

SUPPORTING INFORMATION

MESO-TETRA-(4-PYRIDYL)PORPHYRIN/PALLADIUM(II) COMPLEXES AS ANTICANCER AGENTS

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Table S1. Crystal data and structure refinement for the complex {TPyP[PdCl(dppb)]₄}(PF₆)₄.

CCDC code	2088291
Empirical formula	B ₄ C ₁₅₄ Cl ₈ F ₁₆ H ₁₄₆ N ₈ O ₂ P ₈ Pd ₄
Formula weight	3445.271
Temperature/K	150.03
Crystal system	monoclinic
Space group	P2 ₁ /a
a/Å	21.2707(11)
b/Å	23.0586(12)
c/Å	31.8123(19)
α/°	90
β/°	93.226(4)
γ/°	90
Volume/Å ³	15578.3(15)
Z	4
ρ _{calc} /cm ³	1.469
μ/mm ⁻¹	6.312
F(000)	7029.2
Crystal size/mm ³	0.113 × 0.08 × 0.012
Radiation	Cu Kα (λ = 1.54178)
2θ range for data collection/°	4.74 to 90
Index ranges	-20 ≤ h ≤ 27, -28 ≤ k ≤ 28, -38 ≤ l ≤ 38
Reflections collected	185018
Independent reflections	12550 [R _{int} = 0.3483, R _{sigma} = 0.2043]
Data/restraints/parameters	12550/1824/1477
Goodness-of-fit on F ²	1.477
Final R indexes [I >= 2σ (I)]	R ₁ = 0.1466, wR ₂ = 0.3819
Final R indexes [all data]	R ₁ = 0.1951, wR ₂ = 0.4253
Largest diff. peak/hole / e Å ⁻³	2.59/-1.21

Table S2. Selected bond lengths (Å) and angles (°) for the complex {TPyP[PdCl(dppp)]₄}(BF₄)₄.

Bonds (Å)	lengths (Å)	Bonds (Å)	lengths (Å)	Atoms	Angles (°)
Pd2-Cl2	2.35(1)	N1-C1	1.37(3)	P4-Pd2-Cl2	178.5(3)
Pd2-P3	2.26(1)	N1-C4	1.45(3)	P4-Pd2-P3	92.3(3)
Pd2-P4	2.25(1)	N2-C6	1.33(3)	P3-Pd2-Cl2	89.2(3)
P3-C231	1.83(1)	N2-C9	1.44(3)	N8-Pd2-P4	92.3(6)
P3-C241	1.85(2)	N3-C11	1.44(3)	N8-Pd2-P3	175.3(6)
P4-C221	1.83(2)	N3-C14	1.44(3)	C6-N2-C9	112.0(2)
P4-C211	1.85(2)	N4-C19	1.47(3)	C1-N1-C4	105.0(2)
Pd2-N8	2.08(2)	N4-C16	1.40(3)	C14-N3-C11	104.0(2)

