Triazatruxene Based Covalent Organic Framework and its Quick-response Fluorescence-on nature towards electron rich arenes

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C: Klghei of Environment and Energy Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University. Guangzhou 510275, China. Section 1: Materials and Methods Section 2: Synthesis Section 3: The screening of reaction condition for TAT-COF-1 Section 4: Characterization of TAT-COF-1 and TAT-COF-2 Section 5: The adsorption selectivity of CO₂ toward N₂

Section 5: Fluorescence studies of TAT-COF-2

Section 1: Materials and Methods

2,7,12-Tribromo-5,10,15-triethyltriindole (2-Br-TAT) was synthesized according to the reported method.^[1] Toluene and tetrahydrofuran and 1,4-dioxane were redistilled from sodium. Dichloromethane was redistilled from calcium hydride. All other starting materials and solvents, if not specially mentioned, were obtained from commercial suppliers and used without further purification. IR spectra were recorded on a Thermo-Nicolet 6700 spectrometer using KBr palettes. ¹³C CP-MAS NMR spectra were recorded on a BRUKER AVANCE III 400MHz solid state NMR spectrometer. Thermogravimetric analysis was performed on SDT Q600 V20.9 Build 20 with a temperature ramping rate of 5 $\,^{\circ}$ C min⁻¹ from room temperature to 600 $\,^{\circ}$ C. Scanning electron microscopy (SEM) was performed on S-4300 scanning electron microscope at 15.0 KV. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/max 2500 X-ray powder diffractometer, from 2 θ = 2 $\,^{\circ}$ up to 45 $\,^{\circ}$ or 30 $\,^{\circ}$ with 0.02 $\,^{\circ}$ increment. Nitrogen adsorption-desorption isotherms were carried out with a Micrometrics ASAP 2020 instrument at 77 K. Hydrogen adsorption isotherms were measured at 77 K from 0 to 823 mmHg on Micrometric ASAP 2020 instrument. Carbon dioxide adsorption isotherms were measured at 273 K

from 0 to 823 mmHg on Belsorp-HP. Geometry optimization of the hexagonal lattice pore structure was performed at Forcite Module in Material Studio 6.0.

Section 2: Synthesis

2,7,12-Triformyl-5,10,15-triethyltriindole (2-CHO-TAT):



333 mg (0.5 mmol) 2-Br-TAT was put into a 50 ml two neck bottle under nitrogen atmosphere, then 10 ml anhydrous THF was added with syringe, cooled to -78 $^{\circ}$ C and 1.4ml n-BuLi (2.25mmol, 1.6M in cyclohexane) was added by drop slowly with syringe, and kept stirring for 2 hours. Then 232uL anhydrous DMF (3mmol) was added by syringe, kept the reaction at -78 $^{\circ}$ C for another 0.5h and then warm to room temperature for 1h. After reaction, the reaction was quenched by 3M HCl carefully, then the THF was removed by vacuum distillation. The residue was filtered purified by recrystallization from DCM/PE and titled product was got as a yellow powder (163mg) after dried under vacuum with yield of 64%.

¹H NMR (400 MHz, CDCl₃): δ (ppm) 10.22 (s, 3H), 8.43 (d, J = 8.4 Hz, 3H), 8.23 (d, J = 1.2 Hz, 3H), 7.92 (dd, J = 8.4, 1.4 Hz, 3H), 5.10 (q, J = 7.2 Hz, 6H), 1.68 (t, J = 7.2 Hz, 9H).

¹³C NMR (101 MHz, CDCl₃): δ (ppm) 192.3, 142.0, 140.5, 132.1, 128.4, 123.6, 121.6, 111.7, 100.2, 42.3, 15.9.
HRMS (ESI-): calcd for C₃₃H₂₇N₃O₃: 513.2052, found 513.2043.

2,7,12- triamino-5,10,15-triethyltriindole:



Firstly, 140mg BINAP (10%mol) and 130mg Pd₂(dba)₃ (10%mol) were put into a 50 ml two neck bottle under nitrogen atmosphere, then 30ml anhydrous toluene was added by syringe. The reaction was kept at 110 °C for 0.5h and cooled to R.T., and 500 mg (0.754 mmol) 2-Br-TAT, 495mg t-BuOK (4.4mmol) and 740uL diphenylmethanimine (4.4mmol) were added under nitrogen atmosphere, then warm to reflux for another 36 hours. After the reaction was completed, it was cooled to r.t. and filtered by diatomite. Then toluene was removed under vacuum and the residue was purified by chromatography (PE/EA = 6/1), the titled compound was got as a dark red-brown powder (500mg) when solvent was removed and dried under vacuum with yield of 69%;

Secondly, 300mg compound **a** (0.31mmol) was added to a 50ml two neck flask, 10ml THF was added under nitrogen atmosphere with syringe, followed by 0.5ml 2M HCl was added by drop with syringe. After 30 minutes, the residue was filtered and washed with THF and n-butane and compound **b** was got as a red-brown powder (148mg) after dried in vacuum with yield of 82%;

Finally, 200mg of compound **b** (0.34mmol) was dissolved in water and TEA was added by drop slowly with stirring, gray precipitation appeared and was collected by filtration, after dried in vacuum, the titled compound was received as a gray-green powder (137mg) with yield of 85%.

¹H NMR (400 MHz, DMSO): δ 7.88 (d, J = 8.0 Hz, 3H), 6.85 (s, 3H), 6.61 (s, 3H), 5.13 (s, 6H), 4.72 (s, 6H), 1.39 (t, J = 6.6 Hz, 9H).

