Supporting Information

Rhodium Porphyrin Complexes as Catalysts for Ammonia Borane Hydrolytic Dehydrogenation

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Elemental analysis for all 4 catalysts was carried out with a Perkin-Elmer CHN 2400 instrument.

- TMPyP_Rh ($C_{44}H_{42}N_8O_6Rh$)

  Anal. Calcd. (found): C, 59.93 (59.62); H, 4.80 (4.92); N, 12.71 (12.66)
- TMAP_Rh ($C_{56}H_{66}N_8O_6Rh$)

  Anal. Calcd. (found): C, 64.05 (67.15); H, 6.34 (6.67); N, 10.67 (11.24)
- TSP_Rh ($C_{44}H_{26}N_4O_{14}S_4RhNa_4$)

  Anal. Calcd. (found): C, 45.65 (45.45); H 2.26 (2.29); N, 4.84 (4.81)
- TAP_Rh ($C_{44}H_{32}N_8ClRh$)

  Anal. Calcd. (found): C, 65.15 (64.96); H 3.98 (4.01); N, 13.81 (13.76)

Elemental analyses of the ionic rhodium–porphyrin catalysts (TPyP_Rh, TMAP_Rh and TSP_Rh), purified on an H_2O/NaOH (pH 10) column, are consistent with the formation of axially dihydroxo-coordinated species, with OH^- as counterions for the cationic complexes and Na^+ for the anionic TSP_Rh. The slightly higher H content and the lower C and N values observed for TPyP_Rh and TSP_Rh are attributed to their hygroscopic nature. In contrast, TMAP_Rh shows higher C/H/N percentages likely ascribed to the lower Rh content, compared to the theoretical one, as revealed by ICP analysis. The neutral, non-hygroscopic TAP_Rh displays elemental values in excellent agreement with the calculated composition.

