

Molecular Engineering of Carbazole Dyes for Efficient Dye-Sensitized Solar Cells

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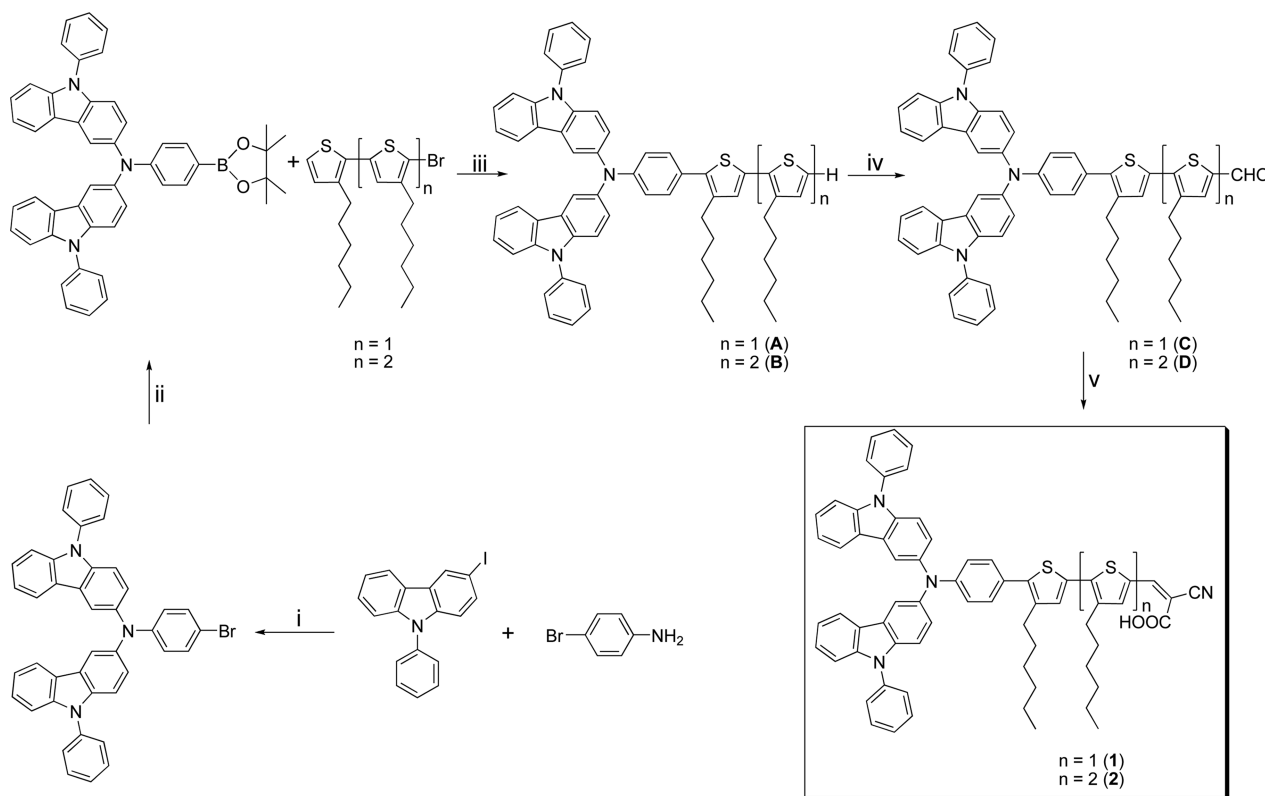
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Organic sensitizers have been recently improved and reached high efficiencies in the range of 8-9% in the performance of dye sensitized solar cells (DSSCs).¹ In particular, carbazole based dyes (MK dyes)² and bis-fluorenylamine based dyes (JK dyes)³ have shown to have high efficiencies and long-term stability in DSSCs performance. Koumura *et al.* has recently reported that the existence of long alkyl chains on the oligothiophene linkage of MK dye molecules can increase the electron lifetime and the open-circuit voltage by suppressing the aggregation of the dyes and electron recombination.⁴ However, for MK dyes, there is a problem to be addressed in terms of relatively low short-circuit current density compared with other efficient organic dyes. The low short-circuit current density (10-14 mAcm⁻²) in MK dyes based DSSCs is originated from weak light harvesting ability

in the long wavelength region (650-750 nm) due to the weak donor ability of carbazole.⁴ While bis-fluorenylamine based JK dyes have shown to have high short-circuit current density (> 14 mAcm⁻²) in DSSCs performance.^{3,5} This high current density can be due to the strong donor ability of amine and absorption in the long wavelength region compared to MK dyes.

