

# Supplementary Material

## Pressure stabilization effect on the donor-acceptor polyiodide chains in tetraethylammonium bis(diodine) triiodide – insights from Raman spectroscopy

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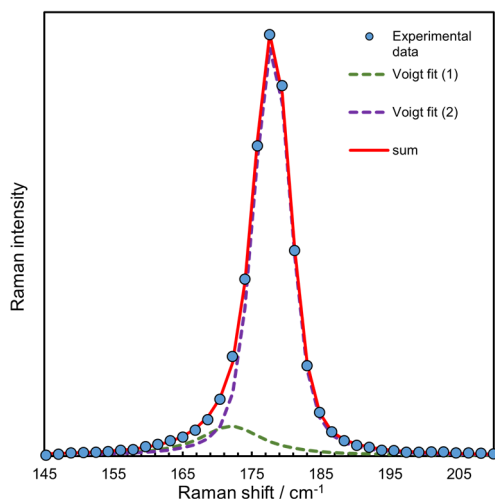
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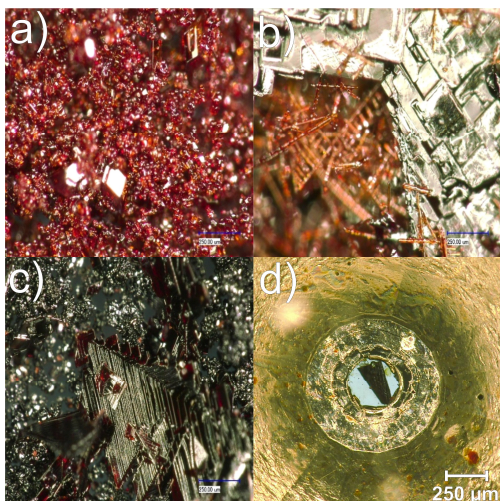
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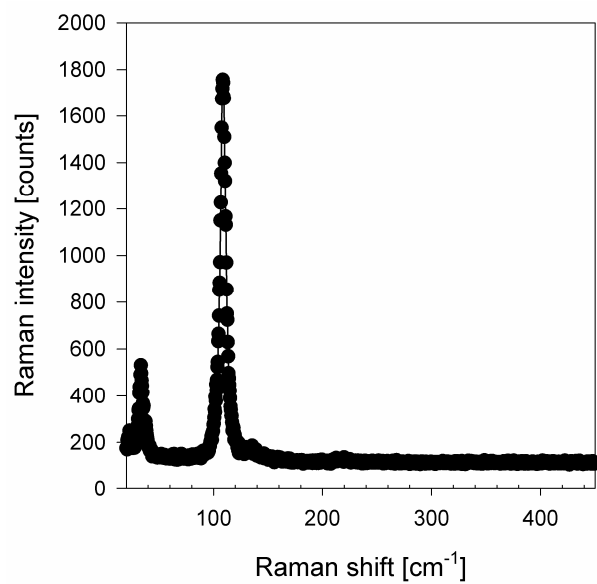
### 1. Raman spectroscopy details on TEAI



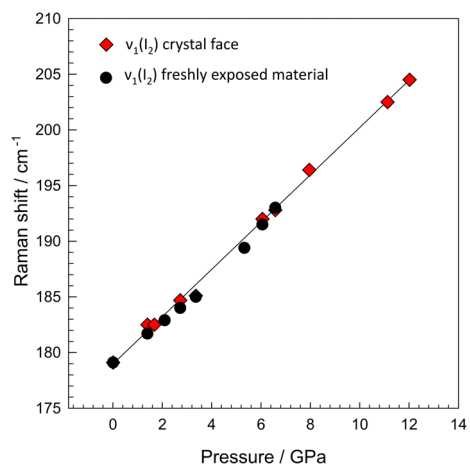
**Figure S1.** Experimental  $\nu(I_2)$  peak profile in TEAI deconvoluted with two Voigt functions centred at 171 and 178 cm<sup>-1</sup>, respectively.



