

Supplementary information for
Charge transport in a liquid crystalline triphenylene polymer
monolayer at air-solid interface

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1. Energy band diagram

In a M-I-M junction, the barrier height (ϕ) can be estimated from the HOMO and LUMO values of triphenylene moiety, 5.38 eV and 1.68 eV respectively (Reference 21). The energy level diagram (Fig. S1) indicates the various energy levels involved in M-I-M junction formed by gold substrate -PHAT monolayer- platinum CSAFM tip. The work functions for platinum and gold are 5.65 eV and 5.1 eV respectively (Reference 26).

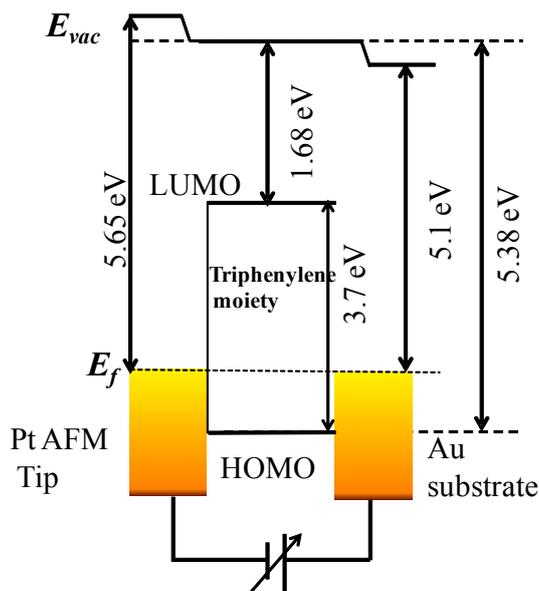


Fig. S1 Energy diagram showing various energy levels for triphenylene moiety with respect to the Fermi levels of platinum and gold electrodes in a junction. The barrier height (ϕ) at $V=0$ is given by $3.7 - (5.38 - 5.1) = 3.42$ eV.

In the absence of applied voltage bias ($V=0$), the energy level diagram gives the barrier height to be 3.42 eV. This is higher than the ϕ value of 1.22 eV determined by our I-V measurements. The difference in the barrier height between that given by the energy diagram and from our experiments can be attributed to:

1. With an applied bias voltage, the interactions of PHAT with Pt and Au electrodes will alter the energy levels.
2. The HOMO-LUMO levels drawn here are for triphenylene moieties in general. The polymer under consideration, PHAT consists of alkyl chains and discs of triphenylene moieties adjacent to one another. The π - π interactions in the columnar structures of the PHAT molecules effect the HOMO-LUMO levels.

2. Liquid crystalline property of PHAT

Polarising optical microscope (POM) images for the monomer 2,6-dihydroxy-3,7,10,11-tetraalkoxy-triphenylene and the polymer derived from it are shown in Fig. S2.

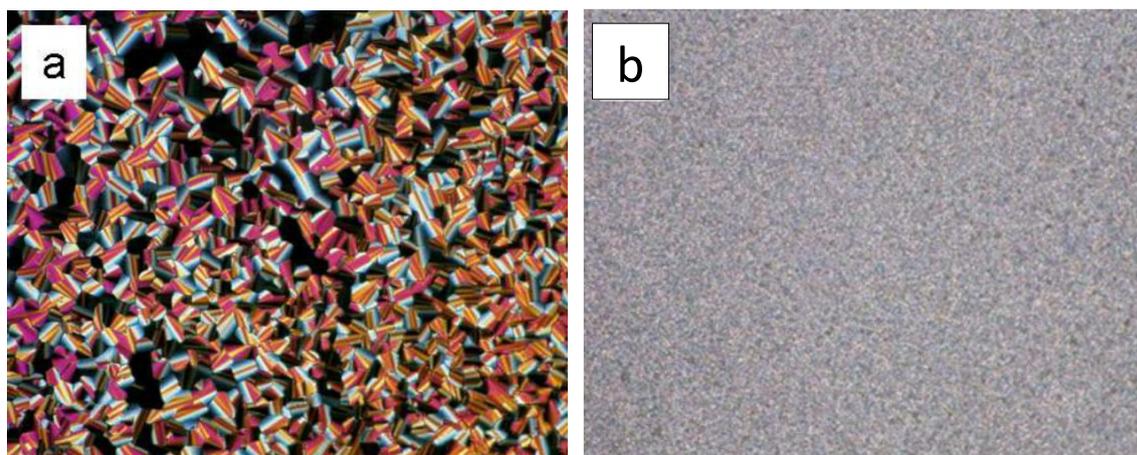


Fig. S2 POM images of (a) Monomer and (b) Polymer material (PHAT) at a temperature of 25 °C on cooling from isotropic phase (crossed polarisers, Magnification is X 200).

The detailed liquid crystalline property of the material PHAT has been described elsewhere (Reference 18). We reproduce some relevant discussion from reference 18 for the convenience of the reader: The liquid crystalline phase behaviour of the polymer was studied by POM, differential scanning calorimetry (DSC) and X-ray diffraction. This highly viscous compound does not show any peak during heating and cooling in the DSC thermogram. Under the polarizing microscope when heated from room temperature the polymer transforms gradually to isotropic state at 89 °C and upon cooling it exhibits a birefringent texture (Fig. S2 (b)). In order to confirm the mesophase structure of the polymer, X-ray diffraction studies were carried out. Only one strong reflection was observed in the small angle region of the X-ray diffraction pattern. Though it is difficult to assign the mesophase structure with only one peak in the small angle region, considering the general mesophase structure of triphenylene based discotic monomers and polymers (Reference 14), we consider this to be a columnar hexagonal phase (Reference 18).

3. Contact area of cantilever tip to sample

We have estimated the cantilever tip-sample area of contact using the Hertz model of contact mechanics (Reference 41). Accordingly the contact radius of sphere with a flat plane is given by

$$a^3 = \frac{3FR}{4E^*}$$

where a is the contact radius, F is the applied load, R is the radius of curvature of the tip and E^* is the reduced elastic modulus of the tip-sample system. Here E^* is given by

$$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2}$$

where E_1 , E_2 are the elastic modulus and ν_1 and ν_2 are the Poisons ratio for the tip and sample respectively.

Taking the value of E_1 , E_2 , ν_1 and ν_2 from literature (Reference 42 and 43) we have estimated the contact radius to be 0.9 nm and the contact area to be 2.6 nm².

We would like to state that it is difficult to determine the exact contact area under an applied force as pointed out by Zhao et al (Reference 32).