Supplementary Information

Asymmetric electron transport realized by decoupling between molecule and electrode

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1. The electron transport of linear models with different molecular proportion

2. The charge distribution calculated by different theoretical methods

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1. The electron transport of linear models with different molecular proportion

To clearly explore the asymmetric electron transport of OPE-Oc induced by the tunneling barrier, we have also calculated the linear system with different molecular proportion. For the linear system, the same saturated ring is used to break the electronic coupling, while conjugated part has different lengths (Figure S1). The first model (Model-**1**) is a benzene ring connected with saturated bridge, which has a molecular proportion of R=1.1. In the Model-**2**, the conjugated wire is diphenylacetypene, which leads to R=3.7. The Model-**3** is OPE-Oc with R=6.4 studied in the manuscript. The methods of geometry optimization and current calculation are described in the manuscript.

Figure S2 shows the current-voltage (*I-V*) curves and the rectification ratio as a function of bias for these three models. As mentioned in the manuscript, the decoupling effect induces asymmetric electron transport in the OPE-Oc. However, this effect becomes weak as the molecular proportion is small in Por-Oc. The same characteristic is observed in these three models. Although pronounced rectification is observed for model-**3** at 2.0 V, almost symmetric *I-V* curves are obtained for the model-**1** and model-**2**, which have small R values (1.1 and 3.7). The longer conjugated part of model-**3** is more easily polarized under the external electric field, which results in pronounced rectification. Therefore, molecular rectification is not only originated from asymmetric coupling, but also correlates to the molecular proportion.

The spatial distribution of model-**1** and model-**2** is displayed in Figure S3. Although the HOMO and LUMO is localized due to the decoupling by saturated ring, the rectification is slight. This result also indicates that the static characteristic cannot give direct insight into the electron transport.

Figure S1

Model-1   S—⬡—⬡—S $L_c / L_s = 1.1$

Model-2   S—⬡≡⬡—⬡—S $L_c / L_s = 3.7$

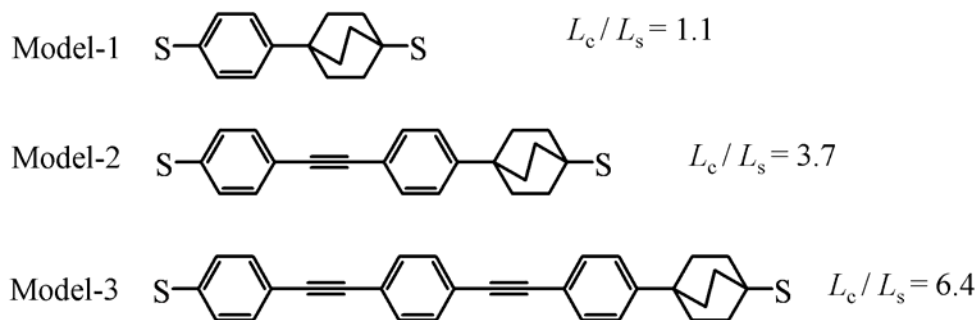Model-3   S—⬡≡⬡≡⬡—⬡—S $L_c / L_s = 6.4$

Figure S1. The molecular structures of linear systems with different molecular proportion.
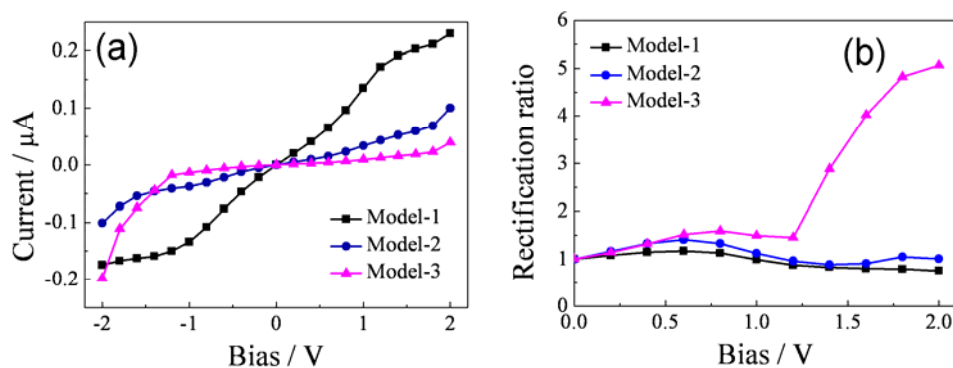
Figure S2

