

Electronic Supplementary Information to Vibrationally Resolved Emission Spectra of Luminescent Conjugated Oligothiophenes from Anharmonic Calculations

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1 Computational settings for the wave-function calculations

Table S-1: Computational details for the calculations for the different molecules, conformations, harmonic and anharmonic calculations with varying number of modes, presented in the main text: Number of VSCF modals, level of couplings in VCI (VCI[n]) and the number of calculated VCI eigenvalues for the ground state. For the excited state, only the first VCI eigenvalue is calculated. Bi-, ter-, quater- and pentathiophene have been abbreviated 2T, 3T, 4T and 5T. The calculation types are anharmonic (anh.), harmonic (harm.) and either coupled or without couplings (no coup.). Calculations denoted by "Anharmonic" include couplings if more than one mode is included. The number of VSCF modals for each mode has been presented in brackets with comma separations.

Structure	Calculation	Modes	No. VSCF of modals	VCI[n]	No. of eigenvalues
<i>trans</i> -2T	Anharmonic	1	[30]	1	20
<i>trans</i> -2T	Anharmonic	2	[20,20]	2	200
<i>trans</i> -2T	Anharmonic	3	[20, 20, 10]	3	300
<i>trans</i> -2T	Anharmonic	4	[10,10,10,10]	4	1500
<i>trans</i> -2T	Anharmonic	5	[8,8,8,8,8]	4	2000
<i>trans</i> -2T	Anharmonic	5	[8,8,8,8,8]	5	1800
<i>trans</i> -2T	Harm. no coup.	5	[8,8,8,8,8]	5	2200
<i>trans</i> -2T	Harm. coupled	5	[8,8,8,8,8]	5	2200
<i>trans</i> -2T	Anh. no coup.	5	[8,8,8,8,8]	5	2200
<i>cis</i> -2T	Anharmonic	3	[20, 20, 10]	3	300
<i>all-trans</i> -3T	Anharmonic	1	[30]	1	20
<i>all-trans</i> -3T	Anharmonic	4	[8,8,8,8]	4	900
<i>all-trans</i> -3T, 2 groups NC	Anharmonic	2	[20,20]	2	200
<i>all-trans</i> -3T, 2 groups	Anharmonic	2	[50,50]	2	50
<i>all-trans</i> -3T, 4 groups	Anharmonic	2	[30,30]	2	50
<i>all-trans</i> -4T	Anharmonic	1	[30]	1	20
<i>all-trans</i> -4T	Anharmonic	4	[8,8,8,8]	4	1000
<i>all-trans</i> -5T	Anharmonic	1	[50]	1	30
<i>all-trans</i> -5T	Anharmonic	4	[8,8,8,8]	4	1500
<i>all-cis</i> -5T	Anharmonic	4	[8,8,8,8]	4	1000
<i>trans-cis-cis-trans</i> -5T	Anharmonic	4	[8,8,8,8]	4	1000

2 Spectra for *trans*-bithiophene

In Fig. S-1(a) we present the same calculation as in Fig. 3(b) in the main text, with the two highest ranked modes, however, with a Lorentzian broadening of 0.05 eV instead of 0.04 eV. The resulting spectrum is very similar to that including the three highest ranked modes, but a broadening of 0.04 eV [c.f. Fig. 3(c)] in the main text. The third-highest ranked mode has with 387 cm^{-1} a rather low harmonic vibrational frequency [c.f. Table 1 in the main text]. It is evident from this example, that the effect of a low-lying frequency can be seen as adding to the overall broadening of the spectrum.

The spectrum including the four highest ranked modes is presented in Fig. S-1(b), and looks indistinguishable from the spectrum with five modes presented in the in Fig. 3(d) in the main text.

