Supporting Information

Giant 2-Dimensional Dielectric Response in a Compressed Hydrogen-Bonded Hybrid Organic-Inorganic Salt

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Table S1. Crystal data and structure refinement details for pyrazinium tetrachloroaurate crystals. X-ray diffraction studies in the function of temperature.

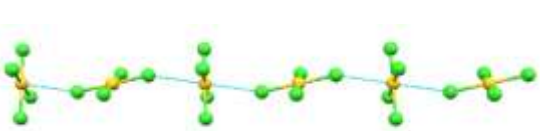
Temperature, K	130(2)	160(2)	190(2)	220(2)	250(2)	270(2)	285(2)
Pressure	0.01 MPa	0.01 MPa	0.01 MPa	0.01 MPa	0.01 MPa	0.01 MPa	0.01 MPa
Formula	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$
Fw, g/mol	419.87	419.87	419.87	419.87	419.87	419.87	419.87
crystal size, mm^3	0.20x0.20x0.50	0.20x0.20x0.50	0.20x0.20x0.50	0.20x0.20x0.50	0.20x0.20x0.50	0.20x0.20x0.50	0.20x0.20x0.50
crystal colour	orange	orange	orange	orange	orange	orange	orange
crystal system	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal
space group, *Z*	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4
a, Å	7.83920(10)	7.84680(10)	7.85600(10)	7.86500(10)	7.87450(10)	7.88180(10)	7.89140(10)
b, Å	7.83920(10)	7.84680(10)	7.85600(10)	7.86500(10)	7.87450(10)	7.88180(10)	7.89140(10)
c, Å	15.7523(3)	15.7718(4)	15.7916(4)	15.8105(4)	15.8305(4)	15.8455(4)	15.8623(3)
β, º	90	90	90	90	90	90	90
V, $Å^3$	968.03(3)	971.11(3)	974.61(3)	978.01(3)	981.61(3)	984.37(3)	987.81(3)
ρ, g/cm^3	2.881	2.872	2.861	2.852	2.841	2.833	2.823
μ, mm^{-1}	16.239	16.188	16.130	16.074	16.015	15.970	15.914
F(000)	760	760	760	760	760	760	760
ϑ range, º	2.59-28.93	2.58-29.03	2.58-28.99	2.58-29.10	2.57-29.10	2.57-29.09	2.57-34.79
limiting indices	-9⇒h⇒10 -10⇒k⇒10 -21⇒l⇒20	-10⇒h⇒9 -10⇒k⇒10 -20⇒l⇒21	-9⇒h⇒10 -10⇒k⇒10 -20⇒l⇒21	-9⇒h⇒10 -10⇒k⇒10 -21⇒l⇒20	-9⇒h⇒10 -10⇒k⇒10 -21⇒l⇒21	-9⇒h⇒10 -10⇒k⇒10 -21⇒l⇒21	-12⇒h⇒12 -12⇒k⇒12 -23⇒l⇒24
reflns collected	5914	5842	5963	5990	6025	6067	14347
R_{int}	0.0766	0.0750	0.0759	0.0757	0.0759	0.0788	0.0586
data/parameters	694/37	691/34	700/34	704/34	706/34	709/34	1145/33
GOF on F^2	1.147	1.138	1.132	1.143	1.110	1.075	1.061
R_1 [I > 2σ(I)]	0.0353	0.0388	0.0375	0.0367	0.0370	0.0361	0.0333
R_1 (all data)	0.0398	0.0441	0.0428	0.0431	0.0447	0.0449	0.0478
wR_2 (all data)	0.1165	0.1199	0.1159	0.1126	0.1117	0.1080	0.1002
completness to theta max.	98.2 %	98.0 %	98.2 %	97.4 %	97.0 %	97.1 %	98.6 %
lrgst diff peak, $e/Å^3$	2.362	3.649	3.456	3.213	2.943	2.738	5.083
lrgst diff hole, $e/Å^3$	-2.415	-2.085	-1.817	-1.460	-1.429	-1.251	-2.307

