Supporting Information

Electrocatalytic O_2-Reduction by Synthetic Cytochrome *c* Oxidase Mimics: Identification of a "Bridging Peroxo" Intermediate Involved in Facile $4e^-/4H^+$ O_2-Reduction

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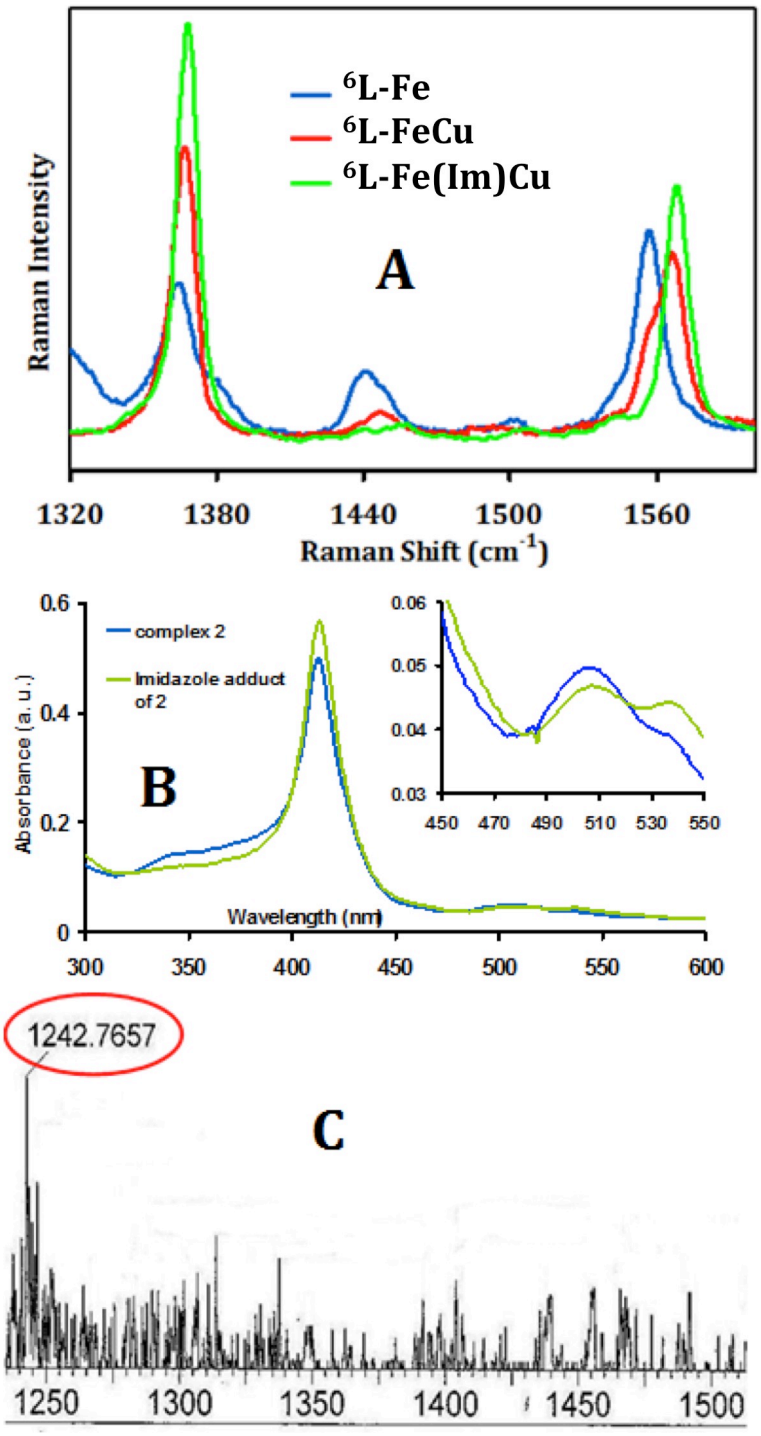

Figure S1. (A) Resonance Raman spectra for complex **1**, **2** and **3** in dichloromethane solution at room temperature using laser of 413.1 nm wavelength. (B) UV-Vis spectra for complex **2** and its imidazole adduct (**3**). (C) ESI mass spectrum of **3**,*m/z*= 1242. This is to be noted that in all the experiments, 1 equivalent of imidazole is added externally to the resting oxidized state of complex **2** to prepare complex **3** which has been further used for other electrochemical and spectroscopic experiments without any chemical treatment**.**

