Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Nonionic Omnisoluble Photosensitizer Reference Material for the Estimation of Singlet Oxygen Quantum Yield

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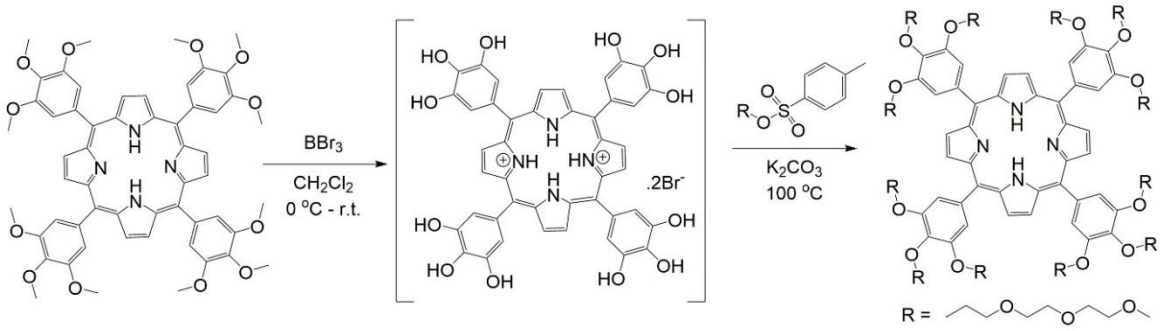

Scheme S1. Preparation of **$TEG_{12}PH_2$** from tetrakis(3,4,5-trimethoxyphenyl)porphyrin**.** Tetrakis(3,4,5-trihydroxyphenyl)porphyrin dihydrobromide was isolated by filtration and used without further purification. Triethylene glycol monomethyl ether tosylate was used as reaction solvent in the O-alkylation step.

Table S1. Absorption maxima and extinction coefficients of **$Teg_{12}PH_2$** in different solvents.

Solvent	λ_{max}	ε / mol^{-1} dm^3 cm^{-1}
Acetone	422, 515, 551, 592, 648	$2.67 \cdot 10^5$, 12300, 5700, 3700, 2900
Acetonitrile	421, 515, 551, 590, 647	$2.86 \cdot 10^5$, 12600, 5200, 3600, 2700
Chloroform	425, 518, 555, 592, 648	$2.98 \cdot 10^5$, 12900, 5800, 4200, 3000
Methanol	420, 516, 551, 590, 648	$2.89 \cdot 10^5$, 13000, 5800, 3900, 2800
Toluene	426, 518, 554, 593, 651	$2.85 \cdot 10^5$, 11700, 5600, 3700, 3000
Water	409, 420, 519, 556, 589, 648	$1.18 \cdot 10^5$, $1.39 \cdot 10^5$, 9000, 4300, 3100, 2100

Table S2. Absorption maxima and extinction coefficients of **$Teg_{12}PZn$** in different solvents.

Solvent	λ_{max}	ε / mol^{-1} dm^3 cm^{-1}
Acetone	427, 557, 597	$3.89 \cdot 10^5$, 14400, 5400
Acetonitrile	426, 557, 597	$4.01 \cdot 10^5$, 14900, 5500
Chloroform	428, 556, 596	$4.11 \cdot 10^5$, 15900, 4800
Methanol	426, 558, 598	$5.00 \cdot 10^5$, 17800, 6700
Toluene	429, 556, 597	$3.64 \cdot 10^5$, 14300, 5000
Water	427, 560, 600	$2.56 \cdot 10^5$, 14000, 6100

Table S3. Fluorescence lifetimes of **$Teg_{12}PH_2$** in different solvents under an atmosphere of argon, air or oxygen.

Solvent	Argon	Air	Oxygen
Acetone	9.85 ns	8.15 ns	5.51 ns
Acetonitrile	9.35 ns	7.92 ns	5.09 ns
Chloroform	7.51 ns	6.88 ns	5.42 ns
Methanol	9.43 ns	8.09 ns	5.27 ns
Toluene	9.51 ns	8.26 ns	5.71 ns
Water	9.58 ns	9.65 ns	9.24 ns

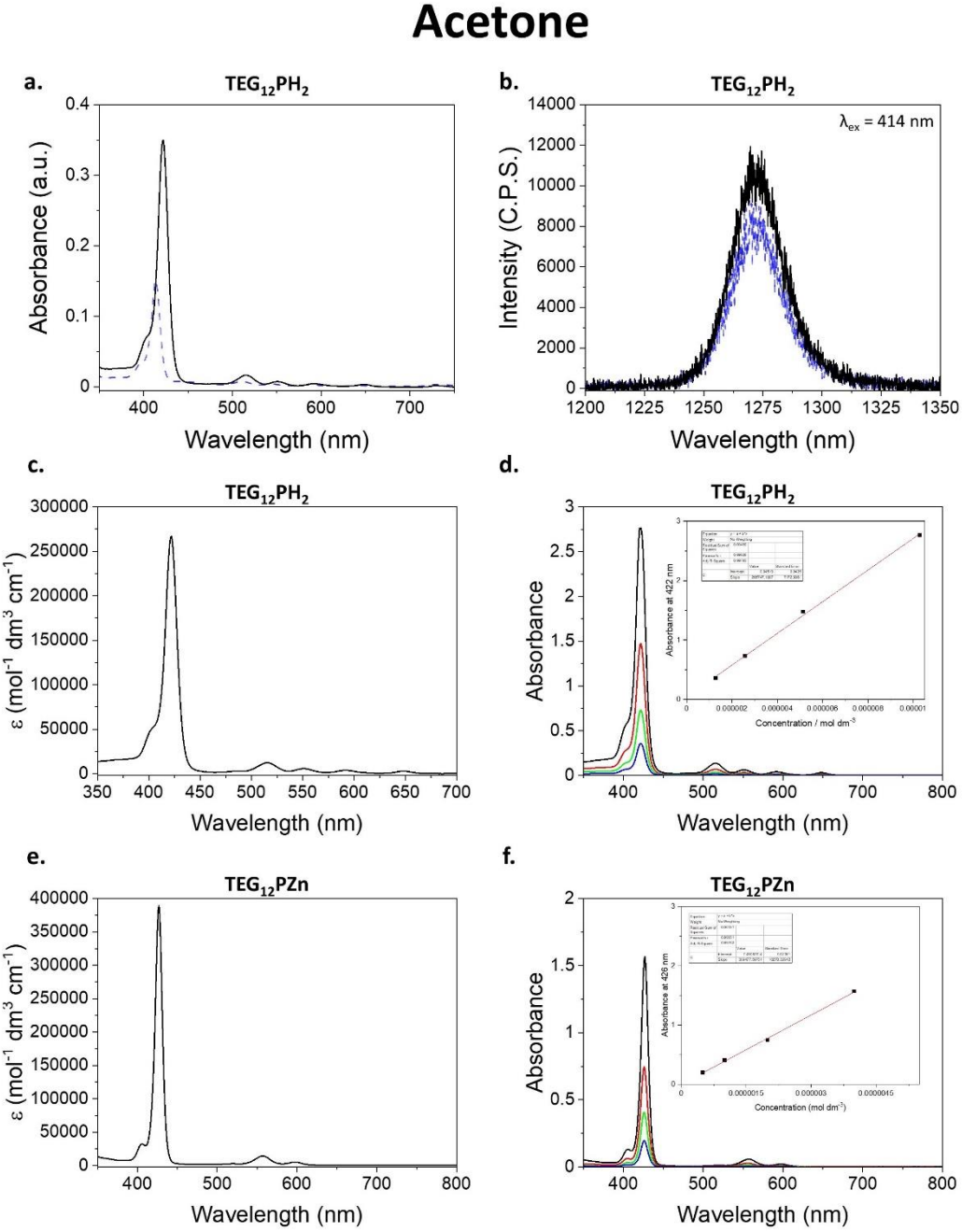

Figure S1. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (black solid lines) and TPP (blue dashed line) in acetone with matched absorption intensity at 414 nm. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** (black solid lines) and TPP (blue dashed line) in acetone after excitation at 414 nm. c. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (5.14×10^{-6} M) in acetone. d. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PH_2$** in acetone used to determine extinction coefficient (inset). e. UV-Vis absorption spectrum of **$TEG_{12}PZn$** (3.99×10^{-6} M) in acetone. f. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PZn$** in acetone used to determine extinction coefficient (inset).

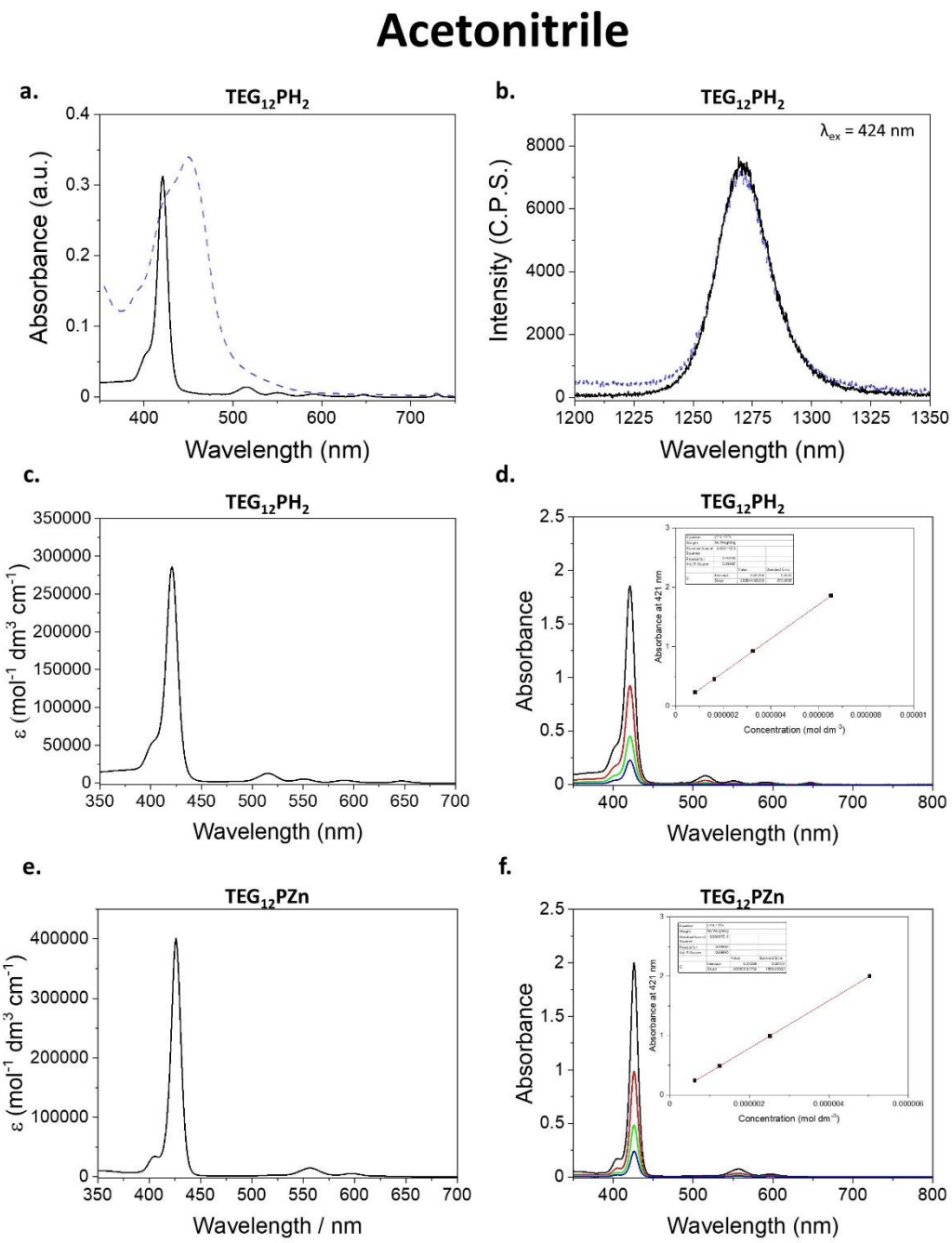

Figure S2. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (black solid lines) and $Ru(bpy)_3Cl_2$ (blue dashed line) in acetonitrile with matched absorption intensity at 424 nm. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** (black solid lines) and $Ru(bpy)_3Cl_2$ (blue dashed line) in acetonitrile after excitation at 424 nm. c. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (6.52×10^{-6} M) in acetonitrile. d. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PH_2$** in acetonitrile used to determine extinction coefficient (inset). e. UV-Vis absorption spectrum of **$TEG_{12}PZn$** (5.03×10^{-6} M) in acetonitrile. f. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PZn$** in acetonitrile used to determine extinction coefficient (inset).

