

## Supporting Information

# Two-dimensional bimetallic phthalocyanine covalent organic framework-based chemiresistive gas sensor for ppb-level NO<sub>2</sub> detection

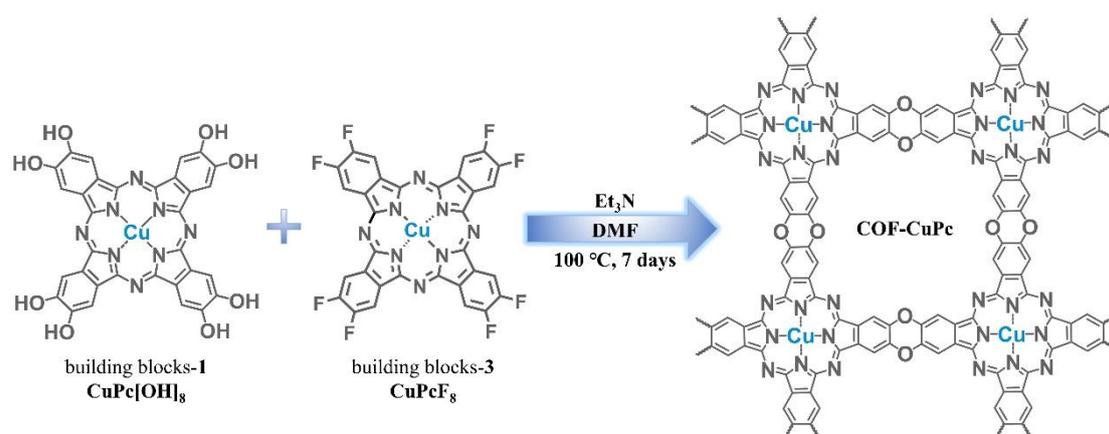


Figure S1. Synthetic route and representative structure of COF-CuPc.

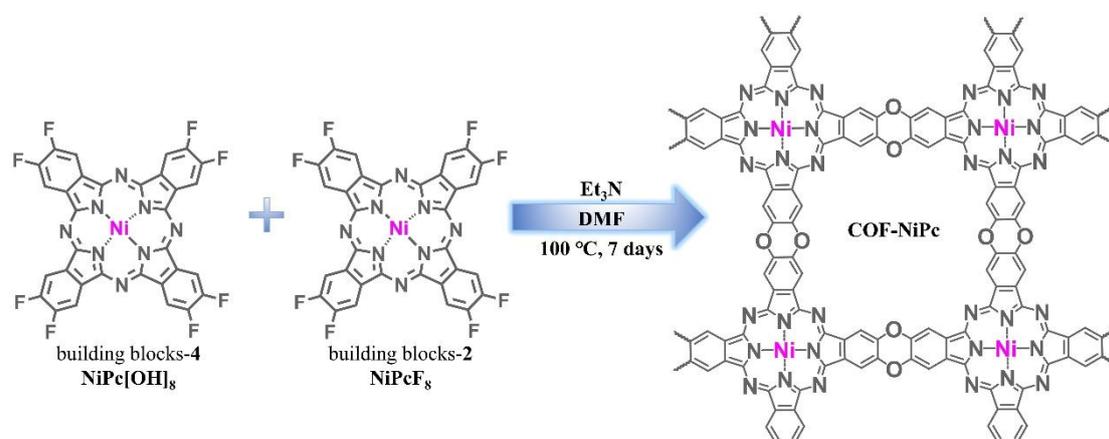


Figure S2. Synthetic route and representative structure of COF-NiPc.

