NEW DESIGNS OF LUMINESCENT SOLAR CONCENTRATORS

Master thesis of Tristan A. Geervliet
ABSTRACT

In the attempt to find bio-based alternatives for PMMA as host matrix for luminescent solar concentrators (LSCs), two types of renewable polyesters were synthesized. A series of random homopolymers from diethyl 2,3:4,5-di-O-methylene galactarate (GxMe) + isosorbide (IGPn) and polymers from 1,3-propanediol + terephthalate + GxMe (GTPn) were prepared in varying molar ratios via a two-step melt-polycondensation reaction with dibutyl tin oxide as catalyst. IGP05, for which the ratio GxMe:isosorbide was 1:1 (M_w=3000 g mole^{-1}) and GTP03, for which the ratio GxMe:terephthalate was 1:1 (M_w=20000 g mole^{-1}), showed optimal thermal properties and optimal compatibility with Lumogen Red 305 (LR). Thin film LSC systems were prepared from four polymers and spectroscopic characterization showed results similar or superior to PMMA-based thin film LSCs. The maximum optical efficiency for the IGP05/LR films was 8.50% at 1.4 wt.% and for the GTP03/LR films it was 7.73% at 1.4 wt.%, which is higher than the 7.41% found for the PMMA/LR 1.4 wt.% film. Both polymers are therefore considered excellent bio-based replacements for the state-of-the-art PMMA as host matrix for thin film LSCs. In addition, it was decided to also prepare films with new fluorophores. Three other organic fluorophores than the state-of-the-art LR were used and based respectively on the benzo[1,2-d:4,5-d’]bisthiazole unit (BBT), the dithieno[3,2-b:2’,3’-d]silole heterocyclic unit (DTS) and eventually one aggregation induced emission fluorophore (TTF). TTF/GTP03 films showed similar behavior as LR/PMMA films in terms of absorption and emission intensity, as well as quantum yield. With a maximum optical efficiency of 7.01% for the 1.4 wt.% TTF/PMMA film, TTF performed almost as well as LR. BBT/PMMA films showed an interesting red-shift at high dye concentrations, probably linked to the formation of red-emitting aggregates in the polymer matrix. The highest optical efficiency of 5.78% was obtained for the 1.4 wt.% BBT/PMMA film. DTS/PMMA films showed poor optical efficiency (3.56%), due to low quantum yields for all dye concentrations, probably linked to the formation of non-emissive aggregates in the polymer matrix. Due to its high optical efficiency, the TTF fluorophore has the most potential to replace LR in large scale LSC production.
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<thead>
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<th>Acronym/abbreviation</th>
<th>Full name</th>
<th>Chemical structure</th>
</tr>
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<tbody>
<tr>
<td>BBT</td>
<td>Fluorophore containing the benzo[1,2-d:4,5-d']bisthiazole unit</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>LR</td>
<td>Lumogen Red 305</td>
<td></td>
</tr>
<tr>
<td>LSC</td>
<td>Luminescent solar concentrator</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
<td></td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
<td></td>
</tr>
<tr>
<td>TTF</td>
<td>Aggregation induced emission fluorophore, adduct of triphenylamine, tetraphenylethene and fumaronitrile.</td>
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INTRODUCTION

The relation between energy consumption and greenhouse gas emissions (i.e. agricultural methane emission, agricultural nitrous oxide emission and carbon dioxide emission) has been investigated thoroughly and confirmed [1]. What is more, the role of the residential sector in global warming has been pointed out to be significant [2]. The building sector accounts for approximately 40% of primary energy consumption in first world countries and 20-30% globally [3]. Energy losses via windows, walls, light, miscellaneous electric loads or plug loads, etc., significantly impact the degree of energy consumption in buildings. From the desire to decrease oil based energy consumption in buildings, a two-step approach has emerged: 1) decrease the amount of energy losses in buildings and 2) use renewable energy as main energy source. More concretely, it has been argued that buildings should have a net zero energy balance [4].

The concept of Net Zero-Energy Buildings (NZEBs) is receiving an increasing amount of attention by the scientific community [5] and policy organizations, such as the European Committee [6]–[8]. NZEBs are buildings that balance their energy consumption with the production of renewable energy on a yearly basis. Currently, NZEBs are technically feasible for individual houses and small buildings due to rooftop photovoltaic (PV) cells and efficient insulation. However, considering that approximately 7 m²/kW of peak power is required for NZEBs [4] the mere use of PVs is not worthwhile for larger buildings. This is mainly due to the problem that conventional PV cells need to be positioned perpendicular to incoming light. Consequently, they can only be used on rooftops.

As possible solution to this problem, luminescent solar concentrators (LSCs) have been the focus of many new studies. LSCs are devices that absorb incoming light, re-emit the light via fluorescence and, subsequently, capture a substantial portion of this re-emitted light in order to convert it into electricity with the use of PV cells. Although the concept of this system is relatively old [9], more efficient techniques in the field of harvesting solar energy [10] and the development of more efficient luminescent systems [11]–[13] have led to a renaissance in the field [4]. Therefore, it is considered a promising approach for finding a solution for the above-mentioned problems.

The major advantage of LSCs is that they are less sensitive to the orientation angle than conventional silicon PV cells. For this reason they could be used on the sides of large buildings, thereby making use of a considerably larger surface area compared to only the roof. Especially in urban areas, this compensates for their lower efficiencies [14], [15]. Furthermore, LSCs are also unaffected by shadowing effects (e.g. clouds) due to indirect illumination of perimeter cells. Therefore, they are a more constant energy supplier than PVs. Lastly, besides these technical advantages, aesthetically, LSCs are attractive as well. As they are semi-transparent, they leave the aesthetics of buildings intact. Moreover, architects can even play with different types of LSCs to increase the aesthetic worth of buildings.

In general, an LSC consists of a host material, usually a polymer matrix, in which fluorophores are mixed. Current state of the art materials are polymethylmethacrylate (PMMA) as host material and Lumogen Red 305 (LR) as fluorophore [13]. However, these materials still have critical drawbacks in terms of renewability, price and overall efficiency. This thesis provides a comprehensive overview of all current state-of-the-art devices and their technical limitations, as well as design strategies for new LSCs. Aiming on developing host matrices superior to PMMA, two types of renewable polymers, one based on GxMe and Isosorbide and one based on GxMe and terephthalate, were synthesized and their characteristics have been compared to PMMA. Moreover, three newly synthesized fluorophores have also been tested as fluorescent dye in LSC systems. They have been compared to LR.

The working of an LSC is schematically depicted in Figure 1. Sunlight penetrates a polymer matrix that is filled with fluorophores. A selection of the photons from the sunlight will collide with fluorophores, thereby bringing them in an excited electronic state. After relaxation of this state, photons with a longer wavelengths are emitted in random directions. Some of these photons remain trapped within the matrix and are concentrated at its side, where they can be converted into electricity by photovoltaic (PV) cells.

In Appendix A, the theory of fluorescence is discussed comprehensively, as well as theory on PV cells. Two important terms, however, deserve special attention: Stokes Shift and Quantum Yield (\(\phi\)). Due to internal
conversion during the fluorescence process, incoming photons possess more energy than radiated photons. The resulting difference in their wavelengths is called Stokes Shift. Furthermore, in some cases, an absorbed photon does not result in a newly emitted photon. The ratio of the amount of absorbed photons relative to the amount of emitted photons is the quantum yield ($\Phi$):

$$\Phi = \frac{\text{#absorbed photons}}{\text{#emitted photons}}$$

The optical efficiency ($\eta_{\text{opt}}$) of LSCs is limited and dependent on multiple factors, due to the nature of both polymer matrix and fluorophore. It may be described by the following equation (based on Goetzberger’s equation [9], [10]):

$$\eta_{\text{opt}} = (1 - R)P_{\text{TIR}} \cdot \eta_{\text{abs}} \cdot \eta_{\text{PLQY}} \cdot \eta_{\text{Stokes}} \cdot \eta_{\text{host}} \cdot \eta_{\text{TIR}} \cdot \eta_{\text{self}}$$

In which:

- $R$ is the reflection of solar light from the waveguide surface,
- $P_{\text{TIR}}$ is the total internal reflection efficiency,
- $\eta_{\text{abs}}$ is the fraction of solar light that is absorbed by the dye,
- $\eta_{\text{PLQY}}$ is the photoluminescent quantum yield of the used luminophore(s),
- $\eta_{\text{Stokes}}$ is the energy lost due to the heat generation during the absorption and emission event,
- $\eta_{\text{host}}$ is the transport efficiency of the waveguided photons through the waveguide,
- $\eta_{\text{TIR}}$ is the reflection efficiency of the waveguide determined by the smoothness of the waveguide surface, and
- $\eta_{\text{self}}$ is the transport efficiency of the waveguided photons related to re-absorption of the emitted photons by another luminophore

All these factors are discussed in detail in Appendix B. Most importantly, two processes that significantly limit the optical efficiency are discussed here: namely the re-absorption problem and fluorescence quenching. When a re-emitted photon is absorbed by another fluorophore before it reaches the PV cell at the edge of the LSC, re-absorption takes place. Emitted photons have lower energy than absorbed photons due to the Stokes shift. The lower the energy a photon has, the higher chance that, when it is absorbed by a luminophore, the excited
luminophore does not emit a new photon [17]. It is due to this scenario, that re-absorption is detrimental to the total efficiency of an LSC. Photons are re-absorbed repetitively until they are not emitted anymore, therefore they do not reach the PV on the side of the LSC and the efficiency of the system decreases. In order to illustrate the magnitude of the re-absorption problem, in Appendix C a mathematical model is presented which illustrates how significant the problem is.

Fluorescence quenching refers to any process that decreases the fluorescence intensity of a sample. Often, two types of quenching are distinguished: dynamic quenching and static quenching. With dynamic quenching, a molecular species is excited, after which an encounter between fluorophore and quencher hinders the emission of a photon during relaxation. With static quenching, a non-fluorescent ground state complex is formed. When this complex absorbs light, it immediately returns to the ground state without emitting any photons [Figure 2].

It may immediately occur to the reader that dynamic quenching is time-dependent and that the quenching effectiveness is related to the time that the fluorescent molecular species remains in the excited state. The longer this is the case, the higher the chance that a fluorescent species interact with its quencher. In Figure 2 it is illustrated that for higher temperatures, the effectiveness of collisional quenching increases (consider that $F_0/F$ is the ratio of fluorescence intensity in absence of the quencher ($F_0$) and the fluorescence intensity in presence of the quencher ($F$)). Indeed, high temperatures increase the chance of collision between fluorescent species and quencher. On the other hand, static quenching is not time-dependent, but dependent on the association constant for the formation of the fluorophore-quencher complex. The easier this complex is formed, the higher the impact of the static quencher is on the system. Assuming that the complex formation is an exotherm process, increasing the temperature will shift the equilibrium of the reaction away from the complex and therefore, the effectiveness of the quencher decreases (illustrated in Figure 2). In Appendix D, a mathematical analysis of fluorescence quenching is provided.

Figure 2. Collisional quenching vs. static quenching [91].
In order to minimize the factors detrimental to the optical efficiency, scientific work has focused on preparing optimal fluorophores and host materials [10]. Here, the main focus is with the design of renewable polymer matrices. The most important characteristic of polymer matrices in LSCs is their compatibility with fluorophores. Good compatibility means homogeneously distributed fluorophores over the matrix and this will lead to the least amount of quenching. Besides their compatibility with fluorophores, there are also several side-requirements in terms of physical properties to the polymers, such as a relatively high $T_g$, good durability, good transparency, good solubility in chloroform, etc. Lastly, with the renewable character of LSC’s in mind, a last criterion for choosing polymer matrices, could be their bio-based background and biodegradability. The central goal of LSCs is producing renewable energy. Therefore, using bio-based materials is of extra importance. In summary, the following requirements should be set for the design of new polymer matrices for LSC’s:

- Good compatibility with fluorophores
- $T_g > 45^\circ C$
- Durable
- Transparent
- Renewable background

Currently, poly(methyl methacrylate) (PMMA) is the state-of-the-art polymer for LSCs. It is a widely available product, compatible with many different fluorophores and its physical properties meet all of the side-requirements. The drawback of PMMA, however, is that it is an oil based product. It is possible to synthesize PMMA from bio-based ethanol which is derived from lignocellulose [18], however, the price of bio-based PMMA is significantly higher than that of oil based PMMA.

