Antioxidant activity of a Mg(II) compound containing ferulic acid as chelator: potential application for active packaging and riboflavin stabilization

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Experimental Section – Starch Films

Casting procedure

Tapioca starch films were done by casting. 1 g of starch (5% m/m), 250 mg (25% m/m) glycerol and 15 mL deonized water were stirred in a hot water bath at 75 °C until gelatinization. 10 mg of Mg(phen)(fer) was added in 5 mL deonized water and this solution was poured into the 15 mL. This final blend was distributed in Petry dishes with 56.75 cm^2 area with 16 g. The films were dried in a ventilated oven for 26h at 37 °C with 60% humidity. For the control films the same procedure was done but the 20 mL of water was added at once. Film thickness was measured with a digital micrometer Mitutoyo (Japan).

Haze

The optical properties of the films were using an UV-vis spectrophotometer Lambda 650 (PerkinElemer, USA). Haze (%) was obtained with the following equation:

$$\%Haze = \left(\frac{T_4}{T_2} - \frac{T_3}{T_1}\right) x\ 100\%$$

The terms T_1, T_2, T_3 e T_4 are defined below:

Term	Sample	Black Body[1]	Standard	Meaning
T_1	No	No	Yes	Incident light
T_2	Yes	No	Yes	Total light transmitted by the film
T_3	No	Yes	No	Light diverted by the equipment
T_4	Yes	Yes	No	Light deflected by equipment and sample

[1]Black body is a device to prevent light dispersion.

Infrared

Attenuated total reflection – Fourier-transform infrared (ATR–FTIR) spectra of the films without and with Mg(phen)(fer) were acquired using a Spectrum 100 FTIR spectrophotometer (PerkinElmer, USA) equipped with a crystal ATR accessory (Ge/Ge) at room temperature. Each film was recorded five times in different position with 64 scans for each measurement with no significant changes.

Experimental section- Antioxidant Activity

pKa value

The pKa was determined by the colorimetric method. Solutions with the same concentration were prepared in the pH range between 2 and 12. Before each measurement, the solution was kept at rest for half an hour so that the system reached equilibrium. To obtain the pKa value was considered the following Equation 1.[1]

$$pKa = -\log K_a = -\log\left(\frac{Abs_{basic\ specie} - Abs_{mixture}}{Abs_{mixture} - Abs_{acidic\ specie}} x\ [H^+]_{mistura}\right) \quad \text{Eq. 1}$$

2,2-Diphenyl-1-picrylhydrazyl (DPPH•) radical assay

Stock solutions were prepared in methanol at the following concentrations: DPPH• radical at 1.2 mmol/L and ferulic acid, 1,10-phenanthroline and BHT at 1.52 mmol/L each one. Stock solution of Mg(phen)(fer) was prepared in distilled water at a concentration equal to 1 mg/mL. To measure the antioxidant activity, the final solutions were consistent of: 150 µL of DPPH•, different volumes (different concentrations between 0 up to 100 µmol/L) from the tested compounds, and variable amount of methanol was added to produce solutions with final volume equal to 2 mL. The reaction solution was vortexed for 30 seconds and left in the dark for 1 hour. After this time, UV-vis spectra of each sample were taken, and the band was monitored at 517 nm.[2] The procedure was done in triplicate.

The IC_{50} value related to the DPPH• radical inhibition percentage was obtained by Equation 2:

$$\%I = \left(\frac{A_0 - A}{A_0}\right) X100\% \quad \text{Eq. 2}$$

Where: %I is percentage inhibition, A_0 is the absorbance of the standard sample without analyte at 517 nm wavelength, A is the absorbance of the sample with analyte at 517 nm wavelength.

2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) radical ($ABTS^{\bullet+}$) assay

Reaction between 5.2 mL of an aqueous solution of the ABTS salt (7 mmol/L) with 92 µL of an aqueous solution of potassium persulfate (140 mmol/L) was kept in the dark for 16 hours for the formation of the $ABTS^{\bullet+}$ radical. Then, stock solutions of the

tested compounds were prepared in methanol at the following concentrations: ferulic acid, 1,10-phenanthroline and BHT at 1.52 mmol/L. Stock solution of Mg(phen)(fer) was prepared in distilled water at a concentration equal to 1 mg/mL. To measure the antioxidant activity, the final solutions were consistent of: 30 µL of $ABTS^{\bullet+}$ radical solution, different volumes (different concentrations between 0 up to 60 µmol/L) from the tested compounds, and variable amount of water was added to produce solutions with final volume equal to 2 mL. The reaction solutions were left in the dark for 10 minutes. After this time, UV-vis spectra of each sample were taken, and the band was monitored at 630 nm.[3] The procedure was done in triplicate. The IC_{50} value related to the $ABTS^{\bullet+}$ radical inhibition percentage was obtained by Equation 3:

$$\%I = \left(\frac{A_0 - A}{A_0}\right) x100\% \qquad \text{Eq. 3}$$

Where: %I is percentage inhibition, A_0 is the absorbance of the standard sample without analyte at 630 nm wavelength, A is the absorbance of the sample with analyte at 630 nm wavelength.

Peroxyl radical (ROO•) assay

The peroxyl radical (ROO•) was generated by thermal decomposition at 37 °C for 30 minutes of 2-2'-azobis-(2-amidinopropane)-dihydrochloride (AAPH).[4] The formation of the peroxyl radical was monitored with the spin trap α-(4-pyridyl-1-oxide)-N-tert-butylnitrone (POBN). 100 µL final volume solutions were prepared containing: 20 µL AAPH (50 mmol/L), 20 µL POBN (50 mmol/L) and for Mg(phen)(fer) complex the concentration varied from 0.8 µg/mL to 16 µg/mL. Each sample was transferred to a quartz capillary and measured from the RPE cavity. RPE spectra were recorded every 30 s. EPR conditions: microwave frequency 9.5 GHz, modulation frequency 100 kHz, microwave power 5.0 mW, modulation amplitude 2 G, scan width 200 G, time constant 0.128 s and temperature 298 K. The procedure was done in triplicate. The IC_{50} value related to the ROO• radical inhibition percentage was obtained by Equation 4:

$$\%I = \left(\frac{A_0 - A}{A_0}\right) x100\% \qquad \text{Eq. 4}$$

Where: %I is percentage inhibition, A_0 is the intensity of the EPR spectrum of the standard sample without analyte, A is the intensity of the EPR spectrum of the sample with analyte.

Singlet oxygen ($^1O_2$) assay

Singlet oxygen ($^1O_2$) was generated by continuous irradiation of riboflavin with 420 nm light for a period of 30 min.[5] The formation of singlet oxygen was monitored with the spin trap 2,2,6,6-tetramethyl-4-piperidinol (TEMP). 1 mL volume solutions were prepared containing: 130 µL TEMP (1.15 mol/L), 150 µL riboflavin (3 mol/L) and Mg(phen)(fer) complex the concentration varied from 165 ng/mL to 4 .95 µg/mL and final volume completed with PBS pH 7.4 buffer. After 30 minutes irradiation of each sample, it was transferred to a quartz capillary and measured from the cavity of the EPR. EPR spectra were recorded every 30 s. EPR conditions: microwave frequency 9.5 GHz, modulation frequency 100 kHz, microwave power 5.0 mW, modulation amplitude 2 G, scan width 200 G, time constant 0.128 s and temperature 298 K

The IC_{50} value related to the $^1O_2$ radical inhibition percentage was obtained by Equation 5:

$$\%I = \left(\frac{A_0 - A}{A_0}\right) x100\% \qquad \text{Eq. 5}$$

Where: %I is percentage inhibition, A_0 is the intensity of the EPR spectrum of the standard sample without analyte, A is the intensity of the EPR spectrum of the sample with analyte.

(1) Salgado, L. E. V.; Vargas-Hernández, C. Spectrophotometric Determination of the PKa, Isosbestic Point and Equation of Absorbance vs. PH for a Universal PH Indicator. *Am. J. Anal. Chem.* **2014**, *05* (17), 1290–1301. https://doi.org/10.4236/ajac.2014.517135.

(2) Sharma, O. P.; Bhat, T. K. DPPH Antioxidant Assay Revisited. *Food Chem.* **2009**, *113* (4), 1202–1205. https://doi.org/10.1016/j.foodchem.2008.08.008.

(3) Abramovič, H.; Grobin, B.; Ulrih, N. P.; Cigić, B. The Methodology Applied in DPPH, ABTS and Folin-Ciocalteau Assays Has a Large Influence on the Determined Antioxidant Potential. *Acta Chim. Slov.* **2017**, *64* (2), 491–499. https://doi.org/10.17344/acsi.2017.3408.

(4) Guo, Q.; Zhao, B.; Shen, S.; Hou, J.; Hu, J.; Xin, W. ESR Study on the Structure-Antioxidant Activity Relationship of Tea Catechins and Their Epimers. *Biochim. Biophys. Acta - Gen. Subj.* **1999**, *1427* (1), 13–23. https://doi.org/10.1016/S0304-4165(98)00168-8.

(5) Choe, E.; Min, D. B. Chemistry and Reactions of Reactive Oxygen Species in Foods. *Crit. Rev. Food Sci. Nutr.* **2006**, *46* (1), 1–22. https://doi.org/10.1080/10408390500455474.

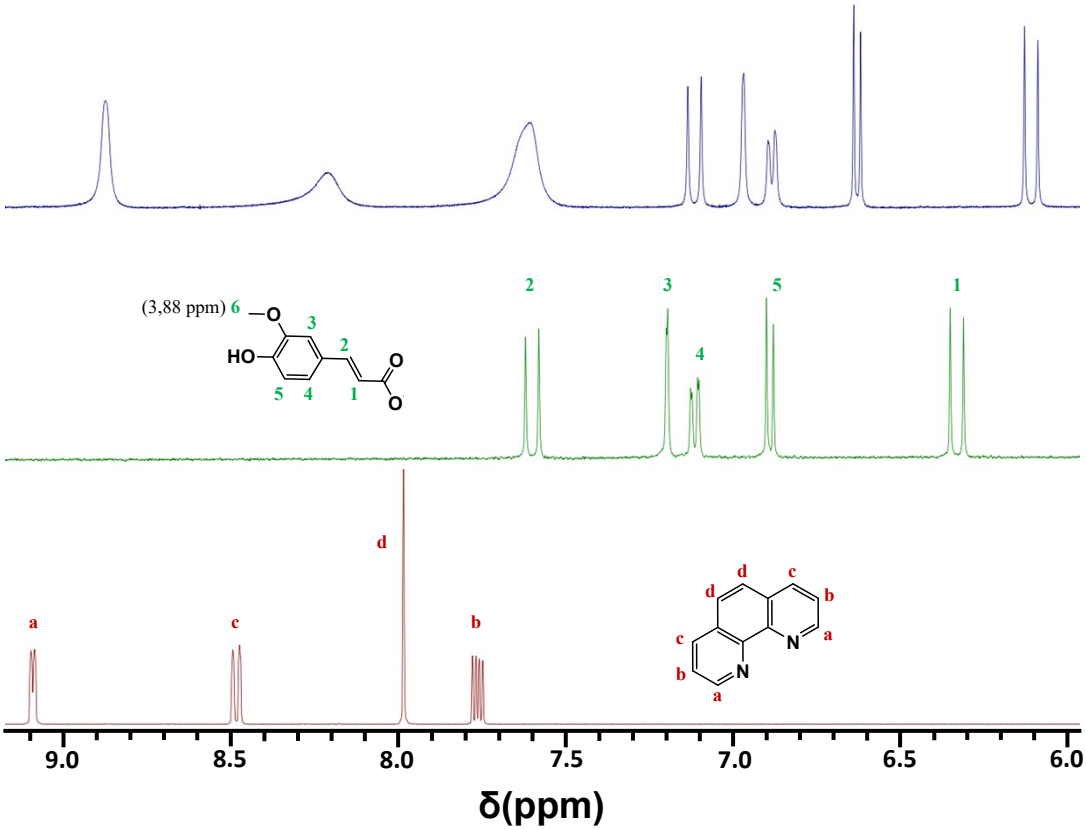


Figure S1. ^{1}H-NMR of the Mg(phen)(fer) complex at 298 K in D_2O (blue) compared with the spectra of ferulic acid (green) and 1,10-phenanthroline (red).

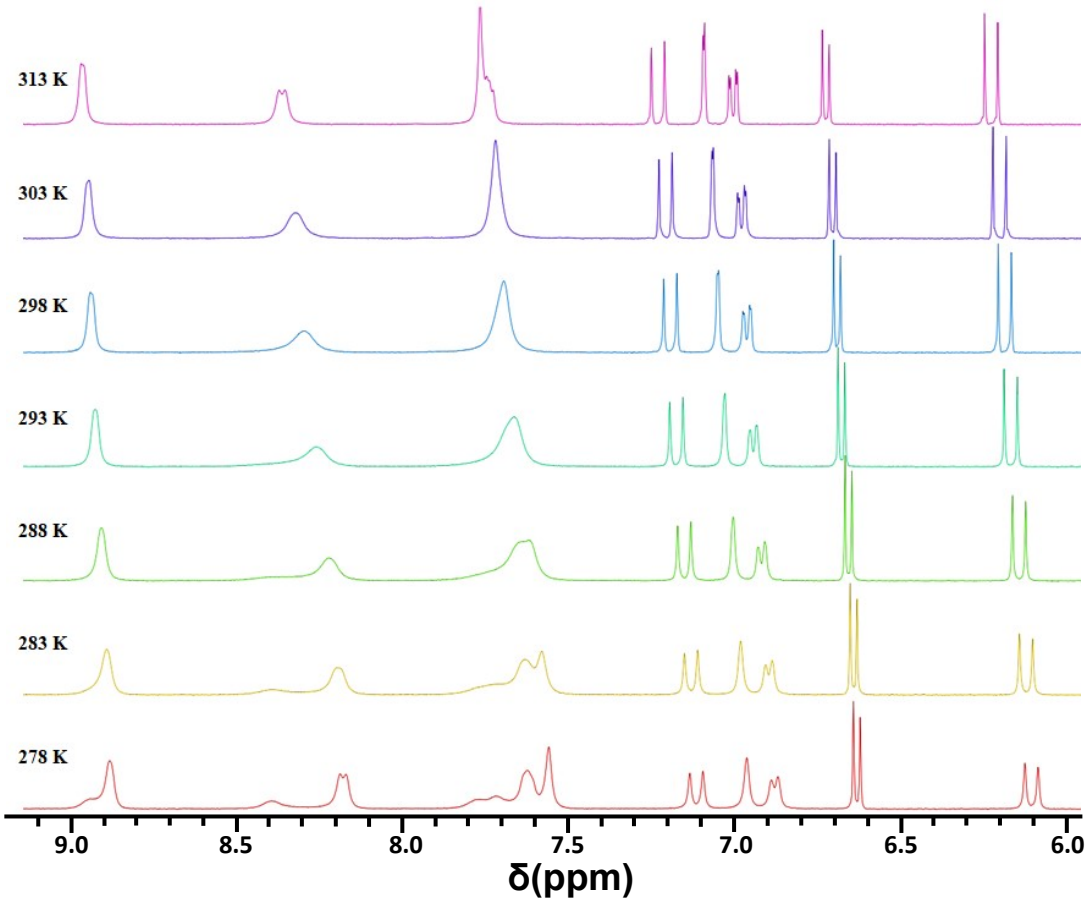


Figure S2. Variable temperature (278K to 313K) ^{1}H-NMR spectra of the Mg(phen)(fer) complex in D_2O.

