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A T-shaped triazatruxene probe for the naked-eye detection of HCl gas with high sensitivity and selectivity†

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A T-shaped Schiff-base triazatruxene derivative (TATNFF) was designed, synthesized, and explored as a sensitive probe to detect HCl gas by the naked eye. The remarkable color change of TATNFF with turn-on behavior in the presence of a trace amount of HCl gas was obviously observed by the naked eye, which opens up a new strategy to explore a novel set of smart responsive materials for sensing applications.

Recently, hydrogen chloride (HCl) gas, which is mainly evolved in the combustion of halogenated polymers, incineration of plants, absorbing towers of semiconductor factories and acid rain, has been of great concern.¹ Due to its hazardous nature, the quantity of HCl gas is strictly regulated in many countries. In order to monitor the release of HCl gas into the environment, an efficient HCl sensor with excellent sensitivity and reliability is highly demanded. Preliminary studies have demonstrated that common analytical methods such as solid electrochemistry² and amperometry³ are not only time-consuming but also lead to wastage of samples, which are thus not suitable for continuous monitoring and remote detection. In contrast, the method based on photochemistry offers distinct advantages in terms of sensitivity, selectivity, response time and local observation. Moreover, optical fibers with a molecular sensor immobilized at the tip⁴ have provided the possibility of remote sensing, promoting the commercial application in the market. Therefore, considerable efforts are being devoted to develop sensitive optochemical sensors for the detection of HCl gas.⁵

Optochemical sensing of small molecules has received much attention in recent years due to its versatility and easy recognition.⁶

For example, porphyrin dyes^{6a,b,d,7} have been widely applied in the detection of HCl gas based on the changes in the absorption spectra, originating from the protonation of the inner nitrogen core of the porphyrin ring.^{6a} More importantly, their excellent photophysical properties, such as evident Stokes shifts and high photostability, make them good candidates for sensing applications.⁸ However, the tedious synthesis of porphyrin dyes with low yields has limited their further development as sensors. Raymond *et al.* introduced difluoroboradiazaindacene (BODIPY) dyes into porous polyacrylate beads to form a solid-state colorimetric and fluorescent sensor for the analysis of HCl in a gas stream and aqueous solution.⁹ Xie *et al.* reported two optochemical sensors based on polymethyl methacrylate (PMMA) films doped with triphenylamine (TPA) segments, in which the detection of HCl gas was achieved by absorption and fluorescence spectra at room temperature.^{6c} However, despite the progress, all the reported detection must be realized by performing measurements of the spectra, leading to inconvenience in practical applications. Therefore, the development of novel sensors for gas detection in a simple and direct way, *i.e.* by the naked eye, is highly desirable.

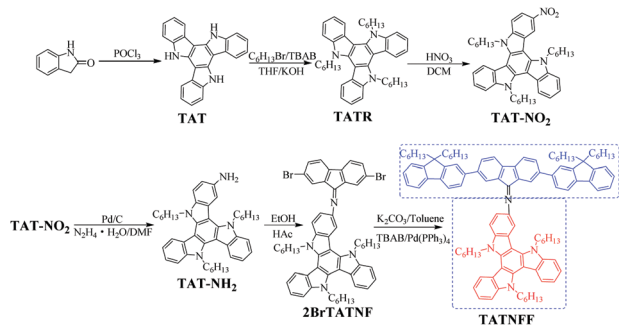
Owing to the excellent optoelectronic properties, triazatruxene (TAT) and its derivatives are widely explored in organic light-emitting diodes,¹⁰ solar cells,¹¹ discotic liquid crystals¹² as well as molecular sensing¹³ for the detection of arenes or G-quadruplexes. In particular, TAT molecules have stood out as good candidates for chemosensors because of their large extinction coefficients and high fluorescence quantum yield. To the best of our knowledge, none of the fluorescence probes based on TAT have been explored for the detection of gas so far.

