Supporting Information

The conductance of porphyrin-based molecular nanowires *increases* with length

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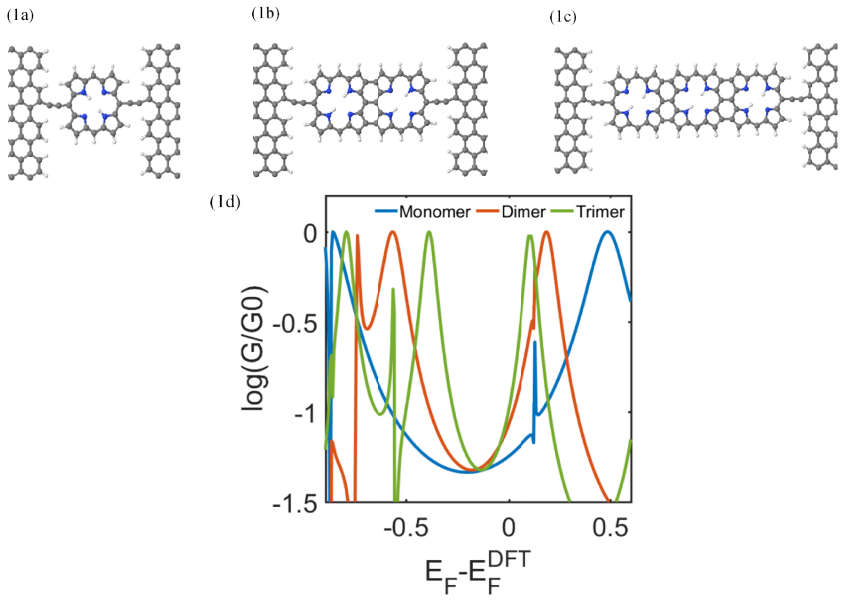


Fig. S1. Transmission coefficient obtained from DFT Hamiltonian for three types of porphyrin connect to graphene electrodes via triple bonds

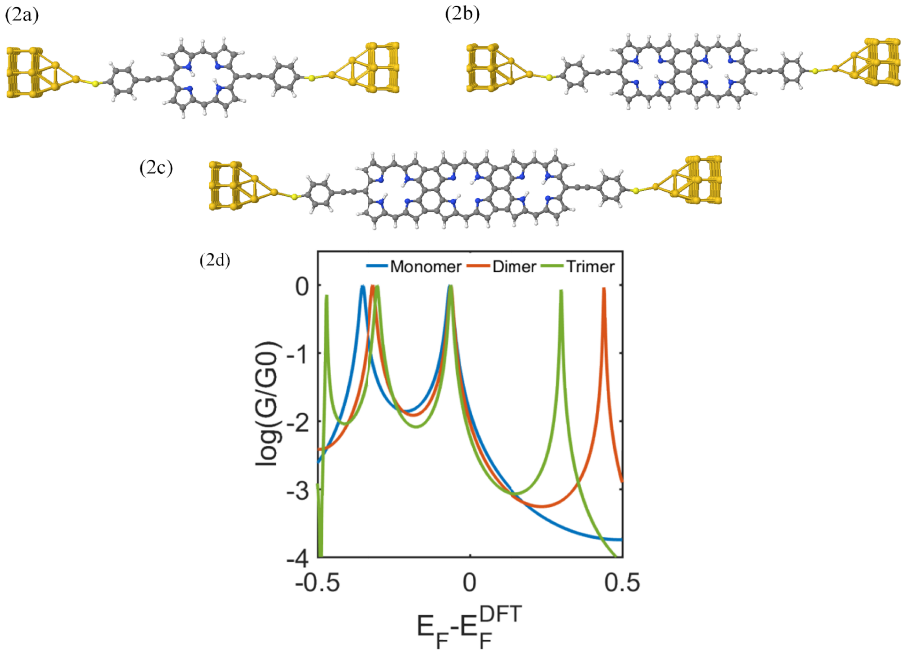


Fig. S2. Transmission coefficient obtained from DFT Hamiltonian for three types of porphyrin connected to gold electrodes via thiol-anchor

