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2	Supporting Information
3	Alteration of nC_{60} in the Presence of
4	Environmentally Relevant Carboxylates
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12	Pages: 26
13	Figures S1-S19
14	Discussion on pH regulating cit/ <i>n</i> C ₆₀ formation
15	Discussion on [Na ⁺] regulating cit/ <i>n</i> C ₆₀ formation
16	Discussion on centrifugation of <i>n</i> C ₆₀ produced indifferent solutions
17	Discussion on the exhaustive extract of <i>n</i> C ₆₀ by toluene
18	Discussion on the adsorption of citrate on <i>n</i> C ₆₀
19	Table S1
20	References



Figure S1 Speciation of citrate as a function of solution pH.



Figure S2 Electrophoretic Mobility (EM) of nC_{60} as a function of stirring time: (A) $[Na_3Cit] = 0-1.0$ mM and (B) $[Na_3Cit] = 5-25$ mM. (Each data point represents the average of three measurements for one sample and the error bar represents the standard deviation. Note: To enhance the clarity of the figures, data for cit/ nC_{60} produced in 0.01, 0.03, 0.05, 0.07, 0.3, 0.7, 3.0, and 15.0 mM Na₃Cit solutions are not presented.)



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Figure S3 Average particle size of nC_{60} as a function of stirring time: (A) $[Na_3Cit] = 0-1.0 \text{ mM}$, (B) [Na₃Cit] = 5-25 mM; Polydispersity index of nC_{60} as a function of stirring time: (C) $[Na_3Cit] = 0-1.0$ mM, (D) $[Na_3Cit] = 5-25 \text{ mM}$. (Each data point represents the average of three measurements for one sample and the error bar represents the standard deviation. Note: To enhance the clarity of the figures, data for cit/ nC_{60} produced in 0.01, 0.03, 0.05, 0.07, 0.3, 0.7, 3.0, and 15.0 mM Na₃Cit solutions are not presented.)

41 **pH Regulation by Citrate.**

In the experiments discussed in the main paper, Na₃Cit was used to adjust the citrate concentration. 42 Unfortunately, the variation in Na₃Cit simultaneously alters both pH and [Na⁺] and thus the results 43 shown in Figure 2 cannot be unambiguously attributed to changes in citrate concentration alone. To 44 evaluate the pH-regulating role of citrate, cit/nC_{60} was produced in citrate buffers over the [total citrate] 45 46 (= [Na₃Cit] + [H₃Cit]) range of 0.1-25 mM. Citrate buffers produce solutions with a fixed [total citrate], 47 but variable pH and ionic strength by adjusting the fractions of H₃Cit and Na₃Cit. In these buffers, solution pH increased with the ratio of [Na₃Cit] to [total citrate] and ranged from 2.66 (25 mM H₃Cit) to 48 7.87 (25 mM Na₃Cit). 49

50 Over the [total citrate] range from 0.1 to 1.0 mM, the EM value of a cit/ nC_{60} suspension was solely dependent upon its pH (Figure S4A). This relationship between EM and pH is consistent with the 51 52 variable [Na₃Cit] experiment (Figure 2) and collectively these results indicate that pH, which is fixed by the citrate content, regulates the cit/ nC_{60} surface charge at low [Na⁺]. Interestingly, despite the fact that 53 their solution pH and EM varied widely, cit/C60 suspensions produced in these buffers generally had a 54 similar average size of ≈ 300 nm after 14-day stirring (Range: 250 to 350 nm; Figure S4B). Cit/ nC_{60} 55 produced in 1 mM H₃Cit was an exception; its larger average particle size (860 ± 3.3 nm) can be 56 attributed to a weak surface charge ($-0.01 \pm 0.02 \times 10^{-8} \text{ m}^2/\text{V-s}$) that enhanced particle destabilization. 57 The general insensitivity of Z_{ave} to pH, [total citrate], and [Na⁺] under these conditions corroborates the 58 59 results obtained with variable [Na₃Cit]. In the cit/ nC_{60} suspensions produced in buffers with [total citrate] \geq 5 mM the EM values generally became more negative with an increase in pH as well. 60 However, the high $[Na^+]$ in these suspensions resulted in low nC_{60} concentrations, leading to significant 61 fluctuations in EM and large $Z_{\mbox{\tiny ave}}$ values with large error bars (data not shown). 62

