Luminescent Solar Concentrators Based on Energy Transfer from an Aggregation-Induced Emitter Conjugated Polymer

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ABSTRACT

Luminescent solar concentrators (LSCs) are solar-harvesting devices fabricated from transparent waveguide that is doped or coated with lumophores. Despite their potential for architectural integration, the optical efficiency of LSCs is often limited by incomplete harvesting of solar radiation and aggregation-caused quenching (ACQ) of lumophores in the solid state. Here, we demonstrate a multi-lumophore LSC design which circumvents these challenges through a combination of non-radiative Förster energy transfer (FRET) and aggregation-induced emission (AIE). The LSC incorporates a green-emitting poly(tetraphenylethylene), p-O-TPE, as an energy donor and a red-emitting perylene bisimide molecular dye (PDI-Sil) as the energy acceptor, within an organic-inorganic hybrid di-ureasil waveguide. Steady-state photoluminescence studies
demonstrate that the di-ureasil host induced AIE from the p-O-PTE donor polymer, leading to a high photoluminescence quantum yield (PLQY) of ~45% and a large Stokes shift of ~150 nm. Covalent grafting of the PDI-Sil acceptor to the siliceous domains of the di-ureasil waveguide also inhibits non-radiative losses by preventing molecular aggregation. Due to the excellent spectral overlap, FRET was shown to occur from p-O-TPE to PDI-Sil, which increased with acceptor concentration. As a result, the final LSC (4.5 cm × 4.5 cm × 0.3 cm) with an optimised donor-acceptor ratio (1:1 by wt%) exhibited an internal photon efficiency of 20%, demonstrating a viable design for LSCs utilising an AIE-based FRET approach to improve the solar-harvesting performance.
1. Introduction

Luminescent solar concentrators (LSC) are solar-harvesting devices fabricated from a transparent waveguide that is doped or coated with a luminescent species (lumophores).\(^1\) LSCs collect solar radiation over a large surface area, upon which it is spectrally converted via a photoluminescence process and redirected to the edges of the device where photovoltaic (PV) cells can be mounted.\(^1\),\(^2\) LSCs are able to collect and concentrate both diffuse and direct sunlight, making them particularly desirable for use in regions with high building density or excessive cloud coverage.\(^3\) These factors, combined with their aesthetic appeal and the diverse range of geometries that can be designed, mean that LSCs offer an excellent complementary approach for the architectural integration of PV technology in cities.\(^4\)

The combination of waveguide and lumophore used in an LSC is critical to its optical efficiency.\(^5\) The ideal waveguide will have high transmittance across the solar spectrum and a refractive index, \(n\), of around 1.5 – 2.0 to minimize the reflective losses at the top surface, while maximizing the trapping efficiency of the radiation emitted within the waveguide.\(^5\) The lumophore must have a photoluminescence quantum yield (PLQY) close to 100%, a high absorption coefficient and broad spectral overlap with the solar spectrum, and a large Stokes shift to minimize reabsorption losses.\(^3\),\(^5\) Both the waveguide and lumophore should have good photo- and thermal stability and easy processability for large scale production.\(^6\)

In recent decades, lumophores with high PLQYs and excellent stabilities, such as quantum dots,\(^7\),\(^8\) metal complexes\(^9\),\(^10\) and organic dyes,\(^11\),\(^12\) have been developed. In particular, \(\pi\)-conjugated polymers have been extensively investigated as lumophores for flexible, light-weight optical devices such as field-effect transistors,\(^13\),\(^14\) organic light-emitting diodes,\(^15\),\(^16\),\(^17\) and PV devices,\(^18\),\(^19\) as well as LSCs,\(^20\),\(^21\) due to their desirable optoelectronic properties and cost-effective solution processability.\(^22\) However, the optical efficiency of conjugated polymers is often undermined by aggregation-caused quenching (ACQ), which occurs due to preferential non-radiative relaxation of excited states as a result of intermolecular \(\pi\)-\(\pi\) interactions.\(^5\),\(^23\),\(^24\) This is
especially problematic at high lumophore concentrations in solid host matrices and can be detrimental to the optical efficiencies of LSCs.\textsuperscript{12,25,26} The effect of ACQ can be mitigated by using lumophores that exhibit aggregation-induced emission (AIE).\textsuperscript{25,27} For AIE-active molecules (\textit{i.e.} AIEgens) non-radiative deactivation is significantly reduced in the aggregated state due to physical restraints on both intramolecular rotations and $\pi$-$\pi$ stacking due to the highly-twisted molecular core.\textsuperscript{28} This leads to preferential radiative relaxation of the excited state upon aggregation, \textit{i.e.} the photoluminescence is “switched on”.

