Exploring an N-Type Conducting Polymer (BBL) as a Potential Gas Sensing Material for NH_3 and H_2S Detection: A Theoretical Study

Sonu Sunny,[†] Shivam Shah,[†,¶] Sushri Soumya Jena,[†,¶] Bhavika Gopalani,[†] Mohit Garg,[†] Arnab Hazra,[‡] and Sarbani Ghosh[*,†]

†*Department of Chemical Engineering, Birla Institute of Technology and Science (BITS), Pilani Campus, Vidya Vihar, Pilani, 333031, Rajasthan, India*

‡*Department of Electrical and Electronics Engineering, Birla Institute of Technology and Science (BITS), Pilani Campus, Vidya Vihar, Pilani, 333031, Rajasthan, India*

¶*These authors contributed equally to this work*

E-mail: sarbani.ghosh@pilani.bits-pilani.ac.in

Supplementary Information

DFT Study

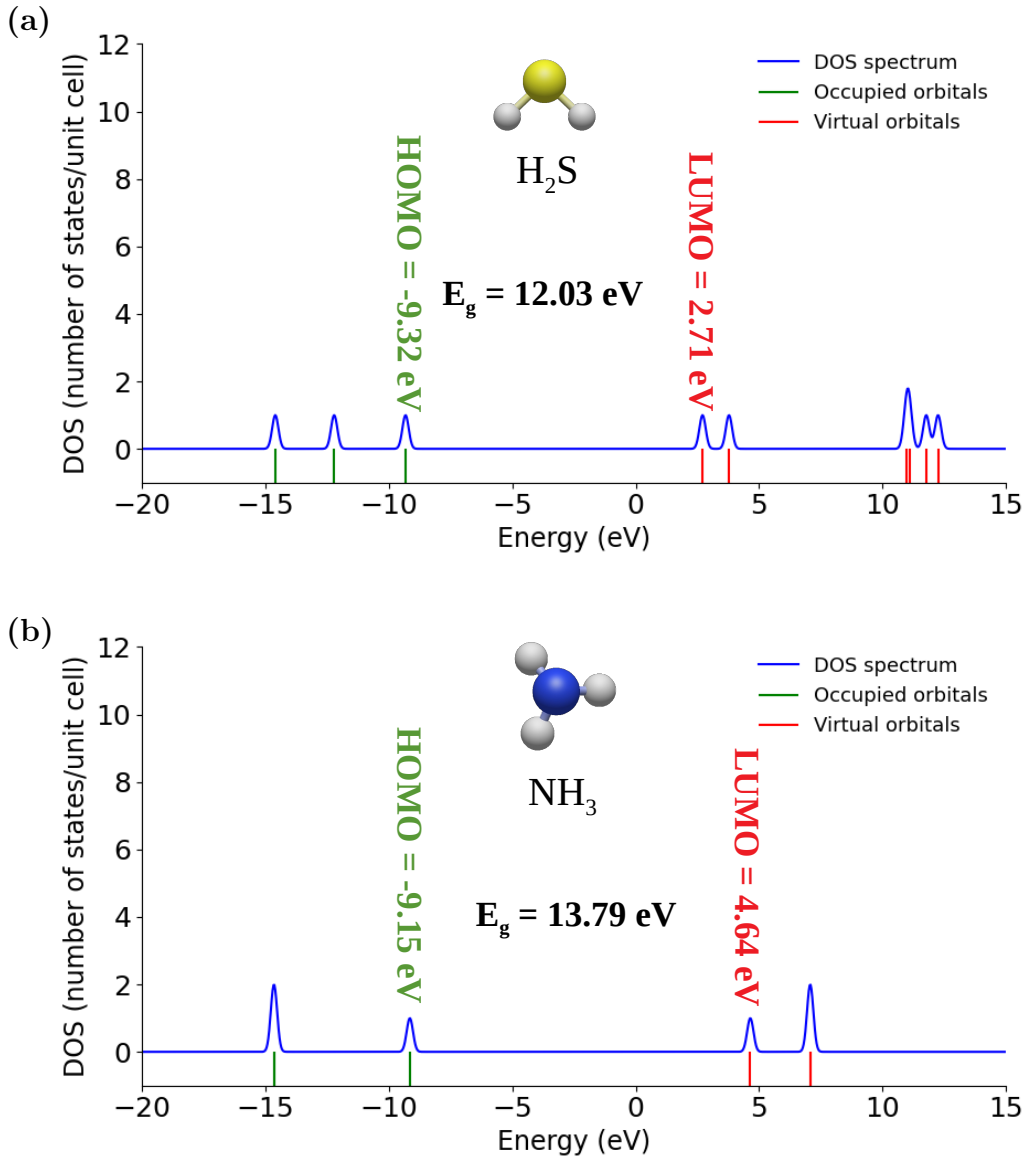

Figure S1: Density of states (DoS) of isolated (a) H_2S and (b) NH_3 molecule. The corresponding HOMO, LUMO, and the HOMO-LUMO bandgap (Eg) are marked within the figure.

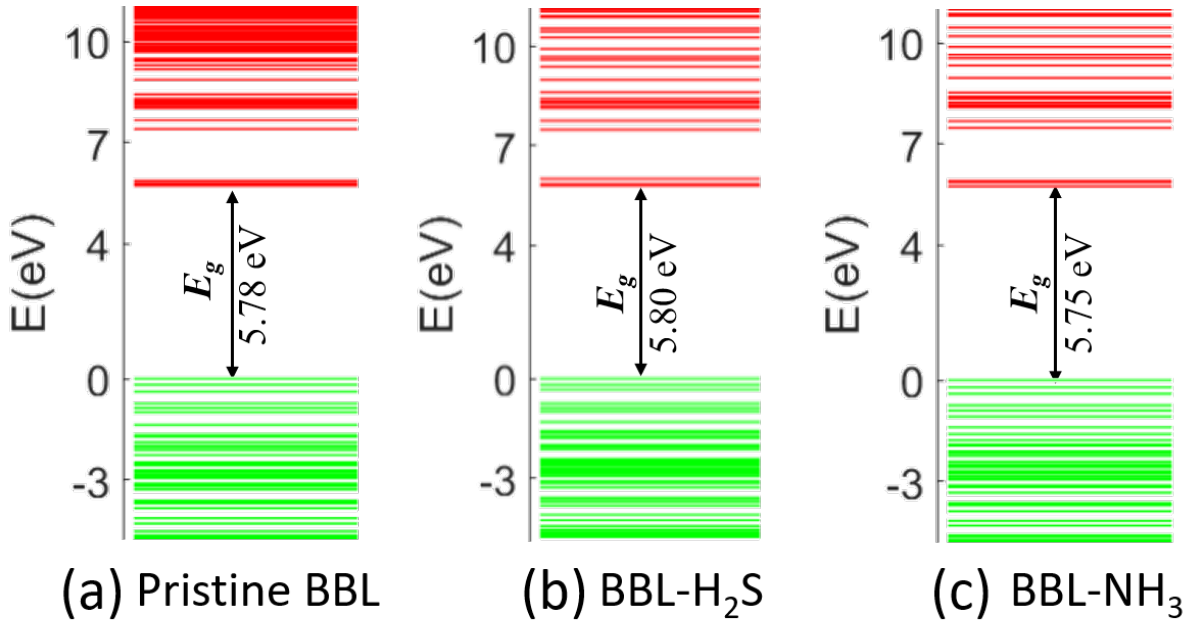

Figure S2: Molecular orbital diagrams of (a) Pristine BBL, (b) BBL-H_2S, and (c) BBL-NH_3. The energy lines in the valence band and the conduction band are shown in green and red, respectively. The corresponding energy gap (E_g) between the valence and conduction band of all three systems are marked.

