Author/s:
Banal, JL;Soleimaninejad, H;Jradi, FM;Liu, M;White, JM;Blakers, AW;Cooper, MW;Jones, DJ;Ghiggino, KP;Marder, SR;Smith, TA;Wong, WWH

Title:
Energy Migration in Organic Solar Concentrators with a Molecularly Insulated Perylene Diimide

Date:
2016-06-23

Citation:
Banal, J. L., Soleimaninejad, H., Jradi, F. M., Liu, M., White, J. M., Blakers, A. W., Cooper, M. W., Jones, D. J., Ghiggino, K. P., Marder, S. R., Smith, T. A. & Wong, W. W. H. (2016). Energy Migration in Organic Solar Concentrators with a Molecularly Insulated Perylene Diimide. Journal of Physical Chemistry C, 120 (24), pp.12952-12958. https://doi.org/10.1021/acs.jpcc.6b04479.

Persistent Link:
https://hdl.handle.net/11343/220173

Energy Migration in Organic Solar Concentrators with a Molecularly Insulated Perylene Diimide

James L. Banal,[1] Hamid Soleimaninejad,[1] Fadi M. Jradi,[2] Maoyuan Liu,[1] Jonathan M. White,[1] Andrew W. Blakers,[3] Matthew W. Cooper,[2] David J. Jones,[1] Kenneth P. Ghiggino,[1]* Seth R. Marder,[2] Trevor A. Smith,[1] and Wallace W.H. Wong[1]*

[1] School of Chemistry, University of Melbourne, Parkville 3010 Australia

[2] School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, USA

[3] Centre for Sustainable Energy Systems, Australian National University, Canberra, ACT, Australia

Abstract

Maintaining high incident light absorption while minimizing luminescence reabsorption is a key challenge for organic luminescent solar concentrators (LSCs). Energy migration and trapping using light harvesting donors and a low energy highly emitting acceptor is one strategy to reduce the reabsorption issue. However, concentration quenching and the potential formation of quenching aggregates is a limiting factor in realizing efficient devices. We describe the synthesis of a novel molecularly insulated perylene diimide that can resist luminescence quenching at concentrations in excess of 50 mM. Photophysical measurements show the insulated perylene diimide has an excitation energy migration diffusion length of 230 ± 10 Å at 60 mM in poly (methyl methacrylate). LSC devices using a mixture of the insulated perylene diimide light absorber and perylene red (LR305) as the low energy trap emitter, exhibit reduced reabsorption and a better current output than LR305 only devices. The results demonstrate that appropriately designed organic molecule dyes can potentially meet the stringent requirements required for efficient LSCs.

Stationary light concentration without external cooling can be realized using luminescent solar concentrators (LSCs), making these devices attractive for building integrated photovoltaic devices. A typical LSC consists of large sheets of plastic or glass containing luminescent molecules that absorb the solar spectrum and then re-emit the absorbed energy into a waveguide mode that directs the luminescence to the thin edges of the concentrator. Edge-mounted solar cells can then harvest the concentrated luminescence for photoelectric conversion. Reabsorption of the emitted light in the waveguide limits the achievable light concentration contributing to parasitic losses such as re-emission into the escape cone or non-unity fluorescence quantum efficiency due to competing non-radiative processes. Separation of both the energy of the peak maxima of absorption and emission (the Stokes shift) and tail absorption of the chromophores in an LSC is crucial in reducing reabsorption.[1, 2]

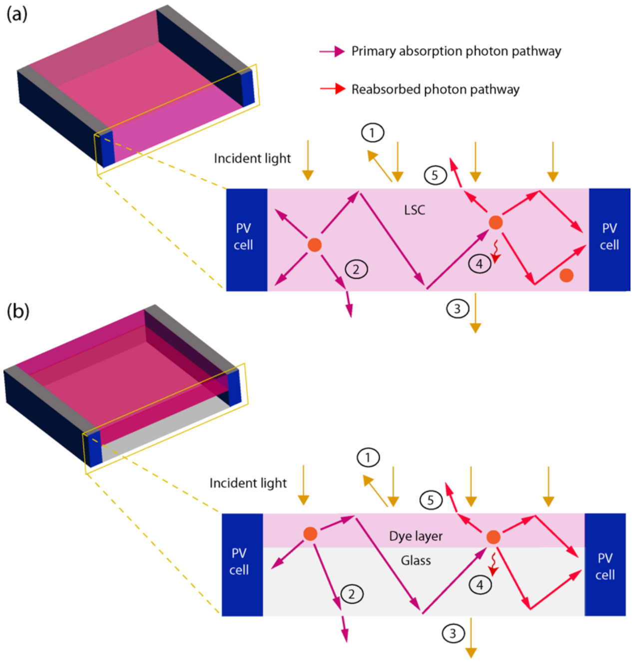

Figure 1. Common embodiments of a luminescent solar concentrator. (a) bulk-doped LSC: first developed LSC configuration wherein the light-emitting chromophores are embedded in a polymeric waveguide. (b) Thin-film LSC: a variation of the first configuration wherein a dye layer is deposited on the surface of an index-matched waveguide (typically glass). Predominant loss mechanisms can reduce the light harvesting efficiency of an LSC regardless of the configuration: (1) surface reflectivity losses, (2) escape cone losses, (3) transmission losses, and reabsorption leading to non-radiative decay (4) or re-emission to an escape cone (5). Scattering losses due to imperfections in the polymer waveguide or large aggregates can exacerbate both reabsorption losses and escape cone losses.

