A molecularly engineered fluorene-substituted Ru-complex for efficient mesoscopic dye-sensitized solar cells

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Abstract

A new high molar extinction coefficient ruthenium(II) bipyridyl complex \( \text{cis-Ru}(L1)(2,2'\text{-bipyridine-4,4'\text{-dicarboxylic acid}}) (\text{NCS})_2 \), BDF, where \( L1 = 4,4\text{-bis}(9,9\text{-dibutyl-9H-fluorene-2-yl})\text{-}[2,2\text{-bipyridine}} \), has been synthesized and characterized by Fourier transform infrared (FTIR), hydrogen nuclear magnetic resonance (\(^1\text{H-NMR}) and electrospray ionization mass (ESI–MASS) spectroscopes. The dye, upon anchoring onto mesoporous nano-crystalline TiO\(_2\) solar cells, exhibited a broader photocurrent action spectrum, with a solar-to-electric energy conversion efficiency (\( \eta \)) of 6.58\% (\( J_{SC} = 14.66 \text{ mA cm}^{-2}, V_{OC} = 640 \text{ mV, fill factor} = 0.71 \)) under sunlight at air mass (AM) 1.5, larger than the reference Z907 sensitized solar cell fabricated under similar conditions, which exhibited an \( \eta \)-value of 4.65\% (\( J_{SC} = 11.52 \text{ mA cm}^{-2}, V_{OC} = 566 \text{ mV, fill factor} = 0.72 \)). Absorption measurements and time-dependent density functional theory (TDDFT) calculations show that the increased conjugation length by introducing 9,9-dibutyl-9H-fluorene moiety relatively enhances the spectral response of the ancillary ligand and the corresponding BDF complex. The calculated dipole moments for BDF and Z907 are 17.71 and 16.34 Debye, respectively. The first three highest occupied molecular orbitals (HOMOs) of BDF have a \( t_{2g} \) character, as observed in Z907, while HOMO-4 and HOMO-5 have considerable sizable mixing from Ru-NCS with \( \pi \)-orbitals of L1.

Keywords: dye-sensitized solar cells, fluorene extended \( \pi \)-system, polypyridyl Ru(II)-sensitizers

Classification numbers: 2.03, 4.02, 5.04

1. Introduction

Dye-sensitized solar cells (DSSC) have attracted intense attention from scientific as well as industrial organizations because of their high photon-to-electricity conversion efficiency and low cost compared to traditional photo-electrochemical cells [1–5]. Since Graetzel introduced the first highly efficient nanocrystalline TiO\(_2\) sensitized solar cell based on a ruthenium(II) bipyridyl complex (N3 as sensitizer), there have been several modifications
proposed to improve the overall performance of the test cell device [6–23]. Among all the components employed in DSSC, the sensitizer plays a key role in photovoltaic performance in respect of efficiency and durability. The important tunable properties of sensitizers for highly efficient DSSCs are a broad absorption (400–900 nm) and a high molar extinction coefficient (thin films and solid state DSSCs), thermal and photochemical stability (long lasting and durable), compatibility with the TiO2 semiconductor conduction band (efficient electron injection) and the redox electrolyte (efficient dye regeneration), non-planar molecular structure, etc [6,8,22–24]. Thiophene-containing oligomers have been extensively explored as the active organic materials for organic field effect transistor (OFET) applications due to the ease of chemical modification of their structures, allowing fine-tuning of their optical and electronic properties [25]. They exhibit high field-effect mobility, which has been related to both the close packing through π–interactions and the high degree of their local order of molecules [26]. Thiophene oligomers display poor stability, especially in the solid state, limiting their practical applications, whereas fluorene-based oligomers have shown both improved stability and a lower HOMO level as compared to thiophene oligomers. The endcapping of oligofluorenes with a diphenylamino group has been shown to offer advantages in terms of lowering their first ionization potentials, enhancing their thermal stability and inducing good amorphous morphological stability [27]. Thus fluorene unit as the core is known to display interesting chemical and electronic characteristics. In this application, we have been engaged in the synthesis of a durable and highly efficient new organic phthalocyanine as well as ruthenium(II) bipyridyl dyes in our laboratory [24, 28–34]. In addition, as part of our continued efforts, we have synthesized a new ruthenium(II) bipyridyl complex by introducing 4,4′-bis(9,9-dibutyl-9H-fluorene-2-yl)-2,2′ bipyridine as an ancillary ligand, to which the influence of an increased conjugation length on photovoltaic performance and thermal stability were evaluated relative to the non-conjugated ancillary ligand 4,4′-dinyonyl-2,2′-bipyridine present in the reference Z907 sensitizer.

