

Supporting Information

Alkylamine-Ligated H93G Myoglobin Cavity Mutant: A Model System for Endogenous Lysine and Terminal Amine Ligation in Heme Proteins such as Nitrite Reductase and Cytochrome *f*

Jing Du,[‡] Roshan Perera,^{‡,#} and John H. Dawson^{‡,§}*

[‡] Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 20208

[§] School of Medicine, University of South Carolina, Columbia, SC 20208

[#] *Present address: Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019-0065. E-mail address: perera@uta.edu (R. Perera)*

* To whom correspondence should be addressed: Department of Chemistry and Biochemistry, 631 Sumter St., University of South Carolina, Columbia, SC 29208. Phone: (803) 777-7234. Fax: (803)777-9521. E-mail: dawson@sc.edu.

Figure Legends

Figure S1. (a) Soret region and (b) visible region electronic absorption spectral changes upon titration of ferric H93G(0.3 M cyclohexylamine) Mb with sodium nitrite in 0.1 M potassium phosphate buffer, pH 7.0, at 4 °C. Vertical arrows indicate the directions of absorbance change on addition of 1, 3, 5, 10, 21, 40, 78 and 144 mM sodium nitrite. The non-vertical short arrows show isosbestic points.

Figure S2. (a) Soret region and (b) visible region electronic absorption spectral changes upon titration of ferric H93G(1 mM Im) Mb with cyclohexylamine in 0.1 M potassium phosphate buffer, pH 7.0, at 4 °C. Vertical arrows indicate the directions of absorbance change on addition of 408, 509, 677, 811, 921, 1012 and 1089 mM cyclohexylamine. The non-vertical short arrows show isosbestic points.

Figure S3. MCD (top) and electronic absorption (bottom) spectra of six-coordinate ferrous-CO complexes of cyclohexylamine-bound H93G Mb (solid line) and ferrous-CO H93G(Im) Mb (dashed line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

Figure S4. MCD (top) and electronic absorption (bottom) spectra of ferric H93G(cyclohexylamine) Mb (0.3 M cyclohexylamine) (solid line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

Figure S5. MCD (top) and electronic absorption (bottom) spectra of ferric H93G(bis-cyclohexylamine) Mb (2 M cyclohexylamine) (solid line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

Figure S6. MCD (top) and electronic absorption (bottom) spectra of cyclohexylamine and nitrite (NO₂)-bound ferric H93G Mb (0.5 M cyclohexylamine, 0.1 M NaNO₂) (solid line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

Figure S7. MCD (top) and electronic absorption (bottom) spectra of cyclohexylamine and Im-bound ferric H93G Mb (0.2 mM Im, 1 M cyclohexylamine) (solid line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

Figure S8. MCD (top) and electronic absorption (bottom) spectra of the deoxyferrous H93G(cyclohexylamine) Mb (0.3 M cyclohexylamine) (solid line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

Figure S9. MCD (top) and electronic absorption (bottom) spectra of the deoxyferrous H93G(bis-methylamine) Mb (144 mM methylamine) (solid line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

Figure S10. MCD (top) and electronic absorption (bottom) spectra of six-coordinate

ferrous-NO complexes of cyclohexylamine-bound H93G Mb (solid line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

Figure S11. MCD (top) and electronic absorption (bottom) spectra of six-coordinate oxyferrous complexes of cyclohexylamine-bound H93G Mb (solid line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

Figure S12. MCD (top) and electronic absorption (bottom) spectra of ferryl complexes of ethylamine-bound H93G Mb (solid line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

Figure S13. MCD (top) and electronic absorption (bottom) spectra of six-coordinate ferrous-CO complexes of cyclohexylamine-bound H93G Mb (solid line). The spectra were recorded in 0.1 M potassium phosphate at pH 7.0 at 4 °C.

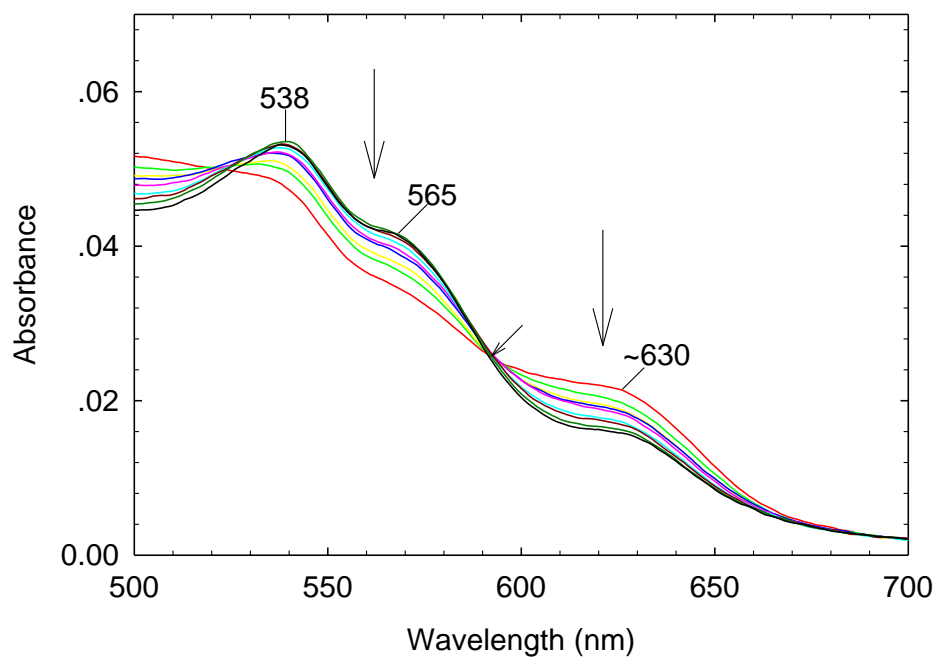
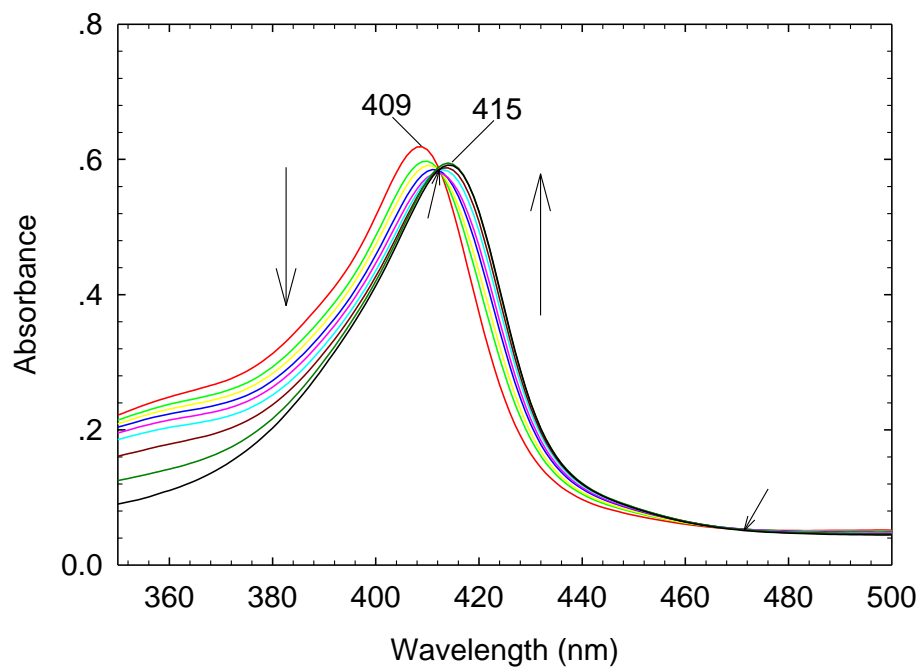


