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DFT calculation for organic semiconductor-based gas sensors: Sensing mechanism, dynamic response and sensing materials

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ABSTRACT

Organic semiconductor materials have demonstrated extensive potential in the field of gas sensors due to the advantages including designable chemical structure, tunable physical and chemical properties. Through density functional theory (DFT) calculations, researchers can investigate gas sensing mechanisms, optimize, and predict the electronic structures and response characteristics of these materials, and thereby identify candidate materials with promising gas sensing applications for targeted design. This review concentrates on three primary applications of DFT technology in the realm of organic semiconductor-based gas sensors: (1) Investigating the sensing mechanisms by analyzing the interactions between gas molecules and sensing materials through DFT, (2) simulating the dynamic responses of gas molecules, which involves the behavior on the sensing interface using DFT combined with other computational methods to explore adsorption and diffusion processes, and (3) exploring and designing sensitive materials by employing DFT for screening and predicting chemical structures, thereby developing new sensing materials with exceptional performance. Furthermore, this review examines current research outcomes and anticipates the extensive application prospects of DFT technology in the domain of organic semiconductor-based gas sensors. These efforts are expected to provide valuable insights for further in-depth exploration of DFT applications in sensor technology, thereby fostering significant advancements and innovations in the field.

1. Introduction

In recent years, organic semiconductor-based gas sensors have gained significant attention for their wide-ranging applications in environmental monitoring, medical diagnostics, industrial safety, and other fields [1–3]. To develop high-performance and cost-effective gas sensors, extensive research is required in several critical aspects, including understanding sensing mechanisms, dynamic responses during the sensing process, and the selection and design of sensitive materials [4–9]. However, traditional experimental approaches can be time-consuming, complex, and inefficient due to the diverse materials and complex sensing mechanisms involved. Therefore, there is a pressing need for a more efficient and accurate research methodology to address these challenges.

In response to these challenges, density functional theory (DFT) [10–15], a computational and simulation technique, has emerged as a powerful tool for understanding and optimizing organic semiconductor-based gas sensors [16–19]. DFT calculations provide insights into the electronic structure, charge transfer processes, and reaction mechanisms of materials, aiding in the design and optimization of gas sensing materials [20–23]. By significantly reducing experimental complexity and costs, DFT simulations enable researchers to gain a deep understanding of the interaction processes between gas molecules and sensing materials and provide theoretical guidance for the design and optimization of gas sensors [24–28].

While previous literature reviews have discussed gas sensor materials and the application of DFT, there is a need for a comprehensive review specifically focusing on the integration of DFT

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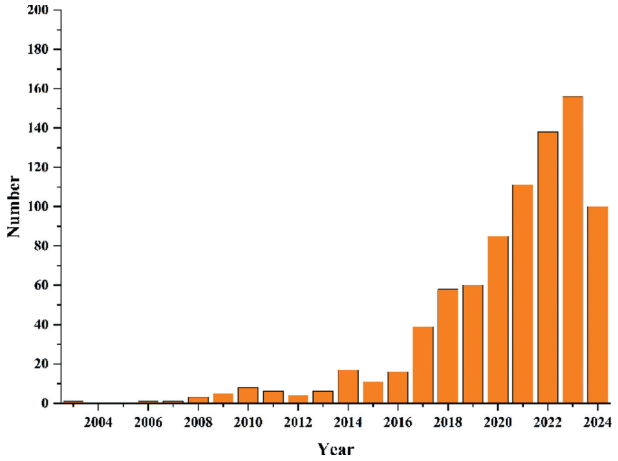

Fig. 1. Number of publications related to the application of DFT in organic semiconductor-based gas sensors per year. Search keywords are organic semiconductor, gas sensors and density functional theory (DFT) *via* web of science on September 30, 2024.

with organic semiconductor-based gas sensors [29–34]. In recent years, a growing number of research papers have applied DFT to explain and predict the behavior of gas sensors based on organic semiconductor materials, indicating sustained academic interest in this area (Fig. 1). Especially, there is rapid increasement of publications since 2015.

In this review, we aim to address the applications and challenges of DFT techniques in the context of organic semiconductor-based gas sensors. These applications can be broadly classified into three categories: elucidating the interaction mechanism between gas molecules and organic semiconductor materials, analyzing the sensor's response mechanism and dynamic performance, and facilitating the screening and design of novel sensitive materials (Fig. 2).

The sensing mechanism and dynamic response are inherently interconnected. The study of sensing mechanism involves employing DFT to analyze the interaction between gas molecules and sensing materials, revealing the working principles of organic semiconductor-based gas sensors. On the other hand, dynamic response simulation utilizes DFT in combination with other computational methods to investigate the adsorption and diffusion processes of gas molecules on the sensor surface, exploring the dynamic behavior of gas adsorption.

During our research, we discovered the close relationship between the sensing mechanism and dynamic response. The interaction between gas molecules and sensing materials directly influences the dynamic response of the sensor. For instance, through DFT calculations, we can elucidate the interaction strength between active sites on the sensing material surface and gas molecules, thus affecting the adsorption and diffusion behavior of gas molecules on the sensor surface. This interaction governs the selectivity and sensitivity of the sensor towards specific gases.

By combining the studies of sensing mechanism and dynamic response, a deep understanding of the working principles and performance characteristics of organic semiconductor-based gas sensors can be achieved. This not only guides the design and optimization of sensors but also provides a theoretical foundation for the development of novel organic sensing materials with outstanding performance.

A comprehensive summary of the literature related to the application of DFT in the field of organic semiconductor gas sensors as shown in Table S1 (Supporting information). By combining theoretical and experimental perspectives, our review aims to deepen the understanding and utilization of DFT techniques in this area. This will provide a more solid theoretical foundation for the design and optimization of organic semiconductor-based gas sensors.

2. DFT calculation for the sensing mechanism of gas sensors

In the context of utilizing organic semiconductors as sensitive materials for gas sensors, the determination of adsorption energy and electron transport properties plays a pivotal role. These parameters directly dictate the performance and response characteristics of the sensors. Employing DFT to calculate these parameters provides invaluable insight into the interaction mechanism between organic semiconductor materials and gas molecules, thereby facilitating the optimization of sensor design and performance.

DFT serves as a pivotal theoretical framework for precisely simulating the adsorption dynamics of gas molecules onto organic semiconductor surfaces and determining the corresponding adsorption energies [35,36]. For example, in NH_3 detection, polyaniline (PANI), an organic semiconductor material, holds significant relevance due to its distinctive characteristics facilitating NH_3 protonation and deprotonation. However, pure PANI exhibits diminished sensitivity to NH_3 and constrained NH_3 adsorption capacity. The introduction of protonic acid doping agents is instrumental in augmenting both the conductivity and NH_3 adsorption capabilities of PANI. DFT computations unveil that X-PANI (where X denotes HCl, H_3PO_4, and H_3BO_3) exhibits a robust π-conjugated architecture characterized by a narrowed bandgap and heightened chemical reactivity. Specifically, HCl-PANI manifests a pronounced dipole moment, thereby fostering enhanced adsorption of positively charged NH_3 molecules and heightened gas response [36]. Furthermore, leveraging DFT calculations provides insights into the intricate interplay between gas molecules and organic semiconductor materials, as exemplified in Fig. 3. Discriminating the sensitivity of diverse sensing materials towards gases necessitates scrutinizing both adsorption energies and non-covalent bonding interactions. DFT empowers the assessment of material adsorption capacities for different gases by precisely predicting the adsorption propensities of various gas molecules on distinct organic semiconductor material surfaces [35]. This predictive capability is indispensable for crafting gas sensors endowed with superior sensitivity and selectivity.

