Flexible, Free-Standing Polymer Membranes Sensitized by CsPbX$_3$ Nanocrystals as Gain Media for Low Threshold, Multicolor Light Amplification

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**ABSTRACT:** Lead halide perovskite nanocrystals (NCs) are highly suitable active media for solution-processed lasers in the visible spectrum, owing to the wide tunability of their emission from blue to red via facile ion-exchange reactions. Their outstanding optical gain properties and the suppressed nonradiative recombination losses stem from their defect-tolerant nature. In this work, we demonstrate flexible waveguides combining the transparent, bioplastic, polymer cellulose acetate with green CsPbBr$_3$ or red-emitting CsPb(Br,I)$_3$ NCs in simple solution-processed architectures based on polymer-NC multilayers deposited on polymer micro-slabs. Experiments and simulations indicate that the employment of the thin, free-standing membranes results in confined electrical fields, enhanced by 2 orders of magnitude compared to identical multilayer stacks deposited on conventional, rigid quartz substrates. As a result, the polymer structures exhibit improved amplified emission characteristics under nanosecond excitation, with amplified spontaneous emission (ASE) thresholds down to $\sim 95 \mu J \ cm^{-2}$ and $\sim 70 \mu J \ cm^{-2}$ and high net modal gain up to $\sim 450$ and $\sim 630 \ cm^{-1}$ in the green and red parts of the spectrum, respectively. The optimized gain properties are accompanied by a notable improvement of the ASE operational stability due to the low thermal resistance of the substrate-less membranes and the intimate thermal contact between the polymer and the NCs. Their application potential is further highlighted by the membrane’s ability to sustain dual-color ASE in the green and red parts of the spectrum through excitation by a single UV source, activate underwater stimulated emission, and operate as efficient white light downconverters of commercial blue LEDs, producing high-quality white light emission, 115% of the NTSC color gamut.

**KEYWORDS:** lead halide perovskites, nanocrystals, amplified spontaneous emission, solution-processed lasers, polymer resonators

**INTRODUCTION**

Inorganic and hybrid lead halide perovskite nanocrystals (LHP NCs) have emerged as versatile, tunable, and low-cost gain media for optically pumped, solution-processed lasers in the visible spectral region. Significant advances include the demonstration of low threshold and air-stable amplified spontaneous emission (ASE) in thin films or simple waveguide structures of perovskite NCs with ambient stability of several hours and thresholds down to $\sim 1 \mu J \ cm^{-2}$ in the femtosecond excitation regime.1−5 Furthermore, efficient optically pumped, single- and multi-mode LHP NC lasers have been realized based on various resonator geometries that include vertical cavities,6−10 distributed feedback,11−14 and whispering gallery architectures.15−17 Despite the significant progress, there are some key challenges that need to be tackled toward the realization of practical and cost-effective optically pumped amplifiers and lasers based on perovskite NCs. Improving the stability and

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lasing even under cw-excitation in properly designed structures. However, these results are typically obtained at cryogenic temperatures, inaccessible by commercial Peltier-type cooling, or implement rigid cavities fabricated by rather elaborate epitaxial and lithographic techniques, that limit the practicality and compromise the cost-effectiveness and mass-production promise of a solution-based fabrication methodology. Finally, the great majority of the work involves the one specific popular emitter—green-luminescent CsPbBr$_3$ NCs—allowing us to thoroughly study effective ligand and encapsulation strategies. To extend the stimulated emission gamut through the visible spectrum, further work is needed to improve the lasing performance and reliability of blue and red LHP NC emitters.

Herein, we introduce a facile, fully solution-processed fabrication methodology to produce flexible waveguide structures combining cellulose acetate (CA) polymer membranes with active gain media based on multilayer stacks of CA with green CsPbBr$_3$ or red-emitting CsPb(Br,I)$_3$ NCs. Upon structure optimization, nanosecond excitation of such freestanding membranes results in air-stable ASE in the green and red parts of the spectrum, with low thresholds down to ∼90 and ∼70 μJ cm$^{-2}$ and high net modal gain up to ∼450 and ∼630 cm$^{-1}$, respectively. Reference structures produced by deposition of the same multilayer CA/NC stacks in rigid quartz substrates also exhibit ASE, but at the expense of higher thresholds and poorer ambient stability. Angle-resolved white-light reflectivity measurements combined with transfer matrix method (TMM) simulations confirm that the improved ASE threshold and net modal gain in the CA membranes are a result of better optical mode confinement that improves photon–exciton coupling. On the other hand, the absence of a bulky substrate and the less thermal dissipative CA/NC interface yields efficient heat exchange with the environment,
significantly improving the operational ASE stability with respect to the reference quartz structures. The versatility and excellent gain properties of such structures allow us also to stack membranes and simultaneously sustain dual-color ASE in the green and red parts of the spectrum using a single nanosecond excitation source and operate as efficient down-converters of commercial blue LEDs, producing high-quality white light emission, 115% of the NTSC.

