

## Electronic Supporting Information (ESI)

### Luminescent Gold-Thallium Derivatives with a Pyridine-Containing 12-Membered Aza-Thioether Macrocycle

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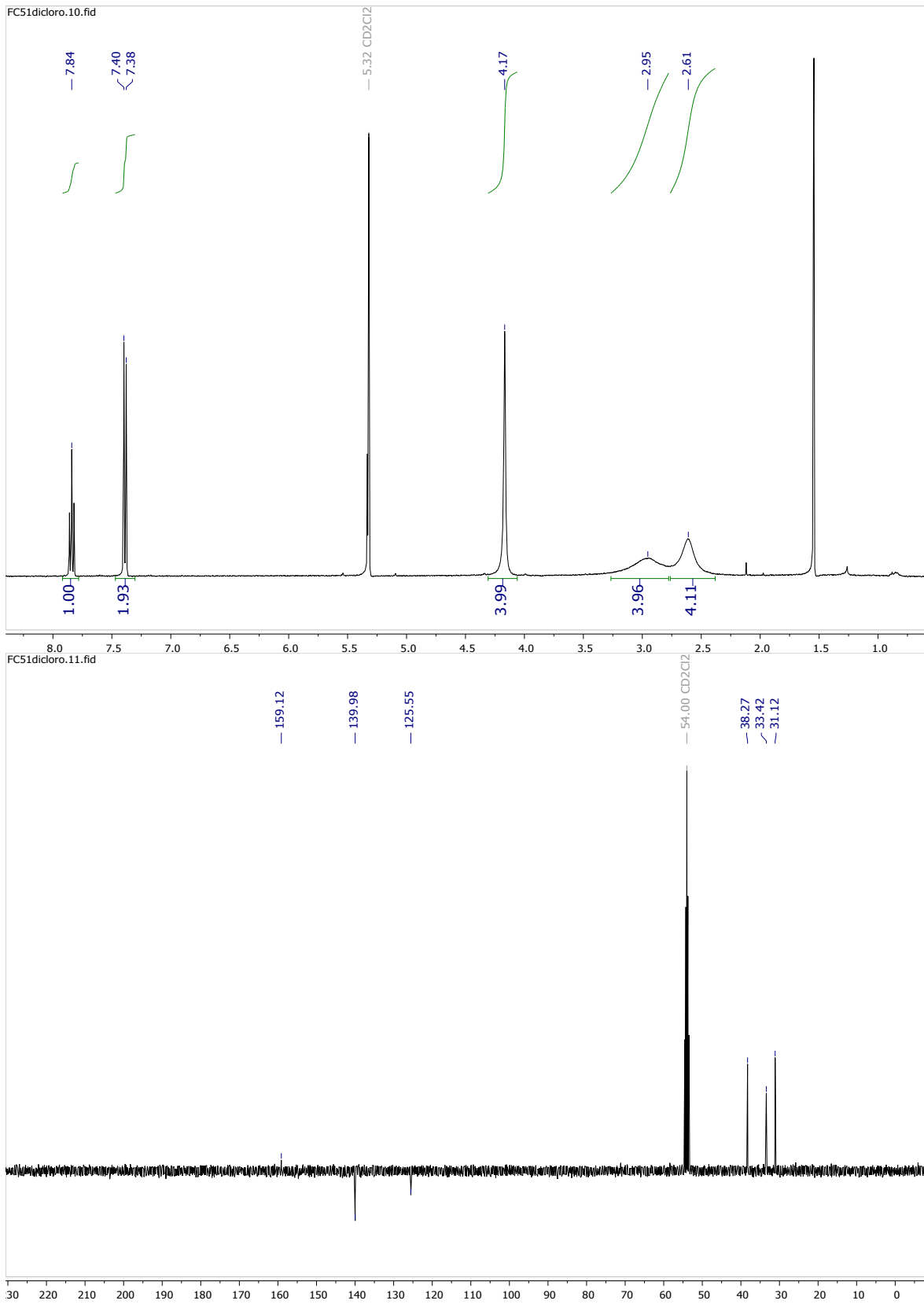


