

Supplementary Information

Photosensitive Schottky Barrier Diode Behavior of a Semiconducting Co(III)-Na Complex With a Compartmental Schiff Base Ligand

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EXPERIMENTAL SECTION

Materials

All starting materials were commercially available, reagent grade and used as purchased from commercial suppliers without any further purification. Cobalt(II) acetate tetrahydrate and sodium azide were purchased from Mark, India. All other chemical and solvents were purchased from Sigma-Aldrich. The reactions and all manipulations were carried out under aerobic conditions.

Caution!!! Even though no troubles were experienced in this work, perchlorate salts containing organic ligands are potentially explosive. Only a small quantity of the material should be prepared and they should be handled with care.

Preparation of $[(N_3)CoLNa(N_3)]_n$

An acetonitrile solution of 2,2-dimethyl-1,3-propanediamine (0.12 mL, 1 mmol) and 5-bromo-3-methoxysalicylaldehyde (462 mg, 2 mmol) was refluxed for ca. 1 h to form the potentially hexadentate Schiff base ligand H_2L . The ligand was not isolated. A methanol solution (10 ml) of cobalt(II) acetate tetrahydrate (250 mg, 1 mmol) was added into the acetonitrile solution of the ligand H_2L to get a dark brown solution. A methanol–water solution of sodium azide (130 mg, 2 mmol) was added into the reaction mixture with constant stirring. The stirring was continued for additional 2 h. Dark brown single crystals, suitable for X-ray diffraction, were obtained after few days by slow evaporation of the solution in open atmosphere.

Yield: 522 mg (75.41 %); Based on cobalt(III). Anal. Calc. for $C_{21}H_{22}Br_2CoN_8NaO_4$ (FW = 692.19): C, 36.46; H, 3.20; N, 16.19%. Found: C, 36.4; H, 3.3; N, 16.1 %. FT-IR (KBr, cm^{-1}): 1628 ($\nu_{C=N}$), 2017 (ν_{N_3}), 2065 (ν_{N_3}), 2914–2962 (ν_{C-H}). UV-Vis, λ_{max} (nm), [ϵ_{max} (L mol $^{-1}$ cm $^{-1}$)] (CH_3CN), 256 (5.38×10^4), 402 (6.03×10^3), 660 (3.15×10^3). Magnetic moment: Diamagnetic.

Crystal data collection and refinement details

Suitable single crystals of the complex were used for data collection using a ‘Bruker SMART APEX II’ diffractometer equipped with graphite-monochromated Mo- K_α radiation ($\lambda=0.71073\text{\AA}$) at 298 K. The molecular structure was solved by direct method and refined by full-matrix least squares on F^2 using the SHELX-97 package.^{1,2} Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in their geometrically idealized

positions and constrained to ride on their parent atoms. Multi-scan empirical absorption corrections were applied to the data using the program SADABS.³ In the ‘checkcif’ an ‘A-level’ alert “VERY LARGE Solvent Accessible VOID(S) in Structure” is present. To resolve this problem we employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules and thereby were able to produce a set of solvent-free diffraction intensities. Details about the SQUEEZE procedure are given in the CIF file. Significant crystallographic data and refinement details of complex are summarized in Table S1. Important bond lengths and bond angles have been given in Tables S2 and S3, respectively.

Table S1: Crystal data and refinement details of the complex.

	Complex
Formula	C ₂₁ H ₂₂ Br ₂ CoN ₈ NaO ₄
Formula Weight	692.28
Crystal System	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
a(Å)	13.0298(3)
b(Å)	27.8366(7)
c(Å)	9.0204(2)
β(°)	109.862(1)
d(calc) [g/cm ³]	1.494
μ [mm ⁻¹]	3.207
F(000)	1376
Total Reflections	45110
Unique Reflections	5763
Observed data [<i>I</i> > 2 σ(<i>I</i>)]	3826
No of parameters	334
R(int)	0.044
R1, wR2 (all data)	0.0683, 0.0912
R1, wR2 ([<i>I</i> > 2 σ(<i>I</i>)])	0.0386, 0.0845
Residual Electron Density (eÅ ⁻³)	0.401, -0.578

Table S2: Selected bond lengths (Å) of the complex.

Co(1)-O(1)	1.917(2)
Co(1)-O(2)	1.904(2)
Co(1)-N(1)	1.915(3)
Co(1)-N(2)	1.928(3)
Co(1)-N(3)	1.970(3)
Co(1)-N(8) ^a	1.971(3)
Na(1)-O(1)	2.376(2)
Na(1)-O(2)	2.399(2)
Na(1)-O(3)	2.467(3)
Na(1)-O(4)	2.474(3)
Na(1)-N(6)	2.552(4)
Na(1)-N(5) ^a	2.396(4)

Symmetry transformation ^a = x, 1/2-y, -1/2+z

Table S3: Selected bond angles (°) of the complex.

