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## Regioselective synthesis of fullerene multiadducts via tether-directed 1,3-dipolar cycloaddition†

Bolong Zhang, Jonathan M. White, David J. Jones and Wallace W. H. Wong\*

The regioselective synthesis of fullerene multiadducts was achieved from commercially available reagents in one pot over two steps. The configuration of the isolated regioisomers was determined using various NMR methods, UV-vis spectroscopy and electrochemical analysis with the structure of one isomer confirmed by single crystal X-ray analysis. Interesting variation in regioselectivity was observed when different amino acid reagents were used in the reactions. Theoretical calculations and additional experiments, such as deuterium exchange, led to a proposed mechanism for the regioselective product formation.

### Introduction

Regiochemistry of fullerenes can be complex given the large number of carbon centres that can participate in reactions.<sup>1,2</sup> An effective strategy is to control the regiochemistry using a tether between two reactive head groups.<sup>3,4</sup> This is known as the tether-directed remote functionalization approach which was first demonstrated by Breslow *et al.*<sup>5</sup> in mimicking highly selective enzymatic reactions on steroid compounds. This tether approach has been demonstrated in regio- and stereo-selective fullerene functionalizations.<sup>6,7</sup> Tethers reported include simple arenes, porphyrins, crown ethers as well as chiral Tröger base units.<sup>2</sup> These previous studies investigated the scope of the tether-directed functionalization strategy but did not look into the application of the materials produced.

A central research theme in our group has been the development of organic electronic materials with particular emphasis on thin film solar cells. Bisadducts of fullerenes have been widely incorporated in solar cell devices but isomeric mixtures are commonly used. There has only been a few attempts to isolate single bisadduct isomers and investigate their performance in devices.<sup>8,9</sup> In one case, a single isomer of indene-C<sub>70</sub> bisadduct (IC<sub>70</sub>BA) was obtained by careful chromatographic separation.<sup>10</sup> This single isomer showed significant device performance improvement compared to samples containing iso-

meric mixtures. However, chromatographic isolation of bisadduct isomers is extremely inefficient in terms of product yield and time required for the processing. There has been a few recent studies on the use of tether-directed functionalization to produce fullerene materials for solar cell applications.<sup>11–13</sup> In particular, our group has developed a one-pot synthesis of a single C<sub>60</sub> bisadduct isomer from commercially available phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM).<sup>14</sup> With the relatively short propyl tether and the azomethine ylide reactive head group, one major product was isolated and subsequently identified as the *cis*-1 C<sub>60</sub> bisadduct derivative, *N*-methyl PC<sub>61</sub>PF (Fig. 1). This pure isomer material showed enhancement in performance compared to the isomer mixtures and the original PC<sub>61</sub>BM material.

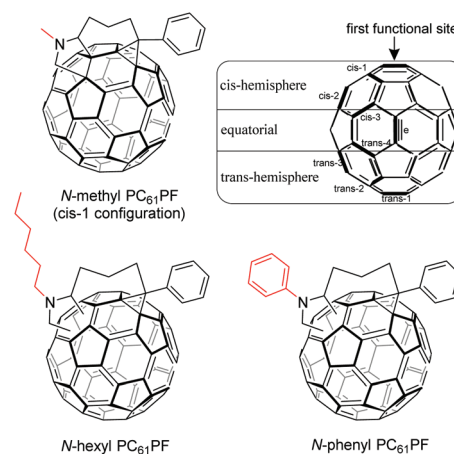


Fig. 1 Chemical structure representation of bisadduct derivatives discussed in this work and an illustration of possible C<sub>60</sub> bisadduct regioisomer configurations.

School of Chemistry, University of Melbourne Bio21 Institute, 30 Flemington Rd, Parkville, Victoria 3010, Australia. E-mail: [wwhwong@unimelb.edu.au](mailto:wwhwong@unimelb.edu.au)

† Electronic supplementary information (ESI) available: Details on the synthesis procedures, characterization and DFT calculations of the materials. Detailed experimental procedures, NMR spectra and other characterization data as well as details on the modelling and theoretical calculations. CCDC 1416759. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ob01630d



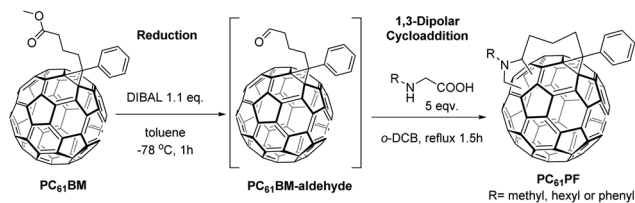


Fig. 2 One-pot two-step synthesis of PC<sub>61</sub>PF derivatives.