2. Experimental

2.1. Materials and instruments

2-bromo fluorene, triisopropyl borate, n-butyllithium, Ba(OH)2•2H2O, Pd(PPh3)4, carbazole, NH4NCS, 1,2-dimethyl-3-n-propylimidazolium iodide (DMPII), 4-tert-butylpyridine (TBP), hexachloroplatinic acid, tetrabutylammoniumhexafluorophosphate (TBA), and chenoxydychloric acid (CDCA) were purchased from Sigma-Aldrich. 4,4′-dibromo 2,2′ bipyridine was procured from Heterocycles & Catalysts, Gundeldingerstrasse 174, CH-4053 Basel, Switzerland. Sephadex LH-20 was procured from GE Healthcare Bio-Sciences AB, SE-75184, Upsala and was used to purify the crude complexes on column chromatography. Dichloro (p-cymene) ruthenium (II) dimer and 2,2′-bipyridine-4,4′-dicarboxylic acid were prepared in accordance to the reported procedures [35, 36]. All solvents and reagents, unless otherwise stated, were of laboratory reagent grade and used as received. A Brucker 300Avance 1H-NMR spectrometer run at 500 MHz was employed to record the 1H NMR spectrum. A Shimadzu LCMS-2010EV with an electrospray ionization (ESI) probe was used to confirm the formation of the ancillary bipyridyl ligand 4,4′-bis(9,9-dibutyl-9H-fluorene-2-yl)-2,2′-bipyridine and the corresponding ruthenium(II) BDF complex. A Shimadzu UV–Vis spectrometer (model 1700) was employed to record the electronic absorption spectrum of the complexes, while their emission measurements were performed in dimethylformamide (DMF) using a Fluorolog 3, JY Horiba fluorescence spectrometer.

2.2. The synthesis of ligand and ruthenium complex

Synthesis of 2-bromo-fluorene (1): N-bromosuccinimide (0.320 g, 1.8 mmol) was added to a solution of fluorene (0.500 g, 1.8 mmol) in dry acetonitrile under nitrogen atmosphere. After maintaining at 80 °C for 3 h, it cooled to room temperature and then ice water was added and then extracted with dichloromethane. The crude compound was purified on silica gel column chromatography using a hexane/ethylacetate mixture in 9/1 as eluent. Yield: 90% 1NMR (δH per ppm in deuterated chloroform CDCl3): 7.75–7.65 (m, 3H), 7.45–7.20 (m, 4H). Chemical formula C33H30Br: ESI–MASS: Calcd for (M + H)+: 246, found: 246.

Synthesis of 2-bromo-9, 9-dibutyl-9H fluorene (2): KI (0.066 g, 0.4 mmol) and dimethyl sulfoxide (DMSO) 20 ml were added to a mechanically stirred mixture of 2-bromo-fluorene (0.980 g, 4.0 mmol), powdered KOH (1.20 g, 20 mmol) and cooled to 10 °C. Bromobutane (1.076 ml, 10 mmol) was added drop wise over 45 min. The reaction mixture turned from red to light purple. After the temperature increased to 20 °C, the reaction mixture was left overnight, with stirring. Then the reaction mixture was poured into water to precipitate and then extracted into dichloromethane. The extract was washed with brine solution and water, and then concentrated with a rotavapour. The compound was purified on silica gel column chromatography using a hexane/ethylacetate mixture in 9/1 as eluent. Yield: 90% 1NMR (δH per 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 C32H32Br: ESI–MASS: Calcd for (M + H)+: 357, found: 357.

