Supplementary Information

Synthesis of Nanoporous 1, 2, 4-Oxadiazoles with High CO_2 Capture Capacity

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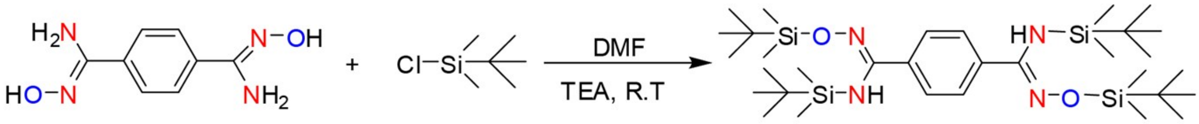
Experimental procedures

1. Materials

Materials for the experiment were 1,3,5-benzenetricarbonyl trichloride, triethylamine, dimethyl formamide (DMF), N-Methylpyrrolidone (NMP) and, *tert*-butyldimethylsilyl chloride (TBS). TBS was supplied from TCI, NMP was purchased from SAMCHUN and others were purchased from Sigma-Aldrich. DMF was purified by solvent distillation equipment and other reagents were used as received. Terephthalamidoxime (TPAO) was synthesized using the amidoxime synthesizing method [1].

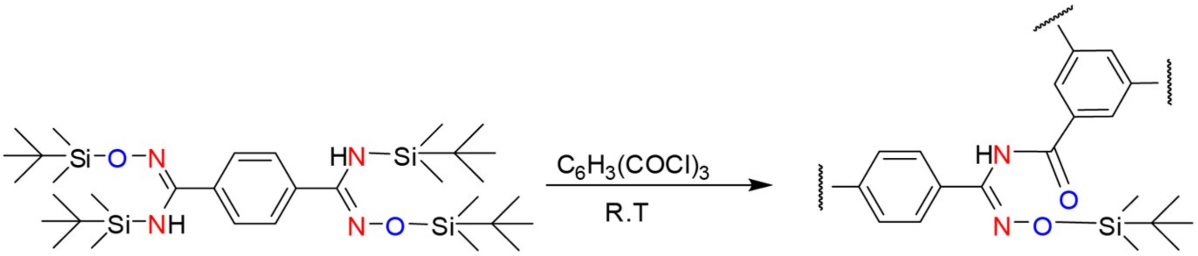
2. Synthesis

2.1 *tert*-butyldimethylsilyl-terephthalamidoxime (TBS-TPAO)



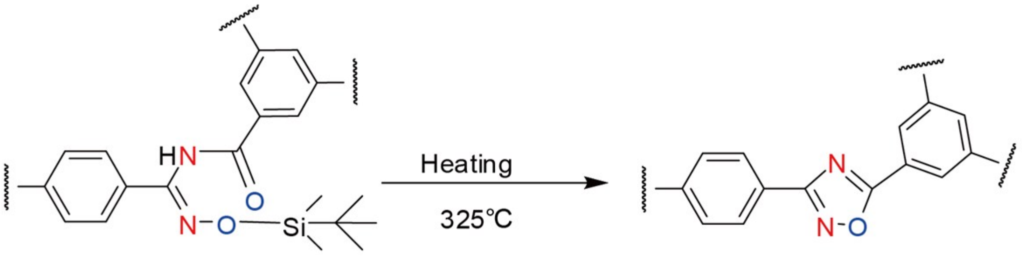
Under argon atmosphere 1g (5.14mmol) of terephthalamidoxime and tert-butyldimethylsilyl chloride (TBS) were dissolved in 50ml DMF. Afterwards 19.3ml of triethylamine was added and then stirred for 24hrs at room temperature. Subsequently the precipitate was filtered and rinsed with water and acetone, then the remaining solvent was removed by a rotary evaporator. Finally, the compound was dried at 80°C for 2hrs. The product showed light brown color the product weighing 1g (yield 30%). ^{1}H NMR (300MHz, DMSO, δ ppm from TMS): 7.70 (Ar-H), 6.15 (N-H), 0.96 (CH_3), 0.1 (CH_3, Si-methyl). FT-IR frequency: 3471 (N-H), 2958 (Ar-H), 2855 (CH_3), 1254 (CH_3). Elemental Analysis (CHN) Calculated: C, 58.8%; H, 10.4%; N, 8.50%. Found: C, 57.5%; H, 9.16%; N, 13.2%.

