

Electronic Supporting Information

Smart covalent organic frameworks: dual channel sensors for acid and base

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Section 1. Experimental Procedures

¹³C solid-state NMR results were recorded on Bruker AVNEO400 Solid NMR. Fourier transform infrared (FT IR) spectra were recorded on a Bruker Alpha infrared spectrometer. Electronic absorption spectroscopy was conducted on a JASCO model v-570 spectrophotometer. The fluorescence spectra and absolute quantum yield were recorded through the same procedures as reported^{S1} on a JASCO model FP-6600 spectrofluorometer, equipped with integral sphere. Time-resolved fluorescence spectroscopy were recorded on a Hamamatsu model compact fluorescence lifetime spectrometer C11367 (Quantaaurus-Tau) which equipped with a light-emitting diode (LED) pulsed light source, monochromator, PMT (photomultiplier tube), iris (aperture) for adjusting light level, and filter for cutting excitation light. Powder X-ray diffraction (PXRD) data were recorded on Bruker D8 advance by depositing powder on the PTMA sample cell. Nitrogen sorption isotherms were measured with a Micromeritics Instrument Corporation model 3Flex Surface Characterization Analyzer. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. Field emission scanning electron microscopy (FE SEM) was taken on a JEOL model JSM-6701F operating at an accelerating voltage of 5.0 kV. The samples were prepared by drop-casting anhydrous ethanol suspension onto silica wafer and coated with gold.

Section 2. Synthesis

Unless otherwise noted, all commercially available reagents were used without further purification. Ethanol (EtOH), sodium methoxide (MeONa), sodium *tert*-butoxide (*t*-BuONa), mesitylene, sodium acetate and 1,4-phenylenediacetonitrile (PDAN) were purchased from Tokyo Chemical Industry Co. Ltd. Tetrahydrofuran (THF), dimethylformamide (DMF), 1,4-dioxane and phosphate buffered saline (PBS) were purchased from Merck Pte Ltd. Sodium hydroxide, potassium chloride, sodium carbonate and sodium bicarbonate were purchase from Dickson Instrument & Chemical Pte Ltd. Hydrochloric acid and acetic acid were obtained from VWR International, LLC.

1,3,6,8-Tetrakis(4-formylphenyl)pyrene (TFPPy) and sp²c-COF were synthesized according to the reported methods.^{S2}

Synthesis of [CO₂H]sp²c-COF. An aqueous solution of sodium hydroxide (10 M, 1 mL) and EtOH (1 mL) were added to a Pyrex tube containing sp²c-COF (6 mg). The rustling mixture was degassed via three freeze–pump–thaw cycles. The tubes were flame sealed and placed in oven at 90 °C for three days. The precipitates were isolated by filtration, washed with deionized water (20 mL), aqueous solution of hydrochloric acid (1 M, 20 mL) and tetrahydrofuran (20 mL). The powder was subjected to Soxhlet extraction with THF for one day. Bright yellow [CO₂H]sp²c-COF powder was collected and dried under vacuum in a 97% yield.

Spectroscopy of [CO₂H]sp²c-COF in Aqueous Solutions of Different pH Values. Multiple buffer systems including potassium chloride/ hydrochloric acid, sodium acetate/acetic acid, phosphate buffered saline (PBS) and sodium carbonate/bicarbonate were made to prepare solutions with different pH values by using NaOH (4 M) and HCl (3 M) to adjust the pH value of the buffer. Buffer solutions with different pH values (1.4, 3.4, 4.5, 5.8, 6.9, 7.4, 9.0, 10.6 and 12.4) were prepared. For spectroscopy, the [CO₂H]sp²c-COF sample (4 mg) was soaked in the buffer solution (8 mL) and sonicated for 5 min. The electronic absorption spectra were then recorded. For fluorescence spectroscopy measurements, the [CO₂H]sp²c-COF sample was soaked in buffer solution (25 ppm, 4 mL). After sonicating for 5 min, fluorescence spectra were recorded upon excitation at 488 nm. During the sensing, the COF dispersion sample was stirred to keep its homogeneity. For the above spectroscopy, each point was repeated for three times to ensure the reproducibility.

Dopamine sensing experiments. Stock solutions of [CO₂H]sp²c-COF in deionized water (400 μM) were prepared. The solution was sonicated for 5 min to ensure homogeneity before use. For dopamine sensing, the [CO₂H]sp²c-COF solution (25 ppm, 200 μL, pH 7.4) was added to an aqueous solution containing dopamine of difference concentrations (0 to 2000 μM, 2 mL). The resulting solution was diluted to 4 mL with the PBS buffer (1.8 mL, pH 7.4), sonicated for 20 min, and

subjected to fluorescence spectroscopy upon excitation at 488 nm and lifetime measurement. Each point was repeated for three times to ensure the reproducibility.

