



Supplementary Material

Bridging Molecular and Periodic Models: A Theoretical Study of the Spectroscopic Properties of Polythiophene †

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† This article is dedicated to Prof. Giuseppe Zerbi in recognition of his outstanding scientific contributions to Spectroscopy.



Table S1. Wavenumbers and intensities of the most prominent IR and Raman bands of TN oligomers of polythiophene (PT). Green characters: B3LYP-V/POB-TZVP results (CRYSTAL code); blue characters B3LYP-V/POB-TZVP results (Gaussian code). For PT, the system is modelled as a 1D crystal (B3LYP-V)—or as T45 oligomer (B3LYP-III). Intensity values of the oligomers are normalized to the number of internal T2 units.

IR	PT-1D crystal T45		T22		T18		T14		T12		T8		T6		T4	
	mode # (code)	ν cm ⁻¹	I km mol ⁻¹	ν cm ⁻¹	I km mol ⁻¹	ν cm ⁻¹	I km mol ⁻¹	ν cm ⁻¹	I km mol ⁻¹	ν cm ⁻¹	I km mol ⁻¹	ν cm ⁻¹	I km mol ⁻¹	ν cm ⁻¹	I km mol ⁻¹	ν cm ⁻¹
1 (B3-V)	808	75	808	67	808	50	803	47	808	61	805 802	80	802 804	82	802	89
1 (B3-III)	805	56	805	63	805	51	805	67	805	59	805	65	804 807	82	806 833	107
2 (B3-V)	1537	445	1538	328	1539	314	1540	289	1541	271	1544	213	1547	170	1553	121
2 (B3-III)	1536	401	1537	363	1538	342	1539	313	1539	289	1543	225	1547	178	1553	126
3 (B3-V)	3192	163	3195	130	3192 3193	124	3193	111	3192 3193	105	3192 3193	81	3193	65	3192	42
3 (B3-III)	3194	152	3194	136	3194	127	3194	114	3194	104	3195	81	3195	65	3195	43
Raman	PT T45		T22		T18		T14		T12		T8		T6		T4	
mode # (code)	ν cm ⁻¹	I 10 ³ A ⁴ amu ⁻¹	ν cm ⁻¹	I 10 ³ A ⁴ amu ⁻¹	ν cm ⁻¹	I 10 ³ A ⁴ amu ⁻¹	ν cm ⁻¹	I 10 ³ A ⁴ amu ⁻¹	ν cm ⁻¹	I 10 ³ A ⁴ amu ⁻¹	ν cm ⁻¹	I 10 ³ A ⁴ amu ⁻¹	ν cm ⁻¹	I 10 ³ A ⁴ amu ⁻¹	ν cm ⁻¹	I 10 ³ A ⁴ amu ⁻¹
1 (B3-V)	703	12	703	7	703	7	702	5	702	4	701	2	700	1	696	0.4
1 (B3-III)	703	15	702	11	702	10	702	7	702	6	701	3	700	2	696	0.4
2 (B3-V)	1070	191	1070	118	1070	101	1070	79	1070	59	1071	25	1071	12	1071	3
2 (B3-III)	1070	209	1070	155	1070	131	1070	97	1070	76	1070	33	1070	14	1071	4
3 (B3-V)	1235	63	1235	32	1235	29	1235	21	1234 1235	17	1236	4	1235	1	1233	0.1
3 (B3-III)	1236	64	1236	50	1236	43	1236	32	1236 1235	25	1236	6	1230–1240	4	1234 1245	0.2
4 (B3-V)	1406	191	1406	113	1406	96	1405	69	1405	54	1404	19	1403	7	1401	1.3
4 (B3-III)	1407	247	1407	187	1407	155	1407	111	1407	83	1406	26	1404	9	1402	3
5 (B3-V)	1477	2281	1478	1315	1478	1142	1479	873	1480	679	1485	319	1491	153	1503	57
5 (B3-III)	1472	2168	1473	1650	1474	1412	1475	1085	1476	872	1483	352	1487	186	1501	61

	PT (1D crystal)	T12
mode 1 (IR)		
ν (cm^{-1})	808	808
mode 2 (IR)		
ν (cm^{-1})	1537	1541
mode 3 (IR)		
ν (cm^{-1})	3192	3192
mode 1 (Raman)		
ν (cm^{-1})	703	702
mode 2 (Raman)		
ν (cm^{-1})	1070	1070
mode 3 (Raman)		
ν (cm^{-1})	1235	1235
mode 4 (Raman)		
ν (cm^{-1})	1406	1405
mode 5 (Raman)		
ν (cm^{-1})	1477	1485

Figure S1. Comparison of the $q = 0$ vibrational eigenvectors associated with the strongest IR and Raman bands of PT as 1D crystal—with those of the corresponding modes of T12 (DFT B3LYP-V/POB-TZVP calculations, CRYSTAL CODE). Blue and green segments indicate bond stretching and contraction, respectively; the segment thickness is proportional to the contribution of each bond deformation to the vibrational eigenvector. Red arrows represent the direction of the atomic displacements within the normal mode. Out-of-plane atomic displacements are shown as red and blue circles, whose radii are proportional to the magnitude of the displacement. For each selected mode, the calculated wavenumber is reported.

