

Enhancing the Photoluminescence Emission of Conjugated MEH-PPV by Light Processing

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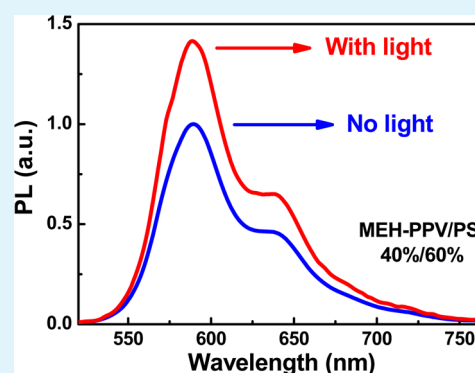
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ABSTRACT: We show here that treatment of thin films of conjugated polymers by illumination with light leads to an increase of the intensity of their photoluminescence by up to 42%. The corresponding enhancement of absorbance was much less pronounced. We explain this significant enhancement of photoluminescence by a planarization of the conjugated polymer chains induced by photoexcitations even below the glass transition temperature, possibly due to an increased conjugation length. Interestingly, the photoluminescence remains at the enhanced level for more than 71 h after treatment of the films by illumination with light, likely due to the fact that below the glass transition temperature no restoring force could return the conjugated chains into their initial conformational state.

KEYWORDS: Conjugated polymers, thin films, processing by light, enhanced photoluminescence, molecular conformation, glass transition temperature



INTRODUCTION

Active layers of semiconductive conjugated polymers are associated with a multitude of fundamental physical phenomena that include exciton diffusion¹ and separation,² charge transport,^{3,4} exciton and charge recombination,⁵ charge carrier migration/mobility⁶ and other interactions of excitons with the polymer chain/network, their trapping and loss,⁶ etc. These phenomena are responsible for the resulting optoelectronic properties, including photoluminescence (PL) and photovoltaic properties (PV), and depend strongly on the material structure at all length scales (from the nanoscale and mesoscale up to the macroscopic scale).^{3,5,7,8} These relations between the molecular conformations and the resulting optoelectronic properties are currently being explored by many research groups all over the world.^{3–5,7–19}

Classical processing methods used to vary polymer chain conformations rely on choosing the solvent quality,²⁰ controlling the solvent evaporation rate,^{21,22} or applying processing treatments like annealing the samples at elevated temperatures²³ or in a controlled solvent vapor atmosphere.^{24–26} When applied to conjugated polymers, these methods lead to a multitude of morphologies containing conjugated polymer chains with various molecular conformations and therefore, various structural but also optoelectronic

properties, including PL emission.^{27,28} PL emission is particularly important for organic light emitting diodes (OLEDs)²⁹ and other display applications. Increasing the PL intensity (using, for example, new processing methods) could lead to an increase of the overall OLED efficiency.

Here, we propose a novel method of physical processing of conjugated polymers that relies on the treatment of thin films of conjugated polymers with white light. We experimentally show that the resulting PL intensity for our system after the treatment is significantly enhanced (up to 42%) and stays at this enhanced level for more than 71 h. This method has the potential to be used as a ‘one-step’ processing method when fabricating OLEDs or when manufacturing other lighting applications and displays as it can be both fully controlled and homogeneously applied over any desired surface area (up to many square meters).

RESULTS AND DISCUSSION

Figure 1 shows normalized PL spectra recorded for films of poly[2-methoxy-5-((2'-ethylhexyl)oxy)-1,4-phenylvinylene]

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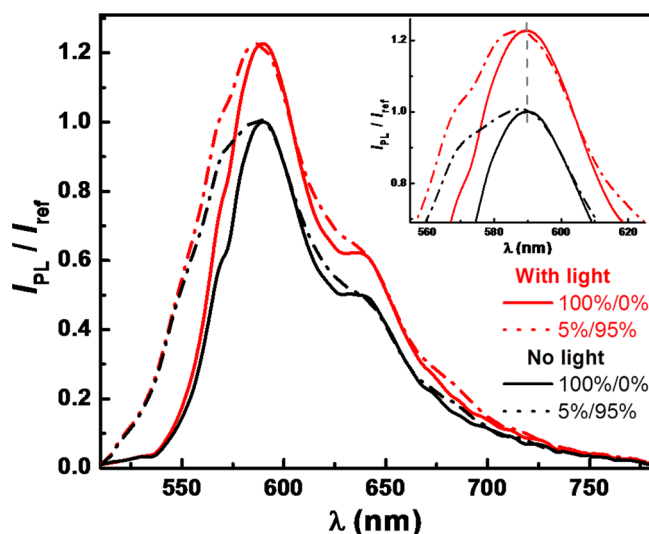


