

Electronic Supplementary Information

Coordination polymers of Ag(I) and Hg(I) ions with 2,2'-azobispyridine: synthesis, characterization and enhancement of conductivity in presence of Cu(II) ions

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Experimental section

Materials and physical methods

Reagents or analytical grade materials were obtained from commercial suppliers and used without further purification. Spectroscopic grade solvents were used for spectroscopic and electrochemical measurements. The C, H, and N content of the compounds were obtained from a Perkin Elmer 2400 series II elemental analyzer. Infrared spectra of the samples were measured from 4000 to 400 cm^{-1} with the KBr pellet at room temperature on a Perkin-Elmer Spectrum RX 1, FT-IR spectrophotometer. Electronic absorption spectra in solution at 298 K were carried out on a Perkin-Elmer Lambda 750 spectrophotometer in the range of 3300–175 nm. Field-emission scanning electron microscope (FESEM) system (Carl Zeiss, Germany make, Model: Sigma) was used for taking FESEM images and FESEM samples were prepared by casting a drop on a Si-wafer and dried at air around 45⁰C.

Syntheses

2,2'-Azobispyridine (abpy) This was prepared by the reported procedure.^{1,2}

[Hg₂(abpy)₂]_n[PF₆]_{2n} (1) To a mixture of abpy (138 mg, 0.75 mmol) and Hg₂(NO₃)₂ (125 mg, 0.25 mmol) in a 50 ml round bottom flux, MeOH (15 ml) and CH₃CN (10 ml) were added and the mixture was stirred at room temperature (298 K) for 12 h. The solution turned reddish and it was filtered. To the filtrate NaPF₆ (171mg, 0.5 mmol) in MeOH (5ml) was added and allowed to evaporate slowly at 298 K. After a few days a reddish orange solid separated out, which was filtered and dried in air and collected. Yield: 200 mg (~ 82% with respect to Hg). Elemental analysis (%) calcd for C₃₀H₂₄Hg₂N₁₂: C 37.78, H 2.54, N 17.62; N; Found: C 37.16, H 2.51, N17.02. IR, cm^{-1} (KBr): ν 3424 (br), 1645 (m), 1601 (vs), 1575 (s), 1470 (s), 1444 (vs), 1312 (m), 1155 (m), 1061 (m), 1025 (s), 830 (vs), 765 (vs), 730 (s).

[Ag(abpy)]_n[PF₆]_n (2) To a solution of abpy (184 mg, 1 mmol) in MeOH (15 ml), AgNO₃ (168 mg, 1 mmol) was added and the mixture was stirred for 4 h. The solution turned deep orange. To this solution, NaPF₆ (167 mg, 1 mmol) in MeOH (5 ml) was added and it was allowed to evaporate slowly in air. After a few days an orange solid separated out, which was collected after filtration and dried in air. Yield 245 mg (~ 84% with respect to Ag). Elemental analysis (%) calcd for C₁₀H₈AgN₄: C 41.12, H 2.76, N 19.18; Found: C 41.05, H 2.75, N 19.01. IR, cm⁻¹ (KBr): ν 3425 (br), 1646 (m), 1575 (m), 1580 (m), 1470 (s), 1438 (s), 1315 (m), 1157 (m), 832 (vs), 764 (s), 575 (s).

X-ray crystallography

Dark red single crystals of [Hg₂(abpy)₂]_n[PF₆]_{2n}(**1**) and [Ag(abpy)]_n[PF₆]_n(**2**) were picked up and mounted on a Bruker APEX-II CCD diffractometer equipped with a Mo-target rotating-anode X-ray source and a graphite monochromator (Mo-KR, $\lambda = 0.71073 \text{ \AA}$). Final cell constants were obtained from least-squares fits of all measured reflections. The structure was readily solved by direct method and subsequent difference Fourier techniques. The crystallographic data of **1** and **2** are listed in Table S1. SHEIXL97³ and SHELXL-2018⁴ program packages were used for the structure solution and for refinement.. The collected data ($I > 2 \sigma(I)$) was integrated by using the SAINT program,⁵ and the absorption correction was done by SADABS.⁶ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters.

