**Directed assembly of optoelectronically active alkyl – π-conjugated molecules by adding *n*-alkanes or π-conjugated species**

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**Abstract**

Supramolecular assembly can yield ordered structures by taking advantage of the cumulative effect of multiple non-covalent interactions between adjacent molecules. The thermodynamic origin of many self-assembled structures in water is the balance between hydrophilic and hydrophobic segments of the molecule. Here we show that this approach can be generalised to use solvophobic and solvophilic segments of fully hydrophobic alkylated-fullerene molecules. Addition of *n*-alkanes results in their assembly, due to the antipathy of the C60 towards *n*-alkanes, into micelles and hexagonally packed gel-fibres containing insulated C60 nanowires. Addition of pristine C60 instead directs the assembly into lamellar mesophases by increasing the proportion of π-conjugated material in the mixture. The assembled structures contain a large fraction of optoelectronically active material and exhibit comparably high photoconductivities. This method is shown to be applicable to several alkyl – π-conjugated molecules, and can be used to construct organised functional materials with π-conjugated sections.

Supramolecular chemistry generates complex structures over a range of length-scales. Structures, including DNA origami,1,2 supramolecular polymers,3,4 or supra-amphiphiles,5 are formed through multiple non-covalent interactions between adjacent molecules that are programmed by their chemical structure. Likewise, in solution, amphiphiles with hydrophilic and hydrophobic sections also assemble through multiple non-covalent interactions. However, their assembly is additionally governed by solution parameters such as concentration and solvent type, as well as the balance of hydrophilic and hydrophobic content within the amphiphile.6 This permits a single amphiphile to be directed to assemble into various structures simply by changing the solution parameters.6

The development of molecular optoelectronics requires the controllable self-assembly of molecules containing π-conjugated units from which the optoelectronic properties derive. The precise organisation of the π-conjugated units directly affects device performance.7 A common concern is that promising molecules with otherwise excellent intrinsic optoelectronic properties often form sub-optimally assembled structures.8 Optimally ordered molecular optoelectronics may be provided by supramolecular liquid crystalline materials containing π-conjugated units.9–11 However, enhanced functionality has yet to be fully demonstrated; a limiting factor is a relatively low content of the π-conjugated moieties in the molecules.12

Here, to address this issue, the amphiphilic assembly concept is extended to include fully hydrophobic amphiphiles comprising mutually immiscible alkyl (long, branched) and π-conjugated (C60, C70, azobenzene) parts. The asymmetric hydrophobic amphiphiles are formed by attaching alkyl chains to just one side of a π-conjugated moiety.13–16 Alkyl chains are routinely attached to π-conjugated molecules to improve solubility and to tune self-assembly.11,12,17–19 In similarity with the directed assembly of conventional hydrophobic-hydrophilic amphiphiles, the introduction of additives or solvents with a selective affinity towards either part of the hydrophobic amphiphile was expected provoke the formation of various complex ordered fluids including micelles, gels and two-component liquid crystals.6 By changing solution parameters, several structures might therefore be formed with a single hydrophobic amphiphile, permitting a level of control over the self-assembly of the π-conjugated units not currently accessible by other means.

To demonstrate the feasibility of this new approach, two hydrophobic alkylated fullerene-C60 derivatives are initially focussed on. The discrepancy in non-covalent interaction strength between the π-conjugated C60 and the attached alkyl chains can control molecular self-organisation in additive-free conditions.15,16 However, the derivativesstudied here form disordered materials without additives. On the other hand, by adding *n*-alkane solvents or pristine C60 to increase either the total alkyl or π-conjugated content of the system, they are directed to assemble into different structures. The driving force for nanoscale phase separation is the solvophobic force generated by the immiscibility of C60 with *n*-alkanes or alkyl chains.19,20 The principle, which is shown to be applicable to other alkyl – π-conjugated molecules, provides a tuneable route to direct the assembly of photoconducting materials.

