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Luminescent Triazene Based Covalent Organic Frameworks Functionalized with Imine and Azine: N_2 and H_2 Sorption and Efficient Removal of Organic Dye Pollutants

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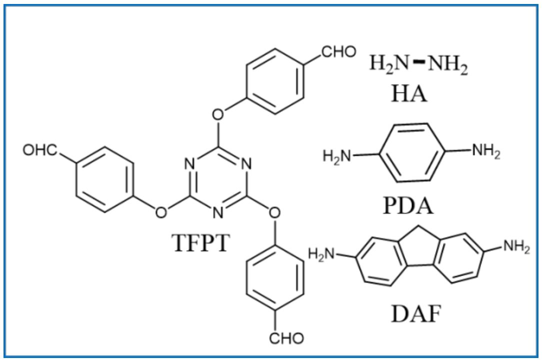
ABSTRACT: Design of adsorbents with high stability, efficiency to achieve rapid uptake and high capacity for the dye pollutants is a key challenge in environmental remedies. Herein, we have design and synthesized three triazene based imine and azine functionalized covalent organic frameworks (COFs **1-3**) *via* the formation of imine bonds by the condensation of a flexible tripodal tri aldehyde (TFPT) with linear diamines. The COFs are characterized by elemental analysis, FTIR, Solid-state NMR, TGA, FESEM, TEM and DRS. They exhibit permanent porosity with high surface areas and N2 uptake capacities of 540, 1600 and 2235 cc/g by COFs **1-3** respectively. They are found to be chemically and thermally stable and exhibit moderate hydrogen storage capacities. Photophysical studies reveals that, COFs **1-3** exhibited low band gap values of 3.0, 2.5 and 2.25 eV respectively, indicating their semiconducting nature. All three materials are highly luminescent and their emission maxima are found to depend on the nature of the diamine linker. Further, COFs **1-3** are highly stable in water, and function as robust adsorbents, as evidenced by its high rapid uptake capacity (>96%) towards anionic (MO, CR) and cationic (MB, CV) organic dye pollutants from their respective aqueous solutions (2.5X10^{-5} M).

The design and synthesis of micro porous materials is an attractive area of research and caters to the day-to-day applicative aspects.[1-3] The quest for zeolite like materials with better prospects for fine tuning the nature of cavities, size, shape and functional properties is ongoing pursuit. MOFs have been widely explored for their zeolitic properties in the past two decades.[4-6] Subsequently, the covalent organic frameworks (COFs) which are new class of materials, built up on covalent bonds, are also gaining importance for their gas sorption, storage and separation, catalysis, sensing, drug delivery, energy storage, magnetic and optoelectronic properties.[7-22] Generally, these COFs are designed using two molecular components that are linked via boronate,[23] boroxine,[24] imine,[25] azine,[26] triazene[27] and imide linkages.[28] In particular, the COFs with imine and azine linkages are of wider interest given their ease of synthesis from simple chemicals, crystallinity and high stability.[29,30] However, unlike MOFs, it is near to impossible to obtain single crystals of COFs given the nature of the reactions involved in their formation. To date only a few single crystal structures of COFs are reported[31-35] and most often the structures are deduced by PXRD, FESEM, TEM, FTIR, solid state NMR and their other properties.[10,25] Despite of poor crystallinity and lack of accurate understanding of the structures, they are widely explored in the fields of gas adsorption, separation, catalysis and removal of dye pollutants from waste water.[36-37]

Several groups have shown that the COFs with triazene core exhibit more basicity which facilitates binding of guest molecules, metals and dyes. In this context, 2,4,6-tris (4-formylphenoxy)-1,3,5-triazine (TFPOT) is an interesting trigonal molecule as it is highly flexible, electron deficient and contain more number of nitrogen atoms. Recently, TFPOT was shown to form COFs with p-phenylenediamine, benzidine and tripodal amine by Pitchumani *et al.* and Zhang *et al.* which exhibit gas sorption, catalysis and photosensitizer properties.[38,39] Further, Li *et al.* have demonstrated the importance of interlayer hydrogen bonds in the COFs of TFPT by introducing the hydrogen bonding functional groups on the linear diamine linker such as benzidine.[40, 41] However, very limited examples have been reported on exploration of COF towards dye, photophysical and photoluminescence properties.