Figure S1

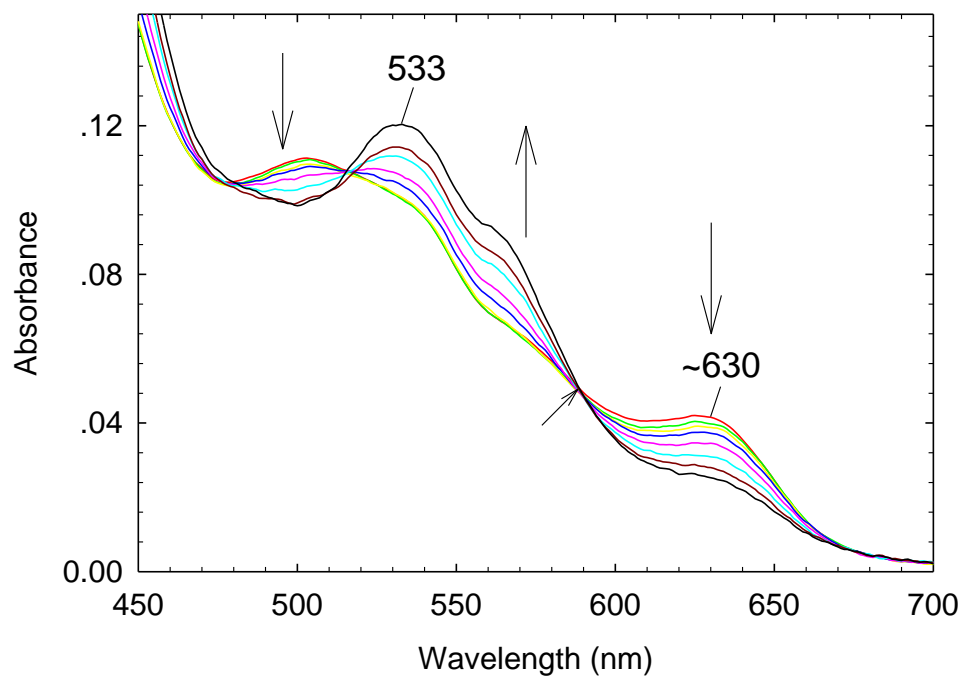
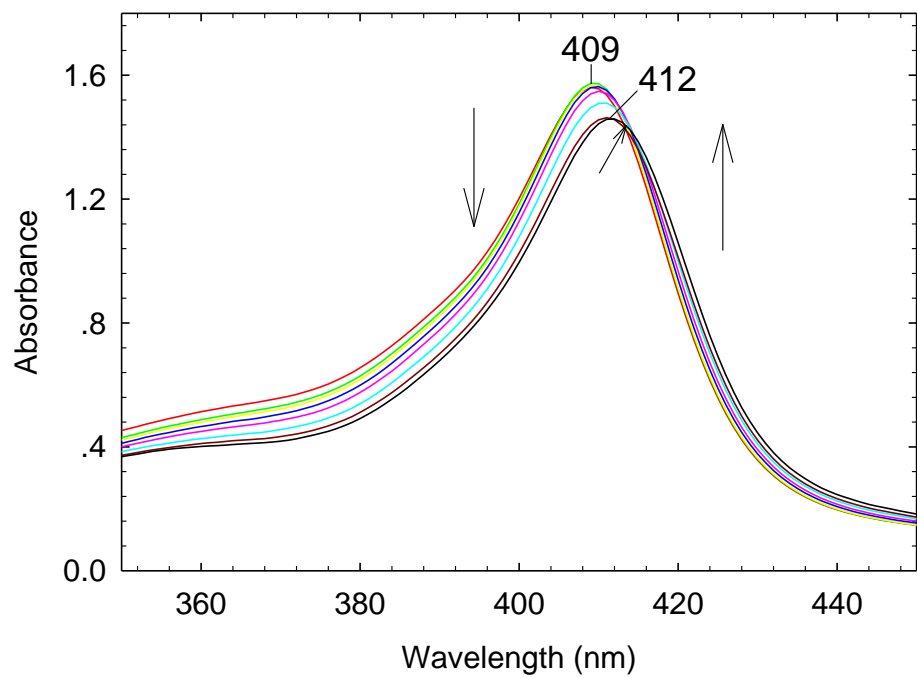


