Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Materials

Can Azulene-like Molecules Function as Substitution-Free Molecular Rectifiers?

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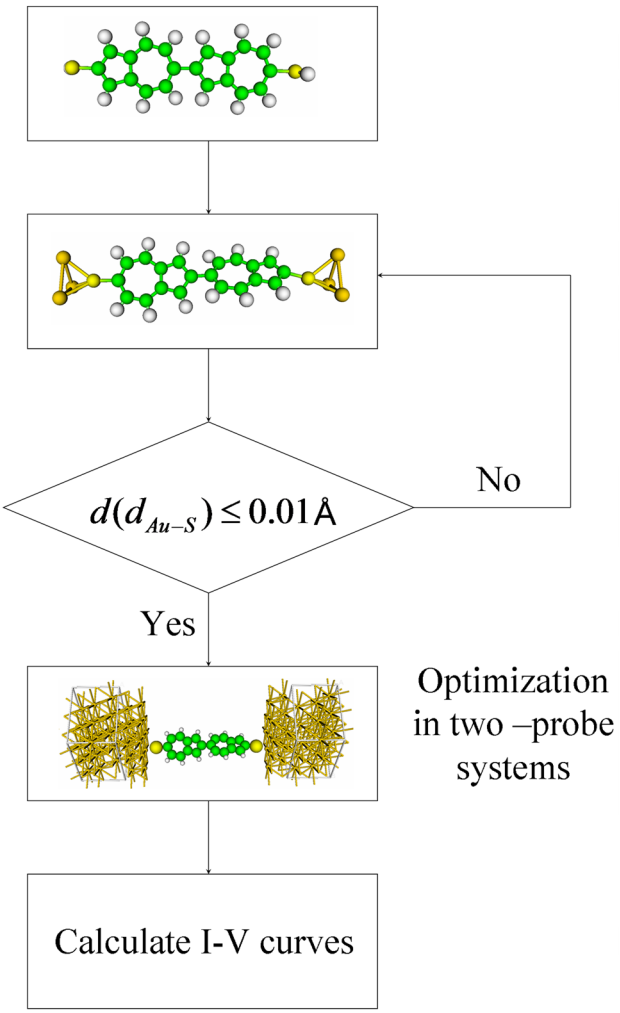
1. Simulation process



Scheme S1. Scheme of simulation process.

The simulation process can be briefly described as below. Firstly, the molecular geometry is optimized with the S atoms saturated by hydrogens. Secondly, the hydrogens on the SH groups are replaced by two frozen gold clusters to simulate the electrodes.[1] The atoms of each cluster are place as equilateral triangle with sides of 2.88 Å. The S atoms are kept above the center of the triangle and distance between S and the plane of gold cluster (d_{Au-S}) are set to 2.01 Å, which is in the reasonable range as reported by most of theoretical investigations,[1-3] and the model is optimized as a molecular system. The second step is recycled until the change of d_{Au-S} is less than 0.01 Å. After relaxation of the cluster-molecule-cluster model completed, the clusters are translated to two 3×3 Au (111) surfaces and there are two gold layers above the electrodes as surface atoms.[2] The distance between S and plane of electrode surface is

set as the distance between S and plane of cluster surface in the second step. The whole two-probe system is optimized at zero bias. The fully relaxed systems are then used to calculate the current-voltage curve (*I*-*V*) with the bias varied from -2.0 V to 2.0 V.

