

Control of the site and potential of reduction and oxidation processes in p-expanded quinoxalinoporphyrins

Paul J Santic, Wenbo E, Zhongping Ou, Jianguo Shao, James A. McDonald, Zheng-Li Cai, Karl M. Kadish, Maxwell J Crossley and Jeffrey R. Reimers.

Supporting Information Figures S1-S14.

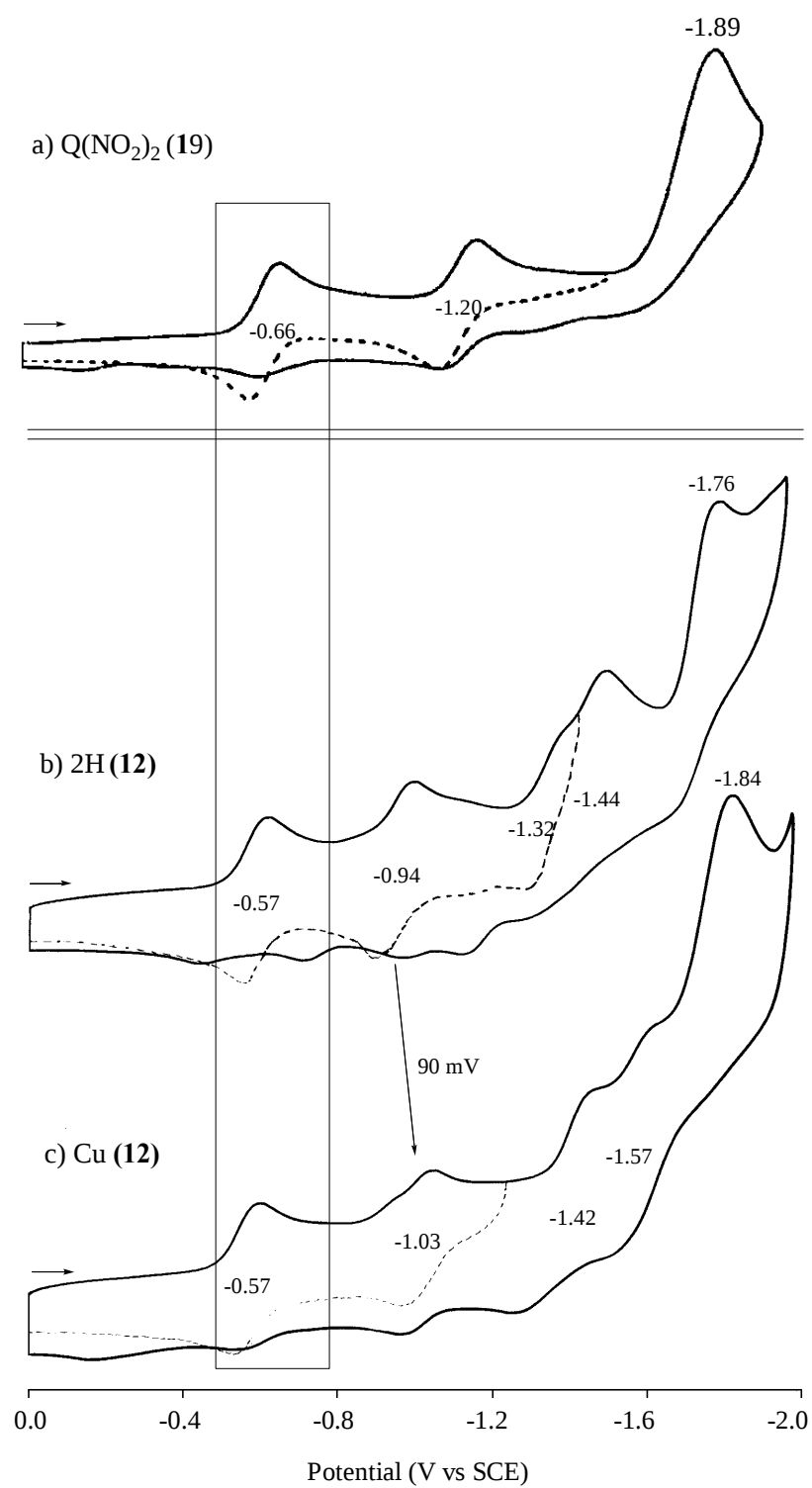


Figure S1. Cyclic voltammograms of dinitroquinoxaline $\text{Q}(\text{NO}_2)_2$ (**19**) and analogous dinitroquinoxalioporphyrins $[\text{PQ}(\text{NO}_2)_2]\text{M}$ **12** in pyridine with 0.1 M TBAP.

