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Photophysical Studies of Poly-Isocyanopeptide Based Photovoltaic Blends

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We report a photophysical study of photovoltaic blends containing perylene-substituted polyisocyanide (pery-PIC) materials, using time-correlated single photon counting (TCSPC) and photo-induced absorption spectroscopy, and compare the key characteristics to analogous perylene-diimide (PDI) monomer blends with polythiophene- and polyfluorene-based conjugated polymers. Pery-PIC consists of semiconducting perylene units, which self-stack in a regular fashion around a rigid helical poly-isocyanopeptide backbone. In particular, the charged state lifetimes in pery-PIC blends are found to be of order 10s of μs ; this being typically less than half those of the perylene-anion in the corresponding PDI blends. We consider the influence of photophysical factors on the superior photovoltaic device performance of the pery-PIC blends, relative to the corresponding PDI-based devices, in addition to the morphological effects described in earlier studies.

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1. Introduction

Substituted polyisocyanopeptides[1,2] are a recently developed class of bio-inspired “supramolecular” materials, where chromophoric moieties may be arranged in an ordered helical array around a polymer template. This helical configuration is indeed reminiscent of those seen in many biological structures, e.g. DNA. In particular, a number of recent studies[3,4] have reported perylene-substituted polyisocyanides, consisting of perylene diimide (PDI) units, which self-stack in a regular fashion around a rigid helical poly-isocyanopeptide backbone, stabilized by hydrogen bonding between peptide units. The perylene units are arranged into chiral “helter-skelter” arrays, which do not form the kind of crystalline molecular aggregates often seen with perylene derivatives, but rather the units overlap continuously along the chain.[5] The resulting polymer is highly rigid, with persistence lengths of up to 76 nm, within an overall supramolecular structure of several hundred nanometers length. The chemical structure and bonding structure of the perylene-substituted polyisocyanide (pery-PIC) material are shown in Figure 1(a) and (b) respectively. PDI (Appendix A), and similar derivatives, are already widely reported and studied as n-type molecular semiconductors in organic photovoltaics.[6] In addition to the highly efficient migrational energy transfer observed in the pery-PIC system,[5] theoretical calculations have indicated that the high degree of ordering and electronic orbital overlap along the rigid PIC backbone result in large transfer integrals.[7] Commensurate investigations of the conductivity and carrier mobility, using thin-film transistor architectures, have also been recently reported.[7,8]

Organic photovoltaics (OPVs) currently represent a key area of interest within research into renewable solar energy,[9-11] with *state-of-the-art* power conversion efficiencies of over 7% now being reported.[12] Great advances have been made regarding issues such as low bandgap and spectral matching, morphology, stability[13] and facility of processing.[14] In our recent work, Foster *et al.*,[15] it was found that introducing arrays of the organic n-type semiconductor perylene onto a backbone of helical polyisocyanopeptide (PIC) had a marked effect on the photovoltaic (PV) properties of blend systems with archetypal p-type polyfluorene and polythiophene conjugated polymers, including up to an order of magnitude increase in device power conversion efficiency, relative to the respective PDI-blend analogues. A summary of the

key results from this earlier work is given in tabular form in Appendix B. It was hence proposed that the use of polyisocyanide chains as a molecular template offers a wide-ranging method by which the morphology and connectivity of bulk heterojunction photovoltaic blends can be modified and enhanced (see figure 1(c)). Indeed, the increased overlap of the perylene units when ordered along a well-defined polymer chain is expected to offer several advantages over the more randomized orientation of a blend containing individual perylene molecules or isolated polycrystalline aggregates.[16] The pery-PIC material and the PDI analogue had been combined in standardised (1:1 by weight) blend systems with each of the notionally p-type polymers P3HT, PFB and F8BT (chemical structures and systematic formulae may be found in Appendix A), for the purposes of photovoltaic device studies. Previous studies had shown these ~1:1 weight ratio blends as giving optimal, or near optimal, performance.[16] The external quantum efficiency (EQE) of the pery-PIC:P3HT and pery-PIC:PFB blends, though not that of pery-PIC:F8BT, were significantly improved relative to the PDI analogues and the power conversion efficiencies (PCEs) were improved by more than an order of magnitude in the cases of P3HT and PFB. Atomic force microscopy images showed that the pery-PIC had significantly altered the morphology of the blend systems causing phase separation on the scale of 100nm in the case of P3HT and PFB blends, compared to 10nm in their PDI counterparts. This separation is possibly suboptimal being somewhat greater than the exciton diffusion radius.[17] The pery-PIC:F8BT blend showed a more complete phase separation at the scale of microns, thought to be too large for efficient exciton diffusion and dissociation. It was argued that this is the cause of the poor overall device performance in this case.

