

## Research Article

# Synthesis and Study of the Physical and Photovoltaic Properties of Novel Heteroleptic Ruthenium(II) Complexes Ligated with Highly $\pi$ -Conjugated Bipyridine Ancillary and Phenanthroline Anchoring Ligand for Dye-Sensitized Solar Cells

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Six new heteroleptic ruthenium(II) complexes (**JM1**–**JM6**), each bearing a highly  $\pi$ -conjugated bipyridine ancillary ligand (a methoxy-substituted analog ( $L_1$ ) and a phenanthroline-type anchoring ligand ( $L_2$ ) (dcphen or dcvphen;  $[\text{Ru}(L)_2(\text{NCS})_2][\text{TBA}]_2$ ;  $L_1 = 4,4'$ -bis{2-(3,4-dimethoxyphenyl)ethenyl}-2,2'-bipyridine (dmpbpy), 4,4'-bis{2-(1,1'-biphenyl)-4-ylethenyl}-2,2'-bipyridine (bpbpy), or 4,4'-bis{2-(4'-methoxy-[1,1'-biphenyl]-4-ylethenyl)-2,2'-bipyridine (mbpbpy);  $L_2 = 4,7$ -dicarboxy-1,10-phenanthroline (dcphen) or 4,7-bis(*E*-carboxyvinyl)-1,10-phenanthroline (dvcphen)) were synthesized, and their physical and photovoltaic properties were investigated. Various dye-sensitized solar cells (DSSCs) were fabricated using heteroleptic ruthenium(II) complexes. Ruthenium(II) complex **JM1**, ligated to dmpbpy (ancillary) and dcphen (anchoring) ligands, exhibited the maximum power conversion efficiency (PCE) value of 3.40%, which was approximately 71% of the efficiency exhibited by the commercially available **N719**-sensitized solar cells. Ruthenium(II) complex **JM5**, ligated to mbpbpy (ancillary) and dcphen (anchoring) ligands, exhibited the second-best PCE value (2.52%), and ruthenium(II) complex **JM3**, ligated to bpbpy (ancillary) and dcphen (anchoring) ligands, exhibited a PCE value of 1.45%. It was observed that the PCE values of the DSSCs could be significantly improved by introducing the electron-donating methoxy group at proper positions of the ancillary ligands present in the heteroleptic ruthenium(II) complexes (such as **JM1** and **JM5**).

## 1. Introduction

Dye-sensitized solar cells (DSSCs) that operate in the presence of sunlight are interesting next-generation energy devices as they are cost-effective and exhibit high-power efficiency [1]. The principles of green energy technology are followed to fabricate and operate DSSCs. DSSCs can be classified into two categories based on the types of dyes used: one is cost-effective metal-free dyes that exhibit high molar extinction coefficient and flexibility in their layout, and the other is metal-based dyes that help achieve high photovoltaic (PV) performance. Among the various metal-based systems

used, systems containing ruthenium(II) complexes are studied extensively as they exhibit interesting electrochemical and photophysical properties. These properties can be attributed to the broad metal-to-ligand charge transfer (MLCT) absorption bands and suitable ground and excited state potentials [2]. The polypyridyl complexes formed with ruthenium(II) have been widely investigated as dye-sensitizers (as they are highly stable and exhibit excellent redox properties). The interest in this field grew after the publication of the results of Grätzel's pioneering research on the development of  $[\text{Ru}(\text{dcbpy})_2(\text{NCS})_2]$  (**N3**),  $[\text{Ru}(\text{dcbpy})_2(\text{NCS})_2][\text{TBA}]_2$  (**N719**) (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine, TBA = tetra

butylammonium), and  $[\text{Ru}(\text{tcterpy})(\text{NCS})_3][\text{TBA}]_3$  (black dye, **BD**) (tcterpy = 4,4',4''-tricarboxy-2,2':6',2''-terpyridine) (Figure 1(a)) [3–6].

A photosensitizer helps convert the energy of the incident sunlight (photon energy) to electrical energy. The most important component in a DSSC is the photosensitizer that helps improve the power conversion efficiency (PCE,  $\eta$ ). It is important to have knowledge on molecular engineering to enhance the efficiency of the DSSCs fabricated using ruthenium(II) based dye-sensitizers. One of the strategies followed to enhance the performance includes the modification of structural features, which can potentially help in the efficient harvesting of light and achieve an improved response. Various ruthenium(II) complexes have been studied by numerous researchers, and numerous ruthenium(II) complexes have been developed using identical *N,N*-ligands or two different *N,N*-ligands (a combination of an anchoring ligand and an ancillary ligand) [7]. The primary role of the sensitizer is to convert the energy of the incident sunlight to electrical energy. In addition, the sensitizer should have the ability to get chemisorbed onto the mesoporous oxide to maximize the overall efficiency of the device. In the case of known ruthenium(II) complex sensitizers, carboxylic acid group-containing bipyridine *N,N*-ligand, 4,4'-dicarboxy-2,2'-bipyridine (dcbpy) was mostly used as the anchoring ligand. The discovery of **BD** led to studies on various terpyridine-type anchoring ligands containing ruthenium(II) for the development of complex sensitizers. Several representative examples of terpyridine-type ligands studied previously, such as 4'-carboxy-2,2':6',2''-terpyridine (cterpy, **1**) [8], 4'-(4-carboxyphenyl)-2,2':6',2''-terpyridine (cpterpy, **2**) [9], 4'-(4-carboxyphenylene-ethylene)-v-terpyridine (cpeterpy, **3**) [10], 4'-(4-carboxyphenylene-ethylene-phenylene-ethylene)-v-terpyridine (cpeterpy, **4**) [10], 4'-thiophene-4,4'-dicarboxy-2,2':6',2''-terpyridine or 4'-(3,4-ethylenedioxythiophene)-4,4'-dicarboxy-2,2':6',2''-terpyridine (R-dcterpy, **5**) [11, 12], and 2,6-bis(4-carboxyquinolin-2-yl) terpyridine (cqterpy, **6**) [13] are shown in Figure 1(b). The power conversion efficiencies of DSSCs fabricated using the reported systems were in the range of 2.2%–10%. The difficulty in derivatizing the ligand limits the synthetic applications of the **BD**-type sensitizers. Therefore, the **N3**-type sensitizer bearing two different types of bipyridine ligands (ruthenium(II) complexes ligated to one dcbpy (anchoring) ligand that could be efficiently chemisorbed onto the mesoporous oxide and one ancillary ligand that bears an appropriate functionality for the conversion of the energy in incident sunlight to electrical energy) has been studied extensively to improve the performance of the solar cells [2, 14].

We have been trying to develop efficient photosensitizers and have primarily focused on the synthesis and application of the heteroleptic ruthenium(II) complexes as they exhibit interesting photophysical and electrochemical characteristics that can be potentially exploited to fabricate DSSC-based devices exhibiting good performances. Consequently, a series of novel heteroleptic ruthenium(II) complexes and dinuclear ruthenium(II) complexes that exhibited satisfactory PCE were synthesized. A series of compounds were

synthesized by varying the ancillary and/or anchoring ligands [15–19]. During the course of our study, we realized that anchoring ligands other than the bcbpy- or terpyridine-type ligands could be used for the fabrication of efficient DSSCs.

