SUPPLEMENTARY MATERIALS

Structure and Spectral Properties of Thianthrene and Its Benzoyl-Containing Derivatives

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Calculated bond lengths (Å) and angles (deg.) for the thianthrene molecule and its derivatives

Parameter	Thian-threne	TBO	T2F	T3F	T4F	T6F
C1–C2	1.396	1.396	1.396	1.396 **1.370**	1.396	1.396
C2–C3	1.394	1.394	1.394	1.394 **1.427**	1.394	1.394
C3–C4	1.400	1.400	1.400	1.400 **1.360**	1.400	1.400
C4–C5	1.404	1.403	1.403	1.403 **1.340**	1.403	1.403
C5–C6	1.400	1.400	1.400	1.400 **1.394**	1.400	1.400
C6–C1	1.394	1.394	1.394	1.394 **1.384**	1.394	1.394
C5–S7	1.786 **1.76**	1.786	1.786	1.786 **1.768**	1.786	1.786
S7–C8	1.787 **1.76**	1.787	1.786	1.786 **1.770**	1.786	1.787
C8–C9	1.404	1.407	1.407	1.407 **1.399**	1.407	1.407
C9–S10	1.787 **1.76**	1.782	1.781	1.782 **1.768**	1.782	1.782
C4–S10	1.787 **1.76**	1.787	1.788	1.787 **1.772**	1.787	1.787
C9–C11	1.400	1.399	1.399	1.399 **1.390**	1.399	1.400
C11–C12	1.394	1.393	1.392	1.392 **1.383**	1.393	1.391
C12–C13	1.396	1.403	1.402	1.403 **1.396**	1.403	1.402
C13–C14	1.394	1.402	1.402	1.402 **1.401**	1.402	1.402
C8–C14	1.400	1.394	1.393	1.394 **1.386**	1.394	1.393
C13–C15	–	1.501	1.499	1.500 **1.494**	1.501	1.495
C15–C16	–	1.500	1.504	1.503 **1.497**	1.498	1.505
C15–O17	–	1.226	1.222	1.225 **1.222**	1.226	1.225
C16–C18	–	1.404	1.401	1.403 **1.399**	1.405	1.405
C18–C19	–	1.391	1.389	1.385 **1.372**	1.389	1.391
C19–C20	–	1.398	1.395	1.393 **1.371**	1.393	1.398
C20–C21	–	1.395	1.396	1.394 **1.380**	1.390	1.394
C21–C22	–	1.395	1.394	1.396 **1.388**	1.394	1.390

C16–C22	–	1.403	1.404	1.403 **1.389**	1.404	1.398
C12–H	1.086	1.084	1.084	1.084 **0.930**	1.084	1.084
C14–H	1.086	1.085	1.085	1.085 **0.930**	1.085	1.085
C18–H	–	1.085	1.343 C18–F	1.084 **0.930**	1.084	1.085–
C19–H	–	1.086	1.084	1.348 **1.359** C19–F	1.084	1.085
C20–H	–	1.086	1.086	1.085 **0.930**	1.346 C20–F	1.086
C22–H		1.085	1.085	1.084 **0.930**	1.084	1.351 C22–F
C4S10C9	101.46 **100**	101.64	101.62	101,66 **102.29**	101,62	101.70
C5S7C8	101.46 **100**	101.49	101.43	101.49 **101.95**	101.43	101.47
C13C15C16	–	120.62	119.27	120.60 **120.81**	120.66	121.05
C15C16C18	–	117.67	120.64	117.16 **117.19**	117.55	117.80
C13C15C16C22	–	30.87	47.14	30.89 **32.86**	29.09	43.59
C13C15C16C18	–	–153.15	–138.17	–153.3 **–151.12**	–155.13	–141.15
C12C13C15C16	–	28.69	20.08	28.53 **24.85**	29.82	19.94
C4S10C9C11	–140.11	–141.66	–141.73	–141.79 **–141.78**	–141.65	–141.70
C5S7C8C14	140.11	141.23	141.11	141.32 **143.8**1	141.00	141.17
C3C4S10C9	140.11	140.61	140.61	140.65 **140.79**	140.46	140.63
C5C4S10C9	–42.03	–41.39	–41.30	–41.32 **–38.36**	–41.48	–41.29

Abbreviations: the second bold number in the columns thianthrene and **T3F** denotes experimental bond lengths (Å) and angles (deg.).

T a b l e S2

Calculated frequencies, IR intensities, corresponding experimental data and assignment of vibrational modes for the thianthrene molecule

No.	Sym.	DFT freq.	Exp. [19]	I_{IR}	Assignment
ν_{60}	a_1	3053		3	=C–H str., s., 1, 3, in-phase
ν_{59}	b_1	3052	3070	38	=C–H str., s., 1, 3, out-of-phase
ν_{58}	b_2	3045		24	=C–H str., as., 1, 3, in-phase
ν_{57}	a_2	3045		0.000	=C–H str., as., 1, 3, out-of-phase
ν_{56}	a_1	3037		0.7	=C–H str., as., 1, 3, in-phase
ν_{55}	b_1	3037		7	=C–H str., as., 1, 3, out-of-phase
ν_{54}	b_2	3028		0.5	=C–H str., as., 1, 3, in-phase

ν_{53}	a_2	3028		0.000	=C–H str., as., 1, 3, out-of-phase
ν_{52}	b_2	1577		2	C=C str., s., 1, 3, in-phase
ν_{51}	a_2	1566		0.000	C=C str., s., 1, 3, out-of-phase
ν_{50}	a_1	1565		0.2	C=C str., s., 1, 3, in-phase
ν_{49}	b_1	1556	1554	9	C=C str., s., 1, 3, out-of-phase
ν_{48}	a_1	1454		3	C=C str., as., 1, 3, in-phase
ν_{47}	b_1	1440	1442	80	C=C str., as., 1, 3, out-of-phase, C–S str., as., 2, in-phase
ν_{46}	b_2	1427 Right sh.	1427 Right sh.	25	C=C str., as., 1, 3, in-phase, CSC bend., 2, out-of-phase
ν_{45}	a_2	1420		0.000	C=C str., as., 1, 3, out-of-phase
ν_{44}	a_1	1310		0.4	C=C str., as. Kekule, 1, 3, in-phase
ν_{43}	b_1	1303		1	C=C str., as. Kekule, 1, 3, out-of-phase
ν_{42}	b_2	1259	1258	13	=CH bend. in-plane., 1, 3, ring str., 1, 3, in-phase
ν_{41}	a_2	1253		0.000	=CH bend. in-plane., 1, 3, ring str., 1, 3, out-of-phase
ν_{40}	a_1	1166		0.002	=CH bend. in-plane., 1, 3
ν_{39}	b_1	1166		0.3	=CH bend. in-plane., 1, 3
ν_{38}	b_2	1133		0.1	=CH bend. in-plane., 1, 3
ν_{37}	a_2	1126		0.000	=CH bend. in-plane., 1, 3
ν_{36}	a_1	1125		1	C–S str., s., 2, in-phase, =CH bend. in-plane., 1, 3
ν_{35}	b_2	1101	1102	28	=CH bend. in-plane, 1, 3, C–S str., as., 2, in-phase
ν_{34}	a_1	1039		1	Ring str., 1, 3, in-phase
ν_{33}	b_2	1039		4	C–S str., s., 2, out-of-phase, ring def., as., 1, 3, in-phase
ν_{32}	b_1	1038	1030	11	Ring str., 1, 3, out-of-phase
ν_{31}	a_2	1019		0.000	C–S str., as., 2, out-of-phase, ring def., as., 1, 3, out-of-phase
ν_{30}	b_2	970		0.001	=CH bend. out-of-plane, as., 1, 3, in-phase
ν_{29}	a_2	969		0.000	=CH bend. out-of-plane, as., 1, 3, out-of-phase
ν_{28}	a_1	934	934	2	=CH bend out-of-plane, as., 1, 3, in-phase
ν_{27}	b_1	933		0.5	=CH bend. out-of-plane, as., 1, 3, out-of-phase
ν_{26}	b_2	860		0.02	=CH bend. out-of-plane, as., 1, 3, in-phase
ν_{25}	a_2	859		0.000	=CH bend out-of-plane, as., 1, 3, out-of-phase
ν_{24}	a_1	753	746	72	=CH bend. out-of-plane, s., 1, 3, in-phase
ν_{23}	b_1	750	746	19	=CH bend. out-of-plane, s., 1, 3, out-of-phase
ν_{22}	b_2	743		0.2	Ring def. in-plane, 1, 3, in-phase, C–S str., s., 2, out-of-phase
ν_{21}	a_2	735		0.000	Ring def. in-plane, 1, 3, out-of-phase, C–S str., as., 2, out-of-phase
ν_{20}	b_2	708		1	Ring def. out-of-plane, 1, 3, in-phase, CSC bend., 2, out-of-phase
ν_{19}	a_2	703		0.000	Ring vib. out-of-plane, 1, 3, out-of-phase
ν_{18}	a_1	662		1	Ring def. in-plane, 1, 3, in-phase, C–S str., s., 2, in-phase
ν_{17}	b_1	660	662	13	Ring def. in-plane, 1, 3, out-of-phase, C–S str., as., 2, in-phase
ν_{16}	b_2	547	554	2	Ring vib. out-of-plane, 1, 3, CSC bend., 2, out-of-phase
ν_{15}	a_2	505		0.000	Ring vib. out-of-plane, 1, 3

