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Tuning the opto-electronic properties of MoS$_2$ layer using charge transfer interactions: effect of different donor molecules

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Abstract

We have performed density functional theory calculations to study the effect of adsorption of a set of organic electron donor molecules on single layer MoS$_2$ to find the optimum condition to tune the charge transfer, as well as to find how it changes the electronic properties of single layer MoS$_2$. We have performed our calculations for three sets of organic Lewis bases. We have found that all the molecules are physisorbed on MoS$_2$. Our calculations show that the charge transfer from the molecules to the MoS$_2$ layer is highly dependent upon the inductive effect and HOMO–LUMO gap of the molecules. Furthermore, we show that the charge transfer interaction tunes the electronic and optical property of MoS$_2$ to a significant amount: for example, the band-gap of the system can be changed from 1.8 eV to even a low value of 0.2 eV, making it interesting for different optoelectronic device applications.

Introduction

Recently, since the last decade, all two-dimensional materials, including transition metal-dichalcogenites (MoS$_2$, WS$_2$, VS$_2$ etc) have become a subject of huge scientific interest because of their possible application in nano electronics [1–9]. They are very promising materials for opto-electronic applications because of their intrinsic semiconducting nature. These materials have layered structure, held by weak van der Waals forces. Therefore, these materials can be easily exfoliated into 2D nano crystals. The combination of lower dimension, high surface area and high band-gap make these 2D nano crystals potential candidates for advanced device applications.

Single layer MoS$_2$, a widely studied transition metal dichalcogenite, has gained attention because of its interesting electronic and electrical properties. It has high carrier mobility [4, 5, 10, 11], and can be used as transistors [11, 12] or energy storage devices such as anodes for Li or Mg ion batteries [13–15]. Also, different forms of MoS$_2$ are commercially available as solid lubricants [16, 17]. Depending upon the atomic arrangements, monolayer MoS$_2$ can stay in different phases, e.g. semiconducting (2H) or metallic (1T) phases [18]. Single layer MoS$_2$ is very easy to fabricate from the bulk and also it is feasible to apply them in different devices [10, 19, 20]. Previously, experiments and theories were used to show that doping of different atoms or small molecules on MoS$_2$ or using an electron beam to create both S and M$_o$ vacancies and adding impurity atoms to the vacant sites can modify the electronic properties of single layer MoS$_2$ [21–26]. Also, organic molecules (such as thiophene, benzothiophene, benzene, naphthalene, pyridine, quinolone, tetrathiofulvalene (TTF) etc) were deposited on MoS$_2$, either to study the charge transfer interactions of the molecules with MoS$_2$, or to tune the band-gap of the systems [27–29]. It was found by most of the studies that, as single layer MoS$_2$ is an electron deficient material at room temperature [30], it can accept electron easily from electron donor molecules, whereas it cannot donate electrons to electron acceptor molecules [29, 31]. Based on these facts, single layer MoS$_2$ transistor was made for gas sensing purposes, as it can sense electron donor gases easily, while electron withdrawing gases will not show any response [32–35].

Inspired by these experimental findings, we have selected three sets of organic electron donor molecules (Lewis bases) for our study; the first set consist of two TTF derivatives, TTF and tetramethyl-tetrathiofulvalene

(TMTTF), while the 2nd set consists of two aromatic diamine moieties, namely 1,5-Napthalenediamine and 1,6-Pyrenediamine. In the last set, there are two aliphatic diamines, viz. 1,3-propanediamine and N,N'-dimethyl-1,2-ethanediamine. The last two molecules have same pKa values both in gaseous and water medium [36]. We consider the deposition of these molecules on single layer MoS_2 in our study. This study aims to show the importance of different groups of molecules as adsorbents, as some of them have better adsorption energy and some of them are better as charge-transfer molecules.

Already some of these donor molecules along with the acceptor molecules are used as room temperature organic ferroelectric materials (naphthalene and pyrene derivatives) [37], organic field effect transistor etc (TTF derivatives) etc [38, 39]. Thus, we believe these MoS_2–donor complexes can easily be used in device applications as already similar systems are synthesized experimentally and have found advanced applications [29].

