Supplementary Material (ESI) for Chemical Communications

C-H bond activation and ring oxidation in nickel carbahemiporphyrazines

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Supporting Information

General Experimental Methods:

All chemicals were purchased from Sigama-Aldrich or Lancaster and used as received. All ^{1}H NMR spectra were recorded on Varian VXR or GEMINI spectrometers at 300 MHz. Absorption experiments were carried out on a Hitachi 3310 single monochromator spectrophotometer. Mass spectrometry experiments were performed at the Mass Spectrometry and Proteomics Facility of Ohio State University on a Micromass ESI-Tof™ II (Micromass, Wythenshawe, UK) mass spectrometer equipped with an orthogonal electrospray source (Z-spray) operated in positive ion mode. Sodium iodide was used for mass calibration for a calibration range of m/z 100-2000. Samples were prepared in a solution containing acidified methanol and infused into the electrospray source at a rate of 5-10 μL min^{-1}. Optimal ESI conditions were: capillary voltage 3000 V, source temperature 110^{o}C and a cone voltage of 55 V. The ESI gas was nitrogen. Data was acquired in continuum mode until acceptable averaged data was obtained. X-ray intensity data were measured at 100 K (Bruker KYRO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operated at 2000 W power. The crystal was mounted on a cryoloop using Paratone N-Exxon oil and placed under a steam of nitrogen at 100 K. The detector was placed at a distance of 5.009 cm from the crystal. Elemental analysis was conducted at the University of Illinois, School of Chemical Sciences Microanalysis Laboratory. The free base hemiporphyrazine macrocycles (**1-3**) were synthesized as described in the literature.[1]

1Ni: The synthesis of this complex by another route was previously described.[2] Free base **1** (30 mg, 6.8×10^{-5} mol) was mixed with bis(1,5-cyclooctadiene)nickel (19 mg, 6.8×10^{-5} mol) in 8 mL of anhydrous pyridine under argon in a glove box. The resultant solution was then refluxed for 1.5 hours. The solution was filtered and the product crystallized by diffusion of anhydrous hexanes to afford dark green crystals suitable for single crystal X-ray diffraction. Yield 15 mg, (34%).

2Ni: Free base **2** (70 mg, 1.6×10^{-4} mol) was weighted into a flask and brought into a glove box. $Ni(COD)_2$ (44 mg, 1.6×10^{-4} mol) was transferred into the dicarbahemiporphyrazine flask and the two reagents dissolved in 10 mL of DMF. The DMF mixture was refluxed for 1.5 h, during which time the solution's colour changed to red. The resultant solution was filtered and layered with methanol, affording red-black blocks of **2Ni**. Yield: 20 mg (25%) ESI MS (positive ion): 495.1 M/z (M+) CHN Analysis Calc. for $NiC_{30.5}H_{25.5}N_{6.5}O_{2.5}$ (**2Ni**·0.5DMF·MeOH·H_2O): C, 62.97; H, 4.42; N, 15.65 Found: C, 62.57; H, 4.03; N, 15.42. ^1H NMR ([D6]DMSO, δ): 5.37, 5.60, 6.22, 6.54, 6.80, 6.93, 7.03, 7.19, 7.47, 7.58 ppm. The UV-visible spectrum of **2Ni** can be seen in Figure S1.

3Ni: The procedure was identical to that for **2Ni** but with **3** (42 mg, 8.8×10^{-5} mol) and one equivalent of $Ni(COD)_2$ (24 mg, 8.8×10^{-5} mol). After refluxing for 1.5 h, the final solution was purple in colour. The resultant solution was filtered, layered with methanol to afford black blocks of **3Ni**. Yield 18 mg, (38%). ESI MS (positive ion): 533.1 M/z (M–H+). CHN Analysis Calc. for $NiC_{34.5}N_{8.5}H_{27.5}O_{1.5}$ (**3Ni**·1.5DMF): C, 64.36; H, 4.31; N, 18.49. Found: C, 64.65; H, 4.57; N, 18.63. ^1H NMR ([D6]DMSO, δ): 6.51, 6.68, 6.89, 7.13, 7.50, 7.65, 7.81, 7.94, 8.05, 8.15 , 10.76 ppm. The UV-visible spectrum of **3Ni** can be seen in Figure S2.

2ONi: The same procedure for the synthesis of **2Ni** was used, starting with 150 mg of **2** (3.4×10^{-4} mol). The resultant DMF solution was removed from the glove box and exposed to air. Red-black crystals were grown by diffusion of this solution with methanol. Yield 31 mg, (18%). ESI MS (positive ion): 511.08 M/z (M+) CHN Analysis Calc. for $NiC_{31}H_{23}N_7O_2$(**2ONi**·DMF): C, 63.73; H, 3.97; N, 16.78. Found: C, 63.01; H, 4.46; N, 16.90. ^1H NMR ([D6]DMSO, δ): 7.35, 7.72, 7.95, 11.85 ppm. The UV-visible spectrum of **2ONi** can be seen in Figure S3.

