# Supplementary Information

## Proximal environment controlling the reactivity between inorganic sulfide and heme-peptide model

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### 1. Mass spectroscopy data

**Table. S1 Theoretical and observed molecular weight of DhHPs and DhAP-6**

| Samples | MS | |
|---|---|---|
| | Theory | Observation |
| DhHP-2 | 771.26 | 771.2995 |
| DhHP-3 | 872.31 | 872.3673 |
| DhHP-4 | 971.37 | 971.3175 |
| DhHP-5 | 1100.42 | 1100.4764 |
| DhHP-6 | 1228.51 | 1228.4230 |
| DhAP-6 | 1162.51 | 1162.4570 |

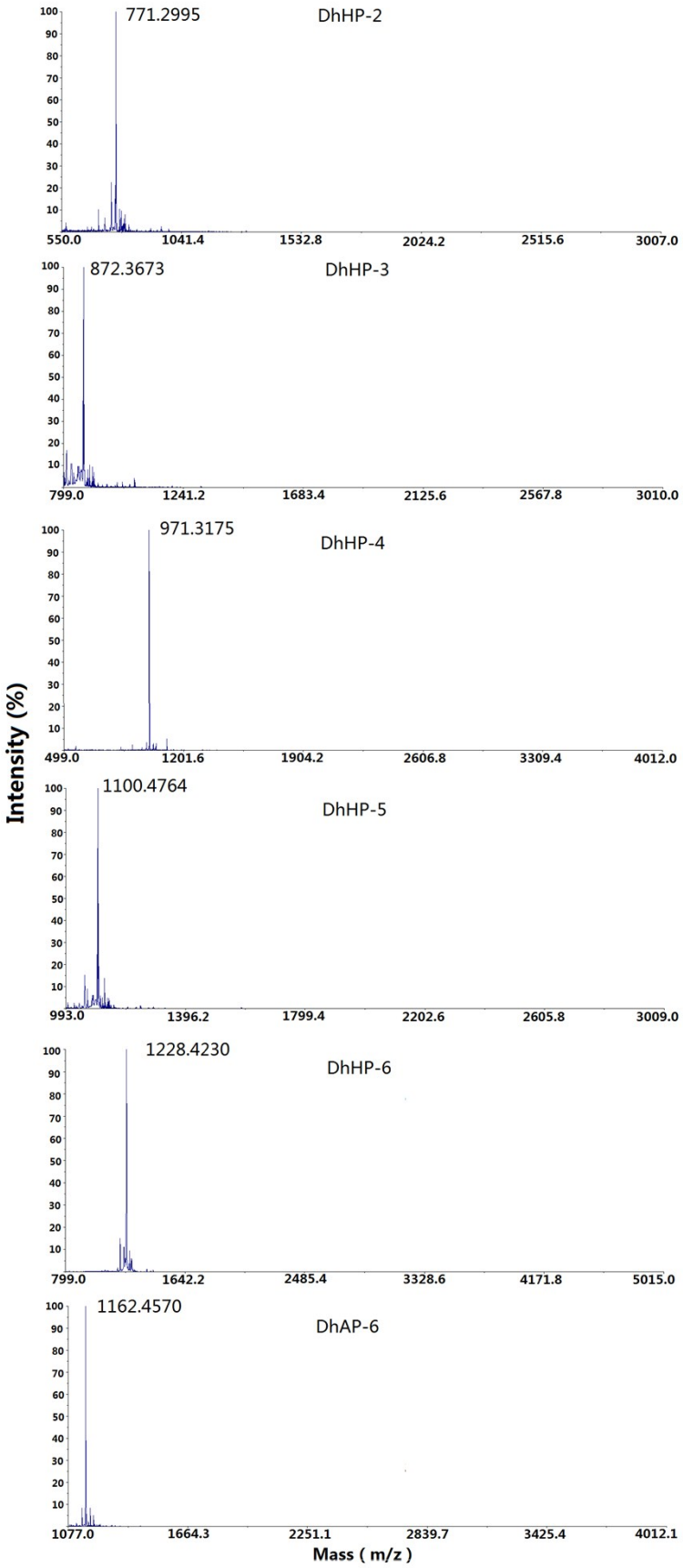


Fig. S1 MS spectra of DhHP-2, -3, -4, -5, -6 and DhAP-6 in the order from top to bottom.