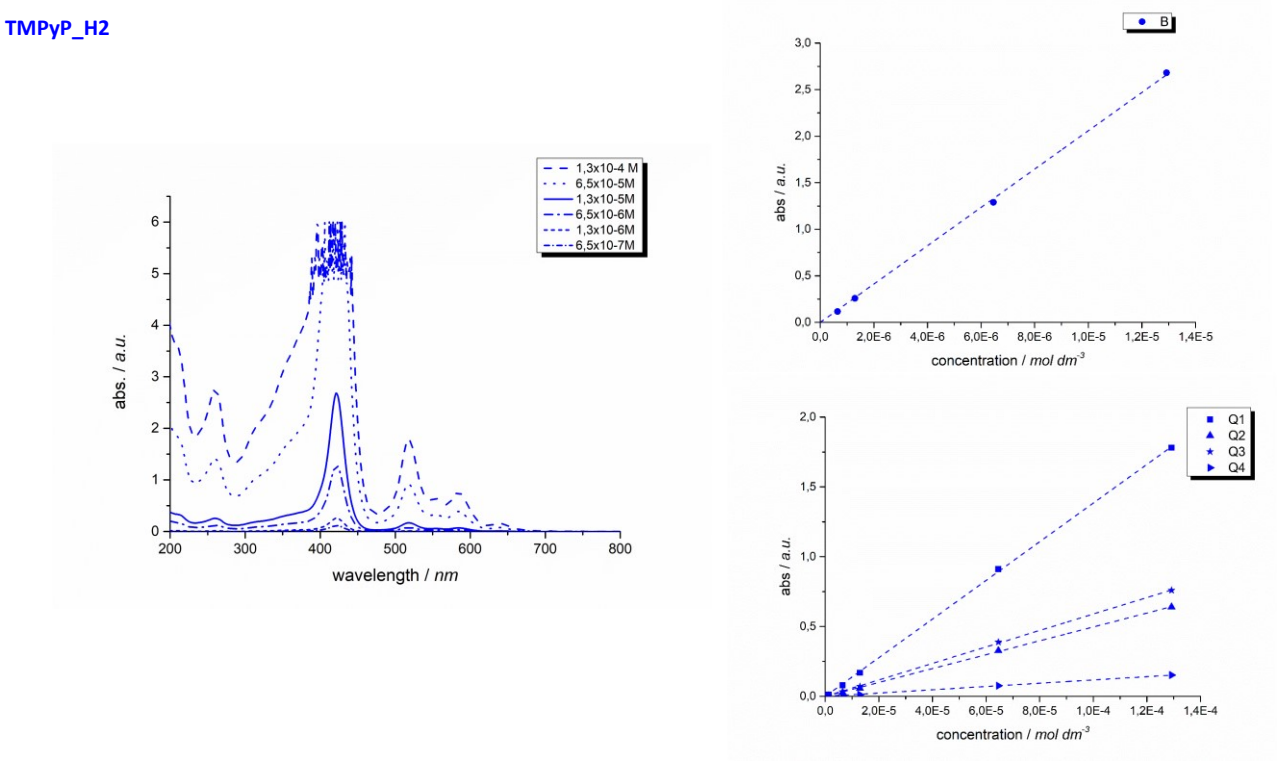

Figure S1. UV-Vis spectra of TMPyP_H_2 in H_2O at various concentrations and Lambert-Beer curve for B and Q bands

TMPyP_Rh

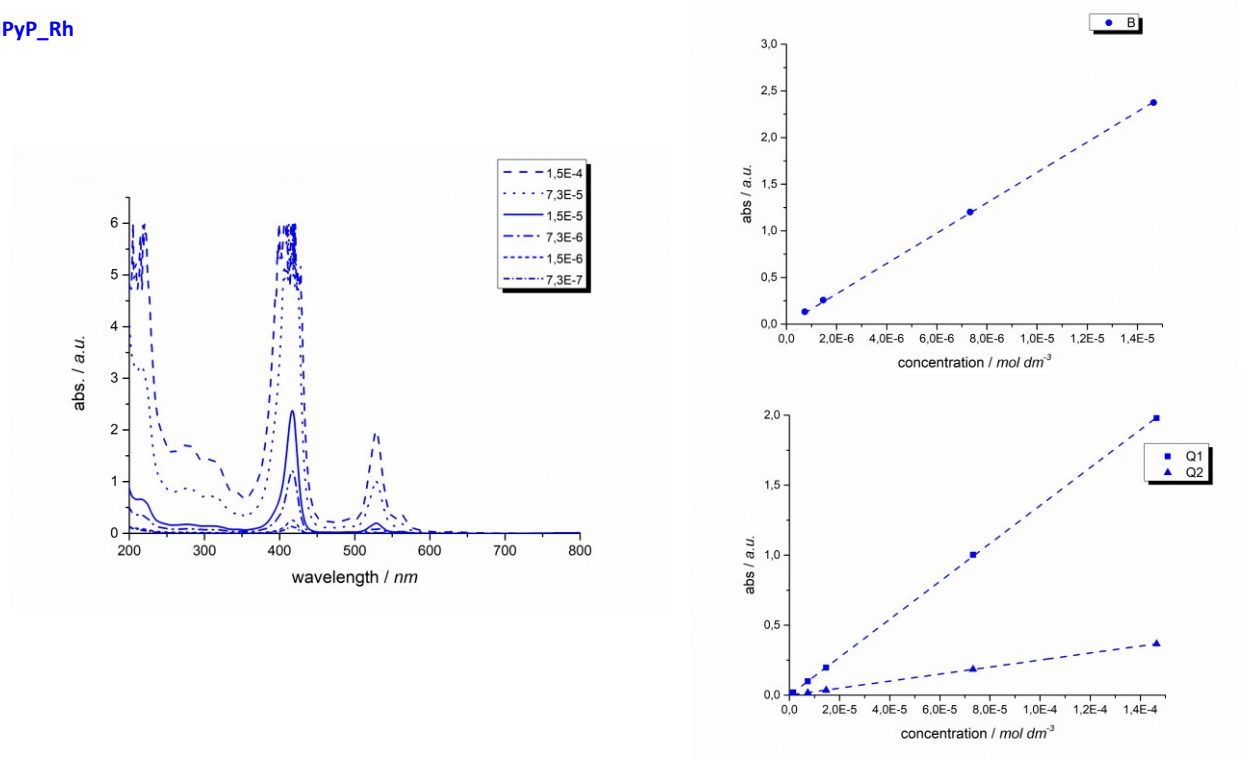

Figure S2. UV-Vis spectra of TMPyP_Rh in H_2O at various concentrations and Lambert-Beer curve for B and Q bands