Table S2. Crystal data and structure refinement details for pyrazinium tetrachloroaurate crystals. X-ray diffraction studies in the function of pressure.

hydrostatic medium	helium	helium	helium	helium	helium	helium	helium
temperature, K	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Pressure, GPa	0.01 MPa	0.40	1.23	2.01	2.77	4.035	6.165
Formula	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$
Fw, g/mol	419.87	419.87	419.87	419.87	419.87	419.87	419.87
crystal size, mm^3	0.02x0.04x0.05	0.02x0.04x0.05	0.02x0.04x0.05	0.02x0.04x0.05	0.02x0.04x0.05	0.02x0.04x0.05	0.02x0.04x0.05
crystal colour	orange	orange	orange	orange	orange	orange	orange
crystal system	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal
space group, *Z*	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4
a, Å	7.88220(10)	7.7706(3)	7.6937(2)	7.62920(10)	7.56550(10)	7.4964(2)	7.38700(10)
b, Å	7.88220(10)	7.7706(3)	7.6937(2)	7.62920(10)	7.56550(10)	7.4964(2)	7.38700(10)
c, Å	15.8523(5)	15.666(12)	15.618(3)	15.259(6)	15.437(5)	15.034(8)	14.791(8)
β, º	90	90	90	90	90	90	90
V, $Å^3$	984.89(4)	946.0(7)	909.8(6)	888.1(4)	867.0(3)	844.9(4)	807.1(4)
ρ, g/cm^3	2.832	2.931	3.065	3.140	3.217	3.301	3.455
μ, mm^{-1}	15.961	16.524	17.278	17.700	18.132	18.607	19.478
F(000)	760	760	760	760	760	760	760
ϑ range, º	3.65-30.28	3.93-36.51	3.97-35.88	4.01-36.39	4.04-36.58	4.08-37.14	4.14-37.62
limiting indices	-11⇒h⇒11 -11⇒k⇒11 -22⇒l⇒22	-12⇒h⇒12 -12⇒k⇒11 -6⇒l⇒7	-12⇒h⇒12 -12⇒k⇒11 -6⇒l⇒7	-12⇒h⇒12 -11⇒k⇒12 -6⇒l⇒7	-12⇒h⇒12 -12⇒k⇒11 -6⇒l⇒6	-12⇒h⇒11 -12⇒k⇒12 -6⇒l⇒6	-12⇒h⇒11 -12⇒k⇒12 -6⇒l⇒6
reflns collected	23555	1570	1475	1454	1429	1393	1375
R_{int}	0.0318	0.0324	0.0356	0.0320	0.0327	0.0310	0.0373
data/parameters	797/38	320/33	298/33	295/33	291/33	280/33	274/33
GOF on F^2	1.181	1.119	1.110	1.150	1.231	1.247	1.269
R_1 [I > 2σ(I)]	0.0130	0.0474	0.0410	0.0499	0.0485	0.0512	0.0543
R_1 (all data)	0.0175	0.0640	0.0526	0.0606	0.0605	0.0619	0.0663
wR_2 (all data)	0.0263	0.0865	0.0830	0.1191	0.1176	0.1204	0.1376
completness to theta max.	98.4 %	25.4 %	25.8 %	24.9 %	24.9 %	23.7 %	23.5 %
lrgst diff peak, e/$Å^3$	0.902	0.700	0.605	0.957	0.987	0.997	1.084
lrgst diff hole, e/$Å^3$	-0.365	-0.640	-0.499	-0.640	-0.702	-0.821	-0.771

Table S2. Crystal data and structure refinement details for pyrazinium tetrachloroaurate crystals. X-ray diffraction studies in the function of pressure.

