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Photosensitization of nanoporous TiO_2 film with porphyrin-linked fullerene

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Abstract

A porphyrin-linked fullerene derivative, which included COOH groups in its fullerene unit, Por-C_{60}(COOH) was synthesized in order to investigate the possibility of promoting the photosensitization of TiO_2. Por-C_{60}(COOH) molecules produced higher photocurrent per molecule than tetrakis(4-carboxyphenyl)-porphyrin molecules. A dye-sensitized solar cell using Por-C_{60}(COOH), in which a C_{60} unit was introduced between the porphyrin unit and TiO_2, yielded an improvement in energy conversion for light collection.
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Keywords: Photosensitization of TiO_2; Donor–acceptor linked molecule; Fullerene derivative having COOH group; Light collection

1. Introduction

The photosensitization of wide-gap semiconductors has gained renewed interest recently, especially since the development of high-efficiency solar cells incorporating dye-sensitized nanocrystalline TiO_2 films [1–3]. The porous nature of the film gives rise to a large surface area, leading to good light collection with just a monolayer of dye. Porphyrins are common photosensitizers because of their strong absorption in the 400–450 nm region (Soret band). There have been several reports of photosensitization by 5,10,15,20-tetrakis(4-carboxyphenyl)-porphyrin (TCPP) and Zn-TCPP, which are both efficient sensitizers for TiO_2 [4–8]. In these dye-sensitized cells, charge separation takes place due to electron injection from the excited state of the dye to the conduction band of TiO_2 on the picosecond timescale. Effective electron transfer from the excited dye to the TiO_2 conduction band requires good electronic coupling between the lowest unoccupied orbital of the dye and the Ti 3d orbitals.

Since buckminsterfullerene (C_{60}) was discovered to be an attractive electron acceptor with novel photo-physical and electrochemical properties, considerable effort has been devoted in recent years to develop donor–acceptor linked molecules (D–A molecules) in which C_{60} is covalently linked to an electron donor [9–12]. One fascinating class of donors that can be covalently linked to C_{60} is porphyrin and its derivatives. Various porphyrin-linked C_{60} dyads have been synthesized and their photoinduced reactions have been investigated [13–16]. Imahori et al. have investigated photoinduced electron transfer in zinc porphyrin-C_{60} dyads and have fabricated highly efficient energy conversion systems [17,18]. Some of these porphyrin-C_{60} linked molecules produce a long-lived charge-separated state with a high quantum yield. Therefore, it may be expected that electron transfer from the excited dye occurs smoothly and consequently enhances energy conversion. However, there is little information available regarding the photosensitization of semiconductors by D–A linked molecules.

For D–A molecules to be usable in the photosensitization of nanoporous TiO_2, they should preferably have COOH groups in their structures so as to promote their adsorption onto TiO_2. Although Imahori et al. have bridged fullerenes onto indium–tin-oxide (ITO) electrodes with COOH units and subsequently reacted the fullerene with porphyrin derivatives [19], almost none of the D–A molecules reported in recent years have used COOH groups. Also, a series of porphyrin–oligothiophene–fullerene dyads containing oligothiophene spacers has been synthesized by Ikemoto et al. [20]. We have attempted the introduction of COOH groups into the fullerene unit of the D–A molecule porphyrin–bithiophene–fullerene (Por-C_{60}(COOH)). Since our D–A molecules can interact with TiO_2 nanoparticles

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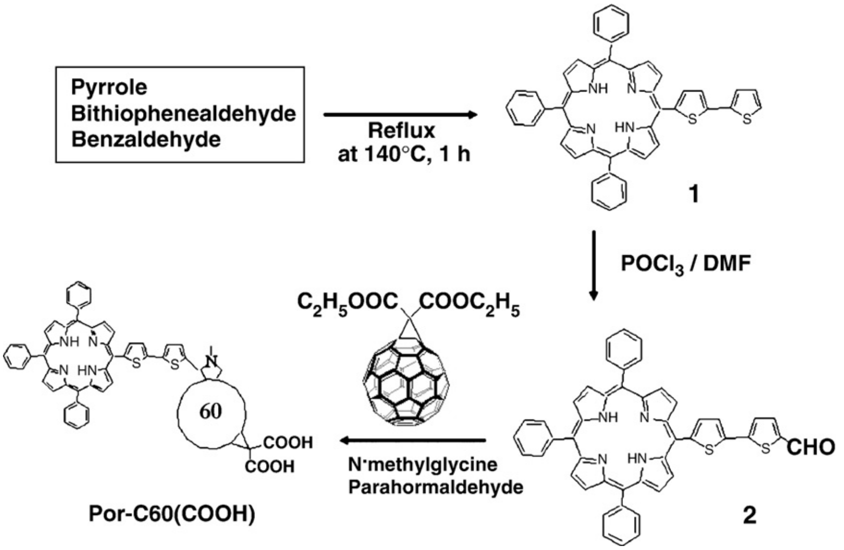

Fig. 1. Synthesis scheme of Por-C_{60}(COOH).

using the COOH groups in the fullerene unit, it was thought that the photoinduced electrons produced by the porphyrin unit would transfer to the C_{60} unit and from thence to the nanoporous TiO_2.