This positive outcome gave us incentive to develop a series of related compounds with different substitution on the pyrrolidine nitrogen (Fig. 1). Interestingly, the substituent variations had significant effects on the regioselectivity of the 1,3-dipolar cycloaddition (Fig. 2). Different products were isolated when *N*-hexylglycine and *N*-phenylglycine was used instead of *N*-methylglycine. In a large proportion of examples, 1,3-dipolar cycloaddition to fullerenes occurred at the [6,6] bonds, namely the C=C bonds between two six-membered rings. This can result in 8 possible regioisomers for C<sub>60</sub> fullerene bisadducts (Fig. 1). With the appropriate tether length, one can limit the 1,3-dipolar cycloaddition to the *cis*-hemisphere only. The *cis*-1 configuration was the most favoured in the case of the *N*-methyl PC<sub>61</sub>PF compound. Therefore, it was intriguing to observe regiochemistry variations for the *N*-hexyl and *N*-phenyl compounds even though the propyl tether was unchanged.

In this study, our efforts in the elucidation of the regioisomer configuration of the isolated products are presented. Through computations and experiments, reaction mechanisms for the product outcomes are proposed. It is noteworthy that these tether-directed reaction resulted in fused ring structures, containing 3, 5, 6 and 7-membered rings, rarely observed in the literature.

## Results and discussion

### Synthesis and configuration identification

Two new C<sub>60</sub> bisadducts, *N*-hexyl PC<sub>61</sub>PF and *N*-phenyl PC<sub>61</sub>PF, were synthesized and fully characterized (Fig. 1). As with the previously reported *N*-methyl PC<sub>61</sub>PF, the hexyl and phenyl analogues were synthesized from PC<sub>61</sub>BM in a one-pot-two-step reaction (Fig. 2). PC<sub>61</sub>BM was treated with the reducing reagent, diisobutylaluminium hydride (DIBAL), to give the aldehyde intermediate. Without isolation, the aldehyde intermediate was heated with *N*-hexylglycine or *N*-phenylglycine in 1,2-dichlorobenzene (*o*-DCB) at 180 °C to form the *N*-hexyl and *N*-phenyl PC<sub>61</sub>PF respectively. It was apparent immediately from thin layer chromatography analysis that the *N*-hexylglycine and *N*-phenylglycine gave different product distributions.

The crude product of *N*-hexyl PC<sub>61</sub>PF was purified by silica chromatography and two major fractions were isolated, *N*-hexyl PC<sub>61</sub>PF-1 and *N*-hexyl PC<sub>61</sub>PF-2, in yields of 9% and 14% respectively. The purity of the two hexyl samples were examined by HPLC analysis with Cosmosil Buckyprep-D column

and found to be 95% and 99% for fraction 1 and 2 respectively (Fig. S22<sup>†</sup>). According to the <sup>1</sup>H NMR spectrum, both fractions contained three distinct proton resonances characteristic to the pyrrolidine moiety, confirming the formation of the fulleropyrrolidine unit. However, the *N*-hexyl PC<sub>61</sub>PF-2 fraction showed two additional singlet resonance at 5.65 and 5.45 ppm compared to *N*-hexyl PC<sub>61</sub>PF-1. This observation corresponded to the mass spectrometry data where *N*-hexyl PC<sub>61</sub>PF-2 was two mass units heavier than *N*-hexyl PC<sub>61</sub>PF-1.