O(1)-Co(1)-O(2)	83.12(9)	O(1)-Na(1)-O(2)	64.13(8)
O(1)-Co(1)-N(1)	91.23(10)	O(1)-Na(1)-O(3)	65.49(8)
O(1)-Co(1)-N(2)	174.48(10)	O(1)-Na(1)-O(4)	127.14(9)
O(1)-Co(1)-N(3)	90.42(10)	O(1)-Na(1)-N(6)	130.72(12)
O(1)-Co(1)-N(8) ^a	90.56(10)	O(1)-Na(1)-N(5) ^a	127.97(11)
O(2)-Co(1)-N(1)	174.34(10)	O(2)-Na(1)-O(3)	127.16(9)
O(2)-Co(1)-N(2)	91.41(10)	O(2)-Na(1)-O(4)	64.15(8)
O(2)-Co(1)-N(3)	90.87(10)	O(2)-Na(1)-N(6)	128.45(10)
O(2)-Co(1)-N(8) ^a	90.23(10)	O(2)-Na(1)-N(5) ^a	135.64(12)
N(1)-Co(1)-N(2)	94.25(11)	O(3)-Na(1)-O(4)	152.00(10)
N(1)-Co(1)-N(3)	89.61(11)	O(3)-Na(1)-N(6)	76.91(11)
N(1)-Co(1)-N(8) ^a	89.39(11)	O(3)-Na(1)-N(5) ^a	88.88(12)
N(2)-Co(1)-N(3)	88.91(11)	O(4)-Na(1)-N(6)	77.34(11)
N(2)-Co(1)-N(8) ^a	90.22(11)	O(4)-Na(1)-N(5) ^a	97.05(12)
N(3)-Co(1)-N(8) ^a	178.62(12)	N(5) ^a -Na(1)-N(6)	79.42(12)

Symmetry transformation ^a = x, 1/2-y, -1/2+z

Instrumentation details

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin Elmer 240C elemental analyzer. Infrared spectrum in KBr (4500-500 cm⁻¹) was recorded with a Perkin Elmer Spectrum Two spectrophotometer. Powder X-ray diffraction was performed on a Bruker D8 instrument with Cu K_α radiation. The magnetic susceptibility measurement was done with an EG & PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants.⁴ Electronic spectrum in acetonitrile medium were recorded on a SHIMADZU UV-1700(E) Pharma Spec UV-Vis spectrophotometer.

Steady state photoluminescence spectrum in acetonitrile medium was obtained in Shimadzu RF-5301PC spectrofluorometer at room temperature. Thermo-gravimetric analyses (TGA) were performed in a Mettler Toledo TGA/DTA instrument using STARe SW 11.00 software. Time dependent photoluminescence spectra were recorded using Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBHDAS6 software. The film thickness was measured by stylus Profilometer.⁵ The current-voltage (I-V) characteristics curve under dark and light condition of the fabricated device was recorded with the help of a Keithley 2635B source meter interfaced with PC.

Description of the Hirshfeld surface analysis method

Generally, a typical Hirshfeld surface is represented by tens of thousands of surface points obtained by triangulation, and two parameters d_i and d_e , (Where, d_i represents distance from the surface to the nearest atom interior to the surface and d_e represents distance from the surface to the nearest atom exterior to the surface) convey information about relevant contact distances from each point. To construct a 2D fingerprint plot the molecular Hirshfeld surface is first obtained using standard methods then Hirshfeld surfaces with d_i and d_e are mapped upon them. As described many of our previous papers,^{6,7} Hirshfeld surface^{8,9} and the associated two-dimensional (2D) fingerprint plots¹⁰⁻¹² were calculated using Crystal Explorer¹³, with bond lengths to hydrogen atoms set to standard values.¹⁴

Device fabrication:

At first ITO (indium tin oxide) coated glass substrate was cleaned by ethanol, acetone and distilled water sequentially by ultrasonication technique. The sample was dispersed in dimethylformamide (DMF) medium until a homogeneous solution appears. Then it was spin

coated on the ITO coated glass (at 800 rpm for 1 min) to produce a thin film. The film was then dried under vacuum condition. The metal (Al) was deposited onto the thin film with the help of shadow mask by thermal evaporation technique to construct metal-semiconductor junction. The film thickness of the device was 1 μm . The effective diode area was maintained at $7.065 \times 10^{-6} \text{ m}^2$. A bias voltage -2 V to +2 V was applied to the Al/complex/ITO device in air at room temperature under dark and light condition for investigation of the electric properties.