Upon the adsorption of gas molecules, the electronic structure of organic semiconductor materials undergoes alterations, exerting a profound influence on sensor efficacy. Leveraging DFT, we can meticulously unravel the intricate dynamics of charge transfer and energy level modulation occurring throughout the adsorption process, discerning the nuances within the material's electronic configuration. As illustrated in Fig. 4a, DFT facilitates an in-depth exploration of the electrostatic potential distribution of X-PANI, thereby pinpointing the most probable NH_3 adsorption sites [36].

Furthermore, the synthesis of experimental observations and DFT insights reveals that NH_3 undergoes physical adsorption devoid of any chemical transformations during the adsorption process, as depicted in Fig. 4b [36]. Coulombic interactions drive the adsorption of NH_3 onto the sensor surface, orchestrating charge transfer phenomena and bolstering the conductivity of p-type compounds. The exchange of electrons between NH_3 and X-PANI, delineated by the alterations in highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) profiles, endows X-PANI with additional charge carriers from NH_3, culminating in an upsurge in the conductivity of organic semiconductor materials until equilibrium is attained. Moreover, owing to their narrower energy bands and augmented dipole moments, NH_3 adsorption onto HCl-PANI is more pronounced, consequently affording superior NH_3 responsiveness. Examining the NH_3 adsorption

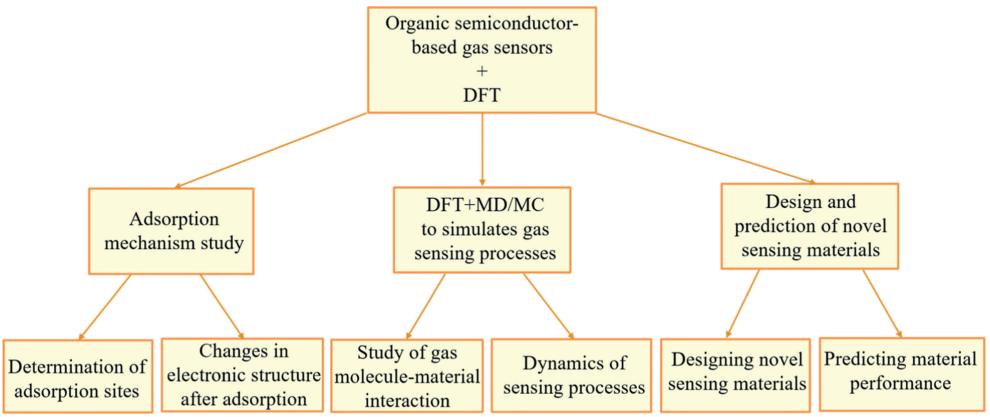

Fig. 2. Application of DFT in organic semiconductor-based gas sensors.

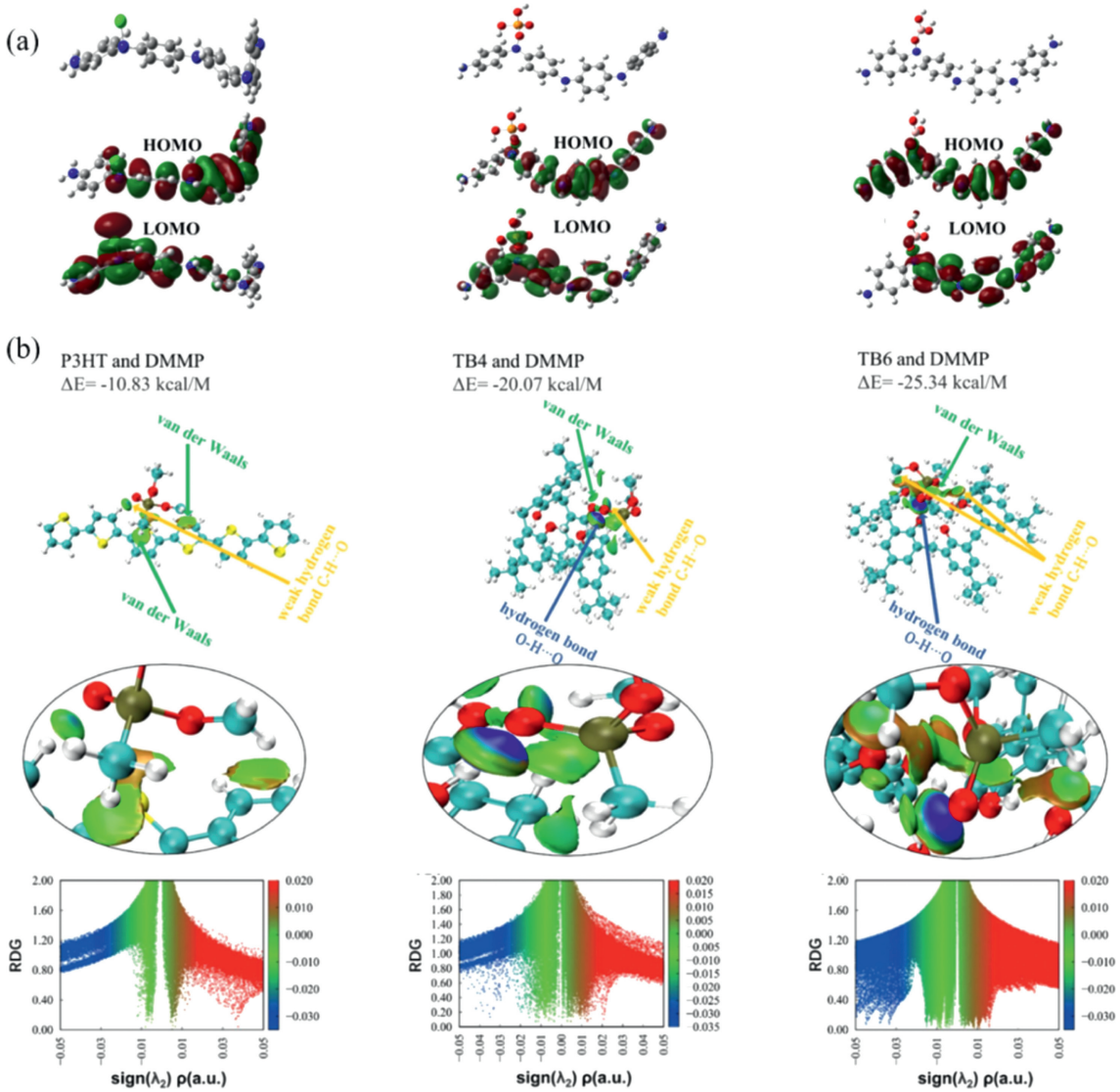

Fig. 3. (a) Geometric structure, HOMO and LOMO of X-PANI (X = HCl, H_3PO_4, H_3BO_3). Copied with permission [35]. Copyright 2023, Elsevier. (b) NCI analysis between DMMP and P_3HT, TB_4, and TB_6. Copied with permission [36]. Copyright 2022, Elsevier.

