Supporting Information

Impact of Sunlight and Humic Acid on the Deposition Kinetics of Aqueous Fullerene Nanoparticles (nC_{60})

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Environmental Science & Technology

This SI includes a total of 11 pages (including this page) with 4 tables and 6 figures.

QCM-D characterization of particle deposition kinetics

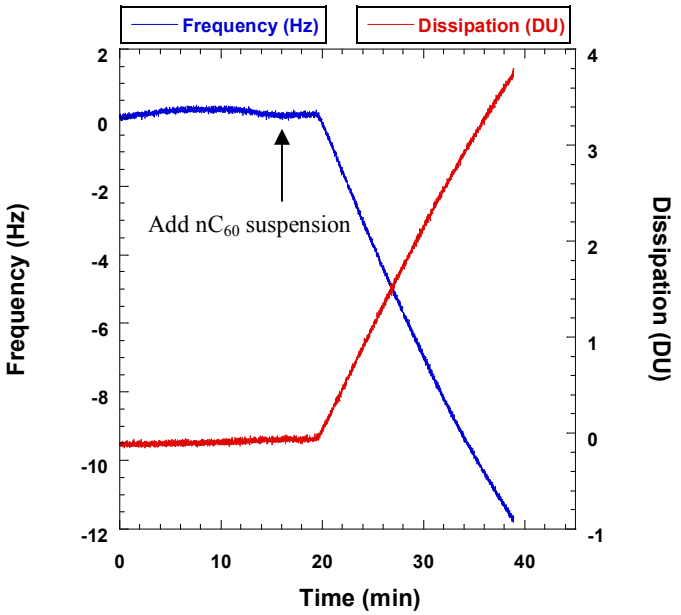

Figure S1. Representative QCM-D measurement data. The figure shows the frequency and dissipation measured at the 3rd overtone as a function of time during the deposition experiment of pristine nC_{60} onto bare silica surface in 20 mM NaCl solution.

Table S1. The initial slop of the measured 3rd overtone frequency shift Δf_3 and the mass deposition rate calculated by the viscoelastic Voigt model for pristine nC_{60} deposition on silica surface at various NaCl concentrations.

NaCl (mM)	Δf_3 (Hz/min)	Mass Deposition Rate (ng/cm^2 min)
5	0.0615	1.5
10	0.5955	16.7
20	0.6525	19.8
40	0.2385	12
80	0.147	7.2
100	0.099	4.9

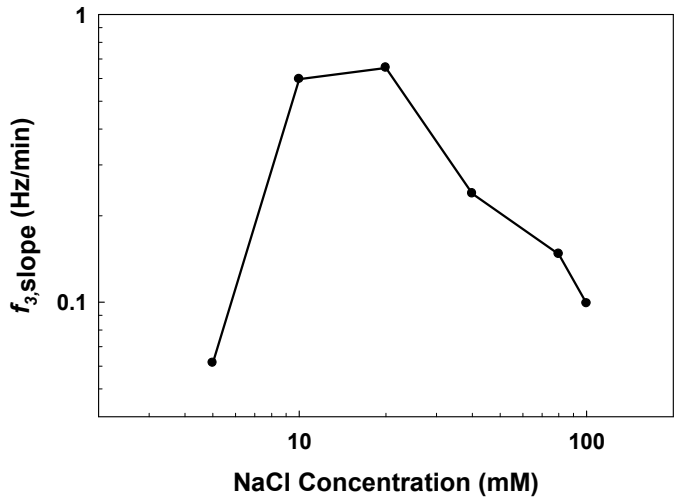

Figure S2a. The initial slop of the measured 3rd overtone frequency shift $f_{3,slope}$ of pristine nC_{60} deposition on silica surface as a function of NaCl concentration.

