Electronic Supplementary Material

Synthesis and ultraviolet/aggregation-induced emission investigation of novel tetraphenylvinyl hydrazone derivatives: efficient multimodal chemosensors for fluoride ion

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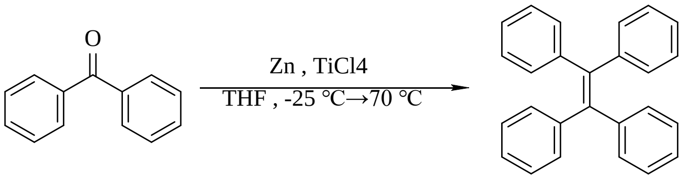
1 Compound synthesis

Part of the compounds were synthesized according to the synthesis route in the reference, and the specific steps are as follows.

1.1 Synthesis of 1,1,2,2-tetraphenylethene (**1**)

The synthesis route of compound **1** is shown in the following figure.

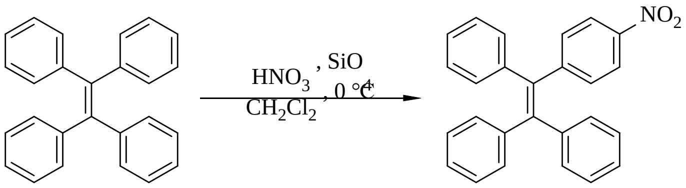


1

Compound **1** is synthesized according to the reference [1]. Under nitrogen atmosphere, benzophenone (4.00 g, 22.0 mmol) was added to a 250 mL three-necked flask, and 100 mL of dehydrated tetrahydrofuran was added and dissolved with stirring at room temperature, and then zinc powder (2.86 g, 0.044 mol) was added. The cold trap was controlled to -25 °C, and titanium tetrachloride (3.0 mL, 27.3 mmol) was added dropwise with vigorous stirring. After the dropwise addition, the mixture was returned to room temperature and stirred, and then warmed up to 70 °C and stirred at reflux for 12 h. After the complete reaction was monitored by TLC, the reaction system was cooled to room temperature, and aqueous sodium carbonate solution with a mass fraction of 10% was added to the reaction. When no more bubbles emerged from the reaction flask, the reaction mixture was transferred to a partition funnel, extracted with dichloromethane, and washed 3-5 times with saturated salt water, and the organic phases were combined. The organic phase was dried over anhydrous sodium sulfate, filtered and evaporated the solvent with rotary evaporator. The crude product was recrystallized with methanol to give a white powder of 3.1 g, yield 84.8%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.25-7.07 (m, 20H).

1.2 Synthesis of 1- (4-nitrophenyl) -1,2,2-triphenylene (**2**)

The synthesis route of compound **2** is shown in the following figure.

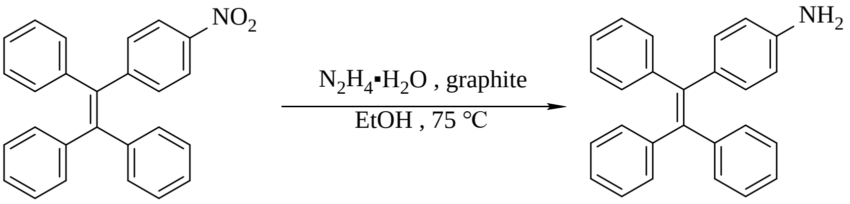


1 **2**

Compound **2** is synthesized according to the reference [2]. At 0 ° C, **1** (2.5 g, 7.5 mmol) and 50 mL of dichloromethane were added to a 250 mL three-necked flask, stirred, and dissolved. Then 3.0g of 200-300 mesh column chromatography silica gel was added with stirring vigorously. Fuming nitric acid (0.5 mL, 12.0 mmol) was added to a constant pressure drip funnel and then slowly added it to the above mixture. After dripping, the mixture continued stirring at 0 °C for 15 minutes. After the TLC monitoring reaction was complete, the reaction mixture was filtered, and the filtrate was extracted with dichloromethane and washed 1-2 times with saturated salt water. The organic phase was merged, dried with anhydrous sodium sulfate, filtered, and the solvent was spin dried. The crude product obtained was recrystallized with methanol to obtain 1.8 g of yellow solid product, with a yield of 63.4%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.96 (d, J = 8.8 Hz, 2H), 7.25–7.10 (m, 11H), 7.01–6.95 (dt, 6H).

1.3 Synthesis of 1- (4-aminophenyl) -1,2,2-triphenylene (**3**)

The synthesis route of compound **3** is shown in the following figure.

