



Carbazole-based organic dye sensitizers for efficient molecular photovoltaics

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ABSTRACT

Efficient dye sensitizers *N,N'*-dialkylcarbazolocarbazole derivatives BG-501 and BG-502 were synthesized and characterized. UV–vis, ¹H NMR and CV were used for the structural characterization. The aim of the synthesis of these molecules is to improve some optical and electronic properties such as molar absorption coefficient, spectral coverage and electron injection properties of the sensitizers. Conjugated organic dyes exhibit higher molar extinction coefficients which allow harvesting more light in thinner semiconductor layer. Carbazole derivative dyes are well known in the literature with their thermal and photochemical stabilities and improved electron donor properties.

We have achieved promising photovoltaic conversion efficiencies with new dyes BG-501 and BG-502 under standard conditions (AM1.5G, 100 mW. cm⁻² light intensity). The conversion efficiencies of solar cells are η :3.18% and η :2.49% with ionic liquid-based electrolyte for BG-501 and BG-502, respectively.

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1. Introduction

Since the report of O'Regan and Graetzel, on high power conversion efficiency [1] dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO₂ have attracted great attention in scientific research due to the potential advantages of low cost production, flexibility and transparency with comparison of silicon solar cell [3]. Over the past 15 years, remarkable progress has been achieved in terms of performance and stability of solar cell [5]. The dye sensitizer is a crucial part for the power conversion efficiency in the devices. Although there is no dye sensitizer reported that has a higher efficiency in comparison with ruthenium complexes, in spite organic dyes have been attracting very intensive research works, owing to ease on synthesis, high molar absorption coefficient, adjustable absorption spectra, and inexpensive production techniques [2,3]. Recently, several groups have developed metal-free organic sensitizers to overcome the prohibitive cost of ruthenium metal complexes, and the impressive photovoltaic performance has been obtained with some organic indoline, coumarin, oligoene, hemicyanine and merocyanine dyes reaching to efficiencies in the range of 5–9% [6–10]. For example DSSC with indoline dye exhibited 9% efficiency which can be attributed to the high molar extinction coefficient of the sensitizer, 68700 M⁻¹ cm⁻¹ in contrast to ruthenium bipyridyl complexes generally have molar extinction coefficient lower than 20000 M⁻¹ cm⁻¹. Organic compounds easily can be modified to

increase molar extinction coefficients and spectral coverage. This allows light harvesting to be accomplished with thinner TiO₂ films [4].

Here we report the synthesis, optical, electrochemical and photovoltaic characterization of two new *N*-alkyl substituted carbazolocarbazole derivative dyes with 3.2% conversion efficiency.

2. Experimental section

2.1. Synthesis and Spectroscopy:

All reactions were carried out under argon atmosphere. All reagents were purchased from Sigma–Aldrich and used without further purification. 5,10-dihydrocarbazolo[3,4-*c*]carbazole was synthesized using the procedure of previous reference [11]. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer. The absorption and the fluorescence spectra were recorded on an Analytic Jena S 600 UV spectrophotometer and PTIQM1 fluorescence spectrophotometer, respectively.

2.2. Electrochemistry:

Electrochemical properties of BG-501 and BG-502 were studied by cyclic voltammetry (CV). CV measurements were recorded by CH 660B model potentiostat from CH Instruments in three electrode cell consist of platinum wire counter electrode (CE), glassy carbon electrode used as a working electrode (WE)

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and Ag/AgCl electrode in 3 M KCl (aq) used as a reference electrode (RE). Measurements were carried out in 0.1 M TBAPF₆ acetonitrile solution as supporting electrolyte. Sweep rate kept constant at 0.1 V/s. The oxidation potential of Ferrocen/Ferrocenium couple was used as an internal reference was exhibited at about +0.41 V.

Electrochemical impedance spectra (EIS) of DSSCs were measured in the dark at –0.66 V forward bias to determine charge transfer resistances (R_{CT}) by using a Zahner IM6 Impedance Analyzer.

2.3. Fabrication of Solar Cells

Electrically conductive oxide-coated glasses were used as transparent electrodes. Dye-sensitized mesoporous TiO₂-coated electrode was used as working electrode and platinized electrode was used as counter electrode.

Anatase nanocrystalline TiO₂ colloids were obtained from a hydrothermal sol-gel method as described in the previous report [12]. The TiO₂ paste was coated on FTO-covered glasses by screen printing technique and sintered at 450 °C for 30 min. The film thicknesses were measured by Ambios XP Stylus Profiler and found about 6 μm. The electrodes were dipped into dye solutions of 0.5 mM BG-501 and BG-502 in chloroform and Z907 in acetonitrile: tert-butanol (1:1) mixture for overnight. Then the electrodes were washed with solvent of the dye solutions.

The counter electrodes were platinized by thermal reduction of hexachloroplatinic acid with the concentration of 1% in 2-propanol and annealed at 400 °C for 20 min. DSSCs was constructed with sandwich geometry. A thermoplastic polymer Surlyn-1702 which had a thickness of 50 μm was used as sealing material. Then the space between two electrodes was filled with electrolyte under vacuum using a pre-drilled small hole on counter electrode. Then the hole was sealed by using piece of Surlyn and cover glass. Electrolyte composition was 0.6 M N-methyl-N-propyl imidasolium iodide (PMII)+0.1 M LiI+0.05 M I₂+0.5 M 4-tert-butyl pyridine (TBP) in 3-Methoxypropionitrile. Active areas of the solar cells were measured as 1 cm².

