Supplementary Information

X-ray Snapshots for Metallopophrin Axial Ligation

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

\[ \text{NiTMP} + \text{py} \xrightleftharpoons[k_1']{k_1} \text{NiTMP-py} \]

\[ \text{NiTMP-py} + \text{py} \xrightleftharpoons[k_2']{k_2} \text{NiTMP-py}_2 \]

Pure pyridine has a concentration of 12.413 M (molecular weight = 79.1 g/mol; density = 0.9819 g/cm³). Pure toluene has a concentration of 9.41 M (molecular weight = 92.14 g/mol; density = 0.8669 g/cm³). 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.

\[
K_1 = \frac{[\text{NiTMP-py}]}{[\text{NiTMP}][\text{py}]}
\]

\[
K_2 = \frac{[\text{NiTMP-py}_2]}{[\text{NiTMP-py}][\text{py}]}
\]

\[
C_0 = [\text{NiTMP}] + [\text{NiTMP-py}] + [\text{NiTMP-py}_2]
\]

\[
I_0 = [\text{py}] + [\text{NiTMP}][\text{py}] + 2[\text{NiTMP-py}_2]
\]

\[
K_1 = \frac{[\text{NiTMP}] + [\text{NiTMP-py}] + [\text{NiTMP-py}_2]}{2[I_0]} - \frac{[\text{NiTMP-py}][\text{py}]}{[\text{NiTMP}][\text{py}]}
\]

\[
K_2 = \frac{[\text{NiTMP-py}_2]}{[\text{NiTMP-py}][\text{py}]}
\]

\[
K_1 = \frac{[\text{NiTMP}] + [\text{NiTMP-py}] + [\text{NiTMP-py}_2]}{2[I_0]} - \frac{[\text{NiTMP-py}][\text{py}]}{[\text{NiTMP}][\text{py}]}
\]

\[
K_2 = \frac{[\text{NiTMP-py}_2]}{[\text{NiTMP-py}][\text{py}]}
\]

\[
K_1 = \frac{[\text{NiTMP}] + [\text{NiTMP-py}] + [\text{NiTMP-py}_2]}{2[I_0]} - \frac{[\text{NiTMP-py}][\text{py}]}{[\text{NiTMP}][\text{py}]}
\]

\[
K_2 = \frac{[\text{NiTMP-py}_2]}{[\text{NiTMP-py}][\text{py}]}
\]

\[
K_1 = \frac{[\text{NiTMP}] + [\text{NiTMP-py}] + [\text{NiTMP-py}_2]}{2[I_0]} - \frac{[\text{NiTMP-py}][\text{py}]}{[\text{NiTMP}][\text{py}]}
\]

\[
K_2 = \frac{[\text{NiTMP-py}_2]}{[\text{NiTMP-py}][\text{py}]}
\]

\[
K_1 = \frac{[\text{NiTMP}] + [\text{NiTMP-py}] + [\text{NiTMP-py}_2]}{2[I_0]} - \frac{[\text{NiTMP-py}][\text{py}]}{[\text{NiTMP}][\text{py}]}
\]

\[
K_2 = \frac{[\text{NiTMP-py}_2]}{[\text{NiTMP-py}][\text{py}]}
\]
An alternative kinetics is one step axial ligation.

\[
\text{NiTMP} + 2\text{py} \rightarrow \text{NiTMPpy}_2
\]

\[
K = \frac{[\text{NiTMPpy}_2]^2}{[\text{NiTMP}][\text{py}]^2}
\]

\[
C_0 = [\text{NiTMP}] + [\text{NiTMPpy}_2]
\]

\[
L_0 = [\text{py}] + 2[\text{NiTMPpy}_2]
\]

\[
K = \frac{[\text{NiTMP}][L_0 - 2[\text{NiTMPpy}_2]]^2}{[\text{NiTMPpy}_2]^2}
\]

\[
\therefore [\text{NiTMPpy}_2] \ll L_0
\]

\[
\therefore K = \frac{[\text{NiTMPpy}_2]}{[\text{NiTMP}]L_0^2} = \frac{[\text{NiTMPpy}_2]}{(C_0 - [\text{NiTMPpy}_2])L_0^2}
\]

\[
[\text{NiTMPpy}_2] = \frac{(KC_0 - KL_0^2)}{L_0^2}
\]

\[
[\text{NiTMP}] = C_0 / (1 + KL_0^2)
\]

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

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.

\[
\frac{OD(\text{py})}{OD(0)} = \frac{[\text{NiTMP}]}{C_0} = \frac{1}{(1 + K_1L_0 + K_2L_0^2)}
\]

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

Because \(C_0 / [\text{NiTMP}] = 1 + K_1L_0 + K_2L_0^2\), fitting this with a polynomial gives

\(K_1 = 0.043 \text{M}^{-1}\), and \(K_2 = 0.10 \text{M}^{-1}\) as shown in the figure below.
Using $K_1$ and $K_2$ values, we calculated fractions of NiTMP, NiTMPpy and NiTMPpy2 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 NiTMPpy2. Therefore, if we must show an apparent equilibrium constant $K$ as defined below.

$$K = K_1K_2 = 0.00414M^{-2} = \frac{[\text{NiTMPpy}_2]}{[\text{NiTMP}][\text{py}]^2}$$