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Towards the Synthesis of Poly(azafulleroid)s: Main Chain Fullerene Oligomers for Organic Photovoltaic Devices

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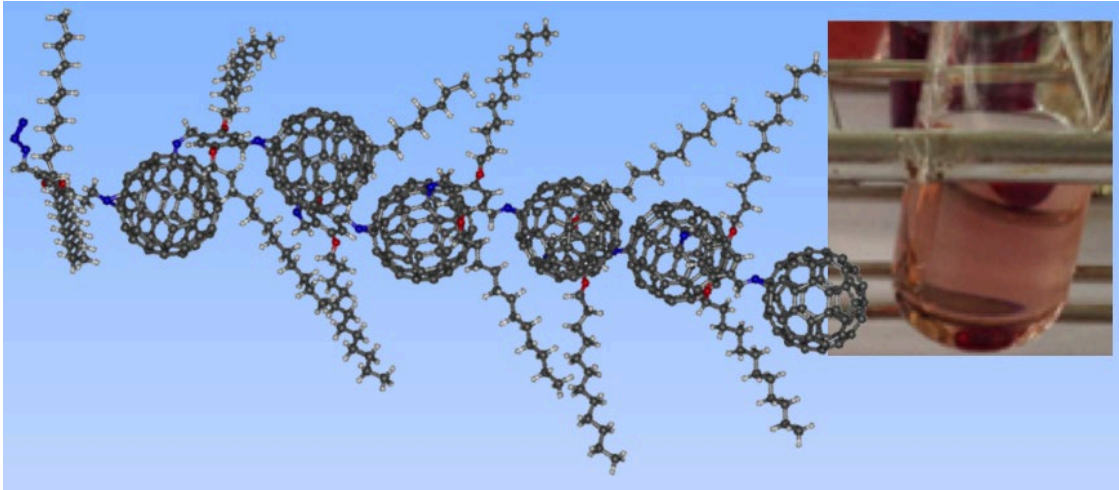
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Abstract: For the first time imino chemistry is explored to synthesize main chain fullerene oligomers and low molecular weight polymers. Oligo(aziridinofullerene)s and low molecular weight poly(aziridinofullerene)s (PAFs) are prepared by 1,3-dipolar cycloadditions of bis(azido-alkyl) comonomers to C₆₀. The effect of the steric bulk of the comonomer is studied and it is found that PAF solubilities and molecular weights are increased with longer comonomer side-chains. Initial and promising photovoltaic characterizations show commensurate improvements in properties. Interestingly, the PAFs exhibit LUMOs close to those of PCBM. Routine characterisations are correlated with DFT/B3LYP/6-31G(d) to understand structural and electronic behaviours. It is expected that higher molecular weights may be obtained through comonomer variations and that this novel methodology will open a route to interesting materials for optoelectronics.

Keywords: oligo(aziridinofullerene); poly(aziridinofullerene); poly(fullerene); fullerene; organic photovoltaic device

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Fullerene is used as a comonomer in this new polymerization.

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Introduction

Polymer-based organic photovoltaic (OPVs) devices have advantages that include their low energy-cost of fabrication, ease of processing, and mechanical flexibility.^{1,2} The photo-charge generating layer is made from a blend of a semiconducting chromophoric electron donating p-type polymer, such as the standard bearer poly(3-hexylthiophene) (P3HT),³ and an acceptor n-type small molecule, typically phenyl-C₆₁-butyric acid methyl ester (PCBM).⁴ While much has been done to vary p-type materials, not least the introduction of the so-called low-band gap polymers to capture greater degrees of available light and reach efficiencies greater than 10%,^{5,6} relatively few papers deal with the modification of the fullerene (C₆₀) derivative. PCBM is widely used because of its excellent electron affinity and good charge mobility.^{1,2} However, through a thermally enhanced leaching process it forms μm -scale crystals that diminish device efficiencies.⁷ Incorporating C₆₀ into an oligomer may permit stabilization of the active layer. Moreover, the creation of a metal-free method of polymerizing C₆₀ would expand possibilities for its use in anti-cancer and anti-viral treatments,⁸⁻¹² as it would make possible the exploration of poly(fullerene) nano- and meso-structures such as micelles and vesicles.¹³

C₆₀ is typically incorporated into polymers as a moiety pendent to the main chain as it is relatively simple to control just one reaction with the sphere.¹⁴⁻²² However, this can lead to aggregation of C₆₀, can make for complex multi-step chemistry, and restricts the possibilities for changing the opto-electronic behaviour of C₆₀. A more interesting possibility is to use C₆₀ as a monomer by incorporating it directly into the main-chain: as its degrees of freedom are reduced this might limit excessive aggregation in the solid state. Furthermore, because there are two points of addition to the sphere, there are more options to vary the C₆₀'s electronic properties.

It should be said that incorporating C₆₀ directly into the polymer main-chain is generally not a simple task as there are 30 [6,6]-double bonds that can react; multiple additions, leading to crosslinking, are common.¹⁵ Nevertheless, a not inconsiderable amount of work has been done in this area. Prior methods included Diels-Alder chemistry,²³ methano-bridges,²⁴ and an elegant tether-directed pre-modification of C₆₀,²⁵

but these also gave cross-linking, intractable products, or required multi-step preparative chemistry, respectively. An attempt to resolve this was made using atom transfer radical addition polymerisation (ATRAP) as the reaction is based on radical bis-additions around just one C₆₀ 1,4-phenylic ring.²⁶⁻²⁸ One down-side of this system through was the high amounts of CuBr required, leading to metal impurities of which even trace amounts can be detrimental to device performances.^{29,30} An alternative and recently discovered method, the so-called sterically controlled azomethine ylide cycloaddition polymerization (SACAP) of C₆₀, showed that it was possible to reach high molecular weight poly(fullerene)s with certain comonomers under forced conditions.³¹ These materials have been of considerable interest, not only as electron acceptors, but as additives, stabilising against thermal degradation.^{31c,32} However, SACAP results in a regio-irregular polymer with a mixture of *trans*-3 and *trans*-2 in-chain isomers. These intra-chain variations can result in different C₆₀ LUMOs along the chain, which may result in electronic traps.³³ Therefore a challenge is to find a facile polymerisation of C₆₀ that results in regioregular polymers.

