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Supporting Information

Interplay Between Singlet and Triplet Excited States in a Conformationally Locked Donor-Acceptor Dyad

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NMR and mass-spectra

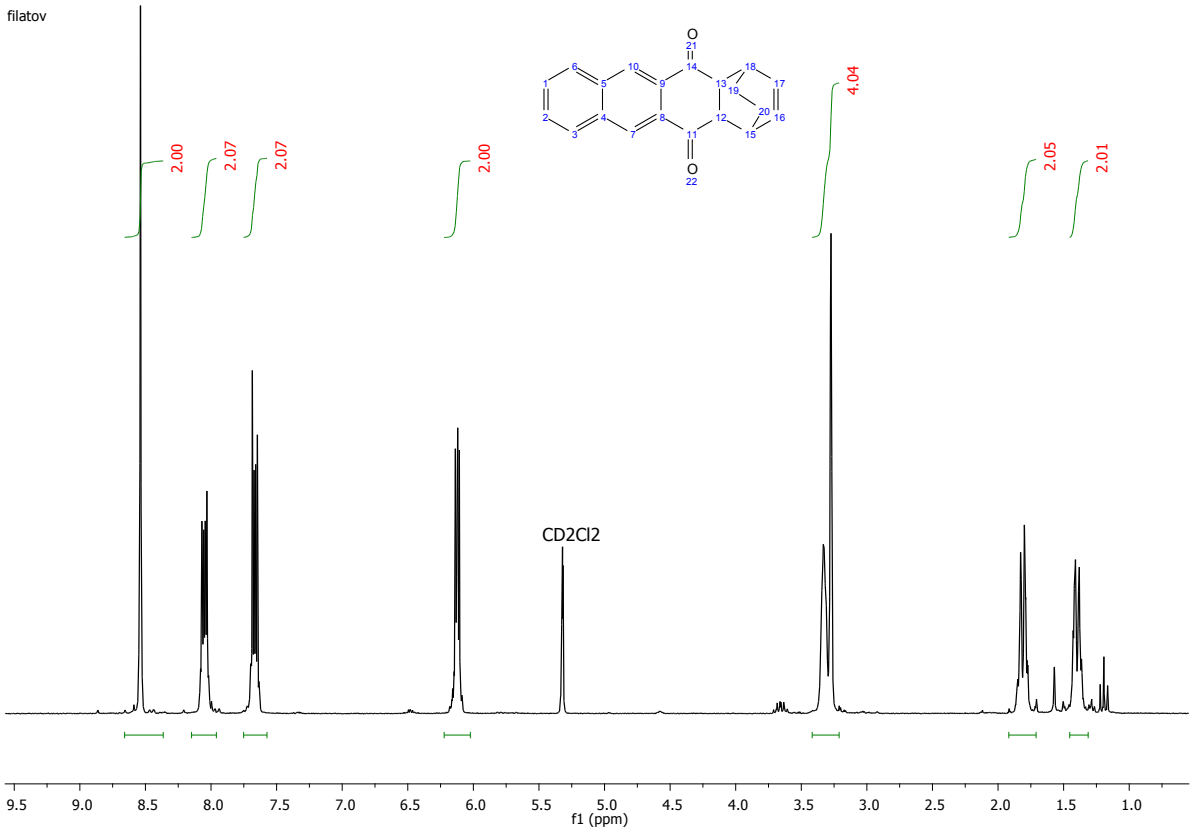


Figure S1. ^{1}H NMR specrum of **2** (250 MHz, CD_2Cl_2, 298 K).

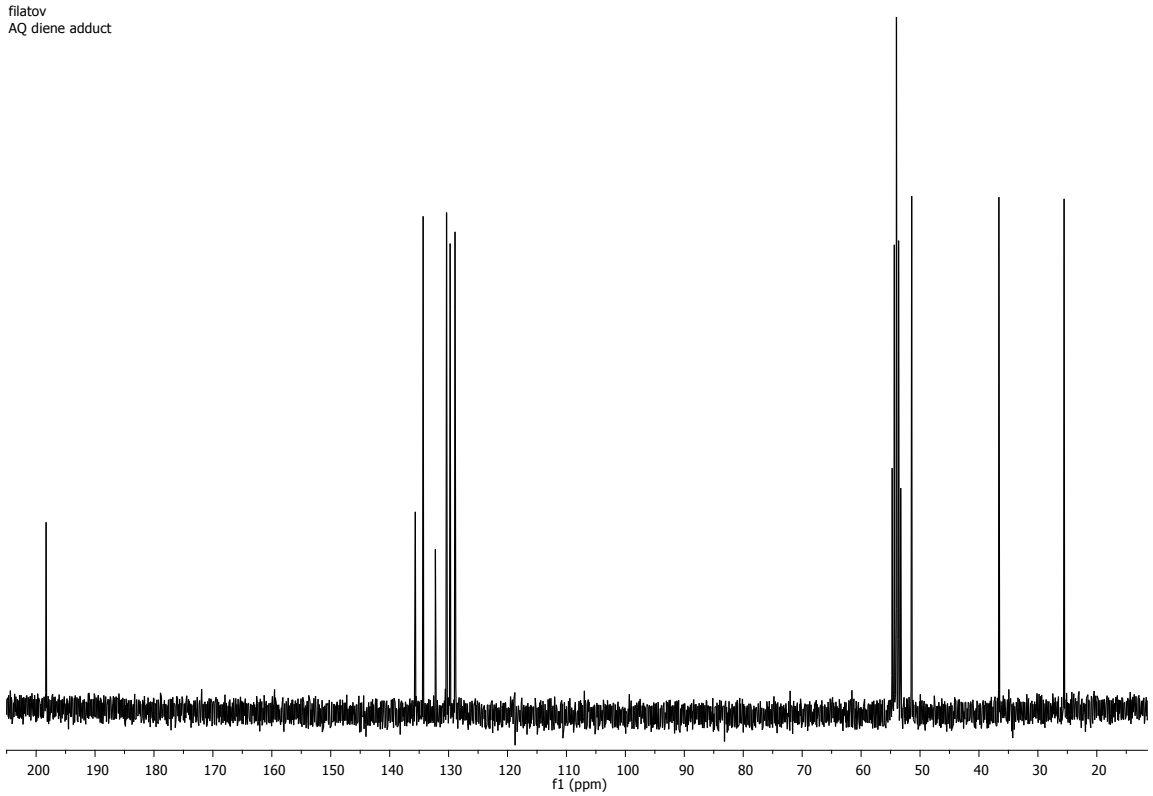


Figure S2. ^{13}C NMR specrum of **2** (75 MHz, CD_2Cl_2, 298 K).

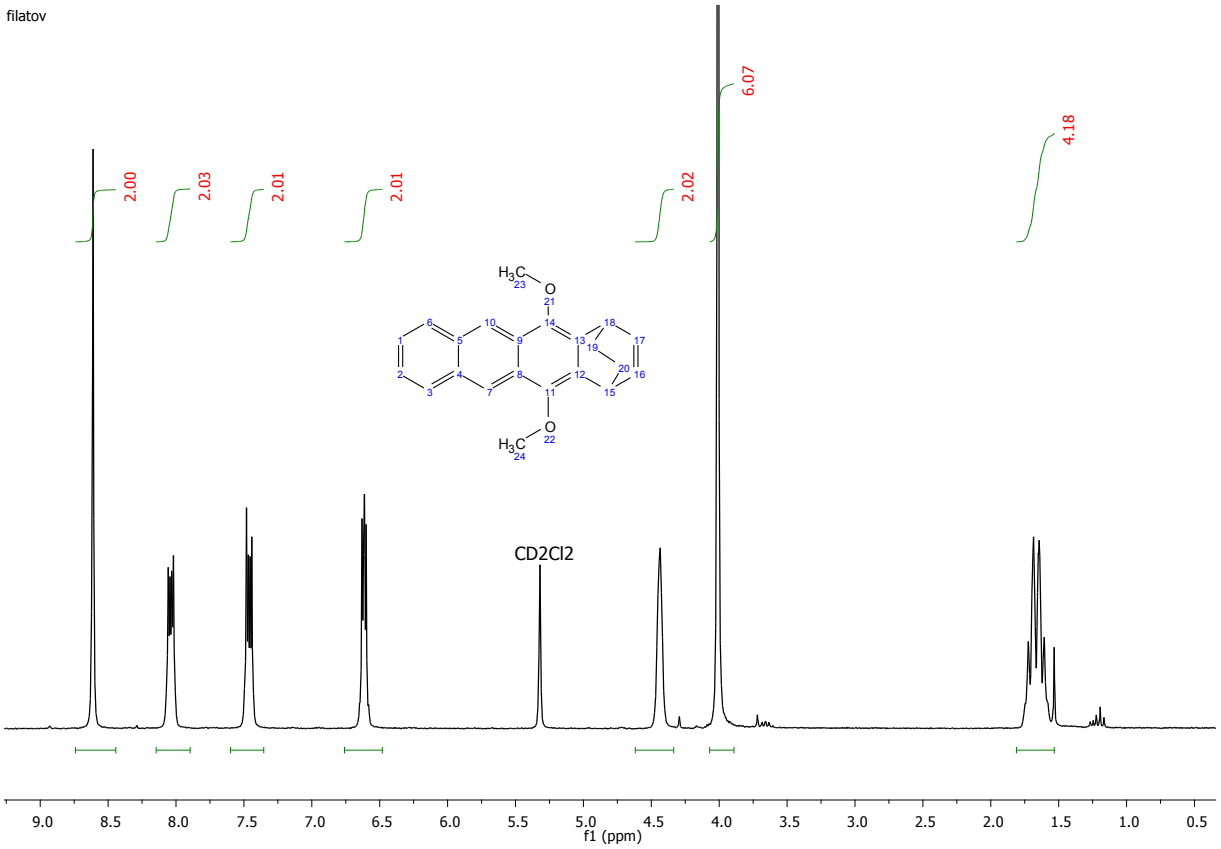


Figure S3. ^{1}H NMR specrum of **3** (250 MHz, CD_2Cl_2, 298 K).