¹³C NMR (100 MHz, DMSO): δ 145.5, 142.6, 134.7, 121.7, 113.5, 108.6, 103.4, 94.7, 40.7, 14.9.

HRMS (ESI-): calcd for C₃₀H₃₀N₆: 474.2532, found 474.2526.

TAT-COF-1:

76.8 mg (0.15 mmol) 2-CHO-TAT and 24.3 mg (0.225 mmol) p-phenylenediamine were added to a 50 ml schlenk tube, 6 ml ethanol and 1.2 ml 3M acetic acid were added with syringe under nitrogen, then three freeze-pump-thaw circles were carried out and then the tube was sealed and put into an oil bath, heated to 90 °C for 7 days. After reaction, the precipitate was collected by filtration, washed with plenty of anhydrous tetrahydrofuran (THF), then soaked in THF for 24h for solvent exchange, filtrated and dried at 120 °C for 12h under high vacuum to give TAT-COF-1 as a brown powder with yield of 79%.

TAT-COF-2:

51.3 mg (0.1 mmol) 2-CHO-TAT and 47.4 mg (0.1 mmol) 2-NH₂-TAT were added to a 50 ml schlenk tube, 7.5 ml ethanol and 1.5 ml 3M acetic acid were added with syringe under nitrogen, then three freeze-pump-thaw circles were carried out and then the tube was sealed and put into an oil bath, heated to 90 °C for 6 days. After reaction, the precipitate was collected by filtration, washed with plenty of anhydrous tetrahydrofuran (THF), then soaked in THF for 24h for solvent exchange, filtrated and dried at 120 °C for 12h under high vacuum to give TAT-COF-2 as a

brown powder with yield of 87%.



Figure S1: ¹H-NMR spectrum of 2-CHO-TAT.







Section 3: The screening of reaction condition for TAT-COF-1

A lot of reaction conditions had been screened for the synthesis of TAT-COF-1, the conditions and their corresponded PXRD were listed in table S1 and Fig S5.

NO.	Solvent (volume ratio)						
	Dioxane	Mesitylene	Ethanol	o-dichlorobenzene	n-butanol	DMAc	AcOH
1	5	15	-	-	-	-	2 (3M)
2	-	-	5	-	-	-	1 (3M)
3	5	15	-	-	-	-	2 (6M)
4	5	5	-	-	-	-	1 (6M)
5	-	_	5	-	-	-	1 (6M)
6	5	_	-	-	-	-	1 (6M)
7	-	5	-	-	-	-	1 (6M)
8	-	5	5	-	-	-	1 (6M)
9	-	_	-	5	5		1 (6M)
10	-	_	-	-	5	5	1 (6M)
11	-	_	5	5	-	-	2 (3M)
12	-	-	-	5	-	5	2 (3M)
13	5	-	-	5	-	-	1 (3M)
14	-	_	-	5	5	-	1 (3M)
15	-	-	5	-	-	5	1 (3M)
16	5	-	-	-	-	5	1 (3M)
17	-	-	-	-	5	5	1 (3M)





Figure S5. The results of conditions screened for TAT-COF-1, a: conditions for 1 to 10; b: conditions for 11 to 17 with condition 2 as comparation, no products were collected in condition 13 and 16.

Section 4: Characterization of TAT-COF-1 and TAT-COF-2



Figure S6. The IR spectrum of TAT-COF-1 (a) and TAT-COF-2 (b).



Figure S7. The ¹³C NMR spectra for TAT-COF-1 (left) and TAT-COF-2 (right). The carbon signal for imine appeared and aldehyde signal disappeared totally for both COFs.



Figure S8. The TGA analysis results of TAT-COF-1 (left) and TAT-COF-2 (right), both COFs were stable under 400 °C.



Figure S9. The SEM of TAT-COF-1 (left) and TAT-COF-2 (right).



Figure s10. a) and c): the staggered models of TAT-COF-1, b) and d): the staggered models of TAT-COF-2.



Figure S11. The BET plot of TAT-COF-1 (up) and TAT-COF-2 (below).

Section 5: The adsorption selectivity of CO₂ toward N₂

The adsorption selectivity (S_{ads}) was calculated based on the following formula^[2]:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

Here q_1 and q_2 are the absolute adsorption, p_1 and p_2 are the related pressure.

Section 6: Fluorescence studies of TAT-COF-2

The Preparation of thin layer samples for test Uv-Vis, the preparation of saturate arenes vapors and the detect of arenes are followed the procedure as reported^[3] except for the cycle test and enhanced and quench cycle test, which had been described in the text.

The calculation of detection limit for guests was based on the stern-volmer formula:

$$F_0/F = 1 + K_D[Q]$$

Here F_0 is the fluorescence intensity without guests and F is the fluorescence intensity with guest, K_D is the quencher coefficient, and [Q] is the concentration of quencher. The fluorescence intensity of limit of detection was assumed as 3% of the fluorescence intensity without guest.



Figure S12. The fluorescence-on and fluorescence-off of TAT-COF-2 in different solvents; the detection limit for Mes and Tol were about 170.5nM and 179.4nM respectively.



Figure S13. The fluorescence-on and fluorescence-off of TAT-COF-2 detected in arene vapors, a: exposed in toluene vapor; b: exposed in chlorobenzene vapor; c: exposed in mestiylene vapor and d: exposed in nitrobenzene vapor.

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