Electron Rich Triphenylamine Based Sensors for Picric Acid Detection

Aniket Chowdhury and Partha Sarathi Mukherjee*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India

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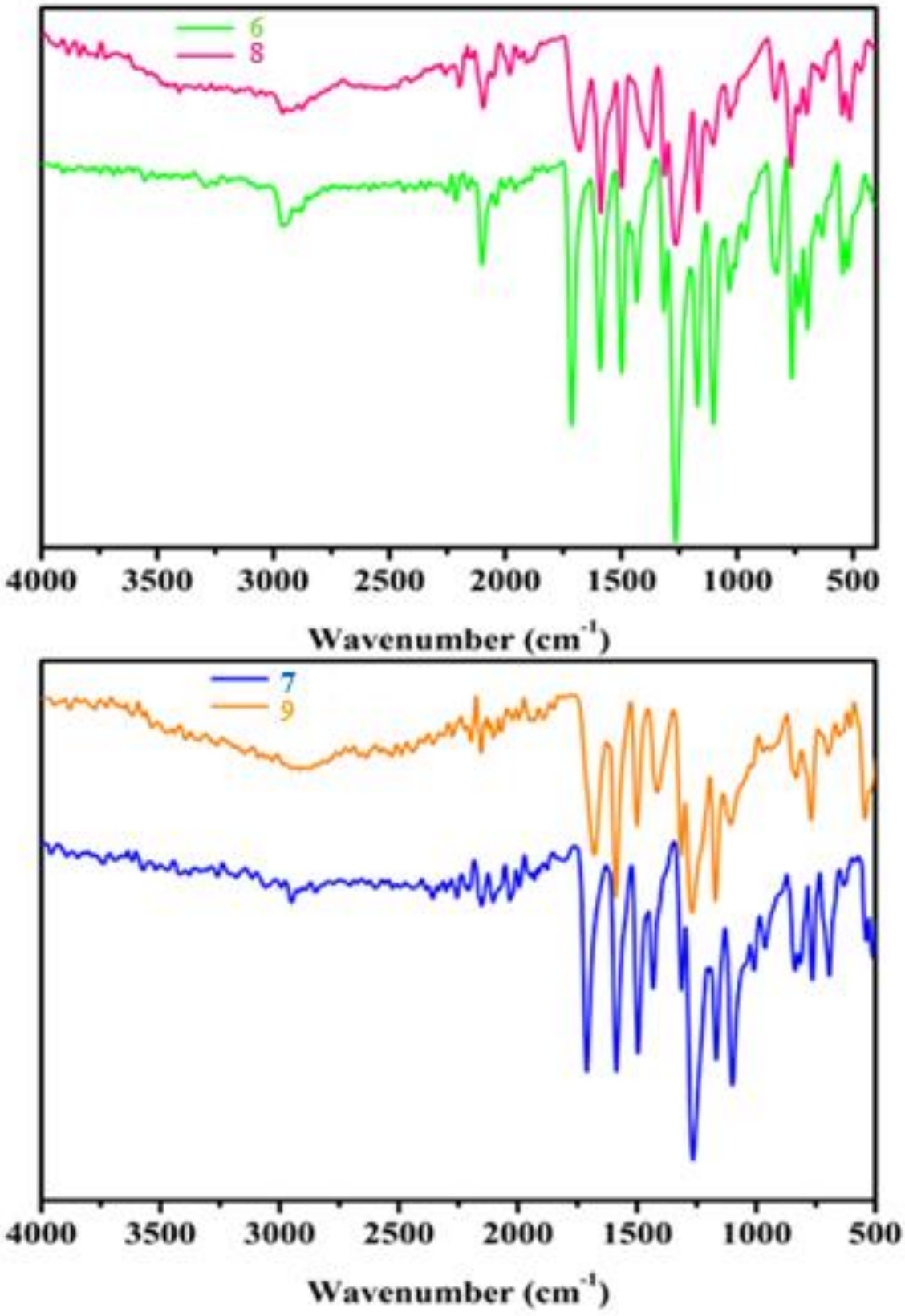


Figure S1. IR spectra of the compounds.

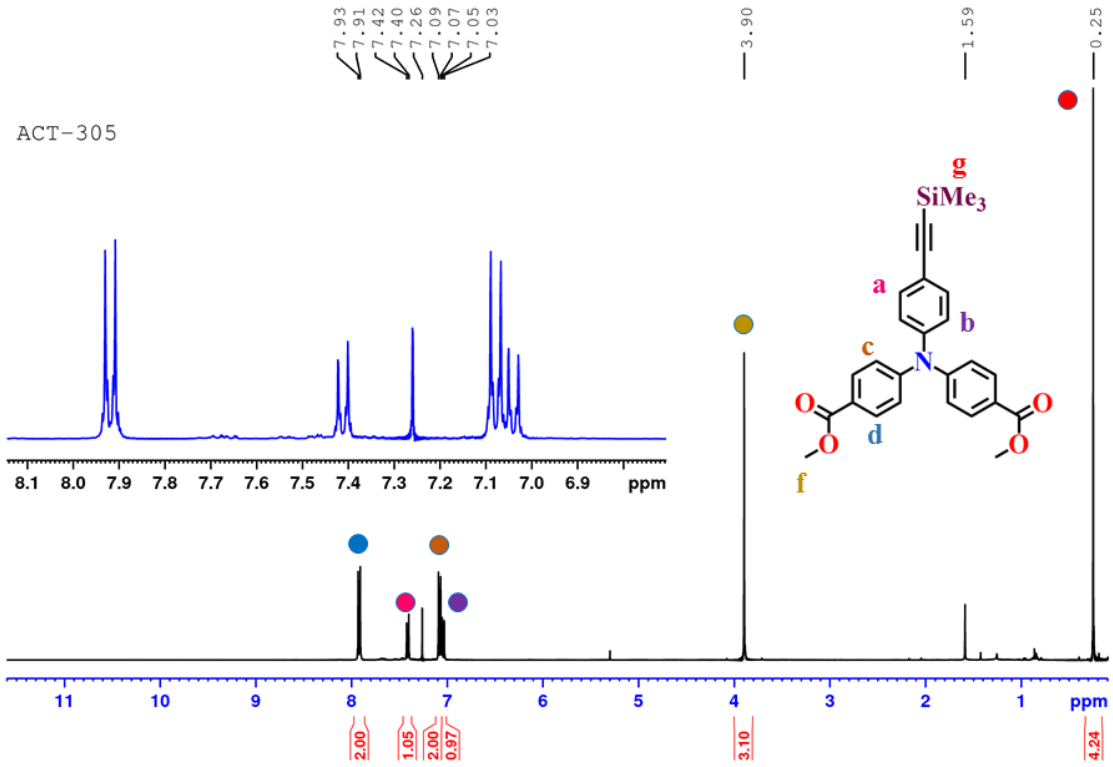


Figure S2. ^{1}H NMR of **4.**

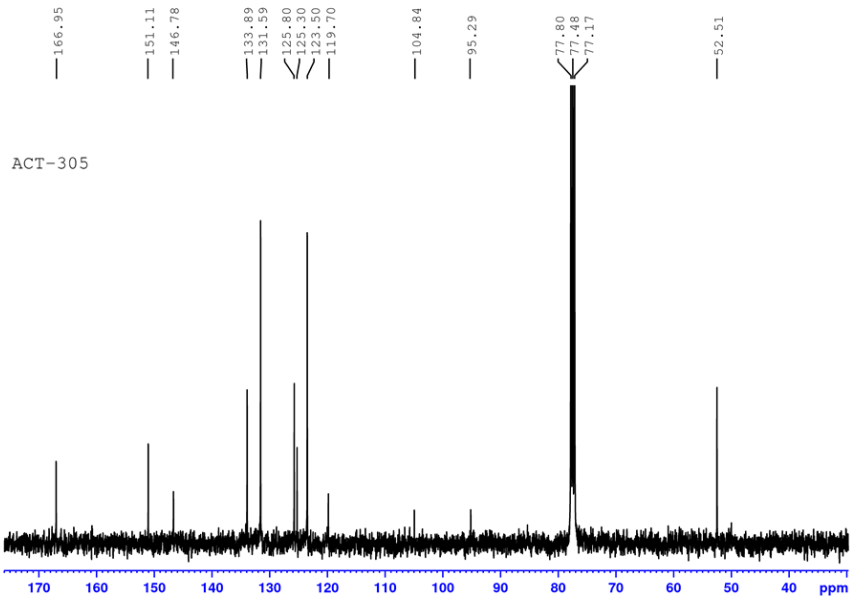


Figure S3. ^{13}C NMR of **4**.

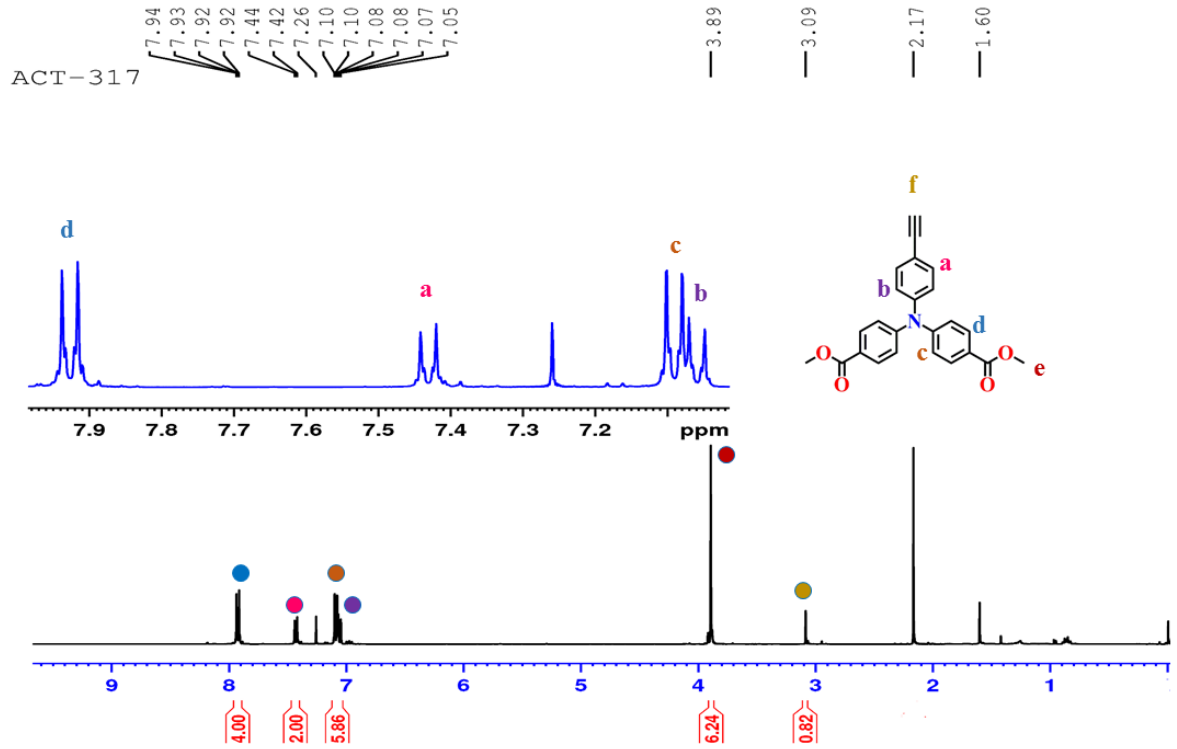


Figure S4. ^{1}H NMR of **5**.

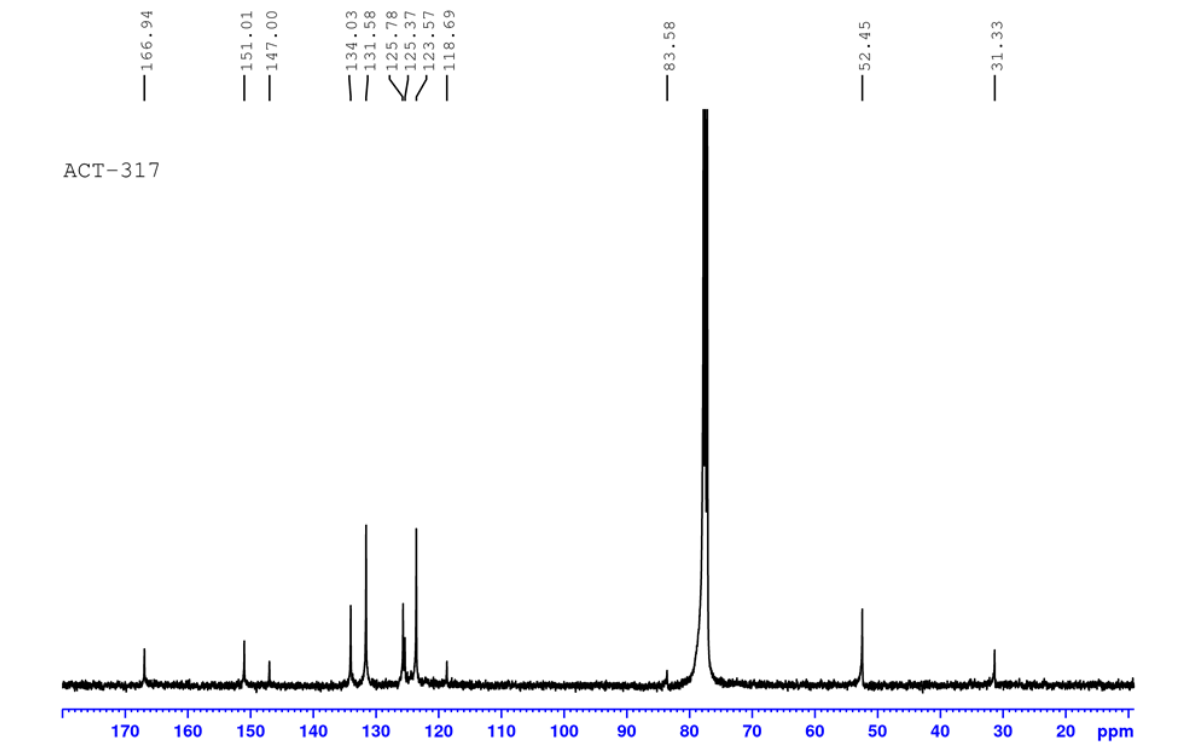


Figure S5. ^{13}C NMR of **5**.