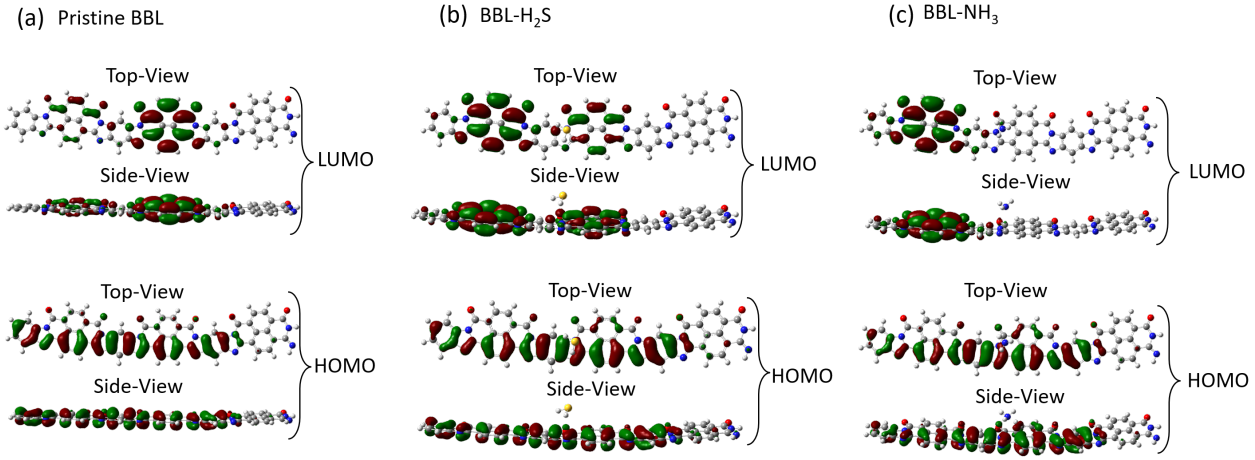

Figure S3: Electronic density distribution of LUMO-HOMO levels of (a) BBL, (b) BBL-H_2S, and (c) BBL-NH_3.

