

Supporting Information

Insights into the Structural and Vibrational Properties of Polaron in Doped Poly(3-alkyl-thiophene), P3HT.

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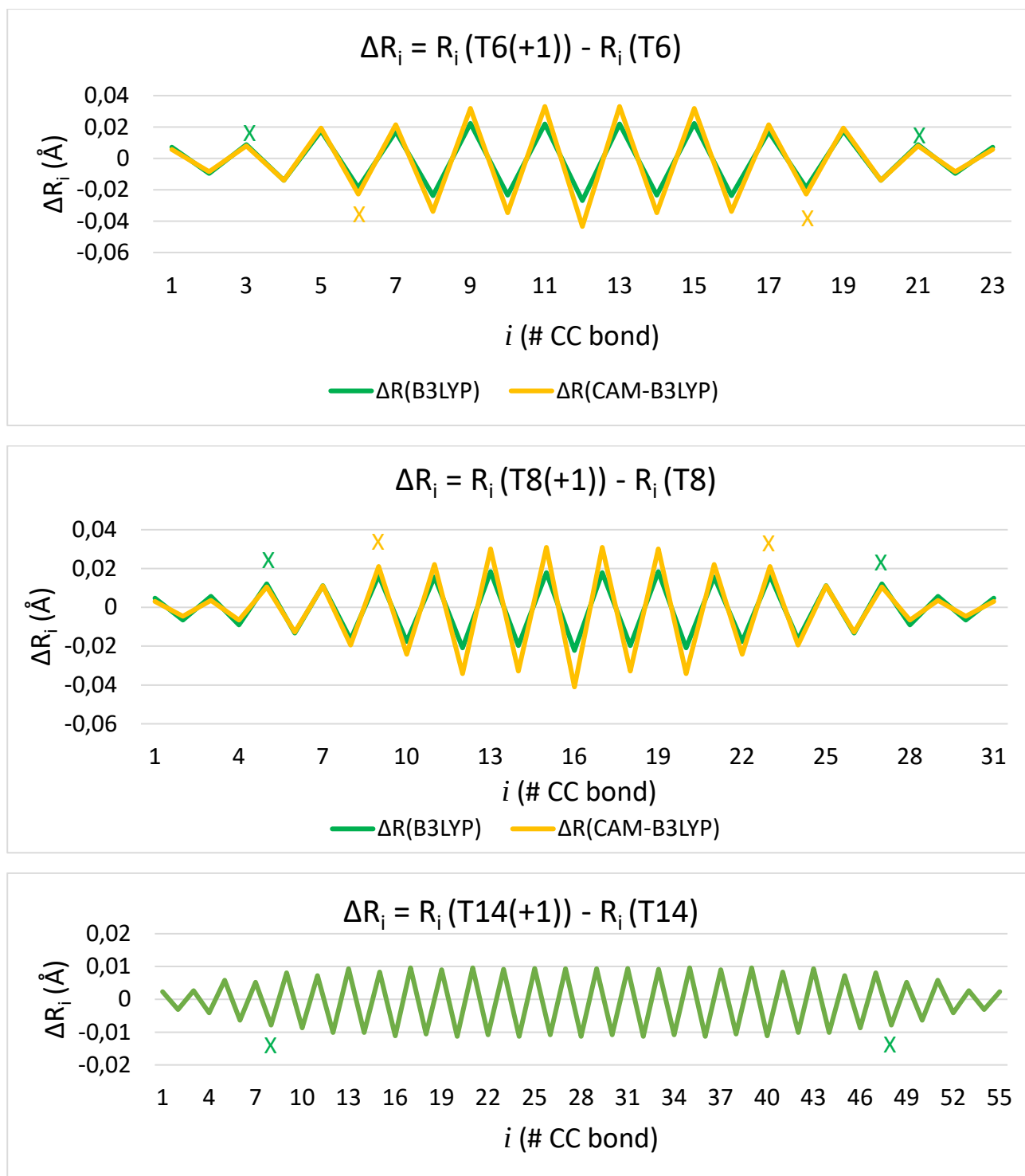


Figure S1. From the top to the bottom: bond length differences ΔR_i between the charged and the neutral species of T6/T6(+1), T8/T8(+1) calculated with both B3LYP and CAM-B3LYP functional and of T14/T14(+1) obtained only with B3LYP.

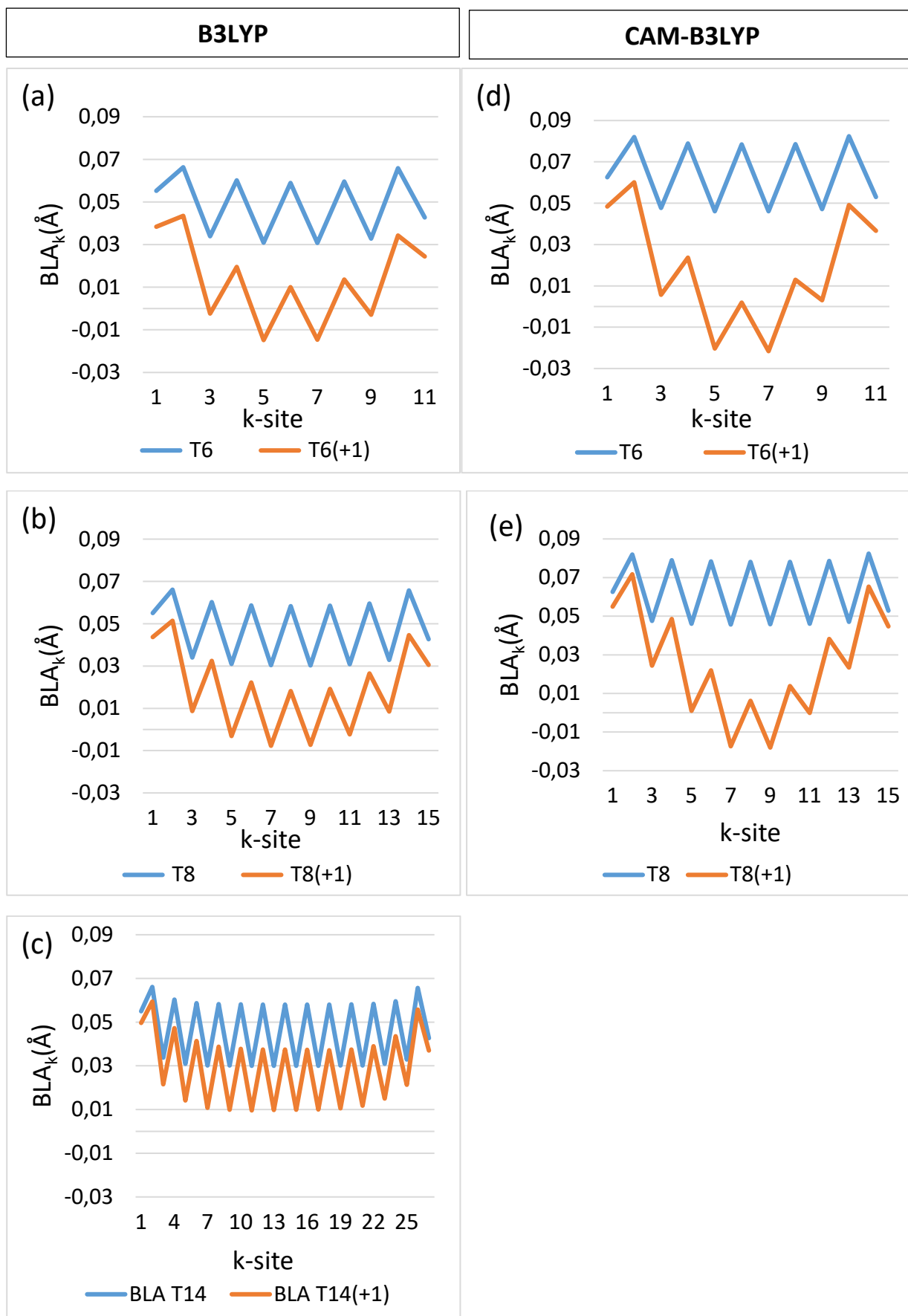


Figure S2. From the top to the bottom: Local Bond-Length-Alternation parameter (BLA_k) of T6/T6(+1), T8/T8(+1) and T14/T14(+1) calculated with B3LYP (left-side panels a.,b.,c.) and CAM-B3LYP (right-side panels d.,e.) functionals.

Table S1. Spatial extent of the polaron predicted by the geometry relaxation of T_n obtained with CAM-B3LYP. In brackets the corresponding B3LYP results.

