ELECTRONIC SUPPLEMENTARY MATERIAL

Electronic structure of positive and negative polarons in functionalized dithienylthiazolo[5,4-*d*]thiazoles: a combined EPR and DFT study

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1. DFT computations

1.1. Positive polaron of Th-DTTzTz

1.1.1. Majority species

Cartesian coordinates (in Å)

C	-1.537047	-0.087268	-0.179879
S	-0.536786	-1.603293	-0.201511
N	-0.832244	1.049156	-0.064904
C	0.468336	0.777751	0.007035
C	0.879487	-0.597589	-0.046532
S	1.884592	1.783440	0.162259
N	2.180080	-0.868983	0.025211
C	2.884891	0.267449	0.140051
C	4.301716	0.331908	0.239597
C	5.240979	-0.748700	0.238683
C	6.559888	-0.272597	0.355909
C	6.682382	1.129973	0.447669
S	5.107377	1.891164	0.386645
C	-2.953848	-0.151700	-0.279809
C	-3.893110	0.928911	-0.278927
C	-5.211984	0.452843	-0.396703
C	-5.334453	-0.949706	-0.488839
S	-3.759469	-1.710918	-0.427508
C	-6.540672	-1.716084	-0.616842
C	-7.861612	-1.236742	-0.677620
C	-8.821784	-2.267968	-0.805187
C	-8.245628	-3.533530	-0.842536
S	-6.524914	-3.474888	-0.722209
C	7.888639	1.896383	0.575082
C	9.209603	1.417061	0.635470
C	10.169807	2.448311	0.762595
C	9.593651	3.713871	0.799992
S	7.872915	3.655214	0.679999
C	4.861629	-2.202533	0.126442
C	-3.513782	2.382719	-0.166272
H	7.434833	-0.933627	0.375696
H	-6.086925	1.113880	-0.416575
H	-8.114196	-0.169049	-0.630201
H	-9.905221	-2.099378	-0.868590
H	-8.749136	-4.504567	-0.935444

H	9.462177	0.349363	0.588164
H	11.253260	2.279733	0.825726
H	10.097176	4.684920	0.892664
C	6.022657	-3.205263	0.145965
C	-4.674932	3.385344	-0.183875
H	4.256889	-2.333172	-0.798209
H	4.138018	-2.436520	0.938421
H	-2.791253	2.617209	-0.979097
H	-2.907851	2.512940	0.757636
C	-4.196844	4.840463	-0.064026
C	5.544500	-4.660468	0.027448
C	-5.335083	5.870460	-0.078344
C	6.682691	-5.690504	0.042740
C	-4.855126	7.324798	0.042937
C	-5.994498	8.349815	0.027781
C	6.202617	-7.144979	-0.076414
C	7.341979	-8.170000	-0.060842
H	6.606296	-3.087755	1.086406
H	6.726449	-2.982970	-0.687180
H	-5.378135	3.161995	0.649486
H	-5.259194	3.268878	-1.124059
H	-3.487686	5.062036	-0.893686
H	-3.606473	4.955427	0.873307
H	4.954142	-4.776275	-0.909790
H	4.835317	-4.881234	0.857300
H	-6.044649	5.647187	0.751092
H	-5.924887	5.755035	-1.016484
H	7.272846	-5.573852	0.980507
H	7.391962	-5.468380	-0.787255
H	-4.144558	7.543833	-0.785612
H	-4.264850	7.436233	0.980240
H	-6.701512	8.182716	0.867390
H	-6.579785	8.291691	-0.913915
H	-5.611000	9.386148	0.117393
H	5.611650	-7.257548	-1.013146
H	5.492654	-7.362987	0.752923
H	7.928088	-8.110592	0.880263
H	8.048264	-8.004077	-0.901296
H	6.958380	-9.206447	-0.148686

Table S1. Principal *g* values and direction cosines (r_x,r_y,r_z) of ***g*** tensor axes in lab frame in which molecular coordinates are defined as obtained via DFT

	g_x	g_y	g_z
value	2.0002685	2.0022987	2.0036143
r_x	0.9779455	-0.0666828	0.1979292
r_y	0.1941104	-0.0596274	-0.9791658
r_z	0.0770956	0.9959909	-0.0453685

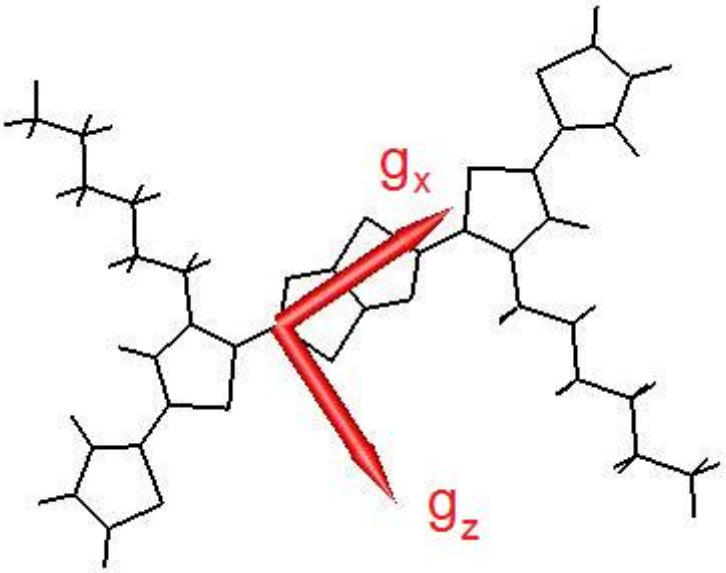

Figure S1. Positions of the g_x and g_z axis versus the molecular structure. Both axes are in the plane of the molecule, the g_y axis being perpendicular to it.

1.1.2. Minority species

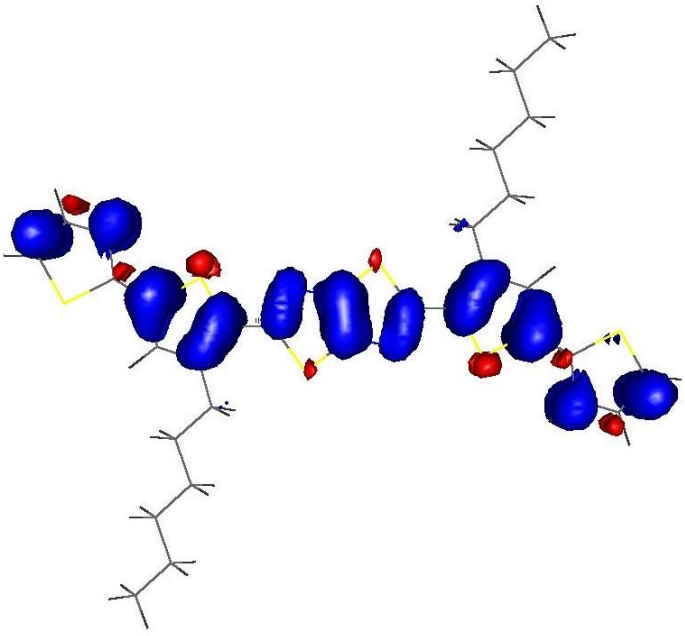

Figure S2. Spin density distribution of a minority conformer of the positive **Th-DTTzTz** polaron. Red: negative spin density, blue: positive spin density. Contour levels are set at -0.0012 and 0.0012, respectively.