In buffers with pH < 3, the EM of cit/nC_{60} fluctuated between negative and positive values during the stirring period. Under these conditions, nC_{60} had a weak and unstable surface charge. Nonetheless,

after 14-day stirring the supernatants of these samples were yellow to light brown in color – indicative 65 of cit/nC_{60} . The presence of cit/nC_{60} in these supernatants was confirmed by UV-Vis and TEM (not 66 shown). nC₆₀ particles in these solutions had a low electrostatic barrier against aggregation and 67 ultimately aggregated and settled out of solutions after 9-months of storage in the dark, leaving clear 68 69 supernatants. For samples with more negative EM values, a significant amount of cit/nC_{60} particles 70 remained in the supernatant after a 9-month extended settling period. The disparity between these cit/nC_{60} suspensions suggests that although surface charge does not necessarily dictate nC_{60} formation, it 71 72 does affect its ultimate aggregation and deposition.



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Figure S4 (A) EM and (B) Z_{ave} of cit/ nC_{60} in citrate buffers after 14-days stirring as a function of pH. (Each data point represents the average of three measurements for one sample and the error bar represents the standard deviation.)

78 [Na⁺] Effects.

In the citrate buffer and variable [Na₃Cit] experiments, [Na⁺] was set by [Na₃Cit]. To isolate the effects 79 of [Na⁺] we conducted experiments wherein [Na⁺] was varied by adding NaCl to solutions of fixed [total 80 citrate] = 0.5 mM at pH values of 3.6 (set by 0.5 mM H_3Cit) and 6.9 (set by 0.5 mM Na_3Cit). These 81 82 experiments were conducted at an elevated temperature of 50 °C to accelerate nC_{60} production (the size and surface charge measurements conducted by Nanosizer was also conducted at 50 °). We note that the 83 surface charge and average size of the particles produced at 50 °C were similar to those produced at 30 84 °C (Figure S5). Similar to the trends described previously, pH dictated the nC_{60} surface charge in 85 solutions with $[Na^+] \le 15$ mM (Figure S6A). The EM values for the low pH samples were less negative 86 than those for the high pH samples irrespective of $[Na^+]$. For solutions with $[Na^+] \ge 15$ mM, however, 87 88 EM became increasingly positive. This result can be explained by the screening effect of the counterion since higher ionic strengths are expected to decrease the surface charge.¹⁻³ 89



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Corroborating the previously presented results, Z_{ave} was insensitive to solution pH and was only affected by [Na⁺] for [Na⁺] > 10 mM. Importantly, a less negative surface charge does not necessarily result in the formation of larger particles. For example, cit/ nC_{60} produced in a solution with 0.5 mM

96 H₃Cit and 3 mM NaCl, had a smaller average size (220.0 ± 4.4 nm) than cit/ nC_{60} (265.0 ± 13.6 nm) produced in a solution with the same [total citrate] and [Na⁺], yet higher pH. However, the EM of the 97 former $(-2.89 \pm 0.05 \times 10^{-8} \text{ m}^2/\text{V-s})$ was considerably less negative than that of the latter $(-4.60 \pm 0.06 \times 10^{-8} \text{ m}^2/\text{V-s})$ 98 10⁻⁸ m²/V-s). Figure S6B and its insets show that in both solution series as [Na⁺] increased the particle 99 size distributions shifted to larger sizes. The argument that high [Na⁺] facilitates the formation of large 100 cit/nC_{60} aggregates is further supported by TEM images of cit/nC_{60} produced in 0.5 mM H₃Cit solutions 101 with variable [Na⁺]. Figure S7 shows images of representative areas on a given TEM grid. As shown in 102 the low resolution images in Figures S7A-D (0.3 mM \leq [Na+] \leq 9 mM), the majority of cit/nC₆₀ were 103 small particles or aggregates comprised of these particles. The similarities in these aggregate structures 104 and morphologies were consistent to their similar EM values and relatively small Z_{ave}. As [Na⁺] 105 increased to 15 and 30 mM, however, large solid particles, whose formation was facilitated by the 106 minimal surface charge became the predominant particle type. 107



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Figure S6 (A) EM and (B) Z_{ave} of nC_{60} on day 14 as a function of $[Na^+]$; Intensity weighted particle size

- distribution of $\operatorname{cit/nC_{60}}$ produced in H₃Cit solutions with variable [Na⁺] (left inset) and in Na₃Cit solutions with variable [Na⁺] (right inset) after 14-day stirring and 24-h settling. (Each data point
- solutions with variable [Na⁺] (right inset) after 14-day stirring and 24-h settling. (Each data point represents the average of three measurements for one sample and the error bar represents the standard
- 113 deviation.)



