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Efficient singlet exciton fission in pentacene prepared from a soluble precursor

Maxim Tabachnyk,¹ Arfa H. Karani,¹ Katharina Broch,^{1,2}
Luis M. Pazos-Outón,¹ James Xiao,¹ Tom C. Jellicoe,¹
Jiří Novák,³ David Harkin,¹ Andrew J. Pearson,¹ Akshay Rao,¹
Neil C. Greenham,¹ Marcus L. Böhm,^{1,a} and Richard H. Friend¹

¹*Cavendish Laboratory, J.J. Thomson Avenue, University of Cambridge, Cambridge CB3 0HE, UK*

²*Fritz-Haber Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, Berlin 1495, Germany*

³*Central European Institute of Technology and Department of Condensed Matter Physics, Masaryk University, Kotlarska 2, Brno 61137, Czech Republic*

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Carrier multiplication using singlet exciton fission (SF) to generate a pair of spin-triplet excitons from a single optical excitation has been highlighted as a promising approach to boost the photocurrent in photovoltaics (PVs) thereby allowing PV operation beyond the Shockley-Queisser limit. The applicability of many efficient fission materials, however, is limited due to their poor solubility. For instance, while acene-based organics such as pentacene (Pc) show high SF yields (up to 200%), the plain acene backbone renders the organic molecule insoluble in common organic solvents. Previous approaches adding solubilizing side groups such as bis(tri-*iso*-propylsilylethynyl) to the Pc core resulted in low vertical carrier mobilities due to reduction of the transfer integrals via steric hindrance, which prevented high efficiencies in PVs. Here we show how to achieve good solubility while retaining the advantages of molecular Pc by using a soluble precursor route. The precursor fully converts into molecular Pc through thermal removal of the solubilizing side groups upon annealing above 150 °C in the solid state. The annealed precursor shows small differences in the crystallinity compared to evaporated thin films of Pc, indicating that the Pc adopts the bulk rather than surface polytype. Furthermore, we identify identical SF properties such as sub-100 fs fission time and equally long triplet lifetimes in both samples. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4968518>]

The power conversion efficiency of commercially deployed, single-junction photovoltaics (PV) is systematically constrained by the Shockley-Queisser limit, mainly because excitations from high-energy photons rapidly cool to the semiconductor band edge.¹ During this cooling process the excess energy of the absorbed photon with respect to the semiconductor bandgap is lost to heat.

One way to overcome this limitation is to make use of the unique excitonic properties of some organic semiconductors (OSCs). In OSCs, the photo-excitation event leads to the formation of coulombically bound electron-hole pairs (excitons), which can either be spin-singlet (spin 0) or spin-triplet (spin 1). In some OSCs, the energy from one highly energetic spin-singlet exciton can be rapidly re-distributed into two triplet excitons, each with approximately half the energy of the original singlet. This process is called singlet exciton fission (SF) and is spin-conserving since the initially combined spin state of the two triplet excitons has spin 0 (see Figure 1(a)).^{2,3}

This energy re-distribution through SF in principle allows for doubling of the photocurrent from high-energy photons, instead of losing the extra energy as heat. Figure 1(b) highlights

^a Author to whom correspondence should be addressed. Electronic mail: mb842@cam.ac.uk

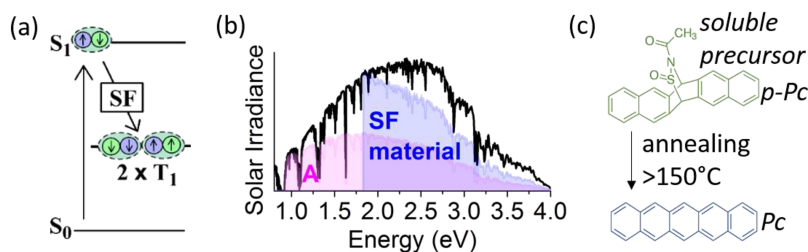


FIG. 1. (a) Singlet exciton fission (SF) in pentacene (Pc). Photo-generated singlet excitons (S_1) in Pc undergo SF into two triplet excitons (T_1) within 80 fs.⁵ (b) Part of the thermalization loss in solar cells from high-energy photons can be avoided by combining a low-bandgap acceptor material (a) with a high bandgap singlet fission material. (c) The solution-processable precursor 13,6-*N*-sulfinylacetamido-pentacene (p-Pc) converts to Pc upon annealing above 150 °C.

the potential photocurrent contribution of an organic SF layer combined with a low-bandgap acceptor.

