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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Truxene based Porous, Crystalline Covalent Organic Frameworks and it's Applications in Humidity Sensing

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Truxene is employed as a building block to successfully synthesize new covalent organic Framework (COF). The condensation reaction between Truxene (10, 15-dihydro-5H-diindeno[1,2-a;1',2'-c]fluorene) (TX) and 1,4-phenylenediboronic acid (DBA) results in boronic ester linkage based crystalline COF-TXDBA with a surface area 1526 m²/g as confirmed by Powder X-Ray Diffraction (PXRD) and Brunauer–Emmett–Teller (BET) surface area measurements. This is the first report where nanochannels generated by periodic layers of COF planar sheets are shown to ease the interaction of boronic ester linkage with the water molecule for efficient humidity sensing application. The COF-TXDBA based %RH sensor exhibits 3 orders of magnitude change in inpedance in 11-98 %RH range with response and recovery times of 37 s and 42 s, respectively. The response transients of COF-TXDBA based %RH sensor by switching back and forth in 4 loops of sensing shows the excellent reversibility of the sensor with a deviation of 2.3% in the switching process.

Introduction

Past century witnesses the structural evolution of porous materials in terms of replacing inorganic components by organic building blocks, achieving larger pores or building rigid to soft dynamic 2D and 3D skeleton.¹⁻³ An important development made in the last decade is the construction of porous organic polymers such as hypercrosslinked polymers (HCPs), polymers of intrinsic microporosity (PIMs), covalent organic frameworks (COFs) and conjugated microporous polymers (CMPs) becomes the main content for advanced applications.

Among these organic porous polymers, covalent organic frameworks (COFs) become very attractive because of their periodic skeletons and ordered pores as the wide pore-size-distribution of other amorphous networks may restrict, to some extent, their further applications.⁴ COFs are devised by manipulating reticular chemistry in which organic building blocks are precisely linked via covalent bonds like boroxine/boronate ester,⁵ imine,⁶ hydrazone,⁷ triazine,⁸ imide bonds,⁹ etc. They are interesting materials from physics perspective as their graphene-like π system triggers interactions with excitons, electrons, holes, spins, ions and molecules in confined space.¹⁰ Due to their exceptional high surface area, large porosity and crystalline nature, COFs have emerged as promising material in applications including semiconductors

conduction,²⁵⁻²⁸ devices,¹¹⁻²¹ capture,²²⁻²⁴ CO₂ proton luminescence,²⁹⁻³¹ catalysis,³²⁻³⁷ energy conversion,³⁸⁻⁴⁰ storage,⁴¹⁻⁴³ and sensing.44-47 The physical and chemical properties of COFs inclusively depend upon the building blocks and the covalent linkage between them. However, a requirement of specific geometries and rigid structures of building blocks to perform reticular chemistry and very few kinetically reversible chemical reactions, which result into crystalline COFs, limits its scope to explore these applications to commercial aspects. To overcome these challenges, continuous design of new building blocks to accelerate this research field is the utmost requirement. Addressing the mentioned challenges, we hereby introduce Truxene based building block of COFs, for the first time.

Truxene (10,15-dihydro-5H-diindeno[1,2-a;1',2'-c]fluorene) is a C3 symmetric, star-shaped π -conjugated polyarene obtained by trimerization of indan-1-one. It can also be formally considered as 1,3,5-triphenylbenzene derivative with three methylene clips, responsible for keeping the four benzene rings coplanar and π conjugated. This induces a strong electron donating as well as strong π - π stacking ability, which hints for the Truxene utility as a building block in the development of advanced functional materials for various applications. Truxene molecular derivatives have been widely investigated in supramolecular chemistry, especially in organic electronics. Truxene based dendrimer, oligomers, and polymers were produced to use them as photosensitizers, photoresists, organic lasers, photoluminescence materials, OLEDs, OFETs and OPVs.⁴⁸ Further, octupolar character combined with polyaromatic and rigid planar structure makes Truxene and its derivatives a good candidate resulting in more efficient non-linear optical (NLO) properties than the conventional dipolar molecules.49,50

In spite of their type, porous materials have been always explored for the sensing applications due to their unique host matrices containing various functional species. The composition of

