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Molecular and electronic structure of cyclo[10]thiophene in various oxidation states: Polaron pair vs bipolaron

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Supporting Information

I. Materials and methods

Solvents and reagents were purified prior to use and dried by usual methods. In spectroscopic application dry solvents were degassed by freeze-pump-thaw-cycles and stored under argon before sample preparation. Quinquethiophene L5T, decithiophene L10T, cyclo[*10*]thiophene and thianthrenium hexachloroantimonate ($ThiSbCl_6$) were prepared according standard literature procedures.[S1-3] UV-vis spectra were recorded on a Perkin Elmer Lambda 19 spectrometer; electrochemical analysis were performed on a Metrohm AutoLab PGSTAT30 potentiostat; EPR spectra in the X-band were recorded with a Bruker System EMX connected with an ER 4131 VT variable temperature accessory.

II. Sample preparation for absorption and ESR measurements under controlled oxidation.

Stock solutions of the respective oligothiophene in 1,1,2,2-tetrachloroethane (TCE) and of thianthrenium hexachloroantimonate in nitromethane were prepared. Defined amounts of the sample solutions were mixed with the corresponding equivalents of the concentrated stock solution of the oxidant prior to dilution with TCE in a volumetric flask. The final sample concentration lies in the range of $9x10^{-6}$ and $1.7x10^{-5}$ Mol/L for absorption measurement and around $5x10^{-5}$ Mol/L for ESR.

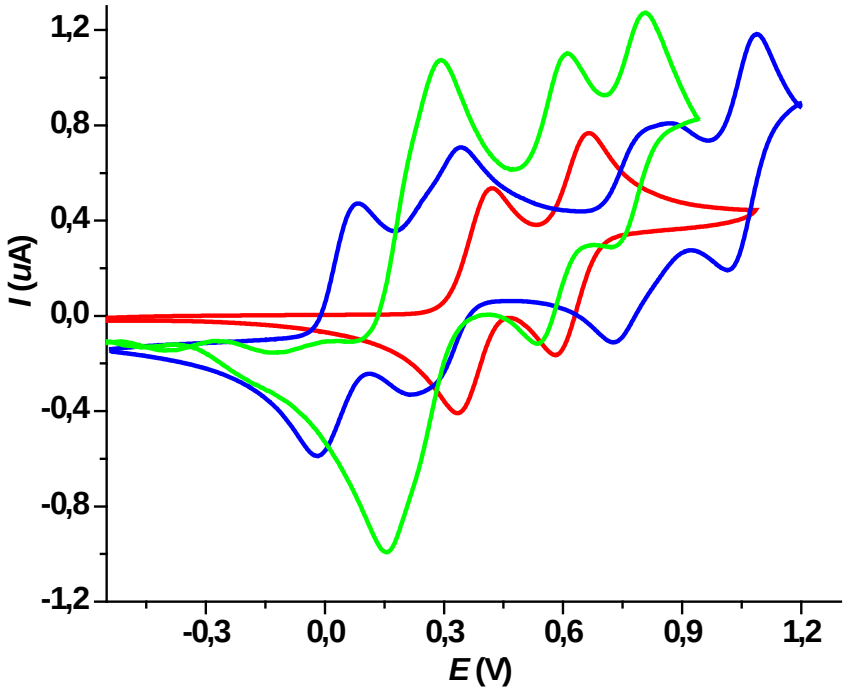


Figure S-1 .Cyclic voltammogram of linear quinquethiophene (red), linear decithiophene (green) and cyclo[*10*]thiophene (blue). The sample concentration is normalized to 7.8 $\times 10^{-4}$ M in 1,1,2,2-TCE/0.1 M $TBAPF_6$, 295 K, ν= 20 mVs^{-1}; potentials vs ferrocene/ferrocenium (Fc/Fc^{+}) (TCE: 1,1,2,2-tetrachloroethane, $TBAPF_6$: tetrabutylammonium hexafluorophosphate).

