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Supporting Information

Chromogenic covalent organic polymer-based microspheres as solid-state gas sensor

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Materials and Methods All the starting materials were purchased and used as received. 2,4,6-tris(*p*-aminophenyl)-1,3,5-triazine (TAPT)[1] and 2,4,6-tris-(*p*-formylphenoxy)1,3,5-triazine (TFPT)[2] was synthesized according to the literature procedure. All the solvents were dried using literature procedure and the solvents were of Analytical Reagent grade. FT-IR, PXRD, BET, TGA NMR and XPS experiments were performed on ThermoScientific INCOLET iS50 spectrometer, Shimadzu D8 DISCOVER X-ray diffractometer, ASI-CT-11 Quantachrome Instrument, Perkin Elmer TG/DTA, Jeol *ECX* 400 MHz spectrophotometer, PHI 5000 Versa Prob III, FEI Inc. with Auger electron spectroscopy module. SEM and TEM studies of as-synthesized material TATF-COM were performed on TECNAI 200 kV TEM with UHV FEI, Germany (Electron Optics) and ZEISS Gemini SEM-500 FESEM instrument. Solid State UV-Vis diffuse reflectance spectroscopy experiment was performed on JASCO UV-Vis spectrophotometer. Fluorescence experiments were performed on Varian Cary Eclipse instrument.

a) Synthesis of TATF-COM The material was synthesized by conventional using Knoevenagel condensation reaction. An accurately weighed amount of 1 and 2 was dissolved separately in mesitylene/dioxane (1:1, v/v) mixture. Then after, 1 mL of 6M acetic acid was added to the reaction mixture and placed in 100mL Teflon autoclave. Then, the autoclave was flushed with nitrogen for about 15min, sealed and heated at 120˚C for 72h. After 72h, the obtained yellow precipitated was collected by filtration and washed successively with acetone, dioxane, methanol and water, dried at 120ºC for overnight. The resulted amorphous yellow colored material named TATF-COM was obtained.

b) Synthesis of Precursors

(**i**) *Synthesis of 2, 4, 6-tris(p-aminophenyl)-1, 3, 5-triazine (TAPT;* ***1****)* [1]

A 25 mL R.B. flask was charged with 1.5 g of *p*-amino benzonitrile and 4.0 mL of trifluoromethanesulfonic acid was added dropwise to it under nitrogen atmosphere at 0˚C. The reaction mixture was further stirred for next 24h at RT under nitrogen atmosphere. To it, 200 mL of deionized water was added and reaction mixture was further neutralized with aq. NaOH solution. The obtained pale-yellow precipitate was washed with plenty of deionized water and dried under *vacuo*. The obtained product was then characterized by NMR techniques. (Yellow solid, Yield: 73%). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 8.36 (d, *J* = 8.8 Hz, 6H), 6.70 (d, *J* = 8.4 Hz, 6H), 5.91 (s, 6H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 169.5, 152.9, 130.6, 130.1, 122.9, 113.1

(**ii**) *Synthesis of 2,4,6-tris-(p-formylphenoxy)1,3,5-triazine (TFPT;* ***2****)* [2]

A 100 ml R.B. flask was charged with a mixture of *p*-hydroxybenzaldehyde (1.89g, 15.5 mmol) and NaOH (0.620g, 15.5mmol) dissolved in 40 ml of acetone and water (1:1 (v/v)) over magnetic stirrer at 0˚C. Then, a solution of cyanuric chloride (0.92 g, 5.0mmol) in 20 mL of acetone was added dropwise to the reaction mixture. After 4h, the reaction mixture was added with 250 ml of deionized water and obtained white precipitate was filtered, washed with water and dried. The as-synthesized crude product was further recrystallized with EtOH. (Off-white, Yield: 89 %). ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): δ 9.99 (s, 3H), 7.97 (d, *J* = 6.3 Hz, 6H), 7.49 (d, *J* = 4.5 Hz, 6H). ^{13}C NMR (DMSO-d_6, 100 MHz, ppm): δ 191.9, 172.7, 155.6, 134.1, 131.1, 122.3

