Supplemental Material

Electron-phonon coupling and mobility modeling in organic semiconductors: method and application to tetracene polymorphs

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Contents

A – Vibrational frequencies in the lattice modes range for P1 with the symmetry assignment, and comparison with the experimental values from ref. [53] of the main text

Table S1: Vibrational Frequencies and symmetry assignment for P1 lattice phonon. Values in red are above the lattice mode range and they are reported only for comparison with experiments.

Symmetry	Freq. calc. [cm^{-1}]	Freq. exp. [cm^{-1}]
Au	33.2	
Ag	45.3	42.3
Ag	48.7	47.8
Ag	60.5	58.5
Au	66.5	
Au	69.4	
Ag	86.2	88.4
Au	98.4	
Au	103.4	
Ag	117.4	117.1
Ag	128.6	129.8
Au	136.1	
Au	144.5	
Ag	164.4	
Au	164.6	
Ag	168.2	168.2
Au	169.3	
Ag	208.3	211.2
Ag	213.5	217.0

B – EPC values

Tables with modes frequency in the different points of the BZ and EPC values are reported. The average atom displacements are around 5.9×10^{-4} Å for the inter-molecular mode and around 5.8×10^{-4} Å for the intra-molecular modes. The order of the bands is referred to the edge at the gap; the 1st VB is the one with the highest maximum whereas the 1st CB is the one with the lowest minimum.

Thus, for the tetracene polymorph P1, about the inter-molecular modes, which are the lowest 16 modes mostly involved in the charge transport limitations, the frequency values are reported in Table S2, the EPC values for the VB are listed in Tables S3 (intra-band in the topmost VB) S4 (intra-band in the lower VB), and S4 (inter-band), and for the CB in Tables S6 (intra-band in the lowest CB), S7 (intra-band in the upper CB), and S8 (inter-band). We also report the EPC for the intra-molecular modes up to 400 cm^{-1}. The frequency are listed in Table S9, the EPC values for the VB are reported in Tables S9, S11 and S12 and for the CB in S12, S13, and S15, in the same way of the inter-molecular: two tables for the intra-band (one for each band) and a table for the inter-band EPC.

In a similar way, for the thin film polymorph, we report in Table S16 the mode and $\boldsymbol{q}$-point specific frequencies for the inter-molecular modes, in Tables S17, S18, and S19 the EPC values for the VB for the

intra-band processes of the topmost VB, the lower VB, and the inter-band processes, respectively, and in Tables S20, S21, and S22 the EPC values for the CB for the intra-band processes of the lowest CB, the other CB, and the inter-band processes, respectively. Then, we report the same information for the intra-molecular modes up to 400 cm^{-1}: the frequency values are listed in Table S23, the EPC values for intra-band and inter-band processes for the VB are reported in Tables S24, S25, and S26, while Table S27 and S28 contain the EPC for the intra-band processes of the two CB and Table 28 reports the inter-band EPC values for the CB.

In Table S29, the mode and $\boldsymbol{q}$-point pairs with the highest EPC values are highlighted in green. These are the Brillouin Zone points and modes which have the most impact on the hole transport in the P1 polymorph.

We report the EPC values DOS-weighted averaged across the Brillouin Zone (BZ) in Tables S30 and S31 for P1 and PF polymorphs, respectively.

The codes used to evaluate the EPC can be found at https://github.com/PatrizioGraziosi/EPHOS.

Tetracene – P1

Inter-molecular modes

Table S2: frequencies in cm^{-1}

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
-0.25	18.18	28.89	33.96	24.76	26.1	22.91	31.59
-0.16	21.79	34.2	42.45	28.44	29.36	22.99	38.66
0.17	23.36	36.62	44.57	48.19	46.56	37.07	40.96
33.18	24.43	41	51.78	49.89	52.9	47.75	45.36
45.35	31.61	48.12	56.74	50.01	56.22	47.78	53.85
48.74	41.47	53.45	60.3	54.75	59.3	51.55	57.52
60.46	59.37	56.73	61.69	75.48	64.11	62.26	70.96
66.47	63.77	59.49	69.11	76.71	66.78	62.94	80.31
69.35	89.83	73.88	72.53	85.13	78.88	66.73	84.75
86.17	92.82	76.47	79.04	87.34	81.29	67.02	86.62
98.43	95.91	93.93	92.07	87.4	91.19	92.63	91.01
103.39	105.75	97.19	97	90.57	93.76	96.89	92.91
117.44	119.69	121.77	104.91	93.53	102.46	121.91	96.81
128.65	129.1	131.8	106.59	99.62	103.31	130.04	103.95
136.14	134.17	136.34	125.98	120.93	122.99	138.18	122.46
144.48	143.38	141.79	129.18	133.9	128.63	144.04	128.23

Table S2: 1st VB, EPC in eV/Å, the largest couplings are highlighted in green, darker the stronger.

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.02	0.01	0.02	0.16	0.12	0.01	0.03	0.02
0.01	0.01	0.25	0.02	0.55	0.01	0.02	0.09
0.02	0.1	0.02	0.35	0.18	0.19	0.01	0.01
0.02	0.01	0.04	0	0.14	0.01	0.01	0.14
0.01	0.17	0.01	0.01	0.01	0.12	0.04	0.01
0.03	0.13	0.07	0.01	0.01	0.01	0.22	0.01
0.1	0.01	0.01	0.1	0.02	0.01	0.12	0.07
0.01	0.06	0.15	0.01	0.06	0.19	0.01	0.06
0.01	0.1	0.01	0.01	0.01	0.01	0.13	0.02
0.02	0.02	0.12	0.06	0.12	0.01	0.02	0.05
0.01	0.05	0.05	0.01	0.01	0.02	0.05	0.06
0.02	0.07	0.02	0.03	0.01	0.06	0.01	0.02
0.03	0.01	0.01	0.09	0.03	0.02	0.05	0.02
0.01	0.01	0.04	0.01	0.1	0.02	0.01	0.01
0.02	0.03	0.02	0.02	0.03	0.08	0.01	0.01
0.01	0.05	0.01	0.04	0.06	0.01	0.04	0.02

