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COMMUNICATION

Chemical reaction mediated self-assembly of PTCDA into nanofibers†

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Uniform and crystalline nanofibers of perylene-3,4,9,10-tetra-carboxylic dianhydride (PTCDA), an insoluble organic semiconducting molecule, have been achieved by self-assembling the molecules using chemical reaction mediated conversion of an appropriately designed soluble precursor, perylene tetracarboxylic acid (PTCA) using carbodiimide chemistry.

Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), a n-type organic semiconducting molecule, has received widespread attention in electronic and opto-electronic devices.[1] It has been found that close contact between the molecules by π-stacking, electrostatic forces and H-bonding allows for efficient charge propagation and therefore they are suitable for use in electronic and opto-electronic devices.[1–6] To enhance the charge-propagation and transport characteristics in organic semiconductors emphasis has largely shifted towards creating more organized 1D nanomaterials such as wires and belts which are more conducive to allow expedient movement of charges across the electrodes.[2,7] Vapour based methods have been widely adopted for the successful assembly of PTCDA and related insoluble perylene based compounds into organized 1D nanostructures.[7–13] Recently, chemical vapour deposition (Ti-CVD) was used to realize 1D nanofiber assembly of the PTCDA primarily driven by π-stacking interaction.[8] In organic semiconductors, crystallinity of the assemblies is known to have pronounced effects towards charge-transport characteristics.[14–19] In general, for large-scale adoption of the organic materials in the area of electronic and opto-electronic devices arguments are based on the ability to use cost effective solution based approaches rather than expensive and intensive vapour based methods.[2,19]
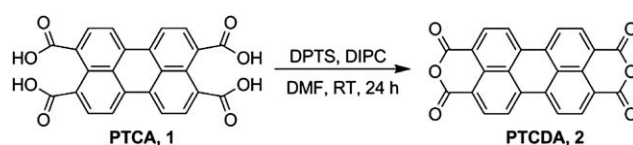
The assemblies of PTCDA using solution based processing are rather challenging, owing to intrinsic insolubility, and are therefore chemically converted to more soluble precursors by reacting with corresponding amine to yield perylene tetracarboxylic diimides

(PTCDI)[20] for realizing solution based 1D assemblies.[2,21–23] The formation of the organized 1D assemblies of PTCDI in non-solvents is promoted largely because of the strong π-stacking interaction amongst the perylene cores and side-chain interdigitation.[20,22]

We hypothesize that if an appropriate perylene precursor having functional groups, allowing reasonable solubility in certain solvents, and amenable to chemical modification to yield PTCDA is designed, it may be possible to provide a solution based medium for obtaining successful 1D assembly of insoluble PTCDA. Indeed, such a precursor exists, namely, perylene-3,4,9,10-tetracarboxylic acid (PTCA) which is highly soluble in dimethylformamide (DMF) and the carboxylic acid groups can be chemically converted to yield PTCDA using carbodiimide chemistry (Fig. 1). While co-crystallization of PTCA with amines has been attempted and shows remarkable propensity to strongly form crystals by H-bonding interactions,[24] to the best of our knowledge, solution based chemical transformation methods to obtain 1D assemblies of PTCDA have yet not been explored.

Carbodiimide chemistry has been widely used for the esterification reaction between a carboxylic acid and an alcohol.[25–27] It has been established that this reaction proceeds *via* formation of acid anhydride. In the absence of an alcohol, monocarboxylic acid undergoes *intermolecular* reaction yielding acid anhydride. Whereas, a dicarboxylic acid in which the carboxylic acid groups are separated by two or three methylene groups undergoes *intramolecular* reaction yielding cyclic anhydride.[27] Thus, PTCA matches quite well the requirements of an ideal precursor, chemically reactive and soluble. Our goals were to explore, firstly, the chemical synthesis of PTCDA from PTCA and finally, attempt to understand if such a chemical synthesis going from a highly soluble form of PTCA to the highly insoluble PTCDA would lead to any *in situ* growth of 1D nanostructures with the final assemblies being composed of PTCDA molecules.

PTCA was synthesized using the known methods from the parent PTCDA (see ESI†).[28] PTCA is highly soluble in DMF (Fig. 2a) and

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† Electronic supplementary information (ESI) available: Synthesis protocols and schemes, plausible mechanism of reaction, additional TEM images, TEM images for stability of fibers after extraction in DCM and aqueous potassium carbonate, detailed FTIR spectra, mass spectroscopy, and XRD of fibers of PTCDA. See DOI: 10.1039/c1nr10579e

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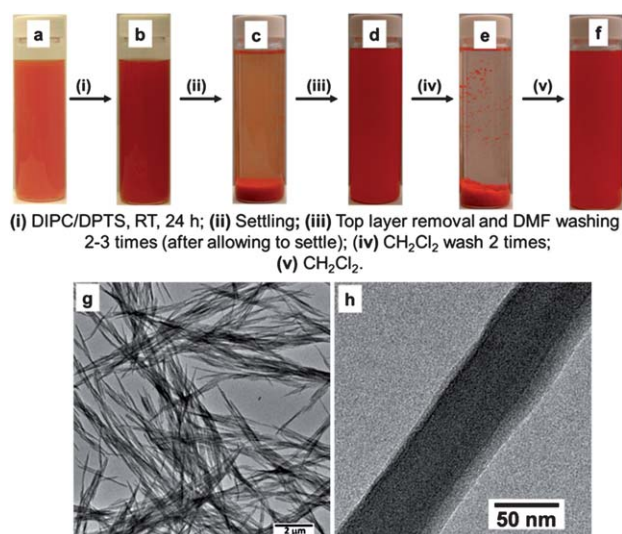

