Dyes and Pigments 91 (2011) 317–323

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Electronically coupled porphyrin-arene dyads for dye-sensitized solar cells

Cheng-Wei Lee [a,b], Hsueh-Pei Lu [b], Nagannagari Masi Reddy [a], Hsuan-Wei Lee [a],
Eric Wei-Guang Diau [b,*], Chen-Yu Yeh [a,*]

[a] *Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan, ROC*
[b] *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 300, Taiwan, ROC*

ARTICLE INFO

Article history:
Received 15 February 2011
Received in revised form
7 April 2011
Accepted 7 April 2011
Available online 21 April 2011

Keywords:
π-Conjugation
Dye-sensitized solar cells
Electronic coupling
Light-harvesting
Perylenes
Porphyrins

ABSTRACT

An acetylene-linked porphyrin-perylene anhydride and an acetylene-linked porphyrin-naphthalic anhydride have been synthesized; the highly conjugated acetylenic bridge in these porpyrins efficiently mediates electronic interaction between the porphyrin and perylene units to extend the π-conjugation of the porphyrin dye and to cause both broadening and red shifts of both the Soret and Q absorption bands. This condition is a useful feature for efficient dye-sensitized solar cell applications. The optical, electrochemical and photovoltaic properties of the new linked anhydrides show that the HOMO–LUMO gap decreased upon extension of π-conjugation, indicating a strong electronic coupling between the porphyrin and the perylene or naphthalene unit.

1. Introduction

To maintain global economic growth and to diminish global warming and environmental pollution, the exploration of renewable energy resources is of great significance. Sunlight is the most abundant resource that can deliver clean and efficient energy to meet the increasing demand worldwide. Nature has chosen porphyrin-related pigments in the light-harvesting antennae of photosynthetic organisms that power biological systems [1]. The chromophores in the photosynthetic reaction center capture sunlight efficiently and convert solar energy into usable chemical energy. The synthesis of porphyrins and related macrocycles has attracted considerable attention because they are ubiquitous in natural systems and have prospective applications in mimicking enzymes [2], catalytic reactions [3], photodynamic therapy [4], molecular electronic devices and conversion of solar energy [5–15]. In particular, numerous porphyrin-based artificial light-harvesting antennae, and donor–acceptor dyads and triads have been prepared and tested to improve our understanding of the photochemical aspect of natural photosynthesis [5–15]. Extensive investigation on these multicomponent systems has disclosed the reaction parameters and the mechanism of transfer of energy and electrons have illuminated the development of the conversion of solar energy.

The development of solar cells of new types is escalating, prompted by increasing energy demand. Dye-sensitized solar cells (DSSC) appear to be a promising approach for the conversion of sunlight to electricity on a large scale. The most efficient DSSC are based on ruthenium polypyridine complexes and have attained efficiencies ∼11% of power conversion [16,17]. However, the application of ruthenium complex devices is significantly limited by the rareness of ruthenium and also by potential environmental pollution issues. Diverse organic dyes including porphyrin-related compounds have consequently been synthesized for use in DSSC [5–15]. Officer et al. have synthesized β-carboxyl-substituted porphyrin monomers and multiporphyrin arrays, and investigated their efficiencies [18]; β-substituted monoporphyrin carboxylic-acid derivatives with a conjugated bridge are effective candidates for DSSC. The best porphyrin dye, which has a butadiene bridge between a carboxyl and the porphyrin ring, attains an efficiency up to 7.1% in its power conversion [10]. The conjugated bridge significantly broadens the absorption bands to increase the light-harvesting ability. To increase the absorption width of a porphyrin, Imahori et al. designed and synthesized a naphthyl-fused porphyrin with elongated π-conjugation. The cell performance of the naphthyl-fused porphyrin is improved by about 50% relative to the non-fused porphyrin derivative [19].

---

* Corresponding authors. Fax: +886 4 22862547.
E-mail addresses: diau@mail.nctu.edu.tw (E.W.-G. Diau), cyyeh@dragon.nchu.edu.tw (C.-Y. Yeh).

