Supplementary Information

Negative Linear Compressibility of Molecular and Ionic-molecular Crystals

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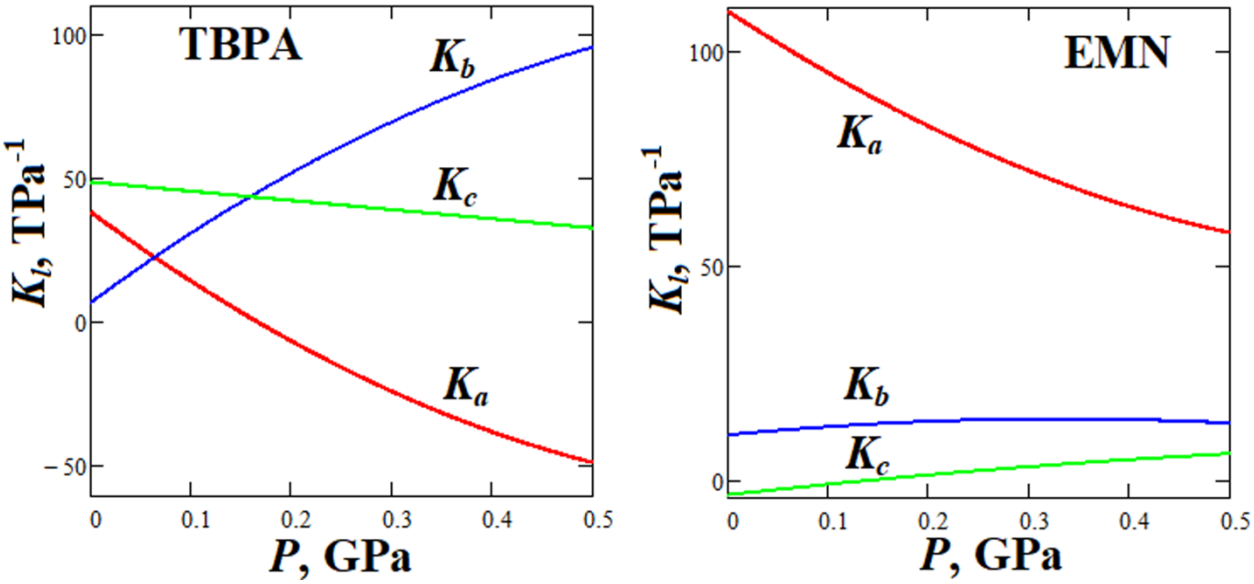

Fig. S1. Calculated linear compressibilities of TBPA (left) and EMN (right) as the functions of pressure: K_a (along *a*-axes), K_b (along *b*-axes), K_c (along *c*-axes).
The *l*-*P* data were fitted by the polynomial functions $l = l_0 + l_1P + l_2P^2 + l_3P^3$ to get a smooth *l*-*P* curves for the linear compressibilities calculations as $K_l = -(\mathrm{d}l/\mathrm{d}P)/l$.

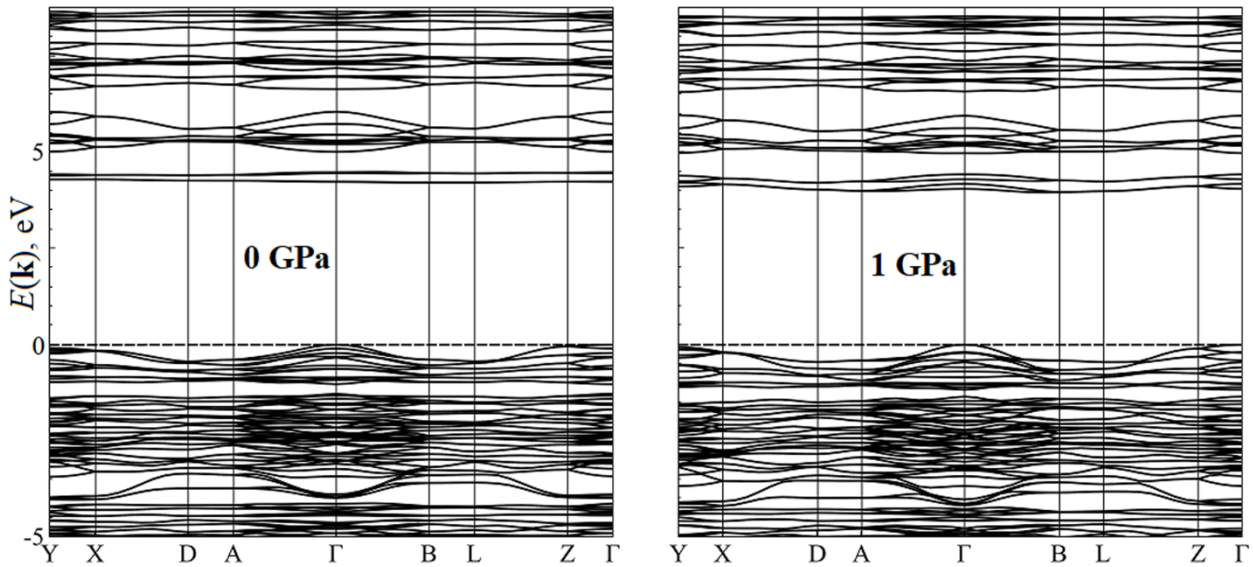

Fig. S2. Band structure of TBPA crystal at pressures of 0 and 1 GPa.
The energy of upper occupied states was set to zero.