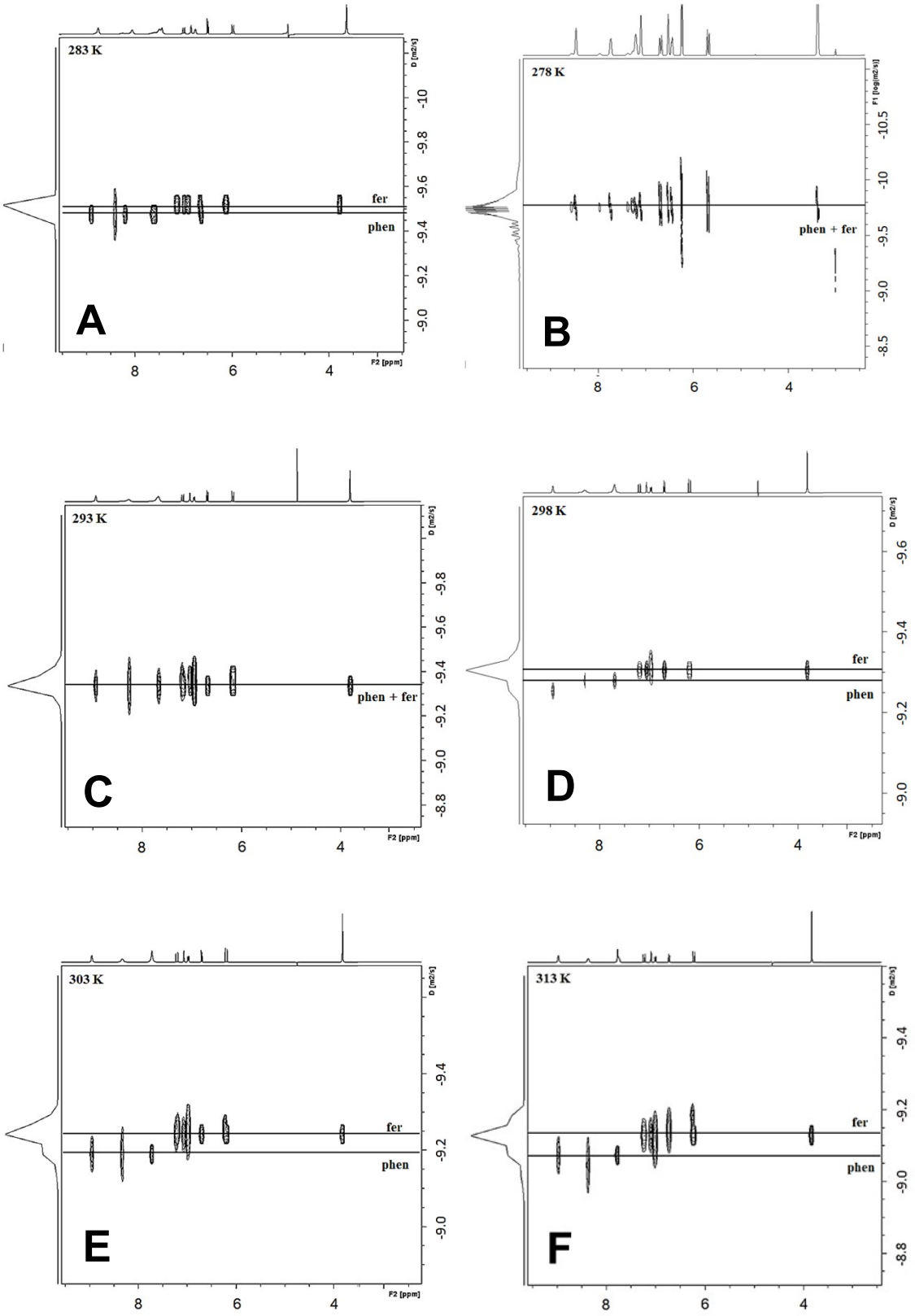


Figure S3. ^{1}H-DOSY-NMR map obtained for the Mg(phen)(fer) complex in D_2O at 283 K (A), 278 K (B), 293 K (C), 298 K (D), 303 K (E) and 313 K (F).

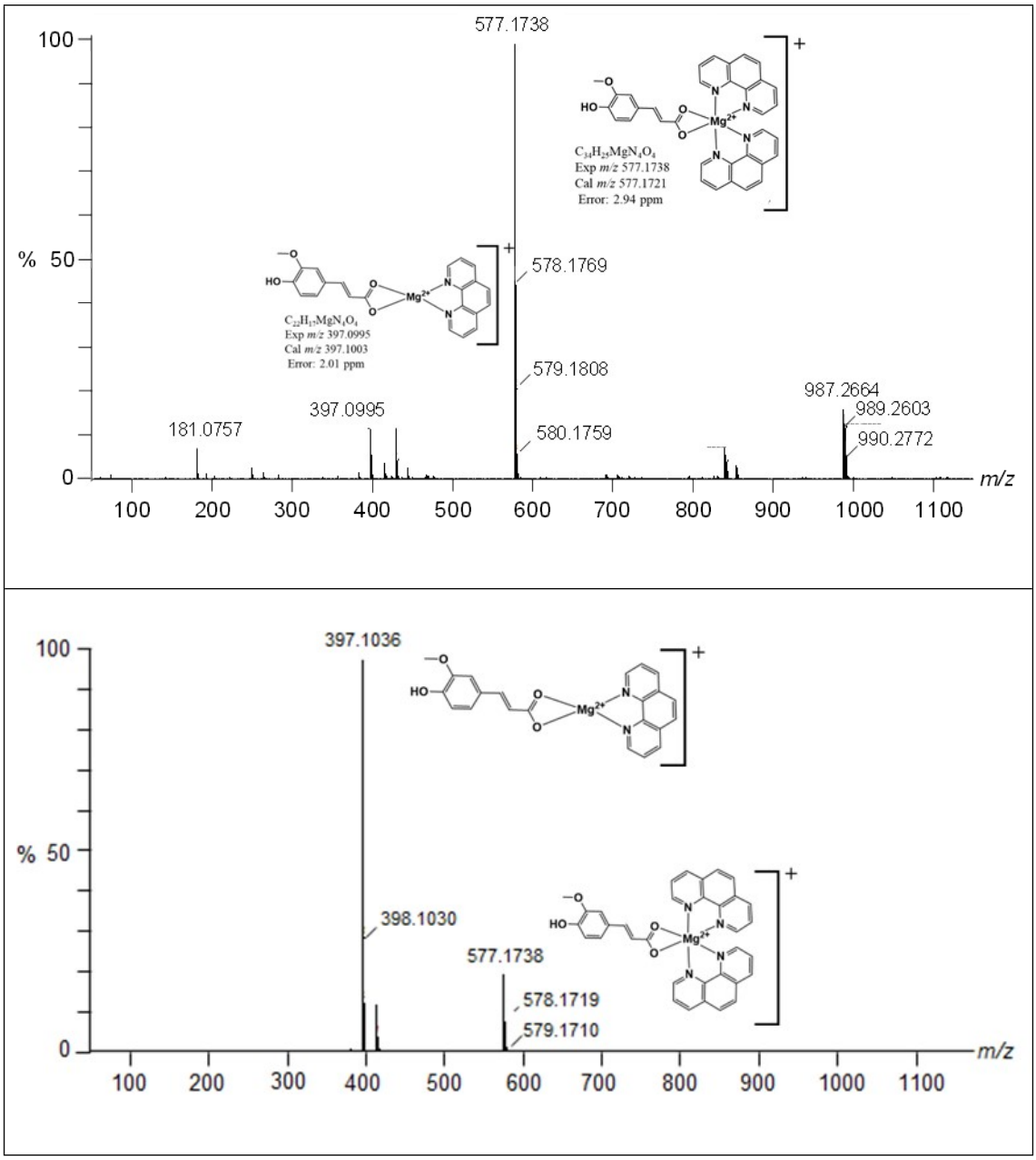


Figure S4. ESI(+)-MS spectrum of a freshly prepared aqueous solution of the Mg(phen)(fer) complex (top painel).

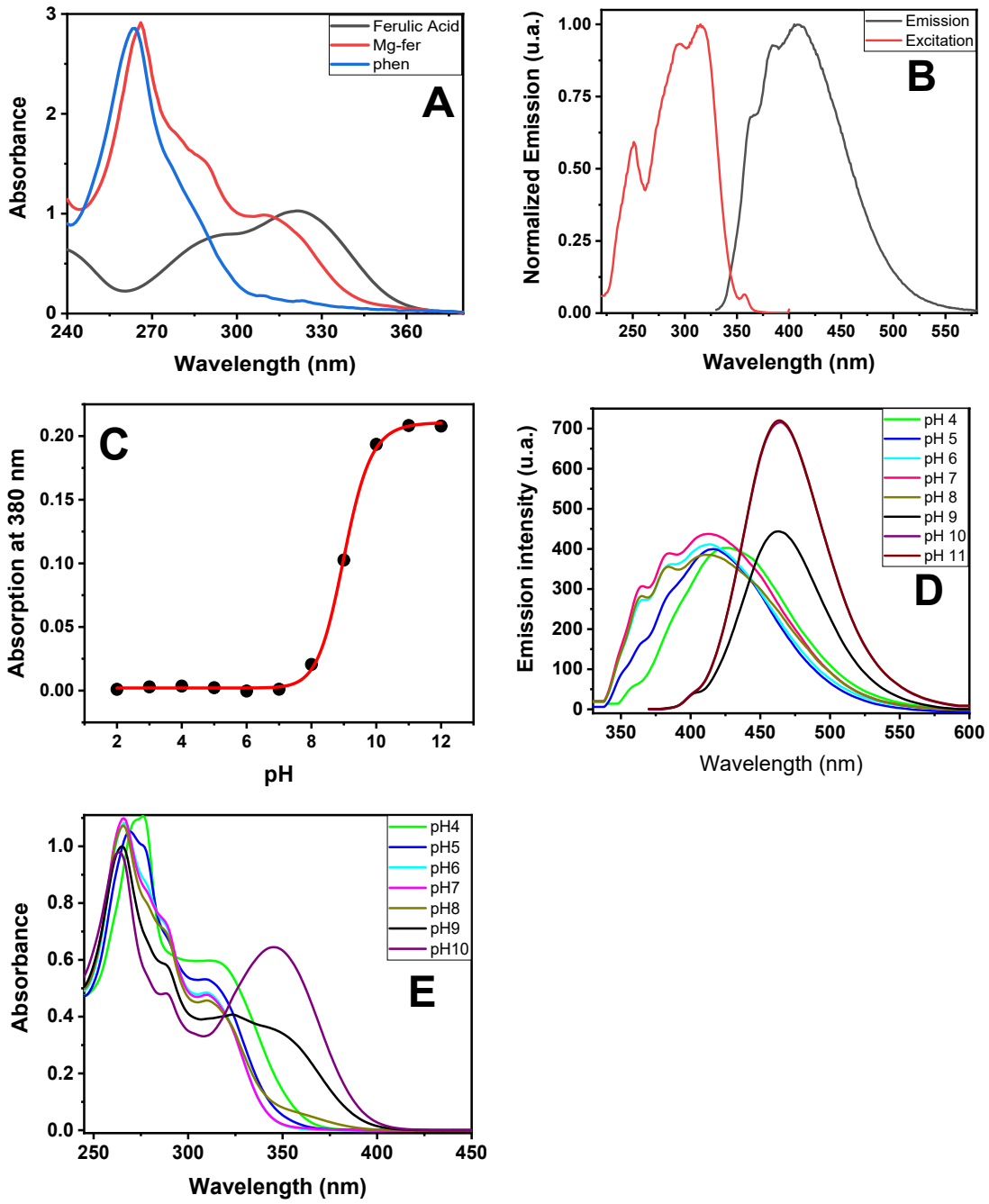


Figure S5. (A) Absorption spectra in water of the Mg(phen)(fer) complex (red) and ferulic acid (black); (B) Emission (λ_{exc}=310 nm) and excitation (λ_{em}=410 nm) spectra of Mg(phen)(fer) in water; (C) Colorimetric determination of the pKa value of Mg(phen)(fer) following absorption at λ=380 nm; (D) Emission spectra (λ_{exc}=310 nm) of Mg(phen)(fer) in the 4-11 pH range. Mg(phen)(fer) concentration was 7.5 µg/mL in all the experiments; (E) Absorption spectra of the Mg(phen)(fer) complex in the pH range 3-10.

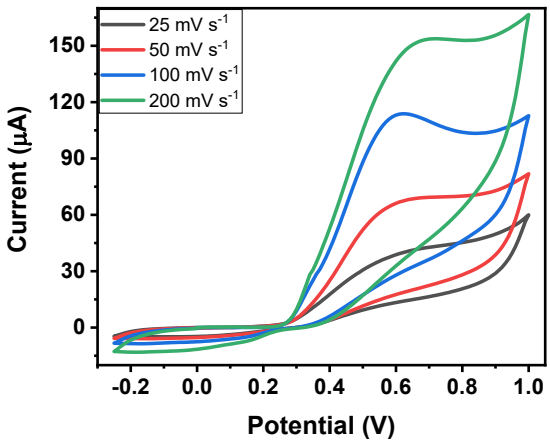


Figure S6. Cyclic voltammograms of ferulic acid in a buffered solution at pH 7.4 with 0.1 M KCl in a screen-printed electrochemical matrix formed by an electrochemical cell with a glassy carbon working electrode (d = 4 mm), silver counter and reference electrodes.