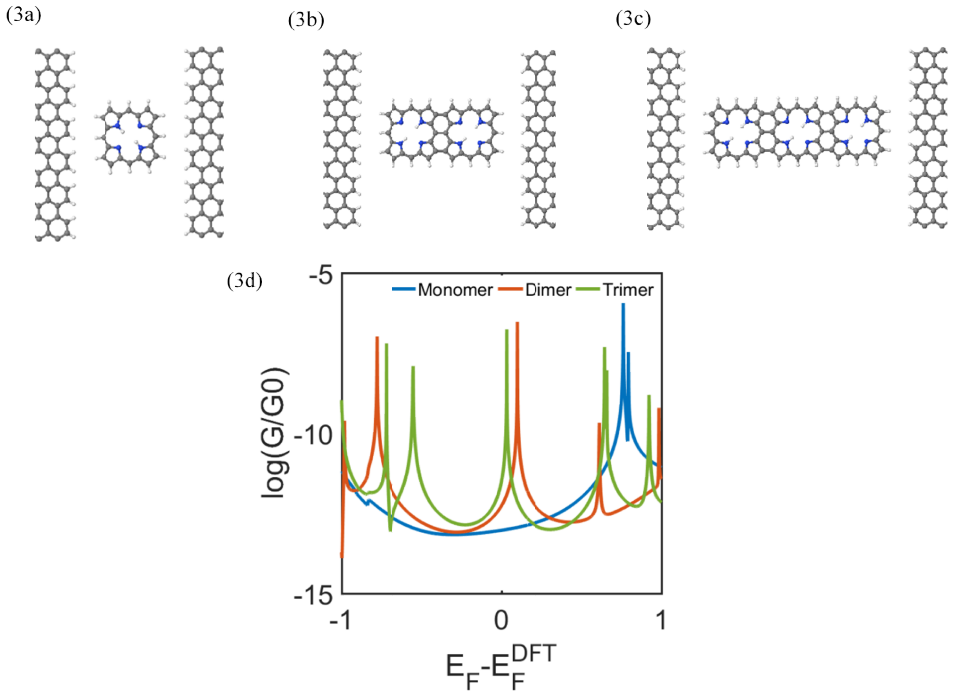


Fig. S3. Transmission coefficient obtained from DFT Hamiltonian for three types of porphyrin between graphene electrodes without specific anchor.

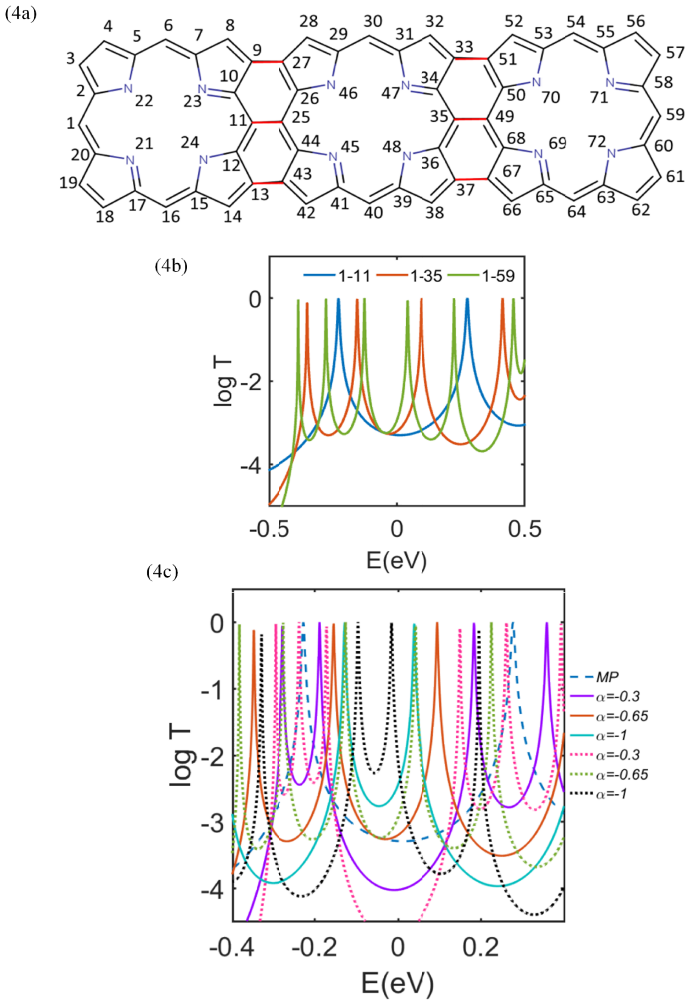


Fig. S4. Transmission coefficient for three types of porphyrin calculated using simple tight binding model