Figure S2

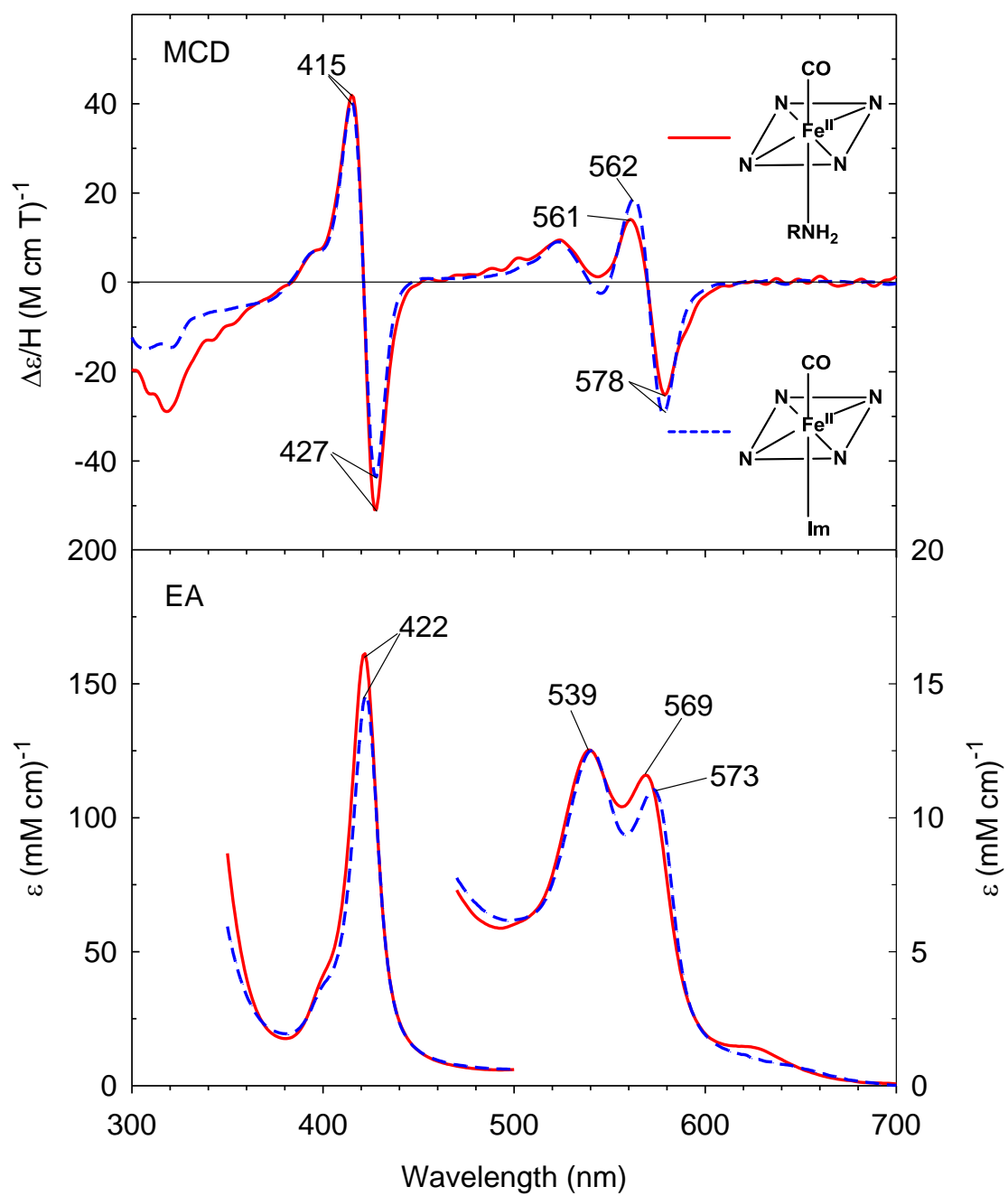


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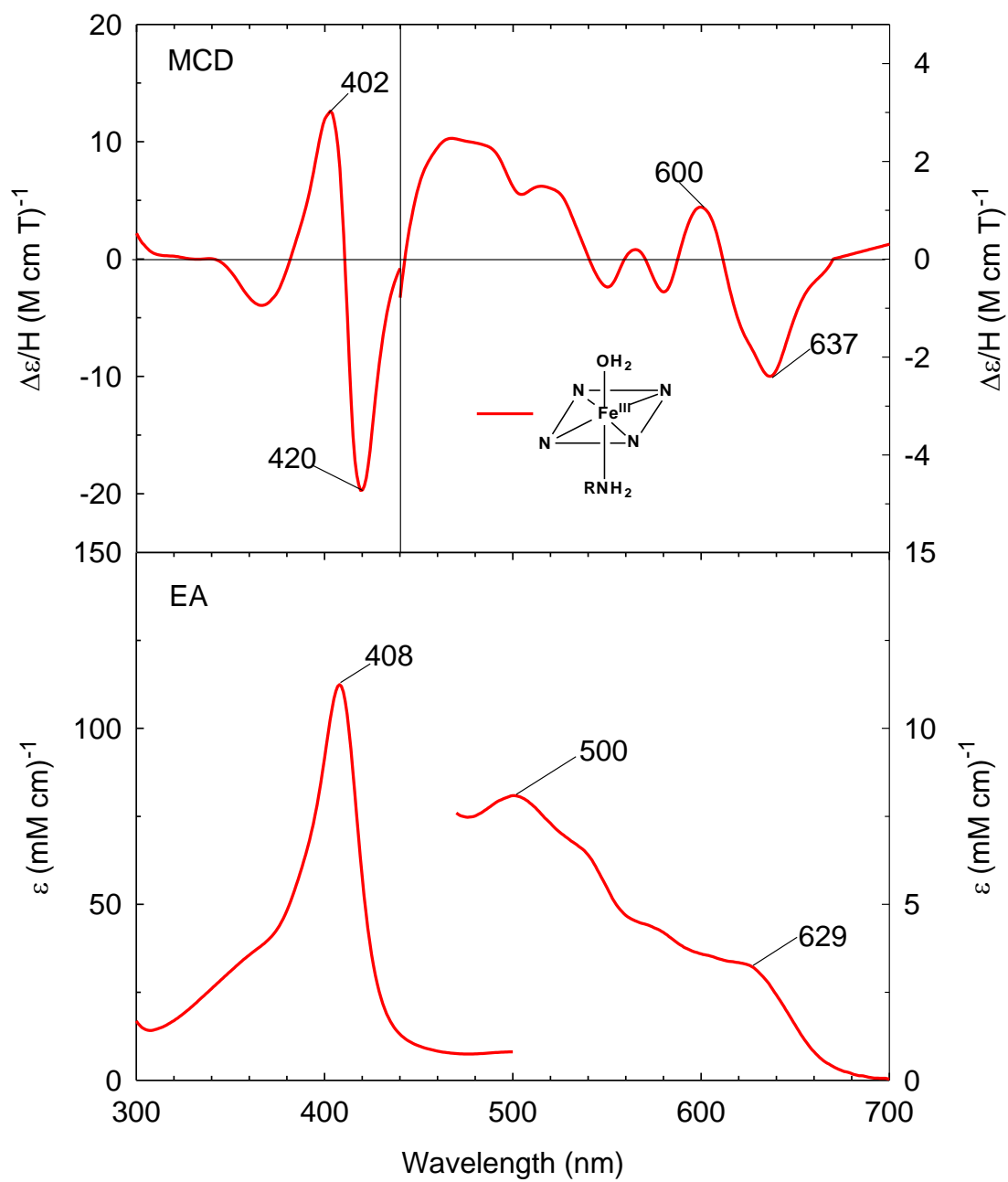


