Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

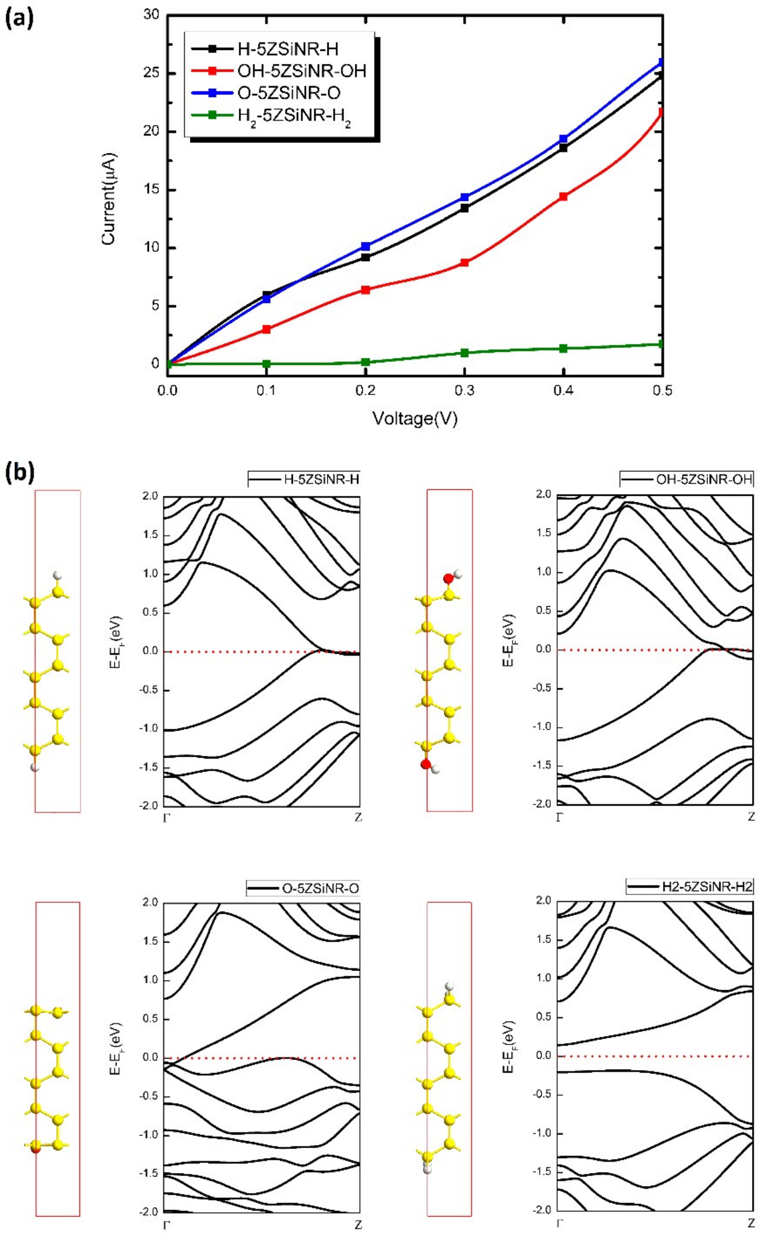

Figure 1. (a) The calculated *I-V* curve of molecular junctions X-5ZSiNR-X (X=H, OH, O, H_2). (b) Bulk structure and band structure of 5ZSiNRs with various edge functional groups: H, OH, O, H_2.

We perform the calculation of transport properties and band structures for the X-5ZSiNR-X (X=H, OH, O, H_2) systems as shown in Figure 1. When the width of ZSiNRs changes to be 5, the X-5ZSiNR-X systems do not satisfy c2 symmetry operation. As a result, we can find that the current turns to increase linearly for X-5ZSiNR-X (X=H, OH, O). Especially, compared with the O-6ZSiNR-O junctions, the current of the O-5ZSiNR-O case under calculated bias voltage remarkably increases, even more than that of H-5ZSiNR-H case. As stated above, the O group can form a band across the Fermi level, which may provide more transmission channels than other three systems. Therefore, from the *I-V* curves, one can see that the current of O-5ZSiNR-O is close to that of H-5ZSiNR-H. But for the O-6ZSiNR-O case, when the bias applied, this band across the Fermi level has no effect on the transport because transmission near the Fermi level is prohibited due to the mismatch of symmetry of electron wave functions of π and π^* subbands of the left and right electrodes. As a result, the current of O-6ZSiNR-O obviously reduces. For OH-5ZSiNR-OH, the band structure of OH-terminated 5ZSiNRs is very close to H-terminated 5ZSiNRs. Since the left and right electrodes are H-terminated ZSiNRs, so the current of OH-5ZSiNR-OH is smaller than that of H-5ZSiNR-H. In addition, for H_2-5ZSiNR-H_2, the current is still very small, which because the introduction of H_2-terminated edge functional group can yield a band gap, so there is no transmission channel to contribute the transport. So we can conclude that for 5ZSiNRs which prevents the symmetry mismatch problem, the transmission channels from central ZSiNRs slices themselves have more significant effect on the transport.