

**Excited-state intramolecular proton transfer based covalent organic  
framework for fluorescence anions sensing**

Zhitao Wang,<sup>ab\*</sup> Yanju Huang,<sup>a</sup> Shuang Wu,<sup>c</sup> Xiu-Mei Li,<sup>a</sup> and Qikun Sun<sup>d\*</sup>

## **Methods**

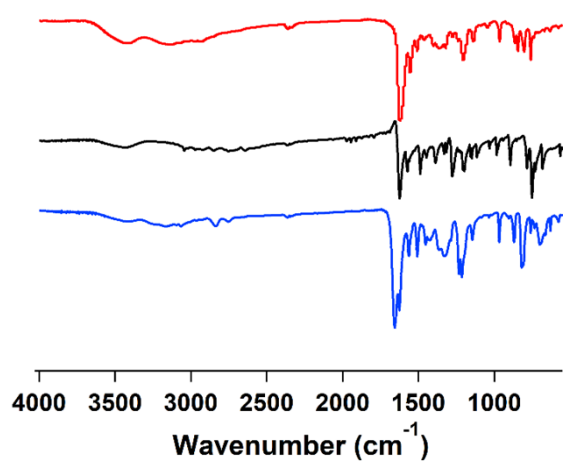
The infrared spectra were recorded from 600 to 3500  $\text{cm}^{-1}$  on an Avatar FT-IR 360 spectrometer. Elemental analyses were measured by an Elementar model vario EL cube analyzer. Powder X-ray diffraction data were performed on a XRD (Ultima IV) diffractometer by depositing powder on glass substrate, from  $2\theta = 3.0^\circ$  to  $35^\circ$  with  $0.02^\circ$ . Field emission scanning electron microscopy and energy dispersive spectroscopy for elemental mapping were recorded on a SU8020 model HITACHI microscope. Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimeter with the heating at a rate of  $10^\circ\text{C min}^{-1}$  from room temperature to  $800^\circ\text{C}$  under nitrogen atmosphere. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F analyzer.

### **Fluorescence measurement**

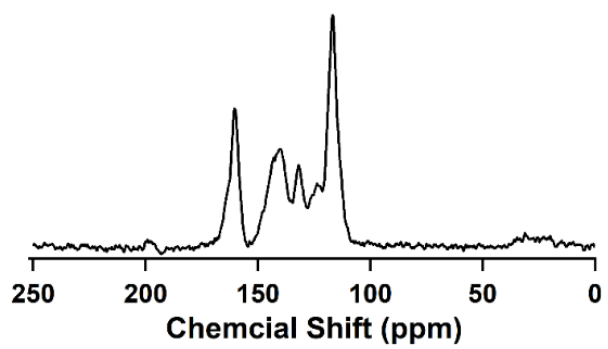
ACOF samples (2 mg) were dispersed in tetrahydrofuran (50 mL), which was sonicated for several mins to give a relatively homogeneous dispersion. The mixture containing 3 mL ACOF in THF with F anions was subjected to fluorescence spectroscopy. The time-dependent fluorescence spectra were recorded. The fluorescence intensity was fixed around 10 mins.

### **Recycle porosity measurement**

We used ACOF 50 mg in THF 2.5 L were added tetrabutylamine fluoride in THF. After 10 mins, the trifluoroacetic acid was added into the mixture. This process operated for 3 times. Finally, the samples were filtered, washed by THF and water, and dried under vacuum.



**Fig. S1.** FT-IR spectra of ACOF (red), 5'-(4-formyl-3-hydroxyphenyl)-3,3''-dihydroxy-[1,1':3',1''-terphenyl]-4,4''dicarbaldehyde (blue), and model compound (black).