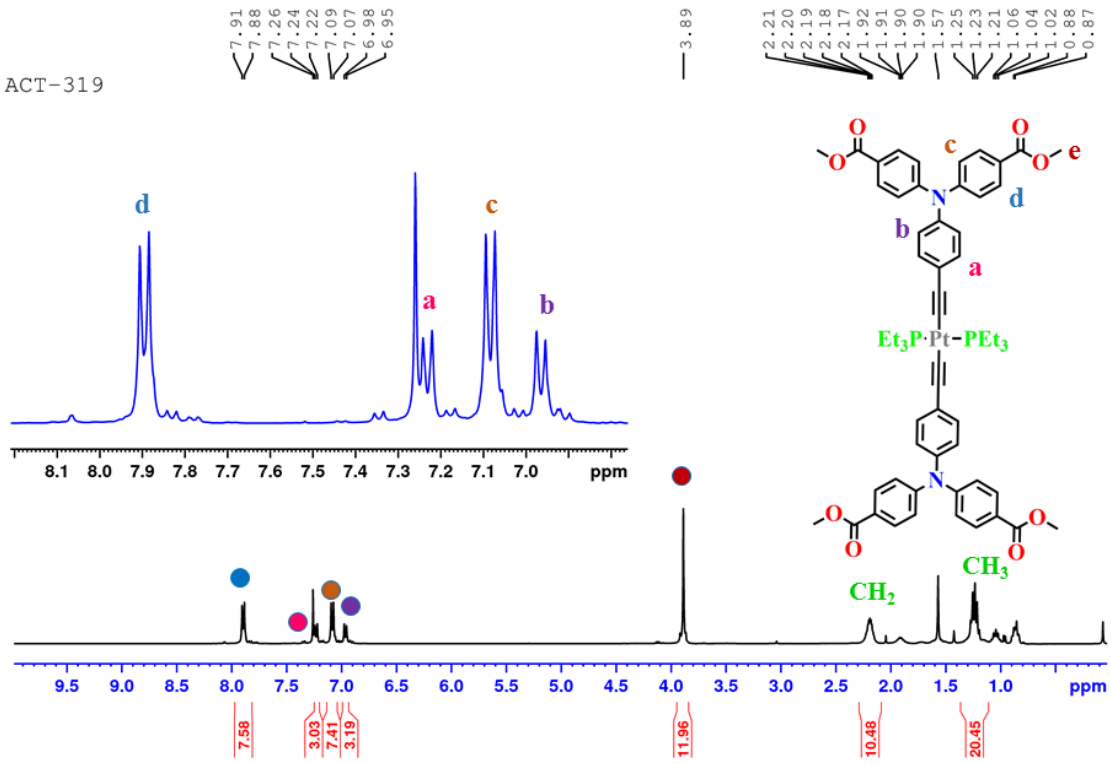


Figure S6. ^{1}H NMR of **6**.

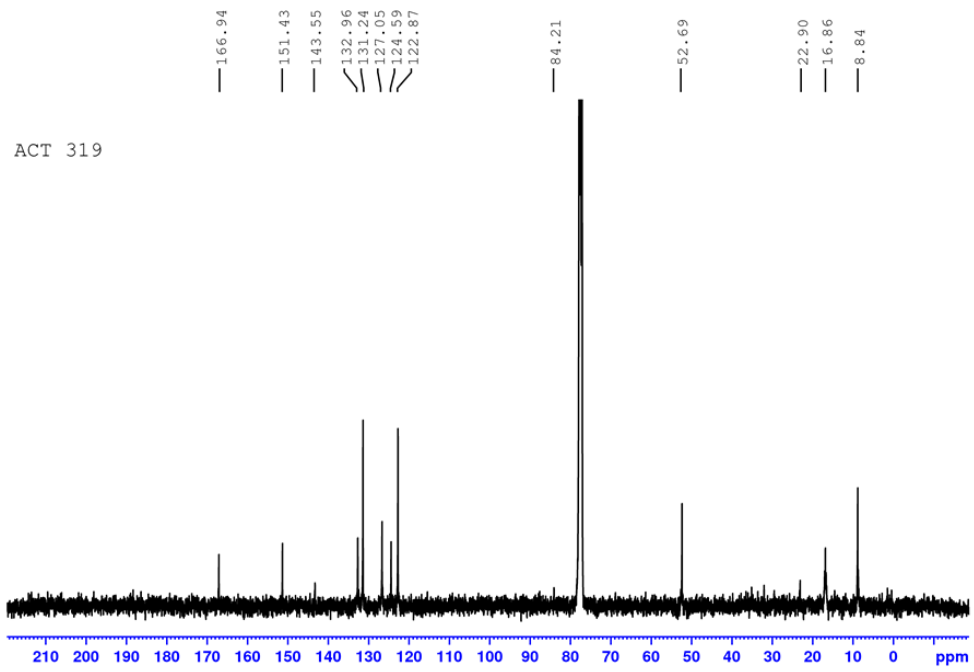


Figure S7. ^{13}C NMR of **6**.

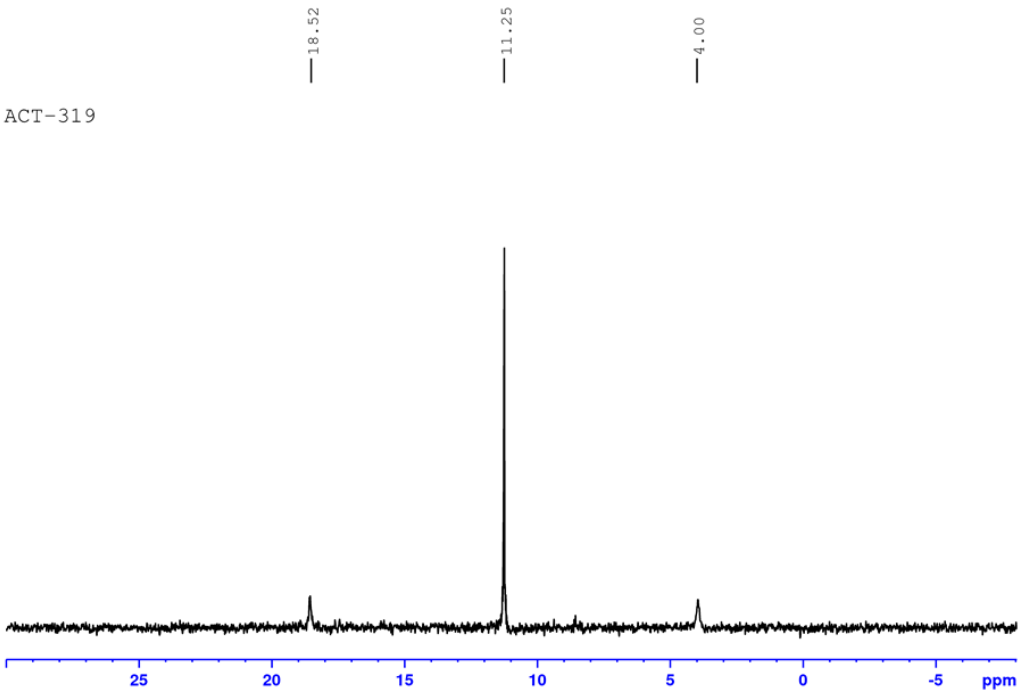


Figure S8. ^{31}P NMR of **6**.

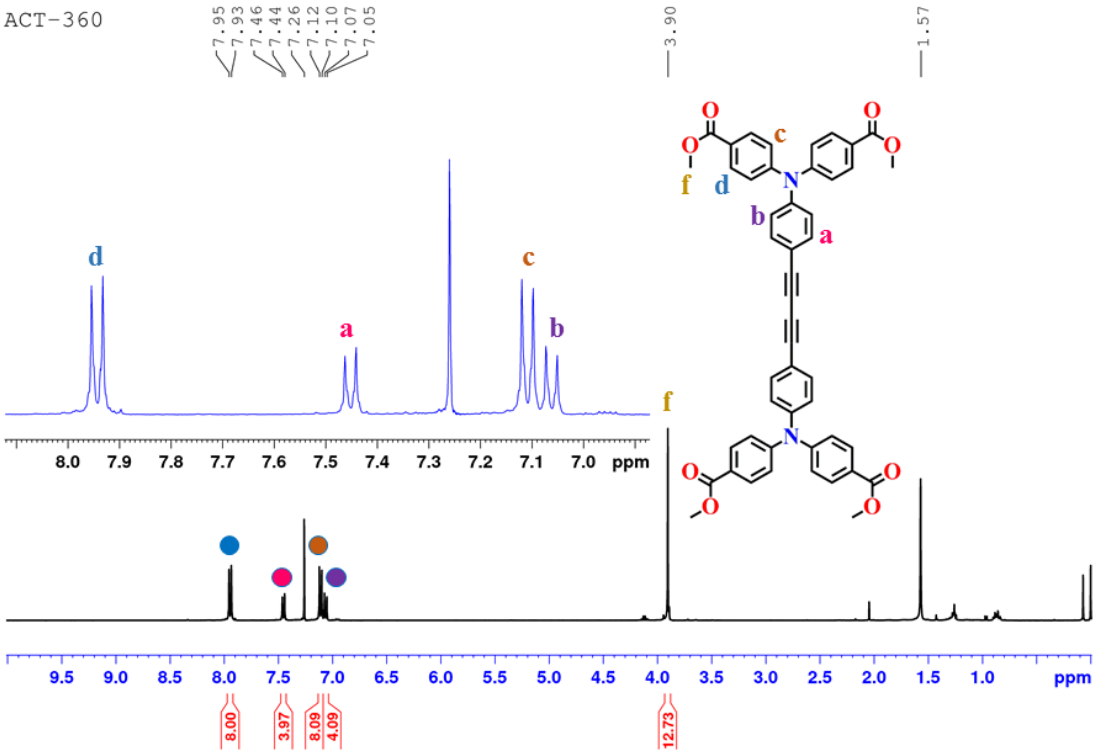


Figure S9. ^{1}H NMR of **7**.

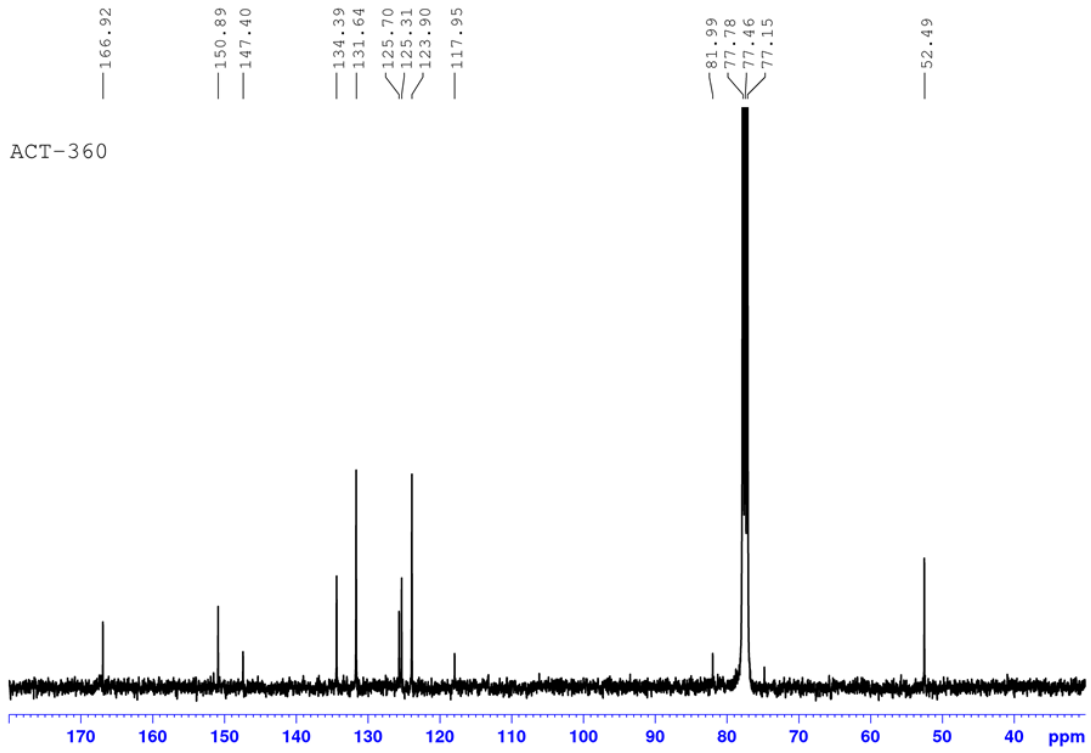


Figure S10. ^{13}C NMR of **7**.

