Nanowire-Intensified Metal-Enhanced Fluorescence in Hybrid Polymer-Plasmonic Electrospun Filaments

Andrea Camposeo,* Radoslaw Jurga, Maria Moffa, Alberto Portone, Francesco Cardarelli, Fabio Della Sala, Cristian Ciraci,* and Dario Pisignano*

Hybrid polymer-plasmonic nanostructures might combine high enhancement of localized fields from metal nanoparticles with light confinement and long-range transport in subwavelength dielectric structures. Here, the complex behavior of fluorophores coupling to Au nanoparticles within polymer nanowires, which features localized metal-enhanced fluorescence (MEF) with unique characteristics compared to conventional structures, is reported. The intensification effect when the particle is placed in the organic filaments is remarkably higher with respect to thin films of comparable thickness, thus highlighting a specific, nanowire-related enhancement of MEF effects. A dependence on the confinement volume in the dielectric nanowire is also indicated, with MEF significantly increasing upon reduction of the wire diameter. These findings are rationalized by finite element simulations, predicting a position-dependent enhancement of the quantum yield of fluorophores embedded in the fibers. Calculation of the ensemble-averaged fluorescence enhancement unveils the possibility of strongly enhancing the overall emission intensity for structures with size twice the diameter of the embedded metal particles. These new, hybrid fluorescent systems with localized enhanced emission, and the general nanowire-enhanced MEF effects associated to them, are highly relevant for developing nanoscale light-emitting devices with high efficiency and intercoupled through nanofiber networks, highly sensitive optical sensors, and novel laser architectures.

The enhancement of the radiative processes in organic and inorganic light-emitting systems has been intensively investigated in the last decades,[1–3] being of interest both for elucidating nanoscale photophysical processes at fundamental level, and for developing applications in the fields of spectroscopy, biodiagnostics, and nanophotonics. Fluorescence enhancement can arise from a cooperative process, such as superradiance found in atoms, quantum wells, and molecular crystals,[4–7] or from the interaction of emitters with dielectric photonic crystals[2] and nanoantennas.[8] In addition, enhanced emission has been evidenced for fluorophores in close proximity of a metal surface or nanostructure.[9] Such metal-enhanced fluorescence (MEF) occurs when a substantial overlap exists for the absorption spectrum of the emitter and the scattering band due to the localized surface plasmon resonance in the metal.[10] Furthermore, MEF requires the emitter-metal separation to be in a well-defined range, in order to prevent fluorescence quenching which takes place at very short distances.[11] MEF has been found with systems emitting in the visible and near-infrared spectral range, and exploited to build biosensors, light-emitting microarrays, and tunable nanolasers.[3,12,13]

However, while metal nanoparticles (NPs) and nanostructures provide large fluorescence enhancement factors and potential confinement of light across subwavelength volumes, they have intrinsically high Ohmic losses. These prevent long-range transport of light, which is relevant for routing and coupling different nanoscale light sources in integrated photonic systems.

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smll.201800187.

© 2018 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA Weinheim. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

DOI: 10.1002/smll.201800187

Dr. A. Camposeo, Dr. M. Moffa, Dr. F. Cardarelli, Prof. D. Pisignano
NEST
Istituto Nanoscienze-CNR
Piazza San Silvestro 12, I-56127 Pisa, Italy
E-mail: andrea.camposeo@nano.cnr.it; dario.pisignano@unipi.it

R. Jurga, Dr. F. Della Sala, Dr. C. Ciraci
Center for Biomolecular Nanotechnologies@UNILE
Istituto Italiano di Tecnologia
Via Barsanti 14, I-73010 Arnesano, Italy
E-mail: cristian.ciraci@iit.it

R. Jurga, A. Portone
Dipartimento di Matematica e Fisica “Ennio De Giorgi”
Università del Salento
via Arnesano, I-73100 Lecce, Italy

Dr. F. Della Sala
Institute for Microelectronics and Microsystems (CNR-IMM)
Via Monteroni
Campus Unisalento I-73100, Lecce, Italy
Prof. D. Pisignano
Dipartimento di Fisica
Università di Pisa
Largo B. Pontecorvo 3, I-56127 Pisa, Italy
systems. Conversely, dielectric structures are highly transparent and can guide photons over macroscopic distances with limited optical losses. These properties have motivated the interest toward crossbreed systems, in which subwavelength light confinement of surface plasmons and long-range propagation of guided modes of dielectric waveguides are hybridized for developing novel and more efficient nanophotonic platforms.

