Supporting Information

Redox-controlled fluorescence modulation (electrofluorochromism) in triphenylamine derivatives

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Table S 23. Atomic coordinates of triphenylaminium cation-radical **5a** after geometry optimization.

Table S 24. Atomic coordinates of triphenylaminium cation- radical **6a** after geometry optimization.

Electrochemistry

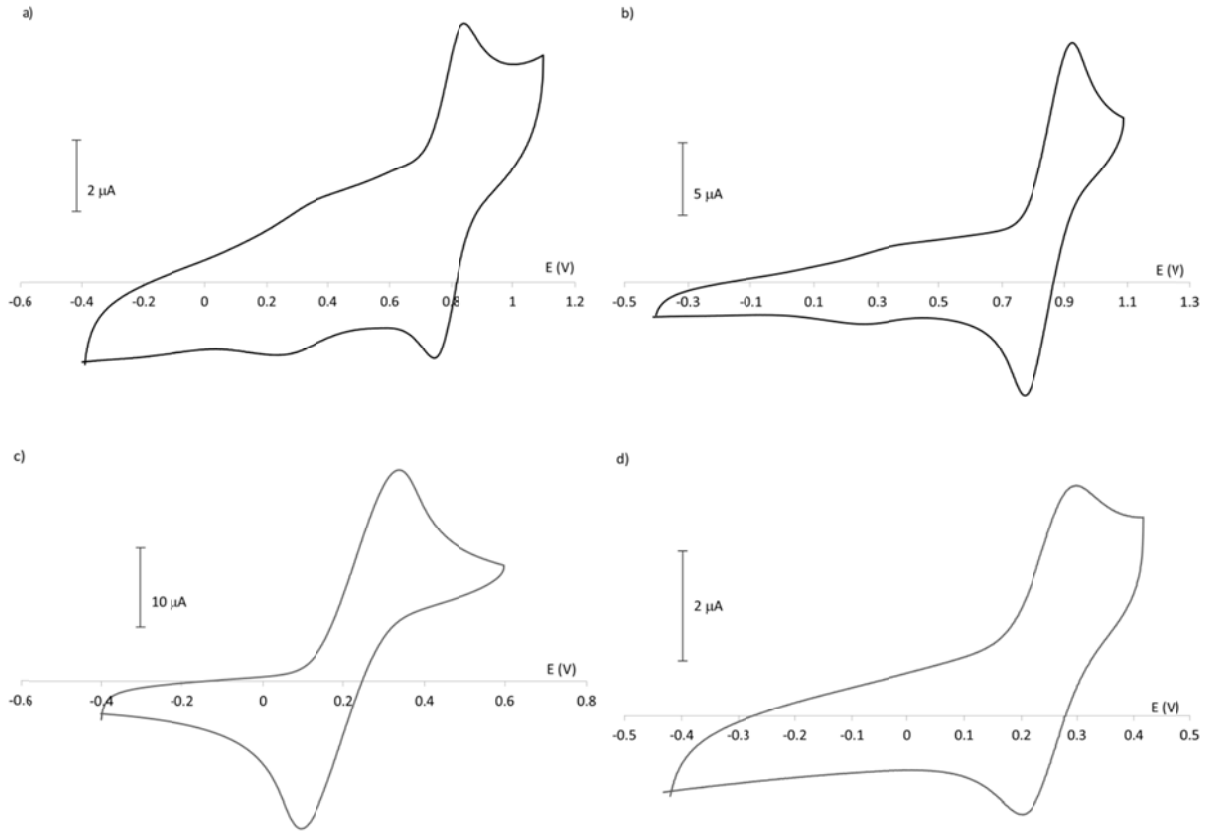

Figure S 1 Cyclic voltammetry in dichloromethane + 0.1M $TBAPF_6$ on C. Potentials referenced to ferrocene. Scan rate: 100 $mV.s^{-1}$. a) compound **1**, b) compound **3**, c) compound **5**, d) compound **6**.

Chemical fluorescence switching

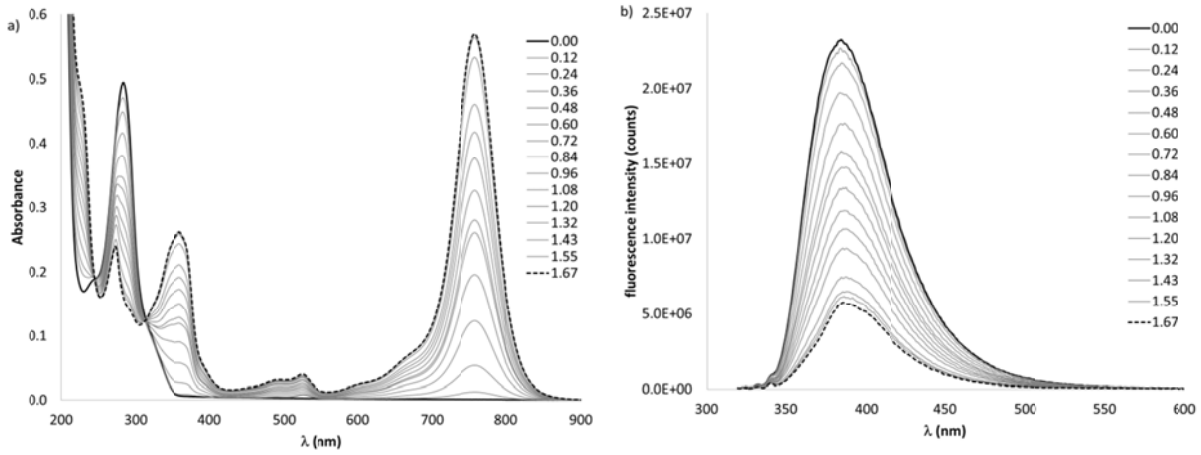

Figure S 2a Spectra recorded upon oxidation of **4** by $Cu(ClO_4)_2$ in CH_3CN as a function of R=[Cu^{II}]/[**4**], [**4**]=1.9 10^{-5} mol.L^{-1}. a) absorption, b) emission, λ_{exc}=309 nm

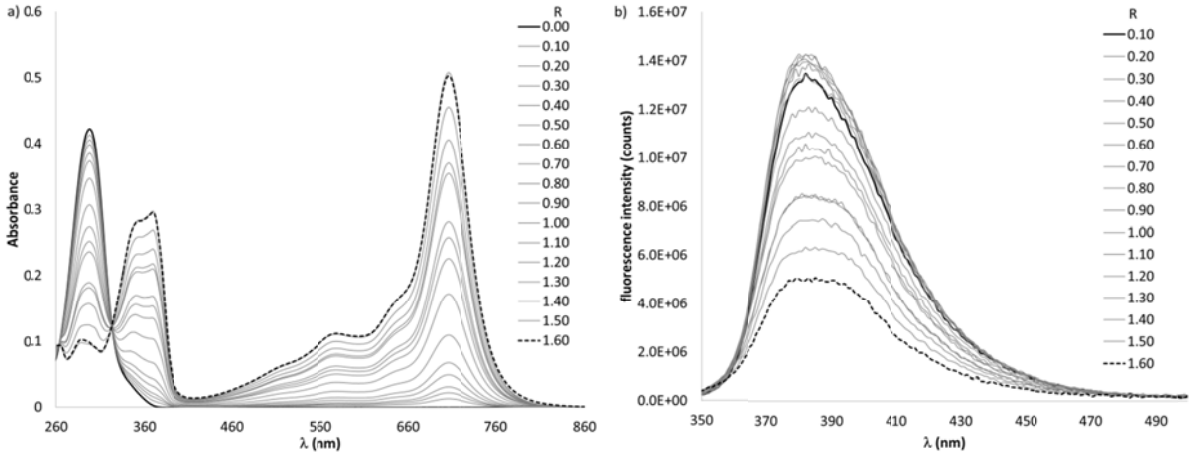

Figure S 2b spectra recorded upon oxidation of **5** by $Cu(ClO_4)_2$ in CH_3CN as a function of R=[Cu^{II}]/[**5**], [**5**]=2.5 10^{-5} mol.L^{-1}. a) absorption, b) emission, λ_{exc}=263 nm

Spectroelectrochemistry

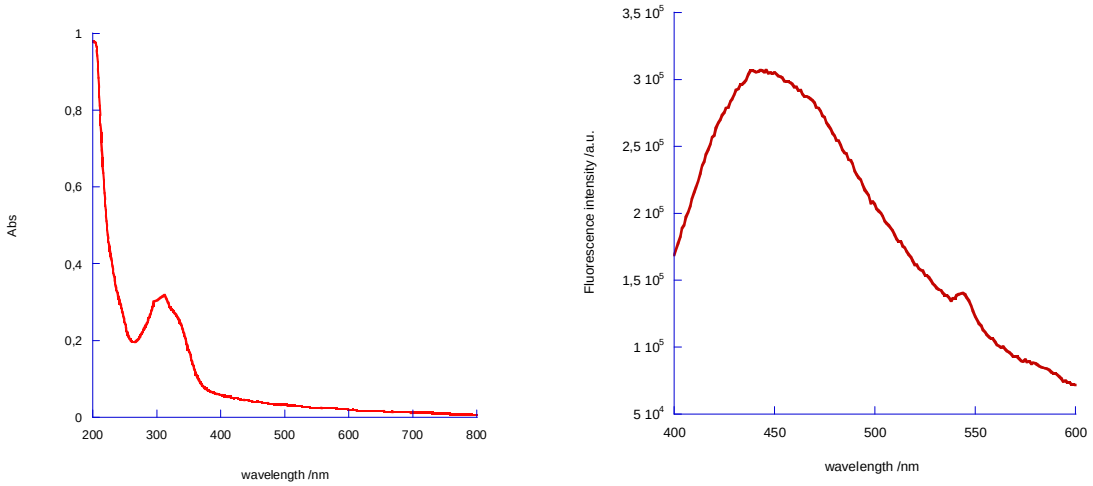

Figure S 3a Absorption and fluorescence spectra (λ_{exc}=330 nm) of **3** recorded in the thin layer spectroelectrochemical cell under open circuit potential.

