



Synthesis, Crystal Structure and Application of New Cobalt(II) Complex [Co(bpy)₂NO₃]·NO₃·5H₂O as Sensitizer in Dye-Sensitized Solar Cells

N. GOSWAMI^{1,*}, P.K. GOGOI^{2,*}, U. SAHA³, M.K. BHATTACHARYYA³ and T.R. CHETIA²

¹Department of Chemistry, Sibsagar College, Sivasagar-785 640, India

²Department of Chemistry, Dibrugarh University, Dibrugarh-786 004, India

³Department of Chemistry, Cotton University, Guwahati-781 001, India

*Corresponding authors: E-mail: nandita_10@rediffmail.com; dr.pradip54@gmail.com

Received: 9 October 2017;

Accepted: 14 December 2017;

Published online: 31 January 2018;

AJC-18765

In this work, the synthesis and X-ray crystallographic study of a new cobalt(II) coordination complex with 2,2'-bipyridine (bpy) and nitrate ions as the ligands are reported. The complex is characterized by single crystal XRD, elemental analyses, FTIR and UV-visible spectroscopic techniques and the results show that it may be used as a potential sensitizer in dye sensitized solar cell (DSSC). Single crystal XRD analysis revealed that crystal structure is stabilized by both intra-molecular and inter-molecular hydrogen bonding in the complex involving the coordinated nitrate ion and water molecules. Photovoltaic performance of the complex was also evaluated by fabricating a prototype cell.

Keywords: Cobalt(II) complex, Crystal packing, Dye sensitized solar cell.

INTRODUCTION

Transition metal complexes involving diimine ligands such as 2,2'-bipyridine (bpy) and its analogues having π -conjugated systems have been extensively studied for their wide applications in electrochemistry, catalysis, biochemistry, analytical chemistry and also in the various fields of material science such as molecular based magnets, chemo-sensors, optoelectronic devices and solar photovoltaic such as in dye sensitized solar cells (DSSC) [1-5]. In search of new materials for application in smart electronic devices, systems having π -conjugated molecules have drawn special attention and thus have been applied as building blocks to develop new classes of such electronic materials [6,7]. Although, coordination bonding and hydrogen bonding interactions act as important driving forces in crystal engineering, several other types of forces, such as π - π stacking and other such electrostatic interactions also have gained significant importance in constructing extended networks [8-10]. Moreover, these complexes show good panchromatic behaviour owing to the enhanced absorption over a broad range due to their large conjugated structure and as well as for the capacity of producing strong charge transfer bands with high molar extinction coefficient; they are preferred as potential photosensitizer dye in DSSC [11-14]. Although, the most efficient cells have been obtained by using Ru-polypyridyl complexes as sensitizer dye, the research has been extended to other charge transfer complexes with other transition metals such as Fe(II), Cu(II), Re(I), Os(II), Pt(II),

Co(II), etc. as potential sensitizers for DSSC owing to the complicated synthetic routes and high cost of these heavy metal complexes [15-19]. In this work, we have synthesized a mixed ligand complex of cobalt with 2,2'-bipyridine and nitrate as ligands. The morphology of complex was studied with the help of single crystal XRD, UV-visible, IR and C,H,N analysis and these studies revealed that it may be used as a sensitizer dye in DSSC. The photoanode was fabricated by applying as-prepared dye solution onto TiO₂ thin films on transparent conducting oxide (TCO) coated glass and the performance of working electrode was investigated by UV-visible spectroscopy. One prototype cell was fabricated by using KI and I₂ as electrolyte and graphene coated TCO as counter electrode. The photovoltaic parameter of the cell was measured with a Keithley 2400-source meter and efficiency of the cell was calculated.