Although all the molecules under our study are strong electron donors, there are still some basic differences in them. While a few of them have some functional groups (the 1st and the 3rd group), the 2nd group has difference in aromaticity. In this study, we find that these factors lead to huge changes in charge transfer and as a consequence to the electronic and the optical properties of the MoS_2 layer. We have shown in this study that to control the ban-gap of the system, different group of molecules can contribute in different manner.
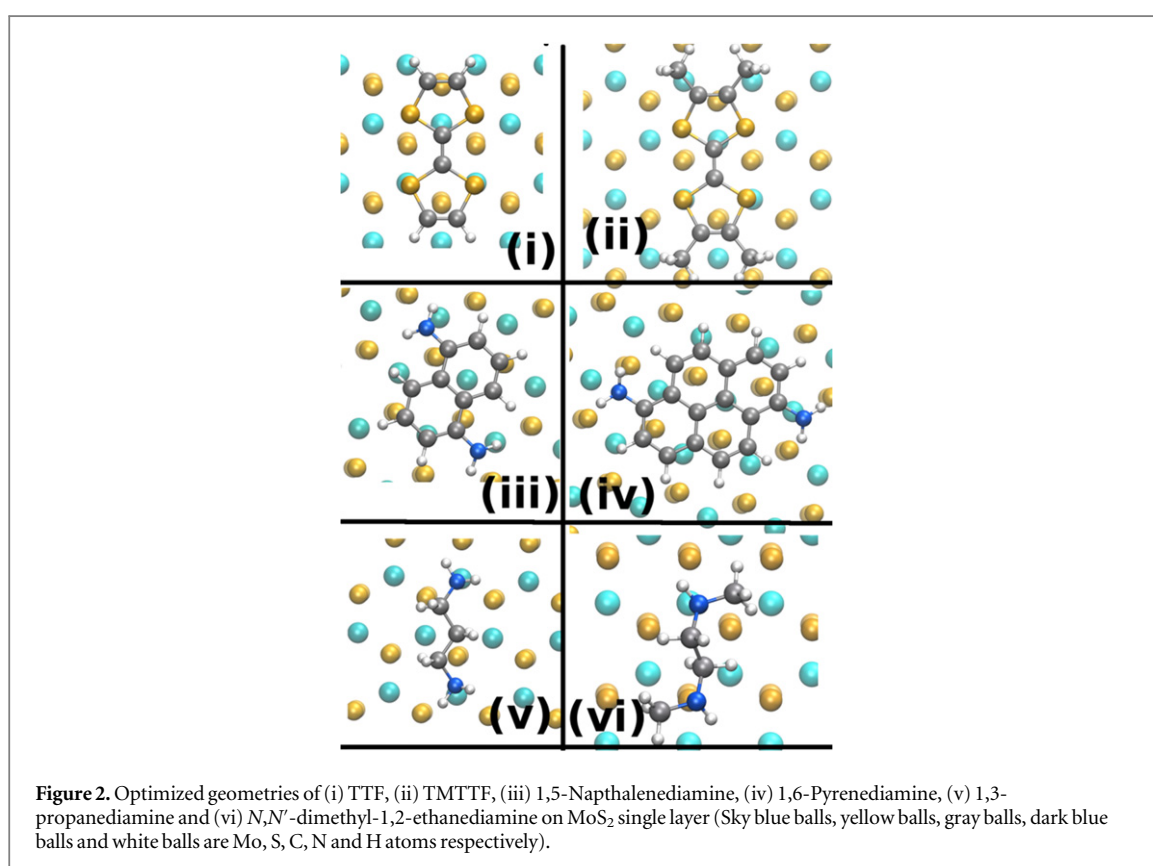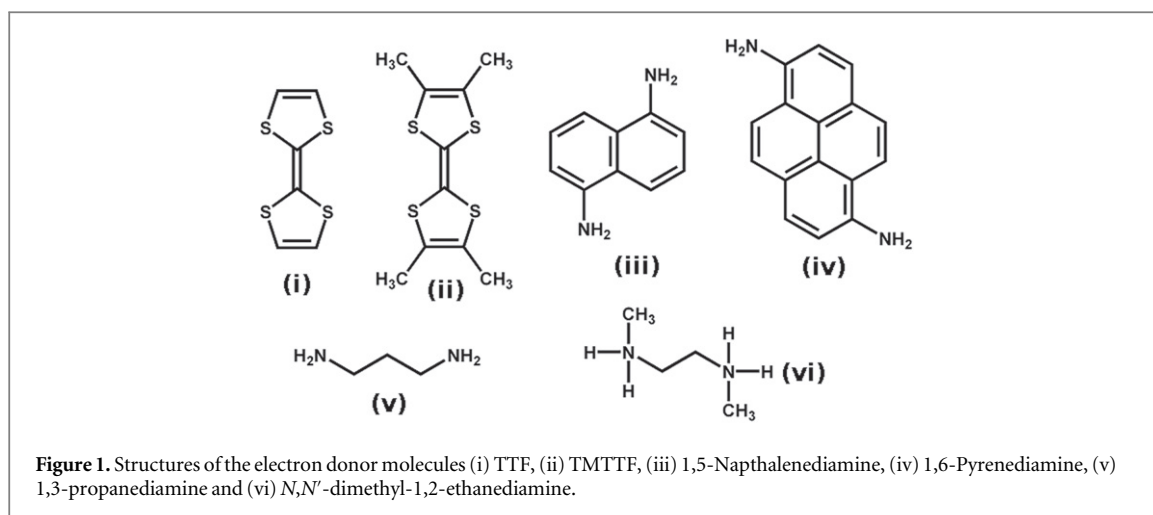
Computational details

In this study, all geometry optimizations are performed using density functional theory (DFT) with exchange-correlation functional in generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form [40], along with Grimme's DFT-D3 dispersion correction [41], as implemented in the QUICKSTEP module of the CP2K package [42]. The norm-conserving Goedecker−Teter−Hutter pseudopotentials [43–45], which are optimized in this software package to use them along with the PBE functional have been used for Mo, S, C, N and H atoms. CP2K package employs a hybrid Gaussian and plane-wave method for the wave function representation. In this present work, double-ζ valence polarized basis sets are used. Along-side with the NN50 smoothing method, a 320 Ry density cutoff is used. Geometry optimizations have been performed using BFGS method, and systems are considered to be optimized until the force on each atom is <0.0001 hartree/Bohr. We have performed Mülliken population analysis and adsorption energy calculations on the systems. We have calculated the band-structures, density of states (DOS) plots and optical properties of the CP2K optimized systems using DFT methods as implemented in the SIESTA package [46]. GGA in the PBE form [40] has been used to take the exchange-correlation function into account. Double ζ polarized atomic-orbital basis sets have been used all the atoms. Molecular dopant adsorption on graphitic systems and inorganic analogues of graphene has been well studied using GGA [10, 47, 48] and they are proved to be sufficient to reproduce the trends in adsorption energies [49]. Norm-conserving pseudo-potentials [50] are considered for all the atoms in the fully nonlocal Kleinman–Bylander form [51]. A reasonable mesh cut-off of 320Ry is used for the grid integration to represent the charge density. We have sampled the Brillouin zone by $10 \times 10 \times 1$ k-points using the Monkhorst-Pack scheme for electronic property calculations. Periodic boundary condition and the supercell approximation are taken in such a way so that the distance between an adsorbate molecule and its periodic image is more than 10 Å to avoid any unintentional interactions between them. We have considered the 2H MoS_2 supercell as it is a thermodynamically stable phase [18]. The MoS_2 supercell is 8×8 in size (it contains 64 Mo atoms and 128 s atoms and one S layer, followed by one Mo and another S layer). We have kept a 15 Å vacuum along the z axis and found that this is sufficient to get the energy convergence and optimized configurations. We found that our calculated band-gap of MoS_2 compares well with experimental findings [5, 10].

