

Redox pathways in the carnosine–manganese system mediated by semiquinone radicals

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Abstract: The interaction of carnosine histidine containing dipeptide with the semiquinone radical of 3,4-dihydroxybenzoic dianion in dimethyl sulfoxide solution under aerobic conditions was investigated in the present study. The interaction of dipeptide–manganese system with the same semiquinone was also studied under the identical conditions. The metal-binding and redox chemistry of these systems were investigated using electronic, ESR, ¹H-NMR spectroscopies and cyclic voltammetry. The *in-situ* formal semiquinone radicals (extensively studied in previous works) were significantly modified upon addition of carnosine, as evidenced by the redistribution of the visible absorption bands and the change of the redox couples of the catecholic product. Subsequent influence of Mn ions induced further spectral and electrochemical changes, consistent with metal centered oxidation and formation of ligand-stabilized manganese species. Paramagnetic broadening in the ¹H-NMR spectra supported the presence of higher-valent Mn intermediates in solution. The combined data support a cooperative redox pathway in which semiquinone species mediate both peptide oxidation and Mn centered electron transfer. These results provide chemical insight into the understanding of multicomponent systems usually present in nature.

Keywords: carnosine; manganese; semiquinone radicals; catechol oxidation; ESR spectroscopy; cyclic voltammetry.

INTRODUCTION

L-Carnosine (β -alanyl-L-histidine) is a naturally occurring histidine-containing dipeptide widely distributed in excitable tissues such as skeletal muscle and brain. It has attracted considerable attention because of its buffering capacity,

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34 antioxidant activity, carbonyl scavenging properties and ability to coordinate tran-
35 sition-metal ions through the imidazole and carboxylate donor groups.^{1,2} These
36 physicochemical characteristics make carnosine an important model compound for
37 studying peptide-mediated redox and coordination processes in solution.

38 Catechol derivatives such as dihydroxybenzoic acids are well known to
39 undergo oxidation in the presence of dioxygen, generating semiquinone radicals
40 and quinonoid products through sequential one-electron transfer processes.^{3–5}
41 Such intermediates are of particular interest because they often display character-
42 istic visible absorption bands, persistent ESR signals and rich electrochemical
43 behavior. In addition, semiquinone species can participate in coupled reactions
44 with nucleophiles, peptides and transition-metal ions, thereby modifying both the
45 redox profile and coordination chemistry of multicomponent systems.⁶

46 Manganese is especially relevant in this context because it can access multiple
47 oxidation states under mild conditions, most commonly Mn(II) and Mn(III), and
48 frequently forms kinetically labile yet spectroscopically informative complexes
49 with O- and N-donor ligands.^{7–10} Redox-active manganese species are central to
50 many chemical transformations, while ligand environment strongly influences
51 their stability, electron-transfer behavior and reactivity toward oxygen-derived inter-
52 mediates.^{11,12} Accordingly, mixed systems containing manganese ions, cate-
53 chol-derived radicals and chemically relevant ligands provide useful models for
54 investigating cooperative electron-transfer pathways.

55 Despite the well-established metal-binding and antioxidant properties of car-
56 nosine, its behavior in radical-mediated manganese redox systems remains insuf-
57 ficiently understood, particularly under non-enzymatic conditions. In our previous
58 studies we have characterized the spectroscopic and electrochemical properties of
59 catechol-derived semiquinone systems and their redox transformations in solute-
60 ion.^{13,14} However, the interplay between such radical intermediates, peptide lig-
61 ands and manganese ions has not been systematically investigated.

62 In systems where catechol derivatives generate semiquinone species, complex
63 reaction pathways may arise involving simultaneous radical transformations, pep-
64 tide modification and metal-centered electron transfer. The present study addresses
65 this gap by examining the interactions among L-carnosine, Mn(II) ions and semi-
66 quinone radicals derived from 3,4-dihydroxybenzoic acid in a controlled chemical
67 environment. By combining spectroscopic (UV–Vis, ESR, ¹H-NMR) and electro-
68 chemical techniques, we aim to elucidate the redox pathways governing this multi-
69 component system and to define the role of semiquinone intermediates in medi-
70 ating manganese oxidation and peptide transformation.

71 It should be emphasized that the present study focuses on a simplified chem-
72 ical model system and does not attempt to directly reproduce enzymatic or bio-
73 logical conditions.

EXPERIMENTAL

Materials and instrumentation

All chemicals were used as received: L-carnosine (99 % crystalline, Sigma-Aldrich), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Merck), manganese(II) acetate tetrahydrate (Merck), tetrabutylammonium hexafluorophosphate (98 %, Fluka Chemical), tetrabutylammonium hydroxide 30-hydrate (Sigma-Aldrich), 2,3-dihydroxybenzoic acid (2,3-DHBA, Sigma-Aldrich), 3,4-dihydroxybenzoic acid (3,4-DHBA, Sigma-Aldrich), EtOH (min. 99.8 %, Carlo Erba), hydrogen peroxide (30 %, Merck), D_2O (99.90 % D, Eurisotop) and high-purity Argon (99.99 %).

UV-Vis spectra were recorded on Hitachi U-2000 and Varian Cary 3E spectrophotometers. IR spectra were recorded on a Perkin-Elmer 883 infrared spectrophotometer. ^1H - and ^{13}C -NMR spectra were recorded on a Varian Unity Plus 300 MHz instrument ($\pm 0.1^\circ\text{C}$). X-Band EPR (ESR) spectra were recorded at NCSR "Demokritos" on a Bruker ER-200D-SCR instrument equipped with an Oxford ESR 900 cryostat. Cyclic voltammetry (CV) was performed on a Pine Research Instrumentation Bipotentiostat (model AFCBP1). Elemental analysis (C, H, N) was carried out on a Perkin-Elmer 2400 analyzer. Raman spectra were obtained using a Renishaw inVia reflex Raman microscope (532 and 785 nm excitation).

Experimental procedures

For UV-Vis spectroscopy, a solution was prepared by dissolving 10 mg (0.065 mmol) of 3,4-DHBA in 25 mL of DMSO, followed by the addition of 0.100 g (0.125 mmol) of tetrabutylammonium hydroxide (TBAH). The UV-Vis spectra were recorded before and after the addition of 0.0147 g (0.065 mmol) of carnosine. Subsequently, 5 mL of a $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ solution (0.0129 g, 0.065 mmol) in DMSO was added. For comparison, the spectrum of a solution containing equimolar isolated carnosine-manganese complex was also recorded.

