Supporting Information for:

High Pressure Behavior of the Organic Semiconductor Salt $(TTF\text{-}BTD)_2I_3$.

Fabio Montisci,[†,⊥] Arianna Lanza,[†] Martin Fisch, [†] Camille Sonneville,[‡] Yan Geng,[†,▽] Silvio Decurtins,[†] Christian Reber,[‡] Shi-Xia Liu,[,†] Piero Macchi*[,†,§]*

[†]Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, 3012-Bern, Switzerland.

[‡]Département de chimie, Université de Montréal, Montréal QC H3C 3J7, Canada.

[§]Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, via Mancinelli 7, I-20131 Milan, Italy.

[⊥]Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, United Kingdom.

[▽]College of Chemistry, Chemical Engineering and Material Science, Shandong Normal University, Jinan 250014, P. R. China.

Table of Contents

Crystallographic coordinates of structures optimized with p-DFT at variable pressure

Optimized structure at ambient pressure.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	21.02217	9.85707	7.12784	110.48785

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	0.500000
I	-0.149453	0.500000	0.387433
S	-0.114635	-0.500000	-0.090222
N	-0.168593	-0.371574	-0.122812
C	0.270208	0.072980	-0.156176
C	0.209785	0.145242	-0.182627
H	0.209254	0.254642	-0.184215
C	0.152797	0.072507	-0.200903
S	0.074131	0.152900	-0.233042
C	0.028112	0.000000	-0.250460
C	-0.038451	0.000000	-0.270036
S	-0.085502	0.151794	-0.286897
C	-0.162777	0.067393	-0.324122
H	-0.206674	0.130499	-0.346021

Optimized structure at 0.5 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	21.01066	9.81226	7.05283	111.59780

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	-0.500000
I	-0.149122	-0.500000	0.390832
S	-0.120293	-0.500000	-0.091616
N	-0.174325	-0.371119	-0.123505
C	0.264249	0.073233	-0.155280
C	0.203919	0.145770	-0.179441
H	0.203258	0.255543	-0.181769
C	0.146832	0.072764	-0.196733
S	0.067872	0.153410	-0.230756
C	0.021981	0.000000	-0.244847

C	-0.044816	0.000000	-0.265657
S	-0.092031	0.152611	-0.284217
C	-0.169496	0.067617	-0.320598
H	-0.213462	0.131194	-0.342769

Optimized structure at 1 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	20.81999	9.71651	6.97238	110.86683

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	-0.500000
I	-0.149503	-0.500000	0.394430
S	-0.116357	0.500000	-0.084257
N	-0.170929	-0.369984	-0.119013
C	0.267066	0.073900	-0.154373
C	0.206161	0.147109	-0.180543
H	0.205533	0.257904	-0.182667
C	0.148609	0.073480	-0.198217
S	0.069190	0.154873	-0.232104
C	0.023128	0.000000	-0.246114
C	-0.044000	0.000000	-0.265364
S	-0.091255	0.154037	-0.282407
C	-0.169331	0.068300	-0.320694
H	-0.213672	0.132508	-0.344580

Optimized structure at 2 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	20.57148	9.58029	6.85686	110.20412

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	-0.500000
I	-0.150011	0.500000	0.399315
S	-0.111465	0.500000	-0.075257
N	-0.166778	-0.368380	-0.113688
C	0.270463	0.074852	-0.153981
C	0.208813	0.149045	-0.182792
H	0.208236	0.261312	-0.184613
C	0.150629	0.074515	-0.200942
S	0.070557	0.156982	-0.235167

C	0.024375	0.000000	-0.248423
C	-0.043120	0.000000	-0.264590
S	-0.090317	0.156076	-0.278668
C	-0.169174	0.069291	-0.318380
H	-0.213962	0.134473	-0.343921

Optimized structure at 5 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	20.14131	9.32806	6.62345	109.48145

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	0.500000	0.500000
I	-0.150781	0.500000	0.404719
S	-0.104280	0.500000	-0.064313
N	-0.160884	-0.365471	-0.107091
C	0.275142	0.076610	-0.154535
C	0.212328	0.152669	-0.186585
H	0.211795	0.267698	-0.188130
C	0.153087	0.076448	-0.204668
S	0.071895	0.160925	-0.239895
C	0.025606	0.000000	-0.252455
C	-0.042647	0.000000	-0.264398
S	-0.089571	0.159850	-0.273354
C	-0.169775	0.071187	-0.314405
H	-0.215346	0.138211	-0.342693