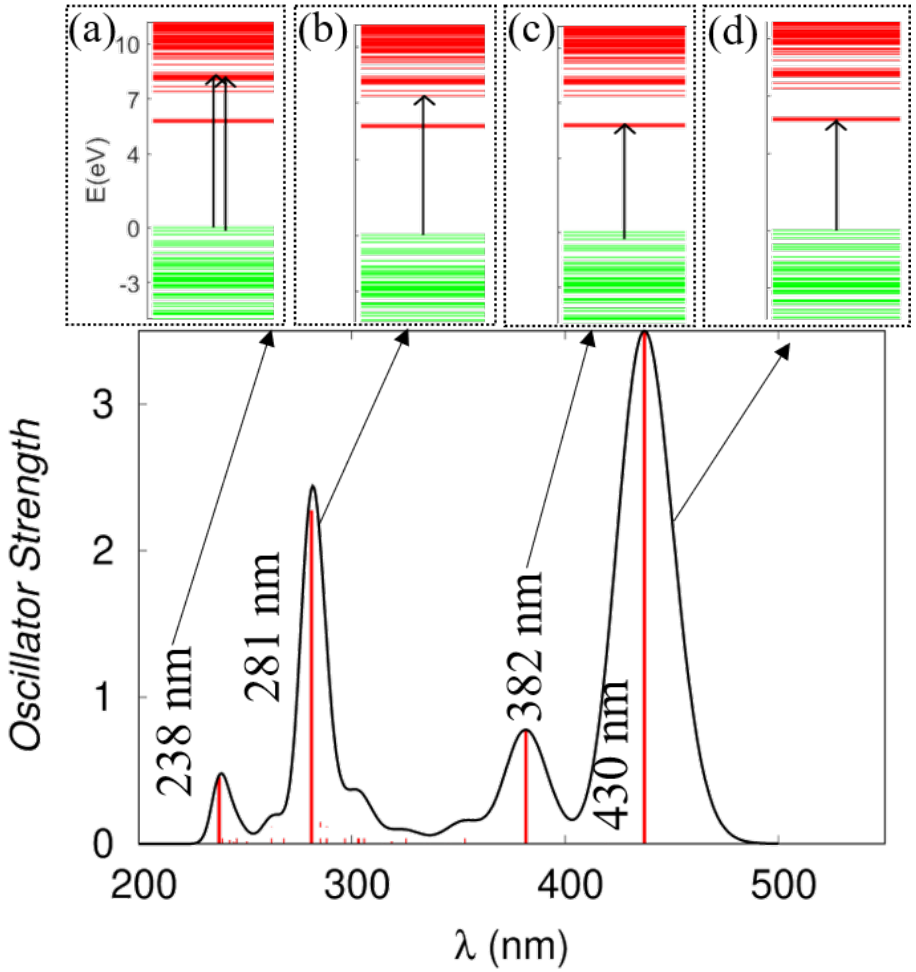

Figure S4: The corresponding electronic transitions of all four peaks present in the UV-vis absorption spectra of Pristine BBL. (a,b)The two peaks in the lower wavelength are due to the electronic transitions from HOMO and HOMO-1 to the higher-lying unoccupied energy levels attributed to the mini-band formation in the conduction band. (c) The peak at 382 nm is due to the electronic transition from HOMO-3 to the LUMO. (d) The peak at the highest wavelength (430nm) is due to the HOMO-LUMO electronic transition.

FTIR Study

In order to understand the structural and chemical changes before and after the gas adsorption, we performed an FTIR analysis of the sample. The FTIR spectra of the sample before and after gas adsorption in the range of 2000 to 600cm^{-1} are shown in Figure S1. We observed the C=O stretching band at 1700cm^{-1}, the C=C stretching band at 1500cm^{-1}, the C=N and C-N strechings in the range of 1400cm^{-1} to 1300cm^{-1} and finally the aromatic C-H bending at 995cm^{-1}.[1] There is no appreciable change in the spectra of pristine BBL, indicating that the neutral BBL has not undergone any structural or chemical changes even after the gas adsorption. This underscores the potential of BBL polymer to act as a promising active material for gas sensing applications. The FTIR spectra were measured in transmission mode with PerkinElmer Spectrum Version Frontier FT-IR, averaging 20 scans with a resolution of 4 cm^{-1}.

