

# Supplementary Information

## On the Inhibition of Hydroxyl Radical Formation by Hydroxycinnamic Acids: The Case of Caffeic Acid as Promising Chelating Ligand of Ferrous Ion

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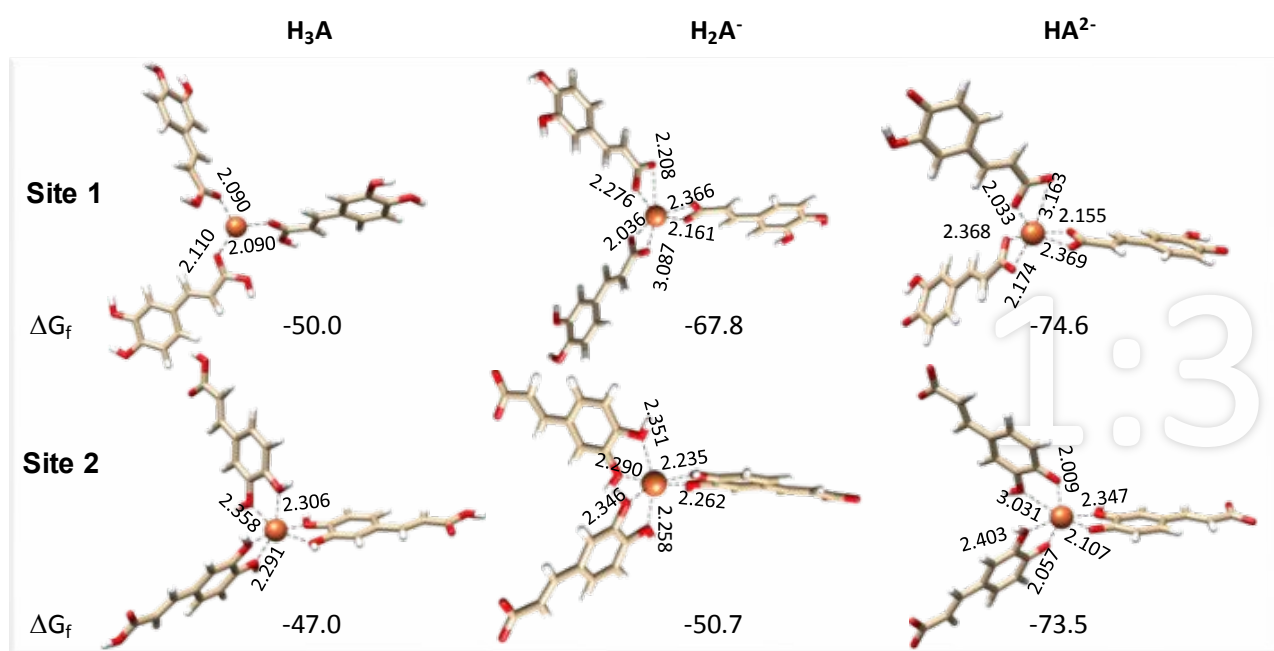
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Figure S1



**Table S1**

| <b>Comp.</b>                      | <b>MO contribution<sup>a</sup></b> | <b><math>\Delta E^b</math></b> | <b><math>\lambda^c</math></b> | <b><math>f^d</math></b> | <b>Exp<sup>e</sup></b> |
|-----------------------------------|------------------------------------|--------------------------------|-------------------------------|-------------------------|------------------------|
| <b>H<sub>3</sub>A</b>             |                                    |                                |                               |                         |                        |
|                                   | H → L (98%)                        | 3.70                           | 335                           | 0.565                   | 321                    |
|                                   | H-1 → L (82%)                      | 4.31                           | 287                           | 0.158                   | 292                    |
|                                   | H → L+1 (76%)                      | 5.10                           | 243                           | 0.352                   | 235                    |
| <b>H<sub>2</sub>A<sup>-</sup></b> |                                    |                                |                               |                         |                        |
|                                   | H → L (98%)                        | 4.04                           | 307                           | 0.582                   | 309                    |
|                                   | H-1 → L (48%); H → L+1 (48%)       | 5.22                           | 238                           | 0.472                   | 240                    |
|                                   | H-1 → L+1 (61%)                    | 5.81                           | 213                           | 0.238                   | 213                    |
| <b>HA<sup>2-</sup></b>            |                                    |                                |                               |                         |                        |
|                                   | H → L (98%)                        | 3.49                           | 355                           | 0.707                   |                        |
|                                   | H-1 → L (80%)                      | 4.90                           | 253                           | 0.332                   |                        |

<sup>a</sup> Only the transitions with high oscillator strengths  $f$  and molecular orbital contributions >10% are reported; <sup>b</sup> main excitation energies in eV; <sup>c</sup> absorption wavelengths in nm; <sup>d</sup> oscillator strengths in a.u.; <sup>e</sup> J.-P. Cornard, C. Lapouge. *A J. Phys. Chem. A*, 2006, 110, 7159-7166.