2.2 Pre-polymer (preOz-COP)



Polymerization was performed under an argon atmosphere. 1g (1.5mmol) of TBS-TPAO was dissolved in 15ml NMP solution. Once the reactor cooled down to 0℃, we added 0.28g (1mmol) of trimesoyl chloride. The mixture was stirred at room temperature for 48h. The solution was poured into methanol to precipitate and centrifuged in 5000rpm, 5000sec at 20℃. Lastly, it was rinsed with water to clearly remove NMP. The compound was dried in the vacuum oven 80℃ for 24h (0.5g). CP/MAS ^{13}C NMR: 175.1 (C=O), 157.8, 157.2 (C=N), 134.0, 129.3 (C-H, arom), 31.7 (CH_3, Si- methyl), 19.5, 18.5 (C-C, alkane) [2]. FT-IR frequency: 3337 (N-H), 1217 (CH_3), 1635 (C=O) [3]. Elemental Analysis (CHN) Calculated: C, 59.5%; H, 6.8%; N, 10.6%. Found: C, 53.3%; H, 4.04%; N, 15.44%.

2.3 Covalent organic polymer linked by 1,2,4-oxadiazole (Oz-COP)



To form oxadiazole covalent organic polymer (Oxadiazole-COP), it was heated at vacuum condition at 200℃ and 325℃ increased, step-by-step. Temperature increasing rate was 2℃/min. The solid obtained dark red color and weighed 10 mg. CP/MAS ^{13}C NMR: 164.9 (C, oxadiazole), 151.2 (C=N, oxadiazole), 136.1, 132.3 (C-H, arom), 121.1 (C, arom) [2]. FT-IR frequency: 900 and 1510 (Oxadiazole) [3]. Elemental Analysis (CHN) Anal. Calculated: C, 64%; H, 2.3%; N, 21%. Found: C, 65.6%; H, 3.5%; N, 17.2%.

3. Characterization and gas sorption measurements

^{13}C NMR spectra solid–state cross polarization magic angle spinning (CP/MAS) of oxadiazole–COP and pre-polymer were collected by a Bruker Avence III 400 WB NMR spectrometer. FT–IR spectra were measured using KBr pellets by a Perkin-Elmer FTIR spectrometer. Thermo gravimetric analysis (TGA) were performed on a SHIMADZU-TG 60A instrument under nitrogen atmosphere and heating the sample to 800°C at a rate of 10°C min−1. To evaluate the porosity and BET surface area (P/P_0=0.01–0.25) of oxadiazole-COP, N_2 adsorption isotherms at 77 K were obtained with a Micromeritics 3Flex surface characterization analyzer, activating the sample at 150℃ for 5 h under vacuum. The CO_2 and N_2 adsorption–desorption isotherms for oxadiazole-COP were measured at 273 and 298 K by using a static volumetric system (3Flex surface characterization analyzer, Micromeritics Inc.). The adsorption and desorption temperature were kept constant by using a PID controller.