116	Figure S7 Low resolution TEM images of cit/nC_{60} formed in 0.5 mM citric acid solutions with variable
117	[Na ⁺]: (A) 0.3 mM, (B) 1.5 mM, (C) 3.0 mM, (D) 9.0 mM, (E) 15.0 mM, and (F) 30.0 mM

118 Collectively the variable $[Na_3Cit]$, pH, ionic strength, and $[Na^+]$ studies have shown that solution pH

119 is the primary parameter determining the surface charge of nC_{60} , that Z_{ave} is generally insensitive to EM

- and pH when $[Na^+] \le 15$ mM, and that charge screening is an important factor that affects the nC_{60}
- surface charge and increases its average size when [Na⁺] exceeds 15 mM.



Figure S8 TEM images of nC_{60} formed in solutions with different sodium citrate concentrations: 0, 0.01, 0.1, 0.5, 1, 5, 10, and 25 mM (A to H).



Figure S9 TEM images of regularly shaped cit/nC_{60} . Similar nanostructures were never observed in the absence of citrate.



Figure S10 TEM images of spherical particles in select areas near cracks and crevices in the largeparticles.



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Figure S11 (A) Normalized spectra (For each sample the absorbance (ABS) at a specific wavelength

was divided by the ABS at 360 nm.) for nC_{60} suspensions produced in four different solutions. Inset: the original UV-Vis spectra for these four suspensions. (B) Spectra of mixtures of aq/nC_{60} and solutions

140 with the added [Na₃Cit] ranging between 0.0 and 5 mM.

142 Centrifugation of *n*C₆₀.

 nC_{60} suspensions were fractionated based on particle size by centrifugation. According to Stokes' law for an ideal suspension consisting of spherical particles,⁴ after a centrifugation period of *t*, the radius *a* of the largest particles remaining in the supernatant will be proportional to the following parameter *S*:

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$$a \propto S = \left[\frac{18\eta}{(\rho_0 - \rho_f)R\omega^2}\right]^{\frac{1}{2}}$$
 (S1)

where ρ_0 is the density of the particle; ρ_f is the fluid density; η is the fluid viscosity; ω is the angular 147 velocity; and R is the distance from the rotor axis. In this experiment, ω and R were fixed while ρ_f and η 148 remained roughly constant within the [Na₃Cit] range of 0 to 5 mM.⁵ Therefore, particle radii obtained 149 from Eqn. S1 for the four tested suspensions $(aq/nC_{60}, 0.1 \text{ mM cit/}nC_{60}, 1.0 \text{ mM cit/}nC_{60}, and 5.0 \text{ mM}$ 150 cit/nC_{60}) should be the same despite their different solution chemistries if the suspensions only 151 152 contained spherical nC_{60} particles. Based upon our observation, there was a decrease in average particle size with centrifugation time for all nC_{60} suspensions (Figure S12). However, despite its largest initial 153 particle size, aq/nC_{60} had the most significant decrease in Z_{ave} following centrifugation. The extent of 154 155 reduction in Zave decreased with [Na₃Cit].



Figure S12 Average particle size of nC_{60} as a function of centrifugation time (The error bar represents the standard deviation of three measurements.).

The discrepancy between the observed Z_{ave} in Figure S12 and the theoretical results based on Eqn. S1 can be accounted for by the variable surface charges of these particles and their inherent heterogeneity that results from extended mixing. As discussed in the main paper, the surface charge of nC_{60} becomes more negative with [Na₃Cit]. The more negatively charged surfaces of 1.0 and 5.0 mM cit/ nC_{60} impede them from aggregating and precipitating during centrifugation. On the other hand, using a modified form of Stokes' law (Eqn. S2)⁶ it is possible to estimate the sedimentation velocity of irregularly shaped particles during centrifugation.

