Supporting Information

X-ray Snapshots for Metallopoprhyrin Axial Ligation

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1. Calculation of the equilibrium constant for the ligation in the ground state NiTMP

$$\text{NiTMP} + \text{py} \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} \text{NiTMP-py}$$

$$\text{NiTMP-py} + \text{py} \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} \text{NiTMP-py}_2$$

Pure pyridine has a concentration of 12.413 M (molecular weight = 79.1 g/mol; density = 0.9819g/cm^3). Pure toluene has a concentration of 9.41 M (molecular weight = 92.14g/mol; density = 0.8669g/cm^3). In the mixed solvent, the molar ratio in pyridine:toluene(v:v=1:3)=(12.413*0.25)/(9.41*0.75)=3.11/7.06 or 1: 2.27, and the pyridine concentration [py] = 3.11 M. Using the above information, we calculated the following, where the variables are self-explanatory.

$$K_1 = \frac{[NiTMPpy]}{[NiTMP][py]}$$

$$K_2 = \frac{[NiTMPpy_2]}{[NiTMPpy][py]}$$

$$C_0 = [NiTMP] + [NiTMPpy] + [NiTMPpy_2]$$

$$L_0 = [py] + [NiTMPpy] + 2[NiTMPpy_2]$$

$$K_1 = \frac{[NiTMPpy]}{\{C_0 - [NiTMPpy] - [NiTMPpy_2]\}\{L_0 - [NiTMPpy] - 2[NiTMPpy_2]\}}$$

$$K_2 = \frac{[NiTMPpy_2]}{[NiTMPpy]\{L_0 - [NiTMPpy] - 2[NiTMPpy_2]\}}$$

$$\because [NiTMPpy] << L_0, [NiTMPpy_2] << L_0$$

$$\therefore K_1 = \frac{[NiTMPpy]}{\{C_0 - [NiTMPpy] - [NiTMPpy_2]\}L_0} \rightarrow [NiTMPpy] = \frac{K_1C_0L_0 - K_1L_0[NiTMPpy_2]}{(1 + K_1L_0)}$$

$$K_2 = \frac{[NiTMPpy_2]}{[NiTMPpy]L_0} \rightarrow [NiTMPpy] = \frac{[NiTMPpy_2]}{K_2L_0}$$

$$\frac{K_1C_0L_0 - K_1L_0[NiTMPpy_2]}{\{1 + K_1L_0\}} = \frac{[NiTMPpy_2]}{K_2L_0} \rightarrow \frac{K_1C_0L_0 - K_1L_0[NiTMPpy_2]}{\{1 + K_1L_0\}[NiTMPpy_2]} = \frac{1}{K_2L_0}$$

$$\{1 + K_1L_0\}[NiTMPpy_2] + K_1K_2L_0^2[NiTMPpy_2] = K_1K_2C_0L_0^2$$

$$[NiTMPpy_2](1 + K_1L_0 + K_1K_2L_0^2) = K_1K_2C_0L_0^2$$

$$[NiTMPpy_2] = \frac{K_1K_2C_0L_0^2}{(1 + K_1L_0 + K_1K_2L_0^2)}$$

$$[NiTMPpy] = \frac{K_1C_0L_0}{(1 + K_1L_0 + K_1K_2L_0^2)}$$

$$[NiTMP] = \frac{C_0}{(1 + K_1L_0 + K_1K_2L_0^2)}$$

An alternative kinetics is one step axial ligation.

$NiTMP + 2py \leftrightarrow NiTMPpy_2$

$$K = \frac{[NiTMPpy_2]}{[NiTMP][py]^2}$$

$$C_0 = [NiTMP] + [NiTMPpy_2]$$

$$L_0 = [py] + 2[NiTMPpy_2]$$

$$K = \frac{[NiTMPpy_2]}{[NiTMP]\{L_0 - 2[NiTMPpy_2]\}^2}$$

$$\because [NiTMPpy_2] << L_0$$

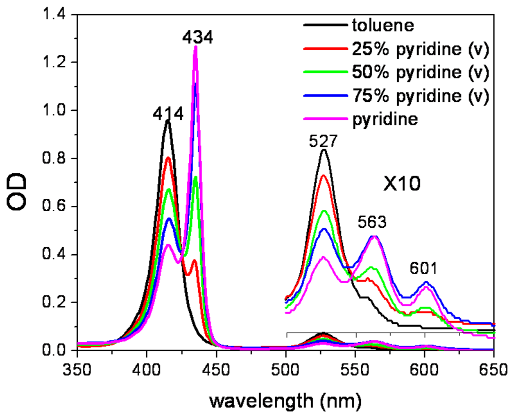
$$\therefore K = \frac{[NiTMPpy_2]}{[NiTMP]L_0^2} = \frac{[NiTMPpy_2]}{\{C_0 - [NiTMPpy_2]\}L_0^2}$$