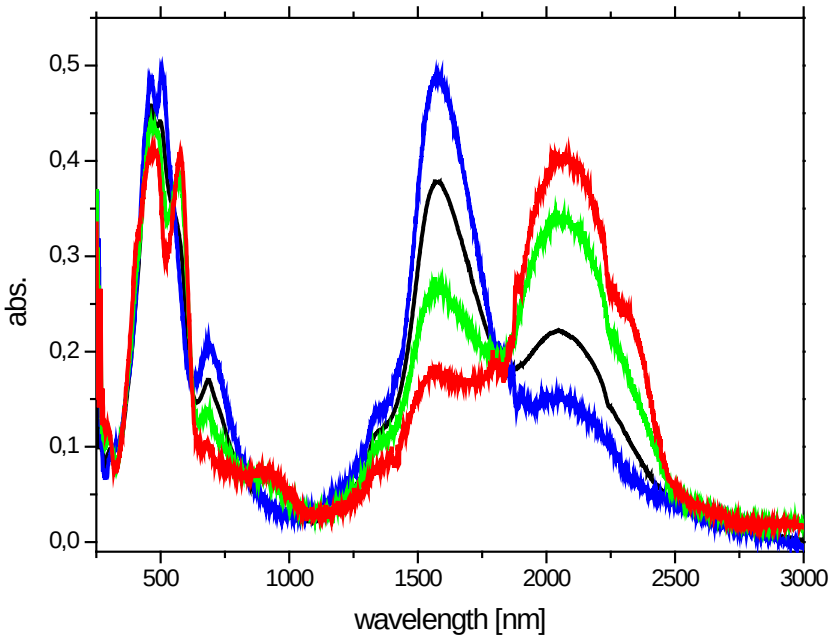
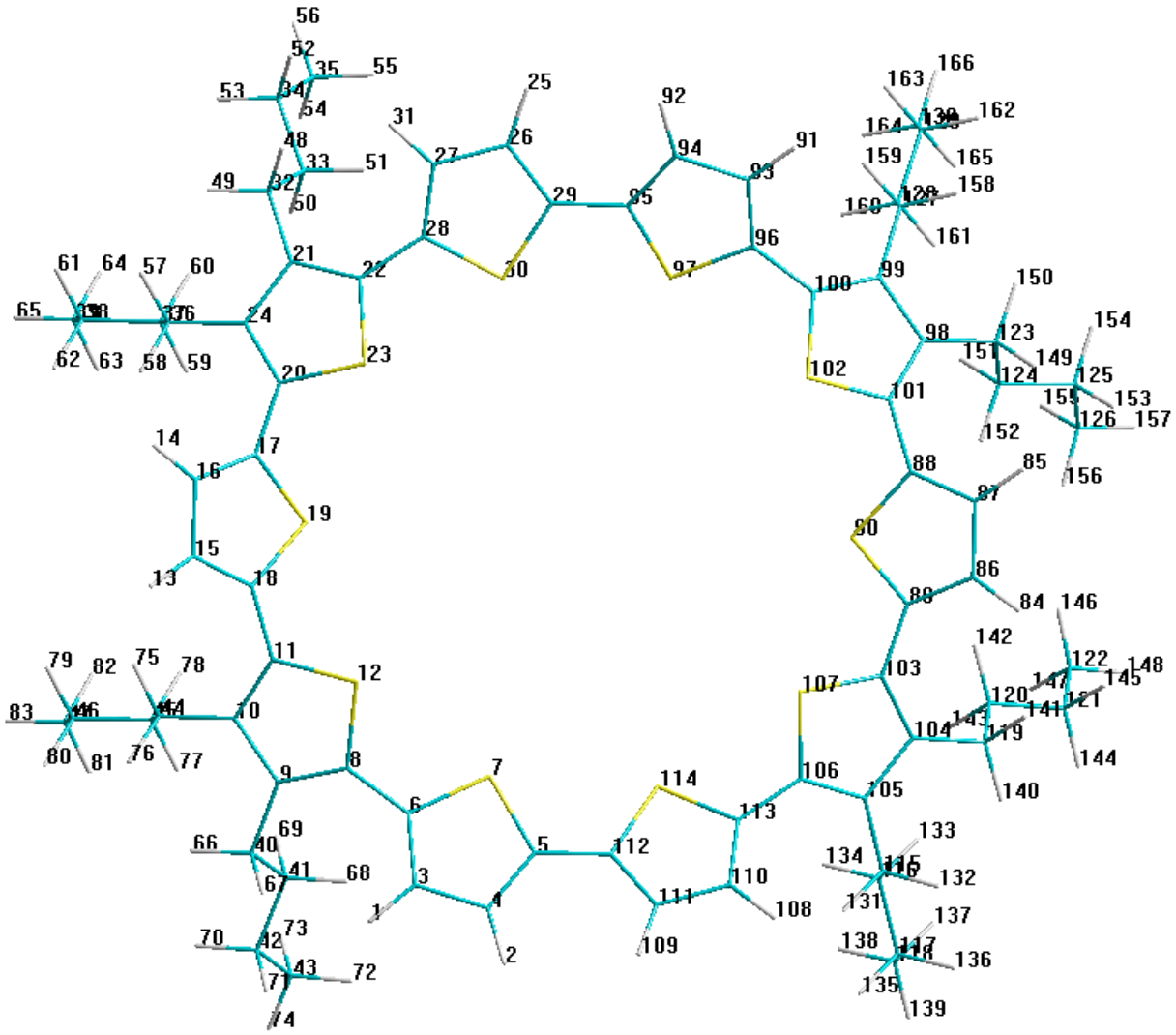