Figure S4

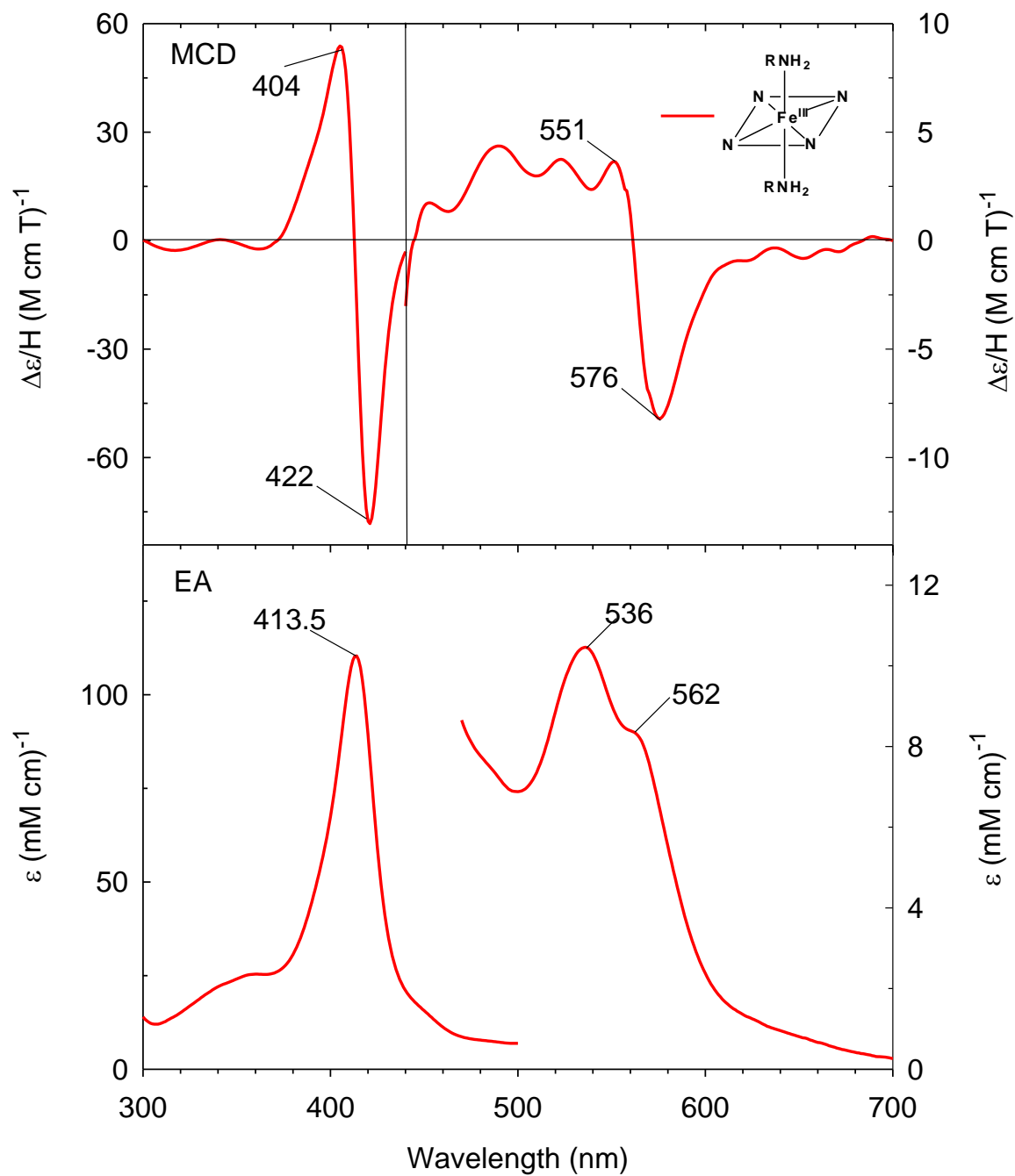


Figure S5

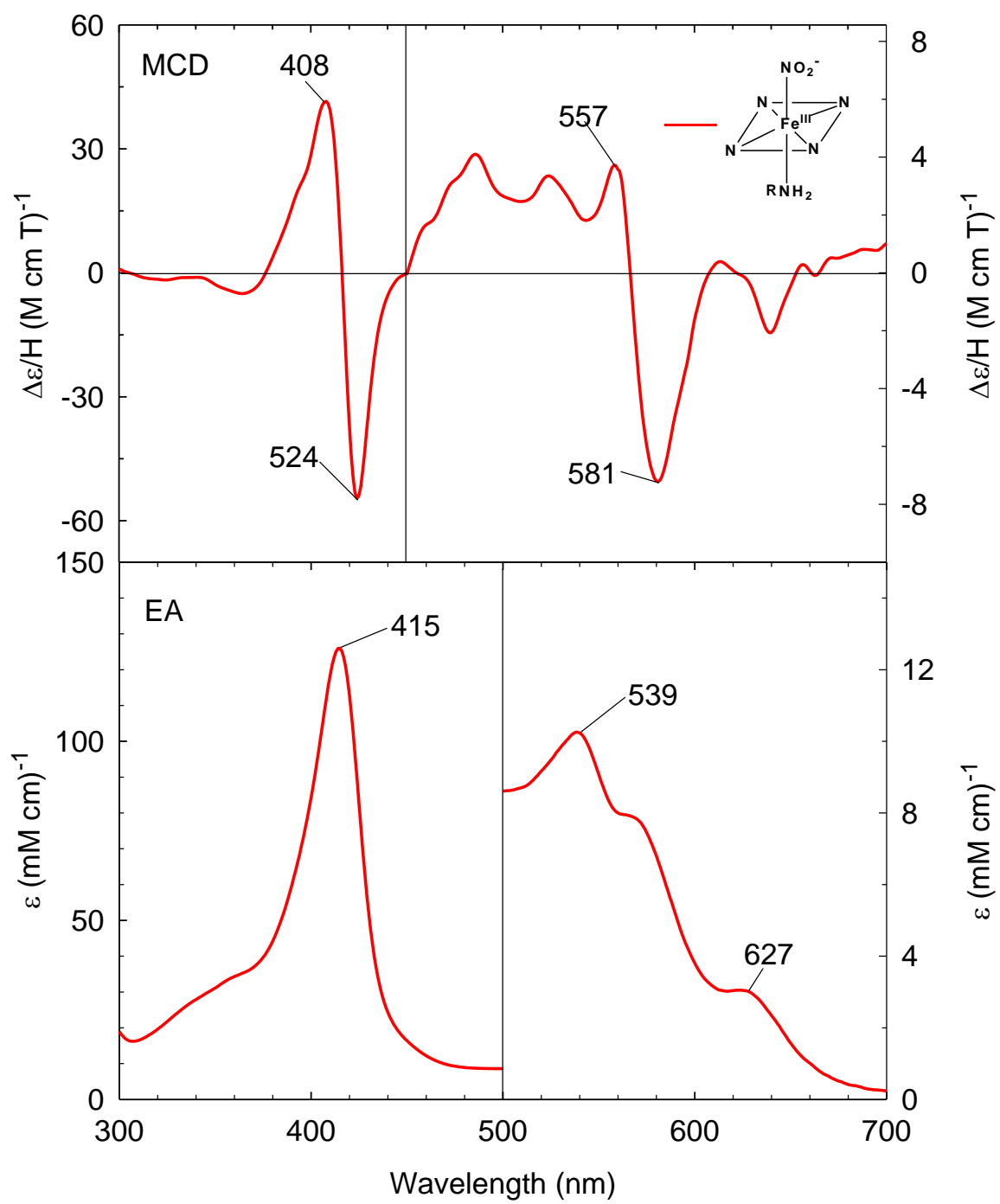