RESULTS AND DISCUSSION

Design and Fabrication of NC-Sensitized Polymer Membranes. The objective of the study has been the demonstration of air-stable and efficient optical amplification in the quasi-cw optical pumping regime by combining robust perovskite NC gain media with a simple, fully solution-processed, mechanically flexible cavity design. To achieve such a target, we implemented mirrorless, polymeric micro-membranes that can weakly confine an optical field due to the refractive index contrast between the organic material and the surrounding air. Free-standing membranes were fabricated by spin casting microns-thick slabs of CA onto quartz, followed by alternate deposition of multiple layers of CsPbBr$_3$ or CsPb(Br,I)$_3$ NCs and CA with layer thickness around 50 and 80 nm for NCs and CA, respectively. Optimization of the structural characteristics of such multilayer stacks is discussed in the following manuscript section. Upon deposition, the membranes were lifted-off from the quartz substrate via a simple peel-off technique, as schematically illustrated in Figure 1a. The figure also contains images of the NC-sensitized membranes under ambient and UV-light conditions, demonstrating their good uniformity, optical quality, and bright emission. Green emitting CsPbBr$_3$ NCs with dimethyldioctadecylammonium bromide (DDAB) ligands have been selected as the active gain media, owing to their structural robustness and good photostability combined with exceptionally high photoluminescence (PL) QY approaching in the liquid phase 100% (larger than 90% in the solid state). The NCs employed were cuboids with mean sizes of $\sim$10 nm, as presented in the TEM images of Figure S1, centered at $\sim$2.40 eV with a full width half maximum (fwhm) of $\sim$80 meV, as shown in Figure 1b. For the red-emitting active gain media, CsPb(Br,I)$_3$ NCs with variable bromine-iodine ratio were obtained via a newly designed synthesis using hot-injection methodology with oleic acid (OA) and two different branched ligands such as dioctylamine (DOAm) and DDAB. Branched ligands with shorter chains are known to have strong binding to the surface of NCs, thus they provide better surface passivation and improvement in the optical properties of these mixed halide NCs, with PL QY exceeding 80% in the liquid phase (larger than 10% in the solid state). In addition, DDA$^+$ cations have a strong affinity to negative sites of cesium lead halide NCs, and Br$^-$ anions from DDAB can substitute I$^-$ in the structure resulting in more stable mixed CsPb(Br$_x$I$_{1-x}$)$_3$ NCs with an easily tunable wavelength.

The size and shape of CsPb(Br,I)$_3$ NCs were confirmed by transmission electron microscopy Figure S2b, showing the presence of two populations of NCs with the average sizes of 16.86 $\pm$ 2.08 and 26.8 $\pm$ 4.23 nm. Powder X-ray diffraction (XRD) of purified CsPb(Br,I)$_3$ NCs shows an orthorhombic perovskite structure (Figure S2d). Bromide and iodide atoms are well intermixed into a solid solution, giving rise to a gradual
shift of XRD reflections. Their PL was centered at \( \sim 1.92 \) eV with an fwhm of \( \sim 100 \) neV as seen in Figure 1c.

