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Gold Nanorod-Enhanced Light Emission in Quantum-Dot-Doped Polymer Nanofibers

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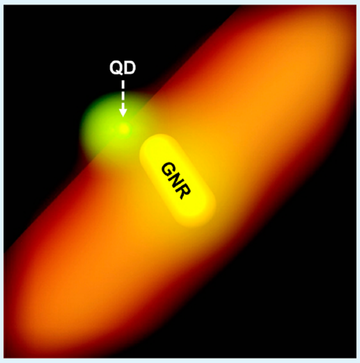
ABSTRACT: One-dimensional nanomaterials have attracted great interest in both fundamental research and technological applications because they can function as device elements and be used to effectively generate, guide, and detect light. Here we report a gold nanorod-enhanced light emission in quantum-dot-doped polymer nanofibers. By incorporating gold nanorods into quantum-dot-doped polymer nanofiber, a 67% increment in 600 nm red light emission efficiency was obtained with an extinction coefficient of 100 cm^{-1}, a low excitation power operation of 100 nW, and a 100 min increment in photostability.



KEYWORDS: *gold nanorod, enhancement, quantum dot, light emission, polymer nanofiber*

Polymer nanofibers are cheap and flexible building blocks for nanophotonic components.[1−7] For high-density nanophotonic integration, both passive and active polymer nanofibers are desirable. In contrast to passive polymer nanofibers, active polymer nanofibers are more desirable because they can act as a light source and waveguide simultaneously. To get active polymer nanofibers, efforts have been focused on light-emitting conjugated polymer nanofibers,[3] dye-doped polymer nanofibers,[4,5] quantum-dot-decorated polymer nanofibers,[6] and quantum-dot-doped polymer nanofibers.[7,8] Among them, quantum-dot-doped polymer nanofibers have been demonstrated as feasible active nanowaveguides, but due to the limitation of self-absorption of the excited light, the concentration of doped quantum dots (QDs) is less than 5.5 $\times 10^3$ μm^{-3}, whereas the light emission efficiency is 10.9%.[8] Therefore, it is difficult to increase light emission efficiency in QD-doped polymer nanofibers simply increase QDs concentration. Fortunately, enhancement of fluorescence by interaction with plasmon resonances of metal nanostructures is a well-established approach to control the rate and efficiency of emission.[9,10] Usually the plasmon-enhanced fluorescence effect are realized in the form of thin films or solutions,[11−13] and employ a free space optical system for excitation and photoluminescence (PL) collection. Compared with those two- and three-dimensional systems, one-dimensional polymer nanofibers may offer a smaller footprint and tighter optical confinement for plasmon-enhanced fluorescence applications with higher density integration, lower power consumption, and better compatibility with nanophotonic circuits. Therefore, in this work, we demonstrate that light emission efficiency can be enhanced by incorporating gold nanorods (GNRs) into low concentration of QDs doped polymer nanofibers.

Polyvinylpyrrolidone (PVP), GNRs, and CdSe-ZnS core−shell QDs were purchased from Boai NKY, NanoSeedz, and Zkwy Bio-Tech, respectively. Figure 1a shows that PVP has a relatively high optical transparency (>80%) in the visible spectral range. Figure 1b shows the extinction spectrum and TEM image of GNRs, whereas Figure 1c shows the absorption and normalized PL spectra of the CdSe-ZnS core−shell QDs.

The GNRs and CdSe-ZnS core−shell QDs codoped polymer nanofibers were fabricated by a direct drawing method from polyvinylpyrrolidone (PVP, $n = 1.48$) ethanol solution. Fabrication details of polymer nanofibers as follows: First, 0.598 g of PVP was dissolved in 0.7 mL of anhydrous ethanol to form homogeneous PVP ethanol solution. Second, 60 μL of GNR (40 nm in diameter, 72 nm in length) aqueous solution (concentration 3.32 $\times 10^{10}$ per mL) and 300 μL of CdSe-ZnS core−shell QD (4.9 nm in diameter) aqueous solution (concentration 4 μM/L) were diluted into PVP ethanol solution. The mixture was then stirred at room temperature for 2 h and followed by 30 min ultrasound, finally a uniform solution with an appropriate viscosity was obtained for drawing. Third, the tip of a tapered silica fiber (diameter ~125 μm) was immersed into the mixture solution for 1−2 s and then pulled out with a speed of 0.1−1 m/s, leaving a GNRs and QDs codoped PVP wire extending between the solution and the fiber tip. With very fast evaporation of the ethanol and finally, a naked polymer nanofiber doped with GNRs and QDs was formed. For comparison, CdSe-ZnS core−shell QD-doped polymer nanofibers were also fabricated by the same method,