Section 3. Supporting Figures

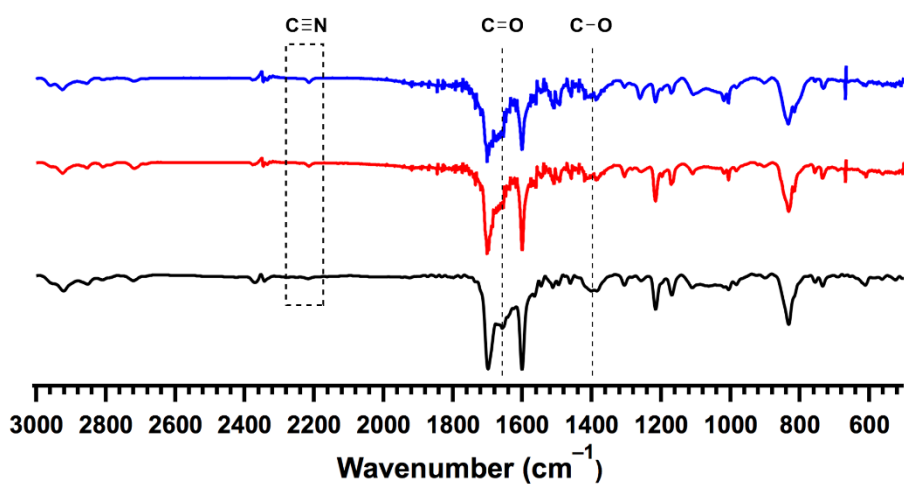


Fig. S1. FTIR spectra of products hydrolyzed in NaOH (black curve), MeONa (red curve), and *t*-BuONa (blue curve), under otherwise same hydrolysis conditions.

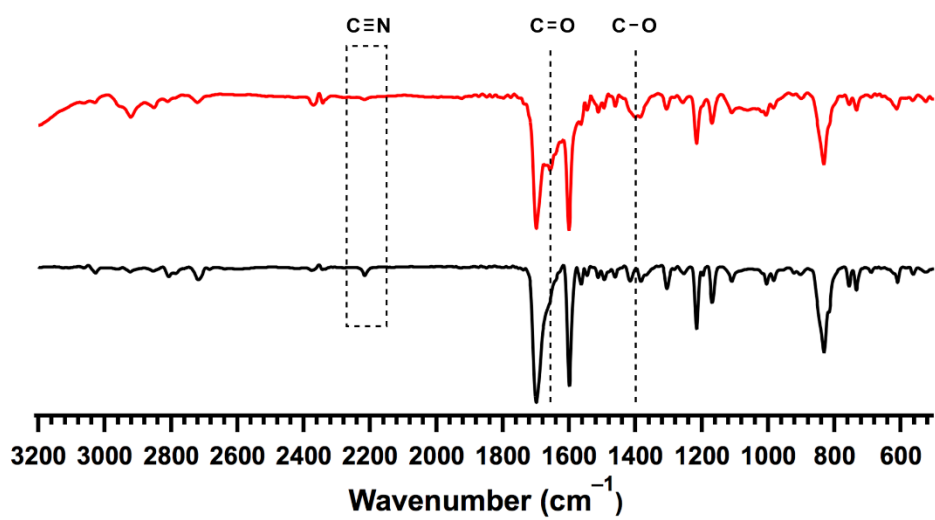


Fig. S2. FT IR spectra of sp²c-COF (black) and [CO₂H]sp²c-COF (red).

