

Design of Oxygen Sensing Nanomaterial: Synthesis, Encapsulation of Phenylacetylde Substituted Pd(II) and Pt(II) *meso*-tetraphenylporphyrins into Poly(1-trimethylsilyl-1-propyne) Nanofibers and Influence of Silver Nanoparticles

Emel Önal^a, Zeynep Ay^b, Zübeyde Yel^a, Kadriye Ertekin^b, Ayşe Gül Gürek^a, Sevinc Zehra Topal^{a,*} and Catherine Hirel^{a,*}

^a *Gebze Technical University, Faculty of Science, Department of Chemistry, P. O. Box 141, Gebze, 41400 Kocaeli, Turkey*

^b *Dokuz Eylül University, Faculty of Science, Department of Chemistry, 35160, Buca, İzmir, Turkey*

Electronic Supplementary Information

Table S1: Microwave promoted Pd(II) metal insertion to **H₂-TPPBr**.

Entry	Metal salt	Organic solvent	Conditions	% yield	Procedure according to Ref
1	2 equiv.PdCl ₂	PhCN	191 °C, Reflux, 1 day	68	26
2	2.5 equiv.PdCl ₂	Acetic acid	Rt. 30 min.	10	34
3	2.5 equiv. Pd(II)acetate	Acetic acid	Rt. 30 min.	5	34
4	3 equiv. Pd(II)acetate	Chloroform-Methanol	Reflux, 45 min.	24	35
5	3 equiv. Pd(acac) ₂	Pyridine	180°C, Reflux, 1 day	49	29
6	3 equiv. Pd(acac) ₂	Pyridine	180°C, MW, 15 min.	-	29
7	3 equiv. Pd(acac) ₂	NMP	180 °C, MW, 15 min.	81	

Table S2: Microwave promoted Pt(II) metal insertion to **H₂-TPPBr**.

Entry	Metal salt	Organic solvent	Conditions	% yield	Procedure according to Ref
1	3 equiv.PtCl ₂	PhCN	191 °C, Reflux, 1 day	-	26
2	3 equiv.Pt(acac) ₂	PhCN	191 °C, Reflux, 1 day	23	36
3	3 equiv.Pt(acac) ₂	PhCN	191 °C, MW, 45 min.	-	29
4	3 equiv.Pt(acac) ₂	Chloroform-Methanol	70 °C, Reflux, 1 day	-	35
5	3 equiv.K ₂ PtCl ₄	NMP	100 °C, MW, 50 min.	-	
6	3 equiv.Pt(acac) ₂	NMP	110°C, MW, 45 min.	25	

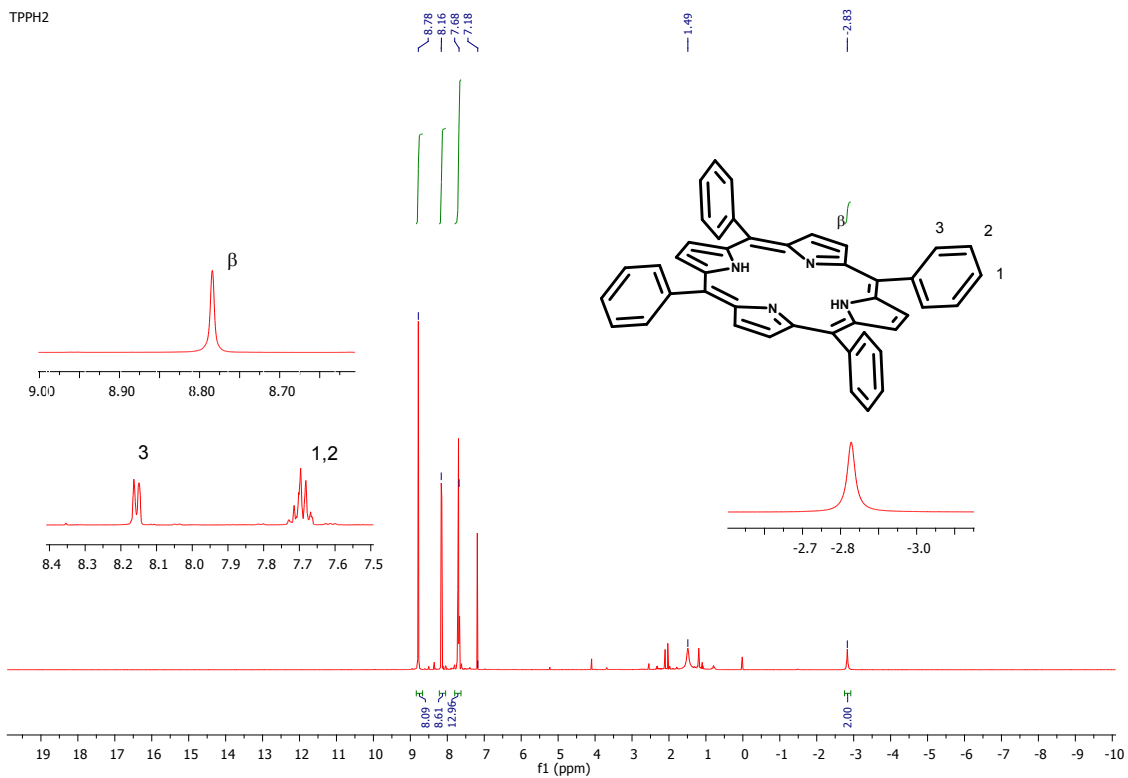


Figure S1. 1H NMR spectrum of *meso*-tetraphenylporphyrin (H_2 -TPP)

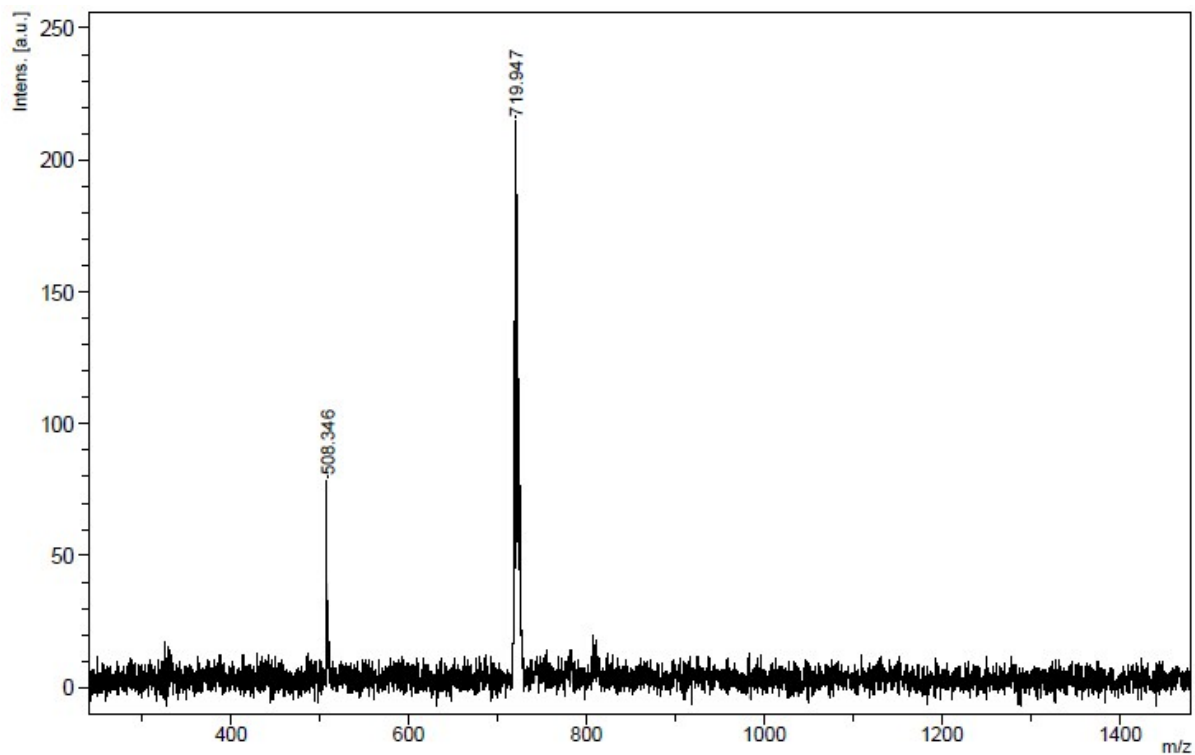


Figure S2. MALDI-MS spectrum of *meso*-tetraphenylporphyrinato palladium (Pd-TPP)

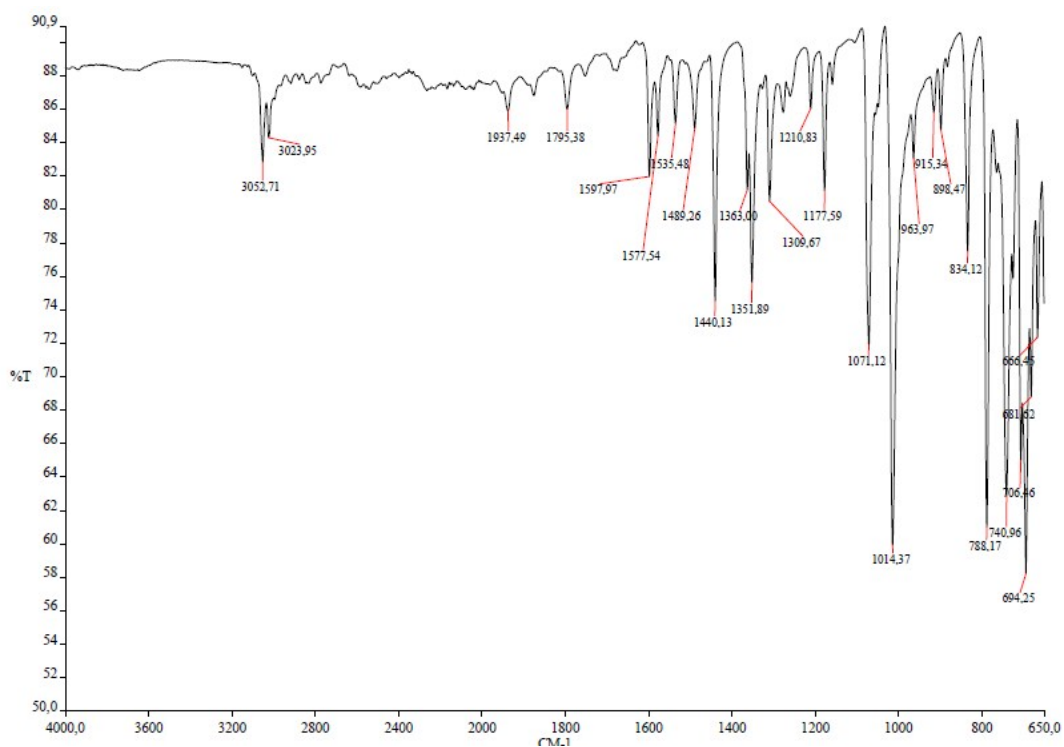


Figure S3. FT-IR spectrum of *meso*-tetraphenylporphyrinato palladium (Pd-TPP)

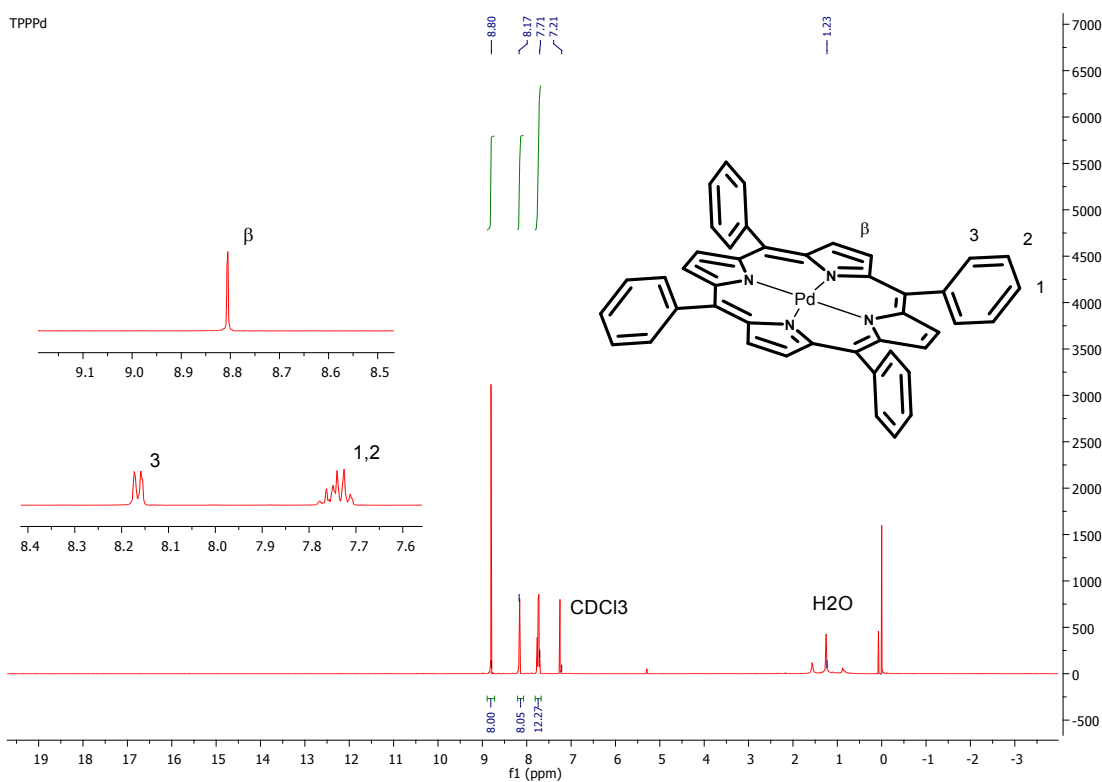


Figure S4. ¹H NMR spectrum of *meso*-tetraphenylporphyrinato palladium (Pd-TPP)

