Millimeter-sized flat crystalline sheet architectures of fullerene assemblies with anisotropic photoconductivity†

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The coassembly of C60 derivatives through arene–perfluoroarene interactions has been used for the first time to develop millimeter-sized flat crystalline sheets. Time-resolved microwave conductivity (TRMC) measurements exhibited anisotropic features with over double the charge carrier mobility in the direction parallel to the plane of the crystal than perpendicular to the plane. This study demonstrates a strategy to obtain large-sized 2-dimensional architectures of C60 with anisotropic optoelectronic functions.

Supramolecular chemistry is known to be a driving force to design versatile building units to create self-assembled functional architectures.1–4 In particular, in recent years the interest in developing assemblies of various organic semiconductors with large photoinduced charge carrier mobility and their use in organic electronics has been growing due to their potential application in advanced low carbon technologies.5 A widely discussed topic in this regard is the crystalline order and nanomorphology of the assemblies to achieve better performance.6 Hence research interest has been directed towards the sensible design of functional molecules, for instance, fullerene (C60), which is one of the good n-type organic semiconductors.5 The recent developments in C60 assemblies rationalised a prerequisite of specific interactions7,8 or a D–A motif9 in arranging the molecules to attain crystalline or bicontinuous order to construct optoelectronically active functional assemblies. Moreover, the design strategies should consider the requirements such as high C60 content, compact C60 packing, high crystallinity, along with better solubility for the molecules in common organic solvents.10,11 Although there have been various studies related to chemical modification of C60, such as amphiphilic,12–14 hydrophobic,15–17 and dendritic18 approaches and its appealing self-assembly performance, the requisite for good optoelectronic materials based on fullerene assembly is the same as for other organic semiconductors.19 In this context, the crystalline order, nanomorphology of the assemblies with high C60 content and fewer insulation units etc. remains the key aspect.5

Here we espouse a new design strategy, C60 derivatives with small substitution to provide high C60 content and their compact packing, thus making an approach towards desirable optoelectronic performance. Arene–perfluoroarene interaction20,21 has been used to control the solubility and assembly properties of C60 derivatives. The ability of weak molecular interactions to achieve precise ordering of the units7 in crystal engineering is well established and arene–perfluoroarene interaction is one among them.20 In fact, the current approach provided millimeter-sized flat sheet crystalline architectures of C60 assemblies with unique anisotropic photoconductivity. The C60 derivatives (1 and 2) were synthesised according to reported procedures (Scheme S1†)11 and characterised by means of 1H NMR and MALDI-TOF-MS. In order to understand the self-organisation of 1 and 2, at first crystallisation using solvent vapour diffusion has been applied. The diffusion of n-hexane vapour into chloroform solutions of 1 or 2 resulted in the formation of flat crystalline sheets with a few submillimeter size. Random surface morphologies and irregular steps are exhibited by atomic force microscope (AFM) images of the surface of the crystals (Fig. 1a and b). The addition of n-hexane to a chloroform solution of 1, monitored by absorption changes, revealed that in the presence of the poor

Fig. 1 Chemical structure of 1 and 2 and tapping mode AFM amplitude images of the sheet crystals of (a) 1 and (b) 2.
The arene–perfluoroarene interactions of their C_60 heads are attributed to the distance of the sum of the molecular length throughout the surface. The height of the steps might be developed a flat plane over submicrometer length scale. The surface pattern (inset of Fig. 2b) exhibits the presence of 1 nm steps on the surface.

Interestingly, it has resulted in the formation of one of the largest flat crystalline sheet assemblies of C_60 having a length of more than 5 mm (Fig. 2a, inset). Optical microscope images of the plates revealed the presence of transparent layered sheets at the edges (Fig. 2a). AFM imaging of the top surface of the coassemblies showed long straight patterns (Fig. 2b) which are absent in the random morphology of the isolated assemblies (both in 1 and 2). A focused AFM height image of the surface pattern (inset of Fig. 2b) exhibits the presence of well-ordered steps with an average height of ~2.0 nm and developed a flat plane over submicrometer length scale throughout the surface. The height of the steps might be attributed to the distance of the sum of the molecular length of 1 and 2 (bimolecular layer), resulting quite possibly from the arene–perfluoroarene interactions of their C_60 heads (vide infra). The supramolecular ordering of C_60 using various procedures resulted in the formation of diverse architectures such as wires, rods and tubes, whiskers, sheets, hexagons, spheres etc. in the nanometer range and even millimeter-sized large crystals. However, the formation of such a large crystalline flat sheet in millimeter size has not been reported yet. Here appropriate substitutions play a crucial role in organising the C_60-molecules to obtain large area crystalline sheet-assemblies with a patterned surface.