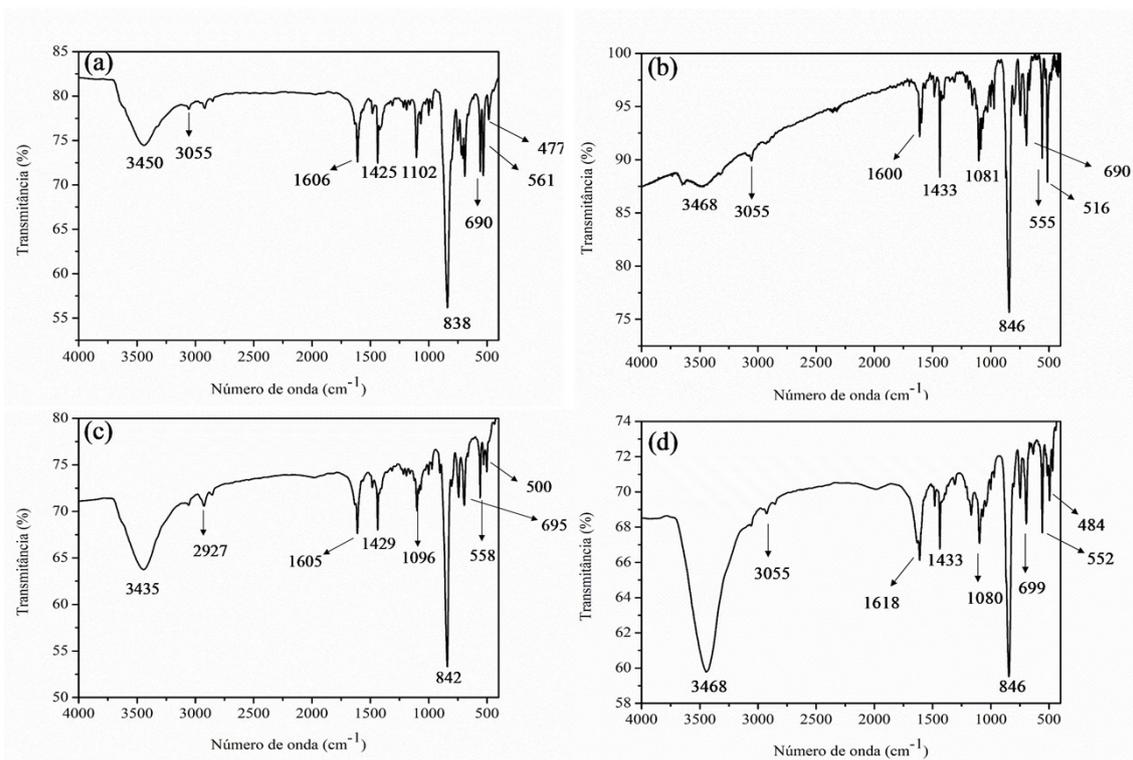


Figure S1. FT-IR spectra (KBr pellets) of the metalloporphyrins (a) $\{\text{TPyP}[\text{PdCl}(\text{dppe})]_4\}(\text{PF}_6)_4$, (b) $\{\text{TPyP}[\text{PdCl}(\text{dppp})]_4\}(\text{PF}_6)_4$, (c) $\{\text{TPyP}[\text{PdCl}(\text{dppb})]_4\}(\text{PF}_6)_4$ and (d) $\{\text{TPyP}[\text{PdCl}(\text{dppf})]_4\}(\text{PF}_6)_4$.

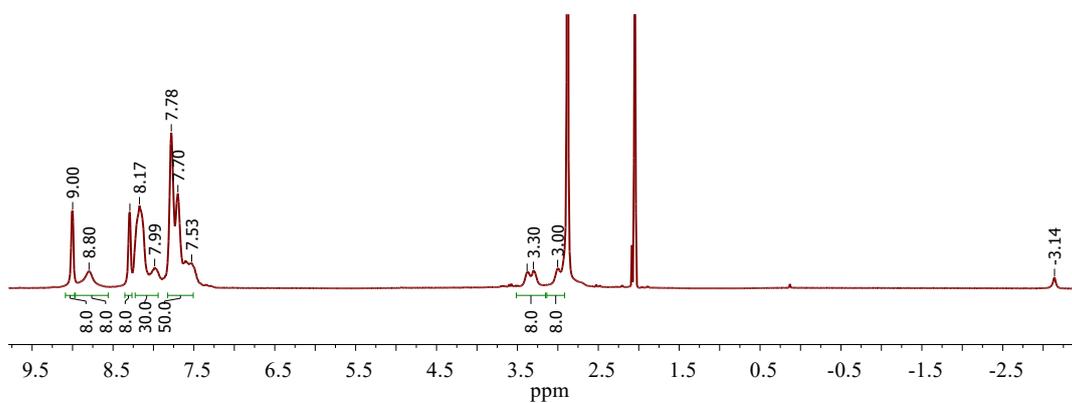


Figure S2. ^1H NMR spectra of the $\{\text{TPyP}[\text{PdCl}(\text{dppe})]_4\}(\text{PF}_6)_4$ complex, in CDCl_3 .