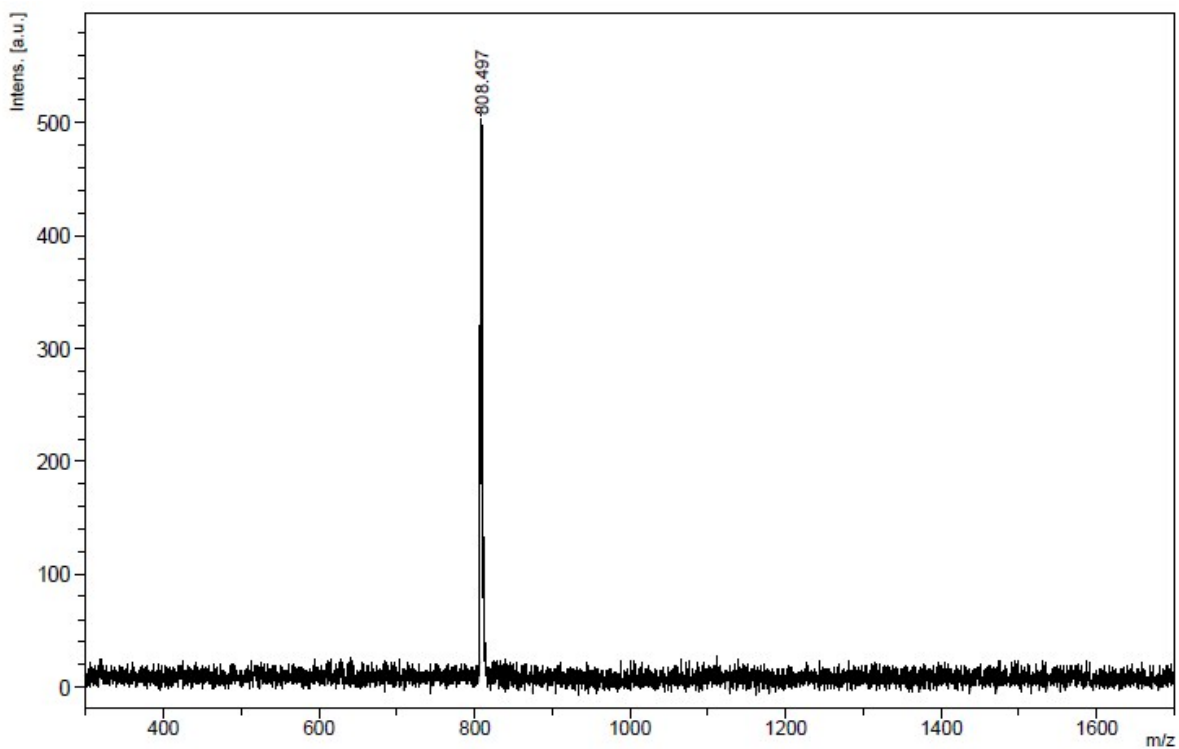


Figure S5. MALDI-MS spectrum of *meso*-tetraphenylporphyrinato platinum (**Pt-TPP**)

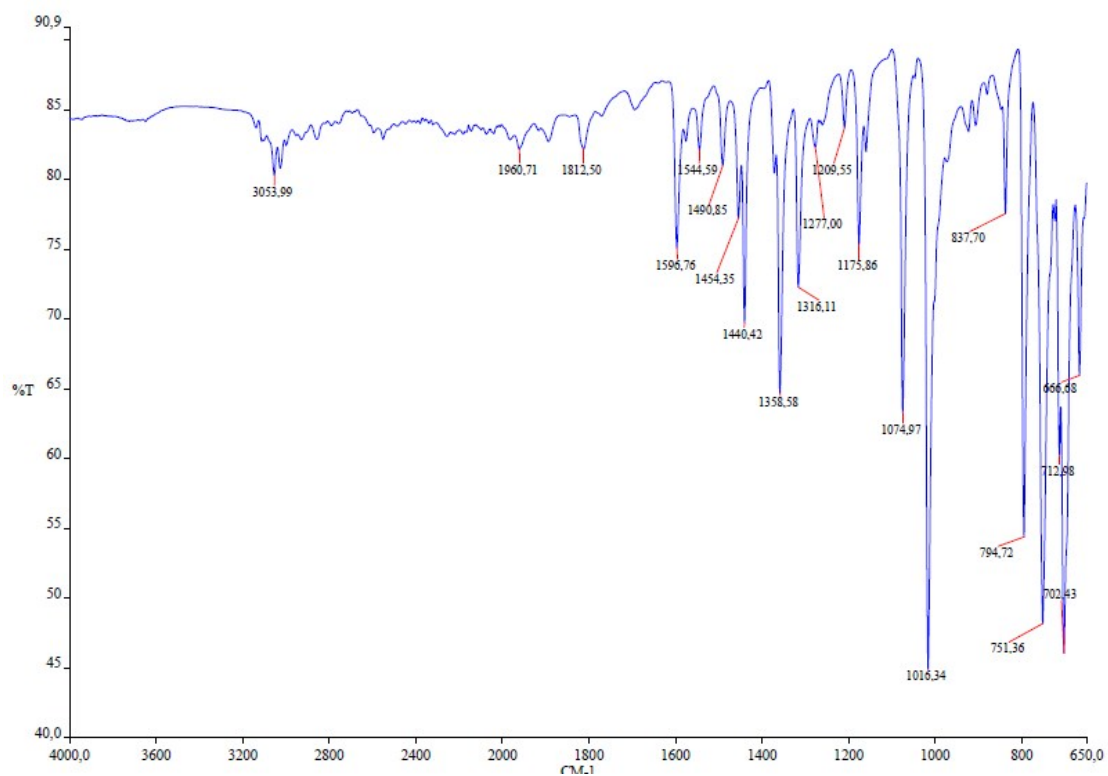


Figure S6. FT-IR spectrum of *meso*-tetraphenylporphyrinato platinum (**Pt-TPP**)

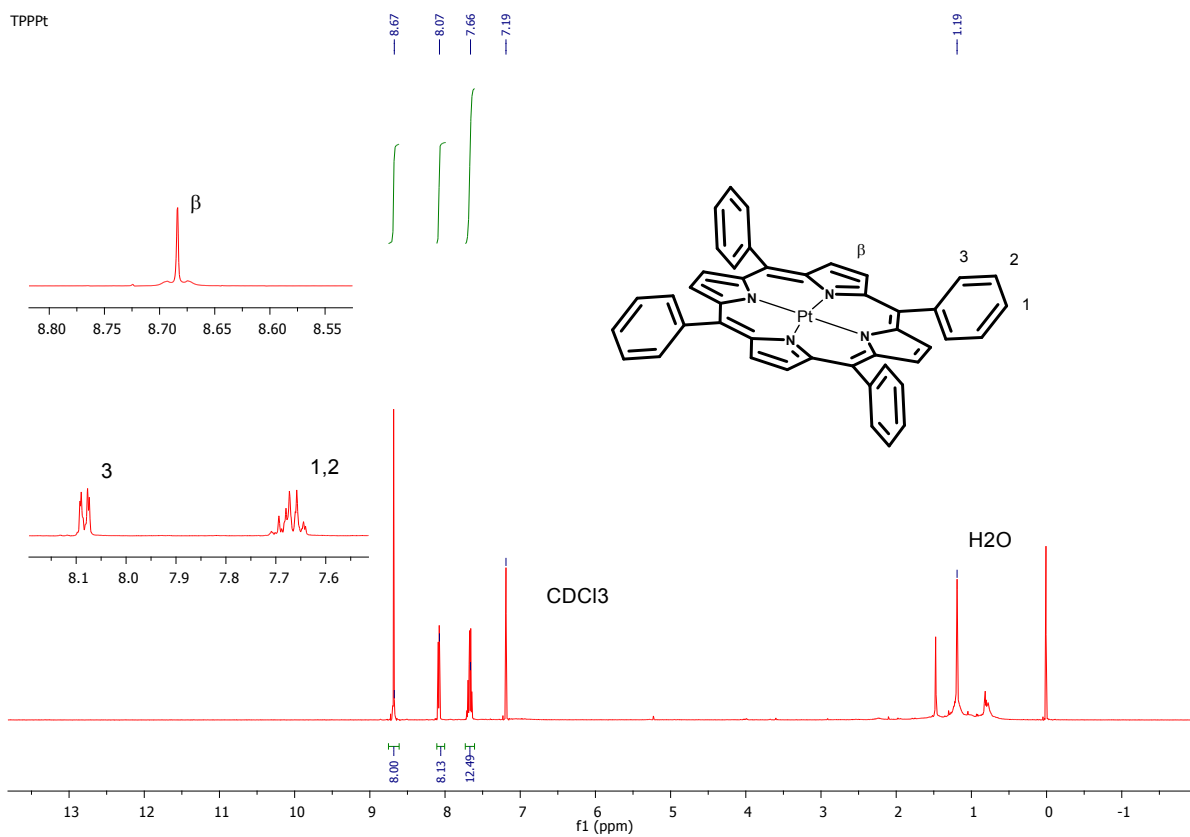


Figure S7. ^1H NMR spectrum of *meso*-tetraphenylporphyrinato platinum (Pt-TPP)

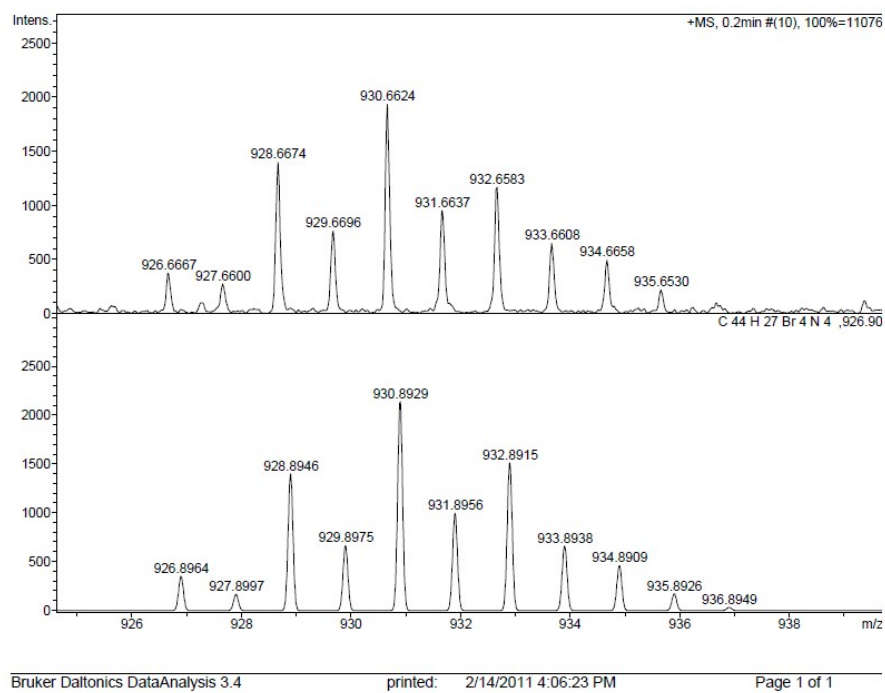


Figure S8.ESI-MS spectrum of *meso*-tetrakis(4-bromophenyl)porphyrin (H_2 -TPPBr)

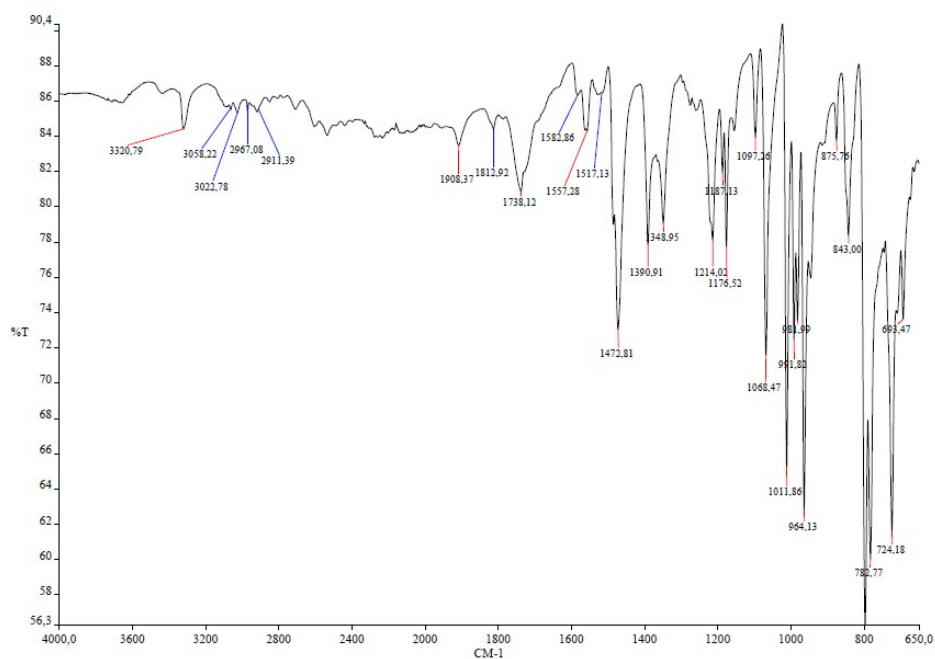


Figure S9.FT-IR spectrum of *meso*-tetrakis(4-bromophenyl)porphyrin (H_2 -TPPBr)

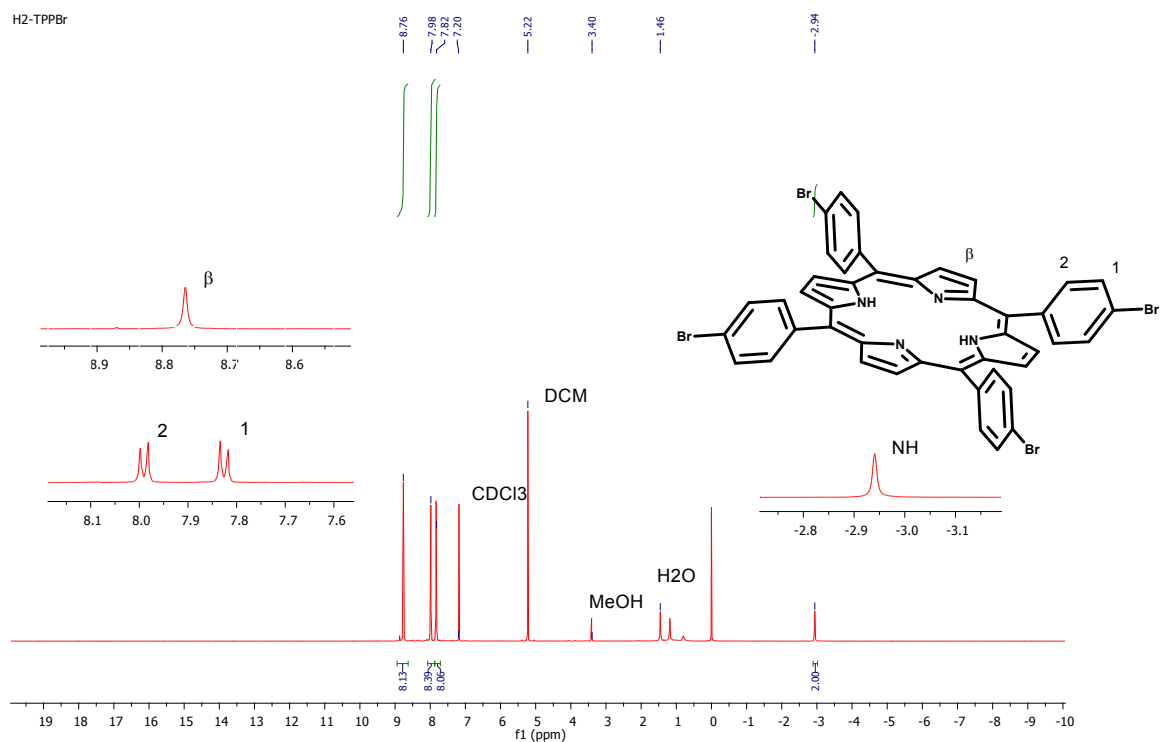


Figure S10. 1H NMR spectrum of *meso*-tetrakis(4-bromophenyl)porphyrin (H_2 -TPPBr) in $CDCl_3$.

