Figure S1. Atom number for the structural description of EDT-TTF-I_2.

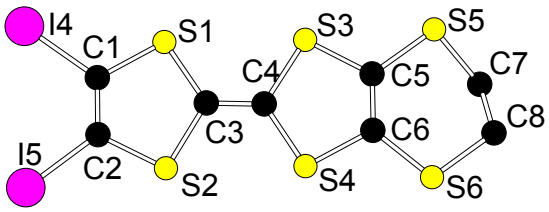

Table S1a. Experimental crystallographic details for ***1***.

Crystal data

Chemical formula weight	1186
Cell setting	triclinic
Space group	*P*-1
a (Å)	7.7818(8)
b (Å)	7.9760(8)
c (Å)	19.9668(2)
α (°)	82.409(12)
β (°)	85.964(12)
γ (°)	61.621(11)
V ($Å^3$), Z	1080.76(19), 2
Dx (Mg m^{-3})	3.6433(7)
Radiation type	Mo K-$L_{2,3}$
Wavelength	0.71069
No of reflections for cell parameters	6567
Temperature (K)	298
Crystal color	black

Data collection

Diffractometer	STOE IPDS
Monochromator	oriented graphite
Crystal form	parallelepiped

Crystal size (mm^3)	$0.16 \times 0.3 \times 0.6$
Absorption coefficient (mm^{-1})	18.073
T min	0.402
T max	0.769
No. of measured reflections	10582
No. of independent reflections	3894
No. of observed reflections	2420
Criterion for observed reflections	$I \geq 2\ \sigma(I)$
R_{int}	0.0490
$\sin(\theta)/\lambda$ max ($Å^{-1}$)	0.65

Refinement

Refinement on	F^2
F(000)	1043
No. of parameters	195
R (obs)	0.0459
wR (obs)	0.0947
S (obs)	1.55
R (total)	0.0814
wR (total)	0.0996
S (total)	1.26
δ/σ max	< 0.0001
Weighting scheme	$1/[\sigma^2(I)+(2*0.016*I)^2]$
$\Delta\rho$ (e $Å^{-3}$)	[-1.86;2.40]

Table S1b. Fractional atomic coordinates, equivalent isotropic displacement parameters ($Å^2$), site occupancy and s.u. for ***1***.

Atom name	x	y	z	U_{eq}	occupancy

$Pb_{5/6}I_2$ layer parameters					
Pb1	0	0.5	1	0.0420(5)	0.874(4)
Pb2	0.33057(10)	0.83150(10)	1.00080(4)	0.0445(3)	0.888(3)
I1	-0.00496(14)	0.86911(15)	0.90383(5)	0.0451(5)	1
I2	0.32786(14)	0.19025(13)	0.91088(5)	0.0402(4)	1
I3	0.33214(13)	0.46411(14)	1.09588(5)	0.0403(4)	1
EDT-TTF-I_2 molecule parameters (I4 as a reference for the rigid body)					
I4	0.04795(14)	0.14160(15)	0.68844(6)	0.0386(4)	
I5	0.570(6)	-0.11(3)	0.747(4)	0.0357(4)	
S1	0.236(3)	0.252(4)	0.5502(7)	0.0298(15)	
S2	0.644(4)	0.06(2)	0.596(3)	0.0285(14)	
S3	0.366(5)	0.418(9)	0.4096(17)	0.0302(15)	
S4	0.771(7)	0.226(18)	0.457(3)	0.0327(15)	
S5	0.460(8)	0.579(15)	0.277(3)	0.0375(16)	
S6	0.932(10)	0.364(18)	0.338(3)	0.0314(16)	
C1	0.285(2)	0.131(7)	0.6340(13)	0.024(5)	
C2	0.465(4)	0.044(17)	0.652(3)	0.026(6)	
C3	0.476(4)	0.206(9)	0.5330(16)	0.020(5)	
C4	0.531(5)	0.278(8)	0.4742(15)	0.026(6)	
C5	0.542(7)	0.448(8)	0.356(2)	0.022(5)	
C6	0.720(8)	0.366(12)	0.377(2)	0.024(6)	
C7	0.850(9)	0.463(11)	0.252(2)	0.029(3)	
C8	0.674(11)	0.449(13)	0.230(2)	0.027(3)	