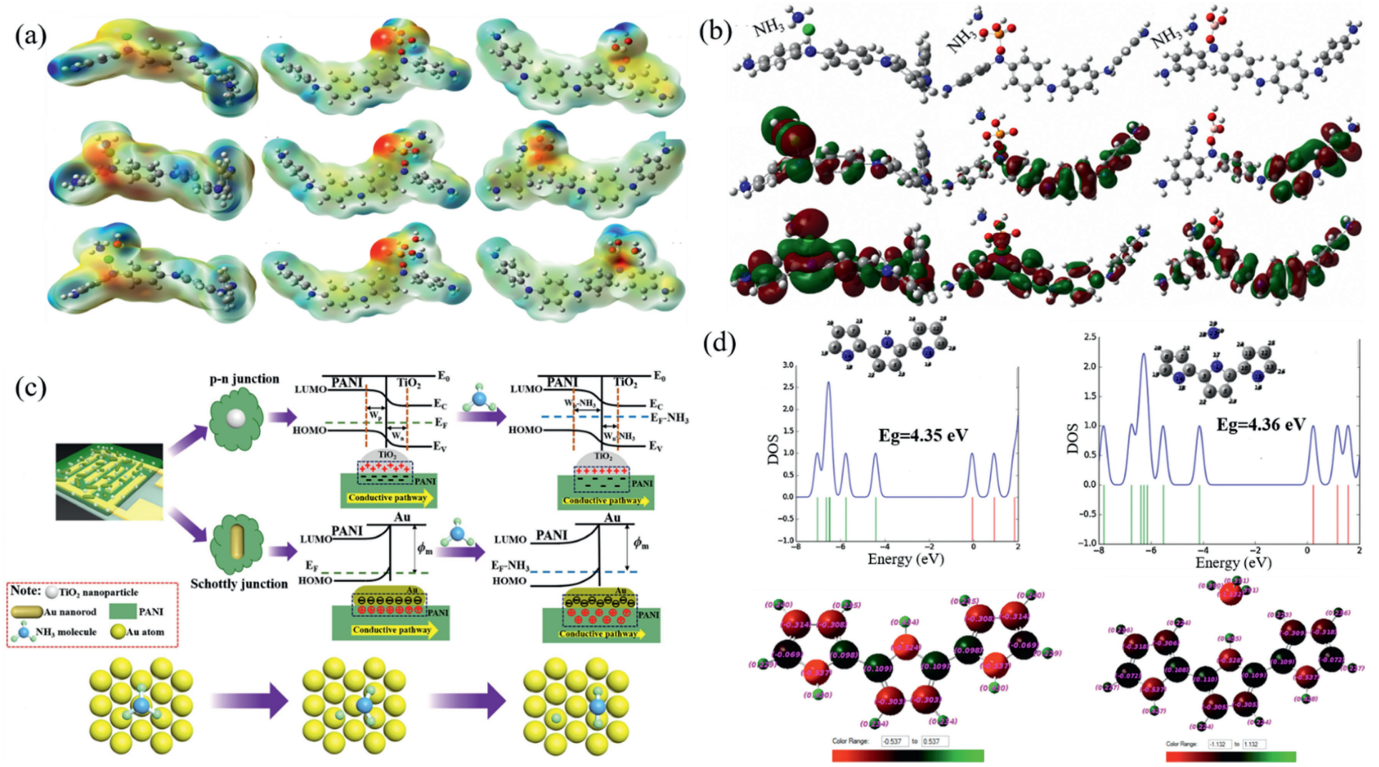

Fig. 4. (a) Electrostatic potential distribution of X-PANI before and after adsorption of NH_3 molecules. Copied with permission [36]. Copyright 2023, Elsevier. (b) Geometric structure, HOMO and LOMO distribution. Copied with permission [36]. Copyright 2023, Elsevier. (c) PANI-TiO_2 before and after NH_3 adsorption Energy band changes of Au composite materials. Copied with permission [37]. Copyright 2017, Elsevier. (d) DOS and charge distribution of 3PPy before and after adsorption of NH_3. Reproduced with permission [38]. Copyright 2015, Elsevier.

mechanism on the X-PANI sensor further through DFT-simulated investigations illuminates the interplay between X-PANI and NH_3, substantiating the influence of protonation type on NH_3 sensitivity [36]. These foundational inquiries offer a theoretical scaffold for subsequent explorations into diverse doped polyaniline derivatives.

The alteration in energy bands pre- and post-gas molecule adsorption was discerned through meticulous DFT calculations, offering profound insights into the underlying sensing mechanism of the gas sensor, as delineated in Fig. 4c [37]. Utilizing PANI-TiO_2-Au composite as the sensing material, NH_3 molecules undergo electron transfer to PANI, resulting in the depletion of hole concentration within the polyaniline framework and consequent reduction in film conductivity. Examination of the energy band variations unveils that the diminishing concentration of holes in polyaniline triggers an expansion of the depletion layer formed by PANI and TiO_2, constricting the conductive pathway of PANI. Concurrently, electrons migrate from PANI to Au nanorods, instigating the formation of a hole accumulation layer within PANI and an electron accumulation layer within Au at their interface. Consequently, it is conjectured that the hole accumulation layer in polyaniline exhibits heightened reactivity towards NH_3 molecules, thereby amplifying the sensor's responsiveness to NH_3 [37].

Electronic properties between sensitive materials and gas molecules can be meticulously scrutinized through DFT calculations. Illustrated in Fig. 4d, density of states (DOS) plots and band gap analyses of 3-polypyrrole (3PPy) and 3PPy-NH_3 complexes unveil remarkably similar band gaps, indicating minimal alteration in electronic properties upon NH_3 interaction with 3PPy. Theoretical computations elucidate that NH_3 interaction with PPy primarily entails electron transfer from NH_3 to 3PPy, resulting in alterations in resistance and band gap characteristics of 3PPy. This charge transfer phenomenon significantly impacts the sensitivity of the interaction while inducing subtle changes in the electronic properties of 3PPy [38].

By comprehensively analyzing the results of DFT calculations and experimental observations, we can find that the adsorption and sensing process of gas molecules involves many physical and chemical processes, such as charge transfer, bond formation and energy band modulation. These processes work together to determine the sensitivity, selectivity and response speed of the sensor. Among them, DFT calculations provide key insights into deeper understanding of these processes.

DFT simulation methods play an important role in studying the sensing mechanisms of gas sensors. By accurately calculating parameters such as adsorption energy and electron transfer, we are able to better understand the interaction mechanisms between organic semiconductor materials and gas molecules and provide guidance for sensor design and performance optimization. However, it is worth noting that the implementation and interpretation of the DFT method needs to be combined with experimental validation, and there are still some limitations and challenges, such as in terms of computational complexity and model accuracy.

The application of the DFT simulation methodology provides us with the ability to gain insight into the working principles and performance modulation mechanisms of gas sensors. By combining experimental observations and theoretical calculations, we can reveal the operation mechanism of the sensor and the interactions of each link, which in turn provides an important reference for sensor design and optimization. However, more research is still needed to further explore and improve the application of DFT simulation methods in gas sensor research.

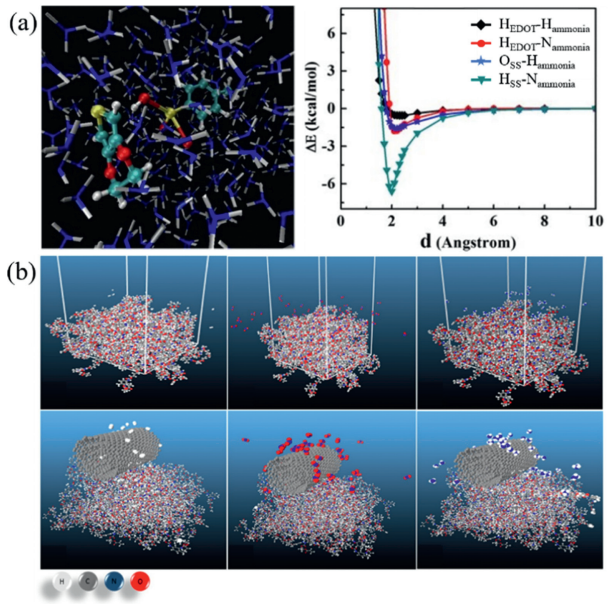

Fig. 5. (a) EDOT:SS in NH_3 gas in MD simulation and interaction energy *vs*. distance. Reproduced with permission [39]. Copyright 2017, Springer Nature. (b) Adsorption of gas molecules by PUA and PUA/MWCNTs composites. Copied with permission [41]. Copyright 2020, Elsevier.