0143-7208/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2011.04.010

Similar to porphyrin derivatives, perylenes are attractive molecular components for application in molecular electronic devices because of their great photostability and unique structures, and their electrochemical and photophysical properties [20–23]. Several perylene dyes for DSSC have been rationally designed and synthesized with introduction of electron-donating groups and bulky substituents to decrease aggregation. The most effective perylene dyes show a power conversion efficiency of up to 6.8% [24,25].

On the basis of previous work, extension of π-conjugation of the porphyrin dye appears to cause broadening of the absorption bands, which is an essential requirement for an efficient sensitizer [5–15,18,19]. We thus aim to construct electronically coupled porphyrin-arene dyads as sensitizers for use in DSSC. Here, we report the synthesis of porphyrin-perylene anhydride dyad **4** and porphyrin- naphthalene anhydride dyad **5**, and their optical, electrochemical and photovoltaic properties. A perylene sensitizer (**P1**) was also synthesized for comparison.

2. Experimental

All reagents and solvents were obtained from commercial sources and used without further purification, unless otherwise noted. CH_2Cl_2 was dried over CaH_2 and freshly distilled before use. THF was dried over sodium/benzophenone and freshly distilled before use. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was recrystallized twice from absolute ethanol and further dried for two days under vacuum. Column chromatography was performed on silica gel (Merck, 70–230 Mesh ASTM).

2.1. Spectral and electrochemical measurements

^1H NMR spectra (Varian spectrometer, 400 MHz), UV–visible spectra (Varian Cary 50), UV–visible–NIR spectra (Shimadzu UV-3600), emission spectra (JASCO FP-6000 spectrofluorimeter), High resolution mass spectra (LTQ Orbitrap XL, Thermo Fisher Scientific) and FAB mass spectra (JMS-SX/SX102A Tandem Mass spectrometer) were recorded on the indicated instruments. Electrochemical tests were performed with a three-electrode potentiostat (CH Instruments, Model 750A) in THF deoxygenated on purging with prepurified dinitrogen gas. Cyclic voltammetry was conducted with a three-electrode cell equipped with a BAS glassy carbon disk (0.07 cm^2) as the working electrode, a platinum wire as auxiliary electrode, and an Ag/AgCl (saturated) reference electrode; the reference electrode is separated from the bulk solution with a double junction filled with electrolyte solution. The working electrode was polished with aluminium (0.03 μm) on felt pads (Buehler) and treated ultrasonically for 1 min before each experiment. The reproducibility of individual potential values was within ±5 mV.

2.2. Device fabrication

The porphyrins were sensitized onto TiO_2 nanoparticulate films to serve as working electrodes in DSSC devices. A paste composed of TiO_2 particles (~20 nm) for the transparent active layer was coated on a $TiCl_4$-treated FTO glass substrate (FTO, 8 Ω/cm^{-2}) with repetitive screen printing to obtain the required film thickness (~10 μm). The TiO_2 film was annealed according to a programmed procedure: (1) heating at 80 °C for 15 min; (2) heating at 135 °C for 10 min; (3) heating at 325 °C for 30 min; (4) heating at 375 °C for 5 min; (5) heating at 450 °C for 15 min; (6) heating at 500 °C for 15 min. For each dye **P1**, **4** and **5**, the electrode was immersed in the dry DMF solution (0.2 mM, 25 °C) containing tetrabutylammonium hydroxide (TBA, 0.2 mM) for dye loading onto the TiO_2 film at 25 °C for 4 h and 8 h. The Pt counter electrodes were prepared on spin-coating drops of H_2PtCl_6 solution onto ITO glass and heating at 380 °C for 15 min. To prevent a short circuit, the two electrodes were assembled into a cell of sandwich type and sealed with a hot-melt film (SX1170, Solaronix, thickness 25 μm). The electrolyte solution containing LiI (0.1 M), I_2 (0.05 M), PMII (0.6 M), 4-*tert*-butylpyridine (0.5 M) in a mixture of acetonitrile and valeronitrile (volume ratio 1:1) was introduced into the space between the two electrodes, so completing the fabrication of these DSSC devices.