Since PMMA’s major drawback is its non-bio-based character, this characteristic forms an excellent starting point from which one can think of other polymers. Especially since the final goal of LSC usage is generating renewable energy, there is an added value in using renewable materials. Over the past decades, attention towards bio-based polymers and bio-based platform chemicals [Figure 3] has increased tremendously, as oil based materials have been found detrimental to the environment. Moreover, oil reserves are likely to run out in the nearby future, which will let us no alternative than to switch to durable alternatives.

![Figure 3. Derivatives of glucose and their application](image)
Vilela et al. (2014) express the importance of research on polyesters based on renewable products [19]. They are bio-based since their monomers are renewable chemicals and biodegradable since they can easily be hydrolyzed. This makes them attractive for applications such as LSCs. One sugar based monomer for the application of polyesters with promising properties receives particular attention in literature due to its easy workability: the formaldehyde derived galactarate unit GalX [20]–[23]. The acetone derived version of GalX 2,3,4,5-di-O-methylene-galactitol (GxMe) and will be further discussed.

GxMe is a bicyclic carbohydrate-based monomer and it is synthesized by intramolecular acetalization of mucic acid (galactaric acid). Mucic acid is synthesized by oxidation of D-galactose with nitric acid. The biggest advantage of this monomer is that copolyesters from GxMe are biodegradable by hydrolysis of its ester groups while the acetal part remains stable against hydrolysis in acidic, basic and neutral conditions [22]. Moreover, the rate of hydrolysis can be increased by adding lipases [21]. A relatively low T_g (−3°C for a polymer of GxMe and hexanediol [23]), on the other hand, makes this monomer by itself unsuited for application in LSCs.

In order to increase the T_g of a polymer with GxMe, a second monomer that increases the T_g should be chosen. Isosorbide (1,4:3,6-Dianhydrohexitol) is an attractive renewable monomer to achieve this. It has already shown to increase the T_g of PET significantly [24]. Isosorbide is a rigid, chiral and non-toxic carbohydrate based aliphatic diol [25], [26]. It is synthesized on industrial scale from starch with D-glucose and D-sorbitol as precursor. One of its hydroxyl groups is in the endo- and one in the exo-position. Isomers of isosorbide are isomannide and isoidide, with respectively both hydroxyl groups in endo- or in exo-position. Due to internal H-bonds of the hydroxyl groups in the endo-position, isomannide has a higher melting temperature but it is also less reactive. Technically, isoidide would therefore be a better alternative than isosorbide, however, its precursor L-idose is quite scarce, which limits possibilities for large production of isoidide [19].

A drawback of using isosorbide in polymers is that high purity of the monomer is required. Initial production processes could not deliver these purity standards, however, newly developed production processes are economically more viable [27], [28]. It is therefore expected that isosorbide will be a promising chemical for the application in renewable polymers.

Besides focusing on increasing the T_g of a GxMe based polymer, it is also important to keep in mind its application, which is the compatibility with fluorophores. Since fluorophores have many aromatic parts, it is expected that implementing an aromatic component in the polymer matrix will be beneficial to their compatibility. Butylene terephthalate is in this case an economically interesting compound. The biggest drawback of polybutylene terephthalate (PBT) is its environmental unfriendliness, due to its resistance to biodegradation. However, in literature, several attempts to incorporate biodegradable compounds into PBT are reported [29], [30], one of which even makes use of GxMe [20].

Taking the aforementioned considerations into account, it was decided to synthesize 2 types of polymers for the use of a matrix in LSCs: GxMe + Isosorbide and GxMe + terephthalate + butanediol. Subsequently, they could be used as polymer matrix in LSCs and their efficiencies of these LSCs can be compared to PMMA based LSCs.

Lastly, as illustrated in Goetzberger’s equation for the optical efficiency of LSCs [Equation 2], the type of fluorophore that is used in the system has great influence on its overall efficiency. Currently, the most intensively researched family of fluorophores are perylene derivatives, perylene-1,7,8,12-tetraphenoxy-3,4,9,10 tetracarboxylic acidbis-(2’6-diisopropylanilide), or Lumogen Red 305 (LR) being the overall best one up to date. [10], [31]–[39] Its high fluorescence quantum yield, excellent photostability, low susceptibility for quenching and good compatibility with a variety of polymers including the state-of-the-art PMMA makes LR an attractive fluorophore for application in LSCs. Another interesting aspect of LR is that, even upon increased concentration in LSC films, this fluorophore does not form aggregates or vibronic structures with altered emission shapes. The shape of its emission spectrum remains unaffected, even at very high dye concentrations. The behavior of LR is therefore easier to predict than the behavior of other fluorophores where aggregates or vibronic structures between fluorophore and matrix emit at different wavelength than monomeric fluorophores.

The largest drawbacks of LR are its small Stokes shift, which makes LR susceptible for re-absorption and its relatively high price (7500 €/kg), which makes it unattractive for large-scale application in LSC systems. In attempt
to find alternatives to LR, researches have focused on synthesizing organic fluorophores with a broad absorption width band and a high absorption intensity over the whole spectrum, a large Stokes Shift (no or low overlap in absorption and emission spectra), a high quantum yield (also in solid state), low energy lost due to the heat generation during the absorption and low susceptibility for photo-degradation and emission events. Besides that, the fluorophores should be soluble in the waveguide and their emitted photons should match the spectral response of the PV-cell. Although there are different luminophore categories (organic dyes, quantum dots and rare earth ions), the focus of this report will be with organic dyes as they are the most extensively studied type of luminophores [40]. They have excellent optical characteristics (high absorbance, good quantum yield, etc.), their organic and optical properties are readily tunable, they are commercially widely available, they have favorable compatibility with organic waveguides and their processing costs are relatively low.

In Appendix E, an overview is presented of state-of-the-art fluorophores. In this report, three newly synthesized organic fluorophores based on the benzo[1,2-d:4,5-d’]bisthiazole unit (BBT), the dithieno[3,2-b:2’,3’-d]silole heterocyclic unit (DTS) and eventually one aggregation induced emission fluorophore (TTF) have been used as organic dye in thin film LSCs. Besides the LSCs based on the newly designed renewable polymers, also LSCs based on these fluorophores are discussed.
EXPERIMENTAL

Materials
The following chemicals from Sigma-Aldrich were used without further purification: 1,3-propanediol (>99%), dibutyltin (IV) oxide (DBTO) (98%), poly(methyl methacrylate) (PMMA, Aldrich, Mw = 350 000 g mol⁻¹, acid number < 1 mg KOH g⁻¹), dimethyl terephthalate, chloroform, acetone, methanol and diethyl ether were HPLC or technical grade. Lumogen Red F350 (LR, BASF) was received from BASF, Benzo[1,2-d:4,5-d′]bisthiazole unit (BBT) and dithieno[3,2-b:2′,3′-d]silole heterocyclic unit (DTS) were kindly provided by the group of Dr. Zani, Institute of Chemistry of Organometallic Compounds (CNR-ICCOM), Sesto Fiorentino, Italy [39], the aggregation induced emission fluorophore (TTF) was kindly provided by Prof. Ben Zhong Tang of the Hong Kong University of Science and Technology [41] and diethyl 2,3,4,5-di-O-methylene-galactarate (>99%) was received from Royal Cosun and used without further purification. Isosorbide was received from TCI Chemicals and used without further purification. x Optically clear glass slides (50 x 50 x 3.0 mm) were obtained by cleaning in 6 M HCl for at least 12 h, rinsing with water, acetone and isopropanol and then drying for 8 h at 120°C.

Methods
Synthesis of the polymers
GTPn copolyesters were obtained from a mixture of 1,3-propanediol, dimethyl terephthalate and diethyl 2,3,4,5-di-O-methylene-galactarate (GxMe) with the selected composition. IGPn polymers were obtained from a mixture of isosorbide and 2,3,4,5-di-O-methylene-galactarate with the selected composition. A reaction setup analogous to an earlier setup was used [20], [21]. The reaction was performed in a three-necked, cylindrical-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. Reactants and catalyst were added to the flask and, subsequently, it was vented with nitrogen several times at room temperature to remove the air and avoid oxidation during the polymerization. The transesterification reaction was carried out under a low nitrogen flow at the selected temperature for the selected time; when the reactants started melting the stirrer was gradually set to 1000 rpm. The polycondensation reaction was left to proceed at the selected temperature, under a 0.01–0.05 mbar vacuum. The reaction mixture was cooled to room temperature, and the atmospheric pressure was recovered with nitrogen to prevent degradation. In [Table 1] all reaction temperatures and reaction times are summarized. The resulting polymers were dissolved in chloroform and precipitated in excess of diethyl ether to remove unreacted monomers and formed oligomers. The product was collected by decanting the methanol and drying the remaining under vacuum.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composition</th>
<th>Reaction temp. (°C)</th>
<th>Time transesterification (h)</th>
<th>Time Vacuum (h)</th>
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<tr>
<td>IGP02</td>
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<td>140</td>
<td>3.5</td>
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</tbody>
</table>

Table 1. Specifications of reactions

Polymer analysis
For determining the thermal behavior of the polymers, DSC tests were performed on Perking Elmer instruments, Pyris Diamond DSC Autosampler. The samples were held at 30°C for 1 minute, after which they were heated until 180°C and subsequently cooled down to 30°C. This cycle was then repeated once. Samples of approximately 5 mg at heating/cooling rates of [10.0 °C min⁻¹] under nitrogen flow of [20.0 mL min⁻¹]. Zinc and indium was used for the calibration. The T_g was determined by Pyris Management.
Thermogravimetric analyses were performed under a nitrogen flow of 20 mL min$^{-1}$ at a heating rate of 10°C min$^{-1}$, within a temperature range of 25–600°C, using Mettler Toledo TGA/SDTA851 equipment. Sample weights of about 5–10 mg were used in these experiments. The data was examined with STAR® software.

Molecular weights and molecular weight dispersity of the polymers were determined by GPC with respect to polystyrene standards. Samples of 3–5 mg were dissolved in 1 ml chloroform and injected in a four-channel pump Jasco PU-2089 Plus chromatograph, equipped with a Jasco RI 2031 Plus refractometer and a multichannel Jasco UV-2077 Plus UV-Vis detector set at 252 and 360 nm. The flow rate was set at 1 ml min$^{-1}$ at a temperature of 30°C which was held constant by a Jasco CO 2063 Plus Column Thermostat. A series composed by two Polymer Laboratories columns PLgel™ MIXED D and a PLgel™ precolumn packed with polystyrenevinylbenzene was used to perform the analysis (linearity range 100 Da – 400 kDa).

$^1$H NMR spectra were recorded in order to confirm the ratio of compounds in the polymers. The tests were performed on a Varian Mercury Plus apparatus operating at 400 MHz, using samples of approximately 50 mg dissolved in 1 mL deuterated chloroform. A total of 64 scans were acquired for each sample.

Preparation of LSC films
All LSC films were prepared with fluorophore to polymer concentrations of 0.1–2.0 wt.%. Fluorophores were dissolved in chloroform in a ratio of 1.2 mg/mL by stirring continuously for 30 minutes at ambient temperature. Specific volumes of these mixtures were added to 60±2 mg polymer and supplemented with extra chloroform so that concentrations in the range of 0.1–2.0 wt.% fluorophore to polymer in 1.4 mL chloroform were obtained. Subsequently, the mixtures were spread out evenly on thoroughly cleaned glass plates (50x50x3 mm). The product was obtained after evaporation at room temperature in a closed environment.