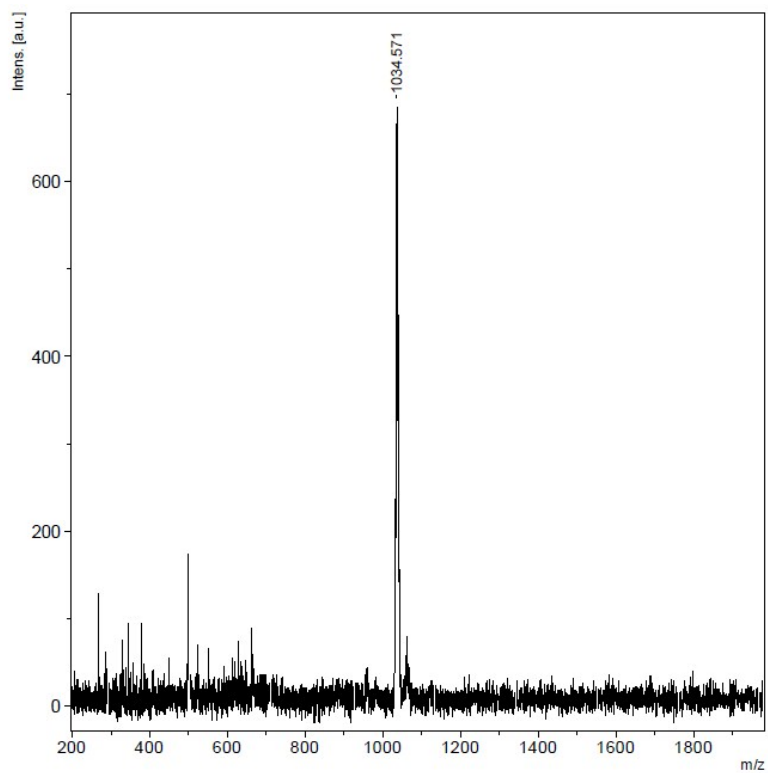


Figure S11. MALDI-MS spectrum of *meso*-tetrakis(4-bromophenyl)porphyrinato Palladium(II) (Pd -TPPBr)

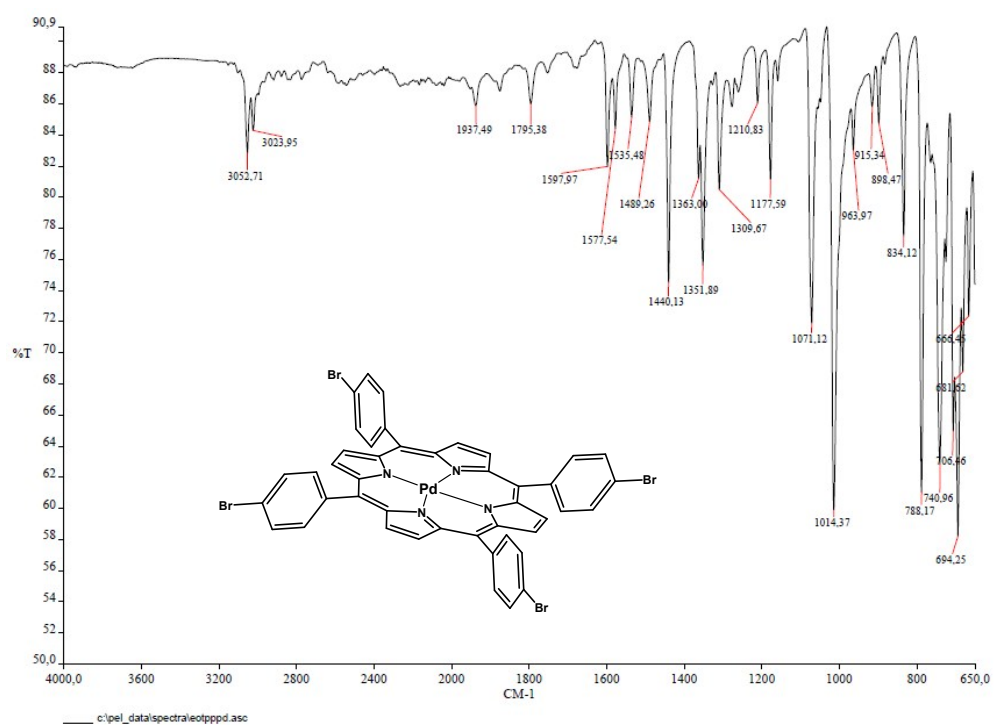


Figure S12. FT-IR spectrum of *meso*-tetrakis(4-bromophenyl)porphyrinato Palladium(II) (Pd-TPPBr)

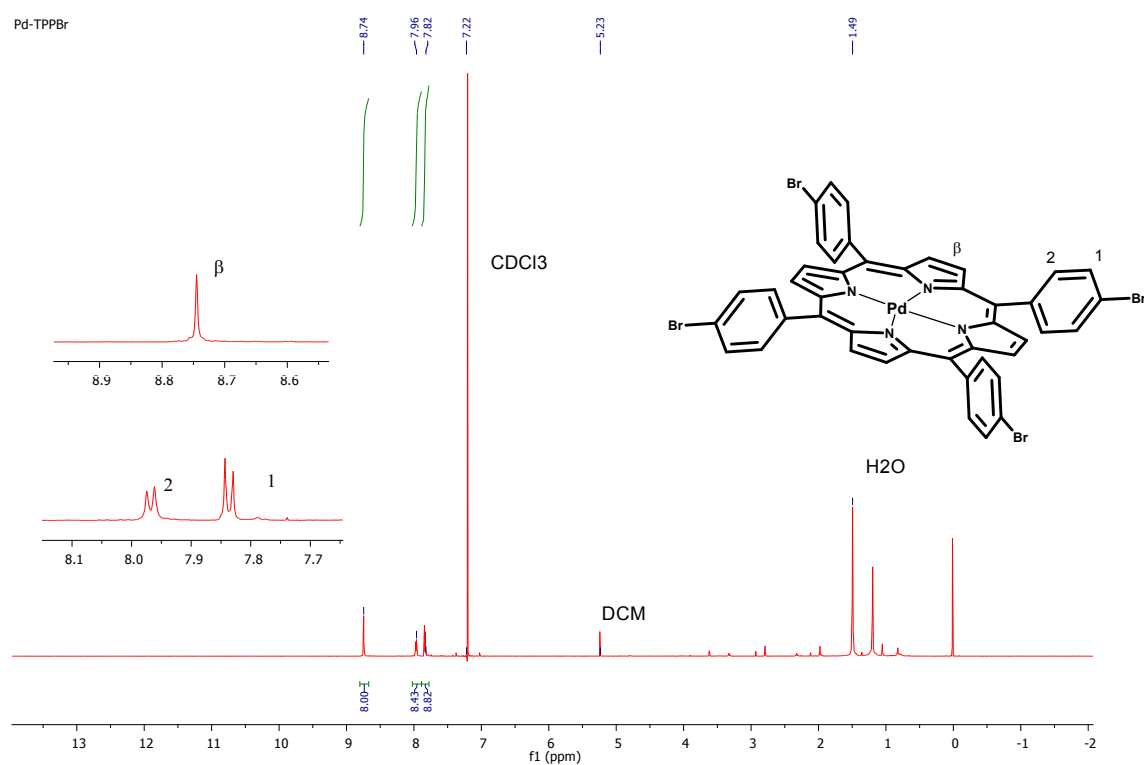


Figure S13. ^1H NMR spectrum of *meso*-tetrakis(4-bromophenyl)porphyrinato Palladium(II) (Pd-TPPBr)

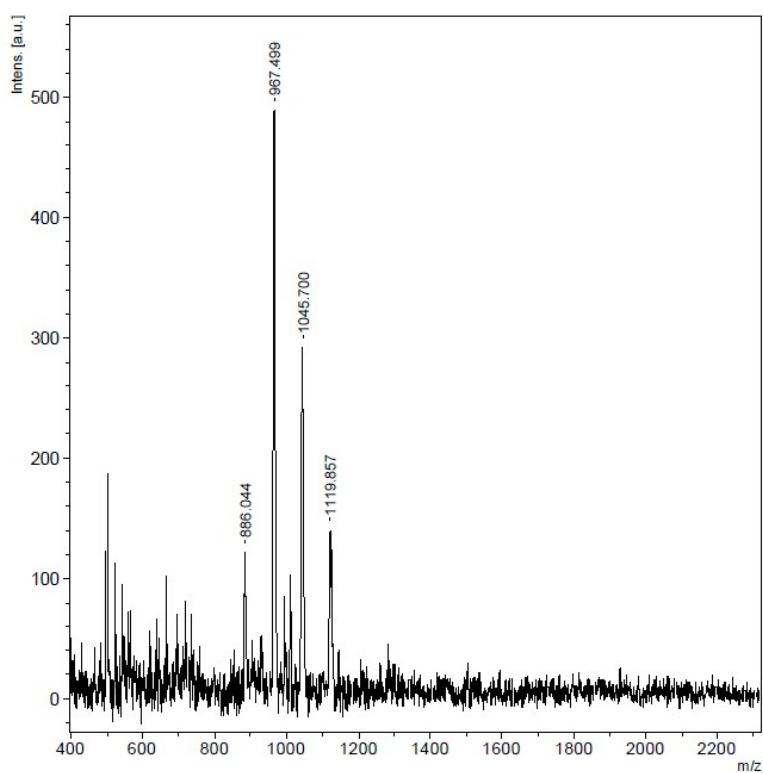


Figure S14. MALDI-MS spectrum of *meso*-tetrakis(4-bromophenyl)porphyrinato Platinum(II) (Pt-TPPBr)

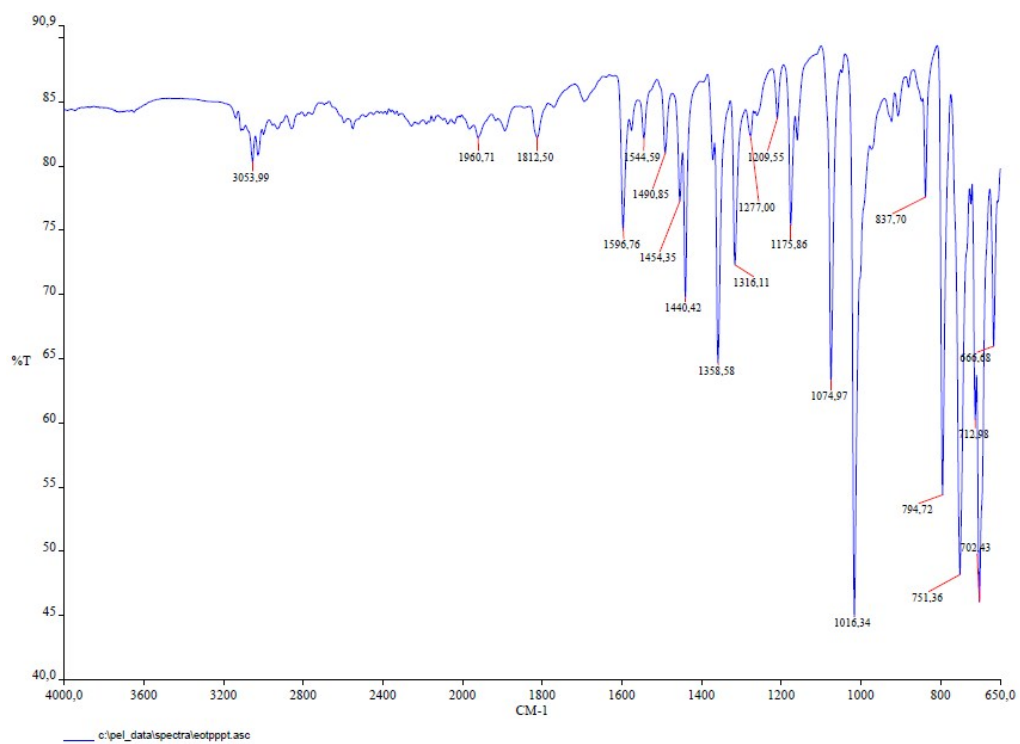


Figure S15. FT-IR spectrum of *meso*-tetrakis(4-bromophenyl)porphyrinato Platinum(II) (Pt-TPPBr)