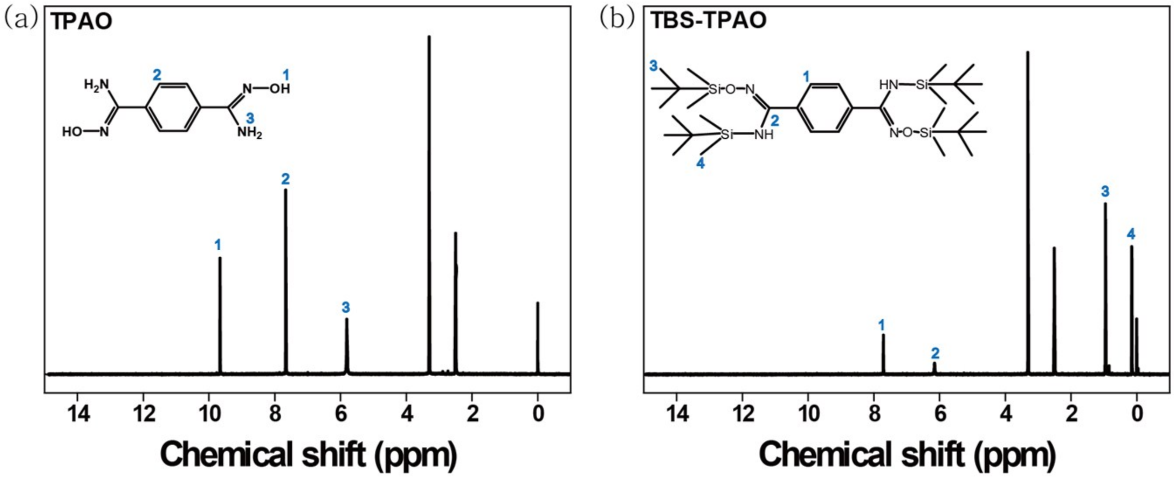


Figure S 1. NMR spectra of (a) Terephthalamidoxime (TPAO) and (b) TBS-TPAO. TPAO: ^{1}H NMR (DMSO), δ (ppm from TMS): 9.66 (2H, O-H), 7.67 (4H, Ar-H), 5.81 (4H, N-H). TBS-TPAO: ^{1}H NMR (DMSO), δ (ppm from TMS): 7.70 (4H, Ar-H), 6.15 (2H, N-H), 0.96 (CH_3), 0.1 (CH_3, Si- methyl)

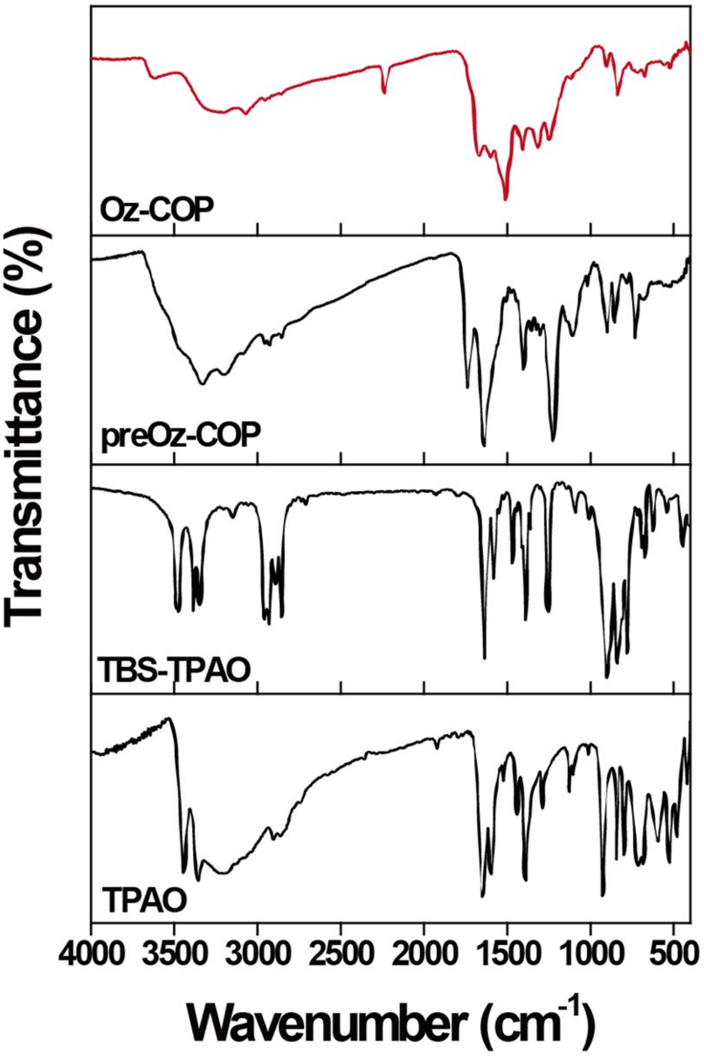
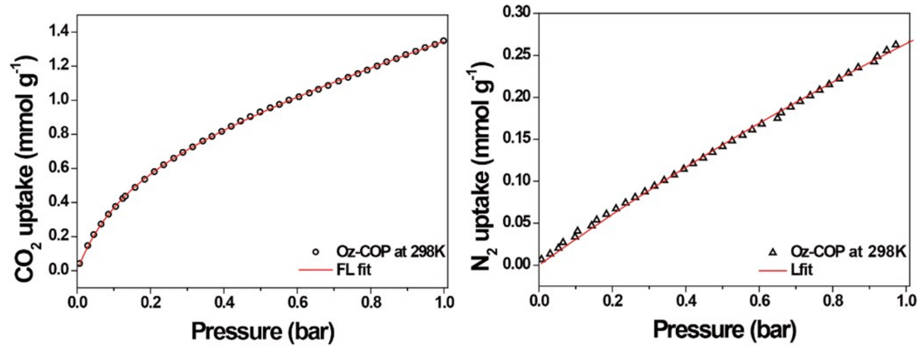
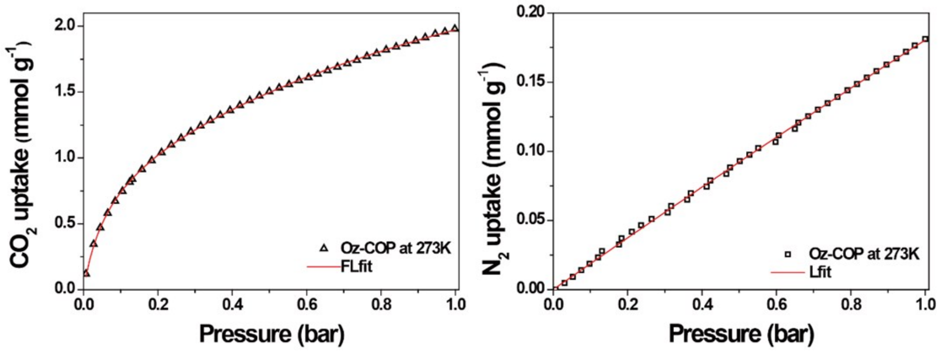


