The realization of an Ultrasensitive and Highly Selective OFET NO₂ Sensor: The Synergistic Combination of PDVT-10 polymer and Porphyrin-MOF

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ABSTRACT: Organic field-effect transistors (OFETs) are emerging as competitive candidates for gas sensing applications due to the ease of their fabrication process combined with the ability to readily fine-tune the properties of organic semiconductors. Nevertheless, some key challenges remain to be addressed, such as material degradation, low sensitivity, and poor selectivity towards toxic gases. Appropriately, a heterojunction combination of different sensing layers with multi-functional capabilities offers great potential to overcome these problems. Here, a novel and highly sensitive receptor layer is proposed encompassing a porous 3D metal-organic framework (MOF) based on an isostructural-fluorinated MOFs acting as an NO₂ specific pre-concentrator, on the surface of stable and ultrathin PDVT-10 organic semiconductor on an OFET platform. Here, with this proposed combination we have unveiled an unprecedented 700% increase in sensitivity towards NO₂ analyte in contrast to the pristine PDVT-10. The resultant combination for this OFET device exhibits a remarkable lowest detection limit of 8.25 ppb, a sensitivity of 680 nA/ppb, and good stability over a period of 4 months under normal laboratory conditions. Further, a negligible response (4.232 nA/%RH) towards humidity in the range of 5% - 90% RH was demonstrated using this combination. Markedly, the obtained results support the use of the proposed novel strategy to achieve an excellent sensing performance with an OFET platform.

KEYWORDS: organic field-effect transistor, conjugated polymer, metal-organic framework, NO₂ sensor, heterojunction

1. INTRODUCTION

Air pollution is one of the most pressing problems facing humanity worldwide. A dangerous gas that is detrimental to human beings and environmental resources is nitrogen dioxide (NO_2). According to the Occupational Safety and Health Administration (OSHA) report, the short time exposure limit (STEL) to NO_2 gas for healthy subjects is 1 ppm for 15 minutes.¹ Hence, we need a sensor to detect NO_2 gas molecules over a wide range of concentrations with high precision, resolution, and accuracy. Several detection techniques exist for gas sensing, such as the electromagnetic spectroscopic method, optical fiber,²⁻⁴ electrochemical,⁵⁻⁶ quartz crystal microbalance (QCM),⁷⁻⁸ microelectromechanical systems (MEMS),⁹⁻¹⁰ resistance changes,¹¹⁻¹³ capacitance changes,¹⁴⁻¹⁶ mass spectrometry,¹⁷ and surface potential measurement.¹⁸⁻¹⁹ Some of the important drawbacks of the aforementioned techniques are their bulky design, environmental interferrants, high operating temperature, and high power consumption, which impede the growth of widely explored gas sensing strategies. As an alternative to silicon dominated electronics (complementary metal oxide semiconductor, or CMOS), recently many research groups have explored the potential of emerging organic and flexible platforms for electronic devices in environmental sensing applications.²⁰⁻²¹ In the field of gas sensors, organic field effect transistor (OFET) devices are preferred due to the ease of their solution processing and reduced device complexity when compared to CMOS technology.²¹⁻²² However, organic semiconductors (OSC) also have drawbacks, such as poor stability and low charge carrier mobility, when compared to the inorganic semiconductors.²³⁻²⁴ To overcome these issues, donor-acceptor (D-A) based conjugated polymers are considered as better alternatives due to their good electronic properties and improved stability.²⁵⁻²⁷ A rapidly emerging D-A conjugated polymer that is at the forefront is the Diketopyrrolopyrrole (DPP) copolymer, which has been successfully explored for various sensing activities.²⁸⁻³⁰ Similarly, conjugated thiophenes (CTs) have also been examined for explosive detection, where CT acts as a donor block for electron deficient explosive

molecules.³⁰⁻³¹ However, to the best of our knowledge, no research groups have demonstrated until now, the NO₂ sensing performance of stable D-A conjugated polymer-based OFET devices.

In this work, we report the fabrication of an NO₂ gas sensor using a new variant of DPP copolymer with thiophene donor blocks (PDVT-10) as a channel layer in an OFET device. PDVT-10 is an air-stable polymer of p-type nature with majority carriers as holes. The (E)-2-(2-(thiophen-2-yl) vinyl) thiophene (TVT) functional unit in PDVT-10 is well-known to be an electron donor and any oxidation process with this material will lead to an increase in the concentration of majority carriers, thereby increasing the conduction. The fact that this polymer has a lower highest occupied molecular (HOMO) level makes it a stable counterpart for similar materials like P3HT. Thus, with all of the above features, this organic semiconductor (OSC) stands as a good candidate for selective detection of an electrophilic analyte such as NO₂. Primarily, the bottom-gate bottom-contact (BGBC) topology of pristine PDVT-10 OFET exhibits a low threshold voltage, a subthreshold swing, and a high charge carrier mobility. Although the pristine OFET device displays appreciable selectivity, however, it has a poor sensitivity towards NO₂ gas. To overcome this issue and to improve the sensitivity, for the first time, we propose a new strategy based on the heterojunction combination of a porous n-type metal-organic framework (MOF) with the PDVT-10 polymer.

