Supplementary Information

Mesoscale aggregation properties of C_{60} in toluene and chlorobenzene

Rong-Hao Guo,[a] Chi-Chung Hua, *,[a] Po-Chang Lin,[b] Ting-Yu Wang[c] and Show-An Chen[d]

[a] Department of Chemical Engineering, National Chung Cheng University, Chiayi 621, Taiwan.

[b] National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan.

[c] Instrumentation Center, National Taiwan University, Taipei 106, Taiwan

[d] Department of Chemical Engineering, National Tsing Hua University, Hsinchu 300, Taiwan.

S1 Absorbance of fullerene solutions

A UV-vis spectrometer (JASCO, V-570) was employed to examine the absorbance of fullerene solutions. The measurement was conducted with a cell having a path length of 2 mm (Hellma, 110-QS) to minimize the scattering associated with large C_{60} clusters. Fig. S1 reveals that C_{60} has negligible absorption at the incident light wavelength (λ_0= 785 nm) for a wide range of concentrations and two different solvent media investigated in this work.

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* Corresponding author. E-mail: chmcch@ccu.edu.tw

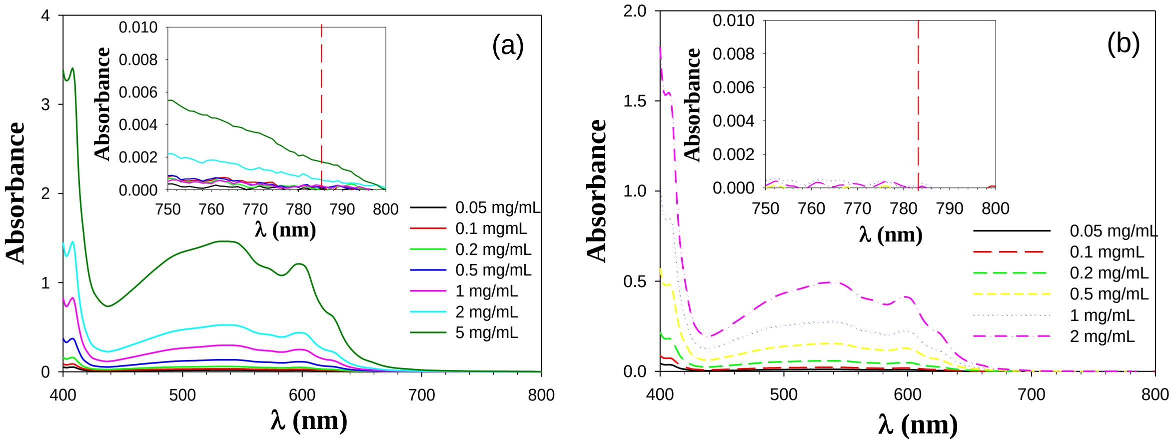
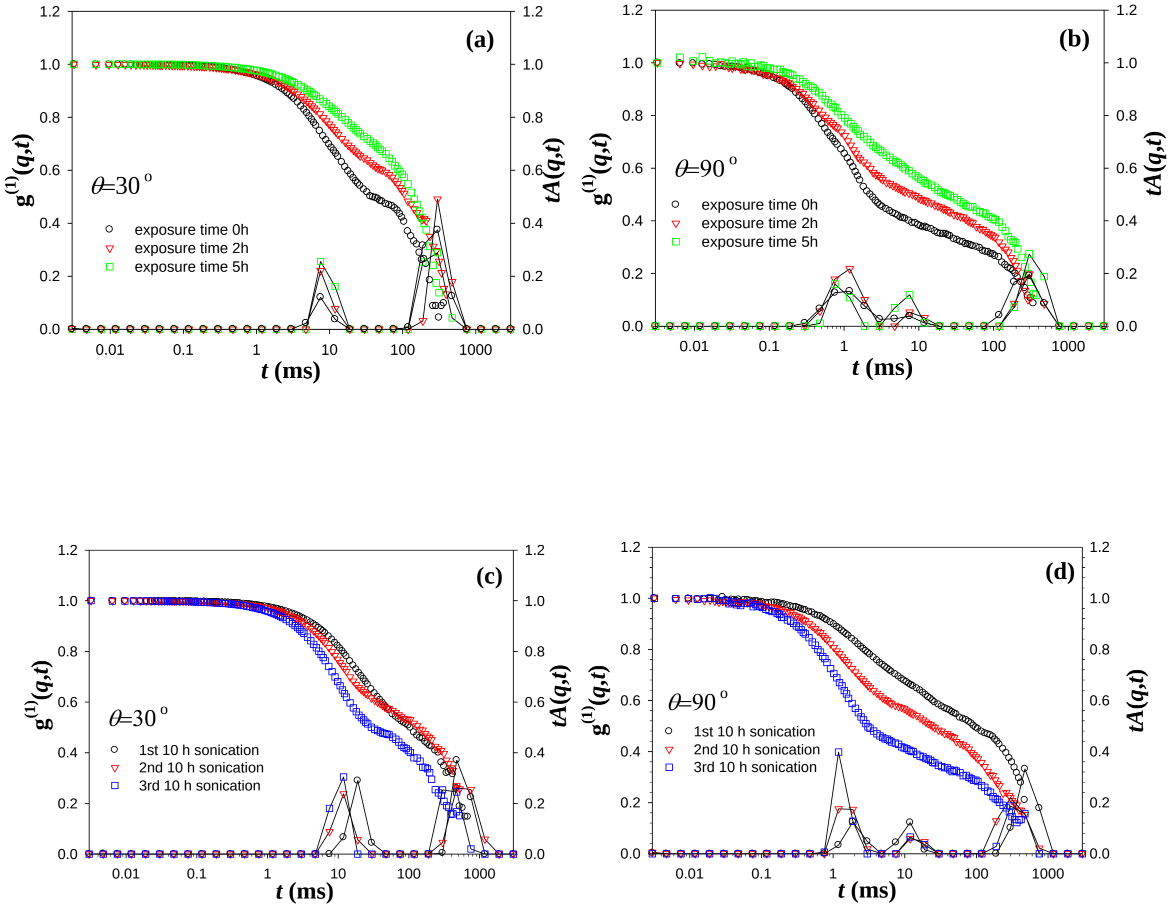


