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A Dual-Function Highly Crystalline Covalent Organic Framework for HCl Sensing and Visible-Light Heterogeneous Photocatalysis

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ABSTRACT: Covalent organic frameworks (COFs) offer great potential for various advanced applications such as photocatalysis, sensing, and so on because of their fully conjugated, porous, and chemically stable unique structural architecture. In this work, we have designed and developed a truxene-based ultrastable COF (**Tx-COF-2**) by Schiff-base condensation between 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 5,5,10,10,15,15-hexamethyl-10,15-dihydro-5*H*-diindeno(1,2-*a*:1',2'-*c*)fluorene-2,7,12-tricarbaldehyde (Tx-CHO) for the first time. The resulting COF possesses excellent crystallinity, permanent porosity, and high Brunauer–Emmett–Teller (BET) surface areas (up to 1137 m² g⁻¹). The COF was found to be a heterogeneous, recyclable photocatalyst for efficient conversion of arylboronic acids to phenols under visible-light irradiation, an environmentally friendly alternative approach to conventiona



SI Supporting Information

irradiation, an environmentally friendly alternative approach to conventional metal-based photocatalysis. Besides, **Tx-COF-2** provides an immediate naked-eye color change (<1 s) and fluorescence "turn-on" phenomena upon exposure to HCl. The response is highly sensitive, with an ultralow detection limit of up to 4.5 nmol L^{-1} .

INTRODUCTION

Covalent organic frameworks (COFs) are the emerging class of porous organic materials, constructed from various building blocks, connected via strong covalent organic bonds.¹⁻⁶ In recent years, COFs have gained immense interest because of their extraordinary properties such as high porosity, low density, extreme crystallinity, and their capability of introducing a new organic moiety inside the stable framework.⁷⁻¹⁰ Because of these properties, COFs have expanded their dimensions into various applications, including gas storage and separation,^{11–13} sensing,^{14–17} energy storage and con-version,^{18–26} proton conduction,^{27,28} optics,^{29–33} cataly-sis,^{34–43} and so on. In terms of photocatalysis, they have acquired enormous attention because of the combination of their π -conjugated skeleton, uniform pore structure, tunable pore channels, high surface area, and, most importantly, their insolubility in all organic solvents, which is the key feature for their heterogeneous character. These features demonstrate that COFs could be considered as a potential candidate for photocatalytic applications.

Among several π -conjugated molecules used as a monomer for the construction of COFs, our particular interest is in the heptacyclic truxene unit. Truxene can be considered as 1,3,5triphenylbenzene clipped through three bridging methylene groups in a plane. These three methylene groups aid planarization of the system and extend the π -conjugation by forming three additional fused five-membered rings.⁴⁴ This unique structural motif provides truxene to be an attractive photoactive core and enhances electron-donating capabilities.^{45,46} The flat trigonal geometry of the truxene has raised interest as a monomer in the construction of functional conjugated microporous polymers (CMPs) and COFs for various applications.^{47–54} Herein, for the first time, we have designed and synthesized a truxene-based [3 + 3] COF using Schiff-base chemistry and demonstrated its dual function both as a heterogeneous photocatalyst and a naked-eye acid sensor.

Recently, photocatalysis has become a vital category in organic synthesis due to its mild reaction conditions such as room temperature and atmospheric pressure, simple setup, and, most importantly, an environmentally friendly alternative to the metal-based catalysts.^{55,56} However, inorganic transition metal complexes 57-63 and organic dyes 64-67 have already shown various chemical transformations as homogeneous photocatalysts. These metal-based photocatalysts and organic dyes are commercially available, and they possess excellent stability. However, their inherent disadvantages, separation cost of homogeneous catalysts after completion of the reaction, and so on restrict their extensive work in large-scale synthesis used for commercial applications. Therefore, the demand for metal-free, heterogeneous catalysts with high stability, easy recovery, and reusability from the reaction mixture could reduce the aforementioned concerns.

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(a)



Figure 1. (a) Synthetic scheme of Tx-COF-2 (inset: the physical appearance of Tx-COF-2). (b) PXRD patterns of Tx-COF-2: experimental (red) and Pawley refined (blue, circled), difference plot (dark gray) between the refined and experimental PXRD patterns, and Bragg positions (green). Simulated PXRD pattern of (c) slipped AA stacking mode (wine) and (d) staggered AB stacking mode (blue) of Tx-COF-2.



