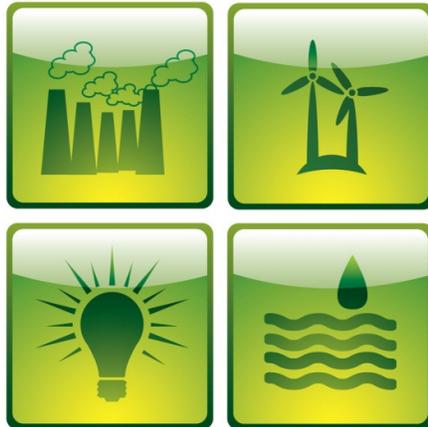




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# E-Futures

Mini-project report

## Preparation of a new electron acceptor for use in plastic solar cells

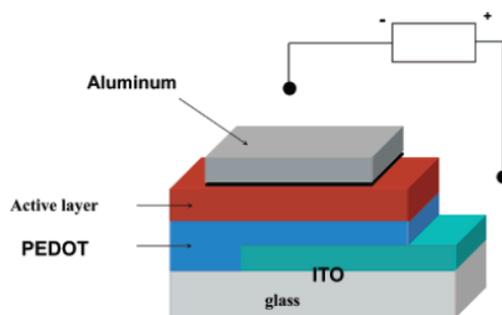
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## Background

The conversion of solar radiation into electricity is an attractive concept, especially given the likelihood of a carbon constrained future. Current efficiencies of different technologies vary: multi junction (34%), crystalline silicon (25%) and organic thin film (10%), but the attractiveness of each is not solely dictated by their efficiency.<sup>[1]</sup> Factors such as the financial and energetic cost of manufacture, material availability and device lifetime must also be considered.

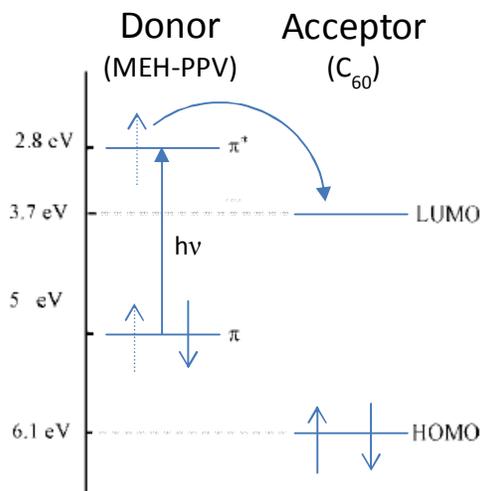


**Fig. 1** – Schematic of bulk heterojunction device structure. The active layer is usually composed of a conjugated polymer donor and a fullerene acceptor.<sup>[2]</sup>

Organic photovoltaics (OPVs) differ from most other types of solar cell because the active layers are made from carbon based molecules instead of silicon or other inorganic semiconductors. This allows solution processing techniques such as spin-coating, doctor blading, screen printing and inkjet printing to be employed, as most polymers are too large for vacuum deposition and decompose at high temperatures. This is a major advantage, as not only are these techniques up-scalable, but they are also less energy intensive than the methods current used in construction or most inorganic devices.<sup>[2]</sup> However, being a relatively new technology OPVs are not without their problems; their absorption spectrums tend not to overlap well with the solar spectrum, excitons have a large binding energy ( $\sim 0.4$  eV), there are high rates of charge recombination, and devices have poor stability (due to  $O_2$ , high temp, UV light degradation).<sup>[3]</sup>

Bulk heterojunction solar cells (Fig. 1) typically contain two phases, a conjugated polymer and a fullerene, as well as two electrodes, a high workfunction metal (eg. ITO) to collect holes and a low workfunction metal (eg. Aluminium) to collect

electrons.<sup>[4]</sup> The process by which they can convert light into electricity is as follows: A photon is absorbed by the conjugated polymer causing exciton formation, this exciton has a limited time to diffuse to a donor-acceptor interface, where charge separation can occur (Fig. 2), and the respective electron and hole (prevented from recombination by being in different materials) can then be conducted to the electrodes.<sup>[2]</sup>