Fig. S1 UV-vis spectra of (a) C_{60}/chlorobenzene solutions and (b) C_{60}/toluene solutions. The absorption at 785 nm is marked with dashed line in the magnified inset figure.

S2 Effects of laser-light exposure time and sonication time on fullerene solution dynamics



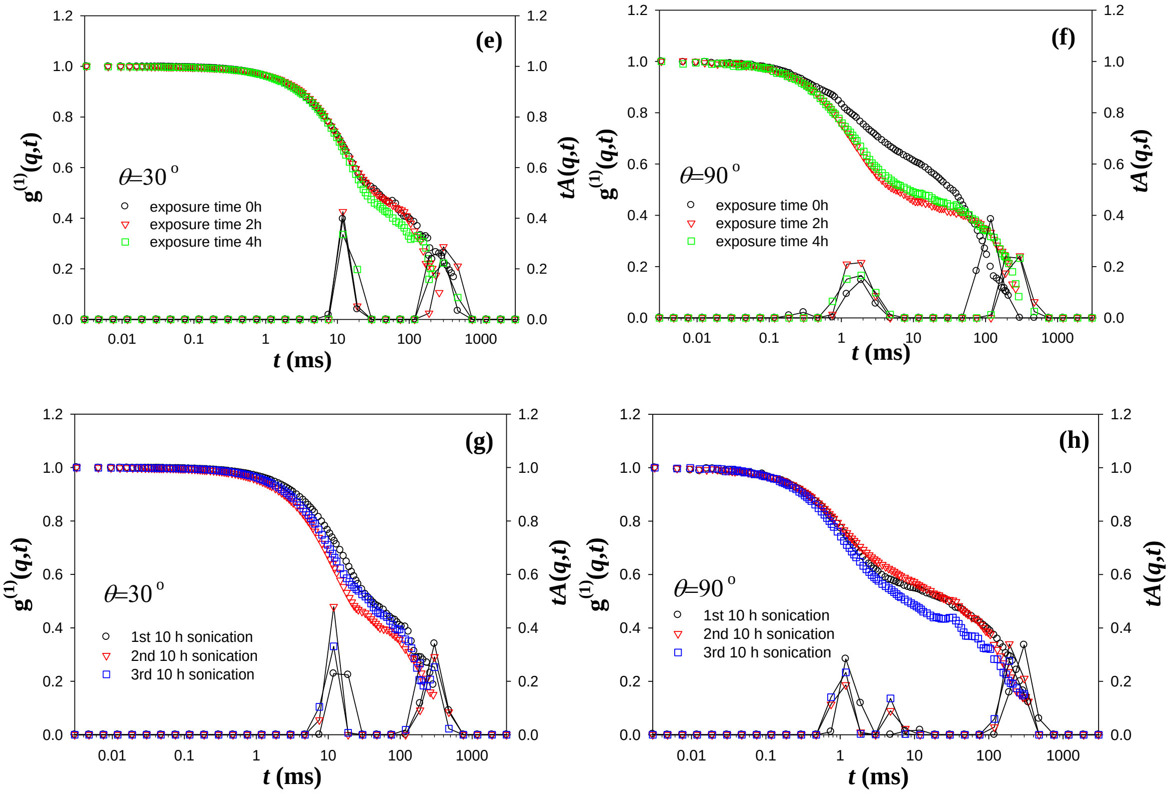


Fig. S2 Effects of laser-light exposure time and sonication time on the field autocorrelation functions $\left|g^{(1)}(q,t)\right|$ and relaxation time distributions $A(q,\tau)$ for (a-d) 2 mg/mL C$_{60}$/toluene solution and (e-h) 5 mg/mL C$_{60}$/chlorobenzene solution.

S3 Examination of micrometer-sized aggregates

Small angle light scattering (SALS) measurements were conducted to discriminate the presence of micrometer-sized aggregates in C$_{60}$ solutions. SALS measurements were performed on a laboratory-built apparatus as described elsewhere.[1] All measurements were conducted at 25 °C in a range of scattering angles $\theta = 2° - 14°$. We selected two representative samples for SALS characterizations. Fig. S3 reveals *q*-independent scattering feature suggesting there are no micrometer-sized aggregate clusters in either solvent system of C$_{60}$ investigated.

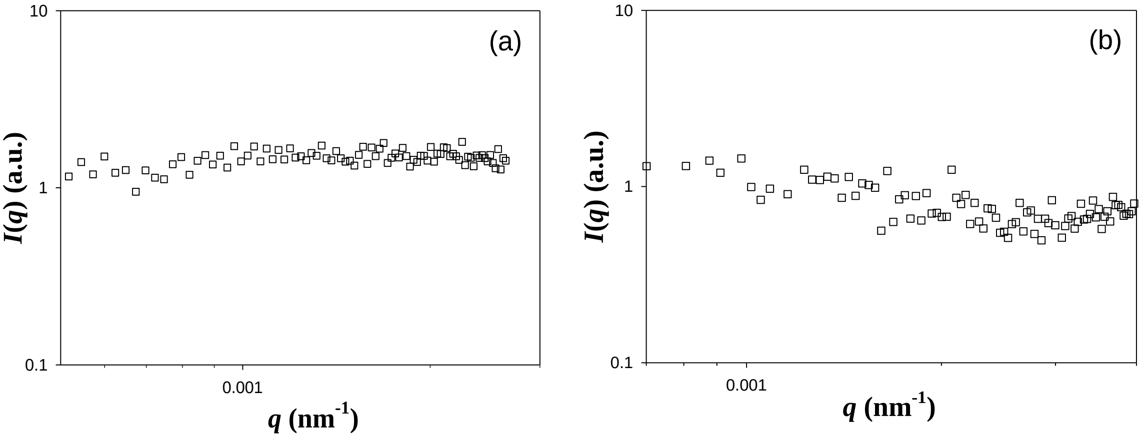


Fig. S3 The SALS intensity profiles of (a) 5 mg/mL C_{60}/chlorobenzene solution and (b) 2 mg/mL C_{60}/toluene solution.