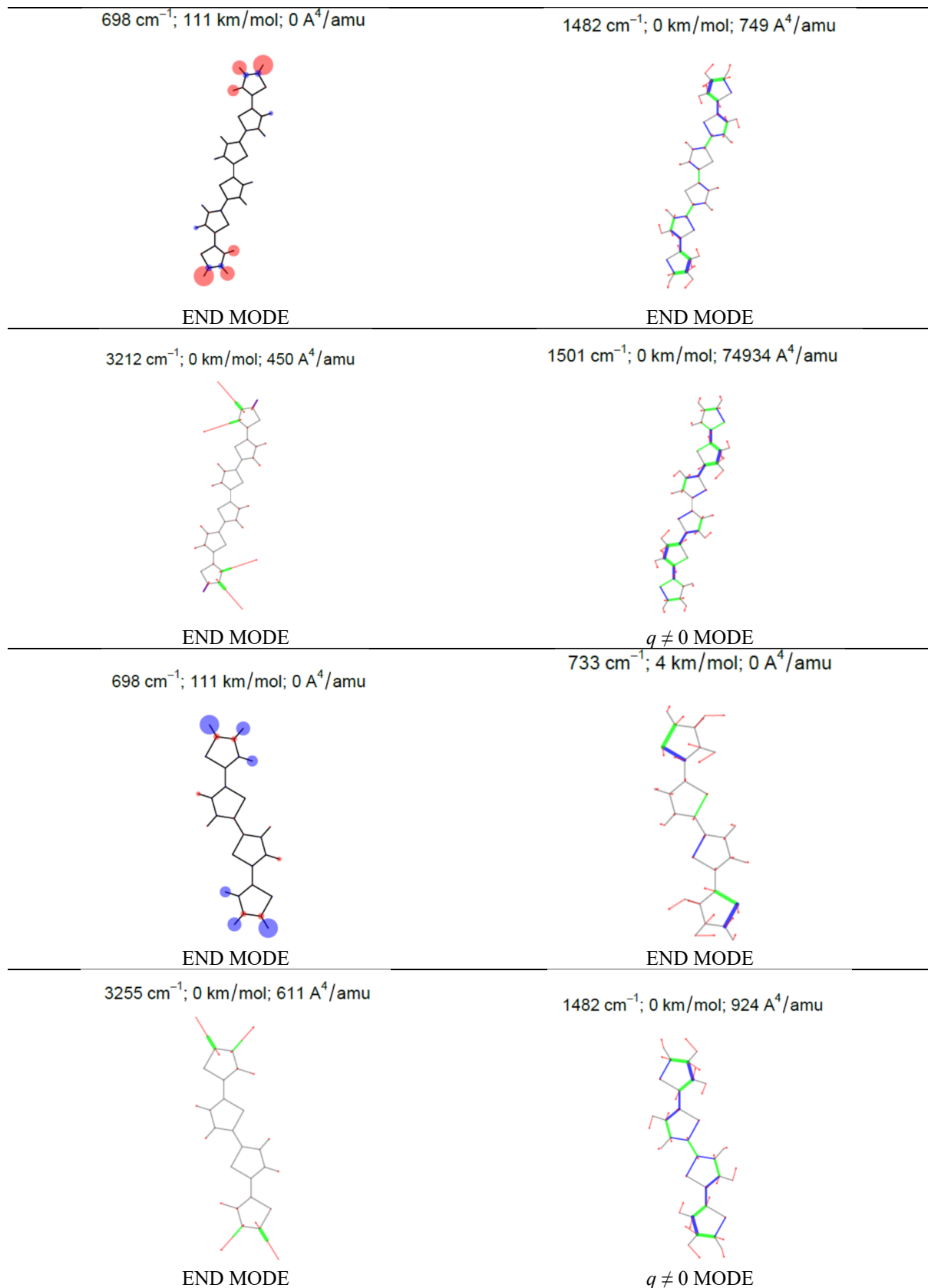


Figure S2. Examples of end modes and modes associated with $q \neq 0$ phonons of the 1D crystal, illustrated through vibrational eigenvectors of T6 and T4, calculated at the DFT B3LYP-V/POB-TZVP level (CRYSTAL code). Blue and green segments indicate bond stretching and contraction, respectively; the segment thickness is proportional to the contribution of each bond deformation to the vibrational eigenvector. Red arrows indicate the direction of atomic displacements within the normal mode. Out-of-plane atomic displacements are depicted as red and blue circles, whose radii are proportional to their magnitude. For each selected mode, the calculated wavenumber and IR or Raman intensity are reported.