$$[NiTMPpy_2] = \{KC_0 - K[NiTMPpy_2]\}L_0^2$$

$$[NiTMPpy_2] = KC_0L_0^2 / \{1 + KL_0^2\}$$

$$[NiTMP] = C_0 / \{1 + KL_0^2\}$$

Experimentally, we measured [NiTMP] as a function of [py] as seen in Figure 2 of the main text, see below. From the first model of the stepwise ligation, we obtained



$$[NiTMPpy_2] = \frac{K_1K_2C_0L_0^2}{(1 + K_1L_0 + K_1K_2L_0^2)}$$

$$[NiTMPpy] = \frac{K_1C_0L_0}{(1 + K_1L_0 + K_1K_2L_0^2)}$$

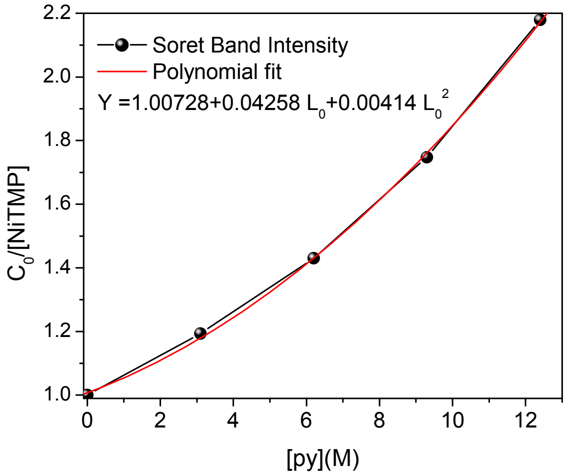
$$[NiTMP] = \frac{C_0}{(1 + K_1L_0 + K_1K_2L_0^2)}$$

Because the most direct measurable property is the optical density change as a function of [py] for unligated [NiTMP] at the B-band of 414 nm, directly from the above spectra, which is directly proportional to the concentration change of NiTMP.

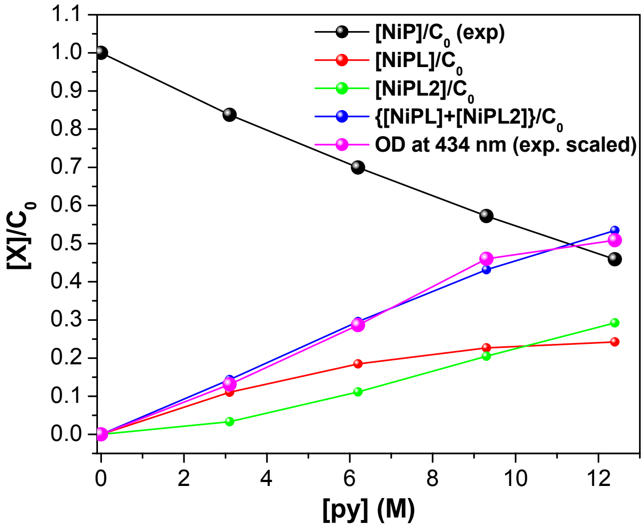
$$\frac{OD(py)}{OD(0)} = \frac{[NiTMP]}{C_0} = \frac{1}{(1 + K_1L_0 + K_1K_2L_0^2)}$$

where $OD(py)$ and $OD(0)$ are optical densities at a certain pyridine concentration and without pyridine at 414 nm, the B-band of unligated NiTMP.

Because $\frac{C_0}{[NiTMP]} = 1 + K_1L_0 + K_1K_2L_0^2$, fitting this with a polynomial gives K_1=0.043M^{-1}, and K_2= 0.10M^{-1} as shown in the figure below.



Using K_1 and K_2 values, we calculated fractions of NiTMP, NiTMPpy and $NiTMPpy_2$ as functions of [py] as shown below. The sum of ligated state appears to fit the shape of the curve from the intensity of 434 nm peak from the experiment in Figure 2 of the main text.



In this case, the 25% pyridine, 3.11 M in toluene could generate 16% of ligated species, but we could not differentiate between NiTMPpy and $NiTMPpy_2$. Therefore, if we must show an apparent equilibrium constant K as defined below.

$$\mathrm{K} = K_1 K_2 = 0.00414 M^{-2} = \frac{[\mathrm{NiTMPpy_2}]}{[\mathrm{NiTMP}][\mathrm{py}]^2}$$