



Polymer communication

Photophysical properties and potential application in photocurrent generation of porphyrin-[60]fullerene polymer linked by metal axial coordination

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ABSTRACT

Porphyrin-[60]fullerene polymers linked by metal axial coordination of fullerenoacetic diacids *e*-isomer with dihydroxo Sn(IV) porphyrin have been prepared and characterized. The polymers display the regular one-dimensional linear arrays with lengths exceeded 200 nm and show good thermal stability. The efficient photoinduced electron transfer from singlet excited porphyrin to fullerene in the polymer has been achieved resulting in the formation of charge separation state with a lifetime as long as 140 μ s in benzonitrile. The long-lived charge separated state is very useful for photoelectric conversion system. The photocurrent generation in organic photovoltaic device was described further, and a steady and rapid cathodic photocurrent response was produced at the irradiation of $\lambda_{\text{ex}} = 429$ nm light. The polymers are expected to provide novel photonic or electronic functions in organic solar cell.

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1. Introduction

Extensive efforts have so far been devoted to the studies of the photoinduced electron transfer (PET) process in donor-acceptor (D–A) systems to develop artificial photosynthetic systems, which is important not only for the photochemical conversion of solar energy into fuels [1], but also for the construction of various optoelectronic devices [2–7]. In the construction of such systems, porphyrin and fullerene (C₆₀) are considered as attractive molecular components due to their ability to form long-lived charge-separated (CS) states upon photoexcitation [8–11]. The long lifetime of the CS state is crucial for the following intermolecular PET to occur [12]. The energy deposited in such a CS state can be further transformed either to electric power or to chemical energy. To this end, various covalent or supramolecular porphyrin and C₆₀ D–A ensembles have already been constructed and studied [13–24]. The CS efficiencies of some of these systems are comparable to those found in natural systems. However, the lifetime of CS state in reported covalently linked porphyrin-C₆₀ systems is general shorter than those in porphyrin-C₆₀ supramolecular ones, which is a great disadvantage for the conversion of light energy to electricity. One

effective strategy to achieve long-lived CS state is to construct multimodular D–A polyad with a suitable redox gradient that mimic the high efficient multistep PET process in photosynthesis [25–34]. In addition, multiple porphyrin and C₆₀ arrays based on supramolecular self-organization or polymers have proven to produce multistep and more efficient PET [35–45]. However, most of these efforts devoted so far have often been hampered by synthesis difficulties to make the number of covalent bonds needed to connect each component.

Recently, we reported on the in-chain porphyrin and C₆₀ polymers [46] with long-lived CS states, but their solubility was not very good, which was disadvantageous for their application in devices. Herein we report the synthesis and characterization of the porphyrin-C₆₀ polymer **3** (Scheme 1) linked by metal axial coordination of fullerenoacetic diacids *e*-isomer (3'H,3''H-dicyclopropa [1,9:16,17][5,6]fullerene-C₆₀-I_h-3',3''-dicarboxylic acid) **1** with dihydroxo Sn(IV) porphyrin **2**, and their photophysical properties and potential application in photovoltaic devices are investigated.

2. Results and discussion

Experimental details are listed in the Supporting Information. Scheme 1 outlined the structures and synthesis routes of the polymers. Here, the dicarboxylic acid *e*-isomer **1** was employed for the present polymerization because of its relatively high solubility.

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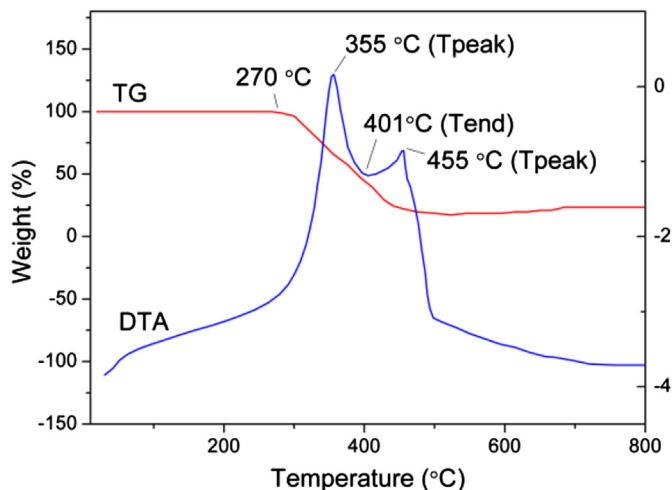
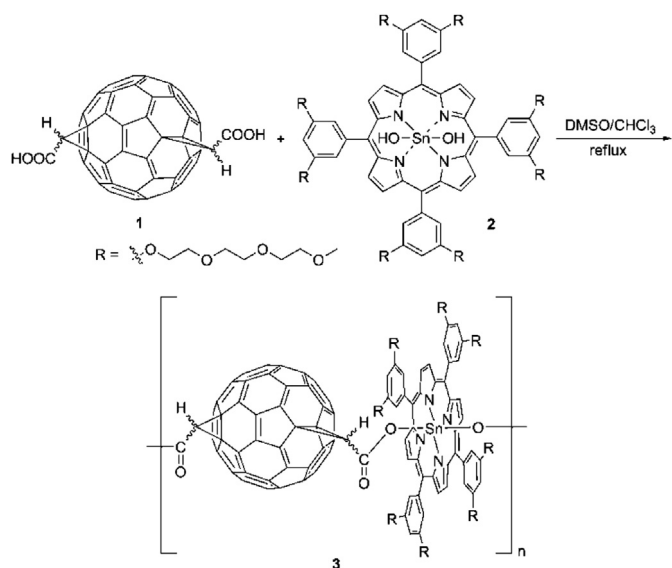


Fig. 1. The TGA-DTA curves of polymer 3.

