Electronic Supplementary Information

A Semiconducting Gyroidal Metal-Sulfur Framework for Chemiresistive Sensing

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General Procedure.   Starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. Elemental analysis was performed with a Vario Micro CUBE CHN elemental analyzer. FT-IR spectra was obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. Solution ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker superconducting magnet high-field NMR spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analysis (TG) was carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 10 °C/min. Optical diffuse reflectance measurements were performed at room temperature with a PerkinElmer Lambda 750 spectrophotometer. The solid sample was finely ground and pressed between two Mylar tapes (sample thickness is about 1.0 mm and much greater than the particle size, and therefore ideal diffuse reflection can be assumed). The sample was held against a white background for data collection. The *I-V* curves were measured by using a Keithley 4200 SCS semiconductor parameter analyzer (Keithley Instruments Inc., Cleveland, Ohio) in 2-probe station.

The electrical device was fabricated by dropping a film onto an Al_2O_3 substrate with pre-deposited interdigital electrodes. Specifically, HTT-Pb was ground gently and dispersed in ethyl alcohol. The mixture was then sonicated to afford a suspension, which was then dropped gently onto the interdigital electrodes/substrate. The thin film device thus deposited was then dried at 50°C.

Powder X-ray diffraction data was collected in reflection mode at room temperature on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with CPS 180 detector using monochromated Cu-Kα (λ = 1.5406 Å) radiation. The X-ray tube operated at a voltage of 30 kV

and a current of 30 mA.

Single crystal X-ray diffraction data for HTT-Pb was collected on a Agilent Technologies SuperNova Single Crystal Diffractometer equipped with graphite monochromated Cu Kα radiation (λ = 1.54178 Å). The crystal was kept at 293 (10) K during data collection. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm, were used. Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement. The structure was solved and refined by full-matrix least-squares on $F_o{}^2$ using SHELXL2014 and SHELXLE Rev714. Selected crystallographic results are summarized in Table S1, with full details of the crystallographic study in cif format having been deposited as CCDC 1506170.

An oxygen atom (O1) is located in hydrogen bonding distance to its symmetry equivalent counterpart across an inversion center. It was refined as being protonated half the time.
A difference electron density peak located in the void space atop of the plane of the aromatic moieties was tentatively refined as a water molecule. Partial occupancy of this site with sodium cannot be categorically excluded. The water molecule is in hydrogen bonding distance to two copies of itself across a threefold axis. H atoms were added and restrained with O-H distances of 0.84(2) Å and H$\cdots$H distances within each molecule of 1.36(2) Å. The distance of one of the two H atoms to the neighboring symmetry created oxygen atom was restrained to 1.95(2) Å.
Two carbon atoms, C1 and C2, were restrained to be close to isotropic.

The structure contains additional solvent accessible voids of 3674 Å^3 combined. No substantial electron density peaks were found in the solvent accessible voids (less than 2.5 electron per cubic

Angstrom) and the residual electron density peaks are not arranged in an interpretable pattern. The hkl file was instead corrected using reverse Fourier transform methods using the SQUEEZE routine (P. van der Sluis & A.L. Spek (1990). Acta Cryst. A46, 194-201) as implemented in the program Platon. The resultant files were used in the further refinement. (The FAB file with details of the Squeeze results is appended to the cif file). The Squeeze procedure corrected for 1040 electrons within the solvent accessible voids.
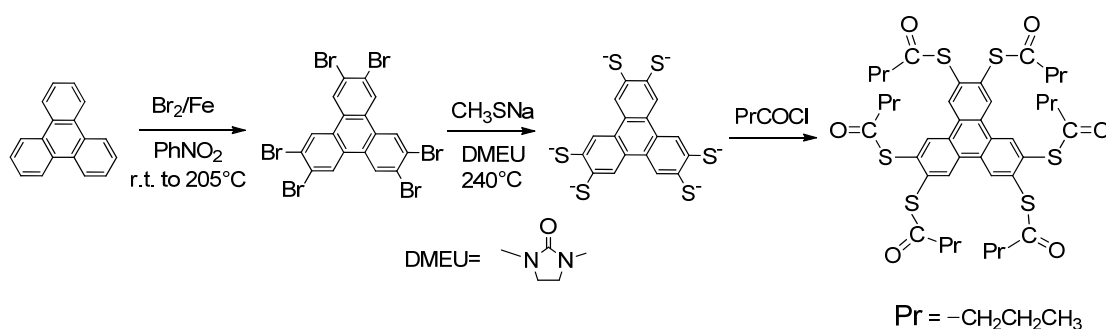
Scheme S1 Synthesis of the HBuTT molecule.

