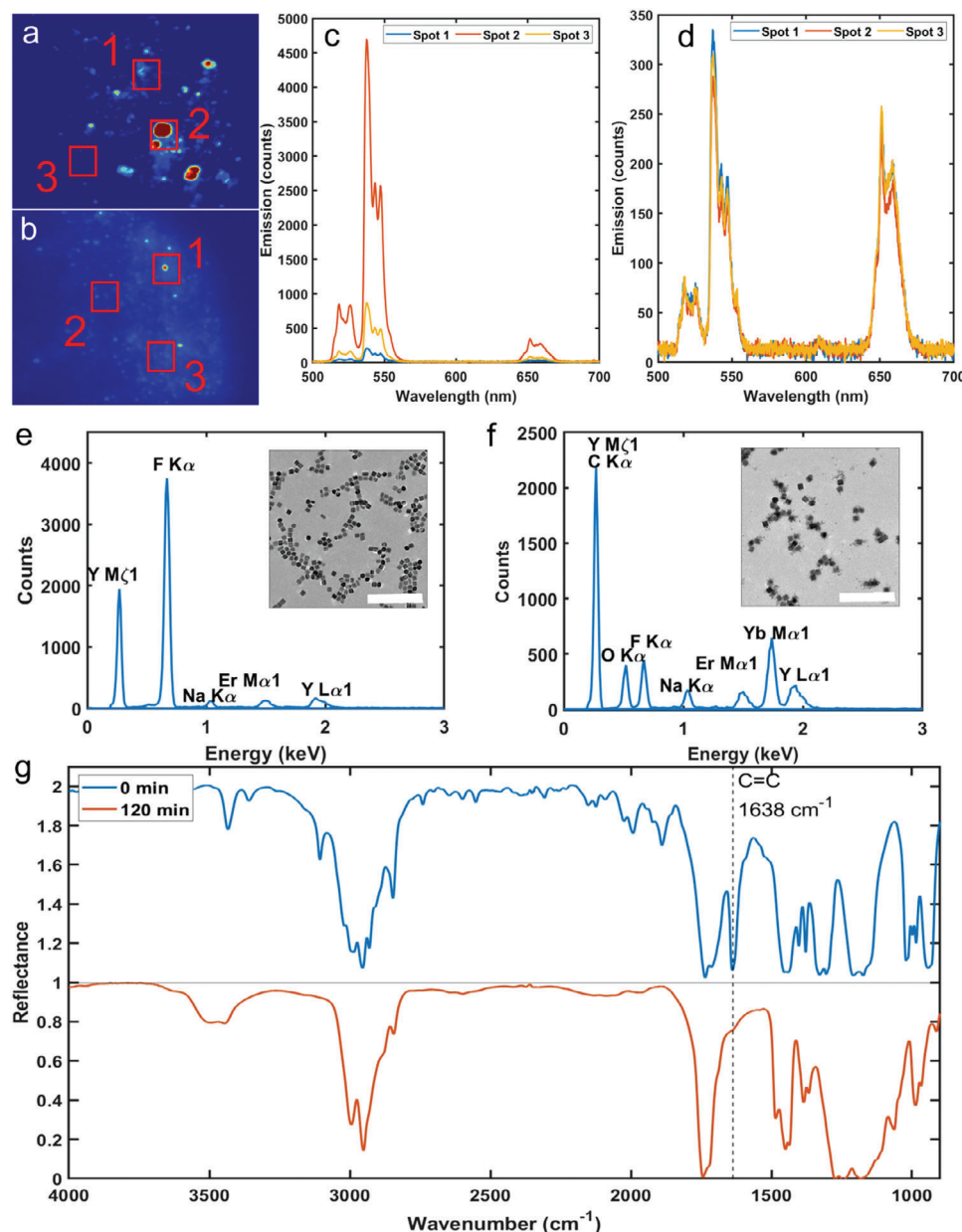


Figure 2. Characterizing polymerization progress over time. a,c,e) Upconversion fluorescence imaging after drop-casting, emission spectra for the marked locations, and the EDX spectrum with a TEM image of the MMA/RENp after 0 min of processing. b,d,f) Upconversion fluorescence imaging after drop-casting, emission spectra for the marked locations, and the EDX spectrum with a TEM image of the MMA/RENp after 120 min of processing. The scale bar on the TEM insets is 200 nm. g) FTIR analysis of the MMA/RENp solution before and after 120 min of processing showed the vanishing peak at 1638 cm⁻¹, indicating polymerization.

spectrum from various locations (Figure 3d–g). The oc-NPs show a large variation in the emission intensity from location to location due to agglomeration of emitters, whereas the f-NP emission is uniform at different locations.