Rigid body (molecule) parameters							
	phi	chi	psi	xtrans	ytrans	ztrans	occupancy
#1	-1(3)	-0.9(6)	2(2)	0.00006(14)	0.00008(15)	0.00000(6)	0.8600(14)
#2	-1(3)	-0.5(6)	0(2)	0.3366(11)	0.3346(18)	0.0004(5)	0.0700(7)

#3	1(3)	-1.2(7)	2(2)	-0.3247(12)	0.6557(18)	0.0006(5)	0.0700(7)

Table S1c. U^{ij} anisoptropic displacement parameters ($Å^2$) for ***1***.

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.0402(6)	0.0463(7)	0.0393(6)	-0.0198(5)	-0.0037(4)	-0.0055(5)
Pb2	0.0501(4)	0.0395(4)	0.0418(4)	-0.0205(3)	-0.0018(3)	0.0006(3)
I1	0.0459(6)	0.0515(6)	0.0404(6)	-0.0243(5)	0.0039(5)	-0.0102(5)
I2	0.0489(6)	0.0344(5)	0.0354(6)	-0.0187(5)	-0.0014(4)	-0.0010(4)
I3	0.0430(5)	0.0425(6)	0.0369(6)	-0.0218(5)	-0.0095(4)	0.0018(4)
I4	0.0292(5)	0.0388(6)	0.0434(6)	-0.0150(5)	0.0052(4)	0.0031(5)
I5	0.0354(5)	0.0414(6)	0.0216(5)	-0.0134(5)	-0.0030(4)	0.0069(4)
S1	0.0210(18)	0.035(2)	0.0254(19)	-0.0081(16)	-0.0036(15)	0.0040(16)
S2	0.0196(17)	0.0346(19)	0.0209(18)	-0.0060(16)	-0.0030(14)	0.0054(15)
S3	0.0221(17)	0.034(2)	0.0257(19)	-0.0081(16)	-0.0026(15)	0.0071(16)
S4	0.0203(18)	0.038(2)	0.0269(19)	-0.0061(16)	-0.0040(15)	0.0092(17)
S5	0.036(2)	0.033(2)	0.0252(19)	-0.0046(18)	0.0025(16)	0.0066(16)
S6	0.0265(19)	0.037(2)	0.031(2)	-0.0162(17)	0.0001(16)	0.0034(17)
C1	0.014(6)	0.021(7)	0.032(8)	-0.006(6)	-0.002(6)	-0.001(6)
C2	0.035(8)	0.023(7)	0.016(7)	-0.012(7)	-0.010(6)	0.007(6)
C3	0.021(7)	0.026(7)	0.011(6)	-0.011(6)	-0.008(5)	0.008(5)
C4	0.040(8)	0.019(6)	0.017(7)	-0.015(6)	-0.009(6)	0.007(6)
C5	0.017(7)	0.020(7)	0.014(6)	0.003(6)	-0.004(5)	0.002(5)
C6	0.037(8)	0.021(7)	0.017(7)	-0.018(6)	0.008(6)	0.002(6)

Table S1d. Electron Probe Microanalysis (EPMA) of ***1***. In bold the theoretical composition which fits the best to the experimental data.