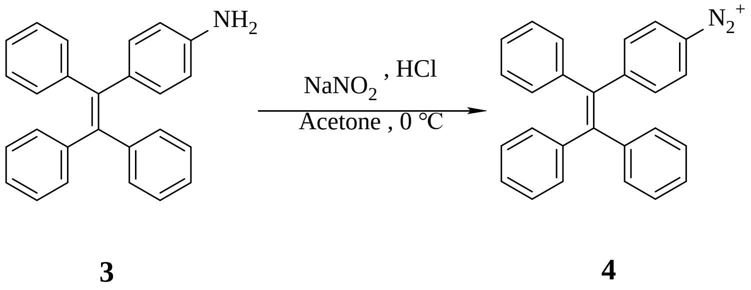


2 **3**

Compound **3** is synthesized according to the reference [2]. **2** (2.0 g, 5.3 mmol) and 80 mL of anhydrous ethanol were added to a 250 mL three-necked flask and stirred to dissolve at 75 °C. Graphite (3.0 g) and 80% hydrazine hydrate (5 mL) were added into the mixture and refluxed under nitrogen atmosphere for 12 hours. After the TLC monitoring reaction was complete, the reaction solution was filtered with diatomaceous earth while it was hot, the filter cake was washed with dichloromethane, the filtrate was spun dry, and cooled to room temperature. The crude product was recrystallized with ethanol to obtain a white solid of 1.23 g, with a yield of 84.5%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.18 (m, 8H), 7.14–7.08 (m, 7H), 6.99 (d, J = 7.6 Hz, 2H), 6.72 (m, 2H), 1.57 (s, 2H).

1.4 Synthesis of tetraphenylethylene-4-diazonium salt (**4**)

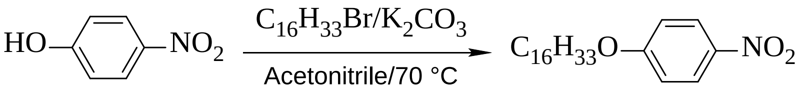
The synthesis route of compound **4** is shown in the following figure.



Compound **4** is synthesized according to the reference [3].**3** (1.00g, 2.85mmol) was added to a 100 mL round bottom flask and dissolved in 8-10mL acetone. concentrated hydrochloric acid (2mL, 37wt%) was added into it, cooled to 0 °C and stirred vigorously. Sodium nitrite (0.24 g, 3.5 mmol) was dissolved in 10 mL of water to obtain an aqueous solution of sodium nitrite. The resulting aqueous solution of sodium nitrite was dropped into a reaction flask. After the drop was completed, continued stirring at 0 °C for 3 hours. Adjust the pH to 6 with saturated sodium acetate aqueous solution, and then added a few grains of urea and stirred to dissolve to obtain an aqueous solution of tetraphenylethylene-4-diazonium salt. The product was stored at 0 °C and immediately put into the next reaction.

1.5 Synthesis of 1-(hexadecyloxy)-4-nitrobenzene (**5**)

The synthesis route of compound **5** is shown in the following figure.

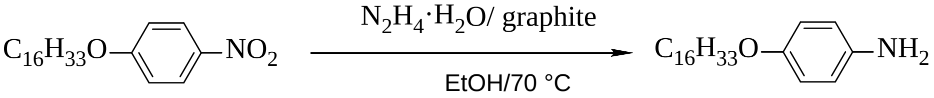


5

Compound **5** is synthesized according to the reference [4]. p-nitrophenol (2.0 g, 14.4 mmol) and 80 mL of acetonitrile were added into a 250 mL three-necked flask, stirred, and dissolved. Then anhydrous potassium carbonate (4.8 g, 35.0 mmol) was added into the mixture and stirred at room temperature for 30 min. $C_{16}H_{33}Br$ (5.3 mL, 17.3 mmol) was added drop by drop, heated up to 70 °C and refluxed overnight. After the TLC monitoring reaction was completed, the reaction mixture was transferred to a partition funnel, extracted with dichloromethane, and washed 3-5 times with saturated salt water, and the organic phases were combined. The organic phase was dried over anhydrous sodium sulfate, filtered, and evaporated the solvent with rotary evaporator. The crude product obtained was recrystallized with petroleum ether and dichloromethane to obtain a white solid of 4.4 g, with a yield of 87%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm):8.21 (d, 2H), 6.96 (d, 2H), 4.06 (t, 2H), 1.83 (m, 2H), 1.48 (m, 2H), 1.27 (m, 24H), 0.89 (t, 3H).

1.6 Synthesis of 4-(hexadecyloxy) aniline (**6**)

The synthesis route of compound **6** is shown in the following figure.

