

Intramolecular Heterojunctions for Highly Sensitive Room-Temperature NO₂ Sensing

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Cite This: *Inorg. Chem.* 2026, 65, 21629–21638

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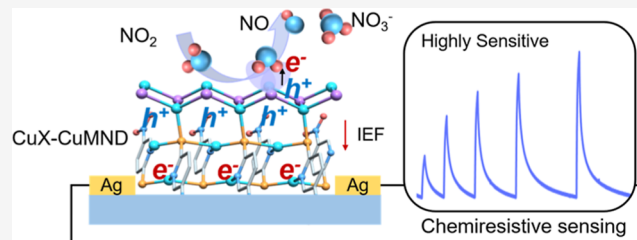


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ABSTRACT: Heterojunction materials achieve efficient charge transfer and carrier separation through built-in electric fields at the interfaces, thereby substantially enhancing the sensitivity and selectivity of gas sensors. However, traditional particle-contact heterojunctions suffer from discontinuous interfaces and limited contact areas, resulting in low charge transport efficiency and restricted gas-sensing performance. Herein, we construct two intramolecular D–A heterostructured frameworks (CuBr–CuMND and CuI–CuMND) by directionally linking CuX chains (donor) and CuMND (acceptor) via Cu–S coordination bonds. The atomically continuous heterointerface achieves spatial highest occupied molecular orbital/lowest unoccupied molecular orbital separation and a strong internal built-in electric field (IEF). CuI–CuMND exhibits a record-low detection limit of 0.05 ppb and a response of 1315% toward 10 ppm of NO₂, along with excellent long-term stability at room temperature without light assistance. Theoretical calculations reveal that, compared with CuBr–CuMND, CuI–CuMND exhibits a larger Fermi level disparity, which generates a stronger IEF that significantly enhances interfacial charge separation and transport, ultimately leading to a higher response value and faster response/recovery time toward NO₂. This study establishes a molecular-scale intramolecular heterojunction engineering strategy for room-temperature trace-gas sensing.



INTRODUCTION

The target gas donates electrons to or extracts electrons from the material upon adsorption onto the surface of the material, leading to the generation of nonequilibrium charge carriers. These carriers are then efficiently separated, and their transport is accelerated by the built-in electric field at the heterojunction interface, which in turn significantly improves the gas-sensing performance.^{1–5} This built-in electric field (IEF) not only accelerates surface reactions and shortens the response time by effectively lowering the activation energy for charge transfer, but also renders the interfacial current exponentially sensitive to the barrier height.^{6–10} As a result, even small surface charge variations cause large resistance changes, imparting high sensitivity to heterojunction materials. Nevertheless, conventional two-component particle-contact heterojunctions, despite generating an IEF at the interface, suffer from limited contact area and discontinuous interfaces between the two constituent particles.^{11–13} These drawbacks lead to low electron-transport efficiency, preventing full exploitation of the IEF modulation and thus restricting further improvement in gas-sensing performance. Therefore, designing room-temperature heterojunction sensing materials with high sensitivity remains a significant challenge (see Scheme 1).

Intramolecular heterojunctions, constructed via chemical bonds (e.g., covalent bonds, coordination bonds) at the molecular scale, feature atomically continuous heterointerfaces.^{14–18} This molecular-scale contact strategy circumvents the bottlenecks of discontinuous interfaces and limited contact

areas in conventional particle-contact heterojunctions, offering a promising route to surpass the sensitivity limits of current gas-sensing devices. Linking electron-donor (D) and electron-acceptor (A) functional groups via chemical bonds at the molecular level can form an intramolecular D–A heterostructure.^{19–23} In this configuration, the coordination linkage serves as an efficient intramolecular bridge for electron transport between the D and A components.²⁴ Moreover, the ordered packing arrangement of D and A units establishes a continuous distribution of the IEF, significantly enhancing the charge transfer efficiency between donors and acceptors.^{25–28} Thus, the intramolecular D–A heterojunction holds great potential to overcome the sensitivity limitation of conventional gas sensors.

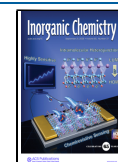
In this work, we directionally linked inorganic CuX chains (donor, D) and organic Cu nitropyridine coordination polymer chains (acceptor, A) at the molecular level via Cu–S coordination bonds. This linkage constructs two-dimensional intramolecular heterostructured frameworks featuring a long-range ordered D–A–D–A parallel arrangement. The resulting

Received: May 28, 2026

Revised: July 21, 2026

Accepted: July 30, 2026

Published: August 6, 2026



Scheme 1. Schematic Diagrams of Particle Contact (a) and Intramolecular Heterojunctions (b)