The utilization of MOFs in the sensing field is a fast-growing research area that anticipates using MOFs in various industrial and environmental applications. The quest for room-temperature stable and sensitive gas sensors has motivated researchers to explore alternative materials such as MOFs as a sensing layer due to their unique properties in terms of reversible physisorption and highly accessible pore system, prompting effective and selective interactions with targeted analytes.³² This sensing can be achieved using different transduction mechanisms, including capacitive, mass and frequency changes. The selectivity of MOF materials for targeted analytes is highly important, nevertheless still not well developed. Molecular sieving is among the possible mechanisms used to introduce molecular selectivity. In such a mechanism, the molecules with smaller size than the MOF's pore-aperture size can diffuse

inside, however larger molecules will be rejected. Another selectivity mechanism is specific interactions between the analyte with the MOF internal surface, via for example hydrogen bonding, or other types of interactions. Our group among others, have applied successfully different types of MOFs as a selective sensing layer for detecting different toxic gases and VOCs using different transduction mechanisms.³⁰

Lately, our group has developed and explored the use of new isostructural 3D fluorinated MOFs, like KAUST-7 and 8 for the selective sensing of humidity, CO₂ and SO₂ using interdigitated electrodes (IDEs) and a quartz crystal microbalance (QCM) as transducers.³³ These isostructural fluorinated 3D MOFs with the formula $[M'_2L_2(M''F_x)]_n$ (where M' is a metal with octahedral geometry, L is a ditopic nitrogen containing linker, and (M''F_x) is an inorganic pillar like SiF₆, TiF₆, NbF₅ etc.), which have shown great properties in terms of gas separation and sensing applications. The structure of this type of MOFs is inherently modular, as each of all three building components can be substituted with a variety of chemical entities and combined in a practically unlimited number of combinations to suit various purposes.³⁴⁻⁴⁵ A relatively unexplored area in the literature concerns the limited number of MOFs based on tetratopic ligand and hexafluorometalates - $[M'L(M''F_6)]_n$.⁴⁶⁻⁴⁷ Therefore, in this study, we have synthesized new isostructural 3D fluorinated MOFs based on the tetratopic linker 5,10,15,20-Tetra(4-pyridyl)porphyrin (TPyP) organic linker and the Ni(TiF₆) as the inorganic pillar. The development of such stable microporous compounds based on porphyrin building blocks is of particularly important because it can offer variety of functionalities/properties.⁴⁸ Porphyrin based MOFs are valued for their unique light-harvesting, optical response, sensing, and catalytic properties. In this study, we aimed to combine these MOFs with the PDVT-10 and explore their sensing properties for NO₂.

We are the first to explore the sensing properties of our porphyrin based-MOF by applying it as a coating over PDVT-10 for the sensing of NO₂. In our study, the employed MOF improved sensitivity by 700% without compromising the selectivity behavior towards NO₂ analyte. Besides, the sensing properties of the MOF/PDVT-10 device combination proved to be highly stable against relative humidity. Finally, we present the sensing mechanism to portray the interaction between the device stack and NO₂

gas analytes. To the best of our knowledge, this is the first time a combined DPP and MOF based OFET sensor has been reported for the detection of NO₂ gas with high sensitivity and reasonable selectivity (both oxidizing and reducing gases).

2. RESULTS AND DISCUSSION

2.1 PDVT Characterization

(**Figure 1a**) presents the chemical structure of the organic semiconductor (PDVT-10), which consists of DPP and Thiophene-Vinyl-Thiophene (TVT) acting as an electron acceptor and donor units, respectively. The donor and acceptor groups of polymer were observed with the help of a Raman spectrum at an excitation wavelength of 473 nm, as shown in (**Figure 1b**). This spectrum consists of 10 peaks associated with three polymer units, as illustrated in (**Table S1**). We adopted a spin coating process for the deposition of PDVT-10 polymer over the surface of Si/SiO₂ substrate, and we observed the same using field enhanced scanning electron microscopy (FESEM), as shown in (**Figure 1c**). These images exhibit the formation of a uniform and conformal film deposition with a thickness of around 17 nm. Furthermore, with the help of atomic force microscopy (AFM) measurement, the roughness of the PDVT-10 thin film was measured to be around 0.9 nm; it is depicted in (**Figure 1d**). The work function (Φ) of a material is defined as the difference between the vacuum level and fermi energy. As shown in (**Figure 1e**), in our work we quantitatively determined the Φ of PDVT-10 (Φ_1) as 4.5981 eV with the help of Kelvin probe force microscopy (KPFM). KPFM helped to determine the electronic bandgap of PDVT-10 along with the ionization potential and electron affinity values. Besides the work function, the ionization energy or HOMO level of a polymer measured around 5.07 eV, which was determined using photoelectron yield spectroscopy in the air (PYS), as shown in (**Figure S1a**). This was followed by the UV-Vis-IR absorption spectroscopy technique, which was employed to observe the optical absorption behavior and optical band gap of a polymer. The obtained absorption spectrum, shown in (**Figure S1b**), exhibited a maximum peak at 715 nm accompanied by a shoulder peak at 789.5 nm, which closely

matches the reported PDVT-10 spectrum.⁴⁹ The optical bandgap of the polymer was approximately 1.415 eV; it was extracted from the tauc plot of the UV-Vis-IR absorption spectrum shown in (**Figure S1c**). This is close to the values reported in the literature.⁴⁹⁻⁵⁰ From (**Table S2**), it is clear that the work function of the polymer is near its ionization energy level. This shows that the polymer is a typical p-type organic semiconductor.

Figure 1. PDVT-10 polymer characterization. (a) Chemical structure; (b) Raman spectrum of the polymer for the spectral range from 1000 to 1700 cm^{-1} and (inset) 2700 to 3000 cm^{-1} ; (c) FESEM image and (inset) magnified version of PDVT-10 thin film on Si/SiO₂ substrate; (d) AFM height image; and (e) surface potential KPFM map of polymer thin film.