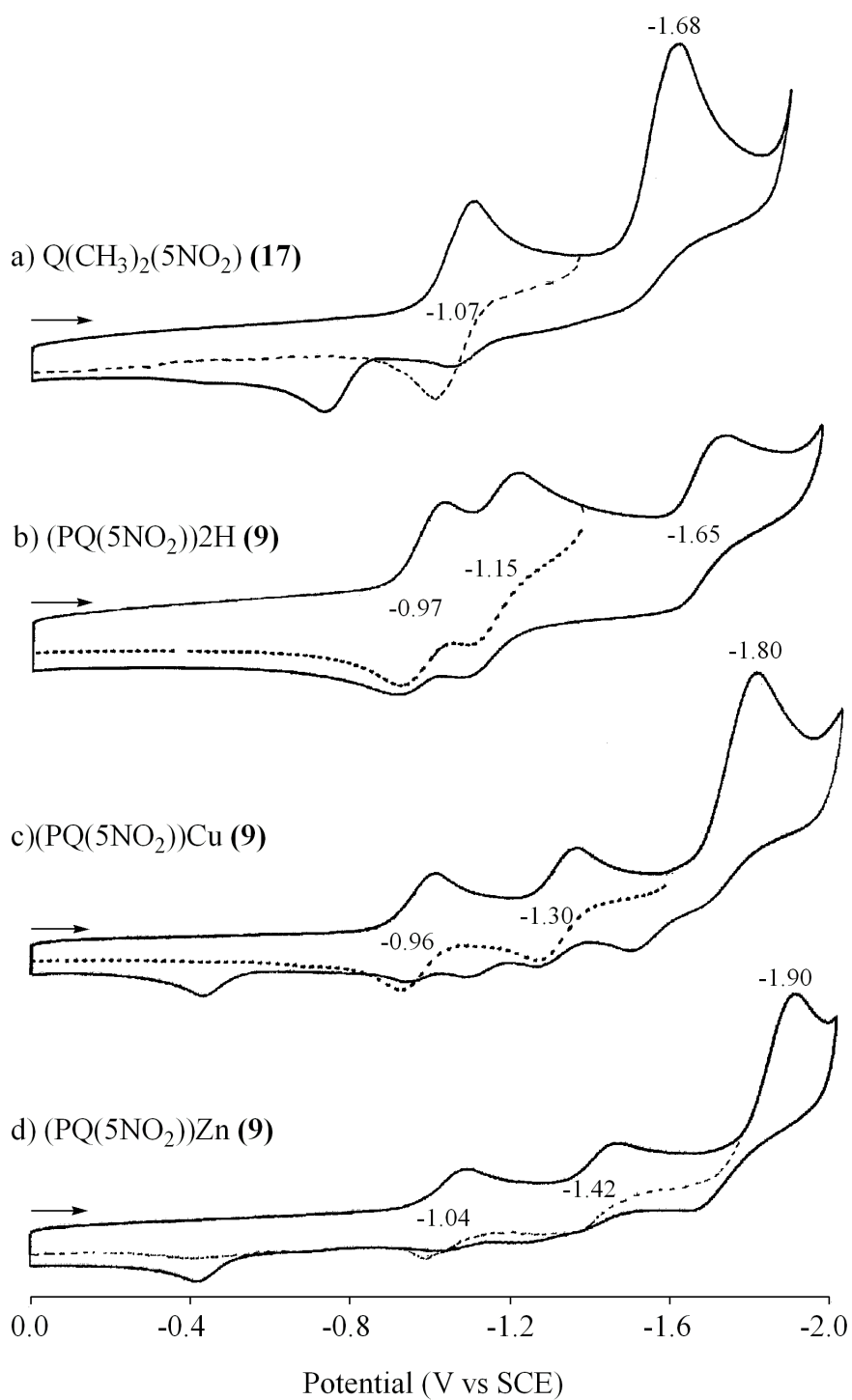


Figure S2. Cyclic voltammograms of the nitroquinoxaline $\text{Q}[(\text{CH}_3)_25\text{NO}_2]$ (**17**) and analogous nitroquinoxalinoporphyrins $[\text{PQ}(5\text{NO}_2)]\text{M}$ (**9**) in pyridine with 0.1 M TBAP.

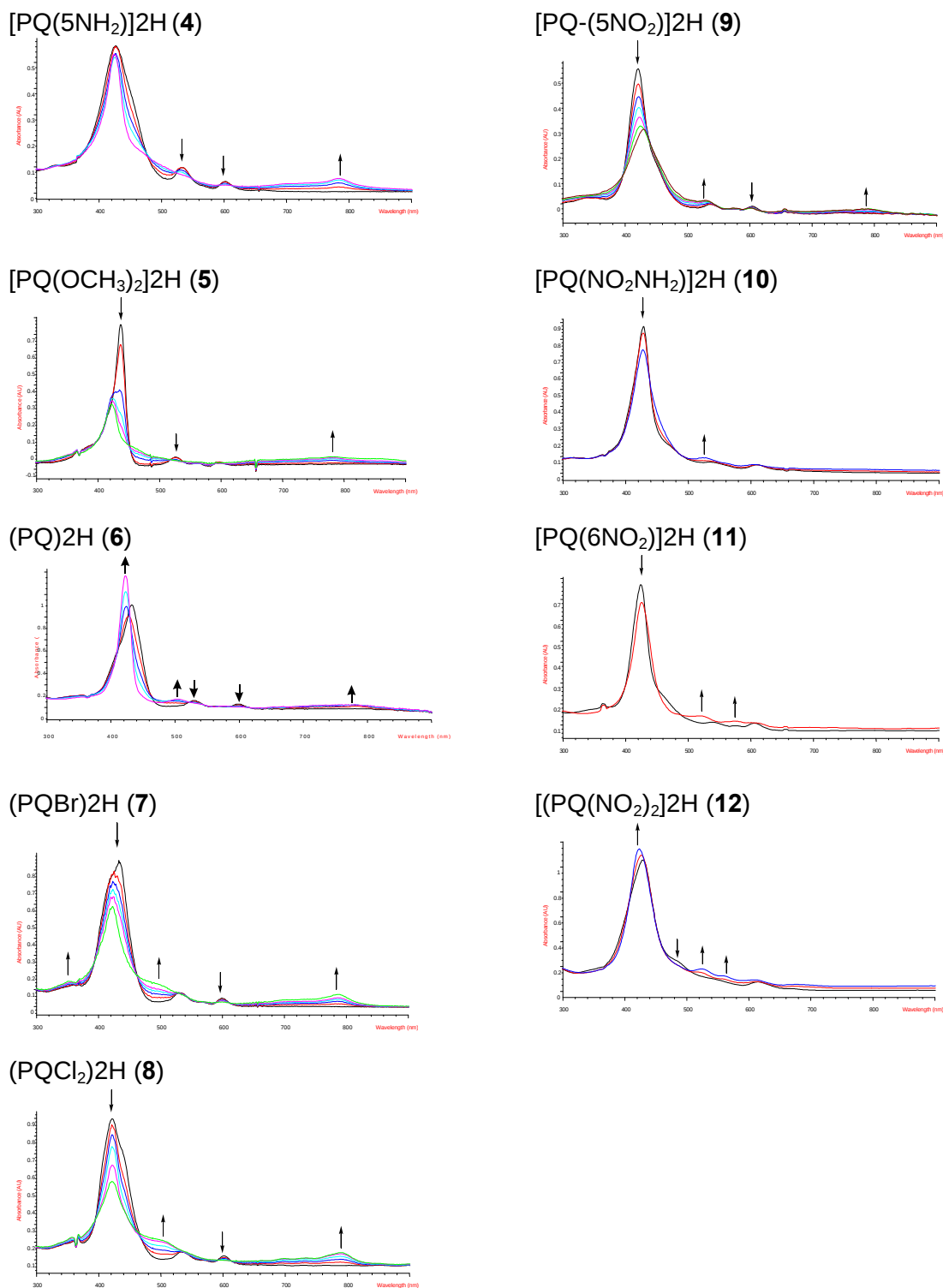


Figure S3. Thin-layer UV-visible spectral changes obtained before and after the first reduction of various quinoxalinoporphyryns [PQ(R₁R₂R₃)]₂H in CH₂Cl₂ solutions containing 0.1 M TBAP.^{ref}

