Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Triazatriangulenium salts – hosts and guests in supramolecular assemblies in solution

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NMR data

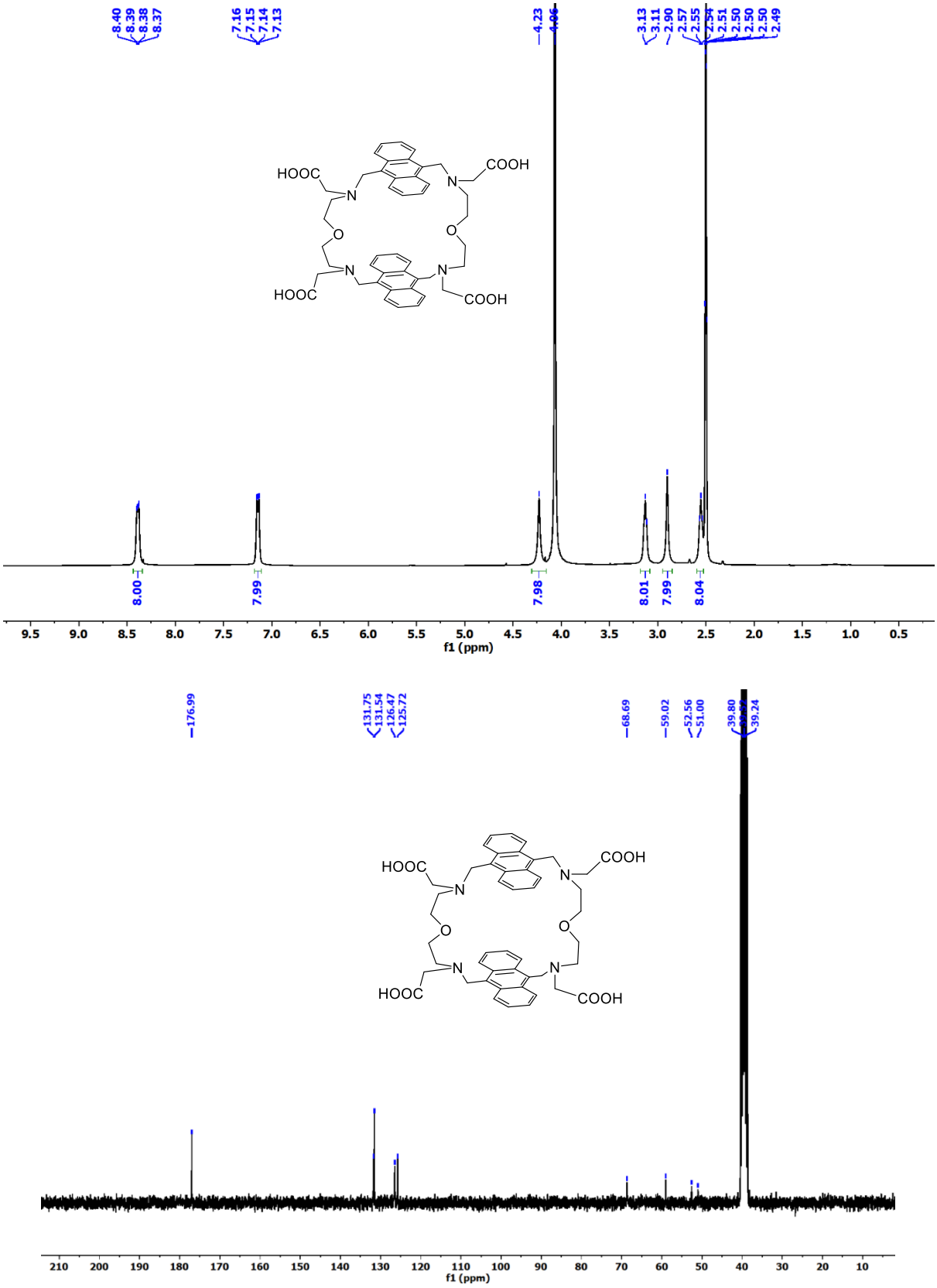


Figure S1. ^{1}H and ^{13}C NMR spectrum of **6** in 5:1 DMSO-d_6-D_2O

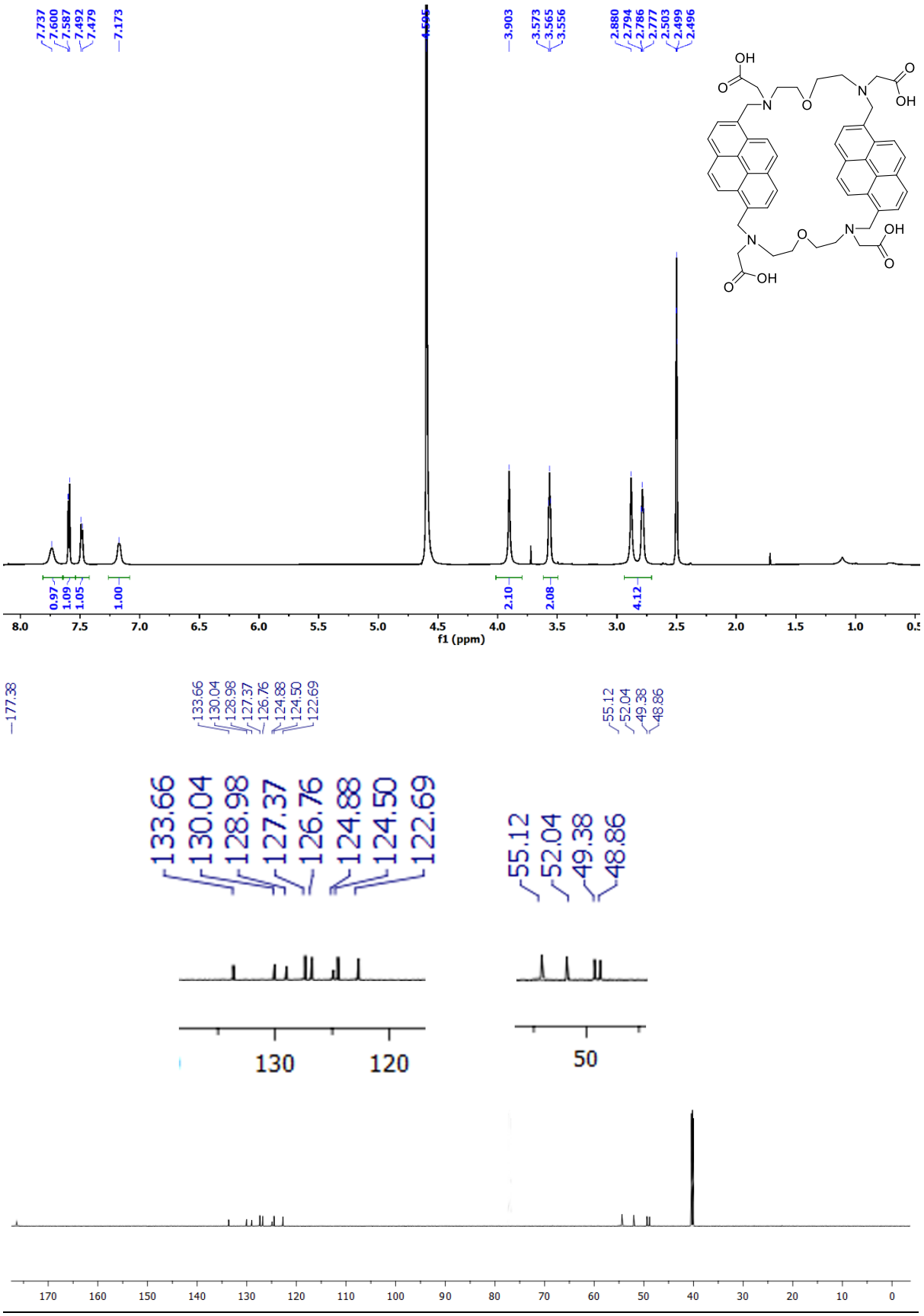


Figure S2. ^{1}H and ^{13}C NMR spectrum of **7** in $DMSOd_6$.

