## **Electronic Supplementary Information for**

# An Ultrafast Responsive NO2 Gas Sensor Based on a Hydrogen-

## **Bonded Organic Framework Material**

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#### General synthesis methods

Key reagents including propionic acid, DMF, methanol, 2-methoxyethanol used as received from the Chemical Corporation. All reactions were carried out under an N<sub>2</sub> atmosphere.

#### Synthesis of 5,10,15,20-tetrakistetra(4-cyanophenyl) porphyrin<sup>1</sup>

Pyrrole (3.52 mL, 50 mmol) and 4-Cyanobenzaldehyde (5.0 g, 7 mmol) in 200 mL propionic acid were heated under refluxing for 1 h. The reaction mixture was cooled down to room temperature and poured into 500 mL of MeOH and stirred for 30 min in an ice bath. The resulting precipitate was filtered off and washed several times with MeOH until the filtrate was clear. Subsequently, the product was washed with 100 mL warm distilled water and dried at 70 °C in a drying oven over night. The residue was purified by silica gel column chromatography with  $CH_2Cl_2$ . 5,10,15,20-tetrakistetra(4-cyanophenyl) porphyrin, <sup>1</sup>H-NMR: (500 MHz

CDCl<sub>3</sub>):  $\delta$ = 8.73 (s, 8H, H-1); 8.27 (d, 8H, H-2);8.04 (d, 8H, H-3); 7.18 (s, 1H, CDCl<sub>3</sub>); MALDI-TOF mass spectrum: calcd for C<sub>48</sub>H<sub>26</sub>N<sub>8</sub>,714.2; found, 714.1.



Synthesis of 5,10,15,20-tetrakis(4-(2,4-diaminotriazine) phenyl) porphyrin<sup>2</sup>

A mixture of 5,10,15,20-tetrakistetra(4-cyanophenyl) porphyrin (586 mg, 0.82 mmol), dicyandiamide (345 mg, 4.1 mmol) and KOH (300 mg, 5.3 mmol) in dry 2-methoxyethanol (20 mL) was heated under refluxing for two days. The resulting precipitate was filtered off and washed several times with MeOH until the filtrate was clear. Subsequently, the product was washed with 100 mL warm distilled water and dried at 70 °C in a drying oven over night. 5,10,15,20-tetrakis(4-(2,4-diaminotriazine)phenyl) porphyrin (H<sub>2</sub>TDPP), <sup>1</sup>H-NMR: (500 MHz DMSO-d6):  $\delta$ = 8.92 (s, 8H, H-1); 8.71 (d, 8H, H-2);8.35 (d, 8H, H-3); 6.89 (s, 16H, H-4), MALDI-TOF mass spectrum: calcd for C<sub>48</sub>H<sub>26</sub>N<sub>8</sub>, 1050.4; found, 1050.5.



### Preparation of UPC-H4 for single crystal x-ray diffraction analysis

 $H_2$ TDPP (3 mg, 0.0028mmol) was dissolved in 1 mL of DMF in a 10 mL uncapped vial, and the vial was put in a 100 mL silk mouth bottle containing 10 mL methanol. The purple rodshaped crystals of UPC-H4 suitable for single crystal x-ray diffraction analysis were grown by vapor diffusion for 3 days at 90°C. Purple needle crystals was obtained with a yield of 80%. Elemental analysis calcd (%) for UPC-H4 ( $C_{72}H_{86}N_{28}O_8$ ): C 58.76, H 5.89, N 26.65; found: C 58.69, H 5.97, N 26.64.

### Synthesis of UPC-H4a for single crystal x-ray diffraction analysis

UPC-H4a was obtained by standing UPC-H4 at room temperature in ambient environment

for more than 8 days. Elemental analysis calcd (%) for UPC-H4a (C<sub>68</sub>H<sub>74</sub>N<sub>28</sub>O<sub>6</sub>): C 59.20, H 5.41, N 28.43; found: C 59.22, H 5.37, N 28.45.