Prior work has demonstrated that imino-C₆₀ bis-adducts show regular, well-defined additions to the C₆₀ sphere and that their mono-adduct homologues can exhibit high charge mobilities.^{34,35} We were therefore interested to see if bis-imino chemistry could be extended to prepare regio-regular oligomers and polymers that might be of use for photovoltaics. We report for the first time the discovery that it is possible to deliver oligo- and poly(aziridinofullerene)s (PAFs) using 1,3-dipolar cyclo-additions of diazido comonomers to C₆₀ under catalyst-free conditions. In effect, metals are avoided in the final synthetic step.

Experimental

Full details of materials, the synthetic procedures used to prepare monomers and oligomers, along with the respective product NMR characterisations, are given in the Supporting Information (SI). The following is a representative example of the synthesis of oligo(aziridinofullerene) (PAF2).

Synthesis of PAF2

Degassed 1,2-dichlorobenzene (DCB, 80 mL) and C₆₀ (1.38 x 10⁻³ mol, 1 g) were stirred under dry N₂ for 30 min at room temperature prior to the addition of the comonomer, 1,4-bis(azidomethyl)-2,5-bis(dodecyloxy)benzene (**7**, 1.38 x 10⁻³ mol, 0.768 g), and subsequently heated to 60 °C for 24 h. The solution was stirred for 2 h at 100 °C. Toluene (5 mL) was added, and the product recovered from precipitation in methanol. Soxhlet cycled washing over periods of 12 h and 3 days with, respectively, methanol and hexane, followed by drying under reduced pressure at 100 °C resulted in 1.24 g (yield, 68 %) of a brown powder. ¹H NMR (400.6 MHz, C₆D₆) δ = 6.95 (broad, -aromatic), 6.3 (d, *J* = 220 Hz, -CH₂-N=), 5.3 (broad, -CH₂-N₃), 4.2 (broad, -OCH₂-), 2.8, 1.6 and 1.3 (broad peaks, -CH₂-), 0.93 (broad, -CH₃).

Cyclic Voltammetry and Reflection Electron Energy Loss Spectroscopy

Cyclic voltammetry was performed in a dry N₂-filled glove-box at ambient temperature using a Ag working electrode (diameter 1.6 mm), Ag/AgCl as counter electrode and a Pt wire as reference electrode. The three-electrode cell was connected to an Autolab potentiostat PGSTAT. The samples were deposited from a 30 mg mL⁻¹ solution in 1,2-dichlorobenzene on top of the working electrode. Acetonitrile and tetrabutylammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Values were corrected with respect to the vacuum level for each reference electrode and solution used. LUMOs were calculated assuming the ferrocene/ferrocenium energy level to be 4.8 eV below the vacuum level, such that:

$$E_{\text{LUMO}} = -(E_{1/2} + 4.8) \text{ eV} \quad \text{Equation (1)}$$

In calculating $E_{1/2}$ values, it was assumed that the Fc/Fc⁺ standard is 0.49 V above that of Ag/AgCl values.^{36,37}

In order to estimate the values of the band-gaps (E_{gap}), reflection electron energy loss spectroscopy (REELS) was employed using thin PAF films formed on a fluorine doped indium tin oxide (FTO) substrate by spin coating (3000 rpm, 30 s) a 30 mg mL⁻¹

solution of each PAF in *o*-dichlorobenzene.³⁸ As the optical band gap is comparable to the electronic gap,³⁹ using equation (2) it was possible to estimate the HOMO, i.e.,

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad \text{Equation (2)}$$

Device Fabrication

Bulk heterojunction organic solar cells were fabricated using glass coated with ITO as transparent substrate. The substrates were cleaned by consecutive sonication in detergent, acetone and isopropyl alcohol in an ultrasonic bath (VWR Model 50T), followed by UV-ozone cleaning (PDC 32G) for 10 min in order to prepare the surface for PEDOT:PSS deposition. PEDOT:PSS (Heraeus Clevios P VP A14083, 40 nm thickness) was spin-coated onto the clean substrate surface, followed by 10 min of annealing in air at 140 °C to remove remaining water. The samples were cooled to room temperature and transferred into a N₂-filled glove-box. P3HT (Rieke 4002-E)/PCBM (American Dye Source), P3HT/PAF1 or P3HT/PAF2 (1:0.6 wt%/wt%) solutions in anhydrous chlorobenzene (40 mg mL⁻¹) were prepared, heated at 60 °C and stirred overnight inside the glove box. Prior to deposition, the solutions were passed through a 0.2 μm filter. The photovoltaic active materials were then spin-coated on top of the PEDOT:PSS layer to produce an active layer of 100 nm, followed by annealing at 130 °C for 10 min. The aluminium cathode (100 nm thick) was thermally evaporated through a shadow mask under high vacuum about 5 x 10⁻⁵ Pa. No electron transport layer (ETL) was inserted between active layer and Al. Solar characterization of the devices was performed in N₂ ambient, using a Keithley 2400 source meter unit and an Oriel Xenon Lamp (450 W) coupled with an AM1.5 filter as a light source and a light intensity of 100 mWcm⁻² was used in all the measurements. Devices parameters were tested for at least 16 devices for each sample.

Conductivity characterisations

The films were deposited over an interdigitated set of electrodes (IDE) of gold with parameters: N = 50 digits with 110 nm height (h), 8 mm length (L) and 100 μm width (w) thus giving, in accordance with $L/A = k_{\text{cell}} = 5.1 \text{ m}^{-1}$ where A is area in m² and L is

in m. PAF solutions were spin coated (1000 rpm, 30 s) and nitrogen-dried from 30 mg mL⁻¹ solutions in 1,2-dichlorobenzene. Conductivities were determined using Equation (3):

$$\tilde{A} = \frac{1}{R} \cdot \frac{L}{A} \quad [\text{S m}^{-1}] \quad \text{Equation (3)}$$

where R is the resistance in Ω .

Results and Discussion

Two similar comonomers of different sizes were chosen to explore the effect of steric bulk on the feasibility of the polymerization. Their structures are shown in Scheme 1. Aromatic-oxy-ether links were chosen for two reasons: first, for their expected photostability;⁴⁰ and second, for their ease of synthesis via a Williamson ether formation.⁴¹ Furthermore, initial attempts to prepare analogous comonomers with simple alkyl side-chains i.e., without ether groups, were made, however, in our hands their subsequent bromomethylation, carried out in accordance with the work of van der Made *et al.*⁴² resulted in very low yields due to the inactivity of the aromatic substrate and the steric bulk of the alkyl chains hindering substitutions.