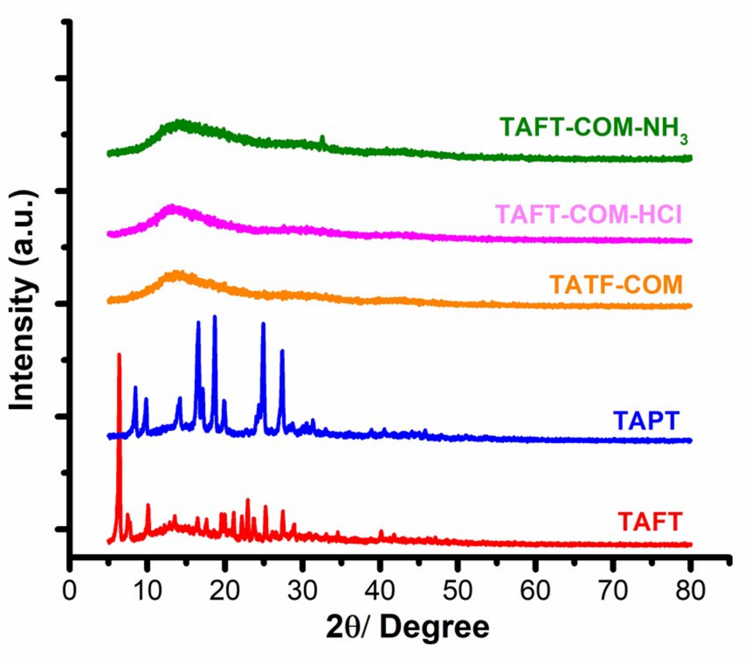

Fig. S1. Stacked view of PXRD pattern of **TATF-COM** compared with precursors and subsequent treatment with HCl and NH$_3$.

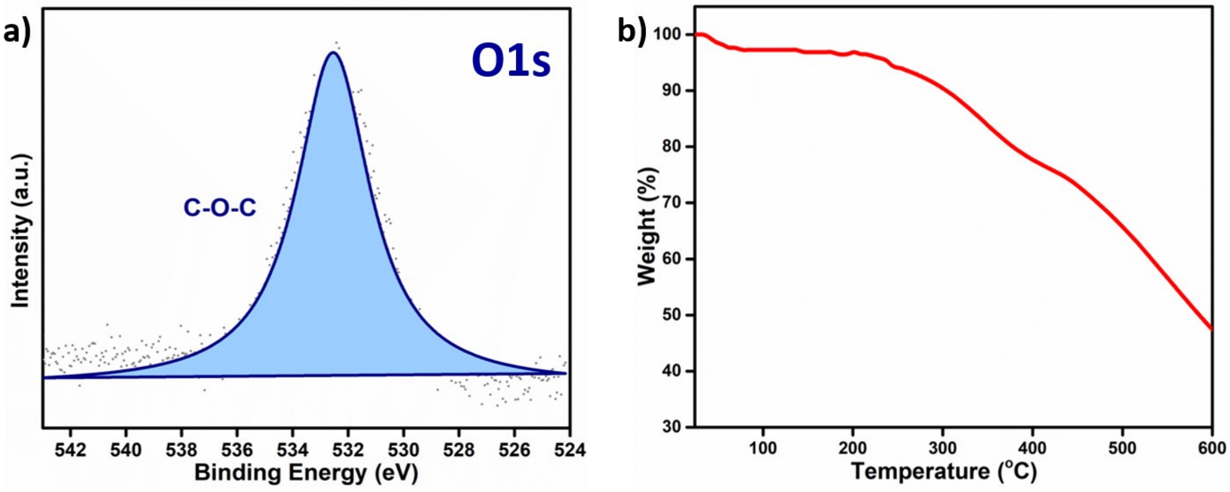

Fig. S2. (a) Deconvoluted XPS spectrum of O1s and (b) TGA thermogram of **TATF-COM**.