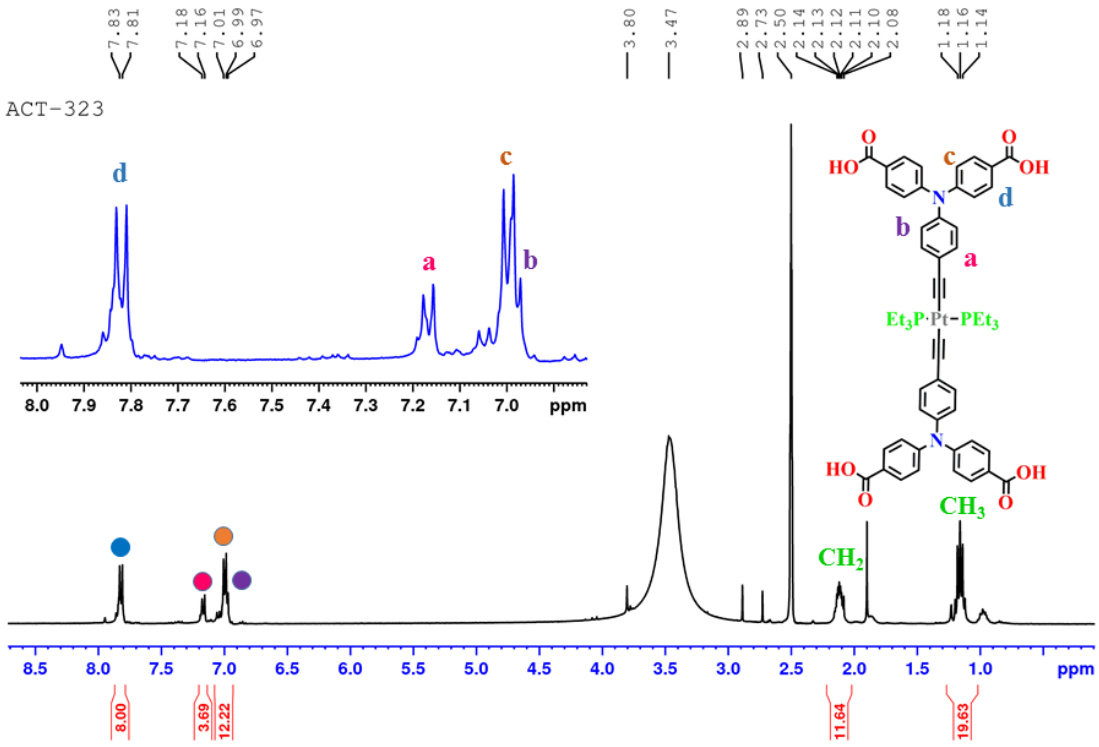


Figure S11. ^{1}H NMR of **8**.

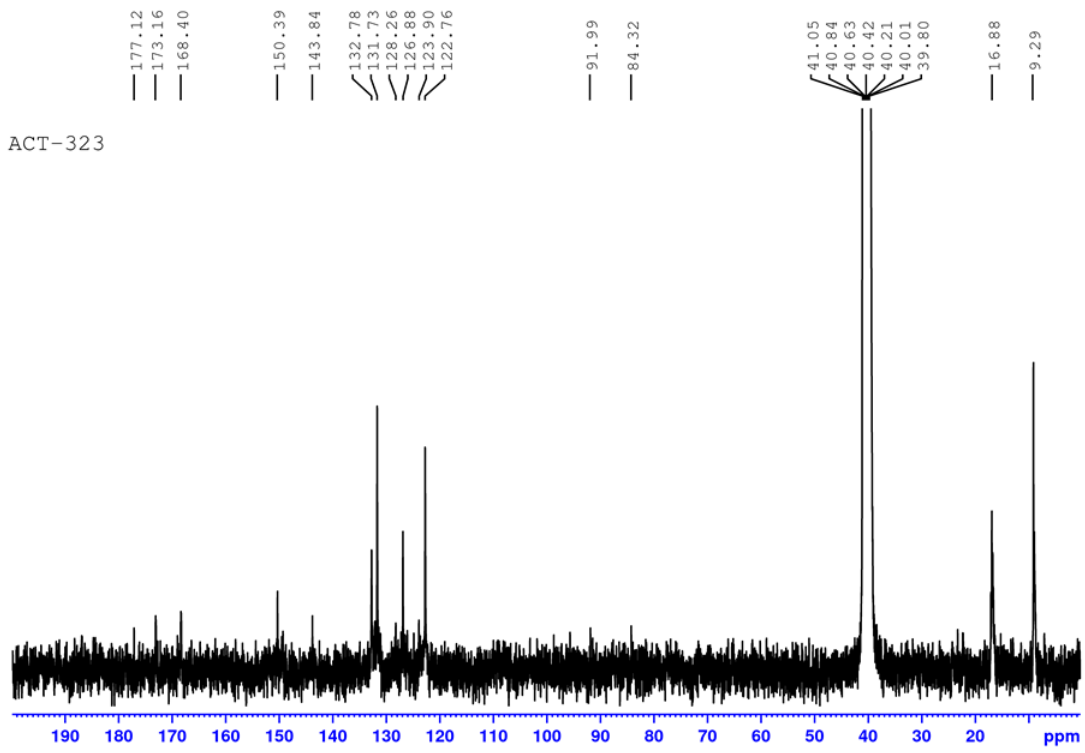


Figure S12. ^{13}C NMR of **8**.

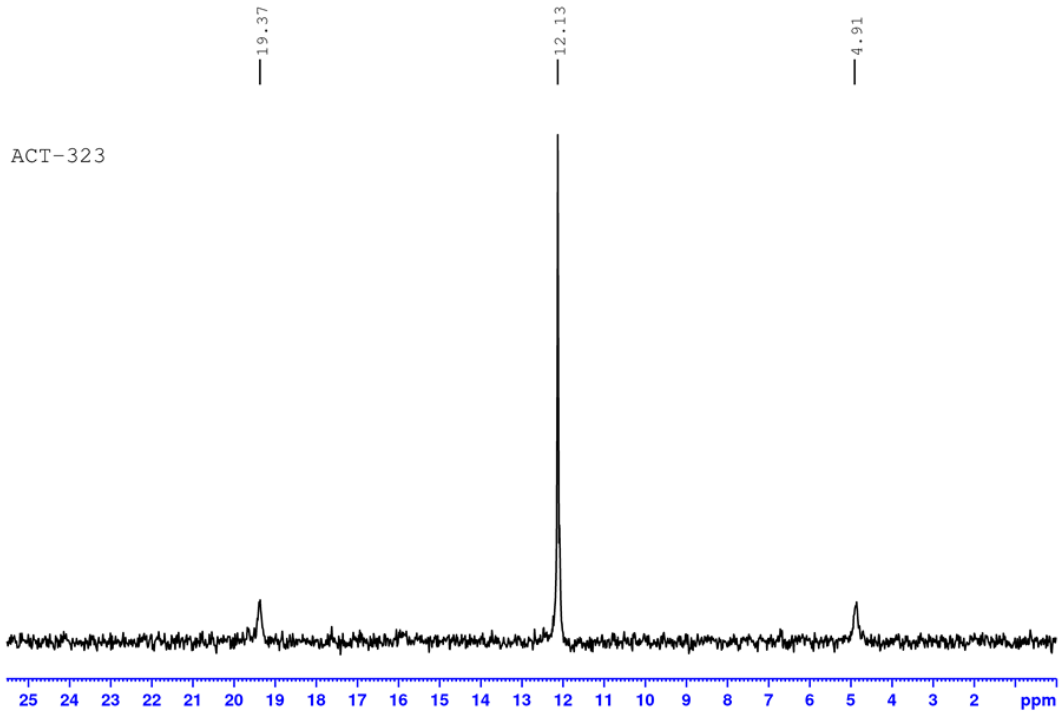


Figure S13. ^{31}P NMR of **8**.

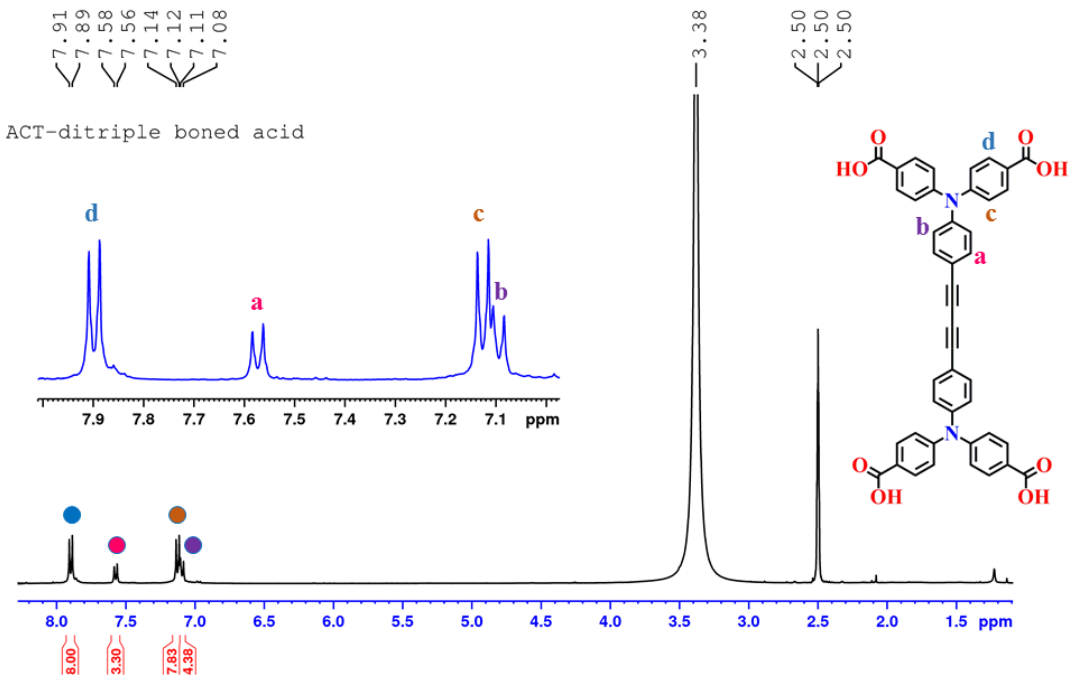


Figure S14. ^{1}H NMR of **9**.

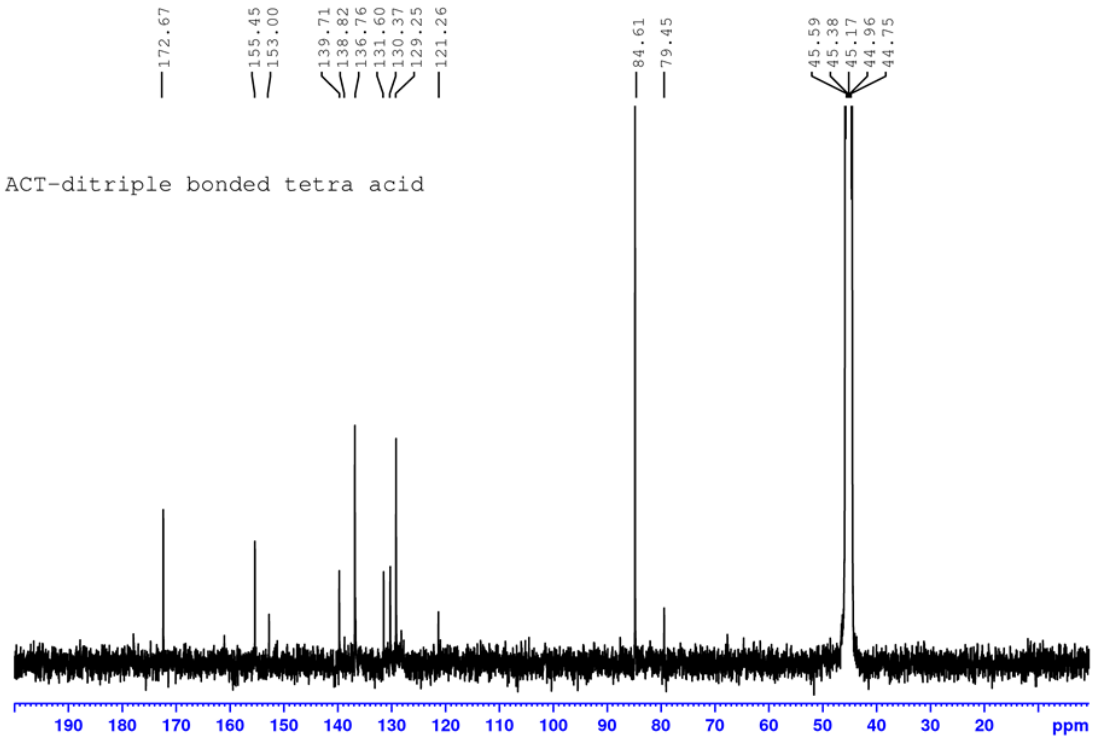


Figure S15. ^{13}C NMR of **9**.

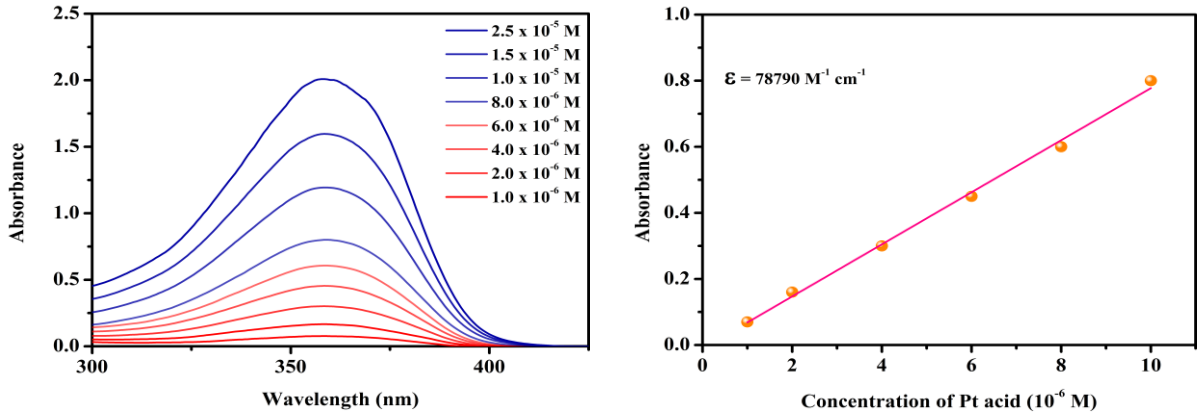


Figure S16: Concentration dependent UV-Vis spectra of **8** in the range of 10^{-6} M to 2.5×10^{-5} M (left) in DMA and the value of extinction coefficient determined form the plot by liner fitting using Beer-Lambert law (right).

