Synthesis of a [60]fullerene-end-capped polyacetylene derivative – a “rod-sphere” molecule from a “coil-sphere” precursor†

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Herein, we report the synthesis of a hybrid material composed of a head-to-head substituted polyacetylene end-capped with [60]fullerene through anionic polymerization. The synthesis was carried out in three successive steps: anionic polymerization of 2,3-diphenyl-1,3-butadiene, anionic addition of the resulting living chains towards C_{60}, and dehydrogenation of the polymer segment in the presence of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Since the precursor polymer is a coil-like polybutadiene derivative and the dehydrogenated polymer is a rod-like conjugated segment, the molecular hybrids underwent a change from a “coil-sphere” to “rod-sphere” conformation before and after dehydrogenation. The structure and properties of the molecular hybrids were investigated via {\textsuperscript{1}}H NMR, FTIR, GPC, FLS, UV and TGA. The self-assembly behaviors of both molecular hybrids in THF were studied using DLS and TEM. Moreover, we also observed an obvious optical limiting property of the hybrid product, which indicates that it may potentially be utilized as a functional opto-electronic material.

Introduction

The conjugation of fullerene with synthetic polymers is able to endow the corresponding fullerene-polymer hybrids specific properties. The covalent connection of polymers to fullerene not only improves the solubility of fullerene so that it becomes solution processable for practical applications, but also effectively avoids the migration and aggregation of fullerene in the casting film, thus enhancing the stability of bulk heterojunction organic photovoltaic devices. To date, different types of fullerene-polymer hybrids, such as side-chain fullerene-polymers, main-chain fullerene-polymers, star-shaped fullerene-polymers, dendritic fullerene-polymers, and fullerene end-capped polymers, have been synthesized through various conjugation strategies.

On the other hand, fullerene-polymer hybrids are used as model molecules to form special morphologies in a solution or solid. In particular, C_{60}-end-capped polymers, such as polystyrene (PS), poly(ethylene oxide) (PEO), polycaprolactone (PCL), poly(acrylic acid) (PAA), poly(methyl methacrylate) (PMMA), and poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA), have been synthesized and employed as “coil-sphere” model structures for self-assembly studies in a

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substituted polyacetylene with head-to-head regio-specificity translated from the monomer. It has been reported that the head-to-head microstructure causes a stronger red shift in UV spectroscopy and higher thermal stability in comparison with its head-to-tail counterparts.\textsuperscript{25} Combining this precursor route with fullerene chemistry,\textsuperscript{26} we synthesize $C_{60}$-end-capped head-to-head substituted polyacetylene functional materials by living anionic polymerization of a template monomer, followed by nucleophilic addition to $C_{60}$ and dehydrogenation of the resulting precursor. The hybrid molecules before and after dehydrogenation are compared with each other from the viewpoint of their structures, behavior and properties. The most interesting issue is, after dehydrogenation, the structure of hybrid molecule is considered to dramatically change from a “coil-sphere” to “rod-sphere” conformation, which suggests significant differences in physical and chemical properties. To the best of our knowledge, there is no report thus far on these changes for $C_{60}$ end-capped polymers.

**Experimental**

**Materials**

Tetrakis(triphenyolphosphine) palladium (≥99%), 1-(4′-butylphenyl)ethanone (≥98%), and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, ≥98%) were purchased from Sigma-Aldrich and used as received. $C_{60}$ (>99.5%) was purchased from J&K and kept in the dark before use. $n$-Butylbenzene (≥99%) (Sinopharm Chemical Reagents) was used as received. sec-Butyllithium (s-BuLi) (Aldrich, 1.0 M solution in cyclohexane/hexane) was titrated before use. Tetrahydrofuran (THF) and toluene were distilled from 1,1-diphenylhexyllithium (DPELi, adduct of s-BuLi with 1,1-diphenylethylened) on a vacuum line before use. All other reagents were purchased from Sigma-Aldrich and used without further purification.