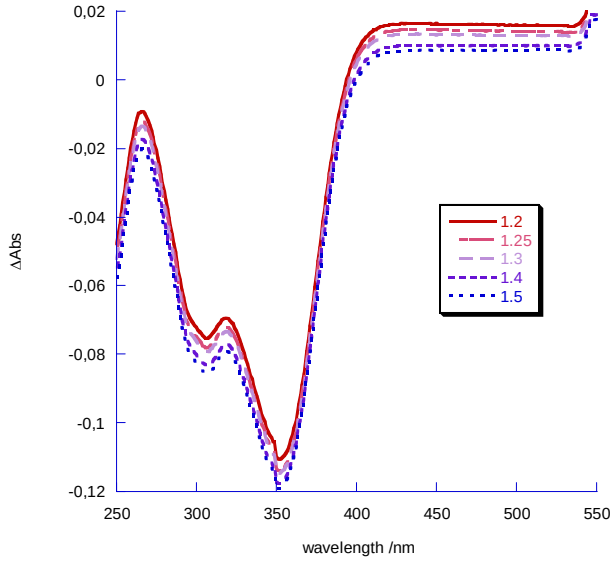

Figure S 3b UV-vis spectroelectrochemistry of **1** upon electrochemical oxidation (potentials in V indicated in the figure). The open circuit potential is subtracted from each subsequent spectrum.

Theoretical calculations

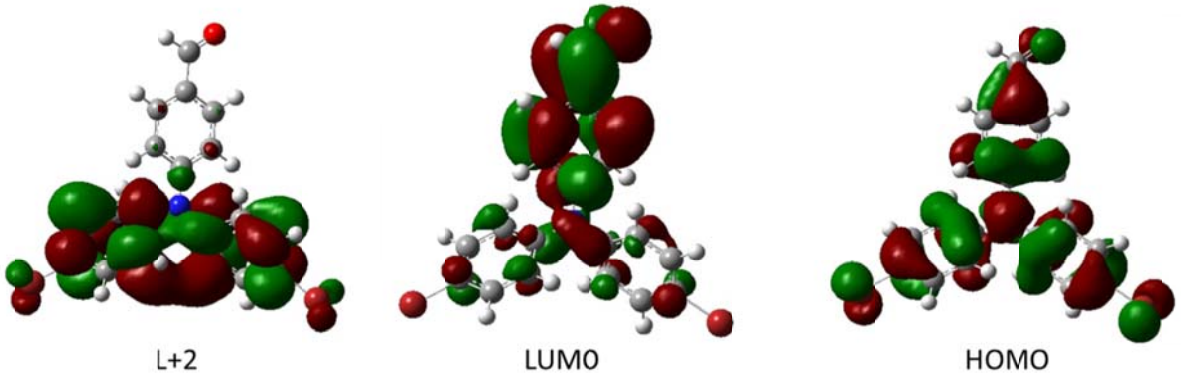

Figure S 3 Representation of the main molecular orbitals involved in the electronic transitions of **1**

Table S 1 Results of TD-DFT calculations for **1**

Wavelength (nm)	Osc. Strength	Major contribs
357	0.49	HOMO->LUMO (87%)
310	0.28	HOMO->L+2 (87%)

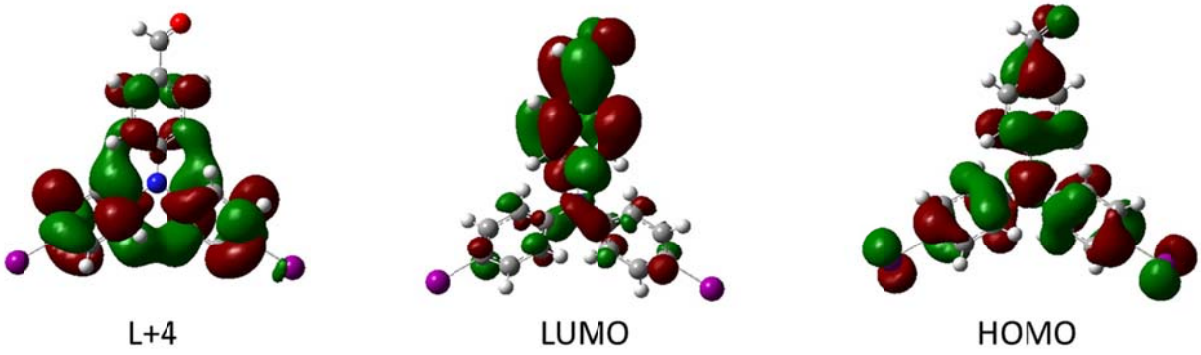

Figure S 4 Representation of the main molecular orbitals involved in the electronic transitions of **2**

Table S 2 Results of TD-DFT calculations for **2**

Wavelength (nm)	Osc. Strength	Major contribs
349	0.47	HOMO->LUMO (79%)
297	0.29	HOMO->L+3 (27%), HOMO->L+4 (65%)

Table S 3 Results of TD-DFT calculations for **3**

Wavelength (nm)	Osc. Strength	Major contribs
333	0.49	HOMO->LUMO (88%)
309	0.28	HOMO->L+2 (90%)

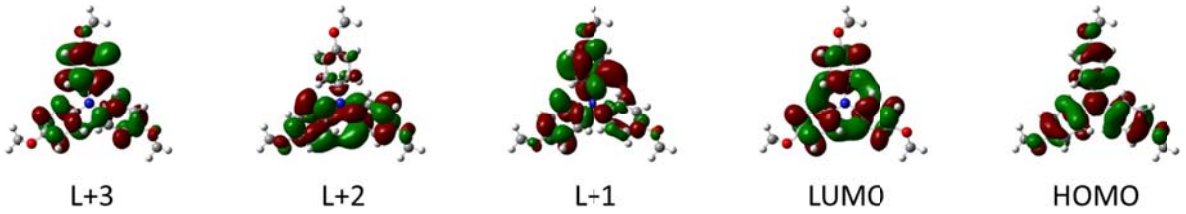

Figure S 5 Representation of the main molecular orbitals involved in the electronic transitions of **4**

Table S 4 Results of TD-DFT calculations for **4**

Wavelength (nm)	Osc. Strength	Major contribs
361	0.20	HOMO->L+1 (21%), HOMO->L+3 (40%), HOMO->L+4 (22%)
360	0.21	HOMO->L+2 (24%), HOMO->L+3 (19%), HOMO->L+4 (41%)

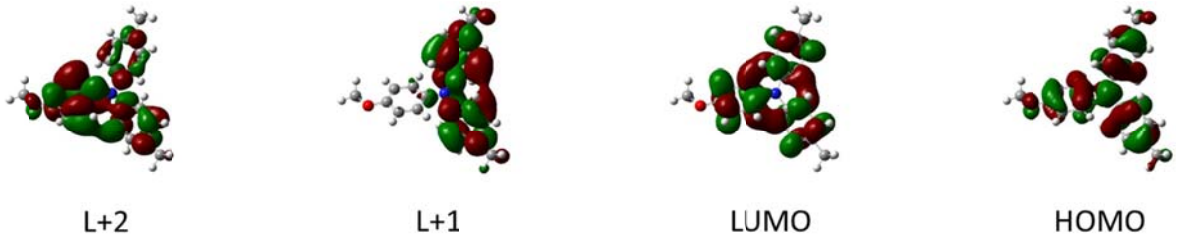

Figure S 6 Representation of the main molecular orbitals involved in the electronic transitions of **5**

Table S 5 Results of TD-DFT calculations for **5**

Wavelength (nm)	Osc. Strength	Major contribs
370	0.19	HOMO->L+1 (81%)
360	0.17	HOMO->L+2 (79%)

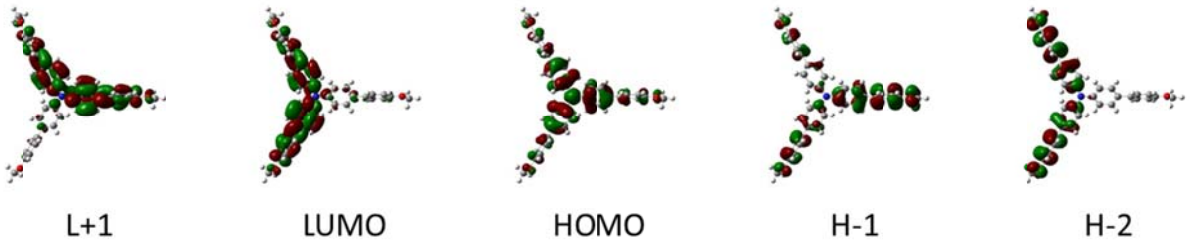

Figure S 7 Representation of the main molecular orbitals involved in the electronic transitions of **6**