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⁺Electronic Supplementary Information (ESI) available: Synthesis details, IR and solid NMR spectra, and XRD. Full synthesis details and characterization of the, TGA, XRD, band gap measurement, solid-state ¹³C{¹H} CP/MAS NMR spectra and 1 H NMR spectra, comparison table. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C7TA05043G Journal Name

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the porous material, crystalline structure, surface area, functionalization, stability, and morphology are crucial parameters which affect crucial sensing attributes including sensitivity, selectivity and response/recovery times.⁵¹ In this respect, COFs possess the above mentioned attributes which makes them potential candidates for sensing applications. In this context, various groups have designed the COF-based sensor for detection of explosives ^{44,45} and toxic metal ions. ^{46,47}

Exploiting the inherent crystallinity, enhanced surface area and electron-rich linker groups, the precise detection of relative humidity (%RH) using COFs is a paradigm shift from tradition metaloxide semiconductor, ⁵² silica, ⁵³ polymer, ⁵⁴ carbon nitrides ⁵⁵ and relatively new MOFs⁵⁶ or inorganic/organic hybrid⁵⁷ based %RH sensors. Keeping in mind, the affinity of boron ester linkage towards water molecule and facilitated interaction between them due to enhanced diffusion effect of nanochannels, we subjected the newly synthesized Truxene-based COF for the detection of %RH at room temperature. As far as we know, this is the first report in which COFs are used for relative humidity (%RH) sensing and we hope that this will open a new dimension for COFs real time application.

Experimental

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Materials and reagents

All chemicals and solvents were of analytical grade quality and used without further purification. 3,4-dihydroxyhydrocinnamic acid, polyphosphoric acid (PPA), 1,4-phenylenediboronic acid, Boron tribromide (BBr₃), potassium carbonate and dimethylsulphate were purchased from Sigma- Aldrich (Bangalore, India). Thin-layer chromatography was performed on aluminium sheets pre-coated with silica gel (Merck, kiesel gel 60, F254). Column chromatographic separations were performed on silica gel (60-120 mesh). Structural characterisation of the compounds was carried out by ¹H NMR, ¹³C NMR (Bruker Biospin, Switzerland, Avance-iii 400 and 100 MHz spectro- meters, respectively), infrared spectroscopy (Perkin Elmer AX3). UV-Vis spectrophotometer 3000+Spectrum Photoluminescence (excitation wavelength 404 nm) and HRMS (Water g-2 synapt gases). NMR spectra were recorded using deuterated chloroform (CDCl₃) & deuterated dimethylsulfoxide (dmso-d₆) and tetramethylsilane as an internal standard. N₂ adsorption-desorption isotherms were measured on Nova Quantachrome at 77 K. Before measurements, the samples were degassed overnight under vacuum at 120 °C. The specific surface area was calculated in the pressure range of $0.01 < p/p_0 < 0.25$ using the BET micropore assistant surface area method. Density functional theory (DFT) method was employed to approximate the pore size distributions of COF-TXDBA sample. Total pore volume was obtained by the amount of N_2 adsorbed at $P/P_0 \simeq 0.9$ and 0.95, assuming that adsorption on the external surface was negligible compared to adsorption in pores. SEM studies were done by using Jeol 7600F model. TEM measurements were carried out using high resolution transmission electron microscope (HRTEM) instrument (JEOL) at an acceleration voltage of 200 kV.

Synthesis

Synthetic route to achieve the hexahydroxy f<u>un</u>actionalized Truxene is given in scheme S1⁺ and synthesis process of all the intermediate is given below in detail.

3-(3,4-dimethoxyphenyl)propanoic acid (a) To obtain compound a, 3,4-dihydroxyhydrocinnamic acid was refluxed with Me₂SO₄ and dry K₂CO₃ in acetone under N₂ atmosphere. After 12 hr, the reaction was stopped and cooled to room temperature. Solid K₂CO₃ was removed by filtration and acetone was removed by vacuum distillation. After distillation, the residue was dissolved in ethyl acetate. Organic laver was washed with water, brine and dried over anhydrous sodium sulphate. A brown coloured organic residue left after vacuum distillation was further refluxed in 50% (v/v) methanol and 10% NaOH solution till that TLC showed a single spot. Reaction mixture was cooled and acidified with conc. HCl. A white colour solid was precipitated, which was filtered and dried. Further purification was done by recrystallization in hexane/ethylacetate solvent mixture. Yield 85.2%; ¹H -NMR (400 MHz, CDCl₃) δ: 6.82 (d, 1H), 6.77 (d, 2H), 3.89 (s, 3H), 3.88 (3H, s), 2.93 (t, 2H), 2.69 ((t, 2H). ¹³C -NMR (100 MHz, CDCl₃): δ179.03, 148.86, 147.52, 132.74, 120.08, 111.57, 111.25, 55.90, 55.81, 35.90, 30.24.