Further analysis for the characterisation of bimolecular ordering in the coassembly has been carried out by X-ray diffraction (XRD) experiments. As shown in Fig. 3, the diffraction patterns up to the (004) reflection in the coassembled sheets are clearly apparent. It indicates that the bimolecular layer structure with the d-spacing of 2.0 nm estimated from the XRD pattern is unique in the sheet architecture. In contrast to the individual assemblies (Fig. S2†), the presence of intense and well-resolved peaks in the XRD strongly supports the ordered packing of molecules in the coassembly, where no phase separated domains exist. If there is such a segregation, some peak splittings should appear, which is not observed in the current case. The signal corresponding to a distance of 0.40 nm (2θ = 22.2°, indicated by ● in Fig. 3) is presumably the average distance of π–π stacking corresponding to the substituent arene–perfluoroarene interaction in the coassembly. It indicates that the intermolecular hydrogen bonding between the hydrogen atom on the phenyl and the fluorine atom on the perfluoro-phenyl parts leads to strong π stacking and thereby results in the formation of dimers of 1 and 2 (see Fig. S3†). The diffraction peak at 2θ = 16.3° (0.54 nm, indicated by ■ in Fig. 3) could be attributed to the diffraction peak from the interplane C_60 ordering, revealing the extended ordering of the dimers using spherical (C_60-C_60) π–π interactions. The ^1H NMR spectrum of the crystalline coassembly in CDCl_3 clearly indicates that in solution, 1 and 2 are molecularly dispersed in 1:1 ratio (Fig. S4†). This is an additional proof for the complexation in an equal ratio between 1 and 2 in the crystals. The thickness of the sheet objects was evaluated by scanning electron microscopy (SEM) analysis, and it was found that the thickness varies from 10–200 μm (inset of Fig. 3). This thickness analysis was further confirmed by 3-dimensional laser scanning microscopy (3D-LSM) of the coassembled objects (Fig. S5†).

In order to understand the detailed molecular packing in the coassembled crystals, single crystal X-ray analysis was performed. Due to the presence of racemic mixtures of 1 and 2 in the coassembly, the exact positioning of the substituent units is not clear, instead the packing of C_60 moieties in the crystal is possibly understood. It indicated that the C_60 moieties in the coassembled crystals are packed in a monoclinic C manner (Fig. 4) with unit cell parameters of a = 14.19 Å, b = 14.23 Å, c = 37.96 Å and α = 90.0°, β = 90.1°, γ = 90.0°. It implies that the presence of arene–perfluoroarene interactions, located at the empty space layers in the multilayered model in Fig. 4b, results in the formation of dimers of 1 and 2, and further π–π interaction of C_60 moieties stabilises the molecules to form a crystalline organization. As shown in Fig. 4a, the length of a unit cell consisting of two bilayers is 3.8 nm. The bimolecular length assumed using optimised molecular structures of 1 and 2 by B3LYP/6-31G* level density functional theory (DFT) calculation is 2.53 nm (Fig. S3†), indicating the interdigitation
of molecules 1 and 2 at the phenyl head groups. The interdigitation observed between the C₆₀ moieties of the bimolecular layers is clearly visible in the single crystal analysis (Fig. 4). Therefore, the centre to centre layer distance of the bimolecular C₆₀ layers obtained from single crystal analysis (1.9 nm) is less than that of the assumed length of the bimolecular unit. However it matches well with the lamellar distance (2.0 nm) from XRD and the average height of the steps (∼2.0 nm) from AFM. This study concludes that arene–perfluoroarene and π stacking interactions enabled a better ordering in the parallel direction of the plane of the crystal (Fig. 4c) whereas π stacking of the C₆₀ part in the bilayer results in formation of layered ordering in the perpendicular direction (Fig. 4b and d).