Table S2. Wavenumbers and intensities of the most prominent IR and Raman bands of P3HT (1D crystal) and its 3HT8 oligomer. The values are obtained from DFT calculations (B3LYP-V/POB-TZVP) with the CRYSTAL code. The intensities of the 3HT8 oligomers are normalized to the number N of internal 3HT units, N = 3.

INFRARED				RAMAN			
P3HT		3HT8		PT		3HT8	
ν cm^{-1}	I km mol^{-1}	ν cm^{-1}	I km mol^{-1}	ν cm^{-1}	I $10^3 \text{ \AA}^4 \text{ amu}^{-1}$	ν cm^{-1}	I $10^3 \text{ \AA}^4 \text{ amu}^{-1}$
855	21	855	13	999	19	998	2
866	41	864–867–868	10	1043	30	1040	3
1407	91	1409	8	1108	93	1109	10
1467	515	1478	88	1206	92	1207	10
1550	247	1556	103	1407	742	1409–1410	64
3186	93	3186	38	1467	1799	1478	241

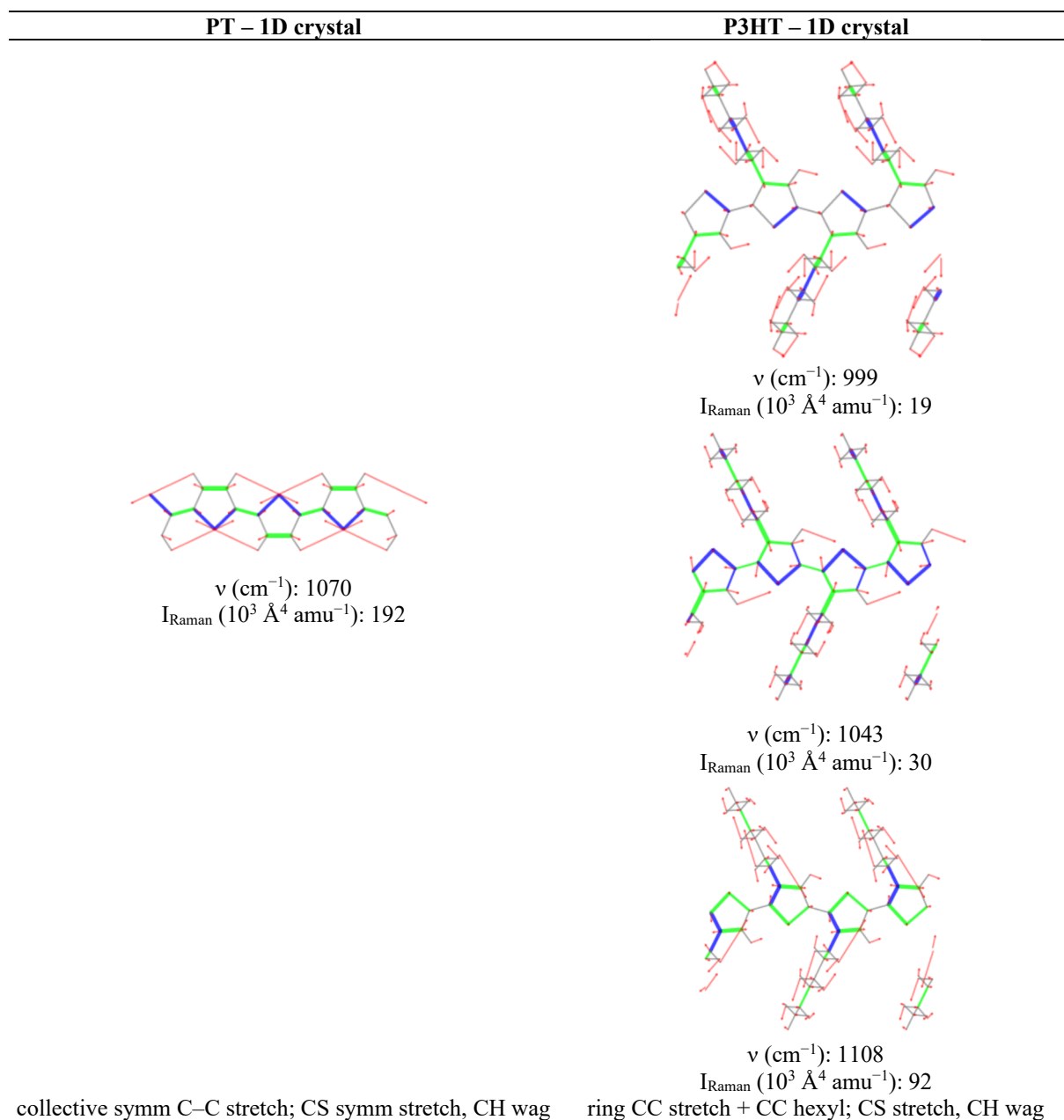