Oligothiophene	Number of non-modified CC bonds before geometry relaxation (starting from one end)	Number of non-perturbed thiophene unit before geometry relaxation (starting from one end)	Polaron spatial extent
T6-T6(+1)	6 [3]	2 [1]	2 Th units + peripheral inter-ring bonds [4 Th units + peripheral inter-ring bonds]
T8-T8(+1)	8 [4]	2 [1]	4 Th units [6 Th units]
T12-T12(+1)	15 [5]	4 [1]	4 Th units + peripheral inter-ring bonds [10 Th units]
T14-T14(+1)	[7]	[2]	[10 Th units + peripheral inter-ring bonds]

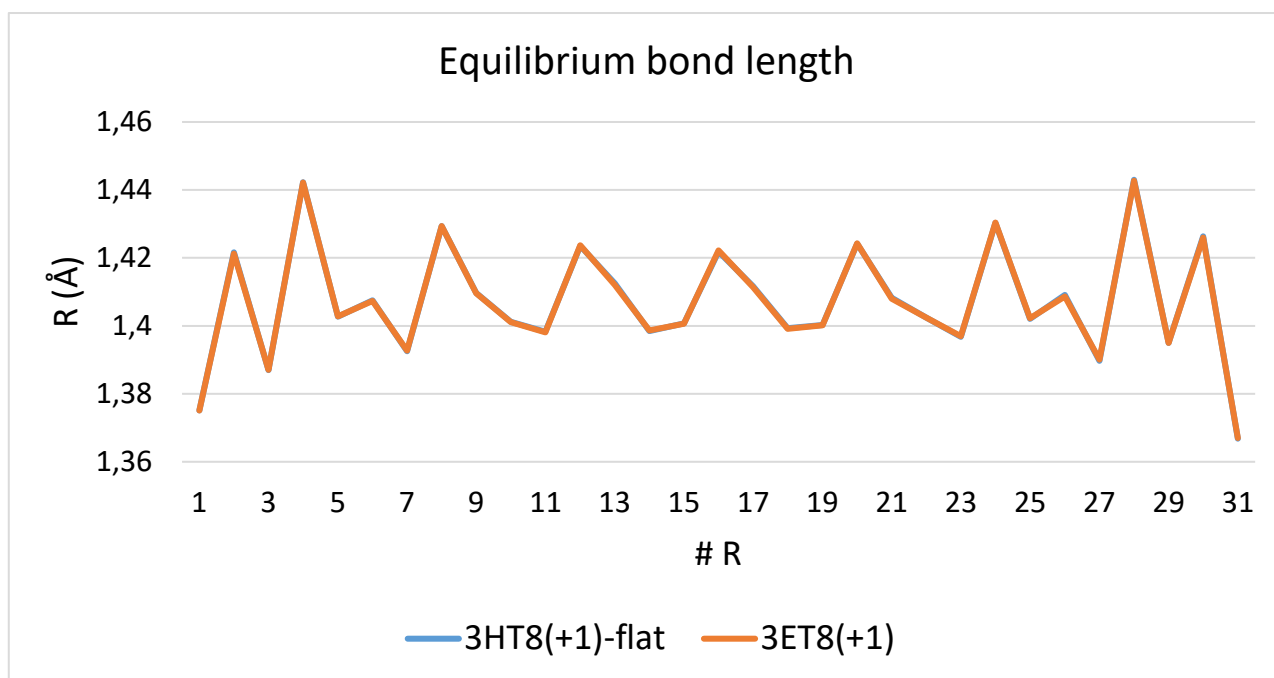


Figure S3. Equilibrium bond length values for the CC bonds of the backbone of 3HT8(+1) and 3ET8(+1).

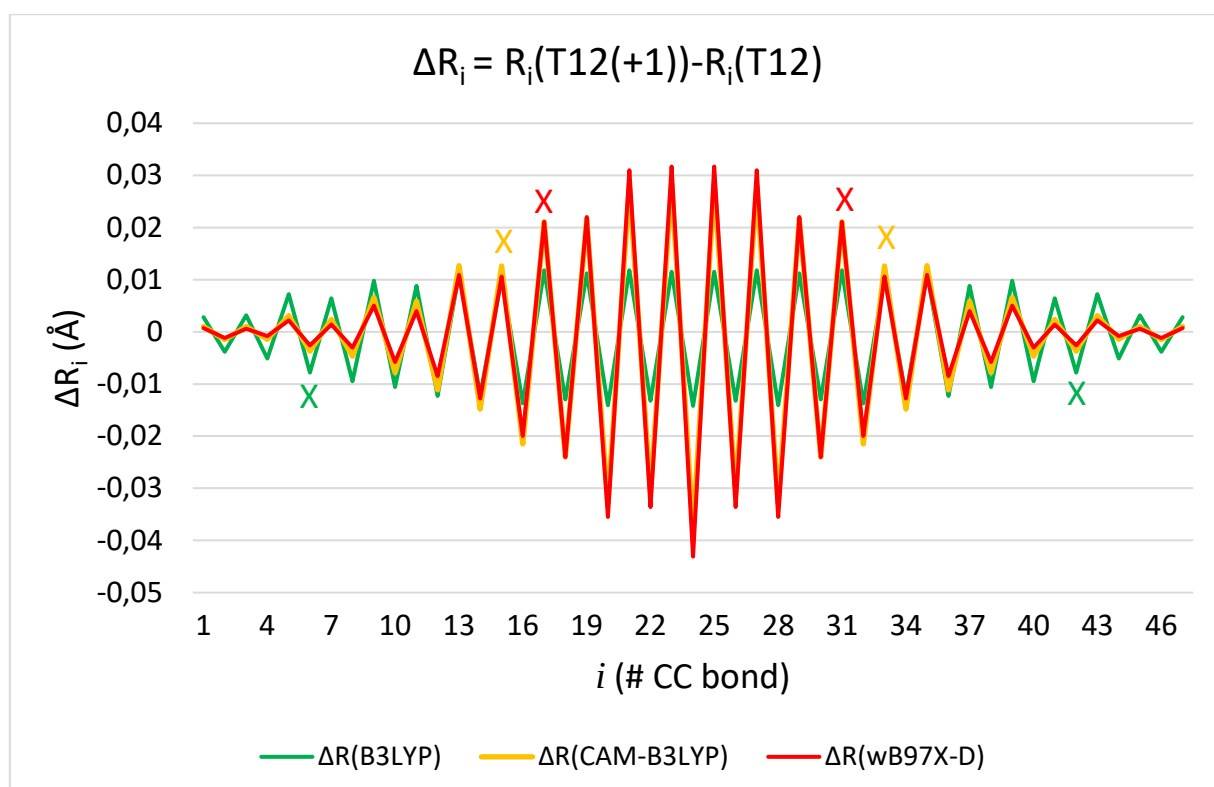
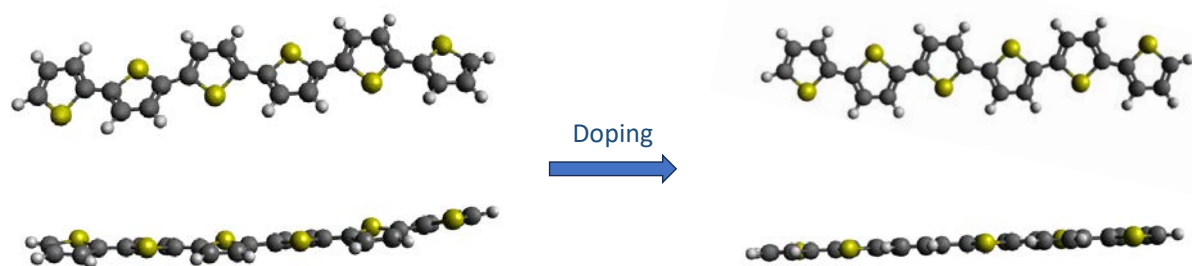


Figure S4. Bond length differences ΔR_i between the charged and the neutral species T12/T12(+1) calculated with B3LYP (green), CAM-B3LYP (yellow) and wb97X-D (red) functionals.

a.



b.

