Novel Metal-Organic Polymer [Ruthenium Bis(II) (2,2′–Bipyridyl 4,4′–Dicarboxylic Acid) (N-Methyl morpholine)]$_n$ $(BF_4)_{2n}$ for Dye-Sensitized Solar Cell Application

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Abstract Herein, we have given the synthesis of a novel Ruthenium based metal-organic polymer dye $[Ru(L_1)_2(L_2)]_n(BF_4)_{2n}$, where L_1 = 2,2′bipyridyl 4,4′-dicarboxylic acid, L_2 = N-Methyl Morpholine, coded as RuMOP-NMM1, centered on long-drawn-out organic base (N-Methyl Morpholine) as linker unit and its photophysical and electrochemical properties. The material was characterized by UV–Vis absorption, Fluorescence, Infrared (FT-IR), Raman and Nuclear Magnetic Resonance (NMR) spectroscopy, Elemental Analyser (CHNS/O), Thermo Gravimetric/Differential Scanning calorimetry (TG/DSC) and Cyclic Voltametry (CV). The polynuclear complex displays an absorption band on longer wavelengths with high molar extinction coefficient. The metal-mediated supramolecular polymer complex, exhibit a strong luminescence emission. Henceforth, these metal-organic polymer (RuMOP-NMM1) have better thermal and chemical stability than the mononuclear complexes. These photoluminescence and electrochemical characterization results strongly suggest that the synthesized metal-organic polymer is kinetically and energetically suitable to aid as sensitizers in energy-relevant applications mainly in dye-sensitized solar cell (DSSC).

Keywords Methyl morpholine · Supramolecular · Polymer · Metal-organic · DSSC · Sensitizer · Ruthenium (II) · Solar cell

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1 Introduction

In the present global scenario, the important need of the hour is to utilize renewable energy sources for commercial applications. In that, solar energy utilization is the prior one and important one. So in the last few years, research on conversion of solar energy into photovoltaic energy becomes a significant one. As a consequence, range of photovoltaic devices (solar cells) was raised such as silicon solar cells, organic Solar cells, dye-sensitized solar cells and polymer solar cells [1–6]. In that, dye-sensitized solar cells (DSSCs) have involved noteworthy attention of recent researchers due to their low production cost. As presence a multilayer stratagem, the efficiency of DSSC mostly rests on the act of sensitizers, TiO_2 photoanode, counter electrode and electrolyte [7]. Among these main components, dye sensitizer is accountable for the photon absorption, electron injection and enlightening the efficiency. Subsequently, dye sensitizer plays an energetic part in the device efficacy, different kinds of dyes have been used in DSSC. Amongst these dye sensitizers, ruthenium polypyridyl based dyes exposed the preeminent concert due to their better light-harvesting properties upon adsorption onto $TiO_{2.}$ [8–11]. Though, Ruthenium polypyridyl based dyes were identified as the most competent sensitizers for DSSC applications. In specific, the dicarboxylated bipyridine ligand-based N3 referred to as the standard. Ruthenium polypyridyl complex centered sensitizers have attained 12% efficiency. So, there is a great entreaty to expand the performance of ruthenium complexes based DSSCs [12, 13].

In mandate to realize higher efficiency, sensitizers with appropriate structural sorts are required. Covering the aromatic units over various ligands, the photophysical electrochemical characteristics of DSSC might be amended. Supramolecular metallo-polymers have increased ample interest in current years [14]. These polymers through extended π—conjugation units can display unusual photophysical and electrochemical properties. Therefore, the transition metal founded main chain coordination polymers show greater photophysical properties and absorption bands within elevation extinction coefficients [15, 16]. These supramolecular metallo-polymers too display the grouping of both organic and organometallic compounds. The structure and the property of the metallopolymers can impart significant differences in the device performances. Ruthenium based metallo-polymers with conjugated units has many advantages, such as long-lived metal to ligand charge transfer (MLCT) and exhibit Ru(II, III) along with ligand centered redox process [17, 18].

In this work, we report the synthesis and characterization of novel Ruthenium based metal-organic polymer dye $[Ru(L_1)_2(L_2)]_n(BF_4)_{2n}$, where L_1 = 2,2′bipyridyl 4,4′-dicarboxylic acid, L_2 = N-Methyl Morpholine, coded as RuMOP-NMM1, structure–property rapport as a sensitizer in DSSC has been considered. The polymeric dye presented exceptional performance closed to that of reference dyes.