Figure S1.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of complex 1

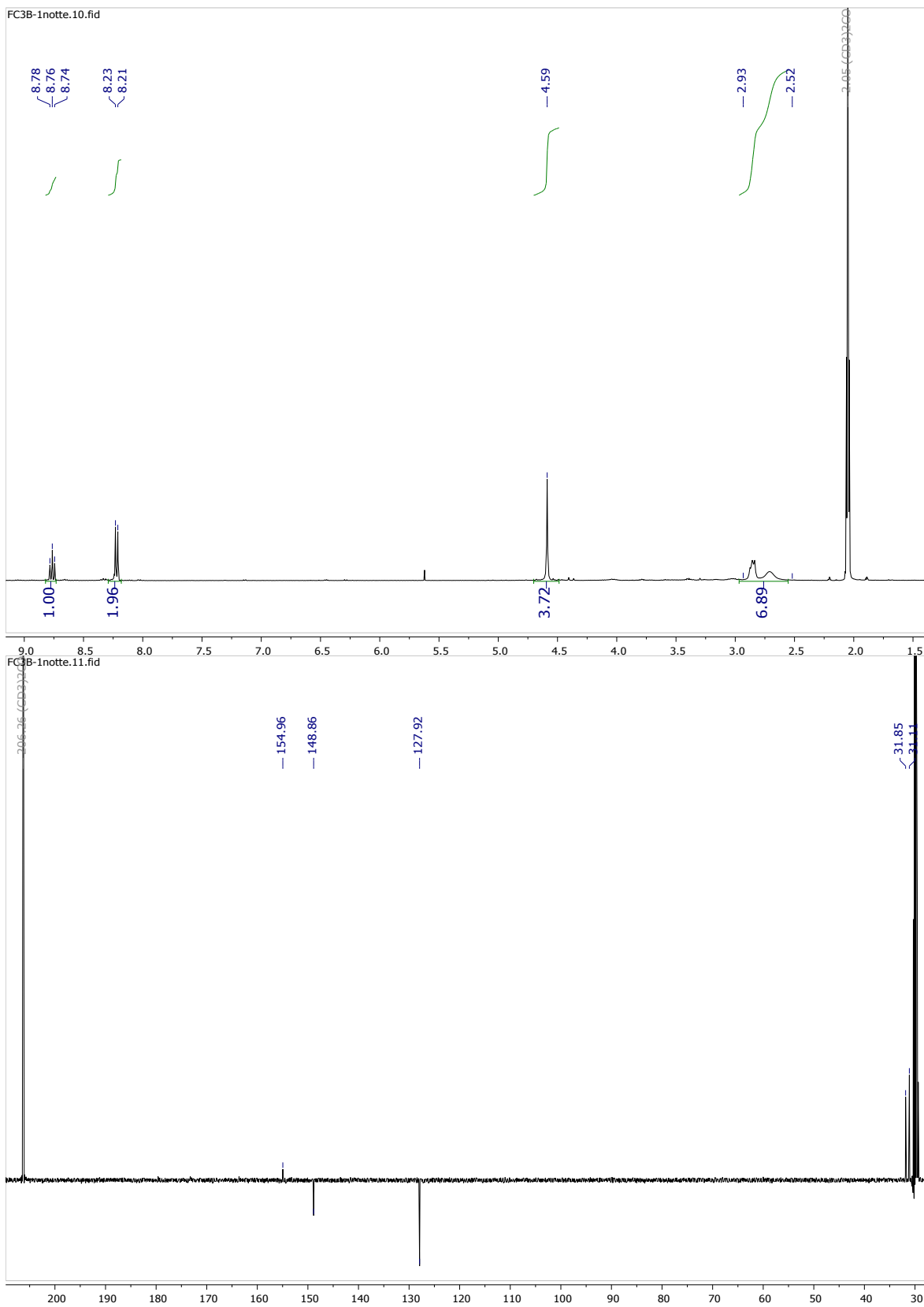


Figure S2.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of complex 2