Table S 6 Results of TD-DFT calculations for **6**

Wavelength (nm)	Osc. Strength	Major contribs
433	0.48	HOMO->LUMO (89%)
433	0.49	HOMO->L+1 (89%)
343	0.25	H-2->LUMO (36%), H-1->L+1 (37%)
343	0.25	H-2->L+1 (38%), H-1->LUMO (35%)

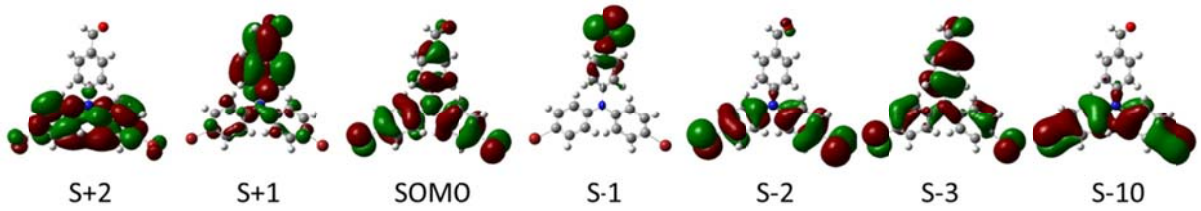

Figure S 8 Representation of the main molecular orbitals involved in the electronic transitions of the cation-radical **1a**

Table S 7 Results of TD-DFT calculations for **1a**

Wavelength (nm)	Osc. Strength	Major contribs
718	0.26	H-1(B)->LUMO(B) (55%), HOMO(B)->LUMO(B) (31%)
633	0.15	H-2(B)->LUMO(B) (82%)
376	0.14	H-3(A)->LUMO(A) (17%), HOMO(A)->LUMO(A) (40%), H-2(B)->L+1(B) (19%)
341	0.12	HOMO(A)->L+1(A) (38%), H-9(B)->LUMO(B) (38%)

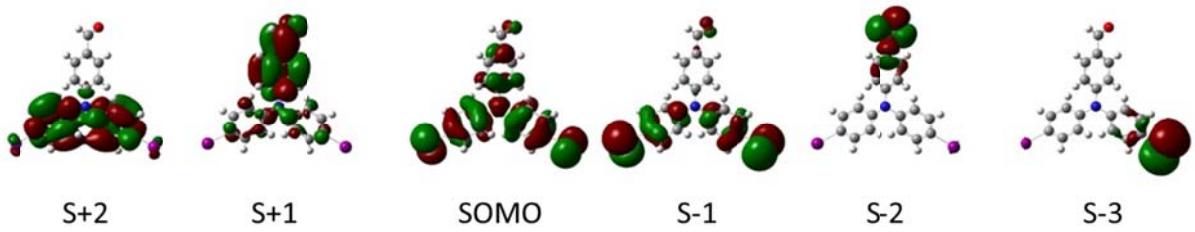

Figure S 9 Representation of the main molecular orbitals involved in the electronic transitions of the cation-radical **2a**

Table S 8 Results of TD-DFT calculations for **2a**

Wavelength (nm)	Osc. Strength	Major contribs
813	0.21	H-1(B)->LUMO(B) (35%), HOMO(B)->LUMO(B) (53%)
699	0.15	H-2(B)->LUMO(B) (90%)

373	0.14	H-5(A)->LUMO(A) (19%), HOMO(A)->LUMO(A) (33%), H-7(B)->L+1(B) (12%), H-2(B)->L+1(B) (13%)
340	0.19	HOMO(A)->L+1(A) (53%)

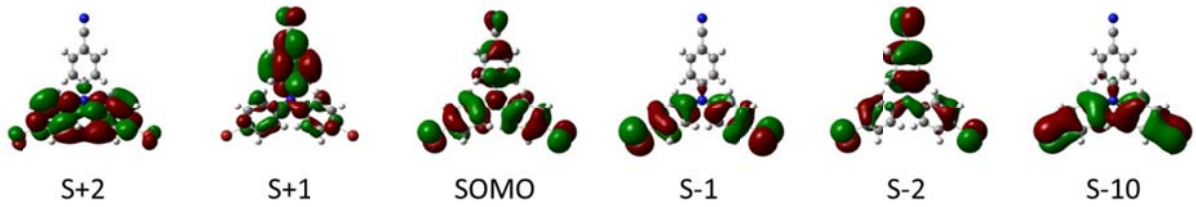

Figure S 10 Representation of the main molecular orbitals involved in the electronic transitions of the cation-radical **3a**

Table S 9 Results of TD-DFT calculations for **3a**

Wavelength (nm)	Osc. Strength	Major contribs
726	0.27	HOMO(B)->LUMO(B) (86%)
650	0.19	H-1(B)->LUMO(B) (86%)
373	0.14	H-2(A)->LUMO(A) (18%), HOMO(A)->LUMO(A) (42%), H-1(B)->L+1(B) (21%)
342	0.12	HOMO(A)->L+1(A) (40%), H-9(B)->LUMO(B) (35%)

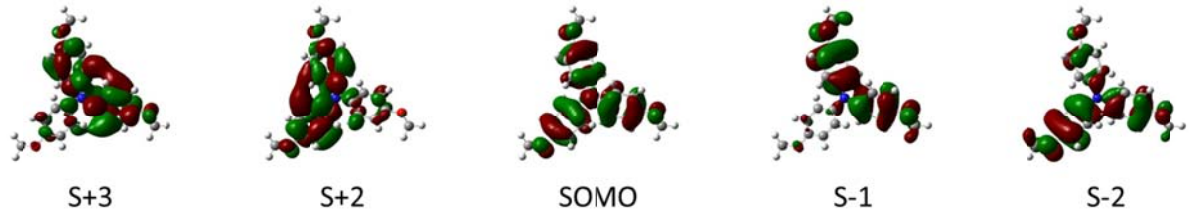

Figure S 11 Representation of the main molecular orbitals involved in the electronic transitions of the cation-radical **4a**

Table S 10 Results of TD-DFT calculations for **4a**

Wavelength (nm)	Osc. Strength	Major contribs
657	0.23	HOMO(B)->LUMO(B) (88%)
657	0.23	H-1(B)->LUMO(B) (88%)
352	0.13	HOMO(A)->L+1(A) (36%), HOMO(A)->L+2(A) (24%)
352	0.13	HOMO(A)->L+1(A) (25%), HOMO(A)->L+2(A) (36%)

Table S 11 Results of TD-DFT calculations for **5a**

Wavelength (nm)	Osc. Strength	Major contribs
648	0.24	HOMO(B)->LUMO(B) (88%)
568	0.13	H-1(B)->LUMO(B) (88%)
345	0.15	HOMO(A)->LUMO(A) (13%), HOMO(A)->L+1(A) (44%)

Figure S 12 Representation of the main molecular orbitals involved in the electronic transitions of the cation-radical **6a**

Table S 12 Results of TD-DFT calculations for **6a**

Wavelength (nm)	Osc. Strength	Major contribs
1126	0.43	H-1(B)->LUMO(B) (11%), HOMO(B)->LUMO(B) (73%)
1126	0.43	H-1(B)->LUMO(B) (73%), HOMO(B)->LUMO(B) (11%)
420	0.23	HOMO(A)->LUMO(A) (29%), HOMO(A)->L+1(A) (18%)
420	0.24	HOMO(A)->LUMO(A) (18%), HOMO(A)->L+1(A) (29%)

Table S 13 Atomic coordinates of triphenylamine **1** after geometry optimization

Number	Atomic number	X	Y	Z
1	7	0	0	0
2	6	0	0	1.416065
3	6	1.213858	0	2.132863
4	6	-1.216046	-0.001193	2.134824
5	6	1.208929	-0.004788	3.521378
6	1	2.148903	0.008968	1.589502
7	6	-1.208423	0.00332	3.518612
8	1	-2.151148	-0.010606	1.591234
9	6	0.001132	0.000208	4.22938

10	1	2.149503	0.002855	4.063838
11	1	-2.130398	-0.004987	4.08855
12	6	1.059185	-0.630437	-0.728793
13	6	1.520614	-1.904602	-0.36494
14	6	1.641682	0.011861	-1.831341
15	6	2.549047	-2.512694	-1.080502
16	1	1.073404	-2.41423	0.478484
17	6	2.658439	-0.608385	-2.552963
18	1	1.294044	0.994798	-2.121073
19	6	3.113376	-1.866142	-2.17432
20	1	2.901995	-3.495289	-0.797728
21	1	3.105445	-0.109895	-3.402411
22	6	-1.051594	0.638473	-0.731881
23	6	-1.530997	1.900182	-0.348125
24	6	-1.608296	0.017271	-1.859865
25	6	-2.551188	2.515969	-1.068676
26	1	-1.105673	2.394294	0.515558
27	6	-2.616641	0.645811	-2.585887
28	1	-1.247705	-0.955956	-2.16593
29	6	-3.089602	1.890788	-2.187592
30	1	-2.918429	3.488151	-0.768895
31	1	-3.043655	0.162975	-3.454467
32	6	-0.032257	0.000892	5.698677
33	8	-1.067786	0.00835	6.375636
34	1	0.973298	-0.00655	6.163594
35	35	-4.492929	2.753216	-3.189381
36	35	4.528068	-2.716949	-3.17151

Number of imaginary frequencies: 0

Table S 14 Atomic coordinates of triphenylamine **2** after geometry optimization

