

## Supporting Information

A water-soluble fluorescent sensor for the quick discriminate H<sub>2</sub>O and D<sub>2</sub>O by notable signal outputs and the real-time monitor food spoilage in a non-contact mode

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## **1. General Information**

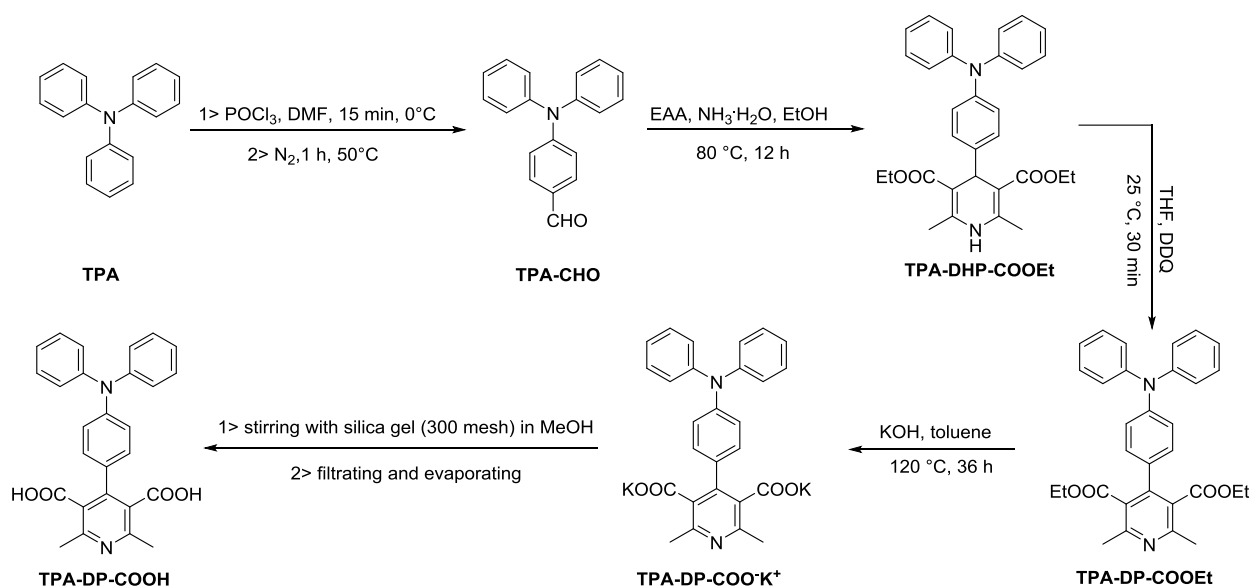
### **1.1 Reagents**

Ethyl acetoacetate (99%), Oleylamine (90%), Phosphorus oxychloride (POCl<sub>3</sub>, 99.5%), Potassium hydroxide (95%), *N, N*-dimethylformamide (DMF), Triphenylamine (98%) were purchased from Aladdin Company. 2,3-Dicyano-5,6-dichlorobenzoquinone (DDQ, 98%), Aluminium oxide (99%), Heavy water (D<sub>2</sub>O, 99.9%), Triethylamine (99.5%), Dimethyl sulfoxide (DMSO), Tetrahydrofuran (THF), Acetic acid, Hydrochloric acid, Methanol, Dichloromethane (DCM, 99.9%), Ethanol and Chloroform were purchased from Energy Chemical Company.

### **1.2 Instrumentations**

<sup>1</sup>H NMR (400/600 MHz) and <sup>13</sup>C NMR (150 MHz) spectra were recorded on MERCURY spectrometer at 25 °C, and all NMR spectra were referenced to the solvent. Mass spectrometric (MS) data were carried out using Thermoscientific Q Exactive instruments. Calculations were performed using the Gaussian09 program package at B3LYP/6-31G\* level. UV-visible absorption spectra (UV) were recorded on a TU-1901 spectrometer. Fluorescence spectra and fluorescence quantum yields were measured using a FluoroSENS 9003 Fluorescence Spectrophotometer.

## **2. Experimental details**



**Scheme S1.** Synthesis of TPA-CHO, TPA-DHP-COOEt, TPA-DP-COOEt, TPA-DP-COO<sup>-</sup>K<sup>+</sup>, TPA-DP-COOH

## 2.1 Synthesis of TPA-CHO.<sup>1</sup>

TPA (4.91 g, 245.33 g/mol, 20 mmol) was dissolved in DMF (20 mL) and placed in a 10 mL round-bottomed flask and the reaction mixture was stirred at 0 °C for 15 min, followed by slow dropwise addition of POCl<sub>3</sub> (10 mL). Finally, the reaction was carried out at 50 °C for 1 h under N<sub>2</sub> environment. The reaction mixture was quenched with distilled water (DMF/H<sub>2</sub>O = 1/100) and a yellow solid was precipitated. The residue was obtained by filtration, and the crude product was purified on a silica gel column using a mixture (petroleum ether/ethyl acetate, 250/1) as eluent to give 4.64 g of product (85% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ (TMS, ppm): 9.80 (s, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.37 - 7.30 (m, 4H), 7.23 - 7.08 (m, 6H), 7.01 (d, *J* = 8.7 Hz, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ (TMS, ppm): 190.38, 153.33, 146.14, 131.26, 129.70, 129.10, 126.33, 125.03, 119.26.

## 2.2 Synthesis of TPA-DHP-COOEt.<sup>2</sup>

TPA-CHO (546 mg, 273.34 g/mol, 2 mmol), ethyl acetoacetate (0.3 mL, 130.14 g/mol, 2.4 mmol) and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (0.4 mL, 35.05 g/mol, 10 mmol) were dissolved in EtOH (20 mL) and placed in a 50 mL round-bottomed flask. Then, the reaction mixture was reacted at 80 °C for 12 h under  $\text{N}_2$  environment and the crude product was obtained by concentrating the mixture by rotary evaporation. The crude product was purified on a silica gel column using the mixture (petroleum ether/ethyl acetate = 50/1) as the eluent to give 903 mg of product (yield: 91%).  $^1\text{H}$  NMR (600 MHz,  $d_6$ -DMSO)  $\delta$  (TMS, ppm): 8.75 (s, 1H), 7.21 (t,  $J = 7.8$  Hz, 4H), 7.05 (d,  $J = 8.5$  Hz, 2H), 6.95 (t,  $J = 7.4$  Hz, 2H), 6.89 (d,  $J = 7.8$  Hz, 4H), 6.83 (d,  $J = 8.5$  Hz, 2H), 4.81 (s, 1H), 4.04 - 3.92 (m, 4H), 2.23 (s, 6H), 1.09 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (150 MHz,  $d_6$ -DMSO)  $\delta$  (TMS, ppm): 167.41, 147.81, 145.72, 145.33, 143.62, 129.79, 128.93, 124.10, 123.7, 122.8, 102.22, 59.38, 18.70, 14.61.