Anal. No.	Vac.(%)	Pb(%wt.)	I	S	Part. Total	Theo. C+H	Total	I/Pb	Pb/S	I/S
Experimental analysis										
1		22.8	49.9	15.0	87.6	8.4	96.1	2.19	1.52	3.32
2		20.4	52.3	15.4	88.0	8.4	96.5	2.57	1.32	3.40
3		20.8	50.3	15.7	86.8	8.4	95.2	2.41	1.33	3.20
4		20.1	51.5	15.8	87.3	8.4	95.7	2.57	1.27	3.27
5		20.6	51.3	15.4	87.3	8.4	95.7	2.49	1.34	3.34
6		21.0	52.4	15.5	88.8	8.4	97.3	2.50	1.35	3.38
7		21.5	51.7	15.4	88.6	8.4	97.1	2.41	1.39	3.36
8		21.2	51.3	15.1	87.5	8.4	96.0	2.42	1.40	3.40
9		20.3	52.3	15.5	88.1	8.4	96.5	2.58	1.31	3.39
10		21.2	51.8	15.5	88.5	8.4	96.9	2.45	1.37	3.34
11		22.4	50.1	14.9	87.4	8.4	95.9	2.24	1.50	3.36
Mean		**21.1(8)**	**51.4(9)**	**15.4(3)**	**88.0(6)**		**96.3(6)**	**2.44(13)**	**1.37(8)**	**3.34(6)**
Theoritical composition										
$D_2(PbI_2)_3$	0	25.1	51.3	15.5	91.9	8.1	100.0	2.04	1.62	3.30
$D_2(Pb_{0.9}I_2)_3$	10	23.2	52.6	15.9	91.7	8.3	100.0	2.27	1.45	3.30
$D_2(Pb_{0.83}I_2)_3$	**16.7**	**21.8**	**53.5**	**16.2**	**91.6**	**8.4**	**100.0**	**2.45**	**1.35**	**3.30**
$D_2(Pb_{0.67}I_2)_3$	33.3	18.3	55.9	17.0	91.2	8.8	100.0	3.06	1.08	3.30

Table S2a. Experimental crystallographic details for ***2***.

Crystal data

Chemical formula weight	1111.3
Cell setting	triclinic
Space group	*P*-1

a (Å)	7.7744(8)
b (Å)	7.9193(8)
c (Å)	19.834(2)
α (°)	87.189(12)
β (°)	83.534(12)
γ (°)	61.602(11)
V ($Å^3$), Z	1067.4(2), 2
Dx ($Mg\ m^{-3}$)	3.4568(7)
Radiation type	Mo K-$L_{2,3}$
Wavelength	0.71069
No of reflections for cell parameters	8000
Temperature (K)	298
Crystal color	black

Data collection

Diffractometer	STOE IPDS	Nonius CAD-4F
Monochromator	oriented graphite	
Crystal form	plate	
Crystal size (mm^3)	$0.03 \times 0.14 \times 0.52$	
Absorption coefficient (mm^{-1})	14.274	
T min	0.13	0.62
T max	0.15	0.59
No. of measured reflections	13399	8319
No. of independent reflections	9233	
No. of observed reflections	3701	
Criterion for observed reflections	2 σ(I)	
Rint (obs)	6.04	
sin(θ)/λ max ($Å^{-1}$)	0.8	

Refinement

Refinement on	F^2
F(000)	1039
No. of parameters	198
R (obs)	0.0508
wR (obs)	0.0997
S (obs)	1.70
R (total)	0.1177
wR (total)	0.2059
S (total)	1.25
δ/σ max	< 0.0001
Weighting scheme	$1/[\sigma^2(I)+(2*0.016*I)^2]$
$\Delta\rho$ (e Å^{-3})	[-1.84,1.74]

Table S2b. Fractional atomic coordinates, equivalent isotropic displacement parameters (Å^2), site occupancy and s.u. for ***2***.