Figure S6

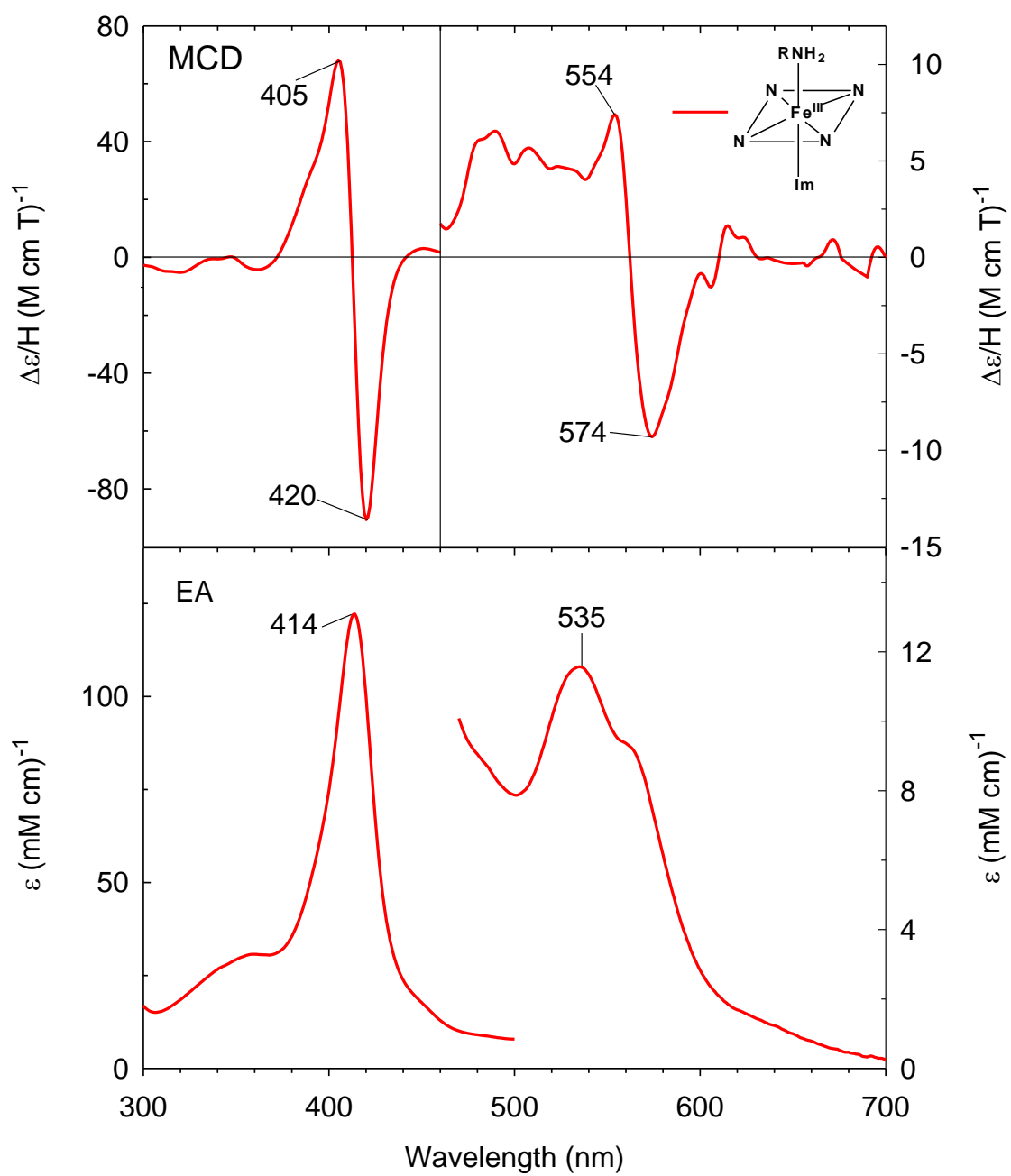


Figure S7

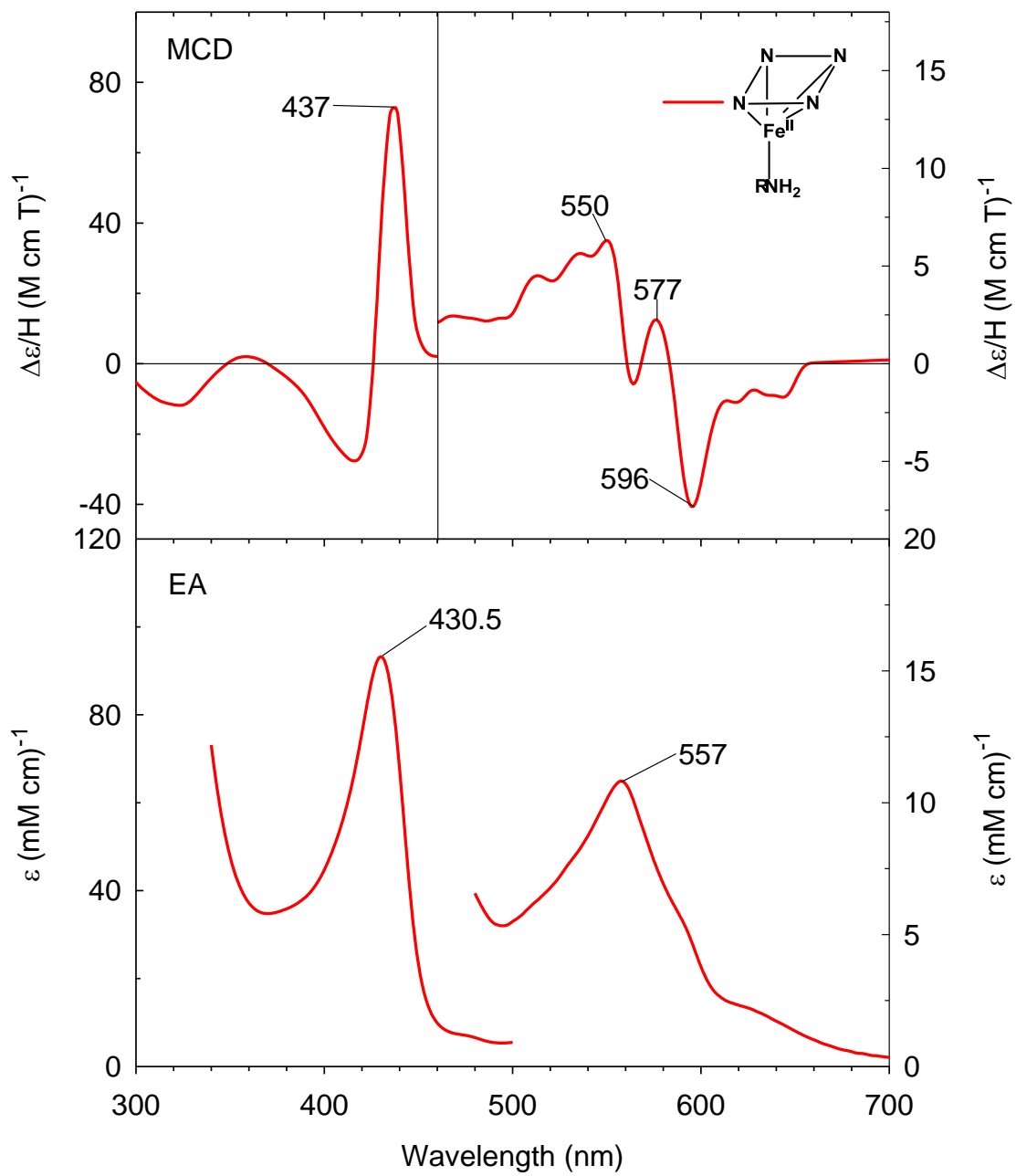