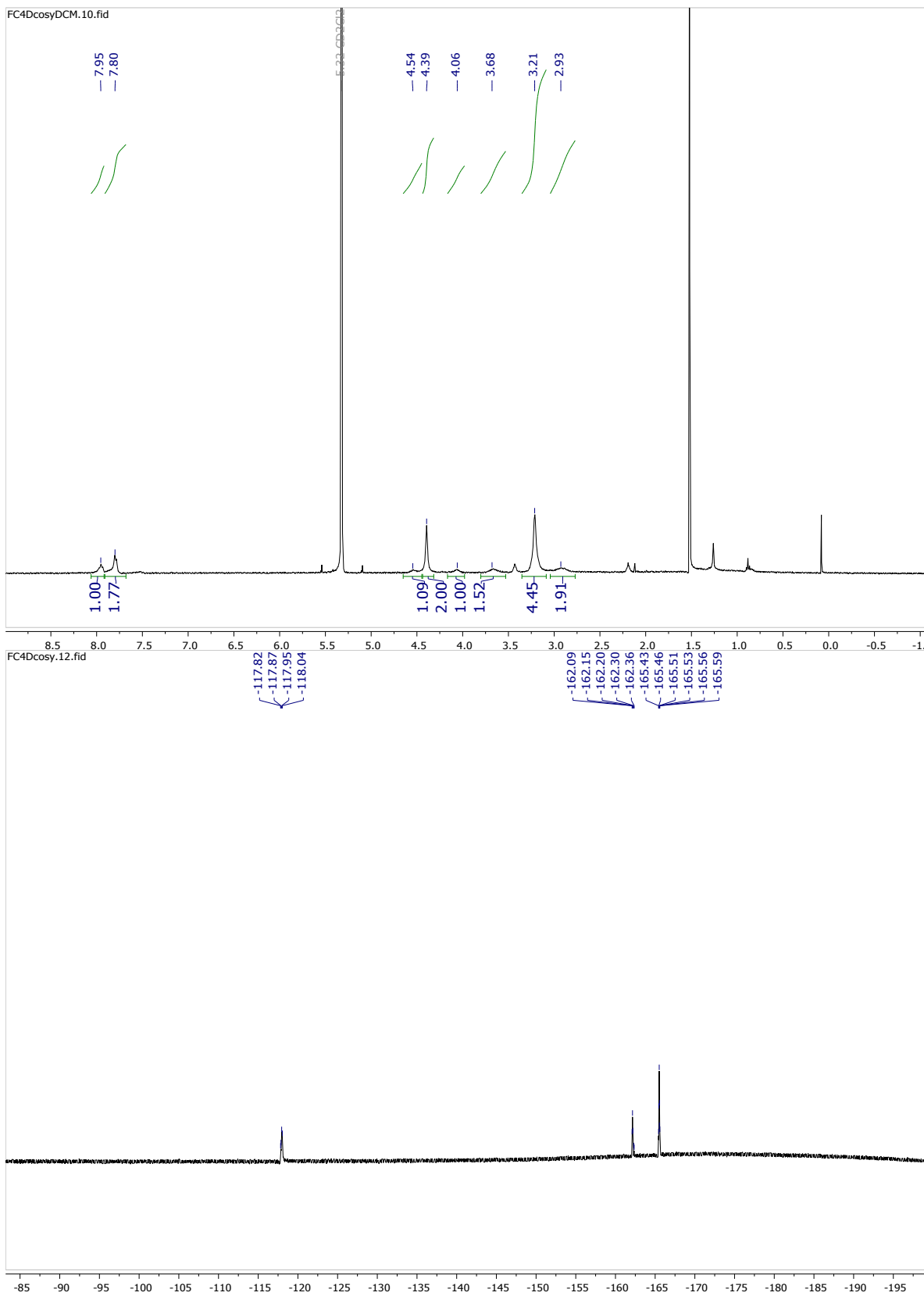


Figure S3.  $^1\text{H}$  and  $^{19}\text{F}$ -NMR of complex 3

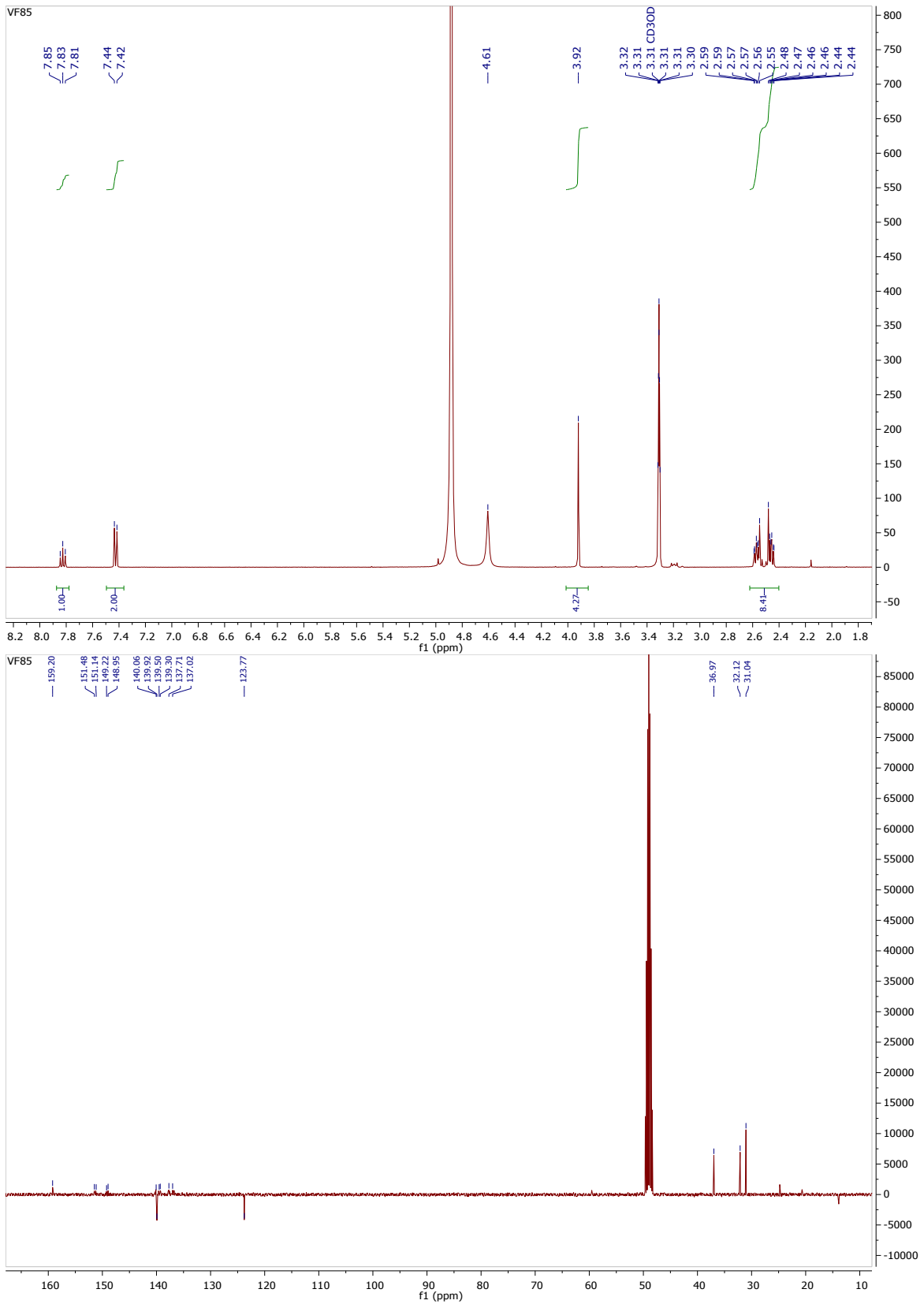
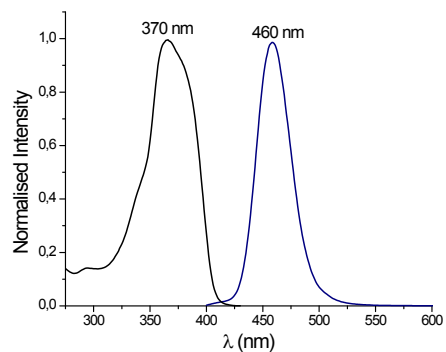
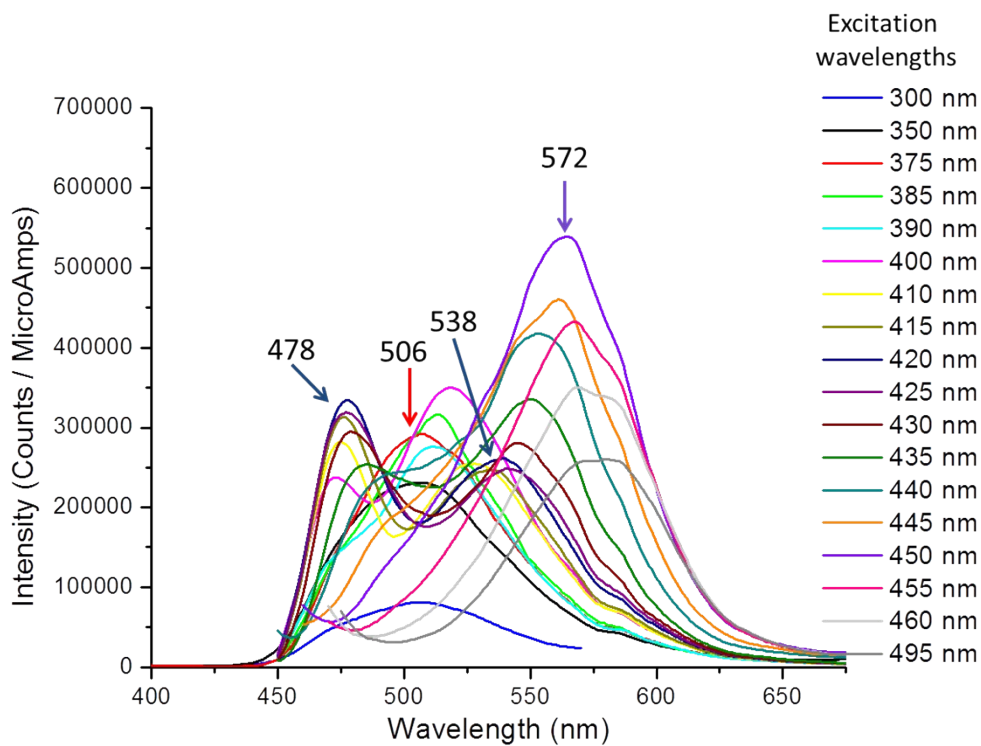


