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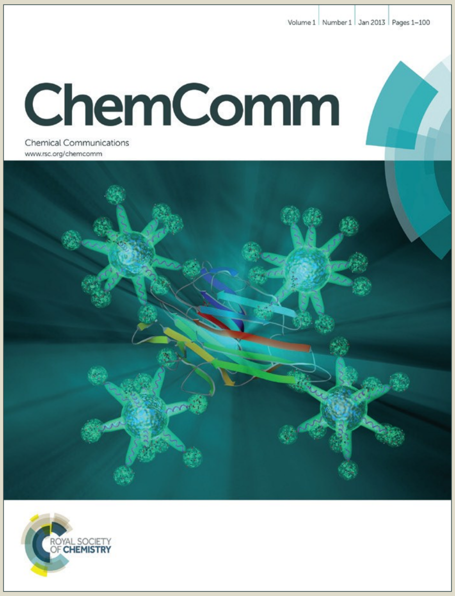

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Sterically Controlled Azomethine Ylide Cycloaddition Polymerization of Phenyl-C_{61}-Butyric Acid Methyl Ester

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Phenyl-C_{61}-butyric acid methyl ester (PCBM) is polymerized simply using a one-pot reaction to yield soluble, high molecular weight polymers. The sterically controlled azomethine ylide cycloaddition polymerization (SACAP) is demonstrated to be highly adaptable and yields polymers with probable $M_n \approx 24\,600$ g mol^{-1} and $M_w \approx 73\,800$ g mol^{-1}. Products are metal-free and of possible benefit to organic and hybrid photovoltaics and electronics as they form thin films from solution and have raised LUMOs. The promising electronic properties of this new polymer are discussed.

Phenyl-C_{61}-butyric acid methyl ester (PCBM) is one of the most common molecules in organic photovoltaics,[1-3] its use cemented as an electron acceptor with poly(3-hexythiophene),[4] and now with numerous low band gap polymers.[5] Its exceptional acceptor properties, ability to transfer charges through bulk heterojunctions (BHJs),[6] and even in perovskite-based solar cells,[7] demonstrate its wide applicability. In BHJs it shows a tendency to self-organize in such a way as to favour electron collection and percolation in both lateral and vertical directions.[8,9] PCBM, however, does show some behaviours that are detrimental to device stability. The fabrication of thin films is sensitive to casting conditions, often leading to excessive aggregation.[10] Furthermore, photonically assisted dimerization may impact device performances.[11]

A possible remediation of these problems is by incorporating PCBM into polymers. While C_{60} is commonly integrated as moieties pendent to the main-chain,[12] as single additions on C_{60} are the simplest to control, such polymers can tend to allow the C_{60} to overly aggregate.[13] By incorporating C_{60} into the main-chain of the polymer the ability for movement is reduced. The polymerization of C_{60}, however, generally leads to crosslinked materials, or necessitates multi-step chemistry precluding industrial applications,[14] or requires metals,[15] which can be detrimental for applications.[16] A challenge with fullerene chemistry is that because there are 30 [6,6]-bonds, most reactions result in a mixture of multi-adducts.[17] Furthermore, a range of isomers can arise; the bis-adduct alone shows eight isomers.[18,19] We recently discovered that it is possible to control additions to C_{60} to yield polymers of reasonable molecular weights in a metal free manner; the sterically controlled azomethine ylide cycloaddition polymerization (SACAP) of C_{60} exploits the use of sterically cumbersome comonomers to ensure that the formation of multi-adducts is reduced, thereby diminishing crosslinking and increasing solubility.[20] SACAP, based on so-called Prato chemistry,[19,20] provides medium molecular weight materials (>15000 g mol^{-1}) under certain controlled conditions.

In this paper, SACAP is surprisingly shown to be applicable to PCBM, opening the possibility that a number of C_{60}-derivatives might be polymerized. Furthermore, when compared to SACAP-formed polyC_{60},[20] PCBM delivers higher yields of high molecular weight polymers with greater solubilities. The product, poly{[bispyrrolidino(phenyl-C_{61}-butyric acid methyl ester)]-*alt*-[2,5-bis(octyloxy)benzene]} (PPCBMB) is facile to recover and metal-free. We also demonstrate the first and promising photovoltaic characterisations of PPCBMB.