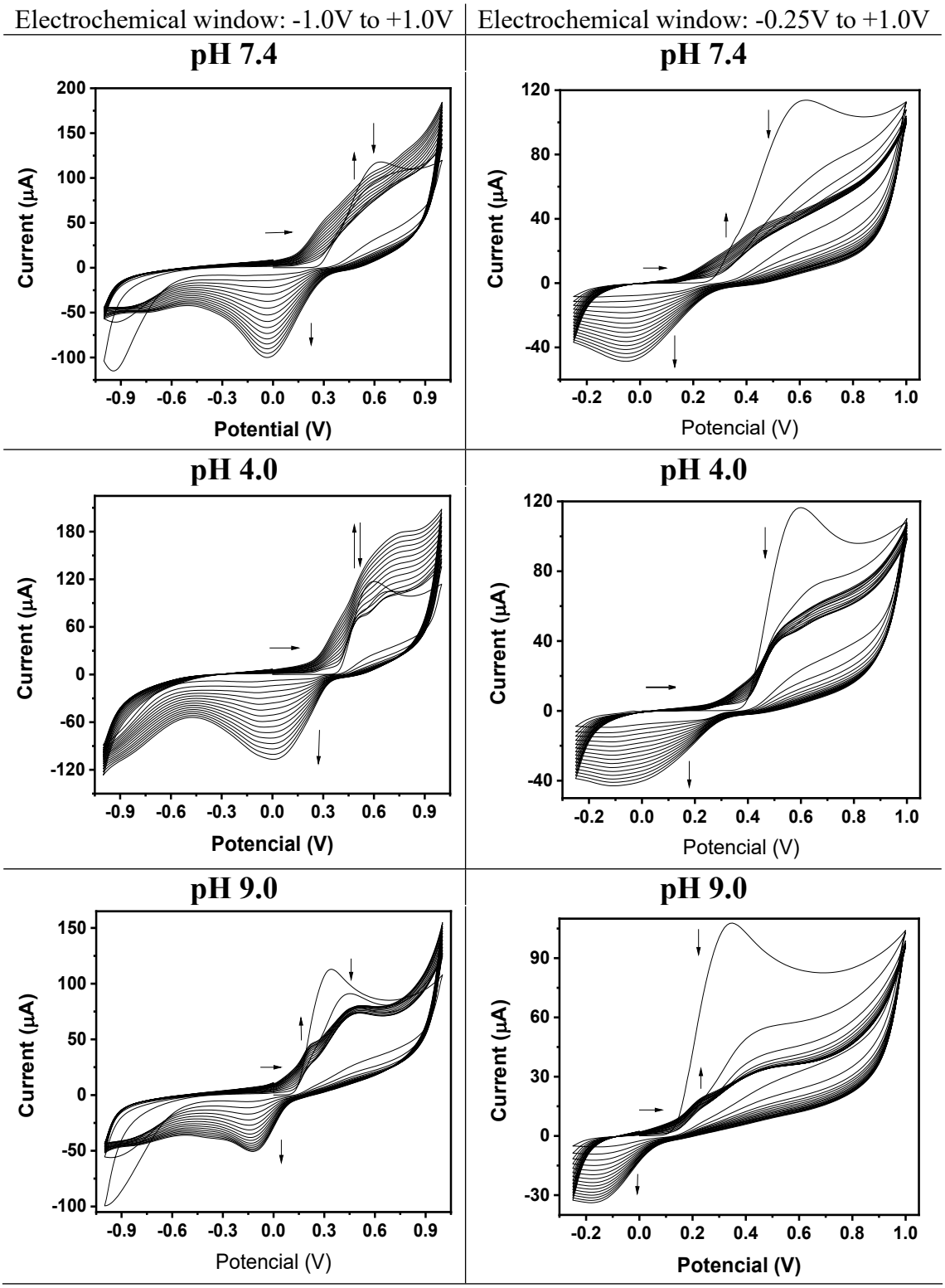


Figure S7. Cyclic voltammograms of ferulic acid in buffered solution at pH 4.0, pH 7.4 and pH 9.0 with 0.1M KCl, v = 100 mV/s and in the range of 1.0 V to -1.0 V (left side) and -0.25V to 1.0V (right side).

Electrochemical window: -0.25 V to +1.0 V

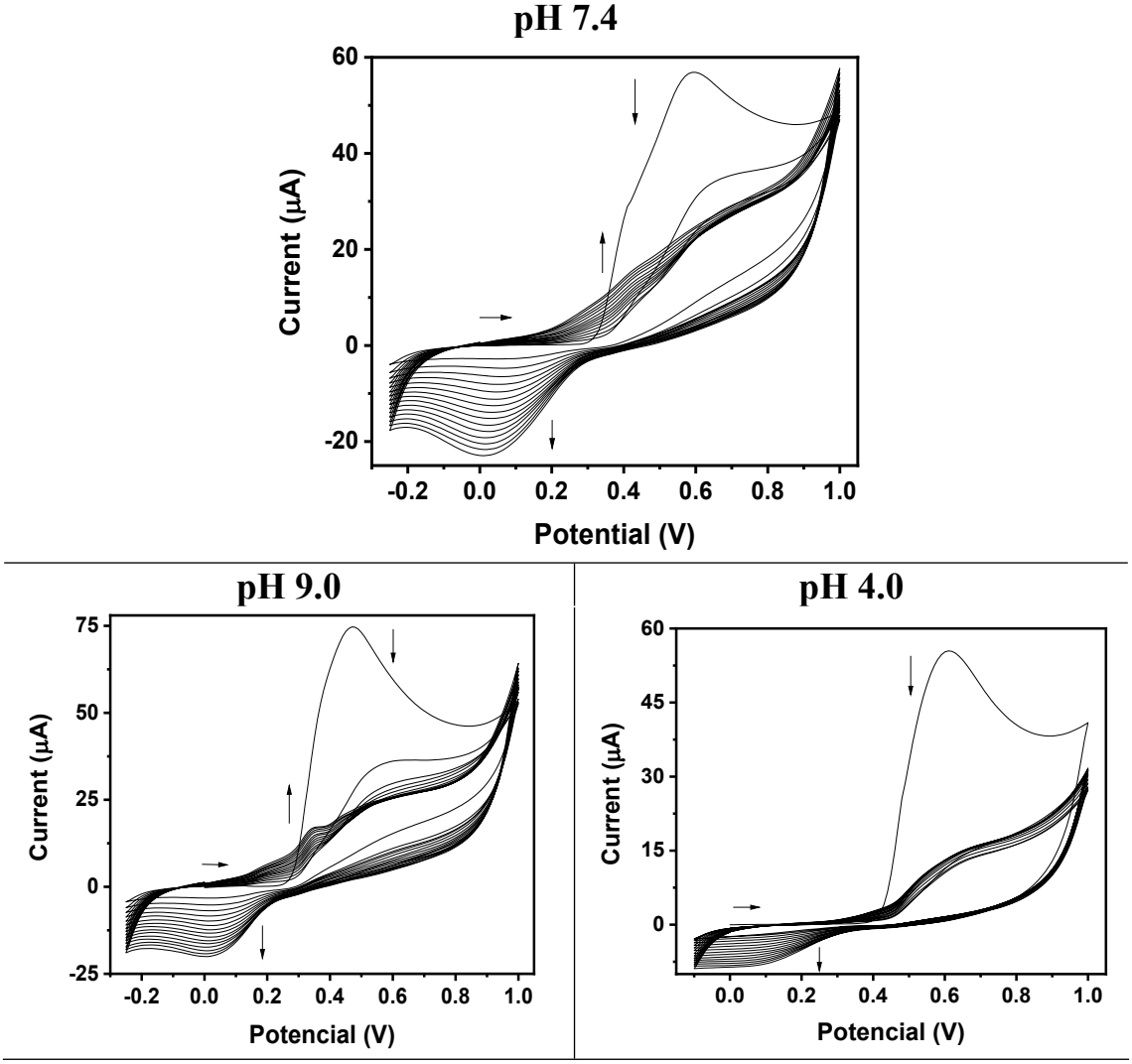


Figure S8. Cyclic voltammograms of Mg(phen)(fer) complex in buffered solution at pH 4.0, pH 7.4 and pH 9.0 with 0.1M KCl, v = 100 mV/s and in the range of -0.25V to 1.0V.

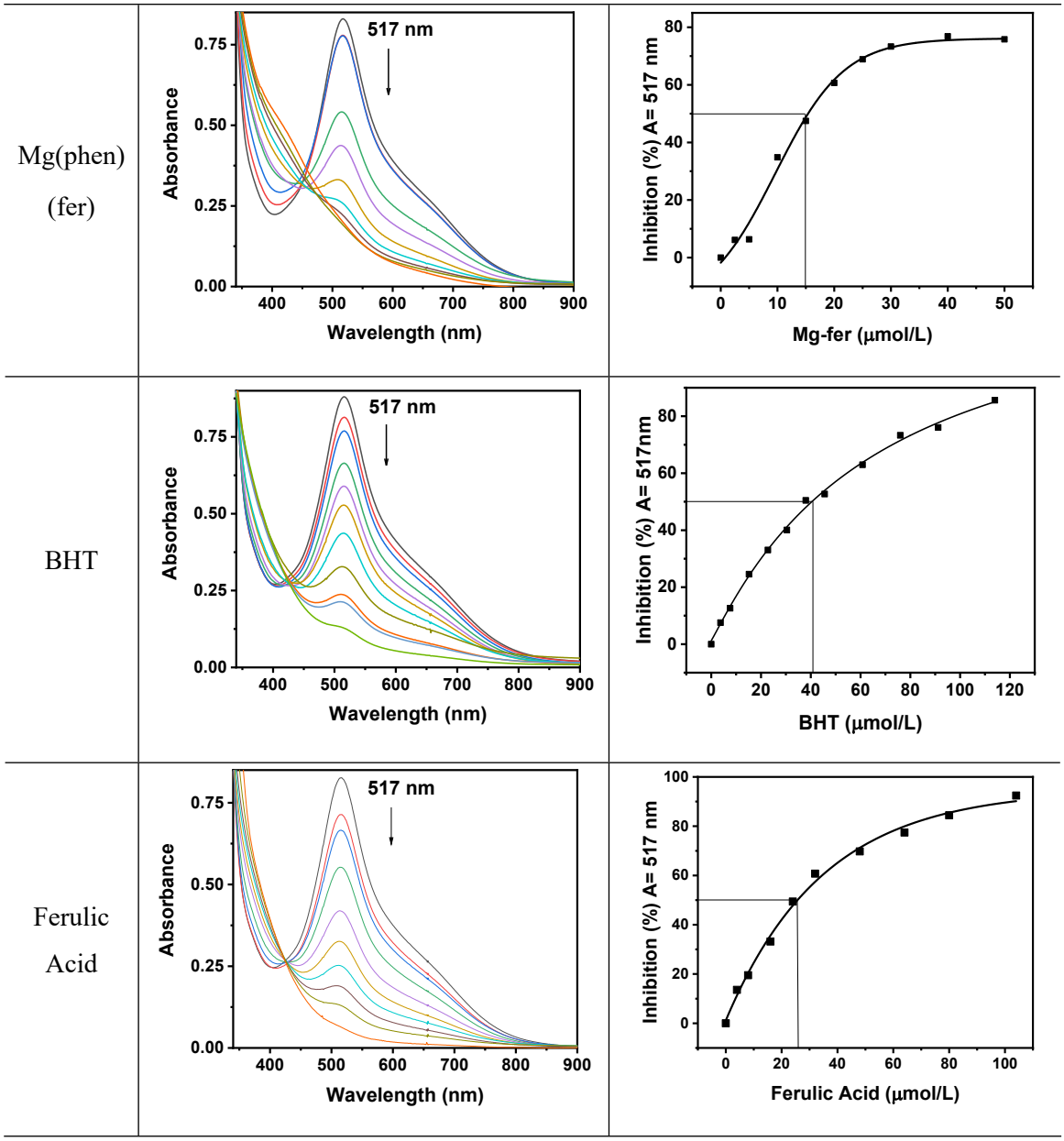


Figure S9. Representation of obtaining the IC_{50} of the inhibition of the DPPH• radical for the Mg(phen)(fer) complex (top panel), for the BHT (middle panel) and for the ferulic acid (bottom panel) using UV-vis spectrophotometer and following the decay of the band at 517 nm. Measurements were performed in triplicate.

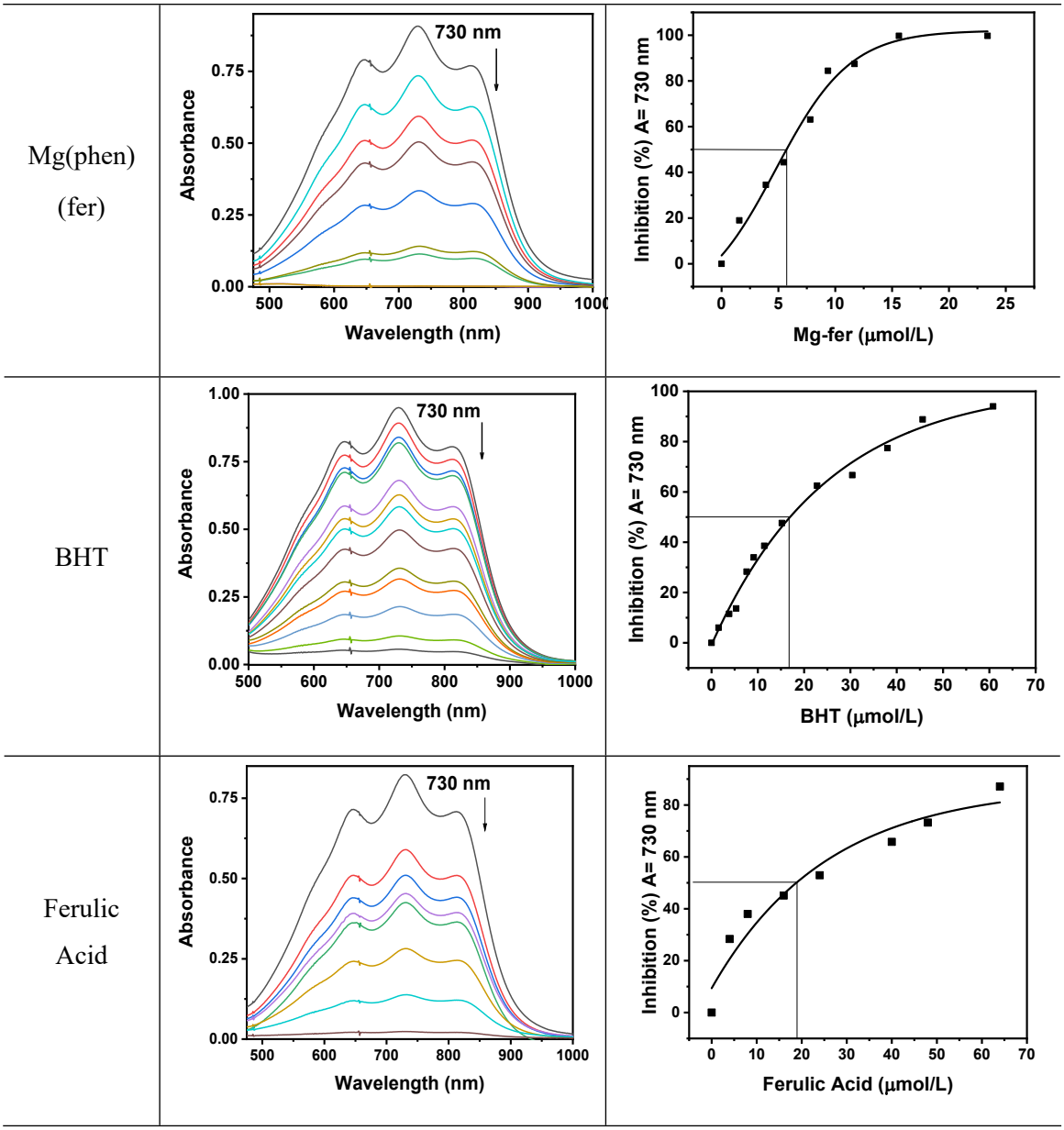


Figure S10. Representation of obtaining the IC_{50} of the inhibition of the $ABTS^{\bullet+}$ radical for the Mg(phen)(fer) complex (top panel), for the BHT (middle panel) and for the ferulic acid (bottom panel) using UV-vis spectrophotometer and following the decay of the band at 730 nm. Measurements were performed in triplicate.