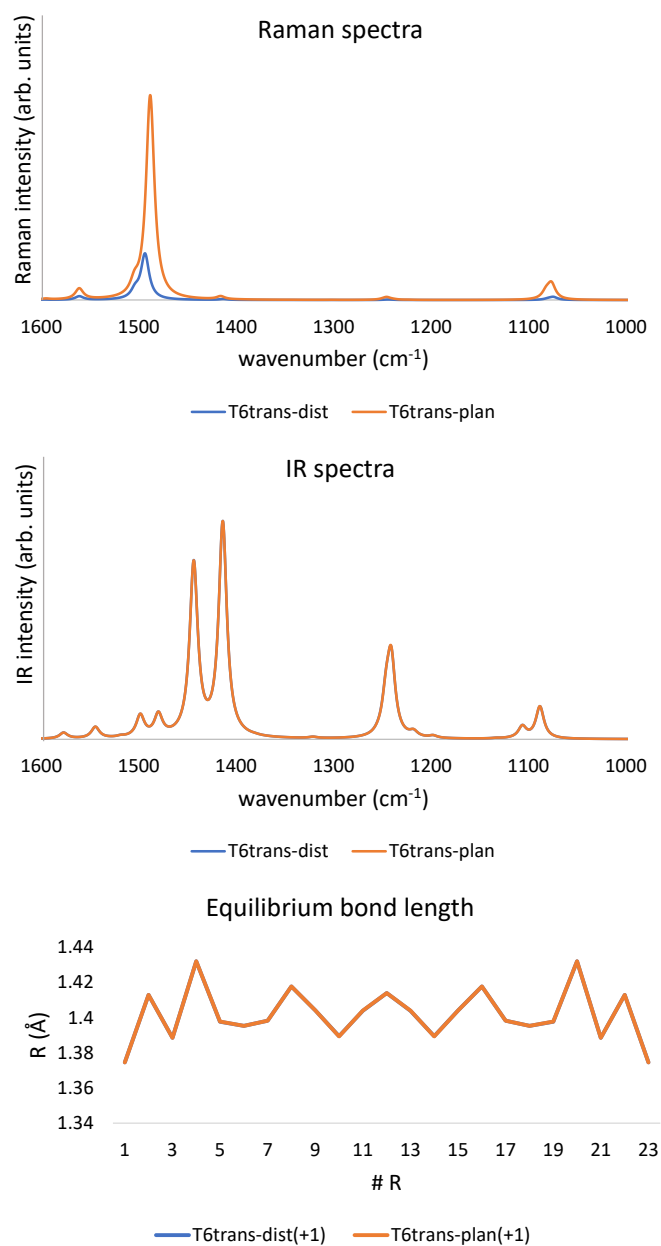


Figure S5. **a.** Sketch of the fully optimized (without any constraint) molecular geometry of a T6 oligothiophene in both the neutral state, showing a distorted structure, and charged state, showing a planar geometry. **b.** From the top to the bottom: comparison between the Raman spectrum of distorted and constrained planar T6, the IR spectrum and the geometry of distorted and constrained planar T6(+1).

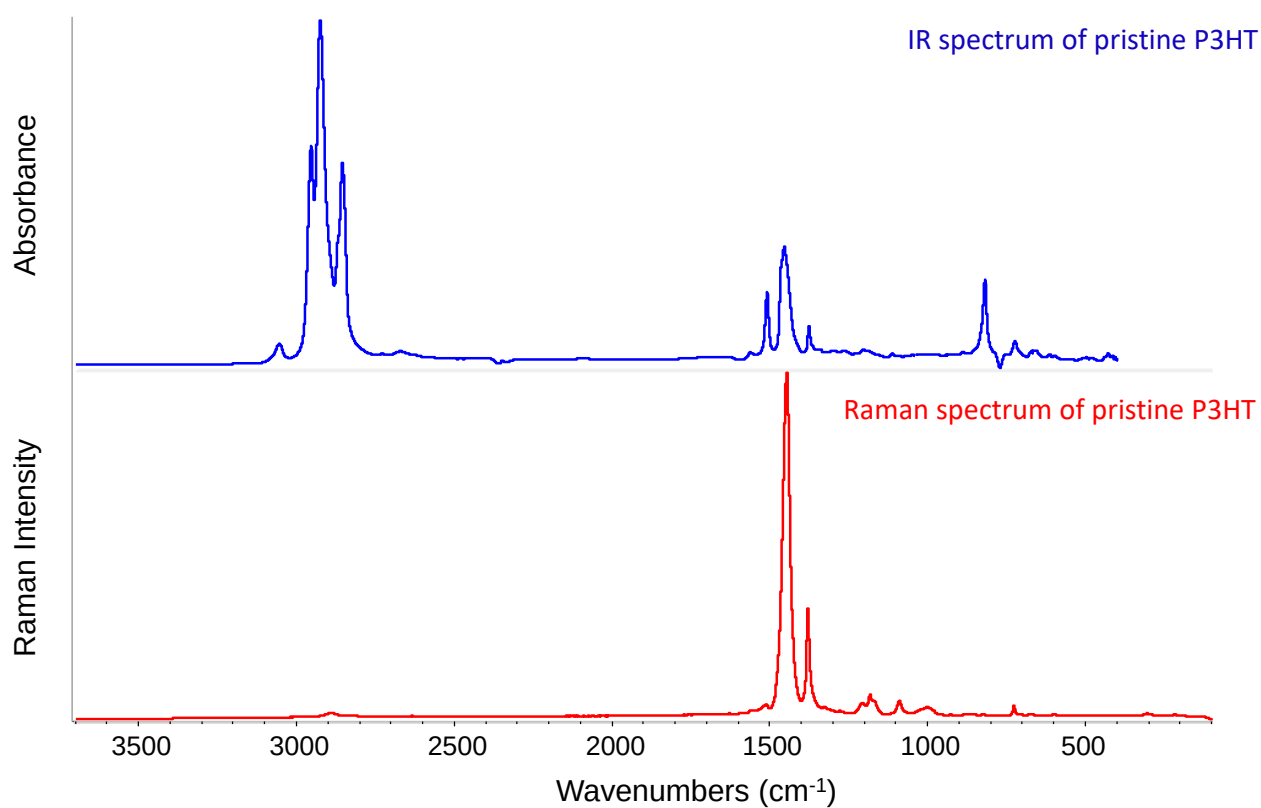


Figure S6. Experimental IR and Raman spectrum ($\lambda_{\text{exc}} = 1064 \text{ nm}$) of a sample P3HT (pristine, undoped film).