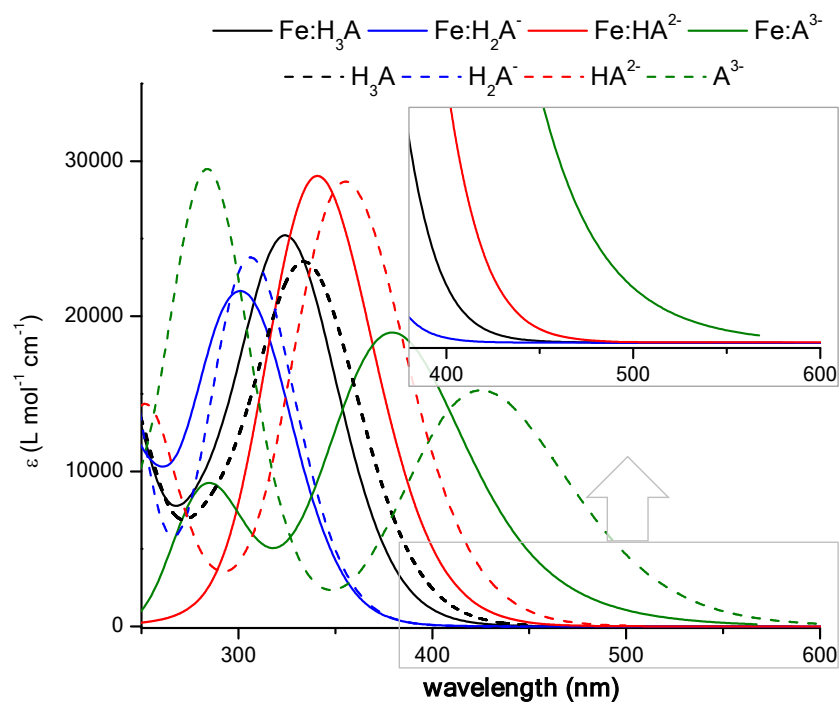
**Table S2**

| Comp.                                       | MO contribution <sup>a</sup>  | $\Delta E^b$ | $\lambda^c$ | $f^d$ |
|---|---|--------------|-------------|-------|
| <b>Fe:H<sub>3</sub>A site 2</b>             |   |              |             |       |
|   | H $\alpha$ $\rightarrow$ L $\alpha$ (49%); H-1 $\beta$ $\rightarrow$ L $\beta$ (49%)  | 3.80         | 326         | 0.601 |
|   | H-2 $\beta$ $\rightarrow$ L $\beta$ (43%)   | 4.37         | 341         | 0.118 |
|   | H-1 $\beta$ $\rightarrow$ L+4 $\beta$ (35%); H $\alpha$ $\rightarrow$ L+2 $\alpha$ (33%)  | 5.16         | 240         | 0.341 |
| <b>Fe:H<sub>2</sub>A<sup>-</sup> site 2</b> |   |              |             |       |
|   | H $\alpha$ $\rightarrow$ L $\alpha$ (47%); H-1 $\beta$ $\rightarrow$ L $\beta$ (49%)  | 4.11         | 301         | 0.599 |
|   | H-3 $\beta$ $\rightarrow$ L+1 $\beta$ (20%); H-3 $\beta$ $\rightarrow$ L $\beta$ (19%);<br>H $\alpha$ $\rightarrow$ L+2 $\alpha$ (17%); H-2 $\alpha$ $\rightarrow$ L $\alpha$ (17%) | 5.26         | 236         | 0.394 |
| <b>Fe:HA<sup>2-</sup> site 2</b>            |   |              |             |       |
|   | H-1 $\beta$ $\rightarrow$ L $\beta$ (14%); H-5 $\alpha$ $\rightarrow$ L $\alpha$ (9%)   | 3.57         | 348         | 0.124 |
|   | H $\alpha$ $\rightarrow$ L $\alpha$ (46%); H-1 $\beta$ $\rightarrow$ L $\beta$ (32%)  | 3.65         | 340         | 0.585 |
|   | H-1 $\beta$ $\rightarrow$ L+3 $\beta$ (78%)   | 4.10         | 302         | 0.082 |
| <b>Fe:A<sup>3-</sup> site 2</b>             |   |              |             |       |
|   | H $\beta$ $\rightarrow$ L $\beta$ (92%)   | 2.78         | 446         | 0.029 |
|   | H $\alpha$ $\rightarrow$ L $\alpha$ (48%); H-1 $\beta$ $\rightarrow$ L $\beta$ (47%)  | 3.26         | 380         | 0.431 |
|   | H-1 $\beta$ $\rightarrow$ L+2 $\beta$ (85%)   | 3.64         | 340         | 0.024 |

<sup>a</sup> Only the transitions with high oscillator strengths  $f$  and molecular orbital contributions >10% are reported;

<sup>b</sup> main excitation energies in eV; <sup>c</sup> absorption wavelengths in nm; <sup>d</sup> oscillator strengths in a.u.

