VII Cyclic Voltammetry of Fullerene Derivatives and Bilayer Devices

It is known that the V_{oc} in polymer/fullerene composite solar cells is limited by the difference between the HOMO of the polymer species (HOMO_{donor}) and the LUMO of the fullerene species (LUMO_{acceptor})^{1,2,3}. Therefore, increasing the HOMO_{donor} – LUMO_{acceptor} separation is a powerful strategy for improving photovoltaic efficiency. In this chapter, cyclic voltammetry is used to assess the ability of a range of fullerene derivatives to increase the donor-acceptor offset. Two candidates, bis-thienyl C₆₁ butyric acid methyl ester (bis-ThCBM), and Er₃N@C₈₀ are then incorporated into basic bi-layer devices, with bis-ThCBM showing significant promise.

VI.I Introduction

Determining the LUMO level of any candidate fullerene derivative is a useful way of screening its applicability before inclusion in a photovoltaic device. The commonly used technique for this is cyclic voltammetry (C-V). In cyclic voltammetry, a dissolved species of interest, in this case a fullerene derivative, is oxidised or reduced via the application of a triangular voltage waveform within a three electrode system. Further information about the technique is presented in Chapter 3. A typical cyclic voltammogram reveals oxidation and reduction peaks which can be compared to voltammograms from other fullerene derivatives

in order to determine relative differences in their electron affinities and therefore their LUMO levels. This is quantified by calculating the mid-point of the first reduction peak couple, which is calculated as the mean of $E_P{}^A$ and $E_P{}^C$; the peak potentials observed during the reverse voltage sweep and forward voltage sweep respectively. Despite the fact that the C-V experiment is solution based, it has been shown to be effective in predicting enhancements in the V_{oc} of solid state polymer fullerene photovoltaic devices.⁴

VI.II Fullerene Species of Interest

A range of fullerene derivatives were investigated for this work and their chemical structures are presented in Figure 2. The redox behaviour of C_{60} has been previously studied by non-aqueous solution-based cyclic voltammetry⁵ and was included in our analyses to provide an additional reference potential. N@C₆₀ is an endohedral fullerene derivative that is used extensively in electron spin resonance experiments for quantum information because it gives a very long lived electron paramagnetic resonance signal⁶. To date, it is difficult to predict how a given endohedral chemistry will affect the fullerene LUMO level. Tri-metallic nitride endohedral fullerenes have been shown to donate multiple electrons to the fullerene cage, significantly raising the lowest unoccupied molecular orbital. ⁷ As such, N@C₆₀ was investigated here to see if the endohedral nitrogen has any effect by itself on the fullerene LUMO. PC₆₁BM has been used extensively in photovoltaics with P3HT, achieving a V_{oc} of 0.58 – 0.64V.^{8,9,10,11} It is measured here to provide a reference against which the potential V_{oc}s of other fullerene derivatives could be compared. PC₆₁BM-d₅ was measured to determine if the deuteration of the benzene ring has any effect on the first reduction potential. C₇₀ was

measured in order to allow comparison to C_{60} . One could expect the reduced symmetry of the C_{70} cage to significantly affect its electrochemical behaviour. The C_{70} cage is more strained than C_{60} and should experience greater strain relief upon accepting an electron, which would tend to increase C_{70} 's LUMO. Conversely, if C_{60} can be considered to be a spherical superbenzopyracylene (Figure 1), C_{70} has fewer pyracylene bonds than C_{60} which should act to reduce C_{70} 's LUMO.