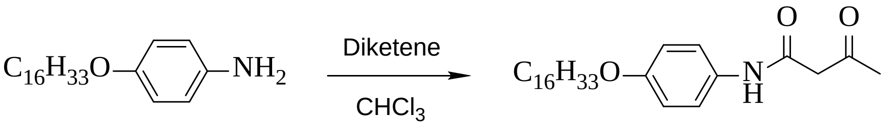


5 **6**

Compound **6** is synthesized according to the reference [4]. **5** (2.5 g, 6.88 mmol), 20 mL of dichloromethane and 80 mL of anhydrous ethanol were added to a 250 mL three-necked flask, stirred, and dissolved. 4.5 g graphite was added into the mixture, and then dropped 80% hydrazine hydrate (5 mL) in N_2 atmosphere, and raised the temperature to 75 °C, refluxed for 48 hours in N_2 atmosphere. After the TLC monitoring reaction was completed, the reaction solution was filtered with diatomaceous earth while it was hot. The filter cake was washed with dichloromethane, the filtrate was spun dry, and a white solid of 1.40 g was obtained by recrystallization with ethanol, with a yield of 61.1%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.71–6.77 (m, 2H),6.60–6.66 (m, 2H), 3.87 (t, J = 6.6 Hz, 2H), 3.39 (s, 2H), 1.70–1.77 (m, 2H), 1.39–1.46 (m, 2H), 1.20–1.36 (m, 24H), 0.88 (t, J = 7.0 Hz, 3H).

1.7 Synthesis of N-(4-(hexadecyloxy) phenyl)-3-oxobutanamide (**7**)

The synthesis route of compound **7** is shown in the following figure.

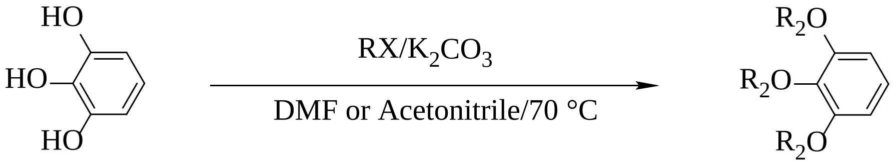


6 **7**

Compound **7** is synthesized according to the reference [2]. **6** (2.0 g, 6.0 mmol) and 50 mL of chloroform was added to a 250 mL three-necked flask. After the solid dissolved, added diethylene ketone (0.8 mL, 9.0 mmol) drop by drop, and stirred at room temperature for 2-5 hours. After the TLC monitoring reaction was completed, the filtrate was spun dry, and the light-yellow solid of 2.15 g was obtained by recrystallization with ethanol, with a yield of 85.8%.

1.8 Synthesis of 3,4,5-tris (alkoxy) benzene (**9**)

The synthesis route of compound **9** is shown in the following figure.



8

RX:$C_{16}H_{33}Br$, $C_{12}H_{25}Br$, CH_3I

9a: R_2 = —$C_{16}H_{33}$
9b: R_2 = —$C_{12}H_{25}$
9c: R_2 = —CH_3

9a:

The synthesis route is the same as **5**. Synthetic raw materials are **8** (2.0 g, 15.9 mmol), 50mL DMF, anhydrous potassium carbonate (13.15g, 95.2 mmol) and 1-bromocectane (17.5mL, 57.1 mmol). The crude product obtained was recrystallized twice with ethanol, resulting in a white solid product of 10.4g with a yield of 82.0%. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.90 (t, 1H, J = 8.6 Hz), 6.54 (d, 2H, J = 8.6 Hz), 3.91- 3.99 (m, 6H), 1.26–1.83 (m, 84H), 0.88 (t, 9H, J = 6.0 Hz).

9b:

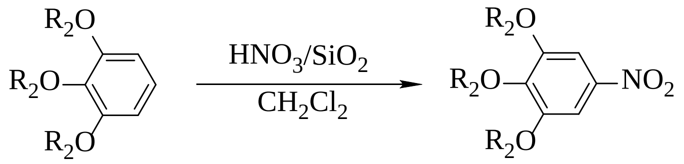
The synthesis route is the same as **5**. Synthetic raw materials are **8** (2.0 g, 15.9 mmol), 50mL DMF, anhydrous potassium carbonate (13.15 g, 95.2 mmol) and 1-bromocectane (13.8 mL, 45.0 mmol). The crude product obtained was recrystallized twice with ethanol, resulting in a white solid product of 8.3 g with a yield of 82.7%. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.93 (t, 1H), 6.56 (d, J = 6.6 Hz, 2H), 3.98-3.88 (dt, 6H), 1.80-1.70 (m, 6H),1.53-1.25 (m, 54H), 0.90(t, 9H).