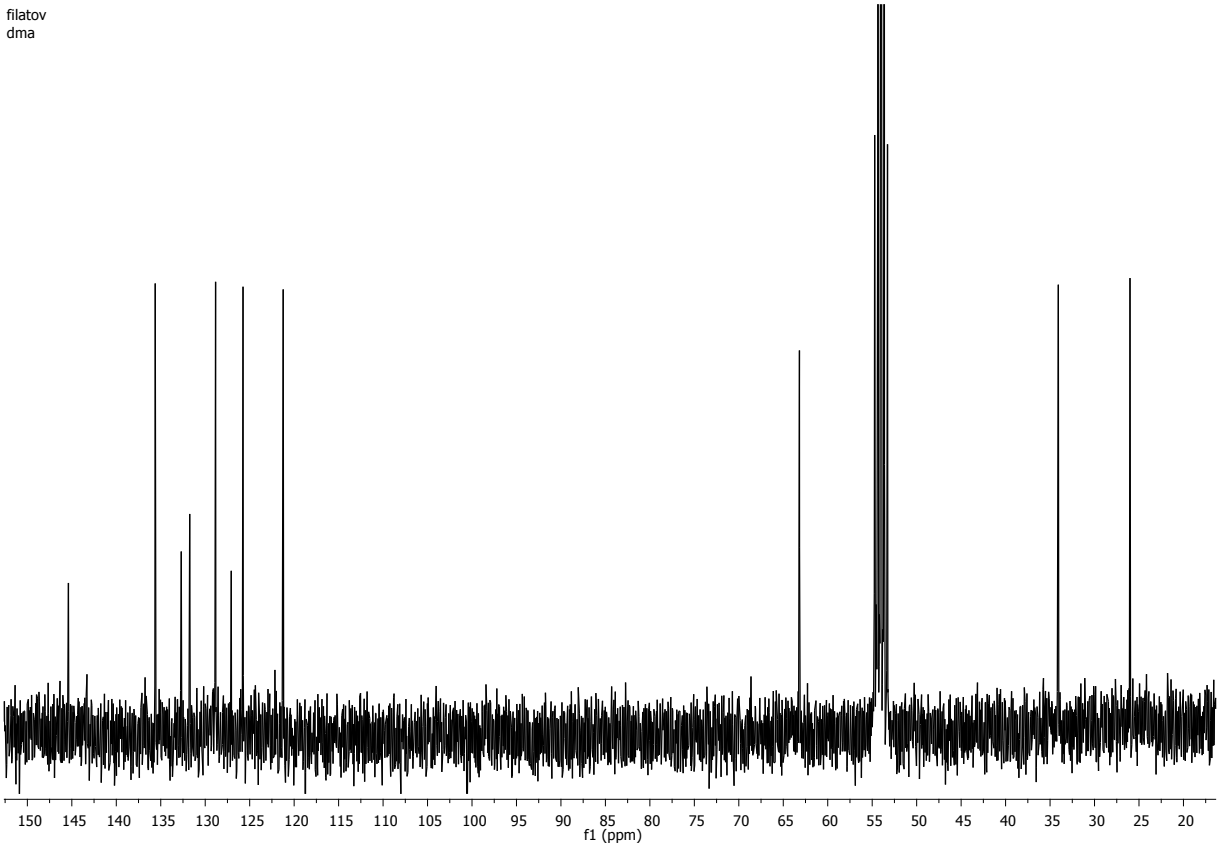


Figure S4. ^{13}C NMR specrum of **3** (75 MHz, CD_2Cl_2, 298 K).

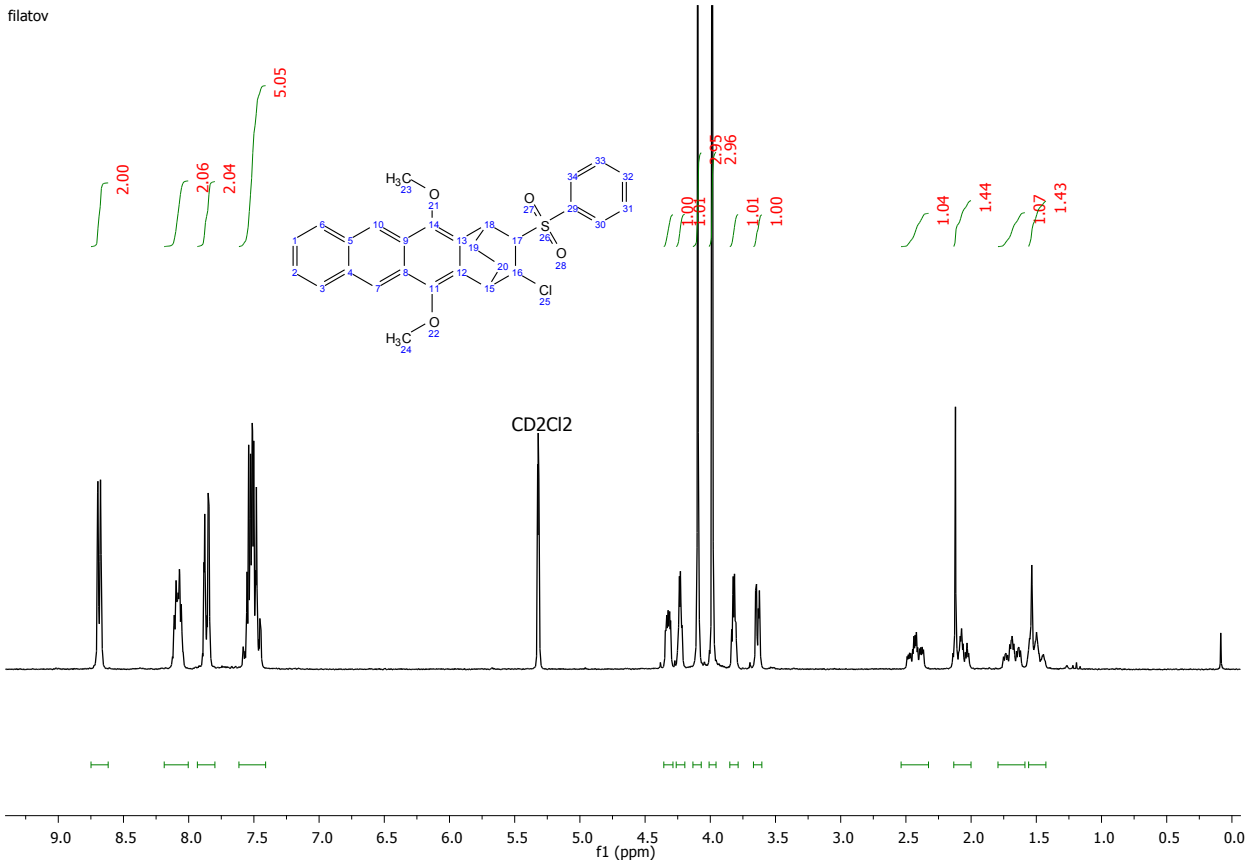


Figure S5. ^{1}H NMR specrum of **4** (250 MHz, CD_2Cl_2, 298 K).

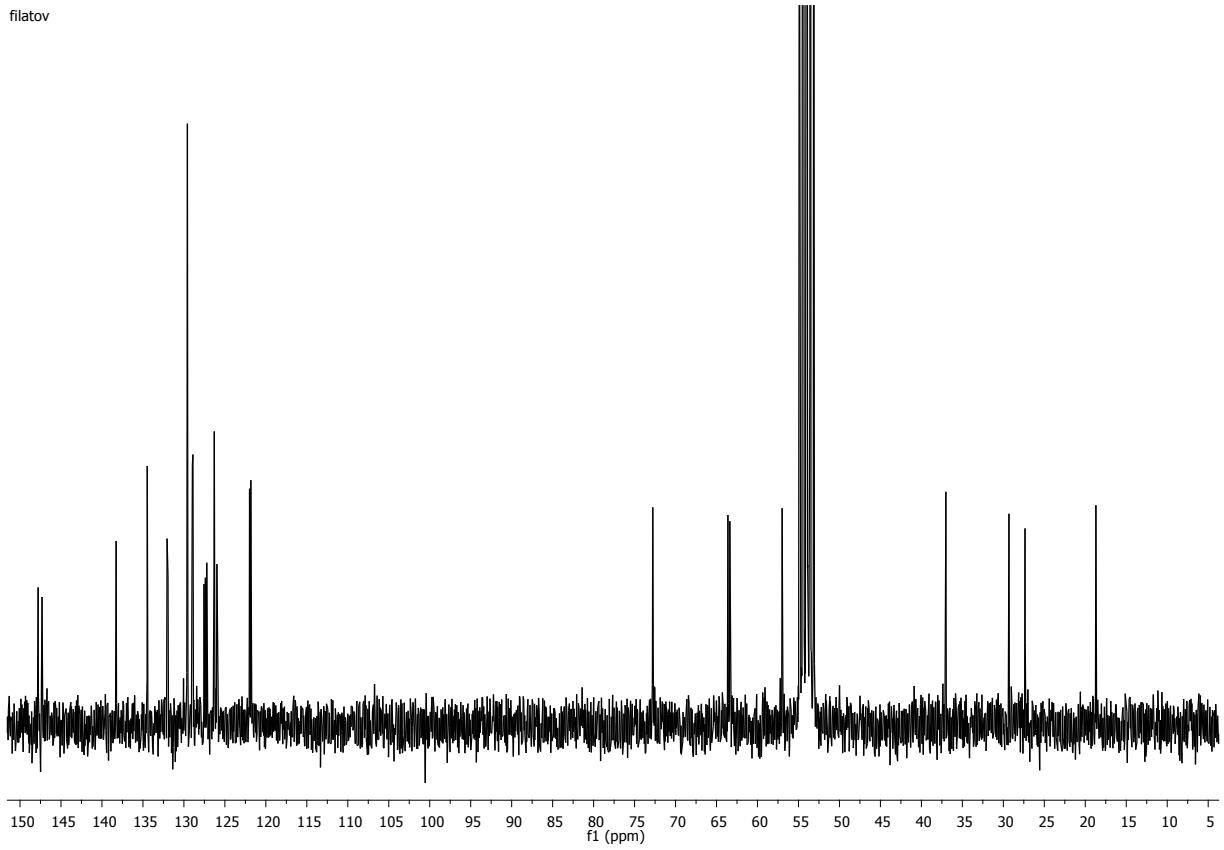


Figure S6. ^{13}C NMR specrum of **4** (63 MHz, CD_2Cl_2, 298 K).

