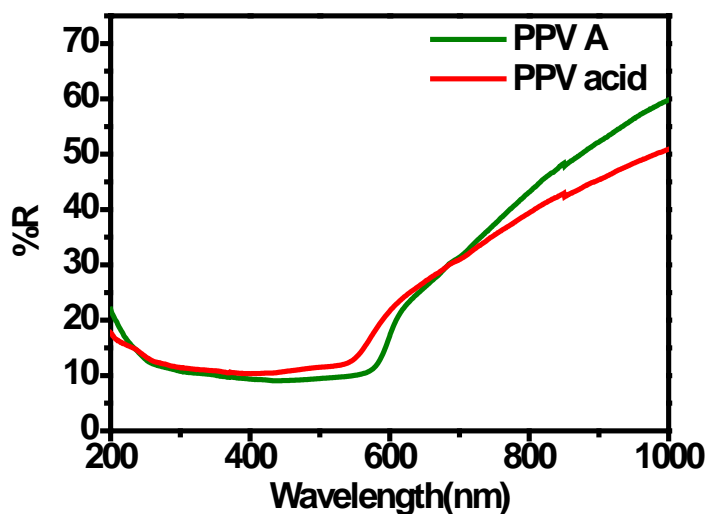


Electronic Supplementary Information (ESI)

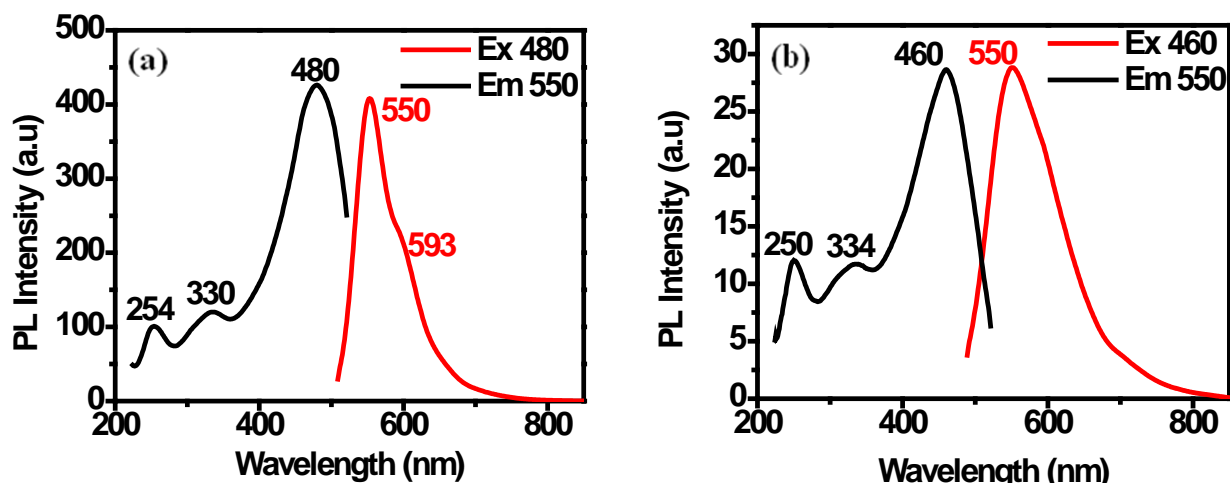
ESI-1. Diffuse reflectance spectra (DRS):

DRS were recorded for the **PPV A** as well as the **PPV acid** in their powder form and data is shown in Fig.1. These spectra exhibited broad absorption of the polymer with a small tail above 600 nm in the case of **PPV acid** as well as small blue shift in the absorption maxima of **PPV acid** from 460 nm (**PPV A**) to 450 nm in accordance with UV-Vis spectra discussed in the text.