Structures produced via single layer deposition of CsPbBr\(_3\) or CsPb(Br\(_3\),I\(_2\)), NCs on quartz or CA membranes do not sustain nanosecond-excited ASE at room temperature. Instead, a multilayer approach was implemented using alternating spin-casted layers of NCs and CA, exploiting the orthogonality of the solvents of the two materials. The method enables the formation of sufficiently thick active gain regions, exceeding the cut-off thickness for the propagation of one optical mode,\(^{27,28}\) while at the same time preserving the optical quality of the layers and reducing the optical losses which single, thick casted films are prone to.\(^{29}\) Representative results of the optimization studies in such multilayers are presented in Figure 1d, where the influence of the number of CsPbBr\(_3\) NC/CA pairs on the light absorption, emission yield, and ASE threshold is demonstrated. The respected emission and absorption data as a function of the number of layers are displayed in Figure S3a,b. Based on such work, activation of nanosecond ASE is typically achieved for an active medium of 1.5 NC/CA layers (a sequence of \( \sim 50 \) nm NC/\( \sim 80 \) nm spacer CA/\( \sim 50 \) nm NC layers), while ASE threshold minimization is obtained for a total multilayer thickness of \( \sim 310 \) nm or equivalently the number of 2.5 NC/CA bilayers (a total NC thickness of \( \sim 150 \) nm). The pronounced reduction of the ASE threshold in the 1.5 to 2.5 layer range is assigned to a combined effect of increased light absorption and more efficient confinement of the optical modes within the thicker active region. The effect appears to dominate over the slight reduction of the emission quantum yield observed across the same thickness range. The addition of more pairs in the multilayer stack, allows the propagation of higher-order cavity modes, effectively reducing the photon–exciton coupling. Furthermore, processes such as re-absorption and light scattering become more prominent, reducing the emission QY and suppressing the overall Q-factor of the cavity. Figure S3c,d contains another parametric study, probing the influence of the CA spacer layers thickness on the ASE threshold; experiments as such yielded optimum thicknesses of around 50 and 80 nm for the NC and CA layers incorporated in the multilayer stack active regions, respectively. The use of such thick CA spacer layers in the optimized waveguide structures also ensures that their optical properties are not affected by electronic interactions between the NC emitters layers.

**Room-Temperature-ASE under Nanosecond Excitation.** The stimulated emission properties of CsPbBr\(_3\) NC/CA multilayers deposited on rigid quartz and flexible CA substrates were examined under optical excitation with a 355 nm nanosecond pulsed laser, with a pulse width of 6 ns and repetition rate of 10 Hz. Both samples exhibit a distinct transition from spontaneous emission to ASE, marked by the linear to superlinear change of slope and the simultaneous collapse of the emission linewidth from \( \sim 100 \) to \( \sim 20 \) meV when the pumping fluence surpasses the characteristic threshold, as seen in Figure 2a,b. The ASE thresholds were extracted via the allometric fitting of the excitation-dependent integrated areas, resulting in the champion structures displayed in Figure 2, to values of \( E_{\text{th}} \sim 150 \) \( \mu \)J cm\(^{-2}\) and \( E_{\text{th}} \sim 95 \) \( \mu \)J cm\(^{-2}\) for multilayers deposited on quartz and CA membranes, respectively. It is worth noting that ASE dominates the background spontaneous emission in both types of samples. For the multilayers on quartz, the ASE is red-shifted by \( \sim 30 \) meV relative to the spontaneous emission peak, which is characteristic of the bi-excitonic optical gain mechanism.\(^{30,31}\)

On the other hand, in the free-standing membrane, the ASE lies in the proximity of the PL peak as the emission couples to the Fabry Perot resonances supported by the micron-thick CA substrate. Such results are further elaborated in Figure S4, containing emission spectra from the two structures below and above the ASE threshold, as well as a comparison of emission data with TMM simulated reflectivity spectra from the CA membrane sample.

On top of sustaining ASE at consistently lower excitation fluences compared to the same gain media deposited in quartz, the polymer membranes also exhibit significantly higher stability during ASE operation. ASE stability for both types of structures was recorded under continuous nanosecond excitation at ambient conditions, at a fluence of 200 \( \mu \)J cm\(^{-2}\) for illumination of up to \( 110 \times 10^3 \) laser pulses or an equivalent of 3 operational hours. Figure 2e contains the results of such a study performed on the same champion devices, the ASE data of which are presented in Figure 2a–d. For the CA membrane structure, the ASE intensity exhibited an initial increase of 10% up at \( \sim 25 \times 10^3 \) laser pulses, followed by a gradual emission quenching down to 85% of the initial intensity, which is a loss of only 15% after 3 h of operation. The initial increase of the ASE intensity was observed also in photostability tests of other free-standing membrane samples and it could be related to the self-healing and annealing effects of the NCs, during the intense photo-excitation.\(^{32,33}\) In contrast, the multilayers deposited on quartz exhibit a rapid loss of the output intensity, with complete quenching of the ASE at \( \sim 40 \times 10^3 \) pulses or equivalently 1 h of operation.