The successful route to the ethylated comonomers is shown in Scheme 1. The first step consisted of the aforementioned Williamson alkylation of hydroquinone, giving straight forward control over the steric bulk of the comonomer by varying the length of the side-chain. The reactions were facile and smoothly formed bis-alkyl ethers **2** and **3**, in respective yields of 54 and 44 %. The reduction in yield with increasing chain length is most likely due to steric hindrance and increasing difficulty in purifying the products; indeed on attempting with higher ethers, for example, $-\text{O}(\text{CH}_2)_{15}\text{CH}_3$, although we managed yields of around 38%, they were generally not consistent. We aimed to make the syntheses as simple as possible so **2** and **3** were recovered pure by reprecipitation in cold methanol. The bisbromomethylation step leading to molecules **4** and **5** was found to be more troublesome. Made *et al.* showed that it was possible to bromomethylate small aromatic compounds using small excesses of HBr in acetic acid and paraformaldehyde.⁴² With these sterically encumbered molecules **2** and **3** we found that

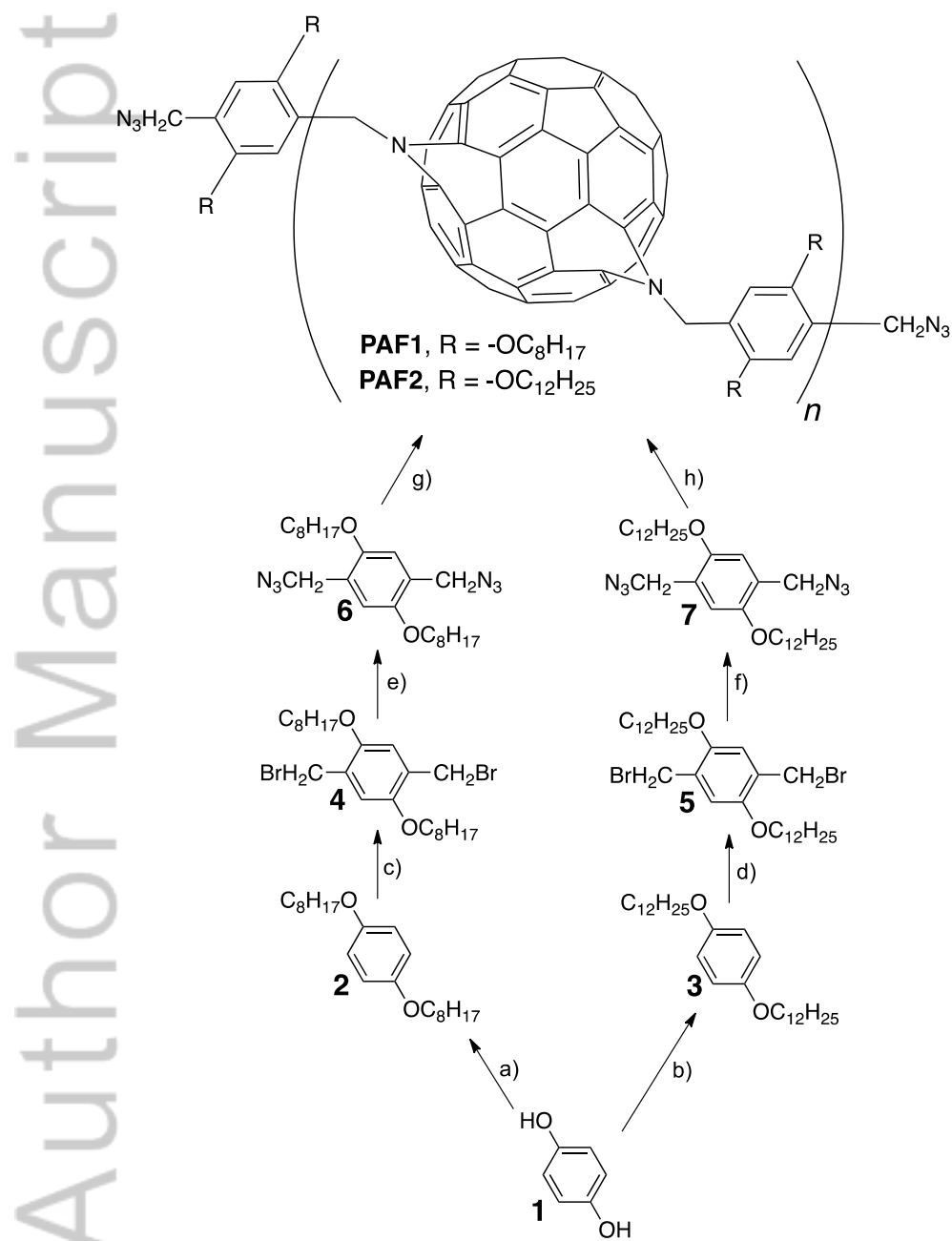
much greater quantities of HBr were required (*ca* 7 times excess); indeed, high temperatures alone did not help and more often led to mixtures of bis- and tris-bromomethylated products. With these conditions consistent yields, not far from 50% could be maintained. Finally, azidization was found to be facile using NaN_3 ,⁴³ where yields were repeatedly of the order of 67%. The Supporting Information (SI) gives full details of the preparative methods along with NMRs (Figure S1-8).

Attempts to prepare analogues of **6** and **7** with bis-azide groups attached directly to the aromatic ring, i.e., 1,4-diazido-2,5-bis(alkyloxy)benzene, to explore the possibility of *peri*-conjugation through proximate phenyl rings,⁴⁴ gave consistently low yields (<20%) in our hands, even when using promoted catalysts as detailed by Zhu *et al.*⁴⁵, and were not further explored. It should be noted that azides are well known for their explosive tendencies when employed with compounds of low carbon to nitrogen ratios.⁴⁶ Therefore, all reactions with sodium azide were above the commonly recognized safety limit for handling, i.e., at least 3 carbon atoms to each nitrogen atom in the azide carrying molecule.⁴⁷

The syntheses of the PAFs were performed using a one-pot, two-step reaction. The mechanism of the cycloaddition of azidoalkyls to C_{60} is well understood.⁴⁸ The first step, at lower temperatures, involves the addition of the azide group to the fullerene [6,6]-bond between adjacent phenyl rings to yield a full 5-membered ring. This intermediate is unstable; on further heating, with the loss of N_2 at around 100 °C, an adjacent [5,6]-bond is brought into the reaction and leads to the synthesis of open [5,6]-bridge azafulleroids as shown in the PAF structure in Scheme 1. A small number of closed [6,6]-bridge aziridino fullerenes also result.^{34,49}

We were greatly encouraged by work identifying the preparation of bisadducts in high yields, even though the chemistry generally required long reaction times and temperatures from 70 °C up to reflux in chlorinated solvents.³⁵ While reflux temperatures could have been chosen in order to drive the reaction forward towards high molecular weights, in this first exploratory work we minimized the risk of tris-additions, which would lead to cross-linking, by working at relatively low temperatures. This meant that long reaction times, of the order of a day, were used. The reactions were

only warmed to higher temperatures at the end so as to drive off N_2 in the second step of the mechanism. We note that the polymerizations can effectively be considered polycondensations,^{50,51} and as such they are expected to deliver high molecular weights only when strictly equimolar quantities of the comonomer and C_{60} are used.