Figure S8

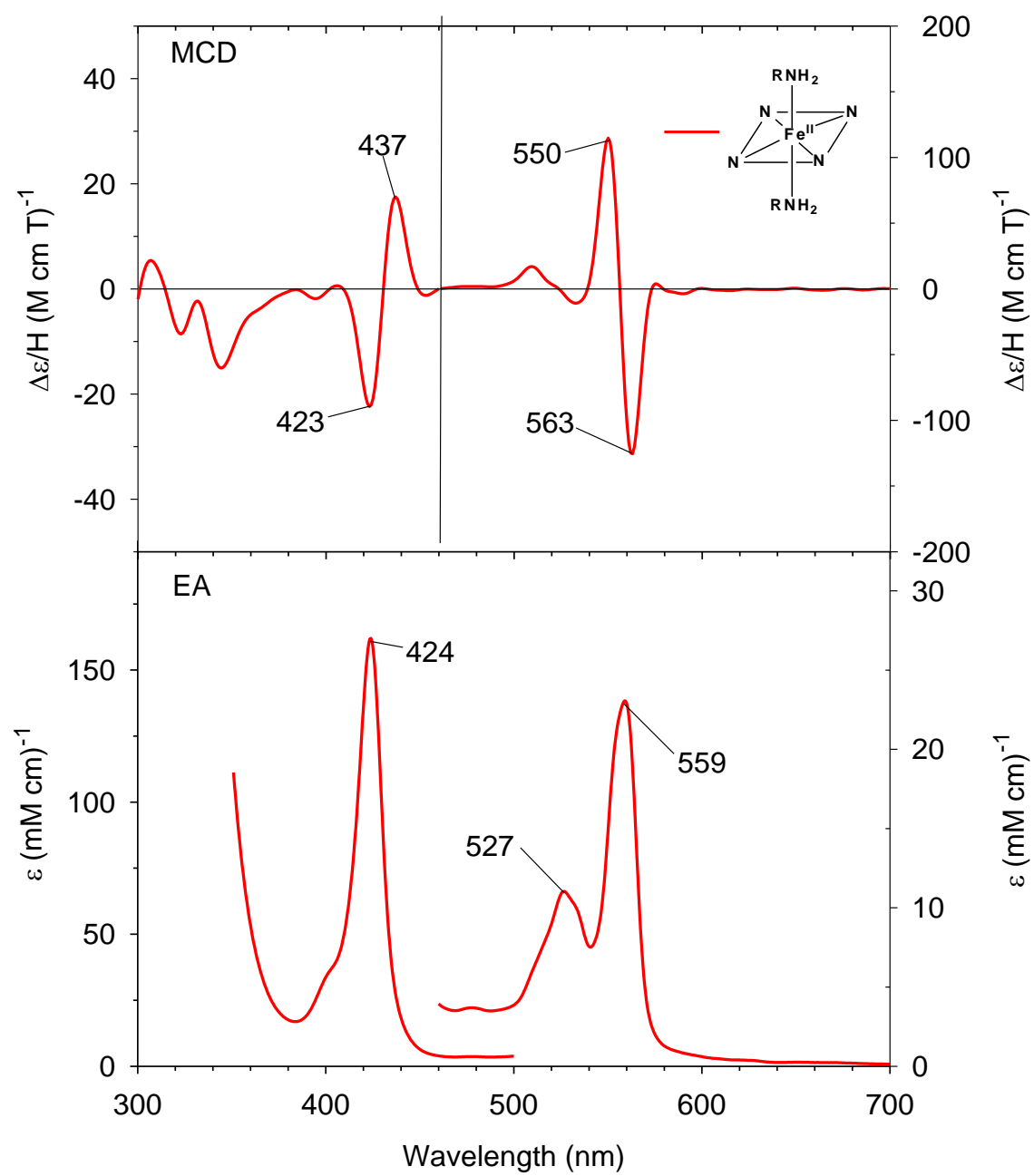


Figure S9