To validate the dispersion of nanoparticles in low-volume structures after printing, we use two-photon 3D printing to fabricate square slabs with side lengths of 200 μm and height of 1.5 μm and map the distribution of NPs by taking images while scanning across the area with the pump laser (Section S6, Supporting Information). The height is deliberately kept small to ensure

that most nanoparticles within the slab remain in focus during imaging and that the pump is not depleted through the height of the structure. There is a clear improvement in nanoparticle loading for both the f-QDs and f-RENPs. Since fluorescence imaging of NPs is diffraction-limited, it is impossible to differentiate between individual emitters and small clusters that still fall under a single pixel. Therefore, emitter-density calculations must be generalized to the number of emitting sites (ESs) rather than individual particles. By determining the number of ESs within printed structures, we find that f-NPs have a higher ES density

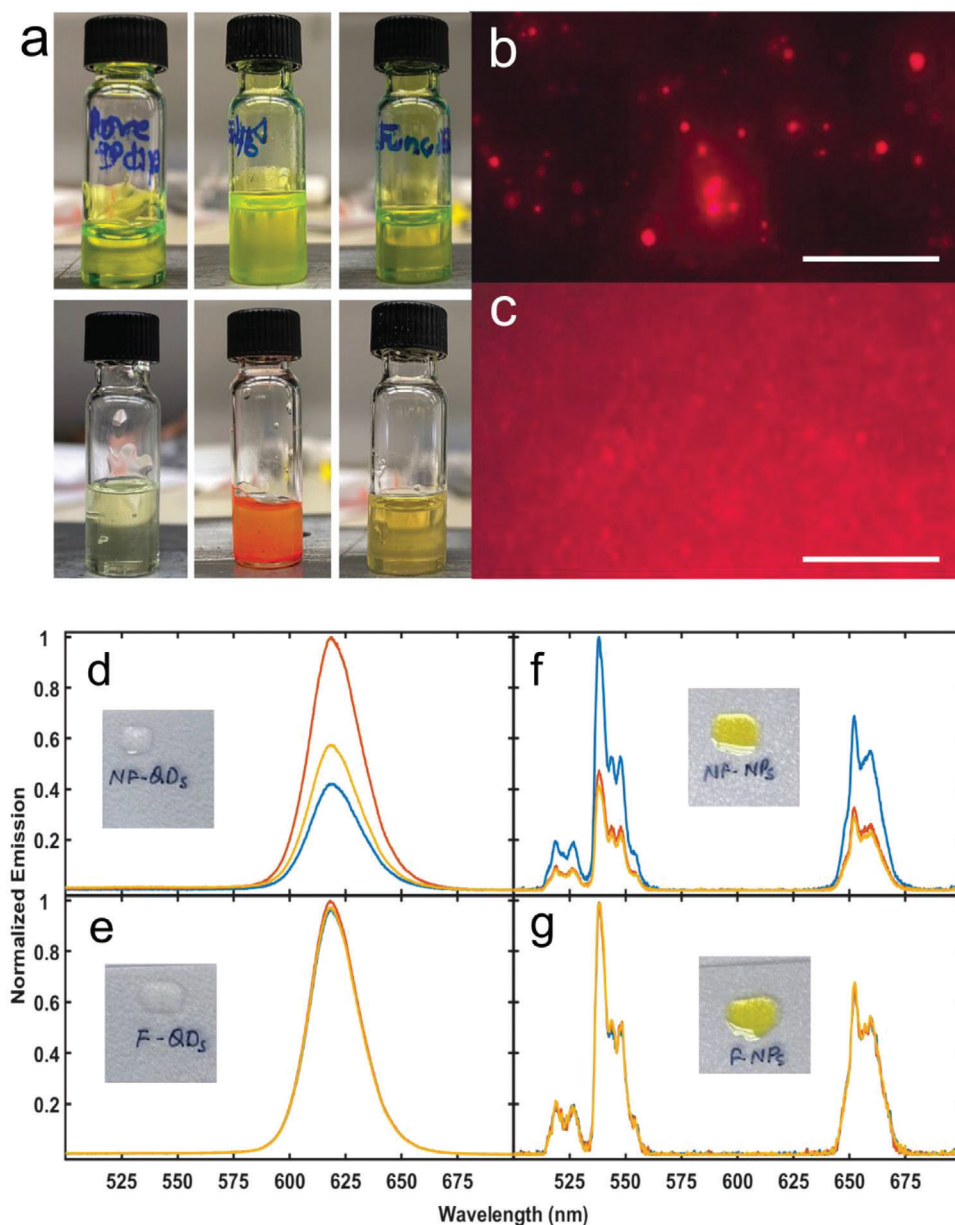


Figure 3. Dispersion of NPs in liquid IP resin. (a) Vial images showing the color and transparency of the photoresist in the pure state (left), with oc-NPs (middle), and f-NPs (right) for RENPs (top row) and QDs (bottom row). (b,c) Fluorescence images of oc-QDs (b) and f-QDs (c) after being mixed into IP-Visio. The scale bar indicates 10 μm . (d–g) Emission spectra for the oc-QDs (d), f-QDs (e), oc-RENPs (f), and f-RENPs (g) composites. The insets show the cured composites after being dropped onto a glass slide. The different colors on the plots indicate different locations from where emission was measured.

compared to oc-NPs. The ES density for oc-QDs is $1.6\text{E}15\text{ m}^{-3}$ and increases to $8.1\text{E}15\text{ m}^{-3}$ for f-QDs. Similarly, the RENPs see a density increase from $3.1\text{E}15$ to $1.19\text{E}16\text{ m}^{-3}$. It is expected that the QDs would see a more dramatic improvement in loading due to their smaller size in comparison to the RENPs. With a statistical analysis of the mean number of individual particles per ES, it is possible to convert the ES density to the nanoparticle density, but this would require a characterization method capable of resolving individual NPs within the polymer slab. However, with the data shown, it can only be claimed that the QD density is at least $8.1\text{E}15\text{ m}^{-3}$. The erbium ion density with f-RENPs was es-

timated to be $4.6\text{E}20\text{ m}^{-3}$ (Section S7, Supporting Information), which is comparable to the standard for Er-doped optical fibers used in amplifiers ($1\text{E}25\text{ m}^{-3}$ – $1\text{E}26\text{ m}^{-3}$).^[22,23] The efficiency of such devices heavily relies on the emitter loading. Lower loading of emitters inherently generates a weaker output, but excessively high loading can also suppress output emissions by means of concentration quenching and other dissipative pathways.^[24]