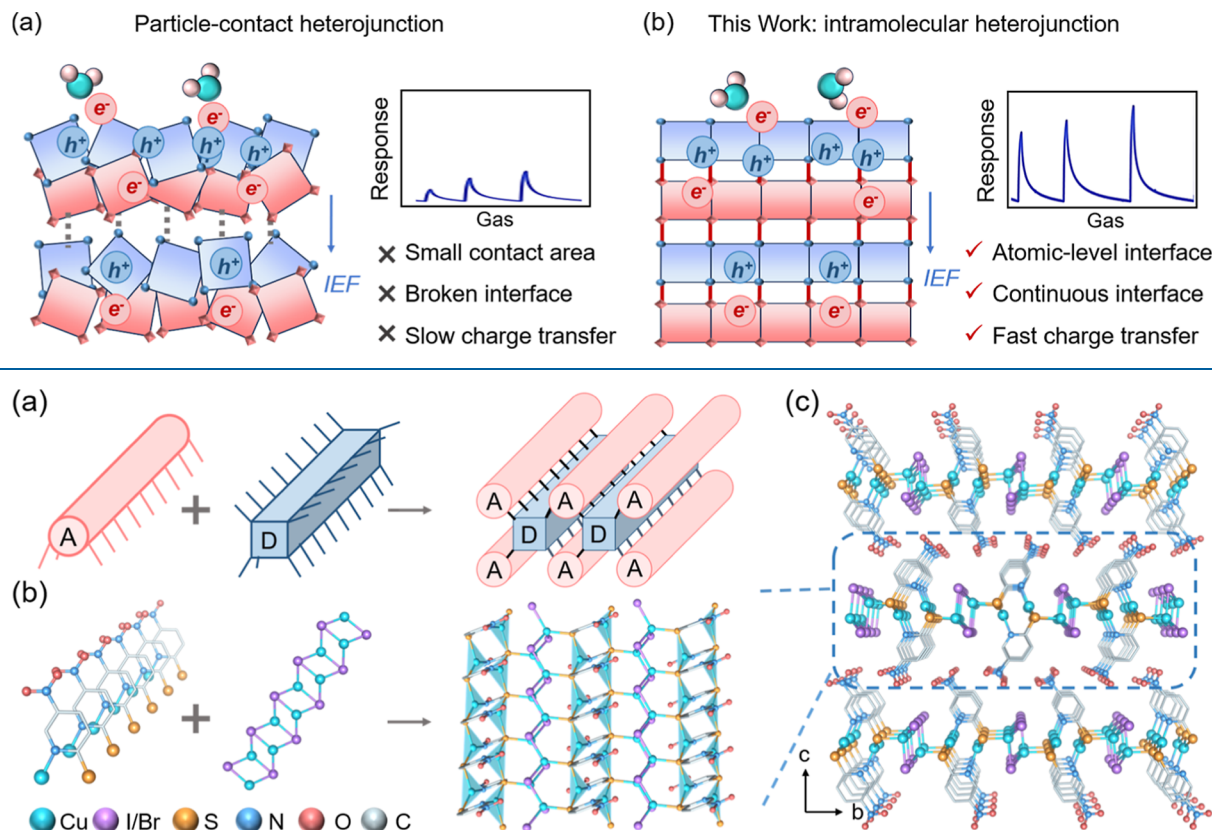


Figure 1. Intramolecular D–A heterostructured frameworks of CuX-CuMND (X = Br, I). (a) Schematic of the construction of CuX-CuMND. (b) Composition of the donor and acceptor chains of CuX-CuMND and coordination connections between the heterointerfaces. (c) Crystal structure of CuX-CuMND.

compounds were designated as CuBr-CuMND ($\text{Cu}_2\text{BrC}_5\text{H}_3\text{N}_2\text{O}_2\text{S}$) and CuI-CuMND ($\text{Cu}_2\text{IC}_5\text{H}_3\text{N}_2\text{O}_2\text{S}$). This architecture achieves spatial localization of the highest occupied molecular orbital (HOMO) on the one-dimensional (1D) inorganic CuI chains (donor) and the lowest unoccupied molecular orbital (LUMO) on the 1D CuMND chains (acceptor), with a strong IEF between the donor and acceptor. Under the same conditions without light illumination, CuBr-CuMND and CuI-CuMND exhibited unique selectivity toward NO_2 , with response values of 251% and 1315% toward 10 ppm of NO_2 and detection limits of 0.78 and 0.05 ppb, respectively. These detection limit values are markedly superior to those of previously reported room-temperature NO_2 sensing materials operating without light assistance. Notably, the detection limit of CuI-CuMND (0.05 ppb) is the lowest reported to date for materials tested under the same conditions. Moreover, CuX-CuMND exhibits excellent reusability, maintaining a response value above 94% in long-term stability tests for up to 35 days. Theoretical calculations revealed that a significant initial Fermi level difference between the inorganic CuX and CuMND chains led to the formation of a strong intramolecular IEF. Upon exposure to an NO_2 atmosphere, this IEF facilitates electron transfer and transport, thereby enabling highly sensitive NO_2 detection. Moreover, a stronger IEF in CuI-CuMND results in a higher response value and faster response/recovery time. This study not only uncovers the intrinsic electronic structure correlation between the IEF strength and gas-sensing performance but also provides a molecular-scale heterojunction engineering strategy based on

coordination chemistry for designing high-performance sensing materials operating at room temperature.

RESULTS AND DISCUSSION

Crystal Structural Analyses

Single-crystal X-ray diffraction analysis showed that CuBr-CuMND and CuI-CuMND possess the same structure, both crystallizing in the monoclinic space group $P2_1/n$ (no. 14). The unit cell parameters of CuBr-CuMND are $a = 3.8499(1)$ Å, $b = 9.1138(2)$ Å, $c = 24.5127(5)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 91.792(2)^\circ$, and $V = 859.66(3)$ Å³, while those of CuI-CuMND are $a = 3.9634(2)$ Å, $b = 9.3509(6)$ Å, $c = 24.1034(13)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 91.229(5)^\circ$, and $V = 893.10(9)$ Å³ (see Table S1 for details). Taking CuI-CuMND as an example, its asymmetric unit contains two distinct copper atoms, Cu1 and Cu2, one iodine atom, and one deprotonated 5-nitropyridine-2-thiolate (MND) ligand (Figure S1a). The MND ligand utilizes its N and S to coordinate with the Cu. Specifically, the Cu1 center adopts a three-coordinate state, binding two sulfur atoms and one pyridine nitrogen atom from three independent MND ligands to form a planar triangular geometry. These triangles are linked via shared organic vertices to generate 1D CuMND chains (Figure S1b). Concurrently, the Cu2 center exhibits a four-coordinate tetrahedral geometry, surrounded by three bridging iodine atoms and one sulfur atom from the organic ligand. Crucially, the copper–iodine bond is shared along the edges, extending into 1D inorganic CuI chains. To construct the intramolecular heterojunction,

