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# Vibronic relaxation energies of acene-related molecules upon excitation or ionization – electronic supplement

Marcin Andrzejak[a,†] and Piotr Petelenz[a]

[a] *Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland*

## 1. Comparison of the CC2 results with the results of alternative calculations.

Table S1.1 Reorganization energies for anthracene and 2-2'-bithiophene calculated using a series of three correlation-consistent basis sets of increasing size. Values in parentheses refer to the reorganization energy for transitions that occur in the reversed direction with respect to that given in column 1.

| | **anthracene** | | | **3T** | | | **6T** | | |
|---|---|---|---|---|---|---|---|---|---|
| | **cc-pVDZ** | **aug-cc-pVDZ** | **cc-pVTZ** | **cc-pVDZ** | **aug-cc-pVDZ** | **cc-pVTZ** | **cc-pVDZ** | **aug-cc-pVDZ** | **cc-pVTZ** |
| **gr. st. → anion** | 852 (825) | 850 (786) | 877 (850) | 1387 (1381) | 1205 (1215) | 1351 (1347) | 1316 (1369) | 1188 (1237) | 1288 (1338) |
| **gr. st. → cation** | 523 (514) | 481 (481) | 532 (515) | 1448 (1437) | 1362 (1333) | 1437 (1424) | 1435 (1503) | 1323 (1441) | 1441 (1502) |
| **anion → $S_1$** | 278 (269) | 261 (272) | 293 (284) | 594 (589) | 612 (591) | 636 (629) | 346 (341) | 334 (353) | (355) |
| **cation → $S_1$** | 457 (440) | 489 (442) | 492 (473) | 347 (345) | 302 (300) | 352 (336) | 208 (205) | 183 (175) | 202 (199) |
| **anion → $T_1$** | 612 (624) | 568 (595) | 624 (633) | 892 (911) | 871 (876) | 933 (947) | 549 (569) | 537 (592) | 594 (609) |
| **cation → $T_1$** | 764 (779) | 782 (753) | 805 (809) | 722 (738) | 681 (683) | 743 (758) | 457 (484) | 431 (445) | 475 (498) |
| **gr. st. → $S_1$** | 1705 (1570) | 1661 (1524) | 1784 (1641) | 2101 (1873) | 1997 (1776) | 2160 (1922) | 1916 (1745) | 1737 (1618) | 1929 (1739) |
| **$S_1 \rightarrow T_1$** | 157 (179) | 137 (152) | 147 (165) | 205 (232) | 204 (235) | 212 (239) | 151 (193) | 155 (198) | 167 (212) |
| **gr. st. → $T_1$** | 2310 (2265) | 2229 (2158) | 2393 (2331) | 2989 (2976) | 2854 (2813) | 3084 (3042) | 2473 (2643) | 2342 (2532) | 2568 (2711) |

[†] Author to whom correspondence should be addressed. Electronic mail: andrzeja@chemia.uj.edu.pl

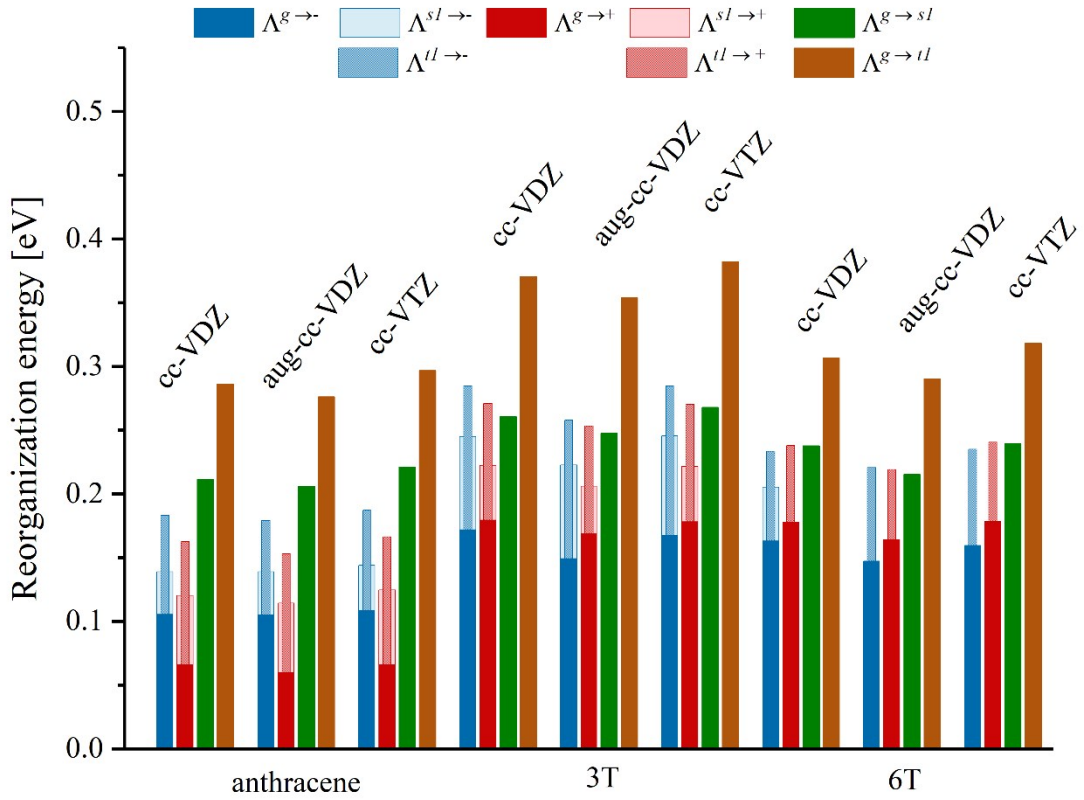


Figure S1.1 Comparison of reorganization energies for the electronic transitions/ionization processes under study calculated for selected compounds using the CC2 method with the cc-pVDZ, aug-cc-pVDZ and cc-pVTZ basis sets.