Table S1. Crystallographic data of **1** and **2**

	1	2
formula	C ₃₀ H ₂₆ F ₁₂ Hg ₂ N ₁₂ OP ₂	C ₁₀ H ₈ AgF ₆ N ₄ P
CCDC No	1993895	1993894
fw	1261.75	437.04
cryst color	orange	orange
cryst system	monoclinic	monoclinic
space group	<i>P2₁/n</i>	<i>Pnna</i>
<i>a</i> (Å)	15.7408(9)	10.6130(10)
<i>b</i> (Å)	16.2559(9)	10.2771(10)
<i>c</i> (Å)	15.888(2)	12.5111(12)
α (°)	90.00	90
β (°)	108.946(6)	90
γ (°)	90.00	90
<i>V</i> (Å ³)	3845.2(6)	1364.6(2)
<i>Z</i>	4	4
<i>T</i> (K)	100(2)	100(2)
refl. collected (2 Θ _{max})	66.2	72.88
ρ calcd (g cm ⁻³)	2.180	2.127
unique refl.	86047	48665
ref (<i>I</i> >2 σ)	12894	3064
μ (mm ⁻¹)	8.163	1.664
λ (Å)	0.71073	0.71073
F(000)	2384	848
R1 ^b /goodness of fit ^c	0.0245/1.103	0.0338/1.136
wR2 ^d [<i>I</i> >2 σ (I)]	0.0558	0.0873
no. of params/restr.	532/0	101/0
residual density (eÅ ⁻³)	1.829/-2.231	2.310/-0.835

^aObservation criterion: $I > 2\sigma(I)$. ^b $RI = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^cGOF = $\{\sum [w(F_o^2 - F_c^2)^2] / (n-p)\}^{1/2}$.

^dwR2 = $\{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2) / 3$

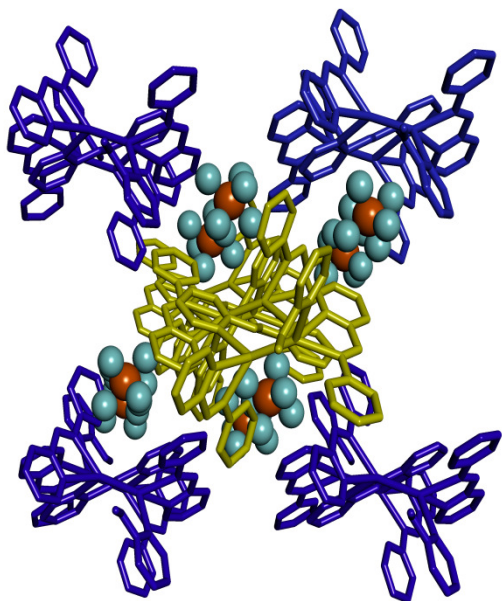


Fig. S1 Arrangement of the polymeric chains and the position of PF₆ units in crystal structure of **1** along with a-axis