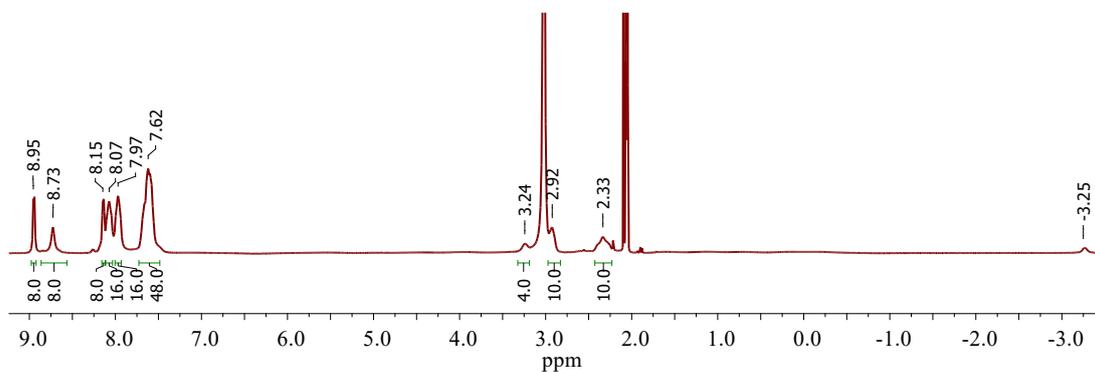


Figure S3. ^1H NMR spectra of the $\{\text{TPyP}[\text{PdCl}(\text{dppp})]_4\}(\text{PF}_6)_4$ complex, in CDCl_3 .

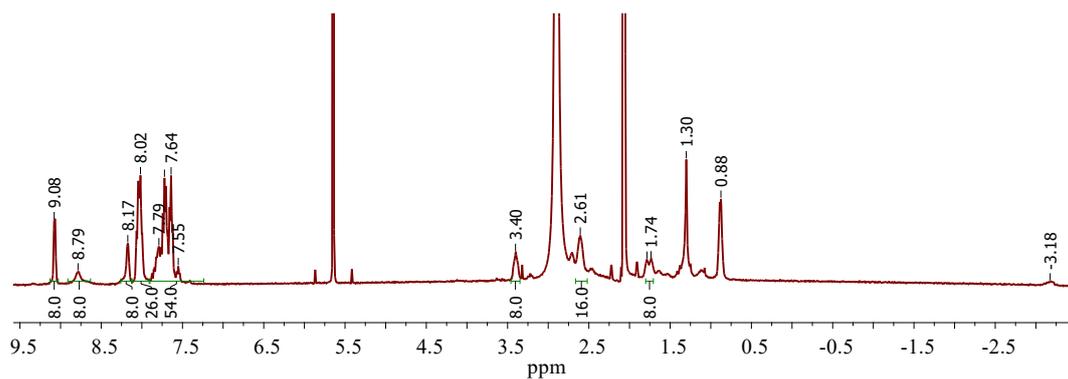


Figure S4. ^1H NMR spectra of the $\{\text{TPyP}[\text{PdCl}(\text{dppb})]_4\}(\text{PF}_6)_4$ complex, in CDCl_3 .

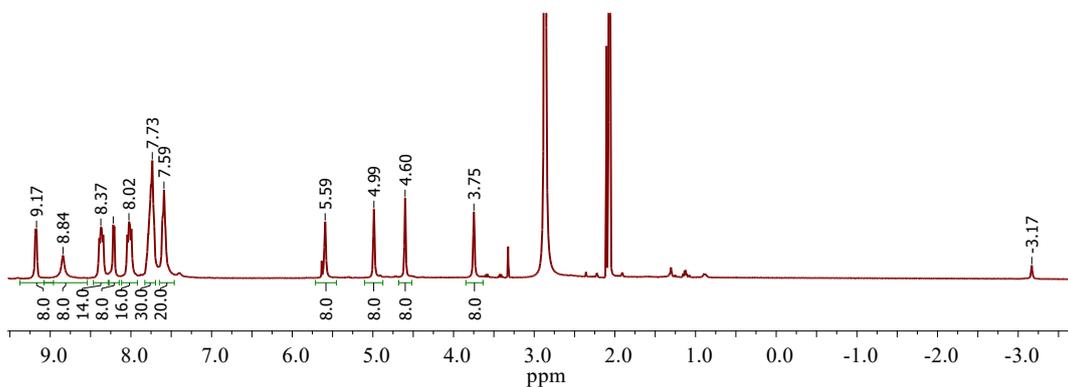


Figure S5. ^1H NMR spectra of the $\{\text{TPyP}[\text{PdCl}(\text{dppf})]_4\}(\text{PF}_6)_4$ complex, in CDCl_3 .