For EPR (ESR) spectroscopy, the spectrum of the 3,4-DHBA dianion ($c = 0.0065\text{ M}$) in DMSO was recorded at $T = 4.2\text{ K}$. Measurements were also performed at 4.2 and 13 K following the addition of an equimolar amount of carnosine (0.0147 g) to 10 mL of the initial solution.

Cyclic voltammetry (CV) measurements involved adding 3 mg (0.020 mmol) of 3,4-DHBA to 20 mL of 0.1 M tetrabutylammonium chloride (TBAC) in DMSO, followed by 32 mg (0.040 mmol) of TBAH. Voltammograms were obtained for the initial solution, after the addition of 4.5 mg (0.020 mmol) of carnosine, and after adding 4 mg (0.02 mmol) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. The electrochemical behavior of the isolated carnosine-Mn complex was also studied using a three-electrode setup: graphite (working), platinum/gold (auxiliary) and Ag/AgCl (reference).

^1H -NMR spectra were obtained by adding carnosine ($c = 0.0065\text{ mmol L}^{-1}$) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ($c = 0.0065\text{ mmol L}^{-1}$) gradually to a solution of 3,4-DHBA/TBAH in $\text{DMSO}-d_6$. Spectra were collected at each titration step. Finally, a spectrum was recorded for a solution containing the isolated carnosine-Mn complex (Mn/carnosine 1:1) in a 1:2 mixture of 3,4-DHBA/TBAH in $\text{DMSO}-d_6$.

Spectra were processed uniformly for baseline correction and visualization purposes without altering the analytical content.

RESULTS AND DISCUSSION

UV-Vis and ESR spectroscopy

The dianionic form of 3,4-DHBA prepared in DMSO under aerobic conditions exhibits broad visible absorption bands centered at 672, 676 and 706 nm (Fig. S-1 of the Supplementary material to this paper). These features are consistent with the

formation of oxygen-stabilized semiquinone radicals arising from catechol oxidation, where overlapping mono- and di-ionized forms contribute to the observed spectral envelope.^{3–5} Additional shoulders in the 320–400 nm region and a strong transition near 300 nm can be attributed to $\pi \rightarrow \pi^*$ excitations associated with partial oxidation of the aromatic framework.^{4,15}

Addition of equimolar carnosine produces an immediate color change to deep purple and generates new absorption bands at approximately 500 and 590 nm (Fig. S-2 of the Supplementary material). The redistribution of visible absorption bands, accompanied by increased molar absorptivity, indicates the formation of a new redox-active species involving chemical interaction between semiquinone intermediates and carnosine. The persistence of semiquinone- and quinonoid-type features suggests that the process involves redox coupling rather than simple radical quenching.⁶

Introduction of Mn^{2+} results in further spectral evolution, producing a brown–yellow solution with weak extended visible absorption (Fig. 1). These features are consistent with the formation of Mn(III) species, likely stabilized through coordination with oxygen- and nitrogen-donor ligands present in the system. Comparable spectral behavior observed after addition of the isolated carnosine–manganese complex (solid 24, Fig. S-3 of the Supplementary material)²⁵ further supports the formation of electronically coupled Mn-containing intermediates.

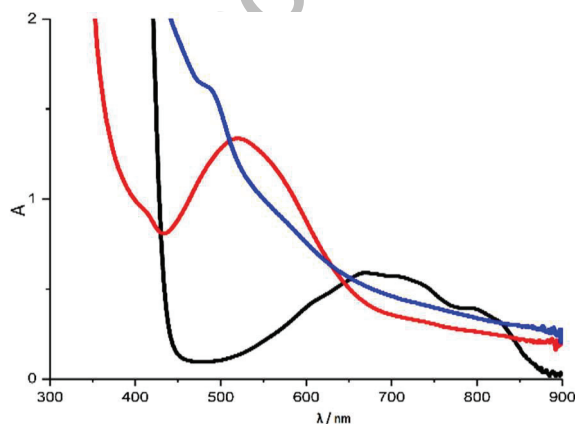


Fig. 1. Electronic spectra of 3,4-DHBA dianion in DMSO (black line), upon addition of carnosine (1:1 ratio, red line) and subsequent addition of equimolar $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (blue line).

A solution of 3,4-DHBA dianion in DMSO under aerobic conditions exhibits a strong ESR signal characteristic of a radical species (Fig. 2). The signal remains largely unchanged upon increasing the temperature to 15 or 30 K, indicating appreciable persistence of the paramagnetic intermediate under the experimental conditions.

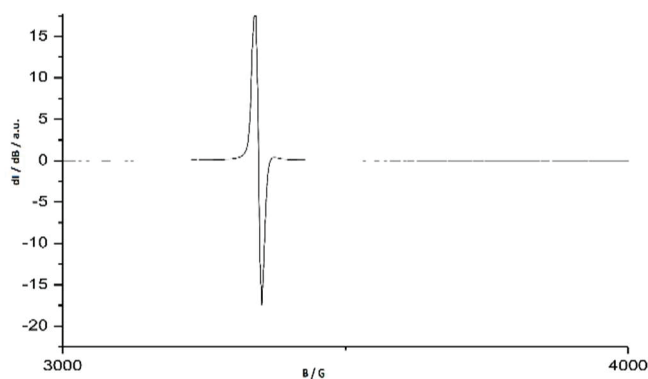


Fig. 2. ESR spectrum of a cyan solution of the 3,4-DHBA dianion ($c = 0.0065$ M) in DMSO under aerobic conditions, recorded at $T = 4.2$ K. Microwave power 0.3 mW, modulation amplitude 1.0 G, receiver gain 26 dB.

The addition of carnosine to the radical-containing solution in a 1:1 mole ratio leads to measurable changes in the ESR spectrum (Fig. 3), indicating interaction between the semiquinone species and the dipeptide. These observations indicate chemical transformation of the radical species upon interaction with carnosine, supporting the involvement of semiquinone intermediates in subsequent redox processes.