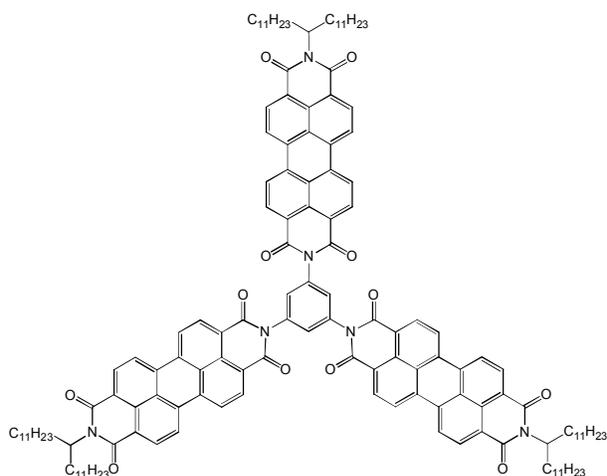
**Fig. 2** – Schematic of the energy levels at a heterojunction; showing exciton formation in the donor and subsequent electron transfer to the acceptor.<sup>[4]</sup>

The donor and/or the acceptor must possess several key properties for the device to function efficiently. Firstly, good light absorption coinciding well with the solar spectrum is required by one or both materials. Since  $C_{60}$  is poor at this it is generally the conjugated polymer layer where light is absorbed creating excitons. However this need not necessarily be the case, with acceptors such as  $C_{70}$  and perylene diimines (PDIs) also having visible absorptions. Secondly, the distance from exciton formation to donor-acceptor interface must be minimised. Polymers and organic semiconductors usually have exciton diffusion lengths of around 10-20 nm,<sup>[5]</sup> so further than this and the exciton is likely to decay. On a device architecture level, increasing the interface between donor and acceptor, and therefore reducing the exciton diffusion distance, is the major benefit of the bulk over the bilayer heterojunction. However, the phase separation of donor and acceptor in a bulk heterojunction must also be correct. Too high and many excitons will

decay before reaching an interface; too low and more pockets will be isolated from their electrode by the other phase. Thirdly, there must be an energetic driving force from donor to acceptor for charge separation to be favourable. But also the energy gap should not be too large as this will reduce device efficiency. Finally, both the donor and acceptor must have sufficient electron mobility to conduct their respective holes and electrons to their electrodes before recombination occurs.

### Why PDIs?

Simple PDIs have similar electron affinity to fullerenes (0.39 eV<sup>[6]</sup> and 0.37 eV<sup>[4]</sup> respectively) and higher electron mobility. Importantly they also have better absorption profiles allowing exciton formation to occur in the PDI phase, and subsequent charge separation to occur by electron donation from the HOMO of the acceptor by the donor. However, despite these advantages, devices using C<sub>60</sub> derivatives, such as PCBM, as the electron acceptor consistently outperform those using PDIs. This is thought to be due to self-trapping of excitons by strongly aggregated PDI regions lowering their efficacy. However, increased control over PDI morphology is likely to be possible due to the many combinations of *peri*-, *bay*- and *ortho*-functionalisation that can be carried out.<sup>[7]</sup>



**Fig. 3** – 1,3,5-tri(N-(12-tricosanyl)-perylene-3,4:9,10-bis(dicarboximide))benzene (**1**)

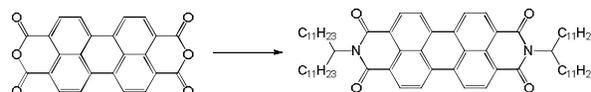
It is with this in mind that the synthesis of (**1**) (Fig. 3) was undertaken, with the aim of obtaining pure material (on the 10s of mg scale) to allow

investigation of its liquid crystal properties and its incorporation into OPV devices. It is also noted that different alkyl groups could be incorporated to modify its properties further.