2.3. Photovoltaic characterization

The current-voltage characteristics of the devices were measured with a solar simulator (AM 1.5, SAN-EI, XES-502S, type class A) calibrated with a Si-based reference cell (VLSI standards, Oriel PN 91150V). When the device is irradiated with the solar simulator, the source meter (Keithley 2400, computer-controlled) sends a voltage (V) to the device, and the photocurrent (I) is read at each step controlled by a computer via a GPIB interface. The efficiency (η) of conversion of light to electricity is obtained with this relation, $\eta = J_{sc} V_{oc} FF/P_{in}$, in which J_{sc} (mA cm^{-2}) is the current density measured at short circuit, and V_{oc} (V) is the voltage measured at open circuit. P_{in} is the input radiation power (for one-sun illumination $P_{in} = 100$ mW cm^{-2}) and FF is the filling factor. The incident monochromatic efficiency for conversion from photons to current (IPCE) spectra of the corresponding devices was measured with a system comprising a Xe lamp (PTi A-1010, 150 W), monochromator (Dongwoo DM150i, 1200 g/mm blazed at 500 nm), and source meter (Keithley 2400, computer-controlled). A standard Si photodiode (ThorLabs FDS1010) served as a reference to calibrate the power density of the light source at each wavelength. Photocurrent densities of both the target device and the reference Si cell were measured under the same experimental conditions (excitation beam size ~0.08 cm^2) so to obtain the IPCE value of the device from comparison of the current ratio and the value of the reference cell at each wavelength.

*2.4. Synthesis of dyes **4**, **5**, and **P1***

*2.4.1. Zinc(II) 5,15-Bis(3,5-di-tert-butylphenyl)-10-(bis(4-octylphenyl)amino)-20-(3- (perylenedicarboxylic-9,10-anhydride) ethynyl)porphyrin (**4**)*

To a solution of porphyrin **2** [5] (26.4 mg, 0.02 mmol) in dry THF (5 mL) was added tetrabutylammonium fluoride (TBAF) 1 M in THF (0.08 mL, 0.08 mmol). The solution was stirred at 25 °C for 30 min under dinitrogen. The mixture was quenched with H_2O and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The residue and 9-bromo-perylene-3,4-dicarboxylic anhydride (16.0 mg, 0.04 mmol) were dissolved in dry THF (5 mL) and NEt_3 (1 mL) and degassed with dinitrogen for 10 min; then $Pd_2(dba)_3$ (2.2 mg, 2.5 μmol) and $AsPh_3$ (6 mg, 0.02 mmol) were added to the mixture. The solution was heated under reflux for 3 h under dinitrogen. The solvent was removed under vacuum. The residue was purified on a column chromatograph (silica gel) using CH_2Cl_2/hexane = 4/6 as eluent. Recrystallization from CH_2Cl_2/CH_3OH gave **4** (13.4 mg, 45%). ^1H NMR ($CDCl_3$, 400 MHz) δ 9.49 (d, $J = 4.4$ Hz, 2H), 9.22 (d, $J = 4.8$ Hz, 2H), 9.00 (d, $J = 8.0$ Hz, 1H), 8.94 (d, $J = 4.4$ Hz, 2H), 8.77 (d, $J = 4.8$ Hz, 2H), 8.42–8.36 (m, 2H), 8.18 (d, $J = 8.0$ Hz, 2H), 8.12 (s, 4H), 7.99 (t, $J = 8.0$ Hz, 1H), 7.83 (s, 2H), 7.71 (br, 2H), 7.52 (br, 1H), 7.45 (br, 1H), 7.24 (d, $J = 8.4$ Hz, 4H), 6.95 (d, $J = 8.4$ Hz, 4H), 2.47 (t, $J = 7.6$ Hz, 4H), 1.55 (s, 36H), 1.25 (m, 22H), 0.84 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.9, 152.5, 152.3, 150.6, 150.3, 150.1, 150.0, 148.6, 143.8, 141.4, 137.3, 137.0, 134.8, 134.5, 133.4, 133.3, 133.1, 131.9, 131.1, 130.8, 130.3, 130.1, 129.6, 129.0, 128.8, 128.7, 128.1, 127.8, 126.8, 126.1, 125.4, 124.5, 124.3, 123.6, 123.5, 122.0, 121.4, 121.3, 120.9, 120.6, 120.5, 108.7, 102.4,