

Electronic Supplementary Information

Chemical Reaction Mediated Self-Assembly of PTCDA into Nanofibers

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1) General Information: Unless otherwise stated, all the starting materials were obtained from commercial suppliers and used without further purification. Perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA), dimethylformamide (DMF) were purchased from Sigma Aldrich. Deionized (DI) water was used for all the experiments.

2) Characterization: All the Fourier transform infrared spectra (FTIR) were obtained on FTIR-8400S Shimadzu instrument by grounding the solid powder of the samples with KBr powder. Transmission electron microscopy (TEM) was performed on JEOL 1230 (acceleration voltage 120 kV), and JEOL 2010 (acceleration voltage 200kV) electron microscope using carbon-coated copper grid which were purchased from Electron Microscopy Sciences (EMS). Powder X-ray Diffraction (XRD) was done on Rigaku D/Max Ultima II Powder XRD instrument using Cu K α X-ray beam of wavelength 1.54 Å. Samples for XRD were prepared by drying the respective aggregates from chloroform dispersion on the glass slides. The data was collected by using 5 mm slit width and a scan rate of 0.5 degree/minute.

3) Synthesis of standard perylene tetracarboxylic acid (PTCA): The synthetic protocol developed by Ferrere et al. has been adopted for the synthesis of PTCA.¹ In a typical synthesis, 1 g of PTCDA powder (2.54 mmoles) was dispersed in ~500 ml water and 715 mg of KOH (12.74 mmoles) was added to this dispersion. This dispersion was heated on hot plate at 80°C for 1 h to form a homogeneous aqueous fluorescent green solution of K₄PTCA. The solution was allowed to cool and filtered so as to remove trace amounts of unreacted PTCDA, if any, and then 1M HCl was added dropwise to this fluorescent green solution at room temperature. There was precipitation of highly water immiscible PTCA in the solution. 1M HCl was kept on adding until all the K₄PTCA is converted into PTCA and there was complete disappearance of green fluorescence in the solution. This dispersion of PTCA was stirred at room temperature for further 1 h. This dispersion was then filtered using a 0.2 μ m pore size filter paper and given several washings with water until the pH of the washings was neutral. The reddish orange solid PTCA powder was dried under vacuum and kept away from heat. Yield = 99%. IR (KBr) ν_{max} 3618, 3122, 1774, 1696, 1586, 1410, 1300, 1296, 857 cm⁻¹.

4) Synthesis of 4-(dimethylamino) pyridinium 4-toluene sulfonate (DPTS): 61 g (0.5 moles) of 4-dimethylaminopyridine (DMAP) was dissolved in around 200 ml THF with vigorous stirring. A clear solution was obtained by occasionally sonicating and heating slightly with the heat gun. Then separately 95.11 g (0.5 moles) of p-toluenesulfonic acid monohydrate (PTSA.H₂O) was dissolved in around 200 ml THF with stirring, sonication and slight heating. Both these solutions are then cooled to room temperature. These two solutions are then mixed. The white aggregates of 4-(dimethylamino) pyridinium 4-toluene sulfonate (DPTS) immediately precipitates out of the solution. This precipitate is allowed to settle and filtered and dried under vacuum. Yield 100%.

5) Synthetic protocol for the conversion of PTCA to 1D nanofibers of PTCDA

(a) Chemical reaction of PTCA in DMF: 7 mg (16 μ moles) of PTCA powder was taken in a 40 ml glass vial. ~ 35 ml dimethylformamide (DMF) was added to this vial and the resulting solution was sonicated for 15 minutes to form a clear homogeneous orange solution. A bright yellow fluorescence was observed when the solution was excited with hand-held UV lamp (365 nm). Then 35 mg (116 μ moles) of DPTS was added to this vial and was dissolved in this solution with slight sonication. The resulting solution was then stirred on the stir plate using a small teflon covered stir bar (10 mm long). Then, 230 mg (0.28 ml, 1.78 mmoles) *N,N'*-diisopropylcarbodiimide (DIPC) was added dropwise to this stirring solution. After 30 minutes addition of DIPC, the initial homogeneous solution started becoming turbid indicating aggregation. After 24 h of stirring, the color of the dispersion became dark red and a very weak fluorescence was observed upon UV light excitation. This fluorescence did not disappear after stirring for additional few hours. Hence, the reaction was stopped at this stage.