Cartesian coordinates (in Å)

C	-7.938179	3.239326	-0.002584
C	-8.806580	2.165294	-0.010311
C	-6.583771	2.838706	-0.001464

C	-6.418865	1.453444	-0.008474
S	-7.983659	0.656180	-0.016823
C	-5.200308	0.698869	-0.009406
C	-5.057540	-0.698029	-0.015137
C	-3.732673	-1.152154	-0.015546
C	-2.816852	-0.065377	-0.009964
S	-3.647990	1.484622	-0.002219
C	-1.401769	-0.029140	-0.009154
S	-0.359857	-1.495162	-0.016013
N	-0.727249	1.128547	-0.003203
C	0.575255	0.909209	-0.003031
C	1.025592	-0.444384	-0.008706
S	1.960705	1.959992	0.003373
N	2.328096	-0.663726	-0.007835
C	3.002617	0.493958	-0.001471
C	4.417698	0.530186	0.000868
C	5.333524	1.616958	0.006480
C	6.658380	1.162810	0.009340
C	6.801131	-0.234099	0.006070
S	5.248826	-1.019827	-0.005254
C	8.019669	-0.988696	0.009598
C	8.184563	-2.373971	0.005327
C	9.538953	-2.774614	0.011177
C	10.407352	-1.700587	0.019678
S	9.584456	-0.191446	0.020305
C	-3.329419	-2.605174	-0.021760
C	4.930288	3.069990	0.010352
H	-8.270281	4.278198	0.002301
H	-9.896463	2.187793	-0.012670
H	-5.744698	3.537138	0.004477
H	-5.918244	-1.366007	-0.019420
H	7.519087	1.830776	0.014873
H	7.345495	-3.072399	-0.001676
H	9.871041	-3.813500	0.009242
H	11.497223	-1.723099	0.025394
C	6.077223	4.087051	0.015532
H	-2.684906	-2.795645	0.856891
H	-2.682958	-2.787571	-0.900684
H	4.283272	3.253591	0.888627
H	4.286337	3.259271	-0.868956
C	5.580701	5.536911	0.017580
C	6.710424	6.571375	0.028089
C	6.218104	8.022701	0.024107
C	-4.476347	-3.622240	-0.027635
C	-3.979810	-5.072084	-0.033499
C	-5.109537	-6.106559	-0.042274
C	-4.617161	-7.557869	-0.044706
H	6.719915	3.923451	-0.867746
H	6.715711	3.919365	0.901105
H	4.928505	5.697960	0.896178
H	4.939355	5.704022	-0.867854
H	7.365270	6.405814	-0.848044
H	7.349310	6.405193	0.915807
H	-5.115980	-3.452642	-0.912013
H	-5.117900	-3.460568	0.856829
H	-3.335797	-5.240625	0.849726

H	-3.330261	-5.231682	-0.914320
H	-5.752288	-5.937753	-0.926704
H	-5.760565	-5.943643	0.837191
C	7.350602	9.050662	0.038975
C	-5.749680	-8.585828	-0.058123
H	5.560312	8.184296	0.897894
H	5.581419	8.186539	-0.864756
H	-3.976889	-7.724388	0.841077
H	-3.962896	-7.716776	-0.921628
H	8.005804	8.939344	-0.841476
H	7.982261	8.939597	0.936488
H	6.959950	10.080545	0.033620
H	-6.384709	-8.472338	-0.952949
H	-6.401572	-8.476936	0.825084
H	-5.358984	-9.615708	-0.057035

Table S2. Principal *g* values and direction cosines (r_x,r_y,r_z) of ***g*** tensor axes in lab frame in which molecular coordinates are defined as obtained via DFT.

	g_x	g_y	g_z
value	2.0013672	2.0022462	2.0025647
r_x	0.9932793	-0.0008975	0.1157383
r_y	-0.1157209	0.0112627	0.9932179
r_z	-0.0021950	-0.9999362	0.0110831

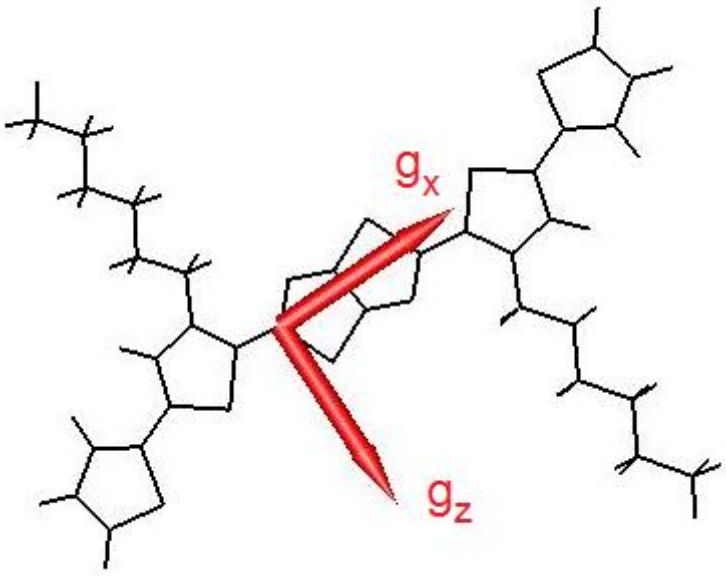

Figure S3. Positions of the g_x and g_z axis versus the molecular structure. Both axes are in the plane of the molecule, the g_y axis being perpendicular to it.

1.2. Negative polaron of Th-DTTzTz

1.2.1. Majority species

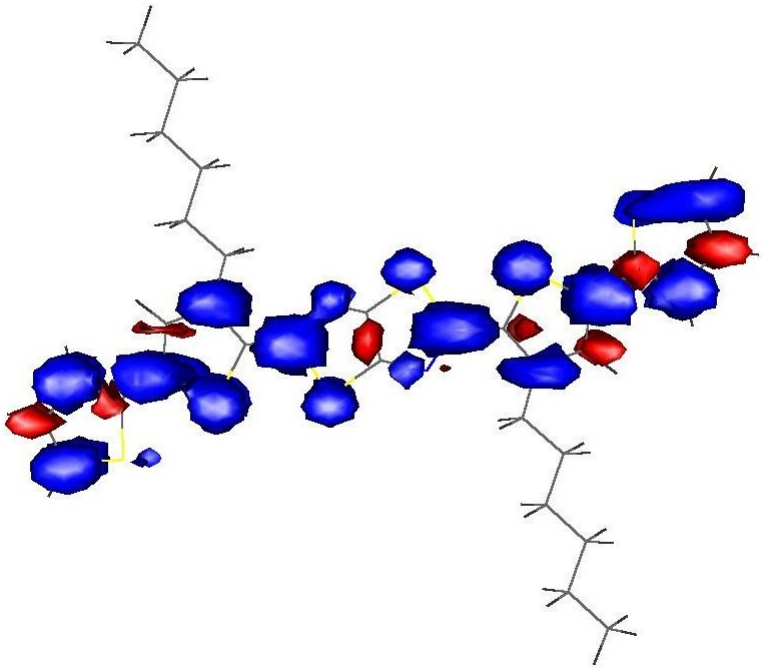

Figure S4. Spin density distribution of a majority conformer of the negative **Th-DTTzTz** polaron. Red: negative spin density, blue: positive spin density. Contour levels are set at -0.0012 and 0.0012, respectively.

Cartesian coordinates (in Å)

C	-1.561115	-0.068342	-0.179065
S	-0.561366	-1.592578	-0.201782
N	-0.834572	1.057542	-0.062202
C	0.468535	0.770300	0.008963
C	0.878998	-0.590417	-0.044852
S	1.908840	1.772415	0.166729
N	2.182162	-0.877613	0.025506
C	2.908735	0.248313	0.141822
C	4.328406	0.312917	0.240919
C	5.276219	-0.750191	0.240549
C	6.601807	-0.276595	0.357677
C	6.739398	1.119984	0.450763
S	5.144893	1.875988	0.389335
C	-2.980690	-0.132838	-0.279637
C	-3.928419	0.930351	-0.280323
C	-5.253914	0.456870	-0.398934
C	-5.391519	-0.939698	-0.492167
S	-3.797153	-1.695849	-0.428867
C	-6.596140	-1.711517	-0.620874
C	-7.929312	-1.269580	-0.684885
C	-8.873937	-2.325449	-0.813211
C	-8.293568	-3.583214	-0.849867