Computational details:

The $P2_1/C$ primitive monoclinic crystal structure of the complex was optimized with the density functional theory method using the DMOL3 program code of Accelrys, Inc.^{15,16} They were relaxed with the experimental unit cell parameters fixed. The calculations were performed within the Generalized-Gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) formulation for the exchange-correlation functional.¹⁷ DMol³ implements Numerical atomic orbitals (NAO) for the basis functions, each function corresponding to an atomic orbital. Double numerical with polarization atomic orbitals (DNP)¹⁵ for the basis function were used. The main advantages for the use of NAO are: according to chemical insight and small basis sets is necessary for good results. All-electron relativistic calculation was used, which eliminates the problems and harms of adding pseudo-potentials in the DFT calculations, treating the electrons of the core in the same way as it does for the valence electrons. The calculations were performed using the spin-polarized methodology. The long-range dispersion correction has been included in the calculations with the Grimme's scheme.¹⁸ The k-mesh points over the Brillouin zone were generated with parameters 2 x 2 x 2 in the Monkhorst-Pack scheme. The energy tolerance for self-consistent field (SCF) convergence was set to 10^{-5} eV/atom . Density of states (DOS) were calculated along the k-vector of the first Brillouin zone (2 x 1 x 3) of the crystal, and total and

local density of states (TDOS and LDOS, respectively) were calculated with respect to the Fermi Level.

The optical properties including dielectric function and optical conductivity of the crystal are calculated with CASTEP software.¹⁹ Ultrasoft pseudopotentials were used in this part of the work with the relativistic treatment of the Koelling-Harmon. A plane-wave basis set with 370 eV cutoff was applied. The k-mesh points over the Brillouin zone were generated with parameters 1x1x2 the Monkhorst-Pack-scheme. The energy tolerance for self-consistent field (SCF) convergence was 1×10^{-4} eV/atom for all calculations. The long-range dispersion correction has been included in the calculations with the Grimme's scheme too. Optical properties are averaged over all polarization directions, thereby imitating an experiment on a polycrystalline sample. A smearing of 0.2 eV was employed. A scissor operator of +0.943 eV was employed for the optical properties calculations of complex.

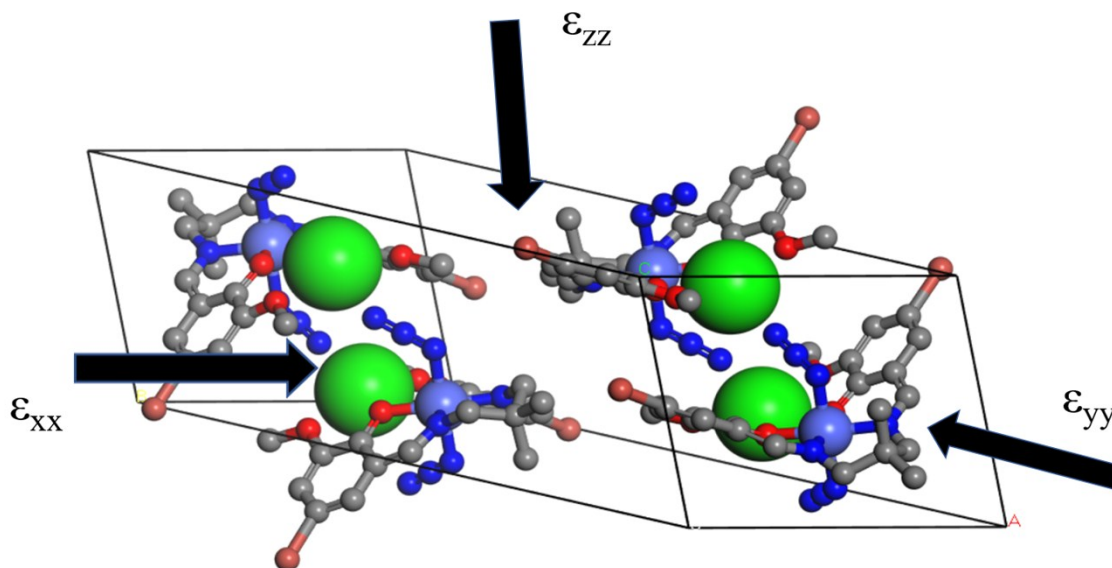


Figure S1: ϵ_{xx} , ϵ_{yy} , ϵ_{zz} specify the incident direction of radiation for optical properties calculation on the cell unit. The direction is specified in fractional (lattice) coordinates. Colour

code: violet CPK= Co, Green CPK = Na, blue ball and stick = N, grey ball and stick = C, red ball and stick = O, brown ball and stick = Br. Hydrogen atoms are removed for clarify.