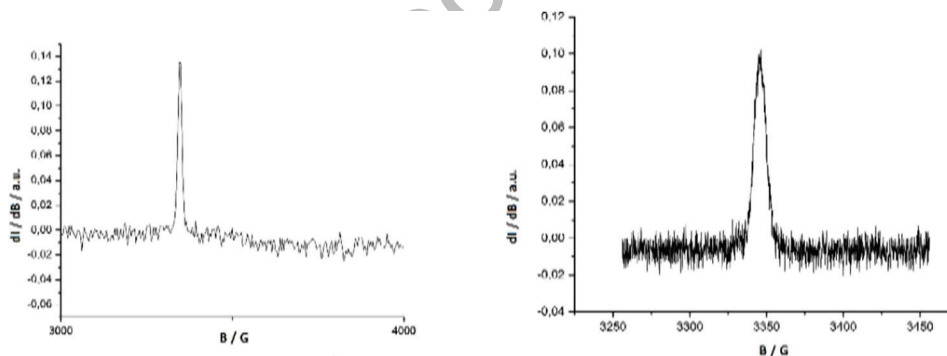
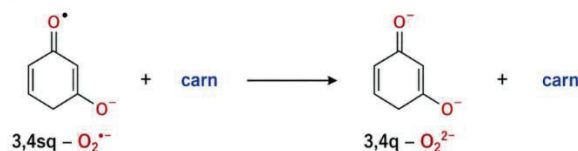
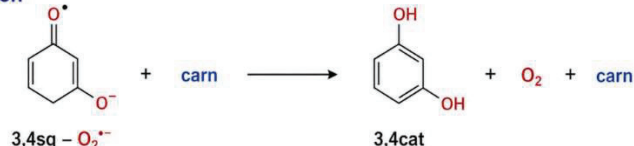


Fig. 3. ESR spectra of a green DMSO solution containing the 3,4-DHBA dianion ($c = 0.0065$ M) and carnosine ($c = 0.0065$ M) recorded at: A) 4.2 and B) 13 K. Microwave power 0.3 mW, modulation amplitude 1.0 G, receiver gain 26 dB.

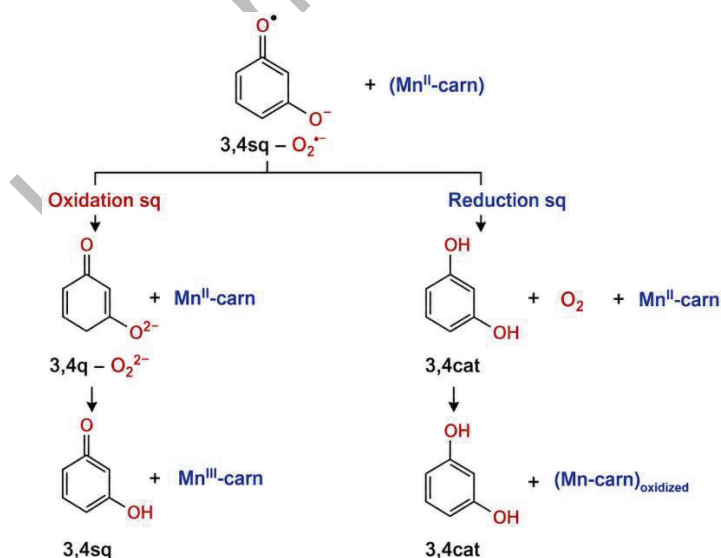
If the reaction between the radical and the dipeptide involves reduction of the semiquinone species (e.g., in a superoxide-associated form, $3,4\text{-SQ}^{\bullet}\text{-O}_2^-$), Scheme 1, regeneration of the catechol form of DHBA would be expected. In such a case, partial decolorization of the solution might occur, as catechol derivatives

typically exhibit weak absorption in the visible region, while the released molecular oxygen would not be expected to react rapidly with carnosine under the present conditions.

Oxidation**Reduction**

Scheme 1. Proposed reaction pathways for the interaction between 3,4-DHBA semiquinone radical and carnosine, illustrating the competitive oxidative and reductive routes.

Conversely, if the process involves oxidation of the semiquinone, Scheme 2, formation of the corresponding quinone species and hydrogen peroxide is plausible. Both species are known to participate in oxidative reactions with nucleophilic sites of peptides, including the imidazole moiety of carnosine. Under these conditions, the development of brown-green coloration is expected, consistent with the experimental observations.



Scheme 2. Proposed mechanism for the metal-assisted electron transfer between 3,4-DHBA semiquinone and the Mn(II)-carnosine complex.

The oxidative pathway likely involves the formation of a semiquinone–carnosine intermediate, which may facilitate interaction with dioxygen-derived species and contribute to charge-transfer stabilization within the system.

Electrochemical behavior

Cyclic voltammetry (CV) of the 3,4-DHBA dianion reveals two well-defined quasi-reversible redox couples (Fig. S-4 of the Supplementary material), consistent with sequential one-electron catechol/semiquinone/quinone transformations.¹ The peak separation suggests moderately fast electron transfer with partial chemical follow-up reactions, likely involving oxygen coordination.

Upon addition of equimolar carnosine, a positive shift in the first redox couple is observed, accompanied by an irreversible oxidation wave at 0.68 V (Fig. 4). This behavior indicates that carnosine perturbs the redox equilibrium through chemical coupling rather than simple hydrogen bonding. The irreversible feature can be attributed to oxidative modification of the imidazole-containing dipeptide or formation of electrochemically unstable quinonoid adducts.

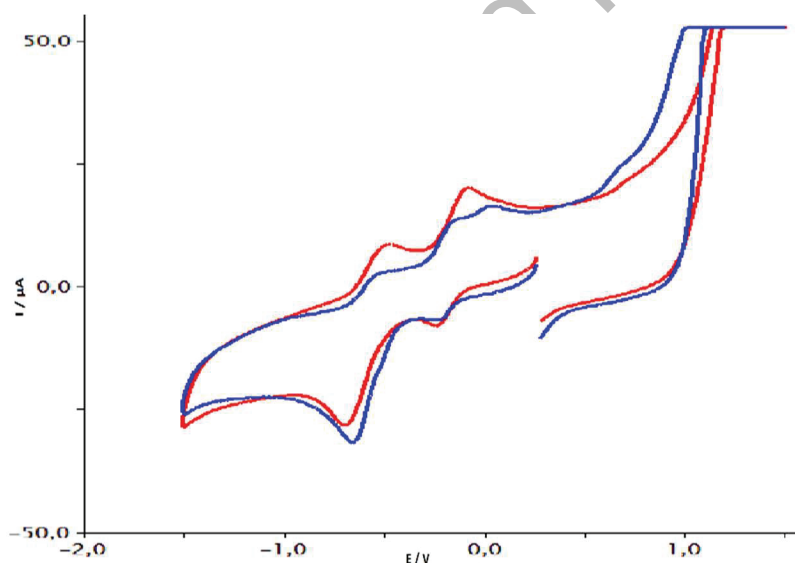


Fig. 4. Cyclic voltammograms of 3,4-DHBA dianion in DMSO before (red line) and after addition of carnosine (blue line). Scan rate: 100 mV s⁻¹.

Introduction of Mn²⁺ dramatically alters the voltammetric profile (Fig. 5). The attenuation of the semiquinone oxidation signal and the emergence of broad irreversible processes between 0.30–0.80 V are consistent with manganese-centered oxidation.

