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Functional group engineering in metalloporphyrin-based covalent organic frameworks for enhancing sensing performance

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Covalent organic frameworks (COFs) face intrinsic limitations in chemiresistive gas sensing due to low carrier concentration and poor charge mobility. In this work, we report a functional group engineering strategy to enhance the performance of porphyrin-based Cu-COF-366 by modulating donor–acceptor (D–A) interactions. By introducing electron-donating/withdrawing groups into the building units, the separation efficiency of photogenerated electron–hole pairs is significantly improved, leading to increased free carrier density and reactive oxygen species generation under visible-light irradiation. The optimized Cu-COF-366-OCH_3 exhibits an ammonia response of 825.9%, representing a 25.9-fold improvement over Cu-COF-366-H. The response of Cu-COF-366-OCH_3 toward NH_3 is at a moderate level among all reported MOF/COF-based sensors. This breakthrough stems from the synergistic effects of methoxy-induced electron enrichment, which improves charge mobility and increases the number of reactive oxygen species as sensing active sites. The material also demonstrates excellent selectivity, repeatability, and long-term stability. This work establishes a mediator-free molecular design paradigm for COF-based sensors, advancing high-performance gas detection technologies.

Introduction

Covalent organic frameworks (COFs), a class of porous crystalline materials constructed from light-weight elements through strong covalent bonds, have attracted broad research interest for various applications like gas storage/separation, catalysis, drug delivery and sensing, *etc.*[1–3] With highly designable molecular structures and well-ordered nanopore systems, COF materials have emerged as promising candidates for next-generation gas sensing.[4,5] Their core advantage lies in enabling precise "customization" of physical and chemical properties at the molecular level through strategic selection and combination of building units.[6–10] Nevertheless, the persistent challenges hindering the application of COFs in chemiresistive gas sensing are their inherently low carrier concentration and poor charge mobility.[11,12] These two fundamental limitations collectively impede the conversion of electronic disturbances caused by gas adsorption into measurable electrical signals.[13] Although conventional strategies attempt to overcome these drawbacks by incorporating conductive additives such as carbon nanotubes or graphene,[14,15] these approaches often obscure the intrinsic functionalities of COFs and compromise access to active sites. Therefore, there is an urgent demand for mediator-free molecular engineering strategies that directly enhance charge separation efficiency and facilitate carrier transport within the COF. Achieving this would represent a pivotal scientific advancement toward unlocking the potential of COFs for high-sensitivity gas sensing applications.

Addressing this need, recent advances have highlighted donor–acceptor (D–A) architectures in COF materials as a promising solution.[16–18] While D–A systems have effectively improved photogenerated carrier separation *via* intramolecular charge transfer in COF-based photocatalysis,[19,20] their potential remains underexplored in gas-sensing applications. Existing research has largely focused on the design of monomers for polymerization,[21,22] overlooking fine-scale control of charge transfer at the functional group level. By strategically introducing or modifying electron-donating/withdrawing groups (*e.g.*, halogen and methoxy) on building units, the local electron density can be tuned without disrupting the topology of the framework.[23] This "functional group engineering"

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strengthens intramolecular charge transfer between donors and acceptors, thereby promoting electron–hole separation under light irradiation.[24] This results in an increase in the concentration of free carriers that facilitates their transfer to adsorbed oxygen molecules, generating abundant reactive oxygen species.[25] These reactive oxygen species act as efficient electronic mediators, amplifying weak gas interactions into significant conductance changes through redox reactions, thus significantly boosting the sensitivity of COF-based gas sensing.[26]

Herein, we successfully engineered a series of porphyrin-based Cu-COF-366-X materials (X = H, Cl, and OCH_3) through rational functional group modification. This strategy effectively tuned the D–A interaction, improving the separation efficiency of electron–hole pairs under light irradiation, which enhanced charge transfer and the quantity of reactive oxygen species in COF pores. Consequently, the chemiresistive NH_3 sensing performance was significantly boosted. Notably, Cu-COF-366-OCH_3 exhibited an exceptional response of 825.9%, representing a 25.9-fold improvement over Cu-COF-366. This improved performance stems from the strong electron-donating ability of the methoxy group, which enriches free charge carriers and generates numerous reactive oxygen species to improve gas-sensing performance. This work demonstrates the efficacy of functional group engineering in enhancing COF-based sensors and provides a new pathway for designing highly efficient gas sensors.