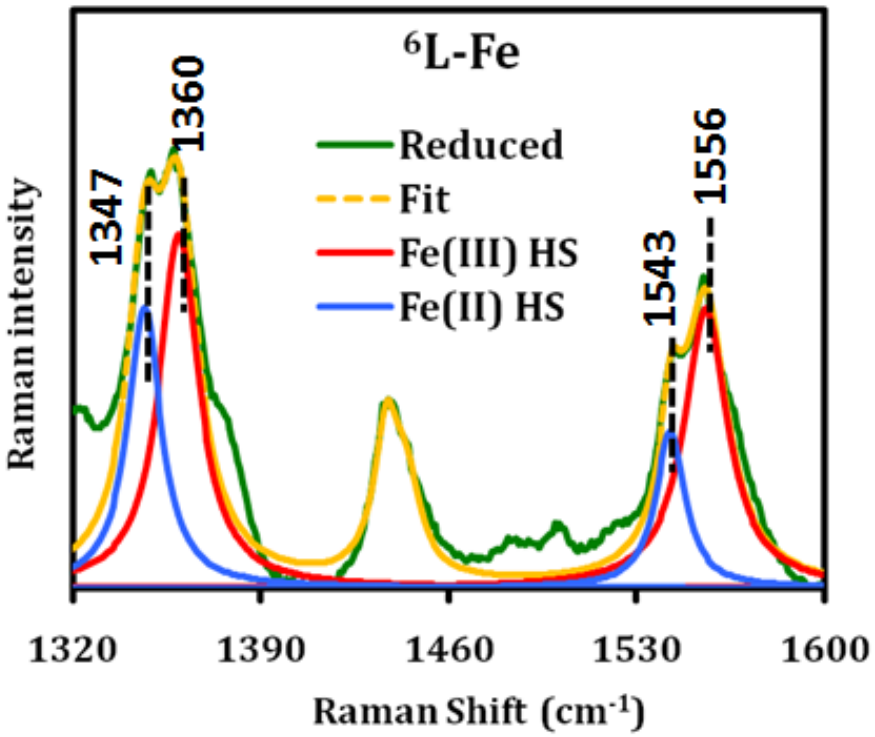

Figure S2. SERRS–RDE data of complex **1** under reduced condition in Ar atmosphere at constant rotation of 200 rpm. The oxidation state marker band (ν_4) and spin state marker band (ν_2) obtained at negative potential have been fit with different components using Lorentzian fit.

