

## **Robust and emissive covalent organic frameworks via intramolecular hydrogen bond interaction**

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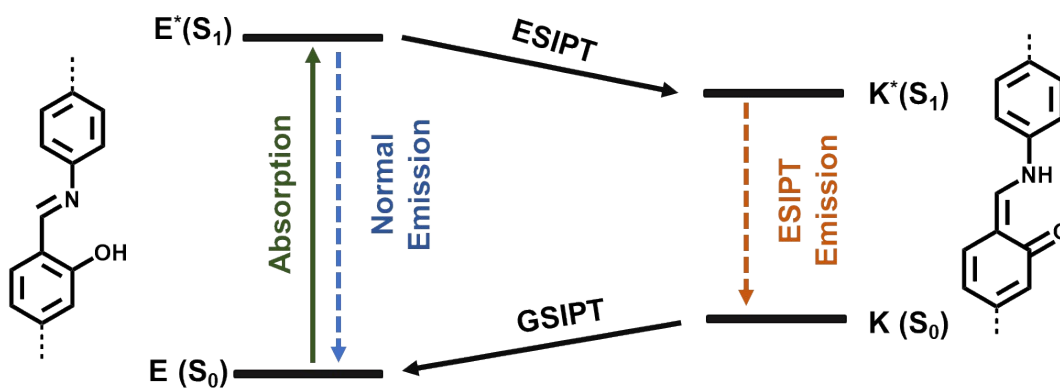
## **Experimental**

### **Materials**

Acetic acid, tetrahydrofuran, n-butanol, o-DCB, DMF, 2,4,6-trinitrophenol, and other chemicals were obtained from J&K Scientific company, TCI, Wako, and Sigma-Aldrich.

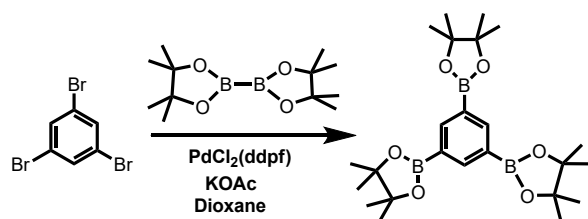
### **Material Characterization**

Recording Fourier Transform Infrared (FT-IR) Spectrum with FT-IR Frontier Infrared Spectrometer with Perkin-Elmer Model. For all FT-IR tests, a small amount of sample can be directly mixed with potassium bromide and ground into a powder, compressed, Photoluminescence spectra were recorded on JASCO model FP-8600 spectrofluorometer. The absolute quantum yield was determined by standard procedure with an integral sphere JASCO model ISF-834 mounted on the FP-8600 spectrofluorometer. Elemental analysis (C, H, and N) was performed on a Euro Vector EA3000 elemental analyzer. Solid-state  $^{13}\text{C}$  CP/MAS NMR measurements were recorded using a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. The samples were prepared for SEM by drop-casting a tetrahydrofuran suspension onto mica substrate and then coated with gold. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from  $2\theta = 1.5^\circ$  up to  $60^\circ$  with  $0.02^\circ$  increment. TGA analysis was carried out using a Q5000IR analyser (TA Instruments) with an automated vertical overhead thermobalance. Before measurement, the samples were heated at a rate of  $5^\circ\text{C min}^{-1}$  under a nitrogen atmosphere. Nitrogen sorption isotherms were measured at 77 K with ASIQ (iQ-2) volumetric adsorption analyzer. Before measurement, the samples were degassed in vacuum at  $150^\circ\text{C}$  for more than 10h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution.



**Scheme S1.** Excited-state intramolecular proton transfer strategy.

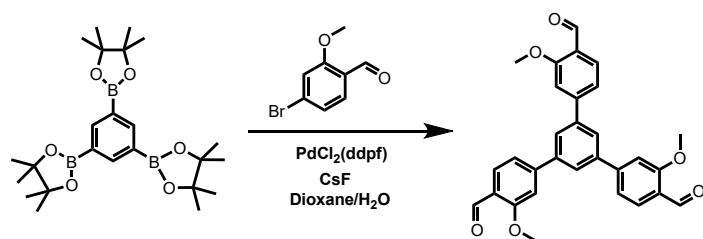
## Synthetic procedures



**Scheme S2.** Synthesis route of 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene.

### 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene <sup>[S1]</sup>

1,3,5-Tribromobenzene (7.87 g, 25.0 mmol), bis(pinacolato)diboron (0.34 g, 0.48 mmol, 4 % equiv.) KOAc (8.10 g, 82.5 mmol) and bis(triphenylphosphine)palladium(II) dichloride (1.75 g, 2.50 mmol) were mixed with degassed dioxane (150 mL) in a 500 mL flask. The flask was cooled to  $-78^{\circ}\text{C}$  and subjected to three freeze-pump-thaw cycles. After the reaction warmed to room temperature, and the reaction mixture was stirred at  $120^{\circ}\text{C}$  for 24 h. After the mixture was cooled at r.t., raw products were collected by filtration, dried under reduced pressure, and recrystallized from EtOAc to lead to a white powder (7.15 g, Yield: 63 %).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta = 8.36$  (s, 3H), 1.33 (s, 36H).

