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Role of perhydroxyl radical in the chelator-mediated Fenton reaction

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Electronic Supplementary information

Table S1. Catecholates ligands classified as electron donor (ED) or electron withdrawer (EW) according to their Hammett parameters. Hammett parameter were calculated by Salgado *et al.*[1].

Name	Hammett parameter		
	σ_m	σ_p	$\Sigma\sigma = (\sigma_{m+}\sigma_p)$
4-tert-butylcatechol	-0.10	-0.20	-0.30 (ED)
4-methylcatechol	-0.07	-0.15	-0.22 (ED)
Catechol	0	0	0
3,4-dihidroxybenzoic acid	0.37	0.42	0.87 (EW)
4-nitrocatechol	0.71	0.78	1.49 (EW)

*ED: electron donor; EW: electron withdrawer

(A)

Radical adduct	Coupling constant (G)			Source
	a_N	a^H_β	a^H_γ	
DMPO-HO•	14.9	14.9		Bruker tech bull. [20]
DMPO-HO_2•	14.2	11.4	1.2	Bruker tech bull. [20]
POBN-HO•	14.97	1.68	0.33	Finkelstein *et al.*[18]
POBN-HO_2•	14.18	1.72		Finkelstein *et al.*[18]
DMPO adduct detected (-HO•)	14.93	14.93		This work
POBN adduct detected (-HO_2•)	14.22	1.69		This work

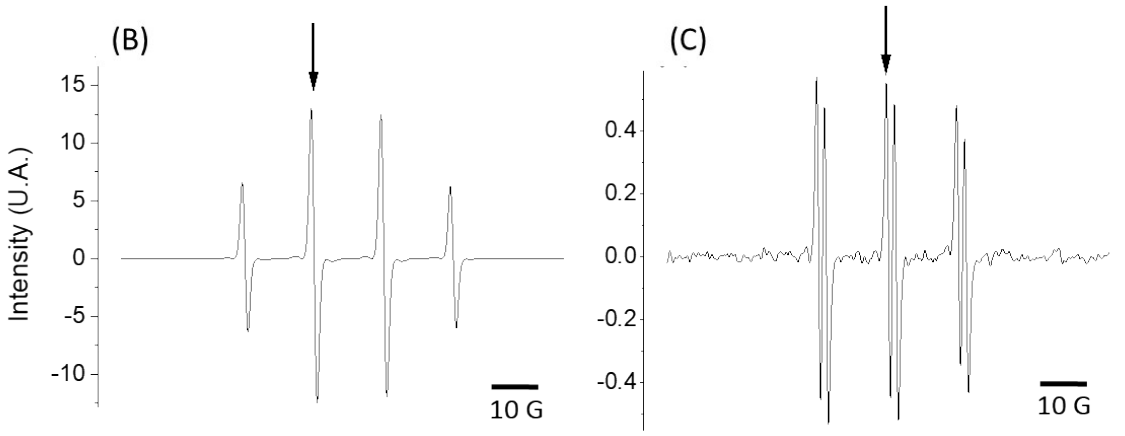

Figure S1. Identification of DMPO and POBN detected in this work by comparison of coupling constants (A) and shape of the DMPO- HO• (B) and POBN-HO_2• (C) adducts. The arrow indicates the selected peak from which the intensity was measured for the construction of 3D surface plots.

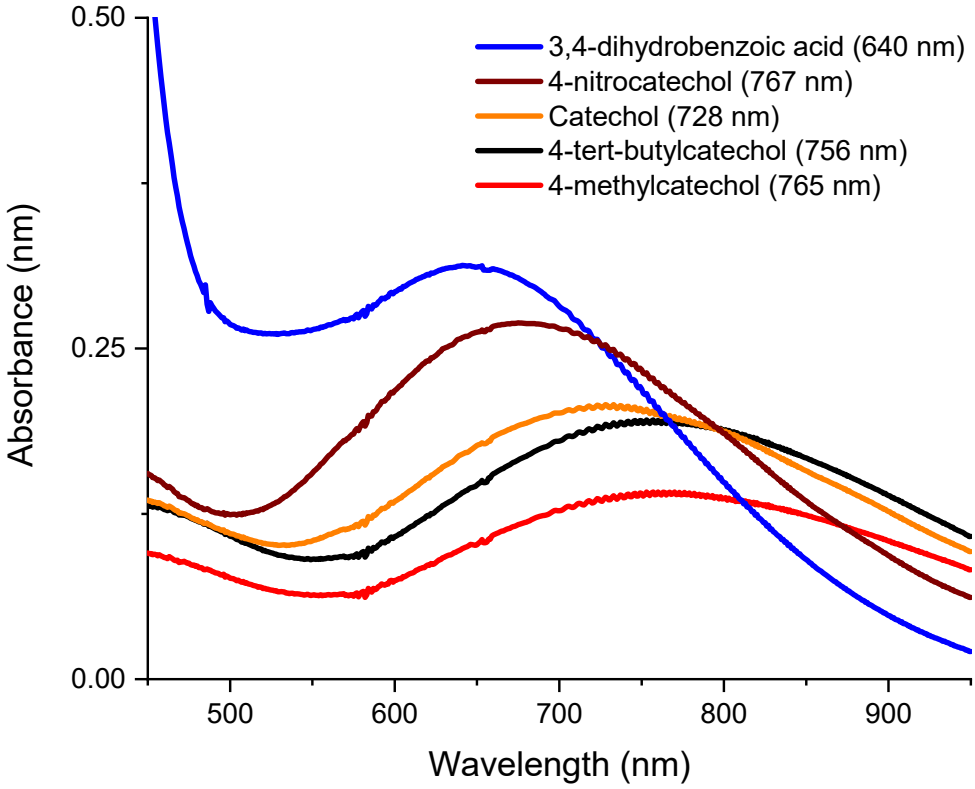

Figure S2. UV-Vis spectra of the ligand-iron monocomplex of catechol-like ligands used in this study and their respective λ maximum in parenthesis.