**Fig. S2.**  $^{13}\text{C}$  NMR spectrum of ACOF

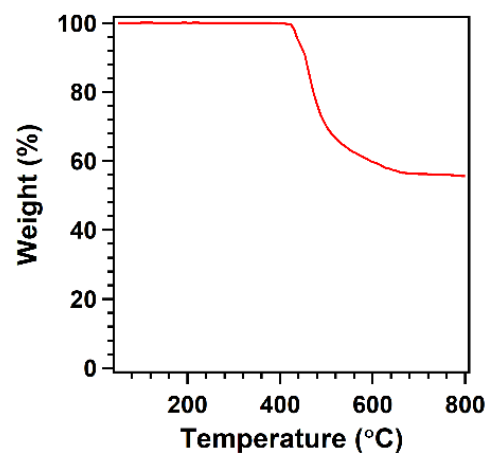
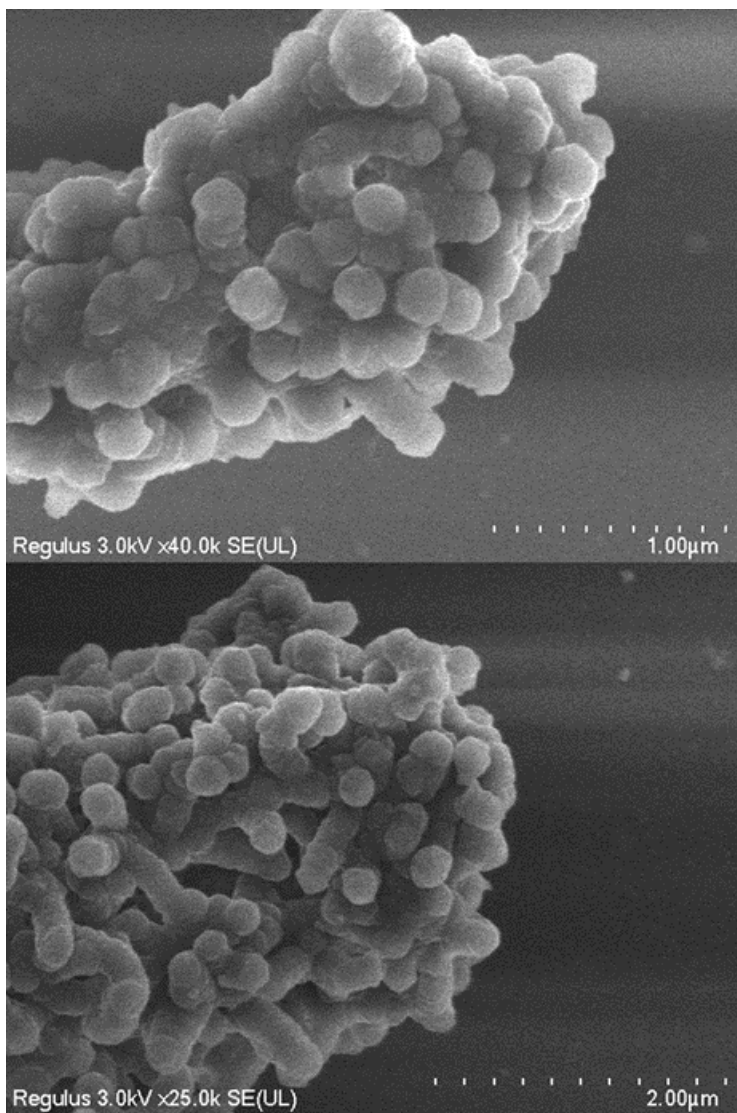
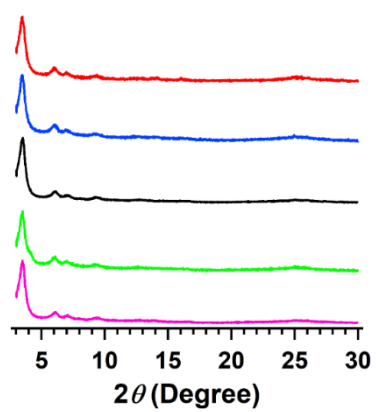


