Supplementary Information

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S1. Transmission spectra at different rotation angle for one triple bond structure.

The peak at -0.5eV is caused by the increase of open channels provided by leads. It is unrelated to the molecular feature. The resonances around -0.6eV and 0eV are dominated by pendent group. The resonances around -1eV and 0.5eV are caused by porphyrin core. The reasons are shown in the following part 2.
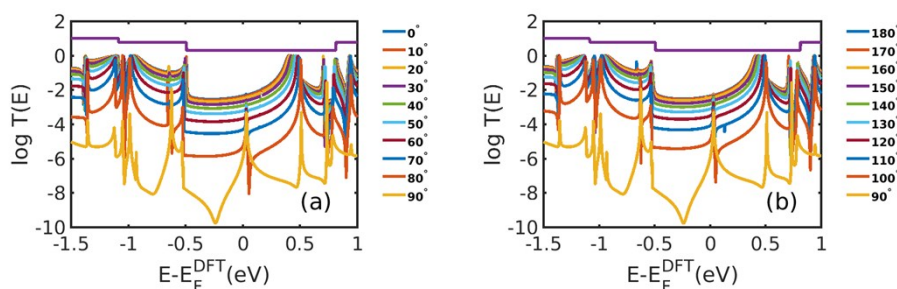

Figure S1. Transmission spectra of different rotating configurations with one triple bond as the spacer on each side.

S2. The frontier orbitals of the molecules.

The 1st, 2nd rows depict Zn-porphyrin with one triple bond each side in the absence of dipole group. The wave functions of HOMO-1, HOMO, LUMO, LUMO+1 are plotted in the 1st row. The following row is the corresponding energies. The gap between HOMO and LUMO is 1.67eV which is consistent with the HOMO-LUMO gap of transmission spectrum shown in Figure S4.

The 3rd ~6th rows show the molecular orbitals for porphyrin in the presence of dipole group. HOMO-2, HOMO-1, HOMO, LUMO are dominated by the pendent group because the states are localised on the pendent group, while HOMO-5, HOMO-4, HOMO-3, LUMO+1, LUMO+2 originate from the porphyrin core in comparison with the orbitals shown in 1st row. The resonances around -1eV stems from the HOMO-4, HOMO-3 and HOMO-2 molecular orbitals respectively while the resonance around 0.5eV stems from the LUMO+1 molecular orbitals In addition, the peak at -0.6eV is due to the HOMO-1 orbitals whereas the HOMO and LUMO

orbitals of the functionalised Zn-porphyrin are the origin of the resonances around 0eV in Figure S1(a) and S1(b).
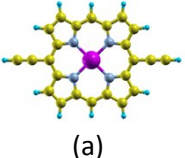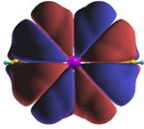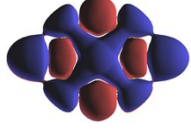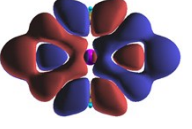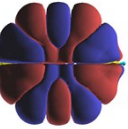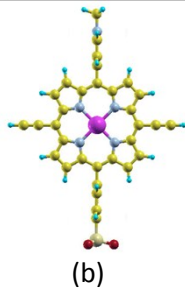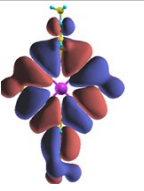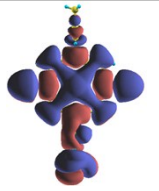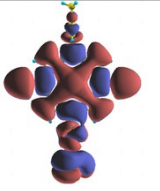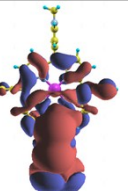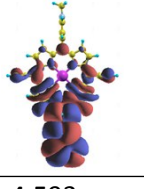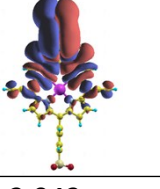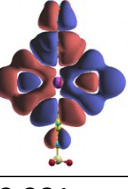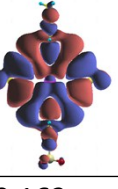
1					
2	$E_F =$ -3.970eV	-5.009eV HOMO-1	-4.753eV HOMO	-3.080eV LUMO	2.847eV LUMO+1	
3						
4		-5.24 HOMO-5	-5.005 HOMO-4	-4.945 isov=0.005 HOMO-3	-4.910 isov=0.0005 HOMO-2	
5						
6	$E_F =$ -3.976eV	-4.593 isov=0.003 HOMO-1	-4.010 isov=0.0005 HOMO	-3.943 LUMO	-3.381 LUMO+1	-3.162 LUMO+2