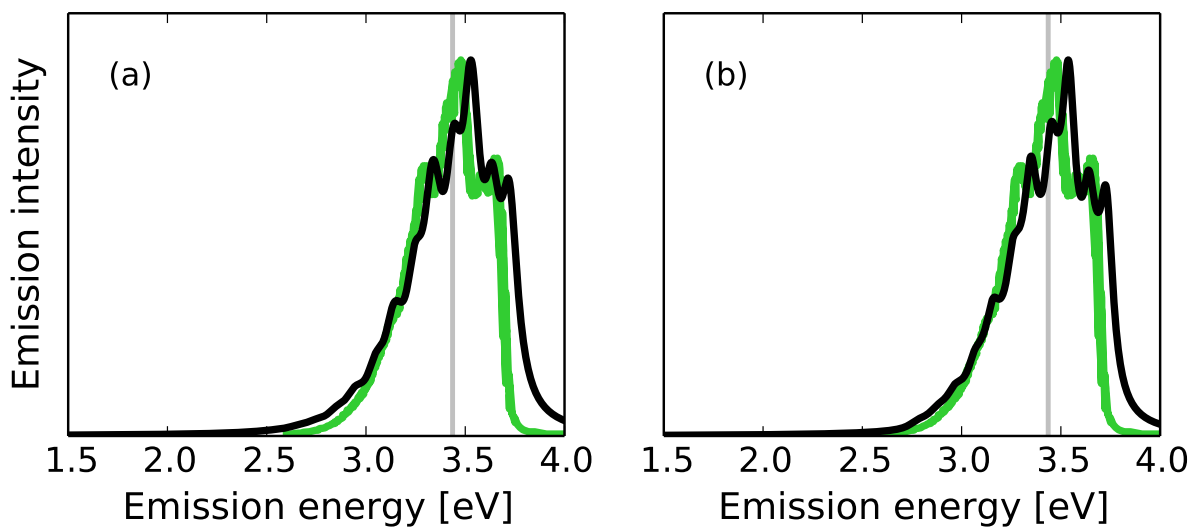


Figure S-1: Anharmonic emission spectra for the $S_1 \rightarrow S_0$ transition of *trans*-bithiophene and experimental spectra (at 77 K in ethanol) from Ref. 19 in the main text. The calculated spectra are represented with black lines, the experiment with green lines and the vertical electronic emission energy with gray lines. (a) Including the two highest ranked modes with half-width at half-maximum of 0.05 eV. (b) Including the four highest ranked modes with half-width at half-maximum of 0.04 eV.

3 Mode ranking

In the tables to follow, we present all the modes ranked for each structure. This includes the absolute value of the dimensionless displacement $|\Delta_i|$, harmonic frequency ν in cm^{-1} and type, sorted according to $|\Delta_i|$. The type is given for a selected few number of the highest ranked modes. The rows written in bold have a dimensionless displacement larger than or equal to 0.6 and a harmonic frequency larger than 161 cm^{-1} .

3.1 *trans*-bithiophene in normal coordinates

Mode	$ \Delta_i $	ν	type
14	1.42e+00	674	Ring breathing
36	1.35e+00	1658	Inter-ring C–C stretch
7	8.24e-01	387	Chain deformation
5	5.29e-01	290	Inter-ring stretch
29	4.46e-01	1214	C–S stretch
35	3.19e-01	1510	
17	3.18e-01	713	
30	2.85e-01	1322	
26	1.77e-01	1111	
25	1.74e-01	1108	
33	1.29e-01	1455	
20	7.02e-02	875	
40	2.01e-02	3263	
38	1.63e-02	3247	
42	1.17e-02	3288	
41	2.85e-03	3287	
37	1.84e-03	3247	
27	6.94e-04	1115	
39	6.10e-04	3262	
24	5.70e-04	1102	
31	3.69e-04	1330	
32	2.15e-04	1450	
3	2.01e-04	117	
1	1.23e-04	69	
28	1.16e-04	1157	
15	6.98e-05	695	
34	6.64e-05	1490	
9	3.36e-05	510	
2	2.94e-05	88	
16	2.54e-05	711	
6	2.08e-05	350	
13	1.49e-05	661	
21	1.33e-05	892	
10	1.17e-05	561	
8	1.16e-05	452	
4	9.99e-06	171	
19	7.79e-06	840	
12	7.25e-06	647	
11	5.21e-06	570	
18	4.22e-06	716	
22	8.41e-07	921	
23	5.07e-07	922	