In order to gain a more complete photophysical understanding of these bulk heterojunction blend systems, in addition to the previous morphological and ellipsometric studies, we report a further study of three pery-PIC-containing blends, using time-correlated single photon counting (TCSPC) and photo-induced absorption (PIA) spectroscopy, and compare the key characteristics to analogous perylene monomer (PDI) photovoltaic blends.

We find the decreased photoluminescence (PL) lifetimes of the pery-PIC component in pery-PIC:P3HT, pery-PIC:PFB and pery-PIC:F8BT to be in good agreement with existing quantum efficiency (PLQE) results, in the context of PL quenching due to charge separation in these blends. The PIA results show photo-induced absorption features, which are attributable to the perylene anion, in all blends studied. The large magnitude of these features in the pery-PIC:P3HT blend being indicative of a particularly efficient generation of free charges, as compared to PDI:P3HT, in spite of the almost complete PL quenching in the PDI blends. The charged state lifetimes in pery-PIC blends are found to be of order 10s of μs ; this being typically less than half those of the perylene-anion in the corresponding PDI blends. It appears that the efficient charge conduits between perylene units, provided by the polyisocyanide template, promote the effective separation of interfacial charges and cause the diffusion of free charges (either to electrodes or to bimolecular recombination trapping sites) to be significantly “speeded-up”. We discuss these results in the context of recent reports of the superior photovoltaic device performance of the pery-PIC blends, relative to the corresponding PDI-based devices.

2. Experimental Procedure and Background Theory

Perylene-substituted polyisocyanide material (pery-PIC) was synthesized at the University of Nijmegen, according to previously reported protocols.[2-5] The particular batch used in these experiments had a mean molecular weight of 9×10^5 g/mol, corresponding to an inferred mean chain length of around 180 nm. Regioregular poly(3-hexylthiophene) (P3HT) was purchased from Plextronics (“Plexcore HP”, lot #05-10192). Poly(9,9'-dioctylfluorene-co-bis(N,N'-(4 butylphenyl))-bis(N,N'-phenyl)-1,4-phenyldiamine) (PFB) and poly(9,9'-dioctylfluorene-co-benzothiadiazole). (F8BT) were supplied by Cambridge Display Technology Ltd., UK. The PFB was characterized as having molecular weights $m_p = 135\text{K}$ and $m_n = 60\text{K}$, polydispersity = 2.8, and quantum-yield efficiency of 27%. The F8BT had $m_p = 147\text{K}$, $m_n = 97\text{K}$, polydispersity = 1.94, and quantum yield of 83%.

The thin-film samples used in this paper were identical in preparation to those used for the morphological studies given in Foster *et al.*[15] In brief, solutions were prepared by measuring a

