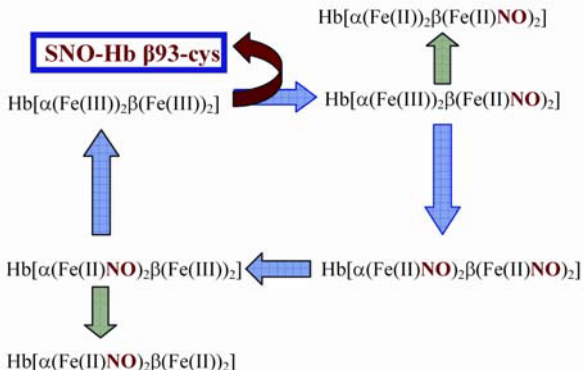


## Subunit Selectivity in NO Hb Reactions



**Figure 5.** Reaction cycle depicting the flexibility of the disposition of the NO group in tetrameric Hb. The blue arrows outline a path beginning (upper left) with met-Hb,  $\text{Hb}[\text{heme-Fe(III)}_4]$ , which is converted through partial reductive nitrosylation to the hybrid  $\text{Hb}[\alpha(\text{Fe(III)})_2\beta(\text{Fe(II)NO})_2]$ , then, upon complete reaction, to  $\text{Hb(NO)}_4$ ,  $\text{Hb}[(\text{heme-Fe(II)NO})_4]$  (lower right). Partial oxidation of  $\text{Hb(NO)}_4$  yields the complementary hybrid  $\text{Hb}[\alpha(\text{Fe(II)NO})_2\beta(\text{Fe(III)})_2]$ , which, upon further oxidation, completes the cycle to yield met-Hb. Reduction of the hybrids (green arrows) generate the corresponding Fe(II)/Fe(II)NO hybrids. SNO-Hb formation (red arrow) can accompany reductive nitrosylation.