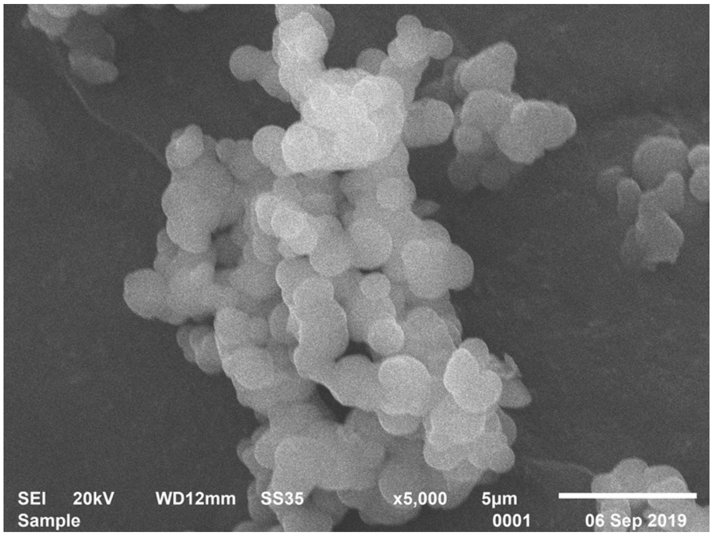

Fig. S3. Scanning Electron Microscopic image of **TATF-COM**.

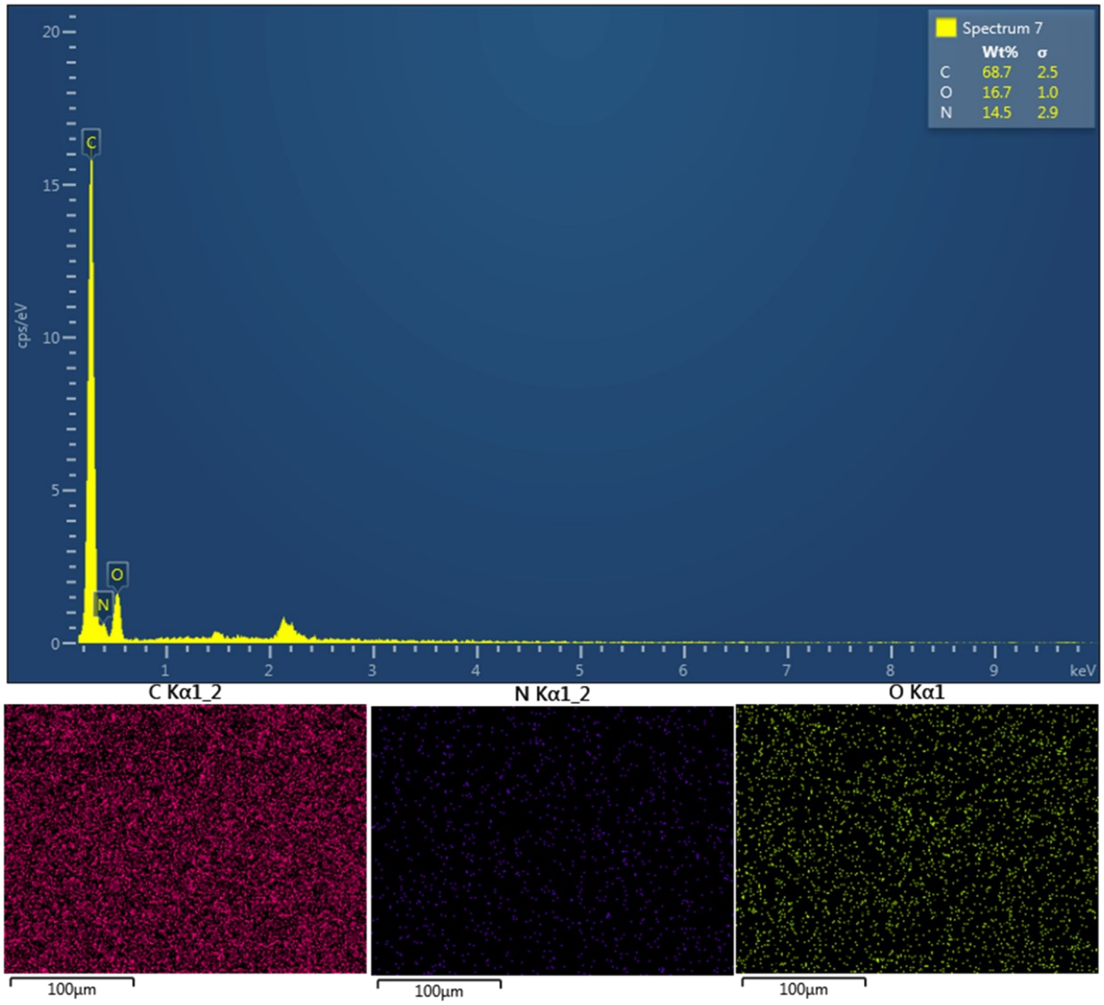

Fig. S4. EDX spectrum of **TATF-COM** and their elemental analysis.