**Measurements**

$^1$H and $^{13}$C NMR measurements were carried out on a Bruker 400 MHz NMR instrument, using CDCl$_3$ as the solvent and tetramethylsilane as the interior reference. Gel permeation chromatography (GPC) analysis was conducted on three TSK gel columns (particle size: 5.0 µm and w ranges: 0–10$^4$, 0–2 × 10$^4$ and 0–4 × 10$^5$ g mol$^{-1}$) calibrated by narrow polystyrene standards. The GPC system was equipped with three detectors: a DAWN HELEOS (14°–154°) (Wyatt multianalyst laser light scattering detector, He–Ne 658.0 nm), ViscoStar (Wyatt), and OptilabEX (Wyatt). THF was used as the eluent at a flow rate of 1.0 mL min$^{-1}$ at 35 °C. UV spectra were obtained on a PerkinElmer Lambda 750 UV-Visible spectrometer with a 1 cm$^2$ quartz cell. Dichloromethane (DCM) was used as the solvent. Fluorescence spectra were obtained using a Perkin-Elmer LS-50B luminescence spectrophotometer. Spectra were acquired using 0.1 and 1 cm quartz cells. The IR spectrum was obtained on a Nicolet 6700 FTIR instrument (KBr pellet). Thermogravimetric analysis (TGA, TA Q5000) was conducted under a nitrogen atmosphere from ambient temperature to 600 °C at a heating rate of 10 °C min$^{-1}$. Dynamic laser light scattering (DLS) was carried out on an ALV/CGS-3 DLS/SLS laser light scattering goniometer system equipped with a multi-t digital correlator (ALV-7004) and an He–Ne laser light source ($\lambda$ = 632.8 nm) at a fixed scattering angle of 90°. Transmission electron microscopy (TEM) images were recorded on a Tecnai G2 20 Twin TEM (FEI). The specimens for TEM observation were prepared by depositing a drop of the sample solution onto a carbon-coated copper grid. The measurement of the optical limiting properties of the samples was carried out using a frequency doubled, Q-switched, mode-locked Continuum ns/ps Nd:YAG laser, which provides linearly polarized 4 ns optical pulses at 532 nm wavelength with a repetition of 1 Hz.

**Synthesis of 2,3-disubstituted butadiene monomer**

**Preparation of 1-(1′-bromovinyl)-4-$n$-butylbenzene.** The synthesis was conducted according to the literature.\textsuperscript{27} Bromine (4 mL, 77 mmol) and anhydrous dichloromethane (200 mL) were mixed at room temperature and the solution was cooled to −60°C under a nitrogen flow. Then, triphenylphosphite (18.5 mL, 70 mmol) and anhydrous triethylamine (12 mL, 84 mmol) were added. The solution was stirred for 30 min while it gradually became pale orange. Subsequently, 1-(4′-butylphenyl)ethanone (11.3 g, 64 mmol) was added and the solution was stirred for 18 h, during which the temperature increased spontaneously from −60°C to room temperature. After concentration of the reaction mixture using a rotating evaporator, the obtained viscous liquid was purified by column chromatography and the first fraction was collected. The product, 1-(1′-bromovinyl)-4-$n$-butylbenzene, was obtained as a dark orange oil. Yield, 10.0 g (65%).

**Preparation of 2,3-di($n$-butylphenyl)-1,3-butadiene (diBBPd).** The synthesis was conducted according to the literature.\textsuperscript{28} The above synthesized 1-(1′-bromovinyl)-4-$n$-butylbenzene (9.6 g, 40 mmol), tetrakis(triphenyolphosphine)palladium (1.2 g, 1.0 mmol), indium (2.3 g, 20 mmol), and lithium chloride (2.6 g, 60 mmol) were added to anhydrous DMF (80 mL) in a 3-necked flask and the mixture was stirred for 2 h at 100°C under a nitrogen atmosphere. NaHCO$_3$ (sat. aq., ~5 mL) was added to quench the reaction. Furthermore, the reaction solution was left standing for 30 min, and the organic layer was collected and washed with water and then with saturated sodium chloride. After drying with MgSO$_4$, the organic layer was concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography, yielding 2,3-di($n$-butylphenyl)-1,3-butadiene as a colorless oil (3.5 g, 55%).

