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Synthesis and characterization of organic dyes containing 2,7-disubstituted carbazole π -linker



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ABSTRACT

New organic dyes containing diphenylamine donor, 2,7-carbazolyl π -linker, and cyanoacrylic acid acceptor have been synthesized and characterized. They possess red-shifted absorption with high molar extinction coefficient when compared to the corresponding dyes with fluorene or phenyl units in the conjugation. The dye-sensitized solar cells fabricated using these dyes as sensitizers exhibited power conversion efficiencies as high as 6.8% which increased to 7.2% when chenodexoycholic acid (CDCA) was used to impede dye aggregation. The DSSCs with ionic liquid electrolytes displayed marked stability over 1000 h. © 2013 Elsevier Ltd. All rights reserved.

Organic materials suitable for application in electronic devices such as organic light-emitting diodes,¹ photovoltaics,² and thin film transistors³ have attracted wide attention in recent years due to the demand for alternate energy resources and energy efficient consumer electronic appliances. In most of these devices, the organic dyes serve as emitters, sensitizers, or charge transporter. So, the synthesis and characterization of organic dyes possessing the above mentioned functional properties are actively pursued.^{1–3} Among the photovoltaic devices, the dye-sensitized solar cells (DSSC or Grätzel cells) demonstrated by Grätzel are considered as a potential alternative as their performance can be fine tuned by architectural alternations and molecular engineering.⁴ In the Grätzel cells, organometallic and organic dyes have been widely used as sensitizers for nanocrystalline TiO₂ semiconductor. Organic dyes possessing donor- π -acceptor configuration have been found to function efficiently in DSSCs.⁵ The following molecular engineering methods have been found to improve the efficiency of the DSSCs: (a) amplification of the electron richness of the donor unit by the introduction of an additional electron donating unit.⁶ (b) Incorporation of electron-rich or low band gap chromophores in the conjugation pathway.⁷ (c) Introduction of auxiliary acceptors in the vicinity of the acceptor end.⁸ All these methodologies were found to be fruitful for the dye molecules which ensured a facile charge migration from the donor to the acceptor via a π -spacer.

Carbazole, a fused aromatic heterocyclic compound, has been widely used in the development of electronic materials due to its excellent hole transporting capability and facile functionalization at various nuclear positions.9 Molecular materials bearing functional chromophores in the C-3, C-6, and N-9 positions of the carbazole have been widely exploited for application in OLED and photovoltaic devices. However, the utility of 2.7-disubstituted carbazole derivatives is limited due to the non-availability of direct methods for chemical modifications at the C-2 and C-7 positions.¹⁰ In this work, we present the synthesis and characterization of two new metal-free organic dyes (Fig. 1) possessing 2,7-carbazolyl bridging unit, diphenylamine donor, and cyanoacrylic acid acceptor. Even though organic dyes containing 2,7-functionalized carbazole in the conjugation have been recently reported, they utilized pyridine as the anchoring group and yielded very low efficiency (1.89%) in the DSSCs.¹¹ The dyes reported in this work showed excellent light-harvesting properties when used as sensitizer in



Figure 1. Structures of the carbazole-based organic dyes.

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DSSCs which illustrate the benefits of the cyanoacrylic acid unit as an efficient acceptor and anchoring segment.

The dyes were synthesized by following a three-step protocol involving Hartwig–Buchwald C–N coupling reaction,¹² Stille reaction¹³, and Knoevenagel¹⁴ condensation (Scheme 1). In the first step diphenylamine was reacted with a slight excess of 2,7-dibro-mo-9-butyl-9*H*-carbazole to obtain 7-bromo-9-butyl-*N*,*N*-diphe-nyl-9*H*-carbazol-2-amine (**2**) in good yield (78%). It was then subjected to the Stille reaction with the tin reagents of the protected aryl aldehydes and subsequent acid hydrolysis generated the required conjugated aldehydes **3a** and **3b**. They were then easily converted to the desired dyes **C1** and **C2** by condensing with cyanoacetic acid in the presence of ammonium acetate in acetic acid. The dyes were thoroughly characterized by NMR and HRMS studies (Electronic Supplementary data).

