

Supplementary Materials: Second Order Nonlinear Optical Properties of 4-Styrylpyridines Axially Coordinated to A₄ Zn^{II} Porphyrins: A Comparative Experimental and Theoretical Investigation

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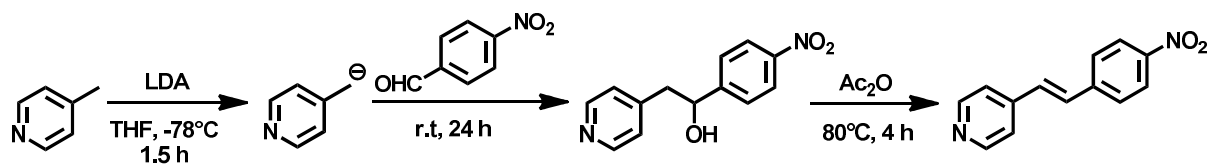
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Materials and Methods

All reagents and solvents were purchased from Sigma-Aldrich and used as received. Milli-Q water was collected from Millipore apparatus, equipped with 0.22 µm filters. Glassware was flame-dried under vacuum before use when necessary. Silica gel for gravimetric chromatography (Geduran Si 60, 63–200 µm) and for flash chromatography (Kieselgel 60, 0.040–0.063 mm) were purchased from Merck. ¹H-NMR spectra were recorded on a Bruker AMX 300 and on a Bruker Avance DRX-400 in CDCl₃ or in THF-*d*₈, to enhance resolution (Cambridge Isotope Laboratories, Inc.). Elemental analyses were carried out with a Perkin-Elmer CHN 2400 instrument in the Analytical Laboratories of the Department of Chemistry at the University of Milan. Electronic absorption spectra were recorded in CHCl₃ solution at room temperature on a Shimadzu UV 3600 spectrophotometer. The starting A₄ Zn^{II} porphyrin complexes were prepared as reported in literature [1].

Synthesis of L1



Scheme S1. Synthetic route for ligand L1.

In a dried schlenk tube 4-methylpyridine (0.559 g; 6.0 mmol) was dissolved in anhydrous THF (6 mL) under nitrogen atmosphere. After cooling at -78 °C, 4 ml of lithium diisopropylamide (LDA) solution in THF (2M) was added dropwise to the reaction mixture which was allowed to react for further 1.5 hours. 15 ml of a 4-Nitrobenzaldehyde (0.906g; 6.0 mmol) solution in THF was then slowly added, then the mixture warmed at room temperature and stirred 24 hours. 30 ml of NH₄Cl-saturated aqueous solution was added to quench the reaction resulting in a two-phase mixture. The aqueous phase was extract with diethyl ether and the collected organic phase washed with deionized water and dried over Na₂SO₄. A yellow-orange thick residue was obtained after removing the solvents and used without further purification for the next dehydration step.

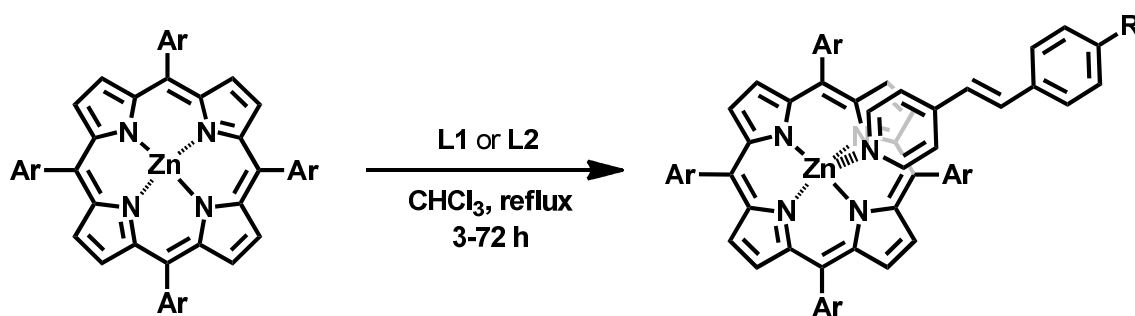
The crude was dissolved in freshly distilled acetic anhydride (20 mL) and refluxed for 4h under vigorous stirring. The solvent was then removed, the brown oil residue dissolved in

dichloromethane and washed first with 10% NaOH aqueous solution and then with deionized water. After drying the organic phase over MgSO_4 and evaporated to dryness the crude was purified by column chromatography over silica gel (ethyl acetate/hexane 8:2 as eluent) to give the pure **L1** as a pale-yellow powder (0.543 g, 40%).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.15 (d, 1H, $J_{\text{trans}} = 16$ Hz), 7.32 (d, 1H, $J_{\text{trans}} = 16$ Hz), 7.37 (d, 2H), 7.64 (d, 2H), 8.19 (d, 2H), 8.59 (d, 2H).

Elemental analysis: calcd (%) C 69.02, H 4.46, N 12.38; found C 69.21, H 4.45, N 12.41.

General procedure for the axial coordination of **L1** and **L2** to A_4 Zn^{II} porphyrins



Scheme S2. Schematic axial coordination of **L1** or **L2** to Zn^{II} porphyrins.

