Electronic Supplementary Information

Additive-Induced Ordered Structures Formed by PC71BM Fullerene Derivative

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Here we present additional experimental and computer simulation data on the systems under study.

S1. Experimental Details and extra experimental results

Materials. PC71BM with purity > 99.95% was purchased from UniRegion Biotech. DIO (b.p. 366 °C) and DBO (b.p. 272 °C) were purchased from Sigma-Aldrich, and ODT (b.p. 270 °C) was purchased from Alfa Aesar. Chlorobenzene was purchased from Sigma-Aldrich. All the chemicals were used as received.

Sample preparation. PC71BM were first dissolved in chlorobenzene at ~25 mg/ml, and then the additives, including DIO, DBO, and ODT, were added into the solutions at the desired amounts. After completely mixing, chlorobenzene was removed in the vacuum oven for 1 h at room temperature.

Due to the high boiling points of the additives, most of the additives remain in the samples.

SAXS and WAXS. SAXS and WAXS measurements were conducted on the BL23A1 beamline in the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The monochromatic beam of wavelength λ = 0.83 Å was used. The sample thickness was 1 mm. The scattering patterns were collected on a Pilatus 1M-F detector. The spectra are shown as plots of the intensity I versus the wave vector $q = 4\pi \sin(\theta/2)/\lambda$ (where θ is the scattering angle), which were obtained by circularly averaging the intensity $I(q)$ for the whole 2-dimensional patterns.

DSC. DSC measurements were performed on a TA Instruments DSC 25 under nitrogen atmosphere at a heating rate of 10 °C/min. Indium was used as the standard for temperature calibration. Samples were encapsulated in sealed aluminum pans, and the weight was ~ 3 mg.

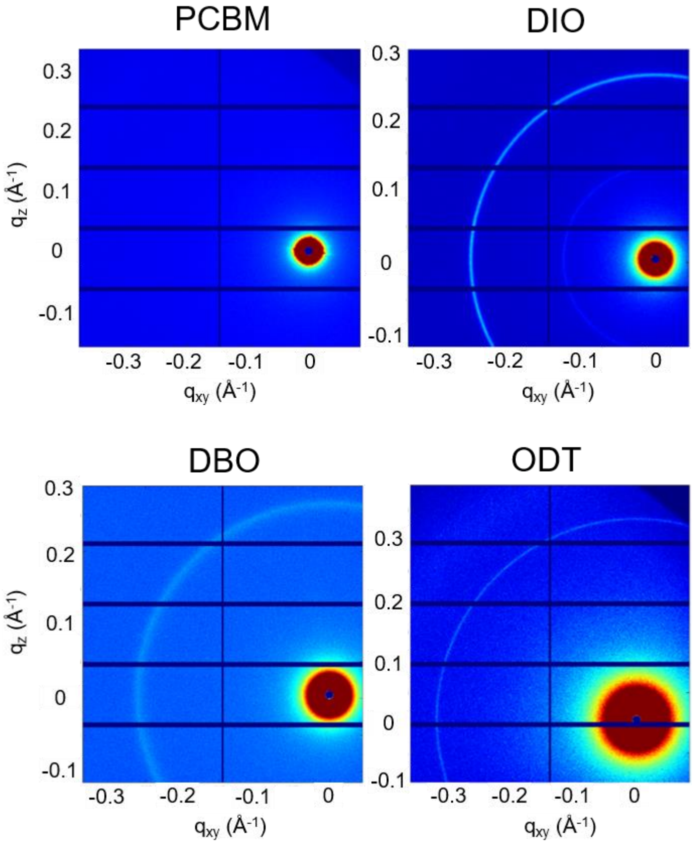

Fig. S1. 2-dimensional SAXS patterns of pure PC71BM, mixtures with DIO, DBO, and ODT casting from solutions.

