Table 2: NPA Atomic charges (e) of the molecules

Atoms	I	II	III	IV	Atoms	I	II	III	IV
C(1)	-0.201	-0.121	-0.165	-0.171	C(17)	-0.192	-0.190	-0.200	-0.195
C(2)	-0.193	-0.204	-0.196	-0.201	C(18)	-0.037	-0.040	-0.042	-0.035
C(3)	-0.192	-0.183	-0.200	-0.194	C(19)	-0.192	-0.190	-0.200	-0.195
C(4)	-0.047	-0.040	-0.035	-0.033	C(20)	-0.156	-0.155	-0.168	-0.164
C(5)	-0.192	-0.184	-0.200	-0.191	C(21)	-0.047	-0.040	-0.035	-0.033
C(6)	-0.193	-0.205	-0.196	-0.192	C(22)	-0.192	-0.184	-0.200	-0.191
C(7)	-0.037	-0.040	-0.042	-0.035	C(23)	-0.193	-0.205	-0.196	-0.192
C(8)	-0.192	-0.190	-0.200	-0.195	C(24)	-0.201	-0.121	-0.165	-0.171
C(9)	-0.156	-0.155	-0.168	-0.164	C(25)	-0.193	-0.204	-0.196	-0.201
C(10)	-0.121	-0.119	-0.105	-0.101	C(26)	-0.192	-0.183	-0.200	-0.194
C(11)	-0.156	-0.155	-0.168	-0.164	S(1)	—	-0.064	-0.149	0.074
C(12)	-0.192	-0.190	-0.200	-0.195	S(2)	—	-0.064	-0.149	0.074
C(13)	0.010	0.011	-0.002	0.008	Au(1)	—	—	0.217	—
C(14)	0.010	0.011	-0.002	0.008	Au(2)	—	—	0.217	—
C(15)	-0.121	-0.119	-0.105	-0.101	Pt(1)	—	—	—	-0.071
C(16)	-0.156	-0.155	-0.168	-0.164	Pt(2)	—	—	—	-0.071

4. Molecular Orbital Analysis

Molecular orbitals are obtained from the combination of atomic orbitals, which predict the location of an electron in an atom. A molecular orbital is a mathematical function describing the wave-like behavior of an electron in a molecule [18,19]. This function can be used to calculate the chemical and physical properties such as the probability of finding an electron in any specific region [19,20]. The most important orbitals in molecules for reactivity are the two so called frontier orbitals known as HOMO and LUMO. HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital [21]. The energy difference between the HOMO and LUMO is termed as the HOMO–LUMO gap (HLG). The charge transport properties [22] of the molecule mainly depends on HLG, hence, it is necessary to examine the variations in HLG and molecular orbital energy levels. Fig.5 illustrates the energy levels of all the molecules calculated from quantum chemical calculations.

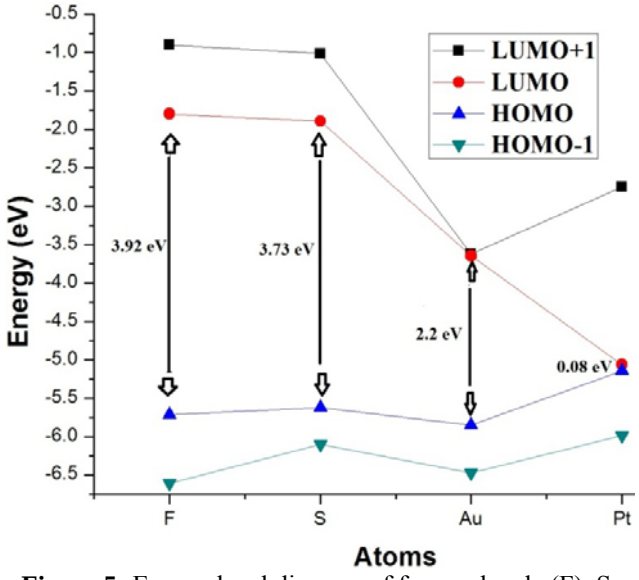
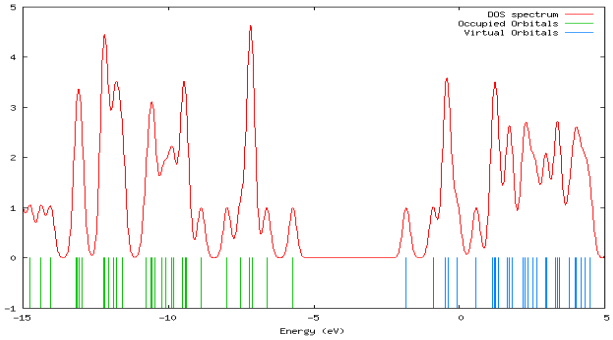
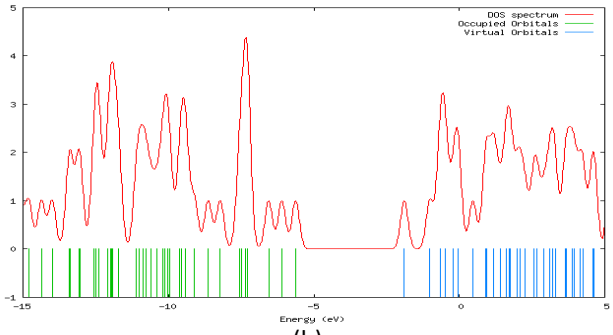