3. Dynamic response simulation between gas molecules and sensing materials

The response characteristics of a sensor are not only determined by its static attributes but also by the dynamic interactions between gas molecules and its surface [39–41]. While DFT calculations provide detailed insights into the atomic and electronic scales, they are computationally intensive and not suitable for directly modeling large-scale dynamic processes. To overcome this challenge, researchers have integrated the adsorption energies and diffusion coefficients obtained from DFT calculations into multiscale kinetic models. By combining microscopic DFT simulations with macroscopic sensor response, these multiscale models offer a comprehensive understanding of the dynamic interactions between gas molecules and the sensor surface, shedding light on the complex gas adsorption and diffusion processes at the sensor interface [39–41]. This integration has proven to be invaluable for unraveling the intricate dynamics that govern sensor performance, significantly advancing our understanding of gas sensing mechanisms.

Fig. 5a showcases an investigation into NH_3 adsorption on 3,4-ethylenedioxythiophene (EDOT), styrene sulfonate (SS), and EDOT:SS using the quantum mechanics/molecular dynamics (QM/MD) method at room temperature [39]. The results demonstrate that NH_3 molecules preferentially bind to the H atoms of EDOT and around the O atoms of SS with a higher probability compared to other atoms. These findings indicate a strong affinity between NH_3 and EDOT:SS, where NH_3 molecules are likely to interact with the H atoms of EDOT through the lone pair electrons on the N atom. This physical adsorption results in electronic charge transfer from NH_3 to EDOT, enabling the interaction between the hole of EDOT and the electron-donating NH_3 [39]. Through DFT-based simulations, we gain valuable insights into the dynamic behavior of gas molecules, which not only enhances our understanding of NH_3 interaction with poly(3,4-ethylenedioxythiophene) (PEDOT) but also elucidates the direct charge transfer sensing mechanism responsible for NH_3 detection by the PEDOT gas sensor.

In addition, Monte Carlo (MC) simulations have been employed to investigate the adsorption behavior of materials, as illustrated in Fig. 5b [41]. Specifically, the adsorption of polyurethane acrylate (PUA)/multiwalled carbon nanotube (MWCNT) composites on gases such as H_2, NO_2, and NH_3 was examined using MC simulations. The simulations reveal that the overall system energy decreases upon gas molecule adsorption, indicating an exothermic adsorption reaction, which is typical for adsorption processes. The integration of MC simulations with other DFT theoretical calculations demonstrates that the presence of MWCNTs significantly enhances the adsorption capacity of PUA and promotes adsorption reactions between the sensor materials and gas molecules, particularly for NO_2. Therefore, PUA/MWCNT composites show great promise as optimal candidates for gas sensor applications [41].

Moreover, the adsorption and diffusion behavior of C_2H_4 and CO gas molecules on the surfaces of Mn@COF (covalent organic framework, COF), Mn@GP, and Mn@GP/COF has been analytically studied through kinetic simulations (Fig. 6a) [42]. The variation of the total and potential energies is investigated to analyze the interaction between the gas molecules and the surfaces. The observed increase in energy indicates the exothermic nature of the adsorption process, signifying the stabilization of gas molecules on the surface. Notably, the temperature *versus* time plots obtained from MD simulations demonstrate the relatively high stability of the Mn@GP/COF surface, indicating its potential as a stable and promising material for C_2H_4 and CO gas adsorption (Fig. 6b) [42]. Overall, the employment of kinetic simulations provides valuable insights into understanding and predicting the adsorption and diffusion behaviors of gas molecules on the sensor surface, thereby facilitating the design and optimization of new gas detection materials [42].

Dynamic response simulation plays a crucial role in understanding the mechanism of 2D COFs in gas sensing, particularly for enhancing the detection selectivity and sensitivity of NO_2. The grand canonical Monte Carlo (GCMC) simulations also predict the gas adsorption distribution, as shown in Fig. 7a for the adsorption distribution of benzene, toluene, ethylbenzene, and xylene (BTEX) in Cu-TCPP-Cu (tetrakis(4-carboxyphenyl)porphyrin, TCPP) [43]. The simulation results highlight the significance of pore size and depth in Cu-TCPP-Cu, which play a vital role in the adsorption and diffusion of BTEX. That is, a specific pore depth maximizes the exposure of adsorption active sites while minimizing spatial resistance during gas molecule diffusion [43]. Furthermore, kinetic simulation studies demonstrate that Cu-TCPP-Cu exhibits exceptional detection properties for benzene vapor, exhibiting ultra-high sensitivity, fast response time, very low detection limit, and excellent selectivity.

As shown in Fig. 7b, GCMC simulations demonstrate the strong gas adsorption capacity and charge transfer capability of COFs [44]. This research contributes to an in-depth understanding and optimization of the design of two-dimensional metal-organic framework (MOF)-based gas sensors through a combination of theoretical simulations and experimental validation [44]. Overall, kinetic simulation studies illustrate the potential of conjugated organic polymers for gas sensing. The kinetic simulations allowed scientists to gain a deeper understanding of the structure-activity relationship, providing important insights into the study of organic semiconductor gas sensors.

Furthermore, molecular dynamics simulations were employed to explore the diffusion behavior of different gas molecules in a zeolite imidazolate frameworks-8 (ZIF-8) ($Zn(mIm)_2$) membrane, as depicted in Fig. 8 [45,46]. Fig. 8a shows the different molecular structure models. These simulations revealed that ethanol exhibited the highest diffusion rate, followed by NO_2, propane, acetone, and ethylbenzene (Fig. 8b). The kinetic simulation study highlights the tunability of gas molecule transport time through the thickness and porosity of the ZIF-8 membrane, providing a strategy for controlling the selectivity and response time of the sensor [45].