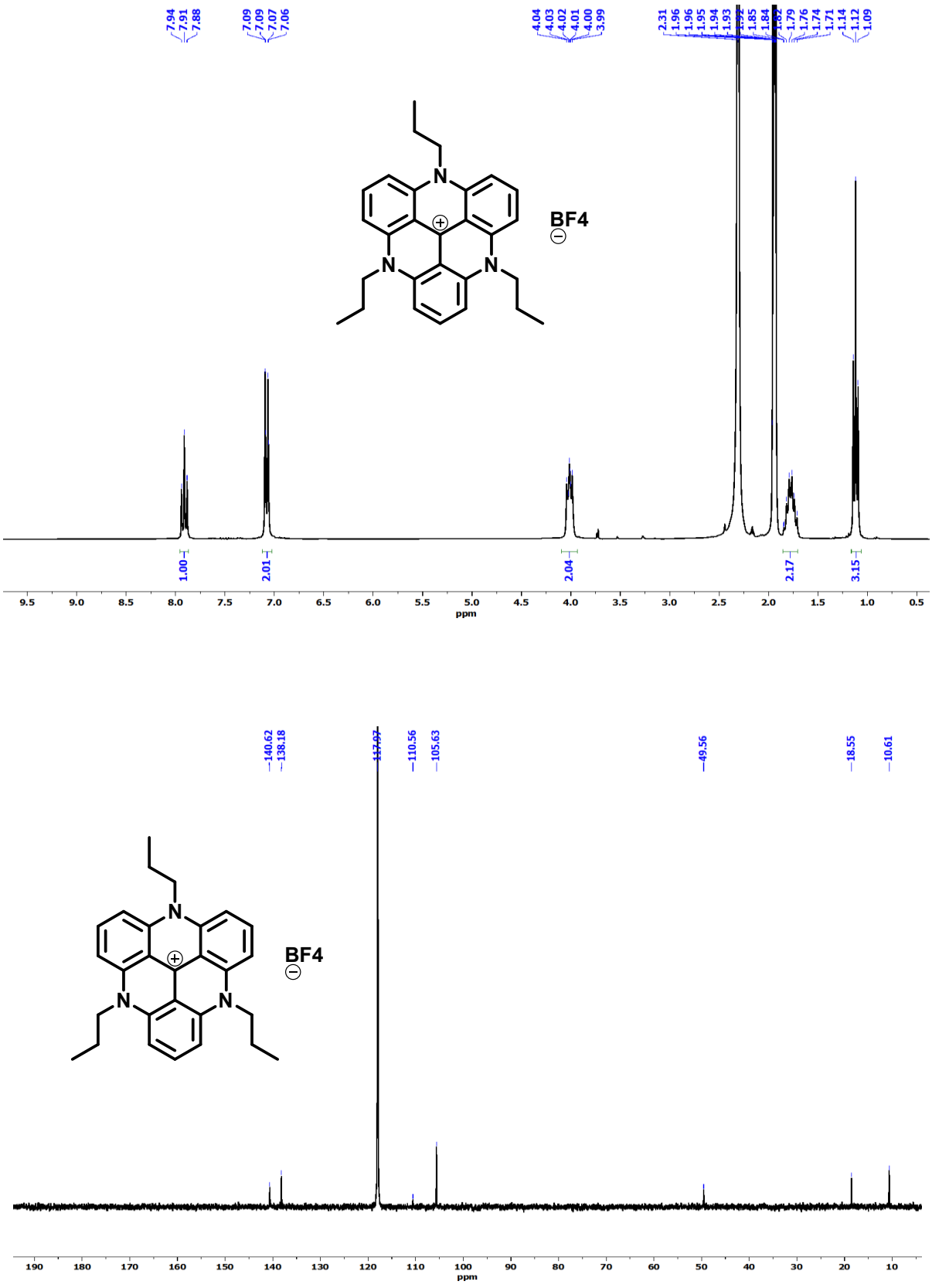


Figure S3. ^{1}H and ^{13}C NMR spectrum (75 MHz) of **1-Pr** in CD_3CN

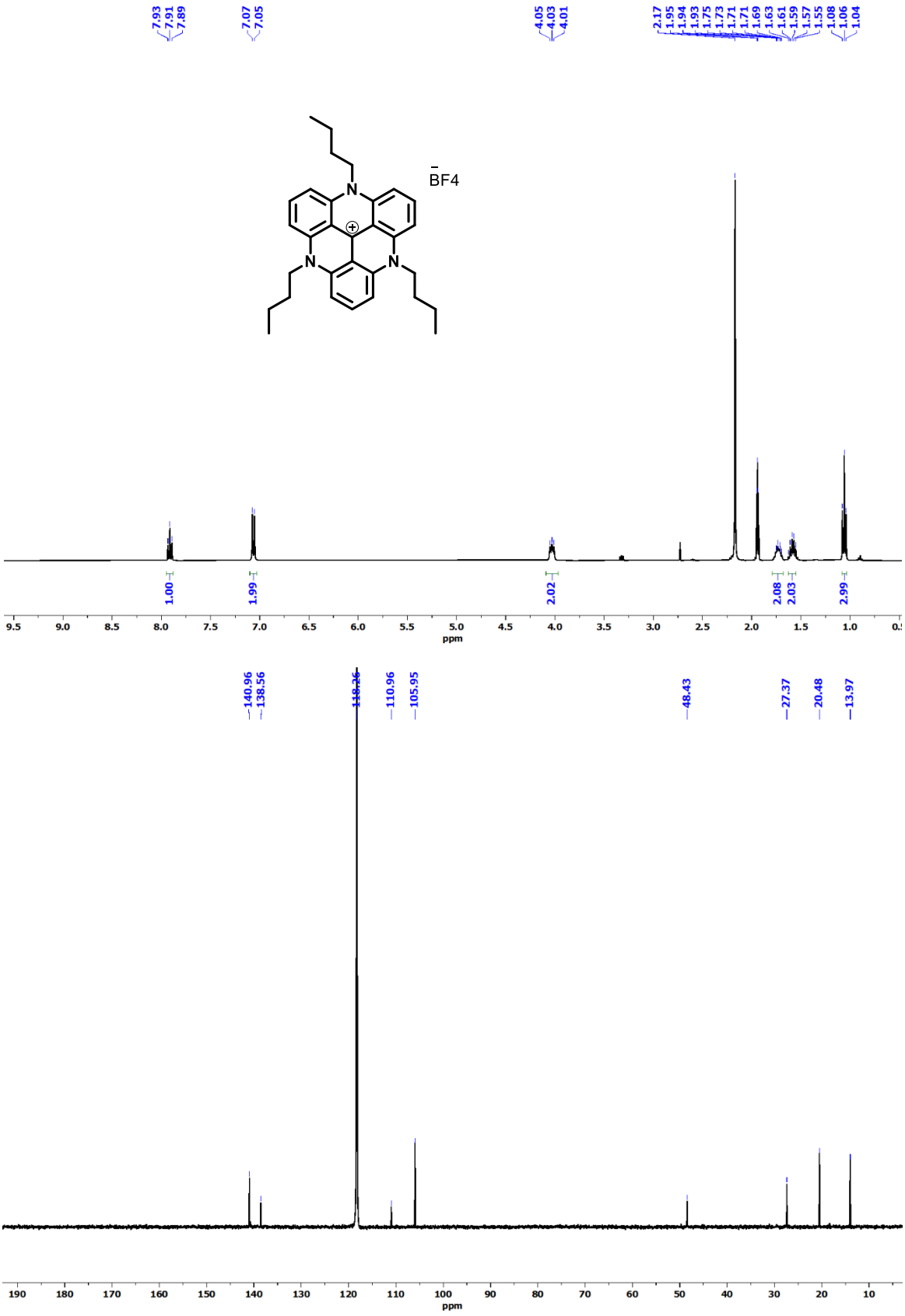


Figure S4. ^{1}H and ^{13}C NMR spectrum (100 MHz) of **1-Bu** in CD_3CN

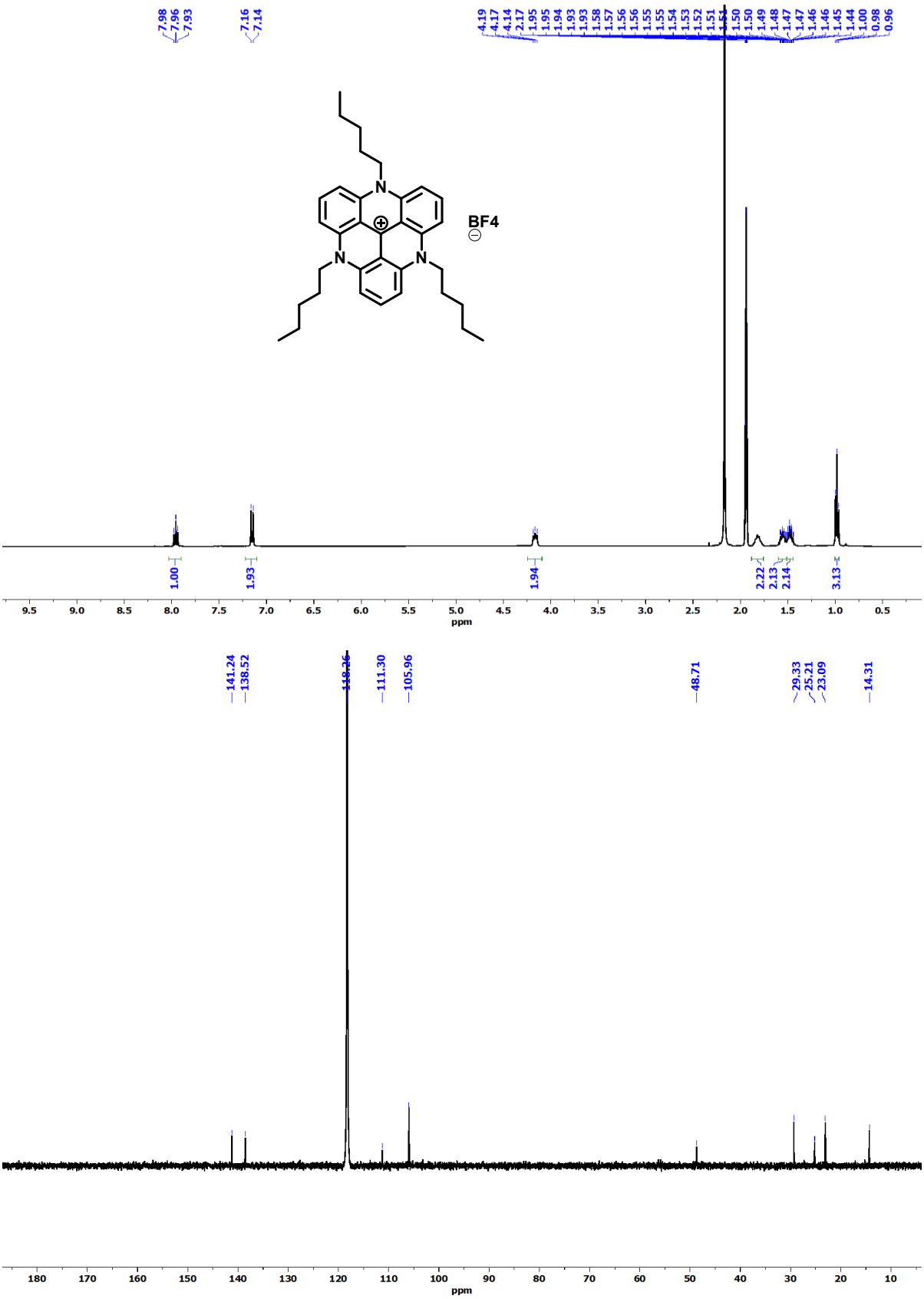


Figure S5. ^{1}H and ^{13}C NMR spectrum (100 MHz) of **1-Pen** in CD_3CN

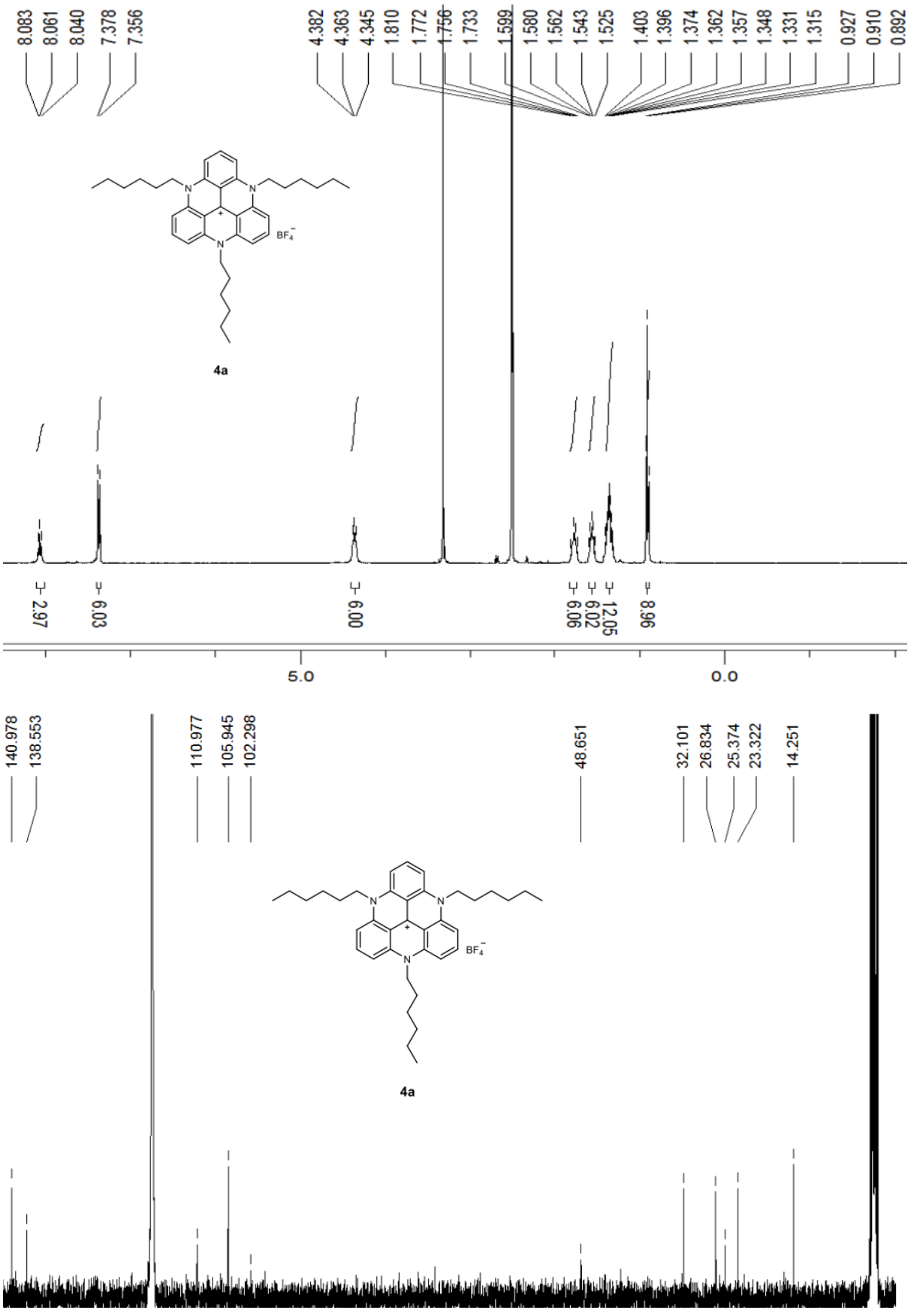


Figure S6. ^{1}H and ^{13}C NMR spectrum (100 MHz) of **1-Hex** in CD_3CN

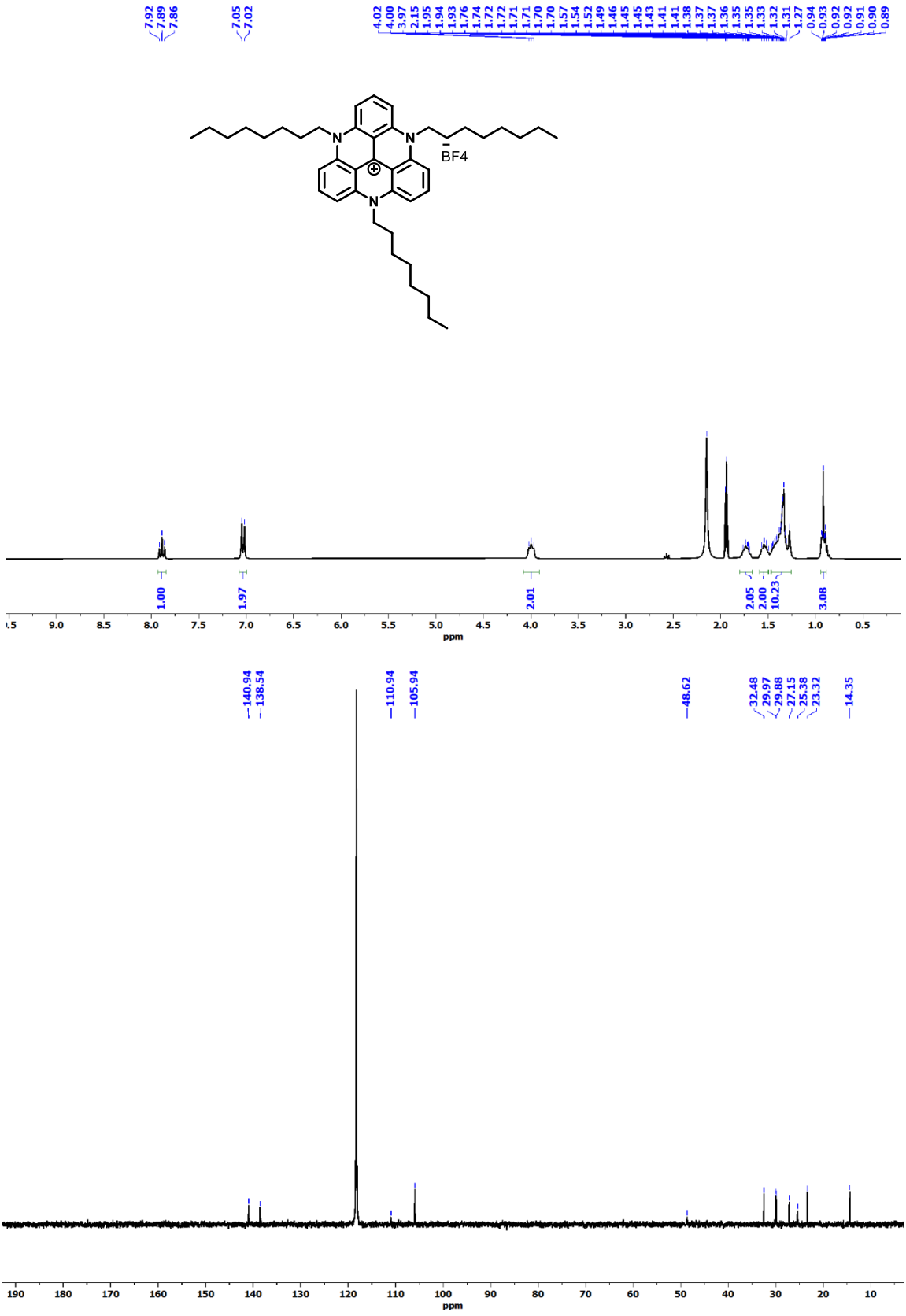
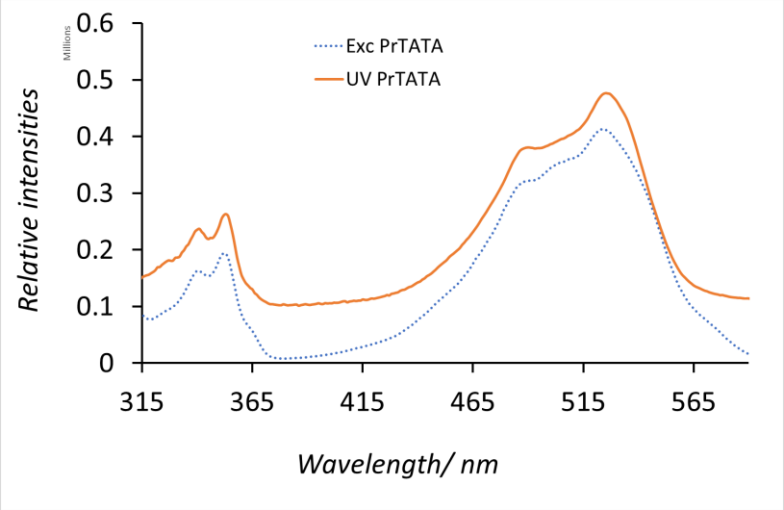


Figure S7. ^{13}C NMR spectrum (75 MHz) of **1-Oct** in CD_3CN

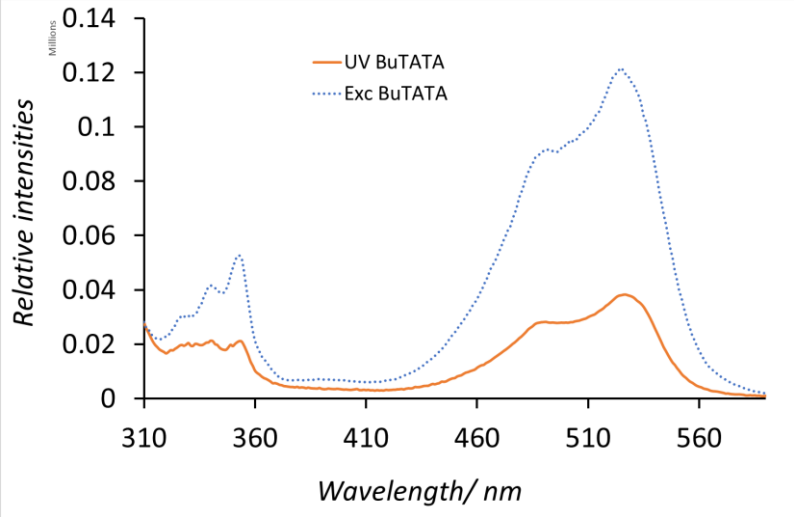
Comparison of the UV and Excitation spectra of Triangulenium salts-

The purity of dyes was checked also by the comparison of excitation and UV-Vis spectrum[1]

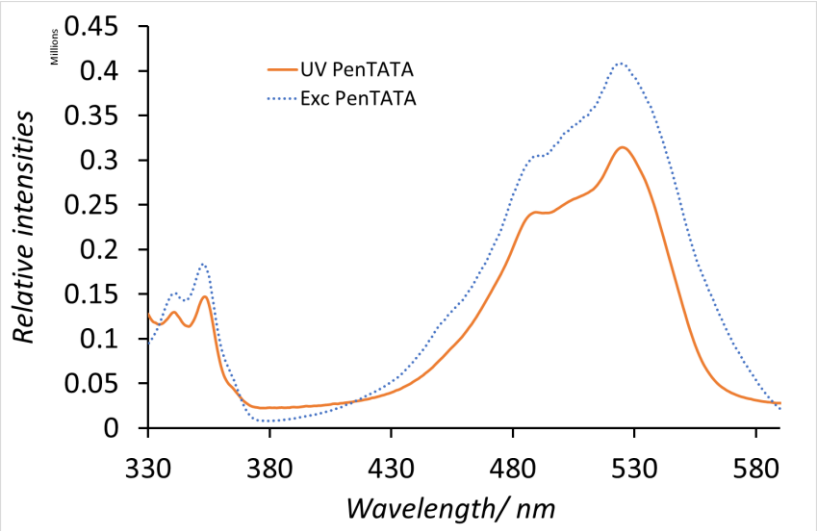
(a)



(b)



(c)



(d)

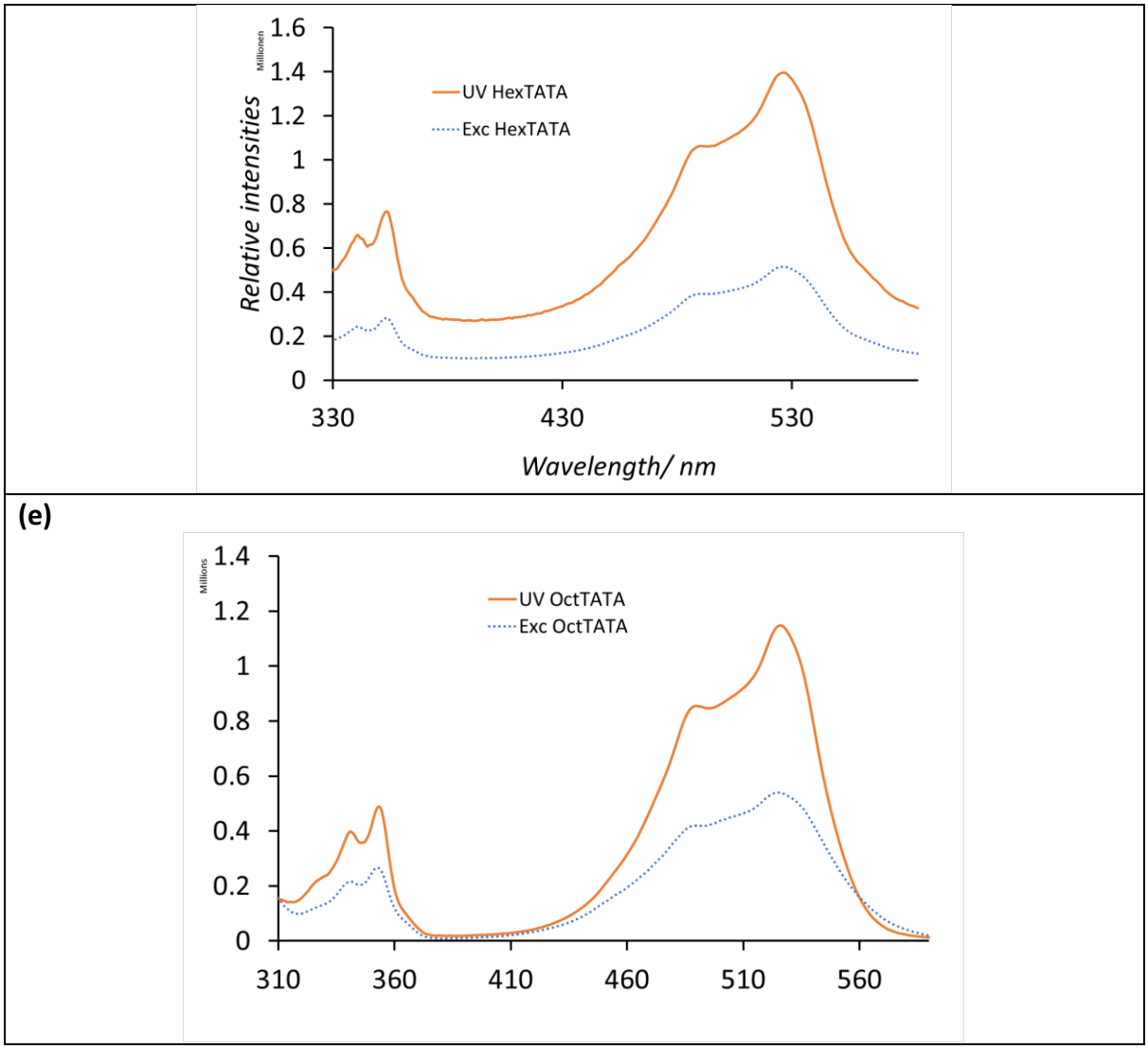
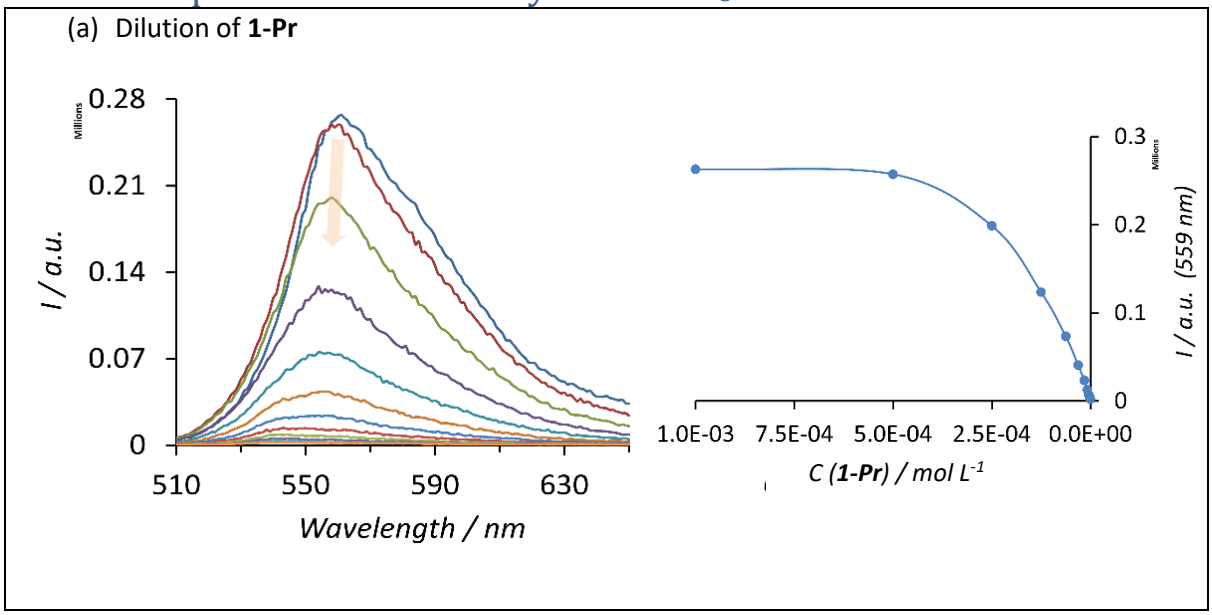
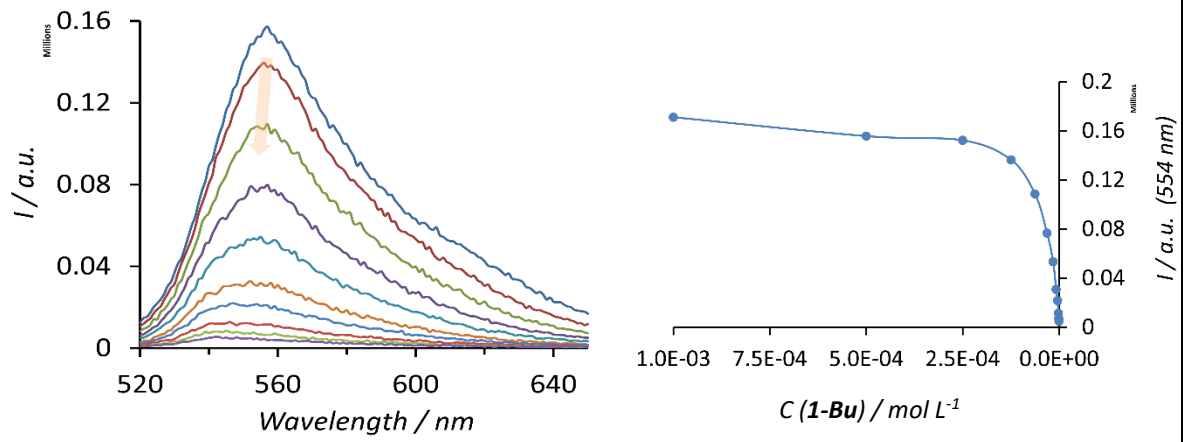


Figure S8. Comparison of the measured UV-Vis spectra of TATA dyes with their excitation spectra.