In a two-neck round bottom flask equipped with a condenser and a dropping-funnel the selected Zn^{II} -porphyrin (1.0 equiv.) was dissolved in chloroform, and the resulting 1.0×10^{-3} M solution was warmed to reflux. After that the appropriate stilbazole-based ligand (1.5 equiv. for **L1** and 1.0 equiv. for **L2**) dissolved in the minimum amount of chloroform was added dropwise to the refluxing solution in 10 minutes. Depending on the specific combination of porphyrin and ligand the axial coordination step required from 3 hours to 72 hours to proceed quantitatively. All desired complexes were purely obtained in almost quantitative yield ($\geq 98\%$) by evaporating the solvent, thoroughly washing the solid with *n*-hexane and recrystallizing from CHCl_3/n -hexane.

ZnTPP-L1 [3 hours]: ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 3.74 (br. s, 2H), 5.98 (br. s, 2H), 6.32 (d, 1H), 6.58 (d, 1H), 7.24 (d, 2H), 7.76 (s, 12H), 8.00 (d, 2H), 8.23 (s, 8H), 8.90 (s, 8H).

Elemental analysis: calcd (%) C 75.70, H 4.24, N 9.29; found C 75.91, H 4.23, N 9.27.

ZnTPP-L2 [3 hours]: ^1H -NMR (400 MHz, CDCl_3) δ (ppm): 2.91 (s, 6H), 6.18 (br. d., 1H), 6.31 (br. d, 2H), 6.52 (d, 2H), 6.80 (br. d., 1H), 7.15 (d, 2H), 7.75 (m, 12H), 8.24 (s, 8H), 8.91 (s, 8H).

^1H -NMR (400 MHz, THF-d_8) δ (ppm): 3.00 (s, 6H), 6.73 (d, 2H), 6.82 (d, 1H), 7.27 (d, 2H), 7.32 (d, 1H), 7.43 (d, 2H), 7.78 (m, 12H), 7.89 (d, 2H), 8.21 (dd, 8H), 8.86 (s, 8H).

Elemental analysis: calcd (%) C 78.53, H 4.91, N 9.31; found C 78.77, H 4.90, N 9.33.

ZnTBP-L1 [24 hours]: ^1H -NMR (400 MHz, CDCl_3) δ (ppm) 4.39 (br. s, 2H), 6.20 (br. s, 2H), 6.48 (d, 1H), 6.71 (d, 1H), 7.35 (d, 2H), 7.82 (s, 4H), 8.08 (d, 2H), 8.12 (s, 8H), 8.99 (s, 8H).

Elemental analysis: calcd (%) C 79.00, H 7.60, N 6.21; found C 79.24, H 7.58, N 6.19.

ZnTBP-L2 [3 hours]: ^1H -NMR (400 MHz, CDCl_3) δ (ppm) 2.94 (s, 6H), 6.21 (d, 1H), 6.32 (br. s, 2H), 6.56 (d, 2H), 6.78 (d, 1H), 7.18 (d, 2H), 7.78 (s, 4H), 8.10 (s, 8H), 8.96 (s, 8H).

Elemental analysis: calcd (%) C 80.89, H 8.06, N 6.22; found C 80.98, H 8.08, N 6.21.

ZnTNP-L1 [72 hours]: ^1H -NMR (400 MHz, THF-d_8) δ (ppm) 1.33 (m, 72 H), 2.51 (br. s, 2H), 7.46 (m, 41H), 7.55 (d, 1H), 7.83 (d, 2H), 8.03 (d, 8H), 8.23 (d, 2H), 8.44 (br. d, 2H), 9.04 (s, 8H).

Elemental analysis: calcd (%) C 81.38, H 6.88, N 6.93; found C 81.60, H 6.90, N 6.90.

ZnTNP-L2 [4 hours]: ^1H -NMR (400 MHz, THF-d_8) δ (ppm) 1.36 (m, 72H), 2.49 (br. s, 2H), 3.01 (s, 6H), 6.73 (d, 2H), 6.89 (d, 1H), 7.49 (m, 43H), 8.09 (d, 8H), 8.42 (m, 4H), 9.04 (s, 8H).

Elemental analysis: calcd (%) C 82.64, H 7.19, N 6.93; found C 82.41, H 7.17, N 6.95.

ZnTFP-L1 [4 hours]: ^1H -NMR (400 MHz, CDCl_3) δ (ppm) 2.44 (br. s, 2H), 5.62 (br. s, 2H), 6.14 (d, 1H), 6.41 (d, 1H), 7.18 (br. s, 2H), 8.00 (d, 2H), 8.95 (s, 8H).

Elemental analysis: calcd (%) C 54.16, H 1.44, N 6.65; found C 54.03, H 1.45, N 6.63.

ZnTFP-L2 [3 hours]: ^1H -NMR (400 MHz, CDCl_3) δ (ppm) 2.99 (s, 6H), 6.39 (d, 1H), 6.61 (d, 2H), 6.71 (br. s, 2H), 7.00 (d, 1H), 7.26 (d, 2H), 8.93 (s, 8H).

^1H -NMR (400 MHz, $\text{THF-}d_6$) δ (ppm): 3.01 (s, 6H), 6.74 (d, 2H), 6.85 (d, 1H), 7.36 (m, 3H), 7.45 (d, 2H), 8.02 (br. s, 2H), 9.11 (s, 8H).

Elemental analysis: calcd (%) C 56.14, H 1.92, N 6.66; found C 56.29, H 1.91, N 6.68.