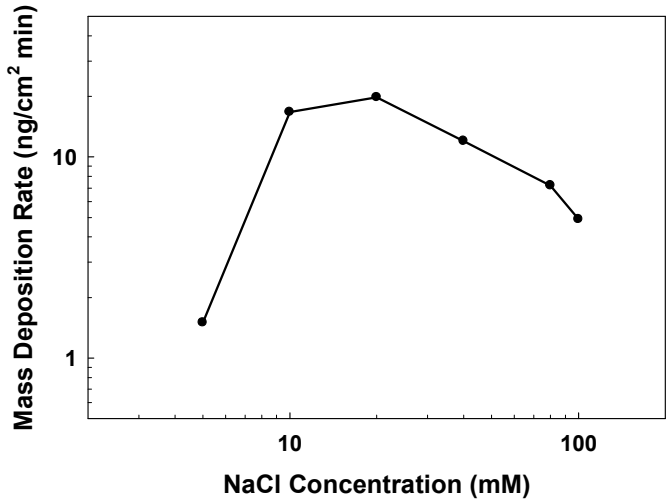

Figure S2b. The mass deposition rate calculated by the viscoelastic Voigt model for pristine nC_{60} deposition on silica surface as a function of NaCl concentration.

Determination of nC_{60} particle size in deposition experiments

In the QCM-D experiments, it took 5 min for the nC_{60} nanoparticles to reach the measurement chamber after being mixed with the NaCl solution. At high ionic strength nC_{60} aggregation occurred. The nC_{60} particle size during deposition in the measurement chamber was therefore determined based on the aggregation kinetics curve (average particle size vs. aggregation time) by setting the aggregation time to

be 5 min.

Table S2. Pristine and 7-day UVA-irradiated (7DUV) nC_{60} particle size during the QCM-D experiments.

Sample	NaCl concentration (mM)	Particle/aggregate size at 5 min (nm)
Prstine nC_{60}	1	162
	5	162
	10	162
	20	163.8
	40	241.8
	60	334.5
	80	449.4
	100	492
7DUV nC_{60}	40	162
	100	162
	150	162
	200	168.9
	250	191.1
	300	244.5
	350	280.8

Packed column experiments

Quartz sand sizing from 250 μm to 300 μm in diameter was obtained by sieving a 50 - 70 mesh quartz sand (sigma-aldrich) with 50 and 60 mesh sieves. Before use, the sand was cleaned by soaking in a 1.5 M HNO_3 solution for 24 h and rinsing with deionized water until the pH reaches neutral. The sand was then oven dried at 100 °C for 24 h. Columns (Omnifit, 1.5 cm in diameter) were wet packed with clean quartz sand to a height of ~5 cm with a porosity of 0.39 as determined gravimetrically. Figure S3 presents the packed column experimental setup. Ten pore volume of deionized water, followed by 10 pore volume of background solution, was passed through the column at a flow rate of 2 mL/min to rinse and condition the sand. The nC_{60} stock suspension and the electrolyte stock solution were mixed to yield the test nC_{60} suspension at 5 mg/L, which was then introduced into the column at a flow rate of 0.84 mL/min until the effluent nC_{60} concentration reached steady state. The effluent was continuously collected by a fraction collector (Pharmacia Fine Chemicals) and the nC_{60} concentration was analyzed using a UV-vis spectrophotometer (UV 2550, Shimadazu) at a wavelength of 350 nm. Representative breakthrough curves of nC_{60} are shown in Figure S4.

To create favorable deposition conditions, clean quartz sand was precoated with poly-L-lysine (PLL) by

soaking in a solution containing 20 mg/L PLL, 100 mM NaCl and 10 mM HEPES, followed by thoroughly rinsing with deionized water and drying at room temperature.

The deposition rate coefficient K_d of nC_{60} in different solution chemistry was determined using following equation: [2]

$$k_d = -\frac{U}{\varepsilon L} In(\frac{C}{C_0})$$

where U is the superficial velocity, ε is the porosity, L is the column length, C is the steady state effluent concentration of nC_{60} (i.e., the plateau of the breakthrough curve), and C_0 is the influent nC_{60} concentration.

