Sterically Engineered Perylene Dyes for High Efficiency Oriented Fluorophore Luminescent Solar Concentrators

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S *Supporting Information*

Luminescent solar concentrators (LSCs) collect and concentrate sunlight for use in solar power generation.[1] First proposed over 30 years ago,[1d] LSCs are simple devices, consisting of a planar waveguide coated or impregnated with a fluorophore. The fluorophore absorbs sunlight, re-emitting it into the waveguide where it travels to a device edge for conversion by photovoltaic (PV) cells. LSCs have attracted attention due to their high theoretical concentration factors, their ability to provide wavelength-to-bandgap matched photons, and because they function equally well under diffuse and direct illumination.[2] Unlike other concentrator designs, LSCs selectively harvest light in a particular spectral band (determined by the absorption range of the fluorophore) allowing other wavelengths to pass through for secondary applications such as thermal generation or interior lighting, increasing the combined-cycle efficiency. Accordingly, LSC performance is expressed in terms of the optical quantum efficiency (OQE), defined as the fraction of absorbed photons concentrated at the edge. Despite several decades of research, LSC OQEs remain too low for most practical applications and decrease rapidly with LSC size. For dyes possessing high fluorescent quantum yield (FQY), light trapping efficiency is limited primarily by waveguide escape cone (EC) losses defined by Snell's Law.[3] An approach to circumvent such losses involves orientation of the dye's emission transition moment perpendicular to the plane of the concentrator, which leads to preferential emission into guided modes.[4] Ballistic photon Monte Carlo simulations predict alignment that can reduce EC losses from about 25% to under 10% *per emission* in an air-clad waveguide with a refractive index of 1.5, depending on the degree of orientational order.[3] Since EC losses compound due to repetitive reabsorption and re-emission caused by overlap of fluorophore absorption and emission spectra, fluorophore alignment, combined with reduced self-absorption,[5] has the potential to significantly improve LSC efficiency. Here, we focus on the former approach.

Previous attempts to prepare oriented fluorophore LSCs demonstrated modest performance gains, limited by the degree of fluorophore orientational order, solubility, or FQY.[4b,6] Here we report a new family of perylenebisimide (PBI) dyes designed for oriented fluorophore LSCs which address these limitations. Incorporation into optically transparent polymerizable liquid crystal (LC) waveguides results in devices with OQE = 74% at a geometric gain $G = 10$, where G is the ratio of facial to perimeter area.

We studied a series of PBIs of the type *N,N*-bis(2,6-diisopropyl-4-octylaniline)-perylene-3,4,9,10-tetracarboximide, containing pendant orthoalkylated anilines with long alkyl tails (Chart 1). The PBI luminophore is widely used for LSC

Chart 1. Abbreviated Molecular Structure(s) of the Full Series of Flourophores Synthesized for This Study and the Complete Molecular Structures of 3 and 4[a]
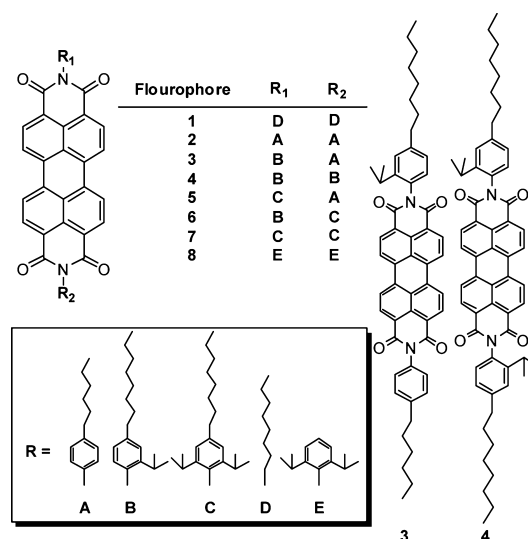
[a]It should be noted that **4** is likely a mixture of *syn-* and *anti-* isomers.

applications[7a] because it confers intense absorbance, good photostability, and near unity quantum yield; however, $\pi-\pi$ stacking in unsubstituted PBIs severely limits their solubility.[7b] Addition of bulky pendant aromatic groups orthoalkylated at aniline positions 2 and 6 (e.g., compound **8**, Chart 1) improves solubility in organic solvents;[7] however, the concomitant reduction in molecular aspect ratio causes poor alignment in LC guest–host systems (the scalar orientational order parameter of the absorption transition moment[8] of **8** in the nematic LC 4'-pentyl-4-cyanobiphenyl (5CB) is $s = 0.22$, Table 1, see also the Supporting Information).[9] Addition of long alkyl tails (compound **7**) to increase the aspect ratio raises s only

