Research Article

High Molar Extinction Coefficient Ru(II)-Mixed Ligand Polypyridyl Complexes for Dye Sensitized Solar Cell Application

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1. Introduction

Among various photo voltaic technologies, dye-sensitized solar cells (DSSCs) are known to be less expensive, easy to fabricate and very efficient at varied incident angle of light. Therefore, intense attention has been devoted in the last two decades to the synthesis of new materials as sensitizers, metal oxide semiconductors, counter electrode materials, electrolytes, and so forth, for applications in high-performance and long-durable DSSCs [1–6]. Especially sensitizer plays an important role in the DSSCs device for obtaining high-efficiency and long-term durability because of the possibility to chemically modify the sensitizer for better anchoring on TiO₂, electron injection property and HOMO-LUMO tuning. To achieve this, many researchers around the world have been working either on modification of various reported sensitzers or designing new sensitizers. A variety of ruthenium(II) polypyridyl, terpyridyl and tetrapyridyl complexes, metal-free organic sensitizers, porphyrins, and phthalocyanines have been developed, since Graetzel introduced the first efficient nanocrystalline TiO₂ solar cell sensitized with cis-bis(thiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis (tetrabutylammonium) (N719) [7–14]. Introduced in 1997, another ruthenium complex, black dye [tri(isothiocyanato)-2,2′,2″-terpyridyl-4,4′,4″-tricarboxylate ruthenium(II)] showed broad spectral absorption (ranging from 400 to 800 nm) and achieved a record 10.4% (air mass 1.5) solar to power conversion efficiency in full sunlight [15, 16]. However, the molar extinction coefficient of the sensitizer is relatively much lower as compared to the most efficient N719 dye. In addition, long-term durability is found to be one of the key limitations of
2. DSSC Device Fabrication

The fluorine-doped SnO2 (FTO) conducting glass plates (Nippon Sheet Glass, 4 mm thick, 8 Ω/sq) were cleaned with a detergent solution, rinsed with water and ethanol to remove organics or any other contaminants, and then dried. The glass plates were treated in a UV-O3 system for 20 minutes and then laid a compact layer by treating the plates with 40 mM TiCl4 aqueous solution and heating at 70°C for 30 minutes to facilitate a good mechanical contact between the nanocrystalline TiO2 and the conducting FTO matrix. Over the glass plate, 9 μm thickness D18T (18 nm TiO2 particles) was laid as transparent layer and then a 4.8 μm thickness HPW-400 (400 nm anatase TiO2 particles) was laid as scattering layer successively one over the other. The electrodes were coated with the TiO2 pastes, thus have an active area of 0.74 cm2, and were heated gradually under air flow for 5 minutes each at 325°C and 375°C and for 15 minutes each at 450°C and 500°C. The TiO2 electrodes were then allowed to cool and when the temperature attained to around 100°C, immersed in dye solutions of ethanol and remained soaked for 16 hours under dark. After taking out from the dye solutions, the electrodes were rinsed with ethanol to remove the unadsorbed dye molecules and then dried under nitrogen gas. The counter electrodes were prepared by treatment of FTO glass plates (TEC 15, 2.2 mm thickness, Lib bey-Owens-Ford Industries) with TiCl4 and further with a drop of H2PtCl6 solution (2 mg of Pt in 1 mL of ethanol) and heated at 430°C for 15 minutes. The dye sensitized TiO2 electrode and Pt counter electrode were assembled into a sealed sandwich type cell by heating with a hot-melt surlon film (Surlyn 1702, 25 μm thickness, Du-Pont) as a spacer between the electrodes. The ionic liquid electrolyte was filled through the predrilled hole present on the counter electrode using vacuum filling technique, the hole was sealed with a Surlyn disk and a thin glass to avoid leakage of the electrolyte.