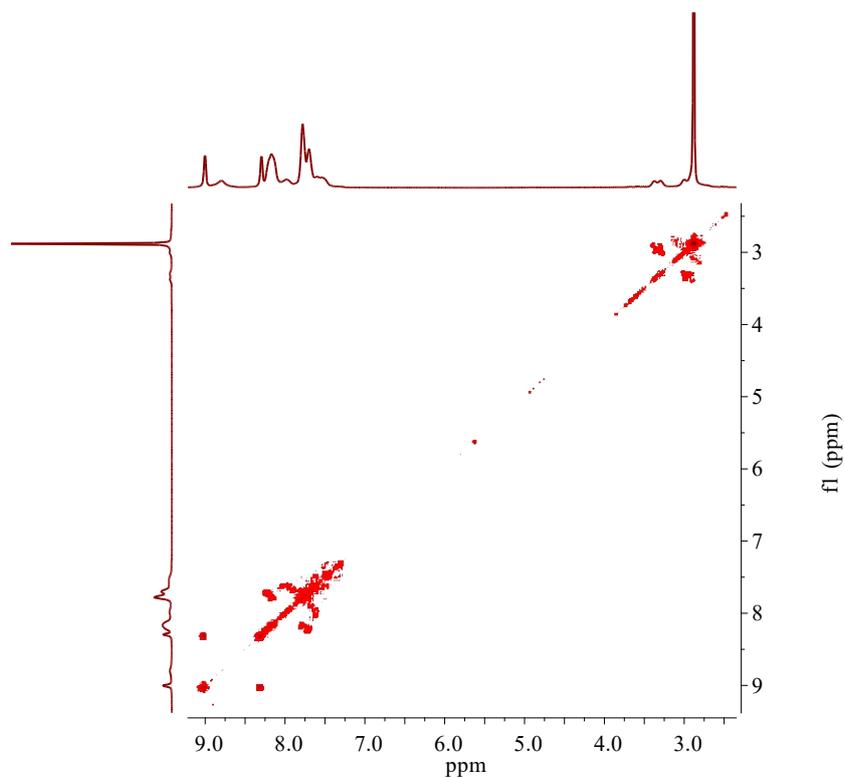


Figure S6. ^1H - ^1H COSY NMR contour map of the $\{\text{TPyP}[\text{PdCl}(\text{dppe})]_4\}(\text{PF}_6)_4$ complex, in CDCl_3 .

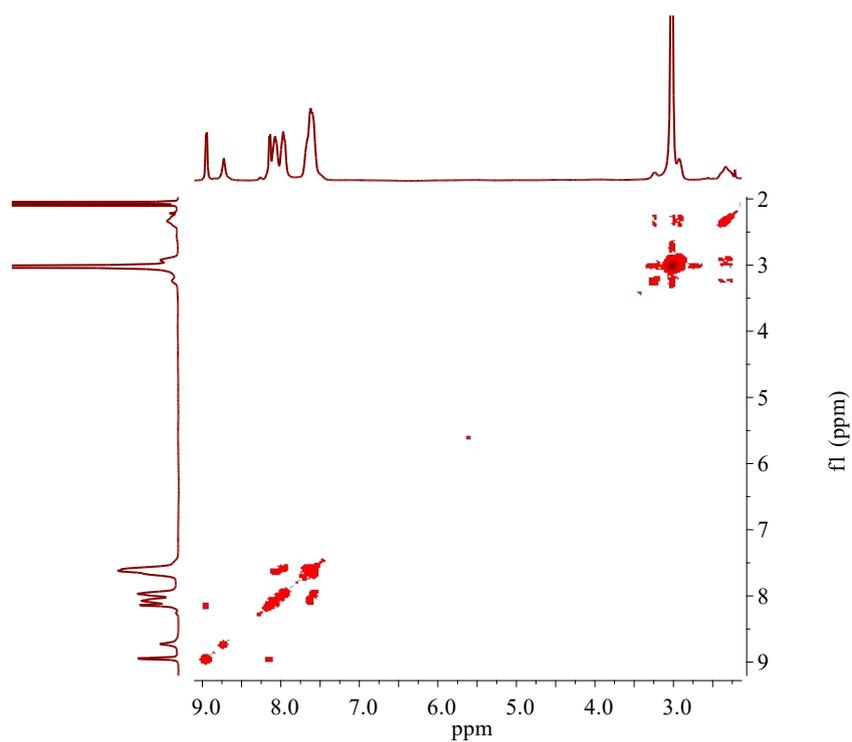


Figure S7. ¹H-¹H COSY NMR contour map of the {TPyP[PdCl(dppp)]₄} (PF₆)₄ complex, in CDCl₃.

