

Electronic Supplementary Information

Unprecedented photosensitivity of heterotrimetallic copper(II)/sodium/mercury(II) coordination polymer based thin film semiconductor device

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Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin Elmer 240C elemental analyzer. IR spectrum in KBr (4500-500 cm⁻¹) was recorded with a Perkin Elmer Spectrum Two spectrophotometer. Electronic spectrum in DMF was recorded on a Perkin Elmer Lambda 35 UV-visible spectrophotometer. Steady state photoluminescence spectrum in DMF was obtained in Shimadzu RF-5301PC spectrofluorometer at room temperature. Time

dependent photoluminescence spectrum was recorded using Hamamatsu MCP photomultiplier (R3809) and was analyzed by using IBHDAS6 software. The emission of the complex was tentatively attributed to the intra-ligand transitions modified by metal coordination. Intensity decay profile was fitted to the sum of exponentials series $I(t) = \sum_i \alpha_i \exp(-t/\tau_i)$, where α_i was a factor representing the fractional contribution to the time resolved decay of the component with a lifetime of τ_i . Bi-exponential function was used to fit the decay profile for the complex, with obtaining χ^2 close to 1. The intensity-averaged life time (τ_{av}) was determined from the

result of the exponential model using $\tau_{av} = \frac{\sum_i \alpha_i \tau_i^2}{\sum_i \alpha_i \tau_i}$, where α_i and τ_i are the pre-exponential

factors and excited state luminescence decay time associated with the i -th component, respectively. Powder X-ray diffraction was performed on a Bruker D8 instrument with Cu K_α ($\lambda = 1.5406 \text{ \AA}$) radiation. In this process, the complex was ground with a mortar and pestle to prepare fine powders. The powders were then dispersed with alcohol onto a zero background holder (ZBH). The alcohol was allowed to evaporate to provide a nice, even coating of powder adhered to the sample holder.

X-ray crystallography

Suitable single crystal of the complex was picked, mounted on a glass fibre and diffraction intensities were measured with an Oxford Diffraction X-Calibur diffractometer equipped with Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$, 50 kV, 40 mA) at an ambient temperature (150 K). Data collection and reduction were performed with the CrysAlis software.¹ The structure of the complex was solved by direct methods using SHELXS-97 and refined by full-matrix least

squares on F^2 , using the SHELXL-2016 program.² Non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached with oxygen atoms were located by difference Fourier maps. All other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. The carbon and hydrogen atom of 1,3-diaminopropane was disordered. Atom C51 was refined as an atom disordered over 2 sites. Programs used included PLATON,³ DIAMOND,⁴ ORTEP⁵ and MERCURY.⁶

Device Fabrication

The morphological study of the thin film of the complex was done by FEI make Inspect F50 field emission scanning electron microscope (FESEM) instrument. The electrical characterization was performed in the complex based metal-semiconductor (MS) junction devices. This device was fabricated by depositing a thin film of well dispersion of as synthesized complex. In order to fabricate active Schottky device, ITO (Indium Tin Oxide) coated glass substrates were used. ITO coated glass substrates were cleaned by acetone, ethanol and distilled water with the help of an ultra-sonicator. Next the complex was separately mixed with acetonitrile in right proportion (20 mg/mL) and sonicated for several minutes until it produces a well stable dispersion. A thin film was prepared by spin coating a well dispersed solution of the synthesised material at 400 rpm for 2 mins. Then the film was dried at 60⁰ C for 2 hours in vacuums. For the characterization of the developed thin film, thickness was measured by surface profiler as ~1 μm . 99.99% pure Al was chosen as the metal-electrode and was deposited on to the active thin film by a Vacuum Coating Unit 12A4D of HINDVAC to prepare the metal-semiconductor (MS) interface through shadow mask by thermal evaporation technique with the help of vacuum coating unit under a base pressure of 10⁻⁶ Torr. The effective areas of the

films were maintained as $7.065 \times 10^{-2} \text{ cm}^2$. For electrical characterization of the devices, the current-voltage (I-V) characteristic was recorded under dark and AM 1.5G radiation with the help of a Keithley 2635B source meter by two-probe technique. All the preparation and measurements were performed at room temperature and under ambient condition. Capacitance, impedance and phase angle were measured as a function of frequency using a computer controlled LCR meter Agilent 4294.

Hirshfeld surfaces

The Hirshfeld surface⁷ is unique⁸ for a given crystal structure provides additional insight into the intermolecular interaction of molecular crystals.⁹ The 2D-fingerprint¹⁰ plot is very important as it provides the contribution of different intermolecular interactions in crystal structure. Crystal Explorer¹¹ was used to determine the Hirshfeld surfaces and the associated 2D-fingerprint plots. 2D-fingerprint plots of each Hirshfeld surface were shown as plots of d_i against d_e . The normalized contact distance (d_{norm}) based on d_e and d_i was given by,

$$d_{norm} = \frac{(d_i - r_i^{vdw})}{r_i^{vdw}} + \frac{(d_e - r_e^{vdw})}{r_e^{vdw}}$$

where r_i^{vdw} and r_e^{vdw} are the van der Waals radii of the atoms. The d_{norm} values were mapped on to the Hirshfeld surface by using a red, blue and white colour scheme: where red is used to highlight shorter contacts, white is used for contacts at distances around the vdW separation and blue is for longer contacts.

Table S1: Selected bond lengths (Å) of the complex.