### 2.3 Synthesis of TPA-DP-COOEt.<sup>3</sup>

TPA-DHP-COOEt (497 mg, 497.61 g/mol, 1 mmol) was dissolved in THF (15 mL) and stirred in a 50 mL round-bottomed flask for 10 min, then DDQ (227 mg, 227 g/mol, 1 mmol) was added. The reaction mixture was stirred at room temperature (25 °C) for 30 min, and following 5 mL of HCl solution (0.1 M) was slowly added. Next, 50 mL of water was added to the reaction mixture and extracted three times with dichloromethane. Finally, the organic layer was concentrated by rotary evaporation to obtain the crude product. The crude product was purified on a silica gel column using the mixture (petroleum ether/ethyl acetate = 20/1) as the eluent to give 350 mg of product (yield: 70%).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (t,  $J = 8.0$  Hz, 4H), 7.12 (d,  $J = 8.6$  Hz, 2H), 7.08 - 7.02 (m, 8H), 4.11 (q,  $J = 7.1$  Hz, 4H), 2.59 (s, 6H), 1.06 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  167.98, 155.30, 147.64, 146.88, 145.45, 130.67, 129.52, 129.27, 126.94, 125.19, 124.13, 122.92, 61.31, 22.85, 13.79.

## 2.4 Synthesis of TPA-DP-COO<sup>-</sup>K<sup>+</sup>.<sup>4</sup>

TPA-DP-COOEt (495 mg, 494.59 g/mol, 1 mmol) and KOH (281 mg, 56.11 g/mol 5 mmol) were dissolved in 15 mL of toluene. The reaction mixture was placed in a 25 mL round-bottomed flask for 36 h at 120 °C. Next, the reaction mixture was concentrated by rotary evaporation to obtain the crude product. The crude product was purified on a neutral alumina column using methanol as eluent to obtain 371 mg of product (yield: 72%). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 4H), 7.04 (d, *J* = 8.0 Hz, 6H), 6.79 (d, *J* = 8.5 Hz, 2H), 2.31 (s, 6H). <sup>13</sup>C NMR (150 MHz, D<sub>2</sub>O) δ 181.41, 176.06, 171.01, 150.29, 147.61, 147.47, 133.64, 129.58, 129.26, 124.55, 123.44, 122.44, 23.33.

## 2.5 Synthesis of TPA-DP-COOH.

TPA-DP-COO<sup>-</sup>K<sup>+</sup> (514 mg, 514.07 g/mol, 1 mmol) was dissolved in 10 mL methanol and 5.14 g silica gel was added. The reaction mixture was placed in a 25 mL round-bottomed flask and reacted at room temperature (25 °C) for 10 minutes. The filtrate was obtained by filtration. The filtrate was concentrated by rotary evaporation to obtain 318 mg of product (yield: 87%). <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO) δ 7.54 (d, *J* = 8.7 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 4H), 7.06 - 6.99 (m, 6H), 6.79 (d, *J* = 8.7 Hz, 2H), 2.29 (s, 6H).