ν_{14}	b_1	491		0.3	C–S str., as., 2, in-phase
ν_{13}	b_2	480		3	Ring vib. out-of-plane, 1, 3, CSC bend., 2, out-of-phase
ν_{12}	a_1	472		11	=CH bend. out-of-plane, 1, 3, in-phase, CSC bend. out-of-plane, 2, in-phase

Abbreviations: No. – mode; DFT freq. calc.. – calculated frequency with scale factor, cm^{-1}; exp.– experimental; I_{IR} – calculated IR intensity, km/mole; def. – deformation; str. – bond stretching; vib. – vibrations; bend. – bending vibrations; s. – symmetric and as. − asymmetric vibrations,

T a b l e S3

Calculated frequencies, IR intensities, corresponding experimental data and assignment of vibrational modes for the TBO molecule

No.	DFT freq.	Exp.	I_{IR}	Assignment
ν_{96}	3060 Left sh.	3063	6	=C–H str., s., 3, 4, in-phase
ν_{95}	3059 Left sh.	3063	6	=C–H str., as., 3, C–H str., s., 4
ν_{94}	3058		3	=C–H str., as., 3, C–H str., s., 4
ν_{93}	3053	3051	22	=C–H str., s., 1
ν_{92}	3051	3051	9	=C–H str., as., 4
ν_{91}	3046	3044 Right sh.	11	=C–H str., as., 1
ν_{90}	3043	3044 Right sh.	29	=C–H str., as., 4
ν_{89}	3039		4	=C–H str., as., 3
ν_{88}	3038		4	=C–H str., as., 1
ν_{87}	3033		9	=C–H str., as., 4
ν_{86}	3030		0.3	=C–H str., as., 1
ν_{85}	3024		0.2	=C–H str., as., 4
ν_{84}	1651	1648	153	C=O str.
ν_{83}	1597	1594	20	C=C str., s., 4
ν_{82}	1577	1576	26	C=C str., s., 1, 3, 4
ν_{81}	1575	1576	12	C=C str., s., 1, 4
ν_{80}	1567	1560	17	C=C str., s., 1, 3
ν_{79}	1560	1560	27	C=C str., s., 1, 3
ν_{78}	1544	1543	7	C=C str., s., 3
ν_{77}	1486		1	C=C str., as., 4
ν_{76}	1456		4	C=C str., as., 1, 3
ν_{75}	1443	1442	9	C=C str., as., 1, 3, 4
ν_{74}	1441	1442	62	C=C str., as., 1, 3, 4
ν_{73}	1424	1426	14	C=C str., as., 1
ν_{72}	1374	1378	61	C=C str., as., 3
ν_{71}	1337		2	C=C str., as. Kekule, 4
ν_{70}	1318	1317	37	Ring str., =CH bend. in-plane, 4
ν_{69}	1312	1317	12	C=C str., as. Kekule, 1, 3
ν_{68}	1304	1307 Right sh.	12	C=C str., as. Kekule, 1, 3
ν_{67}	1274	1281	249	C–C(O) str., as.
ν_{66}	1257	1256 Left sh.	33	Ring str., =CH bend. in-plane, 1
ν_{65}	1247	1243	193	C–C(O) str., as., =CH bend. in-plane, 3, 4

ν_{64}	1183	1176	36	=CH bend. in-plane, 4
ν_{63}	1166		0.3	=CH bend. in-plane, 1
ν_{62}	1165		0.2	=CH bend. in-plane, 4
ν_{61}	1158	1157	7	=CH bend. in-plane, 3
ν_{60}	1145		2	C–C(O) str., s.
ν_{59}	1130		0.1	=CH bend. in-plane, 1
ν_{58}	1126		0.2	=CH bend. in-plane, 1, 3, C–S str., s., 2, in-phase
ν_{57}	1103	1106	40	=CH bend. in-plane, 1, 3, C–S str., as., 2, in-phase
ν_{56}	1089		5	=CH bend. in-plane, 4
ν_{55}	1039	1044 Right sh.	66	=CH bend. in-plane, 1
ν_{54}	1038	1044 Right sh.	9	Ring def. in-plane, as., 1, 3, C–S str. s., out-of-phase
ν_{53}	1035		2	=CH bend. in-plane, 4
ν_{52}	1020		4	Ring def. in-plane, as., 1, 3, C–S str. as., out-of-phase
ν_{51}	997		2	Ring def. in-plane, as., 4
ν_{50}	988		1	=CH bend. out-of-plane, as., `4
ν_{49}	971		0.01	=CH bend. out-of-plane, as., 1
ν_{48}	968	964	8	=CH bend. out-of-plane, as., 3, 4
ν_{47}	959	964	65	CH bend. out-of-plane, as., 3, 4
ν_{46}	956		3	=CH bend. out-of-plane, as., 3, 4
ν_{45}	934		1	=CH bend. out-of-plane, as., 1
ν_{44}	932	934	6	=CH bend. out-of-plane, as., 4
ν_{43}	913	909	7	=CH bend. out-of-plane, 3
ν_{42}	860		0.02	=CH bend. out-of-plane, as., 1
ν_{41}	853	853	4	=CH bend. out-of-plane, as., 3, 4, out-of-phase
ν_{40}	838	838	8	=CH bend. out-of-plane, as., 3, 4, in-phase
ν_{39}	796	795 Left sh.	11	=CH bend. out-of-plane, s., 3, 4, out-of-phase
ν_{38}	783	787	16	Ring. def. in-plane, as., 3, 4
ν_{37}	752	749	48	=CH bend. out-of-plane, s., 1
ν_{36}	740		3	=CH bend. out-of-plane, s., 4, ring vib. out-of- plane, 1, 3
ν_{35}	728	728	30	=CH bend. out-of-plane, s., 3, 4, in-phase
ν_{34}	707	712 Left sh.	10	=CH bend. out-of-plane, s., 4, ring vib. out-of- plane, 1
ν_{33}	701	700	29.	=CH bend. out-of-plane, s., 4
ν_{32}	688		0.1	Ring vib. out-of- plane, 3, 4
ν_{31}	681	683	23	Ring def. in-plane, s., 3, 4
ν_{30}	665	664	14	Ring def. in-plane, s., 3, 4
ν_{29}	661	664	12	Ring def. in-plane, s., 1
ν_{28}	618		0.6	Ring def. in-plane, s., 4
ν_{27}	595		1	CC(O)C bend, ring vib. out-of-plane, 3, 4
ν_{26}	548	551	17	CSC bend out-of-phase, 2., ring vib. out-of-plane, 1
ν_{25}	517		1	C–S str., as., 2, in-phase, CC(O)C bend, ring vib. out-of-plane, 1, 4
ν_{24}	510	510	5	Ring vib. out-of-plane, 1, 3
ν_{23}	489		3	Ring vib. out-of-plane, 1
ν_{22}	473		7	CH bend. out-of-plane, 1, 3, in-phase, CSC bend. out-of-plane, 2, in-phase

Abbreviations: No. – mode; DFT freq. calc.. – calculated frequency with scale factor, cm^{-1}; exp.– experimental; I_{IR} – calculated IR intensity, km/mole; def. – deformation; str. – bond stretching; bend. – bending deformation vibrations; s. – symmetric and as. − asymmetric vibrations.