3.2 *cis*-bithiophene in normal coordinates

Mode	$ \Delta_i $	ν	type
12	1.50e+00	626	Ring breathing
36	1.36e+00	1649	Inter-ring C–C stretch
5	8.14e-01	322	Inter-ring stretch
3	5.89e-01	115	Inter-ring bending
28	5.87e-01	1162	C–H bending
30	2.87e-01	1318	
34	2.57e-01	1489	
26	2.27e-01	1111	
32	1.91e-01	1452	
24	1.83e-01	1070	
18	1.49e-01	721	
40	2.39e-02	3273	
20	1.92e-02	872	
42	1.35e-02	3289	
38	9.89e-03	3249	
35	3.30e-03	1489	
41	1.92e-03	3289	
27	4.59e-04	1118	
1	3.37e-04	62	
25	2.69e-04	1102	
39	1.95e-04	3267	
31	1.95e-04	1341	
11	1.08e-04	585	
33	9.06e-05	1465	
37	8.43e-05	3248	
29	6.69e-05	1221	
6	6.61e-05	339	
2	3.85e-05	86	
7	2.76e-05	353	
15	2.10e-05	706	
8	1.86e-05	460	
19	1.63e-05	858	
14	1.15e-05	659	
17	1.02e-05	717	
23	9.62e-06	922	
9	7.76e-06	488	
21	7.66e-06	901	
13	5.87e-06	639	
10	5.68e-06	558	
22	4.42e-06	922	
16	2.41e-06	709	
4	1.74e-06	176	

3.3 *all-trans*-terthiophene in normal coordinates

Mode	$ \Delta_i $	ν	type
55	1.31e+00	1631	Inter-ring C–C stretch
24	1.05e+00	697	Ring breathing
8	9.25e-01	210	Inter-ring stretch
10	7.41e-01	350	Chain deformation
45	4.54e-01	1264	Inner-ring C–S stretch
26	2.85e-01	740	
54	2.53e-01	1557	
18	2.42e-01	589	

52	2.33e-01	1504
38	1.79e-01	1105
40	1.47e-01	1118
3	1.41e-01	71
43	1.40e-01	1220
47	7.32e-02	1346
32	5.54e-02	894
41	4.82e-02	1132
30	4.69e-02	848
57	1.29e-02	3244
61	1.22e-02	3262
60	8.75e-03	3258
50	4.20e-03	1466
63	3.54e-03	3290
62	2.25e-03	3290
37	9.83e-04	1103
59	8.88e-04	3258
25	7.65e-04	738
23	6.34e-04	693
56	5.73e-04	3244
1	4.24e-04	35
44	3.17e-04	1247
39	2.30e-04	1117
7	1.77e-04	174
4	6.66e-05	87
53	6.66e-05	1548
2	6.36e-05	52
27	5.63e-05	750
29	5.08e-05	787
11	4.95e-05	362
15	4.43e-05	513
22	3.51e-05	689
13	3.11e-05	442
6	2.84e-05	150
9	2.54e-05	281
5	2.20e-05	111
35	1.97e-05	933
12	1.69e-05	391
42	1.58e-05	1172
49	1.50e-05	1440
31	1.50e-05	863
48	1.46e-05	1396
46	1.38e-05	1329
34	1.13e-05	913
21	1.12e-05	685
20	9.35e-06	638
28	8.58e-06	783
58	7.81e-06	3245
33	4.64e-06	899
36	2.34e-06	933
16	1.90e-06	551
51	8.96e-07	1490
17	6.62e-07	586
19	4.23e-07	621
14	4.16e-07	470

3.4 *all-trans*-terthiophene with two groups, no constraints in normal coordinates

Mode	$ \Delta_i $	ν	type
85	1.27e+00	1635	Inter-ring C–C stretch
2	9.47e-01	19	Internal rotation
14	8.43e-01	193	Inter-ring stretch
1	7.65e-01	14	Internal rotation
42	7.48e-01	725	Ring breathing
24	6.80e-01	405	Chain deformation
6	6.61e-01	35	
13	4.72e-01	165	
40	4.32e-01	707	
37	4.08e-01	634	
69	4.05e-01	1270	
12	3.95e-01	146	
83	3.28e-01	1582	
84	3.14e-01	1591	
38	2.80e-01	675	
4	2.72e-01	27	
7	2.27e-01	52	
32	2.23e-01	589	
41	2.17e-01	713	
3	2.12e-01	22	
67	2.00e-01	1251	
44	1.95e-01	755	
43	1.90e-01	750	
78	1.63e-01	1475	
59	1.54e-01	1126	
5	1.29e-01	29	
33	1.10e-01	595	
17	1.09e-01	272	
23	1.06e-01	395	
48	1.06e-01	849	
64	9.36e-02	1202	
27	8.76e-02	465	
39	8.39e-02	694	
54	8.38e-02	912	
34	8.23e-02	603	
80	7.99e-02	1492	
79	7.60e-02	1488	
68	7.13e-02	1265	
19	7.04e-02	301	
75	6.89e-02	1397	
11	6.82e-02	123	
71	6.74e-02	1298	
63	6.58e-02	1192	
55	6.14e-02	972	
15	5.90e-02	239	
73	5.77e-02	1327	
20	5.45e-02	336	
26	5.43e-02	460	
25	4.60e-02	453	
65	4.40e-02	1218	
82	4.39e-02	1531	
21	4.36e-02	341	
29	4.22e-02	533	
70	4.18e-02	1295	