EXPERIMENTAL

All the reagents and solvents *viz.* cobalt nitrate, 2,2'-bipyridine, methanol, ethanol, acetic acid, TiO₂ P25 nanoparticle, Triton-X, etc. were of ACS grade and obtained from Merck (India) Ltd. and used as received unless otherwise stated. C, H, N analyses were carried out using a Perkin Elmer 2400 Series II CHNS/O analyzer. Chemical analyses of cobalt was done gravimetrically by following standard procedures. FTIR spectra were recorded in a Shimadzu FTIR-8400 spectrophotometer in the mid-IR region (4000 to 400 cm⁻¹) for KBr pellets. The UV-visible spectra were obtained using a Shimadzu UV-1700 spectrophotometer.

Deionized water was used as a reaction medium throughout the experiments.

Synthesis of cobalt complex: A solution of 2,2'-bipyridine (0.625 g, 4 mmol) in 10 mL (1:1) CH₃OH/H₂O was added dropwise to a 10 mL solution of cobalt nitrate Co(NO₃)₂·6H₂O (0.582 g, 2mmol), which was mechanically stirred at room temperature for 30 min. The mixture was stirred for an additional 2 h and the resulting red solution was kept for slow evaporation from which the reddish pink block crystal come out after several days. Yield: (83.5%). CHN analysis: Calculated C 48.50, H 3.26, N 16.97; found C 47.96, H 3.12, N 16.45.

Crystallographic analysis: Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structure was solved by Direct Methods using the program SHELXS97. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms of bipyridine ligands were placed in geometrically idealized positions and refined as riding atoms. The hydrogen atoms of water molecules were treated with constraints.

RESULTS AND DISCUSSION

Crystal Structure of [Co(bpy)₂NO₃]₂·NO₃·5H₂O: The description of crystal structure of [Co(bpy)₂NO₃]₂·NO₃·5H₂O are specified in Table-1. The complex consists of [Co(NO₃)(bpy)₂]⁺ as cation, nitrate as counter ion and water molecules (Fig. 1). The Co(II) ion is linked to four N atoms of two bipyridine ligands and to bidentate nitrate ligand through two O atoms. The Co-N distances lie in the range of [1.917(3)-1.941(3)Å] and show difference from each other. The nitrate ligand is found to be coordinated symmetrically to the metal. It is observed that bpy ligands are almost planar with the rings. The angle among N3-Co1-N1 is nearly linear, whereas that for O2-Co1-N4 and O1-Co1-N2 is found to deviate from linearity. On this basis, it was established that equatorial positions are occupied by atoms N1 and N3. The maximum deviation from the basal plane is 0.0782 (18) Å for atom O2. Considerable differences are also obtained for N-Co-N angles in the cationic complex.

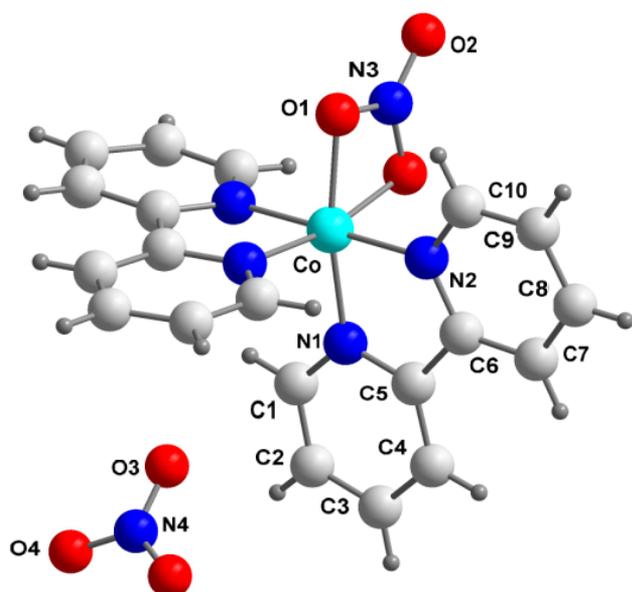


Fig. 1. Molecular structure of [Co(bpy)₂NO₃]₂·NO₃·5H₂O (water molecules in the lattice are not shown for clarity)