Figure 1. Pyracylene (left) and benzopyracylene (right)

Similarly PC₇₁BM was measured in order to compare with PC₆₁BM. Bis-ThCBM was measured in order to determine the effect of the second butyric acid methyl ester group. The addition of an exhohedral addend requires the breaking of a double bond on the fullerene cage. This leads to an increased localization of the electron distribution which should raise the fullerene LUMO. $Er_3N@C_{80}$ is an endohedral metallofullerene consisting of a planar, tri-erbium nitride cluster enclosed in an otherwise unstable C_{80} fullerene. As previously mentioned, trimetallic nitride molecules have been shown to donate multiple electrons to the fullerene cage, however only lutetium based TNEFs have thus far been investigated for use in photovoltaics¹². The promising results of that work, whereby P3HT based devices incorporating $Lu_3N@C_{80}$ exhibited an increased V_{OC} , motivates the investigation of $Er_3N@C_{80}$ presented herein.



Figure 2. Chemical structures of fullerene derivatives investigated by cyclic voltammetry: a) C_{60} , b) $N@C_{60}$, c) $PC_{61}BM$, d) $PC_{61}BM$ - d_5 (5 carbons on the benzene ring are deuterated) e) C_{70} , f) $PC_{71}BM$, g) bis-Th $C_{61}BM$, h) $Er_3N@C_{80}$

All cyclic voltammetry measurements were conducted using an Ivium Compactstat potentiostat at a scan rate of 50 mV/s and were carried out under a constant argon purge. The fullerene solutions contained a solvent mixture of 4:1 (by volume) acetonitrile:orthodichlorobenzene with 0.1 M (NBu)₄BF₄ as the dissolved electrolyte. The fullerene concentrations used were all approximately 0.1 mg/mL (Table 1). A glassy carbon working electrode (7.1 mm²), platinum mesh counter electrode and a non-aqueous Ag/Ag⁺ reference electrode were used. In between measuring each compound, the working electrode was polished with 0.05 μ m γ -alumina to a mirror finish, rinsed with deionized water then sonicated in fresh deionized water for 15 minutes, with the water changed at five minute intervals. As the half cell potential of the reference electrode can drift over time and is influences by the surrounding solution, it is common practice to present all C-V results relative to an internal standard such as ferrocene. In practice, this involved adding ferrocene to the fullerene solution after the C-V response was measured, before recording a second C-V curve which revealed the Ferrocene peak (Figure 3).



Figure 3. Cyclic voltammogram of C_{60} with added ferrocene. The fullerene redox couples are seen on the left side of the graph, below V = 0, while the ferrocene couple is centred at approximately 0.45V.

Errors reported in the redox potential mid-points stem from the variation observed between multiple (typically three or four) C-V curves measured on separate days with separately prepared solutions.

	mg/mL	Mol. Weight, g/mol	mmol/mL
C ₆₀	0.1	720.64	1.39E-04
N@C ₆₀	0.1	734.65	1.36E-04
C ₇₀	0.1	840.75	1.19E-04
PC ₆₁ BM	0.1	910.88	1.10E-04
$PC_{61}BM-d_5$	0.1	915.91	1.09E-04
PC ₇₁ BM	0.1	1030.99	9.70E-05
bis-ThC ₆₂ BM	0.1	1113.16	8.98E-05
Er ₃ N@C ₈₀	0.1	1476.64	6.77E-05

Table 1. Fullerene mass concentrations, molecular weights and molar concentrations of the solutions used in the C-V experiments.

VI.III Cyclic Voltammetry of Fullerene Derivatives

To start with, it is important to recognize that the convention used in this work is that a more negative bias represents a greater driving force for reduction and that a negative current represent a reductive current flow. As all species investigated here are fullerene derivatives it is informative to discuss the electrochemistry of C_{60} , which has been well studied. C_{60} has been shown to have 6 reversible electron transfers, when measured at -10°C, and previously published values for both C_{60} and C_{70} are presented in Table 2.⁵

	C ₆₀	C ₇₀
LUMO	-0.98	-0.97
LUMO+1	-1.37	-1.34
LUMO+2	-1.87	-1.78
LUMO+3	-2.35	-2.21
LUMO+4	-2.85	-2.7
LUMO+5	-3.26	-3.07

Table 2. Published reduction mid-point potentials for C_{60} and C_{70} .⁵ 1:5.4 acetonitrile:toluene solution with 0.1M TBAPF₆ as electrolyte. Fullerene concentrations of 4 – 8 x 10⁻⁴ M. Scan rate of 100mV/s. Measurements taken at -10°C under high vacuum using a 3mm diameter glassy carbon working electrode, platinum counter electrode and silver wire as a pseudo reference.

