Enhanced Photoluminescence in Quantum Dots–Porous Polymer Hybrid Films Fabricated by Microcellular Foaming

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The color conversion efficiency of thin polymeric layers embedding quantum dots (QDs) is limited by their negligible light scattering ability and by the insufficient absorption of the excitation photons. In this study, a route is presented to tackle these optical shortcomings by introducing a tailored network of micropores inside these hybrid films. This is achieved by exploiting the microcellular foaming approach which is rapid, cost effective and only makes use of a green solvent (supercritical carbon dioxide). With an appropriate combination of the applied pressure and temperature during foaming, and by using a proper film thickness, the photoluminescence (PL) intensity is enhanced by a factor of up to 6.6 compared to an equivalent but unfoamed hybrid film made of CdSe/ZnS QDs in a polymethyl methacrylate matrix. Spectroscopic measurements and ray tracing simulations reveal how the porous network assists UV/blue light absorption by the QDs and the subsequent outcoupling of the converted light. The approach improves the PL for various QD concentrations and can be easily scaled up and extended to other polymeric matrices as well as light converting materials.

1. Introduction

In recent years, colloidal quantum dots (QDs) have emerged as an alternative to conventional rare-earth phosphors in display and general illumination applications due to their outstanding properties, such as broad absorption band, narrow emission linewidth, tunable peak emission wavelength, and high photoluminescence quantum yield (PLQY).[1–4] In such applications, QDs are dispersed into a polymeric matrix to form hybrid films, which usually serve as free-standing, remote-type configurations excited by an external UV/blue light source.[5–7] In this layout, the light conversion process is notably hindered by the limited absorption of the excitation light by the QDs. Indeed, the QD nanoscale size does not result in efficient light scattering that could increase the UV/blue light absorption probability.[8–10] Besides, the reabsorption of the converted light by the QDs as well as their current costs prevent the use of too high QD concentrations.[11,12] Lastly, the converted light propagating in the hybrid film can be trapped and guided to the film’s edges upon consecutive total internal reflection events.[13] In order to improve the absorption of the excitation light and the extraction of the converted photons, QDs can be included within photonic crystal slabs or deposited on their surface.[14–16] By engineering the coupling to leaky modes, a high energy density can be obtained at resonance in the direct vicinity of the QDs, and the emission directionality together with its polarization...
dependency can be simultaneously tuned.\textsuperscript{[17,18]} Volumetric light scattering stemming from high refractive index nano/microparticles that are randomly dispersed in the hybrid film can also be employed to assist light conversion.\textsuperscript{[19–22]} The incorporation of such particles nevertheless brings extra material costs and can induce parasitic light absorption. The latter drawback can be tempered by using hollow particles, which additionally exhibit high light diffusion properties.\textsuperscript{[23]} An attractive solution takes inspiration from light scattering biostructures, such as those evolved by the white beetles of the genus \textit{Cyphochilus}.\textsuperscript{[24,25]} It consists in directly introducing a porous network within the polymeric matrix, thus avoiding the use of additional particles. Recently, several fabrication methods have been presented in order to fabricate particle-free optical diffusers, such as the breath figure method,\textsuperscript{[26,27]} electrospinning,\textsuperscript{[28,29]} an extrusion and stretching process,\textsuperscript{[30,31]} as well as the nonsolvent-induced phase separation.\textsuperscript{[32,33]}

In the present study, we propose to enhance the color conversion efficiency of remote hybrid films via introducing a porous network fabricated by microcellular foaming. This technique, often used to improve the mechanical and thermal properties of polymers, combines several advantages: i) it is rapid, cost effective, upscalable, and already established in several industrial applications, ii) it was successfully used to foam various amorphous polymers,\textsuperscript{[44]} and applied to semicrystalline polymers provided a fine control of the foaming temperature,\textsuperscript{[35,36]} iii) it relies on a green process in which no harmful substance is used or produced, and iv) it enables to control the morphology of the porous network.\textsuperscript{[37]} Our approach is exemplified by utilizing hybrid films made of CdSe/ZnS QDs in a micrometer-thick polymethyl methacrylate (PMMA) matrix; however, we emphasize that it is not restricted to that particular system.