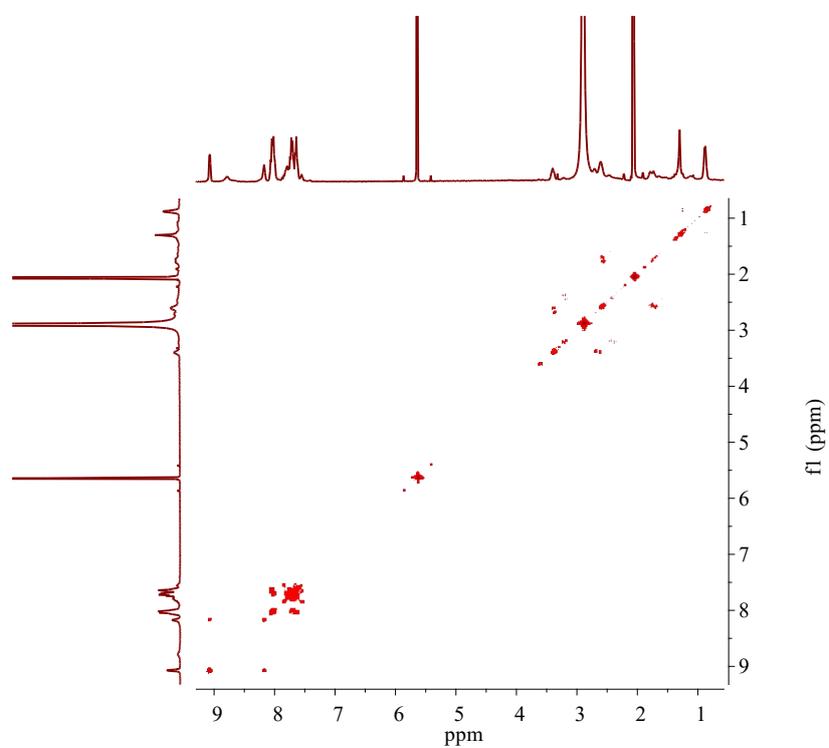


Figure S8. ¹H-¹H COSY NMR contour map of the {TPyP[PdCl(dppb)]₄} (PF₆)₄ complex, in CDCl₃.

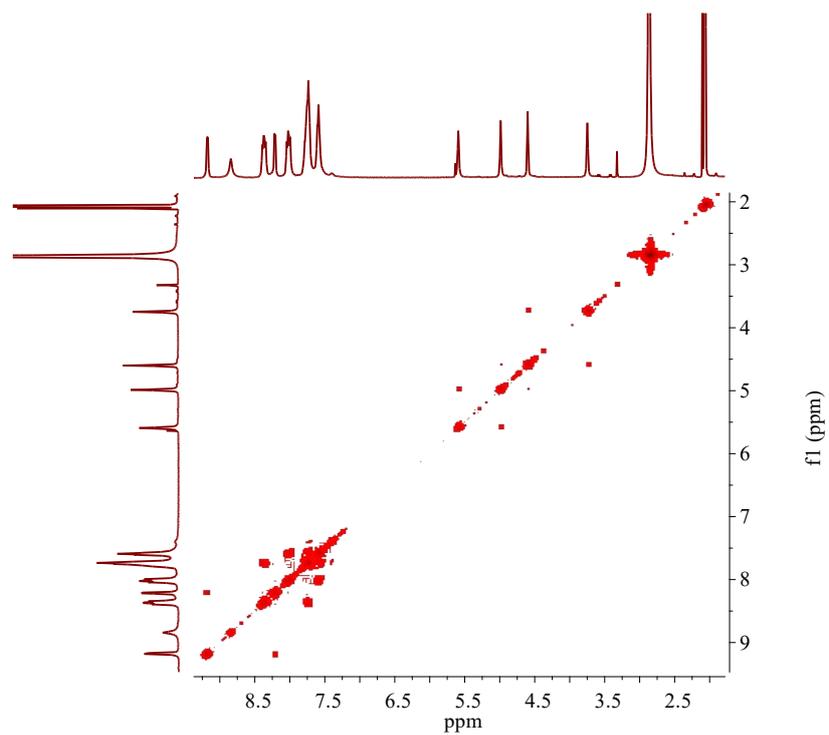


Figure S9. ^1H - ^1H COSY NMR contour map of the $\{\text{TPyP}[\text{PdCl}(\text{dppf})]_4\}(\text{PF}_6)_4$ complex, in CDCl_3 .