Table S1.2: Reorganization energies [in $cm^{-1}$] based on the CASPT2 calculations with the cc-pVDZ basis set. Values in parentheses refer to the reorganization energy for transitions that occur in the reversed direction with respect to that given in column 1.

| | **f3T** | **f4T** | **f3cp** | **f3O** | **f4O** |
|---|---|---|---|---|---|
| **gr. st. → anion** | 1299 (1290) | 1241 (1239) | 1349 (1285) | 1725 (1669) | 1590 (1580) |
| **gr. st. → cation** | 1404 (1370) | 1399 (1327) | 1316 (1221) | 1295 (1254) | 1375 (1292) |
| **anion → $S_1$** | x | 703 (695) | 876 (774) | x | x |
| **cation → $S_1$** | x | 753 (495) | 428 (357) | x | x |
| **anion → $T_1$** | 1072 (1011) | 1051 (940) | 1181 (1172) | 1062 (1075) | 1111 (1135) |
| **cation → $T_1$** | 963 (897) | 920 (807) | 1061 (1074) | 1302 (1311) | 554 (789) |
| **gr. st. → $S_1$** | x | 2117 (1915) | 2531 (2171) | x | x |
| **$S_1 \rightarrow T_1$** | x | 281 (413) | 517 (609) | x | x |
| **gr. st. → $T_1$** | 3131 (3027) | 2836 (2834) | 4104 (3783) | 3551 (3423) | 3246 (3208) |

Compositions of the active spaces (number of orbitals of a given symmetry/number of active electrons):
f3T: $6b_1 5a_2$/14, no convergence for the $S_1$ state
f4T: $7b_g 6a_u$/14, geometry convergence for the $S_1$ state required state-averaging at the CASSCF step over 3 $^1B_u$ states, followed by state-specific CASPT2
f3cp: $6b_1 5a_2$/14 for $S_1$ : geometry convergence for the $S_1$ state required state-averaging at the CASSCF step over 2 $^1B_1$ states, followed by state-specific CASPT2
f3O: $7b_1 6a_2$/14, no convergence for the $S_1$ state
f4O: $6b_g 6a_u$/14, no convergence for the $S_1$ state
[+] Failed convergence of the CASPT2 calculations was caused by energetic proximity of higher lying singlet states of the same symmetry as the lowest singlet state (whose geometry is being optimized) – their mixing with the its wavefunction leads to large rotations between the active/virtual subspaces that strongly depend on molecular geometry, which eventually results in instability of the calculations. This behavior might be attenuated for active spaces that accommodate all the orbitals important for all structures sampled in the process of geometry optimizations, but for such large active spaces geometry optimizations at the CASPT2 level of theory are completely unfeasible.

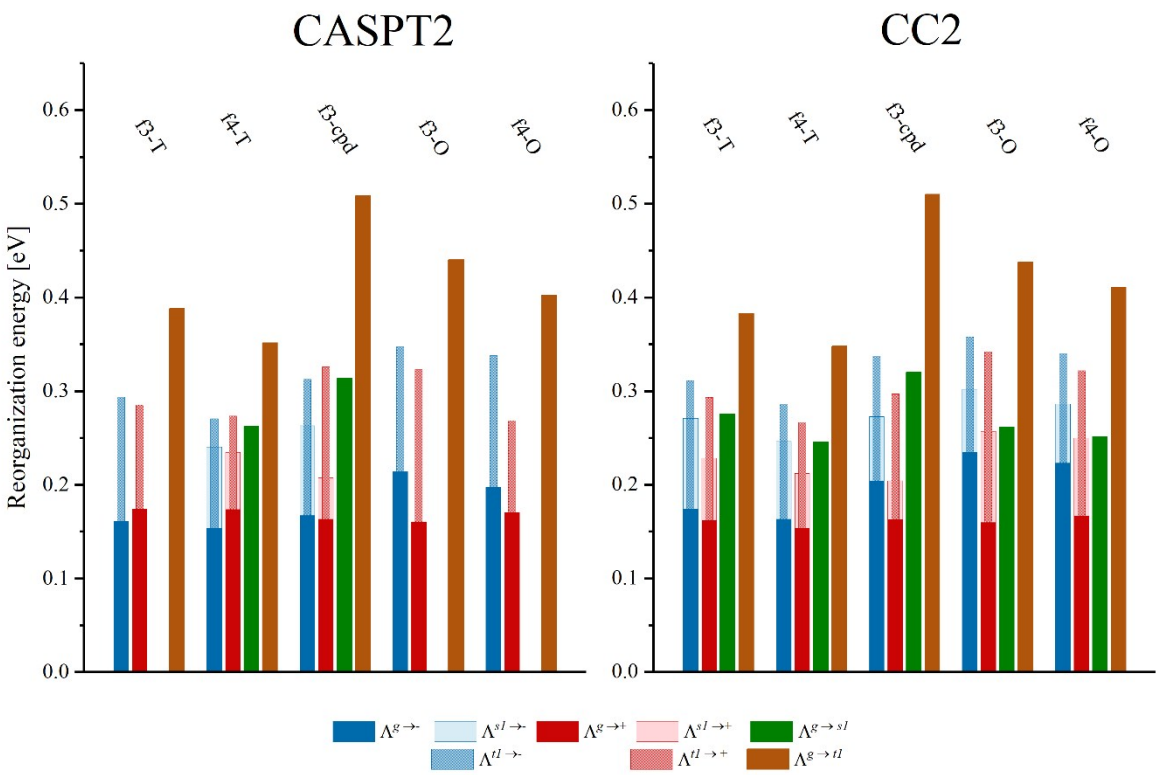


Figure S1.2 Comparison of reorganization energies for the electronic transitions/ionization processes under study calculated for selected compounds by CC2 and CCSD methods using the cc-pVDZ basis set.

On average, the difference between the CASPT2 and CC2-based results is 20.4 cm$^{-1}$. The mean unsigned error is 103.4 cm$^{-1}$, which is 9% of the average CC2-based value.

Table S1.3: Reorganization energies [in $cm^{-1}$] at the CCSD/cc-pVDZ level of theory for the selected hydrocarbons and heterocyclic compounds. Values in parentheses refer to the reorganization energy for transitions that occur in the reversed direction with respect to that given in column 1.

**Hydrocarbons:**

| | **antracene** | **tetracene** | **3cp** | **f3cp** | **f4cp** | **f5cp** |
|---|---|---|---|---|---|---|
| **gr. st. → anion** | 1008 (960) | 879 (856) | 1518 (1573) | 1625 (1651) | 1661 (1725) | 1698 (1805) |
| **gr. st. → cation** | 748 (736) | 675 (656) | 1652 (1712) | 1568 (1554) | 1658 (1661) | 1739 (1770) |
| **anion → $S_1$** | 323 (315) | 275 (266) | 447 (447) | 612 (621) | 517 (523) | 444 (447) |
| **cation → $S_1$** | 469 (455) | 390 (379) | 311 (319) | 447 (459) | 366 (376) | 308 (317) |
| **anion → $T_1$** | 741 (786) | 758 (797) | 1204 (1313) | 1394 (1465) | 1342 (1425) | 1300 (1398) |
| **cation → $T_1$** | 879 (923) | 857 (893) | 1066 (1162) | 1327 (1423) | 1241 (1352) | 1181 (1308) |
| **gr. st. → $S_1$** | 2084 (1981) | 1743 (1621) | 2565 (2324) | 2939 (2699) | 2745 (2468) | 2622 (2323) |
| **$S_1 \rightarrow T_1$** | 205 (236) | 235 (265) | 608 (801) | 657 (811) | 677 (882) | 709 (976) |
| **gr. st. → $T_1$** | 2866 (2971) | 2654 (2687) | 4400 (4956) | 4930 (5175) | 4827 (5210) | 4762 (5322) |

