Electronic Supplementary Information (ESI)

Biogenic approaches using citrus extracts for the synthesis of metal nanoparticles: The role of flavonoids in gold reduction and stabilization

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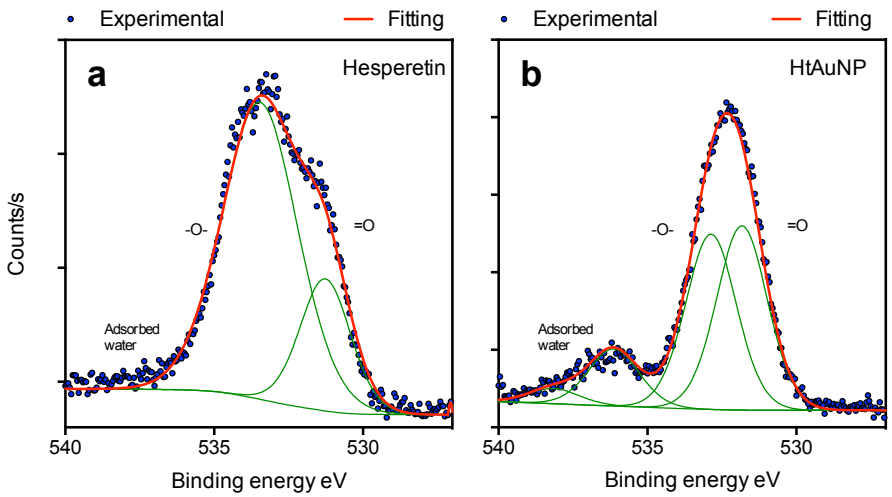

Figure. S1 XPS measurements a) Hesperetin O 1s, and **d)** HtAuNP O 1s envelopes deconvoluted into its components.

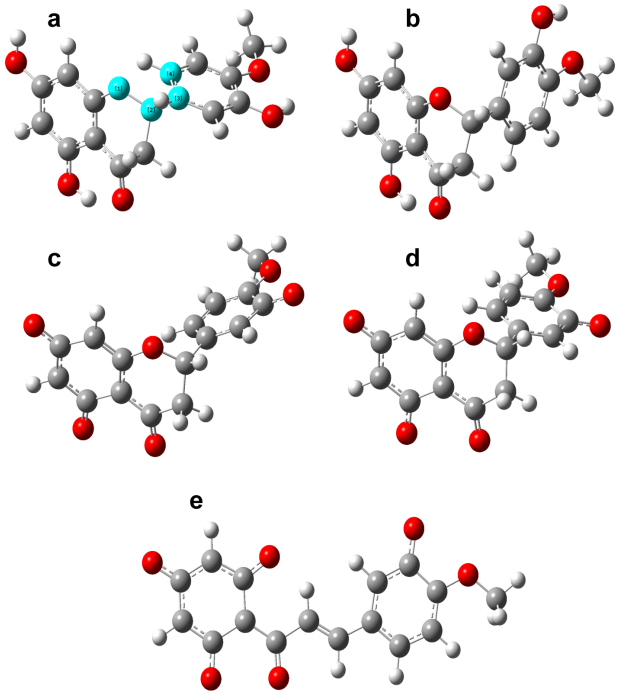

Figure S2. Final structural geometries for optimizations for Hesperetin in **(a)** gas phase and **(b)** water solvent (PCM), hesperetin phenolate Ht^{-3} in **(c)** gas phase and **(d)** water solvent (PCM) and finally hesperetin-chalcone Hc^{-4} **(e)** in water (PCM). Figure (a) indicates the OCCC atoms (presented in cyan), which determine the dihedral angle.