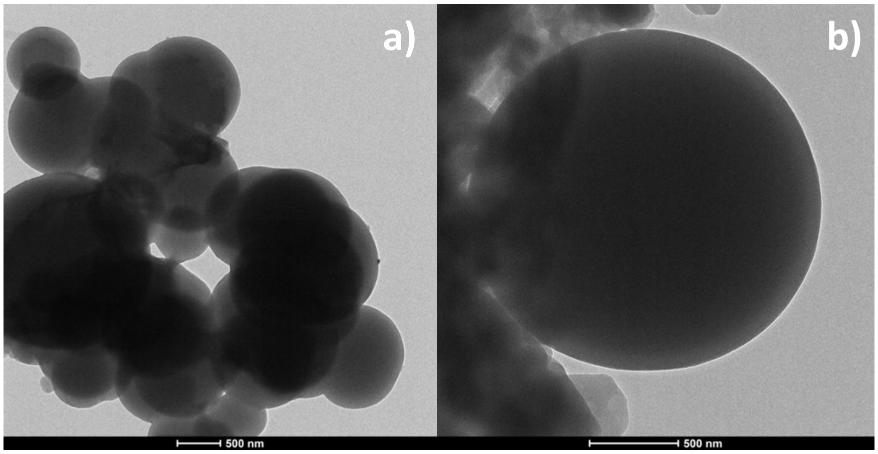

Fig. S5. High-Resolution-TEM images showing (a) an even cluster and (b) single covalent organic microsphere of **TATF-COM**.

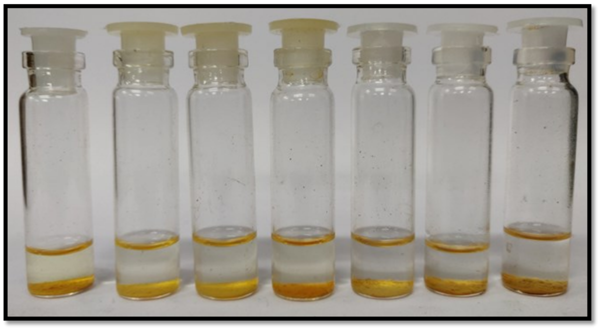

Fig. S6. Insolubility test of **TATF-COM** in different solvents (Left to Right: MeOH, Ethyl Acetate, MeCN, Acetic Acid, DMSO, DMF and Acetone).