These signatures are consistent with Mn²⁺ → Mn³⁺ conversion followed by rapid ligand coordination. The disappearance of the semiquinone oxidation signal

and persistence of a multi-electron reduction wave indicate kinetically slow Mn(II) oxidation to Mn(III), likely occurring within a DHBA-associated coordination environment.

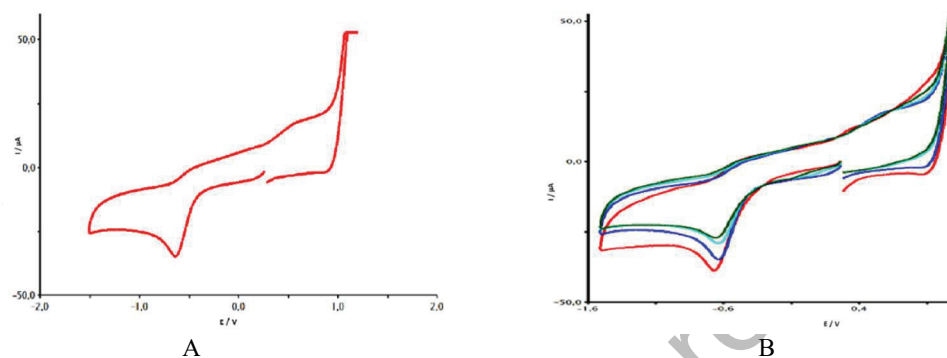


Fig. 5. Cyclic voltammograms of the 3,4-DHBA dianion in DMSO with carnosine: A) immediately after Mn^{2+} addition; B) time-dependent evolution: 0 min (red), 2 min (blue), 4 min (green), 6 min (pink) and 8 min (black). Scan rate: 100 mV s^{-1} .

Comparable irreversible behavior observed for the isolated carnosine–manganese complex (solid 27, Fig. S-5 of the Supplementary material)²⁵ reinforces the assignment of ligand-stabilized Mn(III) intermediates. Overall, the electrochemical data support a mechanism in which semiquinone radicals act as transient electron shuttles, likely promoting manganese oxidation while undergoing peptide-mediated trapping.

A comparative summary of the electrochemical parameters for all investigated systems is provided in Table I.

TABLE I. Summary of redox potentials for the investigated systems in DMSO; E_{pa} : anodic peak potential; E_{pc} : cathodic peak potential; ΔE_p : peak-to-peak separation

System	E_{pa} V	E_{pc} V	ΔE_p V	Electrochemical behavior
3,4-DHBA dianion	~0.45	~0.30	~0.15	Quasi-reversible catechol/semiquinone redox couple
3,4-DHBA + carnosine (1:1)	~0.50	~0.32	~0.18	Positive shift; appearance of irreversible oxidation at ~0.68 V
3,4-DHBA + carnosine + Mn^{2+}	—	—	—	Broad irreversible processes (0.30–0.80 V); Mn-centered oxidation
Carnosine–Mn complex	—	—	—	Predominantly irreversible behavior; ligand-stabilized Mn(III) formation

The stability of Mn(III) species in solution is strongly dependent on ligand environment. In the absence of stabilizing ligands, Mn(III) is typically prone to disproportionation. However, coordination to oxygen- and nitrogen-donor ligands,

224 such as carnosine and catechol-derived species, can provide both kinetic and ther-
225 modynamic stabilization. In the present system, the persistence of electrochemical
226 and spectroscopic signatures attributed to Mn(III) suggests that ligand coordin-
227 ation effectively stabilizes the higher oxidation state, at least on the experimental
228 timescale.

229 *NMR analysis*

230 ^1H -NMR spectroscopy provides complementary evidence for interaction
231 between carnosine and oxidized DHBA species (Fig. 6). Pronounced upfield shifts
232 of the imidazole resonances indicate changes in the electronic environment, con-
233 sistent with possible coordination or interaction with electron-deficient quinonoid
234 structures. Such perturbations are consistent with partial redistribution of electron
235 density within the heteroaromatic ring following oxidative coupling.

236 Following Mn^{2+} addition, the spectrum exhibits substantial line broadening
237 and reduced resolution (Fig. 7), behavior typical of paramagnetic Mn(III) cen-
238 ters.^{22,23}

239 The appearance of a broad resonance near 9.03 ppm is consistent with the
240 formation of metal-associated species undergoing rapid exchange on the NMR
241 timescale. Addition of isolated carnosine-manganese complex to the DHBA dian-
242 ion generates an even more intricate spectral pattern (Fig. 8), suggesting the pre-
243 sence of multiple equilibrating coordination environments rather than a single
244 dominant complex. This observation aligns with the electrochemical evidence for
245 dynamic metal–ligand speciation.