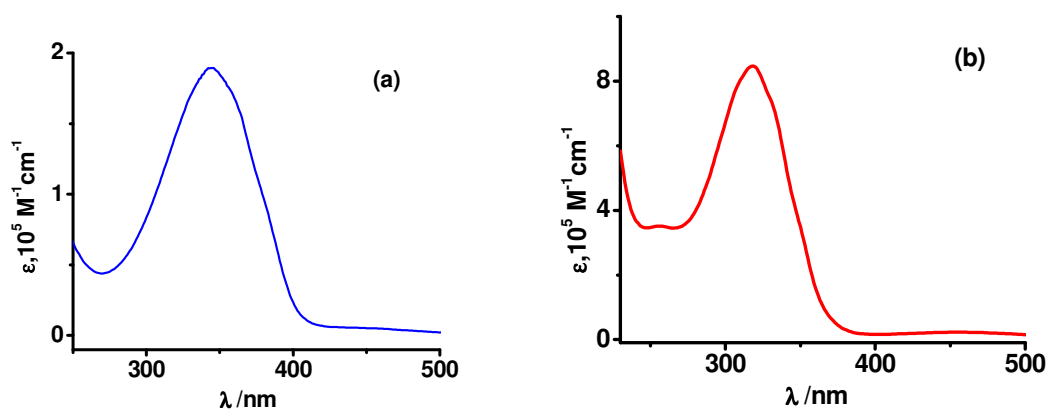


Fig. S2 UV-Vis spectra of (a) **1** and (b) **2** in CH₂Cl₂ at room temperature

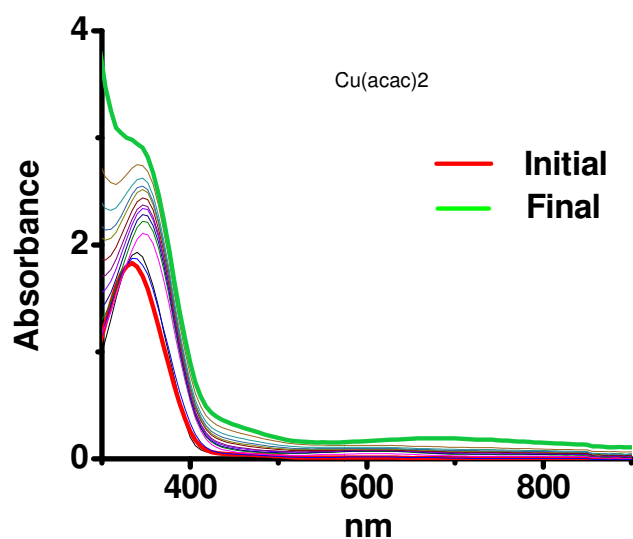


Fig. S3 Change of electronic spectra of **1** with the addition of $\text{Cu}(\text{acac})_2$ solution in CH_3CN .

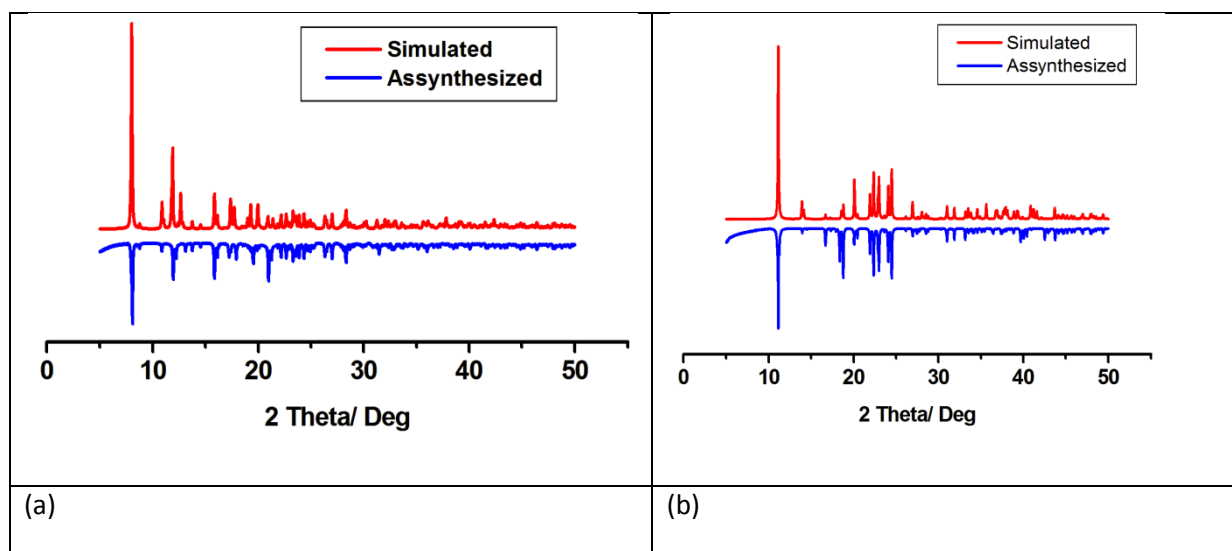


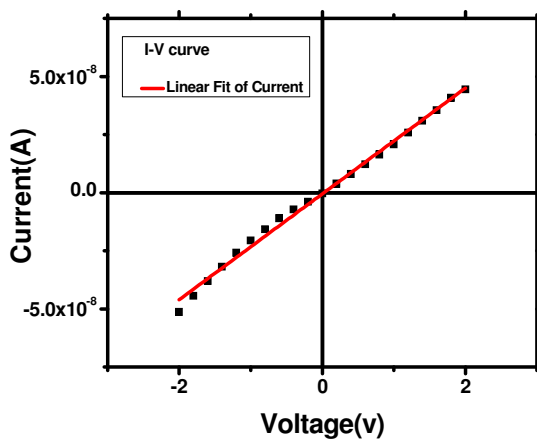
Fig. S4 (a) PXRD patterns of simulated **1** (red) and as-synthesized **1** (blue) and (b) PXRD patterns of simulated **2** (red) and as-synthesized **2** (blue).

