Supplementary materials

to

FLAVONOID-BASED COCRYSTALS: A COMPREHENSIVE STUDY ON THEIR SYNTHESIS, CHARACTERIZATION, PHYSICOCHEMICAL PROPERTIES AND APPLICATIONS

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Table S1. Synthetic routes of flavonoid-based cocrystals reported from 2017 to date in the CSD (accessed January 2025) and solvents employed. See text for a brief description of the methods. NG: neat grinding, LAG: liquid-assisted grinding, SE: solvent evaporation, SL: slurry, CC: cooling crystallization, AS: antisolvent process, GAS-gas antisolvent process, RC: reaction crystallization, OPD: one-pot deracemization. Abbreviations: (+) performed (a) indicates that an additional method was used to obtain single-crystal of cocrystal; (b) indicates that sonication used to dissolve; (c) indicates that various methods used to crystal preparation, and (d) indicates that solvent evaporation preceded by milling.

Flavonoid	Coformer	Solid-based methods									Solution based-methods																																														
		NG	LAG								SE																		SL													CC				AS						GAS		RC			OPD
			ethanol	acetonitrile	methanol	n-butanol	water/ethanol/acetone	Water/ethanol	isopropanol	acetone	methanol	water	acetonitrile	tetrahydrofuran	ethanol/THF	ethanol	propanol	ethanol/ethyl acetate	ethanol/dichloromethane	ethanol/acetone	dichloromethane/isopropanol	dichloromethane/ethyl acetate	acetonitrile/n-butanol/ethanol	water/methanol/ethyl acetate	acetone	methanol/ethyl acetate	ethyl acetae	ethanol/water	ethanol/dichloromethane	methanol	acetonitrile	ethanol	ethyl acetate	isopropylalcohol	isopropyl ether	methanol/ethyl acetate	acetonitrile/ethyl acetate	acetone	dioxane	tetrahydrofuran	water	methanol	ethyl acetate	ethyl acetate/acetonitrile	dichloromethane/methyl isobutyl ketone/acetone	Ethanol/ethyl acetate + n-heptane	isopropanol+ n-heptane	dichloromethane/tetrahydrofuran + n-heptane	ethyl acetate + n-heptane	THF+hexane	DMSO+water	acetone	ethanol	methanol	ethanol	acetone/H_2O	
Flavone	Naringenin [1]	+[a]																																																							
	Diethylstilbestrol [2]										+			+																																											
	Sulfaguanidine [3][c]																																																								
	Dapsone [3][c]																																																								
	Sulfanilamide [3][c]																																																								
Chrysin	Cytosine [4]		+																																																						
	thiamine hydrochloride [4]		+																																																						
	berberine chloride [5]		+[a]																																																						
	4,4'-bipyridine [6]																																										+[b]															
	1,4-bis(pyridin-4-ylmethoxy)benzene [6]																																											+[b]													
	4,4′-vinylenedipyridine [7]														+[b]																																										
	Ethionamide [8]																						+[d]																																		
	isonicotinic acid [9][c]							+																																																	

Apigenin	4,4’-bipyridine [10,11] [c]		+[a]																											+[a]																												
	1,2-di(pyridin-4-yl)ethane [12]															+[a]																																									
	Carbamazepine [12]															+[a]																																									
	(DL)-proline [12]																	+[a]																																							
	δ-valerolactam [12]		+[a]																																																						
	D-proline [12]																	+[a]																																							
	L-proline [12]																	+[a]																																							
	Berberine [13]																													+[a]																											
	Piperazine [14]															+[a]																																									
	Theophylline [15]										+[a]																																															
	Nicotinamide [16]		+[a]																																																						
Luteolin	4,4′-vinylenedipyridine [7]																			+[b]																																						
	Isoniazid [17]		+																																																						
	Caffeine [17]		+																																																						
Fisetin	Caffeine [18]																																									+															
	Nicotinamide [18]																																									+															
kaempferol	Praziquantel [19]																														+[a]																										
	Olaparib [20]																					+																																			
	5-fluorouracil [21] [c]		+[a]																													+[a]																									
	4,4’-bipyridine [22,23]																			+																																					
	Propylthiouracil [24,25] [c]			+[a]							+																																														
	Aripiprazole [26]																																														+	+	+									
	Olanzapine [27]																																																+								
	Palbociclib [28]																																																								
Quercetin	Praziquantel [19]																																+[a]																								
	Theophylline [29] [c]				+																			+																																	
	Olaparib [20]																						+																																		
	Pentoxifylline [30]																																	+[a]																							

