

## Electronic Supplementary Information (ESI)

### ***In-situ* preparation of Fluorescent Polyaniline Nanotubes Doped with Perylene Tetracarboxylic Acids**

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## 1) Experimental Section

### Materials

Aniline monomer (Merck Chemicals) was distilled under reduced pressure. Ammonium persulphate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , APS (Rankem chemicals) was used as a radical oxidant for PANI. 3,4,9,10-Perylenetetracarboxylic dianhydride, 1,4,5,8-Naphthalenetetracarboxylic dianhydride, Benzene 1,2,4,5-tetracarboxylic acid and cyclohexane tetracarboxylic acid were purchased from Aldrich. KOH, Hydrochloric acid and DMF were purchased from local commercial sources as analytical pure reagents. All aqueous solutions were prepared with 18M $\Omega$  water obtained by the purification of deionized water with a Millipore Milli-Q system.

### Apparatus and characterizations

The FTIR spectra were recorded in an FTIR-8400S instrument (Shimadzu) using the KBr pellets of the samples. Raman was recorded with a Renishaw Raman Microscope 1000 operating at 785 nm with a charge-coupled device detector. The UV-Vis spectra of all samples were studied with Hewlett-Packard UV-Vis spectrophotometer (model 8453). Fluorescence studies of all samples were carried out in a Horiba Jobin Yvon Fluoromax 3 spectrometer. XRD of the all samples were measured on Bruker AXS diffractometer (D8 advance) using  $\text{CuK}\alpha$  radiation ( $\lambda=1.54 \text{ \AA}$ ), a generator voltage 40 kV and current 40 mA. Samples were scanned in the range of  $2\theta = 5^\circ - 40^\circ$  at the scan rate of 0.5sec/step with a step width of  $0.02^\circ$ . Confocal laser scanning microscope (CLSM) images were taken with Leica laser scanning confocal microscope (Leica confocal system TCS-SP2 instrument) equipped with an ArKr laser under 100X magnification at an excitation wavelength 520nm. Fluorescence lifetimes were measured using a time-correlated single-photon-counting fluoremeter (Fluorecule, Horiba Jobin Yvon). Average fluorescence lifetimes for exponential iterative fitting were calculated from the decay times and the relative amplitudes.

### 2.a) Synthesis of PTCA:

3,4,9,10-Perylene tetracarboxylic dianhydride (0.39 g, 1 mmol) was dissolved in 20 ml of 5% aqueous solution of KOH under stirring at 60–70°C. After cooling to room temperature, 0.1 M HCl was added drop-wise under stirring till the pH value was 5–6. The precipitate formed was filtered and dried in vacuum at room temperature to yield 0.35 g of red powder (yield 90.0%).<sup>1</sup>

<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): 8.61-8.63 (d, 4H), 8.02-8.04 (d, 4H).

MASS: (MALDI-TOF, dithranol): 430.2 (M<sup>+</sup>+H).

FTIR:  $\nu$ C=O stretch (1693), C–O stretch (1292), O–H bends (1492), and O–H stretch(2987), C=C(perylene core) 1589.23 cm<sup>-1</sup>; C–H (perylene core) 802.3, 748.33 cm<sup>-1</sup>.

**b) Synthesis of NTCA:** Naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (1.0 g, 3.73 mmol) was dissolved in 50 ml of aqueous solution of NaOH under stirring at room temperature. HCl(0.1 M) was added drop-wise under stirring at low temperature till the pH value was 5–6. The precipitate formed was filtered and dried in vacuum at room temperature. Recrystallised the crude product 2-3 times from aqueous-alcoholic solution, 0.98 g of white powder was obtained. (yield 87.0%).<sup>2</sup>

<sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O): 8.58 (d, 4H).

MASS: (HR-MS): 304.1 (M).

FTIR:  $\nu$ C=O stretch (1710), C–O stretch (1288), and O–H stretch (3444),C=C(naphthalene core) 1581.52 cm<sup>-1</sup>; C–H (naphthalene core) 812, 769.54 cm<sup>-1</sup>.