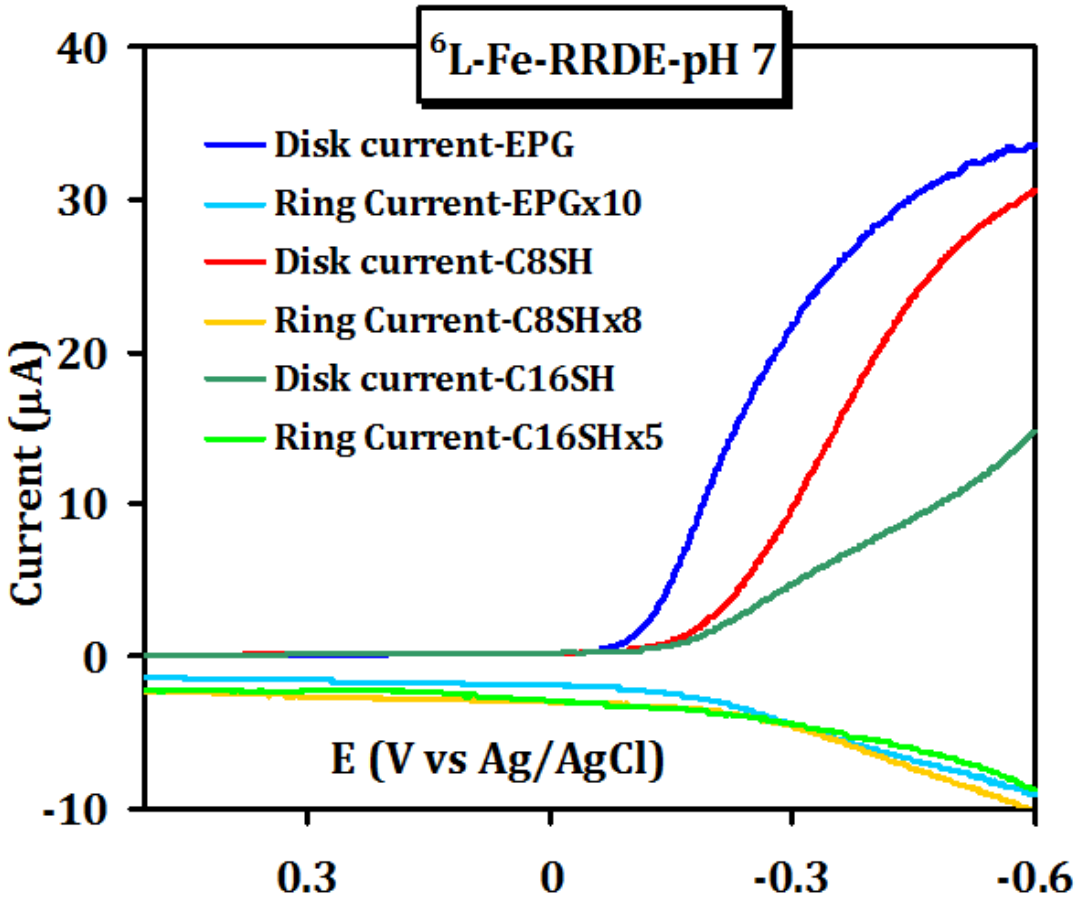

Figure S3. RRDE data of complex **1**, showing the disk and Pt ring currents, physiabsorbed on EPG (blue), C_8SH modified Au (red) and $C_{16}SH$ modified Au (green) in air saturated pH = 7 buffer at a scan rate of 10 mV/s and rotation speed of 300 rpm, using Ag/AgCl reference and Pt wire counter electrodes. The ring currents have been multiplied for better representation of the data.