Characterization of LSC films
Spectrophotometric measurements were performed using a Perkin-Elmer Lambda 650 spectrometer. Fluorescence spectra in the solid state were measured at room temperature by a Horiba Jobin-Yvon Fluorolog®-3 spectrofluorometer equipped with a 450 W Xenon arc lamp and double-grating both excitation and emission monochromators. The emission quantum yields of the solid samples were obtained by means of a 152 mm diameter “Quanta-ϕ” integrating sphere, coated with Spectralon® and mounted in the optical path of the spectrofluorometer, using as excitation source the 450 W Xenon lamp coupled with a double-grating monochromator for selecting wavelengths. The Quanta-ϕ apparatus was coupled to the spectrofluorometer by a 1.5 m fiber-optic bundle in a slilt-round configuration, 180 fibers; slilt-end termination 10 mm O.D. x 50 mm long; round-end termination FR–274; sheath is PVC monocoil. The images at the optical microscopy were recorded via Moticam 2300 digital camera with ½”CMOS sensor and 3.1 Mixels resolution installed on a Reichert Polyrvar polarizer microscope. Far-end absorption of the polymer matrices was measured using the Cary 5000 UV-Vis-NIR spectrophotometer with the universal measurements accessory (UMA).

Optical efficiency measurements
A home-built equipment setup was utilized to measure the efficiency of the LSCs. Each fluorophore concentration was tested in triplicate. A sample holder with the photovoltaic (PV) module (IXYS SLMD121H08L mono solar cell 86 x 14 mm: $V_{oc} = 5.04$ V, $I_{sc} = 50.0$ mA, FF > 70%, $η = 22$%) is placed 2.5 cm above a scattering layer. The PV cell is masked with black tape to match LSC edge (50 x 3 mm) so that limiting the stray light to negligible levels. Silicon was used to grease the LSC edge. The other three edges of the LSC were covered with a reflective aluminum tape. A solar simulating lamp (ORIEL® LCS-100 solar simulator 94011A S/N: 322, AM1.5G std filter: 69 mW/cm$^2$ at 254 nm) was housed 27.5 cm above the sample. The PV module was connected to a digital potentiometer (ADS242) controlled via I2C by an Arduino Uno (https://www.arduino.cc) microcontroller using I2C master library. A digital multimeter (KEITHLEY 2010) was connected in series with the circuit, between the PV module and the potentiometer, to collect the current as a function of the external load. Conversely, the voltage was measured by connecting the multimeter in parallel to the digital potentiometer. Arduino Uno controlled the multimeter via SCPI language over RS-232 bus using a TTL to RS-232 converter chip (MAX232). Arduino Uno was connected to pc via USB port and controlled by a Python script. The measurement cycle began with a signal from PC to Arduino which set the multimeter parameter to measure current. Then, Arduino began the measure loop: (1) set the potentiometer to a given value; (2) send a trigger signal to the multimeter; (3) read the measured data.
and (4) send the data back to PC. The loop is repeated 256 times for potentiometer values ranging 60 Ω to 1 MΩ. Arduino set the multimeter to measure voltage and for each potentiometer value the system recorded 8 data samples which were subsequently processed by the Python script. The optical efficiency was reported as \( \eta_{\text{opt}} \) and obtained from the concentration factor \( (C) \), which is the ratio between the maximal current of the PV cell attached the LSC edges under illumination of a light source and the maximal current of the bare cell put perpendicular to the light source [42].
RESULTS AND DISCUSSION

Synthesis of polymers

Homopolymers of diethyl 2,3:4,5-di-O-methylene galactarate (GxMe) + isosorbide (IGPn) [Figure 4] and co-
polyesters of 1,3-propanediol + terephthalate + GxMe (GTPn) [Figure 5] were synthesized in varying molar ratios
via a two-step melt-polycondensation reaction with dibutyl tin oxide as catalyst. In both syntheses, ethanol was
captured as side product. Transesterification was performed under low nitrogen flow at 140-160°C for as long as
the viscosity increased (ergo, for as long as the rotation resistance on the stirrer kept increasing). Subsequently,
polycondensation reactions were performed at similar temperature as the transesterifications in order to
minimize the decomposition of thermally sensitive sugar compounds, and under vacuum to facilitate the removal
of volatile by-products. The product was purified by dissolving in CHCl₃ and precipitation in diethyl ether.

Higher reaction temperature for GTP06 was used compared to the other reactions, since the mixture did not
melt in its entirety at 140°C. The polycondensation step was terminated after 1h because the mixture had
solidified. Furthermore, GTP06 was badly soluble in CHCl₃ and appeared to be crosslinked. For these reasons, it
was decided that GTP06 would not be suitable as polymer matrix in LSC systems. The composition of the
polymers was determined by ¹H NMR and the molecular weights and molecular weight distributions were
estimated GPC.

Figure 4. Reaction scheme of IGPn polymers.
H NMR results

H NMR samples were prepared by dissolving the polymers in deuterated chloroform. The figures are presented in Appendix F. In order to calculate the ratio between the monomers in the GTPn polymers, the multiplet at 1.51-1.32 was used, which represent the protons of the methyl groups of GxMe, and the multiplet at 8.16-7.97, which represents the protons of the aromatic ring in terephthalate. For the IGPn polymers, the multiplets at 1.51-1.32, representing the protons of the methyl groups of GxMe, and the multiplet at 3.78-4.07, representing 4 CH₂ protons in the isosorbide, were used for calculating the ratio between the monomers. See Table 2 and Table 3 for the calculated ratios.
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<th>Feed</th>
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<th>X&lt;sub&gt;iso&lt;/sub&gt;</th>
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<th>M&lt;sub&gt;w&lt;/sub&gt; (g/mol)</th>
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*Table 2*

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</table>

*Table 3*
IGP02
$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 5.33 – 5.14 (m, 2H), 4.88 (q, J = 4.9, 4.5 Hz, 1H), 4.64 (dd, J = 7.6, 5.8 Hz, 2H), 4.58 (td, J = 5.5, 3.6 Hz, 1H), 4.55 – 4.20 (m, 4H), 4.06 – 3.78 (m, 4H), 1.63 (s, 2H), 1.52 – 1.36 (m, 12H), 1.30 (t, J = 7.1 Hz, 3H).

IGP05
$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 5.38 – 5.12 (m, 2H), 4.88 (t, J = 4.5 Hz, 1H), 4.64 (dd, J = 7.9, 5.7 Hz, 2H), 4.58 (td, J = 5.4, 3.7 Hz, 1H), 4.55 – 4.22 (m, 4H), 4.07 – 3.79 (m, 4H), 3.48 (q, J = 7.0 Hz, 2H), 1.56 (s, 2H), 1.51 – 1.37 (m, 12H), 1.31 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H).

GTP03
$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.16 – 7.97 (m, 4H), 4.61 – 4.50 (m, 4H), 4.49 – 4.40 (m, 4H), 4.37 (t, J = 6.3 Hz, 2H), 4.28 (t, J = 6.3 Hz, 2H), 3.94 (d, J = 1.6 Hz, 6H), 3.80 (d, J = 1.3 Hz, 2H), 2.29 (p, J = 6.2 Hz, 1H), 2.18 (p, J = 6.3 Hz, 2H), 2.06 (p, J = 6.4 Hz, 1H), 1.58 (s, 2H), 1.51 – 1.32 (m, 12H)

GTP04
$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.11 – 8.03 (m, 4H), 4.62 – 4.49 (m, 4H), 4.49 – 4.40 (m, 4H), 4.37 (t, J = 6.3 Hz, 2H), 4.28 (t, J = 6.3 Hz, 2H), 3.94 (d, 6H), 3.80 (d, 2H), 2.29 (p, J = 6.2 Hz, 1H), 2.18 (p, J = 6.3 Hz, 2H), 2.06 (p, J = 6.4 Hz, 1H), 1.57 (s, 2H), 1.51 – 1.37 (m, 12H)

GTP06
$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.08 (tt, J = 5.8, 1.9 Hz, 4H), 4.56 (dt, J = 21.9, 5.7 Hz, 4H), 4.50 – 4.41 (m, 4H), 4.37 (t, J = 6.4 Hz, 2H), 4.28 (t, J = 6.3 Hz, 2H), 3.94 (d, J = 1.5 Hz, 6H), 3.80 (d, J = 3.3 Hz, 2H), 2.29 (p, J = 6.2 Hz, 1H), 2.22 – 2.13 (m, 2H), 2.06 (dd, J = 13.6, 6.6 Hz, 1H), 1.51 (s, 2H), 1.51 – 1.37 (m, 12H).

GPC results
All GPC graphs are presented in Appendix G. GPC results showed a non-homogeneous distribution of the IGP02 chromatogram, which indicated presence of starting compounds in the product. The longer transesterification time of IGP05 compared to IGP02 might have caused more monomer to have reacted, which would explain a smoother peak for IGP05. The significantly higher molecular weight of GTP04 compared to GTP03 might be that monomer was lost before the reaction completed with GTP03. This could have intervened with the overall performance of the reaction. The molecular weights of all polymers are presented in Table 2 and Table 3.

Parasitic absorption of polymers
Parasitic absorption by the host material in LSCs is detrimental to the optical efficiency of the system for two reasons. Firstly, if the polymer is not completely transparent, it will absorb light in the visible region, thereby intervening with the solar harvesting of the fluorophores. Secondly, absorption in the near infrared region (NIR) will heat up the system, which may lead to system degradation with time.

In order to measure the parasitic absorption of the newly prepared copolyesters, empty thin films of host polymer were prepared. The results are presented in Figure 6. For IGP02 and IGP05 an absorption peak is visible around 2850 nm. Since this peak is not found for GTPn copolyesters, it is possibly related to the presence of isosorbide in the backbone. Moreover, although GTPn copolyesters have very limited absorption in the NIR, their absorption in the visible region is higher compared to IGnP copolyesters and PMMA. This is likely due to the aromatic terephthalate in the backbone.
Figure 6. Graph parasitic absorption
Thermal characterization

DSC results

As an example, the DSC results of IGP02 are presented in Figure 7. The first heating curve has several irregularities, probably including the transitions from the thermal history of the material. Therefore, it is unreliable to estimate the $T_g$ from this curve, or to assume that there is a $T_m$. After the first heating cycle, the thermal history of the compounds is lost. The second heating cycle shows therefore the real thermal response of the material. Comparing data from the second heating cycles describes differences between the polymers more adequately. Figure 8 shows the same results as Figure 7, however, scaled to the second heating curve and without the first heating curve. Here, a clear glass transition is visible at 70°C indicating that the material is amorphous. Furthermore, no $T_c$ or $T_m$ is visible. The curves of the other polymers are presented in Appendix H and their results are summarized in Table 4.

Figure 7. DSC results IGP02 (1).

Figure 8. DSC results IGP02 (2).
Table 4. *Temperature at 5% wt. loss. †Temperature at maximum decomposition rate. ‡Remaining wt.% at 600°C. §High molecular weight (i.e., 996,000 GPC, Aldrich, U.S.A) PMMA [43]. ¶Molecular weight 120,000 GPC, Sigma-Aldrich [44].

TGA results

Figure 9 and Figure 10 show the TGA results of IGP02, GTP03 and IGP05. Notably, their weight loss curves have relatively similar shapes. GTP03 is best resistant against heat and deteriorates the slowest, probably due to the higher $M_w$. It is important, however, to note that the difference in thermo resistibility is relatively small for these copolyesters. LSCs will be used in outside environment. Even if placed in direct sunlight, the temperatures to which the devices will be exposed will not be as high as the temperatures at which these polymers start degrading (ca. 200°C). Therefore, they are all suited for the application in LSCs.
Choosing polymers for the preparation of LSC thin films

Earlier in this report it was discussed that important parameters for host materials in LSC systems include good compatibility with fluorophores, a $T_g$ higher than 45°C, transparency, durability and a renewable background. All of the IGPn and GTPn copolyesters are transparent. Moreover, IGP02 and IGP05 have a $T_g$ of respectively 70°C and 60°C, well above the minimally required 45°C. GxMe and isosorbide are both renewable monomers, making the IGPn copolyesters renewable as well. For this reason, IGP02 and IGP05 will both be used for the preparation of thin film LSCs.

Of the GTPn copolyesters, GTP03, GTP04 and GTP06 have an acceptable $T_g$ of respectively 45°C, 48°C and 45°C. GTP07 has a $T_g$ of 35°C, which is too low and will therefore not be used for application in LSCs. Moreover, GTP06 is badly soluble in CHCl₃ and appeared to be crosslinked. It was therefore decided to only use GTP03 and GTP04 for preparation of LSC thin films.