2. The shift of frontier molecular orbitals for substituted molecule G

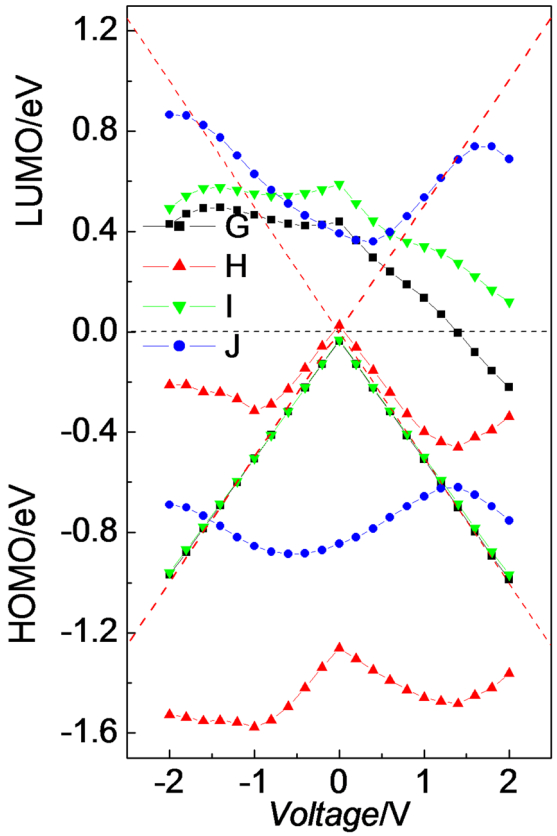


Fig. S1. Shifts of the LUMO and HOMO levels under different bias for molecule G to J. The red dash lines mark the upper and lower limits of the bias window. The dark dash line refers to the Fermi level.

3. Transmission spectra of azulene derivates

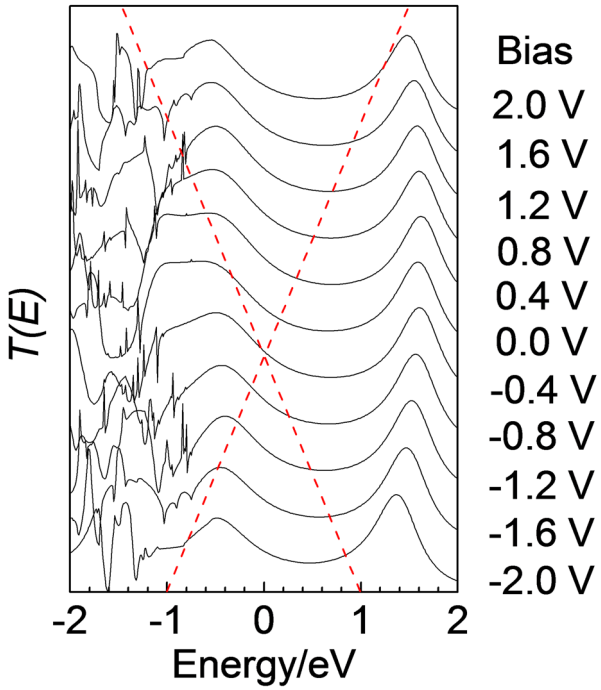


Fig. S2. Transmission spectra of molecule A (azulene) in extent bias. The bias windows are shown by the dash lines.

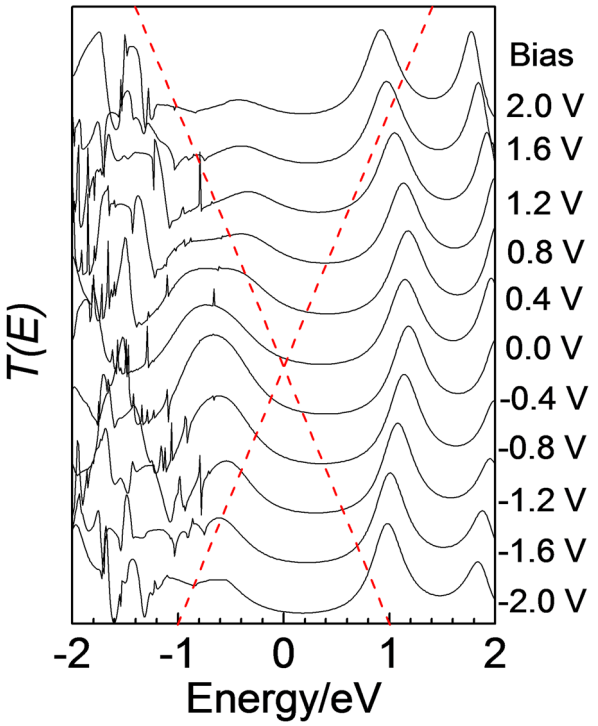


Fig. S3. Transmission spectra of molecule B in extent bias. The bias windows are shown by the dash lines.