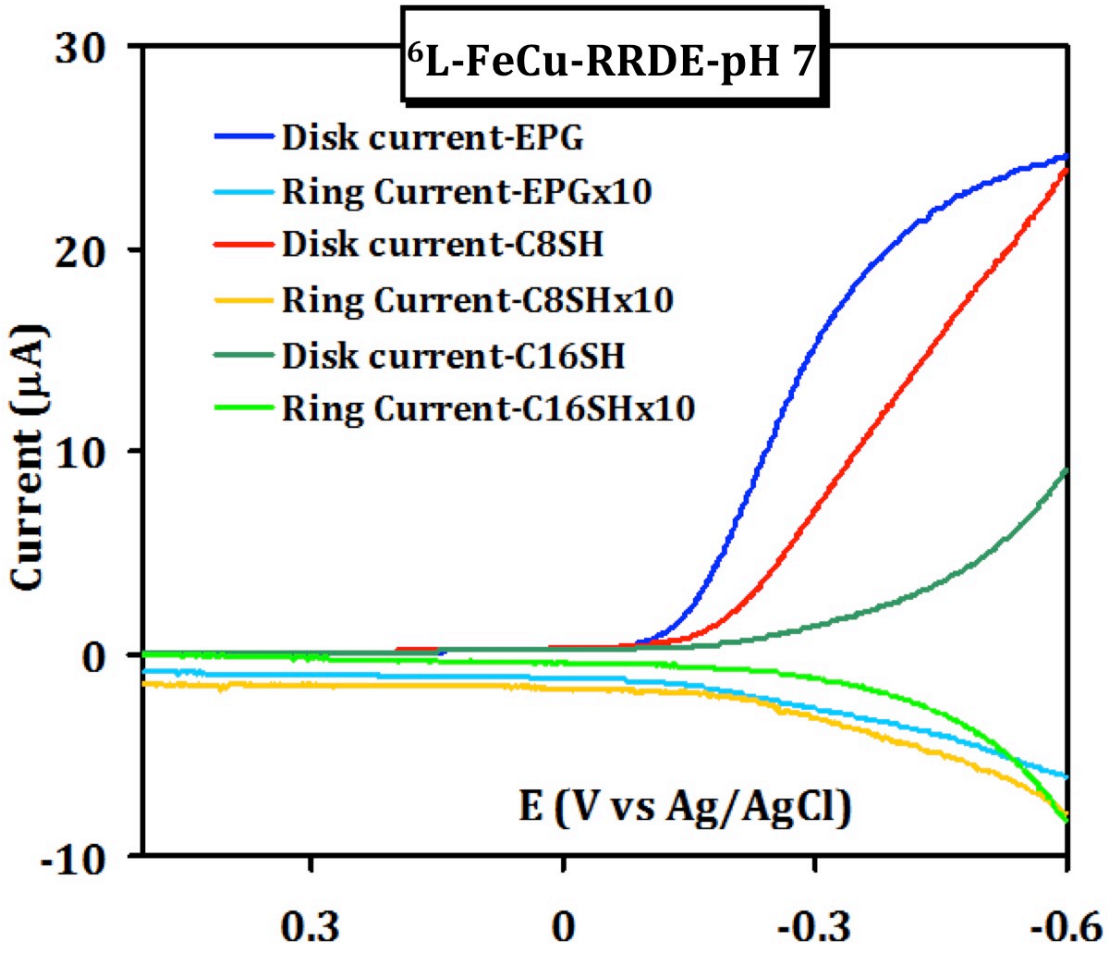

Figure S4. RRDE data of complex **2**, showing the disk and Pt ring currents, physiabsorbed on EPG (blue), C_8SH modified Au (red) and $C_{16}SH$ modified Au (green) in air saturated pH = 7 buffer at a scan rate of 10 mV/s and rotation speed of 300 rpm, using Ag/AgCl reference and Pt wire counter electrodes. The ring currents have been multiplied for better representation of the data.

