Electronic Supplementary Information (ESI)

Hydrazone-linked Covalent Organic Frameworks for Fluorescence Detection of Hg^{2+}

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Experimental Section:

Materials:

Acetic acid (AcOH), 1,2-dichlorobenzene (*o*-DCB), tetrahydrofuran (THF), ethanol, and *N*,*N*-dimethylformamide (DMF) were purchased from Energy Chemical. 2,5-divinylterephthalaldehyde (DvDf) was purchased from Shanghai Haohong scientific Co., Ltd. 5'-(4-(hydrazinecarbonyl)-3-propoxyphenyl)-3,3''-dipropoxy-[1,1':3',1''-terphenyl]-4,4''-dicarbohydrazide (C3XJOPr) was purchased from Yanshen Technology Co., Ltd. All the reagents were used as received. All the solvents were of analytical purity, and used without further purification.

Characterizations:

Attenuated total reflectance Fourier-transform infrared (FT-IR) spectra were acquired on a Nicolet iS50 spectrometer. Nitrogen adsorption and desorption isotherms were measured at 77 K using an ASAP 2020 plus HD88 analyzer. Powder X-ray diffraction (XRD) patterns were recorded with a D8 Advance diffractometer configured for reflection geometry, utilizing a Cu Kα anode (λ = 1.54178 Å) at 30 kV and 40 mA. The thermal stability was evaluated using a TGA-1 thermal gravimetric analyzer (TGA) instrument over the temperature range of 100 to 600 °C under nitrogen atmosphere with a heating rate of 10 °C/min. Specific surface areas (SSAs) and pore size distributions were calculated via the Brunauer-Emmett-Teller (BET) method and density functional theory (DFT) models. Fluorescence excitation and emission spectra were recorded using a Hitachi F-7000 fluorescence spectrometer with a 150 W xenon lamp as the excitation source. The fluorescence lifetimes were measured using an FLS 1000 fluorescence spectrometer with a 450 W xenon lamp as the excitation source and the resolution is 305 fs. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo SCIENTIFIC ESCALAB Xi+ apparatus at a base pressure of 1×10^{-9} bar, and an X-ray source of Al Kα.

Experimental details:

DvDf-C3XJ-COF: A 20 mL pyrex tube was charged with DvDf (16.76 mg, 0.09 mmol), C3XJOPr (39.29mg, 0.06 mmol), 0.1mL of 17 M AcOH, 2 mL of o-DCB. The mixture was sonicated for five minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated at 120℃ for 72 h. After cooling to room temperature, the precipitate was centrifuged and washed constantly with THF until the supernatant was clear. After dried in the vacuum oven at 120℃ overnight, the DvDf-C3XJ-COF COF was synthesized.

Figure S1 -S8:

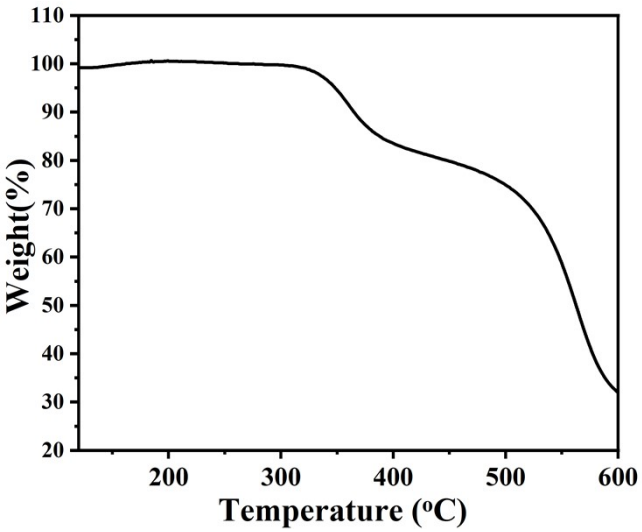

Figure S1. TGA data for DvDf-C3XJ-COF.

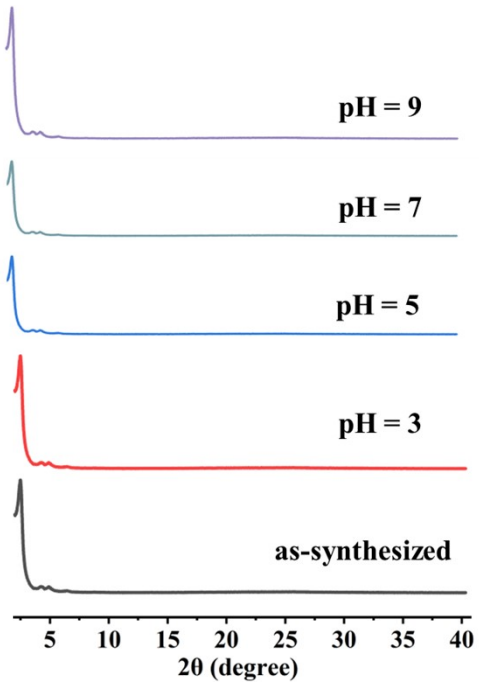

Figure S2. The PXRD patterns of DvDf-C3XJ-COF in aqueous solutions, spanning a pH range from 3 to 9.

