

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

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Introduction

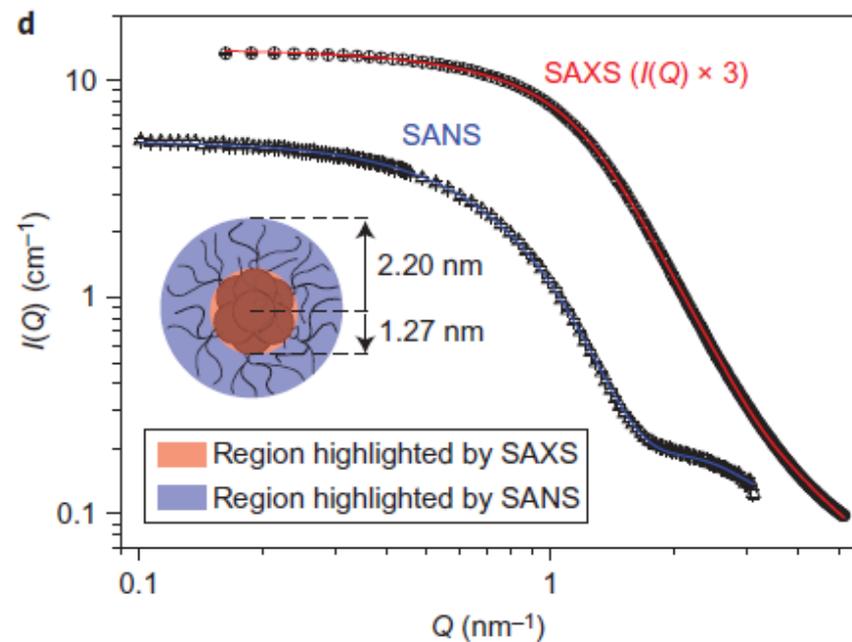
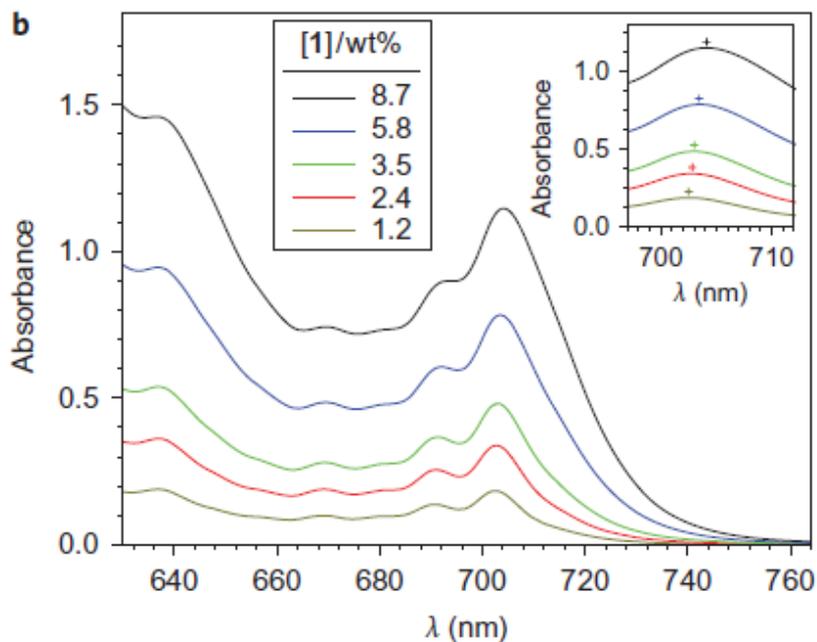
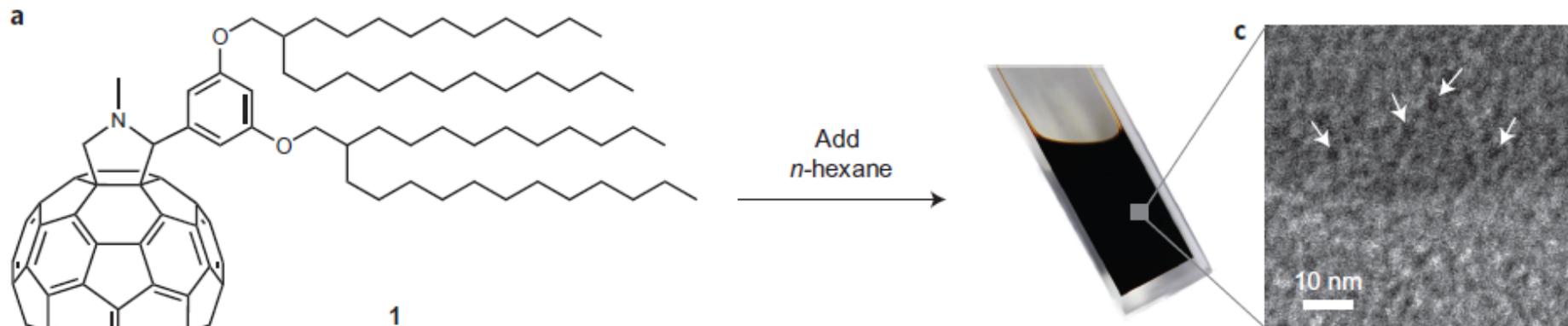
- ❑ Supramolecular chemistry generates complex structures over a range of length scales. Structures such as DNA origami, supramolecular polymers etc. are formed via multiple non-covalent interactions between adjacent molecules that are programmed by their chemical structure.
- ❑ Similarly, in solution, amphiphiles with hydrophilic and hydrophobic sections assemble through multiple non-covalent interactions.
- ❑ However, assembly is also governed by solution parameters such as concentration and solvent type, as well as the balance of hydrophilic and hydrophobic content within the amphiphile.
- ❑ This permits a single amphiphile to be directed to assemble into a range of structures simply by changing the solution parameters.
- ❖ The development of molecular optoelectronics requires the controllable self-assembly of molecules containing π -conjugated units from which the optoelectronic properties derive.
- ❖ Promising molecules with otherwise excellent intrinsic optoelectronic properties often form sub-optimally assembled structures as the precise organization of the π -conjugated units directly affects device performance.

