Mono-, di-, tri-pyrene substituted cyclic triimidazole: A family of highly emissive and RTP chromophores

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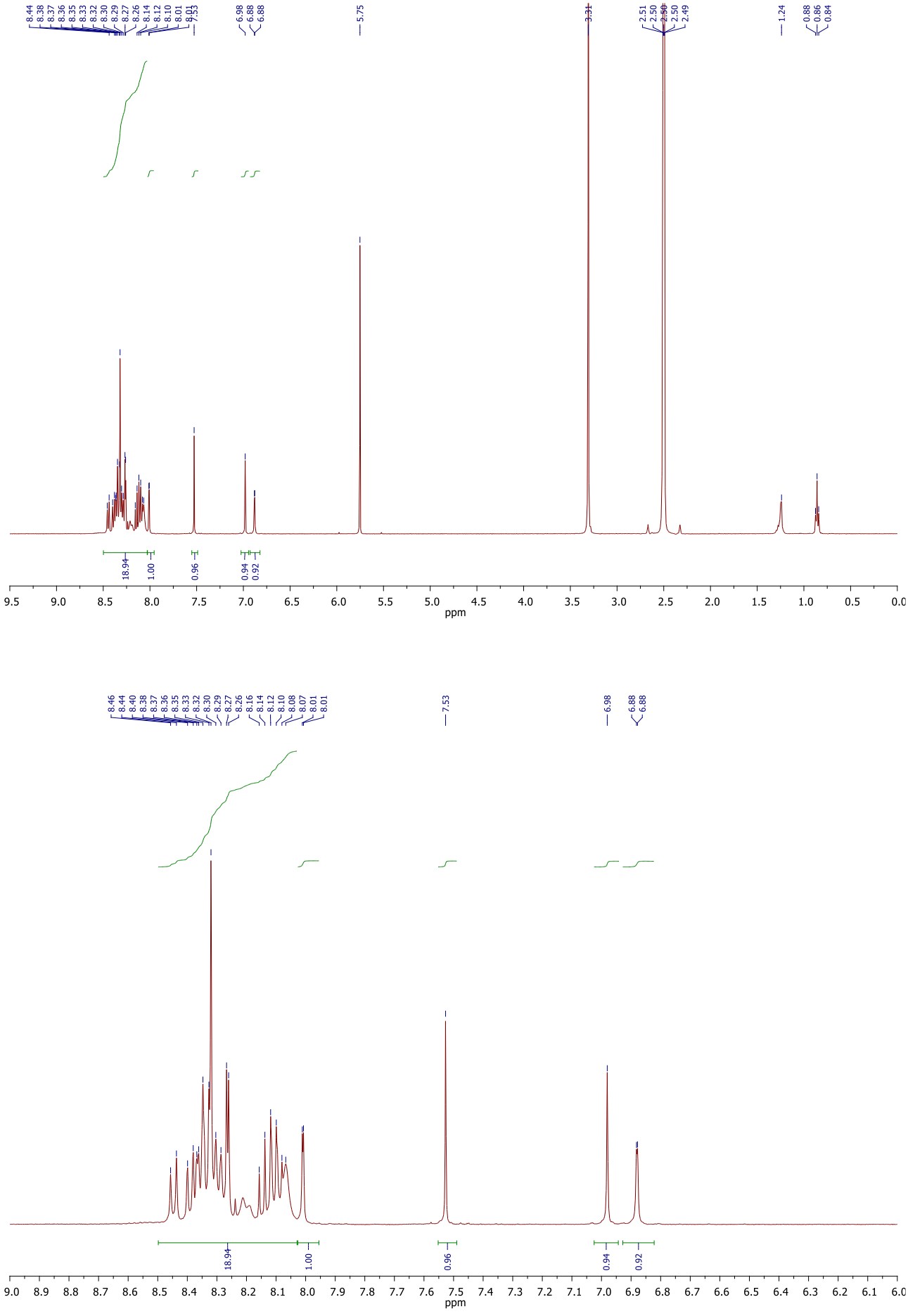


Figure S1. ^{1}H NMR spectrum and expanded region of **TTPyr$_2$** (400 MHz, DMSO-d$_6$)

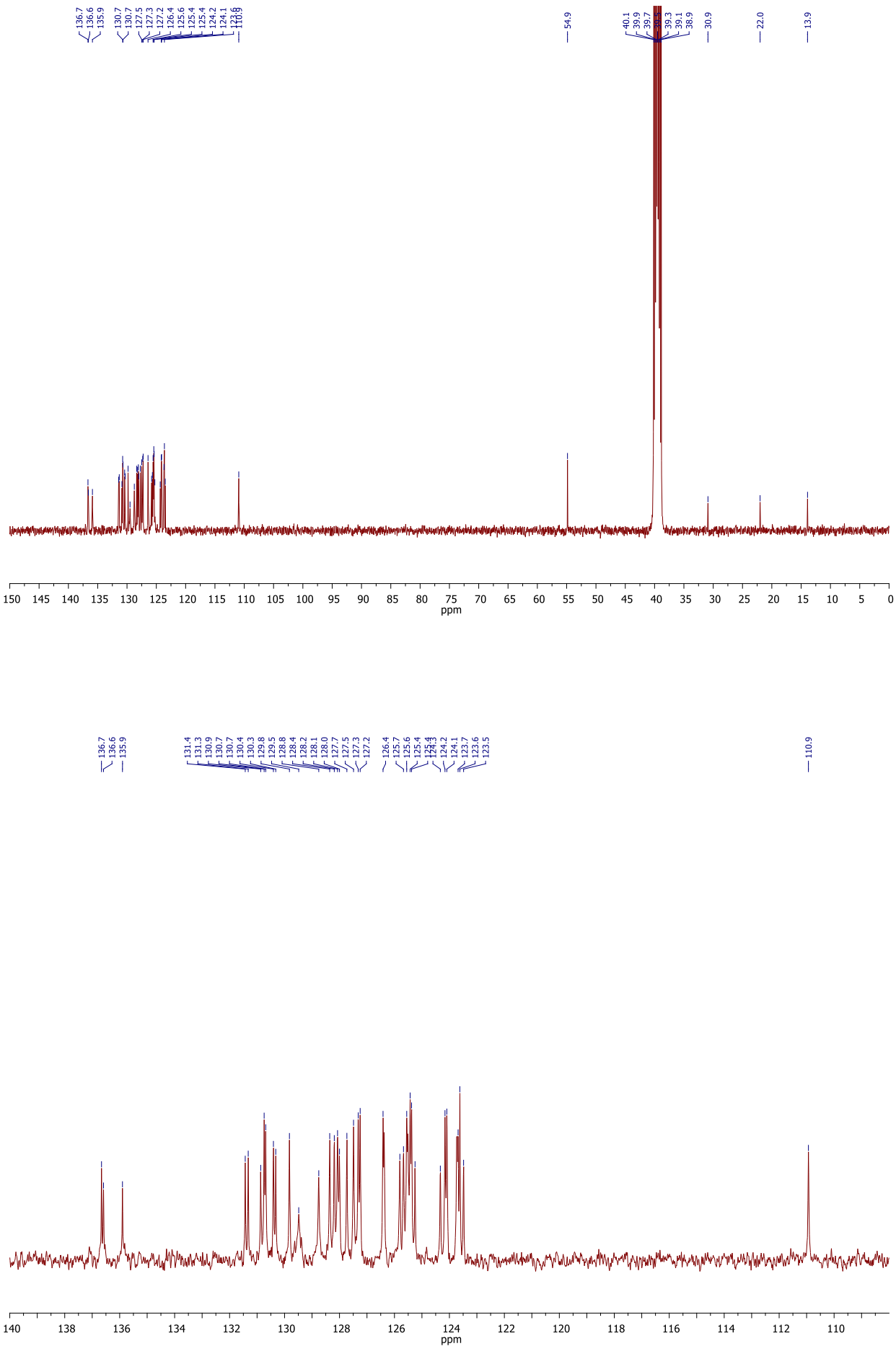


Figure S2. ^{13}C NMR spectrum and expanded region of **TTPyr$_2$** (400 MHz, DMSO-d$_6$)