Full <sup>1</sup>H NMR assignment of the two fractions was achieved using two-dimensional NMR analysis techniques shown in Fig. 3 and 4. The heteronuclear multiple-bond correlation (HMBC) spectrum of *N*-hexyl PC<sub>61</sub>PF-1 showed the C<sub>15</sub> carbon coupled with both H<sub>5</sub> and H<sub>2b</sub> protons (Fig. 3). This coupling was observed for the *N*-methyl PC<sub>61</sub>PF compound with known *cis*-1 regioisomer configuration. This strongly indicated *cis*-1 configuration for the *N*-hexyl PC<sub>61</sub>PF-1 fraction. With two extra proton signals, the HMBC spectrum of *N*-hexyl PC<sub>61</sub>PF-2 was more difficult to analyse (Fig. 4). There were clear HMBC coupling signals for H<sub>18</sub> to C<sub>12</sub> and C<sub>13</sub> as well as H<sub>17</sub> to C<sub>5</sub> and C<sub>14</sub>, but no coupling with C<sub>15</sub> and C<sub>16</sub>. This suggested that C<sub>17</sub> and C<sub>18</sub> were next to C<sub>13</sub> and C<sub>14</sub> but not directly adjacent to C<sub>15</sub> and C<sub>16</sub>. In addition, H<sub>17</sub> and H<sub>18</sub> did not couple to each other. In light of these NMR experiments, a possible configuration of *N*-hexyl PC<sub>61</sub>PF-2 was shown in Fig. 4 with the pyrrolidine ring and the two additional protons occupied both the *cis*-1 and *cis*-2 position, designated as *cis*-1,2 hence forth.

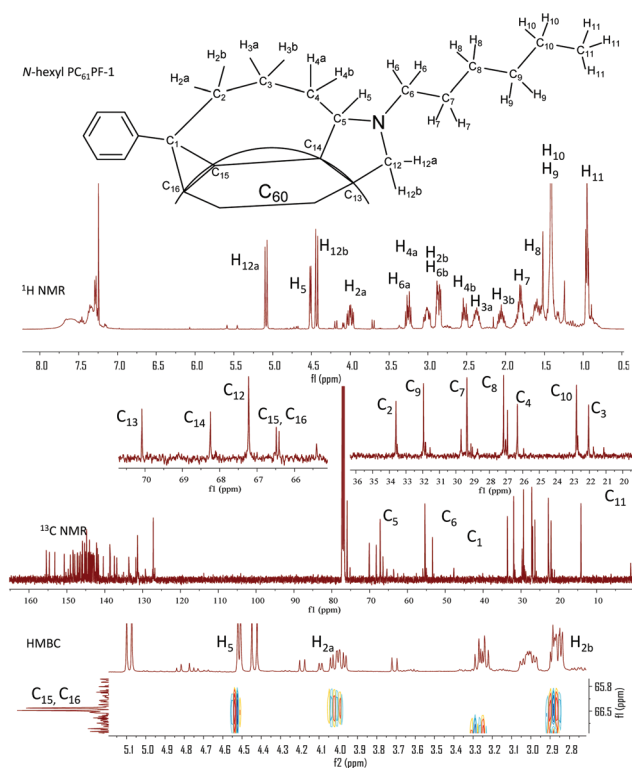


Fig. 3 <sup>1</sup>H, <sup>13</sup>C and HMBC NMR spectrum of *N*-hexyl PC<sub>61</sub>PF-1 with resonances assigned for the key atoms in discussion.