Table S3: 2nd VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.02	0.02	0.02	0.03	0.03	0.01	0.26	0.03
0.02	0.26	0.06	0.02	0.33	0.29	0.03	0.34
0.02	0.16	0.03	0.44	0.3	0.18	0.01	0.02
0.03	0.02	0.1	0.01	0.15	0.02	0.01	0.18
0.06	0.11	0.01	0.06	0.02	0.34	0.12	0.01
0.07	0.13	0.06	0.02	0.01	0.01	0.04	0.02
0.12	0.01	0.01	0.21	0.03	0.02	0.03	0.07
0.01	0.17	0.07	0.02	0.04	0.36	0.01	0.12
0.02	0.08	0.02	0.02	0.01	0.06	0.01	0.02
0	0.02	0.07	0.1	0.15	0.01	0.02	0.05
0.02	0.12	0.04	0.02	0.01	0.02	0.04	0.11
0.02	0.06	0.03	0.02	0.01	0.03	0.02	0.02
0.09	0.01	0.02	0.01	0.22	0.02	0.08	0.02
0.22	0.02	0.11	0.01	0.06	0.18	0.02	0.01
0.02	0.1	0.14	0.02	0.06	0.04	0.01	0.01
0.02	0.19	0.02	0.18	0.09	0.01	0.2	0.03

Table S4: Davydov splitting, VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0.01	0	0.21	0.17	0.01	0.25	0.01
0	0.19	0.03	0	0.21	0.01	0.01	0.04
0.01	0.07	0.01	0.02	0.05	0.04	0	0.01
0.01	0	0.22	0	0.22	0	0	0.09
0.04	0.14	0	0.08	0.01	0.03	0.24	0
0.08	0.15	0.12	0	0	0	0.03	0.01
0.01	0	0	0.08	0.01	0	0.02	0.16
0	0.14	0.29	0.01	0.04	0.15	0	0.15
0.01	0	0	0	0	0.24	0.11	0.01
0.04	0	0.45	0.14	0.15	0	0.01	0.41
0	0.19	0.56	0	0	0	0.23	0.3
0	0.11	0.01	0.25	0	0.24	0.01	0
0.32	0	0	0.43	0.12	0.01	0.23	0
0.91	0.01	0.44	0	0.87	0.33	0	0
0	0.24	0.44	0.01	0.25	0.12	0	0
0	0.77	0	0.65	0.27	0	0.74	0.01

Table S6: 1st CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.03	0.03	0.03	0.17	0.28	0.03	0.1	0.03
0.02	0.05	0.19	0.03	0.34	0.25	0.04	0.38
0.03	0	0.04	0.44	0.33	0.15	0.02	0.03
0.04	0.03	0.02	0.02	0.14	0.03	0.03	0.07
0.03	0.17	0.02	0.06	0.03	0.28	0.01	0.03
0.06	0.11	0.07	0.03	0.03	0.03	0.16	0.03
0.16	0.02	0.02	0.07	0.04	0.03	0	0.06
0.02	0.08	0.07	0.03	0.06	0.22	0.03	0.11
0.03	0.07	0.03	0.02	0.03	0.04	0.04	0.04
0.04	0.03	0.08	0.04	0.09	0.03	0.03	0.1
0.03	0.14	0.05	0.03	0.03	0.03	0.1	0.06
0.04	0	0.04	0.06	0.02	0.04	0.03	0.03
0	0.03	0.03	0.07	0.17	0.03	0.05	0.03
0.15	0.02	0.13	0.03	0.04	0.03	0.03	0.02
0.03	0.05	0.08	0.03	0.06	0.1	0.02	0.02
0.03	0.07	0.03	0.05	0.15	0.03	0.1	0.03

Table S7: 2nd CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.04	0.03	0.04	0.36	0.46	0.03	0.25	0.04
0.03	0.05	0.5	0.04	0.97	0.15	0.05	0.36
0.04	0.02	0.05	0.72	0.44	0.16	0.03	0.03
0.04	0.03	0.17	0.02	0.27	0.03	0.04	0.02
0.19	0.2	0.03	0.07	0.03	0.32	0	0.03
0	0.16	0.13	0.03	0.03	0.03	0.19	0.03
0.05	0.03	0.03	0.14	0.04	0.03	0.16	0.08
0.02	0.07	0.36	0.03	0.06	0.3	0.03	0.08
0.03	0.17	0.04	0.03	0.03	0.05	0.15	0.04
0.02	0.04	0.01	0.14	0.2	0.03	0.03	0.09
0.03	0.15	0.21	0.03	0.03	0.04	0.07	0.04
0.04	0.03	0.04	0.11	0.03	0.12	0.03	0.03
0.16	0.04	0.03	0.01	0.14	0.04	0.11	0.04
0.07	0.03	0.03	0.03	0.02	0.15	0.03	0.03
0.04	0.18	0.09	0.04	0.03	0.09	0.03	0.03
0.03	0.06	0.03	0.03	0.08	0.03	0.09	0.04

Table S8: Davydov splitting, CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.07	0.06	0.07	0.21	0.42	0.06	0.05	0.08
0.05	0.12	0.52	0.08	1.07	0.62	0.08	0.78
0.07	0.07	0.09	1.17	0.7	0.54	0.05	0.06
0.08	0.06	0.33	0.05	0.14	0.07	0.07	0.39
0.05	0.25	0.06	0.08	0.07	0.59	0.07	0.06
0.06	0.21	0.08	0.07	0.06	0.06	0.29	0.06
0.15	0.05	0.05	0.22	0.08	0.07	0.01	0.2
0.05	0.07	0.18	0.07	0.24	0.51	0.06	0.28
0.06	0	0.07	0.06	0.06	0	0.17	0.08
0.13	0.07	0.14	0	0.28	0.06	0.07	0.24
0.05	0.16	0.14	0.06	0.06	0.07	0.05	0.07
0.07	0.08	0.09	0.02	0.05	0.08	0.06	0.07
0.01	0.07	0.07	0.18	0.44	0.08	0.13	0.07
0.34	0.06	0.34	0.06	0.21	0.07	0.06	0.05
0.07	0.03	0.17	0.07	0.1	0.18	0.05	0.05
0.06	0.13	0.06	0.07	0.31	0.06	0.24	0.07