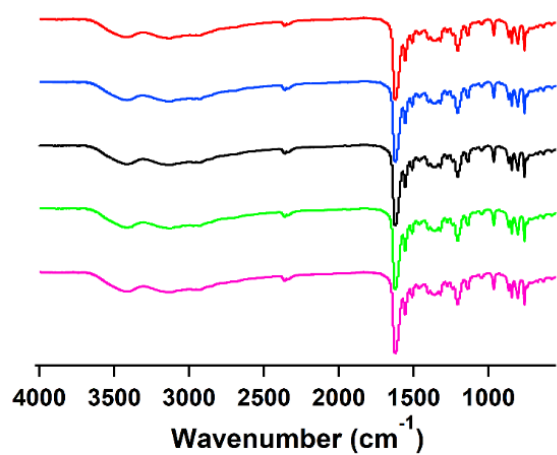
Fig. S3. TGA curve of ACOF



**Fig. S4.** FE SEM images of ACOF

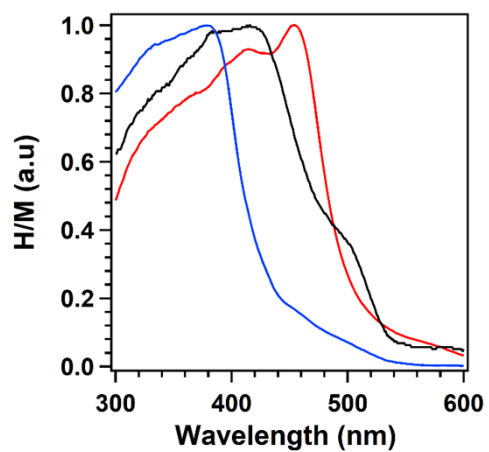


**Fig. S5.** PXRD patterns of ACOF. (As-synthesized: red; water: blue; THF: black; HCl: green; NaOH: purple).

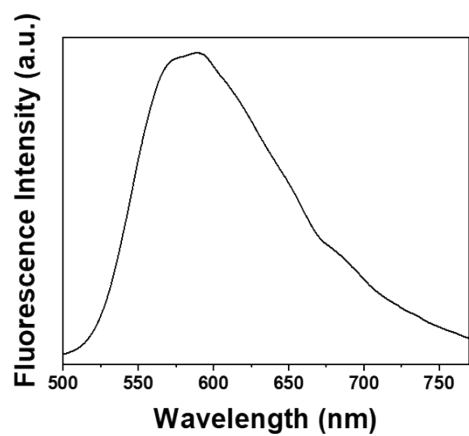


**Fig. S6.** FT-IR spectra of ACOF (As-synthesized: red; water: blue; THF: black; HCl: green; NaOH: purple).

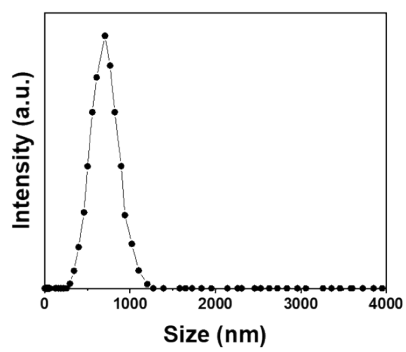