To further characterize the uniformity of each distribution, the mean width of the ESs in each sample is also extracted from NP dispersion maps. The mean number of pixels for each ES is reduced for both types of functionalized NPs, by 40% for the QDs

(3.77 pixels/EC–2.45 pixels/EC) and 58% for the RENPs (7.34 pixels/ES–3.08 pixels/ES). Minimizing the mean size of ECs is essential to the development of polymer-based emitting displays, where a finer dispersion of NPs enables higher-quality color mixing using different QD sizes as well as a more evenly lit pixel, which can improve the total image quality.

The stability of the dispersion of NPs in photo resin is also critical to their printing performance and commercial viability. To achieve uniform nanocomposites, it is essential that NP dispersions can be sustained for extended periods of time. For oc-NPs, the primary source of agglomeration is the depletion force between NPs in a multicomponent solution.^[25] Depletion-induced attraction is typically described using the hard-sphere analogy, which is reasonably applicable to the NPs considered in this work.^[26] Each particle has an “exclusion zone” with a radius approximately double that of its own, which describes the volume within which other solute components are pushed away.^[27] As the interparticle spacing decreases below the diameter of a single particle, the exclusion zones cross, and solute molecules (photoresin, initiators, inhibitors, etc.) are pushed aside, leaving regions depleted of any solute and generating an attractive osmotic pressure. This mechanism is also the reason that agglomerated NPs can be difficult to re-disperse, effectively shortening the shelf life of a suspension. However, theoretical analyses and simulations of NP suspensions have shown that the attractive forces between NPs are overcome as the interparticle distance increases and other solute molecules can move freely.^[26,28,29] Therefore, it is expected that carbon chains with lengths comparable to the NP diameter can prevent the interparticle distance from entering the depletive regime and enable longer periods of stability. From the conservative estimate of 6–10 units/chain obtained from molecular weight measurements (Section S5, Supporting Information) and the published Kuhn length of PMMA (1.5–1.7 nm), the chain length can be estimated as roughly 10nm–20nm.^[30] This, in turn, implies an interparticle spacing of 20–40 nm (depending on chain orientation/bending), which satisfies the general criterion for QD stability. For the RENPs, improvements to dispersibility and stability were still observed, but both can likely be improved by allowing chain lengths to approach 60–65 nm. However, further process optimization is required to controllably achieve longer chains without complete polymerization of the PMMA.