Tetracene – P1

Intra-molecular modes up to 400 cm^{-1}

Table S9: Frequencies in cm^{-1}

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
164.39	152.68	160.8	159.35	164.2	164.15	163.49	156.88
164.55	166.88	161.09	159.87	164.73	164.36	164.77	162.9
168.21	167.47	169.11	167.12	167.17	168.12	168.37	165.91
169.27	168.92	169.53	169.88	167.22	168.46	168.55	169.21
208.34	210.91	211.11	206.85	206.42	207.31	210.63	206.82
213.55	213.7	213	212.77	210.82	210.45	210.83	214.83
268.05	271.92	272.28	271.96	268.23	269.7	270.84	271.74
274.27	275.65	275.29	273.19	271.34	270.15	272.38	273.13
298.9	297.72	298.18	297.67	298.11	298.53	299.01	297.67
299.71	299.96	299.47	299.02	299.59	299.19	299.58	299
314.73	313.32	313.7	313.57	315.26	314.99	315.19	313.77
318.36	315.42	314.51	314.78	318.28	318.28	317.92	314.88
320.57	317.95	318.93	322.96	322.91	323.25	321.3	322.16
322.47	322.32	321.04	323.89	327.21	326.4	321.37	324.62
381.09	380.64	380.72	375.05	375.26	375.94	381.22	373.99
385.28	384.59	384.62	376.37	377.12	376.7	385.34	377.12

Table S10: 1st VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.06	0.01	0.01	0.01	0.01	0.14	0.01	0.01
0	0.01	0.01	0.01	0.12	0	0.07	0.03
0.02	0.09	0.01	0.05	0.01	0.09	0	0.01
0	0.05	0.04	0	0.06	0	0.13	0.01
0.02	0	0	0.05	0	0.01	0.01	0.02
0.01	0	0.06	0	0.01	0.1	0.02	0.1
0.01	0.07	0.07	0.01	0.02	0.01	0.01	0
0.01	0.02	0.01	0.03	0.06	0.07	0.02	0.01
0.01	0	0	0.05	0	0.2	0.01	0.09
0.04	0	0.02	0	0.01	0	0.18	0.18
0.11	0.01	0.1	0.01	0	0.16	0.01	0.1
0.04	0	0	0.27	0.01	0.02	0.24	0.59
0	0.01	0	0	0	0.03	0.05	0.01
0	0.01	0.01	0.1	0.09	0	0	0
0.05	0	0	0.01	0.01	0.02	0.01	0
0	0	0	0.09	0.01	0	0.01	0.07

Table S11: 2nd VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.08
0	0.01	0.01	0.03	0.21	0	0.02	0.07
0	0.14	0.01	0.07	0.01	0.01	0	0.01
0	0.15	0.05	0	0.06	0	0.09	0.01
0.08	0	0	0.11	0	0.01	0.01	0.05
0.04	0	0.09	0.01	0.01	0.18	0.1	0.12
0.01	0	0.04	0.02	0.06	0.01	0.01	0
0.01	0.01	0.01	0.03	0.03	0.11	0.03	0.01
0	0	0.01	0.08	0	0.07	0.01	0.15
0.09	0	0.05	0.01	0.01	0	0.13	0.08
0.15	0.01	0.1	0.01	0	0.01	0.01	0.03
0.08	0	0	0.2	0.01	0.03	0.06	0.27
0.01	0.08	0	0	0.03	0.12	0.07	0.01
0	0.02	0.06	0.19	0.15	0	0.01	0
0.02	0	0.01	0.01	0.01	0.12	0.2	0.05
0.01	0.01	0.02	0.11	0.01	0	0.01	0.07

Table S12: Davydov splitting, VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.02	0	0.01	0	0	0.09	0.01	0.15
0	0	0	0.02	0.09	0	0.32	0.58
0.03	0.02	0.01	0.04	0	0.33	0	0
0	0.01	0.02	0	0.02	0	0.01	0
0.11	0	0	0.68	0	0	0	0.08
0.33	0	0.17	0	0	0.37	0.28	0.2
0	0.04	0.3	0.01	0.11	0	0.01	0
0	0.01	0	0.24	0.14	0.24	0.04	0
0.06	0	0	0.04	0	0.16	0.01	0.11
0.04	0	0.08	0	0	0	0.06	0.18
0.01	0	0	0	0	0.09	0	0.25
0.02	0	0	0	0	0.01	0.05	0.04
0	0.03	0	0	0.02	0.8	0.47	0
0	0.66	0.16	0.17	0.15	0	0.01	0
0.02	0	0	0	0	0.54	0.79	0.16
0.01	0	0.03	0.22	0	0	0	0.56

Table S13: 1st CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.08	0.01	0.08	0.01	0.02	0.27	0.01	0.05
0.01	0.01	0.01	0	0.32	0.01	0.1	0.05
0.01	0.11	0.02	0	0.01	0.19	0.01	0.01
0.01	0.04	0	0.01	0.03	0.01	0.16	0.01
0.03	0.01	0.01	0.05	0.01	0.01	0.01	0.05
0.03	0.01	0.03	0	0.01	0.05	0.06	0.06
0.01	0.02	0.05	0.02	0.01	0.01	0.02	0.01
0.01	0.01	0.01	0.07	0.03	0.02	0.05	0.01
0.01	0.01	0.01	0.12	0.01	0	0.01	0.1
0.01	0.01	0.01	0.01	0.01	0.01	0.05	0.03
0.41	0.01	0.33	0.02	0.01	0.43	0.01	0.36
0.16	0	0.01	0.27	0.01	0.02	0.36	0.35
0.01	0.04	0.01	0.01	0.05	0.01	0.05	0.01
0.01	0.01	0.07	0.09	0.08	0.01	0.01	0.01
0.01	0.01	0.01	0.01	0.01	0.09	0.05	0.05
0.04	0	0.05	0.06	0.01	0.01	0.01	0.02

