## SUPPORTING INFORMATION

# Crystalline Microporous Small-molecule Semiconductors Based on Porphyrin for High-performance Chemiresistive Gas Sensing

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Table S1. Crystallographic data of 2				
Compound name	2			
Empirical formula	C <sub>96</sub> H <sub>57</sub> N <sub>8</sub> O <sub>16</sub> , 2(H <sub>4</sub> N), 2(C <sub>2</sub> H <sub>3</sub> N)			
Formula weight	1948.91			
Temperature/K	293			
Crystal system	monoclinic			
Space group	P21/n			
a/Å	22.6949			
b/Å	9.6108			
c/Å	23.3758			
α/°	90			
6/°	97.186			
٧/°	90			
Volume/Å <sup>3</sup>	7905.5(3)			
Ζ	2			
$ ho_{calc}/g\ cm^{-3}$	1.280			
μ/mm <sup>-1</sup>	0.402			
F(000)	1766			
Radiation	GaK $\alpha$ ( $\lambda$ = 1.34050)			
$2\vartheta$ range for data collection/°	4.448~105.864			
Collected reflections	38175			
Independent reflections	8918 [R <sub>int</sub> = 0.0432, <i>R</i> <sub>sigma</sub> = 0.0360]			
Goodness-of-fit on F <sup>2</sup>	1.075			
Final R indexes [ $I >= 2\sigma(I)$ ]	$^{[a]}R_1 = 0.0477, \ ^{[b]}wR_2 = 0.1313$			
Final R indexes [all data]	$^{[a]}R_1 = 0.0605, \ ^{[b]}wR_2 = 0.1393$			
CCDC No.	2127390			

<sup>[a]</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; [b]  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

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#### Journal Name

#### Powder X-Ray diffraction (PXRD)

PXRD patterns were collected for polycrystalline samples using a Rigaku Dmax 2500 X-ray diffractometer using copper radiation (Cu  $K_{\alpha}$ ,  $\lambda = 1.5418$  Å). Profiles were collected at rt in the angular range 3° < 2 $\vartheta$  < 45° with a step size of 0.02. Molecular modeling was carried out using Reflex Plus, a module implemented in Materials Studio (version 4.4) by Accelrys Inc. The initial structure of **1** was constructed piecewise starting with a triclinic space group *P*-1. The Pseudo-Voigt function was used for whole profile fitting and Berrar-Baldinozzi function was used for asymmetry correction during the refinement processes. The predicted structure was validated with Rietveld refinements against the observed PXRD patterns.

Table S2. Refinement parameters of
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Compound name	1
Refined composition	C <sub>48</sub> H <sub>30</sub> N <sub>4</sub> O <sub>8</sub>
Formula weight	790.76
Crystal system	triclinic
Space group	P-1
a/Å	8.1865
b/Å	16.210
c/Å	19.978
α/°	74.981
6/°	80.473
γ/°	84.737
Volume/Å <sup>3</sup>	2521.9
Z	2
$ ho_{calc}/g \text{ cm}^{-3}$	1.041
$2\vartheta$ range for data collection/°	3~45
R <sub>p</sub> (%) [Rietveld]	6.84
R <sub>wp</sub> (%) [Rietveld]	8.63

#### Table S3. Atomic coordinates of 1

Atom	x	у	Z
01	0.21027	0.13501	0.89336
02	0.30200	0.04124	0.82937
H2	0.32061	0.04035	0.78795
03	-0.06419	0.23397	0.13235
04	0.17990	0.16876	0.15425
H4	0.16068	0.14150	0.12736
05	0.24418	1.00708	-0.00703
H5	0.29629	1.04611	-0.03426
06	0.12329	0.06026	1.08988
07	0.30654	0.94722	0.74702
08	0.55313	0.97604	0.68939
H8	0.62721	0.94969	0.6692
N1	0.28234	0.69579	0.42071
N2	0.29317	0.55402	0.54159
H2A	0.26447	0.56569	0.50052
N3	0.20430	0.43850	0.46015
N4	0.23277	0.59131	0.33549
H4A	0.23221	0.58789	0.37921
C1	0.26269	0.11381	0.83398
C2	0.16265	0.26580	0.77392
H2B	0.11080	0.27318	0.81720
C3	0.24444	0.18810	0.76898
C4	0.32195	0.17707	0.70429
H4B	0.37667	0.12509	0.70099
C5	0.31766	0.24374	0.64455
H5A	0.36952	0.23636	0.60127
C6	0.23587	0.32143	0.64949
C7	0.15836	0.33246	0.71417
H7	0.10364	0.38445	0.71748
C8	0.06046	0.22245	0.16225
С9	0.08994	0.27904	0.20838
C10	0.21704	0.25558	0.24898
H10	0.28422	0.20661	0.24673
C11	0.24373	0.30530	0.29296
H11	0.32876	0.28960	0.32012
C12	0.14331	0.37850	0.29633
C13	0.01622	0.40196	0.25573
H13	-0.05097	0.45093	0.25799
C14	-0.01047	0.35224	0.21176
H14	-0.09551	0.36794	0.18459
C15	0.42574	0.93826	0.70169
C16	0.42062	0.87003	0.65899