Organic solar concentrators that use diluted organic chromophores in inert host matrices are lagging behind their inorganic counterparts due to their small Stokes shifts.[3] A key advantage of organic chromophores over inorganic materials is their solubility in inexpensive host matrices or waveguides, such as poly(methyl methacrylate) (PMMA) or glass, without any complicated processing and the ability to fine tune their properties by simple molecular engineering approaches. This is particularly important for thin-film LSCs where the concentration required to achieve total light absorption over the wavelength range of the chromophore can be high (Fig. 1).

Modification of dyes to achieve a large Stokes shift has achieved only limited success for LSC applications. In some cases, increasing the Stokes shift of the dye has led to a decreased quantum yield and there often remains the long tail absorption of the dye.[4] Energy transfer can also be an effective strategy to induce an apparently large Stokes shift. A number of energy transfer strategies, however, have previously been used to increase the absorption range of LSCs.[5-8] Olson et al. first proposed the use of donor energy migration (Förster energy transfer between similar chromophores) to low concentration traps/acceptors (or Förster energy transfer between a donor and acceptor) to reduce reabsorption losses.[9] As long as the emission energy of the acceptor is separated from the absorption of the donor, reabsorption in an organic solar concentrator is expected to be low.[1] This migration-trapping strategy necessitates a high concentration of donors for diffusive energy migration and efficient trapping.

Most current organic dyes used in LSCs suffer from severe concentration quenching, which hampers the use of this strategy. While the above LSC strategy was proposed three decades ago, it was first demonstrated by Currie et al. that such an approach was feasible,[10] and more recently by Guttierez et al. using conjugated polymers.[11] The fluorescent donor-acceptor pair selected by Currie et al., rubrene/DCJTB, still exhibited significant reabsorption losses even though the trap

(DCJTB dye) concentration was much less than the donor concentration (rubrene). This is mainly because the absorption maxima of rubrene and DCJTB are almost identical and aggravated by significant reabsorption by the tail absorption of rubrene. Recently, we have successfully demonstrated that mere separation of the absorption and emission of both the donor and trap can lead to the reduction of reabsorption losses[12] without requiring the use of triplet traps[10] but at the cost of absorption mismatch between the absorption maximum of the dye and peak photon flux of the solar spectrum. Ideal dyes for migration-trapping should not only be resistant to quenching at the high concentrations required for energy migration but should also have an absorption maximum at the peak solar flux. An elegant approach employed by Guttierez et al., circumvents this problem by using two downconverting conjugated polymers that harvest light at the peak solar flux, yielding effective energy transfer through Förster and electron exchange mechanisms[11] but requires the use of an expensive high refractive index waveguide to match the refractive index of the polymer thin film, which is similar to previous reports on thermally evaporated thin films of molecular materials.[10, 13] Studies on the energy migration approach using molecular materials in luminescent solar concentrators embodying the migration-trapping approach and harvesting the peak flux region of the solar spectrum would be of interest.

Perylene diimides have properties that could make them ideal dyes for organic solar concentrators, in some cases they have high fluorescence quantum yields, excellent spectral matching with the peak photon flux of the solar spectrum, and good photostability.[14] Their use in organic solar concentrators is, however, limited by their small Stokes shift, which leads to significant reabsorption. In addition, perylene diimides are also known to form aggregates at high concentrations, which leads to substantial quenching of fluorescence and therefore has significant implications for thin-film organic solar concentrators.[15] Formation of H-aggregates or excited state aggregates are detrimental to the fluorescence efficiency of perylene diimides.[16] We suggest that perylene diimides can be used as light-harvesting donors in the migration-trapping strategy for organic solar concentrators with proper design of bulky substituents to reduce concentration quenching. The small Stokes shift and high quantum yields of perylene diimides are ideal photophysical properties for efficient energy migration according to the Förster dipole-dipole theory for energy transfer.[17] Perylene diimides are known to form quenching excimers that can quench excited states.[15] Energy trapping to excimers can compete with energy trapping to the desired emissive acceptors[18] leading to a significant decrease in the overall fluorescence efficiency of the system. Here, we describe a strategy to achieve efficient energy migration using perylene diimides with rigid bulky substituents to suppress aggregation, as light harvesting donors to bay-substituted tetraphenoxyperylene diimides, Lumogen® F Red 305 (also known as perylene red, herein abbreviated as LR305), acceptors. By developing the energy migration strategy with this modified perylene diimide donor-acceptor pair, we demonstrate for the first time in a simple two-dye system that a significant reduction in reabsorption can be achieved without sacrificing overall light absorption for state-of-the-art organic dyes for LSCs

There are several strategies to increase the bulkiness of perylene diimides with bay substitution being most commonly used to avoid formation of quenching aggregates.[19] Bay substitutions of perylene diimides, however, can also induce a significant bathochromic shift in the absorption spectrum. For the energy migration strategy to be effective, adequate separation between the absorption of the perylene diimide donor and the emission of LR305 is necessary to avoid reabsorption, which eliminates bay substitution with heteroatom substituents such as the aryloxy group (present in LR305) as a viable strategy. Alternatively, molecular insulation[20] can be introduced on the imide region where electronic effects introduced by bulky substituents are negligible.[21] Fig. 2a shows the structure of perylene diimide **1** (Supplementary Note 1).

