Research Article

Substitution of Carbazole Modified Fluorenes as \( \pi \)-Extension in Ru(II) Complex-Influence on Performance of Dye-Sensitized Solar Cells

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A new high molar extinction coefficient ruthenium(II) bipyridyl complex “\( \text{cis-Ru(4,4} \text{-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2} \text{-bipyridine)(2,2} \text{-bipyridine-4,4} \text{-dicarboxylic acid)(NCS)} \text{2}, BPFC” has been synthesized and characterized by FT-IR, \( \text{H-NMR, and ESI-MASS spectoscopes. The sensitizer showed molar extinction coefficient of 18.5 \times 10^3 \text{M} \text{-1cm}^{-1}, larger as compared to the reference N719, which showed 14.4 \times 10^3 \text{M} \text{-1cm}^{-1}. The test cells fabricated using BPFC sensitizer employing high performance volatile electrolyte, (E01) containing 0.05 M I2, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide, 0.5 M 4-tert-butylpyridine in acetonitrile solvent, exhibited solar-to-electric energy conversion efficiency (\( \eta \)) of 4.65% (short-circuit current density (\( J_{SC} \)) = 11.52 mA/cm², open-circuit voltage (\( V_{OC} \)) = 566 mV, fill factor = 0.72) under Air Mass 1.5 sunlight, lower as compared to the reference N719 sensitized solar cell, fabricated under similar conditions, which exhibited \( \eta \)-value of 6.5% (\( J_{SC} = 14.3 \text{ mA/cm²}, V_{OC} = 640 \text{ mV}, \text{fill factor} = 0.71 \)). UV-Vis measurements conducted on TiO2 films showed decreased film absorption ratios for BPFC as compared to those of reference N719. Staining TiO2 electrodes immediately after sonication of dye solutions enhanced film absorption ratios of BPFC relative to those of N719. Time-dependent density functional theory (TD-DFT) calculations show higher oscillation strengths for 4,4’-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2’-bipyridine relative to 2,2’-bipyridine-4,4’-dicarboxylic acid and increased spectral response for the corresponding BPFC complex.

1. Introduction

Dye sensitized solar cells (DSSCs) attracted intense attention among scientific as well as industrial organizations because of their high photon-to-electricity conversion efficiency and low cost compared to traditional photoelectrochemical cells [1–5]. Since Graetzel introduced the first highly efficient nanocrystalline TiO2 sensitized solar cell based on ruthenium(II) bipyridyl complex, N3 as sensitizer, there have been several modifications to improve the overall performance of the test cell devices [6–22]. Among all the components employed in DSSC, sensitizer plays a key role in photovoltaic performance in respect of efficiency and long-term durability. The important tunable properties of sensitizers for high efficient DSSCs are broad absorption (400 to 900 nm) and high molar extinction coefficient (thin films and solid state DSSCs), thermal and photochemical stability (long durable), compatibility with TiO2 semiconductor conduction band (efficient electron injection) and redox electrolyte (efficient dye regeneration), nonplanar molecular structure, and so forth [6, 8, 22–24]. Thiophene containing oligomers have been extensively explored as the active organic materials.
for OFET applications due to the ease in chemical modification of the structures, allowing fine-tuning their optical and electronic properties [25]. They exhibit high field-effect mobility, which have been related to both, the close packing through π-interactions and the high degree of local order of molecules [26]. Thiophene oligomers display poor diphenylamino group has been shown to o
to thiophene oligomers. Endcaping of oligofluorenes with improved stability and lower HOMO level as compared to thiophene oligomers. Endcaping of oligofluorenes with diphenylamino group has been shown to offer advantages in terms of lowering their first ionization potentials, enhancing thermal stability and inducing good amorphous morphological stability [27]. Thus, fluorene unit as the core is known to display interesting chemical and electronic characteristics. We have been engaged in our laboratory to synthesize notable and high efficient new organic, phthalocyanine as well as ruthenium(II) bipyridyl dyes, [22–24, 28–32] and came across a report of super sensitizer, where carbazole was incorporated on ancillary bipyridyl through conjugation of thiophene moiety [33]. And as a part of our continued efforts in this area of research, we became interested to synthesize a new ruthenium(II) bipyridyl complex BPFC by introducing 4,4′-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2′-bipyridine as an ancillary ligand, and the influence of increased conjugation length on photovoltaic performance and thermal stability was evaluated relative to N719 sensitizer. Multiple performance increasing features such as alkyl groups (n-butyl and t-butyl), triarylamino equivalent (carbazole), biphenyl group in fluorene as extended conjugation have been incorporated in the new ruthenium(II) complex BPFC for achieving better overall performance.