Therefore, we envision that the combination of the oligothiophene linkage with long alkyl chains and carbazole-functionalized amine donor in organic dyes will be highly desirable. Moreover, there is no report on the DSSC performance base on this kind of dyes until now.⁶ These facts prompted us to develop new organic dyes containing carbazole and thiophene linker with long alkyl chain. Herein, we describe the results of our investigation on the preparation,



Scheme 1. Reagent and conditions: i) CuI, Cs₂CO₃, Si(OEt)₄, 145 °C, 38 h, reflux. (ii) *n*-BuLi/THF (−78 °C), 1 h; 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (−78 °C); rt, 15 h; 1 M-HCl, 1 h. (iii) Aliquat[®]336, Pd(PPh₃)₄, 2 M-Na₂CO₃, toluene, 48 h. (iv) POCl₃/DMF (0 °C); 80 °C, 5 h; CH₃COONa, RT (v) piperidine, cyanoacetic acid, CH₃CN in toluene, 15 h, (110-120 °C).

photophysical properties, electrochemical behavior, and DSSC performance of two novel dyes.

Result and Discussion

The organic dyes **1** and **2** are readily synthesized in three steps, which are demonstrated in Scheme 1. The Suzuki coupling of bromo-dihexylbithiophene and bromo-trihexylterthiophene with 1.2 equivalents of 9-phenylcarbazolylaminodioxaborolane produced **A** and **B**. The starting materials, **A** and **B**, were converted into their corresponding carbonyl aldehydes and by means of a Vilsmeier-Haack reaction.⁷ The intermediate aldehydes, **C** and **D**, upon reaction with cyanoacetic acid in the presence of piperidine in acetonitrile, produced the **1** and **2** sensitizers. All compounds have good solubility in a variety of organic solvents except hexane and pentane.

Figure 1 shows the absorption and emission spectra of **1** and **2** observed in THF and the absorption spectra of **1** and **2** adsorbed on nanocrystalline TiO₂ film at ambient temperature. The corresponding absorption maxima, extinction coefficients at absorption maxima, and the emission maxima are deposited in Table 1. The UV-vis spectra of **1** and **2** in THF exhibit two intense absorption bands appearing in the region of 230–260 nm and 400–500 nm. Their maximum values (λ_{max}) are observed at 239, 452 nm for **1** and 242, 469 nm for **2**, respectively. The absorption patterns for all compounds are similar to each other, but molar extinction coefficients at absorption maxima vary significantly. The

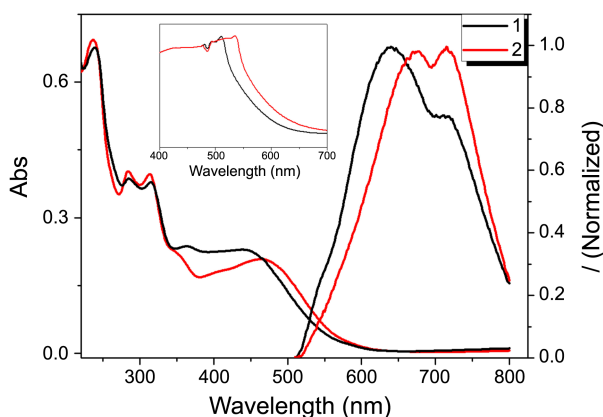


Figure 1. Absorption and emission spectra of **1** (black) and **2** (red) in THF at ambient temperature. Inset: Absorption spectra of **1** and **2** adsorbed on TiO₂ film.

molar extinction coefficient of **2** at 469 nm was 18,000 M⁻¹cm⁻¹, while compound **1** showed 23,000 M⁻¹cm⁻¹ at 452 nm. These values are slightly lower than those ($\epsilon = 30,000$ – $35,000$ M⁻¹cm⁻¹) of **MK-2** (2-cyano-3-[5'''-(9-ethyl-9*H*-carbazol-3-yl)-3',3'',3''',4-tetra-*n*-hexyl-[2,2',5',2'',5'',2''']-quaterthiophenyl-5-yl] acrylic acid)² and **JK-2** ({3,5'-[*N,N*-bis(9,9-dimethylfluorene-2-yl)phenyl]2,2'-bithiophene-5-yl}-2-cyanoacrylic acid).³ As compared to that of standard **N719**⁸ (*cis*-di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxylate) ruthenium(II), $\epsilon = 14,000$ M⁻¹cm⁻¹), however, a relative intense absorption was observed at longer wavelength in our cases. In general, increasing the number of the thiophene units can make the absorption maximum of the sensitizer red shifted as a result of the extended π -conjugation. When **1** and **2** are excited within their π - π^* bands, they exhibit a strong luminescence maximum at around 650 nm with E_{0-0} transition energies of 2.36 and 2.29 eV, respectively.