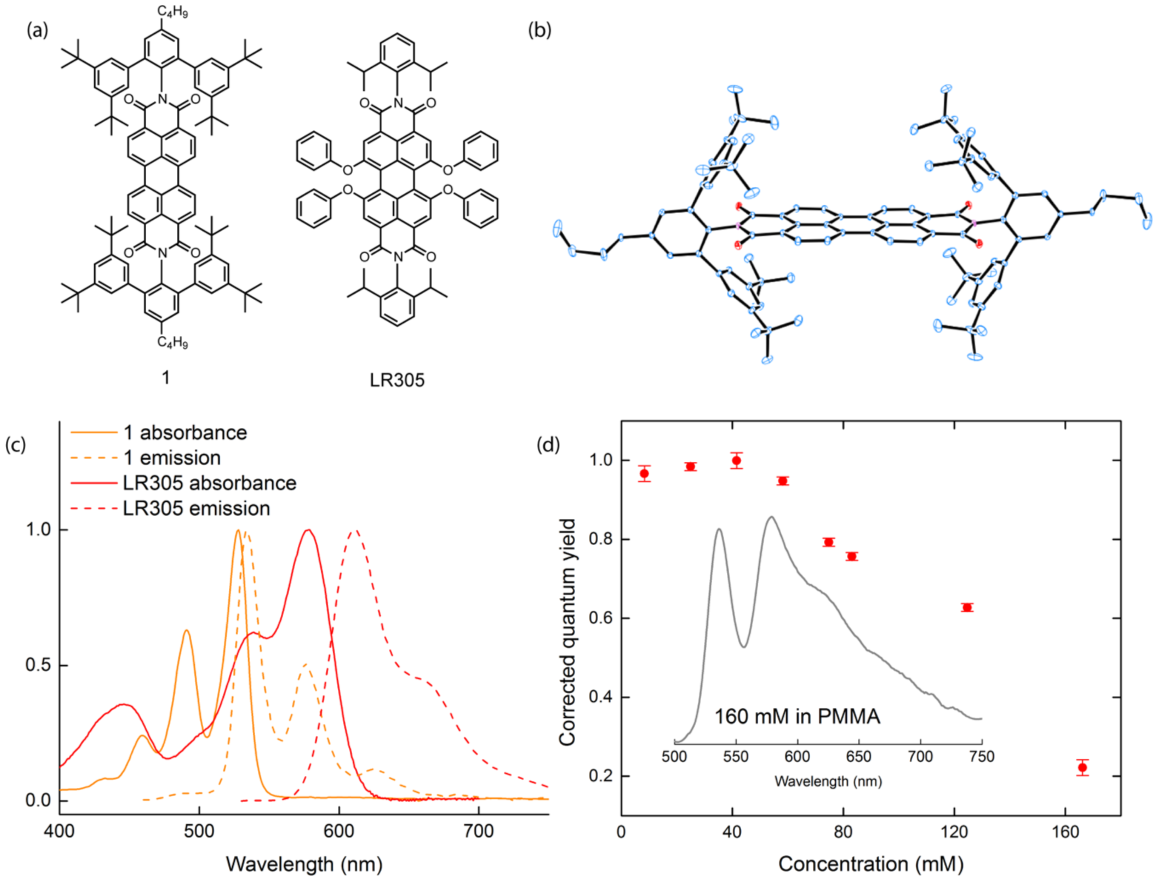

Figure 2. Molecularly insulated perylene diimide. (a) Chemical structures for **1** and LR305. (b) Crystal structure of **1**. (c) Comparison of the normalized absorption and emission spectra of **1** and LR305 in chloroform. (d) Fluorescence quantum yield concentration dependence for **1** in PMMA as host. Samples were excited at 480 nm. Inset shows the loss of vibronic structure in the emission due to the possible formation of excited complexes at the highest concentration studied.

The crystal structure of **1** (Fig. 2b) shows that the di-*tert*-butyl phenyl groups form a dihedral angle of 85° relative to the perylene plane and extending over the core, which served to prevent the close approach of other perylene molecules in the solid-state. The absorption spectrum of **1** is similar to the absorption spectrum of other perylene diimides indicating that this substitution strategy does not perturb the electronic properties of the perylene diimide that could lead to undesired bathochromic shifts (Fig. 2c). The calculated Förster critical radius (R_0) of **1** for energy migration, calculated from UV-Vis absorption and photoluminescence data,[22] is 52 Å. This corresponds to an average concentration of 4.3 mM for dye **1** in PMMA. The clear separation of the absorption of **1** and emission of LR305 demonstrates ideal photophysical properties of the donor-acceptor pair for energy transfer in organic solar concentrators in addition to the large R_0 (70 Å) due to the excellent overlap between the absorption spectrum of LR305 and emission of **1**. The fluorescence quantum yields of **1** at different concentrations in PMMA are shown in Fig. 2d. The quantum yield does not decrease until about 60 mM in PMMA. At this concentration, with the separation of molecules much closer than R_0, the efficiency of energy migration according to Förster theory is close to unity. There is a loss of vibronic structure in the emission at a concentration of 170 mM suggestive of the possible formation of an excited state complex, which occurs at a significantly higher concentration in contrast to unprotected perylene diimides as shown by Haines et al. (~4 mM in PMMA).[15] The significant reduction of quantum yield at 170 mM could be due to the combined contribution of reabsorption and fluorescence quenching by an excited state complex. Further spectroscopic investigations are needed to properly identify the contribution of the excited state complex to the diminution of quantum yield.

