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A new porphyrin bearing a pyridinylethynyl group as sensitizer for dye sensitized solar cells

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ABSTRACT

A novel porphyrin dye extended at one *meso*-position via an pyridinylethynyl group acting as anchoring group and three phenyl —COOMe groups was synthesized and used as sensitizer for the fabrication of dye sensitized solar cells (DSSCs). The overall power conversion efficiencies (PCE) of DSSCs based on this porphyrin dye as sensitizer with and without CDCA coadsorbant are 3.36% and 4.56%, respectively. To improve the PCE of DSSC, we have incorporated Ag nanoparticles into the nano-porous TiO_2 photoanode i.e. FTO/TiO_2/Ag-NPs and found a enhancement up to 5.66%. The improved photovoltaic performance of the DSSCs with modified photoanode is attributed to the (i) the increased light harvesting efficiency due to the plasmon enhanced optical absorption induced by Ag nanoparticles, (ii) reduced back recombination process at TiO_2/dye/electrolyte interface, (iii) improved electron lifetime, and (iv) formation of Schottky barrier at TiO_2/NPs-Ag.

1. Introduction

Dye sensitized solar cells (DSSCs), based on electrochemical devices, are promising alternatives to conventional silicon based photovoltaic technologies for solar energy conversion owing to their high power conversion efficiency (PCE) and low cost of fabrication [1]. One of the major components in the DSSC is the dye molecules that are coated on the surface of nano-crystalline titanium dioxide (TiO_2) film for light harvesting and electron injection into the TiO_2 conduction band [2]. The PCE of the DSSC relies mainly upon the nature of the dye as sensitizer [3], so optimizing the molecular design is paramount to maximizing PCE. High efficient DSSCs have been based on polypyridyl ruthenium complexes as sensitizer and PCE of over 11% has been attained for some DSSCs of Ru(II) based sensitizer [4]. Although such dyes have broad absorption spectra, energetically compatible excited states with other components, relatively long lived excited states and good stability, these dyes are not suitable for cost effective and environmentally friendly photovoltaic systems, because Ru is a rare and expensive metal which may limit the potentially wide application of these dyes. These disadvantages have driven the search for alternative materials as sensitizer for DSSCs.

Recent studies have shown porphyrins, which comprise a family of organic chromophores, to be promising alternatives to Ru(II) dyes due to their high molar extinction coefficients, ease of modification, photochemical stability, low toxicity and potential low cost [5]. Porphyrin chromophores exhibit two absorption bands: the Soret- and Q bands which occur in the blue and red region respectively. With suitable molecular control, these bands can be shifted and broadened, potentially facilitating an increase in total photon absorption and therefore, the achievable photocurrent in DSSC. However, the porphyrin sensitizers based on the light harvesting properties of the basic porphyrin core typically have admittedly moderate cell performance compared with ruthenium polypyridyl complexes. Imahori and coworkers have reported that this occurs mainly because of the insufficient light harvesting ability of typical porphyrins used in optimized cells, especially at around 500 nm and at wavelength beyond 600 nm [5e,5m]. Broadening and red shifting of Soret and Q bands with an enhancement of the light harvesting capability of the Q bands relative to the Soret band in porphyrin dyes are straightforward approaches to increasing their efficiency as sensitizers in DSSCs. As demonstrated for other organic dyes as sensitizers in DSSCs, the introduction of both an electron donating and an electron withdrawing substituent including an anchoring group to a core with a π-system is also appealing for the modulation of light harvesting properties of sensitizers [6]. In 2010, Bessho

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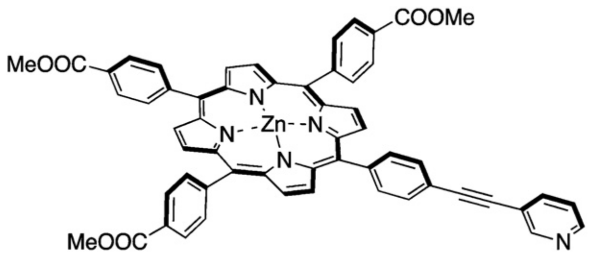

Scheme 1. Chemical structure of tricarboxy-pyridinylethynyl porphyrin dye.

et al. [5g] and Wang et al. [5h] have synthesized porphyrin dyes with electron donating (D) and accepting (A) moieties for intramolecular separation of electron and hole that comprise the excited state. DSSCs based on these dyes have exhibited PCE greater than 10% demonstrating that high efficiencies are attainable from Ru free dyes. Recently a breakthrough in the DSSCs has been achieved by Yella et al. [7], who have used a new cobalt electrolyte conjugation with a push pull porphyrin sensitizer with an electron donating diarylamino group at one *meso* position and an electron withdrawing carboxyphenylethynyl anchoring group at the opposite *meso* position. A remarkably high record PCE of 12.3% was reported. In principle, the molecular design of a porphyrin sensitizer is based on **P–B–A** structure, in which **B** represents a π-conjugation bridge serving as spacer between the porphyrin light harvesting center **P** and the anchoring group **A**.