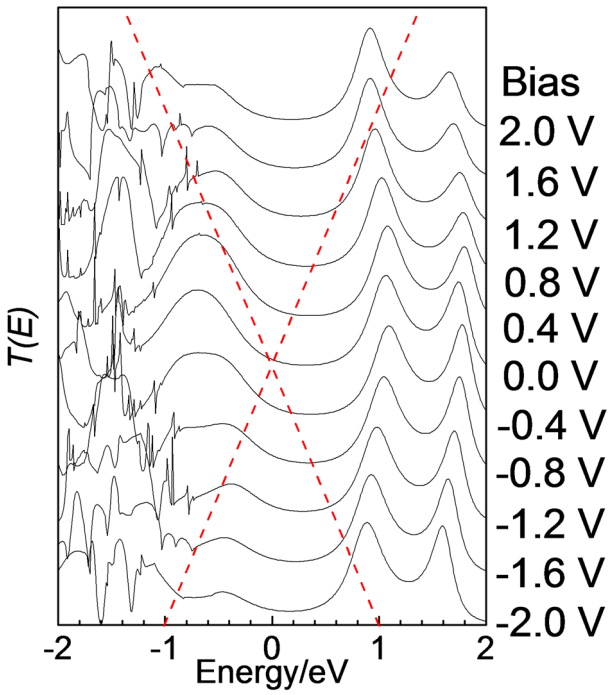


Fig. S4. Transmission spectra of molecule C in extent bias. The bias windows are shown by the dash lines.

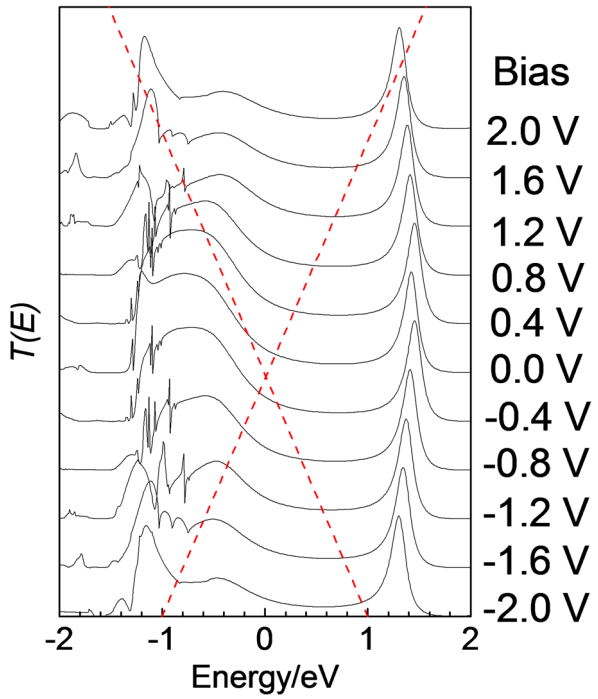


Fig. S5. Transmission spectra of molecule E (anthracene) in extent bias. The bias windows are shown by the dash lines.

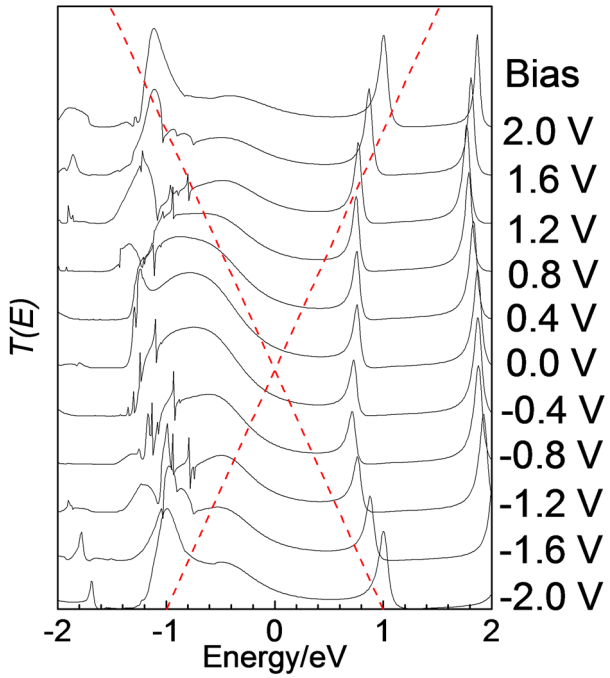


Fig. S6. Transmission spectra of molecule F in extent bias. The bias windows are shown by the dash lines.