56	4.15e-02	978
77	4.06e-02	1438
35	3.86e-02	616
72	3.68e-02	1311
50	3.53e-02	882
22	3.24e-02	365
66	3.16e-02	1230
61	3.16e-02	1154
76	3.00e-02	1421
81	2.94e-02	1518
9	2.86e-02	85
60	2.81e-02	1152
51	2.77e-02	898
45	2.56e-02	775
58	2.50e-02	1014
8	2.48e-02	67
57	2.36e-02	1010
46	2.23e-02	784
53	1.77e-02	910
62	1.61e-02	1173
36	1.59e-02	621
10	1.55e-02	102
31	1.36e-02	571
92	1.35e-02	3237
95	1.20e-02	3261
28	1.14e-02	490
94	1.03e-02	3259
74	9.29e-03	1394
16	9.15e-03	264
87	8.73e-03	1902
18	7.53e-03	288
47	5.08e-03	802
49	4.27e-03	873
30	4.03e-03	550
96	3.39e-03	3277
97	1.78e-03	3315
91	1.32e-03	3105
88	1.18e-03	3051
99	1.11e-03	3782
89	9.85e-04	3054
90	8.98e-04	3096
93	7.94e-04	3245
52	5.23e-04	901
86	5.19e-04	1896
98	4.83e-04	3779

3.5 *all-trans*-terthiophene with two groups, frozen OH in FALCON coordinates

Mode	$ \Delta_i $	ν	type
75	1.27e+00	1635	Inter-ring C–C stretch
10	8.22e-01	216	Inter-ring stretch
34	7.93e-01	725	Ring breathing
17	6.18e-01	392	Chain deformation
31	5.47e-01	643	Ring breathing
35	4.46e-01	725	Ring breathing
61	4.01e-01	1271	
73	3.27e-01	1582	

74	3.14e-01	1591
18	2.36e-01	395
59	2.00e-01	1250
13	1.76e-01	276
28	1.72e-01	594
68	1.67e-01	1474
4	1.62e-01	67
20	1.52e-01	454
53	1.51e-01	1126
60	1.35e-01	1265
27	1.32e-01	584
5	1.30e-01	87
40	1.23e-01	843
21	9.79e-02	457
56	9.34e-02	1201
30	8.60e-02	622
16	8.03e-02	363
70	7.98e-02	1492
46	7.75e-02	903
7	7.71e-02	123
69	7.69e-02	1487
29	6.53e-02	611
1	6.49e-02	39
23	6.27e-02	516
55	6.26e-02	1191
15	6.11e-02	306
12	6.11e-02	267
42	5.75e-02	861
47	5.72e-02	967
64	5.69e-02	1386
48	5.46e-02	972
22	5.31e-02	489
14	5.19e-02	290
2	5.09e-02	49
63	4.77e-02	1324
65	4.57e-02	1388
57	4.48e-02	1217
72	4.41e-02	1531
51	4.00e-02	1111
44	3.88e-02	889
24	3.87e-02	535
39	3.67e-02	790
67	3.40e-02	1435
32	3.31e-02	690
41	3.26e-02	848
25	3.11e-02	558
71	2.90e-02	1518
38	2.78e-02	781
6	2.68e-02	97
58	2.58e-02	1229
50	2.47e-02	1006
66	2.23e-02	1420
9	2.17e-02	170
19	2.05e-02	414
52	1.79e-02	1118
54	1.76e-02	1173
49	1.63e-02	1000
11	1.63e-02	238

26	1.40e-02	580
82	1.35e-02	3237
85	1.20e-02	3261
36	1.06e-02	752
84	1.03e-02	3259
33	1.02e-02	698
8	9.65e-03	153
77	8.39e-03	1892
3	5.46e-03	61
86	3.39e-03	3277
62	2.42e-03	1303
87	1.78e-03	3315
81	1.32e-03	3105
78	1.18e-03	3051
43	1.12e-03	879
76	1.01e-03	1885
79	9.89e-04	3054
80	8.97e-04	3096
83	7.94e-04	3245
45	5.20e-04	901
37	2.68e-04	772

