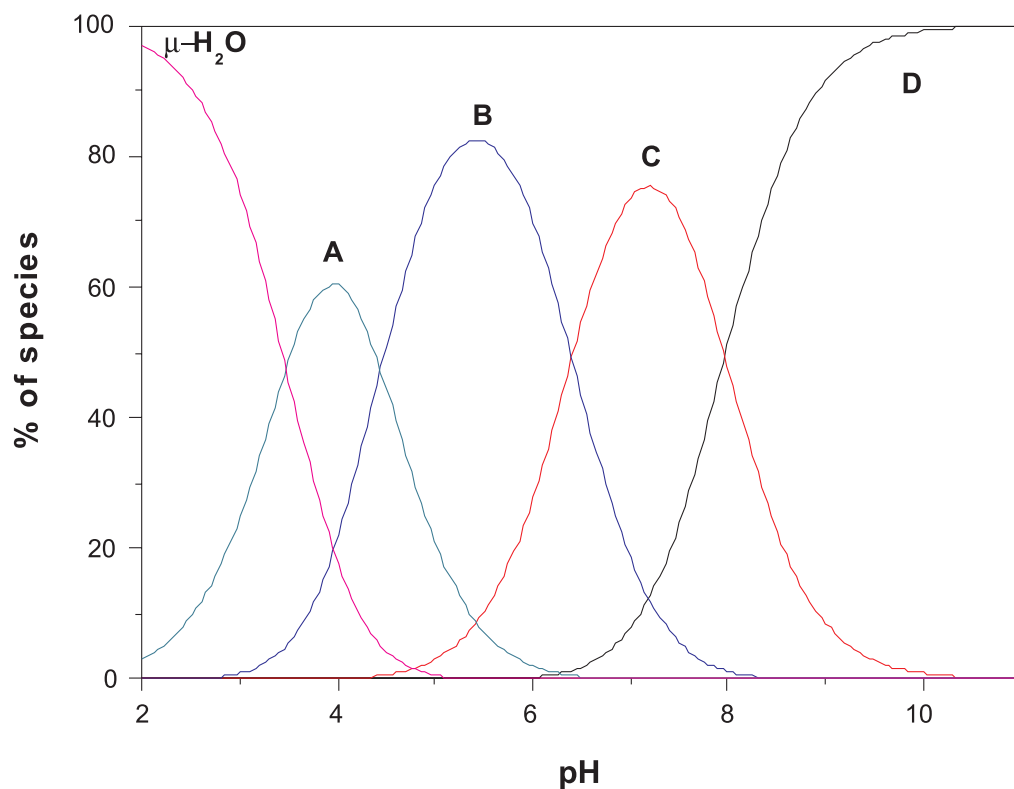


## Catalytic Promiscuity: Catecholase-like Activity and Hydrolytic DNA Cleavage Promoted by a Mixed-Valence Fe<sup>III</sup>Fe<sup>II</sup> Complex

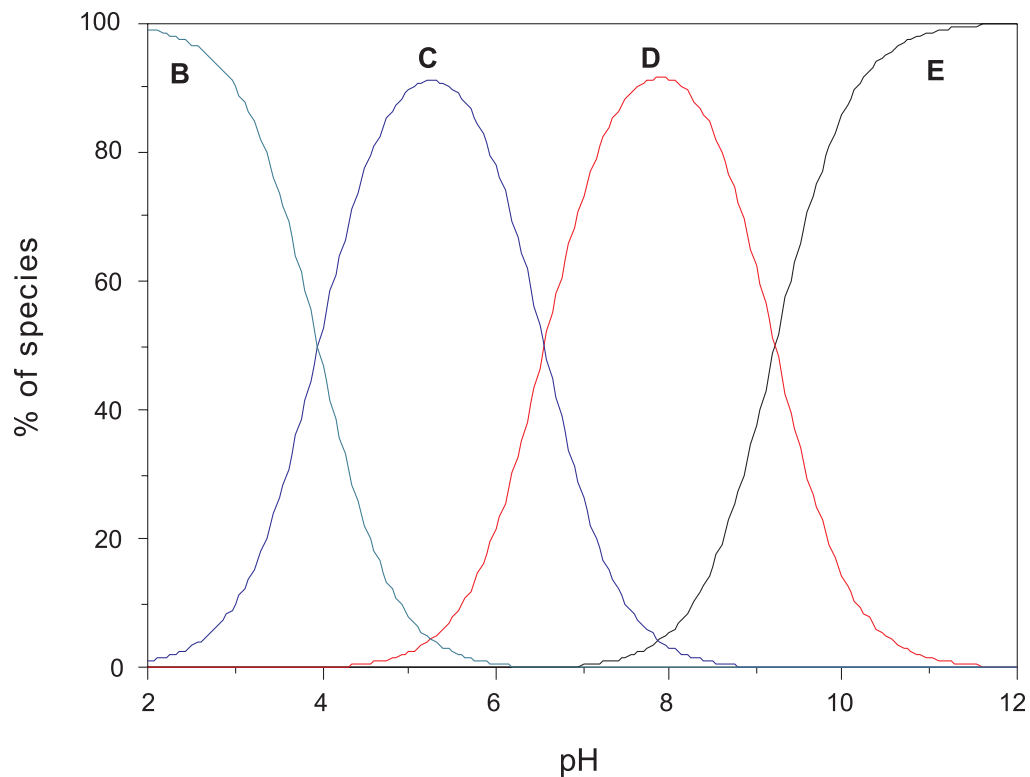
Ademir Neves,<sup>\*,a</sup> Adailton J. Bortoluzzi,<sup>a</sup> Rafael Jovito,<sup>a</sup> Rosely A. Peralta,<sup>a</sup> Bernardo de Souza,<sup>a</sup> Bruno Szpoganicz,<sup>a</sup> Antônio C. Joussef,<sup>a</sup> Hernán Terenzi,<sup>b</sup> Patricia C. Severino,<sup>b</sup> Franciele L. Fischer,<sup>b</sup> Gerhard Schenk,<sup>c</sup> Mark J. Riley,<sup>c</sup> Sarah J. Smith<sup>c</sup> and Lawrence R. Gahan<sup>c</sup>

