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Energy Transfer in Pendant Perylene Diimide Copolymers[†]

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We report the synthesis, characterisation and polymerisation of two novel asymmetric perylene diimide acrylate monomers. The novel monomers form a sensitiser-acceptor pair capable of undergoing Förster resonance energy transfer, and were incorporated as copolymers with *tert*-butyl acrylate. The *tert*-butyl acrylate units act as spacers along the polymer chain allowing high concentrations of dye while mitigating aggregate quenching, leading to persistent fluorescence in the solid state at high concentrations of up to 0.3 M. Analysis of fluorescence kinetics showed efficient energy transfer between the optically dense sensitiser and the lower concentration acceptor luminophores within the polymer. This reduced reabsorption within the material demonstrates that the copolymer-scaffold energy transfer system has potential for use in luminescent solar concentrators.

1 Introduction

Luminescent solar concentrators (LSCs) are devices that concentrate solar energy by absorption and waveguided emission, with large potential for improving PV cost efficiency.^{1,2} A general LSC consists of a luminophore dispersed within a waveguide; direct and diffuse incident light is absorbed by the luminophore and re-emitted, with a portion of the emitted light entering waveguide modes optically coupled to PV cells.³ Due to spectral overlap between the absorption and emission bands of luminescent species in LSCs, reabsorption is one of the major loss mechanisms inhibiting commercialisation.^{4,5} Selecting a chromophore with little overlap between the absorption and emission band is the simplest way to limit reabsorption,⁶ but these spectral properties rarely occur in conjunction with a high luminescence quantum yield necessary for overall device efficiency.^{1,2,7,8} Another solution is to transfer optical excitations to a redder-emitting species which has a greatly decreased optical density across the wave-

guide modes^{9,10} by Förster resonance energy transfer (FRET).¹¹ In this way, the likelihood of reabsorption is decreased compared to the case where only one chromophore is employed.

FRET is an efficient means for spectral management: With suitable chromophores, energy can be transferred from the blue end of the visible spectrum to the red.^{10,12} The strong distance-dependence of FRET efficiency requires that the luminophores are in close proximity. This is a technical challenge in devices employing molecular chromophores, as they tend to aggregate and form quenching states as intermolecular spacing decreases.^{13–16} As such, preventing dye aggregation is of key importance for designing fluorescent organic materials which employ FRET.^{17,18}

Perylene-diimides (PDIs) have found applications in light harvesting systems, organic electronic devices and LSCs due to their range of hues from red to violet, excellent solvent stability, high degree of chemical inertness, and superior thermal stability.^{18–20} As expected for extended π -systems with a large quadrupole moment, PDIs are prone to forming excitation-quenching aggregates at high concentrations. Aggregation is greatly decreased by functionalising the diimide end-groups with bulky substituents that impede cofacial π - π interactions between the PDIs.^{20–27} Accordingly the imide substituents can be used to control solubility and decrease aggregation without impacting the photophysical properties of the PDI chromophore.²⁸ Nevertheless, imide substituted perylenes still aggregate at FRET-enabling concentrations,²⁹ and thus aggregation remains a limiting factor inhibiting efficient FRET in PDI based LSCs.

While previous research has focused on utilising the π - π interactions of perylene monomers for supramolecular assemblies that

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display exciton transport,^{30–33} the use of polymers as a spatial scaffold with controlled inter-chromophore spacing for organising dye molecules is one potential method of allowing higher PDI concentrations without aggregation. Incorporating a low concentration emitter species enables FRET and minimises reabsorption losses. The constitutional control offered by polymers allows different luminophores to be incorporated in specific ratios while being physically separated by inert spacer monomers, reducing aggregation. We report the synthesis and polymerisation of acrylate PDI monomers via conventional radical polymerisation. Specific ratios of luminophores were chosen to reduce reabsorption via FRET, while attachment to a polymer backbone reduces quenching by perylene π - π aggregation at the high concentrations required for FRET.

2 Methods

Fluorescence quantum yields were measured in solution using the comparative method of Williams *et al.*,³⁴ using Perylene Orange (PO) and Perylene Red (PR) as standards. Solid-state and solution absorption spectra were measured with a Varian Cary 4000 UV-Vis spectrophotometer. Steady-state solution fluorescence measurements were carried out on a Varian Cary Eclipse Fluorescence spectrophotometer, while the steady-state fluorescence of solid samples was recorded with an Ocean Optics HR4000 spectrometer. Solution samples were measured in a 1 cm cuvette, and solid samples were drop-cast on a 2 mm thick glass slide. Polymer thin films were prepared by solvent-assisted drop casting and were homogenous over the laser spot area. Film thickness was measured on a Veeco Dektak 150 Stylus Profilometer. Film concentration was measured using the Beer-Lambert Law, over 5 different film regions for each polymer. A Clark MXR CPA-2210 laser and OPA were used for time-correlated single photon counting (TCSPC) measurements. Polymer films were excited at 490 nm by front face illumination and imaged onto a double monochromator with a photomultiplier tube (PMT). This experimental set-up allowed time-resolved measurements of photon emission with sub-nanosecond resolution.