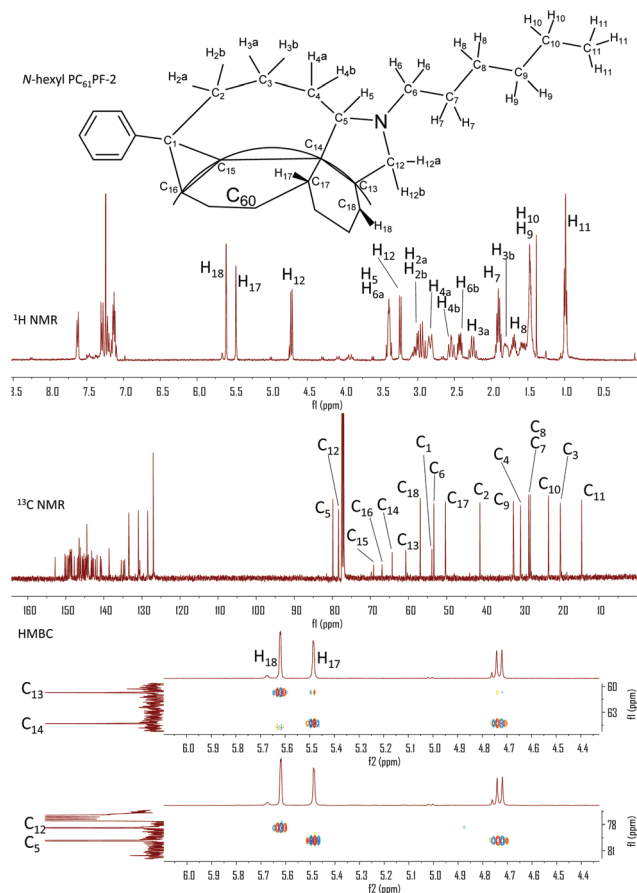


Fig. 4  $^1\text{H}$ ,  $^{13}\text{C}$  and HMBC NMR spectrum of *N*-hexyl  $\text{PC}_{61}\text{PF}$ -2 with resonances assigned for the key atoms in discussion.

Single crystals of *N*-hexyl  $\text{PC}_{61}\text{PF}$ -2 were obtained by recrystallization from chloroform and subsequent X-ray crystallography experiment on the crystals revealed the relative configuration of the sample. The fused ring structure containing the pyrrolidine substituent was in agreement with the NMR assignments where the pyrrolidine ring and the two additional protons were in the *cis*-1,2 configuration (Fig. 4 and 5). Surprisingly, the crystallography data indicated the enantiomeric

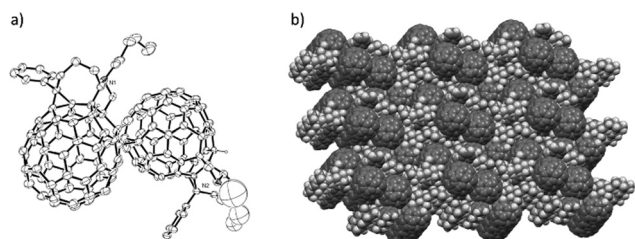


Fig. 5 Single crystal X-ray structure representation of *N*-hexyl  $\text{PC}_{61}\text{PF}$ -2 dimer crystals grown from chloroform: (a) space filling model and (b) dimer packing diagram in single crystal, where  $\text{CHCl}_3$  solvent molecules have been omitted for clarity.

pairs in the crystal existed in a dimerized state (Fig. 5). The dimerization reaction probably proceeded through a photoactivated  $[2 + 2]$  cycloaddition driven by the close packing in the crystal structure.<sup>15</sup> It is important to note that there was no evidence of the covalently linked dimer in mass spectrometry experiments prior to the crystallography analysis with the sample kept in ambient light conditions.

The crude product of *N*-phenyl  $\text{PC}_{61}\text{PF}$  was purified by flash chromatography with one major fraction isolated in a yield of 14%. Some  $\text{PC}_{61}\text{BM}$  starting material and aldehyde intermediate were recovered but the majority of reaction mixture consisted of insoluble material that could not be identified. The purity of the *N*-phenyl  $\text{PC}_{61}\text{PF}$  sample was 77% by HPLC analysis (Fig. S22<sup>†</sup>). The three distinctive proton resonances of the pyrrolidine moiety were clearly observed at the chemical shift of 5.82, 5.47 and 5.35 ppm in the  $^1\text{H}$  NMR spectrum. As with the hexyl compounds, key structure assignments of *N*-phenyl  $\text{PC}_{61}\text{PF}$  was achieved using two-dimensional NMR analysis (Fig. 6 and S13–15<sup>†</sup>). Due to overlapping resonances, it was not possible to identify the regioisomer configuration for *N*-phenyl  $\text{PC}_{61}\text{PF}$  in NMR experiments.

It is well-established that the isomeric configuration of fullerene bisadducts can be identified by comparing the UV-Vis spectrum of materials with known configuration.<sup>6</sup> This is because the absorption bands of fullerene derivatives are closely related to the conjugated surface of the molecules. As shown in Fig. 7, the spectrum of *N*-hexyl  $\text{PC}_{61}\text{PF}$ -1 and *N*-phenyl  $\text{PC}_{61}\text{PF}$  contained a peak at 430 nm. Other  $\text{C}_{60}$  bisadducts of known *cis*-1 configuration, for example *N*-methyl  $\text{PC}_{61}\text{PF}$ <sup>14</sup> and  $\text{C}_{60}$ -benzyl bisadduct,<sup>1</sup> have similar spectral