**Figure S2.** Sample microphotographs: a)  $\text{Et}_4\text{Ni}_3$ , b) mixture of  $\text{Et}_4\text{Ni}_3$  polymorphs at TEAI, c) pristine TEAI, d) TEAI crystal loaded in DAC



**Figure S3.** Raman spectrum of TEAI crystal collected in air (10mW, 10s, 532 nm) presents immediate decomposition to  $\text{Et}_4\text{Ni}_3$



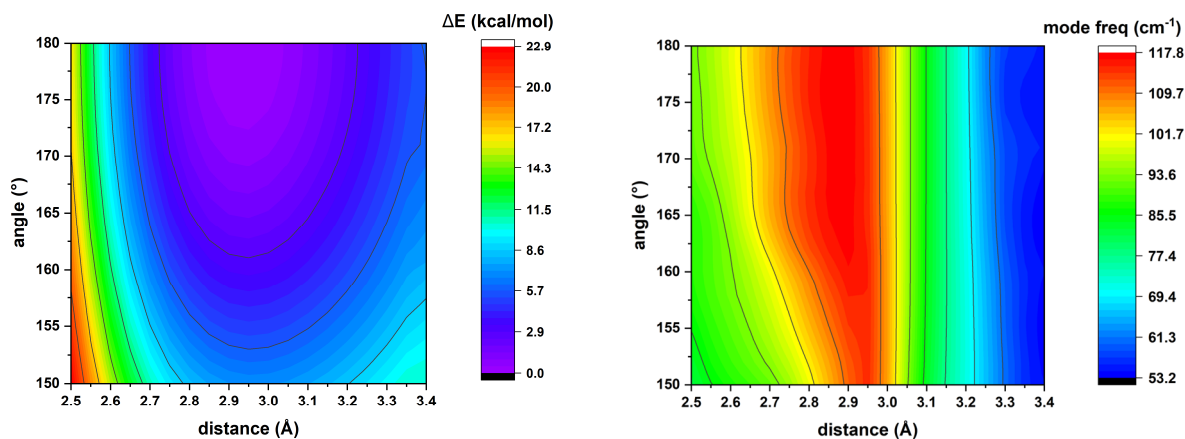
**Figure S4.** Pressure-shift of  $\nu_1(I_2)$  mode in TEAl observed from a region on a surface (diamond) and freshly exposed crystal interior (circles)

**Table S1:** Bond lengths for the studied systems at their energetic minima.

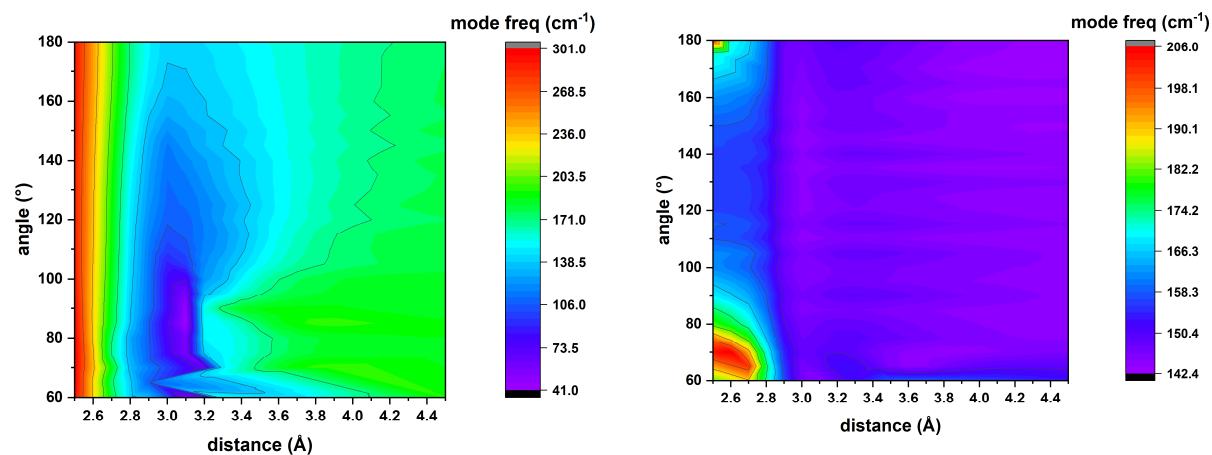
System	Bondlength (Å)	Angle (°)
$I_3^-$	2.933	180.00
$I_2-I_3^-$	3.030 (inner)	109.20
	2.827 (outer)	