Figure 1. PL spectra normalized by setting the maximum PL intensity (I_{ref}) of the untreated films (black color) and recorded for films of MEH-PPV/PS (100%/0% and 5%/95%) that were subsequently treated for 1 h with white light (red color), while kept at 35 °C under nitrogen atmosphere. Inset represents a zoom-in. Gray dotted vertical line in the inset is emphasizing that no detectable spectral shift was observed after the treatment of thin films with light. The 100%/0% film was measured to be 20 nm thick, whereas the 5%/95% film was measured to be 55 nm thick.

(MEH-PPV) and a MEH-PPV/polystyrene (PS) blend (5%/95% by weight) before and after treating the films for 1 h with white light. It is evident that the PL intensity was significantly enhanced after the films were treated with light, independent of the percentage of MEH-PPV contained in the films. Interestingly, with the resolution of the PL setup used here (a fiber optic spectrometer combined with an optical microscope in reflection mode), no changes in peak position could be detected after treating the films with light (see the gray line in the inset of Figure 1).

To scrutinize if the PL enhancement depends on the time of treatment with light, we have treated films with light for up to 150 min and recorded PL spectra during the process (Figure 2a). Note here that while recording the PL spectra (a few

seconds were needed for a spectrum to be recorded), treatment of the film with light was always stopped. These measurements revealed that there was a continuous enhancement of PL emission with treatment time (red plots in Figure 2a). Treating the film with light for longer than ~150 min did not lead to a further enhancement of the PL (note that the rate at which PL is enhanced depends predominantly on the intensity of the illuminating light: when, e.g., a laser was used to illuminate the sample via a confocal laser scanning microscope, the enhanced PL reached the maximum after about 80–100 s of illumination; note though that, for experimental reasons, we preferred to use longer illumination times). PL spectra were recorded after different periods of time of keeping the same sample in the dark (black dash-dotted plots in Figure 2a). Surprisingly, the PL did not decay from the elevated value reached after 150 min of illumination by white light, even after keeping the sample for 71 h in the dark. This observation is illustrated in Figure 2b where we show the evolution of the PL peak intensity (590 nm) during the treatment of the film with white light and after switching off the light. For comparison we also show the evolution of the 590 nm PL peak recorded for an identical film that was not treated with light.

We interpret the observed enhancement of PL intensity upon the exposure of thin films of conjugated polymers to light as a result of conformational changes induced by light (e.g., by photoexcitations). As we have previously shown,³⁰ above the glass transition temperature (T_g), the excited states resulting from absorbed light may partially delocalize along and across conjugated polymer chains and may also induce changes in polymer chain conformations. It was hypothesized that such changes may cause a stiffening of the conjugated polymer chains and thus lead to macroscopically detectable differences in behavior of an ensemble of conjugated molecules, including macroscopic properties such as viscosity.³⁰ Moreover, the enhancement of PL upon treating thin films of conjugated MEH-PPV or MEH-PPV/PS with white light indicates that absorption of light induces weak changes in molecular conformation even below T_g . Experiments using azobenzene functionalized polymers show that exposure to light can lead to a local “light induced plasticization”, allowing limited motion of the polymer chains even below T_g .³¹ It was further shown that

