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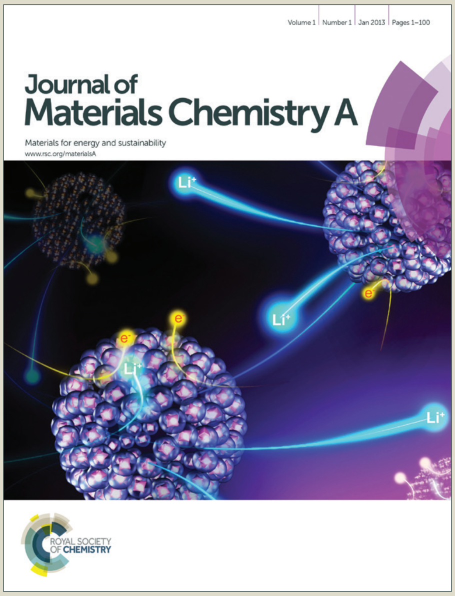

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ARTICLE

# Improved Molecular Architecture of D-π-A Carbazole Dyes : 9% PCE with Cobalt Redox Shuttle in Dye Sensitized Solar Cells

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Saurabh S. Soni,[*a] Kishan B. Fadadu,[a] Jayraj V. Vaghasiya,[a] Bharat G. Solanki,[a] Keval K. Sonigara,[a] Ashish Singh,[b] Dipjyoti Das[b] and Parameswar K. Iyer[*,b, c]

Two new D-π-A dyes (SK2 & SK3) based on carbazole, vinylene-phenylene (π-bridged) with rhodanine-3-acetic acid and cyanoacrylic acid as an electron withdrawing-injecting as well as anchoring groups were designed and synthesised in conditions that were free from precious metal-catalysts and well characterized for dye-sensitized solar cell (DSSC) applications. High power conversion efficiency of 9 % (AM 1.5G, 100 mW.cm$^{-2}$) has been achieved using cyanoacrylic acid as acceptor in D-π-A carbazole dye (SK3) with cobalt based redox shuttle, while PCE of 7.1 % were exhibited in triiodide based redox mediator. A short-circuit current density, $J_{sc}$ of ~18.2 mA.cm$^{-2}$, an open-circuit voltage, $V_{oc}$ of ~725 mV, and a fill factor, FF of ~67 % have been afforded by the SK3 based DSSC incorporating $Co^{2+}/Co^{3+}$ electrolyte as the one-electron redox mediator. In contrast, SK2 dye based DSSC with cobalt based redox mediator has shown a $J_{sc} \approx 8.4$ mA.cm$^{-2}$, a $V_{oc} \approx 587$ mV, and a FF ≈ 48%, yielding a PCE of 2.4%. The devices based on SK3 showed outstanding stability performance without significant degradation even after 1000 h of illumination under standard conditions in $Co^{2+}/Co^{3+}$ electrolyte.

## Introduction

Organic solar cells have attracted considerable attention over the past decades because of their unique advantages. Especially, after the pioneering work by O'Regan and Grätzel,[1] Dye Sensitized Solar Cells (DSSCs) have received considerable attention as an alternative to conventional silicon solar cells. Till date, the power conversion efficiency (PCE) of ~12% have been achieved using the ruthenium (Ru) based dyes with cobalt complex as a redox mediator.[2-5] However, the relatively high cost and environmental concerns associated with the use of Ru-dyes have prompted researchers to develop Ru-free organic dyes which are highly economical, easier to process and could be modified or functionalized as desired as an alternative choice of photosensitizer.[6-9] In particular, the design and development of donor-acceptor π-conjugated (D-π-A) dyes with both electron donating (D) and electron-accepting (A) groups linked by π-conjugated bridges, which possess high molar extinction coefficients, are expected to be one of the most promising organic sensitizers.[10-18]

Due to the excellent hole transporting and facile functionalization possibilities at various positions, carbazole, a fused aromatic heterocyclic molecule has been widely used as a donor in D-π-A sensitizer architecture for DSSC applications. The substituted carbazole dyes with pyridine as the anchoring group were used in DSSC[17,18] but yielded poor PCE (~1.9%) which implies that pyridine is not acting as good anchoring group. Among other D-π-A carbazole based DSSCs reported so far, thiophene derivatives as a bridge shows PCE of 6-10%.[19-28] Wang et al. reported ~8% PCE with a series of $(C_2H_5)_3NH^+$ salts of carbazole based D-π-A sensitizers, functionalized by hexyl substituted oligothiophene moiety as a π-conjugated system.[21] The PCE around 9 % has been reported for the device with dye containing triphenyl amine as donor, phenylene-vinylene bridge and cyanoacetic acid as acceptor, however, this molecule was synthesized using Pd-metal assisted synthetic route.[29] In the formal case, introduction of thiophene derivatives usually required complicated synthetic strategies with the use of metal assisted coupling reactions route which enhance the production cost of dye and have an adverse environmental impact that hamper the commercialization of DSSC technology. To overcome the use of metal catalyzed reactions and promote the practical application of Ru-free D-π-A carbazole dyes as a sensitizer in DSSC technology and extend their utility beyond the laboratory, it is highly desirable to have a metal-free synthetic route and at the same time retain the high efficiency of charge separation and collection. In view of this, a bulky tolyl substituted carbazole dye as synthesized using metal free route shows PCE of ~5% using 1-D ZnO nanowires and nanoparticles with $[Co\text{-}(bpy)_3]^{3+/2+}$ complex as the one-electron redox mediator was reported.[30] It has been reported recently that Co-polypyridyl redox mediators are potential competitors of the triiodide based redox mediators

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[a] Department of Chemistry, SardarPatel University, VallabhVidyanagar – 388 120, Gujarat, INDIA
[b] Center for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, INDIA
[c] Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, INDIA.