166
$$v = \frac{K(\rho_0 - \rho_f)a_{eq}^2 R\omega^2}{18\eta}, K = 0.843lg\left(\frac{A_{eq}}{A \times 0.065}\right)$$
 (S2)

where a_{eq} and A_{eq} correspond to the diameter and surface area of a theoretical sphere that has the same volume as the particle, respectively. Using the established range $K \approx 2-4$ for different shapes this equation indicates that irregularly shaped particles with a given radius of a_{eq} move faster towards the bottom of the centrifuge tube than spheres with a radius of a_{eq} . It can thus be expected that the small spherical particles that exist in the 1.0 and 5.0 mM cit/ nC_{60} suspensions are more resistant to centrifugation induced settling than irregular nC_{60} .



Figure S13 Normalized UV-Vis spectra of centrifuged nC_{60} : (A) aq/ nC_{60} , (B) 0.1 mM cit/ nC_{60} , (C) 1.0 174

mM cit/ nC_{60} , and (D) 1.0 mM cit/ nC_{60} . Insets: the original UV-Vis spectra of centrifuged nC_{60} 175 suspensions. 176



Figure S14 Polydispersity of nC_{60} as a function of centrifugation time (The error bar represents the standard deviation of three measurements.).

180 Exhaustive Extraction.

181 **Experimental Methods.** nC_{60} was extracted into toluene in the presence of 200 mM NaCl. The 182 mixture, consisting of 3 mL of nC₆₀ stock suspension, 0.2 mL of 3.2 M NaCl solution, and 3 mL of toluene, was vortexed in a test tube for 1 min, settled for 15 min to allow the two phases to separate, and 183 184 then the organic phase was transferred to an aqua-regia cleaned test tube. The aqueous phase was then combined with 3 mL of toluene for a second extraction. Extraction operations were repeated three times 185 and the lack of any detectable nC_{60} characteristic absorption bands in the UV-Vis spectrum of aqueous 186 187 phase after three extractions cycles indicated that all of the nC_{60} had been extracted from the aqueous phase. The C_{60} concentration ([C_{60}]_{tol}) in each toluene extract was determined based upon its UV-Vis 188 absorbance at 336 nm and a calibration curve established by a series of C₆₀-toluene solutions with 189 known [C₆₀]. In these experiments the total $[nC_{60}]_{TOT}$ was calculated as the sum of $[C_{60}]_{tol}$ from the three 190 extracts. The recovery efficiency of each extraction is defined as the ratio of $[C_{60}]_{tol}$ in each toluene 191 192 extract relative to $[nC_{60}]_{TOT}$ for each nC_{60} suspension.

Results and Discussion. The extraction efficiency of each extraction was calculated as the ratio of 193 $[C_{60}]$ in each extract to $[C_{60}]_{TOT}$ and is presented in Figure S15. For cit/ nC_{60} produced in solutions with 194 moderate [Na₃Cit] (0.5-5.0 mM), more than 95% of nC_{60} was extracted to toluene in the first extraction. 195 In contrast, only $\approx 50\%$ of the aq/nC₆₀ and in 0.1 cit/nC₆₀ was extracted in the first extraction, with the 196 197 remainder extracted in the second and third operations. It could be hypothesized that the difference in 198 extraction efficiency for the first extraction was caused by the variable initial $[nC_{60}]$ in these samples. However, the results of exhaustive extraction experiments for diluted aq/nC_{60} suspensions suggest that 199 the initial $[nC_{60}]$ for aqueous nC_{60} samples has little effect on the extraction efficiency. For nC_{60} 200 produced in different solutions, 1.0 mM cit/ nC_{60} with a UV-Vis absorbance at 360 nm (ABS(360)) of 201 0.83 had a higher extraction efficiency than 0.1 mM $\operatorname{cit/nC_{60}}$ with ABS(360) = 0.55. We thus conclude 202 that the observed variation in the first extraction efficiency indicates the differential capacity of the 203 different types of nC_{60} to solvation in toluene. The results suggest that surface characteristics of nC_{60} 204

produced in solutions with low or no [Na₃Cit] are dissimilar from those of cit/ nC_{60} produced in solutions with moderate [Na₃Cit]. This dissimilarity is due to the association between citrate and nC_{60} . The particle-solution interface of aq/ nC_{60} contains only surface associated water molecules (Figure S16A), while at sufficient citrate concentrations (> 0.1 mM) citrate is present at the interface in high enough concentrations (Figure S16C) to affect the extraction efficiency. The comparatively higher initial extraction efficiencies for cit/ nC_{60} produced in 0.5-5.0 mM Na₃Cit suggest that the association between citrate and nC_{60} is readily destroyed by high [Na⁺].



