Supporting Information for

Organic–Inorganic Hybrid Metallic Conductor Based on Bis(ethylenedithio)tetrathiafulvalene Cation and Antiferromagnetically Oxalate-Bridged Copper(II) Dinuclear Anion

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Table S1 Crystallographic data of

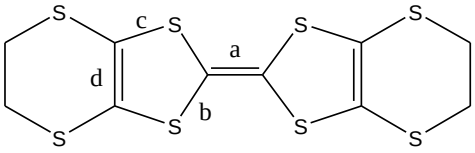
β′′-(BEDT-TTF)$_3$[Cu$_2$(μ-C$_2$O$_4$)(C$_2$O$_4$)$_2$(CH$_3$OH)(H$_2$O)]

T, K	100	180	290
Formula	C37H30Cu2O14S24	C37H30Cu2O14S24	C37H30Cu2O14S24
Fw.	1595.13	1595.13	1595.13
F(000)	806	806	806
crystal system	triclinic	triclinic	triclinic
space group	$P\ \bar{1}$	$P\ \bar{1}$	$P\ \bar{1}$
a, Å	7.4803(3)	7.5040(3)	7.5382(2)
b, Å	9.3547(3)	9.3956(4)	9.4785(2)
c, Å	18.6711(7)	18.6999(7)	18.7231(4)
α, °	95.797(3)	95.930(3)	96.049(2)
β, °	90.974(3)	90.861(3)	90.732(2)
γ, °	93.508(3)	93.745(4)	94.417(2)
V, Å^3	1297.06(8)	1308.26(9)	1326.09(5)
Z	1	1	1
Dc, g/cm^3	2.042	2.025	1.997
μ (Mo K$_\alpha$), mm^{-1}	1.852	1.837	1.812
T_{min} and T_{max}	0.874,1.000	0.866, 1.000	0.880, 1.000
θ_{min}, θ_{max} / °	3.515, 27.868	3.531,27.876	3.565, 27.877
No. total reflns.	28850	29907	29326
No. uniq. reflns.	6139	6184	6285
No. obs.[I⩾2(I$_0$)]	5239	5095	4820
No. params	359	359	359
Restraints	5	5	5
Complete,%	99.4	99.4	99.3
R$_s$/R$_{int}$	0.0255/0.0281	0.0289/0.0311	0.0359/0.0381
R$_1$,wR$_2$[I⩾2σ(I$_0$)]	0.0539, 0.1595	0.0497, 0.1401	0.0488, 0.1277
R$_1$,wR$_2$ (all data)	0.0630, 0.1652	0.0615, 0.1471	0.0674, 0.1386
GOF	1.144	1.098	1.080
[a]Δρ, e/Å^3	1.753, -1.537	1.534, -1.105	1.453, -0.685
[b]Max. and mean Δ/σ	0.001, 0.000	0.000, 0.000	0.001, 0.000
CCDC	2019618	2019619	2019620

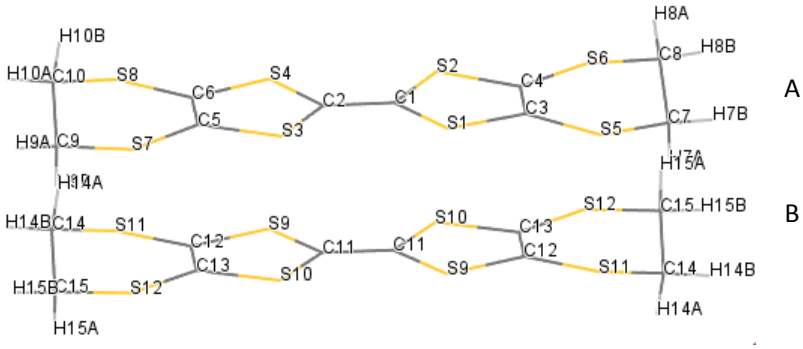
* The distance between O and C of methanol was restrained. The residue peaks higher than 1.0 e/Å^3 were near the Cu atom or S atoms.