T a b l e S4

Calculated frequencies, IR intensities, corresponding experimental data and assignment of vibrational modes for the counter clockwise orientation of the T2F molecule

No.	DFT freq.	Exp.	I_{IR}	Assignment
ν_{96}	3062		6	=C–H str., s., 4
ν_{95}	3060		4	=C–H str., s., 3
ν_{94}	3058		3	=C–H str., as., 3
ν_{93}	3053	3052	22	=C–H str., s., 1
ν_{92}	3052	3052	12	=C–H str., as., 4
ν_{91}	3046		10	=C–H str., s., 1
ν_{90}	3042		12	=C–H str., as., 3, 4
ν_{89}	3040		3	=C–H str., as., 3, 4
ν_{88}	3038		3	=C–H str., as., 1
ν_{87}	3032		0.1	=C–H str., as., 4
ν_{86}	3030		0.3	=C–H str., as., 1
ν_{85}	1665	1653	191	=C=O str.
ν_{84}	1604	1609	54	C=C str., s., 4.
ν_{83}	1577	1579	51	C=C str., s., 1, 3, 4, iph.
ν_{82}	1574	1579	12	C=C str., s., 1, 4, iph.
ν_{81}	1567	1561	15	C=C str., s., 1, 3, iph.
ν_{80}	1560	1561	33	C=C str., s., 1, 3, iph.
ν_{79}	1546	1541	7	C=C str., s., 3
ν_{78}	1482	1482	65	C=C str., as., C–F str., 4
ν_{77}	1455		3	C=C str., as., 1, 3
ν_{76}	1445	1447	24	C=C str., as., 4
ν_{75}	1442	1447	56	C=C str., as., 1, 3, ooph.
ν_{74}	1424	1424	14	C=C str., as., 1
ν_{73}	1375	1381	62	C=C str., as., 3
ν_{72}	1328		21	C=C str., as. Kekule, 4
ν_{71}	1314		10	C=C str., as. Kekule, 1, 3, CSC bend, iph.
ν_{70}	1305		7	C=C str., as. Kekule, 1, 3
ν_{69}	1278	1300?	104	C–C(O) str., as., =CH bend. in-plane, ring str., 3, 4, C–F str.
ν_{68}	1270	1300?	119	C–C(O) str., as., =CH bend. in-plane, ring str., 3, 4
ν_{67}	1245		26	=CH bend. in-plane, 1, 3, 4, C–C(O) str., as.
ν_{66}	1238	1239	60	=CH bend. in-plane, C–F str.
ν_{65}	1228	1214?	224	C–C(O) str., as., =CH bend. in-plane, 3, 4
ν_{64}	1166		0.4	=CH bend. in-plane, 1
ν_{63}	1165	1161	33	=CH bend. in-plane, 4
ν_{62}	1154		4	=CH bend. in-plane, 3
ν_{61}	1146	1147	5	=CH bend. in-plane, 3, 4, C–C(O) str., s.
ν_{60}	1130		0.1	=CH bend. in-plane, 1
ν_{59}	1126		0.3	=CH bend. in-plane, 1, 3, C–S str., s., 2, iph.
ν_{58}	1108		16	=CH bend. in-plane, 4
ν_{57}	1101	1101	36	=CH bend. in-plane, 1, 3, C–S str., as., 2, iph.
ν_{56}	1041	1048	2	Ring def. in-plane, s., 4

ν_{55}	1039	1031	7	Ring def. in-plane, s., 1
ν_{54}	1038	1031	9	Ring def. in-plane, as., 1, 3, iph., C–S str. as., ooph.
ν_{53}	1020		5	Ring def. in-plane, as., 1, 3, ooph., C–S str. as., iph.
ν_{52}	971		0.005	=CH bend. out-of-plane, as., 1
ν_{51}	970		0.3	=CH bend. out-of-plane, as., 4
ν_{50}	958	965	73	=CH bend. out-of-plane, as., 3, 4
ν_{49}	955		0.2	=CH bend. out-of-plane, as., 3, 4
ν_{48}	941	950	22	=CH bend. out-of-plane, as., 3, 4
ν_{47}	934		1	=CH bend. out-of-plane, as., 1
ν_{46}	922	902	8	=CH bend. out-of-plane, as., 3
ν_{45}	862	860	2	=CH bend. out-of-plane, as., 4
ν_{44}	860		0.04	=CH bend. out-of-plane, as., 1
ν_{43}	836	838	15	=CH bend. out-of-plane, as., 3, C–F str., 4
ν_{42}	827	820	11	Ring def., as., in-plane, 4, C–F str., 4
ν_{41}	778	775	17	=CH bend. out-of-plane, s., 3, 4, ooph.
ν_{40}	768		18	=CH bend. out-of-plane, s., 4, ring. def. in-plane, as., 3
ν_{39}	755	748	73	=CH bend. out-of-plane, s., 1, 3, 4, iph.
ν_{38}	752	748	38	=CH bend. out-of-plane, s., 1
ν_{37}	739		0.2	Ring def. in-plane, as., 1
ν_{36}	721		3	Ring vib. out-of- plane, 3, 4
ν_{35}	706		1	Ring vib. out-of- plane, 1
ν_{34}	691	691	2	Ring vib. out-of- plane, 3, 4
ν_{33}	678	676	12	Ring def. in-plane, s., 3
ν_{32}	661	660	11	Ring def. in-plane, s., 1
ν_{31}	652	649	20	Ring def. in-plane, s., 3, 4
ν_{30}	590		2	Ring vib. out-of-plane, 3, 4, CC(O)C bend
ν_{29}	561	560	12	CSC bend ooph. 2, ring vib. out-of-plane, 1, 3, ring def. in-plane, s., 4
ν_{28}	542	548	5	Ring vib. out-of-plane, 3, 4
ν_{27}	527	530	2	Ring vib. out-of-plane, 1, 4
ν_{26}	511		0.7	Ring vib. out-of-plane, 1, 4
ν_{25}	507	507	8	Ring vib. out-of-plane, 1, 3, ring def. in-plane, s., 4
ν_{24}	489		3	Ring vib. out-of-plane, 1
ν_{23}	473		7	Ring vib. out-of-plane, 1, 3, iph., CSC bend. out-of-plane, 2, iph.
ν_{21}	444		2	Ring vib. out-of-plane, 3, CF bend.
ν_{19}	414		9	CF bend.

Abbreviations: No. – mode; DFT freq. calc.. – calculated frequency with scale factor, cm^{-1}; exp. – experimental; I_{IR} – calculated IR intensity, km/mole; def. – deformation; str. – bond stretching; bend. – bending deformation vibrations; s. – symmetric and as. − asymmetric vibrations; iph. – in-phase, ooph. – out-of-phase; sh. – shoulder.

T a b l e S5

Calculated frequencies, IR intensities, corresponding experimental data and assignment of vibrational modes for the clockwise orientation of the T2F molecule (T6F)

