

# Supporting Information

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

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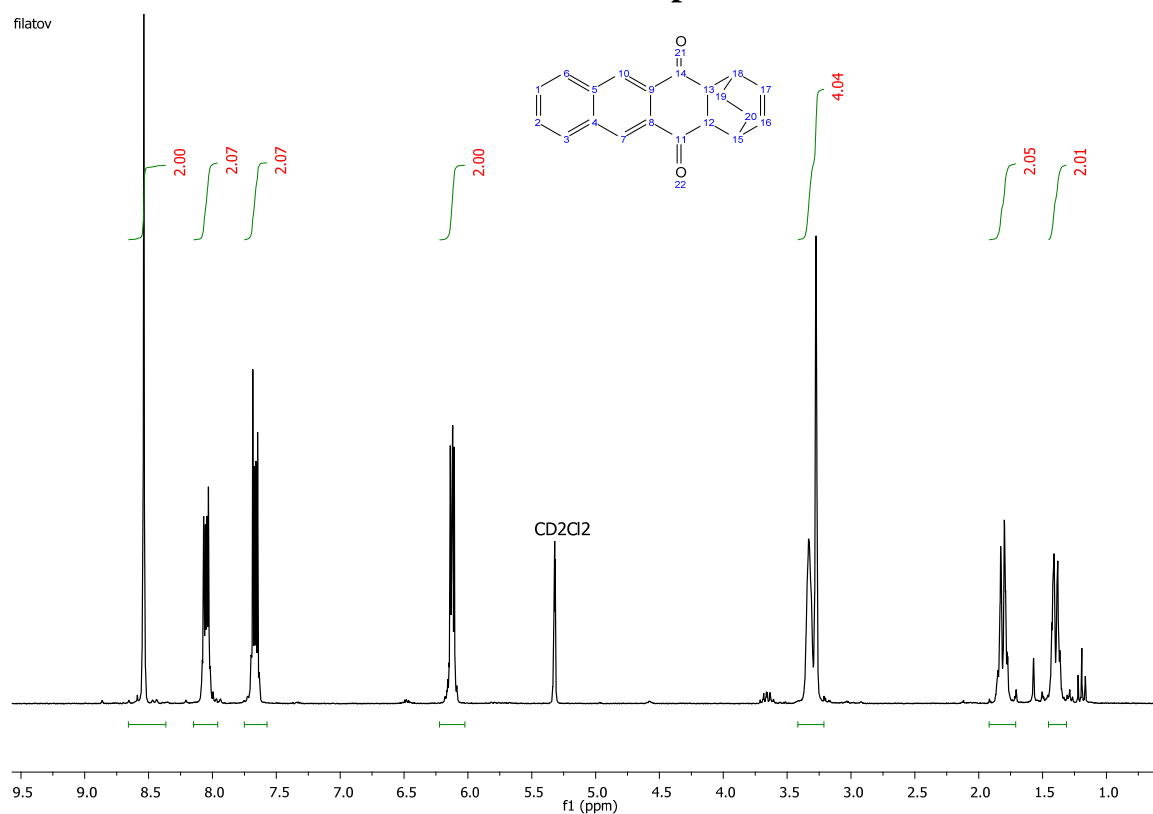
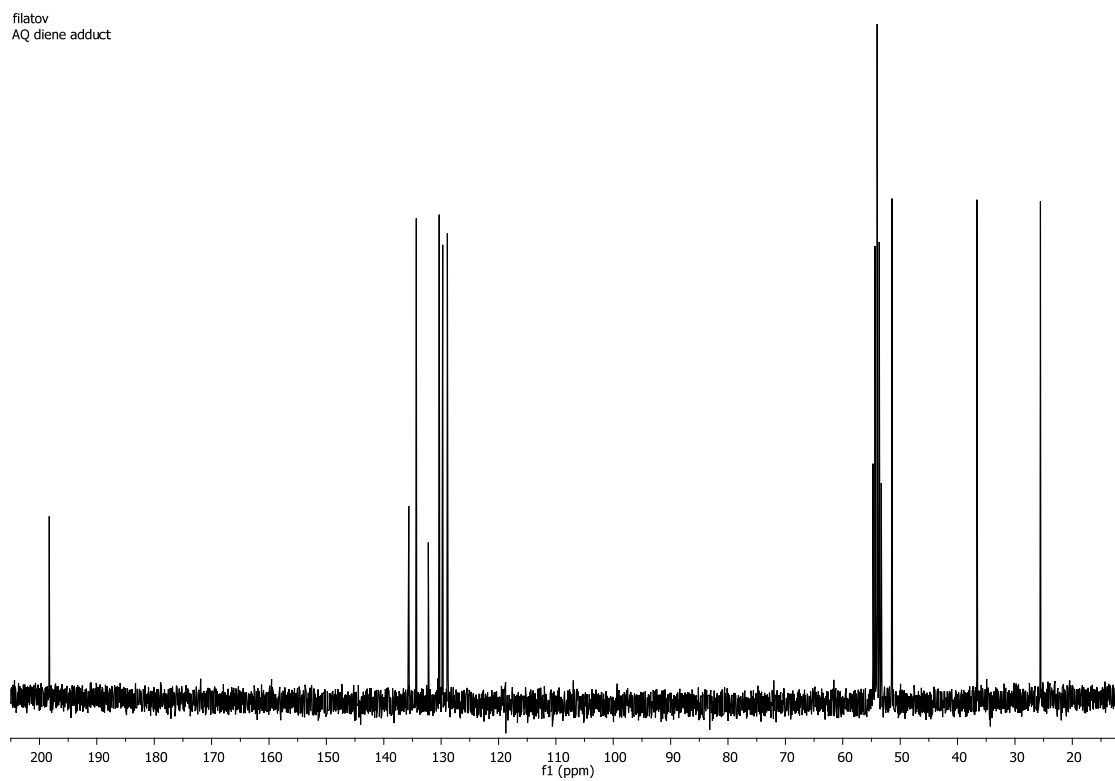
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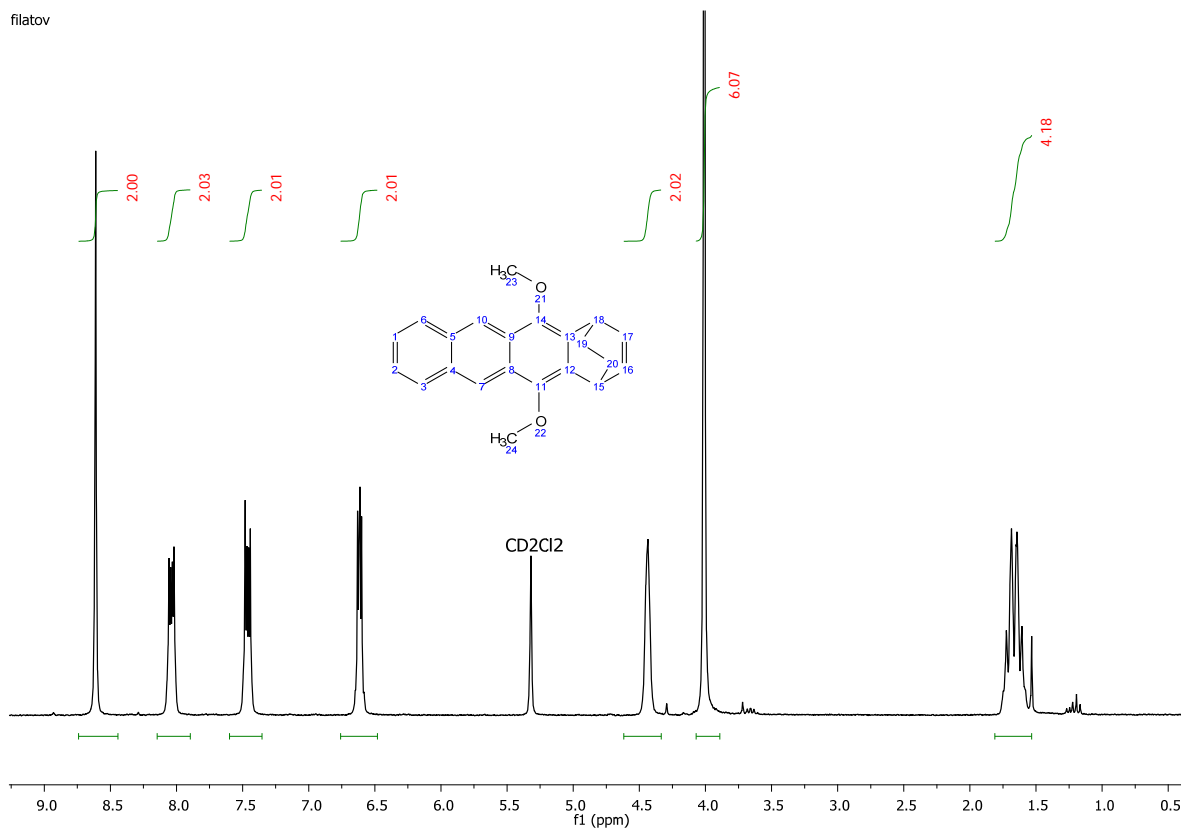
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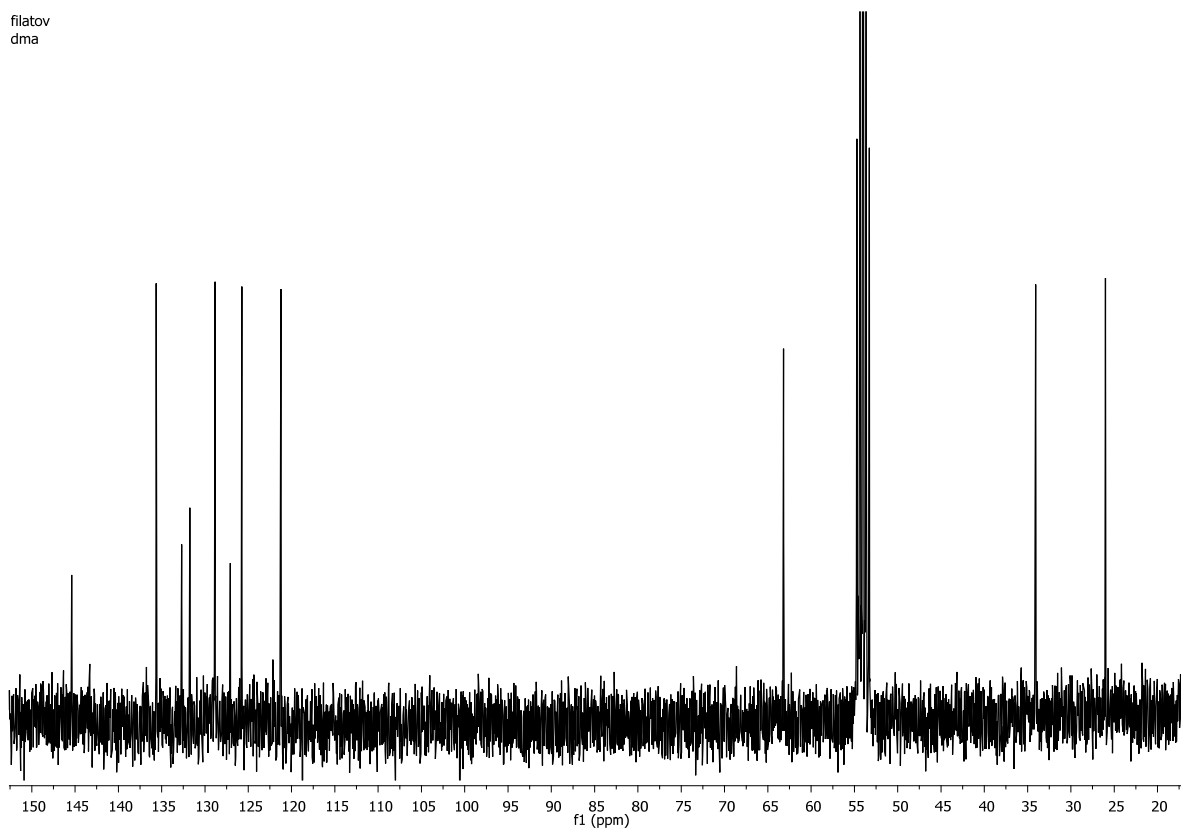
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## NMR and mass-spectra

