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Effect of a novel self-assembly based on coordination polymer with zinc porphyrin in supramolecular solar cells

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ABSTRACT

Within this work, we firstly report the self-assemblies of zinc porphyrin coordination polymers (**CPs**) appended isonicotinic acid ligands by metal–ligand axial coordination approach immobilized on the nanostructured TiO_2 electrode surfaces in photoelectrochemical devices. Compared to the assemblies based on zinc porphyrins integrated isonicotinic acid ligands via metal–ligand axial coordination or metal–ligand edged binding approach, the **CPs**-based assemblies exhibit significantly improved photovoltaic performances. Especially, the assembly based on iminazole-substituted zinc porphyrin coordination polymer exhibits an excellent photovoltaic performance with a short circuit photocurrent density (J_{sc}) of 3.8 mA cm^{-2}, an open circuit voltage (V_{oc}) of 0.31 V, a fill factor (*FF*) of 0.67 and an overall conversion efficiency (η) of 0.48% under AM 1.5 conditions. The results serve as another good testing ground for the fabrication of supramolecular devices techniques in future.

1. Introduction

In nature, porphyrin macrocycle as a basic chromophore framework is used to the photoinduced electron and energy transfer system, because it could collect solar energy from the peripheral light-harvesting antenna and validly convert it into chemical energy [1,2]. Inspired by this intriguing natural principle, researchers have been attempting to mimic such feature to construct artificial light-harvesting devices in solar cells [3–9]. In these biomimic processes, many self-assemble frameworks have successfully served as energy/electron/hole-transferral agents to accomplish efficient charge separation and carrier of separated charges to their respective electrodes. For example, to control the distances and orientations of entities, and achieve long-live charge-separated state, employing multiporphyrin-based assemblies such as triads, tetrads or pentads through metal–ligand axial coordination [10,11] and/or metal–ligand edged binding approach [12,13] for constructing ordered array of different moieties on solid surface have been documented. It is presumed that porphyrin-based coordination polymers (**CPs**)-organic acid self-assemblies via metal–ligand axial interactions with multiple and effective transmission channels for electron and energy transfer could be applied to dye-sensitized photonic devices, and generating significant current–voltage behavior.

Herein, to the best of our knowledge, we firstly report the metal–ligand axial coordination approach to construct the porphyrin-based **CPs**-ionicotinic acid assemblies

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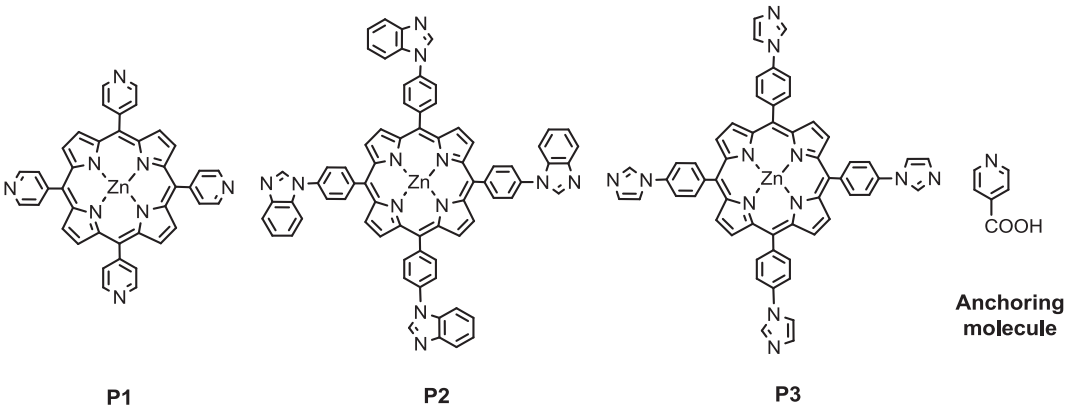