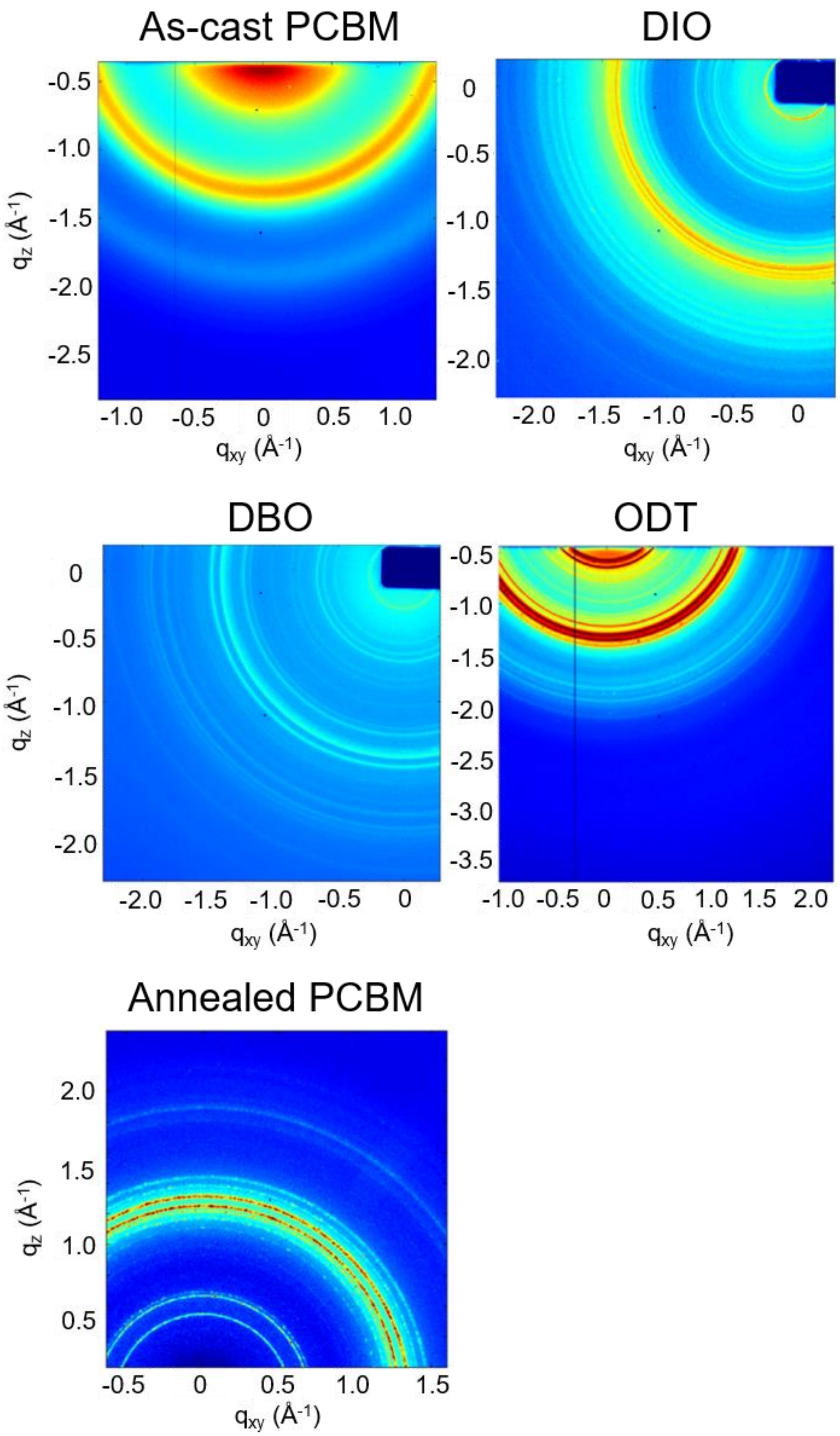

Fig. S2. 2-dimensional WAXS patterns of pure PC71BM, mixtures with DIO, DBO, ODT casting from solutions, and pure PC71BM after annealing at 140 °C for 10 min.