In the next sections, we report on the procedure how to tune the morphology of a micropores network with the aim of fabricating light diffusing films that possess a high optical transmittance. Following the spectroscopic characterization of these films, the developed process is then applied to functional hybrid films to enhance their photoluminescence (PL) intensity. Finally, the influence of the network morphology of the type of emission (edge emission enabled or blocked) and of the QD concentration on the resulting PL intensity enhancement is assessed experimentally and further analyzed by ray optics simulations.

2. Results and Discussion

Figure 1 shows a schematic overview of the developed approach and of the foamed hybrid films. As illustrated in Figure 1a, the foaming process exploited in our approach is based on four main steps: i) the preparation of the light converting layer consisting of (CdSe/ZnS) QDs dispersed in a PMMA matrix (also referred to as “hybrid films” in the following) and processed on a glass substrate; ii) the dissolution of supercritical carbon dioxide (CO\textsubscript{2}) within the PMMA matrix by increasing the pressure to 50 MPa under a fixed temperature of 80 °C, forming a homogeneous system with a resulting glass transition temperature ($T_g$) lower than the applied temperature $T$ (the so-called plasticization effect);\textsuperscript{[18]} iii) the formation of a super-saturated PMMA-CO\textsubscript{2} system by pressure quenching, whereby CO\textsubscript{2} nucleates into numerous small pores; and iv) the growth of the pores by CO\textsubscript{2} diffusion until $T_g > T$. In its supercritical state (above a pressure of 7.38 MPa and a temperature of 31.1 °C),\textsuperscript{[39]} CO\textsubscript{2} exhibits a liquid-like density and a gas-like diffusivity, which enables PMMA to rapidly absorb it (short saturation time required) and in large quantity.\textsuperscript{[40]} Moreover, in the supercritical foaming conditions, the pressure quench carried out at a fixed temperature prevents vapor/liquid boundaries, and hence the degradation of the porous network in the polymer foams.\textsuperscript{[41]} A (micrometer) thin skin layer free from pores nevertheless appears close to the film/air interface as a result of CO\textsubscript{2} diffusing out. This depletion region, originating from a too
low CO2 concentration which does not allow the nucleation of the pores, leads to a mostly planar front side, as indicated in Figure 1a. The porous network introduced in PMMA and close to the substrate assists the luminescence downshifting mechanism in two ways (see Figure 1b): first, by elongating the optical path length of the exciting (UV/blue) light in the light converting medium, thereby increasing its absorption probability by the QDs. Second, by fostering the forward outcoupling of the converted light that could otherwise escape from the rear side (backward propagating light), or be guided within the planar PMMA layer through multiple total internal reflections. We indeed note that the isotropic emission of the converted light and the negligible light scattering induced by the QDs (with a mean diameter of only $\approx 10$ nm) strongly limit the fraction of converted light that is outcoupled in forward direction, the latter being theoretically limited to only 26% for a planar layout without pores (see Figure S1, Supporting Information, for more details).

In the CO2 foaming process, the applied pressure and temperature are two key parameters which determine the mean diameter of the pores, their density as well as their spatial distribution within the PMMA layer. In a previous study, we have shown that the applied pressure plays an even more important role than temperature during the foaming process.$^{[42]}$ More specifically, higher foaming pressures allow i) reducing the pores size, ii) increasing their density, iii) improving their uniformity, and iv) shortening significantly the saturation time which corresponds to the most time-consuming step in the foaming process. For time and energy efficiency, we therefore performed a fast foaming process (saturation time of only 1 min) using a moderate temperature (set at 80 °C) and by working with a pressure of 50 MPa. Such a high foaming pressure enables to rapidly dissolve CO2 in the PMMA layer, provided that the latter has a thickness less than around 10 µm. However, a too thin PMMA layer prevents the formation of a homogeneous porous network because of the previously mentioned “skin layer” effect, although high pressures tend to limit the thickness of this unfoamed region.$^{[43]}$ These counterbalancing effects result in an optimized range of PMMA layer thicknesses between 4 and 10 µm.