2.2 MOF Synthesis and Characterization

The synthesis of the isostructural 3D fluorinated MOF $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ (MOF-A) particles was carried out, for the first time, under ultrasonic irradiation at a frequency of 40 KHz and 60 °C preset in the Branson 2510 Ultrasonic bath. In a typical synthesis, the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.04 mmol) and TPyP (0.02 mmol) were partially dissolved in 6 mL of Dimethylformamide (DMF), and later on 0.4 mL of 0.05 M aqueous solution of $(\text{NH}_4)_2\text{TiF}_6$ (0.02 mmol) was added into a 20 mL scintillation vial. The vial was placed in a pre-heated ultrasonic bath for 10 hours. A clear color change of the initial dispersed phase from dark purple to bright purple indicated the transformation of the reagents. The product was isolated

by centrifugation, and it was washed multiple times with DMF and activated via solvent exchange with methanol. The formed $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A was stable under ultrasound irradiation, which allowed us to effectively separate the product from dissolving starting materials by performing the extensive washing in the sonication bath. (**Figure 2a**) presents the structure of the chosen MOF (MOF-A) and its ancestor (MOF-B), which was accessed by using the tetratopic square ligands, namely TPyP instead of the ditopic (pyrazine (pyr), 4,4'-dipyridine (dpy), etc.). The PXRD analysis shown in (**Figure 2b**) confirms the formation of the $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A and phase purity of MOF-A, via the excellent match between the experimental and simulated patterns. MOF-A adsorb N_2 with characteristic for microporous materials with fully reversible Type-I isotherms. The obtained isotherm is shown in (**Figure 2c**). The apparent BET surface area for heated MOF-A particles was estimated to be $991 \text{ m}^2/\text{g}$, and a pore volume of 0.49 cc/g was projected at 0.85 relative pressure, as the increase of the uptake from 0.9 to 1 relative pressure is associated with the small size of the particles. The estimated pore volume is in good agreement with the theoretical value of 0.49 cc/g . It is worth mentioning that different isorecticular structures of this MOF were obtained using this procedure via changing the inorganic pillar ($\text{M}''\text{F}_x$) like for example SiF_6 , FeF_6 , GeF_6 etc.

Typically, the advantages of using the sonochemical synthesis are shortening the synthesis time and helping to reduce the size of the crystal compared to a typical solvothermal synthesis method. As can be seen in the SEM image of $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A particles presented in (**Figure 2d**), we obtained approximately $1 \mu\text{m}$ by $1 \mu\text{m}$ square plate-like crystals with a thickness in the range of tens of nanometers. Additionally, the elemental analysis showed the presence of expected elements (Ni and Ti) in the right atomic ratio in $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A structure (**Figure S2**). Interestingly, this resulting morphology of the synthesized crystals paved the way for them to be easily dispersed and spin-coated as a thin film on different supports for different applications. The stability of $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ at normal relative humidity was confirmed by the exposure of its particles to the normal lab environment for 2 weeks (20°C and 45% RH), as proven by the preserved PXRD pattern as shown in (**Figure S3**). To understand the

thermal stability of $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A, the same particles (used in the relative humidity experiment) were heated to 200 °C in the presence of air for more than 96 hours. The PXRD pattern and the porosity of the heated sample were not changed and were similar to the as-synthesized one, which confirms the thermal stability of $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A. Furthermore, the UV-VIS spectra (**Figure S4**) showed the typical features of the porphyrin ligand and confirmed that the $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A was not fully metallated during synthesis due to the presence of the characteristic peaks of the non-metallated porphyrin ligand.^{48-49, 51}

Similar to PDVT-10, some of the electronic properties of the $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A particles, such as bandgap, ionization energy, and electron affinity, were experimentally obtained, which are shown in (**Figure S5**) and the corresponding parameter values are displayed in (**Table S2**). The n-type behavior of the $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A was confirmed using the work function, which found to stay very close to the electron affinity level. On one hand, when compared to PDVT-10, due to their high electron affinity, the $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A particles inhibit the tendency to attract electrons from the underlying PDVT-10 layer. On the other hand, higher ionization energy supports the stability of the $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A particles, which is in line with the previously discussed XRD results. To study the interactions and the affinity of the $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A with our targeted gas in this study NO_2 , the corresponding adsorption column breakthrough experiments were performed using a 500 ppm NO_2 in N_2 gas mixture with a 50 cc/min flowrate at 298 K and 1 bar. The breakthrough experiment was carried out with 420 mg of the activated sample of $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A. (**Figure 2e**) displays the normalized retention time for NO_2 600 min/g, which shows a high affinity of the $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A to NO_2 , corresponding to an uptake of 0.66 mmol/g at 500 ppm NO_2 concentration. $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A can also be completely regenerated by applying vacuum or flushing using an inert gas like N_2 .

Figure 2. (a) Structural accessibility of $[\text{M}'(\text{TPyP})(\text{M}''\text{F}_6)]_n$ MOF (MOF-A) from MOF-B based on using tetratopic TPyP ligand; (b) PXRD pattern of $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A; (c) the N_2 adsorption isotherms at 77 K after exchange with methanol and activation at 150°C for 12h; (d) SEM images of MOF-A; (e) breakthrough experiment for MOF-A to estimate the adsorption capacity of the material at 500 ppm NO_2 concentration.

2.3 Electrical and Gas Sensing Performance of PDVT-10 and combined PDVT-10 and $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A OFET Devices

OFET devices with a BGBC geometry were fabricated on the Si/SiO_2 substrate using a standard CMOS compatible process. The interdigitated source and drain contacts were patterned on the surface of the Si/SiO_2 substrate using a photolithography process. (Figure 3a) provides a schematic representation of PDVT-10 OFET (device-1), where the polymer film was deposited on top of the substrate patterned with source and drain electrodes. The formation of an ultrathin channel layer is one of the desired features to improve the interaction with the gas analytes at the dielectric/semiconductor interface. As shown in (Figure 3a), to obtain the transfer characteristics, device-1 was subjected to voltage bias by sweeping gate voltage (V_G) from +20 V to -30 V for different drain voltage steps (V_D) from -5 V to -30 V. It is

evident from (**Figure 3a**) that the device turns “ON” in the negative gate bias region, essentially confirming that PDVT-10 is a p-type organic semiconductor. The transistor parameters such as threshold voltage (V_{th}), charge carrier mobility (μ), subthreshold swing (SS), and current ratio (I_{ON}/I_{OFF}) were extracted from transfer characteristics of the device; their values are tabulated in (**Table 1**). We observed a low threshold voltage in device-1, which can be attributed to the low potential trap states at the semiconductor/dielectric interface region. (**Figure 3b**) depicts the output characteristics of device-1 obtained by sweeping the drain voltage from 0 to -30 V with a gate bias from -5 V to -30 V. The outcome mimics the nearly ideal output behavior of a transistor with good linear and saturation regimes, and thus these devices were investigated for gas sensing application.

