

Supplementary

Metal–Flavonoid Interactions—From Simple Complexes to Advanced Systems

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Abstract: For many years, metal-flavonoid complexes have been widely studied as part of drug discovery programs, but in the last decade, their importance in materials science has increased significantly. A deep understanding the role of metal ions and flavonoids in constructing simple complexes and more advanced hybrid networks will facilitate the assembly of materials with tailored architecture and functionality. In this review, we highlight the most essential data on metal–flavonoid systems, presenting a promising alternative in the design of hybrid inorganic–organic materials. We focus mainly on systems containing Cu^{II} and Fe^{III/II} ions, which are necessary in natural and industrial catalysis. We discuss two kinds of interactions that typically ensure the formation of metal-flavonoid systems, namely coordination and redox reactions. Our intention is to cover the fundamentals of metal-flavonoid systems to show how this knowledge has been already transferred from small molecules to complex materials.

Keywords: hybrid materials; redox; flavonoids; transition metals

Table S1. Structural and physicochemical details on Cu^{II}/Cu^I-flavonoid systems established by coordination or redox interactions.

Cu ^{II} /Cu ^I -flavonoid interaction							
Studied system	Coordination				Redox		
	Coordination sites	Conditions	Physicochemical data	Ref.	Studied reaction	Conditions	Ref.
Cu ^{II} -naringenin	4-C=O/5-OH	H ₂ O-DMF mixture or DMF solution	UV-Vis: band II at λ _{max} = 290 nm charge transfer transitions at λ _{max} = 360 nm	[49]	Cu ^{II} + e ⁻ ⇌ Cu ^I catalysed by naringenin	pH 4.50 and 5.50 established with acetate buffer pH 6.80 and 7.50 established with HEPES or Tris-HCl buffer; gradual and rising profile of reaction specifically at higher pH	[64]
	2x naringenin <i>via</i> 4-C=O/5-OH & H ₂ O or DMF		Solid phase	[49]			
Cu ^{II} -apigenin	4-C=O/5-OH	DMSO or MeOH solution	UV-Vis: hypsochromic shift in band II and bathochromic shift in band I	[22]	Cu ^{II} + e ⁻ ⇌ Cu ^I catalysed by apigenin	pH 4.50 and 5.50 established with acetate buffer pH 6.80 and 7.50 established with HEPES or Tris-HCl buffer; gradual and rising profile of reaction specifically at higher pH	[64]
Cu ^{II} -luteolin	4-C=O/5-OH & 3'-OH/4'-OH	0.16 M NaCl solution	UV-Vis: hypsochromic shift in band II (Δ ~ 15 nm)	[52]	Cu ^{II} + e ⁻ ⇌ Cu ^I catalysed by luteolin	pH 4.50 and 5.50 established with acetate buffer pH 6.80 and 7.50 established with HEPES or Tris-HCl buffer; bell-shaped response of the reaction yield regardless of pH	[64]
	pH < 5.00 no coordination		UV-Vis at pH 5.00-5.80: hypsochromic shift in band II and new peak at 290 nm; band I unchanged	[14]			
	pH 5.00-5.80 4-C=O/5-OH		UV-Vis at pH 6.00-7.20: hypsochromic shift in band II (Δ ~ 60 nm) and bathochromic shift in band I (Δ ~ 4 nm)				
	pH 6.00-7.20 3'-OH/4'-OH		EPR in DMSO at 100K g _⊥ = 2.073 g _∥ = 2.291 A _∥ = 125 and g _∥ = 2.242 A _∥ = 118				
Cu ^{II} -kaempferol	4-C=O/5-OH in DMSO 4-C=O/3-OH in MeOH	DMSO and MeOH solution	UV-Vis in DMSO at RT: new band at 290 nm UV-Vis in MeOH at RT: minor shift in band II (Δ ~ 5 nm); shift in band I (Δ ~ 65 nm)	[22]	Cu ^{II} + e ⁻ ⇌ Cu ^I catalysed by kaempferol	pH 4.50 and 5.50 established with acetate buffer pH 6.80 and 7.50 established with HEPES or Tris-HCl buffer; bell-shaped response of the reaction yield regardless of pH	[64]

	mononuclear complex 4-C=O/3-OH in MeOH		UV-Vis of binuclear complex: bathochromic shift in band I and II				
	binuclear complex 4-C=O/3-OH and 3'-OH/4'-OH in MeOH	MeOH solution and DMSO-d ₆ for ¹ H-NMR	¹ H-NMR: pure quercetin δ 9.60 (s, ¹ H, 3-OH) and lack of this signal in binuclear complex	[55]	Cu ^{II} + e ⁻ ⇌ Cu ^I catalysed by quercetin	pH 7.50 at various M:L 1:1, 2:1, and 3:1	[66,67]
Cu ^{II} -quercetin	mononuclear complex 3'-OH/4'-OH in H ₂ O	H ₂ O solution, pH 10.00	UV-Vis of mononuclear complex: decrease in the intensity of band I	[56]	Cu ^{II} + e ⁻ ⇌ Cu ^I catalysed by quercetin	pH 4.50 and 5.50 established with acetate buffer pH 6.80 and 7.50 established with HEPES or Tris-HCl buffer; bell-shaped response of the reaction yield regardless of pH	[64]
	binuclear complex 4-C=O/5-OH and 3'-OH/4'-OH in H ₂ O		UV-Vis of binuclear complex: decrease in the intensity of band I and band II				
	3'-OH/4'-OH at M:L below 0.0028		UV-Vis at M:L below 0.0028: increase in the intensity of band I	[57]			
	4-C=O/3-OH at M:L in the range from 0.0028 to 3.2	H ₂ O solution, pH 5.00	UV-Vis at M:L in the range 0.0028 – 3.2: bathochromic shift of band II				
Cu ^{II} -catechin	pH 5.50: no coordination pH 7.40: 3'-OH/4'-O	H ₂ O solution, pH 5.50 and 7.40	UV-Vis at pH 7.40: bathochromic shift and small decrease in band I (Δ ~ 16 nm)	[15]	Cu ^{II} + e ⁻ ⇌ Cu ^I catalysed by catechin	pH 4.50 and 5.50 established with acetate buffer pH 6.80 and 7.50 established with HEPES or Tris-HCl buffer; gradual and rising profile of reaction specifically at higher pH	[64]
					Cu ^{II} + e ⁻ ⇌ Cu ^I catalysed by catechin	pH 7.50 at M:L 2:1	[65]
Cu ^I -quercetin	4-C=O/3-OH	MeOH solution	UV-Vis: bathochromic shift in band I (Δ ~ 24 nm) and band II (Δ ~ 34 nm)	[70]			