1:1 weight ratio[16] (6mg/ml each) of pery-PIC/PDI with P3HT/PFB/F8BT in chloroform. A further 5 thin-film samples, one from each pristine material, were prepared for comparative TCSPC readings. Each solution was spin-coated onto a clean spectrosil substrate for 20 seconds at 1000 rpm (pery-PIC blends) or 500 rpm (PDI blends). It was necessary to spin coat the pery-PIC blends at a higher speed of revolution in order to achieve a comparable optical density, given the higher intrinsic viscosity. The absorption spectra of the samples are shown in figure 2(a), with the optical densities of corresponding blends being comparable, as with the previous device studies.[15] In this case, to a first approximation, we do not expect optical density to affect our results, due to the relative nature of the photo-induced absorption measurements. Unfortunately, we do not have access to circular dichroism (CD) spectroscopy that would directly demonstrate the helical morphology of the perylene-polyisocyanide (pery-PIC) molecule in these blends. However, the chiral integrity and extreme rigidity of this molecule in a wide range of media, has been previously characterized by CD (see Schwartz *et al.*[5]) and, most pertinently, in pery-PIC/P3HT blends in a paper by Palermo *et al.*[18] It is therefore considered that the weight of the previous evidence on this matter is sufficiently convincing. We note that, whilst both having a predominantly hydrophilic character, the surface energies of the spectrosil substrates used for optical measurements may be somewhat different from the PEDOT:PSS-planarised substrates used for device work.[15] Whilst the observed top-surface morphologies do not change qualitatively, it is possible that the blend composition and morphology at the substrate is modified, [19,20] with commensurate effects on the orientation of the pery-PIC/PDI chromophores in the interfacial layer.

Photo-induced absorption (PIA) spectroscopy is an experimental method which allows us to probe the optically excited states of a molecules and semiconductors.[21,22] It can be used to identify charged states and to further give information about state origin and lifetimes in the μ s to ms regime. The use of PIA spectroscopy to measure the lifetime of photo-excited states in semiconductors has a well established theory for both mono- and bi-molecular relaxation mechanisms, such as those we expect for charges in photovoltaic- and solar-cells, where the excitation intensities are such that charge-charge interaction (e.g. annihilation) rates are low. In this paper, we probe the charged states of the six aforementioned blends and extract charged-

state lifetimes using frequency-dependent PIA. The film samples were placed under vacuum at room temperature and optically pumped with a mechanically modulated $\lambda = 488\text{nm}$, continuous-wave Ar-ion laser source, at a fixed excitation density of 0.1 W/cm^2 ; with the films having a measured optical density of ~ 1.0 at this wavelength. The sample is then probed for spectral features of photo-induced absorption, using an incandescent white-light source and lock-in amplifier. By measuring the change in fractional transmission, dT/T , as the modulation frequency is varied, it is also possible to infer the lifetimes of the excited states being probed in the PIA experiment, by fitting the frequency dependence of the PIA data to a suitable semi-quantitative model (see fig. 5, insets). These charged state lifetimes may also be estimated from the ratio of the relative intensities of the in-phase (X channel) and quadrature-phase (Y channel) PIA signals.[23] The methods of data acquisition are designed to systematically remove any background signal due to photoluminescence. In addition, the experiments described have been carefully standardized in terms of experimental conditions, such as using a constant pump-laser intensity, in order to allow valid qualitative and quantitative comparisons between samples to be made.

Explicitly, the Beer-Lambert law states that for a material with absorption coefficient α and thickness d , the intensity of transmitted light T is

$$T = T_0 \exp(-\alpha d) \quad \text{Eq.1.}$$

Suppose that at a given laser-modulation frequency, T is the transmission of the sample with the laser ‘off’; that is, taking into account various absorption processes in the blend, substrate etc. but **not** from photo-excited species. Then the laser is ‘on’ creating n such species per unit volume each with absorption cross section σ . There is a small change in transmission $\Delta T \ll T$ and we write

$$\frac{\Delta T}{T} = 1 - \exp(-\alpha d) \approx \alpha d = n \sigma d \quad \text{Eq.2.}$$

