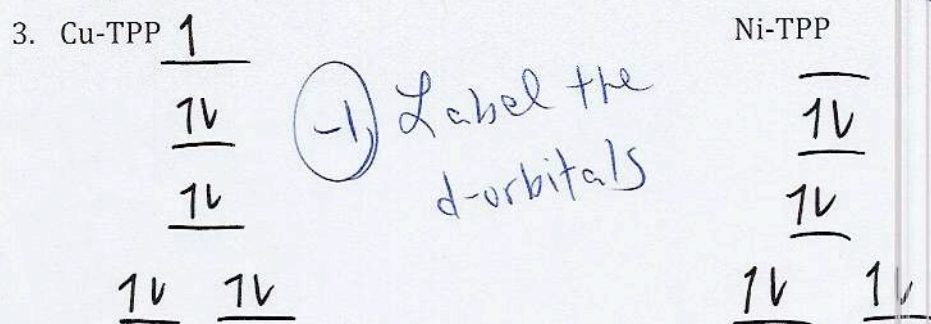


1. The N-H bonds present in tetraphenylporphyrin leads to a single C_2 axis, a vertical reflection axis in the plane of the molecule, and no horizontal reflection axes. This is a relatively low degree of rotational symmetry that is forced by the presence of the 2 N-H bonds on opposite sides of the molecule. When these N-H bonds are removed, the degree of rotational symmetry is increased because the metal-N bonds in the metalloporphyrin (Ni-TPP) are more highly symmetrical. This induces a new axis of higher symmetry, a C_4 axis perpendicularly penetrating the plane of the molecule. This new C_4 axis will cause a change in point group.
2. To get this molecule, replace benzaldehyde with 4-methoxy benzaldehyde.



4. Fluorescence is the emission of absorbed light at a different wavelength, especially the absorption of a high energy photon and the emission of that photon in a lower energy state. The $\pi \rightarrow \pi^*$ transition accounts for the fluorescence of TPP. When the metal binds, the $d_{\pi} \rightarrow \pi^*$ backbonding raises the ΔE , which causes a loss or reduction in the amount of emission encompassing fluorescence. The reason that Ni-TPP causes loss of fluorescence while Zn-TPP does not rests on the fact that there is less $d_{\pi} \rightarrow \pi^*$ backbonding at play in the zinc complex, preventing the increase in ΔE which causes loss of fluorescence.¹ Because of this, the Zn(TPP) complex fluoresces just as the TPP molecule does.

References:

- 1) Marsh, Diane F. and Mink, Larry M., *J. Chem. Ed.*, 1996, 73, 1188.
- 2) Falvo, RaeAnne E. and Mink, Larry M., *J. Chem. Ed.*, 1999, 76, 237.
- 3) Mink, Larry M. and Saucedo, Laura. *J. Chem. Ed.*, 2005, 82, 790.