Results and discussions

We study here the effect of adsorption of different organic Lewis bases (electron donor molecules) on single layer MoS_2. We have found that all the molecules, that is, TTF, TMTTF, 1,5-Napthalenediamine, 1,6-Pyrenediamine, 1,3-propanediamine and N,N'-dimethyl-1,2-ethanediamine are thermodynamically stable on the MoS_2 layer. We have calculated the adsorption energies of the systems using the following formula to assess the relative stability of the systems [47]:

$$\Delta E_{\text{adsorption}} = E_{\text{molecule}+MoS_2} - E_{MoS_2} - E_{\text{molecule}},$$

where $\Delta E_{\text{adsorption}}$, $E_{\text{molecule}+MoS_2}$, E_{MoS_2} and E_{molecule} are the adsorption energy, total energy of the optimized molecule–MoS_2 system, energy of the single layer MoS_2 and energy of the molecule, respectively. In figure 1, we have given the graphical representation of the molecules and in figure 2 we have given the optimized structure of the molecules over MoS_2.

Figure 1. Structures of the electron donor molecules (i) TTF, (ii) TMTTF, (iii) 1,5-Napthalenediamine, (iv) 1,6-Pyrenediamine, (v) 1,3-propanediamine and (vi) *N,N′*-dimethyl-1,2-ethanediamine.

Figure 2. Optimized geometries of (i) TTF, (ii) TMTTF, (iii) 1,5-Napthalenediamine, (iv) 1,6-Pyrenediamine, (v) 1,3-propanediamine and (vi) *N,N′*-dimethyl-1,2-ethanediamine on MoS_2 single layer (Sky blue balls, yellow balls, gray balls, dark blue balls and white balls are Mo, S, C, N and H atoms respectively).

From the optimized geometries (figure 2), it is evident that, all the molecules are almost parallel over the MoS_2 plane and there is no significant bending in any of the structures. For all the molecules, we have found the distance between the molecule and the MoS_2 layer to be $\geqslant 3$ Å. Therefore, there is no possibility of formation of chemical bond between the molecule and the MoS_2 layer.

We have performed the Mülliken population analysis of the systems to calculate the amount of charge (electron) transfer from the molecule to the MoS_2 plane, and we find that for the first set of molecules, that is, the TTF derivatives, the charge transfer increases to a small amount with the introduction of 4 groups showing +I effect (Me groups). We can attribute the charge transfer property of the molecule to its HOMO–LUMO (H–L) gaps also. A system with higher H–L gaps generally is more stable or less reactive [52], and we found that TTF molecule which has more band-gap shows less electron donor property. Because of the increment in the charge transfer, the interaction energy also increases from −1.44 to −1.92 eV (table 1) from TTF to TMTTF.