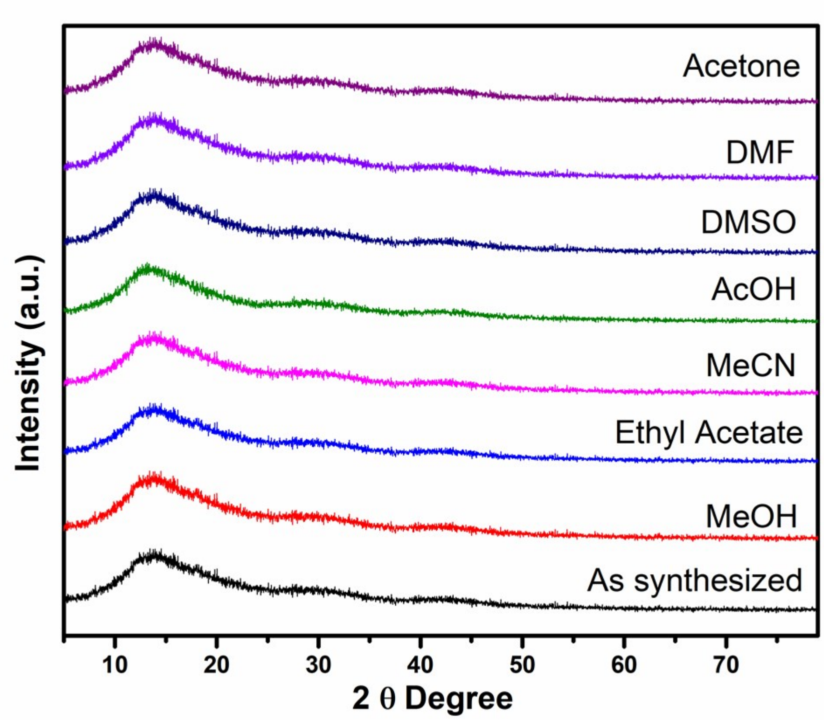

Fig. S7. Stacked view of Powder XRD patterns of **TATF-COM** in different solvents.

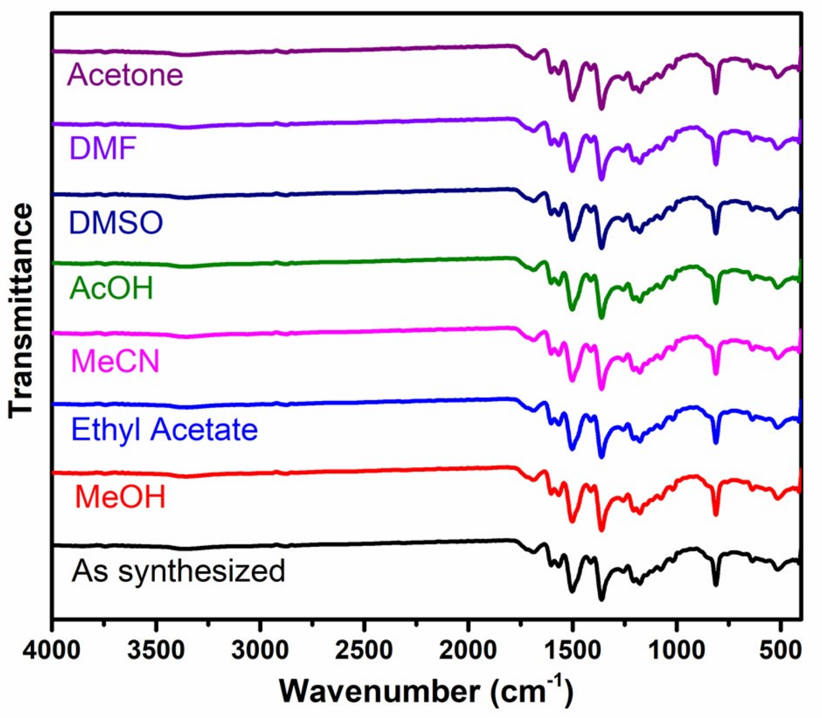

Fig. S8. Stacked view of FT-Infrared spectrum of **TATF-COM** in different solvents.