## 2. UV–vis spectra of DhAP-6 after the reaction.

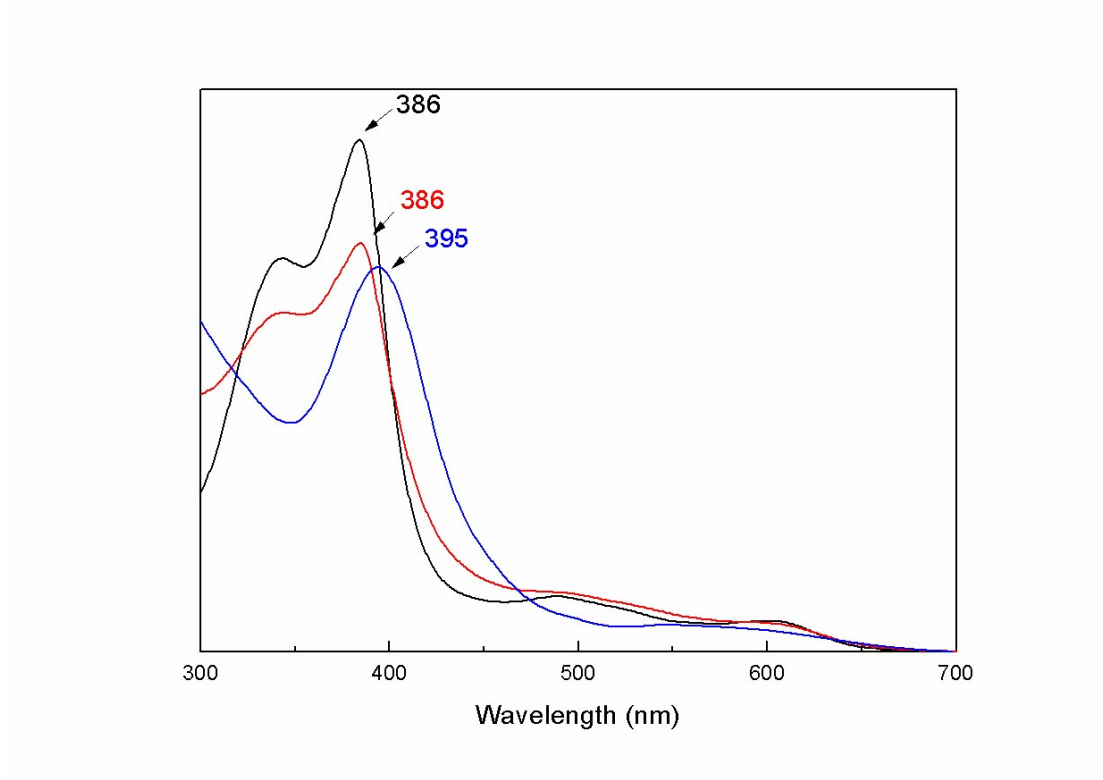


Fig. S2 UV–vis spectra of DhAP-6 in the absence of $H_2S/HS^-$ (black), after addition of $H_2S/HS^-$ for 2 min (red) and after addition of $H_2S/HS^-$ for 10 min (blue). Condition: DhAP-6 (5 μM) reacted with 20 μM $Na_2S$ in degassed PBS at pH 7.0 and 25 ℃.

## 3. Theoretical calculations of Mulliken atomic charges of ferric center in DhHPs

To gain more understanding of the association kinetic results listed in Table 1 and the effect of proximal hydrogen bond network on sulfide binding, We have employed density functional theoretical (DFT) calculations using the B3LYP functional.[1] Geometries and frequencies were generally computed using the LACVP*(Fe)/6-31G(d,p)(rest) basis set using Gaussian 09.[2]