TMAP_H2

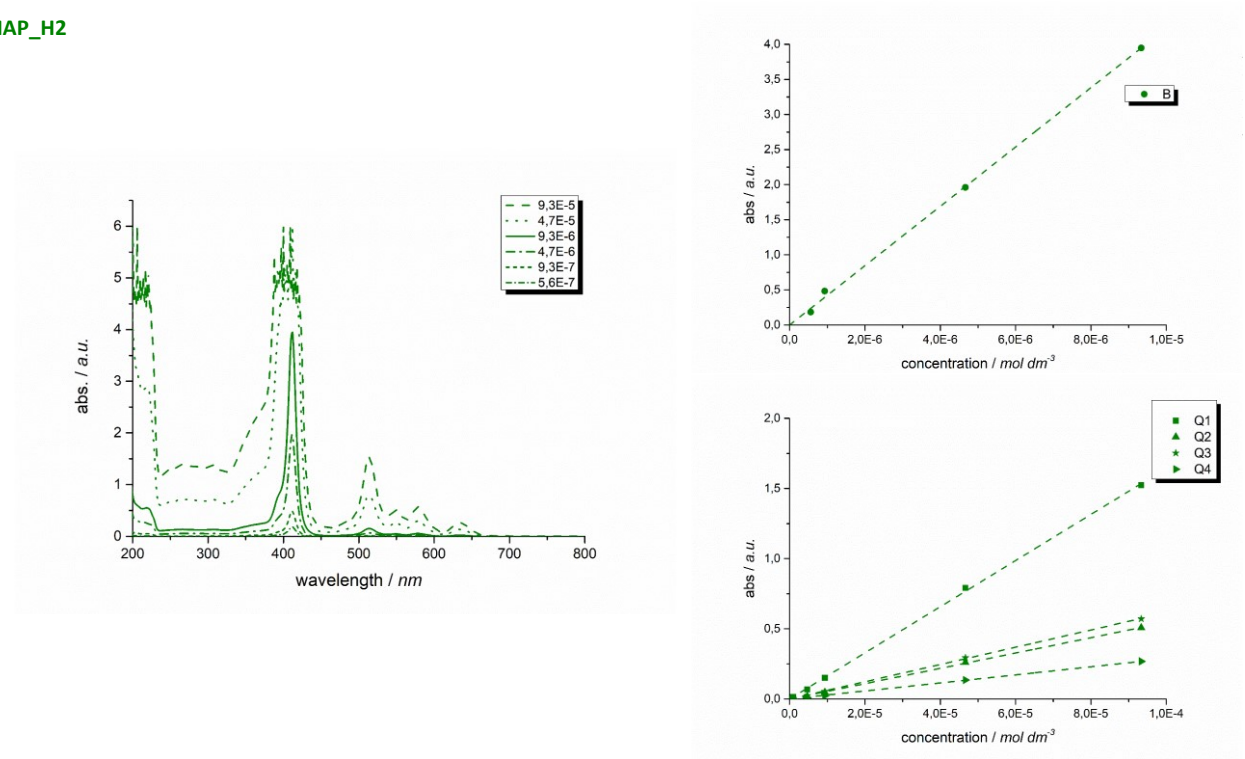

Figure S3. UV-Vis spectra of TMAP_H_2 in H_2O at various concentrations and Lambert-Beer curve for B and Q bands