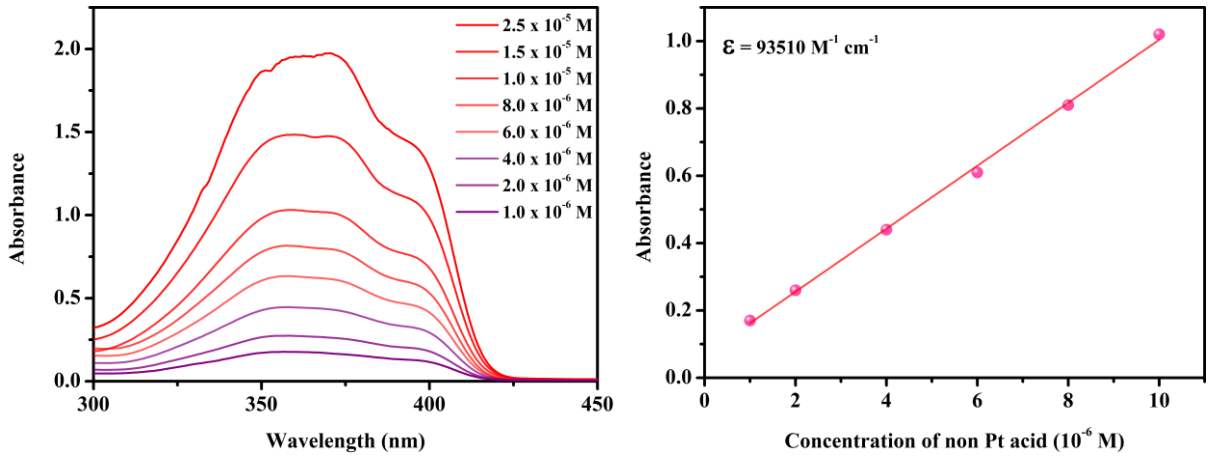


Figure S17: Concentration dependent UV-Vis spectra of **6** in the range of 10^{-6} M to 1.0×10^{-5} M (left) in $CHCl_3$ and the value of extinction coefficient determined form the plot by liner fitting using Beer-Lambert law (right).

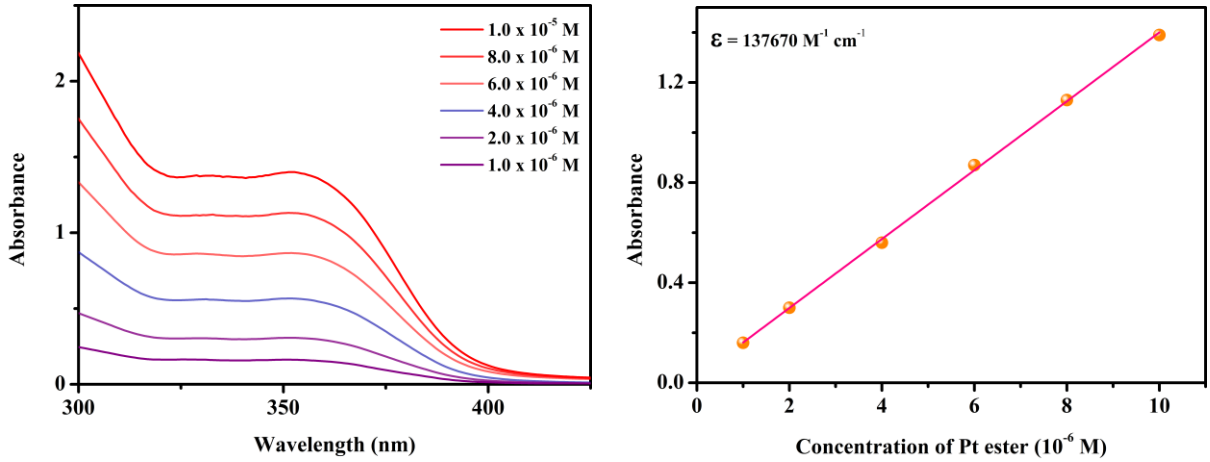


Figure S18: Concentration dependent UV-Vis spectra of **9** in the range of 10^{-6} M to $2.5.0\times10^{-5}$ M (left) in DMA and the value of extinction coefficient determined form the plot by liner fitting using Beer-Lambert law (right).

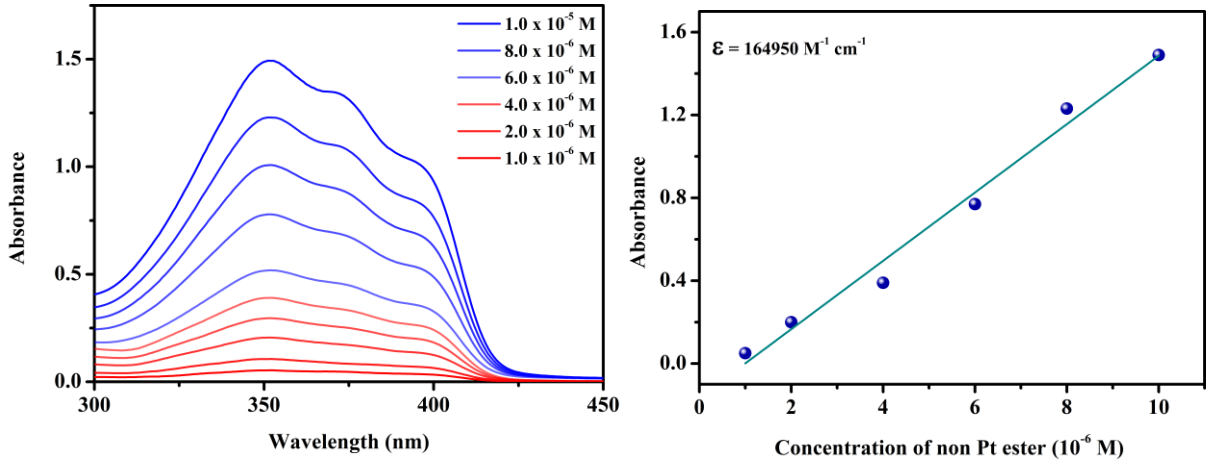


Figure S19: Concentration dependent UV-Vis spectra of **7** in the range of 10^{-6} M to 1.0×10^{-5} M (left) in $CHCl_3$ and the value of extinction coefficient determined form the plot by liner fitting using Beer-Lambert law (right).

Concentration dependent fluorescence spectra of the compounds from 10^{-3} M to 10^{-7} M.

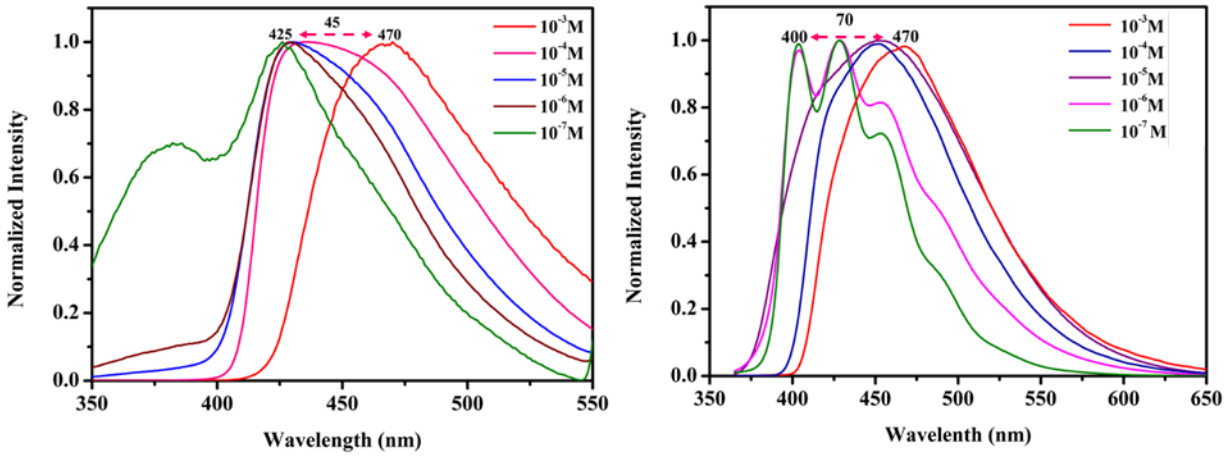


Figure S20. Normalized concentration dependent fluorescence of the **6** in $CHCl_3$ (left). Concentration dependent fluorescence of the **9** in DMSO-d_6 (right).

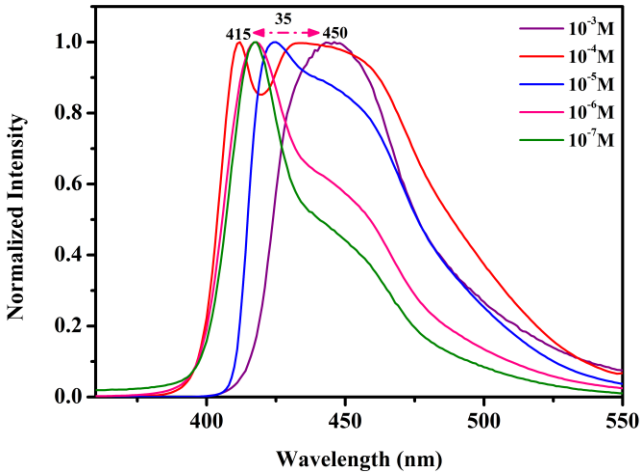


Figure S21: Concentration dependent fluorescence of the **7** in $CHCl_3$.

Solvent dependent absorption and fluorescence spectra of the compounds:

Solvent dependent fluorescence of the compounds were measured by making a 10^{-5} M solution of the individual compounds in corresponding solvents from initial stock solutions either in chloroform or in DMA.

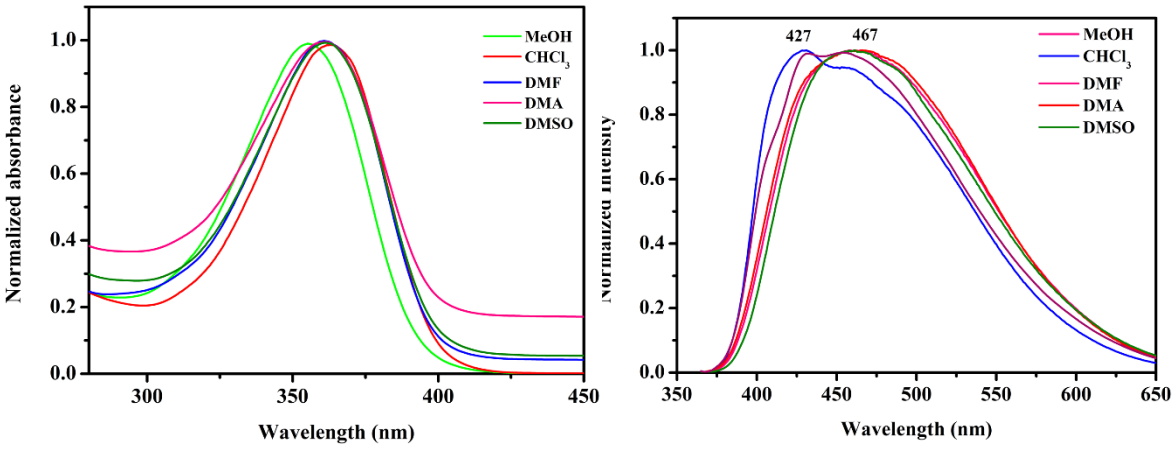


Figure S22. Solvent dependent absorption (left) and emission (right) behaviour of the 10^{-5} M solution of **6.** The compound showed 10 nm blue shift in absorption spectra and 40 nm blue shift in the emission spectra polar protic solvent.

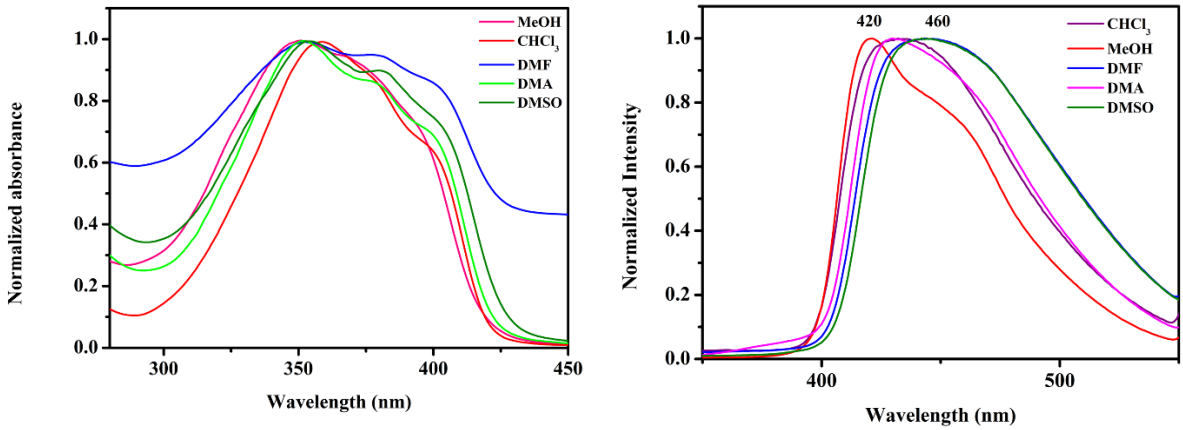


Figure S23. Solvent dependent normalized absorption spectra of the 10^{-5} M solution of **9** (left). The compound showed 10 nm blue shift in absorption spectra and 40 nm blue shift in the normalized emission spectra in the polar protic solvent (right).

