

Supramolecular self-assembly material based on quinoline derivative and sensitively response toward volatile acid and organic amine vapors

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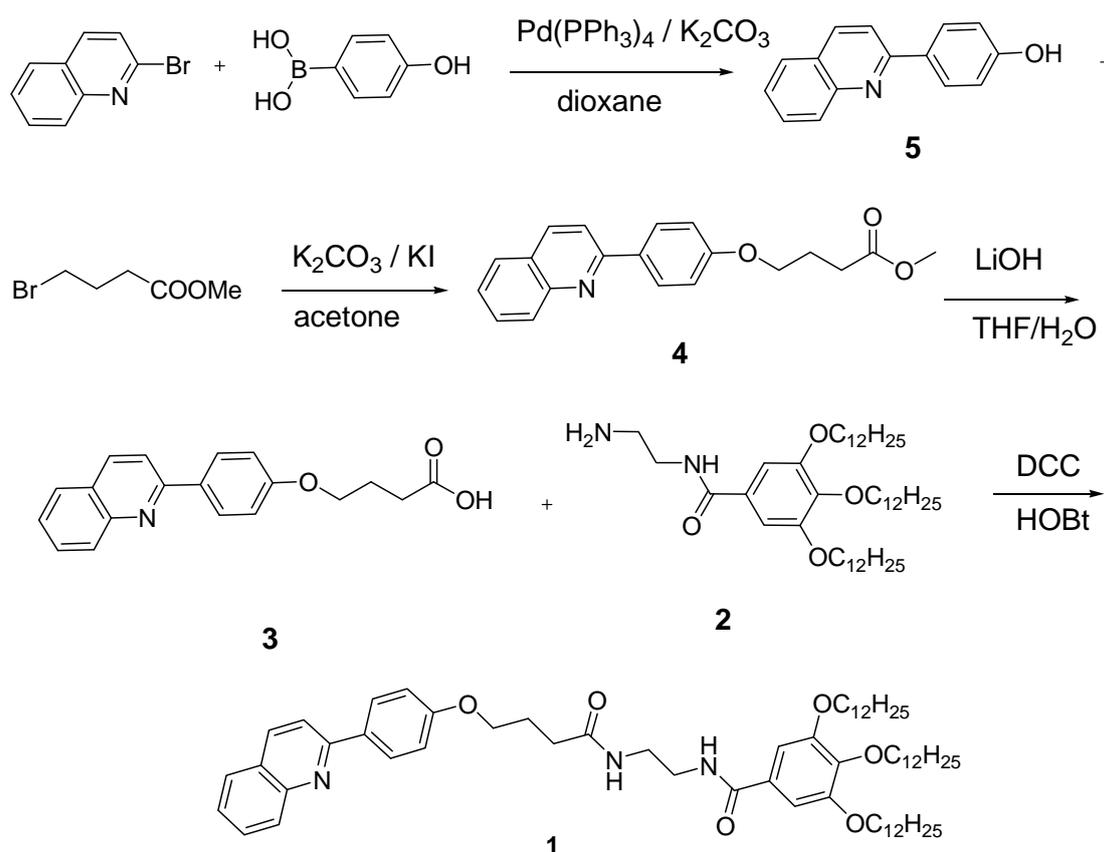
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Scheme S1 The synthesis route of the target product **1**.

Synthesis of compound 5: 2-bromoquinoline (1.5 g, 7.21 mmol), 4-hydroxyphenylboronic acid

(1.19 g, 8.65 mmol), K_2CO_3 (2.98 g, 21.63 mmol) and $Pd(PPh_3)_4$ (0.83 g, 0.72 mmol) were added to dioxane (70 mL), the mixture was heated to reflux for 24 h under nitrogen atmosphere. After the reaction was over, H_2O (200 mL) was added to the above solution, and was extracted for three time by CH_2Cl_2 . The organic phase was combined and removed in vacuo. The crude product was purified by column chromatography with the eluent of petroleum ether / CH_2Cl_2 (1/3, v/v). A pale yellow solid was obtained with the yield of 64%. 1H NMR (400MHz, d_6 -DMSO): δ 9.84 (s, 1H), 8.36 (d, $J = 8.8$ Hz, 1H), 8.14 (d, $J = 8.8$ Hz, 2H), 8.05 (d, $J = 8.8$ Hz, 1H), 8.00 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 7.2$ Hz, 1H), 7.75 (t, $J = 8.4$ Hz, 1H), 7.55 (t, $J = 7.2$ Hz, 1H), 6.93 (d, $J = 8.8$ Hz, 2H). HRMS calculated for $C_{15}H_{12}NO$ $[M+H]^+$ 222.0919, found: 222.0925.