## 3. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum

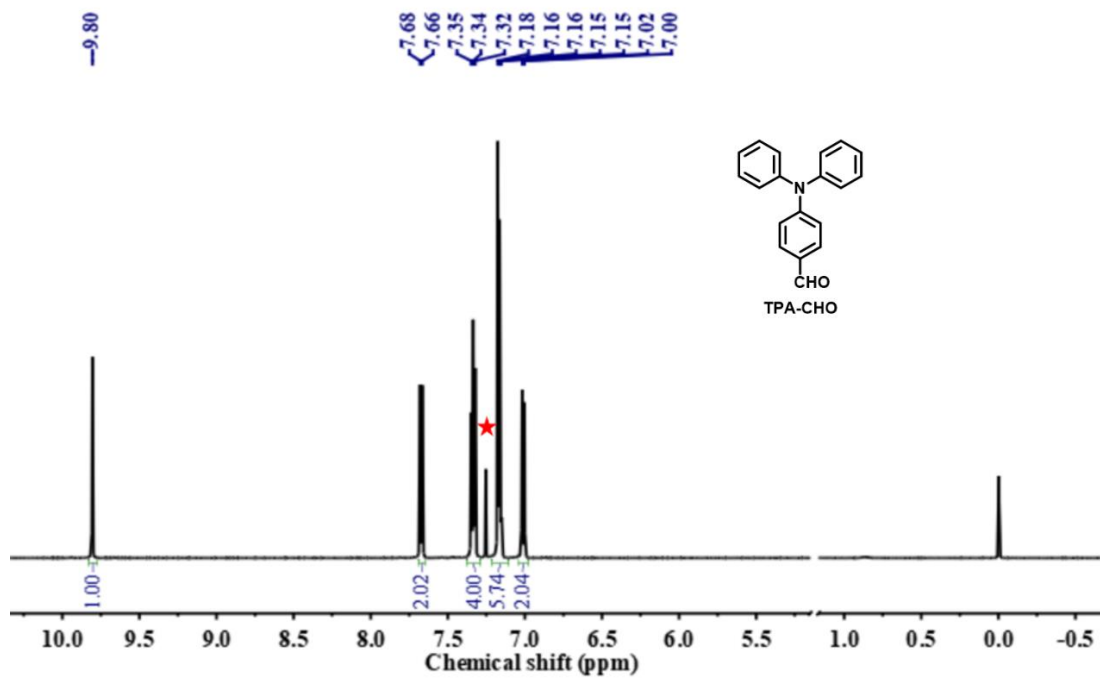


Fig. S1-a. The  $^1\text{H}$  NMR spectrum of TPA-CHO

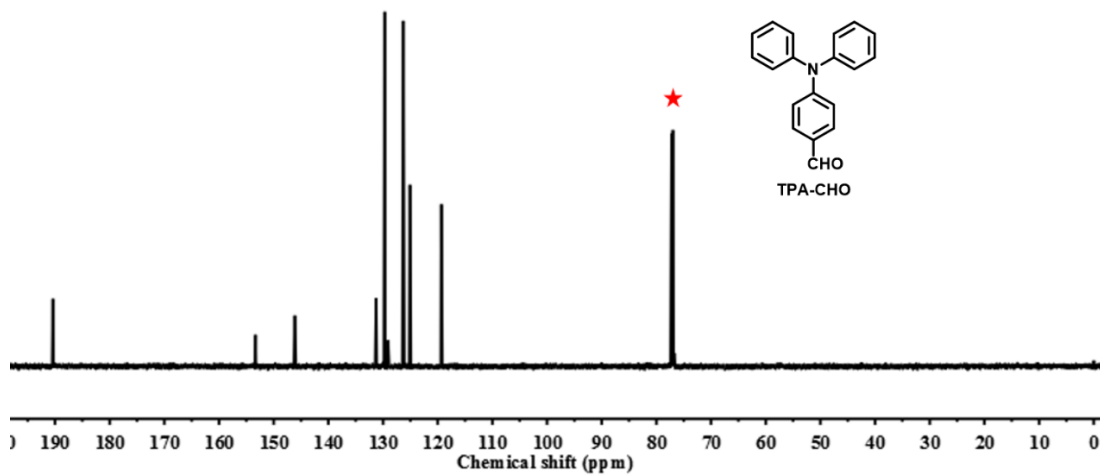


Fig. S1-b. The  $^{13}\text{C}$  NMR spectrum of TPA-CHO

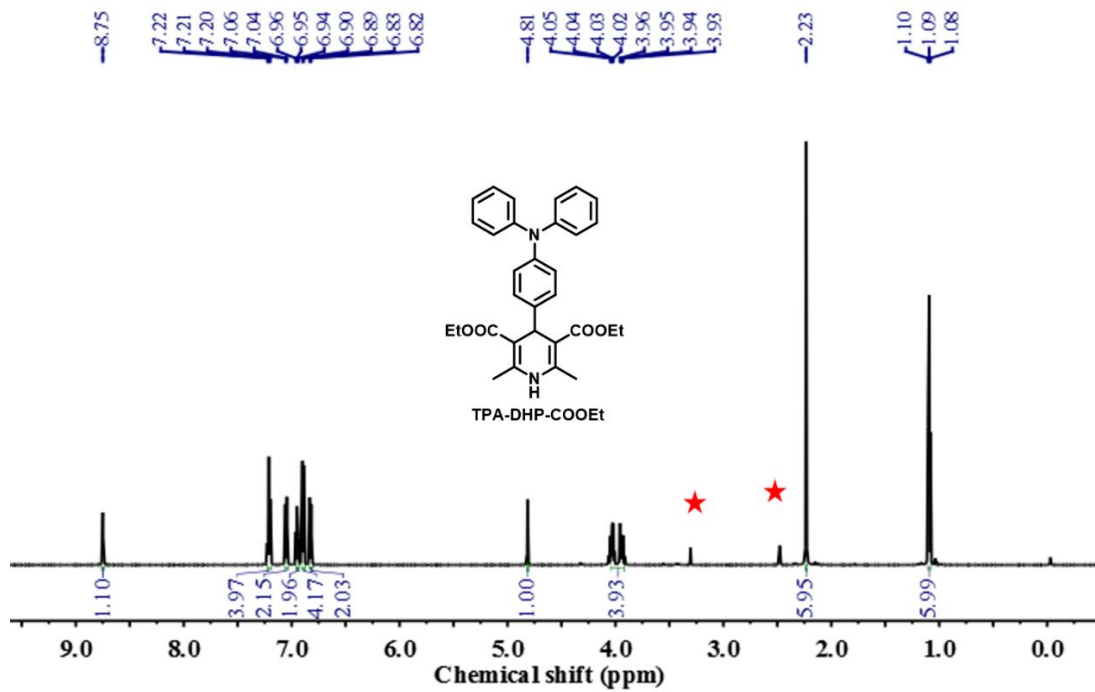


Fig. S2-a. The <sup>1</sup>H NMR data spectrum of TPA-DHP-COOEt