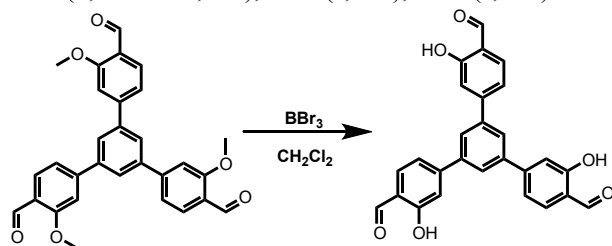


**Scheme S3.** Synthesis route of 1,3,5-Tris(4-formyl-3-methoxyphenyl)benzene.

### 1,3,5-Tris(4-formyl-3-methoxyphenyl)benzene <sup>[S2]</sup>

In a Schlenk flask were added 4-bromo-2-methoxybenzaldehyde (3.9 g, 18.0 mmol) and compound 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2.5 g, 5.0 mmol) followed by vacuum and argon refill three times. In a separate container, cesium fluoride (7.5 g, 50 mmol) was dissolved in 70 mL of argon-sparged deionized water, and this was added to the Schlenk flask followed by  $\text{PdCl}_2(\text{dppf})$  (0.32 g, 0.4 mmol) and 60 mL of dioxane. The mixture was stirred at  $90^{\circ}\text{C}$  for 3 h, and the mixture was allowed to cool to rt. The reaction mixture was then extracted into chloroform (80 mL) and washed with water (50 mL) three times. The aqueous phase was further extracted three times with chloroform (80 mL), combined with the organic phase, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed with a rotary evaporator. The resulting product was boiled in 50 mL of methanol in an Erlenmeyer flask for 15 min, then allowed to cool to rt, followed by further cooling in a freezer overnight. The solids were recovered by vacuum filtration and dried in a vacuum oven at  $50^{\circ}\text{C}$  for 5 h yielding an off-white powder (1.8 g,

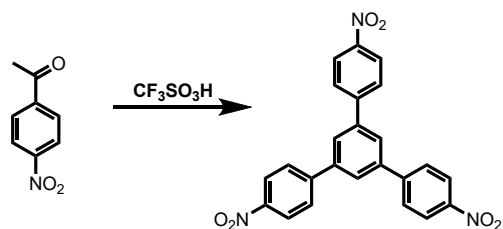
Yield: 68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.51 (s, 3H), 7.95 (d, J = 8 Hz, 3H), 7.80 (s, 3H), 7.33 (d, J = 8 Hz, 3H), 7.21 (s, 3H), 4.02 (s, 9H).



**Scheme S4.** Synthesis route of 1,3,5-tris(4-formyl-3-hydroxyphenyl) benzene.

### 1,3,5-Tris(4-formyl-3-hydroxyphenyl) benzene

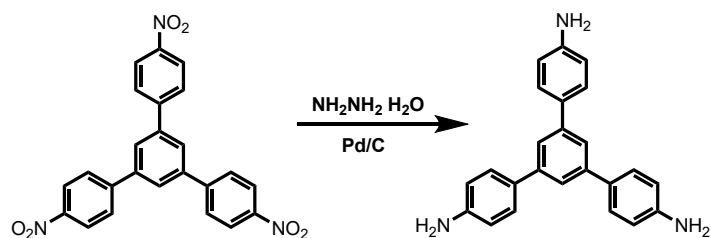
1,3,5-Tris(4-formyl-3-methoxyphenyl)benzene (500 mg, 1.05 mmol) was dissolved in 80 mL of anhydrous nitrogen purged dichloromethane and cooled to  $-78$  °C. Approximately 1 mL of 1 M boron tribromide solution in dichloromethane was added dropwise. The solution stirred at  $-78$  °C for 1 h before being allowed to stir at rt. overnight. Twenty milliliters of methanol were added slowly to the solution. The grayish white product was filtered, washed extensively with methanol, and dried under a vacuum to yield of pure product (0.4g, Yield: 90%). <sup>1</sup>H NMR (400 MHz, DMS-d<sub>6</sub>): δ 10.92(s, 3H), 10.30 (s, 3H), 8.01 (s, 3H), 7.83 (d, J = 8.4 Hz, 3H), 7.54 (d, J = 8 Hz, 3H), 7.46(s, 3H).



**Scheme S5.** Synthesis route of 1,3,5-tris(4-nitrophenyl)benzene.

### 1,3,5-tris(4-nitrophenyl)benzene <sup>[S3]</sup>

4-Nitroacetophenone (10 g, 60 mmol), toluene (40 mL), and CF<sub>3</sub>SO<sub>3</sub>H (1.0 mL) were added to a flask equipped with a water separator and a cooling condenser. The mixture was refluxed for 48 h, during this time the formed water was eliminated as a toluene azeotrope. After being cooled to room temperature, the mixture was filtered and washed with DMF under refluxing to yield a grey-green solid product after drying. This product is insoluble in any common solvent.



**Scheme S6.** Synthesis route of 1,3,5-tris-(4-aminophenyl)benzene.

### **1,3,5-tris-(4-aminophenyl)benzene**

A suspension of 1,3,5-tris(4-nitrophenyl) benzene (3.1g, 7.1 mmol) and Pd/C (5 wt%, 0.5 g) in ethanol (80 mL) was heated to reflux. Hydrazine hydrate (30 mL) was added in portions, and the resulting mixture was refluxed overnight. After that, the mixture was hot filtered through celite and the filtrate was left undisturbed to fully crystallize the product. The solid was collected by filtration and washed with cold ethanol. (2.1 g, Yield 83%). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO): 7.49 (t, 9H, J=5.8 Hz), 6.68 (d, 6H, J=8.4 Hz), 5.21 (s, 6H) ppm.