Scheme 1. Structural drawings for TFPT, HA, PDA and DAF



In this manuscript, we have strategically designed and synthesized COFs **1-3** of TFPT using three diamine linkers namely hydrazine monohydrate, *p*-phenylenediamine and 2,7-diaminofluorene respectively (Scheme-1). The amines are selected such that they increase the pore size gradually and also change the nature of networks given the differences in the chromophores of diamines. Apart from synthesis and characterization of these COFs, the studies are aimed at exploring the differences in their porosities, luminescence and dye sorption properties based on the diamine linkers. These COFs are found to have excellent ability for N_2 and H_2 sorption and also to adsorb both cationic (methylene blue (MB) and crystal violet (CV), and anionic (methyl orange (MO) and congo red (CR) dyes. The band gap values for COFs **1-3** calculated from DRS indicate their semiconducting nature. The luminescence studies reveal that the COFs are highly luminescent and their emissions are found to change with the nature of diamine linker.

RESULTS AND DISCUSSION

The trialdehyde TFPT was synthesized by reacting *p*-hydroxybenzaldehyde with cyanuric chloride in 3:1 ratio in the presence of Na_2CO_3 in benzene. The solvothermal reactions of TFPT with corresponding diamines such as hydrazine monohydrate (HA), *p*-phenylenediamine (PDA) and 2,7-diaminofluorene (DAF) in 2:3 ratio in the presence of catalytic amounts of 6 M acetic acid in dioxane-mesitylene solvent system at 120 °C resulted in the formation COFs **1-3** respectively. These materials are found to exhibit different colors light yellow, green and brown by COFs **1-3**, respectively, and are found to be insoluble in organic solvents such as alcohols, acetone, chloroform, ethers, acetonitrile, N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The materials are thoroughly characterized by elemental analysis, FTIR, solid state NMR, powder XRD, SEM, TEM and DRS. Our efforts to obtain crystalline materials of these COFs are unsuccessful.

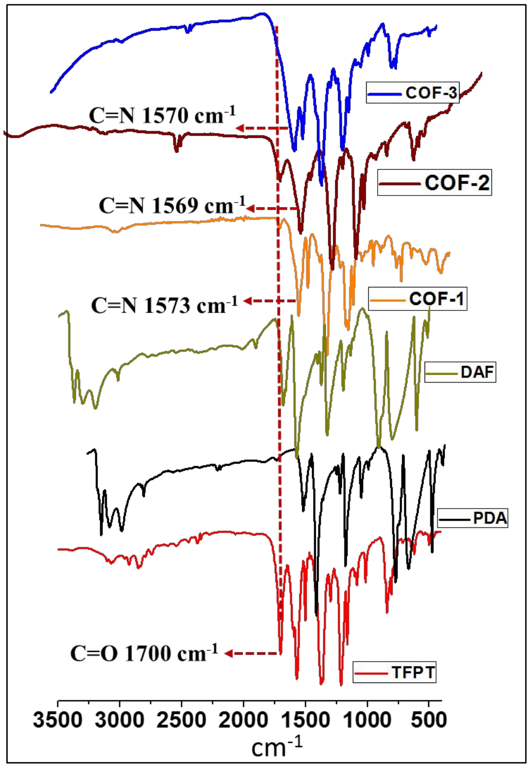


Figure 1. FTIR spectra of TEPT, PDA, DAF, COF-**1**, COF-**2** and COF-**3**.

The polymeric nature of the materials has been confirmed by their lack of solubility in polar solvents such as DMF and DMSO. Further, they are found to be stable under basic conditions as they remain intact in 0.1 M NaOH solution for several days (Figure S8-S10). From TGA it was observed that COF-**1** is stable upto 300 °C, whereas COF-**2** & **3** were stable up to 350 and 390 °C respectively, indicating their high thermal stability (Figure S11). The FTIR spectra (Figure 1) indicates the presence of imine group as C=N stretching frequency appears at 1573, 1569 and 1570 cm^{-1} for COFs **1-3** respectively, and absence of the aldehyde (1700 cm^{-1}). Further, the presence of imine linkages reaffirmed by ^{13}C CP-MAS NMR spectra of COFs **1-3**. The solid-state ^{13}C NMR spectrum of COFs indicate the presence of imine and triazene functionalities as all these materials exhibit signals at ~153 ppm and ~172 ppm respectively (Figure 2).