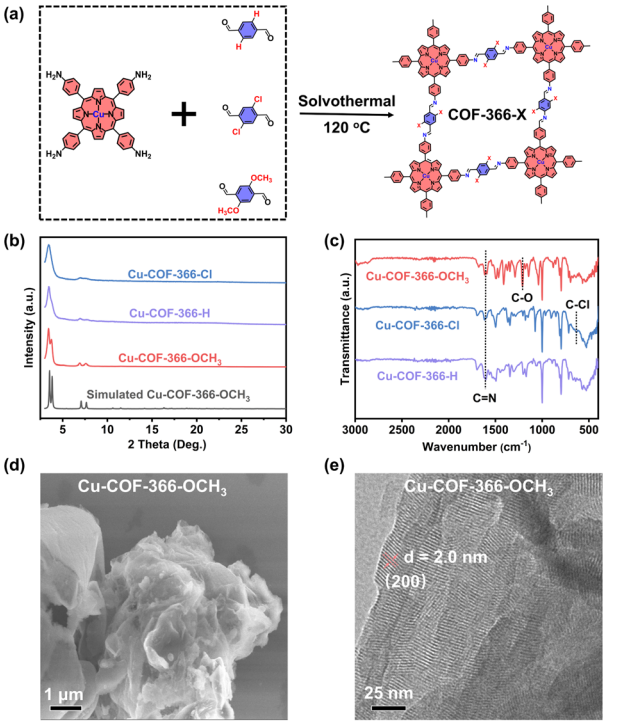

Fig. 1 Structural and morphological characterization of Cu-COF-366-X (X = H, Cl, and OCH_3). (a) Schematic representation of the synthesis procedure and structure. (b) Experimental and simulated PXRD patterns. (c) FT-IR spectra. (d) SEM image and (e) TEM image of Cu-COF-366-OCH_3.

Results and discussion

Copper porphyrin-based covalent organic framework (Cu-COF-366) was prepared through an optimized acetic acid-catalyzed solvothermal condensation reaction between 5,10,15,20-tetrakis(4-aminophenyl)-porphyrin copper (Cu-TAPP) and terephthalaldehyde (TPA) in a mixed solvent system (for details, see the Method section from supporting information).[27] By systematically tuning the species and quantities of Cu-COF-366 precursors, this synthetic approach was successfully extended to produce a series of functionalized COF derivatives denoted as Cu-COF-366-X (where X = H, Cl, OCH_3). In the crystal structure of Cu-COF-366, each Cu-TAPP molecule is covalently linked to four TPA molecules, while each functionalized TPA molecule is connected to two TAPP molecules, forming two-dimensional (2D) π-conjugated macromolecular layers within the *ab* plane (Fig. 1a and S1).

Powder X-ray diffraction (PXRD) patterns confirmed that the phase structures of all Cu-COF-366-X variants (X = H, Cl, and OCH_3) align closely with their respective simulated patterns (Fig. 1b and S2). Fourier transform infrared (FT-IR) spectra revealed a characteristic C=N stretching vibration at 1622 cm^{-1}, verifying imine bond formation in all materials (Fig. 1c). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were applied to investigate the morphology of these samples. Cu-COF-366-X (X = H, Cl, and OCH_3) exhibited large and irregular particle morphologies in SEM images, while a lattice spacing of 2.0 nm observed in the high-resolution TEM (HR-TEM) image was assigned to the (200) crystal plane of Cu-COF-366-OCH_3 (Fig. 1d, e and S3).[27] In the solid-state ^{13}C NMR spectrum of Cu-COF-366-OCH_3 (Fig. S4), the signal around 60 ppm was attributed to the carbon atom of the $-OCH_3$ group; the signals at 116 ppm and 136 ppm were assigned to the carbon atoms on the benzene and porphyrin rings; and the signal at 160 ppm was attributed to the carbon atom of the C=N imine bond. The presence of these characteristic peaks, particularly the imine carbon signal, unequivocally demonstrated the successful formation of imine bonds, thereby further confirming the successful construction of the target structure. These results collectively demonstrate that Cu-COF-366-X (X = H, Cl, and OCH_3) were successfully synthesized.