9c:

The synthesis route is the same as **5**. Synthetic raw materials are **8** (4.0 g, 31.7 mmol), 50mL acetone, anhydrous potassium carbonate (28.25 g, 190.4 mmol) and iodomethane (7.4 mL, 114.1 mmol). The crude product obtained was recrystallized twice with ethanol, resulting in a white solid product of 4.65 g with a yield of 87.2%. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.99 (t, J = 8.4 Hz, 1 H), 6.58 (d, J = 8.3 Hz, 2 H), 3.85 (s, 9 H).

1.9 Synthesis of 3,4,5-tris (alkoxy) nitrobenzene (**10**)

The synthesis route of compound **10** is shown in the following figure.



9a: R$_2$ = —$C_{16}H_{33}$
9b: R$_2$ = —$C_{12}H_{25}$
9c: R$_2$ = —CH_3

10a: R$_2$ = —$C_{16}H_{33}$
10b: R$_2$ = —$C_{12}H_{25}$
10c: R$_2$ = —CH_3

10a:

The synthesis route is the same as **2**. Synthetic raw materials are **9a** (2.0 g, 2.5 mmol), 80 mL dichloromethane, 4 g of 200-300 mesh column chromatography silica gel and fuming nitric acid (0.25 mL, 6.0 mmol). Final crude product was recrystallized twice with methanol to obtain 1.68 g of a light-yellow solid product, with a yield of 79.6%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.47 (s, 2H), 4-4.1 (m, 6H), 0.85-1.84 (m, 93H).

10b:

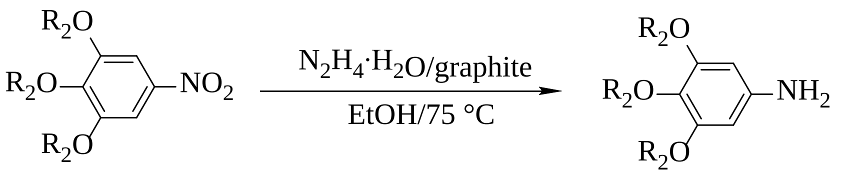
The synthesis route is the same as **2**. Synthetic raw materials are **9b** (2.0 g, 3.2 mmol), 80 mL dichloromethane, 4 g of 200-300 mesh column chromatography silica gel and fuming nitric acid (0.25 mL, 6.0 mmol). Final crude product was recrystallized twice with methanol to obtain 1.72 g of a light-yellow solid product, with a yield of 80.4%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.47 (s, 2H), 4-4.1 (m, 6H), 0.85-1.84 (m, 69H).

10c:

The synthesis route is the same as **2**. Synthetic raw materials are **9c** (2.0 g, 11.9 mmol), 80 mL dichloromethane, 4 g of 200-300 mesh column chromatography silica gel and fuming nitric acid (0.25 mL, 6.0 mmol). Final crude product was recrystallized twice with methanol to obtain 1.92 g of a white solid product, with a yield of 75.7%.

1.10 Synthesis of 3,4,5-tris (alkoxy) aniline (**11**)

The synthesis route of compound **11** is shown in the following figure.



10a: R_2 = —$C_{16}H_{33}$
10b: R_2 = —$C_{12}H_{25}$
10c: R_2 = —CH_3

11a: R_2 = —$C_{16}H_{33}$
11b: R_2 = —$C_{12}H_{25}$
11c: R_2 = —CH_3

11a:

The synthesis route is the same as **3**. Synthetic raw materials are **10a** (2.0 g, 2.4 mmol). 1.56 g of white solid product was obtained with a yield of 80.9%. ^{1}H NMR (400 MHz， $CDCl_3$， δ ppm): 5.91(s, 2H), 3.81-3.92(m, 6H), 3.47(bd s, 2H), 1.26-1.81(m, 84H), 0.88(t, 9H, J=5.8 Hz).

11b:

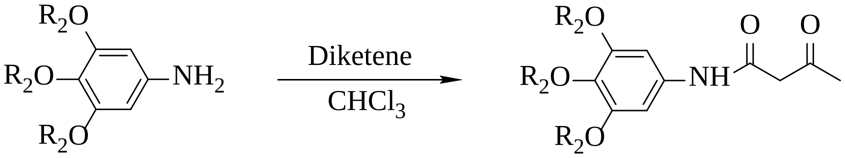
The synthesis route is the same as **3**. Synthetic raw materials are **10b** (2.0 g, 2.9 mmol). 1.78 g of white solid product was obtained with a yield of 93.1%. ^{1}H NMR(400 MHz， $CDCl_3$， δ ppm）： 5.88 (s, 2H), 3.95-3.87 (m, 6H), 2.96 (s, 2H), 1.83-1.73 (m, 6H), 1.49-1.28 (m, 54H), 0.88 (t, 9H).