2.4. Characterization of DSSC:

The cell performances were measured by using Keithley 2400 Source-Meter Unit and Labview data acquisition software. We employed a 100 mW/cm² AM 1.5 light intensity by a solar simulator (KHS equipped with 750 W Xe lamp). The incident light intensity was calibrated with a reference solar cell calibrated by Fraunhofer ISE. The measurements were made at the same day with the cell preparation and the averages of three consecutive measurements were taken. No further long-term stability test was done. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring setup.

2.5. Synthesis

2.5.1. Synthesis of 5,10-dihydrocarbazolo[3,4-c]carbazole

5,10-dihydrocarbazolo[3,4-c]carbazole was synthesized according to procedure described by Zander et al.(11). 2, 7-dihydroxy naphthalene (2.5 g, 1.56 mmol) and phenylhydrazin (3.5 g, 4.17 mmol) were added into a round bottom flask and stirred vigorously at room temperature. After 30 min, 20 mL of K₂CO₃ solution (%36 percent) was added. The final mixture was refluxed for 50 h. The crude product was extracted with 30 mL of ethylacetate for three times at the end of the reaction. Organic phase was evaporated and the pure product was obtained by column chromatography using silica (ethylacetate: hexane-2:3) in

a yield 25%. ¹H NMR (δ) in DMSO-*d*₆: 7.08–7.10 Ar-H (dd), 7.36–7.40 Ar-H (dd), 7.64–7.66 Ar-H(m), 7.64–7.66 Ar-H(m), 7.97–8.0 Ar-H(d), 11.826N-H (s)

2.5.2. Synthesis procedure of N, N-dimethylcarbazolocarbazole

Bromomethyl (2 eq.) was added dropwise into a mixture of carbazolo carbazole (1 eq.) and NaH (2.5 eq.) in DMF, followed by refluxing for 2 h. After the reaction, the mixture was poured into water and extracted with n-hexane for three times. Organic solvent was evaporated and the residue was purified by silica-gel column chromatography using ethylacetate: hexane (1:4) as eluent to afford dimethylcarbazolocarbazole in a yield of 90%. ¹H NMR (δ) in DMSO-*d*₆: 4.48–4.53 Ar-C-H (m), 7.20–7.23 Ar-H (dd), 7.57–7.64 Ar-H (m), 7.57–7.64 Ar-H(m), 7.93–7.97 Ar-H(dd), 7.98–8.02 Ar-H(dd),

2.5.3. Synthesis procedure of N, N-dioctylcarbazolocarbazole

The product was synthesized according to the procedure as described above for the synthesis of N, N-Dimethylcarbazolocarbazole(85%). ¹H NMR (δ) in DMSO-*d*₆: 1.21–1.50 C-H (m), 4.45–4.51 Ar-C-H (m), 7.15–7.21 Ar-H (dd), 7.54–7.62 Ar-H (dd), 7.54–7.62 Ar-H(dd), 7.91–7.96 Ar-H(dd), 7.97–8.0 Ar-H(dd)

2.5.4. Synthesis Procedure of N, N-dialkylcarbazolocarbazole-2-carbaldehyde

Compounds were prepared by Vilsmeier formylations. Phosphoryl chloride (5 eq.) was added dropwise to the DMF (20 eq.) cooled 0 °C and stirred for 1 h. Then a solution of alkyl carbazolo carbazole (1 eq.) in DMF (15 mL) was added into the mixture. After that the final mixture was heated to 90 °C and stirred for 2 h. After the reaction, the mixture was poured into the iced water and extracted with chloroform for three times. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography using chloroform as eluent to give the brown product.

2.5.5. Synthesis procedure of (N, N-dimethylcarbazolocarbazole-2-yl)-isocyanocrylic acid

A mixture of N, N-dimethylcarbazolocarbazole-2-carbaldehyde (1 eq.) and cyanoacrylic acid (2 eq.) was vacuum-dried and added acetonitrile and piperidine(0.01 eq.). The solution was refluxed for 6 h after the reaction, the solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography using chloroform as eluent to give a orange-solid in a yield of 75%. ¹H NMR (δ) in DMSO-*d*₆: 4.40–4.50 Ar-C-H (m), 7.16–7.20 Ar-H (dd), 7.52–7.62 Ar-H (m), 7.54–7.62 Ar-H(m), 7.90–7.94 Ar-H(dd), 8.30–8.34 Ar-H(dd), 8.36 =C-H (s), 10.35 O-H (s)

2.5.6. Synthesis procedure of (N, N-dioctylcarbazolocarbazole-2-yl)-isocyanocrylic Acid

The product was synthesized according to the procedure as described above for the synthesis of (N, N-dimethylcarbazolocarbazole-2-yl)-isocyanocrylic Acid (70%). ¹H NMR (δ) in DMSO-*d*₆: 1.21–1.50 C-H (m), 4.45–4.51 Ar-C-H (m), 7.15–7.21 Ar-H (dd), 7.54–7.62 Ar-H (dd), 7.54–7.62 Ar-H(dd), 7.91–7.96 Ar-H(dd), 8.32–8.35 Ar-H(dd), 8.37 =C-H (s), 10.33 O-H (s)

3. Results and discussion

Novel organic dyes, BG-501 and BG-502 were synthesized by the stepwise synthetic procedures showed in Scheme 1.

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