2,3,6,7,10,11-Hexakis(butyrylthio)triphenylene (HBuTT)

HBT (0.216 g, 0.3 mmol) and CH_3SNa (0.664 g, 9.0 mmol) were loaded into a 50 mL Schlenk flask. Then the flask was evacuated and consequently backfilled with N_2 several times on a Schlenk line. DMEU (anhydrous, bubbled with N_2, 10 ml) was transferred into the flask via cannula. The reaction mixture was then stirred at 240 ºC for 48 h. After the mixture was cooled to 0 ºC (first naturally to rt, then by an ice bath), n-butyric chloride (1.24 ml, 12.6 mmol) was injected under N_2. After being stirred at 0 ºC for 2h, the mixture was poured into ice water (50 ml) and extracted by toluene (3 × 30 ml). The combined organic layer was then washed with water (4 × 30 ml), dried over $MgSO_4$, and volatiles were evaporated in vacuo. The crude product (black solid) was purified by chromatography (3:1 CH_2Cl_2/hexane) to afford an off-white solid (168 mg,

yield 67%). ^{1}H NMR (400 MHz, CDCl$_3$): 8.50 (s, 6H), 2.71 (t, 12H), 1.82 (m, 12H), 1.06 (t, 18H). ^{13}C NMR (100 MHz, CDCl$_3$): 196.56; 132.55; 132.31; 129.82; 45.55; 19.10; 13.65.

Crystal growth of HTT-Pb

HBuTT (9.1 mg, 0.010 mmol), a pre-degassed methanol solution of NaOH (2.0 mL, 70 mmol/L) and ethylene diamine (1.0 mL) were loaded into a vial (10.0 mL) and sonicated until the solid was all dissolved. PbOAc·3H$_2$O (11.4 mg, 0.030 mmol), dissolved in ethylene diamine (1.0 mL) was then added and the reaction mixture was bubbled by N$_2$ for 1 min. The vial was sealed and heated at 90 °C in an oven for 48 h, followed by natural cooling to room temperature, during which yellow, octahedral single crystals suitable for single-crystal X-ray diffraction studies were formed (yield: 45%). The crystals were afterwards collected and stored in degassed MeOH (5 mL) at rt. Chemical analysis of the product C$_{21}$H$_{23}$N$_2$NaO$_4$Pb$_3$S$_6$, corresponding to Pb$_3$Na$_{1.5}$ (OH$_{0.5}$)·(HTT)·(en)·(CH$_3$OH)·(H$_2$O)$_2$, yielded: calcd [C (20.75%), H (1.87%), N (2.30%), S (15.83%)]; found [C (20.69%), H (1.73%), N (2.38%), S (15.51%)]. The presence of sodium was also verified by semi-quantitative EDX analysis (Figure S11).
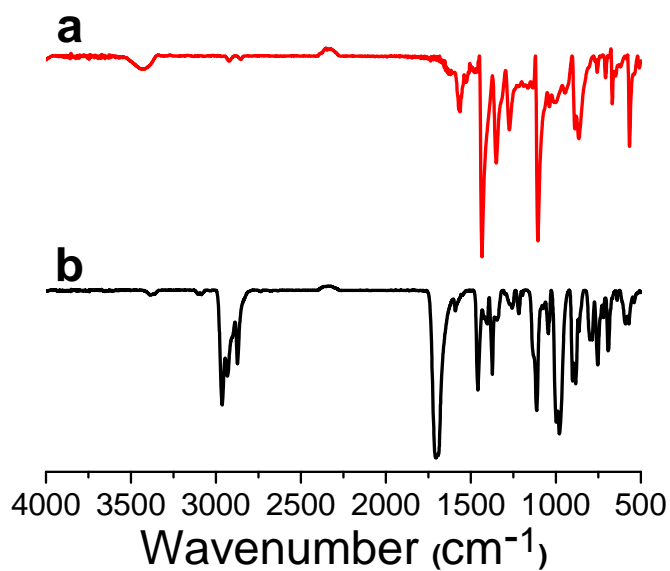
Figure S1. The IR spectrum of an as-made sample of HTT-Pb (a), and a powder of the thioester precursor molecule of HBuTT (b).
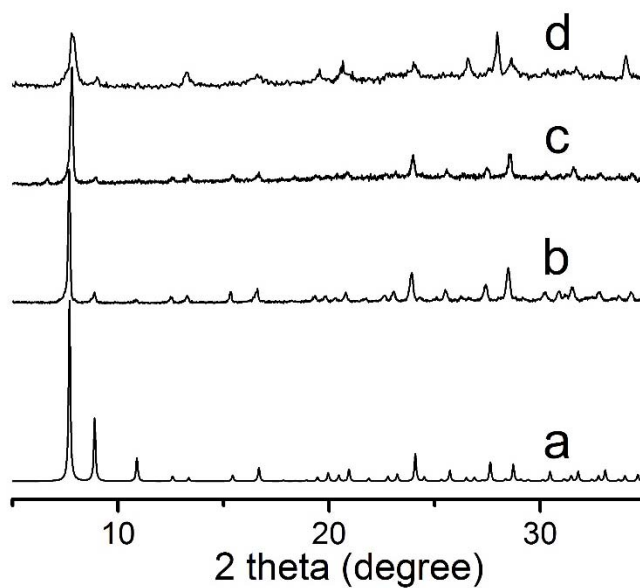