Synthesis of 9, 9-dibutyl-9H-fluoren-2-yloboric acid (3): In a 100 ml two-neck glass flask was placed (2) (0.500 g, 1.4 mmol) in dry tetrahydrofuran (THF) (20 ml) and a magnetic stirrer bar. The solution was cooled to –78 °C by immersing the flask in an acetone/dry ice bath, whereupon n-BuLi (1.05 ml, 1.05 mmol) was added under nitrogen atmosphere, while maintaining good stirring. After stirring for 1 h, triisopropylborate (0.484 ml, 2.1 mmol) was added. After stirring for further 2 h, the reaction mixture was first quenched with water and then aqueous HCl (6 M, 20 ml) was added in a drop wise fashion until the solution turned acidic. The resulting mixture was poured into water and extracted with dichloromethane. The combined organic layers were dried over anhydrous sodium sulfate and concentrated with a rotavapour. Purification was carried out by column chromatography on silica gel using a hexane/ethylacetate
Synthesis of 4,4-bis(9,9-dibutyl-9H-fluorene-2-yl)-2,2′-bipyridine (L1): 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, 1,4-dioxane (4 ml), water (1.35 ml) and 4,4′-dibromo-2,2′-bipyridine (0.180 g, 0.573 mmol) were added. The reaction mixture was refluxed for 24 h under nitrogen gas and then cooled to room temperature. Dioxane was removed and the contents poured into dichloromethane, the precipitate was removed through filter paper and the organic layer was washed with 1 M-NaOH aqueous solution and brine (100 ml), and dried over sodium sulphate. After being concentrated in the rotavapour, a small quantity of methanol was added. The precipitate formed was separated and purified on column chromatography with silica gel using a dichloromethane/methanol mixture (9/1) to collect the pure product as a pale yellow solid, yield 50%. 

β-H NMR (500 MHz, CDCl3) δ (ppm): 9.55 (d, 1H), 9.45 (d, 1H), 8.90 (s, 1H), 8.80 (s, 1H), 8.70 (s, 1H), 8.60 (s, 1H), 8.00–7.20 (m, 4H), 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 (C52H36N2), ESI–MASS: Calcd for (M + H)+: 708, found: 708.

2.4. Photovoltaic characterization

The photovoltaic characteristics of these devices were evaluated under the irradiation of a 450 W xenon light source (Osram XBO 450, USA, equivalent to an AM 1.5 solar simulator). Prior to these measurements, the xenon light was calibrated by using a Tempax 113 solar filter (Schott) and the output power of the solar simulator was calibrated by using a reference Si photodiode equipped with a color-matched IR-cutoff filter (KG-3, Schott) to reduce the mismatch in the region of 350–750 nm between the simulated light and AM 1.5 to <2%. The measurement delay time of photo J–V characteristics of DSSCs was fixed to 40 ms. The incident photon-to-current conversion efficiency was plotted as a function of the excitation wavelength by using the incident light from a 300 W xenon lamp (ILC Technology, USA), which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd) with a light source of Xe 450 W @ AM 1.5 G and a Keithley 2400 source meter.

2.5. Computation

To gain insight into the structural, electronic and optical properties of 4,4′-bis(9,9-dibutyl-9H-fluorene-2-yl)-2,2′-bipyridine (L1), 4,4′-dinonyl-2,2′-bipyridine (L2) and the corresponding protonated ruthenium(II) bipyridyl complexes, BDF and Z907, density functional theory (DFT) calculations were performed by taking into account electron correlations, which are important for transition metal complexes. In these calculations, Beck’s three-parameter functional and the Lee-Yang-Parr functional (B3LYP) method and 6-31G(d) basis set for H, C, N, O and S atoms were used to optimize the electronic ground-state geometries of the ancillary ligands, while an effective core potential basis set; LANL2DZ, was...
and the series of steps involved in A.1 and the spectrum in the Appendix present the related A.9 in the Appendix). The stretching bands in n with was obtained by bromination with NBS, which was prepared starting from fluorene. 2-bromo-fluorene was reacted with triisopropylborate in presence of n-ButLi to form 9,9-dibuty 1. 3. Synthesis of BDF

**Scheme 1.** Synthesis route of BDF sensitizer. (i) N-bromosuccinimide, acetone at 60 °C in 3 h; (ii) bromobutane, powdered KOH, KI and DMSO, RT 12 h (iii) n-BuLi, trisopropyl borate, THF, 2 M HCl, –78 °C, 4 h; (iv) 4,4′-dibromo-2,2′-bipyridine, Ba(OH)\(_2\)·8H\(_2\)O, Pd(PPh\(_3\))\(_4\), dioxane-water, 24 h, reflux; (v) [Ru(p-cymene)\(_2\)Cl\(_2\)], 4,4′-dicarboxy-2,2′-bipyridine, NH\(_4\)NCS, DMF, 12 hours reflux.

used for ruthenium in the optimization of the electronic ground states of fully protonated ruthenium(II) complexes. Based on the optimized electronic ground-state of the ancillary ligands, the time-dependent (TD)-DFT excitation calculations were performed with the B3LYP method and the 6-31G(d) basis set using the Gaussian 09W and Gaussian View 5 interface program [37].