Table S14: 2nd CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.05	0.01	0.03	0.02	0.02	0.47	0.02	0.01
0.01	0.01	0.01	0.12	0.34	0.01	0	0.04
0.01	0.09	0.02	0.01	0.01	0.13	0.01	0.01
0.01	0.22	0.07	0	0.1	0.01	0	0.01
0.05	0.01	0	0.08	0.01	0.02	0.02	0
0.07	0.01	0.06	0	0.02	0.04	0.15	0.02
0.02	0.01	0.01	0.02	0.05	0.02	0.02	0.01
0.01	0.07	0.02	0.1	0	0.02	0.07	0.01
0	0.01	0.01	0.11	0.01	0.11	0.01	0.01
0.02	0.01	0.02	0.01	0.01	0.01	0.09	0.06
0.45	0.02	0.39	0.02	0.01	0.64	0.02	0.6
0.19	0	0.01	0.48	0.01	0.03	0.86	0.98
0.01	0.1	0.01	0.01	0	0.21	0.14	0.02
0	0.06	0.15	0.12	0.07	0	0.01	0
0.05	0.01	0.01	0.01	0.01	0.11	0.1	0.12
0.09	0	0.09	0.06	0.02	0.01	0.02	0.01

Table S15: Davydov splitting, CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.05	0.03	0.09	0.03	0.04	0.7	0.03	0.07
0.02	0.02	0.03	0.12	0.75	0.02	0.01	0.2
0.07	0.47	0.04	0.06	0.03	0.44	0.01	0.02
0.01	0.05	0.07	0.01	0.09	0.01	0.58	0.02
0.01	0.02	0	0.01	0.02	0.03	0.03	0.01
0.01	0.01	0.11	0.01	0.03	0.1	0.01	0.09
0.03	0.09	0.09	0.05	0.05	0.03	0.04	0.03
0.03	0.07	0.03	0.12	0.11	0.15	0.09	0.02
0.02	0.02	0.02	0.09	0.01	0.01	0.03	0.14
0.02	0.01	0.03	0.02	0.03	0.02	0.02	0.06
0.85	0.03	0.81	0.04	0.02	0.74	0.03	0.72
0.35	0	0.02	0.73	0.03	0.06	1.08	1.13
0.02	0.07	0.02	0.01	0.06	0.14	0.17	0.03
0.01	0.1	0.06	0.19	0.09	0.01	0.02	0.01
0.09	0.02	0.03	0.02	0.02	0.25	0.04	0.18
0.06	0	0.07	0.13	0.03	0.01	0.03	0.01

Tetracene – film phase

Inter-molecular modes

Table S16: Frequencies in cm^{-1}

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
-0.27	7.46	23.45	21.41	16.23	31.75	31.1	34.28
-0.19	12.86	25.73	22.94	25.83	34.15	33.93	35.99
-0.12	18.97	35.56	43.07	44.5	44.85	34.86	38.33
16.28	24.15	42.71	49.1	45.49	52.37	37.82	40.74
37.14	36.7	47.95	52.58	45.91	53.87	47.09	48.8
51.58	40.36	48.75	56.98	48.81	55.09	48.46	51.62
63.49	52.91	60.48	63.85	79.75	67.13	60.58	78.41
64.84	67.3	60.79	68.12	84.64	68.53	61.95	82.33
68.14	92.87	73.19	86.03	85	74.29	69.69	84.46
93.06	94.8	74.57	86.97	89.98	78.52	70.65	87.78
94.49	99.61	84.69	92.54	91.36	96.8	101.98	89.73
100.77	105.41	91.7	96.53	92.4	99.33	103.18	90.14
116.49	121.05	123.03	96.58	92.5	107.43	124.92	104.58
124.5	124.16	123.56	100.19	93.81	110.53	125.93	109.6
146.52	139.31	147.62	122.91	121.44	120.66	143	117.6
149.01	147.36	149.12	123.71	126	124.52	144.47	124.48

Table S17: 1st VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0	0	0	0	0	0	0.06
0	0.04	0.04	0.01	0	0.04	0.02	0
0	0	0	0	0	0	0	0.04
0.03	0.01	0.02	0.02	0.01	0.02	0.06	0
0	0	0	0	0	0	0	0.03
0	0.02	0.09	0.08	0.01	0.04	0.04	0.01
0	0	0	0	0.02	0.05	0	0
0	0	0.03	0.01	0.01	0	0.01	0
0	0	0	0.05	0	0.05	0	0
0	0	0	0	0	0	0.01	0.04
0	0	0.01	0.02	0	0	0	0
0	0	0	0.04	0	0.01	0	0.03
0.01	0	0	0	0.03	0.01	0	0.03
0.01	0	0.01	0	0.07	0	0.02	0.04
0	0.03	0	0	0	0	0	0.01
0	0	0.04	0	0	0	0.01	0.01

Table S18: 2nd VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0	0	0	0	0	0	0.27
0	0.1	0.26	0.02	0	0.06	0	0
0	0	0	0	0	0	0	0.12
0.07	0.02	0.05	0.06	0.2	0.01	0.19	0
0	0.06	0	0	0	0	0	0
0.03	0.02	0.28	0.01	0.04	0.06	0.11	0
0	0	0	0	0.23	0.11	0	0
0.01	0.01	0.15	0.05	0.05	0	0.07	0
0	0.01	0	0.09	0	0.14	0	0
0	0	0.08	0	0	0	0.06	0.06
0.01	0.02	0.05	0.01	0	0	0.01	0
0	0	0	0.35	0	0.04	0	0.12
0.01	0	0	0	0.06	0.09	0	0.03
0.31	0	0.23	0	0.26	0	0.04	0.06
0	0.05	0	0	0	0	0	0.15
0	0	0.09	0.02	0	0.25	0.2	0.19

Table S19: Davydov splitting, VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0	0	0	0.01	0.01	0	0.45
0	0.17	0.48	0.08	0	0.17	0.2	0
0	0	0.01	0.01	0	0	0	0.47
0.07	0.03	0.07	0.02	0.29	0.21	0.47	0
0	0.14	0	0	0	0	0	0.05
0.02	0.12	0.33	0.02	0.18	0.06	0.15	0.28
0	0	0.01	0	0.07	0.15	0	0
0	0.02	0.26	0.18	0	0	0.01	0
0	0.05	0.01	0.19	0	0.24	0	0
0.01	0.01	0.01	0	0.01	0	0.15	0.01
0.02	0.01	0.01	0.18	0.01	0	0.04	0
0.01	0.04	0.01	0.06	0.01	0.01	0.01	0.24
0.05	0	0.01	0.01	0.16	0.03	0	0.16
0.01	0	0.02	0.01	0.31	0	0.12	0.11
0	0.16	0	0	0	0.01	0	0.07
0	0.01	0.11	0.02	0	0.05	0.11	0.03

