The production of nitrous oxide (N_2O) by the heme/nonheme diiron center of engineered myoglobins (Fe_BMbs) proceeds through a *trans* iron-nitrosyl dimer

Hirotoshi Matsumura,[1] Takahiro Hayashi,[1,‡] Saumen Chakraborty,[2] Yi Lu,[2] and Pierre Moënne-Loccoz[1*]

[1]Divison of Environmental & Biomolecular Systems, Institute of Environmental Health, Oregon Health & Science University, 3181 SW Sam Jackson Park Road, Portland, Oregon 97239-3098

[2]Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Supporting information

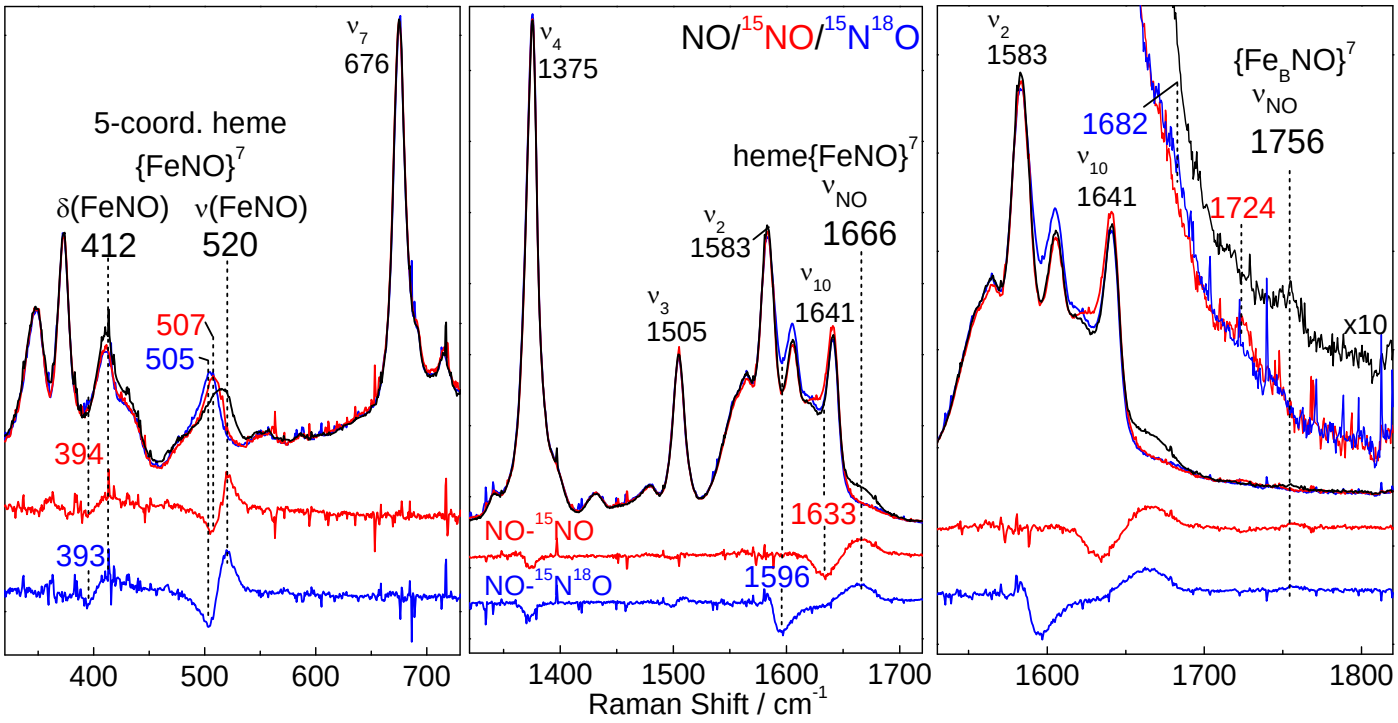

Figure S1. Room temperature RR spectra of the end-product of the reaction of reduced Fe_BMb**1** with excess NO (protein concentration, 100 μM; samples frozen ~ 2 min after the addition of NO; excitation wavelength: 406 nm).

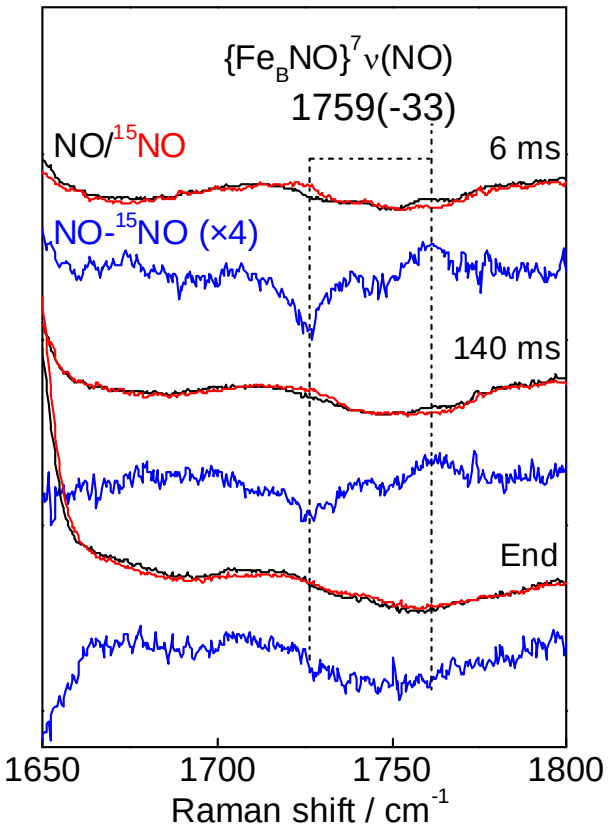

Figure S2. High-frequency region of the RR spectra of the 6-ms and 140-ms RFQ samples of the reaction of reduced Fe_BMb**2** with excess ^{14}NO (back traces), ^{15}NO (red traces), and the resulting ^{14}NO – ^{15}NO difference spectra (blue traces). Also shown are the equivalent spectra for end-point samples (frozen ~2 min after mixing).