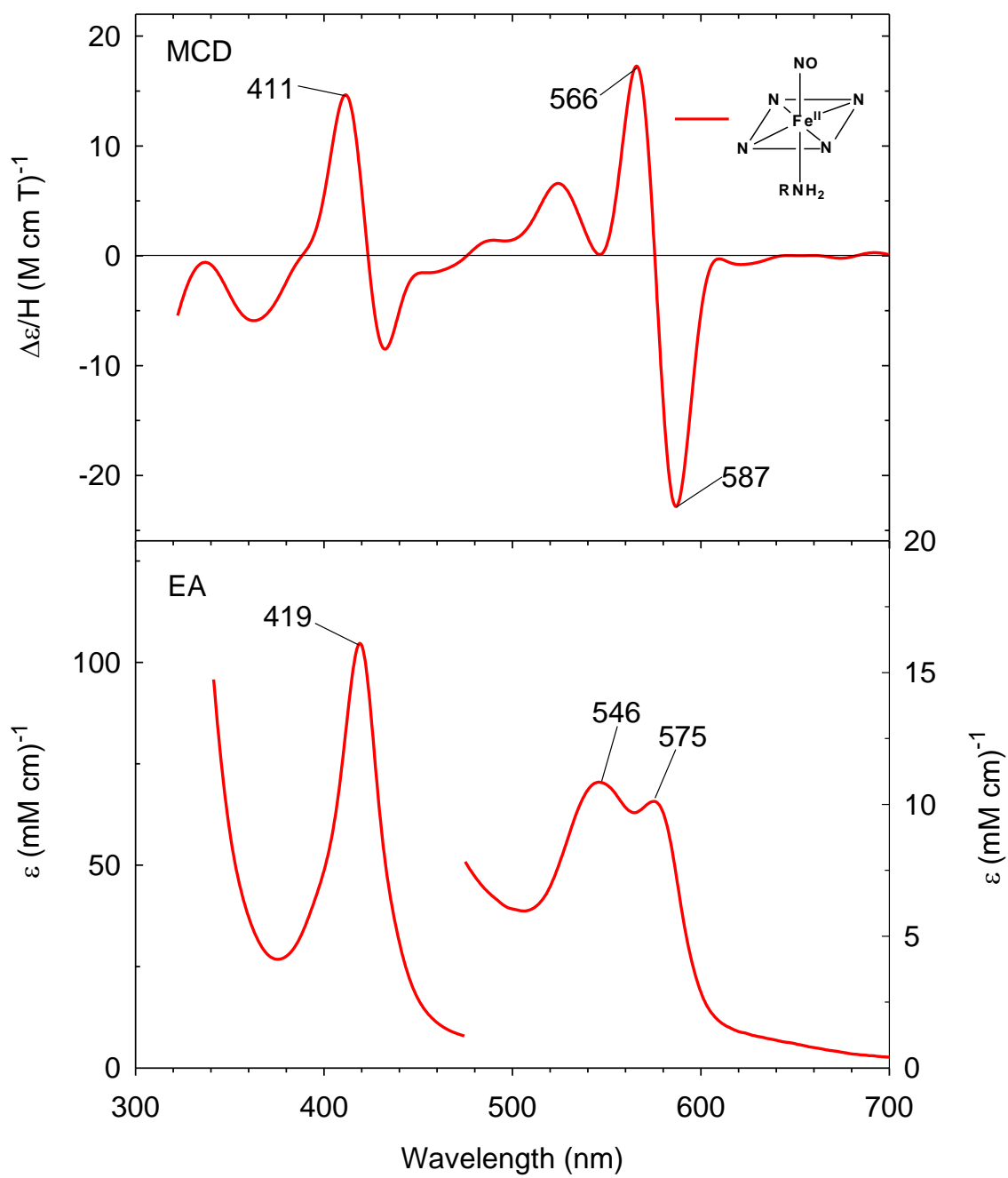


Figure S10

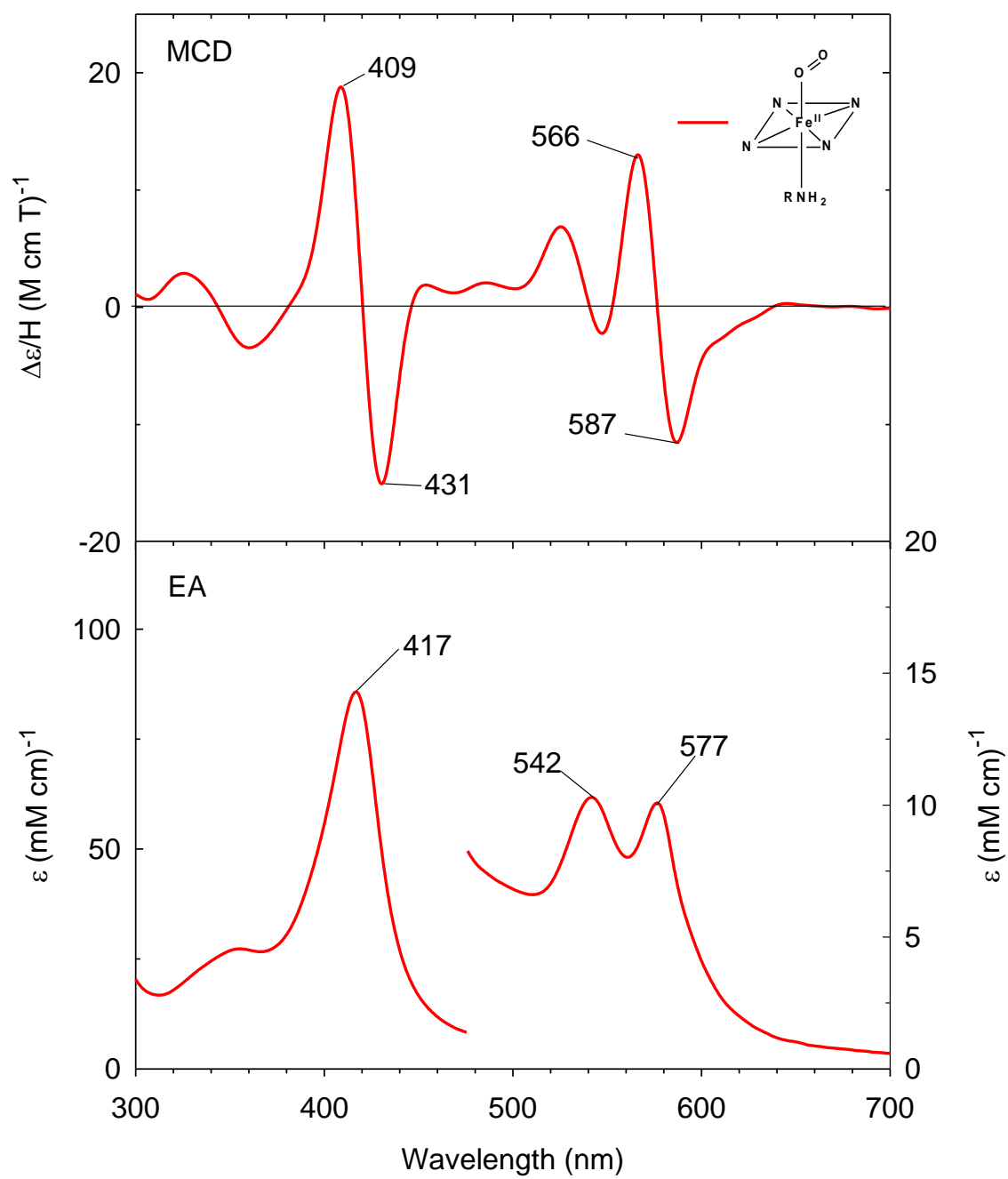


Figure S11