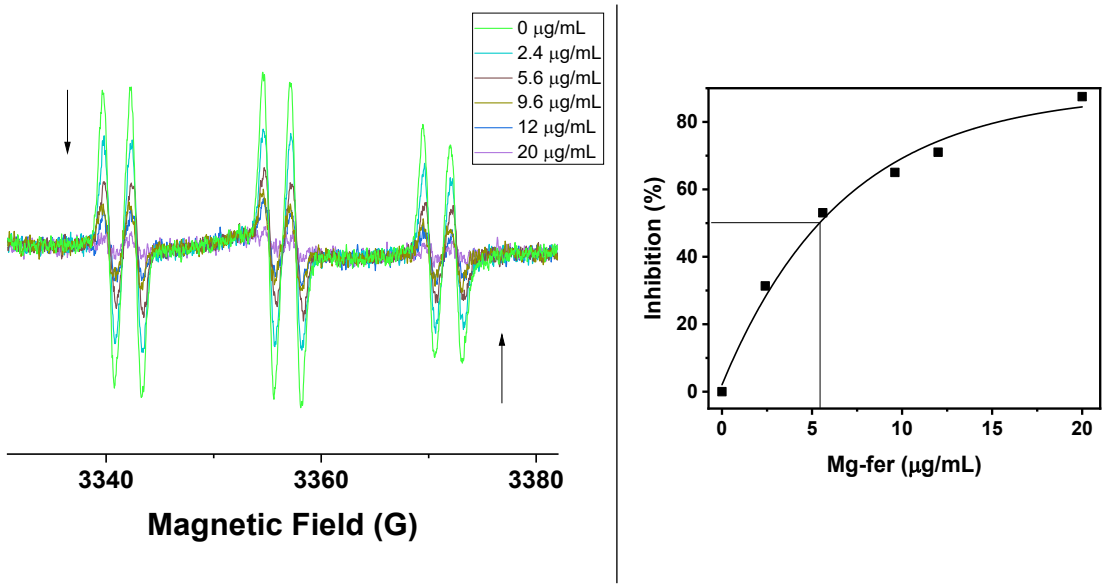


Figure S11. Representation of obtaining the IC_{50} of the inhibition of the peroxyl radical (ROO•) for the Mg(phen)(fer) complex (top panel). Measurements were performed in triplicate.

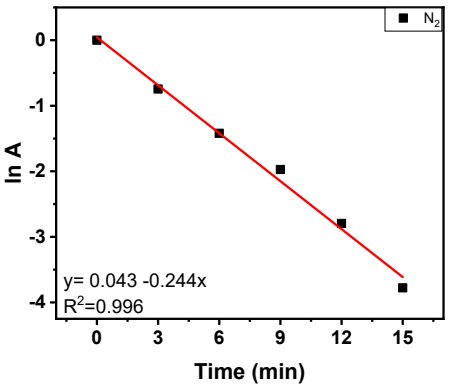
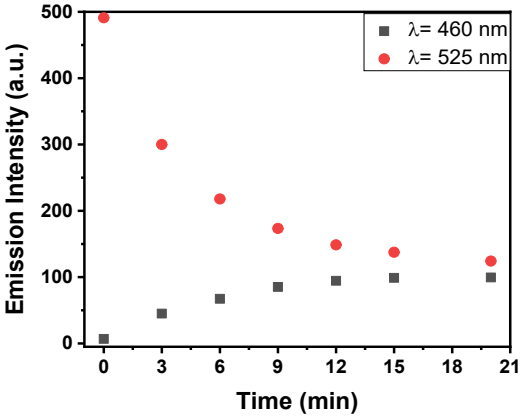
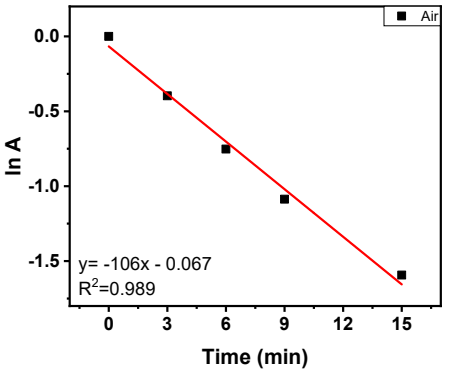
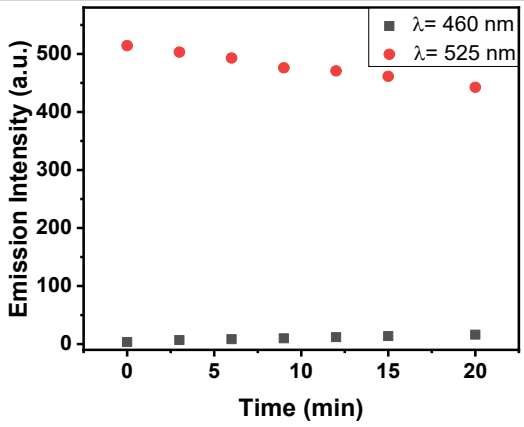
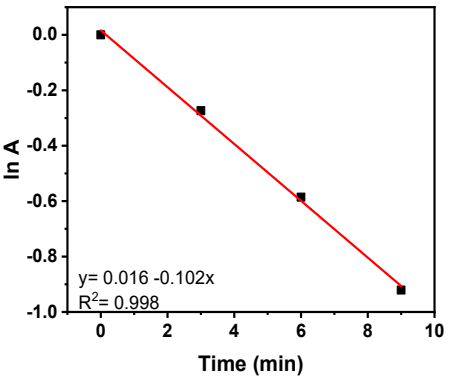
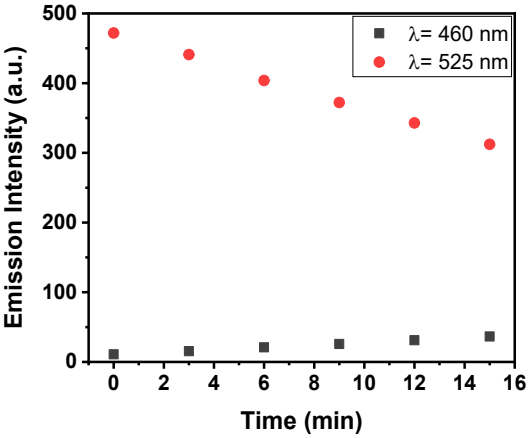
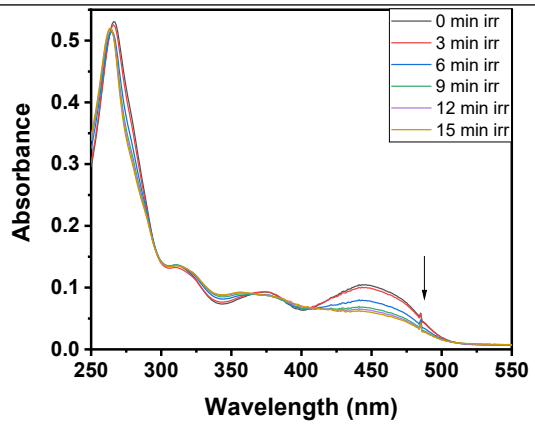
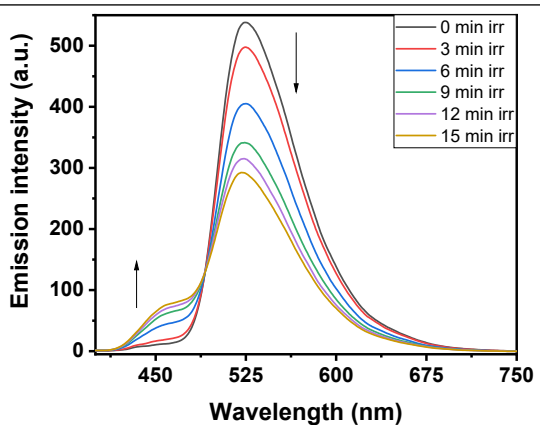
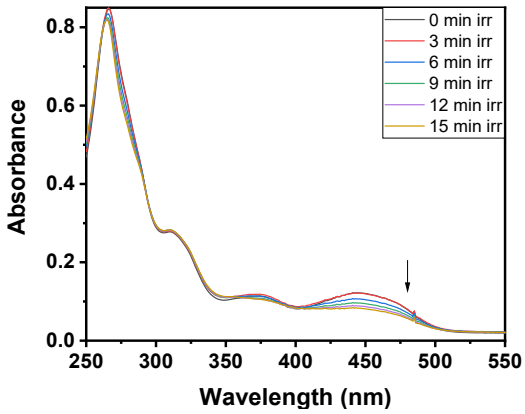
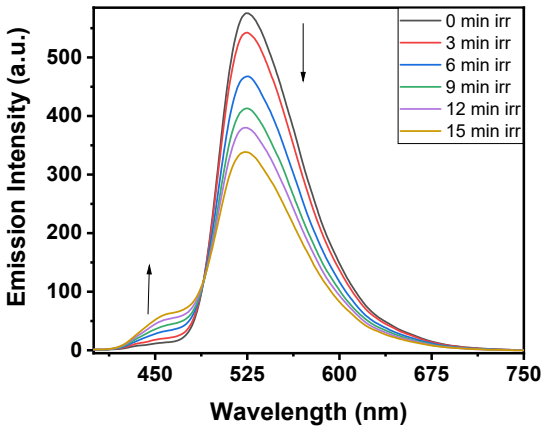
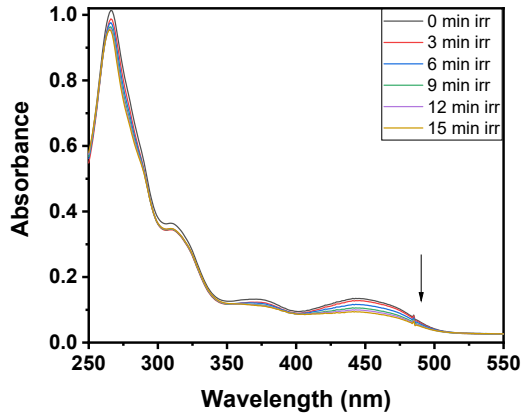
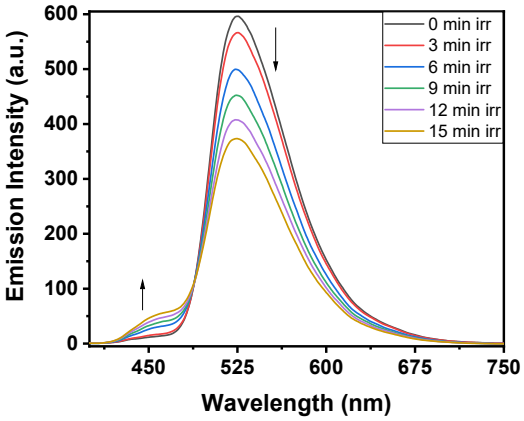
Only Rf in N_2		
Only Rf in Air		
Rf + Mg(phen)(fer) In N_2		

Figure S12. Kinetic treatment of $\ln[(A_{inf} - A_t)/ (A_{inf} - A_{t0})]$ *vs* time in minutes considering a first order process in N_2, air and in N_2 in the presence of Mg(phen)(fer) (left hand side). Decrease in the band at 525 nm referring to excited singlet emission from riboflavin and band increase at 460 nm referring to excited singlet emission of lumichrome in N_2, air and in N_2 in the presence of Mg(phen)(fer) (right hand side).

Mg(phen)(fer) Concenc.	Uv-vis	Emission
4 µg/mL		
7 µg/mL		
9 µg/mL		

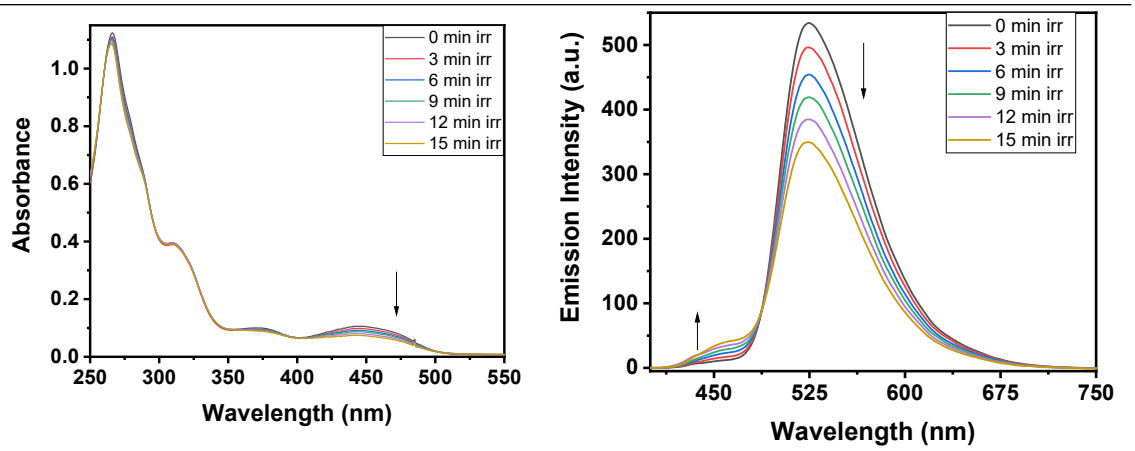
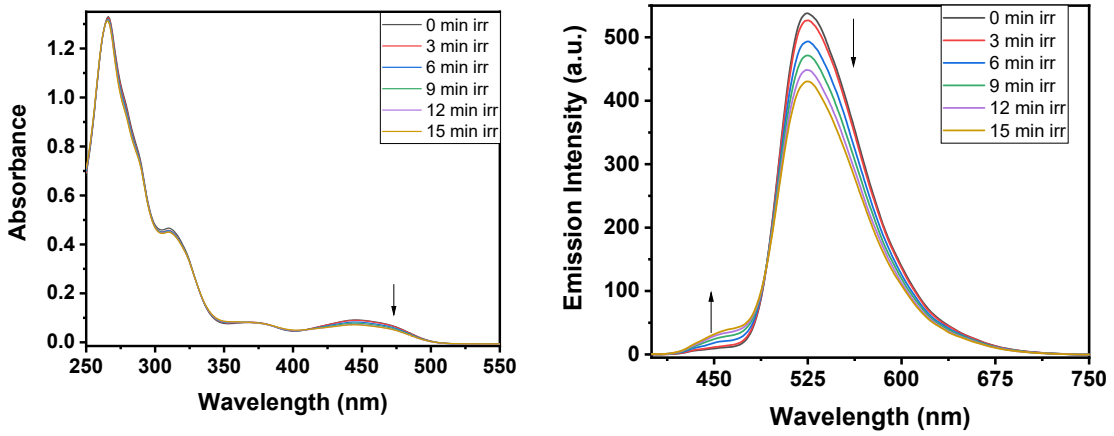
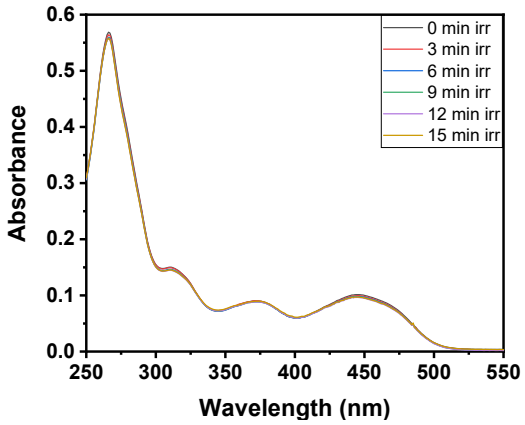
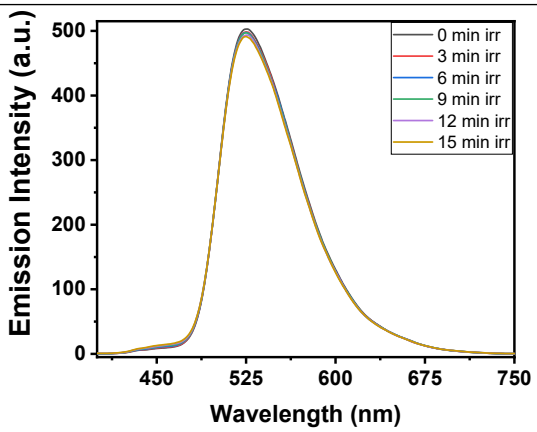
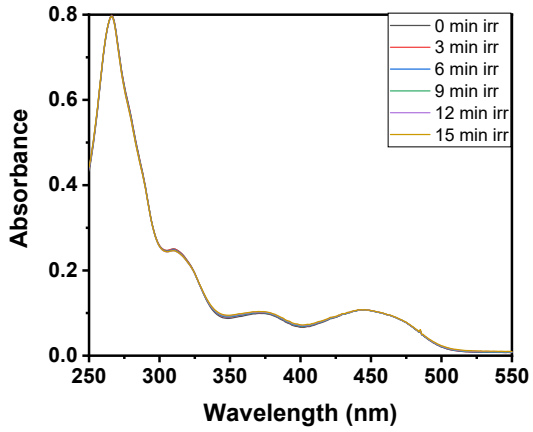
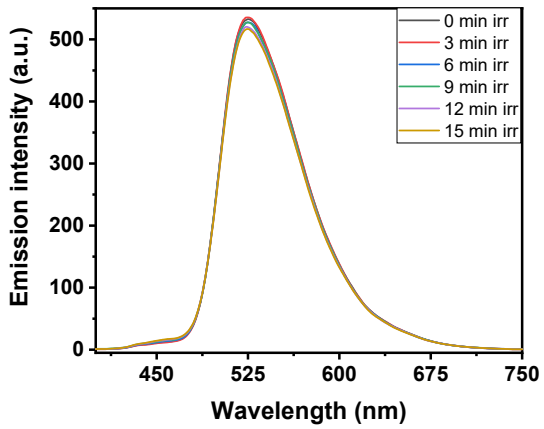
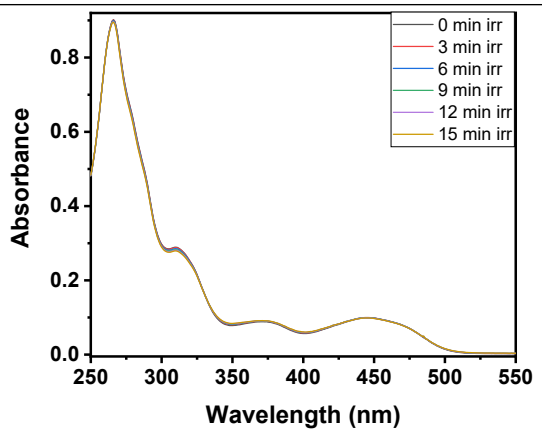
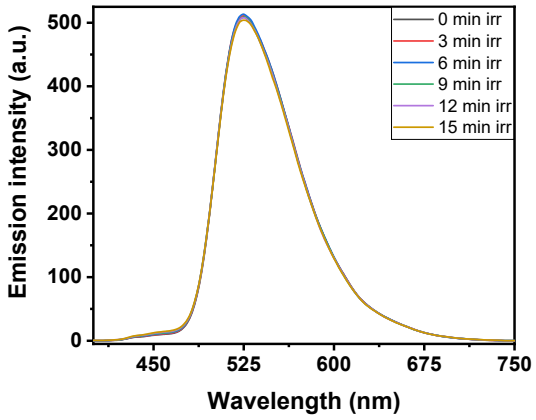
11 µg/mL	
13 µg/mL	