For the 2nd set of molecules, that is, for the diamine derivatives of polyaromatic hydrocarbons, we have found that, though both of the molecules have 2 amine groups as electron donors, the naphthalene derivative has
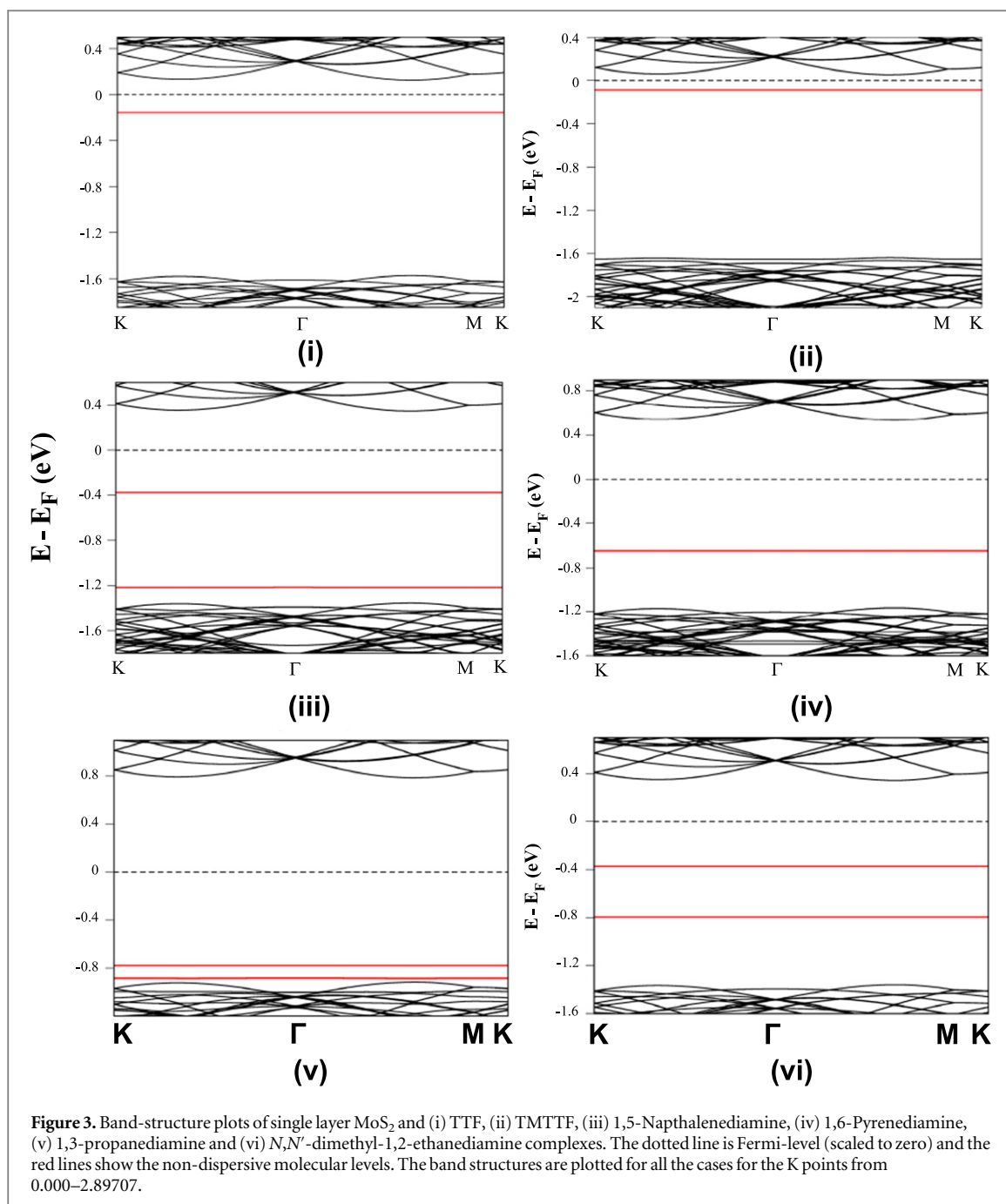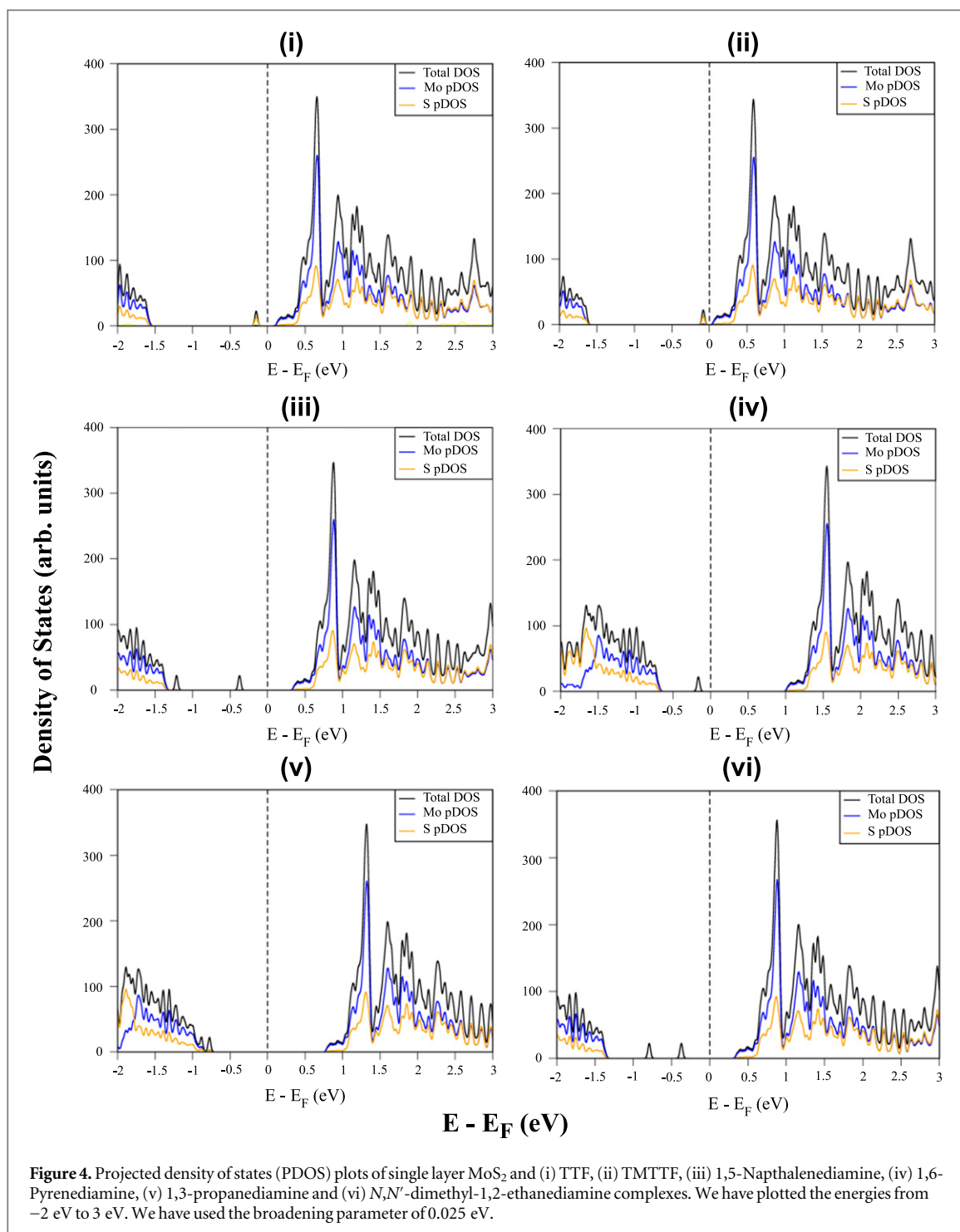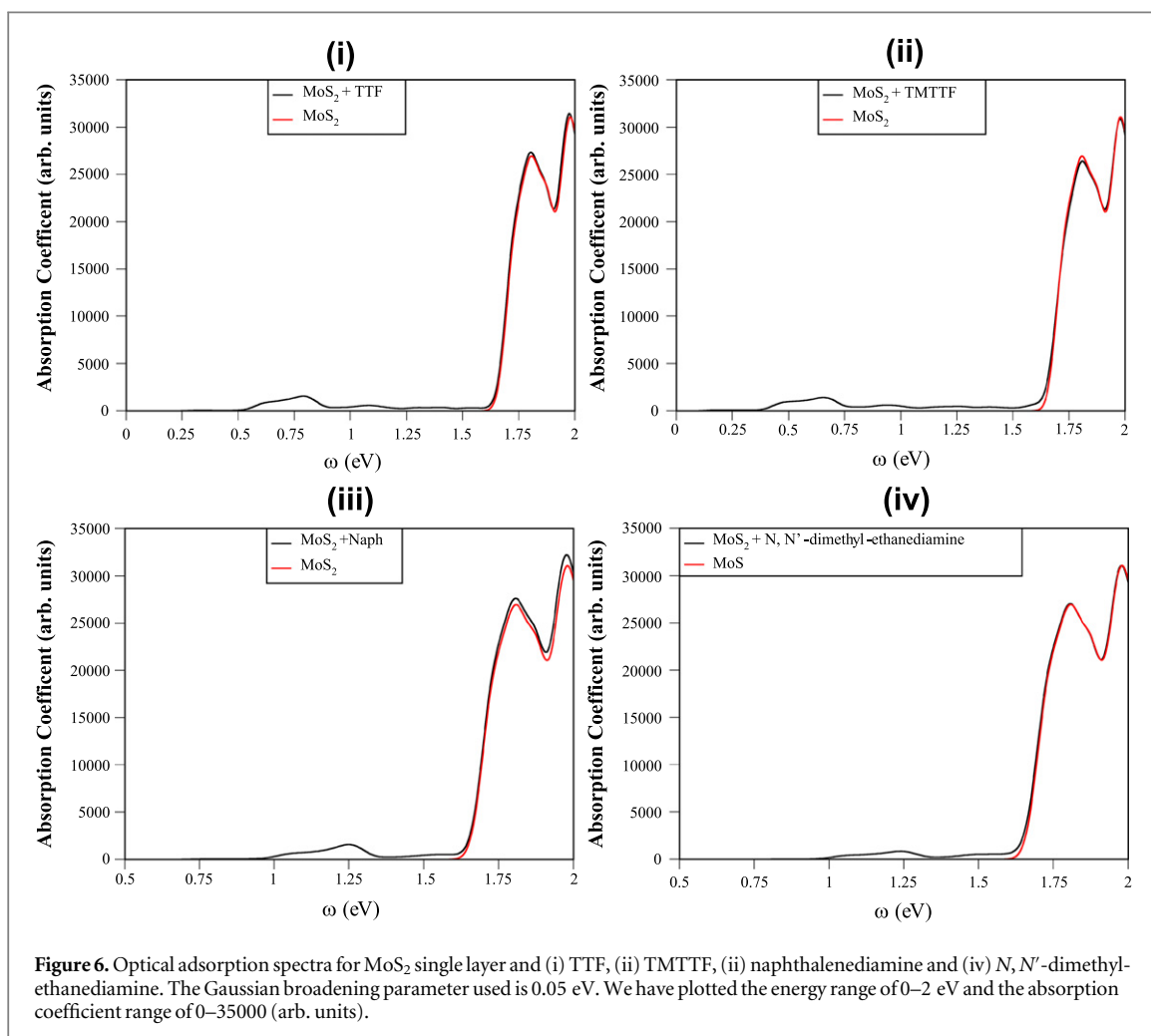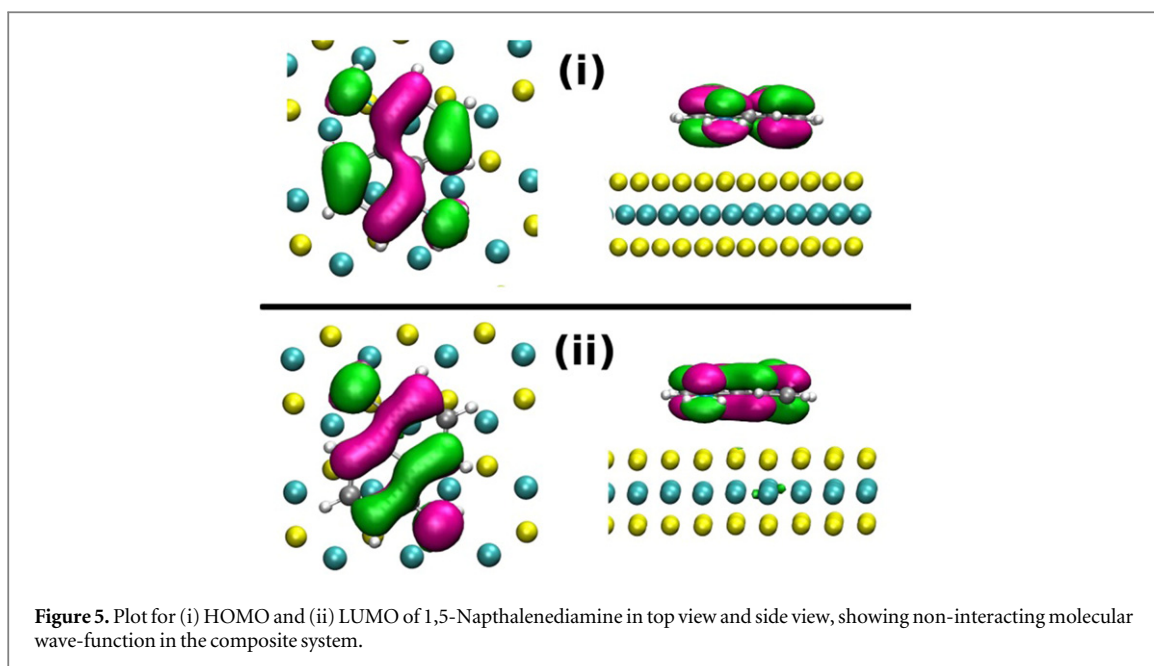
Figure 3. Band-structure plots of single layer MoS$_2$ and (i) TTF, (ii) TMTTF, (iii) 1,5-Napthalenediamine, (iv) 1,6-Pyrenediamine, (v) 1,3-propanediamine and (vi) *N,N'*-dimethyl-1,2-ethanediamine complexes. The dotted line is Fermi-level (scaled to zero) and the red lines show the non-dispersive molecular levels. The band structures are plotted for all the cases for the K points from 0.000–2.89707.