Figure S3. Cont.

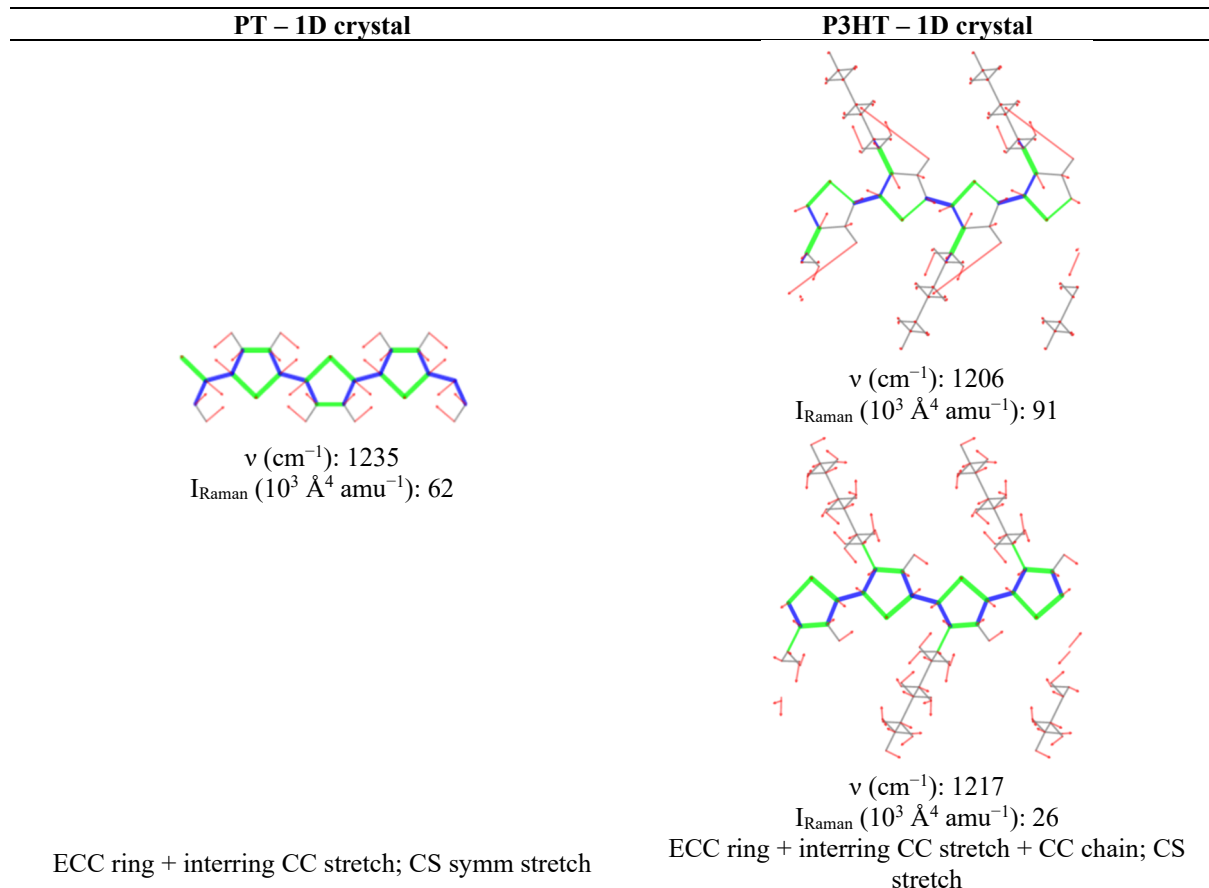


Figure S3. Raman modes of PT showing features shared with multiple P3HT modes (see manuscript). Sketches of the vibrational eigenvectors of PT and P3HT treated as 1D crystals. Blue and green segments indicate bond stretching and contraction, respectively; the segment thickness is proportional to the contribution of each bond deformation to the vibrational eigenvector. Red arrows represent the direction of atomic displacements within the normal mode. Out-of-plane atomic displacements are illustrated by red and blue circles, whose radii are proportional to the displacement magnitude. For each selected mode, the calculated wavenumber, Raman intensity and vibrational assignment are reported.