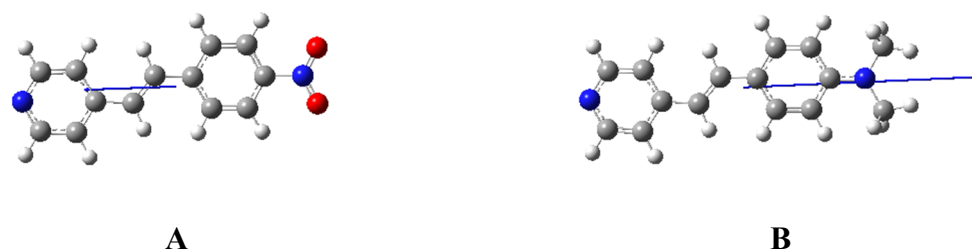


Figure 1. Optimized geometry of 4-styrylpyridine **L1** (A) and **L2** (B).

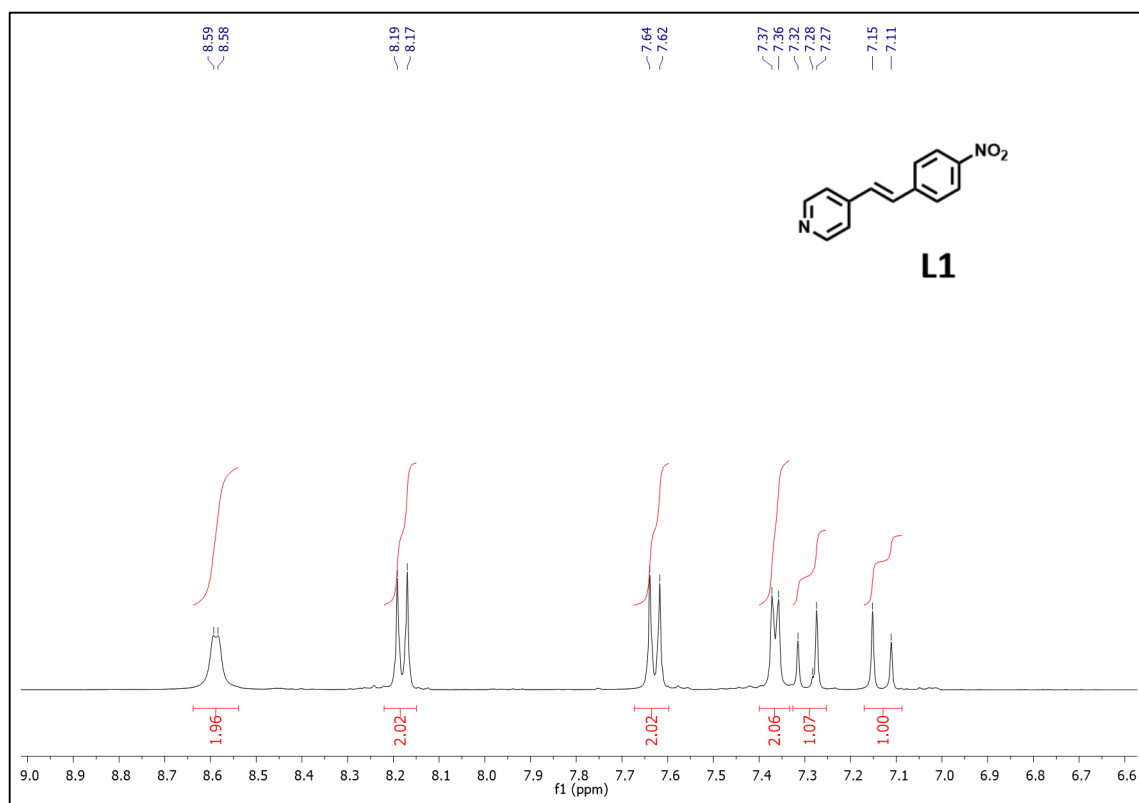


Figure 2. ^1H -NMR spectrum of **L1** in CDCl_3 .