The first reported AIE-based LSC incorporated tetraphenylethylene (TPE) in a poly(methyl methacrylate) (PMMA) film cast on a glass substrate.\textsuperscript{25} This device was able to effectively concentrate light without inducing ACQ, even at an elevated lumophore concentration of 10 wt%. However, the emission range of TPE ($\lambda_{\text{em}} \sim 450$ nm) was not well-matched with the typical band gaps of silicon or GaAs solar cells.\textsuperscript{26} This issue was later circumvented through Förster resonance energy transfer (FRET) from a molecular AIEgen donor (D) to an acceptor (A) lumophore co-doped in the waveguide, leading to an effective red-shift in the emission.\textsuperscript{12,26} An alternative approach to further tune the AIEgen emission to lower energy is to extend the $\pi$-conjugation of the molecule using electron donor and acceptor moieties.\textsuperscript{29} For example, the TPE analogue, TPE-AC, which contains dimethylamine and malononitrile substituents appended to the core, was shown to exhibit intense red emission in both PMMA and polycarbonate matrices; however fluorescence quenching was still observed at concentrations above 0.6-0.7 wt% due to the formation of less emissive supramolecular-amorphous aggregates.\textsuperscript{29} Recently, a tandem-structure LSC consisting of layers of N-doped carbon dots and red-emitting AIEgens was also reported.\textsuperscript{29}

While the potential of both small-molecule AIEgens and conjugated polymers as lumophores for LSCs has been demonstrated, LSCs based on conjugated polymers with AIE characteristics have not yet been reported. A conjugated polymer analogue of TPE, polydiphenoxy-tetraphenylethylene (p-O-TPE) has a high PLQY (52-73\%) and large Stokes shift
(~150 nm) in the solid-state, suggesting it could be successfully implemented in LSCs. However, as p-O-TPE is a green emitter, it would be advantageous to design a FRET-based LSC, that additionally incorporates a red-emitting acceptor lumophore to better match the spectral response of standard Si PV cells. As a π-conjugated polymer, p-O-TPE has the additional advantage of accommodating fast exciton migration along its backbone. This can be easily intercepted by a small amount of FRET acceptors present in the matrix, thus making the FRET process efficient. The choice of waveguide is also important, since both the donor and acceptor lumophores must be well-dispersed through the host. A family of organic-inorganic hybrid polymers known as ureasils have been demonstrated as excellent waveguides for LSCs and other optical applications. As hybrid materials, ureasils combine the easy processability and chemical functionality of organic polymers with the high optical transparency and stability of the typical inorganic waveguides. Moreover, they can be easily fabricated into various shapes through a sol-gel process, making them compatible with a variety of architectural designs. We postulated that the structure of the ureasil, in particular the apolar nature of the alkyl-shielded siloxane backbone, may help to induce the aggregation of p-O-TPE, thus enhancing the emission efficiency in the solid state. As the acceptor, we chose perylene carboxdiimide-bridged triethoxysilane (PDI-Sil), a red-emitter related to the archetypal LSC lumophore Lumogen Red 305 (LR305). While LR305 shows a tendency to aggregate in ureasils, we have recently shown that by covalently grafting the PDI-Sil analogue to the siloxane backbone of the ureasil, aggregation can be effectively reduced, leading to high PLQYs (~80%). Herein, we show that due to excellent spectral overlap, p-O-TPE and PDI-Sil act as an efficient FRET pair in a ureasil waveguide. We observe that FRET also leads to reduced non-radiative relaxation of the p-O-TPE donor and extends the solar-harvesting window of the final LSC, giving rise to improved optical quantum efficiencies.
2. Experimental Section

**Materials:** Bis(2-aminopropyl) polypropylene glycol-block-polyethylene glycol-block-polypropylene glycol (Jeffamine ED-600, $M_w = 600 \text{ g mol}^{-1}$) and 3-(triethoxysilyl)propylisocyanate (ICPTES, 95.0%) were purchased from Sigma-Aldrich. Tetrahydrofuran (THF, ≥99.9%), ethanol (EtOH, 95.0%) and hydrochloric acid (HCl, 37%) were purchased from Fisher Scientific. Water was obtained from Millipore Simpax 2 water purification system. Poly-diphenoxy-tetraphenylethylene (p-O-TPE)$^{30}$ and $N,N$-bis(3-triethoxysilylpropyl)-1,6,7,12-tetra-tert-butylphenoxyperylene-3,4:9,10-tetra-carboxdiimide$^{33}$ were synthesized as previously reported. All materials were used as received.

**Fabrication of di-ureasil-based LSCs:** Samples containing p-O-TPE doped in di-ureasils (denoted p-O-TPE-dU(600)) at different concentrations (wt%) were prepared via a two-step sol-gel process. In the first step, ICPTES (0.91 mL, 3.68 mmol) was mixed with Jeffamine ED-600 (1.00 mL, 1.75 mmol) in THF (5 mL). The reaction mixture was refluxed at 70 °C for 24 h to obtain “one batch” of the organic-inorganic hybrid precursor, di-ureapropyltriethoxysilane (d-UPTES) in solution. The requisite volume, based on the final dopant concentration of 0.001, 0.005, 0.01 and 0.05 wt% (with respect to the mass of the dry monoliths, “one batch” of d-UPTES yields a dry monolith of 1.76 g), of a stock solution of p-O-TPE (1 mg mL$^{-1}$ in THF) was added to the d-UPTES solution under stirring. In the second step, gelling reagents (ethanol, HCl (0.5 M) and water) were added to the d-UPTES in sequence and thoroughly mixed. The molar ratio of Jeffamine ED-600 : ethanol : HCl : water used was 88 : 345 : 1 : 265. The resulting mixture was poured into a polypropylene mould and gelled into free-standing monoliths. The mould was sealed with Parafilm M® to allow slow evaporation of the excess THF in the samples over 5 days, followed by further oven drying at 40 °C for 3 days. “One batch” or “four batches” of the d-UPTES can be used to fabricate “small” (2 cm × 2 cm × 0.3 cm) or “large” (4.5 cm × 4.5 cm × 0.3 cm) monoliths, respectively.
A similar approach was employed for the synthesis of PDI-Sil-dU(600), where the requisite volume of a stock solution of PDI-Sil in THF (1 mg mL\(^{-1}\)) was pre-mixed with the d-UPTES solution under stirring prior to the addition of gelling reagents, to obtain PDI-Sil concentration of 0.0005, 0.0025, 0.005, 0.01 and 0.05 wt% with respect to the mass of the dry monolith. The addition of the gelling reagents triggers the hydrolysis and co-condensation between the triethoxysilyl groups of PDI-Sil and d-UPTES, leading to the covalent grafting of PDI-Sil to the dU(600) framework.\(^{33}\)