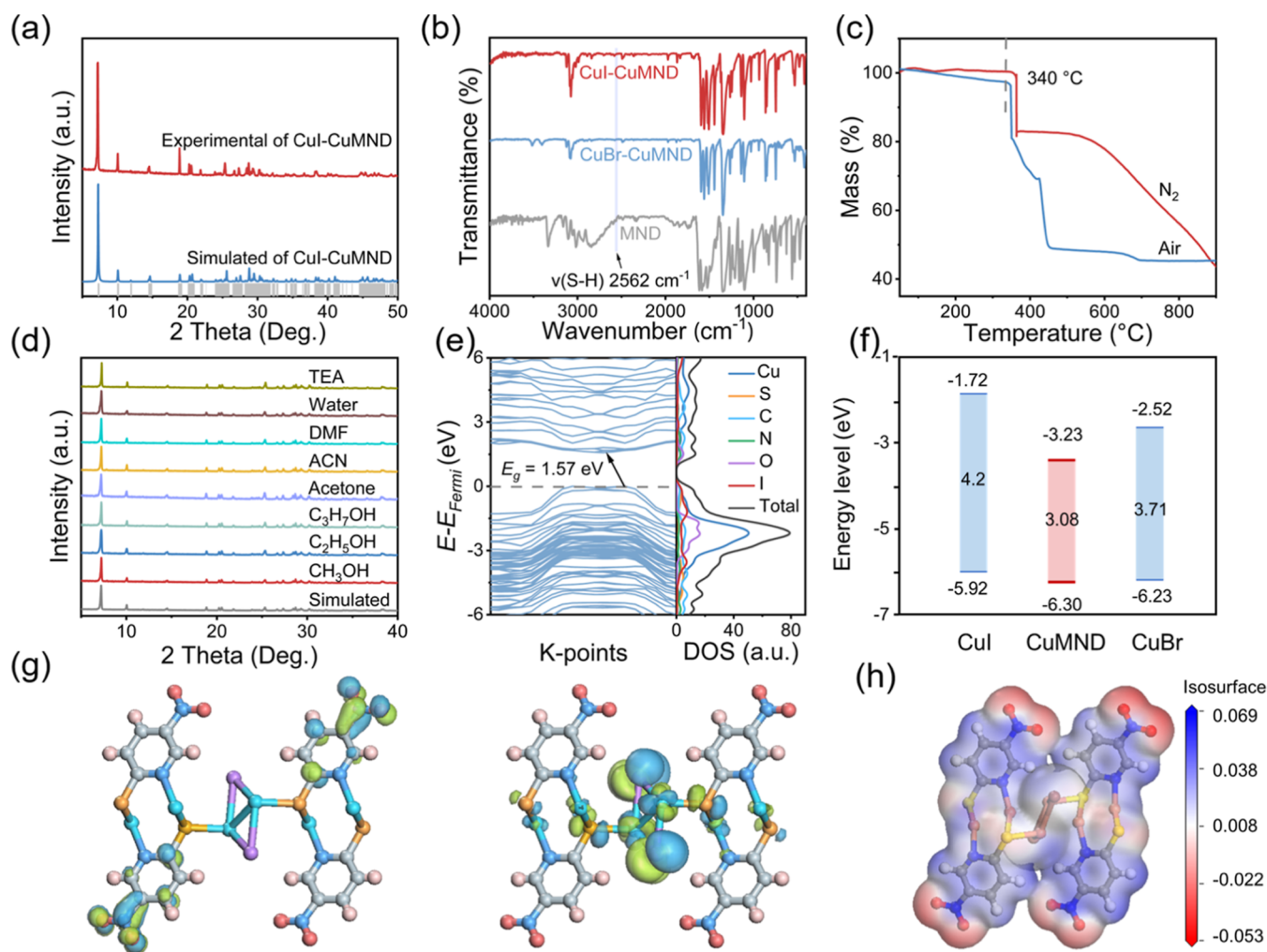


Figure 2. Basic characterization of CuX-CuMND: (a) experimental and simulated PXRD patterns of CuI-CuMND. (b) FT-IR spectra of MND and CuX-CuMND. (c) TG curves of CuI-CuMND. (d) PXRD patterns after immersion in different solvents for 48 h. (e). Calculated densities of states for CuI-CuMND. (f) Band structure diagrams for CuI, CuMND, and CuBr chains. (g) HOMO (left) and LUMO (right) profiles for CuI-CuMND. (h) Electrostatic potential map of CuI-CuMND.

these 1D inorganic CuI chains (donor) and 1D CuMND chains (acceptor) were covalently cross-linked via Cu2–S bonds, thereby forming a two-dimensional D–A–D–A network with long-range order (Figure 1a,b). Finally, adjacent two-dimensional layers are stacked along the *c*-axis via weak van der Waals interactions, establishing a three-dimensional framework (Figure 1c). The structure of CuBr-CuMND is similar to that of CuI-CuMND, as shown in Figure S2. Detailed crystallographic data are provided in Tables S1–S3. The elemental analysis (EA) results were consistent with those calculated based on the molecular formula (Table S4).

The powder X-ray diffraction (PXRD) patterns of the as-synthesized CuX-CuMND samples were in good agreement with the simulated profiles generated from single-crystal data using Mercury software, confirming the high phase purity of the crystalline materials (Figures 2a and S3). Fourier-transform infrared (FT-IR) spectroscopy further confirmed the coordination between the MND ligands and metal ions, as evidenced by the complete disappearance of the characteristic –SH stretching vibration peak at 2562 cm^{−1} (Figure 2b).^{29,30} As shown in Figure S4, the X-ray photoelectron spectroscopy (XPS) survey spectra clearly display characteristic binding energy signals corresponding to Cu 2p, S 2p, N 1s, C 1s, and I