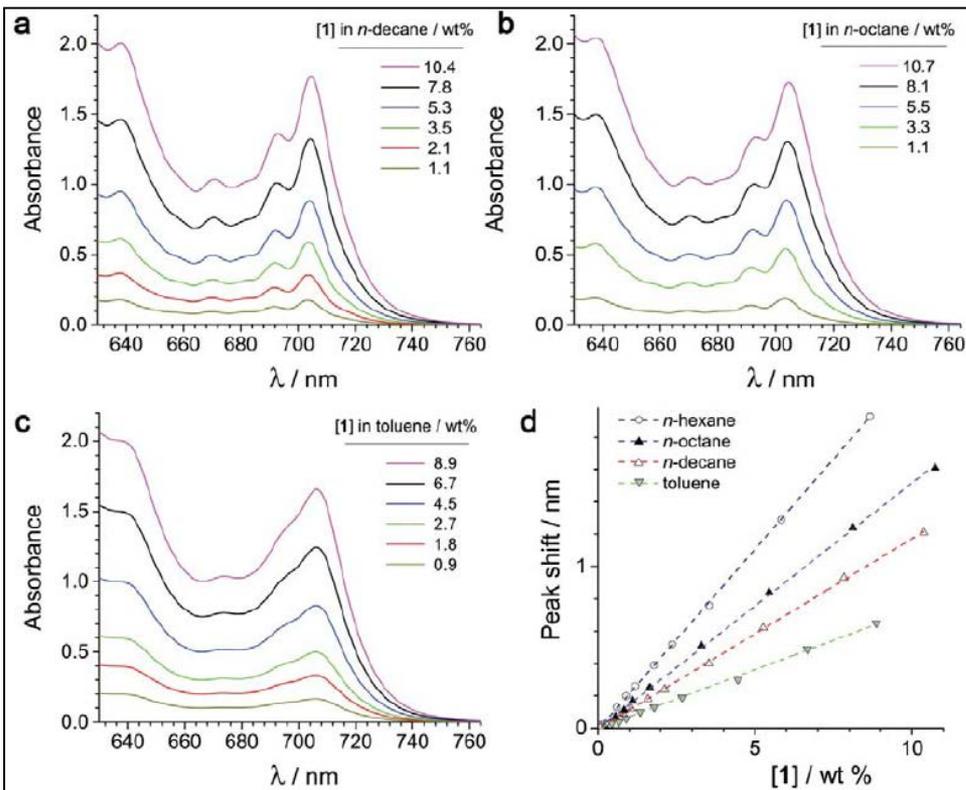
In this paper...