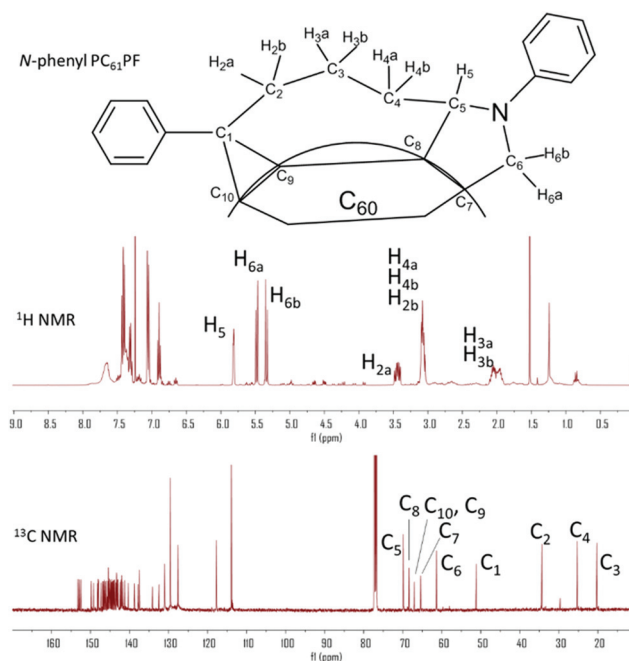


Fig. 6  $^1\text{H}$  and  $^{13}\text{C}$  spectrum of *N*-phenyl  $\text{PC}_{61}\text{PF}$  with resonances assigned for the key atoms in discussion.



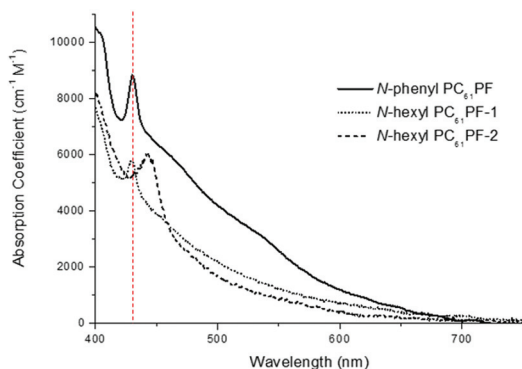


Fig. 7 UV-Vis spectrum of PC<sub>61</sub>PF compounds.

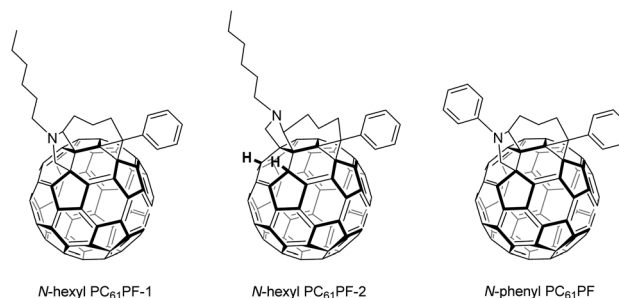


Fig. 8 Chemical structures of *N*-hexyl PC<sub>61</sub>PF-1, *N*-hexyl PC<sub>61</sub>PF-2 and *N*-phenyl PC<sub>61</sub>PF.

features. This provided support for the NMR analysis of the *N*-hexyl PC<sub>61</sub>PF-1 compound and hinted at the *cis*-1 configuration for *N*-phenyl PC<sub>61</sub>PF. Notably, the UV-vis spectrum of *N*-hexyl PC<sub>61</sub>PF-2 was different to that of *N*-hexyl PC<sub>61</sub>PF-1 and *N*-phenyl PC<sub>61</sub>PF with a peak at 442 nm (Fig. 7 and Table 1). Cyclic voltammetry was carried out to estimate the lowest unoccupied molecular orbital (LUMO) energy level of each PC<sub>61</sub>PF material (see ESI for details, Fig. S23†). The half-wave potential of the first reduction process ( $E_{1/2}^{\text{red}}$ ) were measured against the internal ferrocene standard and the LUMO energy can be calculated from this data (Table 1).<sup>16</sup> The *N*-hexyl PC<sub>61</sub>PF-1 sample has higher electron affinity with  $E_{\text{LUMO}}$  at  $-3.67$  eV than *N*-hexyl PC<sub>61</sub>PF-2 with  $E_{\text{LUMO}}$  at  $-3.58$  eV. This corresponds to the increased substitution for *N*-hexyl PC<sub>61</sub>PF-2. The chemical structure of the isolated regioisomers, assigned using the characterisation data, are shown in Fig. 8. In the next section, calculations and discussion on the mechanism of product formation will provide support to the various characterisation techniques presented thus far.