Understanding the dynamics of energy migration for disordered systems is crucial for optimizing the transport properties of the donors to maximize the migration-trapping strategy. Time-resolved fluorescence anisotropy is an experimental observable for energy migration in disordered chromophores in condensed systems. In the absence of rotational diffusion of chromophores, fluorescence depolarization or loss of initial fluorescence anisotropy, results from the randomization of the initially photoselected emission transition dipole orientations through Förster-mediated energy migration. The dynamic fluorescence anisotropy *r(t)* is defined by Eq. 1.

$$r(t)=\frac{I_{||}(t) - GI_{\perp}(t)}{I_{||}(t) + 2GI_{\perp}(t)} \qquad (1)$$

where *G* is a correction factor accounting for the polarization bias of the detection system, and $I_{||}(t)$ and $I_{\perp}(t)$ are the time-dependent fluorescence intensities measured through an emission polarization analyzer oriented parallel and perpendicular to the polarization of the excitation laser pulses respectively. Energy migration in disordered media can be described by a Green's function, $G^{s}(t)$, which is essentially a survival probability of an excitation over time[17]. Gochanour et al. developed a theoretical treatment of energy migration using an infinite order diagrammatic series expansion of the Green's function (colloquially called GAF theory).[17] An analytical form of $G^{s}(t)$ for energy migration was developed earlier by Huber et al[23]. (herein termed as Huber theory) using configuration averaging (Eq. 3), which has been shown to be indistinguishable to GAF theory by Knoester and Van Himbergen[24] for short and moderate time scales. Following Baumann and Fayer,[25] the fluorescence anisotropy *r(t)* can be described by the Green's function $G^{s}(t)$ defined by Huber theory as,

$$r(t)= r_0G^{s}(t) + r_{\infty} \qquad (2)$$

$$\ln G^{s}(t)=-C_D\,\lambda^{\frac{1}{2}}\,\Gamma\left(\frac{1}{2}\right)\left(\frac{t}{\tau}\right)^{\frac{1}{2}} \qquad (3)$$

$$C_D = \frac{4\pi R_0^3}{3}\rho \qquad (4)$$

where r_0 is the initial anisotropy, r_∞ is the residual anisotropy, C_D is the dimensionless donor concentration, λ is a scaling factor which has a value of 2 for energy migration, $\Gamma(1/2)$ is the incomplete gamma function ($\sqrt{\pi}$), τ is the donor fluorescence lifetime (2.8 ± 0.4 ns for **1** across the entire concentration range for the anisotropy measurement), γ is a correction factor for static averaging of the orientation factor (0.845), R_0 is the critical Förster radius for energy migration, and ρ is the dimensionless chromophore density. Fig. 3a depicts the fluorescence anisotropy decay of **1** at different concentrations in PMMA. The concentration range was chosen to avoid the effects of concentration quenching (Fig. 2d) and minimize reabsorption in optically thin films, which can lead to erroneous depolarization decays that are difficult to compare with theory. Increasing the concentration of **1** in PMMA leads to faster emission depolarization, which is a clear evidence for energy migration. The Green's function was found to well describe the anisotropy decays upon global fitting of the decay data of **1** at different concentrations in PMMA using Eq. 2-4 with only R_0 as a shared free parameter and r_∞ as an individual free parameter. The fitted R_0 gave a value of 52 Å, which is the same as the calculated R_0 from the spectral overlap integral and Förster theory. Given the close agreement between experiment and theory, it is possible to infer the characteristic transport properties of energy migration of **1** in PMMA given the calculated parameters in Fig. 3a. The Laplace transform of the mean square displacement $<r^2(\epsilon)>$ is given by,[17]

$$\langle r^2(\epsilon)\rangle = \frac{6}{\epsilon^2} D(0,\epsilon) \qquad (5)$$

where $D(0, \epsilon)$ is the generalized diffusion coefficient defined by GAF theory[17]. Numerical Laplace inversion of $<r^2(\epsilon)>$ using the Talbot algorithm gives the mean square displacement $<r^2(t)>$ shown in Fig. 3b. For diffusive transport at sufficiently long times, $<r^2(t)>$ increases linearly with time with a slope of $6D(0,0)$ - the long time diffusion constant. Increasing the concentration leads to a larger diffusion constant (Fig. 3b), which translates to an increase in the excitation distribution within the lifetime of **1**. A long diffusion length for energy migration L_D, given by $L_D = [D(0,0)\ \tau]^{1/2}$, is necessary for efficient transport in the migration-trapping approach. Ideally, at donor concentrations far exceeding that of the acceptor, the excitation must be efficiently transferred to a trap within the lifetime of the donor for efficient transport.