The signature of a charged species may be identified as a peak (or series of peaks) in the spectrum of $\Delta T/T$ versus wavelength. However, a quantitative approach is possible, by studying the dependence of signal on the laser modulation frequency. Assuming that once generated, charge states undergo monoexponential decay (i.e. recombine) with lifetime τ , we model their population N as

$$\frac{dN}{dt} = g(t) - \frac{N}{\tau} \quad \text{Eq.3,}$$

with the generation rate $g(t)$ modelled as $g(t) = \eta I (\cos(\omega t) + 1)$, proportional to the laser intensity I and carrier photogeneration efficiency η , modulated by chopping frequency ω . Putting in a trial solution $N = X \cos(\omega t) + Y \sin(\omega t)$ gives us the in-phase (X) and quadrature (Y) populations:

$$X = \frac{\eta I \tau}{1 + \omega^2 \tau^2} \quad \text{and} \quad Y = \frac{\eta I \omega \tau^2}{1 + \omega^2 \tau^2} \quad \text{Eqs. 4a and 4b}$$

We further note that

$$\frac{Y}{X} = \omega \tau \quad \text{Eq.5.}$$

X and Y are proportional to the signal magnitude $\Delta T/T$ when the laser is ‘on’ and ‘off’ respectively, hence, these are not independent measurements of lifetime, but are directly correlated. If the lifetime τ is short relative to the modulation time period (i.e. if $\omega \tau \ll 1$) most of the signal will be in X , whereas if $\omega \tau \sim 1$ the signal is distributed more evenly between channels (see Appendix C).

Normal-incidence UV-vis absorption measurements were made using a Hewlett-Packard 8453 spectrophotometer. Photoluminescence (PL) spectra were measured using a calibrated fluorescence spectrophotometer (Cary Eclipse). Finally, time-resolved PL was measured for each of the blends under study, using a technique of time-correlated single photon counting (TCSPC).[24] In brief, the blend samples were excited using a $\lambda = 470\text{nm}$ picosecond pulsed diode-laser source, with the emitted photons being detected and binned based on their lag from the triggering pulse, with the limiting time-resolution of the experiment being ≈ 100 ps. The PL lifetimes were then fitted using non-linear curve-fitting software *Origin 8*.

3. Results

PL spectra for each of the blends studies are shown in figure 2(c), together with thin-film control samples for pristine pery-PIC and PDI. The emission peak seen at around $\lambda = 650$ nm is due to

the perylene component in the blends. Of note, are the extra spectral features in the pery-PIC:F8BT and pery-PIC:P3HT blends, due to the excitation light being partially absorbed by the conjugated polymer component rather than the pery-PIC and/or due to resonant energy transfer between blends components. It is clear, from this incomplete quenching of PL, that not all the excitons created in these blends are dissociated into charges. By contrast, each of the PDI blends show a PL spectrum which is dominated by a broad featureless band due to the perylene component,[16] albeit with a very low intensity, indicating highly efficient quenching due to geminate charge formation in these cases. The TCPSC data and measured lifetimes are shown in Figure 3 and Table 1 respectively, along with PL efficiency and PL quenching efficiency, where known from previous studies.[15] These results have a clear interpretation in the case of the pery-PIC blends, where the PL lifetime of pristine pery-PIC is measured to be 6.5ns; the lower the PLE (and the higher the efficiency of luminescence quenching due to charge separation) the shorter the measured lifetime, commensurately. The lifetimes of emission from the PDI blends are generally rather longer than that of the pristine PDI; the most likely explanation for this is that the emissive state of PDI has been entirely quenched by geminate charge separation and the weak signal observed is from traps within PDI crystallites or aggregates. The apparent absence of these longer lived states in the pery-PIC blends also confirms our earlier assertions that the templating effect of the poly-isocyanide backbone inhibits and suppresses the formation of perylene aggregates in the pery-PIC blends. Finally, the influence of energy transfer in the pery-PIC/F8BT blend is confirmed by the reduced lifetime of emission from the F8BT component of this blend, relative to a pristine film of F8BT (Figure 3b).