TMAP_Rh

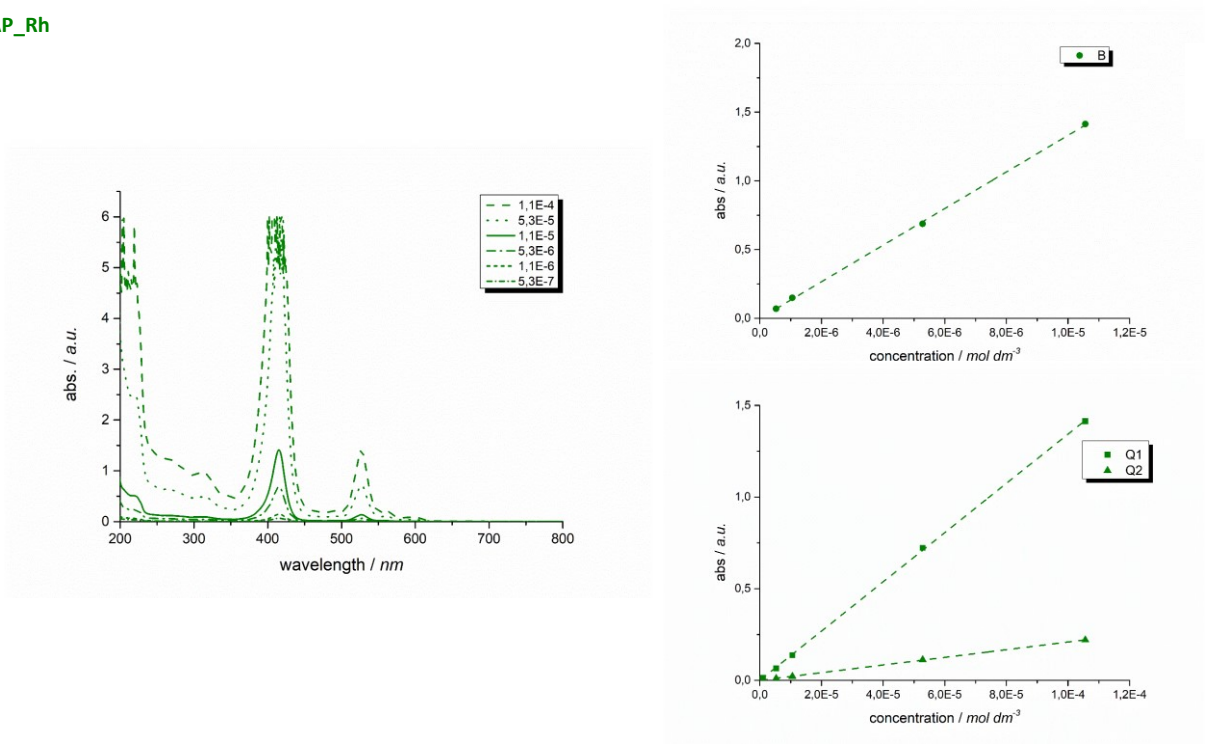

Figure S4. UV-Vis spectra of TMAP_Rh in H_2O at various concentrations and Lambert-Beer curve for B and Q bands