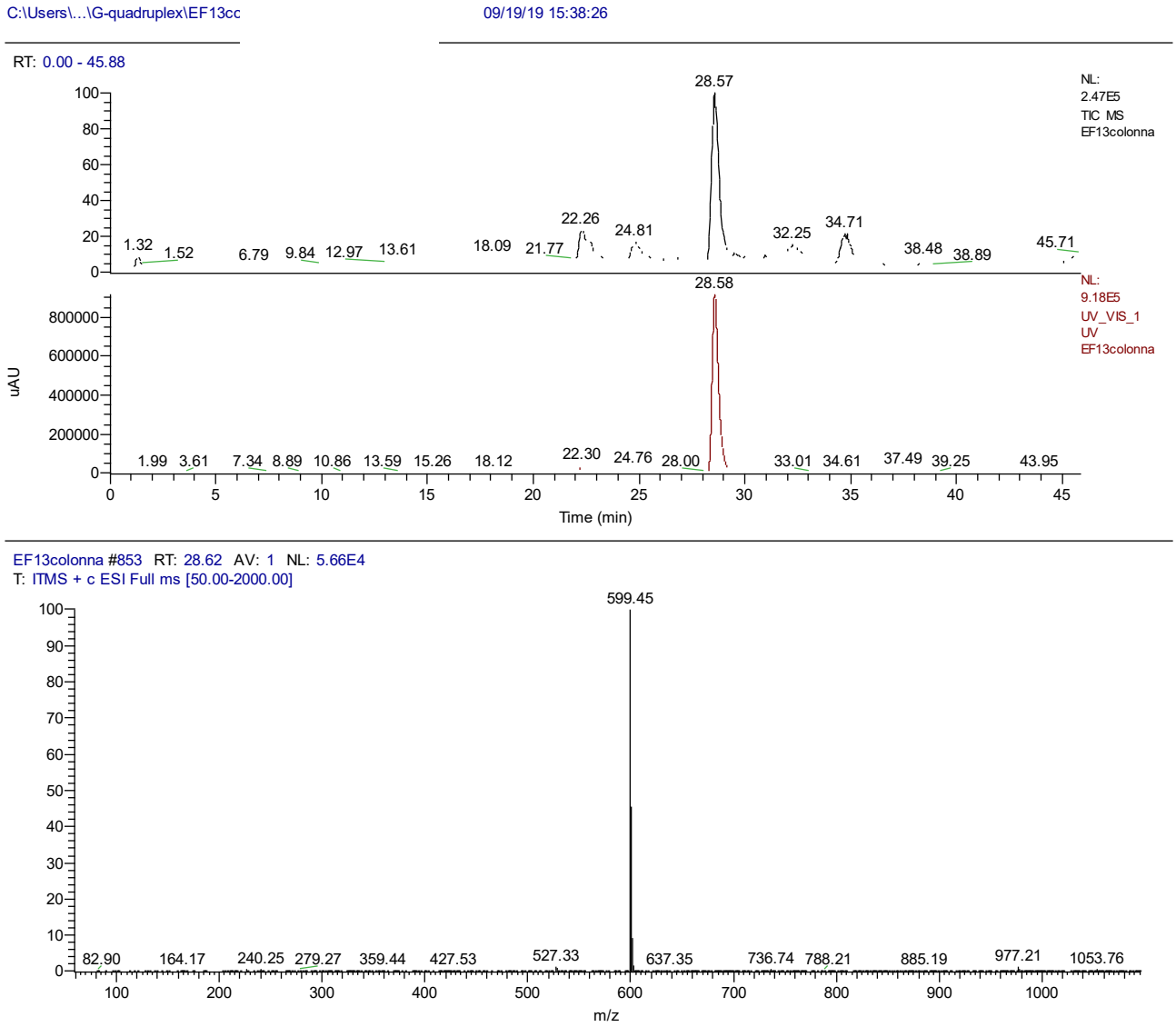
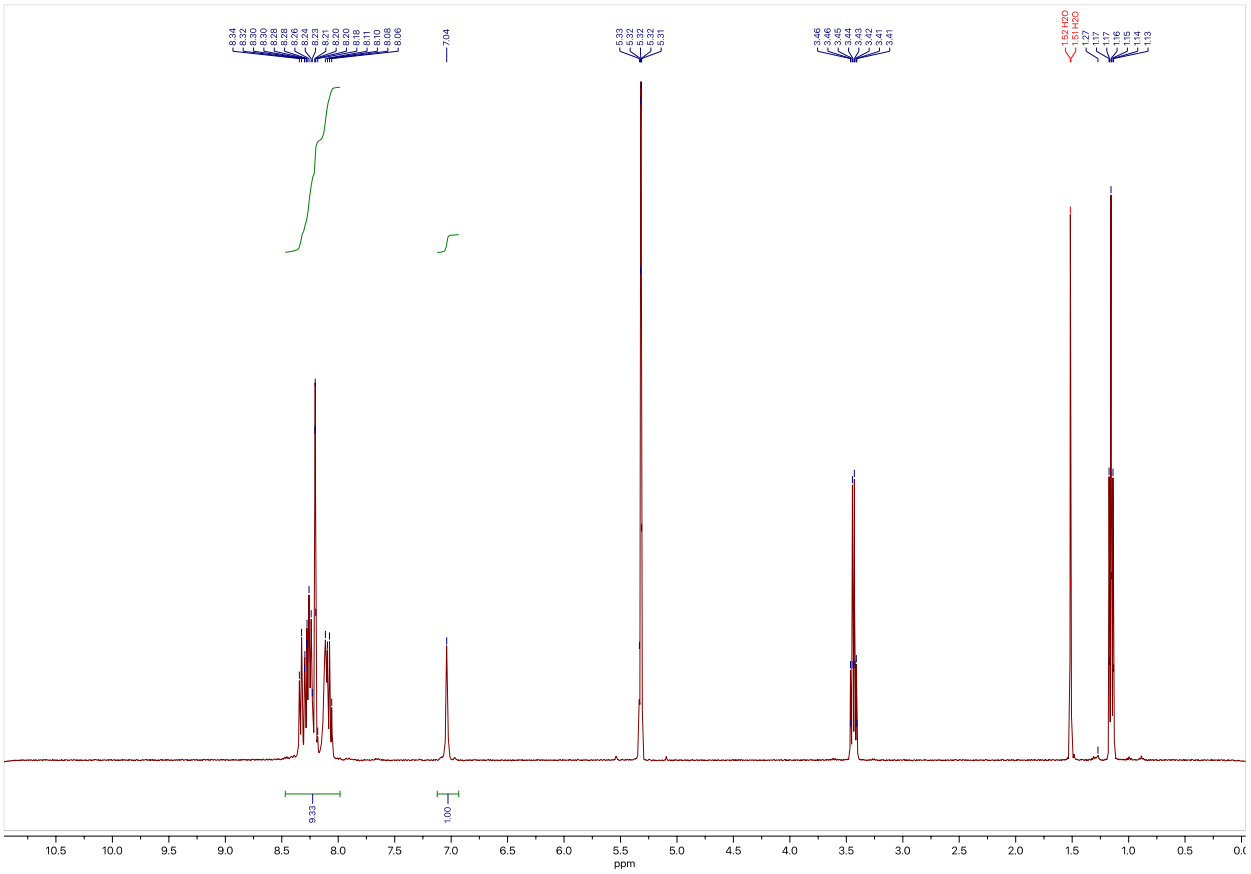