Figure S 2. FT–IR spectrum of TPAO, TBS-TPAO, preOz-COP and Oz-COP. TPAO: 3200-3400 (broad, O–H), 3355 (N–H), 1384 (C-N), 1648 (C=N), 926 (N–O). TBS-TPAO: 3471 (N-H), 2958 (Ar-H), 2855 (CH_3), 1254 (CH_3). PreOz-COP: 3337 (N-H), 1635 (C=O)(COCN), 1217 (CH_3). Oz-COP: 900 and 1510 (Oxadiazole) [3]



Model	FLfit for CO_2	Lfit for N_2
Equation	y=(q1*b1*x)/(1+b1*x) +(q2*b2*x)/(1+b2*x)	y=(q1*b1*x)/(1+b1*x)
Adj. R-Square	0.9998	0.998
q1	0.73227	1.65146
b1	6.74176	0.19011
q2	20.82823	
b2	0.03522	



Model	FLfit for CO_2	Lfit for N_2
Equation	y=(q1*b1*x)/(1+b1*x) +(q2*b2*x)/(1+b2*x)	y=(q1*b1*x)/(1+b1*x)
Adj. R-Square	0.9998	0.9993
q1	3.03938	4.20903
b1	0.56342	0.04479
q2	0.93193	
b2	16.21579	

Figure S 3. IAST selectivity of Oz-COP at 273K and 298K. Freundlich-Langmuir model fits (IAST) selectivity for CO_2 and N_2 adsorption of Oz-COP at 273K.