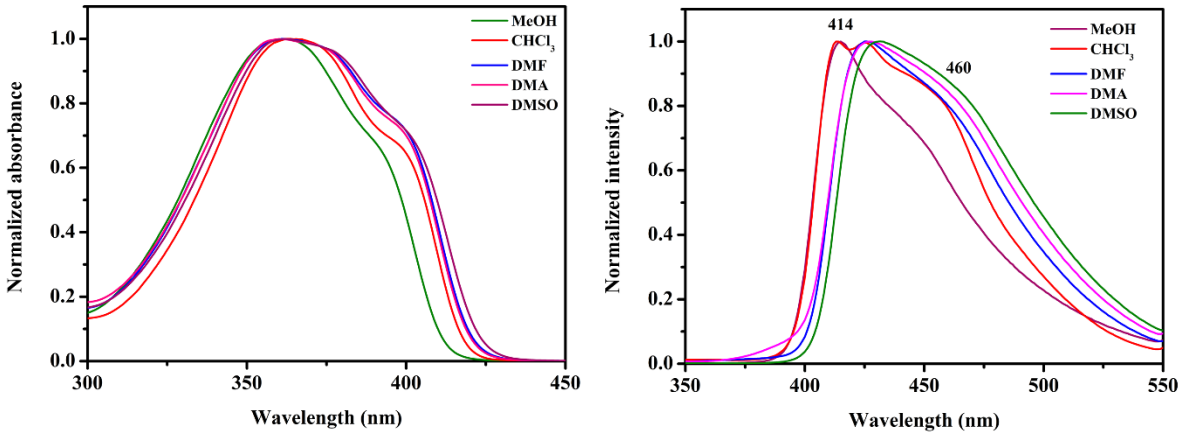


Figure S24. Solvent dependent normalized absorption (left) and emission spectra of the 10^{-5} M solution of **7** (right). The compound showed 10 nm blue shift in absorption spectra and 36 nm blue shift in the emission spectra in the polar protic solvent (right).

Solution state UV-Vis titration study of the compounds with nitroaromatic compounds:

For UV-Vis titration, a 2 mL stock solution (1.0×10^{-5} M) of the corresponding compound in chloroform or DMA was placed in a quartz cell of 1 cm width. Quenchers (1.0×10^{-3} M) solutions were added gradually in an incremental fashion. Their corresponding absorption spectra were recorded at 298 K. Each titration was repeated at least two times to get

reproducible result. For all measurements, the absorption window was taken from 300 nm to 500 nm to exclude absorption of the solvents.

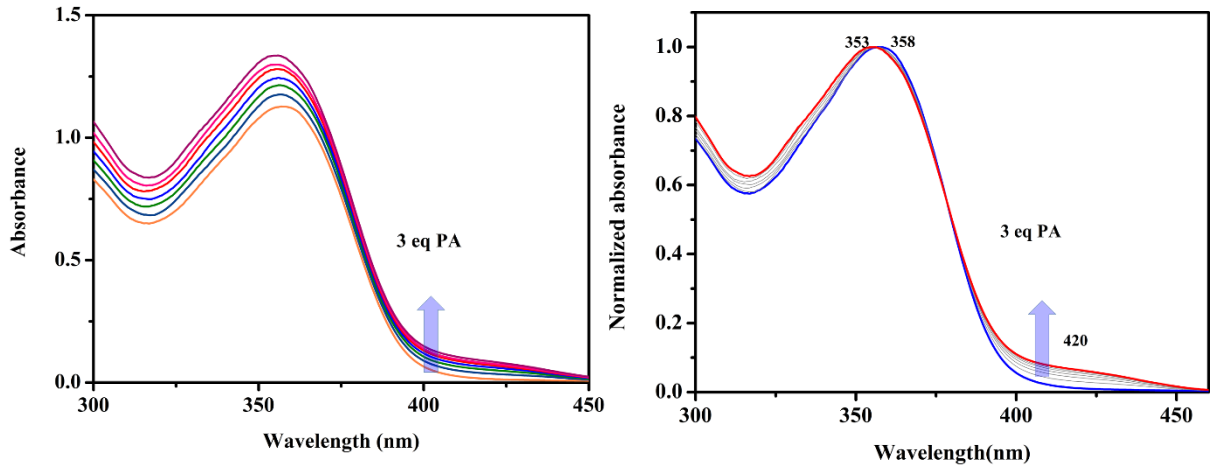


Figure S25: Solution state UV-Vis titration of **6** in $CHCl_3$ with picric acid (left) and corresponding normalized spectra (left). Upon addition of 3 equivalents of PA, a new band was generated at higher wavelength (420 nm) which is the charge transfer band.

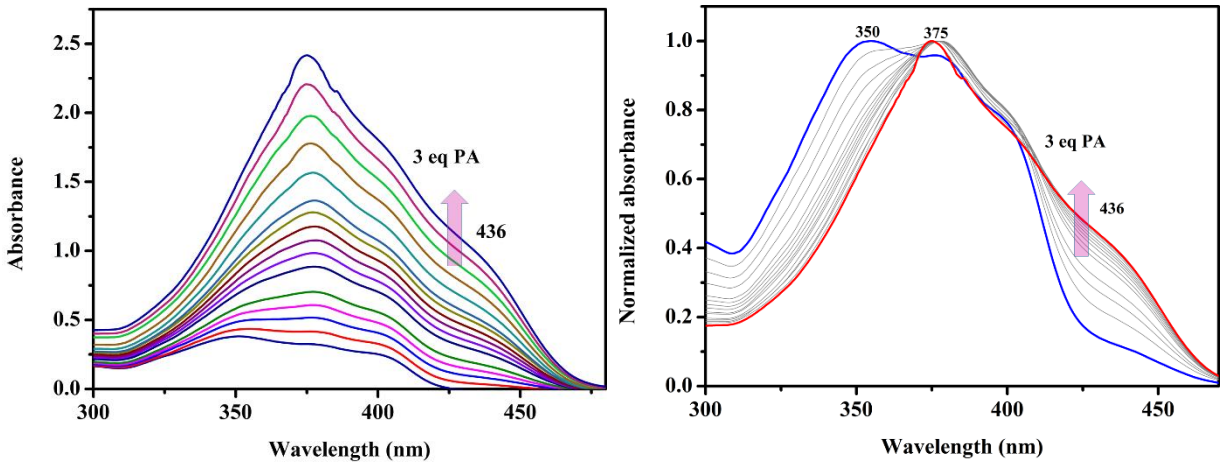


Figure S26: Solution state UV-Vis titration of **9** in DMA with picric acid (left) and corresponding normalized spectra (left). Upon addition of 3 equivalents of PA a new band was generated at higher wavelength (436 nm) which is the charge transfer band.

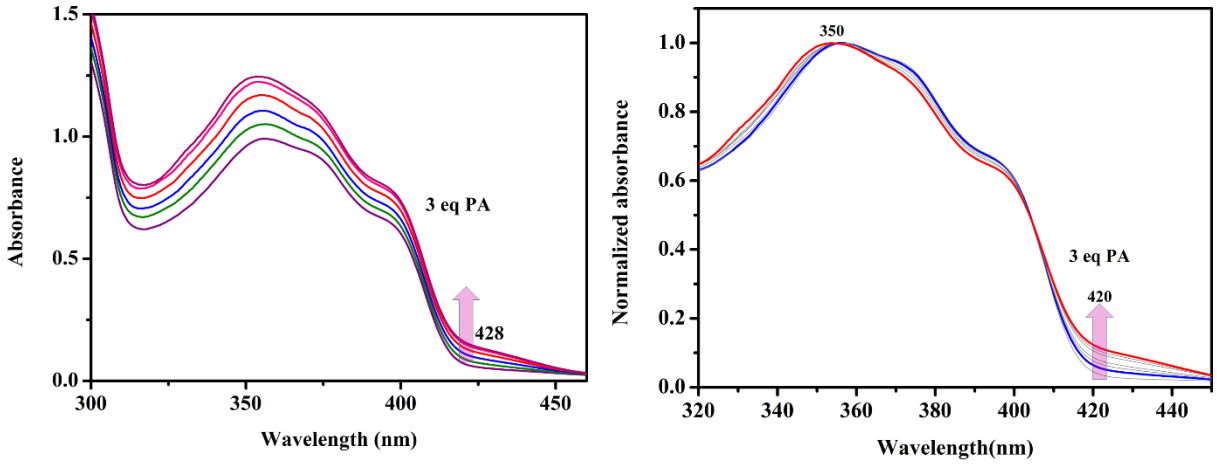


Figure S27: Solution state UV-Vis titration of **7** in $CHCl_3$ with Picric acid (left) and corresponding normalized spectra (left). Upon addition of 3 equivalent of PA a new band was generated at higher wavelength (420 nm) which is the charge transfer band.

Solution state fluorescence titration

For solution state fluorescence titration, a 2 mL stock solution (1.0×10^{-7} M) of the compounds in chloroform or DMA was placed in a quartz cell of 1 cm width and quenchers (1.0×10^{-5} M) solutions were added gradually in an incremental fashion. Their corresponding absorption spectra were recorded at 298 K. Each titration was repeated at least two times to get reproducible result. For all measurement, the compounds were excited at their corresponding absorption maxima and their emission was monitored.

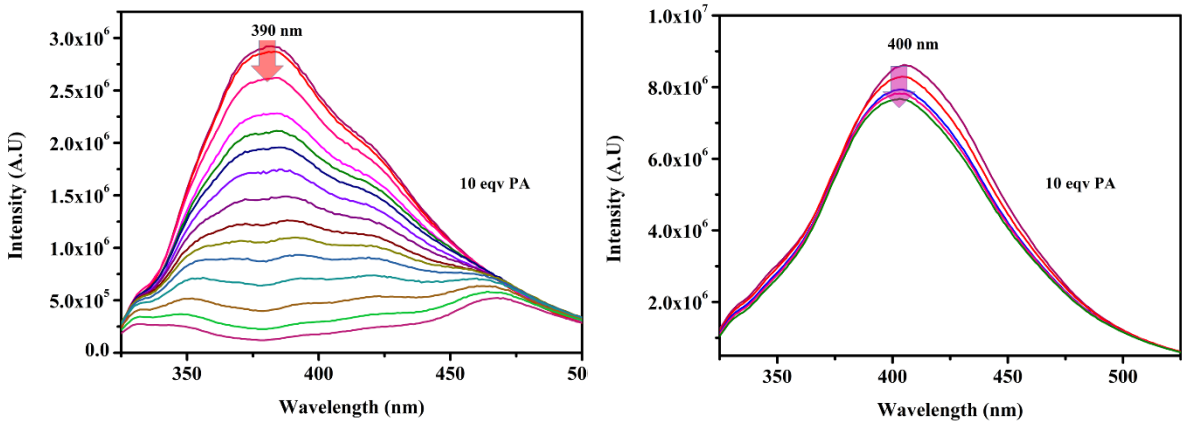


Figure S28: Solution state fluorescence titration of **9** in DMA (left) and **7** in $CHCl_3$ with picric acid (right). Upon addition of 10 equivalents of PA the emission maxima of the **9** at 390 nm quenched gradually, whereas for **7** the quenching effect is negligible.

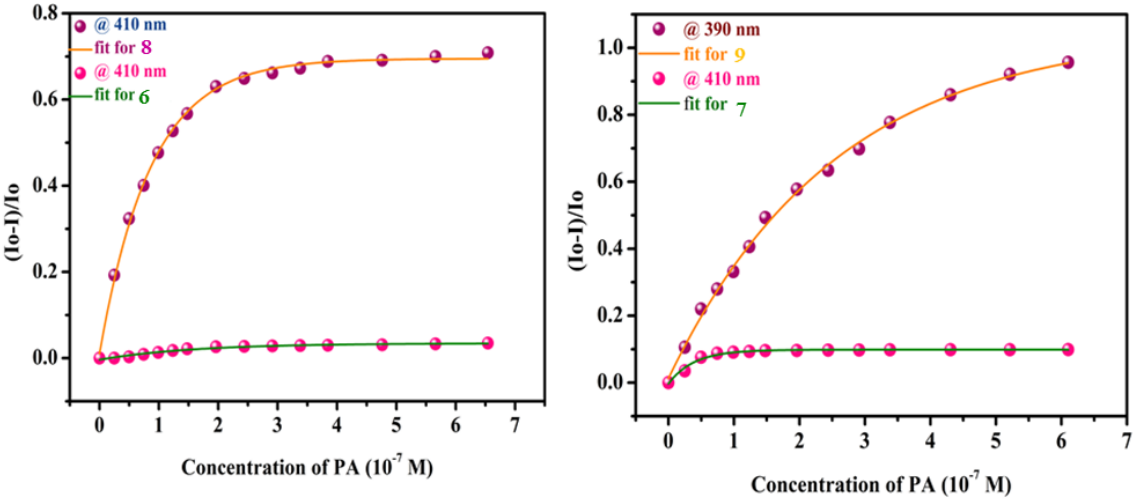


Figure S29: Quenching efficiency plot of solution state fluorescence titration of **8** and **6** with PA (left); and **9** and **7** with picric acid (right).