Hg(1)-Cl(1)	2.517(9)	Cl(2)-Na(1) ^b	2.833(8)
Hg(1)-Cl(2)	2.461(4)	Na(1)-O(11)	2.288(16)
Hg(1)-S(1)	2.562(7)	Na(1)-O(31)	2.308(14)
Hg(1)-S(2)	2.525(7)	Na(1)-O(131)	2.472(14)
Cu(1)-O(11)	1.958(12)	Na(1)-O(291)	2.475(14)
Cu(1)-O(31)	1.932(13)	Na(1)-N(1) ^a	2.500(19)
Cu(1)-N(19)	1.999(15)	Na(2)-O(41)	2.336(14)
Cu(1)-N(23)	1.986(16)	Na(2)-O(61)	2.315(15)
Cu(3)-O(41)	1.945(13)	Na(2)-O(431)	2.512(15)
Cu(3)-O(61)	1.919(14)	Na(2)-O(591)	2.390(17)
Cu(3)-N(49)	1.988(16)	Na(2)-N(1) ^a	2.49(2)
Cu(3)-N(53)	1.951(19)	Na(2)-N(2) ^c	2.44(3)

Symmetry transformations: ^a = 1-x, -1/2+y, 1-z; ^b = 1-x, 1/2+y, 1-z; ^c = 1-x, y, 1/2+z.

Table S2: Selected bond angles (°) of the complex.

Cl(1)-Hg(1)-Cl(2)	109.9(2)	O(31)-Na(1)-O(291)	66.5(5)
Cl(1)-Hg(1)-S(1)	105.7(3)	Cl(2) ^a -Na(1)-O(31)	112.8(4)
Cl(1)-Hg(1)-S(2)	112.1(3)	O(31)-Na(1)-N(1) ^a	139.5(8)
Cl(2)-Hg(1)-S(1)	108.50(19)	O(131)-Na(1)-O(291)	161.7(6)
Cl(2)-Hg(1)-S(2)	117.9(2)	Cl(2) ^a -Na(1)-O(131)	83.2(4)
S(1)-Hg(1)-S(2)	101.7(3)	O(131)-Na(1)-N(1) ^a	77.7(7)
O(11)-Cu(1)-O(31)	79.8(5)	Cl(2) ^a -Na(1)-O(291)	89.9(4)
O(11)-Cu(1)-N(19)	93.3(6)	O(291)-Na(1)-N(1) ^a	86.2(6)
O(11)-Cu(1)-N(23)	171.1(7)	Cl(2) ^a -Na(1)-N(1) ^a	95.5(7)
O(31)-Cu(1)-N(19)	172.1(6)	O(41)-Na(2)-O(61)	64.8(5)
O(31)-Cu(1)-N(23)	91.6(7)	O(41)-Na(2)-O(431)	64.8(4)

N(19)-Cu(1)-N(23)	95.5(7)	O(41)-Na(2)-O(591)	132.2(7)
O(41)-Cu(3)-O(61)	80.3(5)	O(41)-Na(2)-N(1) ^a	139.3(8)
O(41)-Cu(3)-N(49)	91.8(5)	O(41)-Na(2)-N(2) ^c	119.6(7)
O(41)-Cu(3)-N(53)	169.5(6)	O(61)-Na(2)-O(431)	129.5(6)
O(61)-Cu(3)-N(49)	169.9(6)	O(61)-Na(2)-O(591)	67.6(6)
O(61)-Cu(3)-N(53)	91.1(6)	O(61)-Na(2)-N(1) ^a	130.2(6)
N(49)-Cu(3)-N(53)	97.4(6)	O(61)-Na(2)-N(2) ^c	125.3(8)
Hg(1)-Cl(2)-Na(1) ^b	115.3(2)	O(431)-Na(2)-O(591)	162.9(7)
O(11)-Na(1)-O(31)	65.8(5)	O(431)-Na(2)-N(1) ^a	88.4(6)
O(11)-Na(1)-O(131)	66.0(5)	O(431)-Na(2)-N(2) ^c	83.3(7)
O(11)-Na(1)-O(291)	132.2(5)	O(591)-Na(2)-N(1) ^a	77.8(7)
Cl(2) ^a -Na(1)-O(11)	111.3(4)	O(591)-Na(2)-N(2) ^c	85.4(8)
O(11)-Na(1)-N(1) ^a	130.7(6)	N(1) ^a -Na(2)-N(2) ^c	84.3(9)
O(31)-Na(1)-O(131)	131.8(6)	-	-

Symmetry transformations: ^a = 1-x,-1/2+y,1-z; ^b = 1-x,1/2+y,1-z; ^c = 1-x,y,1/2+z.

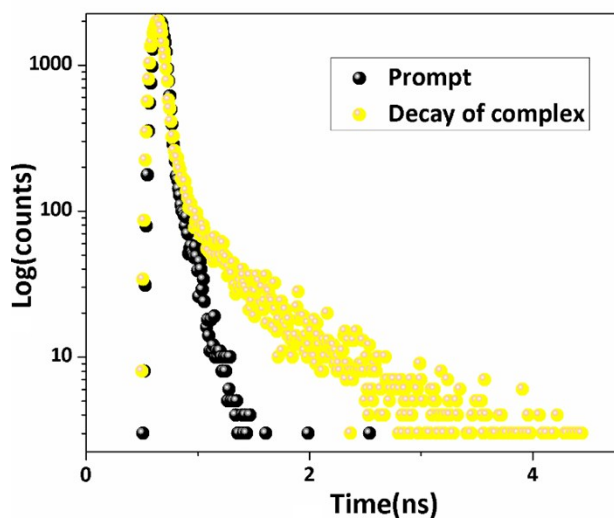


Fig. S1: Decay profile of the complex.

Table S3: Photophysical data for the complex.

Absorption (nm)	Emission (nm)	A ₁ (%)	τ_1 (ns)	A ₂ (%)	τ_2 (ns)	τ_{avg} (ns)	χ^2
280	330	67.54	0.34	32.46	3.63	3.1	1.03

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