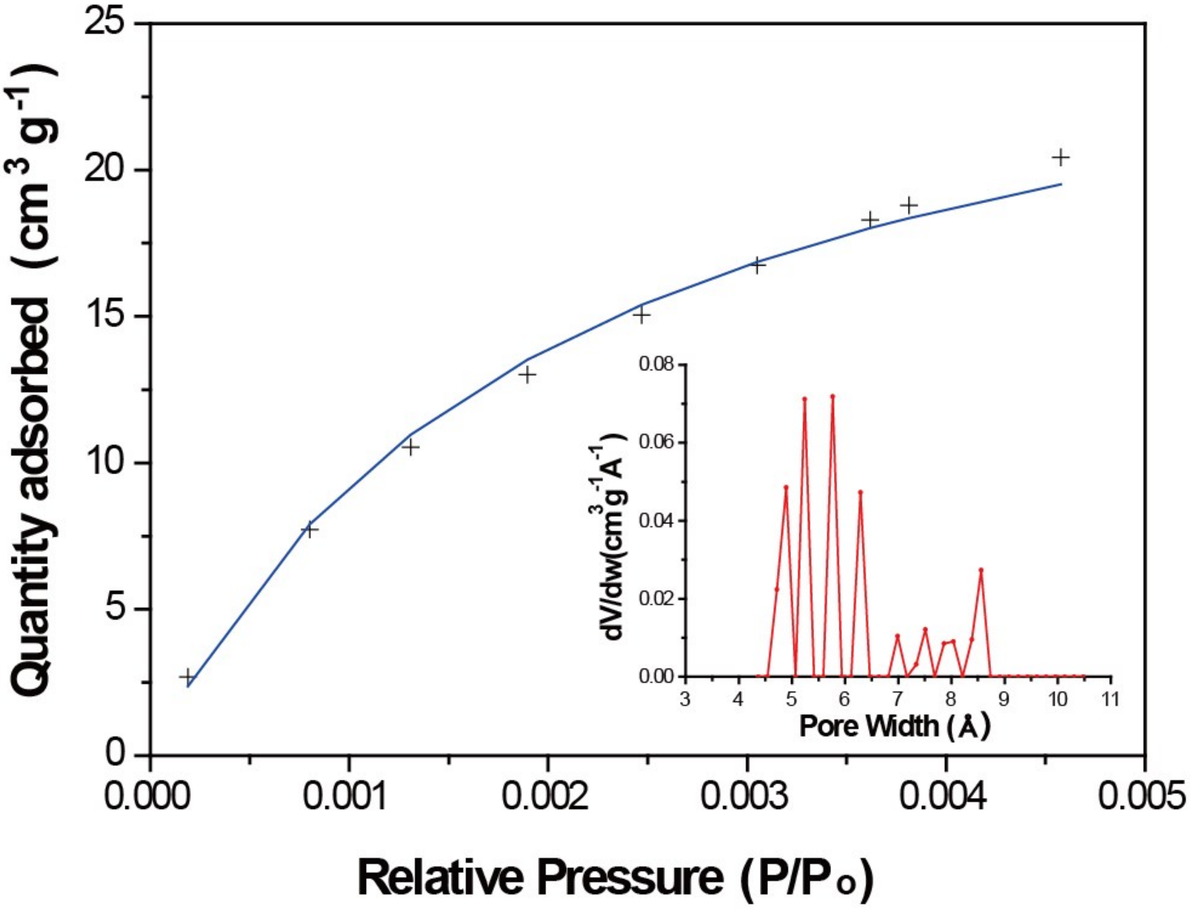


Figure S 4. BET surface area and pore size distribution (inset). BET surface area from CO_2 isotherm at 273K at low pressure (0.15 bar): cross shape plot is the measured isotherm of CO_2 and blue line is fitted data by BET equation. 107.2 m^2/g of BET surface area was found. **Inset:** pore size distribution calculated by DFT, model: CO2 DFT.