Figure S2. X-ray diffraction patterns (Cu Kα, λ= 1.5418 Å) of HTT-Pb: a) calculated from the single-crystal structure; b) freshly prepared bulk sample; c) as-made bulk sample exposed in air for 4 hours; d) as-made bulk sample exposed in air for 24 hours.
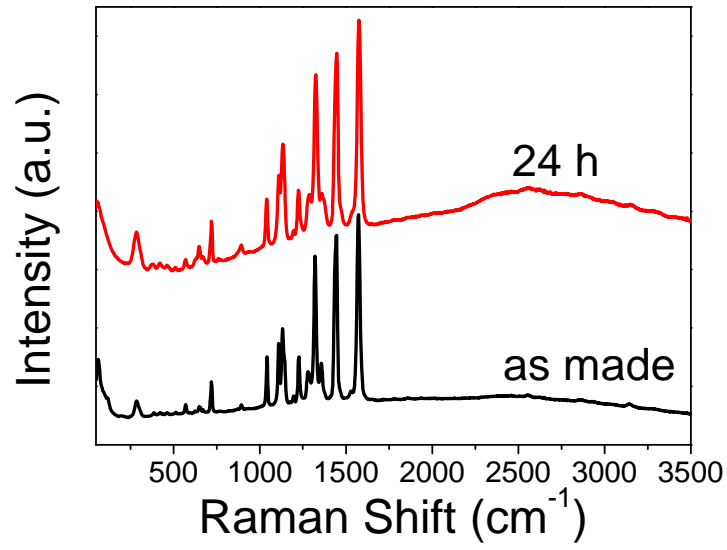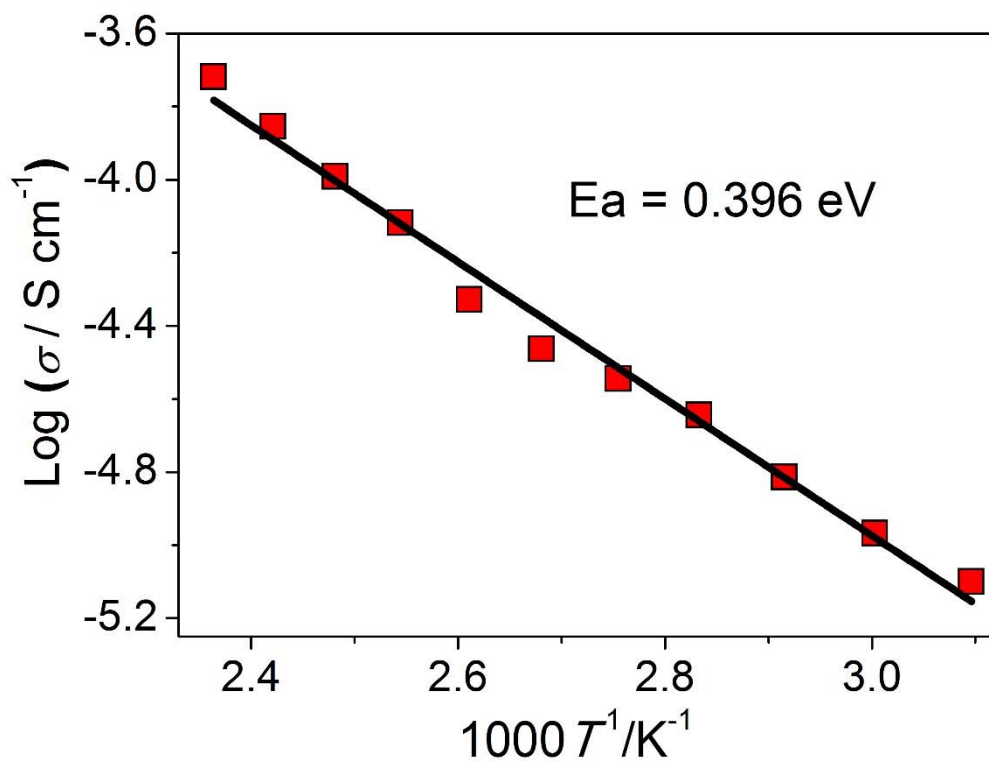