2 Experimental Section

2.1 Materials and Methods

All reagents and solvents used in this synthesis are AR grade. All reactions are carried out under Argon gas atmosphere. The Ruthenium precursor $Ru(dcbpy)_2Cl_2$, reference dye (N_3 dye) was prepared according to the literature. P_{25} TiO_2 powder (<99%) were purchased from Sigma Aldrich.

2.2 Characterization

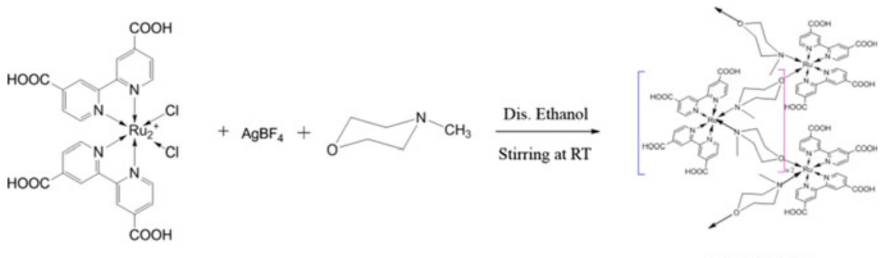
The UV–Vis spectra were obtained by using Shimadzu UV-1800 UV–VIS spectrophotometer (Japan). Flourescence spectra were taken by Shimadzu RF-6000 spectrofluorophotometer (Japan). FTIR spectra were measured in IR Affinity FTIR, (Shimadzu, Japan). ^{1}H NMR spectra were received by 400 MHz NMR spectrometer JEOL JMM-ECS 400. The elemental and mass analysis was completed by Perkin-Elmer elemental analyzer and JEOL GCMATEII correspondingly. The TGA/DSC analysis was conceded out in NETZCH STA Jupiter 4429. Raman analysis was ensured by Horiba Jobin-LabRam-HR UV–vis μ-Raman spe at ambient temperature with Argon laser with an excitation wavelength of 514 nm equipped with CCD detector.

3 Results and Discussion

3.1 Synthesis of RuMOP-NMM1

$[Ru(L_1)_2(L_2)]_n(BF_4)_{2n}$, Where L_1 = 2,2′bipyridyl 4,4′-Dicarboxylic Acid, L_2 = N-Methyl Morpholine]

Preparation of metal-organic polymer dye $[Ru(L_1)_2(L_2)]_n(BF_4)_{2n}$, where L_1 = 2,2′bipyridyl 4,4′-dicarboxylic acid, L_2 = N-Methyl Morpholine, coded as RuMOP-NMM1, was prepared by the following synthetic procedure (1), concerning the replacement of the two chloride ions in Ru(II) precursor $[RuCl_2(dcbpy)Cl_2]$ with the N-Methyl Morpholine as linker unit which is based on extended organic base group.