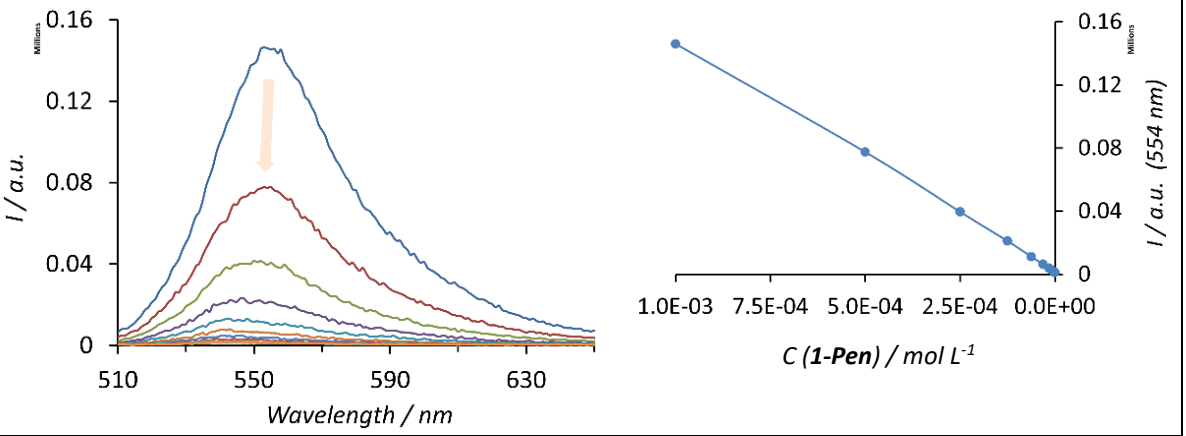
Dilution experiment of TATA dyes in $CHCl_3$



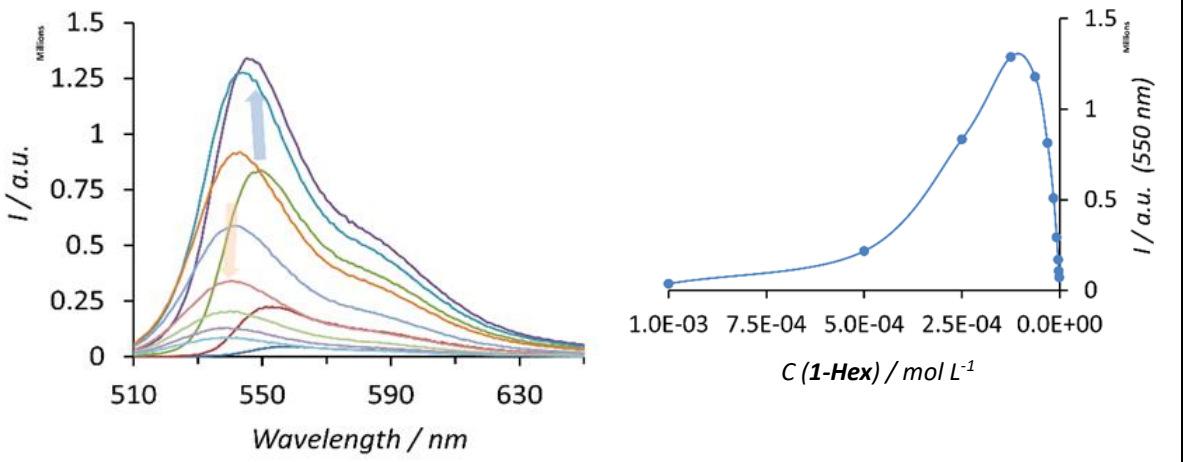
(b) Dilution of **1-Bu**



(c) Dilution of **1-Pen**



(d) Dilution of **1-Hex**



(e) Dilution of **1-Oct**

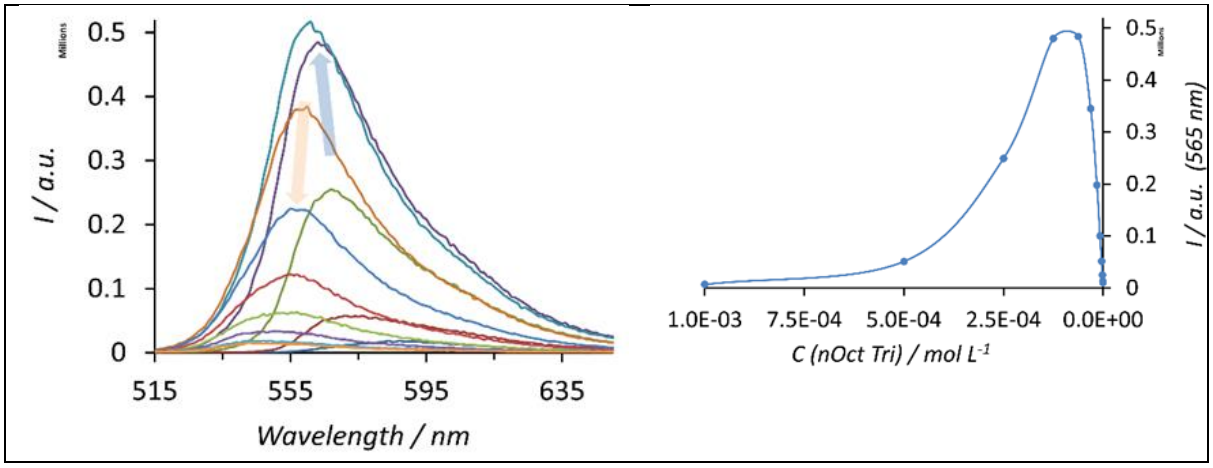


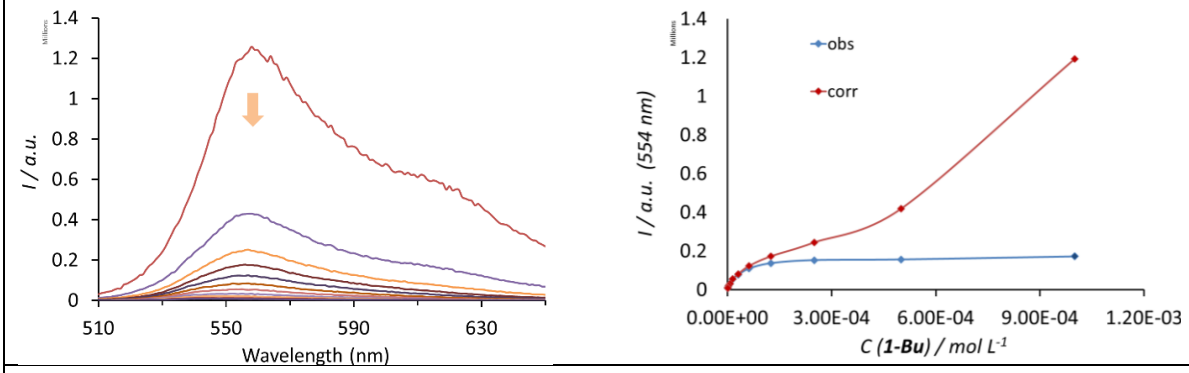
Figure S9. Fluorescence changes of TATA dyes upon dilution (excited at 500 nm, slit 1) in $CHCl_3$.

The equation used for making inner-filter effect correction-

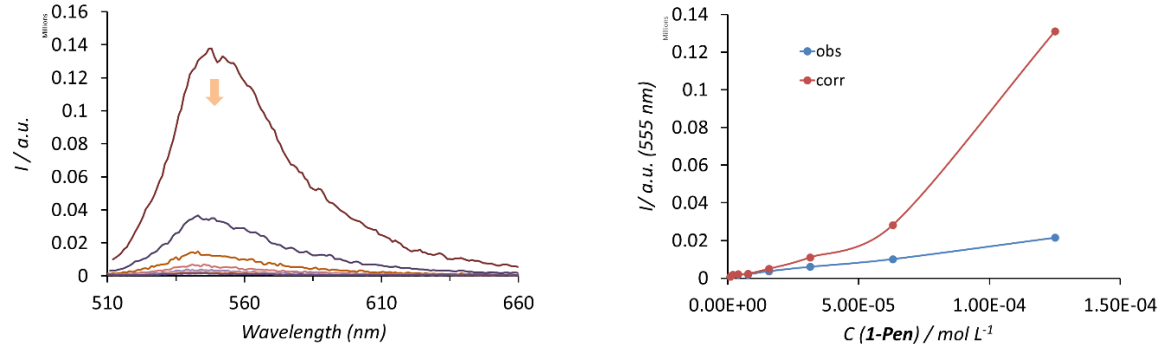
$$F_{corr} = F_{obs} * 10^{[(A_{ex}+A_{em})/2]}$$

F_{corr} is the corrected fluorescence spectrum, **F_{obs}** is the measured or observed fluorescence intensity, **A_{ex}** is the absorbance at the excitation wavelength and **A_{em}** is the absorbance of the sample at the emission wavelength.

(a) Corrected fluorescence spectra for **1-Bu**



(b) Corrected fluorescence spectra for **1-Pen**



(c) Corrected fluorescence spectra for **1-Hex**

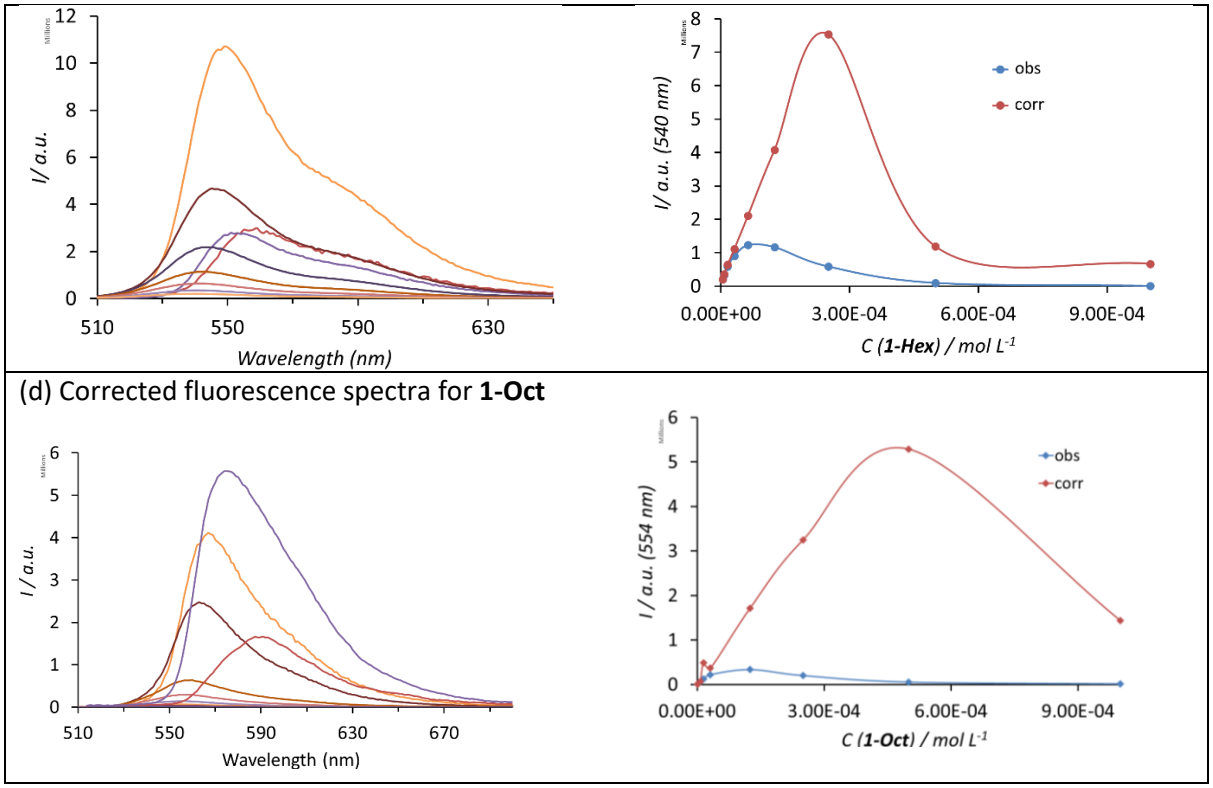
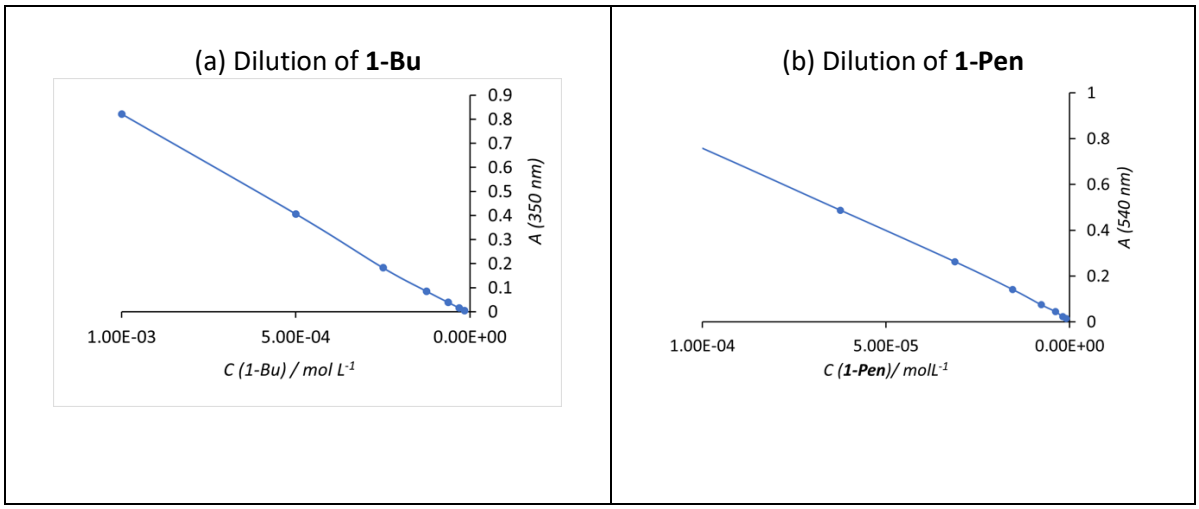


Figure S10. Corrected spectra of **TATA dyes** measured at different concentrations in $CHCl_3$.



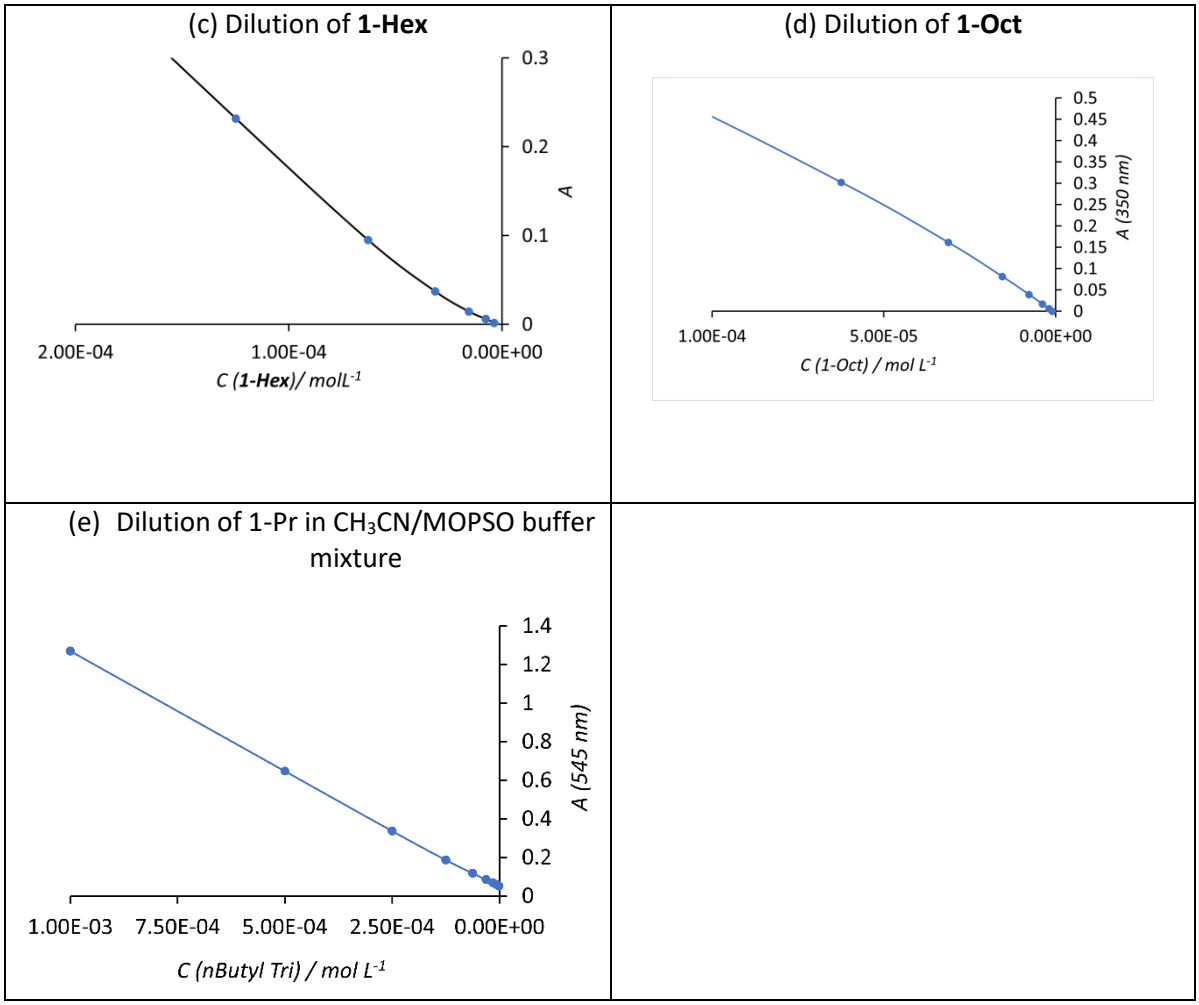
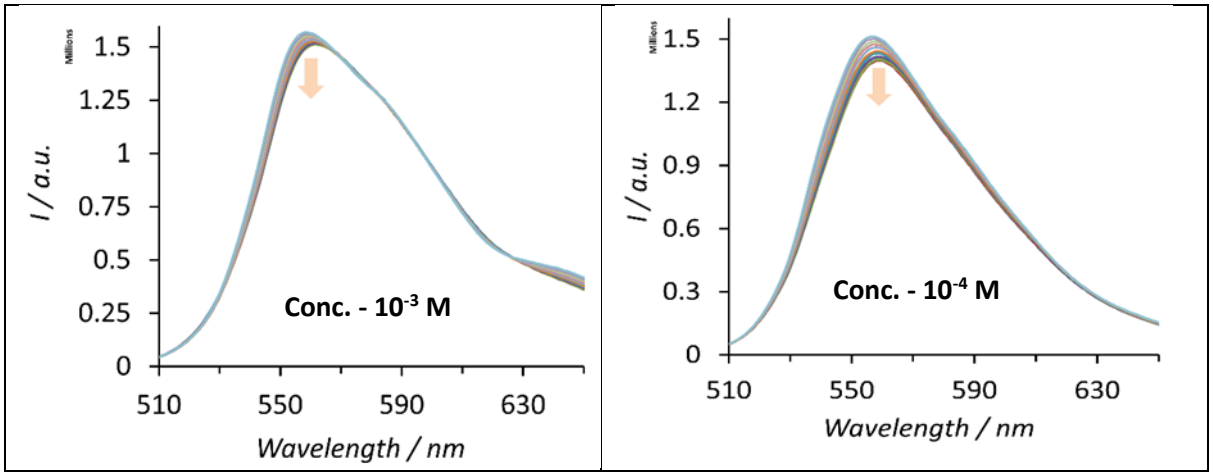