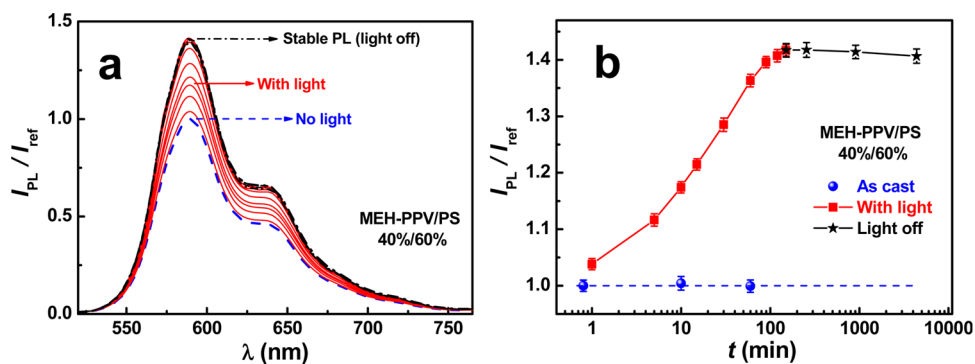


Figure 2. (a) Normalized PL emission spectra recorded for an 80 nm thick film of MEH-PPV/PS (40%/60% weight ratio). The dashed blue line corresponds to PL of an as-spin-cast film that was not exposed to any light. The full red lines correspond to spectra of the same film that was subsequently treated with white light from 1 min (bottom) to 150 min (top), respectively. Dash-dotted black lines correspond to PL of the same film at different time intervals after stopping the illumination. The enhanced PL intensity was found to be rather stable for more than 71 h in the dark. (b) Evolution of the 590 nm PL peak intensity shown in panel (a) during the treatment of film with light (red rectangles) and after subsequently stopping the treatment (black stars). Points symbolized by blue spheres were recorded for an identical film of the same polymer blend and the same thickness that was kept in the dark. Both films were kept at 35 °C and under nitrogen atmosphere during the whole duration of the experiment.

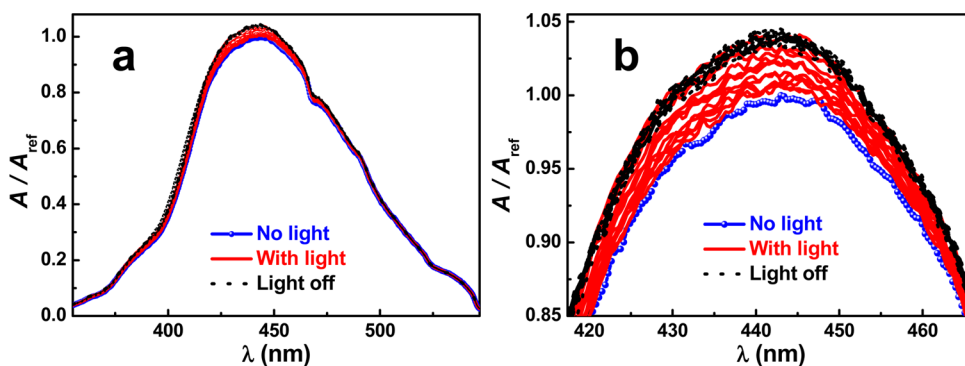


Figure 3. (a) Normalized UV–vis absorption spectra recorded for 80 nm thick films of MEH-PPV/PS (40%/60% weight ratio). The blue line with symbols corresponds to the absorbance of the as spin-cast film. Red lines are absorbance spectra that were recorded for the same film that was then treated with white light from 1 min (bottom red line) to 120 min (top red line), respectively. Black dotted lines correspond to the absorbance of the same film at different time intervals after stopping the illumination. (b) Zoom-in of (a). The enhanced absorbance was found to be stable for more than 24 h in the dark (see the quasi-overlap of black plots). The film was kept at 35 °C and under nitrogen atmosphere during the whole duration of the experiment.