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Figure S15 Extraction efficiencies of individual extraction steps (I, II, and III) for different nC_{60}

suspensions. $1 = aq/nC_{60}$, $2 = cit/nC_{60}$ produced in 0.1 mM, $3 = cit/nC_{60}$ produced in 0.5 mM, $4 = cit/nC_{60}$

produced in 1.0 mM, and $5 = \text{cit/}nC_{60}$ produced in 5.0 mM Na₃Cit solutions; The vertical bar represents

the average of duplicates and the error bar represents the standard deviation of the duplicates.



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Figure S16 Models of nC_{60} particles surfaces for (A) aq/nC_{60} , (B) cit/nC_{60} produced in solutions with low [Na₃Cit] levels, (C), cit/nC_{60} produced in solutions with moderate [Na₃Cit], and (D) aq/nC_{60} with the addition of Na₃Cit after extended mixing.

223 Adsorption of citrate on nC_{60} .

Isolation. To quantitatively estimate citrate adsorption to nC_{60} , cit/ nC_{60} particles were removed from 224 aqueous solutions by ultrafiltration or centrifugation. A cit/nC_{60} stock suspension was ultrafiltrated 225 through a membrane with a cutoff size of 1 kDa at 2 \times 10⁵ Pa; A cit/nC₆₀ stock suspension was 226 centrifuged at 10000 rpm for 30 min. The supernatant was then transferred to a new centrifugation tube 227 and centrifuged at the same speed for 20 min. The filtrate and supernatant were transferred to aqua-regia 228 cleaned test tubes for further characterization. UV-Vis analysis of the filtrate from ultrafiltration or the 229 supernatant from centrifugation indicated that all cit/nC_{60} particles were retained on the membrane or in 230 231 the pellet. Accordingly, the changes in [citrate] in the ultrafiltrate and supernatant reflect the amount of 232 citrate associated with nC_{60} .

Citrate Concentration Measurement. An HP 1090 HPLC with an acid column (Restek Pinnacle ODS Amine) coupled with a refractive index detector was used to measure aqueous phase citrate concentrations. Phosphate buffer (pH = 3.0) was used as mobile phase at a flow rate of 1.0 mL/min.

Results and Discussion. Citrate stabilization of nanoparticle suspensions is an established 236 phenomenon and involves both pH modification and the association of citrate with the nanoparticle 237 surface.^{16,17} Jiang et al.¹⁸ determined that citric acid treated carbon nanotubes (CNT) exhibit more 238 negative zeta potentials than pristine CNT. They hypothesized that citrate associated with the CNT 239 surface, but did not suggest a mechanism. The adsorption of NOM, proteins, and organic pollutants on 240 surfaces of nC_{60} has been studied previously.¹⁹⁻²⁴ Adsorbates interact with nC_{60} via hydrophobic 241 interactions, electrostatic interactions, π - π bonding, or hydrogen bonding. The mechanism by which 242 citrate associates with C60 is presently unknown; however, because of its hydrophilic surfaces, its 243 244 negatively charged surface, and the molecular structure of citrate, hydrophobic interaction, electrostatic interaction and π - π bonding are not likely to be the sources of the association between citrate and nC_{60} . 245 246 The -COOH groups in citrate molecule can act as hydrogen-bonding donors and form hydrogen bonds with the C_{60} molecule, which acts as hydrogen bonding acceptor.²⁵ For electron deficient substrates, the carboxyl- π interaction was found to be energetically favorable.²⁶ Fullerite C_{60} , which is electron deficient²⁷ and has structures similar to aromatic rings, may associate with citrate through the carbonyl- π cloud interaction. It is also well established that C_{60} serves as an electron acceptor in electron-donor acceptor complexes with a variety of organic molecules²⁸⁻³¹ and it appears that citrate can serve as an electron donor enabling production of supramolecular nC_{60} structures. The conversion from the *fcc* crystal structure for aq/ nC_{60} to the *hcp* crystal structure for cit/ nC_{60} also supports this contention.