5,6-dimethoxy-1H-inden-1-one (b) PPA (86.8 g) was heated at 110 $^{\circ}$ C in a 100 ml round bottom flask closed with anhydrous CaCl₂ filled guard tube. Compound **a** (3.0 g) was added to this hot PPA and mixed with glass rod and heated at 110 $^{\circ}$ C for 45 mins. Reaction mixture was cooled and poured into cold water, which was extracted with ethyl acetate. After removing the solvent by vacuum distillation, the crude compound was purified by column chromatography using hexane and ethylacetate solvent mixture. After purification, compound **b** was obtained as a yellow solid. Yield 45 %; ¹H-NMR (400 MHz, CDCl₃) δ : 7.19 (1H, s), 6.90 (1H, s), 3.97 (3H, s), 3.91 (3H, s), 3.06 (2H, t), 2.68 (2H, t). ¹³C-NMR (100 MHz, CDCl₃) δ : 205.84, 155.37, 150.47, 149.34, 129.88, 107.51, 107.42, 104.16, 104.08, 56.31, 56.17, 56.03, 36.53, 25.58.

2,3,7,8,12,13-hexamethoxy-10,15-dihydro-5H-diindeno[1,2-a:1',2'clfluorine (c) Polyphosphoric ester (PPE) (10.4 g) was taken in a 25 mL round-bottom flask which was placed in a preheated oil bath at 140 C. To this preheated PPE compound (b) (3.0 g) was added and stirred for 5 min maintaining the temperature at 140 C. the temperature was subsequently increased to 160 C and reaction mixture was stirred for 25 min. During this reaction condition, excessive foaming occurred. The reaction mixture was then poured in acetone and stirred well. A bright pink coloured solid was settled at the bottom which was collected after repeated centrifugation by washing with DCM until DCM layer will not become clear. Pink coloured solid was dried in vacuum and was subjected to next reaction without purification. (The pink coloured solid obtained was insoluble in nearly all the solvents available in lab, So with an assumption that ~99% of this pink solid is compound (c) we subjected the crude product for the next reaction). Yield 45 %.

Hexahydroxy truxene (d) The pink coloured solid obtained in the previous step was insoluble in nearly all the solvents available in lab, So with an assumption that ~99% of this pink solid is compound **(c)** we subjected the crude product for demethylation and got demethylated product hexahydroxy truxene **d**. Yield 45 %; ¹H-NMR (400 MHz, DMSO-d₆) δ : 9.04 (6H, s), 7.35 (3H, s), 7.13 (3H, s), 3.90 (3H, s), 3.55 (H₂O, s), 4.04 (6H, s). ¹³C-NMR (100 MHz, CDCl₃) δ : 145.11, 137.28, 135.17, 132.04, 112.94, 109.47, 35.61.

Synthesis of COF-TXDBA (e) Compound **d** (150 mg, 1 eqv.) and was dissolved in 30 ml dioxane and stirred till that it is not dissolved completely. Two equivalents of 1,4-phenylenediboronic acid was added to solution and subjected to sonication, make a

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homogeneous mixture. After this 6 ml mesitylene was added to this and subjected to sonication again. Finally 0.2 ml methanol was added to this 5:1 solution of dioxane and mesitylene. This reaction mixture was reflexed at 110 °C under Nitrogen atmosphere. After three days precipitate was filtrate and washed with dry dioxane followed by THF several times. Hence, obtained light brown coloured COFs are dried under vacuum oven at 150 °C. The synthesis scheme of COF-TXDBA is shown in Fig. 1.



Fig. 1 Synthetic scheme of Truxene based COF, COF-TXDBA; (a) Truxene (10, 15-dihydro-5H-diindeno[1,2-a;1',2'-c]fluorene); (b) 1,4-phenylenediboronic acid; (c) and (d) shows the colour change of reaction mixture due to COF formation; (e) Schematic representation of COF-TXDBA.