Figure 4 presents a characteristic cyclic voltammogram for C_{60} , measured as part of this investigation. A total of four reversible oxidation and reduction peaks are visible, before solvent breakdown at -2.55 V (vs. Fc/Fc⁺) obscures the final two. The minima in the lower half of the graph represent reduction events, where electrons are being added to the fullerene LUMO while the maxima present in the upper half of the graph represent oxidation events, with each maximum representing the removal of a single electron from the fullerene. The first reduction couple mid-point, which is the potential at which the first electron is added to the fullerene cage, corresponds to the fullerene LUMO and is indicated by the vertical line at -1.04V. It is calculated by taking the average of the potentials that correspond to the redox current maxima and minima for the rightmost redox couple. Values for the subsequent reduction couple mid-points are presented in Table 3. A movement of the first reduction couple mid-point to more negative values indicates an increase in the fullerene LUMO level. Further details regarding the theory of cyclic voltammetry can be found in Chapter 3.



Figure 4. Voltammogram of C_{60} vs. Ferrocene (Fc/Fc⁺) reference. The first reduction couple mid-point is indicated by the vertical line. The C_{60} concentration is 0.1 mg/mL. The solvent consisted of 4:1 dichlorobenzene:acetonitrile, 0.1M (NBu)₄BF₄ as electrolyte. 7.1 mm² glassy carbon working electrode. Scan rate: 50mV/s.

Figure 5 presents the voltammograms of all the fullerene derivatives investigated with their associated first reduction couple mid-points. Starting on the right hand side, it is clear that C_{60} , N@ C_{60} and C_{70} all exhibit very similar mid-points. The first reduction mid-point potential of C_{70} is slightly more negative than that for C_{60} (-1.06 ± 0.01V vs. -1.04 ± 0.01V) and the values match well with those found in the literature (2), although variations in experimental conditions, especially the solvent system and temperature will cause slight variations in their peak potentials and even their relative magnitudes.

Similarly for N@C₆₀, there is a neglible difference in the first reduction mid-point potential compared to C_{60} , which will most likely prove to be negligible in a photovoltaic device. It is clear that the inclusion of only nitrogen within the fullerene core has very little effect on the fullerene LUMO level. This suggests that it is the inclusion of the rare earth metal that is the key component for raising the fullerene LUMO in endohedral metallofullerenes.

Compared to C_{60} , the first and subsequent reduction mid-point potentials of $PC_{61}BM$ are clearly more negative, indicating that $PC_{61}BM$ possesses a higher LUMO and this is one of the reasons that $PC_{61}BM$ yields a higher V_{0c} than C_{60} when incorporated into polymer based solar cells. As shown in Table 3, the first reduction peak mid-point of $PC_{61}BM C_{60}$ is $0.09 \pm 0.04V$ more negative than C_{60} . This should correspond directly to a difference in V_{0c} in a heterojunction solar cell, and this is investigated in section VI.IV. The raised LUMO is caused by the addition of the butyric acid addend which requires the breaking of a double bond on the fullerene cage.^{13,14} This causes the fullerene electron distribution to become more localised, raising the LUMO level. The effect is analogous to the rise in LUMO level observed in alkenes as one moves from poly(acetylene) down to ethylene.¹⁵



Figure 5. Voltammograms of all the fullerene derivatives investigated vs. Ferrocene (Fc/Fc⁺) reference. Vertical lines represent first reduction couple mid-points. All fullerene solutions are apporximately 0.1 mg/mL, except for $Er_3N@C_{80}$ which was 1mg/mL. The solvent consisted of 4:1 dichlorobenzene:acetonitrile, 0.1M (NBu)₄BF₄ as electrolyte. 7.1 mm² glassy carbon workig electrode. Scan rate: 50mV/s.