Table 1. Summary of Fluorophore Properties

fluorophore	solubility[a]	s^b	FQY[c]	sterics[d]
1	0.13	0.62	0.95	{0,0}
2	0.15	0.68	0.98	{0,0}
3	4.9	0.68	0.92	{1,0}
4	1.1	0.65	0.96	{1,1}
5	7.3	0.53	0.92	{2,0}
6	22	0.62	0.98	{1,2}
7	0.45	0.32	0.98	{2,2}
8	0.14	0.22	0.99	{2,2}

[a]Solubility in 5CB (mg/mL). [b]s is the scalar order parameter for the absorption transition moment. [c]Measured in $CHCl_3$ at 25 °C. [d]Sterics are defined as the number of orthoisopropyl groups on the pendant imide on each side of the PBI molecule.

slightly, to 0.29, insufficient for LSC applications. If the orthoisopropyl groups are removed (compound **2**), s increases sharply, to 0.68, but the solubility is again low. Hence there exists a trade-off in the use of bulky substituents with respect to solubility and alignability, a challenge commonly encountered in guest−host LC systems.[10a] To understand this result we note that, in the absence of directional chemical interactions such as H-bonding, general alignment trends in nematic LC hosts are largely determined by the geometry of the guest's excluded volume, v against rod-shaped nematogens, which for optimal alignment should be such that v is minimized when guest molecules orient parallel to the LC director.[10] A geometry v which disrupts local nematic order also affects solubility, since the free energy density of the LC host is coupled to its order parameter.[11] At the same time, for the dyes studied here, an additional solubility prerequisite is that PBI−PBI π−π stacking should be inhibited, preventing aggregate formation.[12] This suggests the optimal steric design for achieving both high solubility and alignment is a molecular architecture permitting close colinear approach between nematogens and the PBI core but preventing it for pairs of dye molecules.

To achieve this, we studied the effect of asymmetric steric substitution at the aniline in the family of compounds shown in Chart 1. The full compilation of fluorophores synthesized in this study (See Supporting Information for details) and their properties are listed in Table 1. Fluorophores **1** and **8** are commercially available. As expected,[7b] their optical properties ($\lambda_{abs,max}$, $\lambda_{em,max}$, ε, and Φ_f) are virtually identical (Table 1 and Table S1 in the SI), though their solubilities and orientational order parameters in 5CB vary widely. Focusing on the latter, we observe that increasing the number of orthoisopropyl groups {m,n} from {0,0} in **1** and **2** (where m and n are the number of orthoisopropyl groups on the first and second imides, respectively) to {1,2} in **6** results in a steady, significant increase in solubility (from ∼0.1 to 22 mg/mL) as $m + n$ increases from 0 to 3, and uniformly high order parameters. Strikingly though, addition of a fourth orthoisopropyl group in **7** to produce the {2,2} configuration results in a large decrease in both the order parameter and solubility. The values are similar to those obtained for **8** (no alignable tails). The data in Table 1 also show that addition of alkyl chains to the para position of the pendant imide results in an increase in orientational order, consistent with previous studies showing that extension of the long axis leads to higher order parameters up to a chain length of eight carbons, after which longer chains are detrimental to alignment and solubility.[13]

The above results are consistent with a model in which asymmetric substitution (about the long molecular axis of the guest) permits favorable colinear nematogen−PBI core interactions up to $m + n \leq 3$ but inhibits the same for pairs of PBI cores with $m + n > 1$ (Figure 1). Combined with long
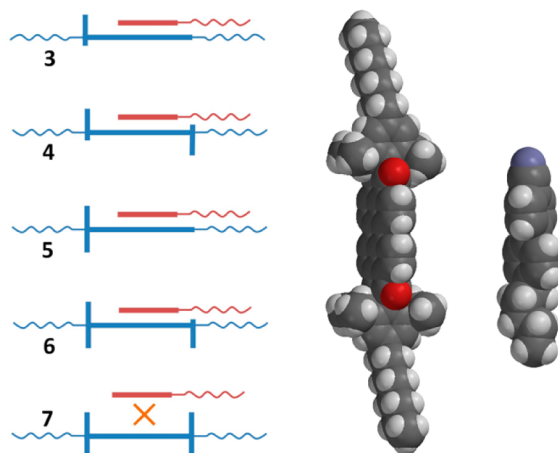

Figure 1. Schematic illustration (left) of the effect of steric placement on nematogen (red)−PBI (blue) colinear interactions in **3**−**7**. Space filling model (right) demonstrating the restricted mesogen access to the perylene core of **7**.

alkyl tails to increase the molecular aspect ratio, the asymmetric fluorophores **3**−**6** having the configurations {1,0}, {1,1}, {2,0}, and {2,1} are both highly soluble and highly oriented.