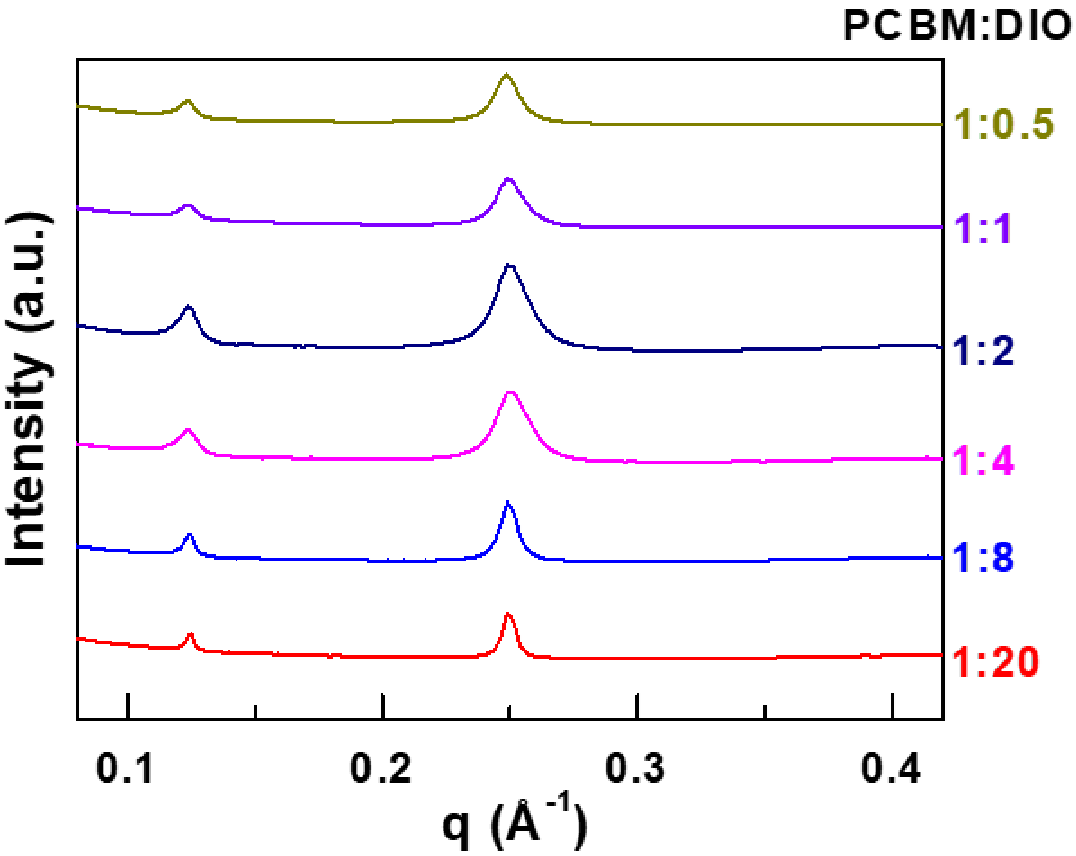

Fig. S3. Small-angle X-ray scattering (SAXS) data of PC71BM mixed with DIO at varying molar ratios. All the samples show similar diffraction patterns, indicating that the structure is not changed in these samples.

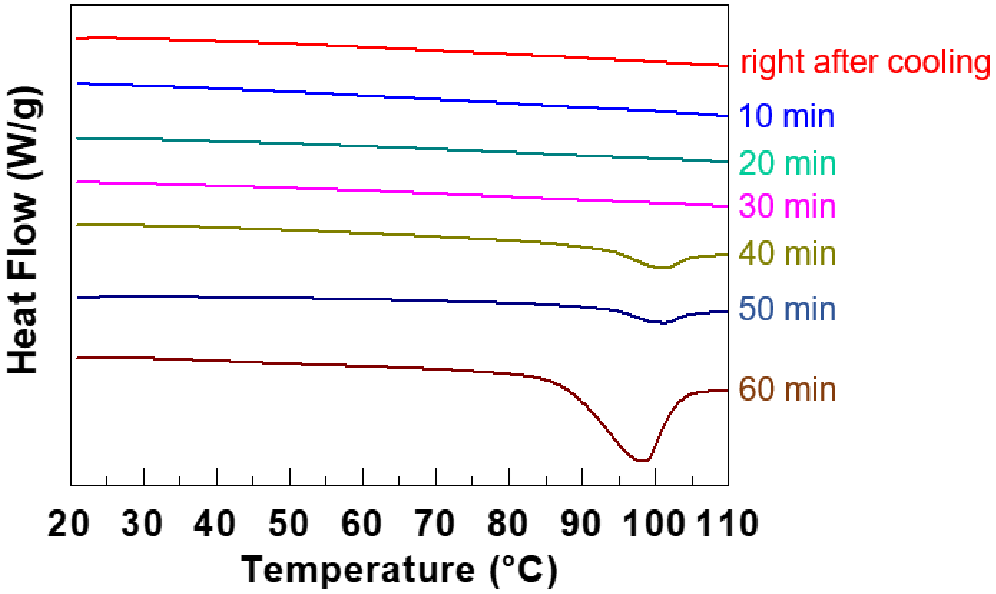

Fig. S4. DSC data of PC71BM mixed with DBO. No phase transition occurs in the second heating run right after the mixture is cooled down from 110 °C. The transition re-appears after the cooled mixture is annealed at room temperature for 40 min. The result indicates that the nanoscaled structure is thermodynamically stable and requires sufficient time to form.

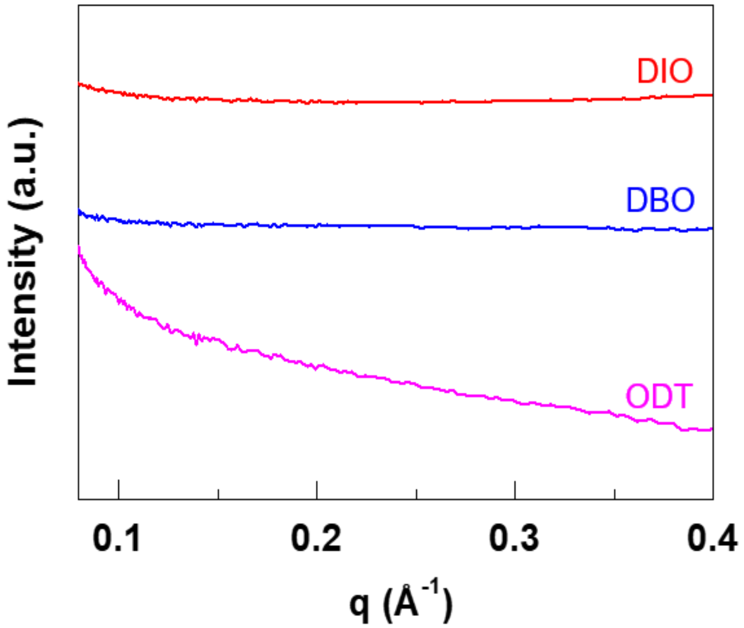

Fig. S5. SAXS data of PC71BM mixed with DIO, DBO, and ODT right after the mixtures are heated to 110 °C.