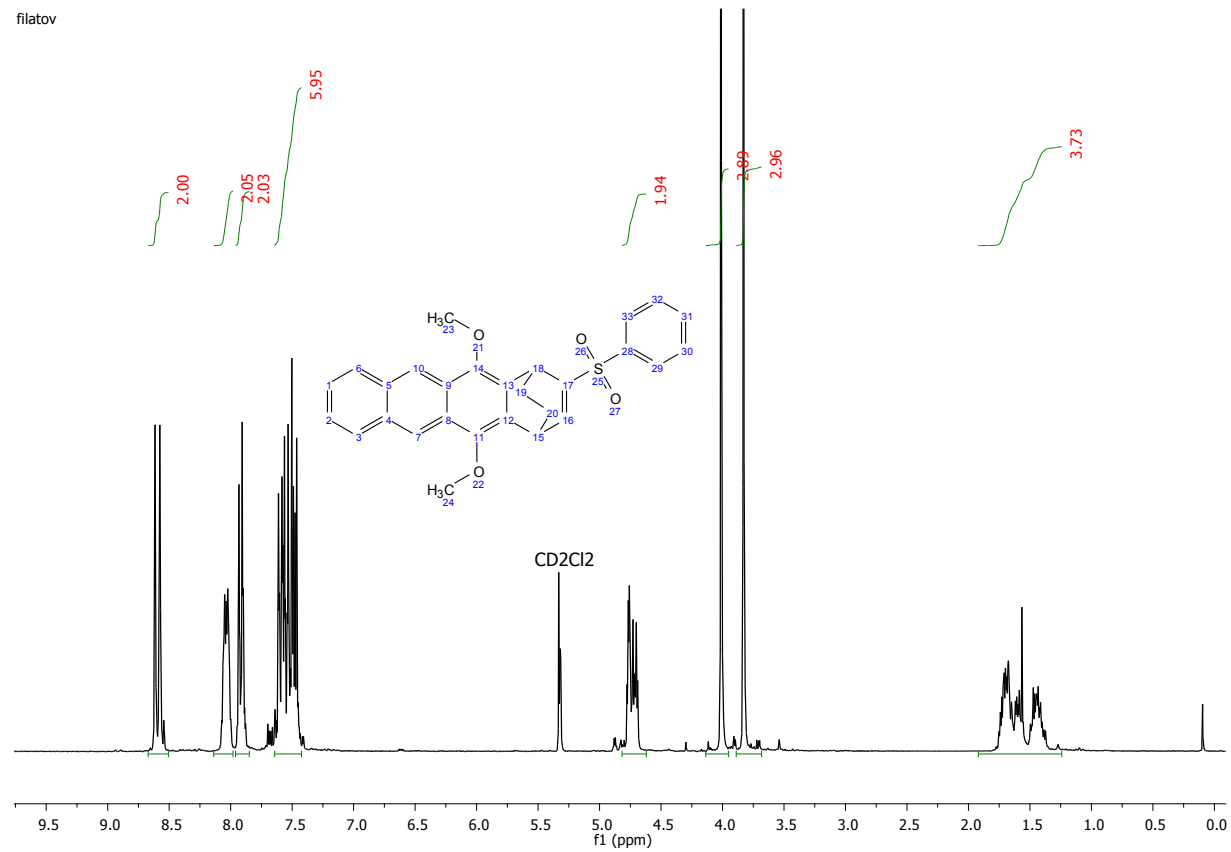


Figure S7. ^{1}H NMR specrum of **5** (250 MHz, CD_2Cl_2, 298 K).

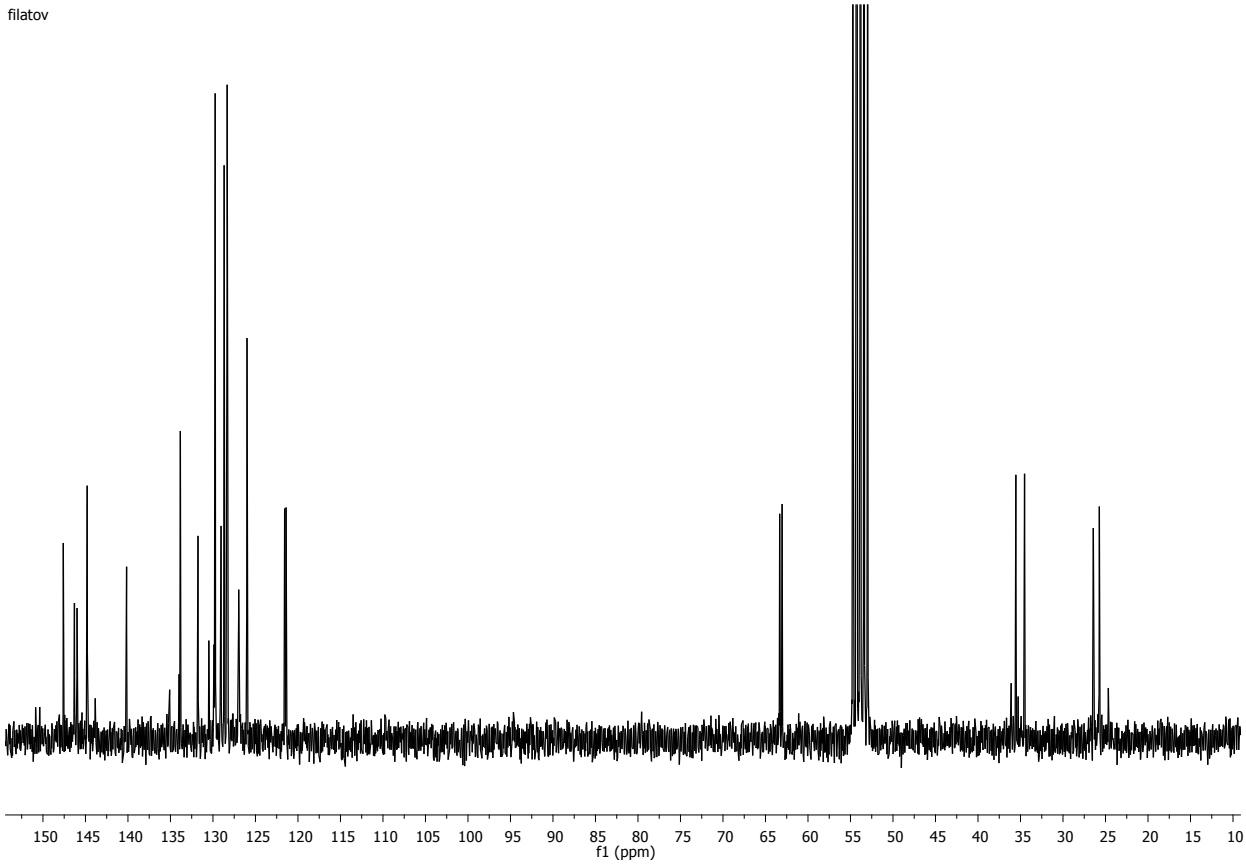


Figure S8. ^{13}C NMR specrum of **5** (63 MHz, CD_2Cl_2, 298 K).

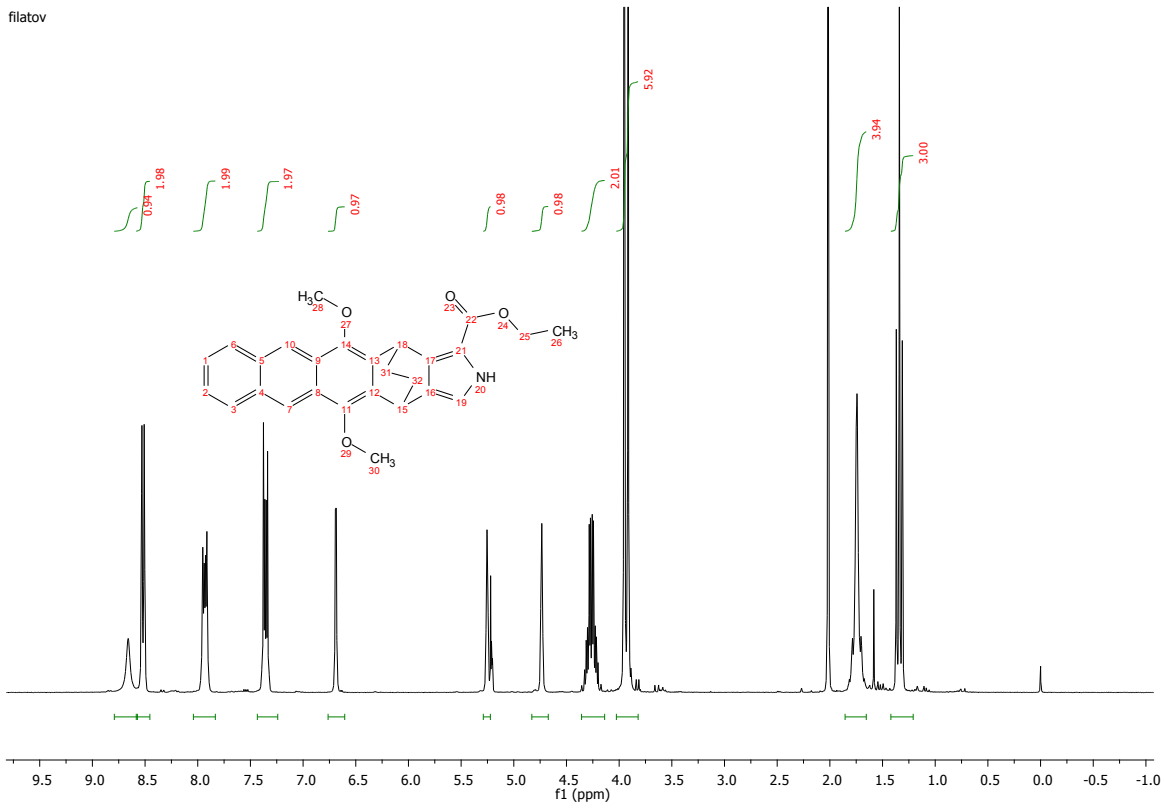


Figure S9. ^{1}H NMR specrum of **6** (250 MHz, CD_2Cl_2, 298 K).