The improved ASE stability in the free-standing membranes is predominantly ascribed to the more efficient heat transfer and the smaller thermal interface resistance of NCs/CA compared to the respective heat conduction and heat dissipation properties of the structures deposited on quartz. Heat extraction through the substrate depends on the material thermal conductivity and the thickness; even though the thermal conductivity of CA (\( \sim 0.17 \) W m\(^{-1}\)K\(^{-1}\))\(^{34}\) is 1 order of magnitude smaller than quartz (\( \sim 1.6 \) W m\(^{-1}\)K\(^{-1}\)),\(^{35}\) the CA membranes are more than 300 times thinner than the conventional 1.1 mm thick quartz substrates employed in our studies, allowing a more efficient heat flow through the CA substrate. Furthermore, the CA polymer is conformable and can displace more of the air entrapped in the CA–NC interfaces than the rigid quartz–NC interface, reducing the thermal interface resistance and, thus, the heat accumulated in the material heterointerface. Further evidence for such an explanation can be found in Figure S5, in which the ASE peak position is monitored as a function of the number of excitation pulses. For the multilayers deposited on quartz, an appreciable \( \sim 20 \) meV blue shift of the ASE builds up during the one-hour operation lifetime of the structure. The blue shift can be predominantly attributed to NC heating arising from the anomalous temperature-dependent variation of the energy gap in CsPbBr\(_3\), NCs.\(^{36}\) In contrast, the ASE peak position in the free-standing membrane is considerably more stable, showing a much smaller \( \sim 7 \) meV red-shift over the course of the 3 h operation. Such a bathochromic shift may originate from the thermal expansion of the CA substrate and/or a small degree of NC sintering during the intense laser illumination.\(^{37}\) Overall, in all membrane samples, the ASE peak position exhibited a small red or blue shift of the order of 5 to 10 meV, being always

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significantly smaller in magnitude compared to the 20 to 30 meV blue shift of the ASE peak in quartz samples, confirming the improved thermal properties of the former structures.

Following an identical fabrication procedure, red-emitting CsPb(Br,I)$_3$ NC/CA multilayers were also produced on quartz and free-standing membranes, examined under optical excitation with a 532 nm nanosecond pulsed laser, with a pulse width of 6 ns and repetition rate of 10 Hz. Similar to the CsPbBr$_3$ NC-based structures, the CsPb(Br,I)$_3$ NC sensitized membranes exhibit consistently lower ASE threshold and higher output stability compared to the respected samples on quartz. The main differences relative to the green-emitting analogous structures are that on the average: (i) the ASE threshold reduces even more in the flexible structures, that is from $\sim$150 $\mu$J/cm$^2$ in quartz to $\sim$70 $\mu$J/cm$^2$ in CA for the champion structures data shown in Figure 3a–d; (ii) the improvement in operational stability is substantial but smaller than that in the green-emitting samples as observed in Figure 3e. It is worth noting that to the best of our knowledge the aforementioned ASE threshold of $\sim$70 $\mu$J/cm$^2$ constitutes a record low value for red-emitting perovskite NC structures in the nanosecond excitation regime.\textsuperscript{30,38,39}

The improved ASE stability can again be attributed to the superior heat transfer properties of the flexible membranes. This is evidenced by experiments summarized in Figure S6 that account for the local heating by monitoring the ASE position shift and further confirmed by the temperature and thermal images of the samples obtained by an IR camera shown in Figure S7. It can be observed that during the first 7 min of ASE operation, the local temperature on the quartz deposited waveguides exhibits a temperature rise of $\sim$1.35 $^\circ$C, which is $\sim$3.5 times higher than the respective temperature rise of the polymer membrane. Furthermore, as presented in Figure S8, the free-standing membranes can sustain ASE under UV (355 nm) nanosecond excitation, albeit at increased threshold values compared to the respected values using green (532 nm) excitation. Importantly though no ASE was observed under 355 nm pumping from multilayer CsPb(Br,I)$_3$ NC structures deposited on quartz, indicative of the better waveguiding and photostability properties of the free-standing membranes, as elaborated further by optical gain measurements and TMM simulations, discussed below.

**Optical Gain Measurements.** The optical gain and waveguiding properties of the green and red-emitting NC multilayers on quartz and free-standing membranes were further investigated via variable stripe length (VSL) experiments.\textsuperscript{30,40–42} A line-shaped excitation beam was focused onto the sample surface via a cylindrical lens. At the same time, the ASE emission was collected from the edge of the sample as a function of stripe length, enabling the estimation of the net modal gain $G$. The optical loss, $\alpha$, related to re-absorption and scattering losses within the structure was evaluated using a fixed stripe length beam by varying the distance of the light stripe from the edge of the sample. The results of the aforementioned VSL experiments at an excitation of $\sim$1.1 $E_{th}$(ASE threshold) are presented in Figure 4a–d for red and green-emitting multilayer stacks deposited on quartz and polymer substrates.