11c:

The synthesis route is the same as **3**. Synthetic raw materials are **10c** (2.0 g, 9.4 mmol). 1.65 g of white solid product was obtained with a yield of 95.9%.

1.11 Synthesis of 3,4,5-tris (alkoxy)-N-acetylacetanilide (**12**)

The synthesis route of compound **12** is shown in the following figure.



11a: R_2 = —$C_{16}H_{33}$
11b: R_2 = —$C_{12}H_{25}$
11c: R_2 = —CH_3

12a: R_2 = —$C_{16}H_{33}$
12b: R_2 = —$C_{12}H_{25}$
12c: R_2 = —CH_3

12a:

The synthesis route is the same as **7**. Synthetic raw material is **11a** (2.0g, 2.5 mmol). 1.85 g of light-yellow solid product was obtained with a yield of 82.4%.

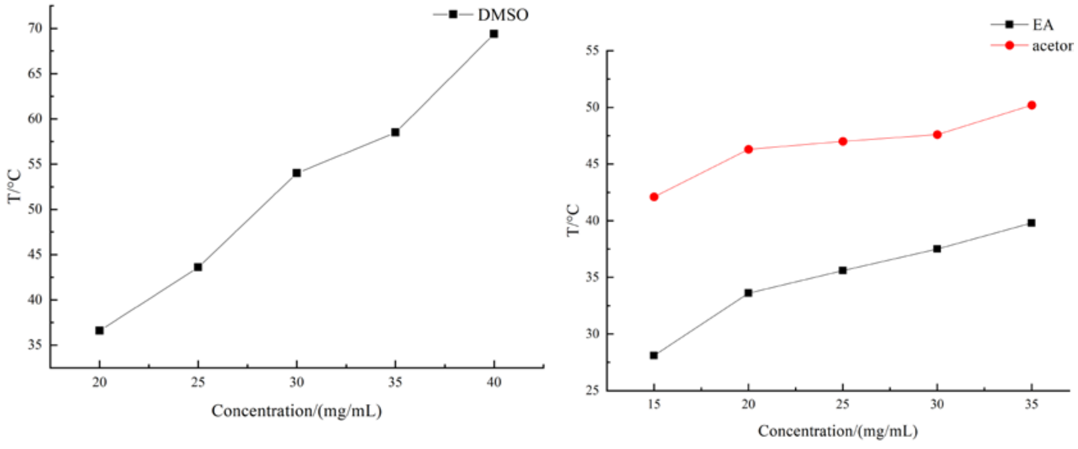
12b:

The synthesis route is the same as **7**. Synthetic raw material is **11b** (2.0g, 3.1 mmol). 1.92 g of light-yellow solid product was obtained with a yield of 84.9%. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 8.85 (s, 1H), 6.88 (s, 2H), 3.94–3.86 (m, 6H), 3.57 (s, 2H), 2.33 (s, 3H), 1.83–1.74 (m, 6H), 1.47–1.24 (m, 54H), 0.87 (t, 9H).

12c:

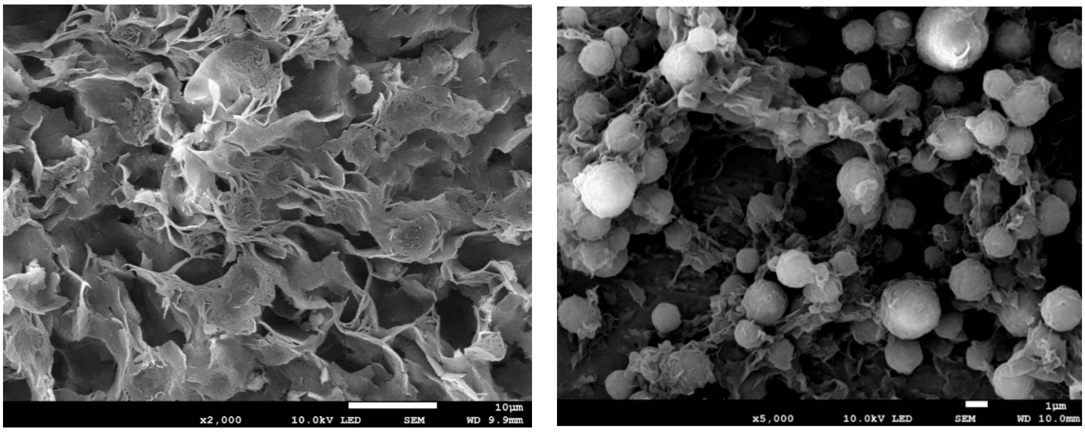
The synthesis route is the same as **7**. Synthetic raw material is **11c** (2.0g, 10.9 mmol). 2.55 g of a light-yellow oily liquid was obtained using a silica gel column separation (PE: EA=1:2), with a yield of 87.6%.