TABLE-1
SINGLE CRYSTAL XRD DATA OF [Co(bpy)₂NO₃]₂·NO₃·5H₂O

Empirical formula	C ₂₀ H ₂₅ N ₆ O ₁₁ Co
Formula weight	584.39
Temperature in K	293(2)
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C2/c
a (Å)	10.92(7)
b (Å)	16.01(9)
c (Å)	14.43(1)
α (°)	90
β (°)	101.83(3)
γ (°)	90
Volume (Å ³)	2471.4(3)
Z, calculated density (Mgm ⁻³)	4, 1.571
Absorption coefficient (mm ⁻¹)	0.766
F(000)	988
Crystal size (mm)	0.32 × 0.27 × 0.12
θ range for data collection (°)	2.54 to 30.07
Index ranges	-15 ≤ h ≤ 10, -22 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected/unique	13626/3585 [R(int) = 0.0261]
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	3585/0/175
Goodness-of-fit ^a on F ²	1.126
Final R indices ^b [I > 2σ(I)] R1/wR2	0.0468/ 0.1457
R indices ^c (all data) R1/wR2	0.0601/ 0.1670
Largest diff. peak and hole (e Å ⁻³)	0.539 and -0.809

O-H...O, C-H...O and π...π interaction: The complex shows extensive hydrogen bonding linking with both coordinated and uncoordinated nitrate ligands. The counter nitrate ion forms C-H...O hydrogen bonds with C-H of pyridine ring of bipyridine ligand [C10-H10...O4 = 2.67Å] (Fig. 2) as well as O-H...O hydrogen bonds with the lattice water molecules [O5-H5a...O3 = 2.23Å, O5-H5A...O4 = 2.02 Å, O7-H7A...O4 = 2.71 Å].

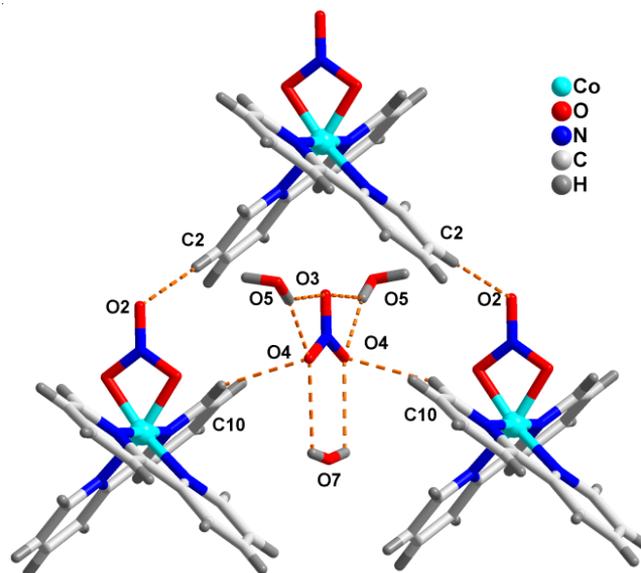


Fig. 2. Nitrate interaction in the complex

The packing diagram clearly shows π...π stacking interactions between pairs of bipyridine with characteristic interplanar distance between the rings of 3.84 Å. The coordinated

nitrate ligand forms C-H...O hydrogen bonds with C-H of bipyridine ring [$\text{C4-H4}\cdots\text{O1} = 2.53 \text{ \AA}$, $\text{C10-H10}\cdots\text{O1} = 2.43 \text{ \AA}$], thus holding the supramolecular chain in the crystal array. The supramolecular network of the complex may be attributed to π - π stacking and H-bonding interactions (Figs. 3 and 4).