3. Results and Discussion

3.1. Synthesis

The synthesis of these complexes is achieved following Scheme 1. The oxidation of 4,4′,4″-triethyl-2,2′:6′:2″-terpyridine to the tricarboxylic acid followed by esterification gives 4,4′,4″-trimethoxycarbonyl-2,2′:6′:2″-terpyridine. The bipyridine ligands L1 and L2 were synthesized by condensing 2,4,6-trimethylbenzaldehyde or 4-tert-butoxybenzaldehyde with tetraethyl 2,2′-bipyridine-4,4″-diylbis(methylene)diphosphonate under Wittig conditions. The reaction of ruthenium trichloride with the triester in presence of EtOH/CHCl3 under reflux for 4 hrs results in the trichloro Ru-complex. The complex is further refluxed for 4 hrs in DMF in presence of bipyridyl ligand (L1 or L2)
Scheme 1: Synthesis route of mLBD dyes; (i) K₂Cr₂O₇, H₂SO₄/H₂O, 80°C, 10 hours; (ii) MeOH, conc. H₂SO₄, reflux, 6 hours (iii) RuCl₃, EtOH/CHCl₃, reflux under dark, 4 hours; (iv) L₁ or L₂, DMF reflux, 4 hours; (v) NH₄NCS, reflux, 2 hours, TEA, water, reflux, 48 hours.

followed by addition of excess NH₄NCS, under refluxing conditions in DMF. The triester mixed ligand complex is finally treated with TEA in water under refluxing conditions for 48 hrs resulted in the formation of mLBD₁ and mLBD₂ complexes. The crude complexes obtained were purified on Sephadex LH20 column chromatography to afford mLBD₁ and mLBD₂ sensitizers as pure compounds. The new sensitizers were fully characterized by UV-Vis, emission, cyclic voltammogram, and other spectroscopic means, and the structures of the compounds are confirmed by ¹H NMR, ESI-MASS, FT-IR spectroscopes.

4.4′,4′′-triethyl-2,2′:6′:2′″-terpyridine was prepared according to reported procedure ref. Tetrabutylammonium-hydroxide, 2, 4, 6-trimethylbenzaldehyde or 4-tert-butoxybenzaldehyde, ammonium thiocyanate, sodiumhydride, and ruthenium trichloride were purchased from Sigma-Aldrich.
All solvents and reagents, unless otherwise stated, were of Laboratory Reagent Grade and used as received. The tetraethyl 2,2'-bipyridine-4,4'-diylbis(methylene)diphosphonate was prepared in accordance to the reported procedure. Sephadex LH-20 was procured from GE Healthcare Bio-Sciences AB, SE-75184, Uppsala and was used to purify the crude complexes on column chromatography. Bruker 300Avance $^1$H-NMR spectrometer run at 500 MHz was employed to record the $^1$H-NMR spectrum. Shimadzu LCMS-2010EV model with ESI probe was employed for MASS analysis. Shimadzu UV-Vis spectrometer (model 1700) and Fluorolog 3, J. Y. Horiba Fluorescence spectrometer were employed to record the electronic absorption and emission spectra.

**Synthesis of 4,4',4''-Tricarboxy-2,2':6',2''-Terpyridine (1).** 4, 4',4''-triethyl-2,2'-6',2''-terpyridine (10 g, 31.55 mmol) was added to a mixture of Conc. H$_2$SO$_4$ and water (150 mL + 150 mL), and dissolved at room temperature. To this solution, K$_2$Cr$_2$O$_7$ (62.1 g, 211.4 mmol) was added in portions for about 4 hours (note: while adding K$_2$Cr$_2$O$_7$, vigorous exothermic reaction takes place, cooling is necessary to avoid the reaction temperature to exceed 50°C). The cooling bath was removed, and the reaction flask was heated to 80°C using heating mantle for 6 hours with stirring. After allowing it to cool to room temperature, the reaction mixture was poured into ice water (1200 mL). After keeping it for 4 hours at 0°C, suspension was filtered by suction. The separated greenish-yellow precipitate was washed thoroughly with distilled water (until the filtrate is colorless) and dried under vacuum to give 4,4',4''-terpyridine acid, which was characterized by $^1$H-NMR spectroscopy. $^1$H-NMR (D$_2$O/NaOD) ppm: 7.72 (2H, dd), 8.22 (2H, s), and 8.62 (2H, d), 8.82 (2H, d). Chemical formula ESIMS: C$_{32}$H$_{32}$N$_2$ (M+H)$^+$: 444 (100%).