DRS spectra of **PPV A** and **PPV acid**

ESI- 2. Photoluminescence spectra (PL):



Photoluminescence spectra of (a) PPV A and (b) PPV acid

Fig 3(a) and Fig 3(b) showed the PL spectra of the **PPV A** and the **PPV acid**, respectively. Both **PPV A** and **PPV acid** showed emission at around 550 nm (2.254 eV) for the excitation maxima at 480 nm (~ 2.583 eV) for **PPV A** and 460 nm (~ 2.695 eV) for **PPV acid**, respectively. In the case of **PPV acid** the e-h binding energy is ~0.441 eV while for the **PPV A** it is ~0.329 eV. This showed a small increase in the band gap energy after modification because of the electron withdrawing effect of -COOH and -CN groups, which corroborates with the UV-Vis spectra (Fig 2), and the band diagram shown in Fig 4 in the manuscript.

ESI- 3. *J-V* characterization of the polymer PPVA, PPV CHO and PPV acid

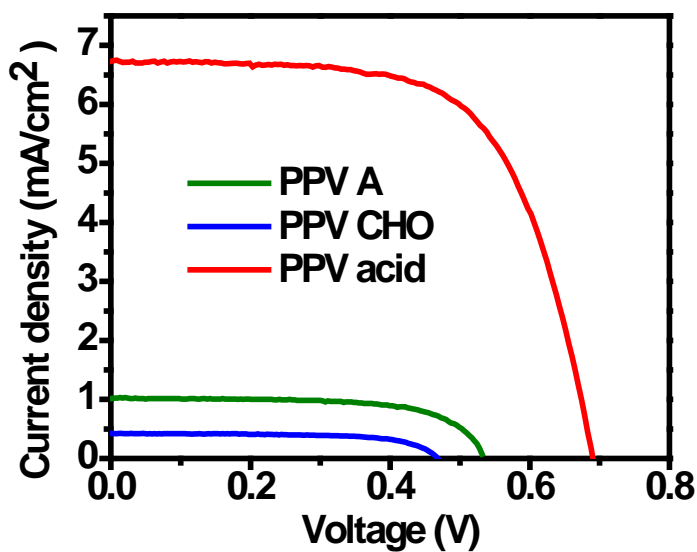


Fig. 3a. Solar cell characteristics for the case of P25 Degussa TiO₂ nanoparticles.