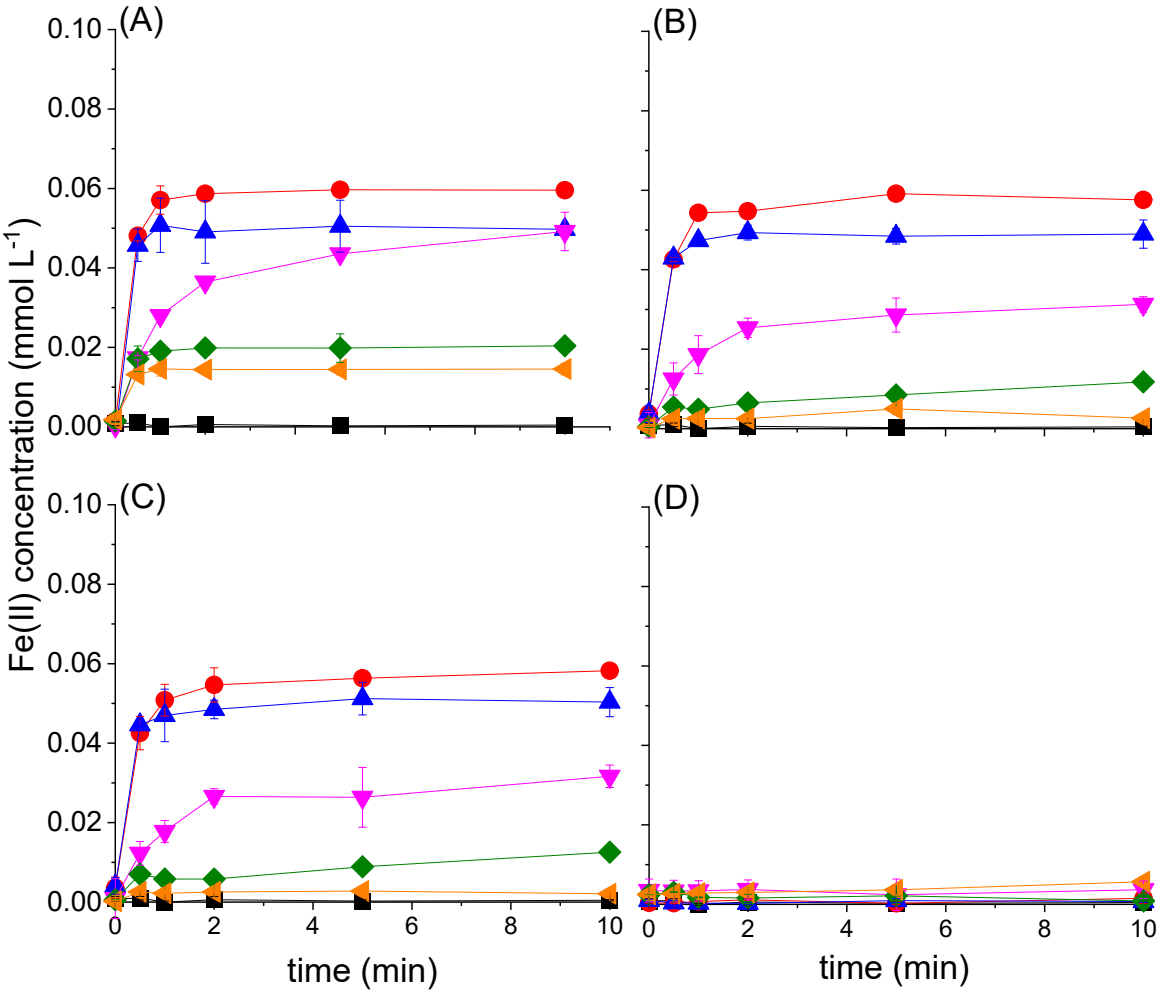

Figure S3. Iron reduction profile of ED ligands 4-tert-butylcatechol (ஜ - red); 4-methylcatechol (◘ - blue); catechol (② - pink), and EW ligands 3,4-dihydroxibenzoic acid (◴ - green); 4-nitrocatechol (♦ - yellow). (A) pH 3.0; (B) pH 4.0; (C) pH 5.0; (D) pH 6.0.

References

1. P. Salgado, V. Melin, Y. Duran, H. Mansilla and D. Contreras, *Environ Sci Technol*, 2017, **51**, 3687-3693.
2. Bruker Biospin, technicall bulletin (available online at www.syntechinnovation.com).
3. E. Finkelstein, G. M. Rosen and E. J. Rauckman, *Molecular Pharmacology*, 1979, **16**, 676-685.