For instance, NPs can be used as local antennas for in- and out-coupling light with waveguides positioned nearby. Moreover, in subwavelength waveguides the significant intensity gradients associated to light confinement lead to coupling the photon spin and orbital angular momentum, which in turn is found to strongly modify the scattering properties of metal NPs across the nanofiber evanescent field. The interaction of two counterpropagating modes with the localized plasmon resonance of an embedded array of NPs is also found to support transparent waveguide plasmon-polariton modes, through classical electromagnetically induced transparency, leading to slow guided light propagation. Metal NPs positioned on the surface of subwavelength waveguides have also been exploited for developing nanoscale acoustic detectors, based on the response of a nanofiber to incident sound waves modulating the NP-fiber separation. Recently, hybrid lasing systems with optical emissions at subwavelength scale have been demonstrated, by coupling Ag nanowires to dielectric perovskite crystals and organic microdisk cavities.

Most of these hybrid systems have been realized by depositing, or lithographically defining metal NPs and nanostructures on the surface of passive waveguides, with coupling allowed by evanescent field. This configuration, however, might limit applications, due to the high sensitivity of the resulting photonic components to ambient perturbations and the consequently frequent need for operation in vacuum. In this respect, metal particles embedded within the core of active waveguides would lead to much more stable and optically robust systems. Various methods are currently available for the production of functional elongated nanostructures and active dielectric filaments embedding NPs, including electrospraying which allows continuous and multifunctional composite nanofibers to be obtained. Single photons and ensemble emission coupling to modes of electrosprun nanofibers have been reported, as well as fluorescent filaments used as active components in lasers, fluorescent barcodes, and UV excitation sources.

Fibers doped with metal NPs have been employed for optical sensing through surface enhanced Raman scattering, for Li ion storage, and for catalysis. Little has been done for developing active organic nanofibers embedding plasmonic NPs, although these devices might feature localized MEF of internal fluorophores and enable improved nanoscale light sources and lasers.

Here we highlight twofold-enhanced fluorescence in hybrid nanowires, namely, the novel nanofiber-enhanced MEF (NE-MEF) effect, realizing fluorescent organic-plasmonic, electrospun nanowires. These hybrid systems are found to exhibit MEF higher than in thin films. The photonic architecture combines active polymer fibers with subwavelength diameter and metal NPs for local enhancement of the emission of incorporated fluorophores. A broadband increase of the fluorescence enhancement is evidenced for fibers compared to films, which is rationalized by finite-element method simulations unveiling the unique features of the field spatial distribution and of the emitter quantum yield in the confined geometry.

Our devices are produced by embedding Au NPs (average size 60 nm, inset of Figure 1a) and Rhodamine 6G (R6G) fluorophores in polyvinylpyrrolidone (PVP), here used as nanofiber matrix for its optical transparency at visible wavelengths and excellent fiber-forming properties via electrosprinning. The absorption and photoluminescence (PL) spectra of R6G-doped PVP exhibit peaks at ~540 and ~565 nm, respectively, whereas Au NPs feature an extinction spectrum with peak wavelength at 538 nm (Figure S1, Supporting Information), well matching the optical features of the fluorophore. Au NPs with smaller (larger) average size having blue (red)-shifted extinction spectra are expected to lead to less efficient fluorescence enhancement.