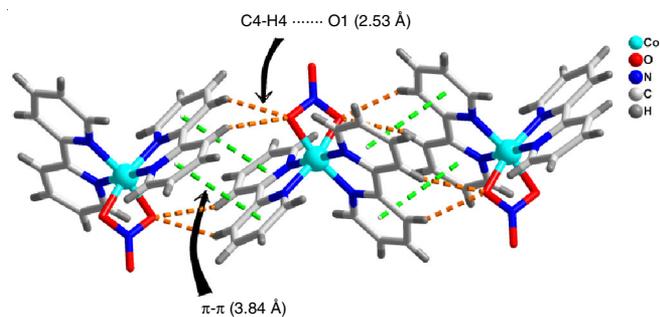


Fig. 3. C-H...O and π - π interaction

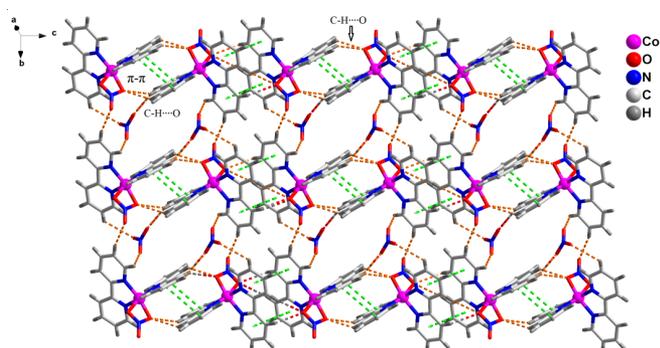


Fig. 4. 2D layered network in complex (π - π interaction shown by green dotted lines and C-H...O shown by orange dotted lines)

IR spectra: The FTIR spectra of the complex is shown in Fig. 5 and the shifting of bands to lower frequency compared to the ligand in free state evidently indicates the coordination of bpy ligand to the metal through two nitrogen atoms. The spectrum shows a broad and intense band located at $3467\text{-}3332 \text{ cm}^{-1}$ which is due to strong H-bonds including the coordinated water molecules. The peaks around $3116\text{-}3033 \text{ cm}^{-1}$ which show weak absorption are due to $\nu(\text{C-H})$ stretching frequency. Strong sharp bands at 1607 cm^{-1} is ascribed to $\text{C}=\text{N}$ stretching vibration of bpy ligand and $\text{C}=\text{C}$ stretching of phenyl ring of bipyridine was observed at 1448 cm^{-1} . The stretching vibration band $\nu(\text{C}=\text{N})$ has been found in the range $1550\text{-}1427 \text{ cm}^{-1}$ which shifted to lower frequency confirming coordination of N atom to the metal atom in the coordination of metal center. The metal-nitrogen and metal-oxygen bands were further confirmed by the presence of stretching vibration of $\nu(\text{Co-N})$ and $\nu(\text{Co-O})$ around $655\text{-}410$ and $472\text{-}308 \text{ cm}^{-1}$, respectively. The IR frequencies at 1641 and 1020 cm^{-1} correspond to $\nu_{\text{asym}}(\text{NO}_2)$ and $\nu_{\text{sym}}(\text{NO}_2)$ modes of NO_3 , respectively.

UV-visible absorption spectra: The UV-visible absorption spectra (Fig. 6) was recorded in a wavelength range of $200\text{-}800 \text{ nm}$ in ethanol. The spectra exhibited two absorption regions in the vicinity of 378 and 518 nm assigned to the transition ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$, respectively and the high intensity strong peaks at 215 , 251 and 304 nm corresponds to the charge transfer bands due to the ligands which favours the complex to be used as a light harvesting dye. The complex is high spin