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170.29020.81210.6828H170.227080.811280.72497C180.274470.755420.64378H180.191110.716660.5598C200.570110.814590.55698H200.571660.815420.51467C210.523670.871270.55605C220.027071.024600.05085C230.224850.955340.11848C240.011170.950130.11947H240.027120.92110.1518C250.125200.881190.23690C260.515720.818440.23333C270.364800.824550.17234C280.351370.8877440.7141C280.351370.887740.7141C280.427330.887740.7141C290.168570.434710.34025C300.168570.434710.34025C310.12530.34690.4273C310.10350.314600.4112C320.168570.347410.5583C330.95420.47240.5583C340.23090.355540.5373C350.39640.267510.55873C350.39640.36790.5385C350.39640.47240.5583C350.39640.37560.5385C350.39640.37560.5385C350.39640.36750.5385 <trr< th=""><th></th><th></th><th></th><th></th></trr<>				
h12     0.22708     0.81128     0.27447       C18     0.27447     0.75542     0.64478       H15     0.15111     0.71666     0.5894       C20     0.50211     0.81452     0.55698       C21     0.52676     0.87127     0.59605       H21     0.6073     0.91033     0.58009       C22     0.20276     1.02460     0.05085       C23     0.22485     0.95634     0.11848       C24     0.01177     0.95013     0.11947       C25     0.12520     0.8819     0.23690       C26     0.5172     0.81844     0.27711       C26     0.5172     0.81844     0.27711       C27     0.36480     0.82465     0.17234       C28     0.45172     0.81844     0.23791       C29     0.16857     0.43471     0.34025       C31     0.16253     0.4460     0.40055       C32     0.16857     0.43471     0.34025       C33     0.16857     0.43471     0.34025       C34     0.23690     0.3254     0.5821       C35     0.16857     0.43471     0.34025       C34     0.1692     0.34849     0.4129       C35     0.32640     0.3576	C17	0.29602	0.81211	0.68286
C180.274470.75620.64378H180.191110.716660.5894C200.502110.814590.55698H200.571660.815420.51487C210.523670.871270.55605H210.607030.910030.56009C220.202761.024600.05985C330.224850.956340.11848C440.027120.952110.1818C550.125200.8817910.23690C450.045540.877040.23771C460.251720.818440.23333C70.364800.824650.17234C480.427030.897740.07411C490.65240.31370.89399C310.163040.400550.41259C320.168570.314600.41259C330.197500.384690.52031C340.239000.395540.52031C350.314600.412590.31461C360.395640.42890.52031C370.391040.568180.64932C360.392640.42890.5332C370.391040.568180.64932C360.392640.42890.5332C370.391040.568180.64932C360.392640.643740.5648C370.392640.568180.64932C360.392640.643740.54932C370.392640.56818	H17	0.22708	0.81128	0.72497
H8         0.3111         0.7566         0.6594           C19         0.37792         0.75666         0.5598           H20         0.55211         0.81493         0.55698           H20         0.53267         0.81717         0.9606           C21         0.52367         0.81717         0.9606           C22         0.20276         1.02460         0.05085           C23         0.22485         0.95613         0.17947           H24         0.02712         0.99211         0.1818           C25         0.15520         0.81819         0.23800           H25         0.49554         0.81819         0.23801           C27         0.36480         0.82465         0.17234           C28         0.35137         0.89374         0.4402           C29         0.16857         0.43471         0.4402           C31         0.16857         0.43471         0.4402           C32         0.16857         0.43471         0.4402           C34         0.2393         0.1412         0.4412           C35         0.23651         0.5526         0.3526           C34         0.1956         0.37691         0.55226	C18	0.27447	0.75542	0.64378
19       0.3772       0.7566       0.5894         220       0.52105       0.81542       0.5168         121       0.52367       0.87127       0.59605         121       0.60703       0.91003       0.50895         122       0.20276       1.02460       0.05985         123       0.22485       0.95634       0.11844         124       0.01717       0.95013       0.17947         124       0.02712       0.92911       0.23890         125       0.04954       0.87704       0.27771         126       0.21520       0.81149       0.33333         127       0.36400       0.82465       0.17234         128       0.42703       0.89774       0.07411         129       0.16857       0.44171       0.34025         131       0.10235       0.21460       0.41259         1431       0.06200       0.27459       0.42281         1432       0.06554       0.24251       0.5884         1432       0.06554       0.42251       0.5884         1432       0.23690       0.32289       0.32391         1432       0.36904       0.43253       0.4388	H18	0.19111	0.71666	0.65974
C20         0.5211         0.81499         0.55989           H20         0.57106         0.81542         0.51467           C11         0.53267         0.87127         0.58005           H21         0.60703         0.91003         0.58009           C22         0.20276         1.02460         0.05685           C33         0.24853         0.95013         0.17947           H24         0.02712         0.9211         0.1818           C25         0.12520         0.8819         0.23333           C27         0.36480         0.82465         0.7724           C28         0.35137         0.89359         0.14627           C29         0.16857         0.43471         0.34025           C31         0.10235         0.31460         0.4328           C32         0.19564         0.26211         0.3583           C33         0.16857         0.43471         0.34025           C34         0.10235         0.1460         0.43125           C34         0.12956         0.32826         0.43125           C35         0.29642         0.47424         0.58684           C36         0.36655         0.48135         0.648	C19	0.37752	0.75666	0.58084
120         0.53106         0.81542         0.5487           C21         0.53367         0.87127         0.59609           C22         0.20276         1.02460         0.65085           C33         0.22485         0.95013         0.17947           C44         0.11177         0.99211         0.1818           C25         0.12520         0.88119         0.23890           C26         0.25172         0.81844         0.27333           C27         0.36480         0.82465         0.11692           C28         0.35137         0.83959         0.1402           C29         0.16657         0.44471         0.7741           C30         0.16357         0.44471         0.7451           C31         0.02020         0.27459         0.4259           C32         0.16957         0.44471         0.7461           C33         0.19750         0.3269         0.52031           H31         0.06200         0.27459         0.4228           C34         0.23809         0.53032         0.3364           C35         0.23642         0.47424         0.55826           C34         0.23809         0.53835         0.56932	C20	0.50211	0.81459	0.55698