We have reported the synthesis of two *meso*-substituted *trans* A2B2 type porphyrin dyes i.e. free base and the corresponding Zn complex, in which two N-N′-dimethylphenyl groups act as donor and two phenyl-carboxylic acids as electron acceptor at *meso* positions and used as sensitizer for DSSCs, yielding a PCE of 6.07% [8]. Recently we have synthesized porphyrin dyes bearing pyridyl groups at different *meso* positions which act as electron anchoring groups, applied them as sensitizer for DSSCs and achieved PCE of 6.12% for porphyrin with two pyridyl groups in *cis*-position related to the porphyrin core [9]. The higher PCE for the *cis*-isomer related to the other two porphyrin dyes having one and four pyridyl functional groups, respectively, is due to the balance of the efficient dye regeneration and electron injection process for the DSSCs.The promising results for porphyrins with pyridyl as anchoring group promoted us for further continuation to our research work and designed a porphyrin dye with a pyridyl group connected through a triple bond to the aromatic porphyrin core (Scheme 1). The overall PCE of the DSSCs based on this sensitizer with and without CDCA as coadsorbant is about 3.36% and 4.56%. The PCE has been further enhanced up to 5.66%, when Ag nanoparticles are incorporated into the nano-porous TiO_2 layer. The addition of Ag nanoparticles can enhance optical absorption of dye by localized Ag plasmons and at the same time the back electron transfer i.e. recombination process has been reduced.

2. Experimental details

2.1. Synthesis of porphyrin dye

^{1}H spectra were recorded on a Bruker AMXDPX-500 or on a 300 MHz spectrometer and referenced to the residual protonated solvent. High-resolution mass spectra were obtained on a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer. Raman spectra were recorded on a DeltaNU 532 Advatage Raman spectrometer, excitation wavelength 532 Nd:Yag laser wave number 200–3400 cm^{-1}. Solvents (ACS for analysis) and chemicals were purchased from Aldrich. All measurements were performed at room temperature.

Synthesis of 5,10,15-tris (4′-carboxymethylphenyl)-20-(4′(-3-pyridinylethynyl)phenyl) porphyrin. 4-(3-Pyridinylethynyl) benzaldehyde was synthesized by Sonogashira coupling [10].

(R_f:0.6 CH_2Cl_2:MeOH 10:0.1,yield 80%)

The synthesis of porphyrin was based on Alder–Longo's method. A mixture of 4′-(-3-pyridinylethynyl) benzaldehyde (2.41 mmol) and methyl-4-formyl benzoate (4.82 mmol) were dissolved in hot propionic acid. Pyrrole (6.43 mmol) was added dropwise and the mixture was refluxed for 1 h. Removal of the propionic acid was followed by repeat washing of the crude mixture with water. The solid was chromatographed on a dry column of SiO_2. Elution of product was achieved as a second fraction by a mixture of solvents CH_2Cl_2/EtOH (100/1.5, v/v), (yield 20%).

HRMS (MALDI-TOF): *m/z* calcd for $C_{57}H_{39}N_5O_6 + H^+$: 890.2979 [M+H]$^+$. Found: 890.2983. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.93 (*s*,1H), 8.89 (d, *J* = 4.5 Hz, 2H), 8.83 (br, 6H), 8.63 (d, *J* = 3.5 Hz), 8,45 (m, 6H), 8.3 (m, 6H), 8.23 (d, *J* = 8 Hz, 2H), 7.96 (m,3H), 7.37 (m, 1H), 4.14 (s, 12H) −2.6 (s, 2H)

Metallation. Metallation with Zn was performed in a mixture of CH_2Cl_2/MeOH (4/2, v/v) with 5eq excess of $Zn(CH_3COO)_2$ at room temperature. The yield was quantitative.

HRMS (MALDI-TOF): *m/z* calcd for $C_{57}H_{38}N_5O_6Zn$ [M+H]$^+$: 952.2114. Found: 952.2118

2.2. Computational methods

DFT calculations were performed using the Gaussian 09W [11] (Revision-A.02) program suite and employing default optimization conditions for tight SCF convergence criteria. The geometry of the dye in air was optimized using density functional theory (DFT) [12] using hybrid B3LYP [13] density functional and the 6-31G* basis set. The optimized structure was subjected to vibrational analysis, and characterized as a minimum due to the absence of imaginary frequency. The time-dependent DFT (TD-DFT) [14] computations at the same level (B3LYP/6-31G*) was further carried out to determine first 10 vertical excitations to the excited state of the molecule. The computations in THF were performed by applying polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM) to describe the electrostatic solute–solvent interactions by the creation of solute cavity via a set of overlapping spheres [15]. The absorption spectra were simulated by using the 10 lowest spin-allowed singlet transitions, mixed Lorentzian–Gaussian lineshape (0.5) and an average full-width at half maximum of 3000 cm^{-1} for all peaks [16].

2.3. Cyclic voltammetry

For the oxidation and reduction potentials of the porphyrin, cyclic voltammetry experiments were performed in DCM with 0.1 M $TBAPF_6$ as supporting electrolyte and a glassy carbon as working electrode, a platinum wire as counter electrode and saturated calomel electrode (SCE) as reference electrode.

2.4. Fabrication and photovoltaic characterization of DSSCs

The TiO_2 paste was prepared by mixing 1 g of TiO_2 powder (P25 Degussa), 0.2 mL of acetic acid and 1 mL of water. Then, 60 mL of ethanol was slowly added while sonicating the mixture for 3 h. Finally, Triton-X was added to obtain a dispersed colloidal (TiO_2) paste and stirred for 4 h at 80 °C to form a transparent colloidal TiO_2 paste. The TiO_2 paste was deposited on the pre-cleaned fluorine doped tin oxide (FTO) coated substrate by doctor blade technique. The thickness of the TiO_2 film was about 14 μm. Finally the TiO_2 coated FTO was sintered at 450 °C for 30 min. After cooling to room temperature, this electrode was immersed into a 40 mM aqueous $TiCl_4$ solution at 80 °C for 30 min, washed with water and ethanol