2. Results and Discussion

2.1. Synthesis. Structure of the new ruthenium(II) bipyridyl sensitizer is shown in Figure 1 and the series of steps involved in synthesis of the complex are illustrated in Scheme 1. The new substituted π-conjugated ancillary bipyridyl ligand “4,4′-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2′-bipyridine” (L1) was prepared in accordance to the reported classical reactions. Fluorene, procured from Sigma-Aldrich, was directly used in the bromination reaction to obtain 2-bromofluorene (1), which was subjected to bromine lithium exchange reaction with n-butyllithium (n-BuLi) followed by addition of n-butylbromide to obtain 2-bromo-9,9-dibutyl-9H-fluorene (2). This was further reacted with trisopropylborate in presence of n-BuLi to form 9, 9-dibutyl-9H-fluoren-2-ylboronic acid (3). The boronic acid derivative was coupled with 4,4′-dibromo-2,2′-bipyridine under palladium catalyzed Suzuki conditions to afford 4,4-bis(9,9-dibutyl-9H-fluoren-2-yl)-[2,2]bipyridine. The bipyridyl derivative thus obtained was treated with elemental iodine to afford 4,4′-bis(9,9-dibutyl-7-ido-9H-fluoren-2-yl)-2,2′-bipyridine (5). The diiodo compound, on further reaction with 3,6-di-tert-butyl-9H-carbazole resulted crude L1, which was purified on silica gel column chromatography to obtain pure L1. The ancillary ligand L1 was subjected to complexation with [RuCl2(p-cymene)]2 in DMF and followed by addition of 2,2′-bipyridine-4,4′-dicarboxylic acid and excess ammonium thiocyanate resulted the formation of crude BPFC. The complex was purified on Sephadex LH-20 column chromatography. The intermediates formed during the several classical reactions and the final ruthenium complex are characterized by FT-IR, 1H-NMR, UV-Vis and ESI-MASS spectroscopes. The reference sensitizer, N719, was synthesized in accordance to the procedure reported.

2.1.1. Synthesis of 2-Bromofluorene (1). To a solution of fluorene (0.500 g, 1.8 mmol) in dry acetic acid was added N-bromosuccinimide (0.320 g, 1.8 mmol) under nitrogen atmosphere. After maintaining at 80°C for 3 hours, cool to room temperature and ice water was added and then extracted with dichloromethane. The crude compound was purified on silica gel column chromatography using hexane/ethyl acetate mixture in 9/1 as eluent. Yield: 90% 1H NMR (δH/ppm in CDCl3): 7.75–7.65 (m, 3H), 7.45–7.20 (m, 4H). Chemical formula C12H10Br: ESI-MS: Calcd for (M + H)+: 246, found: 246 (28%).