S2. Details of Molecular Dynamics Simulations

The Verlet scheme was chosen to integrate the equations of motion [1]. Partial charges of all atoms were determined by PCFF parameterization [2]. Electrostatic interactions were calculated using the particle-particle-grid (P3M) method [3] with an accuracy of 10^{-6}. Since all charges were taken into account explicitly, the dielectric constant of the medium was set equal to 1. All runs were executed with a time step of 1.0 fs.

In order to avoid the occurrence of the effects of hooking of fullerenes with each other and spearing of the fullerenes spheroids by the solvent molecules, the following system preparation protocol was used. The PC71BM molecules, with random orientations, were randomly placed inside the simulation cubic cell with an edge length of 140 Å (with periodic boundary conditions) so that the distance between their centers of mass was not less than 20 Å. The space between them was filled with randomly oriented solvent molecules so that the distance between the atoms of fullerenes and the solvent was not less than 2 Å. After short energy minimization, all systems were compressed under the NPT ensemble conditions at T = 300K and P = 10 atm to the density of 1.2 g/cm^3 (the size of the edge of the simulation cell is 47.7 Å). Temperature and pressure were controlled by the Nose-Hoover thermostat and barostat with relaxation constants of 0.1 ps and 0.5 ps, respectively. Then, the systems were equilibrated under the conditions of the NVT ensemble for 10 ns. During this procedure, the Coulomb interaction was turned off, and the cutoff distance of 2 Å for LJ interactions was used to weaken the intermolecular interaction in order to create a homogeneous distribution of the PC71BM. The samples prepared in this way were used for further study under the NVT ensemble conditions (T = 300 K, the Nose-Hoover thermostat with relaxation constants of 0.1 ps). The structure of these aggregates stabilizes upon reaching 90 ns. In total, a production run of 200 ns (for each sample) was carried out. A cutoff distance of 18 Å with a buffer length of 0.5 Å was used in the production run to reduce the calculation of nonbonding interactions.

The internal structure of the mixture was analyzed by calculating the partial structure factors $S_{\alpha\beta}(q)$ (α and β are types of atoms) [4,5] computed as

$$S_{\alpha\beta}(q) = \frac{1}{4\pi N_{tot}} < \int_{|\mathbf{q}|=q} d\omega \sum_{ij}^{N_{tot}} \exp(-i\mathbf{q}(\mathbf{r}_i^{\alpha} - \mathbf{r}_j^{\beta})) \quad > , \tag{S1}$$

where N_{tot} is the total number of atoms, $\mathbf{r}$ is the position vector of a given atom, $\mathbf{q}$ is the wave vector, the angle brackets <...> denote averaging over the production run, $\int_{|\mathbf{q}|=q} d\omega$ denotes integration over the solid angle $d\omega$ of the wave vector $\mathbf{q}$ while keeping its length q constant. The latter implies that the material sample has no distinguished directions concerning the incident radiation. The local ordering features were studied using the radial distribution function $g_{\alpha\beta}(r)$, which is calculated using the corresponding procedure in LAMMPS.