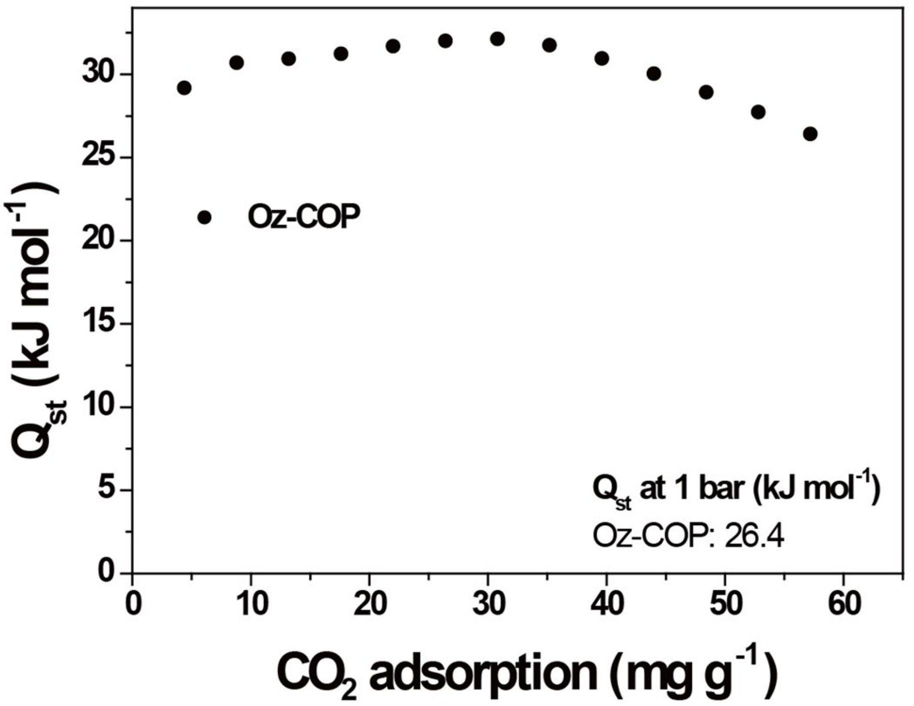


Figure S 5. Isosteric heat of CO_2 adsorption for Oz-COP. Heat of adsorption (Q_{st}) calculated by Van't Hoff equation at 273K, 298K. CO_2 can be uptake to Oz-COP by their low Q_{st} as physisorption. Since only two temperature points are used, the Qst shows increase (although slightly) until 30 mg/g uptake. This slope means initially range before 30 mg/g the pores are started to open and diffused into the pore and it makes the increasing plot.

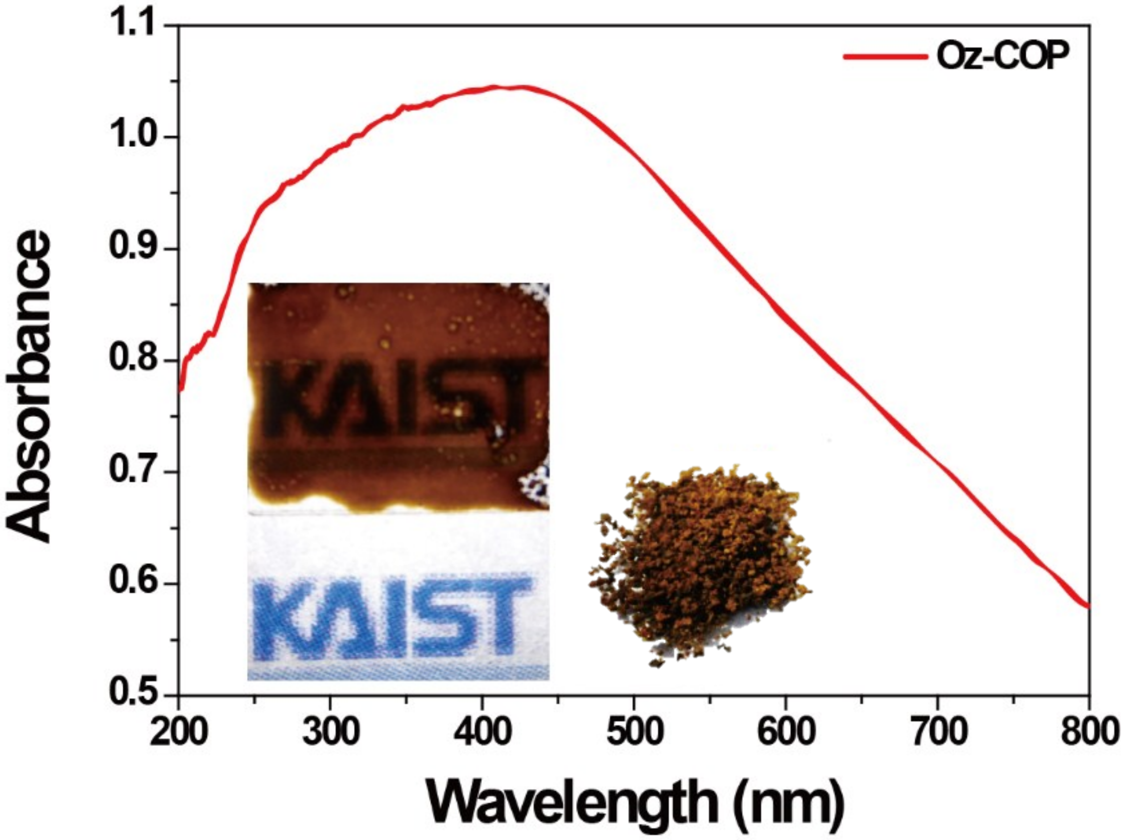


Figure S 6. UV-visible spectroscopy of oxadiazole-COP. Oxadiazole-COP absorb mainly 300nm - 500nm and reflect red region 700nm. The compound color is brown.