C1       0.5267       0.87127       0.59605         H21       0.60703       0.91033       0.59605         C22       0.20276       1.02460       0.05085         C3       0.22485       0.95634       0.11848         C4       0.11177       0.95013       0.17947         H24       0.02712       0.98119       0.23690         H25       0.04954       0.87704       0.27771         C26       0.25172       0.81844       0.23333         C27       0.36480       0.89794       0.07411         C28       0.42703       0.89774       0.07411         C29       0.16857       0.43471       0.3005         C30       0.16904       0.27499       0.44289         C31       0.00235       0.31460       0.4512         H31       0.06200       0.27499       0.43285         C32       0.19564       0.26513       0.5876         C33       0.19750       0.38269       0.53733         C34       0.39084       0.43836       0.64592         H36       0.39084       0.43836       0.64592         H37       0.39084       0.43836       0.64592	H20	0.57106	0.81542	0.51487
H21       0.60703       0.91003       0.58009         C22       0.02076       1.02460       0.05065         C33       0.2485       0.95013       0.11947         H24       0.02712       0.99211       0.1818         C25       0.12520       0.88119       0.23660         H25       0.4954       0.87014       0.27771         C26       0.25172       0.88144       0.23333         C27       0.36480       0.82465       0.17234         C28       0.5137       0.88959       0.11492         H28       0.42703       0.89774       0.34025         C30       0.16807       0.43471       0.34025         C31       0.10325       0.31460       0.45112         H31       0.06200       0.27459       0.32761         C33       0.1956       0.36769       0.52031         H32       0.68654       0.426251       0.5826         C34       0.23609       0.33554       0.64382         C36       0.36655       0.48218       0.64392         C36       0.36655       0.48218       0.64392         C37       0.39104       0.43836       0.63892 <t< th=""><th>C21</th><th>0.52367</th><th>0.87127</th><th>0.59605</th></t<>	C21	0.52367	0.87127	0.59605
C22         0.20276         1.02460         0.05085           C33         0.22485         0.95634         0.11947           C44         0.11177         0.95013         0.12744           C25         0.12520         0.88119         0.23690           H25         0.04954         0.87774         0.23733           C27         0.36480         0.82465         0.11492           C28         0.35137         0.89359         0.11492           C28         0.42572         0.43471         0.34025           C30         0.16304         0.40055         0.41259           C31         0.10235         0.31460         0.45112           H31         0.06200         0.27459         0.52081           C32         0.19550         0.31869         0.52081           C33         0.19750         0.38269         0.52382           C34         0.29842         0.4724         0.5864           C35         0.39064         0.4836         0.68392           C34         0.39064         0.4836         0.68392           C35         0.39064         0.4836         0.66481           C36         0.39076         0.58361         0.	H21	0.60703	0.91003	0.58009
C23       0.22485       0.95634       0.11848         C24       0.1177       0.95013       0.17947         H24       0.02712       0.93211       0.1818         C25       0.04954       0.87704       0.27771         C26       0.25172       0.81844       0.23333         C27       0.36480       0.82465       0.17234         C28       0.35137       0.893754       0.07411         C29       0.16857       0.43471       0.34025         C30       0.16857       0.43472       0.34025         C31       0.0200       0.27459       0.43285         C32       0.1956       0.30769       0.52031         H31       0.06200       0.27459       0.43285         C32       0.1956       0.30769       0.52031         H32       0.06654       0.26251       0.52322         C34       0.29662       0.47424       0.5864         C35       0.29642       0.47424       0.5864         C36       0.39084       0.43836       0.66492         H37       0.33104       0.56015       0.58393         C36       0.39084       0.56015       0.58849 <tr< th=""><th>C22</th><th>0.20276</th><th>1.02460</th><th>0.05085</th></tr<>	C22	0.20276	1.02460	0.05085
C24       0.11177       0.95013       0.17947         H2A       0.02712       0.99111       0.1818         C25       0.12520       0.88119       0.23690         H25       0.04954       0.87704       0.2771         C26       0.25172       0.81844       0.23333         C27       0.34840       0.82465       0.17234         C28       0.35137       0.89379       0.1492         C29       0.16857       0.43471       0.34025         C30       0.15304       0.40055       0.41259         C31       0.02500       0.27459       0.43285         C32       0.11956       0.30769       0.52031         H31       0.06204       0.26251       0.55826         C33       0.19750       0.38269       0.55733         C35       0.29642       0.47424       0.5664         C36       0.36665       0.48118       0.64483         H37       0.33040       0.66017       0.57120         C38       0.34051       0.59336       0.66481         H37       0.33004       0.63074       0.44015         H36       0.34051       0.59336       0.66481      <	C23	0.22485	0.95634	0.11848
H24     0.02712     0.99211     0.1818       C25     0.12520     0.88119     0.23690       H25     0.04954     0.87704     0.23733       C26     0.25172     0.8144     0.23333       C27     0.36480     0.82465     0.17234       C28     0.35137     0.89359     0.11492       H28     0.42703     0.89774     0.30425       C30     0.16304     0.40055     0.41259       C31     0.10235     0.31460     0.45112       H31     0.66200     0.27459     0.4285       C32     0.1956     0.30769     0.52031       H32     0.26654     0.26251     0.55826       C33     0.19750     0.38269     0.52322       C34     0.23809     0.39554     0.58733       C35     0.26654     0.2611     0.55826       C36     0.36655     0.43218     0.64892       C37     0.39104     0.5818     0.64892       C36     0.39084     0.43336     0.68392       C37     0.39104     0.5618     0.5648       C38     0.3017     0.73656     0.4889       C41     0.29867     0.3306     0.37217       H42     0.3704     0.8705 </th <th>C24</th> <th>0.11177</th> <th>0.95013</th> <th>0.17947</th>	C24	0.11177	0.95013	0.17947
C25       0.12520       0.88119       0.23690         H25       0.04954       0.87704       0.27771         C26       0.25172       0.81844       0.23333         C27       0.36480       0.82465       0.17234         C28       0.51377       0.89359       0.11492         H28       0.42703       0.89774       0.07411         C29       0.16857       0.43471       0.34025         C30       0.16304       0.40055       0.41259         C31       0.10235       0.31460       0.45112         H31       0.66200       0.27459       0.43285         C32       0.19750       0.33269       0.52322         C34       0.23694       0.26511       0.55826         C33       0.19750       0.33269       0.52322         C34       0.23694       0.43836       0.64892         C35       0.26651       0.58736       0.58936         C36       0.30645       0.46218       0.64889         C37       0.39104       0.56818       0.64889         C37       0.3317       0.73656       0.4889         C37       0.33074       0.44015       0.57120	H24	0.02712	0.99211	0.1818