Table 1. Adsorption energies, distances and charge transfer values from the molecules to the single layer MoS$_2$.

Molecule	$\Delta E_{adsorption}$ (eV)	Distance (Å)	Charge transfer (e)	Band-gap (eV)	HOMO–LUMO gap of the molecule (eV)
(i) TTF	−1.44	3.13	0.23	0.34	−1.97
(ii) TMTTF	−1.92	3.11	0.27	0.2	−1.80
(iii) 1, 5-Napthalenediamine	−1.8	3.29	0.07	0.78	−2.83
(iv) 1, 6-Pyrenediamine	−1.91	3.17	0.09	1.24	−2.13
(v) 1,3-propanediamine	−0.7	2.95	0.06	1.62	−6.55
(vi) *N,N'*-dimethyl-1,2-ethanediamine	−0.82	3.14	0.07	0.78	−6.53

higher H–L gap, thus it shows lower charge transfer value than the pyrene derivative. This is because of the π-surface area of pyrene is more than that of naphthalene, thus, the van der Waals interactions between the molecule and the MoS$_2$ surface will be more in the case of pyrene. Therefore, combining these two effects, we find the pyrene derivative to be more stable on MoS$_2$ layer.

Figure 4. Projected density of states (PDOS) plots of single layer MoS_2 and (i) TTF, (ii) TMTTF, (iii) 1,5-Napthalenediamine, (iv) 1,6-Pyrenediamine, (v) 1,3-propanediamine and (vi) *N,N'*-dimethyl-1,2-ethanediamine complexes. We have plotted the energies from −2 eV to 3 eV. We have used the broadening parameter of 0.025 eV.

For the last set of molecules, the alkyl-diamines, we have found that *N,N'*-dimethyl-1,2-ethanediamine transfers slightly more amount of charge than 1,3-propanediamine. Surprisingly, the HOMO energies (for propanediamine and *N, N'*-ethanediamine −4.21 and −4.23 eV respectively) are almost the same for both the isolated molecules. Also, the pKa values of these two molecules are found to be almost the same (for propanediamine and *N, N'* ethanediamine pKa values are 9.83 and 9.79, respectively, in gas phase) [36]. We attribute the charge transfer results to the fact that *N, N'*-ethanediamine has a lower H–L gap value. Also, the first molecule is a primary diamine and the second one is a secondary diamine. Therefore, the lone pairs of electron donation capability of the secondary amine would be much higher because of the presence of +I group (Me).However, as these molecules do not have much surface area than the others (no π-surface), they are less stable on single layer MoS_2.

Figure 5. Plot for (i) HOMO and (ii) LUMO of 1,5-Napthalenediamine in top view and side view, showing non-interacting molecular wave-function in the composite system.

Figure 6. Optical adsorption spectra for MoS_2 single layer and (i) TTF, (ii) TMTTF, (ii) naphthalenediamine and (iv) N, N'-dimethyl-ethanediamine. The Gaussian broadening parameter used is 0.05 eV. We have plotted the energy range of 0–2 eV and the absorption coefficient range of 0–35000 (arb. units).

Electronic properties

We plot the band-structure and the DOS and projected density of states (pDOS) to show clearly that the difference in charge transfer indeed affects the electronic properties of MoS_2 in a significant way (figure 3). In the case of TMTTF, we do find that the band gap of the system is very less, i.e. the system shifts towards near metallic

nature (table 1). For the other cases also, band-gap changes significantly. In each of the band structure plot (figure 4), we see that there is a clear evidence of formation of non-dispersive molecular levels. These molecular levels create flat bands near Fermi-energy. When we plotted the HOMO or LUMO wave-functions of the molecules in the complex system, we have found that they do not interact with the MoS_2 wave-functions (figure 5). This indeed proves that there is no bonding interaction present between the molecule and the surface, which leads to the formation of non-dispersive molecular level. The presence of these molecular levels indeed changes the band-gap of the systems. Depending upon the nature of the molecule, the band-gap also can be tuned accordingly. In our study, we have used six different molecules and we obtained five different values for the band-gap, which is very important for using this molecule in different opto-electronic devices, which needs band-gap modulation of the semi-conductor material used in it. Among all the molecules we have used for our study, TMTTF is able to decrease the band-gap of the system to the maximum extent (0.2 eV) as well as it leads to maximum amount of charge transfer.

Optical absorption

We also have analyzed the low frequency optical conduction of the systems (using the complex part of the dielectric constant) [47] to find out the changes in the optical absorption spectra arising because of the charge transfer. We find that for pure MoS_2 layer, the optical absorption peaks arise above 1.75 eV (band gap of MoS_2 single layer is 1.81 eV) (figure 6). But, upon adsorption of some of the Lewis bases, we have observed some low energy absorption peaks in the system (figure 6). This happens because of the presence of the non-dispersive molecular levels in the band structure, which are optically active. But, pyrenediamine and propanediamine do not show any significant changes in the optical absorption spectra, they exhibit the optical absorption nature of pristine MoS_2 layer. Thus, it is clear that, depending upon the nature of the molecule, molecular adsorption can change the optical property of the system, or keep it as the same. These two different types of molecules can be used in two different types of applications.

Conclusions

In this study, we have considered three different sets of organic electron donor molecules to show how the different factors, like +I effect, H–L gap of the molecules, presence of a π-surface and molecular surface area can have an effect in tuning the amount of charge transfer from the molecules to the MoS_2 layer and as a consequence can modify the electronic properties of the single layer MoS_2. With the increment of +I effect and decrement of H–L gap, charge transfer increases, which as a result changes the electronic properties of the systems. We have found that all the molecule-MoS_2 adsorbate systems are thermodynamically stable because they have negative adsorption energy; they become more stable as molecular surface area increases. We have also found that the molecules are physisorbed on the MoS_2 layer because of charge transfer and van der Waals interactions. We have examined the band structure and DOS plots of the systems and how they are affected by the molecular charge transfer interactions, and indeed this type of interactions can tune the electronic band-gap of the systems to a huge extend (0.2–1.8 eV). We have also shown that due to these interactions, for a few molecules the optical absorption peak appears at much lower energy than for pure MoS_2 layer. We believe these types of band-gap as well as optical absorption properties modulated MoS_2 systems can be very useful for device applications.

