

Diamond Rings or Dumbbells: Controlling the Structure of Poly(ethylene glycol)–Fullerene [60] Adducts by Varying Linking Chain Length

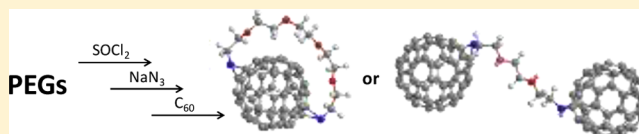
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Supporting Information

ABSTRACT: Fullerene [60] (C_{60}) and poly(ethylene glycol) (PEG) adducts were prepared via 1,3-dipolar cycloaddition of bis-azido-terminated linear PEG (N_3 -PEG- N_3) and C_{60} . While long chain length PEGs ($M_n = 1000$ and 3350 Da) yielded the cyclic diamond ring structures ($C_{PEG1000}^{C_{60}}$ and

$C_{PEG3350}^{C_{60}}$), short-chained PEG ($M_n = 200$ Da) yielded a telechelic dumbbell structure (C_{60} -PEG $_{200}$ - C_{60}). Both dumbbell and diamond ring structures were characterized by MALDI-TOF-MS, 1H NMR, FTIR, UV-vis, and elemental analysis (EA). The results highlight the structural dependence of the PEG- C_{60} adducts on the chain length of the azido-terminated polymer, a factor previously neglected.



INTRODUCTION

Fullerene [60] (C_{60}) has been a focus of scientific attention since its discovery in the mid-1980s,¹ attracting particular interest in its rich chemistry with electron-rich reactive species including carbenes, nitrenes, and azides.² The strong electron-accepting character of fullerenes and the versatility of their grafting chemistry have motivated their incorporation in diverse applications, including organic photovoltaics,^{3,4} as antioxidants,⁵ and as MRI agents.⁶ In many contexts, especially bulk heterojunction solar cells, fullerene's highly hydrophobic nature has a deterministic effect on phase behavior in polymer blends.^{7,8} However, the low solubility of C_{60} in common solvents limits direct use in many circumstances. To enhance the compatibility and processability, C_{60} has been attached covalently to a wide range of polymers, in many different architectures, including "pearl necklace" main chain, side chain pendant, and telechelic configurations;⁹ the properties of various polymer blends incorporating C_{60} -polymer adducts have been tested.^{10–12} Both mono- and double-fullerene-terminated PEGs have received particular attention as simple model systems due to their linearity and ease of preparation.^{13–15} PEG is an appealing backbone for C_{60} end-capped adducts due to its wide solubility, structural inertness, and the commercial availability of a variety of chain lengths and terminations.

Goh and co-workers have promoted the synthesis of dumbbells using the 1,3-dipolar cycloaddition reaction of N_3 -PEG- N_3 (M_n for PEG = 2500, 5000, 10 000 and 20 000 g mol⁻¹) with C_{60} and subsequently prepared blends with poly(acrylic acid), poly(methacrylic acid), and poly(*p*-vinyl-phenol).^{12,16,17} These blends showed an increased glass transition temperature (T_g) compared to their parent polymers, suggesting that addition of PEG- C_{60} alters the phase behavior

of corresponding polymer blends. The synthetic protocol for C_{60} end-capping followed three steps: (i) the conversion of the terminal PEG hydroxyl to chloride with thionyl chloride, (ii) the formation of N_3 -PEG- N_3 using sodium azide, and (iii) the 1,3-dipolar cycloaddition reaction of PEG- N_3 with C_{60} to yield dumbbells.^{12,16–18} Although a well-defined synthetic protocol has been reported, the existing characterization appears ambiguous since it mainly relies on UV-vis analysis of the resulting fullerene-polymer adducts. Other core characterization data, particularly NMR and mass spectrometry characterization, have not been reported, although they are vital in determining the product geometry.^{12,16–18} In addition to dumbbells, a range of monofullerene polymer adducts, including some based on PEG, have been prepared by using end-protected polymers to limit grafting to single fullerenes only.^{17,19} This paper explores the established "PEG dumbbell" reaction¹⁷ using different molecular weight PEG chains to control both mono- and bis-fullerene end-capped poly(ethylene glycol) (PEG) adducts. The distinct nature of these products was established by fully characterizing both starting materials and products using matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS), nuclear magnetic resonance spectroscopy (1H NMR), Fourier transform infrared spectroscopy (FTIR), and ultraviolet visible spectroscopy (UV-vis).