S3. PC71BM/ODT mixture structural characteristics

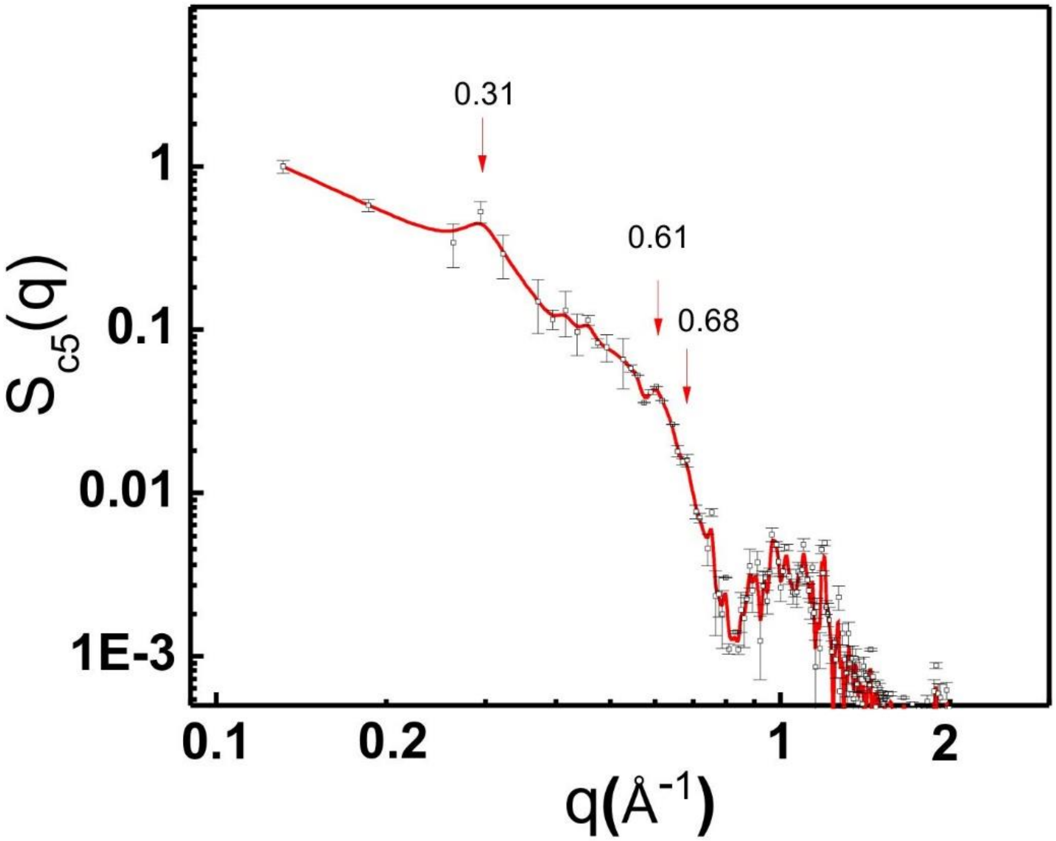

Fig. S6. The calculated fullerene–fullerene static partial structure factor, $S_{c5}(q)$, from our MD simulations of 200ns duration. Atoms of c5 type in PC71BM fullerene spheroid were taking into account (see Fig. 1a). Its amplitude was normalized to the value of the largest reflex $S_{c5}(q^*)$.

The static structure factor $S(q)$ has the maxima at $q \sim 0.31$ Å^{-1} (see Fig. 4) that corresponds to a distance of 20 Å. Simultaneously, the maxima at $q \sim 0.33$ Å^{-1} is observed in the partial structure factor S_{c5} (q), which is in better agreement with the experimental data in Fig. 2.

It should be noted that S (q) and Sc5 (q) (Fig. 4 and S6) were obtained for the mixture of PC71BM with ODT. They differ in the following, S(q) was calculated for all model atoms, except for hydrogen atoms, and Sc5 (q) was calculated only for atoms in the fullerene spheroid (other atoms in PCBM71 and ODT were not taken into account). Thus, we can conclude that the scale 19 Å, observed in the experimental study, corresponds to PC71BM aggregates. It seems that a stack of 4 fullerenes matches such a structural element (see Fig. S9). Both the characteristic thickness of “filaments” composed of such structural elements and distance between these “filaments” are about 20 Å.

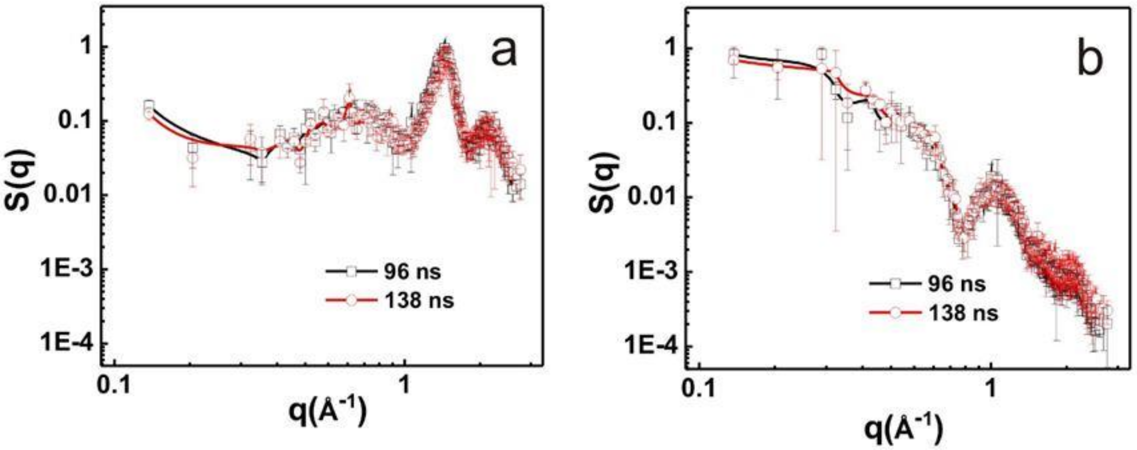

Fig. S7. Partial structure factors $S(q)$ for a) all atoms except hydrogen atoms and b) $S_{c5}(q)$ for c5 atoms (see Fig. 1 and Fig. 4) in the fullerene spheroid. Structure factors were obtained by averaging over 10 ns of productive run with starting time points of 96 ns and 138 ns. Note: These partial structure factors were obtained for the PC71BM / ODT blend.