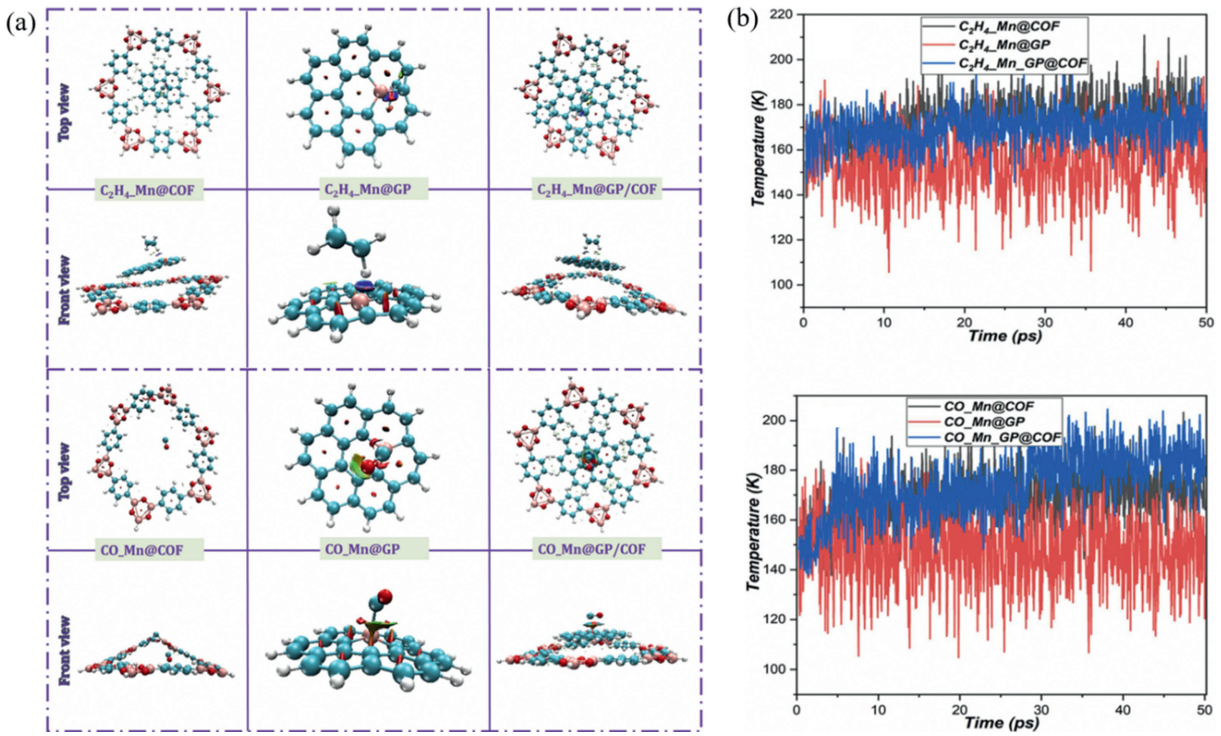

Fig. 6. (a) Isosurfaces of adsorption of C_2H_4 and CO gas molecules on the surface of the composite, and (b) molecular dynamics simulation of adsorption of gas molecules for the formation of complexes. Copied with permission [42]. Copyright 2024, Elsevier.

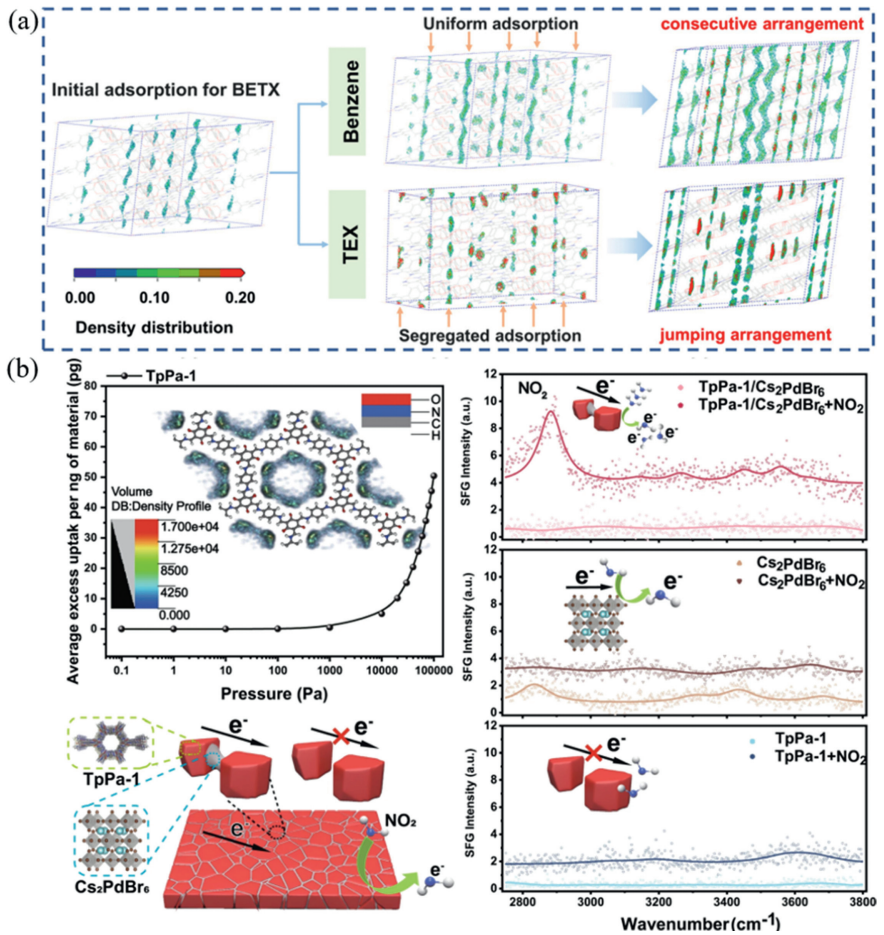

Fig. 7. (a) Adsorption density distribution of benzene and TEX on Cu-TCPP-Cu for different concentrations. Copied with permission [43]. Copyright 2023, Springer Nature. (b) Plot of adsorption density of NO_2 on Tpa-1 simulated by GCMC. Copied with permission [44]. Copyright 2024, American Chemical Society.

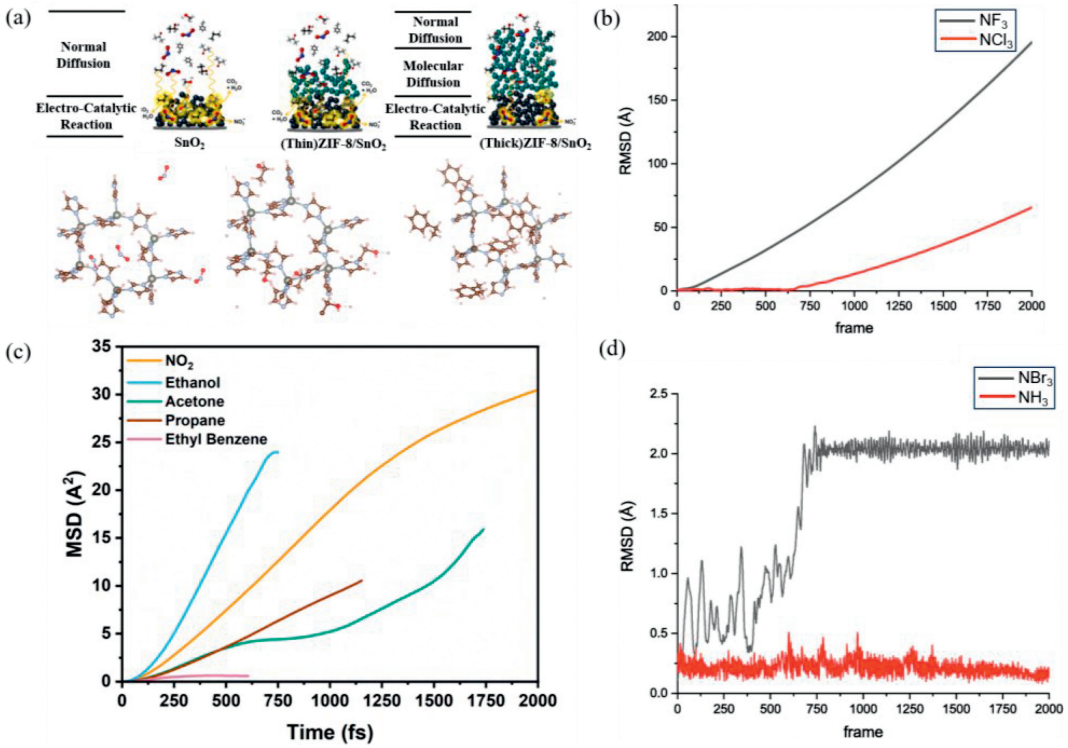

Fig. 8. (a) Snapshots of controlled gas diffusion and MD simulations of NO_2, ethanol, and ethylbenzene molecules in the layered structure. (b) MSD plots of gases passing through the ZIF-8 membrane. Reproduced with permission [45]. Copyright 2024, Royal Society of Chemistry. RMSD curves of the adsorption of (c) NF_3, NCl_3, and (d) NBr_3, NH_3 onto the CTPy. Copied with permission [46]. Copyright 2021, Elsevier.

