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COMMUNICATION

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

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Two new 2D covalent organic frameworks (COFs) with regular honeycomb lattice: TAT-COF-1 and TAT-COF-2 were synthesized based on triazatruxene derivatives. The two COFs, especially TAT-COF-2, has large BET surface area, good crystallinity, moderate to good hydrogen and carbon dioxide adsorption abilities and it also possesses good CO₂/N₂ selectivity. When suspended in ethanol, the fluorescence of TAT-COF-2 could be enhanced or quenched by different solvents. It also shows a rapid fluorescence-on and fluorescence-off nature towards electron rich and deficient arene vapors respectively. After been exposed in electron-rich arene vapors, the enhanced fluorescence intensity can be recovered in 5 minutes in ambient atmosphere, which means the sample could be reused conveniently for detecting electron rich arene vapors.

Covalent organic frameworks (COFs), first reported by O. M. Yaghi and co-workers in 2005, are a new class of micro-crystalline polymers constructed according to reticular chemistry.¹⁻³ COFs are linked by strong covalent bonds, such as boroxine/boronate ester,¹ imine,⁴ hydrazone,⁵ triazine⁶ and imide⁷ rather than metal coordination, which make them more stable and lower in density than MOFs.⁸ These remarkable natures of COFs together with their high porosity, high surface area and outstanding thermal stability endow them with many potential applications such as gas storage, gas separation^{9,10} and catalysis.¹¹⁻¹⁷ Moreover, the highly ordered π - π conjugation and regular pore structures of 2D-COFs make them been widely studied on optoelectronic applications.¹⁶⁻²⁴ But even had been discovered for more than 10 years, the applications of COFs are limited. Herein, based on triazatruxene derivatives, two new 2D-COFs, namely TAT-COF-1 and TAT-COF-2 were synthesized, and the fluorescence property of TAT-COF-2 was studied, the re-

sults show that it possesses a quick response towards electron rich arenes vapor, which may shed light on a new application area of COFs as chemical sensors.

Triazatruxene (TAT) consisting of a C₃ symmetric cyclotrimer of indole, is a star shape planar π -conjugated arylamine derivative with strong electron donating ability.²⁵ It has three potential docking sites at 5, 10 and 15 positions (Fig 1a), and the three phenyl groups could also be modified by varies of functional groups. Consequently, TAT derivatives have been widely investigated in supramolecular chemistry, especially in organic electronics.²⁵⁻²⁷

Imine COFs are less prone to moisture than boroxine/boronate ester COFs,²⁸ so firstly, 2-CHO-TAT (Fig 1b) was designed and synthesized. TAT-COF-1 was synthesized under solvothermal condition by condensation of 2-CHO-TAT and benzene-1,4-diamine (Scheme 1a, see supporting information for all experiment details), but powder X-ray diffraction (PXRD) analysis reveals that the crystallinity of TAT-COF-1 is fairly poor (Fig 2a). However, after screening for many conditions (Tab S1, Fig S5), the crystallinity remains poor. Then, 2-NH₂-TAT (Fig 1c) was designed and synthesized and TAT-COF-2 was synthesized (Scheme 1b). We are excited to see that the crystallinity of TAT-COF-2 improved a lot when compared with TAT-COF-1 (Fig 2b).

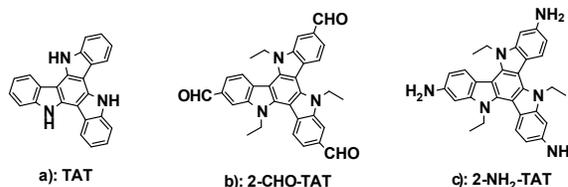


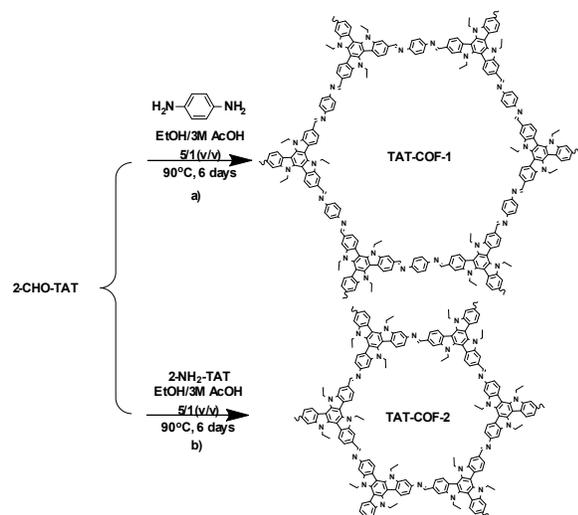
Figure 1. The structures of a) TAT; b) 2-CHO-TAT and c) 2-NH₂-TAT.