**Figure 1.** a,b) SEM images of free-standing R6G-doped PVP nanofibers [highlighted by the arrow in (a)], embedding Au NPs. The fibers are supported by a grid for TEM. Scale bars: a) 50 µm and b) 10 µm, respectively. Insets: Au NPs on an Si substrate (a, scale bar: 500 nm) and individual fiber at high magnification (b, scale bar: 1 µm). c) STEM image of a fiber embedding a single Au NP (arrow). Scale bar: 5 µm. Inset: zoom of the region with the NP. Scale bar: 500 nm. d) Confocal map of the fluorescence intensity collected from the fiber shown in (c). Scale bar: 5 µm. The arrow labeled as “A” highlights the fiber region embedding the Au NP, whereas the arrow labeled as “B” points a region without particles.
mechanisms.\textsuperscript{[10]} The free-standing, hybrid fibers once collected on transmission electron microscopy (TEM) grids, are displayed in Figure 1a,b. The geometry with air surrounding the fibers allows for improving field confinement and light transport through the waveguides. The electrospun fibers have diameter, \(d\), down to 200 nm, and a smooth surface (inset of Figure 1b) that is very important to lower scattering losses, thus leading to propagation lengths of the order of 100 \(\mu\)m.\textsuperscript{[27,28]}

Figure 1c shows a scanning transmission electron microscopy (STEM) image of the fibers, highlighting the incorporation of an individual Au NP. The position of NPs is mainly determined by the dynamics of the entangled network of the polymer macromolecules in the jet during the electrospinning process. Hence, a significant role is played by the viscoelastic properties of the electrified solution, as well as by the very high strain rates (e.g., \(10^3–10^5\) s\(^{-1}\)) promoted by electrospinning. These might lead to a local increase of the polymer density at the jet center as previously probed by X-ray imaging,\textsuperscript{[39,40]} and to the formation of relatively ordered, anisotropic conformations of both the polymer macromolecules and the embedded particles.\textsuperscript{[32,41,42]} In addition, the density of particles in the fibers can be controlled by varying the molar ratio of NPs to the polymer in the electrospun solution.\textsuperscript{[31]} This strategy allows filaments embedding isolated NPs, or linear chains of NPs, to be achieved.

The PL of individual hybrid fibers are investigated by fluorescence confocal microscopy, allowing both intensity and spectral properties to be mapped with a spatial resolution given by the diffraction-limited excitation spot size. Figure 1d shows the confocal map of the fiber displayed in Figure 1c, clearly evidencing a spot with brighter fluorescence in correspondence of the Au NP. The corresponding fluorescence enhancement factor (\(\eta_{\text{fiber}}\)) is obtained by comparing the PL intensity of the brighter spot (\(I_{\text{Au}}\)) with that of nearby regions where no particle is present (\(I_F\)). Such combined STEM and confocal analysis, performed on several fibers with 300 nm diameter, leads to an average enhancement factor, \(\eta_{\text{fiber}} = I_{\text{Au}}/I_F = 1.6 \pm 0.1\). The role of MEF in this effect is highlighted by time-resolved PL measurements performed with confocal detection,\textsuperscript{[43]} which clearly show a decrease of the luminescence lifetime of the chromophores in correspondence of the Au NP (Figure 2a). In fact, while PL time-resolved profiles of nanofiber-embedded chromophores display almost monoexponential decays with average lifetime about 0.8 ns, the PL decay becomes multieponential in presence of Au NPs, with average lifetimes about 0.5 ns.

Furthermore, to unveil the contribution of the filamentous geometry in amplifying the enhancement, namely in leading to NE-MEF, similar measurements are performed on films having identical composition and comparable thickness to the fibers. Interestingly, \(\eta_{\text{fiber}}\) is found to be higher than the fluorescence enhancement factor measured in films (\(\eta_{\text{film}} = 1.3 \pm 0.1\), see Figure S2 of the Supporting Information for details). Therefore, an additional effect is associated to the nanofiber confined geometry, synergistic with the MEF induced by the metal NPs. Furthermore, this effect is dependent on the fiber transversal size, as well as on the polarization of the excitation laser. Figure 2b–d shows the micro-PL (\(\mu\)-PL) intensity profiles measured along the longitudinal axis of three electrospun fibers with different diameter, evidencing a different MEF enhancement factor in correspondence of a single Au NP, depending on the \(d\) value. Decreasing the fiber diameter from 600 to 200 nm leads to an increase of \(\eta_{\text{fiber}}\) by about 60%. Figure 3a displays...
metal particles in the fibers is shown in Figure 3b, together with a spectrum in a region without NPs. Overall, the hybrid polymer-plasmonic nanostructures provide NE-MEF with an almost constant $\eta_{\text{fiber}}$ on a spectral range of about 80 nm (Figure 3c), a property important for those applications where broadband light sources are used, including ultrafast spectroscopy and optical sensing.