Device fabrication and conductivity measurements

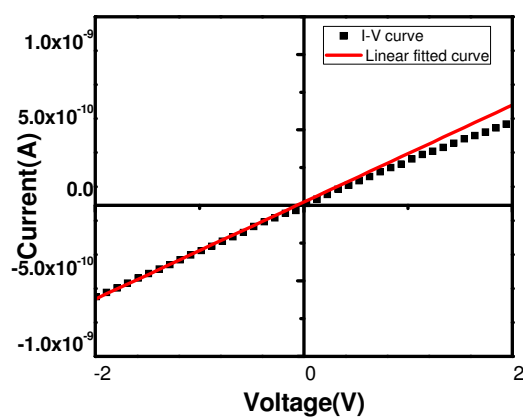
Current-voltage (I-V) measurements were done on individual crystals of **1** and **2**, providing stable electrical contacts between each crystal and tip. The Cu plate was polished thoroughly. The individual block crystals were taken on the Cu plate and the silver paste was used as ohmic contact material. Top and bottom of crystals were connected with two probe knob of

the source meter and the voltage was varied from -2 V to +2 V. The resultant I-V graph was fitted linearly and the slope of the graph was measured. Inverse of the slope is the resistance of the crystal. The bias range was fitted using Ohm's law to determine resistivity (ρ), conductivity (σ), which were calculated using $\rho = R(A/L)$, and $\sigma = 1/\rho$ where L is crystal height and A is contact area between the probe and sample. Crystal heights were determined directly using single crystal X-ray microscope height images. A two-contact probe single crystal device of **1** and **2** were fabricated by using silver paste to attach two copper wires onto both sides of the crystal. The device was loaded into the chamber of a probe station. Probes were connected to a source meter Keithley 2450 source. *I-V* curves were collected every minute by sweeping the voltage from -2 V to +2 V at room temperature. At the end of each step of data collection the electrical resistance remained constant. Therefore, the final measurement was considered as the resistance of the device.

The **Hg@Cu** compound was not isolated as a single crystal. So, the electrical study of it was performed in fabricated by depositing a thin film of well dispersed solution of **Hg@Cu**. In subject to develop the thin film, precleaned Indium tin oxide (ITO) coated glass was used as substrate. Compound **Hg@Cu** was mixed with DMF in right proportion and was sonicated for several minutes until it produces a well dispersion. Then, on the top of the cleaned ITO coated substrate, just prepared dispersed **Hg@Cu** was spun firstly at 500 rpm for 4 min and thereafter, at 1000 rpm for 6 min, with the help of SCU 2700 spin coating unit. Here Aluminium was chosen as the rectifier metal contact to construct metal (Al)-conductor (compound **Hg@Cu**) (MS) junction. Before depositing the aluminum electrode as metal contact, the as-deposited thin film was dried in a vacuum. The contact area was determined using the hertzian elastic contact model.



(a)

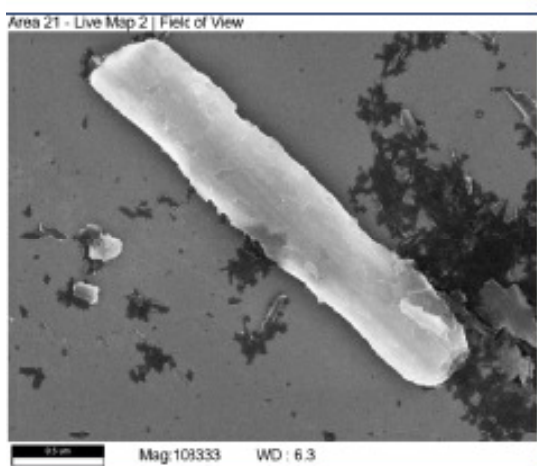


(b)

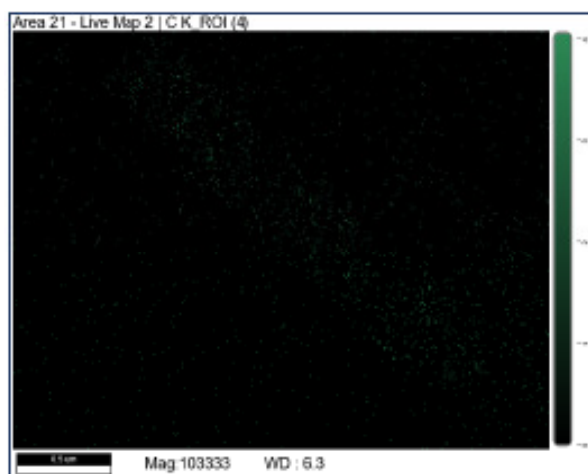
Fig. S5 Current-voltage curves of (a) **1** and (b) **2** using crystals.