**Results and Discussion**

***Micelles***

The alkylated C60 derivative **1** (Fig. 1a) was synthesized and purified using previously described methods.16,21 **1** is a liquid at room temperature and is fully miscible with *n-*hexane, forming dark solutions (*e.g.* photo, Fig. 1a) of low viscosity. This miscibility is counterintuitive given the low solubility of pristine C60 in *n*-alkanes (< 0.1 mM).20 Solubility enhancements are often observed in molecules comprising two parts with widely differing solvophobicity22 including surfactants23, semifluorinated alkanes13 or block copolymers.14 Molecules like this self-assemble in solution to limit contact between the solvophobic part and solvent. It is hypothesised that the solubility increase observed for hydrophobic amphiphile **1** might therefore be due to clustering that minimizes unfavourable interactions between C60­ and the *n*-alkane molecules.

Absorption spectra of **1** in *n*-hexane (Fig. 1b), *n*-octane, *n*-decane and toluene (Supplementary Fig. 1) in the visible region revealed several maxima, typical for C60 derivatives prepared by this route.21 Increasing concentration of **1** from 1 to 11 wt% led to broadening and bathochromic shifts for all peaks in every solvent studied, consistent with aggregation. The magnitude of the shift with increasing concentration was strongly solvent dependent, following the order *n*-hexane > *n*-octane > *n*-decane > toluene. This points to a trend in aggregation mirroring the difference in cohesive energy between the C60 in **1** and solvent.20

**--- Figure 1 ---**

Cryogenic transmission electron microscopy (*cryo-*TEM) confirms the existence of clusters in *n*-decane (Fig. 1c and Supplementary Fig. 2). Owing to the higher electron density of C60, the dark spherical regions (indicated with arrows, Fig. 1c) are likely to be C60-rich cores of core-shell micelles. The micelle cores appear spherical and polydisperse in size, with an average diameter of 2.5 ± 0.3 nm (Supplementary Fig. 2), indicative of small aggregates containing around 6 molecules of **1**.

To further investigate the solutions and to evaluate the influence of concentration and solvent type on micellar properties, small-angle X-ray (SAXS) and neutron (SANS) scattering were applied (Fig. 1d and Supplementary Fig. 3). X-rays scatter from nanoscale electron density inhomogeneities within samples, here effectively highlighting the clustered C60 parts of **1** in the lower electron density *n*-alkane matrix. Conversely, neutrons scatter owing to interactions with nuclei, and in particular scatter very differently from hydrogen and deuterium.24 SANS of **1** added to perdeuterated D-solvents thereby highlights domains comprising H-alkyl chains.

The SAXS and SANS data for **1** in *n*-hexane are shown in Fig. 1d. Both datasets exhibit a region at low *Q* where *I(Q)*, scales as *Q0*, followed by a decay. The decay onsets are inversely related to the radius of gyration of the scattering objects.24,25 As the first decay in the SANS signal occurs at lower *Q* values than in SAXS, the domains scattering neutrons are effectively larger than those probed by the X-ray experiment. On this basis, the data are consistent with the micelle structure suggested by *cryo*-TEM, with a C60-rich core and an alkyl-rich shell (*e.g.* inset schematic, Fig. 1d). The onset of the decay in the SAXS data corresponds to the C60-rich micellar core radii, whereas the first decay in the SANS data represents an overall core+shell dimension. In the SANS data the second decay at around *Q* ≈ 2.2 nm-1 is related to the shell thickness.

SAXS was used to investigate the effect of solvent type (*n*-hexane, *n*-decane, toluene) and concentration (2 - 22 wt%) on micelle size. The scattering objects were modelled as a polydisperse distribution of spherical core-shell micelles (Supplementary Methods). Fitted data and size distributions are shown in Supplementary Fig. 3 and fit parameters for SAXS and SANS data are given in Supplementary Tables 1 and 2 respectively. Micelle core radii, *Rcore* increased with concentration and were larger in *n*-hexane than in *n*-decane, in line with the changes observed by absorption spectroscopy. Average sizes in *n*-hexane and *n*-decane (*Rcore* = 1.27 and 0.94 nm respectively) are in agreement with the results from *cryo*-TEM. In toluene comparatively little aggregation was detected, consistent with the known higher solubility of C60 in this solvent.

In summary, the multi-technique combination of absorption spectroscopy, *cryo*-TEM and SAXS/SANS clearly demonstrates that the solvophobicity for *n*-alkanes of the π-conjugated (C60) part of **1** is sufficient to drive assembly into structured micelles.