Consequently, three sets of PMMA samples with a measured pristine thickness of 4.2, 6.3, and 7.4 µm were foamed for 1 min at 50 MPa and 80 °C (in the following, these samples will be simply referred to as the 4, 6, and 7 µm configurations, respectively). The “pristine” thickness here relates to the PMMA layer thickness measured before foaming, since the introduction of the porous network leads to a volume and thickness increase. As shown in Figure 2a–c, the different pristine PMMA samples considered qualitatively exhibit the same transparency. These samples turn translucent after the foaming process,$^{[42]}$ whereby light diffusion is gradually enhanced as the pristine PMMA layer thickness increases. As revealed by cross-sectional scanning electron microscope (SEM) images, this trend stems from a change in the porous network morphology among the

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**Figure 2.** Influence of the pristine PMMA layer thickness on the porous network morphology and on the resulting light diffusion properties of the foamed samples. Photographs of pristine (left) and foamed (right) PMMA samples shown for increasing pristine layer thicknesses of a) 4 µm, b) 6 µm, and c) 7 µm. The corresponding cross-sectional scanning electron microscope images are displayed in (d)–(f). Scale bars: 4 µm.
Table 1. Dimensional analysis of the porous networks introduced in the three sets of samples displayed in Figure 2.

<table>
<thead>
<tr>
<th>Pristine layer thickness [µm]</th>
<th>Foamed layer thickness [µm]</th>
<th>Average diameter of the pores [µm]</th>
<th>Number of pores per µm (horizontal cut)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 ± 0.1</td>
<td>5.6 ± 0.3</td>
<td>2.2 ± 0.5</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>6.3 ± 0.1</td>
<td>9.8 ± 1.6</td>
<td>2.3 ± 0.6</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>7.4 ± 0.2</td>
<td>11.6 ± 1.4</td>
<td>1.6 ± 0.4</td>
<td>1.8 ± 0.2</td>
</tr>
</tbody>
</table>

different configurations (see Figure 2d–f and the associated quantitative analysis in Table 1). More precisely, the density of the introduced pores increases alongside with the pristine PMMA layer thickness and can be tailored from a single row of micrometer-sized pores to a denser array. The pore array displays reduced pore dimensions with an increasing pristine thickness and extends in three dimensions, hence increasing the resulting thickness of the foamed layers. We always observe the presence of a skin layer with a mean thickness ranging from 1.6 to 2.3 µm which planarizes the front side of the foamed samples.[42] We also stress that the densely packed micropores are most often separated by a thin wall with a submicrometer width.

To demonstrate the tunability of the foamed layers’ optical properties, the overall (diffuse plus specular) transmittance values were measured over the 380–780 nm spectral range, as shown in Figure 3a. It is first noted that these values are stable over the visible range, as expected from layers based on micrometer-sized pores. By increasing the pristine layer thickness from 4 to 7 µm, the overall transmittance of the foamed PMMA layers exhibits a gradual decline from 80.1% to 58.7%, which is significantly lower than that of the unfoamed layers (92.1%). These optical properties are homogeneous over the samples’ surface (several cm²) and can be reproduced with a high fidelity from batch to batch (see example in Figure S2, Supporting Information). In Figure 3b, we additionally report the far-field angular distributions of the transmitted light obtained at 650 nm for the different foamed layers. Our measurements first show a predominant transmittance peak at 0° for all the configurations. This is explained by the limited (lateral) density of the pores, which allows some incident light rays to directly pass through the films without interacting with the pores (see 4 µm configuration) or conversely, by the local clustering of the pores (only separated by a thin wall), which reduces the effective number of light diffusing centers. Despite this, a significant fraction of the light propagates at larger angles, indicating a longer optical path length within the foamed medium. This beneficial effect is more pronounced as the pristine layer thickness increases. To further illustrate the light diffusion properties of the foamed samples, we report in Figure 3 in the Supporting Information the photographs of the far-field transmission patterns of a 650 nm laser beam passing through homogeneous and foamed PMMA layers. They emphasize a more homogeneous angular distribution of the light upon introduction of the micropores. Thus, the pristine thickness of the PMMA layers enables to control the morphology of the porous network after foaming and in turn, to adjust the fraction of diffuse light together with the overall amount of light extracted into air. As will be analyzed in the following, these optical properties are of paramount importance for the performance of QD-based light converting layers.