Table 1. The transistor parameters of OFET devices 1 and 2 are tabulated

Devices	V_{th} (V)	I_{on}/I_{off}	Mobility ($cm^2/V.s$)	Transconductance (S)	Subthreshold swing (V/dec)
1	-3.6	3.2×10^4	4.98×10^{-2}	7×10^{-6}	1.2965
2	9.667	6.59×10^4	7.17×10^{-2}	1×10^{-5}	4.255

Similarly, the $[Ni(TPyP)(TiF_6)]_n$ MOF-A/PDVT-10 OFET (device-2) was fabricated and characterized to understand the effect of the combination of the porous MOF-A particles and PDVT-10 polymer on the device’s characteristics and gas sensing performance. The fabrication process for both device-1 and device-2 was the same until the formation of the polymer channel layer. To complete the device-2 fabrication process, an additional step was drop-casting of $[Ni(TPyP)(TiF_6)]_n$ MOF-A methanolic particles suspension on the surface of the polymer film. Later on, the biasing conditions used to obtain the transfer and output characteristics of device-2 remained the same as those of their pristine device-1 counterpart. In device-1, since the active material is a p-type organic semiconductor, the negative threshold voltage was observed at around -3.6 V. With the addition of $[Ni(TPyP)(TiF_6)]_n$ MOF-A particles, as presented in (**Figure 3d**), a significant positive threshold voltage shift took place from -3.6

V to +9.667 V, as mentioned in (**Table 1**). This was followed by the change in the charge carrier mobility of device-2 to $7.17 \times 10^{-2} \text{ cm}^2/\text{V.s}$, which is around 43% higher than device-1. The positive shift of the threshold voltage and the increase in charge carrier mobility are attributed to the accumulation of excess charge carriers in the channel region formed. This behavior may be the result of the charge transfer process between PDVT-10 and $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A regions, which is explained in detail under the gas sensing mechanism section. The current ratio ($I_{\text{ON}}/I_{\text{OFF}}$) is an important parameter for defining the performance of the desired OFET device. As shown in (**Table 1**), the current ratios of device-1 and device-2 are 3.2×10^4 and 6.59×10^4 , respectively. Compared to device-1, device-2 exhibited a good output behavior with an increase in the drain current level for different gate voltages, as can be seen in (**Figure 3e**). As a result, the improved charge carrier mobility, transconductance, and positive threshold voltage shift of device-2 led to a better device performance when compared to its pristine device-1 counterpart. Hence, the gas sensing properties of both the devices for different gases were further explored.

Figure 3. (a) Transfer behavior with device architecture at the inset, (b) Output behavior and (c) Selectivity behavior of PDVT-10 OFET device. (d) Transfer behavior with device architecture at the inset, (e) Output behavior and (f) Selectivity behavior of MOF-A/PDVT-10 OFET device.

The selectivity behavior of both the devices (1 and 2) was evaluated by recording their drain current responses towards both oxidizing and reducing gases at a fixed concentration of 100 ppm for each gas, as shown in (**Figure S6 and S7**), respectively. We obtained current responses from the transfer characteristics of the devices by sweeping V_G from -20 V to +30 V at constant -20 V_D. As shown in (**Figure 3c**), among all the gases, device-1 showed a good sensitivity of about 225% and an increase in drain current towards 100 ppm NO₂ gas. As a result, device-1 displayed moderate sensitivity with good selectivity towards the targeted NO₂ gas. The same set of gases was employed to study the sensitivity and the selectivity of the combined PDVT-10 and [Ni(TPyP)(TiF₆)]_n MOF-A, device-2. As shown in (**Figure 3f**), its sensitivity towards all tested gases except for NO₂ was not improve. However, in case of 100 ppm NO₂ there was about 3 orders of magnitude enhancement in the sensitivity more than its pristine device -1 counterpart, which is in good agreement with the breakthrough experiments that showed the high affinity of [Ni(TPyP)(TiF₆)]_n MOF-A towards NO₂. Thus, the integration of the [Ni(TPyP)(TiF₆)]_n MOF-A layer plays a significant role in augmenting sensitivity without influencing the selective nature of the pristine device-1 towards the targeted NO₂ gas.

Device-2 was exposed to different NO₂ gas concentrations from 0 to 50 ppm, and the corresponding transfer characteristics were obtained by sweeping the gate voltage from +30 V to -20 V at fixed -20 V drain bias, as shown in (**Figure 4a**). From the obtained transfer characteristics, a significant positive threshold shift from ~ -5 V to -20 V was witnessed, and the drain current increased from 0.1 mA to 1.1 mA with the NO₂ gas concentrations. Sequentially, as displayed in (**Figure 4b**), the output characteristics of device-2 towards different NO₂ gas concentrations (0 to 50 ppm) were obtained by biasing the device with drain voltage from 0 to -30 V at fixed -20 V_G. For the concentrations above 20 ppm, the drain current