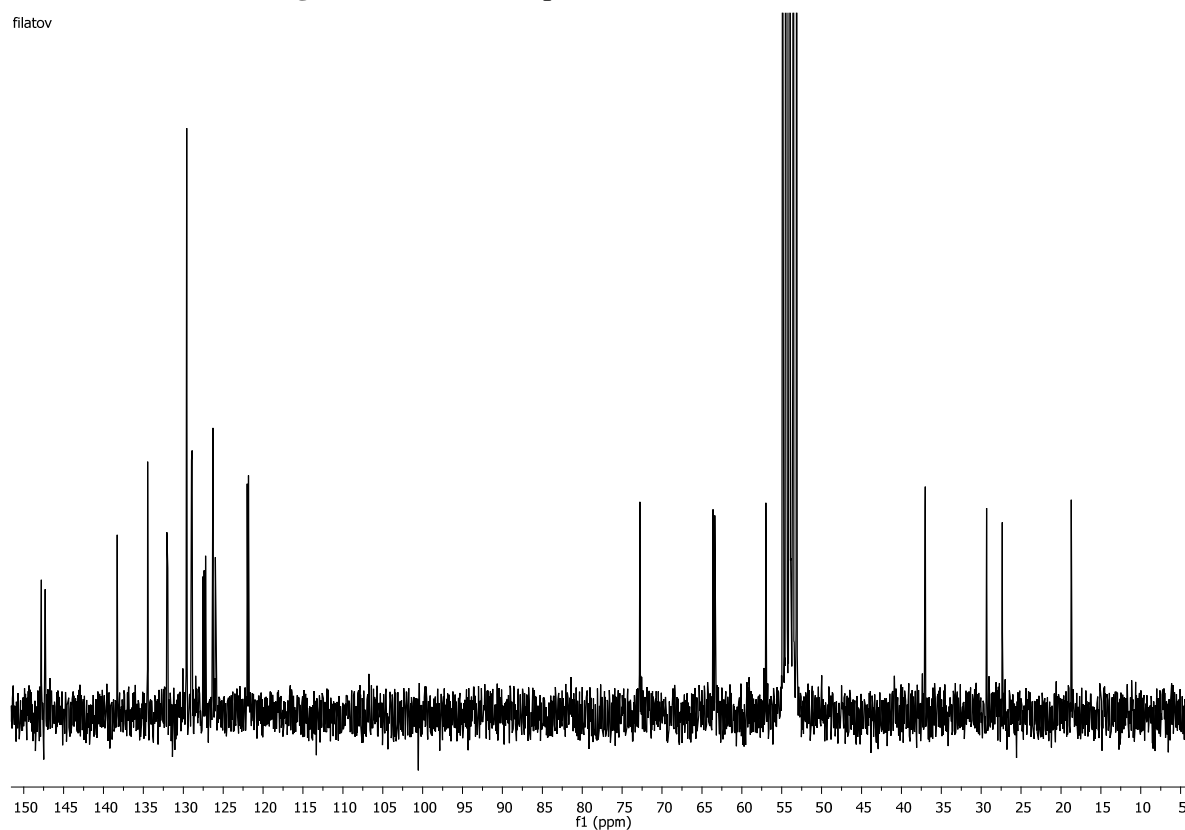
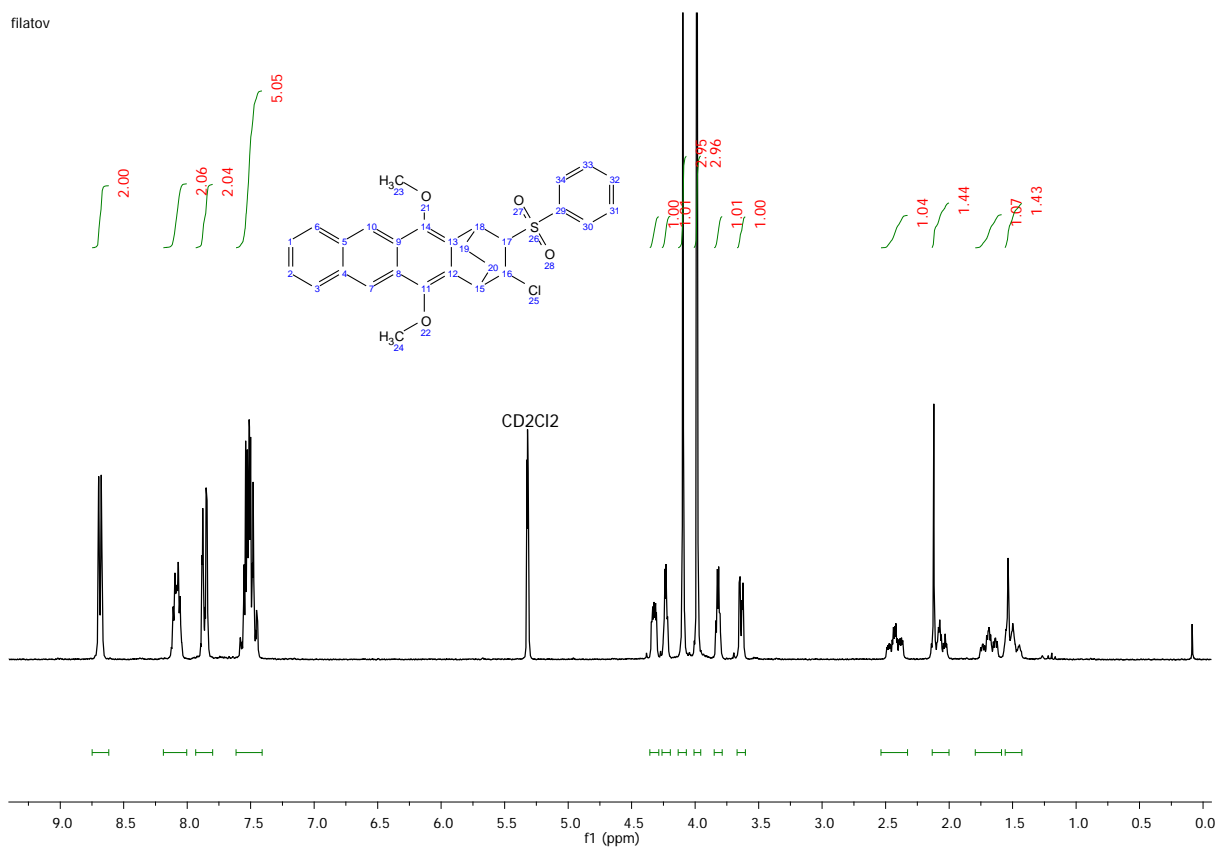
**Figure S1.** <sup>1</sup>H NMR spectrum of **2** (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K).**Figure S2.** <sup>13</sup>C NMR spectrum of **2** (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