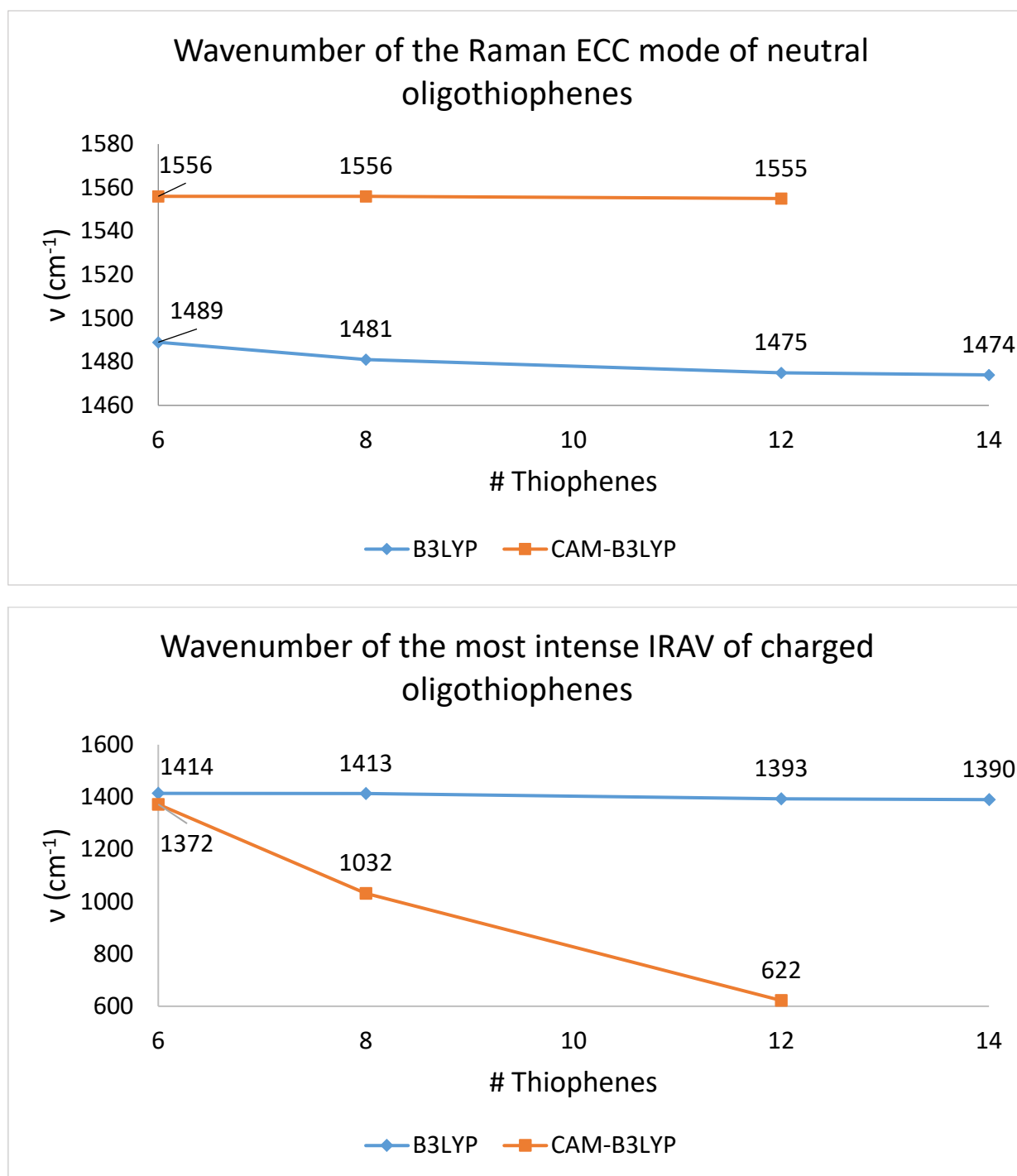


Figure S7. Top panel: frequency dispersion of the Raman ECC mode of neutral oligothiophenes with increasing chain length, from T6 to T14, calculated with both B3LYP and CAM-B3LYP. Bottom panel: frequency dispersion of the most intense IR mode of charged oligothiophenes with increasing chain length, from T6 to T14, calculated with both B3LYP and CAM-B3LYP.

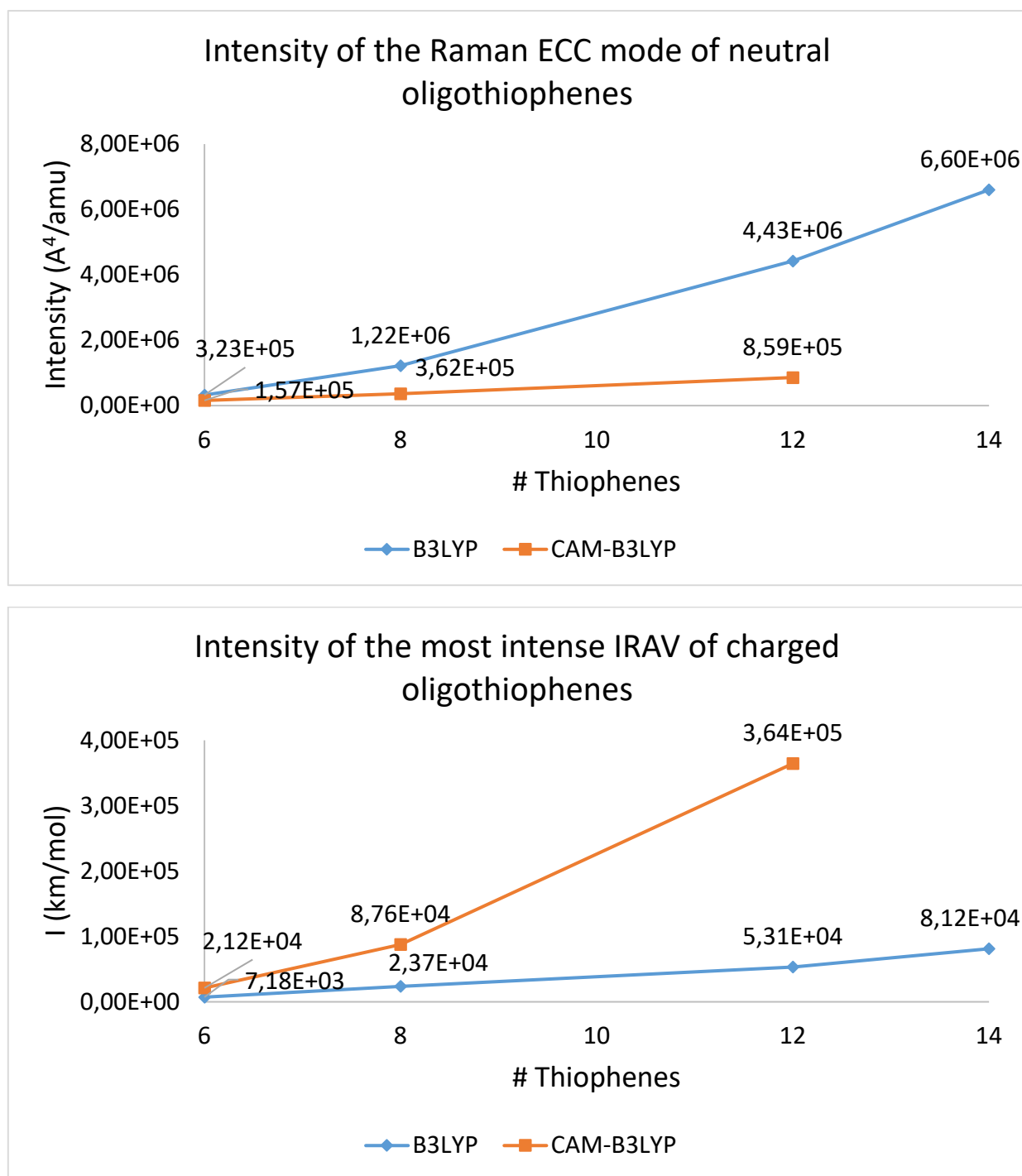


Figure S8. Top panel: intensity of the Raman ECC mode of neutral oligothiophenes with increasing chain length, from T6 to T14, calculated with both B3LYP and CAM-B3LYP. Bottom panel: intensity of the most intense IR mode of charged oligothiophenes with increasing chain length, from T6 to T14, calculated with both B3LYP and CAM-B3LYP.

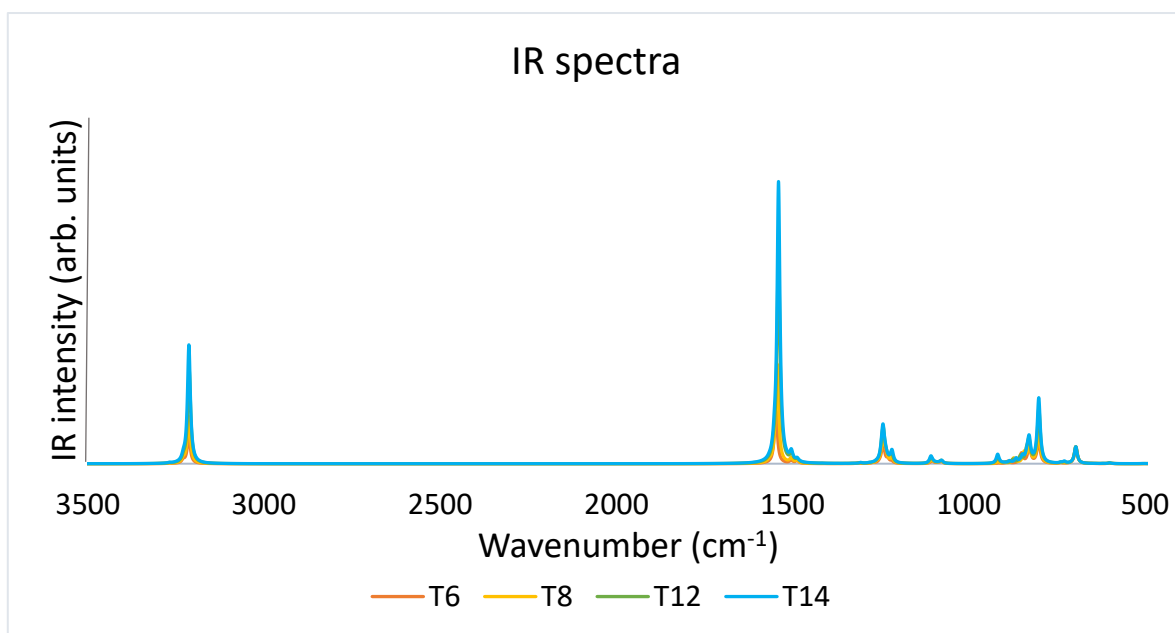
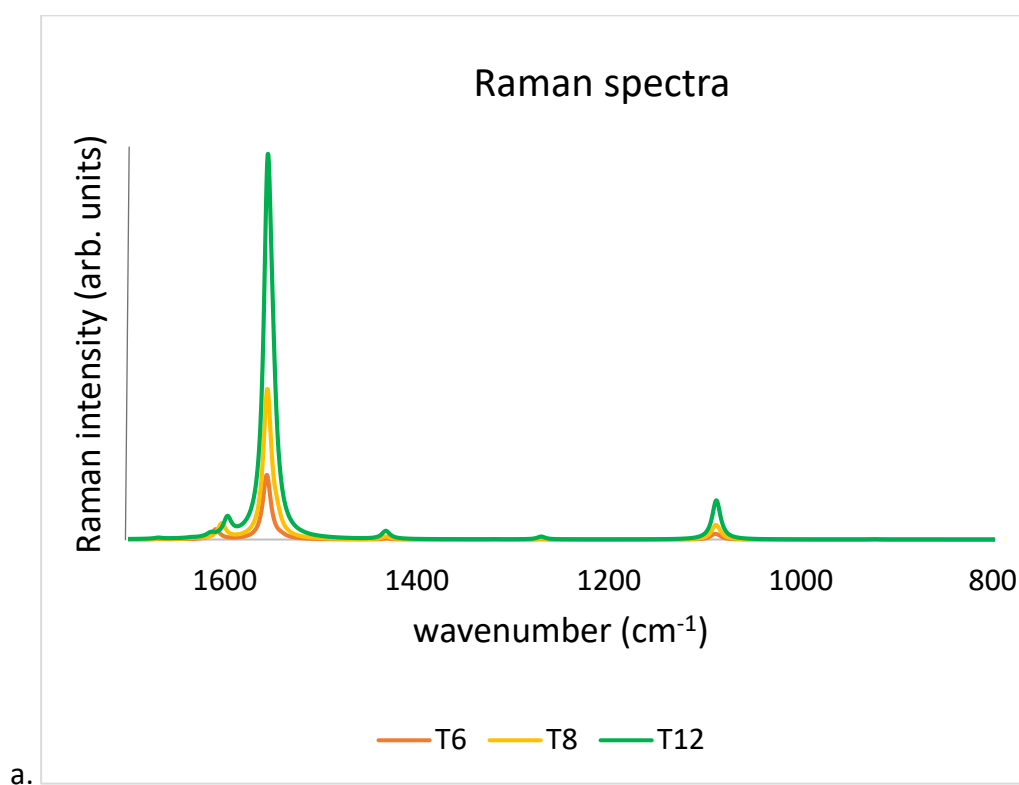