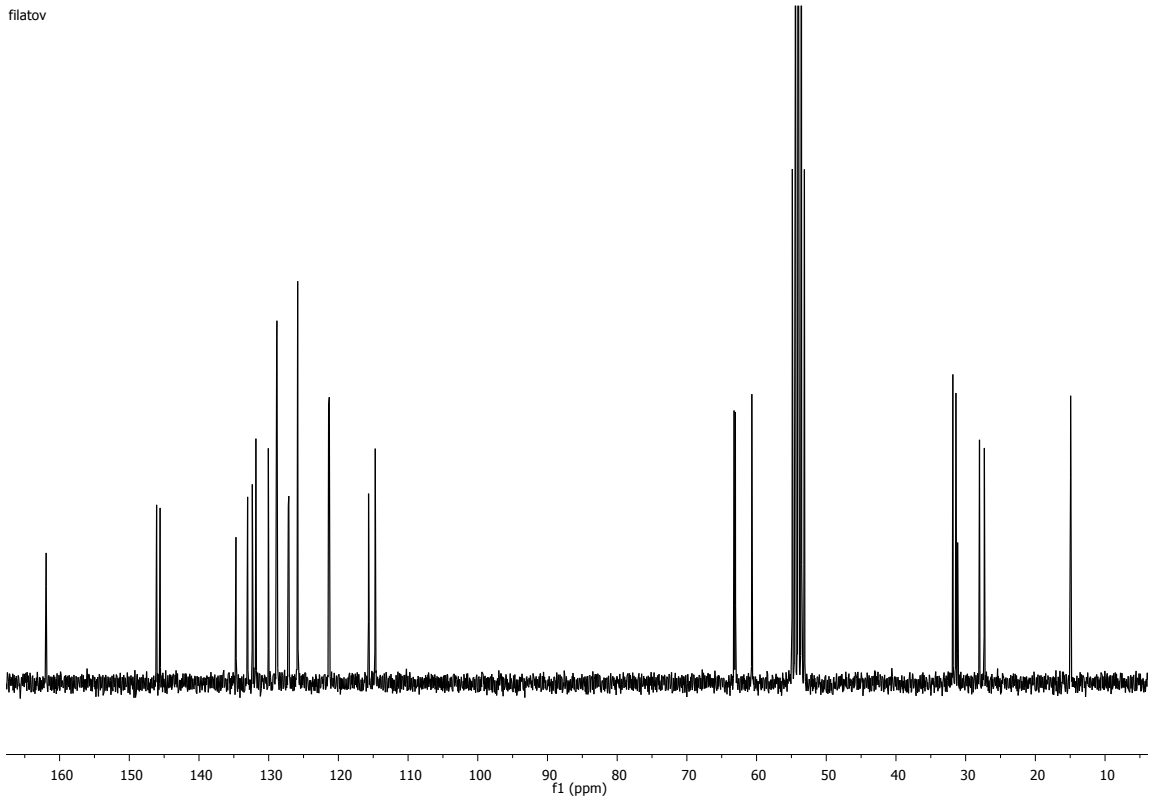


Figure S10. ^{13}C NMR specrum of **6** (63 MHz, CD_2Cl_2, 298 K).

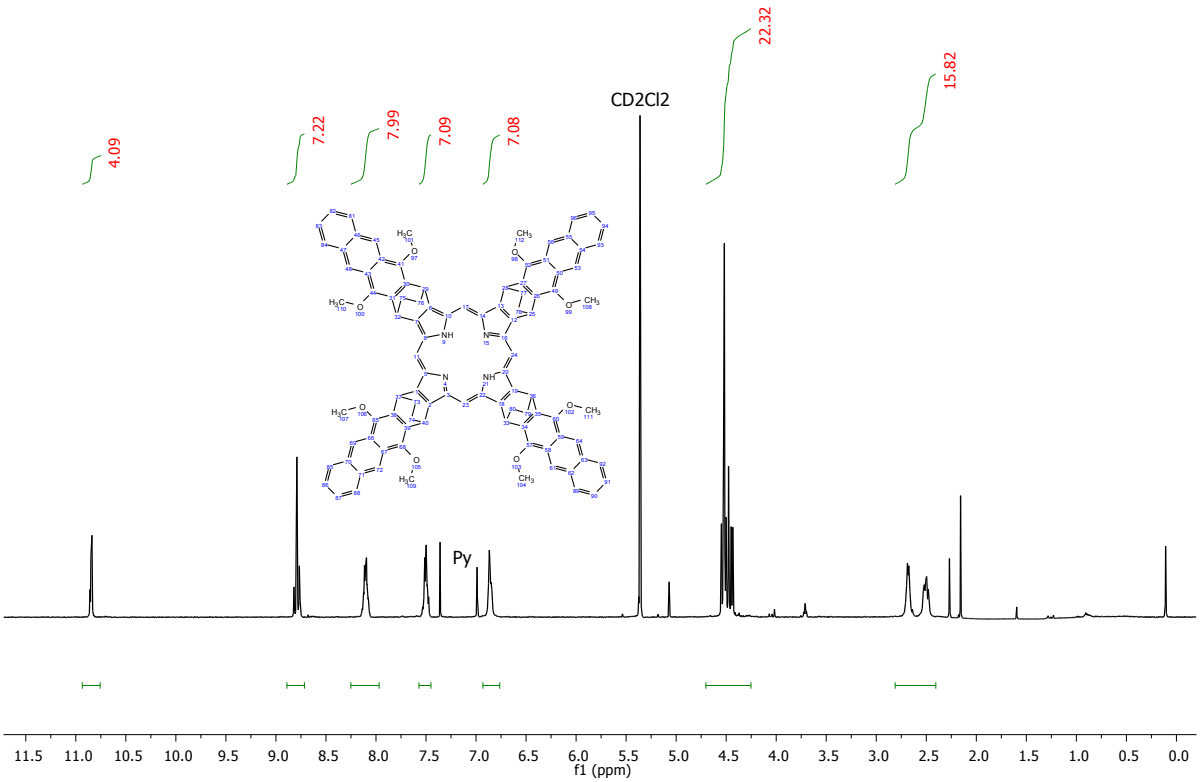


Figure S11. ^{1}H NMR specrum of **8** in a free-base form (250 MHz, CD_2Cl_2, 298 K).

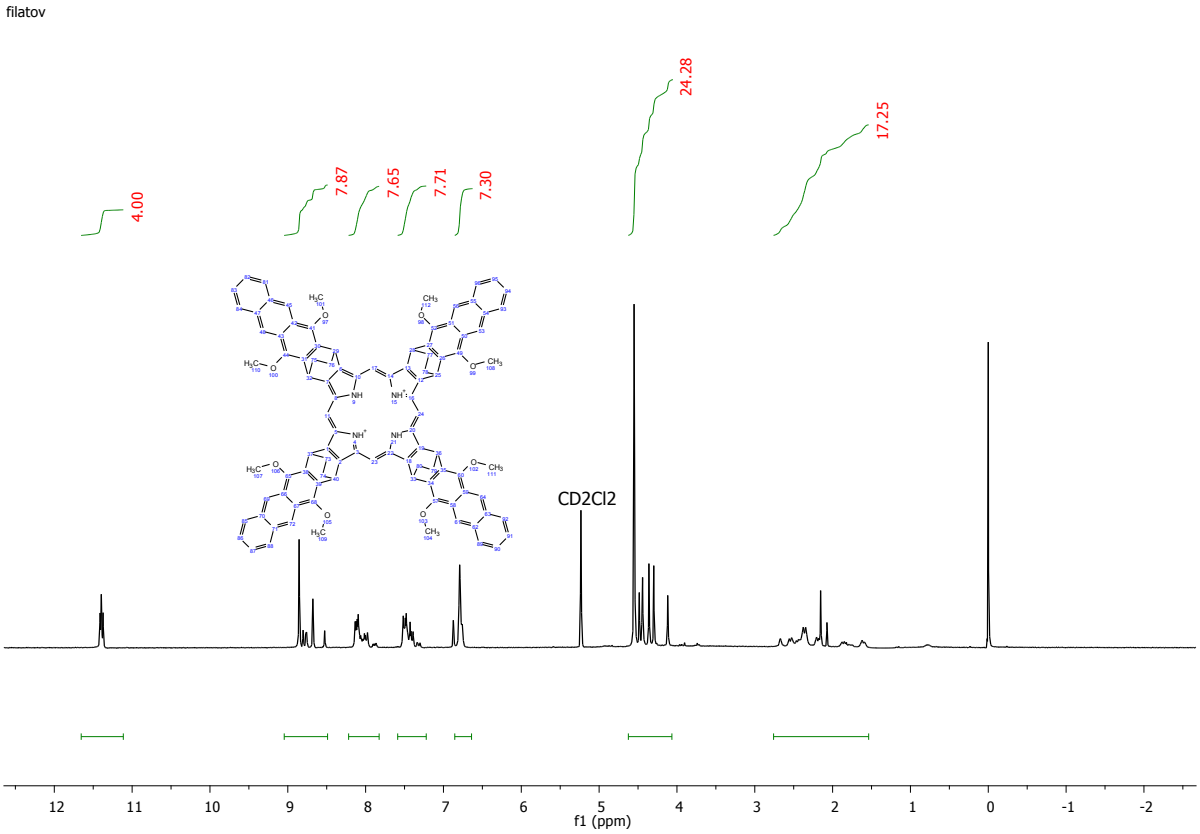


Figure S12. ^{1}H NMR specrum of **8** in a protonated form (250 MHz, CD_2Cl_2, 298 K).