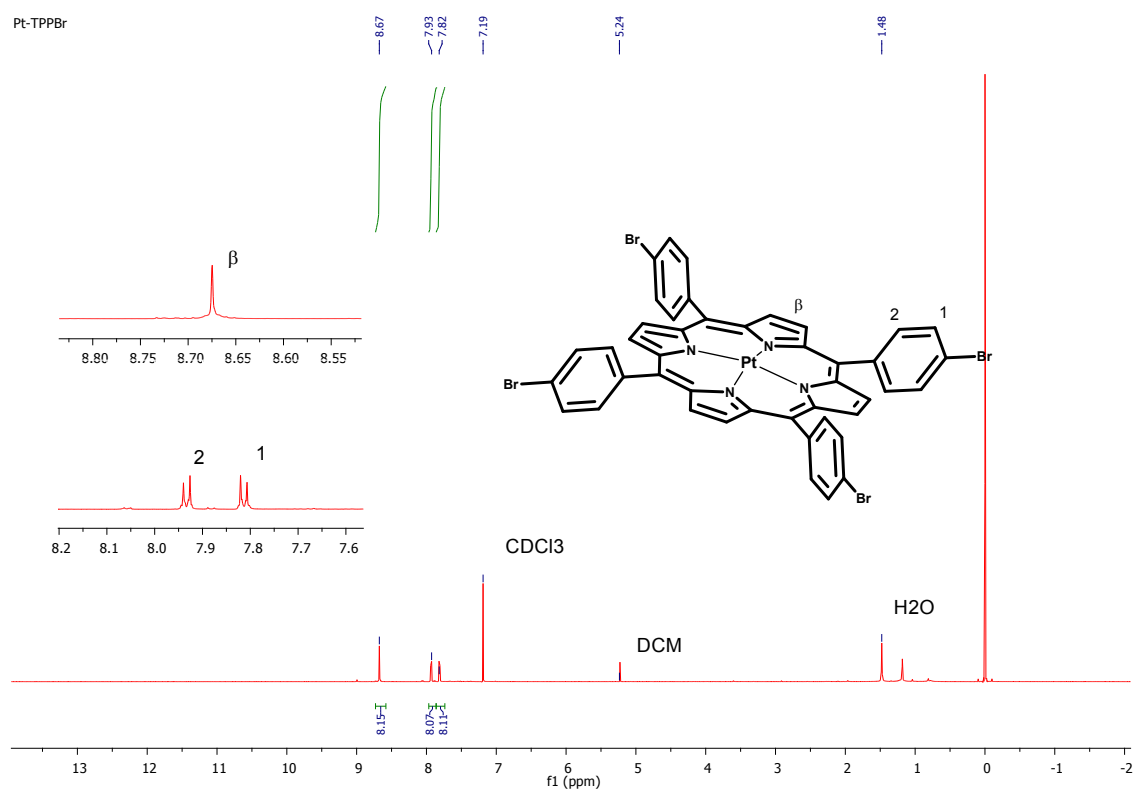


Figure S16. ^1H NMR spectrum of *meso*-tetrakis(4-bromophenyl)porphyrinato Platinum(II) (Pt-TPPBr)

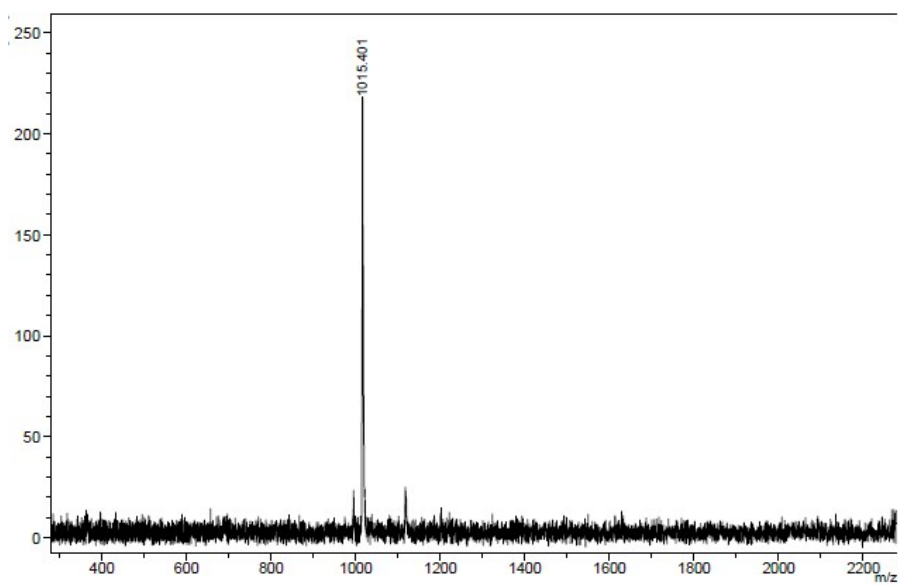


Figure S17. MALDI-MS spectrum of *meso*-tetrakis(4-phenylethynyl)phenylporphyrin (H_2 -TPA)

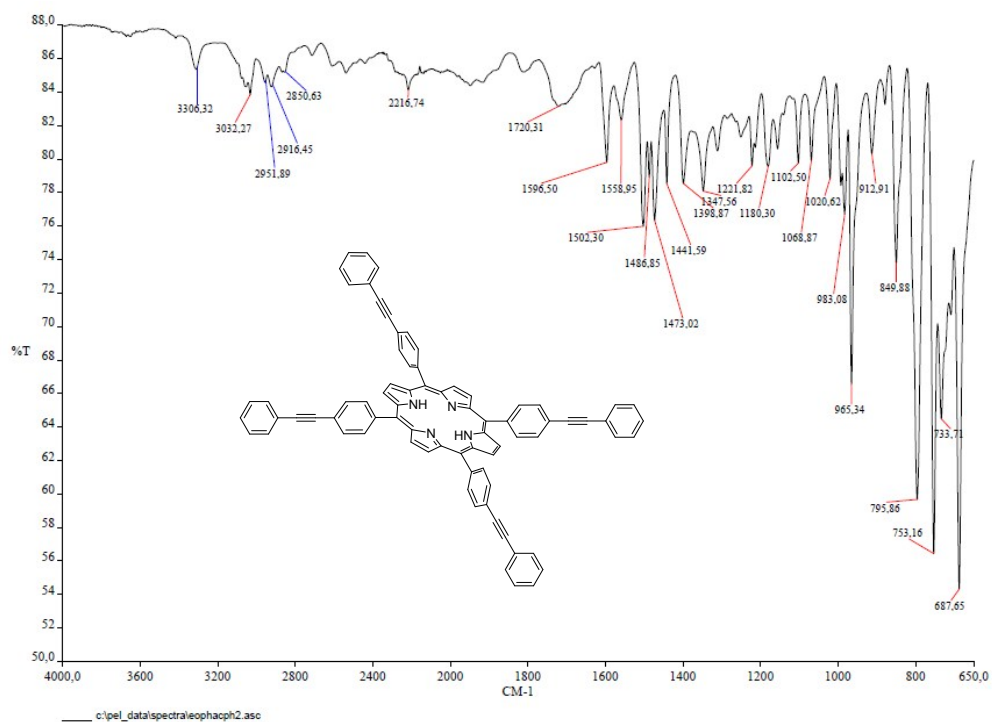


Figure S18. FT-IR spectrum of *meso*-tetrakis(4-phenylethynyl)phenylporphyrin (H_2 -TPA)

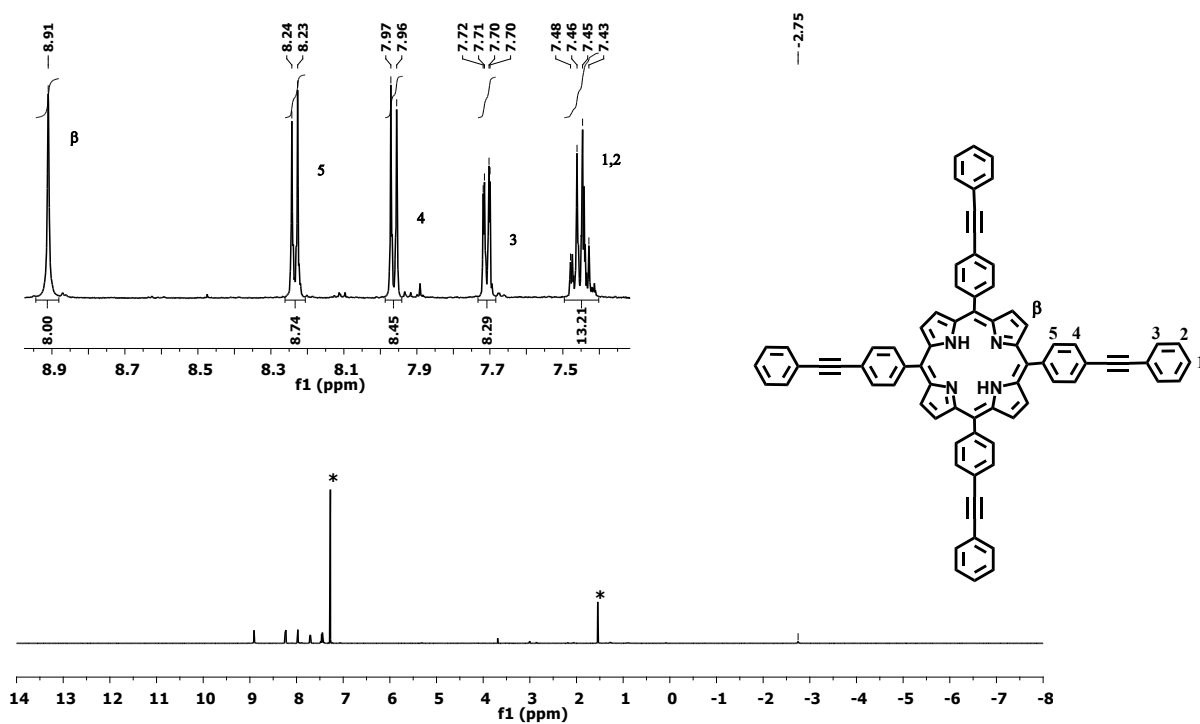


Figure S19. 1H NMR spectrum of *meso*-tetrakis(4-phenylethynyl)phenylporphyrin (H_2 -TPA) in $CDCl_3$.

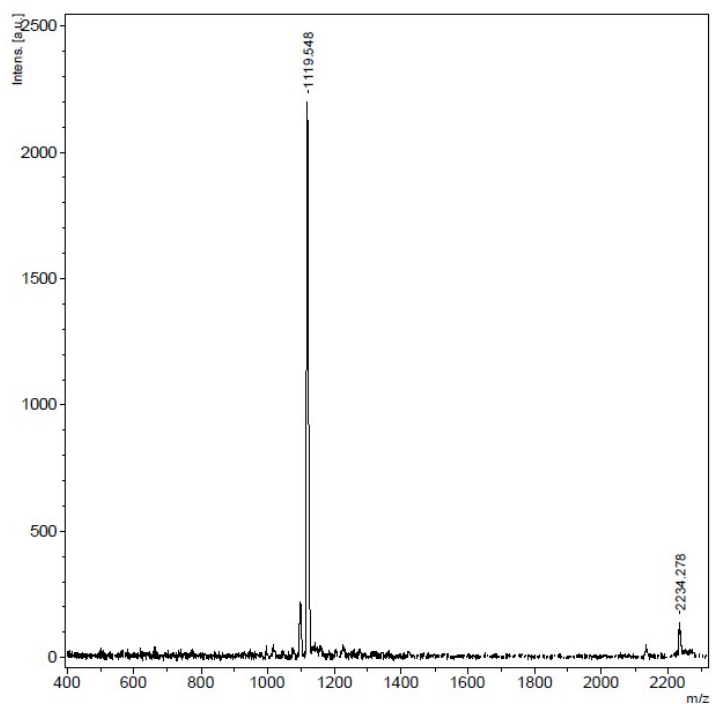


Figure S20. MALDI-MS spectrum of *meso*-tetrakis(4-phenylethynyl)phenylporphyrinato Palladium(II) (Pd-TPA).

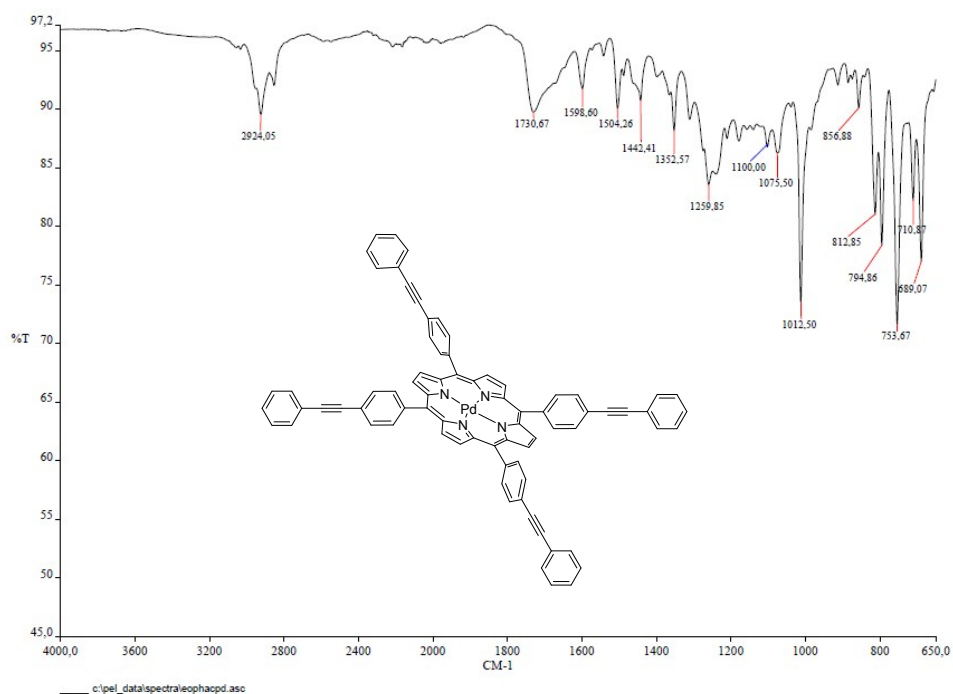


Figure S21. FT-IR spectrum of *meso*-tetrakis(4-phenylethynyl)phenylporphyrinato Palladium(II) (Pd-TPA).