Received: June 6, 2014
Accepted: July 15, 2014
Published: July 15, 2014

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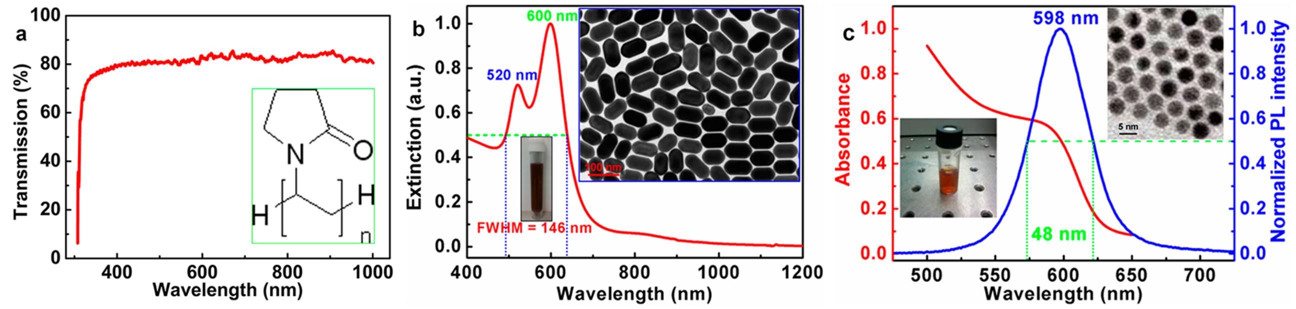
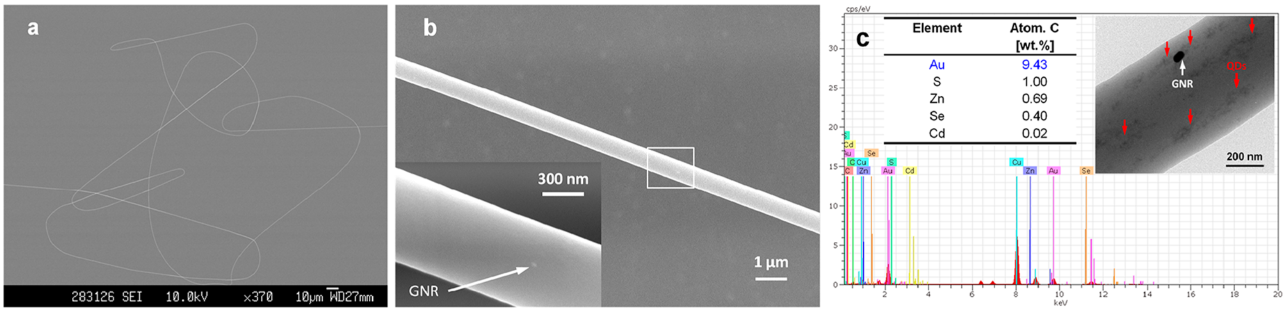


Figure 1. (a) Transmission spectrum and molecular structure of PVP. (b) Extinction spectrum and TEM image of GNRs. Photograph of GNRs solution also shown. (c) Absorption and normalized PL spectra of QDs. Inset: photograph (left) and TEM image (top right) of QDs solution.



Element	Atom. C [wt.%]
Au	9.43
S	1.00
Zn	0.69
Se	0.40
Cd	0.02

Figure 2. SEM image of a GNRs and CdSe-ZnS QDs codoped polymer nanofiber and analysis. (a) Coiled single nanofiber. (b) 630 nm diameter straight nanofiber. (c) EDS spectrum and TEM image of a 560 nm diameter nanofiber.