Ru(II)dcbpy$_2$Cl$_2$ N-Methyl Morpholine RuMOP-NMM1

Scheme 1 Synthesis of RuMOP-NMM1

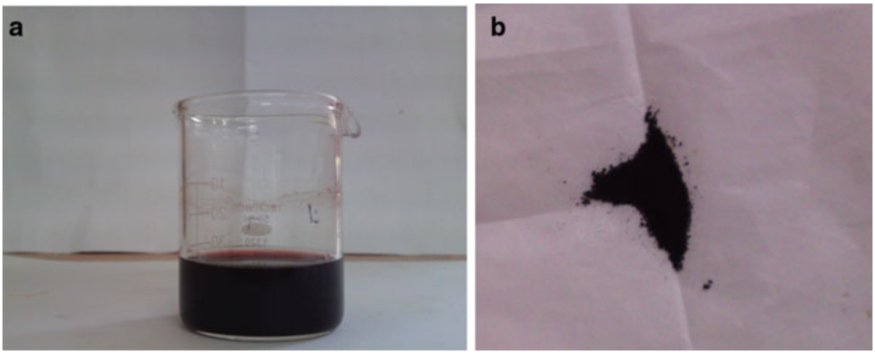


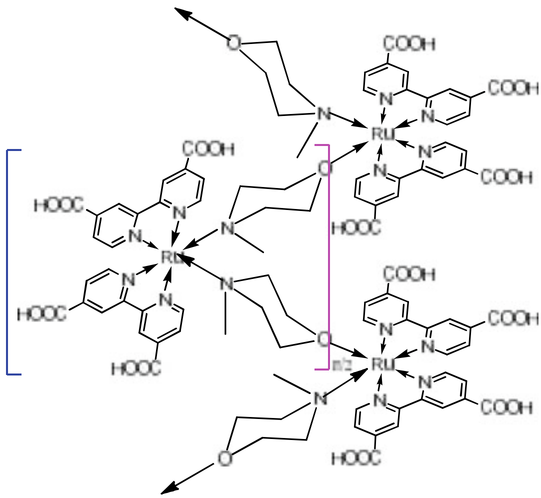
Fig. 1 **a** and **b** RuMOP-NMM1 in Methanol and in powder form

3.2 UV–Visible and Emission Spectroscopy

The UV–Vis spectra of (**RuMOP-NMM1)** show bands in the visible region due to MLCT transitions. The occurrence of carboxylated group exhibit two π to π* intraligand transitions. The two t_2 to π* MLCT bands is due to the visible and near–UV. The absorption and emission values were given in Table 1. The room temperature luminescence of (**RuMOP-NMM1)** complex is displayed the luminescence maximum is positioned centered at 534 nm.

Table 1 Absorption and luminescence properties of (**RuMOP-NMM1**)

Complex	Absorbance (nm)	Emission (nm)
(RuMOP-NMM1)	522	535
	390	
	312	



Structure of RuMOP-NMM1

3.3 FT–IR Spectroscopy

A sturdy band in the area of 3412 cm^{-1}, owing to the occurrence of O–H group of the carboxylic acid group. The quite durable absorption at 1711 cm^{-1} corresponds to the stretching vibration mode of C = O bond and the bands at 1359 cm^{-1} and 1601 cm^{-1} are due to the symmetric and asymmetric stretching in the C = O and C-H bands respectively. Due to the N-coordination from the N-methyl morpholine unit absorption at 2011 cm^{-1} was noted [19].

3.4 Thermal Gravimetric Analysis

The TGA curve of the metal-organic polymer (**RuMOP-NMM1)** is given in Fig. 1. 7.66% weight loss at 70–90 °C is due to the removal of solvent residues. A weight loss observed at 250–345 °C arise due to the loss of coordinated organic ligand. Overhead 400 °C a nearly horizontal curve was obtained due to the realization of metal oxides. The weight fraction of mass change is given in Table 2. The thermal behaviour is consistent with other Ru based dicarboxylic bipyridyl ligands [20].

Table 2 Thermal properties of (**RuMOP-NMM1**) sensitizer

Complex	Temp (ºC)	Mass Change (%)
RuMOP-NMM1	90	7.66
	345	23.81
	400	45.62

Table 3 Photovoltaic properties of DSC $[Ru(dcbpy)_2](NCS)_2$ as sensitizer

Complex	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	Efficiency (%)
(RuMOP-MM1)	2.79	0.582	65.1	1.07

3.5 Fabrication of DSSCs

DSSC has been prepared using the synthesized (**RuMOP-NMM1)** dye as a photosensitizer and with a double layer TiO_2 coating on FTO plate as photo anode entailing of a transparent titania nanoparticles and BMMI electrolyte. We checked the photovoltaic response of the devices. The photovoltaic parameters are listed in Table 3.

The overall conversion efficiencies 2.3% were derived from the equation:

$$\text{IPCE} = J_{sc} \times V_o \times FF,$$

where

J_{sc} is the short circuit current density,
V_{oc} the open-circuit voltage and FF the fill factor.

By using N_3 dye the overall efficiency obtained was 10%. In this report the power conversion efficiencies were 1.07% only, we stress the detail that by tuning all other parameters these dyes can attain the literature mentioned efficiency. We believe that the use of more pi-conjugated extended schemes, with appropriate p-delocalized substituent's also would improve light harvesting possessions and, ultimately, photovoltaic performances.