† Footnotes relating to the title and/or authors should appear here.

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as an electrolyte.[31] Redox potential of the cobalt polypyridyl complex is reported to be 0.56 V which is 150 mV higher than that of iodine based electrolyte and this yields the enhanced photovoltage.[31]

With these multiple motives to have Ru-free and thiophene free dye architecture as well as a metal-catalyst free synthetic route to prepare the dyes, we have designed and synthesized efficient D-π-A carbazole dyes using facile metal free synthetic route. We report two D-π-A carbazole dyes, SK2 and SK3, with rhodanine-3-acetic acid and cyanoacrylic acid molecules as an electron withdrawing-injecting as well as anchoring group respectively, and a vinylene-phenylene unit as a π-bridge. Among these two carbazole dyes, SK3 with cobalt based redox mediator shows excellent photon to power conversion efficiency (9%) high IPCE of 84% along with superior stability.

## Experimental Section

### Materials

Carbazole, NaH, 1-hexyl bromide, $NaBH_4$, triphenyl phosphine hydrobromide, cyano acetic acid, LiI, $I_2$, 4-tert-butyl pyridine, Guanidiniumthiocynate, 3-methoxy propionitrile and rhodanine-3-acetic acid, $CoCl_2·6H_2O$ and 2,2'-bipyridyl were purchased from the Sigma-Aldrich and used without further purification. $POCl_3$, Na metal, piperidine and terphthalaldehyde were purchased from Spectrochem, India. Solvents used for cyclic voltammetry were purified by following standard protocol and stored under 4A molecular sieves. TCO substrates (7Ω/cm$^2$), N719 dye and hot melt tape were purchased from Solaronix Inc. Switzerland.

### Methods

### 1. Fabrication of dye solar cell

DSSCs were fabricated using sandwich type configuration of photoelectrode and counter electrode.[1] A transparent layer of $TiO_2$ with thickness 8 μm, as measured by a profilometer (Veeco Dektak 150 Stylus surface profiler), was used as photoelectrode. This electrode was immersed overnight in ethanol solution containing 3mM organic sensitizer. A platinised FTO was used as a counter electrode. The electrolyte consists of 0.2 M $[Co(bpy)_3]^{2+}$, 0.02 M $[Co(bpy)_3]^{3+}$, 0.1 M $LiClO_4$, and 0.5 M 4-*tert*-butylpyridine in acetonitrile. The $I^{3-}$ /$I^-$ electrolyte composed of 0.5 M Lithium iodide (LiI), 0.05 M Iodine ($I_2$), 0.5 M *tert*-butyl pyridine (TBP), 0.5 M guanidiumthiocynate in 3-methoxy propionitrile. Electrolyte was inserted through the predrilled holes onto the counter electrode. Holes were sealed using epoxy adhesive and the DSSCs were stored in dark at room temperature for 12 h prior to measurements. Active areas of the DSSCs were set to 0.16 cm$^2$ and were maintained constant using the same screen for coating.

### 2. Characterizations

NMR spectra were recorded using Bruker 400 MHz NMR instrument. Elemental analysis was done using EA-3000, Euro Vector Instrument (Italy). Electrochemical Impedance spectroscopy (EIS) measurements were carried out using Solartron 1260+1287 interfaces and data were analyzed using CorrView and Zplot software (Scribner's Associates Inc.). Impedance data were collected by sweeping frequency from 120 kHz to 0.1 Hz having AC amplitude 10 mV. UV-vis spectra were recorded using UV-vis spectrophotometer from Shimadzu, Japan. Cyclic Voltammetry (CV) was recorded using Solartron electrochemical analyzer using three electrode systems in acetonitrile/$TBAPF_6$. The photocurrent density-voltage (J-V) characteristics of the fabricated DSSCs were measured using Keithley-2400 digital source meter controlled by a computer scan rate, 10 mV.s$^{-1}$. An Oriel 500 W xenon lamp, connected with an AM 1.5 Globe filter (Newport, Oriel Sol3A) to remove ultraviolet and infrared radiation, served as the light source, to give 100 mW.cm$^{-2}$ at the surface of the test cell. The incident photon-to-current conversion efficiency (IPCE) of the devices was recorded using Newport Oriel IQE-200, where a 250 W quartz tungsten halogen (QTH) lamp was used as the light source.

### 3. Synthesis of Cobalt based redox electrolyte

Co-polypyridyl complex was synthesized according to the published literature procedure.[32,33] The cobalt(II) and cobalt(III) metal complexes with 2,2'-bipyridyl (bpy) ligand were synthesized by following the protocol reported earlier by Liu et al.[33] For the typical synthesis of $[Co(bpy)_3](PF_6)_2$, $CoCl_2·6H_2O$ (0.25 g) was dissolved in 5.0 mL of distilled water. A solution of 2,2'-bipyridyl (0.55 g) in methanol was then slowly (dropwise) added to the aqueous solution of cobalt under magnetic stirring. The reaction mixture was allowed to stir for another 10 min. An aqueous solution of $NH_4PF_6$ (1.02 g) was then added to precipitate the Co(II) complex. The solid product was filtered, washed with water, and dried in a vacuum to isolate the $[Co(bpy)_3](PF_6)_2$ solid. The complex $[Co(bpy)_3](PF_6)_3$ was synthesized via slight modification of the above procedure. $CoCl_2·6H_2O$ (0.25 g) was dissolved in 5.0 mL of distilled water, followed by the dropwise addition of methanolic solution of 2,2'-bipyridyl (0.55 g) under magnetic stirring. After 10 min of stirring, an equivalent molar concentration of $Br_2$ solution in methanol was added slowly, and the reaction mixture was allowed to stir for 10 min. An orange colored precipitate appeared which was then discarded by filtering the reaction mixture to get a clear solution. The solvent was evaporated by distillation under reduced pressure, and the residue was dissolved inmethanol (15.0 mL). Finally, an aqueous solution of $NH_4PF_6$ (1.02 g) was added under magnetic stirring to precipitate out the Co(III) complex. The product was filtered, washed with water, and dried in a vacuum to yield the $[Co(bpy)_3](PF_6)_3$ solid.