Synthesis of compound 4: Compound 4 (1.0 g, 4.40mmol), methyl 4-bromobutyrate (0.84 g, 4.62 mmol), K_2CO_3 (1.82 g, 13.20 mmol) and KI (catalytic equivalent) were added to acetone (50 mL), the mixture was heated to reflux for 24 h under nitrogen atmosphere. After the reaction was over, K_2CO_3 was removed by filtration. The crude product was purified by column chromatography with the eluent of petroleum ether / CH_2Cl_2 (1/1, v/v). A pale yellow solid was obtained with the yield of 64%. 1H NMR (400MHz, d_6 -DMSO): δ 9.84 (s, 1H), 8.36 (d, $J = 8.8$ Hz, 1H), 8.14 (d, $J = 8.8$ Hz, 2H), 8.05 (d, $J = 8.8$ Hz, 1H), 8.00 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 7.2$ Hz, 1H), 7.75 (t, $J = 8.4$ Hz, 1H), 7.55 (t, $J = 7.2$ Hz, 1H), 6.93 (d, $J = 8.8$ Hz, 2H). HRMS calculated for $C_{15}H_{12}NO$ $[M+H]^+$ 222.0919, found: 222.0925.

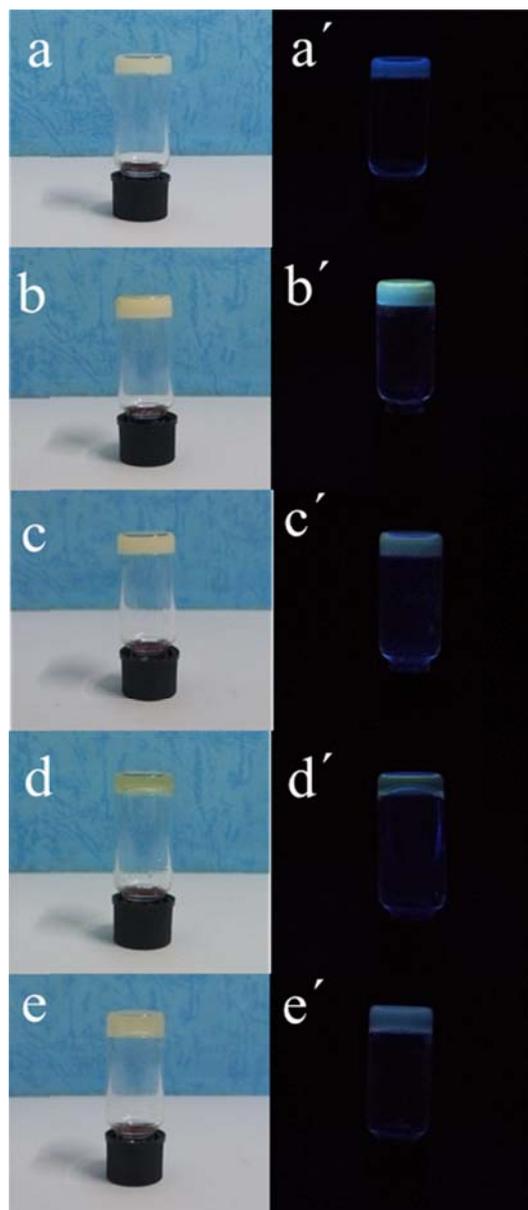


Figure S1 The images of gels **1** in different solvents: a) and a') for ethanol; b) and b) for acetonitrile; c) and c) for hexane; d) and d) for petroleum ether; e) and e) for DMSO. The gel concentration was all at their CGC.

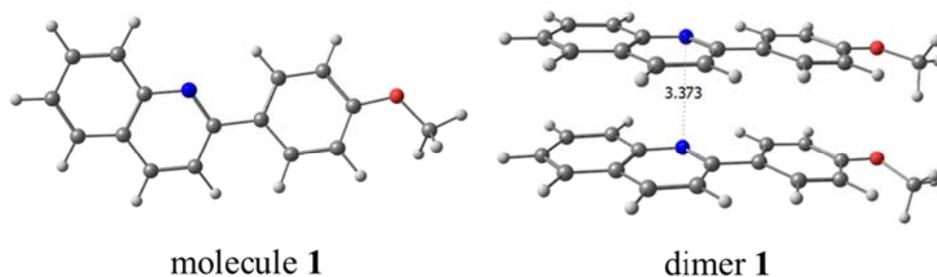


Figure S2. DFT-optimized structure of truncated model of simplified **1** and the dimer of simplified **1** at the B3LYP-D3/6-31G* level using Gaussian 09.

