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Continuous detection of HCl and NH₃ gases with a highperformance fluorescent polymer sensor

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A novel fluorescent triazine-based covalent organic polymer (COP-1) sensor toward HCl and NH₃ gases has been designed and synthesized. Both the COP-1 powders dispersed in solvents and the COP-1 film formed on surface of quartz sheets exhibit stable fluorescence and sensitive HCl/NH₃ response. Immersed in HCl-bubbled solvents weakens and redshifts the fluorescence emission of the COP-1 powders, owing to the protonation induced charge transfer (CT). Subsequent injection of NH₃ into the solvents recovers the fluorescence via deprotonation. Interestingly, the microporous COP-1 film also shows similar fluorescence response to HCl/NH₃ gas with high sensitivity and good reversibility, which could serve as a solid-state optical probe for continuous and quantitative detection of HCl and NH₃ gases. The formation of the red-shifting hydrogen bonds is found to be the origin.

Introduction

Irritating, volatile and colorless hydrogen chloride (HCl) and ammonia (NH₃) gases have been widely applied in industry¹⁻⁴. The main sources of HCl and NH₃ gases in air are fuel burning, chemical and biological metabolic processes.^{5,6} HCl gas is easily dissolved in water to form hydrochloric acid, which is one ingredient of the acid rain.^{7,8} Serious corrosion effect on metals, facilities and buildings has also correlation with HCl and NH₃ gases.⁹ HCl and NH₃ gases could be inhaled into the human body via the respiratory system, and long-term exposure may cause laryngeal mucosal irritation, nasal erosion ulcer and gastrointestinal diseases.^{10,11} In order to mitigate the hazard at utmost, on-site and real-time monitoring of the pollutants is quite important.¹²⁻¹⁶ Traditional detection methods for HCl and NH₃ gases show deficiencies in sensitivity, selectivity and operation.¹⁷⁻¹⁹

Optical detection technology shows great advantages in high sensitivity, good selectivity, easy operation and low cost, which has been extensively applied in environmental, industrial and biological fields.²⁰⁻²² We devote ourselves to develop well-behaved optical sensors for detection of HCl and NH₃ gas, particular for them operated in solid state.²³

Although several optical sensors for HCl and NH₃ gases have

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been reported, the solid-state ones with good reversibility and real-time efficiency are still appealing.²⁴⁻²⁷ Recently, Kalimuthu et al. has reported an optochemical gaseous HCl sensor with a meso-tetramesitylporphyrin (MTMP) deposited glass substrate. The Soret band of the MTMP film was shifted from 434 nm to 452 nm upon exposure to HCl gas, whereas no shift was observed when the film was subsequently treated with NH₃ gas.¹² Deshusses et al. reported a polyaniline composite membrane for the detection of NH₃ gas. However, it requires at least 30 minutes completing the sensing process.¹³

In this work, we synthesized a novel triazine-based covalent organic polymer (COP-1) (Scheme 1). The microporous COP-1 film was formed on surface of the quartz sheets under solvent thermal conditions. The homogeneous pores distributed on the COP-1 film are significant for gas detection. To our delight, the COP-1 film shows strong fluorescence, contrary to usual luminescent materials with aggregation-induced quenching (ACQ) traits.²⁸ Moreover, experimental results show that the COP-1 film could serve as a solid-state probe for HCI/NH₃ gas, which features real-time response, easy operation, high sensitivity and good



Scheme 1 The synthetic route of COP-1.

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reversibility. Quantum chemical calculations were also performed to investigate the detection mechanism.

Experimental

Materials and instruments

Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with Cu K_{\alpha} (λ = 1.5418 Å) radiation in the range of 3-50°. Fourier transform infrared (FT-IR) spectra were obtained with a Thermo Nicolet A370 spectrometer (KBr pellets). X-ray photoelectron spectroscopy (XPS) was obtained using an Escalab 250 instrument. The UV-Vis diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV-3600 spectrometer. Scanning electron microscope (SEM) images were obtained using Quanta FEG250 field emission environmental SEM (FEI, United States). Nitrogen gas and carbondioxide gas porosimetry measurements were performed on an automatic volumetric adsorption equipment(ASIQM0G002-3) and porosity analyzer after the samples were outgassed under vacuum at 70°C for 6 h. Thermogravimetric (TGA) curves were measured using STA449C-QMS403C thermalanalyser. Germany The fluorescence spectra were measured by the Tianjin Gangdong F-380 spectrophotometer. Different humidity environments were created by a Constant Temperature and Humidity Chamber (BPHS-060A, Shanghai Bluepard Experimental Instruments Co., Ltd.).