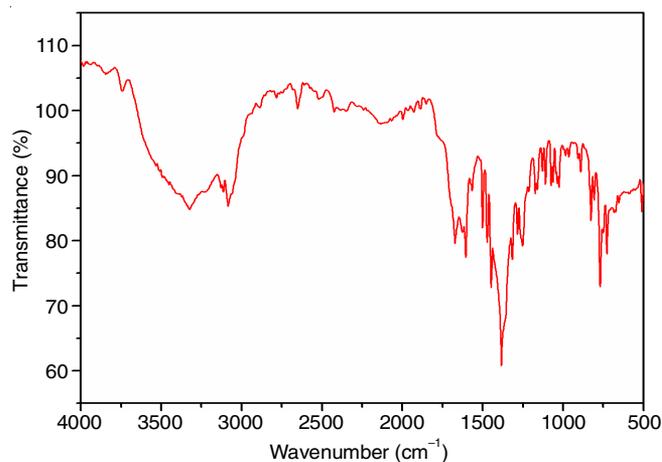


Fig. 5. FTIR spectra of cobalt complex $[\text{Co}(\text{bpy})_2\text{NO}_3]\cdot\text{NO}_3\cdot 5\text{H}_2\text{O}$

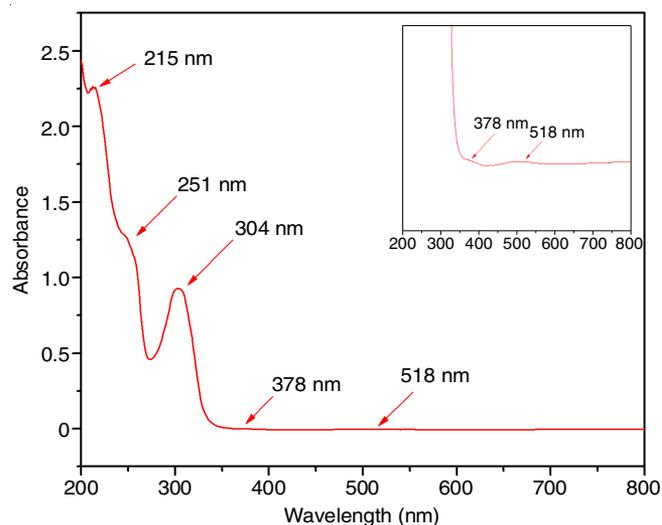


Fig. 6. UV-visible absorption spectra of cobalt complex

and the magnetic moment of cobalt complex was found to be 3.6 , which confirms the $+2$ oxidation state cobalt.

Cyclic voltammetric studies: The cyclic voltammogram of cobalt complex is shown in Fig. 7 and the redox properties was studied using cyclic voltammetry in the potential range $+1.0$ to -1.0 vs. Ag/AgCl electrode was used as reference electrode at room temperature and tetrabutylammonium perchlorate as supporting electrolyte. Fig. 7 showed that the cathodic peak (EP_c) observed at a voltage of 0.72 V coupled with an anodic peak (EP_a) at 0.52 V . The HOMO energy level of the complex can be calculated by using following expression: $E_{\text{HOMO}} = [E_{\text{onset}}(F_c/F_c^+) + 4.8] \text{ eV}$ and is found to be at 5.43 eV (*vs.* F_c/F_c^+).

Fabrication of TiO_2 photoanode: TiO_2 thin film was deposited onto the transparent conducting oxide (TCO) glass substrate which is tin oxide in the present study. Commercially available TiO_2 nano powder was mixed with Triton-X, acetic acid and surfactant and then stirred for 30 min to get a uniform paste. The paste was then deposited on the TCO and sintered at $450 \text{ }^\circ\text{C}$ for 2 h . For the fabrication of photoanode, as-prepared TiO_2 film was dipped in cobalt complex solution by continuous dip coating technique and the film was withdrawn after 24 h , washed and dried in oven at $150 \text{ }^\circ\text{C}$. The comparison of the UV-visible absorption spectra of TiO_2 film and the dye loaded TiO_2