Molecular-orbital calculations demonstrate that the HOMOs of both **1** and **2** are localized over the phenylcarbazolylamino unit through oligothiophene and the LUMOs are localized over the cyanoacrylic unit through oligothiophene (Figure 2). Theoretical calculations for both compounds support the fact that the HOMO-LUMO excitation moves the electron density from the bis(9-phenyl-carbazol-3-yl)amino unit to the cyanoacrylic acid moiety, thus allowing an efficient photoinduced electron transfer from the dye to the TiO₂

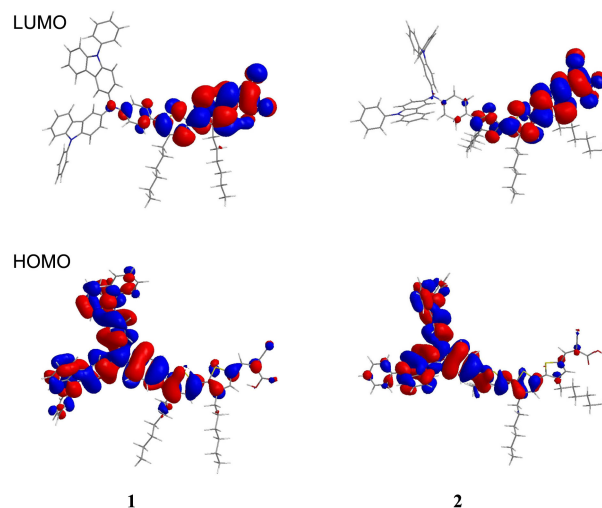


Figure 2. Isodensity surface plots of the HOMO and LUMO1 for **1** and **2** (isodensity contour = 0.03 a.u.); B3LYP/6-31G(d) level.

Table 1. Optical, redox, and DSSC performance parameters of **1** and **2**

Dye	λ_{abs}^a [nm] (ϵ [M ⁻¹ cm ⁻¹], $\times 10^4$)	λ_{em} [nm]	E_{ox}^b [V]	E_{0-0}^c [V]	E_{ox}^{*d} [V]	J_{sc} [mAcm ⁻²]	V_{oc} [V]	ff	η^f [%]
1	239 (6.8), 316(3.8), 452 (2.3)	641	1.32	2.36	-1.04	10.17	0.70	0.75	5.31
2	242 (4.6), 315(2.5), 469 (1.8)	714	1.24	2.29	-1.05	16.04	0.65	0.71	7.43
JK2						14.9	0.72	0.70	7.63

^aThe absorption spectra were measured in THF solution. ^bThe redox potentials of the dyes on TiO₂ were measured in CH₃CN with 0.1 M (N-C₄H₉)₄NPF₆ at a scan rate of 50 mVs⁻¹ (vs. NHE). ^c E_{0-0} was determined from the intersection of the absorption and emission spectra in THF. ^d E_{ox}^{*} was calculated by $E_{\text{ox}} - E_{0-0}$. ^eThe performances of the DSSCs were measured using a working area of 0.18 cm². Electrolyte: 0.6 M DMPImI, 0.05 M I₂, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in CH₃CN.

electrode.

The both **1** and **2** adsorbed on TiO₂ films show a single reversible oxidation at 1.32 V and 1.24 V (*vs* NHE, normal hydrogen electrode), respectively (Figure 3). This reversible redox process can be assigned to the oxidation of 9-phenylcarbazole, as supported by our previous report.^{6,9}

As shown in Table 1, the excited state oxidation potentials (E_{ox}^* , *vs* NHE) of **1** and **2**, which were estimated by the oxidation potentials and the $E_{0,0}$, are -1.05 V and -1.08 V (*vs* NHE) respectively. These values are much more negative than the conduction band edge of TiO₂, which is located at -0.5 V (*vs* NHE), thus providing a thermodynamic driving force for efficient electron injection.¹⁰ In addition, these energies are similar to or more negative than those of **MK-2** (-0.89 V) and **JK-2** (-1.36 V).