* The distance between O and C of methanol was restrained.
* Due to the existence of the disordered CH_3 group of methanol, the anisotropical thermal factor of C19 is large and suggests to be splitted. We tried to split it into two positions, but the refinement result suggested the position to be splitted once more. So the ADP max/min ratio of C19 is 7.4, and the Ueq(max)/Ueq(min) range of it is 10.0.
* The O7 shared by H_2O amd CH_3OH is bonded to Cu with Cu-bond, so its thermos factor is lower than the disordered C19 connected with it.
* When all of reflections are used for least-squares refinement, there are residue peaks from difference Fourier near Cu, S atoms within 1 Å and the least-squares refinement is not convergent. After some disagreeable reflections with Error/esd higher than 6.4 were omitted, the least-squares refinement converges and the highest peak is reduced. The residue peaks higher than 1.0 e/$Å^3$ were near the Cu atom or S atoms.

Table S2 Formal charges of the BEDT-TTF molecules assigned from bond length of the TTF core at 290 and 180 K of β′′-(BEDT-TTF)$_3$[Cu$_2$(μ-C$_2$O$_4$)(C$_2$O$_4$)$_2$(CH$_3$OH)(H$_2$O)].



δ = (b+c)−(a+d), Q = 6.347 − 7.463δ



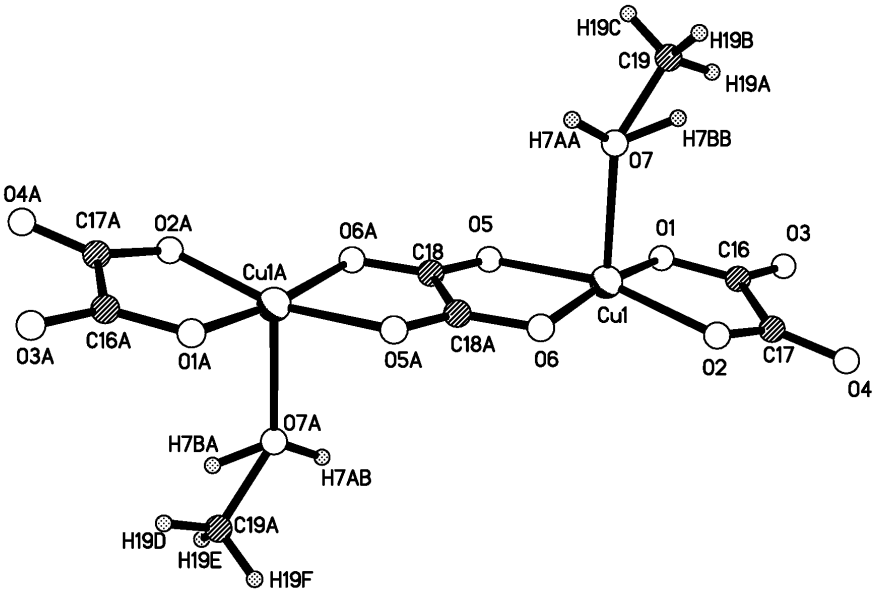
290 K

	a	b	c	d	δ	Q
A	1.375(5)	1.730(3) 1.730(2) 1.726(3) 1.731(3) ~1.729	1.745(3) 1.746(3) 1.739(3) 1.743(3) ~1.743	1.359(4) 1.366(4) ~1.363	0.734	0.869
B	1.375(6)	1.728(3) 1.726(3) ~1.727	1.743(3) 1.741(3) ~1.742	1.360(4)	0.734	0.869
Total						2.6

180K

	a	b	c	d	δ	Q
A	1.372(5)	1.735(4) 1.728(4) 1.730(4) 1.733(4) ~1.732	1.749(4) 1.748(4) 1.739(4) 1.732(4) ~1.742	1.356(5) 1.354(5) ~1.355	0.747	0.772
B	1.375(7)	1.725(4) 1.733(4) ~1.729	1.744(4) 1.750(3) ~1.747	1.356(5)	0.745	0.787
Total						2.33

Table S3. Cu–O bond lengths (Å) in the binuclear anion at different temperatures.