Results and Discussions

Analysis of Hirshfeld surfaces

The Hirshfeld surface analysis is a very powerful technique for gaining information about different types of interactions, and to identify and quantify these interactions. The Hirshfeld surfaces of the complex mapped over d_i , d_e , d_{norm} , shape index and curvedness shown in Figure S2. The surfaces are shown as transparent so that the molecular moieties around which Hirshfeld surfaces are calculated could be visualized. Usually Hirshfeld surface and properties defined by it emphasize a whole-of-molecule approach to understanding inter-molecular interactions, they can also be used in conjunction with a more direct atom...atom based approach to gain a fuller appreciation of the important interactions in a molecular crystal. The dominant interactions of the complex are $\text{H}\cdots\text{H}$, $\text{C}\cdots\text{H}$ / $\text{H}\cdots\text{C}$, $\text{O}\cdots\text{H}$ / $\text{H}\cdots\text{O}$, $\text{N}\cdots\text{H}$ / $\text{H}\cdots\text{N}$, $\text{Br}\cdots\text{H}$ / $\text{H}\cdots\text{Br}$. Red spots on the d_{norm} surface (Figure S2) indicate that these interactions are dominant. In addition, the two dimensional fingerprint plots (Figure S3) exemplify various inter-molecular interaction patterns associated with the complex and their relative contributions in percentage scale. In the two dimensional fingerprint plots inter-molecular interactions become visible as distinct spikes. Complementary regions are visible in the two dimensional fingerprint plots where one molecule act as donor ($d_e > d_i$) and the other as an acceptor ($d_e < d_i$). Fingerprint plots can also be exploited to highlight the selected atoms pair close contacts. This exploitation permits separation of contributions from different interaction types, which overlap in the whole fingerprint plots.^{20,21}

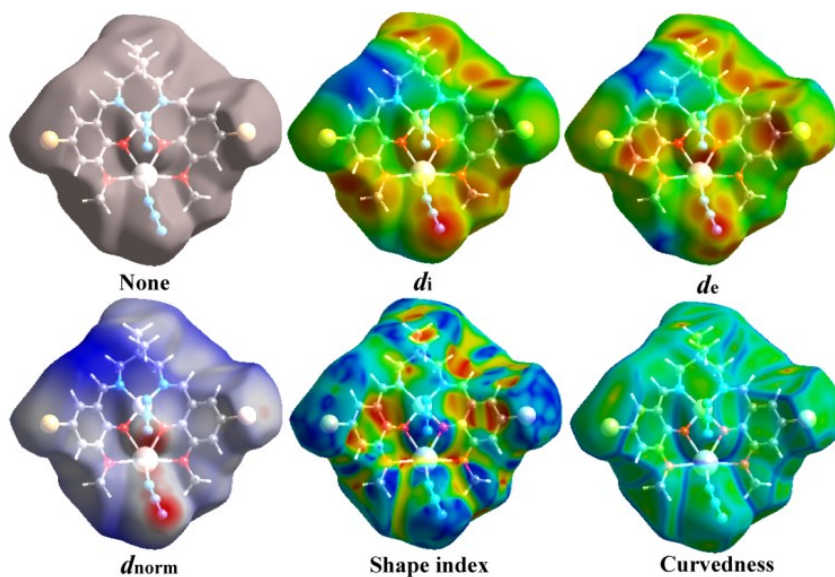


Figure S2: Hirshfeld surfaces mapped with none, d_i , d_e , d_{norm} , shape index and curvedness.

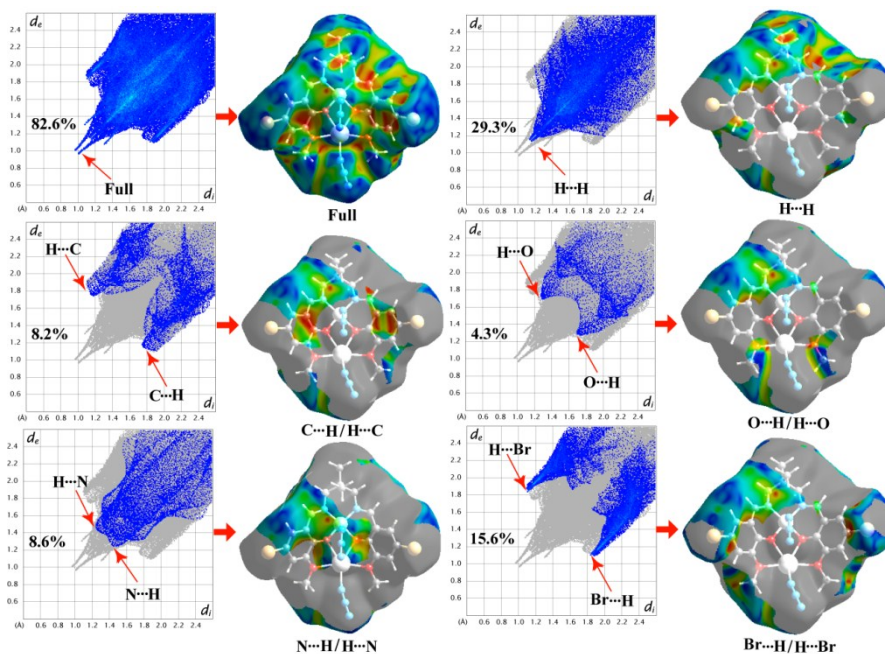


Figure S3: Two dimensional fingerprint plots of the complex: Full and resolved into H...H, C...H / H...C, O...H / H...O, N...H / H...N and Br...H / H...Br contacts showing the percentages of contacts contributed to the total Hirshfeld Surface area of the complex. Surfaces

in the right hand columns highlight the relevant surface patches associated with the specific contacts in the total Hirshfeld Surface area of the complex.