**Synthesis of 4,4',4''-Tricarboxy-2,2':6':2''-Terpyridine (2).** To a suspension of 4,4',4''-tricarboxy-2,2':6':2''-terpyridine (20.0 g, 5.49 mmol) in absolute methanol (850 mL) was added conc. sulfuric acid (115 mL). The mixture was refluxed for 6 hours to obtain a clear solution and then cooled to room temperature. Water (400 mL) was added and the excess methanol removed under vacuum. The pH was adjusted to neutral with NaOH solution, and the resulting precipitate was filtered and washed with water (pH = 7.0). The solid was dried to obtain 17.0 g of desired compound. $^1$H-NMR (300 MHz, CDCl$_3$, $\delta$): 3.95 (3H, s, CH$_3$); 4.05 (6H, s, CH$_2$); 7.98 (2H, d, $J$ = 6 Hz, aryl H on C5 and C5'); 8.88 (2H, d, $J$ = 6 Hz, aryl H on C6 and C6'); 9.00 (2H, s, aryl H on C3 and C3'); 9.20 (2H, d, $J$ = 6 Hz) ESIMS: (C$_{21}$H$_{17}$Cl$_3$N$_3$O$_6$Ru) (M+H)$^+$: 615 (25%).

**Synthesis of Ruthenium Trichloro Complex (3).** Ruthenium tri chloride (642 mg, 2.5 mmol) was dissolved in a mixture of ethanol and chloroform (100 mL). To this, 4,4',4''-tricarboxyterpyridine (1.0 g, 2.5 mmol) was added, and then, the reaction mixture was refluxed for 4 hours under nitrogen atmosphere in the absence of light. The progress of the reaction was monitored by UV-VIS spectrometry. After completion of 3 hours, the solution was concentrated on a rotary evaporator. The crude trichloro compound washed with ethanol and dried under vacuum to obtain white solid (85% yield) $^1$H-NMR (D$_2$O/NaOD) ppm: 8.70 (d, 2H), 8.22 (s, 2H), 8.10 (s, 2H), 7.62 (2H, d), ESI-MS: (C$_{21}$H$_{17}$Cl$_3$N$_3$O$_6$Ru) (M+H)$^+$: 615 (25%).

**Synthesis of L1 and L2 (Representative Procedure).** Sodium hydride (177 mg, 7.38 mmol) was washed with dry hexane (3 x 10 mL). To this suspension, a THF solution of tetraethyl 2,2''-bipyridine-4,4''-diylbis(methylene)diphosphonate derivative (560 mg, 1.23 mmol) was added, and the resulting mixture was stirred at room temperature for a period of 30 minutes. To this, 2,4,6-trimethyl benzaldehyde (546 mg, 3.69 mmol dissolved in THF) or 4-tert-butoxy benzaldehyde (656 mg, 3.69 mmol dissolved in THF) was added dropwise at room temperature while stirring. The reaction mixture was refluxed for 12 hours and then allowed to cool to room temperature. The reaction mixture was filtered through a short plug of silica gel using diethyl ether. The filtrate was concentrated, and methanol was added. The corresponding bipyridyl ligand was precipitated and the precipitate was filtered and washed with cool methanol. The solid was dried to obtain pure L1 or L2.

4, 4'-Bis-[2-(2,4,6-Trimethyl-Phenyl)-Vinyl]-[2, 2']-Bipyridine (L1). $^1$H-NMR (300 MHz, 25°C, CDCl$_3$) 2.35 (s, 18H), 6.58 (d, 1H), 6.62 (s, 4H), 7.25 (s, 2H), 7.31 (d, 1H), 8.63 (d, 2H), 8.71 (d, 2H); ESI-MS: (C$_{32}$H$_{32}$N$_2$) (M+H)$^+$: 444 (100%).

4, 4'-Bis-[2-(2-(Tert-Butoxy Phenyl)-Vinyl)]-[2, 2']-Bipyridine (L2). $^1$H-NMR (200 MHz, 25°C, CDCl$_3$) ppm: 8.67 (d, 2H), 8.54 (s, 1H), 7.46 (m, 8H), 7.06 (m, 6H), 1.40 (s, 18H). Chemical formula (C$_{34}$H$_{36}$N$_2$O$_2$), ESI-MS: Calcd for (M+H)$^+$: 504 (55%).