Figure 10. TGA results derivative
Preparation of LSC thin films

LSC films with the copolymers IGP02, GTP03, GTP04 and IGP05 were prepared using LR as fluorescent dye with dye concentrations varying from 0.2-2.0 wt.%. Approximately 60 mg polymer was dissolved in chloroform with the particular amount of dye. The solution was spread out over optically clear glass (50 x 50 x 3.0 mm) and dried. PMMA-based LSCs were also prepared, in order to compare the results of the renewable polymers with. Notably, the PMMA-based films were significantly tougher than the IGPn- and GTPn-based films, which was expected, because PMMA has a significantly higher $M_w$ (350.000 g/mole) than the IGPn and GTPn copolyesters (2000 g/mole and 20.000-44.000 g/mole, respectively). They could be separated from the glass intact, whereas the GxMe-polymer-based films could only be separated as powder. This is likely related to their low $M_w$ compared to the $M_w$ of PMMA. Moreover, it is assumed that the GxMe-polymers are not only more brittle than PMMA, but they also have stronger interaction with the glass.

Besides LSCs with the polymers, three other organic fluorophores than the state-of-the-art LR were also used in LSC thin films and they were based respectively on the benzo[1,2-d:4,5-d’]bisthiazole unit (BBT), the dithieno[3,2-b:2’,3’-d]silole heterocyclic unit (DTS) and eventually one aggregation induced emission fluorophore, an adduct of triphenylamine, tetraphenylethene and fumaronitrile (TTF) [Figure 11]. An overview of all the films is presented in Table 5.

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<th>Number</th>
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<th>Polymer matrix</th>
<th>Fluorophore</th>
</tr>
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<td>TGIGP2LR</td>
<td>IGP02</td>
<td>Lumogen Red</td>
</tr>
<tr>
<td>2</td>
<td>TGGTP3LR</td>
<td>GTP03</td>
<td>Lumogen Red</td>
</tr>
<tr>
<td>3</td>
<td>TGGTP4LR</td>
<td>GTP04</td>
<td>Lumogen Red</td>
</tr>
<tr>
<td>4</td>
<td>TGIGP5LR</td>
<td>IGP05</td>
<td>Lumogen Red</td>
</tr>
<tr>
<td>5</td>
<td>TGGTP07LR</td>
<td>GTP07</td>
<td>Lumogen Red</td>
</tr>
<tr>
<td>6</td>
<td>TGPMMAQLR</td>
<td>PMMA</td>
<td>DTS based moiety</td>
</tr>
<tr>
<td>7</td>
<td>TGPMMACP07</td>
<td>PMMA</td>
<td>BBT based moiety</td>
</tr>
<tr>
<td>8</td>
<td>TGGTP3TTF</td>
<td>GTP03</td>
<td>TPETPAFN</td>
</tr>
</tbody>
</table>

Table 5. Overview prepared LSC films

Figure 11 A. benzo[1,2-d:4,5-d’]bisthiazole unit. B. aggregation induced emission fluorophore. C. dithieno[3,2-b:2’,3’-d]silole heterocyclic unit.
Spectroscopic characterization polymer based films

Absorption

Figure 12 shows the absorption/emission spectrum of the IGP05/LR film, while Figure 13 shows their maxima as a function of dye concentration. For the absorption, a consistent increase in intensity is visible for increasing concentration. Furthermore, the curves have a similar shape for all concentrations. Logically, it follows that increasing dye concentration in films increases the chance on successful collisions between photons and fluorophores, thereby increasing the absorption intensity with an almost linear behavior. This behavior is also found for the films based on the other polymers, see Appendix I for the spectra of these films. Notably, on the other hand, is the small difference in absolute intensities between the films [Figure 14]. IGP05- and GTP03-based films have a higher absorption intensity than the other films. This could indicate a difference in dielectric constants between these polymers and PMMA, PMMA having the lowest dielectric constant. However, it is expected that the dielectric constants of GTP03 and GTP04 are similar and of IGP02 and IGP05 as well, since the only difference between these polymers are their Mw. The difference in absorption intensity between these films might be attributed to a difference in homogeneity. This difference in homogeneity was visible via microscopy photos and, in some cases, also via photos taken under the illumination of a UV lamp at 366 nm. In Appendix J, an overview is presented of all microscopy and UV photos of the films. In order to give two examples, Figure 15 shows the microscopy photos of GTP03 (A) and GTP04 (B) and the UV lamp photos of IGP05 (C) and IGP02 (D). In the microscopy photos, aggregation spots of the fluorophores are visible for both GTP03 and GTP04, however, the aggregates are significantly larger and more evident for GTP04. This would indicate that the fluorophores are more homogeneously mixed in GTP03 than in GTP04. Similarly, there is an evident difference visible between the photos of IGP05 and IGP02 taken under the illumination of a UV lamp at 366 nm. IGP05 looks significantly more homogeneous than IGP02. These differences in homogeneity could possibly explain the differences in absorption intensity. The more homogeneous the fluorophores are mixed in the film, the higher the absorption intensity. IGP05 could be better compatible to LR than IGP02, due to its higher ratio of GxMe to isosorbide and GTP03 could be better compatible to LR than GTP04 due to its lower molecular weight.
Absorption/emission Spectrum IGP5 and LR

Wavelength (nm)

Absorption (arbitrary numbers)

Emission (arbitrary numbers)

Figure 12
Maximal absorption and emission IGP05 and LR

$R^2 = 0.9927$

- Max absorption
- Max emission
- Lineair (Max absorption)

Figure 13
Figure 14. TGIGP2LR: LSC of LR in IGP02, TGGTP3LR: LSC of LR in GTP03, TGGTP4LR: LSC of LR in GTP04, TGIGP5LR: LSC of LR in IGP05, TGPMMALR: LSC of LR in PMMA.
Figure 15. A. microscopy of GTP03 (breadth = 0.6 mm, dye concentration = 1.0 wt.%). B. microscopy of GTP04 (breadth is 0.6 mm, dye concentration = 1.0 wt.%). C. IGP05 under UV lamp (dye concentration = 1.0 wt.%). D. IGP02 under UV lamp (dye concentration = 1.0 wt.%).
**Emission**

Although one might expect a similar increase for emission intensity as for absorption intensity with dye concentration, another trend is observed for all films. The emission intensity is lowest for the low dye concentration films, however, after reaching a particular intensity, it does not increase further [Figure 16 and Figure 17]. In the case of GTP03, the highest dye concentration films even have a lower emission intensity than the lower dye concentration films. One explanation for this behavior is that the reabsorption problem starts playing a substantial role from these dye concentrations on. The higher the dye concentration, the higher the chance that a photon is reabsorbed before it reaches the glass. In paragraph 2.2.4, it was described for bulk systems how the dye concentration is related to the chance that a photon reaches the edge of the LSC. Albeit the use of thin film systems significantly decrease the chance for reabsorption compared to bulk systems, the problem still plays a substantial role in these films, especially at high dye concentrations.

Another explanation might be that quenching phenomena become more dominant at higher concentrations, thereby counterbalancing the effect of the extra number of fluorophores. High dye concentrations might, for example, provide better circumstances for the fluorophores to form non-emissive aggregates. Especially in the GTP03-based film, this seems plausible, as the emission intensity drops significantly after 1.0 wt.% dye concentration. An important indicator for these speculations is the quantum yield [Figure 18]. For all films, a steady decrease in quantum yield is detected upon increasing dye concentration. These data compliment the theories of reabsorption and quenching phenomena as described above. Indeed, at higher concentrations, the ratio of emitted photons to absorbed photons becomes smaller. Notably, the quantum yield remains higher than 60% for most samples and higher than 50% for all samples, even at higher concentrations. For LSC application, these values are remarkably high.

Notably, the trend of a stagnating emission intensity has been reported in literature abundantly [33], [38], [42], [45]–[49]. Most importantly, finding similar results for the renewable copolysters here, it is expected that their structure does not interfere with the functioning of the LR fluorophores. In terms of compatibility, they are therefore not inferior to PMMA.

Furthermore, the shape of the emission spectra remains unaffected by dye concentration [Figure 19]. This indicates that no aggregates are formed with emission spectra different from the those of individual fluorophores. A trend that is visible, on the other hand, is that the emission peaks shift slightly to a higher wavelength. This behaviour also compliments the theory of reabsorption, since the re-emitted photons with low wavelengths are the ones most likely to be reabsorbed (indeed, their wavelengths are closest to the absorption band). This results in more photons with a relatively high wavelength.
Figure 16. TGIGP2LR: LSC of LR in IGP02, TGIGP5LR: LSC of LR in IGP05, TGPMMA: LSC of LR in PMMA.
Figure 17. TGGTP3LR: LSC of LR in GTP03, TGGTP4LR: LSC of LR in GTP04, TGPMMLAR: LSC of LR in PMMA.
Figure 18. TGIGP2LR: LSC of LR in IGP02, TGGP3LR: LSC of LR in GTP03, TGGP4LR: LSC of LR in GTP04, TGIGP5LR: LSC of LR in IGP05, TGPMALR: LSC of LR in PMMA.
Normalized emission spectrum TGIGP5LR

- Normalized emission 0.2 wt.%
- Normalized emission 0.6 wt.%
- Normalized emission 1.01 wt.%
- Normalized emission 1.4 wt.%
- Normalized emission 2.01 wt.%

Figure 19
Optical efficiency

For measuring the optical efficiency of the prepared LSCs based on polymer thin films, the output of energy of the PV cell connected to the LSC is compared to the output of the PV cell when it is exposed to the same amount of direct light, according to the following equation:

$$\eta_{opt} = \frac{I_{LSC}}{I_{SC} G}$$

[23]

In which:

- $\eta_{opt}$ is the optical efficiency
- $I_{LSC}$ is the short circuit current measured in the case of the cell over the LSC edge
- $I_{SC}$ is the short circuit current of the bare cell put perpendicular to the light source
- $G$ is the geometrical factor of the LSC ($A_{top}/A_{edge}$) and in our case $16 \frac{2}{3}$.

$I_{LSC}/I_{SC}$ is the concentration factor, denoted as $C$.

Therefore:

$$\eta = \frac{C}{G}$$

[24]

It should be noted that, especially in early works, the overall efficiency of LSC systems was measured with different standards [10]. For example, the efficiency of an LSC could be calculated as the total amount of energy that is generated by the PV cell as a function of the energy that is put into the system in the form of light. However, several external factors, such as ambient temperature, other light sources in the room, surface of the exposed area, or type of PV cell used, influence the outcome. Therefore, it has been difficult to compare the results gathered from different research works. Carlotti et al. (2015) proposed that the aforementioned method be used to compare the performance of LSCs, taking these external factors into account [46]. Their method was first suggested by Purcel-Milton et al. (2012) [50] and later supported by McKenna et al. (2017) [13].

An overview of the optical efficiencies calculated for our samples are presented in Figure 20. A similar trend for all films is found. The optical efficiency increases as a function of dye concentration up to a certain point, after which it decreases slightly. This behavior is attributed to two opposing factors. Firstly, increasing the dye concentration increases the amount of emissive fluorophores in the film, which increases the amount of irradiation in the system and thereby the optical efficiency. Secondly, dissipative phenomena, re-absorption and fluorescent quenching, decrease the effectiveness of the fluorophores. Notably, this is also illustrated by a decrease in quantum yield for increasing dye concentrations. Especially at higher concentrations, these effects become so significant that they counterbalance the beneficial effect of fluorophore contents. This explains why there is an optimal dye concentration, for all films at 1.4 w.t.%.

Furthermore, IGP05 and GTP03 show the highest optical efficiencies. The mutual differences in optical efficiency between the films might be related to two factors. Firstly, IGP05 and GTP03 showed the highest absorption intensity, which directly positively relates to optical efficiency. Secondly, the fluorophores are more compatible to these matrices, which means that the dissipative phenomena are slightly less effective. It was already shown in [Figure 15] that the fluorophores in IGP05 and GTP03 are distributed more homogeneously than the ones in IGP02 and GTP04. Highly concentrated areas within the films show intensified dissipative phenomena, resulting in lower optical efficiencies.