Sp. Specifically, the high-resolution Cu 2p spectrum revealed a well-defined Cu 2p^{3/2} peak at 932.26 eV, indicating that copper exists purely in the +1 oxidation state.³¹ The S 2p^{3/2} peak at 162.9 eV represents a characteristic signature of sulfur atoms coordinated to copper.³² Furthermore, the N 1s spectrum exhibited two distinct peaks at 399.5 and 405.9 eV, which can be unambiguously assigned to the nitrogen atoms in the Cu–N coordination bonds and the –NO₂ groups in the structure, respectively.³³ Importantly, comparable XPS profiles and binding energies were observed for CuBr-CuMND (Figure S5), confirming that the bromine derivative shares an identical monovalent Cu⁺ oxidation state and similar coordination environments. Optical microscopy and scanning electron microscopy (SEM) were used to investigate the morphology and dimensions of the two crystals (Figure S6). CuX-CuMND exhibits a well-defined, flattened rod-like morphology, with typical lengths of 70 μm and widths of 5 μm. Additionally, energy-dispersive X-ray spectroscopy elemental mapping verified the homogeneous distribution of Cu, S, N, O, C, and Br/I throughout the entire crystal architecture (Figures S7 and S8). The thermal and chemical stabilities of the CuX-CuMND frameworks were systematically evaluated. As shown in the thermogravimetric analysis (TGA) results in Figures 2c

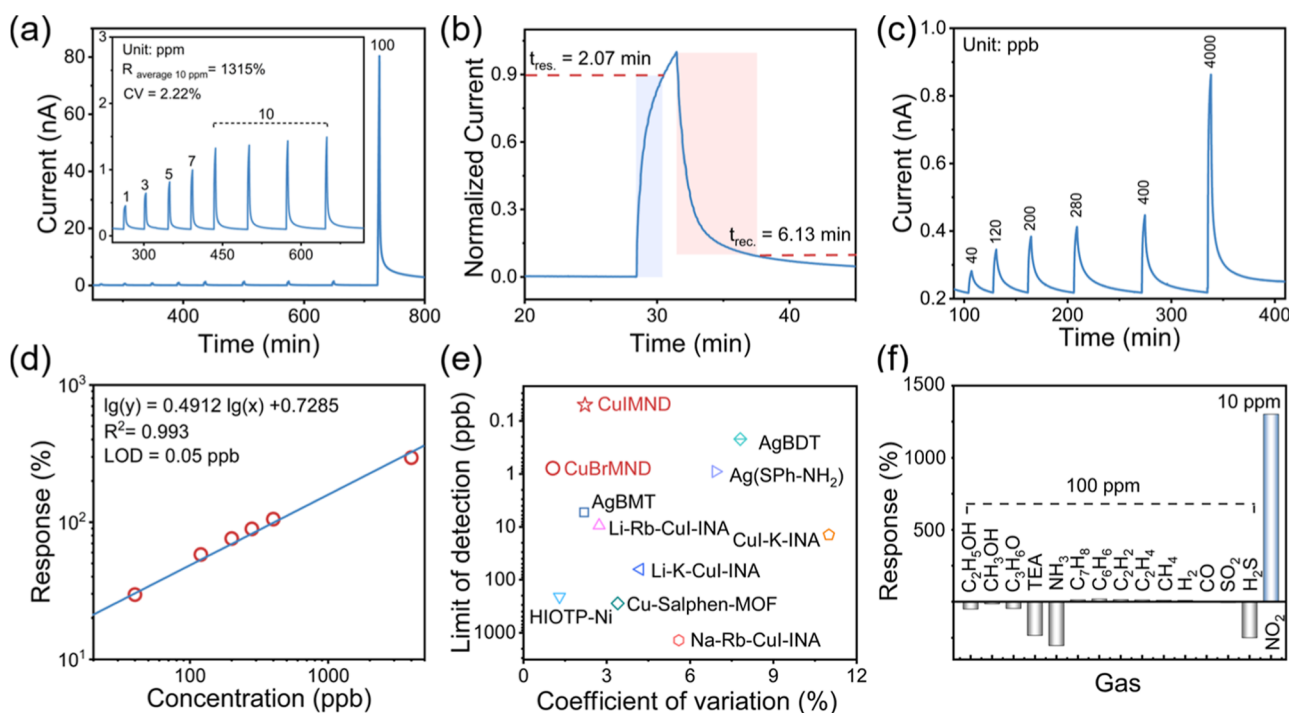


Figure 3. CuI-CuMND sensor: (a) response and recovery curves for NO₂ at different concentrations at room temperature without light assistance. (b) Response and recovery times for 10 ppm of NO₂. (c) Response and recovery curve toward 40–4000 ppb NO₂ at room temperature without light assistance. (d) Log–log linear fitting of the response–concentration plot. (e) Comparison of the limit of detection and CV of CuX-CuMND with those of the reported NO₂ sensors at room temperature without light assistance. (f) Selectivity toward 14 interference gases (100 ppm).

and S9, the CuX-CuMND material exhibited high thermal stability. Among them, CuI-CuMND maintained its structural integrity up to 340 °C in both air and nitrogen environments, whereas CuBr-CuMND maintained its structural integrity up to 300 °C. To assess their chemical durability, the CuX-CuMND powdered samples were immersed in various common laboratory solvents for 2 days. The post-treatment PXRD patterns were in excellent agreement with those of the pristine samples (Figures 2d and S10), with no additional phases or structural degradation observed, thereby confirming the outstanding chemical stability of these crystalline frameworks.

The intrinsic electrical and semiconductive characteristics of CuX-CuMND were investigated using a standard two-probe method. At room temperature, the current–voltage (*I*–*V*) curves of both devices exhibited a linear relationship (Figure S11), demonstrating the establishment of Ohmic contact between the samples and the electrodes. The room-temperature electrical conductivities (σ) were determined to be $4.46 \times 10^{-11} \text{ S cm}^{-1}$ for CuBr-CuMND and a noticeable higher value of $1.96 \times 10^{-10} \text{ S cm}^{-1}$ for CuI-CuMND. Variable-temperature conductivity measurements were performed to verify the semiconducting nature of the materials. As the temperature increased, the conductivities of both materials increased monotonically, behaving as typical semiconductors. Furthermore, the plots of $\log \sigma$ versus $1000/T$ displayed good linear fits (Figures S12 and S13), indicating that the electrical conduction within CuX-CuMND is governed by an Arrhenius-type thermally activated mechanism.