Figure S3. The Raman spectrum of freshly prepared of HTT-Pb (black, bottom), and the same sample exposed to air for 24 hrs (red, top).
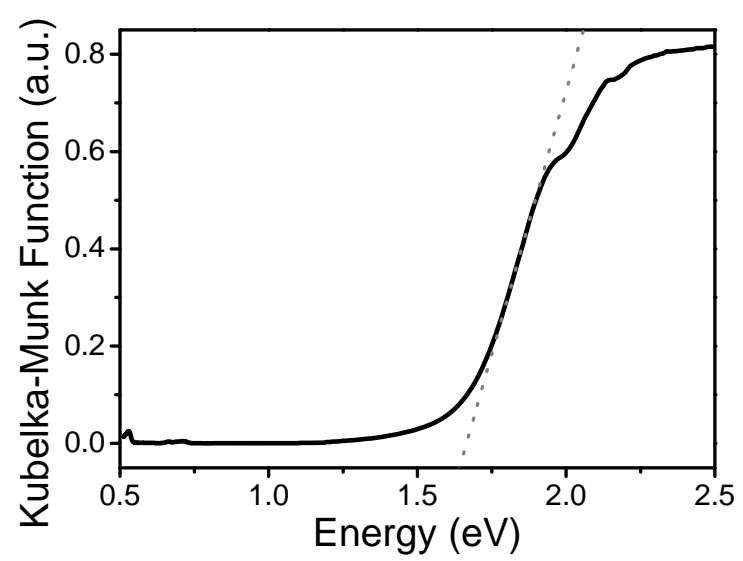
Figure S4. Room temperature optical absorption spectrum for a freshly prepared sample of HTT-Pb.
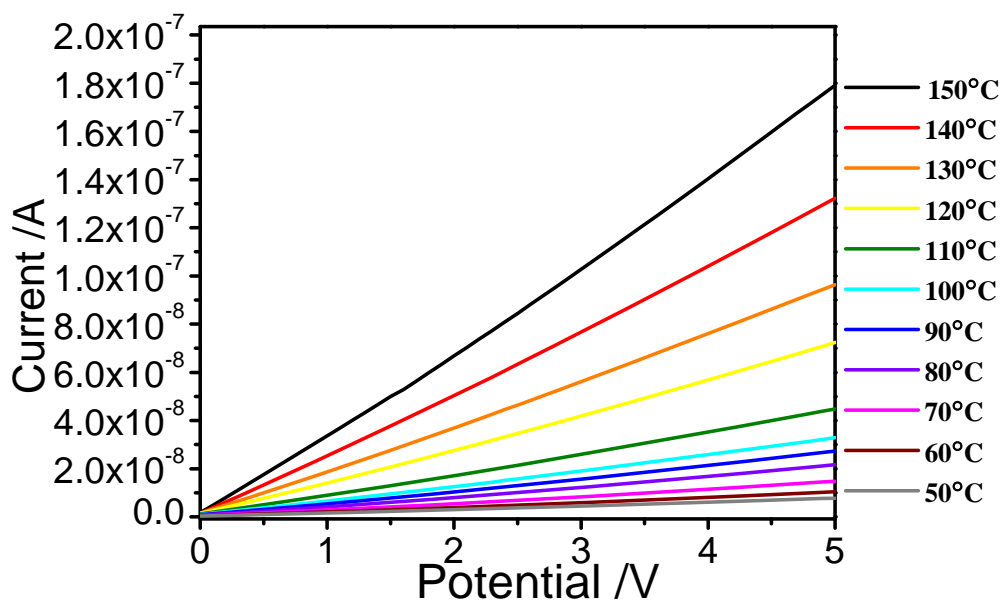
Figure S5. Temperature dependence of the I-V characteristics of a single crystal of HTT-Pb as measured in a two-point configuration.