Cit/nC60 produced in solutions with different [Na3Cit] levels was isolated from solutions by 254 centrifugation. [Citrate] in the original cit/nC_{60} suspensions and their supernatants after centrifugation 255 are present in Figure S17. An obvious decrease in [citrate] was only observed in the 0.1 mM cit/ nC_{60} 256 samples. Less than 10% of the initial citrate remained in the supernatants. In other samples, the 257 decreases in [citrate] were less than 0.05 mM, quite low compared with [Na₃Cit] in original cit/ nC_{60} 258 suspensions. Similar results were observed in ultrafiltration experiments as well. Obvious decreases in 259 [citrate] in ultrafiltrates were only observed for the 0.05 mM and 0.1 mM cit/ nC_{60} samples. Collectively, 260 261 these results indicate that the amount of citrate adsorbed on the surface of nC_{60} is either not large or that the association between citrate and nC_{60} is weak and can be readily destroyed by ultrafiltration and 262 centrifugation. 263



Figure S17 [Na₃Cit] in original cit/nC_{60} suspensions and centrifuged supernatants.



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Table S1 contains a simplified estimation of the amount of adsorbed citrate on the surface of cit/ nC_{60} . Based upon this calculation, when the particle size is larger than 10 nm, the total amount of citrate adsorbed by cit/ nC_{60} is less than 0.01 mM (Figure S18). In cit/ nC_{60} produced via extended mixing, [C₆₀] is usually lower than 20 mg/L and the Z_{ave} is around 200 nm. Therefore, in reality, [citrate]_{adsorbed} would

- be lower than 0.001 mM. This result may explain the fact that we did not observe much difference in
- [citrate] between the original cit/nC_{60} suspension and its ultrafiltrate/supernatant from centrifugation.
- Table S1 Adsorption of citrate on the surfaces of nC_{60} calculation

Some constants and values used in this calculation:

- Size of a C₆₀ molecule: 0.71 nm;
- Avogadro's number: $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$;
- The lattice constant of C_{60} crystal (*fcc*): l = 1.417 nm;
- Surface area of a citrate molecule: $A_{citrate} = 0.38 \text{ nm}^2 \text{ molecule}^{-1}$
- Initial fullerene concentration of $\operatorname{cit/nC_{60}}$ suspension: $[C_{60}] = 400 \text{ mg/L}$.

Assumptions in this estimation:

- The cit/ nC_{60} aggregates are spherical with the same size. The Z_{ave} represents the diameter of these particles.
- Monolayer adsorption.

Calculation: (use 300 nm particle as an example)

1. Number C₆₀ molecules in *n*C₆₀ suspensions of 400 mg/L:
$$N_0 = \frac{[C_{60}]}{Mw_{C_{60}}} \times N_A = 3.34 \times 10^{20}$$
 molecule/L

2. One spherical particle of 300 nm contains $n_0 C_{60}$ molecules: $n_0 = \frac{4\pi}{3} \left(\frac{Z_{ave}}{2}\right)^3 \frac{4}{l^3} = 1.99 \times 10^7$ molecule/particle

3. Number concentration of 300 nm spherical nC_{60} particles: $[nC_{60}]_{\text{particle}} = \frac{N_0}{n_0} = 1.68 \times 10^{13} \text{ particle/L} = 2.80 \times 10^{-11} \text{ mol/L}.$

4. One 300 nm spherical nC_{60} will adsorb $n_{citrate}$ molecule: $n_{citrate} = \frac{A_{surface(nC_{60})}}{A_{surface(citrate)}} = \frac{4\pi \left(\frac{Z_{ave}}{2}\right)^2}{A_{surface(citrate)}} = 7.44 \times 10^5$

citrate molecule/particle

5. [Citrate]_{adsorbed} = $n_{citrate} \times [nC_{60}]_{particle} = 2.08 \times 10^{-5} \text{ mol/L} = 0.002 \text{ mM}.$



Figure S19 (A) Surface charge and (B) average particle size of nC_{60} produced in different carboxylate solutions as a function of the concentration of carboxylate. Each data point represents the average of three measurements for one sample and the error bar represents the standard deviation.

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