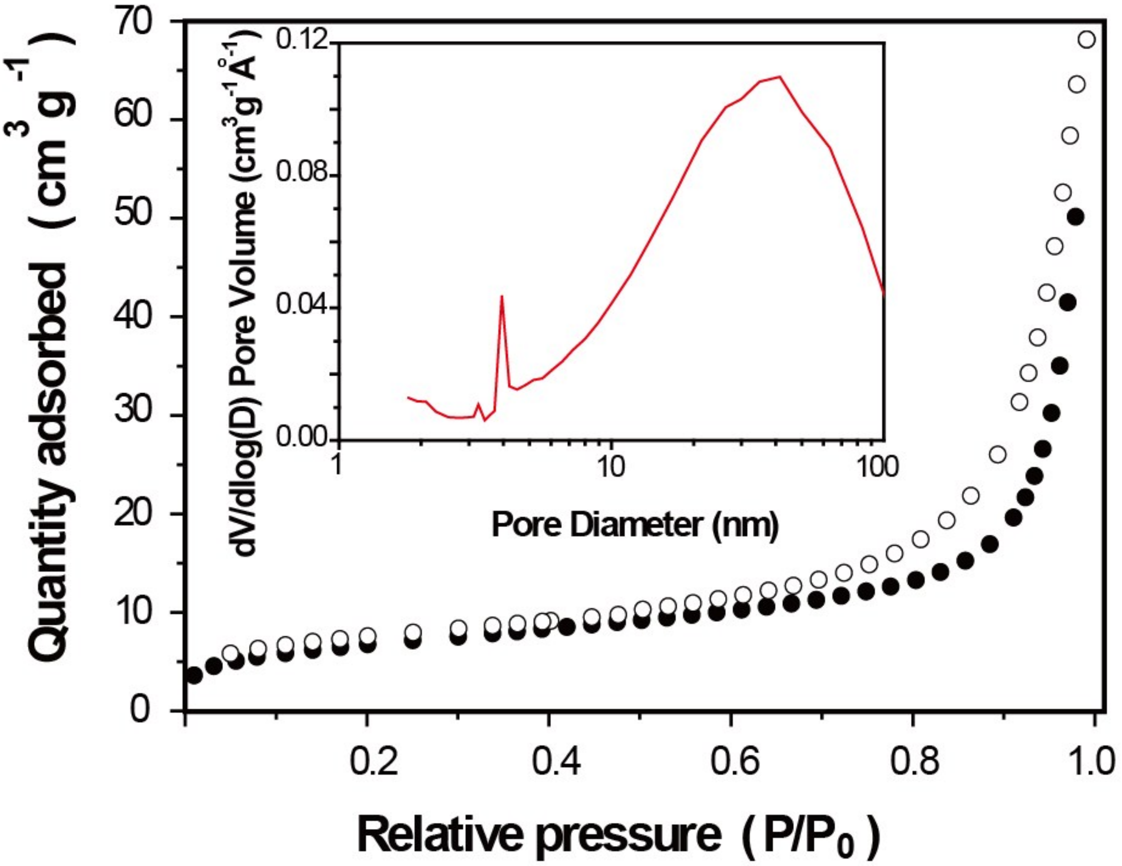


Figure S 7. Nitrogen adsorption-desorption isotherm of oxadiazole-COP measured at 77K. It shows 24.5m^2/g of surface area. Filled and empty symbols represent adsorption and desorption. (Inset: Differential pore size distribution curves from BJH method)