Scheme 1. Syntheses of the comonomers and PAFs: a) 1-bromooctane, K_2CO_3 , **1**, acetonitrile, 54 %; b) 1-bromododecane, K_2CO_3 , **1**, acetonitrile, 44 %, cc) **2**, PFA, HBr, acetic acid, 48%, d) **3**, PFA, HBr, acetic acid, 64 %, e) **5**, NaN_3 , DMSO, 67 %, f) **6**, NaN_3 , DMSO, 68 %, g) C_{60} , **8**, 1,2-DCB, 56 %, h) C_{60} , **9**, 1,2-DCB, 68 %. For visual clarity, only the most probable isomer is shown; please see text for further details.

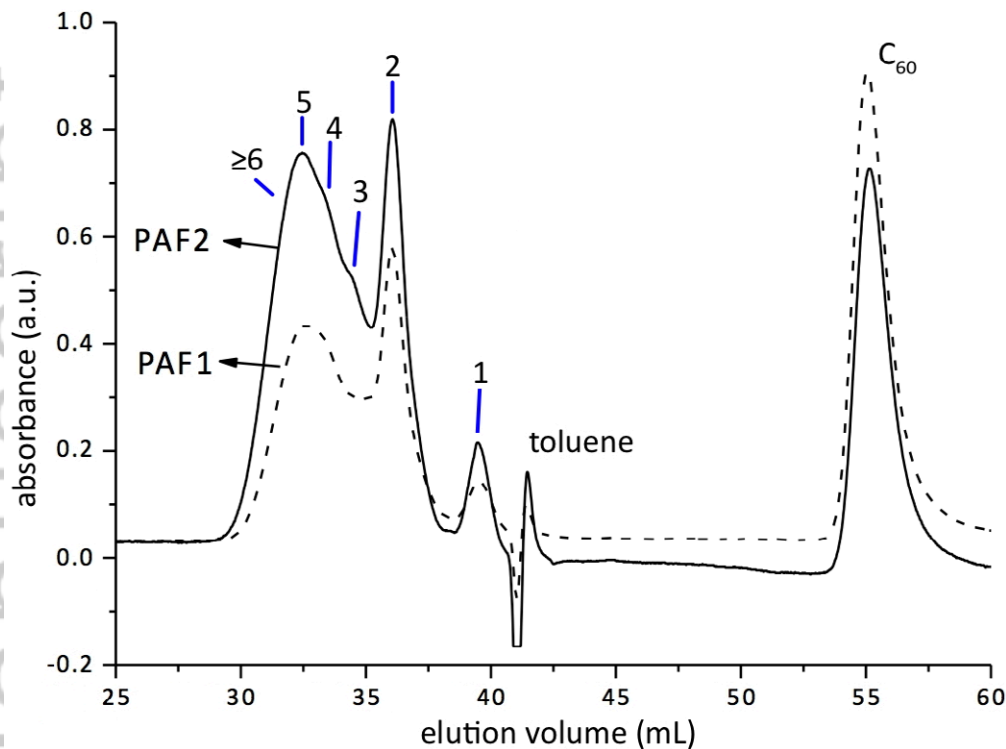


Figure 1. SEC curves of PAF1 and PAF2 (THF, 30 °C, 350 nm) showing C_{60} eluting at *ca* 55 min.

The GPC chromatograms of the products, shown in Figure 1, indicate the formation of oligomers and low molecular weight polymers in both PAF1 and PAF2. C_{60} elutes late from the GPC column, normally appearing after toluene.⁵² Polystyrene standards cannot be used to indicate the correct masses, for example, PAF1 and PAF2 were indicated to have molecular weights and dispersities ($D = M_w/M_n$)^{51,53,54} of $M_n = 1090 \text{ g mol}^{-1}$, $D = 1.49$, and $M_n = 1200 \text{ g mol}^{-1}$, $D = 1.62$, respectively. These values are clearly erroneous given that C_{60} itself has a molar mass of $720.66 \text{ g mol}^{-1}$. A more effective route to calculate the molecular weights was proposed by Gügel *et al.*²³ who assumed that each addition of a repeating unit to the chain resulted in an additional feature to the GPC curve. Using their methodology, i.e., counting off features of the curves, as