That the efficiency of interfacial charge formation appears to be better in the PDI blends compared to the pery-PIC blends is curious, in the context of the superior PV device performance of the latter. However, PIA studies provide a further useful insight into the underlying photophysics of these systems. Figure 4 shows the complete set of PIA spectra for each of the pery-PIC and PDI blends studied. In general, for wavelengths above around 630nm, we are probing photo-induced absorption of excited states in the blends; the X signal is negative (the excitation beam causes a decrease in transmission) and the Y signal positive. For λ below ~600nm, we observe induced transparency (“bleaching”) due to the partial saturation of

absorption processes, which would normally reduce the transmission of the probe beam, by the intense laser light. There are three PIA peaks common to all blends at approx $\lambda = 700, 820$ and 980 nm, which we attribute to the perylene anion.[25] Since the peaks are present in both PDI and pery-PIC blends, we conclude that the polyisocyanide backbone does not substantially alter the photophysics of charged states.

Focussing on the P3HT blends (Fig 4a), in both cases there is a clear signature of the P3HT polaron,[26] both in photo-induced absorption around $\lambda = 600$ nm and in the bleach region, in addition to the perylene anion features. We also note that whilst the Y-signals of the two blends are approximately equal across the spectrum, the X-signal of the pery-PIC is uniformly 2-3 times greater than that of PDI. We expect the magnitude of dT/T to be proportional to the number density of charges,[23] inferring that generation of *free charges* is more efficient in the pery-PIC blend. This is in line with the findings outlined in Foster *et al*, as one would expect greater charge generation efficiency to contribute to the higher EQE and larger short-circuit currents in pery-PIC:P3HT devices.

The pery-PIC:PFB blend has a very weak (and hence noisy) PIA signal, shown in figure 4b, with no obvious difference in magnitude compared to PDI:PFB, suggesting less free charge generation than in the P3HT samples. This is a little unexpected because pery-PIC:PFB has the best EQE of all studied blend devices and a far better power conversion efficiency than PDI:PFB.[15] The data supports previous speculation that in the PFB blend, the pery-PIC improves PV device connectivity and conductivity, but does not significantly affect free charge generation efficiency.

Figure 4(c) shows that pery-PIC:F8BT has a much lower free charge generation efficiency than PDI:F8BT which is consistent with the hypothesis that the micron-scale phase separation in pery-PIC:F8BT is too large for effective exciton dissociation. Additionally, there is a very strong feature present in the PDI:F8BT blend, at $\lambda \sim 580$ nm, which is apparently absent in the case of

perylene-3,4,9,10-tetracarboxylic diimide (PIC):F8BT. This is most likely a photo-induced absorption signature of charges in the F8BT phase,[27] and the absence of this feature is evidence of very poor free charge generation in perylene-3,4,9,10-tetracarboxylic diimide (PIC):F8BT. This could be due to adverse phase-separation, the poor PL quenching efficiency, the adverse orientational effects of the crystalline F8BT phases relative to the perylene-3,4,9,10-tetracarboxylic diimide (PIC) molecules, or a combination of these factors.

The data from modulation-frequency dependent PIA experiments were fit parametrically using *Origin 8*; the full results of these analyses are presented in Table 2. Figure 5 shows a representative lifetime fit of the excited states seen in the PIA experiment, based on the expected modulation-frequency dependence of the X and Y signals. The PIA data for modulation frequencies below $\omega = 2\text{kHz}$ is quite noisy due to problems of interference from electrical sources, such as stray mains lighting and harmonics; this is a well documented limitation of this kind of modulation spectroscopy.[23] As far as care was taken to minimise this artifact, it remains as a significant source of the uncertainty in the fitting of the charged state lifetimes. However, it is considered necessary to take into account these lower frequencies for the sake of the integrity of the overall model. It was generally found that the two extracted values of τ lay within the error margins of one another (see fig.5 caption); as the lifetimes derived from X and Y are also correlated (see eqs.4 and 5), the values produced by the X curve fit are given in the results table (Table 2), since this consistently has the greater signal and smaller fractional error.