(b) Removal of unreacted PTCA: After the reaction the stirring was stopped and the resulting dispersion was allowed to stand undisturbed for 12 h. All the red colored aggregates settled at the bottom of the vial leaving behind almost colorless layer of DMF on the top which when observed under UV light shows slight yellow fluorescence. This top layer of DMF was discarded carefully using a pipette and the lower settled portion of aggregates was again dispersed in DMF. The aggregates were again allowed to settle and the top portion of DMF was again discarded carefully using a pipette.

(c) Removal of DMF, DPTS, DIPC and dispersion of aggregates in dichloromethane: The settled aggregates after removal of top layer of DMF were then dispersed in dichloromethane (CH_2Cl_2). The vial was left undisturbed for 4 h. Again the settling of aggregates was observed and the upper top portion of CH_2Cl_2 was discarded and fresh CH_2Cl_2 was then added for second extraction. Totally, two such extractions were carried out so as to remove all the DMF, DPTS and DIPC from the system and all the fibers are finally suspended in CH_2Cl_2 .

6) Quenching of fluorescence from PTCA upon conversion to PTCDA

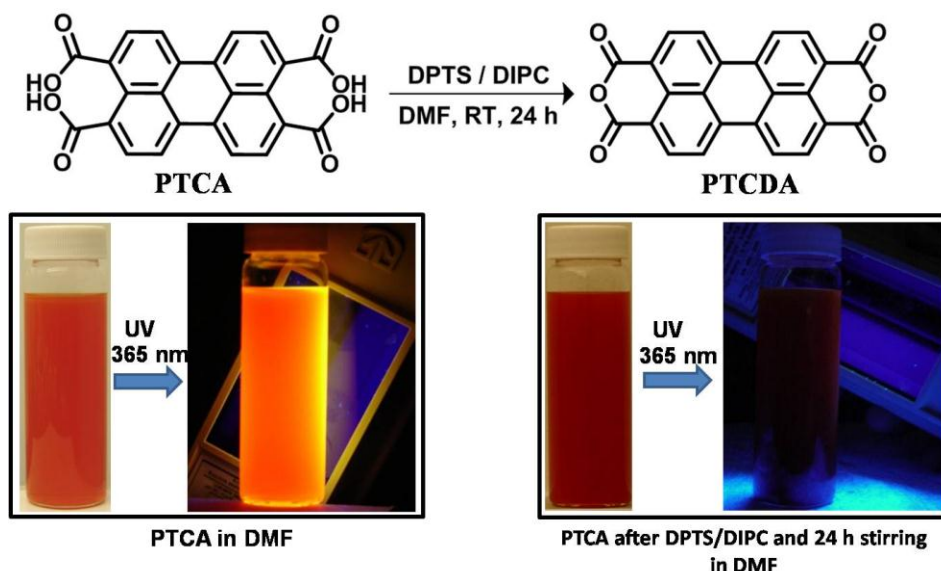
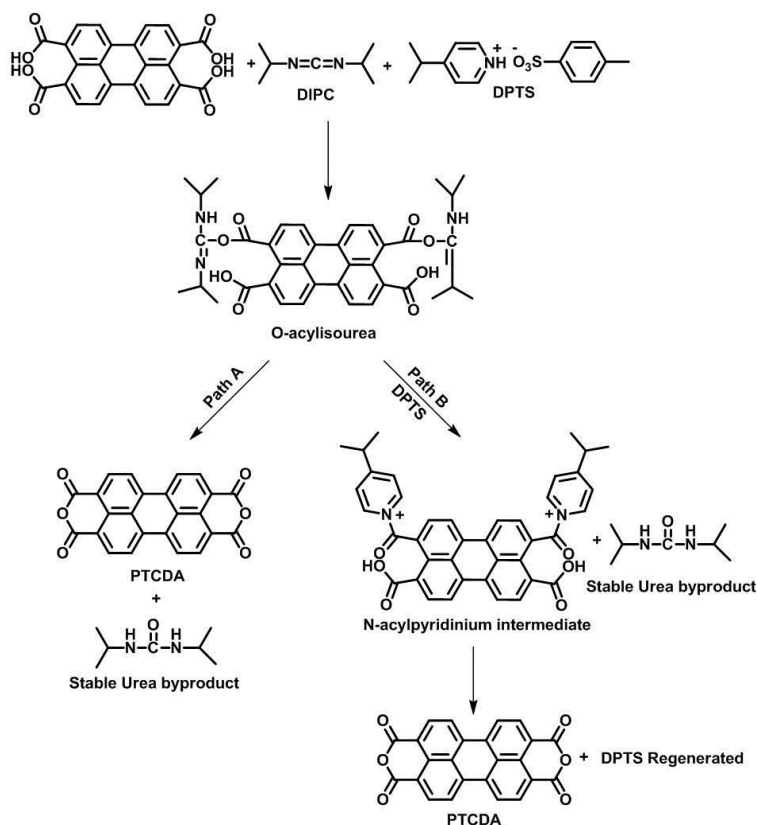


Fig. S1. The precursor, PTCA, is soluble in DMF which exhibits bright yellow fluorescence upon excitation with a hand held UV-lamp. As the reaction progresses there is significant quenching of the fluorescence from PTCA as it gets consumed and converted to aggregates comprised of PTCDA molecules. After 24 h almost no fluorescence can be observed.