To demonstrate that, CdSe/ZnS QDs were incorporated into PMMA films before foaming. The measured absorptance and PL emission spectra of the corresponding QDs dissolved in chloroform are shown in Figure 4a. The QDs considered herein possess a large absorption band ranging from UV (≈360 nm) to green light wavelengths (≈550 nm), whereby the absorptance is more significant toward the UV range. Their emission spectrum exhibits a peak at ≈544 nm with a full width at half maximum (FWHM) of only ≈26 nm. The emission peak wavelength of CdSe/ZnS core–shell QDs can be easily tuned by varying their core size, while the FWHM of their emission peak is correlated to their size distribution.[44] The measured FWHM of ≈26 nm indicates a very uniform size distribution of the QDs, which is desired for high-color-gamut displays. When introduced into homogeneous and transparent PMMA films (see Figure 4b, top panel), the QDs result in a limited emission of the converted light in forward direction. This

![Figure 3](image-url)
can be qualitatively assessed in the bottom panel of Figure 4b which shows a dim brightness over the sample’s surface. Due to the isotropic emission of the QDs and to the absence of light scattering within the film, this sample also exhibits significant edge emission (not visible in Figure 4b). Under the same excitation conditions, the light diffusing foamed hybrid film possesses a much brighter and a homogeneous light emitting surface over few cm², demonstrating the beneficial impact of the porous network. To gain more insights into the spatial distribution of the QDs at different elevations within the foamed PMMA layers, we recorded the downshifted light intensity distribution by confocal fluorescence microscopy. The acquired images suggest that the QDs are homogeneously distributed throughout the foamed PMMA layers. Moreover, a high intensity is observed between the micropores (appearing as dark spots) in a horizontal plane located close to the film/glass interface (Figure 4c), while these pores do not appear in the aforementioned skin layer (Figure 4d). This observation is in agreement with the cross-sectional SEM images of Figure 2, and proves that the micropores are uniformly distributed in the horizontal plane of the films and mostly located close to the substrate.

To evaluate more quantitatively the influence of the porous network on the hybrid films’ PL characteristics, foamed hybrid films with different pristine thicknesses (4, 6, and 7 µm, as indicated in brackets in the following) were characterized in an integrating sphere and under a 405 nm laser excitation from the glass substrate side (as illustrated in Figure 1b). For comparison, equivalent but unfoamed samples were also investigated (QD concentration fixed at 1.5 wt% for all the samples). As shown in Figure 5a, the integrated PL intensity increases using thicker hybrid films for both the unfoamed and the foamed samples, confirming that the limited absorption of the UV light by the QDs is one of the limiting factors. These measurements also underline the enhanced PL intensity of 6.6 (4 µm), 3.3 (6 µm), and 3.0 (7 µm) times obtained with respect to the unfoamed hybrid films (and with blocked edge emission). To analyze the underlying mechanisms responsible for this PL enhancement, both the PLQY and the integrated absorptance values were quantified. Regardless of the pristine thickness considered, it is well noted that these two quantities are improved upon the introduction of the porous network, contributing together to the measured PL intensity enhancements. More precisely, the PLQY increasing ratios are 1.7 (4 µm), 1.1 (6 µm), and 1.0 (7 µm) and the ones relative to the absorptance are 1.8 (4 µm), 1.1 (6 µm), and 1.0 (7 µm). The PLQY enhancement of the foamed samples is attributed to an improved light extraction scheme, by which the normally trapped light can be redirected with a propagation angle lower than 42° (critical angle for total internal reflection, see Figure S1, Supporting Information) as it interacts with pores inside the PMMA layer. Moreover, the absorptance enhancement originates from an extended optical path length of the excitation light in the foamed samples. This is induced by a combination of multiple light refraction/reflection events at the PMMA-pores interface and to a lesser extent, by light scattering by smaller pores or regions in-between the micropores (especially for the 7 µm thick hybrid layers which feature an extended array of smaller pores). In complement...
to the measurements presented in Figure 5a, the PL intensity values were also obtained for a configuration enabling edge emission, shown in Figure 5b. In this case, the introduction of the porous network still leads to a noticeable PL intensity enhancement. More precisely, the relative enhancement for these three configurations are 1.3 (4 µm), 1.1 (6 µm), and 0.8 (7 µm). As expected, the latter is lower than for samples with blocked edge emission since total internal reflection now allows a large fraction of the converted light to be coupled out even for the unfoamed samples. The PL intensity enhancement is instead attributed to the higher absorptance since the PLQY values are similar. Indeed, the PLQY is an intrinsic property of the QDs that only depends on the material's composition and synthesis condition, which means that the introduction of the porous network should not affect the PLQY of QDs provided that all the converted light is extracted. The influence of the excitation direction on the resulting PL properties was additionally tested for the thinnest foamed hybrid film (with pristine thickness of around 4 µm). The results gathered in Figure S4 in the Supporting Information indicate that for both the edge emission enabled and blocked, the PL intensity is higher when the samples are excited from the glass side compared to the air side (by 14.6% and 15.8%, respectively). Given the almost similar PLQY values in both types of excitation, this difference is mainly attributed to the higher absorptance achieved with the substrate side excitation. To demonstrate the universality of our approach in regards to the QDs content, different sets of hybrid films were fabricated using five QD concentrations (and a pristine thickness fixed at 7 µm for all the samples). The corresponding results, reported in Figure S5 in the Supporting Information, prove that the PL intensity is enhanced in all the cases, as a result of the improved exciting light absorption. The PL intensity enhancement decreases as the QD weight ratio ramps up and starts to be negligible only at a concentration of
15%, as a result of the saturation of the exciting light absorption (same value achieved for the foamed and for the unfoamed hybrid films in this case). Thus, our approach can be used to improve the PL at a given QD concentration or alternatively, to maintain a targeted PL value while decreasing the amount of QD used and therefore reducing the costs of the hybrid films.