**Preparation of gas sensor.** The ITO substrate was cut into the size of  $1.2 \text{ cm} \times 0.4 \text{ cm}$  with a glass knife. The tablet was washed ultrasonically three times (10 min/time) in toluene, acetone, absolute ethanol and high purity water, respectively, then dried with N<sub>2</sub> and reserved. The suspension of precursor or UPC-H4a was obtained by dispersing ultrasonically 1 mg activated precursor or UPC-H4a crystal into 2 mL ehanol for 30 min. Subsequently, 5 µL of new-prepared suspension was coated drop to drop on the ITO electrode area (0.2 cm × 0.2 cm) of above-mentioned ITO/glass interdigitated electrodes, then stood to dry.

**X-ray Crystallography.** Single-crystal data of UPC-H4 and UPC-H4 awas measured by an Agilent Super Nova Dual diffractometer using Cu/ K $\alpha$  radiation ( $\lambda$  = 1.54178 Å) at 273 K and focusing multilayer mirror optics. The structures was solved by direct methods using SHELXTL and refined by full-matrix least squares on F2 using SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms attached to C atoms and amino N atoms were located in calculated positions according to isotropic displacement parameters, and hydrogen atoms attached to O atoms were located from the difference electron density maps and refined anisotropically. In order to obtain better crystal data, "SQUEEZE" command was used to remove the lattice ethanol and water molecules in UPC-H4. The crystallographic collection and refinement parameters are listed in Table S1. The crystallographic data was deposited in the Cambridge Crystallographic Data Center (CCDC 1885768 for UPC-H4, and CCDC 1885770 for UPC-H4a). These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk.

**Electrical and sensing measurements.** The fundamental electrical and sensing measurements were performed using a Keithley 6517 electrometer with an incorporated DC voltage supply,

always at room temperature in the range 22-25 °C. The electrometer is controlled by self-made software via the GP-IB board. Current–voltage (I–V) curves were registered in the -10 to 10 V voltage range with 1 V increments, starting and finishing at 0 V bias to avoid irreversible polarization effects. On the other hand, the NO<sub>2</sub>-sensing properties of samples have been examined by exposing the corresponding films to different concentrations of NO<sub>2</sub> and measuring the current changes of the films at a constantly polarized voltage of 5 V. All experiments have been conducted at three times to ensure reproducibility. Conductivity,  $\sigma$ , can be calculated by the following equation:

$$\mathbf{\sigma} = \frac{dI}{(2n-1)LhV}$$

where d is the interelectrode spacing, I is the current, n is the number of electrode digits, L is the overlapping length of the electrodes, and h is the electrode thickness as the film thickness exceeds that of the ITO electrodes in present case.

**Other measurements.** The <sup>1</sup>H-NMR spectra were recorded on a Bruker DRX 500 spectrometer. MALDI-TOF mass spectrometry was performed on a Bruker BIFLEX III ultrahigh resolution. The date of powder X-ray diffraction (PXRD) were recorded on an X-Pert PRO MPD diffractometer with Cu-Kα radiation ( $\lambda$ = 0.154178 nm). Thermal gravimetric analysis (TGA) was proceeded on a Mettler Toledo TGA instrument in the range of 40-900 °C with a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere (100 mL min<sup>-1</sup>). Elemental analysis was conducted on a PerkinElmer 240C elemental analyzer for C, H, and N determination. N<sub>2</sub> and CO<sub>2</sub> adsorption and desorption tests were performed on a Micromeritics ASAP 2020 surface area analyzer. Infrared (IR) spectra were obtained on a Nicolet 330 FTIR spectrometer. UV-vis spectra were performed with UV-vis spectrometer (Specord205, Analytik Jena). The data of luminescence spectra were measured on a Hitachi F7000 fluorescence spectrophotometer. X-ray photoelectron spectroscopy (XPS) was conducted on VG ESCALAB 220i-XL equipped with Al Kα X-ray source.

