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Seeded on-Surface Supramolecular Growth for Large Area Conductive Donor-Acceptor Assembly

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Goudappagouda,^a Chithiravel Sundaresan,^b Kothandam Krishnamoorthy,^b Suresh W. Gosavi,^c
Sukumaran Santhosh Babu*^a

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Charge transport features of organic semiconductor assemblies are of paramount importance. However, large area extended supramolecular structures of donor-acceptor combinations with controlled self-assembly pathways are hardly accessible. In this context, as a representative example, seeded on-surface supramolecular growth of tetrathiafulvalene and tetracyano-*p*-quinodimethane (TTF-TCNQ) using active termini of solution formed sheaves has been introduced to form extended assembly. We demonstrate for the first time, the creation of large area donor-acceptor assembly on surface, which is practically very tedious, using a seeded, evaporation assisted growth process. The excellent molecular ordering in this assembly is substantiated by the good electrical conductivity ($\sim 10^{-2} \text{ Scm}^{-1}$). The on-surface assembly *via* both internally formed and externally added sheaf-like seeds open new ways in supramolecular chemistry and device applications.

Supramolecular assemblies of π -conjugated molecules are highly considered for organic electronic devices to address the existing energy issues.¹ Even though significant developments have been achieved in this direction, there are still many issues to be taken care. For instance, charge transport across the π -conjugated framework, which is created by the ordering of molecules, has an influence on the end use performance of these devices.² Hence, self-organization and related mechanistic pathways are of great significance.³ In this context, the recent reports from the groups of Meijer,^{3b} Sugiyasu and Takeuchi,^{4a} Würthner,^{4b} Aida^{4c} etc. have to be acknowledged for uncovering the complex pathways involved in the self-organization of optoelectronically active molecules. Moreover, the recent finding of seeded, living supramolecular polymerization gathered attention due to the possible control on the nanostructure formation and the intriguing mechanisms involved.^{4,5}

The electronic properties of organic semiconductors for a genuine interest after the discovery of unusually high electrical conductivity in perylene-bromine charge transfer (CT) complex.^{6a} Subsequent demonstrations of CT assisted metallic conductivity at the donor-acceptor interface of TTF-TCNQ assemblies changed the belief of organic materials as insulators.^{6b,c} For the past several decades, the CT heterojunctions of pristine TTF-TCNQ and many analogues have been extensively investigated.^{7,8} The extended supramolecular structures of TTF-TCNQ are hard to achieve in solution,⁹ unless there is sufficient structural modification *via* synthetic manipulation to maintain the aggregation features.¹⁰ Hence, the largest obstacle is to envisage an efficient method for developing large area crystalline assemblies. Even after the successful report of seeded supramolecular polymerization in solution, a useful practical demonstration on surface is still missing. Toward this goal, a seed assisted on-surface large area electron donor-acceptor assembly formation, which may improve the efficiency of substrate-semiconductor interface in charge transport devices,¹¹ will be a promising candidate. Herein, by taking TTF-TCNQ as an example, we introduce seeded on-surface supramolecular growth to obtain large area donor-acceptor assembly. The active termini of the solution formed or externally added TTF-TCNQ sheaf-like structures tailor the assembly on surface.

In order to find a convenient method to form extended TTF-TCNQ (1:1) assembly, an equal volume (0.5 ml) of equimolar CHCl_3 solutions of TTF and TCNQ were mixed simultaneously. Optical microscope (OM) image of the precipitate showed the presence of sheaf-like structures (Fig. S1-3). Field-emission scanning electron microscope (FE-SEM) images of the assembly at lower concentration (3 mM) indicate that the initially formed ribbon-like structures (7-12 μm) radially oriented to its center and self-organized to form sheaf-like assembly having length of 25-40 μm (Fig. 1a and b, respectively). As the concentration is increased to 5 mM, a progressive growth of the sheaf resulted in dendritic-sheaf-like structures (200-250 μm) with increased number of leaves (Fig. 1c,S3,S4). An image of a typical sheaf with leaf and core is

^aOrganic Chemistry Division, CSIR-National Chemical Laboratory (CSIR-NCL), Pune-411 008, India.