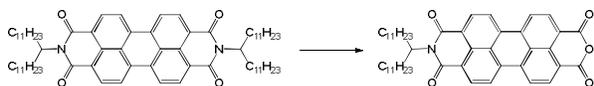
### Experimental



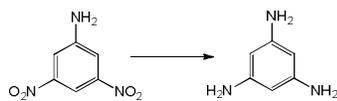
Synthesis of **1-Undecyldodecylamine**.<sup>[6]</sup> [COSHH ID: SH4711] A solution of ammonium acetate (20 g, 259 mmol) and sodium cyanoborohydride (1.6 g, 25.5 mmol) in methanol (100 mL) was poured into a solution of 12-tricosanone (8.9 g, 26.3 mmol) in THF (220 mL). This mixture was stirred for 66 hours at room temperature before conc. HCl (4 mL) was added dropwise. The mixture was concentrated followed by addition of THF (40 mL) and H<sub>2</sub>O (500 mL). The pH of the water phase was adjusted to approx. pH 10 with KOH flakes and the dispersion extracted with CHCl<sub>3</sub> (150, 100, 100 mL). The collected organic phases were dried with magnesium sulphate, filtered and concentrated to obtain a pale yellow oil that was cooled and crystallised to a white solid (8.46 g, 24.9 mmol, 96 % yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.9 (t, 6H), 1.2-1.3 (m, 40H), 2.7 (br s, 1H).



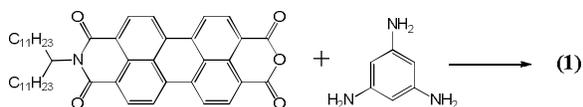
Synthesis of **N,N'-Bis(12-tricosanyl)-perylene-3,4:9,10-bis(dicarboximide)**.<sup>[7]</sup> [COSHH ID: SH4712] A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (1.33 g, 3.4 mmol), 1-undecyldodecylamine (2.9 g, 8.5 mmol) and imidazole (10 g, 147 mmol) was heated to 140°C. After 4 hours the solution [reaction mixture] was cooled down to room temperature and the red solid was dispersed in ethanol (100 mL). 2M HCl (300 mL) was added and the mixture stirred overnight. The red precipitate was broken up using a spatula, filtered, washed with H<sub>2</sub>O until the washing was neutral and dried under vacuum for 6 hours at 100°C. The crude product was further purified by column chromatography on silica gel (100% CHCl<sub>3</sub>), concentrated and dried under high vacuum (2.55 g, 2.52 mmol, 75 % yield). The product gave a single spot on TLC (R<sub>f</sub> = 0.82, 100% chloroform). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.9 (t, 12H), 1.1-1.3 (m, 72H), 1.8-2.0 (m, 4H), 2.2-2.4 (m, 4H), 5.2 (m, 2H), 8.7 (m, 8H).



Synthesis of **N-(12-tricosanyl)-perylene-3,4-dicarboxyanhydride-9,10-dicarboximide (2)**.<sup>[8]</sup> [COSHH ID: SH4715] A mixture of N,N'-Bis(12-tricosanyl)-perylene-3,4:9,10-bis(dicarboximide) (2.99g, 2.88 mmol) in t-BuOH (29 mL) was heated to 89°C before freshly ground KOH (0.684 g, 12.2 mmol) was added. The solution was stirred for 1h 30min before it was cooled down to room temperature to add 10% HCl (7.5 mL) slowly under stirring. After 40 min, 10% HCl (67.5 mL) was added again and the mixture extracted with CHCl<sub>3</sub>. The organic fractions were washed with water until the washing was neutral, dried and then concentrated. The crude product was purified by flash vacuum chromatography on silica gel (99% CHCl<sub>3</sub> / 1% acetic acid) to obtain pure product (0.41 g, 0.577 mmol, 20% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.9 (t, 6H), 1.1-1.4 (m, 36H), 1.8-2.0 (m, 2H), 2.2-2.4 (m, 2H), 5.2 (m, 1H), 8.7 (m, 8H).



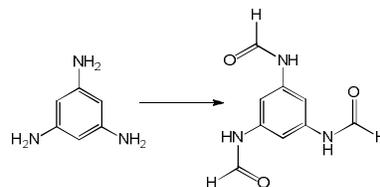
Synthesis of **1,3,5-triaminobenzene**.<sup>[9]</sup> [COSHH ID: SH4792] 3,5-Dinitroaniline (4.95 g, 27.0 mmol) was hydrogenated in THF (100 mL) in the presence of Pd/C (0.15 g) under hydrogen atmosphere (5 atm), room temperature, 24 hours. After filtration, the filtrate was concentrated to dryness by evaporation under reduced pressure to give the product in 91% yield (3.01 g, 24.4 mmol). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 3.5 (br s, 6H), 5.5 (s, 3H).