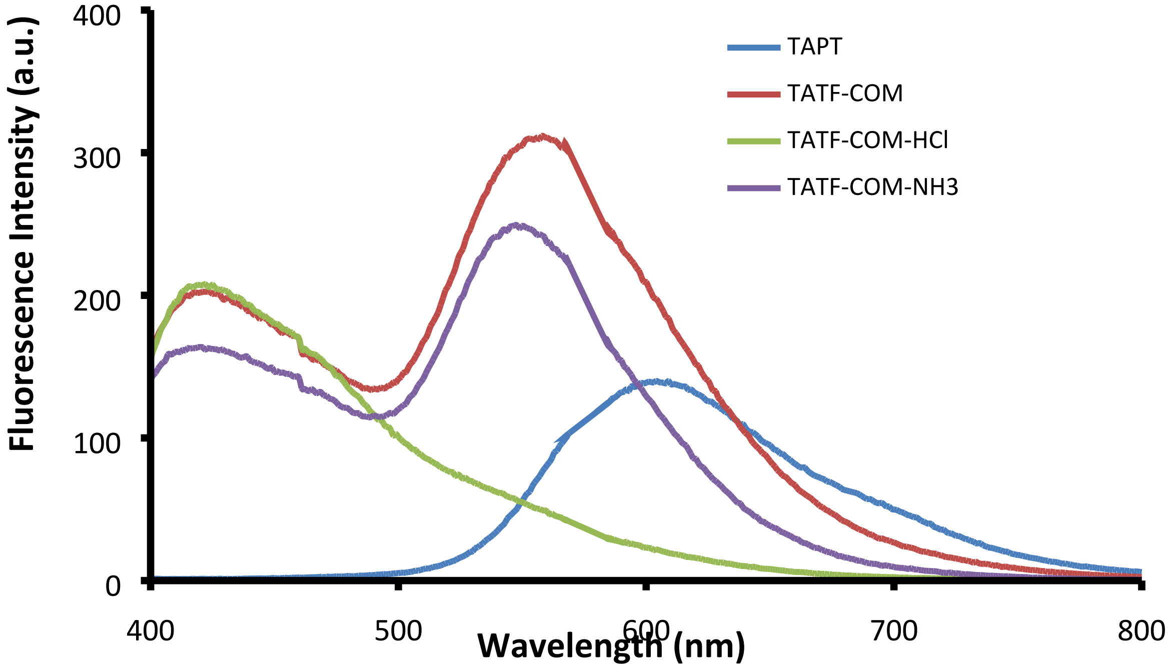

Fig. S9. Comparison of fluorescence spectrum of TAPT, TATF-COM, TATF-COM-HCl and TATF-COM-NH_3.

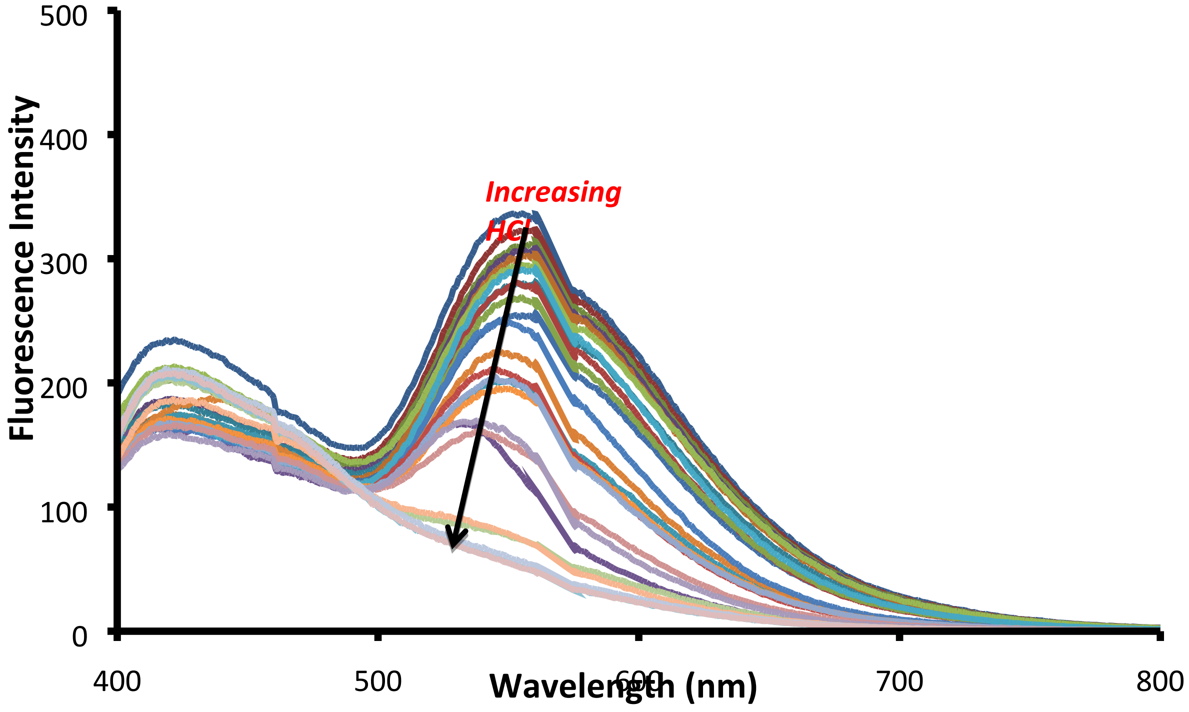

Fig. S10. Fluorescence titration of **TATF-COM** versus HCl. [Conc. of HCl = 100µM].