### **RE-COF-1**

1,3,5-Tris(4-formyl-3-hydroxyphenyl)-benzene (28.2 mg, 0.064 mmol) and 1,3,5-tris(4-aminophenyl)benzene (22.5 mg, 0.064 mmol), o-DCB (0.5 mL), n-butanol (0.5 mL), acetic acid (3 M, 0.2 mL) were added into the system and the mixture was heated about 120 °C for 72 h. After cooling down to room temperature, the sample was filtered, washed by DMF, acetone, and ethanol, Soxhleted by THF for 6 h, and dried in vacuum at 80 °C for 6 h to afford a yellow powder (RE-COF-1, 41.4 mg, Yield: 83%).

### **RE-COF-2**

1,3,5-Tris(4-formyl-3-hydroxyphenyl)-benzene (28.2 mg, 0.064 mmol) and hydrazine hydrate (4.7 uL, 0.096 mmol), o-DCB (0.8 mL), n-butanol (0.2 mL), acetic acid (3 M, 0.2 mL) were added into the system and the mixture was heated about 120 °C for three days. After cooling down to room temperature, the sample was filtered, washed by DMF, acetone, and ethanol, Soxhleted by THF for 6 h, and dried in vacuum at 80 °C for 6 h to afford a yellow powder (RE-COF-2, 31.7 mg, Yield: 84%).

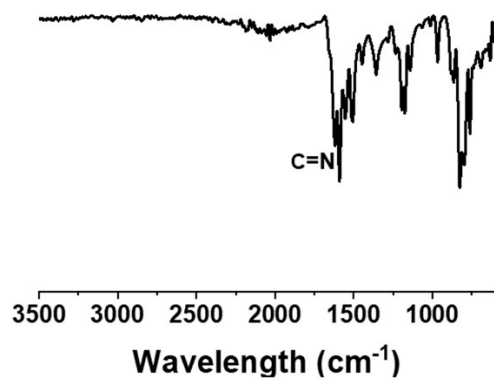
### **Stability measurements**

COF samples were dispersed in water, tetrahydrofuran, aqueous HCl (1 M) and NaOH (1 M) solutions at room temperature for 24 h. The samples were collected by filtration, and washed with THF, water, and acetone. For acid condition, the ammonia water was used to wash for three times. For basic condition, a little acetic acid and large water were used to wash for three times. Finally, the samples were dried under vacuum at 80 °C overnight.

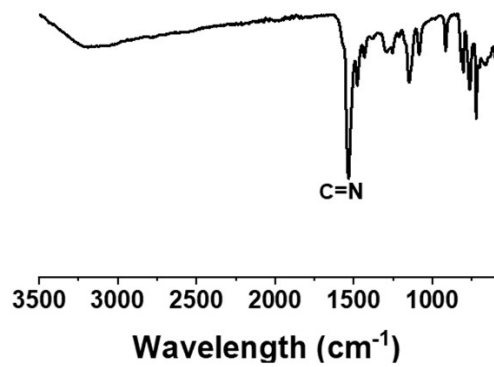
### **Fluorescence experiments**

COF samples were dispersed in tetrahydrofuran to give a homogeneous dispersion which was subjected to fluorescence spectroscopy. After the addition nitrobenzene compound, time-dependent fluorescence spectra were recorded.

(a)

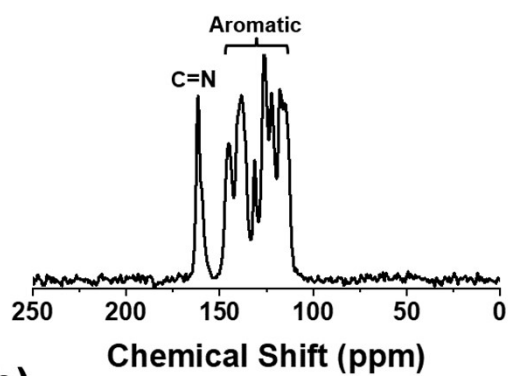


(b)