Figure S11. a)-d) UV-Vis dilution profiles for TATA dyes in $CHCl_3$. In case of **1-Hex** and **1-Oct** non-linear relation is observed. (e) UV-Vis dilution profile of **1-Bu** at Abs 545 nm

Temperature-dependent fluorescence change experiments of triangulenium dyes



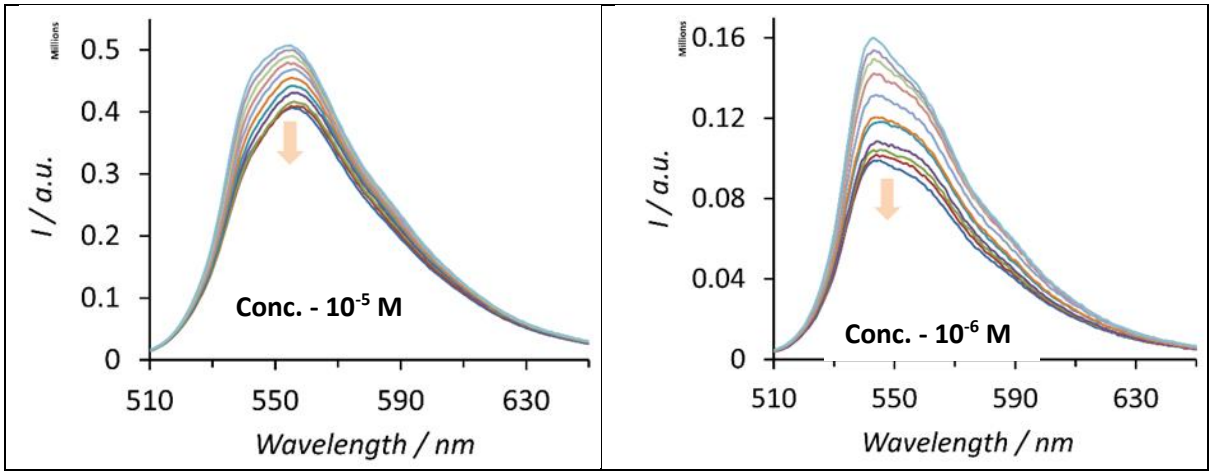


Figure S12. Change of emission spectra (excited at 500 nm, slit 3 and solvent $CHCl_3$) of **1-Pr** in different concentrations upon increasing the temperature of the solution from 0 to 50°C (spectra measured in each 5°C interval).

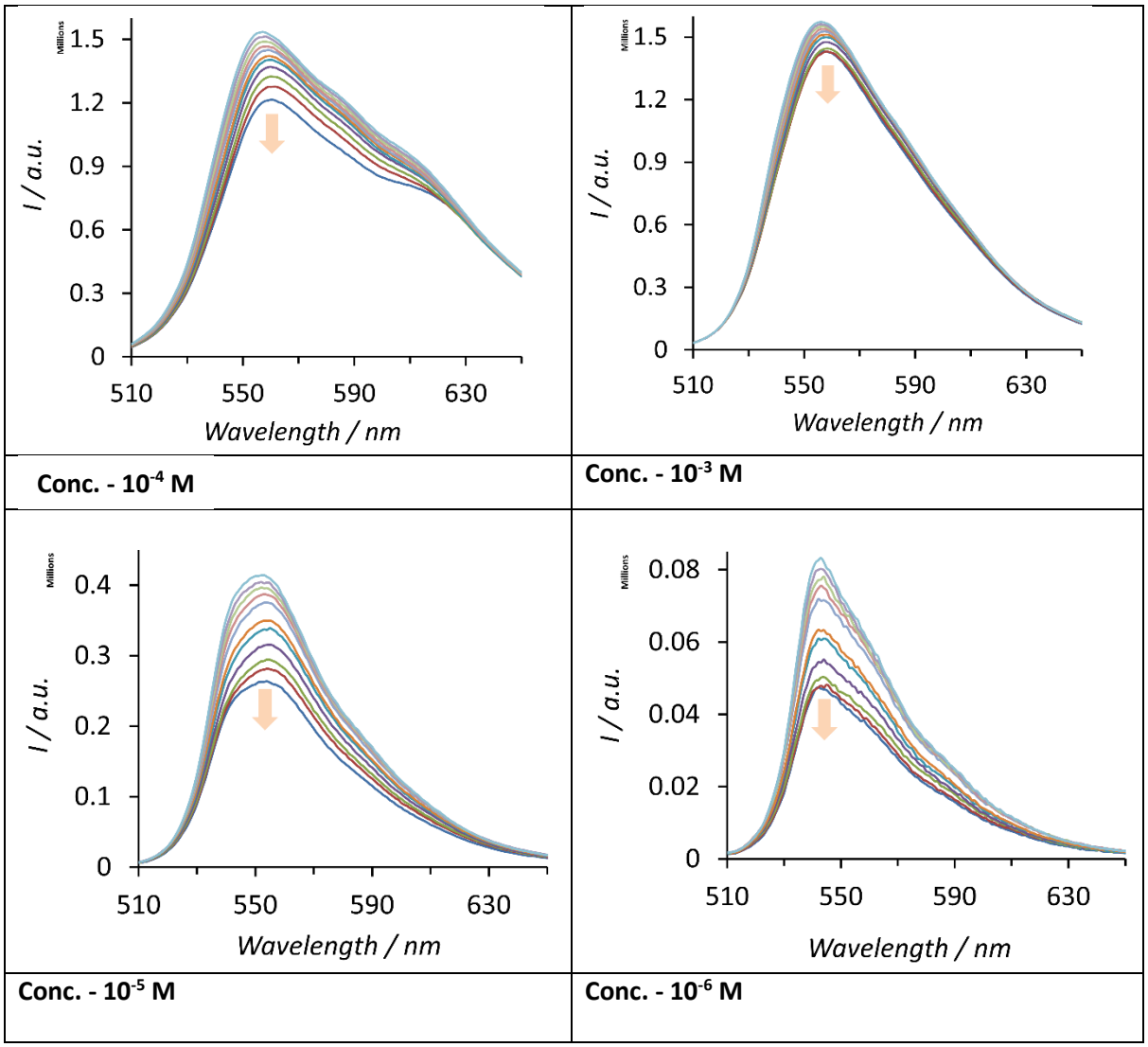


Figure S13. Change of emission spectra (excited at 500 nm, slit 3 and solvent $CHCl_3$) of **1-Bu** in different concentrations upon increasing the temperature of the solution upto 323 K (spectra measured in each 5 K interval).

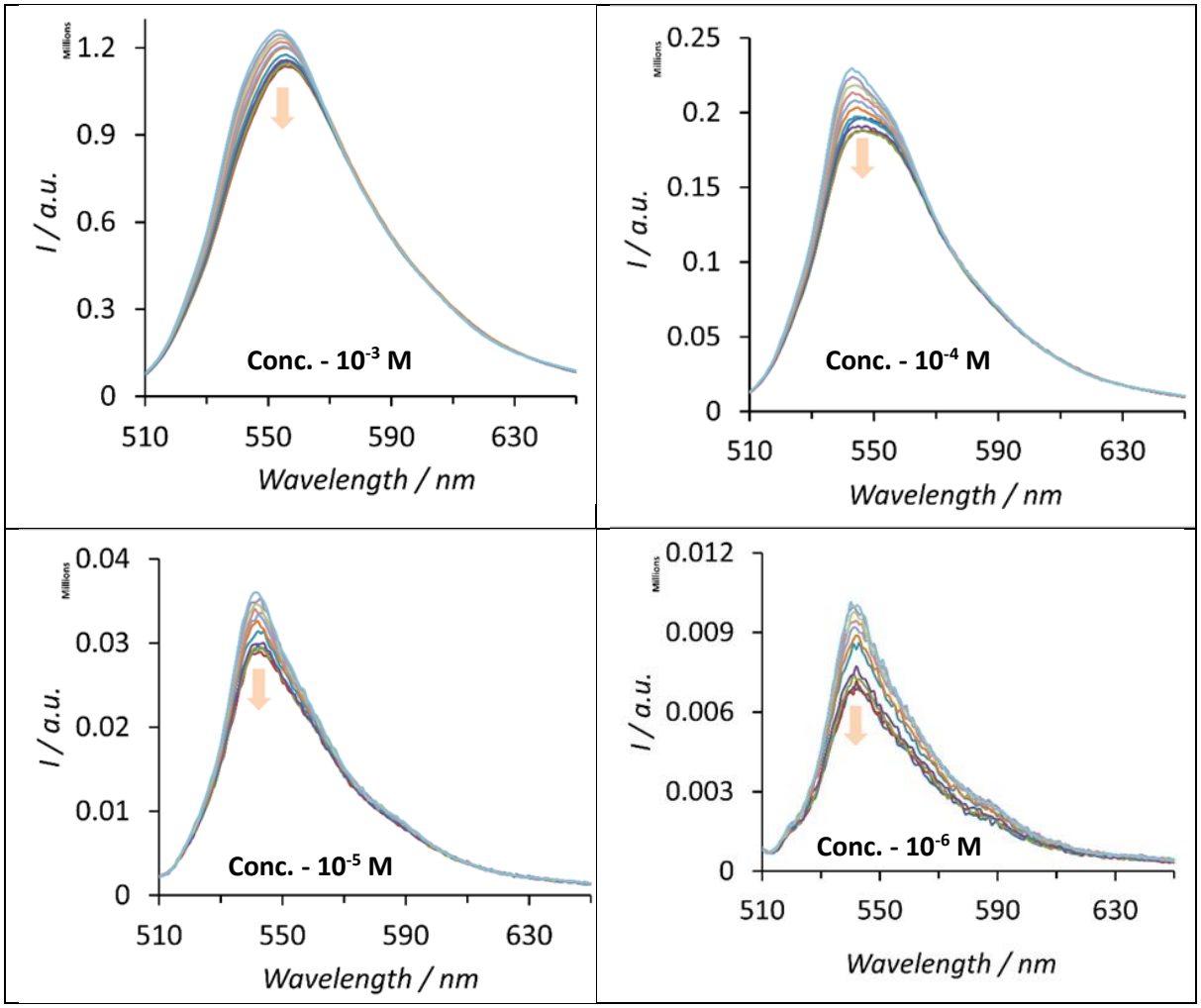


Figure S14. Change of emission spectra (excited at 500 nm, slit 3 and solvent $CHCl_3$) of **1-Pen** in different concentrations upon increasing the temperature of the solution from 0 to 50°C (spectra measured in each 5°C interval).

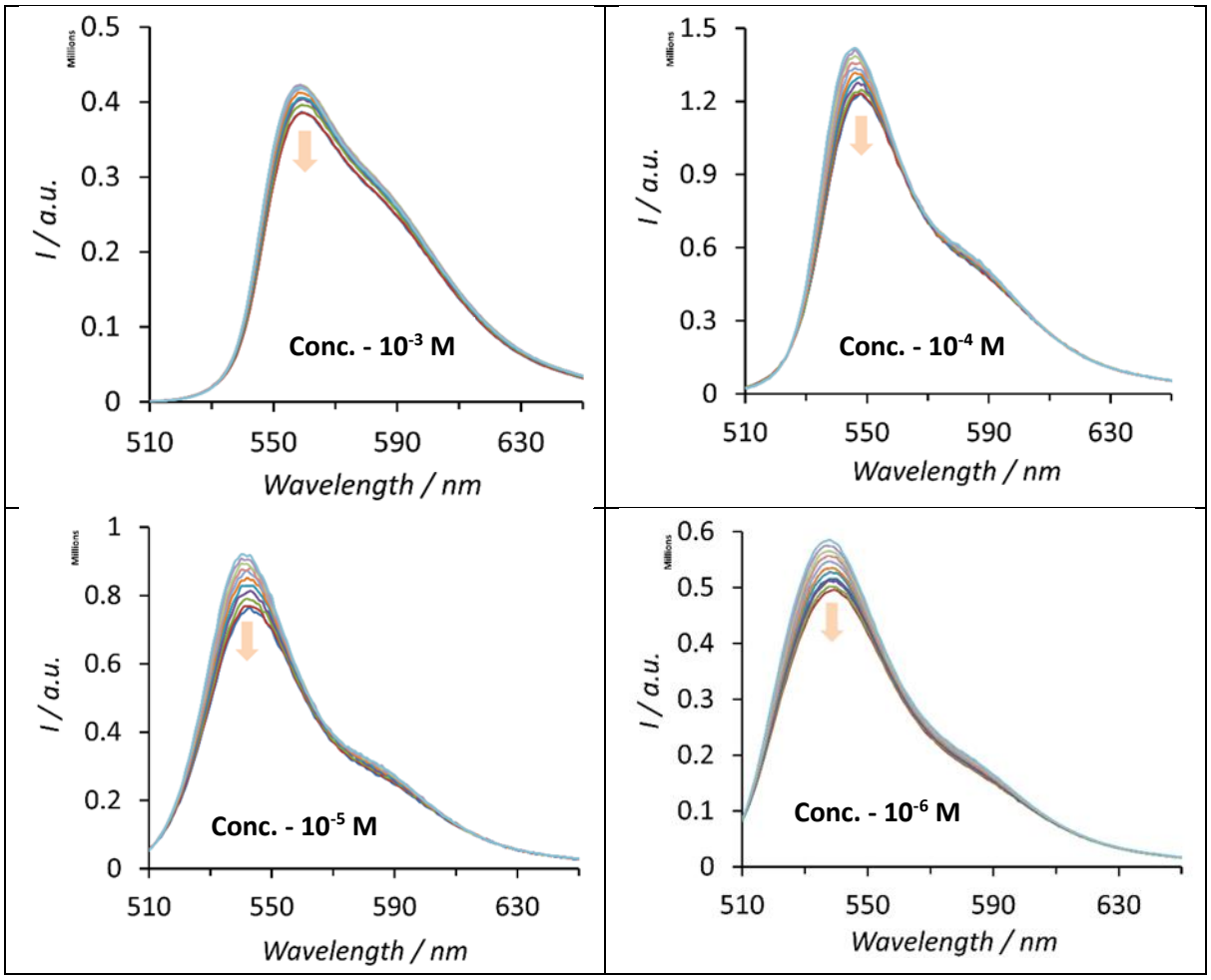
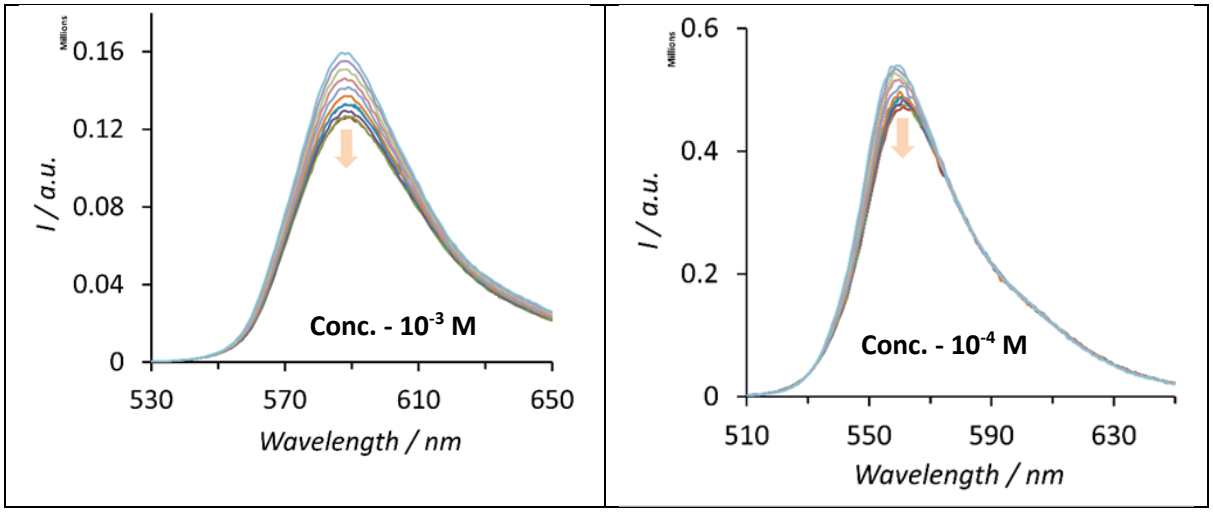


Figure S15. Change of emission spectra (excited at 500 nm, slit 3 and solvent $CHCl_3$) of **1-Hex** in different concentrations upon increasing the temperature of the solution from 0 to 50 °C (spectra measured in each 5°C interval).