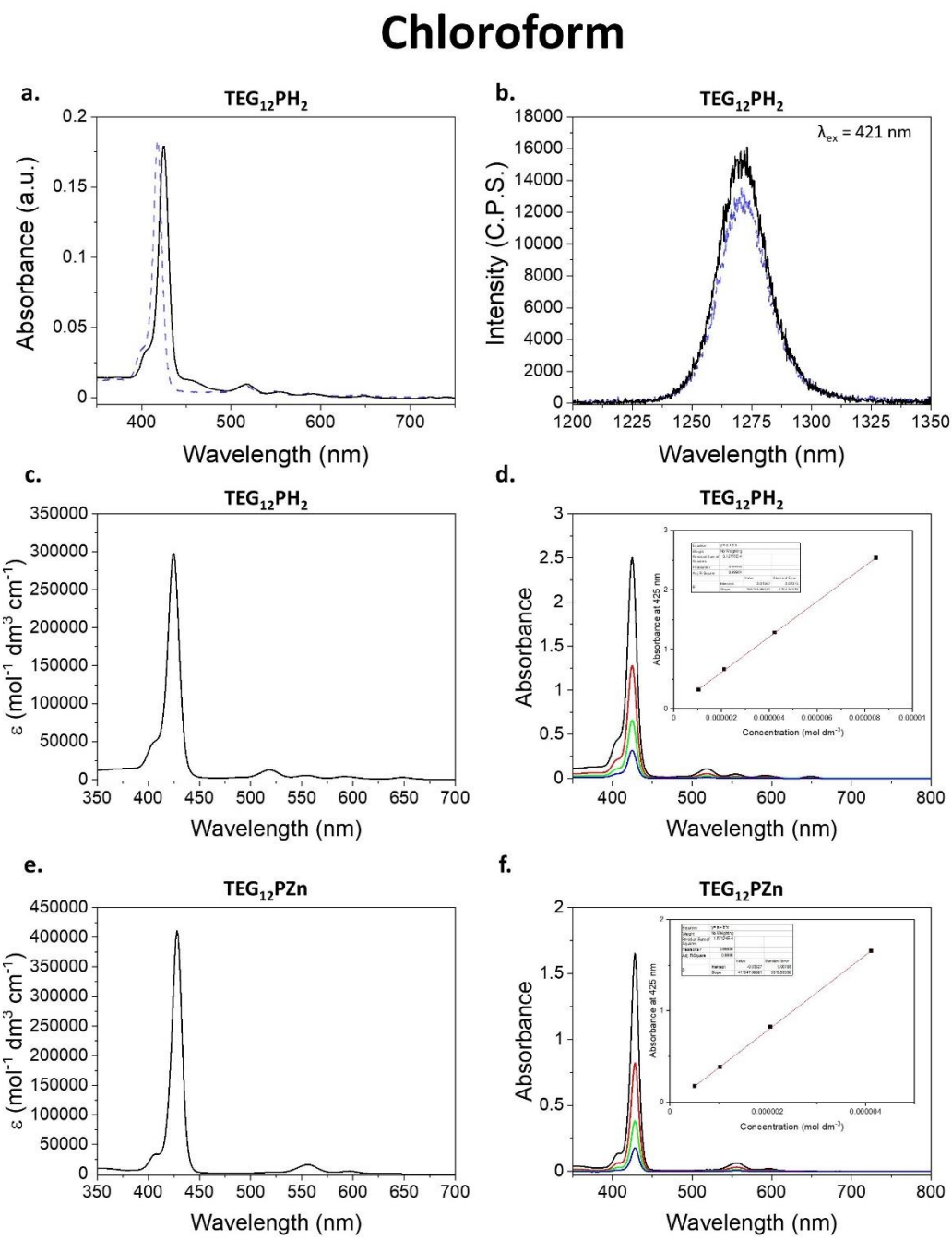

Figure S3. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (black solid lines) and TPP (blue dashed line) in chloroform with matched absorption intensity at 421 nm. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** (black solid lines) and TPP (blue dashed line) in chloroform after excitation at 421 nm. c. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (4.23×10^{-6} M) in chloroform. d. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PH_2$** in chloroform used to determine extinction coefficient (inset). e. UV-Vis absorption spectrum of **$TEG_{12}PZn$** (4.11×10^{-6} M) in chloroform. f. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PZn$** in chloroform used to determine extinction coefficient (inset).

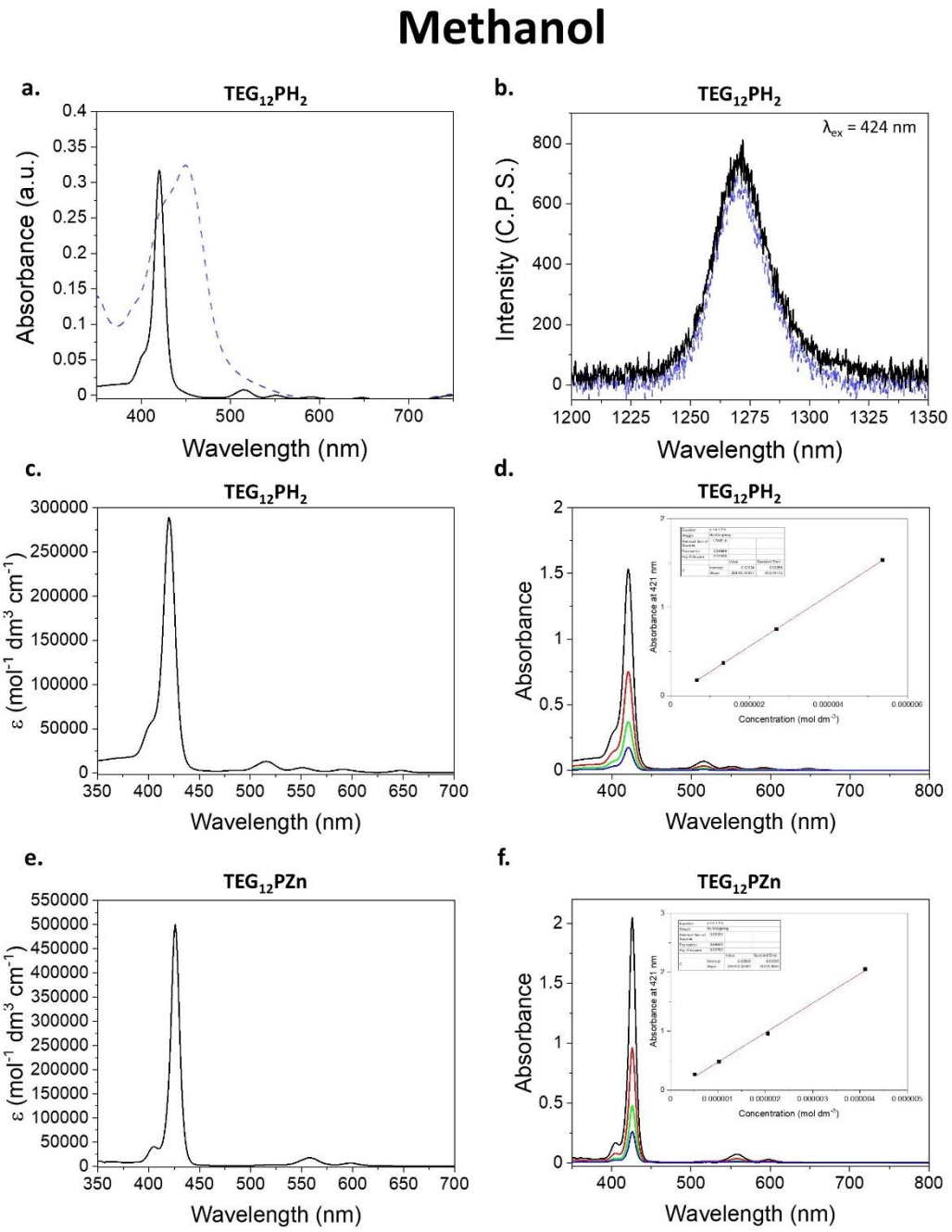

Figure S4. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (black solid lines) and $Ru(bpy)_3Cl_2$ (blue dashed line) in methanol with matched absorption intensity at 424 nm. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** (black solid lines) and $Ru(bpy)_3Cl_2$ (blue dashed line) in methanol after excitation at 424 nm. c. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (5.37×10^{-6} M) in methanol. d. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PH_2$** in methanol used to determine extinction coefficient (inset). e. UV-Vis absorption spectrum of **$TEG_{12}PZn$** (4.11×10^{-6} M) in methanol. f. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PZn$** in methanol used to determine extinction coefficient (inset).

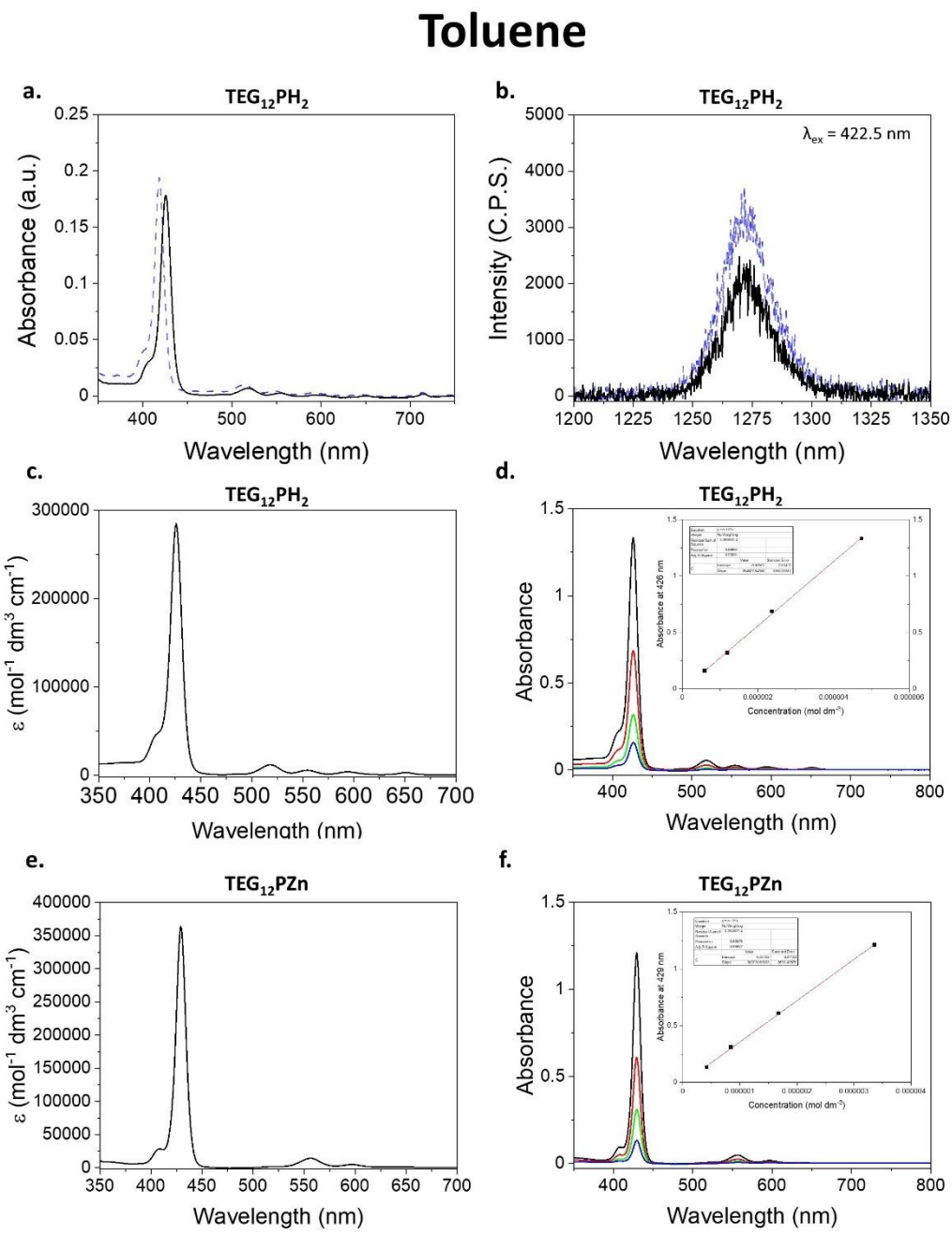

Figure S5. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (black solid lines) and TPP (blue dashed line) in toluene with matched absorption intensity at 422.5 nm. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** (black solid lines) and TPP (blue dashed line) in toluene after excitation at 422.5 nm. c. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (4.74×10^{-6} M) in toluene. d. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PH_2$** in toluene used to determine extinction coefficient (inset). e. UV-Vis absorption spectrum of **$TEG_{12}PZn$** (3.36×10^{-6} M) in toluene. f. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PZn$** in toluene used to determine extinction coefficient (inset).

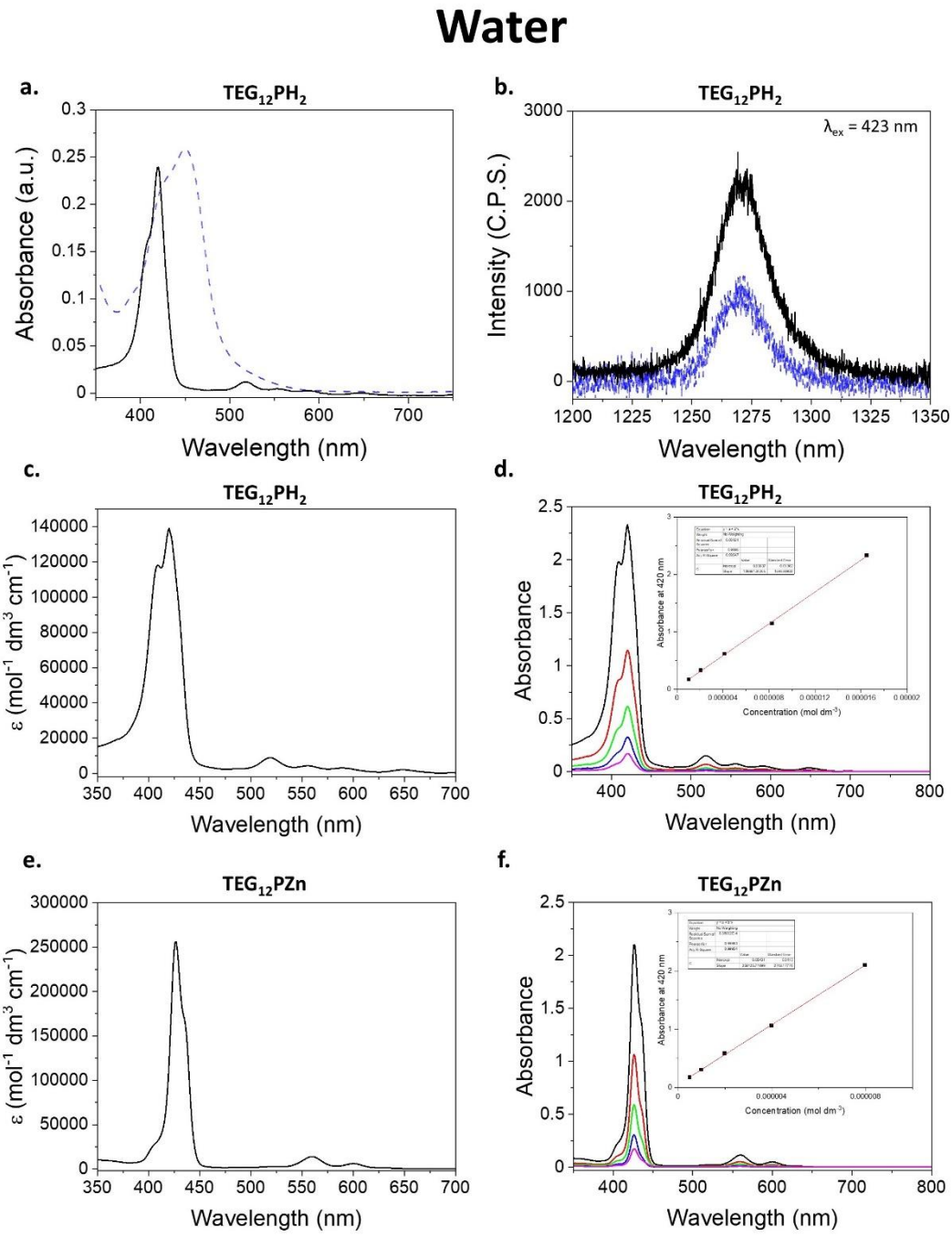

Figure S6. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (black solid lines) and $Ru(bpy)_3Cl_2$ (blue dashed line) in water (D_2O) with matched absorption intensity at 423 nm. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** (black solid lines) and $Ru(bpy)_3Cl_2$ (blue dashed line) in water (D_2O) after excitation at 423 nm. c. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (1.65×10^{-5} M) in water (H_2O). d. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PH_2$** in water (H_2O) used to determine extinction coefficient (inset). e. UV-Vis absorption spectrum of **$TEG_{12}PZn$** (7.98×10^{-6} M) in water (H_2O). f. UV-Vis absorption spectrum of serial dilutions of **$TEG_{12}PZn$** in water (H_2O) used to determine extinction coefficient (inset).