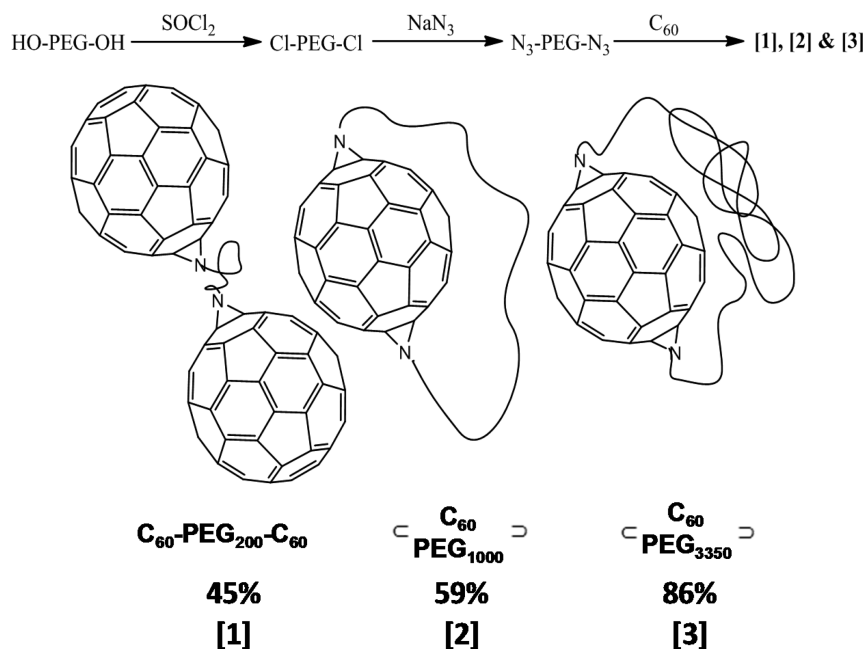
RESULTS AND DISCUSSION

The C_{60} -PEG $_{200}$ - C_{60} dumbbell was synthesized via the 1,3-dipolar cycloaddition reaction of N_3 -PEG- N_3 with C_{60} ,

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Scheme 1. Reaction Scheme for PEG- C_{60} Adducts, Dumbbell [1] and Diamond Rings [2, 3]

following a modified literature procedure;¹⁷ unexpectedly, longer PEG chains produced diamond ring structures ($\text{C}_{60}\text{-PEG}_{3350}$ and $\text{C}_{60}\text{-PEG}_{1000}$). In a typical reaction, bis-azido-terminated PEGs dissolved in *o*-dichlorobenzene (*o*-DCB) were treated with 20 equiv of C_{60} at 140 °C for 24 h, followed by work-up with solvent extraction or column chromatography (see Experimental Section). Fewer equivalents of C_{60} (2.2 equiv, as in the literature procedure) produced similar results; C_{60} content was increased in an attempt to favor dumbbell formation. Three new PEG- C_{60} adducts (1, 2, and 3) were obtained in 45, 59, and 86% yields, respectively (Scheme 1). The structural assignments were based on MALDI-TOF-MS data and ^1H NMR spectra.

The $\text{PEG}_{3350}\text{-C}_{60}$ adduct was selected for the most detailed characterization, as its long PEG chain gave the best solubility. Poor solubility complicated some aspects of spectroscopic analysis (especially NMR, see below) in the case of the PEG_{1000} and PEG_{200} fullerene adducts. In addition, the $\text{PEG}_{3350}\text{-C}_{60}$ adduct is well suited for comparison with the existing literature reports¹² of similar fullerene adducts prepared with PEG_{2000} and PEG_{5000} . The initial Cl-PEG-Cl and $\text{N}_3\text{-PEG-N}_3$ derivatives were prepared following the procedure reported by Goh et al.¹⁷ The electronegativity difference of nitrogen compared to oxygen allows PEG-azide to be identified by ^1H NMR, since the α -proton chemical shift for the $\text{N}_3\text{-PEG-N}_3$ appears at 3.42 ppm (lit. 3.36 ppm)²⁰ compared to 3.75 ppm for OH-terminated PEG (see Supporting Information Figures S1–S3 for ^1H NMR of HO-PEG₃₃₅₀-OH, Cl-PEG₃₃₅₀-Cl, and $\text{N}_3\text{-PEG}_{3350}\text{-N}_3$, respectively). The transformation of chlorides into azides is confirmed by the presence of azido stretching ($\nu_{\text{asymmetric N}_3}$, 2095 cm^{-1}) in FTIR (Figure 1).¹⁷ Further evidence for successful PEG end-group transformation is provided by MALDI-TOF-MS (see Supporting Information Figures S6 and S7 for full MALDI-TOF spectra of Cl-PEG₃₃₅₀-Cl and $\text{N}_3\text{-PEG}_{3350}\text{-N}_3$, respectively); these data are especially helpful for following the transformation from hydroxyl to chloride due to the similar electronegativity of oxygen and