**Heterocyclic compounds:**

| | **f3T** | **f4T** | **3T** | **f3O** | **f4O** | **3O** |
|---|---|---|---|---|---|---|
| **gr. st. → anion** | 1491 (1501) | 1432 (1448) | 1419 (1452) | 1885 (1919) | 1816 (1861) | 1628 (1651) |
| **gr. st. → cation** | 1625 (1615) | 1588 (1579) | 1718 (1754) | 1566 (1523) | 1643 (1602) | 1662 (1709) |
| **anion → $S_1$** | 817 (812) | 723 (711) | 669 (660) | 590 (589) | 555 (552) | 513 (507) |
| **cation → $S_1$** | 504 (502) | 454 (450) | 348 (344) | 769 (775) | 679 (685) | 452 (448) |
| **anion → $T_1$** | 1154 (1192) | 1057 (1086) | 1056 (1098) | 1177 (1218) | 1103 (1141) | 933 (980) |
| **cation → $T_1$** | 1106 (1149) | 959 (994) | 932 (974) | 1614 (1675) | 1387 (1439) | 1101 (1149) |
| **gr. st. → $S_1$** | 2629 (2432) | 2482 (2296) | 2528 (2330) | 2370 (2146) | 2354 (2129) | 2571 (2369) |
| **$S_1 \rightarrow T_1$** | 234 (261) | 172 (193) | 285 (324) | 431 (500) | 347 (406) | 307 (358) |
| **gr. st. → $T_1$** | 3683 (3807) | 3426 (3562) | 3623 (3830) | 4147 (4258) | 3955 (4086) | 3841 (4080) |

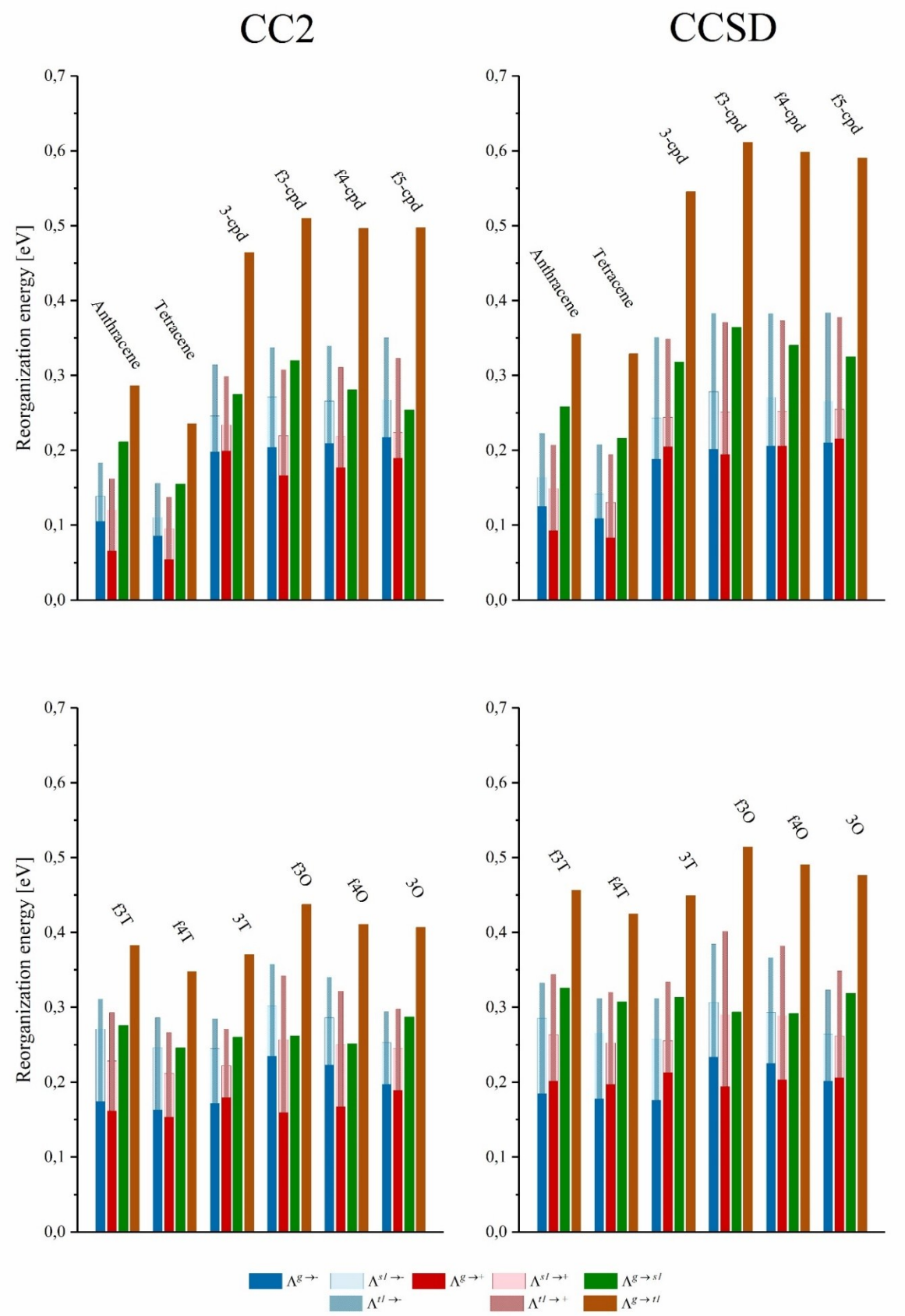


Figure S1.3 Comparison of relaxation energies for the electronic transitions/ionization processes under study calculated for selected compounds by CC2 and CCSD methods using the cc-pVDZ basis set.

The CCSD results are generally higher than the CC2 ones. The average difference between the CCSD and CC2-based reorganization energies is 277 $cm^{-1}$, while the mean unsigned error is 283 $cm^{-1}$, which is 17.9% with respect to the average CC2-based value.

Table S1.4 Reorganization energies for pentacene calculated using CC2 (with two different correlation consistent basis sets) and DFT/TDDFT with the B3LYP exchange-correlation functional and def2-TZVPP basis set. Values in parentheses refer to the reorganization energy for transitions that occur in the reversed direction with respect to that given in column 1.

| | **CC2/ cc-pVDZ** | **CC2/ cc-pVTZ** | **B3LYP/ def2-TZVPP** |
|---|---|---|---|
| **gr. st. → anion** | 565 (541) | 577 (553) | 539 (552) |
| **gr. st. → cation** | 362 (342) | 362 (340) | 385 (395) |
| **anion → $S_1$** | 161 (156) | 171 (165) | 266 (266) |
| **cation → $S_1$** | 268 (260) | 286 (278) | 356 (356) |
| **anion → $T_1$** | 515 (522) | 514 (518) | 604 (597) |
| **cation → $T_1$** | 583 (585) | 600 (601) | 654 (646) |
| **gr. st. → $S_1$** | 930 (828) | 974 (866) | 1182 (1188) |
| **$S_1$ → $T_1$** | 184 (204) | 169 (187) | 130 (133) |
| **gr. st. → $T_1$** | 1571 (1481) | 1603 (1503) | 1784 (1770) |

## 2. Bond length correlations

Figures S2.1 and S2.2 show the calculated lengths of the CC bonds [in Å] for hexaphenyl and sexithiophene ions plotted against the respective lengths in the a) ground state and b) S1 state of the corresponding neutral molecule. It is readily seen that the electronic structure of the ions closely resembles that of the molecule in the excited state, but not in the ground state. Note that much larger differences between the bond lengths of the ions and for the ground state are observed for 6T, which demonstrate the influence of heteroatoms on the molecular geometries in different electronic states.