In order to better elucidate the NE-MEF process and to discriminate the contribution from the metal NP and from the organic filaments to the ultimate values of $\eta_{\text{fiber}}$, classical electromagnetism FEM simulations are carried out for our system. The fluorophore is approximated as a point dipole, assumed to be weakly excited (no saturation) by an external Gaussian beam impinging orthogonally to the fiber longitudinal axis, as sketched in Figure 4a. The calculated spatial distribution of electric field in the hybrid Au NP/fiber is also presented in Figure 4a for a PVP filament with 300 nm diameter (a detailed comparison of the field distribution in and nearby the fiber is performed and shown in Figure S3 of the Supporting Information for filaments either with or without NPs). A local enhancement up to a factor 3.8 is achieved in close proximity of the Au NP, whereas an increase by a factor about 2 is evident in a region nearby the NP with extension of the order of the beam waist. For comparison, we report in Figure 4b the electric field distribution for the case of an Au NP embedded in a PVP film of 300 nm in thickness. The maximum local enhancement factor for the film is ~3.2 around the NP (~40% lower intensity than in the fiber case). Furthermore, the field remains visibly reduced in the surrounding region as well. Additional field enhancement can be achieved by decreasing the fiber size, as shown in Figure S4 of the Supporting Information, where the spatial distribution of the electric field in hybrid filaments is calculated for fibers with diameters of 200 and 600 nm. By decreasing the fiber size, the electric field nearby the Au NP is enhanced up to a factor 4.2.

The ratio of the radiative decay rate ($\gamma_r$) to the total decay rate ($\gamma_{\text{tot}}$), namely, the quantum yield of the fluorophores embedded into the fibers, $q = \gamma_r/\gamma_{\text{tot}} = (\gamma_{\text{sp}} - \gamma_{\text{nr}} - \gamma_{\text{int}})/\gamma_{\text{tot}}$, is derived by obtaining $\gamma_{\text{tot}}$, which represents the internal emission rate accounting for intrinsic decay such as phononic or trapped states, from the measured quantum yield of the chromophores in bulk, and by calculating $\gamma_{\text{int}} = \frac{1}{2} \frac{\gamma_r^2}{W_r} \int_0^{2\pi} \text{Re}[\mathbf{J}^* \cdot \mathbf{E}] dV$. The integration of all metal losses is performed over the NP volume ($\Omega$), and $\gamma_{\text{sp}}$ from the Green’s function, $\mathbf{G}$, of the system

$$\gamma_{\text{sp}} = \frac{2\omega^2}{\hbar c} \left\{ |\mathbf{p}|^2 - 2 \text{Im} \left[ \mathbf{G}(\mathbf{r}_m, \mathbf{r}_m) \cdot \mathbf{n}_m \right] \right\} + \gamma_{\text{int}}$$

where $\mathbf{p}$ is the transition dipole moment, $\omega$ is given by the transition frequency, $\mathbf{n}_m$ is the unit vector of the dipole moment, which accounts for its orientation, and $\mathbf{G}$ is the Green dyadic function calculated at the position $\mathbf{r}_m$ of the emitting dipole. In Figure 4c–e we show the calculated values of the quantum yield, $q = q_{\text{sp}}(\mathbf{r}_m)$, for different orientations of the dipole as a function of its position inside the fiber, normalized with respect to the quantum yield in bulk (the corresponding $\gamma_{\text{sp}}$ values are shown in Figure S5, Supporting Information). We point out that the calculation of
full quantum-yield maps as a function of the position and orientation of the emitter is quite challenging, as about one thousand different FEM calculations are required. The field patterns due to both the fiber and the Au NP are clearly visible in Figure 4c–e. In particular, when the emitter is parallel to the NP surface (Figure 4c), the quenching near the metal allows to appreciate the effect of the fiber confinement, which doubles the quantum yield with respect to its bulk value. In the other cases (Figure 4d,e), the NP enhances the quantum yield up to eight times in the fibers, with a relatively lower effect of fiber confinement. Indeed, such position and orientation dependence of the quantum yield and of the decay rates leads to a complex temporal behavior of the fluorescence following NP addition, as shown in Figure 2a.[44]