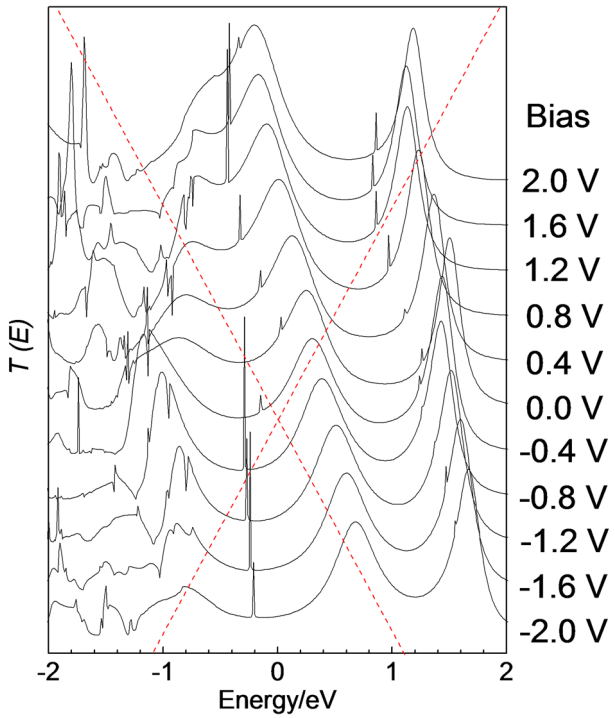


Fig. S7. Transmission spectra of molecule H in extent bias. The bias windows are shown by the dash lines.

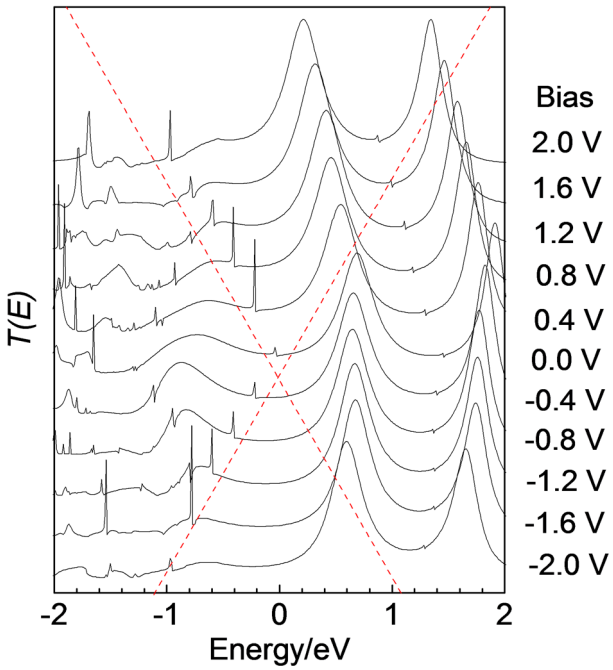


Fig. S8. Transmission spectra of molecule I in extent bias. The bias windows are shown by the dash lines.

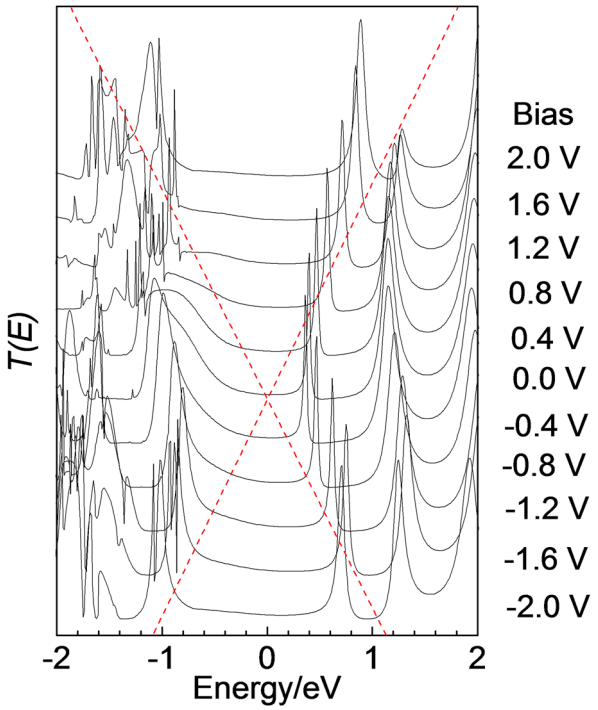


Fig. S9. Transmission spectra of molecule J in extent bias. The bias windows are shown by the dash lines.