S4. Visualization of supramolecular aggregates formed in PC71BM/ODT mixture

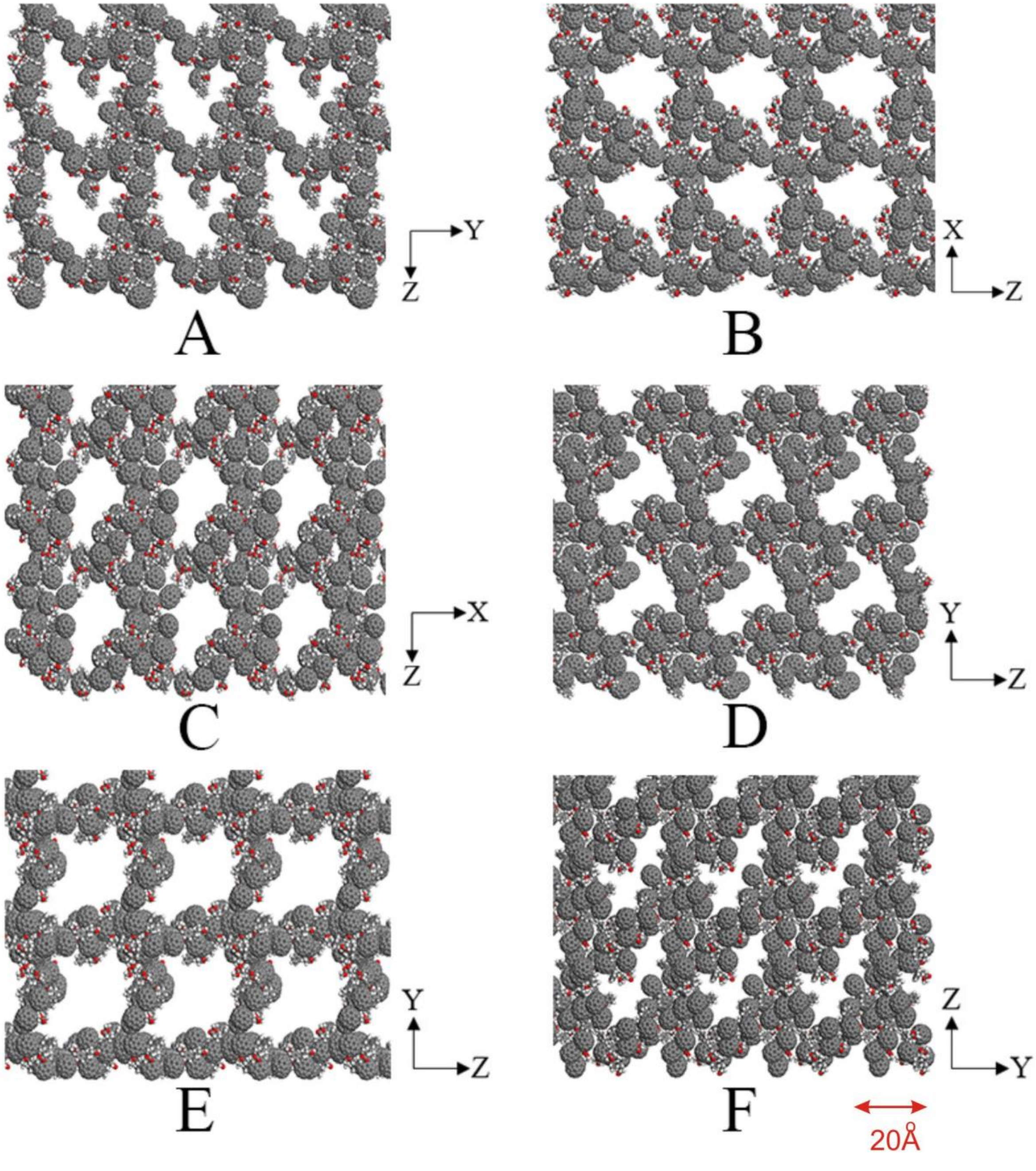

Fig. S8. Examples of snapshots of supramolecular aggregates formed from six independent initial states at the end of the production run of 100 ns. The periodic nature of the system is shown as an MD box multiplied along the principal directions. The coloring of atoms is the same as in Fig. 1. The additive molecules are not shown to simplify the visualization.