S	-6.555706	-3.477701	-0.725362
C	7.944094	1.891900	0.578160
C	9.277366	1.450068	0.640771
C	10.222037	2.506008	0.768175
C	9.641603	3.763721	0.805529
S	7.903644	3.658094	0.682488
C	4.878951	-2.204509	0.126412
C	-3.531137	2.384640	-0.165890
H	7.476846	-0.940337	0.376528
H	-6.128876	1.120686	-0.418747
H	-8.201118	-0.206186	-0.638871
H	-9.960631	-2.165618	-0.877484
H	-8.777188	-4.562923	-0.942091
H	9.549204	0.386693	0.594524
H	11.308804	2.346255	0.831407
H	10.125232	4.743459	0.897404
C	6.032460	-3.215724	0.145641
C	-4.684728	3.395788	-0.183418
H	4.274167	-2.339894	-0.797886
H	4.154125	-2.443238	0.936305
H	-2.807265	2.623865	-0.976523
H	-2.925295	2.519567	0.757754
C	-4.204780	4.849717	-0.063123
C	5.552466	-4.669758	0.026807
C	-5.336008	5.887433	-0.077707
C	6.683695	-5.707463	0.041969
C	-4.852223	7.340227	0.044224
C	-5.985514	8.372692	0.028603
C	6.199811	-7.160418	-0.077628
C	7.333145	-8.192837	-0.062037
H	6.620305	-3.100377	1.084522
H	6.741288	-2.995943	-0.684795
H	-5.393135	3.174940	0.647092
H	-5.273017	3.281535	-1.122157
H	-3.492460	5.069960	-0.890688
H	-3.612814	4.963634	0.873564
H	4.960208	-4.784518	-0.909594
H	4.840403	-4.889246	0.854792
H	-6.049109	5.667812	0.750408
H	-5.927569	5.775558	-1.015824
H	7.275953	-5.594317	0.979494
H	7.396184	-5.488977	-0.786973
H	-4.139023	7.557515	-0.782680
H	-4.261186	7.450112	0.981370
H	-6.695610	8.206704	0.866641
H	-6.571925	8.315543	-0.913178
H	-5.600173	9.409551	0.118789
H	5.607702	-7.271465	-1.013960
H	5.487565	-7.376709	0.750359
H	7.920774	-8.134360	0.878903
H	8.042151	-8.028010	-0.901226
H	6.947708	-9.229829	-0.150269

Table S3. Principal *g* values and direction cosines (r_x,r_y,r_z) of ***g*** tensor axes in lab frame in which molecular coordinates are defined as obtained via DFT.

	g_x	g_y	g_z
value	2.0024173	2.0057904	2.0083760
r_x	-0.0675252	-0.5707032	-0.8183753
r_y	-0.0600949	0.8210847	-0.5676341
r_z	0.9959061	0.0108506	-0.0897402

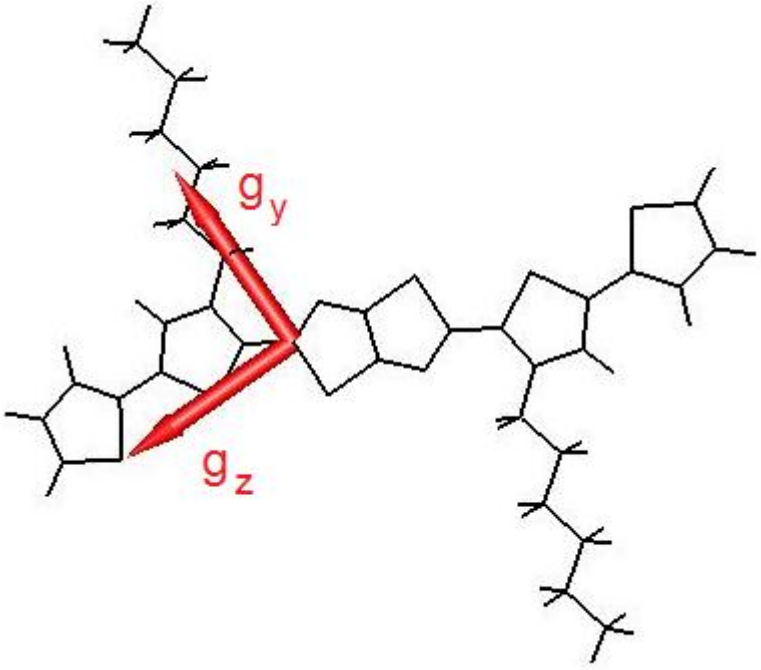

Figure S5. Positions of the g_y and g_z axis versus the molecular structure. Both axes are in the plane of the molecule, the g_x axis being perpendicular to it.

1.2.2. Minority species

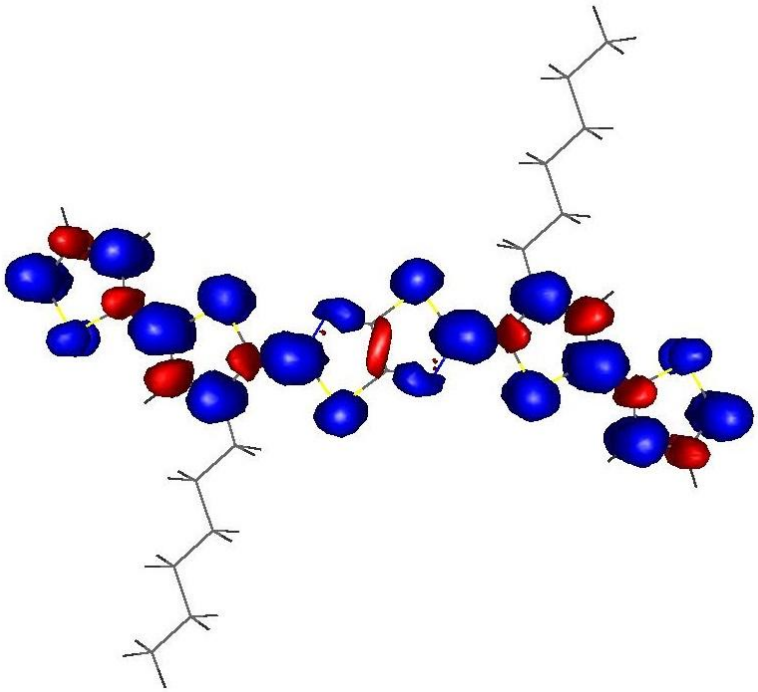

Figure S6. Spin density distribution of a minority conformer of the negative **Th-DTTzTz** polaron. Red: negative spin density, blue: positive spin density. Contour levels are set at -0.0012 and 0.0012, respectively.

Cartesian coordinates (in Å)

C	-8.034140	3.225150	-0.010475
C	-8.911728	2.168228	-0.016949
C	-6.669292	2.825522	-0.009012
C	-6.490474	1.443999	-0.014393
S	-8.065002	0.646994	-0.021409
C	-5.272090	0.684618	-0.014792
C	-5.104315	-0.699610	-0.019570
C	-3.766845	-1.146466	-0.018557
C	-2.848879	-0.070506	-0.012769
S	-3.701102	1.477674	-0.008948
C	-1.428621	-0.021851	-0.009765
S	-0.366218	-1.493098	-0.013022
N	-0.739245	1.126262	-0.004284
C	0.569091	0.899498	-0.002539
C	1.031764	-0.434702	-0.006433
S	1.967073	1.957895	0.003983
N	2.340101	-0.661468	-0.004629
C	3.029479	0.486646	0.000899
C	4.449736	0.535300	0.004046
C	5.367705	1.611261	0.009870
C	6.705174	1.164404	0.011048
C	6.872950	-0.219825	0.006335
S	5.301960	-1.012882	0.000453
C	8.091333	-0.979207	0.006047

C	8.270149	-2.360733	0.001165
C	9.634997	-2.760362	0.002587
C	10.512588	-1.703440	0.008547
S	9.665864	-0.182202	0.012519
C	-3.352326	-2.600948	-0.023065
C	4.953188	3.065744	0.014281
H	-8.357430	4.268811	-0.006812
H	-10.000612	2.188453	-0.019340
H	-5.829861	3.522884	-0.004099
H	-5.959369	-1.377479	-0.023684
H	7.560228	1.842273	0.015227
H	7.430716	-3.058096	-0.003329
H	9.958284	-3.804025	-0.000709
H	11.601472	-1.723665	0.010826
C	6.096500	4.085751	0.019512
H	-2.706782	-2.799971	0.853256
H	-2.703809	-2.793692	-0.898599
H	4.304840	3.258600	0.889919
H	4.307474	3.264657	-0.861938
C	5.604395	5.536765	0.023404
C	6.731418	6.574107	0.029575
C	6.241389	8.026001	0.032366
C	-4.495637	-3.620954	-0.028644
C	-4.003532	-5.071967	-0.032953
C	-5.130557	-6.109308	-0.038928
C	-4.640529	-7.561201	-0.042588
H	6.742676	3.923752	-0.862320
H	6.739756	3.918037	0.902413
H	4.954029	5.699550	0.903321
H	4.958058	5.705647	-0.858332
H	7.382687	6.411784	-0.850461
H	7.377693	6.406711	0.912339
H	-5.138853	-3.452973	-0.911521
H	-5.141852	-3.459223	0.853209
H	-3.356900	-5.241005	0.848537
H	-3.353461	-5.234596	-0.913116
H	-5.777330	-5.941546	-0.921258
H	-5.781330	-5.947350	0.841542
C	7.372264	9.056562	0.039330
C	-5.771408	-8.591759	-0.049259
H	5.590261	8.187244	0.911388
H	5.596198	8.192630	-0.850021
H	-3.994794	-7.728175	0.839335
H	-3.989943	-7.722099	-0.922074
H	8.020519	8.946436	-0.847084
H	8.014097	8.941479	0.929776
H	6.983724	10.088495	0.040801
H	-6.413762	-8.476358	-0.939288
H	-6.419144	-8.481950	0.837573
H	-5.382869	-9.623691	-0.051325