As shown in Figure S14, CuBr-CuMND and CuI-CuMND exhibit optical bandgaps (E_g) of 1.94 and 1.90 eV, respectively, corresponding to absorption edges at 639 and 654 nm, respectively. This bandgap aligns well with their dark red

appearance and endows both materials with a robust absorption capability across the UV–visible region. To further elucidate the electronic band alignment, ultraviolet photoelectron spectroscopy (UPS) analysis was performed (Figures S15 and S16). For CuI-CuMND, the Fermi level (E_F), valence band maximum (VBM) (E_V), and conduction band minimum (CBM) (E_C) were determined to be -4.66 , -5.42 , and -3.52 eV, respectively, whereas the corresponding energy levels for CuBr-CuMND were located at -3.90 , -4.78 , and -2.84 eV. Notably, the E_F positions of both materials were significantly closer to their respective E_V , demonstrating their typical p-type semiconducting nature.

Density functional theory (DFT) calculations were performed to elucidate the molecular-scale electronic structure and interfacial charge-transfer energetics of CuX-CuMND. A comprehensive analysis of the interfacial characteristics (Figure S17) revealed that the initial Fermi level discrepancy between the inorganic CuI chains and the CuMND chains was the source of the IEF. Specifically, the ΔE_F in CuI-CuMND (0.94 eV) is markedly larger than that in CuBr-CuMND (0.39 eV). Driven by this substantial intrinsic energy level alignment disparity, electrons spontaneously migrate from the inorganic CuI chains to the CuMND chain moieties until localized Fermi level equilibration is achieved. This cross-interface correlation establishes a distinct space charge region and a more pronounced IEF directed from the inorganic CuI donor chains toward the CuMND chains. Consequently, this continuous interfacial charge redistribution results in significant electron accumulation on the CuMND chains, while the donor exhibits pronounced electron depletion, thereby creating a hole-enriched p-type transport channel along the CuX chains.

This electronic configuration is further substantiated by the spatial distribution of the frontier molecular orbitals. As

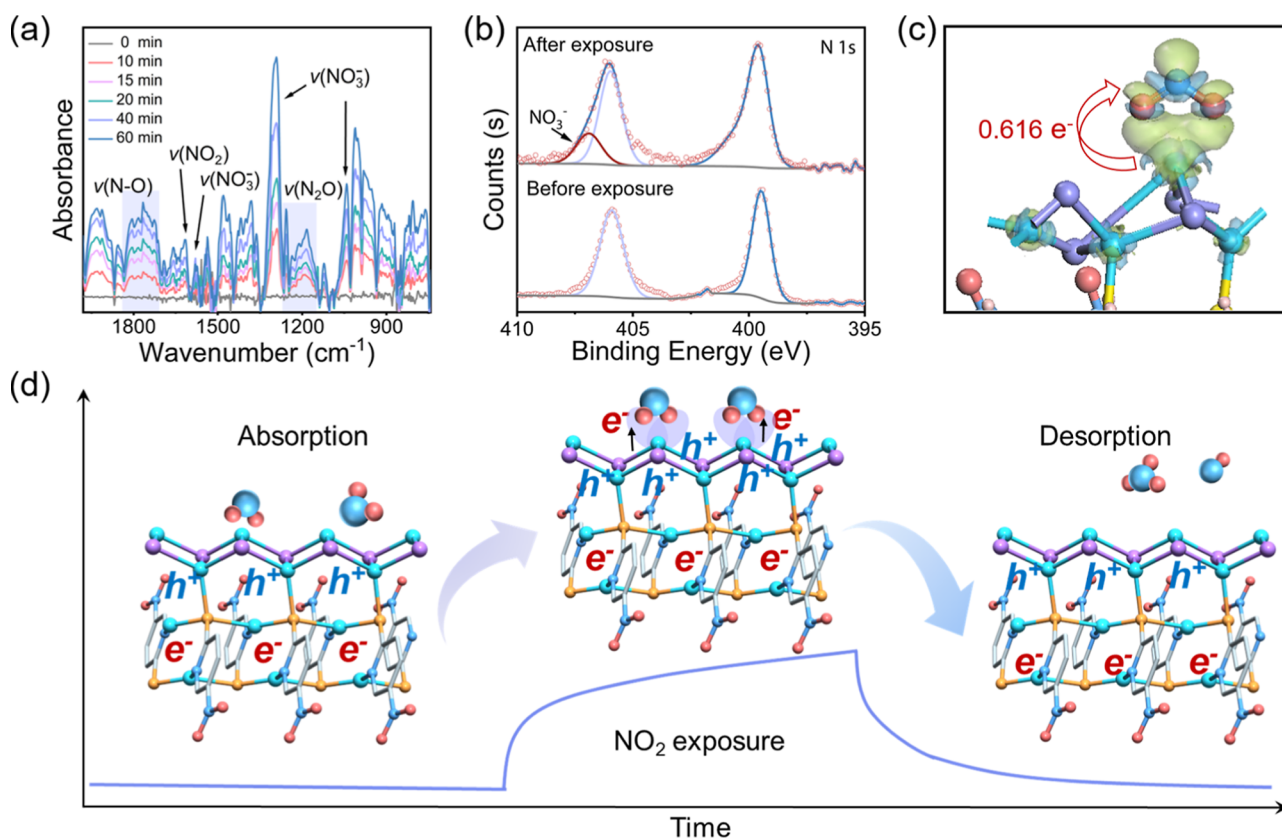


Figure 4. Characterization of the NO_2 sensing mechanism. (a) In situ DRIFT spectra for CuI-CuMND exposed to NO_2 as a function of time. (b) XPS spectra of N 1s in CuI-CuMND before and after NO_2 exposure. (c) Differential charge density between the CuI chains and NO_2 . (d) Possible NO_2 sensing mechanism for CuI-CuMND.

illustrated in Figures 2g and S18, the HOMOs of the CuX-CuMND are predominantly localized on the inorganic CuX chains, whereas the LUMO residing on the CuMND chains. Specifically, the VBM is primarily composed of Cu 3d and I 5p orbitals (Br 4p for CuBr), whereas the CBM is governed by the π^* orbitals of the MND ligands within the CuMND chain (Figures S19 and S20). Crucially, the spatial confinement of the HOMO within the continuous inorganic CuX chains suggests that the inorganic chains can serve as efficient channels for hole carrier transport, whereas the spatially dislocated donor–acceptor of the frontier orbitals inherently promotes the effective spatial separation of activated carriers.