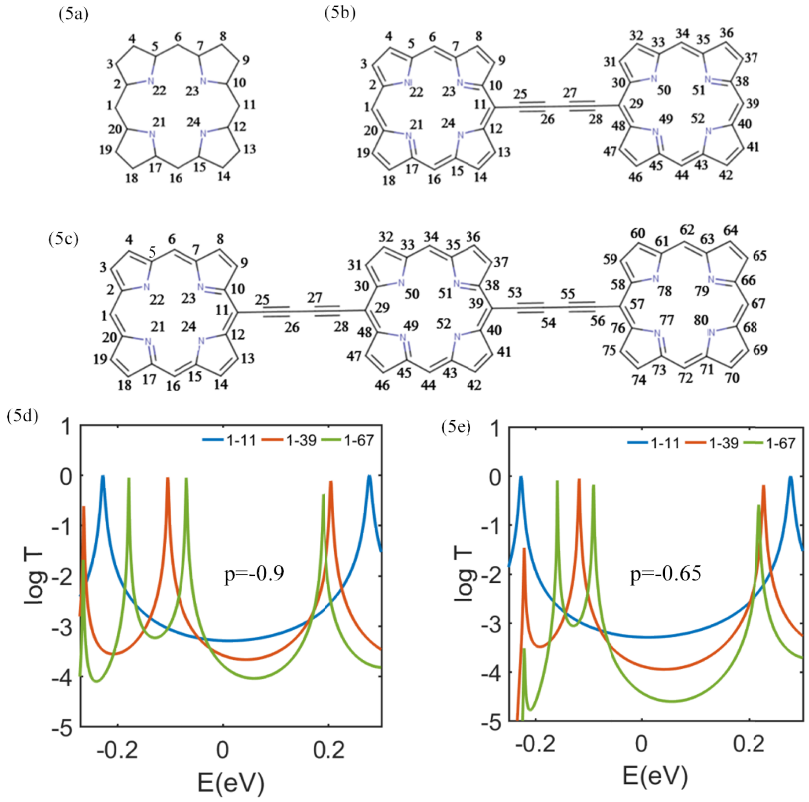
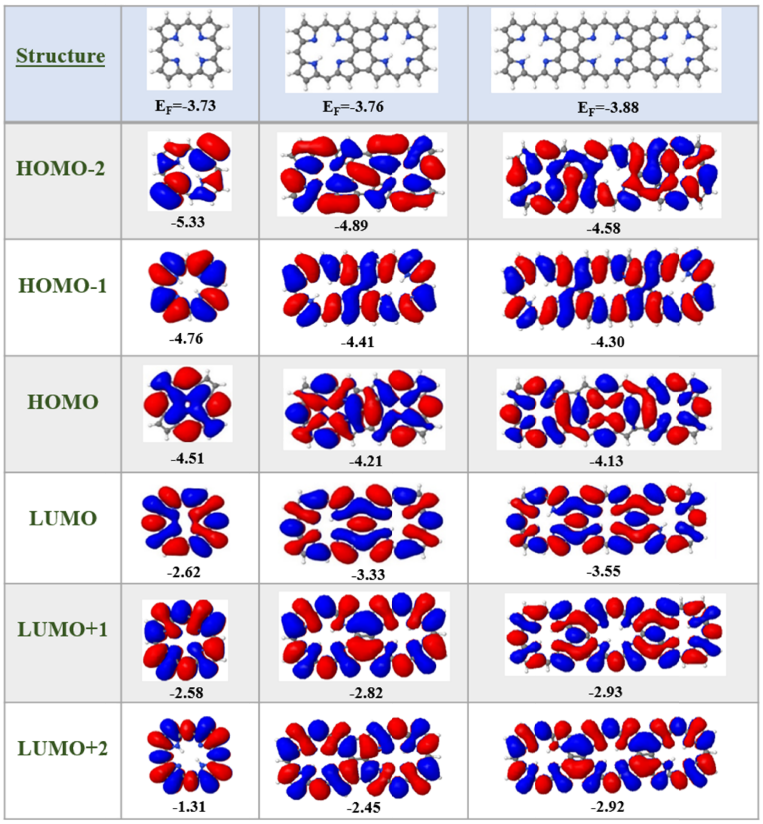