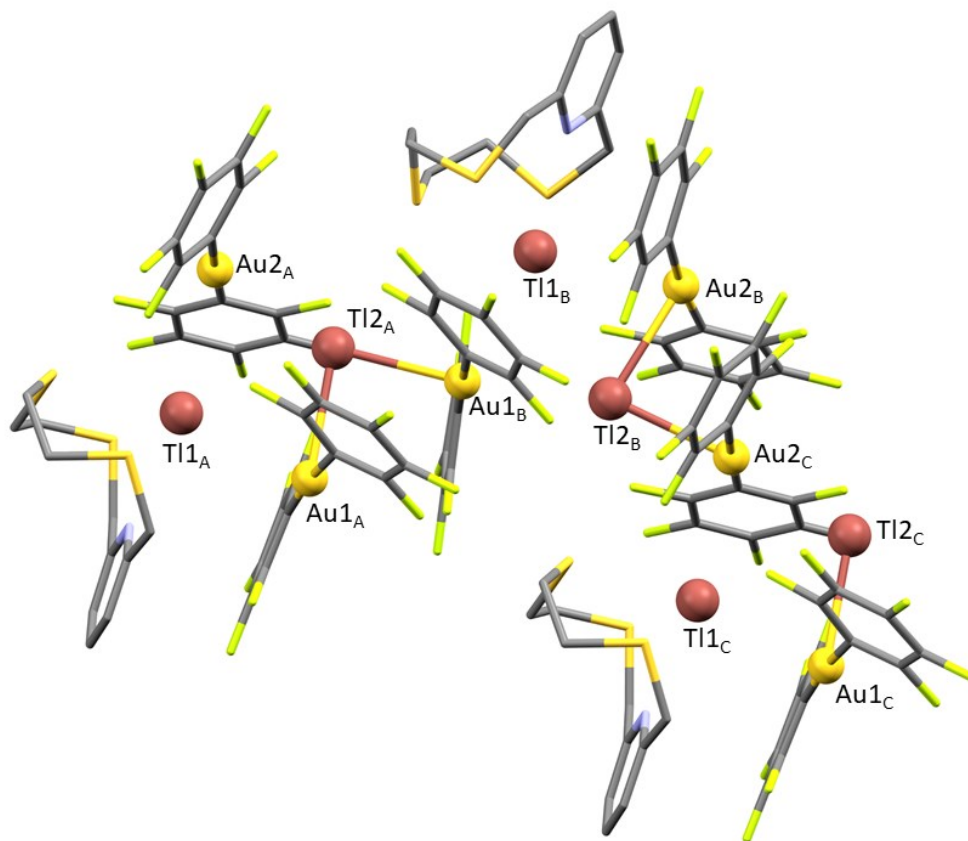
Figure S4.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR of complex 4