	x	y	z	U_{eq}	occupancy
			$Pb_{2/3}Ag_{1/3}I_2$ layer parameters		
Pb1	0.16189(5)	0.67283(6)	0.99929(2)	0.04107(16)	
Pb2	0.5	0	1	0.0532(19)	0.396(18)
Ag2	0.4722(16)	0.051(2)	0.9734(13)	0.141(6)	0.260(16)
I1	0.87314(9)	-0.00290(10)	0.90264(3)	0.0437(3)	
I2	0.53315(9)	0.69009(11)	0.91741(4)	0.0463(3)	
I3	0.18642(9)	0.33961(11)	0.90164(3)	0.0448(3)	
			EDT-TTF-I_2 molecule parameters		
I4	0.88976(9)	0.79953(11)	0.68974(4)	0.0463(3)	
I5	0.34916(8)	1.02986(10)	0.74797(3)	0.0409(3)	
S1	0.7483(3)	0.7313(4)	0.55047(11)	0.0354(9)	

S2	0.3243(3)	0.9097(4)	0.59599(11)	0.0341(9)
S3	0.6646(3)	0.6066(4)	0.40897(11)	0.0339(9)
S4	0.2419(3)	0.7862(4)	0.45569(11)	0.0378(9)
S5	0.6163(3)	0.4856(4)	0.27529(12)	0.0420(10)
S6	0.1230(3)	0.6868(4)	0.33451(12)	0.0383(10)
C1	0.6715(11)	0.8245(13)	0.6336(4)	0.034(3)
C2	0.4803(11)	0.9079(13)	0.6539(4)	0.030(3)
C3	0.5171(11)	0.7797(13)	0.5317(4)	0.032(3)
C4	0.4770(11)	0.7305(12)	0.4746(4)	0.026(3)
C5	0.5071(11)	0.5924(12)	0.3558(4)	0.024(3)
C6	0.3177(11)	0.6726(13)	0.3757(4)	0.031(3)
C7	0.4078(14)	0.6366(18)	0.2307(5)	0.050(5)
C8	0.2328(13)	0.6128(16)	0.2489(5)	0.041(4)

Table S2c. U^{ij} anisoptropic displacement parameters ($Å^2$) for ***2***.

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.03537(18)	0.0415(2)	0.0428(2)	-0.01554(16)	-0.00388(15)	0.00256(18)
Pb2	0.052(3)	0.042(2)	0.062(3)	-0.0163(15)	-0.0161(13)	-0.0125(18)
Ag2	0.151(9)	0.060(6)	0.184(11)	-0.005(4)	-0.112(9)	-0.038(6)
I1	0.0509(3)	0.0378(4)	0.0432(4)	-0.0191(3)	-0.0181(3)	0.0041(3)
I2	0.0367(3)	0.0508(4)	0.0447(4)	-0.0166(3)	-0.0042(3)	0.0151(3)
I3	0.0451(3)	0.0530(4)	0.0402(3)	-0.0280(3)	0.0109(3)	-0.0165(3)
I4	0.0349(3)	0.0502(4)	0.0513(4)	-0.0158(3)	-0.0120(3)	-0.0073(3)
I5	0.0387(3)	0.0499(4)	0.0269(3)	-0.0147(3)	-0.0021(2)	-0.0076(3)
S1	0.0274(9)	0.0427(14)	0.0298(11)	-0.0108(9)	-0.0038(8)	-0.0047(10)
S2	0.0254(9)	0.0435(14)	0.0277(10)	-0.0112(9)	-0.0023(8)	-0.0067(10)
S3	0.0282(9)	0.0443(14)	0.0245(10)	-0.0132(9)	-0.0001(8)	-0.0069(10)
S4	0.0276(9)	0.0504(15)	0.0274(11)	-0.0114(9)	-0.0015(8)	-0.0091(10)