The τ values stretch from 10s to 100s of microseconds, as might have been anticipated for charged excitations in this type of system.[28] We note that the calculated errors are around 10%, although it is recognised there is a distinction to be made between the uncertainty in the measurement of the mean value of τ , and the dispersion of τ . The scope of this paper is to determine *mean* lifetimes in the μs -ms range, which is the most critical timescale for charge relaxation processes in photovoltaic blends. The PIA technique cannot, however, resolve ultrafast (ps-ns) charge-transfer processes[25] or long-lived ($>\text{ms}$) charge-trapping phenomena, which may be present. In general, we observe that for each blend the two excitations around $\lambda = 700\text{nm}$ and 800nm have closely similar lifetimes, with the excitations at 980nm being slightly

longer-lived, but still very much of the same order. This suggests that the excitations belong to successive excited states of a particular charged species (specifically, the perylene anion).

A comparison of the pery-PIC and PDI blends of each donor material yields an interesting result, as the inferred perylene-anion lifetimes in the pery-PIC blends are substantially *shorter* than those of the PDI blends, typically reduced by a factor of at least 2. On the face of it, this is perhaps surprising, because one might assume that due to the facility with which electrons can migrate along the pery-PIC structure, transport away from the bulk heterojunction interfaces would be more efficient and the charges would enjoy longer lifetimes. However, in our experiments, with the relatively low rates of charge generation, we expect the major process to be bimolecular recombination which occurs when charges become ‘trapped’ by discontinuous pathways within the blend.[29] It is possible that the particular ordering of perylene in the pery-PIC blends allows charges to travel much more rapidly along the pery-PIC molecule, away from geminate sites, than is possible in the PDI monomer, increasing the overall diffusive rate. Hence, the processes of diffusion, trapping and decay will be significantly “speeded-up”, resulting in shorter lifetimes for charged species.

It has been proposed here that pery-PIC blends exhibit improved free charge generation at the interfaces (P3HT) and blend connectivity (PFB), relative to bulk-heterojunctions based on PDI. It is unlikely that either of these would have much influence on the charged-state lifetimes, but each would contribute to a more efficient device. Improving connectivity might enhance charge-state lifetimes in a PV device but, importantly, not in quasi-steady state PIA experiments, since there is no applied field causing free charges to migrate. The new results can thus be reconciled with previous findings, although further devices studies, such as transient photocurrent measurements[30] may help to fully elucidate these issues in the future.

4. Conclusion

In conclusion, this paper described a photophysical study of photovoltaic blends containing perylene-substituted polyisocyanide (pery-PIC) materials, using time-correlated single photon counting (TCSPC) and photo-induced absorption spectroscopy (PIA); comparing the key characteristics to analogous perylene monomer (PDI) blends with polythiophene- and polyfluorene-based conjugated polymers. In addition to previous PV device studies,[15,31] which attributed differences in performance to morphological and orientational effects, we find significant photophysical differences, which may be important in the understanding of bulk heterojunction blend systems involving such supramolecular or bio-inspired peptide-based materials.

We find the decreased photoluminescence (PL) lifetimes of the PIC component in pery-PIC:P3HT, pery-PIC:PFB and pery-PIC:F8BT blends to be consistent with an incomplete PL quenching, due to charge separation. The PIA results show characteristic photo-induced absorption features of the perylene anion, in all blends studied. The large magnitude of these features in the pery-PIC:P3HT blend being indicative of a particularly efficient generation of free charges, as compared to PDI:P3HT, in spite of the almost complete PL quenching in the PDI blends. The charged state lifetimes in pery-PIC blends are found to be of order 10s of μs ; this being typically less than half those of the perylene-anion in the corresponding PDI blends, which have been measured as being up to several hundred μs . It appears that the efficient charge conduits between perylene units, provided by the polyisocyanide template, promote the effective separation of interfacial charges and cause the diffusion of free charges to be significantly “speeded-up”. Commensurately, the overall rate of trapping and decay of charge species will be increased, resulting in reduced measured lifetimes. Hence, there is evidence of photophysical factors behind the superior photovoltaic device performance of the pery-PIC blends, relative to the corresponding PDI-based devices, in addition to the morphological effects described in earlier studies.