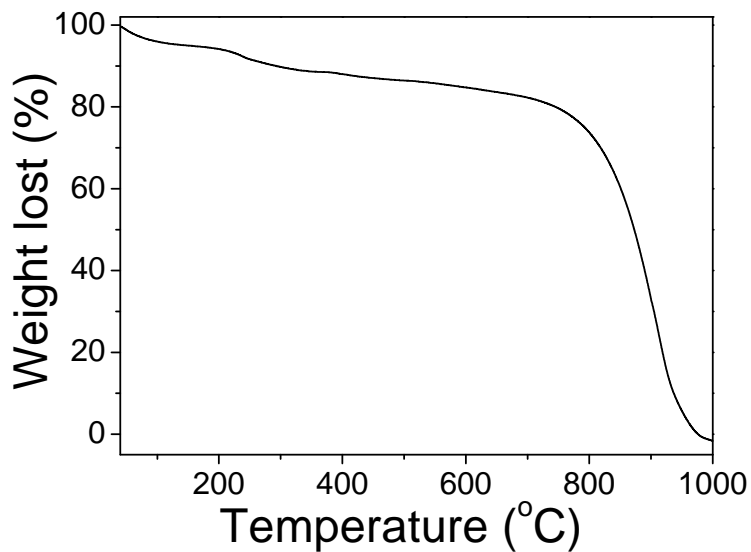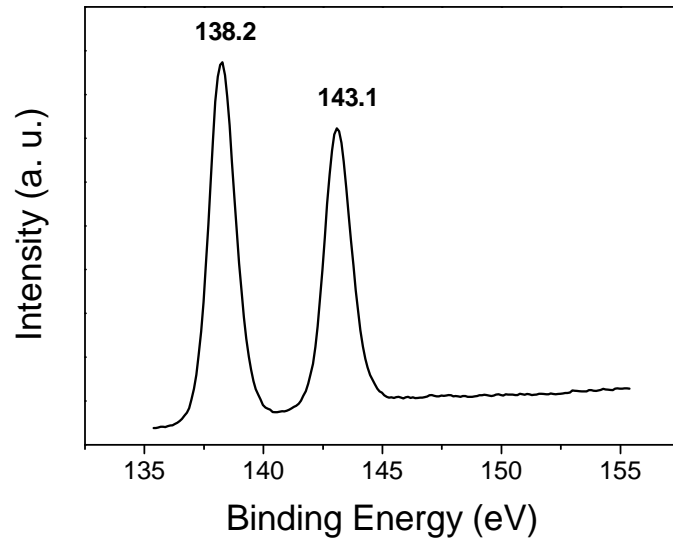
Figure S6 Calculation of the activation energy, determined from the temperature dependence of the conductivity as measured above on a single crystal of HTT-Pb in a two-point configuration.
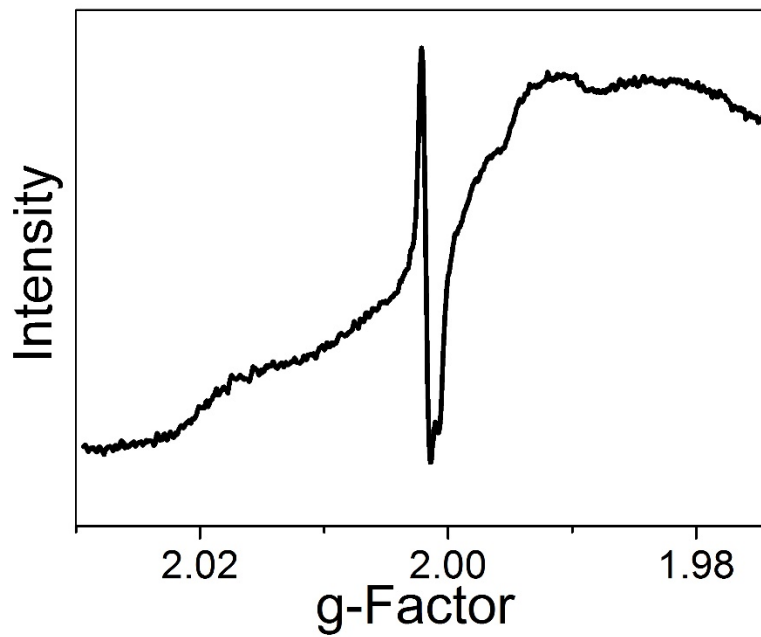