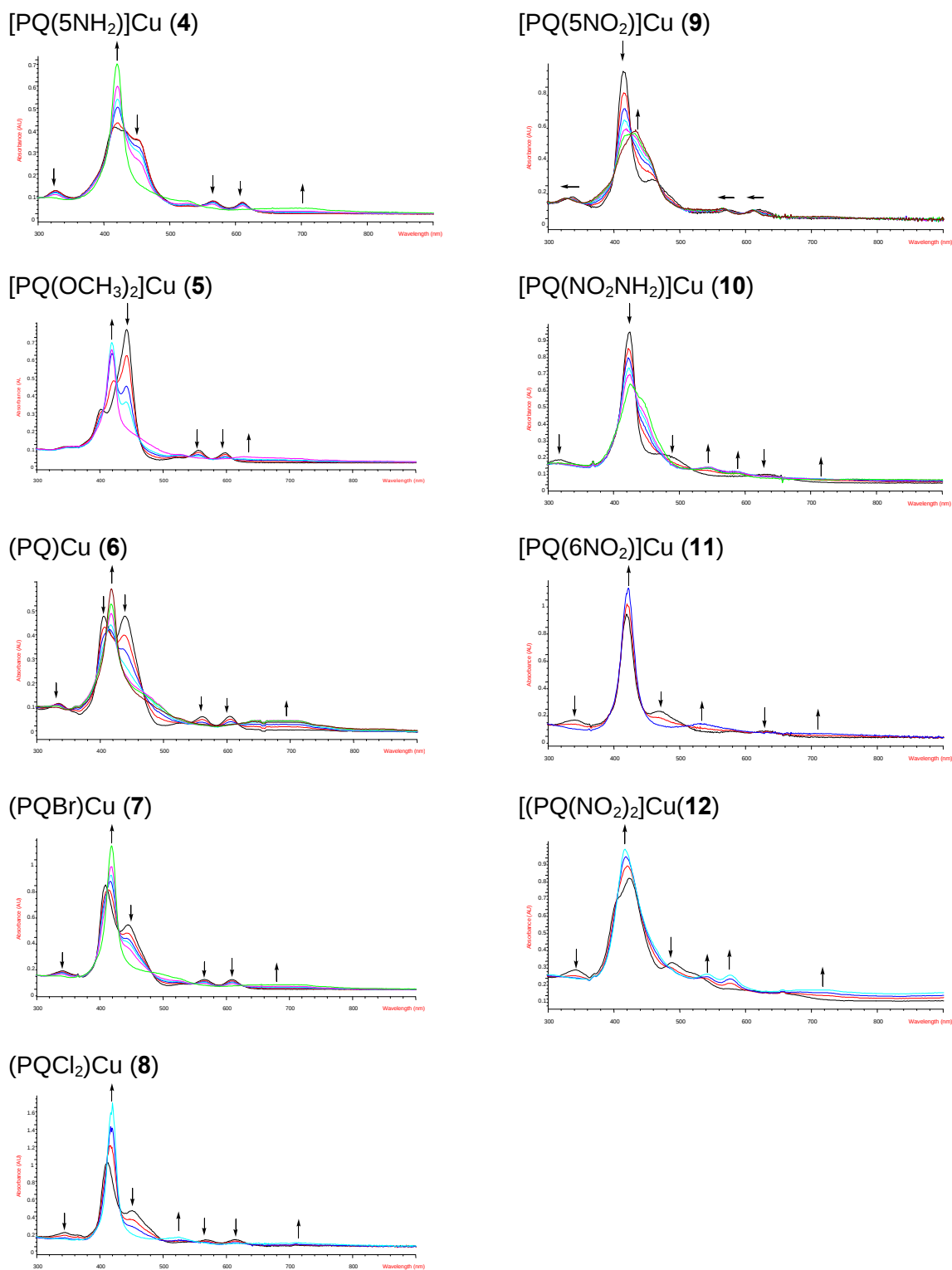
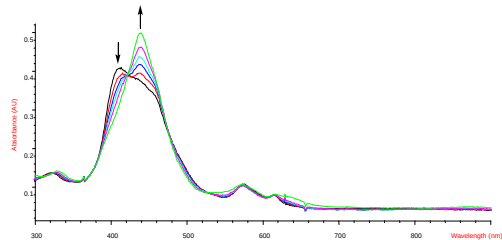
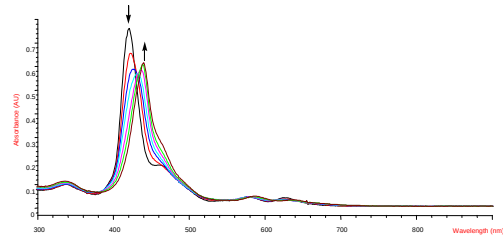


Figure S4. Thin-layer UV-visible spectral changes obtained before and after the first reduction of various quinoxalinoporphyryrins $[PQ(R_1R_2R_3)]Cu$ in CH_2Cl_2 solutions containing 0.1 M TBAP.

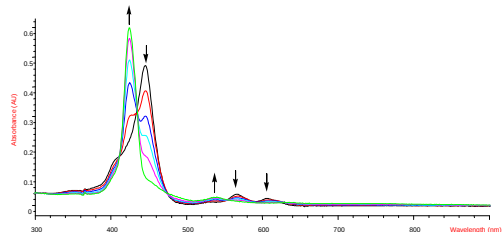
[PQ(5NH₂)]Zn (4)



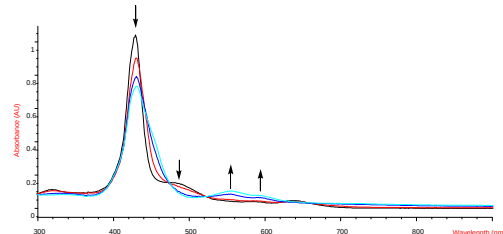
[PQ(5NO₂)]Zn (9)



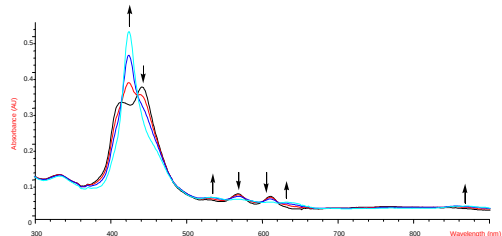
[PQ(OCH₃)₂]₂Zn (5)



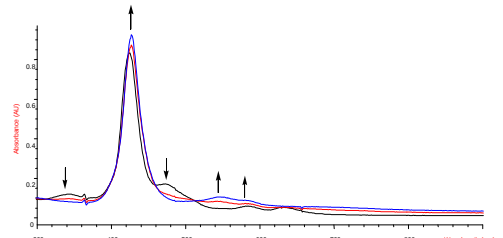
[PQ(NO₂NH₂)]Zn (10)



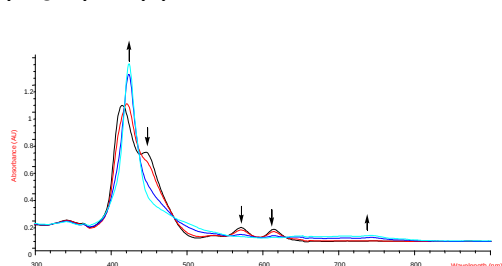
(PQ)Zn(6)



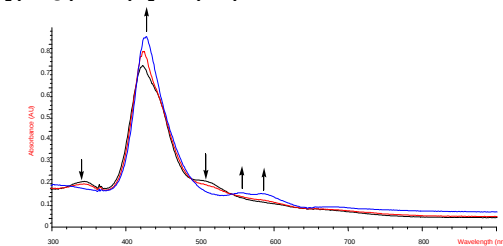
[PQ(6NO₂)]Zn (11)



(PQBr)Zn (7)



[(PQ(NO₂)₂)]Zn(12)



(PQCl₂)Zn (8)

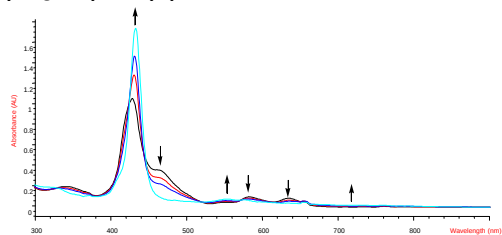


Figure S5. Thin-layer UV-visible spectral changes obtained before and after the first reduction of various quinoxalinoporphyrins [PQ(R₁R₂R₃)]Zn in CH₂Cl₂ solutions containing 0.1 M TBAP.