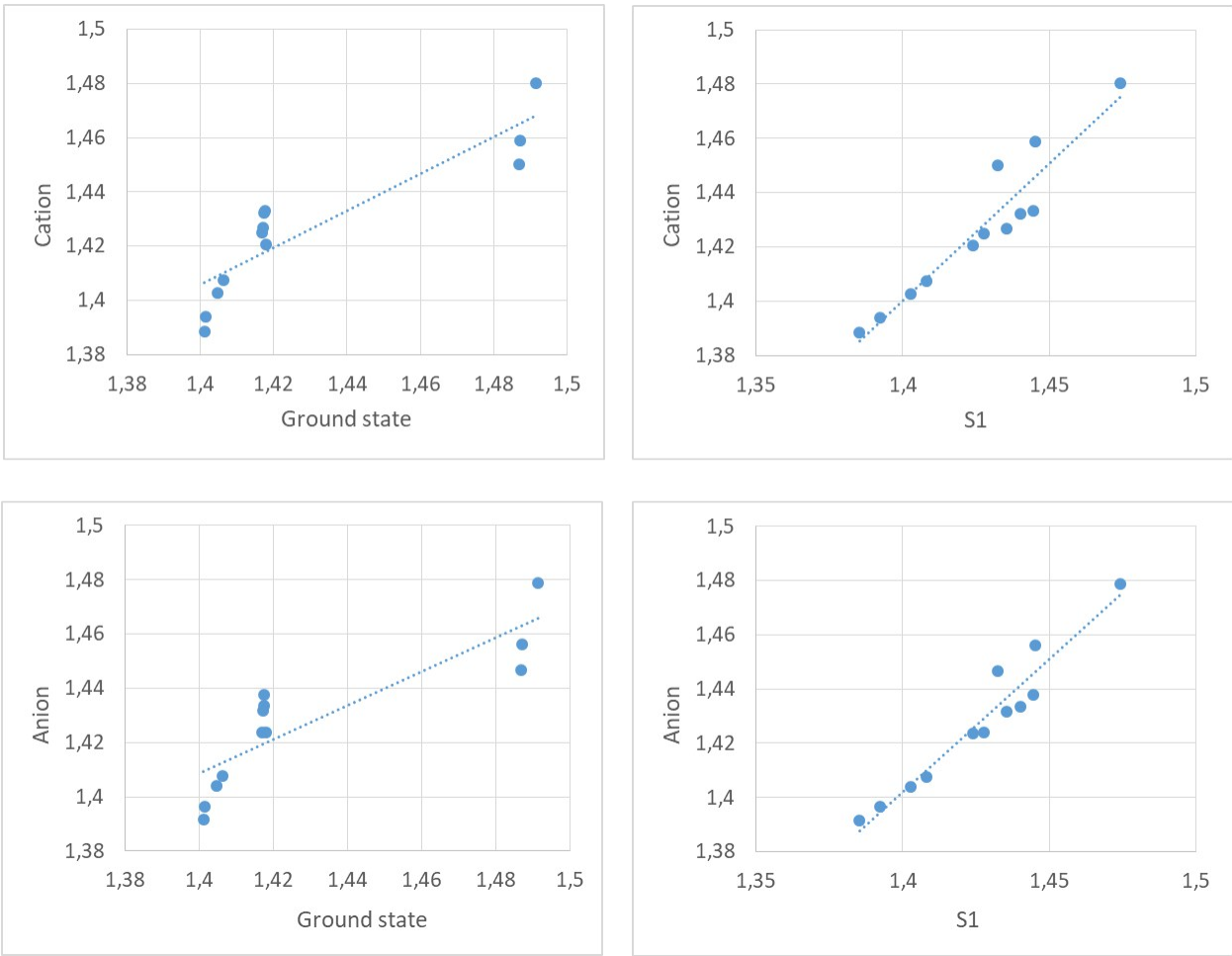


Figure S2.1 Bond lengths [in Å] of the hexaphenyl ions along the carbon skeleton of the molecule against the respective bond lengths of the ground and excited states of 6Ph. The linear regression coefficients $r^2$ for the cation and the anion vs the ground state are equal to 0.81 and 0.76, respectively. The analogous coefficients with respect to the S1 state are equal to 0.90 and 0.93