**Synthesis of mLBD Complex (Representative Procedure).** Dry DMF (100 mL) was placed into 250 mL RB flask, to which ruthenium trichloro complex (200 mg, 0.32 mmol) was added under nitrogen atmosphere, the resulting solution was stirred for five minutes, and then, L1 or L2 (0.391 mmol) was added. The reaction mixture was refluxed for 4 hours under N$_2$ atmosphere. After completion of 4 hours, the mixture was cooled to 80°C, and then, aqueous solution of ammonium thiocyanate (768 mg in 2 mL of water) was added. The mixture was further refluxed for 2 hours. The progress of the reaction was monitored by UV-VIS spectroscopy. After 2 hours, the reaction mixture was cooled to room temperature, and triethylamine was added followed by water (2 mL + 2 mL). The mixture was further refluxed for 48 hours. Then,
This purification procedure was repeated 3-4 times to a MeOH. The main band was collected and concentrated. The crude compound was dissolved in MeOH and methanolic TBA and purified with water and dried under vacuum. The solvent was removed on rotary evaporator, and water was added to get the precipitate. The solid was filtered, washed with water and dried under vacuum. The crude compound was dissolved in MeOH and methanolic TBA and purified with water and dried under vacuum. The crude compound was collected and concentrated. This purification procedure was repeated 3-4 times to afford mLBD1 and mLBD2 dyes in the pure form.

**mLBD1.** \(^1\)H-NMR (300 MHz, CD3OD + CDCl3, \(\delta_{\text{H}}\)): 9.50 (d, 1H), 8.95 (s, 2H), 8.88 (d, 1H), 8.75 (s, 2H), 8.68 (d, 1H), 8.05 (d, 1H), 7.85 (d, 2H), 7.75 (m, 4H), 7.40 (d, 2H), 7.10 (d, 1H), 6.90 (s, 1H), 6.85 (s, 2H), 6.75 (s, 2H), 6.40 (d, 1H), 3.50–0.86 (m, 90H). ESI-MASS: RuC35H34N8O8S(1TBA)(M + 1) = 1272(80%). IR (KBr): \(\nu\) = 2965 cm\(^{-1}\) (CH3), 2095(NCS), 1605(COO\(_{\text{sym}}\)), 1529(BPy), 1474(BPy), 1354(COO\(_{\text{sym}}\)).

**mLBD2.** \(^1\)H-NMR (300 MHz, CD3OD + CDCl3, \(\delta_{\text{H}}\)): 9.65 (d, 1H), 9.10 (s, 2H), 9.00 (s, 1H), 8.90 (s, 2H), 8.70 (s, 1H), 8.20 (d, 1H), 7.85 (d, 2H), 7.75–7.38 (m, 10H), 7.25–6.75 (m, 6H), 3.50–0.86 (m, 90H). ESI-MASS: RuC35H34N8O8S(1TBA)(M + 1) = 1272(80%). IR (KBr): \(\nu\) = 2965 cm\(^{-1}\) (i-butyl), 2095(NCS), 1605(COO\(_{\text{sym}}\)), 1529(BPy), 1474(BPy), 1354(COO\(_{\text{sym}}\)).

### 3.2. Absorption, Emission, and Electrochemical Properties

To have a preliminary evaluation of the light harvesting capacity of the new sensitizers, the electronic absorption spectra were recorded in ethanol and compared with that of black dye. As compared to black dye, these new sensitizers show intense UV absorption band at around 380 nm, which are assigned to the ligand centred \(\pi-\pi^*\) transition of the H3ctpy ligand [25, 26] and other intense low-energy absorption band at around 510 nm. The low-energy absorption band is assigned to metal-to-ligand charge-transfer (MLCT) transition. Absorption spectra of these dyes are very different from that of black-dye, which exhibit intense and broad absorption bands at about 430 and 520 nm and a distinct shoulder low-energy absorption band at around 700 nm extending up to 850 nm (Figure 2). As compared to black dye, the low-energy absorption bands of mLBD dyes are blue-shifted. The dyes showed molar extinction coefficients of 17600 M\(^{-1}\) cm\(^{-1}\) for mLBD1 and 21300 M\(^{-1}\) cm\(^{-1}\) for mLBD2 both at \(\lambda\) maximum of 512 nm, while black dye has shown 8660 M\(^{-1}\) cm\(^{-1}\) at \(\lambda\) maximum of 615 nm. The mLBD dyes increased the light-harvesting ability of the new sensitizers by enhancing their molar extinction coefficients by around 50%, especially in the wavelength region of 400–550 nm, which could be the contribution of extended \(\pi\)-conjugation of these bipyridyl ligands L1 and L2.