The ASE onset is characterized by the steep increase of the integrated emission intensity when the stripe size reaches the required length for the optical gain to surpass the propagation region.
losses. To estimate the net modal gain, the experimental data were fitted using eq 1, near the threshold region.

\[ I_L (\lambda) = G (\lambda) \times e^{\alpha L} \]  

(1)

Where \( I_L (\lambda) \) is the integrated emission intensity, \( G (\lambda) \) is the optical gain, \( \alpha \) is the absorption loss, and \( L \) is the excitation stripe length. For green-emitting CsPbBr\(_3\) NC-based active media, the net modal gain \( G \) is estimated at \( \sim 92 \pm 4 \text{ cm}^{-1} \), for quartz and free-standing membranes, respectively. Lower net modal gain values of \( \sim 37 \pm 3 \text{ cm}^{-1} \) were obtained for mixed halide CsPb(Br,I)\(_3\) NC-based structures on quartz and CA, respectively.

The correlation of optical gain, loss, and net modal gain is given by eq 2.

\[ G (\lambda) = g (\lambda) - \alpha (\lambda) \]  

(2)

The absorption loss \( \alpha \) is extracted by the fitting of the integrated emission versus excitation strip distance from the edge of the sample using the following Beer–Lambert law function.

\[ I (\lambda, d) = I_0 (\lambda) e^{-\alpha d} \]  

(3)

Where \( I_0 \) is the integrated emission for \( d = 0 \) and \( d \) corresponds to the distance of the excitation stripe from the sample edge. The fitting results are shown in the inset graphs of each sample in Figure 4a–d. As can be seen, a substantial reduction of the absorption losses by a factor of \( \sim 2 \) and \( \sim 5 \) for green and

Table 1. ASE Threshold and Optical Gain Properties of the Studied Samples

| sample                     | \( E_{\text{th}} \) (\( \mu \)J cm\(^{-2}\)) | \( \lambda_{\text{exc.}} \) (nm) | \( G \) (cm\(^{-1}\)) @1.1 \( E_{\text{th}} \) | \( g \) (cm\(^{-1}\)) @1.1 \( E_{\text{th}} \) | \( G \) (cm\(^{-1}\)) @16 \( E_{\text{th}} \) |
|---------------------------|----------------------------------|-----------------|---------------------------------|-------------------------------|-----------------|
| quartz \( \text{CsPbBr}_3 \) NC multilayers | 150                              | \( \sim 355 \)   | 30                             | 92                           | 122             |
| membranes \( \text{CsPbBr}_3 \) NC multilayers | 95                               | \( \sim 355 \)   | 15                             | 121                          | 137             |
| membranes \( \text{CsPbBr}_3 \) NC multilayers | 300                              | \( \sim 532 \)   | 70                             | 21                           | 130             |
| membranes \( \text{CsPbBr}_3 \) NC multilayers | 300                              | \( \sim 532 \)   | 70                             | 21                           | 130             |
| membranes \( \text{CsPbBr}_3 \) NC multilayers | 300                              | \( \sim 532 \)   | 70                             | 21                           | 130             |

*The missing data in the first two table columns, refer to samples in which no ASE was observed under the specified experimental conditions. The missing data in the last column, refer to samples in which ASE was not sustained at such high excitation.
red-emitting structures is observed when switching from quartz to free-standing membranes. As re-absorption losses in the rigid and flexible slabs are expected to be similar due to the identical characteristics of the multilayer active region, the reduction of the optical losses can be attributed to a suppression of scattering losses in the free-standing membrane as the emission is more efficiently waveguided through the optical modes supported by the CA slab. The effect of pump excitation energy on the net modal gain for the green and red-emitting flexible waveguides, is presented in Figure 4e,f. For both structures, the net modal gain grows with pump fluence to values as high as $\sim 430$ cm$^{-1}$ at 1.7 mJ cm$^{-2}$ and $\sim 620$ cm$^{-1}$ at 1.2 mJ cm$^{-2}$ for CsPbBr$_3$ and CsPb(Br,I)$_3$ NC-based emitters. The lower $G$ values and the smaller rate with which the net modal gain grows with fluence in the green-emitting samples are attributed to the higher optical losses, such as the Auger and photocharging processes, associated with the UV (355 nm) photoexcitation compared to the green (532 nm) excitation used of the mixed-halide NC-based structures. A summary of the ASE and optical gain properties of the studied samples is listed in Table 1.