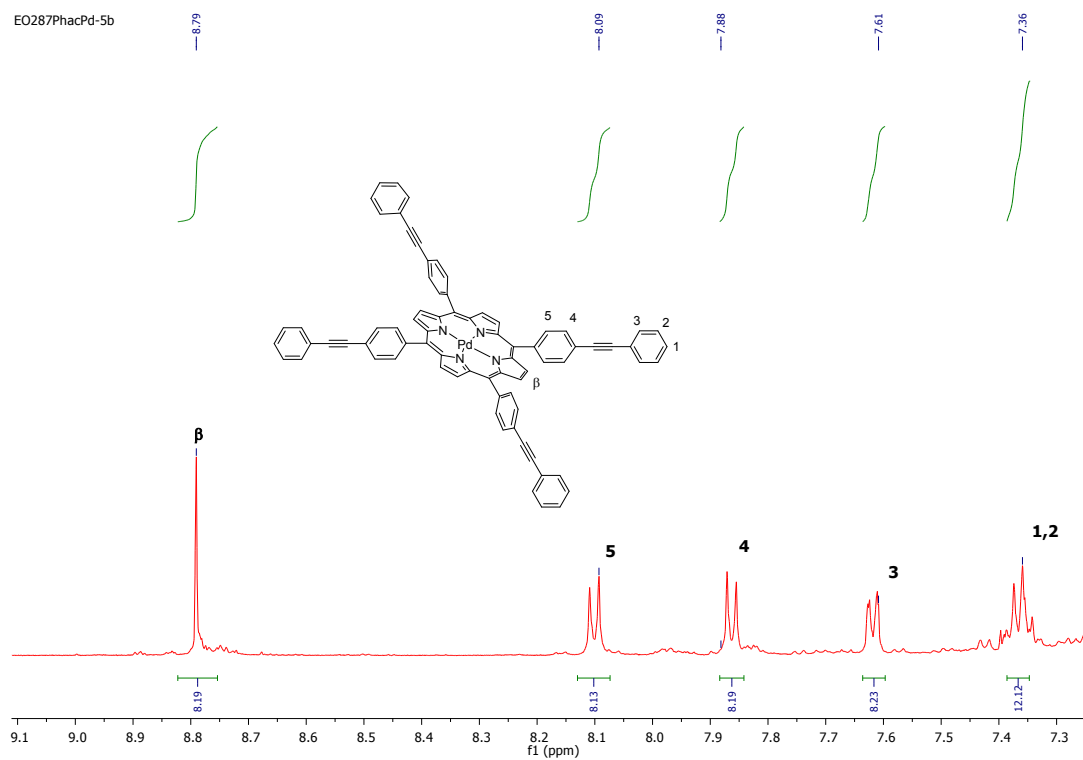
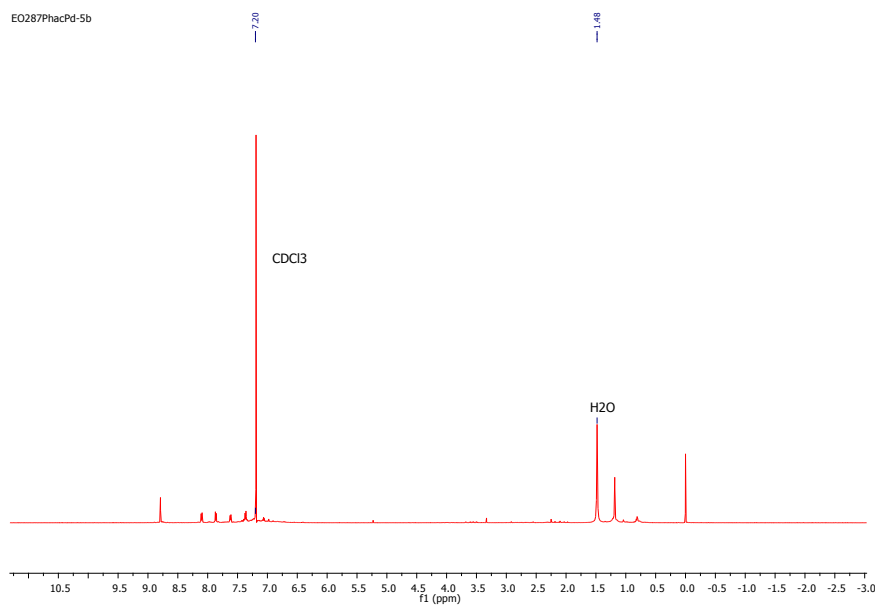


Figure S22. ¹H NMR spectrum of *meso*-tetrakis(4-phenylethynyl)phenylporphyrinato Palladium(II) (Pd-TPA) in CDCl₃.

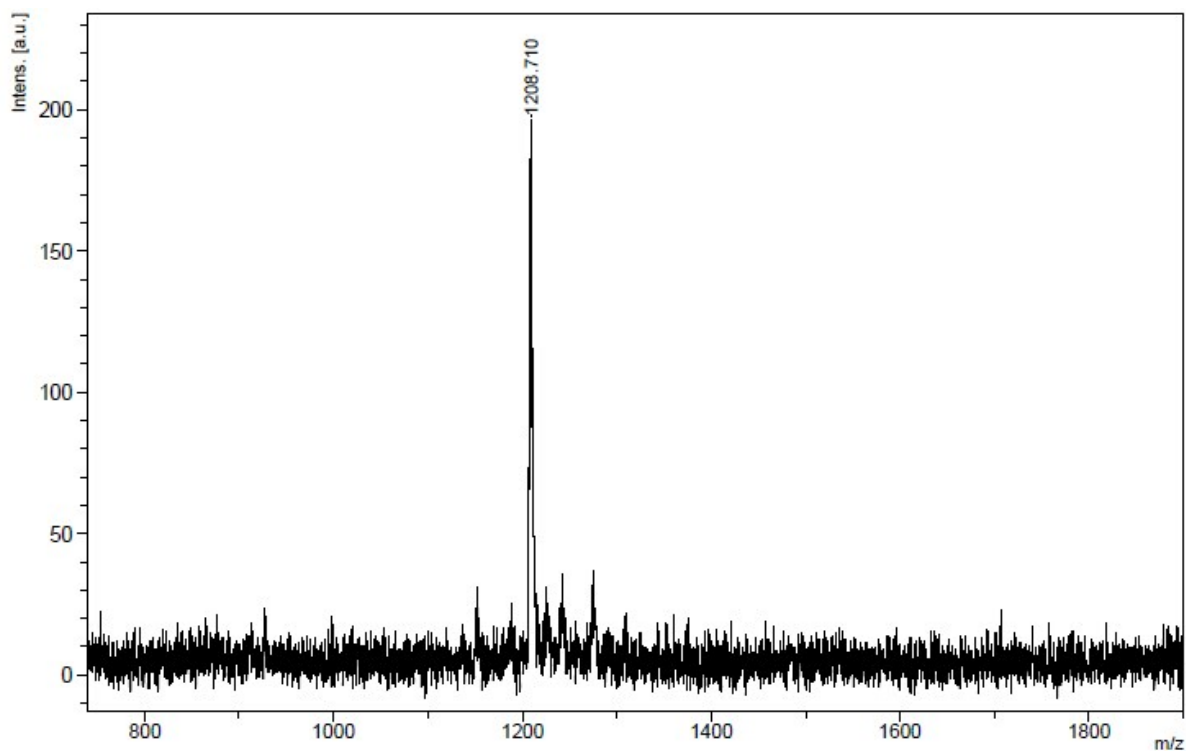


Figure S23. MALDI-MS spectrum of *meso*-tetrakis(4-phenylethynyl)phenylporphyrinato Platinum(II) (**Pt-TPA**).

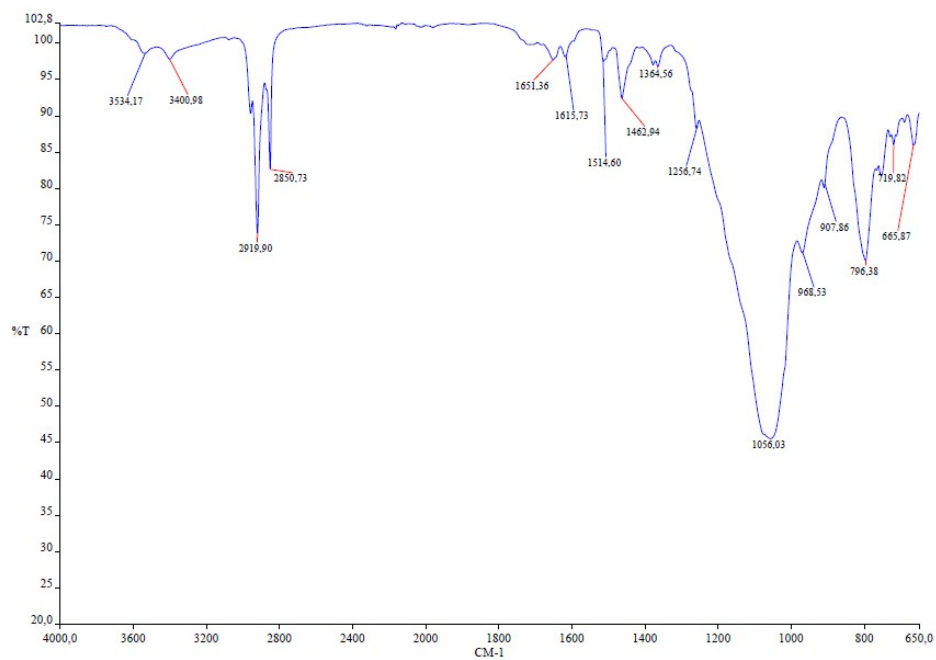


Figure S24. FT-IR spectrum of *meso*-tetrakis(4-phenylethynyl)phenylporphyrinato Platinum(II) (**Pt-TPA**).

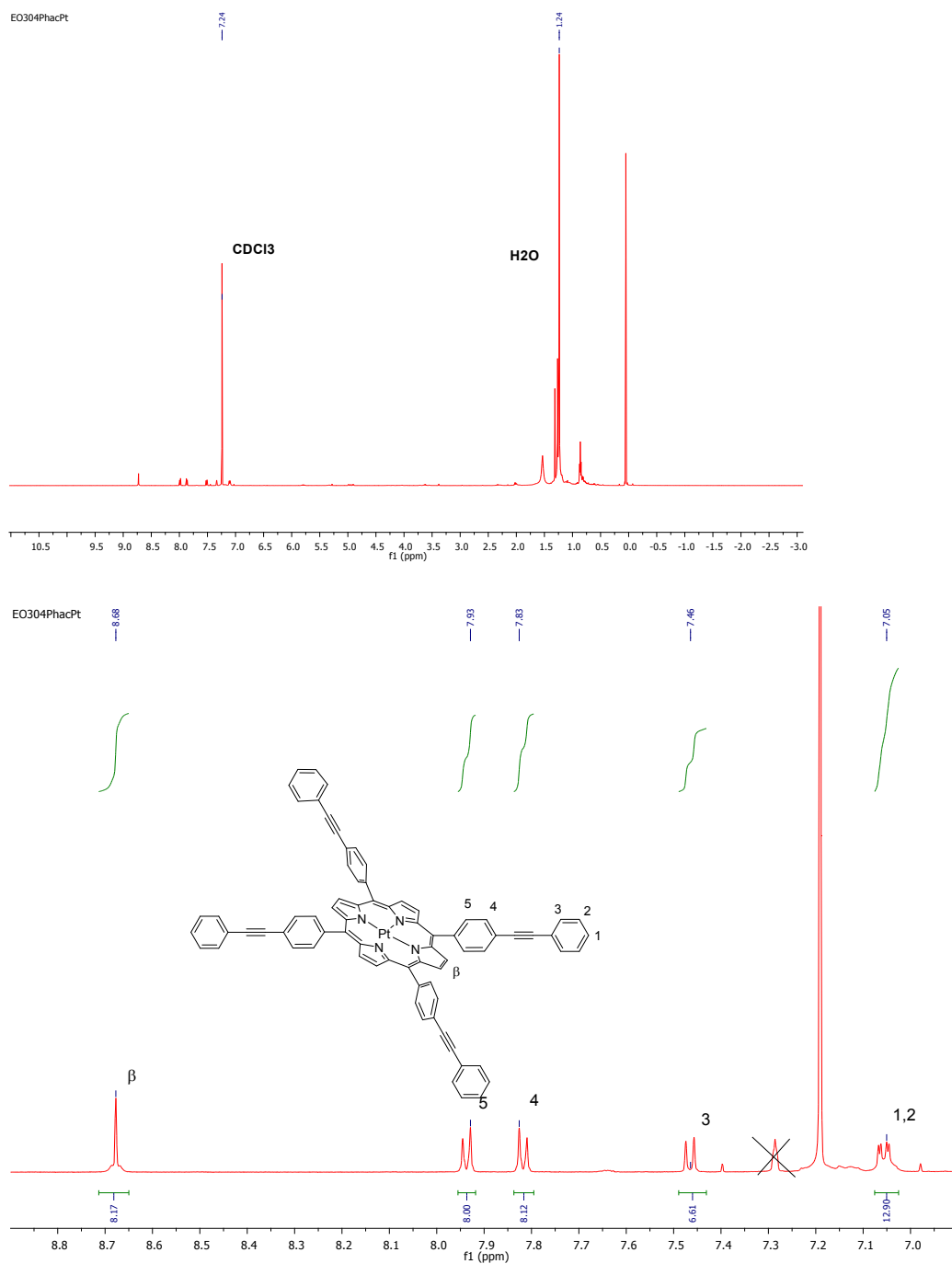


Figure S25. ¹H NMR spectrum of *meso*-tetrakis(4-phenylethynyl)phenylporphyrinato Platinum(II) (Pt-TPA) in CDCl₃.

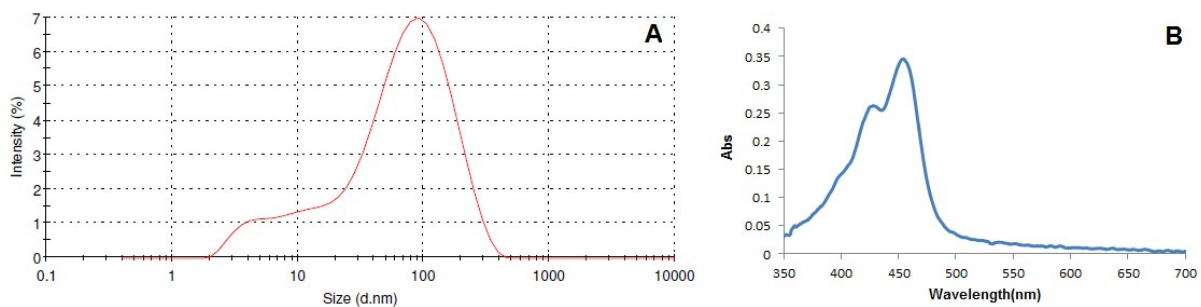


Figure S26: Characterization of silver nanoparticles (AgNPs): A) Size distribution analysis, and B) UV-Vis spectra in THF.