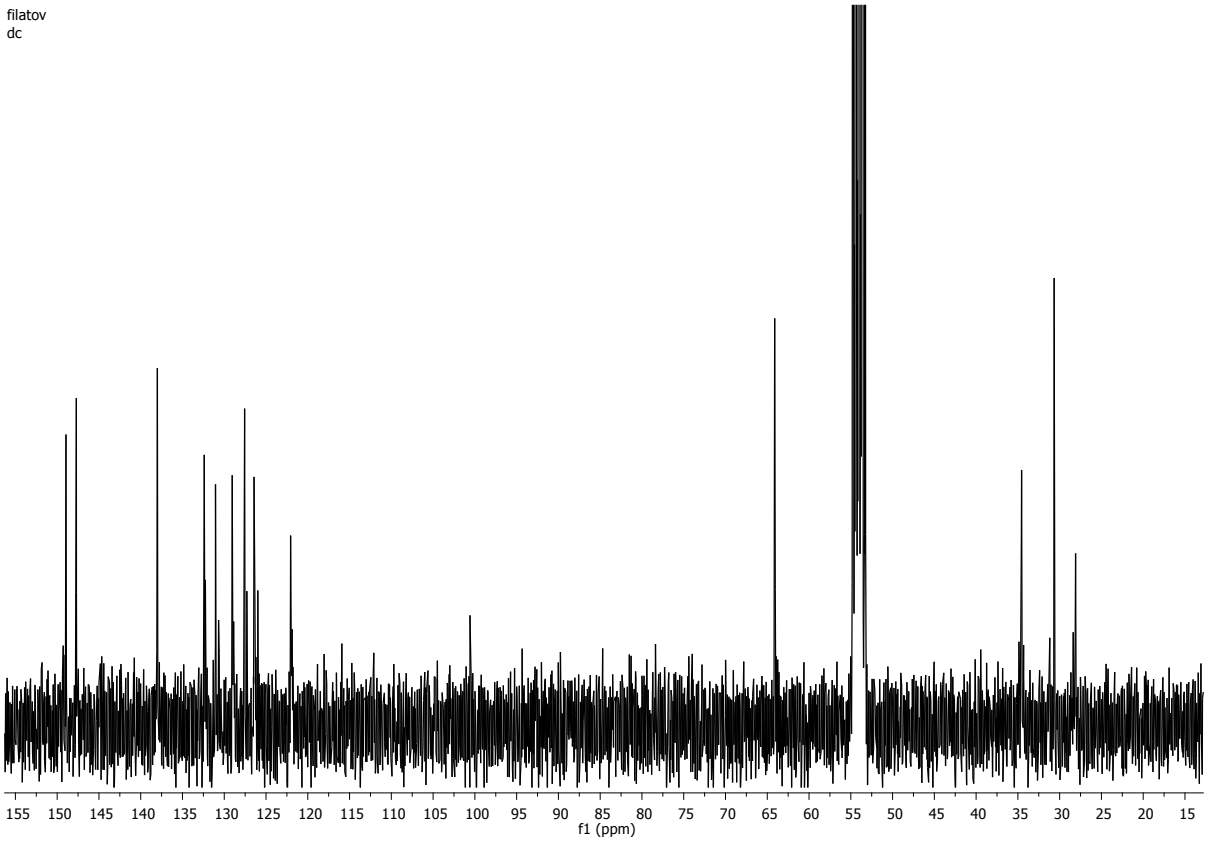


Figure S13. ^{13}C NMR specrum of **8** in a protonated form (75 MHz, CD_2Cl_2, 298 K).

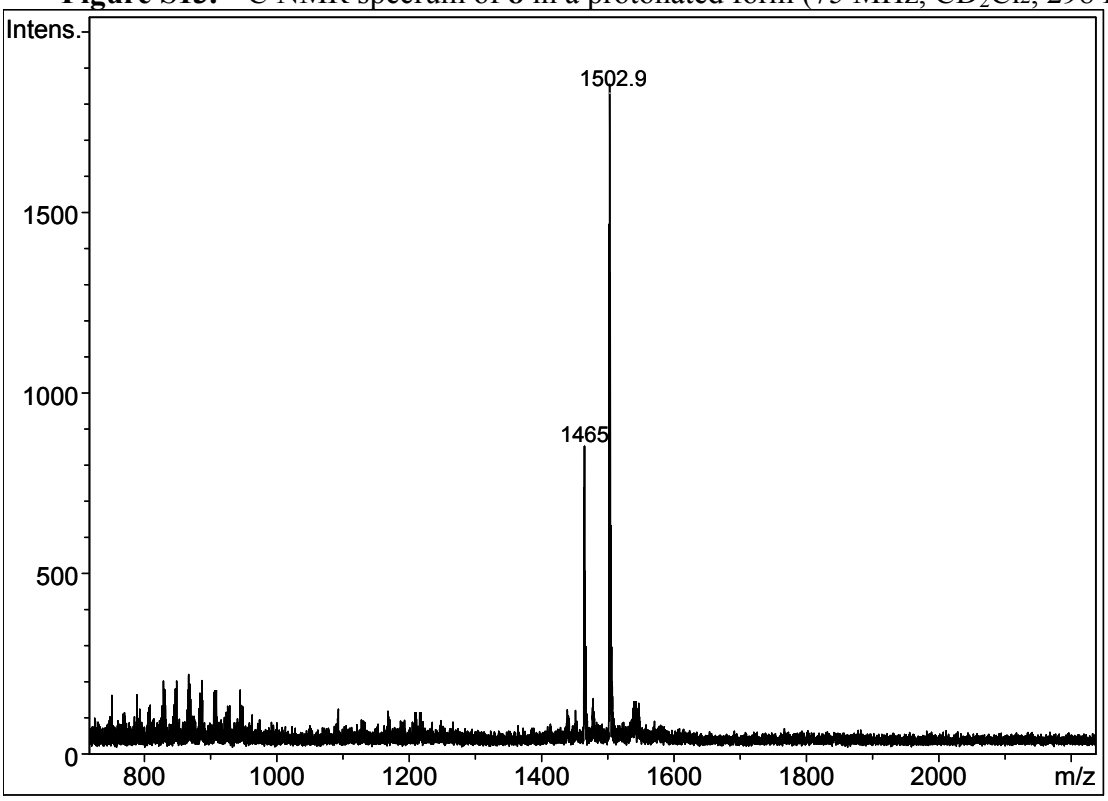


Figure S14. MALDI TOF spectrum **8** (positive mode). Experimentally seen clusters correspond to [M] and $[M+K]^+$ species.

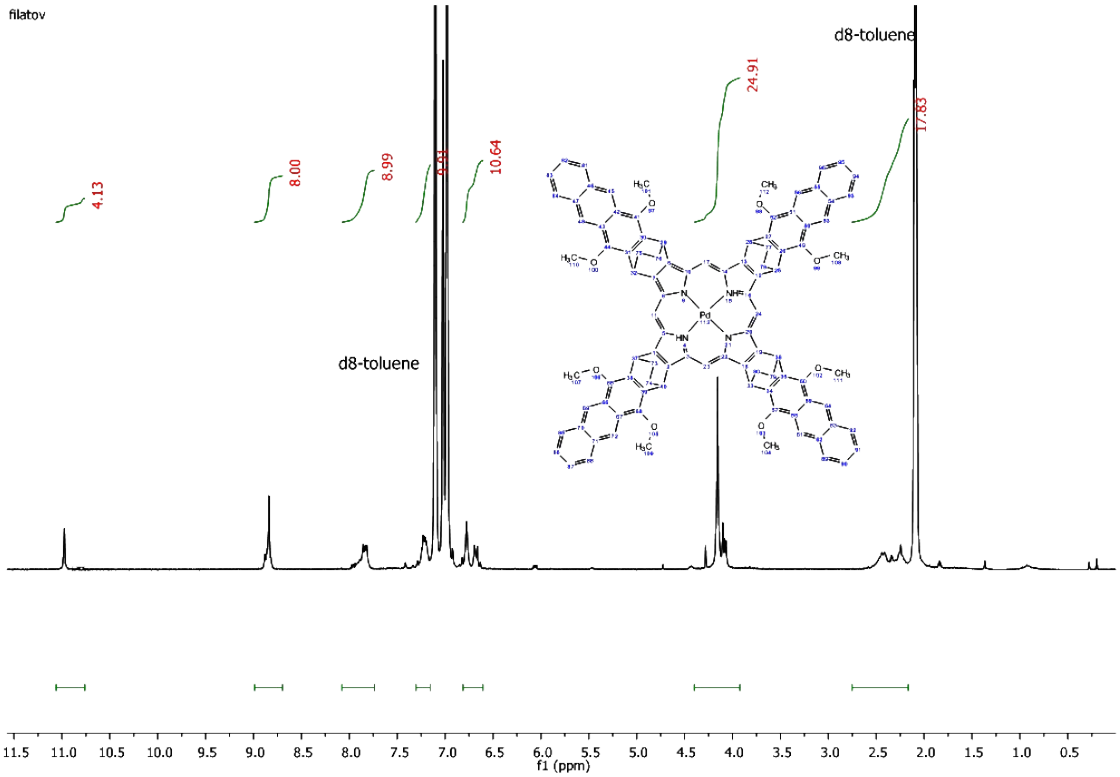


Figure S15. ^{1}H NMR specrum of **9** (250 MHz, d^{8}-toluene, 298 K).

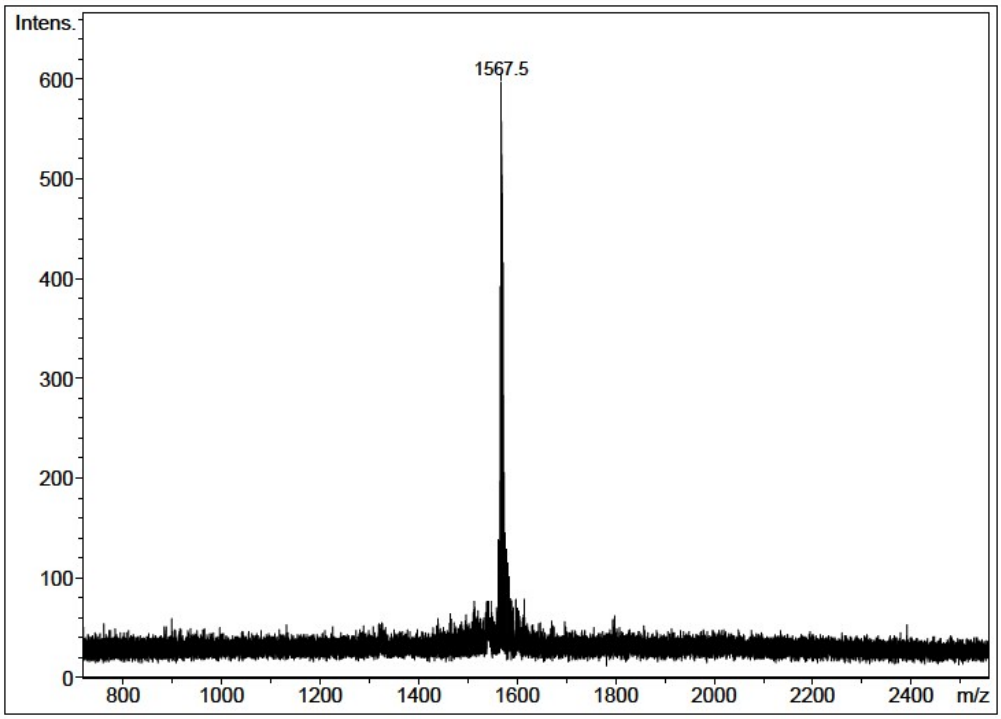


Figure S16. MALDI TOF spectrum of **9** (positive mode).