Optimized structure at 10 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	19.77496	9.08696	6.38014	109.86593

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	0.500000
I	-0.151438	0.500000	0.405733
S	-0.098466	0.500000	-0.058106
N	-0.156412	-0.362789	-0.103416
C	0.278369	0.078269	-0.156884
C	0.214619	0.156076	-0.190306
H	0.214034	0.273740	-0.191801
C	0.154504	0.078246	-0.207111

S	0.072307	0.164726	-0.244465
C	0.026233	0.000000	-0.256279
C	-0.042561	0.000000	-0.263797
S	-0.088837	0.163511	-0.267515
C	-0.170521	0.073062	-0.312299
H	-0.217033	0.141692	-0.345357

Optimized structure at 15 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	19.57910	8.93780	6.22841	111.59542

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	0.500000
I	-0.152996	0.500000	0.395366
S	-0.091294	0.500000	-0.060751
N	-0.150300	-0.361289	-0.107812
C	0.283416	0.079261	-0.164966
C	0.219223	0.158152	-0.196905
H	0.218962	0.277435	-0.195421
C	0.158668	0.079364	-0.212185
S	0.075647	0.167327	-0.253933
C	0.030144	0.000000	-0.262396
C	-0.038043	0.000000	-0.259604
S	-0.083379	0.165669	-0.257139
C	-0.166227	0.074251	-0.304234
H	-0.213674	0.143418	-0.340459

Optimized structure at 20 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	19.35933	8.79453	6.06648	111.19424

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	-0.500000
I	-0.152958	0.500000	0.397303
S	-0.089918	0.500000	-0.058501
N	-0.149573	-0.359728	-0.104948
C	0.283586	0.080203	-0.165036
C	0.219084	0.160076	-0.196844
H	0.218823	0.280898	-0.195671

C	0.158118	0.080351	-0.210458
S	0.074705	0.169690	-0.253697
C	0.029241	0.000000	-0.265023
C	-0.039360	0.000000	-0.260275
S	-0.084315	0.167872	-0.256974
C	-0.167811	0.075451	-0.306334
H	-0.215735	0.145445	-0.345355

Optimized structure at 30 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	18.93607	8.56209	5.79845	109.43095

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	0.500000	-0.500000
I	-0.152691	-0.500000	0.403676
S	-0.087804	-0.500000	-0.051403
N	-0.148775	-0.357163	-0.095941
C	0.283553	0.081615	-0.162030
C	0.218414	0.162934	-0.194561
H	0.217961	0.286313	-0.195558
C	0.156589	0.081716	-0.204922
S	0.072483	0.173664	-0.249111
C	0.026833	0.000000	-0.271302
C	-0.043043	0.000000	-0.264580
S	-0.087569	0.171232	-0.262228
C	-0.171972	0.077604	-0.314854
H	-0.220257	0.149623	-0.356320

Optimized structure at 40 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	18.61084	8.39486	5.61531	108.57679

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	-0.500000
I	-0.152727	0.500000	0.408744
S	-0.085523	0.500000	-0.045227
N	-0.147684	-0.355531	-0.088320
C	0.283770	0.082486	-0.161154
C	0.218037	0.164770	-0.194555

H	0.217510	0.289993	-0.194876
C	0.155412	0.082670	-0.204149
S	0.070745	0.176657	-0.248508
C	0.025155	0.000000	-0.277157
C	-0.045378	0.000000	-0.267028
S	-0.089360	0.173742	-0.263488
C	-0.174531	0.079166	-0.317608
H	-0.223059	0.152952	-0.360033

Optimized structure at 50 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	18.39798	8.27628	5.48321	110.50030

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	-0.500000
I	-0.152552	0.500000	0.423020
S	-0.082097	0.500000	-0.034392
N	-0.145042	-0.353785	-0.071620
C	0.284483	0.082805	-0.155527
C	0.217731	0.165261	-0.194429
H	0.216648	0.291650	-0.199400
C	0.154303	0.082972	-0.202594
S	0.069158	0.179992	-0.250475
C	0.016914	0.000000	-0.352174
C	-0.044464	0.000000	-0.256592
S	-0.088324	0.172899	-0.251831
C	-0.175354	0.080518	-0.317259
H	-0.224139	0.156310	-0.355196

Optimized structure at 60 GPa.