Figure S3. LC-MS profile of **TTPyr$_2$**



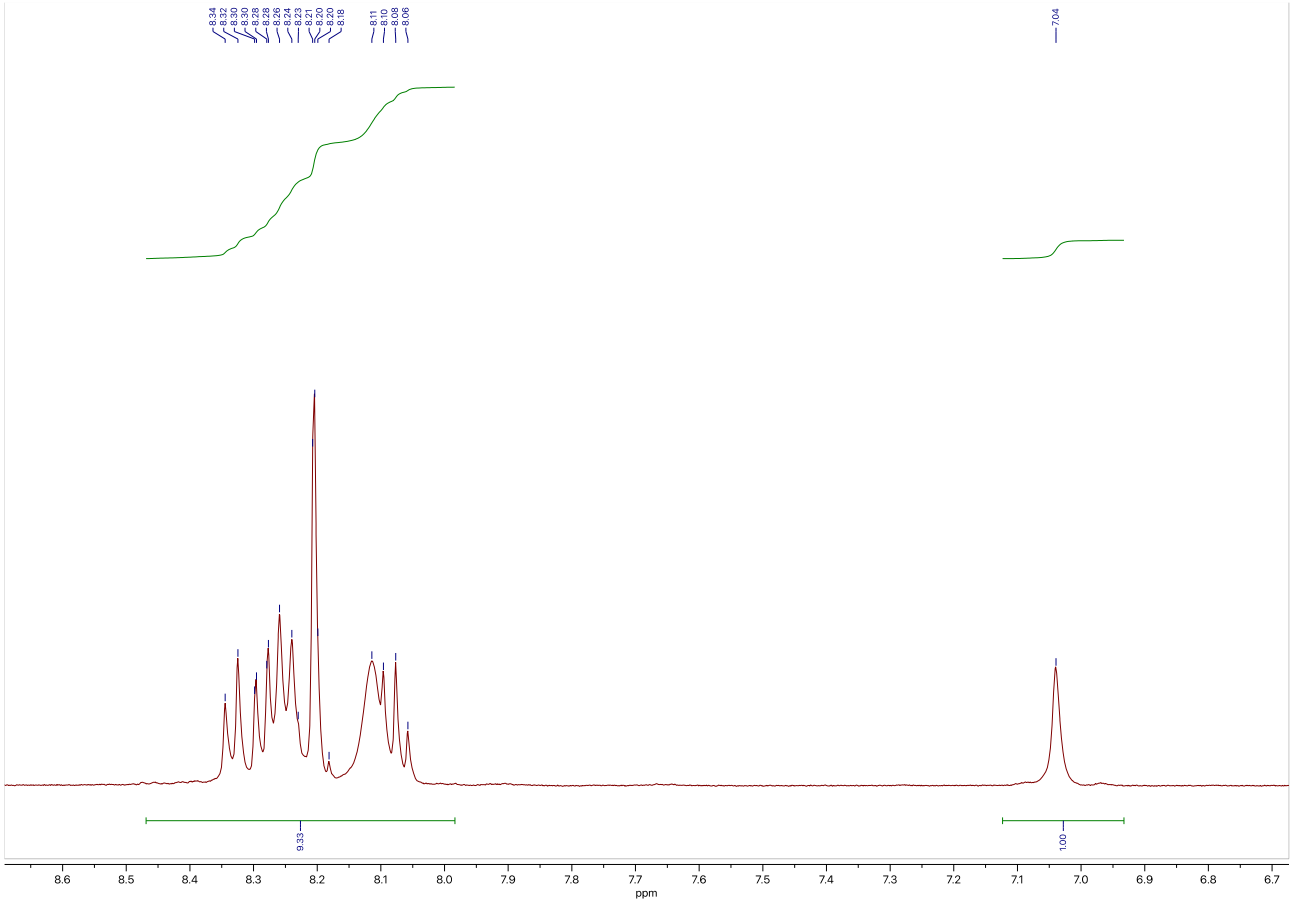


Figure S4. ^{1}H NMR spectrum and expanded region of **TTPyr$_3$** (400 MHz, CD_2Cl_2)

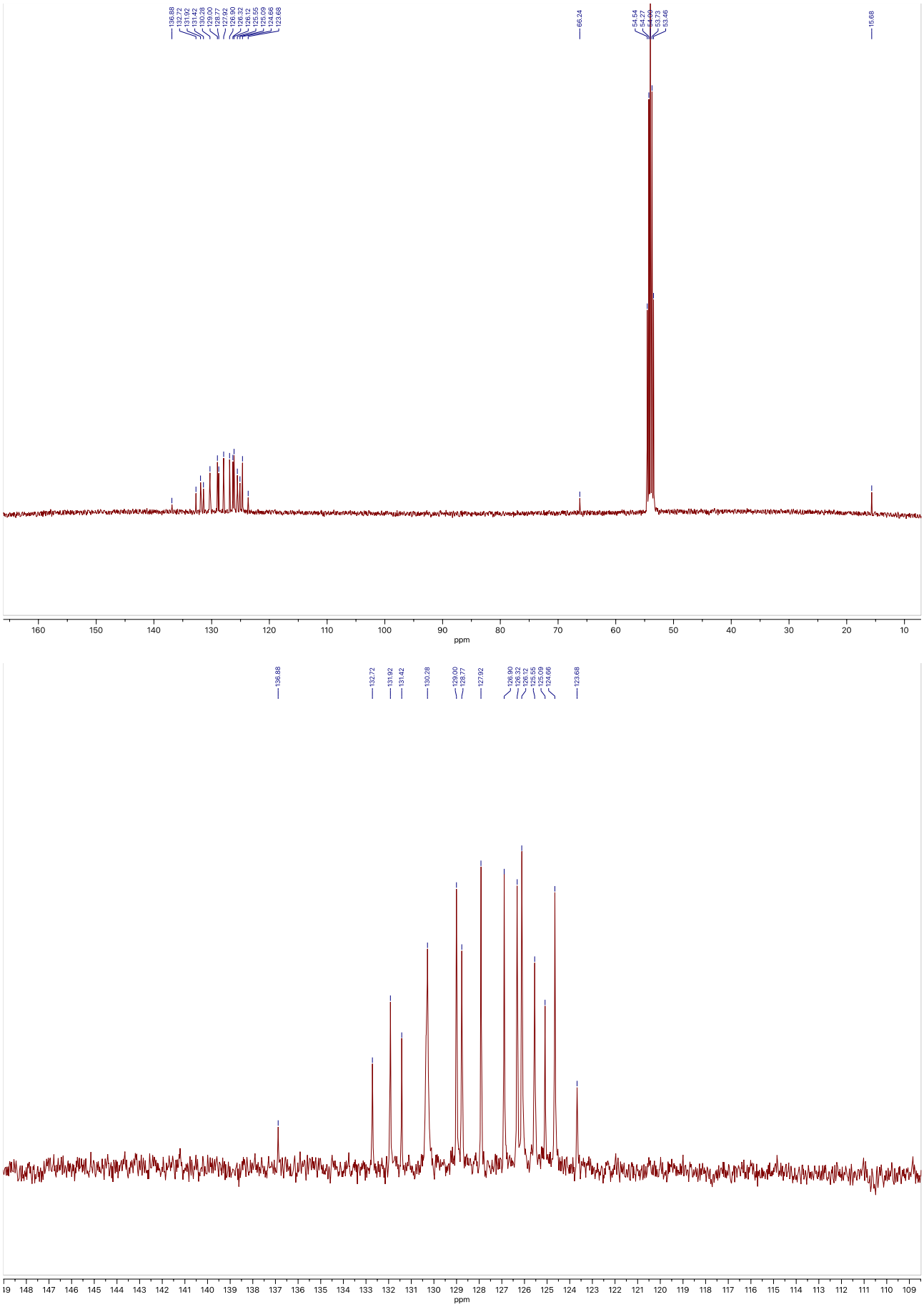


Figure S5. ^{13}C NMR spectrum and expanded region of **TTPyr$_3$** (400 MHz, CD_2Cl_2)