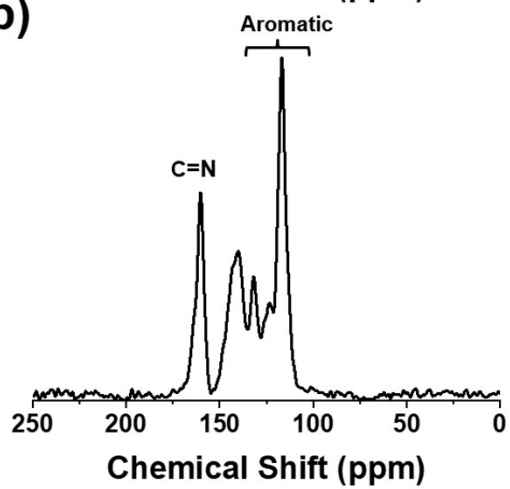


**Fig. S1.** FT-IR spectra of (a) RE-COF-1 and (b) RE-COF-2.

**(a)**

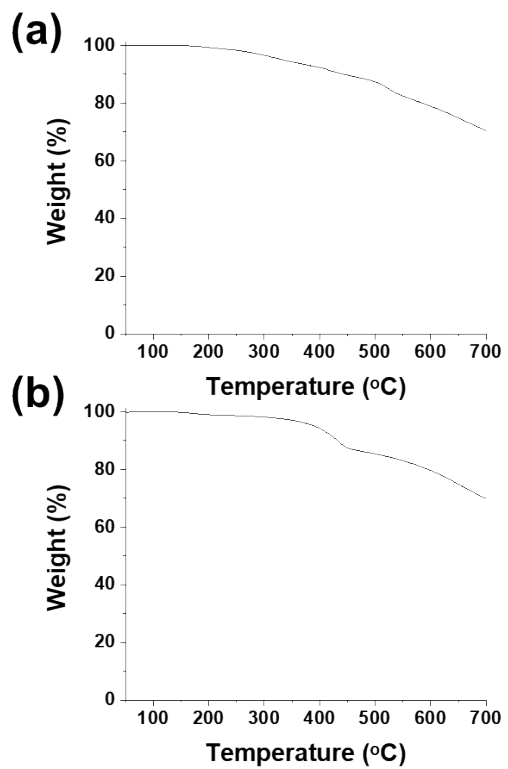


**(b)**

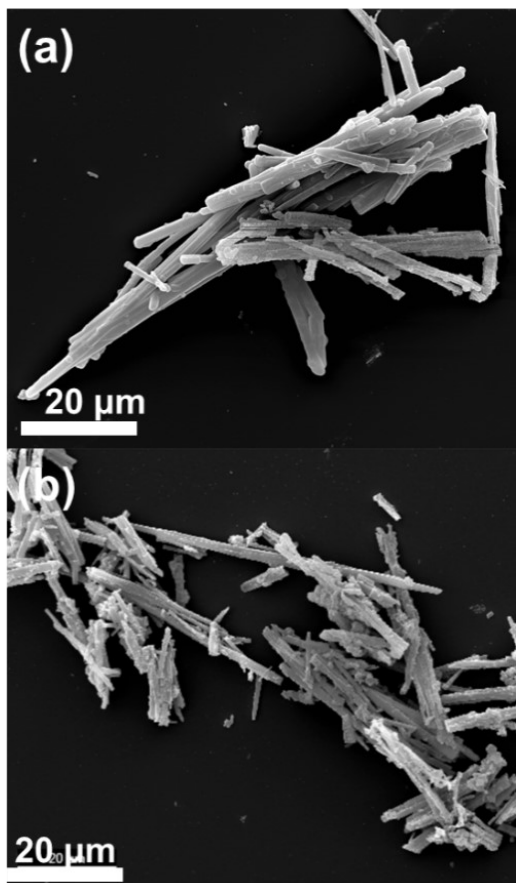


**Fig. S2.** <sup>13</sup>C NMR spectra of (a) RE-COF-1 and (b) RE-COF-2.

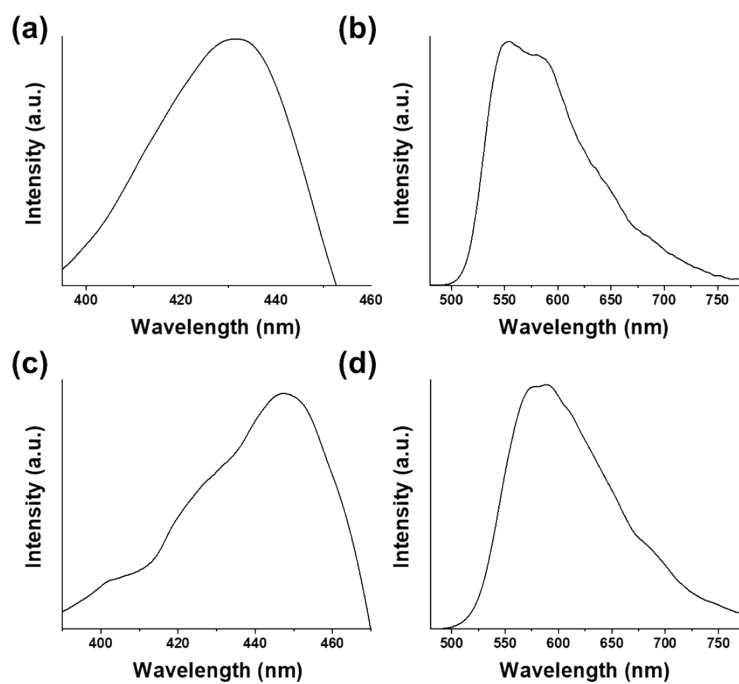




**Fig. S3.** TGA curves of (a) RE-COF-1 and (b) RE-COF-2.

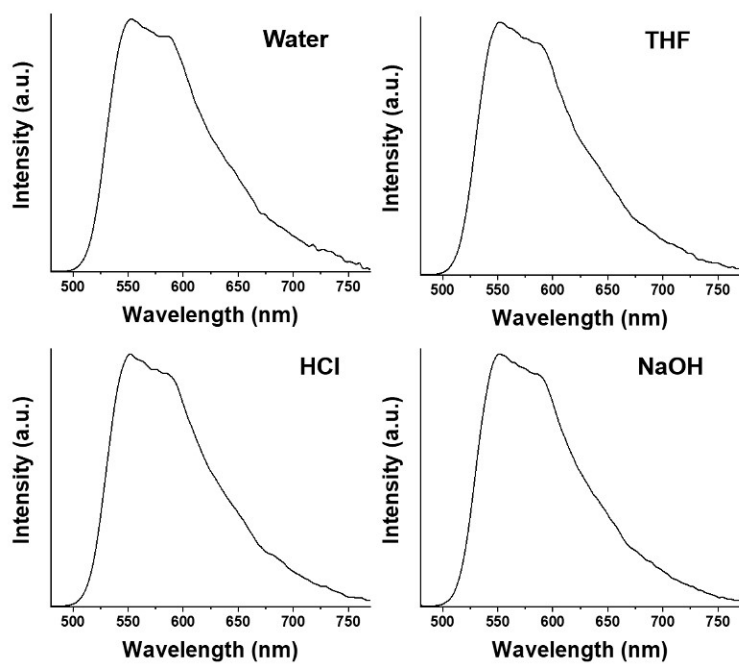