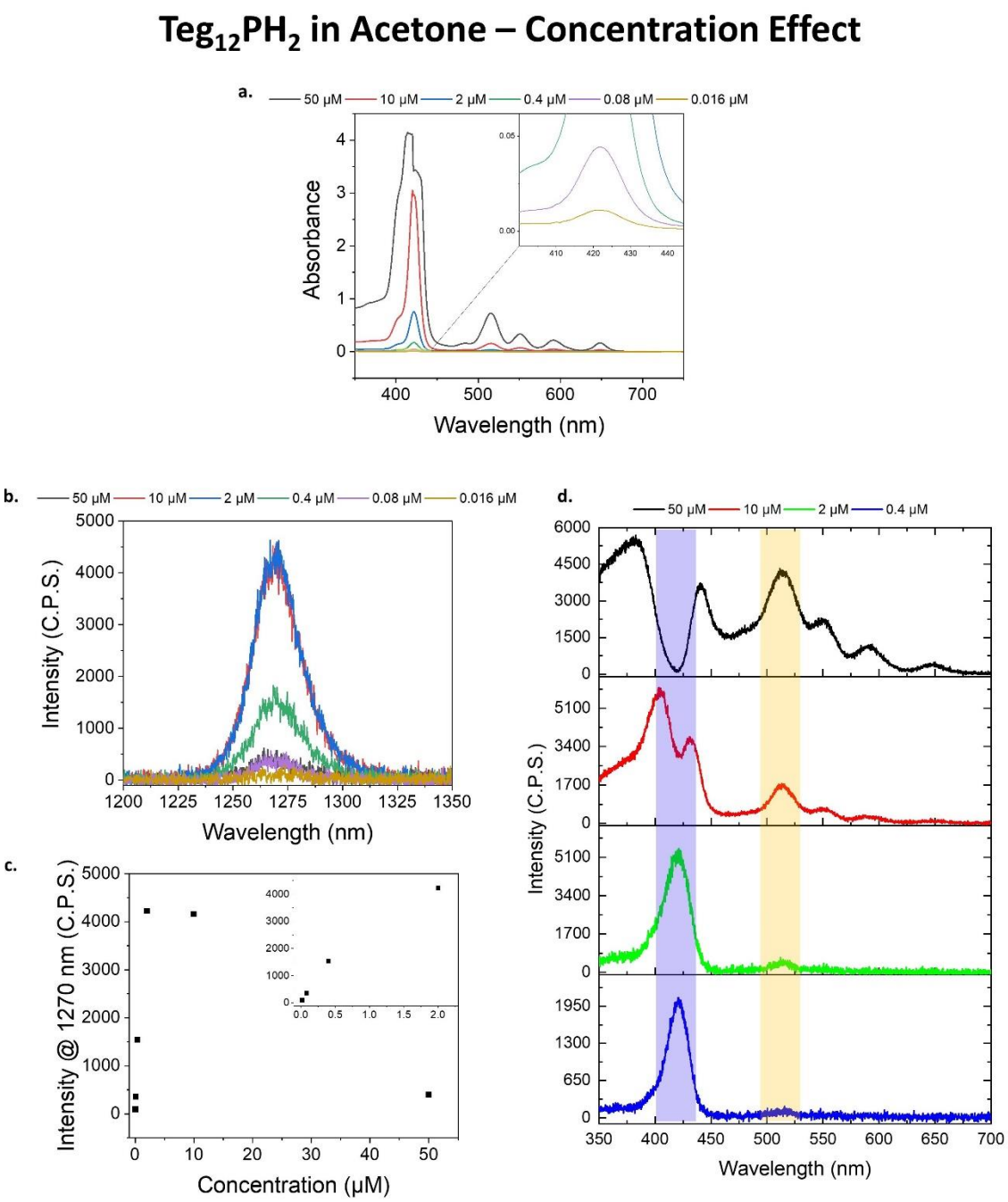

Figure S7. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** in acetone at various concentrations. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** in acetone at various concentrations after excitation at 414 nm. c. Comparison of intensity maxima of **$TEG_{12}PH_2$** at various concentrations in acetone with the linear region inset. d. Excitation spectra (λ_{em} = 1270 nm) of **$TEG_{12}PH_2$** at various concentrations in acetone with the Soret band (blue) and 1st Q-band (orange) regions highlighted.

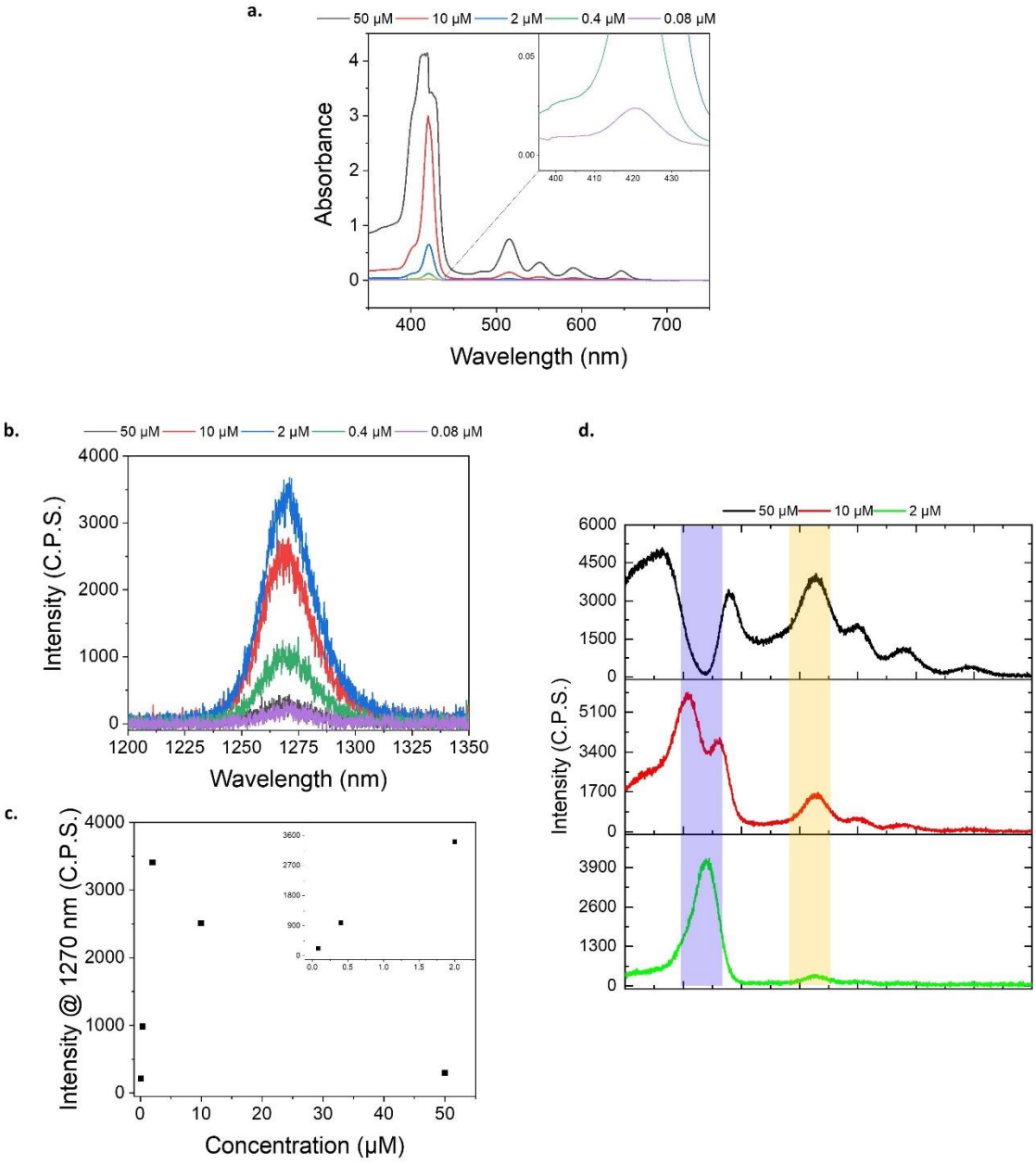

Figure S8. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** in acetonitrile at various concentrations. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** in acetonitrile at various concentrations after excitation at 414 nm. c. Comparison of intensity maxima of **$TEG_{12}PH_2$** at various concentrations in acetonitrile with the linear region inset. d. Excitation spectra (λ_{em} = 1270 nm) of **$TEG_{12}PH_2$** at various concentrations in acetonitrile with the Soret band (blue) and 1st Q-band (orange) regions highlighted.

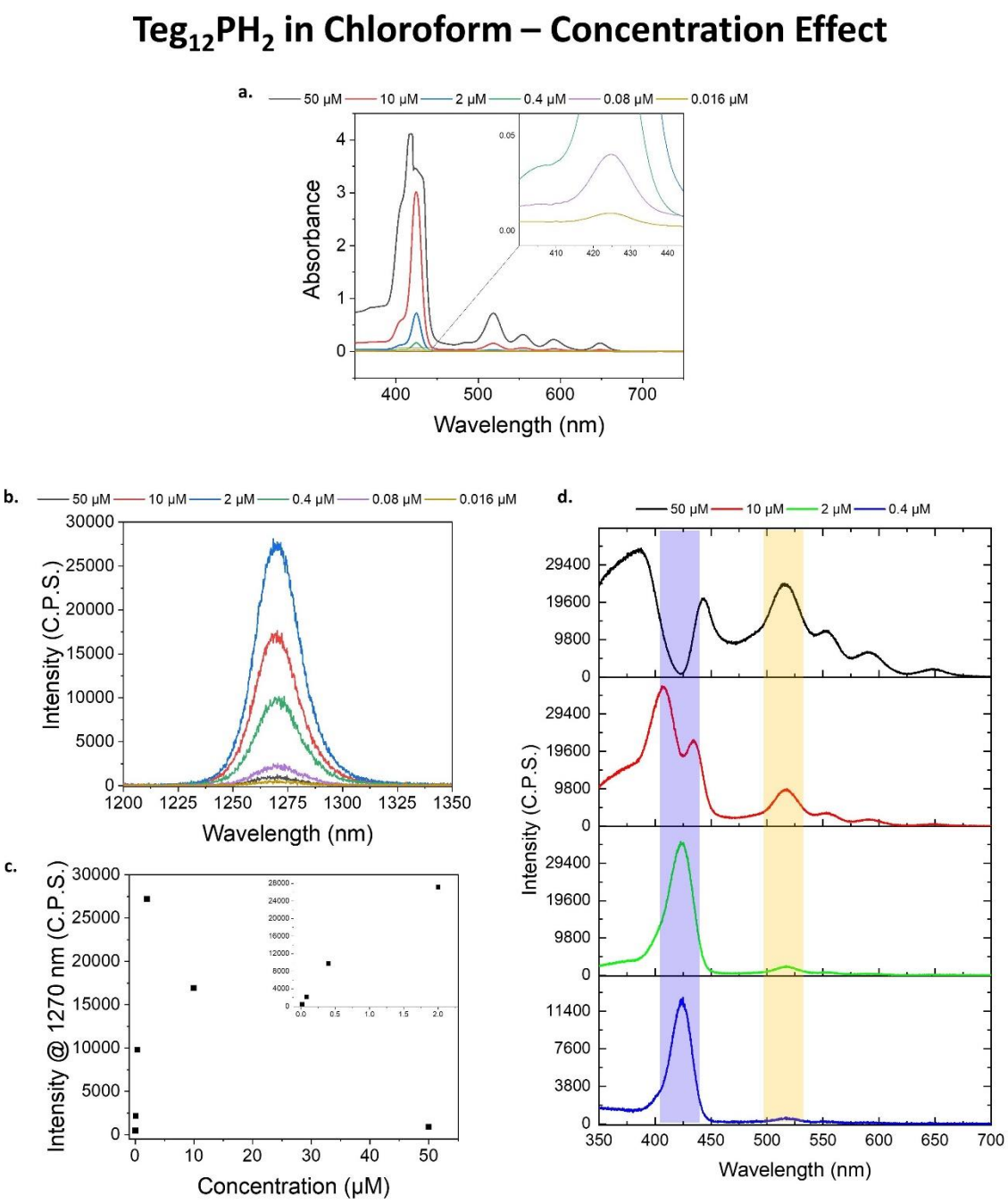

Figure S9. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** in chloroform at various concentrations. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** in chloroform at various concentrations after excitation at 414 nm. c. Comparison of intensity maxima of **$TEG_{12}PH_2$** at various concentrations in chloroform with the linear region inset. d. Excitation spectra (λ_{em} = 1270 nm) of **$TEG_{12}PH_2$** at various concentrations in chloroform with the Soret band (blue) and 1st Q-band (orange) regions highlighted.