The stability of each NP dispersion is studied for multiple weeks for both NP/photoresist mixtures. In the case of the oc-NPs, 70 mg of oc-RENPs and 0.25 mg of oc-QDs are mechanically dispersed in IP Dip and IP Visio, respectively, without any modifications. The nanocomposites are left undisturbed for the duration of the study without any sonication or physical shaking, and the fluorescence of each vial under illumination by a pump laser is imaged at 0 days and 14 days after functionalization. Visual assessment of laser propagation quality and emission distribution at various depths of the oc-NP and f-NP mixtures is compared (Figure 4a,b). In a cloudy mixture, the laser is either scattered or absorbed to the point that the beam is dissipated before reaching the other end of the vial, while the clearer vials enable the laser to pass through as a relatively undisturbed beam. Both functionalized and non-functionalized particles are stable on the first day of dispersion with uniform emission distributions (Figure 4a). However, after 2 weeks, uneven emission distribution is observed

throughout the vial for oc-RENPs and oc-QDs, with less emission at the top and more scattering at the bottom. In contrast, uniform emission is visible throughout the vial for f-RENPs and f-QDs, indicating a stable distribution of both RENPs and QDs in their respective 3D printable resin. Emission spectra were also recorded for both f-NPs at the same time points (0 and 14 days). The spectra were recorded at three different points on the sample and showed a minimal drop in emission after 2 weeks (Figure 4c). In the oc-RENP mixture, there are pronounced changes in the fluorescence intensity as the RENPs settle down over time, but in the f-RENPs, the fluorescence shape is relatively consistent over the duration of the test. Even though the confinement of fluorescence around the pump beam path is clear for the two-photon fluorescence of the RENPs, the single-photon fluorescence of the QDs allows the beam to excite a wider radius despite the beam waist being smaller. This is largely because the emission spectrum of QDs partially overlaps with the excitation spectrum, allowing for neighboring QDs to be excited by the emissions from QDs in the pump beam path. Therefore, the beam appears diffuse even in the better-dispersed f-QD mixture. The agglomeration in the oc-QDs is emphasized by the brighter fluorescence on the right side of the vial where the pump beam is located. The fluorescence intensity drastically decreases over the length of the vial, showing that a significant amount of pump power is dissipated through absorptive bands and scattering.

For quantitative analysis of the stability, the f-NPs are measured using UV–vis spectroscopy over multiple days (Figure 4d,e). Measurements taken after sonication and after five days show no significant differences in the absorbance spectra, such as spectral shifts or variations in intensity. This consistency suggests that the f-NPs maintain their optical properties without experiencing aggregation, degradation, or chemical alteration over this period. The stability observed over the five days can be attributed to the functionalization of the nanoparticles, which provides steric and osmotic stabilization, preventing them from aggregating or reacting with their environment. The unchanged absorbance profile indicates that the functional groups on the nanoparticles effectively prevent any significant interactions or structural changes.

2.3. Printed Structures with Functionalized Nanoparticles

In 2PP printing, polymerization is achieved through two-photon absorption of near-infrared (NIR) photons, which can propagate through polymer resins at lower intensities.^[31,32] Tightly focusing the NIR beam creates a small volume with sufficient power at the focal point for absorption-induced polymerization to occur, while leaving the surrounding volume unaffected (Figure 5a). The resolution capabilities of 2PP-printing are defined by this volume, known as the voxel. While printing, the voxel is often made to overlap with the substrate to ensure adhesion of printed structures. To ensure that the voxel reaches the surface of the substrate, the objective lens is immersed in the photoresist droplet, enabling the use of objectives with lower working distances and higher numerical apertures. After the desired structures are printed, the excess liquid resin is washed away using an organic solvent like propylene glycol methyl ether acetate (PGMEA), followed by an additional wash with isopropanol (IPA).