To obtain p-O-TPE-PDI-Sil-dU(600), a fixed volume of the stock solution of p-O-TPE (1 mg mL\(^{-1}\) in THF) was first added to the d-UPTES solution to obtain a fixed concentration of 0.005 wt% in the final samples. This was followed by the addition of the PDI-Sil stock solution (1 mg mL\(^{-1}\) in THF) with volume adjusted to obtain the desired p-O-TPE:PDI-Sil concentration ratios (by wt%) of 1:0, 1:0.1, 1:0.5, 1:1, 1:5 and 1:10 in the final samples.\(^{33}\)

**UV/Vis absorption spectroscopy:** UV/Vis absorption and transmittance spectra were measured with a Perkin Elmer Lambda 750 spectrophotometer using wavelength scan with a resolution of 1 nm at a scan speed of 1 nm/s and a slit width of 2 nm. Liquid samples were analyzed in a quartz cuvette with a 10 mm pathlength and solid samples were directly mounted to the sample holder.

**Steady-state photoluminescence:** Steady-state photoluminescence (PL) spectroscopy was performed on a Fluorolog-3 spectrophotometer (Horiba Jobin Yvon). Solid-state emission spectra were recorded in both the front-face and edge emission configurations. The excitation and emission slits were adjusted so that the maximum PL intensity was within the range of linear-response of the detector and were kept the same between samples if direct comparison between the emission intensity was required. Photoluminescence quantum yields were measured using a Quanta-phi integrating sphere (Horiba Jobin Yvon) mounted on the Fluorolog-3 spectrophotometer. The values and errors reported are the mean and standard deviation of three repeating measurements. Emission and excitation spectra were corrected for the wavelength
response of the system and the intensity of the lamp profile over the excitation range, respectively, using correction factors supplied by the manufacturer.

**FRET calculations:** The Förster radius, \( R_0 \), defined as the donor-acceptor distance at which FRET is 50% efficient was determined by the following equation:

\[
R_0 = \frac{2.07}{128\pi^5 N_A} \frac{k^2 Q_D}{n^4} \int F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda
\]

where \( N_A \) is the Avogadro’s number, \( k^2 \) is the dipole orientation factor, \( Q_D \) is the quantum yield of the donor, \( n \) is the refractive index of the medium, \( F_D \) is the normalized emission spectrum of the donor, \( \epsilon_A \) is the molar extinction coefficient of the acceptor and \( \lambda \) is the photon wavelength. The calculation was performed using the PhotochemCAD™ 3.0 software.41,42

**LSC characterization:** The optical performance of LSCs was measured using previously reported experimental set-up.6 In brief, the LSC was illuminated using a Class ABB solar simulator (Abet Technologies) equipped with an AM1.5G filter. A black absorptive mask with a circular aperture (d = 3.5 cm) was placed on the top face of the LSC to clearly define the illumination area. The distance between the source of illumination and the LSC was calibrated according to the irradiance of “1 Sun” (1000 ± 10 W m²) using a reference silicon solar cell (ReRa Technologies) coupled to a Keithley 2401 Sourcemeter. The emission from the edge of the LSC was collected by an INS125 integrating sphere (225-1400 nm, International Light Technologies) and directed to a spectroradiometer (SpectriLight ILT 950) through an optical cable. The spectrally-resolved data in photocounts was collected from the spectroradiometer and calibrated into optical power (\( \mu \)W) using the calibration file ILT1007131U1NS123 through the SpectriLight III software. All measurements were performed on a black absorptive background. The parameters used to characterize the optical efficiencies of LSCs are the internal photon efficiency \( \eta_{\text{int}} \) and external photon efficiency \( \eta_{\text{ext}} \), defined by the following equations:
\[
\eta_{\text{int}} = \frac{N_{\text{ph-out}}}{N_{\text{ph-abs}}} = \frac{\sum_{i=1}^{4} \int_{250}^{1050} P_{\text{out}}(\lambda) \frac{\lambda}{hc} d\lambda}{\int_{250}^{1050} P_{\text{in}}(\lambda) \frac{\lambda}{hc} (1 - 10^{-A(\lambda)}) d\lambda}
\]

(2)

\[
\eta_{\text{ext}} = \frac{N_{\text{ph-out}}}{N_{\text{ph-in}}} = \frac{\sum_{i=1}^{4} \int_{250}^{1050} P_{\text{out}}(\lambda) \frac{\lambda}{hc} d\lambda}{\int_{250}^{1050} P_{\text{in}}(\lambda) \frac{\lambda}{hc} d\lambda}
\]