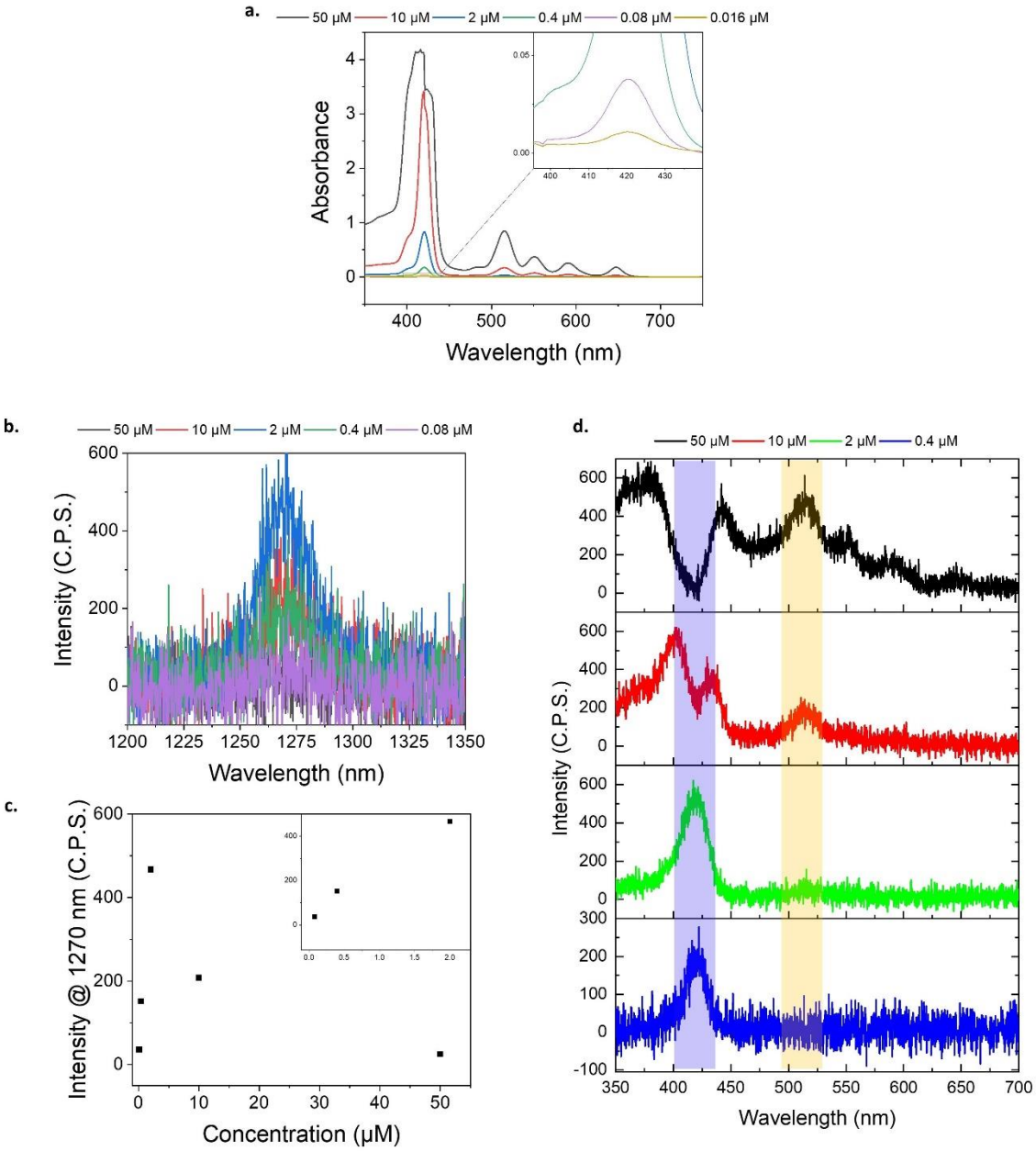

Figure S10. a. UV-Vis absorption spectrum of **TEG$_{12}$PH$_2$** in methanol at various concentrations. b. $^1O_2$ phosphorescence spectrum of **TEG$_{12}$PH$_2$** in methanol at various concentrations after excitation at 414 nm. c. Comparison of intensity maxima of **TEG$_{12}$PH$_2$** at various concentrations in methanol with the linear region inset. d. Excitation spectra (λ_{em} = 1270 nm) of **TEG$_{12}$PH$_2$** at various concentrations in methanol with the Soret band (blue) and 1st Q-band (orange) regions highlighted.

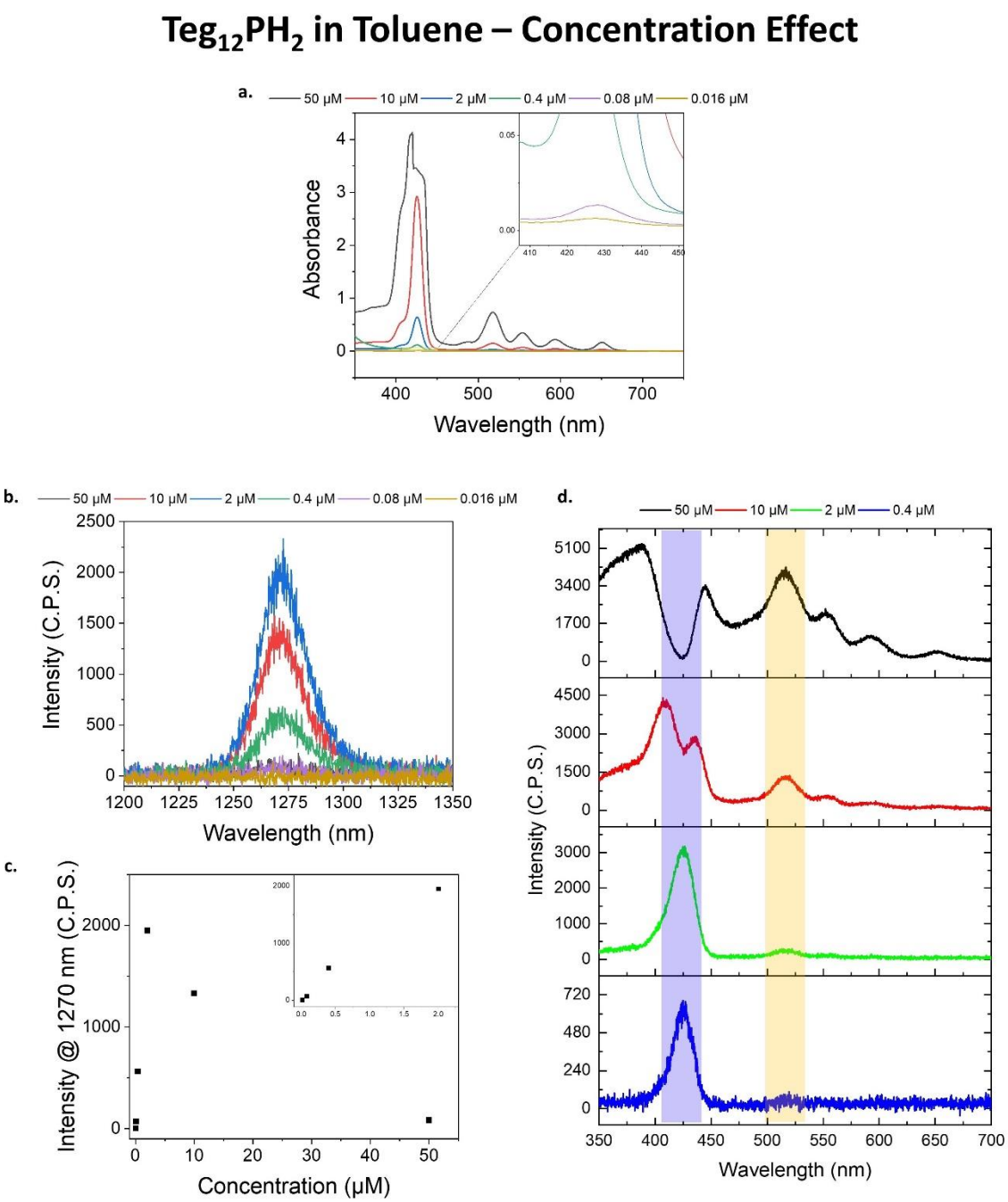

Figure S11. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** in toluene at various concentrations. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** in toluene at various concentrations after excitation at 414 nm. c. Comparison of intensity maxima of **$TEG_{12}PH_2$** at various concentrations in toluene with the linear region inset. d. Excitation spectra (λ_{em} = 1270 nm) of **$TEG_{12}PH_2$** at various concentrations in toluene with the Soret band (blue) and 1st Q-band (orange) regions highlighted.

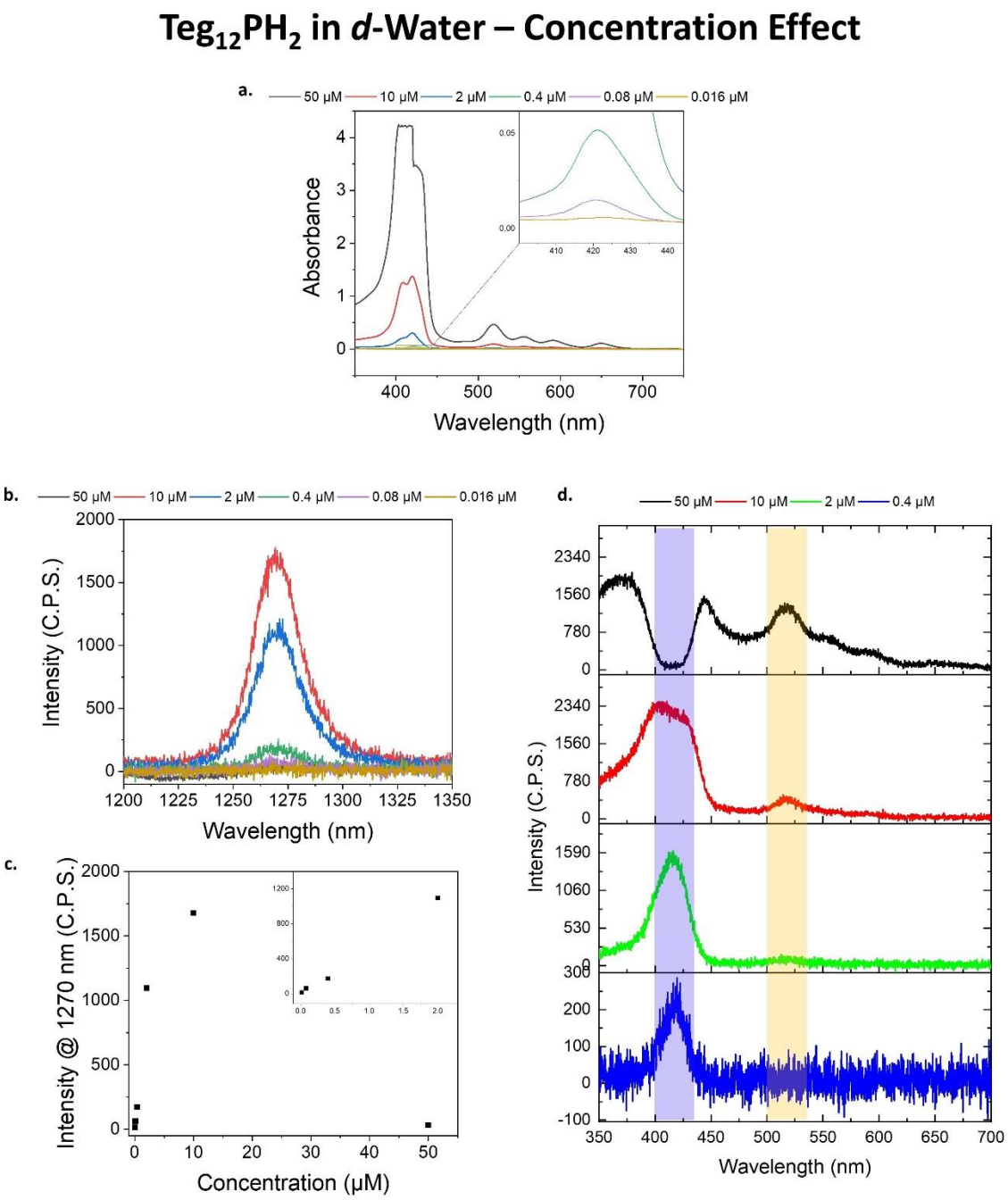

Figure S12. a. UV-Vis absorption spectrum of **TEG$_{12}$PH$_2$** in D_2O at various concentrations. b. $^1O_2$ phosphorescence spectrum of **TEG$_{12}$PH$_2$** in D_2O at various concentrations after excitation at 414 nm. c. Comparison of intensity maxima of **TEG$_{12}$PH$_2$** at various concentrations in D_2O with the linear region inset. d. Excitation spectra (λ_{em} = 1270 nm) of **TEG$_{12}$PH$_2$** at various concentrations in D_2O with the Soret band (blue) and 1st Q-band (orange) regions highlighted.