- The amphiphilic assembly concept is extended to include fully hydrophobic amphiphiles comprising mutually immiscible alkyl (long, branched) and π -conjugated (C_{60} , C_{70} or azobenzene) parts. Alkyl chains attached to π -conjugated molecules improve solubility and tune the self-assembly.
- To the directed assembly of hydrophobic–hydrophilic amphiphiles, the introduction of additives or solvents with a selective affinity towards either part of the hydrophobic amphiphile lead to the formation of various complex ordered fluids including micelles, gels and two-component liquid crystals.
- By changing the solution parameters, several structures were formed from a single hydrophobic amphiphile, permitting a level of control over the self-assembly of the π -conjugated units not currently accessible by other means.

Results and discussion

Micelle formation

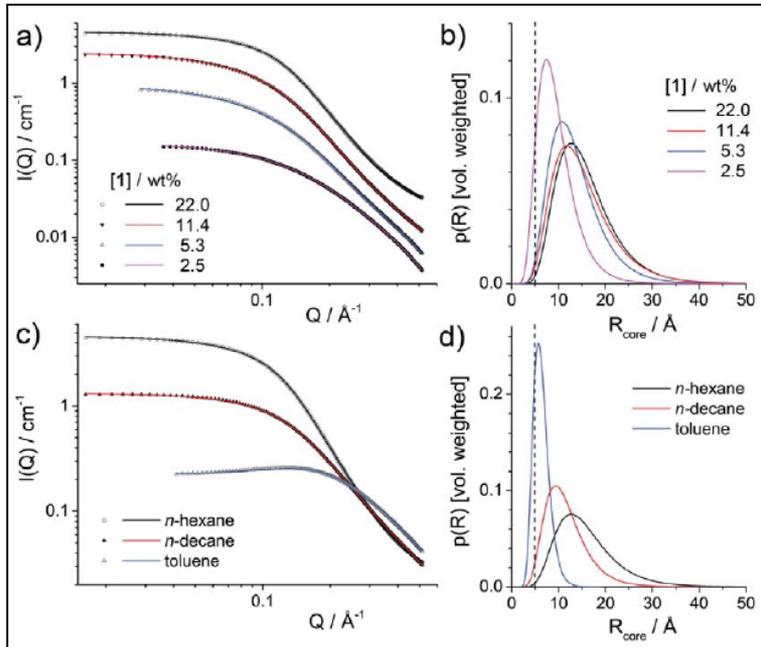




- C_{60} has low solubility in *n*-hexane (.1mM).
- Amphilic molecules are known to self-assemble in solution to limit contact between the solvophobic part and the solvent.

❖ Increasing the concentration of 1 from 1 wt% to 11 wt% led to broadening and bathochromic shifts for all peaks in every solvent studied, consistent with aggregation.