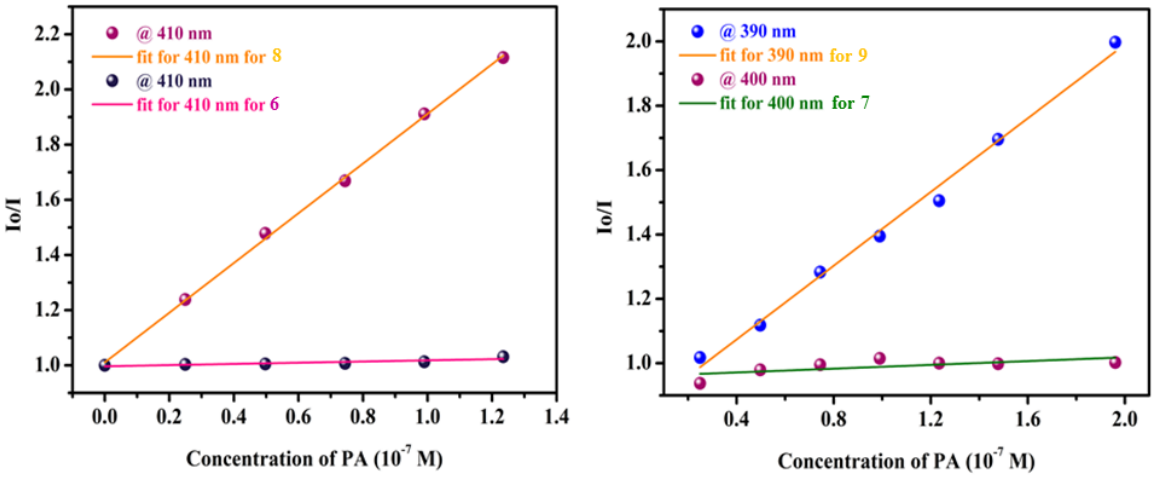
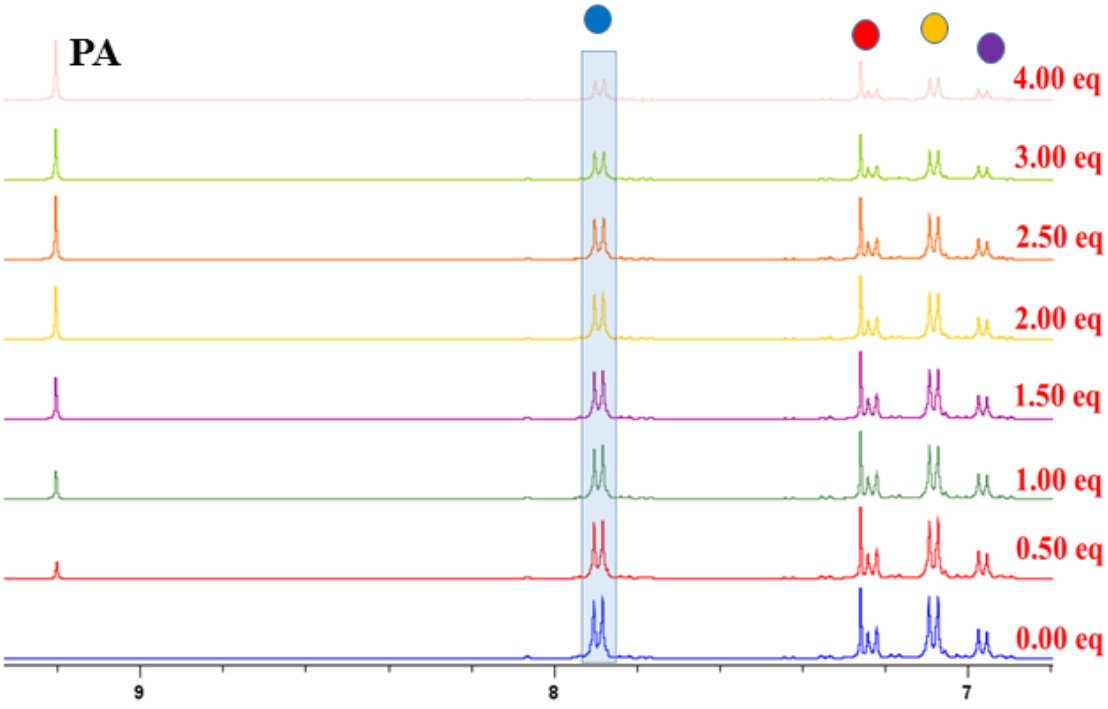


Figure S30. Stern-Volmer plots of solution state fluorescence titrations of **8** and **6** with PA (left); and **9** and **7** with picric acid (right).

NMR titrations of the compounds with picric acid:

In a typical titration 500 μL (10 mM) of compounds were taken in $CDCl_3$ or in DMSO-d_6. To that (10 mM) solution of PA in either $CDCl_3$ or DMSO-d_6 were added gradually and corresponding NMR were recorded at room temperature.



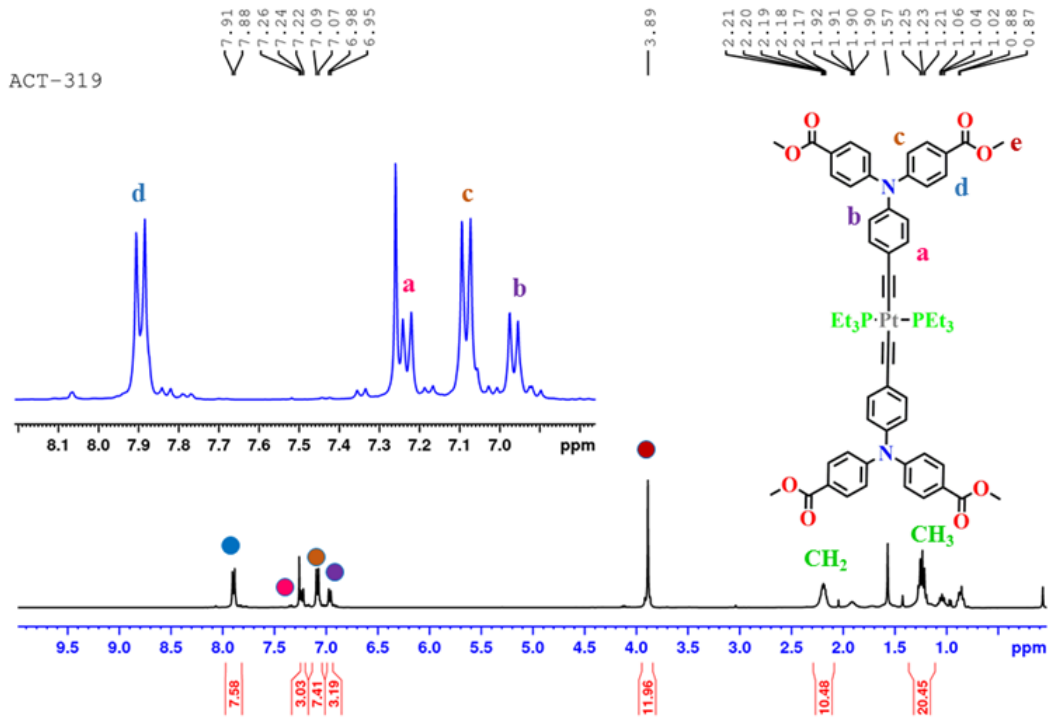
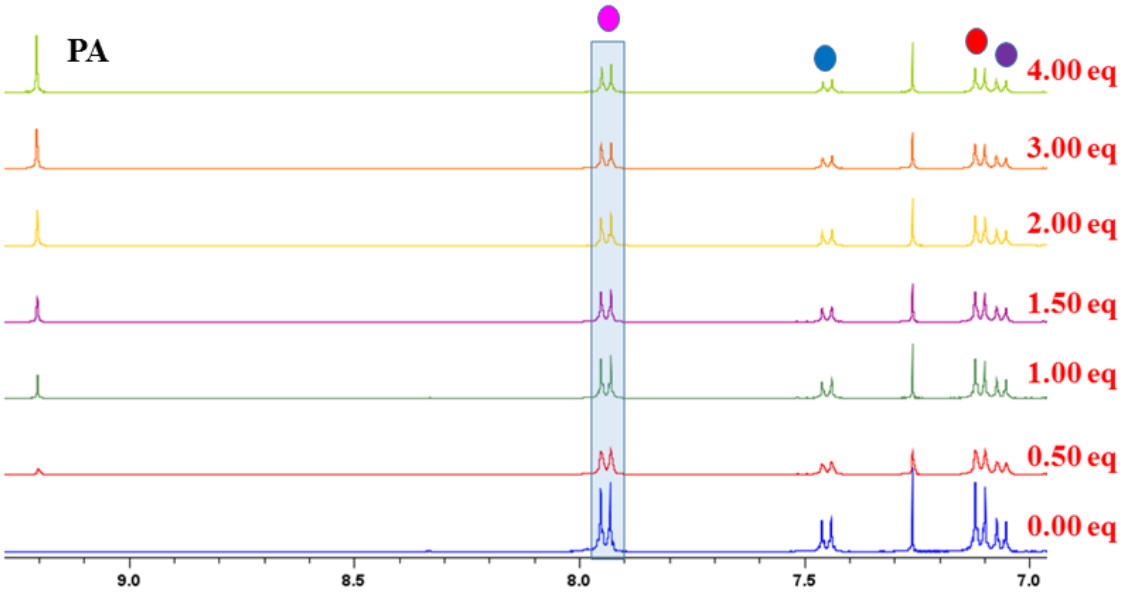


Figure S31: NMR titration of **6** $CDCl_3$ with PA (above) and the peak assignments of **6** (below). No change was observed in the chemical shift of the protons.



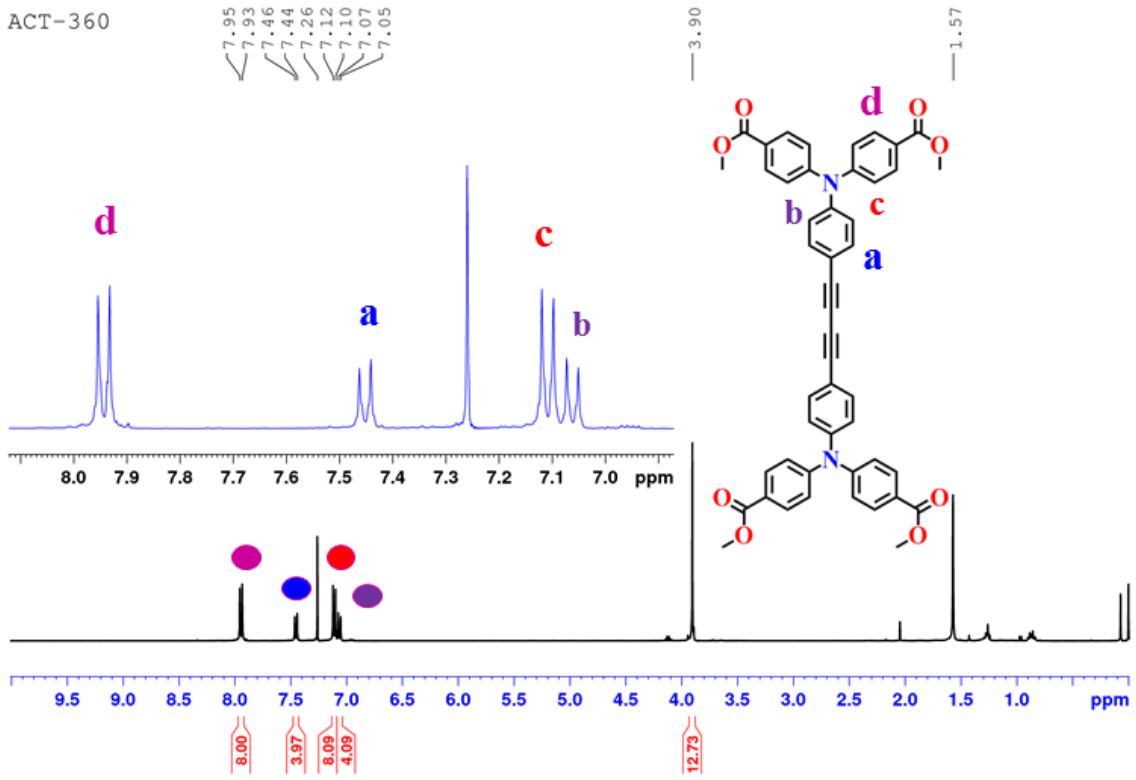


Figure S32: NMR titration of **7 in** $CDCl_3$ (**1**) and the peak assignment (**2**)**.** No change was observed in the chemical shift of the protons.