Table S20: 1st CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0	0	0	0	0	0	0.02
0	0.01	0.05	0.03	0	0.04	0.06	0
0	0	0	0	0	0	0	0.08
0.03	0.01	0.03	0.01	0	0.03	0.02	0
0	0.08	0	0	0	0	0	0
0	0.04	0.08	0.06	0.02	0	0.01	0.02
0	0	0	0	0.01	0.04	0	0
0.04	0.01	0.01	0.02	0.04	0	0	0
0	0.05	0	0.04	0	0.03	0	0
0	0	0.03	0	0	0	0.04	0.01
0.01	0.07	0.1	0.05	0	0	0.07	0
0	0	0	0.01	0	0.03	0	0.03
0.04	0	0	0	0.05	0.05	0	0.01
0.01	0	0.04	0	0.01	0	0.02	0.06
0	0.04	0	0	0	0	0	0.01
0	0	0.02	0.01	0	0.04	0	0.04

Table S21: 2nd CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0.01	0.01	0	0.01	0.01	0	0.17
0	0.07	0.03	0.01	0	0.13	0.15	0
0	0	0.01	0.01	0	0	0	0.21
0.08	0.04	0.1	0.05	0.17	0.06	0.01	0.01
0	0.22	0.01	0.01	0.01	0	0	0.12
0.02	0.05	0.14	0	0.02	0.11	0.05	0.08
0	0.01	0.01	0	0.11	0.08	0.01	0
0	0.04	0.18	0.2	0.14	0.01	0.02	0
0	0.04	0	0	0.01	0.14	0	0
0	0.01	0.09	0.01	0.01	0.01	0.08	0.05
0.01	0.03	0.09	0.07	0.01	0	0.04	0
0.01	0.05	0.01	0.05	0.01	0.01	0.01	0.05
0.14	0	0.01	0.01	0.01	0.07	0.01	0.03
0.06	0	0.1	0.01	0.02	0.01	0.01	0.13
0	0.11	0.01	0	0	0	0	0.12
0	0	0.02	0.04	0	0.03	0.01	0.04

Table S22: Davydov splitting, CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.47
0.01	0.21	0.63	0.01	0.01	0.24	0.38	0.01
0.01	0.01	0.02	0.02	0	0.01	0.01	0.49
0.07	0	0.14	0.04	0.13	0.05	0.01	0.01
0.01	0.3	0.01	0.02	0.01	0.01	0.01	0.21
0.02	0.27	0.17	0.19	0.02	0.03	0.13	0.1
0.01	0.02	0.02	0.01	0.13	0.2	0.01	0.01
0.09	0.05	0.17	0.26	0.39	0.01	0.03	0.01
0.01	0.02	0.01	0.02	0.02	0.16	0.01	0.01
0.02	0.01	0.02	0.02	0.02	0.01	0.04	0.21
0.01	0.03	0.08	0.12	0.01	0.01	0.02	0.01
0.01	0.05	0.02	0.12	0.01	0.06	0.01	0
0.38	0.01	0.02	0.01	0.03	0.01	0.02	0.16
0.05	0.01	0.38	0.02	0.2	0.01	0.06	0.22
0.01	0.3	0.02	0.01	0.01	0.01	0.01	0.25
0.01	0.01	0.11	0.04	0	0.23	0.2	0.2

Tetracene – film phase

Intra-molecular modes, up to 400 cm^{-1}

Table S23: Frequencies in cm^{-1}

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
162.83	148.22	162.45	163.28	163.97	158.94	154.43	160.16
164.98	162.97	164.51	165.84	166.07	160.43	155.69	162.08
165.82	163.94	166.98	171.6	170.58	166.68	165.89	165.12
168.56	167.04	168.03	172.99	171.54	168.5	167.96	166.69
210.72	217.11	213.13	198.76	198.29	202.73	217.54	202.25
218.4	218.64	215.85	201.9	202.18	203.41	218.37	204.97
263.59	271.73	266.88	271.56	271.41	276.57	271.86	276.22
270.86	272.85	267.95	272.66	272.63	277.11	272.37	276.89
295.91	296.32	296.67	297.54	297.57	297.66	296.53	297.64
298.1	297.13	297.46	298.57	298.57	298.1	297	298.09
316.14	313.4	316.59	315.09	316.22	312.39	314.01	313.6
317.65	315.53	317.27	316.19	316.87	312.79	314.21	313.97
325.2	320.01	325.69	318.64	317.37	315.49	322.02	314.02
327.07	326.34	326.45	318.98	318.95	317.14	324.31	316.35
373.12	371.23	373.19	382.86	382.74	381.56	372.16	381.51
373.32	372.92	373.37	382.86	382.82	381.98	372.23	381.98

Table S24: 1st VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0.01	0	0	0	0	0	0
0	0	0.01	0.04	0	0.03	0	0
0	0	0	0.01	0.02	0	0	0.02
0	0	0	0	0.04	0	0	0.01
0.05	0	0	0	0.01	0	0	0
0	0	0.05	0.04	0.04	0	0.04	0
0	0.01	0.01	0.02	0	0.02	0.02	0
0	0.01	0	0	0	0	0	0.03
0.01	0	0	0	0.03	0	0	0
0	0	0.01	0.01	0.01	0.06	0.04	0
0.01	0	0	0	0.06	0	0.06	0
0.01	0	0.01	0.01	0.02	0.03	0	0.02
0	0.05	0	0	0	0	0	0
0	0.01	0.04	0	0	0.03	0.05	0.04
0.01	0	0.01	0.01	0	0.01	0	0
0	0	0	0	0.02	0	0.03	0