Acknowledgments

References

[1] Novoselov K, Geim A, Morozov S, Jiang D, Zhang Y, Dubonos S, Grigorieva I and Firsov A 2004 Electric field effect in atomically thin carbon films *Science* **306** 666–9

[2] Geim A K and Novoselov K S 2007 The rise of graphene *Nat. Mater.* **6** 183–91

[3] Neto A H C, Guinea F, Peres N, Novoselov K and Geim A 2009 The electronic properties of graphene *Rev. Mod. Phys.* **81** 109

[4] Helveg S, Lauritsen J V, Lægsgaard E, Stensgaard I, Nørskov J K, Clausen B, Topsøe H and Besenbacher F 2000 Atomic-scale structure of single-layer MoS_2 nanoclusters *Phys. Rev. Lett.* **84** 951–4

[5] Lebègue S and Eriksson O 2009 Electronic structure of two-dimensional crystals from *ab initio* theory *Phys. Rev.* B **79** 115409

[6] Han W Q, Wu L, Zhu Y, Watanabe K and Taniguchi T 2008 Structure of chemically derived mono-and few-atomic-layer boron nitride sheets *App. Phys. Lett.* **93** 223103

[7] Novoselov K, Jiang D, Schedin F, Booth T, Khotkevich V, Morozov S and Geim A 2005 Two-dimensional atomic crystals *Proc. Natl Acad. Sci. USA* **102** 10451–3

[8] Mak K F, Lee C, Hone J, Shan J and Heinz T F 2010 Atomically thin MoS_2: a new direct-gap semiconductor *Phys. Rev. Lett.* **105** 136805

[9] Xu M, Liang T, Shi M and Chen H 2013 Graphene-like two-dimensional materials *Chem. Rev.* **113** 3766

[10] Ramakrishna Matte H, Gomathi A, Manna A K, Late D J, Datta R, Pati S K and Rao C 2010 Mos$_2$ and Ws$_2$ analogues of graphene *Angew. Chem. Int. Ed. Engl.* **122** 4153–6

[11] Radisavljevic B, Radenovic A, Brivio J, Giacometti V and Kis A 2011 Single-layer Mos$_2$ transistors *Nat. Nanotechnol.* **6** 147–50

[12] Wang H, Yu L, Lee Y H, Shi Y, Hsu A, Chin M L, Li L J, Dubey M, Kong J and Palacios T 2012 Integrated circuits based on bilayer Mos$_2$ transistors *Nano Lett.* **12** 4674

[13] Chang K and Chen W 2011 L-cysteine-assisted synthesis of layered Mos$_2$/graphene composites with excellent electrochemical performances for lithium ion batteries *ACS Nano* **5** 4720–8

[14] Feng C, Ma J, Li H, Zeng R, Guo Z and Liu H 2009 Synthesis of molybdenum disulfide (Mos$_2$) for lithium ion battery applications *Mater. Res. Bull.* **44** 1811–5

[15] Yang S, Li D, Zhang T, Tao Z and Chen J 2011 First-principles study of zigzag Mos$_2$ nanoribbon as a promising cathode material for rechargeable Mg batteries *J. Phys. Chem.* C **116** 1307–12

[16] Cizaire L, Vacher B, Le Mogne T, Martin J, Rapoport L, Margolin A and Tenne R 2002 Mechanisms of ultra-low friction by hollow inorganic fullerene-like Mos$_2$ nanoparticles *Surf. Coat. Technol.* **160** 282–7

[17] Rapoport L, Fleischer N and Tenne R 2005 Applications of Ws$_2$ (Mos$_2$) inorganic nanotubes and fullerene-like nanoparticles for solid lubrication and for structural nanocomposites *J. Mater. Chem.* **15** 1782–8

[18] Lin Y-C, Dumcenco D O, Huang Y-S and Suenaga K 2014 Atomic mechanism of the semiconducting-to-metallic phase transition in single-layered Mos$_2$ *Nat. Nanotechnol.* **9** 391

[19] Zhou K G, Mao N N, Wang H X, Peng Y, Zhang H L and Mixed-Solvent A 2011 Strategy for efficient exfoliation of inorganic graphene analogues *Angew. Chem. Int. Ed. Engl.* **50** 10839–42

[20] Liu K K, Zhang W, Lee Y H, Lin Y C, Chang M T, Su C Y, Chang C S, Li H, Shi Y and Zhang H 2012 Growth of large-area and highly crystalline Mos$_2$ thin layers on insulating substrates *Nano Lett.* **12** 1538–44

[21] He J, Wu K, Sa R, Li Q and Wei Y 2010 Magnetic properties of nonmetal atoms absorbed Mos$_2$ monolayers *App. Phys. Lett.* **96** 082504

[22] Ataca C and Ciraci S 2011 Functionalization of single-layer Mos$_2$ honeycomb structures *J. Phys. Chem.* C **115** 13303–11

[23] Ivanovskaya V V, Zobelli A, Gloter A, Brun N, Serin V and Colliex C 2008 *Ab initio* study of bilateral doping within the Mos$_2$–Nbs$_2$ system *Phys. Rev.* B **78** 134104

[24] Ma Y, Dai Y, Guo M, Niu C, Lu J and Huang B 2011 Electronic and magnetic properties of perfect, vacancy-doped, and nonmetal adsorbed mose2, mote2 and Ws$_2$ monolayers *Phys. Chem. Chem. Phys* **13** 15546–53

