Supporting Information

Phytochemicals as dynamic surface ligands to control nanoparticle-protein interactions

Amanda N. Abraham[†], *Tarun K. Sharma*[†], *Vipul Bansal*[†*] *and Ravi Shukla* [†‡*]

[†]Ian Potter NanoBioSensing Facility, NanoBiotechnology Research Lab (NBRL), School of Science, RMIT University, GPO Box 2476 V, Melbourne (VIC) 3001, AUSTRALIA.

[‡]Centre for Advanced Materials & Industrial Chemistry, School of Science, RMIT University, GPO Box 2476 V, Melbourne (VIC) 3001, AUSTRALIA.

*Email: ravi.shukla@rmit.edu.au (R.S.); vipul.bansal@rmit.edu.au (V.B.)

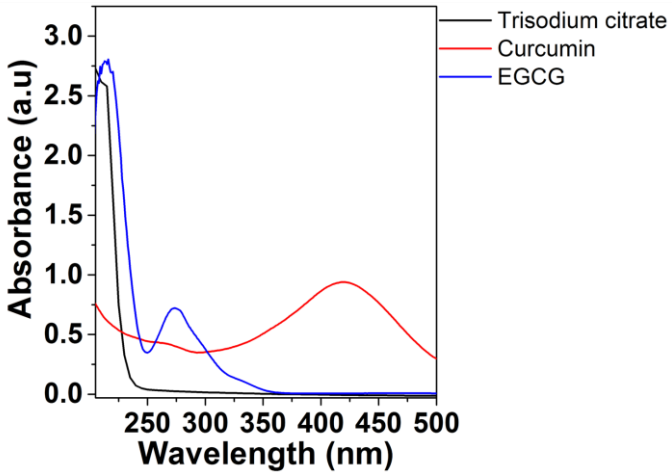

Figure S1: UV-visible absorbance spectra of pristine trisodium citrate, curcumin and EGCG. Trisodium citrate displays a band at 209 nm,[1] curcumin at 263 nm and 417 nm[2] and EGCG at 235 nm and 273 nm.[3]

REFERENCES

1. Krukowski, S. et al. *Journal of Food and Drug Analysis* **2017,** *25* (3), 717-722.

2. Rodrigues, M. A. et al. *American Journal of Chemistry* **2012,** *2* (3), 157-159.

3. Snitsarev, V. et al. *PLoS ONE* **2013,** *8* (11), e79834.

Table S1: Hydrodynamic diameters (obtained from number averaged dynamic light scattering data) and zeta potential for Ct-AgNP, Cur-AgNPs and EGCG-AgNPs. NP concentration was 100 μM in the presence and absence of HSA (3 μM) in phosphate buffer at pH 7.4.

	Ct-AgNPs	Ct-AgNPs + HSA	Cur-AgNPs	Cur-AgNPs + HSA	EGCG-AgNPs	EGCG-AgNPs + HSA
DLS (nm)	55.6 ±5.7	61.6±7.8	44.8±2.5	57.9±6.5	61.5±3.8	67.7±9.5
Zeta potential (mV)	-25.9 ±1.2	-16.5 ±2.5	-41.7 ±3.2	-31.3 ±4.1	-38.9 ±2.6	-32.7 ±3.6

Table S2: Stern-Volmer constants and thermodynamic parameters for Ct-AgNPs.

Temperature (K)	K_{sv} (10^4 M^{-1})	K_q (x10^{13} $M^{-1}s^{-1}$)	K (M^{-1})	ΔG° kJ/mol	ΔH° J/mol	ΔS° J/K mol
293	7.43	0.74	6.66	-1.23	3.99	4.22
303	9.55	0.96	27.71	-1.28	3.86	
313	11.63	1.16	38.46	-1.32	3.74	
323	15.50	1.55	150.54	-1.36	3.62	
333	17.61	1.76	419.13	-1.40	3.51	