Figure S9. B3LYP calculated IR spectra of neutral oligothiophenes with increasing chain length, from 6 to 14 thiophene units.



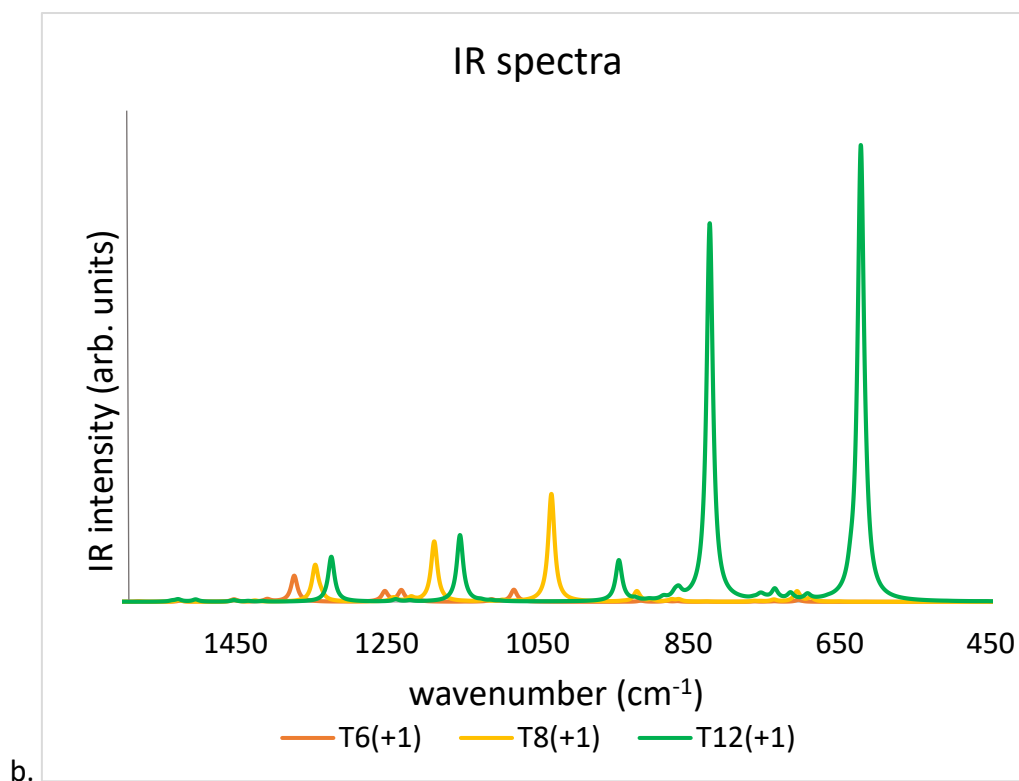


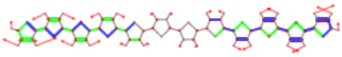
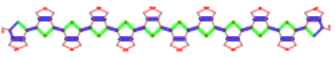
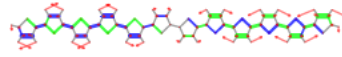
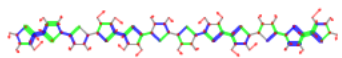
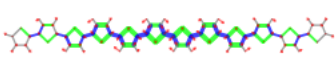
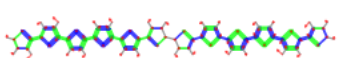
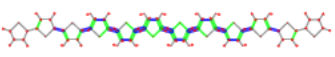
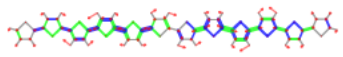
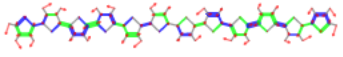
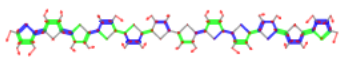
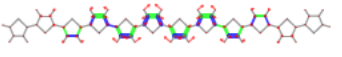
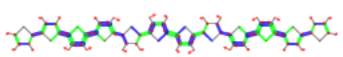
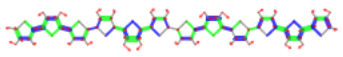
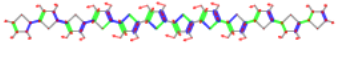
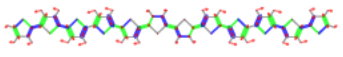
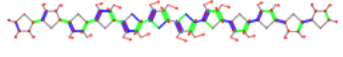
Figure S10. CAM-B3LYP-calculated vibrational spectra of oligothiophenes with increasing chain length, from six to twelve thiophene units: (a.) Raman spectra of T_n oligomers and (b.) IR spectra of T_n(+1) oligomers.

