Dyes and Pigments 105 (2014) 223–231

Contents lists available at ScienceDirect

Dyes and Pigments

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

Cyanovinyl substituted benzimidazole based (D–π–A) organic dyes for fabrication of dye sensitized solar cells

Subbaiah Manoharan, Sambandam Anandan*

Nanomaterials and Solar Energy Conversion Lab, Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, India

ARTICLE INFO

Article history:
Received 13 December 2013
Received in revised form
3 February 2014
Accepted 11 February 2014
Available online 22 February 2014

Keywords:
Benzimidazole
Cyanovinyl
Organic dye
Efficiency
π-bridge
Acceptor

ABSTRACT

Benzimidazole based metal free organic dyes (D–π–A) with and without cyanovinyl unit have been designed and synthesized via one step processes and tested as sensitizers in the dye sensitized solar cells (DSSC). In such donor-π-bridge-acceptor dyes, *N*,*N*-diethylaniline and triphenylamine were act as donors and benzimidazole derivatives were act as π-bridge as well as acceptor. The relationship between molecular structure and optoelectronic properties of the synthesized dyes as well as their DSSC performances were studied by UV–vis and fluorescence spectroscopy, cyclic voltammetry (CV) and Density Functional Theory (DFT) calculation. Introduction of cyanovinyl unit in between the donor and benzimidazole leads to the significant improvement in the optoelectronic properties and DSSC performance. In general, the cyanovinyl unit containing dyes based DSSCs show more than two times higher efficiency than the dyes without cyanovinyl unit based DSSCs. Among the fabricated DSSC, the dye contain triphenylamine donor and benzimidazole with cyanovinyl unit based DSSC shows maximum power conversion efficiency of 3.47% under AM1.5 illumination (85 mW/cm^2).

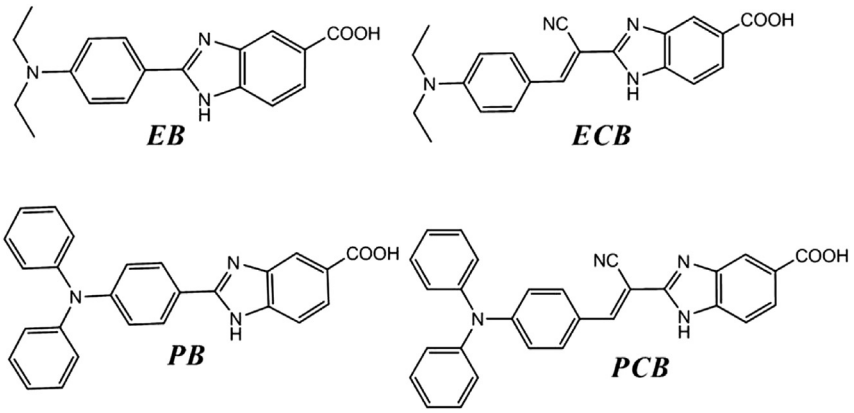
1. Introduction

The current situation in the energetic and environmental crisis has awakened the interest in the conserved utility of renewable energy sources. In this regard, dye-sensitized solar cells (DSSCs) certainly appear as one of the most promising devices for converting the solar energy and have attracted significant attention as low-cost alternatives to conventional semiconductor photovoltaic devices [1]. Among the DSSC components the photoanode play like a heart of the device in which sensitizer molecules were chemisorbed on the TiO_2 surface [2,3]. Recently, metal-free organic dyes possess the common structure of donor-π-bridge-acceptor (D–π–A) have much attention as alternative sensitizers in DSSC compared to their metal organic counterparts due to their high flexibility in structure modification, environmental concerns and low cost [4–6]. In the last decade, variety of organic dyes with D–π–A construction have been investigated for DSSCs, including dyes based on triphenylamine, [7,8] indoline, [9,10] phenothiazine, [11,12] carbazole [13,14], phenoxazine [15,16] and achieved efficiency more than 8%. To improve the efficiency and stability of the DSSC more efforts have been spent through the modification and optimization of dye structure by many research communities [6]. For that variety of donors has been utilized, but predominantly such dyes consist of thiophene or ethenyl derivatives as π-bridges [4]. Even though those π-bridges are very effective, it has some synthetic drawbacks such as multi steps reaction, utilization of expensive catalysts and reagents, finally it needs very rigorous inert atmosphere [17,18]. In this concern, we choose benzimidazole derivatives which are produced from inexpensive and easily available starting materials, simple synthesis methodologies, good electron transporting ability and high thermal stability [19,20]. Introduction of cyanovinyl unit in benzimidazole is very attractive since the presence of cyano group will increase the electron withdrawing nature of the benzimidazole which decreases the lowest unoccupied molecular orbital (LUMO) energy level of the dye molecules. It indicates that the cyanovinyl group helps to increase the intramolecular charge transfer and reduces the optical band gap of the dye molecules [21,22].

Herein we present four benzimidazole based organic dyes namely 2-(4-(diethylamino)phenyl)-benzimidazole-5-carboxylic acid (EB), 2-(4-(diphenylamino)phenyl)-benzimidazole-5-carboxylic acid (PB), 2-(1-cyano-2-(4-(diethylamino)phenyl)vinyl)-benzimidazole-5-carboxylic acid (ECB) and 2-(1-cyano-2-(4-(diphenylamino)phenyl)vinyl)-benzimidazole-5-carboxylic acid (PCB) as a sensitizer towards fabrication of metal free DSSCs (Scheme 1). Triphenylamine and *N*,*N*-diethylaniline were used as donors to

* Corresponding author. Tel.: +91 431 2503639; fax: +91 431 2500133.
E-mail addresses: sanand99@yahoo.com, sanand@nitt.edu (S. Anandan).

http://dx.doi.org/10.1016/j.dyepig.2014.02.010
0143-7208/



Scheme 1. Dye structures.

modify the highest occupied molecular orbital (HOMO) energy levels of the dyes which shows a major contribution in the open circuit voltage (*Voc*). Benzimidazole-5-carboxylic acid with and without cyanovinyl unit was used as π-conjugation bridge and also the acceptor to alter the LUMO energy level and optical band gap of the dyes which predominantly affect the overall photovoltaic performances. The optoelectronic properties of the synthesized dyes were studied by UV–vis and fluorescence spectroscopy, cyclic voltammetry (CV) and Density Functional Theory (DFT) calculation. Finally the synthesized dyes were applied as a sensitizer towards fabrication of DSSCs.