hydrostatic medium	helium	helium	helium	helium	helium	helium
temperature, K	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
Pressure, GPa	7.85	9.23	9.685	10.655	11.98	12.675
Formula	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$	$C_4N_2H_5AuCl_4$
Fw, g/mol	419.87	419.87	419.87	419.87	419.87	419.87
crystal size, mm^3	0.02x0.04x0.05	0.02x0.04x0.05	0.02x0.04x0.05	0.02x0.04x0.05	0.02x0.04x0.05	0.02x0.04x0.05
crystal colour	orange	orange	orange	orange	orange	orange
crystal system	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal	tetragonal
space group, *Z*	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4	$P4_2/ncm$, 4
a, Å	7.3190(2)	7.2677(3)	7.2305(4)	7.1959(5)	7.1293(6)	7.1172(7)
b, Å	7.3190(2)	7.2677(3)	7.2305(4)	7.1959(5)	7.1293(6)	7.1172(7)
c, Å	14.595(13)	14.46(2)	14.50(3)	14.39(3)	14.38(3)	14.30(3)
β, º	90	90	90	90	90	90
V, $Å^3$	781.8(7)	764.0(11)	758.0(13)	745.1(14)	730.8(14)	724.6(14)
ρ, g/cm^3	3.567	3.650	3.679	3.743	3.816	3.849
μ, mm^{-1}	20.107	20.576	20.740	21.098	21.510	21.696
F(000)	760	760	760	760	760	760
ϑ range, º	4.18-35.54	4.21-35.50	4.23-36.03	4.25-35.90	4.28-36.02	4.05-39.20
limiting indices	-11⇒h⇒12 -11⇒k⇒11 -6⇒l⇒6	-11⇒h⇒12 -11⇒k⇒11 -6⇒l⇒6	-11⇒h⇒12 -11⇒k⇒11 -6⇒l⇒6	-11⇒h⇒12 -11⇒k⇒11 -6⇒l⇒6	-11⇒h⇒12 -11⇒k⇒11 -6⇒l⇒6	-11⇒h⇒12 -12⇒k⇒11 -6⇒l⇒6
reflns collected	1341	1264	1252	1234	1135	1685
R_{int}	0.0420	0.0458	0.0510	0.0542	0.0596	0.0433
data/parameters	267/33	255/33	254/33	252/33	251/33	292/33
GOF on F^2	1.139	1.235	1.226	1.187	1.177	1.037
R_1 [I > 2σ(I)]	0.0577	0.0726	0.0767	0.0698	0.0865	0.0822
R_1 (all data)	0.0691	0.0924	0.1045	0.1003	0.1273	0.1457
wR_2 (all data)	0.1451	0.1986	0.1940	0.1853	0.2170	0.3053
completness to theta max.	27.4 %	26.7 %	25.9 %	26.3 %	26.3 %	25.2 %
lrgst diff peak, $e/Å^3$	1.126	1.281	1.093	0.855	0.813	1.519
lrgst diff hole, $e/Å^3$	-0.823	-0.886	-0.659	-0.776	-0.726	-0.676



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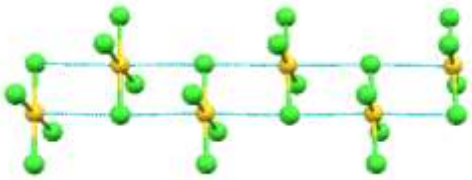

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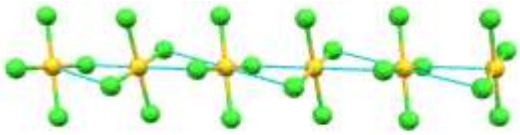

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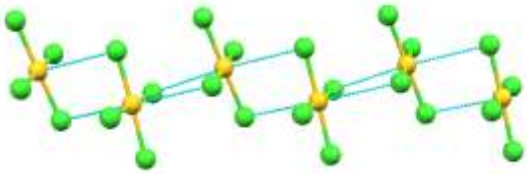