Herein, we report the design and synthesis of new heteroleptic ruthenium(II) complex photosensitizers that are ligated to highly  $\pi$ -conjugated bipyridine ancillary including methoxy-substituted analog and phenanthroline-type anchoring ligands. The systems were examined for the fabrication of DSSCs. It is important to identify appropriate ancillary and anchoring ligands for the design of a sensitizer dye that can be used for the development of DSSCs. An efficient dye must absorb light over a wide range in the electromagnetic region and exhibit a high molar extinction coefficient. Hence, bipyridine ligands containing aromatic rings in their scaffolds and bearing highly  $\pi$ -conjugated ethylene-phenylene and/or substituted alkoxy groups were used as the ancillary ligands. The ancillary ligands were varied to investigate the effect of  $\pi$ -conjugation and/or electron-donating ability of the alkoxy group (lone pair of electrons present in the system participates in conjugation) on the PCE values. The choice of the anchoring ligand is also important as efficient anchoring onto the mesoporous oxide surface can potentially improve the light-harvesting efficiency. In addition to well-known bipyridine- or terpyridine-type anchoring ligands, we attempted the less studied phenanthroline-based anchoring ligands for the fabrication of the sensitizers [16, 18]. As it looks encouraging, we studied the 4,7-dicarboxy-1,10-phenanthroline (dcphen) ligand and its  $\pi$ -conjugated 4,7-bis(*E*-carboxyvinyl)-1,10-phenanthroline (dcvphen) analog extensively in this study and determined their efficiency as anchoring ligands.

## 2. Materials and Methods

Most of the chemical reagents used in the studies were purchased from Aldrich Chemical Co. (St. Louis, MO, USA) and were used as received without further purification. All reactions were carried out under an atmosphere of dry nitrogen unless stated otherwise. The solvents were dried following the standard drying methods. 4,7-Dicarboxy-1,10-phenanthroline (dcphen) and 4,7-bis(*E*-carboxyvinyl)-1,10-phenanthroline (dcvphen) were prepared following previously reported protocols [16]. 4,4'-Bis{2-(3,4-dimethoxyphenyl) ethenyl}-2,2'-bipyridine (dmpbpy), 4,4'-bis{2-(1,1'-biphenyl)-4-ylethenyl}-2,2'-bipyridine (bpbpy), and 4,4'-bis{2-(4'-methoxy-[1,1'-biphenyl]-4-ylethenyl)-2,2'-bipyridine (mbpbpy) were prepared following previously reported protocols [19].

$^1\text{H}$  nuclear magnetic resonance (NMR) spectra were recorded using a 400 MHz NMR system (Jeol, Tokyo, Japan). The chemical shifts were reported in parts per million (ppm) relative to the residual solvent peak. Tetramethylsilane (TMS) was used as an internal standard. The gas chromatography/mass spectrometry (GC/MS) technique was used to characterize the prepared organic ligands and MALDI-TOF mass spectrometry technique was used to characterize the heteroleptic ruthenium(II) complex photosensitizers.

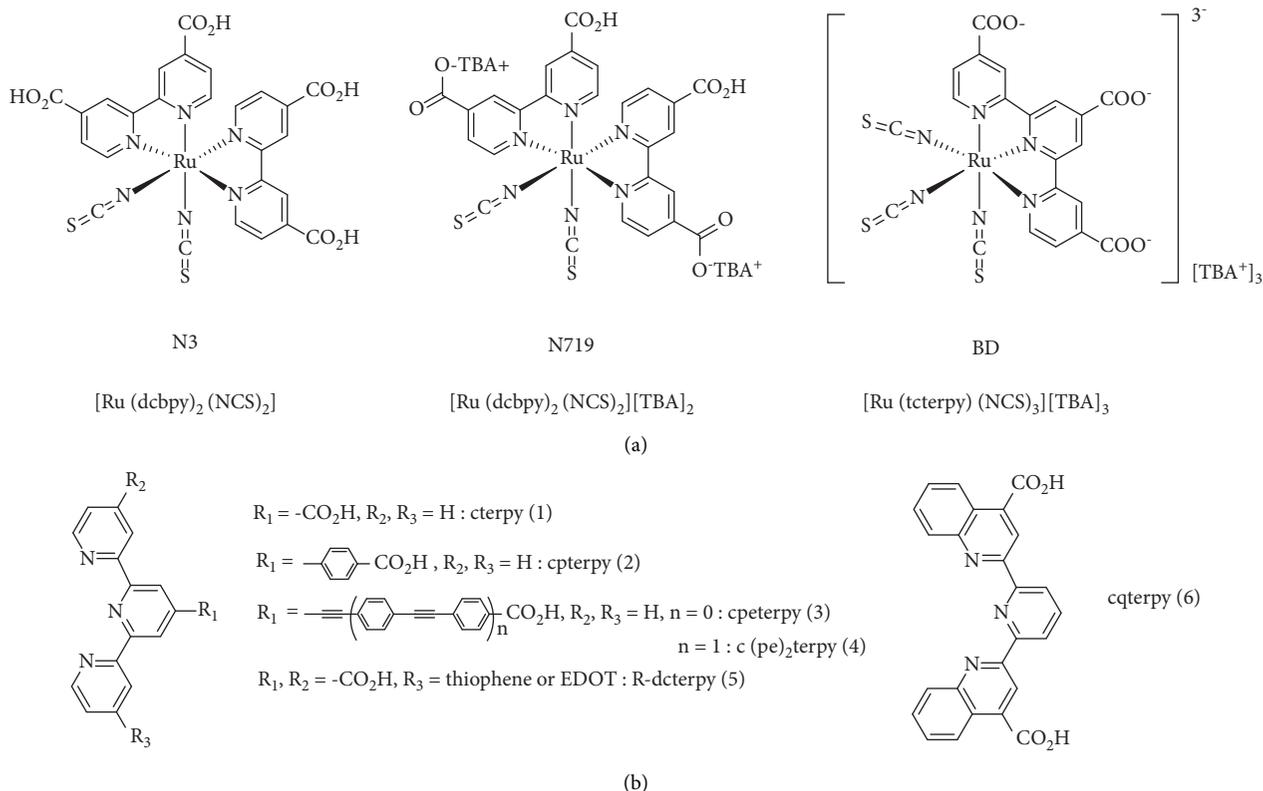


FIGURE 1: (a) Structures of **N3**, **N719**, and **BD**. (b) Terpyridine ligands reported previously in the literature.

The GC/MS experiments were performed using an HP 5973 mass spectrometer connected to an HP 6890 GC system (Hewlett-Packard Co., Palo Alto, California, USA). MALDI-TOF mass spectra were recorded on a JMS-DX303 (Jeol, Tokyo, Japan). The infrared (IR) spectra were recorded on an MB104 Fourier transform infrared (FT-IR) spectrometer (ABB Bomen Inc., Zurich, Switzerland) and the UV-vis spectra were recorded on an S-3100 spectrometer (Scinco, Seoul, Korea). The emission spectra were recorded using a luminescence spectrometer (LS 50B, excitation source: 400 nm; Perkin Elmer, Waltham, MA, USA).