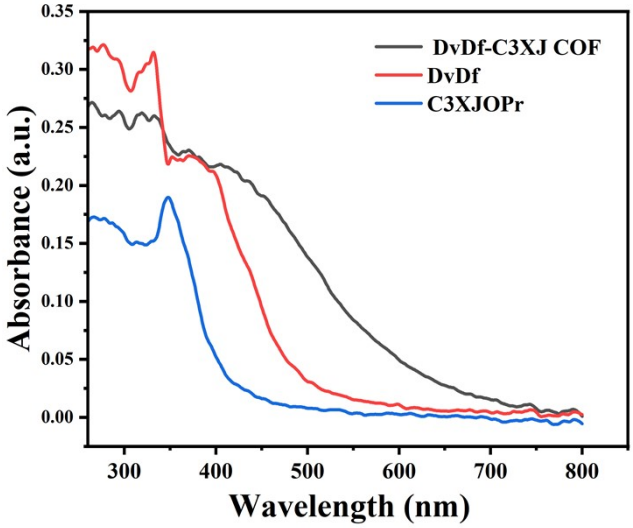

Figure S3. The UV-Vis absorption of DvDf, C3XJOPr, and DvDf-C3XJ-COF.

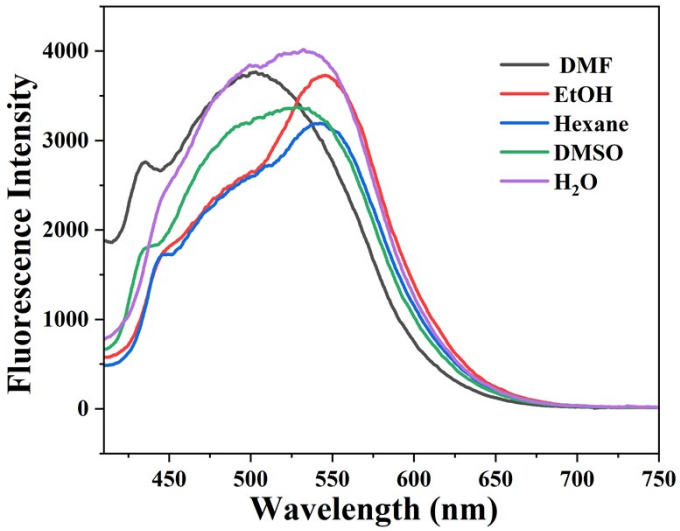

Figure S4. The fluorescence emission spectrum of DvDf-C3XJ-COF dispersed in different solvents.

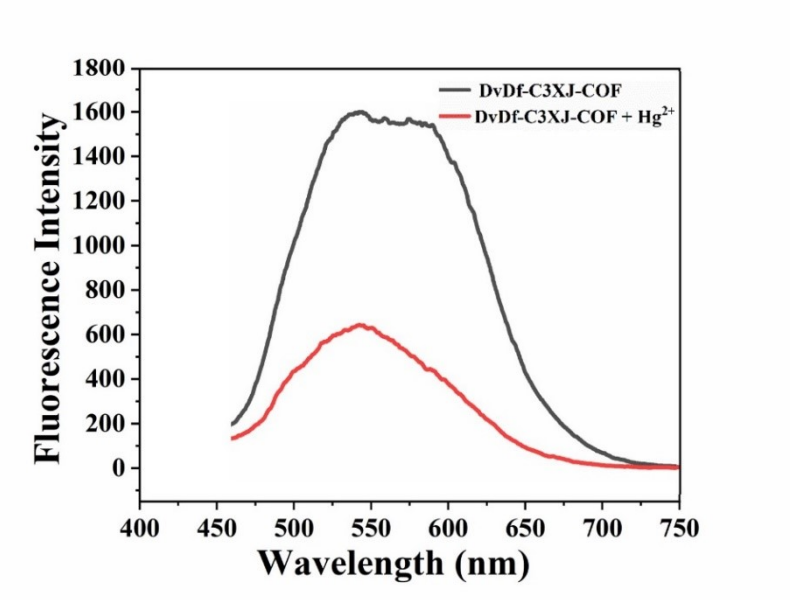

Figure S5. The fluorescence emission spectrum of DvDf-C3XJ-COF dispersed in different solvents.