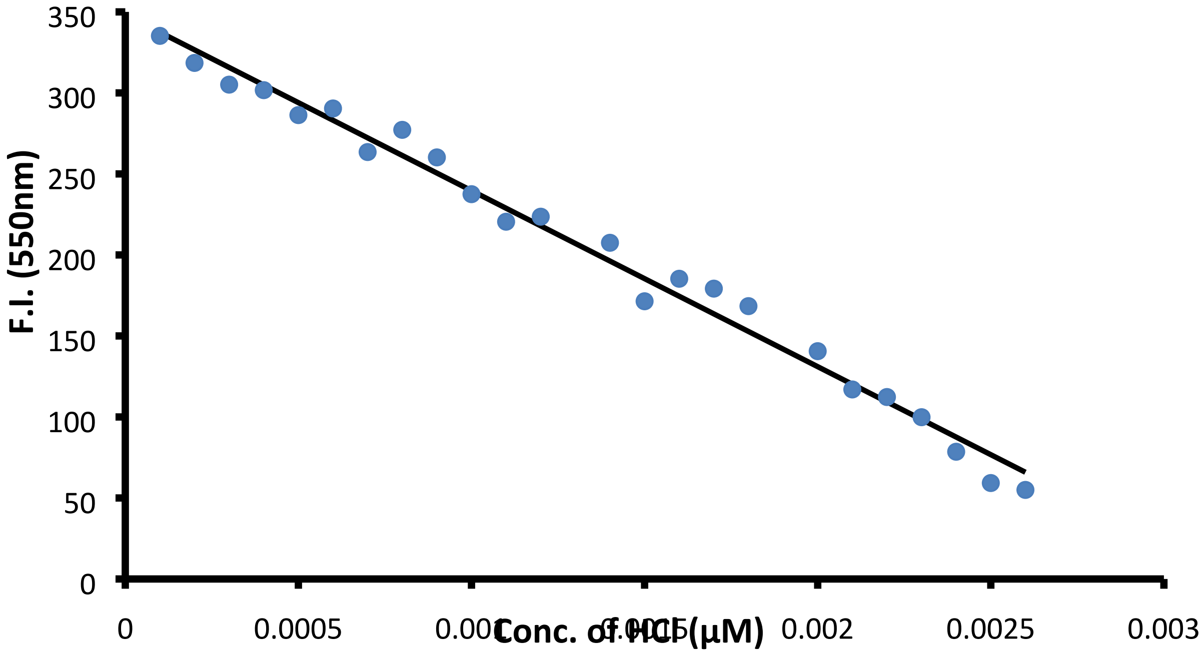

Fig. S11. Detection limit of **TATF-COM** against HCl gas. [Conc. of HCl = 100µM]