The absorption and emission spectra of the dyes recorded in dichloromethane solution are displayed in Figure 2 and the pertinent data presented in Table 1. Both the dyes displayed four distinguishable absorption peaks attributable to the carbazole and diphenylamine localized π - π * transitions, electronic excitation between the π - π ^{*} orbitals delocalized over the entire conjugation pathway and amine to cyanoacrylic acid charge transfer transition in that order. The peaks that appeared at around 260 nm and 310 nm are insensitive to the nature of the π -spacer and are similar to those observed for carbazole and diphenylamine localized electronic transitions.¹⁵ The longer wavelength absorptions observed at 357 nm and 473 nm for the dye C1 is red shifted to 375 nm and 489 nm, respectively in C2. They have also displayed increment in molar extinction coefficients attributable to the elongation of conjugation due to the insertion of additional thiophene unit in **C2**. Extension of conjugation by oligothiophene unit has been found to be beneficial to enhance the electron-richness in the con-



Figure 2. Absorption and emission spectra of the dyes recorded in dichloromethane.

jugation pathway and hike the transition probability of the corresponding transitions.¹⁶ It is interesting to note that the absorption wavelengths of these dyes (**C1** and **C2**) are significantly red-shifted when compared to those containing biphenyl,¹⁷ fluorene,¹⁸ or 9,10-dihydrophenanthrene¹⁹ unit substituted for carbazole or dyes with a pyridine acceptor¹¹ in a similar structural composition.

Electronic distributions observed in the frontier molecular orbitals of the dyes and their energies are illustrated in Figure 3. HOMO of the dyes is mainly located on the amine donor unit and spread up to the carbazole and thiophene units. The LUMO of the dyes are contributed by the cyanoacrylic acid and the thiophene units.



Scheme 1. Synthesis of the dyes.

Table 1

Optical and electrochemical data for the dyes^a

Dye	$\lambda_{abs,} nm (\varepsilon_{max} imes 10^3 \text{M}^{-1} \text{cm}^{-1})$	$\lambda_{\rm em}$ (nm)	E_{ox} (ΔE_P), V ^b	E_{ox}^* , V ^c
C1	473 (29.3), 357 (18.0), 311 (16.8), 267 (33.3)	572	0.38 (65), 0.86 (63)	$-1.18 \\ -1.17$
C2	489 (34.3), 375 (23.5), 311 (16.9), 264 (34.6)	579	0.33 (62), 0.71 (73)	

^a Measured in dichloromethane.

^b Oxidation potentials are reported with reference to the ferrocene internal standard and measured at 100 mV/s.

^c E_{ox}^* is the excited state oxidation potential with reference to NHE.



Figure 3. Energy level diagram showing the electronic distributions observed in the frontier orbitals of the dyes along with the redox potentials.

This clearly indicates an efficient charge migration from the donor unit to the acceptor segment on HOMO to LUMO electronic excitation.

For efficient electron injection into the conduction band of the TiO_2 , the excited state oxidation potential of the dyes must be more negative than the conduction band of the TiO_2 .^{4b} The excited-state oxidation potentials (Table 1) of the sensitizers are

Table 2 Performance parameters of the DSSCs fabricated using the dyes C1 and C2

Dye	$J_{\rm sc}$ (mA cm ⁻²)	V _{oc} (mV)	ff	η (%)	$R_{ m rec}$ (Ω)	R_{ct2} (Ω)	τ_{e} (ms)
C1 C2 C2+A ^a C2+B ^b C2+C ^c	15.30 18.10 19.30 18.30 13.60	660 630 628 620 616	0.60 0.60 0.59 0.61 0.65	6.05 6.83 7.20 6.92 5.45	22.50 12.00 	17.55 14.72 13.02 13.77 18.49	12.50 3.12 3.80 3.80 2.09

^a 1 mM CDCA. ^b 10 mM CDCA.

^c 20 mM CDCA.

20 min coch

more negative than the conduction band of the TiO₂ (-0.5 V vs NHE)²¹ which provides the required thermodynamic driving force for the electron injection from the photo-excited dye to the conduction band of TiO₂. Similarly, the oxidized dyes can be effectively regenerated only if their ground state oxidation potentials are more anodic than the redox potential of the redox electrolyte. The oxidation potentials of the dyes (1.15 V for **C1** and 1.10 V for **C2** vs NHE) are larger than the redox potential of the I⁻/I₃⁻ redox couple (0.4 V vs NHE).²⁰ This predicts a facile regeneration of the dyes by the I⁻/I₃⁻ electrolyte after electron injection.^{4b}

DSSCs were fabricated using the dyes as sensitizers, and an electrolyte composed of 0.1 M Lil, 0.6 M 1-propyl-2,3-dimethyl



Figure 4. (a) *I–V* and (b) IPCE (c) Nyquist and (d) Bode phase plots for the devices measured under 100 mW cm⁻² illumination.

imidazolium iodide (DMPII), 0.05 M I₂, and 0.5 M *tert*-butylpyridine (TBP) in a 1:1 solvent mixture of acetonitrile/3-methoxypropionitrile. The device performance data under AM 1.5, 100 mW cm⁻² illumination are compiled in Table 2. The photocurrent–voltage (*I–V*) curves and the incident photon-to-current conversion efficiencies (IPCE) of the DSSCs are plotted in Figure 4. Both the dyes gave impressive power conversion efficiencies (η = 6.01% and 6.83%) in the DSSCs. The superior performance of the device-based on the dye **C2** is originating from the higher short circuit current attributable to the better light absorption characteristics of **C2**. The dye **C2** exhibits highest IPCE at shorter wavelength region and the devices produced superior photon conversion up to 520 nm.