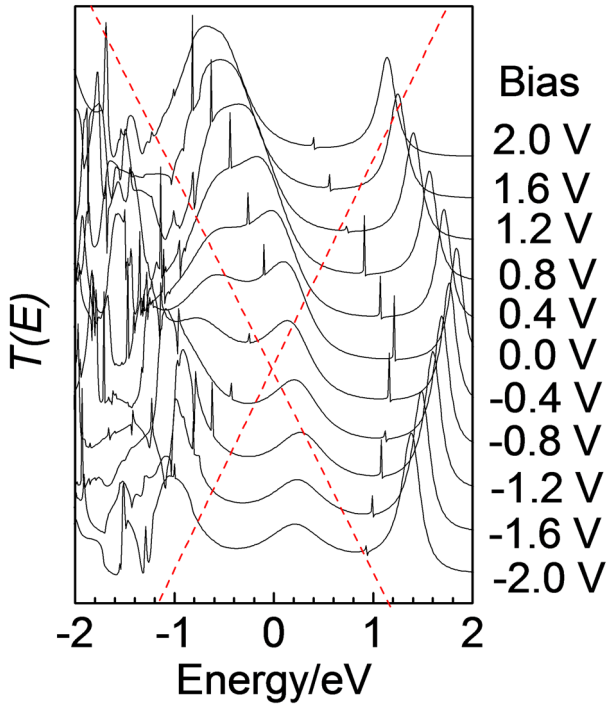


Fig. S10. Transmission spectra of molecule aLi-G (Fig. 8) in extent bias. The bias windows are shown by the dash lines.

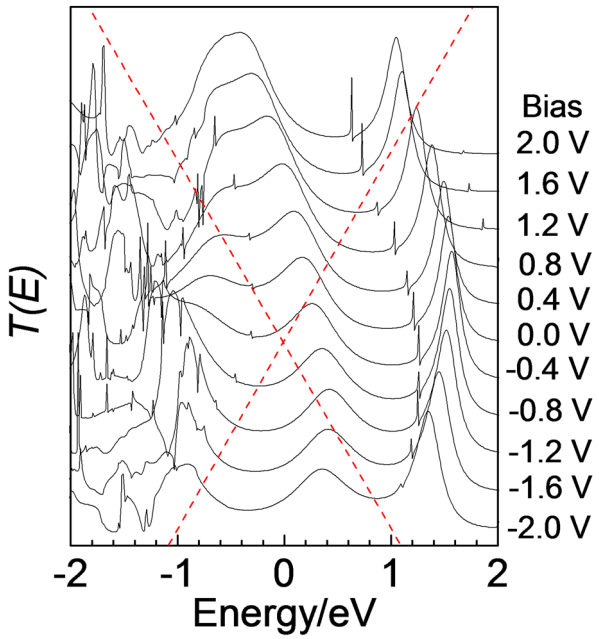


Fig. S11. Transmission spectra of molecule bLi-G (Fig. 8) in extent bias. The bias windows are shown by the dash lines.