H25     0.04954     0.87704     0.27771       C26     0.25172     0.81844     0.2333       C27     0.36480     0.82465     0.17234       C28     0.35137     0.89595     0.11492       H28     0.42703     0.89774     0.07411       C29     0.16857     0.43471     0.34025       C30     0.16304     0.40055     0.41259       C31     0.02020     0.27459     0.32385       C32     0.11956     0.30769     0.5231       H31     0.66200     0.27459     0.32385       C33     0.19750     0.33269     0.52322       C34     0.2809     0.39554     0.58733       C35     0.28642     0.47424     0.58684       C36     0.36665     0.48218     0.64592       H36     0.39084     0.43836     0.64892       C37     0.39104     0.56818     0.58488       H37     0.43219     0.59336     0.66481       C38     0.34174     0.57120     0.33809       C39     0.39074     0.4015     0.59350       C40     0.3017     0.73556     0.4889       C41     0.29867     0.83074     0.4015       H41     0.30704     0.8	C25	0.12520	0.88119	0.23690
C26       0.25172       0.81844       0.23333         C27       0.36480       0.82465       0.17234         C28       0.35137       0.89359       0.11492         H28       0.42703       0.89359       0.1492         C29       0.16857       0.43471       0.3025         C30       0.16304       0.40055       0.41259         C31       0.10235       0.31460       0.45112         H31       0.06200       0.27459       0.43285         C32       0.11956       0.30769       0.52031         H32       0.08654       0.26251       0.53322         C34       0.23809       0.39554       0.58733         C35       0.29642       0.47424       0.56684         C36       0.36665       0.48218       0.64592         H36       0.39084       0.43836       0.68488         H37       0.43329       0.59336       0.66481         C38       0.34124       0.61017       0.57120         C39       0.34095       0.69615       0.53850         C40       0.30317       0.73656       0.46489         C41       0.29867       0.88705       0.3390	H25	0.04954	0.87704	0.27771
C27       0.36480       0.82465       0.17234         C28       0.35137       0.89359       0.11492         H28       0.42703       0.89774       0.07411         C29       0.16857       0.43471       0.34025         C30       0.16304       0.40055       0.41259         C31       0.06200       0.27459       0.43285         C32       0.1956       0.30769       0.52031         H32       0.08654       0.26251       0.58266         C33       0.19750       0.33269       0.52322         C34       0.23809       0.39554       0.5873         C35       0.29642       0.47424       0.58684         C36       0.36665       0.48218       0.64592         H36       0.39084       0.43386       0.68392         C37       0.39104       0.56818       0.63488         H37       0.43329       0.59336       0.66481         C38       0.34124       0.61017       0.57120         C39       0.304095       0.69615       0.53850         C41       0.29867       0.83074       0.46174         C42       0.27848       0.83496       0.37217	C26	0.25172	0.81844	0.23333
C28       0.35137       0.89359       0.11492         H28       0.42703       0.89774       0.07411         C29       0.16857       0.43471       0.34025         G30       0.16304       0.40055       0.41259         G31       0.10235       0.31460       0.45112         G32       0.11956       0.30769       0.52031         G33       0.19750       0.38269       0.52322         G34       0.23809       0.39554       0.58733         G35       0.29642       0.47424       0.5884         G36       0.36665       0.48218       0.68992         G37       0.39104       0.56818       0.63488         G36       0.34025       0.66481       0.57120         G39       0.34124       0.61017       0.57120         G39       0.34124       0.61017       0.57120         G39       0.34035       0.69615       0.53850         G40       0.30317       0.73656       0.46889         G41       0.29867       0.83074       0.46174         G42       0.27505       0.88705       0.3390         G43       0.26255       0.75590       0.35449	C27	0.36480	0.82465	0.17234
H280.427030.897740.07411C290.168570.434710.34025G300.163040.400550.41259G310.102350.314600.45112H310.062000.274590.43285G320.119560.307690.52031H320.86540.262510.55826G330.197500.382690.52322G340.238090.395540.58733G350.296420.474240.5664G360.366550.482180.64592H360.390840.438360.68392G370.391040.568180.66481G380.341240.610170.57120G390.30050.696150.33850C410.298670.830740.44015H410.307040.874260.46124C420.276480.834960.37117H420.275050.887050.3390C430.262510.735590.35449C440.260250.755900.35449C440.260250.755900.35449C440.260250.755900.35449C440.260250.743650.28341C440.268310.660760.28341C450.268310.660750.23151	C28	0.35137	0.89359	0.11492
C29       0.16857       0.43471       0.34025         C30       0.16304       0.40055       0.41259         C31       0.10235       0.31460       0.45112         H31       0.06200       0.27459       0.43285         C32       0.11956       0.30769       0.52031         H32       0.08654       0.26251       0.55826         C33       0.19750       0.3259       0.52322         C34       0.23809       0.39554       0.58733         C35       0.29642       0.47424       0.58684         C36       0.36665       0.48218       0.64592         H36       0.39084       0.43836       0.638392         C37       0.39104       0.56818       0.6481         C38       0.34124       0.61017       0.57120         C39       0.34095       0.66615       0.53850         C40       0.3017       0.73656       0.46889         C41       0.29867       0.83074       0.44015         H41       0.30704       0.87426       0.46174         C42       0.27648       0.83496       0.37217         H42       0.27605       0.75590       0.33409	H28	0.42703	0.89774	0.07411
C30         0.16304         0.40055         0.41259           C31         0.10235         0.31460         0.45112           H31         0.66200         0.27459         0.43285           C32         0.11956         0.30769         0.52031           H32         0.08654         0.26251         0.55826           C33         0.19750         0.38269         0.52322           C34         0.23809         0.39554         0.58733           C35         0.29642         0.47424         0.58684           C36         0.36665         0.48218         0.64552           H36         0.39084         0.43836         0.63488           H37         0.43229         0.59336         0.66481           C38         0.34124         0.61017         0.57120           C39         0.34095         0.69615         0.53850           C40         0.3017         0.73656         0.46889           C41         0.29667         0.83074         0.44015           H41         0.30704         0.84726         0.46174           C42         0.27848         0.83096         0.37217           H42         0.26295         0.88705 <t< th=""><th>C29</th><th>0.16857</th><th>0.43471</th><th>0.34025</th></t<>	C29	0.16857	0.43471	0.34025