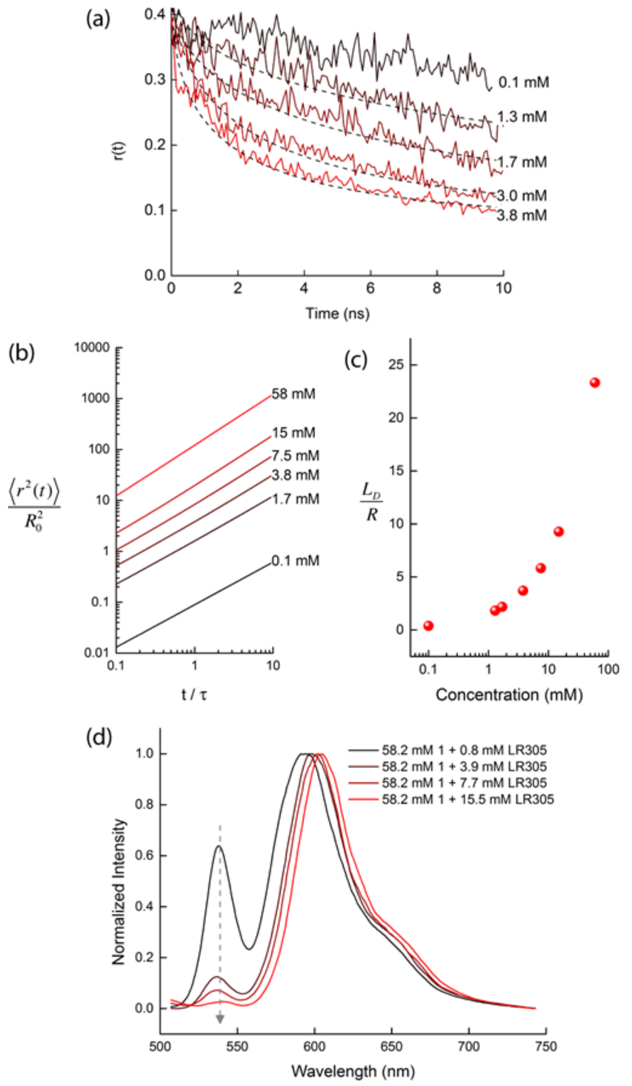

Figure 3. Energy migration and trapping of 1 in PMMA. (a) Concentration dependent fluorescence depolarization of **1** in PMMA. Broken lines are global fits based on Eq. 2-4. Samples were excited at 430 nm. (b) Mean square displacement plotted against t/τ based on experimental parameters derived from Eq. 2-4. (c) Time derivative of the mean square displacement showing the energy migration characteristics of **1** at different concentrations in PMMA. (d) Fluorescence spectra of **1** with different concentrations of LR305 in PMMA.

This condition can be attained at concentrations where L_D exceeds the average donor interchromophore separation R. It is shown in Fig. 3c that only at concentrations exceeding 4 mM is L_D is well above parity with R. At 58 mM, the calculated L_D is 230 ± 10 Å, which is significantly higher than R (30 Å) and longer than the L_D of simple perylene diimides.[18, 26] The long L_D stems from the long fluorescence lifetime of **1** comparable to that in dilute films even at high concentrations such as 58 mM (2.8 ± 0.3 ns), which is unattainable with conventional chromophores used in organic solar concentrators due to the effect of concentration quenching. In comparison, we observed concentration quenching of LR305 in PMMA at 10 mM (Supplementary Table 1) and a much lower quantum yield at 100 mM compared to previous reports.[27] Fig. 3d shows the fluorescence spectrum of a mixture of **1** and LR305 in PMMA. The donor fluorescence is mostly quenched by LR305 at 15.5 mM, which gives Φ_F of 82.0 ± 0.1% upon excitation of the donor. It was noted that only about half of the concentration of LR305 is needed to quench the emission of the donor in our case compared to the perylene orange donor studied previously.[18]

Using the measured parameters for the optimized concentrations of **1** and LR305 in Monte Carlo ray tracing simulations, the simulated optical efficiencies η_{opt}, defined as the number of photons that are collected on the edges of the LSC relative to the number of photons incident on the LSC, as a function of concentrator size show low reabsorption losses even at practical concentrator sizes (≥ 20 cm) (Fig. 4a) comparable with the conjugated polymer-mediated transfer.[11] Simple organic solar concentrators were then fabricated to demonstrate the benefit of the migration and trapping strategy. A mixture of **1** (58 mM in PMMA) and LR305 (15 mM in PMMA), and PMMA dissolved in chloroform were drop casted onto 5 cm × 5 cm × 0.1 cm glass substrates. Two silicon Sliver® cells[28] (open circuit voltage (V_{oc}) = 620 ± 0.1 mV, current density (J_{sc}) = 31.5 ± 0.3 mA cm^{-2}, fill factor (FF) = 74.3 ± 0.2 %, power conversion efficiency (PCE) = 14.5 ± 0.1%) connected in parallel were attached to the opposite edges of the organic solar concentrator. Control concentrator devices with only LR305 (1 mM in PMMA, $\Phi_F = 91.0 \pm 0.1\%$) but varying optical density were also fabricated for comparison. Fig. 4b shows the absorbance spectra of the organic solar concentrator devices. Increasing the absorbance of LR305 from 0.2 (37% absorption, 13.0 ± 1.1 μm thick film) to 0.8 (84% absorption, 54.0 ± 0.8 μm thick film) by increasing the thickness only leads to a non-linear and small increase in current density (c.f. J_{sc} of optically thin LR305 LSC is 0.44 ± 0.1 mA cm^{-2} and J_{sc} of optically dense LR305 is 0.65 mA cm^{-2}), which demonstrates the effect of reabsorption (Fig. 4c). In comparison, the J_{sc} of the organic solar concentrator with **1** and LR305, which has a peak absorbance of >2 (99% absorption, 2.0 ± 0.5 μm thick film) significantly enhances the J_{sc} to 1.02 ± 0.1 mA cm^{-2} (see Fig. 4d for statistical histogram).