No	DFT freq.	Exp.	I_{IR}	Assignment
ν_{96}	3062		9	=C–H str., s., 4
ν_{95}	3061		6	=C–H str., s., 3
ν_{94}	3059		2	=C–H str., as., 3
ν_{93}	3058	3052	6	=C–H str., as., 4
ν_{92}	3053	3052	22	=C–H str., s., 1
ν_{91}	3046	3052	12	=C–H str., as., 4
ν_{90}	3045	3052	11	=C–H str., as., 1
ν_{89}	3041		2	=C–H str., as., 3
ν_{88}	3038		4	=C–H str., as., 1
ν_{87}	3034		3	=C–H str., as., 4
ν_{86}	3030		0.3	=C–H str., as., 1
ν_{85}	1652	1653	167	=C=O str.
ν_{84}	1604	1609	83	C=C str., s., 4
ν_{83}	1578	1579	57	C=C str., s., 1, 3, 4, iph.
ν_{82}	1575	1579	6	C=C str., s., 1, 4, iph.
ν_{81}	1568	1561	17	C=C str., s., 1, 3, iph.
ν_{80}	1561	1561	32	C=C str., s., 1, 3, iph.
ν_{79}	1547	1541	8	C=C str., s., 3
ν_{78}	1479	1482	41	C=C str., as., C–F str., 4
ν_{77}	1457	1455 Left sh.	10	C=C str., as., 1, 3
ν_{76}	1448	1447	28	C=C str., as., 4
ν_{75}	1442	1447	98	C=C str., as., 1, 3, 4
ν_{74}	1424	1424	14	C=C str., as., 1
ν_{73}	1376	1381 1370	63	C=C str., as., 3
ν_{72}	1329		0.4	C=C str., as. Kekule, 4
ν_{71}	1314	1314 Left sh.	20	C=C str., as. Kekule, 1, 3, CSC bend, iph.
ν_{70}	1305	1300	11	C=C str., as. Kekule, 1, 3, ooph.
ν_{69}	1293	1300	335	C–C(O) str., as., =CH bend. in-plane, ring str., 3, 4, C–F str.
ν_{68}	1263	1263 Right sh.	9	=CH bend. in-plane, ring str., 1, 3, 4, C–F str.
ν_{67}	1245	1249	8	=CH bend. in-plane, 1, 3, 4, C–C(O) str., as., C–F str.
ν_{66}	1229 Left sh,	1239	73	C–F str., =CH bend. in-plane, 3, 4, ring str., 4
ν_{65}	1218	1214	128	C–F str., C–C(O) str., as., =CH bend. in-plane, 3, 4
ν_{64}	1166		0.4	=CH bend. in-plane, 1
ν_{63}	1164	1161	23	=CH bend. in-plane, 3, 4
ν_{62}	1154		3	=CH bend. in-plane, 3, 4
ν_{61}	1147	1147	10	=CH bend. in-plane, 3, 4, C–C(O) str., s.
ν_{60}	1130		0.1	=CH bend. in-plane, 1
ν_{59}	1126		0.5	=CH bend. in-plane, 1, 3, C–S str., s., 2, in-phase
ν_{58}	1104	1101	22	=CH bend. in-plane, 4
ν_{57}	1103	1101	33	=CH bend. in-plane, 1, 3, C–S str., as., 2, in-phase

ν_{56}	1042	1048	0.5	=CH bend. in-plane, 4
ν_{55}	1039	1031	8	Ring vib. in-plane, s., 1
ν_{54}	1038	1031	8	Ring def. in-plane, as., 1, 3, iph., C–S str. as., ooph.
ν_{53}	1020		4	Ring def. in-plane, as., 1, 3, ooph., C–S str. as., iph.
ν_{52}	972		7	=CH bend. out-of-plane, as., 4
ν_{51}	971		0.003	=CH bend. out-of-plane, as., 1
ν_{50}	961	965	77	=CH bend. out-of-plane, as., 3, 4
ν_{49}	945	950	2	=CH bend. out-of-plane, as., 3, 4
ν_{48}	944	950	4	=CH bend. out-of-plane, as., 3, 4, ooph.
ν_{47}	934		1	=CH bend. out-of-plane, as., 1
ν_{46}	918	902	7	=CH bend. out-of-plane, 3
ν_{45}	860		0.04	=CH bend. out-of-plane, as., 1
ν_{44}	860	860	2	=CH bend. out-of-plane, as., 3, 4, ooph.
ν_{43}	836	838	17	C–F str., =CH bend. out-of-plane, as., 3
ν_{42}	822	820 Right sh.	4	Ring def. in-plane, as., 4, C–F str., =CH bend. out-of-plane, as., 3
ν_{41}	778	775 Left sh.	8	=CH bend. out-of-plane, s., 3, 4, ooph.
ν_{40}	775	775 Left sh.	17	Ring. def. in-plane, as., 3, 4, C–F str.
ν_{39}	753	748	81	=CH bend. out-of-plane, s., 1, 3, 4, iph.
ν_{38}	752	748	27	=CH bend. out-of-plane, s., 1
ν_{37}	739		0.4	Ring. def. in-plane, as., 1
ν_{36}	713		0.8	Ring vib. out-of- plane, 3, 4
ν_{35}	705		0.8	Ring vib. out-of- plane, 1, =CH bend. out-of-plane, s., 3, 4
ν_{34}	684	691	7	Ring vib. out-of- plane, 3, 4
ν_{33}	678	676	9	Ring def. in-plane, s., 3, 4
ν_{32}	661	660	11	Ring def. in-plane, s., 1
ν_{31}	649	648	19	Ring def. in-plane, s., 3, 4
ν_{30}	595		1	Ring vib. out-of-plane, 3, 4, CC(O)C bend.
ν_{29}	556	560	8	CSC bend ooph., 2, ring vib. out-of-plane, 1, 3, ring def. in-plane, s., 4
ν_{28}	543	548	6	Ring vib. out-of-plane, 1, 3, ring def. in-plane, s., 4
ν_{27}	530	530	18	Ring vib. out-of-plane, 1, 3, ring def. in-plane, s., 4
ν_{26}	520		2	Ring vib. out-of-plane, 1, 4
ν_{25}	508	504	8	Ring vib. out-of-plane, 1, 3, 4
ν_{24}	488		2	Ring vib. out-of-plane, 1
ν_{23}	473		7	Ring vib. out-of-plane, 1, 3, iph., CSC bend. out-of-plane, 2, iph.
ν_{22}	459		7	Ring vib. out-of-plane, 1, 3, 4
ν_{19}	418		2	CF bend., 4
ν_{18}	399		2	CF bend., 4

Abbreviations: No. – mode; DFT freq. calc.. – calculated frequency with scale factor, cm^{-1}; exp. – experimental; I_{IR} – calculated IR intensity, km/mole; def. – deformation; str. – bond stretching; bend. – bending deformation vibrations; s. – symmetric and as. − asymmetric vibrations; iph. – in-phase, ooph. – out-of-phase; sh. – shoulder.

T a b l e S6

Calculated frequencies, IR intensities, corresponding experimental data and assignment of vibrational modes for the T3F molecule

No.	DFT freq.	Exp.	I_{IR}	Assignment
ν_{96}	3073		4	=C18–H str., 4
ν_{95}	3064	3062	5	=C–H str., s., 3, 4
ν_{94}	3061		1	=C–H str., s., 3, C–H str., as., 4
ν_{93}	3058		1	=C–H str., as., 3
ν_{92}	3057	3062	10	=C–H str., as., 3, 4
ν_{91}	3054	3062	22	=C–H str., s., 1
ν_{90}	3046	3046 Right sh.	10	=C–H str., as., 1
ν_{89}	3040		3	=C–H str., as., 3, 4
ν_{88}	3038		3	=C–H str., as., 1
ν_{87}	3037		6	=C–H str., as., 4
ν_{86}	3030		0.3	=C–H str., as., 1
ν_{85}	1653	1646	145	C=O str.
ν_{84}	1602	1602 Right sh.	23	C=C str., s., 4
ν_{83}	1584	1577	44	C=C str., s., 4
ν_{82}	1577	1577	43	C=C str., s., 1, 3, iph., CSC bend.
ν_{81}	1567	1560	21	C=C str., s., 1, 3, iph., CSC bend.
ν_{80}	1560	1560 Right sh.	32	C=C str., s., 1, 3, iph., CSC bend.
ν_{79}	1544	1541 Right sh.	7	C=C str., s., 3
ν_{78}	1479	1474	38	C=C str., as., C–F str., 4
ν_{77}	1456	1458	7	C=C str., as., 1, 3, C–S str., s.
ν_{76}	1443 Left sh.	1438	26	C=C str., as., 1, 3, ooph., C–S str., as.
ν_{75}	1433	1438	135	C=C str., as., 4
ν_{74}	1424 Right sh.	1424	14	C=C str., as., 1
ν_{73}	1375	1377	60	C=C str., as., 3
ν_{72}	1340		5	C=C str., as. Kekule, 4
ν_{71}	1312	1312 Left sh.	16	C=C str., as. Kekule, 1, 3, CSC bend, iph.
ν_{70}	1304	1304 Left sh.	14	C=C str., as. Kekule, 1, 3
ν_{69}	1284	1286	363	C–C(O) str., as., ring str., as., 3, 4, C–F str., =CH bend. in-plane, 3, 4
ν_{68}	1276 Right sh.	1274 Right sh.	81	C–C(O) str., as., =CH bend. in-plane, 3, 4
ν_{67}	1248	1244	52	C–F str., 4, =CH bend. in-plane, 1, 3, 4, C–C(O) str., s.
ν_{66}	1243	1244	8	=CH bend. in-plane, 1, 3, ring str., C–F str., 4
ν_{65}	1212	1213	132	C–C(O) str., as., =CH bend. in-plane, ring str., 3, 4, C–F str., 4
ν_{64}	1166		0.3	=CH bend. in-plane, 1
ν_{63}	1165	1163	6	=CH bend. in-plane, 4
ν_{62}	1152		2	=CH bend. in-plane, 3
ν_{61}	1130		0.1	=CH bend. in-plane, 1