3.6 *all-trans*-terthiophene with four groups, frozen OH in FALCON coordinates

Mode	$ \Delta_i $	ν	type
81	1.23e+00	1612	Inter-ring C–C stretch
10	6.66e-01	215	Inter-ring stretch
40	6.31e-01	732	Ring breathing
37	5.05e-01	686	Ring breathing
42	3.74e-01	736	Ring breathing
28	3.57e-01	530	Ring breathing
9	3.51e-01	177	
80	3.49e-01	1568	
14	3.28e-01	304	
63	3.20e-01	1258	
22	3.01e-01	458	
34	2.86e-01	620	
65	2.55e-01	1275	
17	2.50e-01	344	
74	2.18e-01	1489	
58	2.07e-01	1130	
7	2.04e-01	118	
25	1.97e-01	492	
67	1.91e-01	1284	
19	1.60e-01	396	
4	1.53e-01	99	
3	1.50e-01	82	
69	1.22e-01	1333	
77	1.10e-01	1524	
75	1.05e-01	1509	
12	9.90e-02	242	
83	9.84e-02	1766	
61	8.96e-02	1220	
46	8.81e-02	850	
52	8.59e-02	965	
31	8.01e-02	585	
59	7.93e-02	1134	

45	7.26e-02	797
1	6.46e-02	63
55	5.53e-02	1044
48	3.59e-02	869
54	3.38e-02	1001
71	2.79e-02	1349
21	2.66e-02	417
29	2.59e-02	569
33	2.07e-02	616
93	1.02e-02	3265
43	9.55e-03	780
91	7.64e-03	3248
85	2.93e-03	1861
89	1.16e-03	3178
87	6.30e-04	3120
6	5.86e-04	116
88	3.41e-04	3178
8	3.23e-04	150
56	2.68e-04	1044
15	2.56e-04	306
76	2.06e-04	1509
11	1.06e-04	229
23	9.82e-05	465
2	7.84e-05	71
41	5.62e-05	736
57	5.30e-05	1125
5	4.35e-05	104
27	3.54e-05	526
32	3.19e-05	607
20	2.99e-05	403
26	2.66e-05	505
86	2.60e-05	3120
66	2.59e-05	1278
36	2.26e-05	666
13	2.19e-05	272
78	2.07e-05	1530
51	2.02e-05	964
38	2.02e-05	702
70	1.90e-05	1348
39	1.87e-05	715
47	1.80e-05	856
62	1.75e-05	1237
60	1.50e-05	1183
73	1.47e-05	1422
64	1.39e-05	1262
82	1.36e-05	1754
68	1.14e-05	1312
24	9.90e-06	487
16	9.71e-06	326
72	9.55e-06	1405
79	7.73e-06	1562
50	6.16e-06	926
18	4.19e-06	378
84	4.00e-06	1860
90	3.84e-06	3248
44	3.33e-06	795
53	3.22e-06	1001
30	2.63e-06	570

35	1.45e-06	628
49	1.35e-06	890
92	5.54e-07	3249

3.7 *all-trans*-quaterthiophene in normal coordinates

Mode	$ \Delta_i $	ν	type
74	1.28e+00	1616	Inter-ring C–C stretch
9	1.02e+00	162	Inter-ring stretch
32	8.94e-01	705	Ring breathing
15	6.93e-01	333	Chain deformation
61	4.06e-01	1277	Inner-ring C–S–C stretch
71	3.58e-01	1548	
59	2.35e-01	1261	
28	2.31e-01	640	
52	2.09e-01	1118	
36	2.07e-01	751	
7	1.75e-01	106	
51	1.63e-01	1099	
69	1.53e-01	1500	
73	1.51e-01	1584	
34	9.61e-02	720	
54	6.95e-02	1125	
20	6.66e-02	476	
16	6.51e-02	385	
62	6.07e-02	1336	
64	4.77e-02	1397	
44	3.28e-02	910	
67	2.33e-02	1466	
57	2.28e-02	1221	
42	1.48e-02	863	
82	1.32e-02	3259	
60	1.30e-02	1261	
78	9.95e-03	3243	
80	4.02e-03	3257	
53	1.80e-03	1119	
84	1.32e-03	3291	
76	1.21e-03	3243	
10	1.21e-03	165	
83	1.07e-03	3291	
81	9.80e-04	3259	
79	8.21e-04	3257	
77	7.08e-04	3243	
50	5.11e-04	1095	
55	3.99e-04	1134	
33	1.96e-04	716	
4	1.68e-04	52	
75	1.42e-04	3243	
8	1.22e-04	128	
63	1.05e-04	1342	
70	1.01e-04	1524	
2	8.82e-05	35	
13	7.43e-05	299	
5	7.15e-05	61	
3	6.62e-05	43	
45	6.09e-05	910	
35	5.08e-05	749	
25	4.71e-05	595	