C31       0.10235       0.31460       0.45112         H31       0.06200       0.27459       0.43285         C32       0.11956       0.30769       0.52031         H32       0.08654       0.26251       0.55826         C33       0.19750       0.38269       0.52322         C34       0.23809       0.39554       0.58733         C35       0.29642       0.47424       0.58684         C36       0.39084       0.43336       0.68392         C37       0.39104       0.56818       0.64592         H36       0.39084       0.61017       0.57120         C38       0.34124       0.61017       0.57120         C39       0.34095       0.69615       0.53850         C41       0.29867       0.83074       0.44015         H41       0.30704       0.87426       0.46174         C42       0.27848       0.83496       0.37217         H42       0.26025       0.73505       0.3390         C43       0.26295       0.75350       0.3349         C44       0.26025       0.73565       0.29300         C43       0.26287       0.66076       0.28341	C30	0.16304	0.40055	0.41259
H310.062000.274590.43285G320.119560.307690.52031H320.086540.262510.55826G330.197500.382690.52322G340.238090.395540.58733G350.296420.474240.58684G360.366650.482180.64592H360.390840.438360.68392G370.391040.568180.66481G380.341240.610170.57120G390.340950.696150.53850C400.303740.430260.46174G410.298670.837420.44015H420.275050.887050.3390C430.262550.743650.23300C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.26050.560050.23151	C31	0.10235	0.31460	0.45112
G32       0.11956       0.30769       0.52031         H32       0.08654       0.26251       0.55826         G33       0.19750       0.38269       0.52322         G34       0.23809       0.39554       0.58733         G35       0.29642       0.47424       0.58684         G36       0.36665       0.48218       0.64592         H36       0.39084       0.43836       0.68392         G37       0.39104       0.56818       0.63488         H37       0.43329       0.59336       0.66481         G38       0.34124       0.61017       0.57120         G39       0.34095       0.69615       0.53850         C40       0.30317       0.73656       0.46889         C41       0.29867       0.83074       0.44015         H41       0.30704       0.87426       0.46174         C42       0.27548       0.88705       0.3390         C43       0.26255       0.74365       0.29300         C44       0.26025       0.74365       0.29300         C45       0.24823       0.66076       0.28341         C46       0.25287       0.64230       0.21683	H31	0.06200	0.27459	0.43285
H320.086540.262510.55826C330.197500.382690.52322C340.238090.395540.58733C350.296420.474240.58684C360.366650.482180.64592H360.390840.438360.63488C370.391040.568180.66481C380.341240.610170.57120C390.340950.696150.53850C410.298670.830740.44015H410.307040.874260.46174C420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.263110.680270.7282C470.230560.560050.23151	C32	0.11956	0.30769	0.52031
C330.197500.382690.52322C340.238090.395540.58733C350.296420.474240.58684C360.366650.482180.64592H360.390840.438360.68392C370.391040.568180.66481C380.341240.610170.57120C390.340950.696150.53850C400.303170.736560.46889C410.298670.830740.44015H420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.268310.680270.23151	H32	0.08654	0.26251	0.55826
C340.238090.395540.58733C350.296420.474240.58684C360.366650.482180.64592H360.390840.438360.638392C370.391040.568180.66481H370.433290.593360.66481C380.341240.610170.57120C390.340950.696150.53850C400.303170.736560.46889C410.298670.830740.44015H420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.26050.560050.23151	C33	0.19750	0.38269	0.52322
C350.296420.474240.58684C360.366650.482180.64592H360.390840.438360.68392C370.391040.568180.63488H370.433290.593360.66481C380.341240.610170.57120C390.340950.696150.53850C400.303170.736560.46889C410.298670.830740.44015H410.307040.874260.46174C420.278480.834960.37217H420.260250.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.268310.680270.17282C470.230560.560050.23151	C34	0.23809	0.39554	0.58733
C360.366650.482180.64592H360.390840.438360.68392C370.391040.568180.63488H370.433290.593360.66481C380.341240.610170.57120C390.340950.696150.53850C400.303170.736560.46889C410.298670.830740.44015H410.307040.874260.46174C420.278480.837950.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.68270.17282H460.266310.680270.23151	C35	0.29642	0.47424	0.58684
H360.390840.438360.68392C370.391040.568180.63488H370.433290.593360.66481C380.341240.610170.57120C390.340950.696150.53850C400.303170.736560.46889C410.298670.830740.44015H410.307040.874260.46174C420.278480.834960.37217H420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.268310.680270.17282C470.230560.560050.23151	C36	0.36665	0.48218	0.64592
C370.391040.568180.63488H370.433290.593360.66481C380.341240.610170.57120C390.340950.696150.53850C400.303170.736560.46889C410.298670.830740.44015H410.307040.874260.46174C420.278480.834960.37217H420.275050.887050.3390C430.262550.743650.29300C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.260310.680270.17282C470.230560.560050.23151	H36	0.39084	0.43836	0.68392
H370.433290.593360.66481C380.341240.610170.57120C390.340950.696150.53850C400.303170.736560.46889C410.298670.830740.44015H410.307040.874260.46174C420.278480.834960.37217H420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.260310.680270.17282C470.230560.560050.23151	C37	0.39104	0.56818	0.63488
C380.341240.610170.57120C390.340950.696150.53850C400.303170.736560.46889C410.298670.830740.44015H410.307040.874260.46174C420.278480.834960.37217H420.275050.887050.3390C430.260250.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.260560.560050.23151	H37	0.43329	0.59336	0.66481
C390.340950.696150.53850C400.303170.736560.46889C410.298670.830740.44015H410.307040.874260.46174C420.278480.834960.37217H420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.260310.680270.17282C470.230560.560050.23151	C38	0.34124	0.61017	0.57120
C400.303170.736560.46889C410.298670.830740.44015H410.307040.874260.46174C420.278480.834960.37217H420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.268310.680270.17282C470.230560.560050.23151	C39	0.34095	0.69615	0.53850
C410.298670.830740.44015H410.307040.874260.46174C420.278480.834960.37217H420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.268310.680270.17282C470.230560.560050.23151	C40	0.30317	0.73656	0.46889
H410.307040.874260.46174C420.278480.834960.37217H420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.260310.680270.17282C470.230560.560050.23151	C41	0.29867	0.83074	0.44015
C420.278480.834960.37217H420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.268310.680270.17282C470.230560.560050.23151	H41	0.30704	0.87426	0.46174
H420.275050.887050.3390C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.268310.680270.17282C470.230560.560050.23151	C42	0.27848	0.83496	0.37217
C430.262950.755900.35449C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.268310.680270.17282C470.230560.560050.23151	H42	0.27505	0.88705	0.3390
C440.260250.743650.29300C450.248230.660760.28341C460.252870.642300.21683H460.268310.680270.17282C470.230560.560050.23151	C43	0.26295	0.75590	0.35449
C450.248230.660760.28341C460.252870.642300.21683H460.268310.680270.17282C470.230560.560050.23151	C44	0.26025	0.74365	0.29300
C46         0.25287         0.64230         0.21683           H46         0.26831         0.68027         0.17282           C47         0.23056         0.56005         0.23151	C45	0.24823	0.66076	0.28341
H46         0.26831         0.68027         0.17282           C47         0.23056         0.56005         0.23151	C46	0.25287	0.64230	0.21683
C47         0.23056         0.56005         0.23151	H46	0.26831	0.68027	0.17282
	C47	0.23056	0.56005	0.23151