(3)

where \(N_{\text{ph-out}}\) is the total number of edge-emitted photons summed over four edges (\(i = 1-4\)) of the LSC, \(N_{\text{ph-abs}}\) is the total number of photons absorbed by the LSC, and \(N_{\text{ph-in}}\) is the total number of photons incident on the top surface of the LSC. \(N_{\text{ph-out}}\) is obtained from the sum of the output power spectra, \(P_{\text{out}}(\lambda)\), measured for each edge of the LSC (in W nm\(^{-1}\)), where \(\lambda\) is the wavelength of light (in nm). \(P_{\text{in}}(\lambda)\) is the input power spectrum from the solar simulator incident on the top surface of the LSC (in W nm\(^{-1}\)), \(h\) is Planck’s constant (in J s), \(c\) is the speed of light (in m s\(^{-1}\)), and \(A(\lambda)\) is the absorption spectrum of the LSC. The integrations are performed over the full AM1.5G solar spectrum (250-1050 nm). The values and errors reported for \(\eta_{\text{int}}\) and \(\eta_{\text{ext}}\) are the mean and standard deviation of three repeat measurements, respectively.

3. Results and Discussion

Design strategy

Di-ureasil waveguides (denoted dU(600)) were synthesised via a two-step process, as illustrated in Figure 1. The first step involves coupling of the silane precursor ICPTES to a di-branched commercial polyetheramine, Jeffamine ED-600 to form the intermediate di-ureapropyltriethoxysilane (d-UPTES). The second step involves acid-catalysed hydrolysis and condensation of the siliceous backbone, which after drying, yields the final dU(600) waveguide as a free-standing monolith. The dU(600) structure consists of siliceous nanodomains (~10 Å) covalently bonded to the Jeffamine chains via propylurea linkages.\(^{43}\) To optimise the concentration of the donor p-O-TPE, as well as the concentration ratio between p-O-TPE and the acceptor PDI-Sil,
we prepared three series of samples based on either p-O-TPE, PDI-Sil or their mixtures incorporated into dU(600). In all samples, p-O-TPE is homogeneously mixed throughout the ureasil as a composite, whereas PDI-Sil is covalently grafted to the siliceous domains through the hydrolysis and co-condensation between the triethoxysilyl groups of PDI-Sil and d-UPTES during the sol-gel process.

**Figure 1.** Synthetic route for the preparation of donor-acceptor LSCs. The conjugated polymer donor p-O-TPE is entrapped within the organic domains of the di-ureasil waveguide, while molecular acceptor PDI-Sil is covalently grafted to the siliceous network as a result of the hydrolysis and co-condensation between the triethoxysilyl groups of PDI-Sil and d-UPTES under the acidic conditions of the sol-gel process. The donor-acceptor ratio is varied to tune to emission of the final LSCs, as illustrated by the photograph of the final samples under UV light (365 nm). The concentration of p-O-TPE is fixed at 0.005 wt% for p-O-TPE-PDI-Sil-dU(600) (top row), while the concentration of PDI-Sil is increased from 0 wt% to 0.075 wt%. The ratios correspond to the p-O-TPE to PDI-Sil proportions.

As can be seen in Figure 2, p-O-TPE absorbs light in the UV/blue region (300-450 nm), which is complementary to the absorption range of PDI-Sil (400-600 nm). Therefore, by incorporating both lumophores in the same matrix, a larger portion of the solar spectrum will be absorbed which is expected to enhance the solar-absorption efficiency of the final LSC. Furthermore, Figure 2
demonstrates the excellent spectral overlap between the emission of p-O-TPE, which is centred at around 520 nm, and the absorption of PDI-Sil. This is ideal for efficient FRET to occur between the two lumophores. The calculated critical Förster radius, \( R_0 \), defined as the average \( D-A \) separation required to achieve 50% FRET efficiency, is significantly longer for the p-O-TPE-PDI-Sil pair (~41 nm) than for most previously reported \( D-A \) systems used in LSCs (~10 nm). This means that there should be a higher FRET efficiency for a given \( D-A \) separation (i.e. at a given concentration) in the host matrix. Furthermore, the ureasil waveguide itself can harvest UV radiation and convert it into blue photoluminescence (Figure S1, ESI). A previous study showed that FRET can also occur from the di-ureasil host to embedded lumophores with appropriate spectral overlap, further extending the light-harvesting window of the final LSC.

\[ \text{Figure 2. Normalized absorption (dashed blue) and emission (solid blue, } \lambda_{\text{ex}} = 380 \text{ nm) spectra of the donor (p-O-TPE) measured in 50 vol\% EtOH/THF and normalized absorption (solid red) and emission (dashed red, } \lambda_{\text{ex}} = 520 \text{ nm) spectra of the acceptor (PDI-Sil) measured in THF. FRET is expected from p-O-TPE to PDI-Sil due to the large spectral overlap between the emission spectrum of p-O-TPE and absorption spectrum of PDI-Sil.} \]

**Emission properties of p-O-TPE as an AIEgen**

The aggregation of AIEgens can be induced either by introducing a bad solvent in solution or forcing them to pack in a solid matrix. The AIE behaviour of p-O-TPE was first investigated in solution. In a good solvent (THF), p-O-TPE is only weakly emissive. However, upon addition of
a poor solvent (EtOH), a dramatic increase in the emission intensity up to 530% was observed (Figure S2, ESI). These results clearly demonstrate the AIE behaviour of p-O-TPE in solution. To investigate whether the ureasil host could also induce this AIE behaviour, p-O-TPE was doped into dU(600) at four different concentrations (0.001-0.05 wt% with respect to the dry monolith). Figure 3a shows photographs of the resultant p-O-TPE-dU(600) series under natural light. The green colouration of the samples becomes more intense as the concentration of p-O-TPE increases. The corresponding PL spectra are in good agreement with the solution data, with a broad emission band centred at ca. 513 nm (Figure 3b).