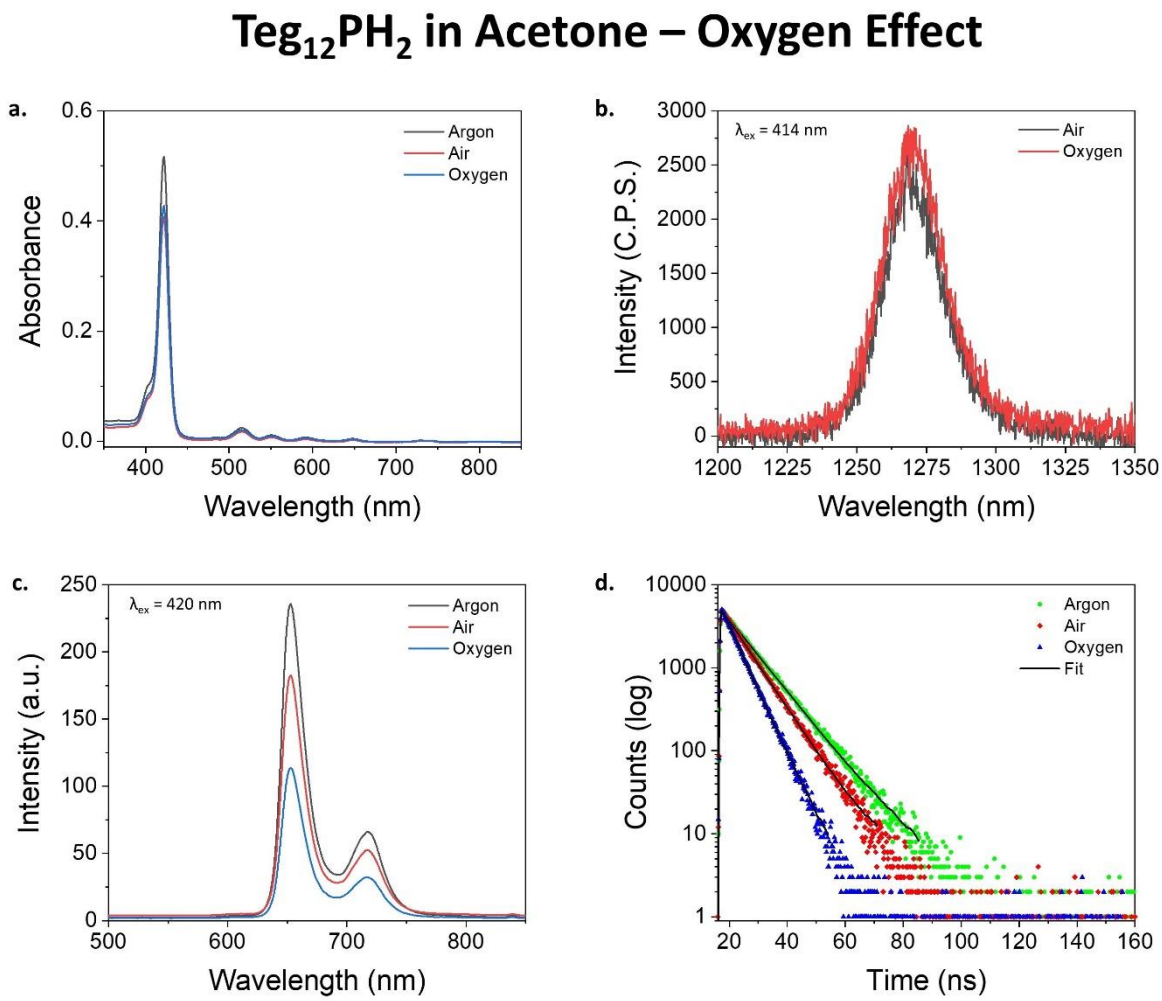

Figure S13. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in acetone with an argon, air or oxygen atmosphere. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in acetone with atmosphere of air or oxygen after excitation at 414 nm. c. Fluorescence emission spectra of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in acetone with an argon, air or oxygen atmosphere excited at 420 nm. d. Fluorescence lifetime measurements (λ_{ex} = 402 nm, λ_{em} = 657 nm) of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in acetone with an atmosphere of argon, air or oxygen.

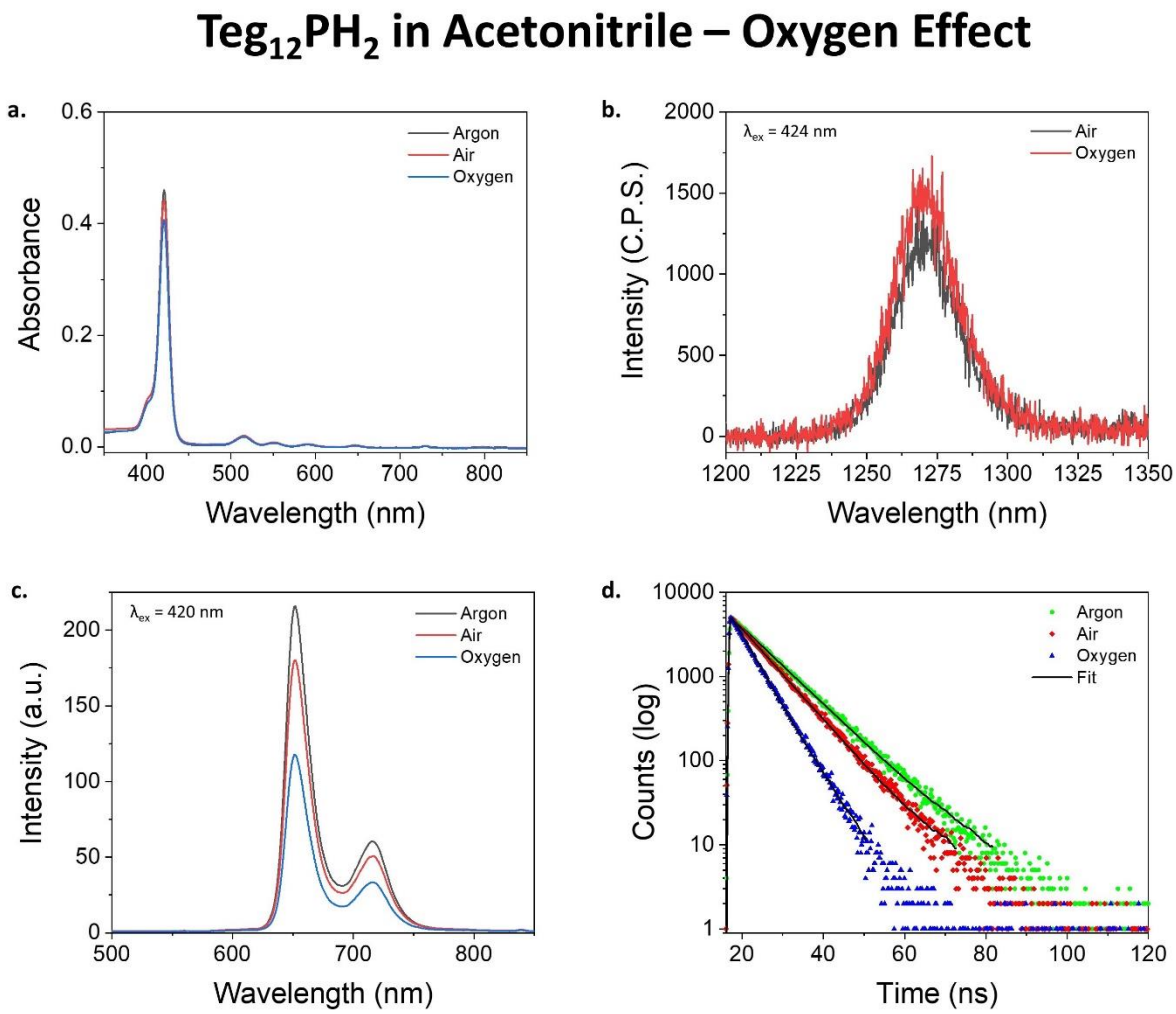

Figure S14. a. UV-Vis absorption spectrum of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in acetonitrile with an argon, air or oxygen atmosphere. b. $^1O_2$ phosphorescence spectrum of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in acetonitrile with atmosphere of air or oxygen after excitation at 424 nm. c. Fluorescence emission spectra of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in acetonitrile with an argon, air or oxygen atmosphere excited at 420 nm. d. Fluorescence lifetime measurements (λ_{ex} = 402 nm, λ_{em} = 657 nm) of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in acetonitrile with an atmosphere of argon, air or oxygen.

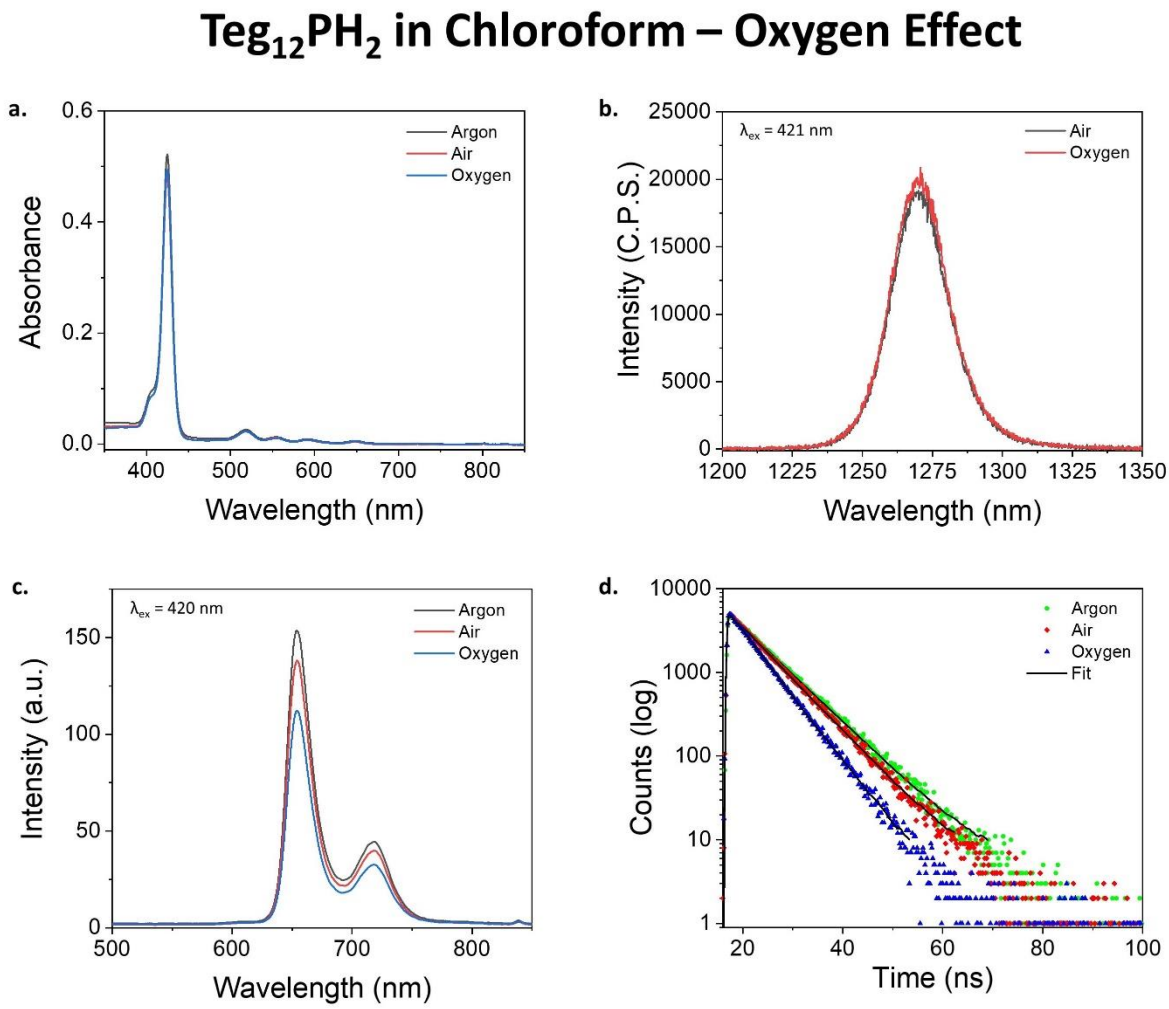

Figure S15. a. UV-Vis absorption spectrum of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in chloroform with an argon, air or oxygen atmosphere. b. $^1O_2$ phosphorescence spectrum of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in chloroform with atmosphere of air or oxygen after excitation at 421 nm. c. Fluorescence emission spectra of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in chloroform with an argon, air or oxygen atmosphere excited at 420 nm. d. Fluorescence lifetime measurements (λ_{ex} = 402 nm, λ_{em} = 657 nm) of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in chloroform with an atmosphere of argon, air or oxygen.

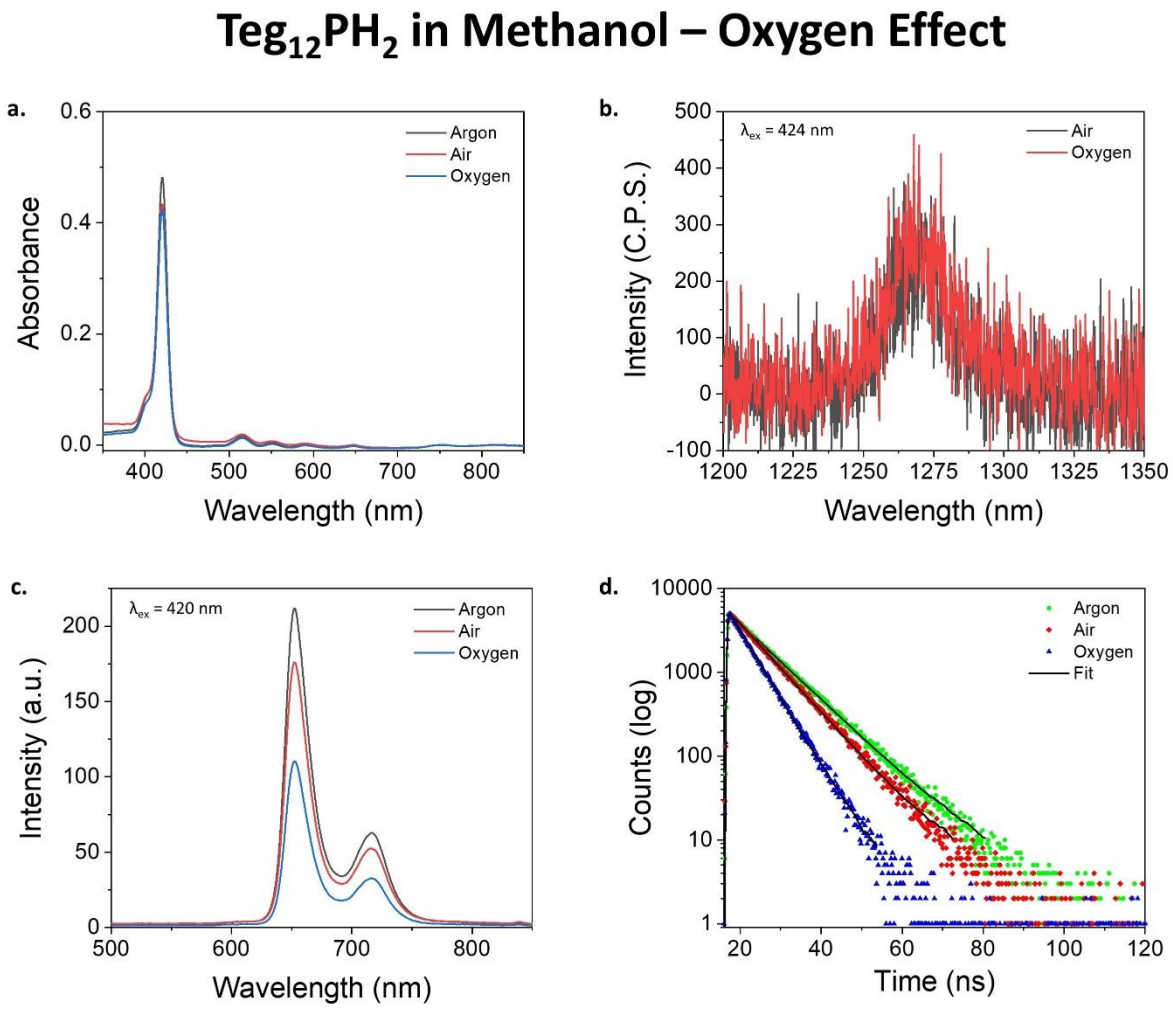

Figure S16. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in methanol with an argon, air or oxygen atmosphere. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in methanol with atmosphere of air or oxygen after excitation at 424 nm. c. Fluorescence emission spectra of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in methanol with an argon, air or oxygen atmosphere excited at 420 nm. d. Fluorescence lifetime measurements (λ_{ex} = 402 nm, λ_{em} = 657 nm) of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in methanol with an atmosphere of argon, air or oxygen.