**Figure S7.** A photograph of the homemade setup for the humidity measurement (MFC: mass flow controller).

Figure S8. A thermogravimetric analysis (TGA) plot of HTT-Pb.

Figure S9. XPS spectrum for the solid sample of HTT-Pb. The peaks at 138.2 and 143.1 eV correspond to the states of Pb 4f.

Figure S10. An EPR (electron paramagnetic resonance) spectrum of HTT-Pb.

Element	Wt%	At%
PbM	71.91	27.54
NaM	1.98	6.89
SK	26.11	65.57
Matrix	Correction	ZAF
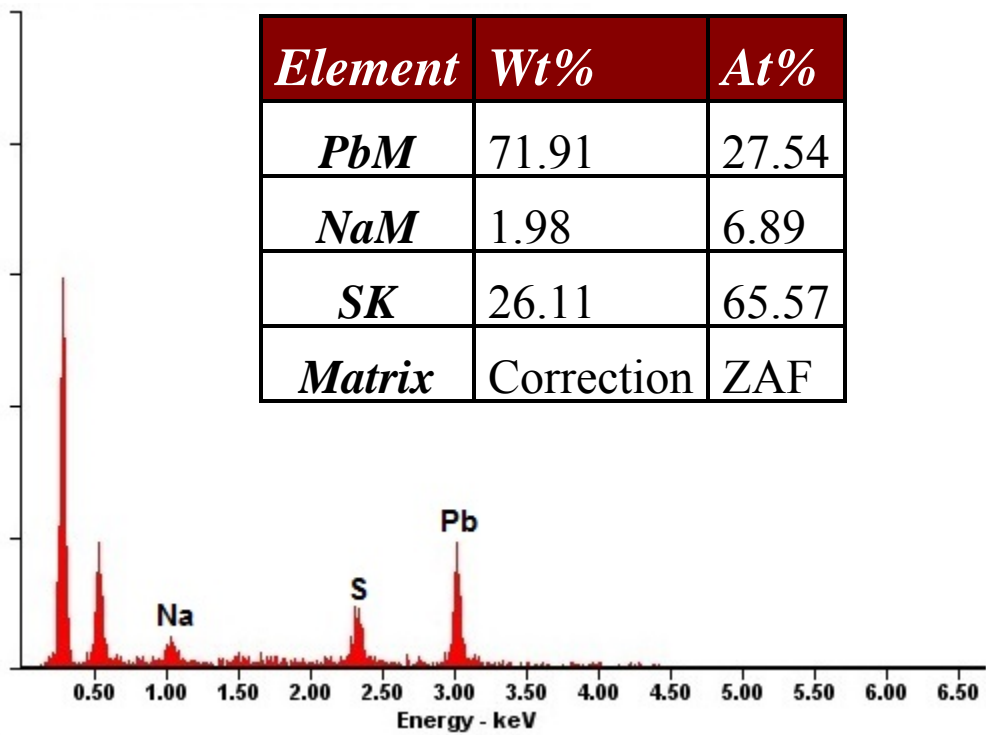
Figure S11. An EDS (Energy-dispersive X-ray spectroscopy) spectrum of HTT-Pb.

Table S1. Crystal data and structure refinement parameters for HTT-Pb.

Compound	HTT-Pb
chemical formula	$C_{36}H_{25}O_8Pb_6S_{12}$
formula weight, fw	2213.48
temperature, K	293(2)
wavelength, Å	1.54178
size, mm^3	0.24 0.16 0.16
space group	$Pa\bar{3}$
a (Å)	19.88410 (10)
V (Å^3)	7861.72(12)
Z	4
ρ_{calcd} (g/cm^3)	1.870
GOF	1.087
$R_1{}^a$ [I >2σ(I)]	0.0574
$wR_2{}^b$ [I >2σ(I)]	0.1535

^{a} $R_1 = \sum ||F_o| - |F_c|| / \sum (|F_o|)$ ^{b} $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$