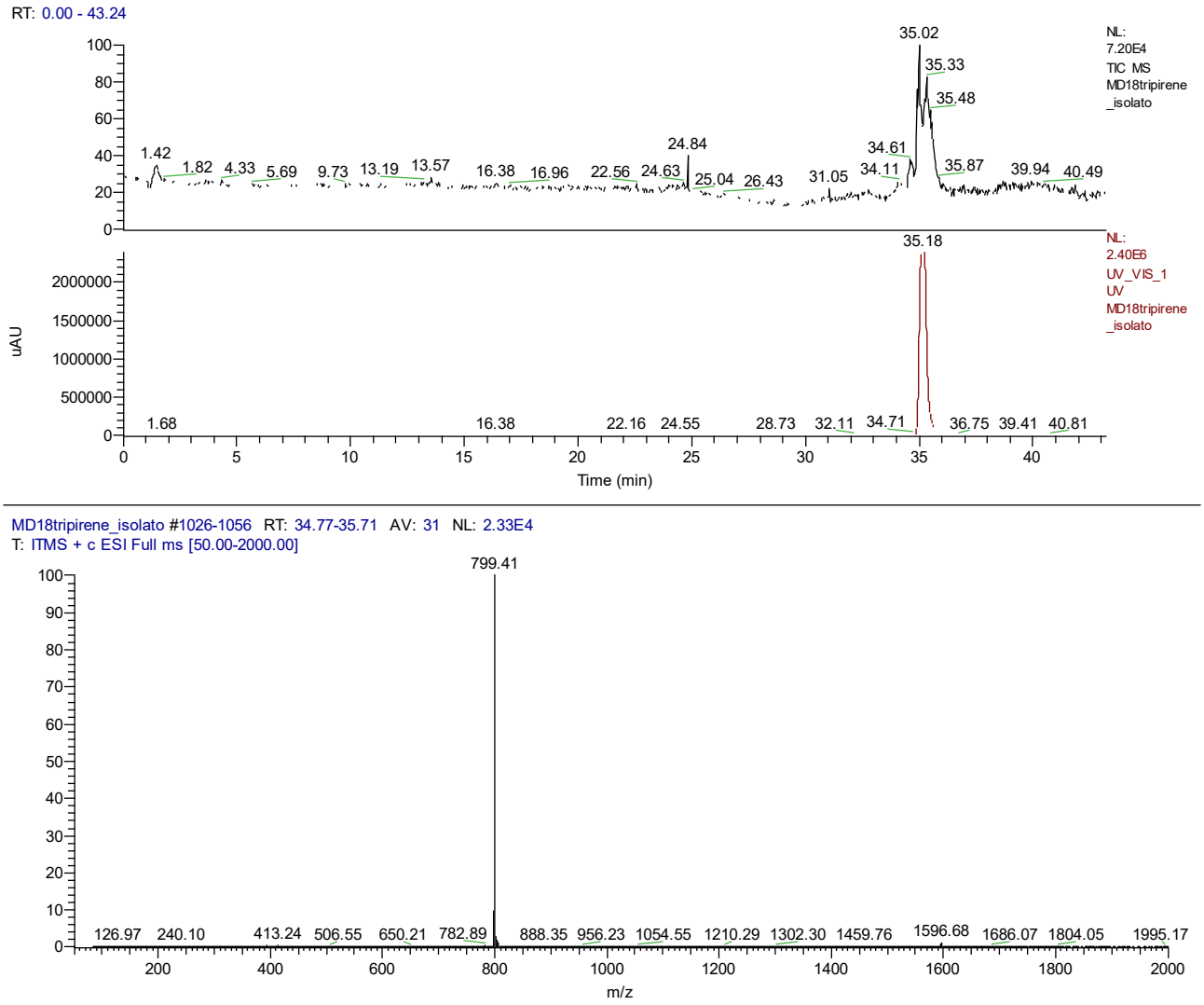


Figure S6. LC-MS profile of **TTPyr$_3$**

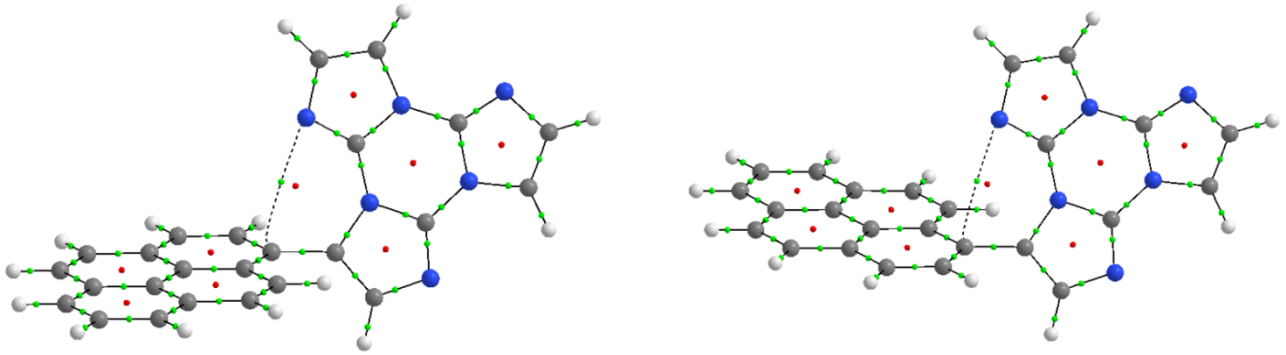


Figure S7. Molecular graphs of **TTPyr$_1$** in ground state RT (left) and HT (right) conformation with bond paths, bond critical points (green circles) and ring critical points (red circles).

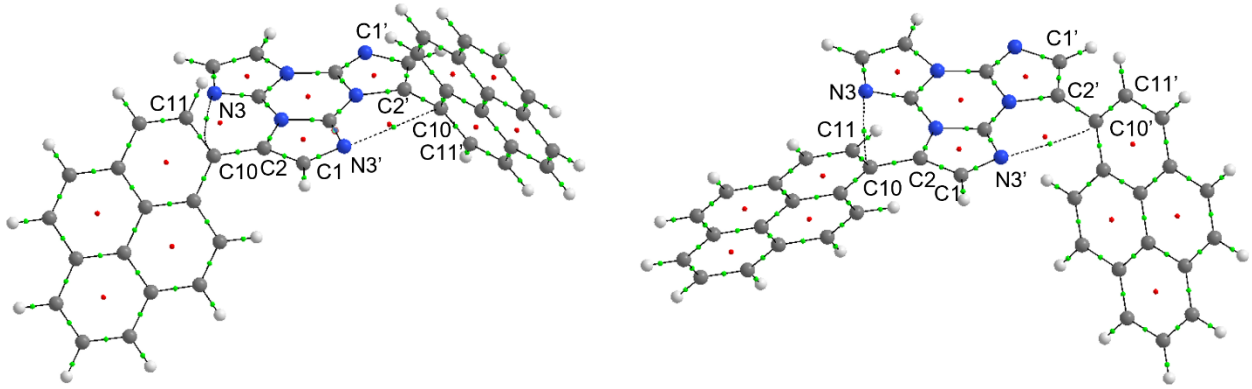


Figure S8. Molecular graphs of **TTPyr$_2$** in ground state RT/RT (left) and HT/HT (right) conformation with bond paths, bond critical points (green circles) and ring critical points (red circles).

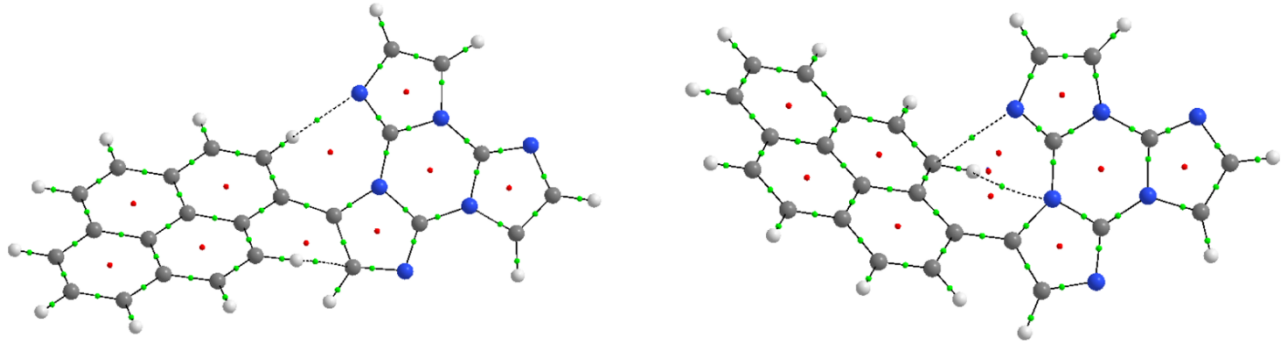


Figure S9. Molecular graphs of **TTPyr$_1$** in excited state RT (left) and HT (right) conformation with bond paths, bond critical points (green circles) and ring critical points (red circles).