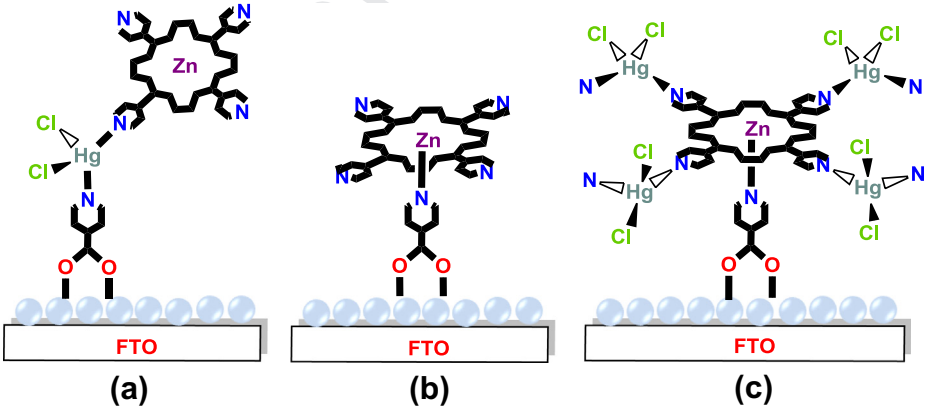
Scheme 1. Structural diagram of **P1**-**P3** and anchoring molecule.

sensitized on TiO_2 electrode surfaces in photosynthesis devices. Three zinc porphyrin bearing different substitutions (denoted as **Px**, **x** = 1–3, shown in Scheme 1) and their corresponding Hg(II) coordination polymers (described as**CPs-x**, **x** = 1–3) were synthesized, and **Px**-isonicotinic acid assemblies via metal–ligand axial coordination (denoted as**Px-a**) and edged binding approach (described as**Px-Hg-e**) were also prepared to further probe the performances of **CPs-x**-isonicotinic acid assemblies (defined as **CPs-x-a**). The detailed assembly modes are shown in Scheme 2.

2. Experiments

2.1. General methods

Electronic absorption spectra were measured on a UV-2550 spectrometer. Elemental analyses of C, H, and N were recorded on a VxRio EL Instrument. Surface topography of the self-assembly films on TiO_2 electrode surface was imaged using an atomic force microscopy (AFM, Nanoscope III, Digital Instruments Co.) in contact tapping mode. Transmission electron microscopy (TEM) (Hitachi Model H-900) was prepared to characterize the morphology and particle size distribution. A LS1000 solar simula-tor (Solar Light Com. Inc., USA) was used to give an irradiance of 100 mW cm^{-2} (the equivalent of one sun at AM 1.5G) at the surface of a testing cell. The current–voltage characteristics were obtained by applying external potential bias to the cell and measuring the dark current and photocurrent with a Keithley model 2602 digital source meter. This process was fully automated using Labview 8.0. A similar data acquisition system was used to control the incident photon-to-collected electron conversion efficiency (IPCE) measurement. Under full computer control, light from a 1000 W xenon lamp was focused through a monochromator onto the photovoltaic cell under test. A computer-controlled monochromator (Omni λ300) was incre-mented through the spectral range (300–900 nm) to generate a photocurrent action spectra with a sampling interval of 10 nm and a current sampling time of 2 s. IPCE is defined by $IPCE(\lambda) = hcJ_{sc}/e\Phi\lambda$, where h is Planck's constant, c is the speed of light in a vacuum, e is the electronic charge, λ is the wavelength (m), J_{sc} is the short-circuit photocurrent density (mA cm^{-2}), and Φ is the incident radiative flux (mW m^{-2}). Photovoltaic performance was measured by



Scheme 2. Structures of coordination-bond-assisted self-assemblies on TiO_2 electrode surfaces, (a) metal–ligand edged binding approach for **P1**-isonicotinic acid assembly; (b) metal–ligand axial coordination for **P1**-isonicotinic acid assembly; (c) metal–ligand axial coordination for **CPs-1**-isonicotinic acid assembly.

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