Based on the previous work of our group,¹⁴ we applied our efforts to exploring a sensitive probe with the introduction of –C=N– as a bridge linkage group onto a TAT unit for HCl detection. A novel T-shaped compound (TATNFF) was designed. The colour of the TATNFF probe in THF solution changed from non-fluorescence emission to bright yellow when it was placed in a HCl atmosphere with visible fluorescence emission under a UV lamp, ensuring the simple and direct convenient detection by the naked eye. In the process of detection of HCl gas, absorption

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Scheme 1 The synthetic route to TATNFF.

and fluorescence spectroscopy was also carried out at room temperature to confirm and investigate the gas sensing behaviours. Such a turn-on fluorescence enhancement may result from hydrogen bonding interaction between the probe TATNFF and HCl, inhibiting the skeletal isomerization and further avoiding quenching processes.¹⁵ Consequently, the naked-eye sensing is realized by the remarkable colour change of TATNFF in the presence of HCl gas, which will be helpful for applications in real-time monitoring by optical signals.

As shown in Scheme 1, TAT was synthesized by trimerization of indolin-2-one in POCl₃. Alkylation of TAT provided TATR. Direct nitration reaction of TATR with nitric acid in dichloromethane afforded TAT-NO₂ in 76% yield. Subsequent reduction with N₂H₄·H₂O using Pd/C as the catalysis offered the key intermediate amino TAT-NH₂ in a high yield of 86%. 2BrTATNF was synthesized through Schiff-base condensation of 2,7-dibromofluorenone with TAT-NH₂ in the presence of acetic acid and ethanol. Suzuki coupling of 2BrTATNF and 9,9-dihexylfluorene-2-bis (boronic acid pinacol ester) occurred smoothly to give TATNFF with high yields using Pd(PPh₃)₄. The structures of all the compounds were well identified by MALDI-TOF mass spectra, ¹H and ¹³C NMR spectra, and elemental analysis (Fig. S20–S37, ESI[†]).

To investigate the sensing properties, a homemade flow cell set-up was used as shown in Fig. S1 (see ESI[†]). The flowmeter was used to monitor the flow rate of air (10 mL min⁻¹). To facilitate the accurate measurements of HCl gas volume, HCl and air was mixed with HCl gas in a volume fraction of 0.1%, namely $\phi_{\text{HCl}} = 0.1\%$. Gaseous HCl at various concentrations was obtained by injecting a certain volume of HCl mixture gas using an airtight syringe into the sealed testing chamber where the sensor was placed. The sensing properties of the sensors exposed to HCl gas were monitored by the variation of absorption and fluorescence spectra. All the measurements were carried out at room temperature.

As shown in Fig. S2 (see ESI[†]), the response of probe TATNFF to various acid gases or proton acids was investigated in tetrahydrofuran (THF) solution. The probe TATNFF did not show fluorescence under a UV lamp at 365 nm. However, a distinct fluorescence change from non-fluorescence emission to brilliant yellow was observed when TATNFF was treated with HCl gas. Meanwhile, a weaker fluorescence change was noticed when TATNFF was contacted with HF gas and HBr gas (*vide infra*). In contrast, upon addition of other analogous analytes, such as

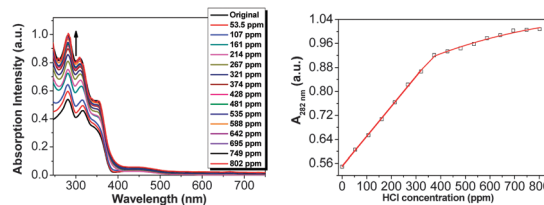


Fig. 1 Absorption spectra of TATNFF (10 μM in THF) exposed to HCl gas with different concentrations (left) and the change of absorption intensity with an increment of HCl gas (right).

HI (gas), SO₂ (gas), NO₂ (gas), CO₂ (gas), SOCl₂, H₂SO₄, HNO₃, and H₃PO₄ to the solution of probe TATNFF, there were no such evident fluorescence changes.

Based on the above phenomena, a quantitative analysis of the probe TATNFF towards HCl gas was carried out in detail to get further insights. As shown in Fig. 1, a weak absorption at 282 nm for TATNFF, was assigned to the π - π^* transition for TAT units.^{10a} Furthermore, two other absorption peaks were observed at 310 nm and 355 nm, respectively, which were attributed to the π - π^* transition resulting from the trifluorene backbone and the extended conjugation between the backbone and the TAT pendant *via* a $-C=N-$ bridge. Upon addition of an increasing volume of HCl gas to the solution of the probe TATNFF (10 μM) in THF, absorption bands at 282 nm, 310 nm and 355 nm increased gradually, and new absorption bands at 454 nm appeared concomitantly, implying the presence of the TATNFF–HCl complex.