***Gel fibres***

The study was broadened to **2** (Fig. 2a), which forms a disordered amorphous solid at room temperature.16 Gentle heating greatly increased the miscibility of **2** with *n-*hexane (Fig. 2b). SAXS data from a sample of 19.8 wt% **2** in *n*-hexane at 55 °C, shown in Fig. 2c, are similar to observations with mixtures of **1** (*e.g.* Fig. 1d), indicating the presence of micelles (*e.g.* schematic illustration, Fig. 2c). These have *Rcore =* 1.1 nm but a higher polydispersity than micelles of **1**, which may indicate more elongated structures.

**--- Figure 2 ---**

Interestingly, the samples gelled upon cooling from the isotropic state (Fig. 2b). This process was reversible, with a transition point, *Ttrans* just above room temperature (Supplementary Fig. 4). SAXS data taken at 5 °C (<<*Ttrans*) are shown in the upper plot in Fig. 2c. In comparison with the data at 55 °C, an increased *I(Q)* at low *Q* and the development of several peaks are noted, indicating an increased order over length scales probed by SAXS (1.5 – 60 nm) . The peaks marked as ***i*** and ***ii*** correspond to *d*-spacings of 5.5 and 3.1 ± 0.1 nm. The difference between *d*-spacings is approximately √3, suggesting a hexagonally-ordered columnar lattice of **2** in which the C60 moieties are in the column centres (*e.g.* inset schematic illustration, Fig. 2c).26

To further characterise the gel structure in *n*-hexane, polarized optical microscopy (POM) and temperature-controlled X-ray diffraction (XRD) were applied (Fig. 3a). Firstly, observations were made in the absence of polarizers: at [**2**] = 19.8 wt%, a network of bundled fibres was observed. Next, the polarizers were introduced in the standard POM configuration: the fibres exhibited textures indicating internal order (for the isotropic state, see Supplementary Fig. 5). Temperature-controlled XRD (Fig. 3a: *T* = 0 °C, [**2**] = 28.7 wt%) also showed peaks ***i*** and ***ii***,at *d*-spacings of 5.0 and 2.9 ± 0.2 nm. Additionally, multiple smaller peaks and shoulders were also noted (***iii***, ***iv*** and ***v*** on Fig. 3a: positions and corresponding *d*-spacings are given in Supplementary Table 3).

The ratio in positions of the peaks ***i****-****v***determined by XRD is approximately 1:√3: √4: √7: √12, as expected for the 2D *p6mm* hexagonal symmetry group.26 This indicates that **2** assembles into hexagonally ordered columnar domains in the gel. While hexagonal ordering is commonly noted in thermotropic C60-containing liquid crystals12, it is uncommon for lyotropic C60-containing gel27,28 and is particularly notable given the lack of gel-promoting hydrogen bonding moieties or tertiary gelators. The two sharp peaks in the region 2*θ* ≈ 9° are likely to correspond to C60-C60 spacing of around 1 nm, indicating a relatively high level of order. Neighbouring C60 units can therefore approach to within 0.3 nm, enabling effective charge transport along the columns. From the SAXS and XRD data, the inter-columnar spacing is 6.0 ± 0.4 nm. As this is larger than twice the length of **2** (≈ 2.5 nm), the hexagonally-packed columns of C60 are likely to be separated by alkyl regions that also contain interpenetrated *n*-hexane molecules (*cf.* C60 wires surrounded by insulator).

The SAXS data in Fig. 2c were therefore modelled as a network of fibres composed of hexagonally spaced monodisperse cylinders representing the C60 columns (Supplementary Methods). Related models have been used to describe gels of conducting polymers.29 The fitted network fractal dimension (2.7) is consistent with the interwoven fibre bundles observed by POM. The cylinder radius (1.6 nm) was similar to the micelle radii for **1** and **2**, suggesting fibre growth from the micellar state.