S4 Evaluation of mean cylinder radius and vertical shifting of SLS profiles

The Guinier approximation may be extended to the rod-like particles in the following way: for a cylinder with length L and radius R, the Guinier approximation at low-q is given by $I(q)=I(0)\exp(-q^2R_\mathrm{g}^2/3)$, where $R_\mathrm{g}^2=L^2/12+R^2/2$. On the other hand, the Guinier approximation at intermediate-q (where a transit from $I(q)\sim q^{-1}$ to $I(q)\sim q^{-4}$ occurs) may be expressed as $I(q)=\left(I(0)/q\right)\exp(-q^2R_{\mathrm{g},R}^2/2)$, where $R_{\mathrm{g},R}^2=R^2/2$. The above formulation can be utilized to extract the mean radius of cylinders (i.e., R) from SLS profiles that fall in the range of $2\pi/L<q<1/R_{\mathrm{g},R}$. Fig. S4 shows the plots of ln $I(q)q$ as a function of q^2 in the indicated region for C_{60}/chlorobenzene solutions. The ln $I(q)q$ vs. q^2 plot exhibits a nearly straight line indicative of fairly monodisperse cross-sectional dimension for R.

Accordingly, to simultaneously fit the SLS and SAXS profiles, the SLS profile was shifted along the vertical axis so that the q value, at which the scaling law of $I_{\mathrm{SLS}}(q) \sim q^{-1}$ intersects with that of $I_{\mathrm{SAXS}}(q) \sim q^{-4}$, should match the reciprocal of $R_{\mathrm{g},R}$ as shown in Fig. S4. Then, the combined SLS and SAXS profiles are described by the z-averaged length-polydisperse form factor that allows for the retrieval of mean cylinder length. Fig. S5 shows the z dependence of the weight-averaged length L_{w}. Obviously, the values of L_{w} are insensitive to the choice of z in the range of 0.001 to 0.1 for C_{60}/chlorobenzene solutions.