2 Experimental test data

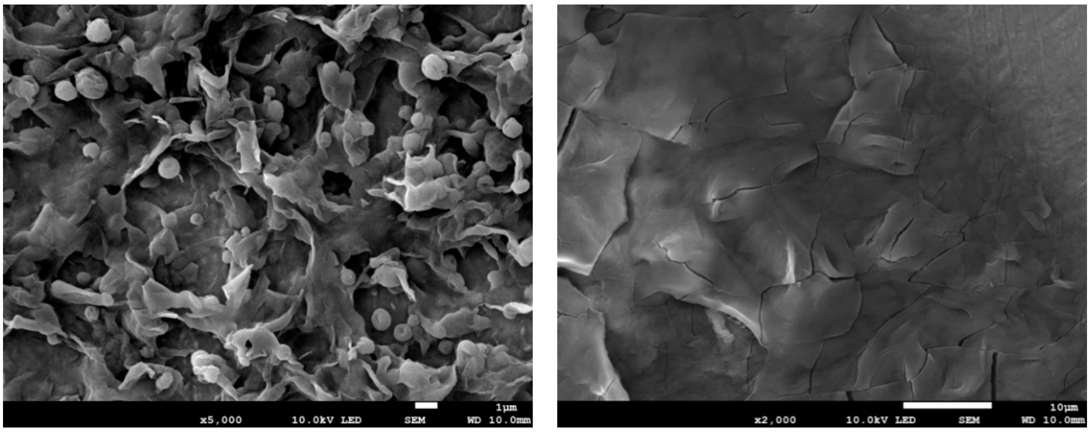


(a) (b)

Fig. S1 Plots of T_{gel} against the concentration of (a) **SC16** in DMSO and (b) **TC16** in EA (black) and acetone (red).



(a) (b)



(c)

(d)

Fig. S2 SEM images of xerogels obtained from the gels of (a) **SC16**-DMSO, (b) **TC16**-acetone, (c) **TC16**-tert-butanol, and (d) **TC16**-EA.

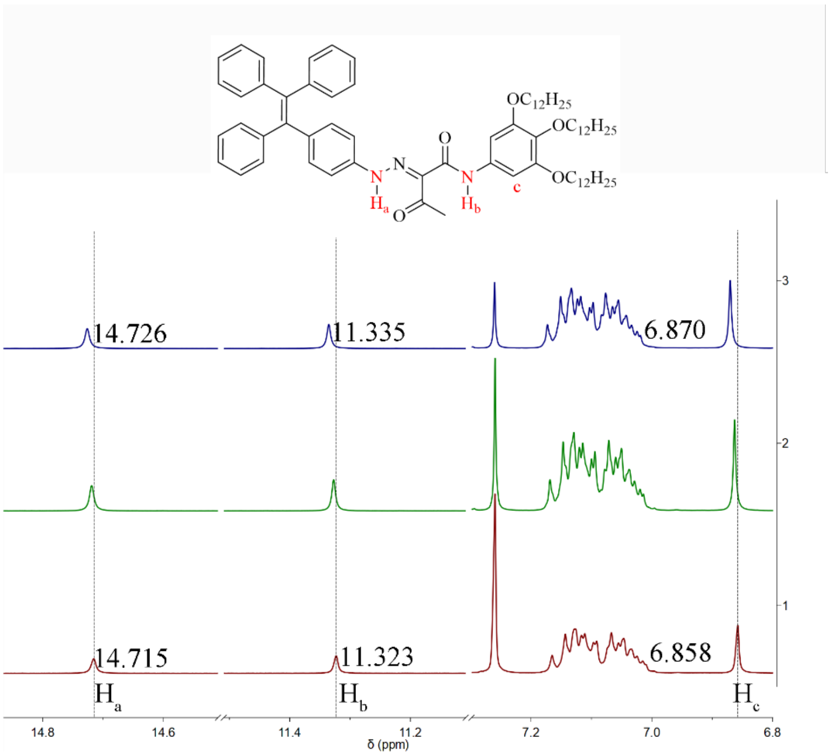


Fig. S3 Partial variable concentration ^{1}H NMR spectra of **TC16** in $CDCl_3$ (from bottom to top: 16.7, 33.3, 50 mg·mL^{-1})