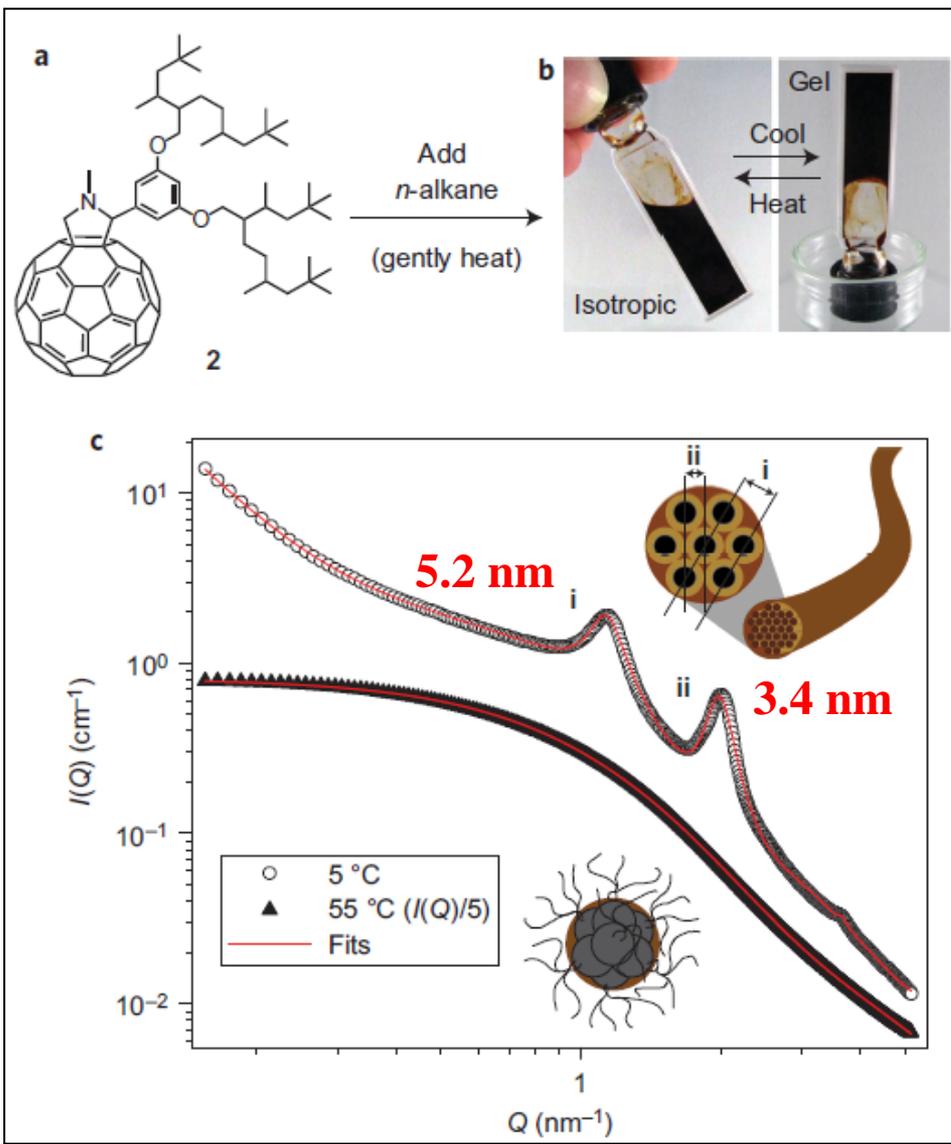
- It is hypothesized that the solubility increase observed for hydrophobic amphiphile 1 might therefore be due to clustering to minimize unfavourable interactions between C_{60} and the *n*-alkane molecules.
- The magnitude of the shift with increasing concentration was strongly solvent-dependent, following the order *n*-hexane > *n*-octane > *n*-decane > toluene.



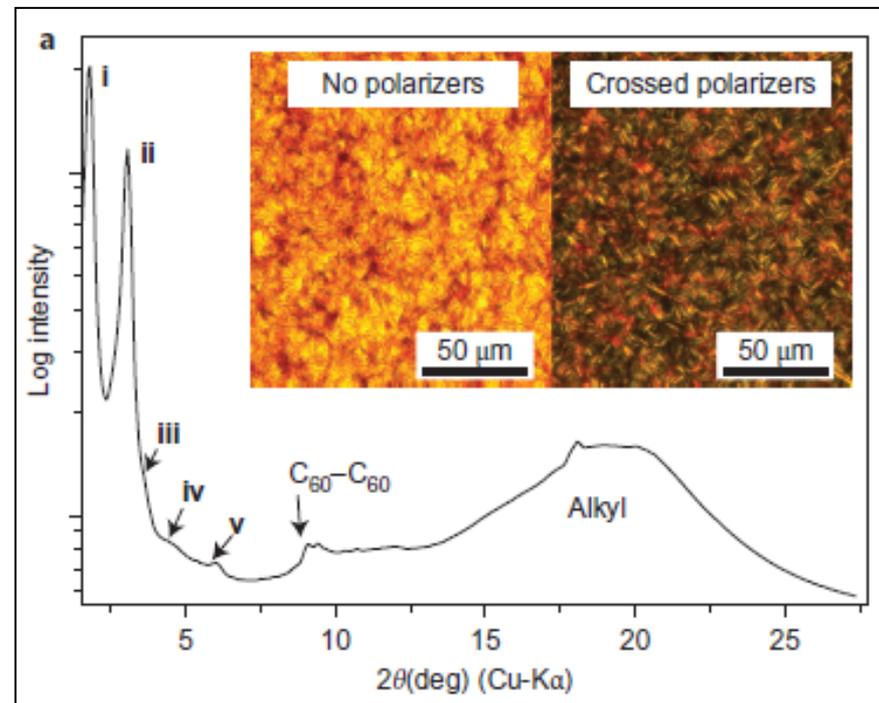
- X-rays scatter from nanoscale electron density inhomogeneities within samples, effectively highlighting the clustered C_{60} parts of 1 in the lower-electron-density n-alkane matrix.
- Neutrons scatter due to interactions with nuclei; in particular, they scatter very differently from hydrogen and deuterium and therefore highlight domains comprising H-alkyl chains (in perdeuterated D-solvents).