All chemicals were obtained commercially and used as received unless otherwise stated. Potassium carbonate (K₂CO₃), potassium hydroxide (KOH), methanol (CH₃OH), dichloromethane (CH₂Cl₂), ethanol (CH₃CH₂OH), acetonitrile (CH₃CN), benzene (C_6H_6), sodium chloride (NaCl), acetic acid (CH₃COOH), NH₃·H₂O were obtained from Kermel Chemical Reagent Co., Ltd. (Tianjin, China). Concentrated sulfuric acid (H₂SO₄) and concentrated hydrochloric acid (HCl) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 1,4-Phthalaldehyde was obtained from Sun Chemical Technology Co., Ltd. (Shanghai, China). Deionized water was obtained from the Sartoriusarium 611DI water 2,4,6-Trimethyl-1,3,5-triazine purification system. was prepared according to literatures.²⁹

Synthesis of 2,4,6-trimethyl-1,3,5-triazine

Anhydrous acetonitrile (53 mL, 1mol), absolute ethanol (58 mL, 1 mol), anhydrous benzene (82 mL, 1 mol) were put into a 500-mL round-bottom flask, then HCl gas (43.1g) was added under stirring. The mixture was stirred at room temperature for 48 h. The solid was collected by filtration and washed three times (10 mL * 3) with dichloromethane (106.4 g, 86.1 %).

The solid (61.75 g, 0.5 mol, dissolved in 100 mL dichloromethane) and K_2CO_3 (86g, 0.6 mol, dissolved in 300 mL distilled water) were rapidly mixed rapidly and stirred for 10 min. The organic phase was separated and the aqueous phase was extracted twice (30 mL * 2) with dichloromethane. The organic phase was dried over anhydrous K_2CO_3 . The fractions below 60°C were removed by distilling to get a pale yellow liquid (acetimide ethyl ester, 36.7 g, 83.7%).

Acetic acid (3 mL, 0.063 mol) was slowly added into acetimide ethyl ester (67.9 g, 0.78 mol) under stirring, and the reaction temperature was maintained between 25°C-30°C. Then the mixture was stirred for 24 h. After completion of the reaction, the fractions below 80°C were removed by distillation, and the residue was diluted with an appropriate amount of methylene chloride. The white solid was removed by pumping filtration. The filtrate was distilled at atmospheric pressure, and the fractions between 149°C-155°C were collected (15.7 g, 16 %).

Synthesis of COP-1

2,4,6-Trimethyl-1,3,5-triazine(0.24 g, 2 mmol), 1,4phthalaldehyde (0.40 g, 3 mmol), potassium hydroxide (0.33 g, 6 mmol) and methanol (75 mL) were put into a 100 mL Teflon reactor. After the mixture was sonicated for 10 min, the reactor was transferred to an oven, and then heated at 80° C for 72 h. Yellow precipitate formed, which was collected by filtration and washed with methanol for three times. The collected sample was dried at 80° C under vacuum for 12 h to give a yellow powder (78 % isolated yield).

Synthesis of the COP-1 film

A quartz sheet (11.0 mm \times 35.0 mm) was immersed into a chromic acid solution at 70°C for 60 min, which was washed thoroughly with acetone and ultrapure water then.

To a reactor (100 mL) was added 2,4,6-trimethyl-1,3,5triazine (0.24 g, 2 mmol), 1,4-phthalaldehyde (0.40 g, 3 mmol), potassium hydroxide (0.33 g, 6 mmol) and methanol (75 mL). The mixture was sonicated for 10 min, to which the quartz sheets were added. The reactor was heated at 80°C for 72 h until a layer of COP-1 film formed on the surface of the quartz sheet. The prepared COP-1 film was washed with methanol and dried at room temperature.

Experimental procedures for detection of HCl and NH₃ gases

A homemade device²³ was constructed for the detection of HCl and NH_3 gas (Scheme 2). Gaseous HCl or NH_3 of various concentrations were obtained by injecting a certain volume (0.05 mL, 0.1 mL, 0.15 mL, 0.2 mL or 0.25 mL) of HCl or NH_3 gas into a 4.3-mL sealed cuvette with an airtight syringe. Fluorescence properties of the COP-1 film exposed to HCl gas were monitored after remaining for 5 minutes. Afterwards,



Scheme 2 Device for detection of HCl and NH₃ gases.