X-ray diffraction of powdered material

Powder X-ray diffraction technique has been used to cross-check the purity of the bulk material. The experimental X-ray diffraction pattern of the bulk material is in excellent concurrence with the simulated XRD pattern, indicating purity of the bulk sample. The simulated patterns were calculated from the single crystal structural data (cif file) using the CCDC MERCURY software. The experimental and simulated powder XRD pattern of the complex is given in Figure S4.

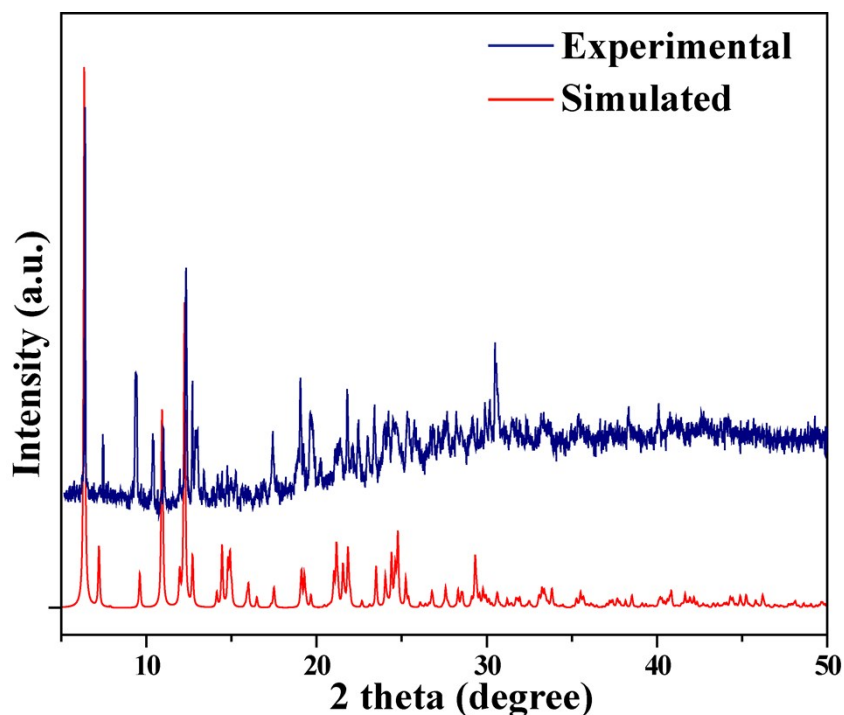


Figure S4: Experimental and simulated powder XRD patterns of the complex, confirming the purity of the bulk materials.

Thermogravimetric analysis

The complex has been subjected to thermal analysis in a dynamic nitrogen atmosphere (100 mL min^{-1}) at a heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ using a thermogravimetric (TG) technique. Figure S5 illustrates the thermogravimetric plot of the complex. The complex is stable up to $\sim 100 \text{ }^{\circ}\text{C}$, as can be observed from thermogravimetric plot (Figure S5). With further increase in temperature, the complex undergoes decomposition.