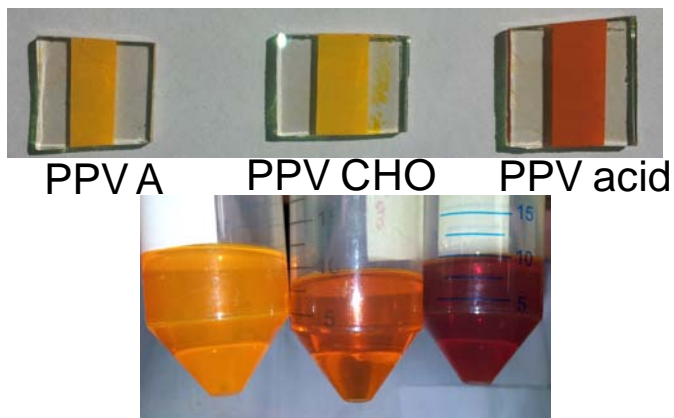
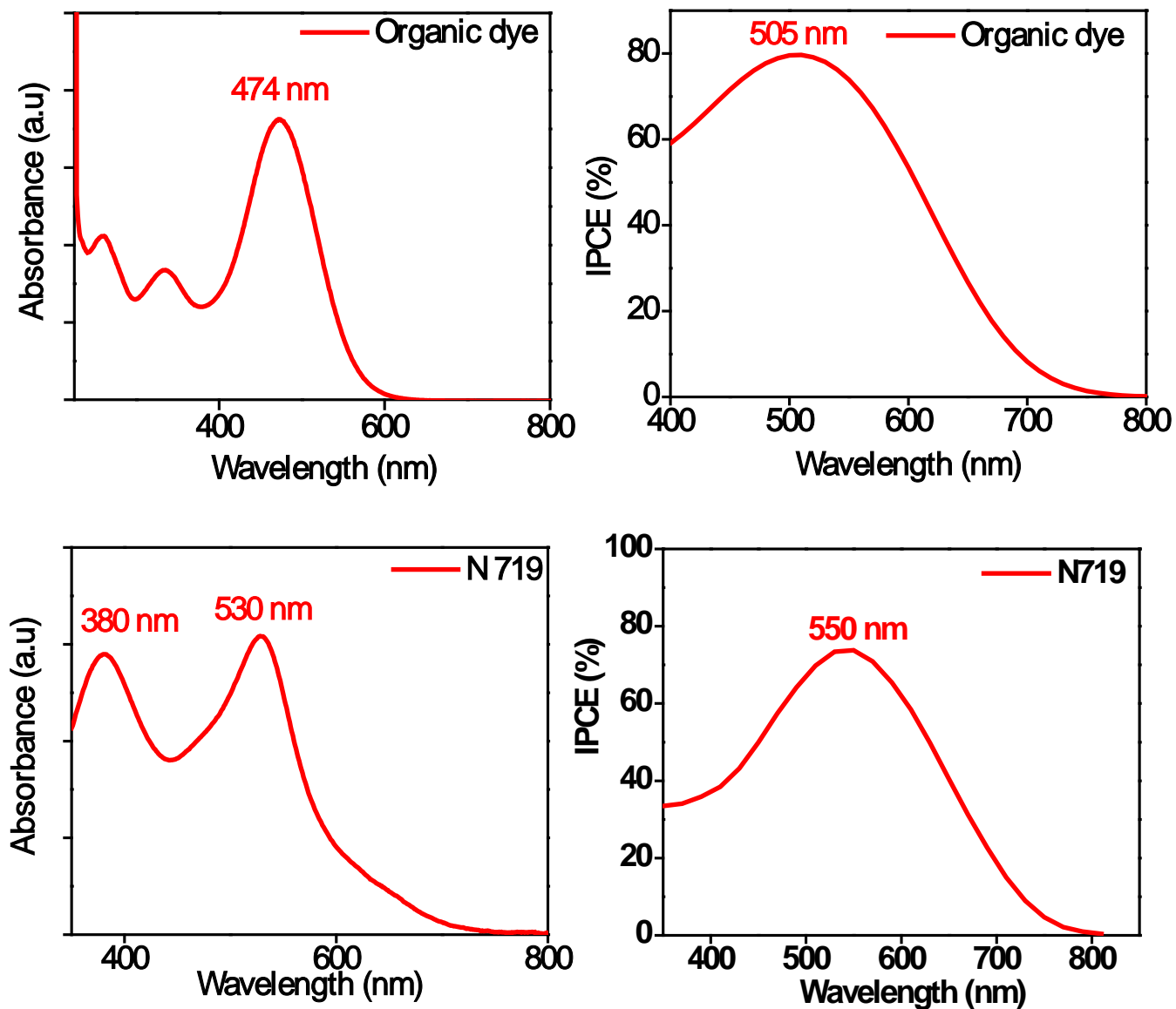


Fig.3b. (Top) TiO₂ films sensitized with PPV A, PPV CHO and PPV acid by dipping in their chloroform solutions (Below).

ESI-4. UV and IPCE data for an organic dye and the N719 dye.

Both dyes show red shift in IPCE as compared to UV absorption maximum.



UV and IPCE data of organic dye and standard N719 dye.

ESI-5. Atomic force microscopy (AFM) and Scanning Tunneling Microscopy (STM) studies on bare and PPV-acid dye loaded TiO₂ thin film.

In order to understand and elucidate the nature of adsorption of PPV-acid on the TiO₂ surface, 200 nm films of anatase TiO₂ were grown by pulsed laser deposition (PLD) on FTO/glass substrates, and these were studied by Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) techniques without and with adsorbed PPV-acid dye molecules. The reason for using PLD films was to ensure reasonable level of surface smoothness to enable proper implementation of the said characterization methods.