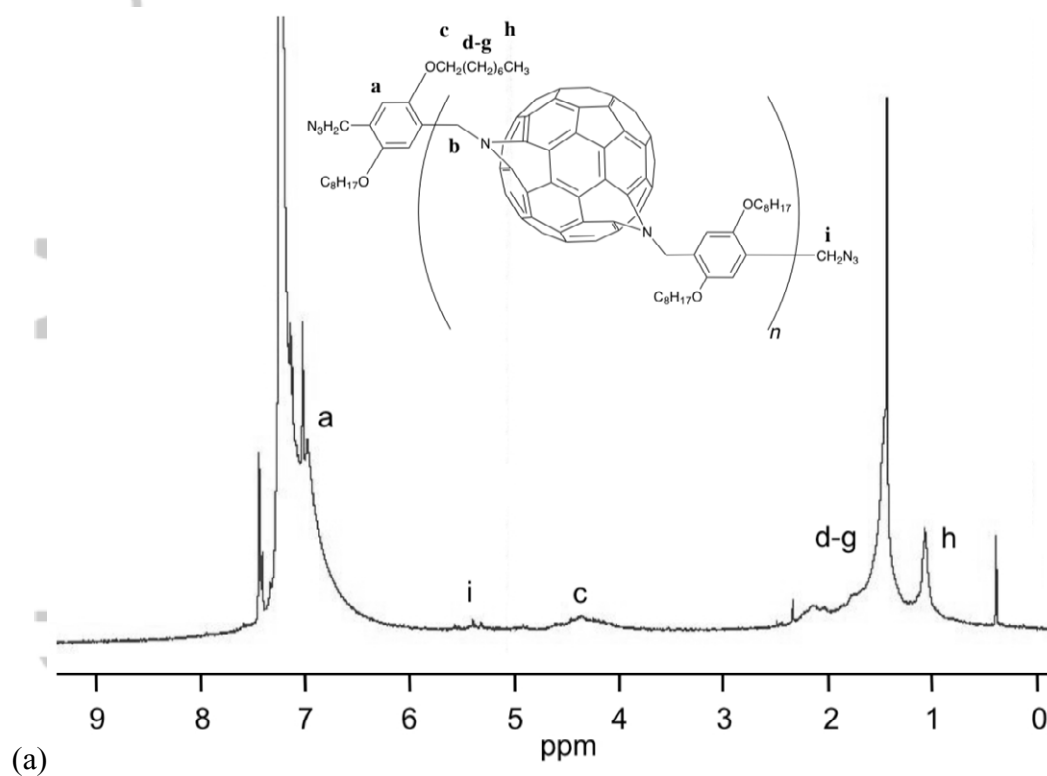
indicated in Figure 1, we find that PAF1 contains a large quantity (*ca* 15% by deconvolution) of bis(azafulleroid) along with oligomers containing between 2 and around 10 C₆₀s. PAF2, however, contains more higher macromolecules, estimated to be up to around 12 repeating or so i.e., equivalent to a molecular weight of *ca.* 17100 g mol⁻¹. That higher molecular weights were not attained was probably due to the low reaction temperatures and/or the comonomers not having long enough side chains to facilitate solubilisation of the products. This will be the focus of future work. Finally we note that while MALDI-TOF characterisations were attempted they were not fruitful due to crosslinking of C₆₀ during lasing.

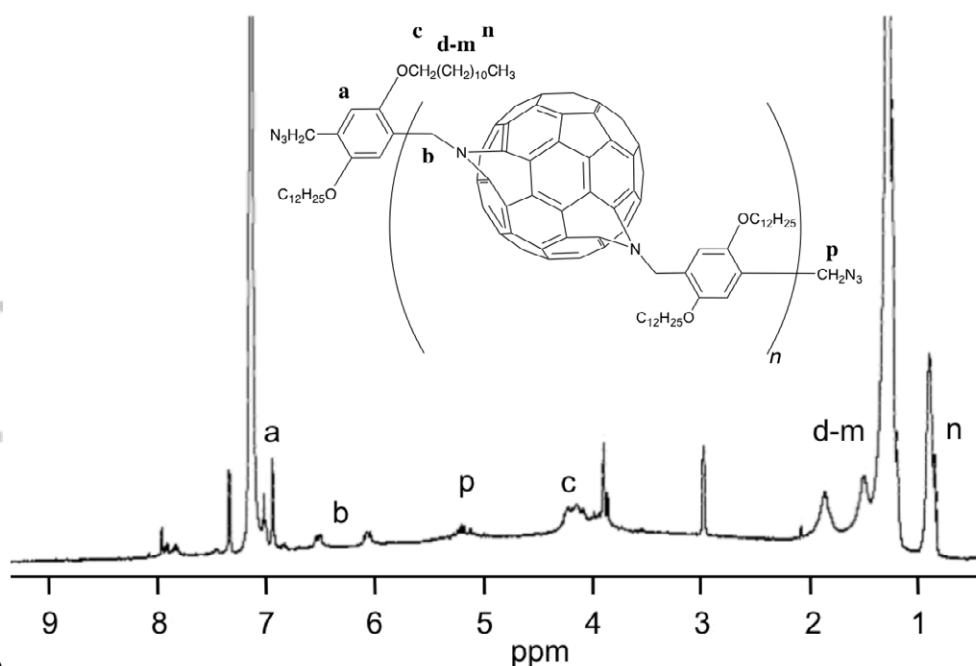
That the reactions had occurred as expected was further confirmed by FT-IR which showed the removal of peaks at 2100 cm⁻¹ due to ½(N₃) vibrations on the comonomers (Figure S9).

It was not possible to easily purify the materials. While reprecipitation from chlorobenzene would have been preferred,⁵⁵ this risked excessive contact between the materials and air. Indeed, fullerenes are known to easily form crosslinked ethers with oxygen.⁵⁶ Therefore all samples were treated with Soxhlet washing using methanol and hexane under dry nitrogen in an attempt to remove comonomers and fullerene, respectively. Assuming that the absorbance of C₆₀ and the repeating unit are the same, deconvolution of the aforementioned GPC curves of PAF1 and PAF2 nevertheless showed that they contained, respectively, 21 and 38 % fullerene. This would either indicate that crosslinking retained impurities, or that non-bonding interactions between the tertiary amines and fullerenes are strong. The GPC, and NMR and UV-visible results discussed *vide infra*, would tend to suggest that the chains are linear, however, further characterisations on more soluble PAF structures would be required to confirm this as only a very small fraction of crosslinking is required to influence the material properties. The products were submitted to simple solubility tests in some commonly used solvents, and the results were found to be in accordance with expectations i.e., in the order PAF2 > PAF1. Images of solutions are shown in Figure S10 in the SI.

Interestingly and in common with many imino-modified C₆₀s, while soluble direct from the reaction, once reprecipitated, their solubilities were greatly reduced. This

difficulty in handling meant that NMR studies were not facile. PAF1 was nevertheless characterised using 1,4-dichlorobenzene-*d*4 as shown in Figure 2(a). The rapidly relaxing alkyloxy side-chains could be well observed with the oxymethylene at *ca* 4.3 ppm and alkyl protons from 0.9 to 2.3 ppm. The chain-end (-CH₂N₃) groups were surmised from peaks at around 5.3 ppm. The intra-chain methylenes (C₆₀=N-CH₂-) could not, however, be observed, most likely due to their low relaxation and the poor solubilisation of the macromolecule. The situation was greatly improved on characterising PAF2. The NMR in Figure 2(b) shows similar peaks to those of PAF1, however, it is now possible to also find a wide doublet centred around 6.3 ppm (*J* = 220 Hz) indicative of the aforementioned intra-chain methylenes and confirming that they are in a highly restrained environment leading to their diastereotopic nature. These variations in relaxations meant that integrals could not reliably be performed in PAF spectra and therefore are not shown here.