### 4. Synthesis of carbazole dyes

### 9-hexyl carbazole (1)

To a 100 mL round flask were added Carbazole (2.0 g, 11.96 mmol) and 1-hexyl bromide (1.7 mL, 12.5 mmol) in DMF,

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followed by NaH (0.3 g, 12.5 mmol). This reaction mass was refluxed for 3h, cooled and added in ice cold water to give light yellow color solid material and filtered. Product was further purified by column chromatography on a silica gel column using hexane and ethyl acetate as eluent [9:1 by vol.], to give white yellow product (2.88 gm, 96%), $^1$H NMR (400 MHz, $CD_3COCD_3$): δ= 0.85 (m, J = 6.8 Hz, 3H), 1.15-1.5 (m, 6H), 1.8-1.9 (m, 2H), 4.45(t, J =6.8 Hz ), 7.2 (m, 2H), 7.35-7.65 (m, 4H), 8.1-8.2 (d, J = 8.8, 2H). Elemental analysis calcd. for $C_{18}H_{21}N$, C (86.05), H (8.47), N (5.55); found C (86.01), H (8.44), N (5.57).

### 9-Hexyl-3-formyle carbazole (2)

The above compound 1 (1.5 g, 5.96 mmol) was subjected to Vilsmeier-Hack procedure using $POCl_3$ (0.55 mL, 6.16 mmol)/DMF (0.47 mL, 6.16 mmol) for formylation. After formylation light yellow oily product was obtained. The products were extracted with chloroform and purified by column chromatography on a silica gel column using petroleum ether and dichloromethane as eluent [4:1 by vol.],to give a faint yellow solid product (1.45 g, 87%). $^1$H NMR (400 MHz, $CD_3COCD_3$): δ = 0.85 (t, J = 7.2 Hz, 3H), 1.2-1.5 (m, 6H), 2.0 (m, 2H), 4.55 (t, J = 4.0 Hz, 2H), 7.35-7.55 (m, 2H), 7.6-7.8 (dd, J = 8.0 Hz, 2H,), 8.0 (m,1H), 8.3 (m, 1H), 8.75 (m, 1H), 10.1 (s, 1H). Elemental analysis calcd. for $C_{19}H_{21}NO$, C (81.66), H (7.61), N (5.04), O (5.70); found C (81.68), H (7.59), N (5.01), O (5.73).

### 9-hexyl-9H-carbazol-3-yl) methanol (3)

The above product 2 (1.3 g, 4.6 mmol) was converted into corresponding alcohol using sodium borohydride (0.176 g, 4.8 mmol) in THF at room temperature to give 9-hexyl-3-hydroxy methyl carbazole. The product was extracted with dichloromethane and purified by column chromatography on a silica gel column using hexane and ethyl acetate as eluent [4:1 by vol.], (1.23 g, 94%). $^1$H NMR (400 MHz, $CD_3COCD_3$): δ = 0.8 (t, J = 7.2 Hz, 3H), 1.2-1.5 (m, 6H), 1.9 (t, J = 7.2 Hz, 2H), 4.1 (s, 1H), 4.45 (t, J = 7.2 Hz, 2H), 4.8 (d, J = 4.0 Hz2H), 7.2 (m, 1H), 7.4-7.65 (m, 4H), 8.15 (m, 2H). Elemental analysis calcd. for $C_{19}H_{23}NO$, C (81.11), H (8.23), N (4.99), O (5.68); found C (81.09), H (8.25), N (4.97), O (5.69).

### ((9-hexyl-9H-carbazol-3-yl) methyl) triphenylphosphonium bromide (4)

The synthesized compound 3 (1.2 g, 4.26 mmol) dissolved in dichloromethane followed by addition of triphenyl phosphine hydrobrimide (1.51g, 4.4 mmol) and reaction mass was stirred at 40◦C for 18 h. After completion of reaction, solvent was evaporated to dryness. Paste like mass was treated with excess diethyl ether to yield white colored solid powder (1.57 g, 75%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.8Hz, 3H), 1.3 (m, 4H), 1.8 (m, 4H), 4.2 (t, J = 7.6 Hz, 2H), 5.45 (d, 13.2 Hz, 2H), 7.05 (t, 7.2 Hz, 2H), 7.3-7.4 (dd, J = 1.6 Hz, 2H), 7.45 (t, 1H), 7.6 (s, 1H), 7.65 (m, 6H), 7.75 (m, 10H). Elemental analysis calcd. for $C_{37}H_{37}NBrP$, C (73.23), H (6.18), N (2.30), P (5.11), Br (13.18); found C (73.25), H (6.14), N (2.32), P (5.11), Br (13.17).