29	4.58e-05	663
18	4.57e-05	411
26	4.51e-05	610
6	4.39e-05	83
58	4.33e-05	1234
66	3.93e-05	1434
12	3.65e-05	251
23	2.42e-05	564
72	2.08e-05	1575
37	2.03e-05	768
21	1.67e-05	505
68	1.62e-05	1492
11	1.62e-05	171
1	1.37e-05	22
17	1.31e-05	391
31	1.30e-05	701
65	1.26e-05	1401
39	1.20e-05	818
49	1.09e-05	936
27	1.02e-05	624
19	9.15e-06	468
41	8.13e-06	849
47	7.31e-06	922
56	5.83e-06	1188
30	4.58e-06	701
22	3.39e-06	537
40	3.18e-06	818
24	2.62e-06	586
48	2.17e-06	936
43	2.03e-06	880
38	1.69e-06	770
14	7.81e-07	312
46	9.65e-08	912

3.8 *all-trans*-pentathiophene in normal coordinates

Mode	$ \Delta_i $	ν	type
11	1.01e+00	137	Inter-ring bendings
92	9.60e-01	1600	Inter-ring C–C stretch
91	8.35e-01	1592	Inter-ring C–C stretch
41	7.95e-01	711	Ring breathing
18	6.90e-01	323	Chain deformation
10	4.63e-01	123	
89	4.21e-01	1551	
77	3.48e-01	1281	
75	2.90e-01	1272	
66	2.80e-01	1114	
37	2.65e-01	663	
46	1.50e-01	756	
88	1.49e-01	1527	
64	1.36e-01	1095	
24	1.35e-01	427	
74	1.14e-01	1251	
20	1.07e-01	344	
86	7.72e-02	1499	
79	7.37e-02	1338	
32	7.18e-02	601	
43	6.69e-02	733	

67	5.03e-02	1124
71	3.40e-02	1221
84	3.15e-02	1468
59	2.24e-02	919
54	1.71e-02	876
69	1.59e-02	1137
52	1.52e-02	851
3	1.50e-02	29
82	1.21e-02	1412
102	9.53e-03	3257
103	9.07e-03	3259
76	8.22e-03	1273
12	6.90e-03	137
97	6.60e-03	3243
95	4.80e-03	3242
94	1.34e-03	3242
65	1.16e-03	1112
93	7.04e-04	1603
45	5.74e-04	755
101	5.70e-04	3257
105	5.36e-04	3291
100	5.21e-04	3257
98	4.96e-04	3243
104	4.96e-04	3291
2	2.59e-04	25
96	2.18e-04	3243
99	2.15e-04	3257
1	1.72e-04	14
19	1.27e-04	331
44	1.10e-04	735
5	8.27e-05	39
4	8.04e-05	35
90	6.82e-05	1569
8	6.61e-05	75
78	6.55e-05	1332
87	5.64e-05	1514
68	5.49e-05	1126
21	5.43e-05	365
85	4.31e-05	1497
6	3.60e-05	58
63	3.48e-05	1089
9	3.04e-05	81
14	2.59e-05	174
38	2.53e-05	674
72	2.44e-05	1240
81	2.37e-05	1389
80	1.83e-05	1384
39	1.46e-05	708
16	1.30e-05	248
34	1.23e-05	614
40	1.16e-05	708
26	1.14e-05	494
15	1.11e-05	231
17	1.09e-05	284
42	9.95e-06	717
70	9.61e-06	1197
7	8.62e-06	73
57	8.22e-06	916