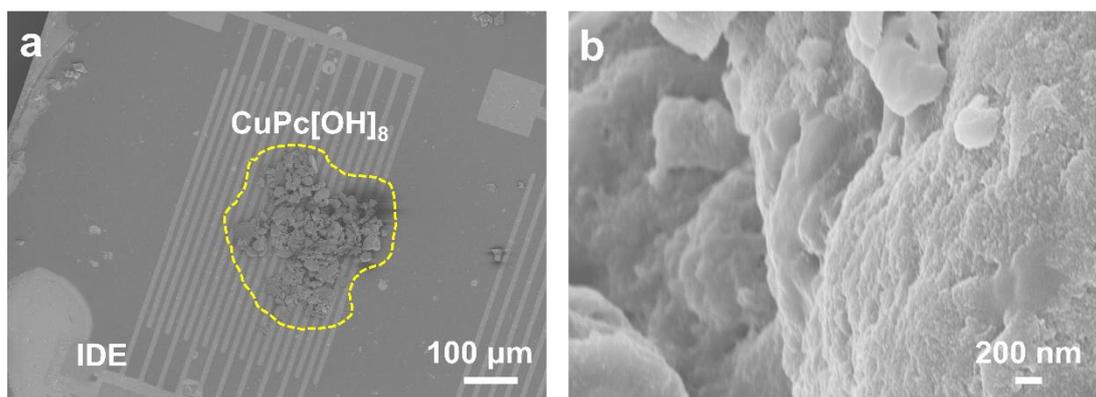


Figure S3. SEM images of CuPc[OH]<sub>8</sub> with a scale bar of (a) 100 μm and (b) 200 nm on IDEs substrate.

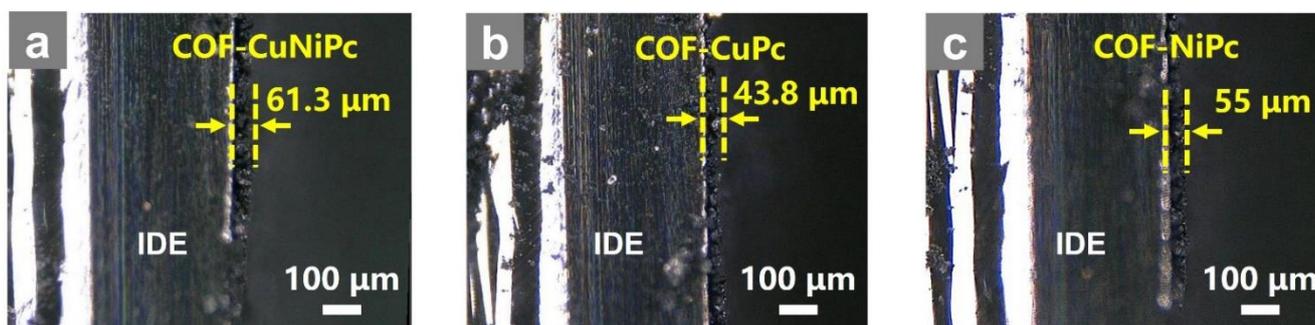


Figure S4. Optical images of the cross-sectional view of the IDE-sensors based on (a) COF-CuNiPc, (b) COF-CuPc, and (c) COF-NiPc.

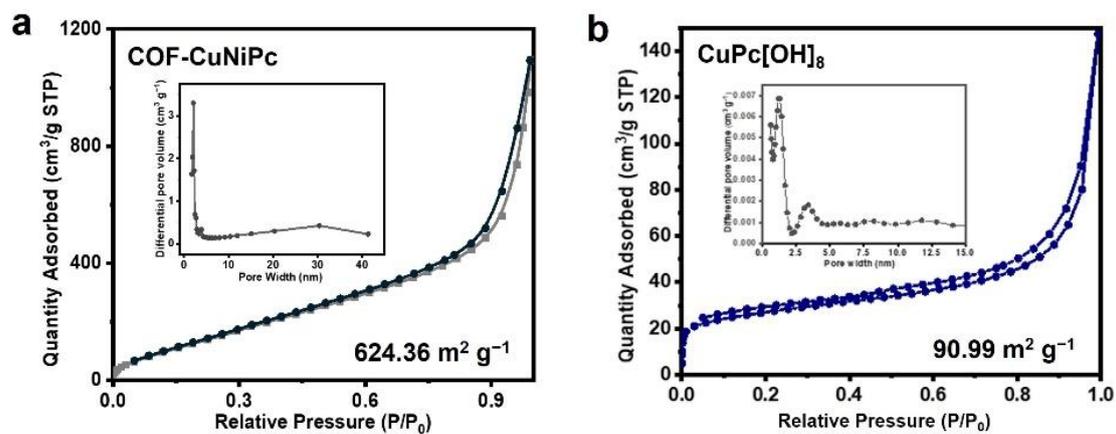


Figure S5. BET Nitrogen sorption isotherm curves and pore size distribution of (a) COF-CuNiPc and (b) CuPc[OH]<sub>8</sub>.