The particle attachment efficiency α was calculated by normalizing the deposition rate coefficient of interest, K_d, by the deposition rate coefficient under favorable conditions, $K_{d,fav}$.

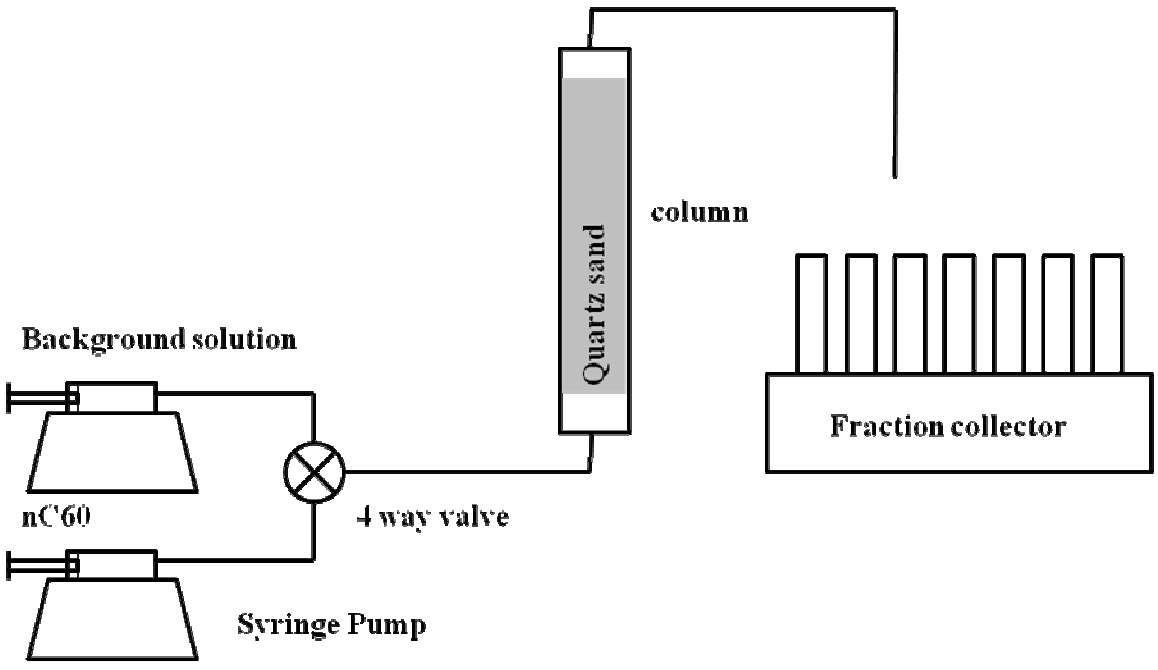

Figure S3. Diagram of the packed column setup

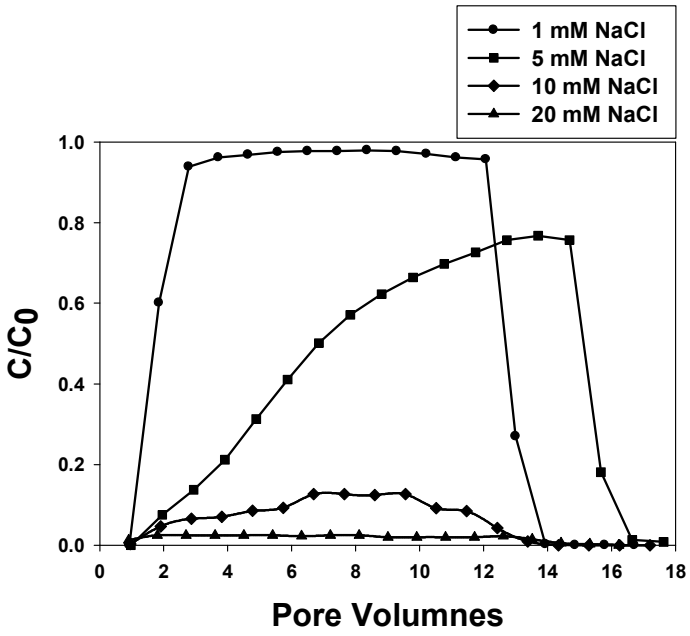

Figure S4. Representative breakthrough curves for nC_{60} (5 mg/L) transport experiments in silica sand packed columns in NaCl solutions.