**Fig. S4.** FE SEM images of (a) RE-COF-1 and (b) RE-COF-2.

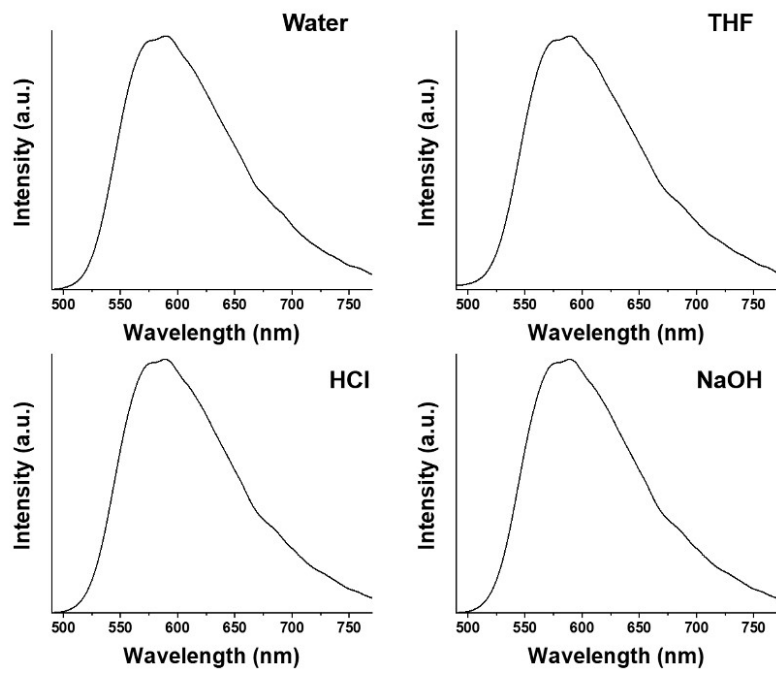


**Fig. S5.** Fluorescence excitation spectra of (a) RE-COF-1 and (c) RE-COF-2 at the solid state.

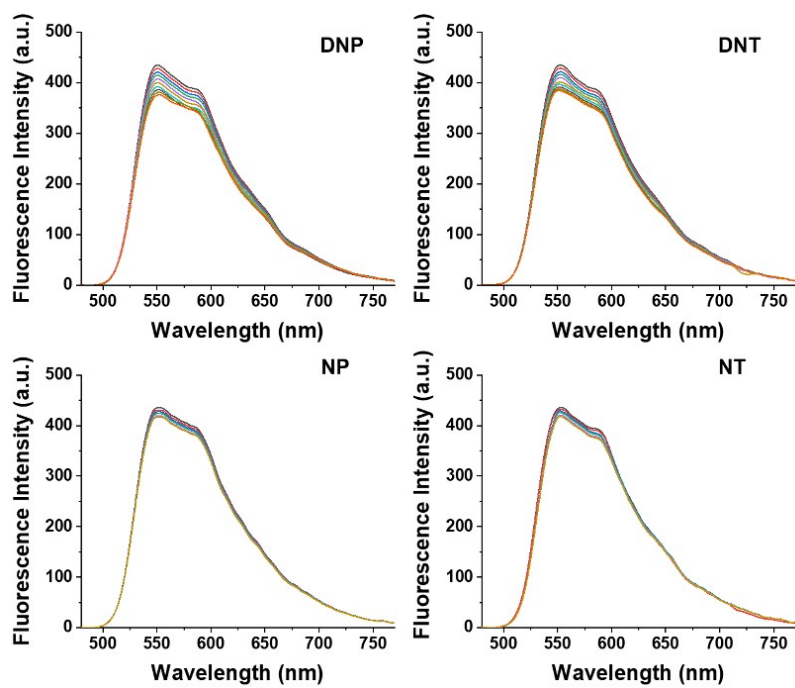
Fluorescence emission spectra of (b) RE-COF-1 and (d) RE-COF-2 at the solid state.



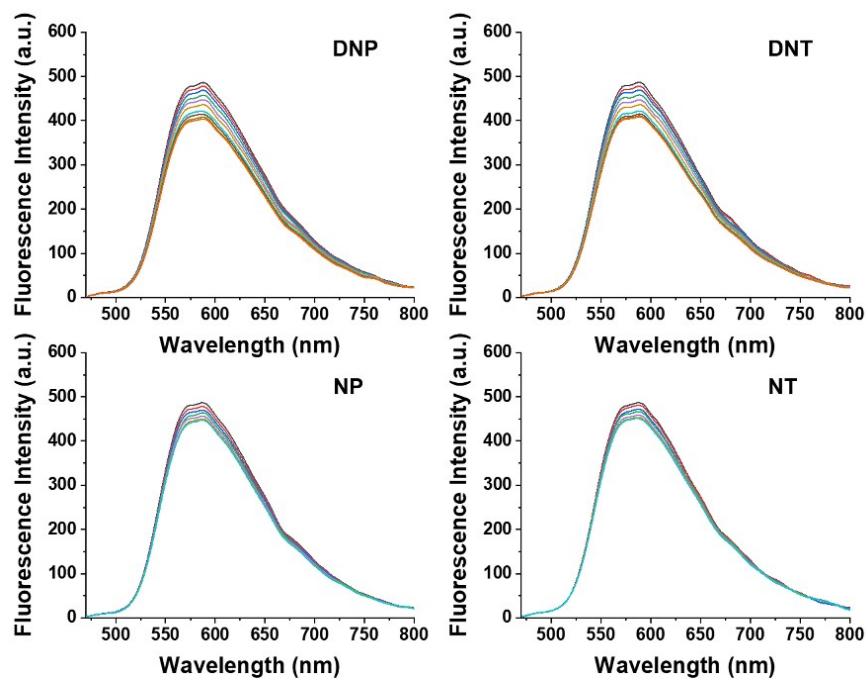
**Fig. S6.** Fluorescent spectra of RE-COF-1 under different conditions.