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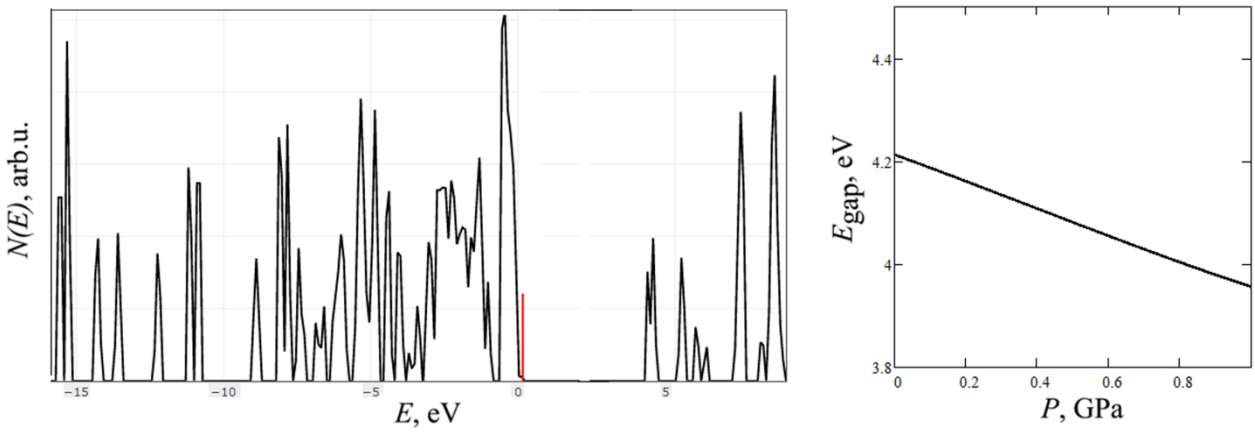

Fig. S3. Density of states $N(E)$ and the pressure dependence of the band gap for TBPA crystal.

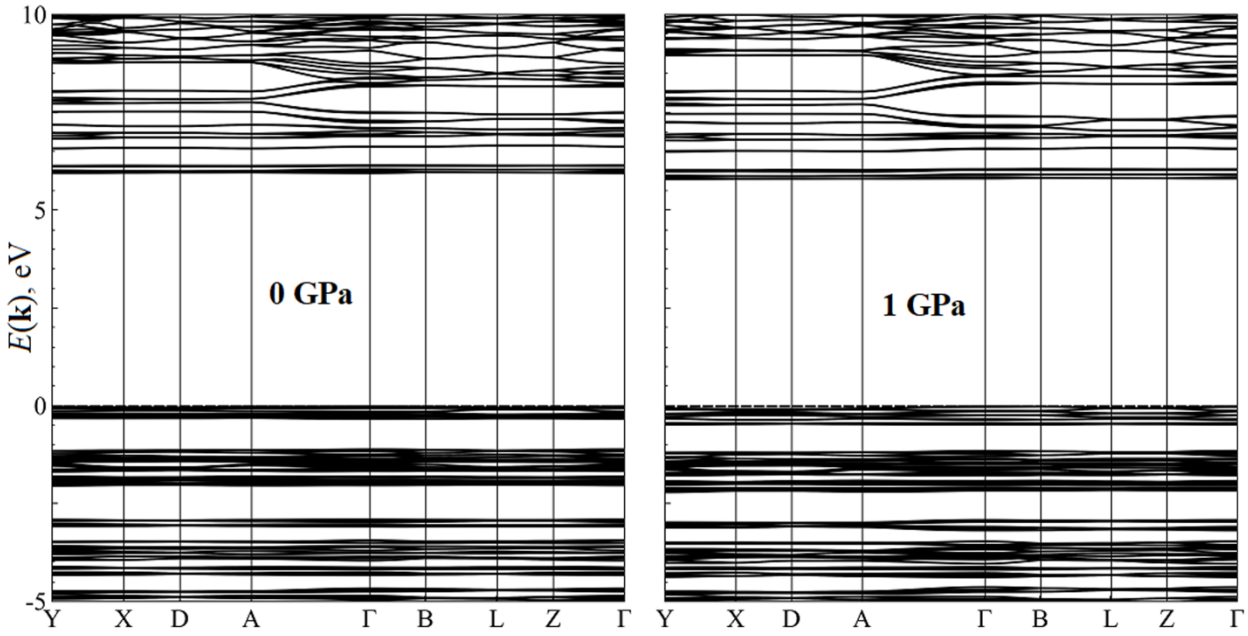

Fig. S4. Band structure of EMN crystal at pressures of 0 and 1 GPa.
The energy of upper occupied states was set to zero.