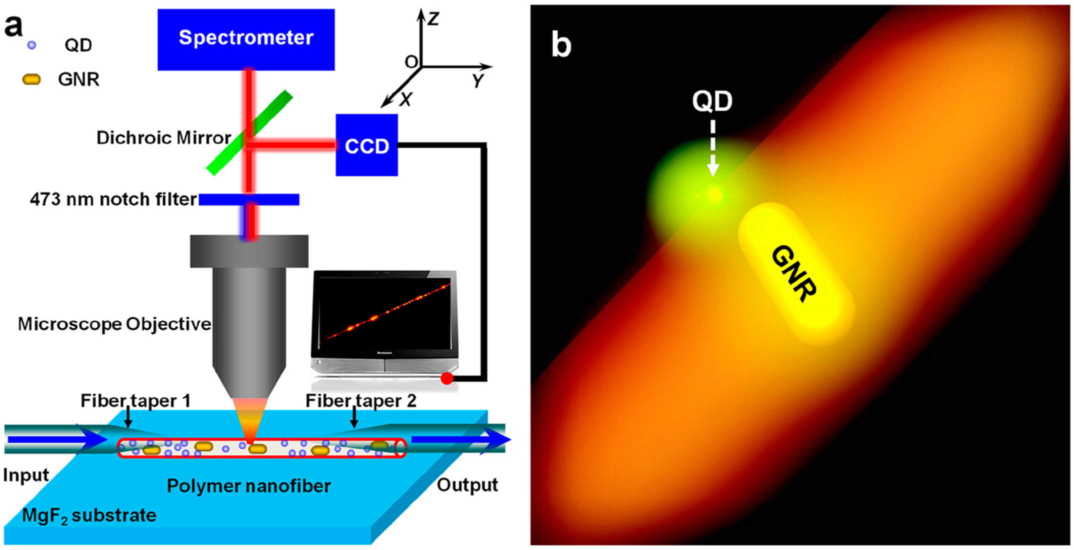


Figure 3. (a) Optical setup for characterization. (b) Schematic shows gold nanorod-enhanced light emission in quantum-dot-doped polymer nanofiber.

just adding 300 μL of QDs aqueous solution into PVP ethanol solution (0.598 g of PVP dissolved in 0.7 mL of anhydrous ethanol) to ensure that they have same QDs concentration.

Figure 2a shows a typical scanning electron microscope (SEM) image of a coiled single polymer nanofiber (average diameter ~500 nm, length ~2 mm) containing GNRs and QDs. Figure 2b shows a typical SEM image of a polymer nanofiber that contained GNRs and QDs with a diameter of 630 nm. To closely inspect the GNRs and QDs distribution in the nanofiber, we performed energy-dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) (operated at 300 kV). Figure 2c shows EDS analysis of a representative nanofiber, whereas the inset shows the TEM image of a 560 nm diameter nanofiber, in which the maximum diameter variation $\Delta D \approx 20$ nm over a length $L = 681$ nm. The GNR (as indicated by white arrow) and QDs (as indicated by red arrows) were doped in the nanofiber. The EDS analysis confirms the existence of Au (9.43 wt %), S (1.00 wt %), Zn (0.69 wt %), Se (0.40 wt %), and Cd (0.02 wt %) elements. The estimated concentration of the GNRs and QDs are 4 μm^{-3} and 3.2×10^3 μm^{-3}, respectively.

Figure 3a shows a schematic of an optical experimental setup. Light from a 473 nm continuous-wave laser was coupled into one end of the polymer nanofiber using a fiber taper 1. The photoluminescence (PL) was picked up using a long working distance objective. Dichroic mirror and 473 nm notch filter