3. Results and discussion

3.1. Synthesis of BDF

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 \(\pi\)-conjugated ancillary bipyridyl ligand \(4,4′\)-bis(9,9-dibutyl-9H-fluoren-2-yl)-2,2′-bipyridine (L1) was prepared starting from fluorene. 2-bromo-fluorene was obtained by bromination with NBS, which was subjected to a bromine lithium exchange reaction with n-butyllithium (n-BuLi) followed by the addition of two equivalents of n-butylbromide providing 2-bromo-9,9-dibutyl-9H fluorene (2). This was further reacted with triisopropylborate 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 L1 (figures A.1–A.8 in the Appendix present the related \(^1\)H-NMR and ESI–MASS spectra). The \(^1\)H-NMR and ESI–MASS spectroscopies confirmed the structure of L1. The new ancillary ligand was subsequently treated with [RuCl\(_2\)\(p\)-cymene\(_2\)] in DMF followed by addition of 2,2′-bipyridine-4,4′-dicarboxylic acid. Finally, excess ammonium thiocyanate was added to afford the ruthenium(II) complex, BDF. The complex was characterized by FTIR, \(^1\)H-NMR and ESI–MASS spectroscopies (related \(^1\)H-NMR, ESI–MASS and FTIR spectra are presented by figures A.9–A.11 in the Appendix). The stretching bands in the FTIR spectrum of BDF at around 1624 and 1363 cm\(^{-1}\) correspond to asymmetric and symmetric stretching modes of the carboxylate groups. The stretching bands at around 2108 cm\(^{-1}\) correspond to NCS groups, indicating that NCS is coordinated to the ruthenium center through the N-atom. The larger broad stretching band centered at 3376 cm\(^{-1}\) is due to the adsorbed moisture of the dye. The reference sensitizer, Z907, was synthesized in accordance to the reported procedure [10].

3.2. Photophysical and electrochemical properties

The electronic absorption spectrum of the BDF sensitizer recorded in ethanol is shown in figure 2 and the spectrum was compared with that of the reference Z907 sensitizer. The complex showed well-defined metal → ligand charge transfer transition absorption bands, one in the long wavelength region and a shoulder type band in the short wavelength region [38]. The molar extinction coefficient of the low-energy absorption band of BDF at \(\lambda_{\text{max}}\) 404 nm is 13 700 M\(^{-1}\)cm\(^{-1}\). Under similar conditions, the reference Z907 sensitizer showed a molar extinction coefficient of 9000 M\(^{-1}\)cm\(^{-1}\) at \(\lambda_{\text{max}}\) 404 nm. When compared to Z907, an increase of around 29% in molar extinction coefficient was observed for the BDF sensitizer. The increase in \(\pi\)-conjugation length effected by introducing 9,9-dibutyl-9H-fluorene is expected to show a higher molar extinction coefficient than that of 4,4′-dinonyl-2,2′-bipiridine in Z907. As compared to the low-energy absorption band of BDF, the high energy absorption band exhibited an increased molar extinction coefficient of 15 500 M\(^{-1}\)cm\(^{-1}\). This indicates that the fluorene moiety substitution on the ancillary bipyridine ligand has not influenced the molar extinction coefficient significantly, but as to the high-energy absorption band, the
much higher molar extinction coefficient could be attributed to the π–π* transitions of fluorene segments, which exhibit strong absorption at around 400 nm.

It is known that the high-energy absorption band of the ruthenium(II)-bipyridyl complex is contributed by two components, one is the metal-to-ligand charge transfer transition, while the other is the π–π* transitions of the ancillary bipyridyl ligand. As compared to 4,4′-dinonyl-2,2′-bipyridine, which showed an absorption band at 290 nm (figure 2(a)), 4,4′-bis(9,9-dibutyl-9H-fluorene-2-yl)-2,2′-bipyridine (L1) has shown two strong absorption bands, one at around 298 nm and the other one at 322 nm, and these absorption bands even exist in the BDF complex, but at slightly at higher wavelengths. This indicates that the π–π* transitions in the ancillary bipyridyl ligand are strong and unfortunately this transition does not exist close to the high-energy metal-to-ligand charge transfer transition of the BDF complex. That is the reason why a shoulder-type high-energy absorption band might have resulted for the BDF complex. The emission spectra of the BDF sensitizer were recorded in a DMF medium by exciting the complex with the absorption maxima of its low-energy absorption band. The emission spectrum was analyzed by the Gaussian reconvolution method to integrate the emission peak to estimate the emission maxima.