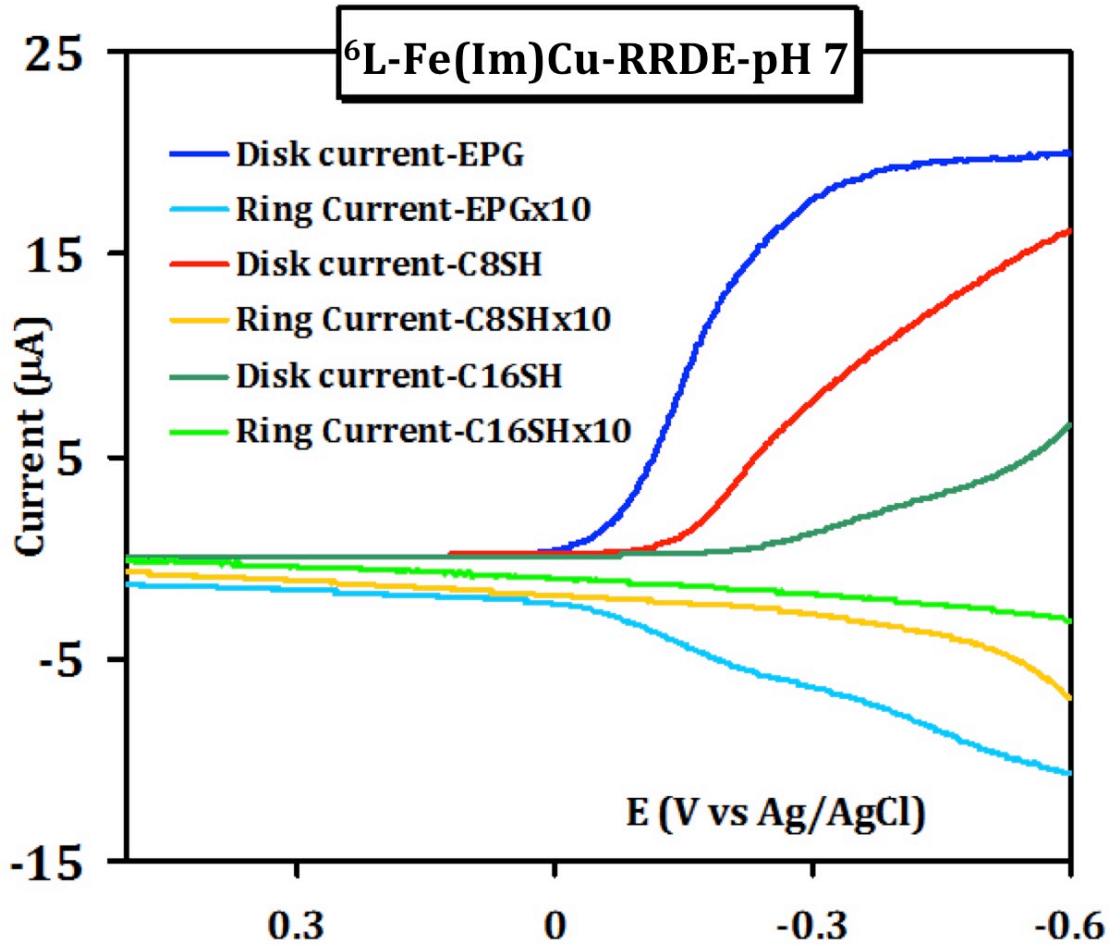

Figure S5. RRDE data of complex **3**, showing the disk and Pt ring currents, physiabsorbed on EPG (blue), C_8SH modified Au (red) and $C_{16}SH$ modified Au (green) in air saturated pH = 7 buffer at a scan rate of 10 mV/s and rotation speed of 300 rpm, using Ag/AgCl reference and Pt wire counter electrodes. The ring currents have been multiplied for better representation of the data.