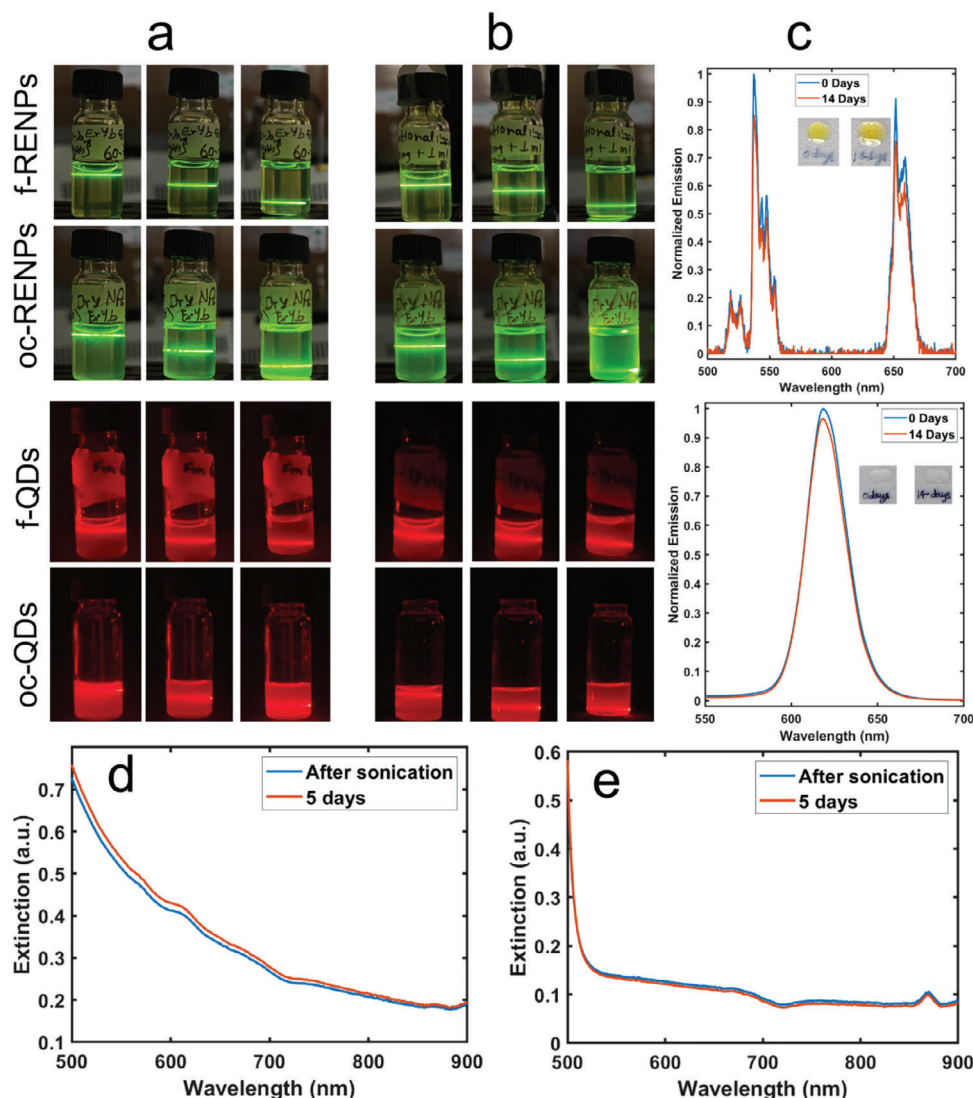