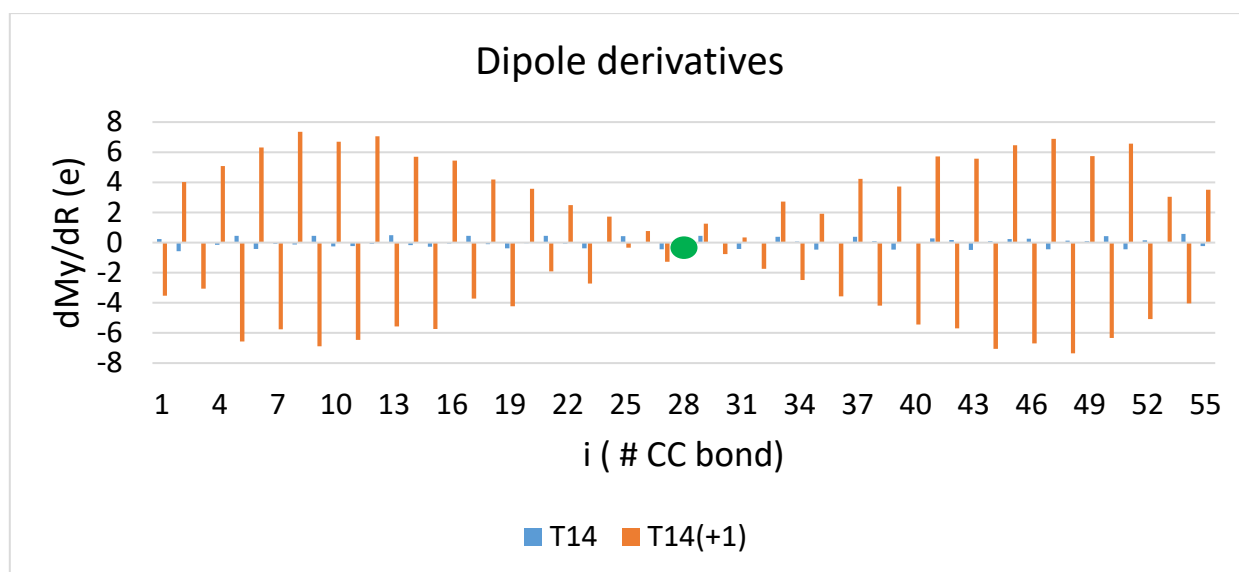
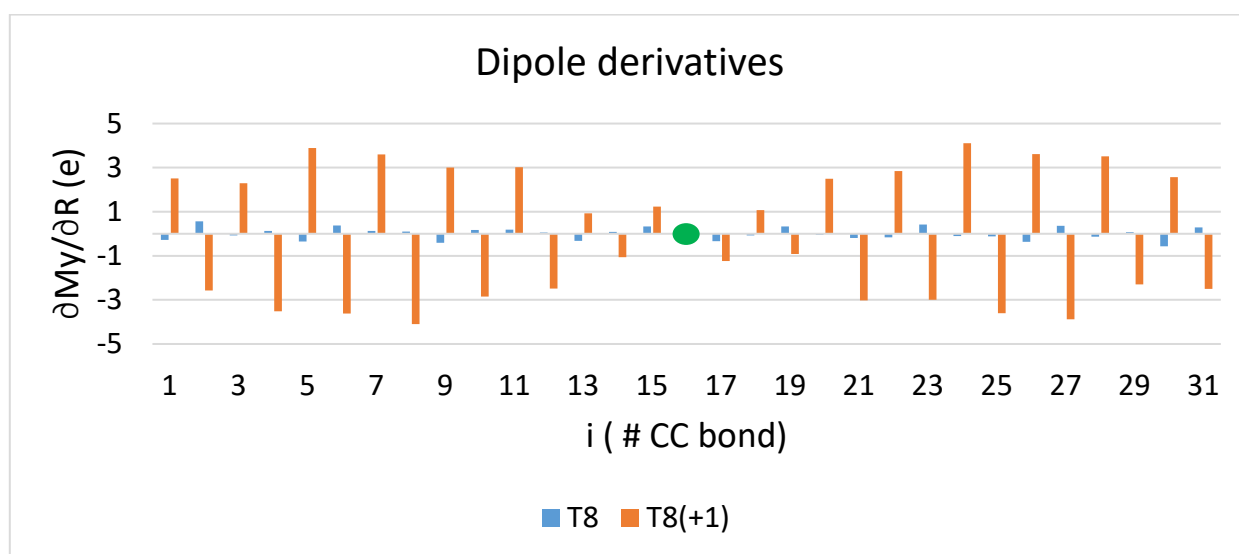
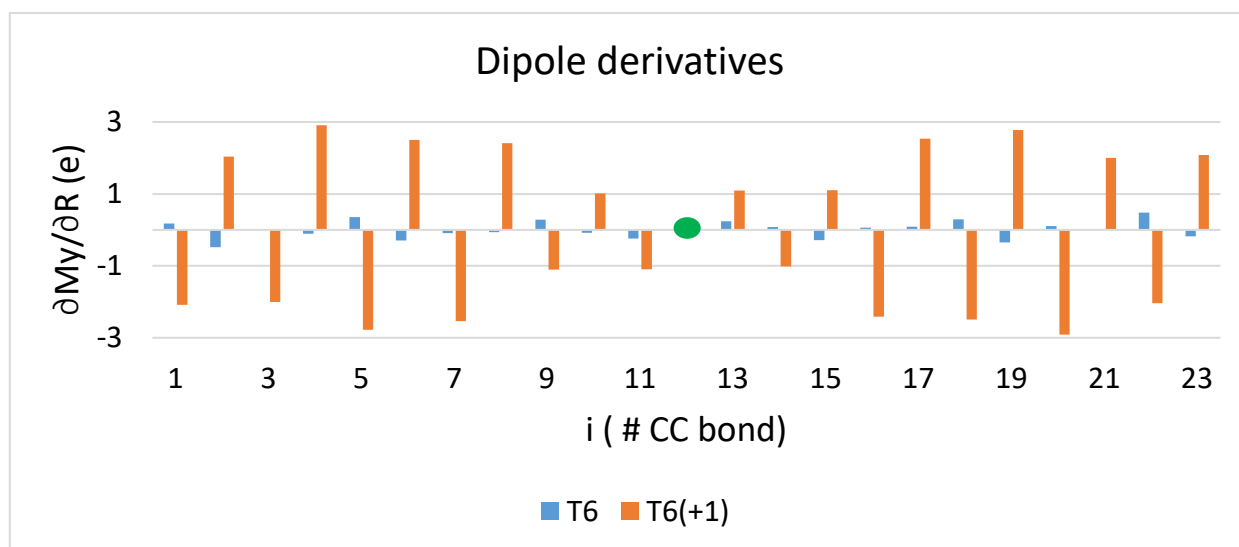
Table S2. DFT (B3LYP/6-311G**) computed IR and Raman vibrational frequencies (unscaled) and band intensities of T12, and computed IR frequencies (unscaled) and intensities of T12(+1). The data are selected considering the intensity of the vibrational transitions: $I_k \geq \frac{I^{MAX}}{100}$, I^{MAX} being the largest band intensity value (in *italics*, boldface). Boldface characters highlight bands with $I_k \geq \frac{I^{MAX}}{10}$. Data relative to transitions which show some correlation (frequency values and/or vibrational eigenvector in different spectra), are reported on the same line. Modes showing a localized character - typically ends modes – are explicitly indicated. The label sy (for symmetric) and a-sy (for anti-symmetric) refers to the phase of the stretching of internal vibrational coordinates which form a pair belonging to the same ring. The labels (a-e), last column, identify strong IR bands, highlighted in the spectrum in Figure 6.

T12						T12 (+1)		
IR spectrum - B3LYP			Raman spectrum - B3LYP			IR spectrum - B3LYP		
ν_k	I_k	assignment	ν_k	I_k	assignment	ν_k	I_k	assignment
cm ⁻¹	km mol ⁻¹		cm ⁻¹	10 ³ Å ⁴ amu ⁻¹		cm ⁻¹	km mol ⁻¹	
697	106	CH opla - ends				309	834	CS str, C-C str
			706	32	sy CS str	701	2671	CS str, C-C str
801	207	CH opla						
802	95	CH opla						
803	47	CH opla						
827	15	CH opla - ends						
830	124	sy CS str						
837	53	sy CS str				841	695	sy CS str

854	42	sy CS str				857	578	sy CS str
875	22	CS str						
918	39	a-sy CS str				911	660	a-sy CS str
1077	15	CC-str,sy CS str	1077	310	CC-str , sy CS str	1078	16022	CC-str , sy CS str (e)
1108	34	C-C str (ring)	1079	64	C-C str, sy CS str	1086	1787	C-C str, sy CS str
1220	57	a-sy CS str, a-sy C=C str ring				1210	525	a-sy C=C str, a-sy CS str
1234	32	a-sy CS, C-C str ring, inter-ring				1214	4058	a-sy C=C str,(C-C)
1243	160	<i>a-sy CS str, C-C str ring, inter-ring</i>	1246	100	ECC ring, interrering CC str - out of phase	1227	41725	ECC ring, interrering CC str out of phase (d)
1246	66	sy CS str, C-C str ring, inter-ring				1231	2033	a-sy C=C str,(C-C interrering), CS str
1248	25	CS str, C-C str ring, inter-ring						
			1419	158	CC str ring (CC str interrering)			
			1475	4427	ECC	1393	53123	ECC (c)
						1394	11487	local ECC (c)
						1417	9894	local ECC (b)
						1436	1122	CC str ring (CC str interrering - out of phase)
1487	19	CC str ring, ends						
1503	35	ECC, nodes	1491	194	ECC, 2 nodes	1457	16789	ECC, 3 nodes (a)
			1500	41	ECC, nodes	1494	610	ECC, nodes
1504	15	CC str ring, ends	1504	35	ECC, ends			
1540	1375	a-sy C=C str	1547	48	a-sy C=C str	1510	1153	a-sy C=C str
1555	51	a-sy C=C str				1552	543	a-sy C=C str
3212	327	a-sy CH str						
3212	214	a-sy CH str						
3212	18	a-sy CH str						
3214	39	a-sy CH str, ends						
3229	18	a-sy CH str, ends						

Table S3. DFT (B3LYP/6-311G**) computed vibrational eigenvectors associated to the most intense IR active normal modes of T12 and T12(+1), and to the most intense Raman active modes of T12. Computed (unscaled) wavenumbers and intensities are also reported. Blue/green lines sketch bond stretching/shrinking. Red arrows are associated to the C-H vibrations.