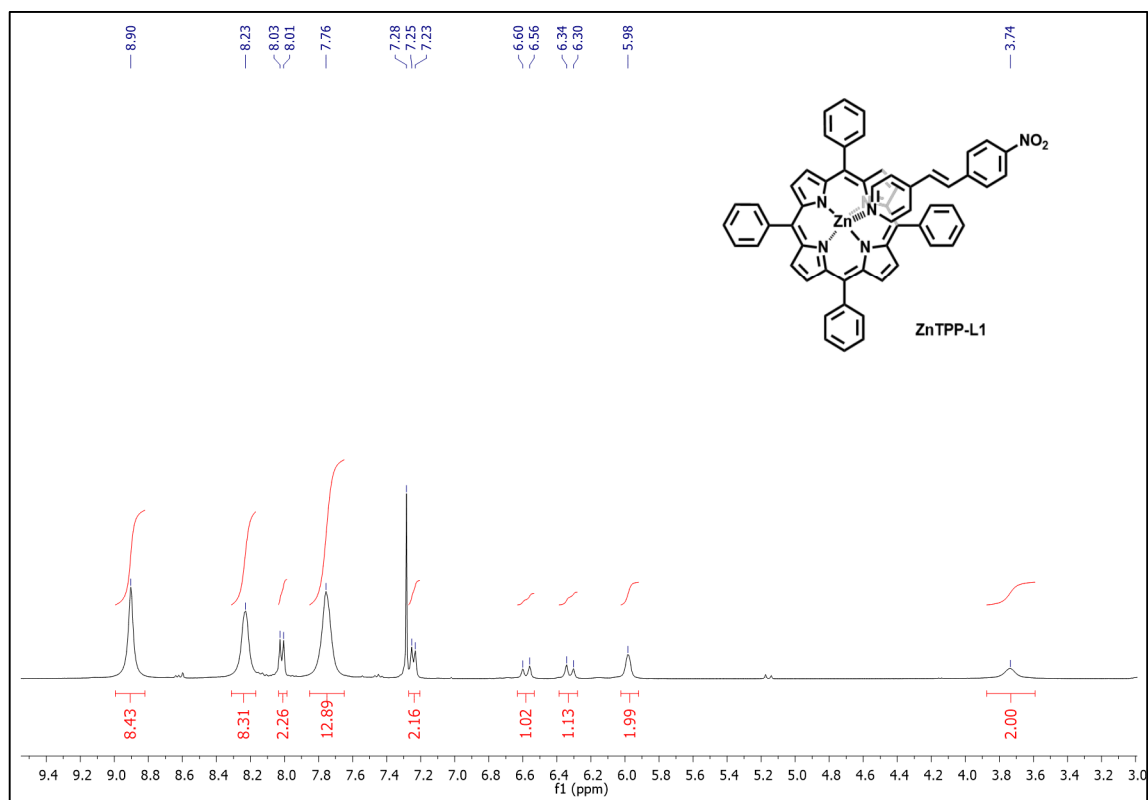


Figure 3. ¹H-NMR spectrum of ZnTPP-L1 in CDCl₃.

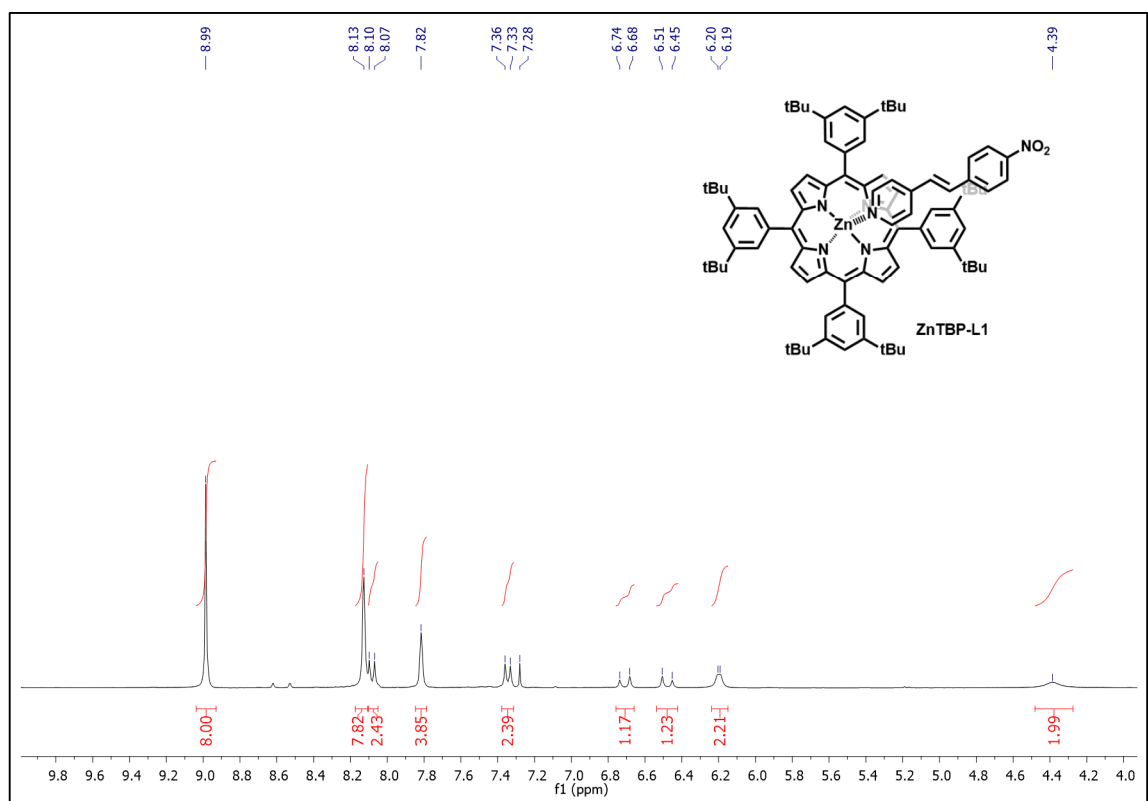


Figure 4. ¹H-NMR spectrum of ZnTBP-L1 in CDCl₃.