exhibited a non-saturation regime for all biases. This can be attributed to the transfer of excess charge carriers in the channel region, preventing the device current from reaching saturation. Using the obtained transfer characteristics, we explored the effect of NO₂ gas concentrations on the transistor parameters of the device-2. As the concentrations increased from 0 to 100 ppm, there was a decrease in threshold voltage of around 3 orders of magnitude, as shown in **(Figure 4c)**. In contrast, the charge carrier mobility increased linearly with NO₂ gas concentration, as also presented in **(Figure 4c)**. As a result, the measured percentage change of charge carrier mobility at 100 ppm was around 400%. **(Figure S8)** displays the obtained relationship between the current ratio (CR) change and different gas concentrations. From this figure, it is evident that the current ratio decreased exponentially with the change of NO₂ gas concentrations from 1 to 100 ppm. From this, we can witness that the percentage of current ratio increase was six orders of magnitude towards 100 ppm NO₂ gas. Another important parameter of a transistor device, the subthreshold swing (SS), was observed with a different NO₂ gas concentration. Interestingly, the SS was inversely proportional to the charge carrier trap density at the dielectric/semiconductor interface (in the concentration range from 1 to 15 ppm), after which SS tends to saturate as the traps were quenched **(Figure S8)**. Moreover, the reduction of trap/defect states at the interface not only lowered the threshold voltage but also augmented the charge carrier mobility of device-2, which is in line with the results in **(Figure 4c)**.

Some important parameters, such as the limit of detection, response and recovery times, were extracted from the transient analysis of device-2 in the presence of NO₂ gas. The transient response was obtained from device-2 ($V_D = V_G = -20$ V) upon the exposure to different NO₂ concentrations from 25 ppb to 50 ppm for 5 min each. After each exposure cycle, device-2 was allowed to recover until the drain current approached the base level. As observed in **(Figure 4d)**, with the increase in gas concentration, the probability of the device for a complete recovery gradually decreased. **(Figure S9)** displays the percentage change in drain current response towards different NO₂ gas concentrations. At 50 ppm NO₂ gas exposure, the drain current (%) of device-2 was increased by 3 orders of magnitude. We measured

the sensitivity of device-2 to NO₂ gas; which was found to be approximately 680 nA ppb⁻¹. The detection limit of device-2 was calculated by the root mean square deviation (RMSD) method, which consists of 3 data points from 25 ppb to 250 ppb NO₂ gas concentrations, as presented in **(Figure S10)**. Using the RMSD method, the limit of detection (LOD) was calculated to be around 8.25 ppb, which is much lower than the LOD values for NO₂ reported in the literature **(Table-2)**. Furthermore, device-2 secured excellent stability against strong relative humidity (RH) conditions with a sensitivity of around 0.005% RH⁻¹ (%), thus outperforming reported devices to date.⁵² The reproducibility test for device-2 was conducted in the presence of 25 ppb NO₂ gas concentration for 4 cycles, and it is shown in **(Figure 4e)**. Device-2 showed excellent reproducibility with the same sensitivity levels for all the cycles. Next, as shown in **(Figure S11)**, the response and recovery time values were obtained from the transient response of device-2 towards 25 ppb NO₂ gas. From this figure, the response and recovery time were measured to be around 43 sec and 438 sec, respectively. Furthermore, bias stress, humidity, temperature, and ambient stability experiments were conducted to study the impact of various conditions on the NO₂ sensing performance. Continuous bias stress was applied at V_D=V_G = -20 V, and a gradual increase in drain current of around 5 μA was observed at the end of 10 hours. During this experiment, the drain current response (of transfer characteristics) was recorded every 2 hours, as presented in the **(Figure S12)**. Interestingly, **(Figure 4f)** shows a negligible change in sensitivity due to bias stress during exposure to 25 ppb NO₂ gas. Furthermore, the drain current was measured at around 23 μA and 19 μA in the 5% and 90% RH conditions, respectively, as shown in **(Figure 4g)**. We calculated the sensitivity of device-2 towards humidity using Equation (1), obtaining approximately 4.232 nA/%RH.

$$S = \frac{I_{90} - I_5}{90 - 5} \text{ (A / \%RH)} \quad (1)$$

where, I₉₀ and I₅ represent the drain current values in the 90% and 5% RH conditions, respectively.

A recent report from Li et al.⁵³ suggests that PDVT-10 is less stable in humid conditions. Thus, the integration of [Ni(TPyP)(TiF₆)]_n MOF-A layer on the surface of thin PDVT-10 serves as a protection

layer, which has shown a significant role in improving the stability of device-2 under different humidity conditions. This is due to the stability of $[\text{Ni}(\text{TPyP})(\text{TiF}_6)]_n$ MOF-A in humid air, as has been proven by PXRD and sorption (**Figure S3 and S4**). (**Figure 4h**) displays the hysteresis curve of device-2 response to 25 ppb NO_2 gas under different RH conditions from 30% to 90%. The mean sensitivity along the adsorption and desorption cycles was around 22.7% and 20.4%, respectively, which has a negligible effect on the actual sensor's response to NO_2 gas (~18%). Furthermore, tests were conducted with varying temperatures, and as (**Figure S13**) clearly shows that the sensitivity was drastically reduced with the increase in temperature. This decrease in sensitivity response with the temperature increase is due to a decrease in the sorption equilibrium of gases decreases in MOF-A as temperature rises, as in the case of most other porous materials. Hence, at temperatures around 100 °C, negligible/no gas adsorption took place on the surface of device-2, as schematically presented in (**Figure S14**). Thus, we speculate that the interaction between the receptor layers and NO_2 gas was negligible at higher ambient temperatures. Finally, the device was put to a shelf-life test over a period of 195 days in the laboratory, as demonstrated in (**Figure 4i**). We observed that the sensitivity of the device was quite stable over this period with insignificant changes in the drain current, thus avoiding any special storage requirements.

Figure 4. (a) Transfer and (b) output characteristics of device-2 towards different gas concentrations from 0 to 50 ppm. (c) The relation between threshold voltage (V_{TH}) and charge carrier mobility (μ) towards different gas concentrations from 1 to 100 ppm. (d) Transient analysis for different concentrations from 25 ppb to 50 ppm; (e) repeatability study of the device at 25ppb NO_2 gas; (f) electrical bias stress effect study towards 25ppb NO_2 gas response of device; (g) effect of humidity on the electrical behavior of the device under N_2 atmosphere; (h) hysteresis adsorption and desorption curve towards a wide range of humidity levels, from 30 to 90% RH, in the presence of 25ppb NO_2 gas; and (i) ambient stability study of MOF-A/PDVT-10 OFET device.