Performance test for %RH sensing

The humidity sensing measurements were performed on Interdigitated electrodes (13.4mm x 7mm x 0.5mm) having 5 tracks of Ag-Pd electrodes. Prior to measurements, a dilute paste of sample in ethanol was dropped onto the electrodes and dried at 60 °C. The controlled environments for %RH were prepared by using air-tight chambers containing saturated aqueous salts solution of LiCl, MgCl₂•6H₂O, MgNO₃•4H₂O, NaCl, KCl and K₂SO₄ generating 11%, 33%, 54%, 75%, 84% and 98% relative humidity, respectively at 25 °C. The electric impedance was measured using a two-probe Keithley source_meter. The measurements were carried out at 1V AC voltage with frequency varying from 100 Hz.

Results and Discussion

The as-synthesized COF-TXDBA was subjected to FTIR and $^{13}C[^{1}H]$ CP/MAS NMR characterization techniques to obtain the bonding structural information. FTIR showed the strong bands at 1398, 1354 and 1295 cm⁻¹ which is attributed to the asymmetric B–O stretches, confirming the formation of boronate ester links. Furthermore, for a boronic–based COF, characteristic band corresponding to C–B stretching vibration in the boronate esters and C–O stretching vibration in the catechol moieties were observed at approximately 1080 and 1241 cm⁻¹, respectively as shown in Fig. S1.⁺ We have further characterized the resulting COF-TXDBA by solid-state $^{13}C[^{1}H]$ CP/MAS NMR spectroscopy. The spectra displayed a dominant aliphatic carbon signal centred at 36 ppm that originates from the methylene bridging units. In the aromatic region, it displays four broad signals at 148, 135, 126 and 106 ppm indicating the ten nonequivalent carbons of the COF structure in Fig. S2.⁺ Thermogravimetric analyses (TGA) revealed that architectural structure of COF-TXDBA is stable upto 410 °C with minimal weight loss. The weight loss at lower temperatures < 200 °C is attributed to the evaporation of THF and dioxane present in the nano channels of COF-TXDBA (Fig. S3).[†]

DOI: 10.1039/C7TA05043G

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The structure and crystallinity of COF-TXDBA has been analysed using density functional theory (DFT) approach. Two possible structural arrangement, in which two truxene units can linked to diboronic acid unit (Scheme S2)⁺, has been considered to build the periodic crystal lattices, Symmetric-COF-TXDBA (s-COF-TXDBA) with symmetric honeycomb like pore and Asymmetric-COF-TXDBA (a-COF-TXDBA) with asymmetric pore shape (Scheme S3)⁺. The periodic crystal lattices with interlayer spacing of 3.74 Å have been built upon the optimized geometries of s-COF-TXDBA and a-COF-TXDBA using 6-311G basis set with B3LYP exchange-correlation functions, as implemented in Gaussian 09 package.⁵⁸ These layers were stacked with 12Å interlayer offset to match the pore size obtained from physisorption measurements. The simulated PXRD of s-COF-TXDBA in its near eclipsed geometry with interlayer upset of 12Å resembles more likely the experimental PXRD patterns at low angle regime with a sharp peak at 3.2°, reflection arising from (100) plane which infers good crystallinity and long range molecular ordering structure of COF-TXDBA with subsequent peaks from (110), (200) and (210) respectively.



Fig. 2 Simulated PXRD of upset geometry of COF-TXDBA with Pawley refinement;(a) Simulated PXRD patterns Experimental PXRD diffraction and PXRD patterns after Pawley refinement;(b) Top view of eclipsed geometry of COF-TXDBA upset by 12Å in order to account for the experimental pore size distribution.