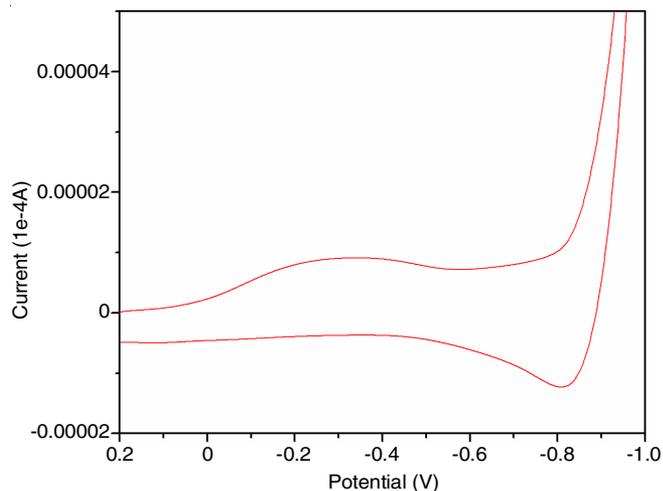
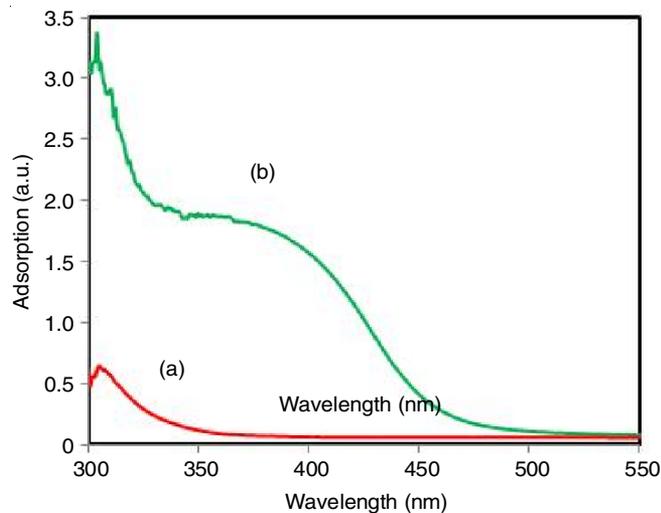


Fig. 7. Cyclic voltammogram of cobalt complex

film are shown in Fig. 8. It is observed from the spectra that the percentage of absorption increases in the dye loaded TiO_2 film towards the visible range around 320-550 nm reflecting the sensitization of TiO_2 . This indicates the good anchorage of the dye on the surfaces of TiO_2 thin film and hence it is found suitable for the fabrication of photoanode for dye sensitized solar cell (DSSC).

Fig. 8. Absorption spectra of TiO_2 thin film (a) and TiO_2 thin film sensitized with cobalt complex (b)

In order to understand excited state charge transfer processes in TiO_2 -dye interfaces, we have performed steady state photoluminescence spectra for both samples, *i.e.*, complex 1 (a) in ethanol and TiO_2 thin film sensitized with the complex (b) as shown in Fig. 9. The excitation wavelength for both samples is 300 nm. In Fig. 9, we have seen that the complex exhibits a strong photoluminescence emission peak at around 430 nm, possibly due to radiative annihilation of excitons, *i.e.*, photogenerated (e^-/h^+) pairs [20]. However, the emission intensity of

cobalt complex is significantly decreased after anchoring with TiO_2 surface, which indicates a preferable photogenerated charge transfer as feasible from the excited state of cobalt complex to the conduction band of TiO_2 [21].

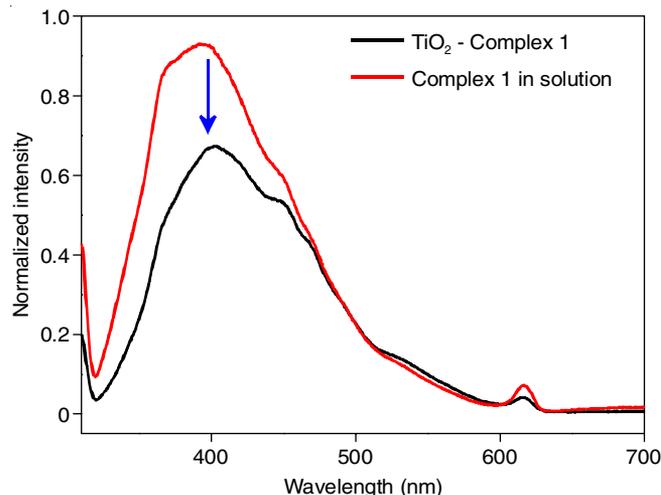


Fig. 9. Photoluminescence spectra of as-synthesized complex (a) in ethanol and photoanode (b)