Fig. S5. (a-c) are the schematic of non-fused porphyrin monomer, dimer and trimer molecular structures. (d-e) are the transmission curves for the non-fused porphyrin calculated using simple tight binding model. Triple bond between two or three Monomer (p) integrals are chosen to be -0.9 and -0.65 in d and e, respectively.

(6a)



(6b)

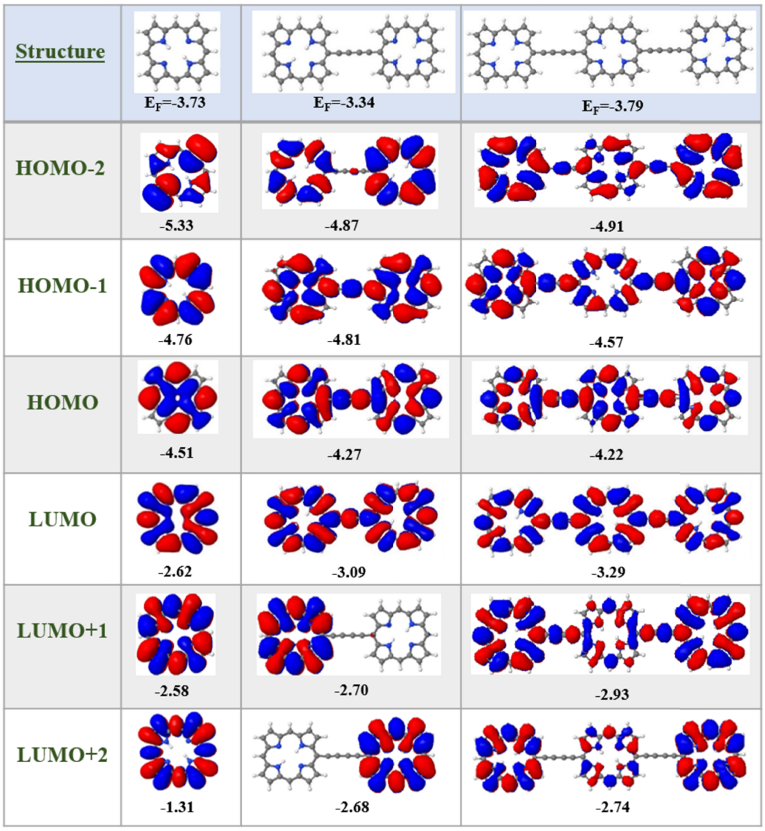


Fig. S6. Comparison between the HOMO and LUMO orbitals for (6a) fused oligo porphyrin and (6b) Non-Fused Porphyrin.