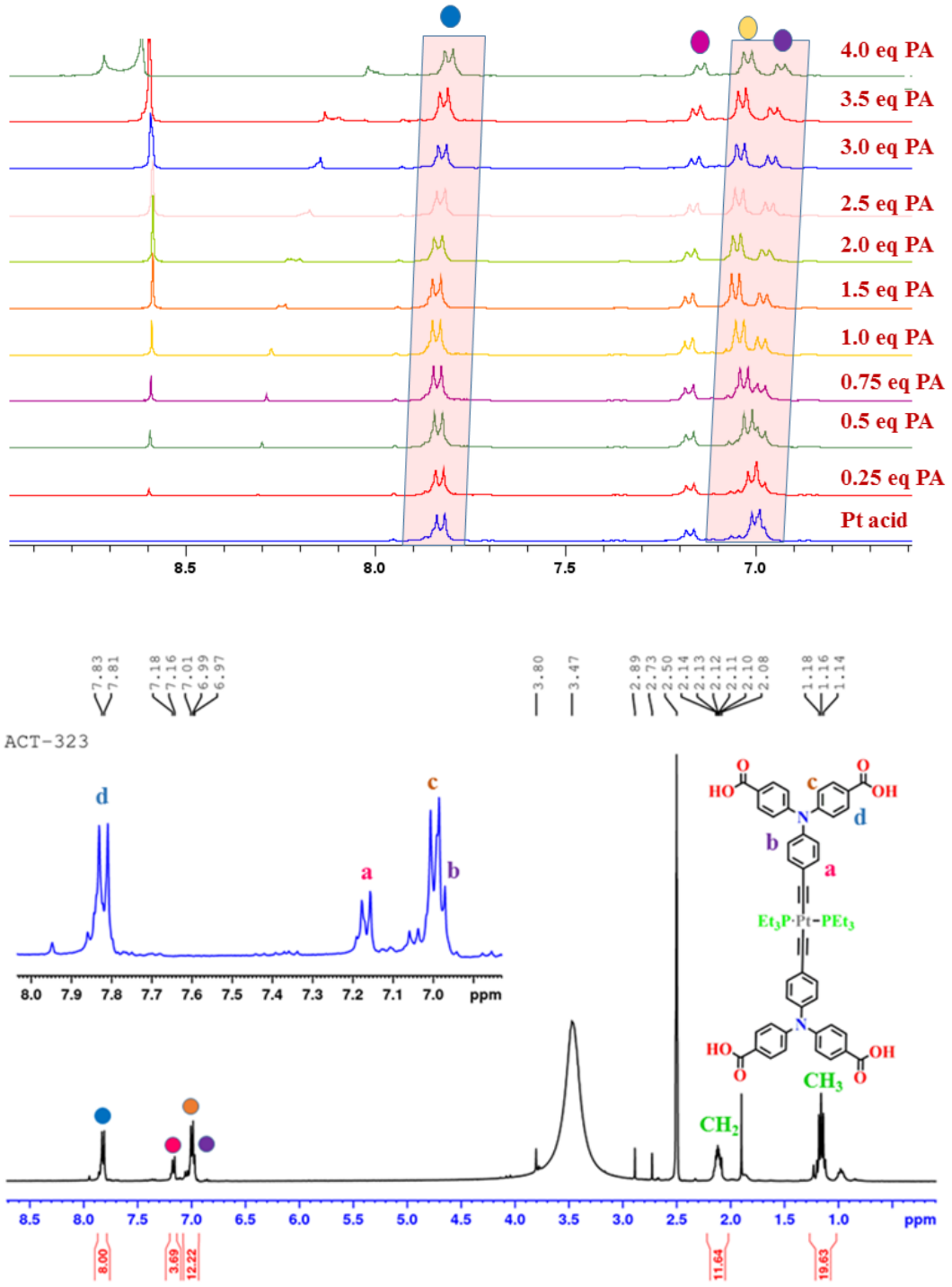


Figure S33: NMR titration of **8** in DMSO-d_6 (above) and the peak assignments (below)**.**

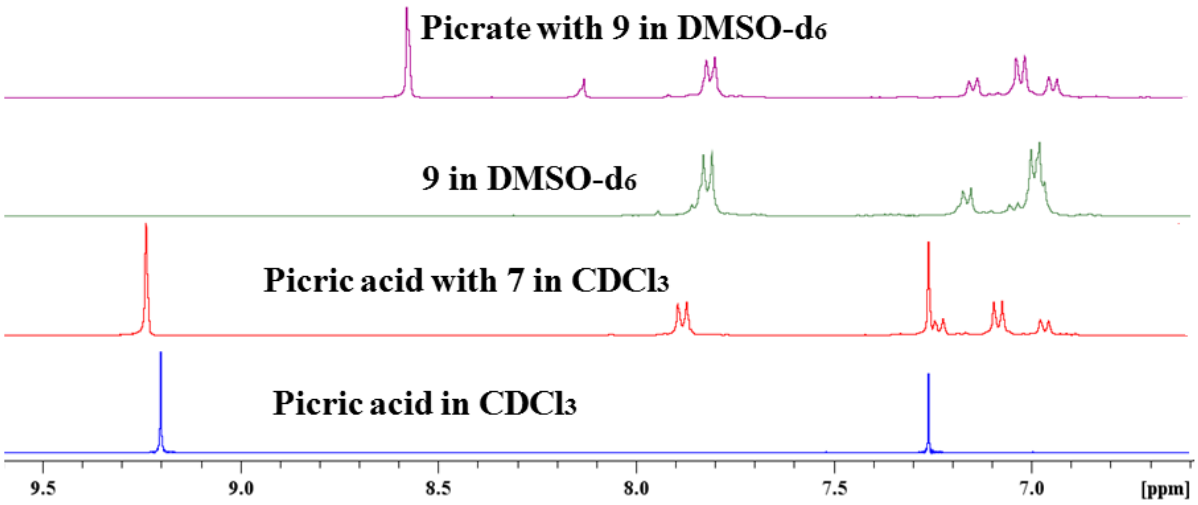


Figure S34. Picric acid and picrate with **7** and **9** in $CDCl_3$ and DMSO-d_6.

Solid state fluorescence sensing of nitroaromatics by the compounds

For solid state fluorescence quenching study thin films of the compounds were prepared by depositing 10 mL of saturated solution of the compounds by spin coating on clean quartz plates and subsequently drying the solvent under vacuum for 4 h.

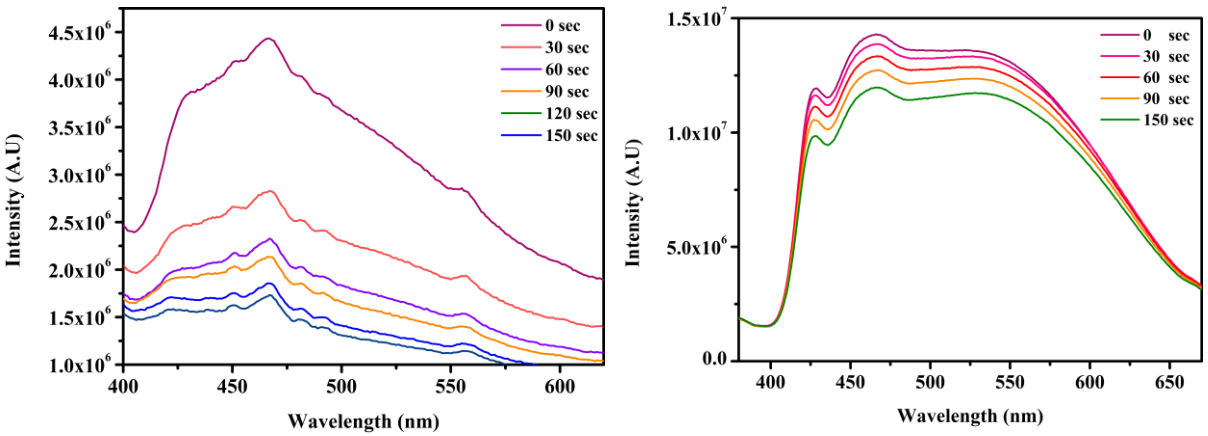


Figure S35: Time dependent solid state fluorescence quenching plot of **9** (left) and **7** (right) with NB.

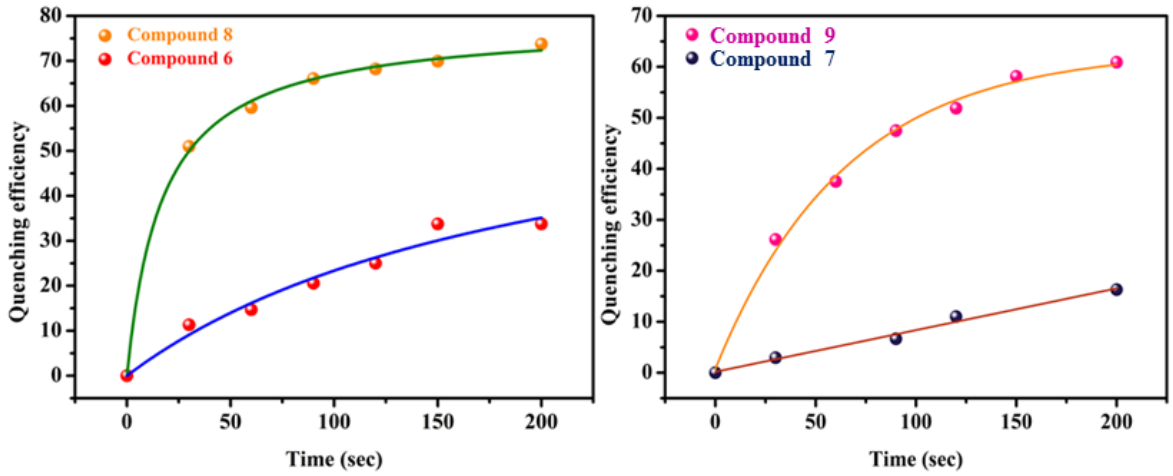


Figure S36. The quenching efficiency pot of the compounds **6** and **8** (left) and **7** and **9** (right).

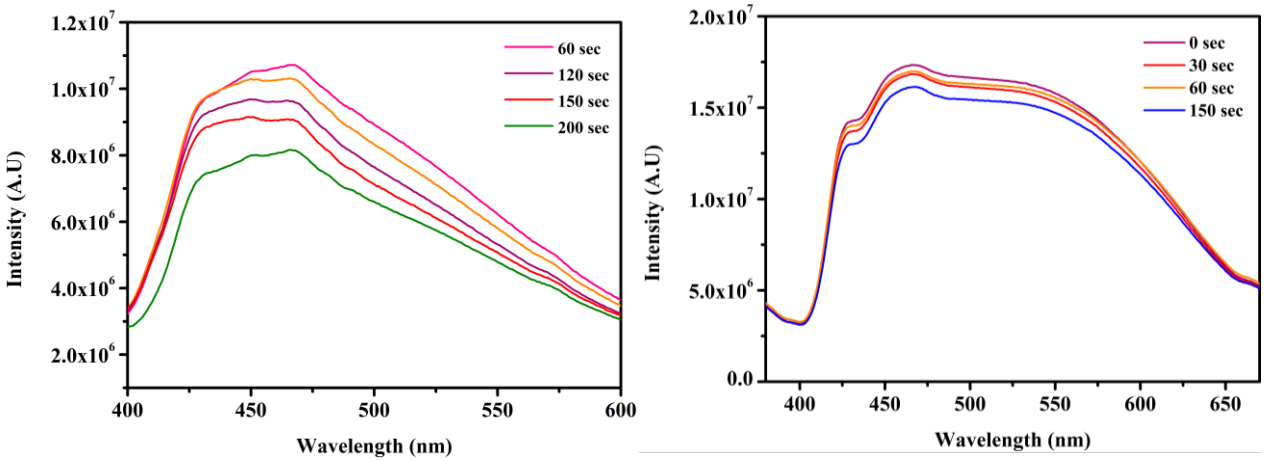


Figure S37: Time dependent solid state fluorescence spectra of **9** (left), **7** (right) upon exposure to PA.

Time-resolved fluorescence titration of 8, 9 with PA

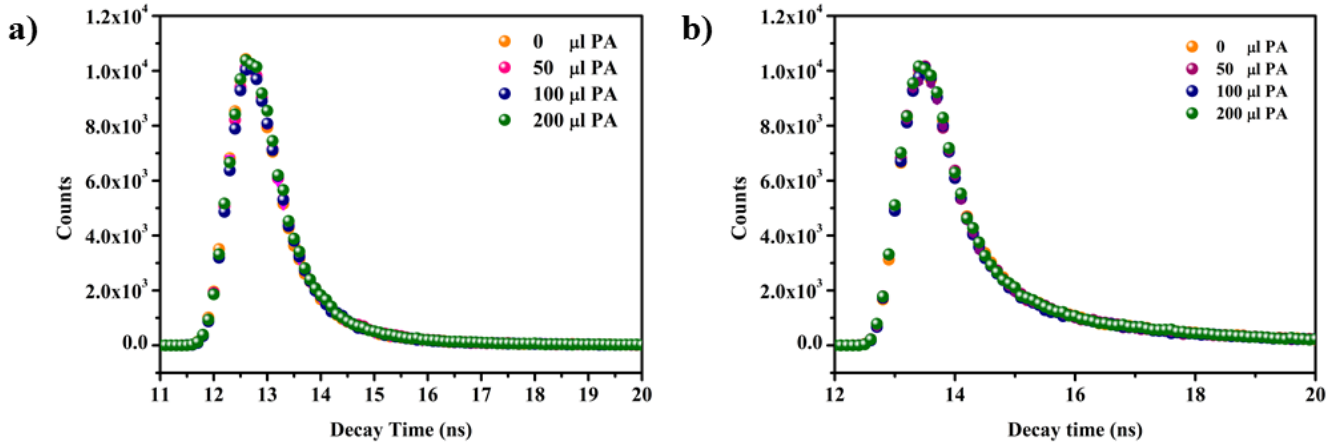


Figure S38. a) Time-resolved fluorescence titration of **9** with PA. b) Time-resolved fluorescence titration of **8** with PA

HOMO-LUMO energy calculation of 7 with Picrate

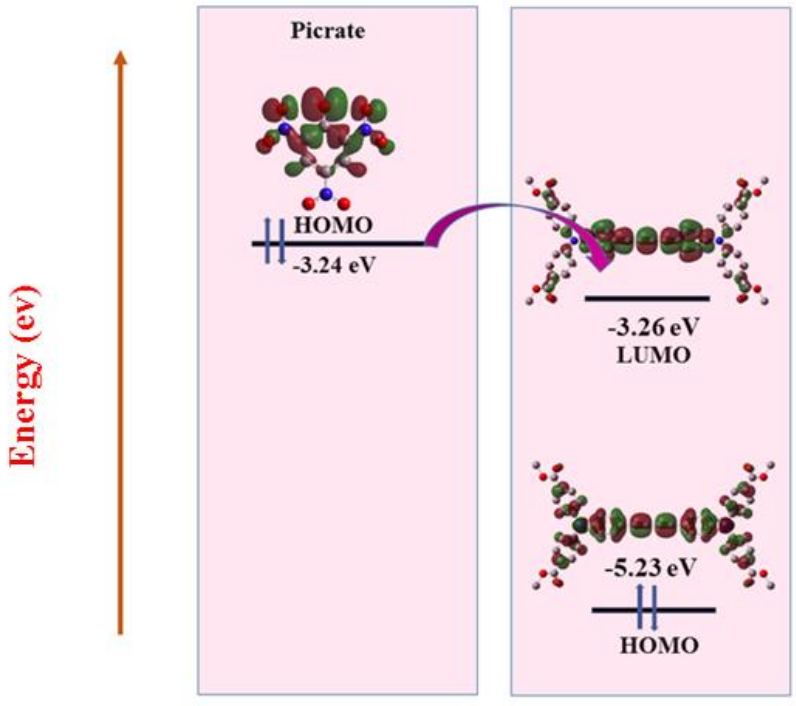


Figure S39. Calculated energy level diagram of **7** and picrate.