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	18.21680	8.16931	5.36529	110.39657

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	0.500000	0.500000
I	-0.152963	-0.500000	0.425170
S	-0.080543	-0.500000	-0.033372
N	-0.144177	-0.353015	-0.066269
C	0.284884	0.083374	-0.156137

C	0.217845	0.166557	-0.195448
H	0.216877	0.294086	-0.200348
C	0.154247	0.083687	-0.201383
S	0.068892	0.182048	-0.252288
C	0.017231	0.000000	-0.351080
C	-0.043449	0.000000	-0.249071
S	-0.087959	0.174765	-0.249816
C	-0.175513	0.081526	-0.318439
H	-0.224510	0.158261	-0.356270

Optimized structure at 40 GPa (relaxed from 50 GPa structure).

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	18.60771	8.40213	5.62087	110.55451

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	-0.500000
I	-0.152251	-0.500000	0.420653
S	-0.083933	-0.500000	-0.035895
N	-0.146114	-0.354774	-0.076985
C	0.284018	0.082154	-0.154761
C	0.217589	0.163726	-0.193453
H	0.216374	0.288779	-0.198324
C	0.154414	0.082103	-0.203832
S	0.069526	0.177572	-0.248721
C	0.016670	0.000000	-0.353448
C	-0.045242	0.000000	-0.263611
S	-0.088612	0.170781	-0.254585
C	-0.174918	0.079350	-0.315575
H	-0.223356	0.154085	-0.352317

Optimized structure at 30 GPa (relaxed from 40 GPa structure).

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	18.85802	8.55946	5.79066	110.63711

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	-0.500000
I	-0.152040	0.500000	0.418115
S	-0.086190	0.500000	-0.038271
N	-0.147514	-0.356162	-0.082579

C	0.283384	0.081323	-0.153845
C	0.217315	0.161748	-0.192287
H	0.215947	0.285097	-0.196848
C	0.154508	0.080994	-0.204972
S	0.069901	0.174590	-0.247449
C	0.016413	0.000000	-0.354962
C	-0.045961	0.000000	-0.270961
S	-0.088963	0.168255	-0.258682
C	-0.174224	0.077922	-0.312965
H	-0.222123	0.151365	-0.346187

Optimized structure at 20 GPa (relaxed from 30 GPa structure).

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	19.32882	8.78758	6.00657	111.50873

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	0.500000	-0.500000
I	-0.154741	-0.500000	0.412889
S	-0.091333	-0.500000	-0.048099
N	-0.150536	-0.359215	-0.089282
C	0.281864	0.080032	-0.153361
C	0.216588	0.159072	-0.191499
H	0.215101	0.279882	-0.198908
C	0.154987	0.079825	-0.207494
S	0.071262	0.170840	-0.252010
C	0.017293	0.000000	-0.353860
C	-0.042866	0.000000	-0.268242
S	-0.086498	0.165118	-0.258563
C	-0.170124	0.075868	-0.306891
H	-0.217385	0.146637	-0.335634

Optimized structure at 10 GPa (relaxed from 20 GPa structure).

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	19.74299	9.10995	6.39733	112.28525

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	0.500000	-0.500000
I	-0.152512	-0.500000	0.411189
S	-0.094591	-0.500000	-0.049435

N	-0.153054	-0.362980	-0.096241
C	0.280517	0.078061	-0.154267
C	0.215655	0.155283	-0.193583
H	0.214571	0.272662	-0.196259
C	0.154673	0.077826	-0.215883
S	0.071593	0.164902	-0.255444
C	0.016753	0.000000	-0.355782
C	-0.043481	0.000000	-0.281632
S	-0.086264	0.160654	-0.263145
C	-0.167978	0.073012	-0.296194
H	-0.213954	0.142017	-0.317267

Optimized structure at 5 GPa (relaxed from 10 GPa structure).

