



JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

J. Am. Chem. Soc., 1998, 120(28), 7103-7104, DOI:[10.1021/ja980432y](https://doi.org/10.1021/ja980432y)

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Supplementary Material

RECEIVED MAY 13 1999

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 $[\alpha A22-l-\alpha H41]_2 : \text{Fe(III)-PP}$ (1:1), $[\alpha H22-l-\alpha H41]_2 : \text{Fe(III)-PP}$ (1:2) and $[\alpha H22-l-\alpha H41]_2 : \text{Fe(III)-PP}$ (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 (ν^2 , 1557 cm^{-1} ; ν^3 , 1503 cm^{-1} ; ν^4 , 1374 cm^{-1}) are totally consistent with low-spin, six-coordinate Fe(III)-PP.¹ Accordingly, the Fe(III)-PP cofactor in $[\alpha A22-l-\alpha H41]_2$ must bridge the two helix-loop-helix monomers.

Figure S2. Low-frequency region of the Soret-excitation resonance Raman spectrum of $[\alpha H22-l-\alpha H41]_2 : \text{Zn(II)-PP}$ (1:2). The key observation is the presence of a moderately strong band at $\sim 158 \text{ cm}^{-1}$, 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- versus 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 metalloporphyrins.^{1b}

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