2.1.2. Synthesis of 2-Bromo-9,9-Dibutyl-9H-Fluorine (2). To a mechanically stirred mixture of 2-bromofluorene (0.980 g, 4 mmol), powdered KOH (1.200 g, 20 mmol), KI (0.066 g, 0.4 mmol), and DMSO (20 mL) were added and cooled to 10°C. Bromobutane (1.076 mL, 10 mmol) was added drop wise over 45 minutes. The color of the reaction mixture turned from red to light purple. After the temperature increased to 20°C, the reaction mixture was left over night, with stirring, poured into water and the precipitate obtained was extracted into dichloromethane. The organic extract was washed with brine solution and water and then concentrated with rotavapour. The compound was purified on silica gel column chromatography using hexane/ethyl acetate mixture in 9/1 as eluent. Yield: 90% 1H NMR (δH/ppm in CDCl3): 7.75–7.65 (m, 3H), 7.45–7.20 (m, 4H), 1.99 (m, 2H), 1.50 (t, 4H), 1.30 (t, 4H), 0.73 (t, 6H), 0.60 (s, 6H). Chemical formula C21H26Br: ESI-MS: Calcd for (M + H)+: 357, found: 357 (100%).

2.1.3. Synthesis of 9,9-Dibutyl-9H-Fluoren-2-ylboronic Acid (3). To a 100 mL two neck glass flask containing 2 (0.500 g, 1.4 mmol) in dry THF (20 mL) and a magnetic stirrer bar at –78°C, n-BuLi (1.05 mL, 1.05 mmol) was added under nitrogen atmosphere while maintaining good stirring. After stirring for 1 hour, trisopropylborate (0.484 mL, 2.1 mmol) was added. After stirring for further 2 hours, the reaction mixture was first quenched with water and then aqueous HCl (6 M, 20 mL) was added drop wise fashion until the solution turned acidic and then extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulphate and concentrated with rotavapour. Purification was carried out by column chromatography on silica gel using hexane/ethanol acetate mixture (4/6 v/v) as eluent. Yield: 50%. 1H NMR (δH/ppm in CDCl3): 7.70 (d, 1H), 7.62 (s, 1H), 7.42–7.27 (m, 5H), 1.99 (s, 2H), 1.92 (m, 4H), 1.10 (t, 4H),
0.73 (t, 6H), 0.60 (s, 6H). Chemical formula C_{21}H_{27}BO_{2}, ESI-MS: Calcd for (M + H)^+: 323, found: 323 (100%).

2.1.4. Synthesis of 4,4-Bis(9,9-Dibutyl-9H-Fluorene-2-yl)-[2,2]-Bipyridine (4). In a 25 mL one-necked round bottom flask equipped with a condenser were placed 3 (0.440 g, 1.375 mmol), barium hydroxide octahydrate (1.355 g, 4.297 mmol), and palladium tetrakis triphenyl phosphine (0.106 g, 0.091 mmol). The reaction flask was evacuated and filled with nitrogen gas, and is charged with 1,4-dioxane (4 mL), water (1.35 mL) and 4,4′-dibromo-2,2′-bipyridine (0.180 g, 0.573 mmol). The reaction mixture was refluxed for 24 hours under nitrogen gas and then cooled to room temperature. The dioxane was removed and the contents were poured into dichloromethane, the precipitate was removed through filter paper, and the organic layer was washed with 1 M-NaOH aqueous solution, NaCl (100 mL) and dried over sodium sulphate. After concentration on rotavapour, small quantity of methanol was added. The precipitate formed was filtered and purified on column chromatography with mixture dichloromethane/methanol, (9/1 v/v) to obtain the pure product as pale yellow solid Yield 50%. 1H NMR (δH/ppm in CDCl_{3}) 8.70 (d, 1H), 8.63 (s, 1H), 7.80 (d, 1H), 7.60 (d, 1H), 7.29–6.63 (m, 6H), 2.0 (m, 4H), 1.50 (m, 4H), 1.10 (m, 4H), 0.86 (s, 6H). Chemical formula (C_{52}H_{56}N_{2}), ESI-MS: Calcd for (M + H)^+: 709, found: 709 (70%).