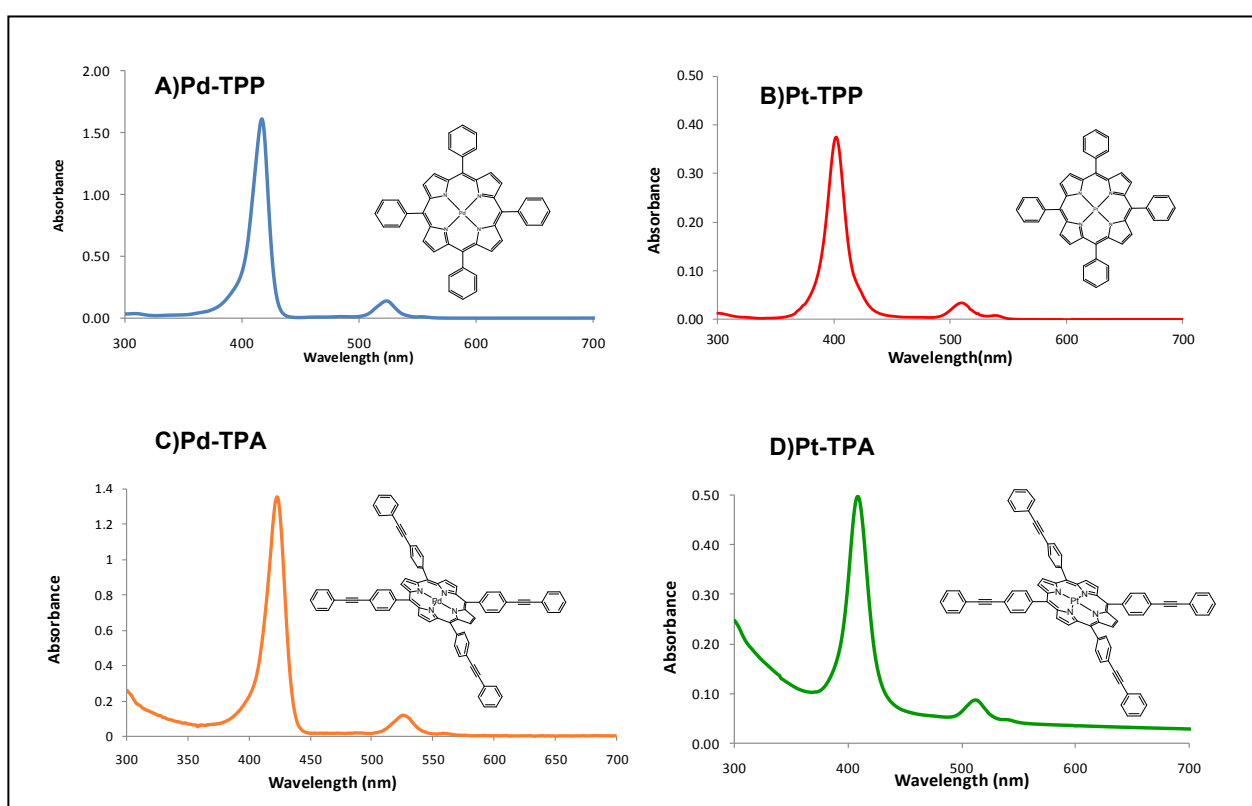


Figure S27. UV-VIS spectra of A) Pd-TPP ($\sim 5 \times 10^{-5}$ M), B) Pt-TPP ($\sim 2 \times 10^{-5}$ M), C) Pd-TPA ($\sim 5 \times 10^{-5}$ M), D) Pt-TPA ($\sim 2 \times 10^{-5}$ M) in toluene.

Table S3. Absorbance spectra related data of the molecules in toluene and poly(TMSP)-based nanofibers.

Compound	Medium	λ_{abs}^{Bband} (nm)	log ϵ	λ_{abs}^{Q1band} (nm)	log ϵ	λ_{abs}^{Q2band} (nm)	log ϵ
Pd-TPP	Toluene	417	5.45	524	4.40	555	*
	Poly(TMSP) ^a	423	-	531	-	*	-
Pt-TPP	Toluene	403	5.43	509	5.40	540	3.80
	Poly(TMSP) ^a	408	-	516	-	546	-
Pd-TPA	Toluene	426	5.02	526	4.01	559	3.23
	Poly(TMSP) ^a	429	-	534	-	569	-
Pt-TPA	Toluene	409	5.12	515	4.35	545	
	Poly(TMSP) ^a	413	-	520	-	550	-

^a thin film coated on mylar support

* The absorbance values were not enough to accurate report.

-Not calculated.

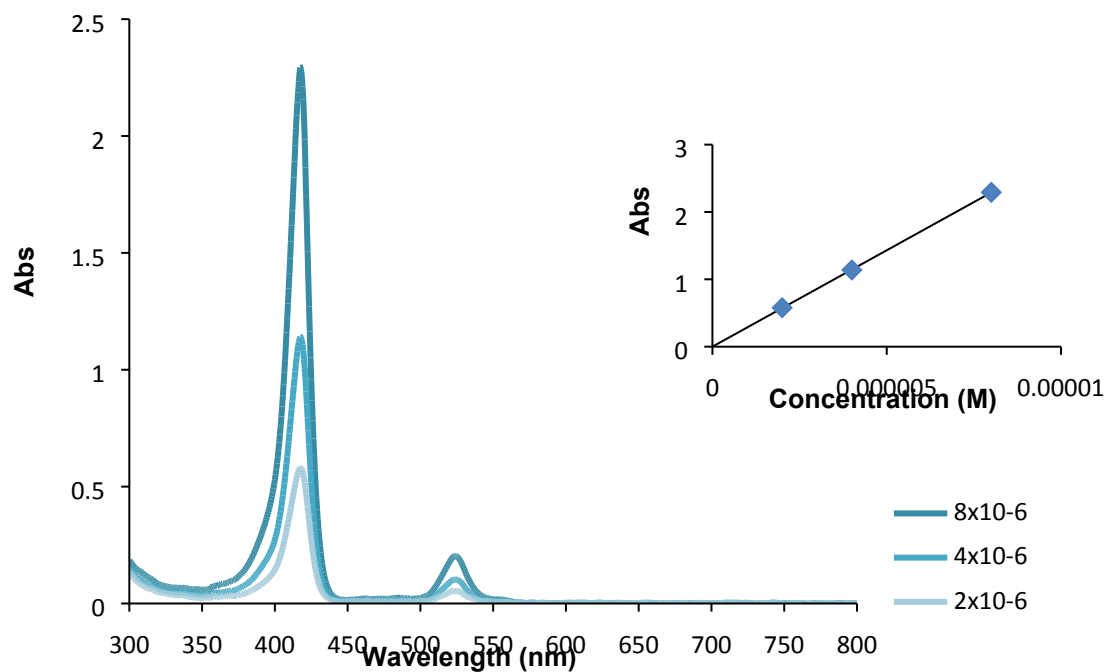


Figure S28: UV-Vis spectra of **Pd-TPP** in toluene at three different concentrations, inset: The plot of B band absorption intensities vs concentration.

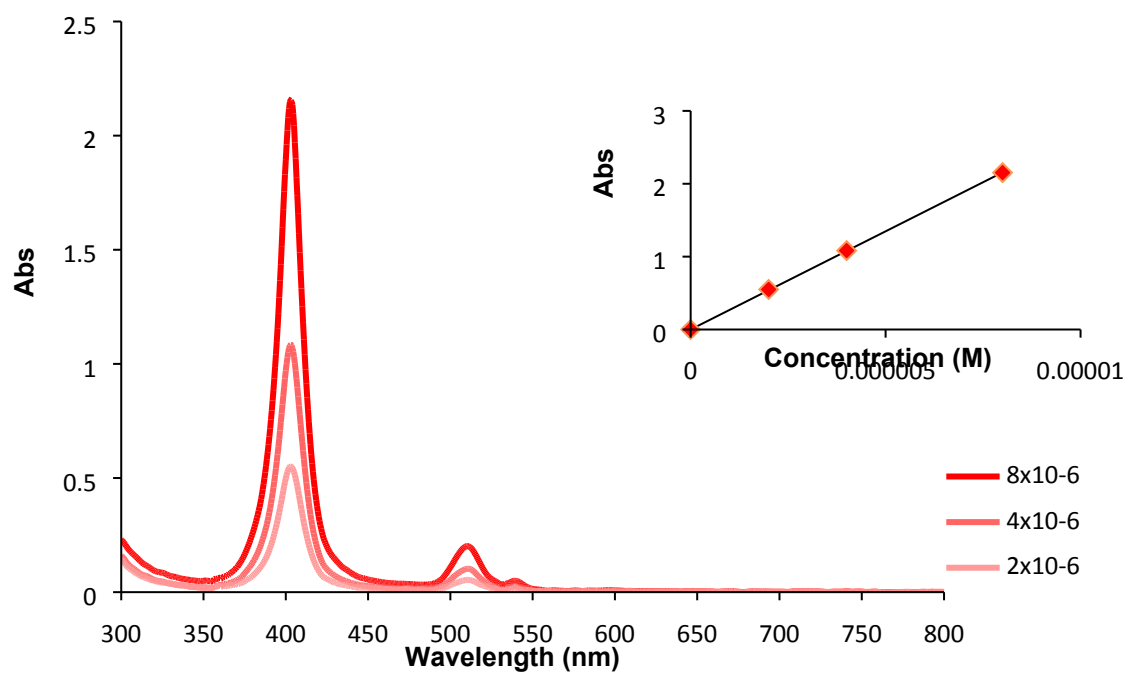


Figure S29: UV-Vis spectra of **Pt-TPP** in toluene at three different concentrations, inset: The plot of B band absorption intensities vs concentration.

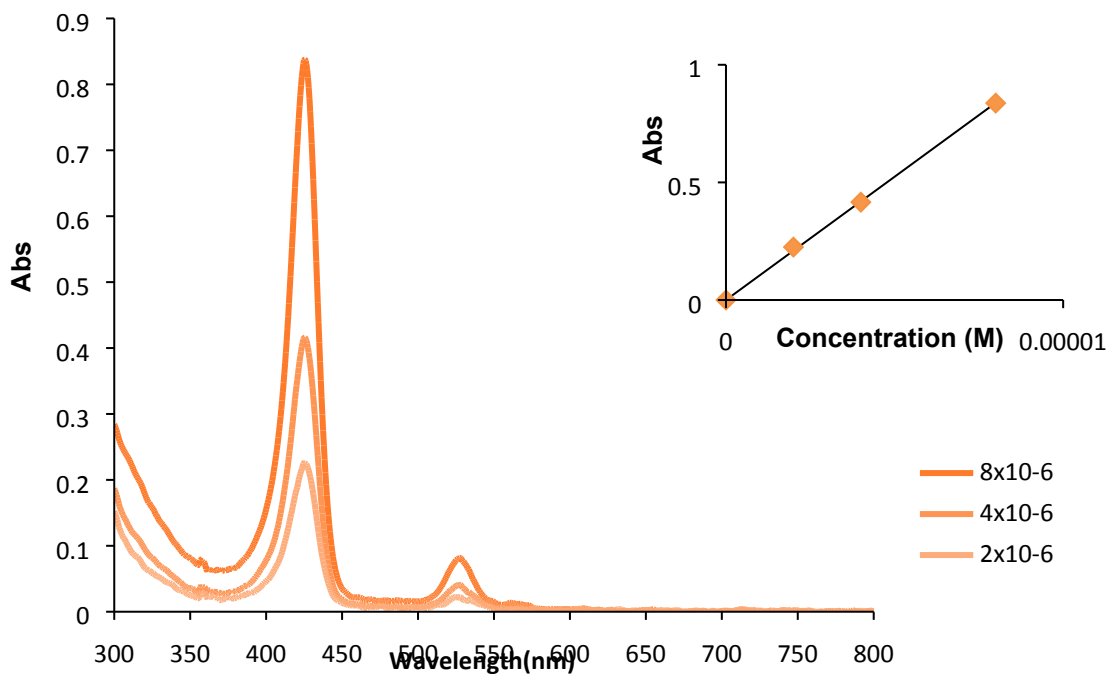


Figure S30: UV-Vis spectra of Pd-TPA in toluene at three different concentrations, inset: The plot of B band absorption intensities vs concentration.

