

Supplementary Information

Sensitive marker bands for the detection of spin states of heme in surface-enhanced resonance Raman scattering spectra of metmyoglobin

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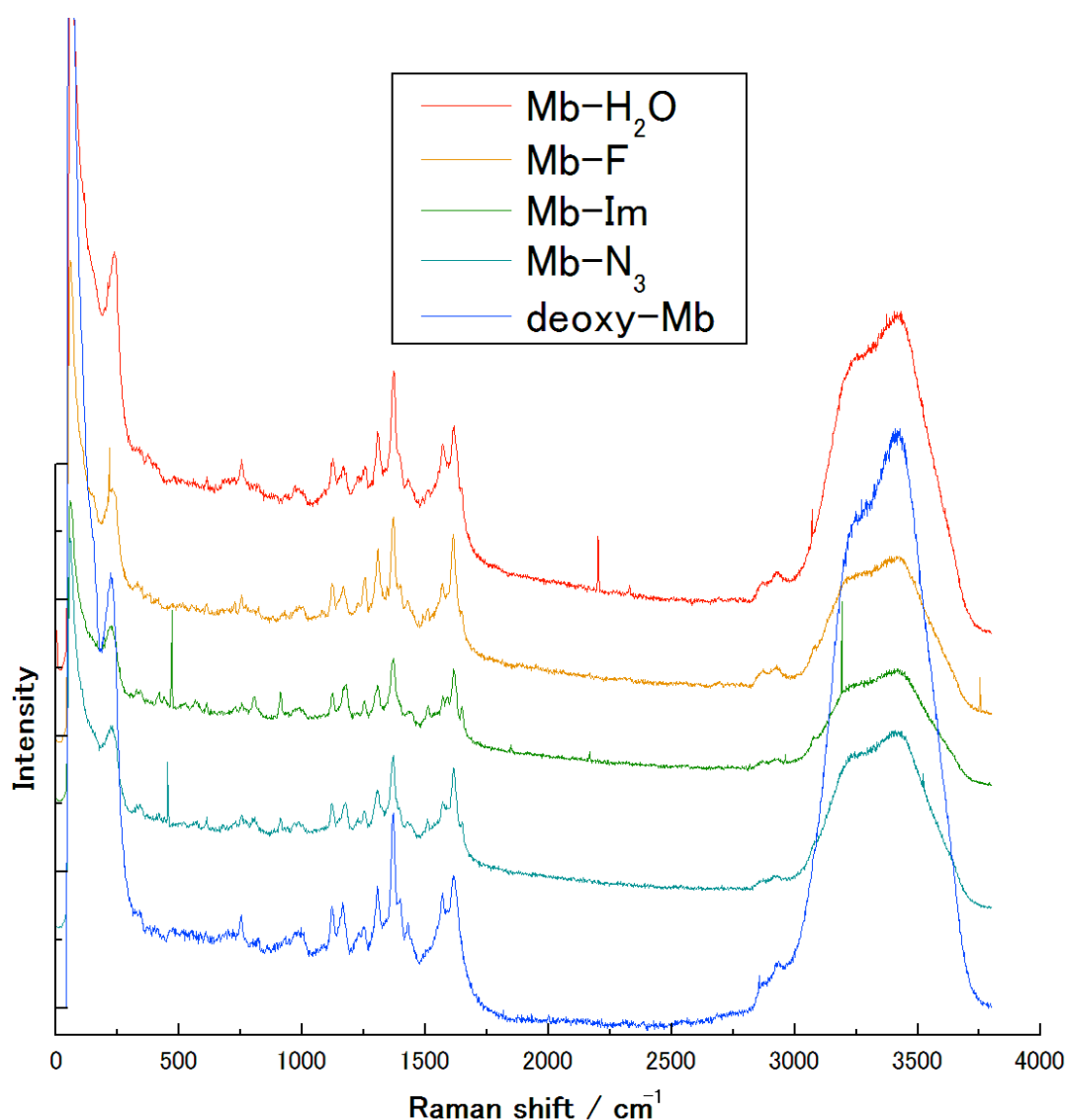


Figure S1 SERRS spectra of the various ligand-binding myoglobin. These were measured from the sample of met-Mb in the high spin state (Mb-H₂O and Mb-F), met-Mb in the low spin state (Mb-Im and Mb-N₃), and deoxy-Mb in the high spin state.