2.1.5. Synthesis of 4,4-Bis(9,9-Dibutyl-7-Iodo-9H-Fluorene-2-yl)-[2,2]-Bipyridine (5). A mixture of 4 (0.200 g, 0.282 mmol), iodine (0.172 g, 0.677 mmol), conc H_{2}SO_{4} (0.036 mL) and water (0.013 mL) in glacial acetic acid (10 mL) were taken into 1-neck 100 mL round bottom flask. Then, the mixture was stirred at 80°C under nitrogen gas for 4 hours, and then, the reaction mixture was cooled to room temperature. The solution was poured into large amount of ice cool water. The resulting mixture was extracted with dichloromethane and then washed with water and then dried over Na_{2}SO_{4} and concentrated on rotavapour, small quantity of methanol was added. The precipitate formed was separated and purified on column chromatography with silica gel using mixture (DCM/methanol, 9/1) to obtain the pure product as pale yellow solid Yield 45%. 1H NMR (δH/ppm in CDCl_{3}) 8.8 (d, 2H), 8.75 (s, 2H), 7.6–7.8 (m, 8H), 7.5 (d, 2H), 7.25 (s, 4H), 2.0 (t, 8H), 1.15 (m, 16H), 0.78 (t, 12H). Chemical formula (C_{52}H_{54}I_{2}N_{2}), ESI-MS: Calcd for (M + H)^+: 961, found: 961 (75%).

2.1.6. Synthesis of 4,4-Bis(9,9-Dibutyl-7,7-Di tert-butyl Carbazole-9H-Fluorene-2-yl)-[2,2]-Bipyridinyl (6). In a 2-neck 250 mL round bottom flask containing 4,4-bis(9,9-dibutyl-7-iodo-9H-fluorene-2-yl)-[2,2]-bipyridinyl (0.100 g, 0.104 mmol), di-tert-butyl carbazole (0.087 g, 0.312 mmol), copper bronze (0.005 g, 0.084 mmol), and K_{2}CO_{3} (0.067 g, 0.487 mmol) freshly distilled nitrobenzene was added, and
the contents were stirred under N\textsubscript{2} atmosphere under reflux at 210 °C for 24 hours. After cooling to room temperature the reaction mixture was concentrated on the rotavapour for complete removal of nitrobenzene. The crude reaction mixture was then subjected to purification on silica gel column chromatography using ethyl acetate/methanol (9/1) as eluent, 45% yield. \textsuperscript{1}H NMR (δH/ppm in CDCl\textsubscript{3}) 8.81 (d, 2H), 8.79 (s, 2H), 7.54–7.85 (m, 18H), 7.35 (d, 4H), 7.12 (d, 4H), 2.0 (t, 8H), 1.50 (m, 16H), 1.35 (s, 36H), 0.86 (t, 12H).

Chemical formula (C\textsubscript{92}H\textsubscript{102}N\textsubscript{4}), ESI-MS: Calcd for (M) +: 1263, found: 1263 (100%).

2.1.7. Synthesis of Ruthenium(II) Complex. Compound 6 (0.100 g, 0.079 mmol) and dichloro (p-cymene) ruthenium(II) dimer (0.024 g, 0.039 mmol) in DMF were heated at 60 °C for a period of 4 hours under nitrogen in dark. Subsequently 4,4′-dicarboxylic acid-2,2′-bipyridine (0.019 g, 0.079 mmol) was added and the reaction mixture was heated to 140 °C for another 4 hours. To the resulting dark green solution, solid NH\textsubscript{4}NCS (0.180 g, 2.37 mmol) was added and then the reaction mixture was further heated for another 4 hours at 140 °C. After rotaevaporation of DMF, water (250 mL) was added to get precipitate. The precipitate was kept in refrigerator overnight, filtered and washed with distilled water and then dried in vacuum desiccator. The crude compound was dissolved in methanol and dichloromethane mixture and further purified on sephadex LH-20 column using methanol/dichloromethane mixture (3/2 v/v) as eluent. The main band was collected and concentrated with rotavapour. Yield: 65%. \textsuperscript{1}H NMR (δH/ppm in CD\textsubscript{3}OD + CDCl\textsubscript{3}) 9.48 (d, 1H), 9.39 (d, 1H), 8.82 (s, 1H), 8.69 (s, 1H), 8.56 (s, 1H), 8.41 (s, 1H), 7.30–8.30 (m, 29H), 7.18 (d, 1H), 1.8 (t, 8H), 1.35 (s, 36H), 1.15 (m, 16H), and 0.85 (t, 12H).