To evaluate the chemical composition and elemental states of the series of Cu-COF-366 with different functional groups, X-ray photoelectron spectroscopy (XPS) measurements were conducted. The full XPS spectra of Cu-COF-366-X (X = H, Cl, and OCH_3) clearly reveal that no additional elements are present in any sample, indicating their high chemical purity (Fig. S5). High-resolution XPS spectra show that the binding energies at 934.36 eV and 954.20 eV correspond to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively, indicating that Cu remains predominantly in its divalent state within Cu-COF-366-OCH_3 (Fig. S6).[27] In addition, N_2 adsorption–desorption measurements were performed at 77 K on the Cu-COF-366-X (X = H, Cl,

OCH_3) series materials to investigate their porosity. Among them, the Cu-COF-366-OCH_3 with the best specific surface area (S_{BET}) was determined to be 748.6 m^2 g^{-1}, revealing the highly porous nature of this material (Fig. 2a and S7). Such porous characteristics facilitate efficient molecular enrichment and localized concentration of analytes, positioning these materials as promising candidates for gas-sensing applications.[28–30]

Solid-state UV/Vis absorption spectra revealed that Cu-COF-366 with different functional groups exhibited broad visible-light absorption ranges, suggesting potential for enhanced performance in light-driven applications (Fig. 2b). Under visible-light irradiation, the series of Cu-COF-366 exhibited significant photoconductivity responses, driven by donor–acceptor (D–A) interactions (Fig. S8). Among these materials, Cu-COF-366-OCH_3 displayed the most pronounced photoconductivity behaviour, owing to strengthened D–A interaction achieved through rational functional group engineering (Fig. 2c). To prove it, the density functional theory (DFT) calculations were conducted to assess the Hirshfeld charge transfer dynamics in Cu-COF-366-X (X = H, Cl, and OCH_3). The calculation results are as follows: for Cu-COF-366-Cl, the charge on the copper porphyrin framework unit was −0.399*e*, while that on the aldehyde monomer bearing the chlorine substituent was +0.403*e*. For Cu-COF-366-H, the charge on the copper porphyrin framework unit was −0.470*e*, and that on the aldehyde monomer was +0.476*e*. For Cu-COF-366-OCH_3, the charge on the copper porphyrin framework unit was −0.576*e*, and that on the aldehyde monomer bearing the methoxy substituent was +0.580*e*. According to the physical definition of Hirshfeld charge analysis, a negative value indicates electron gain (*i.e.*, acting as an electron acceptor), while a positive value indicates electron loss (*i.e.*, acting as an electron donor). The above data indicate that as the functional group systematically varies from the electron-withdrawing chlorine group (–Cl) to neutral hydrogen (–H) and then to the electron-donating methoxy group (–OCH_3), the electron-donating ability of the donor unit exhibits a progressively increasing trend (Fig. 2d–f).[31] Notably, as the functional groups were systematically tuned from Cl to H and then to OCH_3, the electron-donating ability of the donor unit progressively increased, leading to a marked enhancement in the D–A interaction. This enhanced D–A interaction promotes efficient electron transfer and results in superior separation of photogenerated electron–hole pairs. By modulating the D–A interaction *via* functional group engineering, the carrier separation efficiency in Cu-COF-366-OCH_3 was significantly improved, thereby directly facilitating charge transport in materials without reliance on mediating molecules.

To achieve high-performance applications, the stability of materials is crucial.[32–35] It is worth highlighting that Cu-COF-366-X exhibits high chemical and thermal stability. To assess its chemical stability, the sample underwent immersion in various solvents for three days, followed by PXRD analysis. Taking Cu-COF-366-OCH_3, for example, the structural integrity of Cu-COF-366-OCH_3 remains unchanged after immersion in common organic solvents (such as benzene, acetone, and