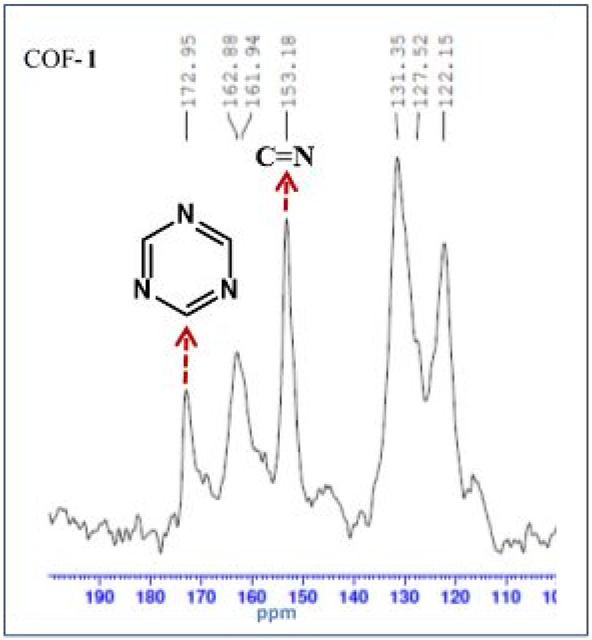
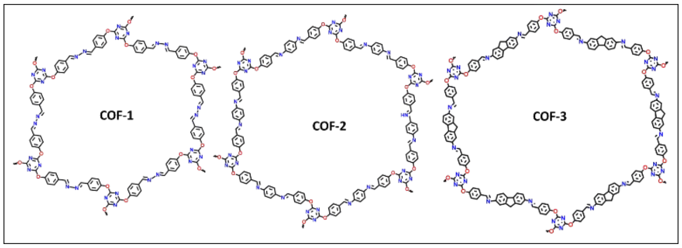


Figure 2. Solid-state ^{13}C NMR spectra for COF-**1**.

Scheme 2. Probable structure for COF-1, COF-2, and COF-3



In case of COF-**3** the presence of signal at 40 ppm confirms the presence of sp^3 carbon corresponding to 2,7-diaminofluorene (Figure S12-S14). The PXRD patterns for COFs **1** and **2** indicate their amorphous nature with some broad peaks while those of COF-**3** exhibit some sharp peaks in the 2θ range of 20-30° (Figure 3). However, indexing of

COF-3 was not successful. To understand the morphology of COFs, microscopic studies such as FESEM and TEM have been performed. The FESEM and TEM images indicate that COFs **1-3** exhibit spherical morphologies (Figure 4), while their starting materials such as aldehyde exhibits rod type morphology and amines exhibit plate-like morphologies (Figure S21). Based on above characterizations, the probable structure of COFs **1-3** have been proposed in Scheme 2.

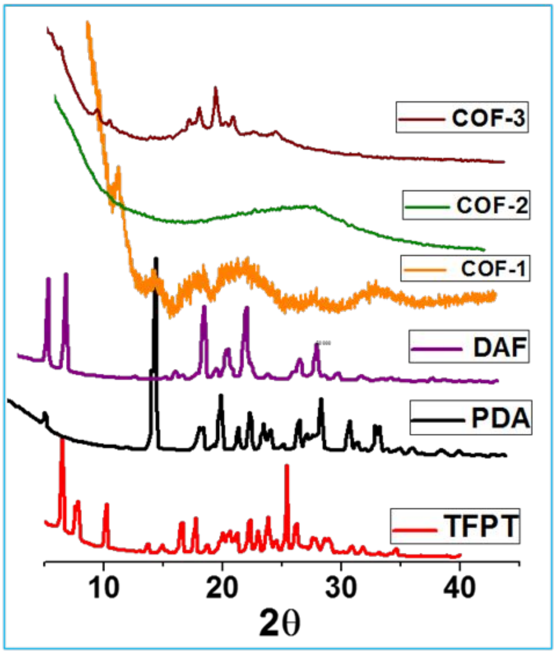


Figure 3. PXRD patterns of TEPT, PDA, DAF, COF-**1**, COF-**2** and COF-**3**.