Electrostatic potential (ESP) maps (Figures 2h and S21) further delineate the holistic charge location in CuX-CuMND. Driven by the spontaneous donor-to-acceptor charge transfer, the CuMND acceptor chains in both systems exhibit a prominently negative potential distribution, which is particularly evident at the highly electrophilic peripheral nitro terminals, which reach a localized minimum of -0.053 (deep red). For CuI-CuMND, the inorganic CuI chains as a collective entity displayed a white-and-blue intertwined distribution with a uniform, moderate positive potential hovering around $+0.038$. This potential contrast unequivocally confirms the establishment of a transversal intramolecular IEF oriented from the CuI donor to the CuMND acceptor. This transversal potential gradient creates an effective electrostatic driving force that efficiently guides carriers and optimizes the surface electronic structure. In contrast, although CuBr-CuMND yields a generally similar ESP, the Br within its inorganic CuBr chains displays a discernible pink color with a

localized negative potential of approximately -0.01 , thereby disrupting the uniform potential continuity of CuX and weakening the intramolecular IEF contrast.

Gas Sensing Properties

Motivated by the unique molecular-scale D–A architecture and the interfacial IEF within CuX-CuMND, we systematically investigated their chemiresistive gas-sensing performance at room temperature without light assistance. Polycrystalline powder-based devices were fabricated by coating ground CuX-CuMND samples onto interdigitated electrodes, which were then integrated into a home-built testing system (Figure S22). The sensing evaluations were conducted at 25°C under dark conditions with a constant bias voltage of 5 V, and the gas detection behavior was captured by real-time monitoring of the conductivity of the device.

As displayed in Figures 3a and S23, both CuX-CuMND devices exhibited a rapid increase in conductivity upon exposure to NO_2 , followed by a gradual recovery to their baseline states during synthetic air purging, which is consistent with a typical p-type semiconducting response. The CuI-CuMND device had a response value of 1315% for 10 ppm of NO_2 , with a response time of approximately 2.07 min and a recovery time of approximately 6.13 min (Figure 3b). In contrast, CuBr-CuMND exhibited relatively poor gas-sensing performance, with a response value of only 251%, and showed a longer response time (approximately 2.47 min) and a slower recovery period (approximately 24 min) (Figure S23c). Furthermore, the investigation of the dynamic sensing behaviors across a wide concentration range of 1–100 ppm revealed that the responses scaled proportionally with the

increased concentrations of NO_2 , demonstrating excellent linearity. Notably, CuI-CuMND also maintained exceptional detection capability within the low-concentration regime of 40–4000 ppb (Figure 3c), while within the same low concentration range, CuBr-CuMND showed almost no response (Figure S24). Both CuBr-CuMND and CuI-CuMND also exhibited low coefficients of variation (CV) of only 1.06% and 2.22% (Figures S23a and 3a), respectively, highlighting their outstanding reproducibility. Based on a response threshold of 10%, the limits of detection (LOD) for CuBr-CuMND and CuI-CuMND were calculated to be 0.78 and 0.05 ppb, respectively (Figures 3d and S23b). The LOD of CuI-CuMND is among the lowest values achieved to date for the reported materials evaluated at room temperature without light assistance (Figure 3e and Table S5). Additionally, both CuBr-CuMND and CuI-CuMND demonstrated exceptional selectivity against 14 common interfering gases (all at 100 ppm) (Figures 3f and S23d), with negligible cross-sensitivities. Moreover, CuBr-CuMND and CuI-CuMND exhibited outstanding long-term stability, retaining over 94% of their initial responses to 10 ppm of NO_2 even after 35 days (stored in a centrifuge tube filled with air at room temperature) of ambient exposure (Figure S25), and the baseline current and response value of the device showed almost no change (Figure S26). However, for high concentration of NO_2 (100 ppm), after multiple cycle tests, the response value of CuI-CuMND will drop to 66% of the original, and the CV after four cycles is 18.67% (Figure S27). This may be attributed to the strong oxidizing nature of NO_2 , possibly causing material oxidation or incomplete desorption of the adsorbed NO_2 .

CuX-CuMND exhibits excellent on–off ratio in photoconductivity, with response values of 2462.09% and 9725.78%, respectively (Figure S28). This indicates that the heterojunction significantly enhances the on–off ratio. However, under illumination conditions, the gas sensing response of CuBr-CuMND and CuI-CuMND are only 199.41% and 128.37%, which are much lower than the response in the dark state. The main reason is that the response is obtained through $\Delta I/I_0$ (current change divided by baseline current). Since the baseline current under illumination conditions is much higher than that in the dark state (approximately 3 orders of magnitude higher, from 10^{-10} A to 10^{-7} A), the relative change $\Delta I/I_0$ decreases accordingly, which is likely the fundamental reason for the relatively small response values. In addition, the gas sensing responses of CuI-CuMND under different humidity conditions were also studied. As shown in Figure S29, within the range of relative humidity (RH) from 10% to 90%, CuI-CuMND exhibited a low humidity response, with the response values all below 100%, indicating that this material has certain antihumidity detection capabilities. The results of the responses to 10 ppm of NO_2 gas under different humidity conditions showed that, regardless of the humidity, the response value caused by NO_2 was always significantly higher than the response value produced by the corresponding humidity itself. As the RH increased, the response to 10 ppm of NO_2 showed a gradually increasing trend, which was consistent with the research results in the literature.^{34,35}

Sensing Mechanism

To gain deep insights into the NO_2 sensing mechanism, time-resolved diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) and postsensing XPS measurements were performed. As shown in Figure 4a, upon exposure to NO_2 ,