^bPolymer Science and Engineering Division, CSIR-National Chemical Laboratory (CSIR-NCL), Pune-411 008, India.

^cDepartment of Physics, Savitribai Phule Pune University, Pune-411 007, India

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shown in Fig. 1d. The sheaf formation could be due to the fast crystallization upon immediate mixing of TTF and TCNQ *via* crystal splitting growth mechanism.¹²

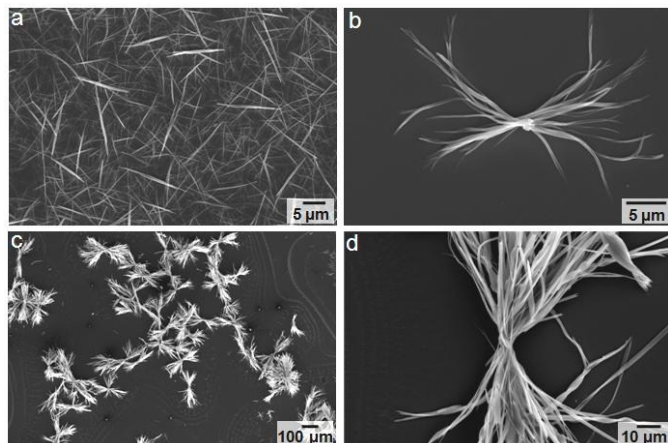


Fig. 1 FE-SEM images of TTF-TCNQ assembly formed by mixing of equimolar CHCl_3 solutions (0.5 mL) of TTF and TCNQ (1:1) and drop casted (10 μL) on silicon substrate. (a) 1 mM and (b)-(d) 3 mM.

The immediate precipitation of TTF-TCNQ from CHCl_3 solution limited the experimental conditions to form extended assembly. However, a seed assisted supramolecular growth experiment has been conducted using TTF-TCNQ assembly in CHCl_3 . Addition of fresh TTF and TCNQ solutions to sheaf-like precipitates in CHCl_3 induced a seeded growth. In an experiment, separate solutions of TTF and TCNQ (1.5 mM, 100 μL each) were added simultaneously to already precipitated TTF-TCNQ sheaf-like assembly (1.5 mM, 1 mL) in CHCl_3 and waited for 2 hours. Interestingly, addition of extra TTF and TCNQ has resulted in an increased length of sheaf-leaves (Fig. S5).

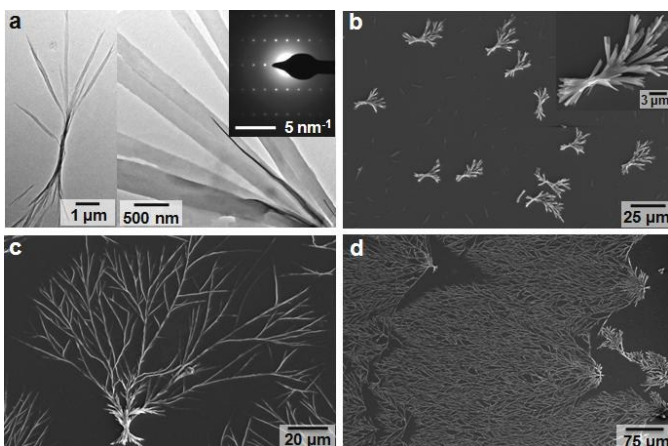


Fig. 2 (a) HR-TEM image of TTF-TCNQ assembly in THF (2 mM), inset shows the SAED pattern of the sheaf leaf. (b)-(d) FE-SEM images of the TTF-TCNQ assembly formed by drop casting THF solution (3 mM, 10 μL) on silicon substrate, inset of (b) shows an unsymmetrical sheaf.