Pentacene is a model system for SF with a fission time of ca. 80 fs thereby outcompeting alternative singlet state decay pathways (e.g., recombination, charge transfer or energy transfer).^{2,4-6} In solar cells where the generated triplets can be ionized at an interface with acceptor materials such as fullerene derivatives, external quantum efficiencies (EQE—charge carrier pairs per incident photon) of up to 126%^{5,7} and internal quantum efficiencies (IQE—charge carrier pairs per absorbed photon) reaching 200%^{5,8} have been demonstrated.

One of the major limitations for the efficiency and applicability of previous pentacene solar cells is the poor solubility of the acene in common organic solvents⁹ which restricts the choice of material deposition method to thermal evaporation techniques only.^{5,8} We note that in order to harvest triplets from SF efficiently, the SF material's domain size is limited to the triplet diffusion length of ca. 40 nm.⁸ As a consequence of these restrictions, only layered device architectures with limited photon absorption in the pentacene domain have been reported. Note that the high EQE values above 100% reported for layered pentacene/ C_{60} devices required light trapping through external mirrors⁵ or distributed Bragg reflectors,⁷ which sets further challenges to the PV device architecture. Solubility of pentacene in common organic solvents can be achieved by adding side groups such as a bis(tri-*iso*-propylsilyl ethynyl) (TIPS) functionality to the acene core.¹⁰ However, the addition of TIPS side groups to the acene core has resulted in lower triplet conversion yields and shorter triplet lifetimes compared to un-functionalized pentacene.¹¹ Among other reasons it is likely that the steric hindrance through the added side groups reduces the electronic coupling of the chromophores between layers,¹² thereby limiting both the yield and the lifetime of triplets produced via singlet fission. As a consequence, only limited device performance in solar cells could be achieved so far.¹³

Another method of combining good solution-processability and close packing of the organic molecules is provided when the solubilizing side groups of a pentacene precursor are cleaved in post-deposition annealing processes, which recovers the un-functionalized acene molecule. Specifically, the pentacene precursor molecule 13,6-*N*-sulfinylacetamido-pentacene (p-Pc) is soluble in common organic solvents and converts into pentacene in a retro Diels-Alder reaction upon annealing in the solid state (see Figure 1(c)).^{9,14} Compared to alternative molecules^{15,16} for solution-processable pentacene precursors, p-Pc provides a facile synthesis route, yields high thin-film hole mobilities (up to $0.89 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),⁹ and therefore promises excellent charge transport properties once integrated in organic photovoltaics. In principle, the low conversion temperature (ca. 150 °C) could also allow low-cost integration of pentacene on plastic substrates. Such a precursor approach thus combines the advantages of both solution-processability and good charge transport in thin films of molecular pentacene.

In this work, we study the formation of crystalline pentacene via thermal annealing of a solution processed p-Pc thin film. We characterize its composition and morphology employing Fourier-transform infrared- (FTIR) and absorption spectroscopy as well as atomic force microscopy (AFM) and X-ray diffraction methods. Using femtosecond laser spectroscopy, we verify identical SF rates and triplet lifetimes for annealed p-Pc and evaporated pentacene (e-Pc).

We base our studies on the comparison of films of annealed p-Pc and thermally evaporated pentacene (e-Pc). The p-Pc films are fabricated *via* spincoating p-Pc on a glass substrate, which

is followed by a thermal annealing process to convert p-Pc into molecular pentacene. The e-Pc samples were prepared by the thermal evaporation of molecular pentacene on a similar glass substrate. Further information to the sample fabrication is provided in the [supplementary material](#). To analyze interconversion from p-Pc to pentacene through thermal annealing, we compare the vibrational modes of p-Pc (before and after annealing at 200 °C for 20 min) with separately prepared e-Pc samples using FTIR (see Figure 2(a)).

All characteristic vibrational signals of p-Pc (i.e., 1372 cm^{-1} N–S group and 1745 cm^{-1} C–O group)¹⁷ disappear after annealing and a similar vibrational profile as for e-Pc emerges showing typical aromatic C–C stretch vibrations (1000–1800 cm^{-1}) and aromatic C–H stretches around 3041 cm^{-1} .¹⁷ Considering the complete loss of the typical *N*-sulfinylacetamide vibrations of p-Pc upon annealing, we suggest that only pure pentacene remains after annealing. We note that FTIR can only detect impurities within pharmacopoeias limits at best¹⁸ and may therefore not be sensitive for trace amounts (<2%)¹⁹ of *N*-sulfinylacetamide decomposition products. This finding is consistent with film absorbance measurements where the featureless profile of the p-Pc upon annealing converts into an absorbance profile which is similar in shape to the e-Pc sample (see Figure 2(b)). In the [supplementary material](#) (Figure S1) we show that changing the annealing temperatures and times of p-Pc between 150 °C and 200 °C as well as 5 min and 60 min, respectively, produces similar absorption spectra. We note that the lowest energy absorption peak in annealed p-Pc is red-shifted by ca. 10 nm compared to e-Pc. Among other effects such small differences in the absorbance spectrum can be generated by a different crystallinity of the two films.