Figure 2. (a) Solid-state ¹³C NMR spectrum of Tx-COF-2. (b) Nitrogen adsorption and desorption isotherms of Tx-COF-2. (c) The pore size distribution (PSD) was calculated from the QSDFT method of Tx-COF-2. (d) HRTEM image of Tx-COF-2. (e) Zoomed-in HRTEM image of the marked yellow area in (d), showing a periodicity of 0.48 nm. (f) FFT filter applied on (e). (g) Corresponding height profiles of the marked line (cyan line) in (f). (h) SAED patterns Tx-COF-2 showing the presence of various crystalline phases. (i) PXRD profiles of Tx-COF-2 as-synthesized (black) and after treating with 12 M NaOH (red), 12 M HCl (blue), TFA (green), water (purple), and visible-light (orange) for 5 days.

In this article, we demonstrate the synthesis of Tx-COF-2 (Figure 1a) by performing a reaction between 1,3,5-tris(4aminophenyl)benzene (TAPB) and 5,5,10,10,15,15-hexamethyl-10,15-dihydro-5H-diindeno(1,2-a:1',2'-c)fluorene-2,7,12 tricarbaldehyde (Tx-CHO). The reaction was conducted under solvothermal conditions and heated at 120 °C for 3 days by

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employing a solvent combination of mesitylene/dioxane (1:1, v/v) and 6 M acetic acid as a catalyst. Interestingly, Tx-COF-2 exhibited high BET surface area (S_{BFT}) up to 1137 m² g⁻¹, extraordinary stability in harsh chemical conditions such as 12 M NaOH or 12 M HCl, and irradiation of visible light for a minimum of 5 days. Tx-COF-2 showed excellent photocatalytic activity for the aerobic oxidative hydroxylation of arylboronic acids. It preserved its crystallinity and activity even after the 10th photocatalytic cycle. Moreover, Tx-COF-2 was shown to be a selective "switch-on" sensor for HCl. Upon exposure to HCl, it became fluorescent and reverted to its negligible fluorescent intensity (pristine) after exposure to NH₃ vapor. Most importantly, a naked-eye reversible change in color from light yellow to orange was also observed when treated alternatively with HCl and NH₃ vapor both in solid and in the dispersed medium of Tx-COF-2.

RESULTS AND DISCUSSION

In a typical synthesis, Schiff-base condensation reaction was used to construct **Tx-COF-2** between 1,3,5-tris(4-amino-

Table 1. Control Experiments^a

ноос		H Visible Tx-CO H DIPEA (: CH ₃ CN/H ₂	light DF-2 5 equiv.) O (4/1), air	ноос-	————————————————————————————————————
entry	visible light	photocatalyst	atmosphere	additives	yield ^{b} (%)
1	on	Tx-COF-2	air	_	99
2	on	Tx-COF-2	O ₂	-	99
3	on	Tx-COF-2	N_2	-	N.D. ^c
4	off	Tx-COF-2	air	-	N.D. ^c
5	on	no catalyst	air	-	N.D. ^c

^{*a*}Conditions: **Tx-COF-2** (10 mg, 0.012 mmol), 4-carboxyphenylboronic acid (0.12 mmol), $CH_3CN:H_2O$ (1.6 mL:0.4 mL), DIPEA (5.0 equiv), irradiation of 20 W white LEDs, 48 h. ^{*b*}Isolated yield. ^{*c*}N.D. = not detected.

phenyl)benzene (TAPB) (27.5 mg, 0.078 mmol), 5,5,10,10,15,15-hexamethyl-10,15-dihydro-5H-diindeno(1,2a:1',2'-c)fluorene-2,7,12-tricarbaldehyde (Tx-CHO, detailed synthesis and characterization are given in Supporting Information, Scheme S1, Figures S1 and S2) (40 mg, 0.078 Table 2. Substrate Scope of Tx-COF-2 in Oxidative Hydroxylation of Arylboronic Acids to Phenols^{*a*}

	он	visible ligh Tx-COF-2	Ar-OH	
Ar-J	OH CH	DIPEA (5 eq H ₃ CN/H ₂ O (4		
entry	substrate	product	time (h)	yield ^b (%)
1	ноос-	н ноос-Дон н	48	99
2	онс-	н онс- Он	48	95
3		н о ₂ N-Он	48	99
4	H₃CO₂C-√_−В́О	н н ₃ со ₂ с-	48	92
5		н NC-ОН	48	99
6	Br-	н вгОн н	48	87
7		н 💭-он	72	74

