Supplementary Material

for

# Differential Binding of Iron(III) and Zinc(II) Protoporphyrin IX to Synthetic Four-Helix Bundles

by

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**Figure S1.**  Stack plot of the high-frequency regions of Soret-excitation resonance Raman spectra for $[\alpha A22\text{-}l\text{-}\alpha H41]_2$ : Fe(III)-PP (1:1), $[\alpha H22\text{-}l\text{-}\alpha H41]_2$ : Fe(III)-PP (1:2) and $[\alpha H22\text{-}l\text{-}\alpha H41]_2$ : Fe(III)-PP (1:1). The spectra of the Fe(III)-PP in all three maquettes are the same within experimental error. The frequencies of the ring skeletal modes ($v^2$, 1557 cm$^{-1}$; $v^3$, 1503 cm$^{-1}$; $v^4$, 1374 cm$^{-1}$) are totally consistent with low-spin, six-coordinate Fe(III)-PP.[1] Accordingly, the Fe(III)-PP cofactor in $[\alpha A22\text{-}l\text{-}\alpha H41]_2$ must bridge the two helix-loop-helix monomers.

**Figure S2.**  Low-frequency region of the Soret-excitation resonance Raman spectrum of $[\alpha H22\text{-}l\text{-}\alpha H41]_2$ : Zn(II)-PP (1:2). The key observation is the presence of a moderately strong band at ~158 cm$^{-1}$, which is assignable to the Zn(II)-His stretching mode.[2] This band is absent from the spectrum of four-coordinate Zn(II)-PP. Accordingly, the Zn(II)-PP is bound to the peptide and must be five-coordinate. There is no issue of whether Zn(II)-PP is five- verses six-coordinate, even under the most severe conditions (such as in the

presence of 4 M imidazole). Also, metal-His stretches are not observed for six-coordinate metallopophyrins.[1b]

## References

1. (a) Choi, S.; Spiro, T. G.; Langry, K. C.; Smith, K. M.; Budd, D.; Lamar, G. N. *J. Am. Chem. Soc.* **1982**, *104*, 4345-4351. (b) Spiro, T. G. in *Iron Porphyrins*; Lever, A. P. B.; Gray, H. B., Eds.: Addison Wesley: Reading, MA, 1983, pp89-160.

2. Feitelson, J.; Spiro, T. G. *Inorg. Chem.* **1986**, *25*, 861-865.

13

$\lambda_{ex}$ = 415.4 nm

$[\alpha A22\text{-}l\text{-}\alpha H41]_2$ :Fe(III)-pp (1:1)

1126, 1171, 1228, 1374, 1502, 1576, 1627

$[\alpha H22\text{-}l\text{-}\alpha H41]_2$ :Fe(III)-pp (1:2)

1127, 1170, 1231, 1308, 1374, 1401, 1428, 1503, 1547, 1577, 1598, 1628

$[\alpha H22\text{-}l\text{-}\alpha H41]_2$ :Fe(III)-pp (1:1)

1128, 1171, 1232, 1306, 1374, 1401, 1428, 1503, 1577, 1598, 1630

Raman Shift (cm$^{-1}$)

$\lambda_{ex} = 415.4$ nm

$[\alpha H22\text{-}l\text{-}\alpha H41]_2$ :Zn(II)-pp (1:2)

x 2