All maximum optical efficiencies are presented in Table 6. Interestingly, in terms of optical efficiency, GTP03/LR and GTP04/LR show comparable results as the state-of-the-art PMMA/LR films. More importantly, IGP05/LR even shows a significantly higher optical efficiency than PMMA/LR, which makes the homopolymer IGP05 an excellent replacement for PMMA in terms of optical performance.
Influence film thickness

In order to gain insight in the ideal film thickness for LSC thin film systems, GTP03 copolyester was used for further investigation. 1.4 wt.% films, having the highest optical efficiency compared to other dye concentrations, was prepared anew, however in bigger quantity. Two extra films, of 120 mg 1.4 wt.% and 200 mg 1.4 wt.%, were made following a similar method as for the other films.

Increasing the film thickness by using 120 mg instead of 60 mg GTP03/LR mixture increases the absorption linearly [Figure 21]. Twice as much fluorophores are present and therefore, the absorption is twice as intensive. On the other hand however, the extra thickness of the film also provide better conditions for reabsorption. Indeed, the average pathlength for the re-emitted photons to the glass becomes longer, therefore, there is a higher chance to re-encounter a new fluorophore. For this reason, the quantum yield is lower for the 120 mg film compared to that of the 60 mg film [Figure 22]. Similarly, the emission intensity and optical efficiency is lower [Figure 23].

Surprisingly, this trend is not continued for the 200 mg films. Firstly, the shape of the absorption spectrum is different than for the other films. The absorption peak at 580 nm is relatively low compared to its shoulder, indicating that relatively more photons with lower wavelengths are absorbed. Moreover, the overall absorption intensity is not linearly related to the dye concentration at 200 mg films and lower than expected. This might be due to the thickness of the film making it impossible for all fluorophores to be reached directly by the incoming light. This accounts for the fluorophores at the bottom, as the fluorophores at the upper part absorb most of the light. Furthermore, the quantum yield of the 200 mg films is lower than that of the other films, implying that more reabsorption and quenching takes place. Notably, the emission intensity is significantly higher for the 200 mg film compared to the others. This might be because the increased emission due to the extra fluorophores outweigh the negative effects of the reabsorption. It is probably due to the higher emission intensity, that the optical efficiency of the 200 mg film is higher than that of the 120 mg film. However, the 60 mg film has the highest optical efficiency and is therefore considered superior.

Table 6. Max optical efficiencies. *data from own research. †data from literature [38], [48]

<table>
<thead>
<tr>
<th>Film</th>
<th>Max. η</th>
<th>Dye concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IGP02/LR</td>
<td>6.50%</td>
<td>1.4</td>
</tr>
<tr>
<td>GTP03/LR</td>
<td>7.73%</td>
<td>1.4</td>
</tr>
<tr>
<td>GTP04/LR</td>
<td>7.65%</td>
<td>1.8</td>
</tr>
<tr>
<td>IGP05/LR</td>
<td>8.50%</td>
<td>1.4</td>
</tr>
<tr>
<td>PMMA/LR</td>
<td>7.41%</td>
<td>1.4</td>
</tr>
<tr>
<td>PMMA/LR</td>
<td>7.2%</td>
<td>1.4</td>
</tr>
</tbody>
</table>

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Figure 20. TGIGP2LR: LSC of LR in IGP02, TGGTP3LR: LSC of LR in GTP03, TGIGP4LR: LSC of LR in GTP04, TGIGP5LR: LSC of LR in IGP05, TGPMMALR: LSC of LR in PMMA.
Absorption/ emission spectra GTP03/LR 1.4 wt.% films

- 60,6 mg absorption
- 120,2 mg absorption
- 200,7 mg absorption
- 60,6 mg emission
- 120,2 mg emission
- 200,6 emission

Figure 21
Spectroscopic characterization of other films

Absorption

More thin film LSCs were prepared based on the fluorophores BBT, DTS and TTF. The trends for absorption maxima of the films with new fluorophores are similar to the ones with LR [Figure 24] (in Appendix I, the emission/absorption spectra for all films are presented). Upon increasing the dye concentration, the absorption increases gradually. The absolute differences in intensity are mostly related to the type of fluorophore used, indeed not all fluorophores are equally effective. Notably, the TTF fluorophore shows relatively similar absorption intensity as LR at all different dye concentrations and the BBT fluorophore even has higher absorption maxima. However, the shape of their absorption band is different, TTF having an absorption band ranging from 420-600 nm, BBT from 370-510 nm and DTS from 350-500 nm. Peaks were at 506 nm, 449 nm and 405 nm, respectively.
Figure 24. TGPMMALR: LSC of LR in PMMA, TGPMMAQL17: LSC of DTS in PMMA, TGPMMACP07: LSC of BBT in PMMA, TGTP3TTF: LSC of TTF in GTP03
Emission

Emission spectra were less regular as a function of dye concentration (these are shown in Appendix I). TTF fluorophores show behavior similar to that of LR. The emission intensity increases for increasing dye concentration, however, after 1.0 wt.% dye concentration, the quenching phenomena and reabsorption problem become so significant that the intensity drops [Figure 23]. The occurrence of quenching phenomena is in line with a decreasing quantum yield found, as a function of dye concentration [Figure 28]. Interestingly, the emission peaks shift to a higher wavelength for high concentrations compared to the peaks of LR. The emission peak shifts from 599 nm for the 0.2 wt.% TTF/GTP03 film to 626 nm for the 2.0 wt.% TTF/GTP03 film [Figure 29], whereas it shifts from 604 nm to 615 for the respectively 0.2 wt.% and 2.0 wt.% LR/GTP03 films [Figure 30]. This suggests that reabsorption plays a more significant role for TTF fluorophores. Lastly, the emission spectra matched the external quantum efficiency of a typical Si-based PV module, making the TTF fluorophores a suitable candidate for application in LSC systems.

Also the emission spectra of BBT/PMMA films were affected by dye concentration. Overall emission intensity of these films increased with the dye concentration and stagnated between 0.6 wt.% and 1.0 wt.%, after which it decreased. Fluorescent quenching occurred, although limited, since the quantum yield decreases with the dye concentration [Figure 28]. Furthermore, the 0.2 wt.% film showed an emission peak at 540 nm. The emission spectra of films with higher concentrations had strongly deviated shapes, which might be the result of the emersion of vibronic structures of the fluorophores. For the highest concentrations (i.e. 1.8 wt.%) a second peak emerged at 600 nm, which might be related to the formation of emissive aggregates within the PMMA matrix. The presence of another peak around 540 nm suggests that quenching of the individual fluorophores has taken place. It should be pointed out that this band shift was reflected on the color change of the films [Figure 25 and Figure 26]. The lowest dye concentration films were green, whereas the highest dye concentrations were yellow. Lastly, the band shift matched the external quantum efficiency of a typical Si-based PV module, making the BBT fluorophores a suitable candidate for application in LSC systems.

Emission of DBT/PMMA films was significantly lower than the other films. Notably, the quantum yield of the DBT fluorophores in PMMA was over 2.5 times lower than the quantum yield of the fluorophores in solution [39]. This behavior suggests that PMMA contributes to the formation of non-emissive aggregates due to compatibility issues. Another factor might be that the broad absorption band favors disadvantageous auto-absorption phenomena (i.e. inner-filter effects). Comprehensively, the DBT fluorophores performed poorly and are considered unsuitable for application in LSC systems.

Figure 25. PMMA/CP07 film lowest dye concentration. Photo taken under UV lamp at 366 nm.

Figure 26. PMMA/CP07 film highest dye concentration. Photo taken under UV lamp at 366 nm.
Maximal absorption and emission GTP03 and TTF

Absorption (arbitrary numbers)

Emission (arbitrary numbers)

$R^2 = 0.9925$

Max absorption
Max emission
Lineair (Max absorption)

Dye concentration (wt.%)
Figure 28. TGPMMALR: LSC of LR in PMMA, TGPMMAQL17: LSC of DTS in PMMA, TGPMMACP07: LSC of BBT in PMMA, TGGTP3TTF: LSC of TTF in GTP03
Normalized emission spectrum TGGTP3TTF

- Normalized emission 0.2 wt.%
- Normalized emission 0.61 wt.%
- Normalized emission 1.01 wt.%
- Normalized emission 1.38 wt.%
- Normalized emission 1.97 wt.%

Figure 29
Figure 30

Normalized emission spectrum TGPMMA-LR

Wavelength (nm)

Emission intensity (arbitrary numbers)

- Normalized emission 0.2 wt.%
- Normalized emission 0.61 wt.%
- Normalized emission 0.98 wt.%
- Normalized emission 1.36 wt.%
- Normalized emission 2.03 wt.%
Optical efficiency

The optical efficiency for the TTF/GTP03 films follow a similar trend as that of the LR/PMMA films [Figure 31]. It increases as a function of the dye concentration after which quenching and reabsorption counterbalances the positive effect of the extra amount of fluorophores. Interestingly, the maximum optical efficiency for TTF/GTP03 is comparable to that of LR/PMMA [Table 7].

After an initial increase in optical efficiency for the CP07/PMMA films at low concentrations, the optical efficiency slowly decreases slightly due to quenching phenomena and reabsorption as earlier discussed. The final increase in efficiency from 1.2 wt.% to 1.4 wt.% is attributed to the higher amount of dye in the film and the progressive red-shift of fluorophore emission (due to formation of highly emissive aggregates. This counteracted re-absorption phenomena, causing a small increase of absolute quantum yield [Figure 28]. Because the increase in optical efficiency stagnates at higher concentration (1.8 wt.%), it is expected that at this concentration fluorescence dissipation has started.

The low optical efficiencies of QL17/PMMA films compared to the other films could be attributed to lower compatibility with PMMA, lower absorption intensity and low quantum yield. The optical intensity does not undergo major changes for different dye concentrations. This confirms that quenching phenomena are already so significant at lower concentrations that they counterbalance the increased amount of fluorophores. Due to its low optical efficiency, QL17 is a bad replacement for LR.

<table>
<thead>
<tr>
<th>Film</th>
<th>Max. $\eta$</th>
<th>Dye concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTF/GTP03</td>
<td>7.01%</td>
<td>1.4</td>
</tr>
<tr>
<td>CP07/PMMA</td>
<td>5.78%</td>
<td>1.4</td>
</tr>
<tr>
<td>QL17/PMMA</td>
<td>3.56%</td>
<td>1.4</td>
</tr>
<tr>
<td>PMMA/LR\textsuperscript{a}</td>
<td>7.41%</td>
<td>1.4</td>
</tr>
<tr>
<td>PMMA/LR\textsuperscript{b}</td>
<td>7.2%</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 7. Max optical efficiencies 2. \textsuperscript{a}data from own research. \textsuperscript{b}data from literature [38], [48].
Figure 31. TGPMMALR: LSC of LR in PMMA, TGPMMAQL17: LSC of DTS in PMMA, TGPMMACP07: LSC of BBT in PMMA, TGGTP3TTF: LSC of TTF in GTP03
This work has demonstrated the potential of replacing state-of-the-art PMMA in LSC systems with renewable GxMe-based polymers. Two types of polymers were synthesized, one from GxMe and isosorbide (IGPn), one from GxMe, terephthalate and 1,3-propanediol (GTPn). IGP02 (GxMe:iso = 3:2), GTP03 (GxMe:Ter = 1:1), GTP04 (GxMe:Ter = 1:1) and IGP05 (GxMe:iso = 1:1) all had the required thermal properties (T_g > 45°C) to be used as host matrix in LSCs. GTP06 (GxMe:Ter = 1:2) was found not dissolvable in chloroform and was not compatible with LR. GTP07 (GxMe:Ter = 2:1) had a T_g < 45°C and was therefore also not suitable as host matrix.

IGP05 had superior compatibility with LR over IGP02, likely due to its higher ratio of GxMe to isosorbide, which probably caused a higher absorption intensity in the IGP05/LR films compared to the IGP02/LR films. Moreover, the superior compatibility most likely also contributed to relatively less fluorescent quenching and reabsorption, which lead to a maximum optical efficiency of 8.50% for the 1.4 wt.% IGP05/LR film. This was even higher than the 1.4 wt.% PMMA/LR film that had a maximum optical efficiency of 7.41%. For this reason, IGP05 has been found an excellent replacement for PMMA.