Table 2. Comparison of the current work with reported NO₂ sensing transistors.

Device stack	Sensitivity	LOD (ppm)	Tested range (ppm)	Selectivity study
BOPET/Al/PMMA/PCDTBT/Au ⁵⁴	16% @ 1 ppm	1	1 to 60	H ₂ S, NH ₃ , NO ₂ , NO, and C ₂ H ₅ OH
Si/SiO ₂ /a-IGZO/Mo ⁵⁵	700% @ 10 ppm	0.5	0.5 to 5	No selectivity study
Glass/ITO/PVA/PS/CuPc/Au ⁵	1600% @ 30 ppm	0.4	1 to 30	NO ₂ , SO ₂ , NH ₃ , H ₂ S, CO ₂
ITO/PMMA/P3HT&PVK/Au ⁵⁶	700% @ 600 ppb	0.3	0.3 to 30	NO ₂ , SO ₂ , NH ₃
Si/SiO ₂ /SiNW/Au ⁵⁷	0.14% ppb ⁻¹	0.1	0.1 to 0.5	No selectivity study
Si/SiO ₂ /a-IGZO/Au ⁵⁸	20% ppm ⁻¹	0.1	0.1 to 5	NO ₂ , SO ₂ , CO ₂ , H ₂ , CO, CH ₄ , and NH ₃
Si/SiO ₂ /ZnPc/Au ⁵⁹	220% @ 20 ppm	0.05	0.05 to 20	NO ₂ , SO ₂ , H ₂ S
Si/SiO ₂ /MoS ₂ /Au ⁶⁰	80% @ 500 ppb	0.02	0.02 to 40	NO ₂ and NH ₃
ITO/SU-8/SiNW/Au ⁶¹	1200% @ 30 ppm	0.02	0.02 to 20	NO ₂ , hexane, and acetone vapors
Si/SiO ₂ /ZnO/Au ⁶²	NA	0.01	0.01 to 1.2	No selectivity study
Polyamide/Au/Al ₂ O ₃ /a-IGZO/Au ⁵²	3.47% ppm ⁻¹	NA	2 to 5	No selectivity study
Si/SiO ₂ /Au/PDVT-10&MOF-A (This work)	1% ppb ⁻¹ 200% ppm ⁻¹ 1750% @ 30 ppm	0.008	0.025 to 50	NO ₂ , SO ₂ , CO ₂ , H ₂ , H ₂ S, H ₂ O, and NH ₃

*NA – Not Available

2.4 Gas Sensing Mechanism

To shed more light and to understand the role of both PDVT-10 and [Ni(TPyP)(TiF₆)]_n MOF-A in improving the sensing characteristics of device-2 towards NO₂ gas we have tried to address some of the following key concepts:

1. The understanding of the interaction between NO₂ molecules and the PDVT-10 organic semiconductor material.
2. The role of the [Ni(TPyP)(TiF₆)]_n MOF-A layer for the enhancement of the interactions and the pre-concentration of NO₂ molecules near the PDVT-10 layer.
3. The charge transfer between the target NO₂ molecules and the [Ni(TPyP)(TiF₆)]_n MOF-A/PDVT-10 heterojunction structure, and its impact on the channel layer in the organic semiconductor/dielectric interface region.

As mentioned earlier, device-1 showed low sensitivity towards different analytes apart from NO₂. The reason behind its unique behavior was quantitatively probed using a KPFM system, as shown in (**Figure 5a**). The contact potential difference (CPD) of the polymer measured was around -0.23 eV in a normal ambient environment. (**Figure 5b**) shows the change in CPD (%) with respect to different analytes, where the response to 5 ppm NO₂ gas was around 120% lower as compared to other analytes (at 100 ppm). This decreasing trend of CPD can be attributed to the increase in the surface electrons trapped by adsorbed NO₂ gas, suggesting a dipole-dipole kind of interaction between the PDVT-10 polymer and NO₂ molecules. (**Figure 5c**) shows the surface potential map of the [Ni(TPyP)(TiF₆)]_n MOF-A layer on the PDVT-10. NO₂ is known to be an electrophile compound that attracts the electrons to the single bond O in the structure (O=N-O). In contrast, an electron donor group (TVT) is available in PDVT-10; which upon interaction with an electrophile like NO₂ induces more holes in the bulk of the OSC. Also, the reaction tendency of NO₂ is strong compared to other oxidizing gases such as CO₂ and SO₂. Thus, the selectivity among other oxidizing gases might be due to the presence of an extra electron in the orbital of N contributing to stronger withdrawing ability.

We also studied the role of [Ni(TPyP)(TiF₆)]_n MOF-A in enhancing the sensitivity and preserving the selectivity towards NO₂ in more detail. Firstly, we deposited only the TPyP porphyrin ligand alone on the PDVT-10. This has led to an enhancement in the sensitivity to all probed gases with the device, but no selectivity was achieved towards any of these probed gases (**Figure S15**). When constructing the

[Ni(TPyP)(TiF₆)]_n MOF-A with the TPyP ligand, there was a small decrease in the sensitivity compared to the pure TPyP ligand, but the selectivity to NO₂ was preserved. This is due to the confined space/pores of the [Ni(TPyP)(TiF₆)]_n MOF-A, which leads to stronger interaction of the NO₂ gas with the [Ni(TPyP)(TiF₆)]_n MOF-A framework compared to other gases. To validate whether this interaction was due to the interaction with the TiF₆ pillar only, we have synthesized the isorecticular [Ni(Py)(TiF₆)]_n MOF-B that has the same pillar as the MOF-A but has the ditopic linker pyrazine (Py) instead of the tetratopic (TPyP) linker (**Figure 2a**) and was spin-coated on the PDVT-10 layer. We then ran the same sensing test using MOF-B (**Figure S15**), and the results showed almost no enhancement in sensitivity, as illustrated in (**Figure S16**). This proves that the enhancement in the sensitivity and the preservation of the selectivity were due to the synergy between the TPyP ligand and its presence in a confined space via its embedding in the MOF network. Thus, the proposed structure selectively allows the target NO₂ molecules to strongly interact with the [Ni(TPyP)(TiF₆)]_n MOF-A layer that leads to their pre-concentration over the surface of the PDVT-10 polymer, which in turn leads to augment the overall sensitivity of device-2, as schematically illustrated in (**Figure 6**).