Crystal data	UPC-H4	UPC-H4a
System	monoclinic	monoclinic
Space group	$P2_{1}/c$	$P2_1/c$
MF	$C_{72}H_{86}N_{28}O_8$	$C_{68}H_{74}N_{28}O_6$
FW	1471.6	1379.5
a/Å	16.6866(6)	16.2396(6)
b/Å	6.5849(3)	6.5461(2)
c/Å	34.8753(18)	33.4443(11)
$lpha/^{\circ}$	90	90
$eta/^{\circ}$	94.826(4)	90.790(3)
γ/°	90	90
Volume/ Å <sup>3</sup>	3818.5(3)	3555.0(2)
Ζ	4	4
Density/g/cm <sup>3</sup>	1.043	1.289
$\mu/\text{mm}^{-1}$	0.561	0.722
<i>F</i> (000)	1256.0	1452.0
$R_1^{a}$ I>2 $\theta$	0.0825 °	0.0723
$R_{w2}^{b}$ I>2 $\theta$	0.2108	0.1787
$R_1^a$	0.1338	0.1054
$R_{ m w2}{}^{ m b}$	0.2433	0.2069
CCDC no.	1885768	1885770

Table S1. Crystallographic and Refinement Parameters for UPC-H4 and UPC-H4a

<sup>a</sup>  $R_1 = \Sigma |F_{o}|F_{c}|/\Sigma |F_{o}|$ , <sup>b</sup>  $R_{w2} = [\Sigma w (F_{o}^2 - F_{c}^2)^2 / \Sigma w (F_{o}^2)^2]^{1/2}$ , and <sup>c</sup> the high value of  $R_1$  is due to the organic molecules made of many light atoms (C and N atoms) and a lot of

disordered solvent molecule filled in the cavity.

Table S2. Hydrogen Bonded parameters in UPC-H4 and UPC-H4a<sup>a</sup>

UPC-H4	<b>D-H</b> …A	Distance of H…A(Å)	Distance of D…A(Å)	Angle of D- H…A(°)
	N6-H6A…N9 <sup>#3</sup>	2.10	2.952(4)	171
	N6-H6B…N8 <sup>#4</sup>	2.31	3.039(4)	143

N1-H1A…N10 <sup>#1</sup>	2.12	2.956(5)	166
$N7-H7B\cdots N3^{\#1}$	2.24	3.093(5)	171
N7-H7A…O2 <sup>#2</sup>	2.02	2.877(7)	178

UPC-H4a	<b>D-H</b> ····A	Distance of H…A(Å)	Distance of D…A(Å)	Angle of D- H…A(°)
	N5-H5A…N10 <sup>#9</sup>	2.06	2.909(4)	168
	N5-H5B…N8 <sup>#10</sup>	2.37	3.099(4)	143
	N6-H6B…N12 <sup>#11</sup>	2.27	3.114(4)	169
	N3-H3A…N11 <sup>#8</sup>	2.19	2.990(4)	155
	O1-H1WA…O2 <sup>#6</sup>	1.71(6)	2.714(11)	165(5)
	N3-H3B…O1#6	2.24	2.992(5)	146
	N6-H6A…O1W <sup>#6</sup>	2.16	2.979(6)	159

<sup>&</sup>lt;sup>a</sup> Symmetric code, #1: -x, -1-y, -z, #2: x, 1+y, z, #3: 1-x, 1/2+y, 1/2-z, #4: 1-x, -1/2+y, 1/2-z, #5: 1-x, -2-y, -z, #6: x-3/2, -y+3/2, z+1/2, #7: 1-x, 1-y, 1-z, #8: 1+x, 1+y, z, #9:1-x,-1/2+ y, 1/2-z, #10: 1-x, 1/2+y, 1/2-z, #11:-1+x,-1+y,z.