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	20.13161	9.33707	6.65058	110.32576

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	-0.500000	0.500000
I	-0.151962	-0.500000	0.398555
S	-0.098698	-0.500000	-0.065009
N	-0.155670	-0.365614	-0.109141
C	0.280127	0.076575	-0.158261
C	0.217051	0.152638	-0.191594
H	0.216693	0.267640	-0.191141
C	0.157642	0.076442	-0.211115
S	0.076126	0.160939	-0.248566
C	0.030145	0.000000	-0.257861
C	-0.037378	0.000000	-0.261623
S	-0.083938	0.159510	-0.266021
C	-0.164397	0.071165	-0.306558
H	-0.210140	0.138009	-0.334229

Optimized structure at ambient pressure (relaxed from 5 GPa structure).

Unit Cell Parameters:

Space Group	a (Å)	b (Å)	c (Å)	β (°)
C2/m	21.19859	9.96882	7.20584	113.22584

Fractional coordinates of the asymmetric unit:

Atom	x	y	z
I	0.000000	0.500000	-0.500000
I	-0.150000	-0.500000	0.397749

S	-0.115697	-0.500000	-0.079215
N	-0.170092	-0.373034	-0.115949
C	0.268172	0.072235	-0.154164
C	0.207293	0.143588	-0.186313
H	0.205849	0.251652	-0.190822
C	0.149878	0.071658	-0.211263
S	0.070753	0.151659	-0.252268
C	0.025637	0.000000	-0.260535
C	-0.038690	0.000000	-0.262937
S	-0.084587	0.150186	-0.269201
C	-0.157872	0.066590	-0.270379
H	-0.198618	0.128895	-0.264805

Band structure and total DOSs plots at variable pressure

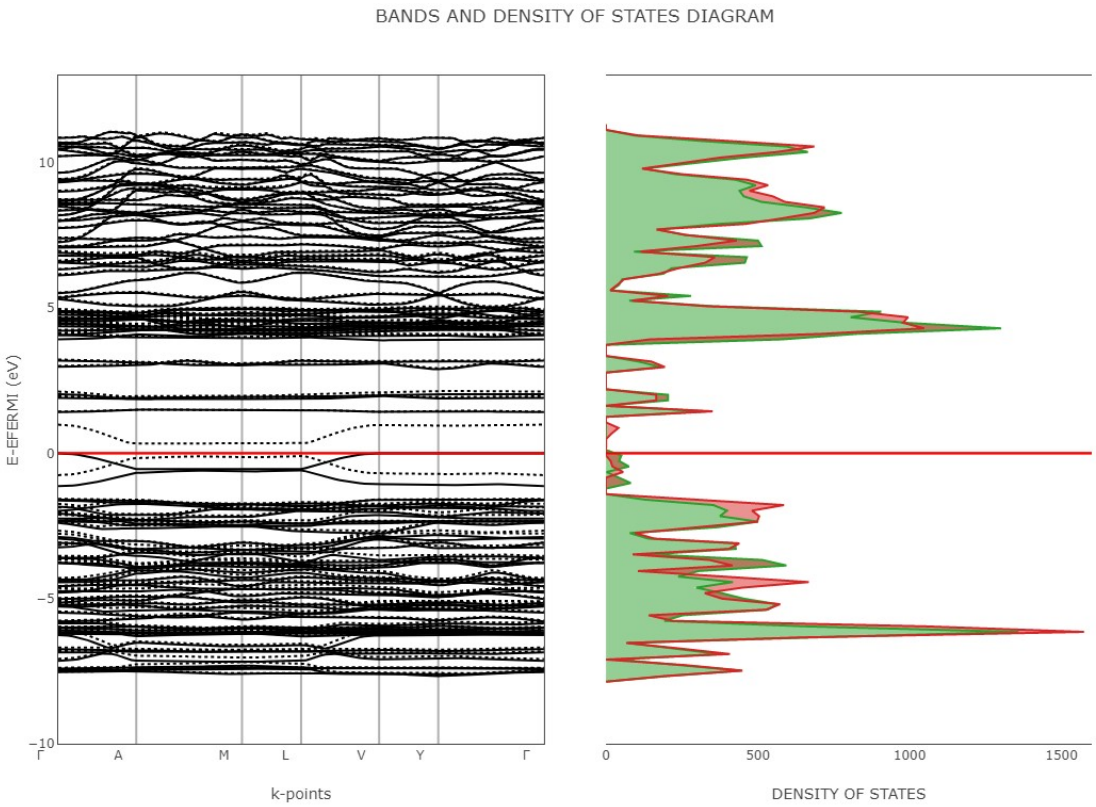

Figure S1. Band structure and Density of States plot for the optimized structure at ambient pressure.