GTP03 copolyesters showed superior compatibility with LR than GTP04, likely due to its lower molecular weight. Similarly to IGP05/LR films, this resulted in a higher absorption intensity for the GTP03/LR films compared to the GTP04/LR films. The maximum optical efficiency of the GTP03/LR films was 7.73% at 1.4 wt.%, which makes GTP03 also an attractive alternative to PMMA.

Notably, relatively low M_w for all synthesized copolyesters (2000 g/mole for IGPn polymers and 20.000-40.000 g/mole for GTPn polymers) compared to the M_w of PMMA (350.000 g/mole for PMMA) had a detrimental impact on the toughness of the thin films made from these polymers. The LSC thin films were quite brittle. Although this did not interfere with their compatibility with fluorophores, future research should devote more time on developing copolyesters with a high M_w, since durable polymers are preferred as host material in LSC systems.

Moreover, IGPn copolyesters showed parasitic absorption in the NIR, possibly related to the presence of isosorbide in the backbone. This negatively affects long term use of LSC systems based on these copolyesters, due to unwanted heating of the system. This negative behavior of isosorbide should be kept in mind for future research. Also, although terephthalate is beneficial to compatibility with fluorophores and simultaneously increases the T_g of GxMe based polymers, it also stimulates parasitic absorption in the visible region, thereby intervening with the solar harvesting of fluorophores. Therefore, the use of terephthalate units in the backbone of polymers for LSC application should be contemplated carefully.

Furthermore, three new fluorophores were used as replacement for LR. One moiety containing the benzo[1,2-d:4,5-d‘]bisthiazole unit (BBT), one containing the dithieno[3,2-b:2‘,3‘-d]silole heterocyclic unit (DTS) and one aggregation induced emission dot (TTF). BBT and DTS were mixed with PMMA. The DTS/PMMA films showed poor quantum yield, likely due to reabsorption phenomena and the formation of non-emissive aggregates, which lead to a low maximum optical efficiency of 3.56%. The BBT/PMMA films, on the other hand showed an interesting red-shift for high dye concentrations, probably linked to the formation of red-emitting aggregates in the polymer matrix. Moreover, the quantum yield remained relatively high for all concentrations. This lead to a maximum dye concentration of 5.78% for the 1.4 wt.% BBT/PMMA film. Lastly, The best results were for the TTF/GTP03 films. These films showed similar behavior as LR/PMMA films in terms of absorption and emission intensity, as well as quantum yield. With a maximum optical efficiency of 7.01% for the 1.4 wt.% TTF/PMMA film, TTF performed almost as well as LR.
REFERENCES


G. W. Chantry, J. W. Fleming, P. M. Smith, M. Cudby, and H. A. Willis, “Far infrared and millimeter-wave


Appendix A. Theory of fluorescence and photovoltaic cells

Fluorescence is the process of emission of photons during the relaxation of molecular species from an excited state into a lower electronic state [51]. This naturally occurring mechanism of radiatively decay, may be controlled and used as method to capture and concentrate sunlight so that it can be effectively converted into electricity. Photo-luminescence refers to the process in which a molecular species is first brought in an excited state by incoming photons and, subsequently, decays back to its ground electronic state, thereby emitting photons with longer wavelengths in random directions [52].

In the beginning of the last century, photons were first conceptualized by Einstein as elementary particles and force carriers of electronic force [53], [54]. Their energy enables them to bring electrons in an excited state, as graphically depicted in Figure 33. When the photon collides with the atom, the electron jumps to a higher shell. Subsequently, the electron ‘relaxes’ back to its ground state, thereby releasing energy in the form of another photon [Figure 32].

The energy states of electrons undergoing excitation and relaxation can best be represented in a Jablonski diagram [Figure 34]. An electron prefers to spin in its most energetically favorable shell, its ground state (S0). Upon excitation it jumps to S1, this occurs within femtoseconds ($10^{-15}$ sec) [52].

The excited state S1 consists of several vibrational states, similar to S0. Within femtoseconds after excitation, the electron will shift to the lowest vibrational state of the S1 level. During these steps, thermal energy is released. It is due to this “internal conversion” that the photon which is released during relaxation contains less energy than the photon that caused excitation. In the Jablonski diagram, this is visualized by the length of the arrows of excitation and fluorescence (the latter being shorter than the first). In reality, the effect of internal conversion is measurable due to difference in wavelength of incoming and radiated photons. Incoming photons are higher in energy and have therefore a shorter wavelength than radiated photons. The difference in wavelength of these photons is called “Stokes shift”, represented in Figure 35.

Figure 33. Graphical representation of excitation

Figure 32. Graphical representation of relaxation

Figure 34. Jablonski diagram [51].
Finally, after staying in the lowest vibrational state of $S_1$ for nanoseconds ($10^{-9}$ sec), the electron relaxes back to its ground state, emitting the released energy as a photon. The direction of this photon depends on the exact time that the electron has stayed in its excited state and is therefore unpredictable. The emission dipole is the angle of the incoming and radiated photon.

In order to understand the principle of absorption in organic fluorophores on a molecular scale, one needs to visualize that these type of luminophores are essentially planar with all atoms of the conjugated chain lying in a common plane and linked by $\sigma$ bonds [55]. The electrons susceptible to absorption are swarming as $\pi$ bonds over the plane (hence the benzene rings present in all organic dyes). These electrons form a charge cloud both on top and on the bottom of the conjugated chain. In their ground state they have a certain distance to the center of the atoms. Upon excitation they are promoted to a higher energy state and their distance to the center increases.

It should be noted that the concept of excitation and relaxation as previously described is an ideal representation of reality. In practice, it might happen that a photon possesses so much energy, that instead of exciting a molecular species, it actually degrades it, thereby removing its luminescent ability [56]. In this case, the incoming photon is not even absorbed.

Another possibility is that an incoming photon possesses so little energy, that it excites the molecular species only to a higher sub-level of the same energy state. In this case, relaxation does not result in the emission of another photon, but in heat release. The ratio of the amount of absorbed photons relative to the amount of emitted photons is the quantum yield ($\Phi$):

\[
\Phi = \frac{\text{#absorbed photons}}{\text{#emitted photons}} \tag{1}
\]

\[\text{Emission} \quad \text{Absorption} \]

\[\text{Stokes shift} \]

- Figure 36. Visualization of the Franck-Codon principle [52].
- Figure 35. Visualization of Stokes shift [52].
The Franck-Codon principle implies that vibrational levels are not significantly altered during electronic transitions [Figure 36]. “According to Franck-Codon principle irradiation into complex [molecules] electronic transitions excites the molecule without causing any change in nuclear geometry” [57]. In other words, during absorption of the photon, the nuclei of the atoms that are involved, are assumed frozen. Transitions can only occur in vertical direction in the energy diagram [52].

Lastly, with fluorescence, the electron relaxes from the excited state to the ground state with similar spin multiplicity. Paired electrons spin in opposite directions, which is the singlet state. When one of these electrons is excited, most often it remains spinning in opposite directions, so the singlet state is maintained. However, it is possible that a so-called “forbidden” spin transition takes place where the spin direction of the excited electron reverses. The electron then spins in the direction parallel to the electron that it formed a pair with, this is the triplet state. This process is called intersystem crossing [58]. Phosphorescence is when the electron relaxes from the triplet state to its ground singlet state [Figure 34].

Notably, until now, luminophores have been denoted as “molecular species”. They can be sub-categorized into fluorophores and phosphors, depending on their type of relaxation (recall the difference between fluorescence and phosphorescence). Our main focus will be with fluorophores, as they bring the highest yield for LSC systems.

**Photovoltaic cells**

Before, it was described how light is concentrated at the side of an LSC, by absorbance and re-emission of luminophores. In LSC systems, an important aspect is the conversion of these photons into electricity. The conversion of light into electricity takes place in solar cells, or (PV) cells [Figure 37].

An inorganic PV cell consists of two layers of a semi-conducting material, most often silicon, in a current circuit: a p-n junction [59]. One layer of the silicon is doped with boron, the n-type, and one layer is doped with phosphorus, the p-type. This is done in order to create different chemical charges between the two layers of silicon, so that a current can be created.

When light penetrates the system, electrons of the p-type silicon are excited in a way that they escape their atomic orbital. They gain so much energy that they do not only go to a higher energy orbital, as is the case with

![Photovoltaic cell](image-url)
fluorescence, but they jump further than the highest orbital and they get separated from the rest of their atom. These electrons move to the n-type silicon.

The p-type silicon is therefore electron-poor (holes) and the n-type silicon is electron-rich (electrons). The electrons in the n-type silicon will subsequently move to the p-type silicon via a circuit in order to cancel the potential between the n-type and p-type silicon and electricity is captured.

Notably, two types of Si-based PV cells can be distinguished. Firstly, the conventional crystalline Si cells, which are the first generation, and, secondly, the amorphous Si cells, which are the second generation. For crystalline Si cells, either monocrystalline silicon (mono-Si), or polycrystalline silicon (multi-Si) is used, mono-Si being the most chemically pure. Amorphous silicon cells use amorphous silicon. Although this is easier to fabricate, the crystalline Si cells are more efficient, and therefore used more often. Figure 39 shows the optical efficiency records of different types of PV-cells. In 2014, Panasonic’s silicon solar cell reached an optical efficiency of 25.6% [60]. Moreover, in 2017, the most efficient solar cell up-to-date was reported by the National Renewable Energy Laboratory (NREL) [61]. It consisted of a dual-junction GaInP/GaAs solar cell, which reached 32.8% one-sun efficiency. Stacked with a Si solar cell, it achieved a record one-sun efficiency of 35.9% for triple-junction solar cells.

Lastly, it is important to note that sun light has the highest radiation intensity for wavelengths between 480-550 nm [Figure 38]. For PV cells it is preferred to have and absorption spectrum suited to the incoming light. In LSCs, the wavelengths of the radiated light are commonly higher (due to the Stokes shift of the fluorophores) and PV cells with a fitting absorption range are required. For example, monocrystalline cells used for this report’s research has a wide spectral sensitivity of 300-1100 nm [62], which is wide enough for application in LSCs.

![Figure 38. Radiation intensity of sun light](image-url)
Figure 39. Best research-cell efficiencies [60].
Appendix B. Factors impacting the optical efficiency of luminescent solar concentrators

Reflection from waveguide surface

The most obvious efficiency factor for LSC systems is the critical angle of reflection of the waveguide. Only incoming light that reaches the waveguide from a specific angle penetrates the system [Figure 40]. Light that hits the waveguide with an angle greater than the critical angle of reflection will, according to Snell’s law, be totally reflected. Only the light that hits the surface more perpendicularly to the surface will penetrate. The critical angle is defined accordingly:

$$\theta_c = \sin^{-1} \left( \frac{1}{n} \right)$$  \[3\]

Where \( n \) stands for the refractive index of the waveguide material. In the aforementioned equation for the LSC efficiency, this factor is implemented as \( R \), which stands for the fraction of the total light that is reflected. The smaller this fraction is, the more light penetrates, so the higher the efficiency will be. The amount of reflected light might be decreased by applying an anti-reflective coating on top of the waveguide [63]. Although it is beneficial to use waveguides that have a high critical angle of reflection, research for new waveguides has not focused on this particular factor [10], [13]. A likely reason is that only approximately 4% of the incoming light is reflected for waveguides with an refractive index of about 1.5 (poly(methyl methacrylate) (PMMA) = 1.49 and poly(carbonate) (PC) = 1.59) [10]. Therefore, the potential increase in efficiency is limited.

Total internal reflection efficiency

Irradiated photons from the fluorophores will escape the waveguide if they hit the surface with an angle lower than the critical angle of reflection. Via this way, 40 – 55% of the energy that enters LSCs is lost [64], [65]. Therefore, when designing waveguides for LSCs, a balance should be sought between the advantage and disadvantage of high/low critical angle of reflection.