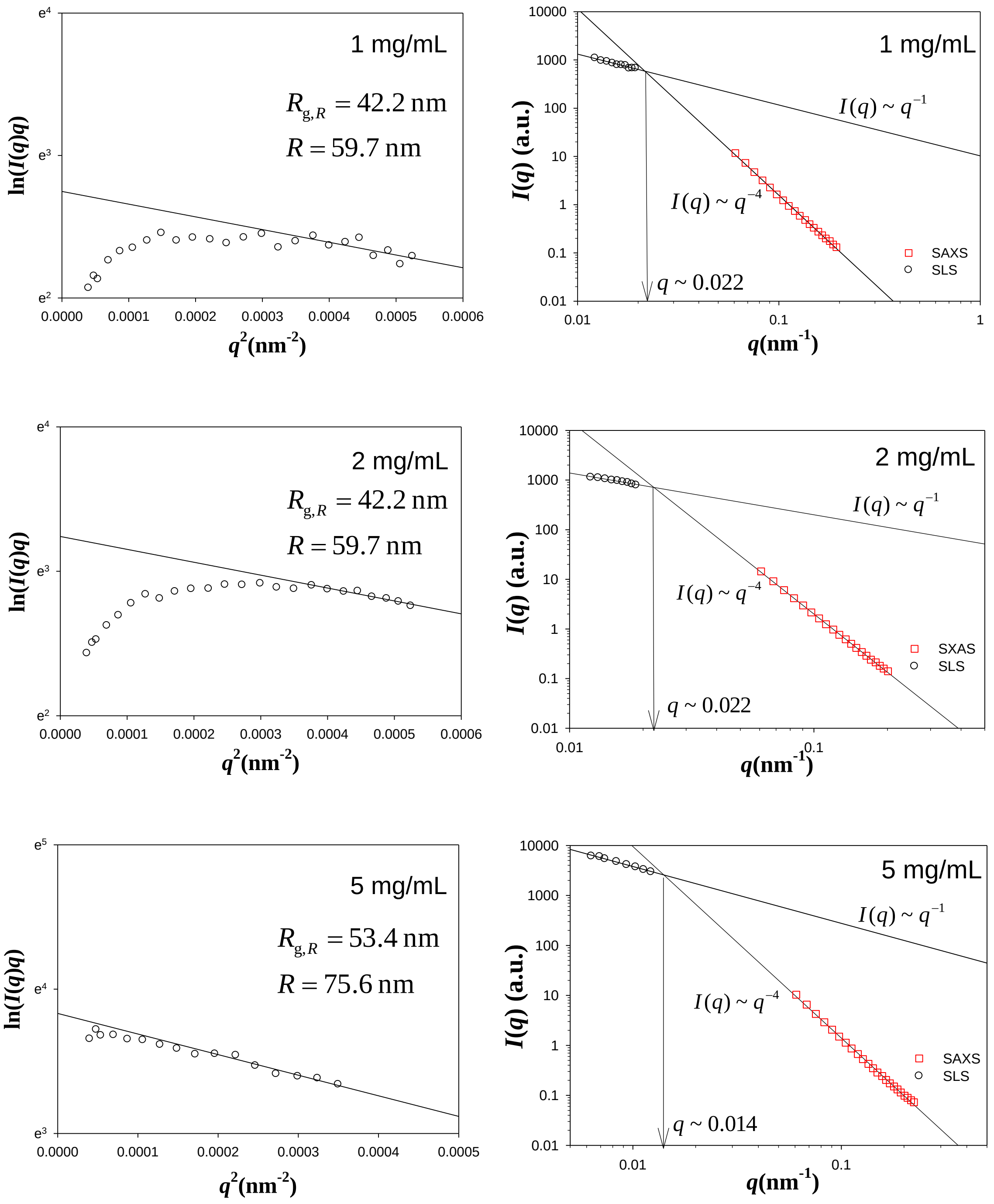


Fig. S4 Plots of ln $I(q)q$ as a function of q^2 for C$_{60}$/chlorobenzene solutions; the crossover of two different scaling laws is demanded to occur at a value of q corresponding to the inverse of $R_{g,R}$.

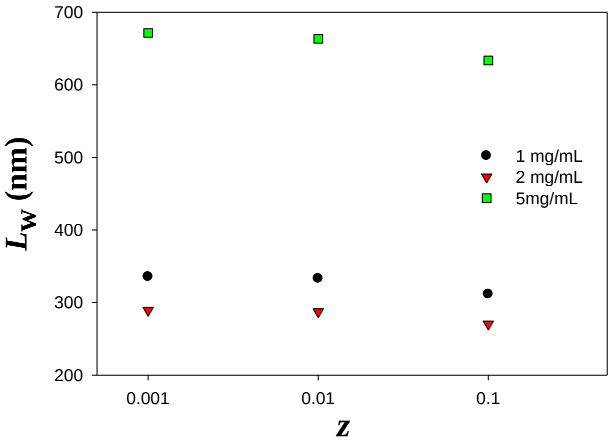


Fig. S5 The weight-averaged length L_{w} as a function of *z* for C_{60}/chlorobenzene solutions.

S5 Evaluation of the scattering intensity contributed by small C_{60} clusters

Fig. S6 shows the fitting of the SAXS profile at high-*q* using the formula $I_{\mathrm{SAXS}}(q) \sim P_{\mathrm{unit}}(q)S(q) + KI_{\mathrm{dimer}}(q)$. The form factors of the packing units were taken to be cylinder and sphere for chlorobenzene and toluene systems, respectively. The contribution of dimers to the scattering intensity can be expressed as $I_{\mathrm{dimer}}(q) = \exp[-(qR_{\mathrm{g,dimer}})^2 / 3]$ ($R_{\mathrm{g,dimer}}$=0.6 nm); *K* is the amplitude factor that depends on, among others, the difference in scattering length density between the cluster and the solvent medium, and is treated as an adjustable parameter here. Notable deviations from SAXS data at high-*q* were generally observable. Therefore, the contributions from isolated dimers and other small clusters were not considered in the main text.