### Density functional theory (DFT) calculations

The unusual *cis*-1,2 configuration for *N*-hexyl PC<sub>61</sub>PF-2 was examined in DFT calculations to support our experimental observations. The proposed reaction pathway leading to the observed products is discussed below (Fig. 9). One can consider the azomethine ylide as the starting point of discussions. For *N*-hexyl PC<sub>61</sub>PF-1 and *N*-phenyl PC<sub>61</sub>PF, the *cis*-1 product can be formed by 1,3-dipolar cycloaddition in one step. On the other hand, the insertion of two additional protons for *N*-hexyl

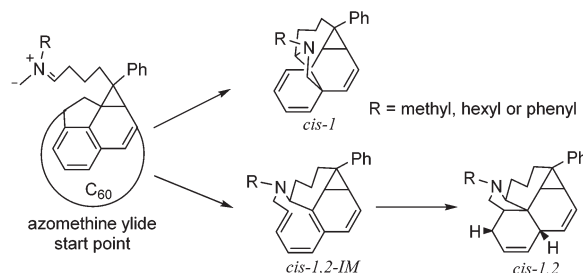


Fig. 9 Proposed reaction pathway for PC<sub>61</sub>PF products with *cis*-1 and *cis*-1,2 configuration.

PC<sub>61</sub>PF-2 with *cis*-1,2 configuration probably involved at least two steps. In detail, the 1,3-dipolar cycloaddition proceeded first to form the pyrrolidine ring on the [5,6] bond followed by protonation to give the *cis*-1,2 product. Therefore, there must be an intermediate between the transition state of the cycloaddition step and the transition state of the protonation step. Using this model and applying DFT at B3LYP-D3 level<sup>17,18</sup> with 6-311G basis set and polarization function (d,p), the relative energy of the azomethine ylide starting point, transition states, possible intermediates and final products were calculated (Fig. 10 and Table S1†).<sup>19,20</sup>

Since the product energy of PC<sub>61</sub>PFs in *cis*-1,2 configuration were much lower than both the intermediates *cis*-1,2-IM<sup>21,22</sup> and the products of *cis*-1, the formation of the *cis*-1,2 product can be considered as irreversible (Fig. 10). On the other hand, an equilibrium may exist between *cis*-1 and *cis*-1,2-IM species. From the calculated Gibbs free energy difference ( $\Delta\Delta G$ ) values

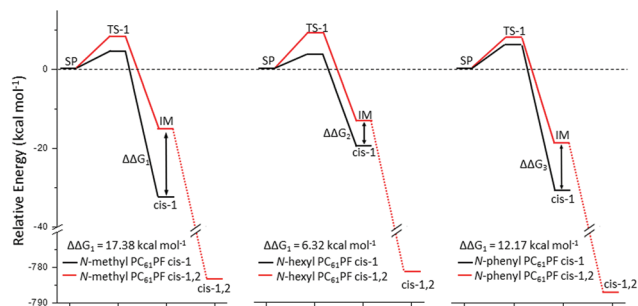
Table 1 Summary of characterization data for PC<sub>61</sub>PF compounds

	Purity <sup>a</sup> (%)	Configuration	UV-vis $\lambda_{\text{max}}$ <sup>b</sup> (nm)	$E_{1/2}^{\text{red}}$ <sup>c</sup> (eV)	$E_{\text{LUMO}}$ <sup>d</sup> (eV)
<i>N</i> -Hexyl PC <sub>61</sub> PF-1	95	<i>cis</i> -1	430 (5.8)	-1.13	-3.67
<i>N</i> -Hexyl PC <sub>61</sub> PF-2	99	<i>cis</i> -1,2	442 (6.0)	-1.22	-3.58
<i>N</i> -Phenyl PC <sub>61</sub> PF	77	<i>cis</i> -1	431 (8.8)	-1.25	-3.55

<sup>a</sup> Calculated by HPLC analysis. <sup>b</sup> Absorption coefficient ( $\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) in brackets. <sup>c</sup> Half-wave reduction potential from cyclic voltammetry. <sup>d</sup>  $E_{\text{LUMO}} = -(E_{1/2}^{\text{red}} + 4.8) \text{ eV}$ .