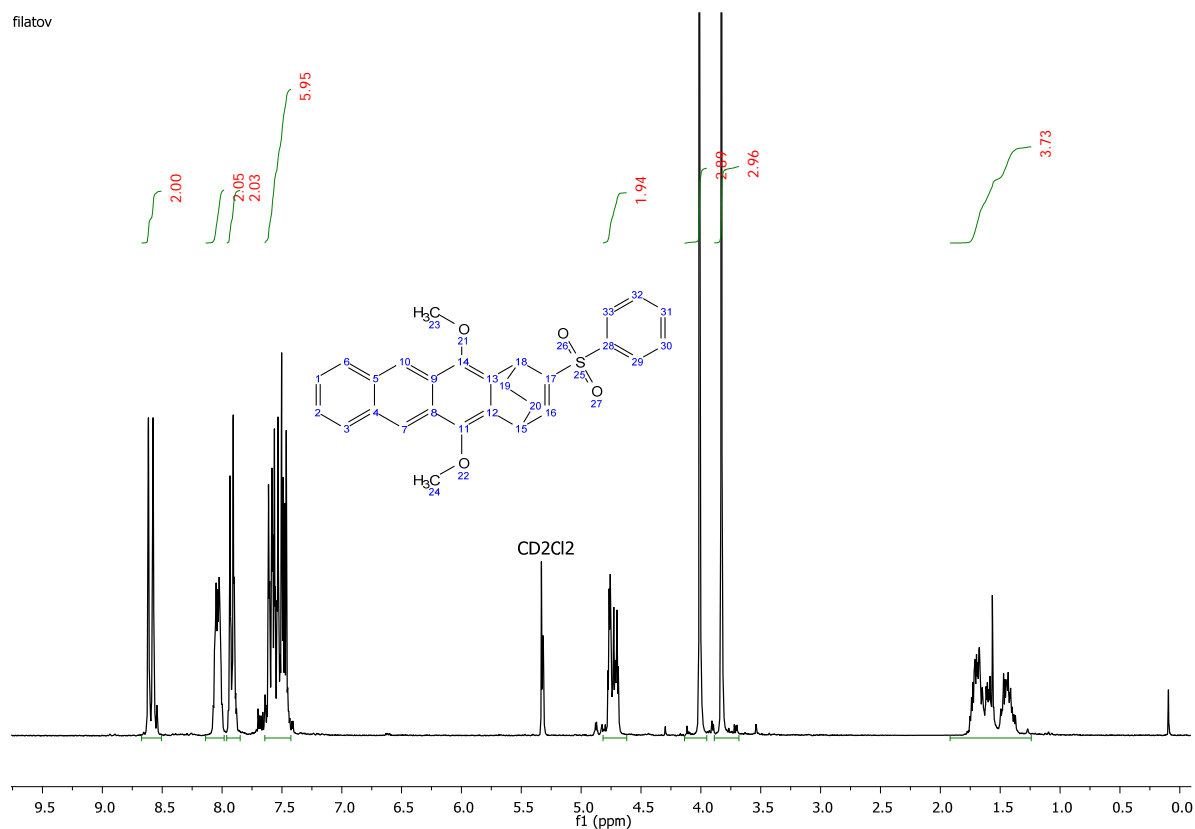


**Figure S3.** <sup>1</sup>H NMR spectrum of **3** (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

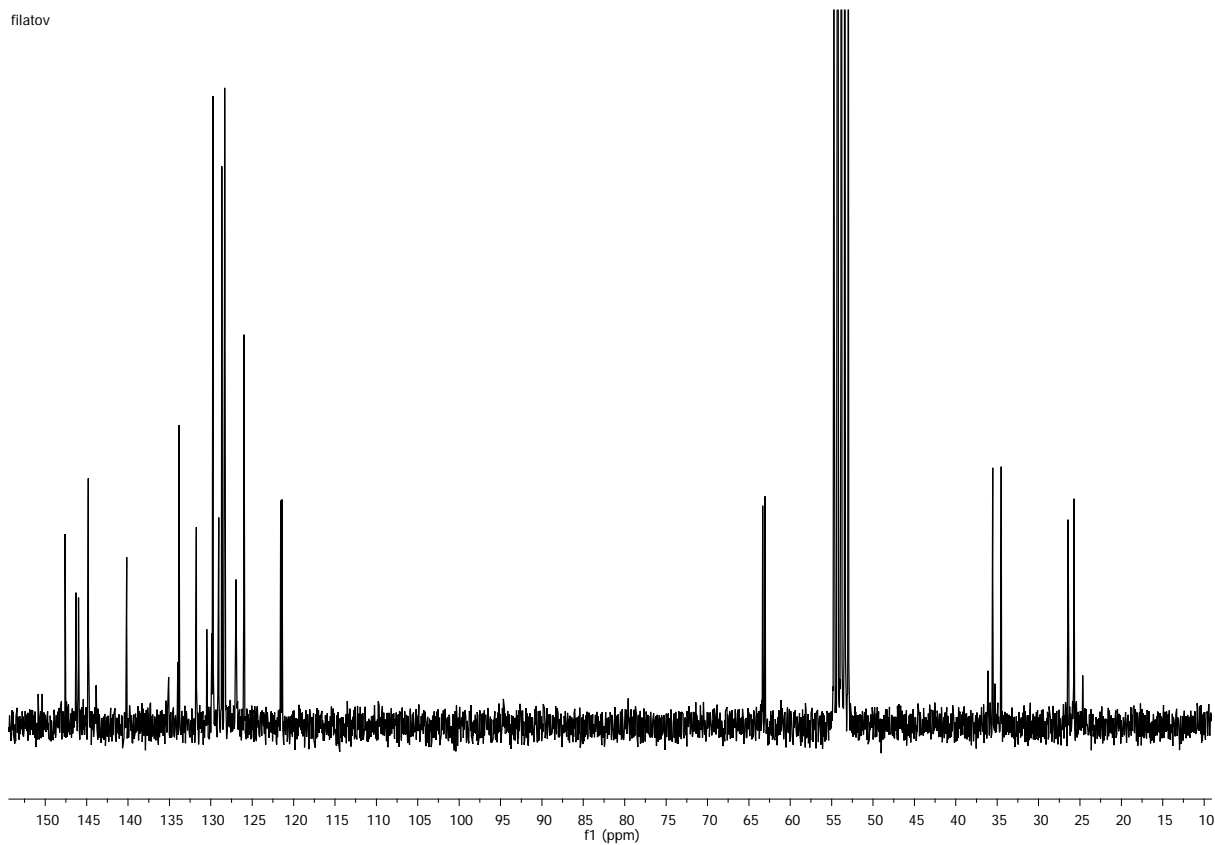


**Figure S4.** <sup>13</sup>C NMR spectrum of **3** (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

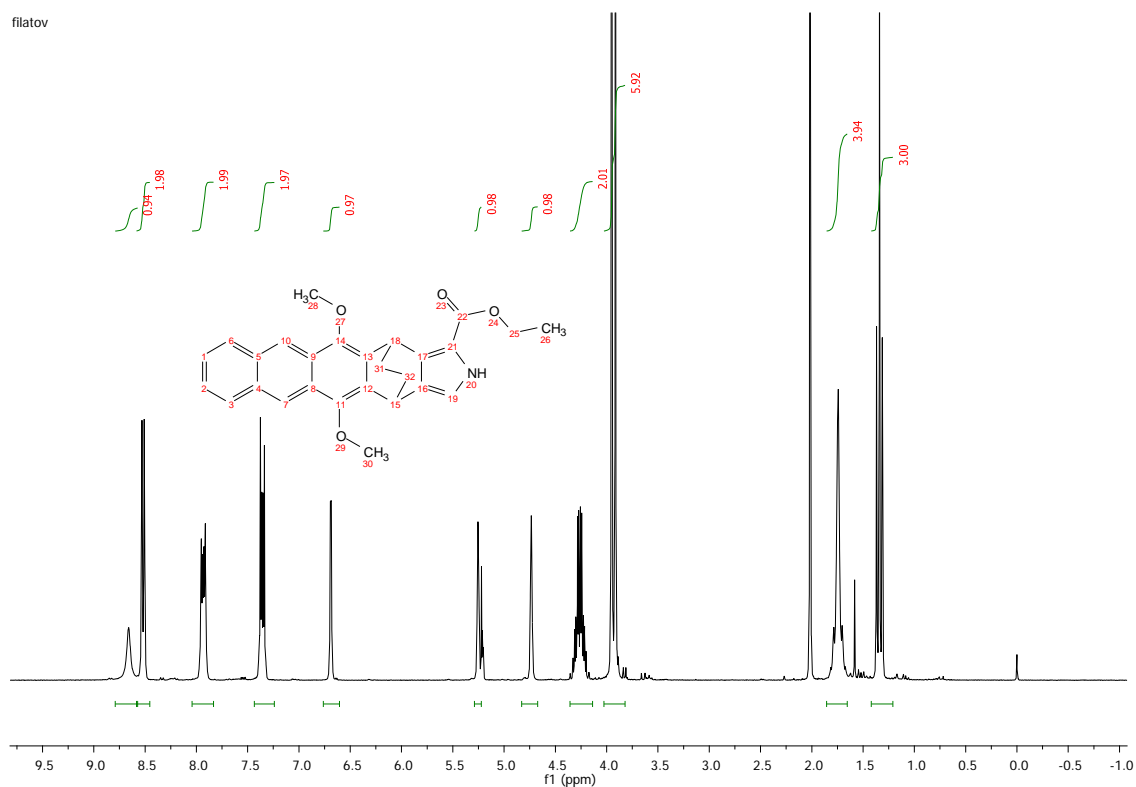




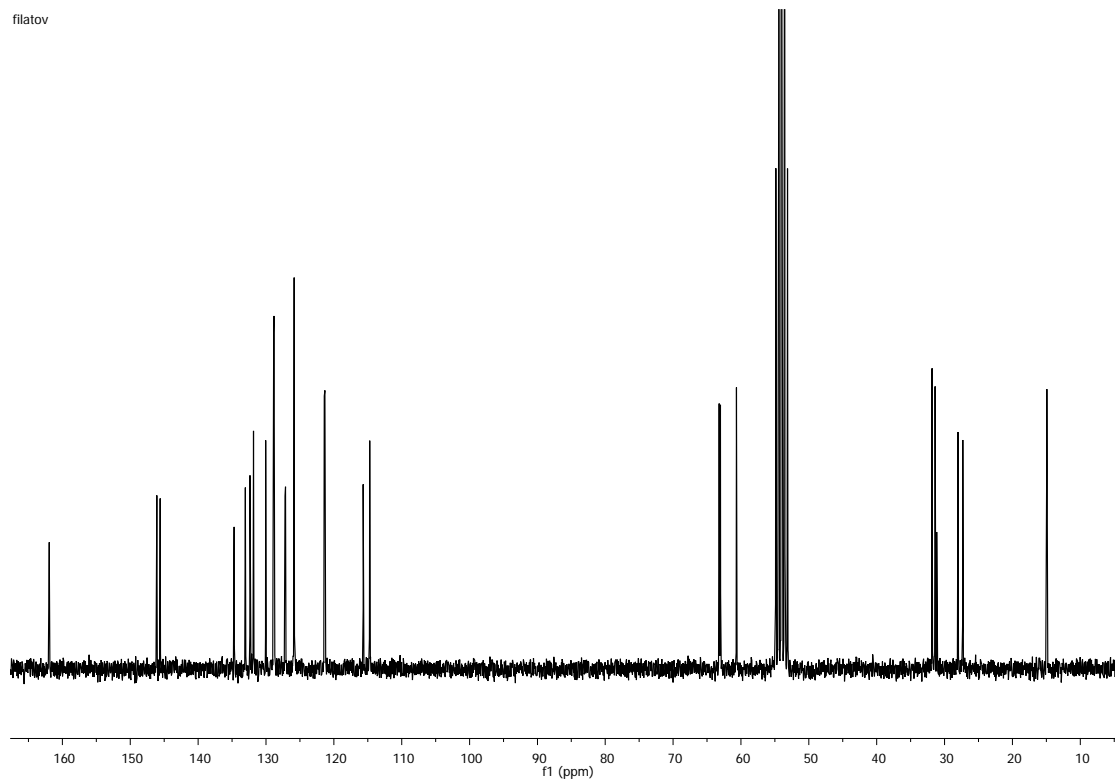
**Figure S7.** <sup>1</sup>H NMR spectrum of **5** (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K).



**Figure S8.** <sup>13</sup>C NMR spectrum of **5** (63 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

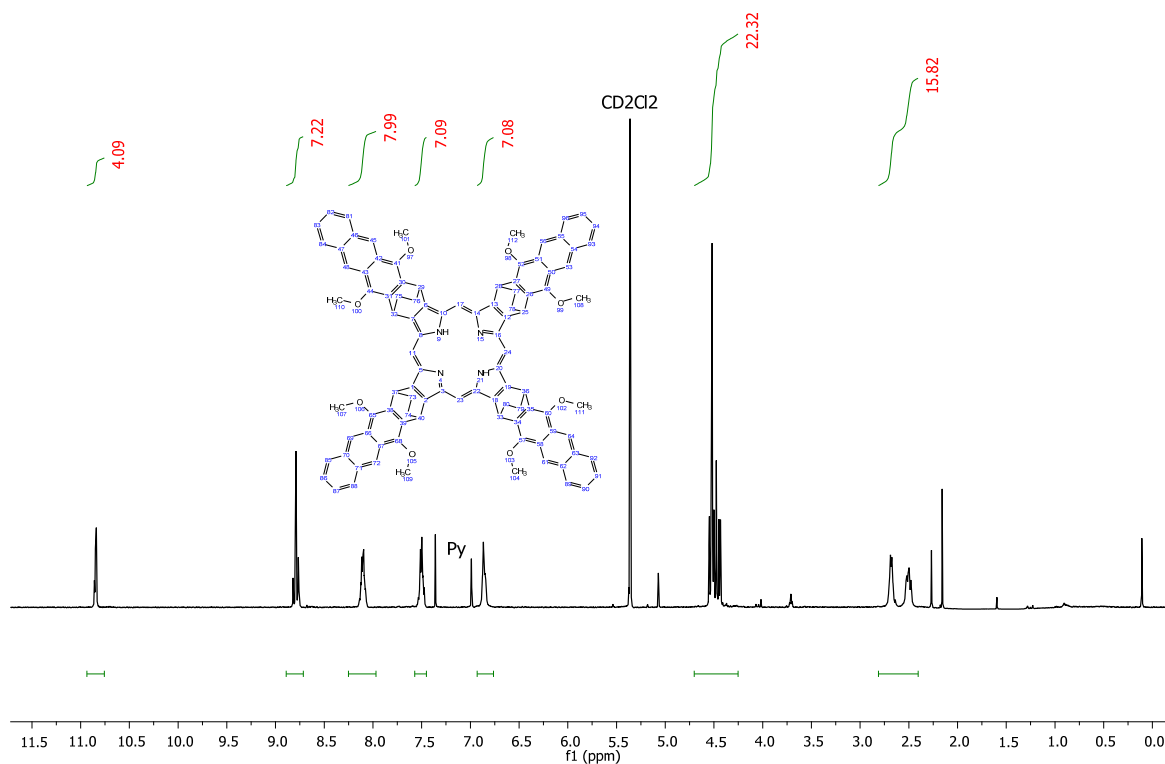