Figure S13. Irradiation with continuous light (450 nm) of an Rf solution (10 µmol/L) in the presence of different concentrations (4-13 µg/L) of the Mg(phen)(fer) complex in a N_2 atmosphere. Irradiation times: 0 min (black), 3 min (red), 6 min (blue), 9 min (green), 12 min (purple) and 15 min (yellow).

Mg(phen)(fer) Concenc.	UV-vis	Emission
4 µg/mL		
7 µg/mL		
9 µg/mL		

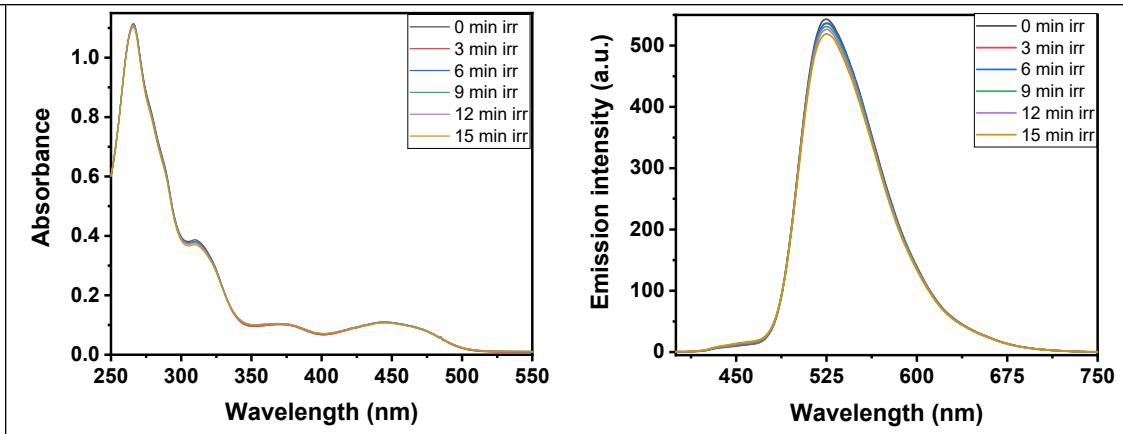
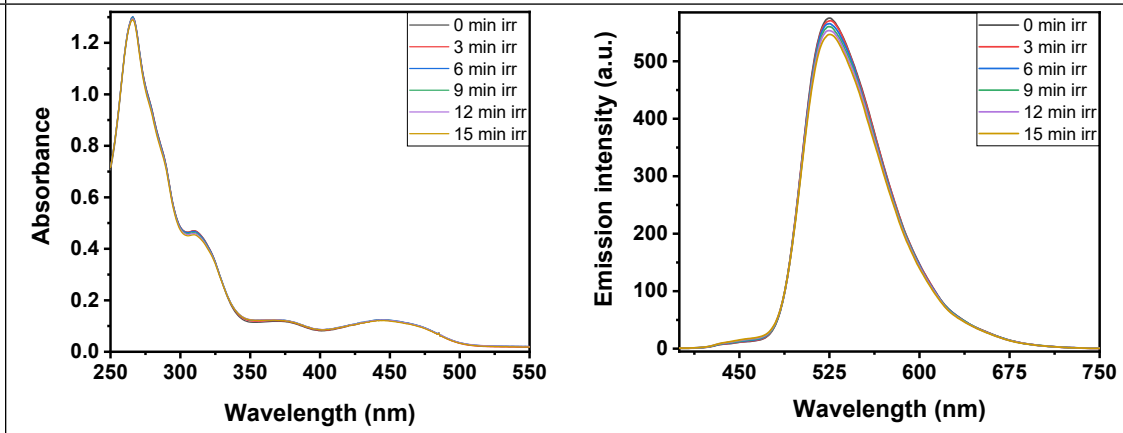
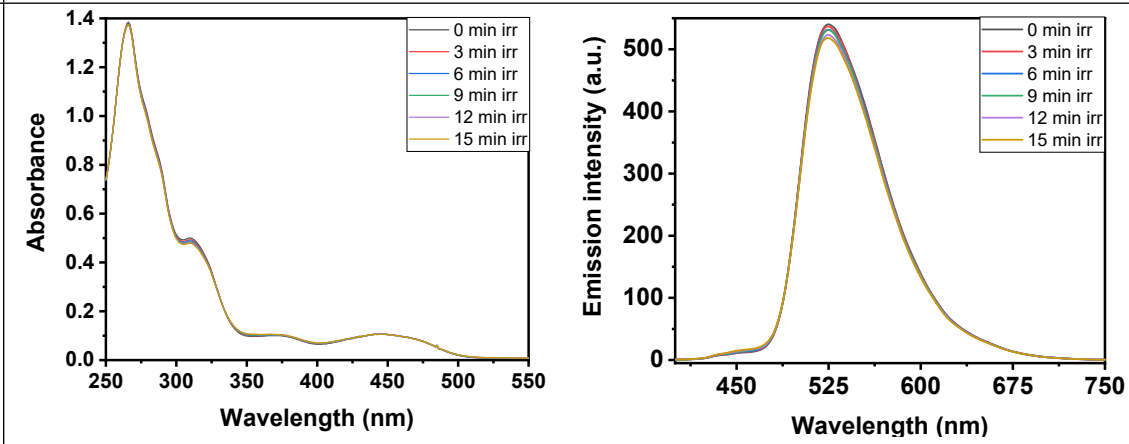
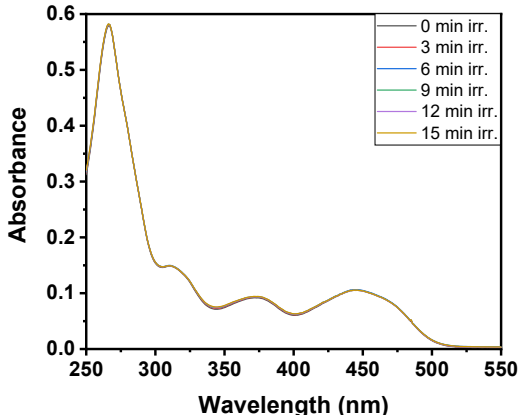
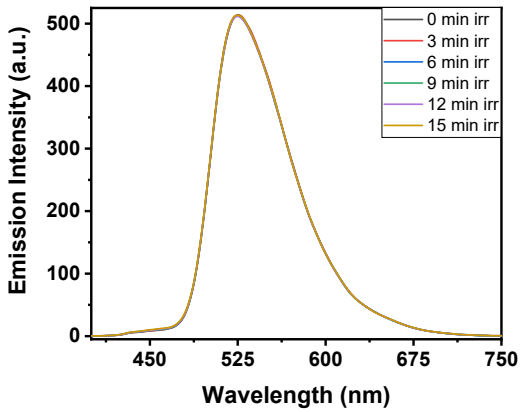
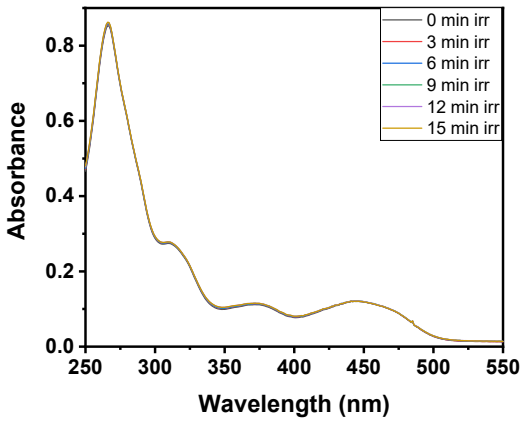
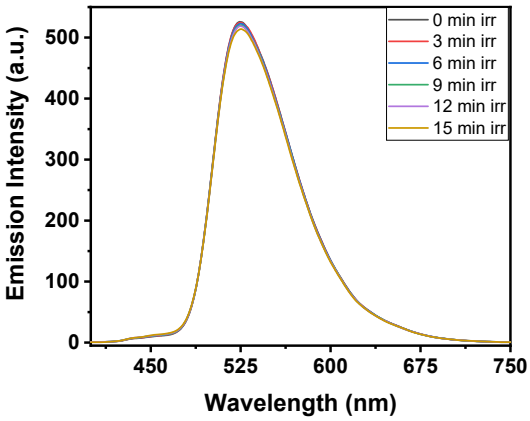
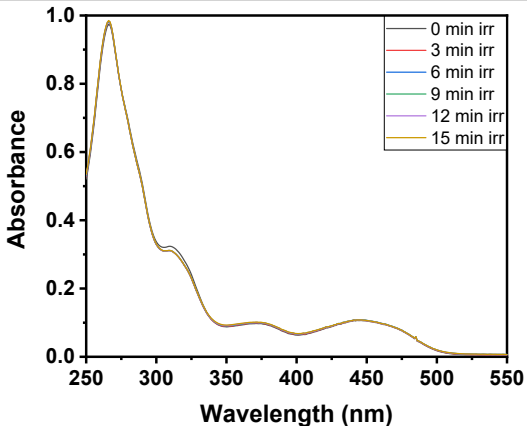
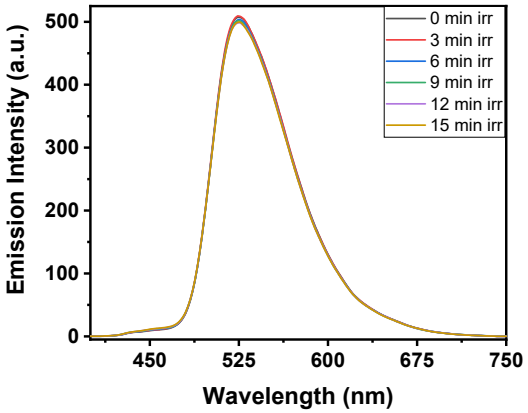
11 µg/mL	
13 µg/mL	
15 µg/mL	

Figure S14. Irradiation with continuous light (450 nm) of an Rf solution (10 µmol/L) in the presence of different concentrations (4-15 µg/L) of the Mg(phen)(fer) complex in air atmosphere. Irradiation times: 0 min (black), 3 min (red), 6 min (blue), 9 min (green), 12 min (purple) and 15 min (yellow).