83	7.84e-06	1434
51	6.31e-06	834
47	5.01e-06	777
73	4.58e-06	1244
23	4.23e-06	422
53	4.04e-06	860
25	3.84e-06	466
33	3.70e-06	605
58	3.67e-06	917
36	3.58e-06	632
31	3.48e-06	586
48	3.41e-06	785
28	3.28e-06	525
61	2.70e-06	938
22	2.47e-06	395
50	2.37e-06	834
27	2.12e-06	495
56	2.07e-06	912
30	1.59e-06	569
62	1.53e-06	938
35	1.35e-06	623
29	1.33e-06	550
49	7.17e-07	789
13	7.15e-07	168
55	2.61e-07	896
60	2.43e-07	927

3.9 *all-cis*-pentathiophene in normal coordinates

Mode	$ \Delta_i $	ν	type
12	1.30e+00	168	Inter-ring stretch
93	1.07e+00	1591	Inter-ring C–C stretch
39	8.46e-01	658	Ring breathing
91	6.41e-01	1581	Inter-ring C–C stretch
73	5.42e-01	1214	Inner-ring C–S–C stretch
3	4.40e-01	25	
89	3.39e-01	1538	
72	3.13e-01	1193	
38	2.62e-01	643	
88	2.62e-01	1527	
35	1.87e-01	624	
75	1.36e-01	1275	
21	1.31e-01	376	
85	1.04e-01	1490	
22	8.24e-02	396	
10	7.70e-02	123	
44	7.05e-02	743	
63	6.94e-02	1090	
67	6.09e-02	1118	
46	6.06e-02	760	
84	4.74e-02	1461	
18	3.25e-02	304	
54	2.51e-02	906	
79	2.11e-02	1371	
77	1.39e-02	1303	
103	1.20e-02	3269	
65	1.18e-02	1097	
61	8.34e-03	941	

82	5.80e-03	1422
95	4.74e-03	3245
53	4.18e-03	873
101	3.34e-03	3264
69	3.16e-03	1126
97	1.84e-03	3249
2	1.14e-03	20
64	1.03e-03	1090
94	8.96e-04	3245
105	6.34e-04	3292
43	6.08e-04	742
104	4.74e-04	3292
13	4.72e-04	170
99	4.60e-04	3260
45	3.88e-04	759
14	2.89e-04	172
71	2.67e-04	1189
92	2.41e-04	1589
5	2.38e-04	35
4	2.16e-04	31
7	1.83e-04	67
6	1.37e-04	55
1	1.21e-04	18
86	1.03e-04	1494
37	1.03e-04	640
8	8.66e-05	71
68	7.98e-05	1124
9	6.66e-05	83
36	6.40e-05	628
96	4.55e-05	3247
87	4.49e-05	1502
83	3.81e-05	1440
19	3.33e-05	335
70	2.81e-05	1161
27	2.67e-05	487
66	2.53e-05	1104
16	2.47e-05	272
23	2.32e-05	421
56	2.27e-05	914
15	2.26e-05	231
52	2.14e-05	872
102	2.01e-05	3266
80	1.91e-05	1382
34	1.67e-05	609
48	1.51e-05	784
33	1.45e-05	601
26	1.29e-05	463
17	1.29e-05	285
57	1.21e-05	915
50	1.17e-05	831
58	1.10e-05	923
42	1.09e-05	732
24	1.06e-05	421
76	9.49e-06	1288
98	8.74e-06	3252
20	8.74e-06	347
78	8.02e-06	1338
47	7.98e-06	774

28	7.37e-06	514
74	7.23e-06	1252
40	6.94e-06	704
32	6.41e-06	592
60	5.74e-06	936
49	5.71e-06	784
31	4.83e-06	584
62	4.35e-06	945
25	3.93e-06	462
55	3.52e-06	911
100	3.22e-06	3260
11	2.62e-06	131
51	2.43e-06	831
29	2.22e-06	541
41	2.10e-06	704
81	1.77e-06	1417
30	1.33e-06	574
59	7.51e-07	936
90	1.68e-07	1559