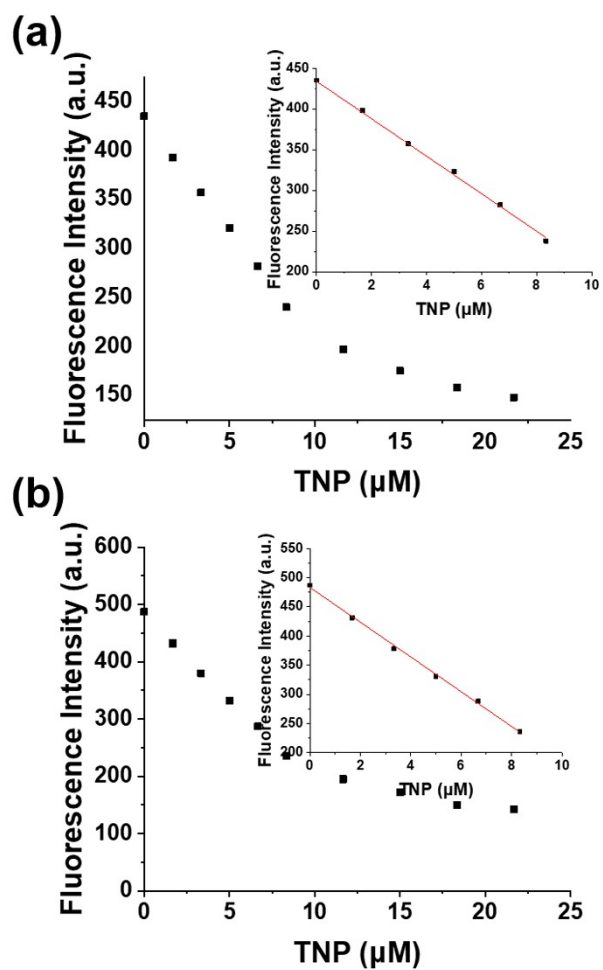
**Fig. S7.** Fluorescent spectra of RE-COF-2 under different conditions.



**Fig. S8.** Fluorescent Sensing of RE-COF-1 for DNP, DNT, NP, and NT. (DNP & DNT: 0, 1.67, 3.33, 5, 6.67, 8.33, 11.67, 15, 18.33, 21.67  $\mu\text{M}$ ; NP & NT: 0, 5, 8.33, 11.67, 18.33, 21.67  $\mu\text{M}$ ).

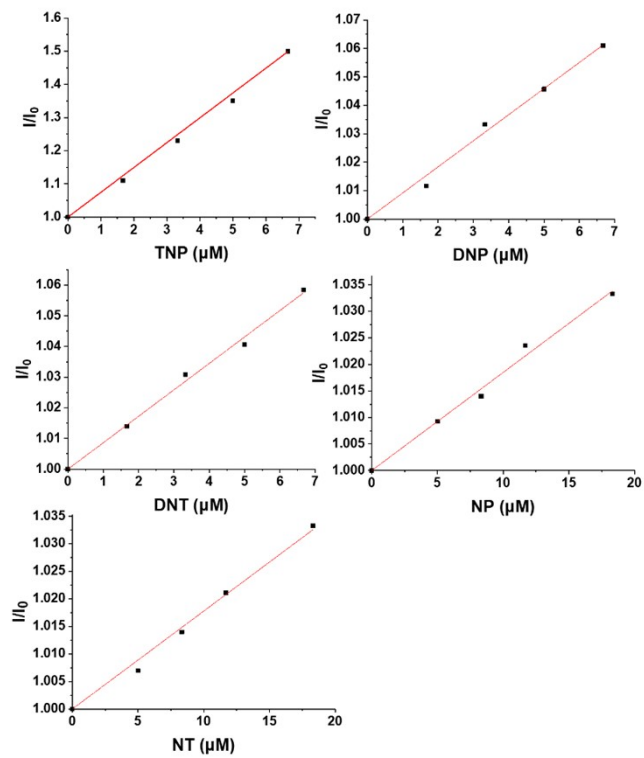


**Fig. S9.** Fluorescent Sensing of RE-COF-2 for DNP, DNT, NP, and NT. (DNP & DNT: 0, 1.67, 3.33, 5, 6.67, 8.33, 11.67, 15, 18.33, 21.67  $\mu\text{M}$ ; NP & NT: 0, 5, 8.33, 11.67, 15, 18.33, 21.67  $\mu\text{M}$ ).