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H47	0.22415	0.52924	0.19879	
C48	0.21765	0.52514	0.30530	



Figure S1. (a, b) SEM images of compound 1; (c, d) SEM images of compound 2.



Figure S2. PXRD patterns of (a) 2 and (b) 3.



**Figure S3.** FT-IR spectra of **1**, **2** and **3**. The as-synthesized samples **1**, **2** and **3** have similar spectra, where the band at 3330<sup>-3300</sup> cm<sup>-1</sup> was assigned to the stretching vibration bond of -NH, the peak near 1390 cm<sup>-1</sup> for the characteristic vibration of  $-C_{\alpha}N$ ,  $-C_{\alpha}C_{\beta}$  and the bands at 1750<sup>-1620</sup> cm<sup>-1</sup> were due to -C = O in carboxylic acid.<sup>[1]</sup>



Figure S4. (a) The hydrogen-bonding node A for 1 (a and c) and node B for 2 (b and d).



Figure S5. Hydrogen bonding chain built of LB and LC nodes for 2.



**Figure S6.** The  $\pi$ - $\pi$  interaction modes between adjacent benzene rings for **1** (a) and **2** (b), and the relative positions of the two neighbouring porphyrins for **1** (c) and **2** (d).



Figure S7. TGA curves of (a) 1 and (b) 2.



Figure S8. Various temperature PXRD patterns of (a) 1 and (b) 2.



Figure S9. PXRD patterns of (a) 1 and (b) 2 samples after soaking in water or organic solvents (acetone, dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), toluene, acetonitrile (CH<sub>3</sub>CN), and *n*-hexane) for at least 12 h.



Figure S10. Temperature-dependent I–V curves of (a) 2 and (b) 3.



Figure S11. I-V curve of 1 at rt and under visible light irradiation



Figure S12. (a) Photographs of sensor devices in this manuscript. (b) Schematic illustration of the gas-detection equipment at rt and under visible light irradiation.



Figure S13. Dynamic response–recovery successive cycling curves for (a) 2 and (b) 3 toward 100 ppm NO<sub>2</sub> at rt and under visible light irradiation.



**Figure S14.** (a) Dynamic response–recovery curves and (b) response and recovery time for **1** toward 100 ppm NO<sub>2</sub> at rt and under visible light irradiation (380 mW cm<sup>-2</sup>).



Figure S15. Transient photocurrent responses of (a) 1, (b) 2 and (c) 3 at rt and under visible light irradiation.



**Figure S16.** Dynamic response–recovery curves of  $NO_2$  sensing properties of (a) **2** and (b) **3** sensor in a concentration ranging of 0.04-100 ppm under visible light irradiation at rt.

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### Table S4. NO<sub>2</sub> sensing performances of different sensor devices at rt.