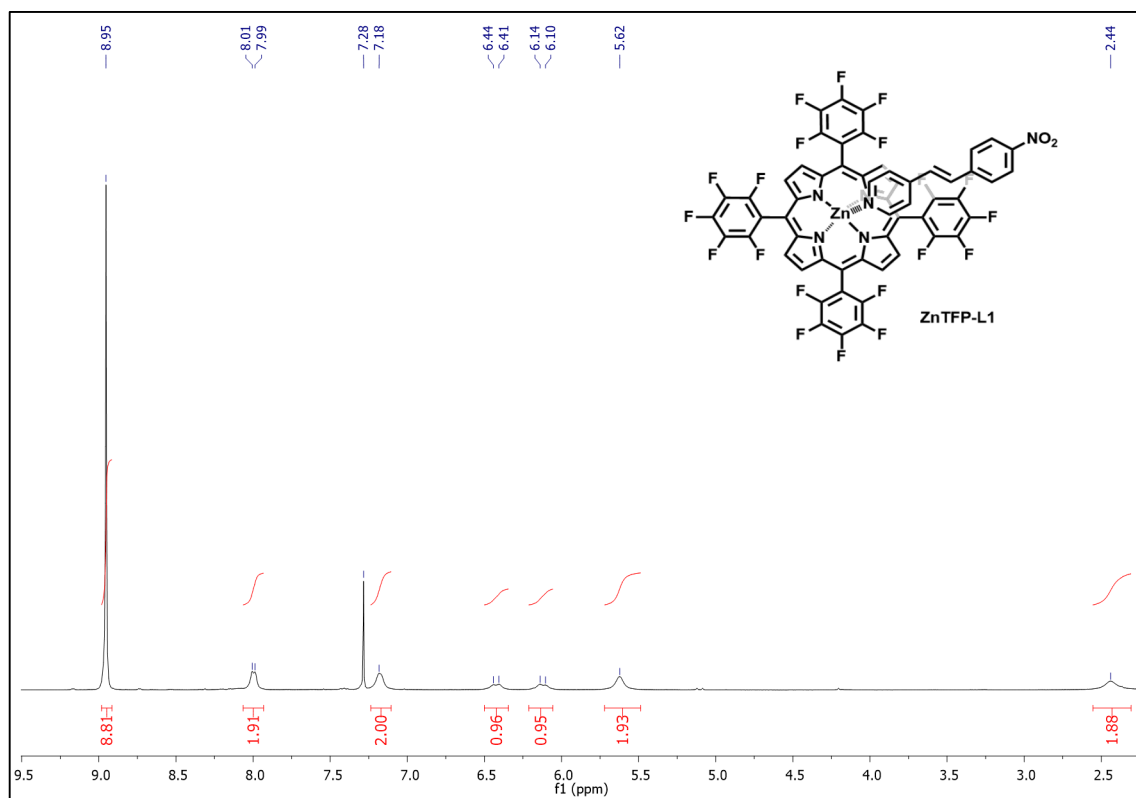


Figure 5. ^1H -NMR spectrum of ZnTFP-L1 in CDCl_3 .

Normalized UV-Vis spectra in CHCl_3 solution

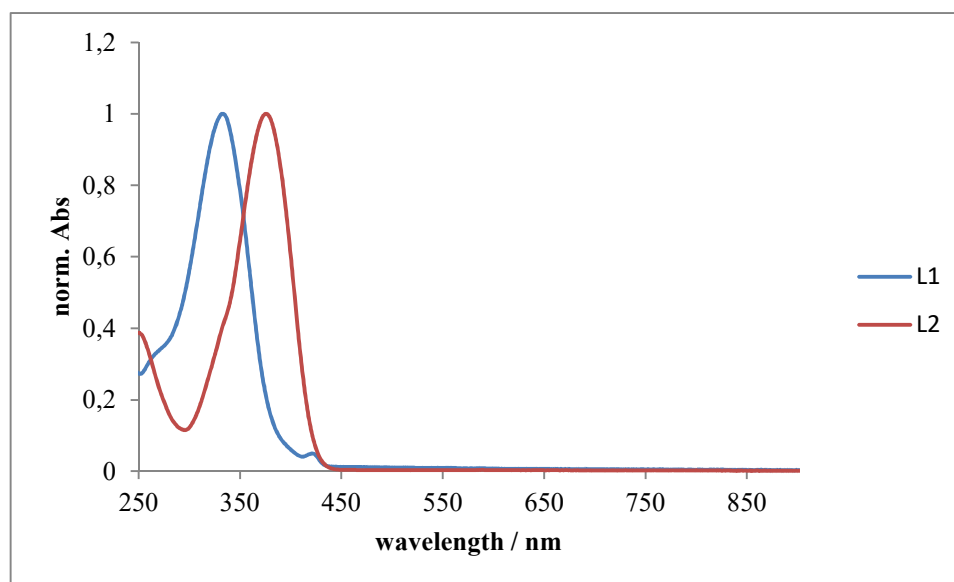


Figure 6. Normalized UV-Vis spectra of ligands L1 and L2.