Table S25: 2nd VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0.23	0	0	0	0	0	0
0	0.03	0.09	0.07	0	0.12	0.1	0
0.02	0	0.02	0.03	0.08	0.05	0.04	0.07
0.01	0.07	0	0	0.06	0	0	0.06
0.07	0	0	0	0.08	0	0	0
0.11	0	0.18	0.17	0.14	0	0.07	0
0	0.01	0	0.03	0	0	0	0.03
0	0	0	0	0	0	0	0.05
0.03	0	0	0	0.04	0	0	0
0	0	0.02	0.03	0.03	0.04	0.02	0
0	0	0	0	0.31	0	0.14	0
0.01	0	0.03	0.01	0.06	0.13	0	0.16
0	0.06	0	0	0	0	0	0
0	0.24	0.03	0.01	0	0.23	0.33	0.29
0	0	0	0	0.02	0.12	0	0
0.02	0	0	0	0.04	0	0.08	0

Table S26: Davydov splitting, VB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0.02	0.01	0	0.01	0.01	0	0
0	0.04	0.22	0.12	0.01	0.17	0.01	0.01
0.01	0	0.09	0.02	0.14	0.09	0.06	0.41
0.02	0.04	0.01	0.01	0.17	0	0	0.16
0.27	0	0	0	0.07	0	0	0
0.06	0.01	0.28	0.24	0.22	0	0.14	0.01
0	0.02	0.05	0.05	0	0.02	0.01	0.04
0	0	0	0	0	0	0.01	0.1
0.06	0.01	0.01	0.01	0.13	0.01	0	0
0	0	0.05	0.05	0.06	0.01	0.07	0
0.01	0	0	0	0.49	0	0.85	0
0.05	0	0.06	0.04	0.14	0.07	0	0.1
0	0.27	0	0	0	0.01	0.01	0
0	0.09	0.14	0.01	0	0.23	0.35	0.27
0.02	0	0.02	0.04	0.01	0.03	0	0.01
0.01	0.01	0	0	0.07	0	0.11	0.01

Table S27: 1st CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0.01	0	0	0	0	0	0
0	0.06	0.04	0.03	0	0.02	0.13	0
0.02	0	0.09	0.11	0.07	0.04	0.07	0.01
0.13	0.01	0	0	0.05	0	0	0.05
0.01	0	0	0	0.07	0	0	0
0.01	0	0.02	0.03	0.02	0.05	0	0
0	0.03	0.07	0.04	0	0.08	0.09	0.06
0	0.08	0	0	0	0	0	0.06
0.01	0	0	0	0.01	0	0	0
0	0	0	0.01	0	0.08	0.04	0
0.03	0	0	0	0.02	0	0.03	0
0.03	0	0.01	0.03	0	0.04	0	0.11
0	0.01	0	0	0	0	0	0
0	0.03	0.02	0.06	0	0	0.03	0.03
0.02	0	0.02	0.03	0.02	0.03	0	0
0.02	0	0	0	0.03	0	0.01	0

Table S28: 2nd CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0	0.07	0.01	0	0.01	0.01	0.01	0
0	0.17	0.04	0.13	0.01	0.11	0.22	0.01
0.02	0	0.07	0.1	0.03	0.15	0.21	0.08
0.11	0.04	0.01	0.01	0.08	0	0	0.17
0.01	0	0	0.01	0.12	0	0	0
0.05	0.01	0.05	0.06	0.03	0.01	0.03	0.01
0.01	0.01	0.04	0.09	0	0.03	0.06	0.01
0	0.06	0.01	0	0.01	0	0	0.07
0.02	0	0.01	0.01	0	0.01	0	0
0.01	0	0.02	0.03	0.01	0.08	0.06	0
0.16	0	0	0.01	0.14	0	0.24	0.01
0.02	0.01	0.07	0.07	0.11	0.04	0	0.25
0	0.05	0.01	0	0	0.01	0	0
0	0.09	0.07	0.01	0.01	0.01	0.05	0.03
0	0	0	0.02	0	0.14	0	0.01
0.02	0	0.01	0	0.03	0.01	0.09	0

Table S29: Davydov splitting, CB, EPC in eV/Å

Γ	Z – ***c***	Y - ***b***	X - ***a***	V	U	T	R
0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.01
0	0.35	0.11	0.12	0.01	0.18	0.32	0.02
0.02	0	0	0.02	0.02	0.22	0.35	0.28
0.06	0.04	0.01	0.02	0.04	0.01	0	0.34
0.05	0.01	0.01	0.01	0.11	0.01	0.01	0.01
0.01	0.01	0.03	0.02	0.05	0.02	0	0.01
0.01	0.06	0.09	0.02	0.01	0.11	0.04	0.06
0.01	0	0.02	0	0.01	0	0.01	0.03
0.05	0.01	0.01	0.02	0.38	0.02	0	0.01
0.02	0.01	0.03	0.06	0.02	0.02	0.24	0.01
0.11	0.01	0.01	0.02	0.66	0.01	0.45	0.02
0.15	0.02	0.16	0.07	0.07	0.06	0	0.37
0.01	0.21	0.01	0	0	0.02	0.01	0.01
0	0.01	0.1	0.11	0.01	0.18	0.21	0.21
0.02	0.01	0.02	0.02	0.01	0.23	0.01	0.01
0.04	0.01	0.01	0.01	0.09	0.02	0.19	0.01

Table S30: DOS-weighted average EPC as used for the charge transport calculation, for the P1 tetracene polymorphs. The EPC are in units of eV/Å.

$\hbar\omega$ [meV]	intra- VB1	intra- VB2	inter- VB	intra- CB1	intra- CB2	inter- CB
3.50	0.08	0.08	0.13	0.13	0.24	0.18
4.01	0.25	0.25	0.10	0.25	0.48	0.65
5.09	0.18	0.23	0.03	0.23	0.35	0.60
5.46	0.07	0.09	0.11	0.06	0.11	0.20
5.97	0.08	0.14	0.10	0.12	0.16	0.23
6.63	0.10	0.06	0.07	0.08	0.10	0.14
7.78	0.07	0.09	0.06	0.08	0.08	0.13
8.41	0.10	0.14	0.16	0.09	0.19	0.22
9.89	0.05	0.04	0.09	0.04	0.09	0.07
10.39	0.07	0.07	0.22	0.06	0.10	0.16
11.50	0.04	0.07	0.26	0.07	0.10	0.09
11.97	0.03	0.03	0.13	0.04	0.07	0.07
13.13	0.04	0.10	0.19	0.08	0.08	0.21
14.52	0.04	0.12	0.48	0.07	0.07	0.19
16.10	0.04	0.07	0.21	0.06	0.09	0.10
16.58	0.04	0.12	0.45	0.08	0.05	0.16

Table S31: DOS-weighted average EPC as used for the charge transport calculation, for the PF tetracene polymorphs. The EPC are in units of eV/Å.