**2.1. General Procedure of Preparing the Monosalt Form of Ruthenium Complexes.** The dimer of dichloro(*p*-cymene) ruthenium(II) (122 mg, 0.20 mmol) and ligand  $L_1$  (0.40 mmol) were dissolved in DMF (40 mL). The process was carried out under an atmosphere of nitrogen gas. The solution was vigorously stirred for 4 h in dark under nitrogen atmosphere at a temperature of 80°C. Following this, ligand  $L_2$  (0.40 mmol) was added to the solution, and the solution was heated at 140°C for 4 h. Subsequently,  $\text{NH}_4\text{NCS}$  (1.24 g, 16.2 mmol) was added to the reaction mixture, and the resulting mixture was heated at 140°C for an additional 4 h. After the evaporation of DMF, the resulting residue was suspended in water, filtered following the process of suction filtration, and dried to obtain the acid form of the ruthenium complexes. The acid form of the ruthenium complex was dissolved in a solution of tetrabutylammonium hydroxide (20 mL; 10%). The solution was stirred for 30 min to 1 h,

following which the reaction mixture was filtered using a sintered glass funnel. The compound was purified using an LH-20 Sephadex column loaded using methanol. The adsorbed complex was eluted using methanol. The compound corresponding to the major band in the column was collected, and the pH of the solution was lowered to 3.8 using an aqueous (aq.) solution of  $\text{HNO}_3$  (0.5 M). At this pH, most of the complex precipitated out. The flask containing the complex was stored in a refrigerator for 12 h. The contents of the flask were filtered using a sintered glass funnel, and the precipitate was collected. The isolated solid was washed with water (5 mL; pH = 3.8). The product was kept in a vacuum oven for drying.

**Tetrabutylammonium [cis-4,4'-bis{2-(3,4-dimethoxyphenyl) ethenyl}-2,2'-bipyridine-(4,7-dicarboxy-1,10-phenanthroline)-di(thiocyanato)]ruthenium(II) (JM1,  $\text{C}_{62}\text{H}_{71}\text{N}_7\text{RuS}_2\text{O}_8$ ):** yield: 48%;  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  9.66 (d, 1H,  $J = 8.0$  Hz), 9.21 (d, 1H,  $J = 3.2$  Hz), 9.05 (d, 1H,  $J = 8.0$  Hz), 8.88 (d, 1H,  $J = 10.8$  Hz), 8.70 (d, 1H,  $J = 11.2$  Hz), 8.45 (s, 1H), 8.08 (d, 1H,  $J = 5.2$  Hz), 8.00 (s, 1H), 7.86 (d, 1H,  $J = 16.0$  Hz), 7.80 (d, 1H,  $J = 5.6$  Hz), 7.55 (d, 1H,  $J = 16.2$  Hz), 7.42–7.36 (m, 2H), 7.33 (d, 1H,  $J = 8.0$  Hz), 7.25–7.21 (m, 2H), 7.17–7.11 (m, 4H), 7.03–7.01 (m, 2H), 3.91 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H), 3.18–3.14 (m, 8H), 1.61–1.54 (m, 8H), 1.35–1.27 (m, 8H), 0.94 (t, 12H,  $J = 7.2$  Hz); IR (neat): 3451, 3043, 2992, 2098, 1702, 1612, 1373  $\text{cm}^{-1}$ ; UV/vis (DMSO) 272, 370, 449, 539 nm; MALDI-TOF:  $m/z = 583.40$  ( $(\text{M-dcphen-2NCS-TBA+H})^+$ , calc. 583.12).

**Tetrabutylammonium [cis-4,4'-bis{2-(3,4-dimethoxyphenyl) ethenyl}-2,2'-bipyridine-(4,7-bis(E-carboxyvinyl)-1,10-phenanthroline)-di(thiocyanato)]ruthenium(II)** (JM2, C<sub>66</sub>H<sub>75</sub>N<sub>7</sub>RuS<sub>2</sub>O<sub>8</sub>): yield: 52%; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.59 (d, 1H, *J* = 5.2 Hz), 9.22 (d, 1H, *J* = 6.0 Hz), 8.91 (s, 1H), 8.73 (s, 1H), 8.61 (d, 1H, *J* = 9.6 Hz), 8.55 (d, 1H, *J* = 4.4 Hz), 8.49 (d, 1H, *J* = 9.2 Hz), 8.43 (d, 1H, *J* = 15.6 Hz), 8.19 (d, 1H, *J* = 15.6 Hz), 8.03 (s, 1H), 7.98 (d, 1H, *J* = 5.2 Hz), 7.57 (d, 1H, *J* = 16.4 Hz), 7.40–7.32 (m, 3H), 7.31 (d, 1H, *J* = 8.4 Hz), 7.27 (d, 1H, *J* = 5.6 Hz), 7.24 (s, 1H), 7.17–7.09 (m, 3H), 7.05–6.99 (m, 4H), 6.77 (d, 1H, *J* = 15.2 Hz), 3.90 (s, 3H), 3.85 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 3.19–3.14 (m, 8H), 1.62–1.54 (m, 8H), 1.37–1.28 (m, 8H), 0.94 (t, 12H, *J* = 7.6 Hz); IR (neat): 3411, 3063, 2962, 2098, 1697, 1612, 1373 cm<sup>-1</sup>; UV/vis (DMSO) 293, 361, 549 nm; MALDI-TOF: *m/z* = 583.46 ((M-dcvphen-2NCS-TBA-H)<sup>+</sup>, calc. 583.12).

**Tetrabutylammonium [cis-4,4'-bis{2-(1,1'-biphenyl)-4-ylethenyl}-2,2'-bipyridine-(4,7-dicarboxy-1,10-phenanthroline)-di(thiocyanato)]ruthenium(II)** (JM3, C<sub>70</sub>H<sub>71</sub>N<sub>7</sub>RuS<sub>2</sub>O<sub>4</sub>): yield: 79%; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.68 (d, 1H, *J* = 5.2 Hz), 9.32 (d, 1H, *J* = 5.6 Hz), 9.07 (d, 1H, *J* = 8.4 Hz), 9.01 (s, 1H), 8.96 (d, 1H, *J* = 9.2 Hz), 8.82 (s, 1H), 8.46 (d, 1H, *J* = 4.8 Hz), 8.06–8.02 (m, 1H), 8.00 (d, 1H, *J* = 16.0 Hz), 7.91–7.83 (m, 4H), 7.82–7.77 (m, 4H), 7.73–7.69 (m, 5H), 7.63 (d, 1H, *J* = 16.0 Hz), 7.59 (d, 1H, *J* = 16.0 Hz), 7.54–7.45 (m, 5H), 7.43–7.37 (m, 3H), 7.32 (d, 1H, *J* = 6.0 Hz), 7.25 (d, 1H, *J* = 16.0 Hz), 3.20–3.16 (m, 8H), 1.65–1.57 (m, 8H), 1.39–1.30 (m, 8H), 0.95 (t, 12H, *J* = 7.6 Hz); IR (neat): 3425, 3061, 2962, 2098, 1682, 1612, 1386, 1028 cm<sup>-1</sup>; UV/vis (DMSO) 276, 350, 448, 550 nm; MALDI-TOF: *m/z* = 613.28 ((M-dcphen-2NCS-TBA-H)<sup>+</sup>, calc. 613.12).