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Scheme 3 Computational models for COM-1-1P (a), COM-1-2P (b), HCl (c), COM-1 (d), COM-1-1HCl (e) and COM-1-2HCl (f).

excess HCl gas was purged with nitrogen gas, and then we injected sufficient NH₃ gas into the sealed cuvette to recover its fluorescence. Until the fluorescence of the COP-1 film recovered to the initial state, we purged excess NH₃ gas and repeated the above procedures for the measurement of another concentration. The COP-1 film used to investigate its fluorescent response to NH₃ gas was pretreated with abundant HCl gas. The aim is to determine an original state with completely quenched fluorescence intensity. Similarly, fluorescence properties of the COP-1 film exposed to NH₃ gas were monitored after remaining for 5 minutes. Afterwards, excess NH₃ gas was purged with nitrogen gas, and then we injected sufficient HCl gas to recover its fluorescence. Until the fluorescence of the COP-1 film recovered to the original state, we purged excess NH₃ gas and repeated the above procedures for the measurement of another concentration. The temperature is 28 $^\circ\!\mathrm{C}$, and the relative humidity is 38% when detecting HCl and NH₃ gases.

Quantum chemical calculations

The monomer model we used as the effective fragment in calculations for COP-1 was named as COM-1. The geometry optimizations and frequency calculations were performed using the density functional theory (DFT) for ground states of COM-1-1P, COM-1-2P, HCl, COM-1, COM-1-1HCl and COM-1-2HCl (Scheme 3) at the B3LYP^{30,31} level with 6-31+G(d) basis set. The local energy minima were ensured by the absence of imaginary frequencies and no symmetry constraint was

adopted. The electrostatic potential (ESP) and natural bond orbital (NBO) analysis were also conducted at the same level. Geometry and frequency calculations for excited S₁ states of COM-1-1P and COM-1-2P were done with the time-dependent DFT (TD-DFT) approach at the B3LYP/6-31+G(d) level. The excited-state transition properties at the optimized geometries were obtained at the range-separated CAM-B3LYP level with 6-31+G(d) basis set.³² All above calculations were carried out with the Gaussian 09 package.³³

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The vibrationally resolved fluorescence spectra, radiative (k_r) and internal conversion (k_{ic}) rate constants for COM-1-1P and COM-1-2P were computed by using the multimode coupled thermal vibration correlation function (TVCF) formalism³⁴ implemented in the Molecular Materials Property Prediction Package (MOMAP),³⁵ in which the photophysics module shows superiority in predicting the optical properties of polymers and solid-state emitters.³⁶

Results and discussions

Synthesis conditions

The influence of raw material ratios or reaction temperature on the yields has been studied. We employed three different raw material ratios to conduct the experiments at three different temperatures. The yields of the obtained products are shown in Table S1. The optimal ratio of raw materials was determined to be 2:3 (2, 4, 6-trimethyl-1, 3, 5-triazine : 1, 4-Phthalaldehyde) and the optimal reaction temperature was determined to be 80° C.

Structure characterizations

The structure of COP-1 was firstly characterized by powder XRD and FT-IR (Fig. S1). The powder XRD pattern shows two strong peaks, suggesting a semi-crystalline nature.^{37,38} The diffraction peaks at 8.5° and 26.3° can be assigned to the (110) and (001) planes, respectively. The FT-IR spectrum of COP-1 shows a characteristic vibrating band at 1631 cm⁻¹, indicating existence of the olefin group. Moreover, the band at 1373 cm⁻¹ can be assigned to the triazine ring.



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Fluorescence intensity (a.u.)

1500

1250

1000

750

500

250

0

curve at 273 K As a powerful tool to evaluate the chemical composition of macromolecules,³⁹ XPS analysis of COP-1 was performed as

shown in Fig. 1, with the total (a) and deconvoluted highresolution C 1s (b) and N1s (c) spectra. The peaks at 284.4 and 284.9 eV on the high-resolution XPS spectrum of C 1s can be assigned to the C-C bond of benzene ring and C=C bond, respectively. The peaks at 286.6 and 288.7 eV can be ascribed to the carbon of the triazine ring. For N 1s, the peaks at 398.7 eV and 399.1 eV correspond respectively to the C-N and C=N in the triazine ring.⁴⁰⁻⁴² Combination with the measurements from the room-temperature UV-Vis DRS, we also obtained the band energies and band gap results of COP-1 (Fig. S2). The valence band (VB) energy and band gap are assessed to be 1.14 eV and 2.50 eV, respectively. By simple addition, the conduction band (CB) energy is 3.64 eV.