**Figure S9.**  $^1\text{H}$  NMR spectrum of **6** (250 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K).



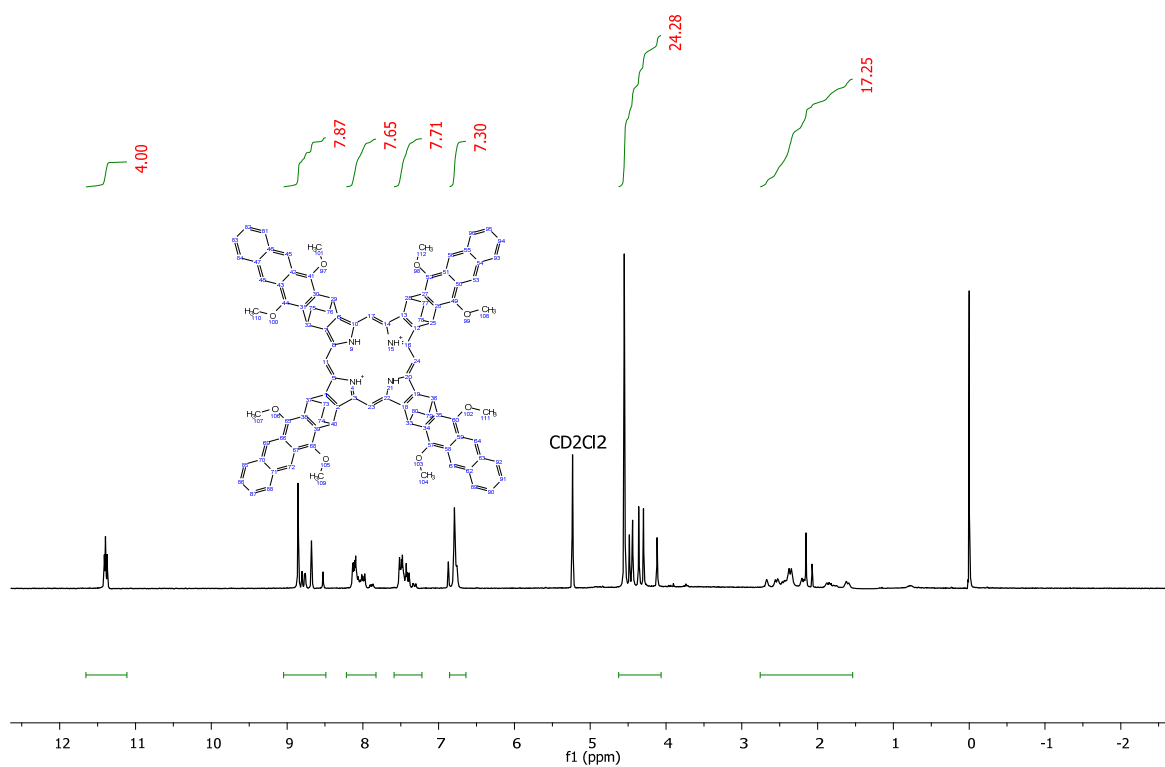
**Figure S10.**  $^{13}\text{C}$  NMR spectrum of **6** (63 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K).

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SMA-FB in CD<sub>2</sub>Cl<sub>2</sub> bei 273.3K

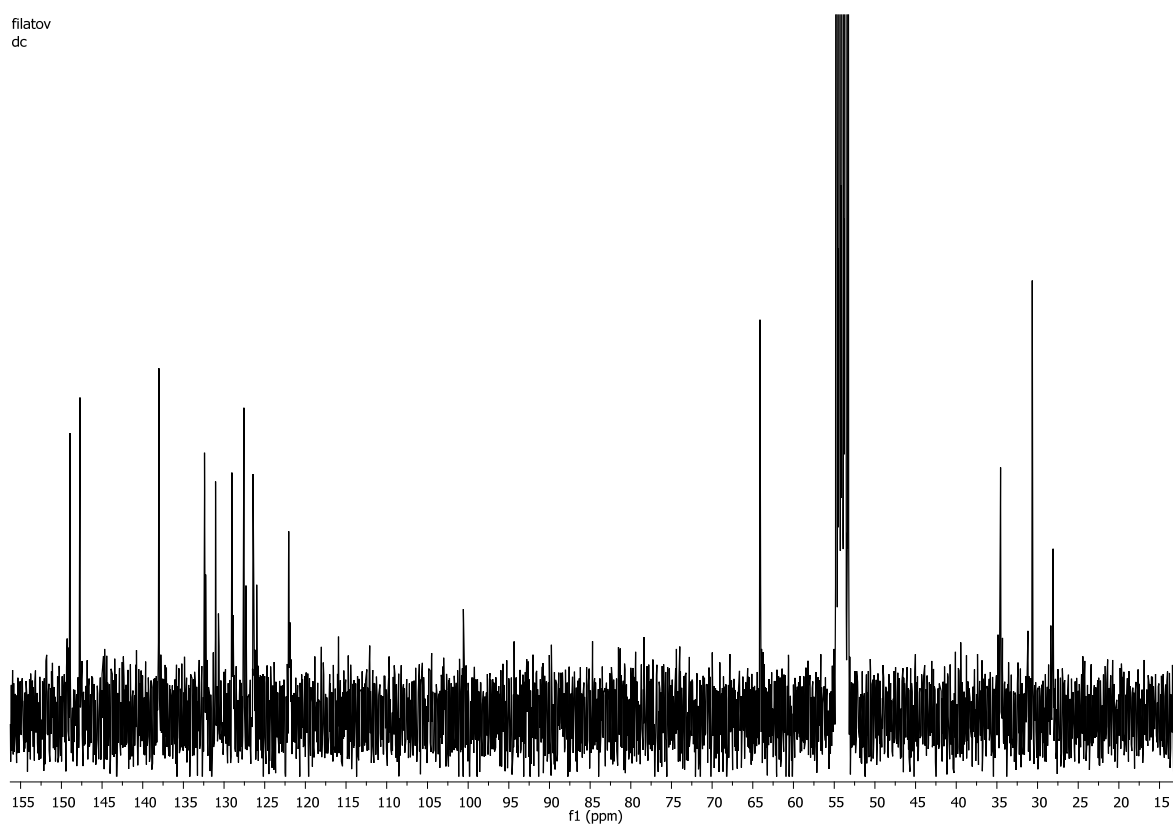


**Figure S11.** <sup>1</sup>H NMR spectrum of **8** in a free-base form (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