The ability of **2** to gel other solvents was studied to assess generality. Gels did not form with toluene, chloroform or cyclohexane, but did with other *n*-alkanes (*n*-octane, *n*-decane). Using near-infrared turbidity measurements (Supplementary Fig. 4), the gel formation temperature *Ttrans* was found to decrease with increasing *n*-alkane chain length and to increase with the concentration of **2**. XRD data (Supplementary Fig. 6 and Table 3) point to similar gel structures with all *n*-alkanes used, within the concentration range of 16.5 to 42 wt%. This assertion was backed up by *cryo*-TEM images taken at the onset of gel formation in *n*-decane (Supplementary Fig. 7). Both micelles and more ordered structures with two primary spacings (*d1* and *d2*) of approximately 4.8 and 3.0 nm are clear in the images. However, one change noted using XRD is the positional shift to higher 2*θ* value and slight broadening of peak ***i*** with increasing alkane chain length (2*θ* = 1.92° and 1.77° for ~20 wt% **2** in *n*-decane and *n*-hexane) and at higher concentrations (2*θ =* 1.96° for 42 wt% **2** in *n*-decane). This may indicate a uniaxial contraction arising from the reduced affinity towards the hyperbranched alkyl chains of **2** of *n*-decane versus *n*-hexane (Supplementary Fig. 6).

**--- Figure 3 ---**

Flash-photolysis time resolved microwave conductivity (FP-TRMC)30 was used to probe the photoconductivity of the C60-rich columnar domains. Measurements of the transient photoconductivity *ϕ*Σ*μ* for a sample of **2** with *n*-decane are shown in Fig. 3b (*ϕ* represents the quantum efficiency of the charge carrier generation and Σ*μ* represents the sum of the nanometre-scale charge carrier mobilities).30 FP-TRMC measurements in the solvated state are difficult and typically suffer from low signal and a higher background noise due to the insulating solvent content. Despite this, clear signals were detected for the gels that were not present for the isotropic clusters (Fig. 3b). The photoconductivity maximum (*ϕ*Σ*μmax* = 3.5 x 10-5 cm2 V-1 s-1) was of similar order as that for solid crystalline C60 derivatives studied using the same technique, including [6,6]-phenyl-C61-butyric acid methyl ester, PCBM (2.8 – 14 x 10-5 cm2 V-1 s-1).31,32 While FP-TRMC evaluates carrier mobility at the nanometer scale, the results indicate that the fibre network transports charge and might be applicable in flexible optoelectronic applications in the gelled state,33 with the potential for unique self-healing or thermally-induced on-off switching properties.

The results above therefore confirm the existence of true solvated-state alkyl – π-conjugated hydrophobic amphiphilicity and provide the first example of the directed assembly of alkyl – π-conjugated molecules into well-defined structures in *n*-alkane solvents. Related approaches using different solvents34–36 or the addition of anti-solvent37,38 to self-organize functional supramolecular structures out of solution have previously been reported, but are not always well understood, can be limited by solubility and furthermore are conceptually different to this current approach. The results from this study indicate a type of directed assembly similar to that of more conventional hydrophobic-hydrophilic surfactants, significantly extending the general concept of a solvophobic-solvophilic balance for inducing and tuning self-assembly in low dielectric and non-aqueous media. The different aggregation extent of **1** and **2** is expected, as the ability of the alkyl chain chemistry to tune chain-chain and chain-solvent interactions has also been noted for conventional surfactants.39,40 It is likely that increased branching yields larger assemblies through reducing the interaction strength between the alkyl chains and solvent molecules, and weakening their ability to interfere in π-π interactions between neighbouring C60 units. The coupling of molecular design with the additive-directed assembly approach appears to provide a powerful new way to construct assembled molecular materials with high functionality and complexity.

To further demonstrate the generality of our approach, a fullerene-C70 derivative **3** and an azobenzene derivative **4** (Supplementary Fig. 8) were investigated. These represent larger (C70) and smaller (azobenzene) π-conjugated systems than C60. Both derivatives are liquid at room temperature, but when dissolved into *n*-alkanes, clusters were detected by SAXS (Supplementary Fig. 8). Micelle core radii (Supplementary Table 4) were larger for **3** (1.22 nm) than for **1** (0.94 nm) under similar conditions (~20 wt% in *n*-decane) and were smaller for **4** (0.50 nm). Reducing the concentration of **3** in *n*-decane was found to also reduce micelle size (Supplementary Fig. 8), in line with the results seen for **1** in *n*-hexane. It is therefore clear that the ability to direct assembly of alkyl – π-conjugated molecules using *n*-alkanes is not only limited to C60-containing species, and that the strength of interaction between the π-conjugated moieties is a key assembly control parameter.