The morphologies of the COP-1 film were characterized by SEM (Fig. S3). The COP-1 film possesses pores with various sizes, indicating its potential applications for adsorption and catalysis. On the surface of the COP-1 film, there distributes homogeneous pores, revealing its sheet-like structure. The N₂ and CO₂ adsorption assays at low temperatures show sufficient porosity of the COP-1 powders, which further suggests its

541nm

541nm

549nm

550

Wavelength (nm) Fig. 3 Fluorescent responses of the COP-1 powders dispersed in aqueous

579nm

600

500

solutions to various pH values (λ_{max} = 453 nm).

microcellular polymeric framework (Fig. 2). The aperture size determined by the pore-size distribution curve was 1.4 nm. The Brunauer-Emmett-Teller (BET) surface area was determined to be 29.1 cm^2g^{-1} , and the pore volume was 0.037 cm³ g⁻¹. All above results indicate the perfect pore distributions.

Thermal and fluorescence stability

As can be seen from the TGA curve, COP-1 shows good thermal stability with the decomposition temperature as high as 450 °C and a total weight loss of 50% after decomposition (Fig. S4), indicating that COP-1 is thermally stable. The fluorescence stability of the solid-state optical material shows great importance in sensing applications. The fluorescence spectra were examined under room temperature as shown in Fig. S5. Even after a month, no obvious changes in band shape and fluorescence intensity were observed for both COP-1 powders and COP-1 film, indicating excellent fluorescence stability.

Detection of HCl and NH₃ in liquid medium

1000

750

500

250

400

450

(a.u.)

Fluorescence Intensity

pH=1

pH=2 pH=3

pH=4

pH=5

pH=7

pH=9

pH=10

pH=12

650

The abundant electron-donating nitrogen (N) atoms of COP-1 tend to accept protons, which offer the opportunity for its application as a pH monitor. Therefore, we studied the fluorescent responses of the COP-1 powders dispersed in aqueous solutions to various pH values (Fig. 3). Results show that the fluorescence intensity declines with the gradually decreased pH values. Particularly, in strong acid medium (pH < 3), significant weakened and red-shifted emission were observed. It was found the thermodynamic pK_a value of the NH⁺ moiety at the N atom of the triazine ring falls in the range of 2.82~3.30.43 Thus, at least one N atom of the triazine core has been protonated when $pH < pK_a$.

To gain deeper insight into the pH-dependent luminescent behavior of the COP-1 powders dispersed in acid

COM-1-1P

COM-1-2P



550

600

650

500

Table 1	Calculated k.	kie and ($\Phi_r(T =$	298 K)	for COM-1	-1P and	COM-1-2P

	$k_{\rm r} ({\rm s}^{-1})$	$k_{\rm ic}({\rm s}^{-1})$	$\Phi_{\rm F}$	
COM-1-1P	2.00×10^{8}	1.85×10^{8}	0.52	
COM-1-2P	1.12×10^{7}	0.46×10^{8}	0.20	



(b) 0.02

0.020

0.01

0.010

0.00

0.000

(cm³g⁻¹

50

40 (cm³g⁻¹

30

---- Adsorption

(a)

STP)

Uptake 20

(c)

(cm³g⁻¹STP)

Uptake

ő

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Fig. 5 Images showing the COP-1 film under visible light (a) and UV lamp (excited at 365 nm) (b) before and after exposed to HCl gas, and recovery by NH₃ gas.

medium (pH < 3), we performed theoretical calculations on COM-1-1P and COM-1-2P (see Scheme 3). We propose more N atoms of triazine moiety are protonated as pH decreases. The calculated vibrationally resolved fluorescence spectra at room temperature are shown in Fig. 4. The fluorescence spectrum of COM-1-2P exhibits a drastic red-shift compared to COM-1-1P, whereas the fluorescence intensity declines remarkably, in good agreement with the experimental observations. Moreover, the fluorescence quantum yield [$\Phi_F = k_r / (k_r + k_{ic})$] predicted by computation also shows a decrease from 0.52 for COM-1-1P to 0.20 for COM-1-2P. The weakened emission arises from the reduced k_r by more than one order of magnitude, overwhelming the reduced k_{ic} by merely four fold (see Table 1).