Figure S2. (a) Representative plot of current-voltage (*I-V*) curves of model **1-3**. (b)

The rectification ratio of the linear system as a function of bias.
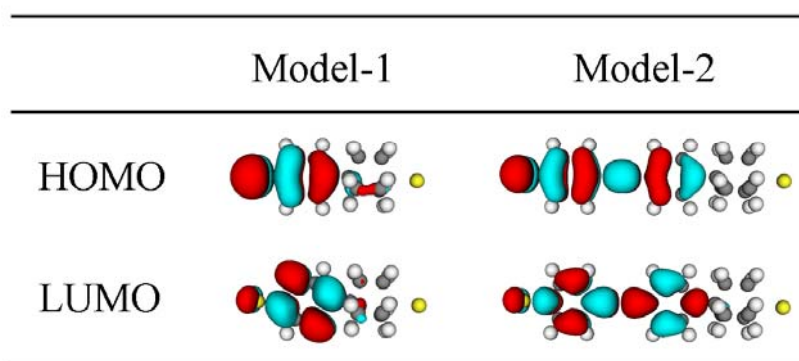
Figure S3

Figure S3. The spatial distribution of HOMO and LUMO for model-**1** and **2** at zero

bias.

2. The charge distribution calculated by different theoretical methods

As the self-interaction/self-repulsion is a prevalent problem in density functional theory (DFT), the hybrid B3LYP functional and local density approximation (LDA) also suffer from self-repulsion in the local functional. Therefore, static polarizability is often greatly exaggerated in elongated molecules.[Phys. Rev. A, 2001, 63(6), 063201] To correct this error, Baer *et al.* developed approaches to DFT with correct long-range behavior.[Phys.Chem.Chem.Phys., 2007, 9, 2932; Chem. Phys. 2006, 329, 266–275; PRL, 2005, 94, 043002] Here, in order to evaluate the influence of the self-repulsion on the molecular polarizability, we have recalculated model OPE-Oc by different methods, i.e. the B3PW91, X3LYP and HF methods and reanalyzed the charge distribution. The same basis set is applied, 6-31G* basis set for molecule and LanL2DZ basis set for Au.

Figure S4 plots the relative charge of every part of free OPE-Oc molecule obtained from four methods. As the Lee-Yang-Parr correlation functional (B3LYP) is changed to the Perdew/Wang 91 gradient-corrected correlation functional (B3PW91), the values of relative charge obtained by two methods are similar. Comparing the result of B3LYP with X3LYP, relative charge is also similar though the exchange functional and the parameters are different. In other words, the influence of changing the exchange-correlation functional is slight for the present system. As the correction functional is not included, taking HF method for example, the evolution trend of relative charge under electric field is similar though the charge value decreases. The HF method does not have the problem of self-interaction, but is not sufficiently

accurate because it neglects the correlation energy. Furthermore, rather than the absolute value of the electric charge, we analyzed the relative charge to eliminate the error of self-repulsion. For all the methods, the conjugated part is more easily polarized than the saturated ring under external electric field.