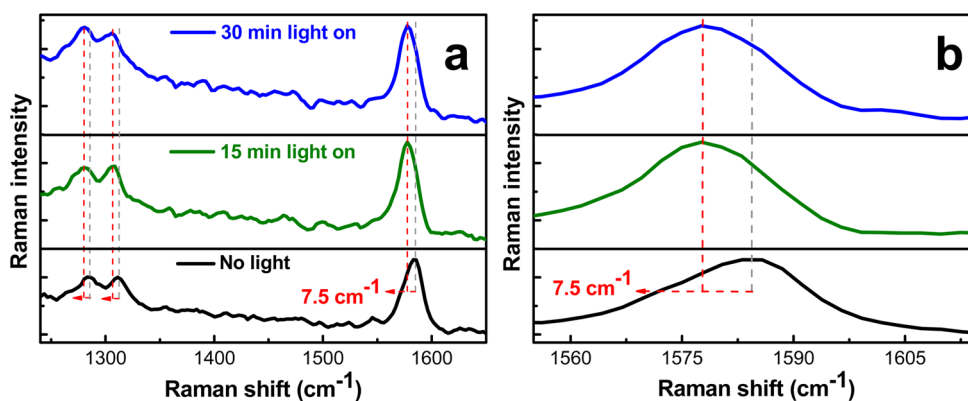


Figure 4. (a) Raman spectra recorded for an 80 nm thick film of MEH-PPV/PS (40%/60%) before (black) and after (color) being treated for 15 and 30 min with white light under nitrogen atmosphere. A weak Raman red shift is indicated by the red arrows. (b) Zoom-in of the peak located at 1584 cm^{-1} in (a).

this “photoinduced motion” of the chains can then, below T_g , be frozen-in by removing the light source.^{31,32}

Simulations previously suggested that absorption of a photon can (temporarily) change the conformation or physical shape of monomers also over some distance along the polymer chain, and can induce chain planarization.³³ Therefore, it cannot be excluded that planarization of conjugated chains upon photoexcitation leads to an increase of conjugation length. Chain planarization, in turn, can lead to a significant enhancement of the PL emission, as experimentally observed in Figures 1 and 2. Such rationale is further supported by previous results reported in the literature.²⁰ There, the PL emission spectra showed that a significant fraction of emission from the β planarized phase of a blue emitting fluorene derivative dominated with respect to the disordered glassy phase, if only a few percent of the chains were planarized.²⁰

Note that the absorption intensity of thin films of MEH-PPV or MEH-PPV/PS exposed to light only increases by 4% compared to the 42% increase in PL, as it can be seen in Figure 3. Here a weak planarization of conjugated chains due to photoexcitations does not lead to a significant increase, as all conjugated chains are absorbing light (compared to the PL contribution that mostly comes from more planarized conjugated chains²⁰ characterized by longer conjugation length and probably, less vibrational coupling to neighboring chains).

Because the chain planarization upon treatment with light can only be weak as the film as a whole is glassy during illumination, a significant red shift in the PL spectra is not expected (the number of monomers for the high molecular weight MEH-PPV polymer used here is rather high and planarization of up to few monomers is not expected to show a significant red shift in the peak position; for example, the Raman frequency dispersion with the number of units for such polymer materials was shown to be extremely small³⁴). One of the few examples include some polypyrroles systems, where a weak frequency dispersion (18 cm^{-1}) was reported and attributed to electron delocalization along the chains despite a significant distortion/twisting of the molecular chain.³⁴ To scrutinize this rationale, we have further investigated whether our films show a weak red shift upon their treatment with light, using a technique that is more sensitive to changes in molecular conformations. In Figure 4 we present Raman spectra of a film of MEH-PPV/PS (40%/60%) before and after being illuminated with white light for 15 and 30 min under nitrogen atmosphere. A weak red shift ($\sim 7.5 \text{ cm}^{-1}$; see Figure 4a) for three different peaks (1285, 1311, and 1584 cm^{-1}) is observed, indicating a weak planarization of the conjugated chains upon their exposure to light. Figure 4b is further emphasizing the red shift of the peak located at 1584 cm^{-1} .

To elucidate the possible mechanism of PL enhancement which could further support our proposed structural changes

induced by light exposure, we have recorded PL lifetime decays for samples that were and were not illuminated with light (Figure 5). Our results clearly show that the PL median

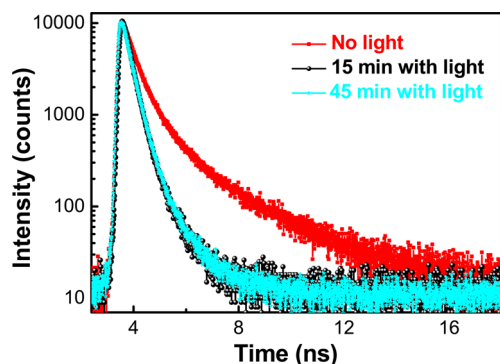


Figure 5. PL lifetime decays recorded for an 80 nm thick film of MEH-PPV/PS (40%/60%) before (red rectangles) and after being treated for 15 (black spheres) and 45 (cyan stars) minutes with white light under nitrogen atmosphere. The excitation wavelength was 510 nm.