The excited-state properties play important roles in determining the excited-state dynamics. The natural transition orbital (NTO) analyses for S₁ states were performed and the corresponding landscapes are shown in Fig. S6. It can be seen that the S₁ state of COM-1-1P exhibits a hybridized local and charge-transfer (HLCT)⁴⁴ feature, with local excitation (LE) on the upper styryl branch and charge transfer (CT) from the bottom styryl branch to the central triazine ring. Instead, almost pure CT character was found for COM-1-2P, with obvious CT from the left two styryl branches to the triazine core and the right styryl branch. The HLCT state in COM-1-1P offers an effective pathway to obtain efficient luminescence as not only LE contributes significant orbital overlap to strengthen k_r but also CT provides full exciton utilization. However, the relative pure CT state in COM-1-2P shows orbital separation, which induces a lower k_r and red-shifted emission compared to COM-1-1P. The calculation result implies protonation could promote the intramolecular charge transfer, thus gives rise to the weak and red-shifted emission.

With the aim to investigate the response of solventdispersed COP-1 powders to HCl/NH₃, the HCl gas was bubbled through different organic solvents. Fortunately, observable fluorescence changes from green to orange take place in all solvents. Subsequent injecting into the solvents with NH₃ gas recovers the fluorescence (Fig. S7). The reason can be ascribed to the protonation via dissociation of HCl and deprotonation upon further contact with NH₃ in liquid, similar to the above-stated pH-dependent luminescent mechanism. As HCl or NH₃ gas cannot be dissolved in organic solvents efficiently, only qualitative results were given to show its sensing ability to HCl/NH₃.



Fig. 6 Electrostatic potential at 0.002 a.u. isosurface of electron density.



Fig. 7 (a) Fluorescent responses of the original COP-1 film to HCl gas with various concentrations ($\lambda_{max} = 453$ nm); (b) Linear relationship between the fluorescence intensities and gaseous HCl concentrations; (c) Fluorescent responses of the pretreated COP-1 film to NH₃ gas; (d) Linear relationship between the fluorescence intensities and gaseous NH₃ concentrations.



Fig. 8 Fluorescence of the COP-1 film upon alternative treatment with HCl and NH_3 gases.

Detection of gaseous HCl and NH_3 with the COP-1 film

Encouraged by its sensing ability in liquid, we endeavor to develop a gaseous HCl/NH₃ sensor with COP-1. As the COP-1 powders are limited in convenient and practical applications, we finally attached them onto the quartz sheets to form a polymer film. Sensor experiments were done with first exposure of the COP-1 film to HCl gas and then to NH₃ gas. Images are shown in Fig. 5. The color of the COP-1 film changes from yellow to orange firstly and recovers to original subsequently under visible light. The fluorescence of the COP-1

film changes from greenish yellow to dark orange at first and recovers afterwards under UV lamp. The structures of the COP-1 powders before and after exposed to HCl gas then to NH₃ gas were also characterized by powder XRD and FT-IR. The major peaks on both the powder XRD patterns and IR spectra experience slight changes (Fig. S8), indicating that the skeleton of COP-1 was hardly damaged upon exposure to HCl/NH₃ gas.

Theoretical calculations were also conducted on HCl, COM-1, COM-1-1HCl and COM-1-2HCl (Scheme 3) to understand the fluorescent response of the COP-1 film to HCl gas. According to the electrostatic potential (ESP) diagram, the adsorption of HCl molecules (Fig. 6a) to the N atoms of the triazine ring of COM-1 (Fig. 6b) could form red-shifting hydrogen bonds⁴⁵ with H–Cl bond lengthening since negative N pulls positive H closer to it, leading to the polarization of the H-Cl bond (Fig. 6c and 6d). The natural population analysis (NPA) charges of significant atoms (Scheme 3) obtained by NBO analysis were listed in Table 2. The NPA charges of the hydrogen (H) atoms in HCl molecules of COM-1-1HCl and COM-1-2HCl are nearly equal to the bonded protons of COM-1-1P and COM-1-2P. Moreover, the bond lengths of the N...H-Cl hydrogen bonds in COM-1-1HCl and COM-1-2HCl are also similar to the N-proton bonds (see Scheme 3). Thus, the adsorption of HCl molecules to the COP-1 film could also enhance the charge transfer during the excited-state transition, which weakens and redshifts the fluorescence intensity. Subsequent exposure to NH₃ gas removes HCl molecules adsorbed on the COP-1 film and recovers the fluorescence.