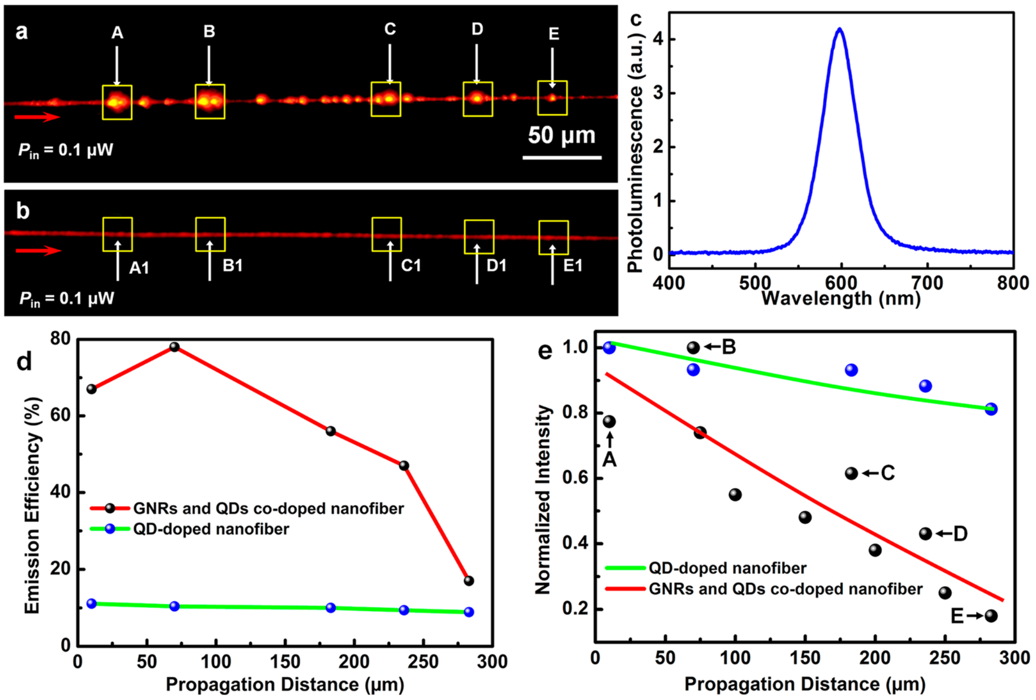


Figure 4. Optical microscope images of (a) GNRs and QDs codoped nanofiber and (b) QD-doped nanofiber. The scale bar in a is applicable in b. The red arrow shows the propagation direction of the light while the yellow line squares show the sum-up region. (c) Representative PL spectrum of QD-doped polymer nanofibers. (d) Red light emission efficiency at different positions along the nanofibers. (e) Normalized intensity of red light along the nanofibers versus propagation distance.

(emission filter) were placed between the samples and the detectors (the spectrometer and the CCD). The excited 600 nm red light was coupled out using a fiber taper 2. The power of the excited red light was measured by an optical power meter (OPHIR NOVA II) integrated with a photodiode (OPHIR PD300-UV). Figure 3b schematically shows gold nanorod-enhanced light emission in quantum-dot-doped polymer nanofiber.

To investigate optical properties, a single GNRs and QDs codoped PVP nanofiber was laid on MgF_2 (n = 1.39) substrate. A 473 nm blue light was coupled into the polymer nanofiber by evanescent coupling method. Figure 4a shows its optical microscope image with red light emission excited by the blue light with an optical power of P_{in} = 0.1 μW, in which positions A−E indicating gold nanorod-enhanced light emission from QDs for measurement. For comparison, a single QD-doped polymer nanofiber, which has similar diameter and QD concentration as the GNRs and QDs codoped polymer nanofiber, was also excited by the blue light with an optical power of P_{in} = 0.1 μW (Figure 4b). Figure 4c shows a representative PL spectrum of QD-doped polymer nanofibers.