### 4-(2-(9-hexyl-9H-carbazol-3-yl)vinyl)benzaldehyde (5)

This above salt 4 (0.8 g, 1.35 mmol) was dissolved in ethanol along with terphthaldehyde (0.81 g, 1.35 mmol) and was stirred at 5◦C followed by sodium ethoxide solution using Na metal (0.3 g, 13.04 mmol) and ethanol (4.94 mL) and stirred for 2 h. This reaction mass was poured in cold water followed by extraction using chloroform. Solvent was removed under vacuum and residues were dissolved in THF in presence of catalytic amount of iodine.[34] This was refluxed for 8 h. in dark and poured into cold solution of 0.1N NaOH followed by extraction using dichloromethane. Solvent was removed under vacuum and residues were purified by column chromatography using hexane and ethyl acetate (1:1 by vol.), (0.247 g, 49%). $^1$H NMR (400 MHz, $CDCl_3$): δ 0.9 (t, J = 6.8 Hz, 3H), 1.35 (m, 6H), 1.6 (s, 1H), 1.9 (2H, m), 4.36 (d, J = 6 Hz, 2H), 7.2 (d, J = 16 Hz, 1H), 7.35 (d, J = 7.6 Hz 1H), 7.35-7.5 (m, 4H), 7.65 ( m, 2H), 7.85 (d, 1H), 8.19 (d, J = 6.8 Hz, 1H), 8.25 (s, 1H), 10.0 (s, 1H). Elemental analysis calcd. for $C_{27}H_{27}NO$, C (85.04), H (7.10), N (3.66), O (4.19); found C (85.01), H (7.11), N (3.66), O (4.19).

### 2-(-5-(4-(-2-(9-hexyl-9H-carbazol-3-yl)vinyl)benzylidene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid (SK2) and 2-cyano-3-(4-((E)-2-(9-hexyl-9H-carbazol-3-yl)vinyl)phenyl)acrylic acid (SK3)

The above aldehyde 5 (0.2 g, 0.52 mmol) was condensed separately with cyano acetic acid (0.088 g, 1.04 mmol) and rhodanine-3-acetic acid (0.198 g, 1.04 mmol) in acetonitrile in presence catalytic amount of piperidine. The orange colored solid was separated out, filtered and dried under vacuum and the products were purified by silica gel column chromatography using dichloromethane and methanol as eluent [9:1 by vol.], to give orange powder SK2 (0.209 g, 72%) and SK3(0.173 g, 74%).

$^1$H NMR (400 MHz, $CDCl_3$) SK2: δ 0.9 (t, J = 4.8 Hz, 3H), 1.32-1.58 (m, 6H), 1.8-1.9 (m, 2H), 4.3 (d, J =7.2 Hz, 2H), 4.5-4.6 (s, 2H), 7.18 (d, J = 17.2 Hz, 1H), 7.3 (d, J = 12.4 Hz, 1H), 7.35-7.45 (m, 2H), 7.45-7.5 (m, 3H), 7.6-7.8 (m, 3H), 7.9-8.1 (m, 2H), 8.15-8.25 (m, 1H), 8.35 (s, 1H). Elemental analysis calcd. for $C_{32}H_{30}N_2O_3S_2$(SK2): C (69.25), H (5.50), N (5.00), O (8.74), S (11.52) found C (69.28), H (5.46), N (5.04), O (8.62), S (11.56). $^{13}$C NMR (DMSO δ / ppm):153.4, 118.0 , 152.9, 152.0, 62.2, 120.0, 40.14, 120.0, 128.6, 128.7, 128.7, 132.0, 132.0, 133.24, 118.3, 131.40, 131.50, 131.98, 118.3, 128.3 , 62.02, 153.4, 51.2, 51.7, 120.0, 39.52 , 39.10, 30.92, 26.09, 39.93, 21.9, 13.47.MS, m/z: calcd. for $C_{32}H_{30}N_2O_3S_2$: 554.72, found: 555.46($M^+$).

$^1$H NMR (400 MHz, DMSO),) SK3: δ $^1$H NMR (400 MHz, DMSO),) SK3: δ 0.81 (t, J = 11.2 Hz, 3H), 1.3 (m, 6H), 1.65-1.78 (m, 2H), 4.36 (t, J = 4.8 Hz, 2H), 6.8 (s, 1H), 6.9 (d, J = 12.4 Hz, 1H), 7.35-7.7 (m, 2H), 7.30-7.65 (m, 4H), 7.81-8.46 (m, 6H). Elemental analysis calcd. for $C_{30}H_{28}N_2O_2$(SK3): C (80.30), H (6.25), N (6.30), O (7.16); found C (80.32), H (6.28), N (6.24), O (7.12).$^{13}$C NMR (DMSO δ / ppm): 162.5, 65.94, 128.66, 128.5, 39.92, 39.72, 120.06, 40.13, 131.90, 135.10, 132.01, 119.4, 130.30, 128.76, 128.6, 120.1, 117.05, 131.40, 151.86, 77.75, 77.37, 128.66, 39.30, 152.49, 86.32, 28.47, 26.09, 22.31, 22.20, 14.1. MS, m/z: calcd. for $C_{30}H_{28}N_2O_2$ 447.95, found: 448.5($M^+$)