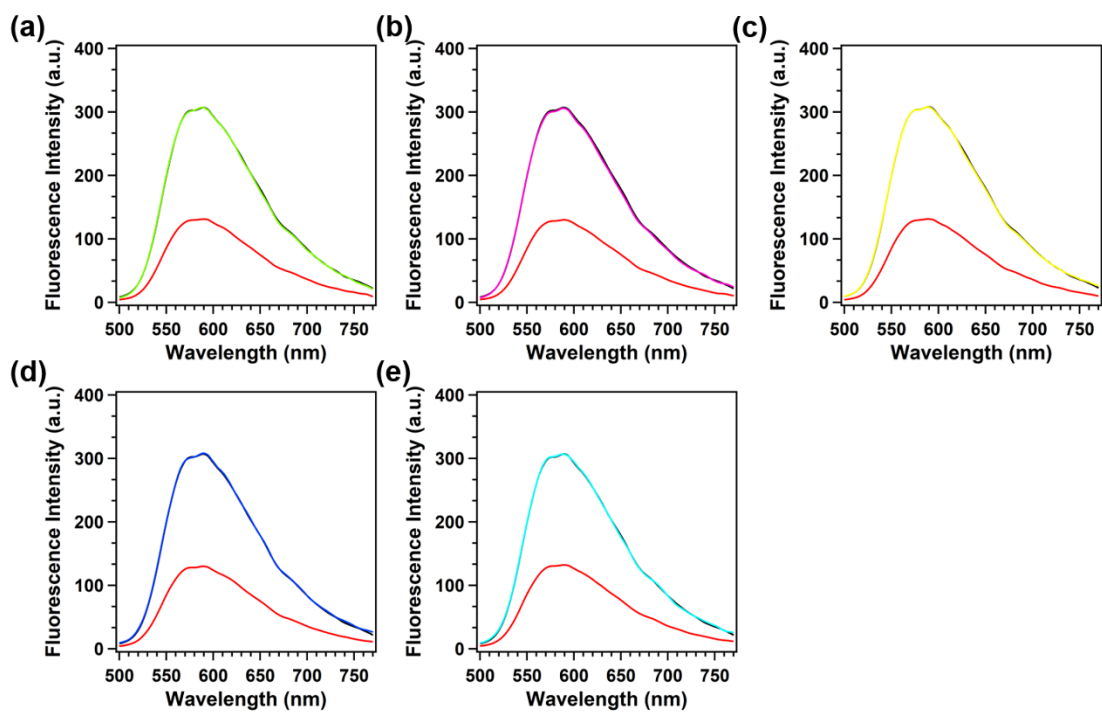
**Fig. S7.** Ultraviolet–visible spectra of ACOF (red), 5'-(4-formyl-3-hydroxyphenyl)-3,3''-dihydroxy-[1,1':3',1''-terphenyl]-4,4''dicarbonyl (blue), and model compound (black).



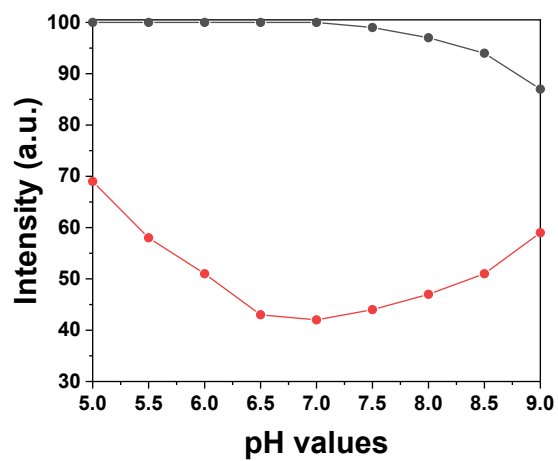
**Fig. S8.** Fluorescence spectrum of ACOF at the solid state.



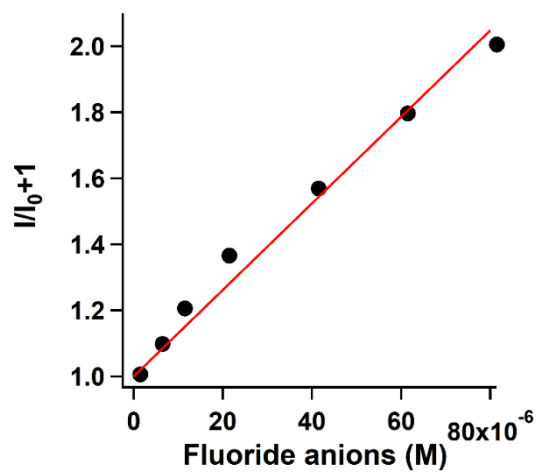
**Fig. S9.** Dynamic light scattering profile of ACOF.