**Preparation of 1-(4′-bromovinyl)-4-butylbenzene.** The synthesis was conducted according to the literature.\textsuperscript{27} The above synthesized 1-(1′-bromovinyl)-4-butylbenzene (9.6 g, 40 mmol), tetrakis(triphenyolphosphine)palladium (1.2 g, 1.0 mmol), indium (2.3 g, 20 mmol), and lithium chloride (2.6 g, 60 mmol) were added to anhydrous DMF (80 mL) in a 3-necked flask and the mixture was stirred for 2 h at 100°C under a nitrogen atmosphere. NaHCO$_3$ (sat. aq., ~5 mL) was added to quench the reaction. Furthermore, the reaction solution was left standing for 30 min, and the organic layer was collected and washed with water and then with saturated sodium chloride. After drying with MgSO$_4$, the organic layer was concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography, yielding 2,3-di($n$-butylphenyl)-1,3-butadiene as a colorless oil (3.5 g, 55%).

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Preparation of a [60]fullerene-end-capped poly(2,3-dibutyl-phenyl butadiene), poly(diBPBd)-C\textsubscript{60}. Anionic polymerization of diBPBd was performed in a mixture of toluene and THF (9 : 1, v : v) under similar conditions as previously reported, using s-BuLi as the initiator.\textsuperscript{24} Living poly(diBPBd)-Li was obtained as a pale red solution. The solution was added dropwise using a syringe to a solution of C\textsubscript{60} in toluene/THF (9 : 1, v : v). A gradual change in color from purple to dark brown was observed. After 2 h, the reaction was deactivated using degassed methanol and the solvent was removed by distillation under vacuum. The crude product was dissolved in THF and the unreacted C\textsubscript{60} was removed by centrifugation (C\textsubscript{60} is insoluble in THF). The supernatant was filtered through a membrane with a pore diameter of 220 nm. The filtrate was distilled to dryness overnight under vacuum at 40 °C. Finally, the product, poly(diBPBd)-C\textsubscript{60}, was obtained \((M_n = 3200 \text{ g mol}^{-1}, \text{PDI} = 1.08)\) using preparative GPC and the subsequent separation process via precipitation (see next), and was preserved under vacuum to avoid oxidation.

Transformation of poly(diBPBd)-C\textsubscript{60} into [60]fullerene-end-capped substituted polyacetylene, sPA-C\textsubscript{60}

Dehydrogenation was conducted according to ref. 24 and 29. The above synthesized poly(diBPBd)-C\textsubscript{60} (0.32 g) was dissolved in anhydrous toluene (5 mL) with the aid of magnetic stirring. The resulting solution was mixed with a solution of DDQ (0.91 g, 4.0 mmol) in toluene (5 mL). The mixed solution was degassed through three freeze–vacuum–thaw cycles. The mixture was stirred for 24 h at 90 °C. After the reaction, the solution was filtered through a membrane with a pore diameter of 220 nm, followed by concentration on a rotatory evaporator and precipitation from a large volume of methanol. Finally, a dark brown powder was obtained after drying overnight under vacuum. The product was preserved under vacuum to avoid oxidation.

Results and discussion

The synthesis of [60]fullerene-end-capped substituted polyacetylene in this study includes three steps: (i) living anionic polymerization of a template monomer, 2,3-di\((\alpha\text{-bromostyrene})\)-1,3-butadiene (diBPBd), to yield a living species poly(diBPBd)-Li; (ii) nucleophilic addition of poly(diBPBd)-Li to C\textsubscript{60}, followed by methanol quenching to produce the precursor poly(diBPBd)-C\textsubscript{60} and (iii) dehydrogenation of the resultant precursor through reaction with DDQ to prepare the target hybrid molecule, substituted polyacetylene (sPA)-C\textsubscript{60} in which the sPA segment has head-to-head enchainment inherited from the template monomer (Scheme 1).