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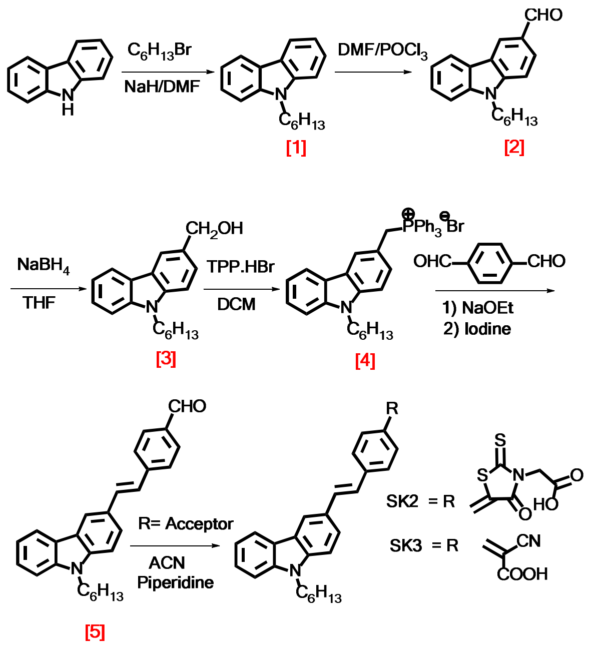
## Results and discussion

### Synthesis of the dyes

The main synthetic pathways along with the structure of new carbazole dyes, SK2 and SK3 are depicted in Scheme 1. The convergent synthetic strategy for SK2 and SK3 relies on two simple building blocks, viz. hexyl substituted carbazole (1) and terphthaldehyde (as a spacer).



**Scheme 1** Synthesis and structure of SK2 and SK3 dyes

Additionally, introduction of a linear hexyl chain to donor component enhances the solubility as well as avoids dye aggregation. The corresponding intermediate aldehyde (2) was synthesized via Vilsmeier-Hack reaction followed by reduction, which was subsequently coupled with terphthaldehyde via economical and facile Wittig phosphonium salt route and treatment of iodine to achieve maximum E-type product.[34] The resultant product is condensed with rhodanine-3-acetic acid or cyanoacetic acid by a Knoevenagel condensation which resulted into SK2 or SK3 dyes. The preparation of these two D-π-A carbazole dyes with vinylene-phenylene bridge was accomplished by metal free low cost route, enabling the development of these dyes in bulk quantity for practical production and large scale DSSC application.

### Optical and Electrochemical properties

The optical properties of SK2 and SK3 dyes were investigated by UV-Vis spectroscopy in ethanol solution (Fig. 1a) and their spectral data are summarized in Table 1. The SK2 and SK3 dyes show strong absorption bands at ~460 nm and ~435 nm respectively, which are assigned to the π-π* electron transition. These absorption bands are quite comparable with those reported with efficient hexyl thiophene bridged carbazole dyes.[21] These bands, however appeared at shorter wavelength with respect to that of N719 but the measured molar extinction coefficients, ε = 34109 $M^{-1}cm^{-1}$ (for SK2) and ε = 34166 $M^{-1}cm^{-1}$ (for SK3) are twofold higher than the values of N719 (14400$M^{-1}$ $cm^{-1}$).[35] The absorption peaks are red-shifted and broadened in case of dyes on titania surface (Fig. 1(b)) compared with those in solvent (ethanol). This might be due to the interaction of the anchoring group with the surface of titanium ion, which enhances the conjugation and results in the decrease of the energy level of the π*-orbital of dyes. These characteristics of interaction enhances the light harvesting capacity of dyes, resulting in higher PCEs.[36,37] The large red-shift for SK3 (~60nm) confirmed a stronger acceptor ability and better intra-molecular charge transfer compared to SK2 (~10 nm).

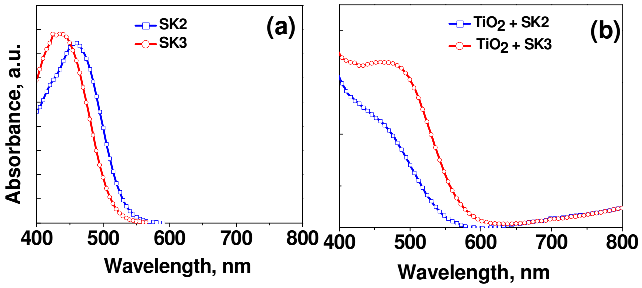


**Fig. 1** Absorption spectra of SK2 and SK3 (a) in ethanol and (b) on $TiO_2$ film

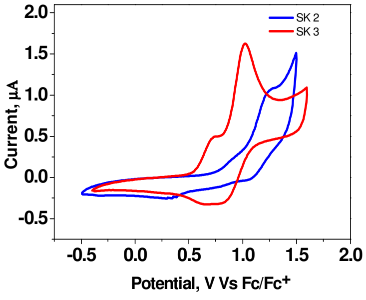


**Fig. 2** CV of SK2 and SK3 in acetonitrile at a scan rate of 25 mV $s^{-1}$

The electrochemical properties of these two dyes were determined using cyclic voltammetry (CV, Fig. 2 and Table 1) with the aim to obtain the energy level position of the frontier orbitals. Under the application of positive potential, CV showed two quasi reversible oxidation waves which correspond to an oxidation-reduction process. These two peaks observed at 0.85 V and 1.25 V for SK2 (0.75 V and 1.00 V for SK3) versus ferrocene/ferrocenium ($Fc/Fc^+$) are attributed to the oxidation of π-conjugated backbone and carbazole donor respectively. The well defined first oxidation peak for SK3 compared to SK2, confirms better charge transfer between D-π-A in case of cynoacrylic acid compared to the rhodanine-3-acetic acid. The HOMO and LUMO energy levels of these two dyes were determined from the spectral analysis and CV data which are summarized in **Table 1**. We have also

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recorded CV of the cobalt based redox shuttle in order to find out the electrochemical potentials and energy level of the same (ESI Fig. S1).

