Electrochemical Synthesis of Transparent, Amorphous, C_{60}-Rich, Photoactive, and Low-Doped Film with an Interconnected Structure

Mao Li,* Shinsuke Ishihara, Kei Ohkubo, Meiyong Liao, Qingmin Ji, Cheng Gu, Yuyu Pan, Xiangfen Jiang, Misaho Akada, Jonathan P. Hill, Takashi Nakanishi, Yuguang Ma, Yusuke Yamauchi, Shunichi Fukuzumi, and Katsuhiko Ariga*

Fullerene (C_{60}) is one of the most investigated species in energy and biological applications[1-3] due to its unique physicochemical properties of electrical conductivity[4] and electron deficiency.[4] For practical applications, including in various electronic devices, preparation of high C_{60} content thin films of high flexibility and transparency (i.e., amorphous and aggregation free) is of great significance. There have been great efforts made in the synthesis of C_{60} polymers,[5-6] but film formation and its control remain difficult. Alternatively, electropolymerization[6] enables in situ preparation of uniform polymeric films directly on the surfaces of conductive substrates with controllable morphologies and thicknesses.[7] However, over the past few decades, use of electropolymerization has been limited to applications where ion-doping is required[8] (i.e. electrochromism, conductive films etc.) because non-quantitative (unlimited) electrochemical coupling reactions usually result in conducting conjugated polymers with an unavoidable highly doped state, and the quantitative electrochemical selection of the polymer structure remains challenging. In fact, the resulting conjugated polymers and highly doped states are often unnecessary (or disadvantageous) for a wide library of building blocks. For example, electropolymerization of thiophene-appended bisC (Scheme 1A) prevents the formation of a conducting conjugated polymer, which tends to lead to highly doped states (Scheme 1B). Our result represents the first example of preparation of a low-doped non-conjugated polymer and is a breakthrough in the broadening of the potential applications of electrochemical synthesis into the field of device fabrications.

Our molecular design involves the starting precursors C_{60}BisC and C_{60}2C (regioisomer mixture) (Scheme 1C) both of which are substituted with two carbazole groups and possess high C_{60} contents of 60 wt% and 53 wt%, respectively. Their UV-vis absorption and electrochemical reduction onset potentials are similar to those of pure C_{60} (Figure S1 and Table S1). C_{60}BisC and C_{60}2C undergo similar electropolymerization processes to Poly[C_{60}BisC] and Poly[C_{60}2C].
Taking C60BisC as a representative case, during the first scan from –0.50 to 1.1 V, the oxidation onset potential appears at 1.0 V as an irreversible wave for carbazole dimerization in a doped state while a reduction peak at 0.64 V, corresponding to the dedoping process of the film, emerges in the reverse scan (Figure 1A). The growth of a brown transparent film by multiple potential sweeping was indicated by the increasing current magnitude (Figure 1B) and UV-vis absorption intensity (Figure 1C). Film growth could be monitored by atomic force microscope (AFM) and scanning electron microscope (SEM) imaging, which revealed the processes of controllable surface coverage (Figure 2A), film thickness (Figure 2B) and patternability (Figure 2C). Films composed of Poly[C60BisC] and Poly[C602C] present onset reduction potentials at ~0.72 V (Figure 1D) similar to pure C60 (Table S1) demonstrating that these films have excellent electron accepting properties as does pure C60. This is in good agreement with electron density distributions calculated using B3LYP/6-31G(d) optimized geometries (Figure S2). The films maintain the intrinsic absorption of C60 at 320 nm and exhibit a significantly enhanced broad absorption in the range 350 – 600 nm (Figure S3) due to electronic interactions between C60 units.[10]

When N-alkylcarbazole and C601C bearing one carbazole were electrochemically treated under identical conditions for the formation of Poly[C60BisC] and Poly[C602C], only their dimers could be detected by MALDI-TOF mass spectroscopy (Figure S4-6 for alky carbazole and Figure S7-8 for C601C) revealing the quantitative (i.e. dimerization) electrochemical reaction of alkylcarbazole. Thus, as depicted in Scheme 1C, Poly[C60BisC] and Poly[C602C] must be interconnected through carbazole dimers. In their FT-IR spectra, Poly[C60BisC] and Poly[C602C] have comparable intensities of absorptions due to the double and triple substitution patterns of the benzene rings of carbazole, also indicating that dimerization is the preferred reaction (Figure S9-10). Despite the high C60 contents of Poly[C60BisC] and Poly[C602C], X-ray powder diffraction (XRD) patterns of the films with thicknesses of 0.4–1.3 µm (Figure S11) contain only broad halos around 20–30 degree (Figure S12). In addition, 2D-SAXS (small angle X-ray scattering) measurements on these films also reveal only weak halos (Figure 3A-B) indicating that these films are amorphous and lack crystallinity of the C60 moieties. The weak GI-SAXS halos should correspond to C60-C60 separated by dimerized carbazoles at an approximate distance of 2.0 nm (Figure 3C-D). Optimized geometries of C60BisC and C602C trimers reveal head-to-tail C60 distances of 3.0 nm and 5.5 nm, respectively.