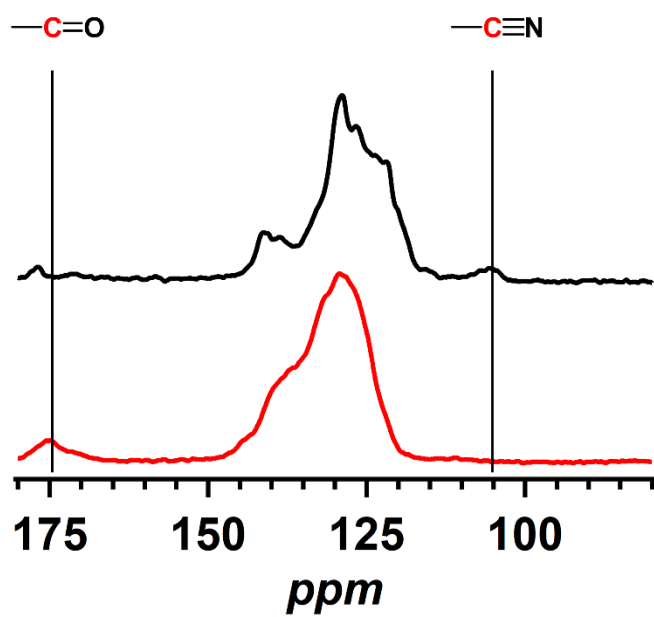


Fig. S3. Solid-state ^{13}C CP/MAS NMR spectra of $\text{sp}^2\text{c-COF}$ (black) and $[\text{CO}_2\text{H}]\text{sp}^2\text{c-COF}$ (red).

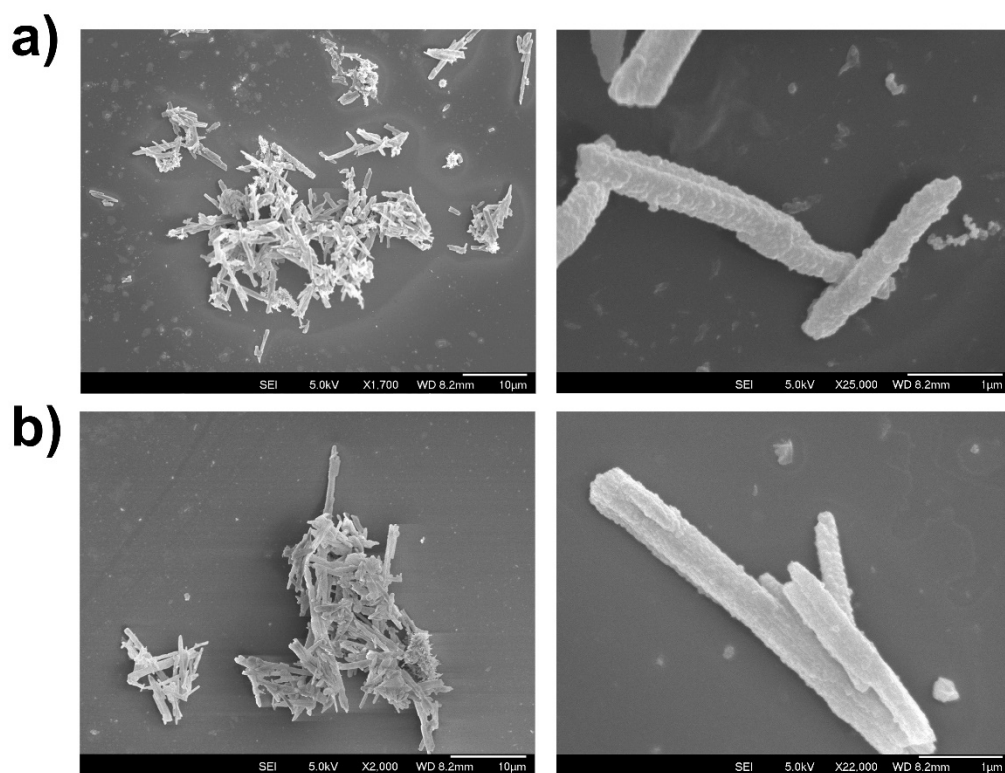


Fig. S4. FE SEM images of (a) sp^2c -COF and (b) $[CO_2H]sp^2c$ -COF.



Fig. S5. Dispersion of [CO₂H]sp²c-COF sample (0.5 mg/mL in buffer solution) after sonication for 5 mins.