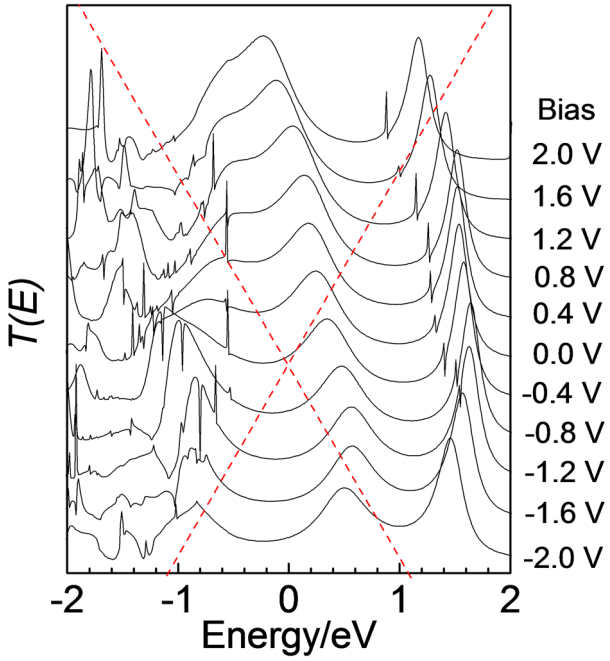


Fig. S12. Transmission spectra of molecule cLi-G (Fig. 8) in extent bias. The bias windows are shown by the dash lines.

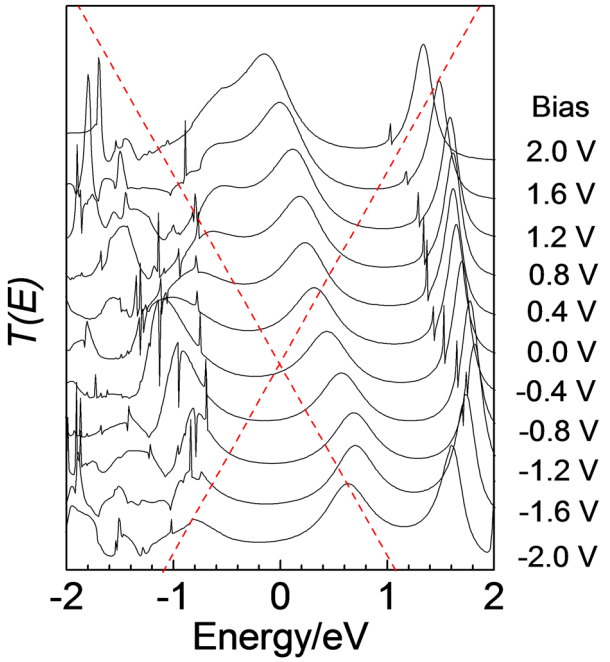


Fig. S13. Transmission spectra of molecule dLi-G (Fig. 8) in extent bias. The bias windows are shown by the dash lines.

4. A five-ring azulene-like molecules

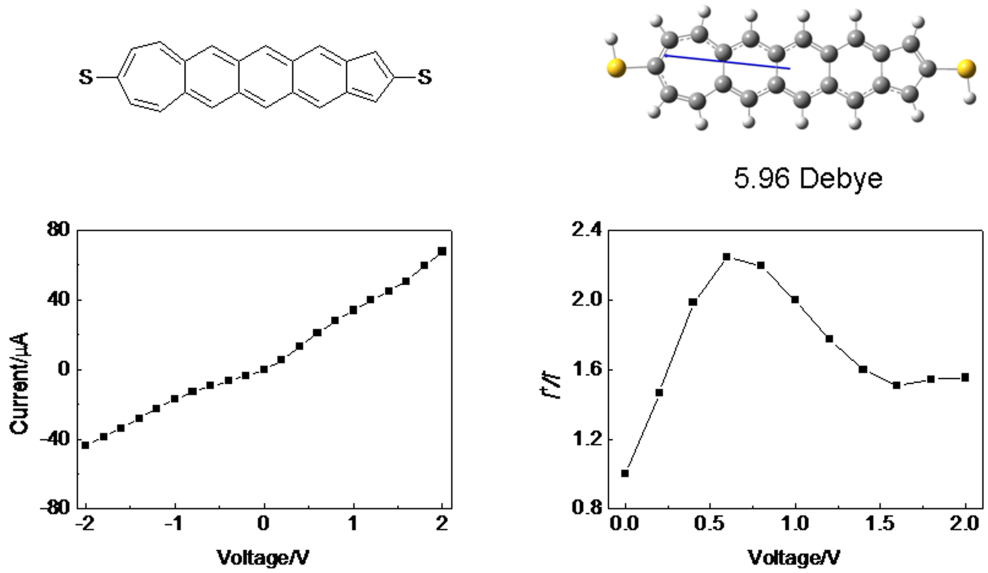


Fig. S14. The electronic transport and rectification performance of a five-ring azulene-like molecule.