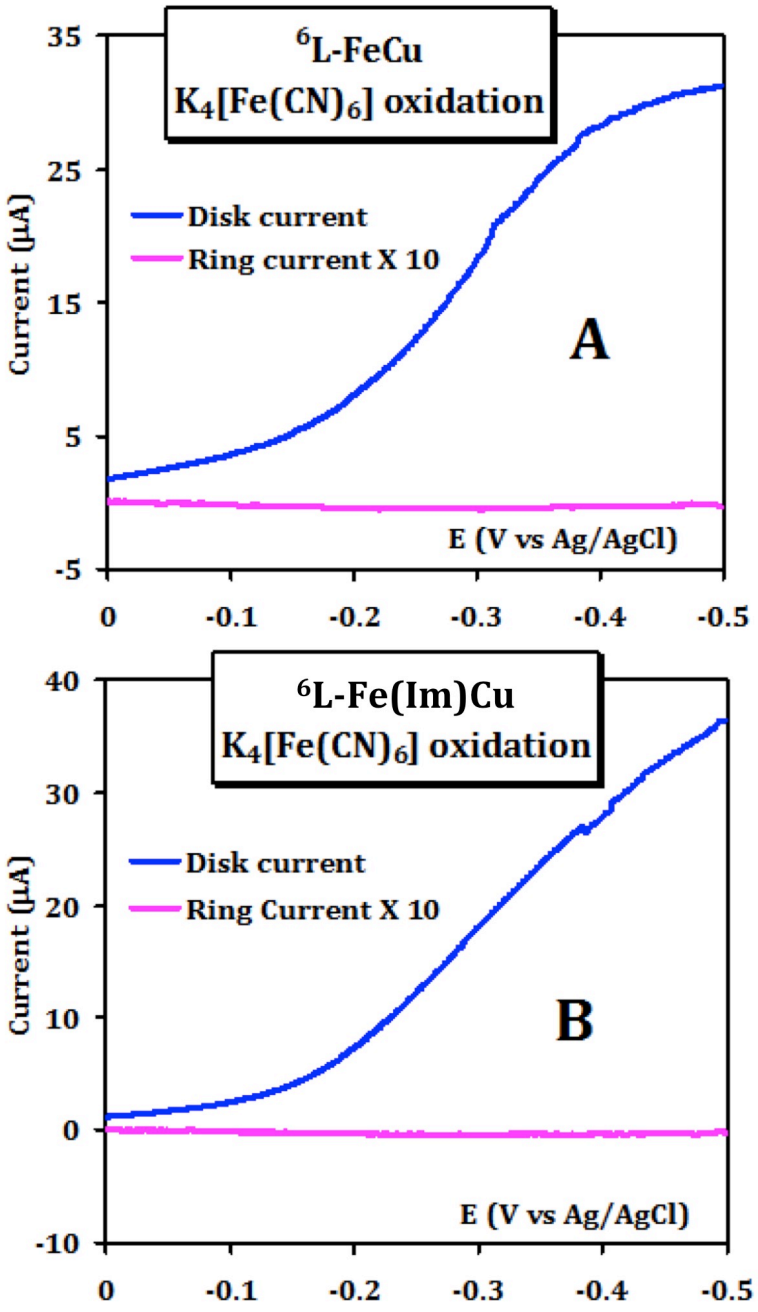

Figure S6. RRDE experiment of complex **2** (A) and **3** (B) when physiadsorbed on C_8SH modified Au surface in pH = 7 buffercontaining 10 mM $K_4[Fe(CN)_6]$using Ag/AgClas reference and Pt wire as counter electrodes.The Pt ring has been held at 0 V (vs Ag/AgCl).

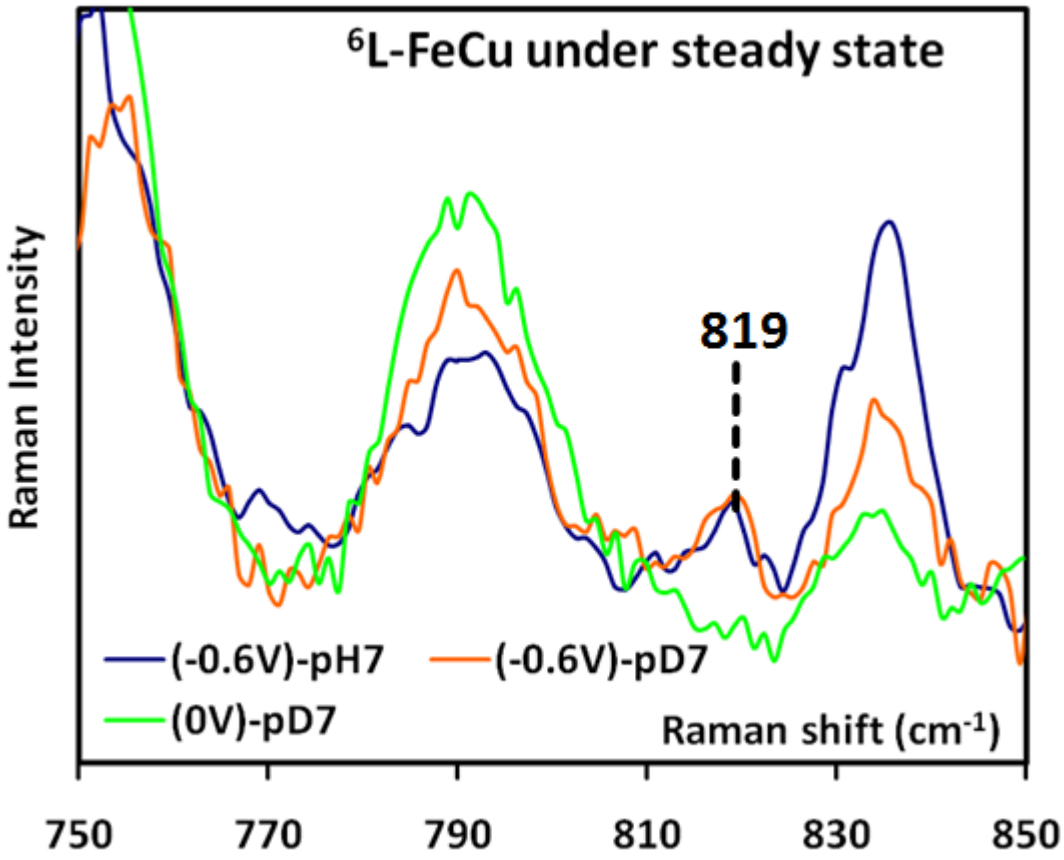

Figure S7. SERRS-RDE data in the low frequency region under oxidized (green) and steady state (blue for pH = 7 and orange for pD = 7) in the presence of pH = 7 and pD = 7 buffer for complex **2** on C_8SH modified Ag surfaces under constant rotation of 200 rpm.