However, deviation at higher angle has been observed moving from eclipsed packing to staggered packing. This infers the geometry of COF-TXDBA is more likely towards the eclipsed form of s-COF-

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TXDBA. PXRD of both s-COF-TXDBA and a-COF-TXDBA in their eclipsed and staggered geometries have also been analysed (Fig. S5, S6, S7 and S8).⁺

Finally s-COF-TXDBA with interlayer upset of 12Å have been considered for Pawley refinement with experimental PXRD result using Reflex module of Accelrys's Materials Studio 7.0 package⁵⁹ to determine the lattice parameters, which results the unit-cell parameters as, a=b= 35.88 Å, c= 3.74 Å, $\alpha = \beta = 90^{\circ}$, and $\gamma = 120^{\circ}$. Pseudo-Voigt function for peak broadening and Berrar-Baldinozzi function for asymmetry correction have been considered simultaneously to improve profile fitting, the refinement converged with residuals; $R_{wp} = 4.11\%$ and $R_p = 2.66\%$, resulting hexagonal space group of P6/M as shown in Fig. 2.

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Fig. 3 SEM image of the COF-TXDBA (a); A higher magnification image of a square portion (yellow highlight) of the Figure 2a (b); Nanorods structures of the same COF at lower (X 10000) (c) and higher magnification (X 50000) (d), respectively. TEM images of COF-TXDBA at different magnifications (e-h)

Scanning electron microscopy images at the different magnifications in Fig. 3a and 3b reveals a uniform spongy morphology of COF-TXDBA sample. However, as shown in Figure 3c and 3d, formation of few hollow nanorods was also observed. Attempts were made to enrich this nanorods phase by changing the dioxane and mesitylene ratio. It was observed that the systematic increase in the mesitylene ratio from 0 to 50% initially increases the crystallite size and promote the formation of vesicles of random size and shape along with the nanorods (Fig. S9).⁺ Further work is going on to optimize the conditions to enrich the nanorod phases,

as these hollow nanorods show similarity, when Fullerene C_{60} crystalized from 2 mM solution in xylene solvent.⁶⁰ It should be noted that, Truxene can also be formally considered as a building block of Fullerene C_{60} , because of its alternative six and five member ring containing skeleton. So, we can expect that it can show the similar behaviour and appearance of similar nanorods with our ongoing work. As it is observed from the TEM images, Fig. 3e to 3h, the edges of the images (especially 3f) at different magnifications show the scrambled sheet-like structural morphology which is in agreement with the XRD data and in-line with DFT calculation results.



Fig. 4 Nitrogen isotherms at 77 K for COF-TXDBA and NLDFT pore size distributions of COF-TXDBA (Inset).

The porous features of COF-TXDBA were determined by measuring nitrogen gas (N₂) adsorption at 77 K, revealing reversible adsorption and desorption curves typical of type-IV isotherms with a sharp uptake below $p/p_0 = 0.01$ Figure 3. The significant adsorption at $p/p_0 < 0.01$ shows the presence of micropores with a narrow distribution which shows the uniform condensation of the monomers to form a boronate ester COF. Further the step observed between $0.01 < p/p_0 < 0.25$ indicates condensation in mesopores. The absence of hysteresis in adsorption-desorption curves is a common nature of hexagonally aligned 1D mesopores materials, as shown by the COF-TXDBA. It exhibit the surface area of around 1526 m²/g calculated in the pressure range of 0.01 < p/p_0 < 0.25 using the BET micropore assistant surface area calculations. Density functional theory (DFT) method was employed to approximate the pore size distributions of COF-TXDBA employing a cylindrical poreoxide surface model, which yielded average pores sizes of 23 Å. Deviation of pore size from theoretical value (ideal pore size of 31 Å is predicted for the eclipsed form) can be taken into account due to the significant offsets between the stacking layers.^{61,62} There is a steep increase of the adsorbed nitrogen at high relative pressures $(p/p_0 < 0.95)$, which is often assigned to outer surface area or interparticle voids of smaller COF-TXDBA particles, which was confirmed by DFT pore size distribution analysis. The total pore volumes calculated at $p/p_0 = 0.95$ is about 0.35 cm³ g⁻¹ and at $p/p_0 =$ 0.99 is about 0.45 $\rm cm^3~g^{-1}.$ These crystalline features of the COF-TXDBA samples and high surface area attributes were utilised for humidity sensing application. Up to our best knowledge this is the first report to use a COF for humidity sensing applications so far.