The HOMO energy levels of SK2 and SK3 are 1.41 and 1.15 V Vs NHE (Normal hydrogen electrode). These values are larger than the redox potential of $I^-/I_3^-$ redox couple (0.4V Vs NHE) of electrolyte. This ensures a facile regeneration of the dyes by the $I^-/I_3^-$ electrolyte after electron injection. The LUMO energy level of SK2 and SK3 are -0.75 and -1.09 V Vs NHE respectively. As evident, these LUMO levels are higher than the conduction band of $TiO_2$ (-0.5V Vs NHE), which ensures that the two dyes can inject electrons to the $TiO_2$ conduction band. Therefore, it is safe to conclude that the red-shifted band observed for SK2 relative to SK3 is attributed to the destabilization of HOMO level and stabilization of the LUMO level on replacement of rhodanine-3-acetic acid with cynoacrylic acid resulting in increase in the band gap. Redox potential of the cobalt based redox shuttle was estimated by CV measurements and found to be 0.5 V which is almost 100 mV higher than that of iodide/triiodide couple. In DSSC, $V_{oc}$ is originated from the energy level difference between $TiO_2$ fermi level and redox potential of electrolyte. Hence, theoretically it is confirmed that the voltage output of the cobalt based redox couple in DSSC will be higher than that of iodine based electrolyte.

Table 1 Optical and electrochemical of SK2 and SK3 dyes

| Dye | $\lambda_{obs}$ [a] (nm) | $\varepsilon$ [a] ($M^{-1}cm^{-1}$) | $E_g$ [b] (eV) | $E°_{onset}$ [c] Vs $Fc/Fc^+$ (V) | HOMO [c] (V) | LUMO [d] (V) |
|---|---|---|---|---|---|---|
| SK2 | 460 | 34109 | 2.17 | 0.788 | 1.41 | -0.75 |
| SK3 | 435 | 34160 | 2.25 | 0.525 | 1.15 | -1.09 |

[a] Measured in ethanol, [b] measured from $\lambda_{onset}$, [c] All potentials were obtained from CV. Potential measured vs. $Fc/Fc^+$ were converted to NHE by addition of +0.63 V (Ref.39). [d] calculated from LUMO = HOMO – $E_g$

### Photovoltaic Characterization

The photocurrent density-voltage (J-V) characteristics of DSSCs sensitized with SK2 and SK3 on 8 µM $TiO_2$ films (without scattering layer) with different redox mediators are shown in Fig. 3 and photovoltaic parameters are depicted in Table 2. SK2I, SK3I, SK2C and SK3C stands for the SK2 dye + Iodine based mediator, SK3 dye + Iodine based mediator, SK2 dye + cobalt based mediator and SK3 dye + cobalt based mediator respectively.In the typical SK3 based device, a short-circuit current density, $J_{sc}$ of 17.2 mA/cm$^2$, an open-circuit voltage, $V_{oc}$ of 645 mV, and a fill factor, FF of 65% affording an overall PCE of 7.1% has been achieved by employing $I^-/I_3^-$ redox electrolyte. The similar device with $[Co(bpy)_3]^{III/II}$ electrolyte exhibited a $J_{sc}$ of 18.3 mA/cm$^2$, $V_{oc}$ of 725 mV, and a FF of 67%, resulting in a PCE of 9.0%. As mentioned, $V_{oc}$ has been remarkably increased by ~80 mV upon the employment of the cobalt-based redox shuttle over the iodide system. Similar trends are also observed in the performance of the DSSC fabricated with SK2 dye. The performance of SK3 based device is quite comparable with similar kind of D-π-A dye, where triphenyl amine has been used instead of carbazole as a donor.[29] However, these dyes were synthesized using Pd-catalyzed route. Moreover, the SK3 based DSSC possessing n-hexyl chain on $TiO_2$ outperformed the tolyl substituted carbazole dye (SK1) on ZnO due to the higher bulkiness of p-tolyl compared to n-hexyl which likely disrupts the packing.[30] The enhanced adsorption of SK3 over SK1 due to its higher solubility and the lower photostabiity of ZnO as compared to $TiO_2$ in the presence of anchoring carboxylic group could possibly be further reasons for higher PCE in SK3. The obtained 9.0 % PCE value for D-π-A carbazole dye (SK3) and Co-polypyridyl complex based redox couple is comparable with the best reported DSSC devices using both metal and thiophene (sulfur) free dyes, thereby enabling access to new dye architecture with economical synthesis and fabrication.[6,7] The reason for lower $J_{sc}$ with SK2 may be assigned to the poor charge injection capacity of this dye (-0.75 V) to the CB of $TiO_2$ (-0.50 V) (see Fig. 4). The IPCE of SK2 and SK3 dyes in DSSCs are shown in Fig. 3(b). SK3 gives higher IPCE value than the SK2 dye, with the highest value of 84% obtained at ~500 nm with cobalt redox shuttle. The higher IPCE value of SK3 dyes indicates that cynoacrylic acid is a very good acceptor or anchoring group in comparison to rhodanine-3-acetic acid. It is also important to note that the SK3 dye with a simple vinylene-phenylene bridge architecture and cyanoacrylic acid as an acceptor gives remarkable solar cell performance than other carbazole dyes where multiple thiophene derivatives were used as a bridge.[38]