(b) **Figure 2.** (a) ¹H NMR (400.6 MHz, 1,4-dichlorobenzene-*d*₄, 85 °C) of **PAF1**; and (b) ¹H NMR (400 MHz, C₆D₆, room temperature) of **PAF2**. Note peaks due to impurities at 2.9 and 3.8 ppm, most likely arising from methanol revealed through long experiment times.

XPS measurements confirmed the presence of the expected groups; Table 1 lists the attributions made. The related spectral data is in Figures S11 and S12 and in Tables S1-S3 in the SI for thin films on FTO. However, and of concern, was the high percentage of oxidised species found, most likely formed during sample preparation for characterisation. This would tend to suggest that these materials may need particular care in handling with respect atmospheric oxygen, and would explain the aforementioned rapid change in handling properties of the materials from their moment of preparation (high solubility) to that on exposure to air or filters where their picking up oxygen leads to the aforementioned etheric cross-links. Their future use may require exclusion of oxygen.

Attribution	Atomic %	
	PAF1	PAF2
C=C	9.34	17.47
C-C	73.63	65.92
C-N	11.71	8.18

C-O	2.73	2.25
C=O	0.86	2.99
COOH/COOR	0.77	-
Shake-up	0.96	3.19

Table 1. XPS peak fitting results for the C1s core level and their attributions.

Thermal gravimetric (TGA) studies, presented in Figure S13, showed that both polymers underwent similar degradation patterns. PAF1 and PAF2 show small losses of around 2 and 1 wt% at 100 and 80 °C, respectively, most likely arising from trapped solvents. Both undergo a second minor degradation from 160 °C up to 350 °C, of the order of 3 wt%. Given the small amount, this is probably due to removal of excess N₂ from in-chain 5-membered rings to form the final aziridinofullerene products. Finally, PAF1 and PAF2 suffer, respectively, losses of 10 wt% at 360 and 4 wt% at 340 °C likely due to oxyalkyl side-chains.

Figure 3 shows the UV-visible absorption characteristics of C₆₀, PAF1 and PAF2 in chloroform. That the PAFs show well-defined UV curves would indicate that the materials are well dissolved, and do not undergo excessive aggregation in solution. Both PAF1 and PAF2 retain the main opto-electronic features of C₆₀. However, there is an increased absorption at around 400-600 nm due to the modification of the C₆₀ sphere, which hints that there are more LUMO states available for charge transfer. Interestingly, it is possible to relate the colours of the solution to the structures of the materials. PAF solutions, shown in Figure S10, present red wine colours, similar to those found by Kim *et al.*⁵⁸ for [5,6]-open azafulleroids. Further evidence that PAFs are based on [5,6]-open azafulleroid repeating units can be found on closer inspection of the UV-visible curves. Notably, the characteristic absorption for [6,6]-closed fullerene derivatives at 420 nm is not observed^{33,58} whereas the shoulder at ~416 nm, characteristic of an open fulleroid structure,⁵⁹ is seen (detailed in Table 2). Therefore this isomer is the most likely for the repeating units in the polymer chain, and has been used for Scheme 1. However, further study of the regioisomers in the chain is required, most likely through extensive ¹³C NMR, a technique unavailable with these materials due to their low solubilities.

Therefore, future work will look at increasing the solubility of the chain through comonomer variations.

Compound	Absorption (nm)
C ₆₀	330, 405, 540, 600, 623(sh)
PAF1	329, 405, 416, 540, 602
PAF2	328, 405, 416, 540, 600

Table 2. Absorption peaks of PAFs and C₆₀ compared.

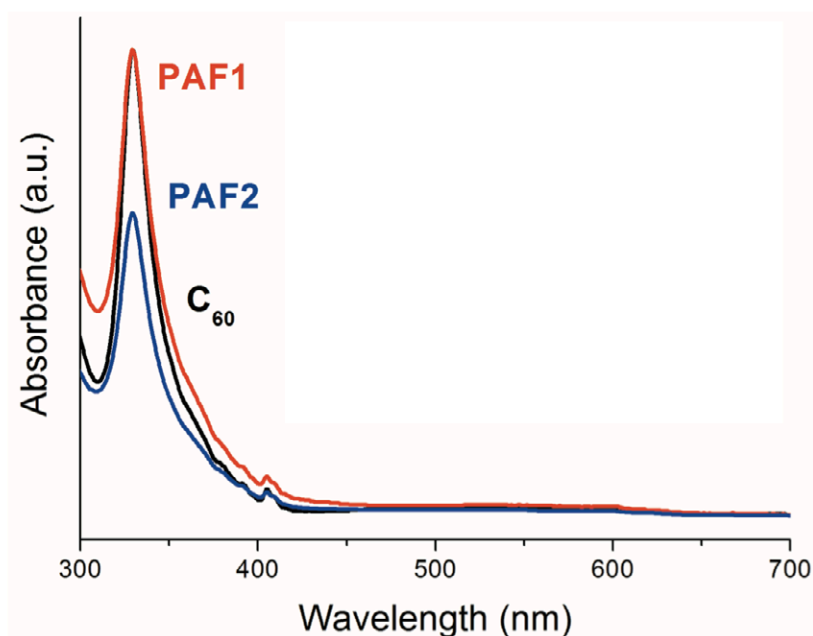


Figure 3. UV-visible absorption spectra of solutions of C₆₀, PAF1 and PAF2 (CHCl₃, ambient temperature).

In order to perform initial modelling of the electronic structure of the PAFs, the aforementioned [5,6]-open azafulleroid repeating unit was studied at the semi-empirical PM6 level, and then subjected to a DFT/B3LYP/6-31G(d) level of theory to reveal predicted HOMOs and LUMOs with frontier energy levels at respectively, -5.42 and -3.09 eV. Figure 4 shows the frontier orbitals wherein one can see that the first LUMO is well and truly on the C₆₀ and the HOMO on the comonomer, again as expected.