Monomer synthesis

The disubstituted monomer, 2,3-di\((\alpha\text{-bromostyrene})\)-1,3-butadiene (diBPBd), was synthesized according to the procedure shown in Scheme 2. First, 4-\(n\)-butyl-\(\alpha\)-bromostyrene was prepared from the corresponding ketone in the presence of triphenylphosphite. The resulting styrene derivative was then coupled to form diBPBd through a palladium-catalyzed intermolecular coupling reaction in the presence of indium and LiCl. The overall yield is usually in the range of 30%–40%. The structure of the monomer was confirmed by \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR (Fig. S1–3). This route consists of only two steps and is much easier than the previously reported method.\textsuperscript{24} The \(n\)-butyl side group in the monomer was introduced to increase the solubility of the corresponding polymers.\textsuperscript{23,20}

Anionic polymerization of diBPBd and the addition reaction of living poly(diBPBd)-Li with C\textsubscript{60}

Anionic polymerization of diBPBd was carried out using s-BuLi as the initiator in a mixed solvent of toluene and THF (9 : 1, v : v) at 40 °C. The polymerization proceeded well under similar conditions as previously reported.\textsuperscript{24} The resulting living poly(diBPBd)-Li was added dropwise into a solution of C\textsubscript{60} in the mixed solvent mentioned above. This titration process was able to keep the molar amount of poly(diBPBd)-Li from large excess to equivalent to that of C\textsubscript{60} along with the reaction, therefore favoring the formation of a monoadduct. Although the process suffered from slight deactivation during the operation, the fraction of termination was small. Upon initial titration of poly(diBPBd)-Li, the purple C\textsubscript{60} solution immediately turned dark brown in color, which was similar in the previous literature.\textsuperscript{22} After termination by acidified methanol, a dark red color was sustained for the reaction mixture. The color change during the reaction implied the end capping of living poly(diBPBd)-Li by C\textsubscript{60} to form the hybrid precursor, poly(diBPBd)-C\textsubscript{60}.

Scheme 1 Synthesis of [60]fullerene-end-capped substituted polyacetylene through successive (i) anionic polymerization, (ii) nucleophilic addition, and (iii) dehydrogenation processes.

Scheme 2 Synthetic route for the 2,3-disubstituted butadiene template monomer.
The precursor was analyzed by GPC equipped with a refractive index (RI) detector and a UV detector with working wavelength at 340 and 370 nm, respectively. Both C<sub>60</sub> and the parent poly(diBPBd) absorb at the former wavelength, whereas only C<sub>60</sub> shows absorption at the latter (Fig. S4 & S5†). Therefore, poly(diBPBd)-Li with and without C<sub>60</sub> end groups become distinguishable. Fig. 1a shows the GPC profiles recorded by different detectors for the reaction products in comparison with the parent poly(diBPBd). All these detecting signals show increasing molecular weight from 2500 to 3200 g mol<sup>−1</sup> before and after the addition reaction, respectively. This GPC result, together with that of TGA *(vide infra)*, indicate monoaddition between poly(diBPBd)-Li and C<sub>60</sub>. It is also notable that a small peak at an extremely large molecular weight appears on the diagram of the UV detector, which could be attributed to the formation of micelles or aggregates of the product poly(diBPBd)-C<sub>60</sub> since C<sub>60</sub> is not soluble in THF.

It is practically very difficult to separate the target poly(diBPBd)-C<sub>60</sub> from the parent poly(diBPBd). Yashima and co-workers reported a purification method for C<sub>60</sub>-end-capped PMMA taking advantage of the self-assembly property of the product in selective solvents.9,31 They obtained a pure substance by collecting the fraction in the extremely high molecular weight region corresponding to the aggregates formed by the product.

Furthermore, we purified the products using a preparative GPC column and then by fractionation upon poor solvent addition. In the first step, fractions corresponding to the broad peak at a similar retention with the parent poly(diBPBd) were collected and the extremely high molecular weight species was removed (Fig. S6†). Then, in the second step, methanol was added dropwise into a solution of crude product in THF to reach a volume fraction of 10% and precipitation was observed. After standing for 24 h, the precipitate was collected (Fig. S7†). The procedure was repeated three times and the products were dried overnight under vacuum. After purification, the product showed narrow unimodal GPC profiles, which indicate the removal of the unreacted parent polymer, as shown in Fig. 1b. Furthermore, the unimodal peak detected at a wavelength of 370 nm with a molecular weight close to that of the parent polymer demonstrates monoaddition between the polymer anion and C<sub>60</sub>.

**Transformation of poly(diBPBd)-C<sub>60</sub> into sPA-C<sub>60</sub> by dehydrogenation**

The obtained precursor poly(diBPBd)-C<sub>60</sub> was converted into sPA-C<sub>60</sub> by dehydrogenation using DDQ as the dehydrogenation agent. A gradual change in color from dark red to dark brown was observed during the dehydrogenation process. After purification, the product was obtained as a dark brown powder.