Cell fabrication: To fabricate the cell, graphene coated counter electrode was prepared by using a pencil on the transparent conducting oxide and photoanode, and the counter electrode was pressed together with the help of blinder clips and finally the electrolytic solution (KI/I_2) was added.

Characterization of cell: The as-fabricated cell was characterized by current-voltage (I - V) characteristics which was measured by a Keithley 2400 source under 1 SUN illumination. The (I - V) curve is shown in Fig. 10 and the observed photovoltaic parameters of the cell are tabulated in Table-2. A conversion efficiency of 0.219 % ($I_{sc} = 0.55 \text{ mA}$; $V_{oc} = 0.85 \text{ mV}$; $\text{FF} = 47$) has been achieved for the cell.

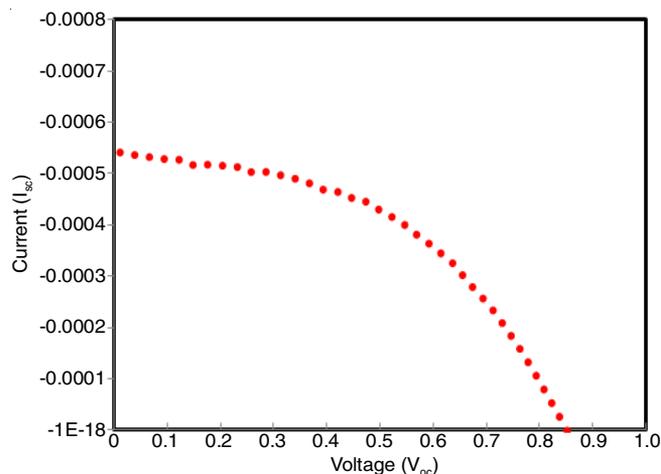
Fig. 10. The I - V characteristic of as-fabricated device

TABLE-2
CURRENT-VOLTAGE PARAMETERS FOR THE CELL AT 100 mW cm^{-2} ILLUMINATION INTENSITY

Solar cell	I (mW cm^{-2})	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	η (%)
TCO/ TiO_2 /Co(II) complex/TCO	100	0.85	0.55	47	0.219

Conclusion

In this work, a new Co(II) complex has been synthesized with 2,2'-bipyridine ligand and the crystallography and morphology of the complex was studied. The study revealed that this cobalt complex may be applied as sensitizer for dye sensitized solar cell (DSSC). The photoanode was prepared by anchoring the complex with TiO₂ film, which was coated on transparent conducting oxide (TCO) and the performance was investigated through UV-visible spectroscopy. Finally, a prototype cell was fabricated using graphene coated TCO as counter electrode and KI/I₂ as liquid electrode. The efficiency as well as the photovoltaic parameters of the cell was found to be 0.219% under 1 SUN illumination. The low efficiency of the cell may be due to the weak anchoring of the complex with TiO₂ semiconductor and also due to the loss of light through interface layers of the cell which may be improved in future for better performance of DSSC.