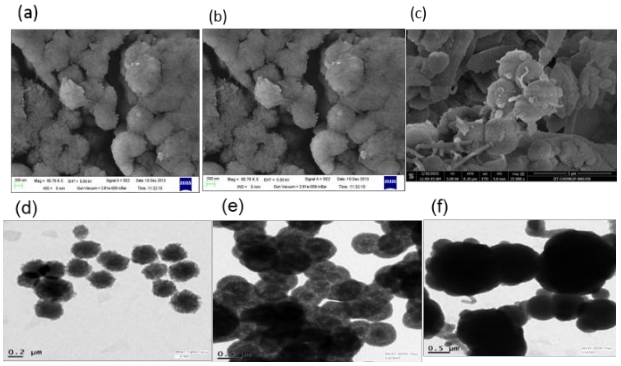


Figure 4. FESEM images for (a) COF-**1**; (b) COF-**2**; (c) COF-**3**; TEM images for the (d) COFs **1**; (e) COF-**2**; and (f) COF-**3**.

Gas adsorption studies.

In order to characterize the porous properties of the resulted COFs, N_2 gas sorption studies were conducted on all the three COFs at 77 K and one bar pressure. The COFs were activated by soaking the as synthesized materials in volatile solvents such as THF, acetone or chloroform for seven days and degasifying at 150 °C under vacuum for 24 h. The N_2 adsorption studies reveal that COFs **1-3** exhibited maximum uptake capacities of 540, 1557, and 2235 cc/g, respectively, at 77 K and one bar pressure. The BET surface areas for COFs **1-3** were found to be 853, 2815 and 1798 m^2/g respectively. These three materials were found to exhibit three different adsorption isotherms: COF-**1** uptakes about 380 cc/g at p/p_o value of 0.15 bar and the uptake gradually reaches to 540 by p/p_o of 1 bar; COF-**2** uptakes about 800 cc/g at p/p_o value of 0.3 bar and the uptake remains constant up to 0.9 bar and suddenly reached to the 1557 cc/g by 1 bar; whereas the uptake of COF-**3** was found to increase gradually up to 2235 cc/g by the p/p_o of 1 bar. These sorption isotherm indicate that COF-**1** and **2** are microporous in nature while **3** is meso-porous in nature (Figure 5a). These N2 sorption values are much better than the recently reported COFs synthesized by the same aldehyde with PDA.[38,39]

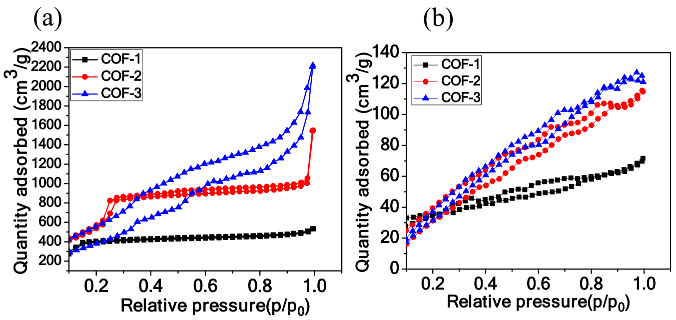


Figure 5. (a) N2 adsorption and desorption isotherms for the COFs **1-3** at 77 K and one bar; (b) H2 adsorption and desorption isotherms at 77 K and one bar for the COFs **1-3**.

Pore size distribution analysis by fitting the uptake of the N_2 isotherms using the nonlocal density functional theory (NLDFT) method reveals that COFs **1-3** exhibit average pore size of 11, 13 and 15 nm (Figure 6). The hydrogen sorption analysis also reveals the similar trends in the uptake values that is increase in uptake as the spacer length increases, COFs **1-3** exhibit 70, 120, and 130 cc/g of uptake respectively (Figure 5b). However, the H_2 isotherms are found to have identical nature for all three COFs that is gradual increase of uptake as the p/p_o values increase.

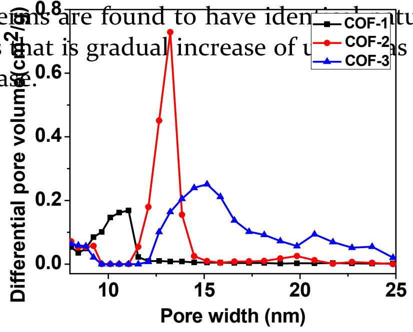


Figure 6. Pore size distribution of COF-**1**, COF-**2**, and COF-**3**.

Diffuse Reflectance Spectra.