The polymerization was carried out in accordance with Scheme 1 as a one-pot reaction using products as supplied. Comonomers with alkyloxy-aromatic groups were chosen due to their expected high solubility and stability against photo-oxidation.[22] Given the relatively low reactivity of C_{60} bonds, the temperature was elevated to 150 ˚C to help the reaction forward. The expected mechanism is based on the Prato reaction, i.e., a [1,3]-dipolar cycloaddition of an azomethine ylide with [6,6]-bonds on the fullerene moiety (Scheme S1).[19,21] The ylide comes from the reaction of *N*-methylglycine (sarcosine) with 2,5-bis(octyloxy)terephthalaldehyde (**1**). The ratio (1:2:1, respectively, PCBM : sarcosine : **1**) was chosen to

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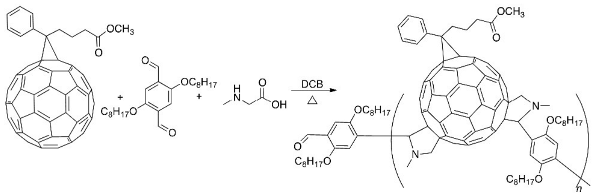
Electronic Supplementary Information (ESI) available: syntheses; spectroscopic, modelling, thermal and photo-CELIV data. See DOI: 10.1039/x0xx00000x avoid multi-adduct formation, known to occur when reaction times are long.[18] Fullerene undergoes reactions on exposure to light,[23] and with oxygen.[24] Therefore the reaction was carried out under anaerobic conditions and under cover from UV light.



Scheme 1. Synthesis of PPCBMB: PCBM, *N*-methylglycine, **1**, 1,2-dichlorobenzene (DCB), 150 ˚C, 18 h, yield: 75%. The calculated most probable regioisomer is shown for clarity (see text for further details).

It is known that purifications of polymers containing fullerene can be troublesome; C_{60} tends to aggregate with the product. However, we found that PPCBMB was easy to purify, necessitating a precipitation from methanol and a Soxhlet-wash with acetone to remove unreacted PCBM. It was found to be well soluble in common organic solvents (e.g., 30 mg mL^{-1} in DCB was feasible), suggesting a low degree of crosslinking.

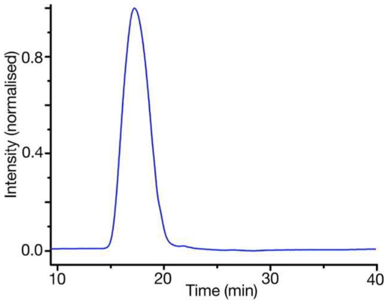


Figure 1. GPC profile (THF, 30 ˚C, 330 nm) of PPCBMB.

A representative GPC curve of PPCBMB in THF is shown in Figure 1. The estimated molecular weights, against polystyrene standards, are 7000 g mol^{-1} (M_n) and 23000 g mol^{-1} (M_w), with a dispersity ($Đ = M_w/M_n$) of 3. Using chlorobenzene as an eluent, we find a slight increase (M_w = 25540 g mol^{-1}, $Đ$ = 3). Under such conditions, values are underestimated due to the retention of C_{60} by the column; for example, C_{60} often elutes after toluene.[25] Deconvolution of GPC curves suggests that the molecular weight of the materials is actually higher by a factor of between 3 and 8 times.[20] The smooth monomodal peak eluting at *ca.* 17 min indicates an absence of oligomers. The bump at 21.85 min corresponds to PCBM, of which deconvolution indicated there to be less than 0.3%.