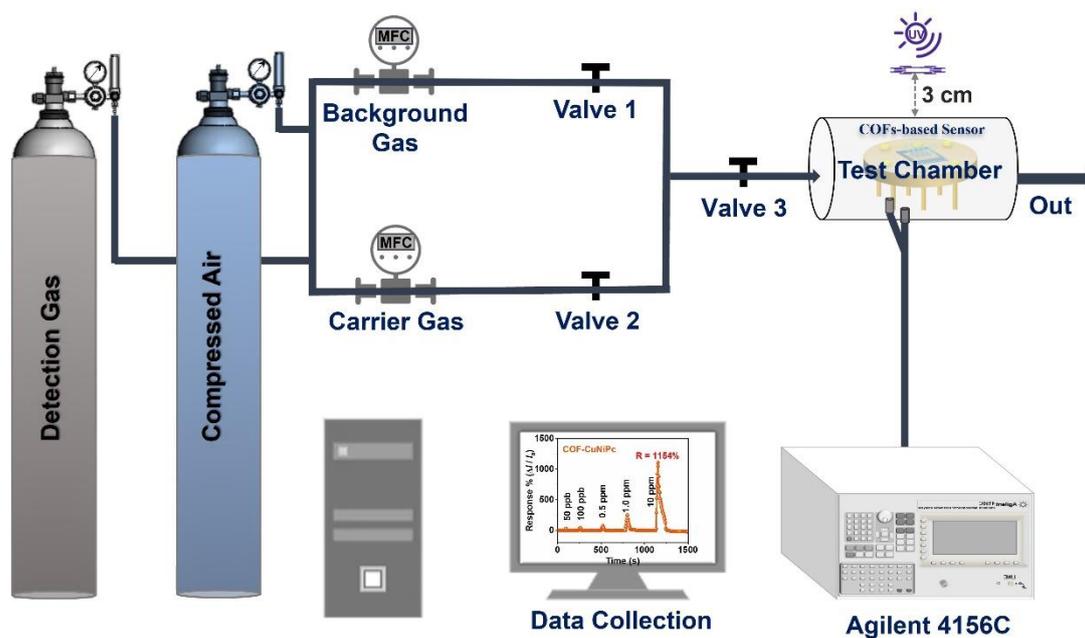


Figure S6. Schematic diagram of the NO<sub>2</sub> sensor test system.