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Electronic Supplementary Information (ESI) available: Detailed experiments, characteristic of compounds and TAT-COFs, fluorescence studies. See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of a) TAT-COF-1 and b) TAT-COF-2.

The FTIR spectrum of both COFs show vibrational peaks for imine at 1567 cm^{-1} for TAT-COF-1 and at 1570 cm^{-1} for TAT-COF-2, the peaks of aldehyde group at 1685 cm^{-1} and amino group at 1623 cm^{-1} for starting materials diminished dramatically, suggesting that reactions were carried out thoroughly (Fig S6). The solid-state ^{13}C CP-MAS NMR spectrum further confirmed the formation of the expected imine bonds (Fig S7). Furthermore, thermo-gravimetric analysis (TGA) under nitrogen atmosphere revealed that both COFs were stable up to $420\text{ }^\circ\text{C}$ (Fig S8). The phase purity of both COFs were confirmed by Scanning electron microscopy (SEM), only one morphologically unique crystalline phase could be seen for each COF (Fig S9). PXRD analysis was used to determine the crystalline structure of both COFs. The result of TAT-COF-1 (Fig 2a) displays peaks at 2.90° , 5.09° , 7.73° , 10.16° , and 22.66° , which can be assigned to the (1, 0, 0), (1, 1, 0), (2, 2, 0) and (0, 0, 1) facets respectively; and the result of TAT-COF-2 (Fig 2b) displays peaks at 4.09° , 7.12° and 23.46° , which can be assigned to the (1, 0, 0), (1, 1, 0) and (0, 0, 1) facets respectively. The reflections reveal that both COFs take honeycomb (hcb) lattice. Eclipsed (Fig 2c ~ 2f) and staggered models (Fig s10) were constructed for both COFs by Material Studio program. The AA stacking models were constructed using space group of $P6$ with the optimized parameters of $a = b = 35.918\text{ \AA}$ and $c = 4.054\text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ for TAT-COF-1 (Fig 2c and 2d) and space group of $P3$ with the optimized parameters of $a = b = 25.076\text{ \AA}$ and $c = 4.135\text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ for TAT-COF-2 (Fig 2e and 2f). The simulated results show both COFs take eclipsed AA arrangement (Fig 2a, 2b).

Nitrogen sorption isotherm measurement at 77 K was used to test the porosity of both COFs. Due to poor crystallinity, the quantity adsorption of TAT-COF-1 is below $25\text{ cm}^3/\text{g}$ at standard pressure. However, for TAT-COF-2, which possesses a good crystallinity, a sharp uptake appears at low pressure ($P/P_0 < 0.1$, Fig 3a), revealing a type I isotherm curve, which is characteristic of microporous materials. The Brunauer-Emmett-Teller (BET) models were applied for TAT-COF-1 and TAT-COF-2 at

P/P_0 between 0.05 and 0.20, which show the calculated BET surface areas were $61.2\text{ m}^2/\text{g}$ and $1166.1\text{ m}^2/\text{g}$ respectively (Fig S11). The total pore volume at ($P/P_0 = 0.99$) were about $0.11\text{ cm}^3/\text{g}$ for TAT-COF-1 and $0.62\text{ cm}^3/\text{g}$ for TAT-COF-2. The density functional theory (DFT) model of TAT-COF-2 was fitted to the isotherm which shows the main pore size distribution was around 1.48 nm (Fig 3b). Low pressure hydrogen adsorption at 77 K (Fig 3c) and low pressure carbon dioxide adsorption at 273 K were measured for TAT-COF-2 (Fig 3d). The maximum H_2 and CO_2 uptake were $109.26\text{ cm}^3/\text{g}$ and $38.99\text{ cm}^3/\text{g}$ respectively. TAT-COF-2 has many bare N sites, which may lead to high CO_2/N_2 selectivity, so low pressure N_2 adsorption at 273 K was also measured (Figure 3e). The calculated selectivity toward CO_2 and N_2 is about 5.9 (Figure 3f, see ESI for detail).