Representative NMR spectra of starting materials and product are in Figure 2a. The new peaks in the PPCBMB spectra are in accordance with the formation of pyrrolidine rings. The peak in the aldehyde region seen with bis(octyloxy)terephthalaldehyde disappears. The ^{1}H NMR in Figure S1 in the Supporting Information (SI) shows a broad signal in the aromatic region peaked at 7.38 ppm and spanning from 8.25 to 7.00 ppm. The general broadness of all the peaks confirm that the material is polymeric in nature. The broad signal centred at 5.02 ppm arises from protons within the pyrrolidine links, whereas the sharper signal at 3.61 ppm is attributed methyl esters and is convoluted with oxymethylene protons in the alkyl side-chain. The pyrrolidine *N*-methyl protons and PCBM propylene protons create a broad signal centred at 2.52 ppm. The aldehyde end groups afford the small broad bump at 10.46 ppm while a sharp peak at 10.03 ppm represents a tiny amount (*ca* 0.1 wt%) of comonomer.

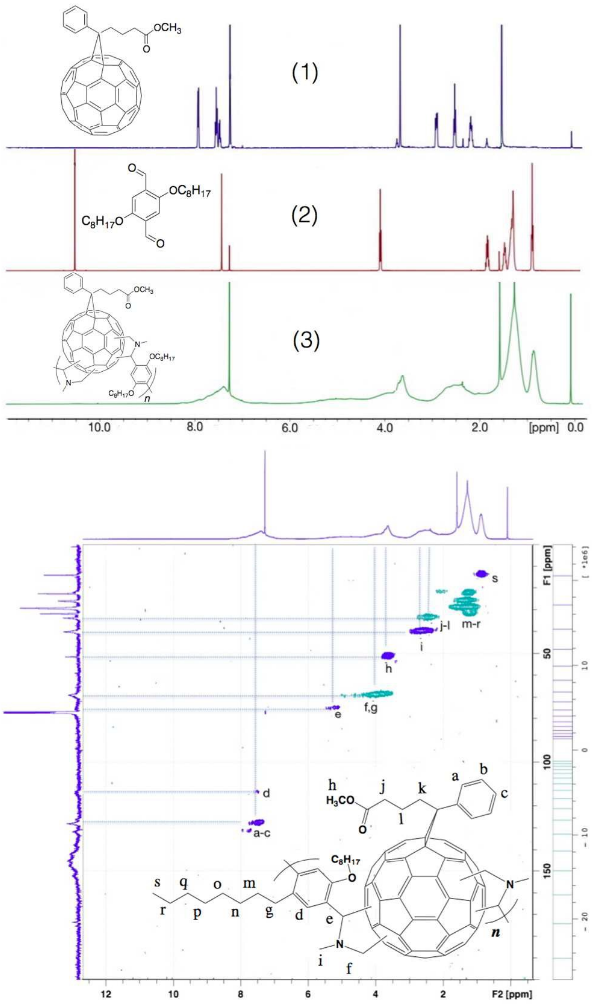


Figure 2. Above, overlay of ^{1}H NMR spectra of: (1) PCBM; (2) **1**; and (3) PPCBMB; and below, HSQC 2D NMR of PPCBMB, all in in $CDCl_3$. Correlations in blue indicate methine and methyl groups and in green, methylenes.

Given the aforementioned mismatch between GPC estimated and real molecular weights, a further estimation was made using ^{1}H NMR (Figure S1). It was assumed that macrocycles were not formed due to the steric bulk of the PCBM, and that each macromolecule carried on average one –CHO group, as the polymerization is a polyaddition.[20]

Integrating the ^{1}H NMR peak at 0.85 ppm for pendent comonomer methyl groups gave a value of 109 *versus* 1 for the aldehyde protons at 10.46 ppm. Assuming a respective ratio of six methyl protons to 1 aldehyde proton in the repeating unit, we infer the degree of polymerization to be 109/6 = 18.2. Multiplying this by the repeating unit molar mass affords M_n = 24670 g mol^{-1}. Assuming $Đ$ = 3, M_w is thus 73800 g mol^{-1}. While an estimate, these are most likely closer to actual values.

The 2-D NMR in Figure 2 details the correlations for methine, methylene and methyl groups of the pyrrolidine linkages. These results are further supported by the ^{13}C NMR of PPCBMB (see Figure S2) in which the peaks associated with the *N*-methyl and methine groups are observed respectively at 40.1 ppm and 69.2 ppm while the peak arising from methylene is obscured by peaks due to chloroform.