5. Dipole moments of azulnene-like molecules

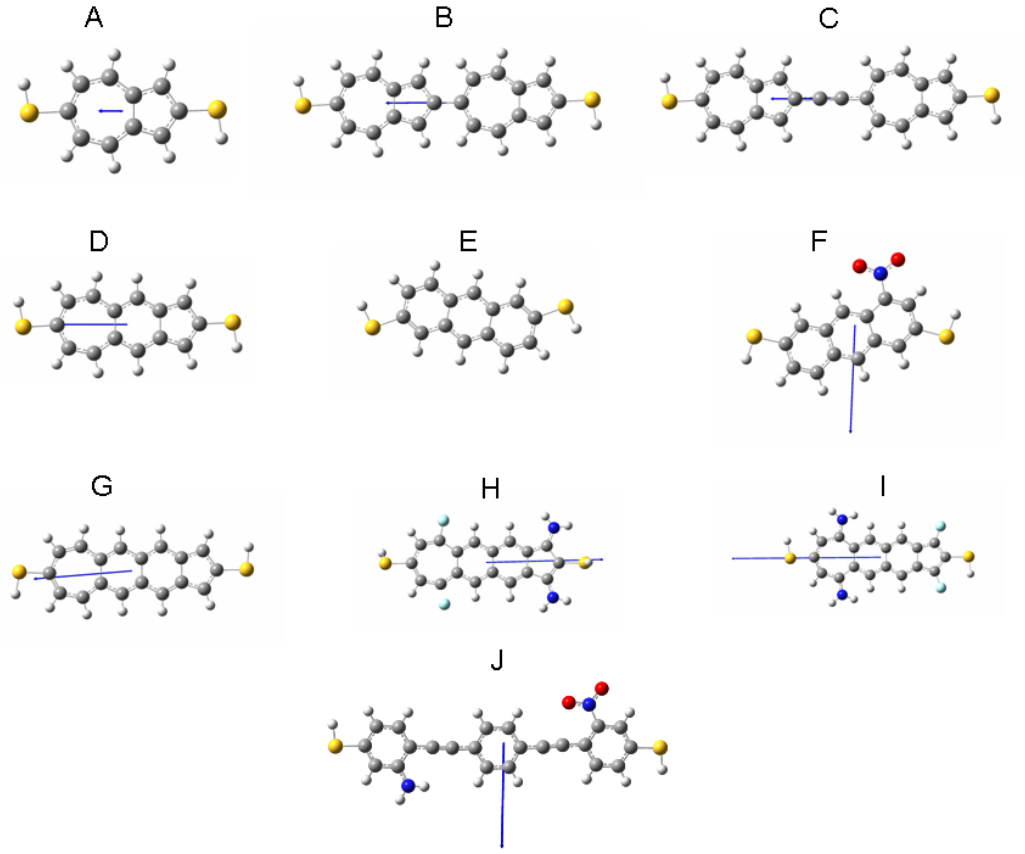
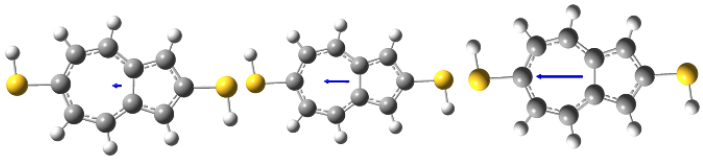


Fig. S15. The dipole vectors for all simulated molecules.

6. Bias induced re-polarization



Bias	-1V	0V	+1V
Dipole	0.36 Debye	1.16 Debye	1.96 Debye

Fig. S16. The dipole vectors of molecule A under different bias.

References

1 S. N. Yaliraki, A. E. Roitberg, C. Gonzalez, V. Mujica and M. A. Ratner, *J. Chem. Phys.*, 1999, **111**, 6997-7002.

2 A. Staykov, D. Nozaki and K. Yoshizawa, *J. Phys. Chem. C*, 2007, **111**, 11698-11705.

3 Y. Xing, L. Hongmei and Z. Jianwei, *J. Chem. Phys.*, 2006, **125**, 094711.