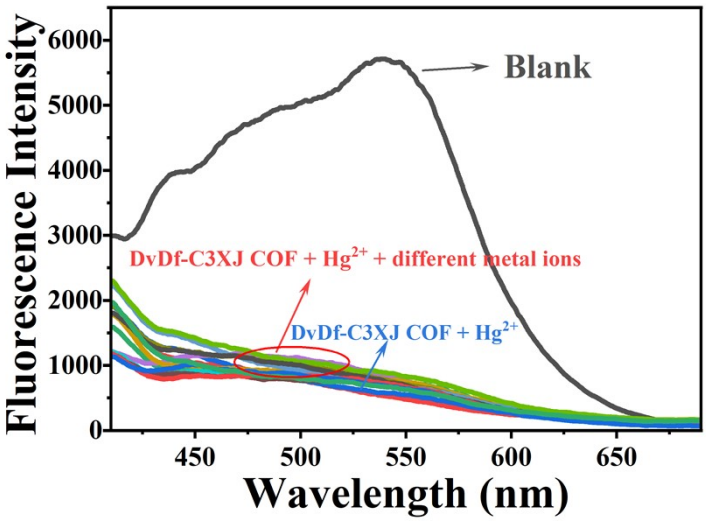

Figure S6. The fluorescence emission spectrum of DvDf-C3XJ-COF, DvDf-C3XJ-COF+Hg^{2+}, and DvDf-C3XJ-COF+Hg^{2+}+ different metal ions.

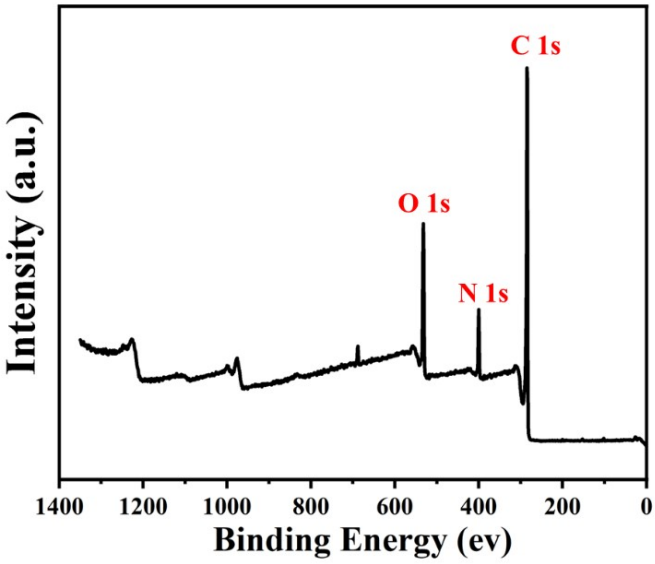

Figure S7. XPS survey spectrum of DvDf-C3XJ-COF.

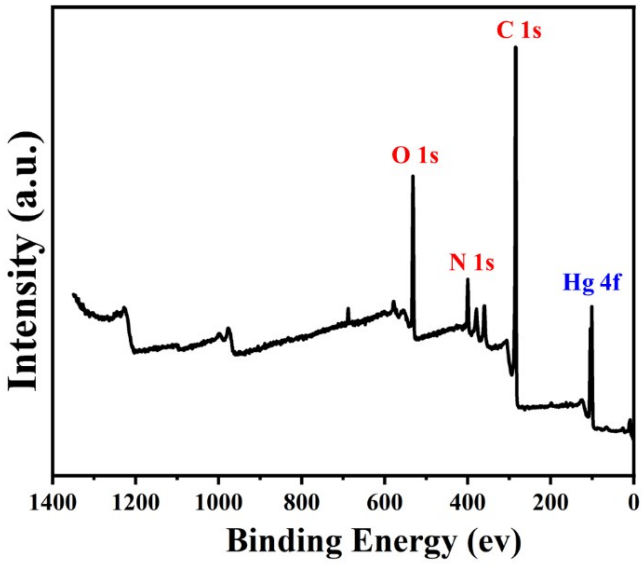

Figure S8. XPS survey spectrum of DvDf-C3XJ-COF+Hg^{2+}.