Waveguiding Properties of the Membrane Structures. The TMM model was used to calculate the cross-sectional electric field distribution within the green- and red-emitting waveguide structures deposited in CA and quartz. The data are presented in Figure 5a,b, along with the refractive index modulation and the layer thicknesses. The striking observation from the simulation data is that the electric field intensity is 2 orders of magnitude larger in the membrane slabs compared to the quartz deposited structures. This is largely a result of the significantly smaller CA slab thickness that effectively confines the optical field within the structure. A more careful look into the model data indicates that the emission of the CsPbBr$_3$ and CsPb(Br,I)$_3$ NC-based structures couples to the 20th and 15th cavity mode, respectively. This confirms that the reduction of the ASE threshold and the simultaneous increase of the net modal gain observed in the membrane samples can be attributed to such efficient light waveguiding properties.
seen in Figure 5c,d. Experimental data show good agreement with simulated data produced via a TMM model. Based on the reflectivity results, quality factors ($Q \sim \lambda/\Delta \lambda$) of $\sim 28$ and $\sim 31$ were estimated for the green and red-emitting cavities, respectively that are comparable with $Q$-factors obtained in dielectric slab microcavities formed electron-beam evaporation of conventional inorganic dielectric materials.\(^{44}\)

**Dual-Color ASE and White Light Generation.** Lasers that can produce dual or multicolor emission toward white light lasing can find niche applications in full-color laser lighting/imaging/displays, spectroscopy, fluorescence sensing, and visible light communications.\(^{45−51}\) Monolithic integration of RGB laser multilayers based on epitaxial semiconductors is challenging though, due to the large lattice mismatch involved. Fabrication of single-chip, multicolor lasers based on soft, solution-processed semiconductor gain media such as polymers, nanowires, or NCs can circumvent the lattice mismatch issue, yet further work is needed toward improvements in the design, capabilities, and reliability of such laser devices. Toward such an objective, a preliminary study of dual ASE emission was performed by optical excitation of stacked up green-emitting CsPbBr$_3$ and red-emitting CsPb(Br,I)$_3$ NC-based membranes.

Optical pumping of the stacked membranes was performed via 355 nm nanosecond pulses, exciting first the CsPb(Br,I)$_3$ NC-based structure, as shown in the schematic of Figure 6a, to minimize reabsorption losses of the green ASE peak by the red-emitting overlayer membrane. The spectral evolution as a function of excitation fluence is presented in Figure 6b, while the combined integrated ASE emission from the stacked membranes and the FWHM of each of the two ASE peaks is plotted against excitation energy density, as shown in Figure 6c. Red ASE is activated at $\sim 90 \mu J \text{ cm}^{-2}$ while green ASE is switched on at $\sim 220 \mu J \text{ cm}^{-2}$ with the dual ASE peaks sustained to densities larger than $1 \text{ mJ cm}^{-2}$. The far-field mixing of the multicolor ASE is displayed on a CIE color map, highlighting the ability to tune the color chromaticity of the output emission from red to green by adjusting the excitation intensity.

The potential of the NC-sensitized free-standing membranes for other applications such as light downconverters for white light generation and underwater light communication was also explored, with blue-green lasers being considered ideal candidates, to satisfy the demand for high-bandwidth, high-speed wireless communication due to the large range data transfer with low propagation losses in aqueous environments. For the former function, green and red-emitting membranes were individually or jointly integrated with blue-emitting InGaN LEDs. As presented in Figure 7a–c, the blue electroluminescence can be partially converted to green or red emission by respected combinations of the InGaN diodes with green or red emissive NC/CA multilayers. Integration of the green and red membranes to the nitride LEDs results in RGB emission. By exploiting the fact that the emission

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**Figure 6.** (a) Schematic illustration of the geometry used to initiate dual ASE from stacked red- and green-emitting free-standing membranes. (b) Evolution of the emission spectra at different pump fluences for stacks of CsPb(Br,I)$_3$/CsPbBr$_3$—CA multilayers demonstrating their ability to sustain dual-color ASE. The inset CIE diagram indicates the tunability of the ASE emission chromaticity via the excitation fluence. (c) Integrated area of the combined emission from the stacked membranes and FWHM of the emission of each of the two membranes plotted against excitation energy density.
chromaticity can be finely tuned via the LED driving current, a pure white color of CIE coordinates 0.34, 0.35 at a color temperature of $\sim$5000 K, and an NTSC 115% wide color gamut can be demonstrated, as shown in Figures 7d and S9. The results indicate that such lightweight, thin, and bendable structures are promising for applications in flexible lighting panels and displays.