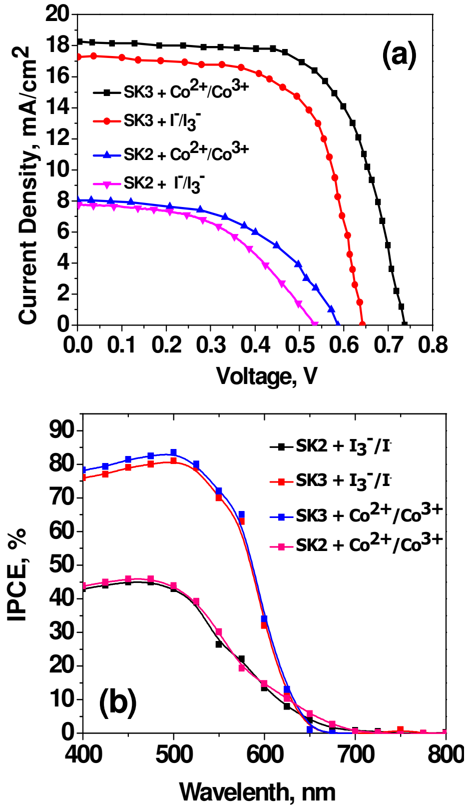

**Fig. 3** (a) Short-circuit photocurrent density–voltage ($J_{sc}$–$V$) curve for the fabricated device with SK2 and SK3 dyes with different redox shuttles at 100 mW/cm$^2$ under AM 1.5G solar irradiation. (b) Incident photon-to-current conversion efficiency (IPCE) plot for the same showing a maximum of ~84% for cobalt based redox mediator.

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**Table 2** Photovoltaic and electron transfer parameters of SK2 and SK3 dyes sensitized cells

| Dye | $J_{sc}$ [a] (mA.cm$^{-2}$) | $V_{oc}$ [a] (mV) | FF [a] (%) | PCE [a] (%) | $R_{ct}$ [b] (Ohm) | $\omega_{max}$ [b] (Hz) | $\tau_{ele}$ [b] (mS) |
|---|---|---|---|---|---|---|---|
| SK2I | 7.1(±0.3) | 534(±010) | 53.0(±1.0) | 2.0(±0.1) | 1.6 | 27.02 | 37 |
| SK3I | 17.2(±0.5) | 645(±016) | 65.0(±2.0) | 7.1(±0.2) | 1.8 | 4.16 | 240 |
| SK2C | 8.4(±0.6) | 587(±011) | 48.0(±1.0) | 2.4(±0.1) | 1.7 | 41.66 | 24 |
| SK3C | 18.3(±0.4) | 725(±012) | 67.0(±1.0) | 9.0(±0.2) | 3.8 | 5.8 | 172 |

[a] From *J-V* measurements, [b] From impedance measurements

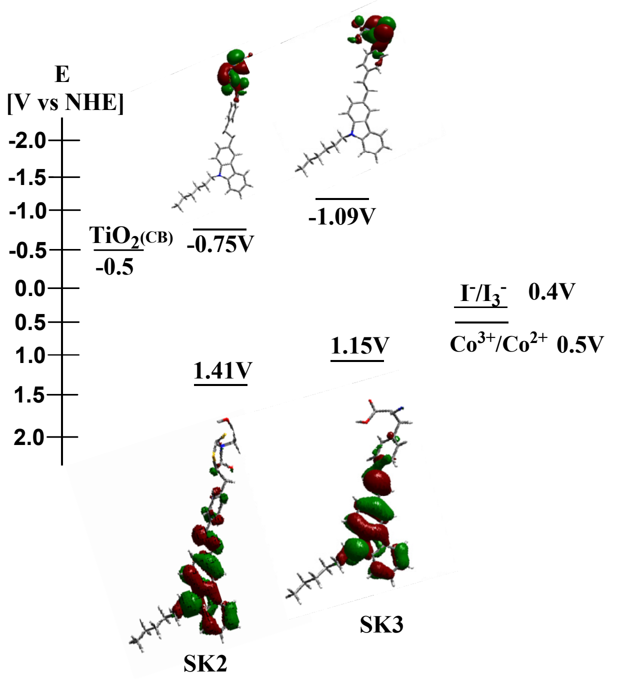

**Fig. 4** Frontier molecular orbitals of SK2 and SK3 dyes with energy level diagram along with redox potentials of iodine and cobalt based redox mediator. (HOMOs; bottom) and (LUMOs; top).

To recognize the huge difference in the performance of DSSCs based on these two carbazole dyes having different acceptors, the density function theory (DFT) calculations were carried out at B3LYP/6-31+G(d,p) level for the geometry optimization. The electronic distribution observed in frontier molecular orbital of the dyes and their corresponding energies are depicted in Fig. 4. For both the dyes, the HOMO is mainly located on donor component and spread up to vinylene-phenylene bridge. However, the LUMO electron density distribution of SK3 dye is located on the cynoacrylic acid group, but for the SK2 dye it is mainly concentrated on the rhodanine-3-acetic acid framework, particularly on the carbonyl and thiocarbonyl. As a result, the SK2 dye prevents the effective injection of electrons into the conduction band of $TiO_2$ via carboxylic group.[39,40]

To further understand the electron injection in detail, the EIS analysis was also performed. Impedance spectra for SK2 and SK3 dye sensitized DSSC devices were measured under illumination of 100 mW/cm$^2$, AM 1.5G light with a forward bias of -0.7V and a frequency range of 0.1Hz-120 KHz. The Nyquist plots (Fig. 5) showed typical two semicircles, the small and large semicircle respectively, located in high and middle frequency region, which were assigned to charge transfer at Pt/electrolyte and $TiO_2$/dye/electrolyte interface respectively.[41,42] The charge transfer resistance ($R_{ct}$) of the Pt/electrolyte interface is quite comparable for all these devices suggesting that reduction of triiodide and $[Co(bpy)_3)]^{3+}$ occurs smoothly. The radius of the large semicircle at intermediate frequency, were increased for SK2 compared to SK3 in both electrolytes, indicating that the electron recombination resistance becomes high for SK2 than SK3. To support these further, an electron life time ($\tau_{ele}$) was calculated from the peak frequency ($\omega_{max}$) of large semicircle.

