Supporting Information

Tetraphenylethene functionalized rhodamine dye for fluorescence detection of HCl vapor in solid state

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1. Materials and methods

Most of the sodium salts and TiCl$_4$ were purchased from Damao Chemical Reagent Factory (Tianjin) and used as received. Rhodamine B and Diphenyl ketone were procured from Sinopharm Chemicals Ltd. The inorganic acids were procured from Xilong Chemical Co., Ltd. Ethanol, THF and CH$_2$Cl$_2$ (AR grade) were purchased from Sinopharm Chemicals Ltd and purified before use. Water used for the experiment was double distilled.

1.1 General Spectroscopic Methods.

Most of the fluorescence spectra were recorded with Jasco FP-6500 fluorescence spectrophotometer by utilizing quartz glass plate as a carrier for the solid sample. Fluorescence changes for acid vapors were measured at different times. In the case of stability and reversibility experiment, RbTPE were determined in sealed testing container (37 L) according to the improved method that reported by Sun and Lu’s group$^{[S1]}$.

![Figure S1. Diagram of gas-sensing measurements for HCl vapor.](image)

In order to make accurate qualitative and quantitative analysis of the entire sample, the detection limit test (Fig.3) and the kinetic curve (Fig.4) was determined using a
simple device test strip by immobilizing the RbTPE stock solution (2×10^{-2} M) on a
common filter paper. The evaporated sample (previously prepared) was exposed to
different concentrations of HCl vapor (0~500 ppm) for 3 minutes, and then sticked to
a quartz cuvette to record the FL spectra under excitation at 365 nm for many times.
The relative FL intensity was calculated by \(I_{580}/I_{463}\).

1.2 Synthesis process

Rhodamine B hydrazide (RbH) was synthesized according to the reported
procedure \[^{S2}\].

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Tetraphenylethene (TPE) was prepared by McMurry reaction \[^{S3}\]. TPECHO was
stepwise synthesized according to Duff reaction \[^{S4}\].

TPE (0.5 g, 1.37 mmol) was added under vigorous stirring to a solution of
hexamethylenetetramine (1.92 g, 13.7 mmol) in trifluoroacetic acid (30 mL), which
was refluxed for 3 h, then 3 M HCl (50 mL) was added and the solution was heated at
100 °C for another 1 h. After cooling to room temperature, the solution was extracted
with CH\(_2\)Cl\(_2\) (3 × 40 mL). The combined organic layers were dried over anhydrous
MgSO\(_4\) and filtered. The solvent was removed under reduced pressure and the residue
was purified by column chromatography with EtOAc/CH\textsubscript{2}Cl\textsubscript{2} (1:1, v/v) as eluent to give TPECHO as a yellow solid (about 50% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 9.89 (s, 1H), 7.85–7.77 (m, 2H), 7.63–7.58 (m, 3H), 7.48 (dd, \(J = 10.6, 4.7\) Hz, 2H), 7.22–7.14 (m, 12H), 7.14–7.06 (m, 20H), 7.06–6.96 (m, 12H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 191.93, 150.57, 143.18, 142.82, 139.76, 134.27, 131.95, 131.44, 131.14, 129.17, 127.94, 127.75, 127.15, 126.77.

References


2. NMR copies of RbTPE

\(^1\text{H}-\text{NMR of RbTPE}\)

\(^{13}\text{C}-\text{NMR of RbTPE}\)
3. ESI-MS data of RbTPE

ESI-MS data of RbTPE (799.4601)

ESI-MS data of RbTPE-HCl (799.4630)
4. FL and UV-vis spectra of RbTPE

Figure S2. FL spectra of RbTPE after exposing to TFA

Figure S3. FL intensity changes of RbTPE without and in HCl vapors
Figure S4. UV-vis spectra of RbTPE before and after exposing in HCl

Figure S5. The fitted relationship of RbTPE after exposing in HCl.