The significance of assembling molecules with a higher degree of ordering in large dimensions is to engage these assemblies as part of devices to investigate their optoelectronic properties. It is known that molecules which organise in 2-dimensional layers exhibit anisotropic properties. In order to investigate the anisotropy in charge transport of the sheet assemblies, time resolved microwave conductivity (TRMC) experiments have been carried out by placing the sheet objects on top of quartz substrates and irradiating with a λ = 355 nm laser pulse. Here, the transient photoconductivity (\(\phi \Sigma \mu\), product of the quantum efficiency of the charge-carrier generation \(\phi\) and the sum of the nanometer-scale charge-carrier mobilities \(\Sigma \mu = \mu_+ + \mu_-\)) was evaluated. Interestingly, the results have shown that the charge carriers exhibited anisotropic transport with a value of \(0.76 \times 10^{-4}\) cm² V⁻¹ s⁻¹ in the parallel direction when compared to the perpendicular direction \((0.36 \times 10^{-4}\) cm² V⁻¹ s⁻¹) of the sheet assembly (Fig. 5a and b). Here the anisotropic effect in the photoconductivity is found to be over double. In the case of individual assemblies, the values in the parallel (and perpendicular) directions were varied: \(0.66 \times 10^{-4}\) cm² V⁻¹ s⁻¹ (and \(0.40 \times 10^{-4}\) cm² V⁻¹ s⁻¹) for 1 as well as \(0.33 \times 10^{-4}\) cm² V⁻¹ s⁻¹ (and \(0.28 \times 10^{-4}\) cm² V⁻¹ s⁻¹) for 2, respectively (Fig. 5f). The observed difference in the photoconductivity and the anisotropic feature of 1 and 2 when compared to that of the coassembled one could be directly correlated to the XRD results (Fig. S2†) and imperfect packing of the molecules in the assemblies. The face centered cubic (fcc) packing in C₆₀ microcrystals enabled 3D charge transport with a higher \(\phi \Sigma \mu\) value of \(3.2 \times 10^{-4}\) cm² V⁻¹ s⁻¹, and a more pronounced long-lived decay component. In contrast, the modification of the C₆₀ surface with phenyl/pentafluorophenyl substituents controls the layer packing within the monoclinic C lattice and reduces the \(\phi \Sigma \mu\) values by roughly one order of magnitude. An emphasis is given to the charge carrier mobility \((\Sigma \mu)\) which would be a few orders of magnitude larger than the values shown above, as the \(\phi\) is typically of the order \(10^{-5}\) or less.\(^{9,35}\)

The anisotropy of charge transport has established that the efficiency is strongly connected to the relative positions of the interacting molecules. In this case, the observed higher mobility in the parallel direction is substantiated by the increased π–π stacking and orbital overlap which is more favorable for the carrier hopping between the molecules along this direction.\(^{37}\) In the coassembled sheets, where molecules organise into layered structures, greater charge transport within the stacked layers is observed whereas the transport between layers is less efficient. It is to be noted that among organic semiconducting materials, sublimation-deposited single crystals exhibited high charge carrier mobilities whereas in other systems such as solution processed single crystals and thin films, a lower mobility is observed.\(^{38}\) In particular, the carrier mobilities in crystalline materials are influenced by many factors including molecular packing, disorder, presence of impurities, charge-carrier density, size/molecular weight, and so on.\(^{36}\) In order to achieve high charge transporting performance, perfect alignment in the crystals or self-assembled molecular layers is needed.

Fig. 4 Crystal packing model of the coassembled objects of 1 and 2 based on single crystal analysis (only packing structure of the C₆₀ part is resolved), (a) a unit cell, (b) multilayered structure, (c) top view and (d) 3-dimensional view.
Most n-type semiconducting materials are quite sensitive to the experimental conditions. Even though the coassembly results in the formation of the largest single crystalline sheets of C<sub>60</sub>, either due to quenching of the generated carriers by oxygen at ambient conditions<sup>39-42</sup> or the trap created by phenyl or perfluorophenyl substituents on the molecule itself, a lower charge carrier mobility is obtained. In order to improve the crystal quality and thereby to attain high mobility values, processes such as chiral separation of the enantiomers<sup>43</sup> and incorporation of various electron donors<sup>44</sup> as a part of the crystalline assembly are currently in progress. In spite of the obtained lower value, this is the first report describing the preparation of large (≈ 5 mm) flat sheet crystals of C<sub>60</sub>. In addition, the fabrication of self-assembled structures of C<sub>60</sub> assemblies with anisotropic emission<sup>7</sup> and charge transport properties<sup>45</sup> are of particular significance.

Conclusions

The incorporation of arene–perfluoroarene interactions in C<sub>60</sub> assemblies, for the first time, resulted in the formation of large flat crystalline sheets with ordered surface pattern and morphology. The resulting coassembled crystals exhibit bimolecular layer organisation of the molecules throughout the crystal. The coassembled crystals exhibits good anisotropy, with higher carrier mobility in the parallel direction due to the dense π stacking along the surface of the crystal. The increased spacing between the C<sub>60</sub> bilayers in the perpendicular direction reduces the carrier hopping frequency. The development of such large flat sheet crystals with anisotropies will be useful in different switchable optoelectronic devices. In addition, the ordered steps on the surface of the crystals could be used for various applications as a template and further as a platform for the crystallisation of other molecules, thereby developing functional crystalline assemblies.

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