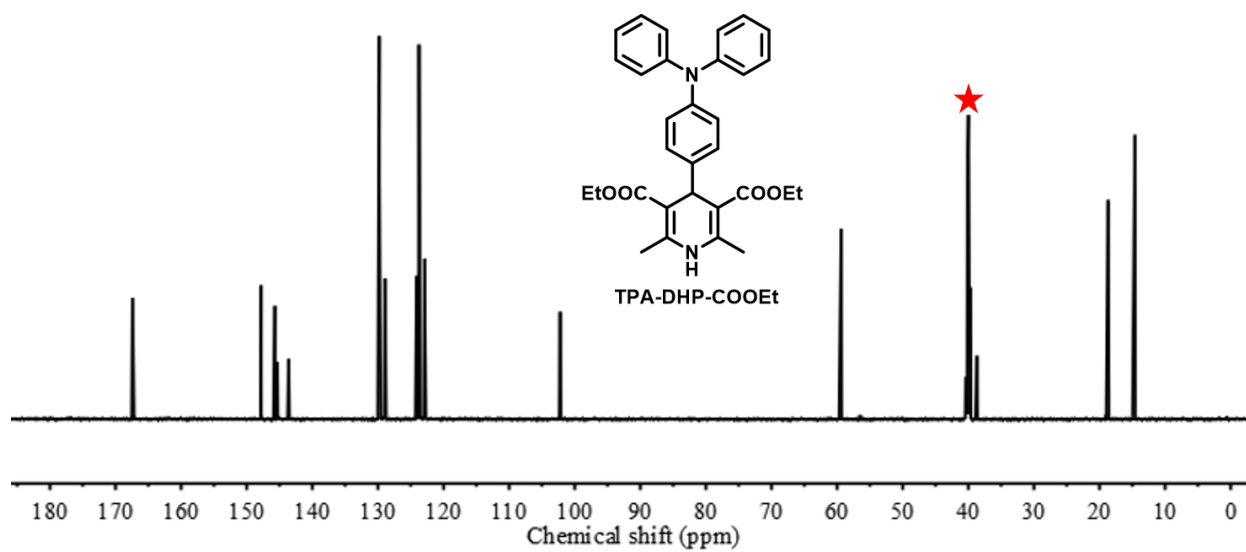


Fig. S2-b The <sup>13</sup>C NMR data spectrum of TPA-DHP-COOEt



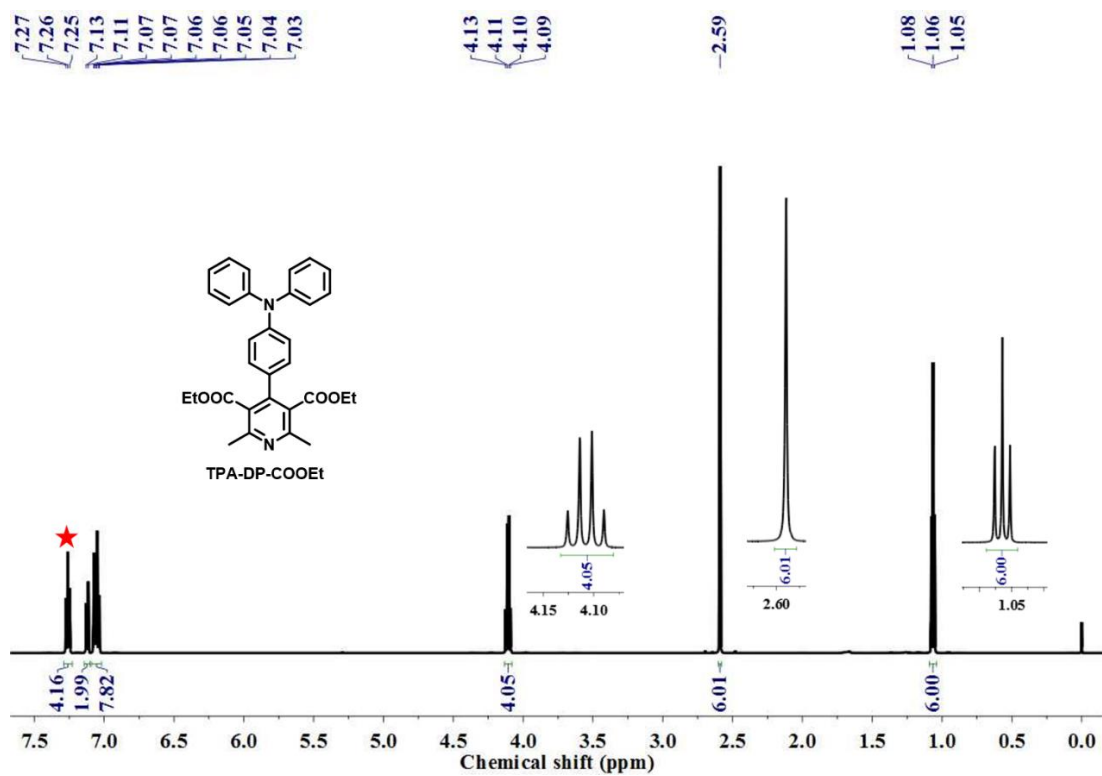


Fig. S3-a The <sup>1</sup>H NMR data spectrum of TPA-DP-COOEt

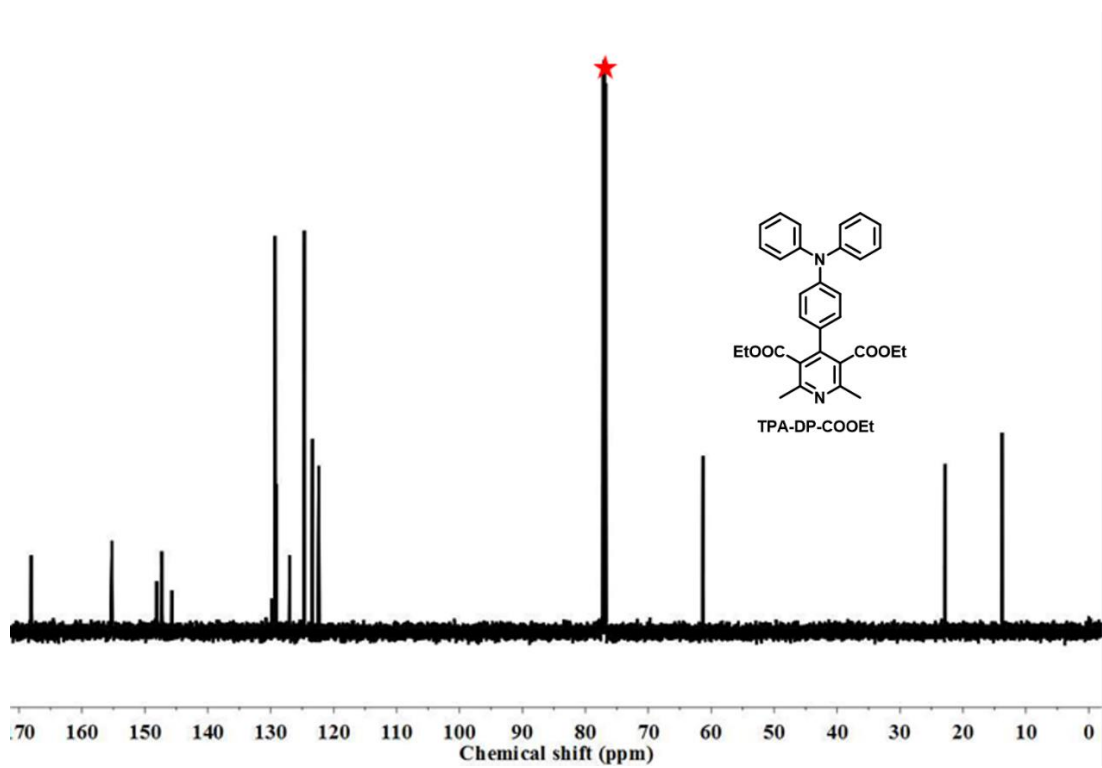


Fig. S3-b The <sup>13</sup>C NMR data spectrum of TPA-DP-COOEt