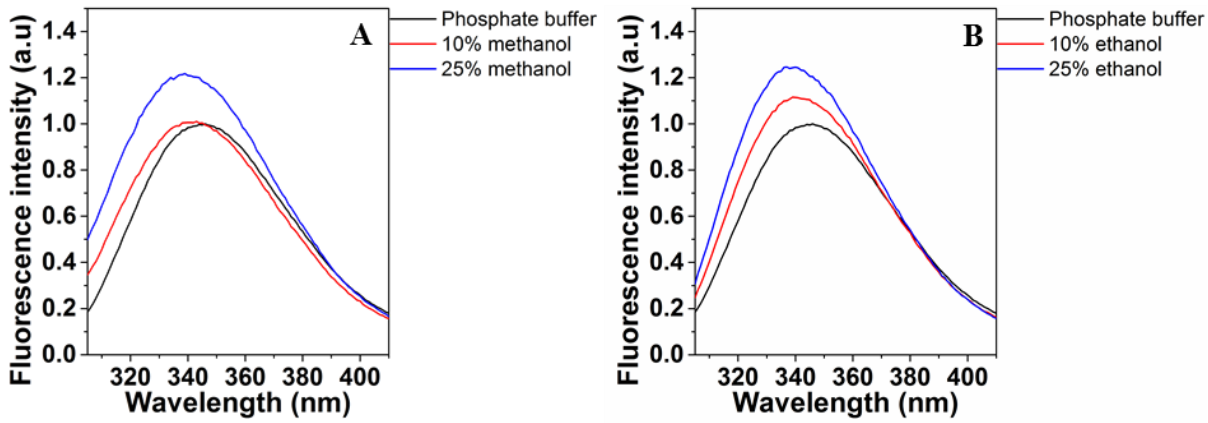

Figure S2. Fluorescence spectra of HSA in a less polar environment obtained through its exposure to either methanol or ethanol (v/v %).

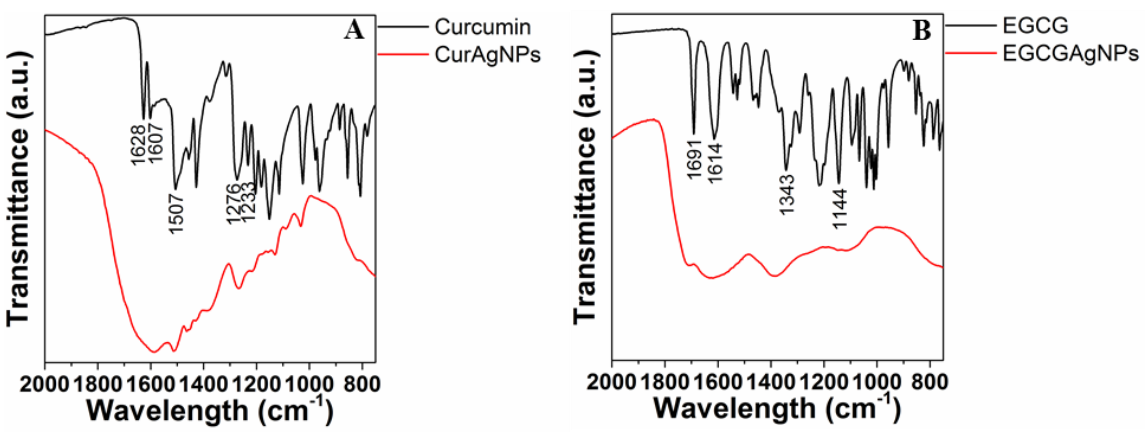

Figure S3. FTIR spectra of (A) Cur-AgNPs and (B) EGCG-AgNPs, in comparison with curcumin and EGCG, respectively. In pristine curcumin, the vibrational band observed at 1628 cm^{-1} corresponds to a mixed C=O and C=C character and the neighbouring 1607 cm^{-1} is attributed to the aromatic ring stretching in curcumin.[1] In Cur-AgNPs, these peaks have been replaced by a broad peak at 1582 cm^{-1}. Additionally, the peak assigned to C=O at 1507 cm^{-1} has also shifted to 1512 cm^{-1}. This indicates that the carbonyl groups in curcumin are involved in the AgNP synthesis. The enol C–O peak at 1276 cm^{-1} and the keto peak at 1233 cm^{-1} have both shifted to 1266 and 1218, respectively, in Cur-AgNPs, which indicates the additional involvement of both these phenol groups in the AgNP synthesis.