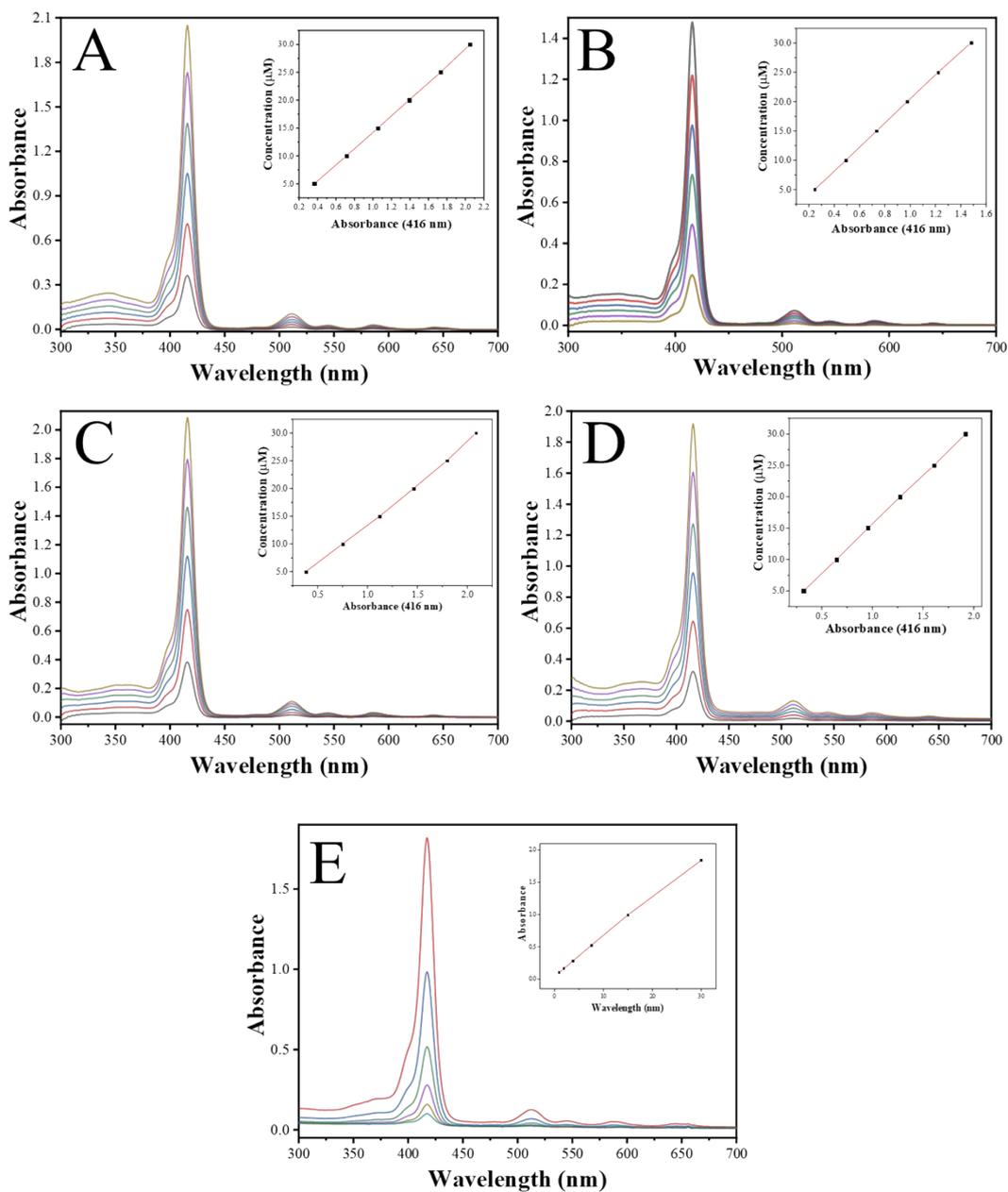


Figure S10. UV-Vis spectra for the complexes A - $\{TPyP[PdCl(dppe)]_4\}(PF_6)_4$, B - $\{TPyP[PdCl(dppp)]_4\}(PF_6)_4$, C - $\{TPyP[PdCl(dppb)]_4\}(PF_6)_4$, D - $\{TPyP[PdCl(dppf)]_4\}(PF_6)_4$, and E - free TPyP, in DMSO, at 298 K.