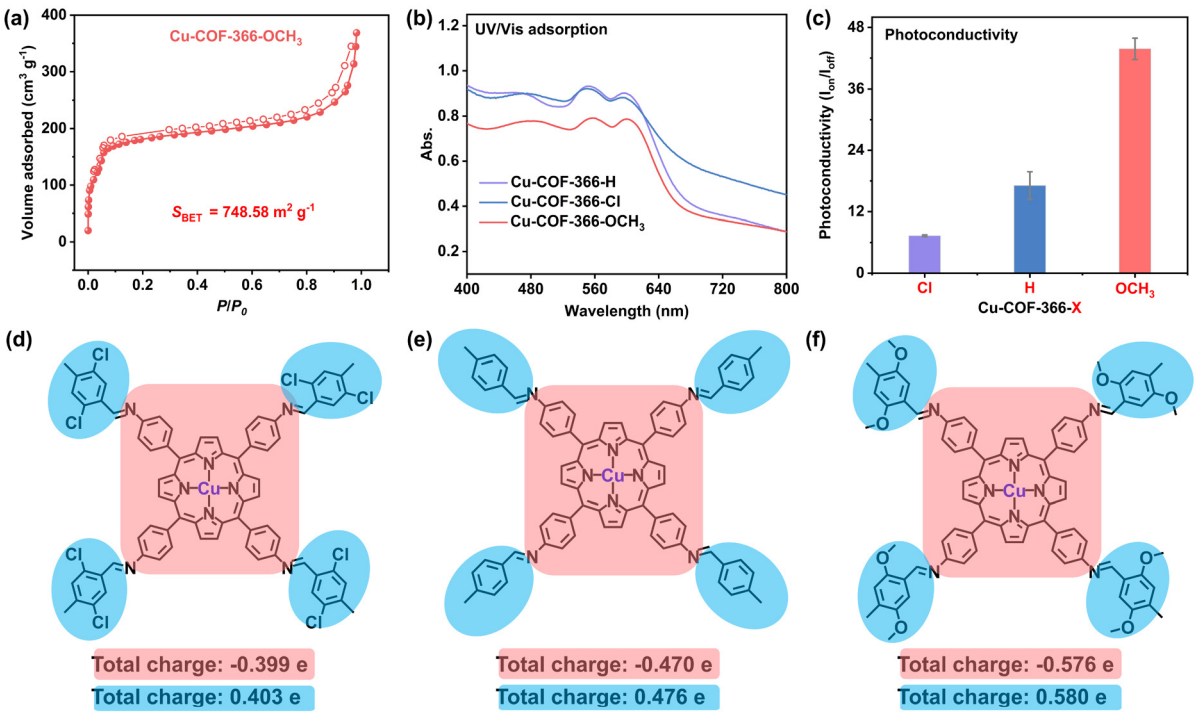

Fig. 2 Characterization and theoretical calculations of Cu-COF-366-X (X = H, Cl, and OCH_3). (a) N_2 adsorption test of Cu-COF-366-OCH_3. (b) Solid-state UV/Vis absorption spectra and (c) photoconductivity of Cu-COF-366-X (X = H, Cl, and OCH_3). Hirshfeld charge analysis of Cu-COF-366-Cl (d), Cu-COF-366-H (e), and Cu-COF-366-OCH_3 (f).

methanol) compared with the as-synthesized one (Fig. S9a). Regarding thermal stability, thermogravimetric analyses (TGA) confirmed that all Cu-COF-366-X (X = H, Cl, and OCH_3) samples maintained their inherent structure up to 200 °C under a nitrogen atmosphere (Fig. S9b).

Cu-COF-366-X (X = H, Cl, and OCH_3), in which the separation efficiency of photogenerated electron–hole pairs is precisely regulated through rational functional group design, exhibits high chemical and thermal stability, as well as excellent photoelectric performance. With this in mind, these materials were applied in chemiresistive gas sensing using a home-made system.[36] Under visible-light and room temperature conditions, all Cu-COF-366-X (X = H, Cl, and OCH_3) samples exhibited a negative response to 100 ppm NH_3, consistent with the characteristic of p-type semiconductors (Fig. 3a and S10–12).[37] With the increase of the electron-donating ability of the functional group, the response of Cu-COF-366 to NH_3 gradually increases (Fig. 3b). Among them, the separation efficiency of photogenerated electron–hole pairs in the OCH_3 is the strongest, demonstrating the optimal NH_3 sensing performance, reaching 825.9%, which is 25.9 times higher than that of Cu-COF-366-H (Fig. 3b). The response of Cu-COF-366-OCH_3 toward NH_3 is at a moderate level among all reported MOF/COF-based sensors (Table S1).[38–43]