In AFM study first the force-distance measurements were performed using a tip with a force constant of about 1 N/m (Please see Fig. ESI-5(a) below). In all the force-distance curves recorded at four different points it is clearly observed that the difference between the sharp dip in the tip approach curve and tip retract curve is not the same for the bare TiO₂ and dye-loaded TiO₂. In case of dye-loaded TiO₂ the required force to detach the tip is higher as compared to bare TiO₂. This increase in force can be attributed to the elastic stretching of polymer or dye chains adsorbed on to the TiO₂ Surface (Ref. 1 and references therein).

In Fig.ESI-5b (next page), we compare the STM based I-V (current voltage) curves taken on bare TiO₂ and dye-loaded TiO₂. These I-V data clearly reveal that the electronic barrier in the case of dye-loaded TiO₂ is higher as compared to bare TiO₂. The STM topographic images (Fig. ESI-5c on the next page) also indicate a uniform distribution of dye molecules on the TiO₂ surface, and more importantly, their contribution to electronic transport exhibits more noise, as expected.

Reference: S. Kale , A. Kale, H. Gholap, A. Rana, R. Desai, A. Banpurkar, S. Ogale, P. Shastry, *J Nanopart Res*, 2012, **14**, 732.

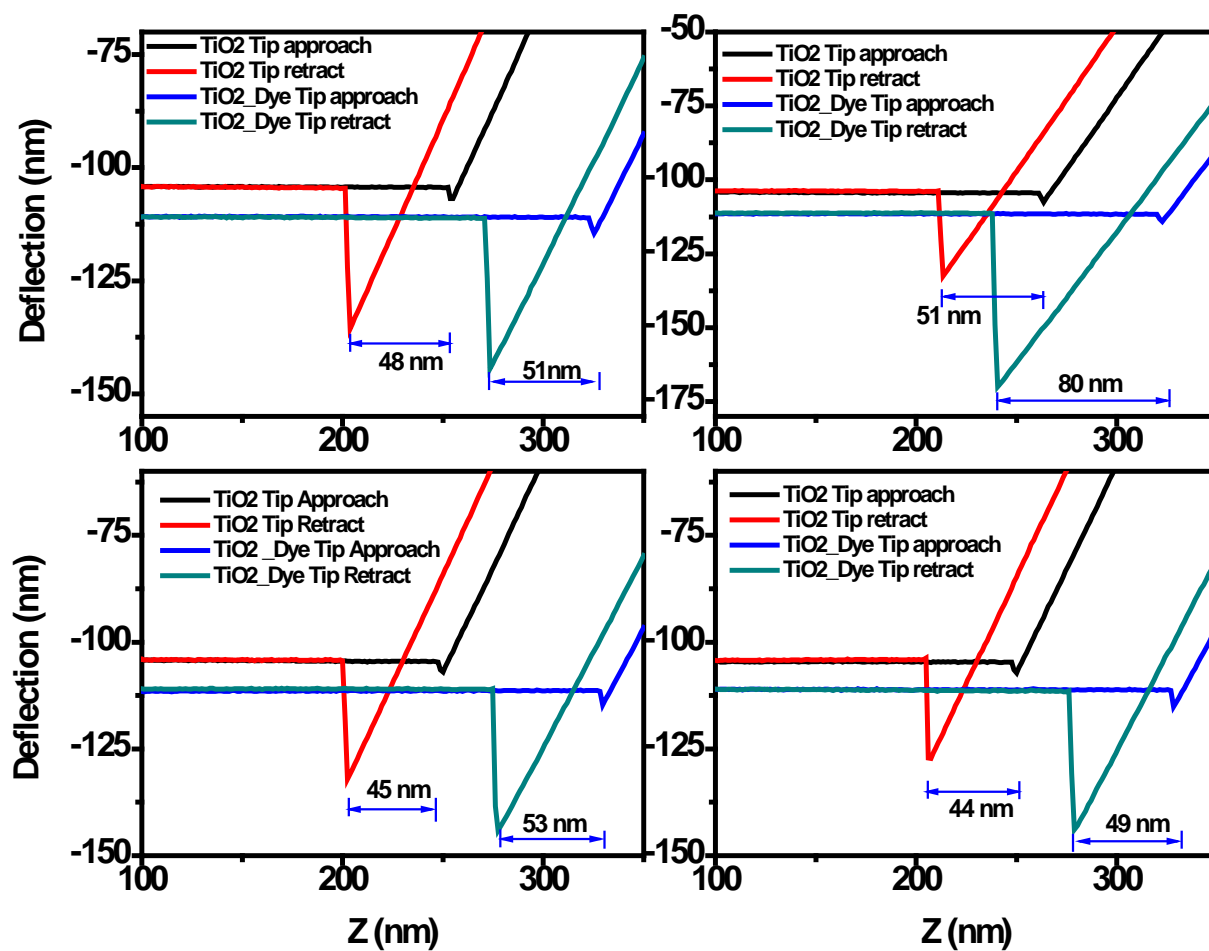


Fig. ESI 5(a): Force-distance curves taken at four different locations on bare and PPV acid dye-loaded TiO₂ surface.