3 Results and discussion

3.1 Synthesis of Monomers and Polymers

PDI-acrylate monomers were prepared from bay-unsubstituted Perylene Orange (PO) and the phenolsubstituted Perylene Red (PR). This dye pair was chosen for the good spectral overlap between PO emission and PR excitation (SI Figure 1), which creates an efficient sensitiser and acceptor pair for FRET.^{29,35} The calculated FRET radius of this pair is $R_0 = 7$ nm.

Sensitiser and acceptor perylene-acrylate monomers were synthesised using modified literature procedures, starting from commercially available 3,4,9,10-perylenetetracarboxylic dianhydride^{36–40} (Figures 1 and 2). Creation of a polymer pendant group based on the PDI center requires an asymmetric PDI monomer. One imide substituent acts to increase the solubility of the perylene core while the other bears a polymerisable acrylate group. A hexylene linker between the acrylate group and chromophore centre was chosen to ensure good separation between

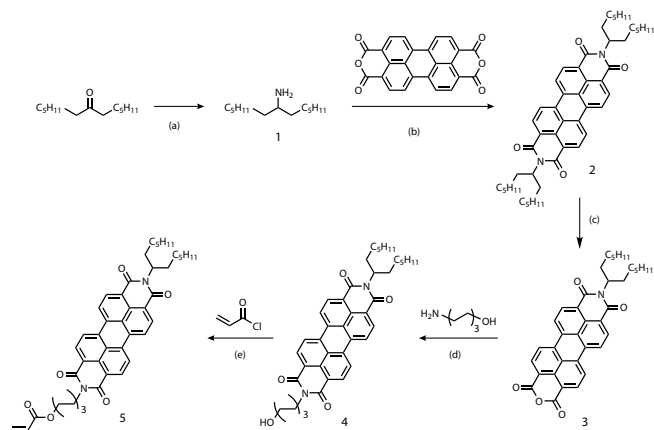


Fig. 1 Reaction scheme for the synthesis of asymmetric perylene sensitiser monomer.

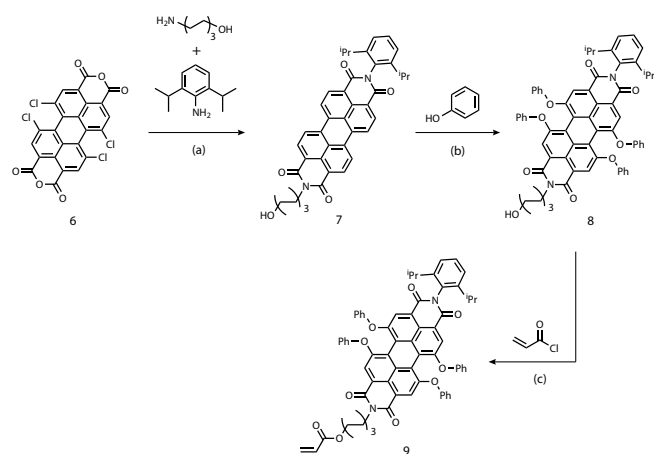


Fig. 2 Reaction scheme for the synthesis of asymmetric perylene acceptor monomer

the chromophore and acrylate so that the spectral properties of the perylene and the reactivity of the acrylate were not altered by conjugation. By varying the properties of the substituents in the bay positions of the perylene core, i.e. electron-withdrawing or donating groups, the absorption and emission spectra of the perylene core can be tuned. The phenyl-ether substituents at the perylene bay positions in the Acceptor Monomer (AM) expand the π -system and induces a torsion of the perylene core.²⁰ These effects cause bathochromic shifting of the absorption spectrum of AM with respect to the Sensitiser Monomer (SM), as required for efficient FRET (Figure 3).

PDI acrylate monomers were co-polymerised in different ratios with *tert*-butyl acrylate (tBA), to form statistical copolymers. Synthesised polymers are henceforth referred to by their tBA:SM:AM number ratio and a two letter code which signifies the type of polymer. Sensitiser Polymers (SP, Figure 4 (a)), comprised only sensitiser and tBA units; Acceptor Polymers (AP, Figure 4 (b)), comprised only acceptor and tBA units; and Sensitiser-Acceptor Copolymers (CP, Figure 4 (c)), comprised both sensitiser and acceptor units, as well as tBA.