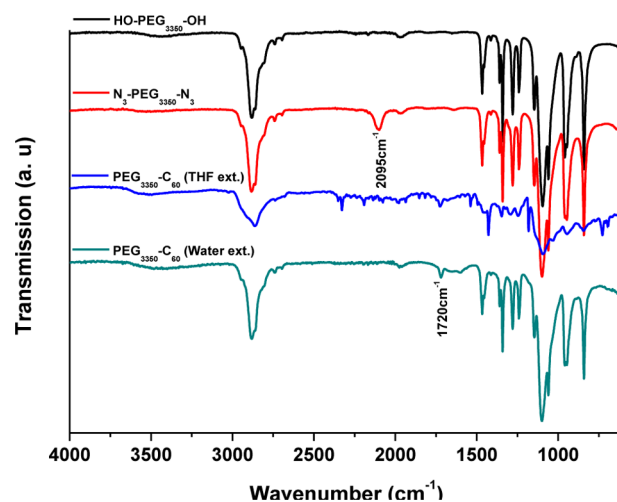


Figure 1. Transmission FTIR spectra of PEG_{3350} derivatives. The feature at 2095 cm^{-1} was assigned to azido stretching whereas the 1720 cm^{-1} peak was assigned to aziridine (C–N) stretching.

chlorine which makes ^1H NMR assignment less conclusive. Isolated $\text{N}_3\text{-PEG-N}_3$ was subsequently reacted with C_{60} to afford C_{60} end-capped PEG adducts.¹⁷

Initially, following the literature protocol,¹⁷ THF extraction was used to isolate the $\text{PEG}_{3350}\text{-C}_{60}$ adduct from the crude mixture (60 mL of THF per 1 g of C_{60}). However, weak absorption bands, characteristic²¹ for pristine C_{60} , at ca. 2000–2500 cm^{-1} in the FTIR spectrum of the $\text{PEG}_{3350}\text{-C}_{60}$ adduct (THF extracted) indicated the continued presence of non-grafted C_{60} (Figure 1), presumably due to the modest solubility of pristine C_{60} in THF (0.06 mg mL^{-1}).²² Instead, after THF extraction, the $\text{PEG}_{3350}\text{-C}_{60}$ product was further extracted with water, exploiting the solubility imparted by its long hydrophilic chain. The FTIR spectrum of water extracted $\text{PEG}_{3350}\text{-C}_{60}$ adduct (Figure 1) confirmed removal of unreacted C_{60} . The FTIR analysis of the $\text{PEG}_{3350}\text{-C}_{60}$ adduct (water extracted) also confirmed successful azide addition by the complete loss of the

characteristic azido absorption band at 2095 cm^{-1} and the appearance of a medium intensity band at 1720 cm^{-1} which can be attributed to the aziridine ring (C–N) stretch (Figure 1). Free aziridine rings show a (C–N) stretch²³ at around 1650 cm^{-1} , but the strain induced by the fullerene shifts the peak to higher wavenumber. The UV–vis spectrum of pure C_{60} shows characteristic UV–vis absorption maxima at 336 and 409 nm, while the PEG itself is featureless in the range measured (Figure 2). The UV–vis spectrum of the $PEG_{3350}\text{-}C_{60}$ adduct

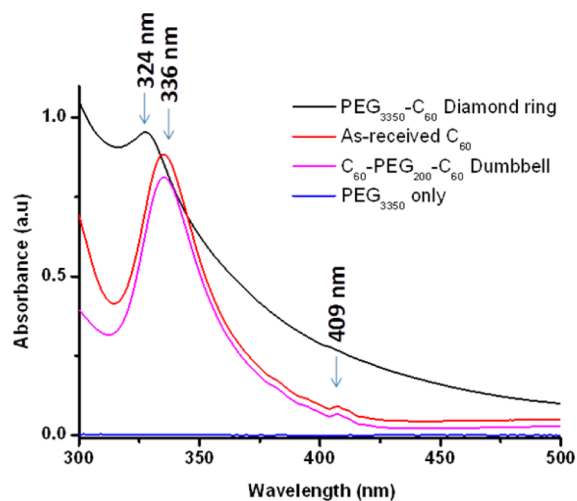


Figure 2. UV–vis spectra of PEG_{3350} and $PEG\text{-}C_{60}$ adducts and pristine C_{60} , recorded in toluene.

showed strong absorbance at around 324 nm, confirming successful incorporation of C_{60} onto PEG. Note that the shift to shorter wavelength is more consistent with the formation of a double addition to the fullerene than a monoadduct.^{24,28}