Figure S1. The TGA curves of UPC-H4 and UPC-H4a in the range of 25-900  $^{\circ}\text{C}$  under  $N_2$  atmosphere.



Figure S2. PXRD patterns of UPC-H4a after activation.



Figure S3. N<sub>2</sub> adsorption/desorption isotherm of UPC-H4a at 77 k.



Figure S4. H<sub>2</sub> adsorption/desorption isotherm of UPC-H4a.



Figure S5. CO<sub>2</sub> adsorption/desorption isotherms of UPC-H4a.



Figure S6. The BET surface area of UPC-H4a obtained from the CO<sub>2</sub> adsorption isotherm at 196 K. SBET =  $(1/(0.02384-0.00214))/22414 \times 6.023 \times 10^{23} \times 0.170 \times 10^{-18} = 210.5 \text{ m}^2\text{g}^{-1}.$ 



Figure S7. The configuration diagram of sensor device.



Figure S8. SEM images of thin film formed on the electrode for precursor (H<sub>2</sub>TDPP).



Figure S9. I-V curves measured for precursor and UPC-H4a.



Figure S10. UV-vis spectra of precursor and UPC-H4a in solid.



Figure S11. The fluorescence spectra of precursor and UPC-H4a in solid. The excited wavelength was 420 nm.



Figure S12. IR spectra of precursor and UPC-H4a in solid.



Figure S13. (a) The response-recovery curve of precursor sensor toward different concentrations of  $NO_2$  at room temperature; (b) the linear relation between R% and concentration; (c) response-recovery time curves to 100 ppb  $NO_2$ ; and (d) responsivity and sensitivity to 1 ppm different gases.

Table S3. The response and recovery times of precursor and UPC-H4a sensors to different concerntrations of  $NO_2$ .

NO <sub>2</sub>	Precursor		UPC-H4a	
Concern.	T <sub>res</sub>	T <sub>rec</sub>	T <sub>res</sub>	T <sub>rec</sub>
0.04 ppm	-	-	17.1	14.6
0.1 ppm	24.8	46.8	17.6	15.4
0.2 ppm	35.6	57.4	21.9	18.3
0.3 ppm	35.8	71.7	26.1	25.0
0.4 ppm	43.0	98.0	28.4	26.8



Figure S14. The response curves of precursor sensor (a) and UPC-H4a sensor (b) toward different concentrations of  $H_2S$  at room temperature.



Figure S15. The response curves of precursor sensor (a) and UPC-H4a sensor (b) toward different concentrations of  $CO_2$  at room temperature.



Figure S16. The response curves of precursor sensor (a) and UPC-H4a sensor (b) toward different concentrations of  $NH_3$  at room temperature.



Figure S17. The response curves of precursor sensor (a) and UPC-H4a sensor (b) toward different concentrations of  $SO_2$  at room temperature.



Figure S18. The response curves of precursor sensor (a) and UPC-H4a sensor (b) toward

different concentrations of  $H_2$  at room temperature.



**Figure S19.** XPS spectra for the activated UPC-H4a fully exposed to the air: (a) full spectrum; and (b) C 1s, (c) N 1s, (d) O 1s level spectra.



**Figure S20.** (a) Reproducibility test of precursor sensor to 1 ppm NO<sub>2</sub>, (b) Stability tests of precursor sensor exposed to 0.1 and 1 ppm of NO<sub>2</sub>, respectively, over a 60-days' time period.



**Figure S21.** (a) Reproducibility test of UPC-H4a sensor to 1 ppm NO<sub>2</sub>, (b) Stability tests of UPC-H4a sensor exposed to 0.1 and 1 ppm of NO<sub>2</sub>, respectively, over a 60-days' time period.



Figure S22. PXRD patterns of UPC-H4a after exposing to 1 ppm NO<sub>2</sub> for 30 min.

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- 2 E. Demers, T. Maris, J. D. Wuest, Cryst. Growth & Des, 2005, 5, 1227-1235.