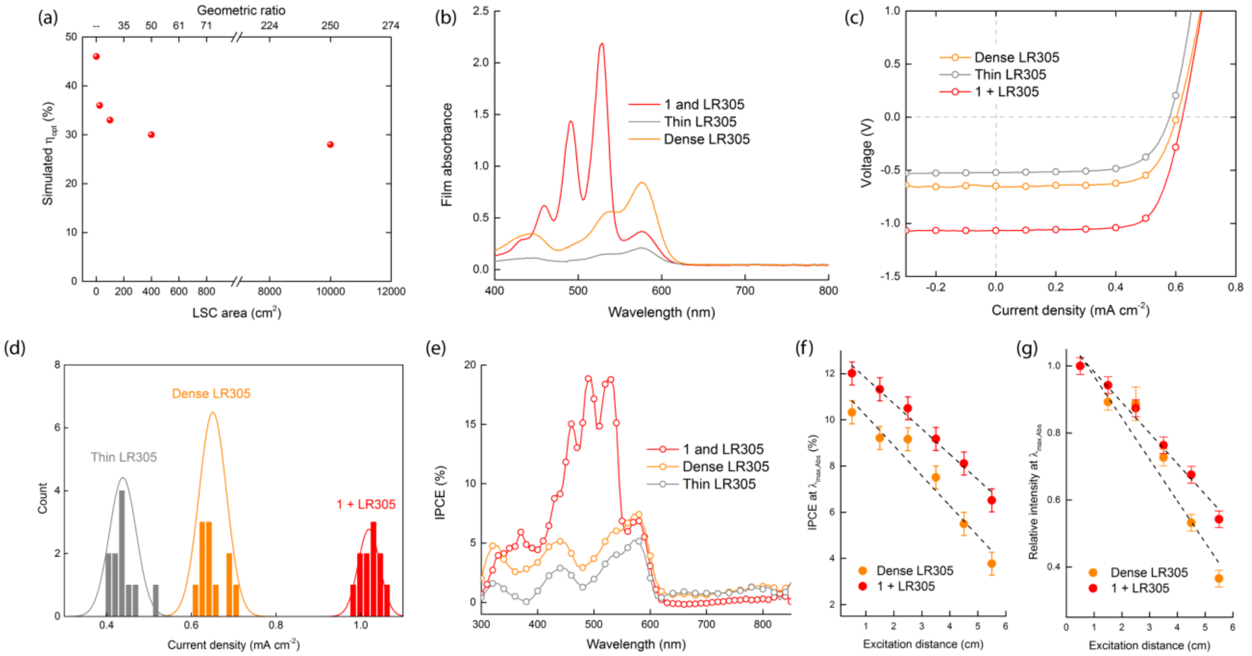

Figure 4. Characterization of organic solar concentrators. (a) Simulated optical efficiency as a function of LSC area. (b) Absorbance spectra of the organic solar concentrators. (c) Current-voltage curves of organic solar concentrators devices. (d) Histogram of current density fitted with Poisson distribution to highlight statistical significance. (e) IPCE curves of the organic solar concentrator devices. Absolute (f) and relative (g) IPCE decrease as a function of excitation distance. Broken lines are arbitrary linear fits only to show trend. Error bars are standard deviations of three independent measurements.

Table 1 summarizes the performance characteristics of each device. The lower power conversion efficiencies of the thin-film organic solar concentrators compared to previously reported bulk doped organic solar concentrators[29] is most probably due to imperfect interface between the dye layer (PMMA + chromophores) and waveguide (glass), which reduces the amount of trapped light that enters the waveguide. It is emphasized that efficiencies are to be taken as relative rather than as an absolute measure of performance. Nonetheless, based on the direct comparison between pure L305 and migration-trapping strategy based organic solar concentrators, we expect high absolute performance surpassing LR305 only devices when the migration-trapping strategy is translated into bulk doped devices[30] with further optimization. Incident photon conversion efficiency (IPCE) of the organic solar concentrator with **1** and LR305 shows that there is no contribution by scattering indicating that the current observed is solely due to trapped emission (Fig. 4e). Comparison between the excitation distance dependence of single wavelength IPCE (Fig. 4f and 4g) of the high absorbing LR305 sample and the energy transfer organic solar concentrator shows that the critical distance (i.e. the distance at which the IPCE drops to half) for the energy transfer LSC is significantly longer than the optically dense LR305 LSC concordant with the observed low reabsorption loss in the simulation. Taken all together, the improved performance of the energy transfer LSC compared to the optically dense LSC confirms that it is possible to achieve high light absorption without compromising luminescence reabsorption in contrast to conventional single dye organic solar concentrators. As the energy transfer LSC described here represents the lowest limit of the possible efficiencies of the device, the energy transfer LSC can still be optimized by reducing the thickness of the film to further minimize reabsorption. A thinner film will lead to smaller absorption of the LR305 in the energy transfer film without significant decrease in the overall light absorption of the LSC due to the very high donor concentration in the film.

Table 1. Performance characteristics of organic solar concentrator devices. Devices were measured using AM 1.5G simulated light under normal ambient conditions. P_{out} is the maximum power output of the LSC device. Devices were masked around the edges with black tape to avoid direct incidence of light to the edge solar cells. All device areas are 25 cm^2.