Figure S5 displays the potential distribution along the OPE-Oc junction calculated by four methods. Although the potential is slightly different obtained by four methods, especially the HF method, the same trend can be clearly observed. Every potential drop is highly non-uniform due to the different degree of coupling. The potential along the saturated ring drops rapidly than that at the conjugated molecular backbone. In summary, the results obtained by B3LYP for the present systems are reliable.
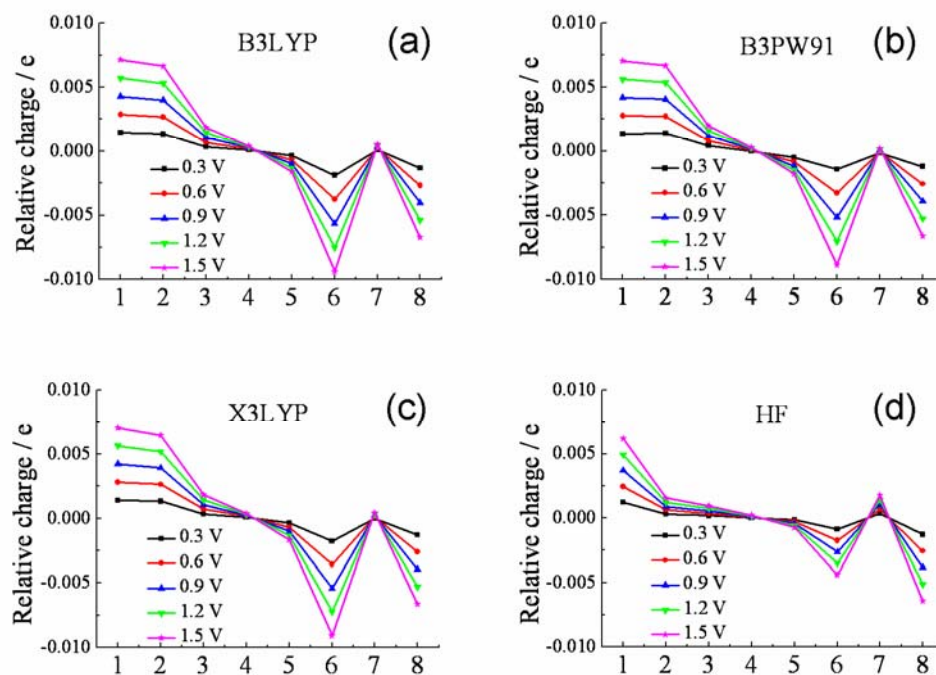
Figure S4

Figure S4. The electric charge of per part relative to zero bias of free OPE-Oc obtained by four methods, (a) B3LYP, (b) B3PW91, (c) X3LYP and (d) HF. 6-31G* basis set is used for molecule.
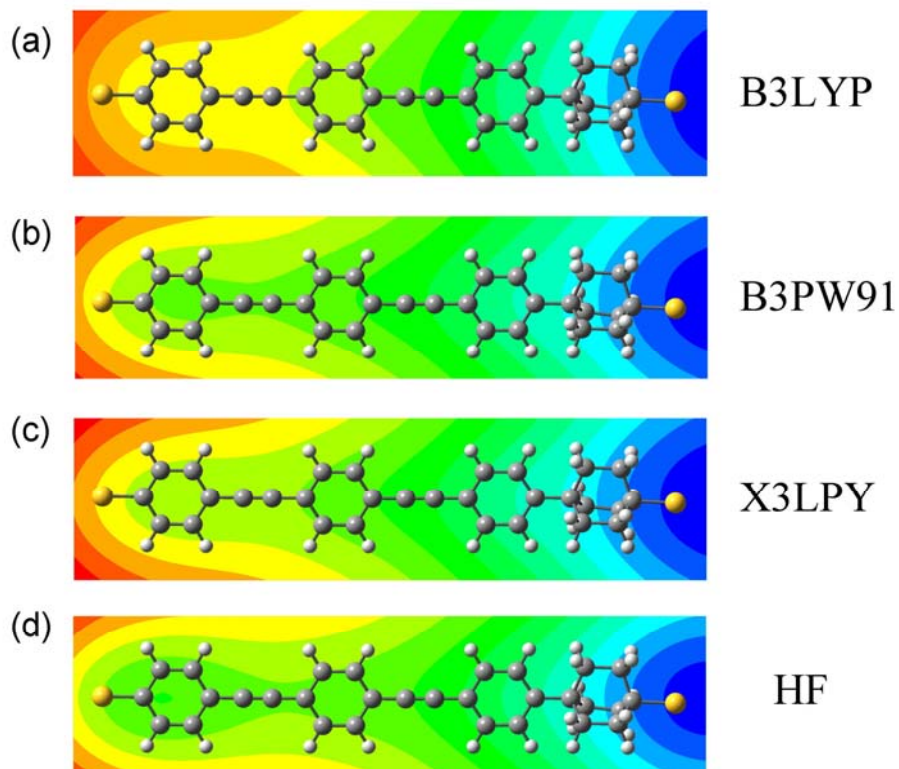
Figure S5

Figure S5. The charge distribution of Au-OPE-Oc-Au at 1.5 V calculated by four

methods, (a) B3LYP, (b) B3PW91, (c) X3LYP and (d) HF. 6-31G* basis set is used

for molecule and LanL2DZ basis set for Au.