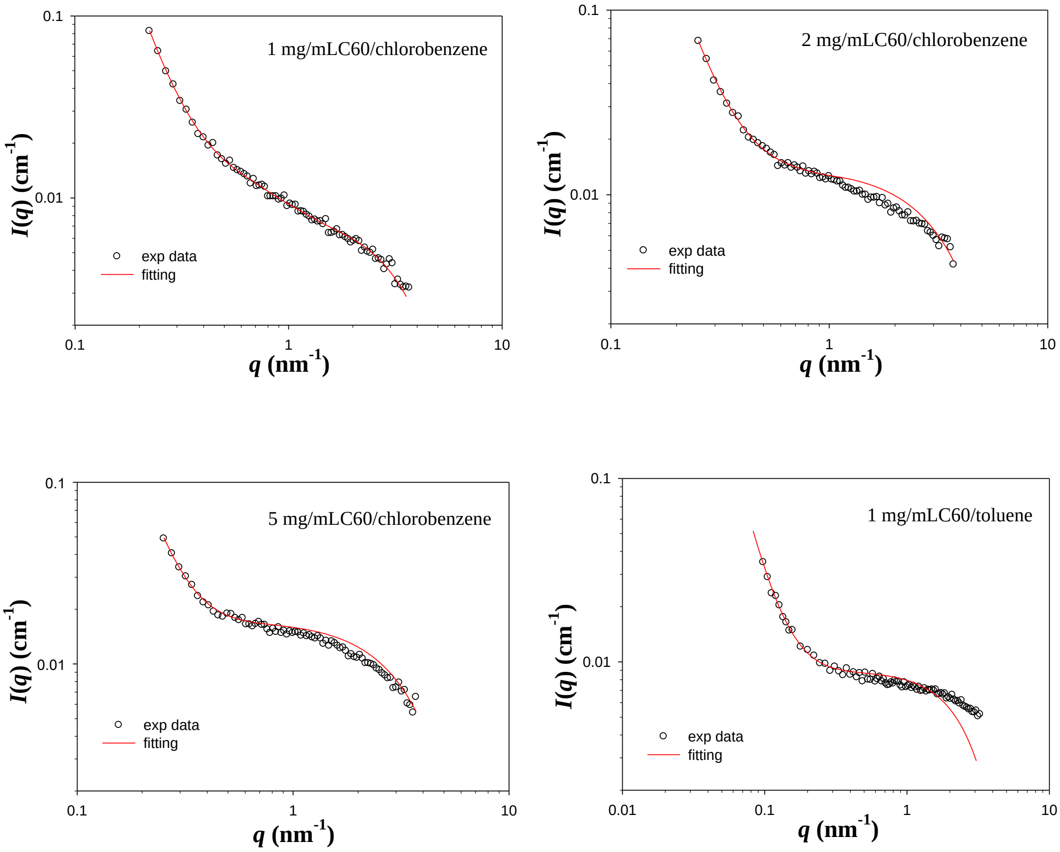


Fig. S6 SAXS intensity profiles for 1 mg/mL, 2 mg/mL, 5 mg/mL C_{60}/chlorobenzene solutions, and 1 mg/mL C_{60}/toluene solution, respectively. The solid lines denote the fitting with the formula $I_{\mathrm{SAXS}}(q) \sim P_{\mathrm{unit}}(q)S(q)+KI_{\mathrm{dimer}}(q)$.

S6 Estimation of number density of C_{60} aggregate clusters in solution

The number density of C_{60} clusters v for a given concentration can be estimated through the relation $v = cN_{\mathrm{A}}/M$, where c and N_{A} are the C_{60} concentration (after the subtraction of isolated C_{60} molecules) and the Avogadro's number, respectively; M represents the mean molecular weight of a C_{60} cluster, which can be estimated using the relation $M = M_{R_e} \times N$ with M_{R_e}

and N being the molecular weight and the total number of building blocks with radius R_e, respectively, in a C_{60} cluster. The number N for a C_{60} cluster of average radius R (obtained from $R_{g}\_S(q)$ in the main text) can be evaluated using the relation $N = k_f \left(R / R_e\right)^D$ with D and k_f being the fractal dimension and a prefactor, respectively; k_f is taken from an existing relation based on intense numerical simulations: $k_f = 4.46D^{-2.08}$.[2] Relevant parameters including the number density of C_{60} clusters so estimated are provided in Table S1. It can be seen the values of v all exceed the overlapping number density v^* for C_{60}/chlorobenzene solutions indicative of semidilute solutions.