**Fig. 10** Relative energy of starting point, transition states, intermediates and products of PC<sub>61</sub>PF compounds with *cis*-1 and *cis*-1,2 configuration from DFT calculations.

between *cis*-1 and *cis*-1,2-IM, relative equilibrium constant ( $K$ ) values can be obtained using the equations:

$$K = e^{\frac{-\Delta\Delta G}{RT}} \quad (1)$$

$$K = \frac{[cis-1, 2-IM]}{[cis-1]} \quad (2)$$

where  $R$  is the gas constant and  $T$  is the reaction temperature. With  $\Delta\Delta G_1$  of *N*-methyl PC<sub>61</sub>PF larger than  $\Delta\Delta G_2$  of *N*-hexyl PC<sub>61</sub>PF (Fig. 10), the corresponding  $K$  for the methyl species was much smaller ( $K_1 = 4.1 \times 10^{-9}$ ) than the hexyl species ( $K_2 = 8.9 \times 10^{-4}$ ). The consequence of this difference was that a much greater proportion of the hexyl species would exist in the *cis*-1,2-IM form compared to the methyl at equilibrium, leading to a greater chance of formation of the *cis*-1,2 product for the hexyl. This corresponded to the *N*-hexyl PC<sub>61</sub>PF-1 and *N*-hexyl PC<sub>61</sub>PF-2 compounds that were isolated. A steric argument can be invoked for the outcome of the calculated  $\Delta\Delta G$  values. The significantly higher energy of the hexyl *cis*-1 species can be attributed to the steric bulk of the hexyl group compared to the methyl group (Fig. S26†). The steric effect of the hexyl moiety in *cis*-1,2-IM configuration was not as significant resulting in similar energies for the hexyl and methyl *cis*-1,2-IM species.

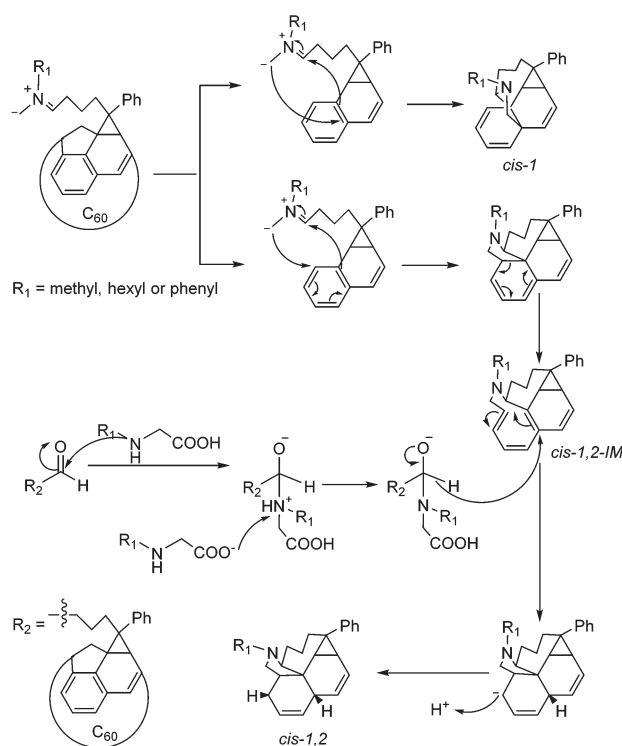
Although the phenyl group should have stronger steric effect than hexyl, *cis*-1,2 product was not observed for *N*-phenyl PC<sub>61</sub>PF. The DFT calculation revealed a relatively large  $\Delta\Delta G_3$  for the phenyl compounds (Fig. 10). This meant that only a small concentration of *cis*-1,2-IM of *N*-phenyl PC<sub>61</sub>PF existed at equilibrium ( $K_3 = 1.3 \times 10^{-6}$ ), resulting in less *cis*-1,2 product compared to hexyl species. A possible reason could be that the phenyl group was able to stabilize the *cis*-1 product by sharing the electron density with the pyrrolidine moiety. According to the DFT optimized molecular models, the orientation of the phenyl ring relative to the pyrrolidine ring was very different for the *cis*-1 and *cis*-1,2-IM species. Only the optimized geometry of *cis*-1 showed electronic stabilization effect of the phenyl group. In the *cis*-1,2-IM species, steric hindrance between the phenyl group and the H<sub>4</sub> proton resulted in an orientation of

the phenyl ring relative to the pyrrolidine ring that did not favor electronic stabilization (Fig. S27†).