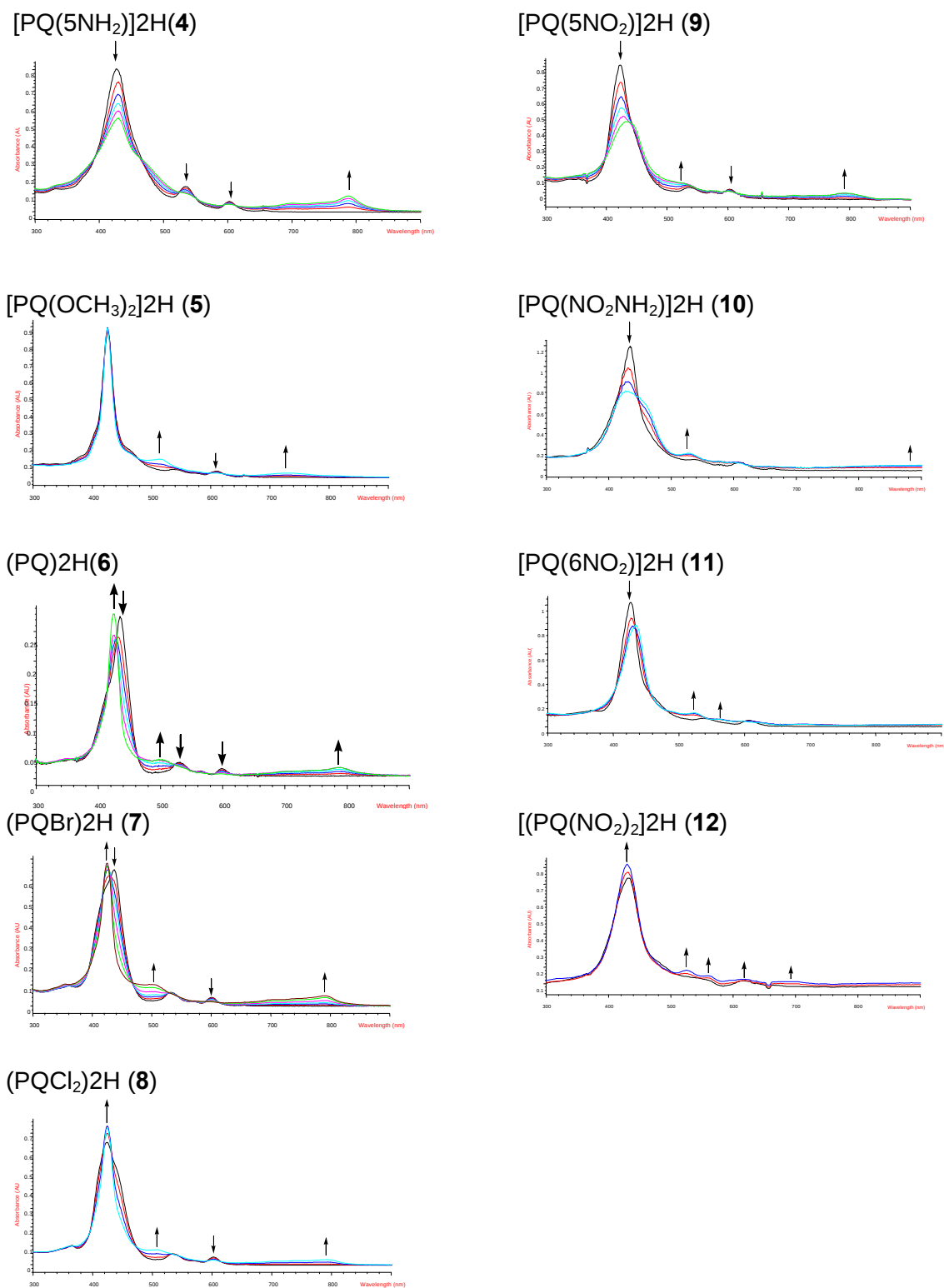
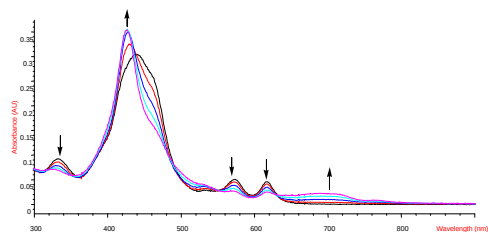
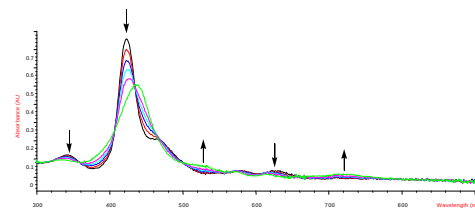


Figure S6. Thin-layer UV-visible spectral changes obtained before and after the first reduction of various quinoxalinoporphyryns [PQ(R₁R₂R₃)]₂H in pyridine solutions containing 0.1 M TBAP.

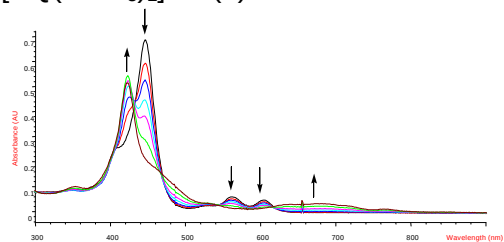
[PQ(5NH₂)]Cu (**4**)



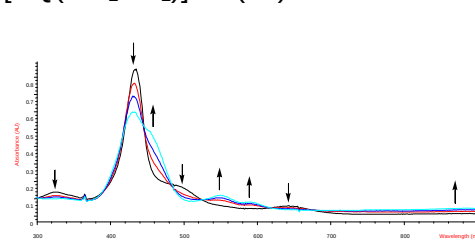
[PQ(5NO₂)]Cu (**9**)



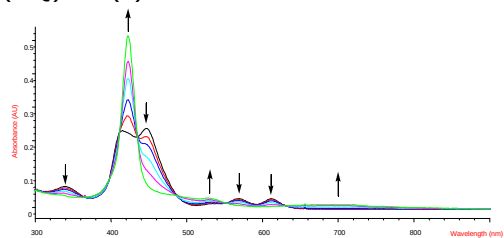
[PQ(OCH₃)₂]**5**]Cu (**5**)



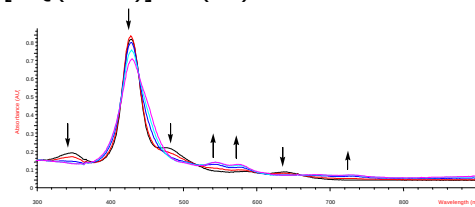
[PQ(NO₂NH₂)]Cu (**10**)