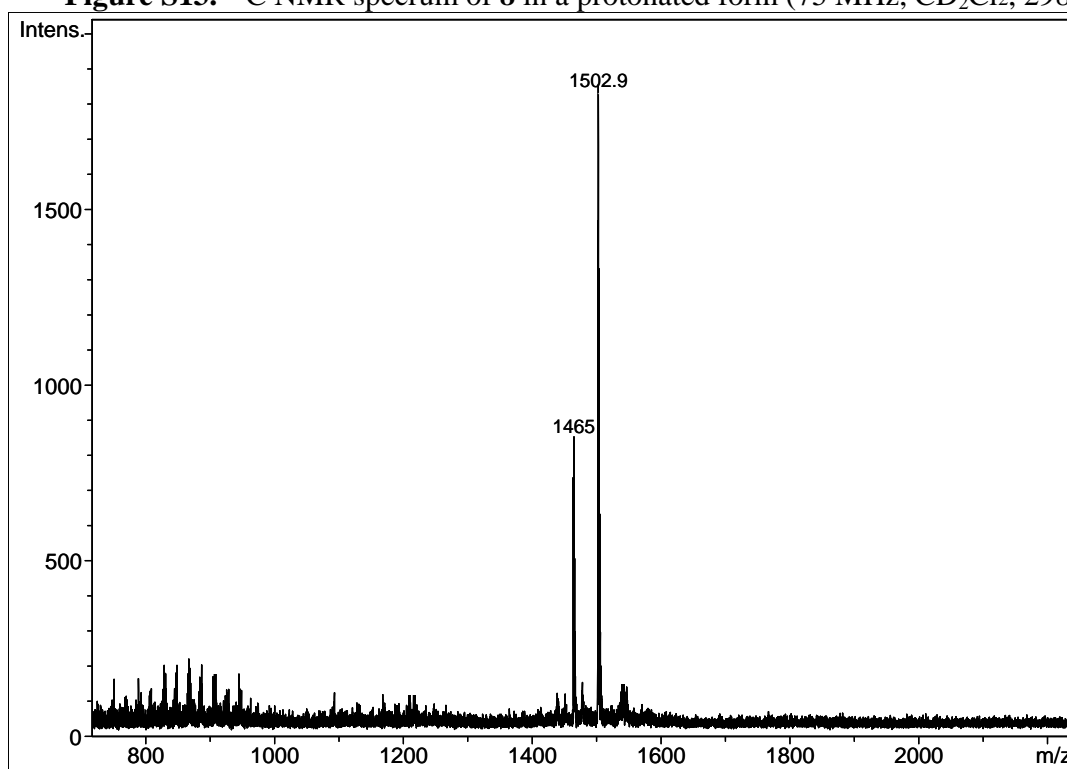
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**Figure S12.** <sup>1</sup>H NMR spectrum of **8** in a protonated form (250 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K).

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**Figure S13.**  $^{13}\text{C}$  NMR spectrum of **8** in a protonated form (75 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K).



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



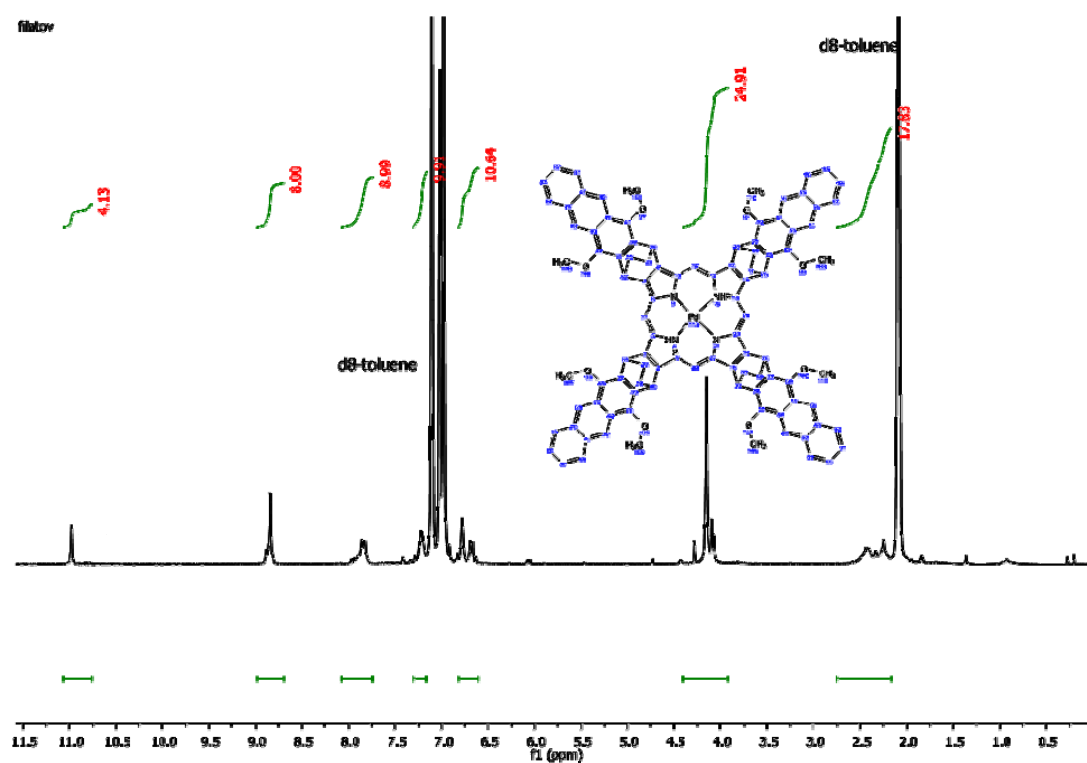


Figure S15.  $^1\text{H}$  NMR spectrum of **9** (250 MHz,  $\text{d}_8$ -toluene, 298 K).

