Supplementary Material (ESI) for Journal of Materials Chemistry

SUPPORTING INFORMATION

Metallic Coordination Supramolecule, $[Cu(I)Cl_{0.2}Br_{1.3}(pyra\text{-}TTF)^{0.5+}]$

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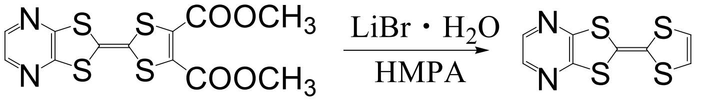
Contents:

1. Synthesis of pyra-TTF

1,3-dithiole-4,5-dicarboxylicacid-2-(1,3-dithiolo[4,5-b]pyrazin-2-ylidene)-dimethyl ester (300 mg, 0.81 mmol) and $LiBr \cdot H_2O$ (677 mg, 3.66 mmol) in HMPA (20 ml) was gradually heated to 80 °C, and stirred for 20 min at this temperature. Then, the mixture was heated to 155 °C, and stirred for 20 min at this temperature. After cooling to room temperature, the mixture was added excess water to obtain the orange solid of crude pyra-TTF. The crude pyra-TTF was filtered, washed H_2O, and dried. The resulting orange solid was purified by column chromatography (silica gel, CH_2Cl_2) to afford pyra-TTF (160 mg, 77.2 %) as an orange solid.

m.p 184 - 186 °C; Mass $M^+ = 256$; ^{1}H-NMR (300MHz, $CDCl_3$) δ 6.379 (s, 2H), 8.007 (s, 2H)

Anal. Calcd: C, 37.48; H, 1.57; N, 10.93, Found: C, 37.35; H, 1.72; N, 10.79



pyra-TTF

Scheme S1. Synthesis of pyra-TTF.

2. X-Ray analyses of [Cu(I)$Cl_{0.2}Br_{1.3}$(pyra-TTF)$^{0.5+}$] (**4**)

Compositions for three samples (4) at 293 K

Table S1. The cell parameters of three samples for **4** (D = pyra-TTF) at 293 K.

	Sample1-this work (ichikawa139_2)	Sample2 (copy2ichikawa122_2)	Sample3 (copy2ichikawa136_2)
composition	$CuCl_{0.188(4)}Br_{1.312(4)}D$	$CuCl_{0.187(5)}Br_{1.313(5)}D$	$CuCl_{0.194(10)}Br_{1.306(10)}D$
FW	431.33	431.33	431.33
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	7.4390(7)	7.440(3)	7.4420(14)
b (Å)	11.964(2)	11.966(6)	11.962(4)
c (Å)	7.0620(12)	7.060(3)	7.0554(11)
α (°)	90.170(14)	90.18(4)	90.202(19)
β (°)	105.226(9)	105.26(3)	105.273(15)
γ (°)	84.984(10)	84.96(3)	84.938(19)
V (Å^3)	603.98(15)	603.9(5)	603.4(2)
Z	2	2	2
D_{calc} (g/cm^3)	2.372	2.372	2.374
μ (cm^{-1})	68.577	68.585	68.644
Ref. data /parameters	2500 / 162	2334 / 162	1329 / 162
R [I > 2.00σ(I)]	0.0377	0.0412	0.0509
R_w [I > 2.00σ(I)]	0.0436	0.0468	0.0510
GOF	0.776	0.831	0.692

3. ESR measurement of 4. The ESR measurement was carried out with a Bruker EMS 9.3 GHz X-band ESR spectrometer at 300, 250, 200, 150, 100, 50 and, 4 K.

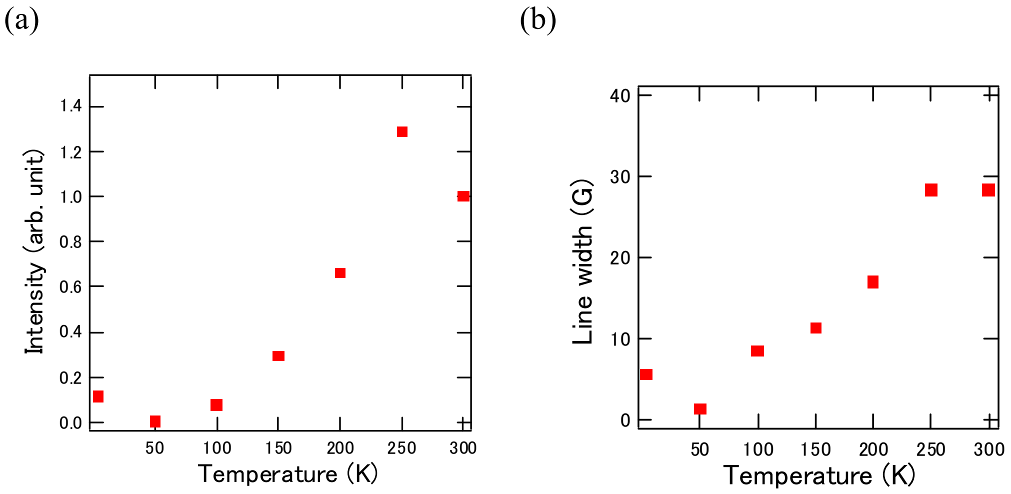


Figure S1. Temperature dependence of (a) intensity and (b) line width of **4**. Sudden decreases of the line width and the intensity were observed at low temperatures. The intensity assumed by Lorentzian signal $I \propto \Delta H^2 h$ (ΔH; linewidth, h; hight of Lorentzian signals), spin susceptibility, decreases below 200 K.