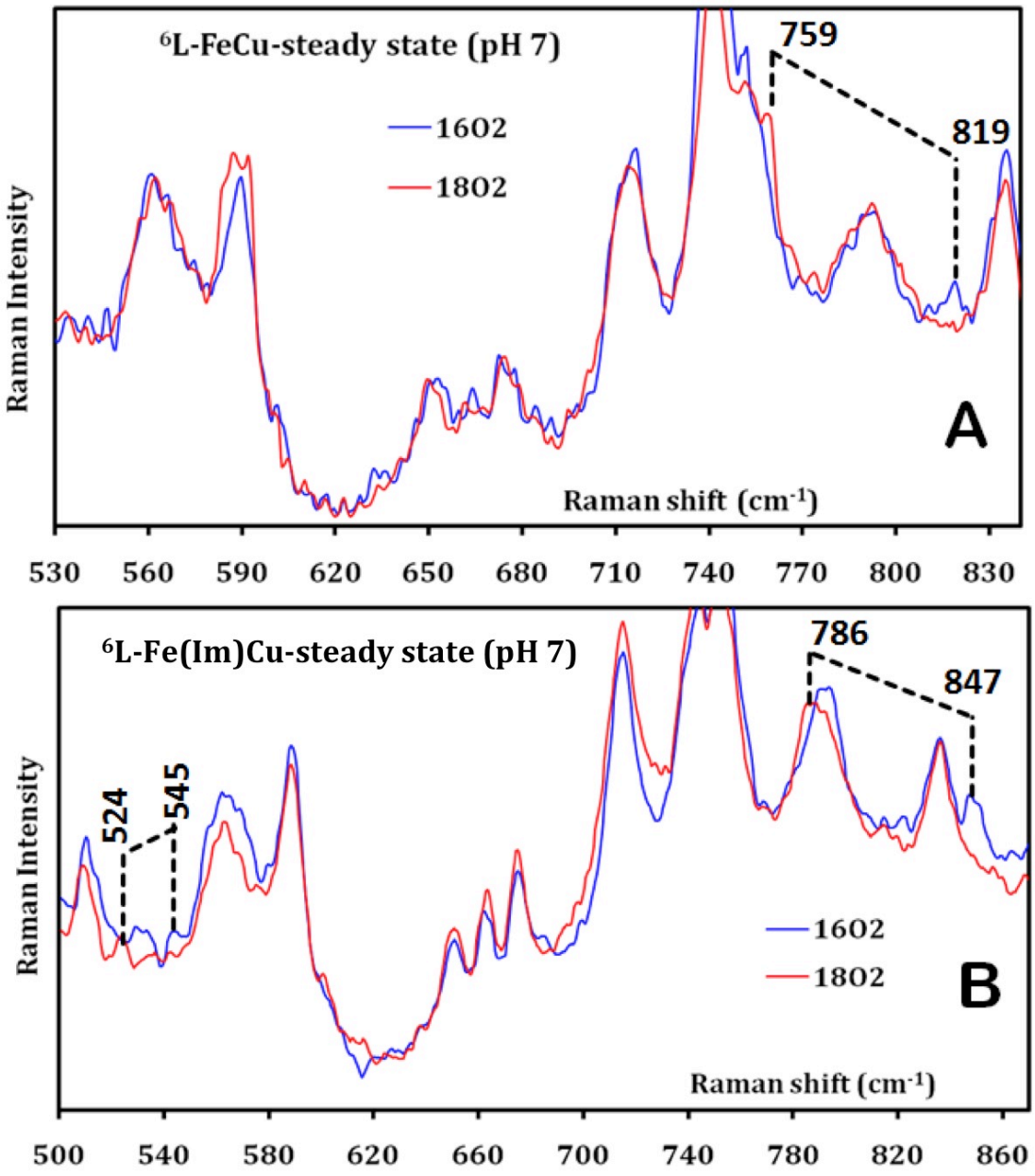

Figure S8. SERRS-RDE data in the low frequency region under steady state in the presence of air (blue) and $^{18}O_2$ (red) saturated pH = 7 buffer for complex **2** (A) and complex **3** (B) on C_8SH modified Ag surfaces showing the $\nu_{Fe\text{-}O/Cu\text{-}O}$ vibrations in the region 500-550 cm^{-1}.