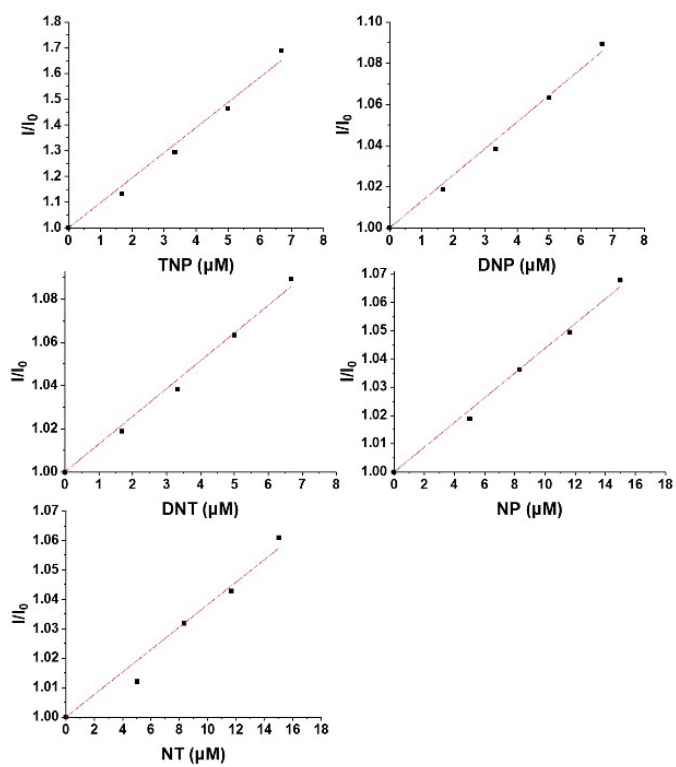


**Fig. S10.** Fluorescent intensity of (a) RE-COF-1 and (b) RE-COF-2 as a function of TNP concentration.





**Fig. S11.** Stern–Volmer plot of relative fluorescence intensity versus of RE-COF-1 for TNP, DNP, DNT, NP, and NT.



**Fig. S12.** Stern–Volmer plot of relative fluorescence intensity versus of RE-COF-2 for TNP, DNP, DNT, NP, and NT.

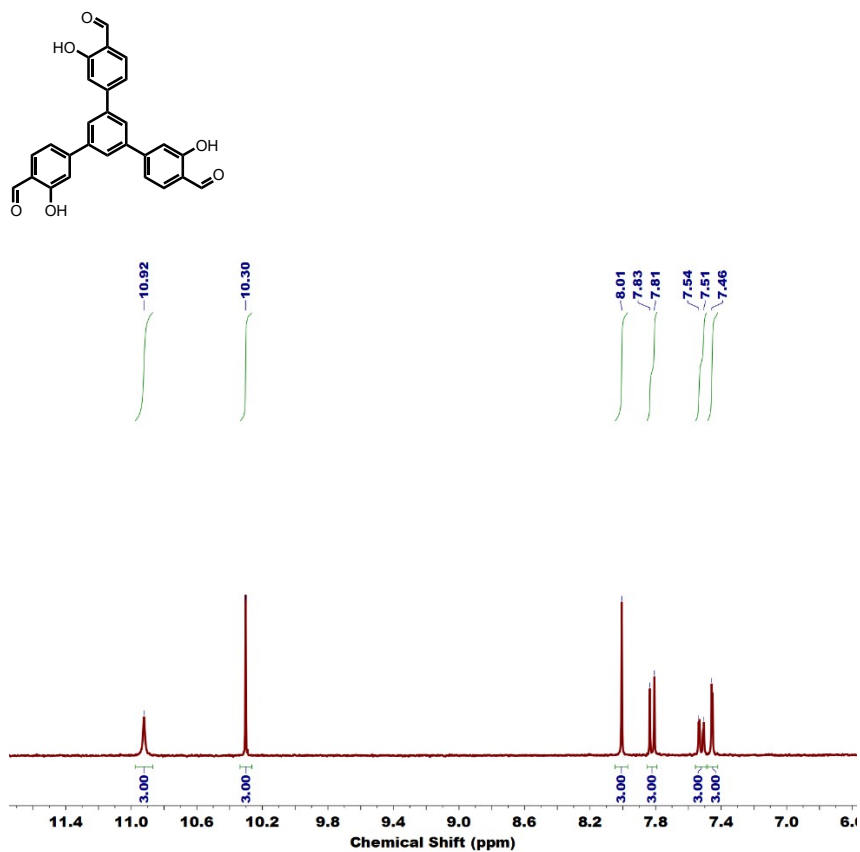


Fig. S13. <sup>1</sup>H NMR spectrum of 1,3,5-Tris(4-formyl-3-hydroxyphenyl)benzene