Device	Concentration of dyes in PMMA	Fluorescence Quantum Yield of films, Φ_F	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	P_{out} (mW cm^{-2})
Optically thin LR305	1 mM LR305	91.0 ± 0.1%	580 ±1	0.44 ±0.01	68.3 ±0.6	0.17 ±0.01
Optically dense LR305	1 mM LR305	91.0 ± 0.1%	600 ±1	0.65 ±0.01	70.5 ±0.3	0.28 ±0.01
Energy transfer dye **1** + LR305	15.5 mM LR305 58.2 mM **1**	82.0 ± 0.1%	620 ±1	1.02 ±0.01	72.4 ±0.2	0.46 ±0.01

In summary, we have demonstrated an organic solar concentrator that has low reabsorption loss by taking advantage of energy migration in highly concentrated films, which show reabsorption reduction on par with state-of-the-art organic solar concentrator devices[12] and consistent with the proposed strategy by Olson et al.[9] Molecular insulation of highly fluorescent chromophores enables a high chromophore density in PMMA necessary for diffusive energy migration previously not possible with conventional dyes used in organic solar concentrators. Energy migration dynamics of **1** in PMMA was characterized and was found to have an L_D significantly higher than any chromophores used in LSCs, which is key in achieving efficient energy migration to traps. Fabricated organic solar concentrator devices using the energy transfer approach show reduced reabsorption by keeping the absorption contribution of the acceptor at a minimum while retaining efficient trapping and re-emission of the absorbed light energy.

Compared to the system that we described previously,[12] there was no mismatch between the absorption maximum of the organic solar concentrator and the solar peak flux. The results presented here provide strong experimental evidence for the optical efficiency enhancement possible with the energy migration and trapping strategy in LSCs. Further improvements can be achieved by increasing the molecular insulation of **1** such that even higher concentrations in PMMA might be reached without resulting in any fluorescence quantum yield loss, maintaining diffusive transport, and further reducing the absorption contribution of the acceptor, which is the current limitation of the energy transfer system described here. Alternatively, optimizing energy migration through vectorial transport (e.g. using organized dye arrays and polymers) rather than random diffusion can also reduce the amount of acceptor required by reducing the average energy migration path length from donor to trap. Nevertheless, the energy migration-trapping approach we described using molecularly insulated donor chromophores can open new strategies for organic solar concentrators to be competitive with their inorganic counterparts.

ASSOCIATED CONTENT

Supporting Information. Synthetic details and characterization data, steady-state photophysical measurement details, fluorescence anisotropy measurement details and LSC characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

KPG: ghiggino@unimelb.edu.au, +613 8344 8939

WWHW: wwhwong@unimelb.edu.au, +613 9035 6154

ACKNOWLEDGMENT

This work was made possible by support from the Australian Renewable Energy Agency which funds the project grants within the Australian Centre for Advanced Photovoltaics. WWHW is supported by an Australian Research Council Future Fellowship (FT130100500). JLB acknowledges an Australian Postgraduate Award and the Eugen Singer Award from the University of Melbourne for financial support. Responsibility for the views, information, or advice herein is not accepted by the Australian Government.

REFERENCES

1. Banal, J. L.; White, J. M.; Ghiggino, K. P.; Wong, W. W. H., Concentrating Aggregation-Induced Fluorescence in Planar Waveguides: A Proof-of-Principle. *Sci. Rep.* **2014,** 4, 4635.
2. Wilson, L. R.; Rowan, B. C.; Robertson, N.; Moudam, O.; Jones, A. C.; Richards, B. S., Characterization and Reduction of Reabsorption Losses in Luminescent Solar Concentrators. *Appl. Opt.* **2010,** 49, 1651-1661.
3. Bradshaw, L. R.; Knowles, K. E.; McDowall, S.; Gamelin, D. R., Nanocrystals for Luminescent Solar Concentrators. *Nano Lett.* **2015,** 15, 1315-23.
4. Turrisi, R.; Sanguineti, A.; Sassi, M.; Savoie, B.; Takai, A.; Patriarca, G. E.; Salamone, M. M.; Ruffo, R.; Vaccaro, G.; Meinardi, F.; Marks, T. J.; Facchetti, A.; Beverina, L., Stokes Shift/Emission Efficiency Trade-off in Donor-Acceptor Perylenemonoimides for Luminescent Solar Concentrators. *J. Mater. Chem. A* **2015,** 3, 8045-8054.
5. Balaban, B.; Doshay, S.; Osborn, M.; Rodriguez, Y.; Carter, S. A., The Role of FRET in Solar Concentrator Efficiency and Color Tunability. *J. Luminescence* **2014,** 146, 256-262.
6. Bailey, S. T.; Lokey, G. E.; Hanes, M. S.; Shearer, J. D. M.; McLafferty, J. B.; Beaumont, G. T.; Baseler, T. T.; Layhue, J. M.; Broussard, D. R.; Zhang, Y.-Z.; Wittmershaus, B. P., Optimized Excitation Energy Transfer in a Three-Dye Luminescent Solar Concentrator. *Sol. Energy Mater. Sol. Cells* **2007,** 91, 67-75.
7. Swartz, B. A.; Cole, T.; Zewail, A. H., Photon Trapping and Energy Transfer in Multiple-Dye Plastic Matrices: An Efficient Solar-Energy Concentrator. *Opt. Lett.* **1977,** 1, 73-75.
8. Batchelder, J. S.; Zewail, A. H.; Cole, T., Luminescent Solar Concentrators. 2: Experimental and Theoretical Analysis of their Possible Efficiencies. *Appl. Opt.* **1981,** 20, 3733-3754.
9. Olson, R. W.; Loring, R. F.; Fayer, M. D., Luminescent Solar Concentrators and the Reabsorption Problem. *Appl. Opt.* **1981,** 20, 2934.
10. Currie, M. J.; Mapel, J. K.; Heidel, T. D.; Goffri, S.; Baldo, M. A., High-Efficiency Organic Solar Concentrators for Photovoltaics. *Science* **2008,** 321, 226-8.
11. Gutierrez, G. D.; Coropceanu, I.; Bawendi, M. G.; Swager, T. M., A Low Reabsorbing Luminescent Solar Concentrator Employing Pi-Conjugated Polymers. *Adv. Mater.* **2016,** 28, 497-501.