Optical spectra

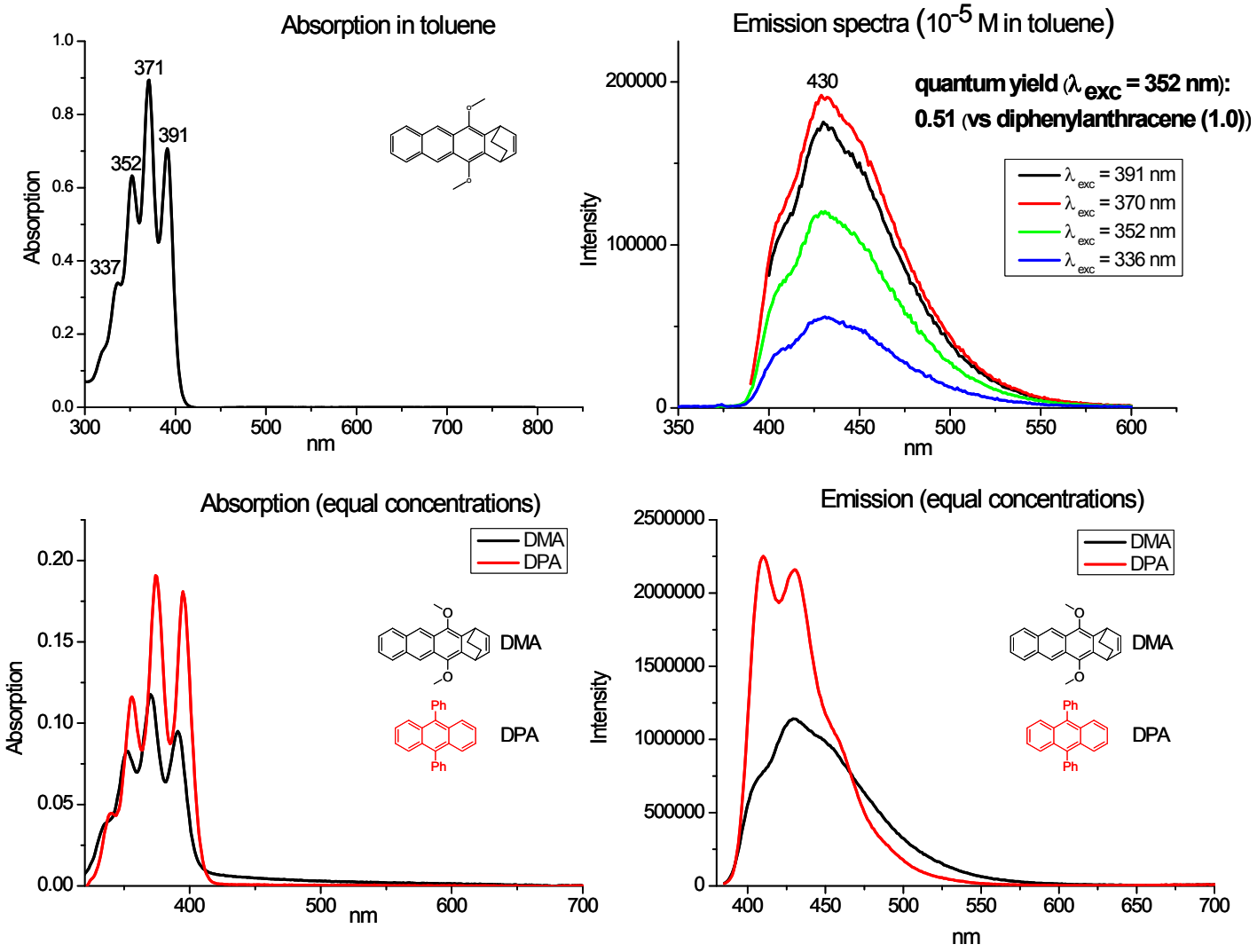


Figure S17. Optical spectra of 5,12-dimethoxy-1,4-dihydro-1,4-ethanotetracene (**3**) in comparison with 9,10-diphenylanthracene.

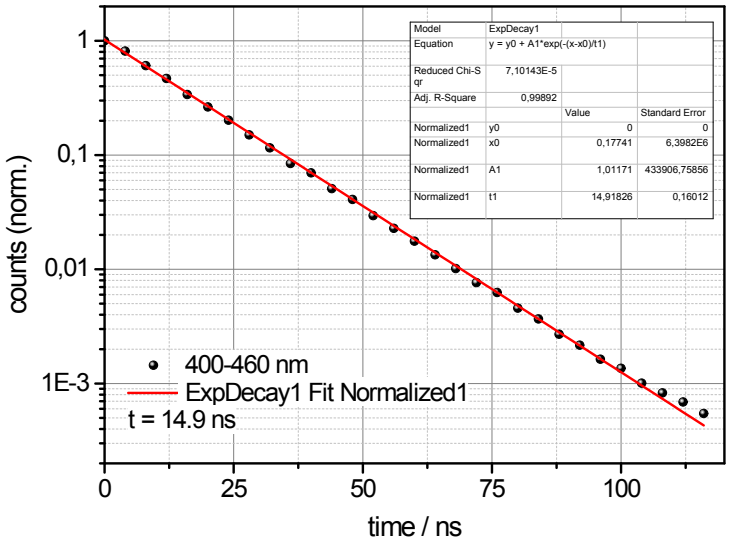


Figure S18. Fit of the fluorescence decay for compound **3**.

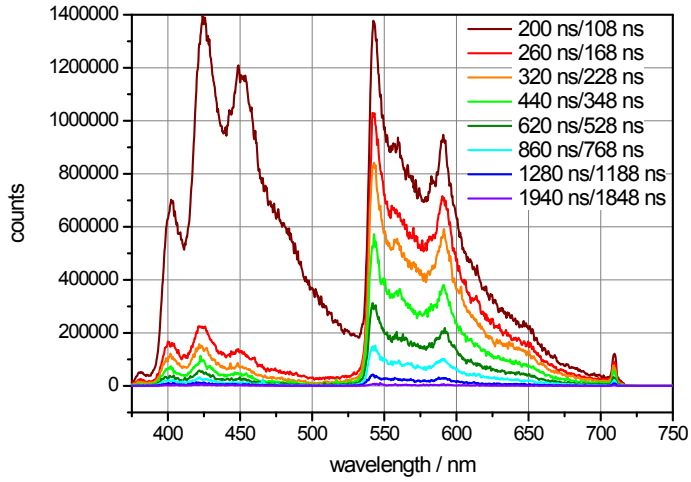


Figure S19. Emission spectrum of **3** at 77 K in methyltetrahydrofuran.

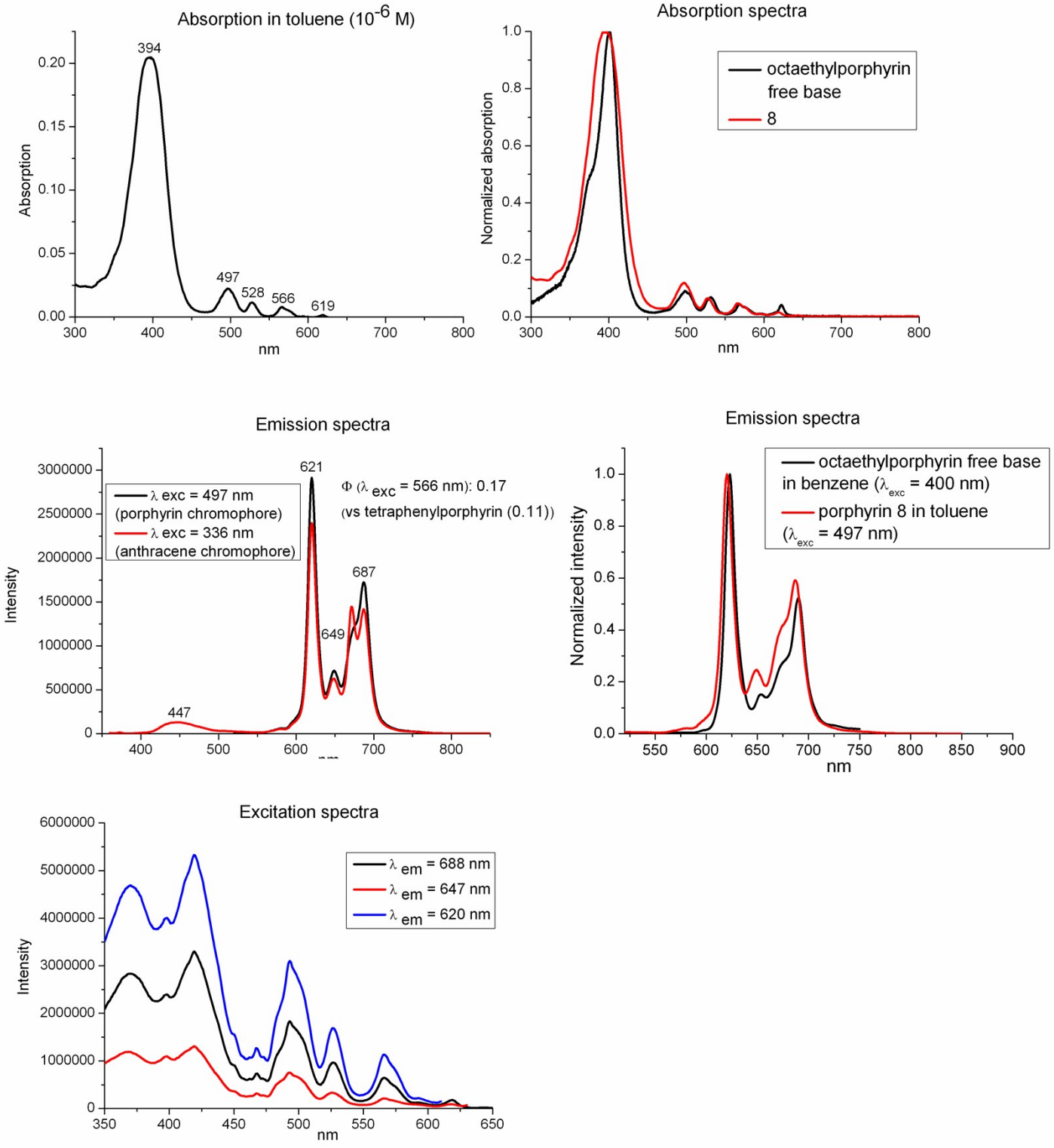


Figure S20. Optical spectra of porphyrin **8** (10^{-6} M) compared with those of octaethylporphyrin free base.