Table S1 Parameter values and estimated number density for C_{60} clusters in solution

System	chlorobenzene			toluene
Concentration [c]	1 mg/mL	2 mg/mL	5 mg/mL	1 mg/mL
Length or radius of C_{60} cluster [nm]	424[a]	377[a]	648[b]	174[c]
Overlapping number density (v^* [1/cm^3])[d]	1.31×10^{13}	1.86×10^{13}	3.68×10^{12}	4.53×10^{13}
Molecular weight of a C_{60} cluster (M [g/mol])[e]	$1.79\sim2.38\times10^{7}$	$2.64\sim3.52\times10^{7}$	$1.29\sim1.72\times10^{8}$	$1.87\sim7.48\times10^{8}$
Number density of C_{60} clusters (v [1/cm^3])	$1.61\sim2.51\times10^{13}$	$1.82\sim2.43\times10^{13}$	$1.04\sim1.39\times10^{13}$	$0.81\sim3.21\times10^{12}$
v/v^*	1.22~1.91	0.98~1.31	2.82~3.77	0.02~0.07

[a] Length obtained from DLS results. [b] Length obtained from DDLS results. [c] Radius obtained from SLS results. [d] $v^*=1/L^3$ for chlorobenzene system and $v^*=1/(4\pi R^3/3)$ for toluene system. [e] $M = M_{R_e} \times N$, where $M_{R_e} = 2160 \sim 2880$ g/mol (i.e., 3~4 C_{60} particles) for chlorobenzene system and $M_{R_e} = 79200 \sim 316800$ g/mol (i.e., 110~440 C_{60} particles) for toluene system.

S7 Estimation of confinement tube diameter

Recall that the number density of C_{60} clusters for all C_{60}/chlorobenzene solutions clearly has reached the semidilute regime. As a result, a "tube diameter" defining the confining space can be utilized to describe the slow mode observed in the DLS analysis. The tube diameter d_{tube} can be evaluated by the relation $d_{\mathrm{tube}} \cong 4/v\pi L^2$,[3] where v and L being the number density and length of C_{60} cluster, respectively. The estimated tube diameters are gathered in Table S2.

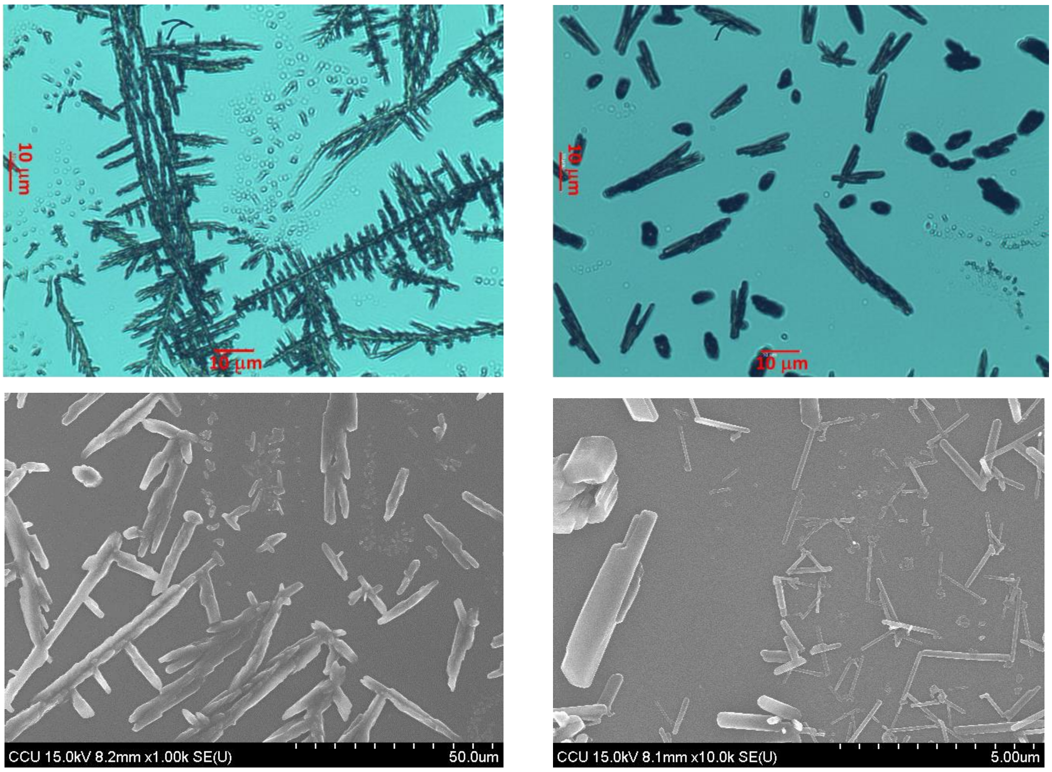
Table S2 Estimated tube diameters for C_{60}/chlorobenzene solutions