The electronic properties of the COFs have been investigated using the solid state UV-vis spectra in comparison with those of parent components. Monomers TFPT, PDA and DAF exhibited absorption bands at 300, 330 and 355 nm respectively (Figure 7a), whereas the COFs **1-3** exhibited absorption bands at 350, 400 and 450 nm respectively (Figure 7b). The absorption bands of the COFs

2 and 3 are red-shifted compared to the parent diamines. COFs **2** and-**3** exhibited much higher red-shifts by 70 and 95 nm than the parent diamines respectively. Further the band gap values for COFs **1-3** have been calculated from the DRS spectra. Interestingly, COFs **1-3** exhibited lower band gap values 3.0, 2.5 and 2.25 eV, respectively, which clearly indicates the semiconducting nature of the materials (Figure S22). These band gap values are comparable and lower than the reported COF-1 constructed by boroxine linkage (3.6 eV) and IRMOF (3.73 eV).[42-44]

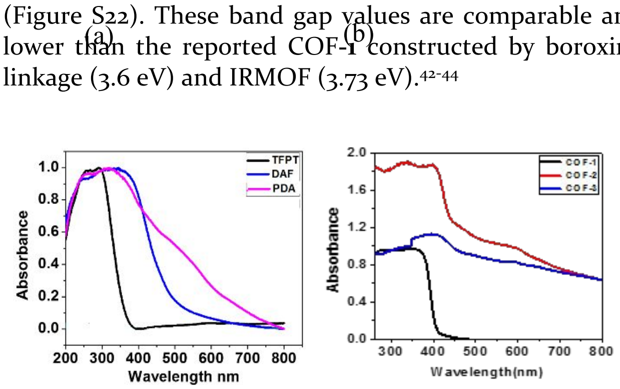


Figure 7. Solid-state UV-vis spectra (diffuse reflectance spectra) for (a) TFPT, PDA and DAF; (b) COFs **1-3**

Solid-State Luminescence Properties.

Recently, luminescent MOFs and COFs have been extensively explored for their applicative aspects such as light emitting diodes, chemical sensing and optoelectronics.[45-47] However, most of the MOFs possess low hydrothermal stability which limits their industrial application, whereas COFs are pure organic low dense materials as they made up of lighter elements and robust towards air and water. Synthesis of organic polymers by judicious selection of conjugated organic spacers offers an efficient methodology for obtaining new type of electroluminescent organic materials.[48,49] The luminescence properties of the COFs **1-3** are studied as they contain electron rich as well as electron deficient aromatic moieties. The COFs **1-3** are found to exhibit the emission maxima at 450, 505 and 540 nm, respectively upon the excitation at 340 nm (Figure 8b). The diamines exhibited λ_{max} at 410 and 450 nm for PDA and DAF respectively, with excitation wavelength of 330 and 340 nm respectively. Figure 8a), while the TFPT is non-luminescent. The emission bands of COFs **2** and **3** were red shifted by 95 and 90 nm compared to their parent diamines, respectively. The observed redshifts for COF **2** and **3**

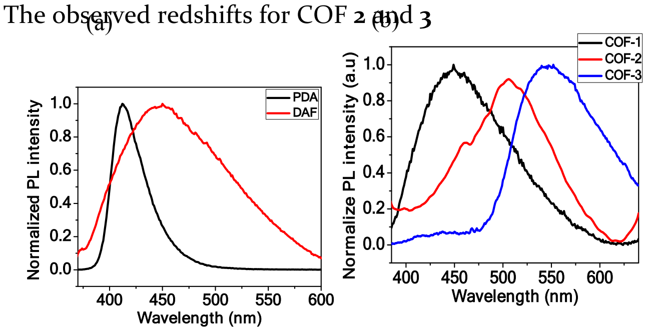


Figure 8. Solid-state luminescence spectra for (a) PDA and DAF; (b) COFs **1-3**

-could be due to the restricted motion of the individual monomer units which leads to enhanced π-conjugation by reducing the energy gap of π-π^* transitions. This phenomenon is consistent with recently reported imine linked porous organic polymers.[50, 51]

Dye Adsorption Studies.