2. Experimental section

2.1. Preparation of Por-C60(COOH)

Por-C_{60}(COOH) was synthesized as shown in Fig. 1. Formyl bithiophene prepared by the Vilsmeier reaction of bithiophene (Tokyo Kasei) was subjected, together with 3 M equiv of benzaldehyde (Aldrich), to hybrid condensation with 4 M equiv of pyrrole (Aldrich) in propionic acid [21]. The triphenyl (bithienyl) porphyrin 1 obtained was converted into its formyl derivative 2 by another Vilsmeier reaction. The formyl derivative 2 was treated with *N*-methylglycine (Aldrich) and di(ethoxycarbonyl)methylene-C_{60} in toluene according to the Prato method [22]. Finally, the ester thus obtained was hydrolyzed with NaOH to obtain Por-C_{60}(COOH). The its identity was confirmed by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) and fourier transform infrared spectroscopy (FTIR). ^{1}H NMR data were recorded at 500 MHz in d_6-dimethyl sulfoxide (d_6-DMSO). Chemical shift δ; −2.927 ppm (2H, s) [23], 2.368 ppm (3H, s), 2.502 ppm (2H, s), 2.634 ppm (1H, s), 6.897 ppm (4H, s), 7.824–7.861 ppm (15H, q), 8.221–8.236 ppm (8H, d), and 10.178 ppm (2H, s). The FTIR data showed peaks at 1735 cm^{-1} due to COOH groups and at 2776 cm^{-1} due to C_{60} units. The signals of the bithiophene unit were observed at 1647 cm^{-1} and 3058 cm^{-1}. Typical peaks due to porphyrin units appeared at 802 cm^{-1}, 978 cm^{-1}, 1440 cm^{-1}, and 1481 cm^{-1}. As the exact position of 1,3-dipolar cycloaddition of azomethine to C_{60} was not identified in these molecules, the C_{60} unit was represented by a large circle in Fig. 1.

2.2. Fabrication of photovoltaic cell

Nanoporous TiO_2 films were prepared by screen-printing a viscous dispersion of colloidal TiO_2 particles on to a conducting

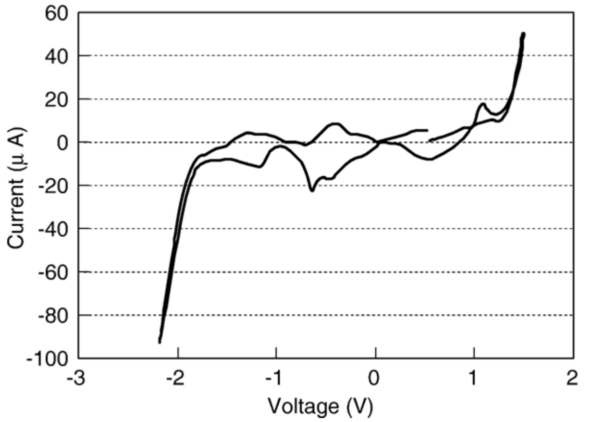

Fig. 2. A cyclic voltammogram of Por-C_{60}(COOH) in dimethyl sulfoxide.

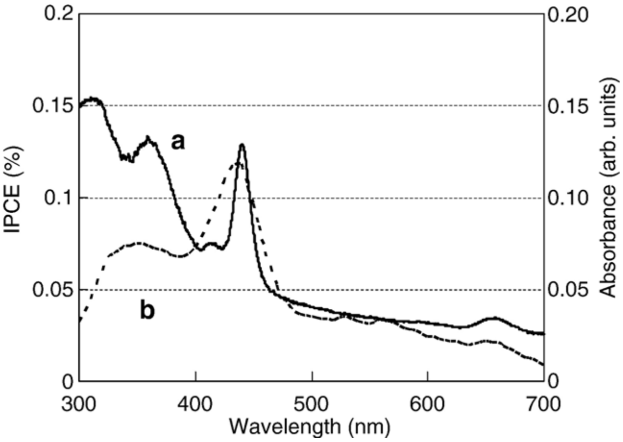

Fig. 3. Photovoltaic properties of Por-C_{60}(COOH); (a) UV–VIS absorption spectrum of a Por-C_{60}(COOH) solution in ethanol, and (b) IPCE profile of a solar cell using a spin-coated film, and respectively. The concentration of Por-C_{60}(COOH) in the ethanol solution was 0.1 mM.

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