This approach contributes to the development of high-performance chemoresistive gas sensors capable of distinguishing and recognizing multiple gas molecules.

MD simulations also demonstrated that NF_3 and NCl_3 molecules can be released from cyclotripyrrole (CTPy) after adsorption without structural damage, suggesting CTPy's potential as a novel gas sensor for detecting NF_3 and NCl_3 molecules (Fig. 8c). Also, NH_3 and NBr_3 interact strongly with CTPy (Fig. 8d). In sum, the kinetic simulation studies provide valuable insights into the adsorption performance and stability of CTPy on NH_3, NF_3, NCl_3, and NBr_3 molecules [46]. CTPy exhibits excellent adsorption performance for these gas molecules due to its unique structure, especially the infinite conjugated and highly active cavities. These simulation results strongly support the potential of CTPy as a sensor material for the detection of these gas molecules.

The dynamic response simulation, built on the foundation of DFT, represents a novel approach in our research. Beyond analyzing static performance metrics, understanding a sensor's response requires considering the dynamic interactions between gas molecules and its surface. Leveraging DFT-based dynamic response simulation enables us to comprehensively assess these molecular dynamics on sensor surfaces. Through meticulous analysis of adsorption, diffusion, and other processes, we gain profound insights into the response mechanism and dynamic performance of gas sensors. With the continuous advancements in computing technology, we expect DFT-based dynamic response simulation to play a pivotal role in gas sensor research, providing more effective solutions for addressing real-world challenges.

4. Screening and design of gas sensitive materials

Organic semiconductor materials offer great potential for advancements in gas sensor technology due to their unique properties, such as molecular modularity, tunable electrical conductivity, and cost-effective fabrication. Materials like polypyridine, polyaniline, and polypyrrole demonstrate exceptional capabilities in gas adsorption dynamics and electron transport phenomena, making them suitable for detecting a wide range of gases, including volatile organic compounds, sulfides, and nitrogen compounds [47–55]. Manipulating the molecular configurations and incorporating functional moieties into organic semiconductors enables highly selective gas detection, opening up possibilities for real-world applications. However, the diverse nature of these materials and the intricate interplay between structure and functionality pose challenges, requiring systematic methodologies for material identification and targeted design strategies. In this context, DFT emerges as a key computational approach that enables the study of the electronic intricacies and gas-responsive characteristics of organic semiconductors. This computational framework not only provides a foundation for material screening and design but also generates innovative paradigms for the development of high-performance gas sensors [56–64].

DFT calculations are instrumental in predicting crucial parameters such as electronic structure, adsorption energy, and charge transfer rates in organic semiconductor materials. These predictive capabilities facilitate the screening and identification of materials with superior gas sensing properties. Computational simulations enable rapid and cost-effective evaluations of a wide range of potential materials, streamlining the development process of advanced sensor materials.

As depicted in Fig. 9a, DFT calculations enable precise comparisons of the interactions between three organic semiconductor materials (furan, pyrrole, and thiophene) and various gas analytes. Notably, polypyrrole exhibits superior sensing capabilities across all analytes compared to polyfuran and polythiophene [49]. Additionally, the response of the band gap indicates the heightened sensitivity of the organic semiconductors to CO, SO_2, and SO_3, suggesting an enhancement in electrical conductivity in their presence.

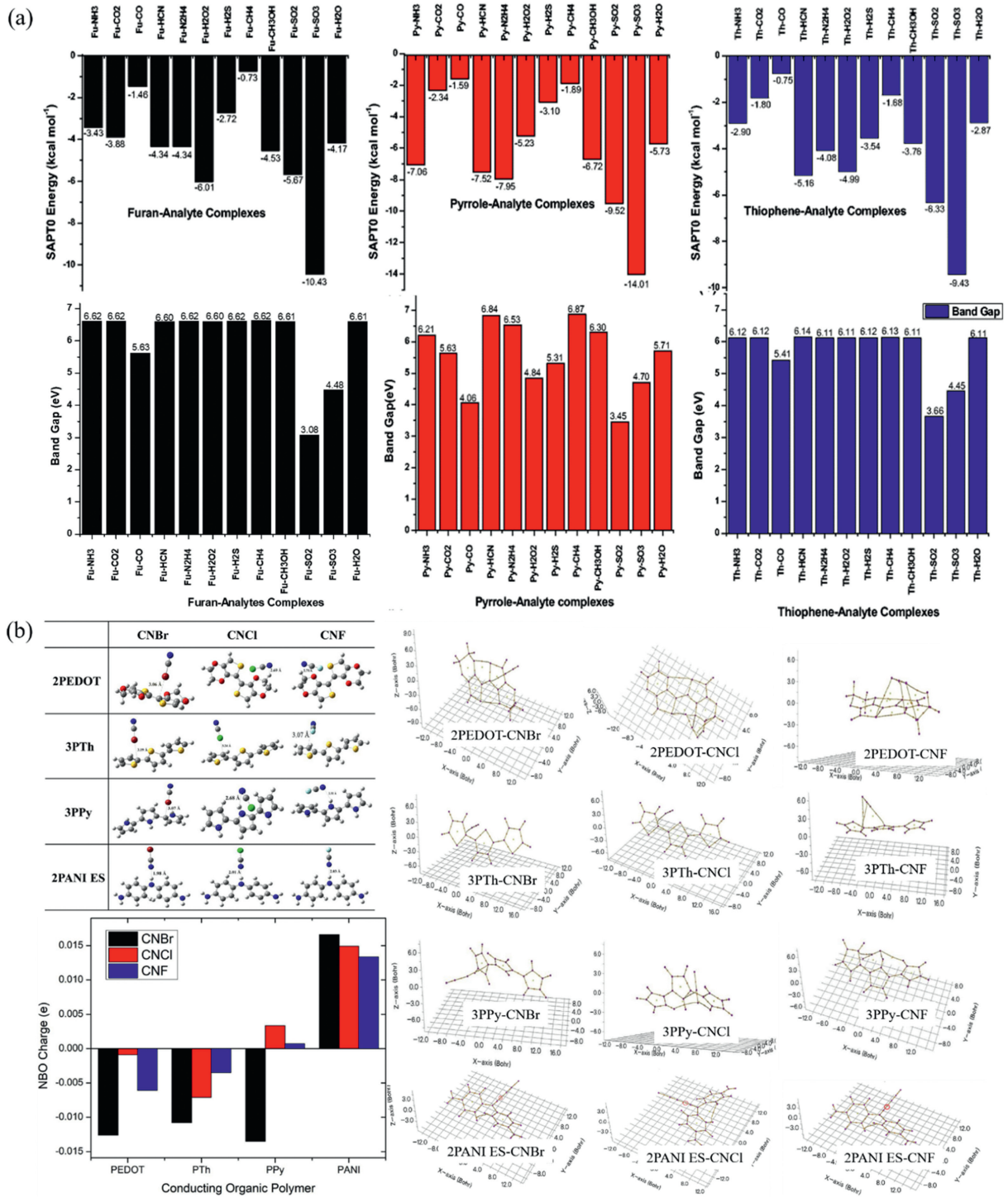

Fig. 9. (a) Interaction energy and band gap characteristics of polymers-CNX complexes. Copied with permission [49]. Copyright 2017, Springer Nature. (b) Structural geometry of polymers-CNX (X = Br, Cl, F) complexes, analysis of charge transfer quantities and topological analysis of electron density. Reproduced with permission [65]. Copyright 2024, Springer Nature.