^{*a*}Conditions: **Tx-COF-2** (10 mg, 0.012 mmol), arylboronic acid (0.12 mmol), $CH_3CN:H_2O$ (1.6 mL:0.4 mL), DIPEA (5.0 equiv), irradiation of 20 W white LEDs. Ar = aryl group. ^{*b*}Isolated yield.

mmol), and 0.5 mL of 6 M aqueous acetic acid, heated in a Schlenk tube for 72 h under solvothermal conditions (Figure 1a, Scheme S2). The solvothermal conditions were screened with various solvent combinations, and the best crystallinity was observed in mesitylene/dioxane (1:1, v/v) solvent mixture (Figure S4). To characterize the successful formation of Tx-COF-2, we first employed Fourier transform infrared (FT-IR) spectroscopy. As shown in the FT-IR spectra of Tx-COF-2 (Figure S3), the stretching band of C=O at 1695 cm^{-1} in Tx-CHO and that of amine $(N-H, \sim 3437, 3357 \text{ cm}^{-1})$ in TAPB disappeared. The appearance of a new vibrational band at ~1624 cm⁻¹ indicated the formation of an imine bond (C= N) in Tx-COF-2, which is consistent with prior studies.⁶ Furthermore, solid-state ¹³C cross-polarization-magic angle spinning nuclear magnetic resonance (CP-MAS NMR) spectroscopy of Tx-COF-2 revealed peaks at 22 and 46



Figure 3. (a) Reusability of Tx-COF-2 for oxidative hydroxylation of 4-carboxyphenylboronic acid. (b) Nitrogen adsorption and desorption isotherms of Tx-COF-2 before (olive) and after (blue) the 10th catalytic cycle.



Figure 4. (a) UV-vis spectrum of the **Tx-COF-2** (inset: Kubelka–Munk function plot to evaluate the bandgap of **Tx-COF-2**). (b) Calculated position of the conduction band and the valence band of **Tx-COF-2**, the reduction potential of $O_{2^{\prime}}$ and the oxidation potential of DIPEA.



Figure 5. Probable reaction mechanism for the photocatalytic conversion of arylboronic acids to phenols by Tx-COF-2 as a photocatalyst.

ppm, originating from the methyl groups and tertiary carbon of the truxene unit, respectively. The other signals in the range 120-150 ppm can be assigned to the aromatic carbons present in the framework. In addition, a signal at 157.9 ppm is indicative of the existence of the imine linkage in **Tx-COF-2** (Figure 2a), which supports the formation of the reticular framework.

The crystalline structure of Tx-COF-2 was confirmed by powder X-ray diffraction (PXRD) analysis. As shown in Figure 1b, the PXRD pattern of Tx-COF-2 showed high crystallinity, with the first intense peak at a low 2θ value of 3.62° , which corresponds to (100) reflection plane, along with minor peaks at 6.31°, 7.30°, 9.68°, 13.22°, and 18.99° corresponding to the (210), (200), (101), (231), and (002) facets, respectively. To elucidate the structure of Tx-COF-2 and to calculate the unit cell parameters, a monolayer of Tx-COF-2 (hcb net) was built, and several stacking configurations were generated, including eclipsed (AA), slipped stacking (slipped AA), and staggered stacking (AB) models (Figure 1c,d and Figure S5). These structural models were optimized by density-functional tightbinding (DFTB) calculations as implemented in DFTB+ 19.1. The comparison between the simulated PXRD pattern and experimental PXRD data indicated that the experimental PXRD profile matched well to the simulated pattern with slipped AA stacking in the triclinic system, P1 space group (Figure 1c and Figure S5). Additionally, the lower value of the stacking energy of the model with slipped AA stacking (-355.1)

kJ/mol) than that of AB stacking (-256.7 kJ/mol) further supported that **Tx-COF-2** adopted slipped AA stacking. The obtained powder pattern was refined by Pawley refinement which gave a unit cell with parameters a = 25.6 Å, b = 26.1 Å, c = 9.4 Å, $\alpha = 94.4^{\circ}$, $\beta = 90.5^{\circ}$, and $\gamma = 62.6^{\circ}$. The final R_{wp} and R_{p} values converged to 5.29% and 2.26%, respectively.