3.10 *trans-cis-cis-trans*-pentathiophene in normal coordinates

Mode	$ \Delta_i $	ν	type
12	1.15e+00	167	Inter-ring stretch
91	1.05e+00	1586	Inter-ring C–C stretch
92	7.07e-01	1597	Inter-ring C–C stretch
37	6.74e-01	642	Ring breathing
39	5.68e-01	691	Ring breathing
10	5.39e-01	119	
71	5.33e-01	1199	
3	4.58e-01	26	
89	3.77e-01	1541	
73	2.56e-01	1241	
21	2.34e-01	356	
18	2.17e-01	303	
76	1.99e-01	1276	
23	1.60e-01	421	
46	1.40e-01	756	
88	1.17e-01	1531	
64	1.09e-01	1092	
85	1.00e-01	1497	
67	8.78e-02	1122	
69	3.20e-02	1127	
54	2.20e-02	899	
53	2.13e-02	862	
82	1.57e-02	1417	
44	1.20e-02	739	
59	1.19e-02	925	
84	1.17e-02	1463	
103	1.13e-02	3269	
65	6.77e-03	1101	
95	5.68e-03	3243	
101	4.79e-03	3261	
34	3.93e-03	614	
93	3.03e-03	1598	
77	2.83e-03	1301	
97	2.71e-03	3243	
100	2.30e-03	3257	

13	1.39e-03	168
99	1.16e-03	3257
94	9.48e-04	3243
79	8.93e-04	1354
68	6.27e-04	1125
105	5.03e-04	3291
45	4.70e-04	754
104	4.66e-04	3291
86	3.52e-04	1498
8	3.13e-04	72
4	2.48e-04	36
63	1.72e-04	1090
6	1.68e-04	58
75	1.57e-04	1270
14	1.54e-04	171
9	1.44e-04	82
2	1.36e-04	24
11	1.03e-04	133
87	8.72e-05	1508
5	8.11e-05	40
1	7.65e-05	19
15	5.84e-05	231
90	5.70e-05	1561
52	5.29e-05	862
72	4.09e-05	1232
24	3.97e-05	422
7	3.87e-05	70
22	2.90e-05	420
20	2.80e-05	351
83	2.69e-05	1445
66	2.46e-05	1110
36	2.46e-05	619
78	2.27e-05	1334
17	2.09e-05	285
74	2.05e-05	1261
30	1.96e-05	570
96	1.51e-05	3243
19	1.49e-05	334
102	1.42e-05	3264
80	1.40e-05	1383
43	1.34e-05	739
25	1.31e-05	462
29	1.25e-05	543
50	1.09e-05	833
48	8.13e-06	785
40	6.06e-06	707
55	5.85e-06	906
58	5.30e-06	916
57	4.79e-06	915
61	4.66e-06	937
38	3.81e-06	672
49	3.80e-06	785
16	3.76e-06	260
33	3.25e-06	612
62	3.23e-06	939
70	2.96e-06	1162
47	2.95e-06	774
56	2.94e-06	912

32	2.86e-06	601
42	2.85e-06	732
31	2.58e-06	581
41	2.49e-06	707
81	2.40e-06	1396
60	2.40e-06	937
51	1.69e-06	833
27	1.41e-06	491
26	9.15e-07	469
98	8.95e-07	3251
28	4.43e-07	524
35	3.04e-07	615

4 Excited-state structures

The applied excited-state equilibrium structures [TDDFT/CAM-B3LYP/6-31+g(d)] for the different oligothiophenes, conformations, and models for a luminescent biomarker are provided in separate files in xyz format in structures.xyz.zip. The naming of the files is listed in Table S-13.

Table S-13: Naming of the separate xyz files with the excited-state structures [TDDFT/CAM-B3LYP/6-31+g(d)] and the figures in the main text, where they are depicted.

Molecule	File name	Depicted in the main text in
<i>trans</i> -bithiophene	2T_trans.xyz	Figs. 2(c)–(f)
<i>cis</i> -bithiophene	2T_cis.xyz	Fig. 2(g), Fig. 6(a)
<i>all-trans</i> -terthiophene	3T_all-trans.xyz	Figs. 2(c)–(d), 5(a)–(b)
<i>all-trans</i> -quaterthiophene	4T_all-trans.xyz	Figs. 5(c)–(d)
<i>all-trans</i> -pentathiophene	5T_all-trans.xyz	Figs. 5(e)–(f)
<i>trans-cis-cis-trans</i> -pentathiophene	5T_trans_cis_cis_trans.xyz	Fig. 6(b)
<i>all-cis</i> -pentathiophene	5T_all-cis.xyz	Fig. 6(c)
<i>all-trans</i> -terthiophene biomarker models		
with two acid groups	3T_all-trans_2groups.xyz	Figs. 7(a)–(b)
with four acid groups	3T_all-trans_4groups.xyz	Fig. 7(c)