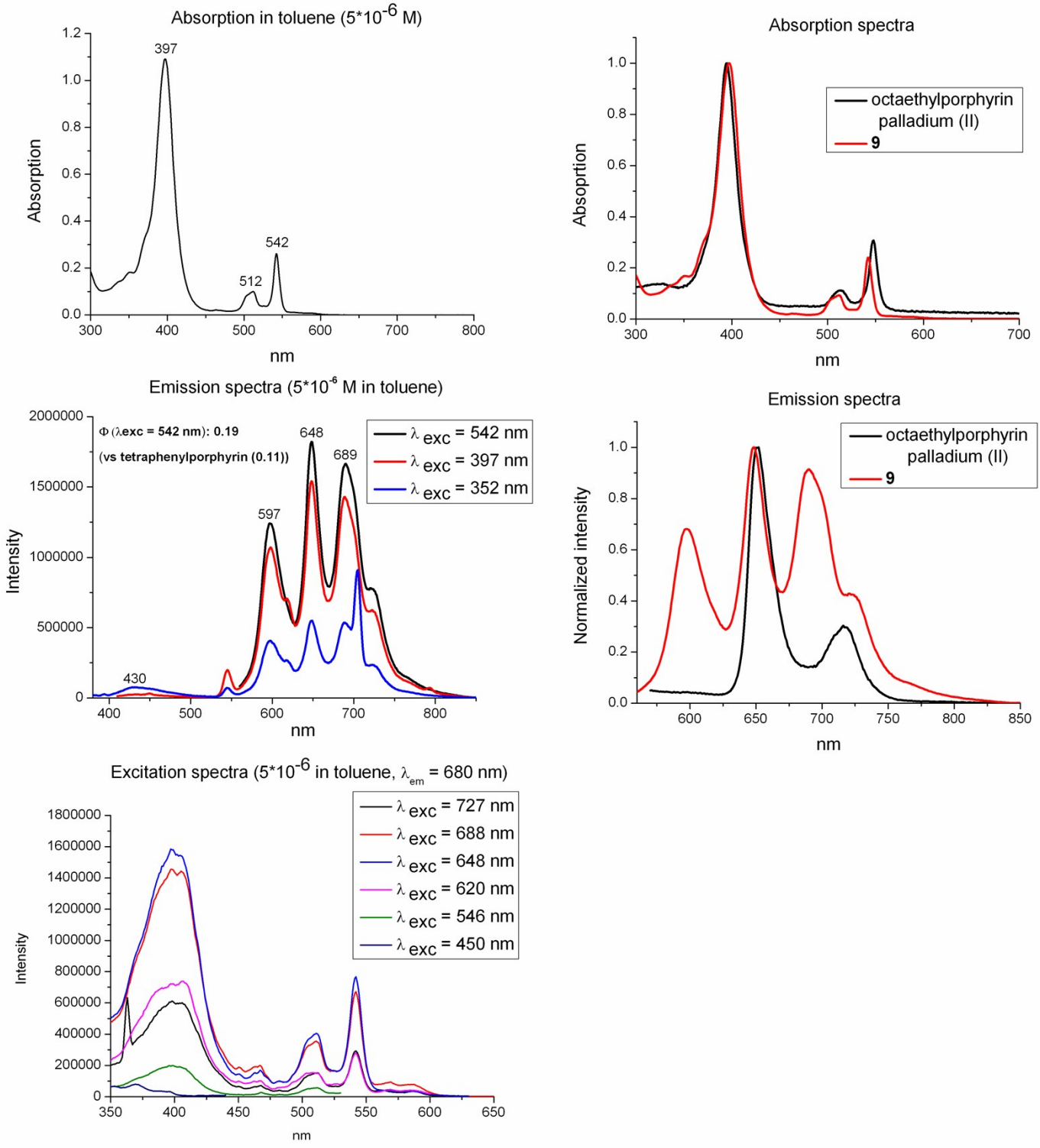
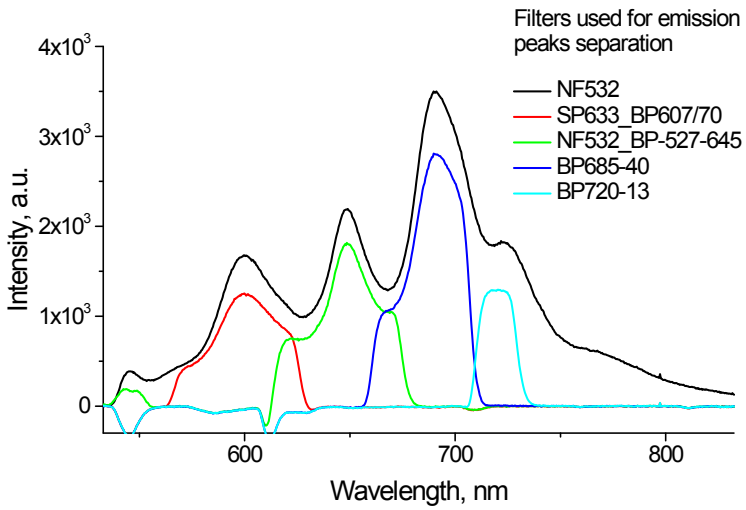
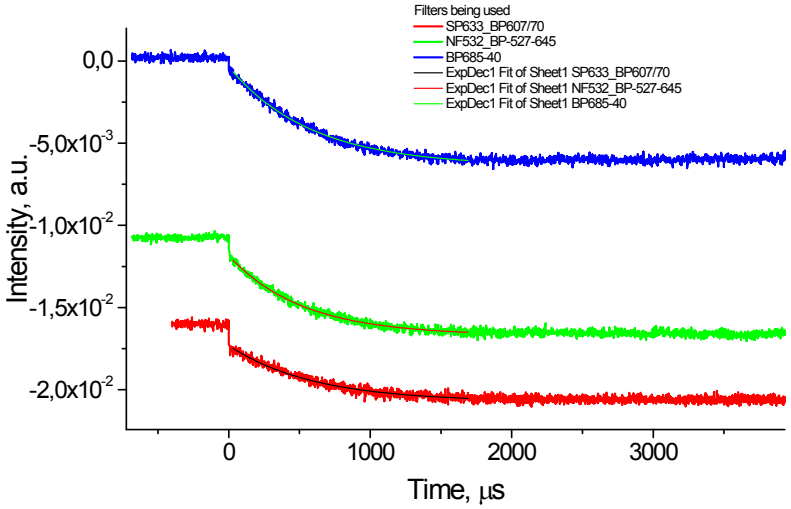


Figure S21. Optical spectra of porphyrin **9** (5×10^{-6} M) compared with those of PdOEP.





Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
		Fitted lifeti	Standa rd Erro
SP633_BP 607/70	**t1**	**601,8 759**	16,749 74
NF532_BP- 527-645	**t1**	**520,3 1492**	8,0478 7
BP685-40	**t1**	**583,7 4688**	8,6064 3

Figure S22. Porphyrin **9** (10^{-5} M) emission lifetimes at different wavelengths, measured using different optical filters.

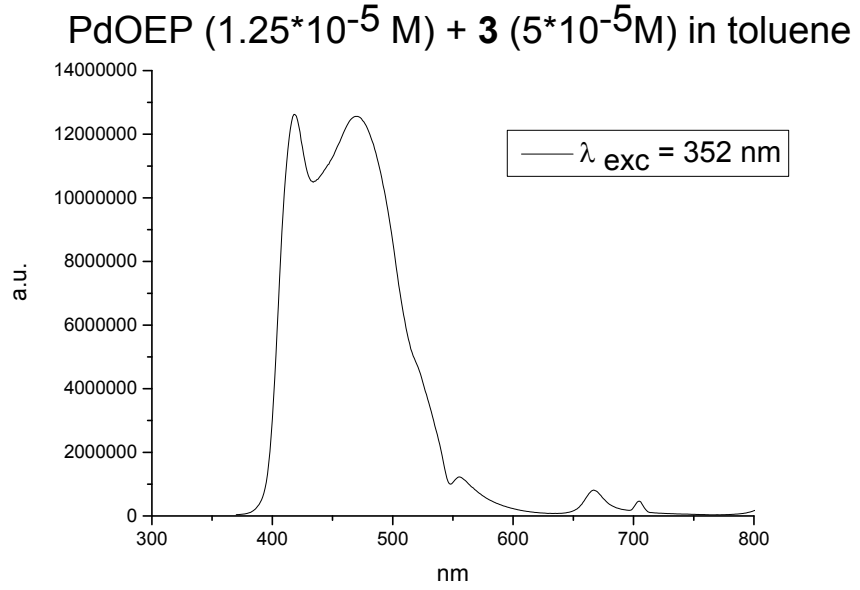


Figure S23. Emission spectrum of the mixture PdOEP – **3** in 1:4 ratio.

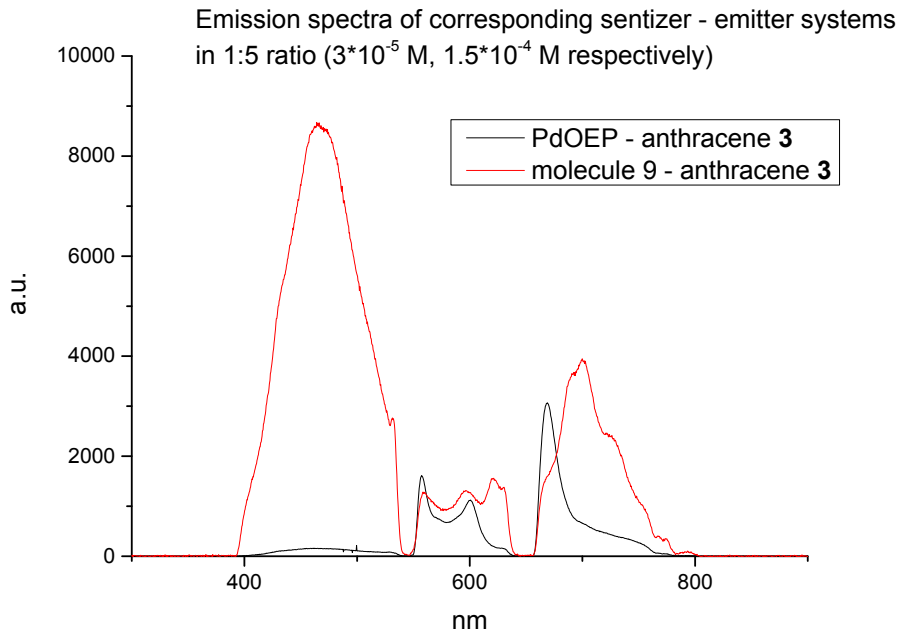


Figure S24. Comparison of the upconversion spectra of the systems based on porphyrin **9** or PdOEP as sensitizers and anthracene **3** as an emitter in 1:5 ratio. Samples were excited at 545 nm (10 $mWcm^{-2}$).