T12 - IR	T12 - RAMAN	T12(+1) - IR
 1077 cm ⁻¹ ; 15 km mol ⁻¹	 1077 cm ⁻¹ ; 310 x10 ³ A ⁴ amu ⁻¹	 1078 cm ⁻¹ ; 16022 km mol ⁻¹
 1243 cm ⁻¹ ; 160 km mol ⁻¹	 1246 cm ⁻¹ ; 101 x10 ³ A ⁴ amu ⁻¹	 1227 cm ⁻¹ ; 41725 km mol ⁻¹
	 (ECC) 1475 cm⁻¹; 4426 x10³ A⁴ amu⁻¹	 1393 cm⁻¹; 53123 km mol⁻¹
		 1394 cm⁻¹; 11487 km mol⁻¹
		 1417 cm⁻¹; 9894 km mol⁻¹
 1503 cm ⁻¹ ; 35 km mol ⁻¹	 1491 cm ⁻¹ ; 195 x10 ³ A ⁴ amu ⁻¹	 1457 cm⁻¹; 16789 km mol⁻¹
 1540 cm ⁻¹ ; 1375 km mol ⁻¹	 1547 cm ⁻¹ ; 47 x10 ³ A ⁴ amu ⁻¹	 1510 cm ⁻¹ ; 1153 km mol ⁻¹



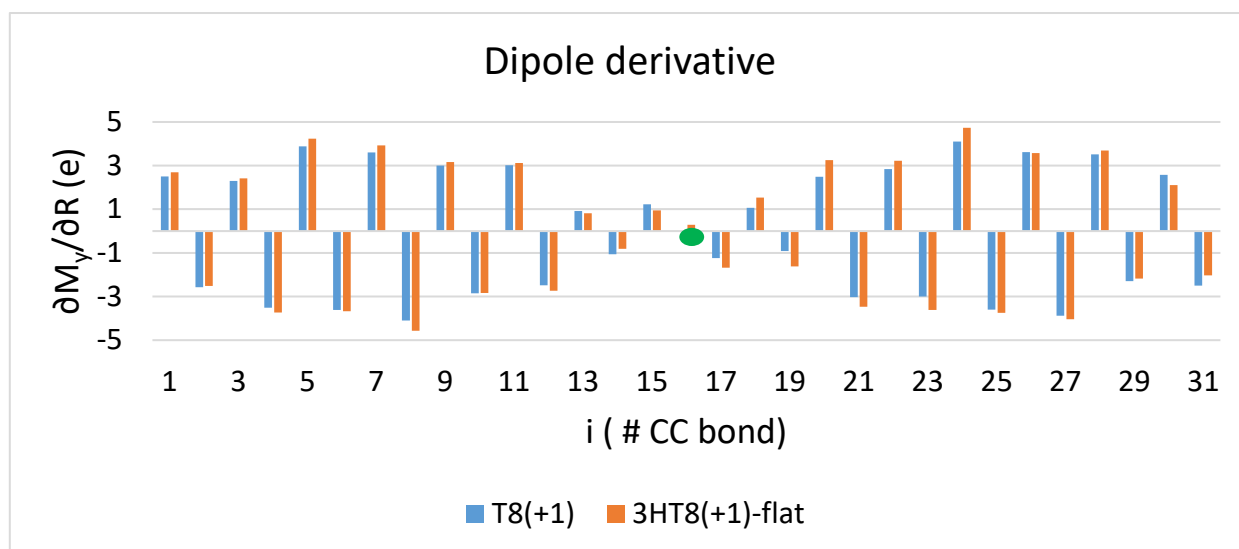


Figure S11. B3LYP-calculated dipole derivatives with respect to individual CC stretchings ($\frac{\partial M_y}{\partial R_i}$) – the y axis is parallel to the chain axis - of neutral and charged oligothiophenes, from T6 (top panel) to T14 (bottom panel).

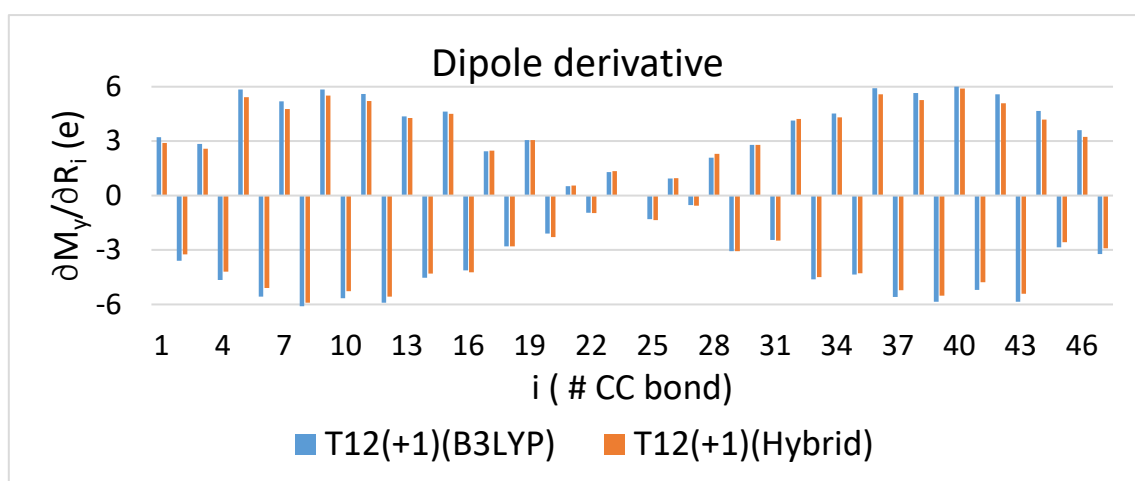


Figure S12. $\partial M_y / \partial R_i$ of T12(+1), calculated with B3LYP and the hybrid approach.

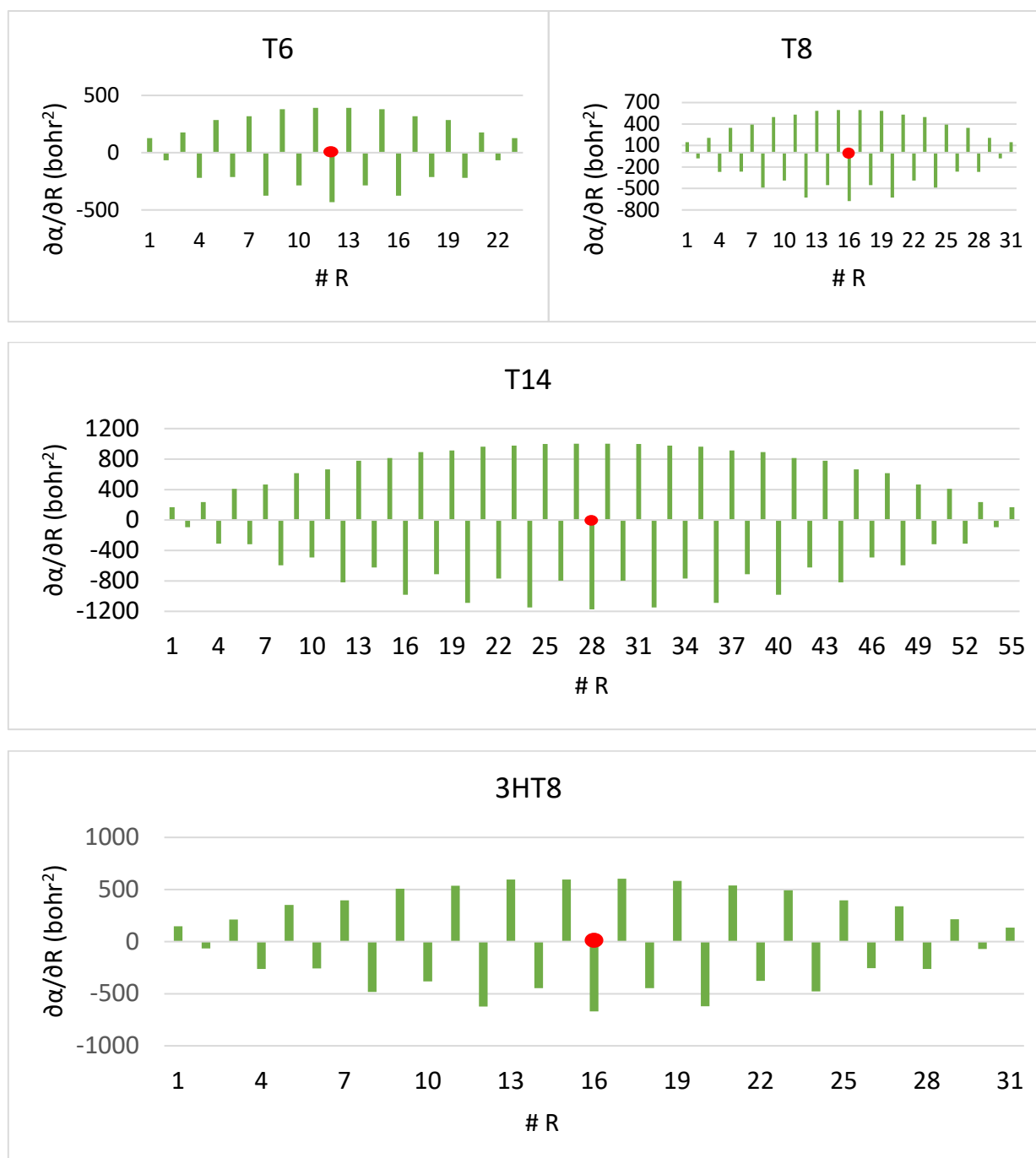


Figure S13. Calculated polarizability derivatives with respect to individual CC stretchings $\frac{\partial\alpha}{\partial R_i} = \text{trace} \left(\frac{\partial\alpha}{\partial R_i} \right)$ for the T6, T8, T14 and 3HT8 molecular models.