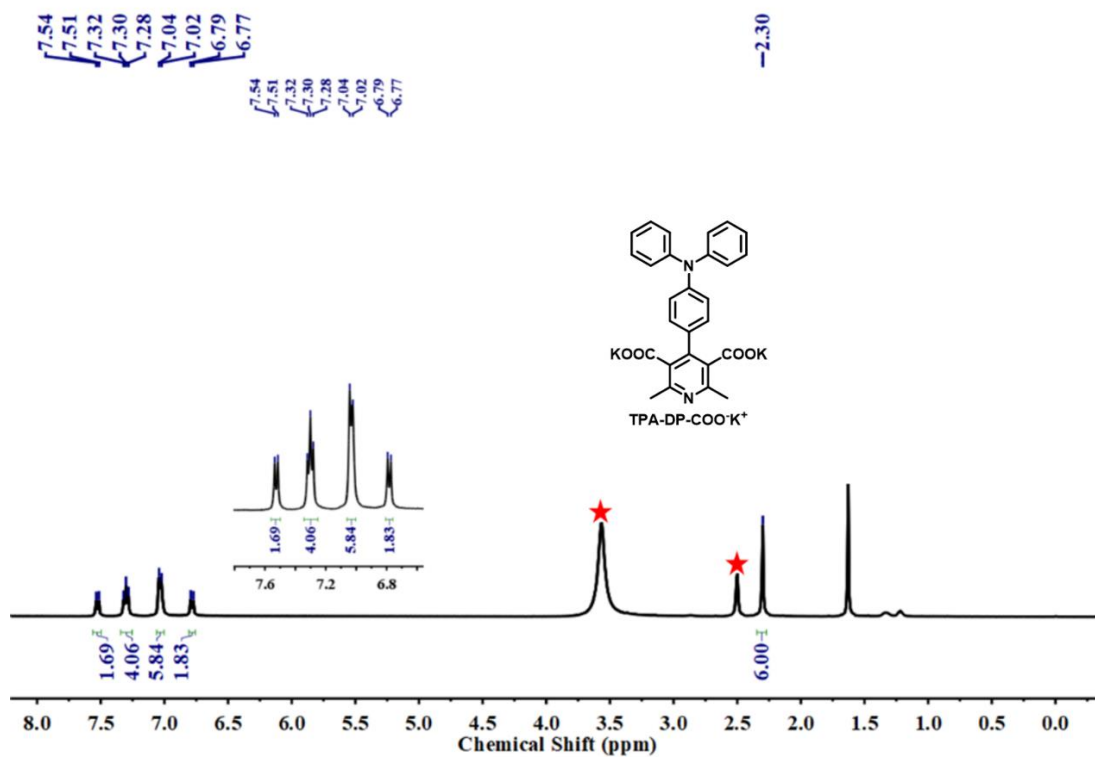


Fig. S4-a The  $^1\text{H}$  NMR data spectrum of TPA-DP-COO $^-$ K $^+$

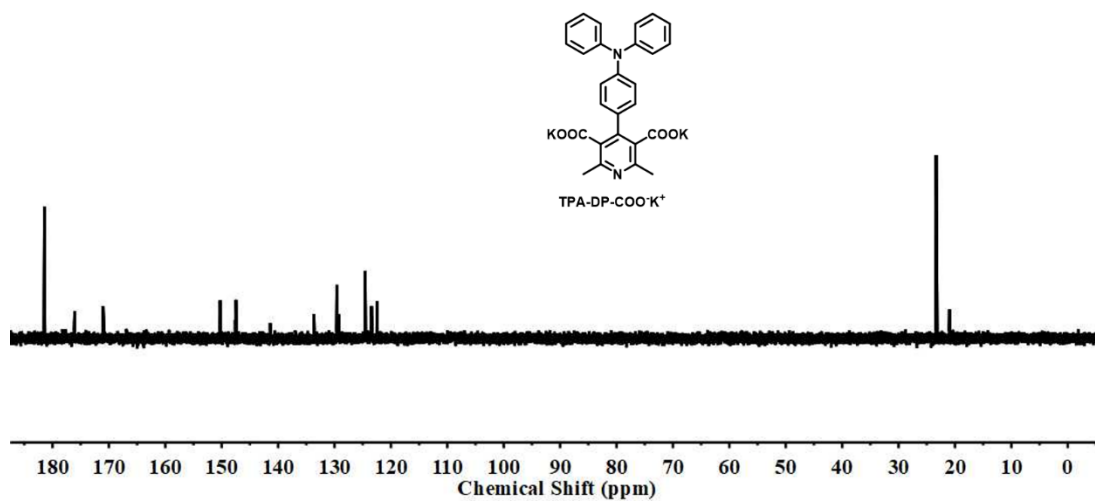


Fig. S4-b The  $^{13}\text{C}$  NMR data spectrum of TPA-DP-COO $^-$ K $^+$

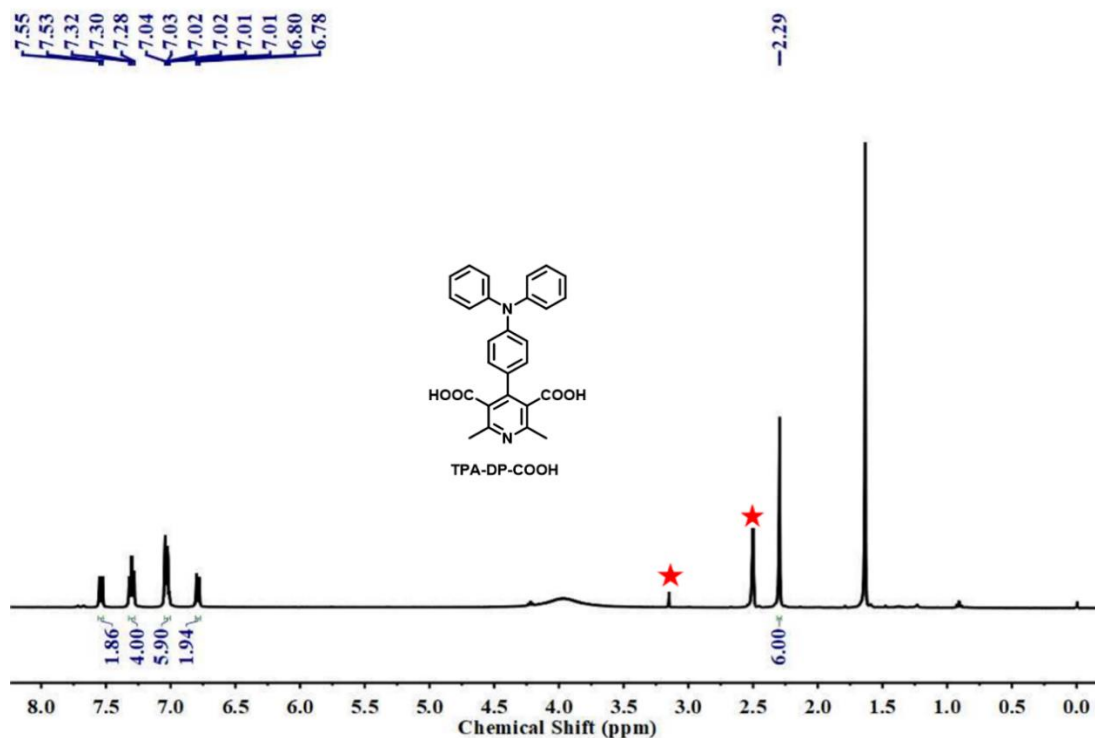


Fig. S5 The <sup>1</sup>H NMR data spectrum of TPA-DP-COOH