After the observation of seeded growth in CHCl_3 , solvent has been changed to THF, expecting to tune self-assembly conditions. The mixed assembly in THF showed moderate color

change from golden to brownish yellow (Fig. S6), indicating a different self-assembly condition than immediate precipitation in CHCl_3 . High-resolution transmission electron microscopy (HR-TEM) images showed that at a concentration of 0.5–2 mM TTF-TCNQ formed randomly oriented flat ribbons, which radially grown to form smaller sheaves (Fig. 2a, S7,S8). Selected area electron diffraction (SAED) pattern of the sheaf leaf exhibited single crystallinity (Fig. 2a, inset). At a concentration of 3 mM, symmetrical and unsymmetrical sheaves were found on drop casted (10 μL) silicon substrate (Fig. 2b). The solution formed symmetrical sheaves undergo on-surface directional growth upon solvent evaporation and result in the formation of unsymmetrical sheaves. Interestingly, upon drop casting THF solution (3–10 mM) containing TTF-TCNQ seeds on substrates such as glass or silicon, branched and long fibrous assembly was formed (Fig. 2c,d).

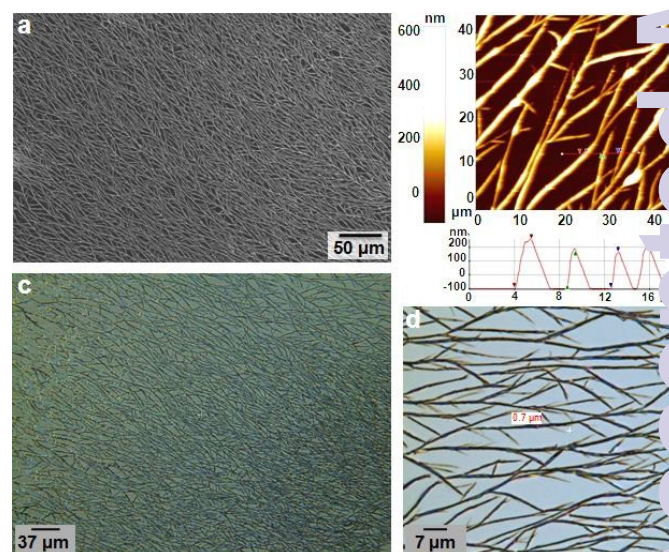


Fig. 3 (a) FE-SEM, (b) AFM and (c), (d) OM images of TTF-TCNQ assembly formed by drop casting THF solution (5 mM, 10 μL) on (a), (b), (d) silicon and (c) on glass substrates.

Solvent evaporation assisted nano/micro-structure formation is a general way to obtain large area ordered arrays of functional organic molecules.¹³ In this particular case, the on-surface growth is due to the combined effect of the available solution formed seeds and evaporation of THF solution. Such an observation of solution formed seeds initiating the formation of extended assembly on surface upon solvent evaporation is hitherto unknown.¹⁴ As shown in Fig. 2c, the solution formed sheaf starts to grow only from the active termini of sheaf-leaves in the direction of solvent evaporation, and as the solvent front moves, it creates unusually long and branched fibrous assembly on surface (Fig. 3, S9–15). The supporting video image clearly demonstrates the on-surface growth process in large area. The extended donor-acceptor assembly formation was imaged by FE-SEM, atomic force microscope (AFM) and OM (Fig. 3). A detailed AFM analysis showed that as the concentration of TTF-TCNQ solution

increased from 5 to 10 mM, the seeds and fibers formed exhibited an average height of 280 and 590 nm, 435 and 830 nm, respectively (Figure 3a, S16). It indicates that the height of the fibrous assembly formed is directly related to the concentration of the TTF-TCNQ solution and height of the seed formed. At higher concentrations, for a minor extent, seeded growth leads to the formation of discontinuous fibrous structures at the edge parts of the substrate due to faster solvent evaporation (Fig. S17).