X-ray diffraction (XRD) measurements show that annealed p-Pc adopts a distinctly different bulk phase crystal structure compared to the reported thin-film phase of e-Pc.²⁰ In Figure 2(c) we show a Bragg peak at $q_z = 0.44 \text{ \AA}^{-1}$ for p-Pc annealed at both studied annealing conditions (150 °C and 200 °C for 20 min), which we assign to the (001) reflection. The corresponding lattice spacing

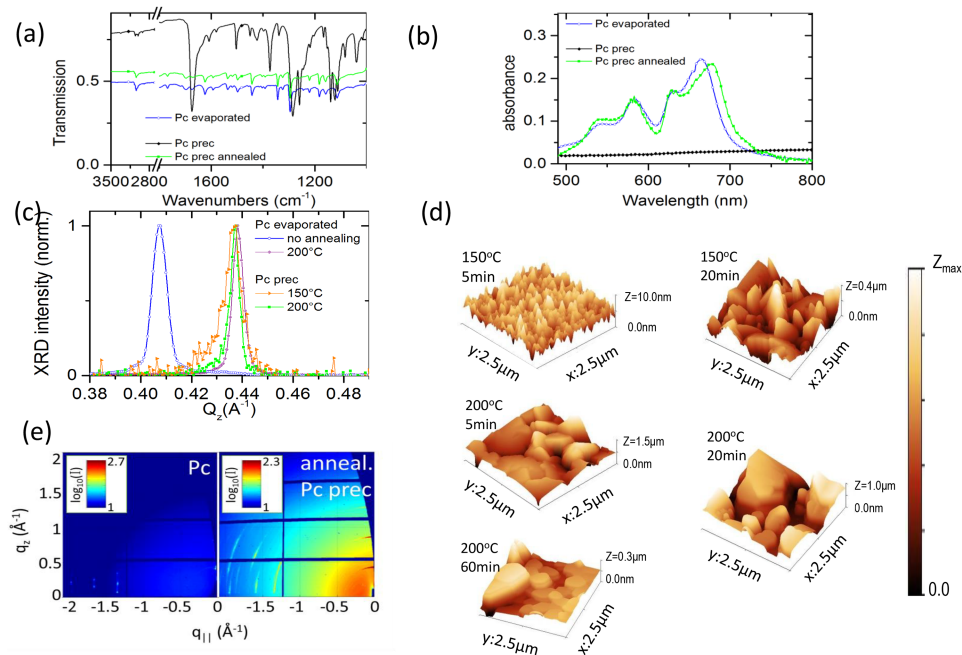


FIG. 2. (a) Infrared transmission of pentacene precursor (p-Pc) changes upon annealing and develops the same spectral profile as observed in evaporated pentacene (e-Pc), verifying complete interconversion and no significant residues. (b) Absorbance spectra, indicating interconversion of p-Pc to molecular pentacene upon annealing. (c) X-ray diffraction (XRD) showing (001)-reflection indicates that films of annealed p-Pc crystallize in the bulk phase of pentacene. (d) Atomic force microscopy (AFM) phase images for annealed p-Pc for various annealing conditions show the growth of clusters with higher annealing temperatures and longer annealing times. (e) Grazing-incidence wide-angle X-ray scattering (GIWAXS) showing that the mosaicity of annealed films of p-Pc is higher than in e-Pc. p-Pc in Figures 2(a), 2(b), and 2(e) was annealed at 200 °C. Annealing time for p-Pc in (a), (b), (c), and (e) was 20 min.