**Figure S2**



**Table S3**

| Comp.                                       | MO contribution <sup>a</sup>   | $\Delta E^b$ | $\lambda^c$ | $f^d$ |
|---|--|--------------|-------------|-------|
| <b>Fe:H<sub>3</sub>A site 1</b>             |  |              |             |       |
|   | H $\beta$ $\rightarrow$ L $\beta$ (89%)  | 2.49         | 498         | 0.019 |
|   | H-1 $\beta$ $\rightarrow$ L $\beta$ (50%); H $\alpha$ $\rightarrow$ L $\alpha$ (48%)     | 3.63         | 341         | 0.594 |
|   | H-2 $\beta$ $\rightarrow$ L $\beta$ (45%); H-1 $\alpha$ $\rightarrow$ L $\alpha$ (38%)   | 4.25         | 292         | 0.178 |
| <b>Fe:H<sub>3</sub>A 1b</b>                 |  |              |             |       |
|   | H $\beta$ $\rightarrow$ L $\beta$ (84%)  | 2.45         | 506         | 0.038 |
|   | H-1 $\beta$ $\rightarrow$ L $\beta$ (52%); H $\alpha$ $\rightarrow$ L $\alpha$ (44%)     | 3.66         | 338         | 0.576 |
|   | H-2 $\beta$ $\rightarrow$ L $\beta$ (45%); H-1 $\alpha$ $\rightarrow$ L $\alpha$ (38%)   | 4.27         | 290         | 0.111 |
| <b>Fe:H<sub>2</sub>A<sup>-</sup> site 1</b> |  |              |             |       |
|   | H $\beta$ $\rightarrow$ L $\beta$ (86%)  | 2.63         | 472         | 0.263 |
|   | H $\alpha$ $\rightarrow$ L $\alpha$ (49%); H-1 $\beta$ $\rightarrow$ L $\beta$ (49%)     | 3.88         | 320         | 0.611 |
|   | H-2 $\beta$ $\rightarrow$ L $\beta$ (33%); H-1 $\alpha$ $\rightarrow$ L $\alpha$ (29%)   | 4.47         | 292         | 0.082 |
| <b>Fe:H<sub>2</sub>A<sup>-</sup> 1b</b>     |  |              |             |       |
|   | H $\beta$ $\rightarrow$ L $\beta$ (93%)  | 2.73         | 455         | 0.028 |
|   | H $\alpha$ $\rightarrow$ L $\alpha$ (48%); H-1 $\beta$ $\rightarrow$ L $\beta$ (49%)     | 3.97         | 312         | 0.607 |
|   | H-2 $\beta$ $\rightarrow$ L $\beta$ (31%); H-1 $\alpha$ $\rightarrow$ L $\alpha$ (28%)   | 4.51         | 275         | 0.054 |
| <b>Fe:HA<sup>2-</sup> site 1</b>            |  |              |             |       |
|   | H $\beta$ $\rightarrow$ L $\beta$ (93%)  | 2.82         | 440         | 0.049 |
|   | H-1 $\beta$ $\rightarrow$ L $\beta$ (43%); H $\alpha$ $\rightarrow$ L $\alpha$ (32%)     | 3.33         | 372         | 0.578 |
|   | H $\beta$ $\rightarrow$ L+7 $\beta$ (49%); H-1 $\alpha$ $\rightarrow$ L $\alpha$ (15%)   | 4.68         | 265         | 0.152 |
| <b>Fe:HA<sup>2-</sup> 1a</b>                |  |              |             |       |
|   | H $\beta$ $\rightarrow$ L $\beta$ (87%)  | 2.96         | 419         | 0.004 |
|   | H $\alpha$ $\rightarrow$ L $\alpha$ (45%); H-1 $\beta$ $\rightarrow$ L $\beta$ (50%)     | 3.32         | 373         | 0.752 |
|   | H $\alpha$ $\rightarrow$ L+4 $\alpha$ (28%); H-1 $\beta$ $\rightarrow$ L+6 $\beta$ (28%) | 4.26         | 291         | 0.007 |

<sup>a</sup> Only the transitions with high oscillator strengths  $f$  and molecular orbital contributions >10% are reported;

<sup>b</sup> main excitation energies in eV; <sup>c</sup> absorption wavelengths in nm; <sup>d</sup> oscillator strengths in a.u.