	Betaine [31]																																		+[a]																						
	Pyrazinamide [32]																						+																																
	o-dianisidine [33]			+[a]																																																			
	1,10-phenanthroline [33]			+[a]																																																			
	4-(5-ethyl-1-benzofuran-2-yl)pyridine [33]			+[a]																																																			
	4-(1-benzofuran-2-yl)pyridine [33]			+[a]																																																			
	4,4′-vinylenedipyridine [7]															+[b]																																									
	4,4'-ethane-1,2-diyldipyridine [34]																													+[a]																											
	4,4′-azobispyridine [34]																													+[a]		+[a]						+[a]	+[a]	+[a]																	
	4,4’-bipyridine [23]																			+																																					
	Caffeine [35]																													+																											
	Isoniazid [36]				+																																																			
	Levofloxacin [37] [c]		+																													+																									
	Ciprofloxacin [37] [c]		+																													+																									
	Nicotinamide [38, 39]															+																																			+					
	L-proline [9, 10]															+																																				+				
	D-proline [9]															+																																									
	Benzamide [41] [c]	+	+																																																						
	Picolinamide [41] [c]	+	+																																																						
	Isonicotinamide [41] [c]	+	+																																																						
	pyrazinoic acid [41] [c]	+	+																																																						
	succinic acid [42]										+																																														
	Arginine [43] [c]										+					+	+																																								
	isonicotinic acid [9] [c]							+								+																																									
	Piroxicam [9]							+																																																	
	4-dimethylaminopyridine [9]															+																																									
Baicalein	Ethionamide [44]		+[a]																																																						
	Metamitron [45]	+[a]																																																							

	Temozolomide [46]																												+																												
	Izoniazide [47]																																																				+			
	Isonicotinamide [47]																																															+				+[a]			
	Caffeine [35,47] [c]																												+																								+[a]			
	Theophylline [47] [c]																							+[b]																													+[a]		+[a]	
	4,4’-bipyridine [48,49]											+							+																																					
	4,4′-vinylenedipyridine [7]														+[b]																																									
	Pyrazinamide [50]					+[a]																																																			
	Betaine [31]				+[a]																					+																															
	Oxaliplatin [51]						+[a]																																																		
	Nicotinamide [52]																										+																														
	Tegafur [53] [c]		+[a]																												+[a]																										
	Praziquantel [19]																																				+[a]																				
	4,4’-ethylenebispyridine [54]																															+[a]																									
	Caffeine [35,55]																													+[a]																										
	Berberine [56]																															+[a]																									
Myricetin	4,4'-bipyridine [23,57]																			+																																					
	Isonicotinatmide [55]																													+[a]																										
	Proline [55]																															+																									
	Nicotinamide [55]																													+[a]																										
	L-carnitine [58]																																+[b]																								
	Levofloxacin [37] [c]		+																												+																										
	Berberine [56]																															+[a]																									
	Caffeine [59]																														+[a]																										
dihydromyricetin	Theophylline [59]																														+[a]																										
	4,4'-bipyridine [60]																			+																																					
	4,4'-(ethene-1,2-diyl)dipyridine [7]														+[b]																																									
	Pentoxifylline [61]																																								+																