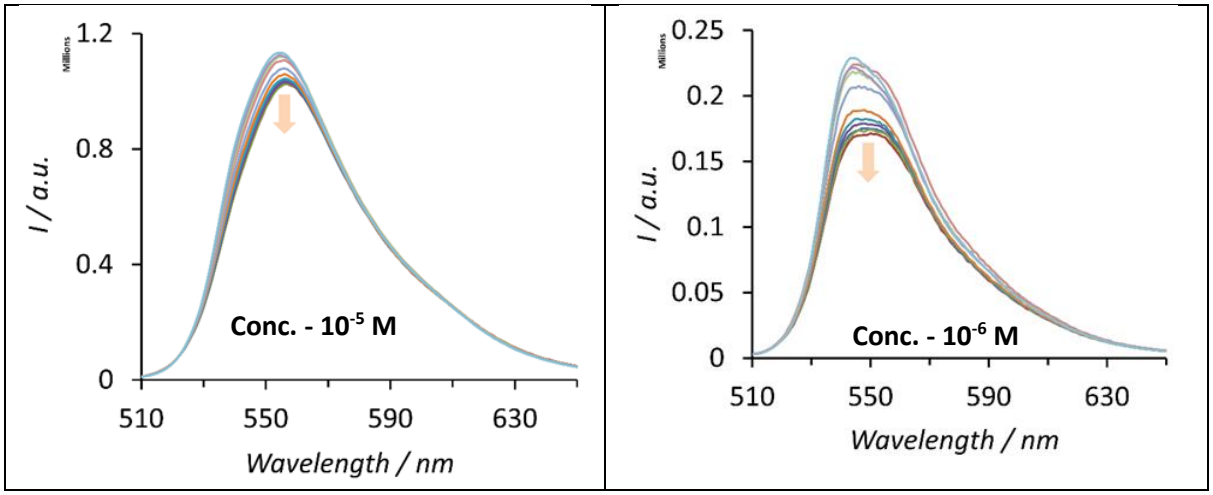
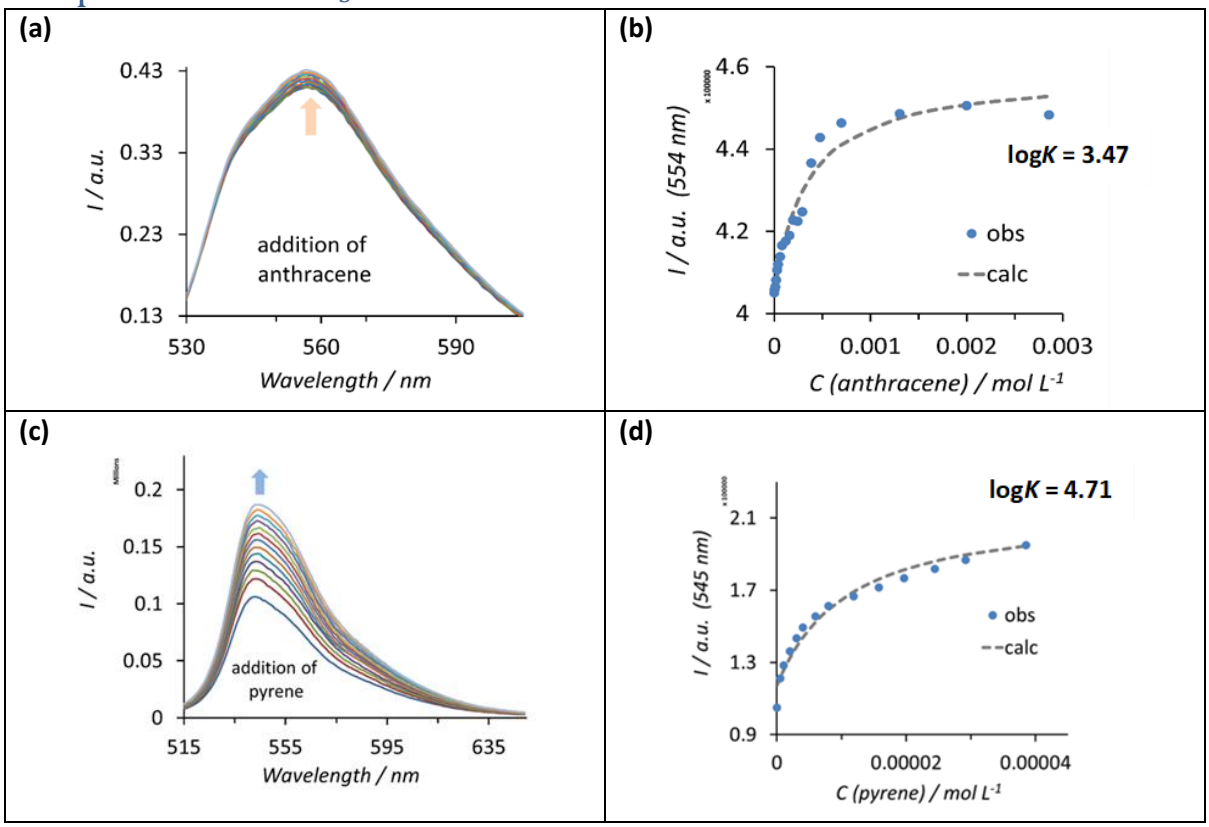


Figure S16. Change of emission spectra (excited at 500 nm, slit 3 and solvent $CHCl_3$) of **1-Oct** in different concentrations upon increasing the temperature of the solution from 0 to 50 °C (spectra measured in each 5°C interval).

Fluorescence titration of trianguleniums dyes with polycyclic aromatic compounds in $CHCl_3$



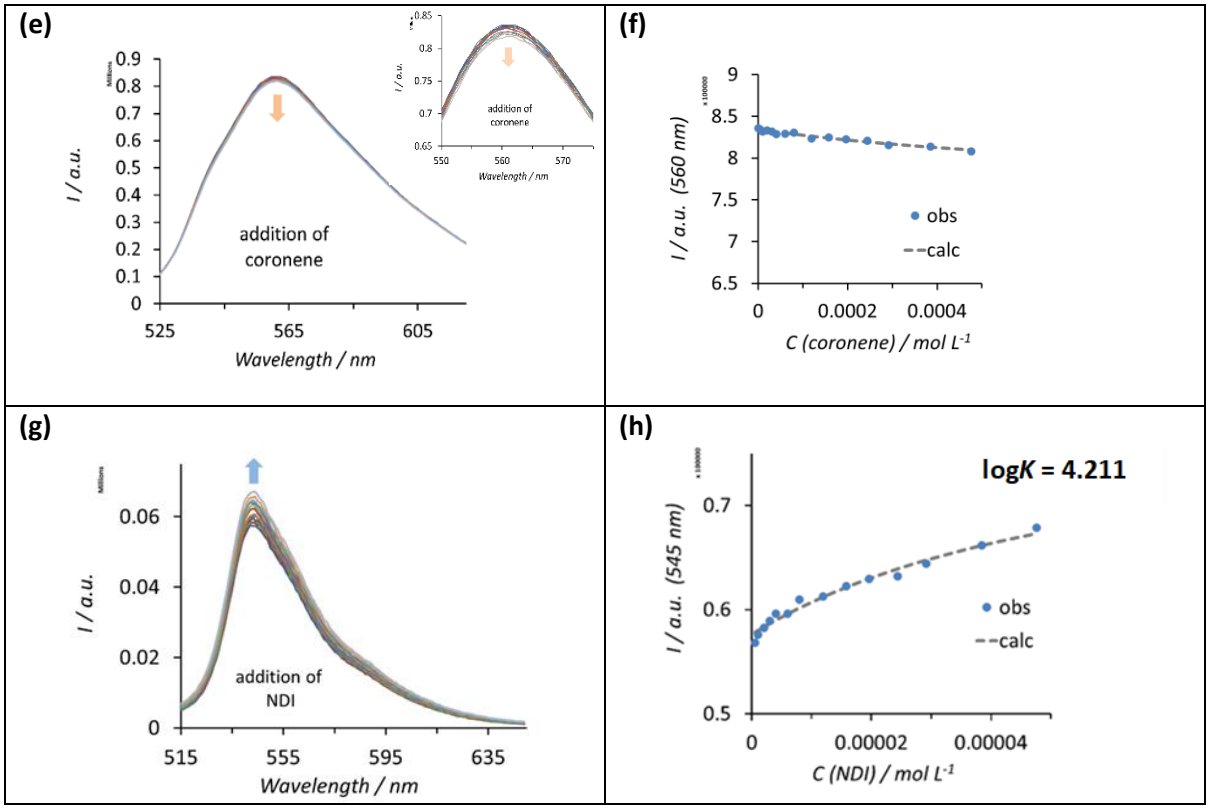


Figure S17. Fluorescence changes of **1-Pr** (10^{-6} M) upon (a) addition of anthracene, (b) fitting curves at 554 nm for addition of anthracene, (c) addition of pyrene, (d) fitting curves at 558 nm for addition of pyrene, (e) addition of coronene, (f) fitting curves at 560 nm for addition of coronene, (g) addition of NDI and (h) fitting curves at 560 nm for addition of NDI; Excitation at 500nm, slit 3 and solvent $CHCl_3$, addition of upto 400 equiv of guests for each cases.

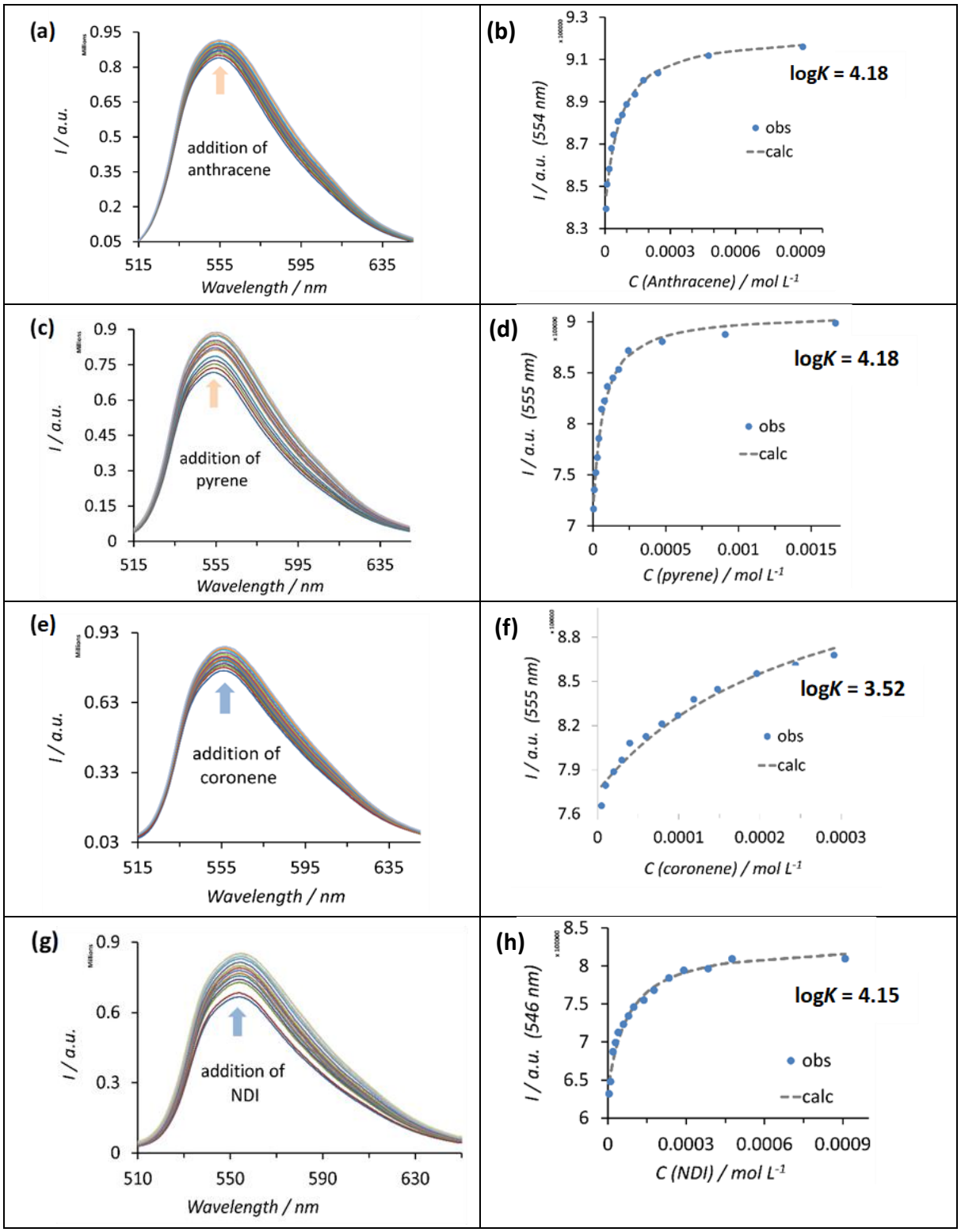


Figure S18. Fluorescence changes of **1-Bu**(10^{-6} M) upon (a) addition of anthracene, (b) fitting curves at 554 nm for addition of anthracene, (c) addition of pyrene, (d) fitting curves at 555 nm for addition of pyrene, (e) addition of coronene, (f) fitting curves at 555 nm for addition of coronene, (g) addition of NDI and (h) fitting curves at 546 nm for addition of NDI; Excitation at 500nm, slit 3 and solvent $CHCl_3$, addition of upto 400 equiv of guests for each cases.

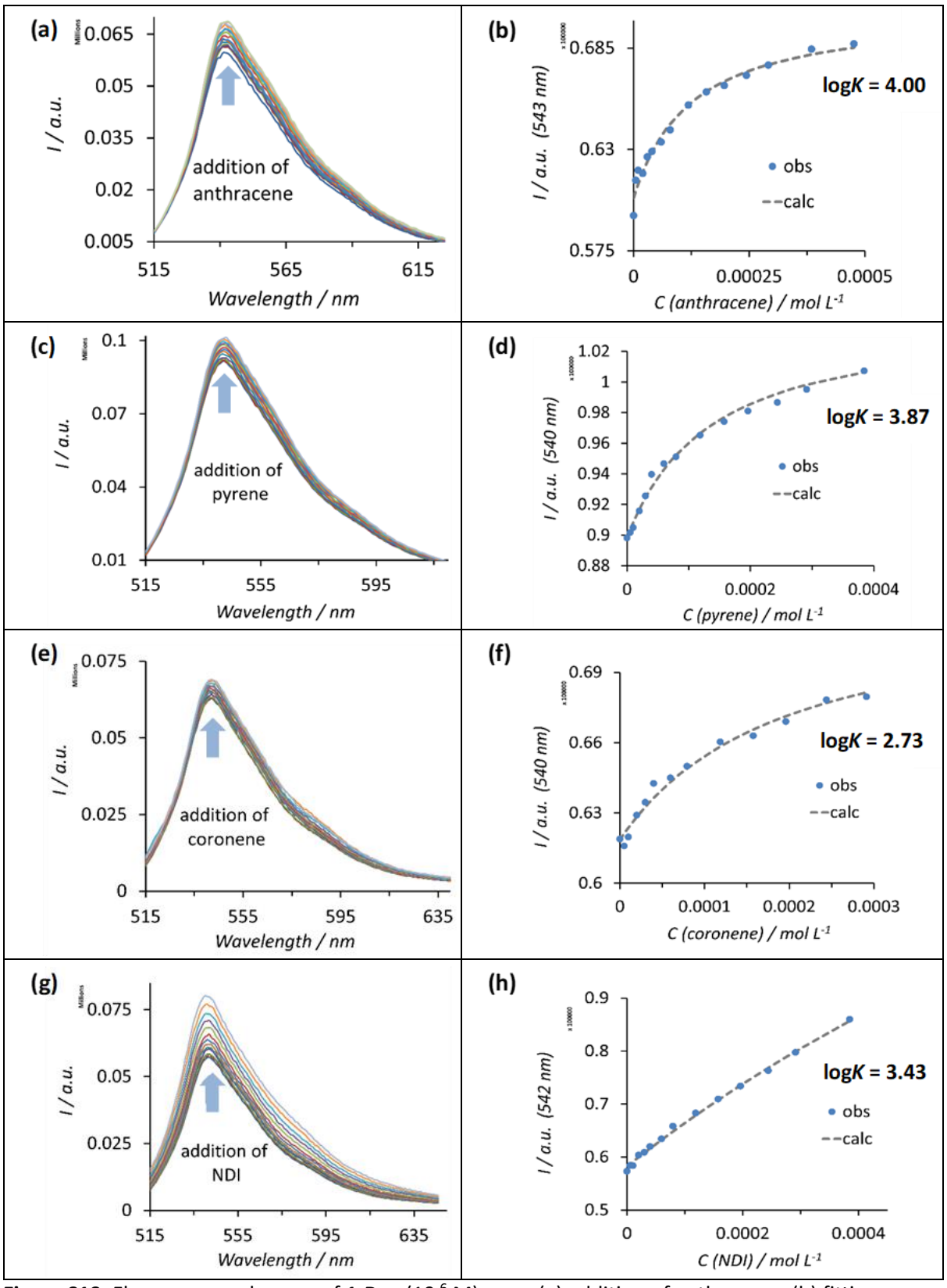


Figure S19. Fluorescence changes of **1-Pen** (10^{-6} M) upon (a) addition of anthracene, (b) fitting curves at 543 nm for addition of anthracene, (c) addition of pyrene, (d) fitting curves at 540 nm for addition of pyrene, (e) addition of coronene, (f) fitting curves at 540 nm for addition of coronene, (g) addition of NDI and (h) fitting curves at 542 nm for addition of NDI; Excitation at 500nm, slit 3 and solvent $CHCl_3$, addition of upto 400 equiv of guests.

UV-Vis measurements

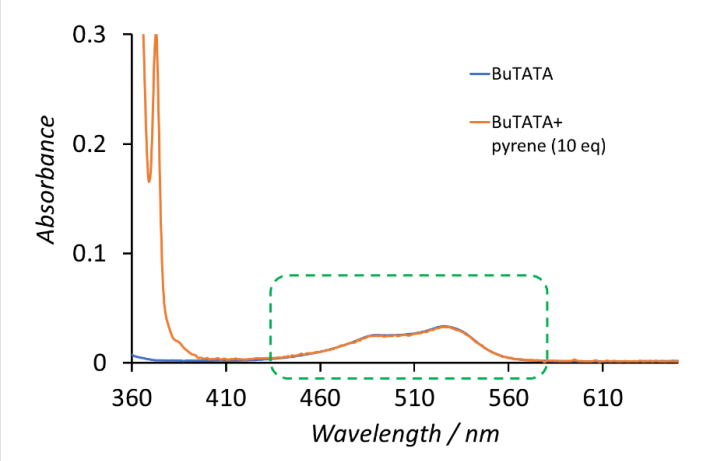
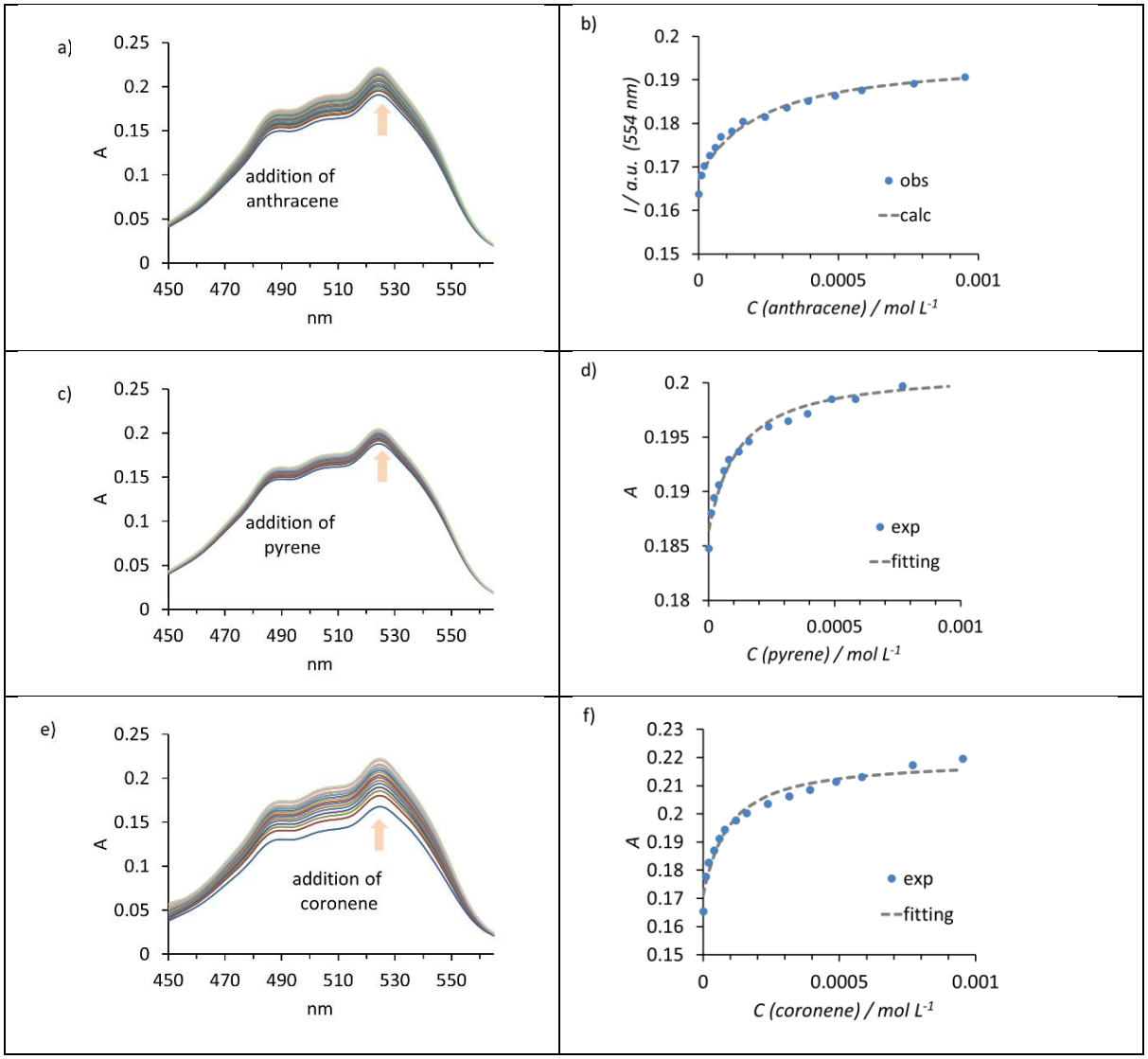


Figure S20. UV-vis of the mixture **1-Bu** ($5x10^{-6}$ M) with pyrene (10 eq) showing no overlap at 500 nm.