Fig. 1 The chemical route used for the self-assembly of the insoluble PTCDA nanofibers. The carbodiimide chemical pathway adopted here allows for the conversion of soluble PTCA to insoluble PTCDA.

Fig. 2 (a–f) The different stages of solution processing to obtain pure PTCDA fibers (f) starting from the homogeneous PTCA in DMF (a). After 24 h of stirring the PTCA solution in DMF with DPTS and DIPC at room temperature there is formation of red colored aggregates (b). The aggregates are allowed to settle (c) and are subsequently washed with DMF and CH$_2$Cl$_2$ (d and e) for the removal of unreacted precursor and the reagents. The pure PTCDA aggregates could be suspended easily in CH$_2$Cl$_2$ as shown in (f). (g) TEM images obtained after drop casting the aggregates from DMF (aggregates shown in (d)) after the completion of the reaction at 24 h. (h) Individual fibers of ∼50 nm diameter and 2–3 mm length are observed.

exhibits a bright yellow fluorescence when excited with a hand-held UV lamp (365 nm) (Fig. S1, ESI†). To perform the chemical transformation of PTCA using carbodiimide chemistry, a homogeneous solution of PTCA was formed in DMF by sonication. Then, 4-(dimethylamino)pyridinium 4-toluene sulfonate (DPTS, synthesis protocol available in ESI†) was added to this vial and further sonicated. The addition of DPTS prevents the formation of unreactive N-acylurea as the by-product and the reaction proceeds via the formation of O-acylisourea intermediate (Scheme S1, ESI†).[29] This was then followed by the addition of 1,3-diisopropylcarbodiimide (DIPC) and the solution was stirred slowly at room temperature. Within 1 h, the solution became turbid red indicating aggregation. When this solution was now excited with the hand-held UV-lamp, there was a large amount of fluorescence from the unreacted PTCA which quenched considerably after 24 h (Fig. S1, ESI†) of reaction leading to dark red colored aggregates in solution (Fig. 2b). The residual weak fluorescence can be attributed to the trace amount of unreacted PTCA in this aggregated dispersion in DMF. This unreacted PTCA was removed by allowing the aggregates to settle and the upper solution layer of the residual PTCA in DMF was discarded (Fig. 2c). This process was repeated by addition of fresh DMF and allowing the aggregates to settle until the upper clear solution showed no detectable fluorescence (Fig. 2d). Typically, this took about 2–3 washings in DMF. A detailed experimental protocol is available in the ESI†.

In general, the chemical products obtained after synthesis are often found to be powdery substances. However, for the products (aggregates in DMF) mentioned above it was interesting to note that the transmission electron microscopy (TEM) revealed the formation of

bundles of uniform 1D nanofiber having widths of 50 nm and lengths of 2–3 μm as shown in Fig. 2g and h (more TEM images are shown in Fig. S2, ESI†). Intrigued by the observation of such a morphology, we set out to understand the chemical species responsible for such a 1D assembly as the reaction proceeds via the formation of a stable urea by-product (Scheme S1, ESI†). Purification of the product was done using a series of extractions in CH$_2$Cl$_2$, after the aggregates were extracted in DMF (Fig. 2e and f). The series of extractions ensures only the removal of starting reagents (PTCA, DPTS, and DIPC) along with the stable urea by-product. This purified product now in CH$_2$Cl$_2$ was then again analyzed using TEM (Fig. S3, ESI†). Similar morphological characteristics are retained as those observed in DMF (Fig. 2g, h and S2, ESI†).

To probe if chemical reaction has occurred, a TEM sample was prepared by casting the aggregates from CH$_2$Cl$_2$. The aggregates left on this TEM grid were then immersed into a potassium carbonate (K$_2$CO$_3$) solution for at least 2 minutes. Following the drying, TEM morphological inspection of the samples was carried out and it was found that there was no destruction in the morphology (Fig. S4, ESI†) and the aggregates were found to retain their original 1D nanostructure (in terms of both widths and lengths). At room temperature, PTCA is highly soluble in K$_2$CO$_3$, whereas PTCDA is not. This qualitatively suggests that indeed the reactants have been consumed and the fibers might be composed of PTCDA.