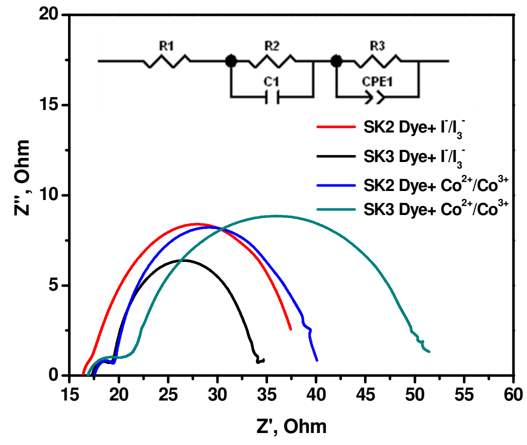

**Fig. 5** Nyquist plot for the DSSC recorded under illumination of light.

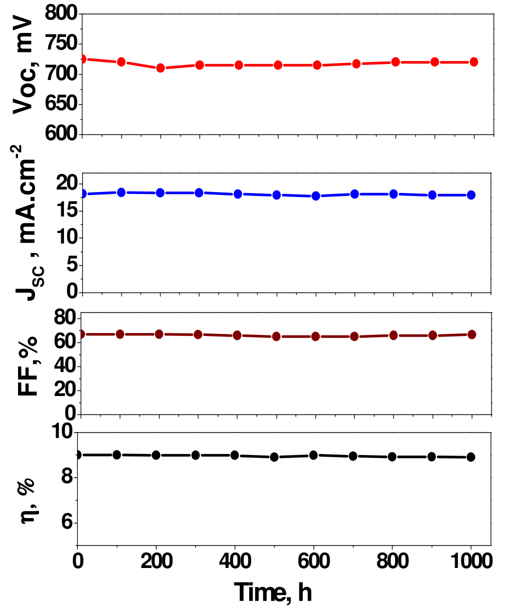

**Fig. 6** Photovoltaic parameters of device (SK3 dye and cobalt redox shuttle) measured under the illumination of sun light for 1000 h.

The obtained values of $\tau_{ele}$ are depicted in Table 2. The longer electron lifetime in $TiO_2$ films observed with SK3 than SK2 dye-sensitized cell indicates the higher electron density and Fermi

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level will be ensured, which might further result in higher $V_{oc}$ for the formal comparison with the latter dye. Moreover, we have found that the electron lifetime for the iodine based devices are a bit higher than those of cobalt based redox shuttle. Hence, it can be anticipated that the recombination of injected electron is higher with one electron redox shuttle ($Co^{2+}/Co^{3+}$).[43,44]

From Fig. 6, it is revealed that the cell exhibits excellent stability with no appreciable degradation of the initial performances even after 1000 h of illumination confirming the high photo stability of the SK3 dye for DSSC applications.

## Conclusions

In conclusion, we designed and synthesized new D-π-A carbazole dyes (ruthenium and thiophene free) possessing vinylene-phenylene group bridged with cynoacrylic acid and rhodanine-3-acetic acid as an acceptor through facile metal catalyst free route allowing scale up of these dyes economically. A prominent PCE of 9.0 % is achieved in combination with one electron Co-based redox mediator and SK3 dye having cynoacrylic acid as an acceptor. These results also confirm that the dye containing a cynoacrylic acid acceptor group has superior performance than dye containing rhodanine-3-acetic acid group with both electrolytes i.e. Iodine based and cobalt complex based. The lower PCE values of SK2 compared to SK3 is attributed to the poor electron injection of dye to the CB of $TiO_2$ and faster charge recombination between the injected electron from the dye and the oxidized electrolyte. The electronic distribution in frontier MO of the dyes shows that the LUMO of SK3 dye has better orbital overlap with the $TiO_2$ conduction band than that of SK2 dye. The DSSC device with SK3 dye and cobalt based electrolyte exhibits good stability under the illumination of AM 1.5G light for 1000 h. We believe that this simple architecture of SK3 dye can be explored further to develop similar structures and utilize them in DSSC devices in larger scale. We expect that the performance of this device can be further improved by modification in dye structure such as improving donating capacity of donor, alkyl chain and optimized bridge structure. The efforts in this direction are in progress in our group.

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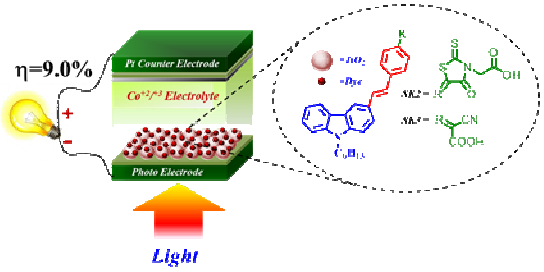
## Graphical Abstract:

# Improved molecular architecture of D-π-A carbazole dyes : 9% PCE with Cobalt redox shuttle in dye sensitized solar cells

Saurabh S. Soni,*[a] Kishan B. Fadadu,[a] Jayraj V. Vaghasiya,[a] Bharat G. Solanki,[a] Keval K. Sonigara,[a] Ashish Singh,[b] Dipjyoti Das[b] and Parameswar K. Iyer *[b,c]



High performance DSSCs with >9 % PCE based on a new dye architecture comprising D-π-A dye (SK3) having carbazole as donor, vinylene-phenylene (π-bridged) and cyanoacrylic acid as electron withdrawing-injecting as well as anchoring groups is reported.