Water contamination with toxic dyes and other water soluble organics has been increasing day by day due to the rapid developments in the industries such as printing, medicine, leather, textile and fertilizer. Most of the dye molecules are stable under adverse conditions, non-biodegradable and their toxicity causes severe problems to aquatic life.[52,53] Thus, removing dyes from waste water quickly and economically remains a great deal of challenge for researchers. Covalent organic frameworks with advantages like tunable porosity, high surface area, water stability and large scale production are envisaged as better candidates for the removal of organic dyes from waste water.[54-56] Being highly chemical and thermal stable with high BET surface area and with more nitrogen content, the utility of COFs **1-3** as potential dye adsorbates from the aqueous solution has been explored. The dye adsorption performance of COFs **1-3** were studied by taking two anionic dyes such as methyl orange (MO), congo red (CR) and two cationic dyes such as methylene blue (MB) and crystal violet (CV). The dye sorption experiments were carried out by immersing 5 mg of COF material in 5 mL of respective 10^{-5} M aqueous solutions of dye. The adsorption was monitored by naked eye as well as by UV-vis spectra of the aqueous solution at different time intervals. Interestingly, COFs **1-3** exhibit good capability for the removal of both anionic (MO & CR) and cationic (MB and CV) dyes. The dye sorption abilities are found to be in the order of COF-**3** > COF-**2** > COF-**1**, which indicates increase in dye absorbing ability with the increase in the length of the spacer. The COF-**2** was found to adsorb MO, MB and CV

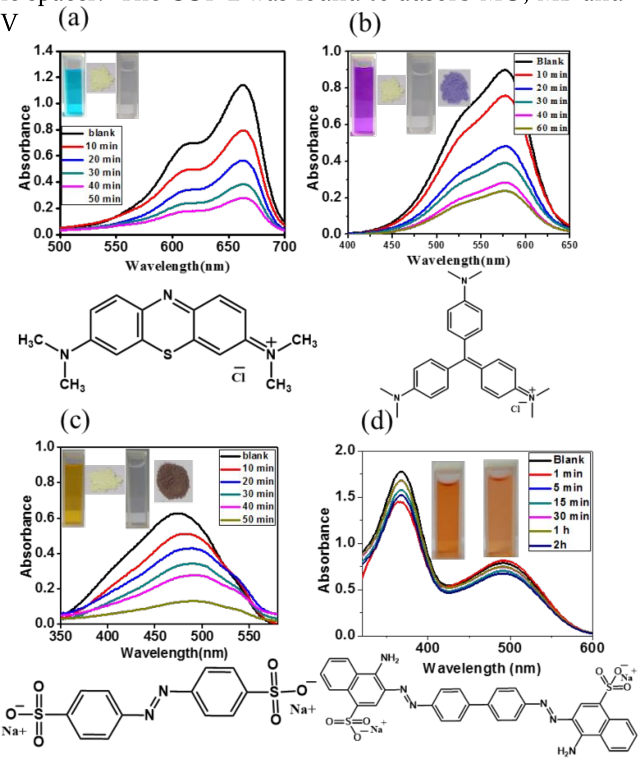


Figure 9. UV-vis spectra for the uptake of different dyes from aqueous solutions at various time intervals by COF-**1** (a) methylene blue; (b) crystal violet; (c) methyl orange; (d) congo red

-rapidly in first 5 minutes and the adsorption reaches to 98 % in 30 minutes. Whereas the adsorption of CR by COF-**2** was found to be somewhat slower and requires about 60 minutes to adsorb 95% of the dye (Figure S23). Similar trends were observed for the COF-**3** also (Figure S24). However, COF-**1** is capable of adsorbing only MO, MB, and CV sluggishly and requires 60 minutes to adsorb 95%, 92% and 92% of the dyes respectively (Figure 9). Interestingly, during the entire process of adsorption and desorption process of dyes, the COFs **1-3** are found to be stable as in dictated by their FTIR spectra (Figure S25-S27). The removal percentages of the dyes have been calculated by the following equation

$$E\% = \frac{(C_0 - C_e)}{C_0} \text{ X } 100$$

Where E% represents the removal percentage of organic dyes; C_o and C_e denotes the initial and equilibrium concentrations (mg/L) of the organic dyes in aqueous solutions respectively.

CONCLUSIONS.