UV spectrometry was performed using an sPA-C<sub>60</sub> solution in DCM. As shown in Fig. 2, while the precursor shows a peak absorption at 340 nm due to the presence of C<sub>60</sub>, the resulting conjugated hybrid, sPA-C<sub>60</sub>, shows a broad band extending to a wavelength larger than 650 nm due to the π-π* electronic transition of the main chain. In addition, the characteristic peak of C<sub>60</sub> at 340 nm is still visible as a shoulder.

**Fig. 2** UV spectra of C<sub>60</sub>, poly(diBPBd), poly(diBPBd)-C<sub>60</sub> and sPA-C<sub>60</sub> in dichloromethane (DCM).

**Fig. 3** FTIR spectra of (A) C<sub>60</sub>, (B) poly(diBPBd), (C) poly(diBPBd)-C<sub>60</sub> and (D) sPA-C<sub>60</sub> (KBr pellets). The right side figure is a partial enlargement of the dashed framework in the left side figure.
peaks at 578 and 526 cm\(^{-1}\) remain after dehydrogenation, which indicate that the reaction did not destroy the chemical link between poly(diBPBd) and C\(_{60}\).

Dehydrogenation was also monitored using NMR spectroscopy. As shown in Fig. 4, while the \(^1\)H NMR spectrum of the precursor is well resolved for all characteristic protons, the signals after dehydrogenation become remarkably broad with very low resolution for these protons. This is because the resulting conjugated chains exhibit a more rigid conformation. Fortunately, one can observe that the signal of the precursor main chain ethylene moiety at 2.0 ppm (peak a in Fig. 4a) disappeared after the reaction, which is evidence of hydrogen elimination. The signal of the resulting olefinic proton overlaps with those of aromatic protons in the chemical shift range of 5.6–8.0 ppm (Fig. 4b). The \(^{13}\)C NMR spectra also show similar changes in the chemical shift range of 120–150 ppm due to the formation of a conjugated structure (Fig. S8†).

The TGA curves of C\(_{60}\), poly(diBPBd), poly(diBPBd)-C\(_{60}\) and sPA-C\(_{60}\) are given in Fig. 5. All samples were measured from 25 \(^\circ\)C to 600 \(^\circ\)C under a nitrogen atmosphere. It is found that while the weight of C\(_{60}\) remains almost constant, the hybrid precursor undergoes a weight loss from 340 \(^\circ\)C to 420 \(^\circ\)C, which is similar to the pure polymer, poly(diBPBd). The marginal residual is approximately 21% after 500 \(^\circ\)C and is attributed to fullerene moiety (calc. 22%, based on monoaddition). After dehydrogenation, sPA-C\(_{60}\) seems to decompose at the much lower temperature of 205 \(^\circ\)C, as compared to that of the precursor, giving, however, a much higher residual (ca. 70%) at 600 \(^\circ\)C. We suggest that the low temperature weight loss is due to elimination and/or decomposition of the defects in sPA-C\(_{60}\) caused by possible incomplete dehydrogenation. The high residual indicates that the conjugated structure after dehydrogenation become much more stable than the precursor material at high temperature.

**Self-assembly behavior of the hybrid molecules**

The self-assembly of the [60]fullerene-end-capped polymers, both poly(diBPBd)-C\(_{60}\) and sPA-C\(_{60}\), was investigated in THF, which is a good solvent for the polymer segment but poor solvent for C\(_{60}\), using TEM and DLS. Both molecules form spherical particles, as shown in Fig. 6a–f for poly(diBPBd)-C\(_{60}\) and sPA-C\(_{60}\), respectively. The TEM observed diameters are smaller than those obtained by DLS (\(R_h\), ca. 100 nm), because the former is in the dry state, whereas the latter is in the solvated state. Since the radii of particles from both molecular hybrids (50–100 nm) are much larger than the length of molecules at the extended states, the particles can be large compound micelles (LCM) formed by the aggregation of primary micelles. Indeed, domains were clearly observable within each particle by close analysis of the morphologies (Fig. 6b and e insets), which are attributable to primary micelles. Similar results for the formation of LCMs were reported previously using C\(_{60}\) conjugated with other polymers, such as poly(methyl methacrylate),\(^{32}\) poly(acrylic acid)\(^{33}\) and poly(ethylene oxide),\(^{34}\) in which the LCMs were in thermodynamic equilibrium with regular micelles and unimers. The tendency for the formation of LCMs is to lower the free energy of the regular core shell structured micelles in the solution. In addition, the aggregates of the precursor are more regular sphere in comparison with those of sPA-C\(_{60}\), whereas the latter exhibits larger particle sizes and domains inside with a broader distribution. These results may indicate the transformation from a “coil-sphere” to “rod-sphere” chain conformation.