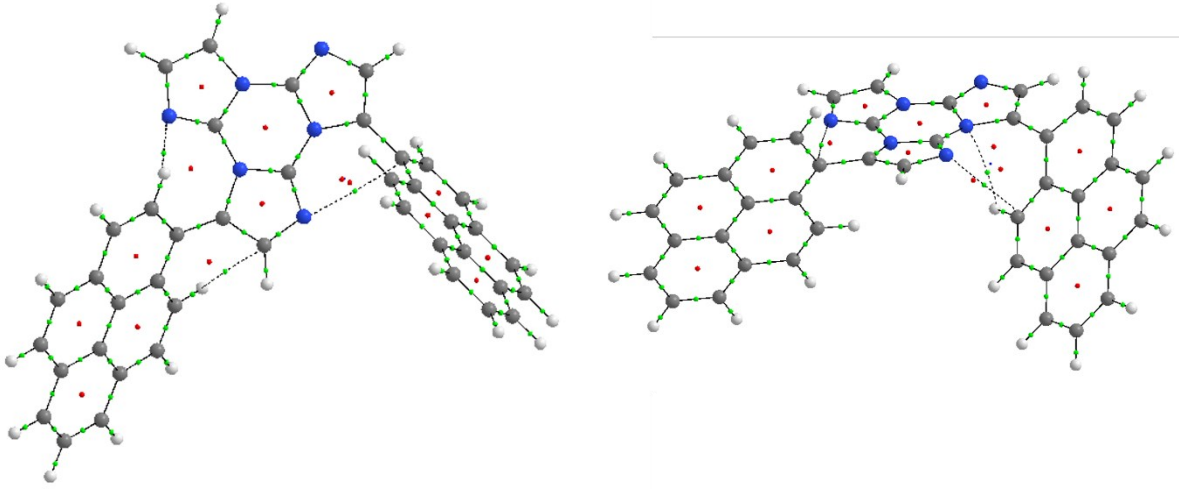


Figure S10. Molecular graphs of **TTPyr$_2$** in excited state RT/RT (left) and HT/HT (right) conformation with bond paths, bond critical points (green circles) and ring critical points (red circles).

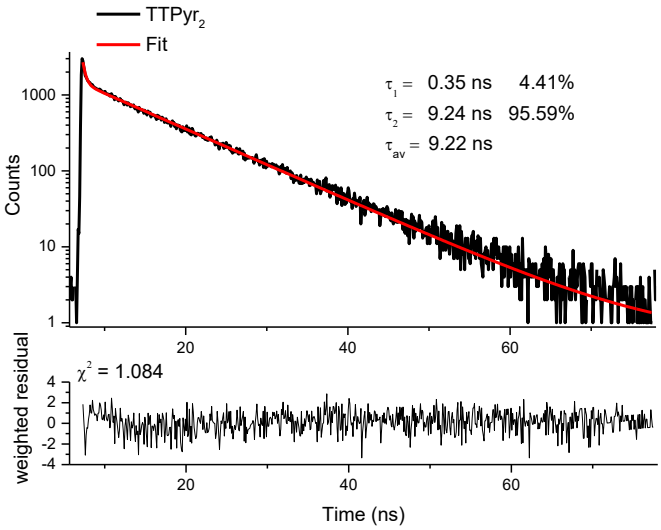


Figure S11. Lifetime measurement (λ_{exc} = 374 nm, λ_{em} = 420 nm) of **TTPyr₂** in DMSO at 298 K.

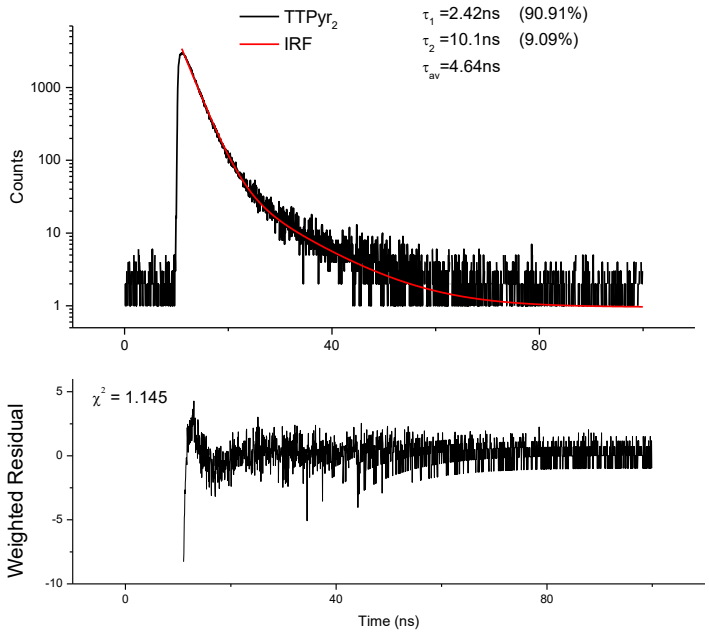


Figure S12. Lifetime measurement (λ_{exc} = 375 nm, λ_{em} = 490 nm) of **TTPyr₂** powders at 298 K.

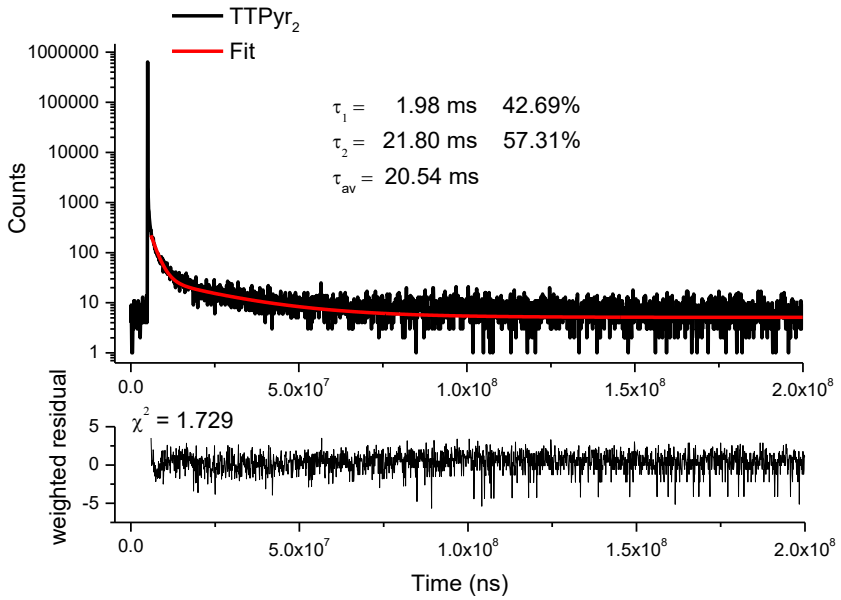


Figure S13. Lifetime measurement (λ_{exc} = 340 nm, λ_{em} = 530 nm) of **TTPyr$_2$** powders at 298 K.

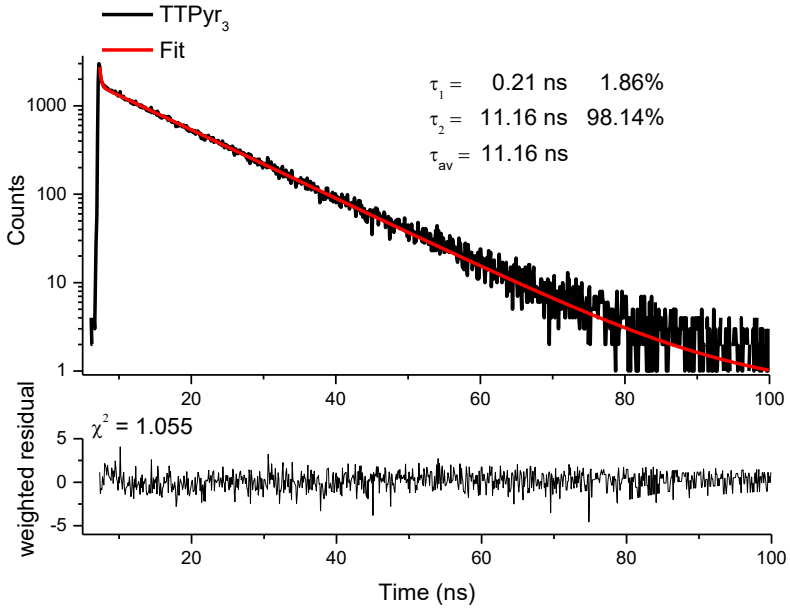


Figure S14. Lifetime measurement (λ_{exc} = 374 nm, λ_{em} = 420 nm) of **TTPyr$_3$** in DMSO at 298 K.