As discussed before, free holes were generated in the bulk region of the polymer due to the physical adsorption of polar NO₂ molecules. These free holes tended to drift towards the dielectric/semiconductor interface region, contributing to increased channel current, as shown in (**Figure 5d**). The corresponding energy band diagram is presented in (**Figure 5e**). Owing to high electron affinity, the MOF-A tended to attract more electrons from PDVT-10. This helped in the increment of dominant free holes in the PDVT-10 bulk region. Due to the applied gate electric field, these additional free holes tended to drift towards the hole accumulation channel layer at the SiO₂/PDVT-10 interface. (**Figure 5f**) displays the effect of the NO₂ gas interaction with the MOF-A/PDVT-10 heterojunction structure. Using the KPFM, the extracted work function established the fact that the MOF-A is an n-type, providing the scope for the formation of an electron-depleted space charge layer at the surface in the presence of oxidizing gas. As is evident from the OFET data, there was an increase in drain current due to further extraction of electrons

(as compared to device-1) from the interface, leading to more hole doping in the channel region. Similarly, for reducing gases like NH_3 , H_2S , and H_2 , the opposite phenomenon took place, hence the evident slump in the drain current (**Figure 3f**).

Figure 5. MOF-A/PDVT-10 OFET Gas sensing mechanism. (a) KPFM experimental setup and (b) relation between contact potential difference (CPD) values of the device and different gases. (c) KPFM surface potential map of MOF-A particles. Schematic representation of (d) interaction of NO_2 gas with PDVT-10 device, (e) heterojunction structure of MOF-A/PDVT-10 sensing layer stack, and (f) interaction of NO_2 gas with MOF-A/PDVT-10 device system.

Figure 6. (Top) Schematic illustration of gas molecules' interaction process in a bottom-gate bottom-contact PDVT-10 / MOF-A OFET transistor device. AFM topography images of (bottom left) PDVT-10 and (bottom right) PDVT-10/MOF-A layers in the OFET device stack.

3. CONCLUSIONS

In summary, we have successfully realized an ultrasensitive and a highly selective OFET sensor for NO₂ gas, via a novel combination of PDVT-10 and an isorecticular fluorinated 3D MOF, namely [Ni(TiF₆)(TPyP)]_n (MOF-A). With the addition of the MOF layer, the sensitivity towards NO₂ analyte increased by 700%, and a negligible effect of humidity on the sensing performance was observed. We achieved an excellent sensitivity of 680 nA/ppb via the synergistic combination of PDVT-10 and MOF-A to detect NO₂, as compared to 7.6 nA/ppb (PDVT-10 alone). The device demonstrated reproducible performance from 8 ppb to 100 ppm, unaffected by humidity and ambient conditions. The sensor device was further subjected to relative humidity changes ranging from 5% to 90% to evaluate its performance in extreme conditions. Bias stress measurements conducted on the devices revealed a negligible effect on the gas sensing performance. Furthermore, we observed that the device has a shelf-life of > 4 months

with insignificant changes in the baseline. Thus, this sensor can act as an alternative to existing sensor platforms due to its reduced complexity in fabrication and its high stability. These results additionally suggest that by choosing a proper synergistic combination of receptor materials, highly sensitive and selective sensors can be realized.

4. EXPERIMENTAL SECTION

PDVT-10. Poly{3,6-dithiophen-2-yl-2,5-di(2-decyltetradecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione-alt-thienylenevinylene-2,5-yl}(PDVT-10) organic semiconductor with molecular weight (MW) >30,000 was purchased from Luminescence Technology Corp. This material was used as received without any further purification. The PDVT-10 material was dissolved in Dichlorobenzene (DCB) organic solvent at a 3mg/mL ratio. The prepared solution was stirred at 350 rpm for a period of 24 hours @110C. With the help of an optimized recipe, as reported before, the PDVT-10 solution was spin-coated on the surface of Si/SiO₂ and Quartz substrate for material characterization. After the film formation, some of the desired features, such as surface coverage, roughness, chemical composition, and electronic bandgap properties, were characterized with the help of field enhanced scanning electron microscopy (FESEM), atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM), Raman spectroscopy, photoelectron spectroscopy in air (PESA), and UV-Vis-NIR spectroscopy instruments.

Synthesis of [M'(M''F₆)(TPyP)]_n (M'=, Ni, M''= Ti) MOF nanoparticles. Synthesis of [M'(M''F₆)(TPyP)]_n was carried out under ultrasonic irradiation at a frequency of 40 kHz preset in the Branson 2510 Ultrasonic bath. The temperature was varied from 20 to 60 °C in all experiments. In a typical synthesis, M'(NO₃)₂·xH₂O (0.04 mmol) and TPyP (12 mg, 0.02 mmol) partially dissolved in 6 mL of DMF and 0.4 mL of 0.05 M aqueous solution (NH₄)₂M''F₆ (0.02 mmol) were added into 20 mL scintillation vials. The vials were placed in the pre-heated ultrasonic bath. After the ultrasonic irradiation for a 4, 4, 10 h for a solution containing (NH₄)₂M''F₆ precursors, respectively, the products were isolated by centrifugation, and they were washed multiple times with DMF and activated with methanol.