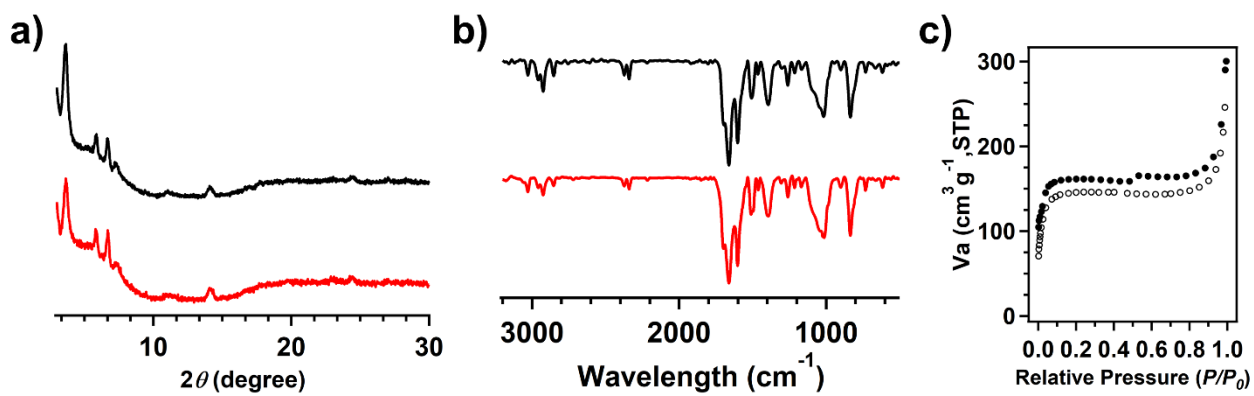


Fig. S6. (a) PXRD patterns of $[\text{CO}_2\text{H}]\text{sp}^2\text{c-COF}$ before (black) and after (red) immersed in acid solution ($\text{pH} = 1$) for 5 days. (b) FTIR spectra of $[\text{CO}_2\text{H}]\text{sp}^2\text{c-COF}$ before (black) and after (red) immersed in acid solution ($\text{pH} = 1$) for 5 days. (c) N_2 sorption spectra of $[\text{CO}_2\text{H}]\text{sp}^2\text{c-COF}$ after immersed in acid solution ($\text{pH} = 1$) for 5 days.

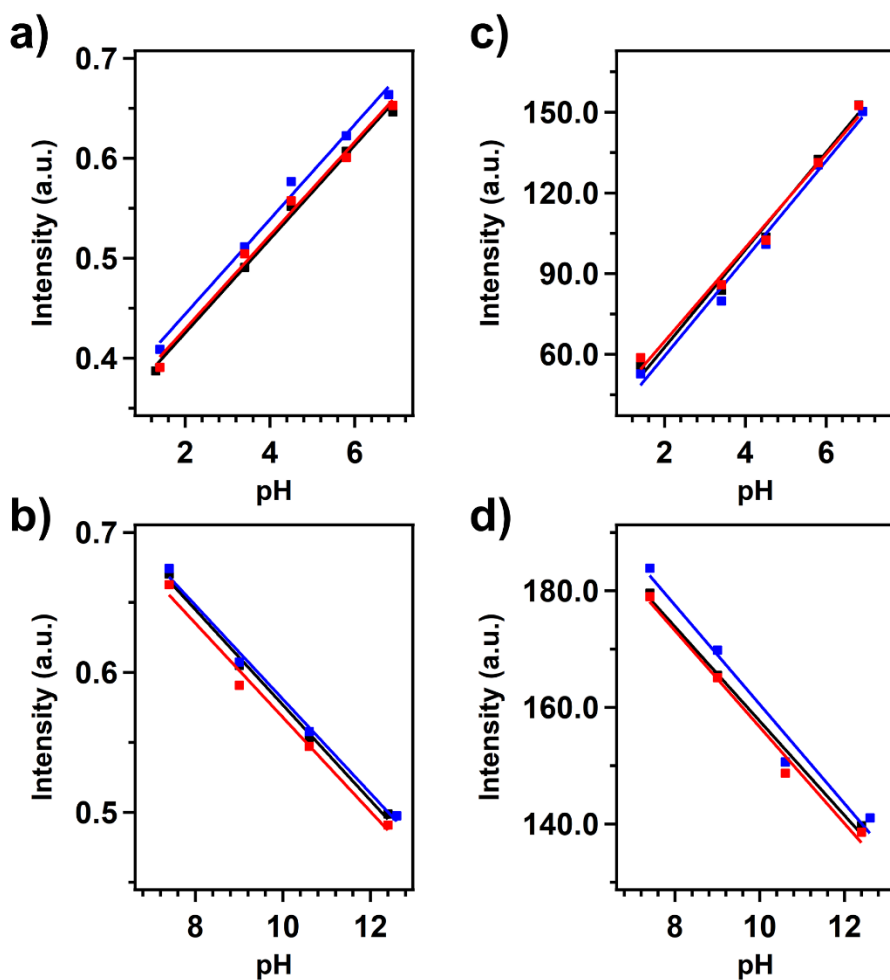


Fig. S7. (a, b) Plot of absorbance versus pH value in acidic (a) and (b) region of [CO₂H]sp²c-COF in the first (black), second (blue) and third (red) cycles. (c, d) Plot of emission intensity versus pH value in acidic (a) and (b) region of [CO₂H]sp²c-COF in the first (black), second (blue) and third (red) cycles.