![Figure 3. Optical properties of p-O-TPE-dU(600) ureasils. (a) Photographs of dU(600) doped with varying concentrations of p-O-TPE under daylight conditions. (b) Emission spectra (λ<sub>ex</sub> = 370 nm), (c) PLQY (λ<sub>ex</sub> = 400 nm) and (d) UV-Vis transmittance spectra of p-O-TPE-dU(600) as a function of p-O-TPE concentration.](image)

The PLQY of p-O-TPE increases dramatically from 2%<sup>30</sup> to 44% when moving from THF solution (used in the synthesis) to the ureasil matrix. Moreover, Figure 3c shows that the PLQY of p-O-TPE increases further with increasing concentration, reaching a maximum of around 60% at 0.05 wt%. This is likely a result of increasing aggregation between p-O-TPE polymer chains in the ureasil matrix, which further rigidifies their molecular conformation.<sup>28</sup> The formation of p-O-TPE aggregates in the ureasil is also apparent upon inspection the samples under daylight conditions (Figure 3a), indicated by the increasing opaqueness. These results demonstrate the
emissive nature of the p-O-TPE aggregates formed in the ureasil matrix, as opposed to the typical ACQ behavior which is often observed for organic lumophores upon translation to the solid state.\textsuperscript{27,48} The latter is often considered detrimental to the efficiency of the LSCs especially at the elevated concentrations required to maximize light harvesting.\textsuperscript{5,3}

Despite the enhanced PLQY, scattering losses emerged as the concentration of p-O-TPE exceeds 0.005 wt\%, caused by the increasing extent of aggregation. This is evident in the corresponding UV/Vis transmittance spectra (Figure 3d), revealed by a significant loss of transmittance in the long-wavelength region where neither the di-ureasil nor p-O-TPE absorb. Such scattering losses will critically limit the optical efficiency of the LSC. Therefore, 0.005 wt\% was chosen as the optimal concentration for the p-O-TPE donor, as it represents the best compromise between a high PLQY without introducing scattering losses.

**Energy transfer from p-O-TPE to PDI-Sil**

According to FRET theory, the energy transfer efficiency, $E$, strongly depends on the physical separation between the donor and acceptor molecules with an inverse 6\textsuperscript{th}-power law.\textsuperscript{44} Therefore, for a fixed concentration of p-O-TPE, the average physical separation between p-O-TPE and PDI-Sil is expected to be reduced by increasing the concentration of PDI-Sil, which will, in theory, lead to a more efficient FRET process. To experimentally investigate the effect of varying PDI-Sil concentration on the FRET efficiency, a series of small LSC samples (2 cm × 2 cm × 0.3 cm) containing different p-O-TPE:PDI-Sil concentration ratios (by wt\%) were fabricated. Figure 4a shows the emission spectra of the resulting p-O-TPE-PDI-Sil-dU(600) samples recorded in the front-face configuration upon excitation at 370 nm; at this excitation wavelength light absorption is expected to occur primarily by p-O-TPE (Figure 2).
Figure 4. Optical properties of dU(600) ureasils (2 cm × 2 cm × 0.3 cm) doped with p-O-TPE and/or PDI-Sil. (a) Front-face and (b) edge emission spectra (λ_ex = 370 nm) of p-O-TPE-PDI-Sil-dU(600) samples with various concentration ratios between p-O-TPE and PDI-Sil. (c) The enhancement in PDI-Sil emission for p-O-TPE-PDI-Sil-dU(600) as a function of the concentration ratio (by wt%) between p-O-TPE and PDI-Sil in arbitrary units.

In the mixed samples, the PDI-Sil emission intensity increases steadily with concentration and is accompanied by a decrease in the p-O-TPE emission, which suggests the occurrence of FRET (of increasing efficiency) between the two lumophores. In addition, the characteristic excitation features of p-O-TPE are present in excitation spectra (Figure S3, ESI) selectively detected for PDI-Sil emission (λ_em = 650 nm), which provides further evidence for the occurrence of FRET. However, PDI-Sil itself can also be moderately excited at 370 nm as the tail of its absorption band lies in this region (Figure 2). Therefore, to determine the actual increase in acceptor emission due to FRET, the emission spectrum of PDI-Sil in the absence of p-O-TPE was investigated. A set of control samples doped with only PDI-Sil (PDI-Sil-dU(600)) at the same wt% were fabricated and their emission spectra were collected at λ_ex = 370 nm (Figure S4, ESI). These spectra were then used to estimate the emission enhancement due to FRET at different D-A concentration ratios based on integrated photon counts (see SI for calculation details). For a p-O-TPE:PDI-Sil concentration ratio up to 1:1, the increase in the PDI-Sil concentration leads to significant enhancement in the emission of PDI-Sil as a result of increasing FRET (Figure 4c). However, a further increase in the PDI-Sil concentration does not lead to additional enhancement in its intensity, despite the continued quenching of p-O-TPE emission (Figure 4a). It is plausible
that, despite the improved spatial isolation expected through grafting, PDI-Sil molecules begin to cluster in the siliceous nanodomains at concentrations higher than 0.005 wt% (the PDI-Sil concentration at which the donor-acceptor concentration ratio is 1:1). This may induce π-π stacking interactions between the PDI-Sil molecules, which is also detectable in the normalized emission spectra of PDI-Sil-dU(600) (Figure S7, ESI), as indicated by the small red-shift in the emission spectrum. As a result, the energy transferred from p-O-TPE to PDI-Sil may subsequently be lost through non-radiative relaxation, decreasing the efficiency. It is also noticeable that, at the concentration ratio of 1:1, the increase in PDI-Sil emission due to the FRET process is greater than the reduction in p-O-TPE emission in number of photons calculated by integrating the emission spectra (Figure S4, ESI). This suggests that the excitation energy that would have been lost due to non-radiative relaxation in p-O-TPE is instead transferred to PDI-Sil via FRET and re-emitted, effectively increasing the PLQY of p-O-TPE from 46% to 67%, which provides further advantages for boosting the optical efficiencies of our LSC system.