Mg(phen)(fer) Concen.	UV-vis	Emission
4 µg/mL		
7 µg/mL		
9 µg/mL		

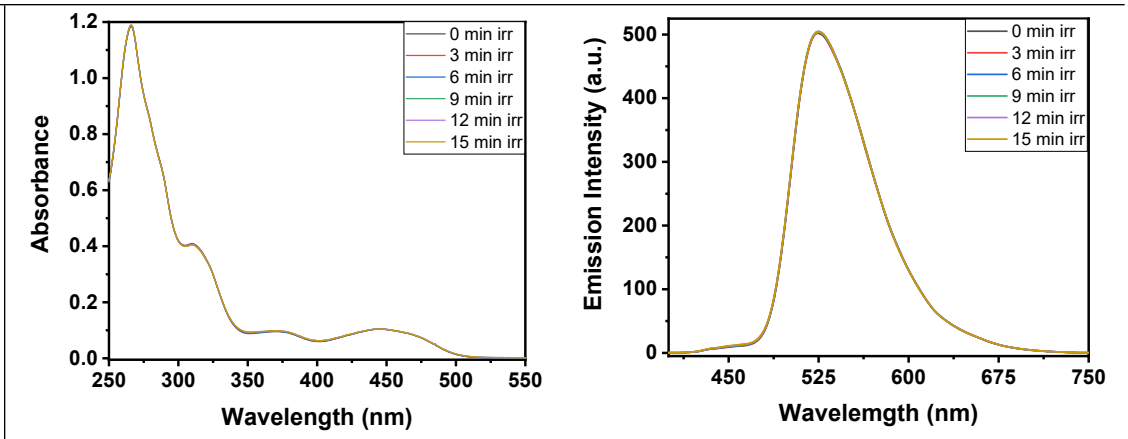
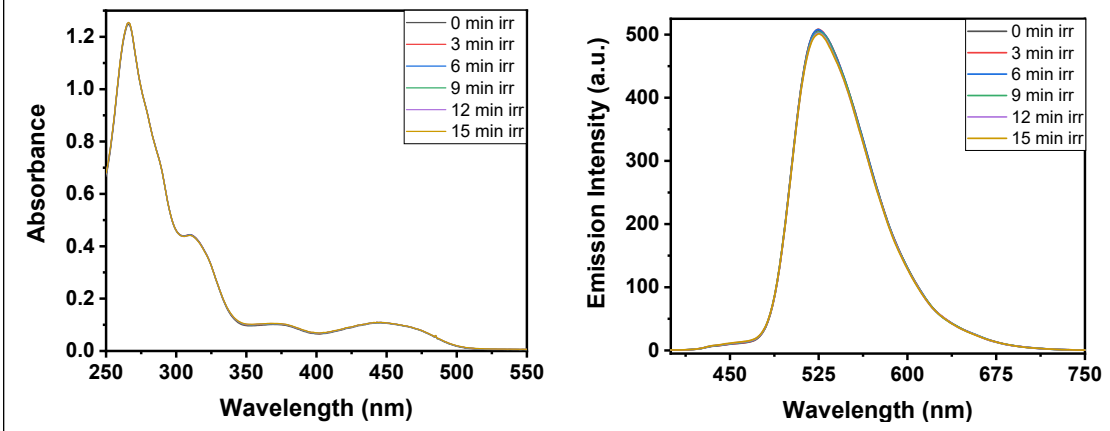
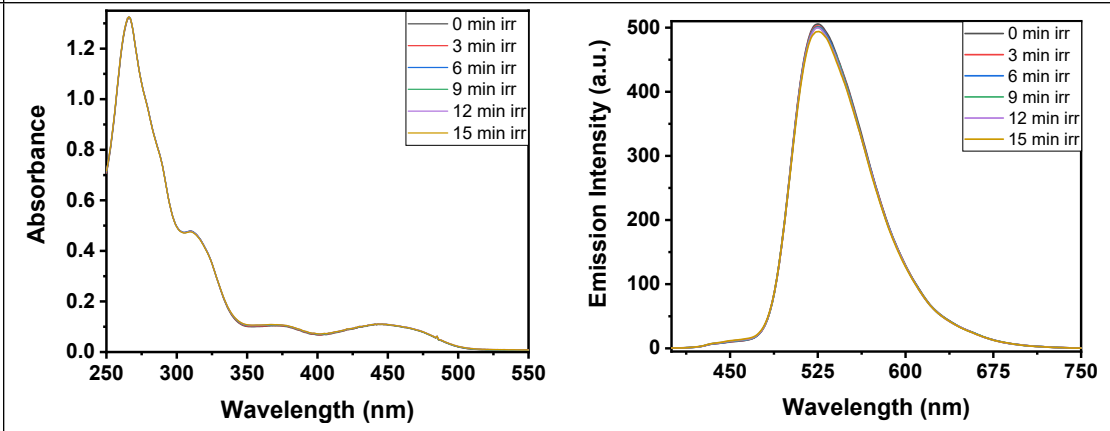
11 µg/mL	
13 µg/mL	
15 µg/mL	

Figure S15. Irradiation with continuous light (450 nm) of an Rf solution (10 µmol/L) in the presence of different concentrations (4-15 µg/L) of the Mg(phen)(fer) complex in an O_2 atmosphere. Irradiation times: 0 min (black), 3 min (red), 6 min (blue), 9 min (green), 12 min (purple) and 15 min (yellow).

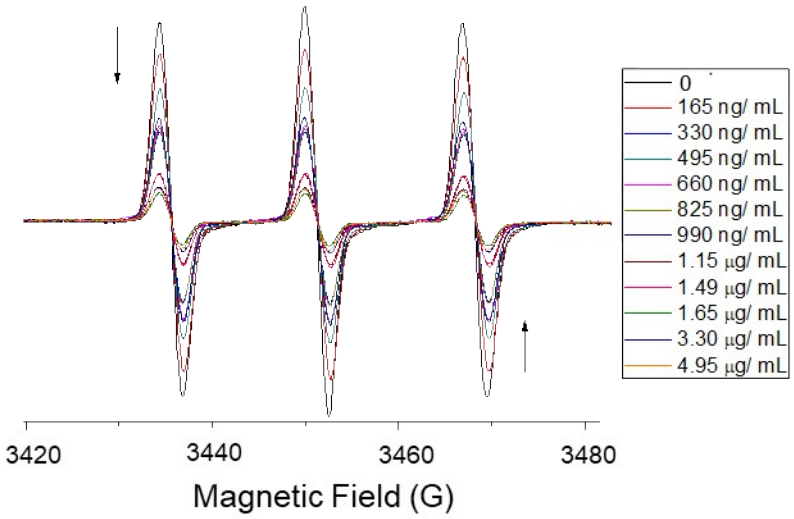
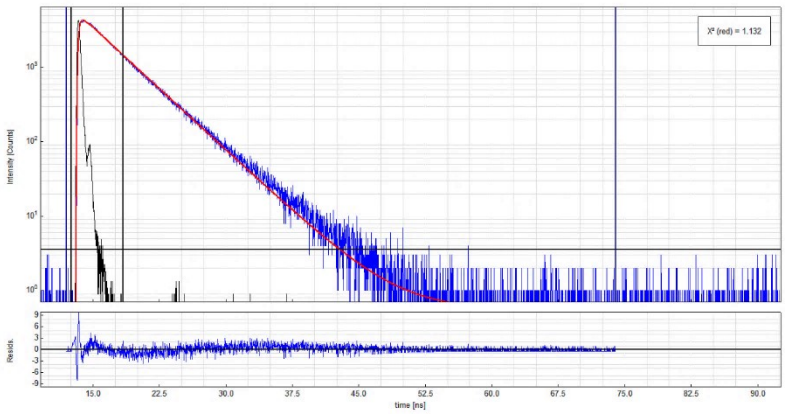
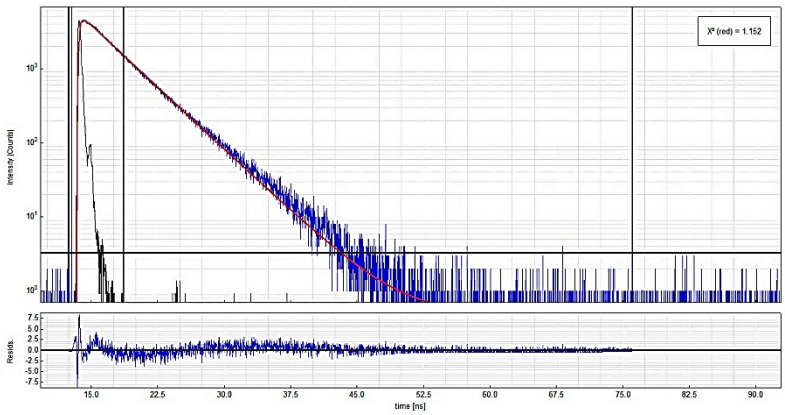
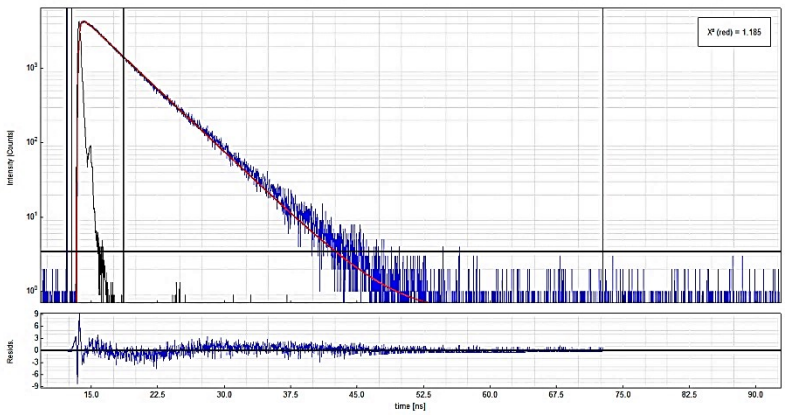
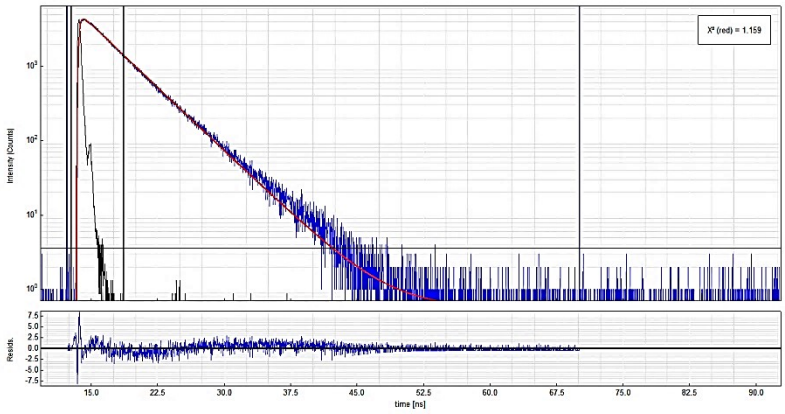
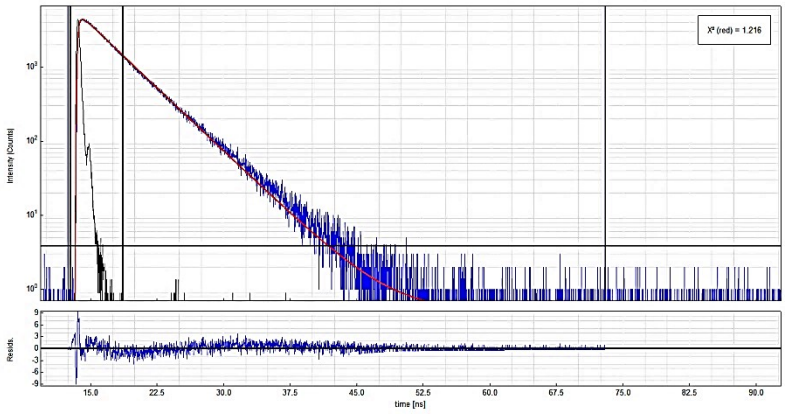
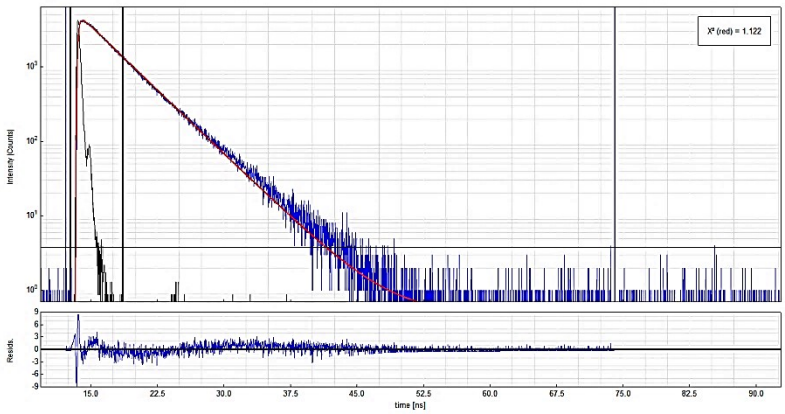


Figure S16. EPR spectra of TEMPO generated *in situ* by the reaction: ^{3*}(Riboflavin) + $^{3}O_2$ → Riboflavin + $^{1}O_2$; $^{1}O_2$ + TEMP → TEMPO (black, control) and $^{1}O_2$ inhibition after adding Mg(phen)(fer) ranging from 0.165 µg /mL to 4.95 µg /mL. Signal decrease through $^{1}O_2$ inhibition reaction with varying concentration of complexes.

Condition in Air	Lifetime Decay profile	τ (ns)
0 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0		3.95
1 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.038 mg/mL		3.90
2 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.076 mg/mL		3.86

3 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.114 mg/mL		3.84
4 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.152 mg/mL		3.83
5 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.190 mg/mL		3.80

