

## Supplementary Information

Figure ESI.1: AFM images a) and c) topography and b and c) current; this 4 images reveal the electrical behavior of different  $K_6$ -P<sub>2</sub> $W_{18}$ 's layers obtained. Clearly the high in plane structuration is not a sufficient to have good electrical behavior.



Figure ESI.2: Spectrum of the threshold of photoemission obtained by UPS. Fitting the rising edge of the threshold gives a workfunction of 5.040 eV for POM.



Figure ESI.3: the XPS binding energy in function of intensity of a thick well organized layer onto ITO of  $K_{6}$ -[ $P_2W_{18}O_{62}$ ] revealed the presence of gap state into the forbidden gap. In insert the all energetic graph is displayed.

Figure ESI.4 : reference I vs V for the structure {ITO/PEDOT:PSS (20nm)/P3HT:PCBM (120 nm)/LiF (8Å)/AI (80 nm); the black curve was performed in the dark, the red curve was performed under light at 75 mW