$\hbar\omega$ [meV]	intra- VB1	intra- VB2	inter- VB	intra- CB1	intra- CB2	inter- CB
3.55	0.03	0.13	0.21	0.01	0.08	0.22
3.75	0.03	0.10	0.22	0.04	0.09	0.31
4.80	0.02	0.04	0.16	0.03	0.07	0.17
5.06	0.03	0.11	0.22	0.02	0.08	0.08
5.61	0.01	0.02	0.06	0.03	0.10	0.14
6.15	0.05	0.12	0.19	0.04	0.08	0.14
8.23	0.02	0.09	0.06	0.01	0.05	0.08
8.90	0.01	0.06	0.11	0.02	0.11	0.20
10.20	0.03	0.06	0.11	0.03	0.05	0.05
10.78	0.02	0.04	0.04	0.01	0.04	0.08
11.61	0.01	0.02	0.07	0.05	0.04	0.06
12.05	0.02	0.12	0.10	0.02	0.03	0.05
13.63	0.02	0.04	0.09	0.03	0.04	0.12
14.16	0.03	0.19	0.14	0.02	0.06	0.17
16.11	0.01	0.05	0.06	0.01	0.05	0.12
16.02	0.01	0.17	0.05	0.03	0.03	0.16

C – convergence in the EPC

The convergence tests of the EPC in respect of the atoms displacement, eq.s (1) and (2) of the main text, focused on the topmost VB of the P1 polymorph of tetracene. These tests are reported in Figure S1. Theoretically the displacement should tend to zero, however we observed a nearly linear increase of the EPC with the decrease of the displacement amount; we chose to use the displacement at which this increase stopped. As an overall estimation of the EPC, we used the sum of all the EPC, denoted as EPC* in Figure S1.

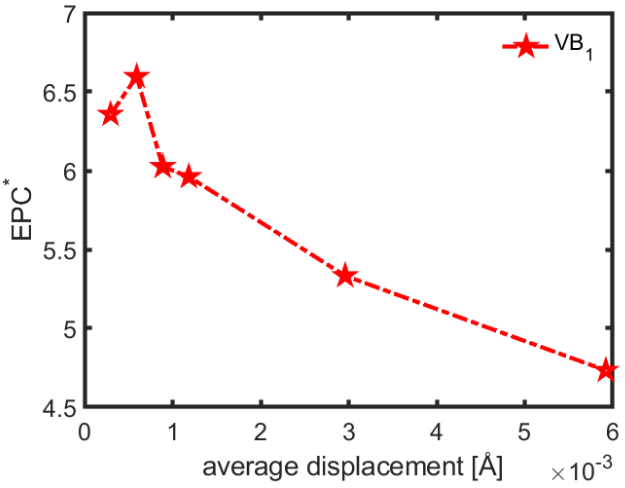

Figure S1: convergence test on the EPC* (sum of the individual EPC values) in respect of the average atoms displacement, performed on the topmost VB (VB_1) of the tetracene bulk polymorph 1. At around 0.001 Å the EPC* appeared to saturate. For smaller displacements, numerical noises started to appear.

D – Deformation potentials for naphthalene, anthracene, and ADP

For the sake of completeness, we report here the DOS-weighted average of the mode and ***q***-point dependent EPC values and related frequency, for naphthalene, Table S32, and anthracene, Table S33. The Table S34 reports the ADP values obtained with eq.s (5) and (6) on the oligoacenes investigated. For comparison, we report also the ADP values reported in literature as obtained with the method of the relative shift of the band edge.[1]

Table S32: DOS-weighted average of the mode and *q*-point dependent phonon frequency and EPC values for naphthalene.

$\hbar\omega$ [meV]	intra- VB1	intra- VB2	inter- VB	intra- CB1	intra- CB2	inter- CB
5.17	0.25	0.20	0.10	0.07	0.18	0.39
5.18	0.03	0.03	0.04	0.01	0.11	0.02
6.44	0.20	0.28	0.35	0.05	0.08	0.18
6.47	0.18	0.17	0.18	0.05	0.14	0.22
7.24	0.06	0.06	0.09	0.04	0.07	0.12
7.38	0.10	0.09	0.11	0.06	0.16	0.24
8.90	0.35	0.40	0.47	0.08	0.15	0.39
9.06	0.15	0.19	0.24	0.03	0.17	0.30
11.14	0.04	0.10	0.23	0.06	0.18	0.45
11.46	0.09	0.08	0.18	0.05	0.15	0.27
13.97	0.04	0.04	0.08	0.04	0.03	0.14
13.92	0.09	0.09	0.10	0.02	0.05	0.11

Table S33: DOS-weighted average of the mode and *q*-point dependent phonon frequency and EPC values for anthracene.

$\hbar\omega$ [meV]	intra- VB1	intra- VB2	inter- VB	intra- CB1	intra- CB2	inter- CB
4.35	0.11	0.16	0.28	0.16	0.24	0.42
4.36	0.07	0.10	0.18	0.17	0.22	0.40
5.60	0.10	0.17	0.33	0.18	0.15	0.31
5.55	0.06	0.18	0.37	0.15	0.18	0.36
6.23	0.13	0.23	0.44	0.22	0.22	0.44
6.35	0.06	0.14	0.24	0.15	0.17	0.31
7.88	0.06	0.16	0.31	0.10	0.13	0.24
8.24	0.03	0.05	0.14	0.07	0.10	0.20
10.01	0.05	0.13	0.29	0.10	0.13	0.28
10.28	0.06	0.15	0.32	0.15	0.14	0.30
13.27	0.08	0.11	0.22	0.08	0.08	0.12
13.59	0.06	0.11	0.22	0.09	0.10	0.24
15.62	0.09	0.12	0.21	0.10	0.09	0.22
15.79	0.12	0.15	0.23	0.10	0.08	0.18