The DOSY ^{1}H NMR spectrum (Figure S3) shows the diffusion profile of PPCBMB. All protons are in the same regime, confirming a monomodal molecular weight distribution.

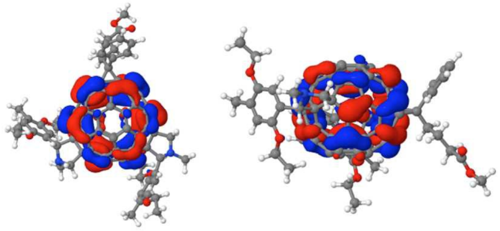
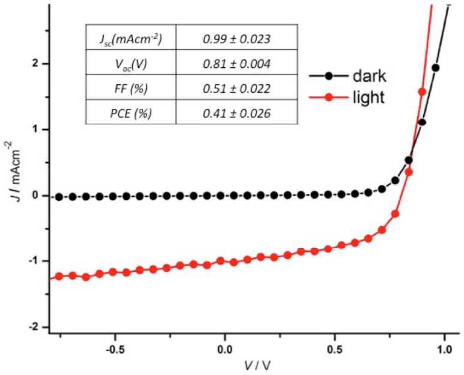


Figure 3. LUMO frontier orbitals for the most probable PPCBMB adducts in DFT B3LYP/6-31G** level of theory.

To model the most probable isomeric structure of the repeating unit, PCBM was treated using DFT with B3LYP/6-31G** theoretical level (see SI, Figure S4).[26] Calculations were carried out assuming the regions of highest LUMO density to be the target of successive attacks,[20] to give the intermediate structure PCBM-1 (Figure S5), and the most probable tris-adduct PCBM-2 shown in Scheme 1 and Figure 3. In accordance with expectations, successive additions raise the LUMO, and reduce the electron affinity and the electrophilicity, as detailed in the SI. The isomeric structure of PPCBMB will be the subject of future work. Cyclovoltammetry confirmed this increase in the LUMO, indicating -3.8 eV for PCBM and -3.34 eV for PPCBMB (Figure S6).

In comparing the solution UV-visible absorption spectra of PCBM, PPCBMB and **1** (Figure S7) it is found that the characteristic absorption maximum of **1** is lost due to disruption of conjugation by the removal of aldehyde groups during the reaction. The absorption maximum of PPCBMB is blue shifted with respect to PCBM owing to a disruption of fullerene conjugation.[27] This disruption will vary depending on which 6,6-bonds are reacted. The contribution of regioregularity, i.e., the various isomers present in the chains, and scattering to the PPCBMB UV curve is under investigation.

Figures S8 and S9 show the thermogravimetric and DSC characterisations, respectively, of PPCBMB. The TGA shows the material to be stable up to 350 ˚C. PCBM degrades at around 400 ˚C.[28] The smooth DSC curve tends to indicate an amorphous quality, however, further studies are required, especially given the shiny appearance of PPCBMB shown in Figure S10, which also shows the visually defect-free film that was blade cast from *o*-xylene.



J_{sc}(mAcm^{-2})	0.99 ± 0.023
V_{oc}(V)	0.81 ± 0.004
FF (%)	0.51 ± 0.022
PCE (%)	0.41 ± 0.026

Figure 4. Representative current-voltage characteristics of non-optimized devices with P3HT:PPCBMB active layer.

Photovoltaic cells were made using PPCBMB as an acceptor with the archetypal poly(3-hexylthiophene) (P3HT) in an 'inverted' bulk heterojunction architecture and processed from industrially applicable neat xylene in an ambient environment. Even though the use of non-halogenated solvents and processing in air are known to be non-optimal for device performances, these conditions were chosen inline with industrial requirements.[29] Figure 4 shows current-voltage curves and a summary of the photovoltaic characteristics. The open circuit voltage (V_{oc}) is found to be *ca.* 200 meV higher with respect to devices made with PCBM acceptors,[30] confirming the elevation of PPCBMB LUMO levels with respect to PCBM and in general agreement with the cyclovoltammetry and modelling studies (see SI). However, the devices are penalized by low short circuit currents resulting in reduced efficiencies. Their fabrication incorporates conditions optimized for PCBM, which may not be the same for PPCBMB. Future studies will concentrate on optimizing conditions for this new material.