The photovoltaic performances of DSSCs employing **1** and **2** under one sun conditions with thin-film TiO₂ electrodes are summarized in Table 1. Compound **1** sensitized cell gave a short circuit photocurrent density (J_{sc}) of 10.17 mA cm⁻², open circuit voltage (V_{oc}) of 0.70 V, and a fill factor of 0.75, corresponding to an overall conversion efficiency η , derived from the equation: $\eta = J_{sc} \cdot V_{oc} / \text{light intensity}$, of 5.31% (Figure 4). However, compound **2** sensitized cell gave a J_{sc} of 16.04 mA cm⁻², V_{oc} of 0.65 V, and a fill factor of 0.71, corresponding to an overall conversion efficiency η of 7.43%. Interestingly, there is a big difference in short circuit photocurrent density (J_{sc}), while the difference of open circuit voltage (V_{oc}) was hardly observed between **1** and **2** based DSSCs. The significant difference for dark current was not observed (see ESI). These results for J_{sc} values can be partially explained by the adsorption amount of the dyes on the TiO₂ film and the extension of π -conjugation through oligothiophene linkage. In general, the relatively low amount of dye adsorbed onto TiO₂ nanoparticles caused the low photo-to-current conversion and the loss of electron in the TiO₂ electrode due to the charge recombination from TiO₂ to I₃⁻.⁴ To confirm these points, however, further investigation is needed.

In summary, we have synthesized a new class of organic dyes featuring oligothiophene with bulky hexyl unit at 3-

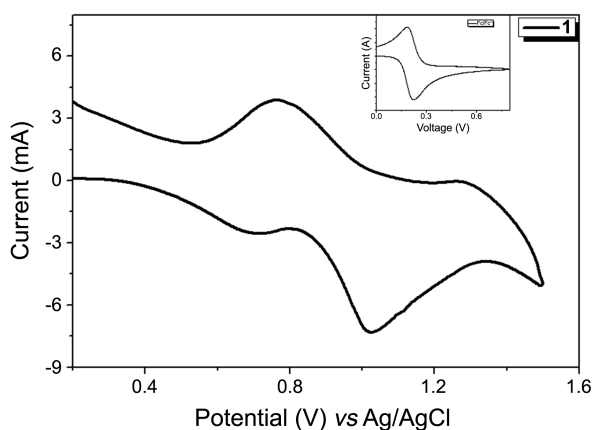


Figure 3. Cyclic voltammetry of **1** attached to a nanocrystalline TiO₂ film deposited on conducting FTO glass. Inset: Fe/Fe⁺.

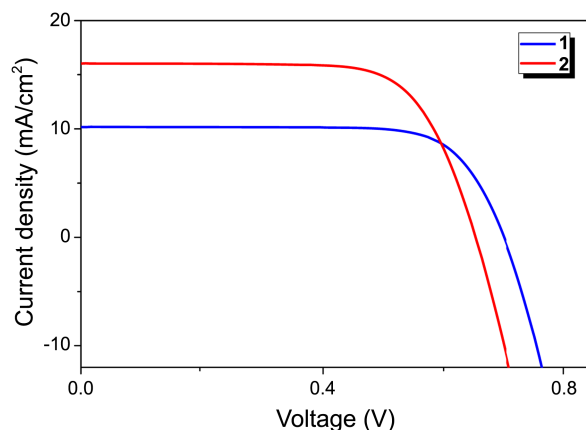


Figure 4. A photocurrent voltage curve obtained with a DSSC based on **1** (blue line) and **2** (red line) and **N-719** (black line) under AM 1.5 radiation.

position as a linker. The performance of DSSC achieved from this new series of dyes is highly efficient. In addition, compound **2**, which has three alkyl-substituted thiophene as a linker between donor and acceptor, exhibits higher conversion efficiency as compared to compound **1** based DSSCs, and the conversion efficiency of which is comparable to that of standard **JK-2** dye. Therefore, it suggests that the development of highly efficient organic alternatives to reference materials can be possible through the more sophisticated structural modifications, and these works are now in progress.

Experimental

Materials and Characterization. The several of 3-hexylthiophen spacers and key starting material were prepared as described in literature.¹¹ The synthetic details of intermediates (**A-D**) are described in supporting information.

General Synthesis of 1 and 2. A mixture of corresponding aldehyde (0.16 mmol), piperidine (0.48 mmol) and cyanoacetic acid (0.32 mmol) was dried under vacuum and MeCN/toluene (20 mL/10 mL) were added. The mixture was refluxed for 15 h (110-120 °C). After cooling the reaction mixture, all volatiles were removed *in vacuo*. The pure products were obtained by column chromatography (silica) in 82-93% yield.