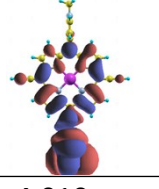Figure S2. The wave functions for (a)Zn-porphyrin with one triple bond each side and (b)functionalised Zn-porphyrin. The 1st and 2nd show the four frontier molecular orbitals for molecule (a). The 3rd ~6th depict the frontier molecular orbitals for molecule (b).

S3. Transmission spectra of different rotation angle for two triple bonds structure.
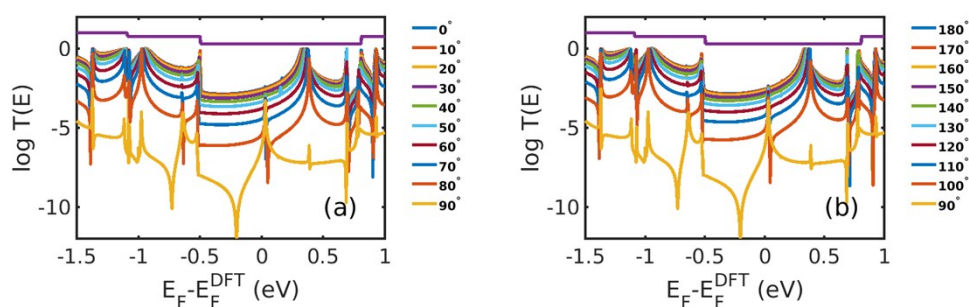
Figure S3. Transmission spectra of different rotating configurations with two spacers (triple bond) on each side.

The resonance around 0.5eV moves to left slightly because of the shrunk energy level spacing due to one more triple bond compared to the one triple bond structure between molecule and each lead.

S4. Transmission spectra for pure Zn-porphyrin
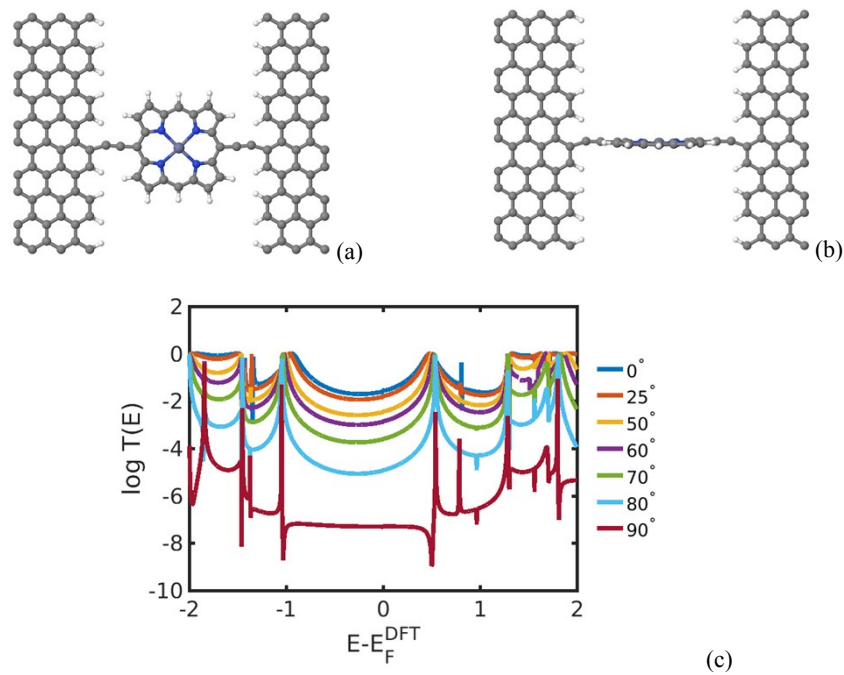

(a)   (b)

(c)

Figure S4. The transmission spectra for Zn-porphyrin molecule bridging the two graphene sheets from 0 (shown in (a)) torsion angle to 90 (shown in (b)) between the molecule and graphene plane.