As a wider consideration, we note that the concept of attaching arrays of chromophoric moieties onto a poly-isocyanopeptide backbone is becoming applicable to a wider range of materials, beyond perylenes; especially in the light of recent advances in modular chemistry techniques, such as the “click” synthesis.[2,32] Such structures potentially offer a very rich platform by which the photophysics of organic bulk-heterojunctions may be studied and by which photovoltaic device performance may be enhanced. Furthermore, if the characteristic self-organisation of substituted polyisocyanides proves favourable, this class of materials could become useful within the field of large scale solution processing, where successful roll-to-roll coating of organic PV devices relies upon the ability of the material to retain the desired morphological structures associated with efficient device performance.[33-35]

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Figures and captions

FIGURE 1

Figure 1; (a) chemical structure of perylene-substituted polyisocyanide (pery-PIC), with a schematic of the resultant helical structure shown in (b). The cartoon in (c) illustrates different bulk-heterojunction blend morphologies in devices; with the typical phase separation of perylene (PDI) monomer blends (left) being contrasted with the enhanced connectivity of a typical pery-PIC blend (right), due to the ordering of PDI moieties on the polyisocyanide backbone.

FIGURE 2

Figure 2; (a) shows the thin-film absorption spectra for 1:1 blends of PDI and PIC, as indicated. The spectra are offset for clarity. (b) shows representative thin-film absorbance spectra for each of the pristine materials, as a guide to the eye. (c) shows photoluminescence spectra for these thin-films, using a $\lambda = 475$ nm excitation source. The spectra are normalised and offset for clarity, however the difference in absolute intensity between the samples may be ascertained from the quantum yield measurements reported in table 1. Spectra for thin-film samples of pristine F8BT and P3HT are also shown for reference, whereas pristine PFB does not luminesce under this excitation wavelength.

FIGURE 3

Figure 3; (a) shows the time-correlated single-photon counting (TCSPC) decay curves for 1:1 blends of pery-PIC, as indicated, together with the data for a control film of neat pery-PIC. Photoluminescence was measured at the emission wavelength of the pery-PIC component. (b) TCSPC decay curves for the 1:1 blend of pery-PIC/F8BT, together with the data for a control film F8BT, as measured at the emission wavelength of F8BT. The lines of best fit to a mono-exponential decay function are shown for clarity in all cases and the extracted lifetime values are given in Table 1.

FIGURE 4

Figure 4; photo-induced absorption (PIA) spectra, showing fractional change in transmission (dT/T) as a function of wavelength for (a) P3HT (b) PFB and (c) F8BT, 1:1 blended with pery-PIC (red) and PDI (black). The PIA peaks at $\lambda \sim 700, 820$ and 980nm are due to the perylene anion species and are indicated by arrow for clarity. The magnitudes of dT/T are proportional to the incidence of charge generation (note the different scales). In all cases, both the X channel (in phase) and Y channel (quadrature) spectra are shown, using a signal-modulation frequency of 225 Hz .

FIGURE 5

Figure 5; Representative example of a frequency dependence curve fit, for the PIA feature at $\lambda = 985$ nm in the 1:1 PDI:F8BT blend. The graph shows the fractional change in transmission (dT/T) as a function of modulation frequency (ω) for the X (in-phase) and Y (quadrature) signals. A fitting algorithm, based on the equations shown as insets, was performed on the X and Y signals separately and the lifetime (τ) values used to reconstruct two curves (shown in red) for comparison. η and I are semi-empirical constants related to the optical cross-section of the sample and the pump beam intensity respectively. In this case, τ (X fit) = 269 ± 33 μ s and τ (Y fit) = 280 ± 15 μ s. All the data fitting was done using non-linear curve-fitting software *Origin 8*.