The polymer obtained was soluble in common solvents, such as CHCl_3 , tetrahydrofuran (THF), *N,N*-dimethylformamide, chlorobenzene and DMSO. In the Fourier transform infrared spectroscopy, the carbonyl groups shifted from 1730 cm^{-1} of **1** to 1710 cm^{-1} after

formation the polymer, and the OH group absorption at 3437 cm^{-1} obviously weakened after coordination (see [Supplementary Materials Fig. S1](#)). The polymer **3** was also investigated by means of NMR spectroscopy. The ^1H NMR spectrum of the polymer **3** showed significant broadening peaks relative to that of dihydroxo Sn(IV) porphyrin **2**. A broad peak at $\delta -7.50$ in the ^1H NMR spectrum of **2** was assigned to the OH group which bound to Sn(IV). It disappeared in that of **3** because of the formation of Sn/carboxylate coordination, which indicated that the coordination reaction of Sn(IV) porphyrins **2** with equivalents of **1** was successful. Solid state ^{13}C NMR of the polymer (see [Supplementary Materials Fig. S2](#)) also exhibited a signal at 175.17 ppm assignable to the carbon atoms of carbonyl groups. Gel permeation chromatography (GPC) measurement in THF indicated that the polymer **3** had weight-average molecular weight (M_w) of about 19,766 with a polydispersity of 1.54, from which it can be deduced that the polymers **3** consist of more than about 7 porphyrin/ C_{60} units.

Thermal stability of the polymer was measured by simultaneous thermogravimetric and differential thermal analysis (TGA-DTA) measurement under air. The results are showed in [Fig. 1](#). As shown in [Fig. 1](#), the polymer **3** started to decompose at about $270\text{ }^\circ\text{C}$, and lost 76.7% of its weight before $800\text{ }^\circ\text{C}$. This is a continuous decomposition process. DTA curve of the polymer has two exothermic peaks at ≈ 355 and $455\text{ }^\circ\text{C}$. The first exothermic peak at $T_{\text{end}} 401\text{ }^\circ\text{C}$ corresponds to a weight loss of 49%, in agreement with the calculated 46% weight loss of the lost of eight chains, and the second exothermic peak at $T_{\text{peak}} 455\text{ }^\circ\text{C}$ corresponds to collapse of the porphyrin skeleton. The residue of combustion at $800\text{ }^\circ\text{C}$ in air is about 23.3%, which is lower the calculated 29% of C_{60} based on 1:1 molar ratio of porphyrin to C_{60} unit in polymer **3**. Considering that C_{60} is very thermally stable, and its decomposition temperature is above $850\text{ }^\circ\text{C}$ in an ultrahigh vacuum [47] and above $725\text{ }^\circ\text{C}$ in air in C_{60} -derived carbonized material [48], the about 23.3% residue should be due to the partial decomposition of C_{60} in the polymer **3**.

Transmission electron microscope (TEM) experiments give some direct visual information about the morphology of the polymer. The TEM image of **3** displays the aggregation of many linear structures with different lengths, and some of those exceed 200 nm ([Fig. 2](#)). From profile of image shown in [Fig. 2b](#), we can see that these nanowires have the same width of about 1 nm, which is a bit wider than that of the diameter of C_{60} . The aggregation originates from strong π - π interaction between porphyrin and C_{60} nanowires. The polymer chains may arrange end to end to form lines, and side by side to form ropes, bundles or agglomeration.

The UV-visible absorption spectra (UV-vis) spectra of the polymer **3** (ca. $2.5 \times 10^{-6}\text{ M}$ based on one porphyrin unit) and porphyrin **2** in diluted *o*-dichlorobenzene (*o*-DCB) solutions are depicted in [Fig. 3](#). As shown in [Fig. 3](#), the characteristic absorption

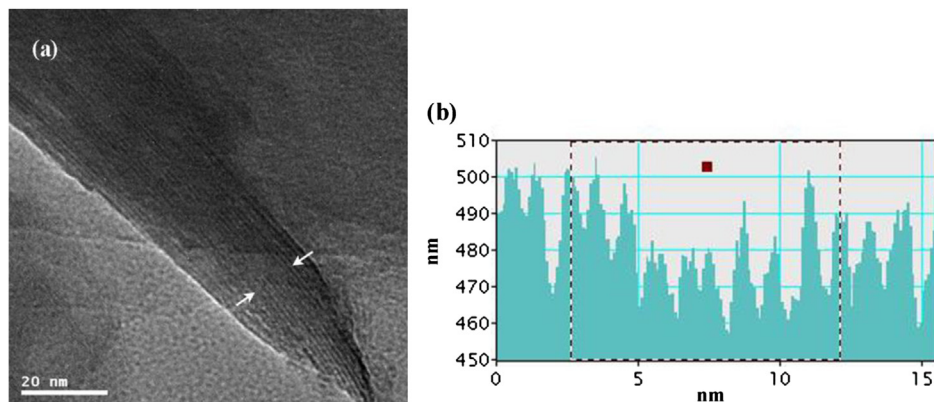


Fig. 2. (a) TEM image of polymer 3, (b) profile of image shown in (a).

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