The seepage velocity used in the packed column experiments was controlled to match the flow velocity used in the QCM-D experiment. This resulted in similar Peclet number in the two systems.

For the QCM-D system, a parallel-plate channel configuration was assumed:[3]

$$P_{e\ QCM} = \frac{3v_m a^3}{2b^2 D}$$

Here, v_m is the flow velocity in the measurement chamber, a is the particle radius, b is the half depth of the channel (0.00032 m), and D is the diffusion coefficient. The flow velocity v_m in the QCM-D chamber is 0.0002 m/s at the volumetric flow rate of 100 μL/min. The particle diameter $2a$ at different ionic strength was determined in Table S1. The diffusion coefficient D is estimated using the *Stokes-Einstein* equation:

$$D = \frac{kT}{3\pi\mu d}$$

where k is the Boltzman constant (1.38×10^{-23} J·K^{-1}), T is the absolute temperature (298 K), μ is the viscosity of water (10^{-3} Pa·s), and the d is the particle diameter.

For packed column system, a sphere in uniform flow configuration was assumed:[3]

87 $$P_{e\,column} = \frac{3A_f v a^3}{R^2 D}$$

88 Here, v is the seepage velocity in the column (0.0002 m/s), a is the radius of nC_{60} nanoparticles, R is the
89 radius of silica sands (137.5 μm), and the dimensionless flow parameter A_f is given by:[4]

90 $$A_f = \frac{3}{2}\left[1 + \frac{0.19R_e}{1 + 0.25{R_e}^{0.56}}\right]$$

91 Where R_e is the Reynolds number, $R_e = 2vR\rho/\mu$. ρ and μ is the density and viscosity of water
92 respectively.

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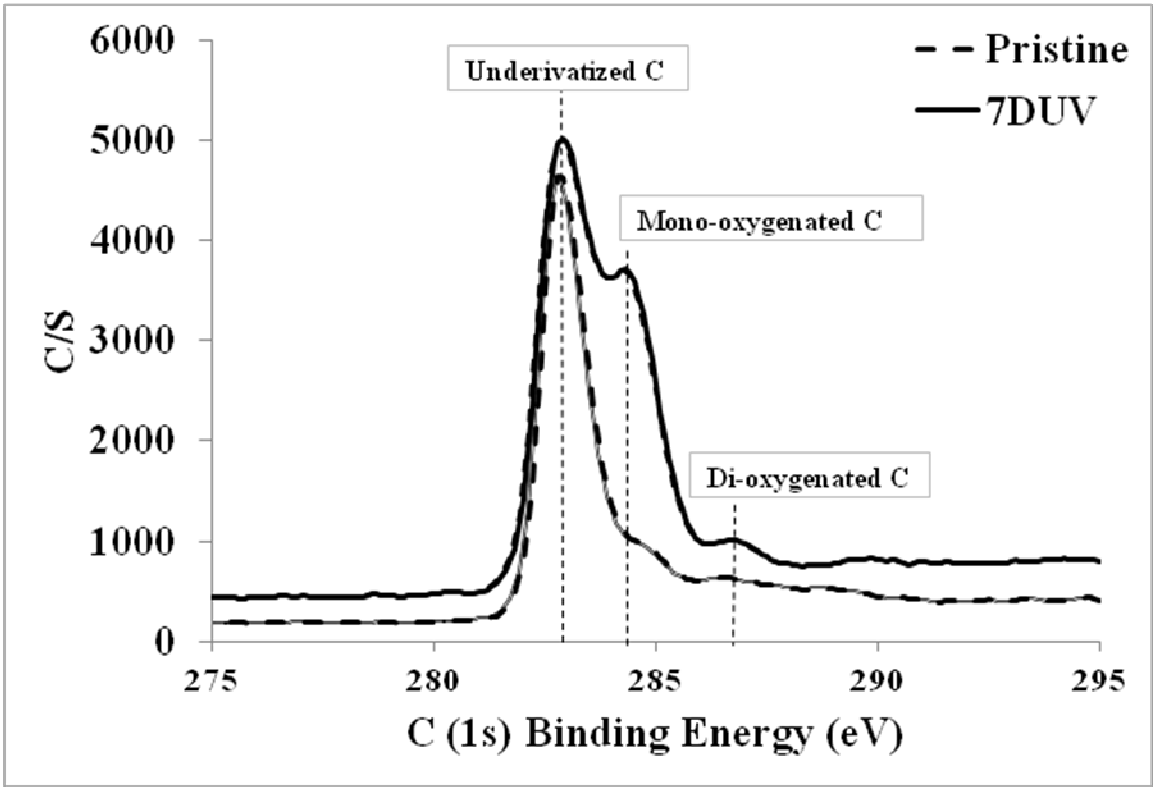
94 **XPS spectra of pristine and 7DUV nC_{60}**