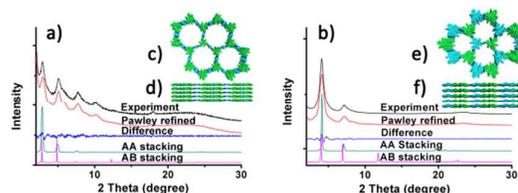


Figure 2. PXRD patterns of a) TAT-COF-1; b) TAT-COF-2; c) and d) AA stacking model of TAT-COF-1; e) and f) AA stacking model of TAT-COF-2

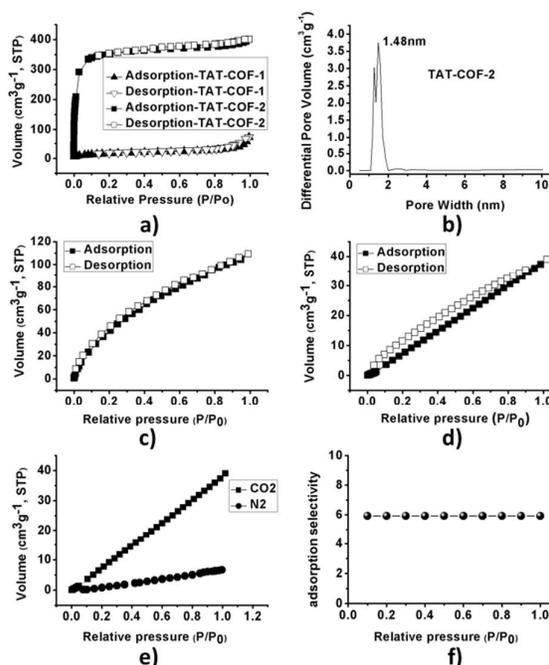


Figure 3. a) Nitrogen adsorption of TAT-COF-1 and TAT-COF-2; b) Average pore distribution of TAT-COF-2; c) Hydrogen adsorption of TAT-COF-2; d) Low pressure carbon dioxide adsorption of TAT-COF-2 at 273 K ; e) Nitrogen and Carbon dioxide adsorption at the same condition; f) The adsorption selectivity of CO_2 toward N_2 .

A highly luminescent conjugated microporous polymer (TCB-CMP) based on a TAT derivative had been synthesized by D. L. Jiang, which possess a sensitive fluorescence-on and fluorescence-off characteristics when exposed to electronic rich and deficient arene vapors respectively, so it can be used to sense chemicals.²⁹ Compared to amorphous polymers, COFs are mi-

cro-crystalline structures, so they may have a quick response when being used as sensors. All parameters of TAT-COF-2 show it was a highly porous microcrystalline material with high BET surface area, so it was selected to do fluorescence research.

Firstly, UV-VIS of thin-layer sample of TAT-COF-2 on quartz was tested (Fig 4a), the result shows that the maximum adsorption is at 485 nm. 2 mg of TAT-COF-2 in 4 ml anhydrous ethanol was sonicated for 30 min to make sure it was uniformly dispersed to get a 500 $\mu\text{g/ml}$ suspension which was then diluted to different concentrations by ethanol and fluorescence were tested immediately with an excitation wavelength of 485 nm. The fluorescence results show that the maximum adsorption of TAT-COF-2 appears at about 100 $\mu\text{g/ml}$ when suspended in ethanol (Fig 4b), and the adsorption diminished but with low extent when the suspension was further diluted (Fig 4b and 4c).