#### 4. HRMS spectrum

##### 4.1 HR-MS Spectra of TPA-DP-COO<sup>-</sup>K<sup>+</sup>.

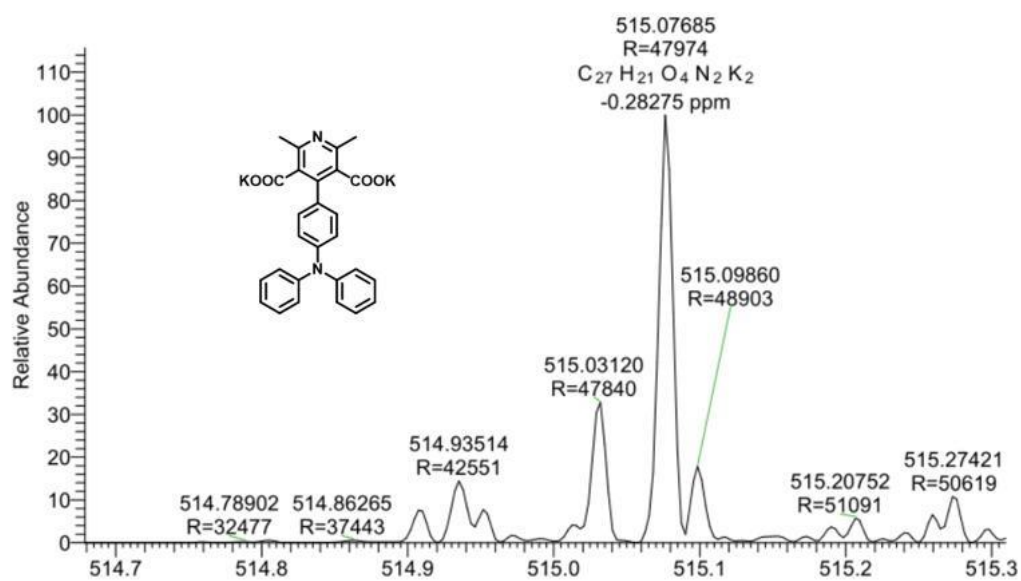


Fig. S6 HR-MS spectra of TPA-DP-COO<sup>-</sup>K<sup>+</sup>.

## 4.2 HR-MS Spectra of TPA-DP-COOH.

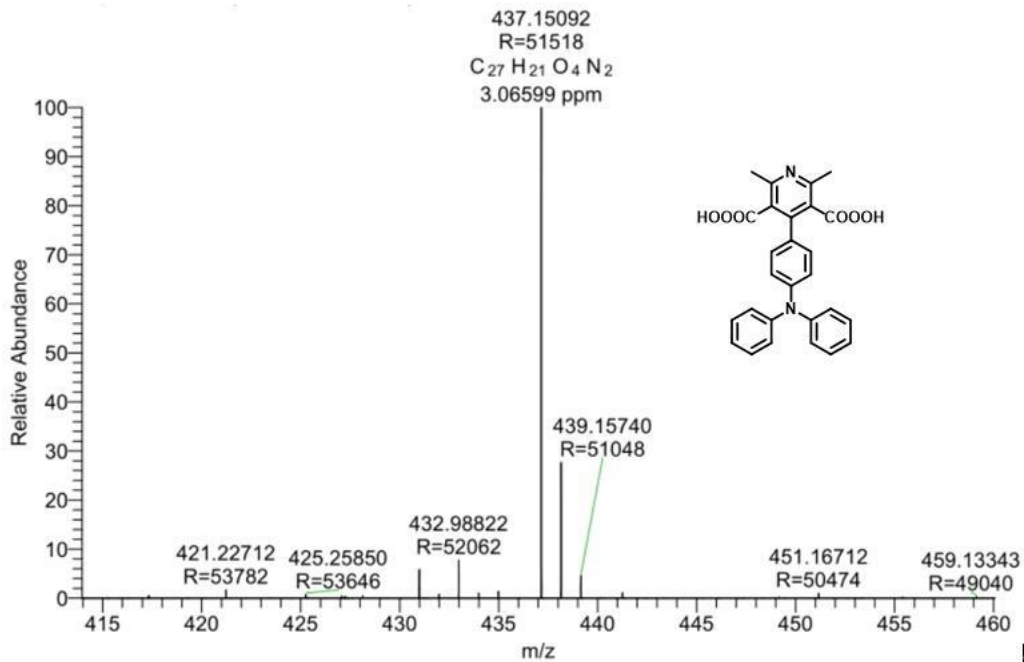


Fig. S7. HR-MS spectra of TPA-DP-COOH.