The porous properties of Tx-COF-2 were evaluated by the nitrogen adsorption-desorption experiment, measured at 77 K. As shown in Figure 2b, Tx-COF-2 displayed a typical type I reversible isotherm, indicating a microporous nature. The BET surface area was calculated to be 1137 m² g⁻¹ (Figure S6) compared to the theoretical surface area of 1357 m² g⁻¹. Furthermore, the quenched solid density functional theory (QSDFT) method was used to calculate the pore size distribution (PSD). The method showed a narrow pore size distribution (PSD) with a prominent peak at 2.3 nm, which is in good agreement with the *d*-spacing value (2.4 nm) at 2θ = 3.62° obtained from the PXRD analysis (Figure 2c). The morphologies of the Tx-COF-2 were studied by electron microscopy. A particulate morphology was revealed by field emission scanning electron microscopy (FE-SEM) of Tx-COF-2 (Figure S7). In addition, the finer details of the internal structure of Tx-COF-2 were revealed by HRTEM analysis. HRTEM analysis showed an ordered, hexagonal porous structure that was in line with the structural model. The observed well-defined lattice fringe with a periodicity of 0.48 nm (Figure 2d,e) corresponds to the (002) plane of the refined

Article



Figure 6. (a) Photographs of **Tx-COF-2** suspension in 1,4-dioxane after exposure to HCl and NH₃ vapor: naked eye (up) and in the UV light (down). (b) Fluorescence spectra of **Tx-COF-2** suspension (0.5 mg mL⁻¹) in 1,4-dioxane at λ_{ex} = 478 nm upon addition of HCl from 0 to 65.3 μ mol L⁻¹. (c) Solid-state UV–vis spectra of **Tx-COF-2**: as-synthesized (black), after treatment with HCl (blue) and NH₃ (red) vapor. (d) Solid-state fluorescence spectra of **Tx-COF-2**: as-synthesized (black), after exposure to HCl (blue) and NH₃ (red) vapor (λ_{ex} = 478 nm). (e) Calibration curve of fluorescence intensity versus HCl concentration. (f) Schematic representation of the protonation and deprotonation mechanism of the **Tx-COF-2** after alternate exposure to HCl and NH₃ vapor.

PXRD pattern $(2\theta = 18.9^{\circ}, d = 0.46 \text{ nm})$ and well-matched with the layer-to-layer distance (0.43 nm) of the slipped AA model. Furthermore, the selected area electron diffraction (SAED) pattern revealed various highly crystalline phases present in the **Tx-COF-2** (Figure 2h).

Tx-COF-2 showed excellent thermal as well as chemical stability. The thermogravimetric analysis indicated that Tx-COF-2 was stable up to 375 °C under a nitrogen atmosphere (Figure S8). PXRD assessed the chemical stability of the Tx-COF-2 after 5 days of treatment in water, TFA, 12 M HCl, and 12 M NaOH. In all these harsh conditions, Tx-COF-2 retained its crystallinity. Furthermore, most of the reported iminelinked COFs degraded upon irradiation of light for a long time;69,70 Tx-COF-2 showed no degradation in the crystallinity after irradiation with 20 W white LED for 5 days (Figure 2i). Furthermore, the high hydrophobic nature (Figure S9) of the synthesized COF protects the imine bonds of Tx-COF-2 from hydrolysis and therefore retains its high crystallinity. This possibly contributes to the high stability of Tx-COF-2 toward harsh acid and base conditions, consistent with the prior reports.⁷¹ The high stability toward harsh chemicals and photostability of Tx-COF-2 render it an excellent candidate for heterogeneous photocatalysis.

The extensively conjugated skeleton, high photostability, and chemical stability of **Tx-COF-2** led us to think whether it could act as a heterogeneous photocatalyst without using metal. We selected visible-light-mediated oxidative hydroxylation of arylboronic acids to phenols to check its photo-activity since metal-free heterogeneous photocatalysis provides an environmentally friendly substitute to the traditional-metal-based redox chemical processes. Additionally, phenols are well-known, adaptable intermediates and constituents in natural products, polymers, and pharmaceutical industries.^{72–74} In previous reports, it was illustrated that oxidative hydroxylation