The orientation-averaged fluorescence intensity, PL(\theta), is obtained as
where \( q_{\rho}(\rho, z) = q_{\rho}(0, y, z) \) and \( q_{\phi}(\rho, z) = q_{\phi}(0, y, z) \) are calculated in the cross-section plane of Figure 4c–e, and \( A \) is a constant. Figure 4f shows the resulting map of the fluorescence enhancement with respect to the bulk, for an averaged random distribution of chromophore orientations: enhancements up to 30 times the bulk values can be achieved. Of course such enhancements are larger than those found in experiments, since the various positions and orientations of the fluorophores are averaged over a volume corresponding to the excitation spot size during measurements. In order to account for such features of experiments, we average PL with respect to the volume included in a sphere of diameter \( D \) around the NP, as depicted in Figure 4f. To this aim, from the definition in Equation (2), it is easy to average over a volume \( \Omega \), as:

\[
\overline{PL} = \frac{1}{\Omega} \int_{\Omega} PL(x) dV.
\]

The resulting, volume-averaged fluorescence enhancement with respect to the case without Au NP, \( \eta_{PL} = \frac{PL_{\text{fiber-NP}}}{PL_{\text{fiber}}} \), is shown in Figure 4g as a function of \( D \), together with the corresponding values calculated for a 300 nm thick film. The effect of the Au NP can be clearly appreciated in a small volume in the vicinity of the NP. Considering the experimental spot used for excitation, a quite good agreement is found with the experimental results shown in Figure 3b, with \( \eta_{PL} \) around 1.5–1.6. More importantly, \( \eta_{PL} \) is found to be larger than the value for the film in all the investigated range of \( D \). A dependence of \( \eta_{PL} \) on the polarization of the excitation light is also obtained (Figure S6, Supporting Information), in agreement with experimental findings (Figure 3a). Moreover, for emitters oriented perpendicularly to the fiber length a large fraction of the emitted light is coupled to modes waveguided along the organic filament (Figure S7, Supporting Information), and the presence of the NP strongly increases the amount of photons available in such modes (Figure 4h).

Such cooperative NE-MEF and improved channeling to guided modes might be exploited for enhancing the coupling efficiency of single-photon emitters embedded in dielectric waveguides.[27] Other applications of these findings embrace coupling metallic particles with nanofiber architectures to achieve active photonic components and integrated systems with higher emission efficiencies, or miniaturized lasers with lower threshold. These include plasmon-enhanced random lasers based on nanofiber networks[37] for optical tagging and fluorescence sensors, and devices combining optical amplifiers based on organic filaments[45] with plasmonic metamaterials.[46] In addition NE-MEF, being inherently localized at subwavelength scales, opens interesting perspectives for imaging, nanolithography, and 3D manufacturing,[47,48] possibly leading to a significant improvement in terms of achievable spatial resolution.

In summary, special features for the enhancement of the fluorescence in hybrid polymer nanofibers embedding plasmonic NPs are found and rationalized. The subwavelength fiber architecture leads to NE-MEF, namely to a significant improvement of the MEF compared to the effect observed for plasmonic particles embedded in films. μ-PL measurements indicate a size-dependent effect, which is significantly improved by decreasing the fiber diameter. In addition, NE-MEF is broadband, being almost insensitive to fluorescence wavelength in a range of about 80 nm. These results are supported by numerical simulations, in which the fiber shows a maximum increase of \( \approx 40\% \) in PL with respect to an extended film of comparable thickness. These hybrid nanostructures, providing improved local field enhancement are an example of how more efficient and tailored emission can be achieved by cooperatively exploiting metal and dielectric nanostructures, which might lead to enhanced performance in multiphoton light-emitting devices with high efficiency, mutually intercoupled through nanofiber circuits and networks for integrated information processing.