- ❑ Both SAXS & SANS data sets exhibit a region at low Q where $I(Q)$ scales as Q^0 , followed by a decay. The decay onsets are inversely related to the radius of gyration of the scattering objects.
- ❑ 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.
- ❑ The data are consistent with the micelle structure suggested by cryo-TEM, with a C_{60} -rich core and an alkyl-rich shell. The onset of the decay in the SAXS data corresponds to the C_{60} -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 is related to the shell thickness.

Gel fiber formation



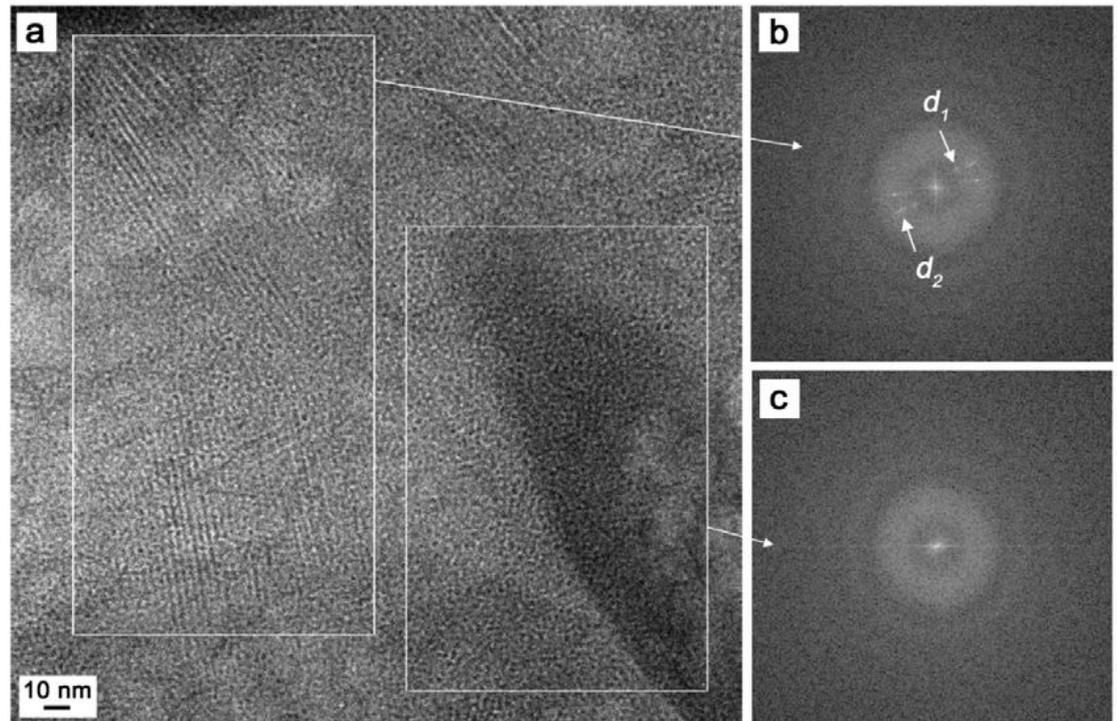
SAXS data from a sample of 19.8 wt% 2 in n-hexane.



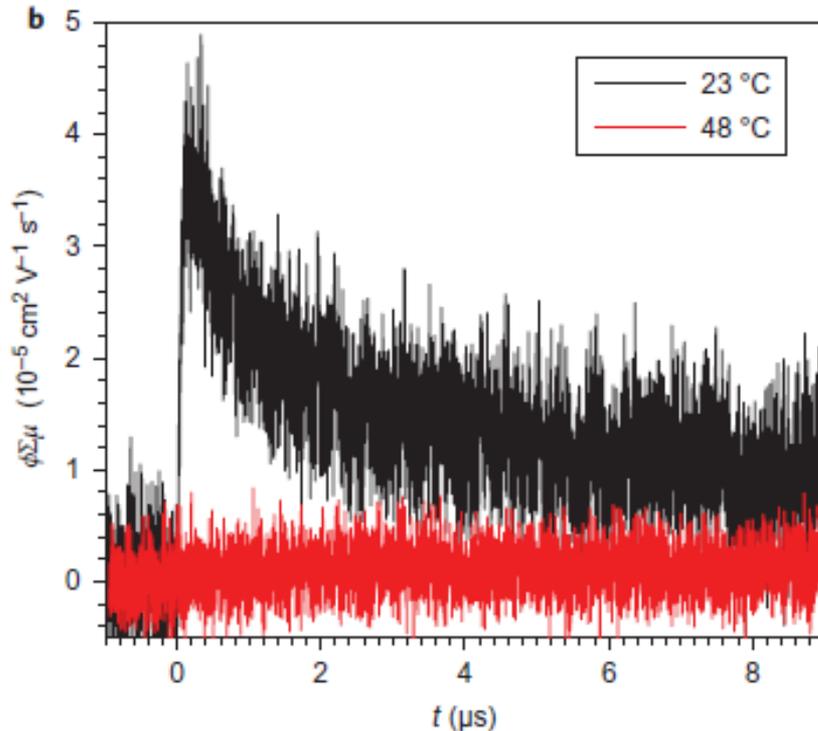
- The ratio of the positions of peaks i–v determined by XRD is $\sim 1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{12}$, as expected for the 2D $p6mm$ hexagonal symmetry group.
- Network of bundled fibers was observed under optical microscope. The fibres exhibited textures indicating internal order when polarizer was introduced.