## 5. UV-vis spectra

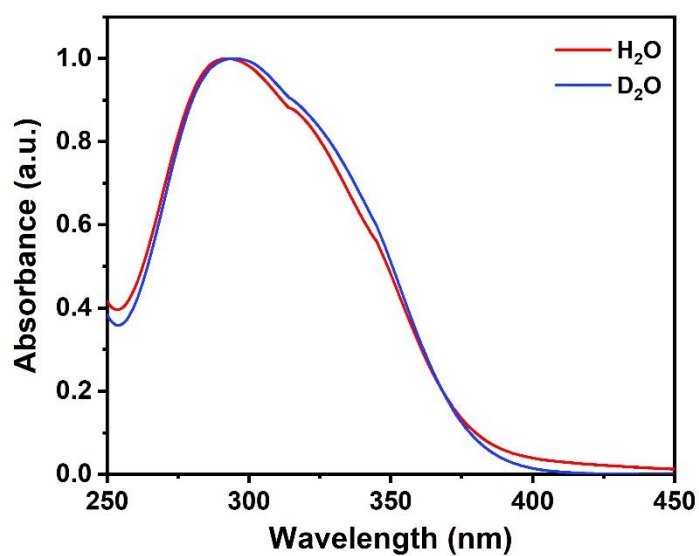
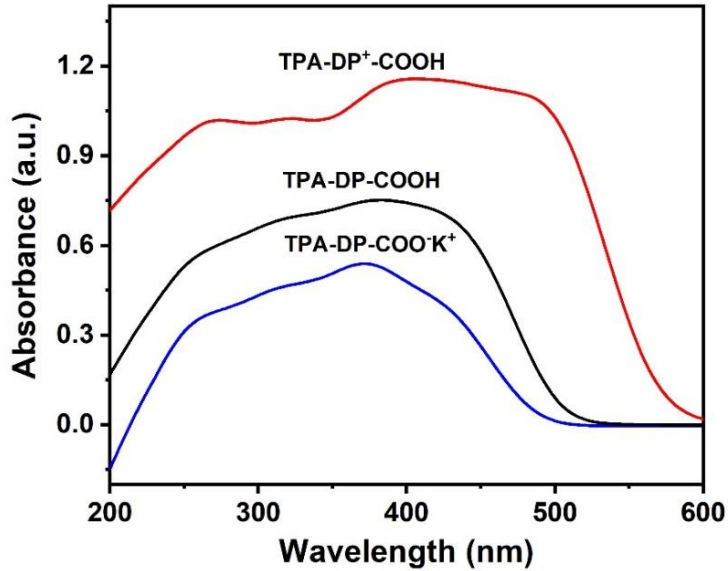
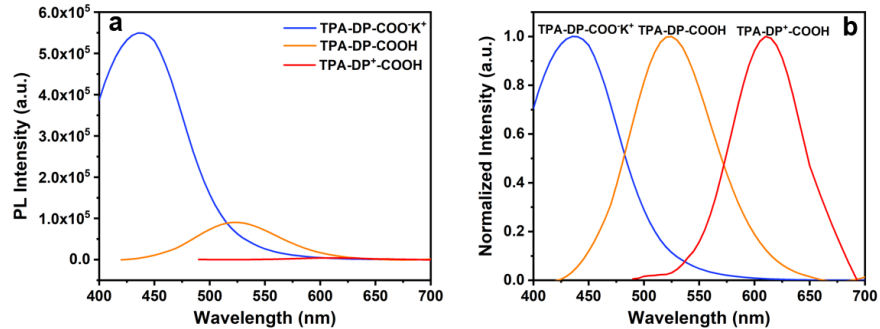


Fig. S8. UV-vis spectra of TPA-DP-COOH, in H<sub>2</sub>O and D<sub>2</sub>O solution (5 μM).