Further evidence for the formation of the $PEG_{3350}\text{-}C_{60}$ adduct is provided by $^1\text{H NMR}$ (Figure 3). Compared to the parent polymer ($\text{HO-PEG}_{3350}\text{-OH}$), the $^1\text{H NMR}$ spectrum of the $PEG_{3350}\text{-}C_{60}$ adduct shows two new signals at 4.45 and 3.80

ppm, associated with the new bond formation. Because of the conjugated, though not superaromatic, π -system, protons closer to the C_{60} surface are deshielded.²⁵ Hence, the most deshielded new signal, at 4.45 ppm, is assigned to α -protons and the other signal at 3.80 ppm to the β -protons (Figure 3). Despite the new signals relating to the covalently functionalized C_{60} , the overall structure of the adduct is not determined. The two possible geometries include either a bis-fullerene adduct with a single PEG chain connecting two fullerenes (dumbbell) or a monofullerene adduct with both ends of the PEG chain attached to the same fullerene (diamond ring). Unfortunately, $^1\text{H NMR}$ does not resolve the two geometries due to the lack of protons on fullerene. No good $^{13}\text{C NMR}$ data were obtained due to the long relaxation times involved.²⁶

Overall, the $^1\text{H NMR}$ data, supported by FTIR and UV–vis, indicate successful covalent addition of $\text{N}_3\text{-PEG}_{3350}\text{-N}_3$ to C_{60} . However, MALDI-TOF-MS was used to confirm that the diamond ring ($C_{60}\text{-PEG}_{3350}$) geometry formed in preference to the dumbbell ($C_{60}\text{-PEG-C}_{60}$) structure; a low laser intensity (90 mW) was used to minimize any fragmentation of the polymer chain or dissociation of terminal C_{60} molecules. The mass spectrum of the $PEG_{3350}\text{-}C_{60}$ adduct shows a Gaussian distribution of positively charged ions ranging from 2297 to 4720 m/z (Figure 4). Taking an average of 65 ethylene oxide repeating units as a representative example for the chain (equivalent to the M_n derived from MALDI,²⁷ Figure 4), the theoretically calculated masses ($[\text{M} + \text{Na}]^+$) for diamond ring ($C_{60}\text{-PEG}_{3350}$) and dumbbell ($C_{60}\text{-PEG}_{3350}\text{-}C_{60}$) can be calculated as 3660.7 and 4380.7 Da, respectively. It is clear from the mass spectrum that the reaction of $\text{N}_3\text{-PEG}_{3350}\text{-N}_3$ with excess C_{60} does not yield a dumbbell structure ($C_{60}\text{-PEG}_{3350}\text{-}C_{60}$) or a double PEG chain structure ($\text{PEG}_{3350}\text{-}C_{60}\text{-PEG}_{3350}$); rather, the data indicate the formation of a diamond ring structure (single fullerene), at around 720 Da ($C_{60} = 720$ Da) less than that of the theoretically calculated mass of $C_{60}\text{-PEG}_{3350}\text{-}C_{60}$. Close inspection of positively charged ions

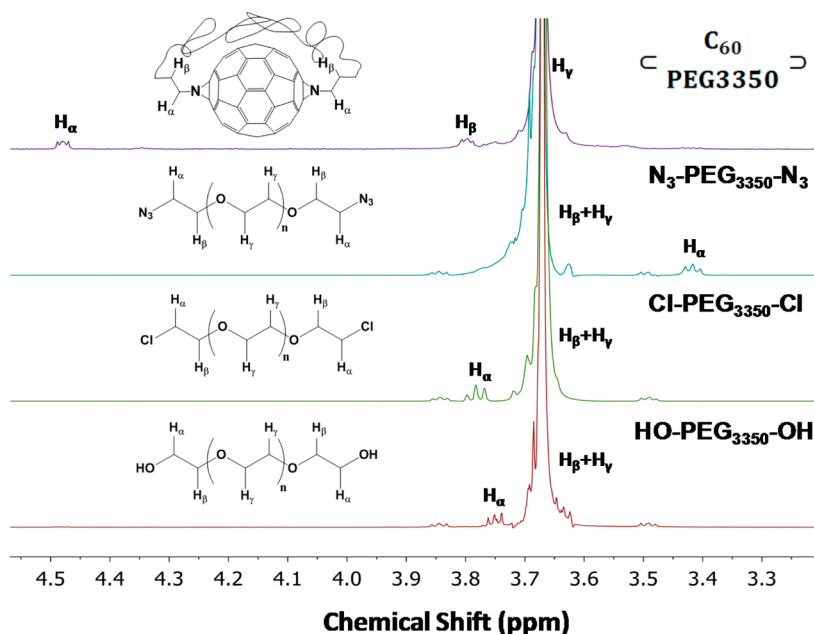


Figure 3. $^1\text{H NMR}$ of PEG_{3350} derivatives and $PEG_{3350}\text{-}C_{60}$ adduct.