Figure S-2. Electronic absorption of C*10*T oxidized with 1.0 eq. of $ThiSbCl_5$ in 1,1,2,2-TCE at different temperatures: 0 ^{o}C (blue), room temperature (black), 40 ^{o}C (green), 60 ^{o}C (red).

III. Theoretical calculations: optimized geometry coordinates



Atom	Z	Charge	Coordinates(Angstrom)			Mass
			x	y	z	
3	6	-0.134852	56.06251	-24.13455	14.93530	12.01100
4	6	-0.137512	54.86061	-24.82156	15.28494	12.01100
5	6	-0.288173	54.91395	-26.16716	14.96356	12.01100
6	6	-0.281151	56.99404	-24.97530	14.35529	12.01100
7	16	0.518858	56.38835	-26.55137	14.23647	32.06400
8	6	-0.300788	58.32115	-24.72482	13.90248	12.01100
9	6	-0.061339	58.87862	-23.61619	13.28041	12.01100
10	6	-0.062350	60.25276	-23.85270	12.91112	12.01100
11	6	-0.303810	60.66858	-25.12529	13.27371	12.01100
12	16	0.541820	59.44924	-25.96625	14.07038	32.06400
15	6	-0.136173	63.19809	-25.39114	13.33436	12.01100
16	6	-0.136333	64.15675	-26.40552	13.03114	12.01100
17	6	-0.296346	63.56297	-27.54439	12.51723	12.01100
18	6	-0.296526	61.90710	-25.79246	13.04132	12.01100
19	16	0.544795	61.89410	-27.34211	12.37462	32.06400
20	6	-0.303364	64.14269	-28.80094	12.17373	12.01100
21	6	-0.061370	65.41219	-30.52190	11.22054	12.01100
22	6	-0.300425	64.46933	-31.23229	11.95082	12.01100
23	16	0.541193	63.43897	-30.19746	12.79321	32.06400
24	6	-0.062422	65.21830	-29.09841	11.35008	12.01100
26	6	-0.137571	64.42795	-34.94859	12.23815	12.01100
27	6	-0.135035	65.10182	-33.70262	12.05939	12.01100
28	6	-0.281023	64.22703	-32.63214	12.05507	12.01100
29	6	-0.288060	63.05878	-34.78983	12.36823	12.01100
30	16	0.518839	62.63071	-33.16112	12.24830	32.06400
32	6	-0.104977	66.49281	-31.12401	10.41019	12.01100
33	6	-0.158738	65.96370	-31.85857	9.19184	12.01100
34	6	-0.158196	67.09661	-32.45397	8.38286	12.01100
35	6	-0.210596	66.58119	-33.19395	7.17564	12.01100
36	6	-0.106336	66.05956	-28.08211	10.68165	12.01100
37	6	-0.156610	65.76673	-27.97517	9.19627	12.01100
38	6	-0.158931	66.66388	-26.94677	8.54036	12.01100
39	6	-0.210487	66.37861	-26.82754	7.06558	12.01100
40	6	-0.104905	58.17533	-22.34122	13.02173	12.01100
41	6	-0.158628	57.07574	-22.48614	11.98541	12.01100
42	6	-0.158211	56.38934	-21.16040	11.73314	12.01100
43	6	-0.210587	55.28729	-21.29644	10.71449	12.01100
44	6	-0.106304	61.11011	-22.86236	12.22444	12.01100
45	6	-0.156613	60.75558	-22.71020	10.75655	12.01100
46	6	-0.158939	61.63372	-21.67089	10.09221	12.01100
47	6	-0.210480	61.29556	-21.51632	8.63194	12.01100
86	6	-0.134498	52.95500	-35.64337	15.22329	12.01100