Number	Atomic number	X	Y	Z
1	7	0	0	0
2	6	0	0	1.41821
3	6	1.216372	0	2.134737
4	6	-1.219097	-0.002332	2.136205
5	6	1.207719	-0.005408	3.526087
6	1	2.155906	0.014169	1.595916
7	6	-1.215706	0.000071	3.524427
8	1	-2.157329	-0.016753	1.59483
9	6	-0.002772	-0.002337	4.241695
10	1	2.149566	0.002551	4.068583
11	1	-2.146209	-0.010794	4.081962
12	6	1.033896	-0.675027	-0.72597
13	6	1.427988	-1.974945	-0.36397
14	6	1.657687	-0.050171	-1.819283
15	6	2.436097	-2.633994	-1.072802
16	1	0.944764	-2.470556	0.470296
17	6	2.655708	-0.711852	-2.54048
18	1	1.363841	0.95365	-2.10424
19	6	3.043996	-1.999995	-2.16077
20	1	2.728018	-3.636115	-0.782937
21	1	3.12915	-0.216591	-3.379536
22	6	-1.028443	0.678414	-0.729646
23	6	-1.444248	1.966544	-0.349815
24	6	-1.625614	0.068554	-1.846329
25	6	-2.447668	2.627675	-1.063355
26	1	-0.982967	2.451763	0.502695
27	6	-2.618043	0.733146	-2.5722

28	1	-1.316261	-0.926316	-2.145697
29	6	-3.028566	2.008896	-2.17447
30	1	-2.757315	3.619779	-0.7578
31	1	-3.070678	0.248969	-3.429048
32	53	-4.566043	3.027588	-3.278185
33	53	4.587781	-3.015762	-3.25862
34	6	0.00395	-0.003367	5.707853
35	8	-1.015201	0.00297	6.422287
36	1	1.00703	-0.010613	6.174129

Number of imaginary frequencies: 0

Table S 15 Atomic coordinates of triphenylamine **3** after geometry optimization

Number	**Atomic number**	**X**	**Y**	**Z**
1	7	0	0	0
2	6	0	0	1.415399
3	6	1.210436	0	2.136086
4	6	-1.210446	0	2.136075
5	6	1.210388	-0.005258	3.523151
6	1	2.148182	0.007605	1.5976
7	6	-1.210415	0.005245	3.523135
8	1	-2.148184	-0.007595	1.597575
9	6	-0.000015	-0.000017	4.24008
10	1	2.148909	0.001206	4.063329
11	1	-2.148938	-0.001216	4.063309
12	6	1.056839	-0.633012	-0.730373
13	6	1.528399	-1.900915	-0.358095
14	6	1.626272	0.001529	-1.84422
15	6	2.554073	-2.510455	-1.076597
16	1	1.09173	-2.405351	0.493947

17	6	2.639825	-0.620578	-2.568554
18	1	1.271022	0.979632	-2.140956
19	6	3.105112	-1.872155	-2.181904
20	1	2.914989	-3.488038	-0.786715
21	1	3.076539	-0.128128	-3.42682
22	6	-1.05682	0.633064	-0.730362
23	6	-1.528281	1.901013	-0.358112
24	6	-1.62633	-0.001477	-1.844166
25	6	-2.553935	2.510597	-1.076605
26	1	-1.091551	2.405444	0.493902
27	6	-2.639861	0.620672	-2.568494
28	1	-1.271155	-0.979616	-2.140876
29	6	-3.105051	1.872297	-2.181871
30	1	-2.914777	3.488213	-0.786746
31	1	-3.076637	0.128224	-3.426726
32	35	-4.514314	2.725464	-3.183363
33	35	4.514399	-2.725266	-3.183412
34	6	-0.000028	-0.000024	5.662656
35	7	-0.00004	-0.00003	6.829513

Number of imaginary frequencies: 0

Table S 16. Atomic coordinates of triphenylamine **4** after geometry optimization

Number	**Atomic number**	**X**	**Y**	**Z**
1	7	-0.030379	-0.016315	0.092326
2	6	1.262968	-0.631249	0.108625
3	6	2.25654	-0.189013	1.001224
4	6	1.568279	-1.68638	-0.758307
5	6	3.510372	-0.780243	1.013111
6	1	2.03364	0.625368	1.678417

7	6	2.822929	-2.296848	-0.732727
8	1	0.813889	-2.035638	-1.451649
9	6	3.807832	-1.845539	0.149956
10	1	4.282404	-0.447148	1.694093
11	1	3.021424	-3.113234	-1.413741
12	6	-0.133958	1.405469	0.109593
13	6	0.791774	2.200242	-0.587842
14	6	-1.151032	2.047882	0.834593
15	6	0.700542	3.588827	-0.554297
16	1	1.583322	1.719753	-1.148221
17	6	-1.242818	3.437729	0.846062
18	1	-1.86589	1.451221	1.386311
19	6	-0.320715	4.235374	0.156148
20	1	1.429431	4.180684	-1.098629
21	1	-2.035884	3.911449	1.415451
22	6	-1.199596	-0.832335	0.065315
23	6	-1.249397	-2.039061	0.780705
24	6	-2.325462	-0.456718	-0.688689
25	6	-2.387635	-2.841839	0.738251
26	1	-0.390022	-2.343538	1.363876
27	6	-3.462709	-1.258119	-0.709715
28	1	-2.299501	0.466655	-1.252791
29	6	-3.516896	-2.466718	0.000186
30	1	-2.401672	-3.770948	1.298615
31	1	-4.318586	-0.947895	-1.300789
32	8	5.087564	-2.370825	0.253736
33	6	5.442573	-3.479692	-0.62418
34	1	6.471804	-3.727891	-0.363677
35	1	4.799068	-4.352198	-0.455775

36	1	5.389084	-3.192631	-1.681691
37	8	-4.695762	-3.27589	-0.020196
38	8	-0.427605	5.661374	0.156322
39	6	-5.83369	-2.454718	-0.295326
40	1	-5.792946	-2.117061	-1.309835
41	1	-6.728056	-3.022255	-0.143961
42	1	-5.831523	-1.610395	0.361951
43	6	0.613415	6.218188	-0.650607
44	1	1.564685	5.943883	-0.244721
45	1	0.530074	5.842894	-1.64916
46	1	0.524432	7.284423	-0.661725

Number of imaginary frequencies: 0

Table S 17. Atomic coordinates of triphenylamine **5** after geometry optimization

Number	**Atomic number**	**X**	**Y**	**Z**
1	7	-0.302371	0.000424	0.052907
2	6	1.107029	-0.223162	0.122505
3	6	1.919078	0.586084	0.935076
4	6	1.703978	-1.255494	-0.620127
5	6	3.294235	0.369167	0.99422
6	1	1.464486	1.380443	1.512256
7	6	3.077751	-1.476557	-0.541955
8	1	1.084392	-1.878667	-1.251863
9	6	3.882503	-0.664732	0.261062
10	1	3.906255	1.001995	1.626906
11	1	3.522065	-2.277378	-1.122142
12	6	-0.812959	1.334788	0.024805
13	6	-0.163676	2.332102	-0.721785
14	6	-1.973541	1.670298	0.741981

15	6	-0.660845	3.633892	-0.740598
16	1	0.728734	2.078199	-1.279173
17	6	-2.474134	2.97032	0.703668
18	1	-2.475478	0.906891	1.321813
19	6	-1.82027	3.961199	-0.033039
20	1	-0.147768	4.391458	-1.322172
21	1	-3.37084	3.21246	1.262794
22	6	-1.200771	-1.109716	0.009471
23	6	-0.964943	-2.251257	0.793941
24	6	-2.335518	-1.078127	-0.818454
25	6	-1.839344	-3.335119	0.741854
26	1	-0.095141	-2.280197	1.437027
27	6	-3.214749	-2.158644	-0.851036
28	1	-2.519965	-0.203335	-1.428572
29	6	-2.971461	-3.295347	-0.075991
30	1	-1.642347	-4.207877	1.354056
31	1	-4.085431	-2.117019	-1.495652
32	6	-3.94057	-4.49129	-0.122318
33	1	-4.69438	-4.36876	0.62712
34	1	-4.401174	-4.53996	-1.086878
35	1	-3.399499	-5.396098	0.060616
36	6	-2.371424	5.398843	-0.064812
37	1	-3.028903	5.51035	-0.901584
38	1	-2.908666	5.594925	0.839524
39	1	-1.559649	6.090135	-0.154452
40	8	5.292911	-0.88956	0.332484
41	6	5.941049	-0.20036	-0.739813
42	1	6.996271	-0.369272	-0.686207
43	1	5.568605	-0.564355	-1.674529

44	1	5.743239	0.848243	-0.661051

Number of imaginary frequencies: 0

Table S 18. Atomic coordinates of triphenylamine **6** after geometry optimization

