Electronic Supplementary Information: Pyrazole analogues of porphyrins and oxophlorins

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Figure 1. UV-vis spectra of pyrazoloporphyrin 25a in 1% Et₃N-chloroform (top spectrum) and 1% TFA-chloroform (bottom spectrum).
Figure 2. UV-vis spectrum of pyrazoloporphyrin 25a in 0.5% Et$_3$N-chloroform.

Figure 3. UV-vis spectra of pyrazoloporphyrin 25a in chloroform with 0 equiv (red line), 1 equiv (orange line), 2 equiv (green line), 3 equiv (blue line) and 5 equiv (purple line) showing the formation of a monoprotonated species.
Figure 4. UV-vis spectrum of pyrazoloporphyrin monocation $25aH^+$ in 1% Et$_3$N-chloroform (top spectrum) and 1% TFA-chloroform (bottom spectrum).
Figure S5. UV-visible spectra of methyl pyrazoloporphyrin $91b$ in 1% triethylamine-chloroform (blue line) and 5% TFA-chloroform (green line).
Figure 6. UV-vis spectrum of pyrazoloporphyrin 25c in 1% Et$_3$N-chloroform.

Figure 7. UV-vis spectra of pyrazoloporphyrin 25c with 20 equiv TFA in chloroform.
Figure 8. UV-vis spectra of pyrazoloporphyrin 25c in 0.5% Et$_3$N-chloroform (red line), chloroform (orange line), 1 equiv TFA in chloroform (green line), 2 equiv TFA in chloroform (blue line) and 5 equiv TFA in chloroform. The chloroform was deacidified by running it through basic alumina, but the chloroform spectrum still shows a small degree of protonation.
Figure 9. UV-visible spectra of ethyl pyrazoloporphyrin 25c in 1% triethylamine-chloroform (blue line) and 5% TFA-chloroform (red line).
Figure 10. UV-vis spectra of nickel(II) pyrazolophyrin 31a in chloroform (green line) and 1% TFA-chloroform (blue line).
Figure 11. UV-vis spectra of palladium(II) pyrazoloporphyrin 32a in chloroform (blue line) and 1% TFA-chloroform (green line).
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Figure 13. UV-vis spectra of palladium(II) pyrazoloporphyrin 32b in chloroform (blue line) and 1% TFA-chloroform (green line).
Figure 14. UV-vis spectra of nickel(II) pyrazoloporphyrin 31c in chloroform (blue line) and with 500 equiv TFA in chloroform (green line).
Figure 15. UV-vis spectra of palladium(II) pyrazoloporphyrin 32c in chloroform (blue line) and with 500 equiv TFA in chloroform (blue line).
Figure 16. UV-vis spectra of oxophlorin analogue $28a$ in 1% Et$_3$N-chloroform (blue line) and 1% TFA-chloroform (red line).

Figure 17. UV-vis spectra of oxophlorin analogue $28a$ in 1% TFA-chloroform (red line), 5% TFA chloroform (green line) and 10% TFA-chloroform (blue line).
Figure 18. UV-vis spectra of oxophlorin analogue 28a in chloroform with 2 equiv (red line), 5 equiv (green line) and 10 equiv of TFA in chloroform (blue line).
Figure 19. UV-vis spectrum of oxophlorin analogue 28b in 0.5% Et₃N-chloroform.

Figure 20. UV-vis spectra of oxophlorin analogue 28b in 0.5% TEA-chloroform (red line), chloroform (orange line), 1 equiv TFA in chloroform (green line), 2 equiv TFA in chloroform (blue line) and 5 equiv TFA in chloroform (purple line).
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Figure 22. UV-vis spectra of oxophlorin analogue 28a in 1% Et₃N-chloroform (blue line) and 1% TFA-chloroform (red line).
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Figure 24. UV-vis spectra of pyrazoloporphyrin 25a in chloroform, 50 equiv TFA in chloroform, 5% TFA-chloroform and 10% TFA-chloroform.
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Figure 28. 125 MHz carbon-13 NMR spectrum of 1-ethyl-3,5-bis(hydroxymethyl)pyrazole in CDCl₃.
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Figure 35.  NOE correlations and partial proton NMR assignments for pyrazoloporphyrin 25b.
Figure 36. 500 MHz proton NMR spectrum of pyrazoloporphyrin 25b in trace TFA-CDCl₃.

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Figure 38. 500 MHz proton NMR and 125 MHz carbon-13 NMR spectra of nickel(II) pyrazoloporphyrin $31b$ in CDCl$_3$. 

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Figure 39. 500 MHz proton NMR spectrum of nickel(II) pyrazoloporphyrin 31b in TFA-CDCl₃.
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Figure 60. 500 MHz proton NMR spectrum of 28c in TFA-CDCl₃.
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Figure 66. $^1$H-$^1$H COSY NMR spectrum of pyrazolophlorin 24a in CDCl$_3$. 
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