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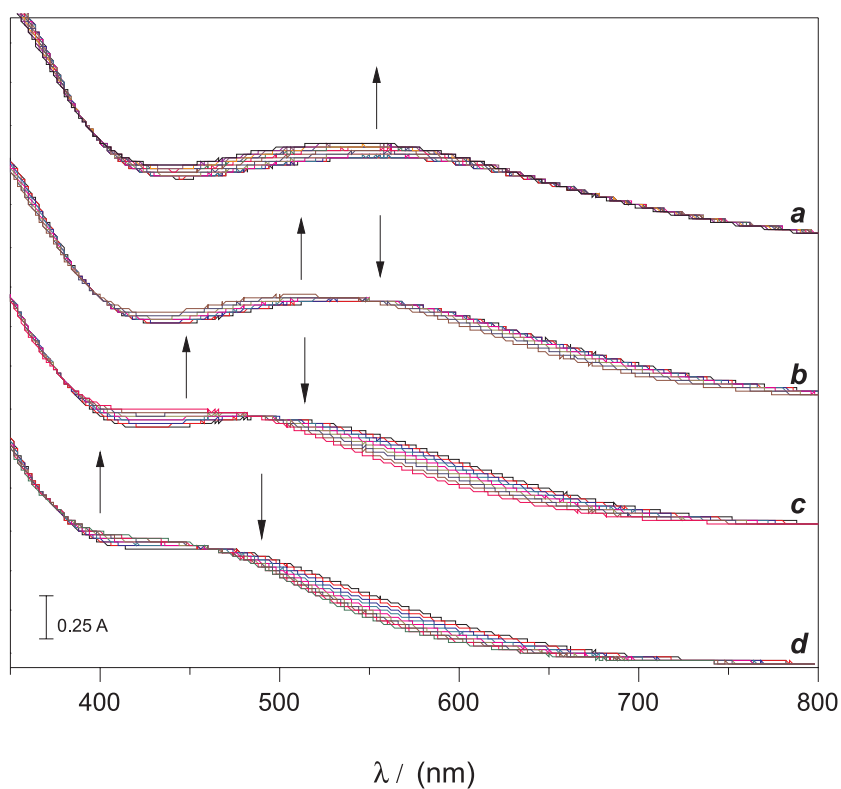
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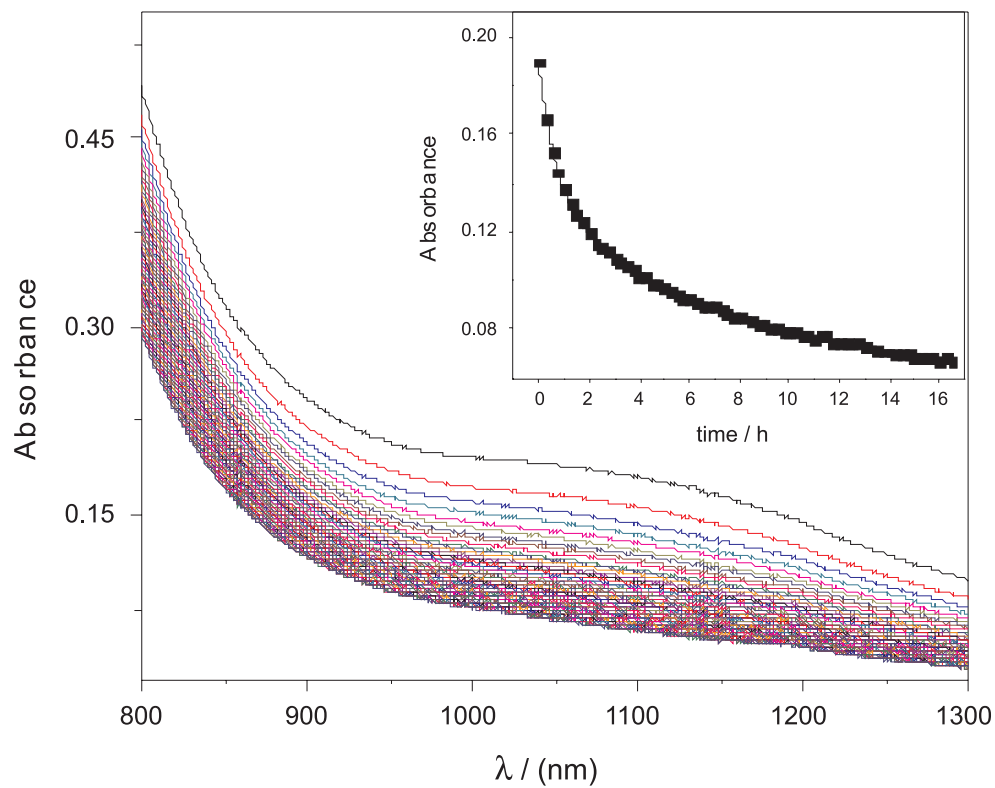
**Figure S1.** Species diagram for the spectrophotometric titration of complex  $[\text{Fe}^{\text{III}}(\text{bpbmp})(\mu\text{-OAc})_2\text{Fe}^{\text{II}}]^+$  in  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  1:1.  $\mu\text{-H}_2\text{O}$ :  $[(\text{OH}_2)\text{Fe}^{\text{III}}(\text{OH}_2)\text{Fe}^{\text{II}}(\text{OH}_2)]$ ; A:  $[(\text{OH}_2)\text{Fe}^{\text{III}}(\mu\text{-OH})\text{Fe}^{\text{II}}(\text{OH}_2)]$ ; B:  $[(\text{OH})\text{Fe}^{\text{III}}(\mu\text{-OH})\text{Fe}^{\text{II}}(\text{OH}_2)]$ ; C:  $[(\text{OH})\text{Fe}^{\text{III}}(\mu\text{-O})\text{Fe}^{\text{II}}(\text{OH}_2)]$ ; D:  $[(\text{OH})\text{Fe}^{\text{III}}(\mu\text{-O})\text{Fe}^{\text{II}}(\text{OH})]$ .