### 3) Synthesis of PANI/PTCA:

Aniline and PTCA at different ratio were dissolved in distilled water by constant stirring for 1h at room temperature. The reaction mixture was cooled to 10°C. An aqueous solution of APS was added over 30 min and the mixtures was allowed to stand for 24 hrs at low temperature (Table-S1). The resulting PANI precipitate was washed several times with water and methanol. Finally the product was dried under vacuum at room temperature for 24 hrs to receive PANI/PTCA nanostructures.

**Table S1: Preparation of Polyaniline using different PTCA concentration.**

Set	Aniline (An) [conc., mmol]	PTCA [conc., mmol]	[PTCA] : [An]	APS (mmol)	[An] : [APS]	Yield (mg)	Avg. fibers Dia.(nm)
a	102mg [1.1]	120mg [0.28]	<b>0.25:1</b>	250 mg [1.1]	1:1	154	185
b	102mg [1.1]	48 mg [0.11]	<b>0.10:1</b>	250 mg [1.1]	1:1	105	175
c	102mg [1.1]	4.8 mg [0.01]	<b>0.01:1</b>	250 mg [1.1]	1:1	72	154

**Molecular weight of PANI** (using viscometry method): ~7000

**Method:** PANI composites ([PTAC]/[An] = 0.25) were treated with aq. NH<sub>4</sub>OH to receive PANI-EB sample that were dissolved in concentrated H<sub>2</sub>SO<sub>4</sub> to prepare 1 w/w % solutions. The solutions were then centrifuged at 3000 rpm for 10 min and the liquid phase was carefully removed. Completely dissolved polyaniline were used for viscosity measurements. The reduced viscosities of these samples were determined at 25°C in concentrated sulphuric acid using an Ubbelohde viscometer, average molecular weights were calculated using the Mark–Houwink relation (1).<sup>3</sup>

$$[\eta] = K \overline{M}_v^\alpha \text{ ----- (1)}$$

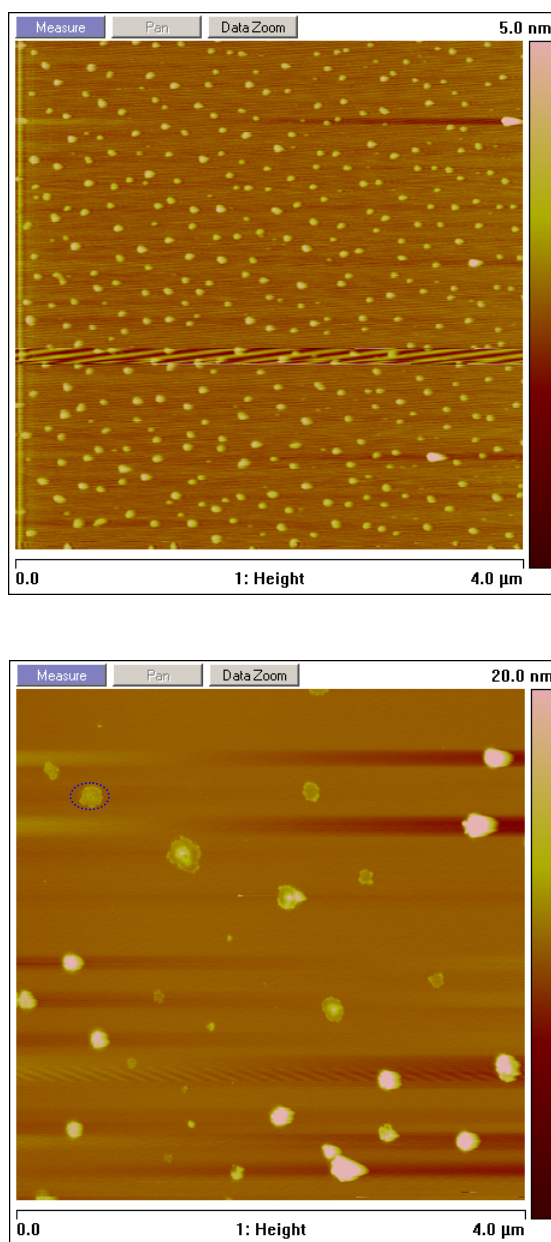
Where  $K = 1.95 \times 10^{-6}$  and  $\alpha = 1.36$  for PANI.<sup>3</sup>