When the volume of HCl gas was increased up to 428 ppm (0.8 μL), the absorption peak at 282 nm changed slowly at even higher HCl concentrations, indicating a 1 : 1 binding stoichiometry between TATNFF and HCl (see ESI[†]). The fluorescence spectra of TATNFF exposed to HCl gas are shown in Fig. 2. When excited at 310 nm, the probe TATNFF was completely non-fluorescent. Upon addition of HCl gas, the fluorescent intensity displayed a remarkable enhancement up to 166-fold at 399 nm in the presence of 1.0 equiv. of HCl. The significant enhancement of fluorescence was mainly attributed to the formation of the TATNFF–HCl complex that inhibited the intramolecular rotational isomerization of TATNFF. The changing trends of the fluorescence intensity at 399 nm matched well with UV-vis titration results, further confirming the binding stoichiometry. In addition, observable UV-vis absorption and fluorescence changes also took place in acetone, *N,N*-dimethylformamide (DMF), cyclohexane and dichloromethane (DCM) solutions (Fig. S3–S10, ESI[†]). Upon addition of HCl gas, the colours of cyclohexane and DCM

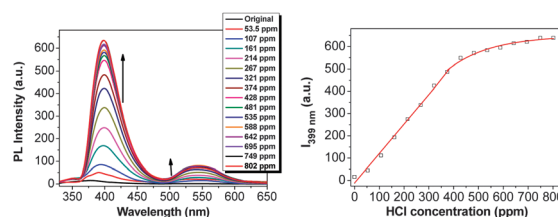


Fig. 2 PL spectra of TATNFF (10 μM in THF) exposed to HCl gas with the different concentrations (left) and the change of PL intensity with an increment of HCl gas (right).

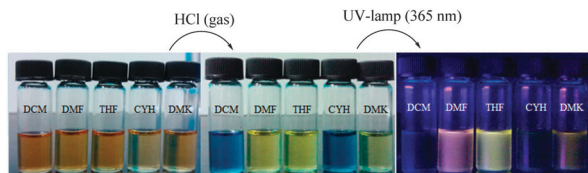


Fig. 3 Solution of **TATNFF** (10 μM in DCM, DMF, THF, cyclohexane and acetone) in the presence of saturated HCl gas without (left) and with (right) a UV-lamp (365 nm).

solutions of **TATNFF** changed immediately from sandy brown to blue without UV light. However, the colours of acetone and DMF solutions of **TATNFF** were almost unchanged. Under a UV-lamp at 365 nm, the weakly fluorescent DMF and THF solutions of the probe **TATNFF** became strongly fluorescent with various colours, respectively (Fig. 3). The significant enhancement of emission could be attributed to effective suppression of $-\text{C}=\text{N}$ -isomerization by intramolecular hydrogen bond.¹⁶

As an important characteristic of the fluorescence probe, the selectivity of **TATNFF** towards different acids was examined by mixing the probe **TATNFF** (10 μM) with saturated HCl gas and other analogous analytes, respectively (Fig. S11, ESI[†]). Among these analytes, HCl gas was the only acid gas that caused a prominent fluorescence enhancement of about 166-fold. Compared with HCl, other testing samples, such as HF, HBr, HI, H_2SO_4 , HNO_3 , H_3PO_4 , HAc, SO_2 , NO_2 , CO_2 , SOCl_2 and KCl exhibited only slight emission enhancement. Keeping all the results in mind, we believe that the probe **TATNFF** displays a very distinctive selectivity for HCl gas.