The devices were studied by electrochemical impedance spectroscopy (EIS) to understand the kinetics of electron transfer at the interfaces. The Nyquist and Bode phase plots observed for the devices under illumination are displayed in Figure 4c and d and the relevant data listed in Table 2. The bigger semicircle in the Nyquist plot (Fig. 4c) corresponds to the electron transport resistance (R_{ct2}) and the calculated value is smaller for the device with C2. It further lowered on addition of chenodexoycholic acid (CDCA) up to 10 mM. Smaller R_{ct2} indicates a favorable electron collection at the photoanode which results in a high photocurrent. This is attributable to the thermodynamically more favorable LUMO in **C2** (Fig. 3).^{5b} The electron lifetime extracted from the angular frequency (ω_{\min}) at the mid-frequency peak in the Bode phase plot (Fig. 4d) using $\tau_e = 1/\omega_{min}$ significantly small for the devices fabricated using C2 which suggests faster charge recombination and larger dark current leading to comparatively low open circuit voltage. Slight enhancement in the electron lifetime was observed on the addition of CDCA. It probably indicates that the addition of CDCA inhibits the intermolecular dye association at the surface of TiO₂.²²

Generally, dye aggregation at the surface of TiO₂ reduces the electron lifetime and facilitates charge recombination in the DSSCs fabricated using organometallic or organic dyes.²² To examine the possibility of dye aggregation, DSSCs were fabricated with various amounts of CDCA co-adsorbed photoanodes. The photocurrent density and power conversion efficiency increased on addition of 1 mM CDCA to the dye solution. However, on addition of higher amounts (10 mM or 20 mM) of CDCA to the dye solution reduced the $V_{\rm oc}$ and $I_{\rm sc}$ which led to comparatively low power conversion efficiency than that observed for the dye alone (Table 2). This outcome can be rationalized by the following explanations: (1) pure dye solution leads to aggregation of the dyes on the TiO₂ electrode which causes inefficient electron injection; (2) an optimum amount of CDCA (1 mM) is sufficient to impede the dye aggregation; (3) the high CDCA concentration reduces the adsorbed amount of the dye on TiO₂ films and the ability to harvest light. As a consequence, the highest η value of 7.20% has been obtained when 1 mM CDCA was present in the dye solution.

In order to investigate the durability of the photoanodes sensitized with **C2** or **C2**/CDCA, DSSCs were also fabricated using binary-ionic liquid electrolyte composed of 1-methyl-3-propylimidazolium iodide (PMII) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) (65:35) in 0.2 M I₂ and 0.5 M TBP due to their advantages such as negligible vapor pressure, high thermal stability, wide electrochemical window, and high ionic conductivity.²³ Though these DSSCs based on ionic liquid electrolytes and sensitized with **C2** or **C2**/CDCA showed slightly lower power conversion efficiencies (4.06% and 4.59%, respectively) than the liquid DSSCs, they were found to be stable for long term up to the tested 1000 h (Fig. 5). These results indicate that the photoanodes sensitized with **C2** or **C2**/CDCA can survive for long duration without significant loss in overall conversion efficiency.



Figure 5. Overall efficiencies of the DSSCs with **C2** and with **C2**/CDCA, obtained at different times for 1000 h; the efficiencies were all measured at 100 mW cm⁻².

In summary, we have synthesized new simple organic sensitizers having diphenylamine donor, 2,7-disubstituted carbazolebased π -spacers and cyanoacrylic acid acceptors. They possess an intense absorption with the peak wavelength longer than 470 nm. High performance liquid DSSCs exhibiting power conversion efficiency as much as 7.20% can be achieved using these dyes as sensitizers. This is the first example of the DSSC with highest power conversion efficiency for a carbazole-based organic sensitizer. Photoanodes sensitized with the newly developed metal-free organic dyes have been found to be stable up to 1000 h. This demonstrates the potential use of the carbazole moiety in the construction of efficient and stable DSSCs and warrants more systematic physicochemical exploration of carbazole-based dyes. The dyes developed in this work may serve as promising candidates for co-sensitized solar cells. We are currently working to optimize the molecular structure as well as device parameters to improve DSSC efficiency.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.05. 069.

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