perpendicular to the substrate surface (out-of-plane direction) for annealed p-Pc is 1.43 nm, which is in agreement with the out-of-plane lattice spacing observed for the bulk phase of e-Pc.^{20,21} The lattice spacing of e-Pc films, however, is slightly larger ($d = 1.53$ nm), confirming that e-Pc grows in the thin-film phase.²⁰ Upon annealing at 200 °C for 1 h, the thin-film phase of e-Pc can be converted into the bulk crystal phase of pentacene showing a lattice spacing of 1.43 nm. This finding is consistent with literature reports where e-Pc samples showed bulk phase properties when no preferential growth direction was provided during the crystal growth²¹ or when the substrate was heated during evaporation.²² Both fabrication methods, however, seem to adopt a similar herringbone structure which is a characteristic for non-substituted pentacene molecules in the solid state (see Figure S2 of the [supplementary material](#)).²³ Furthermore, applying a Scherrer analysis²⁴ on the full width at half maximum (FWHM) of the (001) XRD diffraction peaks to estimate the size of crystallites (perpendicular to the substrate surface), we find that longer annealing times and higher temperatures result in larger crystallites (see Table S1 of the [supplementary material](#)). For instance, when annealed at 200 °C for more than 5 min, we find a crystal size larger than ca. 140 nm, indicating single crystals in the out-of-substrate plane direction, thereby mainly leaving lateral grain boundaries.

We further study the effect of annealing conditions on the film morphology using AFM (Figure 2(e)) and find that annealed p-Pc forms isolated clusters with a diameter of up to 2 μm with extended flat surfaces. If annealed at higher temperatures and for longer times, the clusters increase in size and the initial randomly organized flat surfaces become more oriented with the substrate plane (see Figure S5 of the [supplementary material](#)). Such a transformation from an un-ordered to a substrate-oriented micromorphology with increased annealing temperatures and longer annealing times is consistent with grazing incidence wide-angle X-ray scattering (GIWAXS) measurements (see Figure 2(d)). The e-Pc exhibits distinct and sharp diffraction peaks characteristic of a polycrystalline sample showing a pronounced long-range order and a preferential orientation of the crystallites in the out-of-plane direction with small mosaicity. In the case of the annealed p-Pc samples, these distinct peaks are smeared out into a ring pattern which is characteristic for a sample with low preferential crystallite orientation.²⁵ As discussed in Figure S4 of the [supplementary material](#), higher annealing temperatures and longer annealing times can decrease the mosaicity of the p-Pc samples. However, the practical range of annealing parameters is limited since pentacene sublimates particularly fast above $T_e \approx 170$ °C,²¹ explaining our observation of a reduction in film absorption after annealing (see Figure S1 of the [supplementary material](#)). Long annealing times at low temperature (150 °C) to avoid mass loss does not improve crystallinity significantly (see Figure S3 of the [supplementary material](#)).

Having confirmed the formation of crystalline pentacene, we proceed to discuss the photophysical characteristics of samples prepared via the precursor route. A characteristic behavior of systems such as pentacene with fast and exothermic SF is a very low photoluminescence (PL) yield as the initially formed singlet excitons, which could recombine radiatively, are rapidly converted into pairs of non-emissive triplet excitons. SF is more than four orders of magnitude faster than photon emission from pentacene monomers.²⁶ We note that the emission generated from triplets via triplet-triplet annihilation (TTA) to singlets is negligible because triplet recombination is faster than endothermic TTA.² The p-Pc exhibits weak and broad emission in the red/NIR as presented in Figure 3(a).

However, upon annealing the PL is of a similarly low intensity as for e-Pc films, centered around 700 nm and with a photoluminescence quantum yield below 10^{-4} (see the [supplementary material](#)). This weak PL is therefore consistent with efficient SF in the annealed p-Pc.

To verify that ultrafast SF takes place in annealed p-Pc films, we perform femtosecond transient optical absorption (TA) spectroscopy. In this time-resolved measurement, the Pc films are excited with a 30 fs short laser pulse spectrally centered at 530 nm (FWHM 80 nm) using a fluence of 14 $\mu\text{J cm}^{-2}$ (pump excitation). After a delay, which is mechanically controlled with a retro-reflecting stage, the pump-induced change of absorption of an ultra-short broadband (500-800 nm) pulse is probed. Figure 3(b) shows the change in optical transmission ($\Delta T/T$), normalized by the transmission without the pump excitation. The positive feature at 655-680 nm was previously assigned to the ground state bleach (GSB) and stimulated emission (SE) of pentacene (see Figure S6 of the [supplementary material](#)). The negative feature above 730 nm is associated with a photo-induced absorption (T_1 PIA) of triplet excitons, as has been shown in previous work.^{4,27} SE originates from singlet excitons and the T_1 PIA from triplet excitons, whereas the GSB is proportional to the total excitation density. The