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96 Figure S5. C(1s) XPS spectra of pristine and 7-day UVA-irradiated (7DUV) nC_{60}.

97

98 **Calculation of DLVO interaction energy between nC_{60} and bare/EHA coated silica surface**

99 The DLVO interaction energy was calculated by assuming sphere-plate interactions. The van der Waals

interaction energy was calculated from [24]:

$$\Phi_V = -\frac{Aa}{6h}\left[1+\frac{14h}{\lambda}\right]^{-1}$$

where A is the Hamaker constant of C_{60}-water-silica system (4.71×10^{-21} J [7]), a is the nanoparticle radius, h is the separation distance, and λ is the characteristic wavelength of the dielectric (normally assumed to be 100 nm).

The electrostatic interaction energy was calculated from [25]:

$$\Phi_E = \pi\varepsilon_0\varepsilon_r a\left\{2\psi_p\psi_c\, ln\left[\frac{1+exp\,(-\kappa h)}{1-exp\,(-\kappa h)}\right] + (\psi_p{}^2+\psi_c{}^2)\, ln[1-exp\,(-2\kappa h)]\right\}$$

where ε_0 is the dielectric permittivity in a vacuum, ε_r is the relative dielectric permittivity of water, a is the nanoparticle radius, κ is the inverse Debye length, h is the separation distance, and ψ_p and ψ_c are the ζ potential of the particle and the silica surface respectively.

Table S3. Calculated energy barrier between nC_{60} and bare/EHA coated silica surface at various NaCl concentrations. The ζ potentials used in the calculation are presented in Figure 3b and 6a.

NaCl (mM)	Pristine nC_{60}-silica energy barrier (kT)	7DUV nC_{60}-silica energy barrier (kT)	Pristine nC_{60}-EHA coated silica energy barrier (kT)	7DUV nC_{60}-EHA coated silica energy barrier (kT)
5	159.8	-	30.5	-
10	124.4	-	18.5	-
20	93.4	-	13.4	-
40	80.7	139.3	0	0.4
100	42.3	41.4	0	0
150	-	12	-	0
250	-	0	-	0
300	-	0	-	0
350	-	0	-	0