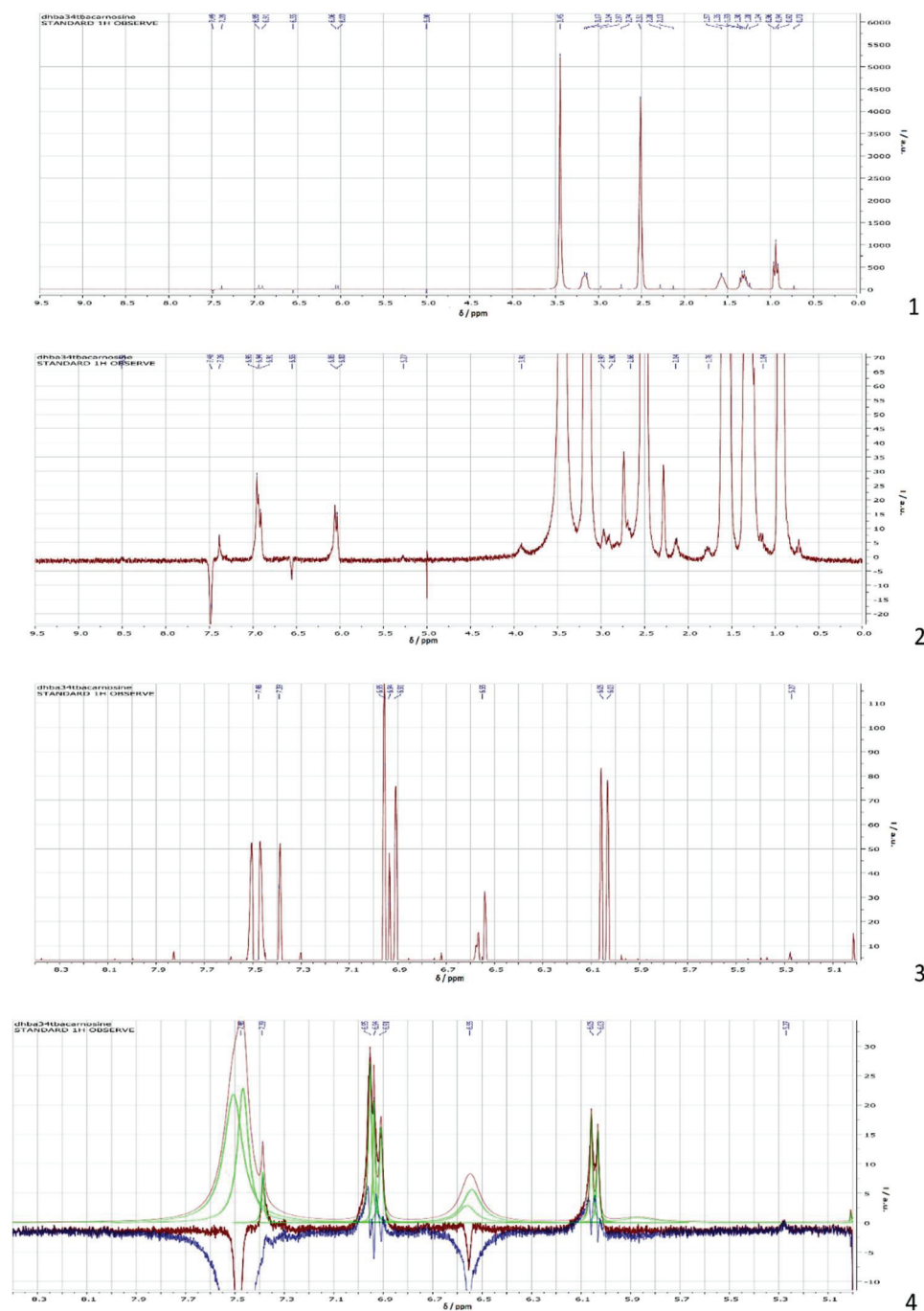
246 Taken together, the NMR data support a model in which carnosine participates
247 both as a redox-active partner and as a ligand scaffold capable of stabilizing higher
248 oxidation states of manganese. The combined observations are consistent with a
249 mechanism involving initial semiquinone formation, followed by peptide-medi-
250 ated oxidative trapping and subsequent electron transfer to Mn(II), yielding ligand-
251 -stabilized Mn(III) intermediates.²⁴

252 *Proposed redox sequence*

253 The spectroscopic and electrochemical results support a cooperative redox
254 sequence in the 3,4-DHBA–carnosine– Mn^{2+} system.

255 1. *Semiquinone formation.* Aerobic oxidation of 3,4-dihydroxybenzoic acid
256 leads to the formation of oxygen-stabilized semiquinone radicals,¹⁶ as evidenced
257 by characteristic ESR signals and visible absorption bands.

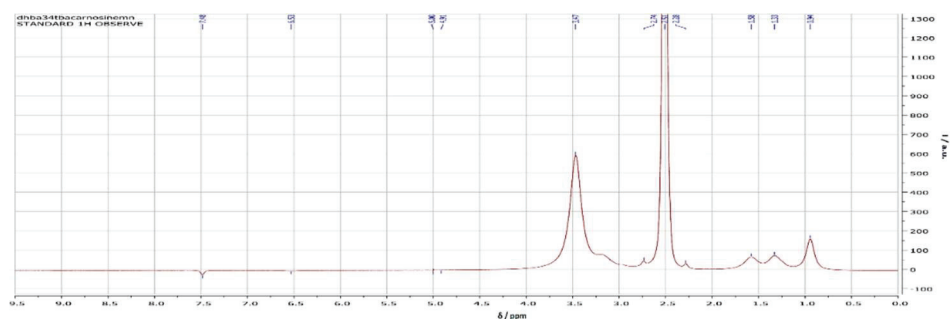
258 2. *Interaction with carnosine.* Carnosine interacts with these intermediates,
259 likely through an imidazole-mediated pathway,^{16,17} leading to attenuation of the
260 ESR signal, redistribution of visible absorption bands and perturbation of the
261 catechol redox couple, consistent with the formation of quinonoid or peptide-
262 -associated species.



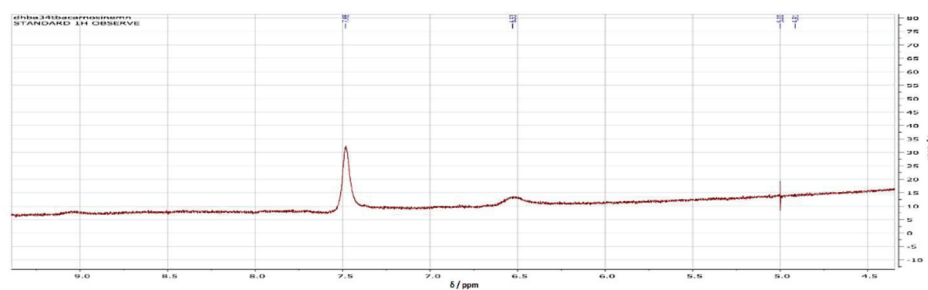
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Fig. 6. ^1H -NMR spectrum of the 3,4-DHBA/carnosine in $\text{DMSO}-d_6$; panels 3 and 4 show the 5–10 ppm region processed with resolution booster and global spectral deconvolution (GSD).

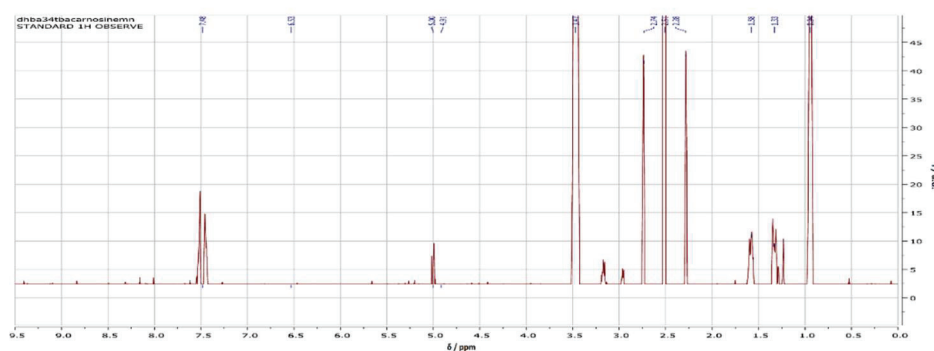
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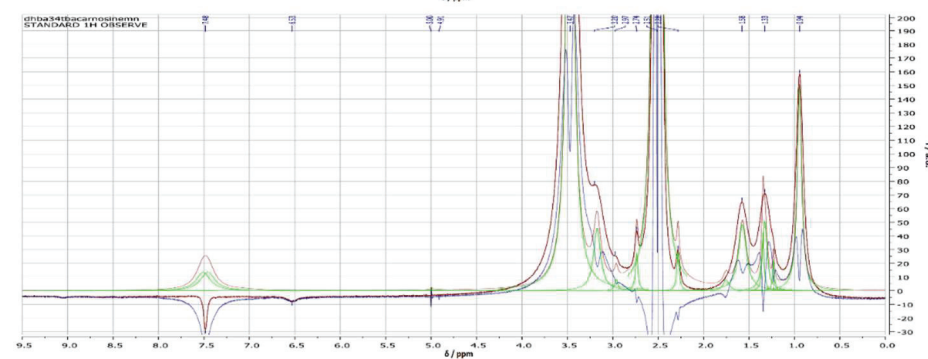
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Fig. 7. ^1H -NMR spectrum of the 3,4-DHBA/carnosine/ $\text{Mn}^{2+}(\text{aq})$ mixture in $\text{DMSO}-d_6$; panels 3 and 4 represent resolution booster and GSD analyses.