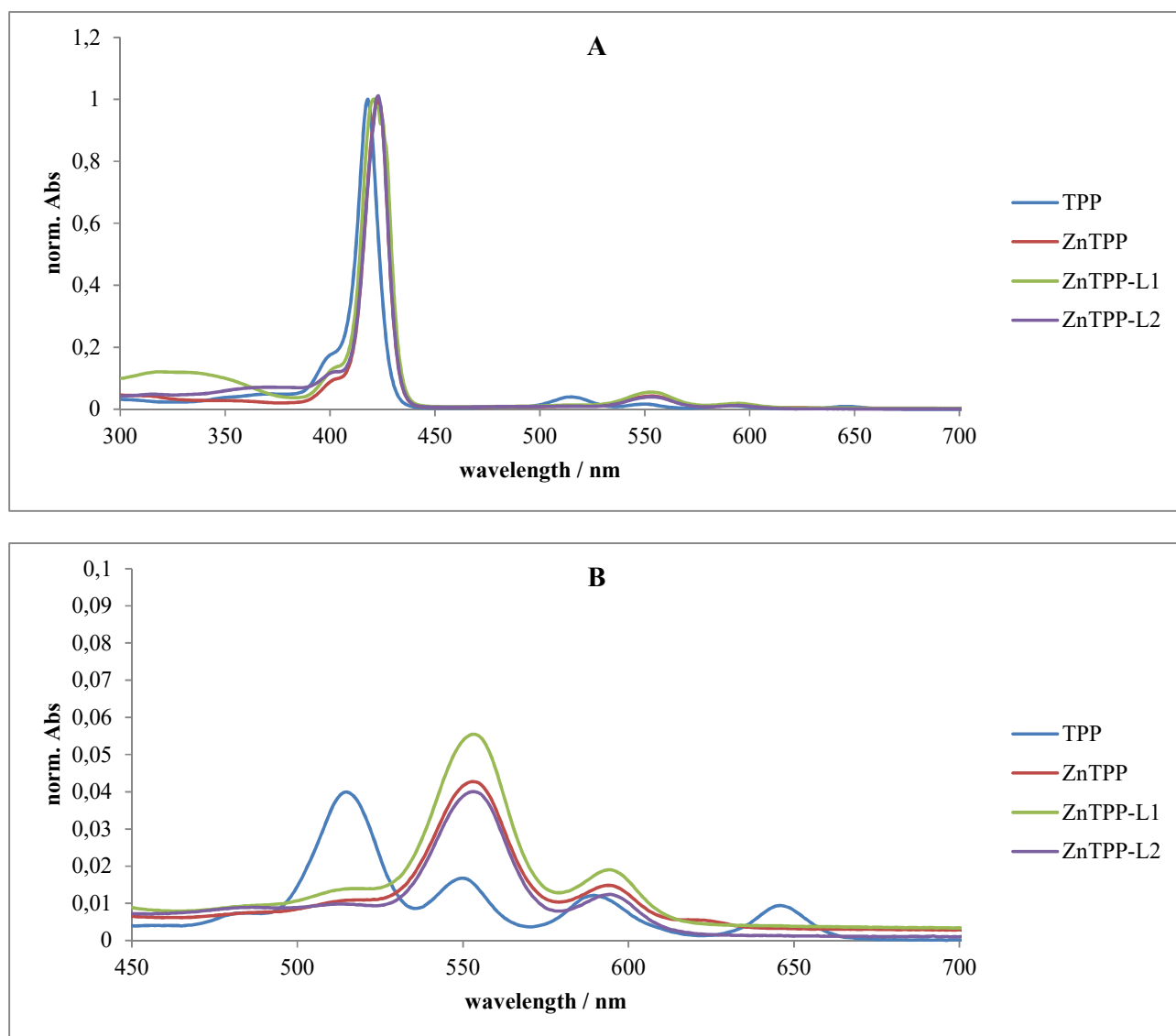
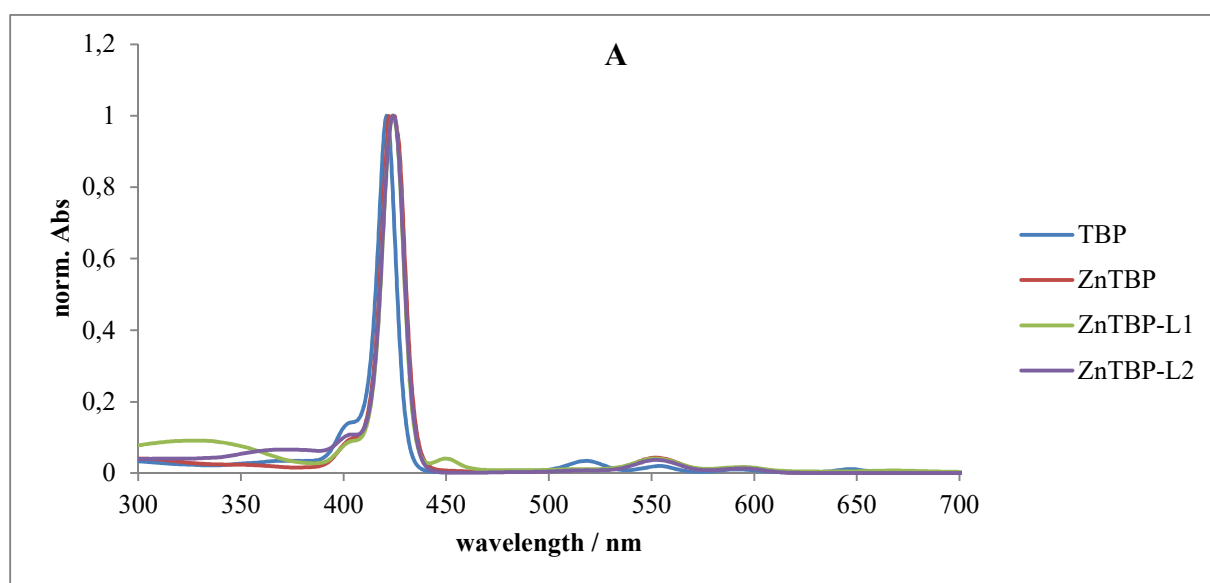


Figure 7. A) Normalized UV-Vis spectrum of the TPP series. B) Expansion of the Q bands.



