Organic Electronics 15 (2014) 266–275

Contents lists available at ScienceDirect

Organic Electronics

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

Carbazole based A-π-D-π-A dyes with double electron acceptor for dye-sensitized solar cell

K.S.V. Gupta [a], Thogiti Suresh [a], Surya Prakash Singh [a], Ashraful Islam [b], Liyuan Han [b], Malapaka Chandrasekharam [a,*]

[a] Network of Institutes for Solar Energy, Inorganic & Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad 500607, India
[b] Photovoltaic Materials Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

ARTICLE INFO

Article history:
Received 26 July 2013
Received in revised form 4 November 2013
Accepted 4 November 2013
Available online 22 November 2013

Keywords:
Dye sensitized solar cells
Double acceptor dye
A-π-D-π-A structure
Anchoring stability
Carbazole
Linker

ABSTRACT

Three novel carbazole-based A-π-D-π-A-featured dyes (**CSG1**–**CSG3**) have been designed, synthesized for applications in dye-sensitized solar cells and fully characterized with NMR, MS, IR, UV–vis and electrochemical measurements. These dyes share the same donor (N-hexylcarbazole) and acceptor/anchoring group (cyanoacrylic acid), but differs in conjugated linkers incorporated, such as benzene, furan or thiophene, to configure the novel A-π-D-π-A framework for effective electron flow. The power conversion efficiencies were observed to be sensitive to the π-bridging linker moiety. The photovoltaic experiments showed that dye with a benzene linker exhibited a higher open-circuit voltage (0.699 V) compared to thiophene and furan linker. Among all dyes, **CSG2** containing a thiophene linker exhibited the maximum overall conversion efficiency of 3.8% (J_{SC} = 8.90 mA cm^{-2}, V_{OC} = 584 mV, FF = 0.74) under standard global AM 1.5 G solar condition. Under similar fabrication conditions, champion dye **N719** exhibited the maximum overall conversion efficiency of 6.4% (J_{SC} = 14.74 mA cm^{-2}, V_{OC} = 606 mV, FF = 0.716).

1. Introduction

Dye-sensitized solar cells (DSSCs), one of the most promising alternatives to crystalline silicon-based photovoltaics for converting clean, inexhaustible sunlight to electricity have received significant research interest due to their low fabrication cost and relatively high power conversion efficiency (η), since the seminal work was reported in 1991 by O'Regan and Graetzel [1–10]. In the past 5 years, such solar cells have witnessed tremendous progress. For example, a power conversion efficiency (η) of 11.9% has been reached with bipyridyl-based ruthenium sensitizer [11] and particularly a certified record η of 11.4% has also been achieved very recently for terpyridine based dyes using a simple co-adsorbent developed by our group [12] under standard AM 1.5 solar light irradiation. Record efficiencies of 12.3% under AM 1.5 conditions have been achieved by using Zn(II)-porphyrin dyes and cobalt poly pyridyl redox electrolyte [13]. Recently, organic–inorganic hybrid perovskites have attracted attention as light-harvesting materials for mesoscopic solar cells [14–18]. Moreover, solar cells based on these hybrids exhibited a highest power conversion efficiency of 15.0% under standard AM 1.5 conditions [18]. Although metal based dyes have high efficiency and long-term stability, they have encountered problems such as relatively low molar extinction coefficient, limited resources, morphological variations, challenging synthesis and tedious purification which might retard future large scale power production based on DSSCs [4].

On the other hand, metal-free organic dyes have been developed for DSSCs. Their advantages are due to their

---

* Corresponding author. Tel.: +91 040 2719 1710; fax: +91 40 2719 3186.

E-mail address: chandra@iict.res.in (M. Chandrasekharam).

1566-1199/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.orgel.2013.11.020

high molar absorption coefficients, inexpensive syntheses by using well-established synthetic methodologies and they present optical, electronic, and electrochemical properties that can be modulated through appropriate molecular design [19–23]. Moreover, organic dyes normally possess higher molar extinction coefficients than Ru dyes (<20,000 M^{-1} cm^{-1}), which make them ideal for solid state DSSCs, utilizing thinner TiO_2 layers. In particular, encouraging efficiency up to 10.3% has been reported by Wang et al. using metal free organic dyes [22]. Among metal-free organic dyes, a common strategy in the design of highly efficient sensitizers for DSSCs is linking the electron donor (D) and acceptor (A) systems (D–A) through the π-conjugated linkers with TiO_2 surface anchoring groups (e.g., carboxylate) integrated onto the acceptor moiety [24]. Variation of the π-conjugated linker seriously affects the efficiency of the intramolecular charge transfer, and partially determines the DSSC performance of the corresponding cells [25]. However, the low conversion efficiency and low stability are important issues still to be resolved [26]. Another crucial factor is the binding strength of dye on the TiO_2 surface, which affects the conversion efficiency and stability of DSSC device. Strong binding of the dye on TiO_2 not only improves adsorption but also induces efficient charge injection. One of the drawbacks of most of the organic dye molecules is the presence of single anchoring functionality which can be a serious constraint for inferior performance as compared to Ru(II) sensitizers, where 1–4 anchoring groups are present [27]. Thus, several di/multi anchoring organic dyes have been synthesized for use in DSSCs, and have demonstrated better cell performance than single D-π-A sensitizers with an improved photoresponse, photocurrent and stability [28–33].