**Experimental Section**

**Electrospinning and Nanofiber Morphology** Hybrid nanofibers were produced by electrospinning a solution of 100 mg of PVP (molecular weight \( 1.3 \times 10^6 \) g mol\(^{-1}\), Alpha Aesar) and 1 mg of R6G (Exciton) dissolved in 1 mL mixture of ethanol (0.85 mL) and distilled water (0.15 mL). The used water dispersion contained 5 \( \times 10^9 \) Au NPs (Sigma-Aldrich), corresponding to a weight ratio of particles with respect to the PVP matrix of about 1:100. Such value is found to allow well-isolated Au NPs to be embedded in the electrospun fibers, as required for optical characterization. Further increase of the weight ratio of Au NPs can be exploited to enhance the macroscopic-averaged fluorescence of the hybrid fibers, because of the higher number of spots with intensified fluorescence. The solution was fed by a syringe pump (Harvard Apparatus), with constant flow rate (0.5 mL h\(^{-1}\)) through a metallic needle (gauge 27), and fibers were collected on a metallic plate positioned at a distance of 15 cm from the spinneret. The voltage bias between the spinneret and the collector was 11 kV. Free-standing fibers were obtained by deposition on TEM grids (TAAB Laboratories Equipment Ltd.), whose supporting structure also provided a reference frame to localize individual fibers to image by scanning electron microscopy (SEM, FEI Nova NanoSEM 450), STEM, and confocal fluorescence microscopy. Fibers were first imaged by an optical inverted microscope (Eclipse Ti, Nikon) in bright field, to be precisely labeled with respect to the grid, and then analyzed sequentially by confocal microscopy and STEM. The combination of the optical and morphological data allows the bright spots observed in confocal microscopy to be univocally correlated to incorporated NPs. Reference thin films were spin-cast on quartz substrates (5000 rpm, 60 s).

**Optical Measurements** Absorption measurements were carried out by using a UV–vis spectrophotometer (Lambda 950, Perkin Elmer). PL spectra were obtained by exciting the samples with a diode laser and collecting the emission by an optical fiber, coupled to a spectrometer (USB4000, Ocean Optics). Samples were mounted in an integrating sphere (Labsphere), which allows the emission quantum yield to be measured (3% for R6G molecules embedded in PVP). A μ-PL analysis was performed by using a confocal microscopy system, based on an inverted microscope (Eclipse Ti, Nikon) equipped with a confocal laser scanning head (A1 MP, Nikon). The samples were excited by an Ar\(^+\) laser (\( \lambda_{exc} = 488 \) nm) through a 20× objective (numerical aperture, NA = 0.5), which was used also to collect the sample emission, and analyzed by means of spectral detection unit with a multianode photomultiplier. To account for the finite collection angle, the ratio \( \eta_{fiber} = I_{fiber}/I_{slit} \) was considered in the analysis, which does not depend on the numerical aperture of the collection optics as shown in Figure S8 of the Supporting Information. The spot size of the focused excitation laser beam was about 300 nm. The intensity of the excitation laser transmitted through the sample was measured by a photomultiplier, simultaneously to the fluorescence signal. Scattering images of thin films were obtained by illuminating the samples at almost grazing incidence with a white light, fiber-coupled tungsten lamp, while collecting the light diffused by the samples by the microscope objective used for confocal fluorescence measurements. Confocal fluorescence lifetime imaging microscopy.
Experimental conditions. In this case, a quartz substrate of index methods were used for the simulations of films. In this approach allows to easily define a converging beam. Analogous Gaussian beam approximation does not hold for such a small beam, being used in order to emulate an infinitely extended geometry. The experimental value) containing an Au NP at its center and surrounded by air. Perfectly matched layers (PMLs) around the geometry have been used to point out that each point of such maps required a separated 3D FEM dependent surface current profile on a spherical simulation boundary placed on the positive quadrant of the –plane at the center of the fiber average of 102–103 photons were collected in each pixel.

**Supporting Information**

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

**Acknowledgements**

The research leading to these results received funding from the European Research Council under the European Union’s Seventh Framework Programme (FP/2007-2013)/ERC Grant Agreement No. 306357 (ERC Starting Grant “NANO-JETS”). The Apulia Networks of Public Research Laboratories WAFITECH (09) and M. I. T. T. (13) are also acknowledged.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

electrospinning, gold nanoparticles, metal-enhanced fluorescence, nanofibers

---

1. V. Giannini, I. Antonio, A. I. Fernández-Domínguez, C. S. Heck, S. A. Maier, *Chem. Rev.* 2011, 111, 3888.

2. N. Ganesh, W. Zhang, P. C. Mathias, E. Chow, J. A. N. T. Soares, V. Malyarchuk, A. D. Smith, B. T. Cunninghan, *Nat. Nanotechnol.* 2007, 2, 515.