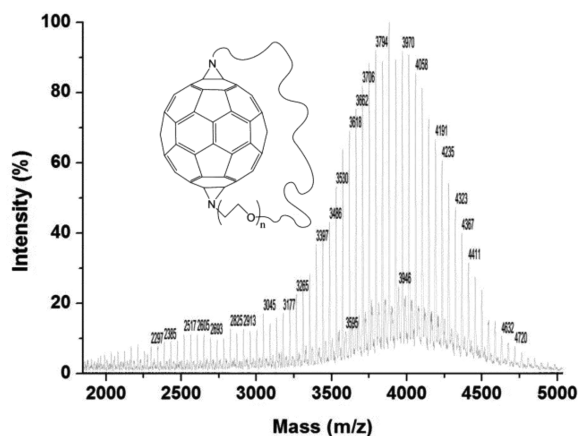


Figure 4. MALDI-TOF of the PEG₃₃₅₀-C₆₀ diamond ring. The offset high/low intensity patterns are formed by the polydispersed polymer with either Na⁺ or K⁺ as counterions.

ranging from m/z 2297 to 4720 (Figure 4) indicates that the observed mass values are not related to fragmentation of a dumbbell structure, as the molecule retains the full chain length distribution of the initial PEG. This finding is further supported by elemental analysis (EA) of the PEG₃₃₅₀-C₆₀ adduct which has composition C (60.23 wt %) and H (7.25 wt %), with a C:H weight ratio of 8.31; the calculated composition for the diamond ring structure (65 repeating units, number-average of the distribution from 2297 to 4720 m/z) is C (63.35 wt %) and H (7.31 wt %), with a C:H ratio of 8.67; the calculated value for the dumbbell structure is C (69.41 wt %) and H (6.10 wt %), with a C:H ratio of 11.38. The calculated value for the bis-PEG/C₆₀ adduct (PEG₃₃₅₀-C₆₀-PEG₃₃₅₀) is C (59.27 wt %) and H (8.14 wt %), with a C:H ratio of 7.28. Only the diamond ring ratio is in good agreement with the experiment.

The MALDI and EA confirm the formation of a monofullerene-substituted PEG₃₃₅₀-C₆₀ adduct. Other monofullerene-substituted linear PEG₃₃₅₀ chains bearing monoazide (C₆₀-PEG₃₃₅₀-N₃), amine (C₆₀-PEG₃₃₅₀-NH₂), or hydroxyl (C₆₀-PEG₃₃₅₀-OH) end groups can also be ruled out as follows. While these alternatives vary only slightly in mass, a detailed comparison of the possible masses is only consistent with a diamond ring structure (see Supporting Information Table S1 for theoretically calculated monoisotopic masses for C₆₀-PEG₃₃₅₀-N₃, C₆₀-PEG₃₃₅₀-NH₂, and C₆₀-PEG₃₃₅₀-OH). Furthermore, the experimental isotopic pattern for the 65 ethylene oxide repeating unit peak ($[M + Na]^+ = 3660.7$ Da) closely matches the theoretical calculated monoisotopic mass of the diamond ring (Figure 5). The FTIR (Figure 1) excludes significant remaining azide content; a control experiment without fullerene showed that the pure N₃-PEG₃₃₅₀-N₃ did not decompose to amine when heated under identical conditions, as monitored by FTIR (not shown). Furthermore, a ninhydrin test on the C₆₀-PEG₃₃₅₀ adduct found no primary amine.

In order to examine the effect of PEG chain length on the structure of fullerene-PEG adducts, two new bis-azido-terminated PEGs, N₃-PEG₁₀₀₀-N₃ and N₃-PEG₂₀₀-N₃ were also synthesized under the same reaction conditions described above for N₃-PEG₃₃₅₀-N₃. In the case of N₃-PEG₁₀₀₀-N₃, the adduct was isolated using THF extraction (×3) since it was insoluble in water probably due to shorter PEG chain length compared to PEG₃₃₅₀. The purity of isolated adduct was verified by FTIR, showing small amount of unreacted fullerene (not

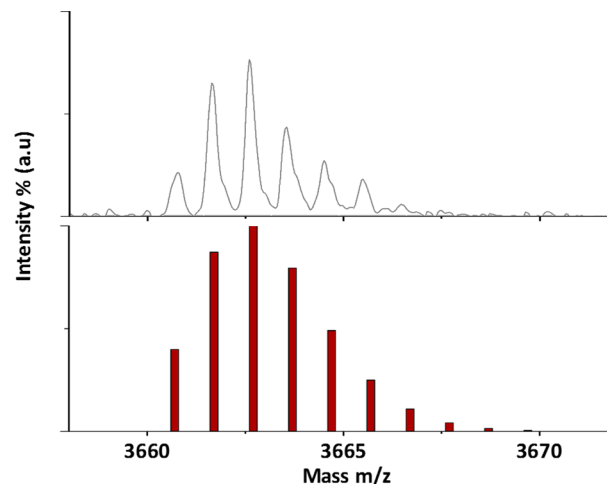


Figure 5. Experimental isotopic pattern for the primary peak of the PEG₃₃₅₀-C₆₀ adduct (top) compared with the simulated monoisotopic pattern for PEG₃₃₅₀-C₆₀ diamond ring with 65 ethylene oxide repeating units (bottom), both including [Na⁺].