The optical absorptivity of the sensitizer anchored on mesoporous TiO2 electrodes influence the light-harvesting capability of dye-sensitized solar cells, which indirectly depends on molecular geometry and size. Therefore the film absorption measurements on a TiO2 surface were carried out by staining 7.0 μm thick TiO2 (18 NRT layered) films in 0.3 mM dye solutions prepared in ethanol for a period of 16 h in the dark. The absorption spectrum of BDF-sensitized TiO2 film was recorded and compared with that of Z907 sensitized TiO2 film (figure A.12 in the appendix). The measurements indicate that the dye molecules are anchored on the TiO2 surface. The film absorbance of BDF is lower than that of Z907, indicating its lower packing density on the titania, which could be due to the enlarged diameter of BDF arising from the presence of the bulky fluorene moieties on the bipyridine ancillary ligand. In dye-sensitized solar cells, a favorite energy offset between the 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 device operation. To measure the electrochemical properties of BDF dye, cyclic voltammetry 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 saturated calomel electrode (SCE). Figure 3 shows the cyclic voltammogram of BDF in acetonitrile. The measured oxidation potential was 0.772 V, while the reduction potential was −0.758 V versus SCE. The more positive potential of the sensitizer, relative to the 1/2 redox couple (0.24 V versus SCE) in the electrolyte, provides a large thermodynamic driving force for the regeneration of the dye by the iodide. Based on absorption and emission spectra, the excitation transition energy (E0–0) of BDF was estimated to be 1.87 eV and the standard potential φ(S*/S+) was calculated from the relation of \([\phi(S*/S+) = \phi(S*/S^+) - E_{0–0}]\) for the sensitizer was −1.063 V versus SCE. So, the φ(S*/S+) value is more negative (or higher in energy) than the conduction band edge of TiO2 (−0.8 V versus SCE) providing a thermodynamic driving force to inject electrons from the dye to the TiO2.

3.3. Computational studies

A geometrical optimization of the electronic ground-state of 4,4′-bis(9,9-dibutyl-9H-fluorene-2-yl)-[2.2] bipyridine was performed and the occupied (highest occupied molecular orbital (HOMO) to HOMO-5) and un-occupied (lowest un-occupied molecular orbital (LUMO) to LUMO+5) frontier orbitals are shown in figure 4, while those of 4,4′-dinonyl-2,2′-bipryidine are shown by figure A.13 in the appendix. In the HOMO of L2, the π-orbitals are over the bipyridine moiety only, while in the HOMO and HOMO-1 orbitals of L1, the π-orbitals are almost delocalized equally among the 9,9-dibutyl-9H-fluorene (π-system) and
bipyridine, which lifts their energy levels. The \(\pi\)-orbital of the HOMO-2 of L1 is over the bipyridine moiety, whose energy corresponds to the HOMO of L2 and has similar \(\pi\)-orbitals over the bipyridine moiety. The HOMO-1 and HOMO-2 of L2 are antinodes formed around the bipyridine moiety, while for L1 the HOMO-3 to LUMO-5 orbitals have antinodes around the bipyridine, with \(\pi\)-orbitals localized on and around the \(\pi\)-system of the new ancillary bipyridine ligand. In the case of the LUMO to LUMO+2 orbitals of L1, the \(\pi^*\)-orbitals are delocalized over the \(\pi\)-system with maximum components on the bipyridine, which depresses their energy levels relative to those of L2 (figure 6). LUMO+3 and LUMO+4 have \(\pi^*\)-orbitals localized on one of the pyridines. The TD-DFT excitation calculations performed for the optimized ground-state of the ancillary bipyridyl ligands, L1 and L2, are summarized in table A.1 in the appendix, which shows basically two \(\pi-\pi^*\) transitions with significant oscillation strengths of 1.12 and 0.74 at 330 and 290 nm, respectively. The 330 nm band results from the HOMO–HOMO-2 to LUMO \(\pi-\pi^*\) transitions, while the 290 nm corresponds to the \(\pi-\pi^*\) transitions of the higher (HOMO-3 to HOMO-5) frontier orbitals to LUMO and it appears that these transitions are from the fluorene moiety to the LUMO orbital. These predicted absorption bands are 8 nm higher than the experimental absorption bands observed at 322 and 298 nm for L1, and this agreement between the experimental and TD-DFT calculated absorption spectra provides useful clues for molecular engineers to further assess the spectral features of the BDF complex relative to Z907, since the only difference in these sensitizers is the ancillary bipyridyl ligand.