Table S34: ADP deformation potential values for naphthalene, anthracene, and tetracene P1, computed with the method in eq.s (5) and (6), and comparison with literature values computed with a different method, which have been computed for unit cell dilation/compression along the *a* and *b* axes, and the corresponding values are indicating with a superscript *a* or *b*, accordingly.[1] Values in eV. We observe that are generally very small numbers if compared with inorganic semiconductors,[2] except for the values of one of the valence band and for the inter-band in the CB in anthracene, which are unphysically high, a point that deserves further investigation.

	naphthalene		anthracene		tetracene P1	
VB_1	0.24	1.31[a]	0.70	1.12[a]	0.17	1.79[a]
VB_2	0.38	1.39[b]	6.32	1.38[b]	0.16	0.47[b]
$VB_{inter\text{-}band}$	0.32		7.39		0.76	
CB_1	0.17	0.96[a]	0.95	0.42[a]	0.25	1.6[a]
CB_2	0.00	0.56[b]	0.00	0.87[b]	0.00	0.53[b]
$CB_{inter\text{-}band}$	0.84		20.39		0.69	

E – Relaxation times

In this section we report the relaxation times along the *a*, *b*, and *c* directions for the hole transport in the valence band of naphthalene, anthracene, and tetracene, along with the corresponding density of states (DOS). These are reported in Figure S2 for the intra- (blue) and inter- (green) band processes, and the DOS related to the two VB bands are reported with a different tones of red color. The zero of the energy corresponds to the VB edge and the positive energy are referred to the hole transport state energy, i.e. they are into the VB. For the case of naphthalene, we report also the case of ADP scattering with acoustic phonon at zone center (red). To highlight at what extent it is larger, and hence negligible. The insets in the naphthalene cases report the same curves without the ADP.

We can note that for naphthalene the intra- and inter- band processes have similar strength, while for anthracene the inter-band processes are much stronger, resulting in shorter relaxation time. In tetracene, the inter-band scattering is negligible, with a relaxation time not defined, set to zero for graphical purposes. This is because in tetracene the two bands are quite split apart with nearly absent overlap, as observable in the DOS in Figure S2 (n), while in naphthalene and anthracene the two bands overlap for the largest part of the energy of interest, thus the inter-band scattering processes are allowed throughout the entire hole energy range of interest in transport. We observe that the relaxation times are larger at the band edge, where only phonon absorption is allowed and the final available DOS is small, and suddenly decreases as soon as the DOS increases and phonon emission is possible.

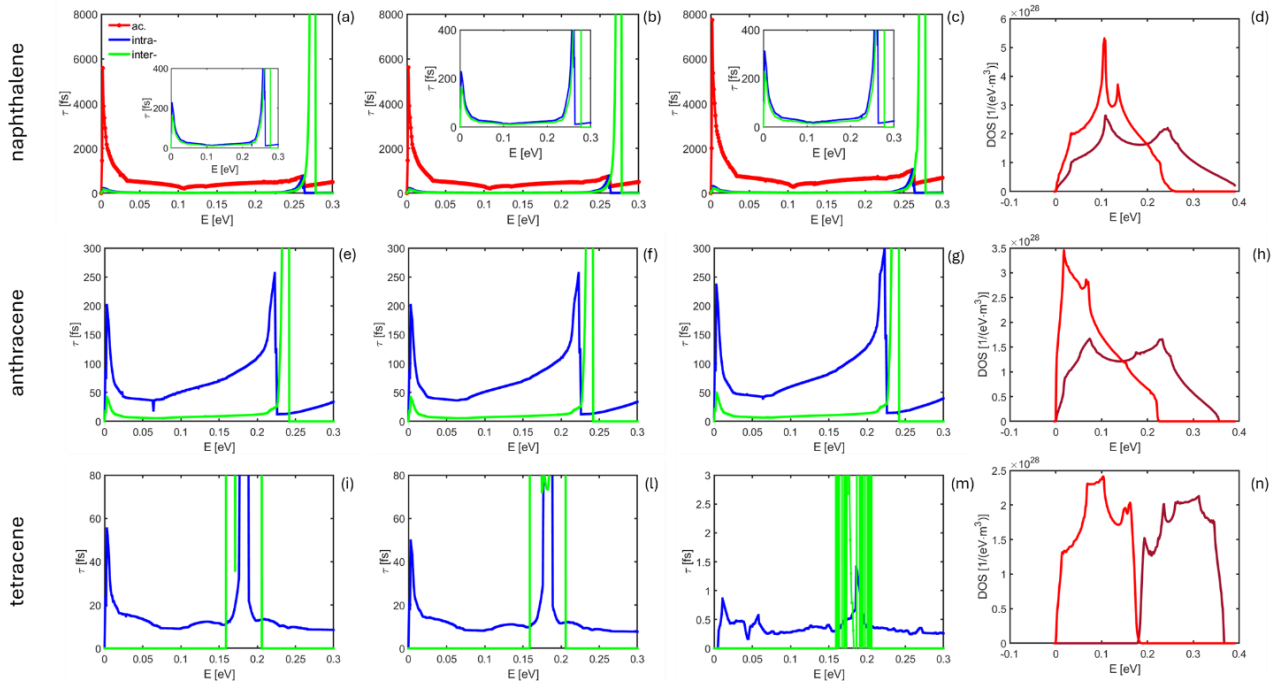

Figure S2: relaxation times for naphthalene (a-c), anthracene (e-g), tetracene(i-m) for the transport along the *a* (a, e, i), *b* (b, f, l), and *c* (c, g, m) axes. In blue and green are depicted the relaxation times for intra- and inter- band

processes, respectively, while the red lines in (a-c) represent the relaxation times for ADP mechanism. The corresponding density-of-states (DOS) are reported in (d), (h) and (n), the two VB are depicted with two red tones. The zero of the energy corresponds to the VB edge and the positive energy are referred to the hole transport state energy, i.e. they are into the VB.

References

[1] L. Tang, M. Long, D. Wang, Z. Shuai, *Sci. China Ser. B-Chem.* **2009**, *52*, 1646.
[2] P. Graziosi, C. Kumarasinghe, N. Neophytou, *Journal of Applied Physics* **2019**, *126*, 155701.