3. K. Aclan, I. Gryczynski, J. Malicka, E. Mateveeva, J. R. Lakowicz, C. D. Geddes, *Curr. Opin. Biotechnol.* 2005, 16, 55.

4. H. M. Gibbs, Q. H. F. Vrehen, H. M. J. Hikspoors, *Phys. Rev. Lett.* 1977, 39, 547.

5. J. Feldmann, G. Peter, E. O. Göbel, P. Dawson, K. Moore, C. Foxon, R. J. Eliot, *Phys. Rev. Lett.* 1987, 59, 2337.

6. F. Meiniardi, M. Cerminara, A. Sassella, R. Bonifacio, R. Tubino, *Phys. Rev. Lett.* 2003, 91, 247401.

7. A. Camposeo, M. Polo, S. Tavazzi, L. Silvestri, P. Spearman, R. Cingolani, D. Pisignano, *Phys. Rev. B* 2010, 81, 033306.

8. R. Regmi, J. Berthelot, P. M. Winkler, M. Mivelje, J. Proust, F. Bedu, I. Ozorov, T. Begou, J. Lumeau, H. Rigneault, M. F. García-Parajo, S. Bialdut, J. Wenger, N. Bonod, *Nanotechnology* 2016, 17, 5143.

9. C. D. Geddes, J. R. Lakowicz, *J. Fluoresc.* 2002, 12, 121.

10. Y. Chen, K. Munecihka, D. S. Ginger, *Nano Lett.* 2007, 7, 690.

11. C. D. Geddes, J. R. Lakowicz, *J. Fluoresc.* 2002, 12, 121.

12. Y. Chen, K. Munecihka, D. S. Ginger, *Nano Lett.* 2007, 7, 690.

13. Y. Liu, Q. Zhang, J. N. Yip, Q. Xiong, T. C. Sum, *Nano Lett.* 2013, 13, 5336.

14. A. Camposeo, L. Persano, R. Manco, Y. Wang, P. Del Carro, C. Zhang, Z.-Y. Li, D. Pisignano, Y. Xia, *ACS Nano* 2015, 9, 10047.

15. W. Ahn, S. V. Boriskina, Y. Hong, B. M. Reinhard, *ACS Nano* 2012, 6, 951.

16. F. B. Arango, A. Kwadrin, A. F. Koenderink, P. J. Rodríguez-Cantó, J. Martínez-Pastor, *Nanotechnology* 2015, 26, 475201.

17. J. Petersen, J. Volz, A. Rauschenbeutel, *Science* 2014, 346, 67.

18. A. Ishikawa, R. F. Oulton, T. Zentgraf, X. Zhang, *Phys. Rev. B* 2012, 85, 155108.

19. Y. Ma, Q. Huang, T. Li, J. Villanueva, N. H. Nguyen, J. Friend, D. J. Sirbuly, *ACS Photonics* 2016, 3, 1762.

20. Y. J. Li, Y. Lu, C.-L. Zou, W. Zhang, J. Yao, Y. S. Zhao, *J. Am. Chem. Soc.* 2016, 138, 2122.

21. Y. Lu, Y. J. Li, J. Li, Y. Yan, J. Yao, Y. S. Zhao, *J. Am. Chem. Soc.* 2017, 139, 11329.

22. L. Zhou, L. Yang, P. Yuan, J. Zou, Y. Wu, C. Yu, J. *Phys. Chem. C* 2010, 114, 21868.

23. X. Wang, C. Niu, J. Meng, P. Hu, X. Xu, W. Wei, L. Zhou, K. Zhao, W. Luo, M. Yan, L. Mai, *Adv. Energy Mater.* 2015, 5, 1500716.

24. I. Lee, M. Y. Park, H.-J. Kim, J.-H. Lee, J.-Y. Park, J. Hong, K.-I. Kim, M. Park, J.-Y. Yun, K. J. Yoon, *ACS Appl. Mater. Interfaces* 2017, 9, 39407.