Table S4. Principal *g* values and direction cosines (r_x,r_y,r_z) of ***g*** tensor axes in lab frame in which molecular coordinates are defined as obtained via DFT.

	g_x	g_y	g_z
value	2.0023616	2.0048085	2.0085009
r_x	-0.0020488	0.1422550	-0.9898279
r_y	-0.0034779	0.9898230	0.1422615
r_z	0.9999919	0.0037340	-0.0015332

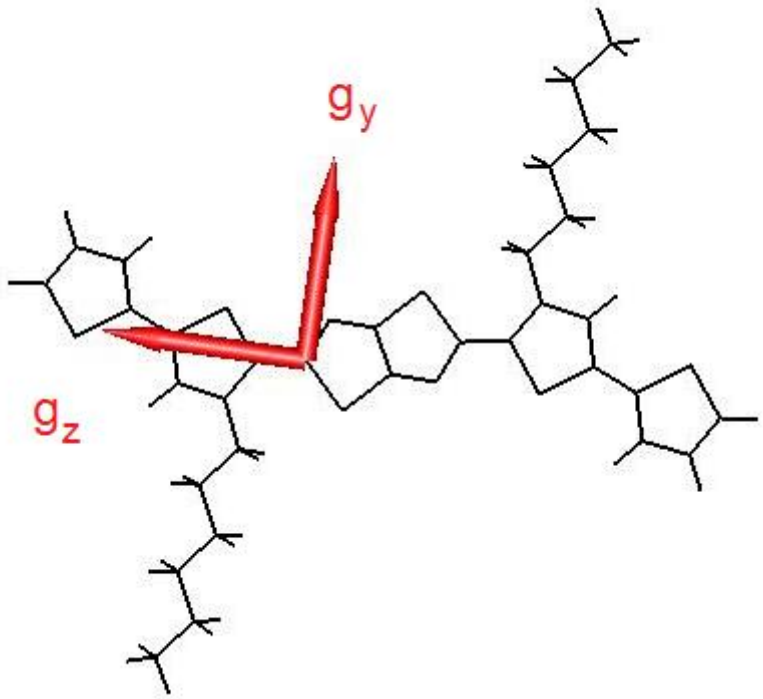

Figure S7. Positions of the g_y and g_z axis versus the molecular structure. Both axes are in the plane of the molecule, the g_x axis being perpendicular to it.

1.3. Positive polaron of 4-CN-Ph-DTTzTz

1.3.1. Majority species

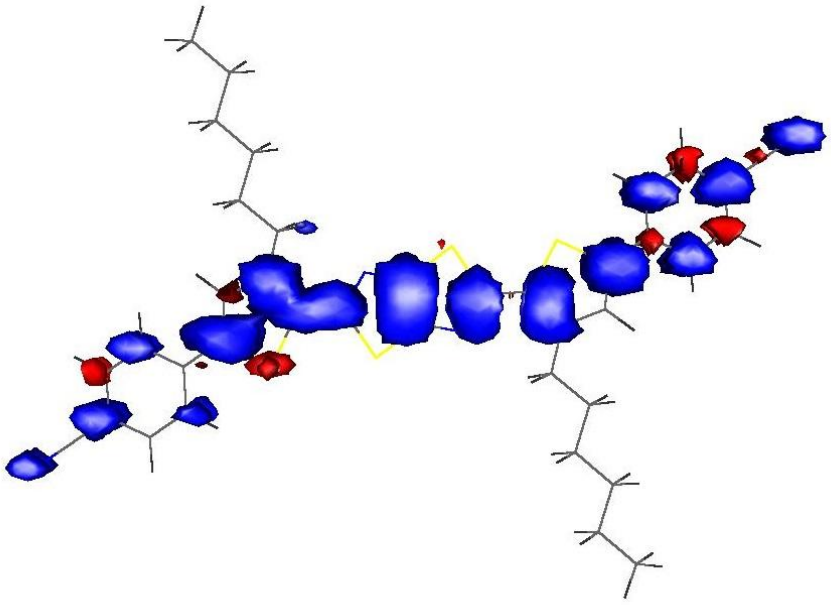

Figure S8. Spin density distribution of a majority conformer of the positive **4-CN-Ph-DTTzTz** polaron. Red: negative spin density, blue: positive spin density. Contour levels are set at -0.0012 and 0.0012, respectively.

Cartesian coordinates (in Å)

C	-1.454450	-0.158790	-0.095962
S	-0.421246	-1.652833	-0.089885
N	-0.773817	0.997377	-0.052780
C	0.533960	0.758599	-0.015145
C	0.974570	-0.611222	-0.026176
S	1.929798	1.800200	0.048394
N	2.282350	-0.849987	0.011682
C	2.962947	0.306202	0.054977
C	4.381239	0.404851	0.103015
C	5.342017	-0.656826	0.112341
C	6.653232	-0.143495	0.165077
C	6.749384	1.260521	0.196971
S	5.155957	1.982896	0.160741
C	-2.872738	-0.257471	-0.143454
C	-3.833556	0.804195	-0.151769
C	-5.144747	0.290861	-0.204978
C	-5.240853	-1.113135	-0.238192
S	-3.647461	-1.835507	-0.201012
C	4.997563	-2.121982	0.071056
C	-3.489149	2.269339	-0.109596
H	7.538671	-0.790050	0.180105
H	-6.030198	0.937407	-0.219883

C	6.185384	-3.093058	0.084170
C	-4.677021	3.240371	-0.121702
H	4.361205	-2.304280	-0.823342
H	4.311679	-2.341495	0.919394
H	-2.803554	2.489444	-0.958020
H	-2.852526	2.451066	0.784725
C	-4.236316	4.711336	-0.074837
C	5.744618	-4.564038	0.038300
C	-5.404877	5.706873	-0.085145
C	6.913124	-5.559628	0.049492
C	-4.965350	7.178116	-0.038017
C	-6.135973	8.167250	-0.048172
C	6.473523	-7.030880	0.003353
C	7.644090	-8.020070	0.014337
H	6.799321	-2.924369	0.997069
H	6.851432	-2.884371	-0.782773
H	-5.342849	3.030997	0.745245
H	-5.291168	3.072339	-1.034581
H	-3.565041	4.920106	-0.938623
H	-3.615939	4.878797	0.834790
H	5.124359	-4.732122	-0.871292
H	5.073214	-4.772147	0.902145
H	-6.076046	5.495895	0.778695
H	-6.025032	5.537477	-0.995042
H	7.533153	-5.389617	0.959360
H	7.584433	-5.349305	-0.814399
H	-4.293637	7.385158	-0.901310
H	-4.344219	7.343487	0.870936
H	-6.805105	8.012658	0.824147
H	-6.754146	8.054615	-0.963462
H	-5.781666	9.217066	-0.013435
H	5.852483	-7.196859	-0.905551
H	5.801702	-7.237277	0.866717
H	8.262168	-7.906821	0.929614
H	8.313327	-7.866131	-0.858018
H	7.289731	-9.069891	-0.019696
C	-6.439400	-1.938176	-0.295615
C	7.947986	2.085586	0.253006
C	-7.729391	-1.337695	-0.326084
C	-8.883586	-2.117455	-0.381630
C	-8.787890	-3.532515	-0.408790
C	-7.508473	-4.145483	-0.378669
C	-6.360222	-3.358246	-0.323116
C	7.868866	3.505684	0.279138
C	9.017166	4.292938	0.333385
C	10.296574	3.679960	0.363561
C	10.392211	2.264872	0.337794
C	9.237966	1.485092	0.283528
C	-9.973420	-4.336831	-0.466400
C	11.482197	4.484231	0.419854
H	-7.831787	-0.243904	-0.306185
H	-9.873538	-1.640218	-0.404769
H	-7.430443	-5.241677	-0.399444
H	-5.377616	-3.855256	-0.300553
H	6.886265	4.002699	0.256512
H	8.939172	5.389155	0.353096