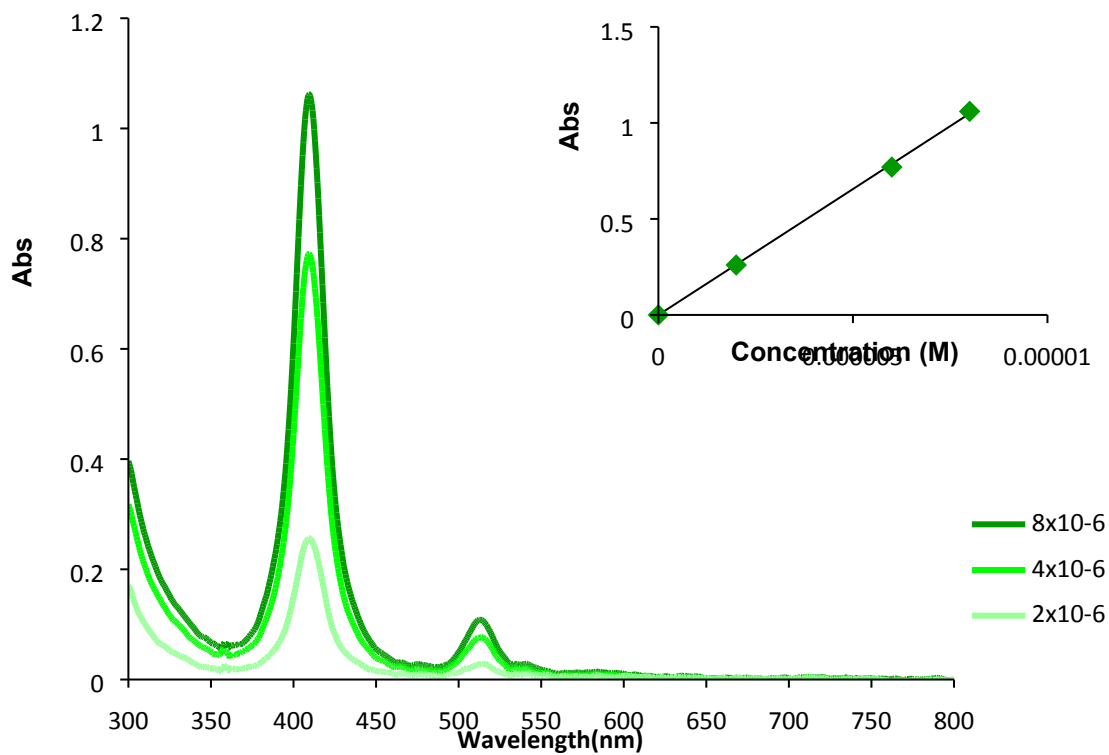


Figure S31: UV-Vis spectra of Pt-TPA in toluene at three different concentrations, inset: The plot of B band absorption intensities vs concentration.

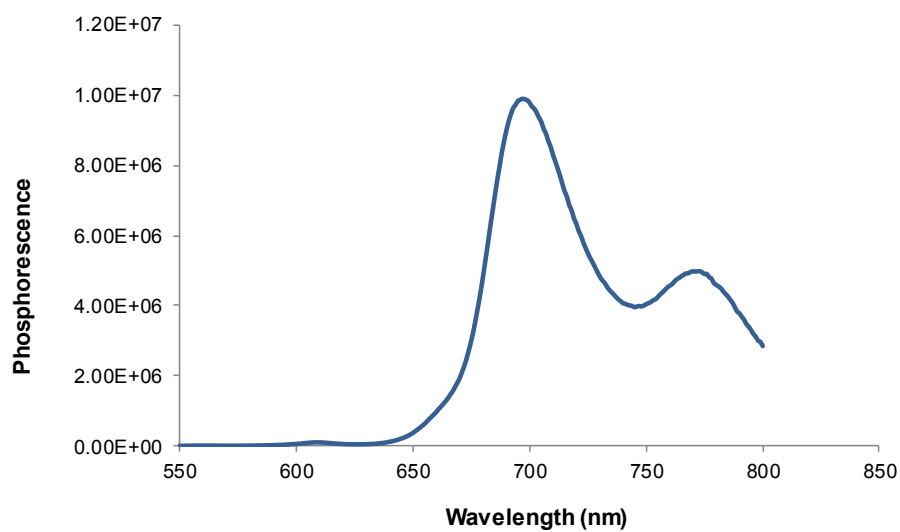


Figure S32. Phosphorescence emission spectra of **Pd-TTP** in toluene after exposure to argon gas ($\sim 8.3 \times 10^{-6}$ M).

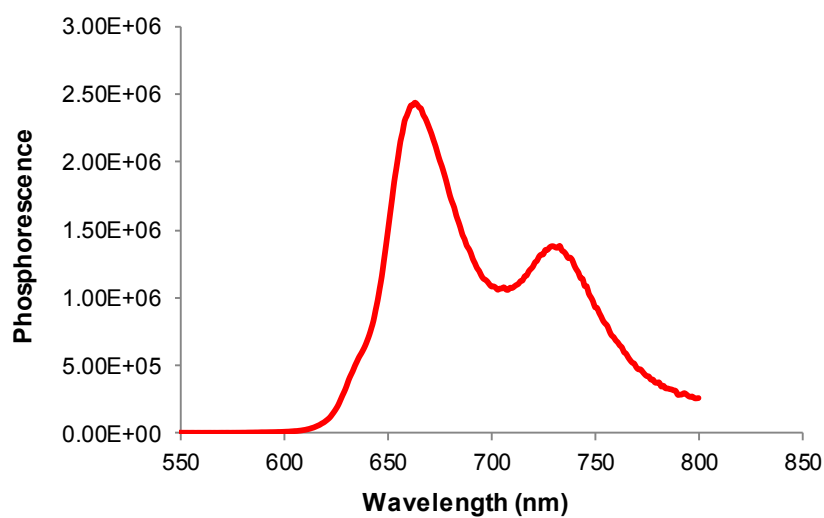


Figure S33. Phosphorescence emission spectra spectra of **Pt-TTP** in toluene after exposure to argon gas ($\sim 5.0 \times 10^{-6}$ M).

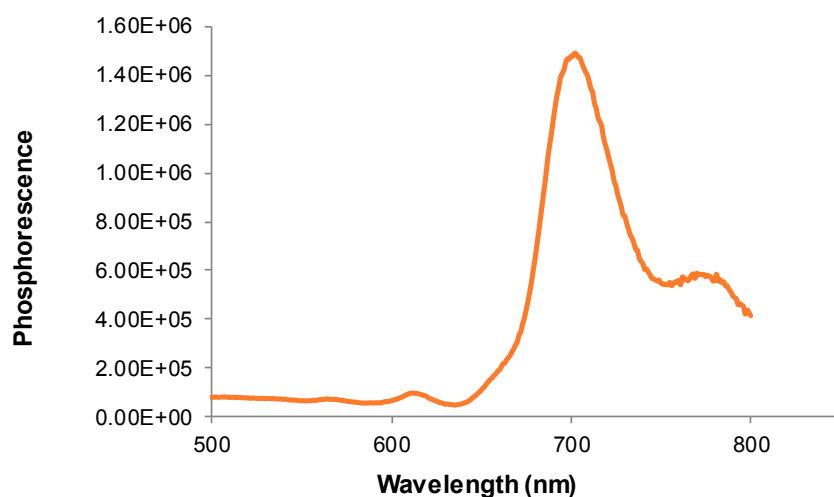


Figure S34. Phosphorescence emission spectra of **Pd-TPA** in toluene after exposure to argon gas ($\sim 5 \times 10^{-6}$ M).

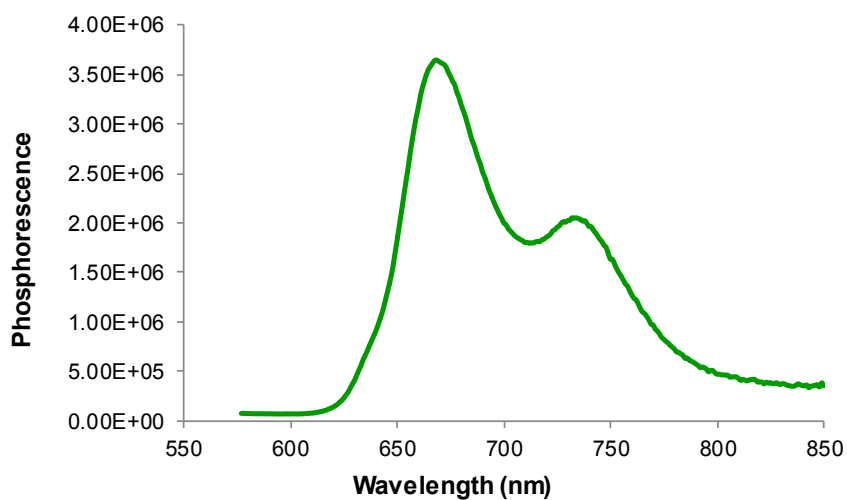


Figure S35. Phosphorescence emission spectra of **Pt-TPA** in toluene after exposure to argon gas ($\sim 3.8 \times 10^{-6}$ M).

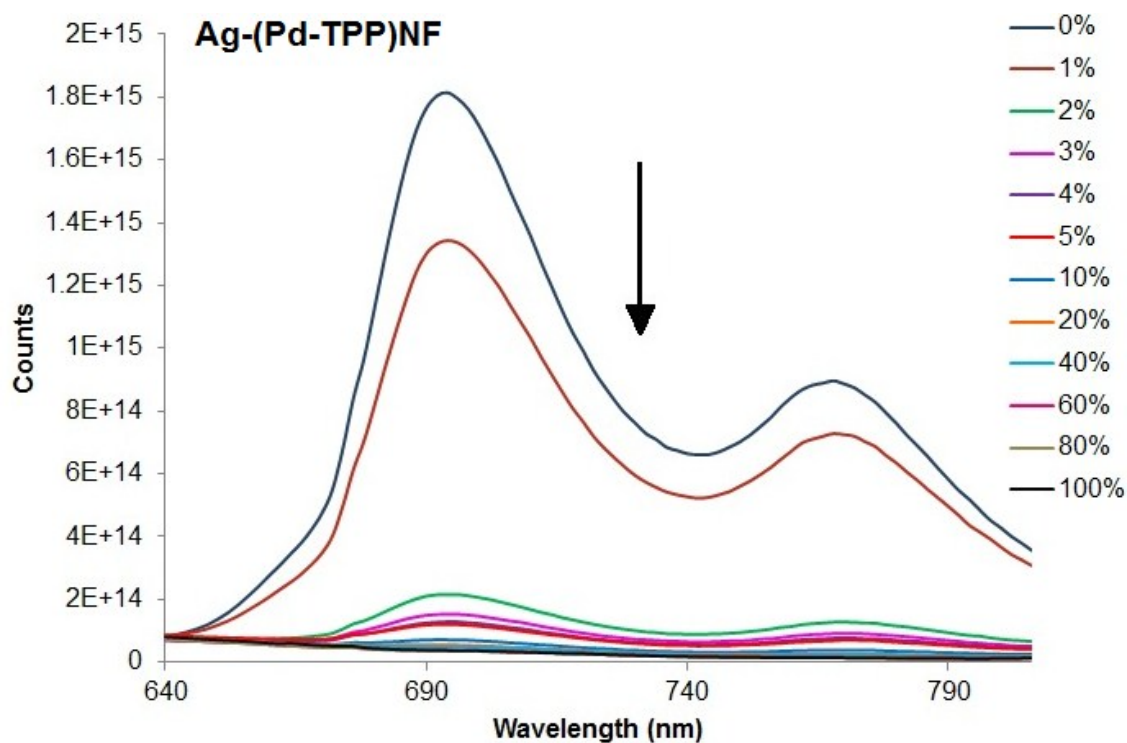


Figure S36. Emission spectra of Ag-(Pd-TPP)NF under small steps of O₂ partial pressures.

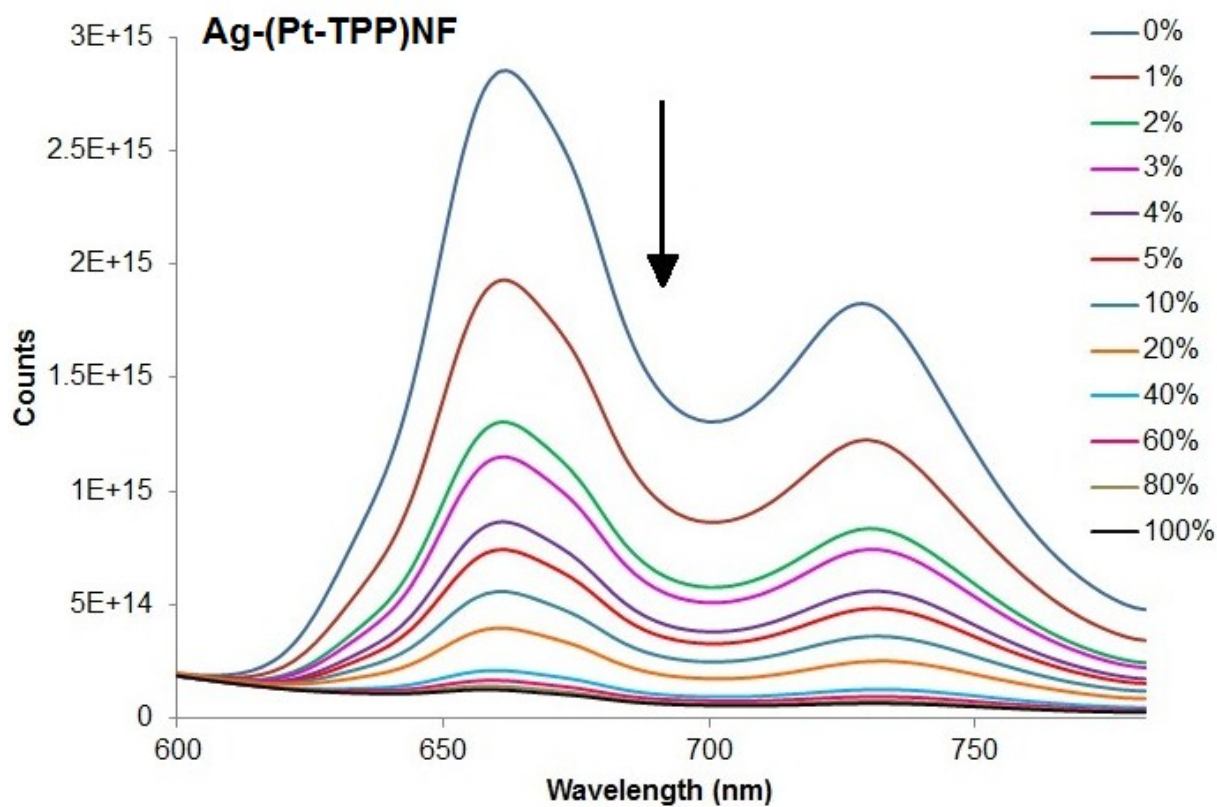


Figure S37. Emission spectra of Ag-(Pt-TPP)NF under small steps of O₂ partial pressures.