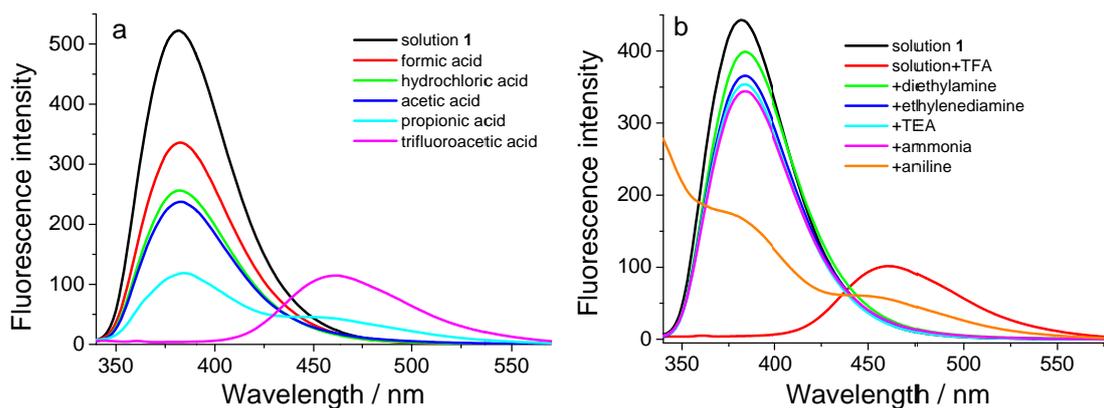


Figure S3 Fluorescence emission change of solution **1** under addition different acid (a) and solution **1** with addition of TFA under addition of different organic amine. The concentration of solution **1** was 10^{-5} M. The addition amount of acid and amine was 0.1 eq and 0.15 eq, respectively.

Association constant (K)

The reaction formulation of **1** to TFA can be written as Eq. 1 with the 1:1 ratio, Where B and A stand for **1** and TFA, respectively.



Therefore, association constant K at room temperature can be determined as the Eq. 2.

$$K = \frac{[BA]_e}{[B]_e [A]_e} = \frac{[BA]_e}{([B]_s - [BA]_e) ([A]_s - [BA]_e)} \quad \text{Eq.2}$$

Where, [BA] stands for the concentration of the complex; [B] stands for the concentration of **1**; [A] stands for the concentration of A; under script e, s stand for states at equilibrium and the beginning, respectively.

$$[BA]_e = \frac{\Delta F_{381 \text{ nm}}}{\varepsilon} \quad \text{Eq.3}$$

Where $\Delta F_{381 \text{ nm}}$ is the fluorescent change (Figure 8a), ε is the illumine coefficient of complex. Therefore, the association constant (K) of **1** to TFA with the ratio of $[TFA] / [1] \leq 1$ and the illumine coefficient ε are determined by the fitting of experimental data in Figure 8a by using equation 4.

$$Y = \frac{x}{K[B]_s \varepsilon} + \frac{1}{[B]_s \varepsilon} \quad \text{Eq.4}$$

The two variables $(1 / [I-I_0])$ Vs $1 / [A]$ were fit very well with the linear fitting: $Y = 0.00635 + 8.4271E-10x$ ($y = A + Bx$). K was calculated as $7.53 \times 10^6 \text{ M}^{-1}$ according to Eq. 4.