87	6	-0.134585	53.91272	-36.65885	14.91879	12.01100
88	6	-0.292185	54.97081	-36.16973	14.17517	12.01100
89	6	-0.292269	53.31584	-34.41486	14.70145	12.01100
90	16	0.530692	54.75941	-34.52944	13.83224	32.06400
93	6	-0.134129	61.01290	-37.74526	13.30957	12.01100
94	6	-0.137834	62.25222	-37.07485	13.08106	12.01100
95	6	-0.293344	62.06974	-35.78349	12.61368	12.01100
96	6	-0.288354	59.92664	-36.94524	13.00629	12.01100
97	16	0.533235	60.42895	-35.44456	12.41507	32.06400
98	6	-0.062521	56.35483	-38.03667	13.10966	12.01100
99	6	-0.060927	57.74237	-38.25229	12.78217	12.01100
100	6	-0.307854	58.53239	-37.18363	13.18104	12.01100
101	6	-0.305164	56.16499	-36.81510	13.74044	12.01100
102	16	0.549977	57.62129	-36.00001	13.95497	32.06400
103	6	-0.305560	52.69667	-33.13875	14.84245	12.01100
104	6	-0.062500	51.37274	-32.75421	14.68237	12.01100
105	6	-0.061012	51.21233	-31.33103	14.84783	12.01100
106	6	-0.308331	52.42201	-30.71041	15.12517	12.01100
107	16	0.550882	53.67826	-31.82510	15.21893	32.06400
110	6	-0.134133	52.16681	-28.38294	16.12611	12.01100
111	6	-0.137781	52.86134	-27.13694	16.07225	12.01100
112	6	-0.293365	53.94070	-27.17729	15.20474	12.01100
113	6	-0.288499	52.73689	-29.33098	15.29658	12.01100
114	16	0.533322	54.04753	-28.68288	14.45076	32.06400
115	6	-0.106105	49.91985	-30.62214	14.73016	12.01100
116	6	-0.156551	49.46524	-30.48631	13.28853	12.01100
117	6	-0.158924	48.13657	-29.76510	13.20455	12.01100
118	6	-0.210474	47.67778	-29.62149	11.77640	12.01100
119	6	-0.103917	50.25838	-33.67777	14.37836	12.01100
120	6	-0.156817	50.34535	-34.24069	12.97104	12.01100
121	6	-0.158371	49.19529	-35.18473	12.69118	12.01100
122	6	-0.210695	49.30052	-35.78708	11.31389	12.01100
123	6	-0.103936	55.27805	-39.00355	12.80475	12.01100
124	6	-0.156832	54.34399	-38.50078	11.71859	12.01100
125	6	-0.158368	53.24911	-39.50713	11.43454	12.01100
126	6	-0.210682	52.29035	-38.99702	10.38983	12.01100
127	6	-0.106104	58.25622	-39.46090	12.10246	12.01100
128	6	-0.156521	57.92614	-39.47556	10.62117	12.01100
129	6	-0.158944	58.45342	-40.73205	9.96097	12.01100
130	6	-0.210458	58.14040	-40.75238	8.48712	12.01100
83	1	0.071880	61.95246	-20.74580	8.16097	1.00800
84	1	0.159192	52.05840	-35.82914	15.81924	1.00800
85	1	0.159183	53.81515	-37.69183	15.26089	1.00800
25	1	0.157327	64.94726	-35.90903	12.27224	1.00800