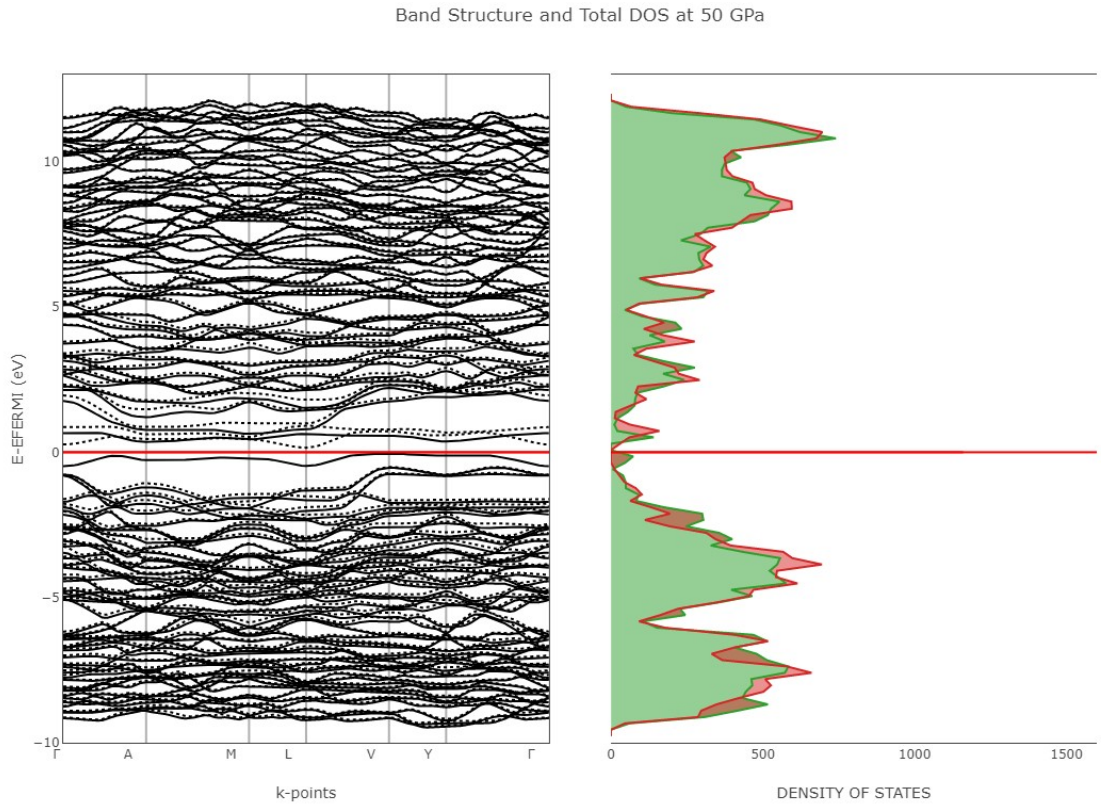

Figure S2. Band structure and Density of States plot for the optimized structure at 50 GPa.