	LUMO	LUMO+1	LUMO+2	LUMO+3
C ₆₀				
$E_m vs Fc/Fc^+$ (V)	-1.04 ± .01	-1.41 ± .01	-1.87 ± .01	-2.33 ± .01
ΔE (V)	0.07 ± .01	0.06 ± .01	0.08 ± .01	0.08 ± .01
N@C ₆₀				
$E_m vs Fc/Fc^+$ (V)	-1.04 ± .02	-1.43 ± .01	-1.88 ± .01	-2.34 ± .01
ΔE (V)	0.07 ± .01	0.07 ± .01	0.08 ± .01	0.08 ± .01
C ₇₀				
$E_m vs Fc/Fc^+$ (V)	-1.07 ± .01	-1.39 ± .01	-1.90 ± .01	-2.36 ± .01
ΔΕ (V)	0.08 ± .01	0.12 ± .01	0.08 ± .01	0.08 ± .01
PC ₆₁ BM				
$E_m vs Fc/Fc^+$ (V)	-1.14 ± .03	-1.51 ± .02	-2.01 ± .02	-2.45 ± .03
ΔΕ (V)	0.07 ± .01	0.06 ± .01	0.06 ± .01	0.07 ± .01
$PC_{61}BM-d_5$				
$E_m vs Fc/Fc^+$ (V)	-1.12 ± .01	-1.50 ± .01	-2.00 ± .01	-2.43 ± .01
ΔE (V)	0.07 ± .01	0.06 ± .01	0.07 ± .01	0.07 ± .01
PC ₇₁ BM				
$E_m vs Fc/Fc^+$ (V)	-1.14 ± .01	-1.50 ± .01	-1.89 ± .01	-2.30 ± .01
ΔE (V)	0.07 ± .01	0.07 ± .01	0.07 ± .01	0.07 ± .01
Bis-ThC ₆₂ BM				
E_m vs Fc/Fc ⁺ (V)	-1.25 ± .02	-1.61 ± .03	-2.21 ± .03	
ΔE (V)	0.12 ± .01	0.11 ± .01	0.11 ± .01	

Table 3. First and subsequent reduction potential mid-points and peak separations for all the fullerenes investigated

As expected, given the electrochemical similarity of C_{60} and C_{70} , $PC_{71}BM$ exhibits a first reduction mid-point very close to that of $PC_{61}BM$. (-1.14 ± 0.1V versus -1.14 ± 0.03V). As a result, solar cells incorporating these materials have been shown to have almost identical $V_{OC}s^{16,17}$. Deuterated $PC_{61}BM$ also shows no significant difference to $PC_{61}BM$, despite the fact that the deuterated benzene should be slightly more electronegative. The lack of an observable effect supports the hypothesis that it is the saturation carbon bonds on the fullerene cage, not the chemical makeup of the addend itself, which drives the change in LUMO level.

Bis-Th₆₂CBM is the first of the fullerene derivatives tested to exhibit a significant improvement over PC₆₁BM with a first reduction peak mid-point of -1.22 \pm 0.02 V vs. -1.14 \pm 0.03V. This is similar to the LUMO increase observed for bis-PC₆₂BM⁴, further supporting the idea that the chemical structure of the addend itself does not affect the LUMO. The result suggests that bis-ThC₆₂BM should be highly effective in raising the V_{oc} in a bulk heterojunction solar cell. In addition, it indicates a potentially effective direction of research for future endohedral fullerene targets. Endohedral fullerene chemistry may benefit from the minimization of the second, third or even fourth addend as their only necessary function is to saturate a double bond on the fullerene cage. Adequate miscibility should be provided by a single butyric acid methyl ester, while subsequent addends could feasibly be as small as a methylene group.