CuI-CuMND exhibited a series of progressively intensifying infrared absorption peaks. The newly emerged peaks at 1614, 1537, 1363, and 1257 cm^{-1} are characteristic of the symmetric and asymmetric stretching vibrations of adsorbed NO_2 , while the bands at 1459 and 1120 cm^{-1} correspond to its bending vibrations, unambiguously confirming the adsorption of NO_2 .³⁶ Concurrently, the distinct peaks at 1580, 1301, and 1041 cm^{-1} can be assigned to the N–O vibrations of bidentate nitrate species (NO_3^-),³⁷ implying a surface-mediated disproportionation reaction of NO_2 molecules upon adsorption. This interpretation is strongly supported by the simultaneous appearance of nitrosyl features ($\text{N}=\text{O}$, $1820\text{--}1700\text{ cm}^{-1}$) representing the NO byproducts.^{38–42} Additionally, the characteristic N–O stretching modes observed around $1300\text{--}1150\text{ cm}^{-1}$ indicate the formation of N_2O , which likely arises from the further reduction or decomposition of nitrogen oxides. This surface reaction mechanism was further validated by the postsensing high-resolution N 1s XPS spectrum (Figure 4b), which successfully resolves the newly generated peak near 407.0 eV, belonging to the surface-bound nitrate (NO_3^-).⁴³

To precisely identify the specific active center of CuI-CuMND, DFT calculations were performed to screen various targeting models (including NO_2 binding onto ligand nitro terminals or copper nodes). The calculation results show that model III (Figure S30), featuring a bidentate O,O-nitro coordination configuration on the open Cu sites, exhibits the highest adsorption energy 2.91 eV, while the same adsorption model of CuBr-CuMND has a relatively lower adsorption energy of 2.18 eV. This suggests that the NO_2 molecule is more likely to adsorb onto the Cu site from the CuX chain. Bader charge analysis (Figures 4c and S31) shows that the CuI-CuMND undergoes a net charge transfer of 0.616 e^- to the NO_2 molecule, while the CuBr-CuMND undergoes a net charge transfer of 0.611 e^- to the NO_2 molecule, thereby triggering the macroscopic resistance response. From the supplementary XPS spectrum (Figure S32), it can be found that after being exposed to the NO_2 atmosphere for 24 h, the binding energy of Cu moved from 952.1 to 952.3 eV. However, no Cu^{2+} satellite peak appeared, indicating that Cu^+ was not oxidized. Therefore, the reason for the poor cycle stability in the high-concentration NO_2 cycle test might be that the NO_2 adsorbed on the material surface was not completely released, resulting in the transfer of electrons from Cu^+ to NO_2 . This further supports the gas-sensing mechanism. Additionally, there were no significant changes in the infrared spectra of the material before and after the test (Figure S33), and the PXRD patterns before and after the test (Figure S34) were almost identical, which further confirmed the excellent structural stability and chemical reversibility of the framework during the perception cycle. The responses curves of CuI, MND monomers, and the CuI/MND mixture to 100 ppm of NO_2 were measured as 60.06%, 102.9%, and 147.99%, respectively, which are substantially lower than that of CuI-CuMND (71110.42%) (Figure S35). The remarkable difference in response underscores the superiority of the atomic-scale continuous interface.

Based on the above analyses, the sensing mechanism of the interaction between the target gas molecules and the material was deduced, as illustrated in Figure 4d. Upon NO_2 exposure, the gas molecules preferentially attach to the active Cu sites of the CuI chains. This adsorption process is profoundly accelerated by the pre-established, potent interfacial IEF, which strongly polarizes the NO_2 molecules and lowers the

energy barrier for charge transfer, thereby enhancing the surface activity. Driven by this built-in potential gradient, electrons are transferred from the CuI chains to the adsorbed NO₂, generating a large number of nonequilibrium hole carriers within the inorganic pathways of CuI. The magnitude of the interfacial electric field plays a crucial role in promoting charge separation, wherein the transferred electrons are stabilized at the chemisorption sites, whereas the injected holes are efficiently delocalized along the conductive CuI chains, leading to a pronounced decrease in resistance. It is worth noting that a strong built-in electric field not only promotes the redistribution of charges, but also accelerates the migration of charge carriers during the recovery process. Upon removal of NO₂, the strong IEF facilitates rapid charge re-equilibration and back-transfer of electrons from NO₂ to the CuI chains, thereby destabilizing the adsorbed species and facilitating their faster desorption. Therefore, CuI-CuMND simultaneously exhibits enhanced sensitivity and accelerated response/recovery dynamics compared to CuBr-CuMND.

CONCLUSIONS

In summary, two two-dimensional intramolecular D–A heterojunctions (CuBr-CuMND and CuI-CuMND) with coordinated bond connections at the interface were successfully constructed through coordination self-assembly. This molecular-scale contact architecture effectively circumvents the limited contact areas and discontinuous interfaces prevalent in conventional particle-contact heterojunctions. By integrating the electron-donating inorganic CuX chains with the electron-accepting CuMND through Cu–S coordination bond, a potent interfacial IEF was successfully established in CuX-CuMND. This strong IEF greatly polarizes the target NO₂ molecules, thereby lowering the barrier for electron extraction and consequently enhancing the gas sensing activity. Consequently, the CuI-CuMND exhibits an outstanding room-temperature NO₂ sensing performance under dark conditions, delivering a high response value of 1315% toward 10 ppm of NO₂, and an ultralow detection limit (0.05 ppb). This LOD is the lowest data among the reported materials evaluated under room-temperature without light-assisted. Furthermore, the material demonstrates exceptional long-term durability, retaining over 94% of its initial response amplitude after a rigorous 35 days stability test. This work provides a feasible molecular engineering design approach for the development of high-performance gas sensing materials that do not require heating or light assistance.