Most optimally, light should easily penetrate the waveguide, but also stay trapped within the LSC when it is radiated from the fluorophores. There are two strategies described in literature for achieving higher efficiency that focus on the internal reflection. Firstly, it was attempted to align fluorophores in such a way, that they mainly emit photons in a specific direction (that of the PV) [66]–[68]. The fluorophores can be aligned parallel to the surface (a), perpendicular (b), or tilted (c) [Figure 41]. Although fluorophores aligned perpendicularly to the waveguide increase the trapping efficiency significantly (65% to more than 80%), their position also results in a decrease of absorption intensity. Therefore, the overall efficiency of the LSC decreases [69]. Fluorophores aligned parallel to the waveguide or tilted have no increased entrapment of photons [10].
Another technique to increase the amount of trapped photons is the use of wavelength selective mirrors [70]–[76]. It was calculated with simulations that the efficiency of entrapping could be increased by 50% using selective mirrors [12]. The principle of a wavelength selective mirror, is that photons with a specific wavelength can penetrate through the film and photons with a different wavelength are reflected [Figure 43]. In an ideal situation, the mirror enables all incoming photons through and keeps the emitted photons inside the waveguide.

The mirrors can be produced from cholesterics, which are nematic liquid crystalline (LC) materials, doped with a chiral molecule [76]. LCs behave like liquids, yet their molecules are oriented in a crystal-like way. In the nematic phase, the molecules are aligned with their long axes in a parallel position [Figure 42]. In a cholesteric film, the chiral molecule rotates through the film, which induces a twist between adjacent layers of the LC, thereby creating a helical structure [10]. This structure is capable of reflecting a certain bandwidth of wavelengths. However, since the chiral molecule is either chiral right handed or left handed, only half of the light (right- or left-circularly polarized light) is reflected.

For incoming light perpendicular to the mirror, the wavelength that is reflected is calculated by Watanabe et al.’s equation [77]:

$$\lambda_m = nP$$ \hspace{1cm} [4]

In which:

- $\lambda_m$ is the central reflective wavelength
- $n$ is average refractive index of the liquid crystal host
- $P$ is the pitch

The pitch is the distance it takes for the liquid crystal director of a plane of molecules in the helix to undergo a 360° twist [10]. For light that approaches the surface from a specific angle, the following formula can be used:

$$\lambda_m = nP \cdot \sin \theta$$ \hspace{1cm} [5]

Where $\theta$ stands for the incidence angle of the light respectively to the normal.

The reflective bandwidth of the light is given by:

$$\Delta \lambda = (n_e - n_o)P$$ \hspace{1cm} [6]

In which $n_e$ and $n_o$ are the extraordinary and ordinary refractive index of the host [10].

Inorganic reflectors have managed to increase edge outputs so that the LSC’s efficiency increased by 20% [70]. The disadvantage of inorganic reflectors, however, is that they are relatively expensive. In order to capture as many photons as possible, the refractive bandwidth should be as large as possible. Ergo, hosts with a high $\Delta \lambda$ should be used for the best performance [72]. Methods to increase bandwidth is using neighboring like-handed cholesterics [10] or employ gradient-pitch cholesterics, in which the pitch continuously varies [78].
Absorbed light

It stands to reason that, in order to achieve high absorption intensity, a fluorophore with a broad absorption spectrum should be used. Indeed, that way a large amount of incoming light can be harvested. Notably, not all incoming light is harvested, some photons within the absorption width band might not be absorbed by the fluorophores. These photons may not collide at all with luminophores when they have penetrated the dye. Or they just might not be absorbed by the luminophores they collide with.

In order to increase the overall optical efficiency of an LSC system, increasing the absorption intensity seems essential. Indeed, the more light is absorbed, the more light is re-emitted and therefore, more energy is converted. This could be achieved by increasing the dye concentration of luminophores. That way, the amount of successful collisions between photons and luminophores is increased, simply because there are more fluorophores in the matrix. It should be noted, however, that increasing the absorption intensity does not necessarily result in an increase of the overall optical efficiency. Although at lower dye concentrations an increase in dye concentration effectuates an increase in optical efficiency, at higher concentrations, this principle is counterbalanced by dissipative processes such as fluorescence quenching and re-absorption. The influence of these phenomena become more significant at high dye concentrations [79].

Other efficiency factors

Irregularities in the waveguide surface, or the presence of dust on top of the waveguides is detrimental for the efficiency of LSC systems [10], [80]. Indeed, it is easiest for light to penetrate a smooth and clean waveguide. This is particularly a challenge when producing relatively large LSCs (i.e. >1 m²). The chance of imperfection increases with size.

Besides the detrimental influence of irregularities, parasitic absorption of waveguide molecules might also decrease the efficiency of LSC systems. Especially for systems in which the fluorophores absorb photons close to the infrared spectrum, this might form losses [32], [33], [81], [82]. PMMA, for example, starts to absorb photons from wavelengths of 880nm.

Summary losses

A graphical representation of the different types of losses that have been previously discussed, is given in Figure 44.

Figure 44. Factors for the loss in LSCs [10]. 1) Light emitted outside capture cone; 2) re-absorption of emitted light by another luminophore; 3a) input light is not absorbed by the luminophore; 3b) limited luminophore stability; 3c) internal quantum efficiency of the luminophore is not unity; 4) solar cell losses; 5a) reflection from the waveguide surface; 5b) absorption of emitted light by the waveguide; 5c) internal waveguide scattering; 5d) surface scattering

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Appendix C. The re-absorption problem: a mathematical analysis

In order to illustrate the magnitude of the re-absorption problem, a mathematical model was presented [79]. Although this is a simplified interpretation of reality, the model provides an adequate approach for a sensitivity analysis of the influence of the dye concentration on the probability that a photon which has entered the system will eventually reach the side of the LSC. This probability is given by:

\[ P_{\text{out}} = (QP_{\text{TIR}})^N \]  \[7\]

Where Q represents the quantum yield, \( P_{\text{TIR}} \) is the likeliness that a photon is re-emitted in a direction so that will undergo total reflection and \( N \) is the number of times the photon is re-absorbed by other fluorophores. \( N \) is related to the radius of the LSC (\( r \)) and the average step length of a photon before it is re-absorbed (\( l \)) and can be presented accordingly:

\[ N = a \left( \frac{r}{l} \right)^2 \]  \[8\]

With \( a \) being a constant that is related to the ratio between \( r \) and \( l \). For system in which \( l >> r \), \( N \) becomes 1 and re-absorption is insignificant. This situation is met when \( l/r > 5 \). For \( l/r < 5 \), Table 8 can be used for finding \( a \) and the calculation of \( N \). \( l \) is related to the dye concentration. Assuming that the average step size \( l \) is the distance travelled by a photon for which the probability of an encounter with the next fluorophore is 0.5, \( l \) can be expressed accordingly:

\[ l = -\frac{\log(0.5)}{\varepsilon C} = \frac{0.3}{\varepsilon C} \]  \[9\]

<table>
<thead>
<tr>
<th>( l/r )</th>
<th>( a(l/r) )</th>
<th>( N(l/r) )</th>
<th>Stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>28.1</td>
<td>1.12</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>18.5</td>
<td>1.16</td>
<td>0.01</td>
</tr>
<tr>
<td>3</td>
<td>10.9</td>
<td>1.21</td>
<td>0.02</td>
</tr>
<tr>
<td>2.5</td>
<td>7.9</td>
<td>1.26</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>5.3</td>
<td>1.32</td>
<td>0.02</td>
</tr>
<tr>
<td>1.5</td>
<td>3.2</td>
<td>1.43</td>
<td>0.03</td>
</tr>
<tr>
<td>1</td>
<td>1.7</td>
<td>1.70</td>
<td>0.03</td>
</tr>
<tr>
<td>0.75</td>
<td>1.1</td>
<td>1.97</td>
<td>0.05</td>
</tr>
<tr>
<td>0.5</td>
<td>0.67</td>
<td>2.67</td>
<td>0.06</td>
</tr>
<tr>
<td>0.33</td>
<td>0.42</td>
<td>3.74</td>
<td>0.11</td>
</tr>
<tr>
<td>0.25</td>
<td>0.33</td>
<td>5.24</td>
<td>0.15</td>
</tr>
<tr>
<td>0.2</td>
<td>0.28</td>
<td>6.87</td>
<td>0.32</td>
</tr>
<tr>
<td>0.17</td>
<td>0.24</td>
<td>8.69</td>
<td>0.22</td>
</tr>
<tr>
<td>0.13</td>
<td>0.20</td>
<td>12.90</td>
<td>0.35</td>
</tr>
<tr>
<td>0.1</td>
<td>0.18</td>
<td>18.09</td>
<td>0.75</td>
</tr>
<tr>
<td>0.05</td>
<td>0.15</td>
<td>58.54</td>
<td>1.38</td>
</tr>
<tr>
<td>0.025</td>
<td>0.13</td>
<td>213.59</td>
<td>1.72</td>
</tr>
</tbody>
</table>

*Table 8. Data retrieved from [79].*
Where \( \varepsilon (\text{m}^2\text{mole}^{-1}) \) represents the molar attenuation coefficient and \( C \) the molar concentration of the dye. When \( l \) is substituted in equation [8], equation [10] can be acquired:

\[
N = a \times \left( \frac{r \varepsilon}{0.3} \right)^2 = 11a \times (r \varepsilon C)^2 \tag{10}
\]

And subsequently:

\[
P_{\text{out}} = (Q P_{\text{TIR}})^{11a(r \varepsilon C)^2} \tag{11}
\]

Notably, equation [10] holds if \( \varepsilon \) is assumed constant over a band of wavelengths. From equation [10] a sensitivity analysis can be made to gain insight in the influence of concentration (\( C \)) on the probability that a photon reaches the edge of the system (\( P_{\text{out}} \)), ceteris paribus. This graph gives insight in how significant the influence of dye concentration is for the re-absorption problem [Figure 45].

**Strategies for tackling the reabsorption problem**

It stands to reason that the use of dyes with relatively high Stokes shifts will be less susceptible to re-absorption. Indeed, re-emitted photons with a wavelength outside of the absorption band width will not be re-absorbed by other fluorophores. Unfortunately, most luminophores have a small Stokes shifts [17]. However, there are also other approaches for decreasing the amount of re-absorption in LSCs [10]. Taleb (2002) introduced a polar dopant (thionin) in the waveguide with luminophores [83]. Due to its polarity, this dopant altered the electronic states of the luminophores, especially the fluorescent state, and increased the Stokes shift. This lead to less re-absorption and therefore allowed for a higher photovoltaic solar conversion.

Another approach was proposed by [31], who tried to stack empty waveguides and waveguides with fluorophores alternately. Although re-absorption decreased, overall absorption decreased as well, leading to a lower photovoltaic solar conversion. [84] stacked layers of different types of fluorophores on top of each other, each absorbing photons with different wavelengths. This was found to benefit mainly luminophores that absorb photons close to the infrared spectrum, however, these LSCs have been found to have lower quantum yields [10].

A promising approach to counter the re-absorption problem seems to be to center all luminophores on top of the waveguide in a dye instead of filling the whole bulk with luminophores [12], [42], [85]–[89]. It was calculated
that layer systems perform as well as bulk systems [90]. Because emitted photons only collide with other luminophores when they hit the top layer for a second time, re-absorption is less common than with bulk systems. Moreover, for large scale production, luminophore layers on top of empty waveguides are superior to bulk filled waveguides since it is cheaper and simpler to manufacture. Conventional spraying or coating techniques could be utilized. On the other, one should be aware that the solubility of luminophores in a dye might form a challenge. Most luminophores have limited solubility [10]. Extra attention should be paid to designing waveguides that can be used as dye and contain dissolved luminophores.
**Appendix D. Fluorescence quenching: a mathematical approach**

The following is based on [91]. For dynamic quenching the Stern-Volmer equation holds:

\[
\frac{F_0}{F} = 1 + k_q \tau_0 [Q] = 1 + K_{SV} [Q]
\]

[12]

In which:

- \( F_0 \) = fluorescence intensity in absence of the quencher
- \( F \) = fluorescence intensity in presence of the quencher
- \( k_q \) = bimolecular quenching constant
- \( \tau_0 \) = lifetime of the fluorophore in absence of the quencher
- \( K_{SV} \) = Stern Volmer quenching constant

Equation [6] may be obtained by considering the fraction of excited fluorophores which decay by emission relative to the total \( \frac{F}{F_0} \). This fraction is given by the ratio of the decay rate in the absence of quencher \( (\gamma) \) to the total decay rate in the presence of quencher \( (\gamma + k_q [Q]) \):

\[
\frac{F}{F_0} = \frac{\gamma}{\gamma + k_q [Q]} = \frac{1}{1 + K_{SV} [Q]}
\]

[13]

As discussed earlier, dynamic quenching depopulates the excited state fluorophores. The lifetimes of the excited fluorophore in absence of the quencher \( (\tau_0) \) and absence of the quencher \( (\tau) \) are given by:

\[
\tau_0 = \gamma^{-1}
\]

[14]

\[
\tau = (\gamma + k_q [Q])^{-1}
\]

[15]

And we see that:

\[
\tau_0 = 1 + k_q \tau_0 [Q]
\]

[16]

Therefore:

\[
\frac{F_0}{F} = \frac{\tau_0}{\tau}
\]

[17]

Here, we see that, indeed, the fluorescence intensity is negatively related to the time that the fluorophore remains in the excited state. The longer a fluorophore remains in the excited state, the more effective the quencher.