7) Formation of stable urea by-product and the final conversion to PTCDA

Scheme S1. Plausible reaction mechanism



Perylene-3,4,9,10-tetracarboxylic acid (PTCA) can react with 1,3-diisopropylcarbodiimide (DIPC) in presence of 4-(dimethylamino) pyridinium 4-toluene sulfonate (DPTS) leading to the formation of o-acylisourea intermediate. This intermediate can react via two paths. **Path A:** O-acylisourea groups can undergo intramolecular reaction with their neighboring carboxylic acid groups leading to formation of perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) and stable urea product. **Path B:** N-acylpyridinium intermediate can be formed from O-acylisourea in presence of DPTS, which undergo reaction with their neighboring carboxylic acid groups leading to PTCDA and stable urea product.

8) TEM sample preparation: The samples for TEM were prepared by casting a droplet of this DMF dispersion on the TEM grid placed. The DMF spreads on filter paper and the aggregates remain on the TEM grid. The TEM sample from dispersion of fibers in dichloromethane was also prepared in the similar way.

9) Morphology of fibers of PTCDA:

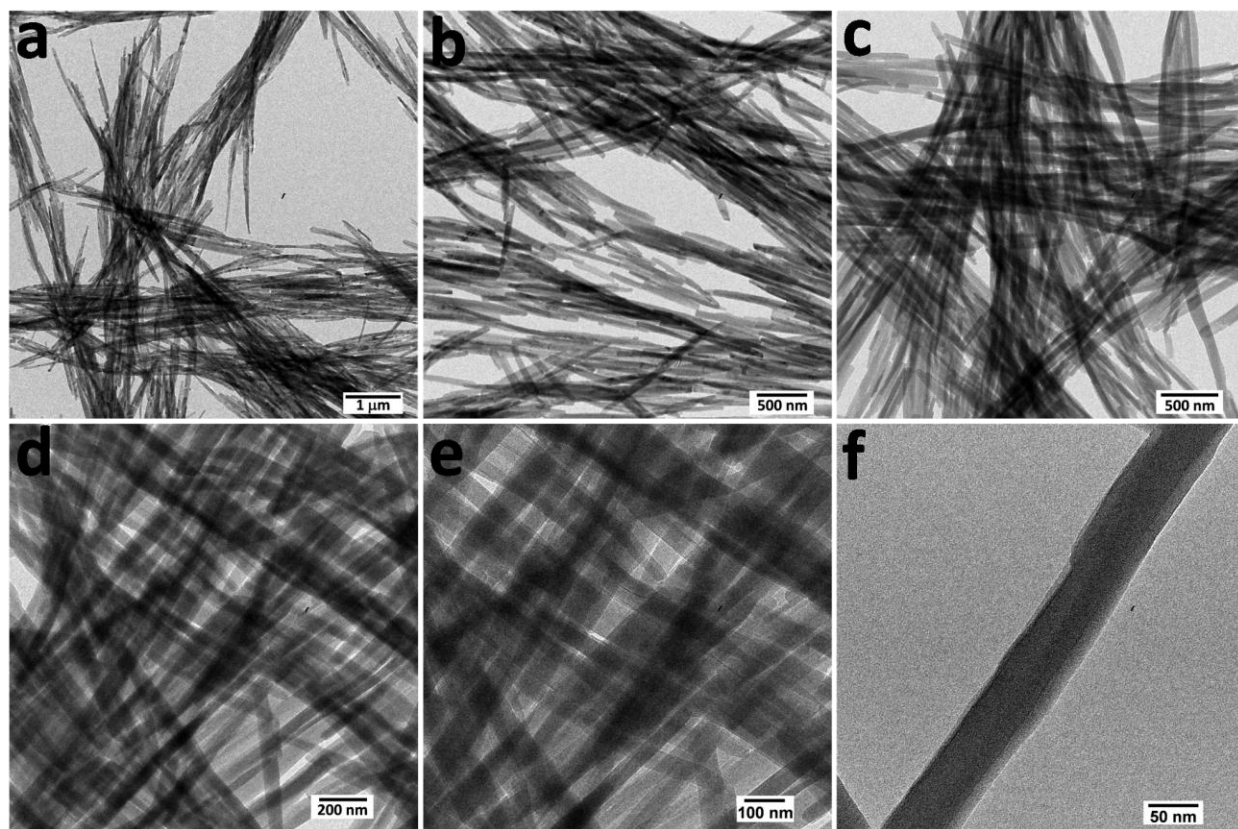


Fig. S2. More TEM images of fibers of PTCDA from DMF dispersion.