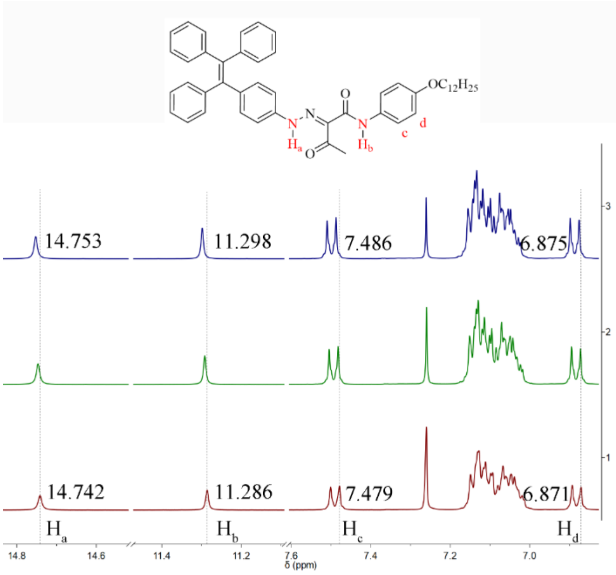
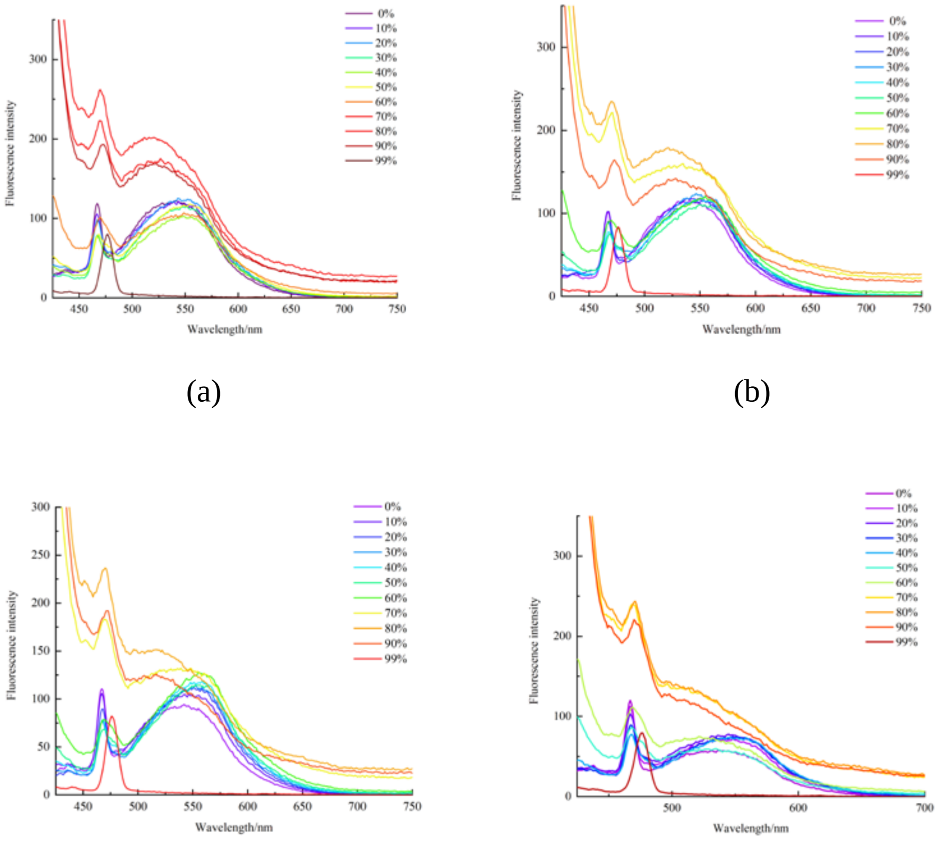


Fig. S4 Partial variable concentration ^{1}H NMR spectra of SC16 in $CDCl_3$ (from bottom to top: 16.7 mg/mL, 33.3 mg/mL, 50 mg/mL)



(a)

(b)

(c)

(d)

Fig. S5 Fluorescence emission spectra of THF/H_2O mixed solutions of (a) SOMe, (b) SC12, (c) TOMe, (d) TC12