31	1	0.160050	66.18618	-33.62348	11.95139	1.00800
13	1	0.159295	63.46882	-24.42789	13.77307	1.00800
14	1	0.159276	65.22683	-26.28823	13.21765	1.00800
1	1	0.160025	56.21422	-23.06892	15.12284	1.00800
91	1	0.159984	60.94975	-38.76147	13.70598	1.00800
92	1	0.157275	63.22472	-37.53107	13.27927	1.00800
2	1	0.157322	54.00710	-24.32961	15.75683	1.00800
48	1	0.088253	67.07258	-31.84305	11.05240	1.00800
49	1	0.090949	67.21278	-30.32845	10.07666	1.00800
50	1	0.085503	65.37273	-31.15308	8.55099	1.00800
51	1	0.092413	65.26658	-32.67284	9.52555	1.00800
52	1	0.076022	67.68980	-33.15412	9.02884	1.00800
53	1	0.076280	67.79318	-31.63726	8.05555	1.00800
54	1	0.072679	66.01024	-32.50630	6.50583	1.00800
55	1	0.074548	65.90208	-34.02561	7.48339	1.00800
56	1	0.071525	67.43039	-33.62802	6.59470	1.00800
57	1	0.089295	67.14429	-28.33491	10.83431	1.00800
58	1	0.093891	65.88324	-27.08040	11.16198	1.00800
59	1	0.087811	64.69293	-27.68949	9.04500	1.00800
60	1	0.085480	65.91695	-28.97514	8.70910	1.00800
61	1	0.075876	67.73777	-27.23384	8.69446	1.00800
108	1	0.159996	51.30494	-28.55695	16.77476	1.00800
109	1	0.157292	52.57786	-26.26755	16.66971	1.00800
62	1	0.078690	66.51450	-25.95050	9.03483	1.00800
63	1	0.073608	65.31968	-26.51714	6.89279	1.00800
64	1	0.072238	66.54471	-27.80500	6.55131	1.00800
65	1	0.071889	67.04998	-26.06573	6.60086	1.00800
66	1	0.090937	58.90680	-21.56138	12.67635	1.00800
67	1	0.088264	57.72861	-21.96914	13.98480	1.00800
68	1	0.092304	56.32573	-23.23962	12.34611	1.00800
69	1	0.085475	57.50756	-22.87564	11.02650	1.00800
70	1	0.076274	57.14320	-20.41013	11.37514	1.00800
71	1	0.076095	55.96610	-20.76898	12.69594	1.00800
72	1	0.074527	54.51456	-22.02303	11.06450	1.00800
73	1	0.072671	55.69384	-21.66103	9.74019	1.00800
74	1	0.071518	54.79277	-20.30991	10.54359	1.00800
75	1	0.093925	62.18562	-23.18055	12.30992	1.00800
76	1	0.089296	61.01844	-21.86705	12.73900	1.00800
77	1	0.085476	59.67728	-22.41462	10.65763	1.00800
78	1	0.087789	60.87931	-23.69595	10.23642	1.00800
79	1	0.078709	62.71076	-21.96695	10.20031	1.00800
80	1	0.075888	61.50841	-20.68551	10.61443	1.00800
81	1	0.072236	60.23223	-21.19916	8.50462	1.00800
82	1	0.073599	61.43957	-22.48211	8.08967	1.00800

131	1	0.093570	50.01678	-29.59651	15.18158	1.00800
132	1	0.089275	49.13674	-31.17103	15.32115	1.00800
133	1	0.085260	49.37345	-31.50458	12.82542	1.00800
134	1	0.087883	50.23745	-29.92234	12.70274	1.00800
135	1	0.078902	48.23158	-28.75009	13.67363	1.00800
136	1	0.075847	47.36589	-30.32983	13.79313	1.00800
137	1	0.072035	47.55512	-30.62363	11.29872	1.00800
138	1	0.073767	48.42128	-29.03882	11.18034	1.00800
139	1	0.071945	46.69725	-29.08865	11.73549	1.00800
140	1	0.090397	49.27461	-33.15097	14.50658	1.00800
141	1	0.089109	50.27959	-34.52752	15.11541	1.00800
142	1	0.090827	51.31997	-34.78388	12.85013	1.00800
143	1	0.084494	50.33539	-33.40301	12.22542	1.00800
144	1	0.076285	48.22426	-34.63054	12.78763	1.00800
145	1	0.077247	49.18616	-36.00253	13.45958	1.00800
146	1	0.073493	50.24298	-36.37920	11.21309	1.00800
147	1	0.072694	49.30444	-34.98833	10.53324	1.00800
148	1	0.071543	48.43532	-36.46597	11.12015	1.00800
149	1	0.089062	54.68384	-39.19269	13.74115	1.00800
150	1	0.090418	55.72011	-39.98624	12.48750	1.00800
151	1	0.084499	54.92501	-38.30097	10.78036	1.00800
152	1	0.090867	53.88947	-37.52749	12.04369	1.00800
153	1	0.077220	52.68977	-39.72971	12.38161	1.00800
154	1	0.076291	53.70740	-40.47099	11.08776	1.00800
155	1	0.072672	52.82716	-38.77763	9.43530	1.00800
156	1	0.073502	51.79332	-38.05759	10.73541	1.00800
157	1	0.071552	51.50009	-39.75856	10.18354	1.00800
158	1	0.089274	57.82619	-40.37684	12.59238	1.00800
159	1	0.093477	59.37269	-39.51136	12.22890	1.00800
160	1	0.087913	58.37462	-38.57407	10.12750	1.00800
161	1	0.085281	56.81410	-39.41297	10.48261	1.00800
162	1	0.075836	58.00130	-41.63260	10.45486	1.00800
163	1	0.078856	59.56368	-40.79589	10.11118	1.00800
164	1	0.073770	58.60622	-39.87691	7.97320	1.00800
165	1	0.072059	57.03724	-40.71100	8.31741	1.00800
166	1	0.071936	58.53457	-41.68677	8.01957	1.00800

III. References

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