Table S4. Sketches of the vibrational eigenvectors associated to the strongest IRAV band of T12(+1) (ECC mode) and of the two IRAV bands of 3ET12(+1) showing a similar ECC-like displacements pattern of the backbone, coupled - with the opposite phase in the two modes - to the CC stretching of the alkyl chain. Sketches of the vibrational eigenvectors associated to the strongest Raman band of T12 (ECC mode) and of the two Raman bands of ET12, showing a similar ECC-like displacements pattern of the backbone, coupled - with the opposite phase in the two modes - to the CC stretching of the alkyl chain.

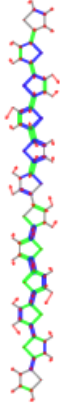
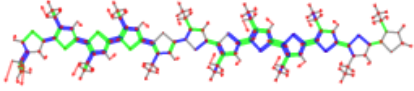
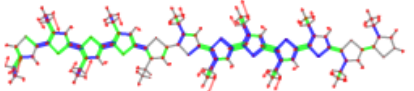
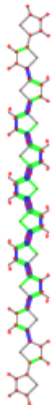
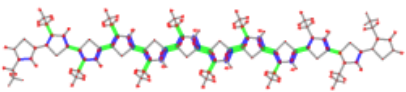
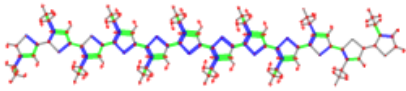
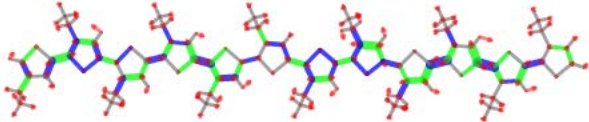
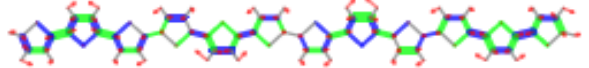
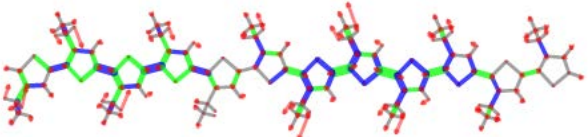
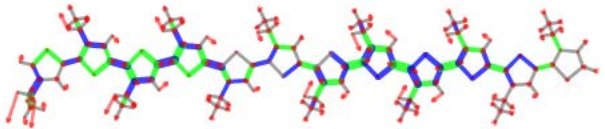
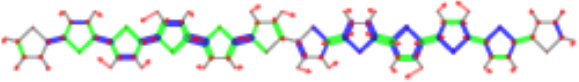
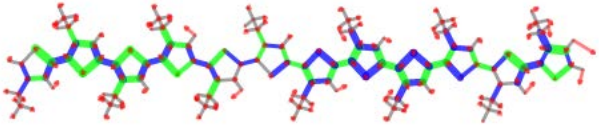
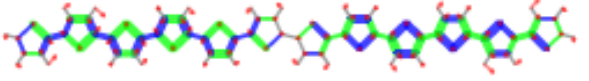
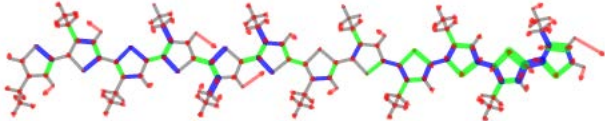
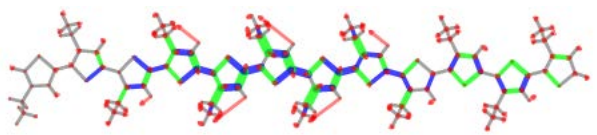
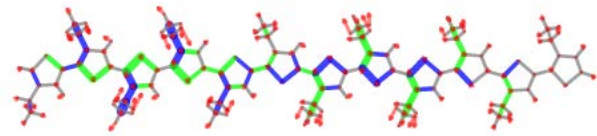
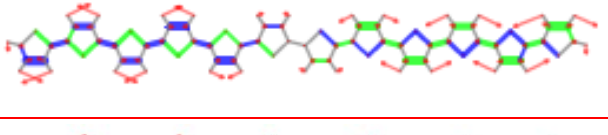
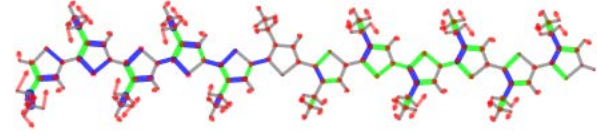
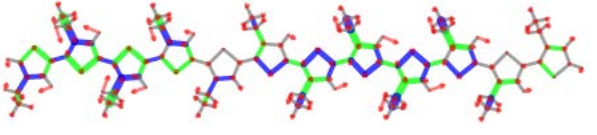
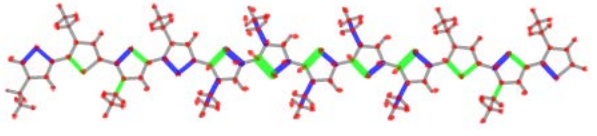
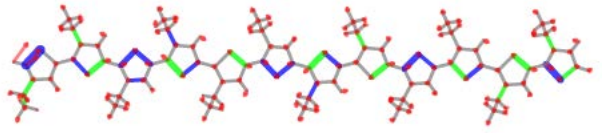
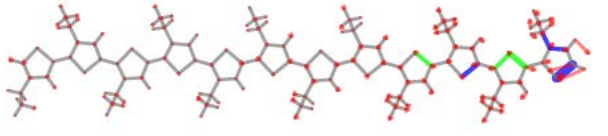
T12(+1)	3ET12(+1)
1393 cm^{-1}; 53123 km/mol; 0 A^4/amu 	1364 cm^{-1}; 33872 km/mol; 2659519 A^4/amu  1352 cm^{-1}; 30399 km/mol; 4495286 A^4/amu 
T12	3ET12
1475 cm^{-1}; 0 km/mol; 4426514 A^4/amu 	1465 cm^{-1}; 906 km/mol; 3255699 A^4/amu  1414 cm^{-1}; 67 km/mol; 1074969 A^4/amu 

Table S5. Comparison between the experimental (P3HT) and the DFT (3ET12(+1)) computed IRAV bands (values after scaling and before scaling - in squared brackets - are reported). DFT IR intensities and sketches of the vibrational eigenvectors. For some IRAVs of 3ET12(+1), we added in the table – subsequent row, grey background – the predicted wavenumbers, IR intensity and eigenvector of the mode of the non-substituted T12(+1) model showing similar vibrational displacements and wavenumber. The first column in Table 4 reports the bands labelling (1-9) adopted in Figure 11. The symbols (i) and (ii) are introduced to indicate the presence of two strong IRAV transitions, close in frequency, which can be associated to a structured band with distinguishable peaks or shoulders in the experimental spectrum. The labels a, b, c, d, e, are the same adopted in Table 2 (last column) and Figure 6.

#	ν (cm ⁻¹) exp	ν (cm ⁻¹) theory	I (Km mol ⁻¹) theory	Vibrational eigenvector
1	1395	1413 [1450]	11134	
a		1419 [1457]	16789	
2(i)	1333	1317 [1352]	30399	
2(ii)	1307	1329 [1364]	33872	
c		1357 [1393]	53123	
3(i)	1197	1201 [1233]	8510	
d		1195 [1227]	41725	
3(ii)	1188	1194 [1226]	8210	

4	1148	1178 [1209]	5113	
5(i)	1077	1062 [1090]	3992	
e		1050 [1078]	16022	
5(ii)	1047	1047 [1075]	7349	
6	979	1010 [1037]	5280	
7(i)	861	840 [862]	1119	
7(ii)	853	836 [858]	1038	
8	825	812 [834]	1025	
9	717	701 [720]	772	