Synthesis of **1,3,5-tri(N-(12-tricosanyl)-perylene-3,4:9,10-bis(dicarboximide))benzene**.<sup>[10] [11]</sup> [COSHH ID: SH4824] N-(12-tricosanyl)-perylene-3,4-dicarboxyanhydride-9,10-dicarboximide (120 mg, 0.174 mmol), 1,3,5-triaminobenzene (47 mg\*, 0.38 mmol), imidazole (0.8 g) and Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (½ micro spatulum) were heated for (5 hours) under nitrogen at 185 °C. The product mixture was cooled to room temperature, diluted with ethanol (5 mL) and 2 M HCl (20 mL), dispersed and stirred for 2 hours. The crude product was collected by vacuum filtration (D4 glass filter), wash with H<sub>2</sub>O until

neutral and dried in air. Pure product was not isolated.

\***Note:** This should have been 4.7 mg to give desired 1:4 ratio of reactants. 1,3,5-triaminobenzene was highly hygroscopic making handling difficult.



Synthesis of **1,3,5-triaminobenzene-tris-formamide**.<sup>[11] [12]</sup> [COSHH ID: SH4940] 1,3,5-triaminobenzene (1.05 g, 8.5 mmol) was dissolved in con. Formic acid (5 mL) and stirred under reflux for 4 hours. Diethylether (20 mL) was added to the cooled solution, decanted and the remaining residue washed with ethanol (2x 50 mL). The crude product was collected by vacuum filtration and dried under vacuum for 4 hours at 40°C (1.20 g)

## Discussion

The three reactions up to the formation of **(2)** had adequate yields and purity's, verifying repeatability of the literature methods. NMR provides a method of quantifying the 12-tricosanone impurity in 1-Undecyl-dodecylamine, using the integrations of the proton closest to the amine functionality δ<sub>H</sub> 2.7(s) and the four closest to the ketone δ<sub>H</sub> 2.4(t). This suggests 7% 12-tricosanone impurity which, although undesirable, should not affect the following reactions.

However, attempts to isolate **(1)** by column chromatography on silica gel were unsuccessful. TLC (82% chloroform, 10% ethanol, 5% Ethyl acetate, 3% acetic acid) of crude **(1)** gave four distinct pink spots (R<sub>f</sub> = 0.45, 0.66, 0.79, 0.87). Using this solvent combination the mono- and di-substituted 1,3,5-triaminobenzene were isolated, identified by MALDI mass spectroscopy, and gave a single spot on TLC (R<sub>f</sub> = 0.45 and 0.66 respectively). The R<sub>f</sub> of 0.87 is consistent with that of the starting material **(2)**, suggesting **(1)** may have an R<sub>f</sub> of 0.79. It is possible that the incorrect ratio of starting materials was responsible for the incomplete substitution of 1,3,5-triaminobenzene. However, significant presence of unreacted starting material does not support this, and another possibility is the oxidation of the 1,3,5-triaminobenzene. This oxidation sensitivity of

electron rich aromatic amines is a common problem and the formamide of 1,3,5-triaminobenzene, which should have similar reactivity with the acid anhydride, may be a better approach than using 1,3,5-triamino benzene directly.<sup>[12]</sup> For this reason the synthesis of 1,3,5-triaminobenzene-trisformamide was attempted, but its NMR (in  $d_6$ -DMSO) contained many unassigned peaks, suggesting a high level of impurity. There are differing procedures for the formylation of triaminobenzene and it is possible that others may give better results. However, it is unclear whether the formylation or preceding hydrogenation reaction is responsible for the mixture of products observed. Although the NMR of 1,3,5-triaminobenzene showed only solvents peak impurities, the solid was only sparingly soluble in  $CDCl_3$  so it is possible that any impurities did not dissolve. This is another possible reason for the incomplete substitution of 1,3,5-triaminobenzene, and should be the first point of investigation in any further work.

During the hydrogenation reaction  $H_2$  consumption caused the pressure to repeatedly drop below 5 atm, the apparatus used requiring manual control of  $H_2$  injection. Increasing the initial pressure to 30 atm would leave a residual pressure of over 5 atm at the end of the reaction, and should be considered if conducting this step again.

## Conclusions

Although the desired product was not isolated, this work has verified the reliability of some literature procedures and highlighted problems with others. Further investigation should focus on the verifying the success of the hydrogenation and formylation steps, which if successful should enable a reliable synthesis of **(1)**.

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