Sample	v [1/cm^3]	L [nm]	d_{tube} [nm]
1 mg/mL	$1.61\sim2.51\times10^{13}$	424	328~438
2 mg/mL	$1.82\sim2.43\times10^{13}$	377	367~490
5 mg/mL	$1.04\sim1.39\times10^{13}$	648	217~290

S8 Morphology and XRD pattern of drop-casting films

The optical microscopy (OM) images were taken in a conventional microscope (Olympus), and the micrographs from CCD (Moticam 2300) were converted to digital images through an image processing software (Motic Image Plus 2.0ML). The scanning electron microscopy (SEM) images were taken in a Hitachi S4800-I instrument. The sample solutions for OM and SEM characterizations were drop-cast onto glass substrates and naturally dried under ambient condition. Fig. S7 shows that branching architectures are ubiquitous in the film produced from C_{60}/chlorobenzene solution, while cylinder clusters prevail in the film made of C_{60}/toluene solution.

Crystallinity of the dried films was characterized using a X-ray diffractometer (Lab XRD-6000, Shimadzu) with Cu Kα radiation (λ=1.54 Å) operating at 30 mA and 40 kV at a scanning rate of 2°/min at room temperature. The specimens for XRD characterization were prepared following a similar procedure as noted above, with the sample solutions drop-cast onto the glass substrates several times so as to gain sufficient film thickness for the subsequent measurement. The results shown in Fig. S8 were indicative of distinct types of solvent-induced crystal structures for the two C_{60} solutions under investigation.



(a) **(b)**

Fig. S7 OM images (top) and SEM images (bottom) of the dried film produced from (a) 2 mg/mL C_{60}/chlorobenzene solution and (b) 2 mg/mL C_{60}/toluene solution.

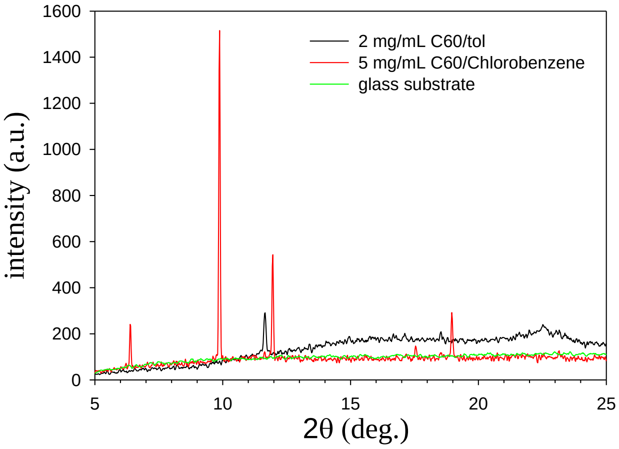


Fig. S8 XRD spectra of the dried films produced from 2 mg/mL C_{60}/ toluene and 5 mg/mL C_{60}/chlorobenzene solutions, respectively.

References

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2. L. Ehrl, M. Soos and M. Lattuada, *J. Phys. Chem. B*, 2009, **113**, 10587-10599.
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