These computational insights highlight the specific gas sensing behaviors exhibited by different organic semiconductor materials and emphasize the superior sensitivity of polypyrrole across all analytes [49].

Furthermore, a detailed investigation into the interactions between PEDOT, polythiophene (PTh), PPy, and polyaniline emeraldine salt (PANI ES) with CNX (X = Br, Cl, F) was conducted using DFT computations, as presented in Fig. 9b [65]. The analysis reveals that CNX primarily interacts with PEDOT, PPy, and PTh through its halogen moieties, whereas PANI ES forms hydrogen bonding interactions *via* N–H functionalities. The quantification of charge transfer and topological analyses highlight the pronounced charge transfer and electrostatic interactions in the PANI ES-CN complex, demonstrating PANI ES as a promising material for CNX sensing applications [65].

The integration of DFT calculations provides valuable insights into the dynamic behavior of organic semiconductor materials in gas sensing. These computational approaches aid in material se-

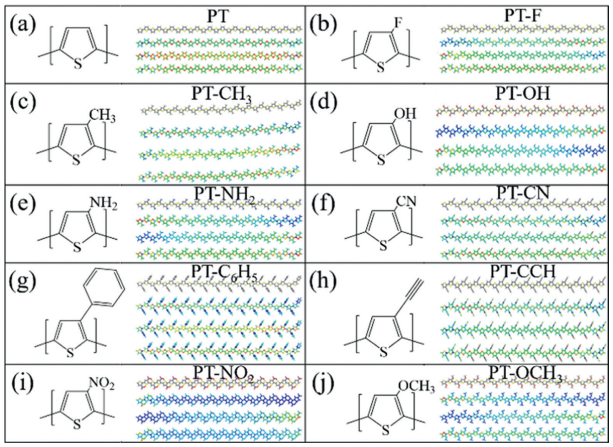

Fig. 10. Schematic diagram of the structures and reaction sites of (a) PT, (b) PT-F, (c) PT-CH_3, (d) PT-OH, (e) PT-NH_3, (f) PT-CN, (g) PT-C_6H_5, (h) PT-CCH, (i) PT-NO_2 and (j) PT–OCH_3. Reproduced with permission [66]. Copyright 2021, Springer Nature.

lection, design optimization, and the development of efficient gas sensors. The combination of computational and experimental efforts fuels advancements in gas sensing technologies and paves the way for future innovations.

In addition to its significant contribution to material screening, DFT plays a pivotal role in guiding the precision-targeted design of organic semiconductor materials for gas sensing applications [36,66]. By carefully controlling the molecular architecture and manipulating dopants, DFT offers unprecedented insights into tailoring the adsorption performance, selectivity, and response kinetics of these materials. This enables researchers to optimize sensor performance by enhancing selectivity and sensitivity towards targeted gases, thus providing heightened discriminatory capacity and improved sensor efficacy [36,66]. The combination of rational design and DFT-guided molecular engineering represents a paradigm shift in sensor fabrication, revolutionizing the field of gas sensing technologies.

In the field of gas sensing, polythiophene (PT) derivatives have been extensively studied for their design and application. However, the synthesis of diverse derivatives and their complex interactions with analytes present significant challenges in developing PT derivatives with enhanced sensing capabilities. Experimental design through trial and error is not feasible due to the large design space. In this context, theoretical studies based on DFT serve as invaluable tools to guide experimental efforts and predict interactions with analytes. Through molecular modeling and simulation, we aimed to explore the modification of PT side chain functional groups, resulting in the generation of ten different PT derivative structures, including unmodified PT, as depicted in Fig. 10 [66].

Adsorption studies of these PT derivatives revealed that sulfur atoms in derivatives such as PT-F, PT-CH_3, and PT-OH exhibited high reactivity. Conversely, derivatives like PT-NH_2, PT-C_6H_5, PT-NO_2, and PT–OCH_3 showed reactivity predominantly at the terminal regions, indicating an efficient electro polymerization process within these systems. Notably, PT-CN and PT-CCH derivatives displayed pronounced reactivity on their side groups, suggesting that the presence of reactive sites on more exposed areas enhances polymer-analyte interactions. Computational analyses confirmed that PT-CN and PT-CCH possess excellent gas adsorption properties and stability, positioning them as promising candidates for gas sensor applications. These DFT predictions are also validated by experimental characterization techniques. PT-CN derivatives exhibited exceptional potential for the high-sensitivity detection of gases such as SO_2 and NH_3 [66]. The high degree of agreement between computational predictions and experimental results confirms the reliability and accuracy of DFT in guiding material selection and design. These findings underscore the importance of leveraging DFT studies to rationally design PT derivatives with superior sensing performance, thereby advancing the development of high-efficiency sensors.

Fig. 11a showcases a meticulous exploration of gas molecule adsorption behavior across various PT derivatives, facilitated by rigorous DFT calculations [66]. Remarkably, PT-CN stands out among the derivatives, exhibiting robust binding energies towards the suite of analytes under investigation. Notably, SO_2 demonstrates the highest affinity towards PT-CN, highlighting its exceptional binding characteristics, while H_2S exhibits comparatively weaker binding energies. Analysis of the HOMO and LUMO profiles reveals intriguing insights, with PT-OH, PT-CH_3, PT-C_6H_5, PT-NH_2, and PT–OCH_3 showing diminished chemical stability compared to pristine PT. Conversely, PT-CN and PT-NO_2 exhibit enhanced stability, accompanied by a discernible reduction in the system's band gap. Furthermore, scrutiny of the density of states diagrams reveals subtle shifts in the boundary energy levels towards higher energies in PT-CH_3, PT-C_6H_5, and PT-CN, indicative of altered electronic structures. Synthesizing these findings, PT-CN emerges as a compelling contender, showcasing both stability and broad-spectrum sensitivity towards analytical gases, positioning it as a promising candidate for integration into gas sensor platforms [66].

DFT serves as a powerful tool for unraveling the complex doping mechanisms that impact the electronic structure and adsorption properties of materials. By elucidating the principles underlying dopant-material interactions, DFT enables informed decisions regarding dopant selection and doping concentration optimization, leading to improved sensitivity and stability of sensors. Fig. 11b exemplifies the transformative potential of DFT in sensor research by investigating the structural and electronic attributes of polypyrene (nPy in nPy, nPy^+, and nPy^- states upon exposure to formaldehyde [67]. Remarkably, it is evident that nPy^- exhibits the highest adsorption energy towards formaldehyde, accompanied by significant changes in its conductive behavior. Analysis of HOMO, LUMO, and density of states profiles provides insights into the charge-dependent interactions between polypyrrole and formaldehyde. The strong affinity observed between negatively charged PPy and formaldehyde highlights its potential as a superior sensing material for formaldehyde detection. Additionally, the profound impact of formaldehyde adsorption on the electronic structure of nPy^-, through alterations in the HOMO energy level and modulation of the HOMO-LUMO gap, further emphasizes its suitability for sensor applications [67]. This study not only positions polypyrrole, particularly in its negatively charged state, as a promising sensing material but also provides invaluable guidelines for doping strategies in organic semiconductor materials and offers a theoretical framework for the design of next-generation gas sensors.