12. Banal, J. L.; Ghiggino, K. P.; Wong, W. W. H., Efficient Light Harvesting of a Luminescent Solar Concentrator Using Excitation Energy Transfer from an Aggregation-Induced Emitter. *Phys. Chem. Chem. Phys.* **2014,** 16, 25358-25363.

13. Giebink, N. C.; Wiederrecht, G. P.; Wasielewski, M. R., Resonance-Shifting to Circumvent Reabsorption Loss in Luminescent Solar Concentrators. *Nat. Photon.* **2011,** 5, 694-701.

14. Slooff, L. H.; Bakker, N. J.; Sommeling, P. M.; Büchtemann, A.; Wedel, A.; van Sark, W. G. J. H. M., Long-Term Optical Stability of Fluorescent Solar Concentrator Plates. *Phys. Status Solidi A* **2014,** 211, 1150-1154.

15. Haines, C.; Chen, M.; Ghiggino, K. P., The Effect of Perylene Diimide Aggregation on the Light Collection Efficiency of Luminescent Concentrators. *Sol. Energy Mater. Sol. Cells* **2012,** 105, 287-292.

16. Würthner, F.; Saha-Möller, C. R.; Fimmel, B.; Ogi, S.; Leowanawat, P.; Schmidt, D., Perylene Bisimide Dye Assemblies as Archetype Functional Supramolecular Materials. *Chem. Rev.* **2016,** 116, 962-1052.

17. Gochanour, C. R.; Andersen, H. C.; Fayer, M. D., Electronic Excited State Transport in Solution. *J. Chem. Phys.* **1979,** 70, 4254-4271.

18. Schlosser, M.; Lochbrunner, S., Exciton Migration by Ultrafast Förster Transfer in Highly Doped Matrices. *J. Phys. Chem. B* **2006,** 110, 6001-6009.

19. Lin, M.-J.; Jimenez, A. J.; Burschka, C.; Würthner, F., Bay-Substituted Perylene Bisimide Dye with an Undistorted Planar Scaffold and Outstanding Solid State Fluorescence Properties. *Chem. Commun.* **2012,** 48, 12050-12052.

20. Frampton, M. J.; Anderson, H. L., Insulated Molecular Wires. *Angew. Chem. Int. Ed.* **2007,** 46, 1028-1064.

21. Huang, C.; Barlow, S.; Marder, S. R., Perylene-3,4,9,10-tetracarboxylic Acid Diimides: Synthesis, Physical Properties, and Use in Organic Electronics. *J. Org. Chem.* **2011,** 76, 2386-2407.

22. Hildebrandt, N., How to Apply FRET: From Experimental Design to Data Analysis. In *FRET - Förster Resonance Energy Transfer*, Medintz, I.; Hildebrandt, N., Eds. Wiley-VCH: Weinheim, Germany, 2014; pp 105-163.

23. Huber, D. L.; Hamilton, D. S.; Barnett, B., Time-Dependent Effects in Fluorescent Line Narrowing. *Phys. Rev. B* **1977,** 16, 4642-4650.

24. Knoester, J.; Van Himbergen, J. E., Excitation Decay Due to Incoherent Energy Transfer: A Comparative Study by Means of an Exact Density Expansion. *J. Chem. Phys.* **1984,** 80, 4200-4203.

25. Baumann, J.; Fayer, M. D., Excitation Transfer in Disordered Two-Dimensional and Anisotropic Three-Dimensional Systems: Effects of Spatial Geometry on Time-Resolved Observables. *J. Chem. Phys.* **1986,** 85, 4087-4107.

26. Colby, K. A.; Burdett, J. J.; Frisbee, R. F.; Zhu, L.; Dillon, R. J.; Bardeen, C. J., Electronic Energy Migration on Different Time Scales: Concentration Dependence of the Time-Resolved Anisotropy and Fluorescence Quenching of Lumogen Red in Poly(methyl methacrylate). *J. Phys. Chem. A* **2010,** 114, 3471-3482.

27. Al-Kaysi, R. O.; Sang Ahn, T.; Muller, A. M.; Bardeen, C. J., The Photophysical Properties of Chromophores at High (100 mM and above) Concentrations in Polymers and as Neat Solids. *Phys. Chem. Chem. Phys.* **2006,** 8, 3453-3459.

28. Verlinden, P. J.; Blakers, A. W.; Weber, K. J.; Babaei, J.; Everett, V.; Kerr, M. J.; Stuckings, M. F.; Gordeev, D.; Stocks, M. J., Sliver® Solar Cells: A New Thin-Crystalline Silicon Photovoltaic Technology. *Sol. Energy Mater. Sol. Cells* **2006,** 90, 3422-3430.
29. Debije, M. G.; Verbunt, P. P. C., Thirty Years of Luminescent Solar Concentrator Research: Solar Energy for the Built Environment. *Adv. Energy Mater.* **2012,** 2, 12-35.
30. Desmet, L.; Ras, A. J. M.; de Boer, D. K. G.; Debije, M. G., Monocrystalline Silicon Photovoltaic Luminescent Solar Concentrator with 4.2% Power Conversion Efficiency. *Opt. Lett.* **2012,** 37, 3087-3089.