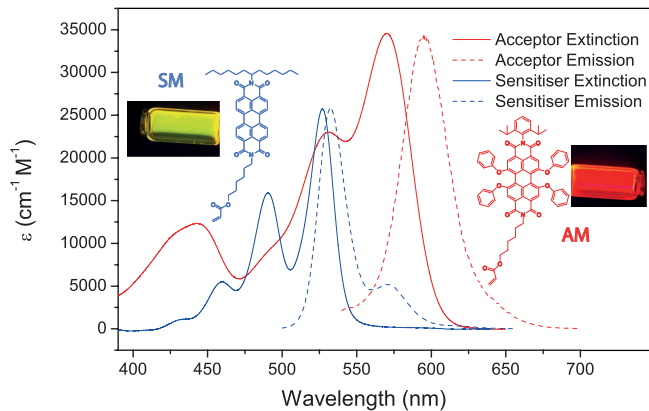


Fig. 3 Absorption and emission spectra of synthesised monomers. Emission spectrum is in arbitrary units and normalised to peak excitation.

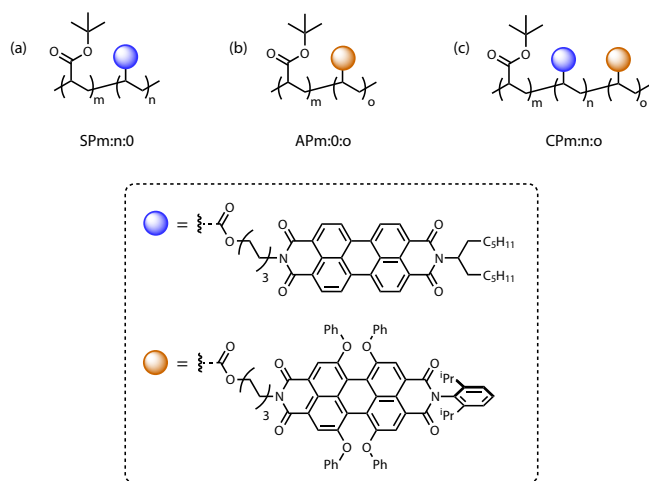


Fig. 4 Structures of the different types of synthesised polymers. (a): SP, (b): AP and (c): CP.

3.2 Solution-phase Photophysics

Prior to polymerisation, both sensitiser and acceptor monomers exhibited fluorescence spectra similar to the model perylenes PO and PR^{19,20,25,35} (Figure 3). Fluorescence quantum yields of the sensitiser and acceptor monomers were determined to be 0.91(5) and 0.90(5). The fluorescence lifetimes were 4.26(1) ns and 5.49(2) ns for the sensitiser and acceptor respectively. Like other imide substituted perylenes,^{20,25} the chromophore core was found to be unaffected by the attachment of the monomer. Upon polymerisation of the monomers in a 1:20 ratio with *t*BA the photophysical properties in solution were found to remain unchanged (SI: Figure 2 and Figure 3), showing that attachment to the polymer chain does not alter to the optical properties of the luminophore monomer.

3.3 Polymer thin-film Photophysics

Fluorescence decays of the solid polymer films, measured by time correlated single photon counting (TCSPC), were well described by single exponential decays. The fluorescence lifetimes of all samples were determined across a range of emission wavelengths