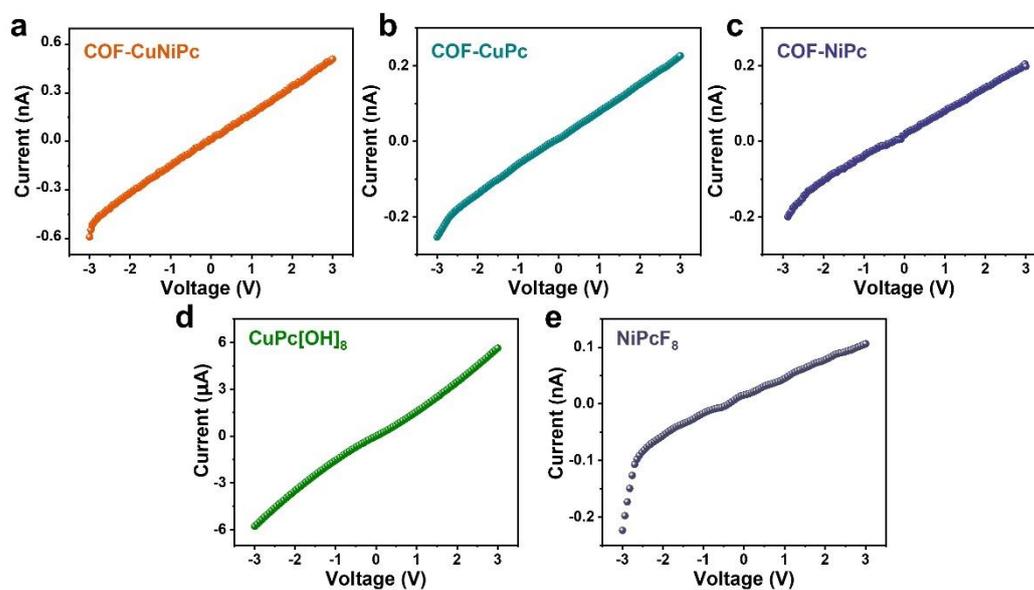
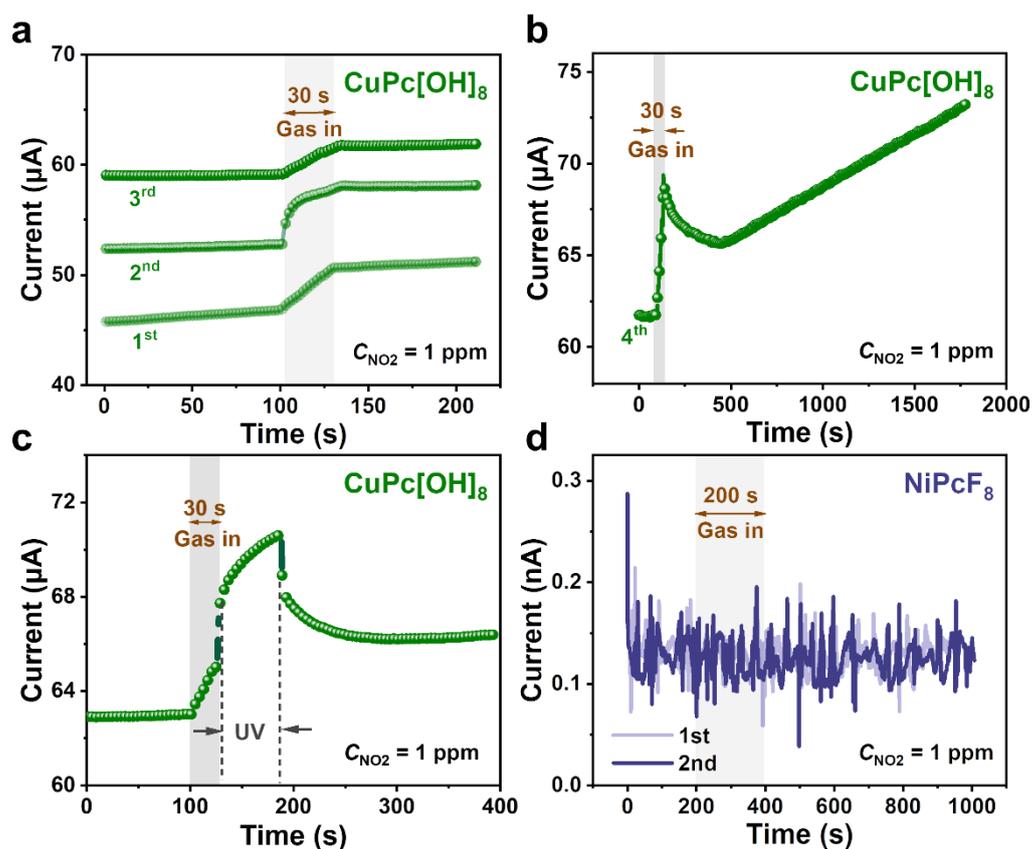
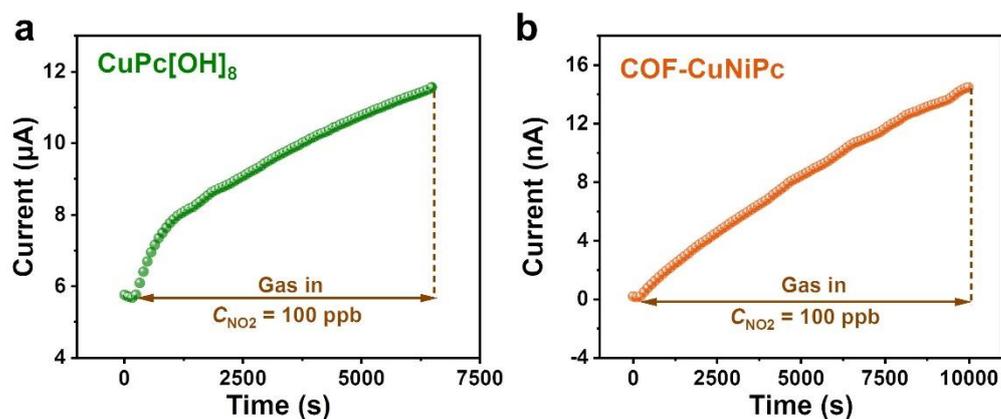