ν_{60}	1127		3	=CH bend. in-plane, 1, 3, 4, C–S str., s., 2, iph.
ν_{59}	1124	1120	9	C–C(O) str., s., =CH bend., ring def. in-plane, 3, 4, C–F str.
ν_{58}	1103	1106	41	=CH bend., ring def. in-plane, 1, 3, C–S str., as., 2, iph.
ν_{57}	1083		2	=CH bend. in-plane, 4
ν_{56}	1039	1031	6	Ring def. in-plane, s., 1
ν_{55}	1038	1031	10	Ring def. in-plane, as., 1, 3, in-phase, C–S str. s., ooph.
ν_{54}	1020		4	Ring def. in-plane, as., 1, 3, in-phase, C–S str. as., ooph.
ν_{53}	1004	1004	8	Ring def. in-plane, as., 3, 4, =CH bend. iph., 4
ν_{52}	998		2	Ring def. in-plane, as., 4
ν_{51}	971		0.002	=CH bend. out-of-plane, as., 1
ν_{50}	965		0.5	=CH bend. out-of-plane, as., 3, 4, iph,
ν_{49}	955		2	=CH bend. out-of-plane, as., 3, 4
ν_{48}	934		1	=CH bend. out-of-plane, as., 1
ν_{47}	916	916	18	=CH bend. out-of-plane, 3
ν_{46}	902	902	1	=CH bend. out-of-plane, as., 3, 4
ν_{45}	887	893	18	=CH bend. out-of-plane, as., 3, 4, ooph,
ν_{44}	867	865	67	Ring def., as., in-plane, 3, 4, C–F str., 4
ν_{43}	860		0.5	=CH bend. out-of-plane, as., 1
ν_{42}	837	836	7	=CH bend. out-of-plane, as., 3
ν_{41}	798	803	10	=CH bend. out-of-plane, as., 3, 4
ν_{40}	761	762 Left sh.	86	=CH bend. out-of-plane, s., 3, 4, iph., C–F str.
ν_{39}	755 Right sh.	754	48	=CH bend. out-of-plane, s., 1, 3, 4, iph.
ν_{38}	752 Right sh.	754	35	=CH bend. out-of-plane, s., 1
ν_{37}	738		2	Benz. def. in-plane, as., 1
ν_{36}	710	708	3	Ring vib. out-of- plane, as., 1, 3, CSC bend, =CH bend. out-of-plane, s., 4
ν_{35}	704		2	Ring vib. out-of- plane, 1
ν_{34}	679	681	8	Ring def. in-plane, s., 3, 4
ν_{33}	675		2	Ring vib. out-of- plane, 3, 4
ν_{32}	661		2	Ring def.. in-plane, s., 1, out-of- plane, s., 4
ν_{31}	660	660	14	Ring def. in-plane, s., 1, out-of- plane, s., 4
ν_{30}	613	611	3	Ring vib. out-of-plane, 3, 4, CC(O)C bend
ν_{29}	549	551	19	CSC bend ooph., 2, ring vib. out-of-plane, 1, 3
ν_{28}	539		0.2	C–S str., as., 2, iph., ring vib. out-of-plane, 1, 3, 4, CC(O)C bend.
ν_{27}	525	524	3	Ring vib. out-of-plane, 1, 3, 4, CC(O)C bend.
ν_{26}	507		3	Ring vib. out-of-plane, 1, 3, ring vib. in-plane, 4
ν_{25}	504	504	4	Ring vib. out-of-plane, s., 1, 4
ν_{24}	488		3	Ring vib. out-of-plane, 1
ν_{23}	473	475	7	=CH bend. out-of-plane, 1, 3, CSC bend. out-of-plane, 2, iph.
ν_{19}	409		7	=CF bend., 4
ν_{18}	402		4	=CF bend., 4

Abbreviations: No. – mode; DFT freq. calc.. – calculated frequency with scale factor, cm^{-1}; exp. – experimental; I_{IR} – calculated IR intensity, km/mole; def. – deformation; str. – bond stretching; bend. – bending deformation vibrations; s. – symmetric and as. − asymmetric vibrations; iph. – in-phase, ooph. – out-of-phase; sh. – shoulder.

T a b l e S7

Calculated frequencies, IR intensities, corresponding experimental data and assignment of vibrational modes for the T4F molecule

No.	DFT freq.	Exp.	I_{IR}	Assignment
ν_{96}	3067		5	=C–H str., s., 4
ν_{95}	3064		3	=C–H str., s., 3, =C–H str., as., 4
ν_{94}	3058		3	=C–H str., s., 3, =C–H str., as., 4
ν_{93}	3058		2	=C–H str., as., 3
ν_{92}	3054		0.3	=C–H str., as., 4
ν_{91}	3054	3061	21	=C–H str., s., 1
ν_{90}	3050	3047	9	=C–H str., as., 4
ν_{89}	3046	3047	10	=C–H str., as., 1
ν_{88}	3039		3	=C–H str., as., 3
ν_{87}	3038		3	=C–H str., as., 1
ν_{86}	3030		0.2	=C–H str., as., 1
ν_{85}	1649	1647	156	C=O str.
ν_{84}	1601	1595	162	C=C str., s., 4
ν_{83}	1579	1575	31	C=C str., s., 4
ν_{82}	1577	1575	16	C=C str., s., 1, 3, iph., CSC bend.
ν_{81}	1567	1572	14	C=C str., s., 1, 3, iph., CSC bend.
ν_{80}	1560	1559	31	C=C str., s., 1, 3, iph., CSC bend.
ν_{79}	1544	1543	8	C=C str., s., 3
ν_{78}	1504	1503	36	C=C str., as., C–F str., 4
ν_{77}	1456		4	C=C str., as., 1, 3
ν_{76}	1443	1444	50	C=C str., as., 1, 3, ooph.
ν_{75}	1424	1428	14	C=C str., as., 1
ν_{74}	1406	1403	22	C=C str., as., 4
ν_{73}	1375	1377	65	C=C str., as., 3
ν_{72}	1330	1336 Right sh.	17	C=C str., as. Kekule, 4
ν_{71}	1312	1313	13	C=C str., as. Kekule, 1, 3, CSC bend, iph.
ν_{70}	1304	1302	12	C=C str., as. Kekule, 1, 3
ν_{69}	1295	1300	45	Ring str., =CH bend. in-plane, 4
ν_{68}	1275	1277	311	C–C(O) str., as., ring str., as., 3, 4, C–F str., =CH bend. in-plane, 3, 4
ν_{67}	1261	1265 Right sh.	102	C–F str., =CH bend. in-plane, 1, 3, 4, C–C(O) str., s.
ν_{66}	1245	1250	25	=CH bend. in-plane, 1, ring str., 1, C–F str.
ν_{65}	1235	1239	186	C–C(O) str., as., =CH bend. in-plane, 1, 3, 4, ring str., 3, 4, C–F str.
ν_{64}	1166		0.2	=CH bend. in-plane, 1
ν_{63}	1159	1155	84	=CH bend. in-plane, 4
ν_{62}	1157		8	C–C(O) str., s., =CH bend. in-plane, 3, 4
ν_{61}	1144		2	C–C(O) str., s., =CH bend. in-plane, 3, 4
ν_{60}	1130		0.1	=CH bend. in-plane, 1
ν_{59}	1126		0.2	=CH bend. in-plane, 1, 3, C–S str., s., 2, iph.
ν_{58}	1103	1099	32	=CH bend. in-plane, 1, 3, 4, ring def. in-plane, 1, 3, C–S str., as., 2, iph.
ν_{57}	1102	1099	17	=CH bend. in-plane, 4
ν_{56}	1039	1028	7	Ring def. in-plane, s., 1