Chemical formula RuC\textsubscript{10}H\textsubscript{11}C\textsubscript{6}N\textsubscript{8}O\textsubscript{4}S\textsubscript{2}, ESI-MASS: Calcd for (M + H) +: 1768, found: 1768 (72%).

2.2. Fabrication of Test Cells. Fluorine-doped SnO\textsubscript{2} (FTO) conducting glass plates (Nippon Sheet Glass, 4 mm thick, 8 Ω/sq) were cleaned with a detergent solution followed by rinsing with water and ethanol and then treated in a UV-O\textsubscript{3} system to remove organics and other contaminants. A compact layer, which will facilitate a good mechanical contact.
between the nanocrystalline TiO$_2$ and the conducting FTO matrix, was coated over the cleaned plates using a 40 mM TiCl$_4$ aqueous solution, and then, the plates were heated at 70°C for 30 minutes. The working electrodes are composed with 9 μm thickness of 18 nm TiO$_2$ particles (D18T) as transparent layer over which 4.8 μm thickness of 400 nm anatase TiO$_2$ particles (CCIC, HPW-400) as scattering layer. The TiO$_2$-coated films were gradually heated under an air flow at 325°C for 5 minutes, at 375°C for 5 minutes, at 450°C for 15 minutes, and at 500°C for 15 minutes. While cooling, when the temperature attained to around 90°C, the electrodes were immersed in 0.3 mM dye solutions of ethanol and soaked for 16 hours under the dark. The dye-sensitized TiO$_2$ electrodes were rinsed with ethanol to remove the unadsorbed dye molecules and then dried under nitrogen gas. The counter electrodes were prepared by coating an FTO plate (TEC 15, 2.2 mm thickness, Libbey-Owens-Ford Industries) with a drop of H$_2$PtCl$_6$ solution (2 mg of Pt in 1 mL of ethanol) and heating it at 430°C for 15 minutes. The dye-sensitized TiO$_2$ electrode and Pt counter electrode were assembled into a sealed sandwich type cell by heating with a hot-melt surlyn film (Surlyn 1702, 25 μm thickness) as a spacer in-between the electrodes. The liquid electrolyte of E01 (I$_2$ 0.05 M, LiI 0.1 M, DMPPII 0.6 M, and TBP 0.5 M in acetonitrile) was filled through the predrilled hole present on the counter electrode, and then, the hole was sealed with a Surlyn disk and a thin glass to avoid leakage of the electrolyte.

2.3. Absorption and Emission Properties. The electronic absorption spectrum of BPFC sensitizer recorded in ethanol is shown in Figure 2(a), and the spectrum was compared with that of the reference N719 sensitizer. The complex exhibited one absorption band at longer wavelength region and a shoulder type band in short wavelength region. The molar extinction coefficient of low-energy absorption band of BPFC is 18.5 × 10$^3$ M$^{-1}$ cm$^{-1}$, which is larger as compared to that of reference N719 sensitizer that showed molar extinction coefficient of 14.4 × 10$^3$ M$^{-1}$ cm$^{-1}$. Compared to N719, the increase in π-conjugation length by introduction of 4, 4′-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2′-bipyridine in BPFC complex increases the molar extinction coefficient and the spectral response of the new complex. The high-energy shoulder type absorption band of the complex with increased molar extinction coefficient could be attributed to the π-π* transitions of the new complex. The high-energy shoulder type absorption band of the complex with increased molar extinction coefficient could be attributed to the π-π* transitions of the new complex. The high-energy shoulder type absorption band of the complex with increased molar extinction coefficient could be attributed to the π-π* transitions of the new complex. The high-energy shoulder type absorption band of the complex with increased molar extinction coefficient could be attributed to the π-π* transitions of the new complex.