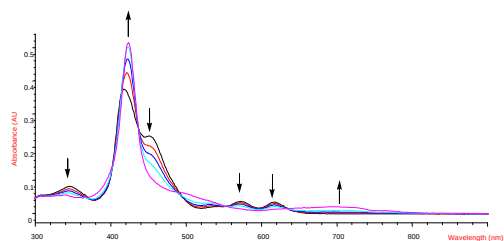
(PQ)Cu (**6**)



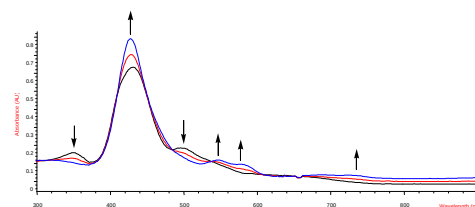
[PQ(6NO₂)]Cu (**11**)



(PQBr)Cu (**7**)



[(PQ(NO₂)₂)]Cu (**12**)



(PQCl₂)Cu (**8**)

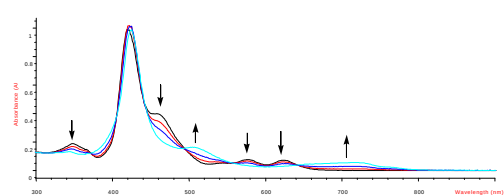
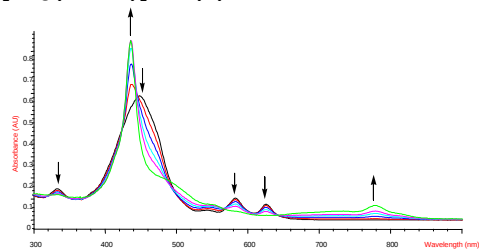
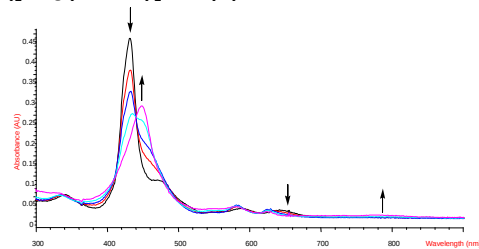


Figure S7. Thin-layer UV-visible spectral changes obtained before and after the first reduction of various quinoxalinoporphyrins [PQ(R₁R₂R₃)]Cu in pyridine solutions containing 0.1 M TBAP.

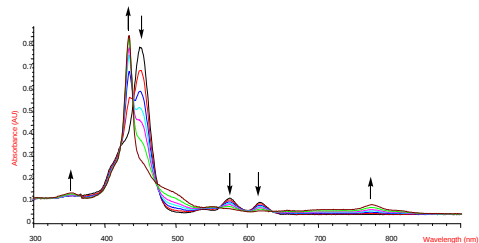
[PQ(5NH₂)]Zn (4)



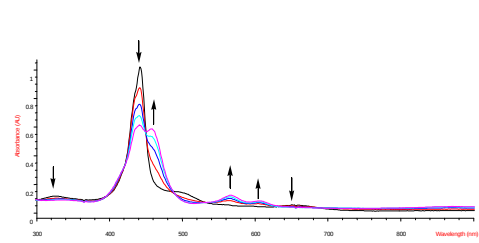
[PQ(5NO₂)]Zn (9)



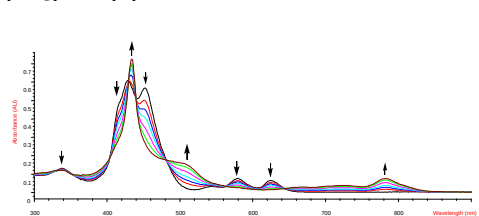
[PQ(OCH₃)₂]]Zn (5)



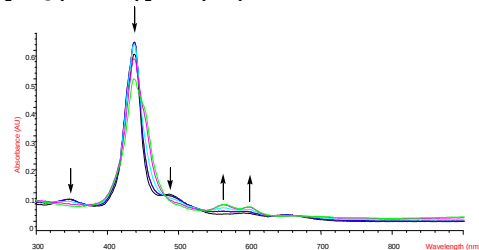
[PQ(NO₂NH₂)]Zn (10)



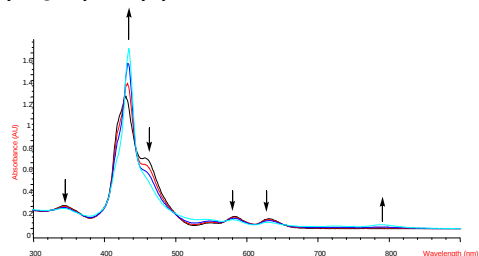
(PQ)Zn (6)



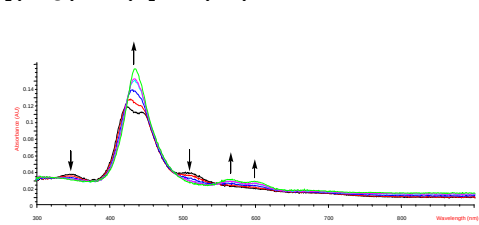
[PQ(6NO₂)]Zn (11)



(PQBr)Zn (7)



[(PQ(NO₂)₂)]Zn (12)



(PQCl₂)Zn (8)

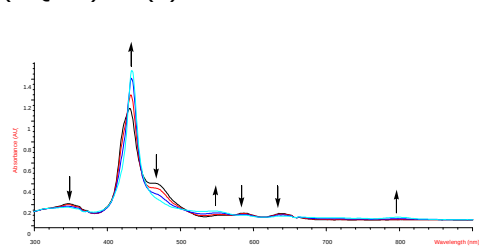


Figure S8. Thin-layer UV-visible spectral changes obtained before and after the first reduction of various quinoxalinoporphyrins [PQ(R₁R₂R₃)]Zn in pyridine solutions containing 0.1 M TBAP.