The reduced viscosity  $\eta_{red}$  (dL/g) was determined using the viscometer drain times:

$$\eta_{red} = \frac{t - t_0}{ct_0} \text{ ----- (2)}$$

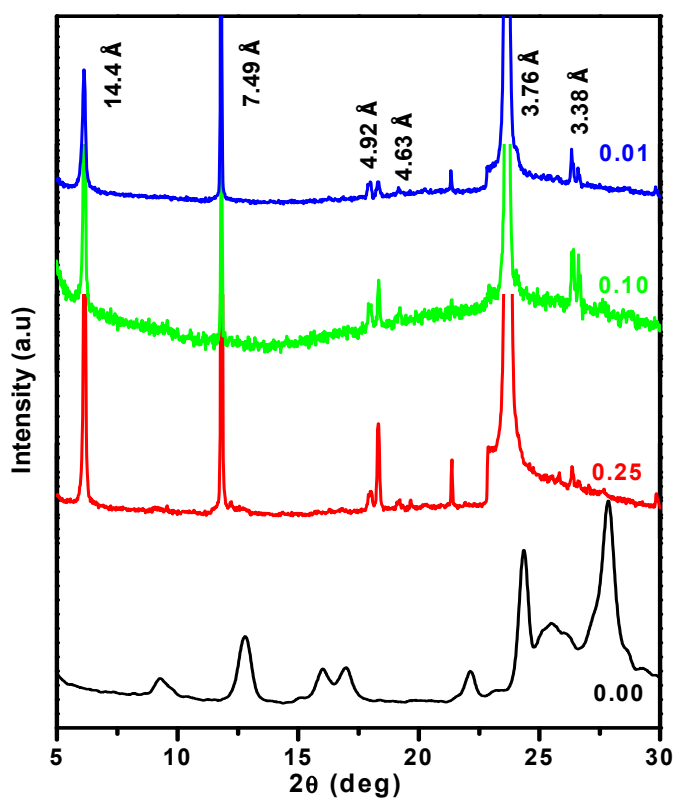
where  $t_0$  was the viscometer drain time of sulfuric acid only, 't' was the viscometer drain time for a polyaniline solution of a known concentration (s), and 'c' was the known polyaniline concentration (g/dL).  $\eta_{red}$  was then plotted versus the polyaniline concentration for four concentrations, and a linear extrapolation to zero concentration produced the value of  $[\eta]$  (0.332 dL/g). After putting the values of  $[\eta]$ , K and  $\alpha$  in the Mark–Houwink equation (1), the viscosity average molecular weight of the PANI was come out ~7000.

#### 4) AFM topology of PTCA and PTCA/ Aniline aggregates



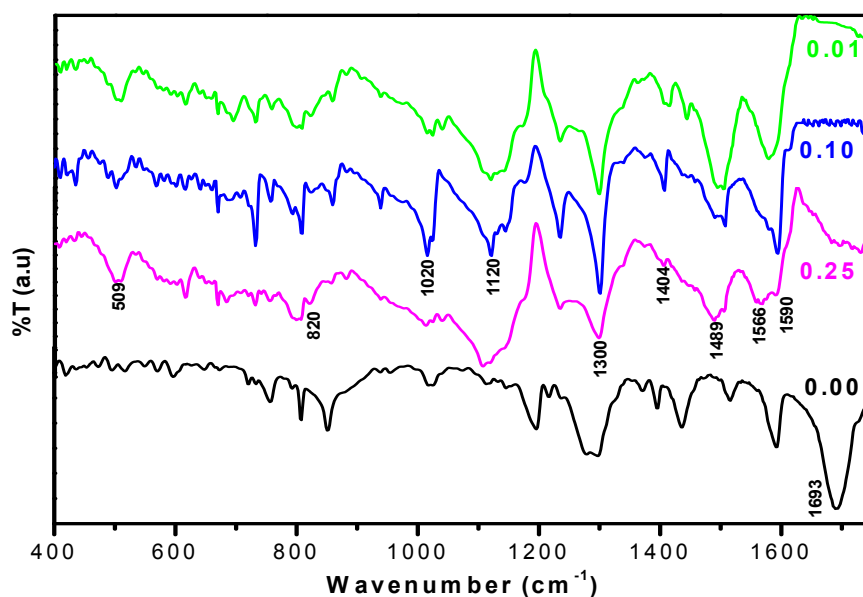
**Fig.S1.** AFM topology of dispersed PTCA (top) and PTCA/aniline ( $[PTCA]/[An] = 0.01$ ) aggregates in water on freshly prepared mica surface under identical experimental condition. AFM studies reveal the formation of PTCA vesicle (indicated by blue circle) in solution in presence aniline whereas PTCA only in water forms the random blobs