H	11.382154	1.787624	0.361004
H	9.340329	0.391280	0.264744
N	-10.944492	-4.996274	-0.513551
N	12.453556	5.143330	0.465895

Table S5. Principal *g* values and direction cosines (r_x,r_y,r_z) of ***g*** tensor axes in lab frame in which molecular coordinates are defined as obtained via DFT.

	g_x	g_y	g_z
value	2.0007548	2.0021805	2.0028763
r_x	0.9677636	-0.0287185	0.2502176
r_y	0.2497583	-0.0186572	-0.9681285
r_z	0.0324715	0.9994134	-0.0108831

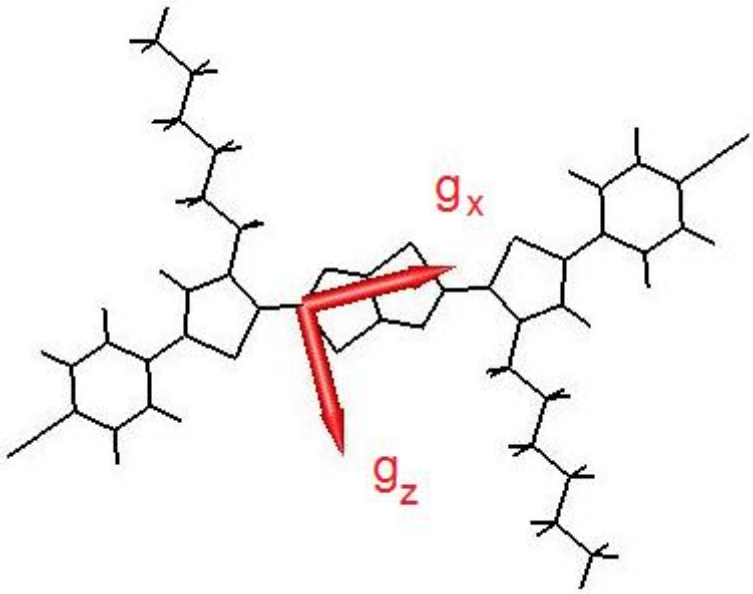

Figure S9. Positions of the g_x and g_z axis versus the molecular structure. Both axes are in the plane of the molecule, the g_y axis being perpendicular to it.

1.3.2. Minority species

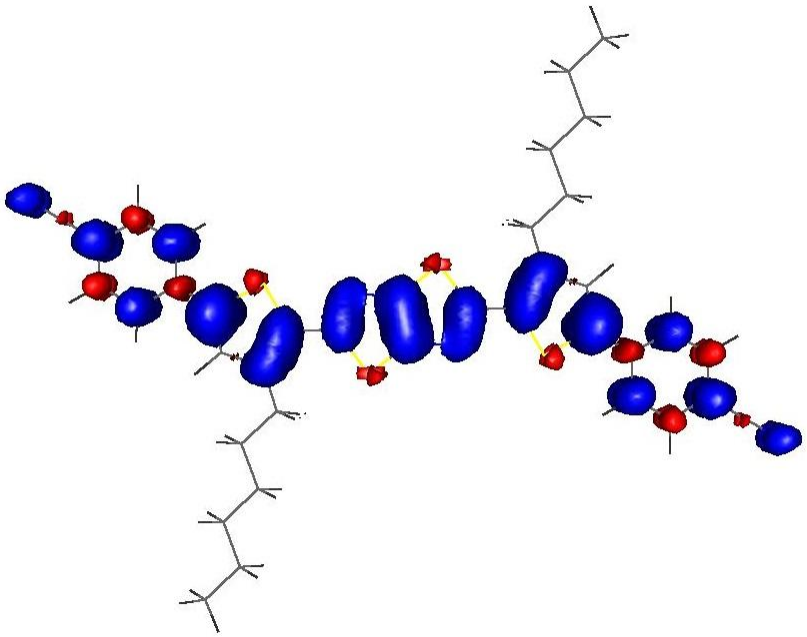

Figure S10. Spin density distribution of a minority conformer of the positive **4-CN-Ph-DTTzTz** polaron. Red: negative spin density, blue: positive spin density. Contour levels are set at -0.0012 and 0.0012, respectively.

Cartesian coordinates (in Å)

C	-7.679189	3.436001	0.024262
C	-8.904475	2.739068	0.036042
C	-6.481176	2.734793	0.017194
C	-6.459880	1.320363	0.021599
C	-5.202311	0.582117	0.014053
C	-5.027156	-0.808755	0.003753
C	-3.691805	-1.236781	-0.002069
C	-2.801907	-0.128692	0.004321
S	-3.668972	1.398195	0.017175
C	-1.387824	-0.060978	0.002241
S	-0.315711	-1.504295	-0.008779
N	-0.739514	1.112838	0.008690
C	0.565969	0.922960	0.005172
C	1.045886	-0.423887	-0.004360
S	1.927564	2.003370	0.009620
N	2.351368	-0.613766	-0.007849
C	2.999679	0.560049	-0.001443
C	4.413761	0.627769	-0.003342
C	5.303651	1.735865	0.002866
C	6.639006	1.307845	-0.002334
C	6.814170	-0.083030	-0.011972
S	5.280840	-0.899119	-0.015512
C	8.071749	-0.821270	-0.018688

C	8.093086	-2.235679	-0.010087
C	9.291111	-2.936875	-0.016354
C	10.516364	-2.239950	-0.031517
C	-3.258078	-2.680395	-0.013947
C	4.869909	3.179480	0.014163
H	-7.677952	4.527483	0.020434
H	-5.544958	3.298222	0.007125
H	-5.864764	-1.502828	-0.000768
H	7.476612	2.001919	0.002432
H	7.156895	-2.799093	0.002902
H	9.289908	-4.028340	-0.009200
C	5.993950	4.221990	0.019685
H	-2.608376	-2.859809	0.863410
H	-2.609295	-2.845761	-0.894703
H	4.222246	3.345465	0.895643
H	4.219086	3.358249	-0.862477
C	5.464498	5.660199	0.030641
C	6.570610	6.719899	0.036676
C	6.044934	8.159455	0.046888
C	-4.382132	-3.722876	-0.021685
C	-3.852694	-5.161080	-0.034162
C	-4.958819	-6.220751	-0.042509
C	-4.433160	-7.660290	-0.055639
H	6.636198	4.077108	-0.867196
H	6.639016	4.064687	0.902396
H	4.815516	5.803060	0.914727
H	4.813085	5.815623	-0.849532
H	7.220089	6.574827	-0.847045
H	7.221813	6.562945	0.917090
H	-5.026585	-3.564349	-0.904623
H	-5.024991	-3.579207	0.864952
H	-3.202033	-5.317691	0.846355
H	-3.202963	-5.302769	-0.917887
H	-5.609965	-6.061964	-0.922637
H	-5.608350	-6.077502	0.841470
C	7.153726	9.212872	0.053326
C	-5.541966	-8.713678	-0.064187
H	5.394779	8.301110	0.929784
H	5.393557	8.313164	-0.833087
H	-3.781776	-7.815788	0.824016
H	-3.783017	-7.800165	-0.938828
H	7.798951	9.122647	-0.836805
H	7.799945	9.110725	0.941445
H	6.739192	10.233281	0.060396
H	-6.188275	-8.609642	-0.952022
H	-6.187099	-8.625328	0.826199
H	-5.127446	-9.734074	-0.073458
C	-8.900524	1.329665	0.040618
C	-7.697889	0.635402	0.033501
C	9.309724	-0.136316	-0.033980
C	10.512370	-0.830567	-0.040323
H	-9.847579	0.787045	0.050078
H	-7.725152	-0.454853	0.038341
H	9.336943	0.953920	-0.042388
H	11.459400	-0.287956	-0.052512
C	11.757346	-2.959844	-0.037934