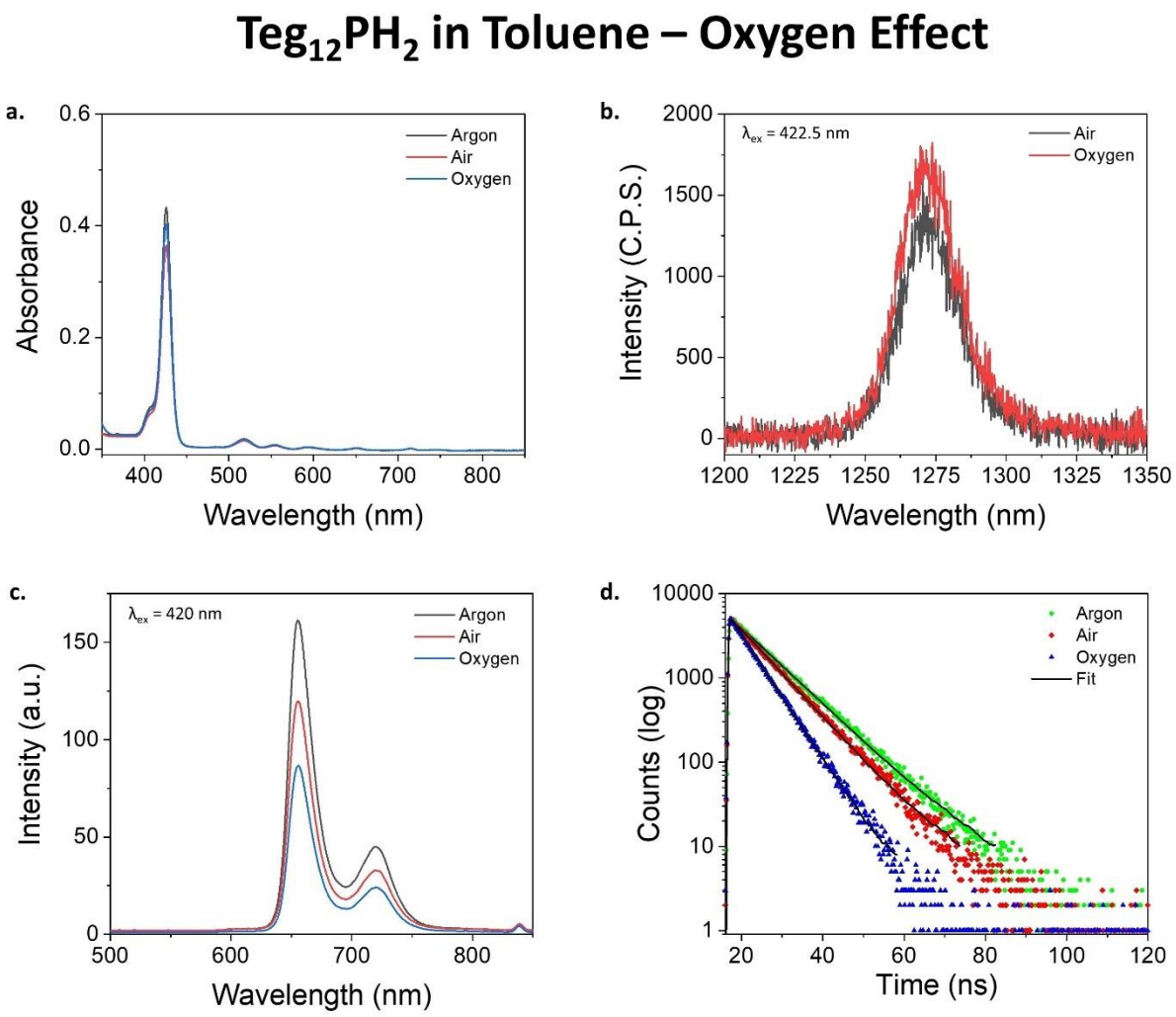

Figure S17. a. UV-Vis absorption spectrum of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in toluene with an argon, air or oxygen atmosphere. b. $^1O_2$ phosphorescence spectrum of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in toluene with atmosphere of air or oxygen after excitation at 422.5 nm. c. Fluorescence emission spectra of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in toluene with an argon, air or oxygen atmosphere excited at 420 nm. d. Fluorescence lifetime measurements (λ_{ex} = 402 nm, λ_{em} = 657 nm) of **$TEG_{12}PH_2$** (1.30×10^{-6} M) in toluene with an atmosphere of argon, air or oxygen.

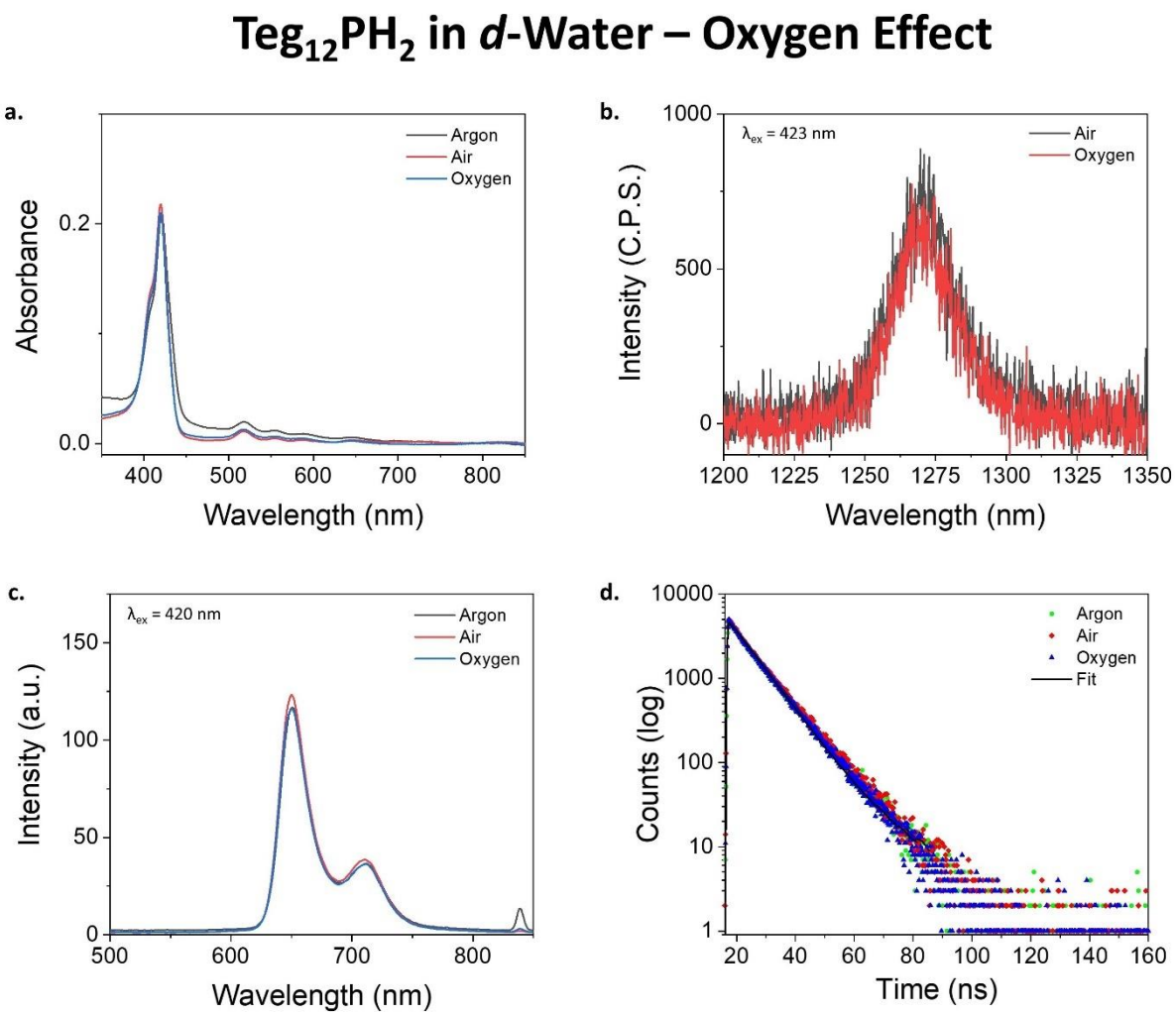

Figure S18. a. UV-Vis absorption spectrum of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in D_2O with an argon, air or oxygen atmosphere. b. $^1O_2$ phosphorescence spectrum of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in D_2O with atmosphere of air or oxygen after excitation at 423 nm. c. Fluorescence emission spectra of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in D_2O with an argon, air or oxygen atmosphere excited at 420 nm. d. Fluorescence lifetime measurements (λ_{ex} = 402 nm, λ_{em} = 657 nm) of **TEG$_{12}$PH$_2$** (1.30×10^{-6} M) in D_2O with an atmosphere of argon, air or oxygen.