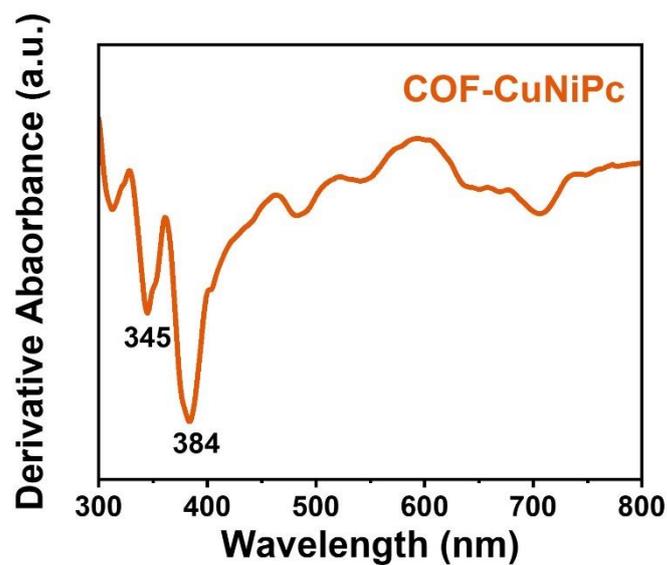
Figure S7. *I-V* curves of the (a) COF-CuNiPc, (b) COF-CuPc, (c) COF-NiPc, (d) CuPc[OH]<sub>8</sub>, and (e) NiPcF<sub>8</sub>-based chemiresistive device under  $\pm 3$  V bias in a dry compressed air atmosphere at RT.



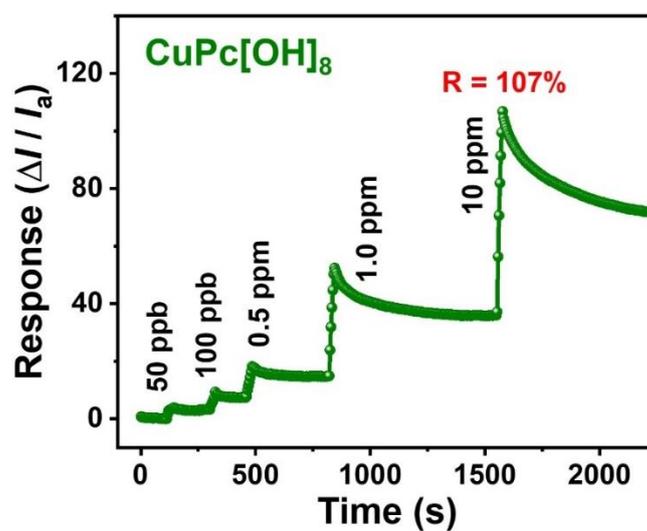
**Figure S8.** (a) The 1<sup>st</sup>, 2<sup>nd</sup>, and 3<sup>rd</sup>, (b) 4<sup>th</sup>, and (c) UV-light-assisted dynamic response characteristic curves of CuPc[OH]<sub>8</sub> (building block-1)-based chemiresistive device exposed to 1 ppm NO<sub>2</sub> for 30 s at RT. (d) Dynamic response characteristic curves of NiPcF<sub>8</sub> (building block-2)-based device.