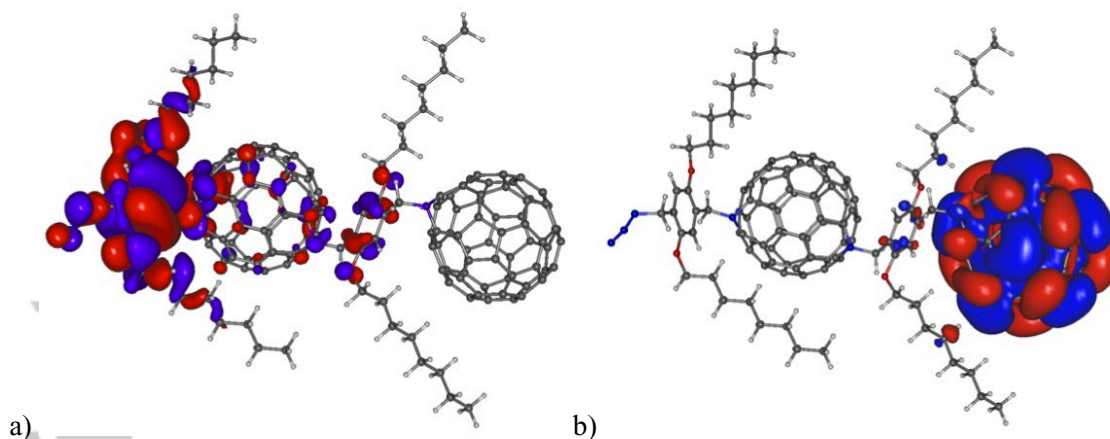


Figure 4. Representations of (a) HOMO and (b) LUMO frontier orbitals calculated at the DFT/B3LYP/6-31G(d) theoretical level.

To empirically determine the HOMO and LUMO levels for the synthesised PAFs, cyclic voltammetry was performed on PAF1, PAF2 and a standard, PCBM. It is important to highlight that the samples were submitted to 30 cycles without evident degradation, demonstrating the high stability of the PAFs under anaerobic conditions. The reduction potential, $E_{1/2}$, was calculated from the reduction peak using equations indicated in the experimental section and employed as shown in Figure S14. The gap, E_{gap} , was estimated using REELS (Figure S15), again in accordance with the assumptions and equations given in the experimental section. The calculated values are given in Table 3. Surprisingly, we find that the PAF LUMO values are very close to those of PCBM, even though the former have two additions to the sphere and a quite definitive modification of the C_{60} sphere, while the latter has just one broken double bond. Given the aforementioned modelling work, one would normally expect the LUMO to be quite substantially raised. However, it should be remembered that here we are dealing with [5,6]-open bis-adducts, and this may allow for greater electronic interactions between the adduct and the C_{60} moieties, and this may limit any rise in the LUMO. Indeed, prior work has also shown similarly small decreases with respect to PCBM LUMOs for [5,6]-open mono-adduct imino modified C_{60} .³⁴ There, the unexpected deepening of the C_{60} LUMO was explained by way of a reduced electron density in the fullerene shell caused by the higher electronegativity of the nitrogen atom in the imino adduct relative to carbon atoms in the C_{60} . Again here this may explain this

unexpected quality. Furthermore, we see on going from PAF1 to PAF2 an additional, small but non-negligible, decrease in the LUMO and E_{gap} . This would again tend to suggest greater crossover and interactions between the C_{60} orbitals in PAF2 and the comonomers. While unexpected, it might be due to the PAF2 $-OC_{12}H_{25}$ groups permitting greater solubilisation and thus more flexibility in the chain-structure than the PAF1 $-OC_8H_{17}$'s, allowing the former's imino groups a better electronic exchange with the fullerene.

Sample	$E_{1/2}$ ^a	E_{LUMO} (eV) ^a	E_{gap} (eV) ^b	E_{HOMO} (eV) ^b
PCBM	-1.00	- 3.80	2.32 ^c	-5.5
PAF1	-0.96	-3.84	3.33	-7.17
PAF2	-0.94	-3.86	2.73	-6.59

Table 3. Estimated band energy levels for PCBM, PAF1 and PAF2. Notes: (a) calculated using cyclic voltammetry data (see SI, Figure S15); (b) calculated employing REELS data (see Figure S11); (c) literature data shown for comparison, however, note is from CV.⁵⁷

Normal configuration organic solar cells (ITO/PEDOT:PSS/active layer/aluminium) were made combining P3HT with the as-prepared PAFs. Devices with commercial PCBM were also fabricated and used as reference cells to compare PAF1 and PAF2. Figures 5 and S16 show representative J - V curves for all three types of device. Performances with PAFs were lower than those found for PCBM-based devices, with average power conversion efficiencies around 0.2% and 1.4% for PAF1 and PAF2 respectively and 2.6% for PCBM based devices, as indicated in Figure S17 and Table 4. Notably, we find that the V_{oc} s are considerably lower than those using PCBM. This would tend to point to losses through poor interfacial contacts between the acceptor and the electrodes or the donor material. This may have arisen from preparative effects, as the devices were made using solvents and techniques optimised for PCBM, and as such are outside of the scope of this initial study. Suffice that this will be a consideration of future work. In comparison to PAF1, PAF2 shows an enhanced final performance (V_{oc} , J_{sc} , and FF). The improvement of short circuit current and fill factor can be related to a

better electron transport favoured for the PAF2 structure. Recalling that these devices were made with electrodes and solvents that were not optimised for the PAF materials, these initial results remain encouraging.

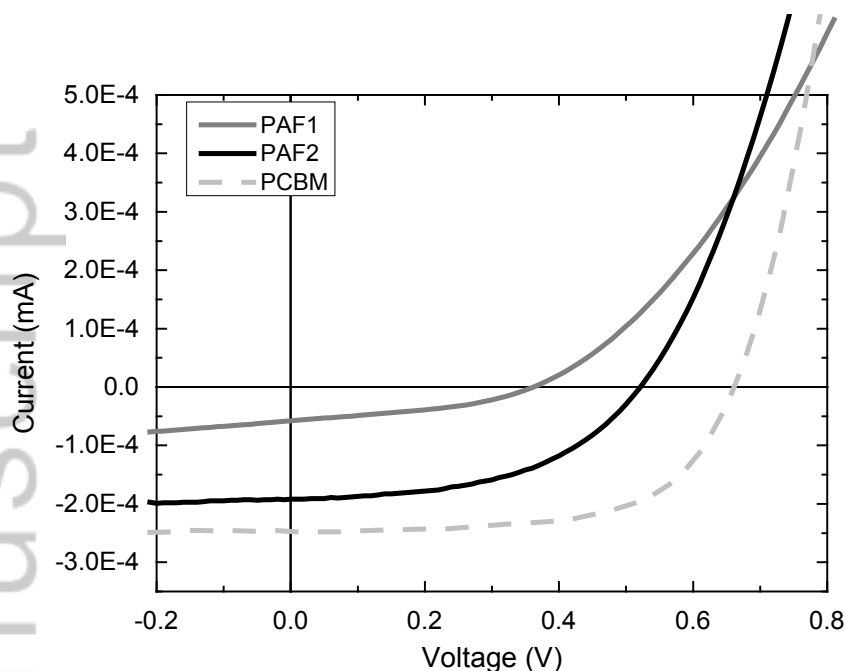


Figure 5. J - V curves of photovoltaic devices made using P3HT with PAF1, PAF2 or PCBM.