**Table S2:** Raman data (frequency and activity) for studied compounds for which an energetic minimum has been found.

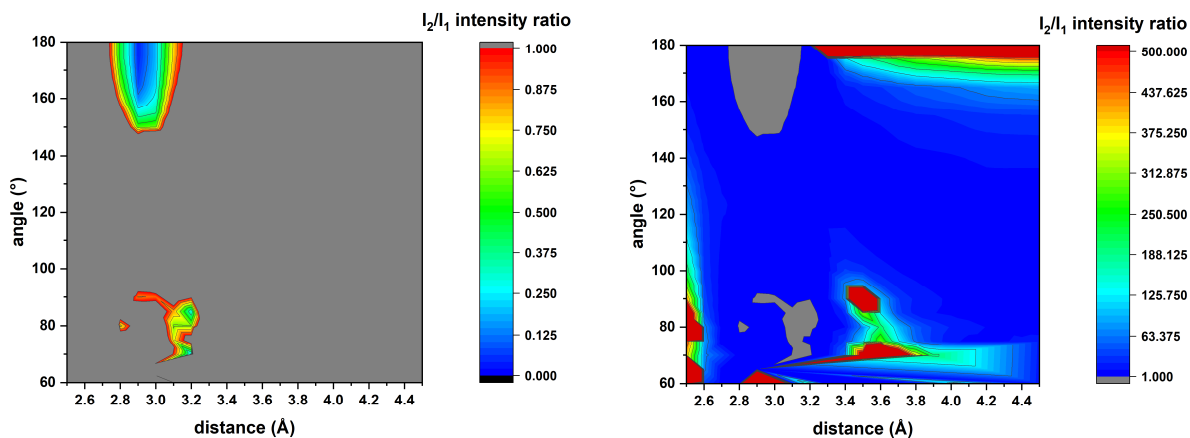
System	Frequency [ $\text{cm}^{-1}$ ] (activity)		
	Bending	Assym. Stretch	Symmetric Stretch
$\text{I}_3^-$	58.66 (0)	115.92 (46.6)	145.42 (0)
$\text{I}_2\text{-I}_3^-$	-	144.37 (50.2)	160.26 (149.4)



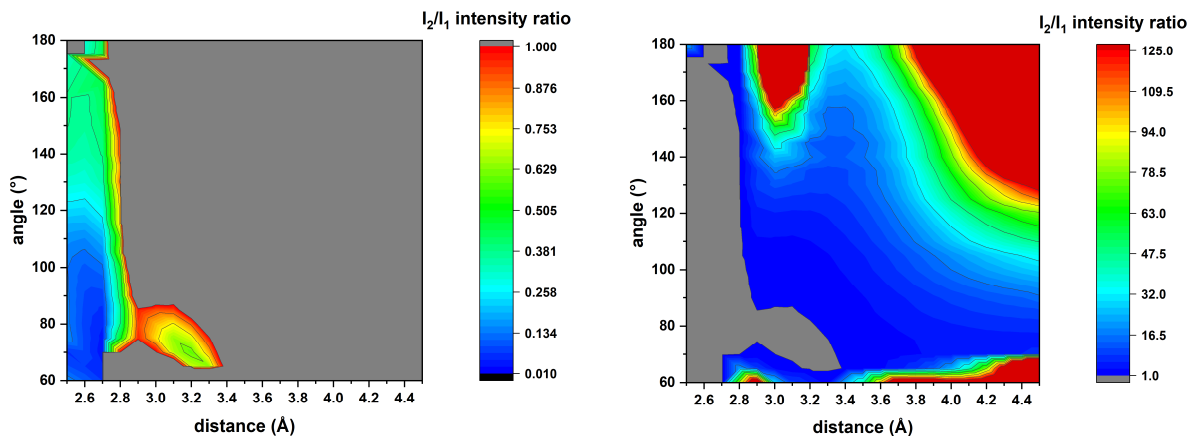
**Figure S5.** Potential energy surfaces calculated for triiodide fragment with different geometries are shown (left) along with the calculated Raman shifts (right), for the corresponding geometries, of I-I stretch for triiodide ( $\text{I}_2\cdots\text{I}$ )