[25] Komsa H P, Kotakoski J, Kurasch S, Lehtinen O, Kaiser U and Krasheninnikov A V 2012 Two-dimensional transition metal dichalcogenides under electron irradiation: defect production and doping *Phys. Rev. Lett.* **109** 35503

[26] Sorescu D C, Sholl D S and Cugini A V 2004 Density functional theory studies of the interaction of H, S, Ni–H, and Ni–S complexes with the Mos$_2$ basal plane *J. Phys. Chem.* B **108** 239–49

[27] Moses P G, Mortensen J J, Lundqvist B I and Norskov J K 2009 Density functional study of the adsorption and van der waals binding of aromatic and conjugated compounds on the basal plane of Mos$_2$ *J. Chem. Phys.* **130** 104709

[28] Raybaud P, Hafner J, Kresse G and Toulhoat H 1998 Adsorption of thiophene on the catalytically active surface of Mos$_2$: an *ab initio* local-density-functional study *Phys. Rev. Lett.* **80** 1481–4

[29] Dey S, Matte H, Shirodkar S N, Waghmare U V and Rao C 2013 Charge-transfer interaction between few-layer Mos$_2$ and tetrathiafulvalene *Chem. Asian J.* **8** 1780

[30] Zhan Y, Liu Z, Najmaei S, Ajayan P M and Lou J 2012 Large-area vapor-phase growth and characterization of Mos$_2$ atomic layers on a Sio$_2$ substrate *Small* **8** 966–71

[31] Bandyopadhyay A and Pati S K 2013 Organic molecules adsorption on single layer Mos$_2$: a theoretical study *SMC Bull.* **4** 1–4

[32] Perkins F K, Friedman A L, Cobas E, Campbell P M, Jernigan G G and Jonker B T 2013 Chemical vapor sensing with monolayer Mos$_2$ *Nano Lett.* **13** 668–73

[33] Li H, Yin Z, He Q, Li H, Huang X, Lu G, Fam D W H, Tok A I Y, Zhang Q and Zhang H 2012 Fabrication of single- and multilayer mos2 film-based field-effect transistors for sensing no at room temperature *Small* **8** 63–7

[34] He Q, Zeng Z, Yin Z, Li H, Wu S, Huang X and Zhang H 2012 Fabrication of flexible Mos$_2$ thin-film transistor arrays for practical gas-sensing applications *Small* **8** 2994–9

[35] Late D J *et al* 2013 Sensing behavior of atomically thin-layered Mos$_2$ transistors *ACS Nano* **7** 4879–91

[36] Bryantsev V S, Diallo M S and Goddard W A 2007 Pka calculations of aliphatic amines, diamines, and aminoamides via density functional theory with a Poisson–Boltzmann continuum solvent model *J. Phys. Chem.* A **111** 4422–30

[37] Tayi A S *et al* 2012 Room-temperature ferroelectricity in supramolecular networks of charge-transfer complexes *Nature* **488** 485–9

[38] Sakai M, Sakuma H, Ito Y, Saito A, Nakamura M and Kudo K 2007 Ambipolar field-effect transistor characteristics of (bedt-ttf)(tcnq) crystals and metal-like conduction induced by a gate electric field *Phys. Rev.* B **76** 045111

[39] Bandyopadhyay A and Pati S K 2015 Photophysical properties of charge transfer pairs encapsulated inside macrocycle cage: a density functional theory study *Chem. Phys. Lett.* **624** 64–8

[40] Burke K, Perdew J P and Ernzerhof M 1997 Why the generalized gradient approximation works and how to go beyond it *Int. J. Quantum Chem.* **61** 287–93

[41] Grimme S, Antony J, Ehrlich S and Krieg H 2010 A consistent and accurate *ab initio* parametrization of density functional dispersion correction (Dft-D) for the 94 elements H–Pu *J. Chem. Phys.* **132** 154104

[42] VandeVondele J, Krack M, Mohamed F, Parrinello M, Chassaing T and Hutter J 2005 Quickstep: fast and accurate density functional calculations using a mixed gaussian and plane waves approach *Comput. Phys. Commun.* **167** 103–28

[43] Goedecker S, Teter M and Hutter J 1996 Separable dual-space Gaussian pseudopotentials *Phys. Rev.* B **54** 1703–10

[44] Hartwigsen C, Goedecker S and Hutter J 1998 Relativistic separable dual-space gaussian pseudopotentials from H to Rn *Phys. Rev.* B **58** 3641–62

[45] Krack M 2005 Pseudopotentials for H to Kr optimized for gradient-corrected exchange-correlation functionals *Theor. Chem. Acc.* **114** 145–52

[46] Soler J M, Artacho E, Gale J D, García A, Junquera J, Ordejón P and Sánchez-Portal D 2002 The siesta method for *ab initio* order-N materials simulation *J. Phys.: Condens. Matter* **14** 2745

[47] Manna A K and Pati S K 2009 Tuning the electronic structure of graphene by molecular charge transfer: a computational study *Chem. Asian J.* **4** 855–60

[48] Tang Q, Zhou Z and Chen Z 2011 Molecular charge transfer: a simple and effective route to engineer the band structures of bn nanosheets and nanoribbons *J. Phys. Chem.* C **115** 18531–7

[49] Das B, Voggu R, Rout C S and Rao C 2008 Changes in the electronic structure and properties of graphene induced by molecular charge-transfer *Chem. Commun.* **41** 5155–7

[50] Troullier N and Martins J L 1991 Efficient pseudopotentials for plane-wave calculations *Phys. Rev.* B **43** 1993
[51] Kleinman L and Bylander D 1982 Efficacious form for model pseudopotentials *Phys. Rev. Lett.* **48** 1425–8
[52] Yamijala S S, Bandyopadhyay A and Pati S K 2014 Nitrogen-doped graphene quantum dots as possible substrates to stabilize planar conformer of Au20 over its tetrahedral conformer: a systematic dft study *J. Phys. Chem.* C **118** 17890–4