In the case of EGCG system (B), the characteristic vibrational mode in pristine EGCG at 1343 cm^{-1} corresponding to the O–H in-plane bending[38] has disappeared in the EGCG-AgNPs, whereas the 1144 cm^{-1} feature corresponding to the O–H aromatic vibration[2] is replaced by a broad peak. The peaks at 1691 cm^{-1} and 1614 cm^{-1} which correspond to the C=O[38] have shifted to 1704 cm^{-1} and a broad peak at 1620 cm^{-1}, respectively. This indicates the likely involvement of a number of phenol groups in EGCG in AgNP synthesis.

REFERENCES

1. Mohan, P. R. K. et al. *Vibrational Spectroscopy* **2012,** *62*, 77-84.
2. Zhu, H. et al. *Sensors and Actuators B: Chemical* **2013,** *185*, 608-619.

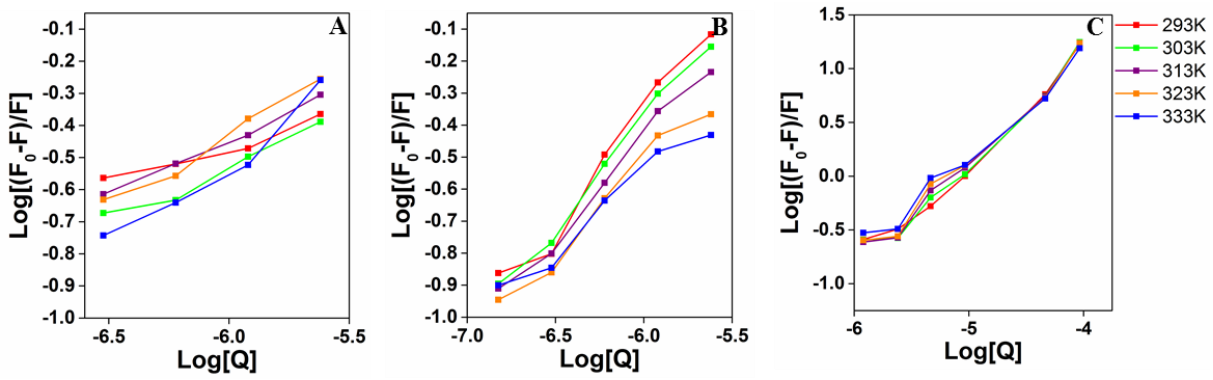

Figure S4. Double logarithmic regression plots of log[(F_0-F)/F] versus log[Q] for binding of (A) Ct-AgNPs, (B) Cur-AgNPs and (C) EGCG-AgNPs to HSA, from which the binding constants (*K*) were calculated.

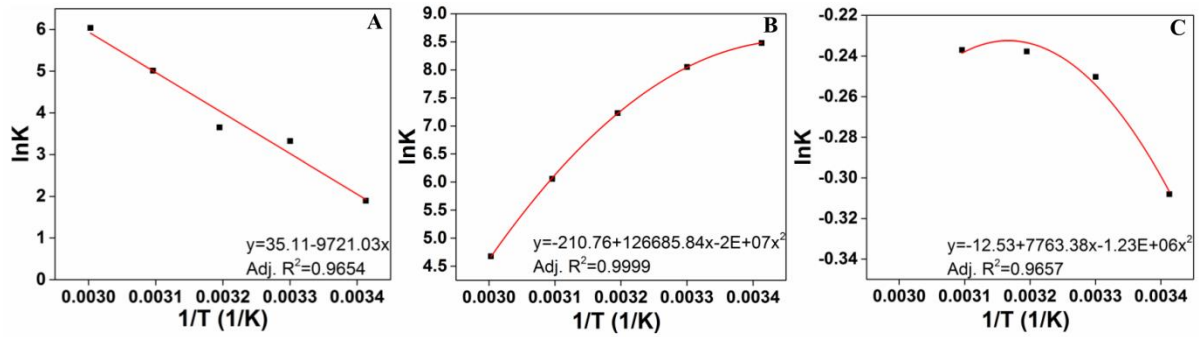

Figure S5. van't Hoff plots for (A) Ct-AgNPs, (B) Cur-AgNPs and (C) EGCG-AgNPs, from which the thermodynamic parameters were calculated to determine the nature of binding involved in the interaction of the AgNPs to HSA.