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The %RH dependent impedance response of the prepared COF-TXDBA in the 11-98 %RH range is shown in Fig. 5a. As can be seen, at low %RH, the sample exhibit very high impedance, however, as the %RH increases, a dramatic decrease in impedance was observed. The COF-TXDBA exhibits ~3 orders of magnitude change in impedance in 11-98% RH range. Hysteresis is another important attribute to estimate the reliability of sensor and is defined as the maximum difference between the processes of adsorption and desorption. Generally, a sensing material undergoes hysteresis effect at increasing and decreasing %RH. The hysteresis was measured by switching the sensor between the closed chambers (11 - 98 %RH and 98 - 11 %RH). The hysteresis curves for COF-TXDBA based humidity sensor are shown in Fig. 5b, where solid circle line represents the process of adsorption (11-98 %RH) and hollow circle line represents the process of desorption (98-11 %RH). The maximum humidity hysteresis error was ~2.5% for COF-TXDBA in the range of 11-98 %RH.



Fig. 5 Humidity sensing curves showing decrease in impedance with increase in %RH (a). The hysteresis curve showing adsorption-desorption responses measured in the 11-98 %RH range (b).

The response and recovery time are other important parameters to evaluate the performance of humidity sensor and defined as the time taken by a sensor to achieve ~90% of total impedance change in case of the process of adsorption and desorption, respectively. ⁵³ Fig. 6(a) shows the response and recovery curve of COF-TXDBA measured continuously in the lowest and highest humidity environment. The response time (humidification from 11-98 %RH) was about 37 s and the recovery time (desiccation from 98-11 %RH) was around 42 s.The response transients of COF-TXDBA based %RH sensor were measured by switching back and forth the sensor in 4 loops of 11 %RH and 98 %RH, respectively Fig. 6b. It was observed that the impedance of the sensor retains its original value, when humidity is restored to the initial state, which indicates the excellent reversibility of the sensor. The standard deviation in process of switching of sensor response was 2.3%. A comparison of humidity sensing performance with those of published literature in Table - T1⁺ shows that our material exhibit satisfactory %RH sensing attributes as compared to than that of conventional %RH sensors under the similar test conditions.

Thus the high surface area and ordered micropores/ mesopores in this COF-TXDBA are effectively utilized for addressing any target oriented, here in, effective humidity sensing which further opens up the broad role the COFs can play in different applications. These functional designed COFs will be good candidates for being explored in sensing of different other analytes like VOCs.



DOI: 10.1039/C7TA05043G

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Fig. 6 Response and recovery curves of COF-TXDBA (a). Repeated response and recovery characteristics of COF-TXDBA measured at consecutive intervals of time in four loops (b).

To study the effect of humidity on the stability of COF-TXDBA, PXRD patterns were recorded for 5 loops after every cycle (11 \rightarrow 98 \rightarrow 11 %RH) of measurement. The sample was scratched out from the sensing substrate and dried at 100 °C for 10 mins. As can be seen in Fig S10a, the crystallinity of the COF-TXDBA remains intact during the test experiments as can be seen from characteristic sharp peak of COF peak at 3.2° in PXRD. However very low intensity extra peaks also appeared near $2\Theta = 18^{\circ}$ and 25° , which shows very few boronic ester bond are dissociating during the experiment. The SEM image of COF-TXDBA (Fig S10b)[†] after fifth cycle of humidity sensing experiment also confirms that the morphology of the COF was retained and confirms the excellent stability of the material. Thermogravimetric analyses (TGA) of COF- the sensing experiment shows nearly 10% weight loss after 250 °C as compare to as synthesized COF-TXDBA, which can be attributed to formation of small amount of oligomers during interaction of water molecule and COF-TXDBA. Which also confirm that condition used during the sensing experiment is not affecting the COF much (Fig. S3)^{\dagger}. The PXRD patterns as a result of time-dependent stability test for COF-TXDBA were recorded by placing the sample in chamber containing 98 %RH for 10 min, 20 min, 30 min and 50 min time interval. PXRD was recorded after drying the sample at 100 °C for 10 mins. The PXRD patterns of COF-TXDBA measured as a result of time dependent stability test in Fig S11 shows that the sample can sustain its long range order and structural morphology in high humidity conditions (98 %RH) as well. The BET measurement study for COF-TXDBA after exposing the sample to 98%RH and thereafter drying overnight (120 °C) shows that the porous feature of the COF remain intact after this treatment. However, a decrease in the surface area was observed for the treated COF (1048 m²/g) as compared to the as synthesized COF (1526 m²/g). The long-term stability in response of the COF-TXDBA sensor was measured by recording the sensor impedance at each %RH for 70 days (Fig S12)[†]. A standard deviation of just 2.3% which is calculated as the average value of impedance at each %RH level accounts for the excellent stability of the COF-TXDBA material.