***Lamellar mesophases***

Additives with higher affinities for the C60 part than for alkyl chains are also expected to drive assembly; for example, the addition of pristine C60 to **1**. Coassembly structures of C60 with polymers41,42 and planar π-conjugated groups such as porphyrins43 have been described,15,44 but to our knowledge the coassembly of pristine C60 with C60 derivatives to direct assembly has yet to be realized. Pure **1** forms an unstructured liquid at room temperature. When C60 and **1** were mixed in toluene at molar ratios of C60:**1** of 1:2 and 1:10, absorption spectroscopy indicated little interaction between the two species (Supplementary Fig. 9). However, thick pastes were formed after removal of the solvent by evaporation.

**--- Figure 4 ---**

POM images of the pastes (Fig. 4a,b) exhibit marbled textures similar to those noted for smectic phases of C60-containing thermotropic liquid crystals.12,17,19 The rheological behaviour (Fig. 4c,d) of the pastes is distinctly different to that for **1** alone, with higher complex viscosity *η\**, storage modulus *G’*, and loss modulus *G’’* values throughout almost the entire applied angular frequency (*ω*) range. The pastes shear thin as indicated by the reduction in *η\** with increasing *ω*. Similarly to **1**, 1:10 C60:**1** exhibits liquid viscoelastic behaviour, with *G’’* > *G’*. However, solid-like behaviour is noted for 1:2 C60:**1**, with *G’’* < *G’* at this strain amplitude (0.1%). In general, large increases in intermolecular interactions are observed on adding C60 to **1**, in line with directed assembly formation.

TEM (Fig. 4e-g) and XRD (Fig. 4h) confirms the existence of extended lamellar domains. The lack of any discernible peaks in the XRD corresponding to the fcc phase of C60 suggests C60 is mostly incorporated into the lamellar structure. Several evenly-spaced peaks (labelled ***I-V*** on Fig. 4h) were detected, corresponding to the (001) - (005) reflections of a lamellar mesophase.26 For 1:2 C60:**1** the peaks are broader and shifted to higher 2*θ* values than for 1:10 C60:**1**, indicating a smaller lamellar spacing (3.4 *vs.* 3.7 nm) and a reduced persistence length45 of the lamellar structure (19 *vs.* 31 nm). As 1:2 C60:**1** contains proportionally more C60, there may also be more C60 incorporated within the lamellar structure, which would lead to closer contact between layers due to a proportionally reduced amount of alkyl spacer. Echoing the results from XRD, TEM images of 1:10 C60:**1** show lamellar domains with a persistence length of ≥ 20 nm in the lamellar growth direction, and at least 50 nm in the lamellar plane (Fig. 4e). Within the layers, dark regions corresponding to assembled C60 units can be distinguished, which are interdigitated at an angle of ~60° (Fig. 4f). Lamellar and C60-C60 *d*-spacings are 3.6 and 1.1 nm respectively (Fast Fourier Transfrom, FFT, Fig. 4g), in agreement with the XRD results. FP-TRMC (Fig. 4i) measurements gave *ϕ*Σ*μmax* = 0.9 and 1.5 x 10-5 cm2 V-1 s-1 for the 1:2 and 1:10 C60:**1** blends respectively, which are both higher than values obtained for pure **1** (0.4 x 10-5 cm2 V-1 s-1). Interestingly, the highest *ϕ*Σ*μmax* was obtained for 1:10, for which the more extensive mesophases were noted by XRD.

The assembly of **1** can clearly therefore be induced by adding of C60, just as by adding an *n*-alkane solvent. That such a small quantity of C60 (1:10 contains 4.4 wt% C60) causes a significant change in both the nanoscale and bulk properties of the initially is interesting and perhaps points to the C60 units acting as seeds for mesophase growth. When generalised to other additives and other alkyl – π-conjugated molecules, this can become a particularly useful assembly tool of relevance to the developing field of functional organic fluids.46,47 With this in mind, a different C60 derivative **5**, was synthesised (see Supplementary Synthesis). Like **1**, molecule **5** is a liquid at room temperature. Adding either C60 or PCBM to **5** resulted in the formation of lamellar-type assemblies, as verified by XRD and POM results (Supplementary Fig. 10). While this new system has yet to be studied in depth, it is clear that the reported phenomenon is neither restricted to **1**, nor to the use of C60 as an additive.