![Fig. 4](image-url) \(^1\)H NMR spectra of (a) poly(diBPBd)-C\(_{60}\) and (b) sPA-C\(_{60}\).

![Fig. 5](image-url) Thermograms of C\(_{60}\), poly(diBPBd), poly(diBPBd)-C\(_{60}\) and sPA-C\(_{60}\).

![Fig. 6](image-url) TEM images and dynamic laser light scattering results of spherical LCM formed by the self-assembly of poly(diBPBd)-C\(_{60}\) and sPA-C\(_{60}\) in THF: (a)–(c) for poly(diBPBd)-C\(_{60}\) and (d)–(f) for sPA-C\(_{60}\), in which (b) and (e) are partial enlargements of (a) and (d), respectively.

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Opto-electronic property

The hybrid molecule synthesized in this study contains two different systems of π-electron conjugation, specifically, a two-dimensional sPA segment and three dimensional C₆₀. This very specific structure may render the molecule interesting opto-electronic properties.

The fluorescent emissions of poly(diBPBd)-C₆₀ and sPA-C₆₀ were measured in DCM. As shown in Fig. 7, under excitation at 320 nm, the precursor displays three emission peaks at 370, 390 and 415 nm, whereas sPA-C₆₀ gives practically no fluorescence signal. The emission of the precursor may arise from the stilbene structure in the parent polymer and C₆₀ moiety. It was reported that bare C₆₀ does not show emission, whereas C₆₀ attached to a polymer chain becomes fluorescent with the wavelength of 400 nm. Comparing the spectra of the precursor (Fig. 7) and the parent polymer (Fig. S9†), it can be deduced that the former is an overlap of the emission of the latter and the attached C₆₀. However, after dehydrogenation, the fluorescence is quenched because photogenerated electrons in the conjugated polymer chains may flow to the C₆₀ cages via the photo-induced charge-transfer process.

Both (substituted) polyacetylene and C₆₀ have well-known non-linear optical properties that arise from their delocalized π-electron systems. These properties facilitate the application of the corresponding substance as an optical limiting material. In the present study, we studied the optical limiting behavior of the obtained precursors and product with π-conjugations. As shown in Fig. 8, the parent polymer and hybrid molecule, poly(diBPBd) and poly(diBPBd)-C₆₀, show a nearly linear increase of output fluence along with the incident fluence. This indicates that the content of C₆₀ in the precursor is not enough to cause optical limiting behavior. Nevertheless, the dehydrogenated product, sPA-C₆₀, shows very strong non-linearity in the curve of incident-output fluence. The optical limiting amplitude is approximately 0.21 J cm⁻². Therefore, the hybrid compound, sPA-C₆₀, is a promising optical limiting material for practical application.

Conclusions

A hybrid material, [60]fullerene-end-capped polyacetylene derivative, was successfully synthesized through a precursor route containing three steps, specifically, living anionic polymerization of a 2,3-disubstituted butadiene, end capping of the living polymer to C₆₀, and subsequent dehydrogenation of the polymer segment. During dehydrogenation, the hybrid molecule underwent a conformation change from “coil-sphere” to “rod-sphere” due to the conjugated structure of the sPA segment. These reaction processes were monitored using various analytical methods. Both the “coil-sphere” and “rod-sphere” like molecules tend to self-assemble into spherical LCMs in selective solvent. The hybrid material after dehydrogenation possesses two systems of π-conjugation and thus exhibits a red-shift in UV absorption, fluorescent quenching and optical limiting property. All these interesting findings should provide valuable insight into the relationship between the structure and properties of fullerene-containing polymers.

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