To evaluate the high selectivity of the probe **TATNFF** towards HCl gas, the ^1H NMR test was performed to further explore the detailed binding mode of the **TATNFF**-HCl complex. As shown in Fig. S13 (see ESI[†]), all signal changes of protons implied the alteration of the chemical circumstances, originating from probe **TATNFF** coordinated with HCl (from 8.5 to 6.5, the protons of aromatic rings). The shift of proton at 8.7–10.2 ppm was ascribed to a typical intramolecular hydrogen bond ($\text{N}\cdots\text{H}-\text{Cl}$). By increasing the volume of HCl gas to the solution of probe **TATNFF**, the shift of the proton was gradually enhanced to 10.2. Meanwhile, the protons of aromatic rings Ha (7.88 ppm) and Hb (7.82 ppm) shifted downfield to 8.47 ppm (H_a) and 8.05 ppm (H_b), respectively. The proton signals of HCl around 8.83 ppm displayed a significant downfield shift, which indicated that the decrease of the electron density on the phenyl ring was attributed to the π - π conjugative effect after the cyclization reaction. It is worthwhile to mention that the proposed sensing mechanism of the sensor **TATNFF** for the detection of HCl gas is speculated in Fig. 4. The conjugated geometric configuration of **TATNFF**-HCl complex is thus confirmed, which indicates that the stability of the complex is enhanced because of intramolecular hydrogen bonding. In this system, the probe **TATNFF** is coordinated with HCl gas by intramolecular hydrogen bonding, inhibiting the skeletal isomerization. The fluorescence decay is plotted in Fig. S16 (see ESI[†]). Both the 400 nm and the 544 nm emission peaks of **TATNFF**-HCl complex showed biexponential decay, with the average decay lifetimes of 9.0 ns and 9.7 ns, respectively.

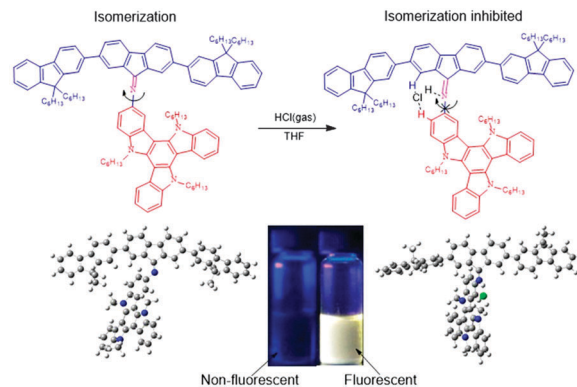


Fig. 4 The proposed sensing mechanism of the probe **TATNFF** for the detection of HCl gas.

Consequently, the conjugated Schiff base moiety with HCl formed a highly rigid fluorophore.

In addition, density functional theory (DFT) calculations were conducted in an attempt to better understand the “turn-on” behaviour of the **TATNFF**-HCl complex. The sketches of the frontier molecular orbital for both compounds are shown in Fig. S17 (see ESI[†]). It is noticed that **TATNFF** shows a distinct charge separation of electronic density over the entire molecule. The increased rigidity of the **TATNFF**-HCl complex could significantly reduce the non-radiative decay. The binding-induced increase in molecular rigidity should be therefore mainly responsible for the fluorescence enhancement of the **TATNFF**-HCl complex.¹⁷

Fig. S18 (see ESI[†]) shows the changes of emission spectra of sensor **TATNFF** exposed to HCl gas for 10 to 90 s. The emission intensities were progressively augmented by increasing the exposure time in HCl gas. In this case, the emission bands around 399 nm could change from the “off” state to the “on” state due to intramolecular hydrogen bonding that inhibits the skeletal isomerization. To evaluate further the photostability of the probe, the PL properties of **TATNFF** (10 μM in THF) exposed to saturated HCl gas were recorded with increasing the exposure time in both N_2 and air. As shown in Fig. S19 (see ESI[†]), the PL intensity of the probe **TATNFF** remained almost identical with increasing the exposure time from 20 min to 80 min under a UV lamp even in air. The results indicated that the **TATNFF** probe exhibited excellent photostability while keeping identical selectivity and sensitivity during the test in both N_2 and air atmosphere.

In conclusion, we have developed a sensitive probe **TATNFF** for the facile detection of HCl gas in air in a simple and direct approach. The probe displayed good selectivity and sensitivity for HCl. Upon exposure to HCl gas, the probe emitted brilliant yellow fluorescence because of the inhibition of skeletal isomerization, which is ascribed to the formation of intramolecular hydrogen bonds. In addition, the detailed binding modes of the probe **TATNFF** were confirmed by ^1H NMR titration and DFT computational studies, further revealing the fluorescence mechanism. More importantly, the colour of the **TATNFF** probe changed from non-fluorescence emission to bright yellow when it was placed in a HCl atmosphere with visible fluorescence emission under a UV lamp, which can be easily observed by the

naked eye. As a result, the distinct colour switch behaviours based on the TATNFF probe show great promise for potential applications as chemical sensors. Inspired by this fluorescence mechanism, a novel set of smart responsive materials could be explored, which will open up a new strategy to develop simple and sensitive chemical sensors for practical sensing applications by the naked eye.

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