In case of mLBD dyes, the increased molar extinction coefficient is expected due to extension of \(\pi\)-conjugation, which is akin to the molecular cosensitization for efficient panchromatic DSSC sensitizers [27]. What is expected of these dyes is maintaining the absorption spectrum of black-dye, while enhancing the molar extinction coefficient. But the introduction of these bipyridyl ligands shifted the absorption spectrum towards blue region. To understand the molar extinction coefficient’s augment and the blue-shifted absorption spectrum, time-dependent density functional theory calculations were run based on DFT optimized structure in ethanol medium. The conductor-like polarizable continuum model (C-PCM), which accounts for the effects of the solvent molecule ethanol was used along with the calculations. In mLBD dyes, the replacement of two thiocyanato anions by a single chelating \(\pi\)-conjugated bipyridine ligand stabilizes the ground state with less electron donation to the centre ruthenium(II), and this causes a decrease in the overall energy of the t2g metal orbitals. For these complexes, the low-energy MLCT transition bands from this orbital to LUMO exhibit significant blue shift [28].

Besides the molar extinction coefficient, the photovoltaic performance of DSSC is also influenced by quantity of absorbed dye and its pattern over TiO2 surface, which is further dependent on the size and geometrical structure of photosensitizer. To investigate further, the absorption measurements over TiO2 films were carried out by staining 7 μm thick TiO2 electrodes in 0.3 mM dye solutions prepared in ethanol for 16 hours under the dark. After that the electrodes were washed with ethanol to remove unadsorbed dye molecules and dried under nitrogen purging. The absorptions recorded using UV-Vis spectrometer showed relatively decreased film absorptions as compared with that of black dye. The substitution of two NCS anions by 4,4’-bis(2,4,6-trimethylstyryl)-2,2’-bipyridine and 4,4’-bis(4-tert-butoxy styryl)-2,2’-bipyridine in the black dye increased the molecular size by more than one and half times, and additionally, this influenced the packing densities of these molecules on TiO2 films.

Prior to fabrication of DSSC devices, cyclic voltammetry measurements of the sensitizers were conducted to ensure that the LUMOs of these complexes are suitable for injecting electrons into the conduction band of TiO2 and also whether their HOMOs match the energy level of the I2/iodide redox couple. The cyclic voltammogram of these dyes were measured using tetrabutyl ammonium perchlorate (0.1 M in acetonitrile) as an electrolyte and ferrocene as an internal standard.
density distribution mainly located on the metal centre and NCS anions. TD DFT calculations showed the highly allowed transition from HOMO−2/HOMO−3 to LUMO+2 orbital, in which the electron densities of HOMO−2 and HOMO−3 are located at the metal centre, NCS ligand and the chelating L1 or L2 bipyridine, whereas that of LUMO+2 orbital is contributed to mainly by L1 or L2 bipyridine moieties. The HOMO/LUMO band gaps predicted through the DFT optimization are 2.035 and 2.045 eV for mLBD1 and mLBD2, respectively, while the band gap for parental black-dye optimized under similar conditions is 1.89 eV.

3.4. Thermal Stability. The incorporation of the ancillary bipyridine ligands into the parental black dye make the dye more hydrophobic and one of the advantages of these mixed ligand dyes could be their stability obtained by the replacement of NCS anions by stable panchromatic chelating ancillary bipyridine ligand [29]. One of the desirable parameters to retain the initial photovoltaic performance of the DSSC is the high thermal stability of the ruthenium(II) sensitizer [30], and hence, the TGA analysis of the sensitizers was performed using a TGA/SDTA 851-e thermal system (Mettler Toledo, Switzerland) at heating rate of 10°C/min in the temperature range of 25°C–600°C under N2 atmosphere (flow rate of 30 mL/min). Film samples ranging from 8 to 10 mg were placed in the sample pan and heated, while weight losses are recorded against temperature difference. The thermograms of mLBD dyes are shown in Figure 6, in which the derivative of % conversion plotted against to temperature. The thermograms show a very good thermal stability (310°C for mLBD1 and 350°C for mLBD2), while under comparable conditions the black dye showed 290°C.