**Tetrabutylammonium [cis-4,4'-bis{2-(1,1'-biphenyl)-4-ylethenyl}-2,2'-bipyridine-(4,7-bis(E-carboxyvinyl)-1,10-phenanthroline)-di(thiocyanato)]ruthenium(II)** (JM4, C<sub>74</sub>H<sub>75</sub>N<sub>7</sub>RuS<sub>2</sub>O<sub>4</sub>): yield: 71%; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.62 (d, 1H, *J* = 5.6 Hz), 9.28 (d, 1H, *J* = 4.8 Hz), 8.97 (s, 1H), 8.79 (s, 1H), 8.60–8.54 (m, 2H), 8.48–8.40 (m, 2H), 8.18 (d, 1H, *J* = 14.4 Hz), 8.01 (d, 1H, *J* = 6.0 Hz), 7.98–7.94 (m, 2H), 7.87–7.80 (m, 5H), 7.75–7.63 (m, 10H), 7.56–7.53 (m, 2H), 7.39–7.32 (m, 3H), 7.30 (m, 3H), 7.23 (d, 1H, *J* = 16.0 Hz), 7.07 (d, 1H, *J* = 14.4 Hz), 6.72 (d, 1H, *J* = 16.0 Hz), 3.34–3.20 (m, 8H), 1.61–1.53 (m, 8H), 1.36–1.26 (m, 8H), 0.92 (t, 12H, *J* = 6.8 Hz); IR (neat): 3441, 2962, 2098, 1697, 1612, 1311, 1018 cm<sup>-1</sup>; UV/vis (DMSO) 299, 341, 466, 555 nm; MALDI-TOF: *m/z* = 613.26 ((M-dcvphen-2NCS-TBA-H)<sup>+</sup>, calc. 613.12).

**Tetrabutylammonium [cis-4,4'-bis{2-(4'-methoxy-[1,1'-biphenyl]-ylethenyl)-2,2'-bipyridine-(4,7-dicarboxy-1,10-phenanthroline)-di(thiocyanato)]ruthenium(II)** (JM5, C<sub>72</sub>H<sub>75</sub>N<sub>7</sub>O<sub>6</sub>RuS<sub>2</sub>): yield: 75%; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.69 (d, 1H, *J* = 5.0 Hz), 9.31 (d, 1H, *J* = 6.4 Hz), 9.08 (s, 1H), 8.98–8.94 (m, 2H), 8.78 (s, 1H), 8.45 (d, 1H, *J* = 4.6 Hz), 8.12–8.05 (m, 2H), 7.97 (d, 1H, *J* = 16.0 Hz), 7.88–7.84 (m, 2H), 7.81–7.77 (m, 3H), 7.74–7.61 (m, 9H), 7.54 (d, 1H, *J* = 16.0 Hz), 7.30 (d, 1H, *J* = 6.4 Hz), 7.23–7.17 (m, 2H), 7.10–7.01 (m, 4H), 3.85 (s, 3H), 3.82 (s, 3H), 3.20–3.16 (m, 8H), 1.65–1.57 (m, 8H), 1.37–1.30 (m, 8H), 0.95 (t, 12H, *J* = 7.2 Hz); IR (neat): 3427, 3064, 2966, 2095, 1686, 1617, 1390, 1024 cm<sup>-1</sup>; UV/vis (DMSO) 270, 363, 439, 536 nm;

MALDI-TOF: *m/z* = 673.23 ((M-dcphen-2NCS-TBA-H)<sup>+</sup>, calc. 673.14).

**Tetrabutylammonium [cis-4,4'-Bis{2-(4'-methoxy-[1,1'-biphenyl]-ylethenyl)-2,2'-bipyridine-(4,7-bis(E-carboxyvinyl)-1,10-phenanthroline)-di(thiocyanato)]ruthenium(II)** (JM6, C<sub>76</sub>H<sub>79</sub>N<sub>7</sub>O<sub>6</sub>RuS<sub>2</sub>): yield: 75%; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 9.68 (d, 1H, *J* = 5.6 Hz), 9.28 (d, 1H, *J* = 4.8 Hz), 8.91 (bd s, 1H), 8.72 (bd s, 1H), 8.62 (d, 1H, *J* = 4.8 Hz), 8.51 (s, 1H), 8.46 (s, 1H), 8.28–8.24 (m, 2H), 8.07 (d, 1H, *J* = 5.5 Hz), 7.96 (s, 1H), 7.92 (s, 1H), 7.89–7.84 (m, 3H), 7.83–7.79 (m, 3H), 7.75–7.63 (m, 9H), 7.50 (d, 1H, *J* = 16.0 Hz), 7.29 (d, 1H, *J* = 4.8 Hz), 7.22–7.15 (m, 2H), 7.10–7.01 (m, 4H), 6.76 (d, 1H, *J* = 16.0 Hz), 3.84 (s, 3H), 3.81 (s, 3H), 3.21–3.17 (m, 8H), 1.65–1.58 (m, 8H), 1.40–1.31 (m, 8H), 0.96 (t, 12H, *J* = 7.2 Hz); IR (neat): 3450, 2977, 2102, 1702, 1634, 1326, 1056 cm<sup>-1</sup>; UV/vis (DMSO): 269, 294, 353, 551 nm; MALDI-TOF: *m/z* = 673.23 ((M-dcvphen-2NCS-TBA-H)<sup>+</sup>, calc. 673.14).

**2.2. Fabrication and Characterization of DSSCs.** The TiO<sub>2</sub> colloid was prepared: TiO<sub>2</sub> (3.0 g, Degussa P25) and acetylacetone (0.27 mL) were added to a container containing distilled water (17 mL). The mixture was ultrasonicated for 10 min, following which the surfactant Triton X-100 (0.13 mL), polyethylene glycol (0.75 g, PEG-20000), and poly(ethylene oxide) (0.15 g, PEO-2000000) were added to the solution. The porous TiO<sub>2</sub>-film was then deposited on a well-cleaned indium tin oxide (ITO) conducting glass following the doctor blade method. Following this, the material was sintered at 450°C for 30 min. A complex dye sensitization process was conducted using JM1–JM6 by soaking the porous film for 18 h in isopropyl alcohol (0.20 wt.%; 2.0 mg H-series/1 g isopropyl alcohol). The dye N719 was used as a reference (Solaronix SA, Aubonne, Switzerland). An electrolyte (consisting of I<sub>2</sub> (0.05 M), LiI (0.50 M), and *tert*-butylpyridine (0.50 M) dissolved in acetonitrile) was then spread on the sensitized semiconductor layer following the process of spin coating. Following this, the Pt counter-electrode was introduced into the system. The DSSCs were fabricated using a glass substrate/ITO/porous TiO<sub>2</sub>/JM-series complex dye/electrolyte/Pt. The performances of the DSSCs were determined under an illumination intensity of 100 mW·cm<sup>-2</sup> generated by an AM 1.5 light source (96000 Solar Simulator, Newport Corporation, Irvine, CA, USA). The active area of the DSSCs was set to 0.36 cm<sup>2</sup>. The photocurrent characteristics were measured using a source meter (2400 Keithley, Cleveland, OH, USA). A reference solar cell (BS-520, Bunkohkoiki, Tokyo, Japan) was used for calibration. The devices were characterized at room temperature under ambient conditions.