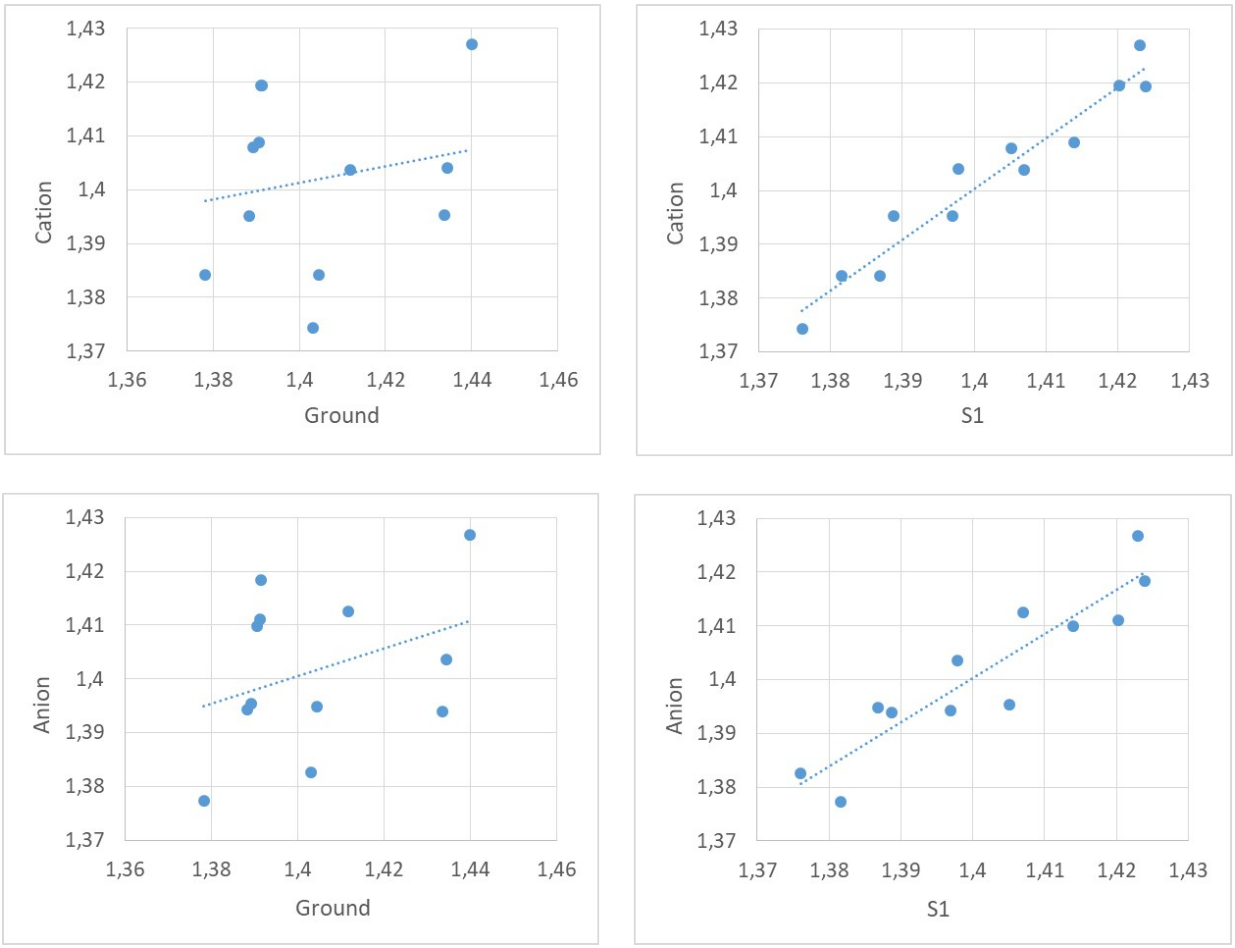


Figure S2.2 Bond lengths [in Å] of the sexithiophene ions along the carbon skeleton of the molecule against the respective bond lengths of the ground and excited states of 6T. The linear regression coefficients $r^2$ for the cation and the anion vs the ground state are equal to 0.04 and 0.13, respectively. The analogous coefficients with respect to the S1 state are equal to 0.94 and 0.84

**3. Comparison of the relaxation energies upon singlet and triplet excitation**

Table S3 clearly shows that the relaxation energy for the singlet-to-triplet transition is marginal with respect to those for singlet or triplet excitation from the ground state.

Table S3. Relaxation energies [in $cm^{-1}$] for singlet ($\Lambda^{g\rightarrow S1}$) and triplet ($\Lambda^{g\rightarrow T1}$) excitation, and for the singlet to triplet transition ($\Lambda^{S1\rightarrow T1}$).Values in parentheses refer to the reorganization energy for transitions that occur in the reversed direction with respect to that given in column 1.

**Oligoacenes**

| | **antracene** | **tetracene** | **pentacene** | **hexacene** |
|---|---|---|---|---|
| **gr. st. → $S_1$** | 1705 (1570) | 1252 (1132) | 930 (828) | 692 (610) |
| **$S_1$ → $T_1$** | 157 (179) | 171 (188) | 184 (204) | 192 (213) |
| **gr. st. → $T_1$** | 2310 (2265) | 1898 (1820) | 1571 (1481) | 1298 (1206) |

**Oligophenyls**

| | 3Ph | 4Ph | 5Ph | 6Ph |
|---|---|---|---|---|
| **gr. st. → $S_1$** | 2276 (2133) | 2131 (2020) | 2040 (1968) | 1955 (1922) |
| **$S_1$ → $T_1$** | 88 (100) | 74 (85) | 66 (79) | 67 (82) |
| **gr. st. → $T_1$** | 2669 (2800) | 2440 (2592) | 2245 (2426) | 2081 (2304) |

**Oligocyclopentadienes (*n*-cpds) and fused oligocyclopentadienes (f*n*-cpds)**

| | f3-cpd | f4-cpd | 2-cpd | 3-cpd | 4-cpd |
|---|---|---|---|---|---|
| **gr. st. → $S_1$** | 2581 (2322) | 2265 (1946) | 2691 (2475) | 2579 (2300) | 2105 (1718) |
| **$S_1$ → $T_1$** | 480 (598) | 567 (767) | 507 (605) | 493 (675) | 584 (972) |
| **gr. st. → $T_1$** | 4114 (4111) | 4004 (4047) | 4021 (4063) | 3744 (3920) | 3732 (4233) |

**Oligothophenes**

| | 2T | 3T | 4T | 5T | 6T |
|---|---|---|---|---|---|
| **gr. st. → $S_1$** | 2562 (2351) | 2101 (1873) | 1961 (1736) | 1923 (1719) | 1916 (1745) |
| **$S_1$ → $T_1$** | 303 (309) | 205 (232) | 189 (226) | 167 (205) | 151 (193) |
| **gr. st. → $T_1$** | 3430 (2419) | 2989 (2976) | 2765 (2813) | 2602 (2710) | 2473 (2643) |

**Oligofurans**

| | 2O | 3O | 4O | 5O | 6O |
|---|---|---|---|---|---|
| **gr. st. → $S_1$** | 2691 (2475) | 2319 (2088) | 2219 (2000) | 2190 (2005) | 2168 (2031) |
| **$S_1$ → $T_1$** | 280 (290) | 218 (250) | 188 (228) | 166 (207) | 156 (203) |
| **gr. st. → $T_1$** | 3722 (3726) | 3281 (3319) | 2842 (3022) | 2842 (3022) | 2680 (2933) |

**Fused oligothiophenes**

| | f3T | f4T | f5T | f6T |
|---|---|---|---|---|
| **gr. st. → $S_1$** | 2224 (2040) | 1983 (1810) | 1879 (1699) | 1785 (1609) |
| **$S_1$ → $T_1$** | 178 (198) | 141 (156) | 115 (129) | 107 (121) |
| **gr. st. → $T_1$** | 3087 (3083) | 2805 (2793) | 2620 (2611) | 2482 (2478) |

**Fused oligofurans**

| | f3O | f4O | f5O | f6O |
|---|---|---|---|---|
| **gr. st. → $S_1$** | 2110 (1891) | 2026 (1804) | 1974 (1752) | 1928 (1702) |
| **$S_1$ → $T_1$** | 344 (396) | 273 (319) | 241 (282) | 232 (274) |
| **gr. st. → $T_1$** | 3529 (3525) | 3316 (3315) | 3186 (3192) | 3092 (3122) |