Characterization of MOF. Powder X-ray diffraction (PXRD) patterns of the silica foam and all obtained MOF thin films were recorded on a Panalytical X'pert PRO MPD X-ray diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm, 45 kV, 40 mA). Ultraviolet-visible spectra were collected using a PerkinElmer Lambda 950 UV/vis spectrometer. SEM and EDX were performed using an FEI Quanta 600 field emission scanning electron microscope (accelerating voltage: 30 kV). Gas sorption measurements were performed on a fully automated micropore gas analyzer, Autosorb-1C (Quantachrome Instruments), at relative pressures of up to 1 atm. The cryogenic temperatures were controlled using a liquid nitrogen bath at 77 K. The apparent surface area was determined from the nitrogen adsorption isotherms by applying the Brunauer-Emmett-Teller (BET) model using adsorption points in the relative pressure (P/P_0) range of 0.015 to 0.046. Pore size analyses were performed using a cylindrical NLDFT pore model system by assuming an oxidic (zeolitic) surface.

OFET device fabrication process. Industry purchased, highly doped n-type (n++) silicon with thermally grown chlorinated SiO₂ layer wafers were employed to fabricate bottom-gate bottom-contact (BGBC) OFET devices. First, the wafer samples were ultrasonically cleaned in acetone and isopropyl alcohol (IPA) solvents, for 5 minutes each. The cleaned samples were then rinsed in deionized (DI) water and blown under an N₂ gas flow for a few seconds, and they were then dehumidified at 120 °C for 5 minutes. It is important to note that the IDE patterns were formed using a standard photolithography process. Initially, AZ5214 photoresist was spin-coated on top of the Si/SiO₂ substrate and pre-baked at 110 °C for 2 mins. Followed by exposure to UV light of dose 80 mJ/cm² through mask plate for 7 seconds. Without any further delay, the substrate was developed in AZ 726 developer for 1 min before cleaning in DI water. Thereafter, the substrate was dried with N₂ gas and enclosed in a black box before leaving the yellow room. Ti (10 nm)/Au (100 nm) metals were deposited on top of the developed substrate with radio frequency (RF) sputter machine. Finally, the source and drain interdigitated electrodes (IDE), with a channel length and width of around 10 μ m and 583640 μ m, were obtained after sonication in Acetone

for a suitable time. Thin-film of PDVT-10 organic semiconductor was spin-coated, using a previously reported recipe,⁴⁹ on the surface of the IDE devices using the as-prepared 3 mg/mL PDVT-10 solution. Subsequently, the PDVT-10 coated device was annealed by slowly increasing the temperature at a rate of 450 °C/hr from 25 °C to 180 °C. This high temperature was maintained for 5 min, and the device was then cooled down to room temperature. This resulted in the fabrication of device-1. The IDE devices were considered for the fabrication of both PDVT-10 (Device-1) and MOF-A/PDVT-10 (Device-2) OFET devices. The common feature in both devices was the formation of a PDVT-10 organic channel film. An additional step in the device-2 fabrication process was the deposition of MOF-A particles on the surface of PDVT-10 film. To maintain consistency in the MOF-A film formation, a fixed quantity of 5 μ L MOF-A solution was drop cast on the surface of the PDVT-10 OFET device. The MOF-A coated device was annealed at 100 °C for 5 min to evaporate the residual solvents.

Gas sensing measurements. The electrical behavior of the OFET devices in the presence of different gases was measured using the Keithely 4200 SCS system connected to a homemade gas testing chamber. The pristine PDVT-10 device was subjected to bias by sweeping the gate voltage (V_G) = 20 to -30 V for different drain voltages stepped from -5 to -30 V and the corresponding transfer characteristics were recorded. Whereas, for output characteristics, the drain voltage was swept from 0 to -30 V and the corresponding gate voltages were stepped from -5 to -30 V. These biasing conditions were applied using commercial 4200 Semiconductor Characterization system (SCS) and it was connected to gas set up, as shown in Figure S5c. Here, we used two mass flow controllers (MFCs) and one mass flow meter (MFM) to keep track of the gases flowing. Initially, the device was connected to electrical wires in gas chamber (as shown in Figure S5c) and the corresponding lid was enclosed tightly to avoid any leakages. To get rid of any moisture present in the chamber N_2 gas was purged at 200 SCCM till a baseline is reached for both the transfer and output characteristics. Thereafter, with the help of two MFCs desired concentration of any gas is passed through the chamber by manipulating the ratio between target gas and N_2 gas while

maintaining the overall flow rate constant at 200 SCCM. Like preceding measurements transfer and output characteristics of the device were obtained at individual gas concentrations before purging the chamber. The complete details about the gas set up employed during this measurement are presented elsewhere.⁶³ The effects of different gases on the surface potential of PDVT-10 thin film were characterized using the KPFM feature in the Bruker AFM system. In this experiment, the sample under study was initially exposed to target gases of different concentrations for 5 min. Without any further delay, the exposed sample was then subjected to KPFM characterization. The important parameters such as integral gain, amplitude set-point, drive frequency, and lift scan height were optimized at 7.609, 35.17 nm, 61.29741 kHz, and 108.1 nm, respectively.

Supporting Information Available:

Supporting information file contains the details of different material characterization of the active channel layer PDVT-10 and [Ni(TiF₆)(TPyP)] metal-organic framework (MOF). It also briefs about the gas setup used to conduct the exposure studies with different gases. All the measurements related to the pristine OFET and the OFET with MOFs are presented with transfer plots. OFET device parameters were extracted from these characteristics and plotted separately. Further, data related to sensitivity and selectivity with different gases and the mechanism involved in the process have been depicted accordingly.

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Notes

The authors declare no competing financial interest

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