### 5) X-ray diffraction:



**Fig.S2.** X-ray diffraction studies of PANI/PTCA synthesized using different molar ratios of PTCA to aniline.<sup>4</sup>

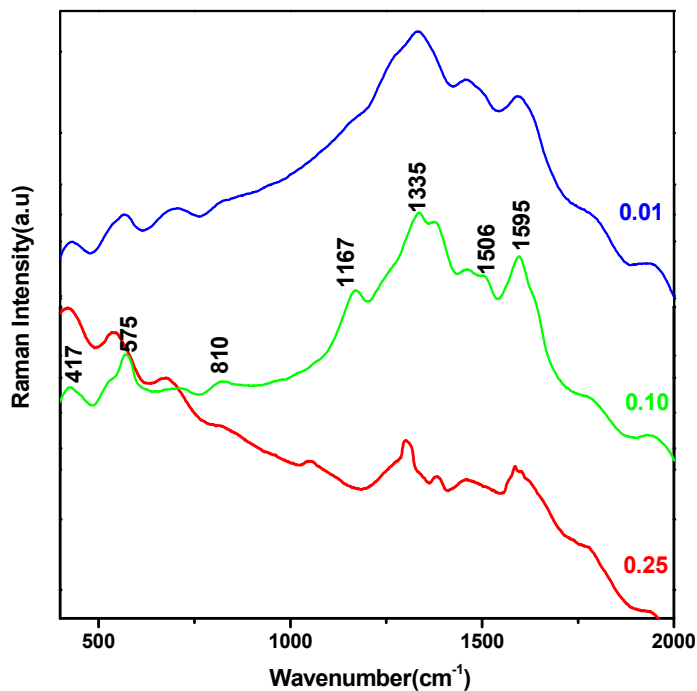
## 6) FT-IR studies:



**Fig.S3.** FT-IR-spectral analysis of PANI/PTCA synthesized using different molar ratios of PTCA to aniline. The characteristic stretching vibrations at 1556 cm<sup>-1</sup> ( $\nu_{C=C}$  for quinoid rings), 1489 cm<sup>-1</sup> ( $\nu_{C=C}$  for benzenoid rings), at 1300 cm<sup>-1</sup> ( $\nu_{C-N}$  for the secondary aromatic amine), 1120 and 820 cm<sup>-1</sup> ( $\nu_{C-H}$  aromatic in plane and the out of plane deformation for the 1,4-disubstituted benzene) support the formation of PANI. The presence of peak at 1590 cm<sup>-1</sup> ascribes to perylene core.