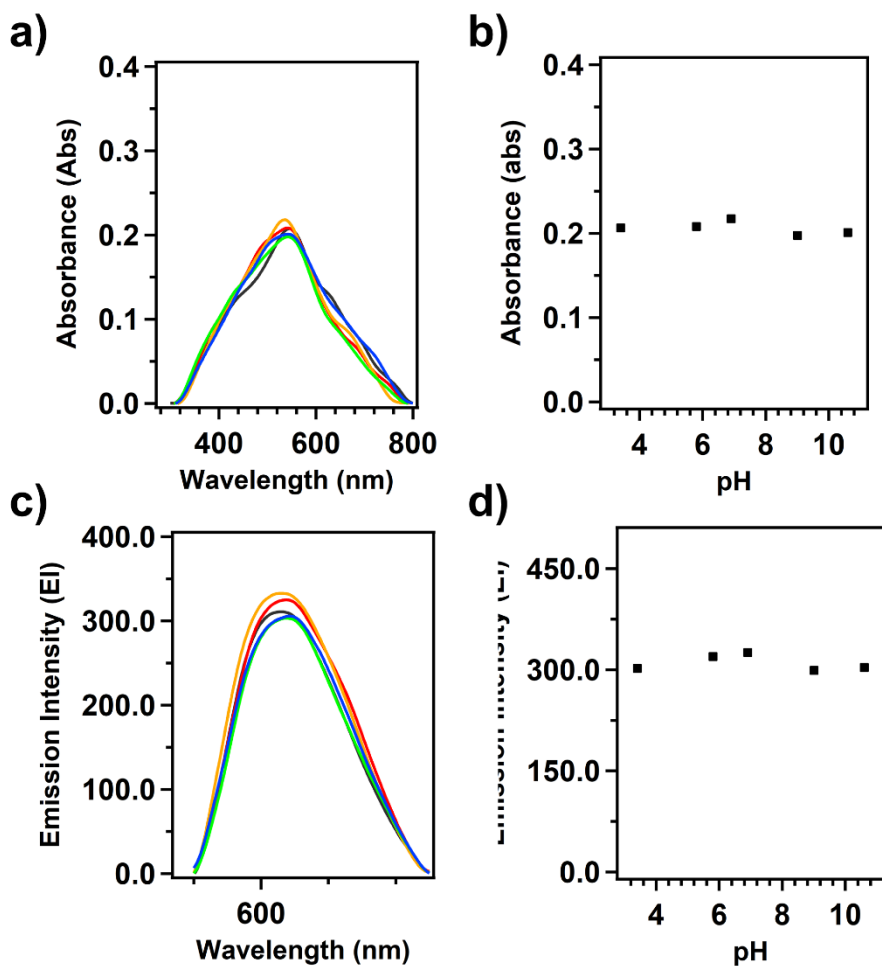


Fig. S8. (a) Absorption spectral change of sp²c-COF at different pH values (black: pH = 1.4; red: pH = 3.4; orange: pH = 5.8; green: pH = 6.8; blue: pH = 9.0; purple: pH = 10.6; pink-red: pH = 12.4). (b) Plot of absorbance versus pH value. (c) Fluorescence spectral change of sp²c-COF at different pH values (black: pH = 1.4; red: pH = 3.4; orange: pH = 5.8; green: pH = 6.8; blue: pH = 9.0; purple: pH = 10.6; pink-red: pH = 12.4). (d) Plot of emission intensity versus pH value.

Section 4. Supporting Table

Table S1. Comparison of dopamine sensing.

Sensors	Time required (min)	Detection limit (nM)	Sample	Recovery (%)	Ref.
[CO ₂ H]sp ² c-COF	20	260	-	-	This work
ECP nanoflakes	5	21	Human serum	90-99	3
C2-F127 organic nanoparticles	90	35	-	-	4
Fe ₃ O ₄ @SiO ₂ -NH-EDTATb(III)	-	820	Human serum	97 - 101	5
Silicon nanoparticles	180	0.3	-	-	6
Abtz-CdI ₂ -MOF	50	57	Urine	94.5 - 102	7
MoS ₂ QDNS	5	0.9	Human blood	88 - 104	8
Eu-MOF	1	15	Human serum	102 - 114	9
NaGdF ₄ :Tb Nanoparticles	5	33	Serum, urine	79 - 90	10
GEAB _{DA1m}	Real-time	130	<i>In vivo</i>	-	11
GRAB _{DA1h}		10		-	

Section 5. Supporting References

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