Lastly, to estimate the elongation of the average path length in the sole light converting medium (i.e., without accounting for the path length in the pores), the foamed sample based on the pristine thickness of 4.2 μm (shown in Figure 2d) was modeled according to the measured parameters reported in Table 1 and analyzed using ray optics simulations (see the Experimental Section for details). Beforehand, our model was validated by computing the overall reflectance (R) and transmittance (T) of the foamed layer under normal incidence. The simulated values, reaching \( R = 21\% \) and \( T = 79\% \), are in very good agreement with the measured ones (\( R = 20\% \) and \( T = 80\% \), compare with Figure 3a), hence the same model was used to determine the average path length. The latter, which equals the physical thickness of 4.2 μm for the unfoamed configuration, was found to be increased by a factor of 4.3 in the light converting medium owing to the porous network and the associated angular redistribution of the exciting light. This enhanced path length increases the absorption probability of the UV light by the QDs, and positively impacts the performance of the light converting hybrid films.

3. Conclusion

In summary, we presented a rapid and reproducible method for enhancing the color conversion efficiency of hybrid films made of CdSe/ZnS core–shell QDs embedded in a polymeric (PMMA) matrix. This is achieved by introducing micropores into the films via the microcellular \( \text{CO}_2 \) foaming technique, which requires a saturation time of 1 min only. We have shown that the morphology of the porous network can be easily adjusted by tuning the pristine thickness of the hybrid films between 4 and 7 μm. The micropores enable to increase the angular spread of the excitation UV/blue light in the medium containing the homogeneously dispersed QDs, while preserving a high optical transmittance reaching up to 80% over the visible range. Upon introduction of the porous network, we measured a maximum PL enhancement factor of 6.6. As confirmed by ray tracing simulations, this improvement originates in part from the elongated optical path length of the excitation light in the converting medium, which increases the absorption of these high-energy photons by the QDs. Furthermore, the PLQY is simultaneously enhanced since the micropores offer a better light extraction scheme compared to the planar, unfoamed layouts. We have additionally shown that our approach is effective for various QD concentrations up to the saturation of the exciting light absorption, here reached at a QD weight ratio of 15% in hybrid films with a pristine thickness of 7 μm. More generally, the method presented herein can be extended to other QD-polymer composites. The porous network, whose optical properties are mostly governed by ray optics and stable over the visible spectrum, offers an efficient light management scheme for different QDs emitting at various wavelengths.