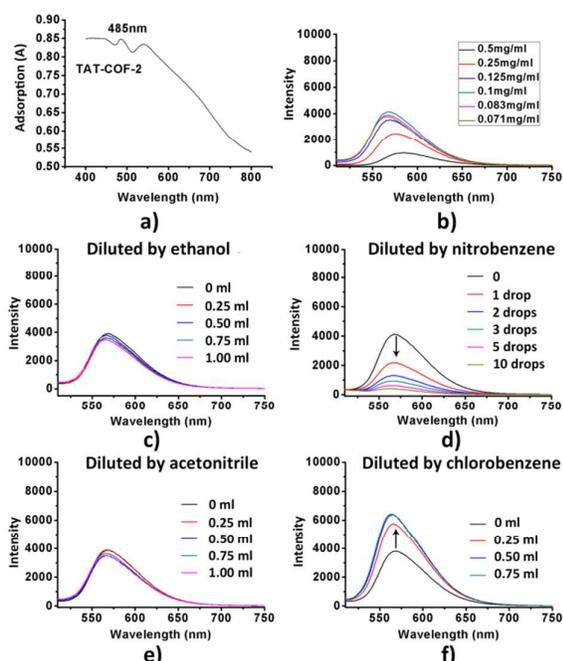


Figure 4. a): UV-Vis adsorption of TAT-COF-2, b): Fluorescence of TAT-COF-2 suspended in ethanol at different densities; 100 μg TAT-COF-2 suspended in 1 ml ethanol and diluted with c): ethanol, d): nitrobenzene, the calculated detection limit (see ESI for detail) is about 10 mM; e): acetonitrile and f): chlorobenzene, the calculated detection limit is about 198 mM.

Then, the fluorescence nature of TAT-COF-2 suspended in ethanol was studied. 1 ml of the 100 $\mu\text{g/ml}$ suspension was diluted with different solvents and the changes of fluorescence intensities were recorded. The results show that the fluorescence intensities vary widely (Fig 4c~f, S12): if further diluted with ethanol, the fluorescence intensity almost kept no change (Fig 4c); when diluted with nitrobenzene, methanol, 2-nitrotoluene, water, n-butanol, tetraethylene glycol, dioxane and phenol solution, the intensities were quenched (Fig S12). Especially nitrobenzene, when 1 drop of it was added to the suspension, the fluorescence intensity almost quenched by

50%, and 5 drops could almost totally quench the intensity (Fig 4d), 2-nitrotoluene and phenol could also quenching the fluorescence significantly (Fig S12). When diluted with acetonitrile (Fig 4e) or acetone, the intensity can be retained. When diluted with N-methylpyrrolidone, tetrahydrofuran, toluene, chlorobenzene (Fig 4f), o-dichlorobenzene, mesitylene, brombenzene, 1,2-dimethylbenzene, ether, triethylamine, pyridine, dimethylformamide, ethyl acetate, dimethylacetamide, dimethyl sulfoxide, hexane and chloroform the fluorescence intensities could be enhanced. The regularity is not very clear, but for arenes analytes, it can be concluded that the fluorescence could be enhanced by electron rich arenes can quenched by electron deficient arenes. The reasons for these phenomenons may due to the electron transfer: when electrons were transferred from TAT-COF-2 to arenes, the fluorescence was quenched, and otherwise, the fluorescence was enhanced.²⁹

Since TAT-COF-2 is stable and insoluble in most common solvents, it will be convenient for it to application at solid state. The solid state fluorescence characteristics of it were studied by exposing thin-layer samples of TAT-COF-2 to saturate arene vapors for 60 and 120 seconds at ambient temperature. The results (Fig 5, S13) were concordant with the results tested by suspended in ethanol: the fluorescence intensities were enhanced by electron-rich arene vapors and quenched by electron-deficient nitrobenzene. For example, when exposed to toluene and mesitylene vapors for 60 seconds, the fluorescence intensities were increased by 60%, upon exposure to chlorobenzene for 60 seconds, the intensity was almost doubled; when exposed to nitrobenzene vapor for 60 seconds, the intensity was quenched by about 50%. However, when exposed to these vapors for about 120 seconds, the intensities did not increase much compared with 60 seconds, which means TAT-COF-2 could be saturated by arene vapors quickly. These results further confirmed the deduction mentioned above: when exposed in electron rich arenes, the electrons were transferred from arenes to TAT-COF-2, which lead to an increase of the electron cloud density of TAT-COF-2, as a result, the fluorescence could be enhanced. On the contrary, electron deficient arene could decrease the electron cloud density of TAT-COF-2, and the fluorescence was quenched.