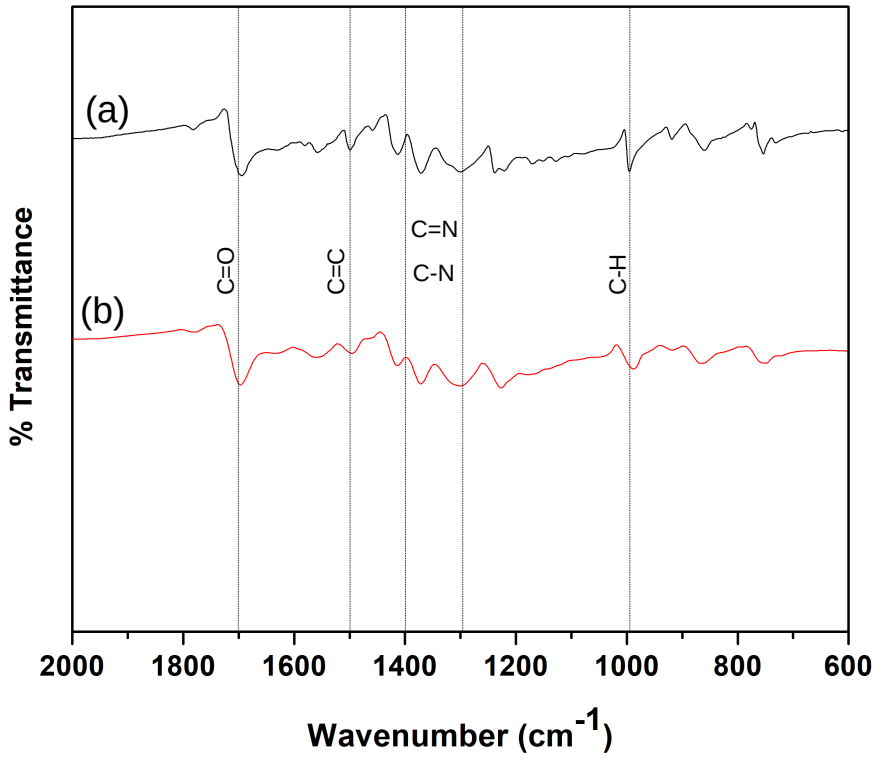

Figure S5: FTIR Spectra for neutral BBL film (a) before, and (b) after gas adsorption.

PSD Analysis

To analyze the nanoporous structure, we conducted calculations for free volume, surface area, and pore size distribution (PSD) using the Zeo++ package. The free volume representation of BBL-H_2S and BBL-NH_3 systems without polymer chains and analyte gas molecules are given in FigureS6.

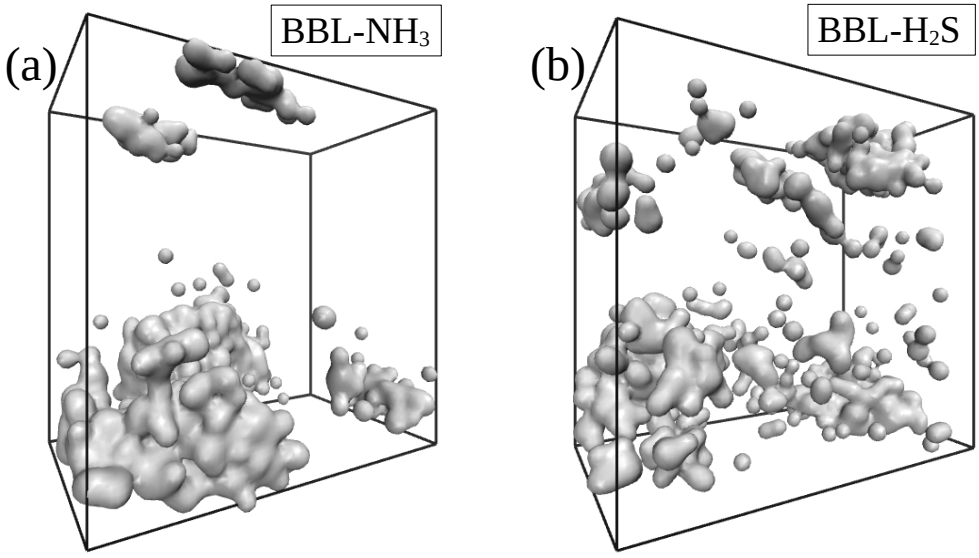

Figure S6: (a) Free volume distribution of (a) BBL-NH_3 and (b) BBL-H_2S systems.

Table S1: Calculated available volume, AV (Å^3), non available volume, NAV (Å^3), available surface area, ASA (Å^2) and non available surface, NASA area (Å^2) of unloaded, and NH_3 and H_2S loaded BBL.

System	AV(Å^3)	NAV (Å^3)	ASA (Å^2)	NASA (Å^2)
Unloaded	74337.1	22353.1	36941.3	29384.3
BBL-H_2S	73526.2	9190.77	63712.9	20688.9
BBl-NH_3	73791.3	26158.3	-30814.7	37078.7

References

(1) Wang, S.; Ruoko, T.-P.; Wang, G.; Riera-Galindo, S.; Hultmark, S.; Puttisong, Y.; Moro, F.; Yan, H.; Chen, W. M.; Berggren, M.; others Sequential doping of ladder-type conjugated polymers for thermally stable n-type organic conductors. *ACS Applied Materials & Interfaces* **2020**, *12*, 53003–53011.