The voltammogram of $Er_3N@C_{80}$ differs significantly from those of the other fullerene derivatives tested, and its interpretation is more difficult. Instead of four highly reversible redox couples we see only irreversible redox behaviour, similar to results published for $Lu_3N@C_{80}$.¹² Manipulation of the scan rate from 0.2 Vs⁻¹ up to 200 Vs⁻¹ did not affect the reversibility of the redox peaks and a higher fullerene concentration of 1 mg/mL was necessary in order to observe discernable redox peaks. The molecular weight of $Er_3N@C_{80}$

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(1170.15 gmol⁻¹) is only slightly greater than bis-ThC61BM (1101.12gmol⁻¹) so the increased concentration by mass also indicates a significantly increased molar concentration. As can be seen, the reduction onset is significantly reduced in $Er_3N@C_{80}$, occurring at -1.32V. This is the lowest reduction onset observed for any of the fullerene derivatives investigated and makes $Er_3N@C_{80}$ a promising candidate for an enhanced V_{OC} solar cell.

The first reduction mid-point potentials of the fullerenes discussed above are summarized in Figure 6 below.



Figure 6. First reduction peak mid-points of the fullerene derivatives under investigation

VI.IV Bi-layer Solar Cells

The C-V results suggest that bis-Th₆₂CBM and $Er_3N@C_{80}$ should both show improved V_{oc} in heterojunction solar cells, relative to PC₆₁BM. To confirm this, all of the fullerene derivatives

were incorporated into bi-layer photovoltaic devices with P3HT. Bi-layer devices were fabricated in a similar manner to that outlined in Chapter 2. ITO coated glass substrates were cleaned in 0.5% detergent solution, deionised water, acetone and propanol before being dried over night in a vacuum oven. A layer of PEDOT:PSS was then spin cast at 5000 rpms before being heat treated in air at 140°C for 10 minutes. The substrates were then transferred to an oxygen and moisture free glovebox where a 50 nm thick layer of P3HT was spin cast from a 10 mg/mL chlorobenzene solution, at 800 rpm. A fullerene film was then deposited by thermal evaporation under vacuum (base pressure of 5 x 10^{-7} torr) before a 70nm thick top electrode of Aluminium was deposited, also by thermal evaporation. The devices were then annealed at a range of temperatures from 150°C to 220°C in order to maximise the V_{oc}.

A bi-layer architecture with an evaporated fullerene film was necessary due to the relative insolubility of some of the derivatives such as C_{60} , $N@C_{60}$, C_{70} and $Er_3N@C_{80}$. In addition, this architecture has the advantage of a relatively simple morphology, compared to a bulk heterojunction cell. This allows for direct comparisons between devices without the complication of trying to account for differences in phase separation between the different materials

Figure 7 presents the V_{oc} values for the fabricated devices. It is clear that the trend in V_{oc} is very similar to that of the first reduction potential mid-points, with distinct differences between the bare, mono-adduct and bis-adduct fullerene derivatives. Within each grouping,

slight differences observed in the reduction mid-point values are virtually indistinguishable in the V_{oc} results. The V_{oc} of 0.79V obtained with bis-ThCBM is one of the highest yet obtained in a P3HT:fullerene based, single-junction solar cell, and the highest excluding metallofullerenes.¹²



Fullerene Derivative

Figure 7. Voc values for P3HT:fullerene bi-layer devices

Interestingly, all of the devices incorporating Er₃N@C₈₀ exhibited very poor photovoltaic function, with a V_{oc} of 0.12V and a short circuit current of 0.23 \pm 0.031 \pm 0.05 mA/cm². A characteristic I-V curve is presented in Figure 8. A number of annealing regimes were investigated, included annealing above the P3HT melting point, in order to induce penetration of the fullerene into the P3HT layer, but none yielded positive results.