### Deuterium exchange experiments and proposed mechanism

To gain further insight into the reaction mechanism, deuterium exchange experiments were performed. The reactions to form the hexyl compounds were carried out as before except with the addition of deuterium oxide in the reaction mixture of the 1,3-dipolar cycloaddition step (see Experimental section for details). The <sup>1</sup>H NMR spectrum showed that deuterium exchange occurred at two protons (H<sub>4a</sub> and H<sub>4b</sub>) in *N*-hexyl PC<sub>61</sub>PF-1 and four (H<sub>4a</sub>, H<sub>4b</sub>, H<sub>17</sub> and H<sub>18</sub>) in *N*-hexyl PC<sub>61</sub>PF-2 (Fig. S16 and S17†). The exchanges at the H<sub>4a</sub> and H<sub>4b</sub> proton could be simply attributed to the keto–enol tautomerisation of the aldehyde starting material. The deuterium exchange at H<sub>17</sub> and H<sub>18</sub> for the *N*-hexyl PC<sub>61</sub>PF-2 material provided information on the source of those protons (Fig. 11). It was noteworthy that the percentage of deuterium exchange at H<sub>15</sub> and H<sub>18</sub> were both around 80% by integration. The following is a description of the proposed reaction mechanism for the formation of the *cis*-1 and *cis*-1,2 products taking into account all experimental data and calculations.

The mechanism of formation of the *cis*-1 product proceeded via 1,3-dipolar cycloaddition of azomethine ylide to *cis*-1 bond of the C<sub>60</sub> derivative (Fig. 11). This reaction, known as the Prato reaction, is commonly observed in the literature but usually proceeds without regioselectivity.<sup>23,24</sup> In order to



**Fig. 11** The proposed mechanism for the formation of PC<sub>61</sub>PF compounds in either *cis*-1 or *cis*-1,2 configuration.



achieve the *cis*-1,2 product outcome, the 1,3-dipolar cycloaddition would be required to occur at the [5,6] bond between the *cis*-1 and *cis*-2 positions (Fig. 11).<sup>21,22</sup> This open cage intermediate *cis*-1,2-IM would then be converted to the close cage intermediate *via* a hydride transfer reaction. Further protonation would lead to the *cis*-1,2 product. It is feasible that the hydride source is from the fullerene aldehyde substrate leading to a fullerene amide by-product. This proposal is in agreement with the observed product yields. A reaction with deuterated DIBAL reagent was performed in an attempt to gather further evidence for the proposed mechanism (see ESI, Fig. S18†). In agreement with the azomethine ylide formation mechanism, the H<sub>5</sub> proton on the pyrrolidine ring was deuterated. However, deuteration was not observed for either the H<sub>17</sub> or H<sub>18</sub> on the fullerene surface. It was found that the acidity of H<sub>17</sub> and H<sub>18</sub> was such that there was facile proton exchange under the reaction conditions (Fig. S19†). Attempts were made to identify intermediates and by-products from the reaction mixture using mass spectrometry. While some relevant fragments were observed, these experiments did not provide conclusive evidence for the proposed reaction mechanism.

## Conclusions

The regioselective synthesis of three fullerene derivatives was presented. Starting from commercially available PC<sub>61</sub>BM, the multi-adducts were obtained *via* reduction of the methyl ester followed by 1,3-dipolar cycloaddition of the azomethine ylide in one pot. While the yields were moderate, intriguing regioselectivity variations were observed when different amino acid reagents were used. With a range of NMR methods, UV-Vis spectroscopy and electrochemical analysis, it was possible to confidently assign the configurations of the isolated regioisomers *N*-hexyl PC<sub>61</sub>PF-1 (*cis*-1), *N*-hexyl PC<sub>61</sub>PF-2 (*cis*-1,2) and *N*-phenyl PC<sub>61</sub>PF (*cis*-1). The relative configurations for *N*-hexyl PC<sub>61</sub>PF-2 was confirmed by single crystal X-ray analysis. Mechanism for the product formation was proposed with the aid of DFT calculations and deuterium exchange experiments.

## Acknowledgements

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