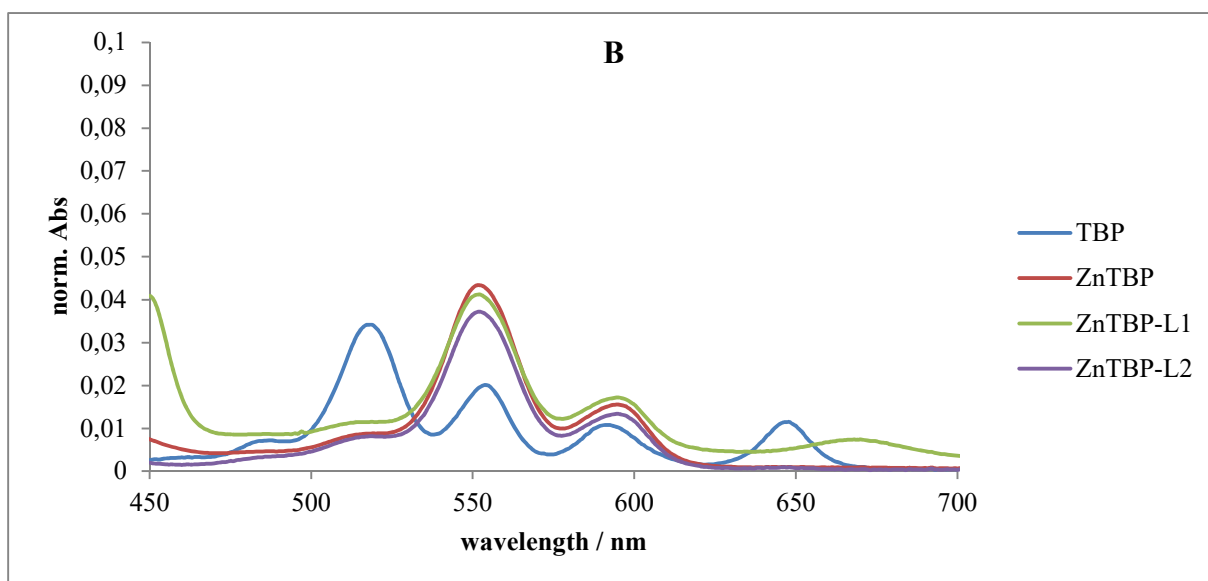


Figure 8. A) Normalized UV-Vis spectrum of the TBP series. B) Expansion of the Q bands.

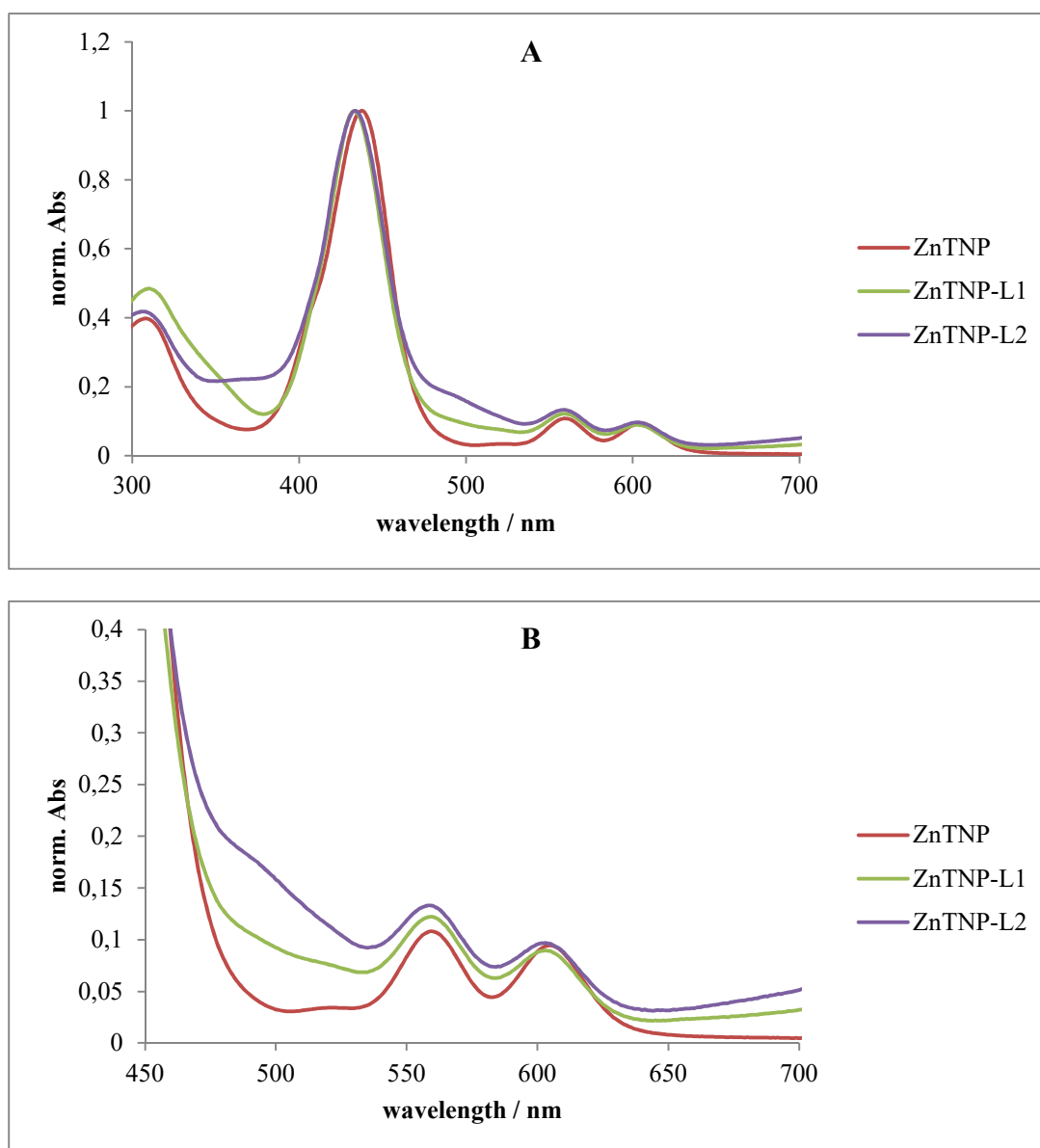


Figure 9. A) Normalized UV-Vis spectrum of the TNP series. B) Expansion of the Q bands.