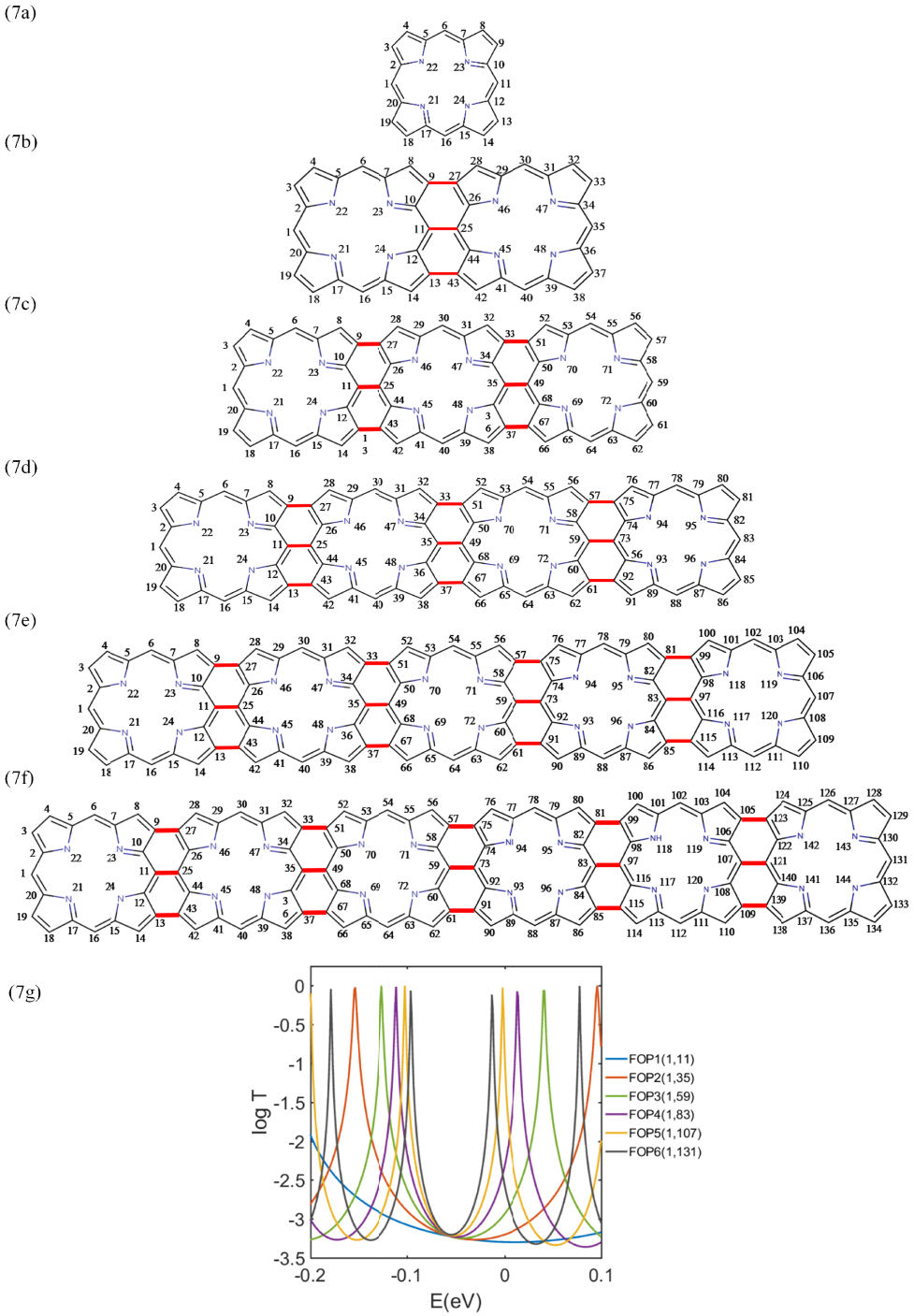


Fig. S7. Transmission coefficient for fused oligo porphyrins with different length upto 6 porphyrin units calculated using simple tight binding model. The red bonds are chosen to be $\alpha = -0.65$.

A simple model based on coupling the frontier orbitals of a chain of monomers

Here we note that the qualitative features of the figure 2 can be reproduced by a simple tight binding model of independent transport through the HOMOs and LUMOs. Let $T(E, n, -\gamma_L, \varepsilon_L)$ be the transmission coefficient for a chain of n monomer LUMOs, with energies ε_L and coupled by nearest neighbour matrix elements $-\gamma_L$. Similarly let $T(E, n, +\gamma_H, \varepsilon_H)$ be the transmission coefficient of an independent chain of monomer HOMOs, with energies ε_H and coupled by nearest neighbour matrix elements $+\gamma_H$. Note that from fig 4b, since the splitting of the LUMO resonances is greater than that of the HOMO resonances, $\gamma_L > \gamma_H$. Then if we assume no interference between the HOMO and LUMO, the total transmission coefficient is

$T(E,n) = T(E,n,-\gamma_L,\varepsilon_L) + T(E,n,+\gamma_H,\varepsilon_H)$. Without loss of generality, we choose $\varepsilon_H = -\varepsilon_L$, which fixes the energy origin. As shown in figure S9, with an appropriate choice of parameters, this simple model captures the qualitative features of figure 2 and the tight-binding results of figure 4a.