In contrast to dynamic quenching, static quenching is not time related, but concentration related. For static quenching the following formula holds:

\[
\frac{F_0}{F} = 1 + K_S [Q]
\]

[18]

In which:

- \( K_S \) = association constant for the formation of the fluorophore-quencher complex

This equation may be obtained by considering the reaction constant for complex formation. This constant is given by:

\[
K_S = \frac{[F-Q]}{[F][Q]}
\]

[19]

In which:

- \([F-Q]\) = the concentration of the complex
- \([F]\) = the concentration of uncomplexed fluorophore
- \([Q]\) = the concentration of quencher
If we remember that:

\[ [F]_0 = [F] + [F - Q] \]  \hspace{1cm} [20]

We can rewrite the reaction constant of the formation of the fluorophore-quencher complex into:

\[ K_S = \frac{[F]_0 - [F]}{[F][Q]} = \frac{[F]_0}{[F][Q]} - \frac{1}{Q} \]  \hspace{1cm} [21]

When we substitute the fluorophore concentration for fluorescence intensity, we find after some re-arrangement:

\[ \frac{F_0}{F} = 1 + K_S[Q] \]  \hspace{1cm} [22]

In case of LSCs, only static quenching plays a significant role, since the film is in a solid state and the fluorophore is usually immersed in a glassy environment. When designing new polymer/fluorophore films for LSCs, one must remember the importance of the complex formation between fluorophore and quencher. If this complex is easily formed, quenching becomes increasingly important. Reaction conditions for the formation of the complex should also be considered.

This raises the following question: which molecular species may act like a quencher in a system and at which conditions is it most effective? In literature, it was proposed that the formation of aggregates in high dye concentration system causes fluorescence quenching [92], [93]. Reciprocal interactions between fluorophores in these aggregates might the formation of excimers (excited dimers) as well. Excimer formation might therefore be detrimental to the emission intensity and optical efficiency.

Logically, one would expect that the intensity of these emissive excimer complexes is lower than the emission intensity of single fluorophores. Indeed, in general excimer formations, dynamic molecular motions generate friction between excimer and medium, which results in a transformation of photonic to thermal energy (Förster’s quenching). However, there are several situations known where an increase in dye concentration of thin LSC films show an emission spectrum with increased intensity and emission peaks at higher wavelengths [34], [39], [47], [94]–[97], [41].

An example is presented in Figure 46.A. An emission intensity spectrum is shown of nanostructure aggregates of perylene diimide derivatives (PDI-1) dispersed in LSC thin films at different dye concentrations. Two emission peaks are visible at wavelengths of 485 nm and 530. The last peak is most intense for higher dye concentrations, suggesting that it belongs to excimer complexes that are more frequently present at high dye concentrations. Note that in Figure 46.B Lumogen Red 305 shows an emission spectrum that is unaffected by dye concentration. It is an important characteristic of LR that it does not form aggregates in LSC systems thanks to its molecular structure, which bears sterically hindered peripheral functional moieties.

Furthermore, the life time of an excited excimer complexes is longer than of single molecules. [35] found that average life times of perylene derivatives in their excited state were both approximately 4 ns and 12-17 ns (thin films of perylene derivative in PMMA). The shortest time is attributed to single molecules and the longer life time is attributed to aggregates. Increasing the dye concentration, a higher percentage of long lifetimes was found compared to short lifetimes.

Tang (2016) suggested that the reason for an increasing emission intensity due to formation of aggregates could be explained by the following: In general excimer formations, dynamic molecular motions generate friction between excimer and medium, which results in a transformation of photonic to thermal energy (Förster’s quenching) [36]. However, in solid nano-aggregates, structural rigidity hinder the excimer complexes to undergo intermolecular and inter-ring motions, which enhances emission intensity. This idea was also proposed by [47], [97], who argued that limiting the effects of restricted intramolecular rotation of the fluorophore enabled more effective non-radiative decay channels. It should be noted that an emission spectrum with a shifted and/or increased intensity is not directly related to increased optical efficiency. It might actually lead to an overall lower quantum yield or emitted photons with wavelengths that are less compatible with used PV cells.
Figure 46. Emission spectra of nanoparticles loaded with different PDI-1 (A) and Lumogen Red (B) weight concentrations. Excitation wavelengths were 485 nm and 530 nm, respectively [94].
Appendix E. Overview of state-of-the-art fluorophores

Debije et al. (2013) have presented an extensive overview of fluorophores used in LSCs up until 2013 [10]. Another extensive overview of state-of-the-art fluorophores up to 2017 was presented by McKenna et al. (2017) [13]. Notably, different methods are used to determine the overall optimal efficiency for the LSCs, which makes it difficult to objectively compare them. For example, the optical efficiency ($\eta$) in this report has been measured by comparing the amount of energy a PV cell generates when light directly shines on it, with the amount of energy that same PV cell generates when it is attached to the side of an LSC system. However, Olsen et al. (2016) report the optical efficiency as Power Conversion Efficiency (PCE), including in their calculation an efficiency factor of the PV cell they use [98]. In order to avoid confusion, the overview presented here merely presents fluorophores used by our group for which the calculation for optical efficiency ($\eta$) is done as presented earlier in this report, using equation [23]:

$$\eta_{opt} = \frac{I_{LSC}}{I_{SC} \cdot G}$$ [23]

For other fluorophores, the reader is referred to Debije et al. (2013) [10] and McKenna et al. (2017) [13].

<table>
<thead>
<tr>
<th>Name fluorophore</th>
<th>Chemical structure</th>
<th>Waveguide</th>
<th>Optical Efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>perylene-1,7,8,12-tetraphenoxy-3,4,9,10 tetracarboxylic acidbis-(2′6′diisopropylanilide) (Lumogen red 305)</td>
<td><img src="https://example.com/chemical_structure.png" alt="Image" /></td>
<td>PMMA</td>
<td>7.2%</td>
<td>[38]</td>
</tr>
<tr>
<td>2-amino-7-acceptor-9-silafluorene</td>
<td><img src="https://example.com/chemical_structure.png" alt="Image" /></td>
<td>PMMA</td>
<td>9.6%</td>
<td>[42]</td>
</tr>
<tr>
<td>N,N0-bis(2-hydroxy-1-naphthylidene)-diaminomaleonitrile</td>
<td><img src="https://example.com/chemical_structure.png" alt="Image" /></td>
<td>PMMA</td>
<td>7.0%</td>
<td>[37]</td>
</tr>
<tr>
<td>Check this!</td>
<td><img src="https://example.com/chemical_structure.png" alt="Image" /></td>
<td>PMMA</td>
<td>6.8%</td>
<td>[38]</td>
</tr>
<tr>
<td>3,6-bis(5-(4-methoxyphenyl)thiophene n-2-yl)-2,5-dioctyl-2,5-dihydro pyrrole[3,4-c]pyrrole-1,4-dione</td>
<td><img src="https://example.com/chemical_structure.png" alt="Image" /></td>
<td>PMMA</td>
<td>5.8%</td>
<td>[39]</td>
</tr>
<tr>
<td>Fluorophore containing the benzo[1,2-d:4,5-d′]bisthiazole unit</td>
<td><img src="https://example.com/chemical_structure.png" alt="Image" /></td>
<td>PMMA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>PMMA</td>
<td>Conversion</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td>------------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>3-(2-Benzothiazolyl)-N,N-diethylumbelliferylamin (Coumarin 6)</td>
<td>PMMA</td>
<td>6.9%&lt;sup&gt;a&lt;/sup&gt;</td>
<td>[99]</td>
<td></td>
</tr>
<tr>
<td>Adduct of triphenylamine, tetraphenylethene and fumaronitrile</td>
<td>PMMA</td>
<td>7.0%</td>
<td>Not yet published, based on this report</td>
<td></td>
</tr>
</tbody>
</table>

Table 9. Overview of state-of-the-art fluorophores published by our group. \( \eta_{\text{opt}} = \frac{I_{\text{SC}}}{I_{\text{ISC}}G} \)
Appendix F. Overview of all $^1$H NMR results

Figure 47. IGP02

Figure 48. GTP03
Figure S1. GTP06
Appendix G. Overview GPC results

**Figure S2. IGP02**

**Figure S3. GTP03**
Figure 54. GTP04

Figure 55. IGP05
Figure 56. GTP06

Figure 57. GTP07
Appendix H. DSC results of all films

DSC results GTP03

DSC results GTP04

DSC results IGP05
DSC results GTP06

DSC results GTP07
Appendix I. Absorption/Emission spectra all films

Absorption/emission Spectrum IGP2 and LR

Absorption/emission Spectrum GTP3 and LR
Absorption/emission Spectrum GTP03 and TTF

Absorption (arbitrary numbers)

Absorption/emission Spectrum GTP03 and TTF

Wavelength (nm)

0,2 wt.% absorption
0,61 wt.% absorption
1,01 wt.% absorption
1,38 wt.% absorption
1,97 wt.% absorption
0,2 wt.% emission
0,61 wt.% emission
1,01 wt.% emission
1,38 wt.% emission
1,97 wt.% emission
Absorption/emission spectra CP07/PMMA

Absorption (arbitrary numbers)

Wavelength (nm)
Absorption/emission Spectrum PMMA and QL17

Emission (arbitrary numbers)
Absorption (arbitrary numbers)
Wavelength (nm)

- 0.2 wt.% absorption
- 0.6 wt.% absorption
- 1.0 wt.% absorption
- 1.4 wt.% absorption
- 0.2 wt.% emission
- 0.6 wt.% emission
- 1.0 wt.% emission
- 1.4 wt.% emission
Figure S8. IGP02 (1.0 wt.%) under UV lamp (366 nm)
Figure 59. GTP03 (1.0 wt.%) under microscope (breadth = 0.6 nm)

Figure 60. GTP03 (1.0 wt.%) under UV lamp (366 nm)
Figure 61. GTP04 (1.0 wt.%) under microscope (breadth = 0.6 mm)

Figure 62. GTP04 (1.4 wt.%) under UV lamp (366 nm)
Figure 64. IGP05 (1.0 wt.%) under microscope (breadth = 0.6 mm)

Figure 63. IGP05 (1.0 wt.%) under UV lamp (366 nm)
Figure 65. PMMA (1.0 wt.%) under microscope (breadth = 0.6 mm)

Figure 66. PMMA (1.0 wt.%) under UV lamp (366 nm)
The author is excited to note that the results of the LSC thin films based on PMMA/BBT and PMMA/DTS have been published in the European Journal of Chemistry in the issue of the 1st of June 2018 (DOI: 10.1002/ejoc.201800242).

ACKNOWLEDGMENTS

The author is grateful to Prof. Andrea Pucci, Ms Ionela Gavrila and Prof. Francesco Picchioni for their comprehensive feedback of the concept version of this report. In addition, the author would like to thank Ms. Ionela Gavrila for her assistance in the preparation of the polymers and their characterization and Mr Giuseppe Iasilli for his assistance in the preparation of the LSC thin films and determination of their performances.