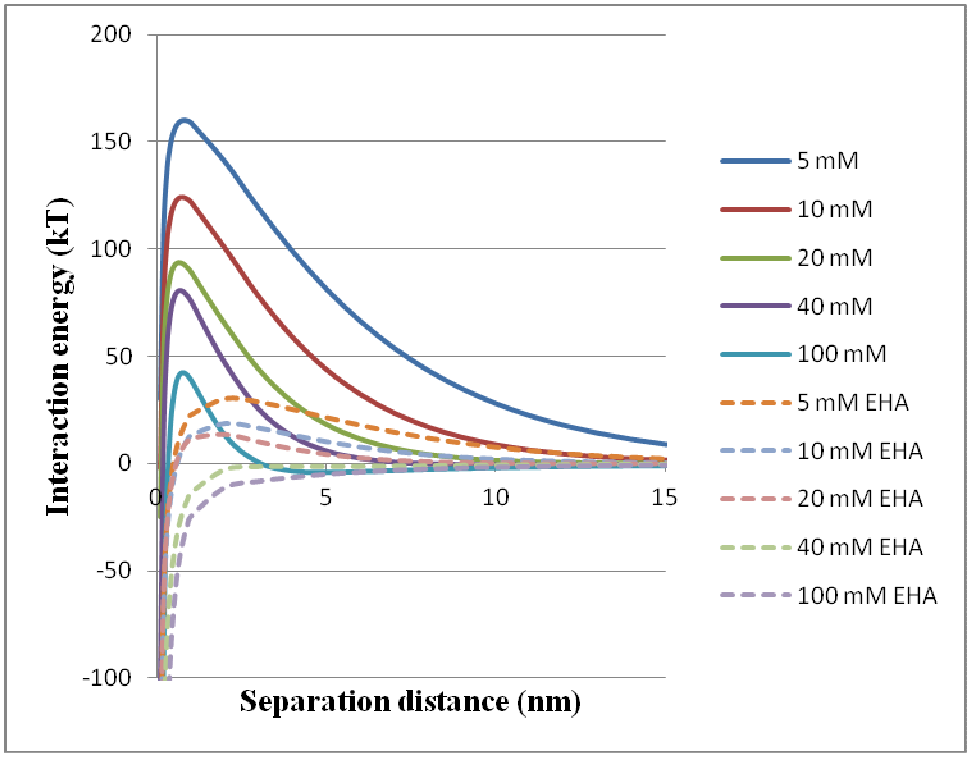

Figure S6a. Calculated DLVO interaction energy profiles for pristine nC_{60} approaching a flat silica or EHA coated silica surface at various NaCl concentrations.