In conclusion, the thermodynamic origin of aggregation for conventional hydrophobic-hydrophilic amphiphiles is an appropriate balance between hydrophobic and hydrophilic interactions. Here, that concept is generalised to encompass solvophilicity and solvophobicity within hydrophobic amphiphiles and the antipathy between alkyl and π-conjugated moieties is used to drive self-assembly. Materials of different micro- and macroscopic properties have been produced by changing the balance of alkyl and π-conjugated content using selective solvents or additives, and by changing the structure of the hydrophobic amphiphiles. The materials have the additional benefit of localised and aligned π-conjugated content, and potential for unique and switchable optoelectronic properties. The method has notable advantages over existing solution-state, hydrophilic-hydrophobic C60-amphiphile strategies12,48,49 in ease of application, increased solution processability of the materials and the uniformity and bulk-scale of the assemblies. The combination of advanced molecular design strategies with this approach has the potential to build and optimise functional materials based on π-conjugated molecules with nanoscale control.

**Methods**

The synthesis of both molecules **1** and **2** has been reported elsewhere.16 Solutions of **1** and **2** in *n*-alkanes were prepared simply by dissolving the required amount of the alkylated C60 derivative in the *n*-alkane solvent. Solutions of molecules **3** and **4** (syntheses reported in Supplementary Methods) in *n*-alkanes were prepared in the same manner. **1**, **3** and **4** were clearly highly soluble in *n*-alkanes and a solubility limit was not found in any case. As noted in the text, slight heating (*i.e.* over the *Ttrans* shown in Supplementary Fig. 4, but below the boiling point of the solvent) was required to dissolve molecule **2** and form a homogeneous (micellar) solution. At this elevated temperature, a solubility limit was not found; the highest concentration tested was 42 wt% in *n*-decane.

In the case of the samples for SANS analysis, perdeuterated *n*-hexane-*d*14 was used as the solvent. Solvent deuteration is expected to have minimal effects on self-assembly24 as the relative strengths of CH−π and CD−π interactions are similar.50

The compositions of solutions of **1**-**4** are given in wt% throughout for clarity. One point to note is that in the case of samples of **1** in different solvents for SAXS analysis (for example), compositions were designed such that the vol% of **1** was approximately similar, to facilitate comparison. The value of vol% is not given, as the exact density of **1**-**4** is unknown. For example, while 22.0 wt% **1** in *n*-hexane and 17.5 wt% **1** in toluene might seem quite different compositions, the vol% and molarity are similar in both cases. The same point applies for samples of **2**, unless otherwise noted (*e.g.* Supplementary Fig. 7).

Blends corresponding to molar ratios of C60:**1** of 1:2 and 1:10 were formed by mixing dilute solutions of the two components in toluene, followed by fast solvent evaporation. The process was repeated three times for increased homogeneity, then the material was dried for at least 24 hours under vacuum at 50 °C. Blends of C60 + **5** (synthesis reported in Supplementary Methods) and PCBM + **5** were formed using the same method.

All other experimental details, including the synthesis, techniques used and details of model fitting are provided in the Supplementary Information.

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**Figure Legends**

**Figure 1:** **Micelle formation by 1, driven by addition of *n*-alkane solvents.** (**a**) Chemical structure of molecule **1** and photograph of a solution in *n*-hexane. (**b**) Visible absorption spectra for **1** with *n*-hexane for concentrations of **1** as indicated. The inset shows magnified spectra indicating the shift in the position of the maxima centred around 703 nm with increased concentration that suggests aggregation. (**c**) *Cryo*-TEM image of micelles of **1** in *n*-decane. The dark regions indicated by white arrows are the C60-rich cores of the micelles. The full image is provided in Supplementary Fig. 2, alongside an image for *n*-decane alone. (**d**) SAXS and SANS data for **1** with *n*-hexane and *n*-hexane-*d*14 respectively, taken at 25 °C and [**1**] = 22 wt%. (Inset) Proposed aggregate structure, indicating the parts that would be expected to be highlighted by SAXS (C60-rich core) and SANS (alkyl-rich shell), as discussed in the text. Inferred dimensions corresponding to the core and core+shell radii are shown, which were obtained by fitting the SAXS and SANS data in (**d**) respectively.