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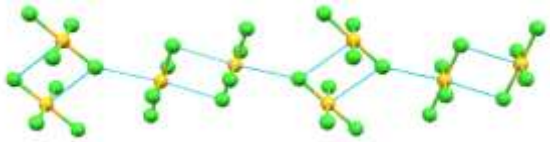

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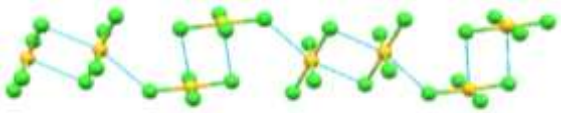

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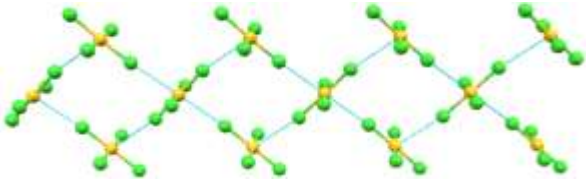

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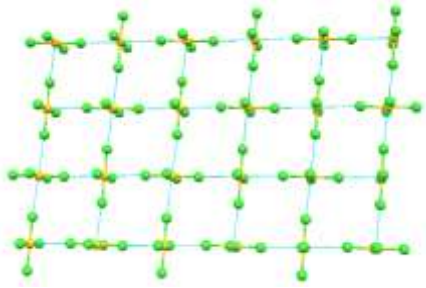

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Figure S1. Aggregation types of tetrachloroaurate anions in the crystal structures retrieved from the Cambridge Structural Database. The illustrated aggregates are described by the deposit refcode.[1]

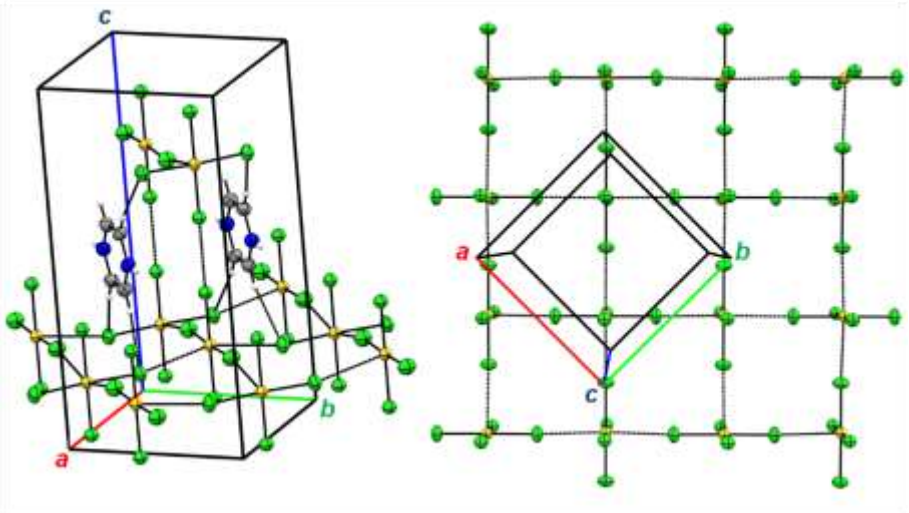

Figure S2. Short interionic contacts in the structure of pyrazinium tetrachloroaurate: a perspective view of the structure with the contacts indicated by black lines (left) and one sheet of $AuCl_4^-$anions linked by Au···Cl interactions (right).