In summary, three porous triazene based imine and azine functionalized covalent organic polymers COF-**1**, COF-**2** and COF-**3** were synthesized using imine linkages between flexible tripodal tri aldehyde (TFPT) and linear diamines via solvothermal technique. The COFs are shown to be thermally stable (>350 °*C*) and exhibited excellent N_2 sorption values. The N_2 sorption values are found to increase with increasing the size of the spacer diamine. The N_2 uptake capacities of COF **1-3** are found to be 540, 1557 and 2235 cc/g respectively. The photophysical properties of COFs **1-3** have been studied which shows their semiconducting nature with low band gap values of 3.0, 2.5 and 2.25 eV respectively. Further, the luminescent studies reveals that COFs **1-3** are highly luminescent and their emission maximas are red-shifted compared to their parent compounds. Further, the COFs **2** & **3** exhibited high sorption capacity towards organic dyes such as MO, MB, CV and CR from aqueous solutions, whereas COF-**1** adsorbed MO, MB and CV only.

EXPERIMENTAL DETAILS

All the reagents and solvents like N,N′-dimethylformamide, dimethyl sulfoxide, dioxane mesitylene, benzene, acetic acid, ethyl acetate Na_2CO_3 p-hydroxybenzaldehyde, hydrazine monohydride, p-phenylenediamine were purchased from local chemical suppliers and used further distilled the solvents. The solvents like methanol, THF, chloroform, acetone and acetonitrile were HPLC grade. 2,7-diaminofluorene and cyanuric chloride were purchased from Sigma-Aldrich. (FTIR) spectra were recorded with a Perkin-Elmer Instrument Spectrum Rx Serial No. 73713. Elemental analysis has been carried out by Perkin-Elmer Series II 2400, the diffuse reflectance spectra (DRS) were recorded with a Cary model 5000 UV-vis-NIR spectrophotometer, the PXRD patterns were recorded with Bruker D8-advance diffractometer, ^{1}H NMR spectra was recorded on BRUKER-AC 400 MHz spectrometer, melting points were taken using a Fisher Scientific melting point apparatus, Cat. No.12-144-1, Solid-state luminescence was carried out by using Spex Fluorolog-3 FL3-22) spectrofluorimeter and Solid-state NMR was recorded on Varin INOVA 400 MHz solid state spectroscopy. The absorption of the dye solution was monitored by Shimadzu UV-1601 UV-vis spectrophotometer.

Synthesis of 2,4,6-tris (4-formylphenoxy)-1,3,5-triazine (TFPOT). TFPOT was prepared by literature procedure p-hydroxybenzaldehyde (1.6 g, 1.31 mol (1.3 excess)) and cyanuric chloride (0.6 g, 3.25 mol) were added to a suspension of Na_2CO_3 (10 g) in 50 mL of benzene. The mixture was refluxed for 20 h. The reaction mixture was then cooled and the solid was removed by filtration and washed with hot AcOEt twice. The filtrate was extracted with 10% Na_2CO_3 twice and with H_2O once and the organic layer was dried over anhydrous Na_2SO_4 and then concentrated. The white powder was recrystallized from 20 mL of AcOEt to afford a white fluffy precipitate. IR (KBr) ν 2833, 1702, 1567, 1361, 1211, 842 cm^{-1}, ^{1}H NMR ($CDCl_3$) 6 7.32 (d, 6H, J=8.5 Hz), 7.92 (d, 6H, J=8.5 Hz), 10.00 (S, 3H).

Synthesis of COF-1. COF-**1** was prepared by taking (TFPT) (44.1 mg, 0.1mmol) and hydrazine monohydrate (7.5 μmL, 0.15 mmol) were suspended in mixed anhydrous 1,4-dioxane (4.0 mL) and mesitylene (2.0 mL) in the presence of aqueous acetic acid (6.0 M) in a Pyrex tube. The sealed tube was heated at 120° *C* for 3 days to yield a light yellow solid, which was filtered and washed with THF, acetone and methanol and ethyl acetate to remove any unreacted building unit. The resulting powder was dried in vacuum. Melting point of the material is above 320 °C elemental analysis calcd (%) for $C_{30}H_{25}N_6O_3$: C 75.45, H 5.86, N 13.56; found: C 76.49, H 4.98, N 14.23. FTIR (KBr): ν = 1573 (C=N), 1504, 1360, 1202, 1165, 1015, 1013, 806, 623 and 511 cm^{-1}; Solid state; ^{13}C NMR: d= 153 (C=N), 172, 162, 161, 153, 131, 127 and 122 ppm.