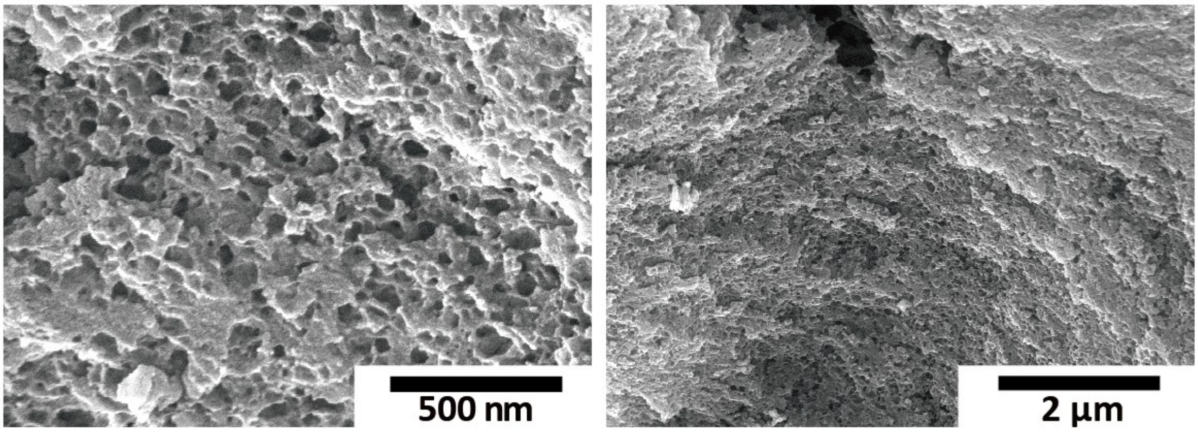


Figure S 8. SEM imaging of the Oz-COP. SEM micrographs show porous morphology and the continuity in the network formation of the oxadiazole covalent organic polymer.

Table S1. Numerical values of CO2 adsotpion for Oz-COPs at 273K and 298 K.

	CO$_2$ adsorption at 273K		CO$_2$ adsorption at 298K	
	Pressure, bar	mmol/g	Pressure, bar	mmol/g
1	0.006492	0.120146	0.006737	0.042177
2	0.027559	0.344697	0.028978	0.147738
3	0.044996	0.47033	0.045767	0.212342
4	0.065234	0.581149	0.065742	0.27409
5	0.084982	0.672007	0.085472	0.330451
6	0.10493	0.747757	0.105037	0.377154
7	0.124471	0.816592	0.124801	0.423401
8	0.131168	0.83909	0.131466	0.437243
9	0.157401	0.91238	0.157913	0.488043
10	0.183576	0.980123	0.184286	0.535831
11	0.209859	1.042024	0.210815	0.580837
12	0.235936	1.09995	0.23602	0.621245
13	0.26229	1.150208	0.263488	0.659322
14	0.288766	1.19912	0.288579	0.694194
15	0.314946	1.243841	0.31493	0.726437
16	0.340947	1.285153	0.342547	0.760503
17	0.36756	1.324072	0.367528	0.788165
18	0.394141	1.361219	0.393819	0.817371
19	0.42059	1.399726	0.420207	0.846696
20	0.447034	1.43695	0.445914	0.877569
21	0.473417	1.470976	0.47237	0.904628
22	0.499881	1.503993	0.498753	0.930921
23	0.526344	1.531882	0.526551	0.955753
24	0.552632	1.558567	0.551276	0.975322
25	0.579143	1.589214	0.577473	1.001013
26	0.605585	1.610822	0.604897	1.020436
27	0.630269	1.637262	0.632939	1.043168
28	0.656776	1.663821	0.657612	1.064014
29	0.683172	1.691231	0.684226	1.0869
30	0.709694	1.716762	0.712246	1.111748
31	0.735352	1.742004	0.738464	1.134324
32	0.762101	1.77208	0.765019	1.156417
33	0.788444	1.793696	0.790779	1.176926
34	0.81409	1.82147	0.817721	1.2008
35	0.841001	1.843712	0.843466	1.225352
36	0.867334	1.866898	0.870223	1.244533
37	0.893728	1.889151	0.895784	1.267862
38	0.919371	1.914522	0.922753	1.287667
39	0.94629	1.941606	0.948194	1.308569
40	0.972278	1.957264	0.975191	1.327592
41	0.998581	1.979881	0.99873	1.349274

Supplementary References

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3. D. Grant, R. Dahl and N. D. P. Cosford, *The Journal of Organic Chemistry*, 2008, **73**, 7219-7223.