shown). The MALDI-TOF spectrum of the PEG₁₀₀₀ adduct displayed a Gaussian distribution of positively charged ions in the range of 1450–2100 m/z , centered around the theoretically expected mass for the diamond ring PEG₁₀₀₀ adduct ($[M + Na]^+$); the experimental monoisotopic peak pattern for the adduct with 20 ethylene oxide repeating units (the most intense signal in the starting PEG₁₀₀₀ mass distribution) ($[M + Na]^+ = 1679.5$) was consistent with the formation of diamond ring structure (see Supporting Information Figure S9 for full MALDI-TOF spectrum of C₆₀-PEG₁₀₀₀).

The only difference between C₆₀-PEG₁₀₀₀ and C₆₀-PEG₃₃₅₀ is the length of the polymer backbone. However, the longer PEG chain offers a benefit in purification. As mentioned above, THF alone was not sufficient to remove all unreacted fullerene. Having a relatively long PEG chain in the fullerene/PEG adducts (PEG₃₃₅₀) makes the adduct water-soluble, simplifying the complete removal of free fullerene since pristine C₆₀ is insoluble in water. Unlike the longer PEG-C₆₀ analogues (C₆₀-PEG₁₀₀₀ and C₆₀-PEG₃₃₅₀), the PEG₂₀₀-C₆₀ adduct was not easily isolated by extraction in water or THF. The combination of the short PEG₂₀₀ chain and bis-addition of fullerene (see below) makes the adduct insoluble in both water and THF; instead, unreacted fullerene was removed by column chromatography using toluene as eluent. In contrast to the PEG₃₃₅₀ and PEG₁₀₀₀/fullerene products, the mass spectrum of the isolated PEG₂₀₀-C₆₀ adduct showed no peaks related to diamond ring (C₆₀-PEG₂₀₀) formation, around the theoretically expected mass range (975.1 m/z for four ethylene oxide repeating units). Instead, a Gaussian mass distribution of positively charged ions ranging from 1100 to 2300 m/z was observed, consistent with the formation of dumbbell structure (C₆₀-PEG₂₀₀-C₆₀) (see Supporting Information Figure S8 for full MALDI-TOF spectrum of C₆₀-PEG₂₀₀-C₆₀). The UV-vis spectrum (Figure 2) for C₆₀-PEG₂₀₀-C₆₀ shows no shift in the primary fullerene absorbance, consistent with the addition of a single PEG chain to each fullerene, in this case, rather than the double PEG addition/diamond ring structure.^{24,28}

It appears that the PEG chain length determines the molecular structure of the resulting PEG- C_{60} adducts. Simple space filling models of C_{60} -PEG- C_{60} and $C_{\text{PEG}}^{C_{60}} \supset$ based on four ethylene oxide repeating units demonstrate that the PEG₂₀₀ chain is insufficiently long enough to wrap around the fullerene for *trans-1* addition (the conformation requiring longest PEG chain, Figure 6). Other regioisomers may be unfavorable due to

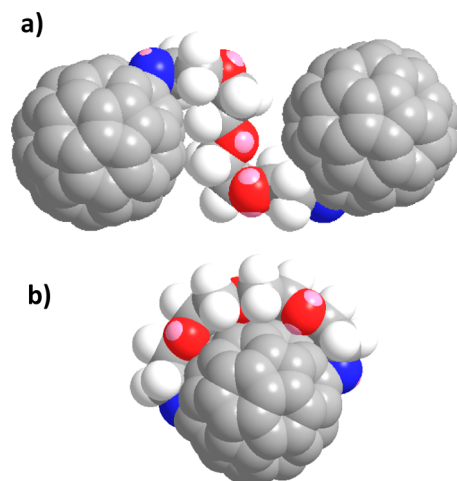


Figure 6. Space-filling models of C_{60} -PEG₃₃₅₀- C_{60} dumbbell and hypothetical PEG₂₀₀- C_{60} diamond ring.