**Figure 2: Gel formation by 2, driven by addition of *n*-alkane solvents.** (**a**) Chemical structure of **2** and (**b**) photographs showing the gelled and isotropic states that arise on dissolving **2** in *n*-decane. (**c**) Fitted synchrotron SAXS data for **2** with *n*-hexane, **2** at 19.8 wt%, taken at 5 °C (gel state) and 55 °C (isotropic state), respectively. Red lines indicate fits to the data. For clarity the SAXS data and fit for the isotropic state have been divided by a factor of 5. (Inset, **c**) Schematic depictions of the structures (micelles and gel fibres) present in the system in both states. The peaks in the SAXS data taken at 5 °C marked ***i***and ***ii*** arise from an hexagonal arrangement of the C60-rich columns within the fibres, with *d*-spacings corresponding to the distances indicated on the schematic of the gel fibre. The steep increase in *I(Q)* at low *Q* suggests a fractal-like network structure, indicating that individual fibres are bundled and substantially interwoven.

**Figure 3: Structure and photoconductivity** **of the gel fibres formed by 2.** (**a**) XRD data for the gelled state of 28.7 wt% **2** with *n-*hexane, taken at 0 °C. The labelled peaks and shoulders ***i-v*** correspond to expected reflections for a *p6mm* hexagonal symmetry group, in the ratio 1:√3: √4: √7: √12. The broad peak at higher angles represents the alkyl content of **2** and *n-*hexane, as indicated. (inset, **a**) Polarized optical microscopy (POM) images of the gelled state without and with crossed polarizing filters. Ordered regions can be observed in both images that correspond to fibre bundles. (**b**) Solution-state FP-TRMC data for 42 wt% **2** with *n*-decane, taken at 23 °C (gelled state, 12 hours aging) and 48 °C (isotropic state), *λ*ex = 355 nm. Upon laser excitation at *t* = 0 s, the gelled state gives a clear peak (*ϕ*Σ*μmax*) in the FP-TRMC, indicating its ability to transport charge, whiles the isotropic state gives no clear signal above the baseline.

**Figure 4: Structure, rheological properties and photoconductivity of the lamellar mesophase formed by 1, driven by addition ofC60.** (**a**, **b**) POM images 1:10 and 1:2 molar ratios of C60 and **1** at room temperature, respectively. (**c**, **d**) Rheology data showing the change in complex viscosity *η\**, storage modulus *G’*, and loss modulus *G’’* values with angular frequency *ω* for1:10 and 1:2 molar ratios of C60 and **1**, and **1** alone. Tests were carried out at 0.1% strain amplitude in the linear-viscoelastic region at 25 °C. (**e**) TEM image of lamellar mesophase formed by the 1:10 molar ratio of C60 and **1** at room temperature. (**f**) Magnified area, showing the interdigitated C60 units. (**g**) Fast Fourier transform (FFT) of the image shown in panel (**e**). Spots corresponding to the lamellar spacing (001, 002 and 003), and to the C60-C60 separation are indicated. (**h**) XRD data for both ratios, highlighting the different positions of labelled peaks ***I-V****,* corresponding to the (001) - (005) reflections of a lamellar mesophase, for1:10 and 1:2 molar ratios of C60 and **1**. (**i**) FP-TRMC result for the two ratios and for pure **1** in the solvent-free condensed phase, *λ*ex = 355 nm.

**Author Contributions**

MJH and TN are joint principal investigators – they designed the work, carried out research, analyzed data and wrote the paper. MK helped to characterise the lamellar mesophases; PHHB and NAJMS performed the *cryo*-TEM experiments; AS and SS performed the TRMC studies; H. Minamikawa contributed to the temperature-dependent XRD studies; IG, PB and JE helped acquire the SANS data and advised on presentation and English; BRP helped acquire, reduce and analyse the SAXS data. H. Möhwald was involved in developing the concept and in the work discussion. All authors discussed the results and commented on the manuscript.

**Supplementary Information**

This indexed section, which includes supplementary methods (experimental details, model fitting details, fit parameters), plus supplementary figures and tables, is available online.

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