	Diphenylprolinol [61]																																																						+
Dihydroquercetin	4,4'-bipyridine [60]																		+																																				
	Isonicotinamide [62]																									+																													
Naringenin	Metamitron [62]	+[a]																																																					
	4-(1H)pyridine [1]	+[a]																																																					
	Piperazine [1]	+[a]																																																					
	Anthranilamide [1]	+[a]																																																					
	4,4’-bipyridine [1]	+[a]																																																					
	Flavone [1]	+[a]																																																					
	permethylated β-cyclodextrin [63]											+																																													
	Isonicotinamide [64]																																+[a]																								
	Betaine [64]																															+[a]																									
	picolinic acid [64]																																+																								
	4,4'-(ethene-1,2-diyl)dipyridine (4,4′-vinylenedipyridine) [7]										+[b]																																														
	Carbamazepine [65,66] [c]		+													+																																			+						
	Oxaliplatin [51]						+[a]																																																		
	Lobaplatin [67]								+[a]																																																
	Norfloxacin [68]																		+																																						
	isonicotinic acid [9]															+[a]																																									
	Nicotinamide [9]							+																																																	
Hesperetin	4,4’-ethylenebispyridine [54]																															+[a]																									
	Tetraethylammonium [69]																													+[a]																											
	Sophocarpinium [70]																																		+																						
	Temozolomide [71] [c]																																																								
	Carbamazepine [72-74]																																																						+[a]		
	Pirfenidone [75]																																								+[a]																
	Caffeine [76]		+																																																						
	Nicotinamide [76]		+																																																						

	picolinic acid [76]		+[a]																																																				
	palmatine chloride [77] [c]																												+[a]		+[a]																								
	4,4′-vinylenedipyridine [7]														+[b]																																								
	Piperine [78]																																																					+[a]		
	Levofloxacin [37]		+																																																				
	4,4 ′-bipyridine [79] [c]																								+[a]						+[a]																									
	nicotinic acid [9]							+																																															
	4-dimethylaminopyridine [9]														+[a]																																								
Nobiletin	Urea [80]		+[a]																																																				
	oxalic acid [80]		+																																																				
	gallic acid [80]		+																																																				
	salicylic acid [80]		+																																																				
	formic acid [80]		+[a]																																																				
Daidzein	4,4’-bipyridine [81]																+[a]																																						
	Piperazine [82]																																																					+[a]		
	Berberine [83]				+[a]																																																		
	Isonicotinamide [84]		+																																																				
	Theobromine [84]		+																																																				
	Cytosine [84]		+																																																				
	Theophylline [85]									+																																													
Genistein	4,4’-ethylenebispyridine [54]																														+[a]																								
	4,4’-bipyridine [86]																		+																																				
	4,4′-vinylenedipyridine [7]														+[b]																																								
	Ligustrazine [87] [c]				+[a]																										+[a]																								
	Piperazine [88]								+[a]																																														
	Pirfenidone [75]																																							+[a]																
	Palmatine [89]																																																				+[a]			
	Theophylline [90]																																																							+

Pratensol	4,4’-ethylenebispyridine [54]																															+[a]																									
	4,4’-vinylenedipyridine [7]																			+[b]																																					
xanthohumol	Caffeine [91]												+																																												
	Nicotinamide [91]												+																																												
	glutarimide (piperidine-2,6-dione) [91]												+																																												
	Acetamide [91]												+																																												
Phloretin	Isoniazid [92]										+																																														
	Betaine [31]				+[a]																																																				
	β-cyclodextrin [93]																											+																													
	Nicotinamide [94,95] [c]				+[a]																									+[a]																											
	Isonicotinatmide [95]																													+[a]																											
Catechin	Barbituric acid [96]															+																																									
	Urea [97]	+[a]																																																							
L-epicatechin	4,4’-vinylenedipyridine [7]										+[b]																																														

Table S2. Techniques and methods commonly used to characterize flavonoid cocrystals and physicochemical and biological properties of the cocrystals reported in CSD from 2017 to date. SCXRD - single-crystal X-ray diffraction; PXRD – powder X-ray diffraction; IR - infrared spectroscopy; DSC - differential scanning calorimetry; PK - in vivo pharmacokinetic experiment; IDR - intrinsic dissolution rate; DVS - dynamic vapor sorption; SFS - solid state fluorescence spectra.