C_{60} wires surrounded by insulator

- ❑ Two sharp peaks in the region $2\theta \approx 9^\circ$ correspond to a C_{60} - C_{60} spacing of ~ 1 nm, indicating a relatively high level of order.
- ❑ Neighboring C_{60} units can therefore approach to within 0.3 nm, enabling effective charge transport along the columns.
- ❑ The cylinder radius (1.6 nm) was similar to the micelle radii for 1 and 2, suggesting fibre growth from the micellar state.
- ❑ 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 C_{60} are probably separated by alkyl regions that also contain interpenetrated n-hexane molecules.



Photoconductivity of the gel fibres

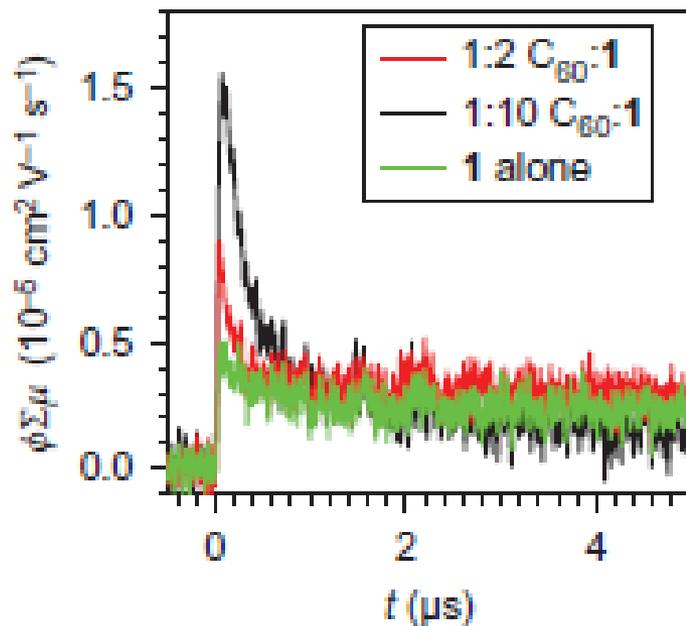
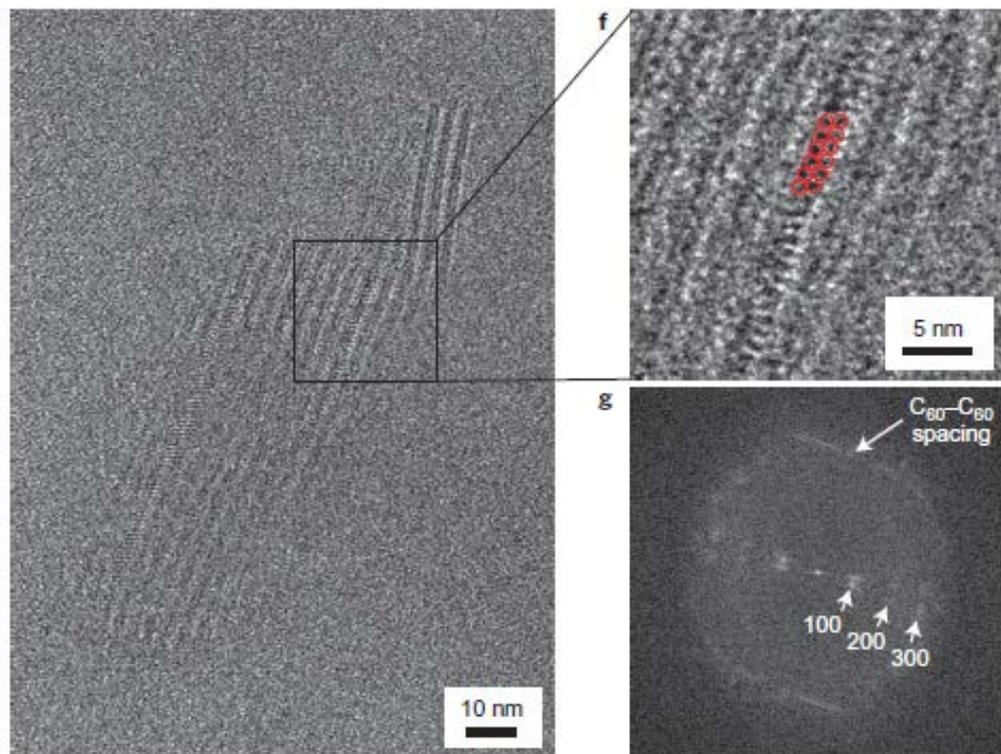
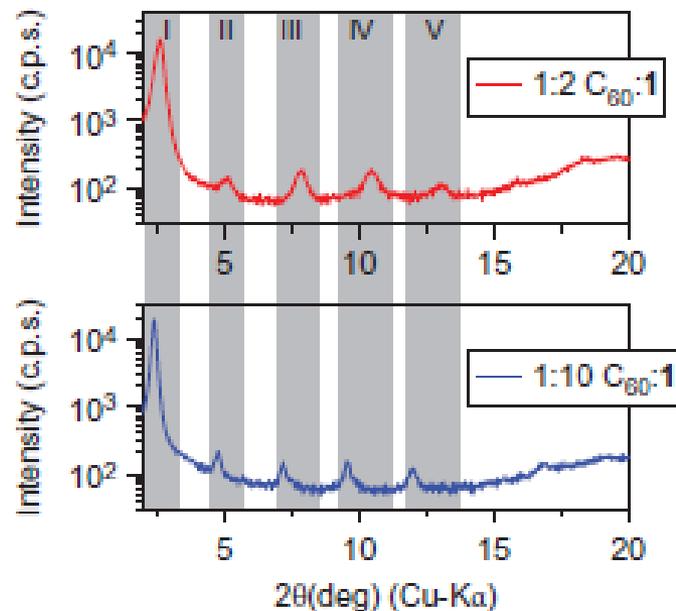
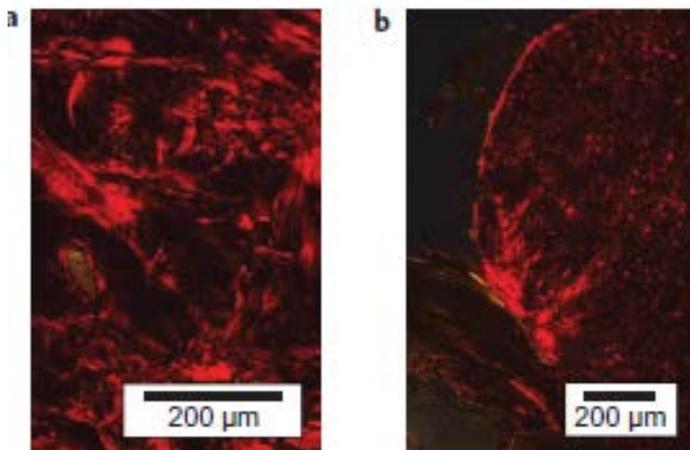


Flash-photolysis time-resolved microwave conductivity (FPTRMC)

The flash-photolysis time resolved microwave conductivity (FP-TRMC) measurement was carried out using a X-band (9 GHz) microwave circuit at low power (approximately 20 mW) and a nanosecond laser irradiation at 355 nm with photon density of $9.1 \times 10^{15} \text{ photons cm}^{-2} \text{ pulse}^{-1}$.

- ❑ The photoconductivity maximum ($\phi \Sigma \mu_{\text{max}} = 3.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was of similar order as that for solid crystalline C60 derivatives studied using the same technique (ϕ represents the quantum efficiency of the charge carrier generation and $\Sigma \mu$ is the sum of the nanometre-scale charge carrier mobilities).
- ❑ Although FPTRMC evaluates carrier mobility at the nanometre scale, the results indicate that the fibre network transports charge and might be applicable in flexible optoelectronic applications in the gelled state, with the potential for unique self-healing or thermally induced on-off switching properties.