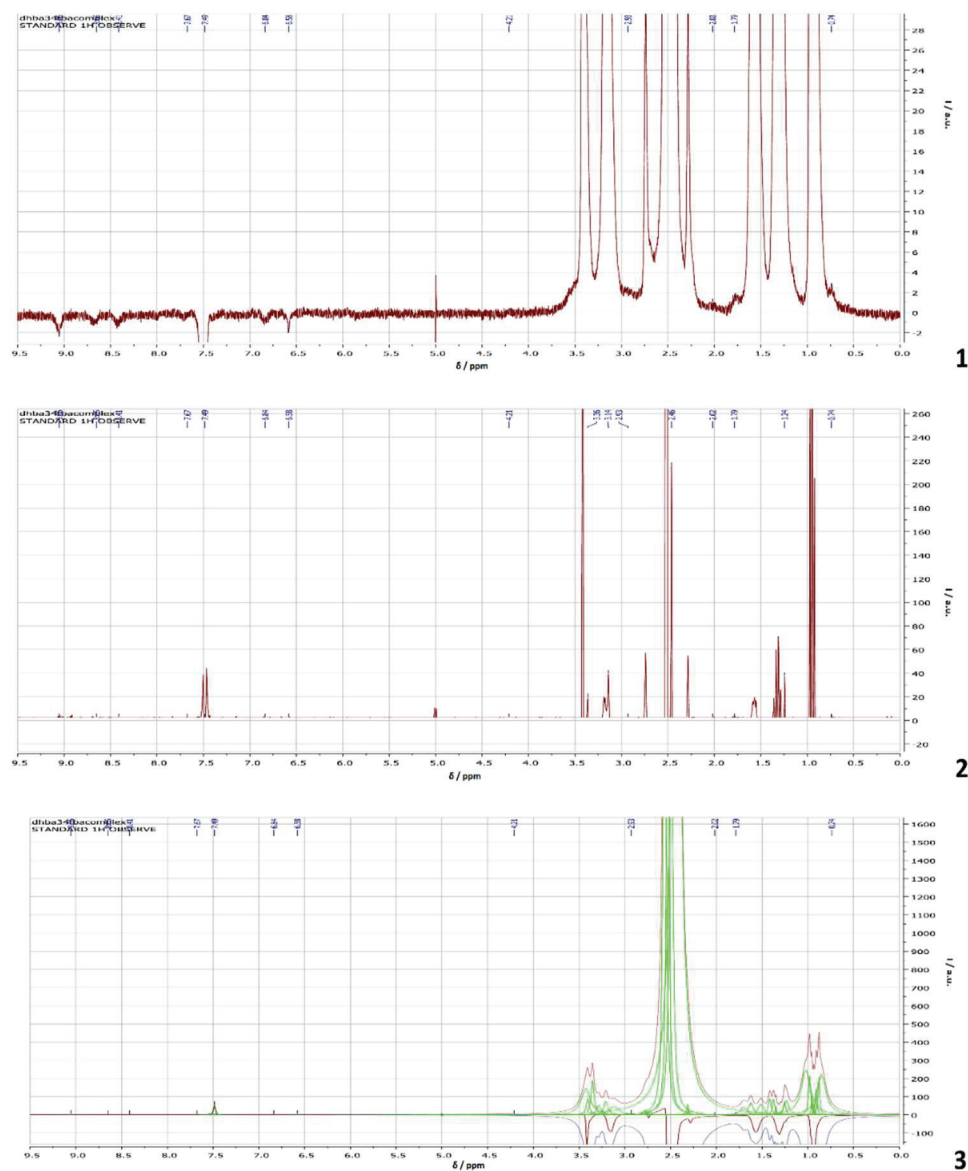
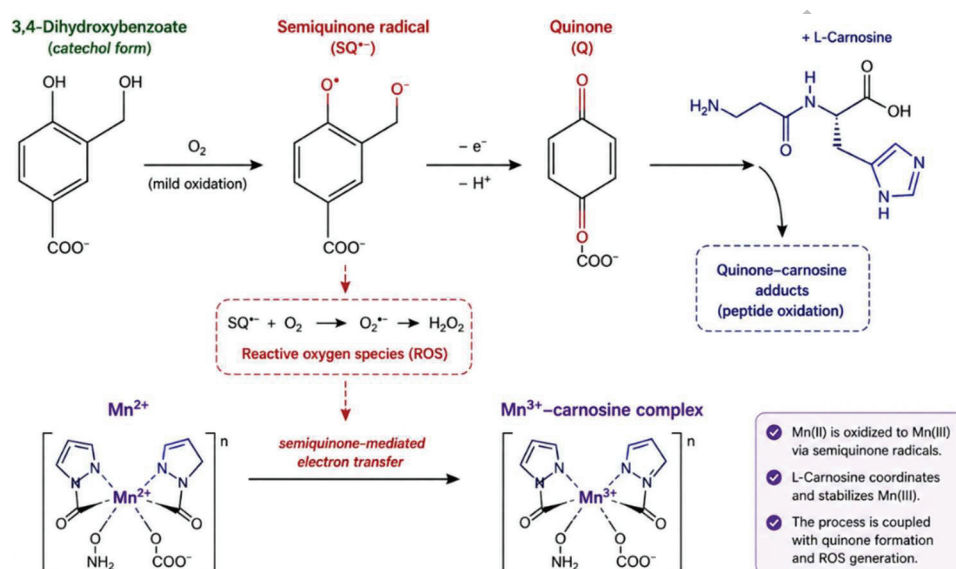


Fig. 8. ^1H -NMR spectrum of the 3,4-DHBA/ isolated carnosine-manganese complex (solid 24)²⁵ in $\text{DMSO}-d_6$; panels 2 and 3 show GSD and resolution booster analyses.