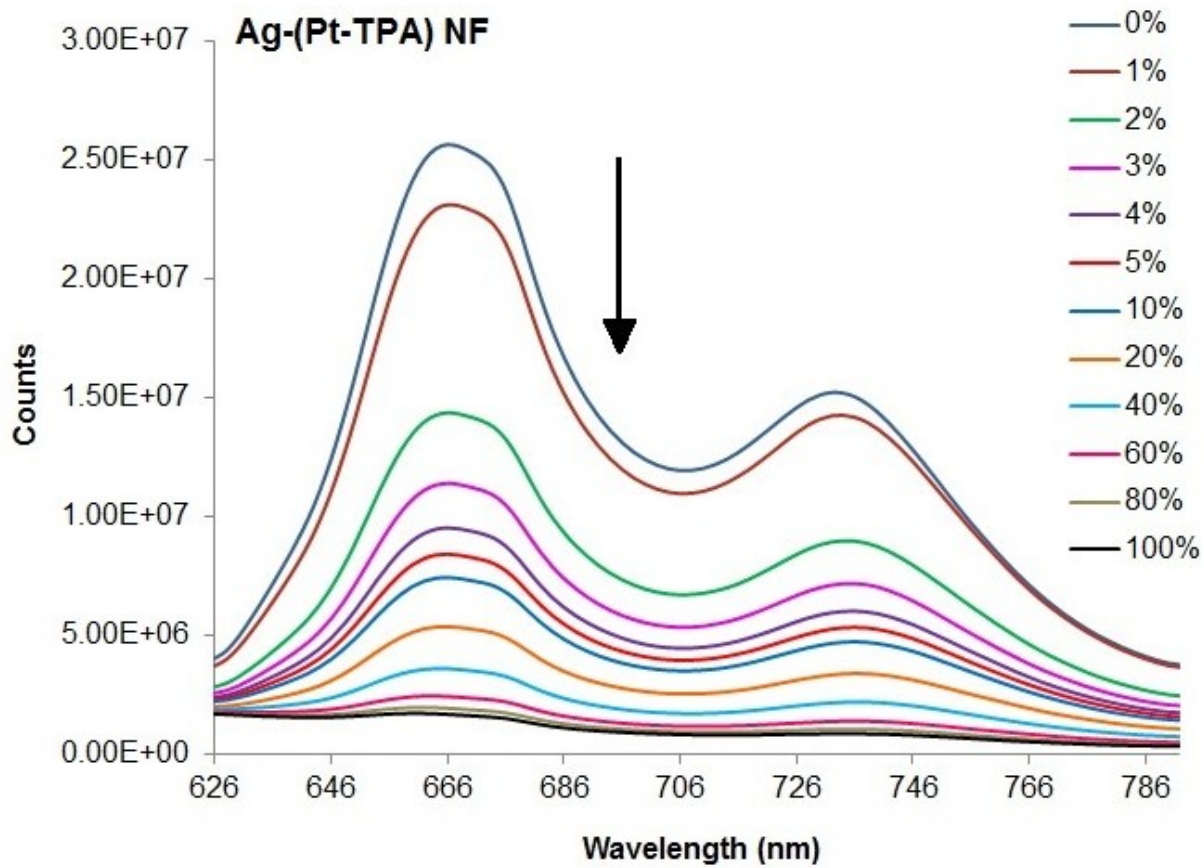


Figure S38. Emission spectra of Ag-(Pt-TPA)NF under small steps of O₂ partial pressures.

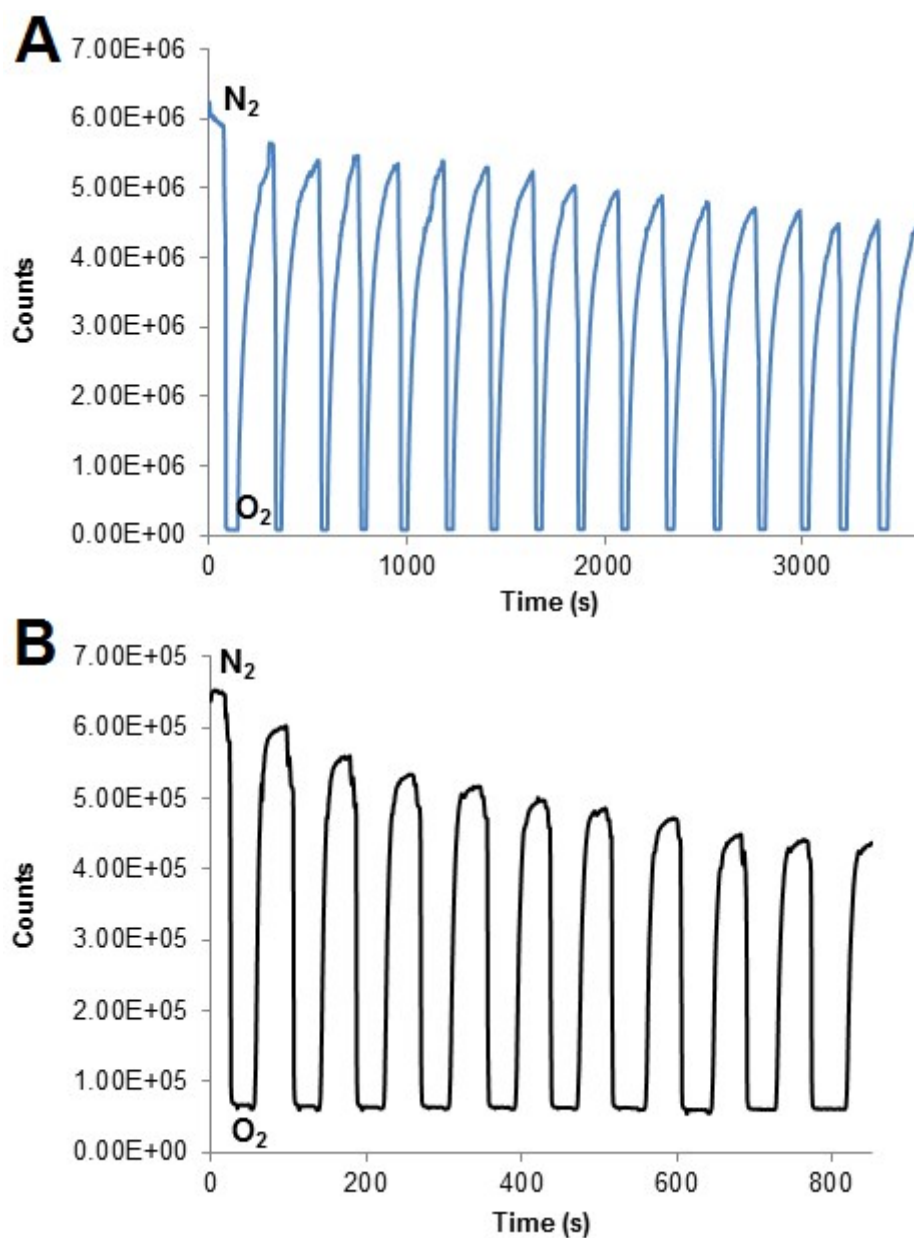


Figure S39. Time-based emission of **Pd-TPP** based nanofiber on going from 100 % O_2 to 100 % N_2 : (A) Nano Ag free nanofiber (B) nanofiber with nano Ag additive.

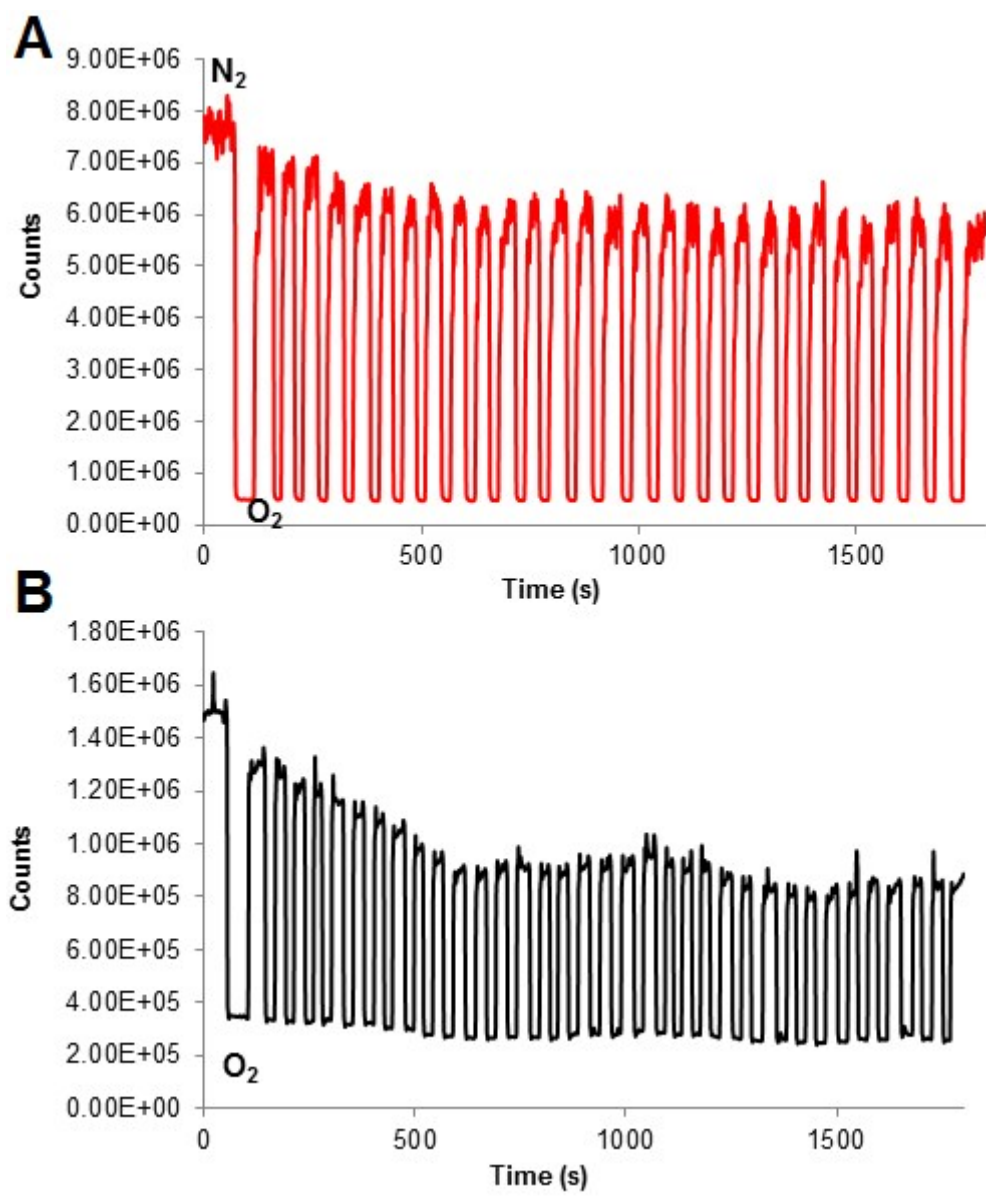


Figure S40. Time-based emission of **Pt-TPP** based nanofiber on going from 100 % O₂ to 100 % N₂ : (A) Nano Ag free nanofiber (B) nanofiber with nano Ag additive.

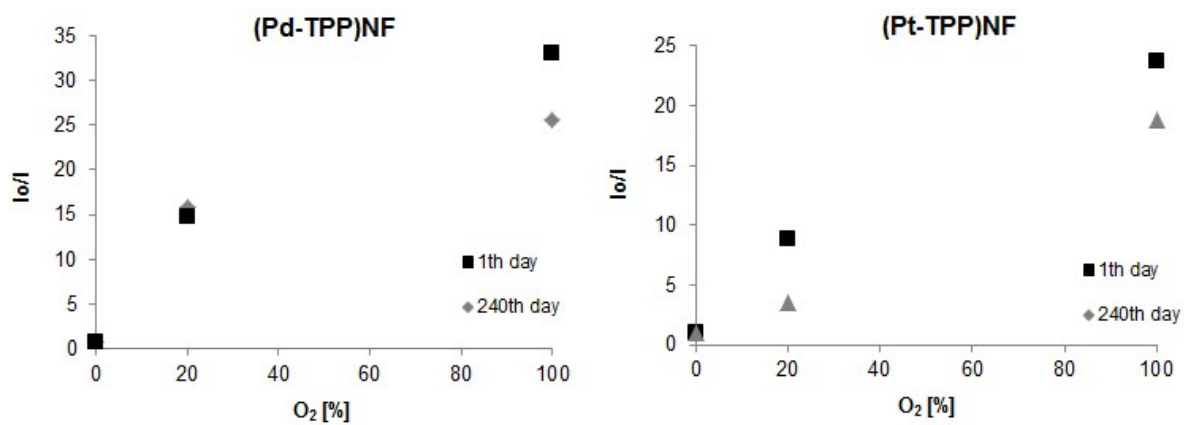


Figure S41. Repeatability test results of (Pd-TPP)NF and (Pt-TPA)NF.

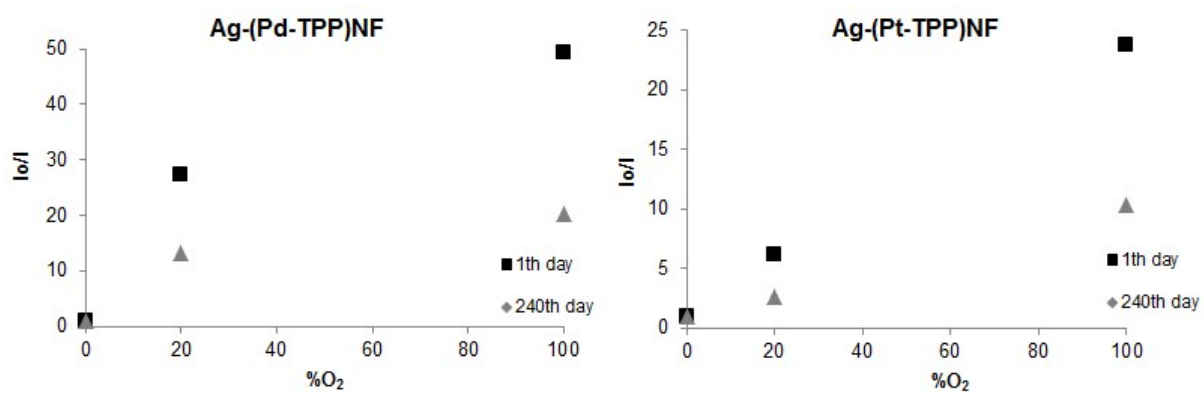


Figure S42. Repeatability test results of A) Ag-(Pd-TPP)NF and B) Ag-(Pt-TPP)NF.