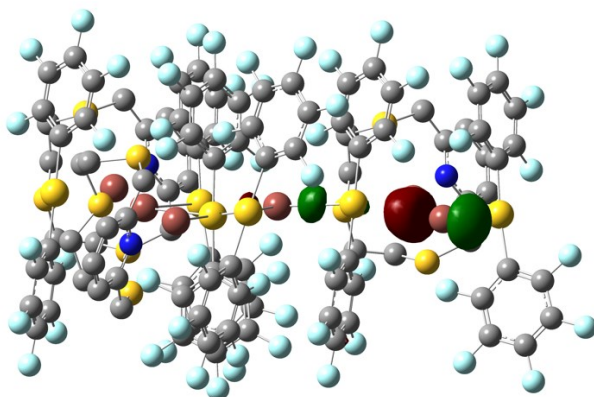
**Figure S5.** Emission and excitation spectra of **3** recorded at in solid state at 77 K.



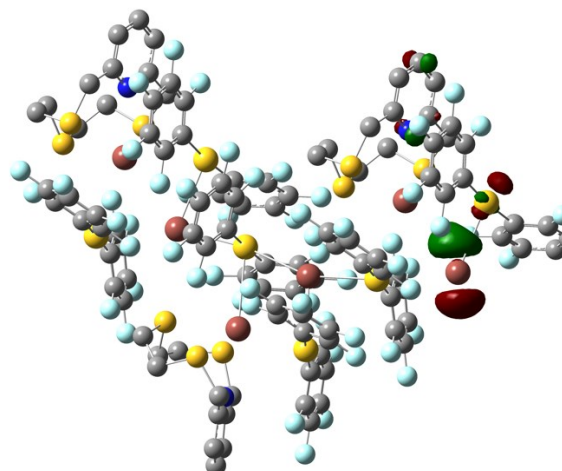
**Figure S6.** Emission spectra of **4** recorded at different excitation wavelengths (77 K)



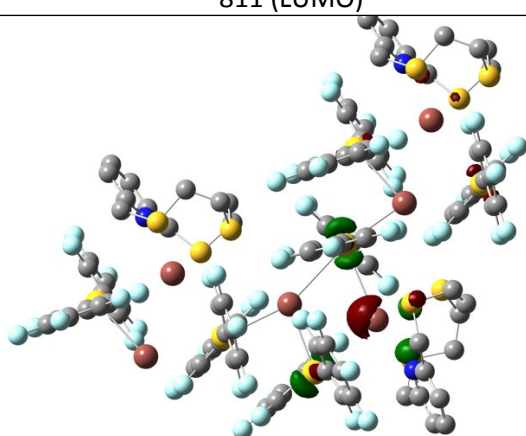
**Figure S7.** Molecular drawing and atom labelling scheme for the oligomeric portion  $\{\text{LTl}_2[\text{Au}(\text{C}_6\text{F}_5)_2]_2\}_3$  (**4'**), selected as model for **4** for DFT calculations.



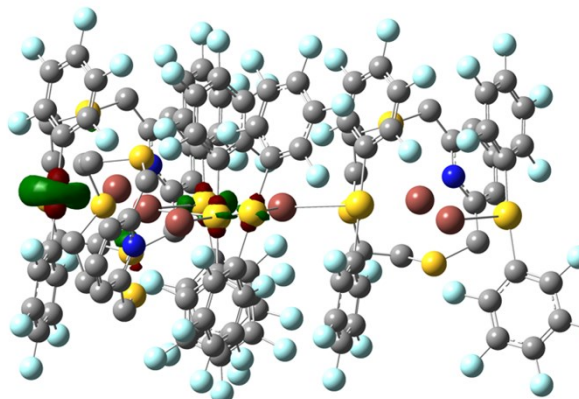
811 (LUMO)



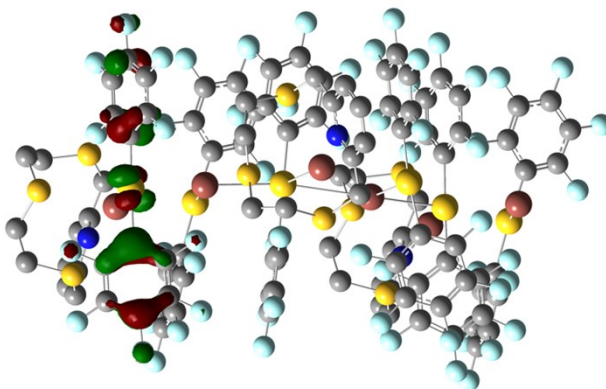
814 (LUMO+3)