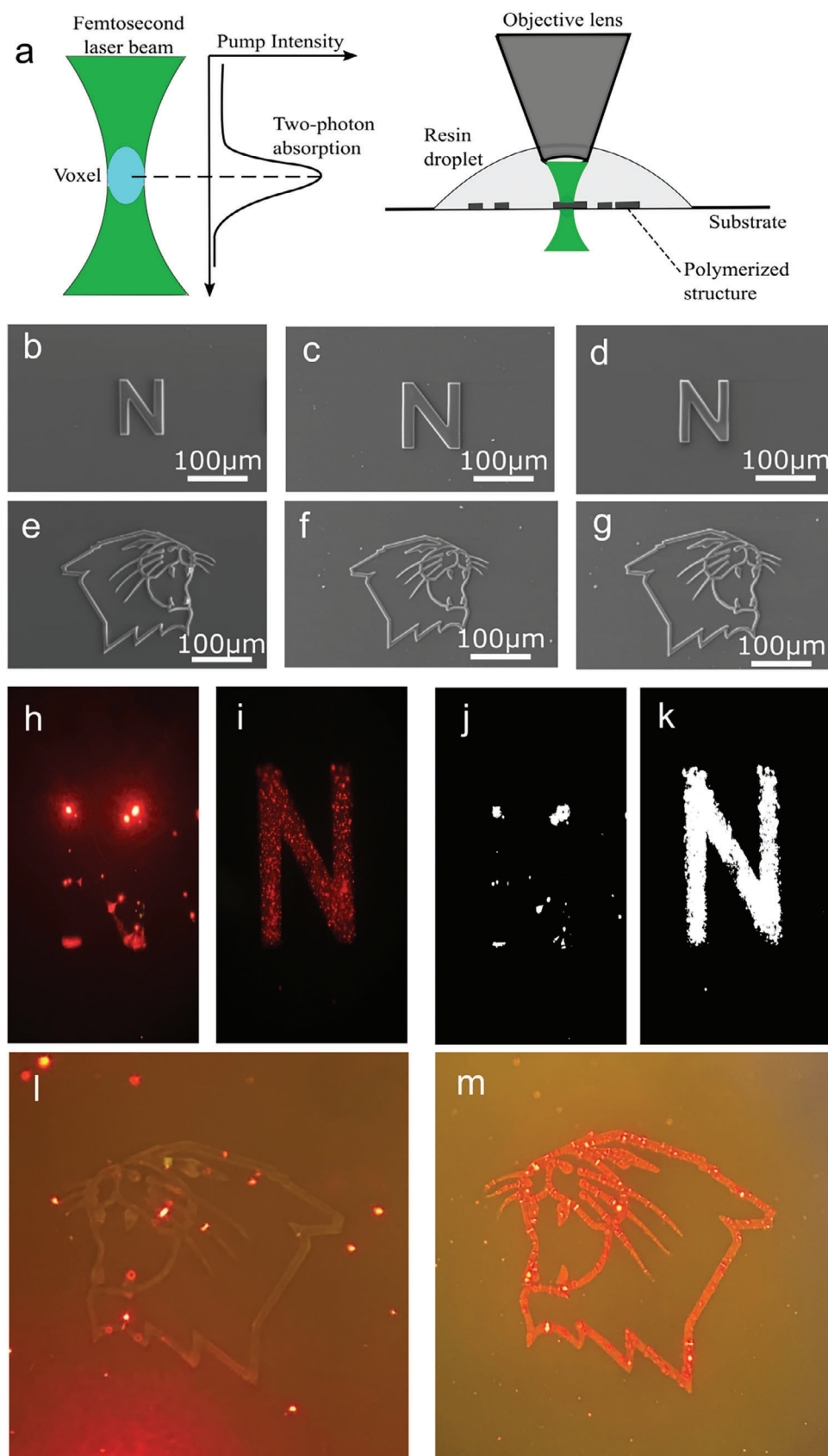