In order to augment the molar extinction coefficient with the \(\pi\)-conjugation extension through 4,4′-bis(9,9-dibutyl-9H-fluorene-2-yl)-[2,2] bipyridinyl of BDF relative to 4,4′-dinonyl-2,2′-bipyridine in the Z907 complex, the electronic ground state of these fully protonated complexes are optimized and the corresponding occupied (HOMO to HOMO-6) and unoccupied (LUMO to LUMO+6) frontier orbitals of BDF are shown in figure 5, while those of Z907 are shown in figure A.14 in the appendix. As expected, the occupied and unoccupied molecular orbitals of BDF are similar to those of Z907. The first three occupied (HOMO to HOMO-2) orbitals of BDF exhibit a ruthenium \(t_{2g}\) character with size mixing from the thiocyanate ligand; while HOMO-4 and HOMO-5 have considerable mixing of the Ru-NCS with \(\pi\)-bonding orbitals of 4,4′-bis(9,9-dibutyl-9H-fluorene-2-yl)-[2,2] bipyridine (L1) and 4,4′-dicarboxylicacid-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 is favorable for lifting their energy levels (figure 6). As can be seen in the electronic...
Figure 5. Frontier molecular orbitals of BDF: (a) LUMO + 6; (b) LUMO + 5; (c) LUMO + 4; (d) LUMO + 3; (e) LUMO + 2; (f) LUMO + 1; (g) LUMO; (h) HOMO; (i) HOMO-1; (j) HOMO-2; (k) HOMO-3; (l) HOMO-4; (m) HOMO-5 and (n) HOMO-6.

absorption spectrum of BDF, two absorption bands in the UV region (one at 300 nm and another one at 339 nm) correspond to the $\pi-\pi^*$ transitions of bipyridyl ligands (shown in figure 2(a)), in which the L1 metalation with ruthenium(II) increases the spectral response along with bathochromic shift. However, the increase in the conjugation length through the adoption of fluorene moiety resulted in a slight increase in the molar extinction coefficient of metal-to-ligand charge transfer (MLCT) absorption bands, which could possibly be due to lifting their occupied molecular orbitals energy levels as compared to those of Z907. The calculated dipole moment for BDF is 17.707 Debye is slightly larger compared to that of Z907 (16.343 Debye). For Z907, the HOMO-3 is a non-bonding combination localized on the NCS ligand, while the HOMO-3 orbital of BDF is also a non-bonding combination localized only on the NCS ligand. The HOMO-4 and HOMO-5 of BDF are combinations of the $\pi$-bonding orbitals of 4,4-bis(9,9-dibutyl-9H-fluorene-2-yl)-[2,2]bipyridine, the NCS ligand and the ruthenium center, which lifted their energy levels as compared to those of the corresponding occupied molecular orbitals of Z907. In the case of LUMO, the electron distribution moves toward anchoring groups, while assuming similar molecular orbital geometry when
adsorbed on the 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. In the case of the higher unoccupied molecular orbitals of the ancillary bipyridyl ligand, L1, the $\pi^*$-orbitals move from the $\pi$-system to bipyridine moieties and this transfer in BDF significantly depresses the LUMO $+$ 4 and LUMO $+$ 5 orbitals and moderately extends the LUMO $+$ 1 orbital relative to those of Z907.

### Table 1. Detailed photovoltaic parameters of DSSCs.

| Sensitizer | $J_{\text{SC}}$ (mA cm$^{-2}$) | $V_{\text{OC}}$ (mV) | ff | $\eta$ (%) |
|-----------|-------------------------------|----------------------|----|---------|
| BDF       | 14.66                         | 640                  | 0.71 | 6.58    |
| Z907      | 11.52                         | 566                  | 0.72 | 4.65    |

Short-circuit photocurrent density ($J_{\text{SC}}$), open-circuit voltage ($V_{\text{OC}}$), fill factor (ff). The electrolyte composition of E01 is 0.05 M I$_2$, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-π-propylimidazolium iodide, 0.5 M 4-tert-butylpyridine in acetonitrile solvent.