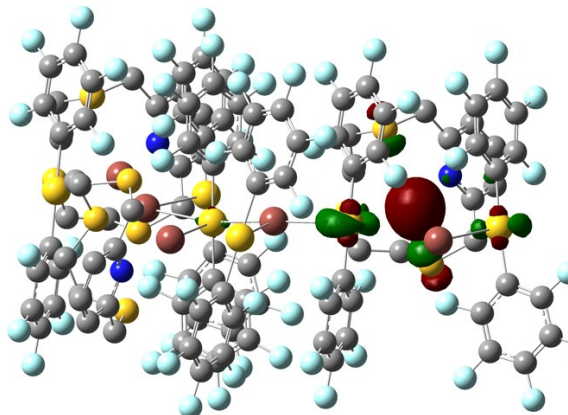
809 (HOMO-1)



810 (HOMO)

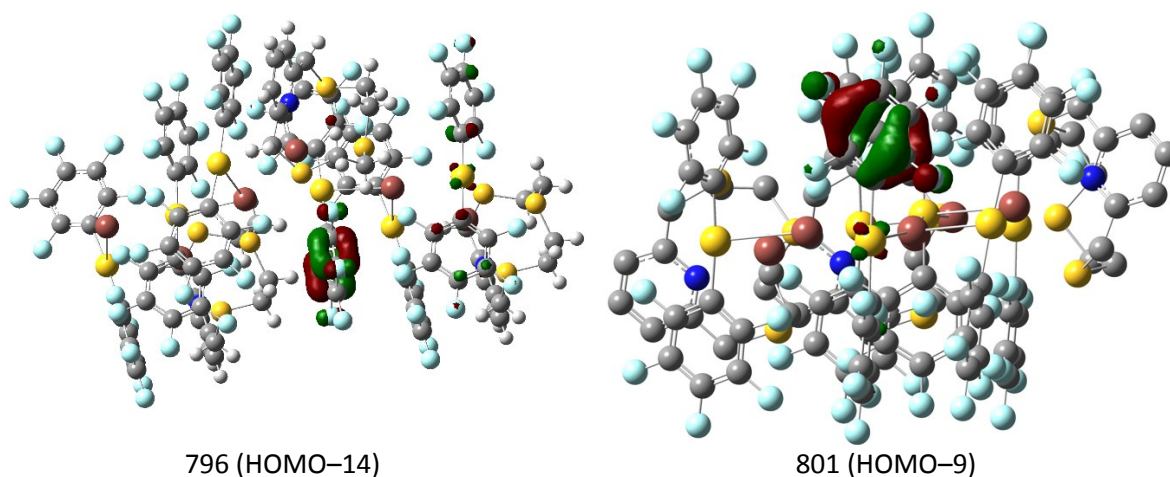


807 (HOMO-3)



808 (HOMO-2)





**Figure S8.** Drawing of selected frontier Kohn-Sham molecular orbitals involved in mono-electronic excitations calculated for compound **4'** at TD-DFT level (see Table 3 in the text). The absolute ordering number of each MO is reported (in parentheses as referred to HOMO and LUMO for occupied and virtual MOs, respectively). Hydrogen atoms have been omitted for clarity. Cutoff value = 0.05 |e|.

**Table S1.** Geometry used for the DFT calculations on oligomeric portion **4'** in orthogonal Cartesian coordinate format (total charge = 0, spin multiplicity = 1; Z = atomic number).