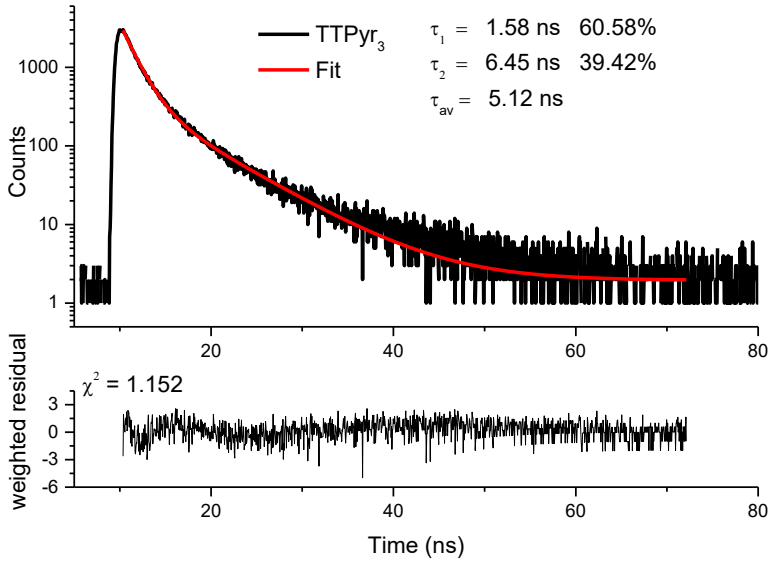


Figure S15. Lifetime measurement (λ_{exc} = 300 nm, λ_{em} = 470 nm) of **TTPyr$_3$** powders at 298 K.

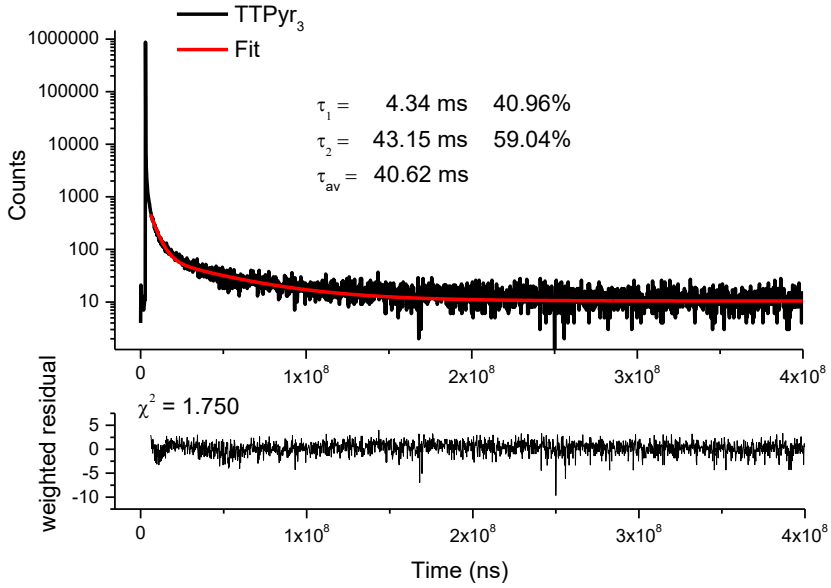


Figure S16. Lifetime measurement (λ_{exc} = 340 nm, λ_{em} = 520 nm) of **TTPyr$_3$** powders at 298 K.

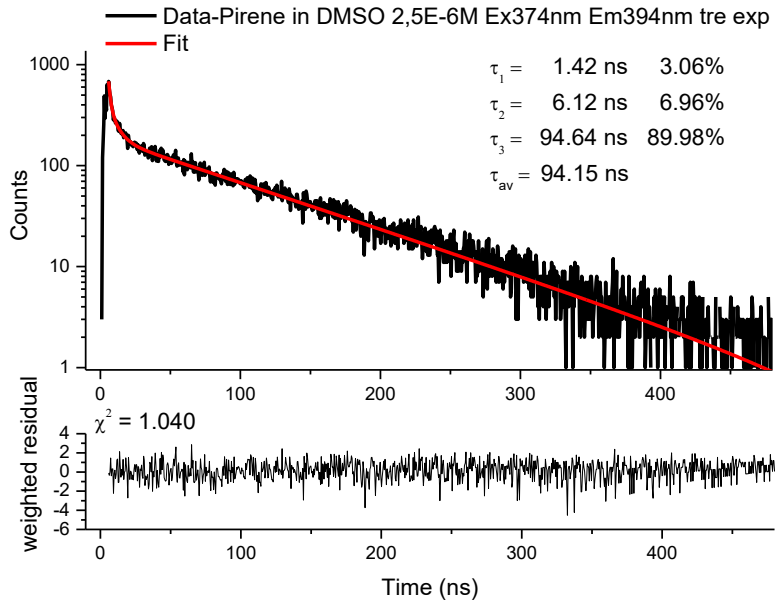


Figure S17. Lifetime measurement (λ_{exc} = 374 nm, λ_{em} = 394 nm) of **Pyrene** in DMSO at 298 K.

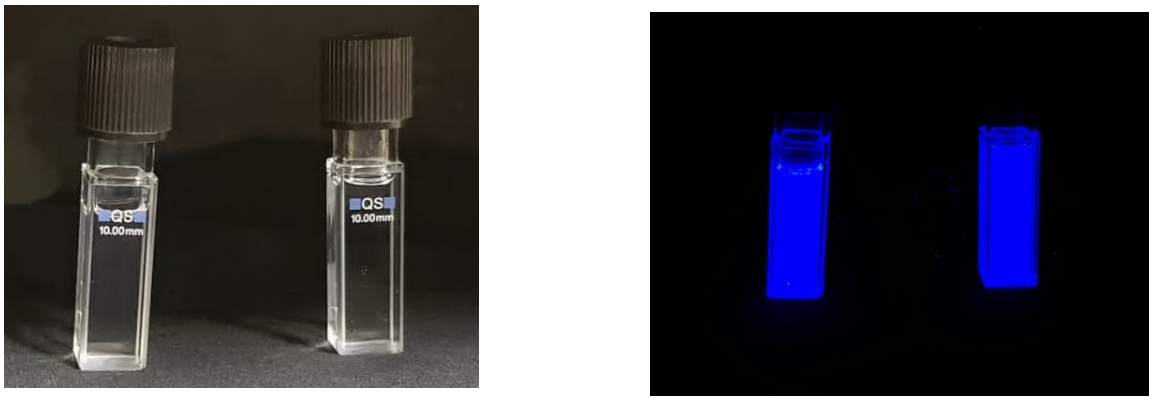


Figure S18. Photographs of **TTPyr$_2$** (left) and **TTPyr$_3$** (right) solutions under UV light OFF (left) or UV light ON (right, λ_{exc} = 366 nm)

Figure S19. Photographs of powders of **TTPyr$_2$** (left) and **TTPyr$_3$** (right) under UV light OFF (left) or UV light ON (right, λ_{exc} = 366 nm)

Table S1. Excitation energies (nm), oscillator strength (*f*) and composition of the first singlet transitions computed for pyrene, **TT-Pyr$_1$** (HT and RT conformations) and **TT-Pyr$_2$** (HT/HT and RT/RT conformations).[a]

Molecule	S_1, *f* weights	S_2, *f* weights	S_3, *f* weights	S_4, *f* weights	S_5, *f* weights	S_6, *f* weights	S_7, *f* weights	S_8, *f* Weights
Pyrene	ES_1		ES_2					
	301, *0.0003* H-1→L (**44**%) H→L+1 (**52**%)	294, *0.347* H→L (**87**%)	249, *0.0000* H→L+5 (**86**%)	231, *0.526* H-1→L (**54**%) H→L+1 (**46**%)				
TT-Pyr$_1$ conf. HT	ES_1		ES_2					
	304, *0.229* H-1→L (21%) H→L (**42**%) H→L+1 (26%)	302, *0.257* H-1→L (17%) H→L (**47**%) H→L+1 (22%)	249, *0.0045* H-5→L (13%) H→L+9 (**64**%)	237, *0.718* H-1→L (**43**%) H→L+1 (**35**%)				
TT-Pyr$_1$ conf. RT	304, *0.060* H-1→L (**35**%) H→L (10%) H→L+1 (**43**%)	302, *0.498* H→L (**79**%)	251, *0.008* H→L+9 (**66**%)	238, *0.570* H-1→L (**42**%) H→L+1 (**31**%)				
	ES_1				ES_2			
TT-Pyr$_2$ conf. HT/HT	306, *0.380* H-1→L+1 (**33**%) H→L (**35**%)	304, *0.101* H-3→L (16%) H-2→L+1(14%) H-1→L+2 (12%) H→L+2 (12%)	303, *0.066* H-3→L+1 (15%) H-2→L (12%) H-1→L+2 (12%) H→L+3 (12%)	301, *0.445* H-1→L (**35**%) H→L+1(**37**%)	249, *0.003* H-1→L+13(**34**%) H→L+15(17%)	249, *0.007* H-1→L+15 (**22**%) H→L+13 (**20**%) H→L+15 (12%)	238, *1.272* H-3→L+1 (**20**%) H-2→L (**22**%) H-1→L+3 (12%) H→L+4 (12%)	237, *0.198* H-3→L (10%) H-2→L+1 (17%)
TT-Pyr$_2$ conf. RT/RT	ES_1				ES_2			
	306, *0.709* H-1→L (**35**%) H-1→L+1(10%) H→L (11%) H→L+1 (**30**%)	304, *0.011* H-2→L+1(**34**%) H→L+3 (**38**%)	303, *0.132* H-3→L (**25**%) H-1→L+2(**28**%) H→L+1 (18%)	301, *0.258* H-1→L (**41**%) H→L+1(**27**%)	251, *0.012* H→L+13(**53**%)	249, *0.004* H-1→L+14 (**34**%) H-1→L+15 (**19**%)	240, *0.641* H-2→L+1 (**37**%) H→L+3 (**22**%)	237, *0.758* H-3→L (**37**%) H-1→L+2 (**26**%)

[a]H and L stand for HOMO and LUMO, respectively; only contributions with weight ≥ 10% are reported.