Our approach is therefore compatible with other color conversion materials based for example on perovskite, organic dyes and so on, and the supercritical foaming conditions enable to use lower foaming temperatures (below 80 °C) if temperature-sensitive QDs are involved. Additionally, the versatility of the microcellular \( \text{CO}_2 \) foaming technique enables to process various matrices ranging from amorphous to semicrystalline polymers. The developed foamed hybrid layers could be integrated in liquid crystal display panels in order to homogenize the pattern of the exciting blue light and to improve its absorption by the QD light converting film. This design would allow to reduce the amount of necessary QDs and to avoid the use of additional light scattering particles and light diffusing films, thereby decreasing the overall costs of the display panels. In the continuation of this work, we will adapt the foaming process to scale down the size of the pores below the micrometer and investigate the light conversion and extraction mechanisms in this different light scattering regime.

4. Experimental Section

Hybrid Films Preparation: CdSe/ZnS core–shell QDs (Beida Jubang Co., Ltd) was first dissolved with chloroform (Sigma-Aldrich) in a vial. Then PMMA powder with a molecular weight of \( \approx 15 \, 000 \) (Aldrich) was also dissolved with chloroform in another vial. To prepare the QDs-PMMA solutions prior to spin coating, these two solutions were then mixed together to obtain a homogenous solution of all components. Before processing QDs-PMMA hybrid layers, glass substrates with a size of \( 3.5 \times 1.5 \, \text{cm}^2 \) and a thickness of 0.95 cm were cleaned in isopropanol (5 min) and later in isopropylene (5 min) in an ultrasonic bath, and then dried with compressed nitrogen. Afterward, glass substrates were treated with oxygen plasma for 2 min to further clean them and to lower down their surface energy. These substrates were immediately used for spin coating after the plasma treatment. During the spin-coating process, the PMMA-chloroform weight ratio and the spin-coating speed were varied to obtain hybrid films with different thickness. The same processes (except for the addition of the QDs solution) were used in order to fabricate the PMMA-only films. All the samples were stored for more than 12 h to ensure the total evaporation of chloroform before subsequent microcellular foaming.

Microcellular Foaming Process: PMMA films and QDs-PMMA hybrid films were foamed according to the method described in our previous study.[36] To this end, the samples were placed in a high-pressure vessel connected to a \( \text{CO}_2 \) feeding system, allowing to compress \( \text{CO}_2 \) to adjust the pressure, and to a heating system so as to set the autoclave temperature. A pressure of 50 MPa and a temperature of 80 °C were used in all the experiments. After 1 min of saturation, pressure quenching was triggered by quickly opening the venting valve, leading to the foaming of the samples.

Thickness Measurement: The unfoamed layers’ thicknesses were measured using a profilmometer (Bruker DektakXT). During the thickness measurement, the height between positions with and without PMMA film was obtained and the final thickness value was averaged based on at least four measured positions. In addition, the foamed layers’ thicknesses were obtained by analyzing the captured SEM images.

Morphological Analysis: Prior to SEM observation, the foamed samples were immersed into liquid nitrogen and subsequently broken to expose their cross-sections. Afterward, a thin gold layer was sputtered to improve the image resolution. The cross-sections of the different foamed samples were characterized by using an SUPRA 55 VP SEM (Zeiss) with an accelerating voltage of 1 KV. To extract the pores’ dimensions, the pores were fitted with an ellipse using the ImageJ software (version 1.52a) and the diameter of a circle with the same area as the ellipse was derived.[45] In addition, the pores density was calculated as...
the number of pores per micrometer along a line parallel to the polymer/glass interface. The dimension analysis of each configuration was based on three samples and at least three SEM images, as the ones displayed in Figure 2, were analyzed for each sample.

Spatial Distribution of the QDs in the QDs-PMMA Layers: Fluorescence images were acquired by confocal microscopy with an inverted Zeiss laser scanning confocal microscope (Zeiss LSM 510 META, Carl Zeiss Inc.). A laser diode with a peak wavelength of 405 nm was used as the exciting source and the emission ranging from 505 to 550 nm was collected. An apochromat 63× oil immersion objective with a numerical aperture of 1.4 was adopted during the scanning process. An area of 20 × 20 μm² with <200 nm lateral and 400 nm axial resolution was scanned to visualize the hybrid films in three dimensions.