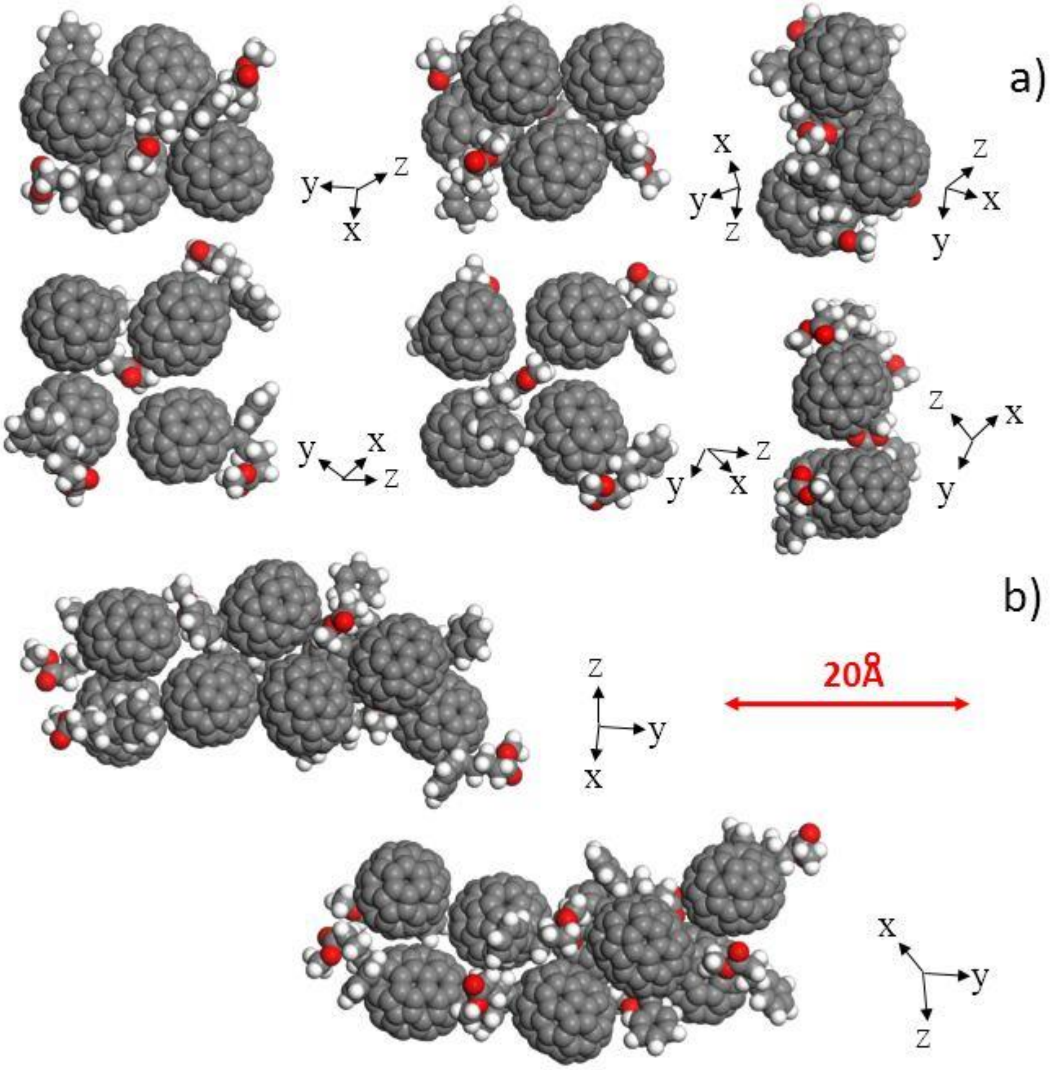

Fig. S9. Selected fragments of the local structure of the aggregate (shown in Fig. 5) are represented from different angles. a) A fragment formed from four fullerenes, b) a filamentous fragment formed from seven fullerenes.

Visualization of the local structure of the formed aggregates (Fig. S9) shows that they consist of PC71BM dimers. In turn, the dimers are combined into clusters composed of four PC71BMs (also mainly due to the interaction between fullerene spheroids). At the same time, their functional groups can both contact the adjacent fullerenes by their phenyl rings and be turned outward. Further aggregation is characterized by the appearance of a periodic structure of ~ 20 Å scale.

S5. The radial distribution functions

The nature of the local ordering of the fullerenes can be determined using the radial distribution function $g_{\alpha\beta}$(r) (RDF) calculated for selected pairs of atoms αβ belonging to different molecular fragments. The following types of atoms were chosen (see Fig. 1) viz. c5 - carbon atoms belonging to five-member cycles in the fullerene spheroids; cp – carbon atoms in the composition of six-membered aromatic rings in the fullerene spheroid and in the phenyl group; c_1 – carbon atoms in methyl ester group; sh – sulfur atom in ODT; c2 – carbon atoms in alkyl fragments of ODT and methyl butyrate group.

The function g_{c5c5}(r) (see Fig. S10a and Fig. 1a where designations of atom types are shown) reveals the features of the structure of the fullerene (series of sharp peaks in the interval 2.5 Å < r < 7.5 Å). It also shows the presence of the long-range correlations in the distribution of the fullerenes, which is indicated by the presence of maxima at ~10 Å and ~16 Å, and a weakly pronounced broad maximum at ~20 Å. Thus, the main motif of the structure factor is determined by the ordering of the fullerenes induced by strong C_{70}-C_{70} dispersion interaction [6]. Note that a series of high peaks at r < 7.5 Å refer to the intra-molecular correlations, which also manifest themselves in the existence of a series of sharp maxima at q ~ 1 - 2 Å^{-1}on the curve $S_{c5}(q)$ (see. Fig. S6). The gaps at 7.5 and 8 Å on $g_{c5c5}(r)$ and $g_{c5cp}(r)$ approximately reflect characteristic sizes of the fullerene spheroid C_{70}. The profile $g_{c5c\_1}(r)$ reflects characteristic intramolecular distances between the fullerene spheroid and surface functional group atoms. The character of correlations between fullerene spheroid with polar and nonpolar parts of the ODT (see $g_{c5sh}(r)$ and $g_{c5c2}(r)$ in Fig. S10b) indicates a weak interaction of the fullerenes with ODT. The same conclusion can be made from the shape of functions $g_{cpsh}(r)$ and g_{cpc2}(r) (see Fig. S10c). The RDF $g_{c\_1sh}(r)$, which characterizes a correlation of ester-thiol groups, reveals the high affinity of these groups (see Fig. S10d). This fact is indicated by a well-pronounced maximum at r ~ 5 Å. The similar maximum in $g_{c\_1c2}(r)$ corresponds to the intramolecular correlations. In general, this RDF shows a weak interaction of the ester group with the nonpolar part of the solvent molecule.