DFT calculations offer powerful advantages in materials design for gas sensors, but it is also important to acknowledge the limitations and potential sources of error associated with this computational method. Despite its remarkable predictive capabilities, DFT calculations are based on certain assumptions and approximations that may introduce inherent limitations. These include the choice of exchange-correlation functionals, the treatment of van der Waals interactions, and the consideration of spin-orbit coupling, among others. It is crucial to recognize that the accuracy of DFT calculations can vary depending on the specific system and level of theory employed.

To validate and refine DFT calculations, it is essential to integrate experimental techniques and other computational methods. Experimental validation can provide crucial insights into the behavior and properties of gas sensing materials. It is important to consider the influence of external factors, such as temperature, pressure, or environmental conditions, on the performance of gas

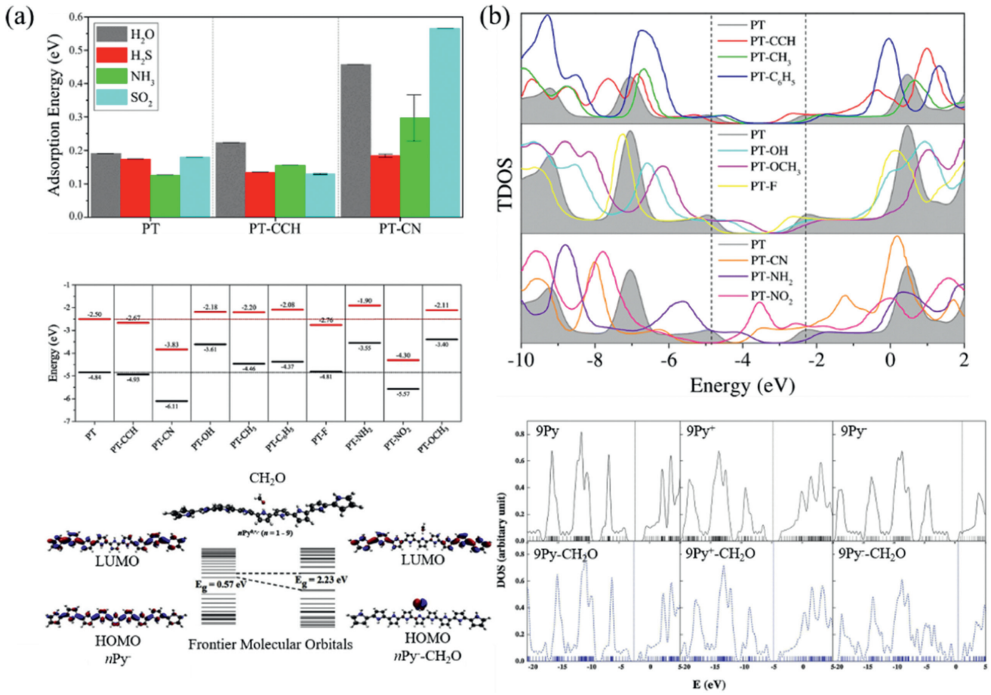

Fig. 11. (a) Adsorption energy, HOMO-LUMO and density of states of PT derivatives. Reproduced with permission [67]. Copyright 2021, Springer Nature. (b) HOMO-LUMO and density of states of gas molecules adsorbed on Py with different charges. Reproduced with permission [66]. Copyright 2017, Elsevier.

sensors. Incorporating these factors into computational modeling can enhance the understanding of sensor behavior under realistic conditions. By embracing a holistic approach that combines DFT calculations with experimental validation and the application of complementary computational methods, they can enhance the reliability and predictive capabilities of DFT in materials design for gas sensors.

The use of DFT methods in gas sensing helps in material selection, design optimization and development of efficient gas sensors. The precise manipulation of molecular architectures and careful consideration of doping mechanisms allow for the fine-tuning of sensor characteristics, paving the way for continuous evolution and innovation in gas sensor technology. With the ongoing advancements in computational power and the refinement of theoretical frameworks, DFT is poised to make further strides in gas sensor research, providing unparalleled contributions to the realization of sensor platforms with exceptional performance metrics and cost-effectiveness.

5. Conclusions and perspectives

In this review, we provide an in-depth discussion of the integration of DFT simulations with organic semiconductor-based gas sensors and summarize the significant findings and advances in related research. This area of research provides us with an in-depth understanding of the working principle and performance modulation of organic semiconductor-based gas sensors.

Through DFT simulations, we can reveal the molecular-level interactions and self-assembly behaviors in organic semiconductor-based gas sensors, thus providing theoretical guidance for designing efficient and selective sensor materials. Through systematic calculations and simulations, we can predict and optimize the response characteristics and sensing mechanisms of the sensors, accelerating the development process of novel gas sensors.

By combining DFT simulation and experimental techniques, we are able to provide important insights to further improve the performance and stability of sensors by investigating the structure-property relationship of sensor materials. This integrated approach provides us with new ways to study and develop novel functional materials and devices.

In addition to the insights gained from DFT simulations, it is crucial to explore future research directions and overcome the challenges encountered in current research. One key area of interest is the integration of emerging machine learning techniques to improve the efficiency and accuracy of DFT in materials design. By combining DFT with machine learning algorithms, researchers can enhance the exploration of large chemical spaces, accelerate material discovery, and improve the prediction of sensor performance. Machine learning approaches can facilitate the analysis of complex datasets, enabling the identification of correlations and patterns that may not be apparent through traditional methods. This integration of DFT and machine learning holds promise in advancing materials design by providing insights into structure-property relationships, optimizing material properties, and reducing the need for laborious and expensive experimental trials. Future research efforts should focus on developing new machine learning algorithms specifically tailored for DFT calculations, as well as exploring innovative ways to leverage existing algorithms. Moreover, collaborative efforts between the materials science and machine learning communities can further advance the development and application of these techniques in gas sensor research. By embracing the opportunities offered by emerging machine learning techniques, we can enhance the efficiency and accuracy of DFT in materials design, paving the way for the discovery of novel and improved gas sensing materials.

The application of DFT simulation to organic semiconductor-based gas sensors holds great promise and continued research is needed to further advance the integration of DFT simulation with organic semiconductor-based gas sensors. Future efforts should focus on the incorporation of novel experimental techniques to validate simulation results and optimize sensor performance. Moreover, exploring the utilization of DFT simulations in multi-scale modeling, understanding interface properties, and investigating the

effect of environmental factors on sensor performance are promising directions for further research.

Despite the current challenges, the potential impact of DFT simulations on the development of organic semiconductor-based gas sensors is immense. The ability to predict, design, and optimize sensor materials using accurate theoretical models opens up new possibilities for achieving highly efficient and reliable gas sensors. Furthermore, the insights gained from DFT simulations can provide valuable guidance for the design and optimization of sensors for specific applications, such as environmental monitoring and healthcare.

The combination of DFT simulations with organic semiconductor-based gas sensors has demonstrated tremendous potential in advancing this field. By embracing emerging computational techniques, such as machine learning, and addressing current challenges, we can expedite the discovery of novel materials and optimize gas sensor performance. With continued research and collaboration between different scientific disciplines, we are poised to witness transformative advancements in gas sensing technology. The future holds exciting opportunities for the application of DFT simulations, and we anticipate that this technology will continue to shape the development of organic semiconductor-based gas sensors for a wide range of applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Zhongchao Zhou: Writing – original draft, Investigation, Formal analysis, Data curation. **Jian Song:** Writing – review & editing, Supervision, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Yinghao Xie:** Formal analysis, Data curation. **Yuqian Ma:** Investigation, Formal analysis. **Hong Hu:** Investigation, Formal analysis. **Hui Li:** Writing – review & editing, Supervision, Methodology. **Lei Zhang:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Charles H. Lawrie:** Writing – review & editing, Investigation, Conceptualization.

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Supplementary materials

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