of arylboronic acids to produce corresponding phenols could be done by using homogeneous photoredox catalysts, such as Ir or Ru complexes⁷⁵ and methylene blue (MB).⁷⁶ Ruthenium and iridium complexes such as Ru(bpy)₃Cl₂ and Ir(PPy)₃ are most commonly used for visible light photocatalysts.7 $Ru(bpy)_3Cl_2$ and similar complexes also have been used for the water splitting 78,79 and the reduction of CO₂ to methane,⁸ OLEDs,^{81,82} and initiator for polymerization reactions^{83–85} or in photodynamic therapy.⁸⁶ $Ru(bpy)_3Cl_2$ has also been used as visible light photoredox catalyst for α -alkylation of aldehydes,⁸ $\begin{bmatrix} 2 + 2 \end{bmatrix}$ cycloaddition,⁸⁸ and reductive dehalogenation of activated alkyl halides.⁸⁹ Compared to these earlier works, our designed COF is the first example of highly stable truxenebased functional material constructed by Schiff-base chemistry. Tx-COF-2 could provide a heterogeneous catalytic environment in mild and harsh reaction conditions, which helps to easily achieve the reusability and recyclability of the photocatalyst.

In the recent past, a couple of COFs containing benzoxazole core^{69,70} and vinylene-bridged COFs⁹⁰ have already shown photocatalytic activity for the transformation of boronic acids to corresponding phenols. We believe that in our work the photocatalytic activity of **Tx-COF-2** could be a result of the highly electron-rich truxene (Tx-CHO) unit.^{91–93} Thus, we selected the conversion of 4-carboxyphenylboronic acid to 4-hydroxybenzoic acid as a standard reaction for the precise evaluation of the reaction. The elements that influence this transformation, such as photocatalyst, light source, oxygen source, and sacrificial agent, were evaluated systematically. As shown in Table 1, the yield of the reaction can be obtained up to 99% with *N*,*N*-diisopropylethylamine (DIPEA) as a sacrificial agent and **Tx-COF-2** as a photocatalyst under an oxygen atmosphere or air in the presence of visible light. In the absence of **Tx-COF-2**, no conversion was observed (Table 1,

entry 5), which suggested that Tx-COF-2 has a significant part as a photocatalyst. Similarly, the transformation of the reaction was hard to observe when conducted in the absence of visible light and the nitrogen atmosphere (Table 1, entries 3 and 4). It could be concluded from all these control experiments that light source, oxygen, and photocatalyst are necessary for this reaction.

The superiority of Tx-COF-2 as a photocatalyst was further examined by recycling experiments. Because of the insoluble nature of Tx-COF-2 in all organic solvents, it was simply removed from the reaction mixture by centrifugation after the completion of the reaction. The experiment was performed on 4-carboxyphenylboronic acid. As shown in Figure 3a, without any reactivation procedure or specific treatment, Tx-COF-2 gave excellent results for the conversion of 4-carboxyphenylboronic acid to 4-hydroxybenzoic acid even after 10 runs as a photocatalyst. The crystallinity of recycled Tx-COF-2 catalyst was fully comparable with that of the as-synthesized Tx-COF-2, as observed from PXRD, with a small decrease in the intensity^{69,70} (Figure S12). Furthermore, after the 10th catalytic run, Tx-COF-2 retained its microporous nature with a slight drop in the BET surface area, as shown by the nitrogen adsorption and desorption isotherms (Figure 3b, Figures S13 and S14).

We then tested the versatility of the **Tx-COF-2** as a photocatalyst for the conversion of different derivatives of arylboronic acid to the corresponding phenols. As shown in Table 2, **Tx-COF-2**, as a photocatalyst, can easily convert all the substituted arylboronic acids to the corresponding phenols. Usually, the reaction rate is faster with the substrates bearing electron-deficient groups (Table 2, entries 1–5) than that of the substrates bearing electron-rich groups (Table 2, entries 6 and 7). In reported literature, this selectivity has been explained according to the fact that the empty p-orbital of boron atoms present in electron-deficient arylboronic acid substrates are more available for the O₂^{•-} radical anion.⁹⁴