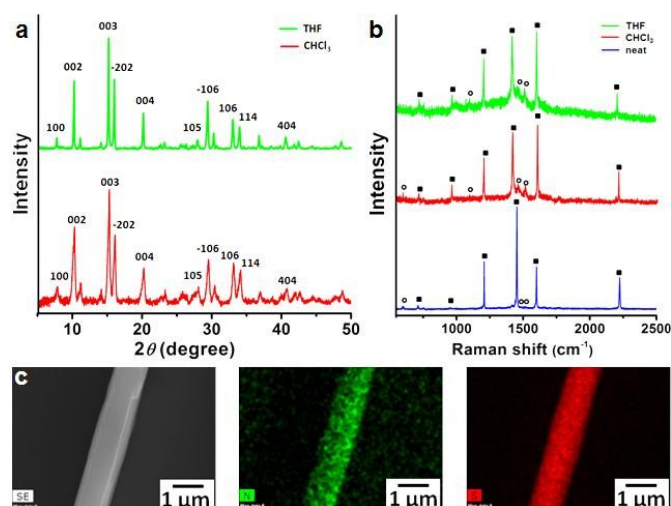


Fig. 4 (a) XRD and (b) Raman spectra of TTF-TCNQ assemblies from THF and CHCl_3 . Raman spectrum of as ground TTF-TCNQ complex is provided as reference. (c) SEM image (left) and corresponding STEM mapping images for nitrogen (middle) and sulfur (right) of a single TTF-TCNQ sheaf leaf formed from CHCl_3 .

The assembly formation on surface has been characterized by using XRD, Raman and UV-Vis-NIR spectroscopy and STEM mapping. XRD profile of TTF-TCNQ assemblies suggest a monoclinic space group $\text{P2}_1/\text{C}$ (Fig. 4a, S18).¹⁵ The presence of sharp peaks in TTF-TCNQ assemblies clearly indicate high crystallinity. As reported for TTF-TCNQ systems, the XRD data reveals the domination of homologous columns of separately stacked cations and anions.^{15b} Raman spectra of the TTF-TCNQ assembly along with that of as ground TTF-TCNQ CT complex confirmed the presence of both TTF and TCNQ in the assembly (Fig. 4b). The respective peaks of TTF (marked by open circles) and TCNQ (marked by filled rectangles) show that the assembly is composed of TTF and TCNQ molecules (Fig. S19). The CT interaction between TTF and TCNQ is clearly observed in the solid state UV-Vis-NIR spectra of the assemblies (Fig. S20). In addition, STEM mapping for nitrogen and sulfur confirmed the uniform distribution of TTF and TCNQ (Fig. 4c, S21).

To elucidate the seeded on-surface supramolecular growth, a sequential placement of the sheaf formed from CHCl_3 solution of TTF-TCNQ as the seed followed by THF solution on silicon substrate has been planned. The concentration of TTF-TCNQ in THF was selected in such a way that it excludes the solution formed sheaf. In order to avoid the larger dendritic-sheaf, supernatant CHCl_3 solution (2 μL , 3–10 mM) containing smaller sheaf was deposited on silicon

substrate. A dilute THF solution (2 μL , 0.5–3 mM) of TTF-TCNQ was carefully placed on the silicon substrate containing sheaf from CHCl_3 . Remarkably, OM images showed that the seeds from CHCl_3 are also found to be successful in initiating the on-surface growth (Fig. 5a). But a large area assembly similar to that from THF solution was not feasible due to the surface inhomogeneity created by the initially deposited CHCl_3 sheaves. However, it confirmed the concept of seeded on-surface growth assisted donor-acceptor assembly formation. One point to be noticed is in both seeded assembly formations (THF and CHCl_3 generated sheaves), the fiber growth starts only from the active termini formed by the segregated stacks of TTF and TCNQ.^{4b,14} Moreover, no fiber growth is initiated from the surface perpendicular to the long axis of the sheaf. The experiments repeated at various concentrations justified the genuinity of this concept (Fig. S22–25), which may be definitely useful in electronic device applications. Since the sheaf from CHCl_3 is bigger than that of THF, the fibers formed *via* seeded growth is bigger in diameter than from THF. The on-surface growth initiated from THF and CHCl_3 sheaf seeds are schematically represented (Fig. 5b,c).