10) Stability of fibers in dichloromethane (CH_2Cl_2):

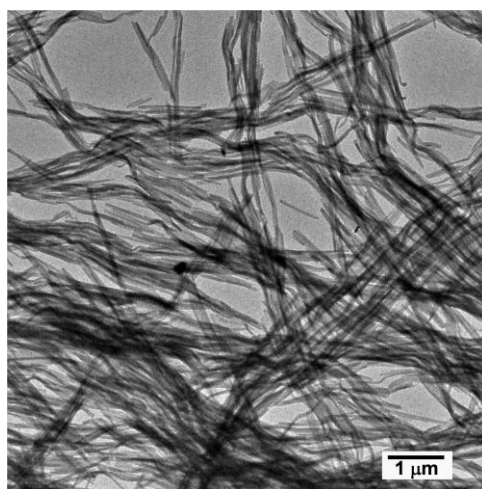


Fig. S3. TEM image of fibers obtained by casting the fibers dispersed in dichloromethane. The morphology of the fibers remains the same as those observed in DMF.

11) Stability of fibers towards potassium carbonate:

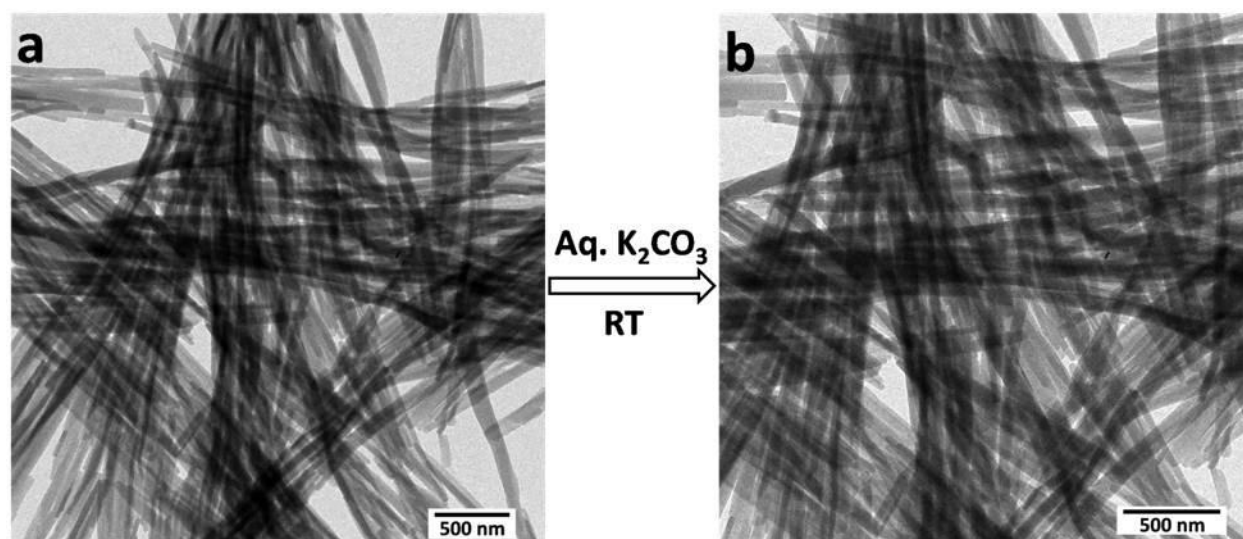


Fig. S4. TEM image of fibers of PTCDA (a) before and (b) after treating with aqueous solution of K₂CO₃. For this purpose, a particular region on the TEM grid was identified and was imaged. This grid was then dipped in aqueous solution of K₂CO₃ for at least 2 minutes. The grid was then dried and then the same region was identified and imaged again. There was no destruction of fibers and the morphology of the fibers remained intact. This further proved that the PTCA was converted to fibers of PTCDA after the chemical reaction.