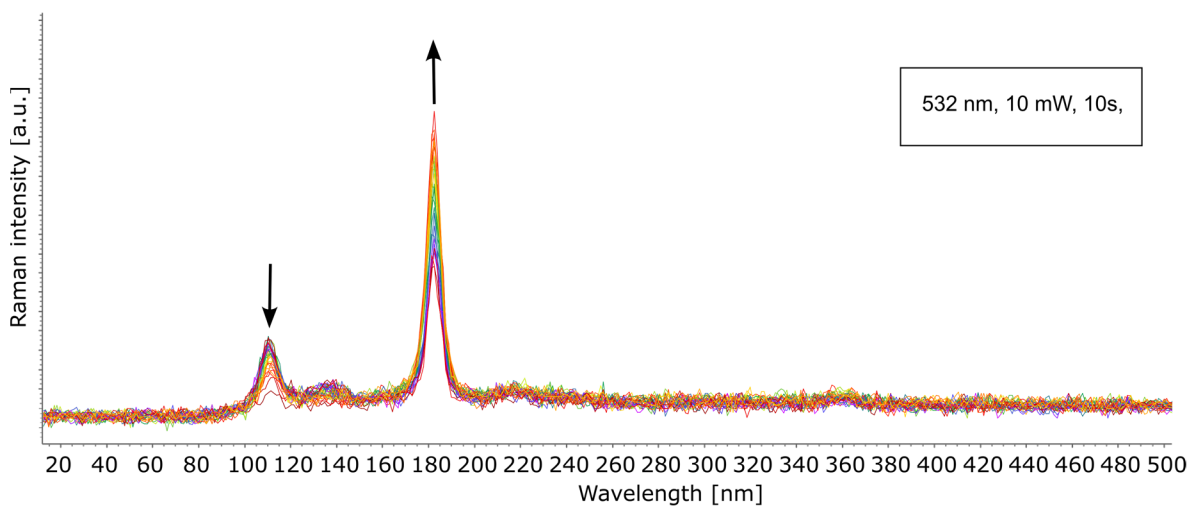
**Figure S6.** Asymmetric stretch,  $\nu_2(\text{I}_3^-)$  (left) and  $\nu_2(\text{I}_5^-)$  (right), mode frequencies calculated for various geometries



**Figure S7.**  $v_2/v_1$  ( $\sigma_u$ ,  $\sim 140\text{ cm}^{-1}$  and  $\sigma_g$ ,  $\sim 102\text{ cm}^{-1}$ ) modes intensity ratios calculated for various  $I_3^-$  geometries: below (left) and above (right) 1.



**Figure S8.**  $v_2$  (symmetric outer stretch)/ $v_1$  (asymmetric outer stretch) [ $\sigma_g$ ,  $\sim 165\text{ cm}^{-1}$  and  $\sigma_u$ ,  $\sim 144\text{ cm}^{-1}$ ] modes intensity ratios calculated for various  $I_3^-$  geometries: below (left) and above (right) 1.



**Figure S9.** Linear decay of  $v_1(I_2)$  and emergence of  $v_1(I_3)$  in TEAL upon continuous 532 nm laser irradiation kept in air.

## 2. Experimental structures containing donor-acceptor polyiodides

**Table S3.** Experimental I-I distances and the respective Raman shifts extracted from literature. Only structures containing V - or L-shaped I<sub>2</sub>·I<sub>3</sub> fragments were considered.