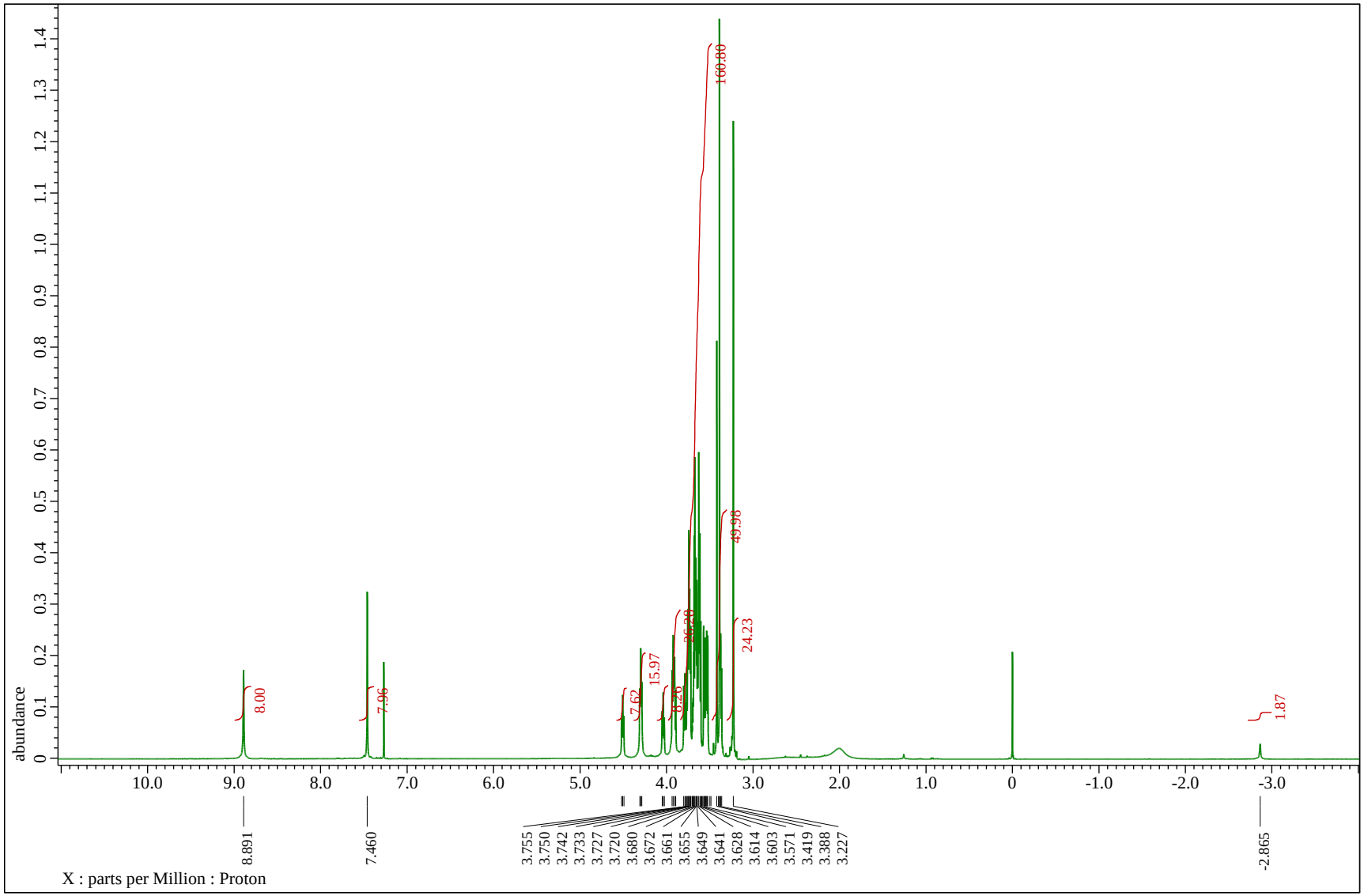

Figure S19. ^{1}H NMR spectrum of **TEG$_{12}$PH$_2$**

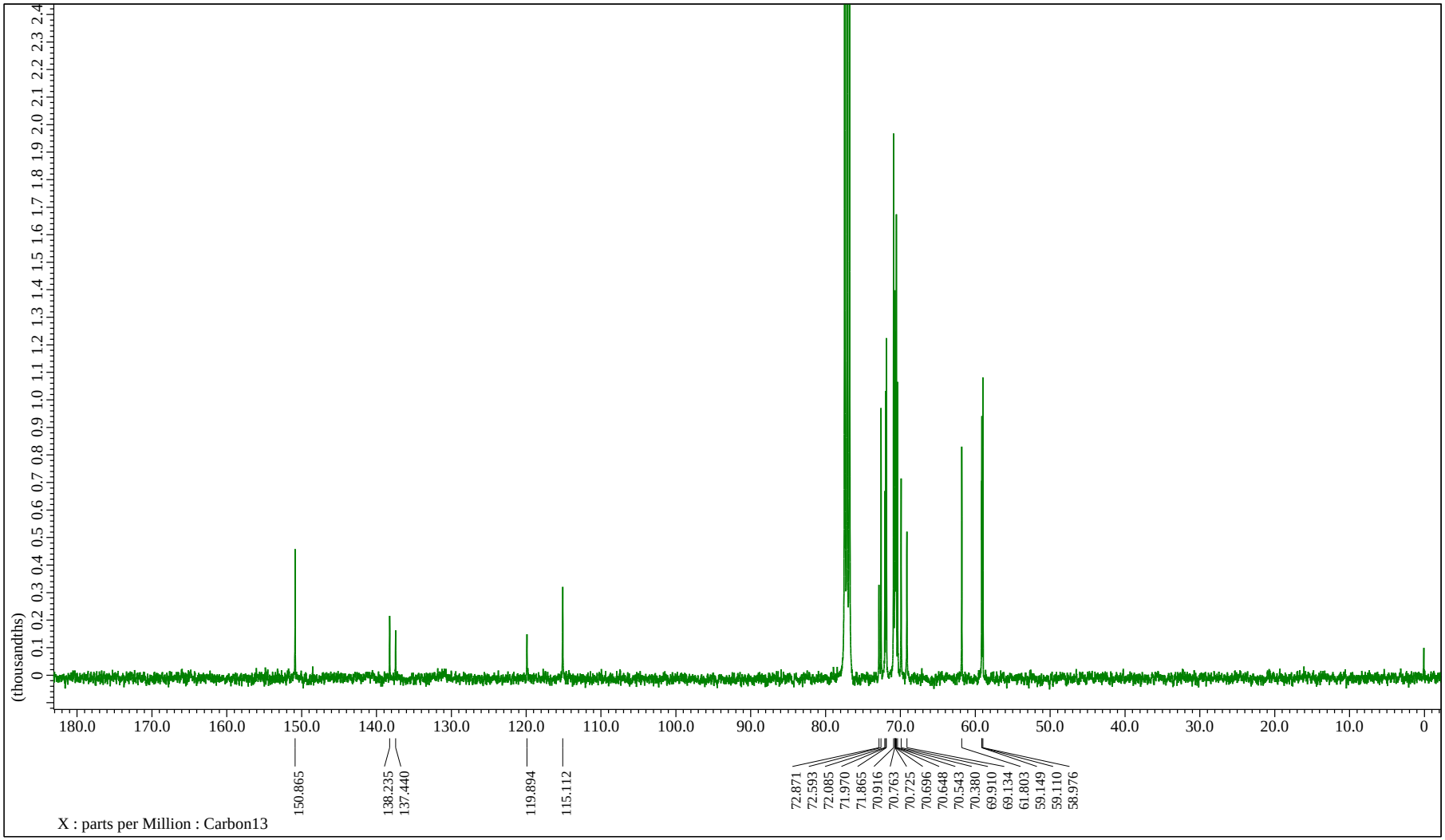

Figure S20. ^{13}C NMR spectrum of **$TEG_{12}PH_2$**

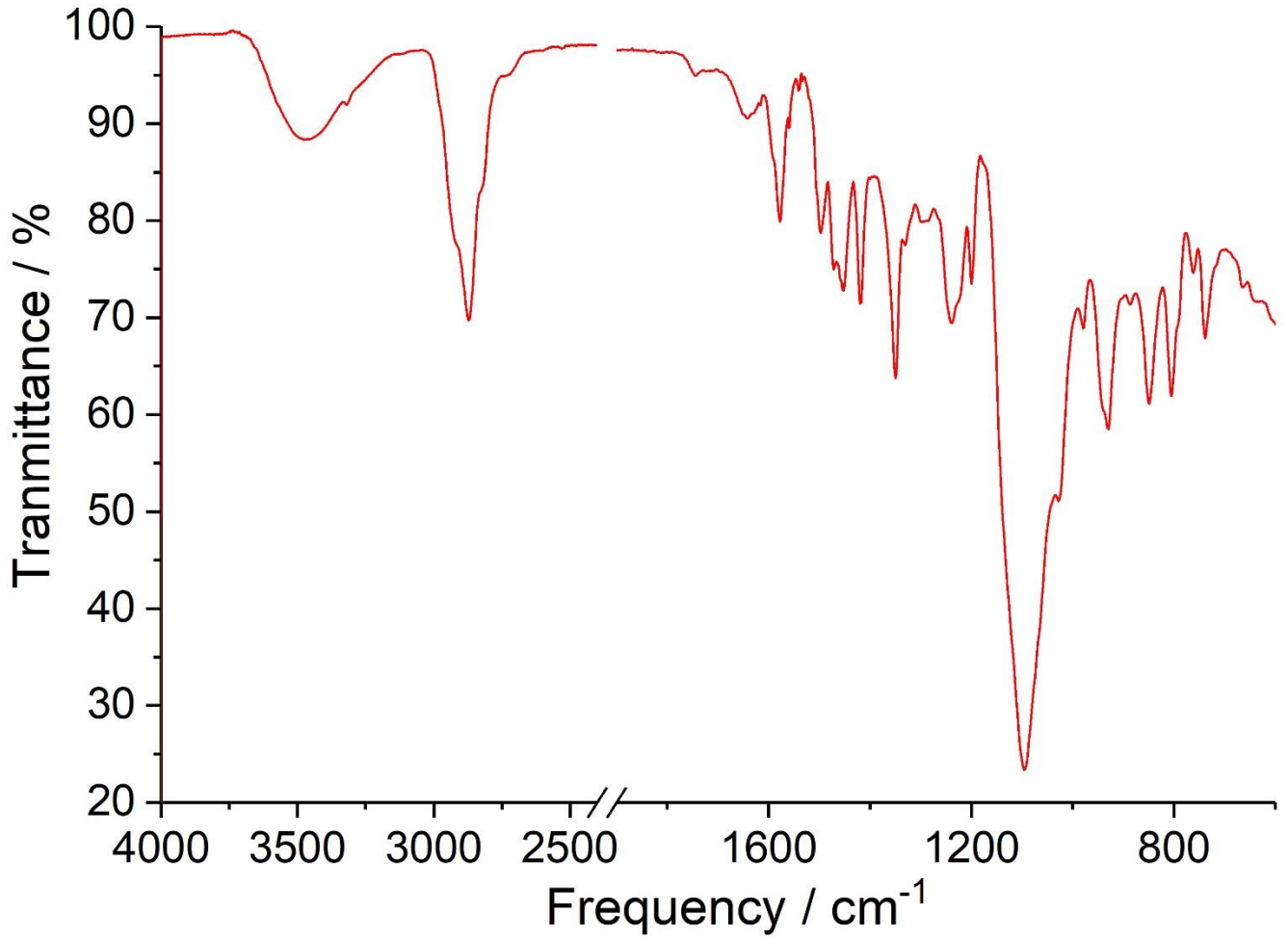

Figure S21. FTIR-ATR spectrum of $TEG_{12}PH_2$.

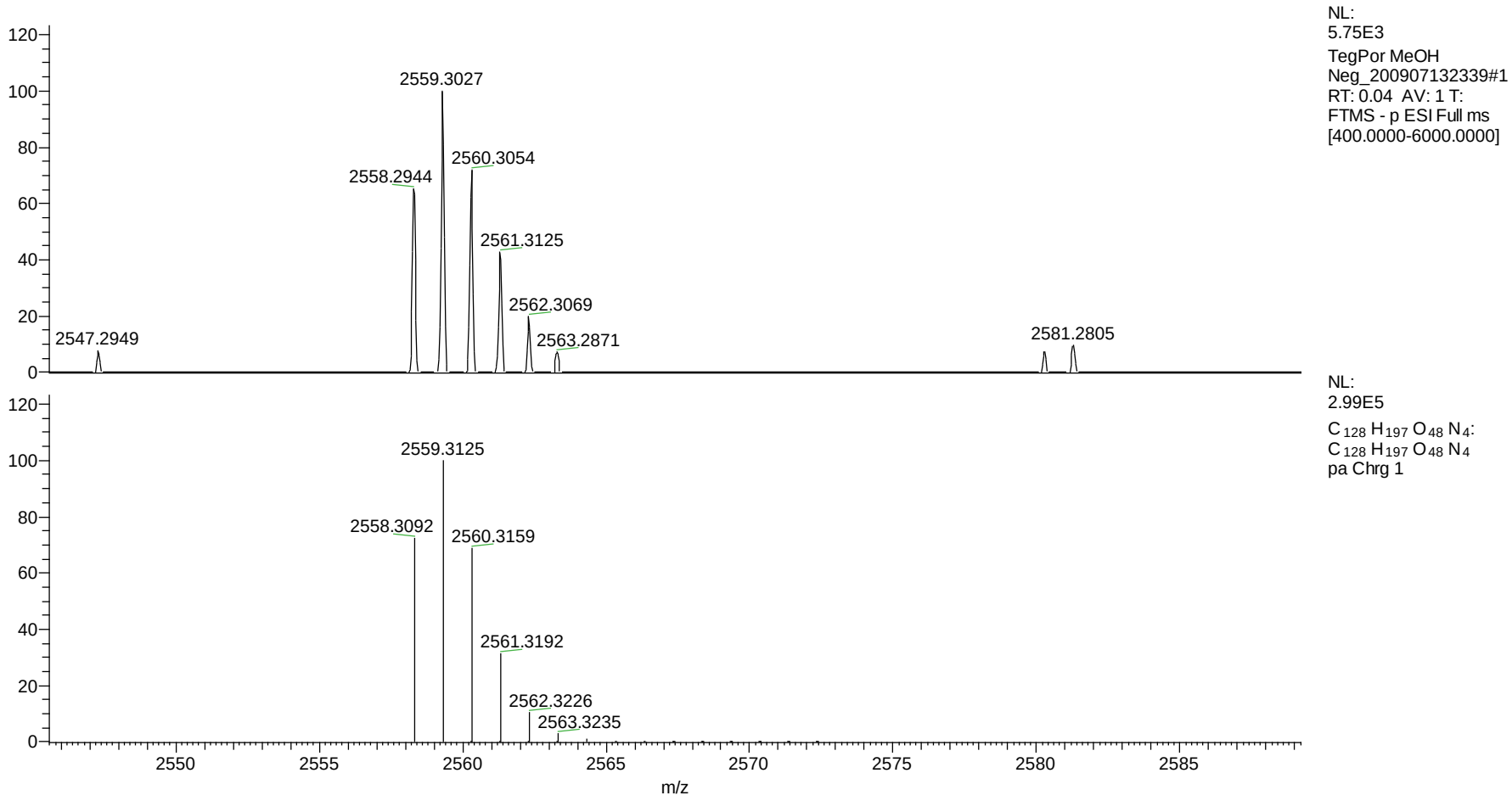

Figure S22. Mass spectrum (ESI-TOF-HRMS) of **$TEG_{12}PH_2$** (top) and a simulation (bottom)