Flavonoid	Coformer	Diffraction methods			Spectroscopic methods								Microscopic methods						Thermal methods		Physicochemical properties																							Biological properties											Computational studies
		SCXRD	PXRD	VT-PXRD	IR	Raman	Solid state NMR	HNMR in solutiom	CNMR in solutiom	LC-MS	Solid UV-VIS	XPS	Polarizing Microscopy (PM)	Hot-Stage Microscopy (HSM)	Light Microscopy	optical microscope	SEM	TEM	TGA	DSC	Solubility	Saturation Solubility	Dissolution test	Selective dissolution experiments	Equilibrium solubility studies	Phase Solubility Analysis.	IDR	DVS	FluxMeasurements	Accelerated Stability studies	Hygroscopic test	Powder compaction	Specific surface area determination	Leaching experiments in the soil column	herbicidal activity	Tabletability	ternary phase diagram	Sublimation Kinetics.	SFS	PK	Antioxidant activity	Antihemolytic activity	Anti-inflammatory evaluation	Antibacterial properties	Hepatotoxicity Study	DPPH scavenging	ABTS scavenging	Cytotoxicity test	Antitumor activities	toxicity test	interaction of AP and AP-Nico pharmaceutical cocrystal with human serum albumin	
flavone	naringenin [1]	+	+		+															+	+																															
	diethylstilbestrol [2]	+	+										+						+	+							+													+											
	sulfaguanidine [2]		+											+					+	+																															
	dapsone [2]		+											+					+	+																															
	sulfanilamide[2]		+											+					+	+																															
chrysin	cytosine [4]		+		+		+													+					+		+													+	+	+	+								
	thiamine hydrochloride [4]		+		+		+													+					+		+													+	+	+	+								
	berberine chloride [5]	+	+																	+								+													+											+
	4,4’-bipyridine [6]	+	+		+														+	+			+																									+				
	1,4-bis(pyridin-4-ylmethoxy)benzene [6]	+	+		+														+	+			+																									+				
	4,4′-vinylenedipyridine [7]	+	+		+															+																																+
	ethionamide [8]	+	+		+														+	+			+				+													+											
apigenin	4,4’-bipyridine [10, 11]	+	+		+	+													+	+		+	+		+	+													+				+					+		
	1,2-di(pyridin-4-yl)ethane [12]	+	+		+										+				+	+			+		+																									
	carbamazepine [12]	+	+		+										+				+	+			+		+																									
	(DL)-proline [12]	+	+		+										+				+	+			+		+																									
	δ-valerolactam [12]	+	+		+										+				+	+			+		+																									
	D-proline [12]	+	+		+										+				+	+			+		+																									
	L-proline [12]	+	+		+										+				+	+			+		+																									
	berberine [13]	+																																																	
	piperazine [14]	+	+		+														+	+																															+
	theophylline [85]		+			+		+	+				+						+	+					+		+	+	+											+											+
	nicotinamide [16]		+		+			+	+											+		+	+				+	+																				+	+
luteolin	4,4′-vinylenedipyridine [7]	+	+		+															+																																+
	isoniazid [17]		+		+			+												+		+																			+											+
	caffeine [17]		+		+			+												+		+																			+											+
fisetin	caffeine [18]		+		+												+			+		+					+													+			+							