Table S2. Structural and physicochemical details on Fe^{III}/Fe^{II}-flavonoid systems established by coordination or redox interactions.

Fe ^{II} /Fe ^{III} -flavonoid interaction								
Studied system	Coordination			Ref.	Studied reaction	Redox		
	Coordination sites	Conditions	Physicochemical data			Conditions	Ref.	
Fe ^{III} -naringenin	4-C=O/5-OH	H ₂ O solution, 0.5 M NaClO ₄ ionic strength, 25°C, pH range 1–3	Kinetic studies based on UV-Vis	[95]	Fe ^{II} - e ⁻ ⇌ Fe ^{III} catalysed by narin- genin	H ₂ O solution at pH 6.50 and 7.00		[59]
	4-C=O/5-OH	H ₂ O solution, pH 6.50	UV-Vis: bathochromic shift in band I (λ _{max} = 350 nm, sh)	[60]		DMSO solution		[69]
Fe ^{III} -apigenin	4-C=O/5-OH	H ₂ O solution, pH 2.00	UV-Vis: Ligand-to-Fe ^{III} -Charge Transfer (LMCT) transitions (λ _{max} = 520 nm); bathochromic shift in band I and II	[59]	Fe ^{III} + e ⁻ ⇌ Fe ^{II} catalysed by luteolin	H ₂ O solution, 90°C		[70]
Fe ^{III} -luteolin	3'-OH/4'-OH	EtOH solution	UV-Vis: bathochromic shift in band I and II	[61]				
	3'-OH/4'-OH	H ₂ O solution, pH 6.50	UV-Vis: bathochromic shift in band I (λ _{max} = 420 nm) and II (λ _{max} = 270 nm) and new band from πτ→dπ LMCT (λ _{max} = 550 nm)	[60]				
Fe ^{III} -kaempferol	4-C=O/5-OH	H ₂ O solution, pH 4.00 and 8.00	UV-Vis: bathochromic shift in band I	[62]				
	4-C=O/5-OH	H ₂ O solution, pH 6.50	UV-Vis: bathochromic shift in band I (λ _{max} = 420 nm)	[60]				
Fe ^{II} -quercetin	4-C=O/5-OH	MeOH solution	UV-Vis: bathochromic shift in band I and band II; new band from πτ→dπ LMCT (λ _{max} = 425 nm)	[78]				
Fe ^{III} -quercetin	3'-OH/4'-OH in the dominant species Fe(H) ₅ (H ₅ Que) ₂ ²⁻	H ₂ O solution, pH range 2.00- 4.50, 0.16 M NaCl, 37°C Fe(H) ₅ (H ₅ Que) ₂ ²⁻ species with M:L 1:2, pH 2.00	Potentiometric titration and DFT	[80]	Fe ^{III} + e ⁻ ⇌ Fe ^{II} catalysed by quercetin	MeOH-H ₂ O mixture 1:1 with 0.1 % ace- tic acid; final pH 3.00		[71]
		Fe(H) ₄ (H ₅ Que) ⁻ with M:L 1:1, pH 3.00						
		Fe(H) ₆ (H ₅ Que) ₂ ³⁻ with M:L 1:2, pH 3.00						
	4-C=O/3-OH	DMSO-d ₆	¹ H-NMR, ¹³ C-NMR and maps of the molecular electrostatic potential (MEP)	[80]	Fe ^{III} + e ⁻ ⇌ Fe ^{II} catalysed by quercetin	0.1 M HCl-MeOH 1:1, 37°C		[72]
					Fe ^{III} + e ⁻ ⇌ Fe ^{II} catalysed by quercetin	MeOH-H ₂ O mixture 1:1 under aerobic and anaerobic atmosphere		[74]

					$\text{Fe}^{\text{III}} + \text{e}^- \rightleftharpoons \text{Fe}^{\text{II}}$ catalysed by quercetin	50 mM acetate buffer, pH 5.50	[15]
Fe^{III} -catechin	3'-OH/4'-OH	aqueous solution, pH 7.40	UV-Vis; new LMCT band at $\lambda_{\text{max}} = 491$ nm, pH range 9.71-10.10 and $\lambda_{\text{max}} = 551$ nm, pH 7.40	[82]	$\text{Fe}^{\text{III}} + \text{e}^- \rightleftharpoons \text{Fe}^{\text{II}}$ catalysed by catechin	nano-ESI-MS analysis; MeOH- H ₂ O mixture 1:1	[54]