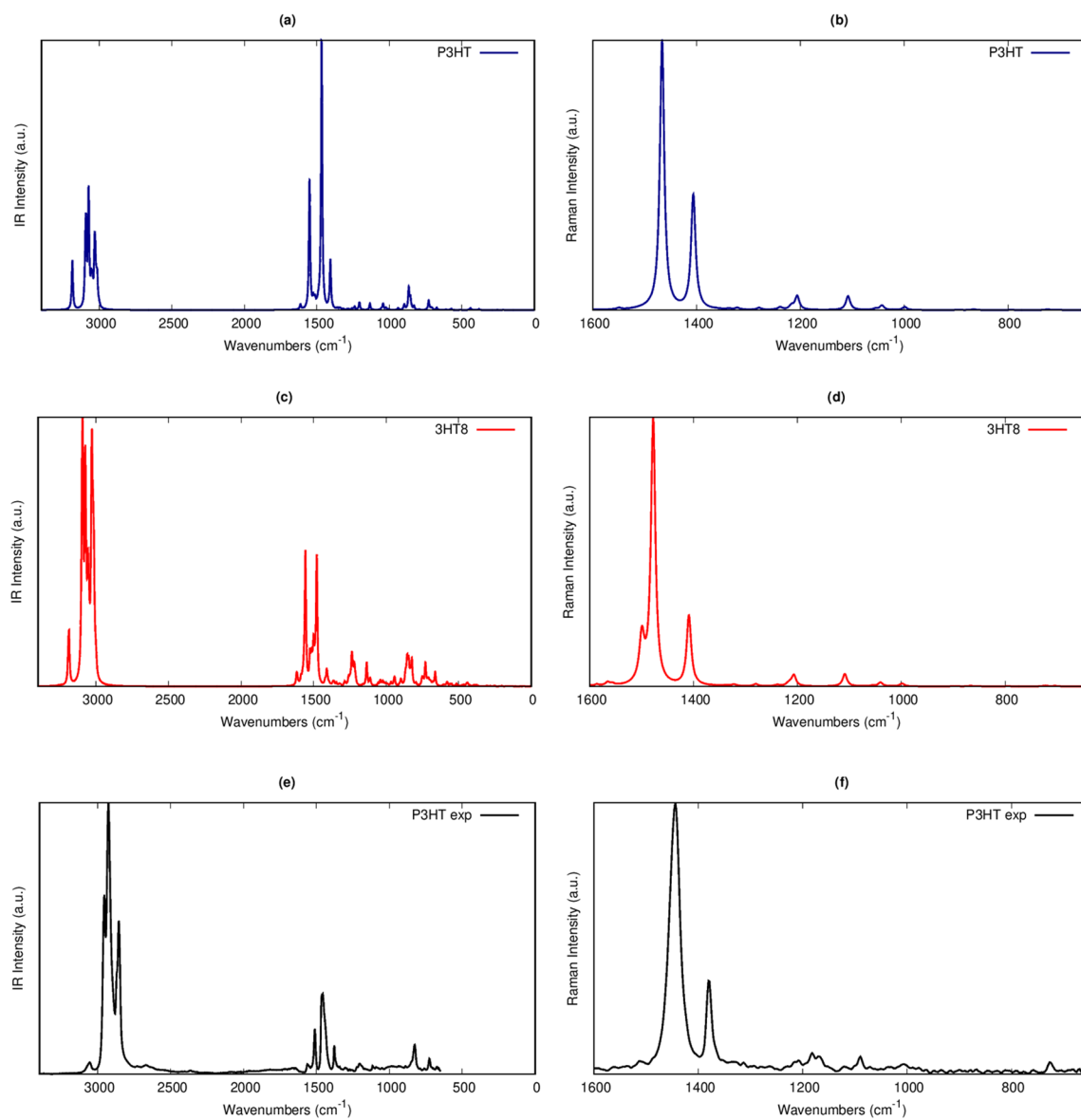


Figure S4. Calculated IR and Raman spectra for the 1D crystal model of P3HT (panels (a,b)) and for the 3HT8 molecule (panels (c,d)). Calculations were performed using the CRYSTAL code at DFT B3LYP-V/POB-TZVP level. Panels (e,f) report the experimental IR and Raman spectra of a solid sample of P3HT.