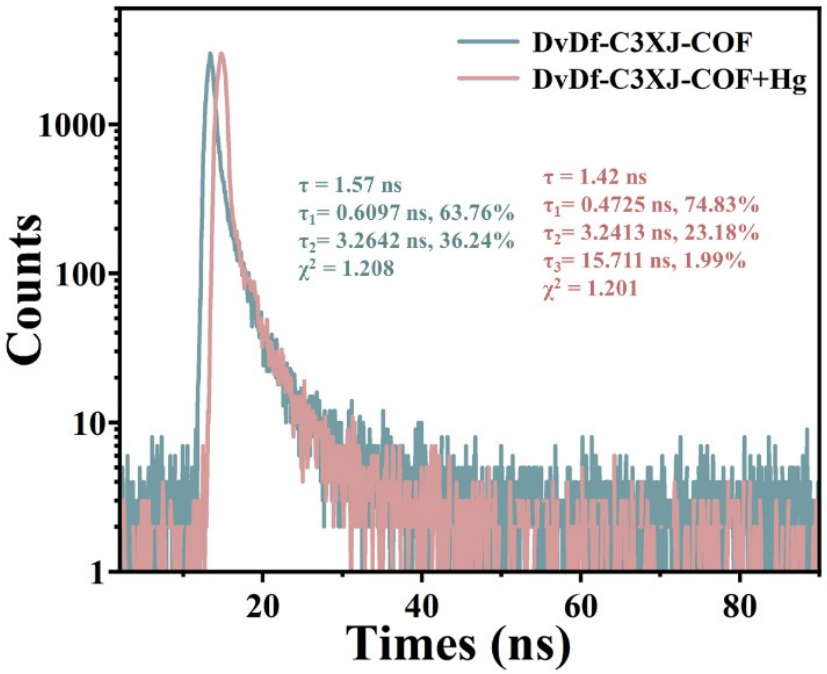

Figure S9. The fluorescence decay spectra of DvDf-C3XJ-COF and DvDf-C3XJ-COF+Hg^{2+} dispersed in EtOH: H_2O=1:1.

Table S1. Fractional atomic coordinates for DvDf-C3XJ-COF: space group *P*6/m; *a* = *b* = 41.99 Å, *c* = 3.53 Å; alpha=beta=90°, gamma=120°

Atom	x(Å)	y(Å)	z(Å)
C1	0.32144	0.69017	0.07092
C2	0.35718	0.7021	0.07092
C3	0.38051	0.73795	0.07092
C4	0.41625	0.74988	0.07092
C5	0.44012	0.78551	0.07092
C6	0.42824	0.80921	0.07092
C7	0.3925	0.79728	0.07092
C8	0.36863	0.76165	0.07092
C9	0.45211	0.84485	0.07092
N10	0.44024	0.86903	0.07092
O11	0.48786	0.85678	0.07092
O12	0.38062	0.82098	0.07092
C13	0.34488	0.80905	0.07092
N14	0.46411	0.90466	0.07092
C15	0.46368	0.98791	0.07092
C16	0.5113	0.97566	0.07092
C17	0.45224	0.92836	0.07092
C18	0.47555	0.96373	0.07092
C19	0.52317	0.95196	0.07092
C20	0.55892	0.96389	0.07092
C21	0.33301	0.83323	0.07092
C22	0.29726	0.82129	0.07092
H23	0.31116	0.71068	0.07092
H24	0.42653	0.72937	0.07092
H25	0.47088	0.79567	0.07092
H26	0.33787	0.75149	0.07092
H27	0.41029	0.85917	0.07092
H28	0.33245	0.79046	0.32866
H29	0.33183	0.79166	-0.19314
H30	0.43293	0.97778	0.07092
H31	0.42145	0.91809	0.07092
H32	0.50266	0.92117	0.07092
H33	0.57066	0.95073	-0.12532
H34	0.57796	0.98733	0.26717
H35	0.34543	0.85182	-0.18681
H36	0.34362	0.85123	0.33498
H37	0.28163	0.79096	0.1525
H38	0.28839	0.82485	-0.2243
H39	0.29097	0.83779	0.28457

Table S2. The comparison of detection limit and linear range between DvDf-C3XJ-COF and other fluorescent probes.

Material	LOD (μM)	Linear range (μM)	References
PET	1.2	0–40	1
AgNPs	2.85	5–30	2
L	0.989	0–20	3
GSH	4.3	0–72	4
COF-Ag	0.0037	0.05–10	5
SH-COF	0.239	0–80	6
TFPPy-CHYD COF	0.017	0–4	7
Bpy-sp2c-COF	0.00242	0–0.02	8
AH-COF	20 ppb	/	9
DvDf-C3XJ-COF	**1.65**	**0–300**	**This work**

References

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