Number	Atomic number	X	Y	Z
1	7	0.000172	-0.003912	0.116689
2	6	1.27431	-0.647422	0.116832
3	6	1.494785	-1.805684	-0.646963
4	6	2.336554	-0.13699	0.881378
5	6	2.734636	-2.435844	-0.635662
6	1	0.683899	-2.213302	-1.236521
7	6	3.579121	-0.76155	0.873396
8	1	2.182911	0.758526	1.469311
9	6	3.804474	-1.926412	0.120118
10	1	2.875355	-3.34321	-1.211685
11	1	4.39227	-0.335699	1.449748
12	6	-1.193976	-0.7859	0.116415
13	6	-1.284291	-1.959423	0.883238
14	6	-2.305447	-0.399683	-0.650891
15	6	-2.445788	-2.724335	0.873041
16	1	-0.433108	-2.272288	1.473905
17	6	-3.470348	-1.159212	-0.641717
18	1	-2.251766	0.505467	-1.241746
19	6	-3.56546	-2.339478	0.115487
20	1	-2.483924	-3.640993	1.450084
21	1	-4.325002	-0.828597	-1.220528
22	6	-0.079933	1.421096	0.117609
23	6	0.816356	2.191402	-0.641897
24	6	-1.056178	2.085757	0.878398

25	6	0.742504	3.580126	-0.630416
26	1	1.577351	1.693033	-1.228173
27	6	-1.136196	3.474215	0.870474
28	1	-1.757397	1.504908	1.463375
29	6	-0.236723	4.252021	0.121284
30	1	1.460877	4.155419	-1.202929
31	1	-1.914019	3.96542	1.443621
32	6	5.129676	-2.597983	0.123851
33	6	5.866299	-2.732675	1.313522
34	6	5.681929	-3.112002	-1.062634
35	6	7.107424	-3.364413	1.318082
36	1	5.448229	-2.360754	2.241718
37	6	6.922311	-3.745075	-1.057466
38	1	5.144223	-2.988391	-1.995514
39	6	7.643153	-3.869263	0.131963
40	1	7.676275	-3.466528	2.233716
41	1	7.356622	-4.121451	-1.975305
42	6	-4.808635	-3.15294	0.114772
43	6	-5.290593	-3.735741	1.299957
44	6	-5.530678	-3.366083	-1.072738
45	6	-6.455086	-4.499564	1.298675
46	1	-4.759304	-3.566358	2.229341
47	6	-6.696053	-4.128377	-1.073335
48	1	-5.157187	-2.953199	-2.002642
49	6	-7.160281	-4.703603	0.111247
50	1	-6.824609	-4.95125	2.210768
51	1	-7.239714	-4.310241	-1.992025
52	6	-0.31749	5.735498	0.124775
53	6	-0.57694	6.441159	1.312697

54	6	-0.140868	6.470555	-1.060684
55	6	-0.650769	7.831881	1.316052
56	1	-0.695621	5.893579	2.240475
57	6	-0.213021	7.861214	-1.056648
58	1	0.026457	5.942915	-1.992475
59	6	-0.473919	8.547866	0.130846
60	1	-0.852832	8.375869	2.23022
61	1	-0.098474	8.425286	-1.973898
62	8	8.909879	-4.477545	0.135292
63	8	-8.31654	-5.502164	0.106283
64	8	-0.581208	9.949011	0.132451
65	6	9.265896	-5.122448	-1.140744
66	1	9.284723	-4.397538	-1.963736
67	1	10.263592	-5.53668	-0.988826
68	1	8.562268	-5.925812	-1.391184
69	6	-9.175943	-5.300486	-1.073465
70	1	-10.018261	-5.980625	-0.939389
71	1	-9.536902	-4.266329	-1.131742
72	1	-8.64421	-5.543887	-2.001465
73	6	-0.130118	10.583804	-1.118367
74	1	-0.72107	10.241001	-1.976535
75	1	-0.2776	11.654561	-0.97071
76	1	0.929542	10.376078	-1.311171

Number of imaginary frequencies: 0

Table S 19. Atomic coordinates of triphenylaminium cation-radical **1a** after geometry optimization

Number	**Atomic number**	**X**	**Y**	**Z**
1	7	0.008066	0.637252	0.018853
2	6	0.089492	2.050706	0.046384

3	6	-0.906267	2.813665	0.689507
4	6	1.169051	2.720627	-0.570983
5	6	-0.824689	4.199649	0.709854
6	1	-1.73167	2.307466	1.171279
7	6	1.244441	4.101952	-0.53627
8	1	1.931771	2.141897	-1.074297
9	6	0.250403	4.858868	0.101845
10	1	-1.593062	4.777547	1.214469
11	1	2.060547	4.635159	-1.010185
12	6	-1.26438	-0.019504	0.014703
13	6	-2.295908	0.420867	-0.828402
14	6	-1.49357	-1.127045	0.844333
15	6	-3.529778	-0.224922	-0.829131
16	1	-2.12865	1.268896	-1.479519
17	6	-2.724093	-1.778775	0.827043
18	1	-0.705444	-1.475463	1.498874
19	6	-3.740748	-1.324657	-0.005111
20	1	-4.322663	0.116743	-1.480762
21	1	-2.897276	-2.632308	1.468415
22	6	1.194187	-0.164049	0.00541
23	6	2.277624	0.141685	0.843084
24	6	1.283981	-1.282897	-0.836179
25	6	3.425849	-0.646025	0.826743
26	1	2.219209	0.99748	1.50278
27	6	2.428361	-2.076197	-0.835583
28	1	0.455546	-1.529121	-1.487288
29	6	3.498485	-1.754922	-0.008593
30	1	4.259064	-0.406285	1.473389
31	1	2.493763	-2.937469	-1.48661

32	6	0.363766	6.324118	0.113689
33	8	1.291179	6.958975	-0.403526
34	1	-0.472372	6.827858	0.637581
35	35	5.085265	-2.849787	-0.018128
36	35	-5.446177	-2.22518	-0.018613

Number of imaginary frequencies: 0

Table S 20 Atomic coordinates of triphenylaminium cation-radical **2a** after geometry optimization

Number	**Atomic number**	**X**	**Y**	**Z**
1	7	0.000000	0.000000	0.000000
2	6	0.000000	0.000000	1.428190
3	6	1.222740	0.000000	2.127944
4	6	-1.224847	-0.000322	2.129131
5	6	1.216427	0.001725	3.517596
6	1	2.155182	0.024763	1.579795
7	6	-1.214658	-0.002790	3.513269
8	1	-2.157345	-0.025079	1.580909
9	6	0.001501	-0.000507	4.213175
10	1	2.153529	0.018359	4.063462
11	1	-2.131935	-0.020124	4.089814
12	6	0.934460	-0.799538	-0.703829
13	6	1.309617	-2.062087	-0.196585
14	6	1.498852	-0.338155	-1.912517
15	6	2.221104	-2.846862	-0.887197
16	1	0.861962	-2.429305	0.717219
17	6	2.414656	-1.123052	-2.597799
18	1	1.239492	0.642918	-2.287646
19	6	2.775774	-2.379670	-2.088572
20	1	2.487850	-3.822468	-0.503430

21	1	2.858743	-0.753874	-3.512552
22	6	-0.938731	0.795262	-0.702308
23	6	-1.319506	2.056093	-0.194517
24	6	-1.504756	0.329893	-1.908897
25	6	-2.238891	2.834535	-0.881650
26	1	-0.872094	2.425846	0.718367
27	6	-2.428500	1.108403	-2.590585
28	1	-1.241494	-0.649994	-2.284282
29	6	-2.796024	2.362731	-2.080206
30	1	-2.511073	3.808156	-0.496626
31	1	-2.874617	0.735741	-3.502896
32	53	-4.213733	3.557058	-3.127211
33	53	4.178108	-3.585337	-3.144112
34	6	-0.047226	-0.001300	5.701148
35	8	-1.106636	-0.004192	6.329874
36	1	0.941100	0.000768	6.189436

Number of imaginary frequencies: 0

Table S 21. Atomic coordinates of triphenylaminium cation-radical **3a** after geometry optimization

Number	Atomic number	X	Y	Z
1	7	0.000003	0.689173	0.00004
2	6	-0.000011	2.104572	0.000017
3	6	1.035341	2.825259	-0.627041
4	6	-1.035386	2.825248	0.627057
5	6	1.03801	4.212324	-0.622541
6	1	1.833517	2.286773	-1.119321
7	6	-1.03809	4.212308	0.622532
8	1	-1.83355	2.286748	1.119342
9	6	-0.000043	4.929253	-0.000007

10	1	1.83743	4.752502	-1.114264
11	1	-1.837524	4.752482	1.114236
12	6	1.23191	-0.041188	-0.005973
13	6	2.292076	0.331114	0.834251
14	6	1.390278	-1.155047	-0.843701
15	6	3.485166	-0.387376	0.824306
16	1	2.179873	1.183166	1.491921
17	6	2.57951	-1.879369	-0.836618
18	1	0.579724	-1.451802	-1.496296
19	6	3.625853	-1.492695	-0.007109
20	1	4.300297	-0.097476	1.473521
21	1	2.697961	-2.737644	-1.484058
22	6	-1.2319	-0.041201	0.006022
23	6	-2.292013	0.331025	-0.834305
24	6	-1.390312	-1.154993	0.843827
25	6	-3.485094	-0.38748	-0.824384
26	1	-2.179772	1.183029	-1.49203
27	6	-2.579533	-1.879333	0.836719
28	1	-0.579798	-1.451684	1.4965
29	6	-3.625825	-1.492734	0.007107
30	1	-4.300185	-0.097639	-1.473675
31	1	-2.698021	-2.737556	1.484219
32	35	-5.273212	-2.494242	0.007403
33	35	5.273251	-2.494187	-0.007433
34	6	-0.000064	6.351829	-0.000017
35	7	-0.000083	7.518686	-0.000025

Number of imaginary frequencies: 0

Table S 22. Atomic coordinates of triphenylaminium cation-radical **4a** after geometry optimization