the relatively bulky PEG substituents which may hinder the addition at an adjacent position. In this case, with diamond ring formation suppressed, the dumbbell is the favored conformation. Previous literature suggests that the use of large excess of monoprotected linear polymer favors the addition of two or more polymer chains to each fullerene (10:1 equiv of grafting polymer to C_{60}).²⁸ In the current experiment, excess C_{60} (1:10 relative to azide chain ends) was used in an attempt to favor dumbbell formation. Nevertheless, the diamond ring structure was favored when the PEG chain was sufficiently long. Most examples of more than one polymer attached to fullerene in the literature are synthesized via multiple azomethine ylide addition²⁸ of independent substituents. A recent example demonstrated a *trans-4* isomer of a fullerene bis-adduct in which the fullerene is connected to a metallocene bis-aldehyde to give a cyclic diad (diamond ring) via the Prato reaction.²⁹ The main focus of current paper is to demonstrate the geometry of PEG- C_{60} adduct with various PEG chain lengths; therefore, no HPLC was performed, and the resultant product was believed to be mixture of regioisomers.

CONCLUSIONS

Both diamond ring and dumbbell structures were successfully synthesized using the 1,3-dipolar cycloaddition reaction of N_3 -PEG- N_3 with C_{60} . The final structure of the polymer–fullerene adducts is determined by the polymer chain length. Previous studies had assumed a dumbbell structure would be formed for all bis-azido-terminated PEG reactions with fullerene, but without sufficient spectroscopic evidence to identify the final structure fully. The current study shows that it is necessary to perform detailed characterization, particularly using MALDI to establish the structure. In fact, diamond ring structures dominate, except where they are sterically frustrated by the shortness of the linking PEG chain. This finding may be

generally applicable to polymer/fullerene functionalization via telechelic reactive groups. This new type of fullerene diamond ring structure is potentially relevant to polymer blend and organic bulk heterojunction photovoltaics, as a means to increase the fullerene loading or control the critical phase separation of the charge carrying components.³⁰ Fullerene aggregation remains a major challenge in the polymer/fullerene active layer in bulk heterojunctions (BHJ) photovoltaics (PV).⁷ Controlling the resultant structure of the fullerene derivative may provide an alternative route to enhance current fullerene-based PV performance since dumbbell and diamond ring structures are believed to have different degrees of aggregation. If dumbbells are specifically required, more rigid spacers such as polythiophene or polyphenylene might restrict the formation of the diamond ring structure, as well as providing specific electronic function.

EXPERIMENTAL SECTION

Materials and Methods. C_{60} (purity >99%) was obtained from SES Research, Houston, TX. PEG with $M_n = 200, 1000,$ and 3350 Da were purchased from Sigma-Aldrich and azeotropically dried overnight using toluene. Azeotropic distillation was performed with Dean–Stark trap and reflux condenser under N_2 . As water is denser than toluene, residual water is trapped in the bottom of the Dean–Stark trap. Sodium azide (99%), tetrabutylammonium iodide ($\geq 99.5\%$), toluene (HPLC grade), anhydrous dichlorobenzene (*o*-DCB), anhydrous dimethylformamide (DMF), and *trans-2*-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) ($\geq 98\%$) were obtained from Sigma-Aldrich. Thionyl chloride ($\geq 99.5\%$) was obtained from Fluka. All other solvents were purchased from VWR and used without further purification.

¹H NMR spectra were acquired on a Bruker 400 MHz NMR spectrometer operating at 9.4 T. The recycle delays for all spectra were one second, with 16 scans per spectrum unless otherwise specified. Fourier transform infrared spectra were recorded on a PerkinElmer ATR Spectrum 100 spectrometer with a resolution of 4 cm^{-1} and 32 scans per spectrum. Elemental analysis was determined by Mr. Stephen Boyer at London Metropolitan University, Science Centre, Elemental-Analysis service. UV–vis spectra were recorded on PerkinElmer Lambda 950 spectrometer in toluene. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF) data were acquired on a Waters MICROMASS MALDI micro MX with a nitrogen laser at 333 nm in the positive reflectron mode with delayed extraction. Samples (1–2 mg) dissolved in toluene (10 μL) were added to the mixture of 10 μL of predissolved matrix (10 mg/mL DCTB in THF) and 3 μL of NaI (3 mg/mL in THF). Small aliquots of mixture were loaded on to a stainless steel target plate and allowed to air-dry at room temperature. The instrument was calibrated in the range of 500–5000 Da using a standard poly(ethylene glycol). The simulated isotopic peak patterns were constructed using online software MolE - Molecular Mass Calculator v2.02 (<http://rna-mdb.cas.albany.edu/RNAmods/masspec/mol.htm>).