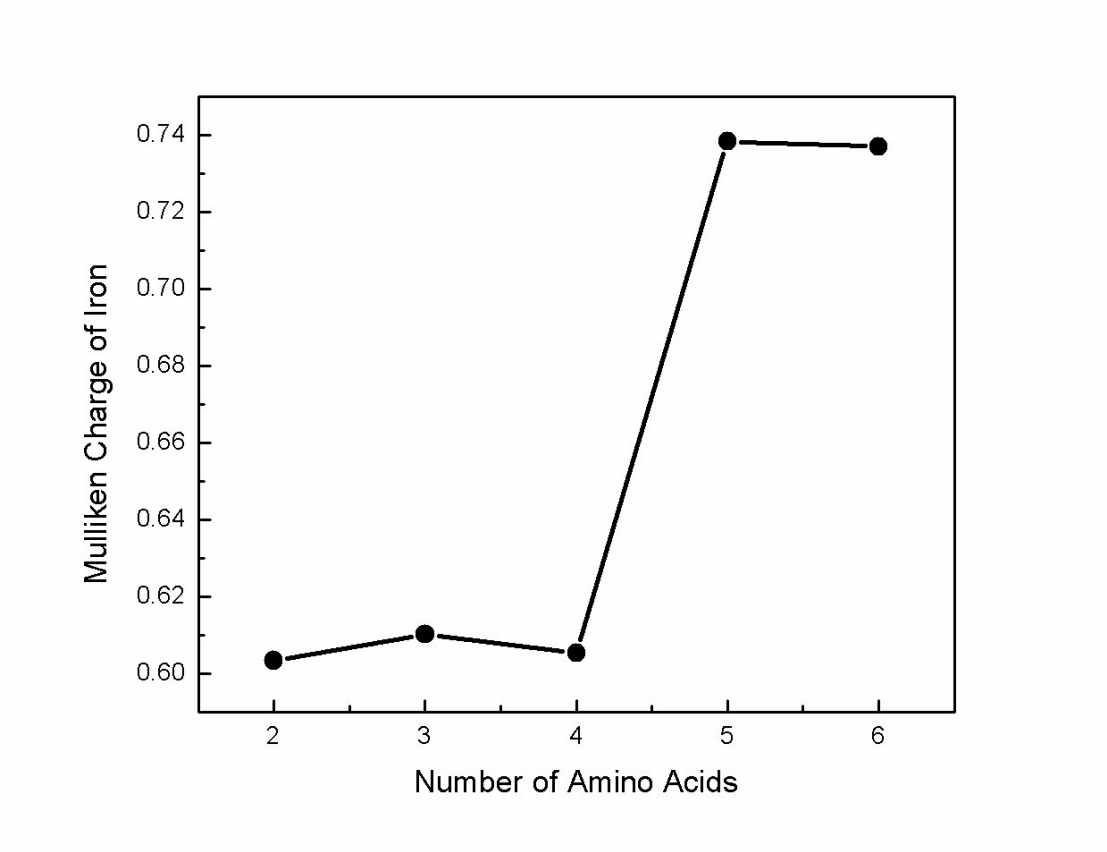


Fig. S3 Mulliken atomic charges of $Fe^{III}$ center in DhHPs where 2, 3, 4, 5, and 6 on x-axis are DhHP-2, -3, -4, -5 and -6 respectively

The DFT calculations have been performed on DhHP-2, DhHP-3, DhHP-4, DhHP-5 and DhHP-6. Fig. S2 reveals that Mulliken atomic charges showing a substantial increase, especially when the peptide length increased to 5 or 6. This increase agrees well with their larger association kinetic constants compared with the other DhHPs. We believe that the introduction of Glu5 in DhHP-5 or-6 does enhance the intensity of H-bond network as a consequence of high charge density on the ferric center to promote the sulfide coordination.

1. (a) Becke, A. D. J. Chem. Phys. 1992, 96, 2155−2160. (b) Becke,A. D. J. Chem. Phys. 1992,97, 9173−9177. (c) Becke, A. D. J. Chem.Phys. 1993, 98, 5648−5652. (d) Lee, C.; Yang, W.; Parr, R. G. Phys.Rev. B 1988, 37, 785−789.
2. Frisch, M. J. et al. Gaussian 09, Revision D01, Gaussian, Inc., Wallingford CT, 2009.