	nicotinamide [18]		+		+											+			+		+					+													+			+									
kaempferol	praziquantel [19]	+	+		+															+					+																											+
	olaparib [20]	+	+		+												+		+	+			+				+			+																			+				+
	5-fluorouracil [21]		+		+												+		+	+			+					+		+																							
	4,4’-bipyridine [22, 23]	+	+		+			+	+											+	+											+													+									+
	propylthiouracil [24, 25]	+	+														+		+	+			+		+																												+
	aripiprazole [26]	+	+		+														+	+			+																														
	olanzapine [27]	+	+	+	+														+	+			+																														+
	palbociclib [28]	+			+												+		+	+			+							+		+																	+				+
quercetin	praziquantel [19]	+	+		+															+					+																											+
	theophylline [29]	+	+		+			+		+							+		+				+		+						+																					
	olaparib [20]	+	+		+												+		+	+			+				+			+																			+				+
	pentoxifylline [30]	+	+																+	+			+							+										+												
	betaine [31]	+	+				+													+			+					+		+	+																					
	pyrazinamide [32]	+																					+																	+												
	o-dianisidine [33]	+	+		+	+						+				+	+																																			
	1,10-phenanthroline [33]	+	+		+	+						+				+	+																																			
	4-(5-ethyl-1-benzofuran-2-yl)pyridine [33]	+	+		+	+						+				+	+																																			
	4-(1-benzofuran-2-yl)pyridine [33]	+	+		+	+						+				+	+																																			
	4,4′-vinylenedipyridine [7]	+	+		+															+																																	+
	4,4'-ethane-1,2-diyldipyridine [34]	+	+								+								+	+										+																							+
	4,4′-azobispyridine [34]	+	+								+								+	+										+																							+
	4,4’-bipyridine [23]	+	+		+			+	+																																			+									
	caffeine [35]		+		+															+	+																															+
	isoniazid [36]		+		+															+			+				+			+															+					+		
	levofloxacin [37]		+	+				+											+																									+									
	ciprofloxacin [37]		+	+				+											+																									+									
	nicotinamide [38, 39]		+		+	+											+		+	+			+																	+												
	L-proline [9, 40]		+			+											+			+			+										+																				+
	D-proline [9]		+																																																	+
	benzamide [41]		+		+														+																																	
	picolinamide [41]		+		+														+																																	
	isonicotinamide [41]		+		+														+																																	
	pyrazinoic acid [41]		+		+														+																																	
	succinic acid [42]		+		+												+			+			+																													
	arginine [43]		+		+	+							+				+			+		+																														
	isonicotinic acid [9]		+																																																	+
	4-dimethylaminopyridine [9]		+																																																	+
	piroxicam [9]		+																																																	+
baicalein	ethionamide [44]	+	+																	+		+					+													+					+					+		
	metamitron [45]	+	+			+													+	+			+		+					+				+	+																	+
	temozolomide [46]	+	+		+															+			+							+																						
	izoniazide [47]	+	+		+									+					+	+			+					+												+												
	isonicotinamide [47]	+	+		+									+					+	+			+					+												+												
	caffeine [35, 47]	+	+		+									+					+	+			+					+												+												+
	theophylline [47, 98]	+	+		+									+			+		+	+			+					+												+												
	4,4’-bipyridine [48, 49]	+	+		+														+				+																													
	4,4′-vinylenedipyridine [7]	+	+		+															+																																	+
	pyrazinamide [50]	+	+		+														+	+							+													+					+							
	betaine [31]	+	+				+													+			+					+		+	+																					
	oxaliplatin [51]	+	+		+														+	+		+	+																									+				+
	nicotinamide [52]		+														+			+			+																	+												
myricetin	tegafur [53]	+	+		+			+											+	+			+					+		+		+				+																
	praziquantel [19]	+	+		+															+					+																											+
	4,4’-ethylenebispyridine [54]	+	+		+														+	+			+																									+	+			
	caffeine [35, 55]	+	+		+															+			+				+																									+
	berberine [56]	+	+																+	+					+			+																					+			+
	4,4'-bipyridine [23, 57]	+	+					+	+																						+																					+
	isonicotinatmide [55]	+	+		+															+			+				+																									+
	Proline [55]	+	+		+															+			+				+																									+