In a working LSC device, the photons concentrated at the edge of the LSC travel through a much longer distance than those escaping from the surface, resulting in a significantly higher number of reabsorption events. This is noticeable in the emission spectra detected at the edge of the samples (Figure 4b), where the quenching of p-O-TPE emission occurs much more rapidly due to additional radiative reabsorption events by PDI-Sil molecules along the long optical pathway to the edge, leading to the depletion of the p-O-TPE emission at concentration ratios higher than 1:1. In contrast, the relatively slower quenching of p-O-TPE emission detected at the front face of the slab (Figure 4a) is mostly due to the non-radiative FRET process from p-O-TPE to PDI-Sil. More importantly, as the p-O-TPE:PDI-Sil concentration ratio increases from 1:0.1 to 1:10, the emission from PDI-Sil undergoes significant spectral distortions and red-shifts (Figure 4b) due to the increased reabsorption effects of the edge emission, leading to greater losses of the PDI-Sil emission despite the increasing FRET efficiency. It was calculated that the LSC with
a concentration ratio of 1:1 emits the highest number of photons at the edge (Figure S8, ESI), as a result of a balance between the increasing FRET efficiency and the growing reabsorption losses.

**Optical efficiencies of the LSCs**

Based on the results above, p-O-TPE-PDI-Sil-dU(600) with a concentration ratio of 1:1, containing 0.005 wt% of both p-O-TPE and PDI-Sil, was considered as the most promising candidate for a working LSC with a larger geometry, since overall it exhibited the highest FRET efficiency without introducing excessive scattering losses, non-radiative relaxation and reabsorption at the edge of the slab. To evaluate the optical efficiency of this donor-acceptor system, a set of larger doped LSCs (4.5 cm × 4.5 cm × 0.3 cm) based on the dU(600) waveguide, containing: (1) both p-O-TPE and PDI-Sil (p-O-TPE-PDI-Sil-dU(600)) (2) only p-O-TPE (p-O-TPE-dU(600)) and (3) only PDI-Sil (PDI-Sil-dU(600)) were fabricated (Figure 5). All samples had the same concentrations of p-O-TPE (0.005 wt%) and/or PDI-Sil (0.005 wt%).

One of the key parameters to characterize the performance of LSCs is the internal photon efficiency (\(\eta_{int}\))\textsuperscript{49,52,53}, defined as the ratio of the number of photons emitted from the edges to those absorbed by the LSC (Equation 2), which quantifies the quality of the light-guiding process irrespective of the lumophore absorption range. Experimental \(\eta_{int}\) values were determined by illuminating the top face of the planar LSCs using a solar simulator and measuring the edge output using a spectroradiometer-integrating sphere system (see Experimental section for further details). To achieve a high \(\eta_{int}\), the lumophore needs to have a large Stokes shift to minimize reabsorption losses and a high PLQY to reduce non-radiative relaxation pathways.\textsuperscript{54} In addition, scattering losses and internal emission trapping of the lumophore emission due to the waveguide material should be minimized.\textsuperscript{54} The obtained \(\eta_{int}\) values are summarized in Table 1.
Figure 5. Photographs of p-O-TPE-dU(600) (left), p-O-TPE-PDI-Sil-dU(600) (middle) and PDI-Sil-dU(600) (right) under daylight (top) and UV irradiation (365 nm). Each sample contains 0.005 wt% of p-O-TPE and/or 0.005 wt% of PDI-Sil.

Table 1. Internal ($\eta_{\text{int}}$) and external ($\eta_{\text{ext}}$) photon efficiencies of p-O-TPE-dU(600), p-O-TPE-PDI-Sil-dU(600) and PDI-Sil-dU(600), determined over all four edges of the LSC with the illumination of full AM1.5G spectrum (250 nm – 1050 nm). The values and errors reported are the mean and standard deviation of three repeat measurements, respectively.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>$\eta_{\text{int}}$ (%)</th>
<th>$\eta_{\text{ext}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-O-TPE-dU(600)</td>
<td>8.9 ± 0.4</td>
<td>1.9 ± 0.1</td>
</tr>
<tr>
<td>PDI-Sil-dU(600)</td>
<td>18.0 ± 0.1</td>
<td>4.6 ± 0.1</td>
</tr>
<tr>
<td>p-O-TPE-PDI-Sil-dU(600)</td>
<td>20.0 ± 0.1</td>
<td>5.5 ± 0.1</td>
</tr>
</tbody>
</table>

As can be seen from Table 1, p-O-TPE-PDI-Sil-dU(600) demonstrates the highest $\eta_{\text{int}}$ of 20.0%, which is an improvement of 125% and 11% when compared to p-O-TPE-dU(600) and PDI-Sil-dU(600), respectively. Since comparison of $\eta_{\text{int}}$ values among the three LSC samples is independent of both the lumophore absorption and waveguide, the resulting improvement in $\eta_{\text{int}}$ of p-O-TPE-PDI-Sil-dU(600) is directly attributed to the reduced reabsorption losses through the excitation energy cascade and the improved effective PLQY of the donor p-O-TPE as a result of
the FRET process. The $\eta_{\text{int}}$ value of 20.0% of our system is comparable to recent literature values reported for LSCs calculated over the full AM1.5G spectrum (see Table S1, ESI).