To calculate emission efficiency of the excited red light from QDs doped in the polymer nanofiber, we define light emission efficiency $\zeta = P_{em}/(P_{in}\eta)$,[8] where P_{em} is the excited red light power along the polymer nanofiber, P_{in} is the injected blue light power at the input end of the nanofiber. The coupling efficiency $\eta \approx 90\%$, which is attributed to the tapered fiber and the nanofiber is in parallel and contacted each other tightly by the van der Waals force. By measuring the red light power at position A (60 nW), B (70 nW), C (50 nW), D (42 nW), E (15 nW), A1 (10 nW), B1 (9.4 nW), C1 (9 nW), D1 (8.5 nW), and E1 (8 nW) using a fiber taper, which was moved step by step to different positions along the polymer nanofiber, the calculated corresponding $\zeta \approx$ 67, 78, 56, 47, 17, 11.1, 10.4, 10, 9.4, and 8.9%. Figure 4d shows the light emission efficiency at positions A−E (with GNRs) and positions A1−E1 (without GNRs). The emission enhancement reaches the maximum at position B in which plasmon wavelength is equal to emission peak wavelength of QDs.[14−16] The mechanism of the enhancement on the QD emission is as follows: First, by injecting a 473 nm blue light into nanofiber, the doped QDs are excited and emit 600 nm red light. Second, the 600 nm light excites the localized plasmon resonance of GNRs which results in an enhancement of local electromagnetic field. Third, the locally enhanced electromagnetic field increases the stimulated radiative decay rate of QDs in the coupled exciton−plasmon system, thus resulting in the increase of quantum yields and the decrease of fluorescence lifetime.[17] As a result, the QD emission is enhanced under the same excitation power. Theoretically, quenching effect maybe occur because electrons can easily be transferred from QDs to GNRs when the QD is very close to a GNR. Although this effect was not observed in our experiment, it could be achieved via proper materials, architectures, and excitation light. For example, PL quenching of QDs by gold nanoparticles has been reported in previous work.[18,19] Enhancement of light emission can be attributed to an increase in the local density of optical states in the vicinity of the GNRs, which explains the locally enhanced unevenly distributed bright PL spots along the polymer nanofiber shown in Figure 4a. To improve the discontinuous behaviors of emission light, we can link QDs and GNRs by direct chemical coupling method with the assistance of molecular/biological linkers,[13,17] which will ensure their interaction. It is worth noting that the emission efficiency ζ of the red light is related to quantum efficiency of the QDs, self-absorption of the excited light by QDs, surface plasmon resonant properties of GNRs, and propagation loss of the excited red light. To measure the PL intensity, the optical microscope images were transformed from the RGB (additive

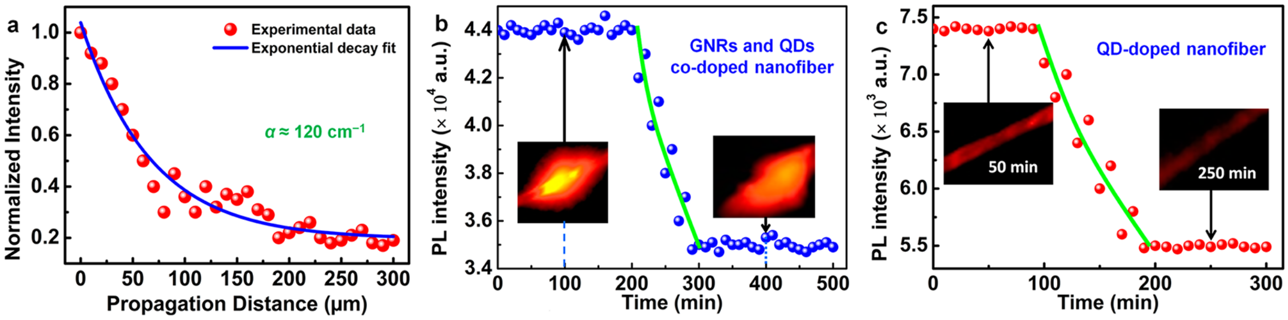


Figure 5. (a) Normalized intensity of blue light in the polymer nanofiber as a function of propagation distance. (b) PL intensity of GNRs and QDs codoped polymer nanofiber and (c) QD-doped polymer nanofiber as a function of time. Insets: PL images of polymer nanofibers.