We demonstrate the effect of dye orientation on LSC performance in a device based on a representative member of this group (**4**) incorporated into the photopolymerizable LC RMM28A (Merck). **4** was selected due to its intermediate solubility, alignability, and relative synthetic ease (compared to fluorophores **3**, **5**, and **6**).[14] LSCs were fabricated as 1−5 μm thick films spin-cast onto borosilicate glass coverslips, photo-polymerized to produce uniform homeotropic alignment to the plane of the film. The order parameter for the absorption transition moment of **4** was measured to be s = 0.77 in the photopolymerized matrix, somewhat higher than in 5CB.[15] LSCs were uniformly illuminated with 485 nm monochromatic light and emission from an aperture of length l = 0.7 cm centered on one edge was collected by an integrating sphere coupled to a fluorometer. The remaining device edges were blackened. Samples measured 2.5 × 2.5 × 0.16 cm, resulting in a geometric gain G = 10. Facial absorption and edge emission spectra for a representative device are shown in Figure 2. Experimental details are presented in the Supporting Information.

After correcting for the aperture size and edge-escape cone angle (see Supporting Information for discussion), we find OQE = 74%, the highest efficiency observed so far in a LSC device and significantly exceeding the previous highest reported OQE of ∼50%.[16] The results are in good agreement with predictions from ballistic Monte Carlo simulations (predicted OQE = 70%) performed using a model based on the experimentally measured absorption and emission spectra, film refractive indices, dye order parameter, FQY, and device absorbance and dimensions.[15] For comparison, the limiting upper theoretical OQE for an LSC incorporating fluorophores with an order parameter s = 0.8 is approximately 84%, assuming unity FQY, a single escape cone loss, and a waveguide refractive
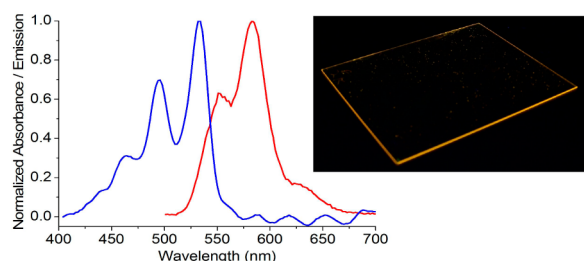
Figure 2. Normalized absorption (blue) and emission (red) spectra of **4** in photopolymerized RMM28A. Inset: photograph of an LSC device imaged under UV illumination.

index of 1.5.[3] The somewhat lower efficiency observed here can be accounted for by self-absorption resulting from the small Stokes shift, which leads to repeated escape cone losses as well as nonunity FQY. Although devices were prepared using a relatively low dye concentration (1000 ppm) to isolate the effects of alignment, attenuation of the highest energy vibronic peak in the emission spectrum shown in Figure 2 (relative to the intensity of the second and third transitions) indicates some self-absorption in these devices.[17]

In summary, a systematic analysis of the effects of molecular structure on solubility and guest−nematic host alignment in a series of perylenebisimide fluorophores was undertaken, and a model is proposed for optimal steric architecture based on asymmetric pendant anilines having long alkyl tails. Incorporation of one such fluorophore into a LSC device with homeotropic alignment resulted an optical quantum efficiency of 74%, the highest reported to date. Further efficiency improvements may be possible through the use of oriented fluorophores having larger Stoke's shifts and higher FQY. Finally, we note that the steric design principles articulated here should be applicable to a wide range of other guest−nematic host systems, including guest−host LC displays.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, *s* determination, selected spectra, device fabrication, and description of mathematical model. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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(14) It should be noted that **4** may be a mixture of the *syn-* and *anti-* isomers. Only one product was separable via chromatography and temperature-dependent NMR indicated only a single product was present.

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