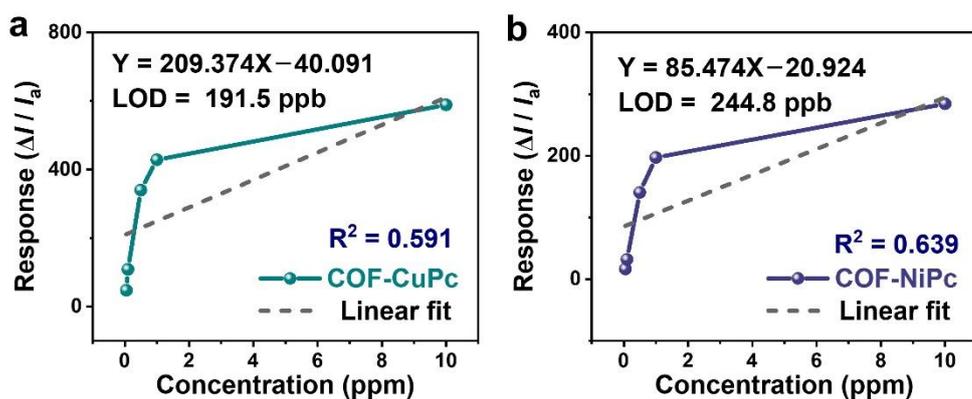
**Figure S9.** (a) Dynamic response characteristic curves of CuPc[OH]<sub>8</sub>-based device, and (b) COF-CuNiPc-based chemiresistive device exposed to 100 ppb NO<sub>2</sub> for a long time (>6000 s) at RT.



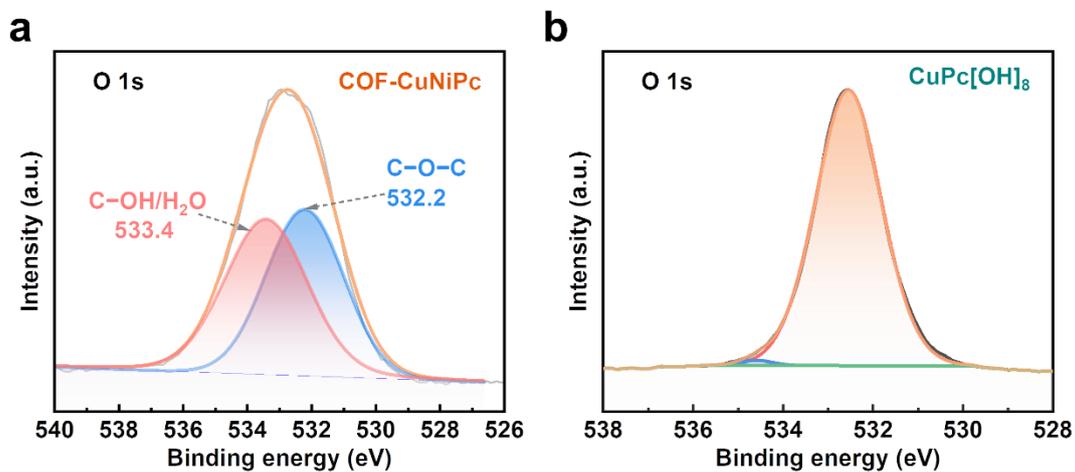
**Figure S10.** The absorption peak positions of COF-CuNiPc were differentiated once with the assistance of the absorption spectrum of UV-Vis DRS.



**Figure S11.** Dynamic current characteristic curve of CuPc[OH]<sub>8</sub>-based sensor exposed to different concentrations of NO<sub>2</sub> (0.05, 0.1, 0.5, 1.0, and 10 ppm) with UV-assisted recovery.



**Figure S12.** The linear fit curve of response versus the concentration absorption for the gas sensors based on (a) COF-CuPc and (b) COF-NiPc.



**Figure S13.** High-resolution O 1s core-level XPS spectra of (a) COF-CuNiPc and (b) CuPc[OH]<sub>8</sub>.