T, K	100	180	290
Cu1-O1, Å	1.937	1.937	1.929
Cu1-O2, Å	1.930	1.931	1.923
Cu1-O5, Å	2.000	2.003	2.001
Cu1-O6, Å	2.001	2.003	2.000
Cu1-O7, Å	2.231	2.240	2.261

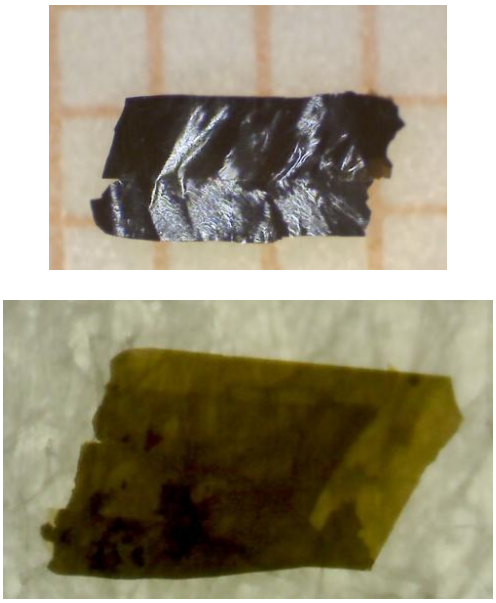


Figure S1. Morphologies of the crystals. Viewed with reflectance mode(top) and transmission mode (bottom).