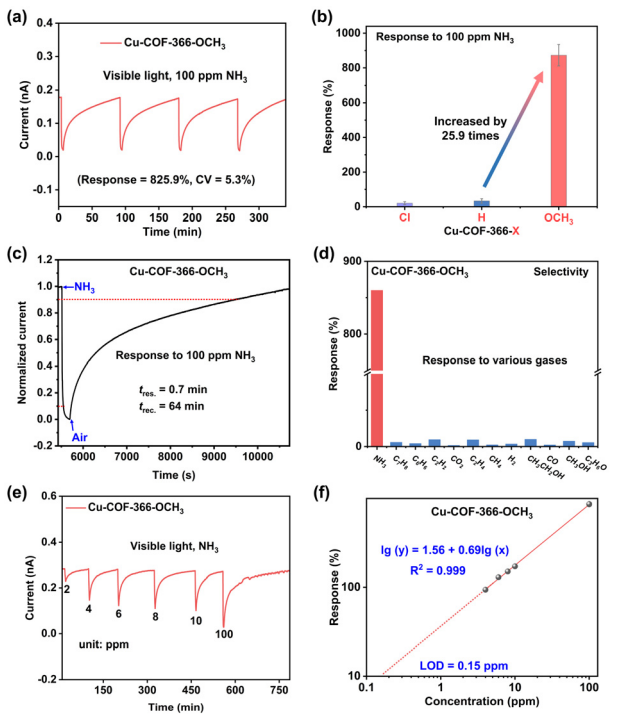

Fig. 3 Gas sensing performance of the devices at room temperature. (a) Recycle sensing of Cu-COF-366-OCH_3 towards 100 ppm NH_3. (b) Column chart of responses toward 100 ppm NH_3 of Cu-COF-366-X (X = Cl, H, and OCH_3). (c) Response–recovery time curves for 100 ppm NH_3. (d) Sensing response to various gases (100 ppm). (e) Response–recovery curves toward NH_3 at different concentrations. (f) Response–concentration log–log plots for Cu-COF-366-OCH_3.

Cu-COF-366-OCH_3 exhibited four cyclic responses to 100 ppm NH_3 with a low coefficient of variation (CV = 5.3%), demonstrating its excellent repeatability (Fig. 3a). The response and recovery times of the material were estimated to be 0.7 minutes and 64 minutes, respectively. The prolonged recovery time is mainly attributable to the strong coordination interaction between NH_3 molecules and the Cu active sites in the material, which undergo a relatively slow natural desorption process under dry air purging. To prove the promoting effect of light on the recovery of sensing capabilities, we systematically evaluated the effect of different light intensities on the recovery characteristics of the material. The results indicate that at a light intensity of 20 A, the material achieves a reasonably satisfactory recovery time while maintaining a relatively high response value (Fig. 3c and S13). Cu-COF-366-OCH_3 also demonstrated excellent selectivity for NH_3 over 11 commonly existing interfering gases (Fig. 3d). In addition, Cu-COF-366-OCH_3 displayed a concentration-dependent response to NH_3 within the range of 1 to 100 ppm (Fig. 3e), and the theoretical limit of detection (LOD) was calculated to be approximately 0.15 ppm based on the linear equation by setting the response at 10% (Fig. 3f). After 30 days, the material retained about 90% of its initial response to 100 ppm NH_3, indicating outstanding long-term stability (Fig. 4a). The structural integrity of Cu-COF-366-OCH_3 remained intact after prolonged gas stability experiments, which was confirmed by PXRD analysis (Fig. 4b).

To reveal the sensing mechanism, the NH_3 sensing performance of COF-366-OCH_3 and Cu-TAPP was determined for comparison under conditions similar to those used for Cu-COF-366-X (X = H, Cl, and OCH_3). The results demonstrated that the response of Cu-COF-366-OCH_3 was 49.5 times higher than that of COF-366-OCH_3, highlighting the significance of Cu active sites in enhancing performance (Fig. S14). To further

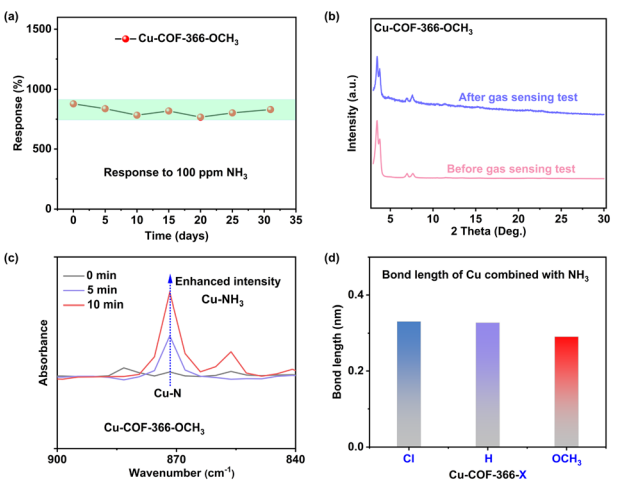

Fig. 4 Sensing performance stability and mechanism. (a) Long-term stability of Cu-COF-366-OCH_3 (b) PXRD patterns of Cu-COF-366-OCH_3 before and after the sensing test. (c) Time-resolved DRIFTS spectra of Cu-COF-366-OCH_3 under NH_3 mixed air. (d) High-resolution O 1s XPS of Cu-COF-366-OCH_3 without and under light irradiation.