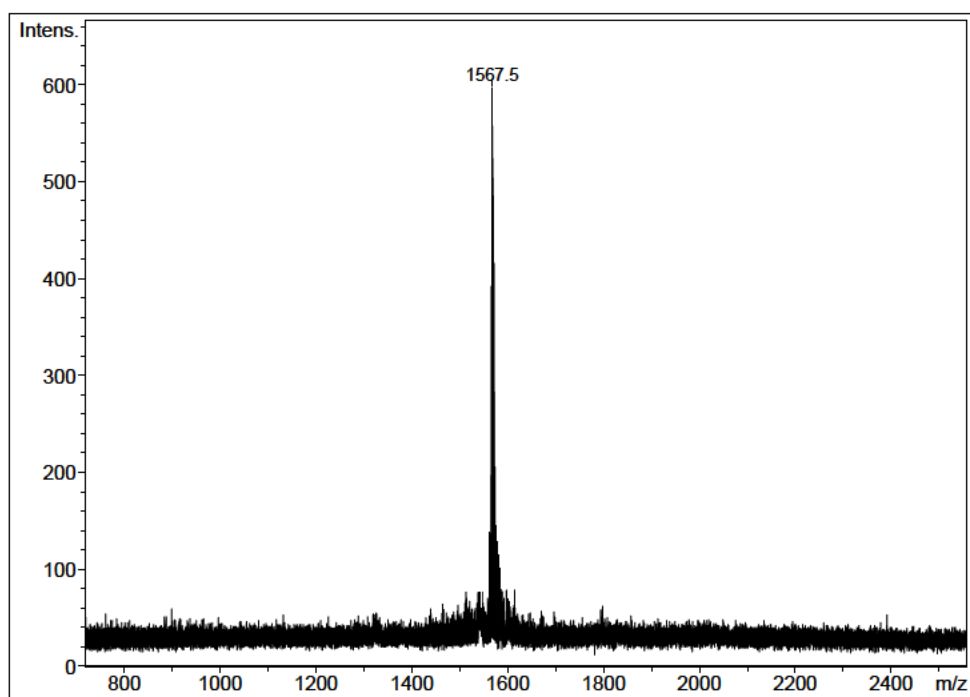
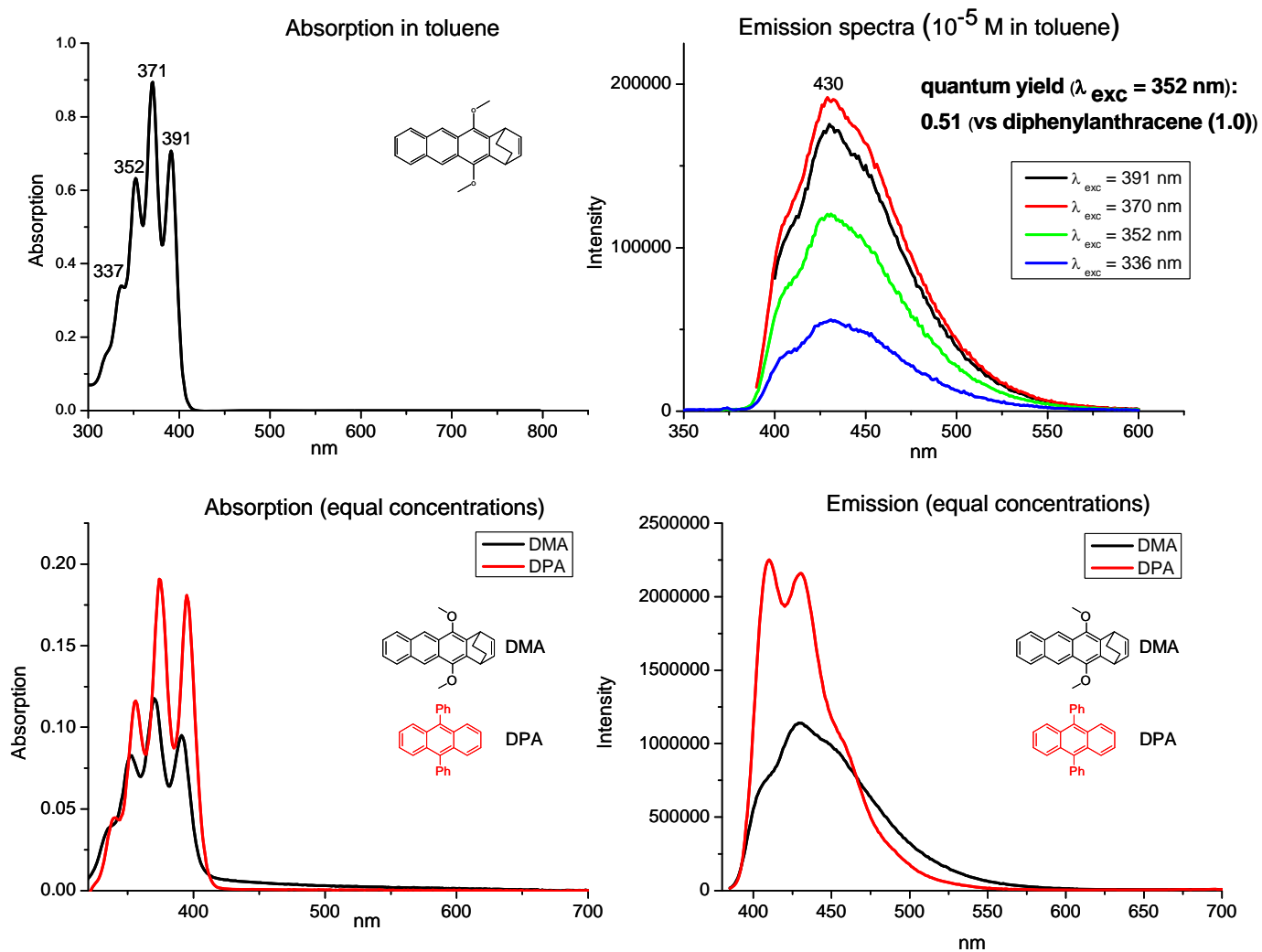
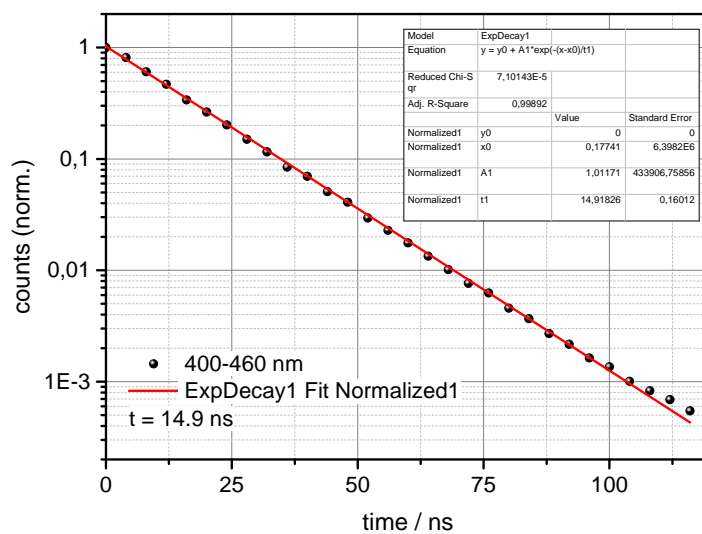


Figure S16. MALDI TOF spectrum of **9** (positive mode).

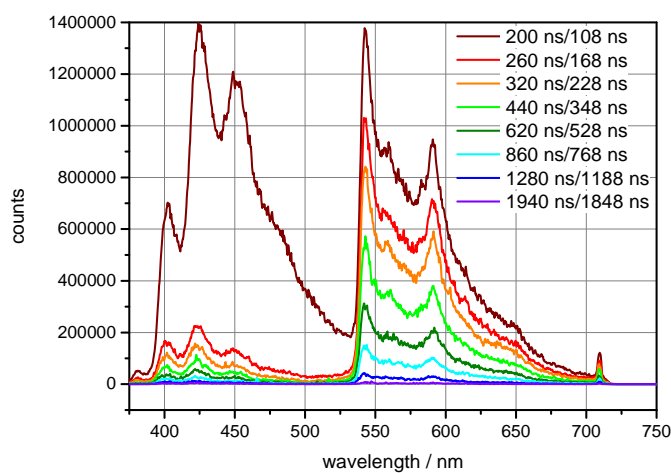
## Optical spectra



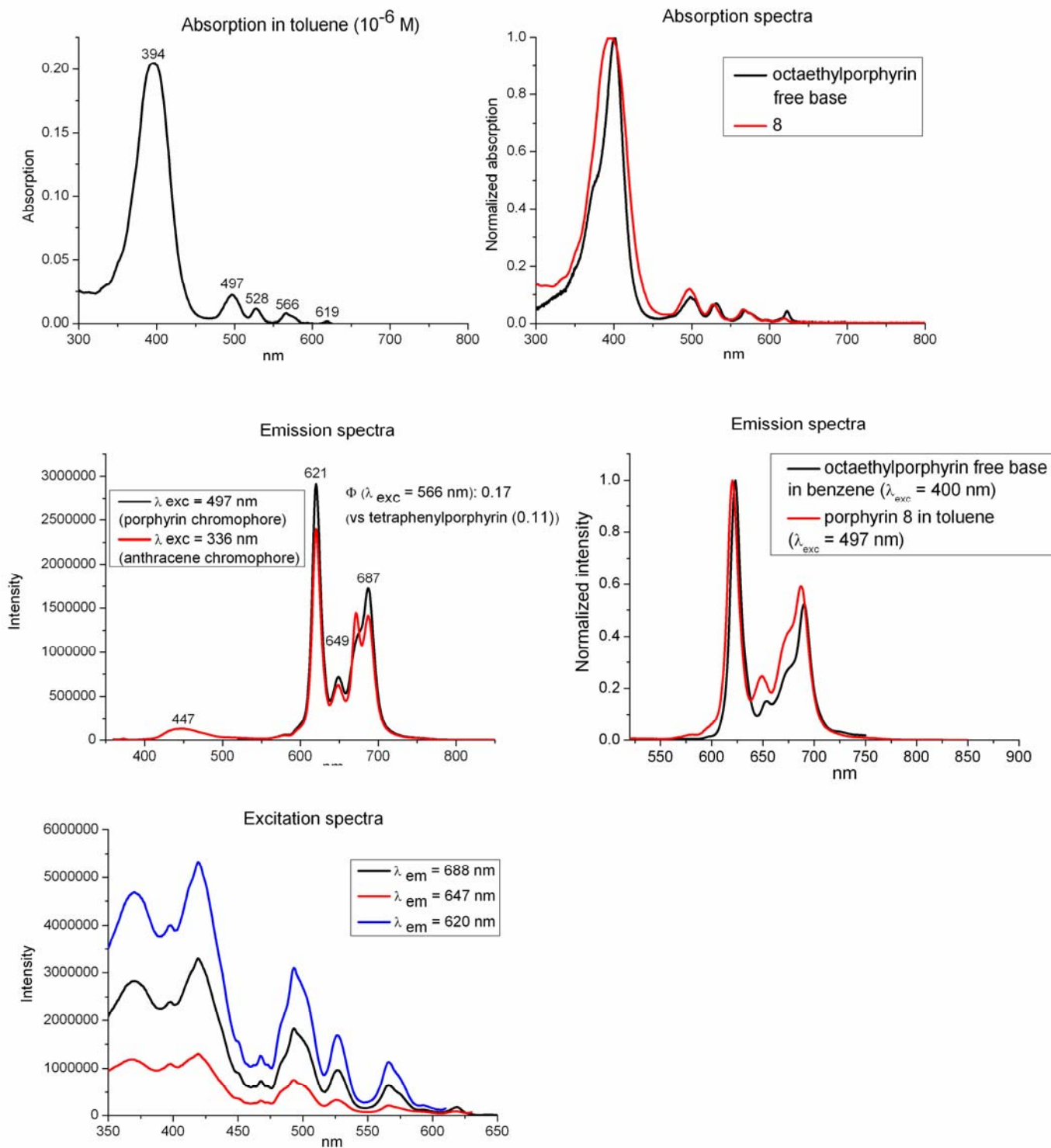
**Figure S17.** Optical spectra of 5,12-dimethoxy-1,4-dihydro-1,4-ethanotetracene (**3**) in comparison with 9,10-diphenylanthracene.