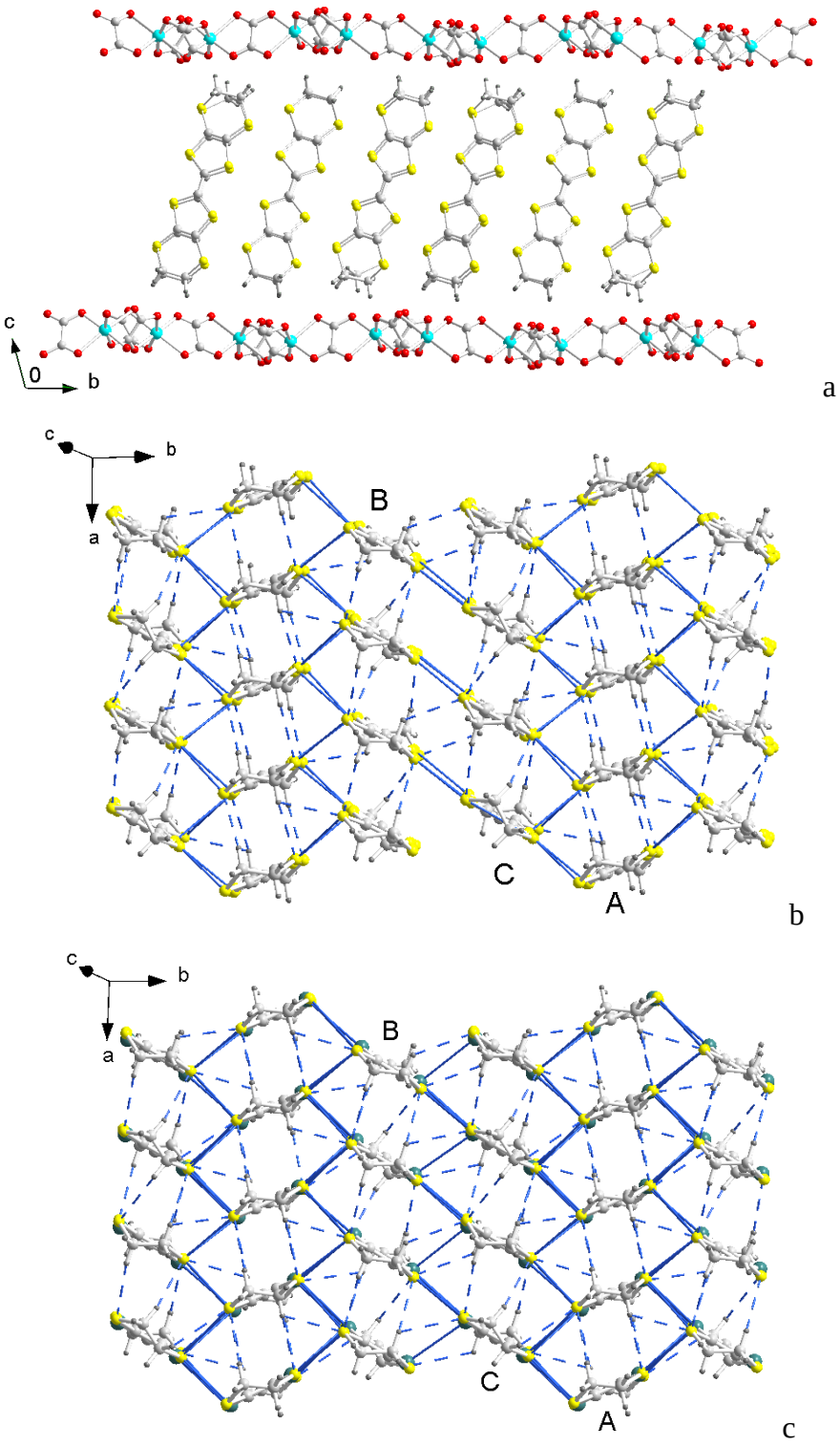


Figure S2. (a) Crystal structure of θ^{21}-(BEDT-TTF)$_3$[Cu$_2$(μ-C$_2$O$_4$)$_3$]·2CH$_3$OH without solvent molecules, viewed along the *a* axis; (b) Donor arrangement of θ^{21}-(BEDT-TTF)$_3$[Cu$_2$(μ-C$_2$O$_4$)$_3$]·2CH$_3$OH viewed along the *c* axis; (c) Donor arrangement of θ^{21}-(BETS)$_3$[Cu$_2$(μ-C$_2$O$_4$)$_3$]·2CH$_3$OH viewed along the *c* axis. Color code: Cu, cyan; O, red; S, yellow; Se, teal; C, grey; H, dark grey; hydrogen bonds, blue dash lines; S ··S, S ··Se, and Se ··Se contacts, blue solid lines.