### 3. Results and Discussion

**3.1. Synthesis.** Two phenanthroline-based anchoring ligands functionalized with carboxylic acid groups and three highly  $\pi$ -conjugated and/or methoxy-incorporated conjugated bipyridine ancillary ligands were prepared for the synthesis of the new heteroleptic ruthenium(II) complex sensitizers

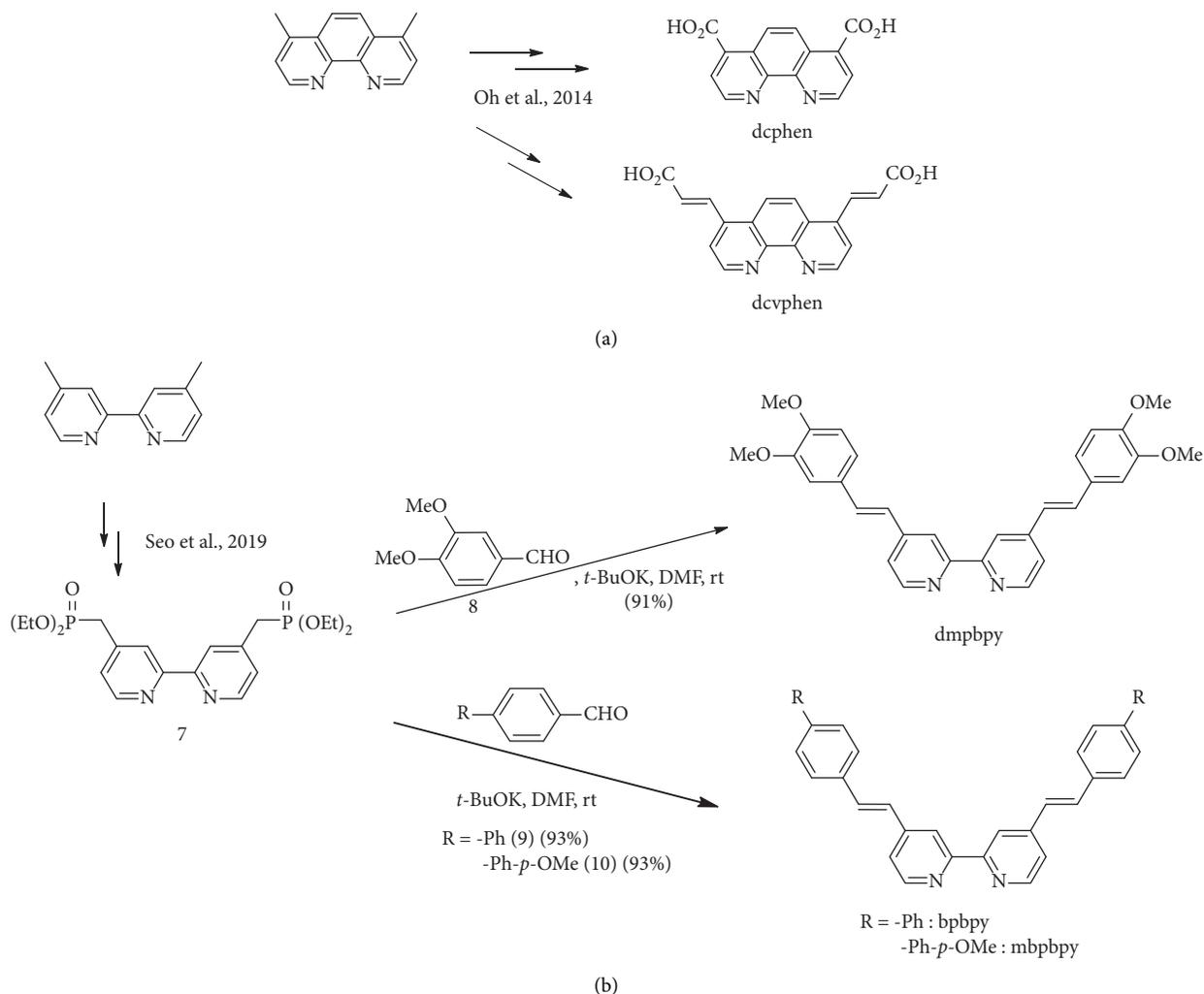
for the fabrication of DSSC materials (Scheme 1). The anchoring ligands, which would enable the efficient chemisorption of the sensitizers onto the mesoporous oxide (dcphen and its  $\pi$ -conjugated dcvphen analog), were synthesized following reported protocols (Scheme 1(a)) [16, 18]. Three ancillary ligands (4,4'-bis{2-(3,4-dimethoxyphenyl)ethenyl}-2,2'-bipyridine (dmpbpy), 4,4'-bis{2-(1,1'-biphenyl)-4-ylethenyl}-2,2'-bipyridine (bpbpy), and 4,4'-bis{2-(4'-methoxy-[1,1'-biphenyl]-4-ylethenyl)-2,2'-bipyridine (mbpbpy)) were synthesized over multiple steps starting from 4,4'-dimethylbipyridine following the methods reported in the literature [19]. First, 4,4'-dimethylbipyridine was converted to the phosphonate-functionalized bipyridine intermediate 4,4'-bis (diethylphosphonomethyl)-2,2'-bipyridine (**7**). The compound could be used as a precursor of the ancillary ligands. The prepared compound was used as a substrate in the Wittig cross-coupling reaction and was reacted with the appropriate benzaldehyde derivative (**8**, **9**, or **10**) to synthesize the three essential ancillary ligands needed for our studies (Scheme 1(b)).

Prepared two anchoring ligands and three ancillary ligands were used for the synthesis of six new heteroleptic ruthenium(II) complexes (Scheme 2). Ruthenium(II) complexes (**11a–11f**; [Ru(L<sub>1</sub>)(L<sub>2</sub>)(NCS)<sub>2</sub>]) containing carboxylic acid-functionalized anchoring and ancillary ligands were prepared following a typical one-pot procedure (Seo et al., 2019). [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> was reacted with an ancillary ligand (L<sub>1</sub> = dmpbpy, bpbpy, or mbpbpy) in *N,N'*-dimethylformamide (DMF) as the solvent under an atmosphere of nitrogen in the dark. The synthesized compound was further reacted with an anchoring ligand (L = dcphen or dcvphen), and the resulting product was treated with a large excess of ammonium thiocyanate (Scheme 2). Following this, the prepared acid form of the precipitate (**11a–11f**) was dissolved in a solvent system consisting of 10% tetrabutylammonium hydroxide and MeOH. The impurities were filtered off, and the solvent was removed. The solution was purified using a Sephadex LH-20 column with methanol as the eluent. The resulting solid was treated with HNO<sub>3</sub> (0.1 N) to obtain the desired products (**JM1–JM6**; [Ru(L<sub>1</sub>)(L<sub>2</sub>)(NCS)<sub>2</sub>] [TBA]). The products were obtained in moderate yields (48–79%; two-step complexation reaction).