3.4. Photovoltaic performance of DSSCs based on the dyes

The photovoltaic performance of BDF was evaluated by employing a high-quality double-layer titania film (9.0 $\pm$ 4.8 $\mu$m) and a high-efficiency liquid electrolyte to construct 0.54 cm$^2$ active area dye-sensitized solar cells. To see the influence of 4,4-bis(9,9-dibutyl-9H-fluorene-2-yl)-2,2-bipyridine as the $\pi$-conjugation extension in BDF relative to the 4,4′-dinonyl-2,2′-bipyridine in Z907, the incident photon-to-current conversion efficiencies (IPCEs) of the sensitizers plotted as a function of excited wavelength were compared (figure 7). The photocurrent action spectrum of BDF showed a broad plateau IPCE spectrum with exceeding IPCE of 83%, while that of Z907 exhibited a broad plateau relatively red-shifted IPCE spectrum with a maximum IPCE reaching 81%. The BDF sensitizer gives the short-circuit photocurrent density ($J_{\text{SC}}$), open-circuit voltage ($V_{\text{OC}}$) and a fill factor (ff) of 14.66 mA cm$^{-2}$, 640 mV and 0.71, respectively, yielding an overall energy conversion efficiency ($\eta$) of 6.58%, while the test device fabricated under identical conditions with Z907 dye gave $J_{\text{SC}}$ of 11.52 mA cm$^{-2}$, $V_{\text{OC}}$ of 566 mV and an ff of 0.72 yielding an overall energy conversion efficiency of 4.65%. When compared to the Z907 sensitized solar cell, the BDF sensitized solar cell is expected to show a lower power conversion efficiency due to its lower packing density over the TiO$_2$ surface, but the higher $J_{\text{SC}}$ of BDF relative to that of Z907 could probably be favored by a more localized electron cloud over the 4,4′-dicarboxylic-2,2′-bipyridine in LUMO orbital as compared to the corresponding LUMO orbital of Z907. The sum of Mullikan atomic charges calculated for the LUMO orbital of BDF is $-0.27413$, larger as compared to the corresponding orbital of a Z907 sensitizer ($-0.26613$). This indicates that a larger charge transfer from HOMO to LUMO takes place in the BDF complex relative to that of Z907, which...
may favorably support better anchoring and better electron injection onto the TiO$_2$ surface.

One of the desirable parameters to sustain the initial photovoltaic performance of the DSSC over a long period is the high thermal stability of the ruthenium(II) sensitizer. TGA analysis of the new ruthenium(II) sensitizer, BDF, was performed using a thermo-gravimetric/simultaneous differential thermal analysis (TGA/SDTA) 851° thermal system (Mettler Toledo, Switzerland) by heating at a rate of 10°C min$^{-1}$ in the temperature range of 50–600°C under N$_2$ atmosphere (flow rate of 30 ml min$^{-1}$) to see the influence of fluorene substitution on thermal stability. 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 thermo-gram of BDF obtained was compared under identical conditions with that of Z907. Figure 8(b) shows the derivative of % conversion with respect to temperature, in which both the thermo-grams of BDF and Z907 initially follow a similar trend up to around 200°C and, then, BDF loses its mass quickly and thereby a decrease in thermal stability by around 100°C was observed as compared to that of Z907. In order to investigate further the factors contributing to the decreased thermal stability of the ruthenium(II) complex, TGA analysis was performed under similar conditions for the ancillary ligands 4,4-bis(9,9-dibutyl-9H-fluorene-2-yl)-[2,2] bipyridine and 4,4′-dinonyl-2,2′-bipyridine and the derivative of per cent of conversion versus temperature are shown in figure 8(a). The thermo-gram of L$_2$ shows a transition at 420°C, while that of L$_1$ shows it at around 470°C yielding an increase in thermal stability by 50°C, which could be attributed to the conjugation of aromatic phenyl units against nonyl moieties with bipyridine. During the metal complex formation, these aromatic alkyl-fluorene-substituted units might have weakened the chelating bonds of the ruthenium-bipyridine due to the presence of the bulky fluorene moieties. 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.