12) Mass spectroscopic analysis: Samples were analyzed by chemical ionization on a Waters Autospec Premier double-focusing magnetic sector mass spectrometer using methane as the reagent gas and internal calibration with perfluorokerosene. Solid samples were introduced using a direct exposure technique: a small amount of solid material was packed into a glass melting point capillary, which was scored approximately 20 mm from the closed end and placed upright into a coil of 0.006" tantalum wire mounted on an insertion probe. The capillary was broken along the score, and the probe/capillary assembly was inserted into the source. Approximately 1.6 amps of current were run through the tantalum wire to heat the capillary and vaporize the sample. (Courtesy: Dr. Karin Keller, UT-Austin).

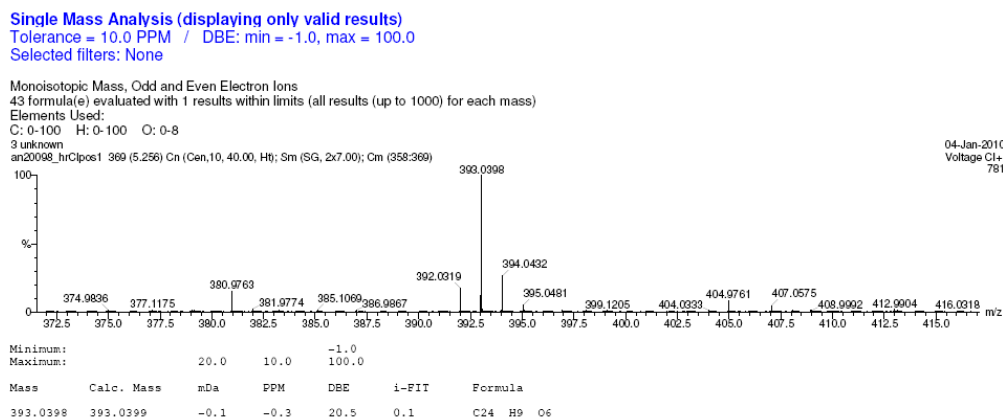


Fig. S5. Mass spectra of the PTCDA-fibers. The spectral features match well with the standard PTCDA powder shown below in Fig. S7.

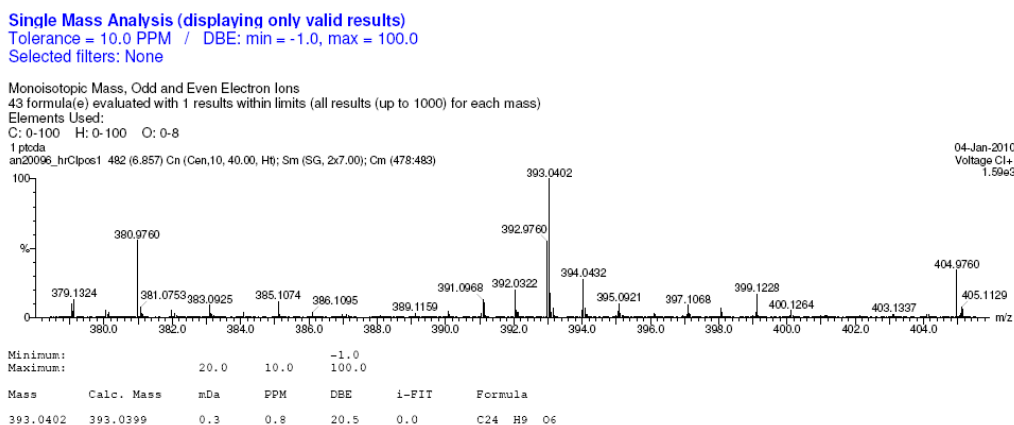


Fig. S6. Mass spectra of the standard commercially available PTCDA powder. A 100% relative abundance peak for m/z at 393 corresponds to $(\text{PTCDA}+\text{H})^+$ as expected for the standard PTCDA powder (m/z calculated = 392.32).

13) Selected area electron diffraction pattern obtained from a single PTCDA nanofiber:

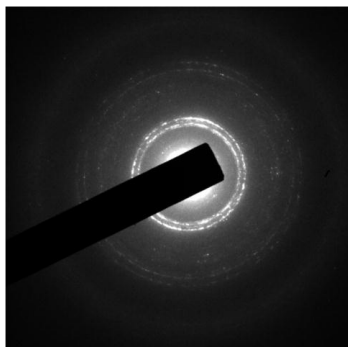


Fig. S7. Selected area e-diffraction pattern obtained from a single PTCDA nanofiber.

14) Supporting References

- (1). S. Ferrere, A. Zaban and B. A. Gregg, *J. Phys. Chem. B*, 1997, **101**, 4490.