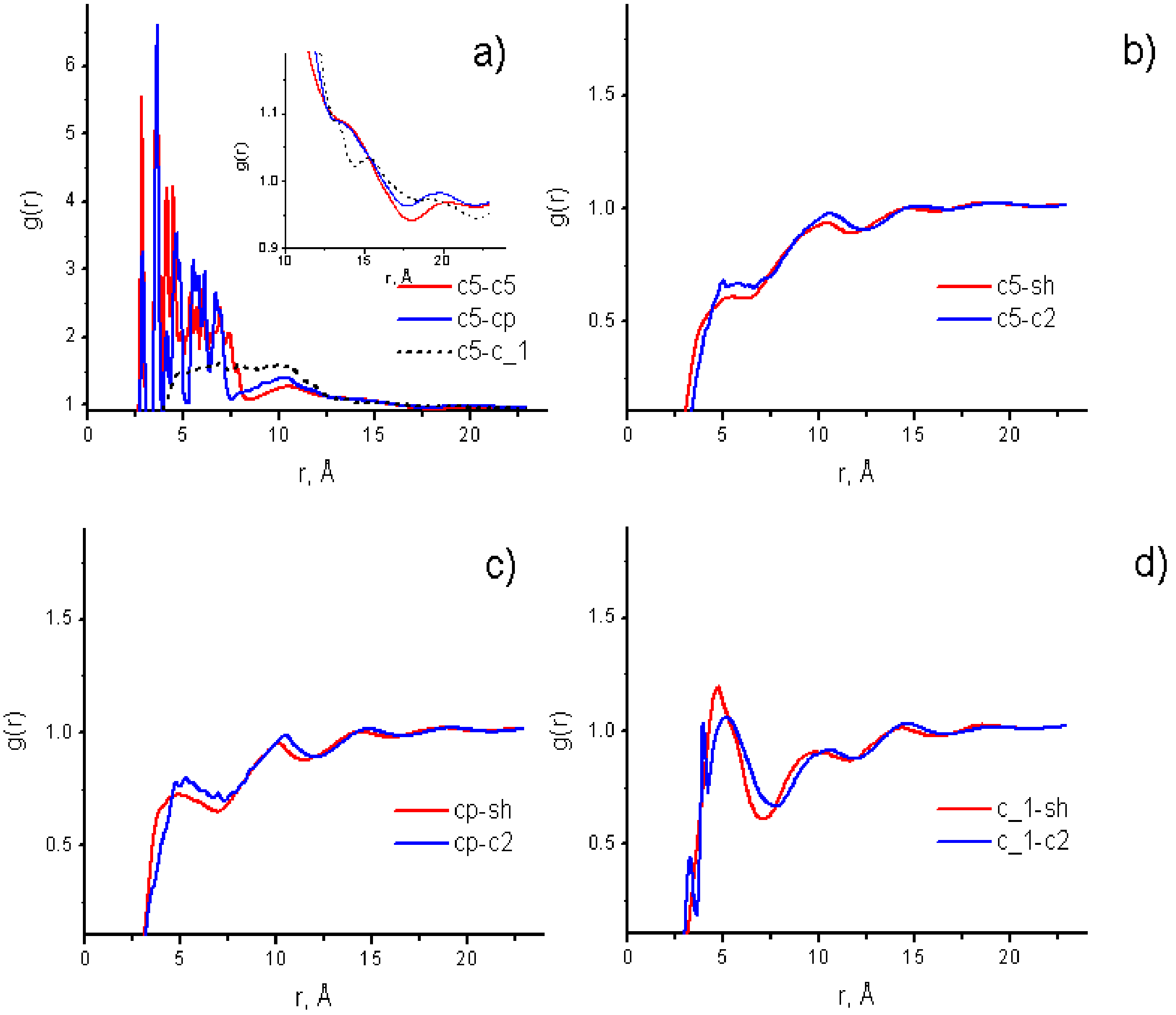

Fig. S10. The radial distribution functions *g*(r) for (a) the fullerene-fullerene correlations (c5-c5, c5-cp, c5-c_1 atoms of the different parts of fullerenes, see Fig. 1), the inset shows the same plot over a longer distance. (b) The fullerene-ODT correlations (c5-sh, c5-c2 atoms of the fullerene spheroid and different fragments of ODT molecules). (c) The phenyl-ODT correlations (cp-sh, cp-c2 atoms of the phenyl ring, and different fragments of ODT molecules). (d) Ester group-ODT (c_1-sh, c_1-c2 atoms of the ester group and different fragments of ODT molecules).

References

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