To get a deeper understanding of the photocatalytic procedure, various electronic properties of Tx-COF-2 were studied. Initially, the UV-vis absorption spectrum of Tx-COF-2 showed a broad light absorption edge in the range 300–700 nm, indicating that Tx-COF-2 can absorb light in the visible region (Figure 4a). The optical band gap (E_{σ}) of Tx-COF-2 was determined by the Kubelka-Munk plot and estimated to be 2.65 eV, indicating its semiconducting nature (Figure 4a, inset). Cyclic voltammetry (CV) was further recorded to determine the oxidative potential of Tx-COF-2. The CV experiment displayed an oxidation peak with an onset value of +0.93 V versus the saturated calomel electrode (SCE), which corresponds to the valence band potential $(E_{\rm VB})$ (Figure S10).⁷⁰ The approximate conduction band potential (E_{CB}) was evaluated by using the formula $E_{CB} = E_{VB} - E_{g}$. Thus, the E_{CB} value of Tx-COF-2 was estimated to be -1.72 V. The reduction potential (E^{red}) of O_2 and the oxidation potential (E^{ox}) of DIPEA versus SCE are -0.86 V and +0.90 V, respectively. For oxidation of DIPEA and reduction of O₂, a photocatalyst is expected to possess a $E_{\rm VB}$ value greater than E^{ox} of DIPEA and a E_{CB} value less than E^{red} of O₂.⁹⁴ The E_{CB} and $E_{\rm VB}$ of Tx-COF-2 entirely meet the above-mentioned criteria (Figure 4b). In addition, electron paramagnetic resonance (EPR) spectroscopy was performed to confirm the generation of $O_2^{\bullet-}$ upon addition of the superoxide radical scavenger 5,5-dimethyl-1-pyrroline N-oxide (DMPO), shown in Figure S11. A probable reaction mechanism for the

conversion is shown in Figure 5. Initially, an excited intermediate **Tx-COF-2*** was formed, upon irradiation of visible light, followed by an electron extraction from DIPEA by single-electron transfer (SET) pathway to generate a radical anion **Tx-COF-2^•** which left a radical cation DIPEA^{•+}. Then the **Tx-COF-2•** was oxidized by molecular oxygen to restore **Tx-COF-2**, used in upcoming cycles. In addition, $O_2^{\bullet-}$ was filled in the vacant p-orbital of boron atom, leading to the generation of **A**. A hydrogen atom was pulled out from DIPEA^{•+} to produce intermediate **B**. Next, loss of a $-OH^-$ ion and rearrangement formed intermediate **C**. Finally, intermediate **C** hydrolyzed to afford the desired phenolic product **D**.

As mentioned earlier, the Tx-COF-2 was very stable in contact with 12 M HCl, which also caused a visual change of the color from yellow to orange. This phenomenon motivated us to examine the sensing properties of Tx-COF-2 toward HCl. Upon exposure to HCl vapor, the suspension (0.5 mg mL^{-1} in 1,4-dioxane) of Tx-COF-2 went through a naked-eye color change from light yellow to orange. When the HCl treated suspension was subjected to light at 365 nm of wavelength, an orange fluorescence emission color was also observed (Figure 6a). This color change was completely reversible when HCl treated Tx-COF-2 exposed to the NH₃ vapor. The color changes occurred in fractions of a secondfaster than those previously reported COF-based HCl sensors.^{95,96} Notably, as-synthesized Tx-COF-2 was very weakly fluorescent, but the HCl-treated suspension of Tx-COF-2 showed remarkable enhancement in the fluorescence intensity. Thus, Tx-COF-2 could be used as a "turn-on" sensor because it offered a high increment in the fluorescence intensity after treating with HCl vapor and reverted to its pristine weakly fluorescent nature after exposure to NH₃ vapor. Besides, no degradation in the fluorescence intensity as well as in naked-eye color changes up to 10 alternating cycles of exposure to HCl and NH₃ vapor confirmed the outstanding reversibility and structural integrity of Tx-COF-2 as HCl sensor. We then investigated the relationship between the fluorescent intensity of 1,4-dioxane suspended Tx-COF-2 (0.5 $mg mL^{-1}$) and the HCl concentration (diluted in 1,4-dioxane). We observed that upon the addition of a very little amount of HCl concentration (8 μ mol L⁻¹) to Tx-COF-2 suspension the weak-intensity peaks at 495 and 515 nm started disappearing, and a new peak appeared at 558 nm (λ_{ex} = 478 nm) (Figure 6b). The fluorescence intensity enhanced gradually upon increasing the HCl concentration from 8 to 65.3 μ mol L⁻¹ and remained unchanged after that. The lowest limit of detection was found to be 4.5 nmol L^{-1} from the calibration curve in the range of HCl concentration from 1 to 55 μ mol L⁻¹, which showed linear correlation ($R^2 = 0.9864$) with detection at 558 nm (Figure 6e). The fluorescence lifetime decay of Tx-COF-2 was found to be 0.49 ns at 65.3 μ mol L⁻¹ HCl concentration (Figure S18). A possible mechanism of sensing toward HCl is shown in Figure 6f. The Tx-COF-2 presumably undergoes protonation at the imine nitrogen atom, which takes part in the conjugation of the COF and results in an apparent change in fluorescence emission as well as in color.⁹⁷ Previously reported COFs support the fact of protonation at the nitrogen atom present in the COFs.⁹⁸ Next, the reusability and recyclability of Tx-COF-2 as HCl sensor were investigated and shown in Figure S16. Tx-COF-2 was recovered by the addition of a solution of triethylamine (1.6 mmol L⁻¹) from the HCl-treated **Tx-COF-2** at a concentration (1.6 mmol L^{-1}) until the pH is equal to 7. Moreover, the selectivity of the Tx-COF-2 toward