TSP_H2

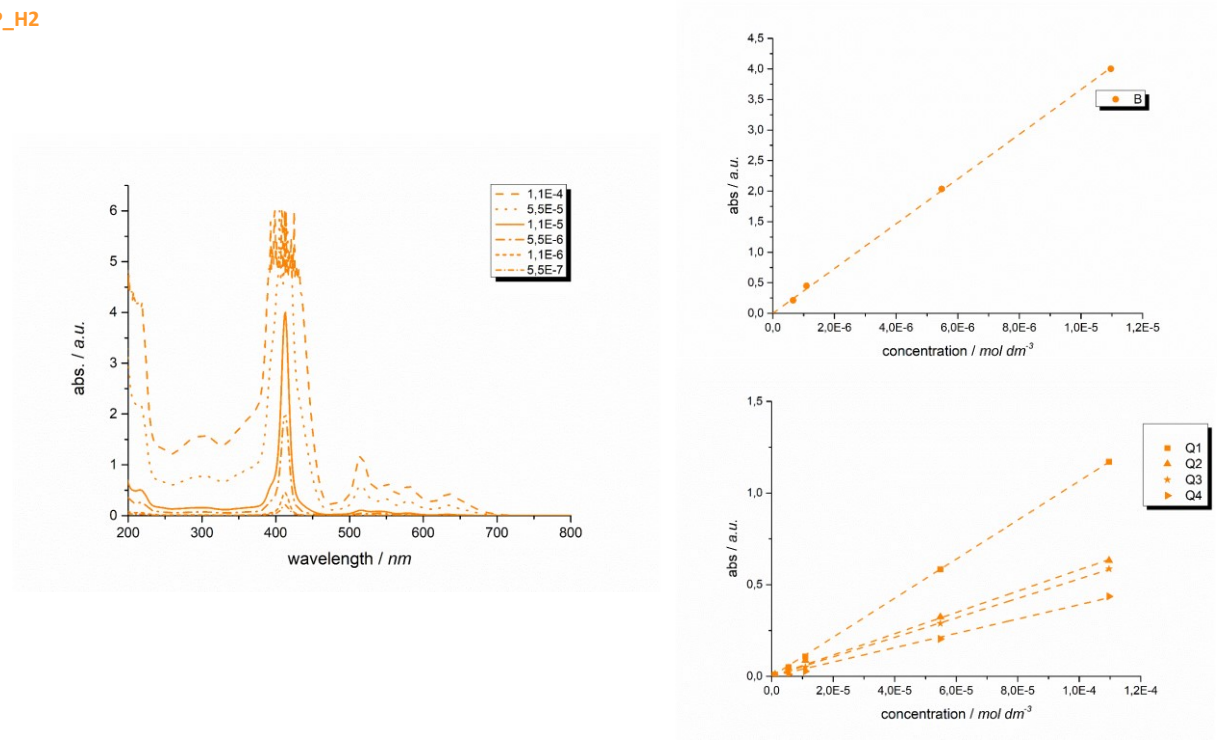

Figure S5. UV-Vis spectra of TSP_H_2 in H_2O at various concentrations and Lambert-Beer curve for B and Q bands