ν_{55}	1038	1028	9	Ring def. in-plane, as., 1, 3, iph., C–S str. s., ooph.
ν_{54}	1020		5	Ring def. in-plane, as., 1, 3, ooph., C–S str. as., ooph.
ν_{53}	1011		2	Ring def. in-plane, as., =CH bend. in-plane, 4
ν_{52}	971		0.007	=CH bend. out-of-plane, as., 1
ν_{51}	965	963	40	=CH bend. out-of-plane, as., 3, 4, iph.
ν_{50}	960	963	25	=CH bend. out-of-plane, as., 3, 4, iph.
ν_{49}	956		6	=CH bend. out-of-plane, as., 3, 4
ν_{48}	945	944	13	=CH bend. out-of-plane, as., 3, 4
ν_{47}	934		1	=CH bend. out-of-plane, as., 1
ν_{46}	912	913	8	=CH bend. out-of-plane, as., 3
ν_{45}	860		0.02	=CH bend. out-of-plane, as., 1
ν_{44}	848	848	29	CH bend. out-of-plane, as., 3, CH bend. out-of-plane, s., 4
ν_{43}	836	838	4	=CH bend. out-of-plane, as., 3, =CH bend. out-of-plane, s., 4, C–F str.
ν_{42}	828	821	19	=CH bend. out-of-plane, as., 3,= CH bend. out-of-plane, s., 4, C–F str.
ν_{41}	819		5	=CH bend. out-of-plane, s., 4
ν_{40}	768	775	18	Ring def., as., in-plane, 3, 4
ν_{39}	760	758	51	=CH bend. out-of-plane, s., 3, 4, iph.
ν_{38}	752	758	41	=CH bend. out-of-plane, s., 1
ν_{37}	738		0.4	Ring def. in-plane, as., 1
ν_{36}	713		1	Ring vib. out-of- plane, 3, 4
ν_{35}	705		1	Ring vib. out-of- plane, 1
ν_{34}	682	689	7	Ring vib. out-of- plane, 3, 4
ν_{33}	676	679	7	Ring vib. in-plane, s., 3, 4
ν_{32}	661	660	11	Ring vib. in-plane, s., 1
ν_{31}	634	634	2	Ring def. in-plane, s., 4
ν_{30}	614	617	24	Ring def. in-plane, s., 1
ν_{29}	589		0.4	CC(O)C bend., ring vib. out-of-plane, s., 3, 4, ooph.
ν_{28}	540	532	26	CSC bend. ooph., 2, ring vib. out-of-plane, 1
ν_{27}	520		1	CC(O)C bend., C–S str., as., 2, iph., ring vib. out-of-plane, as. 1, ring vib. out-of-plane, s. 4,.
ν_{26}	507	507	8	Ring vib. out-of-plane, s., 4, ring vib. out-of-plane, as., 1, 3
ν_{25}	499		10	Ring vib. out-of-plane, s., 3, 4, ring vib. out-of-plane, as., 1
ν_{24}	487		2	Ring vib. out-of-plane, 1
ν_{23}	472		7	=CH bend. out-of-plane, 1, 3, CSC bend. out-of-plane, 2, iph.
ν_{19}	407		2	CF bend., 4
ν_{18}			2	CF bend., 4

Abbreviations: No. – mode; DFT freq. calc.. – calculated frequency with scale factor, cm^{-1}; exp. – experimental; I_{IR} – calculated IR intensity, km/mole; def. – deformation; str. – bond stretching; bend. – bending deformation vibrations; s. – symmetric and as. − asymmetric vibrations; iph. – in-phase, ooph. – out-of-phase; sh. – shoulder.

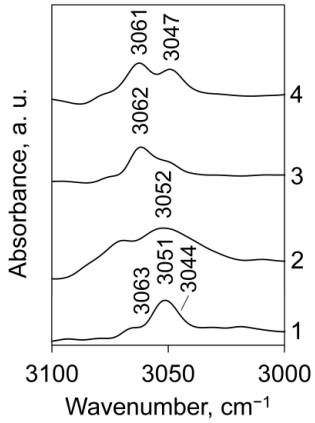


Figure S1. Experimental IR spectra of solid-state samples of the studied compounds in the 3100–3000 cm^{-1} range: curve 1 – IR spectrum for compound **TBO**; curve 2– IR spectrum for compound **T6F (T2F** clock-wise orientation); curve 3 – IR spectrum for compound **T3F**; curve 4 – IR spectrum for compound **T4F**

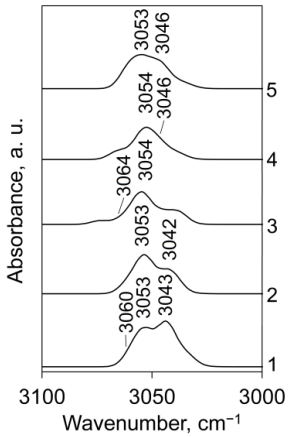


Figure S2. Calculated absorption IR spectra of the benzoylthianthrene and fluorobenzoylthianthrene derivatives in the 3100–3000 cm^{-1} range: curve 1 – IR spectrum for molecule **TBO**; curve 2 – IR spectrum for molecule **T2F**; curve 3 – IR spectrum for molecule **T3F**; curve 4 – IR spectrum for molecule **T4F**; curve 5 – IR spectrum for molecule **T6F**

T a b l e S8

Assignment of selected bands in the IR absorption spectra of the thianthrene, benzoylthianthrene (TBO) and its fluorobenzoylthianthrene derivatives. For each mode (column) the first two numbers denote calculated frequency with scaling factor (cm^{-1}) and intensity (km/mole); the third bold number in each column denotes experimental IR frequency (cm^{-1})

Type of normal vibrations	**Thian-threne**	**TBO**	**T2F counter clock-wise**	**T3F**	**T4F**	**T6F (T2F clock-wise)**
=C–H str., s., 1	3052 38 **3070**	3053 22 **3051**	3053 22 –	3054 22 **3062** **3052**	3054 21 **3061**	3053 22 **3052**
=C–H str., as., 1	3045 24 –	3046 11 **3044**	3046 10 –	3046 10 **3046**	3046 10 **3047**	3045 11 **3046**
=C–H str., as., 4	–	3043 29 **3044**	3052 12 –	3037 6 **3038**	3050 9 **3047**	3046 12 **3046**
C=O str.	–	1651	1665	1653	1649	1652

		153 **1648**	191 –	145 **1646**	156 **1647**	167 **1653**
C=C str., s., 4	–	1597 20 **1594**	1604 54 –	1602 23 **1602**	1601 162 **1595**	1604 83 **1609**
C=C str., s., 4 (in **T2F** and **T6F** C=C str., s., 1, 4)	–	1577 26 **1576**	1574 12 –	1584 44 **1577**	1579 31 **1575**	1575 6 **1579**
C=C str., s., 1, 3, in-phase (in **T2F** and **T6F** C=C str., s., 1, 3, 4)	1577 2 –	1575 12 **1576**	1577 51 –	1577 43 **1577**	1577 16 **1575**	1578 57 **1579**
C=C str., s., 1, 3, in-phase	1565 0.2	1567 17 **1560**	1567 15 –	1567 21 **1560**	1567 14 **1559**	1568 17 **1561**
C=C str., s., 1, 3, in-phase	1556 9 **1554**	1560 27 **1560**	1560 33 –	1560 32 **1560**	1560 31 **1559**	1561 32 **1561**
C=C str., s., 3	–	1544 7 **1543**	1546 7 –	1544 7 **1541**	1544 8 **1543**	1547 8 **1541**
C=C str., as., 4	–	1486 1 –	1482 65 –	1479 38 **1474**	1504 36 **1503**	1479 41 **1482**
C=C str., as., 1, 3	1454 3	1456 4	1455 3	1456 7	1456 4	1457 10
C=C str., as., 4	–	–	1445 24 –	1433 135 **1438**	1406 22 **1403**	1448 28 **1447**
C=C str., as., 1, 3, out-of-phase	1440 80 **1442**	1441 62 **1442**	1442 26 –	1443 26 **1438**	1443 50 **1444**	1442 98 **1447**
C=C str., as., 1	1427 25 **1427**	1424 14 **1426**	1424 14 –	1424 14 **1424**	1424 14 **1428**	1424 14 **1424**
C=C str., as., 3	–	1374 61 **1378**	1375 62 –	1375 60 **1377**	1375 65 **1377**	1376 63 **1381**
C=C str., as. Kekule, 4	–	1337 2 –	1328 21 –	1340 5 –	1330 17 **1336**	1329 0.4 –
C=C str., as. Kekule, 1, 3, CSC bend, in-phase	1310 0.4 –	1312 12 **1317**	1314 10 –	1312 16 **1312**	1312 13 **1313**	1314 20 **1314**
C=C str., as. Kekul e, 1, 3, out-of-phase	1303 1 –	1304 12 **1307**	1305 7 –	1304 14 **1304**	1304 12 **1302**	1305 11 **1300**
C–C(O) str., as., ring str., CH bend. in-plane, 3, 4	–	1318 37 **1317**	–	-	1295 45 **1300**	-
C–C(O) str., as., ring str., =CH bend. in-plane, 3, 4, C–F str.	–	1274 249 **1281**	1278 104 –	1284 363 **1286**.	1275 312 **1277**	1293 335 **1300**