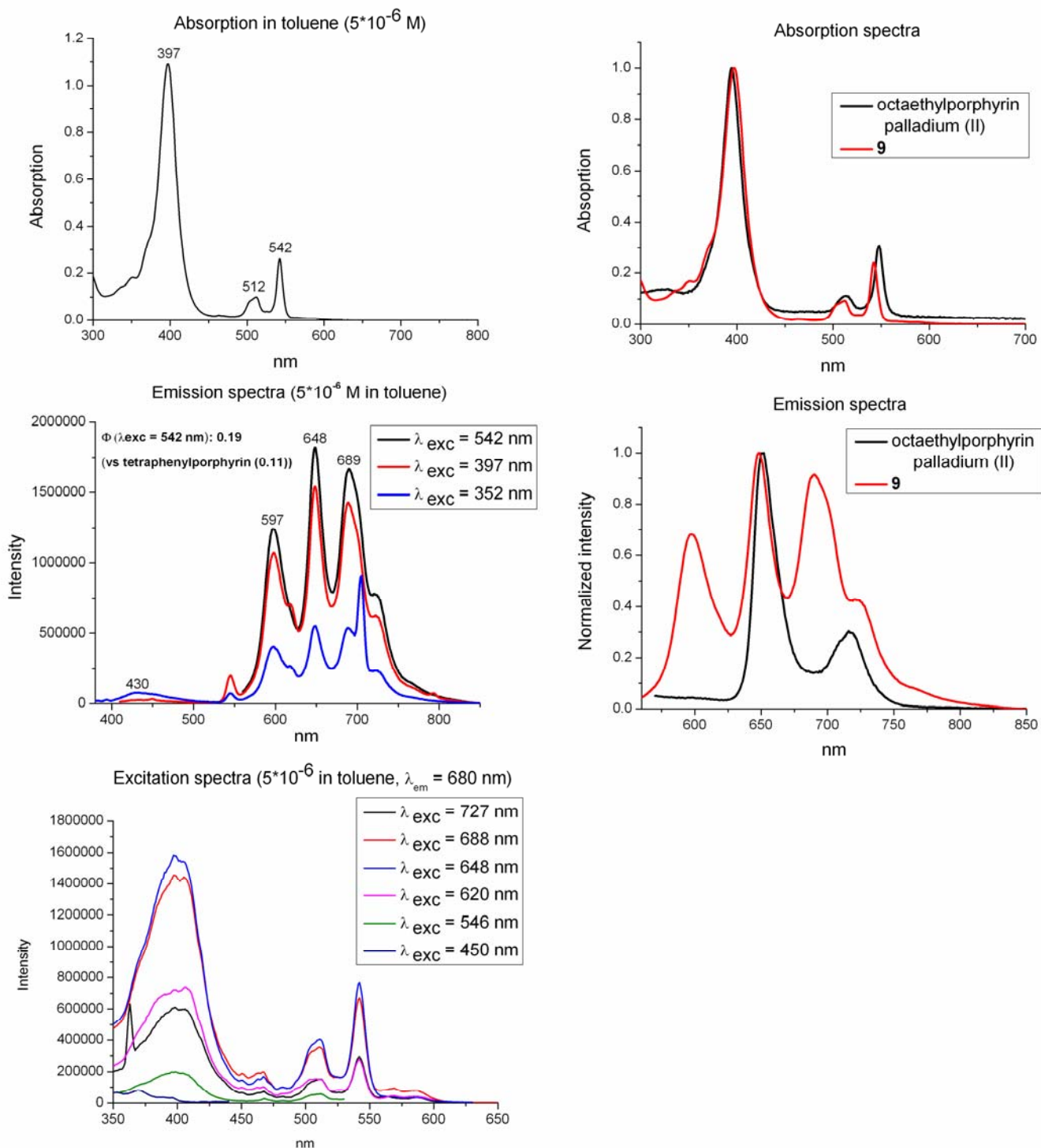
**Figure S18.** Fit of the fluorescence decay for compound **3**.



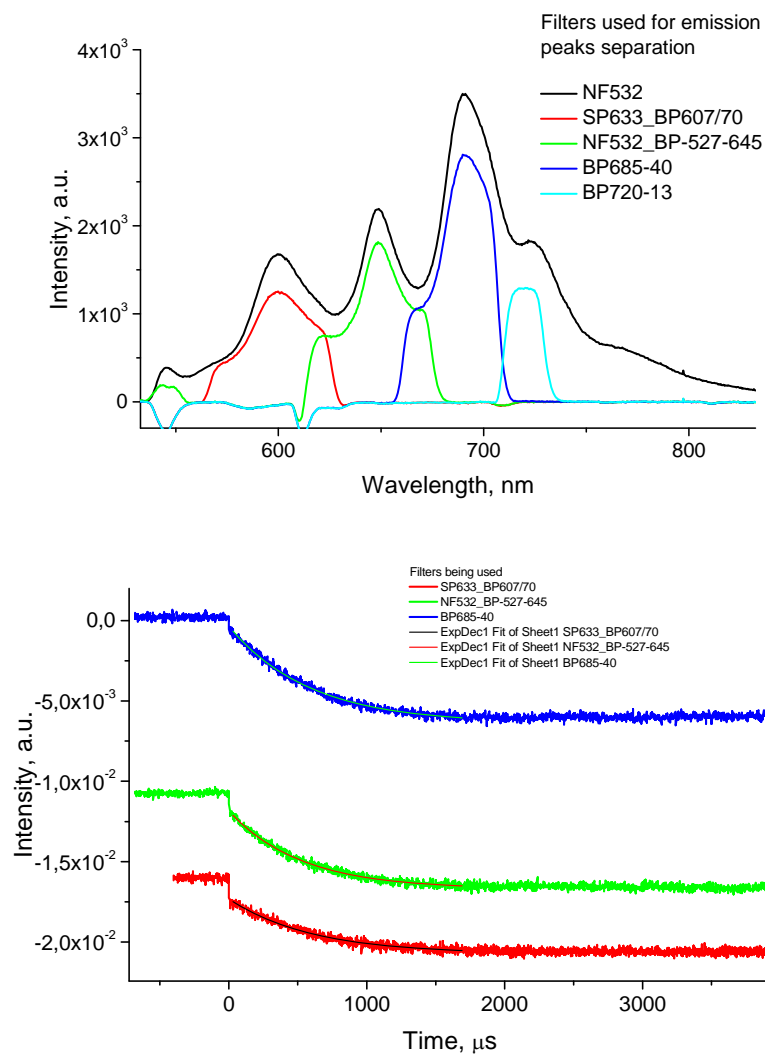
**Figure S19.** Emission spectrum of **3** at 77 K in methyltetrahydrofuran.



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

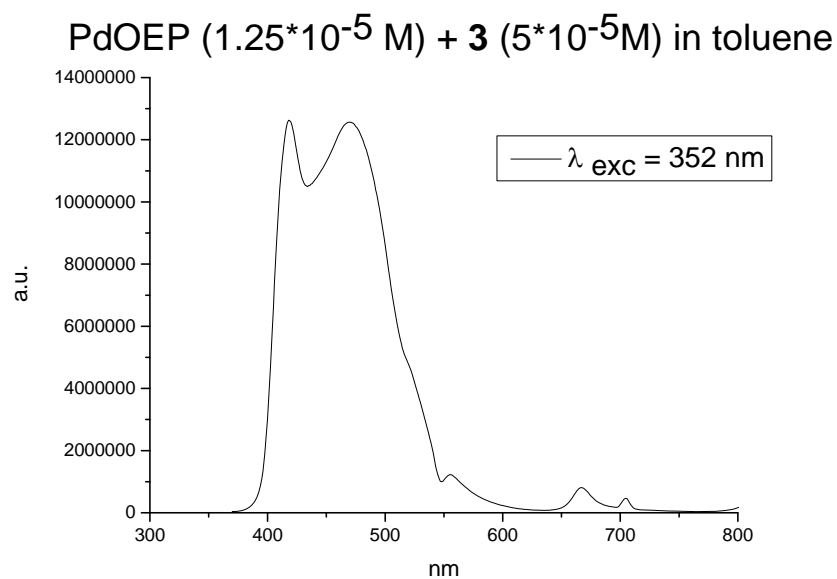


**Figure S21.** Optical spectra of porphyrin **9** ( $5 \cdot 10^{-6}$  M) compared with those of PdOEP.

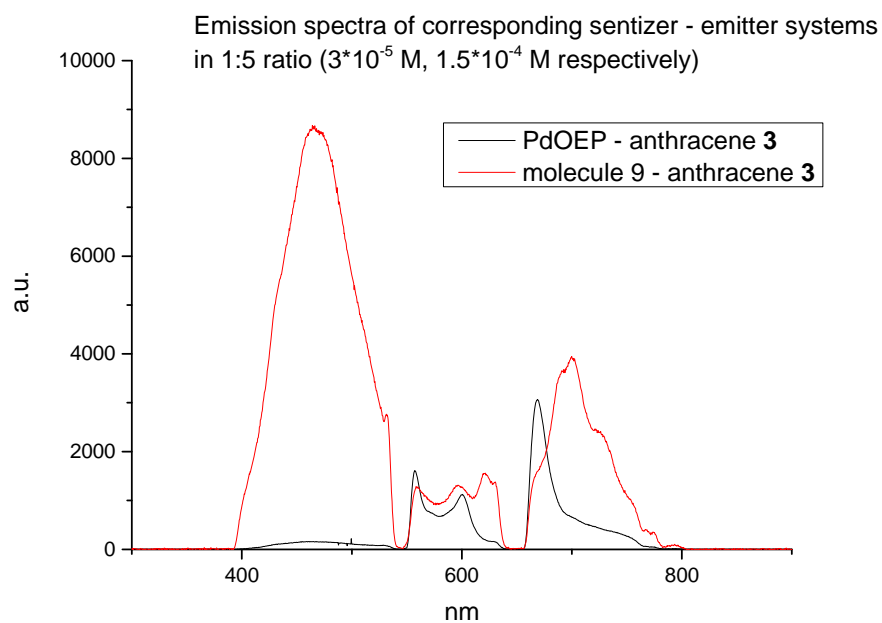


Model	ExpDec1		
Equation	$y = A1 * \exp(-x/t1) + y0$		
		Fitted lifeti	Standar Erro
SP633_BP607/70	t1	<b>601,8</b> <b>759</b>	16,749 74
NF532_BP-527-645	t1	<b>520,3</b> <b>1492</b>	8,0478 7
BP685-40	t1	<b>583,7</b> <b>4688</b>	8,6064 3