confirm Cu as the functional motif for gas sensing, time-resolved *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was conducted on Cu-COF-366-OCH_3 exposed to NH_3 mixed air. As the exposure time increased, a gradual intensification of the Cu–N bond peak was observed, strongly indicating the adsorption of NH_3 onto Cu sites (Fig. 4c).[44] Additionally, compared with Cu-TAPP, Cu-COF-366-OCH_3 exhibited significant advantages, underscoring the critical role of porous structural features in improving gas sensing performance (Fig. S15).

By leveraging the electronic induction effects of various functional groups, we effectively modulated the separation efficiency of photogenerated electron–hole pairs in Cu-COF-366, thereby enhancing its performance. Further analysis *via in situ* XPS measurements revealed the underlying mechanism. Under light irradiation, Cu-COF-366-OCH_3 exhibited an O 1s peak that could be attributed to adsorbed oxygen, which was absent under dark conditions (Fig. 4d). This observation indicates that the material generated a large amount of adsorbed oxygen under light exposure. The quantity of such adsorbed oxygen directly influences the sensitivity of the sensing response. As the functional group was varied from Cl to H and then to OCH_3, the number of photogenerated charge carriers increased, resulting in a higher concentration of adsorbed oxygen and a marked improvement in gas-sensing performance. Through fine-tuning the separation efficiency of photogenerated electron–hole pairs by functional group manipulation, Cu-COF-366-OCH_3 achieved optimal NH_3 sensing properties.

Based on the above discussion, a possible sensing mechanism of Cu-COF-366-OCH_3 can be described as follows (Fig. S16). Firstly, the inductive effect of functional groups promotes the accumulation of a large number of photogenerated electrons in the COF material under visible-light irradiation. A large number of photogenerated free carriers are transferred to the adsorbed oxygen, generating numerous reactive oxygen species, which significantly improves the reactivity of the COF material. Secondly, the material exhibits p-type semiconductor characteristics, with its conductivity primarily determined by the concentration of hole carriers. As an electron-donating gas, NH_3 injects electrons into the material upon adsorption onto its surface, thereby reducing the number of holes. As shown in Fig. 3c, the current decreases significantly upon exposure to NH_3, which directly reflects a reduction in conductivity. Finally, NH_3 molecules desorb from the surface of the material, the previously transferred electrons are released, and the electrical conductivity of the material is restored.

Conclusions

This work successfully demonstrates that rational functional group engineering represents a powerful mediator-free strategy to overcome the intrinsic limitations of COFs in chemiresistive gas sensing. By systematically introducing electron-donating or withdrawing substituents into porphyrin-based Cu-COF-366 building units, we precisely tuned donor–acceptor (D–A) interactions to achieve unprecedented photogenerated charge separation efficiency. As a result, Cu-COF-366-OCH_3 exhibited a response of 825.9% at room temperature and under visible-light conditions. The response of Cu-COF-366-OCH_3 toward NH_3 is at a moderate level among all reported MOF/COF-based sensors. The established molecular design paradigm directly links electronic modulation at the functional group level to sensing efficacy, revealing three fundamental mechanisms: (1) D–A interaction optimization for photogenerated carrier separation, (2) light-driven reactive oxygen species production, and (3) metal coordination-mediated analyte recognition. This work demonstrates how enhanced charge transfer in metalloporphyrin-based COFs without mediator molecules can break sensitivity bottlenecks, offering a universal approach for designing high-performance gas sensors.

Author contributions

Y.-J. C. and G. X. conceived the idea. J.-L. J. and T.-H. W. designed the experiments and collected and analysed the data. Y.-M. X. carried out the theoretical calculations. J.-F. L. and G.-E. W. assisted with the experiments and characterization. J.-L. J. and Y.-J. C. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Supplementary information (SI): synthesis, IR, SEM, and sensing property tests. See DOI: https://doi.org/10.1039/d6nr00531d.

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