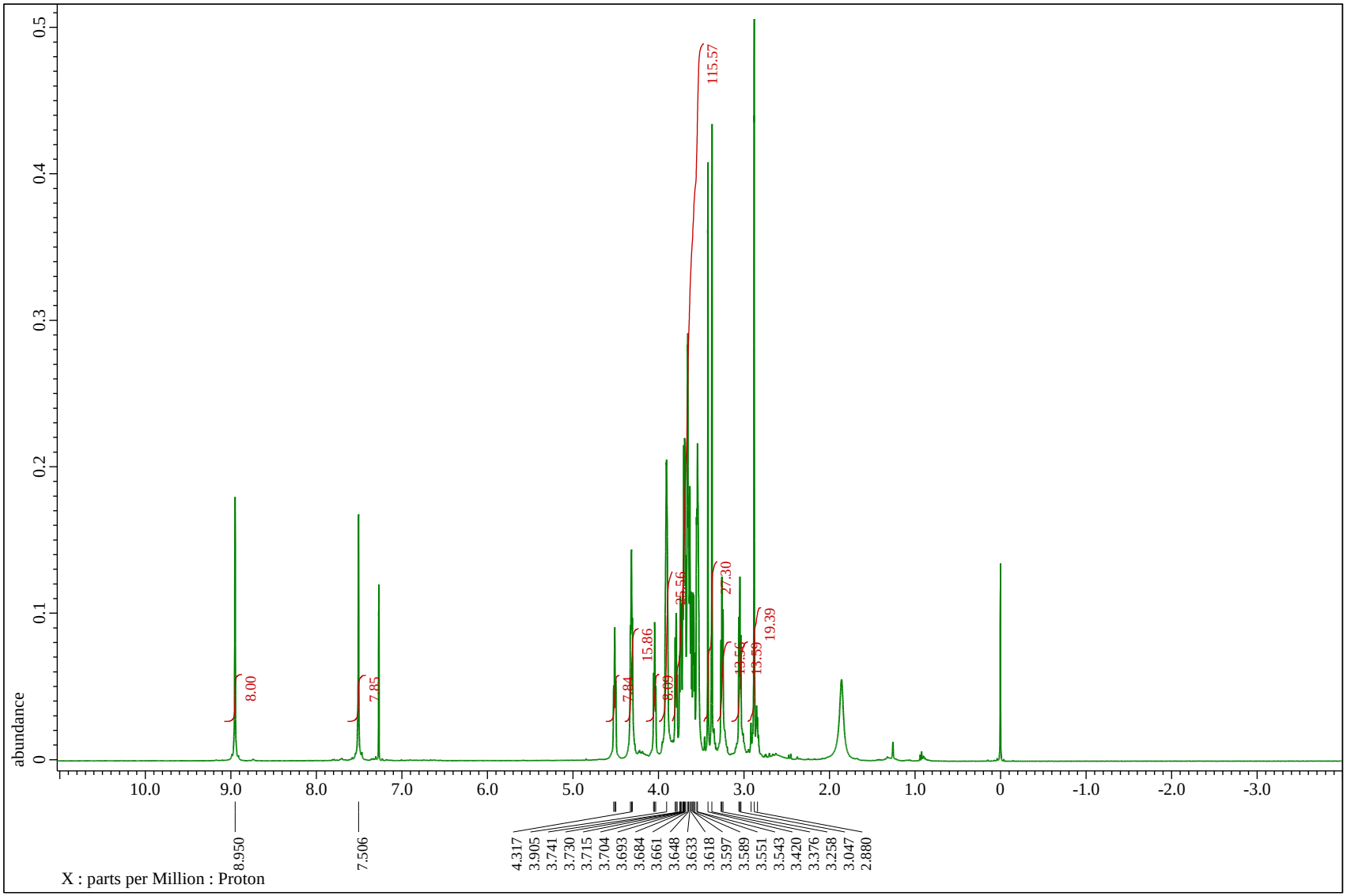

Figure S23. ^{1}H NMR spectrum of **TEG$_{12}$PZn**

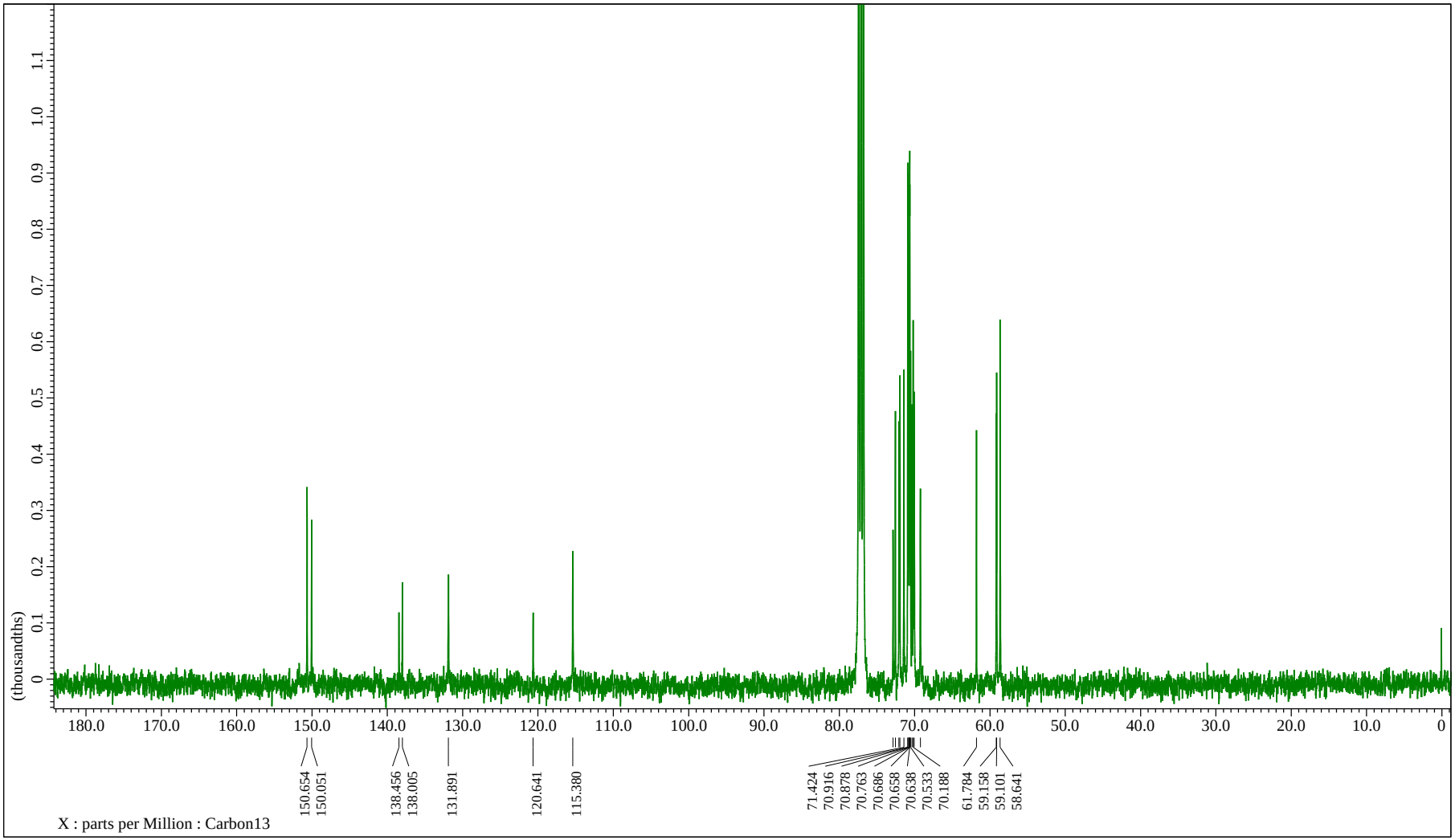

Figure S24. ^{13}C NMR spectrum of **TEG$_{12}$PZn**

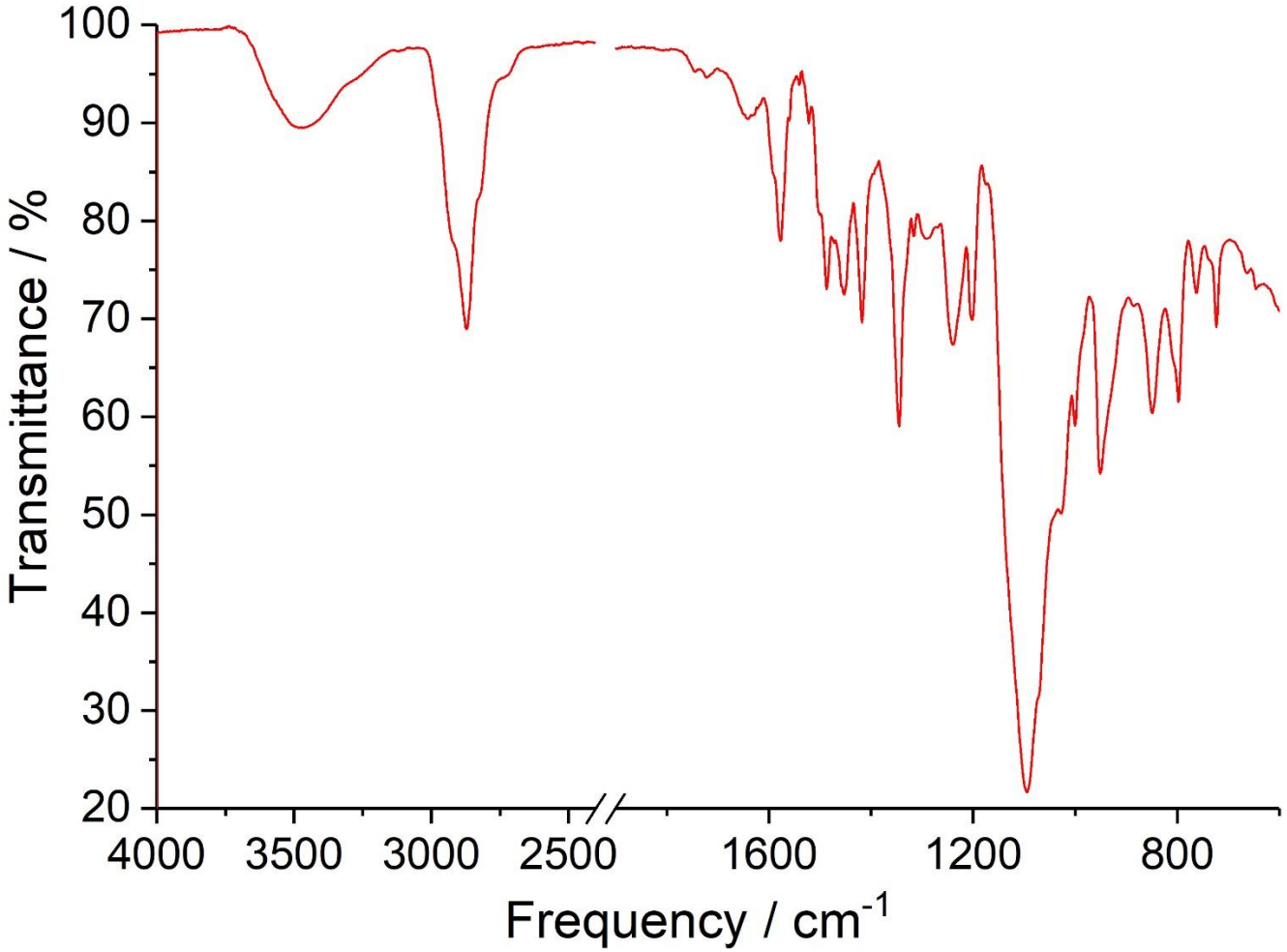

Figure S25. FTIR-ATR spectrum of **$TEG_{12}PZn$**,

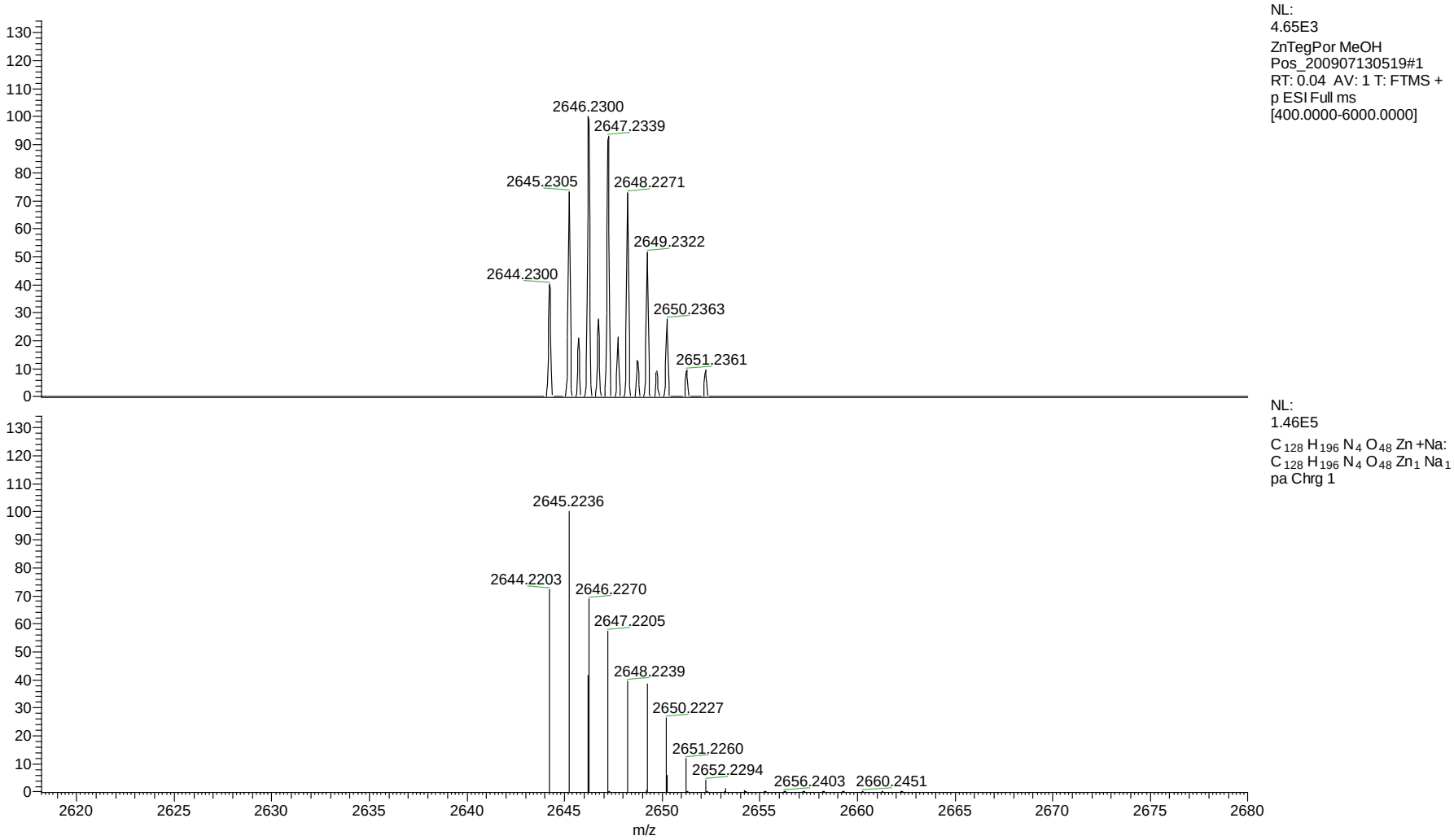

Figure S26. Mass spectrum (ESI-HRMS) of **TEG$_{12}$PZn** (top) and a simulation (bottom)