5'-{4-(*N,N*-Bis[9-phenyl-9*H*-carbazol-3-yl]phenyl)-3,4'-di-*n*-hexyl-[2,2']-bithiophenyl-5-cyanoacrylic Acid (1**):** Eluent:EtOH/CHCl₃ = 1/4 (v/v), R_f = 0.2) Yield: 93%. ¹H-NMR (CDCl₃, 300 MHz) δ 8.23 (d, J = 5.32 Hz, 2H), 7.72-7.64 (m, 4H), 7.58-7.52 (m, 2H), 7.46-7.22 (m, 6H), 7.18 (s, 1H), 6.94-6.91 (d, J = 8.72 Hz, 1H), 2.78-2.62 (dt, J = 26.76 Hz, J = 8.49 Hz, 4H), 1.60-1.55 (m, 4H), 1.36-1.11 (12H, m), 0.94-0.82 (6H, m). ¹³C-NMR (DMSO-*d*₆, 100 MHz) δ 163.2, 150.3, 149.6, 143.5, 143.0, 141.0, 140.9, 140.4, 139.9, 139.6, 138.8, 138.4, 137.8, 137.7, 137.1, 133.5, 131.4, 130.5, 130.2, 129.7, 129.6, 129.0, 128.0, 127.0, 126.8, 126.0, 124.2, 124.1, 124.0, 123.9, 122.8, 121.1, 120.3, 118.7, 118.5, 118.3, 118.1, 111.2, 110.8, 60.3, 40.5, 40.3, 40.1, 39.9, 39.7, 39.4, 39.2, 33.2, 31.6, 31.3, 30.5, 29.9,

29.4, 28.9, 28.8, 28.7, 28.5, 28.4, 26.4, 25.1, 22.5, 22.4, 22.3, 22.0, 21.1, 14.2. Mass (*m/z*): 1102.39. Anal. Calcd for C₆₆H₅₈N₄O₂S₂: C, 79.01; H, 5.83; N, 5.58; found: C 79.11, H 5.59, N 5.49.

5''-{4-(*N,N*-Bis[9-phenyl-9*H*-carbazol-3-yl]phenyl)-3,4',4''-tri-*n*-hexyl-[2,2',5',2'']-terthiophenyl-5-cyano-acrylic Acid (2): Eluent:EtOH/CHCl₃ = 1/4 (v/v), *R_f* = 0.1) Yield: 82%. ¹H-NMR (CDCl₃, 300 MHz) δ 8.27-8.24 (d, *J* = 7.21 Hz, 4H), 8.11 (m, 1H) 7.77-7.69 (m, 12H), 7.62-7.57 (m, 2H), 7.51-7.40 (m, 8H), 7.36-7.27 (m, 5H), 7.20 (s, 1H), 6.99-6.97 (d, *J* = 8.65 Hz, 2H), 2.82-2.78 (m, 6H), 1.68-1.65 (m, 6H), 1.47-1.11 (m, 18H), 0.90-0.81 (m, 9H) ¹³C-NMR (DMSO-*d*₆, 150 MHz) δ 170.3, 170.2, 170.1, 167.4, 163.7, 163.6, 163.5, 149.6, 141.5, 141.1, 140.5, 140.2, 138.7, 138.6, 137.9, 137.2, 133.9, 132.7, 132.2, 132.0, 131.9, 131.7, 130.9, 130.7, 129.9, 129.4, 129.1, 129.0, 128.2, 127.1, 127.0, 126.1, 124.4, 124.3, 122.9, 121.3, 120.5, 118.9, 118.6, 118.0, 124.3, 124.0, 122.9, 121.3, 120.5, 118.9, 118.6, 117.9, 111.4, 110.1, 79.6, 69.8, 66.1, 65.8, 34.1, 33.0, 32.3, 31.7, 31.4, 30.6, 30.3, 29.9, 29.4, 29.3, 29.1, 29.0, 28.9, 28.6, 27.4, 22.9, 22.5, 21.2, 19.8, 19.4, 16.7, 14.4, 12.5. Mass (*m/z*): 1168.46. Anal. Calcd for C₇₆H₇₂N₄O₂S₃: C, 78.04; H, 6.20; N, 4.79; found: C, 78.28; H, 6.18; N, 4.73.

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Supporting Information. Synthetic details of key starting materials; NMR, Mass and dark current data.

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