**3.2. Ultraviolet-Visible (UV-Vis) Studies.** The UV-vis absorption spectra recorded for **JM1–JM6** (ruthenium(II) complexes) have been shown in Figure 2. The energy maxima ( $\lambda_{\max}$ ) and coefficients ( $\epsilon$ ) are summarized in Table 1. For comparison, the UV-vis absorption spectrum of the well-known **N719** has been shown in Figure 2. The data obtained by analyzing the UV-vis spectra recorded with **N719** and the previously reported compound **H3** (ruthenium(II) complex ligated to 4,4'-bis(*E*)-styryl)-2,2'-bipyridine (bsbpy) and dcphen [18]) have also been listed in Table 1 for reference. The experiments were conducted with the compounds dissolved in DMSO (concentration:  $1 \times 10^{-4}$  M). The series of six new heteroleptic Ru(II) complexes exhibited unique  $\lambda_{\max}$  and  $\epsilon$  values. The recorded  $\lambda_{\max}$  and  $\epsilon$  values were different than the values recorded for

the reference **N719** and **H3** dyes, which have absorption bands covering a wide spectral range (from near UV to visible range). Absorption bands shown in the high-energy region in the UV region at approximately 300 nm were assigned to the intraligand  $\pi$ - $\pi^*$  transitions, while the absorption bands shown in the low-energy region in the visible region (between 430 and 560 nm) were assigned to the  $\pi$ - $\pi^*$  and metal-to-ligand charge transfer (MLCT) transitions. When the spectra recorded for **JM1** was compared with the spectra recorded for **H3**, it was observed that the spectra of **JM1** exhibited a hypsochromic shift which was observed for both  $\pi$ - $\pi^*$  (blue-shifted by 20 nm; from 292 to 272 nm) and MLCT (blue-shifted by 11 nm; from 550 to 539 nm) transitions as the methoxy groups were introduced to the phenyl rings of the ancillary ligands of the complex. As shown in Figure 2(a) and Table 1, though absorption maxima of  $\pi$ - $\pi^*$  and MLCT for **JM1** are blue shifted compared to **H3**, corresponding molar extinction coefficients are increased or reduced. A similar trend was observed for **JM3** and **JM5**. When the methoxy group was introduced to the tail of the ancillary ligand of **JM3**, a hypsochromic shift was observed for both  $\pi$ - $\pi^*$  (276 to 270 nm) and MLCT (550 to 536 nm) transitions. A decrease by 6 and 14 nm was observed, respectively. The results indicated that the electron-donating methoxy substituent helped increase the energy gap (for  $\pi$ - $\pi^*$  and MLCT transitions). An analysis of the absorption spectra of the ruthenium(II)-complexes **JM2**, **JM4**, and **JM6** revealed that the compounds exhibited extended  $\pi$ -conjugation (anchoring ligand: dcvphen). The extent of conjugation in these compounds was greater than the extent of conjugation exhibited by **JM1**, **JM3**, and **JM5**. The wavelengths were red-shifted by 21, 23, and 24 nm for the  $\pi$ - $\pi^*$  transitions ( $\pi$ - $\pi^*$  transition in **JM5**: 294 nm) and 10, 5, and 15 nm for the lower-energy MLCT transitions. However, the broad bands appeared in the range of 320–470 nm for **JM2**, **JM4**, and **JM6**. The broad nature of the bands could be attributed to the presence of the highly  $\pi$ -conjugated system and the ancillary and anchoring ligands. These features resulted in difficulties in determining the values of  $\lambda_{\max}$ .

**3.3. PV Performance of the DSSCs Fabricated with Ruthenium(II) Complexes.** The DSSCs were successfully fabricated using the synthesized heteroleptic ruthenium(II) complex sensitizers. The PV performances of the DSSCs fabricated using the prepared ruthenium(II) sensitizers were examined under conditions of 1 sun (AM 1.5 G, 100 mW·cm<sup>-2</sup>). The performance was compared to the performance of the reference (**N719**-sensitized DSSC) under the same conditions. Figures 3(a) and 3(b) show the typical photocurrent-voltage (*J-V*) curves recorded for the DSSCs fabricated using **JM1–JM6**, **H3**, and **N719**. As shown in the figures, the DSSCs exhibited characteristic PV performances. Characteristic open-circuit voltages ( $V_{OC}$ s), short-circuit current densities ( $J_{SC}$ s), fill factors (*FF*s), and PCEs were observed. The  $V_{OC}$ ,  $J_{SC}$ , and *FF* values of the reference DSSC fabricated with **N719** were 0.69 V, 12.2 mA·cm<sup>-2</sup>, and 0.67, respectively. The result corresponded to a PCE value of approximately 5.63%. The recorded value agreed well with



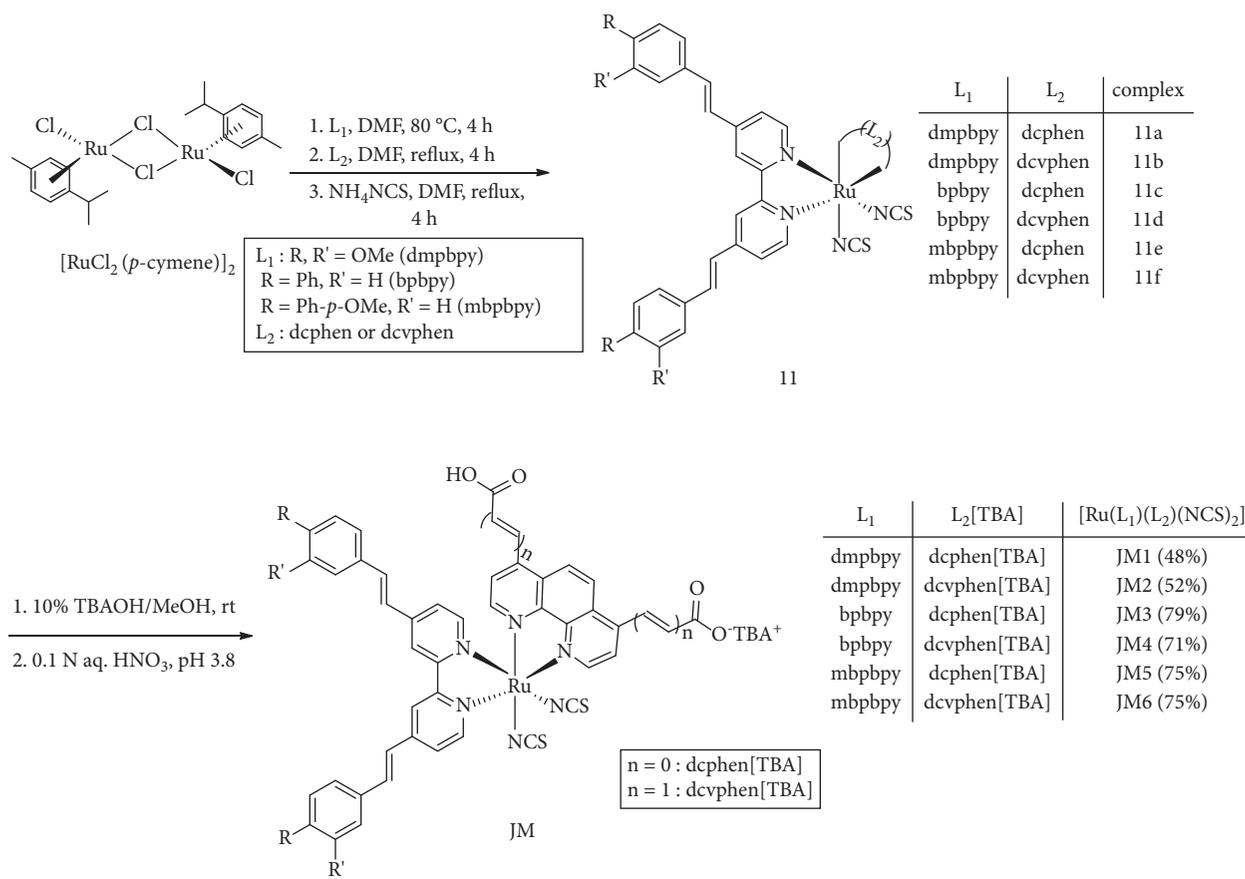
SCHEME 1: Synthetic route for the preparation of the ligands under study.

the values previously reported by us [18]. The  $V_{OC}$ ,  $J_{SC}$ , and  $FF$  values of an **H3**-sensitized DSSC were 0.64 V, 6.65 mA·cm<sup>-2</sup>, and 0.69, respectively. The values corresponded to a PCE value of 2.98%. The PV performance of this system was better than the performances of the **H**-series-sensitized cells studied previously (PCE in the range of 0.64–2.98%) [18].