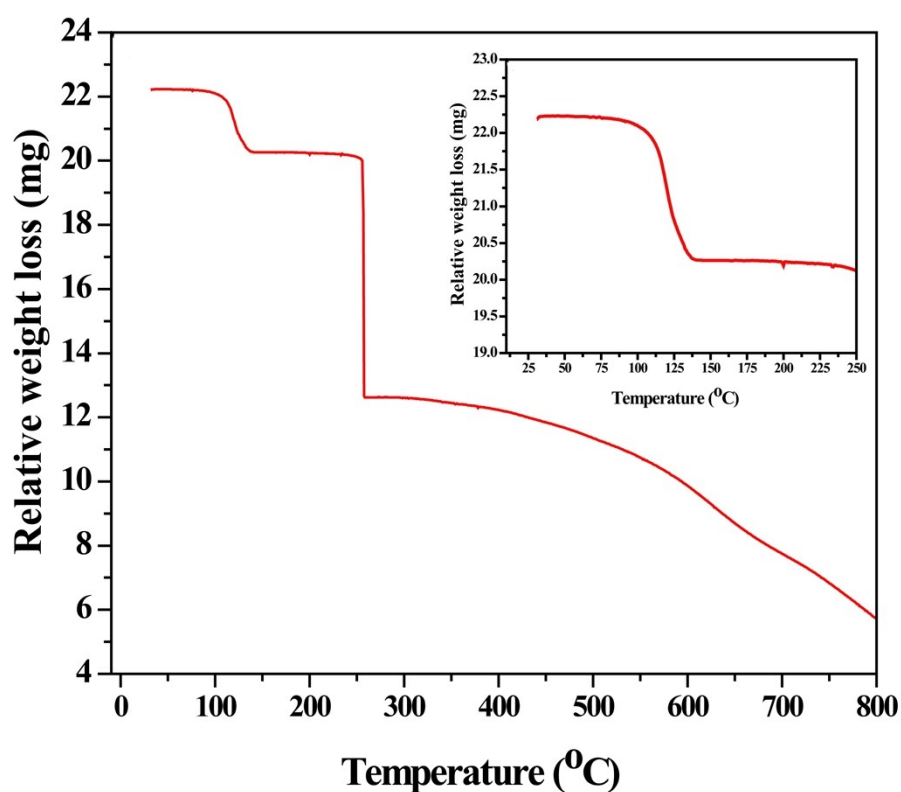


Figure S5: Thermal analysis of the complex.

Characterization of the complex layer

IR and UV-Vis spectral analysis of the complex layer has been performed to characterize the complex layer fabricated on the ITO electrode. IR and UV-Vis spectra of the complex layer are illustrated in Figure S6 and S7, respectively.

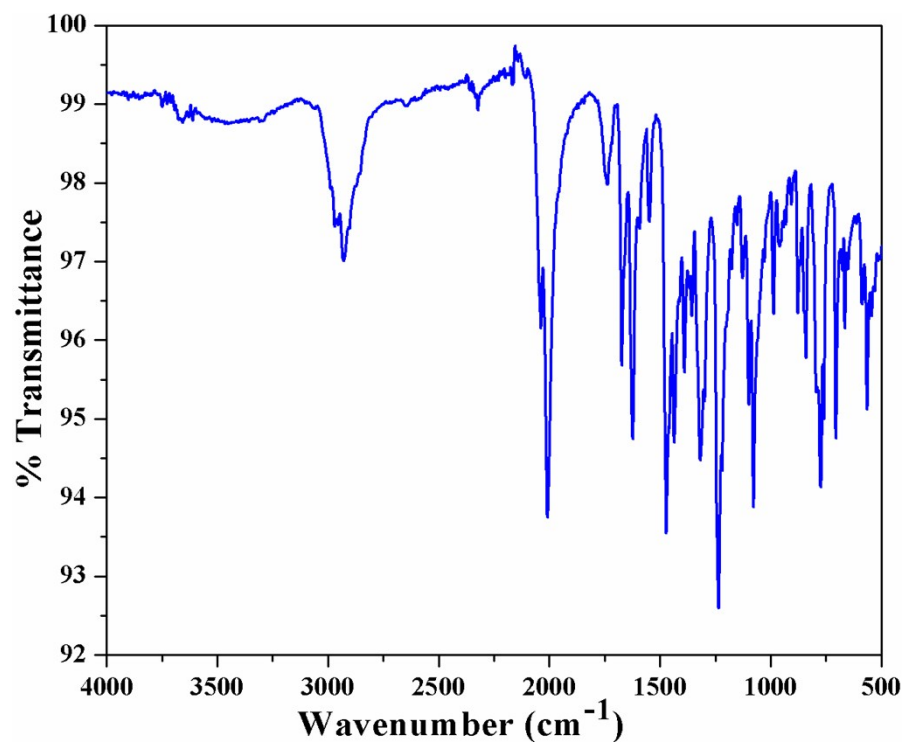


Figure S6: IR spectrum of the complex layer.