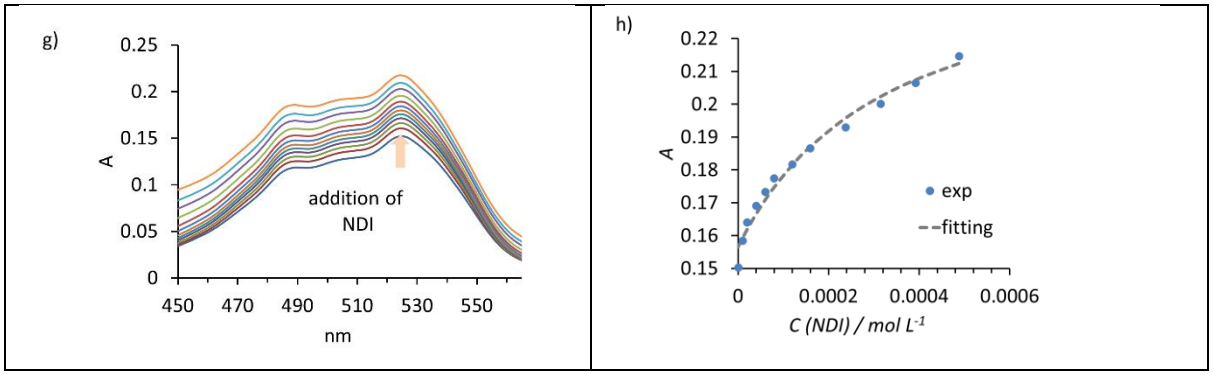
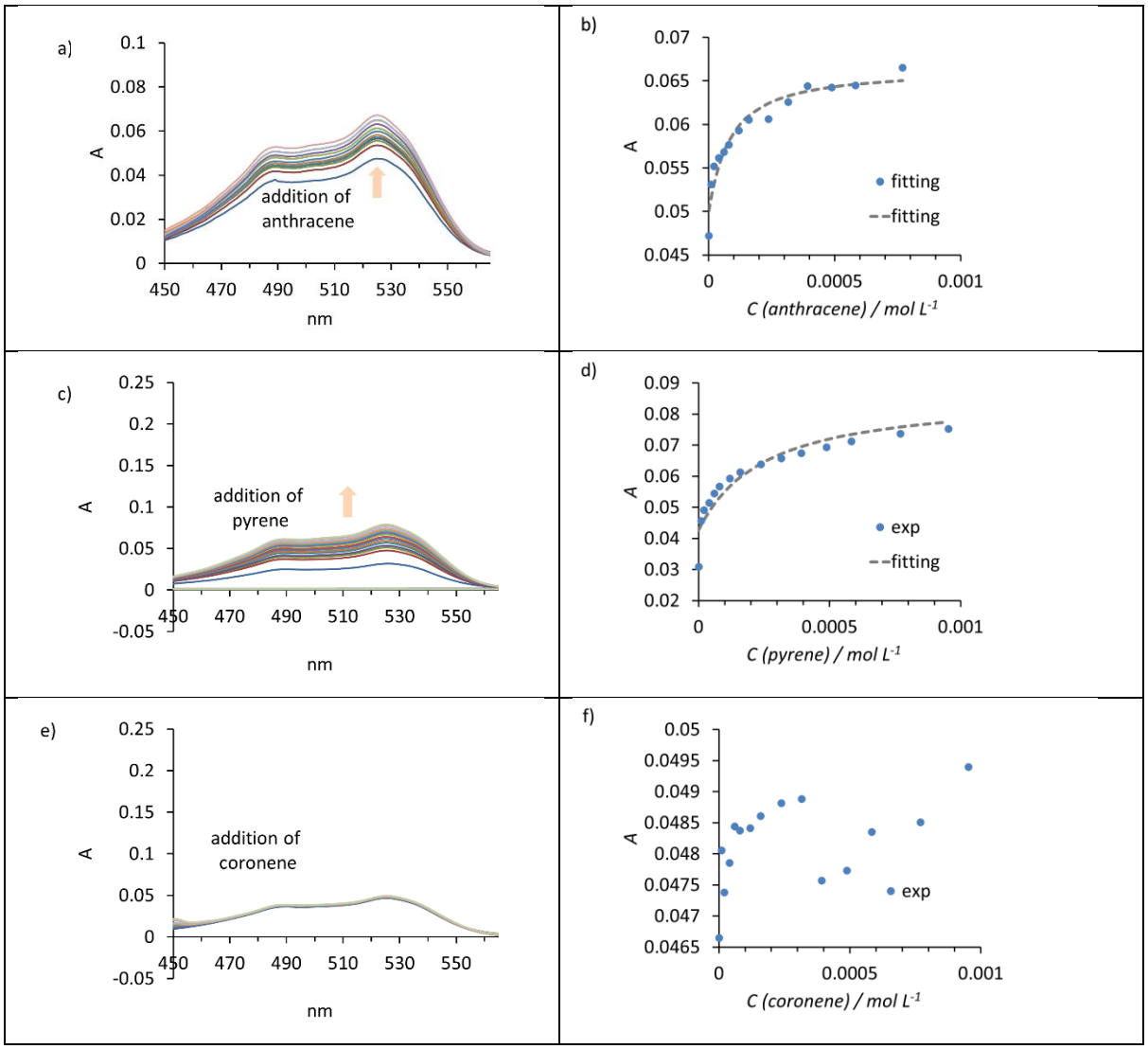


Figure S21. UV-vis titrations of **1-Pr** ($2x10^{-5}$ M) with aromatic compounds.



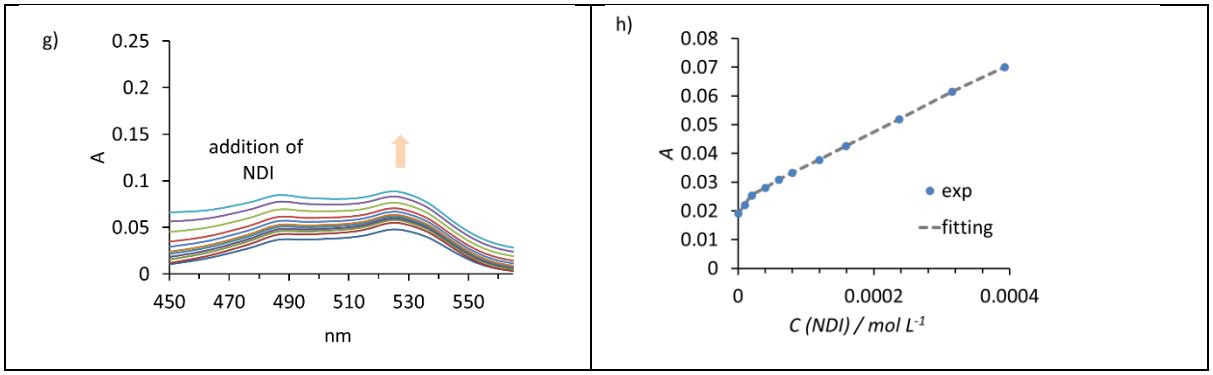


Figure S22. UV-vis titrations of **1-Bu** ($2x10^{-5}$ M) with aromatic compounds.

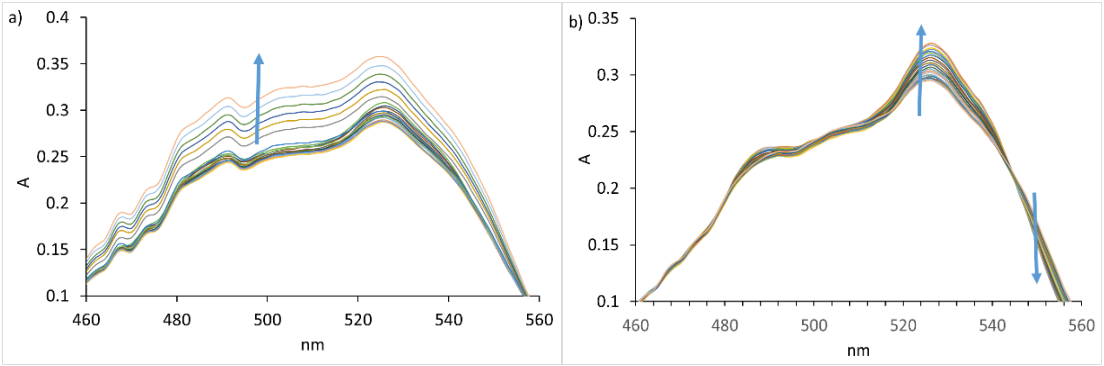


Figure S23. Temperature dependent studies of a) **1-Bu** and b) **1-Hex** (also for **1-Oct**) in $CHCl_3$. Temperature range 0°C ->50°C. **1-Pen** shows similar behaviour as **1-Bu**.

Fluorescence titration data of macrocycles 6 and 7 with 1-Bu

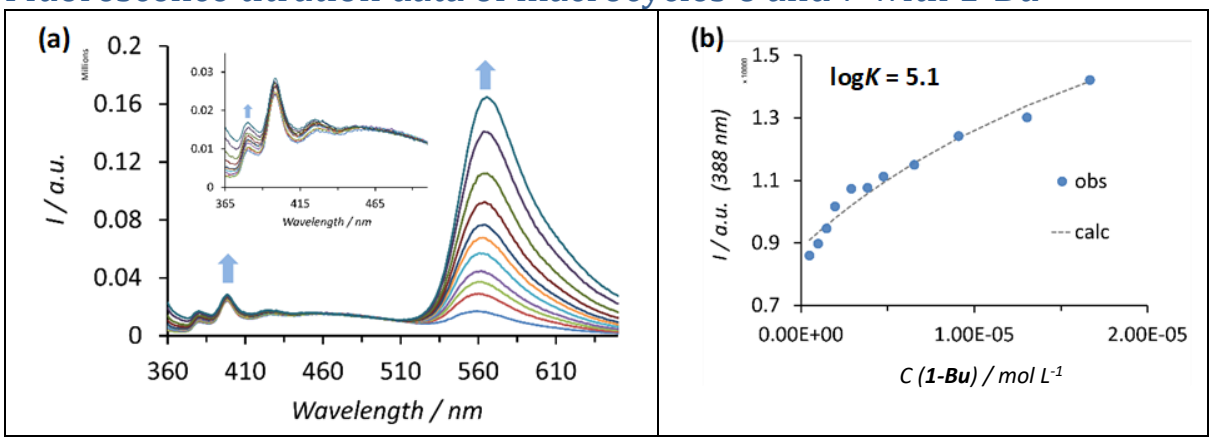


Figure S24. (a) Fluorescence changes of **6** (10^{-6} M) upon addition of **1-Bu** (upto 20 equiv) in 1% CH_3CN-MOPSO buffer (50mM) pH 7.4, (b) fitting curves at 388 nm for addition of **1-Bu**; Excitation at 350 nm, slit 4.

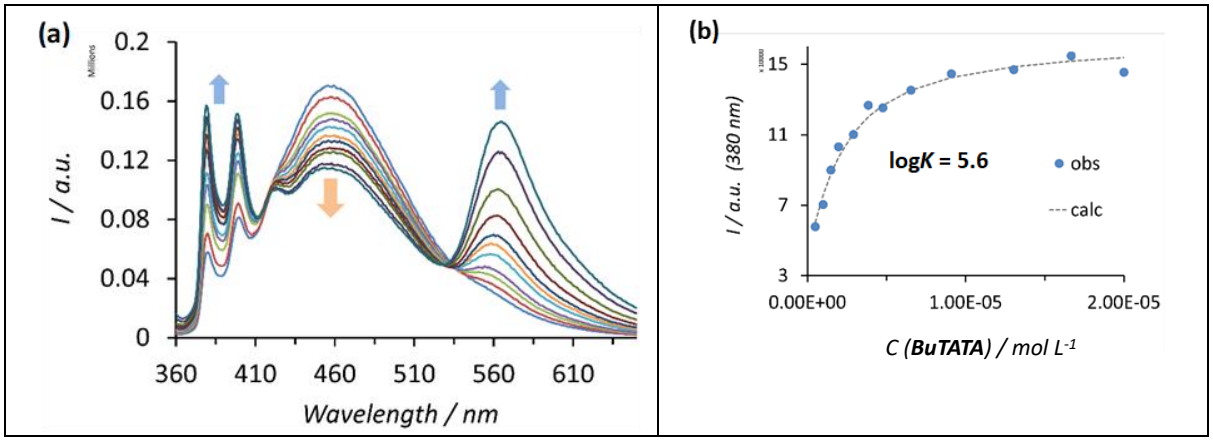


Figure S25. (a) Fluorescence changes of **7** (10^{-6} M) upon addition of **1-Bu** (upto 25 equiv) in 1% CH_3CN-MOPSO buffer (50mM) pH 7.4, (b) fitting curves at 380 nm for addition of **1-Bu**; Excitation at 350 nm, slit 4.

Fluorescence titration data of triangulenium dyes (1-Pr and 1-Bu) with macrocycles 6 and 7

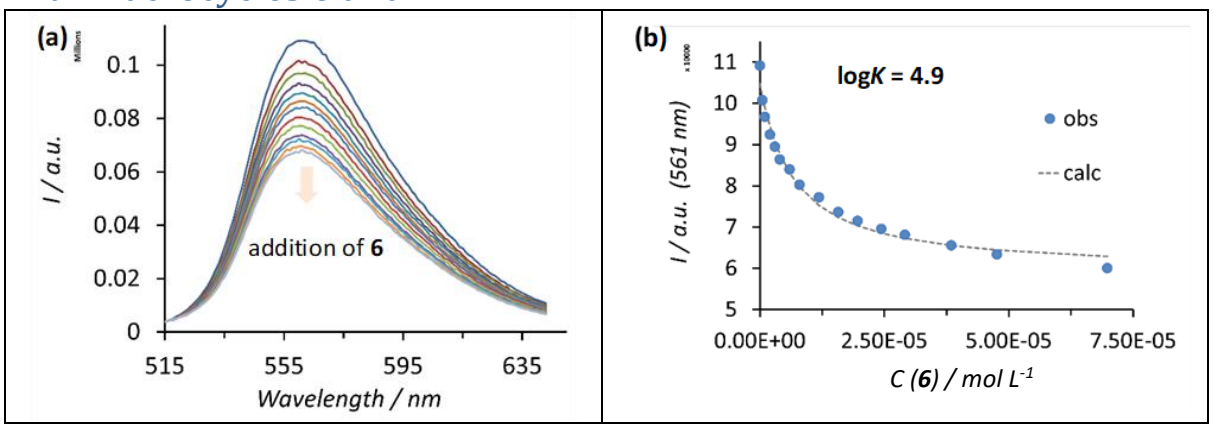


Figure S26. (a) Fluorescence changes of **1-Pr** (10^{-6} M) upon addition of **6** (upto 75 equiv) in 1% CH_3CN-MOPSO buffer (50mM) pH 7.4, (b) fitting curves at 561 nm for addition of **6**; Excited at 500 nm, slit 4.

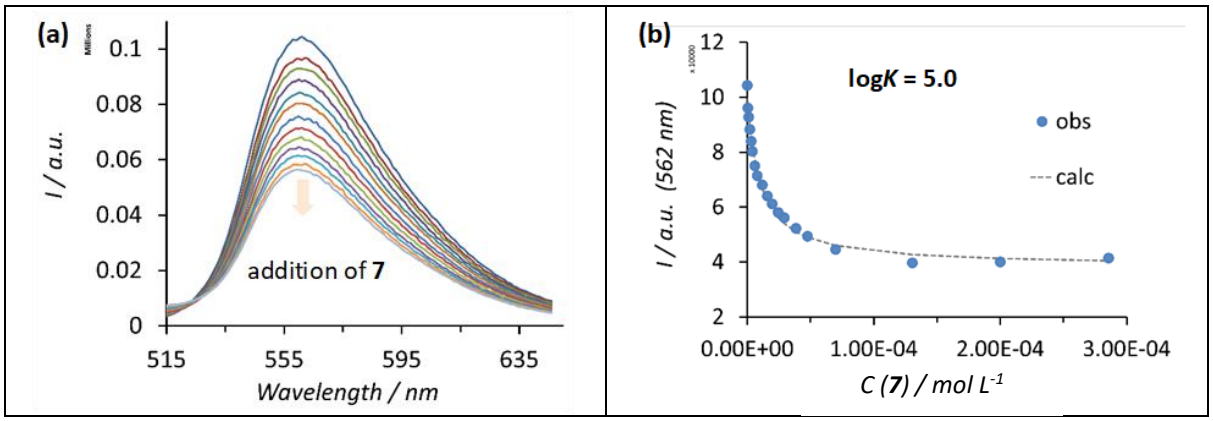


Figure S27. (a) Fluorescence changes of **1-Pr** (10^{-6} M) upon addition of **7** (upto 400 equiv) in 1% CH_3CN-MOPSO buffer (50mM) pH 7.4, (b) fitting curves at 562 nm for addition of **7**; Excited at 500 nm, slit 4.