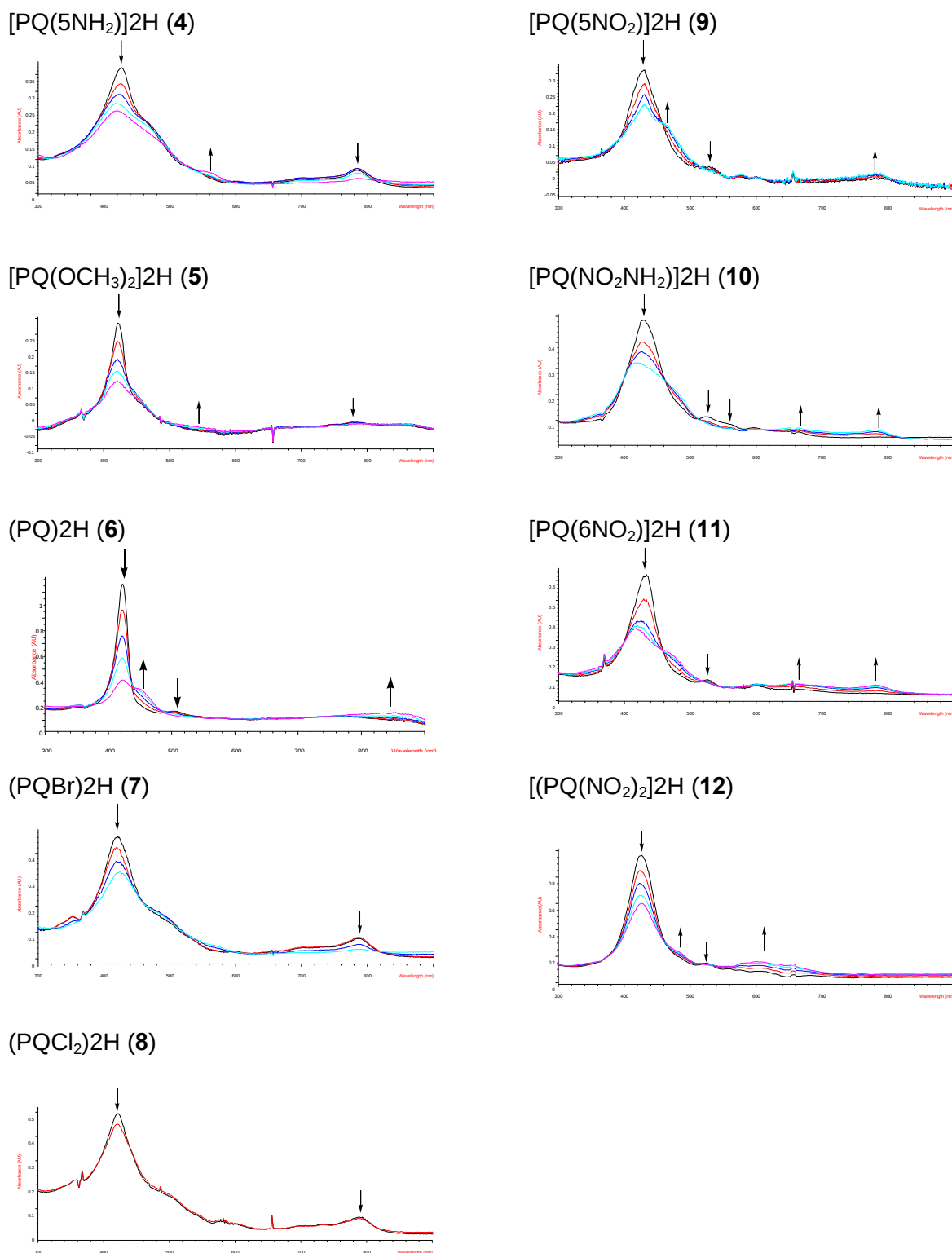
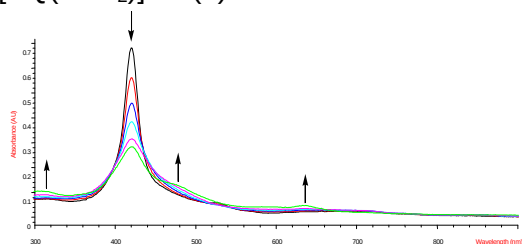


Figure S9. Thin-layer UV-visible spectral changes obtained before and after the second reduction of various quinoxalinoporphyryns $[PQ(R_1R_2R_3)]2H$ in CH_2Cl_2 solutions containing 0.1 M TBAP.

[PQ(5NH₂)]Cu (4)



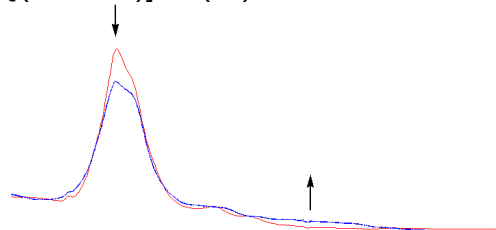
[PQ(5NO₂)]Cu (9)

Data not presented due to slow chemical reaction on the spectroelectrochemical time scale

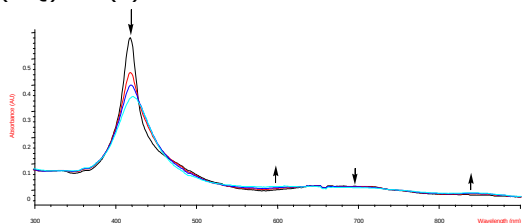
[PQ(OCH₃)₂]₂Cu (5)

Data not presented due to slow chemical reaction on the spectroelectrochemical time scale

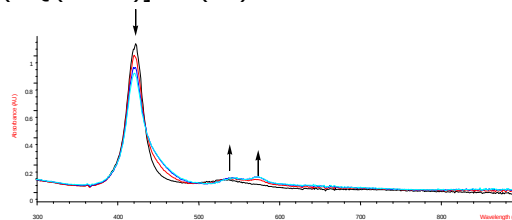
[PQ(NO₂NH₂)]Cu (10)



(PQ)Cu (6)



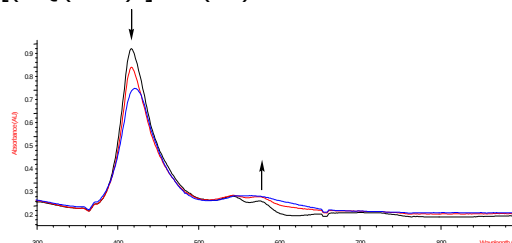
(PQ(6NO₂)]Cu (11)



(PQBr)Cu (7)

Data not presented due to slow chemical reaction on the spectroelectrochemical time scale

[(PQ(NO₂)₂)]Cu (12)



(PQCl₂)Cu (8)

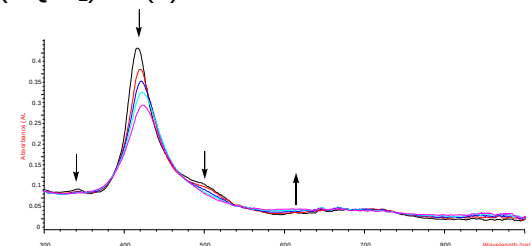
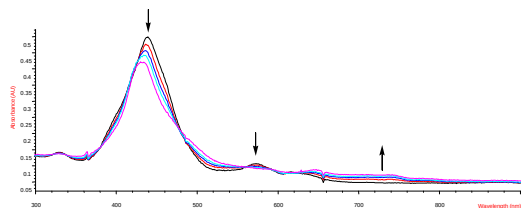


Figure S10. Thin-layer UV-visible spectral changes obtained before and after the second reduction of various quinoxalinoporphyrins [PQ(R₁R₂R₃)]Cu in CH₂Cl₂ solutions containing 0.1 M TBAP.