Compound	I-I bond length in I <sub>2</sub> [Å]	Raman shift [cm <sup>-1</sup> ]	References
nicotine-1,1'-dium bis(triiodide)-diiodine	2.740	177	[1]
1-(Iodomethyl)-1,2-dihydro[1,3]thiazolo[3,2-a]quinolin-10-ium tri-iodide hemikis(di-iodine)	2.765	165	[2]
solid iodine	2.715	180	[3,4]
(Z)-4-chloro-5-((2-((4-chloro-5H-1,2,3-dithiazol-5-ylidene)amino)phenyl)amino)-1,2,3-dithiazol-1-ium oligoiodide	2.732	179	[5]
(E)-3-(iodomethylene)-2,3-dihydro-[1,4]oxazino[2,3,4-ij]quinolin-4-ium triiodide diiodine	2.747	172	[6]
4-benzoyloxy-2,2,6,6-tetramethylpiperidiny-1-oxy tetrakis(diiodine) di(pentaiodide)	2.829	141	[7]
4-benzoyloxy-2,2,6,6-tetramethylpiperidiny-1-oxy tetrakis(diiodine) di(pentaiodide)	2.813	156	[7]
5,10,15,20-tetraphenylprophyrinium bis(pentaiodide)	2.740	174	[8]
tetraethylammonium bis(diiodine) triiodide	2.734	178	[9,10]
tetramethylammonium pentaiodide	2.799	155	[10,11]
N-Propylurotropinium heptaiodide	2.740	176	[12,13]
Tetra(n-propyl)ammonium bis(iodine) triiodide	2.740	164	[14,15]
N-propylurotropinium pentaiodide	2.780	163	[13,16]
N-propylurotropinium pentaiodide	2.815	149	[13,16]
bis(N-methylurotropinium) octaiodide	2.773	164	[13,17]
tris(morpholinecarbodithioato-S,S')manganese(IV)pentaiodide–dichloromethane (2/1)	2.810	144	[18]
tris(morpholinecarbodithioato-S,S')manganese(IV)pentaiodide–dichloromethane (2/1)	2.750	165	[18]
morpholinium pentaiodide	2.783	164	[19,20]
bis(3,5-Di-(N-morpholinio)-1,2,4-trithiolane) hexadecaiodide	2.741	174	[20,21]
bis(phenacetinium) pentaiodide	2.748	178	[22,23]
bis(phthalocyaninato)niobium(IV) octaiodide, 1-chloronaphtalene solvate (3.5/1)	2.771	167	[24]
bis(N-methylbenzothiazole-2(3H)-selone)-μ-iodonium heptaiodide	2.771	157	[25]
bis(N-methylbenzothiazole-2(3H)-selone)-μ-iodonium heptaiodide	2.746	175	[25]
cesium octaiodide	2.762	170	[26,27]

<b>(acetonitrile)-(3,6,9-trithia-1(2,9)-1,10-phenanthrolinecyclodecaphane)-nickel(II) triiodide pentaiodide</b>	2.784	167	[28]
<b>bis(1,4,7-trithiacyclononane)-cobalt(III) tris(tri-iodide) iodine</b>	2.787	168	[29]
<b>bis(1,4,7-trithiacyclononane)-cobalt(III) tris(tri-iodide) iodine</b>	2.825	150	[29]
<b>bis(1,4,7-trithiacyclononane)-nickel(II) bis(pentaiodide)</b>	2.780	164	[29]
<b>bis(1,4,7-trithiacyclononane)-nickel(II) bis(pentaiodide)</b>	2.815	145	[29]
<b>(1,4,8,11-tetrathiacyclotetradecane)-palladium(II) bis(pentaiodide) acetonitrile solvate</b>	2.760	168	[29]
<b>(1,4,8,11-tetrathiacyclotetradecane)-palladium(II) bis(pentaiodide) acetonitrile solvate</b>	2.840	154	[29]
<b>(1,4,8,11-tetrathiacyclotetradecane)-palladium(II) bis(pentaiodide) acetonitrile solvate</b>	2.798	163	[29]
<b>catena-((<math>\mu_2</math>-Iodo)-bis((tetrathia-16-crown-4)-palladium(II)) undecaoidide)</b>	2.836	149	[30]
<b>catena-((<math>\mu_2</math>-Iodo)-bis((tetrathia-16-crown-4)-platinum(II)) undecaoidide)</b>	2.789	158	[30]
<b>catena-((<math>\mu_2</math>-Iodo)-bis((tetrathia-16-crown-4)-platinum(II)) undecaoidide)</b>	2.833	153	[30]

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