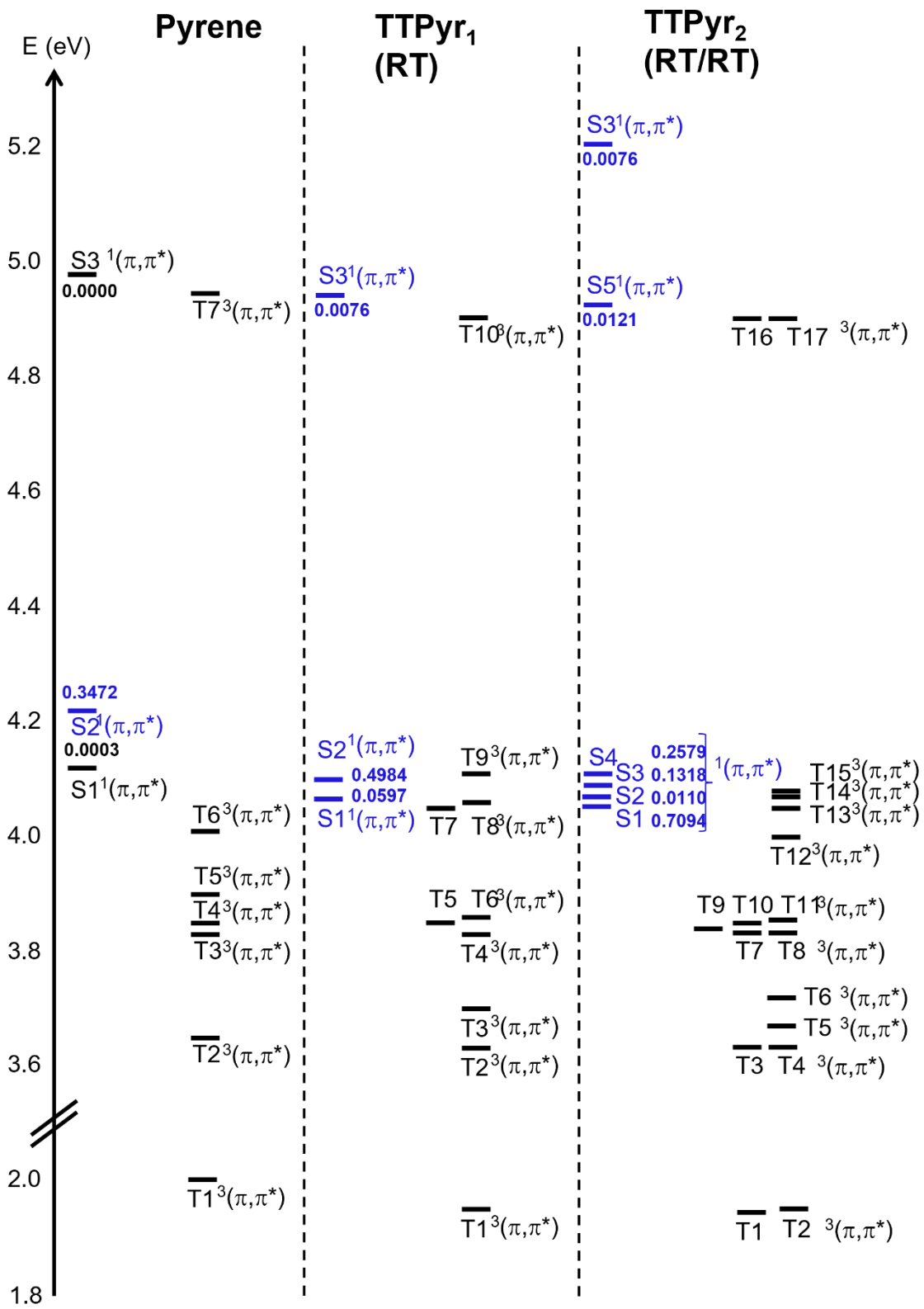


Figure S20. Electronic levels computed for pyrene, **TTPyr$_1$** and **TTPyr$_2$** at molecular level. In blue are reported the singlet levels with oscillator strength $f \geq 0.001$ and the corresponding values of f (see detailed information in Table S1).

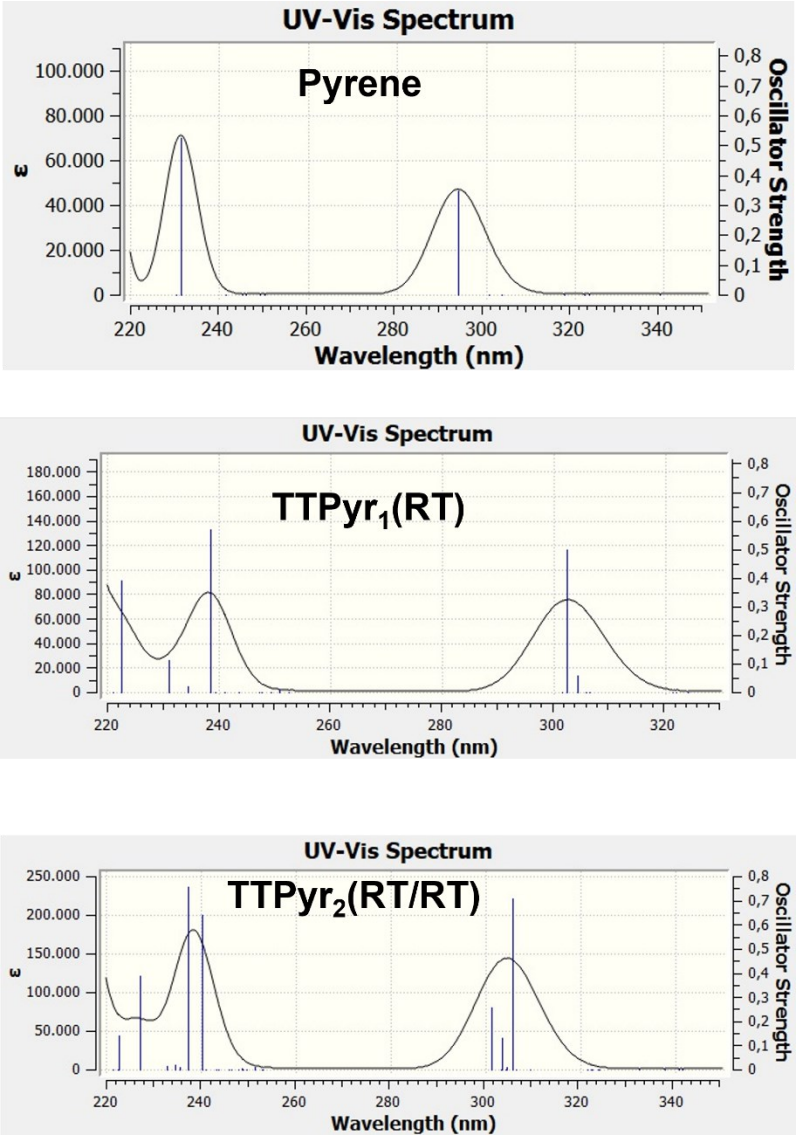


Figure S21. Simulated absorption spectra of pyrene (top), **TTPyr$_1$**, RT conformation (middle) and **TTPyr$_2$**, RT/RT conformation (bottom) at ωB97X/6-311++G(d,p) level of theory, resulting from convolution of the singlet excitation energies with 0.1 eV of half-bandwidth (singlet levels plotted as blue sticks according to their oscillator strength).