Synthetic Procedures. *Synthesis of Cl-PEG-Cl and N_3 -PEG- N_3 .* Cl-PEG-Cl and N_3 -PEG- N_3 were synthesized following the literature procedure reported by Goh et al.¹⁷ In brief, the bis-hydroxyl-terminated PEG was first converted to bis-chloro-terminated PEG (Cl-PEG-Cl) by reaction with thionyl chloride. The Cl-PEG-Cl was then reacted with sodium azide to afford bis-azido-terminated PEG (N_3 -PEG- N_3).

Synthesis of the C_{60} -Terminated PEG₃₃₅₀ Diamond Ring ($C_{\text{PEG}}^{C_{60}} \supset$). Azido-terminated PEG₃₃₅₀ (0.1 g, 1 equiv) was dissolved in 15 mL of *o*-dichlorobenzene in a two-necked 50 mL round-bottom flask fitted with a condenser and connected to vacuum line. C_{60} (0.43 g, 20 equiv) was dissolved in 20 mL of *o*-dichlorobenzene and transferred into a pressure equalizing dropping funnel and fitted to the round-bottom flask. The C_{60} solution was then added dropwise into the stirring PEG solution to ensure the mixture

was mixed thoroughly. Once addition of azide was completed, the mixture was then heated to 140 °C and stirred for 24 h. Solvent was evaporated *in vacuo*, and 25 mL of THF was added to the remaining solid. The THF solution was stirred at room temperature overnight and filtered under gravity to yield a dark brown solid. The solid was then dissolved in 20 mL of water to give a yellow solution and unreacted C₆₀ was filtered off under gravity. The water was evaporated *in vacuo*, and the solid was then freeze-dried *in vacuo* (liquid nitrogen, 0.11 mbar, overnight) to yield a dark brown solid C_{PEG3350}^{C₆₀} (0.08 g, 86%). Characterization data for C_{PEG3350}^{C₆₀}: R_f = 0.26 toluene/methanol (9/1 v/v). ¹H NMR (400 MHz, CDCl₃, D1 20 s): δ 4.48 (t, 4H, J = 4 Hz, C₆₀-CH₂-CH₂-O-), 3.80 (t, 4H, J = 4 Hz, C₆₀-CH₂-CH₂-O-) 3.67 (m, 292H, main PEG) ppm. FT-IR (ATR) ν/cm⁻¹: 3462, 2889, 2871, 1728, 1468, 1361, 1342, 1281, 1242, 1150, 1102, 1062, 961, and 843. MALDI-TOF m/z: C₁₉₂H₂₆₄O₆₅N₂Na [M + Na]⁺ calcd 3660.7310; found 3660.9 Da. EA calcd for C₁₉₂H₂₆₄N₂O₆₅: C, 63.33; H, 7.31; N, 0.77; O, 28.58. Found: C, 60.23; H, 7.25; N, 0.90; O, 31.62. All values are given as percentages.

Synthesis of the C₆₀-Terminated PEG₁₀₀₀ Diamond Ring (C_{PEG1000}^{C₆₀}). The C₆₀-terminated PEG₁₀₀₀ was synthesized following the same procedure described above for C_{PEG3350}^{C₆₀}. The resulting crude product after solvent removal was extracted by THF (3×) since it was not water-soluble. Removal of THF *in vacuo* afforded a dark brown solid C_{PEG1000}^{C₆₀} (0.056, 59%). Characterization data for C_{PEG1000}^{C₆₀}: R_f = 0.34 toluene/methanol (9/1 v/v). FT-IR (ATR) ν/cm⁻¹: 3391, 2972, 2877, 1729, 1463, 1431, 1384, 1353, 1292, 1249, 1184, 1105, 1044, 954, 856, and 752. MALDI-TOF m/z: C₁₀₂H₈₄O₂₀N₂Na [M + Na]⁺ calcd 1679.5515; found 1679.0 Da.

Synthesis of the C₆₀-Terminated PEG₂₀₀ Dumbbell (C₆₀-PEG₂₀₀-C₆₀). The C₆₀-terminated PEG₂₀₀ was synthesized following the same procedure described above for C_{PEG3350}^{C₆₀}. The resulting crude product was purified by silica gel column chromatography with toluene/methanol (9/1 v/v) as eluent, giving C₆₀-PEG₂₀₀-C₆₀ (0.04 g, 45%) as a dark brown solid. Characterization data for C₆₀-PEG₂₀₀-C₆₀: R_f = 0.55 toluene/methanol (9/1 v/v). FT-IR (ATR) ν/cm⁻¹: 3404, 2936, 2883, 1738, 1642, 1431, 1360, 1183, 101, and 729. MALDI-TOF m/z: C₁₃₀H₂₀O₄N₂Na [M + Na]⁺ calcd 1607.0796; found 1605.1 Da.

■ ASSOCIATED CONTENT

● Supporting Information

Full MALDI-TOF-MS and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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