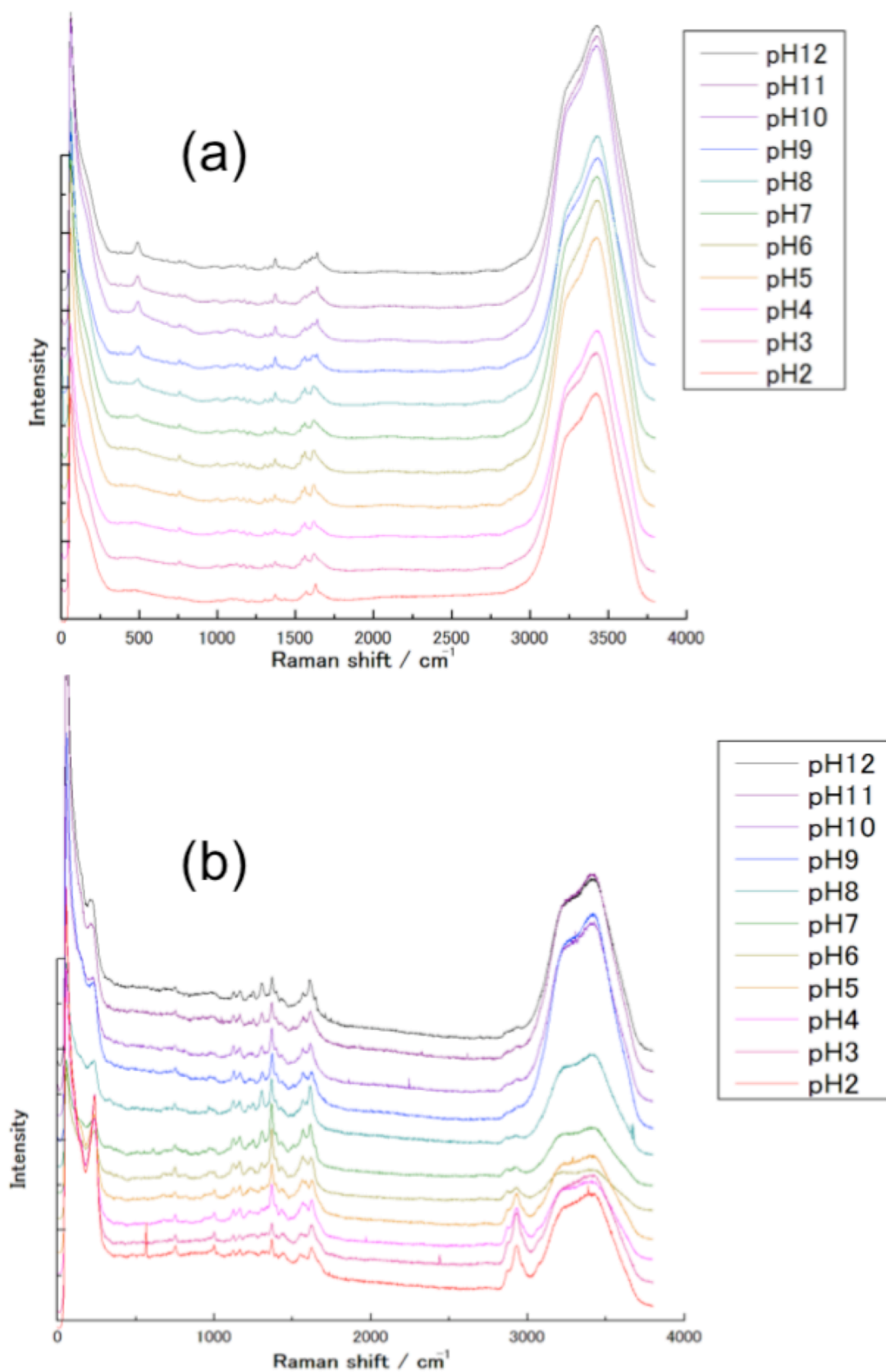


Figure S2 (a) Resonance Raman and (b) SERRS spectra of met-Mb in the low and high spin states (Mb-OH and Mb-H₂O, respectively) at pH from 12 (top) to 2 (bottom) at intervals of one.

It can be shown that the SERRS peaks around at 250 and 2800—3000 cm^{-1} were increased in the low spin state (Figure S1) and at $\text{pH} \leq 5$ (Figure S2b). Figure S2a shows that the peaks in the RRS spectra at $\text{pH} \geq 8$, which may be marker band for the low spin state, were observed around at 500 cm^{-1} . In the previous report,¹ the marker band appears at 677 cm^{-1} . These will be discussed elsewhere.

The SERRS peak intensity was defined as height from a datum line, which shown as a vertical arrow in Figure S3. The datum line was estimated by linear interpolation between the points at the bases of the peak, which shown as a broken line in Figure S3. For the peak at 1560 and 1620 cm^{-1} , we adopted the points around at 1520, 1600 and 1600, 1640 cm^{-1} , respectively. These points were local minima of the spectrum, which can be confirmed by local maxima of its second derivative. The intensity ratio is estimated in the range of the error bar in Figure 5 even by that we adopt different points at the bases of the peak, around at 1520, 1600, and 1640 cm^{-1} .

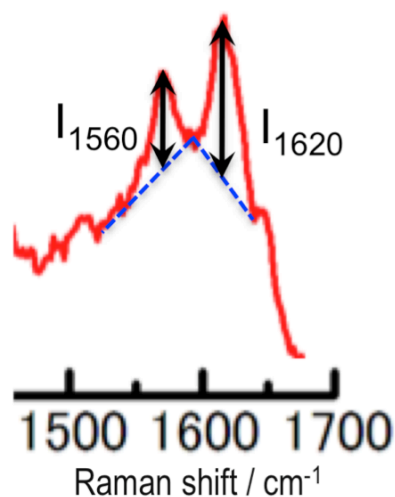


Figure S3 Schematics of estimation of the SERRS peak intensity at 1560 and 1620 cm^{-1} .

Reference for Supplementary Information

- 1 Y. Ozaki, T. Kitagawa and Y. Kyogoku, *FEBS Lett.*, 1976, **62**, 369–372.