Substance	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	η (%)
PCBM	0.65 (SD 0.01)	7.5 (SD 0.62)	0.54 (SD 0.05)	2.64 (SD 0.33)
PAF1	0.37 (SD 0.042)	1.36 (SD 0.25)	0.36 (SD 0.02)	0.19 (SD 0.04)
PAF2	0.48 (SD 0.035)	5.74 (SD 0.75)	0.50 (SD 0.03)	1.38 (SD 0.25)

Table 4. Summary of OPV results, where SD denotes standard deviation.

To confirm the electronic effects of side-chains, the conductivities of the PAFs were characterised using interdigitated gold electrodes as shown in Figure S18 and using the exact techniques described in detail elsewhere.⁶⁰ PAF1 and PAF2 were found to have conductivities of 0.42 and 0.81 nS m^{-1} . That the conductivity is greater for PAF2 than PAF1 would tend to confirm the OPV results. Considering the relation between the bulk drift mobility, conductivity and charge concentration, i.e., $\tilde{A} = N_m e \mu$,

where N_m is the concentration of mobility charge carriers per unit volume, and assuming that there are the same amount of each charge carrier,⁶¹ it is possible to state that the mobility of PAF2 is of the order of $10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. This relatively high value is of interest and may be due to either the polymeric structure or the presence of the heteroatom; future studies will consider this in greater detail.

Conclusions

A novel route to polymerise fullerene has been discovered. Oligo- and poly(azafulleroid)s are formed *via* a [1+3] cycloaddition mechanism to give rise to a quite regio-regular polymer based on [5,6]-open azafulleroids. While further work is required to ascertain the isomeric regioregularity of the structures, these initial studies do not indicate any regio-irregularities. The materials obtained are soluble in various organic solvents. The LUMOs of the polymers are comparable to those of PCBM, and raised, as expected, from those with respect to C_{60} . However, this effect is not as great as expected and may be due to imino-fullerene electronic interactions. Solvation and opto-electronic properties are improved with the longer comonomer side-chains, and future studies will concentrate on varying side-chains so as to increase chain-lengths, improve solubilities and permit extensive NMR studies. However, a concern with this system is its apparent high sensitivity to oxygen, with reactions rendering the materials insoluble due to crosslinking via ether formation and hindering characterisations. Nevertheless, the initial photovoltaic results with the non-optimised hero-cell based on PAF2 exhibiting 1.84 % efficiency and a FF comparable to standard PCBM devices make them worthy of further attention.

Supporting Information details: materials; equipment; syntheses of the comonomers and polymers; NMR, FT-IR, TGA, DSC, UV-visible, CV, OPV and conductivity data; and pictures of the polymers in solution.

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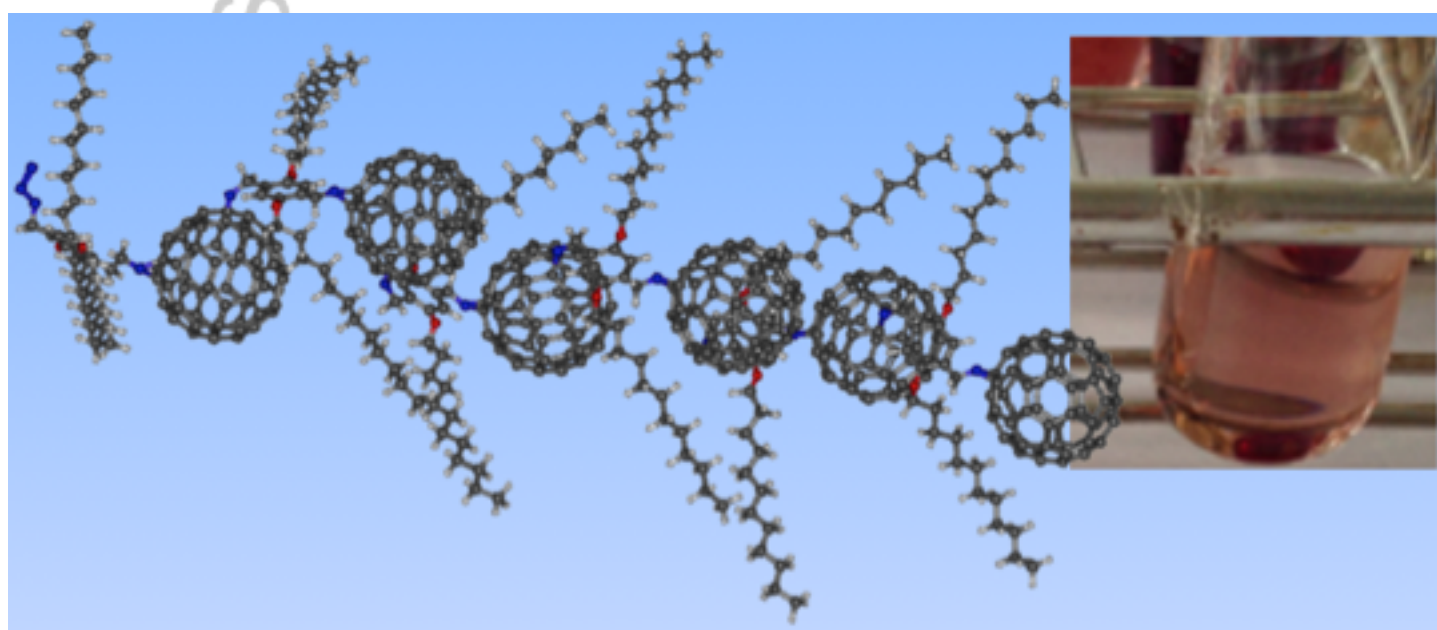
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