References:

[1] J. A. Elvidge, J. P. Linstead, J. Chem. Soc., 1952, 5008; P. F. Clark, J. A. Elvidge, R. P. Linstead, *J. Chem. Soc.,* 1954, 2490; J. A. Elvidge, J. H. Golden, *J. Chem. Soc.,* 1957, 700.

[2] 11 E. Agostinelli, D. Attanasio, I. Collamati, V. Fares, *Inorg. Chem.,* 1984, **23**, 1162.

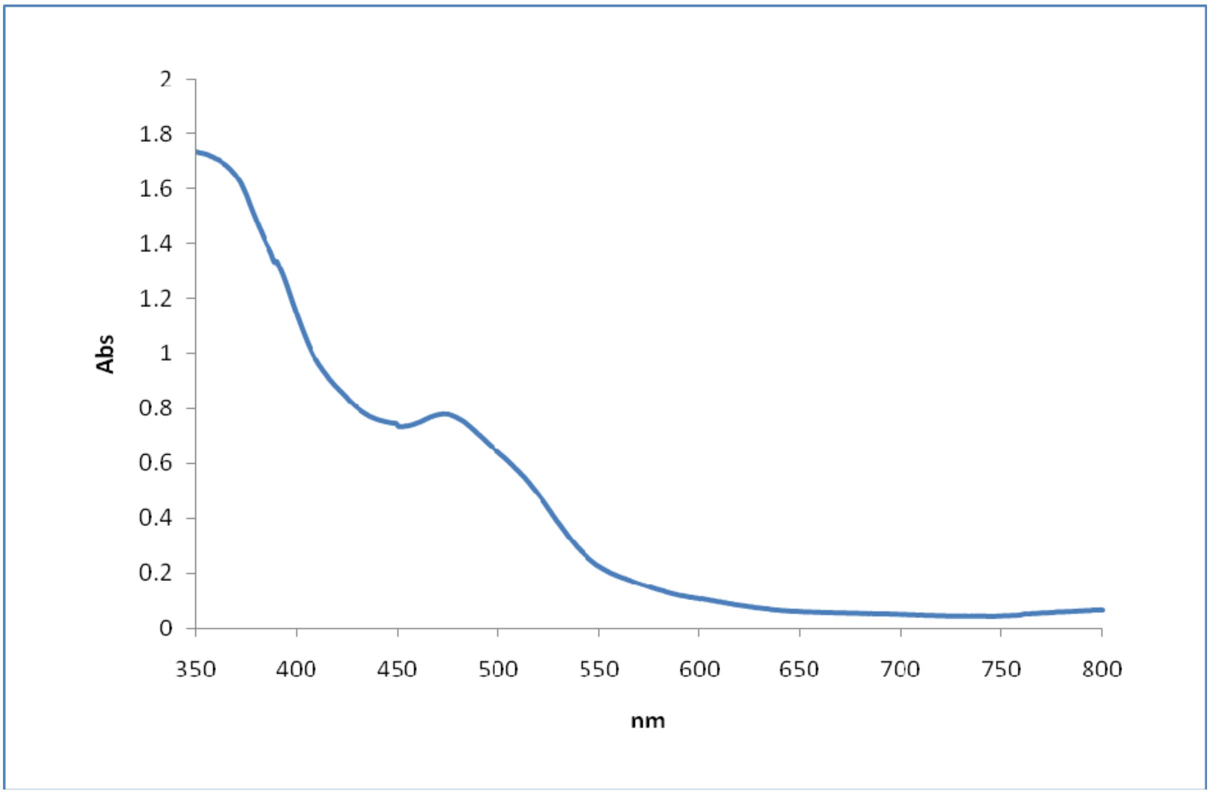

Figure S1: The UV-visible speectrum of **2Ni** in DMF.