Another key figure of merit for evaluating the performance of an LSC is the external photon efficiency ($\eta_{\text{ext}}$),\textsuperscript{7,53} defined as the ratio of the number of photons emitted from the edges of the LSC to that incident on top (Equation 3). Unlike $\eta_{\text{int}}$, $\eta_{\text{ext}}$ is largely dependent on the absorption range of the lumophores. For a given $\eta_{\text{int}}$, the more incident photons the LSC absorbs, the higher the resulting $\eta_{\text{ext}}$ will be. As can be seen from Table 1, p-O-TPE-PDI-Sil-dU(600) again exhibits the highest $\eta_{\text{ext}}$ value of 5.5%, exceeding those of the individual p-O-TPE-dU(600) and PDI-Sil-dU(600) LSCs. The greater improvement in $\eta_{\text{ext}}$ compared to $\eta_{\text{int}}$ is believed to be due to the additional benefit from the extended absorption range provided by the two-lumophore system (Figure S9, ESI).

4. Conclusions

In summary, we have demonstrated a viable dual-lumophore system for LSCs based on FRET from p-O-TPE, an AIE conjugated polymer donor, to a red-emitting molecular acceptor (PDI-Sil), incorporated in a di-ureasil lightguide. The di-ureasil host was shown to effectively induce AIE from p-O-TPE, although at higher concentrations the formation of large polymer aggregates led to scattering losses. A p-O-TPE concentration of 0.005 wt% was shown to be the best compromise between PLQY enhancement and minimized scattering losses. To reduce the extent of aggregation and prevent ACQ, the PDI-Sil acceptor molecules were covalently grafted to the siliceous domains of the di-ureasil. The concentration of PDI-Sil relative to p-O-TPE was optimized to give the highest FRET efficiency possible without introducing non-radiative decay losses and/or significant reabsorption of the emitted photons within the lightguide. The resulting LSC based on the optimized p-O-TPE-PDI-Sil system showed improvement in its internal photon efficiency compared to the single lumophore (p-O-TPE or PDI-Sil) LSCs, which was attributed to
reduced loss of absorbed photons as a result of the FRET process. Enhancement in the external photon efficiency of the donor-acceptor LSC was also observed due to the extended solar-harvesting window provided by the complementary absorption spectra of the dual lumophore system. The results also demonstrate the importance of lumophore-waveguide interactions in determining the final LSC efficiency. Here, the di-ureasil waveguide is used to promote aggregation and thus switch-on emission from the AIE-donor, while simultaneously covalent grafting of the acceptor reduces ACQ. This study therefore demonstrates that the bottom-up design of integrated lumophore-waveguide materials is a viable strategy to overcome the intrinsic optical losses of LSCs and to boost their solar-harvesting performance.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information file is available free of charge on the ACS Publication website at DOI: XX.XXX/XX

Photoluminescence properties of dU(600) lightguides, AIE behavior of p-O-TPE in THF/EtOH solution, absorption spectra of large LSCs and literature comparison of LSC efficiencies.

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Notes

The authors declare no competing financial interests

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Electronic Supporting Information

Luminescent Solar Concentrators Based on Energy Transfer from an Aggregation-Induced Emitter Conjugated Polymer

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1. Photoluminescence properties of dU(600) waveguides
Figure S1. (a) Photoluminescence excitation ($\lambda_{em} = 360$ nm) and (b) emission spectrum ($\lambda_{ex} = 350$ nm) of dU(600) waveguides.

2. Aggregation-induced emission (AIE) behaviour of p-O-TPE in THF/EtOH system

Figure S2. (a) Emission spectra ($\lambda_{ex} = 373$ nm) of p-O-TPE in THF/EtOH solutions of varying EtOH concentration. (b) Variation of peak intensity of p-O-TPE emission ($\lambda_{ex} = 373$ nm) in THF/EtOH (black) and CHCl$_3$/EtOH (red)\(^1\) with varying EtOH concentration. Inset: variation of peak position of p-O-TPE emission in THF/EtOH.
3. Steady-state photoluminescence studies of p-O-TPE-PDI-Sil energy transfer in dU(600) host

3.1 Excitation spectra

![Normalized excitation spectra](image)

**Figure S3.** (a)-(e) Normalized excitation spectra ($\lambda_{em} = 650$ nm) of p-O-TPE-dU(600) (solid black), p-O-TPE-PDI-Sil-dU(600) (solid coloured) and PDI-Sil-dU(600) (dash coloured) with varying concentration ratios between p-O-TPE and PDI-Sil. A concentration ratio of 1 : 1 represents 0.005 wt% of p-O-TPE and 0.005 wt% of PDI-Sil.
3.2 Emission spectra

The enhancement in PDI-Sil emission as a result of FRET is calculated by comparing the PDI-Sil emission in p-O-TPE-PDI-Sil-dU(600) and PDI-Sil-dU(600) (Figure S4). Firstly, the p-O-TPE emission in p-O-TPE-dU(600) is normalized by the peak intensity of p-O-TPE emission in p-O-TPE-dU(600) (Figure S5). Subsequently, it is subtracted from the emission of p-O-TPE-PDI-Sil-dU(600) to get the emission of PDI-Sil in p-O-TPE-PDI-Sil-dU(600) and compared to the emission of PDI-Sil in PDI-Sil-dU(600) (Figure S6). The difference in integrated photon counts between the PDI-Sil emission in p-O-TPE-PDI-Sil-dU(600) and PDI-Sil-dU(600) corresponds to the increase in PDI-Sil emission due to FRET from p-O-TPE.