lifetimes τ_m become shorter upon illumination of thin films, (from about $\tau_{mni} = 0.668 \pm 0.015$ ns for samples before illumination with light to $\tau_{m15} = 0.358 \pm 0.010$ ns and $\tau_{m45} = 0.351 \pm 0.010$ ns for samples that were illuminated with light for 15 and 45 min, respectively). We attribute this to an increase of the radiative rate rather than a decrease in the nonradiative constant. Such a picture is also supported by the absorbance data displayed in Figure 3. Note also that according to the Strickler–Berg model for a single chromophore, an increase of the absorbance implies an increase of the radiative rate constant and higher PL yield.^{35,36} In addition, we like to highlight that the recorded PL lifetime curves show a multiexponential behavior and the best fit was obtained using a sum of three exponential functions. The median lifetime values τ_{mni} , τ_{m15} , and τ_{m45} were computed by taking the weighted sum of the three lifetime components recovered from the multiexponential fit of the decays (e.g., $\sum (\alpha_i \times \tau_i)$)

Once the treatment of thin conjugated films with white light was stopped by switching off the light, the newly induced planarized conformations are ‘frozen-in’ in their final state. In the glassy state, thermal energy is not sufficient to move molecules; only very local conformational changes are possible upon light induced plasticization. This explains why the PL emission stays at an enhanced intensity level for many tens of hours as shown in Figure 2b. Our experiments (not shown here) proved that the enhancement of PL can be eliminated in few minutes by heating the MEH-PPV/PS films to temperatures above the T_g of PS ($T_g = 88$ °C) under nitrogen atmosphere, i.e., by bringing thin films out of the glassy state where molecular conformations can be easily changed.

According to recent studies performed irradiating samples at temperatures below the T_g , we should expect rearrangements at the level of polymer chain segments that are sufficient to partially relax local ‘frozen-in’ out-of-equilibrium chain conformations.³⁷ Taking into account that during the treatment of our films with light the energy pumped into the system is about 100 times the thermal energy, the partial relaxation of ‘frozen-in’ local chain conformations will occur at slower time scale once the treatment with light is stopped (e.g., in the presence of thermal energy only). Thus, an eventual relaxation of enhanced PL to its initial value before treatment of

conjugated films with light is expected to take periods of time much longer than hundreds of minutes (only a very weak decrease of enhanced PL can be observed on a logarithmic scale in Figure 2b; see black symbols). The same rationale can be applied to the absorption data showing that the slightly enhanced absorption intensity stays at the enhanced level for more than 24 h (Figure 3b) of experimental time (no measurements were conducted beyond this time). This eventual and extremely slow relaxation of the enhanced PL has important implications as the here proposed treatment with light method has a real potential to be employed, for example, as an additional processing step in the future development of display applications and OLED devices.

EXPERIMENTAL SECTION

MEH-PPV with a weight average molecular weight (M_w) of 150 000–250 000 g/mol and with a polydispersity index (PDI) around 5 was purchased from Sigma-Aldrich. MEH-PPV was used without further purification. Low molecular weight polystyrene (PS) was bought from Polymer Standards Service with $M_w = 3250$ g/mol and $PDI \leq 1.05$. The 6 mg/mL mixture of MEH-PPV and PS was dissolved in a solvent blend of equal amounts of toluene, tetrahydrofuran, and cyclohexanone. For reference films, MEH-PPV alone was dissolved in toluene (2 mg/mL). All vials used for solution preparation were at all times wrapped in aluminum foil for protection against light. Solutions of both MEH-PPV/PS and MEH-PPV were stirred at 60 °C overnight and then filtered using 0.2 μ m pore size polyvinylidene difluoride (PVDF) filters.