2. Experimental section

2.1. Materials and methods

Triphenylamine (Sigma–Aldrich), 4-diethylaminobenzaldehyde (Alfa Aesar), 3,4-diaminobenzoic acid (Alfa Aesar), Ethyl cyanoacetate (Sigma–Aldrich), Copper (II) acetate ($Cu(OAc)_2$), Tetrabutylammonium perchlorate (TBAP) (Sigma–Aldrich) were purchased and used without further purification. Phosphorus oxychloride ($POCl_3$), *N*,*N*-dimethylforamide (DMF) were purchased from Merck. ^1H and ^{13}C NMR analysis were measured on Bruker 500 MHz NMR Spectrometer using tetramethylsilane as internal standard. Agilent liquid chromatography-mass spectrometry (LC-MS) was used to record LC-MS spectra. The FT-IR spectra were obtained with a Thermo Scientific Nicolet iS5 FT-IR spectrometer. All reactions were monitored by using TLC plates. All chromatographic separations were carried out on silica gel (60–130 mesh).

2.2. Photophysical and electrochemical measurements

Absorption and fluorescence spectra were measured in DMF solution on a T90+UV–vis spectrometer and Shimadzu RF-5301 PC spectrofluorophotometer respectively. Electrochemical measurements were performed on a Metrohm Autolab PGSTAT potentiostat/galvanostat-84610. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a glassy carbon (GC) working electrode, a platinum wire auxiliary electrode, and a silver wire was used as the reference electrode. The potentials were reported vs ferrocene as standard using a scan rate of 0.1 V/s. The CV experiments were performed with 3×10^{-4} M dye solution and 0.1 M tetrabutylammonium perchlorate (TBAP) in anhydrous DMF as a supporting electrolyte under Argon atmosphere. Electrochemical impedance spectroscopy (EIS) measurements were done under 85 mW/cm^2 light illumination by using an Autolab PGSTAT potentiostat/galvanostat-84610. The impedance spectra were recorded with a frequency ranging between 10 kHz and 0.1 Hz at their open circuit potential (OCP).

2.3. Synthesis

2.3.1. 2-(4-(diethylamino)phenyl)-benzimidazole-5-carboxylic acid (EB)

3,4-diaminobenzoic acid (0.5 g, 2.82 mmol) was suspended in 1:1 methanol water mixture (24 mL). A solution of the 4-diethylaminobenzaldehyde (0.7 g, 3.95 mmol) in methanol (12 mL) was added and followed by addition of aqueous copper (II) acetate (0.76 g, 4.17 mmol, 12 mL). The resulting mixture was refluxed for 6 h and then filtered while hot. The precipitate was washed with 1:1 mixture of water and methanol. This precipitate was dried and dissolved in ethanol (20 volumes) containing 1.2 mL of concentrated HCl. An aqueous solution of Na_2S (2 mL, 50%) was added and the mixture was refluxed for 2 h. The resulting mixture was filtered while hot to remove the Cu_2S. The filtrate was concentrated to half of the volume, diluted with water twice and then the mixture was made alkaline with aq. NaOH solution (l0%) and filtered. The filtrate was acidified with acetic acid solution (10%) and the precipitate was collected and dried under vacuum to give a pale yellow coloured product with the yield of 73% (0.92 g). ^1H NMR (DMSO-d_6, ppm): δ 1.12 (t, 6H), 3.39–3.43 (q, 4H), 6.78–8.10 (ArH, 7H), 12.62 (s, 1H). ^{13}C NMR (DMSO-d_6, ppm): δ 12.90, 44.18, 111.02, 111.55, 114.37, 115.73, 123.55, 124.30, 128.77, 149.47, 152.38, 155.12, 168.42. IR (KBr pellet, cm^{-1}): 3402, 3159, 2969, 1685, 1607, 1515, 1354, 1160, 945, 819. Anal. Calcd for $C_{18}H_{19}N_3O_2$: C, 69.88; H, 6.19; N, 13.58. Found: C, 70.16; H, 6.30; N, 13.60. LC-MS Anal. Calcd. for $C_{18}H_{19}N_3O_2$: 309.36. Found: 310.10 $[M + H]^+$.

2.3.2. 2-(4-(diphenylamino)phenyl)-benzimidazole-5-carboxylic acid (PB)

First, the starting material 4-(diphenylamino)benzaldehyde was synthesized from triphenylamine according to the Vilsmeier–Haack formylation reaction [23]. Then 3,4-diaminobenzoic acid (0.3 g, 1.97 mmol) was suspended in 1:1 methanol water mixture (24 mL). A solution of the 4-(diphenylamino)benzaldehyde (0.65 g, 2.36 mmol) in methanol (45 mL) was added and followed by addition of aqueous copper (II) acetate (0.53 g, 2.92 mmol, 25 mL). The resulting mixture was refluxed for 6 h and then filtered while hot. The precipitate was washed with 1:1 mixture of water and methanol. This precipitate was dissolved in ethanol (20 volumes) containing 1 mL of concentrated HCl. An aqueous solution of Na_2S