**4. Duschinsky rotations among the totally symmetric normal modes of pentacene**

Table S4. The Duschinsky matrices for all the studied transitions of pentacene obtained in B3LYP/def2-TZVPP calculations. For the sake of clarity the values smaller than 0.1 have been omitted.

| **S1/gr** | **264** | **617** | **648** | **764** | **797** | **1019** | **1186** | **1209** | **1333** | **1410** | **1433** | **1497** | **1558** | **1576** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **262** | 1.0 | | | | | | | | | | | | | |
| **613** | | -0.96 | | | | | | | | | | | | |
| **628** | | | -0.96 | | | | | | | | | | | |
| **757** | | | | 1.0 | | | | | | | | | | |
| **804** | | | | | 1.0 | | | | | | | | | |
| **1048** | | | | | | -0.99 | | | | | | | | |
| **1183** | | | | | | | -0.99 | | | | | | | |
| **1221** | | | | | | | | -0.99 | | | | | | |
| **1312** | | | | | | | | | -0.87 | -0.32 | 0.35 | | | |
| **1382** | | | | | | | | | -0.38 | | -0.85 | | | |
| **1426** | | | | | | | | | | 0.93 | | | | |
| **1511** | | | | | | | | | | | | 0.88 | | -0.33 |
| **1536** | | | | | | | | | | | | | -0.94 | |
| **1578** | | | | | | | | | | | | 0.34 | | 0.88 |

| **+/gr** | **264** | **617** | **648** | **764** | **797** | **1019** | **1186** | **1209** | **1333** | **1410** | **1433** | **1497** | **1558** | **1576** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **263** | 1.0 | | | | | | | | | | | | | |
| **615** | | 1.0 | | | | | | | | | | | | |
| **639** | | | -1.0 | | | | | | | | | | | |
| **764** | | | | 1.0 | | | | | | | | | | |
| **805** | | | | | -1.0 | | | | | | | | | |
| **1040** | | | | | | 1.0 | | | | | | | | |
| **1198** | | | | | | | 0.99 | | | | | | | |
| **1221** | | | | | | | | 0.99 | | | | | | |
| **1330** | | | | | | | | | -0.96 | | | | | |
| **1409** | | | | | | | | | | | -0.93 | | | |
| **1426** | | | | | | | | | | -0.93 | | | | |
| **1510** | | | | | | | | | | | | 0.95 | | |
| **1551** | | | | | | | | | | | | | 0.90 | 0.35 |
| **1578** | | | | | | | | | | | | | -0.40 | 0.88 |

| -/gr | 264 | 617 | 648 | 764 | 797 | 1019 | 1186 | 1209 | 1333 | 1410 | 1433 | 1497 | 1558 | 1576 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **263** | 1.0 | | | | | | | | | | | | | |
| **617** | | 1.0 | | | | | | | | | | | | |
| **640** | | | 1.0 | | | | | | | | | | | |
| **755** | | | | -0.99 | | | | | | | | | | |
| **796** | | | | | 0.99 | | | | | | | | | |
| **1033** | | | | | | -1.0 | | | | | | | | |
| **1171** | | | | | | | 1.0 | | | | | | | |
| **1210** | | | | | | | | 1.0 | | | | | | |
| **1310** | | | | | | | | | 0.96 | | | | | |
| **1391** | | | | | | | | | | 0.36 | -0.88 | | | |
| **1410** | | | | | | | | | | 0.90 | 0.39 | | | |
| **1498** | | | | | | | | | | | | 0.96 | | |
| **1535** | | | | | | | | | | | | | 0.95 | |
| **1563** | | | | | | | | | | | | | | -0.94 |

| T1/gr | 264 | 617 | 648 | 764 | 797 | 1019 | 1186 | 1209 | 1333 | 1410 | 1433 | 1497 | 1558 | 1576 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **261** | -1.0 | | | | | | | | | | | | | |
| **613** | | -0.93 | 0.36 | | | | | | | | | | | |
| **631** | | 0.36 | 0.93 | | | | | | | | | | | |
| **755** | | | | -0.98 | | | | | | | | | | |
| **807** | | | | | -0.97 | | | | | | | | | |
| **1051** | | | | | | -0.99 | | | | | | | | |
| **1183** | | | | | | | 0.98 | | | | | | | |
| **1216** | | | | | | | | 0.97 | | | | | | |
| **1271** | | | | | | | | | 0.86 | 0.36 | | | | |
| **1358** | | | | | | | | | | | -0.85 | | | 0.35 |
| **1435** | | | | | | | | | 0.37 | -0.89 | | | | |
| **1496** | | | | | | | | | | | | 0.68 | -0.54 | -0.33 |
| **1535** | | | | | | | | | | | | -0.61 | -0.77 | |
| **1592** | | | | | | | | | | | | | | -0.87 |

| +/S1 | 262 | 613 | 628 | 757 | 804 | 1048 | 1183 | 1221 | 1312 | 1382 | 1426 | 1511 | 1536 | 1578 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **263** | 1.0 | | | | | | | | | | | | | |
| **615** | | -0.98 | | | | | | | | | | | | |
| **639** | | | 0.98 | | | | | | | | | | | |
| **764** | | | | -1.0 | | | | | | | | | | |
| **805** | | | | | 1.0 | | | | | | | | | |
| **1040** | | | | | | -1.0 | | | | | | | | |
| **1198** | | | | | | | -1.0 | | | | | | | |
| **1221** | | | | | | | | 1.0 | | | | | | |
| **1330** | | | | | | | | | 0.96 | | | | | |
| **1409** | | | | | | | | | | 0.94 | | | | |
| **1426** | | | | | | | | | | | -0.97 | | | |
| **1510** | | | | | | | | | | | | 0.98 | | |
| **1551** | | | | | | | | | | | | | -0.95 | |
| **1578** | | | | | | | | | | | | | | 0.96 |

| **-/S1** | **262** | **613** | **628** | **757** | **804** | **1048** | **1183** | **1221** | **1312** | **1382** | **1426** | **1511** | **1536** | **1578** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **263** | -1.0 | | | | | | | | | | | | | |
| **617** | | -0.98 | | | | | | | | | | | | |
| **640** | | | -0.98 | | | | | | | | | | | |
| **755** | | | | 1.0 | | | | | | | | | | |
| **796** | | | | | -1.0 | | | | | | | | | |
| **1033** | | | | | | 1.0 | | | | | | | | |
| **1171** | | | | | | | -1.0 | | | | | | | |
| **1210** | | | | | | | | 1.0 | | | | | | |
| **1310** | | | | | | | | | -0.97 | | | | | |
| **1391** | | | | | | | | | | 0.90 | 0.34 | | | |
| **1410** | | | | | | | | | | -0.34 | 0.93 | | | |
| **1498** | | | | | | | | | | | | 0.96 | | |
| **1535** | | | | | | | | | | | | | -0.97 | |
| **1563** | | | | | | | | | | | | | | -0.98 |