Sensing materials	tres/trec (min)	Response (R <sub>eas</sub> /R <sub>air</sub> -1)%	Concentration (ppm)	LOD (ppb)	Ref.
1	2.5/0.6	1.7×10 <sup>5</sup>	100	20(exp.)	This work
3D graphene Flowers	33/0.03	1411	10	100(exp.)	[2]
3D graphene	8.3/50	74	10	_k	[3]
Graphene	~ <sup>j</sup> 10/10	27	5	-	[4]
Graphene/MoS <sub>2</sub>	10/10	12	0.5	50	[5]
Graphene/CeO <sub>2</sub>	0.31/4.1	5	10	5000	[6]
RGO	3.3-5/5	4	100	-	[7]
RGO	>5/>10	150	100	2000	[8]
RGO	15/20	815	100	-	[9]
RGO@Cu <sub>2</sub> O	5/8	67	2	400	[10]
RGO/PET	3/5	6	10	500(exp.) <sup>n</sup>	[11]
sulfonated RGO	~ 8.3 /41	~ 640	20	2000	[12]
RGO/MoS <sub>2</sub>	5/7.5	~ 40	10	53	[13]
3D FRGOH <sup>a</sup>	7/13	8	10	57	[14]
3D S-RGOH <sup>b</sup>	~6.5/0.18	23	4	200(exp.)	[15]
RGO–IDTO <sup>c</sup>	>10/ > 16	1100	100	300(exp.)	[16]
Ag-S-RGO	0.2/0.33	90	100	500(exp.)	[17]
RGO/ SnO <sub>2</sub>	1.1/incomplete recovery	120	10	1000 (exp.)	[18]
CNT <sup>d</sup>	3/10	84	100	250(exp.)	[19]
CNT	10/10	90	10	44	[20]
CNTs/Au	_k	10	1	100	[21]
CNTs/SnO <sub>2</sub>	₽4.5/₽3.5	40	25	-	[22]
SnO <sub>2</sub>	1/12	~80	10	2000(exp.)	[23]
SnO-SnO <sub>2</sub>	0.95/5	500	10	100	[24]
amine-terminated SnO <sub>2</sub>	1.8/1.25	2100	0.4	250 (exp.)	[25]
ZnO	3.7/2	410	20	-	[26]
ZnO	15/48	120	20	-	[27]
ZnO1-x	13.7/15	259	1	-	[28]
$SnO_{1-\alpha}@ZnO_{1-\beta}@SnO_{2-\gamma}$	17.6/23.4	236	1	-	[29]
ZnO /RGO	1.25/2.2	119	1	-	[30]
ZnO-Ag	2.5/2.16	110	1	-	[31]
CdS/ZnO	0.45/3.8	337	1	5(exp.)	[32]
SnO <sub>2</sub> /ZnO	1.5/3.7	619	5	1000(exp.)	[33]
ZnO/SnO <sub>2</sub>	7/8	1×10 <sup>5</sup>	0.5	200(exp.)	[34]
ZnO/PbS	3/4	500	10	-	[35]
MoS <sub>2</sub> /SnO <sub>2</sub>	6.8/1.2	28	10	500(exp.)	[36]
P₃HT <sup>f</sup> /ZnO	15/45	90	10	-	[37]
Au/ZnO	25/⊠40	60	5	-	[38]
$TiO_{2-x}N_x$	~ 6/6	~ 14	10	-	[39]
Polypyrrole /WO <sub>3</sub>	10/~91	16	10	5000(exp.)	[40]
RGO/WO₃	9/18	769	5	-	[41]
DBSA doped PPy–WO <sub>3</sub>	4.8/99.8	72	100	-	[42]

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Polypyrrole–NiO	2.08/8.3	8	10	10000(exp.)	[43]
In <sub>2</sub> O <sub>3</sub> /RGO	4/24	725	30	-	[44]
In <sub>2</sub> O <sub>3</sub>	10/15	61800	0.5	50 (exp.)	[45]
MoS <sub>2</sub>	8/25	60	100	-	[46]
MoS <sub>2</sub>	11.3/5.3	11	10	1000	[47]
MoS <sub>2</sub> -Pt	>30/30	18	5	-	[48]
CdS	0.73/1.88	89	5	100	[49]
WS <sub>2</sub> @MTCNF <sup>e</sup>	3.73/10	28	4	10	[50]
Ag/WS <sub>2</sub>	~5/10	58	25	1000(exp.)	[51]
PbS CQDs <sup>g</sup>	0.2/0.61	2170	50	500 (exp.)	[52]
Si	1.38/0.3( $t_{50\%}$ , microheater )	80	100	1000	[53]
Те	1.4/13 (t <sub>50%</sub> ) <sup>m</sup>	62	10	100(exp.)	[54]
Black Phosphorus	0.08/10	100	100	100(exp.)	[55]
Phosphorene	~10/10	9000	1	~ 20(exp.)	[56]
polythiophene	4.95/9.75	9	10	10000(exp.)	[57]
Electrospun polyaniline	1/-	80	1	~50	[58]
VOPc/F <sub>16</sub> CuPc <sup>h</sup>	10/12	700	5	500(exp.)	[59]
PTCDI-Ph/p-6P <sup>i</sup>	~ 30/60	670	30	5000(exp.)	[60]
CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3x</sub> (SCN) <sub>x</sub>	3.7/6	300	5	200	[61]
CuTAP(t-Bu)4 <sup>p</sup>	4.5/9	500	50	-	[62]
metal-thiourea complex	2.9/9.2	19000	10	-	[63]
polythiophene	3.7/26.7	33	100	-	[64]
Ag(SPh-NH <sub>2</sub> )	1/2.3	852	10	100	[65]
rGO/P NFs	4/10	250	5	150(exp.)	[66]
graphene	5/10	15	5	5000 (exp.)	[67]
graphene nanomesh	15/20	12	10	1000 (exp.)	[68]
rGO/Au	7/28	25	20	1000 (exp.)	[69]
rGO/Au	5/>11	50	8	200 (exp.)	[70]
CuPc	1.3/1.6	17	0.5	50 (exp.)	[71]
MnPS <sub>3</sub>	1.6/2.6	9530	35	100 (exp.)	[72]
MoS <sub>2</sub>	1/>10	200	1	120 (exp.)	[73]
SnO <sub>2</sub> /MCN <sup>0</sup>	7/12	1.1×10 <sup>5</sup>	0.1	100 (exp.)	[74]
$g-C_3N_4/SnS_2$	-/2.76	1750	6	125 (exp.)	[75]
SnS <sub>2</sub> /MoS <sub>2</sub>	0.03/0.5	2490	100	50 (exp.)	[76]
Black Phosphorus	8.3/5	30	0.04	5 (exp.)	[77]
MoS <sub>2</sub> /GR	0.36/0.58	30	100	100000(exp)	[78]
UPC-H4a	0.28/0.26	43	2	40(exp)	[79]
Si-doped graphene	2.1/6.3	21.5	50	18(exp)	[80]
Pd-SnO <sub>2</sub> -rGO	0.21/1.75	292	1	50(exp)	[81]
B-RGOH	-/1.58	25.3	0.8	20(exp)	[82]
N-RGOH	-/0.16	13	0.8	50(exp)	[82]
Metal phthaloc	yanine/ 1.67/1.67	1480	50	50(exp)	[83]
cobalt phthalocyanine	1.67/1.67	512	50	50(exp)	[84]
GaN/TiO <sub>2</sub>	2.3/2.6	32	500	1(exp)	[85]
MoS <sub>2</sub>	0.26/1.08	670	0.4	20(exp)	[86]