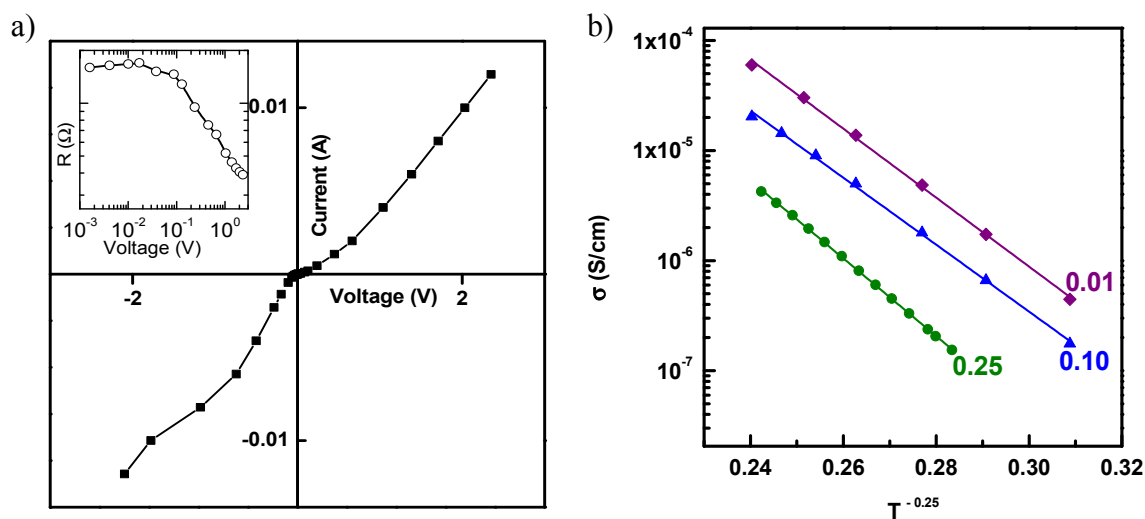


## 7) Raman Studies



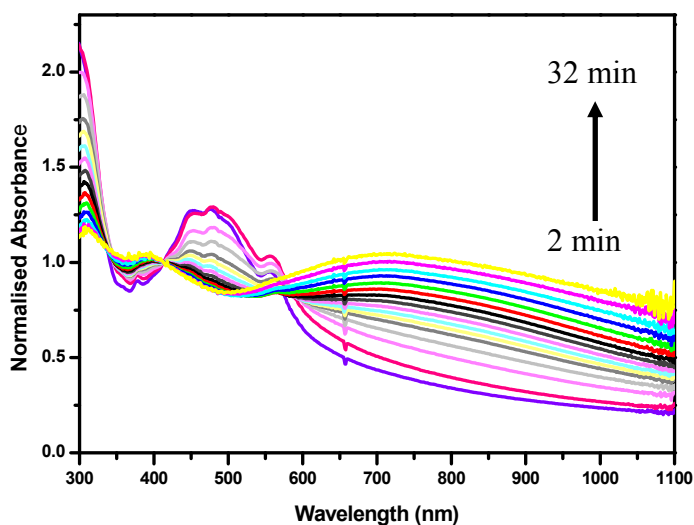
**Fig. S4.** Raman spectra of PANI/PTCA composites synthesized using different molar ratios of PTCA to aniline. The bands at 1506, 1335 and 1167 cm<sup>-1</sup> corresponding to the N-H stretching mode, the C-N stretching mode of the cationic radical and the C-H bending vibration are also observed. The bands at 417 and 810 cm<sup>-1</sup> are related to the C-H deformation.

## 8) I-V and temperature dependent conductivity results



**Fig. S5.** (a) I-V curve of the PANI/PTCA nanocomposites ([PTCA]/[An] = 0.25). Inset shows the log-log plot of resistance vs. voltage. Both the curves show non-linear electrical characteristics of the sample. (b) Temperature dependent conductivity plot of the samples, showing variable range hopping conductivity.<sup>5</sup>