Figure 5: Energy level diagram of free molecule (F), S, Au and Pt substituted molecules

The HLG can also be determined from the density of states (DOS) spectrum [23]. DOS of a system describes the number of states per interval of energy at each energy level that are available to be occupied by electrons. A high DOS at a specific energy level means that there are many states available for occupation. A DOS of zero means that no states can be occupied at that energy level [24]. Fig.6 [(a)-(d)], shows the density of states (DOS) for the molecules- I, II, III and IV in which the green lines indicate the HOMO and the blue is LUMO, the decrease of HLG is also shown. Here, the hybridization of the molecular level with that of the gold atom broadens the DOS peaks. The HLG of molecules-I, II, III and IV are 3.92, 3.73, 2.20 and 0.08 eV respectively. The large decrease of HLG of the molecule-III and molecule-IV facilitates large electron conduction through the molecule [7], hence, the Au or Pt substituted molecule can act as an efficient molecular nanowire.



(a)



(b)

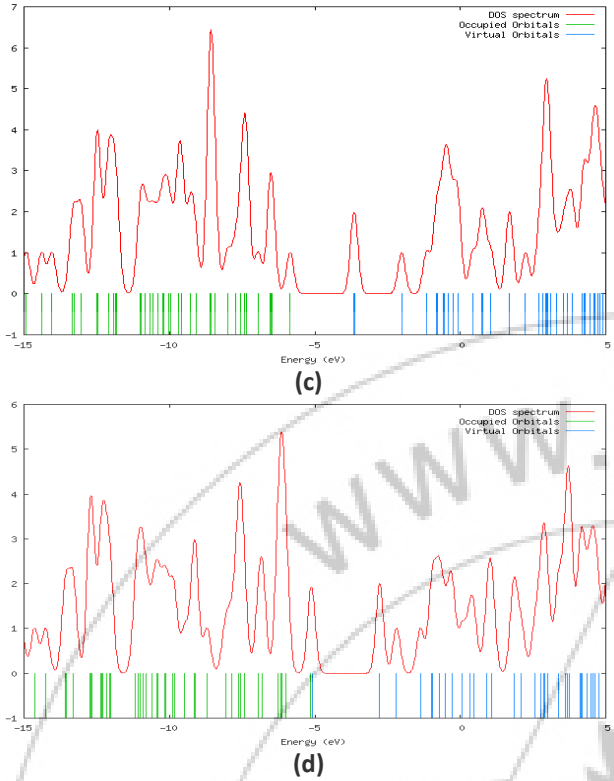


Figure 6: [(a)-(d)], Shows the density of states (DOS) for the molecules-I, II, III and IV.

5. Conclusion

The present computational study on 1, 2-di (biphenyl-4-yl)ethyne molecular nanowire describes the difference in atomic charges of the molecule substituted with thiol, Au and Pt atoms. The linker thiol atoms on either ends [S(1) and S(2)] possess same MPA charge for molecule-II (0.038e), molecule-III (0.084e) and molecule-IV (0.095e). The charges of Au atom at both ends of the molecule-III are equal (-0.054e). Similarly, the charges of Pt atom at both ends of the molecule-IV are equal (-0.213e). Similarly, the NPA charges of thiol, Au and Pt atoms at both ends of the molecules are equal; however, there is slight difference between MPA and NPA charges of all atoms. Further, it is found to be MPA and NPA charges of linker thiol atoms gradually increases for substituting Au and Pt metal electrodes. From the DOS spectrum, the HLG of molecules-I, II, III and IV are found to be 3.92, 3.73, 2.20 and 0.08 eV respectively. The large decrease of HLG of the molecule-III and molecule-IV facilitates large electron conduction through these molecules, hence, charge transport increases for the Au or Pt substituted molecules. However, Au electrodes are user friendly than Pt electrodes, hence, 1, 2-di (biphenyl-4-yl)ethyne molecule using Au as electrodes with thiol as linker can act as efficient molecular nanowire.

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