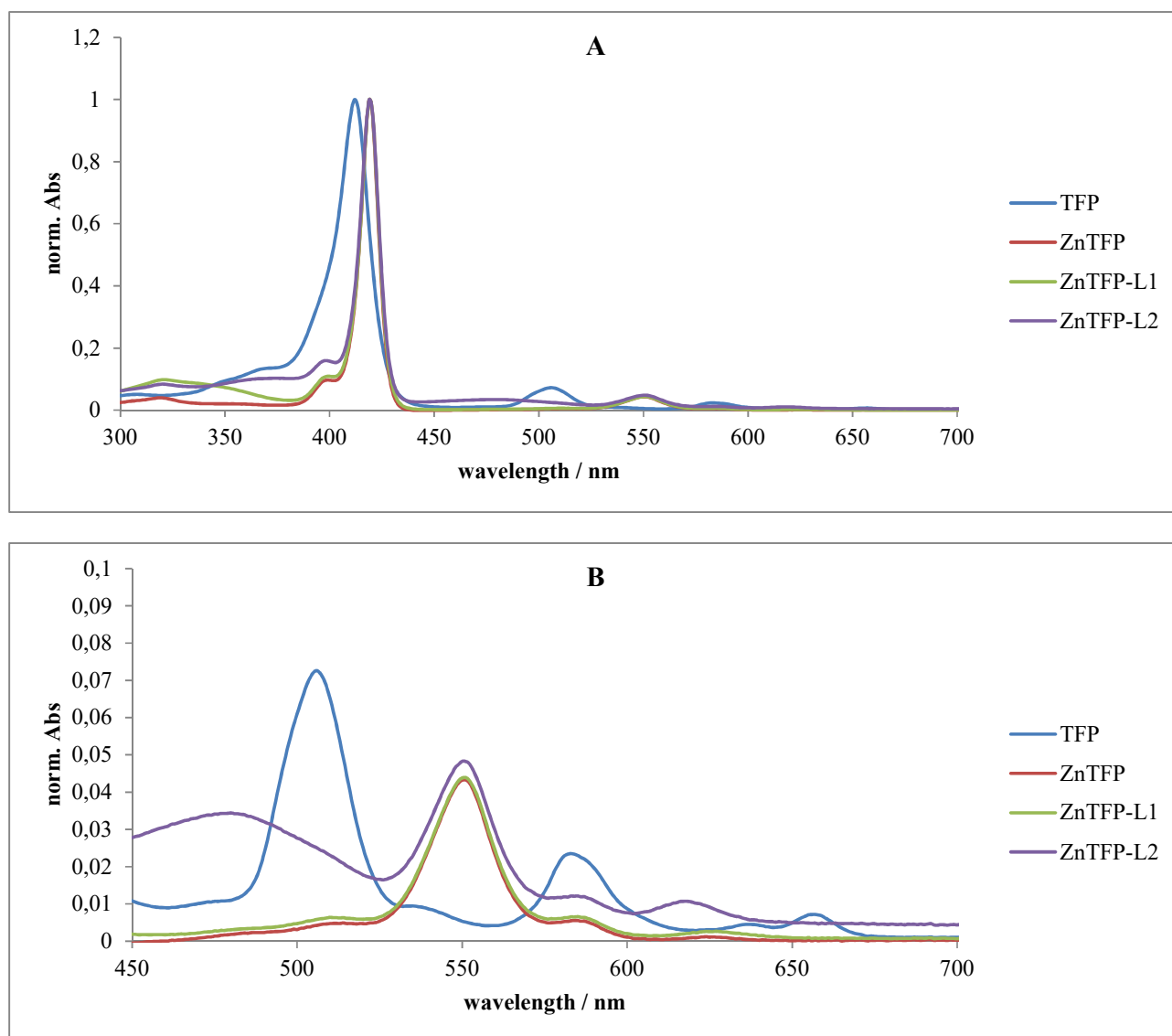


Figure 10. A) Normalized UV-Vis spectrum of the TFP series. B) Expansion of the Q bands.

Table 1. Distances between Zn and the pyridine nitrogen atom, $R_{\text{Zn-N}}$, in the axially coordinated A_4 Zn^{II} porphyrins described at the M06/6-311G(d) level of theory.

Compound	$R_{\text{Zn-N}}$ (Å)
ZnTFP-L1	2.167
ZnTPP-L1	2.187
ZnTBP-L1	2.189
ZnTNP-L1	2.187
ZnTFP-L2	2.140
ZnTPP-L2	2.164
ZnTBP-L2	2.165
ZnTNP-L2	2.163

References

- Di Carlo, G.; Orbelli Biroli, A.; Pizzotti, M.; Tessore, F.; Trifiletti, V.; Ruffo, R.; Abboto, A.; Amat, A.; De Angelis, F.; Mussini, P.R. Tetraaryl Zn^{II} porphyrinates substituted at β -pyrrolic positions as sensitizers in dye-sensitized solar cells: A comparison with meso-disubstituted push-pull Zn^{II} porphyrinates. *Chem. - Eur. J.* **2013**, *19*, 10723–10740, doi:10.1002/chem.201300219.