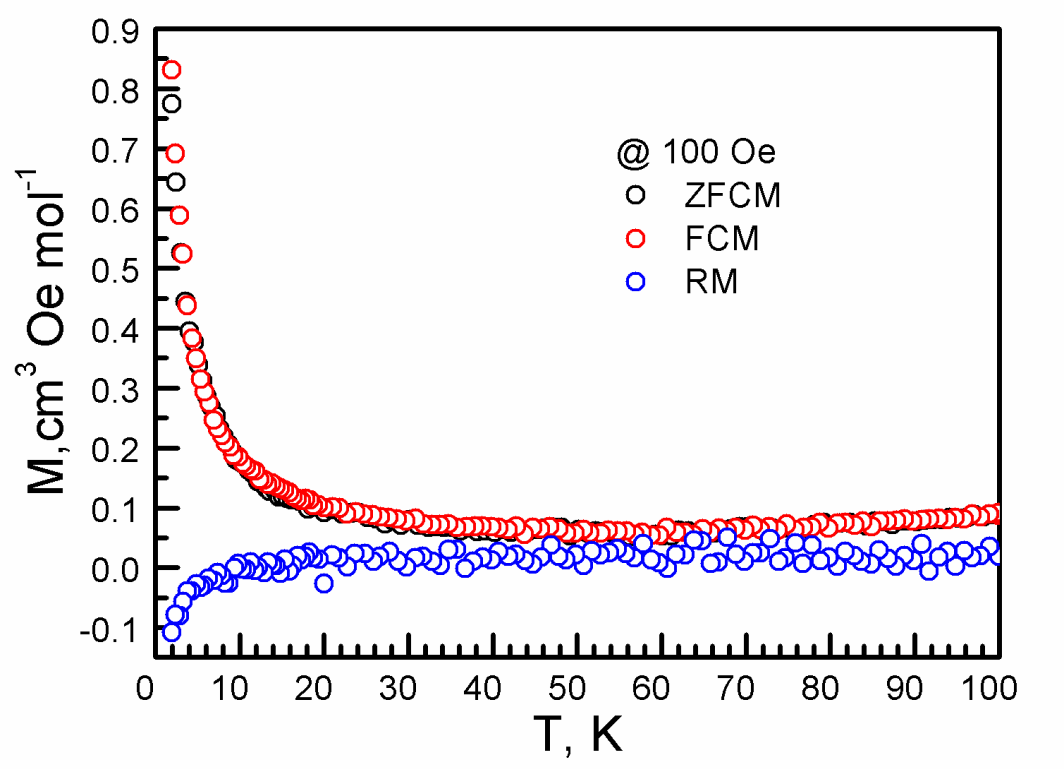


Figure S3. ZFCM/FCM/RM of polycrystal under 100 Oe.

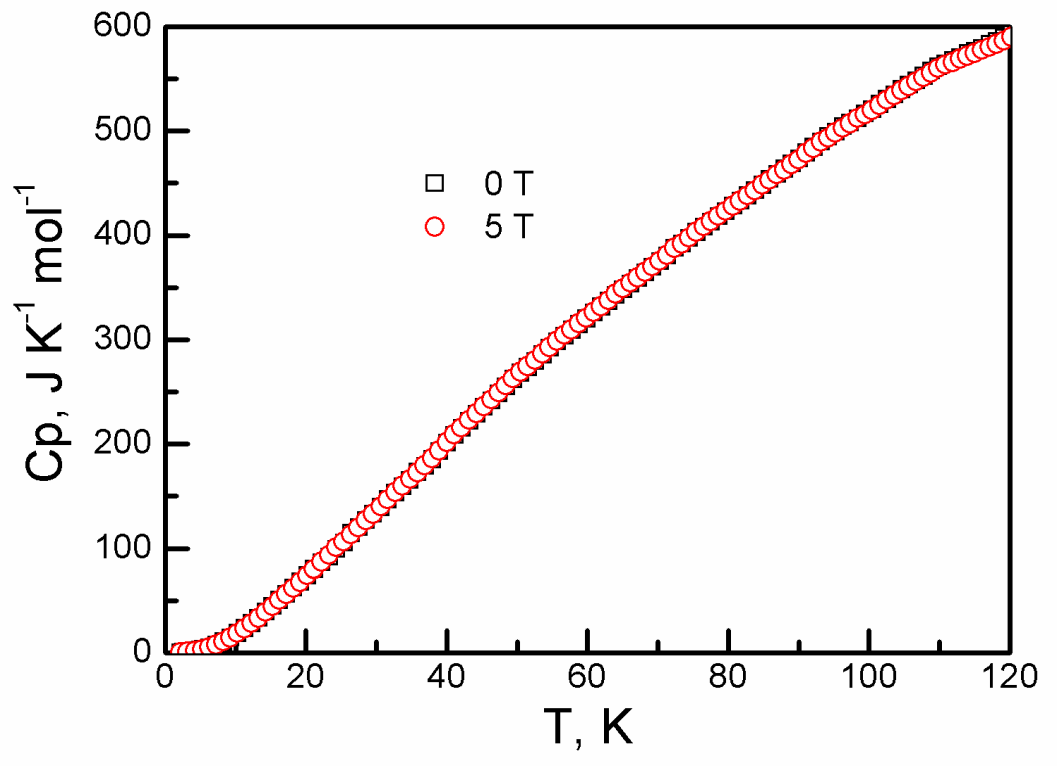


Figure S4. Specific heat measurement form 120 to 2 K under 0 T (black square) and 5 T (red circle).