N	12.761541	-3.542775	-0.043103
C	-10.145433	3.458994	0.043350
N	-11.149539	4.042068	0.049670

Table S6. Principal *g* values and direction cosines (r_x,r_y,r_z) of ***g*** tensor axes in lab frame in which molecular coordinates are defined as obtained via DFT.

	g_x	g_y	g_z
value	2.0006758	2.0021811	2.0030564
r_x	-0.9560462	-0.0014943	-0.2932122
r_y	-0.2932070	-0.0029610	0.9560444
r_z	-0.0022968	0.9999945	0.0023927

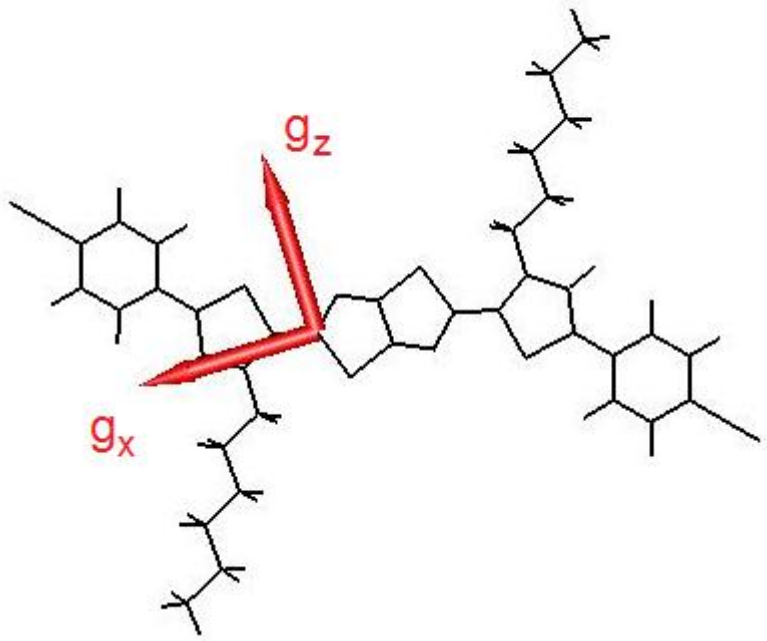

Figure S11. Positions of the g_x and g_z axis versus the molecular structure. Both axes are in the plane of the molecule, the g_y axis being perpendicular to it.

1.4. Negative polaron of 4-CN-Ph-DTTzTz

1.4.1. Majority species

Cartisian coordinates (in Å)

C	-1.475585	-0.147994	-0.094742
S	-0.440555	-1.644051	-0.087125
N	-0.779088	0.999966	-0.050551

C	0.533115	0.749546	-0.011985
C	0.975186	-0.602370	-0.022480
S	1.948827	1.791205	0.053479
N	2.287412	-0.852761	0.015473
C	2.983903	0.295203	0.059226
C	4.405556	0.397743	0.107125
C	5.374762	-0.645748	0.116646
C	6.689590	-0.136621	0.168610
C	6.801683	1.265763	0.200550
S	5.185881	1.979231	0.165573
C	-2.897200	-0.250498	-0.143922
C	-3.866399	0.793024	-0.153814
C	-5.181163	0.283939	-0.207903
C	-5.293223	-1.118434	-0.241331
S	-3.677523	-1.831974	-0.203041
C	5.012568	-2.112913	0.074861
C	-3.504244	2.260169	-0.110765
H	7.574752	-0.786072	0.182865
H	-6.066317	0.933410	-0.223141
C	6.193607	-3.091882	0.085947
C	-4.685267	3.239156	-0.122545
H	4.375355	-2.298331	-0.818048
H	4.327800	-2.336271	0.922844
H	-2.818558	2.484027	-0.957886
H	-2.867994	2.445046	0.782952
C	-4.242792	4.709018	-0.075206
C	5.751113	-4.561782	0.040071
C	-5.404702	5.712204	-0.085254
C	6.913073	-5.564915	0.049209
C	-4.961413	7.182059	-0.037608
C	-6.126337	8.178642	-0.047505
C	6.469799	-7.034813	0.002763
C	7.634779	-8.031336	0.011770
H	6.813133	-2.925738	0.996257
H	6.863107	-2.885200	-0.779574
H	-5.355749	3.031916	0.742091
H	-5.303772	3.073615	-1.033669
H	-3.568987	4.916910	-0.937467
H	-3.620297	4.875252	0.833412
H	5.127429	-4.728588	-0.867622
H	5.078453	-4.769170	0.903342
H	-6.078743	5.504444	0.777781
H	-6.027280	5.546385	-0.994778
H	7.536711	-5.398652	0.957919
H	7.586086	-5.357519	-0.814711
H	-4.287770	7.387718	-0.899893
H	-4.338766	7.345683	0.870776
H	-6.797797	8.024796	0.823910
H	-6.746393	8.067161	-0.962382
H	-5.770115	9.228955	-0.012345
H	5.846104	-7.198888	-0.904818
H	5.797172	-7.240101	0.865927
H	8.255860	-7.919443	0.925897
H	8.305248	-7.877832	-0.860466
H	7.278564	-9.081678	-0.022548
C	-6.479629	-1.939436	-0.298283

C	7.988164	2.086845	0.254485
C	-7.787657	-1.359587	-0.330729
C	-8.935378	-2.142684	-0.386087
C	-8.850820	-3.565055	-0.412790
C	-7.556762	-4.157882	-0.380830
C	-6.412813	-3.368249	-0.325430
C	7.921302	3.515636	0.281778
C	9.065320	4.305346	0.334335
C	10.359477	3.712610	0.363133
C	10.444078	2.290259	0.336259
C	9.296287	1.507085	0.283727
C	-10.028818	-4.369819	-0.470141
C	11.537557	4.517434	0.417599
H	-7.895054	-0.265151	-0.311823
H	-9.925819	-1.663636	-0.409947
H	-7.466976	-5.254425	-0.400435
H	-5.427231	-3.859713	-0.301875
H	6.935641	4.007015	0.260753
H	8.975508	5.401869	0.354169
H	11.434598	1.811291	0.357679
H	9.403711	0.412675	0.264512
N	-11.002446	-5.033116	-0.517631
N	12.511307	5.180695	0.462722

Table S7. Principal g values and direction cosines (r_x,r_y,r_z) of $\boldsymbol{g}$ tensor axes in lab frame in which molecular coordinates are defined as obtained via DFT.

	g_x	g_y	g_z
value	2.0023625	2.0049263	2.0075836
r_x	-0.0339109	-0.4027183	-0.9146956
r_y	-0.0193461	0.9153150	-0.4022737
r_z	0.9992376	0.0040543	-0.0388302

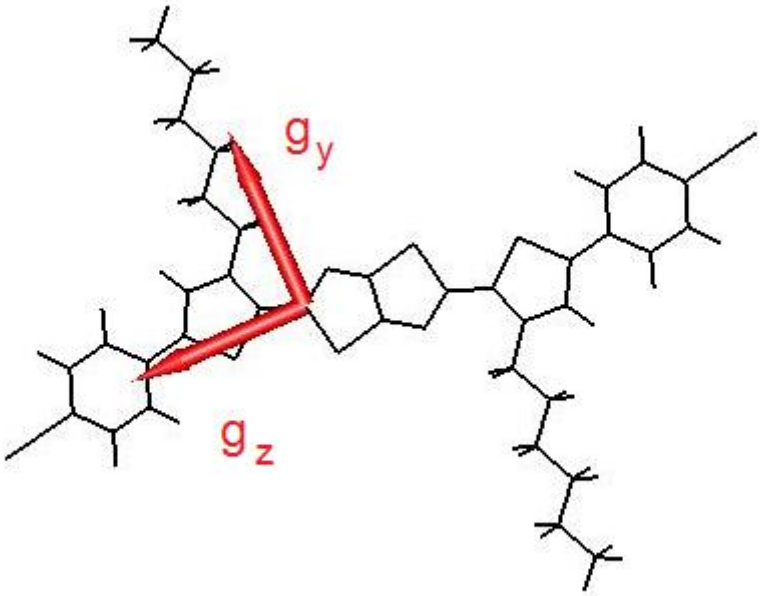

Figure S12. Positions of the g_y and g_z axis versus the molecular structure. Both axes are in the plane of the molecule, the g_x axis being perpendicular to it.