Tables and captions

Table 1

sample	λ (nm)	TCSPC lifetime (ns)	PLE %	Quenching efficiency %
Pery-PIC:P3HT	650	0.38	1.3	84.1
Pery-PIC:PFB	635	4.17	6.0	26.8
Pery-PIC:F8BT	620	5.68	7.9	3.7
Pery-PIC only	640	6.52	8.2	
PIC:F8BT	565	1.00		
F8BT	545	1.93		
PDI:P3HT	650	8.97	$\ll 1.0$	≈ 100
PDI:PFB	650	5.90	$\ll 1.0$	≈ 100
PDI:F8BT	650	6.07	$\ll 1.0$	≈ 100
PDI only	650	3.52		

Table 1; time-correlated single photon counting (TCSPC) data for all blends studied, giving the PL lifetime at the emission wavelengths indicated, the limiting time-resolution of the experiment being ≈ 100 ps in all cases. The photoluminescence efficiency (PLE) and quenching efficiency are also given, where available.

Table 2

Sample	$\lambda(\text{nm})$	$\tau(\mu\text{s})$	$\lambda(\text{nm})$	$\tau(\mu\text{s})$	$\lambda(\text{nm})$	$\tau(\mu\text{s})$
Pery-PIC: P3HT	700	54 ± 6	810	55*	980	74 ± 7
PDI:P3HT	700	158 ± 28	810	135*	985	251 ± 34
Pery-PIC: PFB	715	82 ± 8	810	66 ± 12		
PDI:PFB	725	151 ± 17	805	153 ± 18		
Pery-PIC: F8BT	700	81 ± 10	820	59 ± 6	980	95*
PDI:F8BT	715	215 ± 18	805	206 ± 12	985	269 ± 33

Table 2; lifetime values of photo-induced absorption features of perylene anion, for all blends studied. These values are based upon fitting of X-channel frequency-dependent PIA data. *No frequency dependence data available, estimate of lifetime found by direct comparison of X and Y signals in dT/T spectra.

Appendix A

Appendix A; full chemical structures of materials described in this paper. Namely, perylene (N,N'-bis(1-ethylpropyl)-3,4:9,10-perylene bis(tetracarboxyl diimide)), P3HT (Poly(3-hexylthiophene)), F8BT (Poly(9,9-di-n-octylfluorene-alt-benzothiadiazole)), and PFB (Poly(9,9-dioctylfluorene-co-bis-N,N-(4-butylphenyl)-bis-N,N-phenyl-1,4-phenylenediamine)).

Appendix B

Sample	V_{oc} (V)	I_{sc} (mA/cm ²)	Fill-factor	Peak EQE (%)	ε
PDI/P3HT	0.30	4.7×10^{-4}	0.21	1.0	
pery-PIC/P3HT	0.19	4.8×10^{-3}	0.41	2.7	12.6
PDI/PFB	0.07	4.5×10^{-4}	0.24	0.6	
pery-PIC/PFB	0.42	6.4×10^{-4}	0.31	3.6	10.8
PDI/F8BT	0.27	6.6×10^{-4}	0.26	1.3	
pery-PIC/F8BT	0.35	4.4×10^{-4}	0.30	0.6	1.0

Appendix B; Summary of recent photovoltaic (PV) device studies from S. Foster *et al.*, 2009 *Macromolecules* **42** 2023, which analysed the blends described in the current paper in planar PV architectures. The table gives representative values for the open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), fill factor, and peak external quantum efficiency (EQE) for each of the 1:1 by weight pery-PIC and PDI blends studied, together with the relative enhancements (ε) of the power extraction efficiencies between analogous pery-PIC and PDI blends.

Appendix C

Appendix C; Schematic depiction of the variation of photo-induced absorption signal (grey) with laser intensity function, as determined by the chopping frequency (black line) for (a) $\omega\tau \ll 1$ (b) $\omega\tau \approx 1$. Symbols and terms are as previously defined in the main text. Source: Dhoot A S, *Optical Probing of Excited States in Conjugated Polymer Devices* (Ph.D. Thesis, University of Cambridge, U.K., 2002)