Number	Atomic number	X	Y	Z
1	7	-0.000069	-0.002925	0.12831
2	6	-0.109317	1.421263	0.116801
3	6	-1.07109	2.075586	0.91026
4	6	0.737547	2.204412	-0.677225
5	6	-1.180408	3.457196	0.896173
6	1	-1.731935	1.486156	1.532438
7	6	0.642421	3.596846	-0.67521
8	1	1.482005	1.718452	-1.294673
9	6	-0.321606	4.236889	0.107199
10	1	-1.91709	3.967714	1.502495
11	1	1.318644	4.167117	-1.297706
12	6	-1.179047	-0.80824	0.116025
13	6	-2.288073	-0.453631	-0.662171
14	6	-1.259104	-1.980002	0.893169
15	6	-3.446812	-1.231655	-0.661619
16	1	-2.244661	0.443247	-1.266555
17	6	-2.401589	-2.764401	0.877337
18	1	-0.413239	-2.267605	1.503912
19	6	-3.512827	-2.39844	0.103255
20	1	-4.284214	-0.920965	-1.27177
21	1	-2.470607	-3.666559	1.470908
22	6	1.287955	-0.619023	0.116439
23	6	2.341732	-0.097624	0.891699
24	6	1.538932	-1.756387	-0.66123
25	6	3.59432	-0.690548	0.875666
26	1	2.165271	0.779063	1.501145
27	6	2.794216	-2.366523	-0.660841

28	1	0.741894	-2.170036	-1.265513
29	6	3.836293	-1.836138	0.103066
30	1	4.409373	-0.29545	1.467753
31	1	2.946975	-3.246292	-1.271334
32	8	-0.510953	5.610574	0.177987
33	6	0.3617	6.459014	-0.624161
34	1	0.040295	7.47863	-0.409557
35	1	1.415496	6.338214	-0.343257
36	1	0.251285	6.256145	-1.696816
37	8	5.123365	-2.35314	0.169308
38	8	-4.607546	-3.250064	0.17064
39	6	5.416252	-3.548124	-0.612366
40	1	5.288487	-3.3715	-1.687759
41	1	6.461432	-3.775685	-0.400694
42	1	4.78653	-4.394702	-0.311104
43	6	-5.783967	-2.907341	-0.618757
44	1	-6.203815	-1.937984	-0.321969
45	1	-5.560548	-2.887198	-1.692848
46	1	-6.505196	-3.698008	-0.409804

Number of imaginary frequencies: 0

Table S 23. Atomic coordinates of triphenylaminium cation-radical **5a** after geometry optimization

Number	Atomic number	X	Y	Z
1	7	0.331561	0.00564	0.02619
2	6	-1.084233	-0.205184	0.073454
3	6	-1.640446	-1.145419	0.960048
4	6	-1.94705	0.519276	-0.75649
5	6	-3.010337	-1.353775	1.001814
6	1	-0.984871	-1.711862	1.608786

7	6	-3.328	0.326112	-0.700393
8	1	-1.53263	1.244721	-1.444808
9	6	-3.8722	-0.61666	0.175872
10	1	-3.448692	-2.075383	1.678448
11	1	-3.964496	0.90791	-1.353075
12	6	1.209696	-1.117056	-0.003248
13	6	0.866039	-2.27743	-0.717736
14	6	2.430214	-1.099137	0.691527
15	6	1.715924	-3.379764	-0.729896
16	1	-0.072922	-2.307577	-1.255226
17	6	3.280718	-2.201737	0.65729
18	1	2.705411	-0.217516	1.255829
19	6	2.941885	-3.362625	-0.049832
20	1	1.426583	-4.265374	-1.286539
21	1	4.217396	-2.165295	1.203992
22	6	0.847209	1.335201	0.015142
23	6	0.234579	2.348989	0.768376
24	6	1.972212	1.667295	-0.760272
25	6	0.731488	3.650625	0.741659
26	1	-0.633844	2.110092	1.368449
27	6	2.469642	2.966742	-0.765555
28	1	2.450661	0.89868	-1.353409
29	6	1.859441	3.984655	-0.017835
30	1	0.239822	4.417454	1.331309
31	1	3.338148	3.199099	-1.373708
32	6	2.419734	5.39576	-0.02295
33	1	3.343119	5.451882	0.56809
34	1	2.654638	5.722185	-1.04263
35	1	1.702033	6.102521	0.405371

36	6	3.879203	-4.555939	-0.099569
37	1	4.456562	-4.560222	-1.033567
38	1	4.588804	-4.530666	0.7338
39	1	3.321113	-5.49718	-0.046277
40	8	-5.224539	-0.896269	0.307685
41	6	-6.158864	-0.154739	-0.531062
42	1	-7.144945	-0.528272	-0.253756
43	1	-6.106484	0.924427	-0.340262
44	1	-5.981136	-0.340082	-1.597687

Number of imaginary frequencies: 0

Table S 24. Atomic coordinates of triphenylaminium cation- radical **6a** after geometry optimization

Number	Atomic number	X	Y	Z
1	7	0.006266	0.000184	0.119156
2	6	1.433617	-0.004968	0.116967
3	6	2.148288	-0.946044	-0.642776
4	6	2.157158	0.931741	0.873696
5	6	3.539013	-0.952863	-0.636263
6	1	1.604346	-1.678629	-1.224839
7	6	3.547853	0.931926	0.859513
8	1	1.620155	1.666567	1.459348
9	6	4.270725	-0.011638	0.108772
10	1	4.069341	-1.706214	-1.207282
11	1	4.084562	1.682753	1.427913
12	6	-0.712134	-1.233436	0.114483
13	6	-0.268311	-2.327147	0.876158
14	6	-1.880468	-1.381748	-0.651317
15	6	-0.964792	-3.530866	0.860267
16	1	0.633425	-2.229203	1.46664

17	6	-2.584044	-2.581464	-0.645421
18	1	-2.238915	-0.544812	-1.236476
19	6	-2.139908	-3.684815	0.104093
20	1	-0.587704	-4.37029	1.433021
21	1	-3.499251	-2.663698	-1.220328
22	6	-0.703712	1.238578	0.118272
23	6	-0.250225	2.327347	-0.644915
24	6	-1.874452	1.396293	0.878562
25	6	-0.941365	3.53428	-0.638204
26	1	0.654019	2.222792	-1.230388
27	6	-2.57205	2.599365	0.864233
28	1	-2.239331	0.564168	1.466584
29	6	-2.120074	3.69656	0.110382
30	1	-0.558411	4.369499	-1.213248
31	1	-3.488802	2.688926	1.435591
32	6	5.755481	-0.011755	0.100042
33	6	6.489908	0.223025	1.279597
34	6	6.473902	-0.24465	-1.080974
35	6	7.876455	0.223831	1.27228
36	1	5.961136	0.379358	2.21264
37	6	7.869418	-0.246074	-1.095533
38	1	5.935135	-0.401315	-2.0085
39	6	8.582808	-0.01089	0.083077
40	1	8.446641	0.392932	2.176282
41	1	8.386409	-0.41987	-2.029588
42	6	-2.884688	-4.969205	0.096862
43	6	-3.048943	-5.720829	1.27745
44	6	-3.446465	-5.475798	-1.083395
45	6	-3.74336	-6.921006	1.271937

46	1	-2.647327	-5.340847	2.209629
47	6	-4.147232	-6.682623	-1.096133
48	1	-3.311752	-4.932469	-2.01172
49	6	-4.301406	-7.415853	0.083748
50	1	-3.882201	-7.498048	2.176743
51	1	-4.555579	-7.045125	-2.02985
52	6	-2.865238	4.980803	0.101728
53	6	-3.432352	5.500227	1.282586
54	6	-3.030239	5.715808	-1.080421
55	6	-4.130979	6.697935	1.275194
56	1	-3.297771	4.966349	2.216109
57	6	-3.73115	6.922561	-1.094992
58	1	-2.627527	5.326468	-2.008526
59	6	-4.288425	7.423474	0.084784
60	1	-4.560456	7.107813	2.17989
61	1	-3.845989	7.454183	-2.029965
62	8	9.964475	0.012515	0.185617
63	8	-4.972667	-8.623614	0.187994
64	8	-5.004368	8.605435	0.187007
65	6	10.7449	-0.251078	-1.01847
66	1	10.572135	0.511633	-1.787723
67	1	11.784917	-0.214916	-0.693413
68	1	10.522756	-1.240694	-1.436285
69	6	-5.62619	-9.149381	-1.005818
70	1	-6.126465	-10.059788	-0.674903
71	1	-6.366541	-8.445497	-1.405286
72	1	-4.89984	-9.392586	-1.791062
73	6	-5.170204	9.41157	-1.017549
74	1	-5.740519	8.876731	-1.786998