Conductivities of the films were evaluated by using conductive AFM analysis (Figure 4A-B) giving values in the range 10⁻³–10⁻² S cm⁻¹, which is 4 orders of magnitude lower than the typical value for C60 containing highly doped conducting polymers.[11] Therefore, use of dimers of carbazole as linkers apparently inhibits electrochemical doping processes. Conductivity of Poly[C60BisC] film (~2.0 × 10⁻³ S cm⁻¹) is lower than that of Poly[C602C] film (~8.0 × 10⁻³ S cm⁻¹) probably because the disordered Poly[C60BisC] polymer chains can facilitate easy diffusion and better dedoping processes of ions through the entire film since Poly[C60BisC] film prepared by switching at 1.0 V does not show any doping by PF₆⁻ (Figure S13), which usually exists as a counterion to the polycarbazole cation.[9] This film has an unusually low level of doping in contrast to those prepared by using conventional electrochemical synthesis, which are unavoidably highly doped. A strong and stable switching photocurrent...
Figure 2. AFM images of bare ITO (indium tin oxide) substrate (A) and Poly[C₆₀BisC] films prepared by 5 cycles (B) and 10 cycles (C) of CV (cyclic voltammetry) on ITO. Cross-sectional SEM images of bare gold substrate (D) and Poly[C₆₀BisC] films prepared by 5 cycles (E) and 10 cycles (F) on gold substrate. (G) Poly[C₆₀BisC] films prepared on a patterned gold surface.

Figure 3. GI-SAXS diffraction diagrams and patterns of Poly[C₆₀BisC] (A) and Poly[C₆₀C₂] (B) films (weak halo is shown by dash line). Optimized geometries of C₆₀BisC (C) and C₆₀C₂ (D) trimers and distances between fullerene moieties calculated using B3LYP/6-31G(d).
response of Poly[C_{60}BisC] film sandwiched between ITO and Al electrodes as a simple device was obtained under irradiation with 400 nm light (Figure 4C,E), as revealed by the photocurrent spectra (Figure S14). As can be seen in Figure 4C, the metal Al is positively biased and the photocurrent is lower than that of the negative bias. As has been described for a semiconductor diode,\textsuperscript{12} since the work function of Al (\(-4.2\) eV) is lower than that of ITO (\(-5.5\) eV) this film is demonstrated to be composed of an n-type material.

In comparison, the Poly[C_{60}2C] film shows high conductivity and a more highly doped state (Figure S13), and similar but much weaker photovoltaic device performance (Figure 4D,F) probably due to trace amounts of residual doped carbazole dimer acting as trapping defects (the capture of photogenerated carriers). This was verified by femtosecond transient absorption spectroscopy measurements (Figure 4G,H) which revealed an exponential decay for exciton quenching (\(k = 4.9 \times 10^{10} \text{ s}^{-1}\)) of Poly[C_{60}2C] film (Figure 4I,J). Since the
film can be fabricated on conducting or semiconducting electrodes (c.a. Si) as the electrode of an electronic device, it is reasonable to claim that this C_{60} film is a promising material for device applications. By integrating C_{60} through one or two positions of C_{60} into polymers, Poly[C_{60}BisC] and Poly[C_{60}2C] films exhibited an unexpected strong contrast in their photophysical properties. This should be emphasized as an important design feature of promising high C_{60} content materials which have substantial further possibilities for optimization.

In conclusion, we report the first quantitative electrochemical reaction of N-alkylcarbazole for the synthesis of high C_{60} content (60 wt%) polymer film with an interconnected structure. These photoactive C_{60} films with amorphous and transparent structures possess a low level of doping and have similar physicochemical properties to pure C_{60}, which might lead to extensive applications in various fields including biomedical,[14] nonlinear optics,[15] optical limiters,[16] and energy-related devices.[17] Extensive investigations regarding their potential applications are underway in our laboratory. Herein, our strategy fills the void which once existed for electrochemical preparation of non-conjugated polymers, and also represents a breakthrough in broadening the potential applications of electrochemical synthesis where a high degree of control over the predictable molecular structure or nanostructure of a large library of molecules, building blocks, nanoparticles, etc., may be exerted.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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