Mechanism: The reason for this good response towards humidity sensing is due to the presence of boronic ester linkages, which interacts with the water molecules in the planar sheets of COF backbone. Due to the high surface area and ordered micropores/ mesopores in this COF-TXDBA, a large number of boronic ester active site is exposed for the interaction of water molecule. Under the conditions of low %RH, the little amount of water molecules are adsorbed on the surface of sensor and form first chemisorbed layer

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through Lewis acid-base interaction, where empty orbitals of boron atom interact with the electron lone pair of oxygen atom of water molecule. This little amount of water molecules forms a discontinuous layer and causes hinder in the free movement of water molecules as a result high impedance was observed under low %RH conditions. However, high %RH pushes the system for multilaver adsorption of water molecules and helps in the formation of continues array of water molecules in nanoporous channels. This continues array of water molecules provides a favourable condition for the process of charge transportation followed the Grotthuss chain reaction ($H_2O + H_3O^+ \rightarrow H_3O^+ + H_2O$) and an abrupt increase in conductivity of the sensor was observed.⁶³ Under high %RH conditions, the electric field ionizes the water molecules to produce hydronium ions (H_3O^{\dagger}) as charge carriers, which upon hydration produces protons $(H_3O^+ \rightarrow H_2O + H^+)$ and hopping of these protons between adjacent water molecules become easier at high %RH.

In addition to the sensing attributes, we tried to explore the optical properties of COF-TXDBA samples for their application in the related areas. The diffuse reflectance spectra show the sample has wide absorbance in the visible region centred at around 450 nm with the significance tail absorption from 800 nm onwards, see Fig. 7a. The bandgap is estimated using Kubelka-Munk function to be around 2.3 eV, (Fig. S13).⁺ The emission spectra of the photoluminescence spectra with peak at around 565 nm shows the applicability of these frameworks in optical sensing applications (Fig. 7b).



Fig. 7 Diffuse-reflectance UV-Vis spectra (a) and Photoluminescence spectra (b) of the COF-TXDBA sample.

Conclusion

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In this report, we have demonstrated the first example in which Truxene was used as a building block for the COF-TXDBA synthesis. DFT calculation shows a good agreement with experimental PXRD and the pore size distribution of this framework. The interaction of boronic ester linkage with the water molecules in the nanoporous channels of COF-TXDBA helps in humidity sensing. The COF-TXDBA based %RH sensor shows efficient sensing capabilities with 3 orders magnitude change of impedance in 11-98 %RH range with response time and recovery time of 37 s and 42 s, respectively. They show excellent reversibility with a deviation of 2.3% in process of switching back and forth in the process of adsorption and desorption. The quick recoverability ad stability of the COF-TXDBA is through repeated humidity exposure. sensing measurements followed by PXRD analysis. These features unfold the additional role that the COFs can play in the emerging applications.

Acknowledgements

This work was carried out with the financial support from IISER, Mohali and INST, Mohali. Dr. SK Pal is grateful for INSA Medal for Young Scientist 2015 and the financial support from INSA bearing Sanction No. SP/YSP/124/2015/433. K Kailasam thanks DST-SERB Early Career Research Award (ECR), File the for No. ECR/2016/001469 and DST-Nano Mission funded Technology Project, File No. SR/NM/NT-06/2016. Dr. V K Tomer and Dr. D Nepak thank INST Mohali for the postdoctoral fellowship and Mr. N Jena and Ms. N Sharma also thank INST Mohali for the doctoral fellowship. We are grateful to NMR, HRMS, SEM and SAXS/WAXS facility at IISER Mohali. We sincerely thank Mr. Indrajit Singh for helping with SEM measurements at IISER Mohali. We also thank INST, Mohali for providing N_2 Physisorption and TEM facility. ADS and NSJ remain highly thankful to Center for Development in Advanced Computing (CDAC), Pune for providing its supercomputing facilities on PARAM-YUVA-II.

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DOI: 10.1039/C7TA05043G

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Sensing mechanism illustrating proton hopping between the water molecules physisorbed on the COF-TXDBA surface