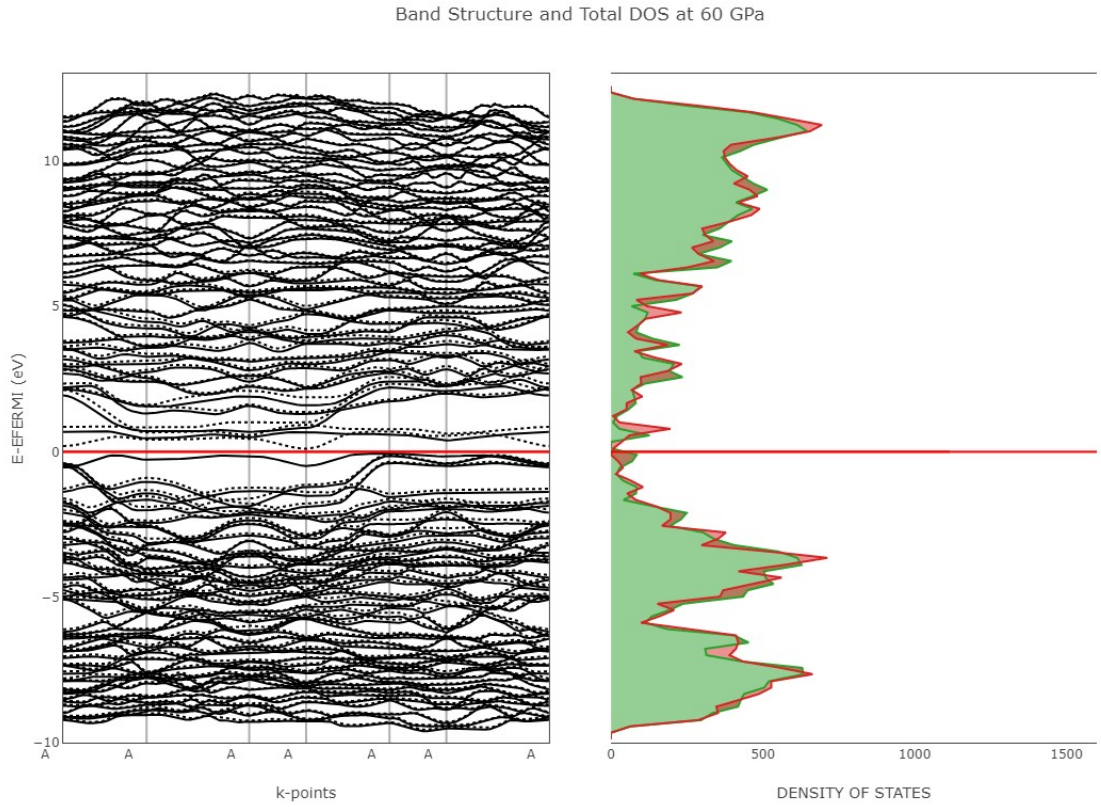

Figure S3. Band structure and Density of States plot for the optimized structure at 60 GPa.

Forces calculated with semi-empirical potential

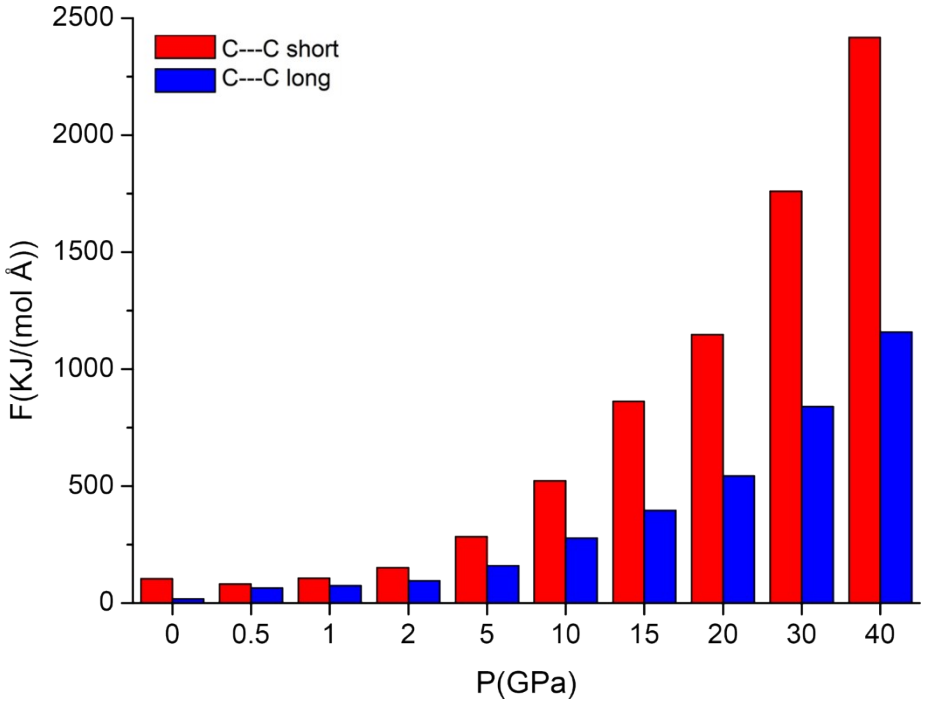

Figure S4. Intermolecular interaction forces computed with the semi-empirical potential FF on the calculated crystal structures of $(TTF\text{-}BTD)_2I_3$ up to 40 GPa for the molecules containing the $C\cdots C_{short}$ and $C\cdots C_{long}$ contacts.