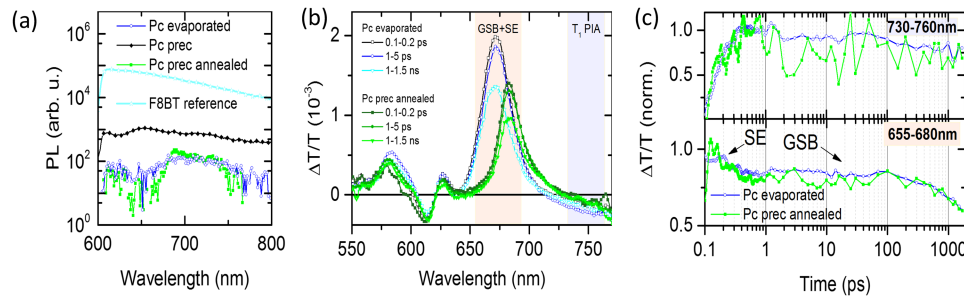


FIG. 3. (a) Steady-state photoluminescence (PL) from films of thermally evaporated pentacene (e-Pc), as-deposited pentacene precursor (p-Pc), annealed p-Pc (200 °C for 20 min), and poly(dioctylfluorene-alt-benzothiadiazole) (F8BT) as a reference for the PL yield. Low PL from annealed p-Pc indicates efficient singlet exciton fission. (b) Transient optical absorption ($\Delta T/T$) spectra, exciting at 530 nm and averaging the probe response in the indicated time interval. The ground state bleach (GSB), stimulated emission (SE), and triplet exciton photoinduced absorption (T_1 PIA), originating from the excitation population, the singlet exciton and triplet excitons, respectively, are highlighted. (c) Temporal evolution of $\Delta T/T$ amplitude averaged over the indicated spectral region (top right) of GSB, SE as well as T_1 PIA. Singlet exciton fission is as fast (83 fs) and as efficient in annealed p-Pc as in e-Pc. The generated triplets have similar lifetimes (ca. 5 ns).

lowest-energy GSB of the annealed p-Pc is red-shifted by 12 nm compared to e-Pc, as expected from the shift in absorption shown in Figure 2(b).

We first consider the singlet and triplet dynamics in Figure 3(c) where the evolution of the signal amplitude over time is averaged over the spectral regions of GSB, SE, and T_1 PIA. Both e-Pc and annealed p-Pc show a rapid decay of the SE and simultaneous rise in T_1 PIA with a time constant of 83 ± 7 fs for e-Pc and 78 ± 14 fs for annealed p-Pc (see Fig. S8 of the [supplementary material](#)). Since there is no indication for an additional loss in singlet excitons before fission occurs, we argue that the identical signal rise characteristics of the T_1 PIA are indicative of similar SF properties in both samples. Note that previous measurements on e-Pc have shown SF yields close to 200%,^{5,8} indicating that the SF yield is similarly high in annealed p-Pc. Furthermore, the SF rate seems to be stable within the range of molecular packing distances characterized here (i.e., a 1 Å variation in lattice spacing and 0.1 Å variation in $\pi - \pi$ stacking), supporting recent results questioning the necessity of distinct molecular arrangements to drive efficient SF.²⁸ Additionally, the similar kinetics on the ns timescales suggest that the triplet states produced in both e-Pc and p-Pc decay with similarly long lifetimes of 5.0 ± 0.5 ns (see Figure S9 of the [supplementary material](#) for detailed analysis). The lifetime is in agreement with previous measurements²⁹ on e-Pc and indicates that there are no extra pathways for triplet exciton quenching in the annealed p-Pc compared to e-Pc. It is interesting to note that while TIPS pentacene has shown fast singlet fission, high process quantum yields, and moderately long-lived triplet states (80–1 ps, 144% and 125 ps, respectively),^{11,30} these figures of merit are significantly worse compared to the solution processable precursor route discussed here, thereby underlying the potential of p-Pc for operational solar cells.

In summary, we show complete conversion of films of the soluble pentacene precursor p-Pc into molecular pentacene and analyze their micromorphology in the solid-state. Ultrafast transient absorption measurements indicate identical SF characteristics in both the converted precursor p-Pc and e-Pc films. Our results widen the scope for future optoelectronic devices by enabling solution processability for otherwise insoluble acene-based semiconductors, while retaining their unique properties such as SF and high thin film mobilities—a combination which has the potential for an efficient integration of the SF mechanism into solar cells operating beyond the Shockley-Queisser limit.

See [supplementary material](#) for detailed film and device fabrication methods, additional absorption-, X-ray and photoluminescence spectra as well as AFM images and solar cell characterization data.

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