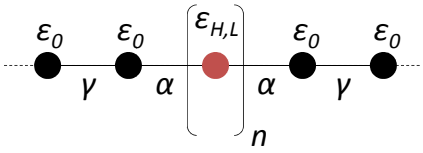


Figure S8. A tight binding (Hückel) model of 1, 2 or 3 site scattering region (depicted in red), coupled to one-dimensional leads. The scattering region represents either a chain of coupled monomer LUMOs or a chain of coupled monomer LUMOs. After calculating their separate transmission coefficients, they are simply added to give the total transmission coefficient.

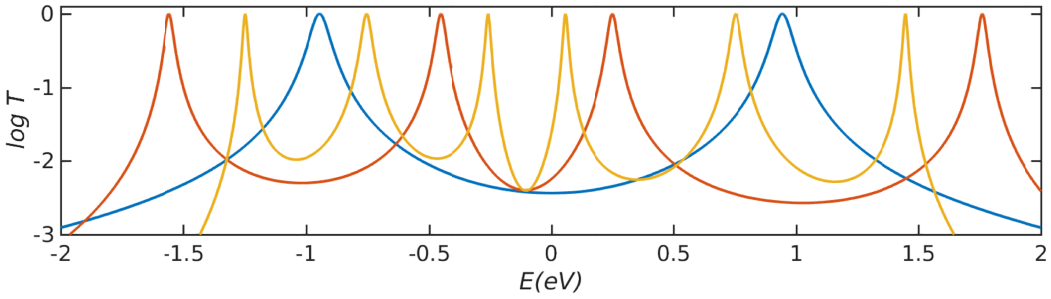


Fig. S9. Sum of transmission coefficient $T(E,n) = T(E,n,-\gamma_L,\varepsilon_L) + T(E,n,+\gamma_H,\varepsilon_H)$ through independent HOMO and LUMO levels for a monomer n=1, dimer n=2 and trimer n=3. For the monomer, $\varepsilon_L = 0.935$; for the dimer, $\varepsilon_L = 1.0, \gamma_L = 0.75, \gamma_H = 0.55$ and for the trimer, $\varepsilon_L = 0.75, \gamma_L = 0.5, \gamma_H = 0.35$. In these plots, the coupling between the molecule and the one-dimensional leads is $\alpha = -0.1$ and the leads are represented by a chain of sites with site energies $\epsilon_0 = 0$ and nearest neighbour couplings $\gamma = -1$.

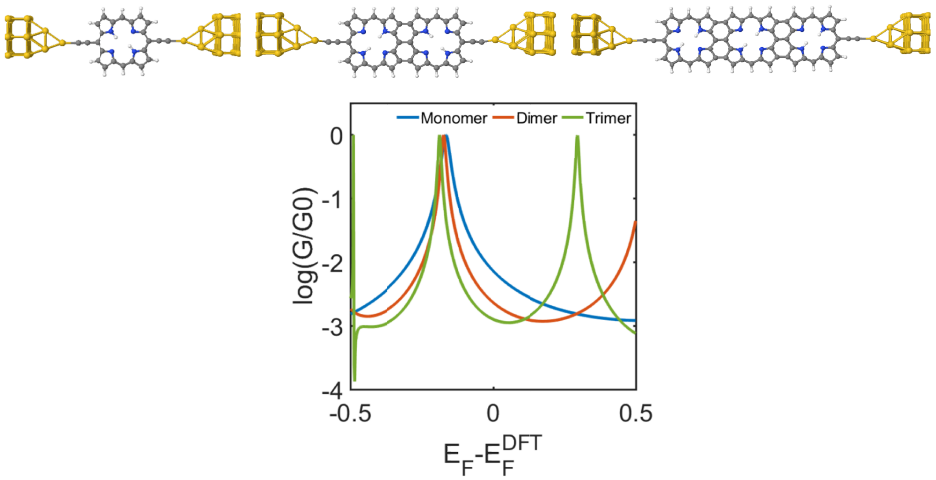


Fig. S10. Transmission coefficient obtained from DFT Hamiltonian for three types of porphyrin connected to gold electrodes through a direct Au-C bond.