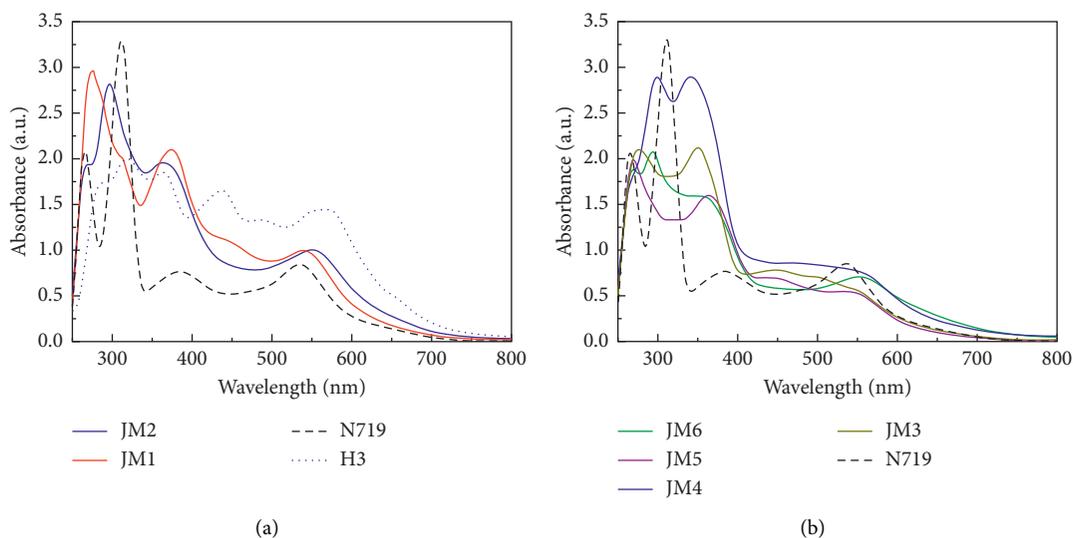
When the dimethoxy group was introduced in the scaffold of the bsbpy (ancillary) ligand in **H3**, i.e., dmpbpy (**JM1**), the **JM1**-sensitized DSSC exhibited the best device performance. The performance was better than the performance of the compounds in the **JM**-series reported herein. The  $V_{OC}$ ,  $J_{SC}$ , and  $FF$  values for the system were 0.63 V, 8.06 mA·cm<sup>-2</sup>, and 0.67, respectively. The PCE value was 3.40%. The PV performance of the **JM1**-sensitized DSSC was significantly better than the performances of the previously studied **H**-series-sensitized DSSCs (PCE in the range of 0.64–2.98%) (Lee et al.). The PCE value (3.40%) recorded for the **JM1**-sensitized DSSC was approximately 71% of the PCE value recorded for the reference **N719**-sensitized DSSC (5.63%). The lower PCE value of the **JM1** system can be attributed to the extended  $\pi$ -conjugation. Extended

$\pi$ -conjugation can potentially result in a decrease in electron-collection efficiency. It can also promote the process of harvesting light. The second and third best performances (among the **JM**-series-sensitized DSSCs under study) were recorded for the **JM5**- and **JM3**-sensitized solar cells, respectively. The  $J_{SC}$  value was 6.41 mA·cm<sup>-2</sup> for the **JM5** system (and 3.55 mA·cm<sup>-2</sup> for the **JM3** system). The  $V_{OC}$  value was 0.60 V for the **JM5** system (and 0.60 V for the **JM3** system). The  $FF$  value was 0.66 for the **JM5** system (and 0.68 for the **JM3** system). The PCE value was 2.52% for the **JM5** system (and 1.45% for the **JM3** system). The **JM2**-, **JM4**-, and **JM6**-sensitized DSSCs exhibited poor PV performances (the PCE values were lower than 0.1%). The PV performances of the DSSCs under study are summarized in Table 2.

The data presented in Table 2 revealed that an appropriate combination of the ancillary and anchoring ligands helps in optimizing the PV performances of the DSSCs fabricated using the heteroleptic ruthenium(II) complexes. Appropriate structural modifications for the ancillary and anchoring ligands also help in optimizing the PV performance of the DSSCs. First, the ancillary ligand of bsbpy (**H3**) was modified by introducing the dimethoxy (dmpbpy, **JM1**)



SCHEME 2: Synthesis of heteroleptic ruthenium(II) complexes.

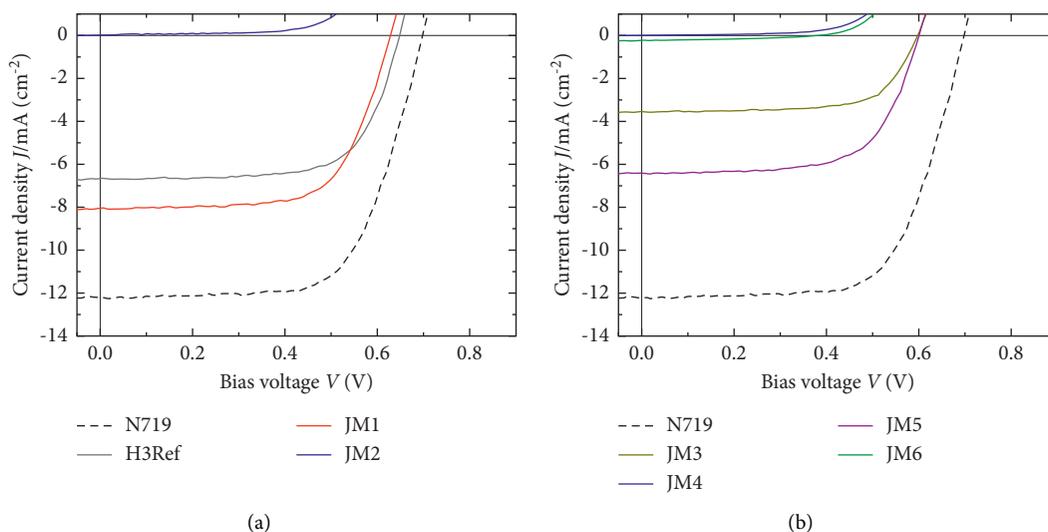
FIGURE 2: UV-vis absorption spectra of (a) **JM1–JM2** including **N719** and **H3** and (b) **JM3–JM6** including **N719** measured at 298 K under ambient conditions (solvent: DMSO).

group. The lone pair of electrons present in oxygen in the system helped in achieving extended conjugation. The PCE value of the **JM1**-sensitized DSSC increased significantly from 2.98% to 3.40%, although the  $\pi$ - $\pi^*$  and MLCT bands were blue-shifted. When the  $\pi$ -conjugation in the ancillary

ligand of bsbpy (**H3**) was extended by introducing the extended phenyl (bpbpy, **JM3**) group, the PCE value of DSSC reduced significantly (from 2.98% to 1.45%). Significant and interesting changes in the PV performances were observed when the electron-donating methoxy groups were

TABLE 1: Absorption maxima ( $\lambda_{\max}$ ) and molar absorption coefficients ( $\epsilon$ ) of **JM1–JM6** and **N719** (standard solution in DMSO;  $1 \times 10^{-4}$  M).