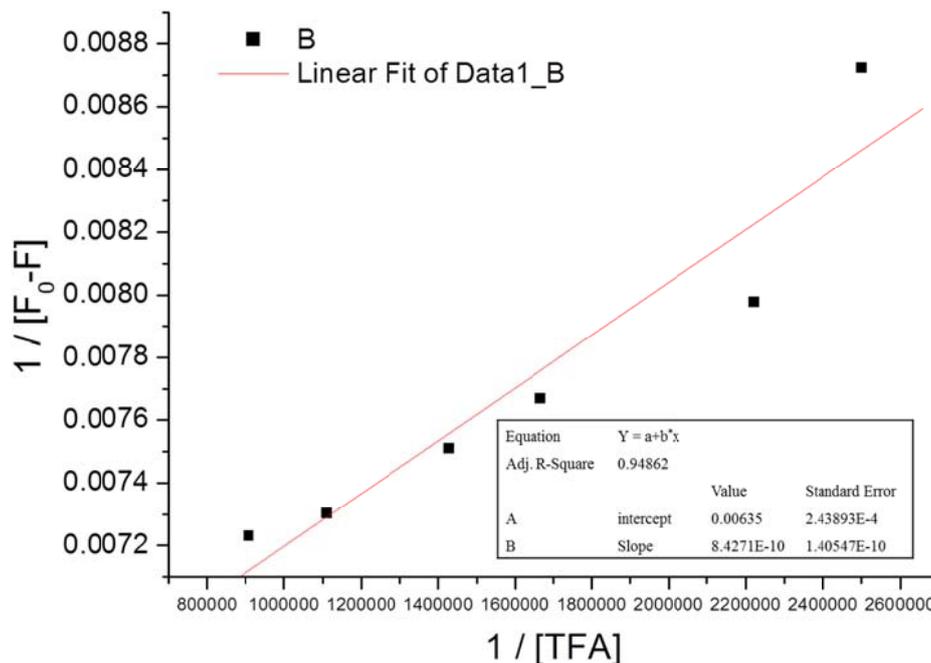


Figure S4 The linear fitting curve of fluorescence change of **1** with the addition of TFA.

Limit of detection calculation

The limit of detection (LOD) was determined with the following equation: $LOD = 3\sigma/b$ [1] where σ was the standard deviation (SD) of 10 blank samples (10^{-5} M) of **1** measurement and b was the slope of the linear fit using the ratio of fluorescence emission intensity versus TFA concentration (Fig. S5 and Table S1), respectively.

From Figure S4, $LOD = (3 \times 0.7) / 369.44571 \mu\text{mol/L} = 5.68 \times 10^{-9} \text{ mol/L}$.

Table S1 Detection limit of **1** toward TFA in acetonitrile by fluorescence intensity changes at 381 nm

n	1	2	3	4	5	6	7	8	9	10
Intensity (X _n)	168	169	167	168	169	169	167	168	167	167

$$X_{\text{average}} = 167.9 \quad \sigma_{\text{wb}} = \sqrt{\sum (X_n - X_{\text{average}})^2 / n} = 0.7$$

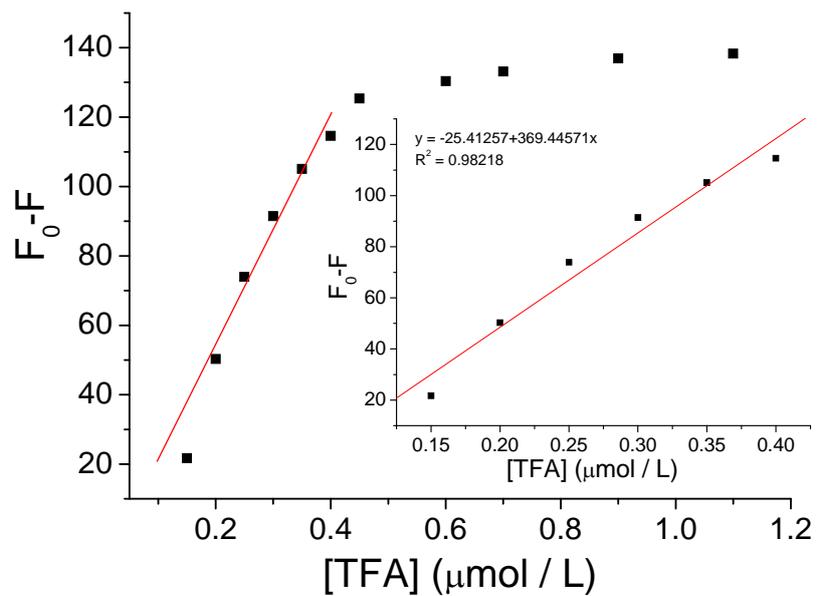


Figure S5 The curves of the fluorescence emission intensity at 381 nm versus the concentration of TFA. Inset: Calibration curve in the concentrations range of 0-0.4 $\mu\text{mol/L}$ of TFA.