75	1	-5.72706	10.291005	-0.693332
76	1	-4.203631	9.7197	-1.434717

Number of imaginary frequencies: 0

NMR characterizations

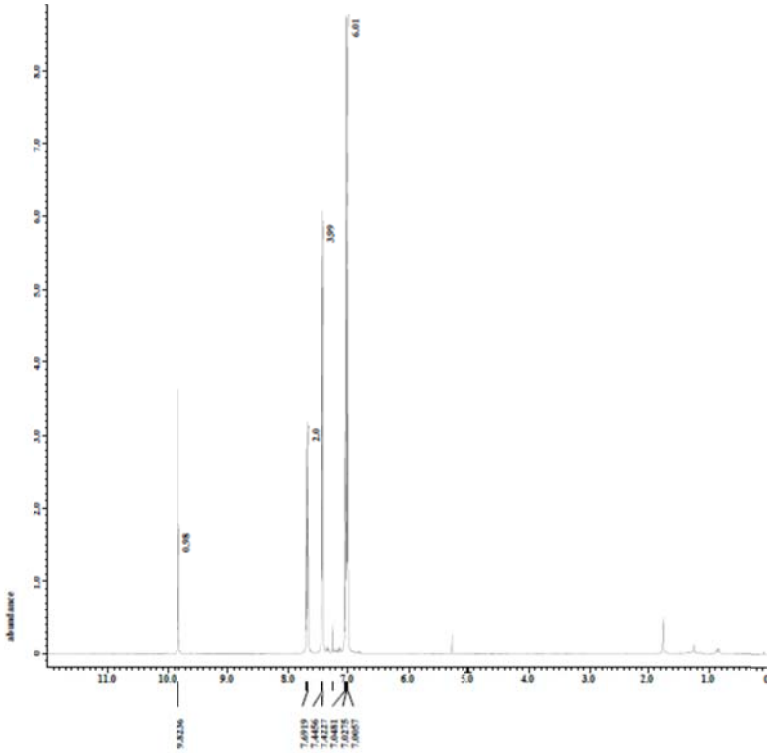

Figure S 13 ^{1}H NMR of **1** in $CDCl_3$

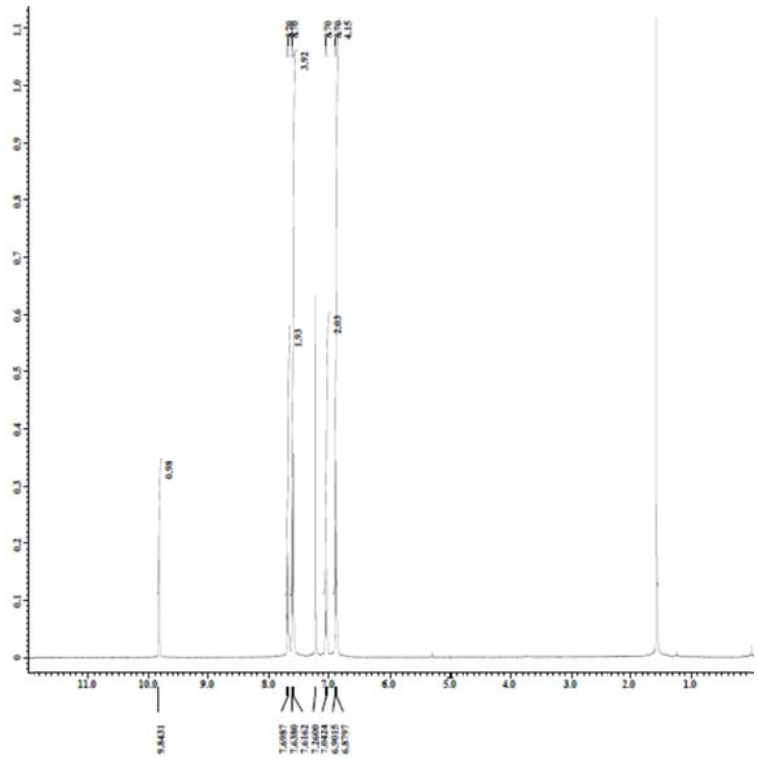

Figure S 14 ^{1}H NMR of **2** in $CDCl_3$

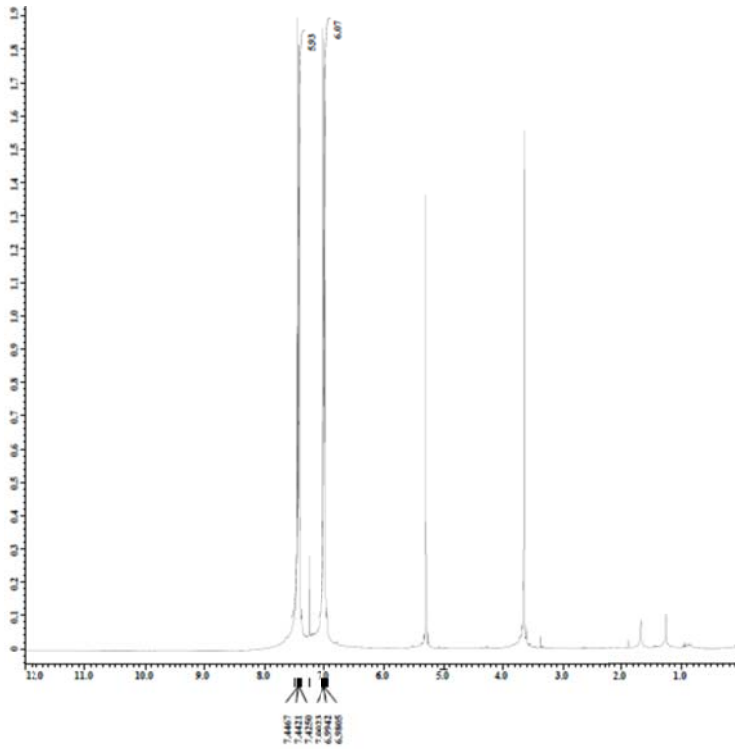

Figure S 15 ^{1}H NMR of **3** in $CDCl_3$

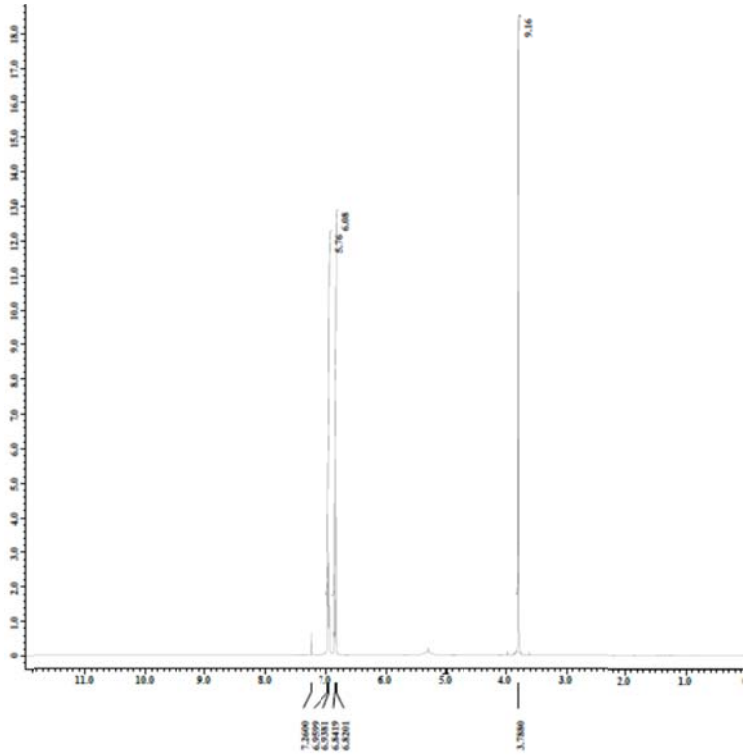

Figure S 16 ^{1}H NMR of **4** in $CDCl_3$