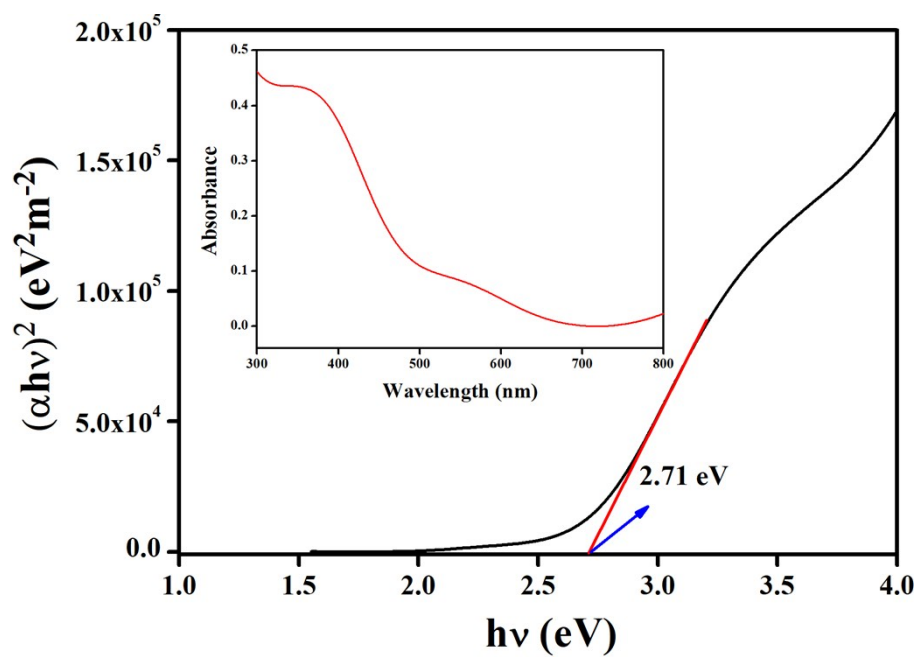


Figure S7: Tauc's plot and UV-Vis absorption spectra (inset) of the complex layer.

Thickness and temperature dependent current-voltage (I-V) characteristics:

The conductivity (Figure S6) is measured with the variation of film thickness (800 nm, 1000 nm and 1200 nm). The temperature dependent I-V characteristics of Al/complex SBD are analyzed in temperature range from 303 K to 423 K, which confirms the semiconducting behavior of our synthesized complex. Temperature dependent I-V curve and conductivity plot are portrayed in Figure S8.