| **T1/S1** | **262** | **613** | **628** | **757** | **804** | **1048** | **1183** | **1221** | **1312** | **1382** | **1426** | **1511** | **1536** | **1578** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **261** | 1.0 | | | | | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **613** | | 0.99 | | | | | | | | | | | | |
| **631** | | | -1.0 | | | | | | | | | | | |
| **755** | | | | 0.99 | | | | | | | | | | |
| **807** | | | | | 0.99 | | | | | | | | | |
| **1051** | | | | | | 1.0 | | | | | | | | |
| **1183** | | | | | | | -1.0 | | | | | | | |
| **1216** | | | | | | | | 0.98 | | | | | | |
| **1271** | | | | | | | | | -0.97 | | | | | |
| **1358** | | | | | | | | | | 0.99 | | | | |
| **1435** | | | | | | | | | | | -1.0 | | | |
| **1496** | | | | | | | | | | | | 0.92 | 0.36 | |
| **1535** | | | | | | | | | | | | -0.37 | 0.93 | |
| **1592** | | | | | | | | | | | | | | -1.0 |

**5. Sensitivity of Franck-Condon parameters for excited state ionization to consistency of input data**

Table S5 demonstrates the importance of consistency in evaluation of FC parameters for ionization from the excited state. The pertinent $b^{S1\to\pm}$ values are deduced from the corresponding FC parameters for singlet excitation and ground-state ionization. The FC parameters for ground state ionization being fixed at their values from TDDFT calculations, in some modes the change of the FC parameter for singlet excitation from its TDDFT value to that obtained from the CC2 method changes the resultant $b^{S1\to\pm}$ parameter by a factor of 2 to 5.

Table S5. Franck-Condon parameters $b^{S1\to\pm}$ for ionization of a singlet-excited pentacene molecule, calculated from Eq.(1) as the differences between the corresponding values for singlet deexcitation to ground state ($b^{S1\to g}$) and for transitions from ions to the ground state ($b^{\pm\to g}$), based on consistent and inconsistent input. Columns 1-6 are consistent TDDFT values, whereas the resultant $b^{S1\to\pm}$ values from columns 8, 9 are derived from the CC2 singlet excitation $b^{S1\to g}$ values (column 7) by subtracting the $b^{+\to g}$ or $b^{-\to g}$ of TDDFT origin.

| Freq. [cm$^{-1}$] | $b^{+\to g}$ | $b^{S1\to+}$ | $b^{-\to g}$ | $b^{S1\to-}$ | $b^{S1\to g}$ | $b^{S1\to g}$ | $b^{S1\to+}$ | $b^{S1\to-}$ |
|---|---|---|---|---|---|---|---|---|
| | DFT | **DFT** | DFT | **DFT** | DFT | **CC2** | **CC2/DFT** | **CC2/DFT** |
| **264** | 0.262 | **-0.928** | -1.063 | **0.397** | -0.666 | **-0.647** | **-0.909** | **-0.416** |
| **617** | 0.00 | **-0.221** | -0.300 | **0.079** | -0.221 | **-0.128** | **-0.128** | **0.172** |
| **648** | 0.00 | **-0.049** | -0.034 | **-0.015** | -0.049 | **-0.044** | **-0.044** | **-0.010** |
| **764** | -0.063 | **-0.280** | -0.161 | **-0.182** | -0.343 | **-0.294** | **-0.231** | **-0.133** |
| **797** | 0.089 | **0.043** | 0.116 | **0.016** | 0.132 | **0.059** | **-0.030** | **-0.057** |
| **1019** | -0.117 | **-0.057** | -0.068 | **0.106** | -0.174 | **-0.095** | **-0.022** | **-0.027** |
| **1186** | 0.164 | **0.171** | 0.209 | **0.126** | 0.335 | **0.273** | **0.109** | **0.064** |
| **1209** | 0.325 | **0.251** | 0.347 | **0.229** | 0.576 | **0.361** | **0.036** | **0.014** |
| **1333** | 0.027 | **0.062** | 0.040 | **0.049** | 0.089 | **0.151** | **0.124** | **0.111** |
| **1410** | -0.393 | **-0.330** | -0.457 | **-0.266** | -0.723 | **-0.514** | **-0.121** | **-0.057** |
| **1433** | 0.157 | **0.230** | 0.280 | **0.107** | 0.387 | **-0.588** | **-0.431** | **-0.308** |
| **1497** | 0.059 | **0.068** | 0.090 | **0.037** | 0.127 | **0.163** | **0.194** | **0.073** |
| **1557** | -0.422 | **-0.124** | -0.194 | **-0.352** | -0.546 | **-0.398** | **0.024** | **-0.204** |
| **1576** | -0.147 | **-0.115** | -0.120 | **-0.142** | -0.262 | **-0.113** | **0.034** | **0.007** |

## 6. Complete set of reorganization energies for all the studied oligomers

Table S6. Reorganization energies [in $cm^{-1}$] for all the studied systems calculated at the CC2/cc-pVDZ level of theory. Values in parentheses refer to the reorganization energy for transitions that occur in the reversed direction with respect to that given in column 1.

**Oligoacenes**

| | **antracene** | **tetracene** | **pentacene** | **hexacene** |
|---|---|---|---|---|
| **gr. st. → anion** | 852 (825) | 691 (666) | 565 (541) | 462 (442) |
| **gr. st. → cation** | 523 (514) | 439 (419) | 362 (342) | 293 (274) |
| **anion → $S_1$** | 278 (269) | 209 (202) | 161 (156) | 128 (125) |
| **cation → $S_1$** | 457 (440) | 345 (333) | 268 (260) | 218 (213) |
| **anion → $T_1$** | 612 (624) | 562 (569) | 515 (522) | 469 (476) |
| **cation → $T_1$** | 764 (779) | 664 (672) | 583 (585) | 517 (520) |
| **gr. st. → $S_1$** | 1705 (1570) | 1252 (1132) | 930 (828) | 692 (610) |
| **$S_1$ → $T_1$** | 157 (179) | 171 (188) | 184 (204) | 192 (213) |
| **gr. st. → $T_1$** | 2310 (2265) | 1898 (1820) | 1571 (1481) | 1298 (1206) |

**Oligophenyls**

| | **3Ph** | **4Ph** | **5Ph** | **6Ph** |
|---|---|---|---|---|
| **gr. st. → anion** | 1354 (1355) | 1254 (1269) | 1170 (1195) | 1092 (1126) |
| **gr. st. → cation** | 1029 (1040) | 1005 (1028) | 965 (999) | 914 (955) |
| **anion → $S_1$** | 423 (412) | 366 (355) | 339 (329) | 324 (314) |
| **cation → $S_1$** | 427 (404) | 374 (354) | 351 (333) | 338 (323) |
| **anion → $T_1$** | 622 (644) | 542 (564) | 485 (510) | 449 (481) |
| **cation → $T_1$** | 671 (684) | 567 (583) | 501 (522) | 463 (494) |
| **gr. st. → $S_1$** | 2276 (2133) | 2131 (2020) | 2040 (1968) | 1955 (1922) |
| **$S_1$ → $T_1$** | 88 (100) | 74 (85) | 66 (79) | 67 (82) |
| **gr. st. → $T_1$** | 2669 (2800) | 2440 (2592) | 2245 (2426) | 2081 (2304) |