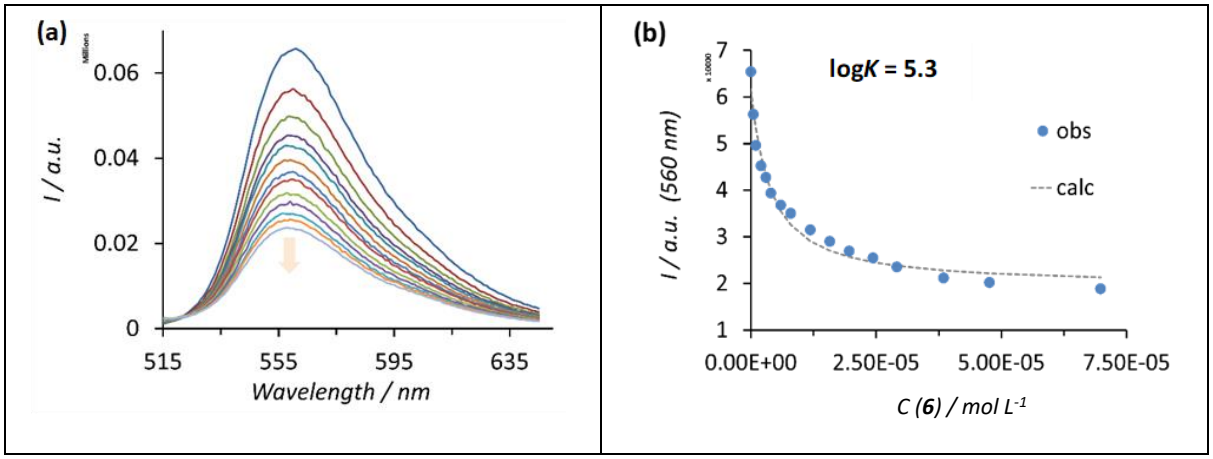


Figure S28. (a) Fluorescence changes of **1-Bu** (10^{-6} M) upon addition of **6** (upto 75 equiv) in 1% CH_3CN-MOPSO buffer (50mM) pH 7.4, (b) fitting curves at 560 nm for addition of **6**; Excited at 500 nm, slit 4.

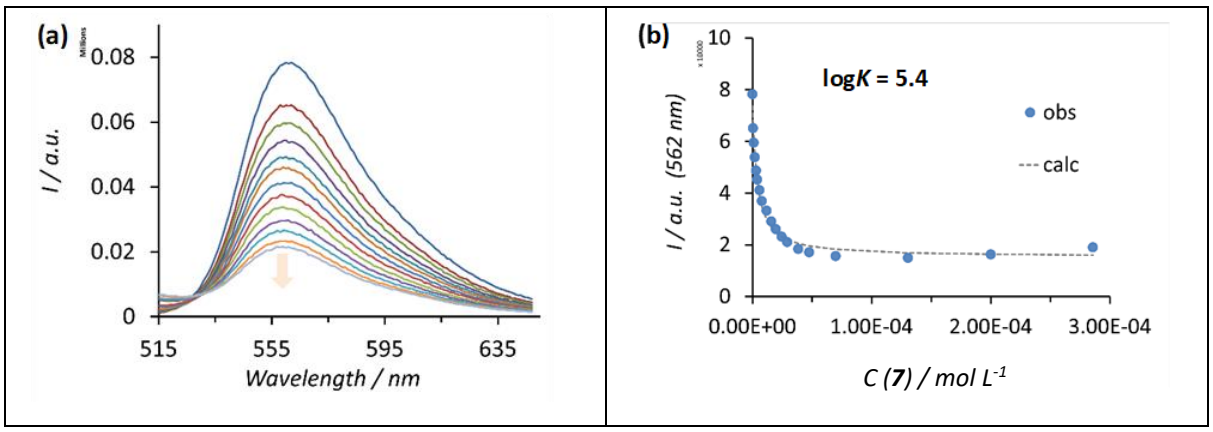


Figure S29. (a) Fluorescence changes of **1-Bu** (10^{-6} M) upon addition of **7** (upto 400 equiv) in 1% CH_3CN-MOPSO buffer (50mM) pH 7.4, (b) fitting curves at 562 nm for addition of **7**; Excited at 500 nm, slit 4.

logK binding constants of triangulenium receptors (**ProTATA** and **BuTATA**) for macrocycles **6** and **7** obtained by fluorescence titrations in 1% CH_3CN-MOPSO 7.4 (50mM); excitation 500 nm.

Host	ProTATA	BuTATA
6	**4.90**	**5.33**
7	**5.01**	**5.44**

The emission of BuTATA at 564 nm undergoes a 4 nm bathochromic shift after the addition of 30 equiv of compound **7**.

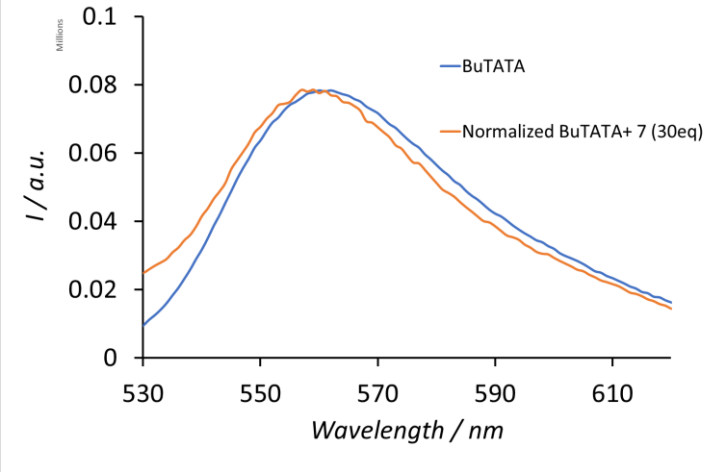


Figure S30. Emission of **1-Bu** without and with compound **7** (30 eq)

Temperature-dependent and lifetime studies of the mixtures of 1-Bu and 7

a) Fluorescence titration at different temperatures (and Stern-Volmer plot)

To prove the static quenching of **1-Bu** by **7**, we conducted titrations at two different temperatures: at 298K and at 323K. At 323K the linear Stern-Volmer plot shows smaller slope value than the titration at 298K. The dissociation of supramolecular complexes at higher temperatures is more effective and hence the quenching is weaker.

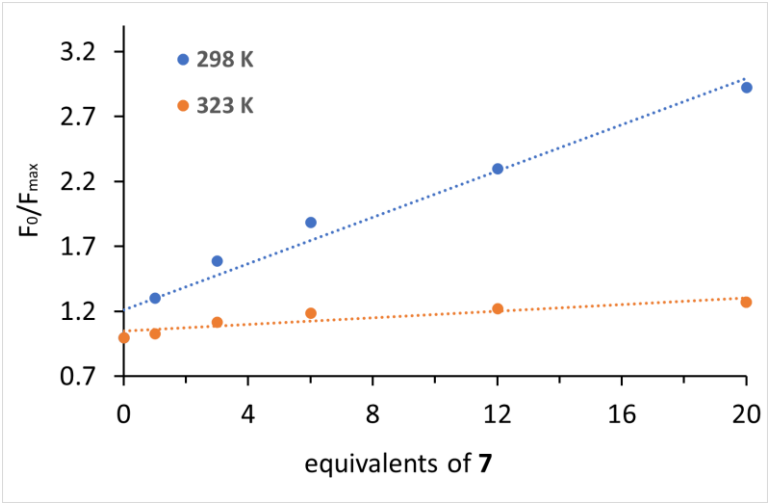


Figure S31. Plotted data of (a) F_o/F_{max} vs equivalents of **7** added to the solution of **1-Bu** (10^{-6} M^{-1}); (b) Fluorescence titration of **1-Bu** (10^{-6} M^{-1}) with **7** at 298K; and (c) Fluorescence titration of **1-Bu** (10^{-6} M^{-1}) with **7** at 323K.

b) Lifetime measurement studies of 7 to understand the excimer and monomer lifetime-

equiv of 1-Bu	τ, ns
0	4.22
1	4.21
5	4.17
10	4.12
20	4.05

Figure S32. Lifetimes of excimer of **6** upon addition of 20 equiv of **1-Bu.** Excitation laser 370 nm.

UV-vis and Fluorescence spectra of Compound 6 and 7 at different pH values

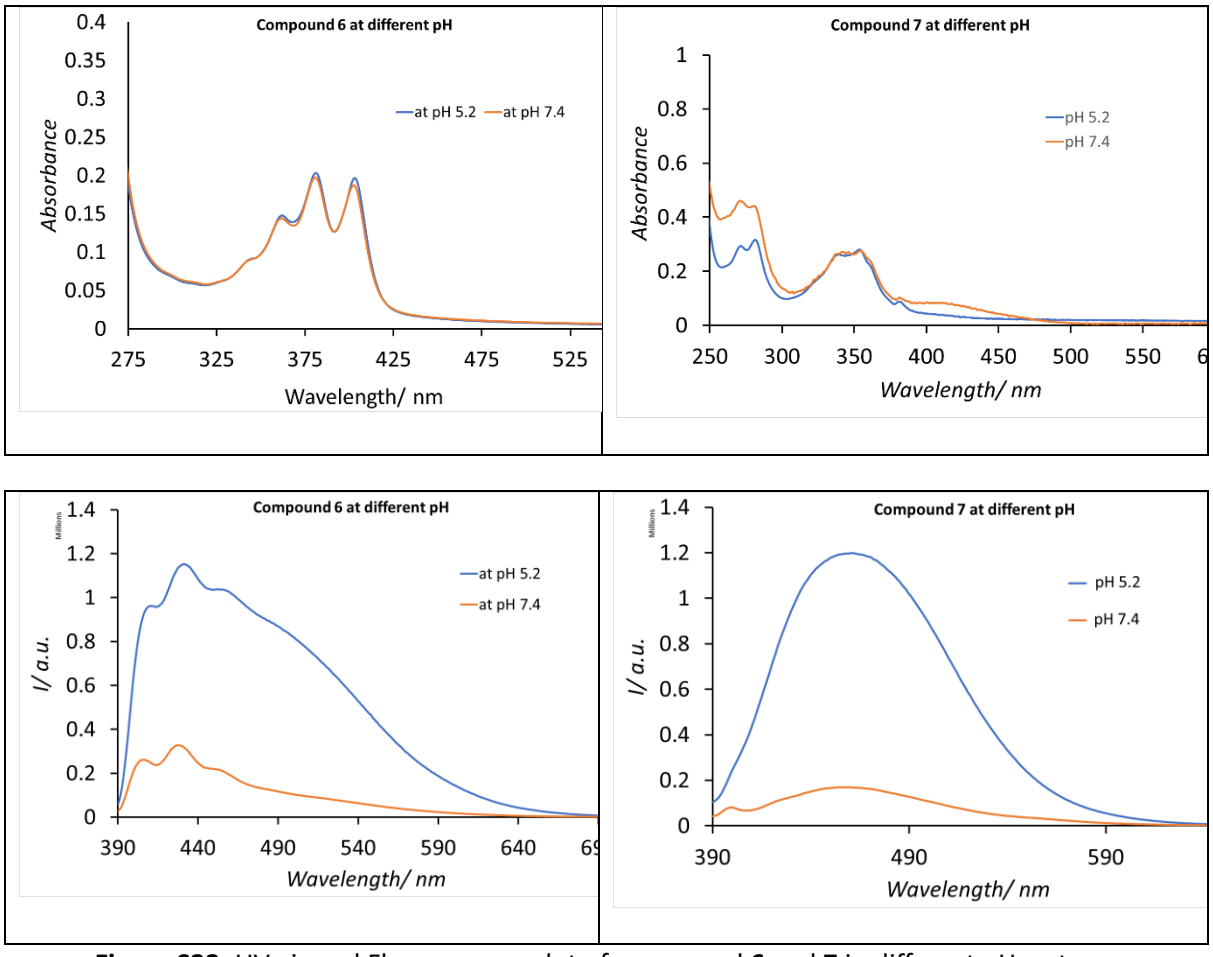


Figure S33. UV-vis and Fluorescence plot of compound **6** and **7** in different pH systems

UV-vis and Fluorescence of compound 7 with and without 1-Bu

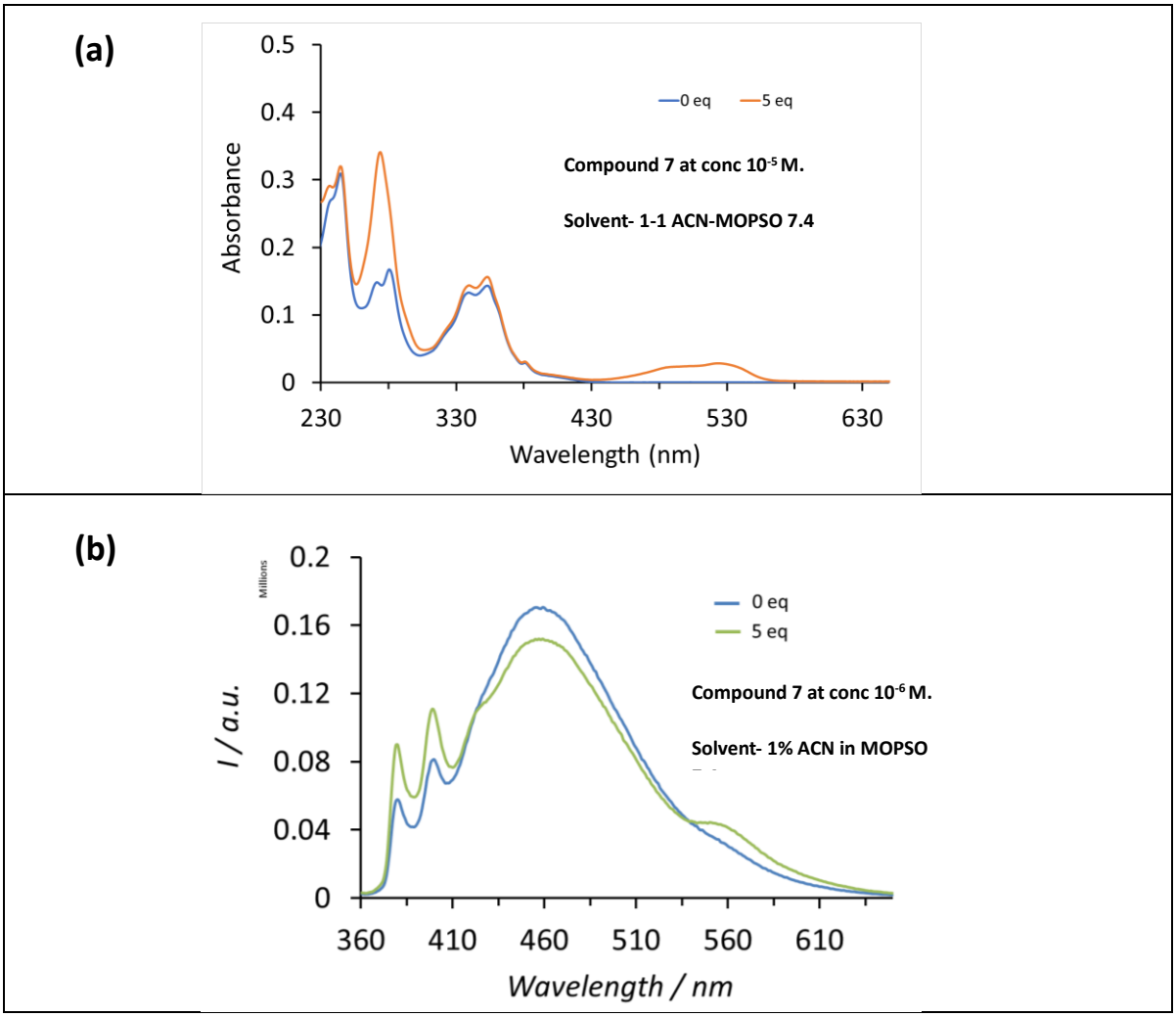
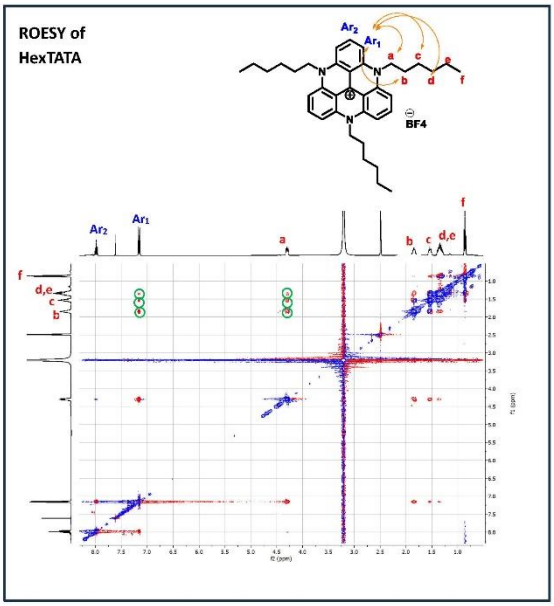
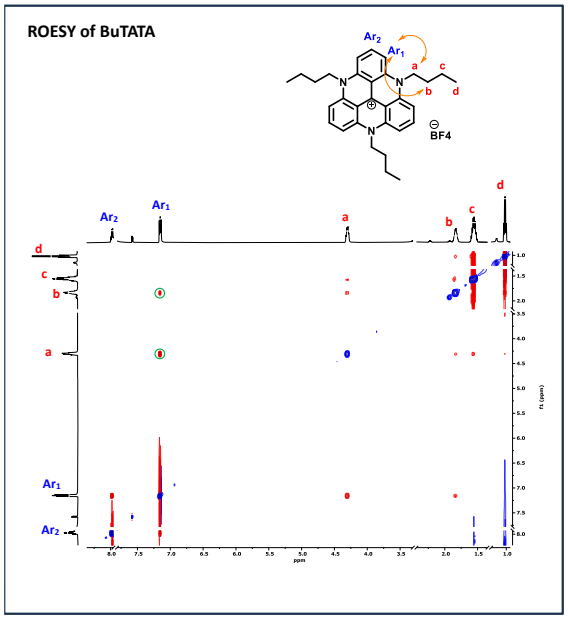
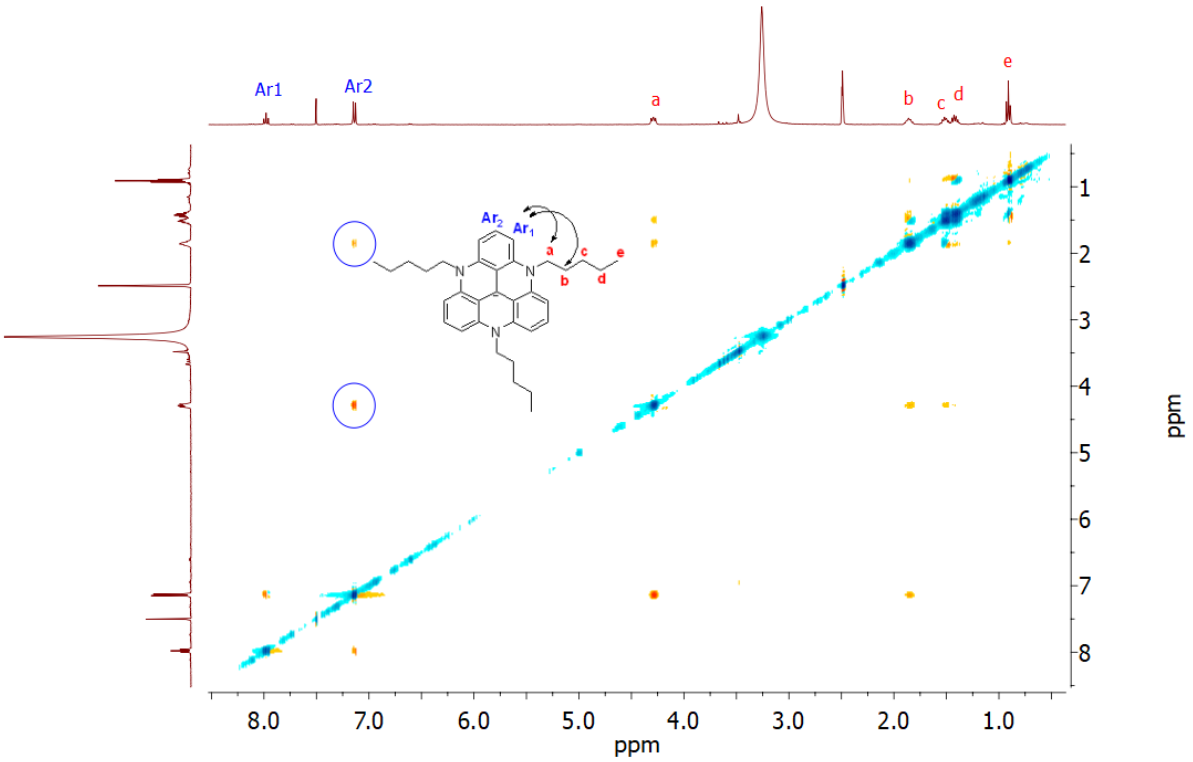