![Figure 2: Absorption spectrum of BPFC (---) relative to N719 (----) (a) equi-molar in ethanol (b) on TiO$_2$ films.](image-url)
in 0.3 mM dye solutions prepared in ethanol for a period of 16 hours under dark. The absorption spectrum of BPFC-sensitized TiO$_2$ film was recorded and was compared with that of N719 sensitized TiO$_2$ film (Figure 2(b)). The measurements indicate that the dye molecules are anchored on TiO$_2$ surface, and the film absorbencies for both the dyes are similar. To compare the anchoring pattern and surface morphology of the new sensitizer, the absorbance maxima of low energy absorption band of BPFC sensitizer is normalized by the corresponding absorbance maxima of N719, while their molar extinction coefficients are normalized by the molar extinction coefficient of N719. The film absorbance ratio of BPFC calculated is lower than that of N719 indicating its lower packing density of the dye molecules on TiO$_2$ surface. Staining TiO$_2$ electrodes immediately after sonication of BPFC dye solution showed much higher film absorption ratios as compared to those TiO$_2$ films stained for prolonged soaking times in the BPFC dye solutions, and this indicates the necessity of sonication before staining the TiO$_2$ electrodes, particularly when sensitizers with larger diagonal diameter are employed.

2.4. Electrochemical Properties. In dye-sensitized solar cells, favorite energy offset between dye and titania is a basic requirement for any high-efficiency solar cell, in which the sensitizer’s immediate charge generation yield from the excited state has a direct influence on the performance of DSSC device. To measure the electrochemical properties of BPFC dye, cyclic voltmammetry was employed using tetra-butyl ammonium perchlorate (0.1 M in acetonitrile) as an electrolyte and ferrocene as an internal standard at 0.42 V versus SCE (Figure 3). The oxidation and reduction potentials of BPFC are 0.79 V and −0.80 V, respectively. The more positive potential of the sensitizer, relative to $\Gamma^-/\Gamma_3$ redox couple in the electrolyte provide a large thermodynamic driving force for the regeneration of the dye by iodide. Based on absorption and emission spectra, the excitation transition energy ($E_{0-0}$) of BPFC was estimated to be 1.87 eV and the standard potential ($\varphi_{0}^{b}(S+/S^\ast)$) calculated from the relation of $\varphi_{0}^{b}(S+/S^\ast)=\varphi_{0}^{b}(S+/S^\ast)−E_{0-0}$ for the sensitizer was −1.08 V versus SCE. So, $\varphi_{0}^{b}(S+/S^\ast)$ value is more negative (or higher in energy) than the conduction band edge of TiO$_2$ providing a thermodynamic driving force to inject electron from the dye to TiO$_2$.

2.5. Computational Studies. In order to augment the molar extinction coefficient with the $\pi$-conjugation extension through 4, 4’-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2’-bipyridine (L1) in BPFC relative to 2,2’-bipyridine -4,4’-dicarboxylic acid in N719 complex, the electronic ground state of fully protonated complex is optimized. To see the influence of the ancillary ligand, L1 on the corresponding ruthenium(II) complex, the electronic ground state of the ligand was optimized using B3LYP/6-31G(d) method. Based on the optimized structures, TD-DFT calculations were performed to see the optical properties of the ligand and the corresponding ruthenium(II) complex. The unoccupied (LUMO+4 to LUMO) and occupied (HOMO to HOMO+4) orbitals of L1 are shown in Figure 4. The HOMO and HOMO−1 orbitals of L1 are degenerate and the $\pi$-orbitals are almost delocalized among carbazole modified fluorenes on ancillary bipyridine, which lifts their energy levels. In case of HOMO−2 and HOMO−3, the $\pi$-orbitals are almost localized on the carbazole chromophore. In case of LUMO to LUMO+2 orbitals of L1, the $\pi^*$-orbitals are delocalized over $\pi$-system with maximum components on the bipyridine, which depresses their energy levels. LUMO+3 and LUMO+4 have $\pi^*$-orbitals localized on carbazole chromophore. The TD-DFT excitation calculations performed for the optimized ground state of the ancillary bipyridyl ligand, L1 shows basically two $\pi-\pi^*$ transitions with significant oscillation strengths at 303 and 322 nm, respectively, as observed in the case of the absorption spectrum of the ancillary ligand, L1.