Optical Characterization: The overall (diffuse and specular) transmittance of the porous PMMA layers without QDs was obtained over the 380–780 nm spectral range for an unpolared light and under normal incidence using a PerkinElmer Lambda 1050 UV/Vis/NIR spectrometer with an attached integrating sphere. The transmittance results were averaged based on at least six samples for each configuration. With the same instrument (PerkinElmer Lambda 1050 UV/Vis/NIR spectrometer), the absorptance spectrum of the QDs-chloroform solution was obtained over the 360–800 nm spectral range for an unpolared light and under normal incidence. A fluorescence spectrometer (Agilent Cary Eclipse) was used for measuring the emission spectrum of the QDs-chloroform solution between 420 and 800 nm and the wavelength of the exciting light was set at 405 nm.

A UV–vis–NIR spectrometer (Agilent Cary 5000) equipped with a universal measurement accessory was used to measure the angular distribution profile of the transmitted light. During the measurements, the samples were fixed to ensure a normal incidence of the unpolarized light while the detector was rotated with steps of 5° around the samples to collect the transmitted light. The samples were illuminated with 650 nm light and a 2° plate was used in front of the detector to set the collection aperture.

Photoluminescence Measurements: The measurements of PL intensity, PLQY and absorption of QDs-PMMA hybrid films were based on the 3M procedure shown in Figure S6 in the Supporting Information. All the measurements were conducted on four samples and these results were averaged. The measurements were conducted in a home-built optical system, which consists of a light source, an integrating sphere, a charge-coupled device (CCD) spectrometer ( AvaSpec-ULS2048x64-TEC, Avantes BV). For the excitation of QDs, a laser diode with a peak wavelength of 405 nm and a maximum power of 80 mW (DL-7146-101S, Rotheiner Laserotechnik GmbH) was used, which was mounted on a mount (TCLDM9, Thorlabs) and driven by a laser diode controller (ITC4001, Thorlabs GmbH). For the adjustment of an excitation power, a rotatable neutral density filter (NDC-100C-2, Thorlabs) was adopted. During the measurements, samples were placed in the middle of the integrating sphere with the help of a sample holder. A high OH optical fiber with a diameter 1 mm (FP1000UURT, Thorlabs) collected the emission from the integrating sphere and transferred the light to the CCD spectrometer. Before measurements, spectral correction of the detection system was conducted using a certified halogen calibration lamp (HL-3plus, Ocean Optics). Due to the different power values of laser light and QDs emission light, different integration and measuring times were picked to enable a large signal-to-noise ratio. Background errors and errors caused by a red tale of an excitation light were excluded in all the measurements. When measuring the PL properties of the hybrid films with a blocked edge emission, the samples’ edges were coated with a black absorber (black polish, p2 Cosmetics GmbH) to block side emission.

Ray Optics Simulations: Due to their dimensions of several micrometers, the interaction of light with these pores can be well described by ray optics. To assess the influence of pores on the geometrical path length in the polymer material, ray tracing simulations were performed on a simplified geometric model corresponding to the 4.2 μm thick (before foaming) samples using the commercial software LightTools (Synopsys). The pores were modeled as spherical air inclusions (n = 1) in a 5.6 μm thick cuboid PMMA sheet (n = 1.49), which corresponds to the total layer thickness (including skin layer) of the 4.2 μm thick unfoamed layers after the foaming process (see Table 1). All pores have a radius of 1.1 μm and are placed inside the PMMA layer so that they are just touching the upper surface, mimicking the real geometry of the 4 μm thick samples (see Figure 2d). In analogy to ref. [48], their arrangement in the lateral direction follows a hexagonal grid incorporating a normally distributed displacement (standard deviation = 1 μm) in an arbitrary (lateral) direction. The distance between nearest neighbors of the underlying hexagonal grid was chosen to be 3.3 μm, which leads to a void density per unit length close to the experimental value of ≈0.3 μm⁻¹. The total area of the PMMA sheet simulation model was chosen to be ~3245 μm² and a central region of ~480 μm² was illuminated with 10⁶ parallel light rays under normal incidence. The outer boundaries of the PMMA sheet model are equipped with mirrors to keep light rays from exiting the sheet to the sides. A simulation model with these parameters is depicted in Figure S7 in the Supporting Information.

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.

Keywords
microcellular foaming, photoluminescence, porous polymers, quantum dots, ray tracing simulations