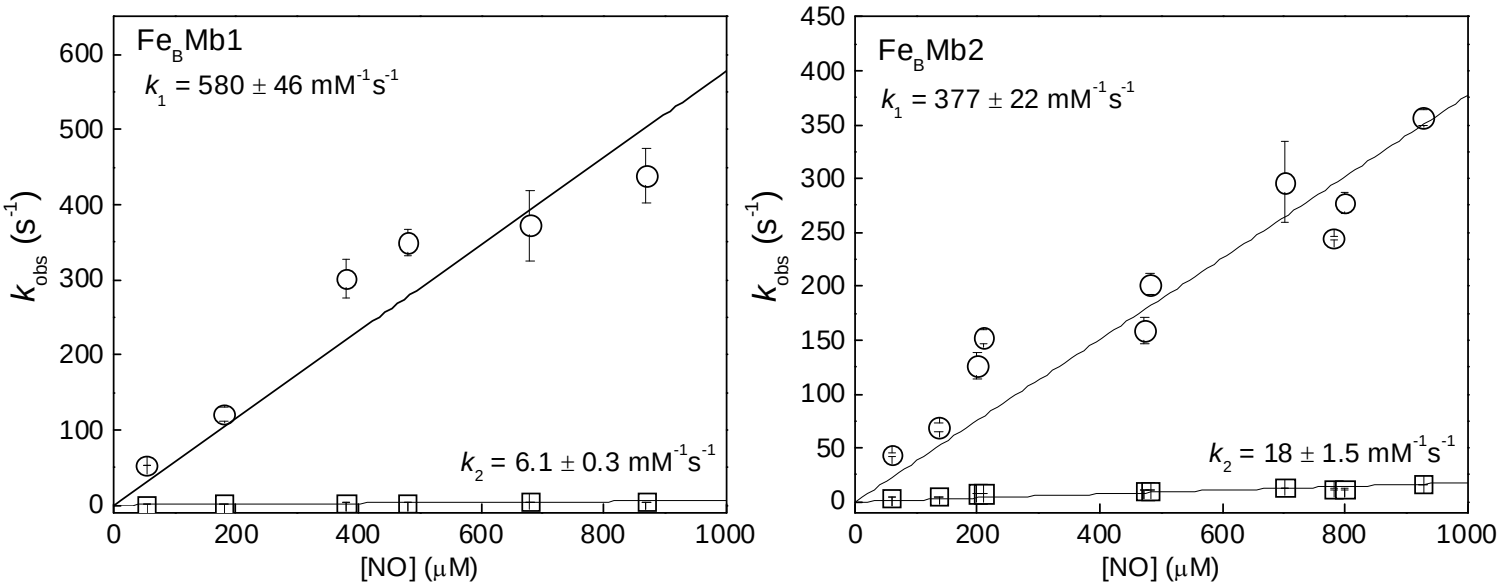

Figure S3. The dependence of the rate constants of k_1 and k_2 on NO concentration.

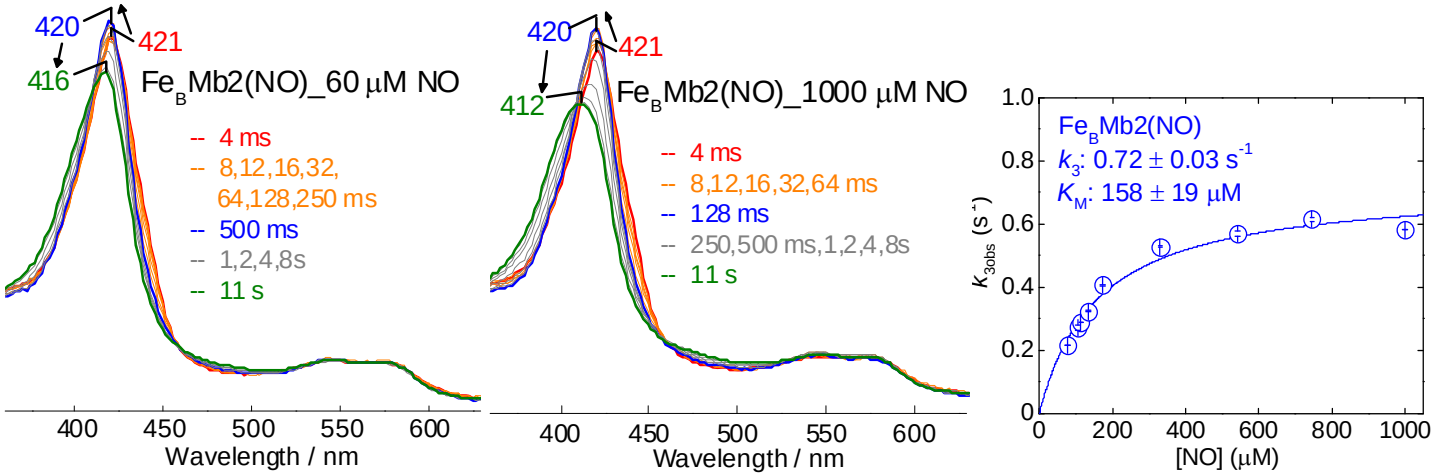

Figure S4. Stopped-flow UV-vis absorption spectra of the reaction of Fe$_B$Mb**2**(NO) with 60 and 1000 μM NO at 4.0 °C. Also shown, is the dependence of the last rate constant on NO concentration.