Figure 4. Stability of f-NPs and f-QDs in IP-Dip and IP-Visio, respectively. (a) initial stability of f-NPs and f-QDs on day 1 using NIR and green lasers for RENPs and QDs, respectively, the emission is compared with oc-RENPs and oc-QDs vials (b) stability after 2 weeks showed uneven emission in oc-RENPs and oc-QDs compared to the emission from f-RENPs and f-QDs vials (c) Emission spectra over 2 weeks with a minimal drop in emission averaging three points. (d,e) the UV-Vis spectra of (d) f-QDs and (e) f-RENPs immediately after sonication and after five days.

To highlight the effect of improved dispersibility in the printed structures, some example designs are printed using the f-RENP and f-QD mixtures. Momper et al. highlight how scattering and absorption from NP clusters lead to substantial deformations or resin degradation in the printed structures.^[19] However, our prints show that f-NP photoresin composites achieve printing qualities comparable to unmodified resins (Figure 5b–g). The oc-QD and f-QD prints of the letter N (Figure 5h,i) are processed in ImageJ (Figure 5j,k) to find the integrated pixel intensity. An increase in intensity by almost two orders of magnitude is observed in the f-QD print (Section S8, Supporting Information). To similarly test the functionalization method with a structure involving finer features, the Northwestern Wildcat logo is printed over an area of $\approx 200 \times 200 \mu\text{m}$ (Figure 5l,m) with the smallest features, like the whiskers, having a width of $\approx 500 \text{ nm}$ as measured by SEM (Section S9, Supporting Information). It is evident that even

sub-micron features can still be printed with the same quality as the pure polymer. The images are well-resolved despite the small regions with lower concentrations of nanoparticles, whereas the oc-QD prints are almost unidentifiable without any background contrast. A similar comparison is also made for the RENPs in the N-shaped structure, but the quality of the images is limited by pump power (Section S10, Supporting Information). Both types of f-NPs are mostly contained within the smaller features of the prints, indicating that the functionalization method can be utilized for a variety of micro-photonic applications.

Overall, our functionalization method demonstrates a strong improvement in nanoparticle dispersibility in 3D-printable resins, but certain aspects of our approach still require improvement. As shown in Figure 5i, some clusters can still be observed in printed structures. Since the NP suspensions show long-term stability, we believe that these clusters come from the



agglomeration of NPs during extraction from their native solvent prior to functionalization. While the partial polymerization process keeps individual NPs separated, it can also cement existing NP clusters and prevent them from being mechanically separated by sonication. We expect that this can be alleviated with proper filtration of larger clusters prior to functionalization, effectively only allowing single NPs to be functionalized. Another issue is the presence of residual NPs on top of printed structures and regions of the substrate without printing. Sonication during development was found to be effective for removing excess NPs, but the vibrations also damaged the printed structures on occasion. It is likely that extremely light stirring of the solvent during development would remove clusters from the surface while allowing the structures to remain intact. Finally, outside of restricting the polymerization time to 120 min, the control over the reaction rate is somewhat limited, and the reaction rapidly accelerates to completion soon after. It would likely be beneficial to explore chemical inhibitors and other targeted means of stopping the reaction for growing chains on larger particles.

3. Conclusion

In this work, we have developed a surface-functionalization method for oleic acid-capped NPs that reduces agglomeration in nonpolar polymers. Our method functionalizes short PMMA chains alongside native oleic acid ligands onto the surface of NPs. This allows for separation and re-suspension of functionalized NPs into a variety of photoresins and circumvents the need for ligand stripping. Our method is validated on different fluorescent NPs with sizes ranging from 10 to 60 nm using multiple resins compatible with 2PP printing. Functionalized NP suspensions remain stable over extended time periods (at least 14 days) compared to oc-NPs. Using these nanocomposite resins, printed structures with varying feature sizes show that the printing quality is not compromised by the introduction of the f-NPs. Ultimately, by providing a route toward uniform NP dispersion in photoresins, this work marks an important step toward increasing the resolution and quality of 3D-printed nanostructures for active photonic and optical applications.

4. Experimental Section

Materials: $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, oleic acid, 1-octadecene, sodium hydroxide, ammonium fluoride, methanol, n-Butyl acetate, methyl methacrylate, 2,2'-azobis-isobutyronitrile were purchased from Sigma Aldrich. All chemicals were of analytical grade and utilized without further purification. Commercial photo-resins (IP Dip and IP Visio) were obtained from Nanoscribe GmbH. The quantum dots were acquired from NNCrystal US Corporation under the product number HECZ620-25.

Synthesis of oc-RENPs: The core/shell RENPs were synthesized using thermal decomposition method from previously reported articles.^[33,34] The Supporting Information offers a detailed explanation of the synthesis process.

Table 1. Dispersion of f-RENPs and f-QDs in 3D printable resin.