Table S1. HOMO-LUMO energies, energy gap, dihedral angle, total energies and gold Mulliken charges for hesperetin and its charged especies

System	HOMO (a.u.)	LUMO (a.u.)	Gap (eV)	Φ (°)	Total Energy (a.u.)
Ht (gas)	-0.224	-0.065	4.33	-7.76	-1069.540
Ht (PCM)	-0.227	-0.072	4.20	55.64	-1069.559
Ht^{-3} (gas)	0.178	0.214	0.98	-56.80	-1067.583
Ht^{-3} (PCM)	-0.161	-0.010	4.09	-13.17	-1068.105
Hc^{-4} (PCM)	-0.134	-0.032	2.76	n.a.	-1028.290

n.a. Not applicable

Table S2. Optical information for the complex 2b at an Au:Ht ratio 1:1

λ (nm)	f	Main contributions to the configuration interaction
1029	0.1640	HOMO-3→LUMO (37%), HOMO-1→LUMO (62%), HOMO→LUMO (12%)
1088	0.0807	HOMO-3→LUMO (53%), HOMO-1→LUMO (39%)
539	0.0491	HOMO-6→LUMO (95%)
441	0.0383	HOMO-11→LUMO (14%), HOMO-5→L+1 (79%)
801	0.0202	HOMO-4→LUMO (90%)

f is the oscillator strength.

Table S3. Optical information for 1:2 Au:Ht structures.

λ (nm)	f	Major contrib. for 1:2	Transitions
374.0	0.119	H-12→L (10%), H-7→L+2 (15%), H-6→L+1 (24%), H-2→L+1 (33%)	LMCT/ILCT
446.0	0.060	H-10→L (96%)	LMCT
375.0	0.056	H-12→L (82%)	ILCT
684.0	0.051	H-4→L (44%), H-2→L (45%)	LMCT

Note: Transitions are ordered from higher to lower oscillator strength and H and L stand for HOMO and LUMO, respectively

Table S4. Optical information for 2:1 Au:Ht structures.

λ (nm)	f	Major contrib. for 2:1	Transitions
509.6	0.027	H-9→L (49%), H-9→L+1 (32%)	MLCT/ILCT
912.5	0.021	H-2→L (26%), H-2→L+1 (32%), H-1→L+1 (24%)	MLCT/ILCT
1070.9	0.019	H-1→L (58%), H-1→L+1 (37%)	MLCT/ILCT
622.1	0.018	H-7→L (24%), H-7→L+1 (10%), H-4→L (34%), H-4→L+1 (21%)	MLCT/ILCT
737.8	0.017	H-9→L+1 (13%), H-4→L (26%), H-4→L+1 (36%)	MLCT/ILCT

Note: Transitions are ordered from higher to lower oscillator strength and H and L stand for HOMO and LUMO, respectively

Table S5. Optical information for system 6a, Au^{+3}:$2Hc^{-4}$ interaction.

λ (nm)	f	Major contrib. 1:2	Transitions
519.3	0.2667	H-2→L+1 (13%), H-1→L+1 (73%)	LMCT/ILCT
778.3	0.0872	H-2→L (94%)	LMCT/ILCT
487.1	0.0708	H-1→L+2 (61%), H→L+2 (31%)	LMCT/ILCT
513.9	0.0702	H-3→L+1 (10%), H-3→L+2 (12%), H-2→L+1 (49%), H-1→L+1 (17%)	LMCT/ILCT
484.8	0.0651	H-1→L+2 (31%), H→L+2 (62%)	LMCT/ILCT
460.0	0.0580	H-11→L (78%)	LMCT/ILCT

Note: Transitions are ordered from higher to lower oscillator strength and H and L stand for HOMO and LUMO, respectively

Table S6. Optical information for system 6b, Au^{+3}:$2Hc^{-4}$ interaction.

λ (nm)	f	Major contrib.	Transitions
758.4	0.0360	H-11→L (43%), H-8→L (38%)	MLCT/ILCT
771.7	0.0192	H-12→L (14%), H-10→L (42%), H-7→L (28%)	MLCT/ILCT
753.0	0.0116	H-14→L (20%), H-12→L (61%), H-7→L (11%)	MLCT/ILCT
804.7	0.0087	H-11→L (33%), H-9→L (30%), H-8→L (31%)	MLCT/ILCT
525.4	0.0033	H→L+2 (99%)	MLCT/ILCT
538.5	0.0027	H→L+1 (99%)	MLCT/ILCT

Note: Transitions are ordered from higher to lower oscillator strength H and L stand for HOMO and LUMO respectively.