REFERENCES

- O.B. Berryman, F. Hof, M.J. Hynes and D.W. Johnson, *Chem. Commun.*, 506 (2006); <https://doi.org/10.1039/B511570A>.
- S. Demeshko, S. Dechert and F. Meyer, *J. Am. Chem. Soc.*, **126**, 4508 (2004); <https://doi.org/10.1021/ja049458h>.
- H. Casellas, C. Massera, P. Gamez, A.M.M. Lanfredi and J. Reedijk, *Eur. J. Inorg. Chem.*, 2902 (2005); <https://doi.org/10.1002/ejic.200500138>.
- B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991); <https://doi.org/10.1038/353737a0>.
- J. Bisquert, J. García-Cañadas, I. Mora-Seró and E. Palomares, *Proc. SPIE 5215*, Organic Photovoltaics IV (2004); <https://doi.org/10.1117/12.506907>.
- Mudasir, N. Yoshioka and H. Inoue, *Anal. Lett.*, **29**, 2239 (1996); <https://doi.org/10.1080/00032719608002245>.
- R. Soriego, L. Farias and S.A. Moya, *Polyhedron*, **16**, 3487 (1997); [https://doi.org/10.1016/S0277-5387\(97\)00130-7](https://doi.org/10.1016/S0277-5387(97)00130-7).
- J.C. Mareque-Rivas and L. Brammer, *Coord. Chem. Rev.*, **183**, 43 (1999); [https://doi.org/10.1016/S0010-8545\(98\)00183-0](https://doi.org/10.1016/S0010-8545(98)00183-0).
- I. Unamuno, J.M. Gutiérrez-Zorrilla, A. Luque, P. Román, L. Lezama, R. Calvo and T. Rojo, *Inorg. Chem.*, **37**, 6452 (1998); <https://doi.org/10.1021/ic9805224>.
- M. Mascal, A. Armstrong and M.D.J. Bartberger, *J. Am. Chem. Soc.*, **124**, 6274 (2002); <https://doi.org/10.1021/ja017449s>.
- M. Grätzel, *J. Photochem. Photobiol. Chem.*, **4**, 145 (2003); [https://doi.org/10.1016/S1389-5567\(03\)00026-1](https://doi.org/10.1016/S1389-5567(03)00026-1).
- N. Shekhar and V.Y. Gehlot, *Resonance*, **15**, 819 (2010).
- G. Sauve, M.E. Cass, G. Coia, S.J. Doig, I. Lauermaun, K.E. Pomykal and N.S. Lewis, *J. Phys. Chem. B*, **104**, 6821 (2000); <https://doi.org/10.1021/jp0002143>.
- S. Ferrere, *Chem. Mater.*, **12**, 1083 (2000); <https://doi.org/10.1021/cm990713k>.
- G.M. Hasselmann and G.J. Meyer, *Z. Phys. Chem.*, **212**, 39 (1999); https://doi.org/10.1524/zpch.1999.212.Part_1.039.
- N. Alonso-Vante, J.-F. Nierengarten and J.-P. Sauvage, *J. Chem. Soc., Dalton Trans.*, 1649 (1994); <https://doi.org/10.1039/dt9940001649>.
- T. Bessho, E.C. Constable, M. Graetzel, A. Hernandez Redondo, C.E. Housecroft, W. Kylberg, M.K. Nazeeruddin, M. Neuburger and S. Schaffner, *Chem. Commun.*, 3717 (2008); <https://doi.org/10.1039/b808491b>.
- A. Islam, H. Sugihara, K. Hara, L.P. Singh, R. Katoh, M. Yanagida, Y. Takahashi, S. Murata and H. Arakawa, *Inorg. Chem.*, **40**, 5371 (2001); <https://doi.org/10.1021/ic010391y>.
- A. Islam, H. Sugihara, K. Hara, L. Pratap Singh, R. Katoh, M. Yanagida, Y. Takahashi, S. Murata and H. Arakawa, *New J. Chem.*, **24**, 343 (2000); <https://doi.org/10.1039/b001472j>.
- Y. Zhang, Q. Pan, G. Chai, M. Liang, G. Dong, Q. Zhang and J. Qiu, *Sci. Rep.*, **3**, 1943 (2013); <https://doi.org/10.1038/srep01943>.
- Y.-P. Zhu, M. Li, Y.-L. Liu, T.-Z. Ren and Z.-Y. Yuan, *J. Phys. Chem. C*, **118**, 10963 (2014); <https://doi.org/10.1021/jp502677h>.