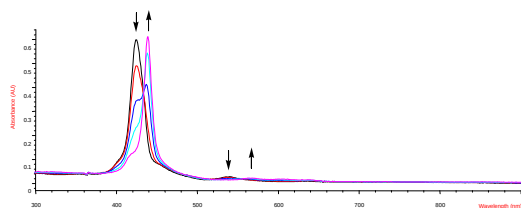
[PQ(5NH₂)]Zn (**4**)



[PQ(5NO₂)]Zn (**9**)

Data not presented due to slow chemical reaction on the spectroelectrochemical time scale

[PQ(OCH₃)₂]**Zn** (**5**)



[PQ(NO₂NH₂)]Zn (**10**)

Data not presented due to slow chemical reaction on the spectroelectrochemical time scale

(PQ)Zn (**6**)

Data not presented due to multiple reduction products

[PQ(6NO₂)]Zn (**11**)

Data not presented due to slow chemical reaction on the spectroelectrochemical time scale

(PQBr)Zn (**7**)

Data not presented due to slow chemical reaction on the spectroelectrochemical time scale

[(PQ(NO₂)₂)]Zn (**12**)

Data not presented due to slow chemical reaction on the spectroelectrochemical time scale

(PQCl₂)Zn (**8**)

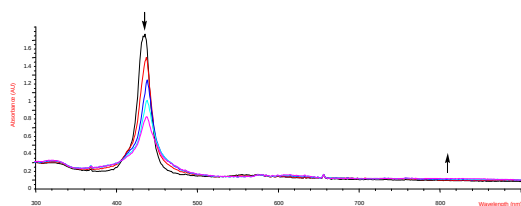
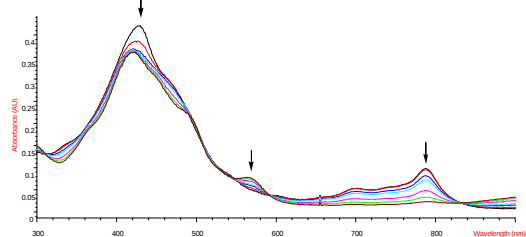
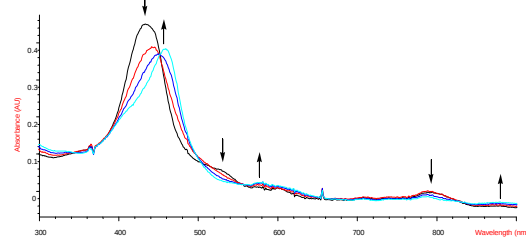


Figure S11. Thin-layer UV-visible spectral changes obtained before and after the second reduction of various quinoxalinoporphyrins [PQ(R₁R₂R₃)]Zn in CH₂Cl₂ solutions containing 0.1 M TBAP.

[PQ(5NH₂)]2H (4)



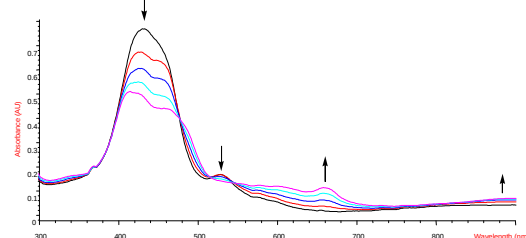
[PQ(5NO₂)]2H (9)



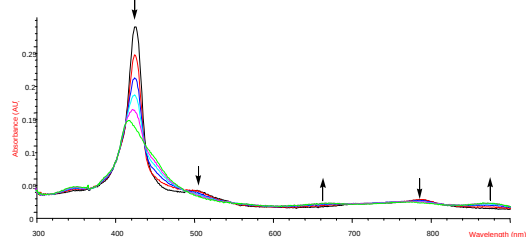
[PQ(OCH₃)₂]]2H (5)

Data not presented due to slow chemical reaction on the spectroelectrochemical time scale

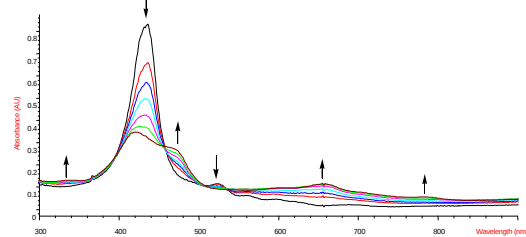
[PQ(NO₂NH₂)]2H (10)



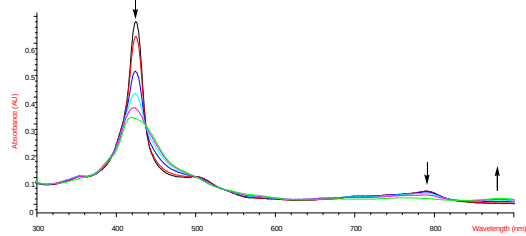
(PQ)2H (6)



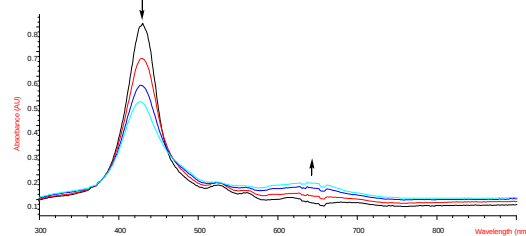
[PQ(6NO₂)]2H (11)



(PQBr)2H (7)



[(PQ(NO₂)₂)]2H (12)



(PQCl₂)2H (8)

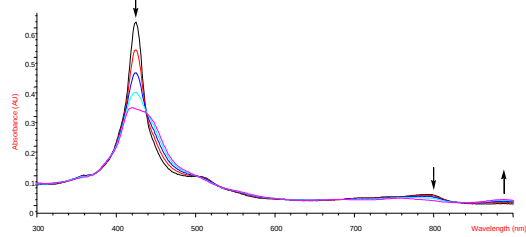
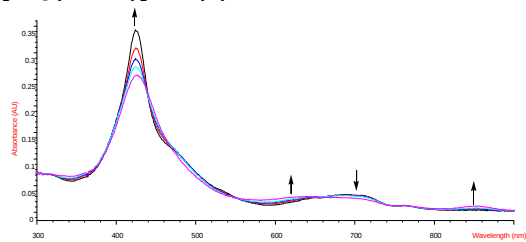
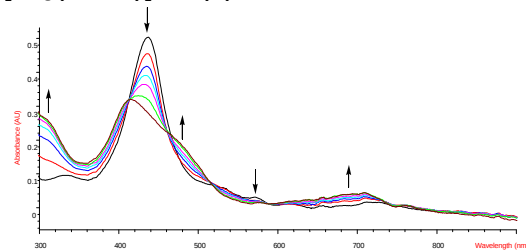


Figure S12. Thin-layer UV-visible spectral changes obtained before and after the second reduction of various quinoxalinoporphyrins [PQ(R₁R₂R₃)]2H in pyridine solutions containing 0.1 M TBAP.