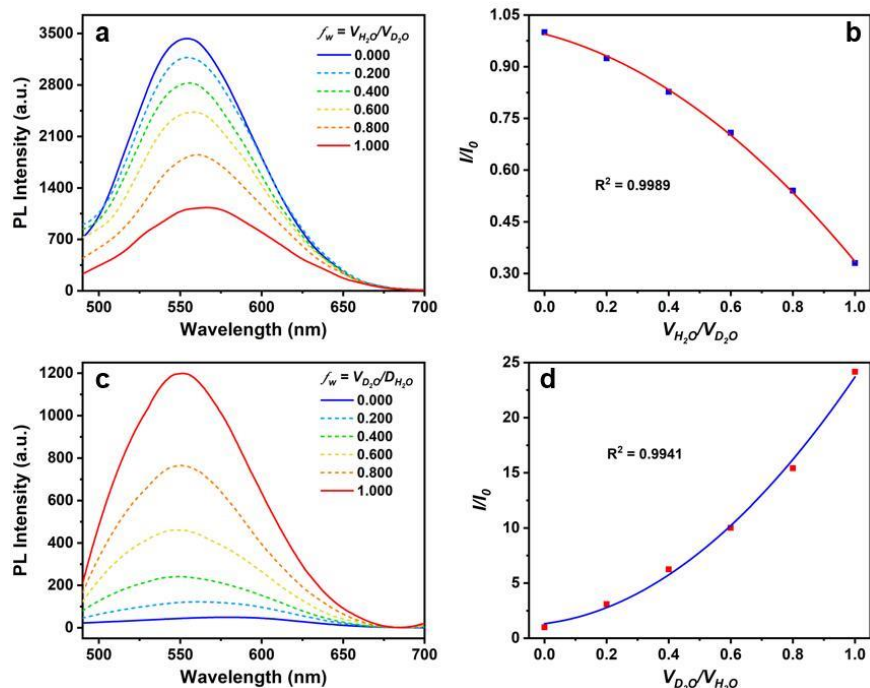


**Fig. S9.** UV-vis spectra of TPA-DP-COO<sup>-</sup>K<sup>+</sup>, TPA-DP-COOH, TPA-DP<sup>+</sup>-COOH in solid state.

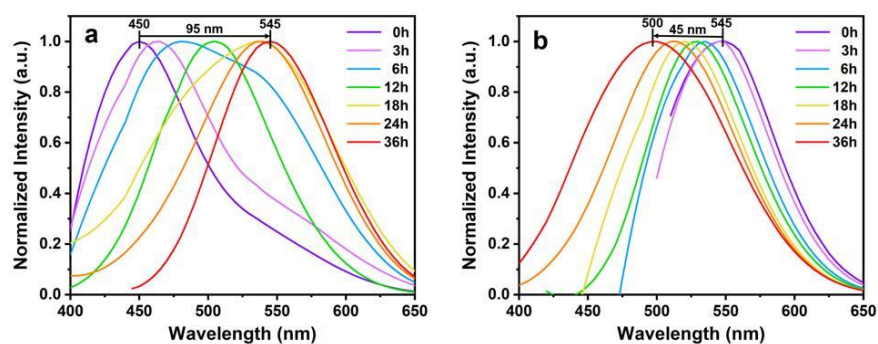
## 6. The PL spectrum



**Fig. S10.** (a) PL spectra of TPA-DP-COO<sup>-</sup>K<sup>+</sup>, TPA-DP-COOH, TPA-DP<sup>+</sup>-COOH in solid state ( $\lambda_{\text{ex}} = 400, 420, 490 \text{ nm}$ ). (b) Normalized spectra of TPA-DP-COO<sup>-</sup>K<sup>+</sup>, TPA-DP-COOH, TPA-DP<sup>+</sup>-COOH in solid state ( $\lambda_{\text{em}} = 435, 525, 620 \text{ nm}$ ).

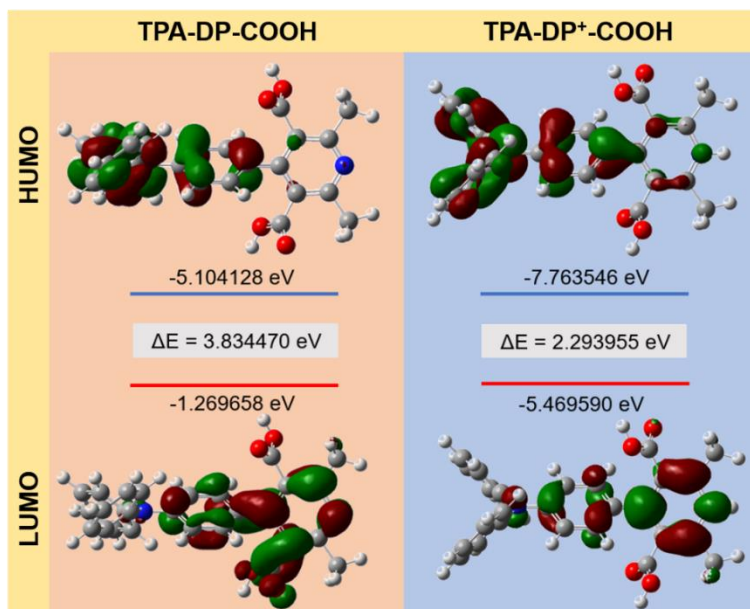


**Fig. S11.** (a) The PL spectrum of TPA-DP-COOH in H<sub>2</sub>O/D<sub>2</sub>O mixtures with different H<sub>2</sub>O fractions (0-1.0, v/v) (conc. = 2 μmol/mL, λ<sub>ex</sub> = 490 nm). (b) Relationship between ratiometric values of TPA-DP-COOH with H<sub>2</sub>O contents in D<sub>2</sub>O. (c) The PL spectrum of TPA-DP-COOH in D<sub>2</sub>O/H<sub>2</sub>O mixtures with different D<sub>2</sub>O fractions (0-1.0, v/v) (conc = 2 μmol/mL, λ<sub>ex</sub> = 490 nm). (d) Relationship between radiometric values of TPA-DP-COOH with D<sub>2</sub>O contents in H<sub>2</sub>O.



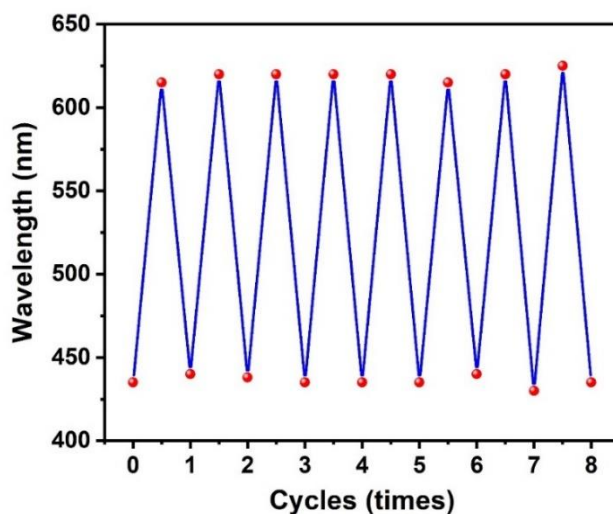
**Fig. S12.** Normalized PL spectra of (a) TPA-DP-COO<sup>-</sup>K<sup>+</sup> sensor in sealed packages *Dimocarpus longan* Lour (b. TPA-DP-COOH sensor in sealed packages white-leg shrimp) stored at room temperature (25 °C) for 0, 3, 6, 12, 18, 24, 36 hour.

## 7. Molecular orbital amplitude plots



**Fig. S13.** Molecular orbital amplitude plots of HOMO and LUMO energy levels of compounds TPA-DP-COOH and TPA-DP<sup>+</sup>-COOH calculated using the B3LYP/6-31G\*basis set.

## 8. Reversibility testing



**Fig. S14.** Wavelength change of TPA-DP-COO<sup>-</sup>K<sup>+</sup> filter paper strip after repeated cyclic exposure to triethylamine and hydrochloric acid vapor.

## 9. Table of details of LOD values

**Table S1.** Detection Limit and Related Date of Trace D<sub>2</sub>O in H<sub>2</sub>O (H<sub>2</sub>O in D<sub>2</sub>O)

mixtures	S.D.	A (Slope)	B (Intercept)	R <sup>2</sup>	LOD (ppm)
Trace D <sub>2</sub> O in H <sub>2</sub> O	16.8243	-4.7604	0.9867	0.9932	49.0791
Trace H <sub>2</sub> O in D <sub>2</sub> O	1.0270	13.5895	0.9693	0.9936	0.2267

## REFERENCES

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