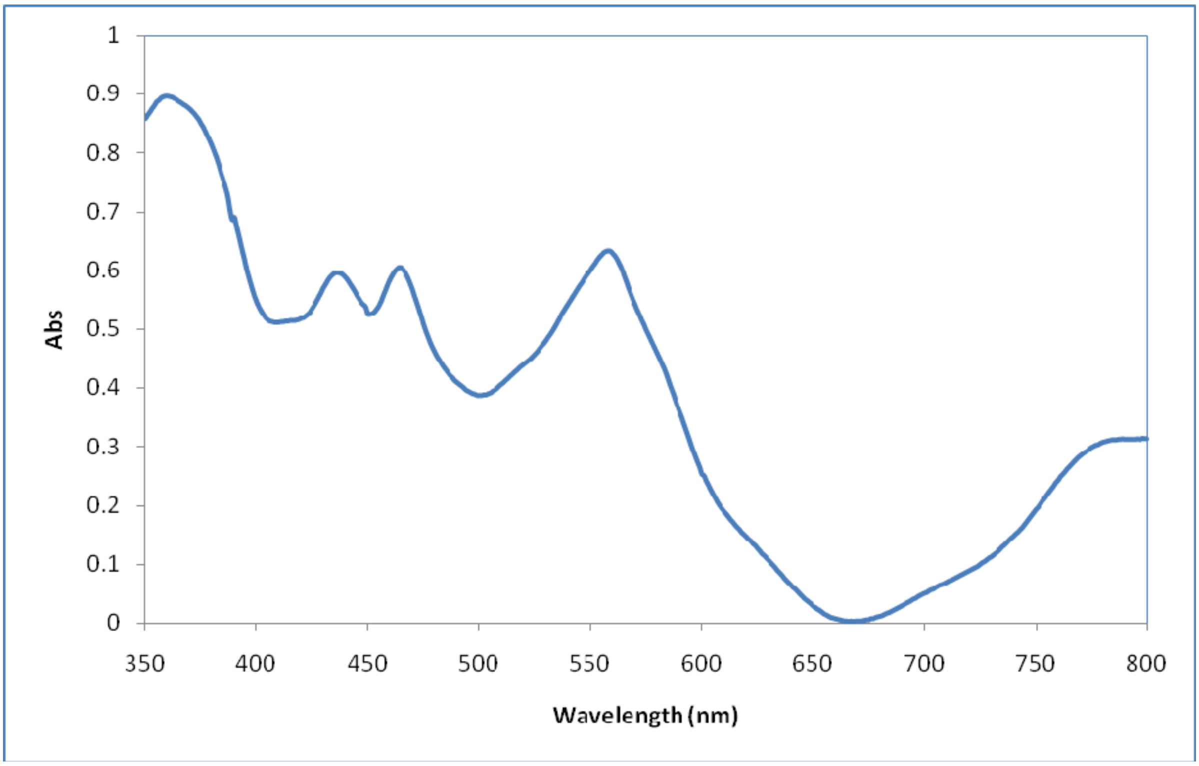

Figure S2: The UV-visible spectrum of **3Ni** in DMF.

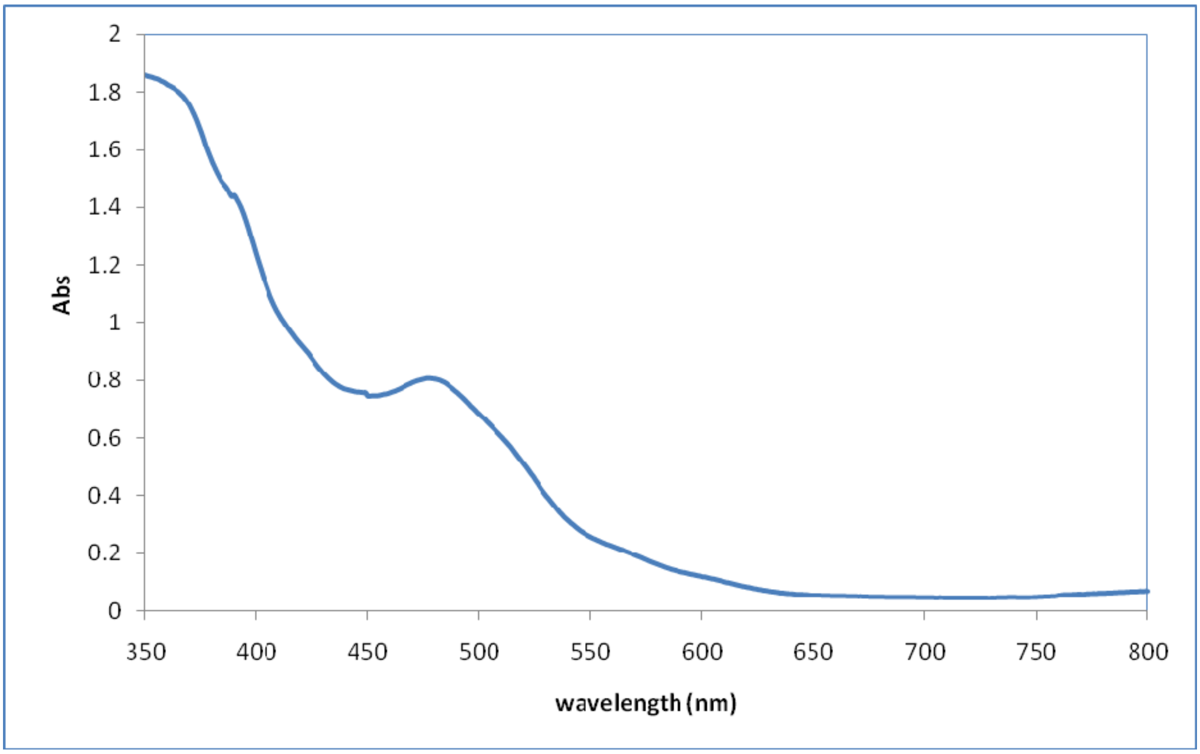

Figure S3: The UV-visible spectrum of **2ONi** in DMF.