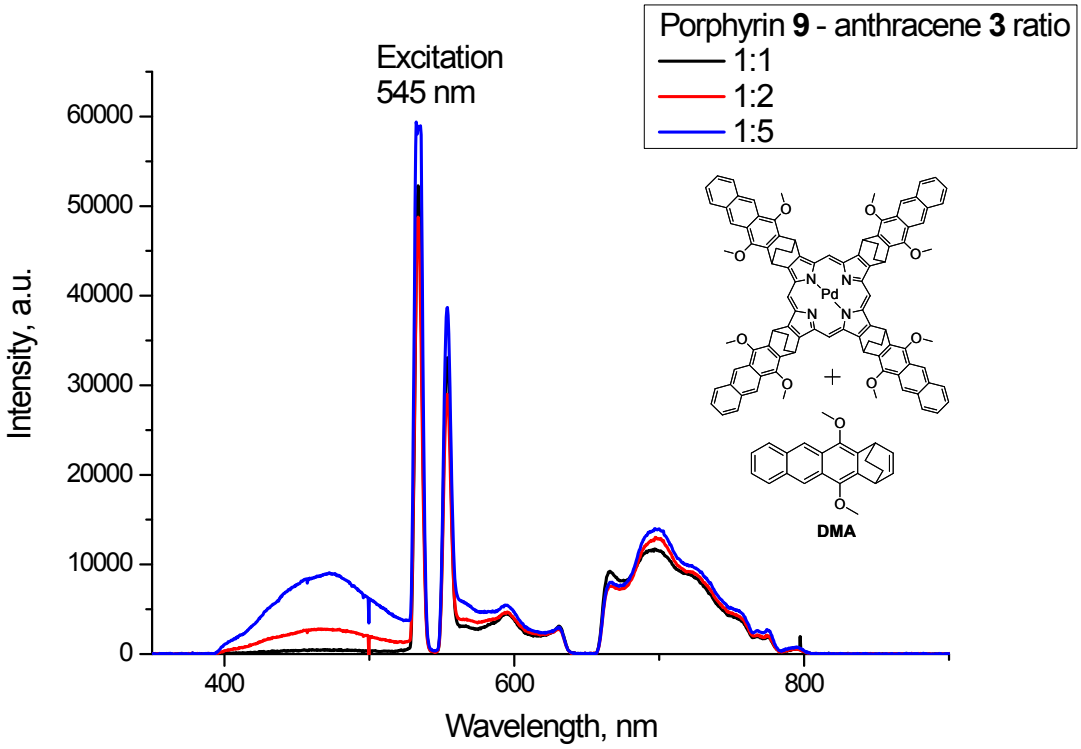


Figure S25. Upconversion spectra of samples containing $3 \cdot 10^{-5}$ M of **9** and 1, 2 or 5 equivalents of **3** as an emitter (solvent – toluene). Samples were excited at 545 nm (10 $mWcm^{-2}$).

Transient absorption spectra

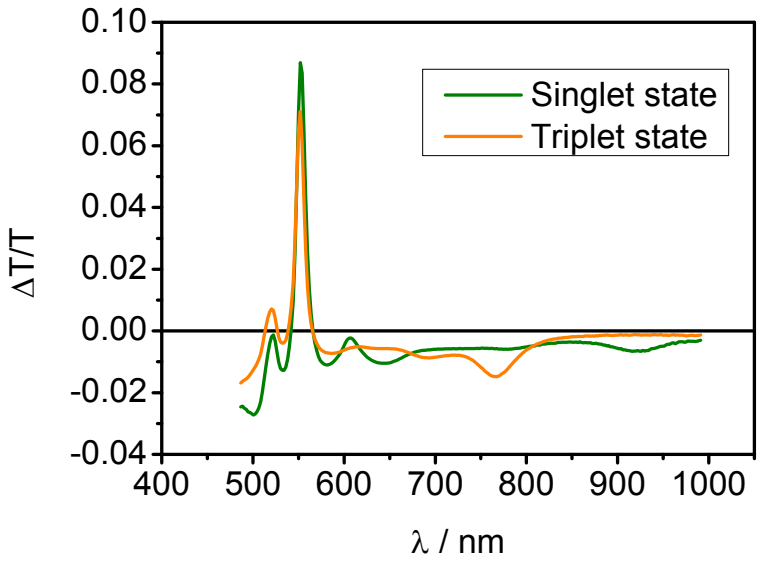


Figure S26. Component spectra of singlet and triplet states of PdOEP (10^{-4} M) obtained by global analysis.

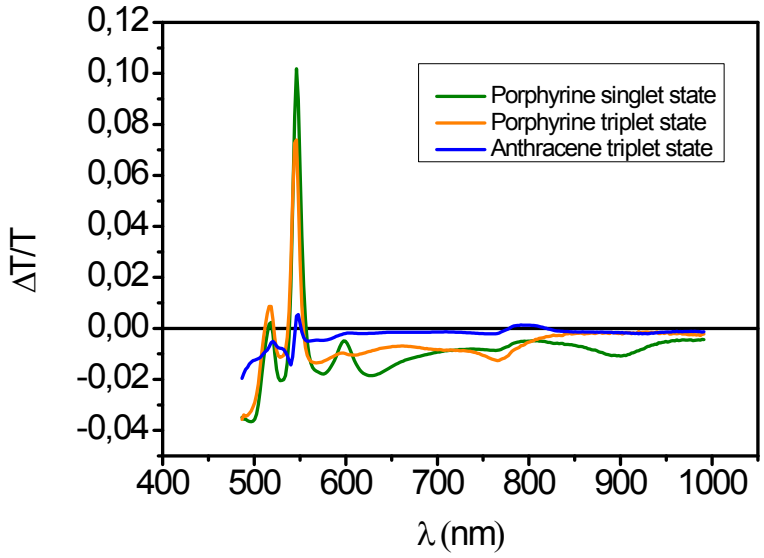


Figure S27. Component spectra of compound **9** (10^{-4} M) obtained by global fitting.

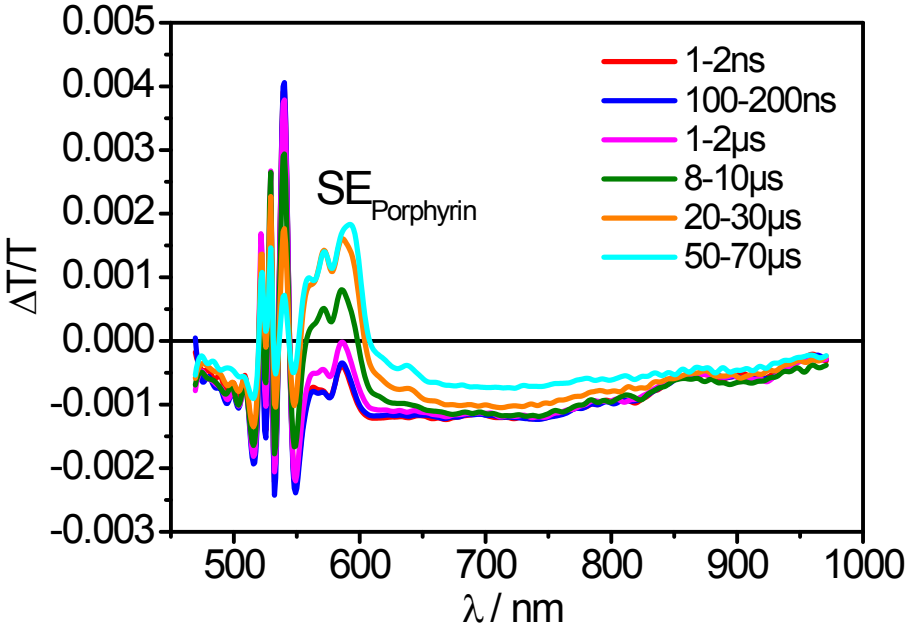


Figure S28. ns-μs Vis-NIR TA spectra of compound **9** (10^{-4} M).

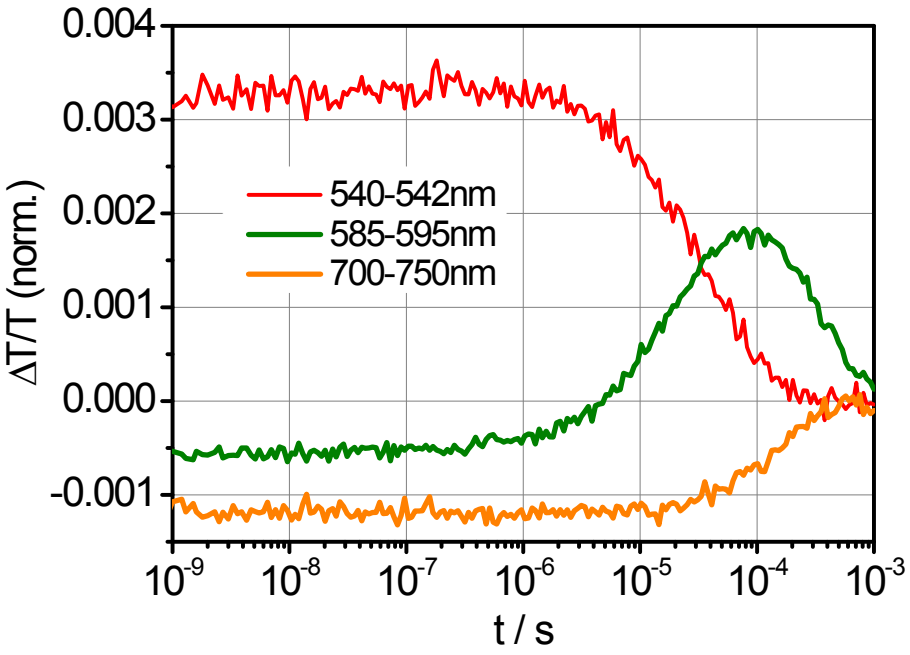


Figure S29. ns-μs dynamics obtained on compound **9** at selected wavelength regions corresponding to the porphyrin's ground state bleach (540-542 nm), the region of stimulated emission from the porphyrin (585-595 nm) and the triplet-induced absorption (700-750 nm).