3. *Semiquinone-mediated Mn oxidation.* In the presence of Mn^{2+} , semiquinone intermediates can act as electron-transfer mediators, promoting oxidation of the metal center to higher oxidation states.¹⁸ Attenuation of semiquinone electrochemical signals and the appearance of irreversible anodic processes are consistent with coupled metal-centered redox processes.

277 4. *Stabilization of Mn(III)*. The resulting Mn(III) species are likely stabilized
 278 through coordination to oxygen-donor groups and the imidazole functionality of
 279 carnosine, forming dynamic solution structures.^{18–21} Paramagnetic ¹H-NMR
 280 broadening and irreversible voltammetric behavior in the 0.30–0.80 V region sup-
 281 port the presence of ligand-stabilized high-spin Mn(III) species.^{9,18,21}

282 The proposed sequence is consistent with the observed ESR attenuation, irre-
 283 versible voltammetry, and paramagnetic NMR effects, as summarized schematic-
 284 ally in Fig. 9.



285 Fig. 9. Schematic representation of the proposed redox sequence in the 3,4-DHBA–carnosine–
 286 –Mn²⁺ system illustrating semiquinone-mediated electron transfer leading to oxidation of
 287 Mn(II) to Mn(III) and stabilization of the resulting metal complex by L-carnosine.
 288

289 CONCLUSION

290 This study establishes a coherent redox framework for the interactions
 291 between L-carnosine, Mn²⁺ and semiquinone radicals derived from 3,4-dihydroxy-
 292 benzoic acid under non-enzymatic conditions. Combined UV–Vis, ESR, ¹H-NMR
 293 and cyclic voltammetry measurements demonstrate that semiquinone intermedi-
 294 ates participate in both peptide oxidation and manganese-centered electron-trans-
 295 fer processes.

296 Carnosine acts as both a redox-active component and a coordinating ligand,
 297 interacting with semiquinone species and contributing to the stabilization of
 298 higher-valent manganese intermediates. The formation of ligand-stabilized Mn(III)
 299 species is supported by spectroscopic and electrochemical evidence, including
 300 paramagnetic NMR behavior and irreversible voltammetric features.

Overall, the results support a cooperative redox pathway in which semiquinone radicals function as transient electron-transfer mediators within a multicomponent system. These findings provide insight into redox interactions between manganese ions, catechol-derived species and peptide ligands in solution, offering a chemically consistent basis for understanding such processes in complex environments.

NOMENCLATURE

3,4-DHBA: 3,4-dihydroxybenzoic acid
 DMSO: dimethyl sulfoxide
 ESR: electron spin resonance
 CV: cyclic voltammetry
 NMR: nuclear magnetic resonance
 UV–Vis: ultraviolet–visible spectroscopy
E_{pa}: anodic peak potential
E_{pc}: cathodic peak potential
 ΔE_p : peak-to-peak separation
g: g-factor (ESR spectroscopy)
 δ : chemical shift (NMR spectroscopy)

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/13801>, or from the corresponding author on request.

ИЗВОД

РЕДОКС РЕАКЦИЈЕ У КАРНОЗИН–МАНГАН СИСТЕМУ У ПРИСУСТВУ СЕМИХИНОНСКИХ РАДИКАЛА

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У овом раду испитивана је интеракција карнозина, дипептида који садржи хистидин, са семихинонским радикалом дианјона 3,4-дихидроксибензојеве киселине у раствору диметил-сулфоксида у аеробним условима. Поред тога, испитивана је интеракција система дипептид–манган са истим семихинонским радикалом при истим условима. Координација за метал и редокс хемија ових система испитивани су применом електронске, ESR и ¹H-NMR спектроскопије, као и цикличне волтаметрије. *In-situ* формирану семихинонски радикали (детаљно проучавани у претходним радовима) били су значајно модификовани након додавања карнозина, што је потврђено прерасподелом апсорпционих трака и променом редокс парова катехолног производа. Утицај јона мангана изазвао је додатне спектралне и електрохемијске промене, у складу са оксидацијом усмереном на јон метала и формирањем комплексних врста мангана стабилованих лигандом. Параметро магнетно ширење сигнала у ¹H-NMR спектрима указало је на присуство интермедијера

мангана виших оксидационих стања у раствору. Комбиновани подаци указују на кооперативни редокс механизам у којем семихинонске врсте посредују и у оксидацији пептида и у преносу електрона усмереном на јон мангана. Ови резултати пружају увид у разумевање вишекомпонентних система који су често присутни у природи.

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Supplementary material

SUPPLEMENTARY MATERIAL TO
**Redox pathways in the carnosine–manganese system mediated
by semiquinone radicals**

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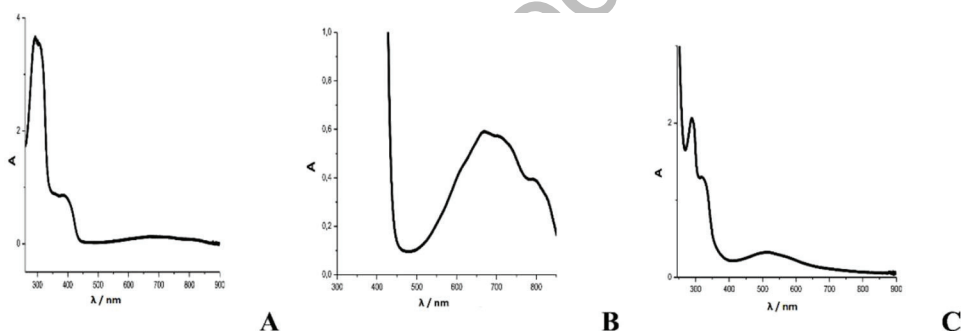


Fig. S-1. Electronic spectrum of 3,4-DHBA dianion ($c = 2.6 \times 10^{-3}$ M) in DMSO under aerobic conditions: (A, B) UV and Vis regions for the cyan form and (C) for the green form.