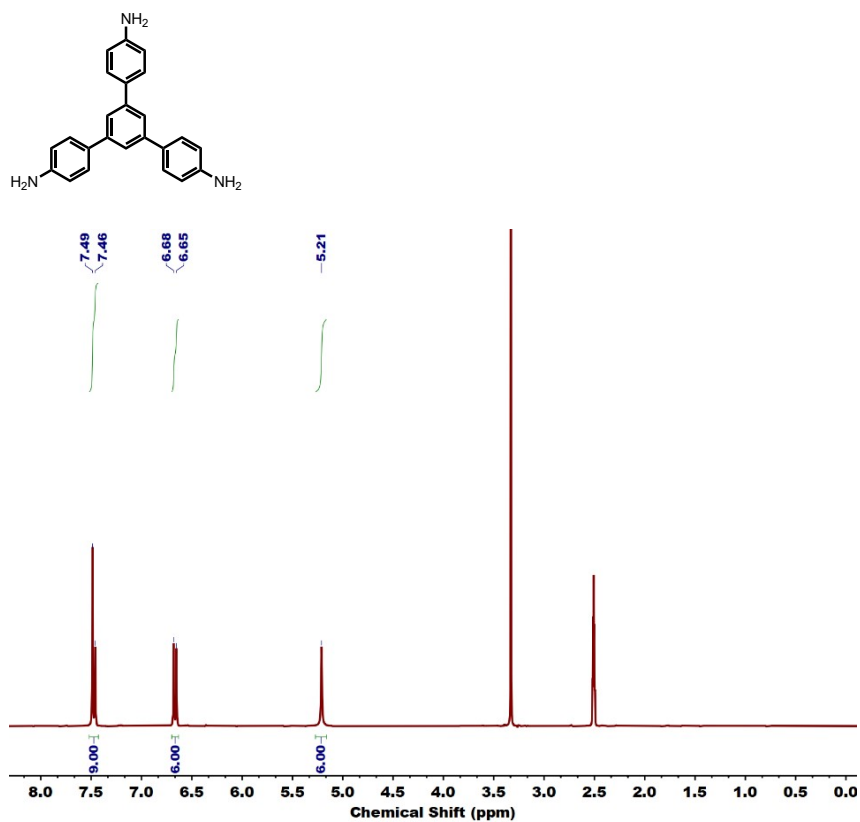


Fig. S14. <sup>1</sup>H NMR spectrum of 1,3,5-tris-(4-aminophenyl)benzene

**Tab. S1.** Elemental analysis of COFs.

		C (%)	H (%)	N (%)
RE-COF-1	Observed	82.35	6.09	5.03
	Calculated	83.11	5.13	5.49
RE-COF-2	Observed	73.79	5.70	9.10
	Calculated	75.15	4.73	9.39

**Tab. S2.** Atomistic coordinates of RE-COF-1.

<b>Space group: P3/M</b>			
<b>a = b = 25.375 Å, c = 3.65 Å,</b>			
<b><math>\alpha = \beta = 90^\circ, \gamma = 120^\circ</math></b>			
<b>Rp = 3.84%, Rwp = 2.98%</b>			
C	0.29629	0.69101	0.33813
C	-0.30100	1.30381	0.90068
C	-0.26962	0.36667	0.89232
C	-0.20565	0.40003	0.84777
C	-0.16856	0.37625	0.95308
C	-0.10809	0.40686	0.89041
C	-0.07989	0.46322	0.72304
C	-0.11563	0.48755	0.62293
C	-0.17617	0.45765	0.68187
N	-0.01825	0.49558	0.64926
C	0.12422	0.49994	0.66934
C	0.18356	0.53337	0.58350
C	0.20680	0.59036	0.41688
C	0.16504	0.60927	0.34247
C	0.10563	0.57566	0.43551
C	0.08331	0.51921	0.60112
C	0.02158	0.48007	0.70842
C	0.27004	0.62842	0.35082
O	0.07023	0.60003	0.36042
H	0.26702	0.71022	0.35676
H	-0.18812	1.33275	1.08935
H	-0.08202	0.38616	0.97720
H	-0.09521	0.53127	0.48872
H	-0.20204	0.47803	0.58496
H	0.10945	0.45690	0.80384
H	0.21337	0.51648	0.66155
H	0.17980	0.65233	0.20842
H	0.01114	0.43752	0.83585
H	0.03428	0.57603	0.48961
H	0.71954	0.44409	0.88765

**Table S3.** Atomistic coordinates of RE-COF-2.

<b>Space group: P6/M</b> <b>a = b = 28.979 Å, c = 3.50 Å,</b> <b><math>\alpha = \beta = 90^\circ, \gamma = 120^\circ</math></b> <b>Rp = 3.78% Rwp = 2.71%.</b>			
H	0.73066	1.43284	0.50000
C	0.68726	0.29904	0.50000
C	0.72136	0.35375	0.50000
C	0.77606	0.37438	0.50000
C	0.79678	0.34037	0.50000
C	0.85150	0.36111	0.50000
C	0.88552	0.41584	0.50000
C	0.86477	0.44985	0.50000
C	0.81006	0.42909	0.50000
C	0.94025	0.43649	0.50000
O	0.89800	0.50352	0.50000
N	0.97372	0.49012	0.50000

**Tab. S4.** Detection Limit and K<sub>SV</sub> value of the reported porous frameworks

	<b>Detection Limit (TNP) nM</b>	<b>K<sub>SV</sub> (TNP) M<sup>-1</sup></b>	<b>Ref.</b>
<b>RE-COF-1</b>	165	$7.48 \times 10^4$	<b>This work</b>
<b>RE-COF-2</b>	128	$9.76 \times 10^4$	
<b>Py-Azine COF</b>	70 ppm	$7.8 \times 10^4$	<i>J. Am. Chem. Soc.</i> , 2013, <b>135</b> , 17310-17313.
<b>TfpBDH-CONs</b>	---	$2.6 \times 10^4$	<i>Chem. Sci.</i> , 2015, <b>6</b> , 3931-3939.
<b>COF-BABD-BZ</b>	1250	$5.7 \times 10^4$	<i>Chem. Commun.</i> , 2018, <b>54</b> , 2308-2311.
<b>3D-Py-COF</b>	---	$3.1 \times 10^4$	<i>J. Am. Chem. Soc.</i> 2016, <b>138</b> , 3302–3305.
<b>DTZ-COF</b>	357	$8.71 \times 10^4$	<i>RSC Adv.</i> , 2019, <b>9</b> , 30937-30942.
<b>TRIPTA</b>	546	$2.7 \times 10^6$	<i>RSC Adv.</i> , 2016, <b>6</b> , 28047-28054.
<b>DTF</b>	722	$2.08 \times 10^3$	<i>Talanta</i> , 2017, <b>165</b> , 282-288.

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**S2.** W. A. Braunecker, K.E. Hurst, K. G. Ray, Z. R. Owczarczyk, M. B. Martinez, N. L., A. Keuhlen, A. Sellinger, J. C. Johnson, *Cryst. Growth Des.* 2018, **18**, 4160-4166.

**S3.** A. Kasprzak, P. A. Guńka, *Dalton Trans.*, 2020, **49**, 6974–6979