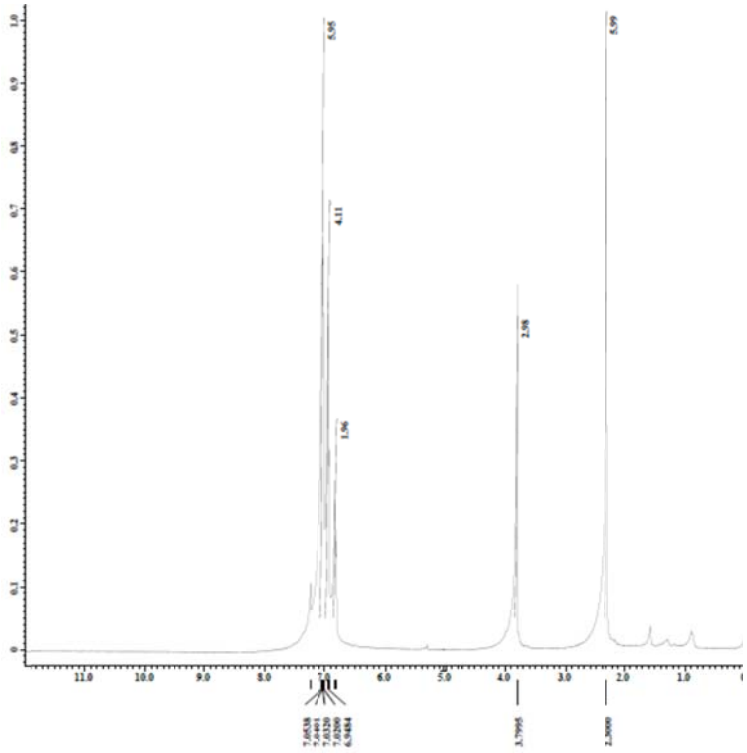

Figure S 17 ^{1}H NMR of **5** in $CDCl_3$

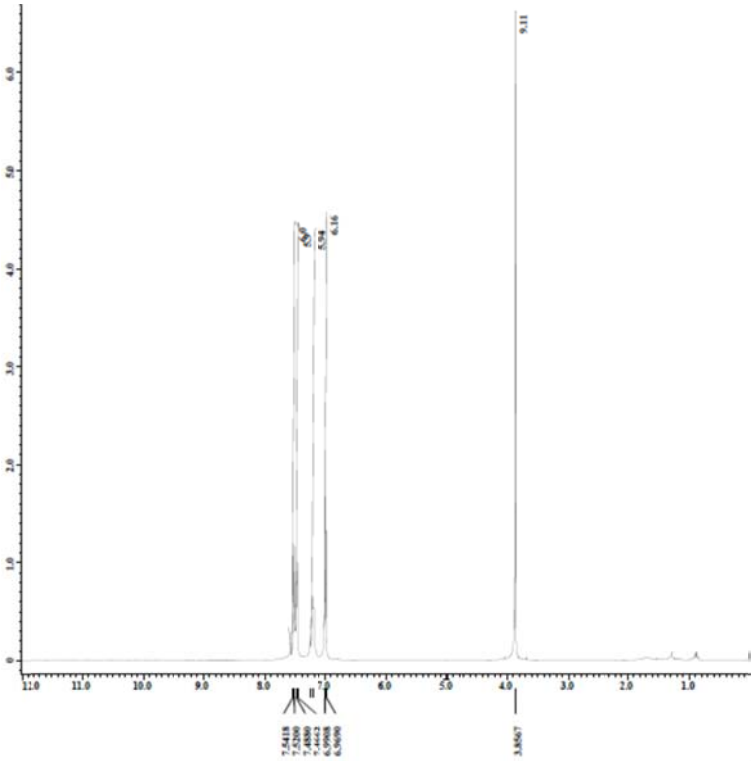

Figure S 18 ^{1}H NMR of **6** in DMSO

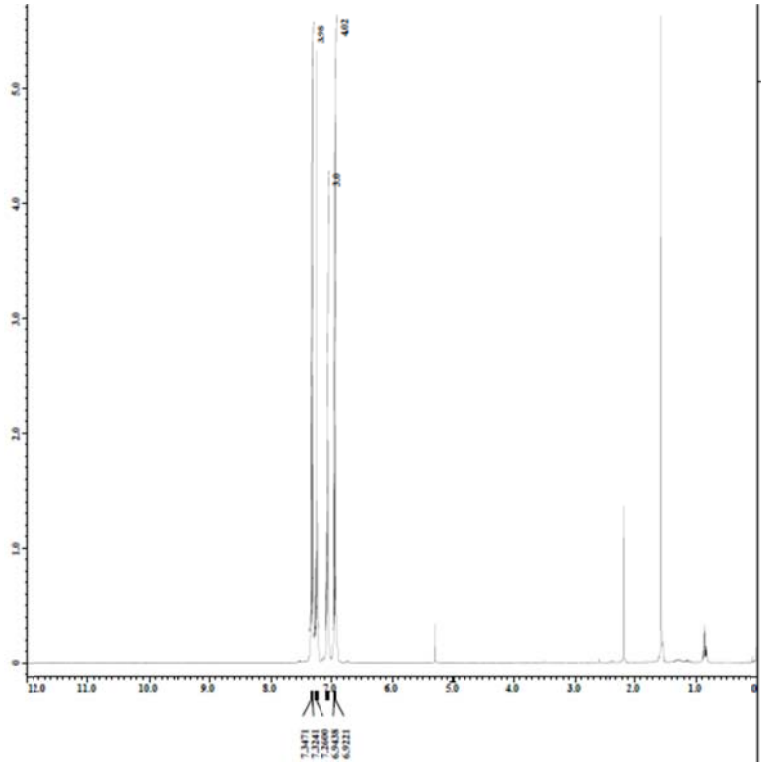

Figure S 19 ^{1}H NMR of **7** in $CDCl_3$

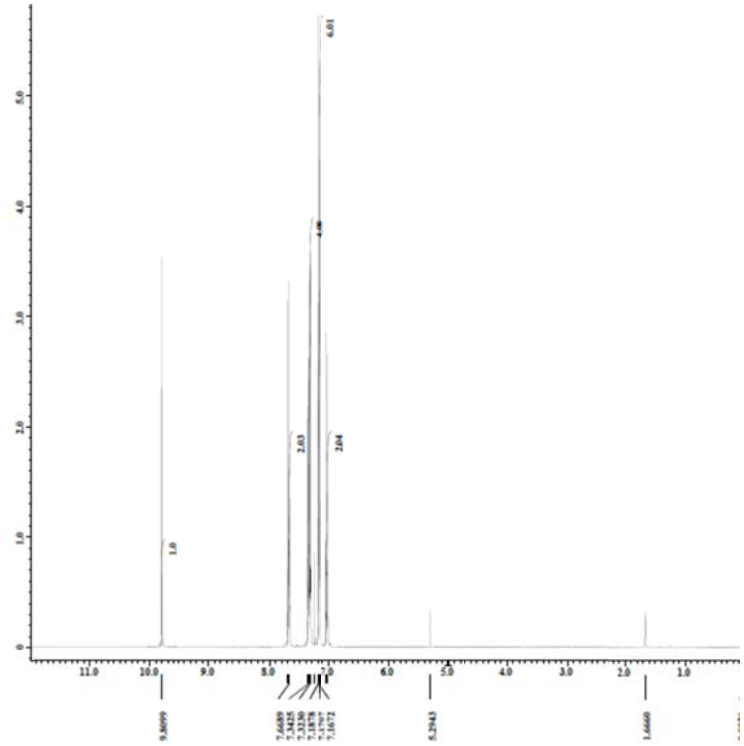

Figure S 20 ^{1}H NMR of **8** in $CDCl_3$

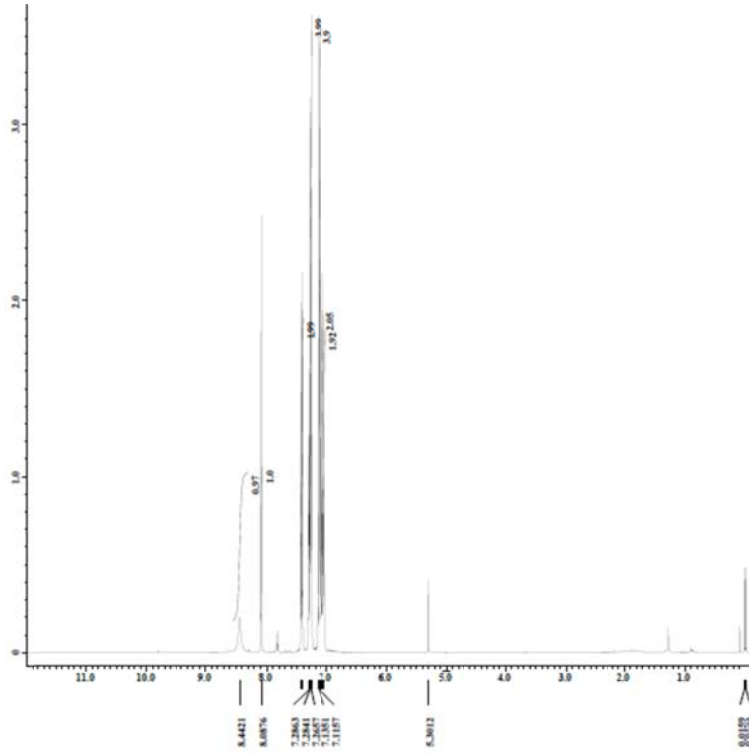

Figure S 21 ^{1}H NMR of **9** in $CDCl_3$

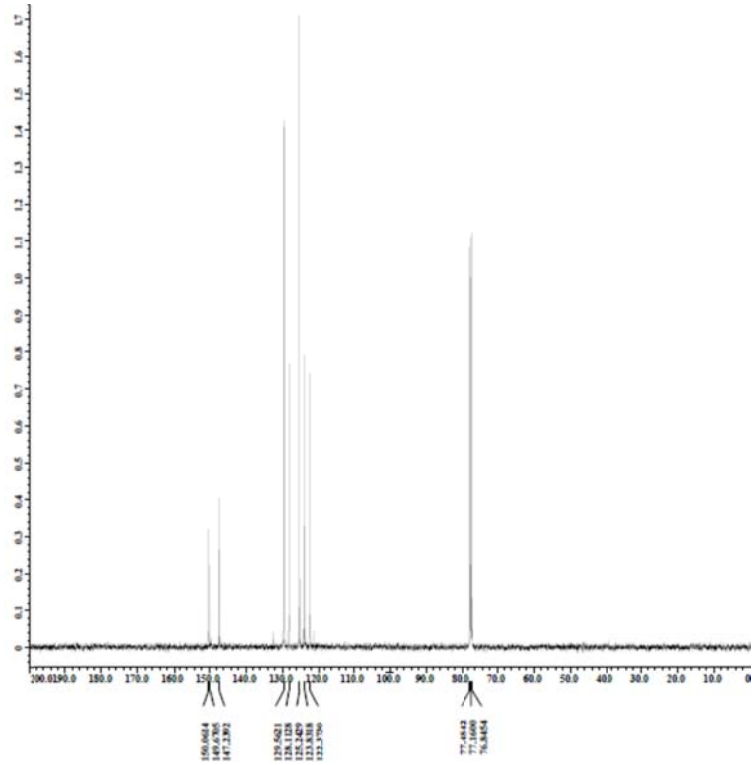

Figure S 22 ^{13}C NMR of **9** in $CDCl_3$