3,6-Functionalized carbazole is a nonplanar compound which can improve the hole transporting ability of the materials and prevent the formation of dye aggregates [34]. Due to its unique optical, electrical, and chemical properties, carbazole has been used widely as a functional building block or substituent in the construction of organic molecules for use as light-emitting and hole-transporting layers in OLED devices [35–42], as host materials for electrophosphorescent applications [43], and as active components in solar cells [44,45]. Moreover, upon introduction of a carbazole unit into the structure, the thermal stability and glassy state durability of the organic molecules improves significantly [46,47].

Furthermore, alkyl-functionalized carbazole dyes have been designed and used in DSSCs to improve both performance and stability. Kohjiro Hara et al. showed that the presence of hexyl substituents increased the electron lifetime and consequently open circuit voltage [48–53]. We and others reported that the substitution of alkyl chains on dye peripheral can inhibit the recombination losses in DSSC [48,54–57]. As mentioned above, the introduction of π-linker moieties were expected to allow red-shift of the spectrum, and broaden the spectral region of absorption. Based on the above consideration, and our experience on metal free organic sensitizers and carbazole substituted ruthenium [58–60], we have designed and synthesized three new efficient organic carbazole-based double electron acceptor dyes (**CSG1**–**CSG3** shown in Fig. 1) with cyanoacrylic acid moiety acting as the anchoring group and variation of π-conjugated linkers. Finally, the three new sensitizers have been applied successfully to the sensitization of nanocrystalline TiO_2-based solar cells and the corresponding photovoltaic properties, electronic and optical properties are also presented.

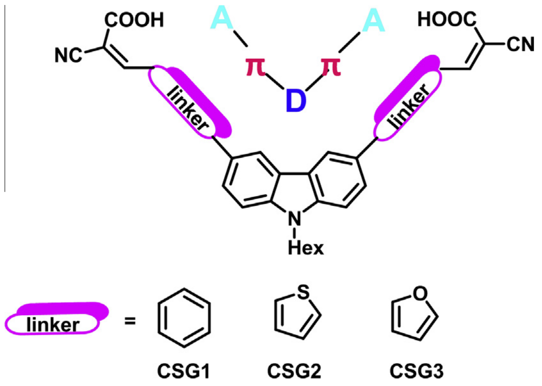

Fig. 1. Chemical structures of organic dyes **CSG1**–**CSG3**.

2. Experimental

2.1. Materials and instruments

All reactions were carried out under nitrogen atmosphere. Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma–Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on Avance 300 or 500 MHz spectrometer. Chemical shifts were reported in parts per million (δ) downfield from tetramethylsilane (TMS) as an internal standard in $CDCl_3$. Low resolution mass spectrometry was performed using LCQ iontrap mass spectrometer (Thermo Fisher, Sanjose, CA, USA) equipped with an ESI source. IR spectra were recorded on a Perkin–Elmer 1800 series FTIR spectrometer and samples were analyzed as thin films on KBr pellets.

The optical spectra of dyes in solution were recorded with a UV–vis spectrophotometer (Shimadzu) while their emission measurements were performed using a Fluorolog 3, JY Horiba fluorescence spectrometer. Electrochemical data were recorded using Autolab potentiostat/ Galvanostat PGSTAT30. The cyclic voltammogram curves were obtained from a three electrode cell in 0.1 M Bu_4NPF_6 *N,N*-dimethylformamide solution at a scan rate of 100 mV s^{-1}, Pt wire as a counter electrode and an Ag/AgCl reference electrode and calibrated with ferrocene.

2.1.1. Synthesis of 3,6-dibromo-9 hexyl-9H carbazole(**3**)

To a solution of 3,6-dibromo-9H-carbazole (0.200 g, 0.615 mmol) in dry *N,N*-dimethylformamide was added KOH (0.105 g, 1.845 mmol) and allowed to stir for 30 min. To this, 1-bromo hexane (0.962 mL, 0.799 mmol) dissolved in dry *N,N*-dimethylformamide was added drop wise and allowed to room temperature with stirring for 12 h. After complete consumption of the dibromocarbazole (TLC), crushed ice was added and stirred well. The