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VO-rich ZnO nanowires	0.51/2.4	708	1	20(exp)	[87]
MoS <sub>2</sub> /ZnO	0.33/0.33	607	1	50(exp)	[88]
ZnO quantum dots	2.5/1	650	1	50(exp)	[89]
TiO <sub>2</sub> /graphene	0.5/1.5	330	1.75	70(exp)	[90]
SnO <sub>2</sub>	0.11/0.42	3400	10	100(exp)	[91]
Pd-SnO <sub>2</sub> -RGO	0.21/1.75	292	1	50(exp)	[92]
Pt-In <sub>2</sub> O <sub>3</sub>	-/5.96	2290	1	10(exp)	[93]
Pd-In <sub>2</sub> O <sub>3</sub>	4.5/4.7	950	0.5	100(exp)	[94]
MoTe <sub>2</sub>	/2.7	7000	2	20(exp)	[95]
ZnO	2.9/6.2	100	0.15	25(exp)	[96]

a: 3D FRGOH ( 3D chemically functionalized reduced graphene oxide hydrogel); b: 3D S-RGOH ( 3D sulfonated RGO hydrogel); c: RGO–IDTO ( Indium-doped SnO<sub>2</sub>-graphene), d: CNT (single walled carbon nanotube); e: WS<sub>2</sub>@MTCNFs (WS<sub>2</sub> edge functionalized carbon nanofibers); f: P<sub>3</sub>HT (poly(3-hexylthiophene)); g: PbS CQDs (PbS Colloidal Quantum Dots); h: VOPc/  $F_{16}$ CuPc (vanadyl phthalocyanine/ copper hexadecafluoro-phthalocyanine); i: PTCDI-Ph/p-6P ( N,N'-diphenyl perylene tetracarboxylic diimide / para-hexaphenyl) ; j: "~" means estimated value of figure obtained; k: "-" means cannot extracted the information from the article; m: the response time  $t_{50\%}$  is defined as the time to achieve 50% of its steady resistance in the response process, and the recovery time  $t_{50\%}$  is defined as the time to reach 50% of its original resistance in the signal recovery process; n: "exp." means experimental detection limits; o: MCN (multiwalled carbon nanotubes). p: CuTAP(t-Bu)<sub>4</sub> (tetra-(tert-butyl)-5,10,15,20-tetraazaporphyrin copper)



Figure S17. Dynamic response-recovery curves of three different 1 sensor toward 100 ppm NO<sub>2</sub> at rt and under visible light irradiation.



**Figure S18.** Dynamic response curves of **1** sensor against 100 ppm of typical interference gases under visible light at rt. (a) SO<sub>2</sub>, (b) CO<sub>2</sub>, (c) C<sub>6</sub>H<sub>6</sub>, (d) CH<sub>4</sub> and CH<sub>3</sub>-CH<sub>3</sub>, (e) NH<sub>3</sub>, (f) CH<sub>3</sub>NH<sub>2</sub>.



**Figure S19.** Dynamic response curves of **1** sensor against 100 ppm of typical interference gases under visible light at rt. (a)  $CH_2=CH_2$ , (b)  $CH\equiv CH$ , (c)  $H_2S$ , (d)  $Me_2CO$  (e) MeOH, (f)  $CH_3CH_2OH$ , (g)  $C_6H_5CH_3$ , (h) CO, (i)  $H_2$ .



Figure S20. Sensing results of 1 toward  $H_2O$  at rt and under visible light irradiation, (a) real-time dynamic response-recovery curve in the concentration range of 5%~100% RH, (b) response versus [RH%] graph.



Figure S21. (a-f) the response-recovery curves of 1 towards NO2 in 7 weeks.



Figure S22. The long-term stability of 1 for NO<sub>2</sub> detection.

$2NO_2 + O^2 \rightarrow NO_3^- + NO_2^-$	(1)
$NO_2 + e^- \leftrightarrow NO_2^-$	(2)
$NO_2 + O_2^- + 2e^- \leftrightarrow NO_2^- + 2O^-$	(3)
$NO_2 + 2e^- \leftrightarrow NO_3^- + NO^-$	(4)

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