The small solubility of CA in DI water combined with encapsulation of the flexible membranes by the Hyflon AD 60 fluoropolymer, enabled the demonstration of nanosecond-excited ASE in an aqueous environment, as presented in Figure 7e. Upon UV-excitation of CsPbBr$_3$ NC-based structures, an increase of fluence results in the activation of ASE at $\sim$2.33 eV with an ASE onset at $P_{\text{th}} \sim 320 \mu J$ cm$^{-2}$, as presented in Figure 7f. The increase of the threshold by a factor of $\sim$3, compared to the respective samples investigated in ambient conditions, can be assigned to the reduction of the refractive index contrast between the membrane ($n_{\text{CA}} \sim 1.46$) and the surrounding medium ($n_{\text{DI water}} \sim 1.33$ vs $n_{\text{air}} \sim 1$) resulting in higher optical losses of the resonator as well as the degradation of the water-soaked structure.

CONCLUSIONS

In summary, we have demonstrated the facile, fully solution-processed fabrication of flexible, free-standing structures, combining CA polymer membranes with active gain media based on multilayer stacks of CA with green CsPbBr$_3$ or red-emitting CsPb(Br,I)$_3$ NCs. Such flexible membranes act as low Q waveguides supporting optical modes that can effectively couple with the perovskite gain media emission resulting in nanosecond-excited ASE with a lower threshold, higher net modal gain, and suppressed optical losses compared to identical multilayers deposited on rigid quartz substrates. Furthermore, they exhibit higher ASE operational stability compared to the latter samples as a result of the better heat outflow properties arising from the absence of a supporting substrate and the smaller thermal interface resistance between the two soft and comfortable CA and NC media. The exceptional optical amplification properties of such membranes are witnessed by their ability to stack up and sustain dual-color ASE in the green and red parts of the spectrum, while their versatility for other photonic applications is confirmed by demonstrations of white light generation and underwater ASE. The presented results demonstrate the high potential of simple,
solution-processed waveguides based on polymer resonators and LHP NC gain media for practical, scalable, flexible, and low-cost spontaneous and stimulated emission applications.

MATERIALS AND METHODS

**NC Synthesis.** CsPbBr$_3$ DDAB NCs. The synthesis of CsPbBr$_3$ DDAB NCs is similar to the method described in ref 53. CsPb(Br,I)$_3$ DDAB NCs. Preparation of Cesium Olate Precursor Solution. (Cs-olate, 0.4 M). Cs$_2$CO$_3$ (814 mg, 2.5 mmol) was mixed with octadecene (10 mL) and OA (2 mL, 6.34 mmol) in a vial. The mixture was stirred and heated to ca. 125 °C on a hot plate until it became clear and then cooled to room temperature.

Synthesis of CsPb(Br,I)$_3$ NCs. Pb$_2$ (200 mg, 0.434 mmol) and DDAB (92.5 mg, 0.2 mmol) were added to 10 mL mesitylene in a 100 mL 3-necked flask. The mixture was heated to 110 °C under a nitrogen atmosphere and, after the reaction mixture reached set temperature, OA (1 mL, 3.17 mmol) and DOAm (2 mL, 6.63 mmol) were injected simultaneously. Then the temperature of the mixture was raised to 140 °C forming a clear yellowish solution, and then, the Cs-olate (0.3 mL, 0.12 mmol) precursor was swiftly injected. After 10s the reaction mixture was cooled down to RT with a water/ice bath.

**Isolation and Purification of CsPb(Br,I)$_3$ NCs.** The purification procedure was performed in the nitrogen glove box using anhydrous solvents. The crude solution was centrifuged at 5000 rpm (3438g) for 7 min. The supernatant was discarded, and the precipitate was dispersed in 10 mL of anhydrous hexane and then centrifuged at 3700 rpm (1883g) for 2 min. The precipitate was discarded, and 7 mL of anhydrous methyl acetate was added to the supernatant, followed by centrifugation at 10,000 rpm (13751g) for 5 min. The resulting precipitate was dispersed in 3 mL anhydrous cyclohexane, followed by centrifugation at 3700 rpm (1883g) for 2 min. The precipitate was discarded, and the obtained colloidal solution of CsPb(Br/I)$_3$ NCs was filtered with a PTFE-syringe filter (pore size 0.2 μm) and used for further studies.

**Sample Preparation.** Quartz substrates with dimensions of 2 × 1.5 cm were used for the deposition of the NC/CA multilayers and the CA slabs. Prior to the deposition process, the substrates underwent sequential cleaning with n-butyl acetate, acetone, and IPA. The substrates were then kept in nitric acid for 8 h allowing them to form a highly hydrophilic surface. The samples were then washed with deionized water, followed by sequential cleaning with n-butyl acetate, acetone, and IPA and dried under compressed air.