S5. Conductance as the function of Fermi levels and energy landscapes for three and four triple bonds structure at room temperature.

Figure S5-1. (a), (b) Electrical conductance in units of the conductance quantum $G_0=2e^2/h$) without gate electric field as a function of the Fermi level E_F of the electrodes relative to the DFT-predicted value in zero bias limitation at 300K. (c) Potential landscape under a series of perpendicular electric field 0.0 V/nm, 0.2 V/nm, 0.4 V/nm, 0.6 V/nm shown in (d). The dots represent the total energies relative to the energy at $0°$ and 0 V/nm calculated by DFT which are fitted by $y = a\sin^2\theta + b$. (d) Corresponding Boltzmann distribution probability (obtained by formula (2), (3)) against the rotation of porphyrin under different gate electric fields at 300K. 'Three' indicates the number of triple bonds between the molecule and each electrode.
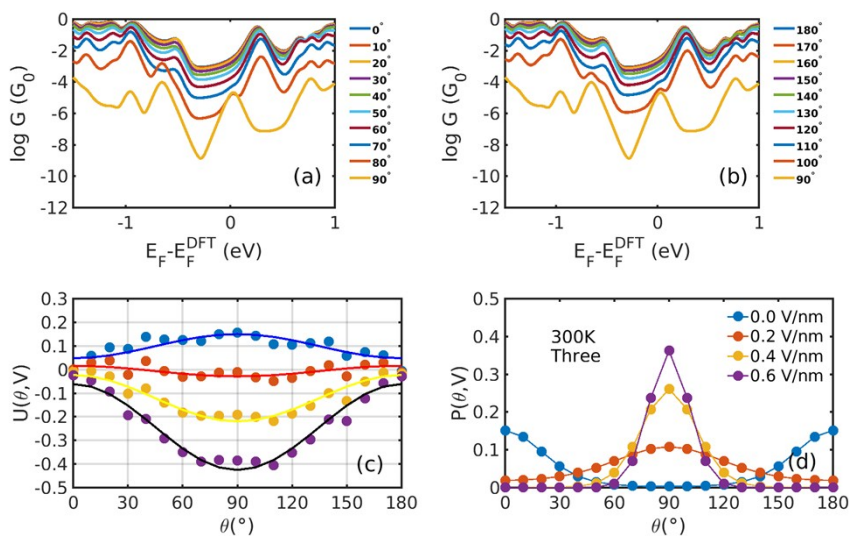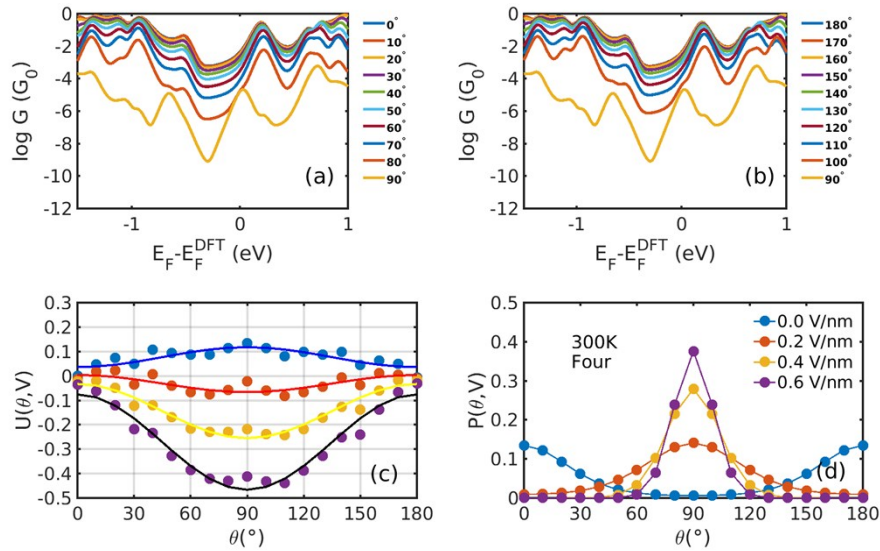