S5	0.0345(11)	0.0431(15)	0.0325(12)	-0.0044(10)	-0.0044(9)	-0.0089(11)
S6	0.0259(9)	0.0449(15)	0.0398(13)	-0.0129(9)	-0.0007(9)	-0.0104(11)
C1	0.028(4)	0.034(5)	0.025(4)	-0.001(3)	-0.003(3)	-0.005(4)
C2	0.027(4)	0.034(5)	0.023(4)	-0.008(3)	-0.004(3)	-0.004(4)
C3	0.023(3)	0.031(5)	0.024(4)	0.001(3)	0.002(3)	-0.003(4)
C4	0.026(3)	0.027(4)	0.021(4)	-0.010(3)	-0.002(3)	0.004(3)
C5	0.035(4)	0.021(4)	0.019(4)	-0.017(3)	0.000(3)	0.005(3)
C6	0.023(3)	0.028(5)	0.030(4)	-0.001(3)	-0.010(3)	-0.001(4)
C7	0.044(5)	0.067(8)	0.036(5)	-0.022(5)	-0.013(4)	-0.005(5)
C8	0.042(5)	0.059(7)	0.031(5)	-0.031(5)	-0.006(4)	0.007(5)

Table S2d. Electron Probe Microanalysis (EPMA) of ***2***. In bold the theoretical composition which fits the best to the experimental data.

Anal. No. of ***2***	Vac.(%)	Pb(% wt.)	I	S	Ag	Part. Total	Theo. C+H	Total	I/Pb	Pb/S	I/S	I/Ag	Pb/S	I/S
Experimental analysis														
1		17.4	51.1	15.2	3.0	86.8	8.4	95.2	2.93	1.15	3.36	16.81	5.00	5.73
2		17.7	51.4	15.3	3.1	87.5	8.4	95.9	2.90	1.16	3.37	16.36	4.86	5.63
3		18.7	52.0	15.3	3.1	89.1	8.4	97.5	2.78	1.22	3.40	16.55	4.87	5.96
4		17.3	51.1	15.4	3.1	86.8	8.4	95.3	2.95	1.13	3.33	16.47	4.95	5.58
5		17.2	49.8	15.2	3.0	85.2	8.4	93.7	2.89	1.14	3.29	16.67	5.07	5.77
6		17.0	51.6	15.2	3.4	87.2	8.4	95.6	3.03	1.12	3.39	15.08	4.45	4.97
7		18.7	50.8	15.5	2.8	87.7	8.4	96.1	2.72	1.20	3.28	18.33	5.60	6.73
Mean		**17.7(7)**	**51.1(7)**	**15.3(1)**	**3.1(2)**	**87.2(1.2)**		**95.6(1.2)**	**2.89(11)**	**1.16(4)**	**3.34(5)**	**16.61(95)**	**4.97(34)**	**5.77(53)**

n		**7)**	**7)**	**1)**	**)**	**1.2)**		**1.2)**	**11)**	**4)**	**5)**	**1(95)**	**34)**	**53)**
Theoritical composition														
$D_2(Pb_{0.83}I_2)_3$	16.7	21.8	53.5	16.2	0.0	91.6	8.4	100.0	2.45	1.35	3.30	-	-	-
$D_2(Pb_{0.73}Ag_{0.20}I_2)_3$	6.7	19.2	53.4	16.2	2.7	91.6	8.4	100.0	2.78	1.19	3.30	19.58	5.93	7.03
$D_2(Pb_{0.72}Ag_{0.23}I_2)_3$	5	18.8	53.4	16.2	3.2	91.6	8.4	100.0	2.85	1.16	3.30	16.80	5.09	5.90
$D_2(Pb_{0.71}Ag_{0.24}I_2)_3$	**4.7**	**18.7**	**53.4**	**16.2**	**3.3**	**91.6**	**8.4**	**100.0**	**2.86**	**1.15**	**3.30**	**16.34**	**4.95**	**5.71**
$D_2(Pb_{0.70}Ag_{0.27}I_2)_3$	3.3	18.3	53.4	16.2	3.6	91.6	8.4	100.0	2.92	1.13	3.30	14.72	4.46	5.05
$D_2(Pb_{0.67}Ag_{0.33}I_2)_3$	0	17.4	53.4	16.2	4.5	91.6	8.4	100.0	3.06	1.08	3.30	11.76	3.57	3.84

Note that theoretical composition for ***2*** where calculating assuming a constant charge of the inorganic layer (*i.e.* 2*%Pb(II) + %Ag(I) = 5/3)