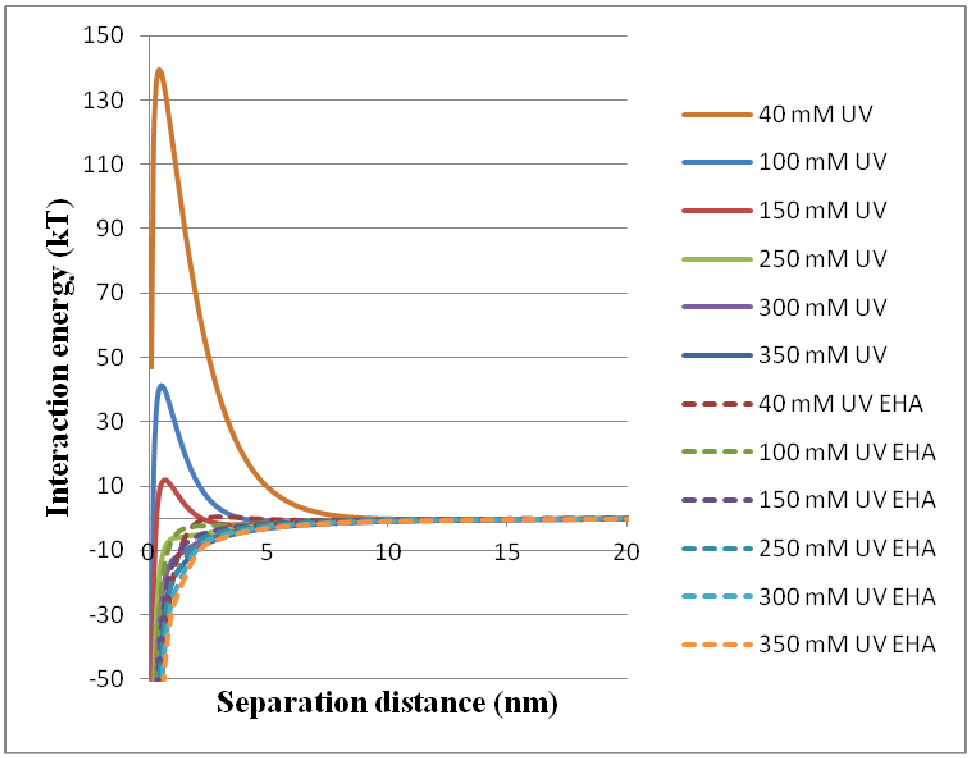

Figure S6b. Calculated DLVO interaction energy profiles for 7-day UVA-irrdiated nC_{60} approaching a flat silica or EHA coated silica surface at various NaCl concentrations.

Humic acid adsorption experiments

Humic acid (HA) adsorption by the pristine and 7DUV nC_{60} in deionized water was measured by batch sorption experiments. The EHA stock solution was filtered through centrifugal filters equipped with 30 kDa MWCO ultrafiltration membranes (Millipor, Carrigtwohill, Co. Cork, Ireland). The resulting EHA solution was used in the adsorption experiment. Both pristine and 7DUV nC_{60} solutions were concentrated using centrifugal filters to 250 mg/L. 1 mg/L EHA was mixed with 200 mg/L nC_{60} in 10 mL PTFE-lined screw cap glass vials and agitated on a shaker bed at room temperature for 24 h. Then the samples were filtered with the 30 kDa MWCO centrifugal filters to separate nC_{60} and the residual dissolved EHA. The dissolved humic acid concentration was determined by measuring UV absorbance at 254 nm.

Table S4. Humic acid adsorption on pristine nC_{60} and 7-day UV-irradiated nC_{60} (7DUV nC_{60}) in 1 mg/L humic acid solutions. *SRHA adsorption data was reported by our previous paper.[1]

	SRHA* K_d (mg/Kg)/(mg/L)	EHA K_d (mg/Kg)/(mg/L)
Pristine nC_{60}	1722	1648
7DUV nC_{60}	Non-detectable	Non-detectable

Adsorption of SRHA onto pristine nC_{60} nanoparticles in 10 mM and 40 mM NaCl solutions was studied by QCM-D. After coating the silica crystal surface with PLL, 5 mg/L nC_{60} in 1 mM NaCl was flowed across the crystal for 1 h to allow nC_{60} deposition. The nC_{60} deposit layer was then rinsed with the background NaCl solutions. After a stable baseline was achieved, a 5 mg/L SRHA solution in 10 mM or 40 mM NaCl was introduced into the measurement chamber, allowing SRHA to adsorb on nC_{60} until reaching adsorption equilibrium. The amount of SRHA adsorbed was calculated using the Sauerbrey Equation. The SRHA adsorption density on nC_{60} was quantified by normalizing the total amount of SRHA adsorbed with the surface area of the crystal.

Literature Cited

(1) Qu, X. L.; Hwang, Y. S.; Alvarez, P. J. J.; Bouchard, D.; Li, Q. L., UV Irradiation and Humic Acid Mediate Aggregation of Aqueous Fullerene (nC(60)) Nanoparticles. *Environ. Sci. Technol.* **2010,** *44*, (20), 7821-7826.

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(3) Gregory, J.; Jia, X.; Williams, R., *Particle deposition and aggregation: measurement, modelling and simulation*. Butterworth-Heinemann: 1998.
(4) Adamczyk, Z.; Warszynski, P.; Szyk-Warszynska, L.; Weronski, P., Role of convection in particle deposition at solid surfaces. *Colloid Surf. A-Physicochem. Eng. Asp.* **2000,** *165*, (1-3), 157-187.