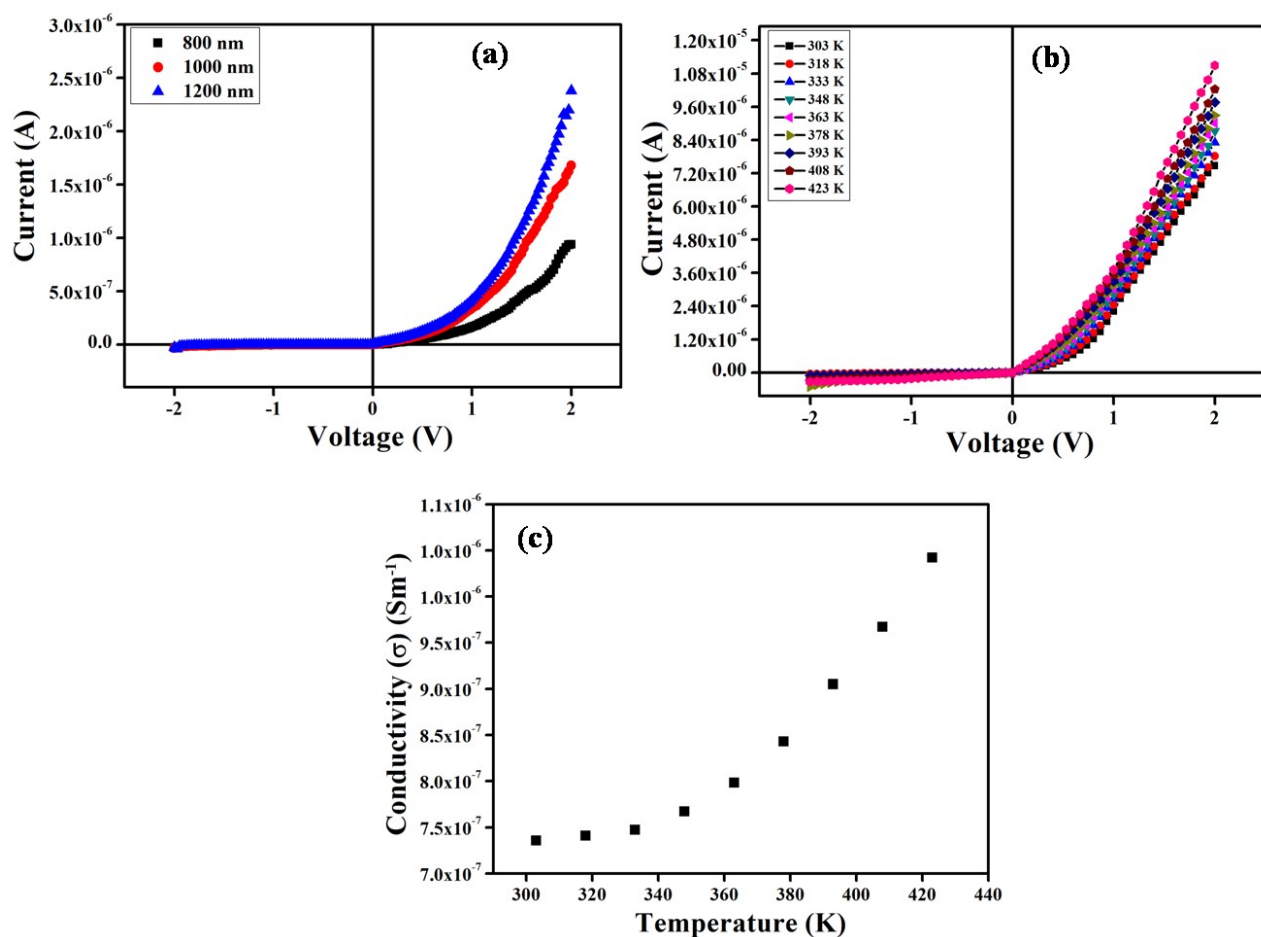


Figure S8: (a) Thickness dependent I-V characteristics and temperature dependent (b) I-V characteristics curve, (c) conductivity plot.

Spectral and magnetic characterization

The IR and electronic spectra of the complex are in excellent concurrence with its crystal structure. Some of the extremely informative infrared and electronic absorptions which assist in the structural characterization of the complex are gathered in the Experimental section (ESI). In the IR spectra of the complex, a distinct band due to the azomethine (C=N) group at 1628 cm^{-1} is routinely noticed.²²⁻²⁴ Strong bands at 2017 and 2065 cm^{-1} , for the anti-symmetric and symmetric stretching vibrations of end-to-end bridged azide respectively, are noticed in the IR spectrum of the complex.^{25,26} Broad bands in the range of 2914 - 2962 cm^{-1} due to alkyl C-H stretching vibrations are consistently detected in IR spectrum of the complex.^{27,28} Figure S9 illustrate the IR spectra of the complex.

The electronic spectrum of the complex in acetonitrile medium consists of three most fundamental bands around 256 nm , 402 nm and 660 nm . An octahedral cobalt(III) complex, in presence of Schiff base like strong field ligand, is expected to have two d-d transitions, ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{2g} \leftarrow {}^1A_{1g}$ in the visible range along with higher energy charge transfer transitions. Broad absorption band around 660 nm may thus be assigned as one of these two expected d-d transitions, as was also observed in similar type low spin octahedral cobalt(III) complexes.^{29,30} Bands around 403 nm may be attributed to charge transfer transitions from the coordinated ligands to the cobalt(III) centre. The intense absorption band in the high energy region around 256 nm corresponds to intra-ligand $\pi\text{-}\pi^*/\text{n-}\pi^*$ transition.³¹⁻³³

Magnetic susceptibility measurement at room temperature confirms that the complex is diamagnetic in nature, as expected for low spin octahedral cobalt(III) complexes.^{27,34}

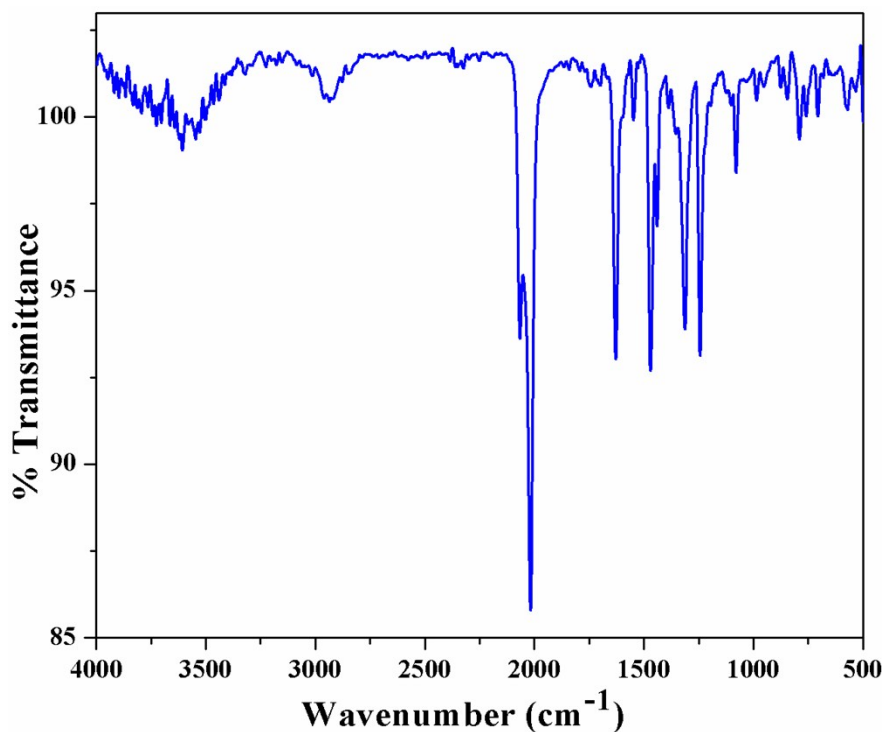


Figure S9: IR spectra of the complex.

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