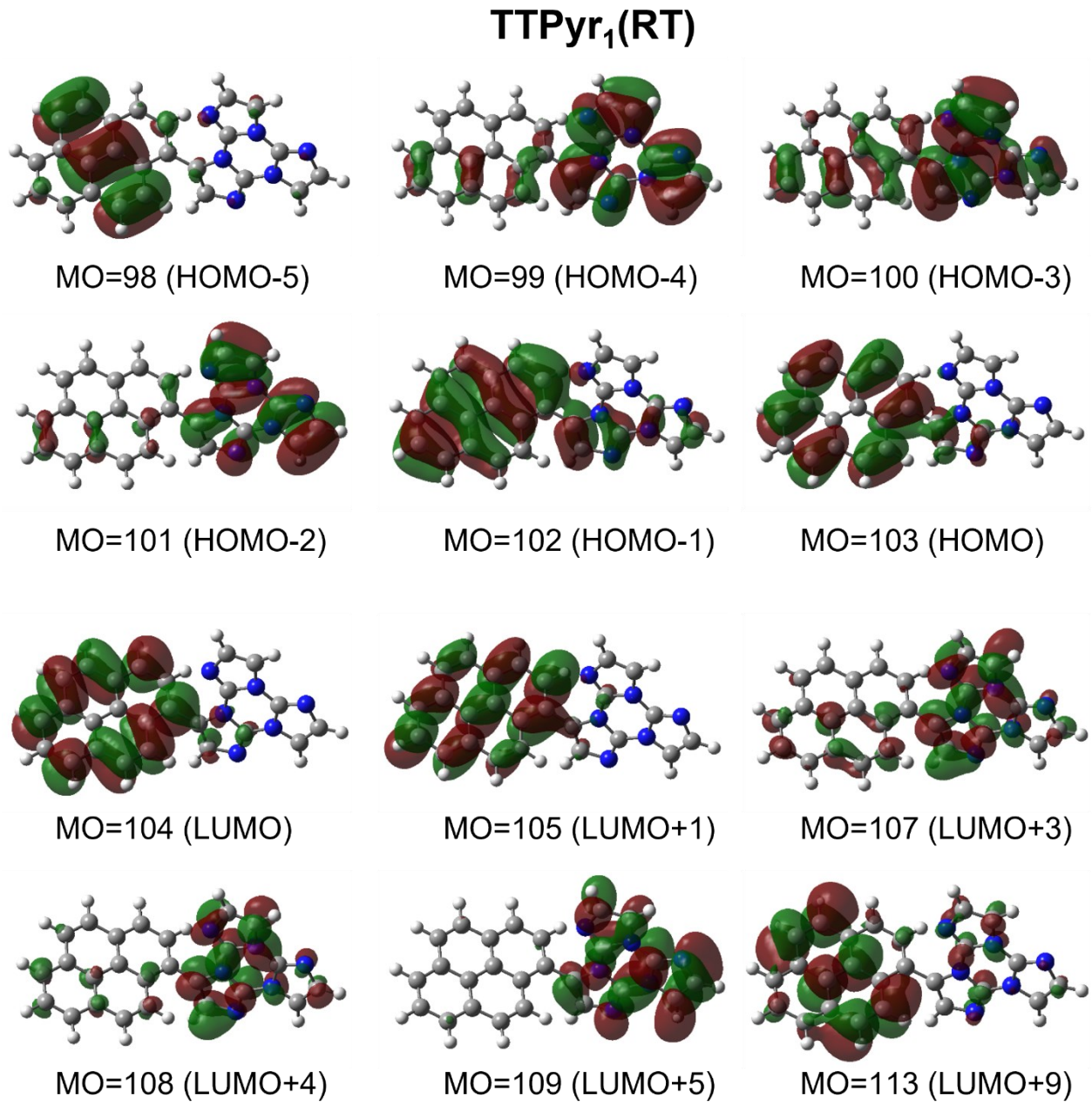


Figure S22. Plots of the ωB97X/6-311++G(d,p) MOs mainly involved in the lowest energy transitions of **TT-Pyr$_1$** in RT conformation (isosurfaces value 0.02).

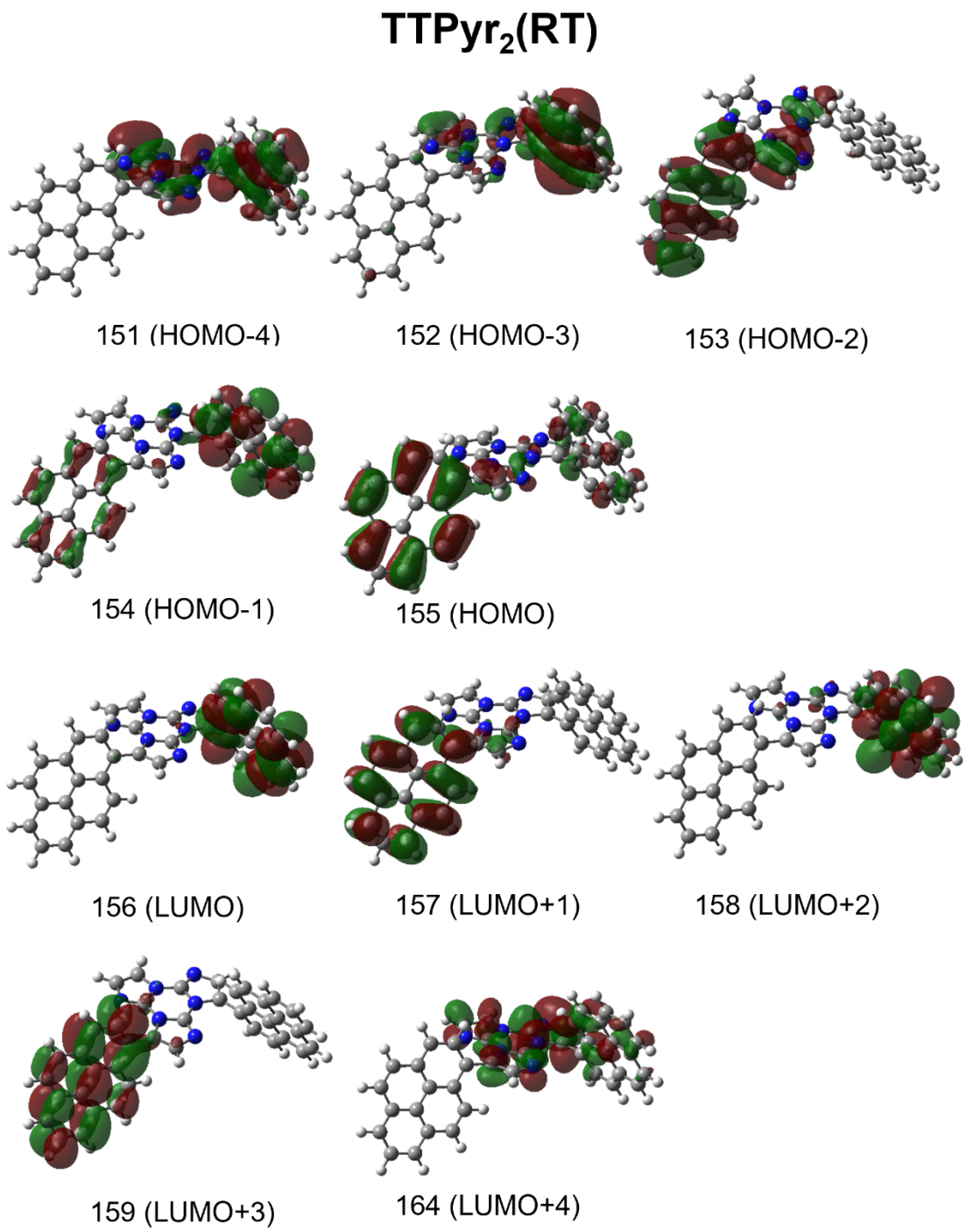


Figure S23. Plots of the ωB97X/6-311++G(d,p) MOs mainly involved in the lowest energy transitions of **TT-Pyr$_2$** in RT/RT conformation (isosurfaces value 0.02).