**Fig. S10.** Fluorescence spectra of ACOF@F<sup>-</sup>@anions {(a) Cl<sup>-</sup>, (b) Br<sup>-</sup>, (c) I<sup>-</sup>, (d) NO<sub>3</sub><sup>-</sup>, and (e) PF<sub>6</sub><sup>-</sup>}.



**Fig. S11.** Effect of pH on luminescence intensity of ACOF with fluoride anions.



**Fig. S12.** Plot of PL quenching efficiency ( $I/I_0$ ) as a function of fluoride anions.

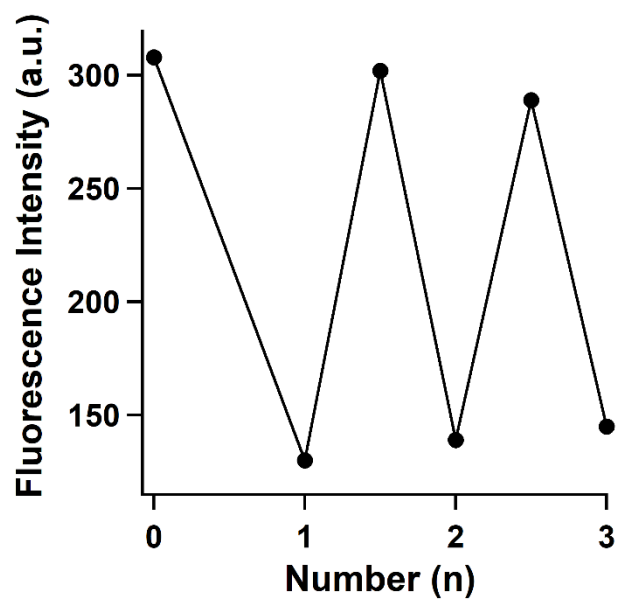


Fig. S13. Fluorescence spectra of ACOF@F<sup>-</sup>@H<sup>+</sup>@F<sup>-</sup>@H<sup>+</sup>@F<sup>-</sup>.

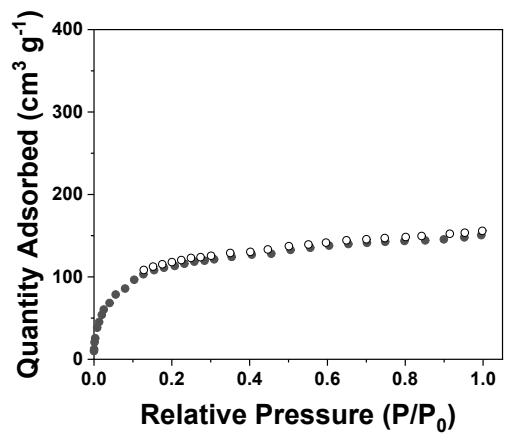


Fig. S14. Nitrogen adsorption-desorption isotherms of recycled-ACOF measured at 77 K (●: adsorption, ○: desorption).



**Tab. S1.** The detection limit and Ksv values of the reported porous organic polymers.

	Detection limit	Ksv	Ref.
ACOF	2.5 $\mu$ M	$1.2 \times 10^4 \text{ M}^{-1}$	This work
DATGCl-iCONs	5 ppb	$2.25 \times 10^3 \text{ M}^{-1}$	<i>ACS Appl. Mater. Interfaces</i> 2020, <b>12</b> , ,13248–13255.
CMP-A	141 nM	$1 \times 10^4 \text{ M}^{-1}$	<i>Mater. Chem. Front.</i> , 2020, <b>4</b> , 3040–3046.
CMP-B	272 nM	$1 \times 10^4 \text{ M}^{-1}$	
TFPPy-DETHz-COF	50.5 ppb	...	<i>J. Am. Chem. Soc.</i> , 2018, <b>140</b> , 12374–12377
BCMP-3	...	...	<i>Chem. Eur. J.</i> , 2015, <b>21</b> , 17355–17362.
BN-ph-ac	...	...	<i>J. Mater. Chem. A</i> , 2013, <b>1</b> , 13878–13884.