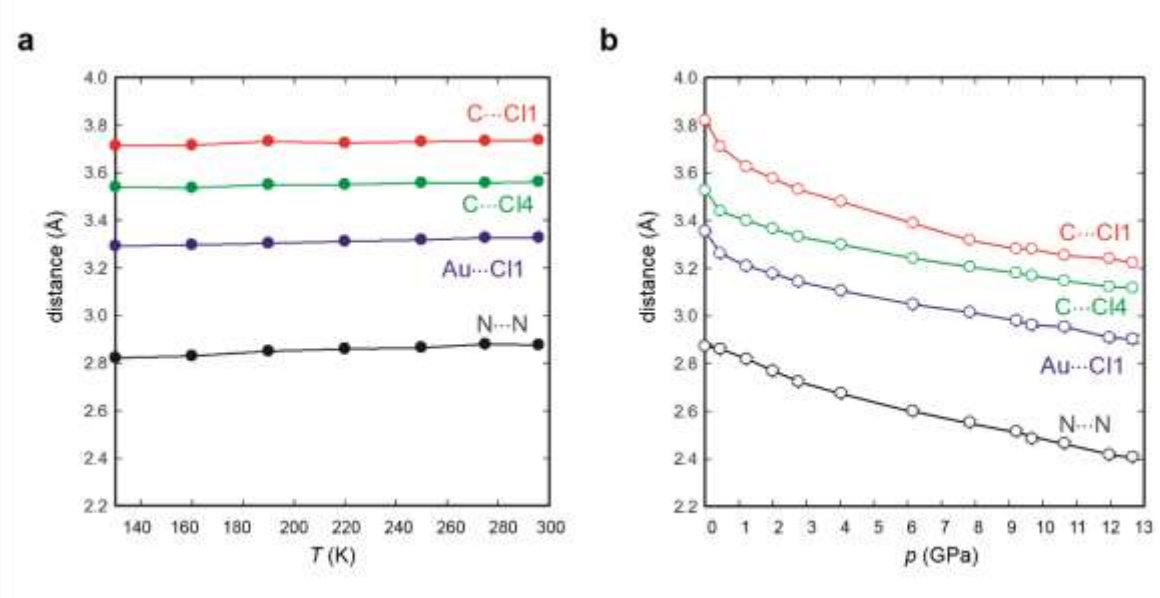

Figure S3. Short interionic contacts in the structure of pyrazinium tetrachloroaurate $PyrH^+AuCl_4^-$ as a function of temperature and pressure (*cf.* Figure 3). Note the estimated standard deviations smaller than the symbols.

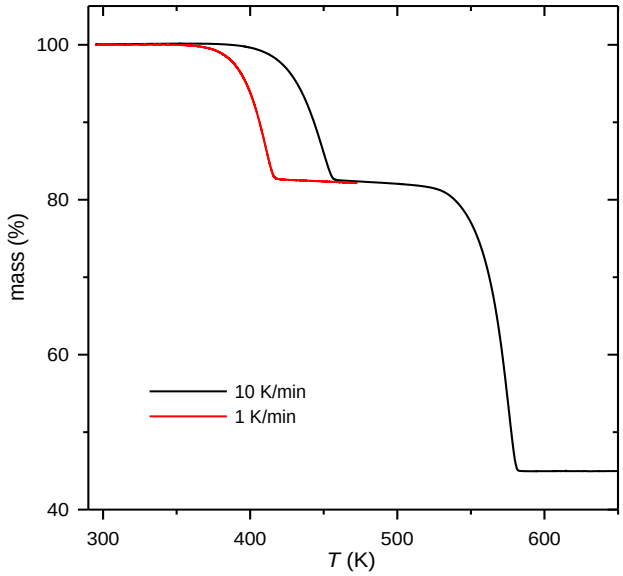

Figure S4. TGA runs measured for $PyrH^{+}AuCl_4^{-}$ at the rate of temperature changes 10 and 1 K/min.