Figure S34. (a) UV-vis and (b) Fluorescence of compound **7** with and without **1-Bu** (5 eq)

ROESY and NMR titrations







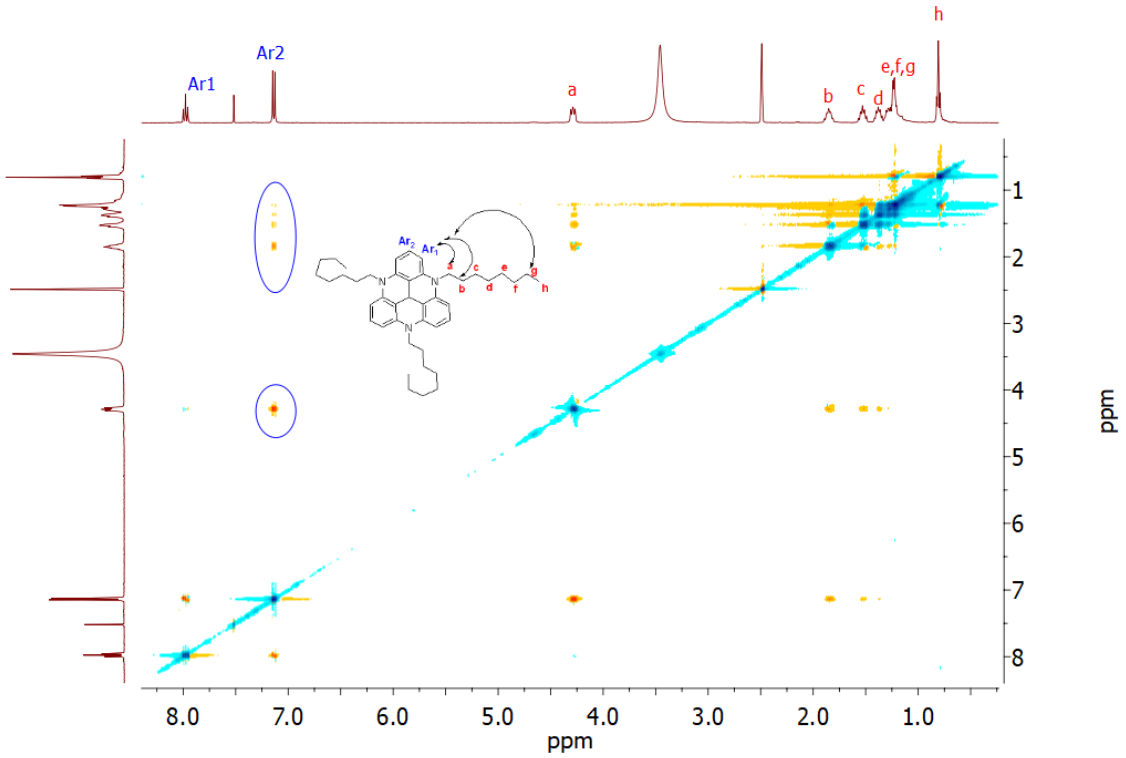


Figure S35. ROESY plots of **1-Hex**, **1-Bu**, **1-Pen** and **1-Oct** ($5x10^{-4}$ M) in $CDCl_3$ containing 5% DMSO-d_6

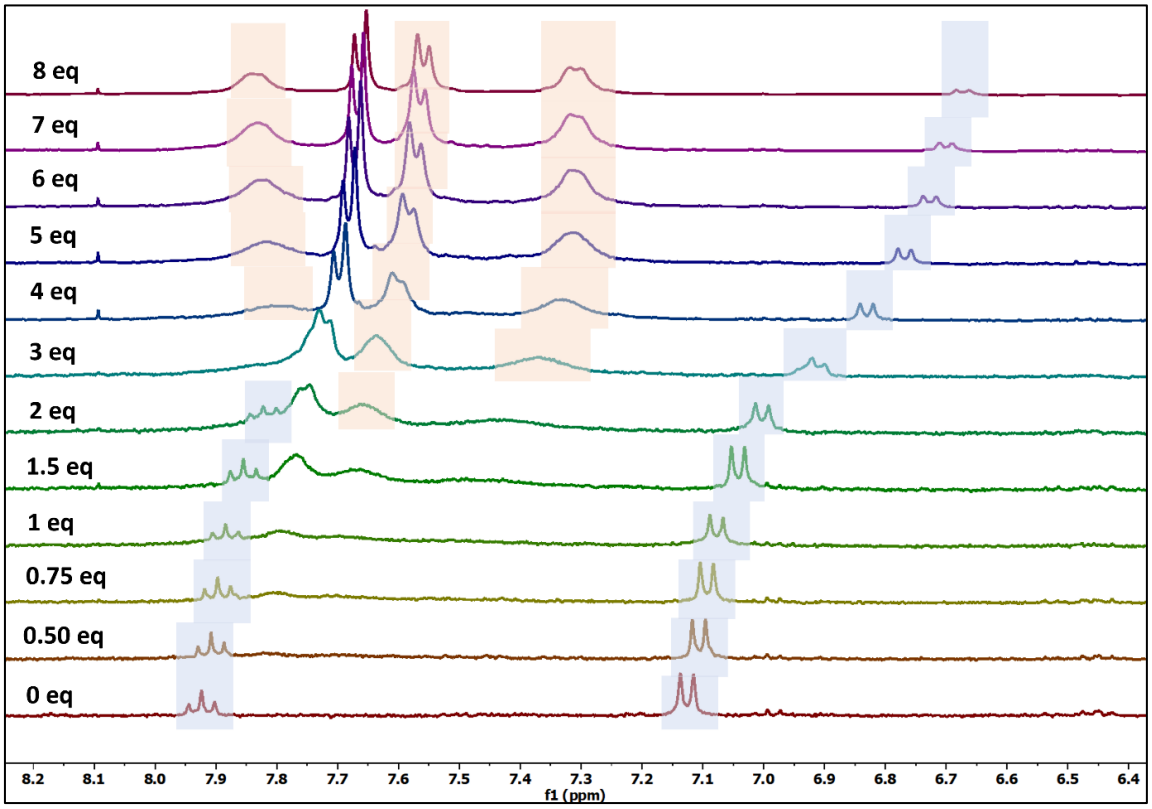


Figure S36. NMR titration of **1-Pr** (1mM) with **7** (up to 8 equiv) in 1:1 CD_3CN-MOPSO pH 7.4 (50mM).
Mass spectra

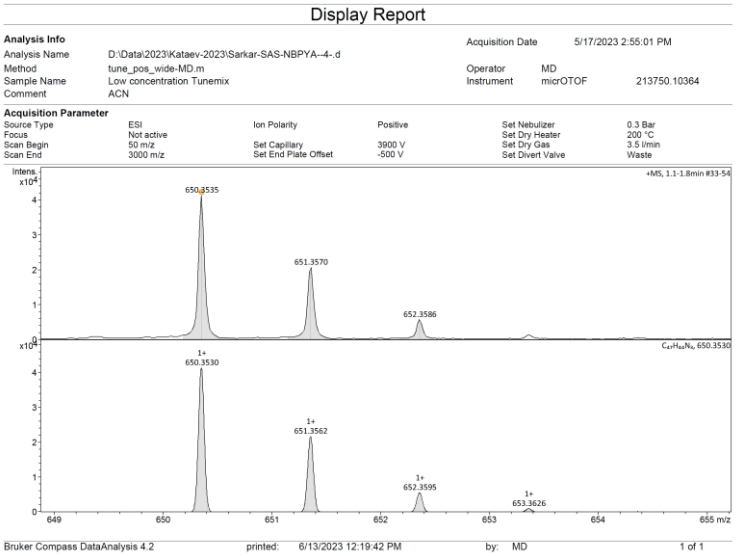


Figure S37. Mass spectrum of the observed adduct between pyrene and **1-Bu**.

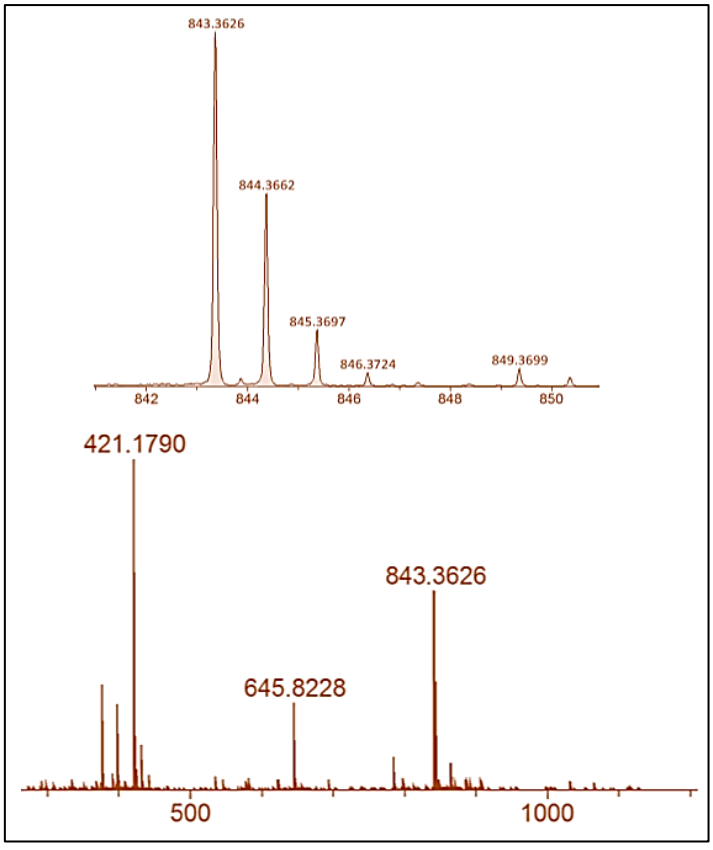


Figure S38. Mass spectrum (HRMS) of **6**

DFT calculations

CARTESIAN COORDINATES (ANGSTROEM)

O 5.854230 -2.191570 -0.366173

N	-5.112405	0.912763	-2.553644
N	5.687037	0.467172	-1.900151
C	-6.196046	0.091913	-3.100328
H	-5.742617	-0.740136	-3.681649
H	-6.831171	0.696885	-3.795714
C	-4.062814	1.203058	-3.542574
H	-4.408944	2.016002	-4.231039
H	-3.953672	0.300865	-4.170797
C	-2.695590	1.609855	-2.993189
C	-2.522258	2.882943	-2.403067
H	-3.392754	3.554134	-2.310868
C	-1.266738	3.331238	-1.977012
H	-1.173075	4.317729	-1.495357
C	-0.097997	2.563097	-2.192446
C	-0.226810	1.279886	-2.822563
C	-1.539364	0.789687	-3.183309
C	-1.611380	-0.514328	-3.787975
H	-2.594828	-0.939461	-4.026608
C	-0.485699	-1.246346	-4.069180
H	-0.578592	-2.235357	-4.540740
C	0.826867	-0.767671	-3.744038
C	1.989756	-1.515386	-4.032436
H	1.883528	-2.504291	-4.506310
C	3.255958	-0.993690	-3.757418
H	4.150957	-1.569577	-4.043663
C	3.434310	0.264833	-3.154125
C	2.273432	1.018232	-2.788279
C	0.957087	0.510352	-3.104911
C	1.215388	3.027848	-1.839034
H	1.303128	3.992758	-1.315081
C	2.345018	2.294747	-2.125800
H	3.328974	2.676256	-1.822301
C	4.853089	0.822437	-3.053862
H	5.378734	0.516004	-3.996680
H	4.790800	1.928499	-3.101280
C	6.657640	-0.604239	-2.124775
H	7.572972	-0.331771	-1.553637
H	6.949495	-0.656813	-3.211632
C	6.222748	-2.022476	-1.714645
H	5.325368	-2.331223	-2.294555
H	7.052735	-2.723788	-1.998920
C	6.872343	-2.157808	0.639977
H	7.641106	-1.386810	0.409666
H	7.362995	-3.163009	0.691626
C	6.284427	1.653198	-1.265484
O	-6.539714	-1.620598	-1.356650
N	5.250303	-2.722894	2.493530
N	-5.175687	-3.041177	0.887145
C	6.251749	-1.779146	1.986635
H	5.808611	-0.769817	1.876624
H	7.076514	-1.645874	2.725265
C	4.035282	-2.117026	3.027671
H	4.146336	-1.944968	4.129568
H	3.934336	-1.110816	2.574723
C	2.753920	-2.886889	2.751719
C	2.796287	-4.175689	2.189843
H	3.778712	-4.555175	1.876596
C	1.636998	-4.942606	2.011545
H	1.706302	-5.960996	1.594873
C	0.361161	-4.426044	2.327066
C	0.269981	-3.068267	2.796276
C	1.474996	-2.309867	3.033163

C	1.334245	-0.945472	3.472342
H	2.239213	-0.354531	3.668717
C	0.097733	-0.353048	3.587644
H	0.016651	0.709102	3.869606
C	-1.113001	-1.073037	3.301384
C	-2.385832	-0.458274	3.334966
H	-2.453200	0.610047	3.594726
C	-3.535653	-1.179167	3.004233
H	-4.510346	-0.666359	2.989565
C	-3.495777	-2.546191	2.664112
C	-2.229762	-3.204687	2.635088
C	-1.024917	-2.458354	2.931226
C	-0.852922	-5.167498	2.111323
H	-0.779062	-6.210160	1.763548
C	-2.092436	-4.594733	2.268517
H	-2.996024	-5.186577	2.060922
C	-4.802421	-3.239117	2.296282
H	-5.602172	-2.777988	2.913516
H	-4.782035	-4.327550	2.536683
C	-6.595785	-3.127736	0.577754
H	-6.804910	-4.032538	-0.037183
H	-7.186735	-3.267676	1.510900
C	-7.166601	-1.880982	-0.107667
H	-7.038965	-0.992561	0.563939
H	-8.270546	-2.026924	-0.254459
C	-7.125727	-0.526513	-2.054105
H	-8.057740	-0.868846	-2.573066
H	-7.447577	0.258605	-1.328187
C	-4.350880	-3.803534	-0.046741
C	5.828471	-3.761036	3.338492
C	-5.555790	2.128288	-1.875878
H	-4.582953	-3.468550	-1.078473
H	-3.291810	-3.536261	0.130035
C	-4.428142	-5.377022	0.007049
O	-3.672252	-5.951076	-0.823691
O	-5.196221	-5.887403	0.873776
C	6.407168	-3.332586	4.769724
H	5.073861	-4.551542	3.540584
H	6.655728	-4.261439	2.790178
O	6.991738	-4.277317	5.358807
O	6.194573	-2.144724	5.129413
C	-5.964599	3.351815	-2.771860
H	-6.420617	1.885233	-1.220656
H	-4.751714	2.446412	-1.187692
O	-5.636559	4.480909	-2.287872
O	-6.560092	3.102660	-3.852499
C	6.961428	1.336295	0.111106
H	5.471949	2.386261	-1.096956
H	7.050215	2.136856	-1.936423
O	8.114312	0.829589	0.059240
O	6.271825	1.599803	1.145438
C	-1.568465	-0.480013	-0.140977
N	-0.402343	-1.224834	-0.296537
C	0.849313	-0.662463	-0.056371
C	-1.503580	0.821744	0.459888
C	-1.279329	4.681498	2.241365
C	1.169036	4.506534	2.306470
C	-0.017492	5.207642	2.546437
C	-0.245678	1.374754	0.788962
C	0.938444	0.652302	0.510112
N	2.254074	2.469202	1.476647
C	1.110623	3.214171	1.724446

C	-0.170402	2.662936	1.396600
C	-1.373910	3.388177	1.669774
N	-2.602491	2.798326	1.385022
C	2.032305	-1.383054	-0.292192
C	3.262526	-0.795988	0.003101
C	3.378679	0.486552	0.561145
C	2.214320	1.211341	0.846421
C	-3.976342	-0.291585	-0.198178
C	-2.813901	-0.991570	-0.519935
C	-2.707182	1.534947	0.772691
C	-3.938211	0.935140	0.484470
C	-0.483357	-2.704232	-0.337611
C	-0.283913	-3.468553	-1.657772
C	-1.558832	-3.924957	-2.376079
C	-1.264714	-4.826825	-3.577418
H	0.289410	-3.038937	0.371274
H	-1.449443	-2.982388	0.119334
H	0.299978	-4.379028	-1.393866
H	0.372135	-2.880997	-2.329584
H	-2.143526	-3.039894	-2.706298
H	-2.216319	-4.502773	-1.684501
H	-2.203489	-5.154130	-4.069572
H	-0.627324	-4.329757	-4.343327
H	-0.727584	-5.744682	-3.254764
C	-3.818362	3.544123	1.726395
C	-4.227317	4.608187	0.700807
C	-5.451083	5.411652	1.156944
C	-5.845835	6.488980	0.140357
H	-4.637558	2.817875	1.874681
H	-3.653421	4.008263	2.722118
H	-4.474254	4.159560	-0.286221
H	-3.371455	5.295234	0.522565
H	-5.262895	5.861716	2.162280
H	-6.304495	4.708481	1.296099
H	-6.771175	7.023210	0.446649
H	-5.038525	7.247100	0.038147
H	-5.997801	6.016920	-0.855188
C	3.555072	3.043440	1.842606
C	4.078753	4.043427	0.807008
C	5.421790	4.648887	1.223493
C	6.032658	5.539131	0.138516
H	3.452783	3.517562	2.840271
H	4.301915	2.235957	1.944941
H	3.324563	4.838966	0.611432
H	4.206939	3.494832	-0.149060
H	6.104499	3.801410	1.450382
H	5.290095	5.232188	2.164760
H	7.000735	5.976621	0.461933
H	6.228540	4.952837	-0.783981
H	5.357707	6.379021	-0.139911
H	-2.885014	-1.935211	-1.063407
H	-4.931002	-0.726084	-0.497728
H	-4.884795	1.426400	0.723074
H	2.005717	-2.391282	-0.717812
H	4.185803	-1.368861	-0.158469
H	4.390275	0.885897	0.746266
H	-2.172544	5.284965	2.431843
H	0.042685	6.215949	2.986323
H	2.128979	4.969601	2.555743

Dispersion correction -0.599324955

FINAL SINGLE POINT ENERGY -4346.526526807825