The unoccupied (LUMO to LUMO+4) and occupied (HOMO to HOMO−4) frontier orbitals of BPFC are shown in Figure 5. The first three occupied (HOMO to HOMO−2) orbitals of BPFC exhibit ruthenium $12g$ character with size mixing from thiocyanate ligand and with $\pi$-bonding orbitals of 4,4’-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2’-bipyridine (L1). The $\pi$-clouds for HOMO−3 orbital for both the dyes are nonbonding combination localized on the NCS ligands. The HOMO−4 and HOMO−5 of BPFC are combinations of $\pi$-bonding orbitals localized over carbazole moiety of 4,4’-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2’-bipyridine. In HOMO and HOMO−1 orbitals of the new ancillary bipyridine, the $\pi$-orbitals are more delocalized over the $\pi$-system and bipyridine, and this favors lifting their energy levels. The conjugation length of BPFC resulted in increase in the molar extinction coefficient of MLCT absorption bands, which could probably due to lifting their occupied molecular orbitals energy levels as compared to those of N719. In case of LUMO, the electron distribution move toward anchoring groups, while assuming similar molecular orbital geometry when adsorbed on TiO$_2$.
surface, the close position of the LUMO to the anchoring moieties is expected to enhance the overlap with the 3d orbitals of TiO$_2$ leading to favored electron injection.

2.6. Thermal Stability. One of the parameters desired to sustain the initial photovoltaic performance of the DSSC over a long period is the high thermal stability of the ruthenium(II) sensitizer. In order to evaluate the thermal stability of the new sensitizer relative to N719, TGA analysis were performed using a TGA/SDT A 851 e thermal system (Mettler Toledo, Switzerland) at heating rate of 10°C/min in the temperature range of 50–600°C under N$_2$ atmosphere (flow rate of 30 mL/min) and the influence of 4,4′-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2′-bipyridine on thermal stability of BPFC complex was studied. Film samples ranging from 8 to 10 mg were placed in the sample pan and heated, while weight loss and temperature difference were recorded as a function of temperature. The thermogram of BPFC obtained under identical conditions with that of N719 was compared. Figure 6 shows the derivative of % conversion with respect to temperature, in which both the thermograms of BPFC and N719 initially follow similar trend up to around 200°C and after this, BPFC loses its mass quickly and hence a decrease in thermal stability by around 50°C was observed as compared to that of N719. This indicates that the substitution of 4,4′-bis(9,9-dibutyl-9H-fluorene-2-yl)-2,2′-bipyridine reduces the thermal stability of the ruthenium(II) sensitizer.