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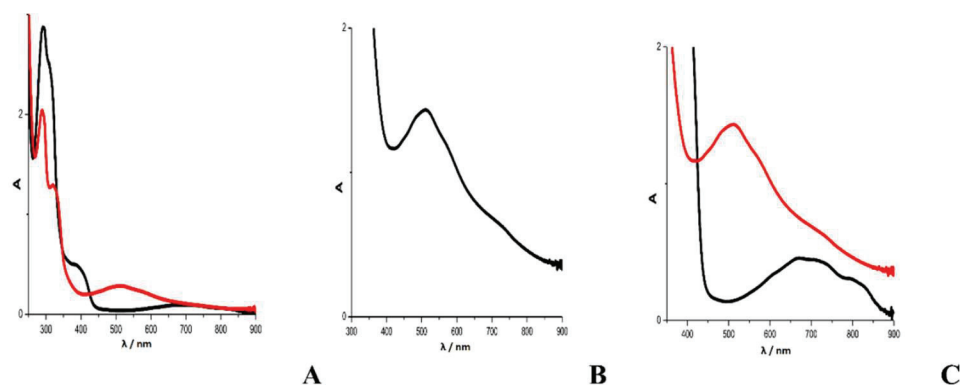


Fig. S-2. Electronic spectra of a 1:1 mixture of 3,4-DHBA dianion and carnosine in DMSO under aerobic conditions: A) comparison between 3,4-DHBA dianion (black line) and its mixture with carnosine (red line); B) visible region showing the blue form; C) comparison of the visible region.

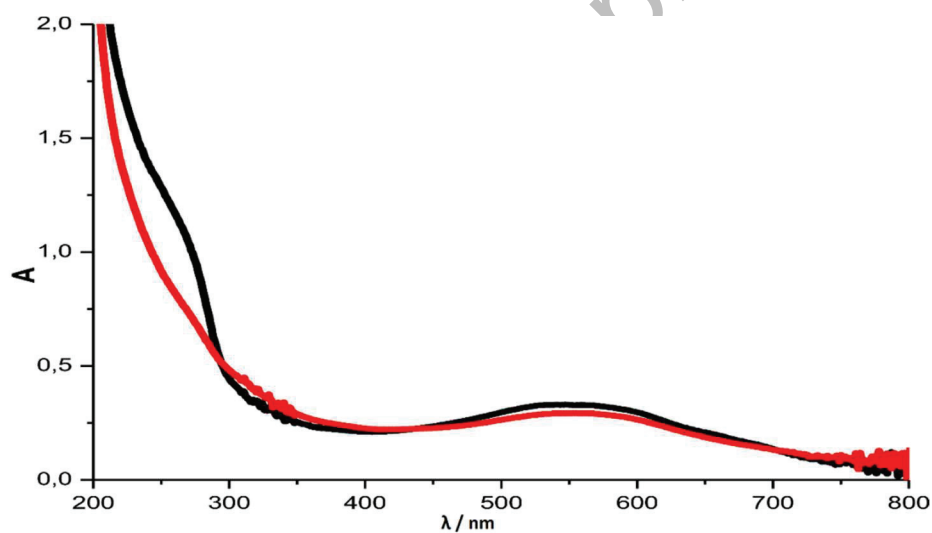
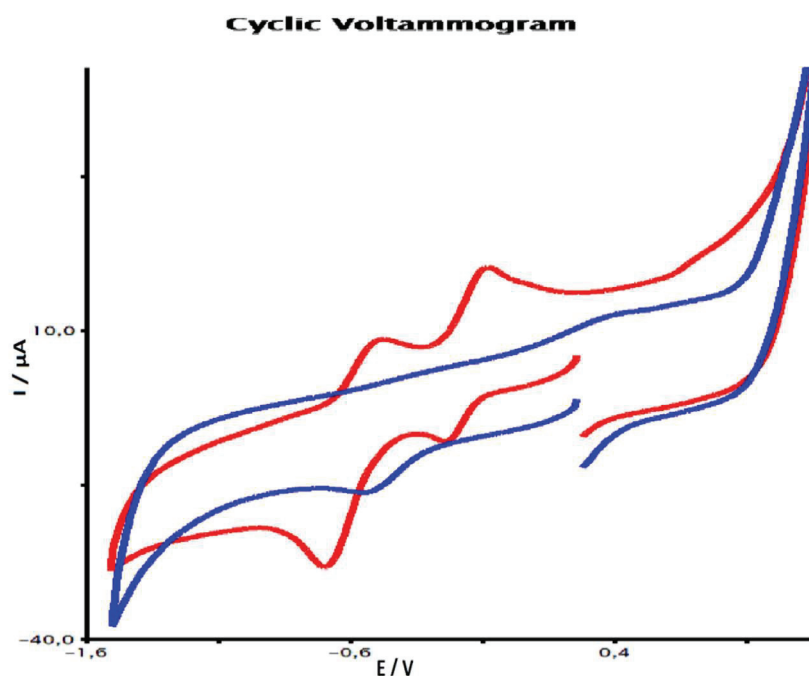
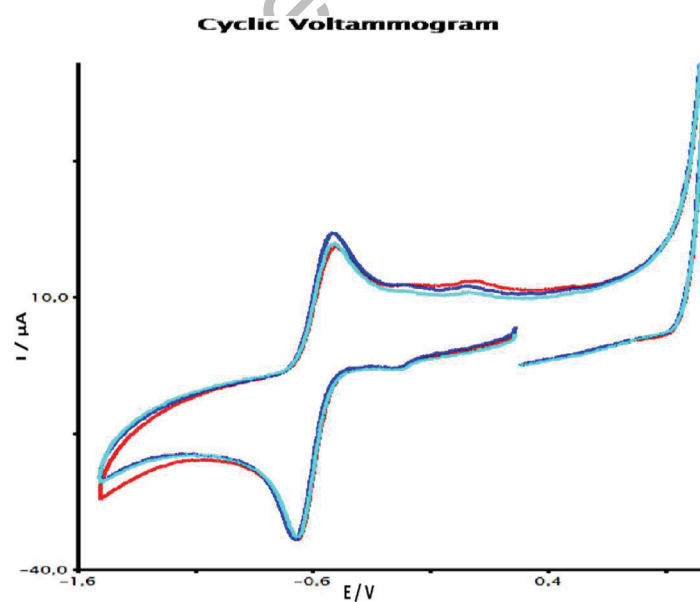


Fig. S-3. Electronic spectrum of the 3,4-DHBA dianion mixture in DMSO (black trace) compared with the spectrum after addition of an equimolar solution of isolated carnosine-manganese complex (solid 24)²⁵ (red trace).



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Fig. S-4. Cyclic voltammograms of 3,4-DHBA dianion in DMSO before (red line) and after 25 min of electrolysis (blue line). Potential range: -1500 to 1500 mV; scan rate: 100 mV s⁻¹.



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Fig. S-5. Cyclic voltammograms of isolated carnosine-manganese complex (solid 27)²⁵ ($c = 10^{-3}$ M) in a DMSO solution of 3,4-DHBA dianion at $t = 0$ min (red), 10 min (blue), and 25 min (green). Scan rate: 100 mV s⁻¹.