In order to obtain the chemical entities responsible for the formation of 1D assembly, FTIR and mass spectroscopy of the final fiber products were performed and compared to the starting compound PTCA and the commercially available PTCDA (standard). The FTIR spectra of the fibers obtained after reaction showed distinct sharp vibrational modes corresponding to the carboxylic dianhydride and match very well with the commercially available PTCDA powder, and are different from the starting material PTCA (Fig. 3a).[30] Thus, from the FTIR data it was very clear that the free carboxylic acid groups in PTCA upon reaction get converted into dianhydride groups leading to the formation of PTCDA. A 100% relative abundance peak for m/z at 393 corresponding to (PTCDA + H)$^+$ was found from the mass spectroscopy measurements of the PTCDA fibers and matches perfectly with the standard PTCDA powder (Fig. S5 and S6, ESI†). The chemical analysis by FTIR and mass spectroscopy clearly demonstrate that the fibers are indeed composed of PTCDA molecules.

The X-ray diffraction (XRD) pattern from the bundles of fibers of PTCDA shows that the assemblies are highly crystalline in nature. The peaks obtained could be indexed by matching with the standard PTCDA powder (Fig. 3b).[9] The selected area electron diffraction (SAED) patterns obtained from the PTCDA nanofibers show the presence of mixed phases (Fig. S7, ESI†) and corroborate the crystalline nature of the as obtained assemblies. The exact mechanism for the formation of the crystalline fibers of PTCDA by this chemical reaction mediated self-assembly is not very clear at the moment. It is likely that various intermolecular forces like π–π interactions, hydrogen bonding and electrostatic interactions play a critical role, as observed in small size aggregates of PTCDA from the vapor phase, when the intermediates are converted to the final fiber product (PTCDA).[1,7,24,31–36] One plausible explanation is that the insoluble PTCDA seeds formed upon the reaction initiation allow for controlled crystallization as more and more PTCA molecules get converted to PTCDA in DMF leading to highly crystalline 1D assembly.
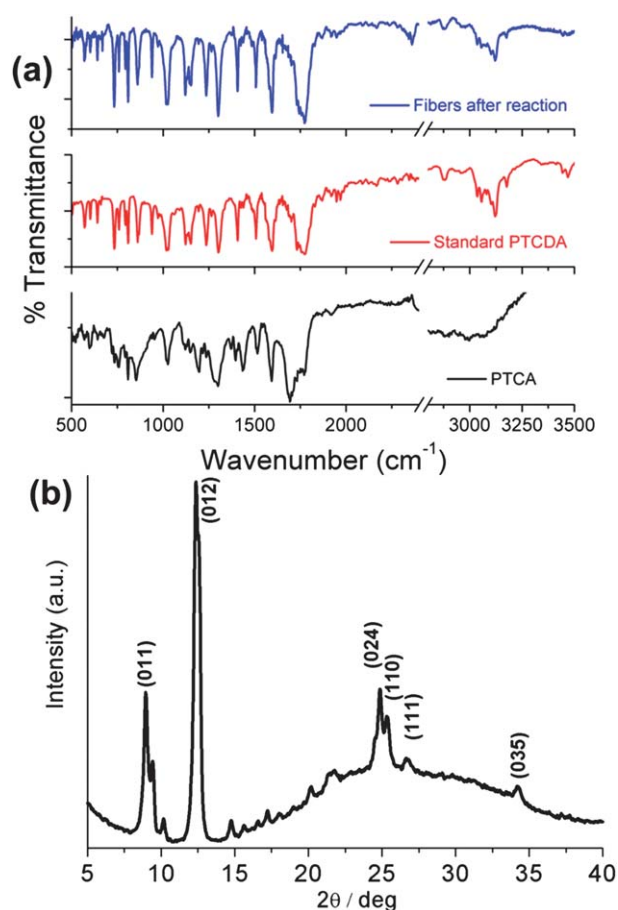
Fig. 3 (a) FTIR spectra of the product obtained after the chemical reaction (blue curve) and its comparison to commercially available PTCDA powder (red curve). There is a perfect match of the two spectra which are distinctly different from the starting material, PTCA (black curve) implying that indeed the reactants have been consumed and the final products are composed of PTCDA. (b) XRD pattern obtained for the PTCDA fibers shows highly crystalline nature of the aggregates formed because of the chemical reaction. The indexing of the peaks was done by matching the peaks with the standard PTCDA.[9]

Conclusions

Thus, in conclusion we have for the first time demonstrated a carbodiimide based chemical reaction mediated self-assembly of PTCDA into 1D nanofibers using PTCA as a starting material. The fibers prepared by this approach are highly crystalline in nature. The chemical compositions of the fibers were confirmed by FTIR and mass spectroscopy analysis. This kind of *in situ* self-assembly by a chemical reaction leads to the expedient formation of organized 1D nanostructures of PTCDA under ambient conditions, which is otherwise impossible by any other solution processing technique. This generic protocol of the carbodiimide chemistry can be further extended to similar π-conjugated chemical systems, with carboxylic acids, to yield the assembled structures of the π-conjugated cores without any side-chains. The demonstrated approach additionally opens new avenues for exploring other chemical reaction for the wide range of π-rich organic semiconducting molecules, oligomers and polymers, depending on the available functional group of the starting precursor to yield self-assembled crystalline structures without any

side-chains. In general, such chemical approaches will allow for an understanding of the applicability of π-rich cores in electronic and opto-electronic applications, as there are no side-chains involved.

Acknowledgements

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