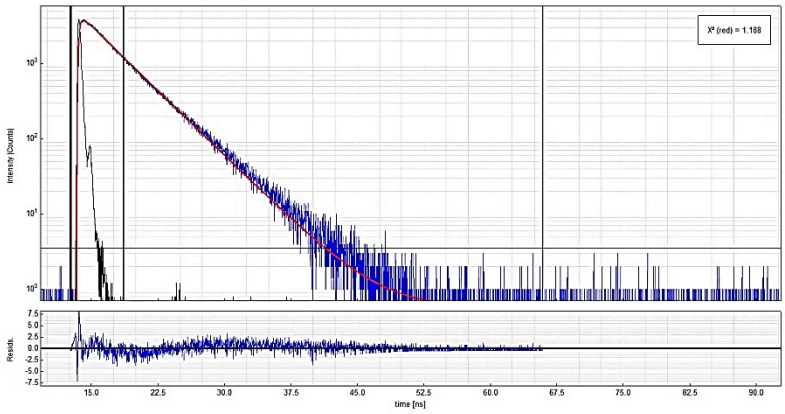
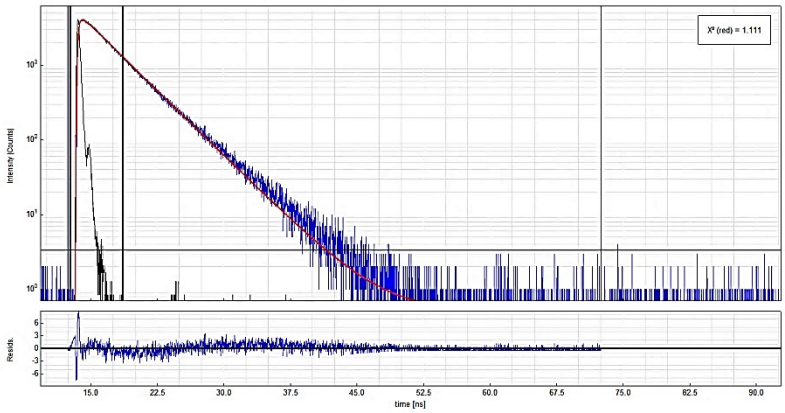
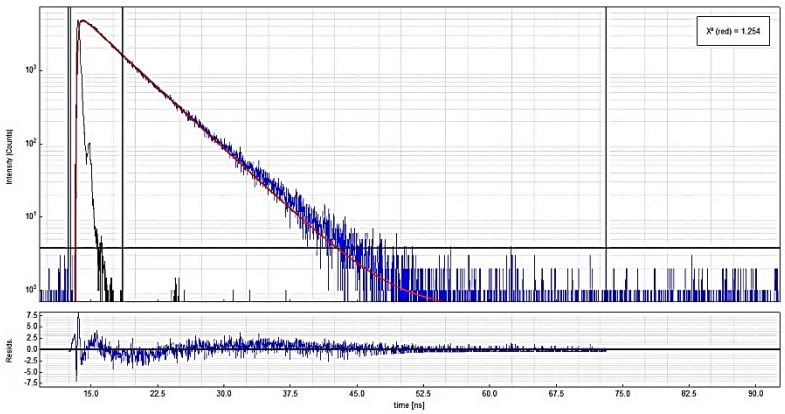
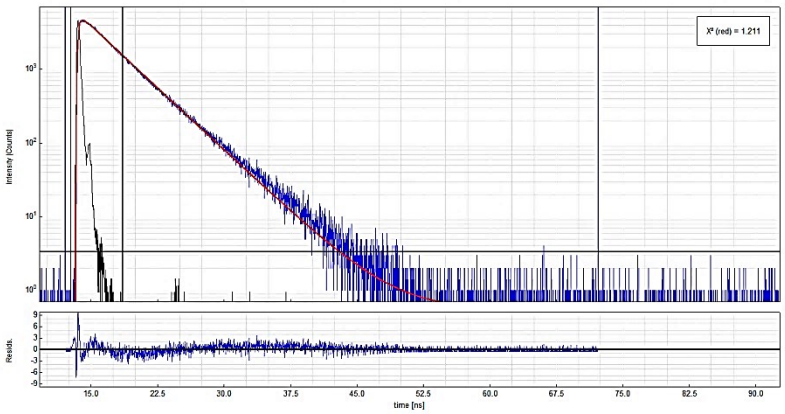
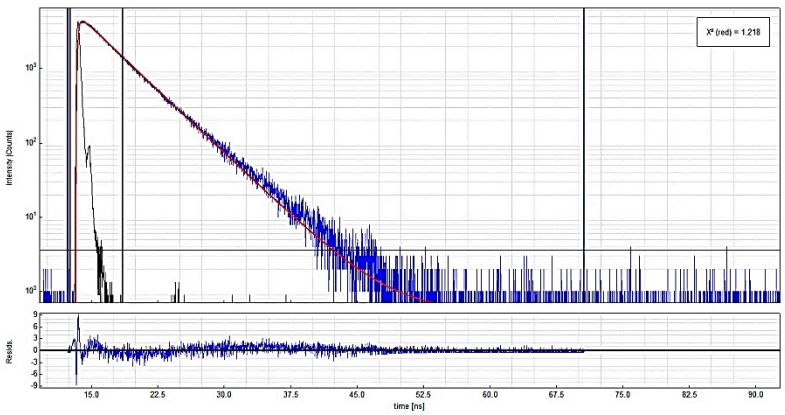
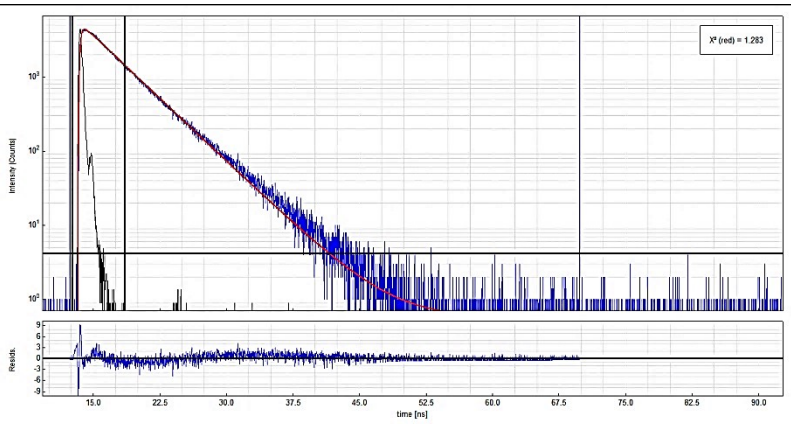
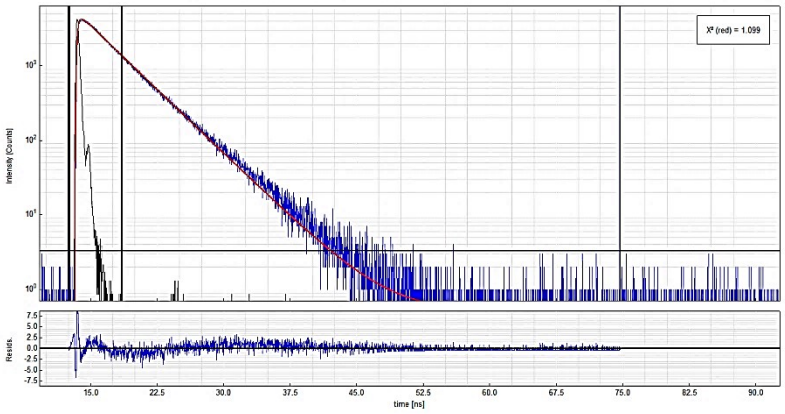
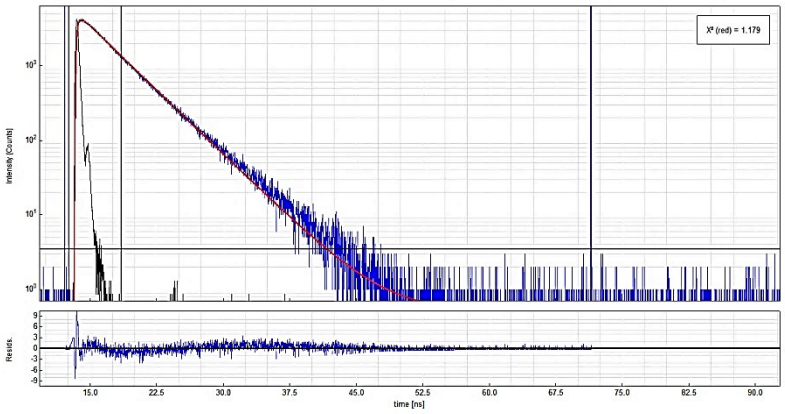
6 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.228 mg/mL		3.79
7 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.266 mg/mL		3.75

Figure S17. Selected riboflavin fluorescence lifetime decay traces recorded in phosphate buffer pH 7.4 at a specific concentration (C_{Rf}= 0.38 mg/mL) with variable concentration of Mg(phen)(fer) complex (C_c= 0.38 to 2.66 mg/mL) in air atmosphere, blue fit decay profile in each condition. Measurements were performed in triplicate. Red decay profile is the IRF decay. The quality of the fit is indicated by the plots of the weighted residues shown below the luminescence decays.

Condition in N_2	Lifetime Decay profile	τ (ns)
0 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0		3,90
1 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.038 mg/mL		3,88
2 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.076 mg/mL		3,86

3 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.114 mg/mL		3,85
4 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.152 mg/mL		3,82
5 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.190 mg/mL		3,79

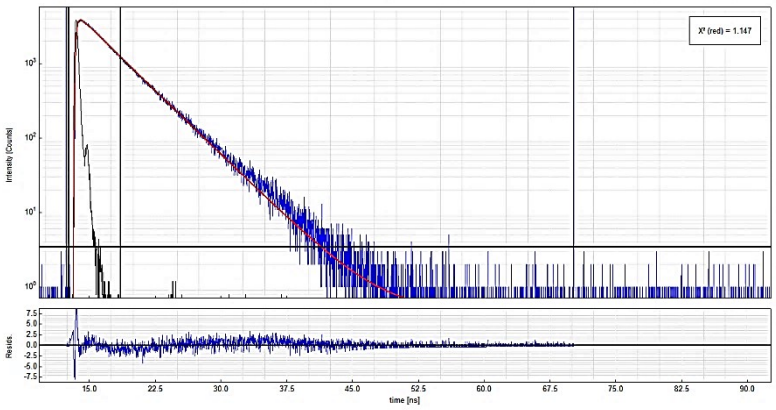
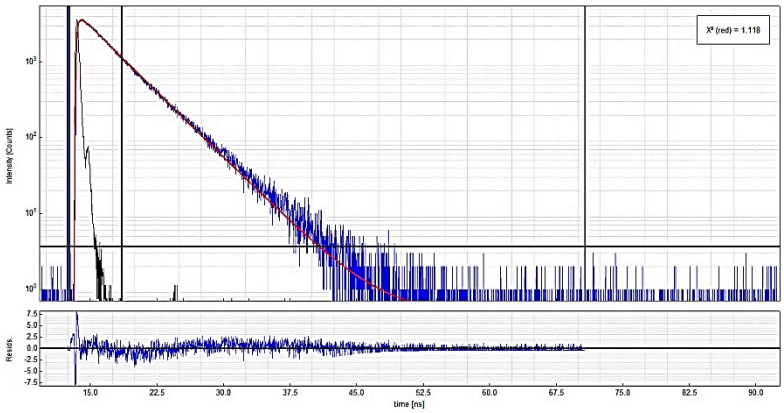
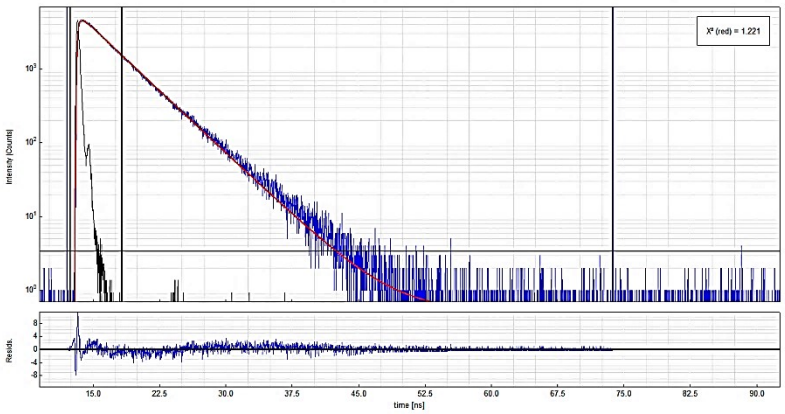
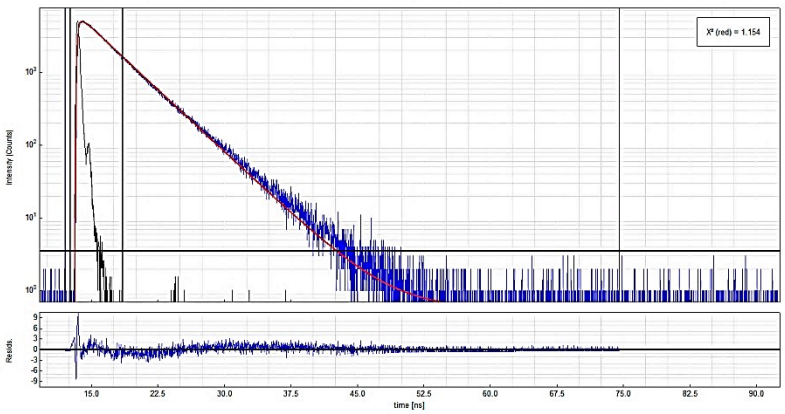
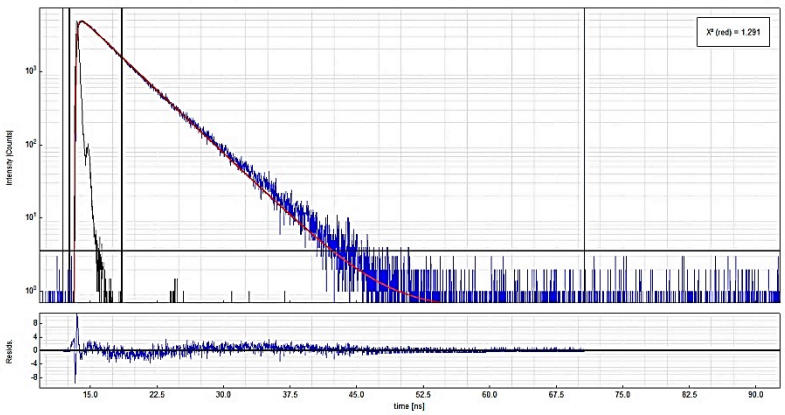
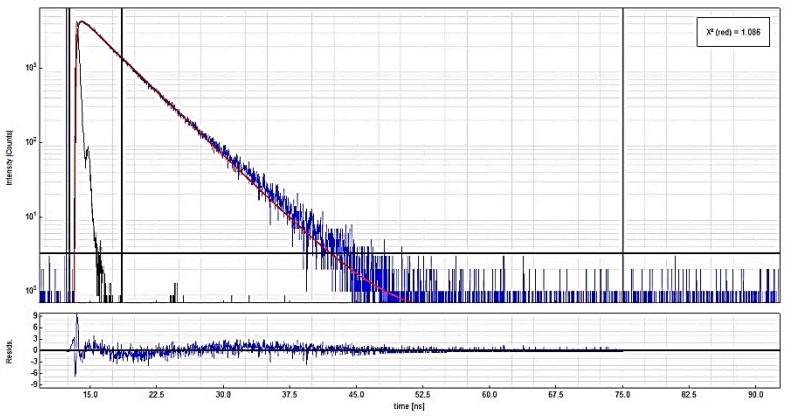
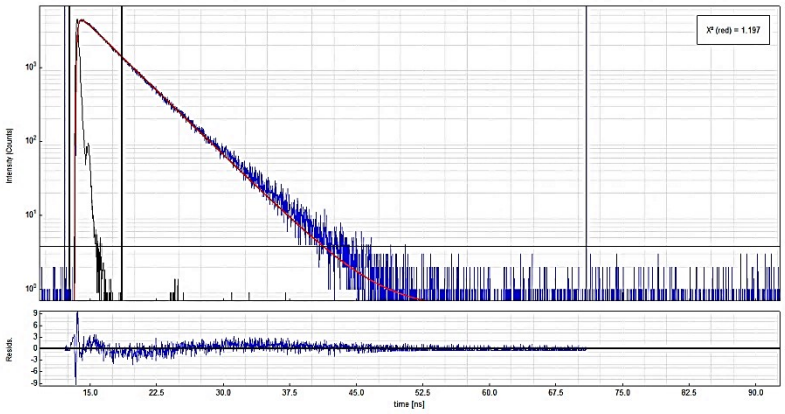
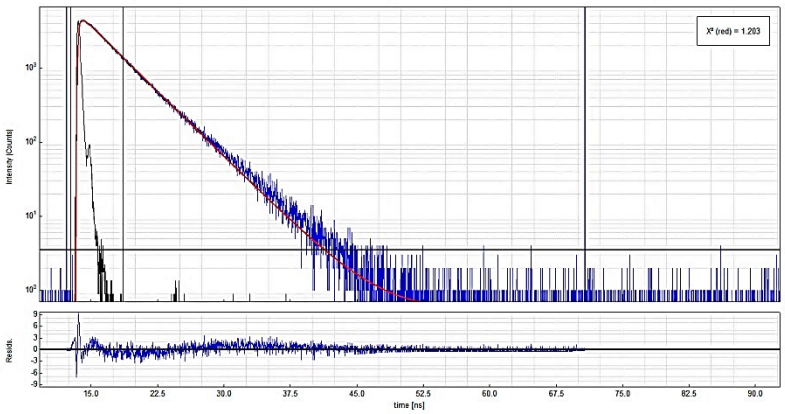
6 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.228 mg/mL		3,79
7 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.266 mg/mL		3,77

Figure S18. Selected riboflavin fluorescence lifetime decay traces recorded in phosphate buffer pH 7.4 at a specific concentration (C_{Rf}= 0.38 mg/mL) with variable concentration of Mg(phen)(fer) complex (C_c= 0.38 to 2.66 mg/mL) in N_2 atmosphere, blue fit decay profile in each condition. Measurements were performed in triplicate. Red decay profile is the IRF decay. The quality of the fit is indicated by the plots of the weighted residues shown below the luminescence decays.