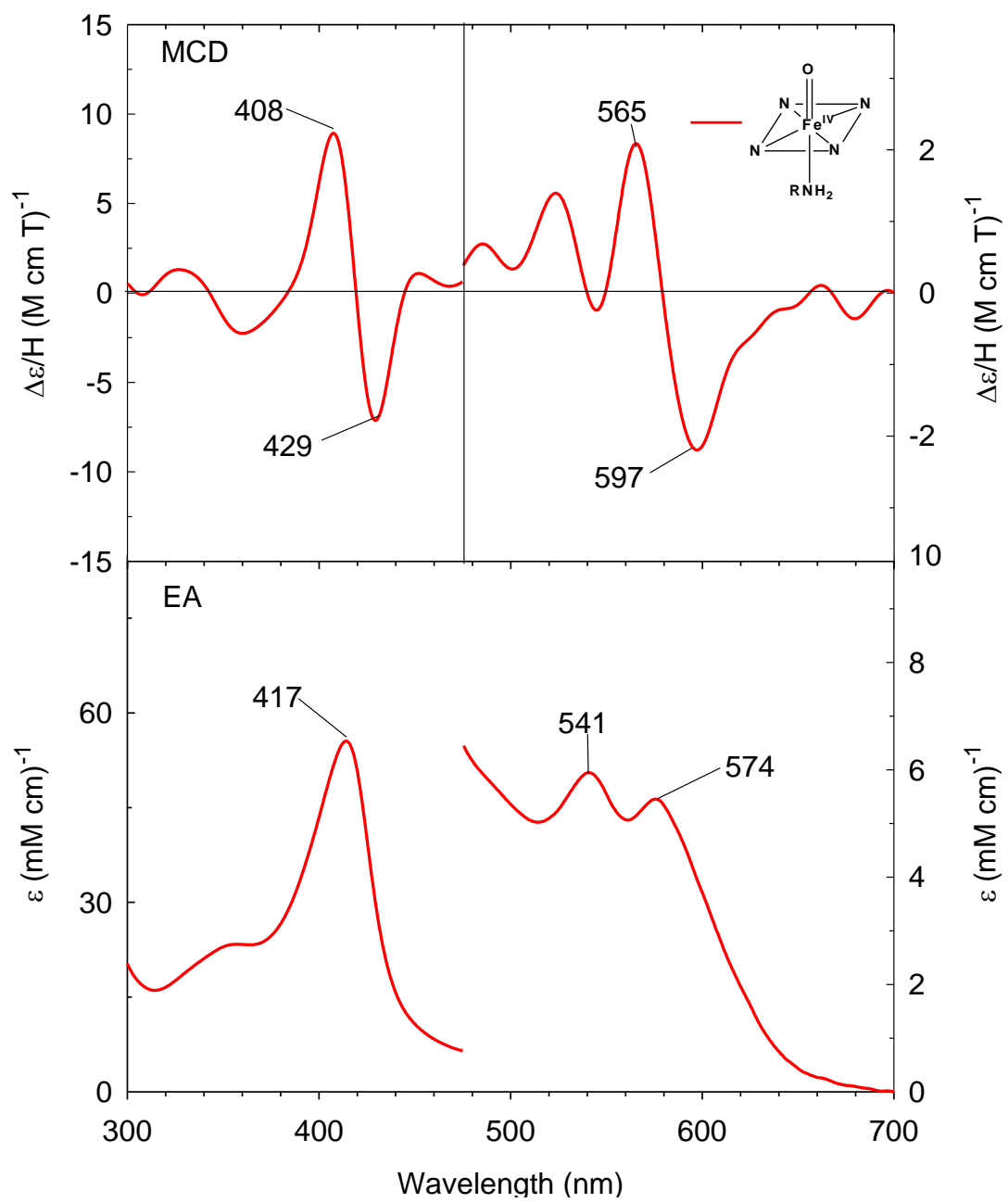


Figure S12

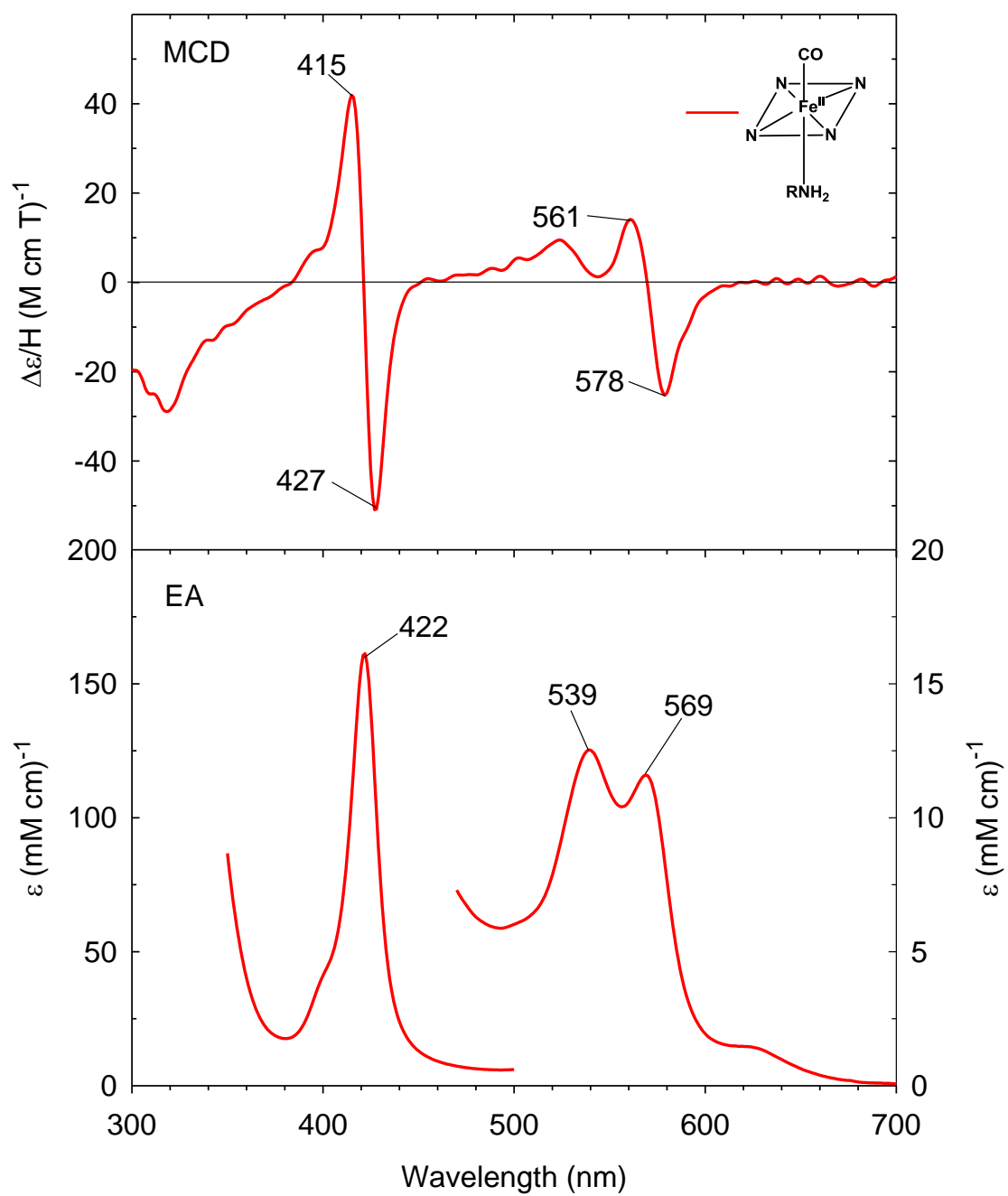


Figure S13