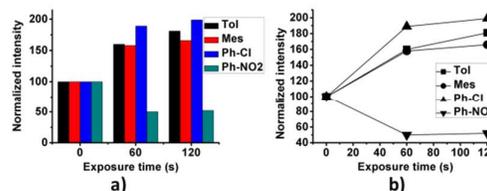


Figure 5. The fluorescence results of TAT-COF-2 thin-layer samples tested in arene vapor. a): column form; b): trend line form (■: toluene; ●: mesitylene; ▲: chlorobenzene; ▼: nitrobenzene).

Due to the presence of regular pore structures, when the thin-layer sample of TAT-COF-2 was removed from electronic rich arene vapor the fluorescence intensity went down quickly since the vapors can escape from the pore easily, which means

it has a quick responsibility towards electronic rich arenes vapor. Take toluene vapor as an example, firstly, the thin-layer sample was exposed in the toluene vapor for 60 seconds, then, the vapor was removed, and fluorescence intensity decreased rapidly, and stabilized to normal level after 5 minutes (Fig 6a, cycle 1). When the sample was exposed into the toluene vapor for another 60 seconds, the fluorescence intensity increased, and then, when the toluene vapor was removed again, the fluorescence intensity decreased once more and stabilized in another 5 minutes (Fig 6a, cycle 2). After three cycles, the fluorescence intensity decreased to a stable level (Fig 6a, cycle 3 and cycle 4) which was higher than normal level due to the small remnant of toluene vapor in the COF pores. If the thin-layer sample was firstly exposed in electron-rich vapor 30 seconds, like chlorobenzene, the fluorescence intensity was enhanced (Fig 6b, cycle 1); and then if it was exposed in electron-deficient vapor 120 seconds, like nitrobenzene, the fluorescence intensity was quenched and could not recovery automatically at ambient environment or even exposed in chlorobenzene vapor for 120 seconds again (Fig 6b, cycle 2 and cycle 3). This may due to the TAT-COF-2 are electron-rich COF, Which may has a stronger interaction with those electron-deficient arenes than electronic rich arenes at ambient atmosphere.

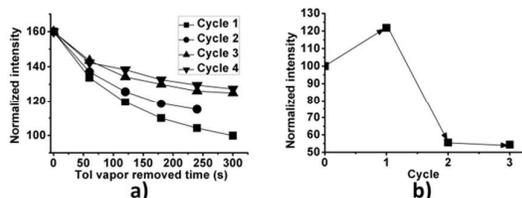


Figure 6. Cycling tests of TAT-COF-2 exposed a): in toluene vaor and b): first in chlorobenzene vapor, then in nitrobenzene vapor and thirdly in chlorobenzene vapor again.

Conclusions

In conclusion, two new COFs based on TAT derivatives have been synthesized. And we found that the electron-rich TAT-COF-2 has a weak interaction with electron-rich arenes, so the fluorescence-on sensing of electron-rich arenes could be re-used conveniently. Furthermore, its electron-rich nature may be able to be used as optoelectronic materials, which is under our research currently.

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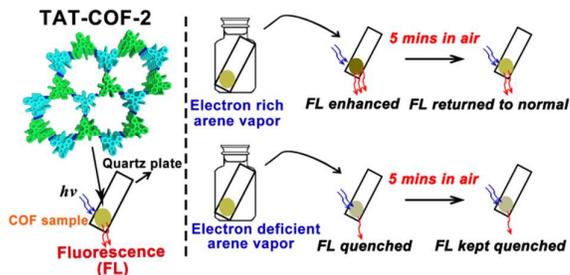
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Triazatruxene Based Crystalline Covalent Organic Framework and Its Quick-response Fluorescence-on Nature towards Electron Rich Arenes

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Two new 2D covalent organic frameworks were synthesized based on triazatruxene unit, which could be as potential fluorescent sensors for electron rich/deficient arene vapors.