Next we quantitatively investigated the fluorescent responses of the original COP-1 film to HCl gas with various concentrations (0.0116, 0.0232, 0.0348, 0.0464, 0.0580, HCl/N₂, v/v). The HCl gas was gradually injected into a 4.3-mL cuvette containing the COP-1 film with the increasing gaseous HCl concentration, and the procedures are detailed in the experimental section. Weakened and red-shifted fluorescence were found (Fig. 7a), and the fluorescence intensities of the COP-1 film decreases linearly with the increased gaseous HCl concentrations (Fig. 7b). The detection limit for HCl gas was calculated to be 1.0967×10^{-4} . Similar procedures were applied to study the quantitative fluorescent responses of the pretreated COP-1 film to NH₃ gas with given concentrations. As expected, enhanced and blue-shifted emission were observed (Fig. 7c), and the emission intensities increase proportionally to the rising gaseous NH₃ concentrations (Fig. 7d).

Table 2 NPA charges (in e) on selected atoms for HCl, COM-1 and four complexes obtained by NBO analysis							
	N1	N2	N3	H1	H2	C11	C12
HC1				0.282		-0.282	
COM-1	-0.515	-0.516	-0.515				
COM-1-1HCl	-0.569	-0.513	-0.516	0.440		-0.773	
COM-1-2HCl	-0.573	-0.572	-0.510	0.435	0.432	-0.747	-0.743
COM-1-1P	-0.570	-0.495	-0.501	0.450			
COM-1-2P	-0.570	-0.567	-0.491	0.463	0.463		

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Fig. 9 Responses of the COP-1 film toward other potential co-existing interference gases: (a) acid gases; (b) volatile organic compounds.

The detection limit for NH_3 gas was determined to be 5.8925 × 10^{-4} . The above results show that the COP-1 film could be applied to the continuous and quantitative detection of HCl and NH₃ gases with high sensitivity. The reversibility is one important factor for fluorescent chemosensors in practical applications. The reversibility of the COP-1 film was investigated by cycling the reaction of the probe with HCl and NH₃ gases (Fig. 8), due to the high affinity of NH₃ toward HCl. These reversible cycles, fluorescence bright green and weak orange, could be repeated for five or more times under the same condition, demonstrating the good reversibility of the COP-1 film toward HCl and NH₃ gases. In addition, we also studied the fluorescence sensor stability of the COP-1 film (Fig. S9). The experimental results show that there was no significant change in the fluorescence intensity of COP-1 film after three hours, indicating its good detection stability.

Moreover, we created different humidity environments (40%, 50%, 60%, 70% and 80%) by a Constant Temperature and Humidity Chamber, to study the effect of humidity on the detection of HCl gas by COP-1 (Fig. S10). The cuvette containing COP-1 film was placed in the Constant Temperature and Humidity Chamber under a specific humidity for 15 minutes. After that, 0.3 ml of dry HCl gas was injected into the 4.3-mL cuvette, and then the fluorescence intensity was measured. Results revealed that humidity put almost no influence on the fluorescence intensity of COP-1 when detecting HCl gas.

To examine the responses of the COP-1 film toward other potential co-existing acid gases, we investigated its responses to CO₂, SO₂, H₂S and Cl₂. Upon exposure to CO₂ and SO₂, no obvious changes in the fluorescence intensity were observed as shown in Fig. 9a. The presence of H₂S and Cl₂ could result in a little decrease of the fluorescence intensity (~25%). Volatile organic compounds (VOCs) are also important interference gases in some cases, four different VOCs (benzene, methylbenzene, dimethylbenzene, trichloromethane) were chosen as interfering gases to verify the effect on the detection of hydrogen chloride gas by COP-1. Upon exposure to these VOCs, no obvious changes in the fluorescence intensity were observed (Fig. 9b).

Conclusions

In conclusion, we have synthesized a fluorescent triazinebased covalent organic polymer (COP-1) sensor toward HCl and NH_3 gases. Both solvent-dispersed COP-1 powders and microporous COP-1 film exhibit stable fluorescence and sensitive HCl/NH₃ response. The COP-1 powders were used to successively detect HCl and NH₃ in liquid medium. The asprepared COP-1 film was applied for reversible detection of HCl and NH₃ gases. Quantum chemical calculations show that the weak and red-shifted fluorescence response of the COP-1 powders/film to HCl originates from the adsorption of proton/HCl to the N atoms of triazine rings. The interaction between negative N of the triazine ring and positive H of proton/HCl could lead to a charge-transfer (CT) state. Subsequent exposure of the HCl-pretreated COP-1 powders/film to NH₃ cause deprotonation/desorption and recovers the fluorescence. As a visible and easy-operating detection strategy, it paves a new way for continuous detection of acidic and alkaline gases.

Conflicts of interest

There are no conflicts to declare.

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