### 9) Time dependent UV-Vis spectra of PTCA/PANI mixtures

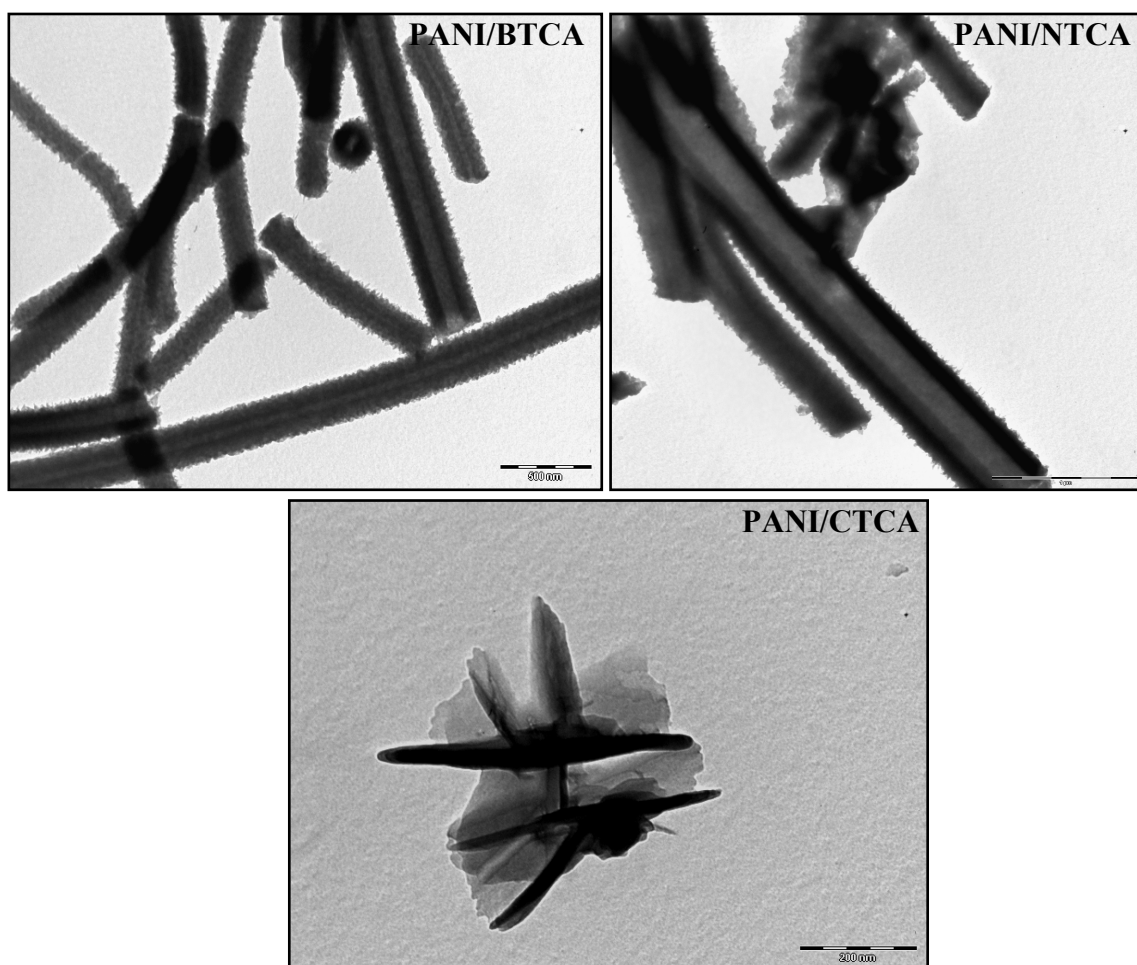


**Fig. S6** Time dependent UV-Vis spectra of PTCA/aniline mixtures ( $[PTCA]/[An] = 0.01$ ). The reaction was carried out in a temperature-controlled 1cm quartz cuvette at 25 °C. Spectra clearly indicate that the formation of PANI takes place using PTCA by insitu polymerisation method. The spectra shows that intensities of both bands (above 350 nm ascribed to the  $\pi$ - $\pi^*$  transition in the benzenoid rings of PANI and a dominant band at around 840 nm representing  $\pi$ -polaron transition of quinoid rings on PANI chains) are gradually increasing with increasing time. These two bands are the characteristics band of polyaniline.<sup>6</sup>

**10) Table S2:** Time resolved fluorescence data of PTCA and PANI/PTCA composites. The average life time (ns) and their amplitude are taken from Fig.3d.

<b>Sample name</b>	<b><math>\langle\tau\rangle</math> (ns)</b>
PTCA only	3.54
PANI/PTCA <b>0.25</b>	5.33
PANI/PTCA <b>0.10</b>	5.10
PANI/PTCA <b>0.01</b>	4.07

11) TEM observations:



**Fig. S7.** TEM images of PANI/BTCA, PANI/NTCA and PANI/CTCA composites.

## 12) Reference:

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