Atom number	Z	x	y	z	Atom number	Z	x	y	z
1	79	3.854015	-2.570436	-1.165593	118	6	-4.713105	-5.853624	0.306121
2	79	7.664002	0.894943	0.485121	119	6	-4.775200	-7.230847	0.169245
3	81	7.161715	-2.272556	-0.618170	120	1	-4.583422	-7.799971	0.905329
4	6	3.269831	-1.595084	-2.865670	121	6	-5.117635	-7.757770	-1.049588
5	6	1.952221	-1.657353	-3.265685	122	1	-5.138924	-8.697919	-1.174879
6	6	1.469051	-1.071120	-4.435090	123	6	-5.430964	-6.908819	-2.090669
7	6	2.341104	-0.425301	-5.261820	124	1	-5.670584	-7.259267	-2.940980
8	6	3.682874	-0.336551	-4.917839	125	6	-5.390249	-5.536776	-1.878860
9	6	4.098155	-0.892973	-3.734140	126	6	-5.831066	-4.615197	-2.975843
10	6	4.293796	-3.697480	0.492826	127	1	-6.759906	-4.329119	-2.784777
11	6	4.354516	-5.077028	0.434854	128	1	-5.850798	-5.129960	-3.823484
12	6	4.564434	-5.885114	1.529619	129	6	-3.131570	-3.771298	-3.288354
13	6	4.766951	-5.320970	2.768320	130	1	-3.074222	-4.589647	-2.735424
14	6	4.745599	-3.948686	2.886160	131	1	-2.895240	-4.011288	-4.218765
15	6	4.500296	-3.190108	1.765887	132	6	-2.147927	-2.733444	-2.766145
16	9	1.042086	-2.299837	-2.508712	133	1	-2.256961	-1.906348	-3.297690
17	9	0.168617	-1.156872	-4.760214	134	1	-1.230051	-3.067961	-2.926464
18	9	1.899191	0.140969	-6.409232	135	6	-4.684357	1.868434	-1.145830
19	9	4.535297	0.300240	-5.740903	136	6	-4.939974	3.219671	-1.285732
20	9	5.421025	-0.745901	-3.426102	137	6	-4.855213	3.901266	-2.494869
21	9	4.213130	-5.701439	-0.761741	138	6	-4.483873	3.210132	-3.634028
22	9	4.604578	-7.230580	1.414257	139	6	-4.267641	1.859522	-3.549815
23	9	5.022352	-6.092275	3.828108	140	6	-4.356950	1.236211	-2.334334
24	9	4.953870	-3.381890	4.087652	141	6	-4.874870	0.096607	2.541089
25	9	4.493766	-1.833770	1.953005	142	6	-3.869141	-0.610916	3.168104
26	16	10.128238	-2.362291	-1.215024	143	6	-3.990562	-1.248696	4.387432
27	16	8.726252	-3.691672	1.620673	144	6	-5.195165	-1.202721	5.042777
28	16	7.600694	-3.186230	-3.439182	145	6	-6.233399	-0.494427	4.478954
29	7	7.389604	-5.072183	-0.880393	146	6	-6.049560	0.130616	3.272311
30	6	10.652737	-3.917335	-0.440273	147	9	-5.276052	3.968005	-0.207147
31	1	10.125161	-4.667360	-0.811541	148	9	-5.109927	5.228541	-2.564742
32	1	11.606824	-4.083158	-0.641123	149	9	-4.337716	3.849065	-4.800610
33	6	10.452169	-3.850734	1.071325	150	9	-3.964127	1.170984	-4.664996
34	1	10.965868	-3.079582	1.421366	151	9	-4.077321	-0.096609	-2.321291
35	1	10.834939	-4.670634	1.473502	152	9	-2.642327	-0.727531	2.561387
36	6	8.110164	-5.376231	1.470024	153	9	-2.956112	-1.924949	4.932394
37	1	8.806593	-5.979682	1.832965	154	9	-5.374571	-1.823359	6.213443
38	1	7.321499	-5.457344	2.063590	155	9	-7.417454	-0.444946	5.117142
39	6	7.709587	-5.912005	0.108414	156	9	-7.121223	0.829336	2.789212
40	6	7.647410	-7.289230	-0.028409	157	79	-2.285810	4.073057	1.541603
41	1	7.839101	-7.858336	0.707711	158	79	1.438278	0.573115	-0.231182
42	6	7.305021	-7.816180	-1.247243	159	81	-7.972725	0.307005	-0.009134
43	1	7.283677	-8.756333	-1.372497	160	81	0.999970	3.744900	0.889495

44	6	6.991818	-6.967251	-2.288380	161	6	-2.824684	3.102589	3.259349
45	1	6.752231	-7.317718	-3.138693	162	6	-4.128306	3.177182	3.700929
46	6	7.032610	-5.595202	-2.076625	163	6	-4.579437	2.595112	4.885001
47	6	6.591927	-4.673639	-3.173675	164	6	-3.687381	1.941076	5.683446
48	1	5.663094	-4.387492	-2.982684	165	6	-2.358135	1.839885	5.296911
49	1	6.572218	-5.188436	-4.021296	166	6	-1.975849	2.392671	4.100575
50	6	9.291500	-3.829933	-3.486041	167	6	-1.888338	5.196671	-0.129896
51	1	9.348757	-4.648262	-2.933073	168	6	-1.813048	6.575566	-0.073511
52	1	9.527876	-4.069976	-4.416426	169	6	-1.630443	7.382095	-1.174304
53	6	10.275177	-2.792122	-2.963808	170	6	-1.472327	6.816611	-2.418733
54	1	10.166234	-1.965041	-3.495395	171	6	-1.510132	5.444729	-2.535958
55	1	11.193042	-3.126707	-3.124053	172	6	-1.727061	4.687977	-1.408497
56	6	7.739179	1.809761	-1.344430	173	9	-5.055900	3.828322	2.973107
57	6	7.483718	3.161028	-1.484321	174	9	-5.867943	2.692746	5.251251
58	6	7.568429	3.842596	-2.693476	175	9	-4.097784	1.378730	6.844411
59	6	7.939552	3.151400	-3.832668	176	9	-1.485968	1.195062	6.092413
60	6	8.155622	1.800764	-3.748462	177	9	-0.664835	2.233435	3.750344
61	6	8.066371	1.177480	-2.532963	178	9	-1.910641	7.200753	1.126933
62	6	7.548605	0.038241	2.342626	179	9	-1.574217	8.727069	-1.059914
63	6	8.554207	-0.669378	2.969737	180	9	-1.243296	7.585918	-3.485975
64	6	8.432672	-1.306970	4.189152	181	9	-1.345330	4.876281	-3.743403
65	6	7.228079	-1.260688	4.844492	182	9	-1.752088	3.331929	-1.595425
66	6	6.189971	-0.552284	4.280574	183	16	3.984633	3.806996	1.391963
67	6	6.373921	0.072561	3.073845	184	16	2.505666	5.150141	-1.397918
68	9	7.147857	3.909419	-0.405708	185	16	1.536640	4.653765	3.695124
69	9	7.313875	5.169903	-2.763338	186	7	1.261823	6.542243	1.144261
70	9	8.085657	3.790299	-4.999275	187	6	4.498957	5.357174	0.601043
71	9	8.458921	1.112172	-4.863668	188	1	3.990390	6.111914	0.988912
72	9	8.345831	-0.155375	-2.519934	189	1	5.460507	5.513902	0.771857
73	9	9.780999	-0.786297	2.363034	190	6	4.250062	5.292904	-0.903454
74	9	9.467002	-1.983336	4.734204	191	1	4.745279	4.517149	-1.269588
75	9	7.048562	-1.881135	6.015242	192	1	4.627481	6.109359	-1.317522
76	9	5.005927	-0.502502	4.918756	193	6	1.910233	6.840164	-1.227859
77	9	5.302384	0.771409	2.590653	194	1	2.600224	7.437363	-1.612513
78	81	4.450784	0.248851	-0.207621	195	1	1.103811	6.928857	-1.796109
79	79	-8.568984	-2.512259	-0.967491	196	6	1.557950	7.379459	0.145992
80	79	-4.759624	0.953583	0.683700	197	6	1.512775	8.757137	0.284907
81	81	-5.261267	-2.214182	-0.420277	198	1	1.686192	9.324851	-0.456670
82	81	-1.746545	1.249409	0.564818	199	6	1.213837	9.286458	1.514102
83	6	-9.153335	-1.536732	-2.667410	200	1	1.205054	10.226790	1.640275
84	6	-10.470950	-1.599098	-3.067393	201	6	0.926050	8.439981	2.564531
85	6	-10.954225	-1.012754	-4.236699	202	1	0.716667	8.792035	3.421908
86	6	-10.082273	-0.366714	-5.063364	203	6	0.947777	7.068254	2.351291
87	6	-8.740504	-0.277857	-4.719412	204	6	0.533912	6.150541	3.461796
88	6	-8.325121	-0.834400	-3.535806	205	1	-0.403130	5.872978	3.300548
89	6	-8.128860	-3.639437	0.690745	206	1	0.546035	6.665413	4.309514
90	6	-8.067751	-5.018959	0.632558	207	6	3.233817	5.281906	3.688588
91	6	-7.857589	-5.827156	1.727194	208	1	3.280914	6.099839	3.134077