**Oligocyclopentadienes (*n*-cpds) and fused oligocyclopentadienes (f*n*-cpds)**

| | f3-cpd | f4-cpd | 2-cpd | 3-cpd | 4-cpd |
|---|---|---|---|---|---|
| **gr. st. → anion** | 1648 (1621) | 1687 (1658) | 1561 (1522) | 1597 (1583) | 1731 (1781) |
| **gr. st. → cation** | 1344 (1318) | 1428 (1387) | 1473 (1463) | 1609 (1620) | 1809 (1890) |
| **anion → $S_1$** | 543 (552) | 451 (460) | 540 (535) | 385 (387) | 280 (281) |
| **cation → $S_1$** | 428 (432) | 326 (334) | 474 (480) | 274 (281) | 193 (194) |
| **anion → $T_1$** | 1039 (1074) | 997 (1052) | 1066 (1113) | 879 (941) | 781 (885) |
| **cation → $T_1$** | 1097 (1140) | 1014 (1080) | 983 (1011) | 758 (803) | 650 (734) |
| **gr. st. → $S_1$** | 2581 (2322) | 2265 (1946) | 2691 (2475) | 2579 (2300) | 2105 (1718) |
| **$S_1$ → $T_1$** | 480 (598) | 567 (767) | 507 (605) | 493 (675) | 584 (972) |
| **gr. st. → $T_1$** | 4114 (4111) | 4004 (4047) | 4021 (4063) | 3744 (3920) | 3732 (4233) |

**Oligothiophenes**

| | 2T | 3T | 4T | 5T | 6T |
|---|---|---|---|---|---|
| **gr. st. → anion** | 1494 (1488) | 1387 (1381) | 1356 (1362) | 1338 (1366) | 1316 (1369) |
| **gr. st. → cation** | 1506 (1495) | 1448 (1437) | 1448 (1456) | 1448 (1486) | 1435 (1503) |
| **anion → $S_1$** | 855 (852) | 594 (589) | 463 (457) | 390 (383) | 346 (341) |
| **cation → $S_1$** | 556 (569) | 347 (345) | 271 (268) | 231 (228) | 208 (205) |
| **anion → $T_1$** | 1141 (1173) | 892 (911) | 596 (617) | 623 (641) | 549 (569) |
| **cation → $T_1$** | 950 (973) | 722 (738) | 734 (753) | 510 (532) | 457 (484) |
| **gr. st. → $S_1$** | 2562 (2351) | 2101 (1873) | 1961 (1736) | 1923 (1719) | 1916 (1745) |
| **$S_1$ → $T_1$** | 303 (309) | 205 (232) | 189 (226) | 167 (205) | 151 (193) |
| **gr. st. → $T_1$** | 3430 (2419) | 2989 (2976) | 2765 (2813) | 2602 (2710) | 2473 (2643) |

**Oligofurans**

| | 2O | 3O | 4O | 5O | 6O |
|---|---|---|---|---|---|
| **gr. st. → anion** | 1751 (1719) | 1593 (1579) | 1542 (1553) | 1507 (1546) | 1468 (1535) |
| **gr. st. → cation** | 1484 (1496) | 1525 (1543) | 1569 (1616) | 1577 (1662) | 1554 (1674) |
| **anion → $S_1$** | 632 (638) | 449 (447) | 295 (365) | 331 (329) | 280 (277) |
| **cation → $S_1$** | 661 (661) | 455 (454) | 432 (354) | 309 (304) | 313 (310) |
| **anion → $T_1$** | 946 (983) | 751 (779) | 636 (668) | 555 (587) | 504 (541) |
| **cation → $T_1$** | 1158 (1171) | 866 (879) | 713 (736) | 619 (647) | 564 (604) |
| **gr. st. → $S_1$** | 2691 (2475) | 2319 (2088) | 2219 (2000) | 2190 (2005) | 2168 (2031) |
| **$S_1$ → $T_1$** | 280 (290) | 218 (250) | 188 (228) | 166 (207) | 156 (203) |
| **gr. st. → $T_1$** | 3722 (3726) | 3281 (3319) | 2842 (3022) | 2842 (3022) | 2680 (2933) |

**Fused oligothiophenes**

| | f3T | f4T | f5T | f6T |
|---|---|---|---|---|
| **gr. st. → anion** | 1407 (1406) | 1318 (1310) | 1248 (1241) | 1200 (1190) |
| **gr. st. → cation** | 1304 (1286) | 1239 (1215) | 1212 (1184) | 1191 (1166) |
| **anion → $S_1$** | 783 (779) | 678 (669) | 613 (602) | 555 (598) |
| **cation → $S_1$** | 545 (538) | 477 (472) | 421 (414) | 381 (304) |
| **anion → $T_1$** | 1082 (1102) | 977 (992) | 893 (903) | 824 (832) |
| **cation → $T_1$** | 1042 (1060) | 893 (910) | 782 (797) | 699 (712) |
| **gr. st. → $S_1$** | 2224 (2040) | 1983 (1810) | 1879 (1699) | 1785 (1609) |
| **$S_1$ → $T_1$** | 178 (198) | 141 (156) | 115 (129) | 107 (121) |
| **gr. st. → $T_1$** | 3087 (3083) | 2805 (2793) | 2620 (2611) | 2482 (2478) |

**Fused oligofurans**

| | **f3O** | **f4O** | **f5O** | **f6O** |
|---|---|---|---|---|
| **gr. st. → anion** | 1894 (1908) | 1799 (1814) | 1720 (1732) | 1668 (1680) |
| **gr. st. → cation** | 1288 (1253) | 1347 (1304) | 1401 (1357) | 1451 (1409) |
| **anion → $S_1$** | 540 (542) | 510 (509) | 470 (467) | 433 (429) |
| **cation → $S_1$** | 788 (784) | 673 (669) | 590 (588) | 524 (523) |
| **anion → $T_1$** | 971 (993) | 924 (946) | 881 (904) | 839 (863) |
| **cation → $T_1$** | 1454 (1472) | 1226 (1248) | 1063 (1084) | 945 (967) |
| **gr. st. → $S_1$** | 2110 (1891) | 2026 (1804) | 1974 (1752) | 1928 (1702) |
| **$S_1$ → $T_1$** | 344 (396) | 273 (319) | 241 (282) | 232 (274) |
| **gr. st. → $T_1$** | 3529 (3525) | 3316 (3315) | 3186 (3192) | 3092 (3122) |