C–C(O) str., as., =CH bend. in-plane., 3, 4	–	–	1270 119 –	1276 81 **1274**	–	–
=CH bend. in-plane, 1, 3, 4, C–F str.	–	–	–	1248 52 **1244**	1261 102 **1265**	1263 9 **1263**
C–C(O) str., as., ring str., =CH bend. in-plane, 1, 3, 4	1259 13 **1258**	1257 33 **1256**	1245 26 –	1243 8 **1244** C–F str.	1245 25 **1250**	1257 8 **1249** C–F str.
C–C(O) str., as., CH bend. in-plane, 3, 4	–	1247 193 **1243**	1228 224 –	1212 132 **1213** C–F str.	1235 186 **1239**	1218 128 **1214** C–F str.
=CH bend. in-plane, 4	–	1183 36 **1176**	1165 33 –	1165 6 **1163**	1159 84 **1155**	1164 23 **1161**
C–C(O) str., s., =CH bend. in-plane, 3, 4	–	–	1146 5 –	–	–	1147 10 **1147**
=CH bend. in-plane, 1, 3, C–S str., as., 2, in-phase	1101 28 **1102**	1103 40 **1106**	1101 16 –	1103 41 **1106**	1103 32 **1099**	1103 33 **1101**
Ring vib. in-plane, as., 1, 3, in-phase, C–S str. as., out-of-phase	–	1041 4	1041 5	1041 4	1041 5	1041 4
Ring vib. in-plane, as., 1, 3, out-of-phase, C–S str. s., out-of-phase	1038 11 **1030**	1038 9 **1044**	1038 9 –	1038 10 **1031**	1038 9 **1028**	1038 8 **1031**
Ring vib. in-plane, as., =CH bend. in-plane, 4	–	997 2 –	–	1004 8 **1002**	1011 2 –	–
=CH bend. out-of-plane, as, 3, 4, in-phase	–	959 65 **964**	958 73 –	965 0.5 –	965 40 **963**	961 77 **965**
=CH bend. out-of-plane, as., 3, 4, out-of-phase	–	956 3 –	941 22 –	955 2 –	945 13 **944**	944 4 **950**
=CH bend. out-of-plane, as., 1	934 2	934 1	934 1	934 1	934 1	934 1
=CH bend. out-of-plane, 3	–	913 7 **909**	922 8 –	916 18 **916**	912 8 **913**	918 7 **902**
=CH bend. out-of-plane, as., 3, 4, out-of-phase	860 0.02 –	853 4	–	887 18 **893**	–	860 2 –
=CH bend. out-of-plane, as., 3, =CH bend. out-of-plane, s., 4	–	–	–	–	848 29 **848**	–
=CH bend. out-of-plane, as., 3, C–F str. (in **T3F** C–F str. is absent)	–	838 8 **838**	836 15 –	837 7 **836**	836 4 **838**	836 17 **838**

Ring def. in-plane, as., 4, C–F str., 4, =CH bend. out-of-plane, as., 3	–	-	827 11 –	–	828 19 **821**	822 4 –
=CH bend. out-of-plane, s., 3, 4, out-of-phase	–	796 11 **795**	778 17 –	798 10 **803**	–	778 8 **775**
Ring def. in-plane, as., 3, 4, C–F str.	–	783 16 **787**	768 18 –	867 67 **865**	768 18 **758**	775 17 **775**
=CH bend. out-of-plane, s., 1 (in thianthrene1, 3)	750 19 **746**	752 48 **749**	752 38 –	752 35 **754**	752 41 **758**	752 27 **748**
=CH bend. out-of-plane, s., 1, 3, 4, in-phase	–	–	755 73 –	755 48 **754**	–	753 81 **748**
=CH bend. out-of-plane, s., 3, 4, in-phase	–	728 30 **728**	–	761 86 **754** C–F str.	760 51 **758**	–
Ring vib. out-of- plane, 1, CH bend. out-of-plane, s., 3, 4	708 1 –	707 10 **712**	–	704 2 –	705 1	–
=CH bend. out-of-plane, s., 4	–	701 29 **700**	–	710 3 –	–	–
Ring vib. out-of- plane, 3, 4	–	688 0.1 –	691 2 –	675 2 –	682 7 **689**	684 7 **681**
Ring def. in-plane, s., 3, 4	–	681 23 **683**	678 12 –	679 8 **680**	676 7 **679**	678 9 **676**
Ring def. in-plane, s., 1	660 13 **662**	661 12 **664**	661 11 –	660 14 **657**	661 11 **660**	661 11 **658**
CSC bend out-of-phase, 2., ring vib. out-of-plane, 1, 3, ring def. in-plane, s., 4	547 2 –	548 17 **551**	561 12 –	549 19 **553**	540 26 **532**	556 8 **560**
=CH bend. out-of-plane, 1, 3, in-phase, CSC bend. out-of-plane, 2, in-phase	472 11 –	473 7 –	473 7 –	473 7 **475**	472 7 –	473 7 –

Abbreviations: def. – deformation; str. – bond stretching; bend. – bending deformation vibrations; s. – symmetric and as. − asymmetric vibrations; sh. – shoulder.

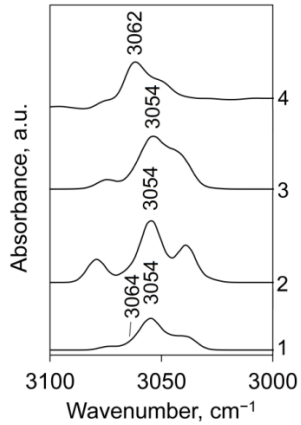


Figure S3. Absorption IR spectra of the 3-fluorobenzoylthianthrene derivatives in the 3100–3300 cm^{-1} range: curve 1 – calculated IR spectrum for **T3F** molecule, curve 2 – calculated IR spectrum for **T3F** dimer 1, curve 3 – calculated IR spectrum for **T3F** dimer 2, curve 4 – experimental IR spectrum for **T3F** compound