Thin solid films of a blend of MEH-PPV and PS or neat films of MEH-PPV with a thickness varying from 20 to 80 nm were obtained by spin-casting (varying the rotation speed from 2000 to 500 rpm) from mixed solutions of MEH-PPV/PS (5%/95%, 40%/60% weight ratio) or neat MEH-PPV solutions onto UV-cleaned silicon wafers. The obtained films were used fresh and subsequently treated with light while kept at 35 °C on a hot stage. The films were kept at 35 °C on a hot stage to avoid heating of the sample by the lamp. The hot stage’s only cooling mechanism was exchange with ambient air, so 35 °C was chosen to allow ample cooling power. The glass transition temperature of the polystyrene used here is 88 °C so 35 °C is well below this temperature and no temperature effects are expected. Additionally, simply placing two samples at different temperatures (35 and 40 °C, not shown here), did not lead to any difference in PL. All experiments were performed in an inert nitrogen atmosphere (under continuous nitrogen flow). Treatment of thin films with light in the presence of oxygen led to decreased PL emission due to degradation of the conjugated polymer caused by photo-oxidation. Similar experiments were also performed on films that were stored for prolonged times (days) in a vacuum so that effects due to remaining solvent can be ruled out.

To experimentally evaluate the effect of treatment with light, two identical films were placed simultaneously on the same hot stage while only one was exposed to light. The two films were separated from each other by an aluminum foil in order to avoid scattering of light from one film to the other. For the film that was not exposed to light, half of the hot stage window was also covered so that no light of any kind could access the film. The other film was treated with light coming from a cold light source (Schott KL 750) using a 75 W halogen lamp producing a maximum light intensity of 15 Mlx. Distance between the light source and the thin films was about 2 cm. Note that, in order to exclude effects induced by heating of thin films with the lamp during the treatment with light compared to films covered with aluminum foil, we have chosen a temperature of 35 °C controlled by a Linkam hot stage (at a set point of 25 °C of the Linkam hotstage, treatment by light for a few hours led to a warming up of noncovered films up to 29 °C due to insufficient cooling power). At 35 °C, additional effects not directly related to the light treatment were ruled out. Furthermore, experiments performed at higher temperatures but still below the glass

transition temperature of polystyrene (65 °C; not shown here) also emphasized the increase of PL when the films were treated with light.

UV-vis absorption and PL emission spectra were acquired using a USB2000 fiber optic spectrometer from Ocean Optics combined with an optical microscope (Zeiss Axio Scope.A1) in transmission and reflection mode, respectively. Note here that every time we have been recording a PL spectrum, the light source used for the film treatment with light was switched off and a LED light source for recording the spectrum was used. The diameter of focus area when using a 50 μm (or 600 μm) optical fiber and the 50 \times objective was about 1 μm (or 12 μm). For all PL spectra, we used an excitation wavelength range of 450–490 nm.

Raman spectra were recorded using a WiTec alpha 300R confocal Raman microscope equipped with charge coupled device (CCD), Raman spectroscopy system UHTS 300 using, as the excitation source, a 632.8 nm He-Ne laser. All Raman measurements were performed using a 100 \times microscope objective with a numerical aperture of 0.9 at an integration time of 10 s/spectrum. Each Raman spectrum presented here is an average of four Raman spectra recorded in four different regions of the film.

PL lifetime measurements were performed on a PicoQuant MicroTime 200 time-resolved confocal microscope system based on an inverted microscope (IX 71, Olympus) equipped with a PL 40 \times /NA = 0.65 PlanApochromat objective. The excitation beam was provided by a 1 μW picosecond diode laser head (LDH-D-C-510, PicoQuant) operating at 510 nm and 40 MHz repetition rate. The samples were deposited on microscope cover glass substrate. Experimental decay curves were tail-fitted with exponential decay curves.

CONCLUSIONS

We show that illuminating thin films of conjugated polymers (or polymer blends containing conjugated polymers) with white light significantly enhanced their PL intensity. The enhancement of PL was tentatively attributed to changes in molecular conformations even below T_g , i.e., planarization of chains induced by photoexcitations as shown by Raman spectroscopy. PL lifetime measurements along with absorbance data indicated as a possible photophysical mechanism of PL enhancement an increase of the radiative rate rather than a decrease in the nonradiative constant. The observed 42% increase in PL remained almost unchanged for more than 71 h after ending the treatment with light. Although no experimental observations were made beyond this time, the enhancement of PL intensity seemed to remain almost constant on the logarithmic scale, indicating that processing of conjugated materials by light might, in the future, find its place in the device fabrication technology. Additional processing by light illumination could be a versatile method with potential to be used when fabricating OLEDs or when manufacturing other lighting applications and displays with the advantage that it can be both fully controlled and homogeneously applied over any desired surface area.

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Notes

The authors declare no competing financial interest.

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