TSP_Rh

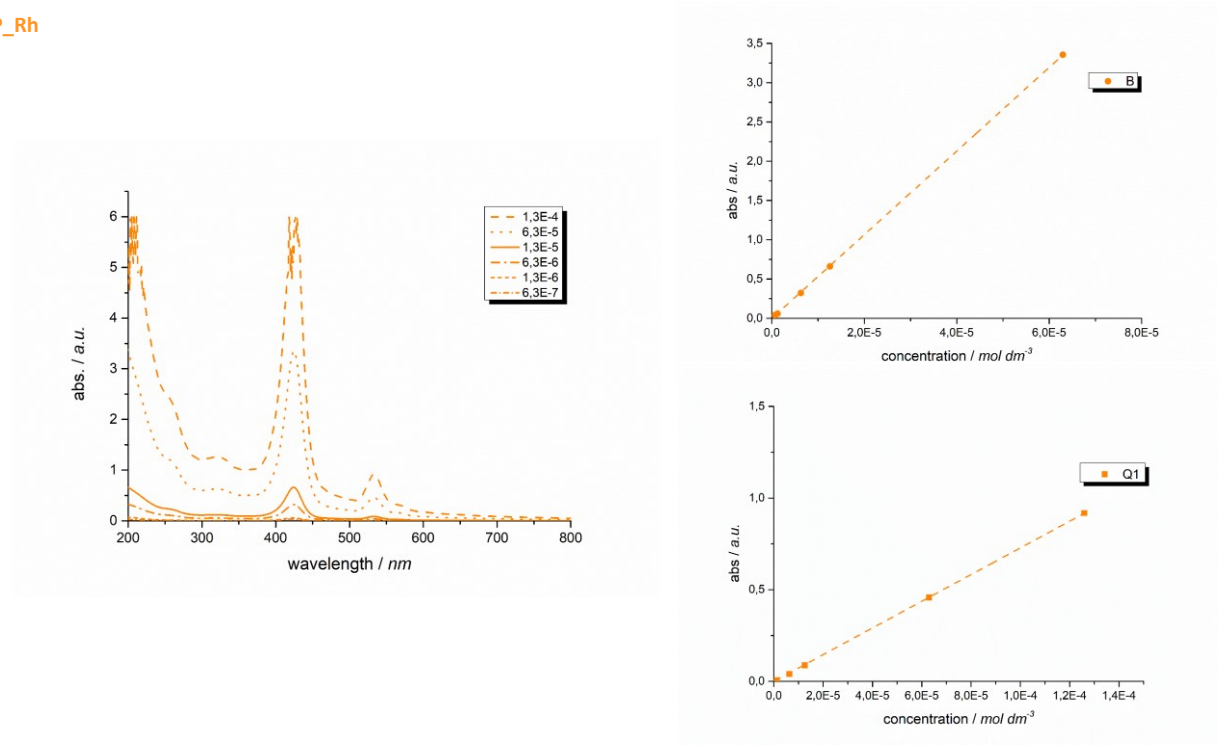

Figure S6. UV-Vis spectra of TSP_Rh in H_2O at various concentrations and Lambert-Beer curve for B and Q bands

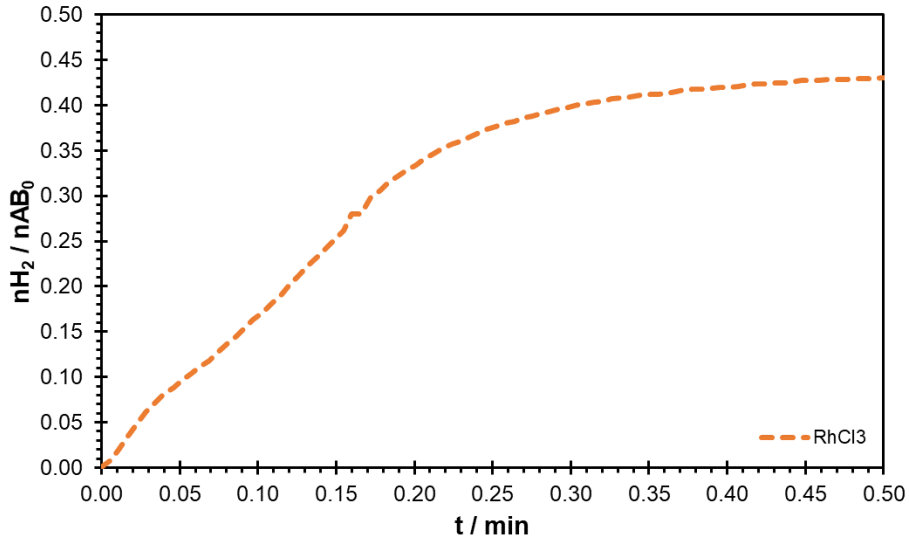

Figure S7. kinetic profile of the RhCl3 * 3H2O employed in the metalation process. Tested at 30 °C, 1400 rpm, AB/Cat molar ration 1000/1 and 0.4 mmol of AB.