Particles	Size	Used 3D printable resin	Concentration	Sonication
RENPs	50–65 nm	IP-Dip (1 mL)	60 mg mL ⁻¹	20 min
CdSe/ZnS QDs	8–12 nm	IP-Visio (1 mL)	2.5 mg mL ⁻¹	20 min

Carbon Chain Growth: The chemical composition was adapted from the article reported by Yang et al.^[18] In a single-necked flask, 10 g of MMA was combined with 2 mL of n-Butyl acetate and 0.01 g of 2,2'-azobis-isobutyronitrile was utilized to grow carbon chain on NPs (as shown in Figure 1b). Following pre-polymerization at 70 °C for 2 h, 4 mL of n-Butyl acetate containing 0.2 mmol of oc-NPs (RENPs and QDs) was added into the flask dropwise. Subsequently, the temperature of the flask was increased from 70 to 95 °C for copolymerization. The temperatures for the pre-polymerization and copolymerization steps have been adjusted from the published procedure, with 70 °C for pre-polymerization and 95 °C for copolymerization observed to give the desired growth of the carbon chain. At 120 min, the f-NPs were retrieved by centrifugation of the nanocomposite at 3000 rpm for 15 min. The f-NPs were washed in cyclohexane to remove any unbound polymer chains and centrifuged again for extraction.

Dispersion of f-NPs in Resin: All 3D printable resins were commercial and were used without any purification or modification. The f-NPs were directly dispersed in the IP resist. After adding the f-NPs, the mixture was sonicated for uniform dispersion. The f-RENPs and f-QDs both required 20 min of sonication for uniform dispersion. More details about the particle size, concentration, and dispersion are shown in the following table (Table 1).

2PP Printing Parameters: 2PP printing was performed using the NanoScribe Photonic Professional (GT) 3D printer. The structures were printed inside a small droplet of 3D printable negative photoresin (IP-Dip/IP-Visio) using dip-in laser lithography. A 25x N.A immersion objective was used to focus the laser at the voxel point, and a standard glass microscope slide was used as the substrate. After printing, the excess resin was rinsed off the structure via immersion in propylene glycol methyl ether acetate (PGMEA) for 15 min, followed by immersion in isopropanol (IPA) for 5 min. The printing parameters, such as scan speed and laser power, were optimized for the resin type and the structure morphology.

Measurements/Imaging: All emission spectra were collected using a Nikon Ti-U inverted microscope connected to a cooled Andor Newton 971 EMCCD camera through an Andor SR-303i monochromator. The pump sources were a PicoQuant LDH-P-C-375 laser for the quantum dots and a PicoQuant LDH-D-C-975 laser for the RENPs. For the stability images involving the pump laser, the QD vials were illuminated with a PicoQuant LDH-P-C-510 instead of the UV laser to prevent the IP-Visio from polymerizing. NP dispersion maps were constructed by scanning the elliptical beam spot of each laser across the sample area using a translation stage as a laser mount and stacking the resultant images. Both the emission spectra and the NP dispersion maps were collected using a Nikon 20x/0.4 objective lens. Fluorescence images for the QD samples were taken using a Zeiss Axio Observer Z1.m inverted microscope. The pump source was a broadband tungsten lamp with a 450 nm long-pass dichroic mirror to isolate the pump wavelengths. UV-vis spectra were obtained using the Agilent Technologies Cary 60 UV-vis. Infrared reflectance measurements were conducted with a Bruker Vertex 70 FTIR coupled to a Bruker Hyperion 3000 microscope. Gas chromatography-mass spectrometry measurements were done using the Bruker Rapiflex MALDI-TOF, using FlexControl data acquisition software, and processed using FlexAnalysis software for data analysis.

Figure 5. Overview and analysis of printed structures using composite resins. a) A schematic of the 2PP-printing process. b–g) SEM images of the printed N (top) and wildcat (bottom) designs using pure resin (left), f-RENPs (middle), and f-QDs (right). Fluorescence images of the N structures for oc-QDs (h) and f-QDs (i). j,k) ImageJ decompositions of (h) and (i) for integrated intensity calculations. l,m) Fluorescence images of the wildcat design using the oc-QD (l) and f-QD (m) composites.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

3D printing, dispersion, functionalization, nano-emitters, two-photon polymerization

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