![Emission spectra](image)

**Figure S4.** (a)-(e) Emission spectra ($\lambda_{em} = 370$ nm) of p-O-TPE-dU(600) (solid black), p-O-TPE-PDI-Sil-dU(600) (solid coloured) and PDI-Sil-dU(600) (dash coloured) with varying concentration ratios between p-O-TPE and PDI-Sil. A concentration ratio of 1 : 1 represents 0.005 wt% of p-O-TPE and 0.005 wt% of PDI-Sil.
Figure S5. (a)-(e) Emission spectra ($\lambda_{em} = 370$ nm) of p-O-TPE-dU(600) (solid black, normalized by the peak intensity of p-O-TPE emission in p-O-TPE-PDI-Sil-dU(600)), p-O-TPE-PDI-Sil-dU(600) (solid coloured) and PDI-Sil-dU(600) (dash coloured) with varying concentration ratios between p-O-TPE and PDI-Sil. A concentration ratio of 1 : 1 represents 0.005 wt% of p-O-TPE and 0.005 wt% of PDI-Sil.
Figure S6. (a)-(e) Emission spectra ($\lambda_{em} = 370$ nm) of PDI-Sil in p-O-TPE-PDI-Sil-dU(600) (solid) and PDI-Sil-dU(600) (dash) with varying concentration ratios between p-O-TPE and PDI-Sil. A concentration ratio of 1 : 1 represents 0.005 wt% of p-O-TPE and 0.005 wt% of PDI-Sil.

Figure S7. Optical properties of PDI-Sil-dU(600) ureasils. (a) Photograph of PDI-Sil-dU(600) samples doped with varying concentration of PDI-Sil under UV illumination (365 nm). The value above each sample represents the concentration (wt%) of PDI-Sil in dU(600). (b) Normalized emission spectra ($\lambda_{ex} = 530$ nm) of PDI-Sil-dU(600) samples with varying concentrations of PDI-Sil.
3.3 Integrated photon counts of edge emission

![Graph showing integrated photon counts of edge emission as a function of p-O-TPE : PDI-Sil concentration ratio.]

**Figure S8.** Number of photons emitted from the edge of p-O-TPE-PDI-Sil-dU(600) samples as a function of p-O-TPE : PDI-Sil concentration ratio in arbitrary units.

4. Absorption spectra of large LSCs

![Graph showing UV/Vis absorption spectra of p-O-TPE-dU(600), PDI-Sil-dU(600), and p-O-TPE-PDI-Sil-dU(600).]

**Figure S9.** UV/Vis absorption spectra of the p-O-TPE-dU(600), PDI-Sil-dU(600) and p-O-TPE-PDI-Sil-dU(600).
5. Literature comparison of LSC efficiencies

Table S1. Performance metrics of the luminescent solar concentrator of this work in comparison to that of the recent literature.

<table>
<thead>
<tr>
<th>Type</th>
<th>Dimension</th>
<th>Light Source</th>
<th>$\eta_{int}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>4.5 cm × 4.5 cm × 0.3 cm</td>
<td>AM1.5G Solar simulator</td>
<td>20.0%</td>
</tr>
<tr>
<td>CdSe/ZnS core/shell-Aleca Fluor 546 dye$^2$</td>
<td>4 cm × 4 cm × 0.27 cm</td>
<td>AM1.5G Solar simulator</td>
<td>19.8%</td>
</tr>
<tr>
<td>Silica-coated CdSe/CdZnS1-1 core/alloyed shell$^3$</td>
<td>10 cm × 10 cm × 0.16 cm</td>
<td>Sunlight</td>
<td>21.0%</td>
</tr>
<tr>
<td>Perovskite nanoplatelets$^4$</td>
<td>10 cm × 10 cm × 0.2 cm</td>
<td>Sunlight</td>
<td>26.0%</td>
</tr>
<tr>
<td>PbS/CdS core/shell$^5$</td>
<td>10 cm × 10 cm × 0.2 cm</td>
<td>Solar simulator</td>
<td>4.5%</td>
</tr>
<tr>
<td>CulInSeS2In/ZnS core/shell$^6$</td>
<td>10 cm × 10 cm × 0.3 cm</td>
<td>Solar simulator</td>
<td>16.7%</td>
</tr>
<tr>
<td>Silicon quantum dots$^7$</td>
<td>12 cm × 12 cm × 0.26 cm</td>
<td>Solar simulator</td>
<td>30%</td>
</tr>
<tr>
<td>CdSe/CdS core/shell$^8$</td>
<td>21.5 cm × 1.3 cm × 0.5 cm</td>
<td>Solar simulator</td>
<td>10.2%</td>
</tr>
</tbody>
</table>
6. References