Formation of lamellar mesophase by addition of C_{60}

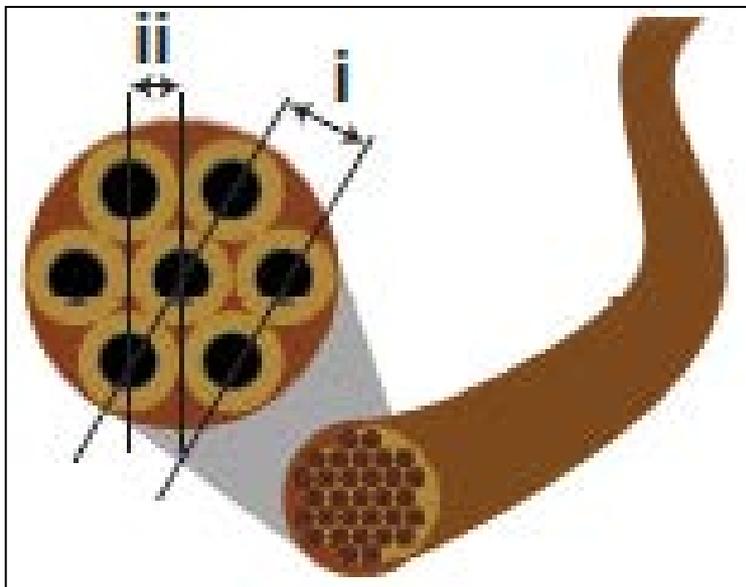


Summary and conclusions

- The thermodynamic origin of aggregation for conventional hydrophobic–hydrophilic amphiphiles is an appropriate balance between hydrophobic and hydrophilic interactions. The same antipathy between alkyl and π -conjugated moieties is used here 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 localized 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 strategies in terms of ease of application, increased solution processability of the materials, and the uniformity and bulk scale of the assemblies.

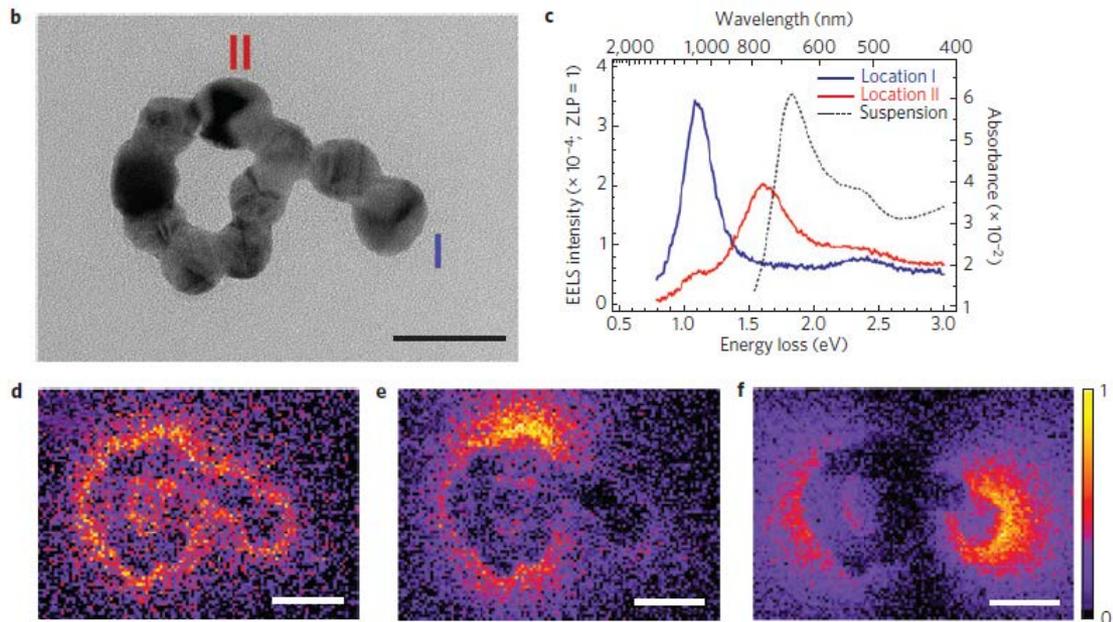
Future directions

- ❖ Similar strategy can be utilized to form self-assembled structures of clusters. Properties like photoconductivity of clusters can be probed in this self assembled structures.
- ❖ Columnar assembly of plasmonic clusters can be used for low dissipative information processing (waveguiding).



Multimodal plasmonics in fused colloidal networks

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Thank
you