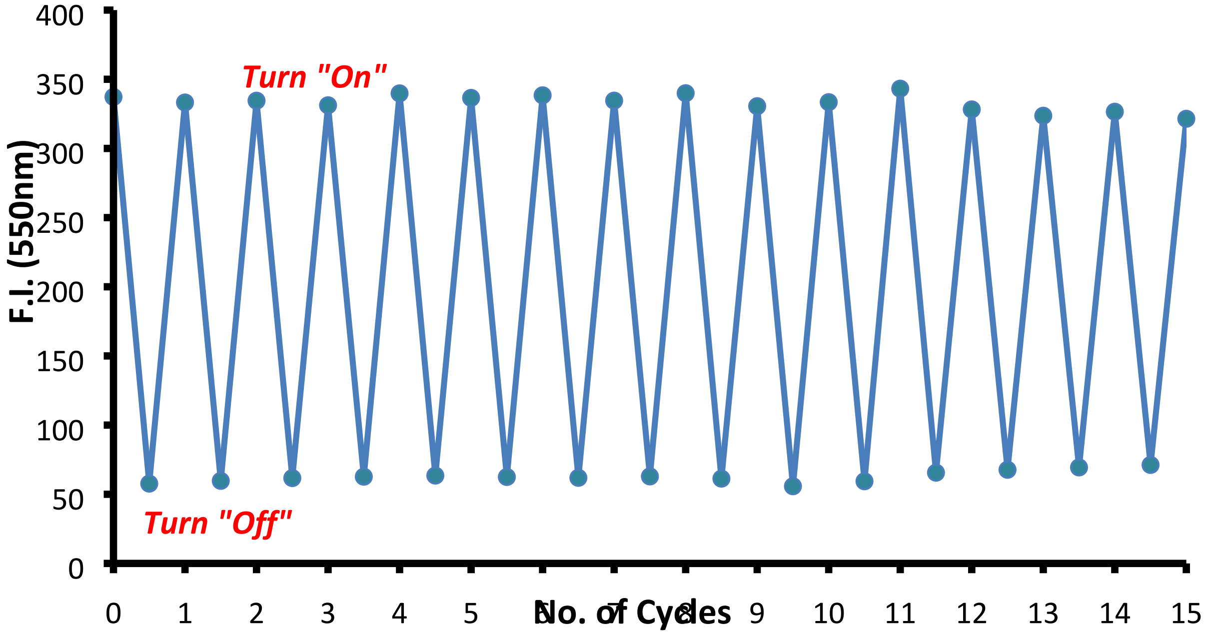

Fig. S12. Reversible cycles of **TATF-COM** upon alternative treatment with HCl and NH_3 vapors.

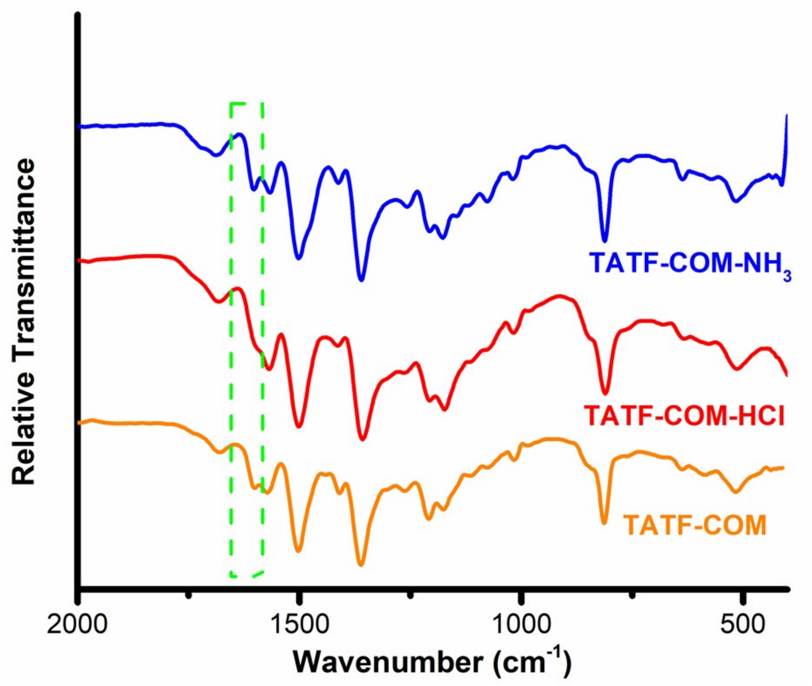

Fig. S13. Comparison of FT-IR spectra in as-synthesized **TATF-COM** upon alternative treatment of HCl and NH_3 vapors.

Table. S1. Comparison table of reported optical chromogenic sensors for HCl sensing.

Material	**Method**	**Detection limit/ Response time**	**References**
TCPPH2-SiO_2 HPNFM	Fluorescence/ Colorimetric	17 ppb/ 5 s	[3]
Porphyrinated PI honeycomb film	Fluorescence	-/ 10 s	[4]
Cu_4I_4–MOF (1)-based MMM	Visual/Luminescent	3.2 ppb / <60 s	[5]
Polyaniline-Functionalized Nanofibers	Colorimetric	~0.09 ppm/ 5 min	[6]
Troger's base functionalized porous N-rich polymer	Colorimetric	269 ppm/ 10 s 1345 ppm/ 2 s	[7]
CC-TAPT-COP	Colorimetric	1μM/-	[8]
COP-1	Fluorescence	1.0967×10^{-4} M/-	[9]
COF-ETBA-DAB	Fluorescence	4.7 ppm/ -	[10]
TATF-COM	**Colorimetric**	**2.38 ppb/ 3 s**	**Present Work**

References:

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