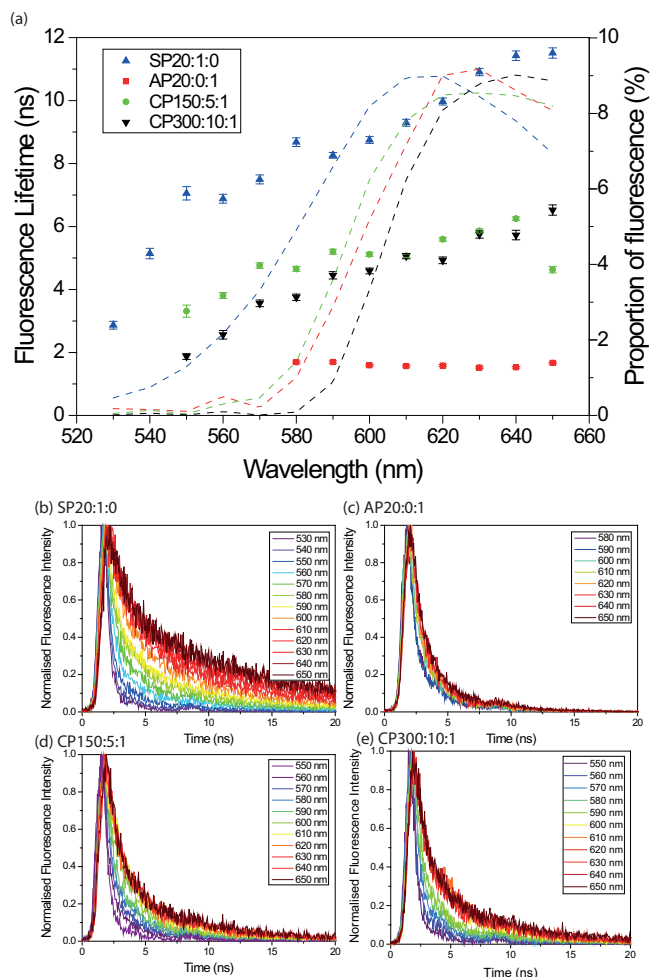


Fig. 5 (a) Fluorescence lifetimes of all solid polymer films (right) and fluorescence yields as a percentage of the total fluorescence at individual wavelengths (left). (b)-(e) Transient decays of individual polymers at different emission wavelengths under 490 nm excitation.

(Figure 5 (a)). Solid SP20:1:0 has an effective sensitiser concentration of 0.17 M or 20.79 wt%. Compared to free monomer in solution, SP20:1:0 showed a large hypsochromic shift in absorption, and a bathochromic shift in emission, from 532 to 615 nm (Figure 6 (a)). Solid SP20:1:0 showed short emission lifetimes at shorter wavelengths, increasing at longer wavelengths (Figure 5 (a) and (b)). Like other luminophores in polymeric systems,⁴¹⁻⁴⁷ the SM luminophores display a range of excitation energies due to aggregation, different microenvironments and conformations in the disordered solid polymer. Homo-FRET between like-luminophores in different energy configurations is then possible, leading to the large observed redward shift. The large Stokes shift and the increased width of the new broad emission feature relative to the free SM suggests that this effect is due to exciton-transfer and subsequent emission from lower energy chromophore-aggregate states.^{48,49} The pure acceptor polymer AP20:0:1 has an effective acceptor concentration of 0.054 M or 29.51 wt%. AP20:01 also showed a bathochromic shift in emission in the solid state, though to a lesser extent than SP20:1:0 (Figure 6 (b)). Like SP20:1:0, this polymer exhibited short life-

times at shorter wavelengths, increasing at longer wavelengths (Figure 5 (a) and (c)). The smaller change in fluorescence lifetime and smaller bathochromic shift in emission implies that the acceptor dye is less sensitive to the microenvironment of the solid polymer film. This lends support to reports that out-of-plane phenols lead to a more isolated luminophore.²⁰

Copolymer CP150:5:1 was synthesised using a similar *t*BA spacer-to-PDI monomer ratio to that of SP20:1:0 and AP20:0:1 and is calculated to have an overall perylene concentration of ≈ 0.3 M. We estimate the maximum distance to an acceptor chromophore to be about 2.6 nm, well within the FRET radius of 7 nm. Indeed, it was found that the emission spectrum was independent of the excitation wavelength. This implies efficient energy transfer from the sensitiser to the acceptor. The fluorescence decay lifetimes (Figure 5 (a)) show the effect of FRET between higher energy sensitiser states and lower-energy acceptor states as an increase in fluorescence lifetimes with increasing wavelength.

Polymer CP300:10:1 is calculated to have a similarly high dye concentration. The maximum distance to an acceptor chromophore is estimated to be 3.3 nm. CP300:10:1 shows excitation-independent peak emission at 640 nm (Figure 6 (d)) and exhibits short lifetimes at lower wavelengths. These lifetimes increased at longer wavelengths, characteristic of exciton migration to lower energy sites via FRET (Figure 5 (a)). The decrease in spectral overlap compared to CP150:5:1 arises from decreasing the concentration of acceptor units, which decreases the strength of the absorption peak at 570 nm.