Synthesis of COF-2. COF-**2** was prepared by following same procedure instead of hydrazine, p-phenylenediamine was taken which resulted as light green color solid. Melting point of the material was above 320 °C, elemental analysis calcd (%) for $C_{40}H_{28}N_6O_3$: C 79.55, H 6.76, N 12.66; found: C 78.89, H 7.48, N 13.23. FTIR (KBr): ν = 1569 (C=N), 2367, 1698, 1362, 1211, 1162, and 840 cm^{-1}. Solid state ^{13}C NMR: d= 154 (C=N), 192, 172, 145, 134, and 121 ppm.

Synthesis of COF-3. COF-**3** was prepared following same procedure instead of hydrazine, 2,7-diaminofluorene was used and resulted as brown color solid melting of the solid was above 320 °*C*. Elemental analysis calcd $C_{25}H_{15}N_6O_3$: C 55.65, H 3.76, N 12.36; found: C 56.26, H 3.20, N 13.34: FTIR (KBr): ν = 1570 (C=N), 3421, 2344, 2362, 1363, 1205, 1159, and 806 cm^{-1}. Solid state ^{13}C NMR: d= 154 (C=N), 44, 122, 129, 134, 148, 153 and 173 ppm

Field Emission Scanning Electron Microscope (FESEM). A field emission scanning electron microscope (FESEM, Zeiss, Supra- 40) operating at 5-10 kV was used to obtain the micrograph. For electron micrographs, the polymer samples were dispersed in MeOH and drop casted on the aluminum foil, allowed to dry at room temperature, and then dried in desiccators for 24 h. A layer of gold was sputtered on top to make a conducting surface, and finally, the specimen was transferred into the microscope.

Transmission Electron Microscope (TEM): The polymer materials were examined by a transmission electron microscope (FEI-TECNAIG20S-TWIN, Type-5022/22). The sample was prepared by placing a drop of MeOH dispersed material on a carbon-coated copper grid.

Gas Sorption Study. Powdered polymer materials have been used for the gas adsorption study. The polymer materials have been dried under vacuum for the gas adsorption study. The gas sorption experiment was performed using a Quantacrome autosorb iQ automated gas sorption analyzer. Generally, 20-25 mg of sample was taken in a 6 mm sample holder without a rod. Prior to the sorption experiment, the samples were employed for degassing at 150 °C under vacuum for 24 h

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org."

FTIR, XRPD, solid-state ^{13}C NMR analysis, TGA profile, SEM, TEM images, band gap calculations and dye adsorption studies. (PDF)

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Notes

The authors declare no competing financial interest.

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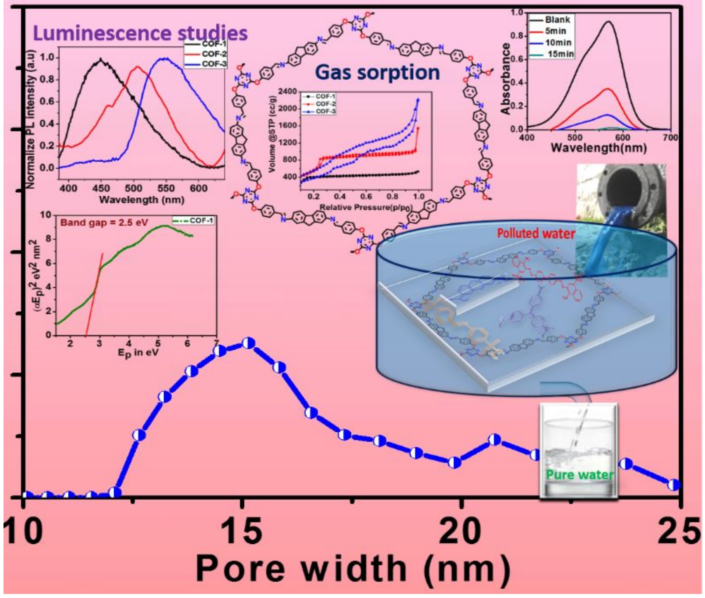
SYNOPSIS TOC

Three triazene based imine and azine functionalized covalent organic frameworks (COFs **1-3**) have been designed and synthesized via the formation of imine bonds from the condensation of a flexible tripodal tri aldehyde (TFPT) and linear diamines and characterized by different techniques . The gas and dye adsorption of COFs **1-3** have been explored successfully. Further their luminescence and photo physical properties have been studied.



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