1.4.2. Minority species

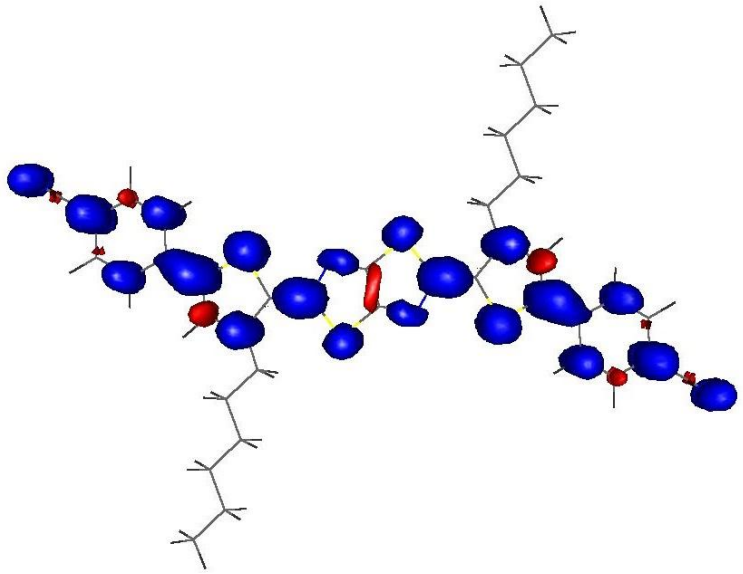

Figure S13. Spin density distribution of a minority conformer of the negative **4-CN-Ph-DTTzTz** polaron. Red: negative spin density, blue: positive spin density. Contour levels are set at -0.0012 and 0.0012, respectively.

Cartesian coordinates (in Å)

C	-7.760581	3.426308	0.045590
C	-8.997182	2.739994	0.046607
C	-6.562662	2.730153	0.036975
C	-6.519888	1.307304	0.028814
C	-5.272304	0.581426	0.019762
C	-5.070393	-0.801616	0.008040
C	-3.726839	-1.219294	-0.000365
C	-2.833753	-0.121822	0.005244
S	-3.716247	1.401848	0.023412
C	-1.413368	-0.046462	-0.000542
S	-0.327810	-1.495230	-0.016929
N	-0.749494	1.114026	0.005418
C	0.563698	0.912472	-0.000769
C	1.048136	-0.413324	-0.011728
S	1.939634	1.994401	0.001448
N	2.361334	-0.614894	-0.015584
C	3.025210	0.545582	-0.008250
C	4.445607	0.620913	-0.008721
C	5.338682	1.718387	-0.002079
C	6.682251	1.300679	-0.003921
C	6.884185	-0.082389	-0.011495
S	5.328142	-0.902803	-0.019961
C	8.131787	-0.808289	-0.013517
C	8.174579	-2.231153	-0.017472
C	9.372518	-2.927326	-0.019285
C	10.609118	-2.241017	-0.017231
C	-3.280765	-2.664063	-0.014639
C	4.892581	3.163189	0.007029
H	-7.754414	4.518981	0.051602
H	-5.626385	3.293601	0.036208
H	-5.901888	-1.505727	0.004284
H	7.513734	2.004790	0.001706
H	7.238302	-2.794599	-0.018827
H	9.366365	-4.020013	-0.022209
C	6.011374	4.209871	0.013875
H	-2.628056	-2.851470	0.858699
H	-2.631384	-2.835068	-0.893770
H	4.241370	3.336822	0.884312
H	4.241695	3.347976	-0.868202
C	5.483770	5.648354	0.022497
C	6.585365	6.712538	0.029930
C	6.059492	8.151793	0.037742
C	-4.399575	-3.710722	-0.022281
C	-3.871995	-5.149162	-0.037372
C	-4.973603	-6.213326	-0.045808
C	-4.447747	-7.652523	-0.061522
H	6.659641	4.066152	-0.869537
H	6.658945	4.055335	0.895977
H	4.831090	5.792549	0.903850
H	4.832303	5.803572	-0.857881
H	7.238799	6.568763	-0.851676
H	7.236816	6.558477	0.911266
H	-5.049470	-3.553008	-0.902105
H	-5.045511	-3.570203	0.863354

H	-3.218353	-5.307505	0.840837
H	-3.221496	-5.290213	-0.920842
H	-5.627945	-6.055477	-0.924326
H	-5.624138	-6.073370	0.838552
C	7.164764	9.209555	0.045626
C	-5.553032	-8.710267	-0.070171
H	5.406265	8.294261	0.918402
H	5.408796	8.304743	-0.843033
H	-3.794079	-7.809209	0.816394
H	-3.797497	-7.791225	-0.944980
H	7.813584	9.118321	-0.842427
H	7.810781	9.108002	0.934602
H	6.750460	10.231218	0.050903
H	-6.202124	-8.604856	-0.956454
H	-6.198773	-8.622916	0.820513
H	-5.138742	-9.731888	-0.081333
C	-8.974241	1.324139	0.038665
C	-7.774498	0.633434	0.030145
C	9.386399	-0.134422	-0.011728
C	10.586160	-0.825144	-0.013430
H	-9.918577	0.774221	0.039493
H	-7.799753	-0.457830	0.024645
H	9.411641	0.956853	-0.009310
H	11.530497	-0.275230	-0.012038
C	11.846846	-2.954000	-0.018994
N	12.857666	-3.533634	-0.020392
C	-10.234881	3.452973	0.055453
N	-11.245629	4.032687	0.063030

Table S8. Principal g values and direction cosines (r_x,r_y,r_z) of ***g*** tensor axes in lab frame in which molecular coordinates are defined as obtained via DFT.

	g_x	g_y	g_z
value	2.0023395	2.0047815	2.0071833
r_x	0.0018132	0.1321774	-0.9912244
r_y	-0.0058382	0.9912106	0.1321649
r_z	0.9999813	0.0055473	0.0025689

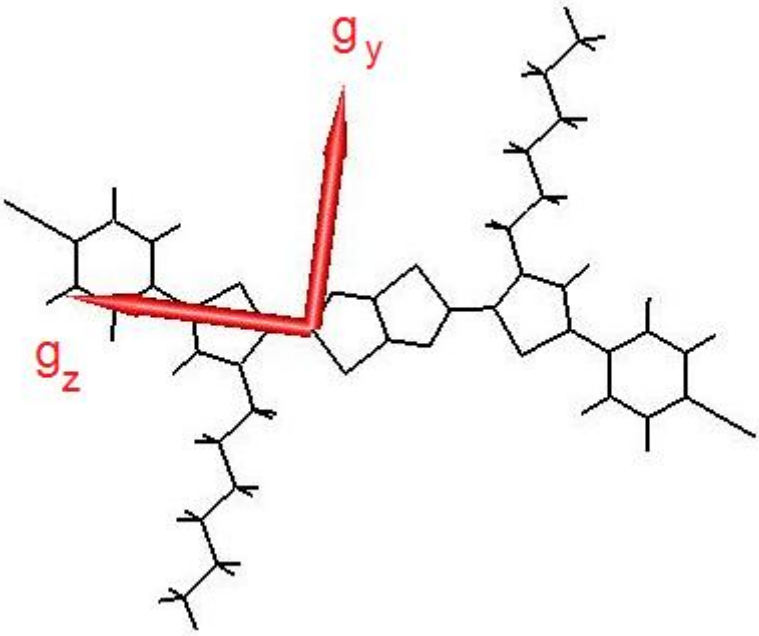

Figure S14. Positions of the g_y and g_z axis versus the molecular structure. Both axes are in the plane of the molecule, the g_x axis being perpendicular to it.

1.5 Rotation barrier for alkyl side chain

The alkyl rotation barrier was calculated for the dominant species of the positive polaron of **Th-DTTzTz** (Figure S15). The computations were performed in vacuum using the same functional/basis set combinations as for the other computations. The computations support that rotational disorder can be the reason why no clear contribution of the H^E protons is found in the ENDOR spectra (see main text).