color) mode to gray levels using Adobe Photoshop, and then summed up the gray values to obtain the corresponding intensity as reported in previous work.[20] In this work, the sum-up region is considered as a rectangular region as indicated by the yellow line squares in panels a and b in Figure 4 with a size of 21 × 18 μm^2. The results are I_A = 256145, I_B = 330981, I_C = 203493, I_D = 142452, and I_E = 59525 for GNRs and QDs codoped polymer nanofiber while I_{A1} = 43332, I_{B1} = 40429, I_{C1} = 40394, I_{D1} = 38255, and I_{E1} = 35174 for QD-doped polymer nanofiber. Figure 4e shows the normalized intensity of red light along the GNRs and QDs codoped polymer nanofiber (red line) and QD-doped polymer nanofiber (green line) as a function of propagation distance. The extinction coefficient γ = 100 cm^{-1} for GNRs and QDs codoped polymer nanofiber and γ = 68 cm^{-1} for QD-doped polymer nanofiber, which were calculated according to the equation: $I = I_0\exp(-\gamma d)$,[3,4,20] where I_0 is the initial PL intensity, I is the measured output PL intensity, and d is the propagation distance. Similar extinction coefficients were determined for several other polymer nanofibers studied under same conditions. It is worth noting that waveguiding properties are affected by the presence of gold nanorods. The extinction coefficient of GNR- and QD-codoped polymer nanofiber being larger than that of QD-doped polymer nanofiber can be attributed to the increased scattering induced by gold nanorods. In addition, possible local regions with nonuniform refractive index, GNR density, or crystallinity produce bulk scattering in the GNR- and QD-codoped nanofiber. These local regions affect the resulting emission, whose PL intensity exhibits abrupt enhancement along the nanofiber axis and higher local optical losses.

The absorption of the injected blue light in the polymer nanofiber was estimated by measuring the output optical power at different positions along the nanofiber using the fiber taper 2 as shown in Figure 3a, which was connected to an optical power meter. We basically assumed 473 nm blue light was confined within the polymer nanofibers. For instance, light confinement in polymers may suffer due to their low refractive index, n. For this reason, polymer nanofibers are generally based on passive high-n resists, possibly incorporating inorganic or metallic nanostructures (e.g., QDs and GNRs), which can modify the local photonic environment of the polymer nanofibers.[21,22] Thus, the absorption coefficient measurement using Lambert–Beer Law was acceptable. Figure 5a shows the measured normalized optical intensity. It was found that the intensity is exponentially decreased with increasing propagation distance along the nanofiber, obeying the Lambert–Beer law: $I = I_0\exp(-\alpha d)$.[3,4,8,20] The blue line in Figure 5a is the fitting curve of the experimental data according to first order exponential decay fit. The calculated absorption coefficient α is about 120 cm^{-1} for 473 nm blue light. The absorption coefficient α = 120 cm^{-1} is for both the QD-doped nanofiber and the codoped nanofiber. The injected light absorption is mainly due to the doped QDs. The absorption from GNRs is negligible because 473 nm is beyond the FWHM of GNRs extinction spectrum. The extinction coefficient γ indicates waveguiding properties of excited 600 nm light while absorption coefficient α indicates the absorption of nanofiber to injected 473 nm light. The relatively high absorption coefficient indicates that the injected blue light was efficiently absorbed by the QDs, which is desirable in active polymer nanofibers. Photostability is one of the most important concerns for practical applications of active polymer nanofibers. The result was measured by collecting PL emissions at positions from GNRs and QDs codoped polymer nanofiber with an interval of about 10 min. The PL intensity almost remained unchanged for 200 min (Figure 5b), but dramatically decreased from 200 to 300 min, which is an irreversible photochemical reaction.[7,8] After 300 min, about 80% of initial PL intensity still remained. For reference, the photostability of QD-doped polymer nanofiber was also measured (Figure 5c). The photobleaching of QDs under laser excitation can be attributed to the nonradiative transfer in excited QDs.[23] As long-term high-stability dopants in polymer nanofibers, GNRs are intrinsically immune to photobleaching.[22] Incorporation of GNRs changes the local photonic environment of QDs and reduces nonradiative transfer resulting in a much higher photostability.[24] These indicate that the photostability of GNR- and QD-codoped polymer nanofibers increases 100 min, which makes the GNR- and QD-codoped polymer nanofibers much more promising candidates for practical applications.

In conclusion, we demonstrate a facile strategy based on plasmon-enhanced fluorescence effect for realizing light-emission enhancement in QD-doped polymer nanofibers. The polymer nanofibers exhibit PL efficiency (78%), higher photostability (100 min increment), relatively high absorption coefficient (120 cm^{-1}), and low extinction coefficient (100 cm^{-1}) for guiding excited 600 nm red light under optical wave guiding excitation. We believe that the polymer nanofibers would be a promising component in future nanophotonic devices.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (11274395) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT13042).

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