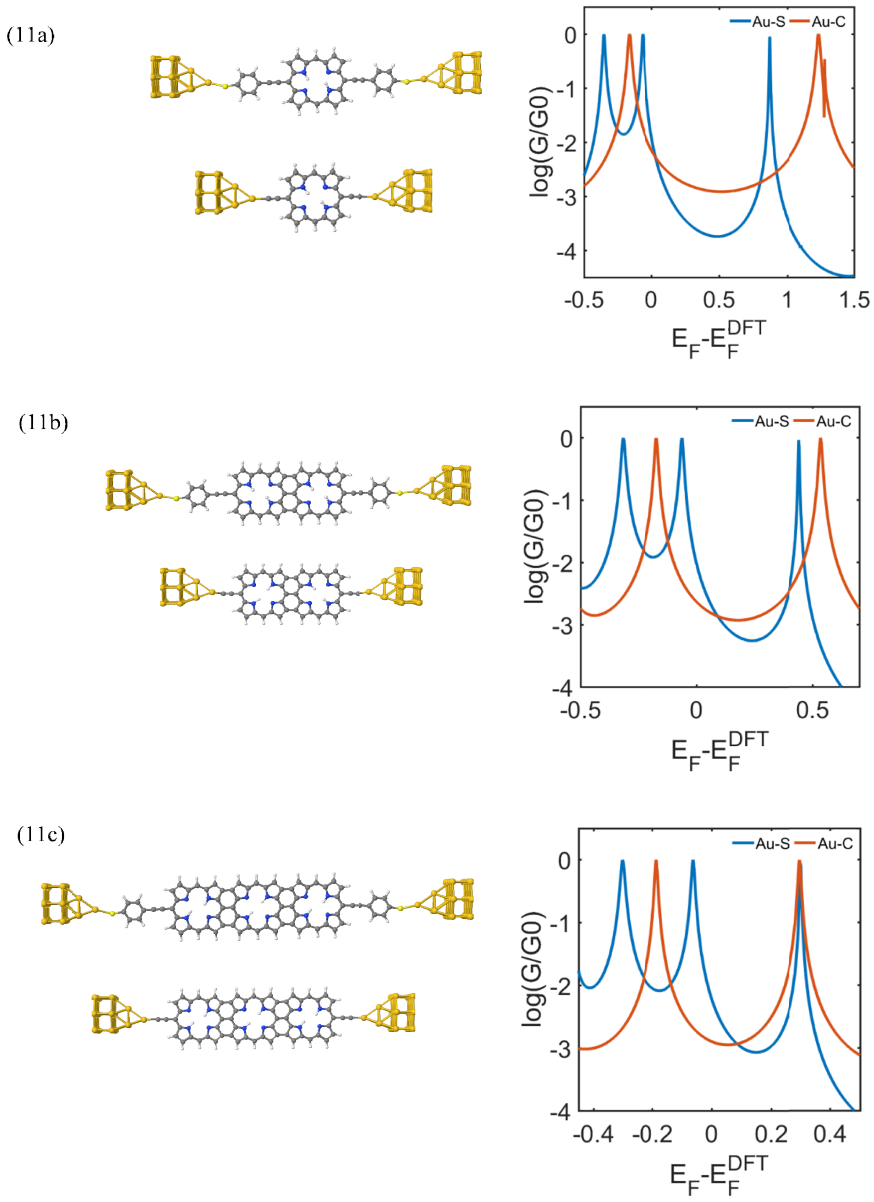


Fig. S11. Transmission coefficient obtained from DFT Hamiltonian for three types of porphyrin connected to gold electrodes with two anchors, thiol- and direct Au-C bond. (a) monomer, (b) dimer and (c) trimer