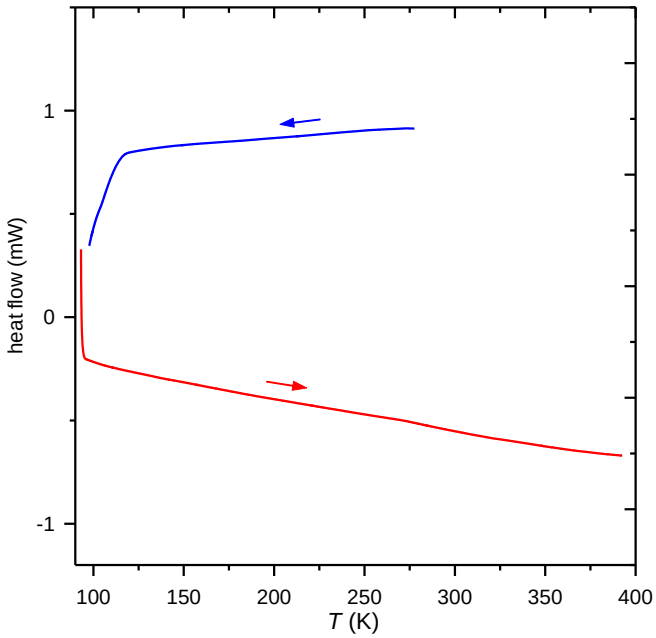

Figure S5. DSC cooling and heating runs measured for $PyrH^{+}AuCl_4^{-}$ at the temperature rate of 10 K/min.

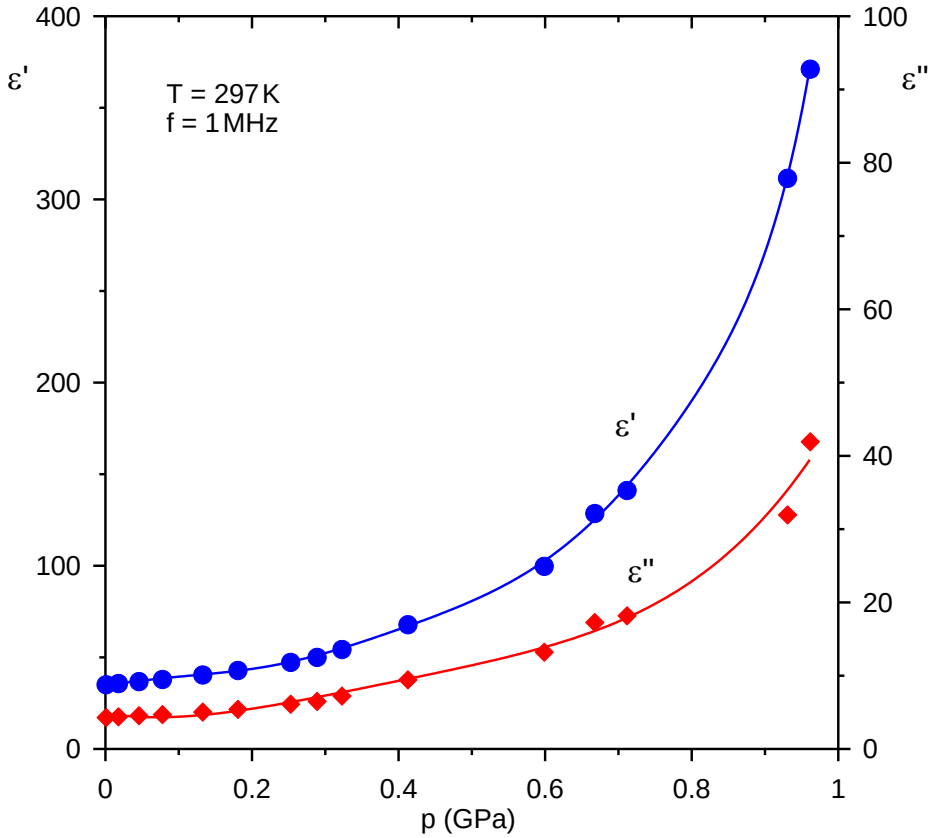

Figure S6. Pressure dependence of the real and imaginary parts of electric permittivity measured at 297 K for the 1 MHz frequency of electric field.

References:

[1] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, The Cambridge Structural Database, *Acta Cryst. Sect. B* **2016**, *72*, 171-179.