Table S2. Conductivity and resistivity of **1**, **2** and **Hg@Cu**

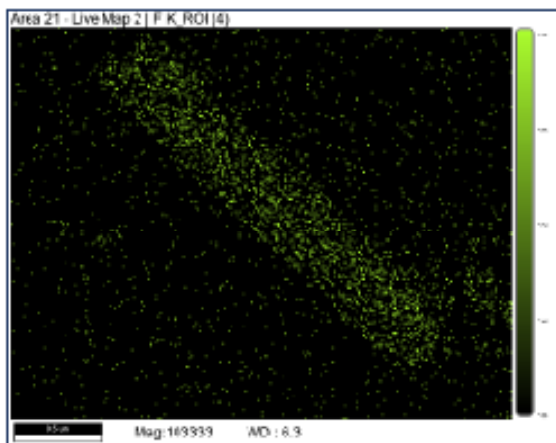
	1	2	Hg@Cu
Resistivity(ohm-cm)	0.0031	0.195	4.27×10^{-5}
Conductivity(Siemens/cm)	323	5.1	2.34×10^4



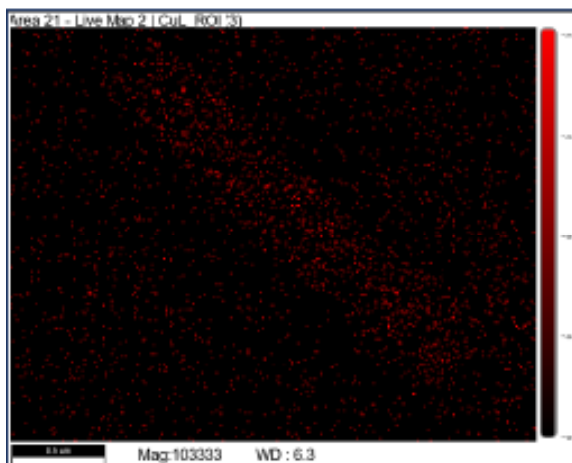
(a)



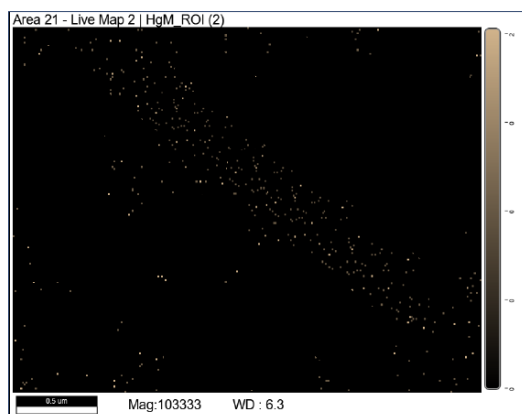
(b)



(c)



(d)



(e)

Fig. S6 (a) SEM image of in compound **Hg@Cu**, (b) EDS mapping of C, (c) EDS mapping of F, (d) EDS mapping of Cu and (e) EDS mapping of Hg.

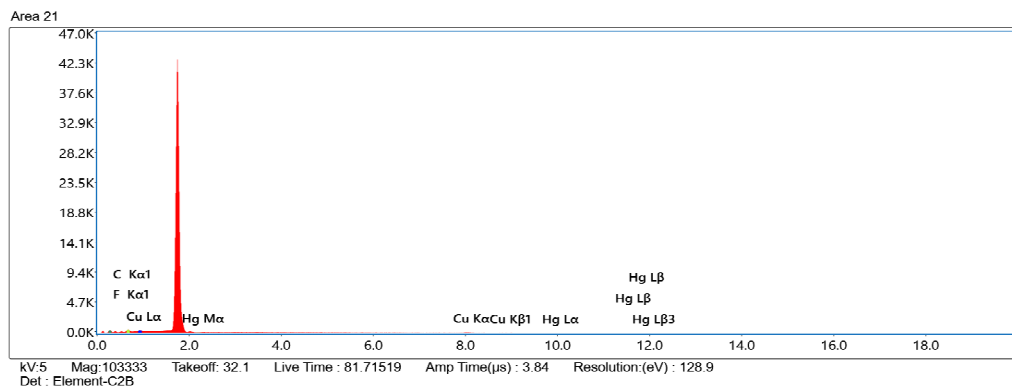


Fig. S7 EDS spectrum of compound **Hg@Cu**.

Table S3. Elemental analysis for compound **Hg@Cu**

Element	Weight %
C K	20.68
F K	25.78
Cu L	29.41
Hg M	24.13

References

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