HCl was investigated by treating **Tx-COF-2** suspension to several acids with a concentration of 2.0 mmol L^{-1} . As shown in Figure S17, in comparison with the other acids, only HCl produced a notable enhancement in the fluorescence intensity of **Tx-COF-2** when excited at 478 nm.

Next, we investigated the naked-eye detection of HCl vapor by Tx-COF-2 in a solid state. A color change from yellow to orange was observed when Tx-COF-2 powder was exposed to HCl vapor and returned to its natural color after the exposure of NH₃ vapor (Figure S15 and Video S1). In the UV-vis spectra, a red-shift in the absorbance maxima was observed after exposure to the HCl vapor and regenerated with NH₃ vapor (Figure 6c). In addition, when we recorded fluorescence spectra of Tx-COF-2 powder, fluorescence emission was observed for the HCl-treated Tx-COF-2 powder and returned to as-synthesized nonfluorescent powder when exposed to NH₃ vapor (Figure 6d). Moreover, the crystallinity of Tx-COF-2 remained unaltered after alternate exposure to HCl and NH₃ vapors (Figure S19). In conclusion, these phenomena were observed presumably because of the protonation at the nitrogen center in the Schiff-base backbone of the Tx-COF-2.99 As the crystallinity of Tx-COF-2 remained unchanged after exposure to HCl, we believe that the structural integrity due to the presence of truxene core in Tx-COF-2 might also be contributing toward HCl sensing. Compared to the previous reports, this is the first report in COFs where we simultaneously observed a "turn-on" fluorescence phenomena and a naked-eye color change when Tx-COF-2 was exposed to HCl.

CONCLUSIONS

In summary, we have synthesized a novel dual-function truxene-based COF using Schiff-base chemistry. Based on our results, Tx-COF-2 was found to be highly crystalline with permanent porosity and high chemical stability even in harsh chemical conditions, for example, 12 M HCl, 12 M NaOH, and so on. Tx-COF-2 has been used for visible-light heterogeneous photocatalytic transformation of arylboronic acids to phenols with high efficiency. Most importantly, Tx-COF-2 has many advantages as a photocatalyst such as a reusability and insolubility in various organic solvents. Hence, we believe that Tx-COF-2 could be a promising photocatalyst for chemical transformations. Besides, we tested Tx-COF-2 for HCl sensing and found very high sensitivity and selectivity toward HCl. We observed the "turn-on" phenomenon in the fluorescence spectroscopy accompanied by naked eye color change in solid as well as in the dispersed state in rapid response time (<1 s). Tx-COF-2 can sense HCl up to 4.5 nmol L⁻¹, which is the first example of very low detection for HCl sensing in COFs. This COF was found to be an excellent photocatalyst and sensor for HCl vapor. We believe that our work will open up several new strategies to develop simple and smart materials for practical applications, from naked eye readable sensors to photocatalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c00574.

Detailed synthetic procedure of monomers and Tx-COF-2, ¹H and ¹³C NMR spectra of substrates (Figures S23–S40), FT-IR spectra, FE-SEM images, TGA curve,

cyclic voltammetry (CV), fluorescence experiments and computational details (Figures S20–S22, Tables S1–S3) of **Tx-COF-2** (PDF)

Video S1 (MP4)

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Notes

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