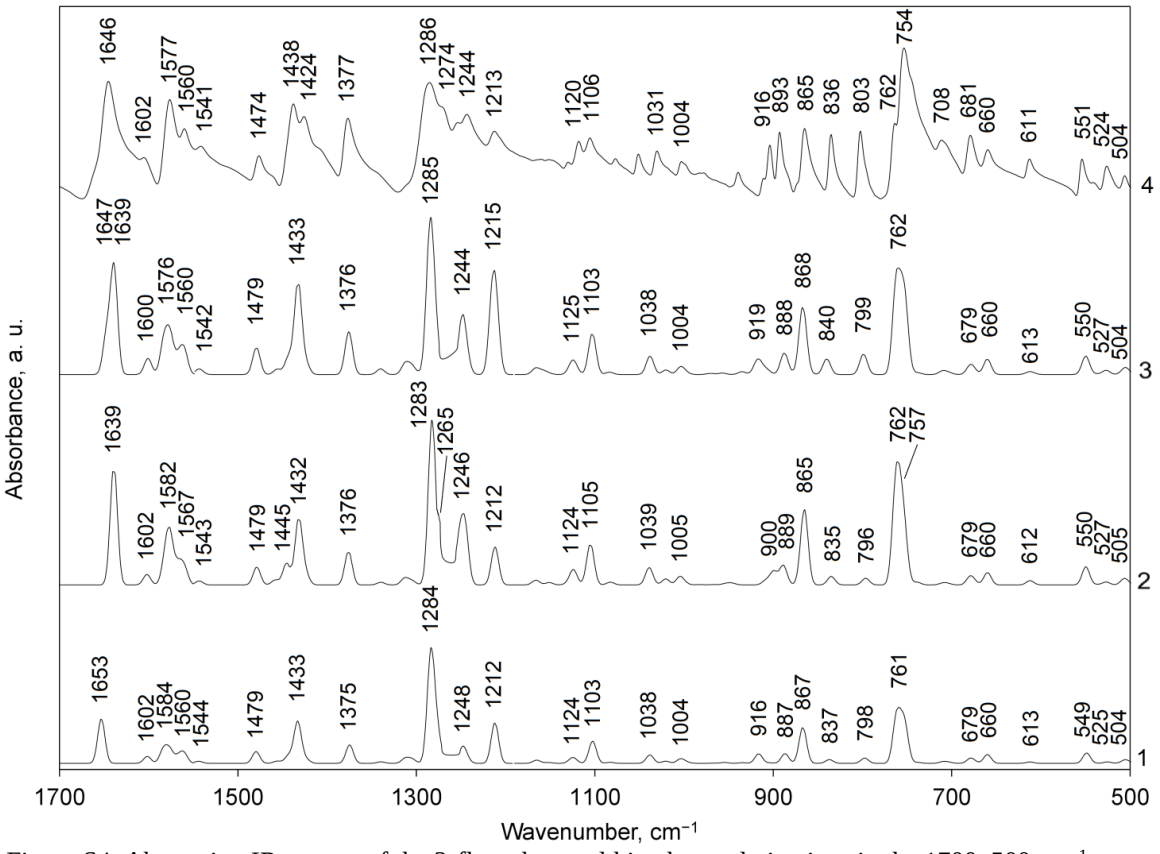
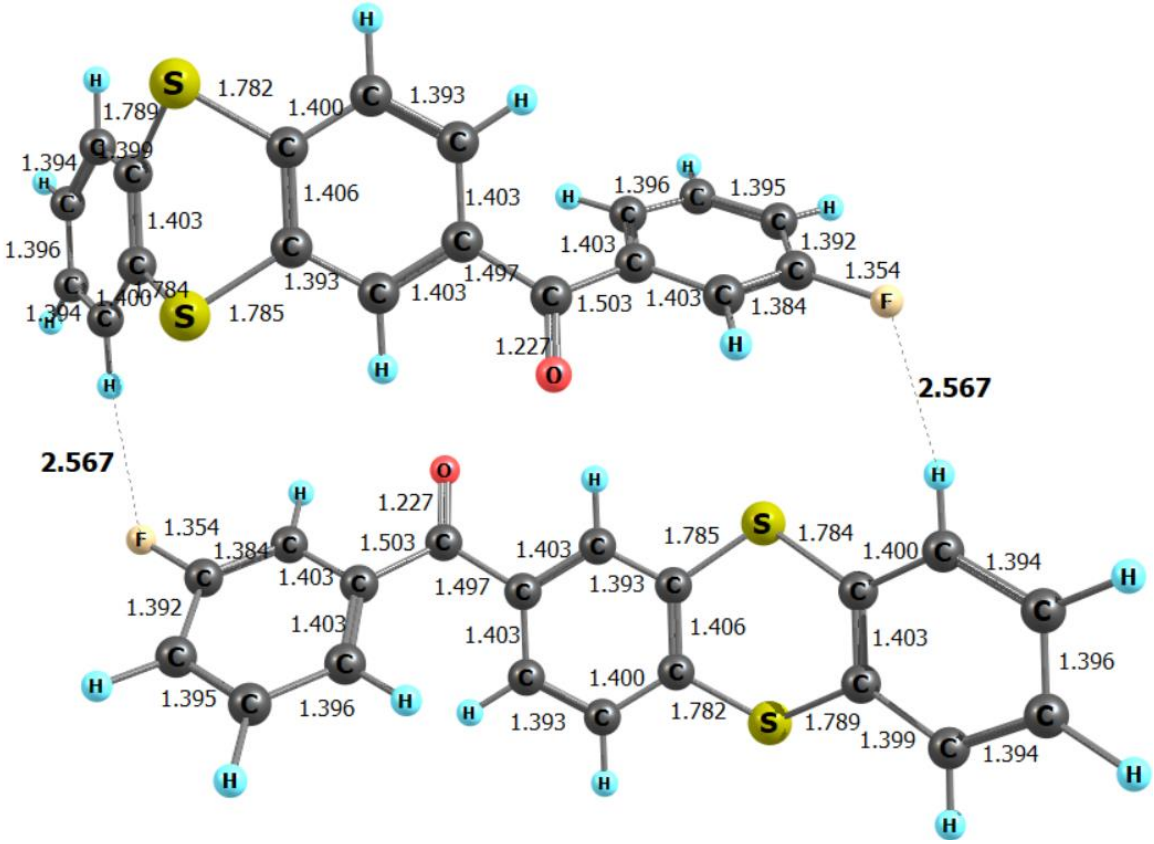
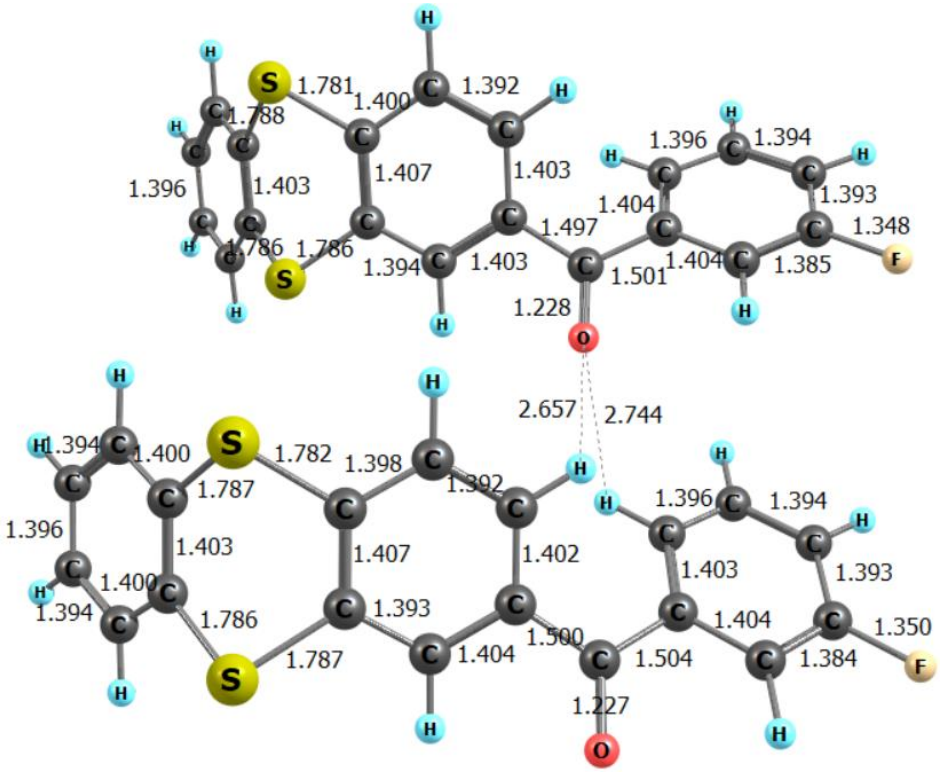


Figure S4**.** Absorption IR spectra of the 3-fluorobenzoylthianthrene derivatives in the 1700–500 cm^{-1} range: curve 1 – calculated IR spectrum for **T3F** molecule, curve 2 – calculated IR spectrum for **T3F** dimer 1, curve 3 – calculated IR spectrum for **T3F** dimer 2, curve 4 – experimental IR spectrum for **T3F** compound



Dimer 1



Dimer 2

Figure S5. The structures of the corresponding dimers selected from crystals of **T3F**, optimized at the B3LYP/6-31G(d,p) theory level