TAP_H_2

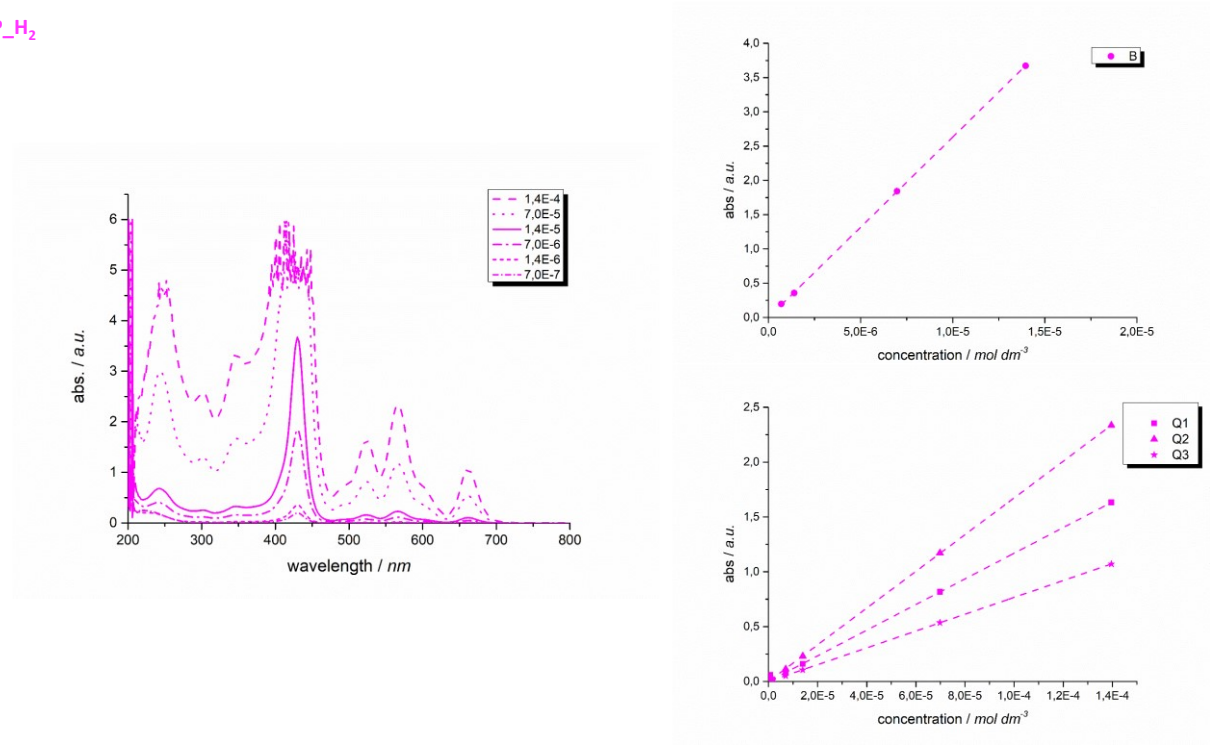

Figure S8. UV-Vis spectra of TAP_H_2 in THF at various concentrations and Lambert-Beer curve for B and Q bands