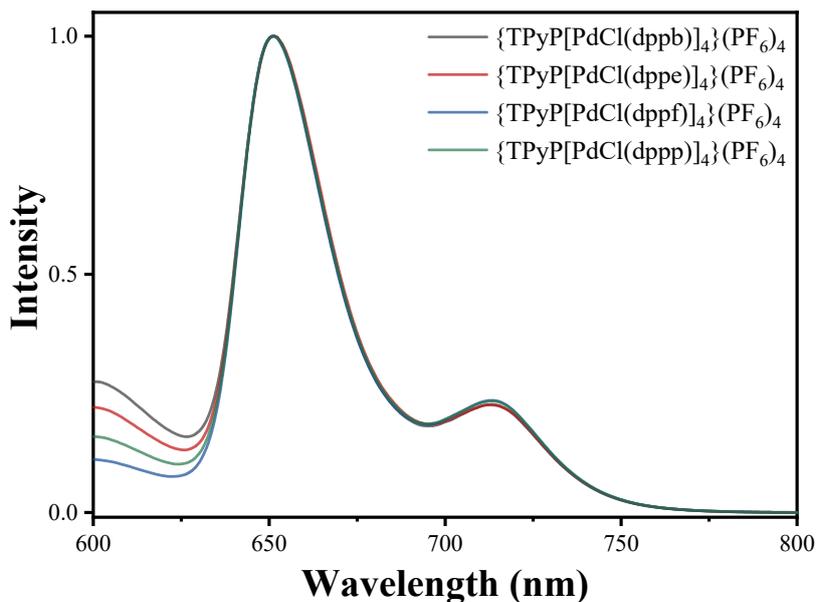


Figure S11. Fluorescence emission spectra of the palladium/TPyP complexes in DMSO, at 298 K.