	nicotinamide [55]	+	+		+															+			+				+																										+
	L-carnitine [58]		+		+	+	+												+	+			+								+					+																
	levofloxacin [37]		+	+				+												+																													+								
dihydromyricetin	berberine [56]	+	+																	+	+					+			+																								+				+
	caffeine [99]	+	+															+							+																+																	+
	theophylline [99]	+	+															+							+																+																	+
	4,4'-bipyridine [60]	+	+		+															+	+			+								+																						
	4,4'-(ethene-1,2-diyl)dipyridine [7]	+	+		+															+																																	+
	pentoxifylline [61]	+	+																	+		+	+					+																					+			
	diphenylprolinol [100]	+																																																		
dihydroquercetin	4,4'-bipyridine [60]	+	+		+															+	+			+								+																						
naringenin	isonicotinamide [62]		+										+							+			+																					+												
	metamitron [45]	+	+			+															+	+			+		+					+				+	+																			+
	4-(1H)pyridone [1]	+	+		+															+		+																															
	piperazine [1]	+	+		+															+		+																															
	anthranilamide [1]	+	+		+															+		+																															
	4,4’-bipyridine [1]	+	+		+															+		+																															
	flavone [1]	+	+		+															+		+																															
	permethylated β-cyclodextrin [63]	+																																																			+
	isonicotinamide [64]	+	+		+		+	+												+			+																													
	betaine [64]	+	+		+		+	+												+			+																													
	picolinic acid [64]	+	+		+		+	+												+			+																													
	4,4'-(ethene-1,2-diyl)dipyridine [7]	+	+		+															+																																	+
	carbamazepine[65, 66]	+	+		+		+	+									+		+	+		+			+		+				+								+	+												
	oxaliplatin [51]	+	+		+														+	+		+	+		+		+																					+					+
	lobaplatin [67]	+	+		+			+											+	+		+	+																												+			
	norfloxacin [68]	+	+		+			+									+	+		+												+																+					+			
	isonicotinic acid [9]	+	+																																																	+
	nicotinamide [9]		+																																																	+
hesperetin	4,4’-ethylenebispyridine [54]	+	+		+														+	+			+																										+	+			
	tetraethylammonium [69]	+	+	+															+	+																																
	sophocarpinium [70]	+	+		+														+	+					+		+	+		+																								+
	temozolomide [71]	+	+		+			+													+			+					+		+																								
	carbamazepine [72, 73, 101]		+		+	+								+		+		+	+			+																	+														+
	pirfenidone [75]	+	+		+														+	+					+		+	+																									+
	caffeine [76]		+		+		+														+			+		+															+		+	+			+						
	nicotinamide [76]		+		+		+														+			+		+															+		+	+			+						
	picolinic acid [76]	+	+		+		+														+			+		+															+		+	+			+						
	palmatine chloride [76]	+	+		+														+	+		+	+					+																									+
	4,4′-vinylenedipyridine [7]	+	+		+															+																																	+
	piperine [78]	+	+		+														+	+			+		+															+												
	levofloxacin [37]		+	+				+												+																													+								
	4,4 ′-bipyridine [79]	+	+		+															+					+																												+
	nicotinic acid [9]		+																																																	+
	4-dimethylaminopyridine [9]	+	+																																																	+
nobiletin	urea [80]	+	+																	+	+			+																													
	oxalic acid [80]		+																	+	+			+																													
	gallic acid [80]		+																	+	+			+																													
	salicylic acid [80]]		+																	+	+			+																													
	formic acid [80]	+	+																	+	+			+																													
daidzein	4,4’-bipyridine [81]	+	+		+									+						+			+		+																												
	piperazine [82]	+	+		+														+	+			+		+				+	+											+													+
	berberine [83]	+																																																		
	isonicotinamide [83]		+		+		+														+					+		+			+											+		+	+			+						
	theobromine [83]		+		+		+														+					+		+			+											+		+	+			+						
	cytosine [83]		+		+		+														+					+		+			+											+		+	+			+						
	theophylline [85,90]		+			+		+	+				+						+	+					+		+	+	+											+													+
genistein	4,4’-ethylenebispyridine [54]	+	+		+														+	+			+																										+	+			
	4,4’-bipyridine [86]	+	+		+														+	+			+		+																			+								
	4,4′-vinylenedipyridine [7]	+	+		+															+																																	+

	ligustrazine [87]	+	+		+												+		+	+			+															+		+											+
	piperazine [88]	+	+		+														+	+			+							+										+											+
	pirfenidone [75]	+	+		+														+	+					+		+	+																							+
	palmatine [89]	+																																																	
pratensol	4,4’-ethylenebispyridine [54]	+	+		+														+	+			+																								+	+			
	4,4’-vinylenedipyridine [54]	+	+		+															+																															+
xanthohumol	caffeine [89, 91]	+	+		+	+										+							+		+																										+
	nicotynamide [89]	+	+		+	+										+							+		+																										+
	glutarimide (piperidine-2,6-dione) [91]	+	+		+	+										+							+		+																										+
	acetamide [91]	+	+		+	+										+							+		+																										+
phloretin	isoniazid [92]	+	+		+			+											+	+			+		+															+						+	+		+			+
	betaine [31]	+	+				+													+			+					+		+	+																					
	β-cyclodextrin [93]	+																																																		+
	nicotinamide [94, 95]	+	+			+							+						+	+			+		+		+	+											+													+
	isonicotinatmide [95]	+	+			+							+						+	+			+		+														+													+
catechin	barbituric acid [96]	+	+			+													+	+			+		+																										+
	urea [97]	+	+	+															+	+					+																											
L-epicatechin	4,4’-vinylenedipyridine [7]	+	+		+															+																															+

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