Photo-CELIV measurements carried out on the aforementioned devices (Figure S11) provided a mobility value of 2 x 10^{-4} cm^2 V^{-1} s^{-1} for the blend, similar to that of blends of P3HT:PCBM (6 x 10^{-4} cm^2 V^{-1} s^{-1}) prepared in the same manner,[31] and comparable to many high-performing blends.[32] This suggests that the blends possess reasonable mobilities and is not a limiting factor in terms of device performance.

To sum, the SACAP route can be extended to PCBM to yield thermally stable, soluble materials that exhibit raised LUMOs and film forming properties making them extremely promising for organic electronic and other applications. The use of PCBM in place of C_{60} leads to more soluble macromolecules in higher yields. It is expected that this polymerization technique can be extended to a range of comonomers and fullerenes. The photovoltaic properties of this material will be further studied, and initial modelling studies furthered to complement spectroscopic techniques to elucidate the regioregularity of this interesting new system.

Notes and references

Experimental

Synthesis of PPCBMB. 2,5-Bis(octyloxy)terephthalaldehyde (0.21 g, 0.55 mmol), $PC_{60}BM$ (0.50 g, 0.55 mmol) and *N*-methylglycine (0.10 g, 1.11 mmol) were dissolved in degassed 1,2-dichlorobenzene (20 mL) and stirred at 150 °C for 18 h, then poured into methanol (250 mL). The precipitate was recovered by filtration directly into a Soxhlet thimble, acetone washed for 3 days, and recovered as a shiny black powder, yield: 75% (0.48 g). GPC: M_w = 23000 g mol^{-1}; M_n = 7500 g mol^{-1}; $Đ$ = 3.00 (THF, 30 ˚C, 330 nm). NMR: ^1H NMR (400.6 MHz, 5 mg ml^{-1},$CDCl_3$) δ = 10.46 (broad, -CO*H*), 8.26 – 6.84 (broad, *aromatics*), 5.41-4.62 (broad, -*CH*-N-, -$\mathit{CH_2}$-N-), 4.18 – 3.41 (broad, -O$\mathit{CH_2}(CH_2)_6CH_3$, -COO$\mathit{CH_3}$), 2.82-2.17 (broad, -$\mathit{CH_3}$-N-, -$(\mathit{CH_2})_3COOCH_3$), 1.68-1.07 (broad, -$OCH_2(\mathit{CH_2})_6CH_3$), 0.93 (broad, -$OCH_2(CH_2)_6\mathit{CH_3}$) ppm. ^{13}C NMR (100.16 MHz, 5 mg ml^{-1}, $CDCl_3$) δ = 173.5 (s, -*C*$OOCH_3$), 152.1-113.9 (m, *aromatics*), 69.2 (m, -*C*H_2-N-, O-*C*$H_2(CH_2)_6CH_3$), 51.6 (s, -COO*C*H_3) 40.1 (s, -*C*H_3-N-), 34.1-31.9 (m, -$(\mathit{CH_2})_3COOCH_3$), 29.4-22.2 (m, -$OCH_2(\mathit{CH_2})_6CH_3$), 14.2 (s, -$OCH_2(CH_2)_6$*C*$H_3$) ppm. 2D-HSQC NMR (5 mg ml^{-1}, CDCl3), d=δ=7.44, 128.0 (*aromatics*); 5.41, 76.7 (-*CH*-N-); 4.81-3.87, 69.2 (-$\mathit{CH_2}$-N-, -O$\mathit{CH_2}(CH_2)_6CH_3$); 3.62, 51.6 (-COO$\mathit{CH_3}$); 2.80-2.61, 40.1 (-$\mathit{CH_3}$-N-); 2.63-2.28, 34.1-33.8 (-$(\mathit{CH_2})_3COOCH_3$); 1.68-0.99, 31.9-22.2 (-$OCH_2(\mathit{CH_2})_6CH_3$); 0.93,14.22 ($OCH_2(CH_2)_6\mathit{CH_3}$) ppm.

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