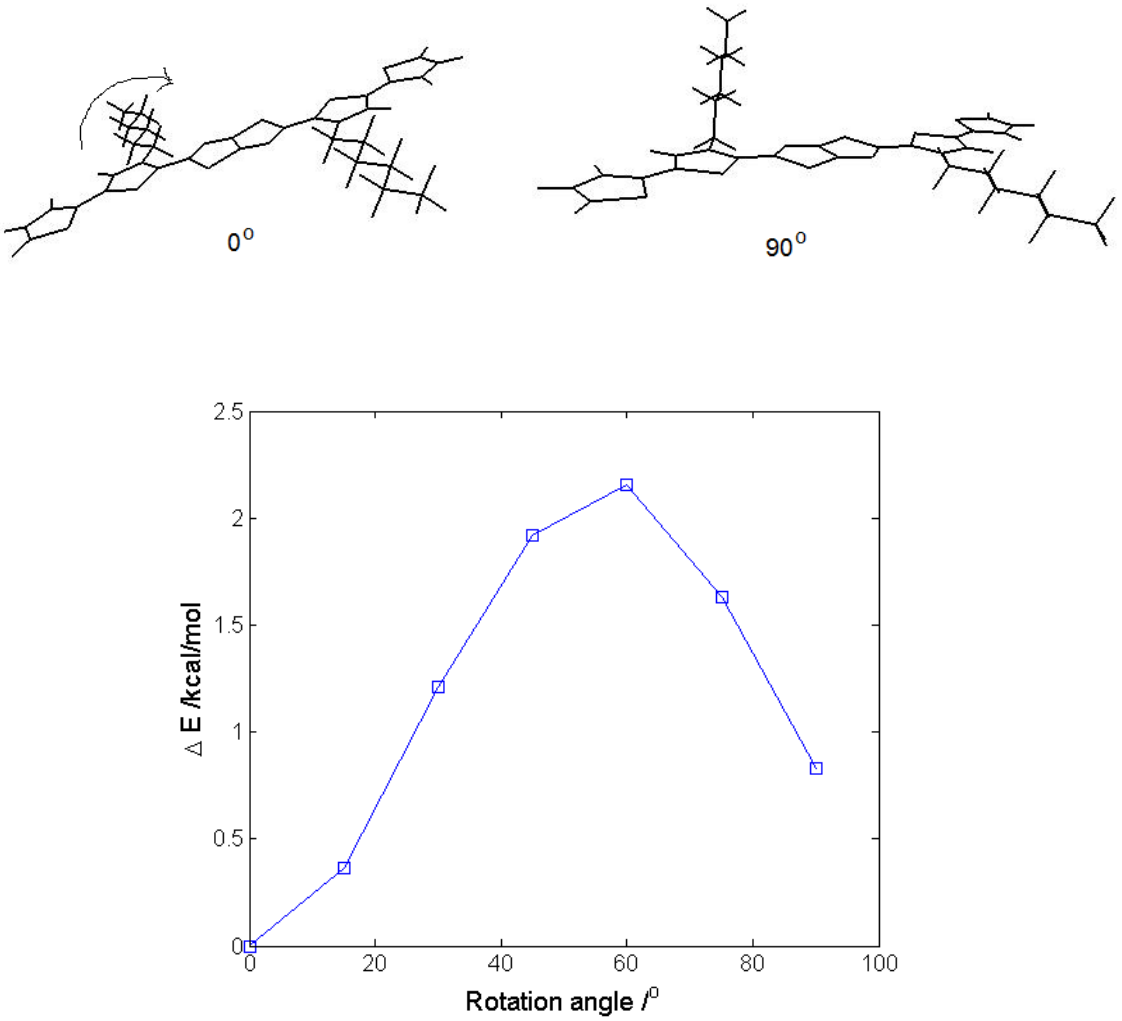

Figure S15. Computation of the rotation energy barrier. Rotation around one bound was considered as indicated in the top cartoon.

2. Experimental results

2.1 ^{14}N HYSCORE of positive polaron of Th-DTTzTz

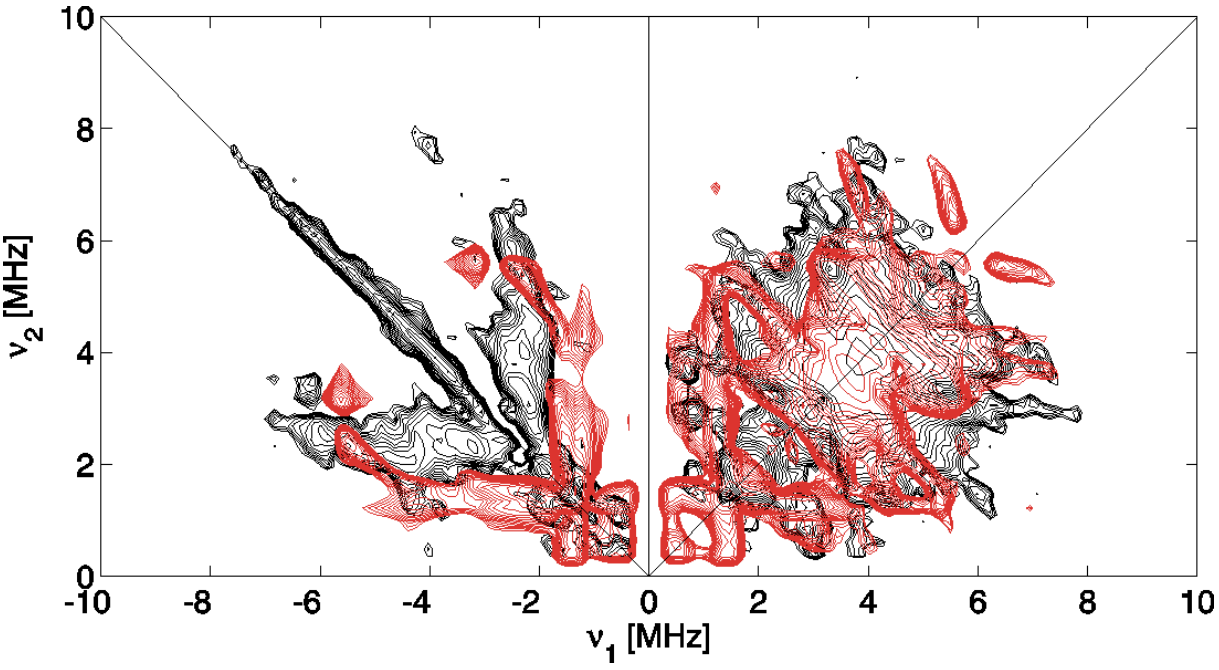

Figure S16. Comparison of the experimental (black) and simulated (red) HYSCORE spectrum of an I_2-induced positive **Th-DTTzTz** polaron. The simulations are done assuming the DFT-computed spin Hamiltonian values of Table 3 (main text) (the contributions of both equivalent nitrogen nuclei are included).

2.2 Light-induced EPR spectrum of the 4-CN-Ph-DTTzTz:MDMO-PPV blend

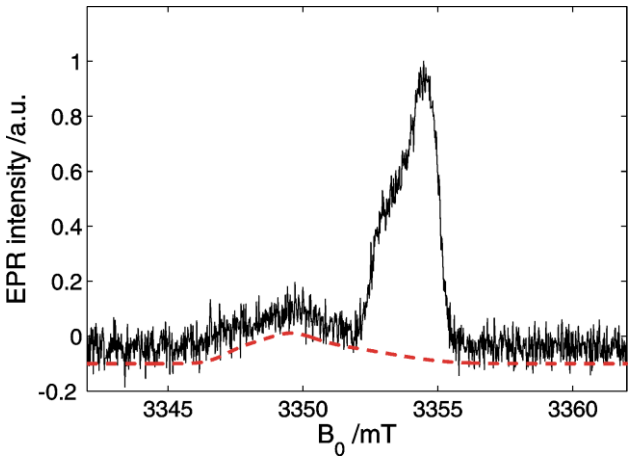

Figure S17. Light-induced W-band ESE-detected EPR spectrum of a **4-CN-Ph-DTTzTz:MDMO-PPV** (1:1) blend. The experiment is given in solid black, The simulation (red dashed line) is performed using the principal *g* values of Table 1 (main text). The second signal corresponds to the positive MDMO-PPV polaron (see reference 14 of main text).