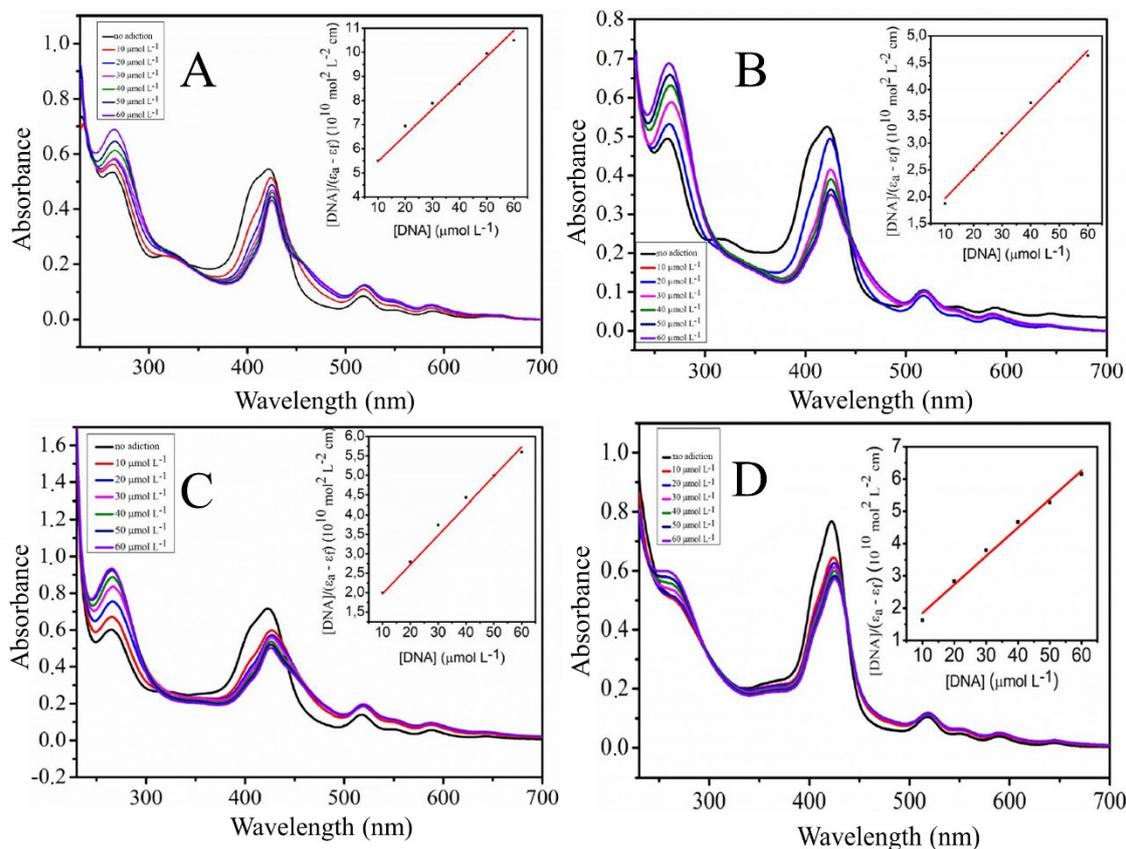


Figure S12. UV/Vis spectra of the complexes A - $\{\text{TPyP}[\text{PdCl}(\text{dppe})]_4\}(\text{PF}_6)_4$, B - $\{\text{TPyP}[\text{PdCl}(\text{dppp})]_4\}(\text{PF}_6)_4$, C - $\{\text{TPyP}[\text{PdCl}(\text{dppb})]_4\}(\text{PF}_6)_4$ and D - $\{\text{TPyP}[\text{PdCl}(\text{dppf})]_4\}(\text{PF}_6)_4$, (initially $2 \mu\text{M}$) in DMSO (5%) / Tris-HCl solution (pH 7.4), with increasing amount of CT-DNA, solutions.

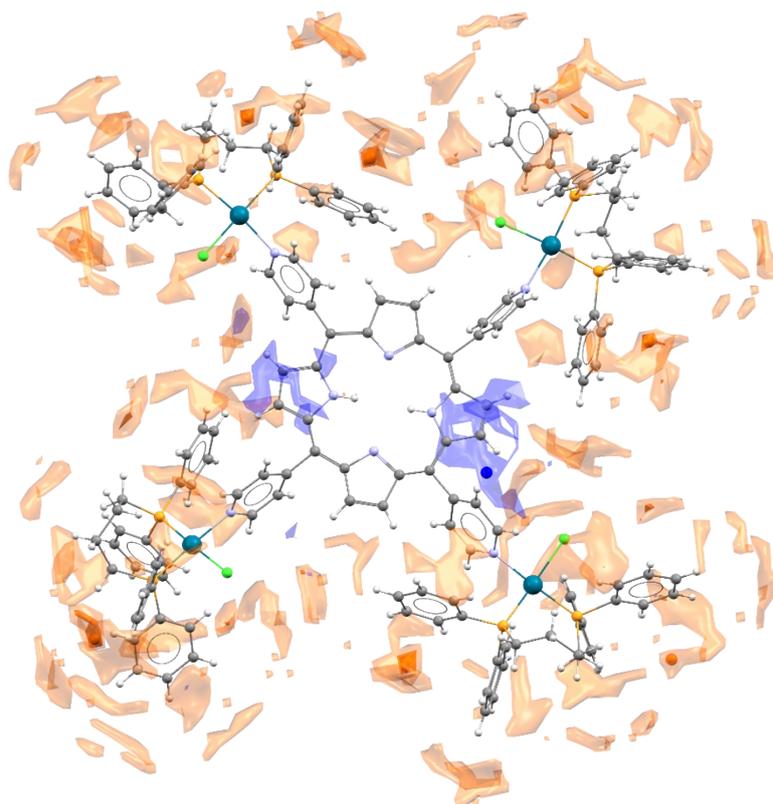


Figure S13. Full interaction map obtained for the crystal structure for the $\{\text{TPyP}[\text{PdCl}(\text{dppb})]_4\}(\text{BF}_4)_4$ complex, displaying the regions with probability to perform aromatic interactions.