92	6	-7.655212	-5.263148	2.965979	209	1	3.501742	5.519680	4.610971
93	6	-7.676950	-3.890889	3.084033	210	6	4.190991	4.235317	3.135261
94	6	-7.922483	-3.132205	1.963882	211	1	4.091351	3.409225	3.670016
95	9	-11.380987	-2.241796	-2.310484	212	1	5.116494	4.561409	3.266449
96	9	-12.254659	-1.098612	-4.561795	213	6	1.562778	-0.342636	1.595320
97	9	-10.524289	0.199668	-6.210681	214	6	1.298785	-1.691272	1.743534
98	9	-7.888180	0.359151	-5.542412	215	6	1.415130	-2.373722	2.949558
99	9	-7.002258	-0.687216	-3.227788	216	6	1.829045	-1.686296	4.076218
100	9	-8.208979	-5.643223	-0.564133	217	6	2.055285	-0.337870	3.985198
101	9	-7.817067	-7.172593	1.611621	218	6	1.933447	0.286398	2.773038
102	9	-7.399577	-6.034547	4.025643	219	6	1.272241	1.431244	-2.084187
103	9	-7.468820	-3.324222	4.285611	220	6	2.264491	2.129341	-2.742884
104	9	-7.929394	-1.775898	2.151212	221	6	2.110732	2.768266	-3.958069
105	16	-2.294778	-2.303695	-1.017333	222	6	0.885561	2.733819	-4.575080
106	16	-3.696486	-3.633286	1.818403	223	6	-0.141090	2.035528	-3.978520
107	16	-4.822416	-3.127710	-3.241356	224	6	0.074764	1.408787	-2.778076
108	7	-5.033210	-5.013783	-0.682631	225	9	0.921482	-2.436240	0.676313
109	6	-1.770124	-3.858735	-0.242681	226	9	1.150214	-3.698638	3.027719
110	1	-2.297675	-4.608780	-0.613945	227	9	2.005833	-2.326730	5.237841
111	1	-0.816039	-4.024487	-0.443601	228	9	2.400395	0.347392	5.090132
112	6	-1.970595	-3.792210	1.268933	229	9	2.225307	1.616473	2.750864
113	1	-1.456924	-3.021039	1.618971	230	9	3.510878	2.234031	-2.175378
114	1	-1.587744	-4.612102	1.671051	231	9	3.133973	3.434667	-4.535370
115	6	-4.312473	-5.317880	1.667726	232	9	0.675178	3.356280	-5.739605
116	1	-3.615979	-5.921299	2.030595	233	9	-1.344953	1.997517	-4.579116
117	1	-5.101093	-5.399069	2.261341	234	9	-0.987613	0.720260	-2.261289

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**Table S2.** Selected NBO charges  $Q$  ( $|e|$ ) calculated for **4'** in the gas phase (labelling scheme as in Figure S7).

	$Q$
Tl1 <sub>A</sub>	0.543
Tl2 <sub>A</sub>	0.819
Au1 <sub>A</sub>	0.157
Au2 <sub>A</sub>	0.214
Tl1 <sub>B</sub>	0.586
Tl2 <sub>B</sub>	0.866
Au1 <sub>B</sub>	-0.054
Au2 <sub>B</sub>	0.174
Tl1 <sub>C</sub>	0.548
Tl2 <sub>C</sub>	0.944
Au1 <sub>C</sub>	0.159
Au2 <sub>C</sub>	-0.049