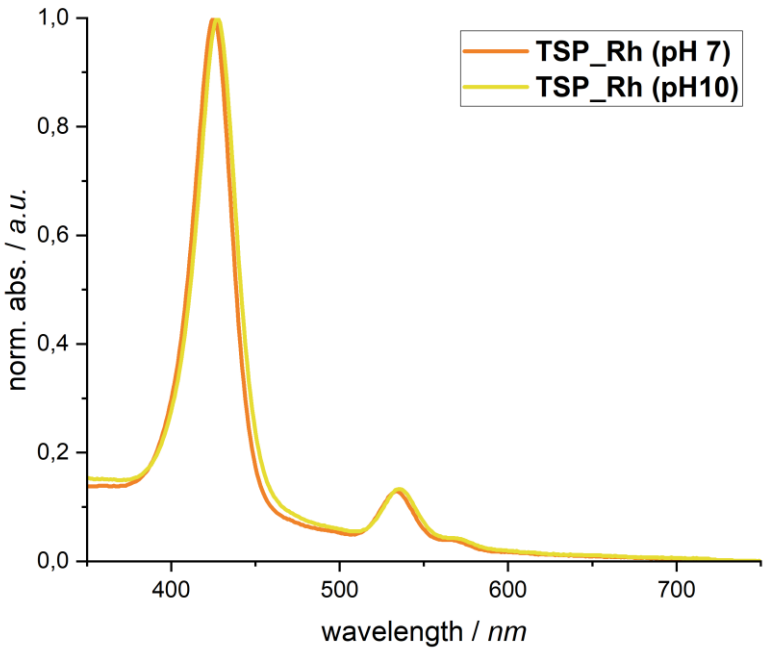

Figure S9. Comparison of UV-Vis spectra of pristine TSP_Rh at pH 7 and pH 10

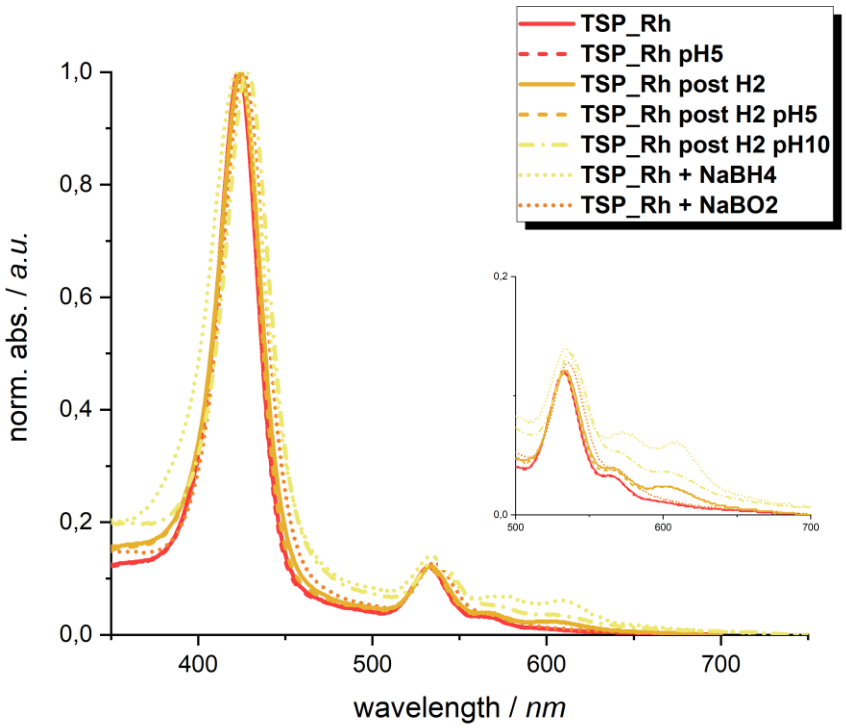

Figure S10. UV-Vis spectra of TSP_Rh after treatment with H_2 for 2h, addition of $NaBH_4$ and addition of $NaBO_2$

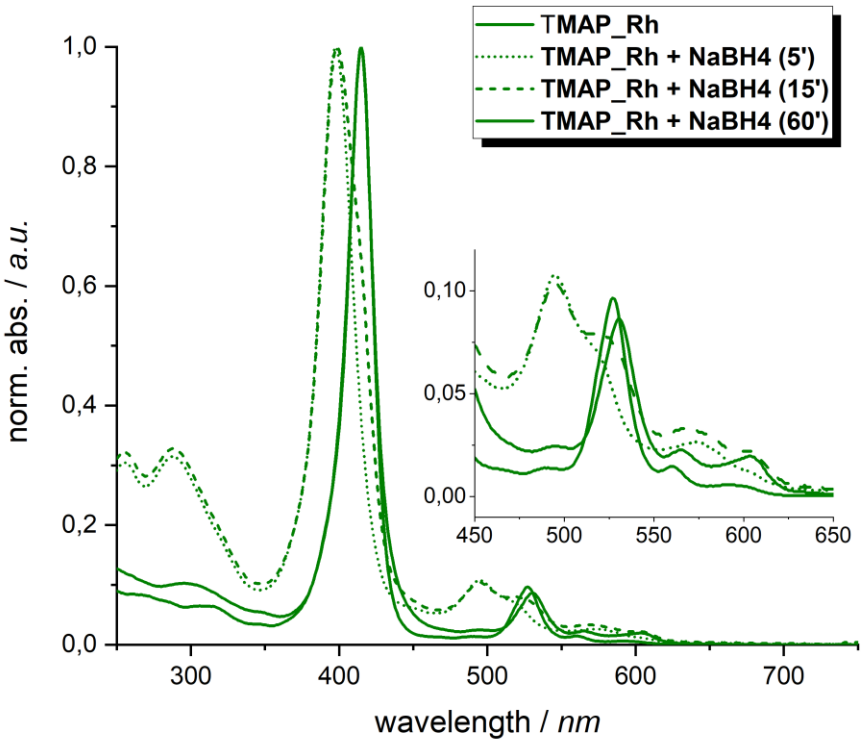

Figure S11. UV-Vis spectra of TMAP_Rh after addition of $NaBH_4$ at different times