25. P. Wang, Y. Wang, L. Tong, *Light: Sci. Appl.* 2013, 2, e102.

26. L. Persano, A. Camposeo, D. Pisignano, *Prog. Polym. Sci.* 2015, 43, 48.

27. M. Gaio, M. Moffa, M. Castro-Lopez, D. Pisignano, A. Camposeo, R. Sapienza, *ACS Nano* 2016, 10, 6125.

28. V. Fasano, A. Polini, G. Morello, M. Moffa, A. Camposeo, *D. Pisignano, *Macromolecules* 2013, 46, 3935.

29. S. Krämmé, C. Vannahme, C. L. Smith, T. Grossmann, M. Jenne, S. Schierle, L. Jørgensen, I. S. Chronakis, A. Kristensen, H. Kalt, *Adv. Mater.* 2014, 26, 8096.

30. C. Huang, B. Lucas, C. Vervaat, K. Braeckmans, S. Van Calenbergh, I. Karalic, M. Vandewoestyne, D. Deforce, J. Demeester, S. C. De Smedt, *Adv. Mater.* 2010, 22, 2657.

31. G. Morello, R. Manco, M. Moffa, L. Persano, A. Camposeo, D. Pisignano, *ACS Appl. Mater. Interfaces* 2015, 7, 21907.

32. D. He, B. Hu, Q.-F. Yao, K. Wang, S.-H. Yu, *ACS Nano* 2009, 3, 3993.

33. S. H. Nam, H.-S. Shim, Y.-S. Kim, M. A. Dar, J. G. Kim, W. B. Kim, *ACS Appl. Mater. Interfaces* 2010, 2, 2046.

34. E. Formo, E. Lee, D. Campbell, Y. Xia, *Nano Lett.* 2008, 8, 668.
[35] R. Jurga, F. Della Sala, D. Pisignano, C. Ciraci, Opt. Lett. 2016, 41, 1632.
[36] H. Sugimoto, R. Zhang, B. M. Reinhard, M. Fujii, G. Perotto, B. Marelli, F. G. Omenetto, L. Dal Negro, Appl. Phys. Lett. 2015, 107, 041111.
[37] R. Zhang, S. Knitter, S. F. Liew, F. G. Omenetto, B. M. Reinhard, H. Cao, L. Dal Negro, Appl. Phys. Lett. 2016, 108, 011103.
[38] X. Lu, Y. Zhao, C. Wang, Adv. Mater. 2005, 17, 2485.
[39] I. Greenfeld, A. Arinstein, K. Fezzaa, M. H. Rafailovich, E. Zussman, Phys. Rev. E 2011, 84, 041806.
[40] I. Greenfeld, K. Fezzaa, M. H. Rafailovich, E. Zussman, Macromolecules 2012, 45, 3616.
[41] M. Richard-Lacroix, C. Pellerin, Macromolecules 2013, 46, 9473.
[42] T. Aubert, L. Palangetic, M. Mohammadimasoudi, K. Neyts, J. Beeckman, C. Clasen, Z. Hens, ACS Photonics 2015, 2, 583.
[43] S. Kühn, U. Häkansson, L. Rogobete, V. Sandoghdar, Phys. Rev. Lett. 2006, 97, 017402.
[44] G. M. Akselrod, C. Argyropoulos, T. B. Hoang, C. Ciraci, C. Fang, J. Huang, D. R. Smith, M. H. Mikkelsen, Nat. Photonics 2014, 8, 835.
[45] L. Persano, A. Camposeo, P. Del Carro, V. Fasano, M. Moffa, R. Manco, S. D’Agostino, D. Pisignano, Adv. Mater. 2014, 26, 6542.
[46] Z. Wang, X. Meng, S. H. Choi, S. Knitter, Y. L. Kim, H. Cao, V. M. Shalaev, A. Boltasseva, Nano Lett. 2016, 16, 2471.
[47] T. L. Andrew, H.-Y. Tsai, R. Menon, Science 2009, 324, 917.
[48] R. L. Truby, J. A. Lewis, Nature 2016, 540, 371.