Condition in O_2	Lifetime Decay profile	τ (ns)
0 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0		3,86
1 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.038 mg/mL		3,83
2 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.076 mg/mL		3,79

3 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.114 mg/mL		3,78
4 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.152 mg/mL		3,74
5 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.190 mg/mL		3,71

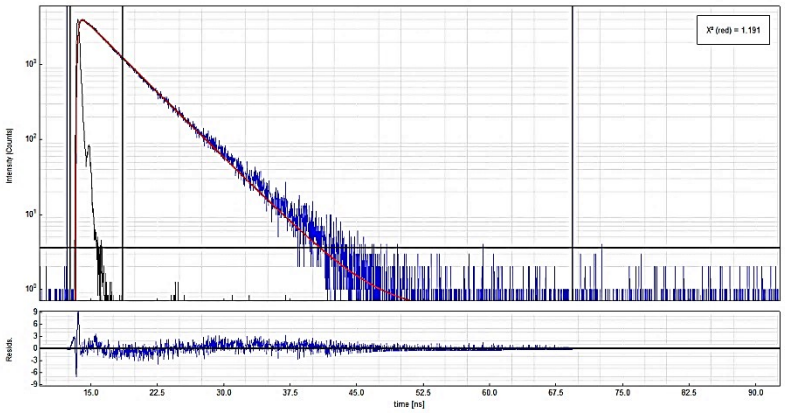
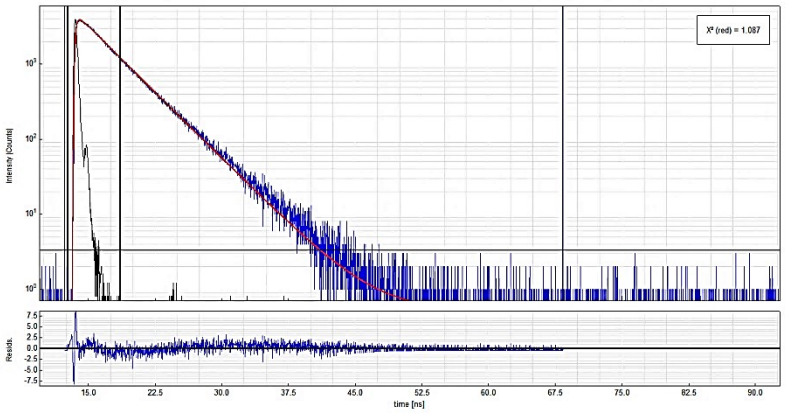
6 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.228 mg/mL		3,71
7 Mg(phen)(fer): 1 Rf C_{Rf}= 0.038 mg/mL C_c= 0.266 mg/mL		3,69

Figure S19. Selected riboflavin fluorescence lifetime decay traces recorded in phosphate buffer pH 7.4 at a specific concentration (C_{Rf}= 0.38 mg/mL) with variable concentration of Mg(phen)(fer) complex (C_c= 0.38 to 2.66 mg/mL) in O_2 atmosphere, blue fit decay profile in each condition. Measurements were performed in triplicate. Red decay profile is the IRF decay. The quality of the fit is indicated by the plots of the weighted residues shown below the luminescence decays.

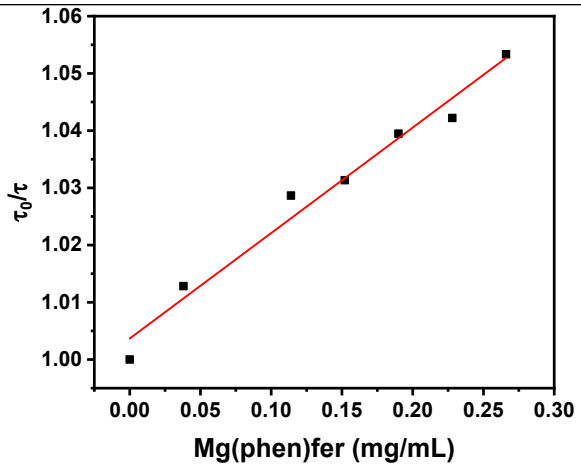
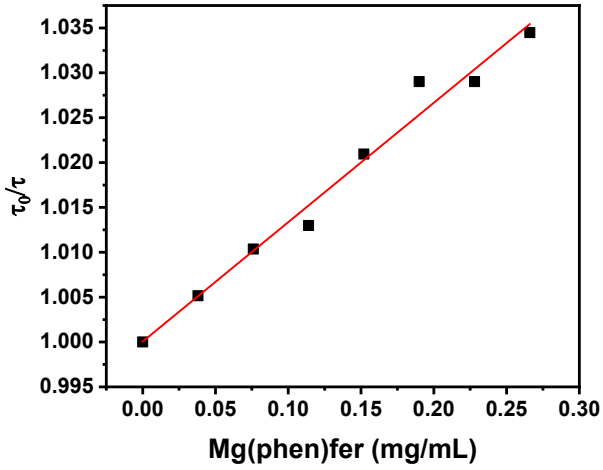
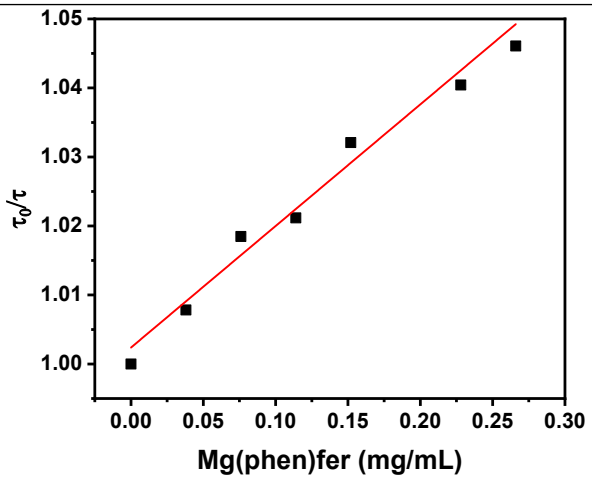
Air		K_{SV}= 0,1844±0,0134 $(mg/mL)^{-1}$ k_q= 8.11 x 10^{11} l/mol.s
N_2		K_{SV}= 0,1330±0,0177 $(mg/mL)^{-1}$ k_q= 1.35 x 10^{12} l/mol.s
O_2		K_{SV}= 0,1762±0,0118 $(mg/mL)^{-1}$ k_q= 8.48 x 10^{11} l/mol.s

Figure S20. Stern-Volmer plots for suppression of the singlet excited state of Rf by the Mg(phen)(fer) complex in different atmospheres and concentrations: N_2 (top), air (center) and O_2 (bottom) in phosphate buffer pH 7.4. Values of the Stern-Volmer constant (K_{SV}) and bimolecular rate constant of singlet state suppression by the complex (k_q). Measurements were performed in triplicate.

Sample	Starch	
	% Haze	Visual test
Control	20,05 %	
Mg(phen)(fer)	13,50 %	

Figure S21. Haze (%) values and visual transparency test for starch films produced by casting.

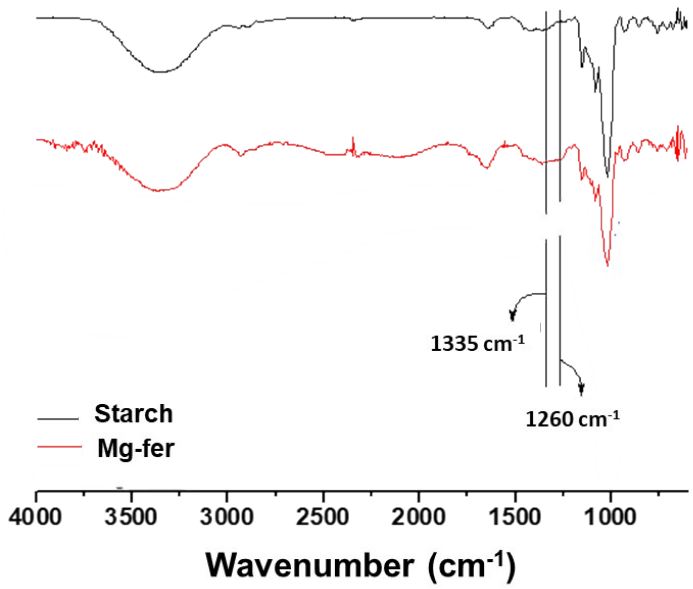


Figure S22. Starch films Fourier transform infrared attenuated total reflectance (ATR–FTIR) spectroscopy: control (black) and containing Mg(phen)(fer) (red).

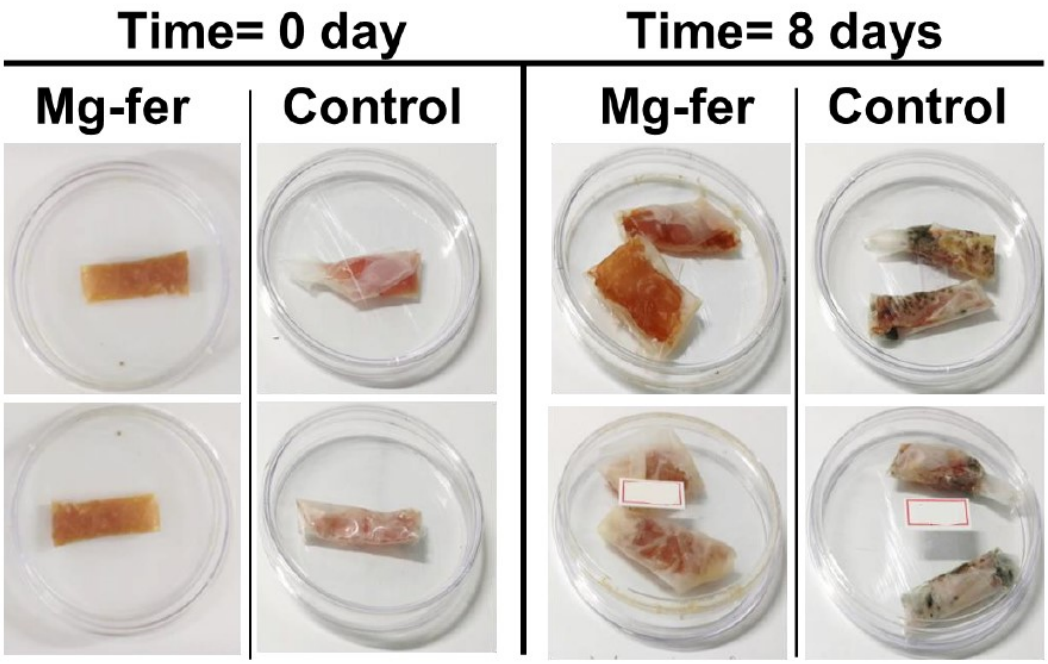


Figure S23. Qualitative activity of Mg(phen)fer as active compound in active starch film compared to the film control under the following conditions: continuous white light at 8°C for 8 days.

Table S1. First-order rate constants (k_{obs}) for Rf photobleaching under anaerobic condition with different concentrations of the complex in phosphate buffer pH 7.4

Mg(phen)(fer)	k (min^{-1})

concentration (μg/mL)	
0	0,244
4	0,233
7	0,207
9	0,199
11	0,102
13	0,080

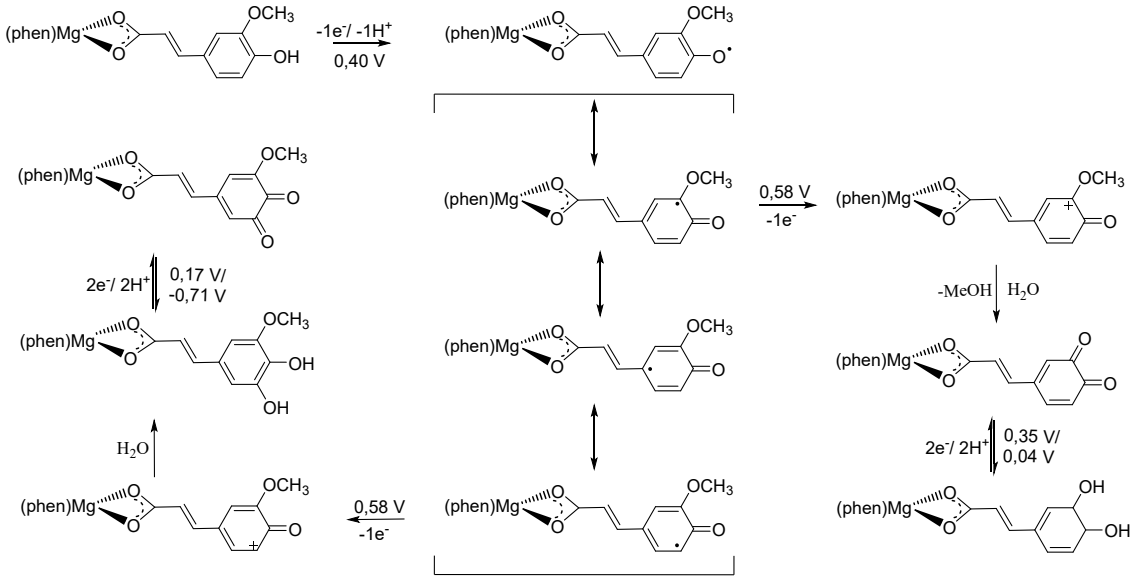
Table S2. Halo diameter in cm for different concentrations of Mg(phen)fer against *A. niger, P. nonatum and R. oryzae*

Mg(phen)(fer)

Fungi / Concentration	*A. niger*	*P. nonatum*	*R. oryzae*
Control	1.32 cm	1.00 cm	1.75 cm
0.001 mg/mL	1.30 cm	0.90 cm	1.74 cm
0.005 mg/mL	1.15 cm	0.88 cm	1.44 cm
0.01 mg/mL	1.00 cm	0.75 cm	1.45 cm
0.05 mg/mL	0	0	0
0.1 mg/mL	0	0	0

Table S3. Halo diameter in cm for different concentrations of ferulic acid against *A. niger, P. nonatum and R. oryzae*

Fungi / Concentration	Ferulic acid		
	A. niger	*P. nonatum*	*R. oryzae*
Control	0.92 cm	0.69 cm	1.12 cm
0.70 mg/mL	0.68 cm	0.60 cm	0.59 cm
1.05 mg/mL	0.58 cm	0.45 cm	0.61 cm
1.40 mg/mL	0.59 cm	0.45 cm	0.44 cm
1.75 mg/mL	0.58 cm	0.31 cm	0.41 cm
2.10 mg/mL	0.42 cm	0 cm	0.42 cm



Scheme S1**.** Proposed mechanism for the electrochemical process of the Mg(phen)(fer) complex.