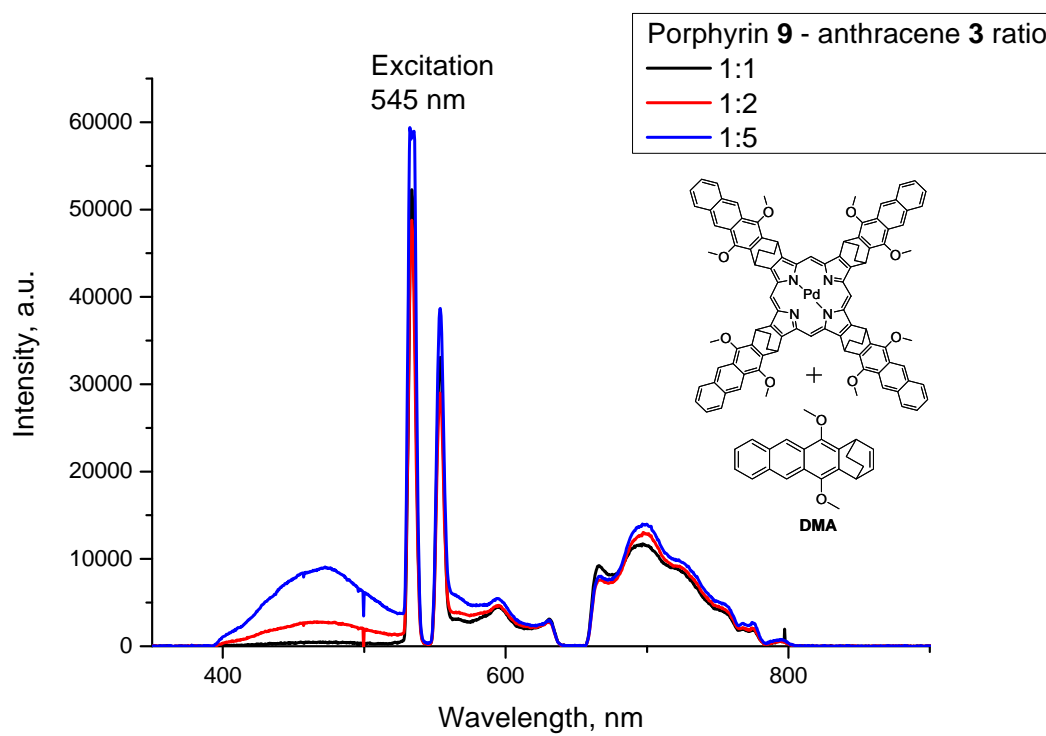
**Figure S22.** Porphyrin **9** ( $10^{-5}$  M) emission lifetimes at different wavelengths, measured using different optical filters.



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



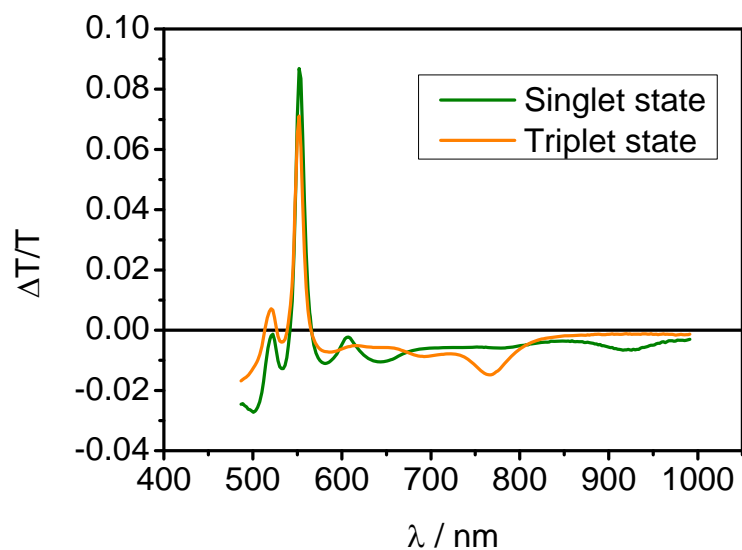
**Figure S24.** Comparison of the upconversion spectra of the systems based on porphyrin **9** or PdOEP as sensitizers and anthracene **3** as an emitter in 1:5 ratio. Samples were excited at 545 nm ( $10 \text{ mWcm}^{-2}$ ).



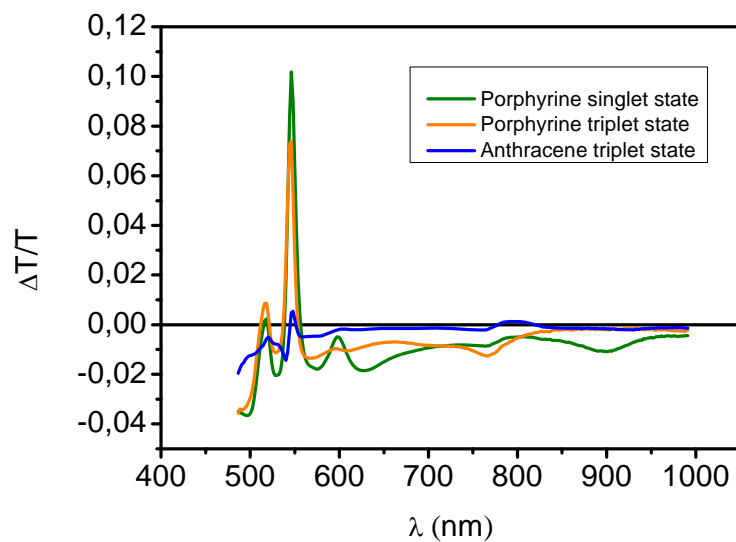
**Figure S25.** Upconversion spectra of samples containing  $3 \cdot 10^{-5}$  M of **9** and 1, 2 or 5 equivalents of **3** as an emitter (solvent – toluene). Samples were excited at 545 nm ( $10 \text{ mWcm}^{-2}$ ).



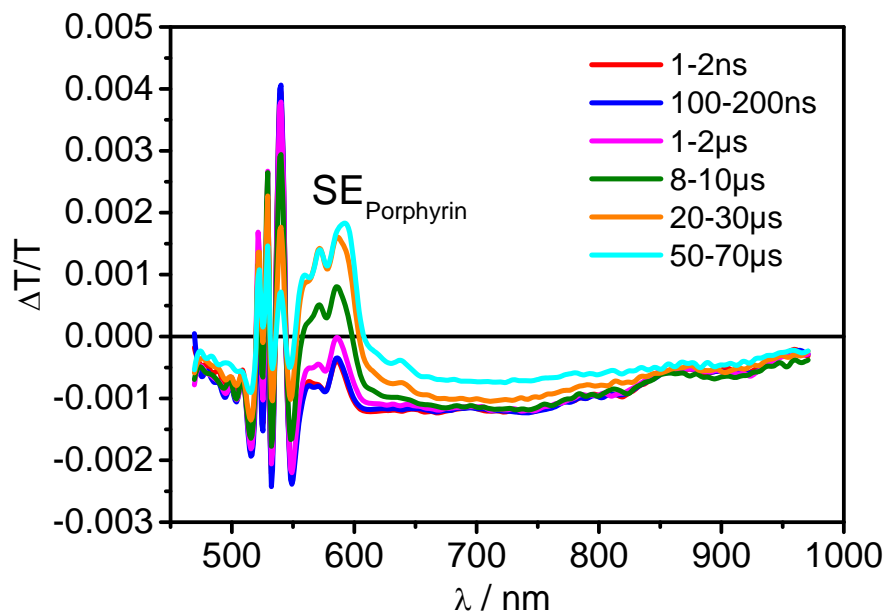
### Transient absorption spectra



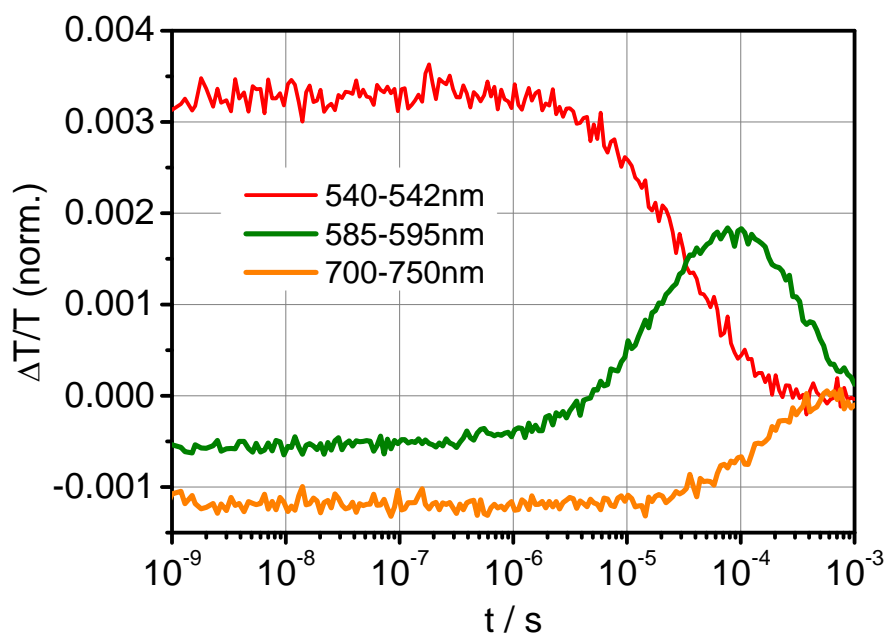
**Figure S26.** Component spectra of singlet and triplet states of PdOEP ( $10^{-4}$  M) obtained by global analysis.



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



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



**Figure S29.** ns- $\mu$ s 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).