**Flexible Membranes.** CA (CA, Mn = 30,000, η$_{av}$ ~ 1.46) dissolved in acetonitrile at 120 mg/mL was prepared for the formation of free-standing and spacer layers used in the samples. For the formation of the free-standing membranes, cellulose acetate was spin cast under static conditions on a quartz substrate at 4000 rpm for 30 s. The thickness of the free-standing membranes was determined via the single-point ellipsometry method, measured by a ThetaMetrisz ellipsometer (FR-PRO).

LHP NCs/CA Multilayers. Multilayers were deposited either directly on top of quartz substrates or to the CA flexible substrates via spin casting. Initially, CsPbBr$_3$ or CsPb(Br/I)$_3$ NCs dispersed in toluene (∼30 mg/mL) was deposited under static coating conditions, at 1000 rpm for 30 s, followed by a drying step at 4000 rpm for 10 sec. CA diluted in acetonitrile (13 mg/mL), was used as the spacer layer deposited via dynamic deposition of CA at 5000 rpm. The bilayer deposition was repeated as many times as needed to produce multilayers. In the case of the membranes, subsequent to multilayer deposition, they were peeled off from the substrate.

**TMM Model.** A TMM model was used to simulate the reflectivity from the studied waveguides as well as produce the cross-sectional distribution of the electric field within the structures. The TMM model is described in detail in the book “Basics of Optics of Multilayer Systems”. The absorption spectra of the CsPbBr$_3$ and CsPb(Br/I)$_3$ NCs were used as the input of the TMM model, with the amplitude of the excitonic absorption corresponding to the oscillator strength of the excitonic species.

**Optical Spectroscopy.** Steady-State PL and Optical Absorbance. The absorbance of films was acquired using a PerkinElmer Lambda 1050 spectrophotometer with a spectra range of 200−3000 nm. Steady-state PL was excited by a 405 nm diode laser and detected via a combination of a 0.75 m Acton 750i Princeton spectrometer and a 1024 × 256 pixels PIXIS charge-coupled device (CCD) camera.

**White-Light Angle-Resolved Reflectivity.** A custom-made goniometer was used, equipped with a fiber-coupled tungsten-halogen white light source coupled to a 600 μm core multimode fiber. The white light beam was focused onto the sample’s surface using a collimating and a focusing lens mount on the excitation arm, in a 2 mm spot diameter. A second rotating arm was then used to collect the reflected light via a fiber-coupled Ocean-Optics CCD spectrometer, with a spectral resolution of ~1 nm.

**Amplified Spontaneous Emission Experiments.** The optical excitation of the films was performed via Quantel Brilliant Nd/YAG laser either 355 or 532 nm wavelength, producing a 4 mm beam with a pulse width of ~6 ns and repetition rate of 10 Hz. The excitation energy density was varied via neutral density optical filters. The excitation was performed using a line-shaped beam, focused on the sample via a cylindrical lens. The PL and ASE were collected from the sample side using a Mitutoyo 10X, 0.28 NA long working distance objective coupled to a 100 μm core multimode fiber. The collected emission spectra were dispersed in a 0.75 m Acton 750i Princeton spectrometer equipped with a 1024 × 256 pixels PIXIS CCD camera.

**Optical Gain Properties.** For the estimation of the optical gain properties of our samples, VSL experiments were used. The excitation beam was focused via a cylindrical lens in a 5 × 1 mm spot. The length of the strip was adjusted via a precision-adjustable slit with a micrometer sensitivity of 5 μm. For the optical loss measurements, the excitation beam was initially placed at the edge of the sample. By keeping the excitation beam size, intensity, and position constant, the sample was moved in 50 μm intervals away from the light collection side.

**Transmission Electron Microscopy.** TEM images were collected using a JEOL JEM2200FS microscope operating at 200 kV accelerating voltage.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsphotonics.2c00426.

TEM images of CsPbBr$_3$ NCs; synthetic procedure and structural characterization of CsPb(Br/I)$_3$ NCs; opti-
mization of the ASE threshold based on multilayers of CsPbBr$_3$ NCs-CA on quartz substrates; ASE data and simulated reflectivity spectra from of CsPbBr$_3$ NC multilayers deposited on quartz and CA; ASE stability of CsPbBr$_3$ and CsPbBr$_3$(Br,I)$_3$ NCs on quartz and membrane substrates; thermal images of bilayers deposited on CA membranes and quartz substrates; ASE studies under nanosecond UV (355 nm) excitation; light downconversion properties of NC-sensitized polymer membranes (PDF)

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Notes

The authors declare no competing financial interest.

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