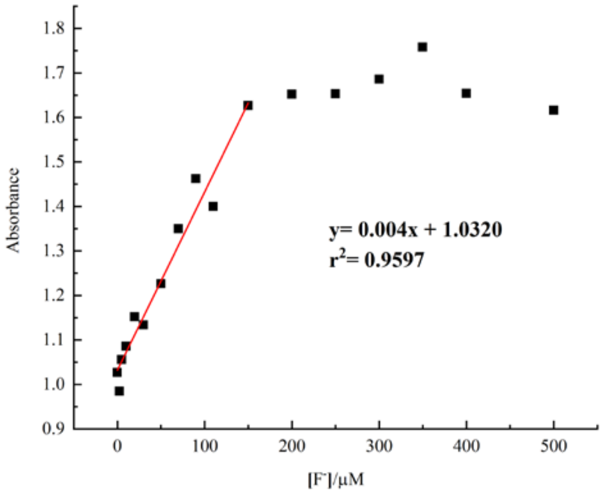


Fig. S6 Absorbance change and fitting curve of TC12 with the addition of F⁻ at 438 nm

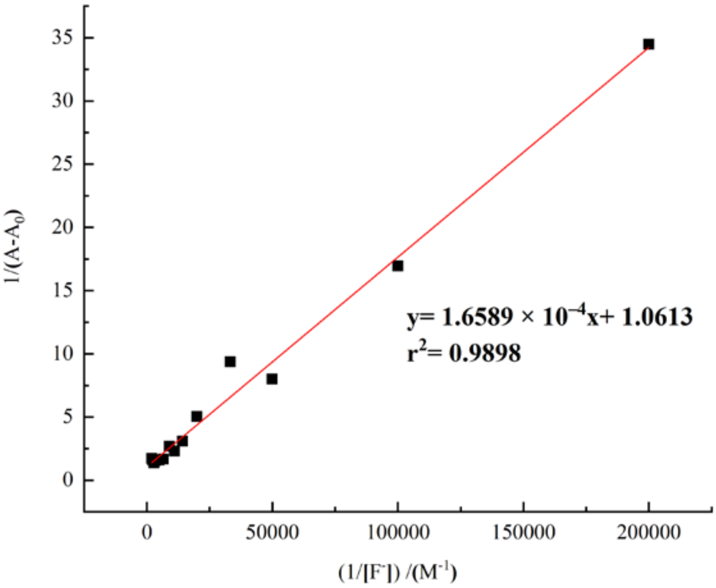


Fig. S7 Benesi-Hilderbrand plot of TC12 with F⁻

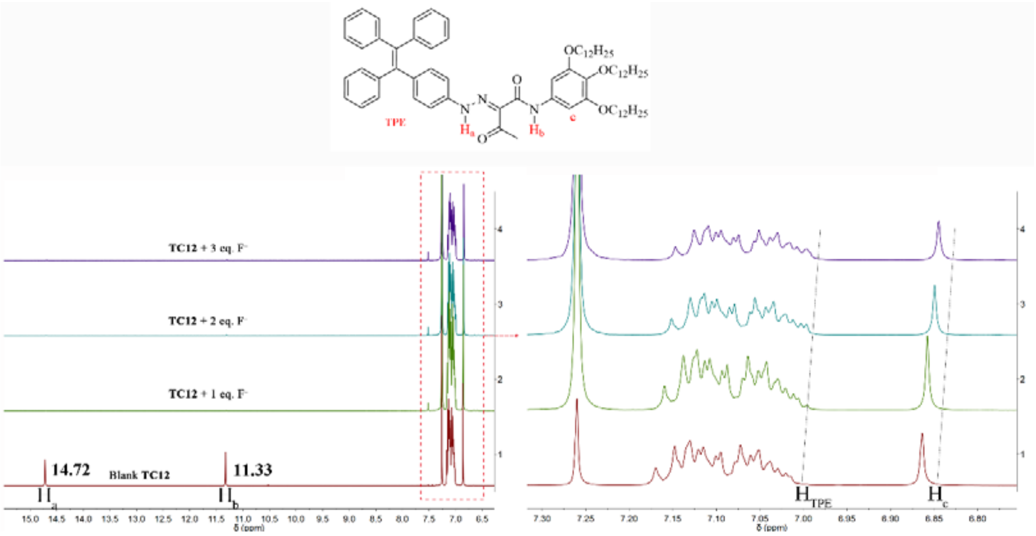


Fig. S8 ^{1}H NMR titration of **TC12** in the presence of different equivalents of TBAF in $CDCl_3$.

3 Reference

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