3.6 I-V Characteristics

The current density (J) against voltage (V) curves of the DSSC is exposed in Fig. 2. The photovoltaic dimensions of open-circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), and the PCE (η) values were abridged in Table 3. The metal-organic polymer ***(RuMOP-Pyz-1)***, based DSSC showed the photoconversion efficiency value (η) of 1.07% with short circuit current (J_{sc}) 2.79 mA/cm^2; open-circuit voltage (V_{oc}) 0.582 V and Fill Factor (*FF)* 65.1%. In compared with the reference dye. The main-chain metal-organic polymer-based supramolecular ruthenium which has linker units, has better photovoltaic properties. So, in this synthesized main-chain metal-organic polymer which has efficient electron injection on TiO_2 surface (Fig. 3).

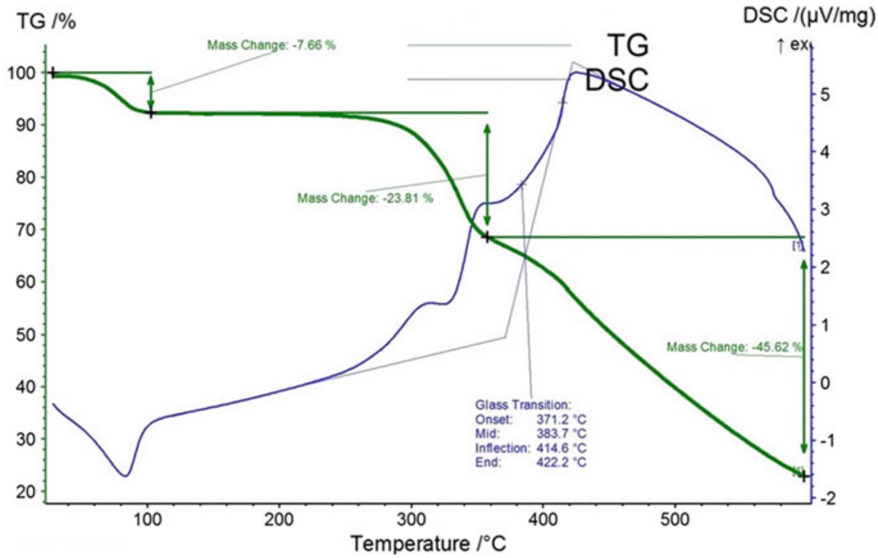
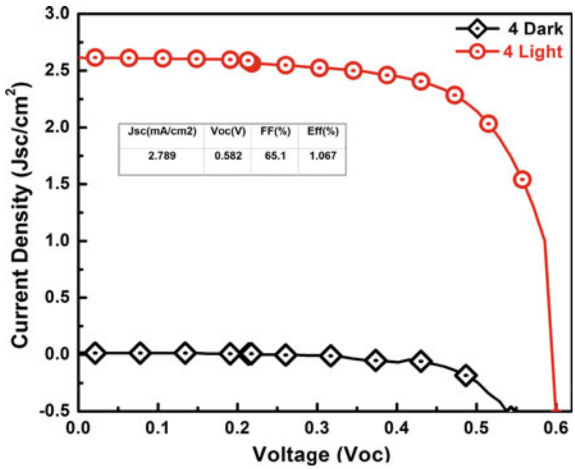


Fig. 2 TGA and DSC curves of (**RuMOP-NMM1)**

Fig. 3 *J-V* curves of (**RuMOP-NMM1)** as sensitizer in DSSC



Jsc(mA/cm2)	Voc(V)	FF(%)	Eff(%)
2.789	0.582	65.1	1.067

4 Conclusions

In summary, **$[Ru(L_1)_2(L_2)]_n(BF_4)_{2n}$, where L_1= 2,2′bipyridyl 4,4′-dicarboxylic acid, L_2= N-Methyl Morpholine,** metal-organic polymer **RuMOP-NMM1** was effectively prepared and engaged as an energy material in the form of sensitizer in DSSC. The synthesized metal-organic polymer was characterized using several spectroscopic and microscopic techniques. A maximum conversion efficiency of 1.07% with short circuit current (J_{sc}) 3.22 mA/cm^2; open-circuit voltage (V_{oc}) 0.582 V and Fill Factor (FF) 65.1%. Under Air Mass (AM) 1.5 G simulated sunlight at a light intensity of 100 mW/cm^2 was obtained.

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