Raman spectra at variable temperature

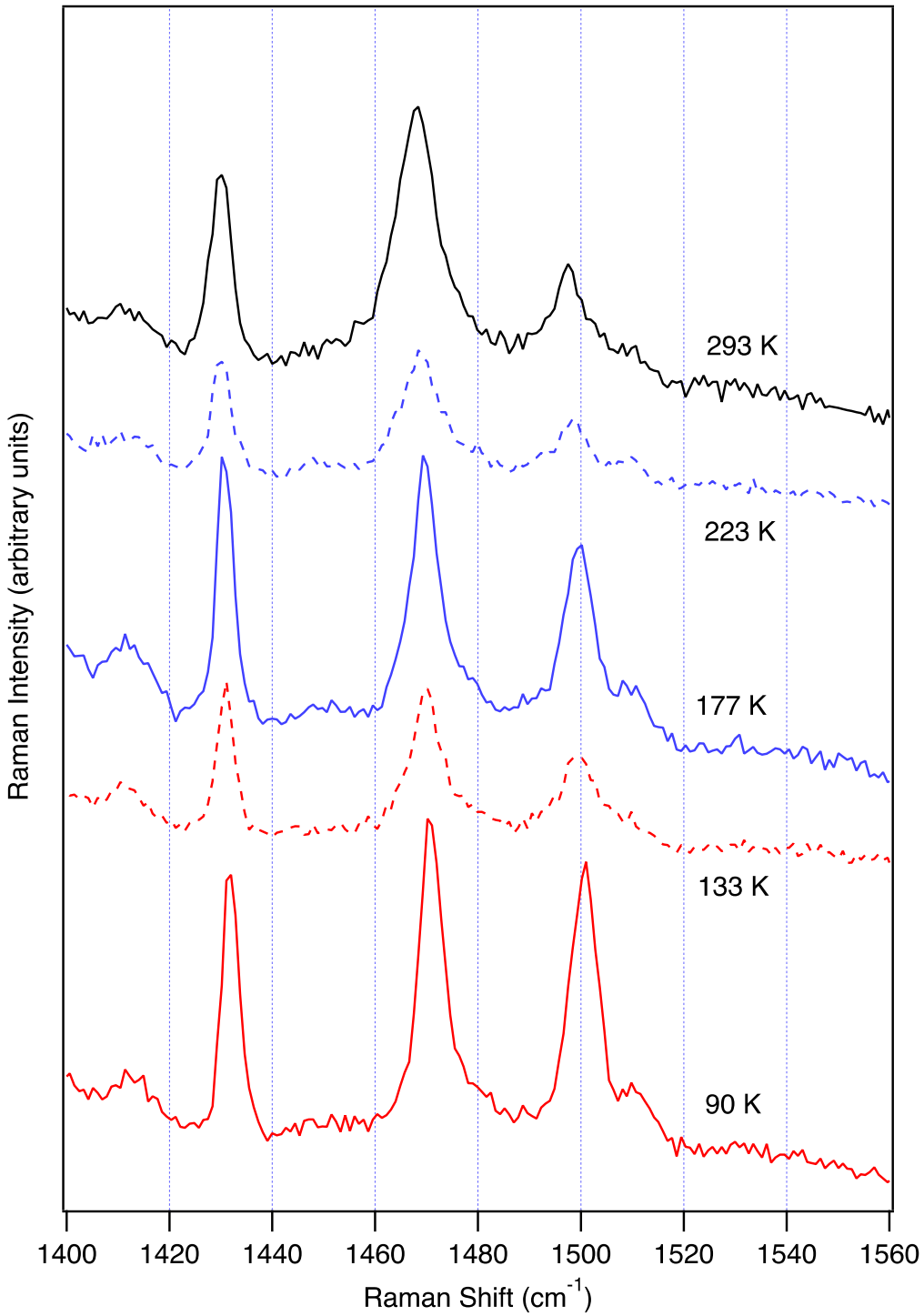

Figure S5. Raman spectra at variable temperature and ambient pressure in the region of C=C stretching modes shown in the same range as for variable pressure in Figure 4. Peaks broaden and maxima shift to slightly lower frequency with increasing temperature. Excitation wavelength: 785 nm.