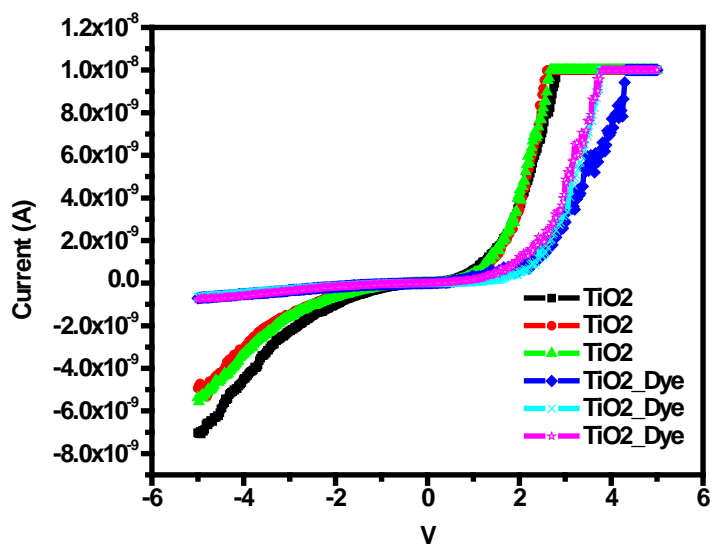


Fig. 5 (b): STM Spectra taken on bare TiO₂ and **PPV acid** dye loaded TiO₂

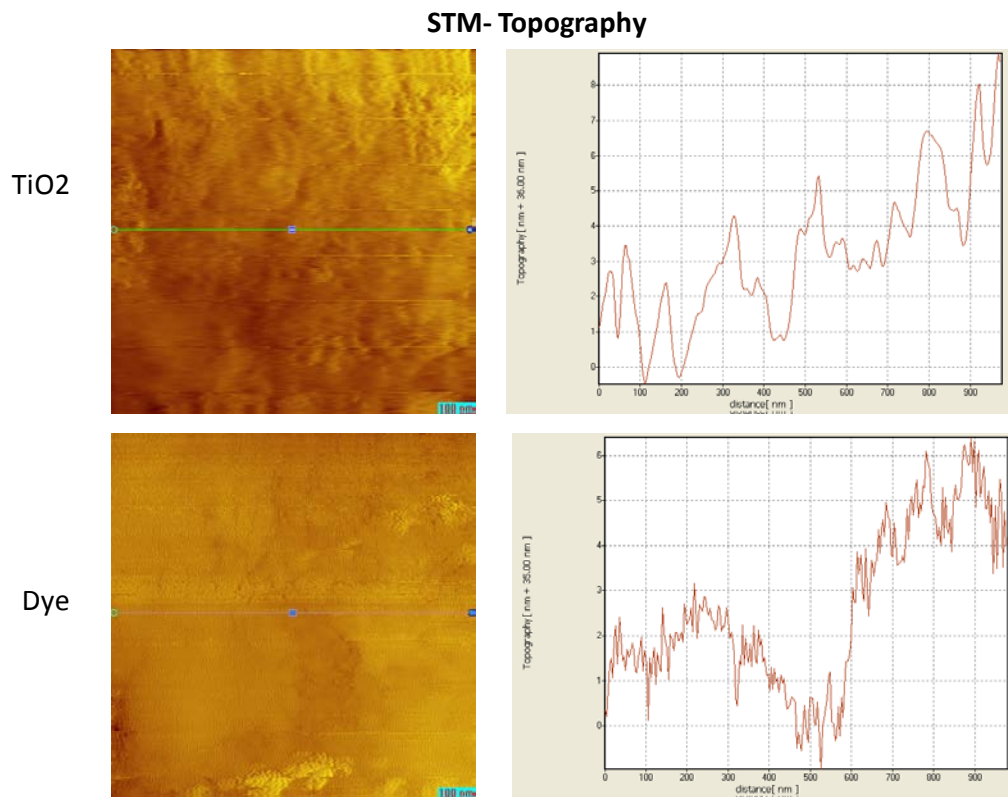


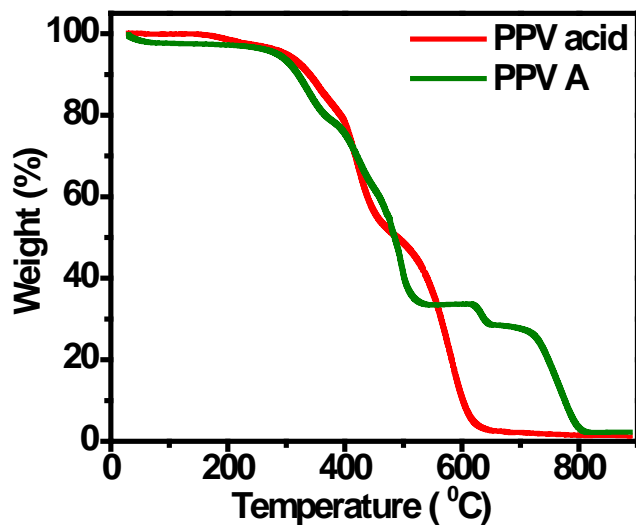
Fig. ESI 5 (c): STM Topography and line scan on bare TiO₂ and **PPV acid** dye loaded TiO₂

ESI-6. Thermal stability of PPV-acid polymeric dye:

To investigate thermal stability of DSSC made with the **PPV acid** and traditionally used **N719** dye, heat treatment studies were performed on the sensitized TiO₂ based cells. The results are shown in Fig. 7. The solar cells were subjected to heating at different temperatures for 30 min, allowed to cool and then efficiency was measured at room temperature. For Ru based **N719** dye the power conversion efficiency started decreasing when annealed above 50°C while in case of **PPV acid** it is stable for heat treatment up to 100°C. The Ru based dye showed drop in the efficiency from 5% to less than 0.3% at 200°C after interval of 30 min at every annealing step from room temperature to 200°C. In the case of **PPV acid** total the conversion efficiency remained stable up to 100°C and gradually started decreasing from 2.8 % at 100°C, 1.8% at 200°C to 0.9% at 300°C. This showed that the **PPV acid** is thermally stable as compared to Ru based dyes at higher temperature which was in agreement with the TGA data of the polymer.

ESI -7. Thermogravimetric Analysis of PPV-A and PPV- acid:

Thermogravimetric analysis (TGA) was performed in air for the **PPV A** and the **PPV acid** and thermograms are shown in Fig.2. Both **PPV A** and PPV acid are stable up to $\sim 250^{\circ}\text{C}$ (T_{10} value).



TG curves of **PPV A** and **PPV acid**