2.7. Photovoltaic Properties. To study the influence of 4,4′-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2′-bipyridine as π-conjugation extension on the photovoltaic performance of DSSC relative to 2,2′-bipyridine-4,4′-bicarboxylic acid, double-layer titania film (9.0 + 4.8 μm) 0.16 cm$^2$ active area TiO$_2$ electrodes and high-efficiency liquid electrolyte were employed for fabrication of DSSC test cells. The fabrication and evaluation of DSSC test cells were in accordance to the procedures already reported and the volatile electrolyte, (EO1) containing 0.05 M I$_2$, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide, 0.5 M 4-tert-butylpyridine in acetonitrile solvent was employed [31]. The incident photon-to-current conversion efficiency (IPCE) of the sensitizer plotted as a function of excited wavelength was compared with that of N719 sensitized solar cell, fabricated and evaluated under identical conditions (Figure 7). The photocurrent action spectrum of BPFC showed broad plateau IPCE spectrum with exceeding IPCE of 55%, while that of N719 exhibited maximum IPCE reaching 78%. The BPFC sensitizer gives short-circuit photocurrent density ($J_{SC}$), open-circuit voltage ($V_{OC}$), and fill factor (ff) of 11.52 mA/cm$^2$, 566 mV, and 0.72, respectively, yielding an overall energy conversion efficiency ($\eta$) of 4.65%, while the test device fabricated under identical conditions with N719 dye gave $J_{SC}$ of 14.36 mA/cm$^2$, $V_{OC}$ of 640 mV, and ff of 0.71 yielding an overall energy conversion efficiency of 6.5%. When compared to N719 sensitized solar cell, BPFC-sensitized solar cell is expected to show lower power.

Figure 4: Frontier molecular orbitals of 4,4′-bis(9,9-dibutyl-7-(3,6-di-tert-butyl-9H-carbazol-9-yl)-9H-fluoren-2-yl)-2,2′-bipyridine (L1); (a) LUMO+4; (b) LUMO+3; (c) LUMO+2; (d) LUMO+1; (e) LUMO; (f) HOMO; (g) HOMO−1; (h) HOMO−2; (i) HOMO−3; (j) HOMO−4.
Figure 5: Frontier molecular orbitals of BPFC: (a) LUMO+4; (b) LUMO+3; (c) LUMO+2; (d) LUMO+1; (e) LUMO; (f) HOMO; (g) HOMO−1; (h) HOMO−2; (i) HOMO−3; (j) HOMO−4.

Table 1: Detailed photovoltaic parameters of DSSCs.

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>J_SC (mA/cm^2)</th>
<th>V_OC (mV)</th>
<th>ff</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPFC</td>
<td>11.52</td>
<td>566</td>
<td>0.72</td>
<td>4.6</td>
</tr>
<tr>
<td>N719</td>
<td>14.36</td>
<td>640</td>
<td>0.71</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Short-circuit photocurrent density (J_SC), open-circuit photovoltage (V_OC), fill factor (ff).

conversion efficiency due to lower J_SC and lower IPCE of BPFC relative to that of N719 Table 1.

3. Conclusions

The new sensitizer BPFC was carefully designed considering the following (1) The alkylgroups (two n-butyl and two t-butyl on each pyridyl of ancillary ligand) not only increase the solubility of the sensitizer in organic solvents but also serve as electron donating apart from inhibiting water induced desorption of the sensitizer from the TiO_2. (2) Carbazole is a triarylamine equivalent which is known to improve the efficiency of the sensitizer. (3) The biphenyl group in Fluorene moiety serves as extended conjugation for enhancing the molar extinction coefficient and provides aromatic stability to the molecule. (4) The bipyridine dicarboxylic acid provides excellent anchoring of the complex on to the TiO_2 surface facilitating easy electron injection. Thus, the multiple performance increasing features of the BPFC sensitizer makes the ruthenium(II) complex unique for DSSC application and showed solar-to-electric energy conversion efficiency (η) 4.6%, while under similar fabrication and measurement conditions, standard N719 showed 6.5% efficiency. The new ruthenium(II) bipyridyl sensitizer showed relatively high molar extinction coefficient. Upon
sensitization with nano-crystalline TiO$_2$, the dye showed decreased film absorption ratios, whereas staining the TiO$_2$ electrodes with freshly sonicated dye solutions showed relatively increased film absorption ratios on TiO$_2$ surface. The lower solar-to-electrical energy conversion efficiency could be result of lower IPCE value and lower film absorption ratios. Design and development of super sensitizers with similar high performance features but with less bulky nature are under progress.

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