**Figure S2.** Species diagram for the spectrophotometric titration of complex  $[\text{Fe}^{\text{III}}(\text{bpbmp})(\mu\text{-OAc})_2\text{Fe}^{\text{III}}]^{2+}$  in  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  1:1. B:  $[(\text{OH})\text{Fe}^{\text{III}}(\mu\text{-OH})\text{Fe}^{\text{III}}(\text{OH}_2)]$ ; C:  $[(\text{OH})\text{Fe}^{\text{III}}(\mu\text{-O})\text{Fe}^{\text{III}}(\text{OH}_2)]$ ; D:  $[(\text{OH})\text{Fe}^{\text{III}}(\mu\text{-O})\text{Fe}^{\text{III}}(\text{OH})]$ ; E:  $[(\text{OH})\text{Fe}^{\text{III}}(\mu\text{-O})\text{Fe}^{\text{II}}(\text{OH}_2)]$ .



**Figure S3.** Spectral changes of the complex  $[\text{Fe}^{\text{III}}(\text{bpbmp})(\mu\text{-OAc})_2\text{Fe}^{\text{III}}]^{2+}$  during titration. The spectra were recorded on  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  1:1 at successive pH.  $[\text{complex}] = 3 \times 10^{-4} \text{ mol L}^{-1}$ . pH range *a*: 2.4-3.7; *b*: 3.6-4.7; *c*: 5.5-8.1; *d*: 8.1-10.9.



**Figure S4.** Spectral change of the intervalence band for the mixed-valence complex  $[\text{Fe}^{\text{III}}(\text{bpmpmp})(\mu\text{-OAc})_2\text{Fe}^{\text{II}}]^+$  over time under kinetic conditions: 3:2  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  at pH 7.0.  $[\text{complex}] = 4 \times 10^{-3} \text{ mol L}^{-1}$ ,  $[\text{buffer}] = 0.1 \text{ mol L}^{-1}$ . Inset: Decay of the absorbance at 1050 nm during 16 h.