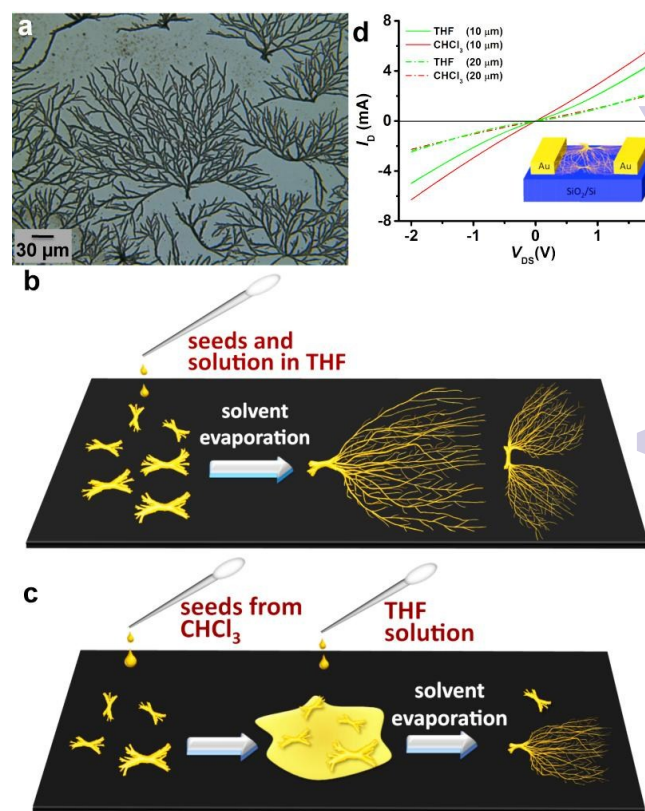


Fig. 5 (a) OM image of seeded supramolecular polymers of TTF-TCNQ obtained by sequential deposition of THF solution (2 μL , 1 mM) of TTF and TCNQ (1:1) onto silicon substrate containing CHCl_3 sheaf (2 μL , 5 mM). Schematic illustration of the on-surface self-assembly processes from (b) THF and (c) CHCl_3 sheaf seeds. (d) Typical I-V curves for TTF-TCNQ assemblies from THF and CHCl_3 deposited on Au electrodes with channel widths of 10 μm and 20 μm ; inset shows the schematic of the typical I-V device.

CT assemblies of TTF-TCNQ are considered as quasi-one-dimensional metals composed of segregated molecular stack

of highest conductivity along the stacking direction.¹⁶ However, the challenging task is to obtain ordered molecular assemblies in larger dimensions with optimum performance. In order to take advantage of the branched structures with higher connective density, current-voltage (I-V) measurement was performed (Fig. 5d, Table S1). The I-V characteristics were recorded by scanning the applied voltage from 0 to +2 V and then to -2 V, followed by a reverse scan. The conductivity values upto 0.30×10^{-2} , 0.22×10^{-2} for 10 μm and 0.11×10^{-2} , $0.09 \times 10^{-2} \text{ Scm}^{-1}$ for 20 μm channel widths of Au electrodes were observed for assemblies from CHCl_3 and THF (10 mM), respectively. The comparable values obtained in both the cases clearly indicate the excellent ordering obtained by on-surface growth. Noteworthy, the concentration of TTF-TCNQ solution used for assembly formation is found to be important for the conductivity measurements (Figure S26, S27, Table S2). The high conductivity obtained at a concentration of 10 mM could be attributed to the larger size/height of the solution formed sheaves and thereby resulted fibers, leading to higher connective density and maximum coverage of the channel area.

In summary, an effective method of seeded on-surface growth has been introduced to create extended donor-acceptor assemblies in large area. Here, we have demonstrated for the first time, both the solution formed and the externally added seed assisted on-surface growth of functional organic molecules. Furthermore, by taking advantage of the high connective density, thus formed branched donor-acceptor structures exhibit excellent conductivity in the range of $\sim 10^{-2} \text{ Scm}^{-1}$. We envision that the concept of seeded on-surface growth will open a new door to various applications in supramolecular assemblies. The ongoing studies in our lab include detailed mechanistic aspects of assembly formation and extension of this concept to other potential π -systems.

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Table of Content

A seeded on-surface supramolecular growth leads to large area conductive donor-acceptor assembly via evaporation assisted growth from active termini of solution formed sheaf-like seeds