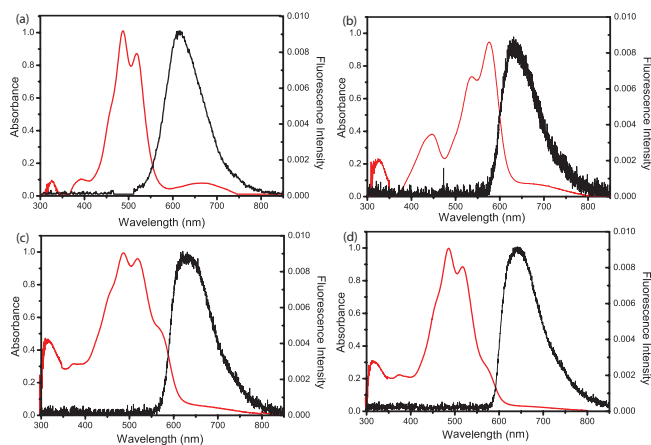


Fig. 6 Absorption (red line) and emission (black line) spectra of polymer films (a) SP20:1:0, (b) AP20:0:1, (c) CP150:5:1 and (d) CP300:10:1.

The emission spectra of CP150:5:1 and CP300:10:1 are similar to AP20:0:1, while differing from SP20:1:0 (SI Figure 4). The lack of emission from the sensitiser indicates efficient FRET from the sensitiser to the acceptor units in both CP150:5:1 and CP300:10:1. All copolymers exhibited lifetimes in between the two homo-polymers indicating that although the majority of the emission is out the acceptor units, the sensitizers in low energy microenvironments do play a role. It is worth noting that we were unable to simulate the solid state emission spectra by attenuating the monomer emission with its absorption spectrum (SI Figure 5), showing that the spectral shifts described above are not the

result of reabsorption.

Reabsorption of a chromophore system has been quantified by Currie *et al.*⁵⁰ in terms of a self-absorption ratio *S*, defined as the ratio of the absorption coefficients at absorption and emission maxima. *S* is intrinsic to each dye species in a specific host material, and has a direct impact on reabsorption. Table 1 shows an increase in *S* in the solid state due to exciton transfer to low energy microenvironments. The increase in *S* from CP150:5:1 to CP300:10:1 arises from decreasing the concentration of acceptor units, which decreases the absorption peak at 570 nm. These systems exhibit FRET from sensitiser to acceptor subunits and the sensitiser-to-acceptor ratio allows concentration of excitons into the acceptors. Due to the increased Stokes shift these two solid-state copolymers show potential application for LSCs.

Table 1 Self-absorption ratio (*S*) of synthesised monomers and polymers. ^a toluene solution. ^b solid state.

Sample	<i>S</i>
SM ^a	1.3
AM ^a	3.6
SP20:1:0 ^b	10.3
AP20:0:1 ^b	9.5
CP150:5:1 ^b	13.7
CP300:10:1 ^b	33.7

The polymer films reported in this paper have high concentrations of perylene units. While highly concentrated perylene-doped polymer films (1 – 3 M) have been prepared in previous work,^{14,29,43} the majority of the literature reports perylene doped polymer films of $5 \times 10^{-4} - 5 \times 10^{-2}$ M^{44,45} and weight percentages of 0.006 – 5%.^{35,46,47,51} We present perylene films with concentrations in the range of 0.05-0.31M and 18-30 wt%. Although aggregation was found to occur, all polymer samples still exhibited fluorescence at this high concentration. The polymer scaffold does not completely prevent aggregation but does reduce quenching of excited states by preventing complete aggregation through spacing, as well as assisting in the energy transfer system by supporting lower energy chromophore sites. These two attributes make the use of polymer scaffolds desirable as an LSC material.

We have shown that increasing the sensitiser-to-acceptors ratio decreases spectral overlap, but this is also predicted to decrease the relative proportion of FRET as sensitiser acceptor distance increases. Further optimisation of the sensitiser to acceptor ratio, using photophysical simulations, will enable tuning of FRET efficiency.

4 Conclusion

We have explored perylene-based polymer films for addressing the reabsorption and quenching by aggregation problems in LSCs. We report the convergent synthesis and photophysical characterisation of two novel asymmetric perylene acrylate monomers. These PDI dyes were designed to operate as a sensitiser-acceptor pair capable of undergoing FRET for the purpose of minimising reabsorption in LSCs. Both dyes were found to have high fluorescence quantum yields and a large overlap between sensitiser emission and acceptor absorption, making them suitable candidates for FRET-assisted LSCs. These monomers were copoly-

merised with tert-butyl acrylate, an optically inert monomer used to control space between the dyes, reducing quenching via aggregation at high concentrations. A variety of copolymers were prepared, producing polymers that exhibited solid-state fluorescence. These polymers demonstrated efficient FRET from sensitizer to acceptor units, resulting in energy transfer from a dense absorber to a low-concentration emitter, effectively reducing reabsorption. The use of polymers as a scaffolding structure enabled the preparation of high concentration films with persistent fluorescence. These two key findings demonstrate that the copolymer-scaffold energy transfer strategy presented here has potential for use in LSCs.

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