Figure 8. Typical J-V curves for a P3HT: Er₃N@C₈₀ bi-layer solar cell

It is unlikely that the absence of photovoltaic activity is due to the $Er_3N@C_{80}$ LUMO being too high to provide an adequate driving force for exciton dissociation. The C-V results show that the first reduction mid-point potential of $Er_3N@C_{80}$ is -1.32eV, indicating that the LUMO level is 0.19 eV higher than $PC_{61}BM$, well within the 0.8 eV limit discussed in Chapter 3. Solubilised metallofullerenes containing lutetium have been successfully used as acceptor molecules in polymer:fullerene photovoltaics and have been reported with first reduction mid-points as low as -1.5 V.

Moving from left to right across Figure 7, the fullerene derivatives become increasingly difficult to evaporate, in that they required greater current before a film began to register on the quartz thickness monitor. This is most likely due to increased bond interactions caused by the addition of the addends and the endohedral erbium. The bare fullerenes, C_{60} , $N@C_{60}$ and C_{70} , evaporated easily to form films on the order of 50 – 100nm thick. The exohedral fullerenes, $PC_{61}BM$, $d5-PC_{61}BM$, $PC_{71}BM$ and bis-ThCBM evaporate more slowly and required

greater current, but still produce films that are photovoltaic. $Er_3N@C_{80}$ was the most difficult of all to evaporate with the deposited film measuring only 17nm in thickness. It is possible that the fullerene may have been chemically altered by the evaporation process. Alternatively, the $Er_3N@C_{80}$ may have evaporated intact and there may be something intrinsic to the molecule that prevents photovoltaic activity. C_{80} is not a stable cage structure by itself so we were unable to investigate the effectiveness of the empty cage in a solar cell and photoluminescence (PL) quenching experiments of P3HT; $Er_3N@C_{80}$ solutions were ruled out due to the very poor solubility of $Er_3N@C_{80}$.

In accordance with the theory that V_{OC} is proportional to the HOMO_{donor} – LUMO_{acceptor} offset, a plot of V_{OC} versus the first reduction mid-points should yield a straight line with a gradient of unity. Such a graph is presented in Figure 9.



Figure 9. First reduction potential mid-point vs. $V_{oc}s$ for the fullerene derivatives. Blue diamonds represent thermally evaporated bi-layer devices. Red circles represent solution processed bulk heterojunction devices. The dotted trend line has a gradient of 1 and is included as a guide to the eye.

The expected trend is evident for the right hand side of the graph, dealing with the exohedral mono and bis-adduct fullerenes. However, the bare fullerenes fall significantly below the trend line. These results match those obtained with solution processed devices, also shown in Figure 9, suggesting that the result is not due to the fabrication process. It appears that there are additional factors limiting the V_{oc} in devices containing bare fullerenes. One contributing factor could be that the bare fullerenes allow better packing in the polymer, which would increase the polymer conjugation length and raise the polymer HOMO, leading to a reduced V_{oc} .¹⁸

VI.V Conclusions

In conclusion, a range of bare, exohedral, and endohedral fullerene derivatives have been assessed for the ability to achieve an increased V_{oc} in polymer heterojunction solar cells. Cyclic voltammetry experiments indicated that both bis-ThC₆₂BM and Er₃N@C80 as promising targets in this regard and that for exohedral modification, it is the breaking of double bonds on the fullerene cage that drive the increase in LUMO level. This presents an interesting and synthetically achievable target for further rational modifications of exhohedral fullerenes. Since only one butyric acid methyl ester addend is required in order to achieve a suitable level of solubility, subsequent addends should ideally be as small as possible, as their sole role is to saturate a bond on the fullerene cage. Bi-layer photovoltaic devices were fabricated to verify this potential but interestingly, devices containing $Er_3N@C_{80}$ exhibited no photovoltaic response. Solar cells containing bis-Th₆₂CBM , on the other hand, exhibited significantly higher V_{oc} s, and showed shifts equal to the shift in electron affinity predicted by C-V. As a result P3HT:bis-ThC₆₁BM bulk heterojunction solar cells shall be further investigated and optimised in the following chapter.

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