3.5. Photovoltaic Properties. To evaluate the influence of 4, 4′-bis(2,4,6-trimethylstyryl)-2,2′-bipyridine and 4,4′-bis(4-tert-butoxy styryl)-2,2′-bipyridine on the photovoltaic performance, a high-quality double-layer titania films (9 + 4.8 µm) were employed to fabricate 0.74 cm² active area DSSC cells in combination with a high durable electrolyte, Z580, containing 0.2 M I2, 0.5 M guanidinium thiocyanate and 0.5 M N-methylbenzimidazole in a mixture of 1-propyl-3-methylimidazolium iodide/1-ethyl-3-methylimidazolium tetracyanoborate (65/35, v/v). Photon-to-current conversion efficiency spectrum was recorded as a function of excitation wavelength using a 300 W xenon lamp (ILC Technology, USA), which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.). The incident photon-to-current conversion efficiencies (IPCEs) of the DSSCs constructed based on these dyes are shown in Figure 7(a). The monochromatic incident photon-to-collected electron conversion efficiencies of 60.71% and 75.89% were obtained for mLBD1 and mLBD2 dyes, respectively, over the entire visible range extending into the NIR region, which are less than unity suggesting a low-charge collection yields. The photo current-voltage measurements were executed under air mass (AM) of 1.5 sunlight and the resultant I−V curves are shown in Figure 7(b). The photovoltaic parameters of mLBD dyes are compared with that of black dye-sensitized solar
Figure 4: Frontier molecular orbitals of mLBD: (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.

cell, fabricated, and evaluated under comparable conditions (Table 1).

The energy conversion efficiencies of mLBD1 and mLBD2 dyes are 3.15% ($J_{SC} = 11.86 \text{ mA/cm}^2$, $V_{OC} = 613 \text{ mV}$, $ff = 0.4337$) and 3.36% ($J_{SC} = 12.71 \text{ mA/cm}^2$, $V_{OC} = 655 \text{ mV}$; $ff = 0.4042$), respectively, under air mass of 1.5 sun light, the reference black-dye sensitized solar cell, fabricated, and evaluated under identical conditions exhibited $\eta$-value of 2.69% ($J_{SC} = 10.95 \text{ mA/cm}^2$, $V_{OC} = 655 \text{ mV}$, $ff = 0.3750$). Although the film absorptions of mLBD dyes over TiO$_2$ films are little lower as compared to that of black dye, the newly designed mLBD dyes were endowed with improved over
Figure 5: Frontier molecular orbitals of mLBD: (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/cm²)</th>
<th>$V_{OC}$ (mV)</th>
<th>ff</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mLBD1</td>
<td>11.86</td>
<td>613</td>
<td>0.4337</td>
<td>3.15</td>
</tr>
<tr>
<td>mLBD2</td>
<td>12.71</td>
<td>655</td>
<td>0.4042</td>
<td>3.36</td>
</tr>
<tr>
<td>BD</td>
<td>10.95</td>
<td>655</td>
<td>0.3750</td>
<td>2.69</td>
</tr>
</tbody>
</table>

Short-circuit photocurrent density ($J_{SC}$), open-circuit photovoltage ($V_{OC}$), fill factor (ff).

all conversion efficiencies. This could be probably due to more charge transfer to the LUMO orbitals for these dyes as compared to black dye. In the LUMO orbitals of these complexes, the electron density distributions mainly located on H$_3$tctpy ligand, while for black dye it is only ascribed to the centre pyridine of H$_3$tctpy [31]. As compared to the black dye-sensitized solar cell, the mLBD dyes showed higher current densities, which could be probably because of their increased incident photon to-current conversion efficiencies spectra. The mLBD2 sensitized solar cell gives $J_{SC} = 12.71$ mA/cm², which is slightly higher as compared to that of mLBD1 sensitized solar cell. Although there is no much change in their film absorptions over TiO$_2$ films, we presume that the increased photocurrent density and hence the efficiency of mLBD2 could be probably resulting from efficient dye regeneration mediated by redox electrolyte [32].

4. Conclusions

In conclusion, the new panchromatic ruthenium(II) terpyridyl-based mixed ligand dyes, mLBD1 and mLBD2 synthesized, showed much higher molar extinction coefficients at 400–550 nm remarkably with blue shift in absorption spectrum as compared to black-dye. Incorporation of conjugated light-absorbing ancillary bipyridine ligands into the new mixed ligand ruthenium(II) complexes provide a combined benefit of electron donor from ancillary conjugated bipyridyl ligand as well as electron acceptor anchoring terpyridine tricarboxylic acid in the sensitiser to achieve better charge transfer from HOMO to LUMO. Though these ancillary bipyridines do not directly interfere with active sites of TiO$_2$ electrode, the molecular diameter increased significantly and to some extent influenced the packing densities.
of the sensitizers over TiO$_2$ films. These heteroleptic sensiti-
zizers exhibited better solar energy conversion efficiencies as
compared to the standard black dye and mLBD2 sensitizer
that showed an efficiency of 3.36%, highest among the three.

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