4. Conclusions

In summary, a new ruthenium(II) bipyridyl sensitizer was synthesized with the adoption of 4,4-bis(9,9-dibutyl-9H-fluorene-2-yl)-[2,2] bipyridine as an ancillary ligand, where the increase of conjugation length through 9,9-dibutyl-9H-fluorene resulted in an increased spectral response relative to that of the reference Z907 sensitizer. The sensitizer exhibited a comparable photocurrent action spectrum, but a larger power conversion efficiency of 6.58% compared to that of 4.65% for Z907 sensitized solar cell fabricated and evaluated under similar conditions. TGA analysis showed relatively less thermal stability for the BDF complex. The agreement between the experimental absorption measurements and the TDDFT calculations allows for detailed assessment of the main spectral features of the BDF complex and provides valuable information for designing new sensitizers with desirable absorption properties.

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Appendix

In this appendix some supporting information is presented.

Figure A.1. $^1$H-NMR (δ ppm) spectrum of 2-bromo-fluorene (1).
Figure A.2. ESI–MAAS spectrum of 2-bromo-fluorene (1).

Figure A.3. $^1$H-NMR ($\delta$ ppm) spectrum of 2-bromo-9,9$'$-dibutyl-9H fluorene (2).

Figure A.4. ESI–MASS spectrum of 2-bromo-9,9$'$-dibutyl-9H fluorene (2).
Figure A.5. $^1$H-NMR ($\delta$ ppm) spectrum of 9,9$'$-dibutyl-9H-fluorene-2-yl-boronic acid (3).

Figure A.6. ESI–MASS spectrum of 9,9$'$-dibutyl-9H-fluorene-2-yl-boronic acid (3).

Figure A.7. $^1$H–NMR ($\delta$ ppm) spectrum of 4,4$'$-bis(9,9-dibutyl-9H-fluorene-2-yl)-[2,2$'$] bipyridine (L1).
Figure A.8. ESI–MASS spectrum of 4,4′-bis(9,9-dibutyl-9H-fluorene-2-yl)-[2,2′] bipyridine (L1).

Figure A.9. $^1$H-NMR (δ ppm) spectrum of BDF.

Figure A.10. ESI–MASS spectrum of BDF.
Table A.1. Transition assignments calculated at B3LYP/6-31G(d).

| Ancillary ligand                      | Transition energy nm$^{-1}$ | Oscillator strength | Transition assignments*                   |
|--------------------------------------|-----------------------------|--------------------|------------------------------------------|
| 4,4′-Bis(9,9-dibutyl-9H-fluorene-2-yl)-[2,2]bipyridinyl (L1) | 330 314 291            | 1.12 0.74 0.08    | H-2 → L(0.14); H-1 → L(−0.61);          |
|                                      |                             |                    | H → L(0.23); H → L + 1(0.20)             |
|                                      |                             |                    | H → L + 2(−0.37)                           |
| 4,4′-dinonyl-2,2′-bipyridine (L2)    | 287 274 272 255           | 0.002 0.496        | H-1 → L(0.7015)                           |
|                                      |                             |                    | H-4 → L(−0.133); H → L(0.669); H → L + 2(0.133) |
|                                      |                             |                    | H-4 → L(0.674); H-1 → L + 1(−0.177)       |
|                                      |                             |                    | H-2 → L + 1(−0.478); H-1 → L + 2(0.507)   |

*H = HOMO, L = LUMO, etc.

Figure A.11. FT-IR spectrum of BDF.

Figure A.12. TiO₂ film absorbance of BDF (solid line) and Z907 (dotted line).

Figure A.13. Transition involved molecular orbitals of L2: (a) LUMO + 3; (b) LUMO + 2; (c) LUMO + 1; (d) LUMO; (e) HOMO; (f) HOMO-1; (g) HOMO-2; (h) HOMO-3 and (i) HOMO-4.
Figure A.14. Frontier molecular orbitals of Z907: (a) LUMO + 5; (b) LUMO + 4; (c) LUMO + 3; (d) LUMO + 2; (e) LUMO + 1; (f) LUMO; (g) HOMO; (h) HOMO-1; (i) HOMO-2; (j) HOMO-3; (k) HOMO-4 and (l) HOMO-5.

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