Figure S5-2. (a), (b) Electrical conductance in units of the conductance quantum $G_0=2e^2/h$) without gate electric field as a function of the Fermi level E_F of the electrodes relative to the DFT-predicted value in zero bias limitation at 300K. (c) Potential landscape under a series of perpendicular electric field 0.0 V/nm, 0.2 V/nm, 0.4 V/nm, 0.6 V/nm shown in (d). The dots represent the total energies relative to the energy at $0°$ and 0 V/nm calculated by DFT which are fitted by $y = a\sin^2\theta + b$. (d) Corresponding Boltzmann distribution probability (obtained by formula (2), (3)) against the rotation of porphyrin under different gate electric fields at 300K. 'Four' indicates the number of triple bonds between the molecule and each electrode.

S6. Current under finite bias.

Transmission spectra of the four devices with one, two, three, four triple bonds are presented in (a)s. S6(b)s show the currents corresponding to each rotation angle under finite bias obtained by Landauer formula shown in S7. S6(c)s depict the Boltzmann-averaged currents under different gates on the basis of the current shown in Figure (b)s. We can see the current increases linearly as the bias arises in a reasonable range. The corresponding On-Off ratios extracted from Figure 6(c)s are presented in Figure (d)s. Figure S6-5 presents the On-Off ratios of the four devices under three finite biases (Vb=0.1eV, 0.2eV, 0.3eV) at room temperature. It is found that there is no big difference in the On-Off ratios under the three finite biases.
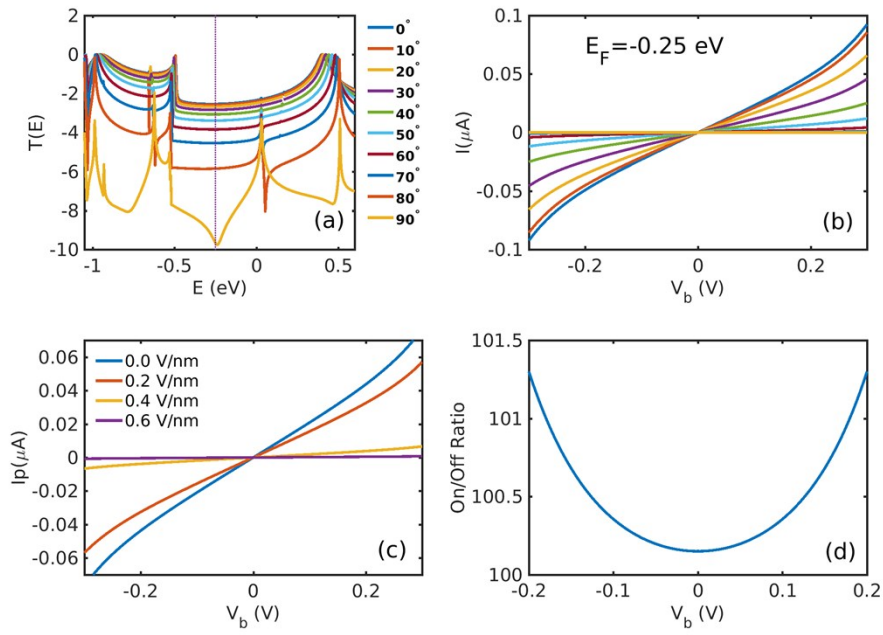
Figure S6-1. Transmission spectra and I-V curves of the device with one triple bonds.
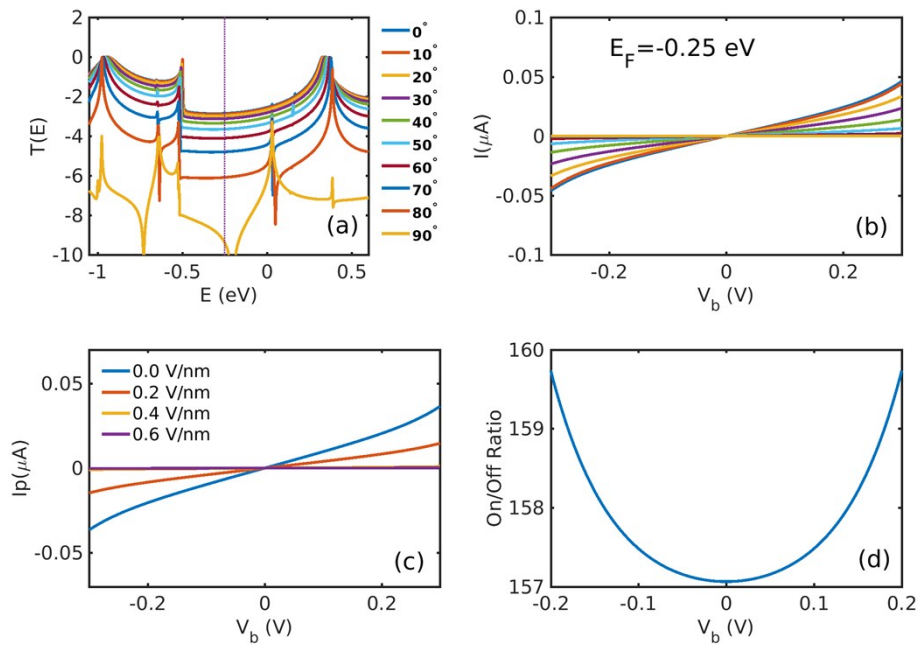