EXPERIMENTAL SECTION

General Information

Materials and Preparation of the CuX-CuMND Samples. All experimental reagents used in this study were of analytical grade and no require further purification. Cuprous iodide (CuI, 99.9%) and cuprous bromide (CuBr, 99.9%) were purchased from Aladdin Holdings Group Co., Ltd., China. 2-Mercapto-5-nitropyridine (MND, 99.9%) was purchased from Adamas-beta, China. EtOH and ACN was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ag–Pd interdigital electrode plates with a channel width of 200 μ m were obtained from Hangzhou Jinbo Tech. Co., Ltd., China. All target gases were sourced from Beijing Huayuan Gas Chemical Industry Co., Ltd., China.

Synthesis of CuX-CuMND

CuI-CuMND was synthesized by CuI (38 mg), 2-mercapto-5-nitropyridine (31 mg), 2.0 mL of ACN, and 2.0 mL of EtOH, sealed

in a 20 mL container, heated at 85 °C for 3 days, and then cooled to room temperature. Red-brown, rod-shaped crystals were obtained, washed with ethanol, and then dried in air. CuBr-CuMND was synthesized using the same procedure as for CuI-CuMND, except that CuBr (28 mg) was substituted for CuI.

Characterization

Single crystals of CuI-CuMND and CuBr-CuMND were selected for the experiments. Diffraction data were collected using a ROD Synergy single-crystal diffractometer equipped with a copper target (Cu K α , λ = 1.54184 Å) X-ray source and a mixed-pixel area detector. The structure was determined using the direct method with the ShelXT program embedded in Olex2, and full-matrix least-squares fitting was performed using ShelXT. The detailed crystallographic data and structural refinement parameters are summarized in Table S1–S3.

PXRD measurements were performed on the samples using a Rigaku Smart Lab X-ray diffractometer (Cu K α 1, λ = 1.5406 Å) with a scanning speed of 5°/min (2θ range: 5–50°, step size: 0.02°/2 θ). Simulated PXRD patterns were generated from single-crystal structural data using Mercury software (developed by the Cambridge Centre for Crystallography, version 1.4.2). FTIR spectra were recorded on a Bruker VERTEX 70 FT-IR spectrometer (Germany). TGA was performed using a NETZSCH STA449F3 analyzer (Germany) with an Al₂O₃ fusion crucible. Measurements were conducted in the temperature range of 30–800 °C, with a heating rate of 10 K/min. EA for C, H, and N was performed using an Elementar Vario EL III instrument (Elementar, Germany). The (SEM, ZEISS-300) was operated at 3.0 kV. XPS and UPS data were obtained using a Thermo Fisher Scientific ESCALAB 250 Xi XPS system. UV–vis–NIR diffuse reflectance spectra were acquired using a PerkinElmer Lambda 950 spectrophotometer. Barium sulfate powder was used as a nonadsorptive background. DRIFTS was employed. The test on a 6700 FTIR spectrometer (Nicolette) equipped with a stainless-steel in situ IR flow cell. All spectra were obtained by scanning in the range of 2000–650 cm^{−1} with a resolution of 4 cm^{−1}. The conductivity (σ) is determined by fitting the linear region of the current–voltage curve to Ohm's Law. The powder sample is pressed into a 2.5 mm-diameter sheet, and silver paste and silver wires are connected between the two electrodes. The test is conducted using Keithley 4200-SCS in a dark environment, and temperature changes are controlled through a gas sensing test platform.

Gas Sensors Fabrication and Measurement

10 mg of the sample was ground and dispersed in C₃H₇OH solution. 10 μ L of the prepared sample suspension was directly applied onto the interdigitated electrode via drop coating. The resulting electrode was dried under vacuum at 65 °C for 8 h before sensor testing. The sensor characterization was performed using a homemade system reported in a previous study. A constant gas flow rate of 600 mL/min was maintained, and the current data were recorded using a Keithley source meter. The target gas was mixed with dry air at a specific ratio using a mass flow controller to generate a gas of precise concentration, which was then injected into a quartz tube. The nitrogen dioxide gas used in the tests was a mixture of 100 ppm dry nitrogen dioxide gas and dry air. All tests were conducted at room temperature.

Responsivity (*R*): evaluates the effect of NO₂ on the response ($\Delta I/I_0$, where I_0 is the current in air and ΔI represents the change in current in the circuit after exposure to the analyte gas). The CV was estimated as $R_{SD}/R_{avg} \times 100\%$, where R_{SD} and R_{avg} are the standard deviation (SD) and average of the response, respectively. The response and recovery times were defined as the time required to reach 90% of the total resistance change. The calculation method of LOD is based on the log–log fitting curve of the response and concentration, using the concentration corresponding to the response value of 10%.

DFT Calculations

DFT calculations were performed to investigate the interaction between NO₂ molecules and CuX-CuMND. With the exception of Bader charges, all other calculations were performed using the CASTEP and DMol3 modules in Materials Studio 2020 (Materials

Studio 20.1, BIOVIA, San Diego, CA, USA). Exchange–correlation interactions were modeled using the generalized gradient approximation with the Pedev-Burke-Enzshof functional. Atomic positions were optimized using the conjugate gradient method (cutoff energy 400 eV) until the force on all atoms was less than 0.05 eV/Å. Atomic positions and lattice constants were optimized using the same cutoff energy and tolerance; in all calculations, reciprocal space was sampled only at the Γ point. Bader charge analysis was performed on the charge density from VASP calculations to investigate charge transfer in the system.

■ ASSOCIATED CONTENT

Data Availability Statement

Data supporting the findings of this study are available upon reasonable request by contacting the corresponding author.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.6c02751>.

Experimental details, crystal data, and additional gas sensing information for CuBr-CuMND and CuI-CuMND (PDF)

Accession Codes

Accession Codes Deposition Numbers 2554019 and 2554020 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

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■ ACKNOWLEDGMENTS

This work was financially supported by the Strategic Priority Research Program of the Chinese Academy of Sciences, Grant No. (XDB1170000), National Natural Science Foundation of China (22271281, 22422508, 22325109, 62227815, 22494633, 22505265), Self-deployment Project Research Program of Haixi Institutes, Chinese Academy of Sciences (CXZX-2023-GS03), the Key Research Project of Chinese Academy of Sciences under Grant (KGFZD-145-25-21).

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