Complex	Absorption maxima ( $\lambda_{\max}$ (nm)) ( $\epsilon$ ( $10^4$ M $^{-1}$ cm $^{-1}$ ))		
	$\pi$ - $\pi^*$	$\pi$ - $\pi^*$ or MLCT	MLCT
<b>H3</b> <sup>a</sup>	292 (1.63)	320 (1.83) 437 (1.54)	550 (1.33)
<b>JM1</b>	272 (2.91)	370 (2.09) 449 (1.09)	539 (0.99)
<b>JM2</b>	293 (2.78)	361 (1.95)	549 (1.00)
<b>JM3</b>	276 (2.09)	350 (2.11) 448 (0.78)	550 (0.55)
<b>JM4</b>	299 (2.88)	341 (2.88) 466 (0.86)	555 (0.76)
<b>JM5</b>	270 (1.98)	363 (1.59) 439 (0.70)	536 (0.55)
<b>JM6</b>	269 (1.86) 294 (2.07)	353 (1.59)	551 (0.71)
<b>N719</b>	311 (3.29)	383 (0.76)	533 (0.84)

<sup>a</sup>Ref [18].FIGURE 3: Photocurrent density-voltage ( $J$ - $V$ ) characteristic curves of **JM1–JM6** and **N719**-sensitized  $\text{TiO}_2$  nanocrystalline solar cells under conditions of 1 sun (AM 1.5G). Electrolyte mediator:  $\text{I}_2$  (0.05 M),  $\text{LiI}$  (0.5 M), and *tert*-butylpyridine in acetonitrile (0.5 M).TABLE 2: Photovoltaic parameters of the DSSCs sensitized using **H3**, **JM1–JM6**, and **N719** dyes under the 1 sun (AM 1.5 G,  $100 \text{ mW}\cdot\text{cm}^{-2}$ ) illumination condition.

Dyes	$V_{\text{OC}}/V$	$J_{\text{SC}}/\text{mA}\cdot\text{cm}^{-2}$	FF/(%)	PCE/(%)
<b>H3</b> <sup>a</sup>	0.64	6.65	0.69	2.98
<b>JM1</b>	0.63	8.06	0.67	3.40
<b>JM2</b>	0.00	0.00	—	0.00
<b>JM3</b>	0.60	3.55	0.68	1.45
<b>JM4</b>	0.00	0.00	—	0.00
<b>JM5</b>	0.60	6.41	0.66	2.52
<b>JM6</b>	0.38	0.24	0.39	0.04
<b>N719</b>	0.69	12.2	0.67	5.63

<sup>a</sup>Ref [18].

introduced into the scaffolds of the ancillary ligands. The results were further validated when the **JM5**-sensitized DSSC was studied. The  $\pi$ -conjugation in the ancillary ligand of the phenyl-extended bsbpy in the **JM5**-sensitized DSSC was extended by introducing the electron-donating methoxy (mbpbpy, **JM5**) group. This resulted in the improvement of the PCE values (from 1.45% to 2.52%). Improved PCE values were recorded for **JM1** and **JM5** when the electron-donating methoxy groups were substituted at the appropriate positions of the ancillary groups.

The anchoring ligands were structurally modified by replacing the dcphen (anchoring) ligands of the **JM1**, **JM3**, and **JM5** with dcvphen (**JM2**, **JM4**, and **JM6**, respectively). The PV performances of the **JM2**-, **JM4**-, and **JM6**-sensitized DSSCs significantly decreased, and the PCE values recorded were less than 0.1%. Extended  $\pi$ -conjugation in the anchoring ligand should improve the light-harvesting ability of the sensitizers. It was observed that the **JM2**, **JM4**, and **JM6** sensitizers were significantly less efficient (in conserving power) than the **JM1**, **JM3**, and **JM5** sensitizers. However, we could not explain the lower efficiencies of the **JM2**-, **JM4**-, and **JM6**-sensitized DSSCs could be potentially attributed to the fact that the solubilities of these systems in the given solvent (isopropyl alcohol) were lower than the solubilities of the **JM1**, **JM3**, and **JM5** sensitizers. This resulted in significantly reduced adsorption on the  $\text{TiO}_2$  surfaces.

#### 4. Conclusions

Six new heteroleptic ruthenium(II) complexes (**JM1–JM6**), each containing a highly  $\pi$ -conjugated bipyridine ancillary ligand including methoxy-substituted analog ( $L_1$ ) and a phenanthroline-type anchoring ligand ( $L_2$ ) (dcphen or

dcvphen;  $[\text{Ru}(\text{L})_2(\text{NCS})_2][\text{TBA}]_2$ , where  $\text{L}_1 = \text{dmpbpy}$ ,  $\text{bpbpy}$ , or  $\text{mbpbpy}$  and  $\text{L}_2 = \text{dcphen}$  or  $\text{dcvphen}$ ) were synthesized and characterized, and their physical and photovoltaic properties were investigated. Among the DSSCs fabricated with the heteroleptic ruthenium(II) complexes, the ruthenium(II) complex ligated with  $\text{dmpbpy}$  as the ancillary ligand and  $\text{dcphen}$  as the anchoring ligand (**JM1**) exhibited the maximum PCE (3.40%). The PCE value recorded for the commercially available **N719**-sensitized solar cell (used as a reference) was 5.63%. The ruthenium(II) complex ligated to  $\text{mbpbpy}$  as the ancillary ligand and  $\text{dcphen}$  as the anchoring ligand (**JM5**) exhibited the second-best efficiency (PCE value: 2.52%), and the ruthenium(II) complex ligated to  $\text{bpbpy}$  as the ancillary ligand and  $\text{dcphen}$  as the anchoring ligand (**JM3**) exhibited a PCE value of 1.45%. Interestingly, when the appropriate sites of the ancillary groups in **H3** (or **JM3**) were substituted with the electron-donating methoxy groups, the PCE values of the DSSCs fabricated using **JM1** or **JM5** increased significantly. In contrast, the sensitized DSSCs fabricated using the ruthenium(II) complex ligated to  $\text{dcvphen}$  as the anchoring ligand (**JM2**, **JM4**, and **JM6**) exhibited poor PV performance. The PCE values of these systems were lower than 0.1%.

## Data Availability

All data used to support this study are included in the article.

## Conflicts of Interest

The authors declare no conflicts of interest.

## Acknowledgments

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