Figure S6-2. Transmission spectra and I-V curves of the device with two triple bonds.
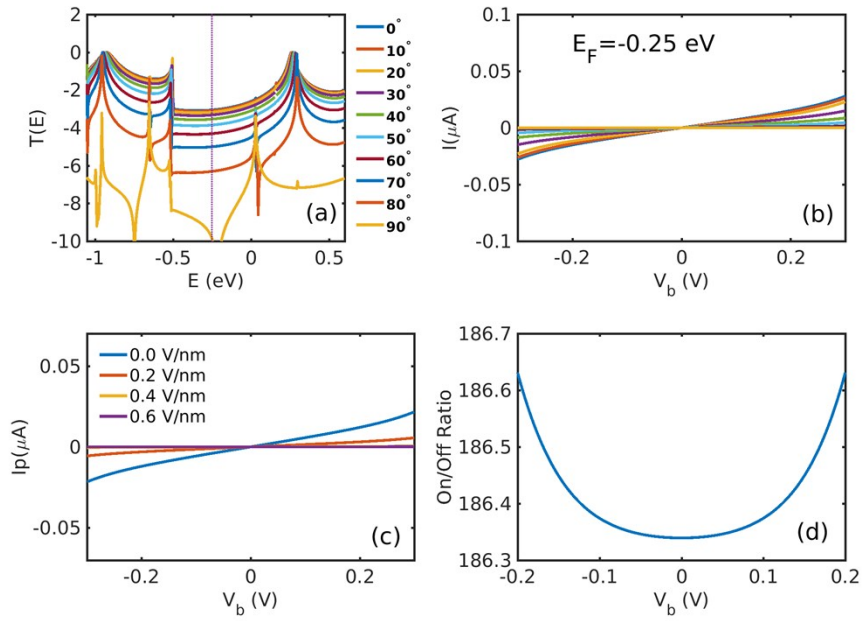
Figure S6-3. Transmission spectra and I-V curves of the device with three triple bonds.
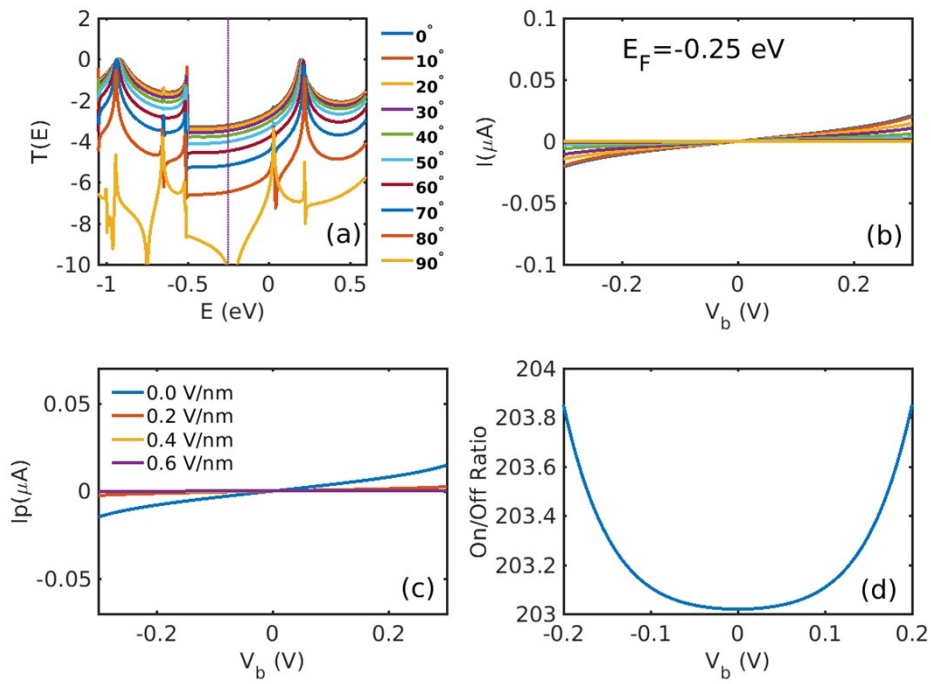
Figure S6-4. Transmission spectra and I-V curves of the device with four triple bonds.
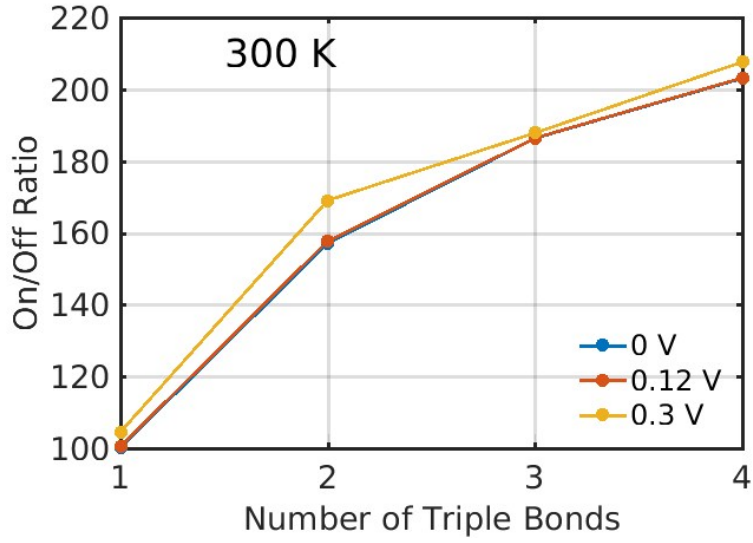
Figure S6-5. On-Off ratio of four devices with one, two, three, four triple bonds under finite biases.

S7. Formula for the current utilised in S6

$$I = \frac{2e}{h} \int_{-\infty}^{\infty} dE T(E)[f_l(E,E_F,T) - f_r(E,E_F,T)]$$

$-e$ is the charge of a electron; $f_{l,r} = (1 + exp(E - E_F/k_BT))^{-1}$ is the Fermi-Dirac probability distribution function, E_F is the Fermi energy and T is the temperature.