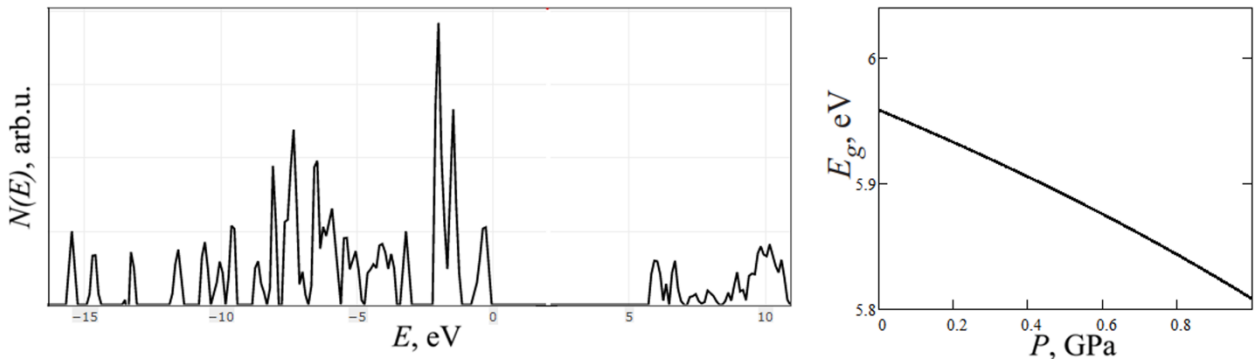

Fig. S5. Density of states $N(E)$ and the pressure dependence of the band gap for EMN crystal.

Table S1. The computed coefficients of pressure dependences $f_0 + f_1P + f_2P^2 + f_3P^3$ for lattice parameters a, b, c (Å) and unit cell volume V (Å^3) of TBPA and EMN (R is a correlation coefficient).

Crystal	Parameter	f_0	f_1	f_2	f_3	R^2
TBPA	a	13.326	-0.5075	1.7211	-0.7343	0.9947
	b	6.2264	-0.0400	-0.8080	0.3605	0.9977
	c	12.750	-0.6175	0.2218	-0.0120	0.9989
	V	1057.9	-96.981	17.875	-1.2658	0.9999
EMN	a	8.5820	-0.9363	0.7029	-0.3219	0.9984
	b	15.902	-0.1673	-0.1771	0.1802	0.9926
	c	12.489	0.0426	-0.1610	0.0556	0.9784
	V	1703.5	-199.21	99.669	-37.502	0.9992

Table S2. The computed coefficients of pressure dependences $f_0 + f_1P + f_2P^2 + f_3P^3$ for $R_{C\text{-}C}$ distances between carbon atoms of neighboring molecules and for L_1 and L_2 linear dimensions of TBPA molecules along the a and c axes, respectively (R is a correlation coefficient).

Crystal	Parameter	f_0	f_1	f_2	f_3	R^2
TBPA	$R_{C1\text{-}C1}$	6.5673	-0.3218	1.0085	-0.4502	0.9908
	$R_{C2\text{-}C2}$	6.5742	-0.3172	1.0089	-0.4601	0.9905
	$R_{C3\text{-}C3}$	6.5581	-0.3160	1.0200	-0.4634	0.9915
	L_1	6.1215	-0.1922	0.6819	-0.3223	0.9931
	L_2	5.3463	-0.1878	-0.1686	0.1403	0.9947

Table S3. Computed coefficients of pressure dependences $f_0 + f_1P + f_2P^2 + f_3P^3$ for the length of H…O hydrogen bond between cations and anions, and for angles between C-N bonds of molecular 1-ethyl-3-methylimidazolium cations and the c axis (R is a correlation coefficient).

Crystal	Parameter	f_0	f_1	f_2	f_3	R^2
EMN	$\alpha_{C1\text{-}N1}$	42.981	-1.3793	0.4880	0.0899	0.9956
	$\varphi_{C2\text{-}N2}$	33.452	-7.5797	9.0938	-4.6756	0.9993
	$R_{H\ldots O}$	2.1262	0.1209	-0.5086	0.0000	0.9621

Table S4. Computed coefficients of pressure dependences $f_0 + f_1P + f_2P^2$ for the electron density ρ_c, quantum electronic pressure QEP_c and H-bond energy in EMN crystal (R is a correlation coefficient).

Crystal	Parameter	f_0	f_1	f_2	R^2
EMN	ρ_c	0.0188	-0.0052	0.0210	0.9793
	QEP_c	-0.0072	0.0011	-0.0046	0.8517
	E_{HB}	16.615	-5.9886	24.5714	0.9721