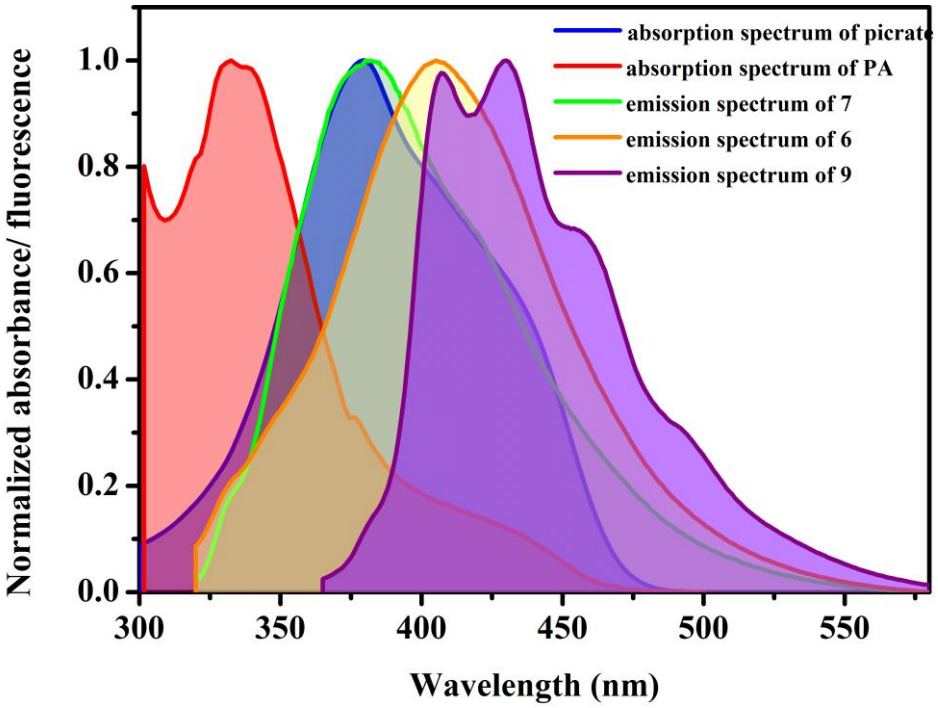


Figure S40. Spectral overlap between absorption spectra of PA and picrate with emission spectra of **6**, **7** and **9**.

Table S1. Computational result of optimized structure of **9**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	9.672794	-2.639434	2.582814
2	6	0	8.491592	-3.055554	1.943421
3	6	0	7.810436	-2.191592	1.090831
4	6	0	8.292832	-0.886533	0.863424
5	6	0	9.474811	-0.468492	1.509755
6	6	0	10.155546	-1.338238	2.354187
7	7	0	7.587703	0.000002	-0.000010
8	6	0	8.292823	0.886550	-0.863432
9	6	0	6.156417	-0.000052	-0.000040
10	6	0	5.443710	0.017868	-1.213280
11	6	0	4.052429	0.023938	-1.213934
12	6	0	3.326209	-0.000155	-0.000083

13	6	0	4.052393	-0.024205	1.213791
14	6	0	5.443671	-0.018032	1.213178
15	6	0	7.810314	2.191547	-1.090978
16	6	0	8.491473	3.055524	-1.943548
17	6	0	9.672789	2.639489	-2.582789
18	6	0	10.155652	1.338361	-2.354023
19	6	0	9.474918	0.468596	-1.509608
20	6	0	1.905460	-0.000188	-0.000108
21	6	0	-4.052347	0.024066	1.213738
22	6	0	-5.443628	0.017989	1.213157
23	6	0	-6.156401	-0.000017	-0.000043
24	6	0	-5.443714	-0.018074	-1.213298
25	6	0	-4.052438	-0.024240	-1.213981
26	7	0	-7.587684	0.000027	0.000003
27	6	0	-8.292863	-0.886466	-0.863439
28	6	0	-8.292771	0.886533	0.863495
29	6	0	10.426862	-3.518467	3.488764
30	6	0	10.426859	3.518544	-3.488713
31	8	0	11.474343	3.219373	-4.081358
32	8	0	9.852121	4.769088	-3.640061
33	8	0	11.474218	-3.219200	4.081585
34	8	0	9.852220	-4.769066	3.640003
35	6	0	-9.474820	0.468534	1.509726
36	6	0	-10.155526	1.338259	2.354204
37	6	0	-9.672680	2.639392	2.582979
38	6	0	-8.491409	3.055472	1.943683
39	6	0	-7.810280	2.191535	1.091050
40	6	0	-9.474848	-0.468372	-1.509722
41	6	0	-10.155636	-1.338074	-2.354158
42	6	0	-9.672932	-2.639278	-2.582834
43	6	0	-8.491724	-3.055453	-1.943488

44	6	0	-7.810515	-2.191536	-1.090894
45	6	0	-10.427052	-3.518264	-3.488788
46	8	0	-9.852437	-4.768867	-3.640097
47	8	0	-11.474403	-3.218941	-4.081590
48	6	0	-10.426717	3.518403	3.488973
49	8	0	-9.851986	4.768947	3.640342
50	8	0	-11.474151	3.219185	4.081684
51	6	0	0.679113	-0.000188	-0.000143
52	6	0	-0.679093	-0.000162	-0.000167
53	6	0	-1.905440	-0.000142	-0.000204
54	6	0	-3.326189	-0.000106	-0.000147
55	1	0	8.123294	-4.060072	2.109900
56	1	0	6.908305	-2.522997	0.590716
57	1	0	9.845682	0.537004	1.351671
58	1	0	11.060498	-1.021738	2.860256
59	1	0	5.985836	0.022952	-2.151914
60	1	0	3.511774	0.033592	-2.153698
61	1	0	3.511709	-0.033909	2.153539
62	1	0	5.985770	-0.023087	2.151828
63	1	0	6.908097	2.522891	-0.590982
64	1	0	8.123086	4.059993	-2.110129
65	1	0	11.060691	1.021921	-2.859975
66	1	0	9.845882	-0.536850	-1.351426
67	1	0	-3.511647	0.033779	2.153476
68	1	0	-5.985701	0.023126	2.151821
69	1	0	-5.985858	-0.023192	-2.151921
70	1	0	-3.511802	-0.034011	-2.153756
71	1	0	10.399286	5.307486	-4.250396
72	1	0	10.399353	-5.307432	4.250395
73	1	0	-9.845770	-0.536916	1.351534
74	1	0	-11.060530	1.021785	2.860196

75	1	0	-8.123037	4.059945	2.110271
76	1	0	-6.908098	2.522916	0.591012
77	1	0	-9.845685	0.537131	-1.351598
78	1	0	-11.060593	-1.021532	-2.860192
79	1	0	-8.123463	-4.059979	-2.110002
80	1	0	-6.908382	-2.522984	-0.590814
81	1	0	-10.399591	-5.307193	-4.250507
82	1	0	-10.399118	5.307310	4.250738

Table S2. Computational result of optimized structure of compound **7**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	7.587759	0.000055	-0.000027
2	8	0	11.524048	-5.027910	0.577360
3	6	0	9.471687	1.413824	-0.714664
4	1	0	9.835385	0.604291	-1.336255
5	6	0	8.294609	1.236607	0.040652
6	8	0	11.525198	5.027175	-0.576942
7	6	0	6.157477	0.000057	-0.000003
8	6	0	9.684319	-3.686895	-0.114399
9	6	0	3.326182	-0.000028	0.000044
10	6	0	4.052830	-0.905254	0.808748
11	1	0	3.512409	-1.600368	1.441503
12	6	0	8.507066	3.512077	0.862329

13	1	0	8.152561	4.333719	1.474279
14	6	0	8.294468	-1.236617	-0.040774
15	6	0	5.443927	0.900502	-0.813035
16	1	0	5.985581	1.591543	-1.448662
17	6	0	10.377126	4.986934	0.187497
18	6	0	9.684846	3.686709	0.114210
19	6	0	10.160123	2.623084	-0.673283
20	1	0	11.060148	2.758351	-1.259780
21	6	0	0.679096	-0.000111	0.000136
22	6	0	9.471124	-1.414251	0.715108
23	1	0	9.834609	-0.604947	1.337125
24	6	0	7.820346	2.302893	0.831876
25	1	0	6.921559	2.172928	1.422791
26	8	0	9.998730	-5.962955	-0.855535
27	6	0	4.052743	0.905227	-0.808684
28	1	0	3.512275	1.600313	-1.441429
29	6	0	1.905497	-0.000075	0.000089
30	6	0	5.444004	-0.900445	0.813049
31	1	0	5.985737	-1.591448	1.448649
32	6	0	7.820423	-2.302543	-0.832568
33	1	0	6.921935	-2.172240	-1.423867
34	6	0	10.159381	-2.623604	0.673697
35	1	0	11.059074	-2.759242	1.260616
36	8	0	9.999191	5.962975	0.854733
37	6	0	8.506964	-3.511846	-0.863063
38	1	0	8.152629	-4.333230	-1.475456
39	6	0	10.376447	-4.987210	-0.187747
40	6	0	12.274252	-6.289320	0.560929
41	1	0	13.129444	-6.112650	1.210470
42	1	0	12.593366	-6.525338	-0.456563
43	1	0	11.652526	-7.103470	0.939799

44	6	0	12.275589	6.288470	-0.560511
45	1	0	13.130898	6.111585	-1.209840
46	1	0	12.594529	6.524561	0.457021
47	1	0	11.654074	7.102675	-0.939605
48	7	0	-7.587773	-0.000098	0.000074
49	8	0	-11.523854	5.029314	-0.566089
50	6	0	-9.471835	-1.415376	0.711381
51	1	0	-9.835579	-0.607200	1.334708
52	6	0	-8.294652	-1.236535	-0.043395
53	8	0	-11.525541	-5.028293	0.565313
54	6	0	-6.157485	-0.000153	0.000111
55	6	0	-9.684145	3.686693	0.122622
56	6	0	-3.326204	-0.000158	0.000194
57	6	0	-4.052780	0.906689	-0.806758
58	1	0	-3.512302	1.603036	-1.438106
59	6	0	-8.507090	-3.510178	-0.870117
60	1	0	-8.152539	-4.330487	-1.483825
61	6	0	-8.294413	1.236517	0.043539
62	6	0	-5.444011	-0.902229	0.811396
63	1	0	-5.985728	-1.594510	1.445619
64	6	0	-10.377312	-4.986437	-0.198806
65	6	0	-9.684983	-3.686409	-0.122552
66	6	0	-10.160317	-2.624510	0.667233
67	1	0	-11.060422	-2.761037	1.253316
68	6	0	-0.679116	-0.000147	0.000187
69	6	0	-9.471070	1.415887	-0.711934
70	1	0	-9.834607	0.607978	-1.335732
71	6	0	-7.820323	-2.301095	-0.836902
72	1	0	-6.921452	-2.169873	-1.427410
73	8	0	-9.998408	5.961136	0.868764
74	6	0	-4.052826	-0.906985	0.807106

75	1	0	-3.512401	-1.603333	1.438499
76	6	0	-1.905518	-0.000156	0.000214
77	6	0	-5.443955	0.901938	-0.811127
78	1	0	-5.985650	1.594219	-1.445367
79	6	0	-7.820296	2.300668	0.837678
80	1	0	-6.921802	2.169020	1.428669
81	6	0	-10.159269	2.625179	-0.667828
82	1	0	-11.058962	2.762163	-1.254435
83	8	0	-9.999293	-5.961042	-0.868092
84	6	0	-8.506779	3.509931	0.870866
85	1	0	-8.152394	4.329944	1.485065
86	6	0	-10.376214	4.986873	0.198867
87	6	0	-12.273985	6.290728	-0.546831
88	1	0	-13.129334	6.115474	-1.196548
89	1	0	-12.592846	6.524622	0.471230
90	1	0	-11.652299	7.105639	-0.924131
91	6	0	-12.275977	-6.289521	0.545966
92	1	0	-13.131504	-6.113970	1.195369
93	1	0	-12.594566	-6.523457	-0.472173
94	1	0	-11.654626	-7.104547	0.923564