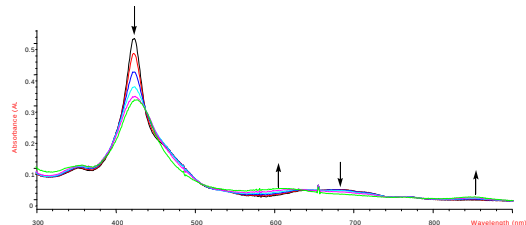
[PQ(5NH₂)]Cu (4)



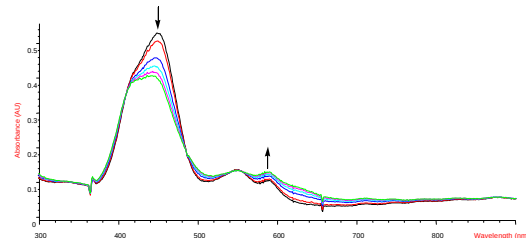
[PQ(5NO₂)]Cu (9)



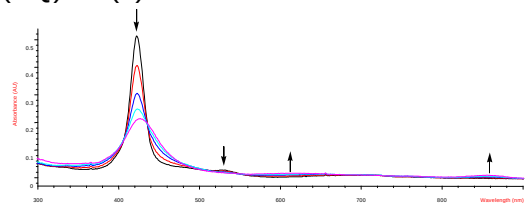
[PQ(OCH₃)₂]₂Cu (5)



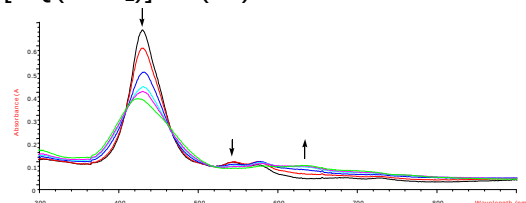
[PQ(NO₂NH₂)]Cu (10)



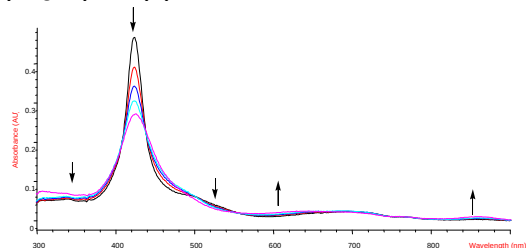
(PQ)Cu (6)



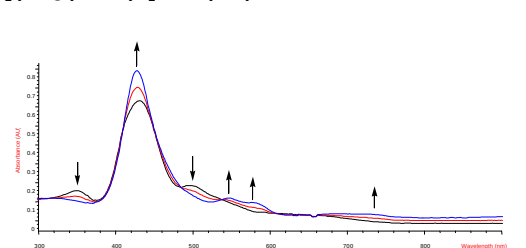
[PQ(6NO₂)]Cu (11)



(PQBr)Cu (7)



[(PQ(NO₂)₂)]Cu (12)



(PQCl₂)Cu (8)

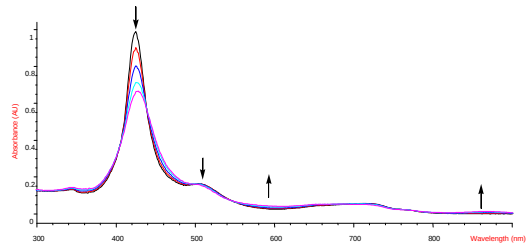
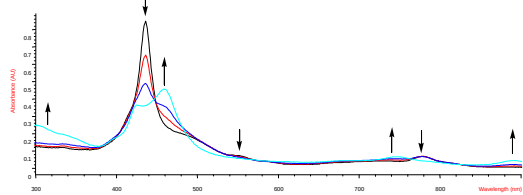
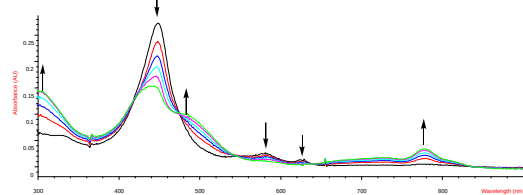


Figure S13 Thin-layer UV-visible spectral changes obtained before and after the second reduction of various quinoxalinoporphyrins [PQ(R₁R₂R₃)]Cu in pyridine solutions containing 0.1 M TBAP.

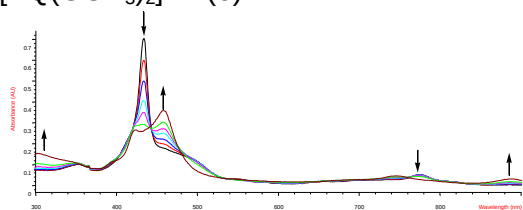
[PQ(5NH₂)]Zn (4)



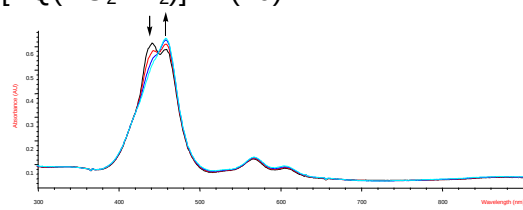
[PQ(5NO₂)]Zn (9)



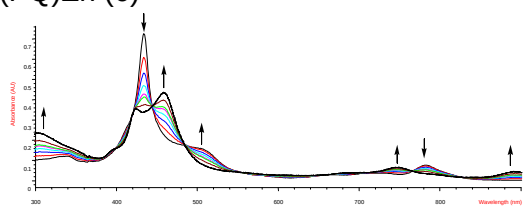
[PQ(OCH₃)₂]]Zn (5)



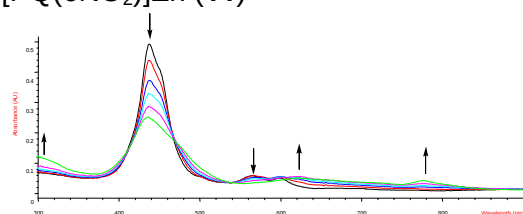
[PQ(NO₂NH₂)]Zn (10)



(PQ)Zn (6)



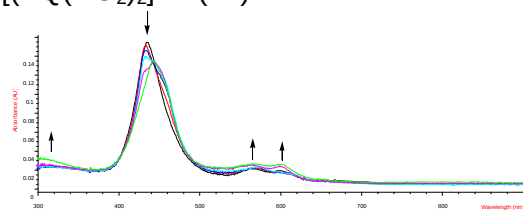
[PQ(6NO₂)]Zn (11)



(PQBr)Zn (7)

Data not presented due to slow chemical reaction on the spectroelectrochemical time scale

[(PQ(NO₂)₂)]Zn (12)



(PQCl₂)Zn (8)

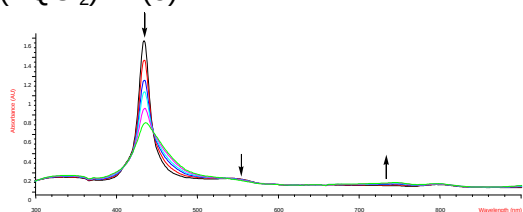


Figure S14. Thin-layer UV-visible spectral changes obtained before and after the second and possibly third reduction of various quinoxalinoporphyrins [PQ(R₁R₂R₃)]Zn in pyridine solutions containing 0.1 M TBAP.