Supporting information for

Dual Functional sp^2 Carbon-Conjugated Covalent Organic Frameworks for Fluorescence Sensing and Effective Removal and Recovery of Pd^{2+} Ions

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1. Supplementary Materials

1.1 Materials

1,3,6,8-tetrakis(4-formylphenyl)pyrene (TFPPY) was purchased from Jilin Chinese Academy of Sciences Yanshen Technology Co., Ltd. $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, $PdBr_2$ and $Pd(OAc)_2$ were purchased from Energy Chemical. The following salts utilized in the experiments: $PdCl_2$, $NaNO_3$, KCl, $AgNO_3$, $ZnCl_2$, $CaCl_2$, $CoCl_2$, $MgCl_2$, $CuCl_2$, $MnCl_2$, $NiCl_2$, $Pb(NO_3)_2$, $CdCl_2$, $SnCl_2$, $HgCl_2$, $AlCl_3$, $CrCl_3$, $FeCl_3$, KNO_3 and NaCl all purchased from Bide Pharmaceutical Technology Co., Ltd. 4-cyanomethylphenylboronic acid was obtained from Bide Pharmaceutical Technology Co., Ltd. Tetrabutylammonium hydroxide was purchased from Macklin Company. All the chemicals involved in this work were utilized with no further purification.

1.2 Instruments

The powder X-ray diffraction (PXRD) characterization was performed on D8 ADVANCE with Cu Kα radiation (λ = 1.5405 Å) with a 2θ range from 2° to 30° at room temperature. Fourier transform infrared (FT-IR) Spectra were recorded on Bruker ALPHA FT-IR Spectrometer ranging from 500 to 4000 cm^{-1}. ^1H NMR spectra were acquired on Bruker Avance 400 MHz NMR spectrometers. Solid-state ^{13}C NMR spectrum was exploited on a Bruker Avance III 400 MHz instrument. Thermogravimetric analysis (TGA) was collected on TGA/SDTA851e in N_2 atmosphere at 10 °C min^{-1} from 30 °C to 1000 °C. Scanning electron microscopy (SEM) images were recorded on a SUB010 instrument. Transmission electron microscopy (TEM) analysis was conducted on Hitachi HT7700 electron microscope. The Brunauer-Emmett-Teller (BET) surface areas were tested on an ASAP 2020/TriStar 3000 (Micromeritics) at 77 K. Ultraviolet-visible (UV-Vis) spectra was

performed on a Hitachi U-4100 spectrophotometer. Fluorescence spectra were collected on with F-4600 FL Spectrophotometer (Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) spectra were obtained from PHI Versaprobe II. Inductively coupled plasma (ICP) measurement was performed on an IRIS Intrepid (II) XSP and NU AttoM spectrometer. The elemental analysis test was performed on the elementar vario el III instrument.

2. Supplementary Experimental Section

2.1 The synthesis of 4,4'-(benzoselenadiazole-4,7-diyl)diacetonitrile (SEA)

4,7-dibromo-2,1,3-benzoselenodiazole (578 mg, 1.7 mmol),[1] 4-cyanomethylphenylboronic acid (820 mg, 5.1 mmol), $Pd(PPh_3)_4$ (250 mg) and sodium carbonate (1.27 g) were put into a 100 mL round bottom flask. 30 mL of tetrahydrofuran (THF) and 6 mL of water were added as solvents and the mixed system was heated to reflux at 85 ℃ in a nitrogen atmosphere for 48 h. After the reaction was completed, 50 mL of water was added into the system. The crude product was extract with dichloromethane (DCM) and purified by silica gel column with DCM as eluent and finally a yellow-green solid with yield about 60% was obtained. ^{1}H NMR (400MHz，$CDCl_3$): δ 7.91 (d, J＝8.2 Hz, 4H), 7.65 (s, 2H), 7.51 (d, J＝8.2 Hz, 4H), 3.86 (s, 4H).

2.2 The stability test of PY-SE-COF

PY-SE-COF was soaked in water, ethanol, dioxane, acetone, DCM, THF, HCl (pH = 2) and NaOH (pH = 12) for 24 h, respectively. After filtered and dried, the crystallinity of PY-SE-COF was rechecked by PXRD.

2.3 The influence of solvent on fluorescence intensity of PY-SE-COF

PY-SE-COF powder was dispersed in different solvent (like DMF, water, THF, DCM, methanol, ethanol, acetone, acetonitrile and DMSO) and the concentration was kept at 0.1 mg mL^{-1}. The fluorescence spectra were collected. Unless otherwise stated, all fluorescence measurements were excited at 420 nm, and the corresponding emission wavelengths were measured between 440 nm and 800 nm.

2.4 The influence of pH on fluorescence intensity of PY-SE-COF

200 μL stock solution of PY-SE-COF (0.1 mg mL^{-1}) was put into a quartz cuvette and diluted to 2 mL with solution with pH = 2, 4, 6, 7, 8 and 10, respectively. Record the fluorescence spectra.

2.5 The fluorescence responses of PY-SE-COF towards different palladium salts

The stock solution of PY-SE-COF (200 μL) and Pd^{2+} solution ($Pd(OAc)_2$, $PdBr_2$, $PdCl_2$, 1 mM, respectively) were put into a quartz cuvette and the mixture were diluted to 2 mL. After incubated for 2 h, the fluorescence spectra were collected.

2.6 The adsorption selectivity

PY-SE-COF (4 mg) was added to beaker containing 100 mL of mixed aqueous solution of $PdCl_2$, $MnCl_2$, $NiCl_2$, $CaCl_2$, $CrCl_3$, $CoCl_2$ and $AlCl_3$ (each concentration was 0.4 mM, pH = 5) . The mixture was stirred at room temperature for 60 min and then was filtered. The solid powder was washed by water and ethanol and then was dried and analyzed by ICP.

3. Supplementary Figures and Tables

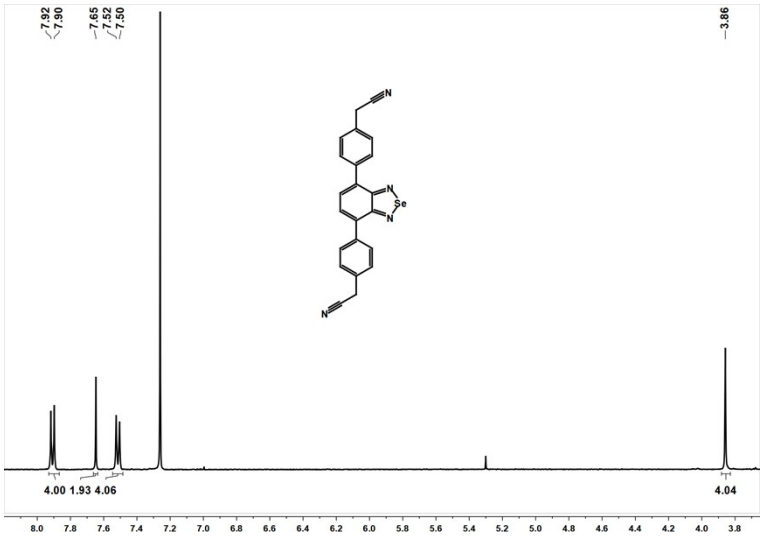


Fig. S1 The ^{1}H NMR spectrum of SEA.

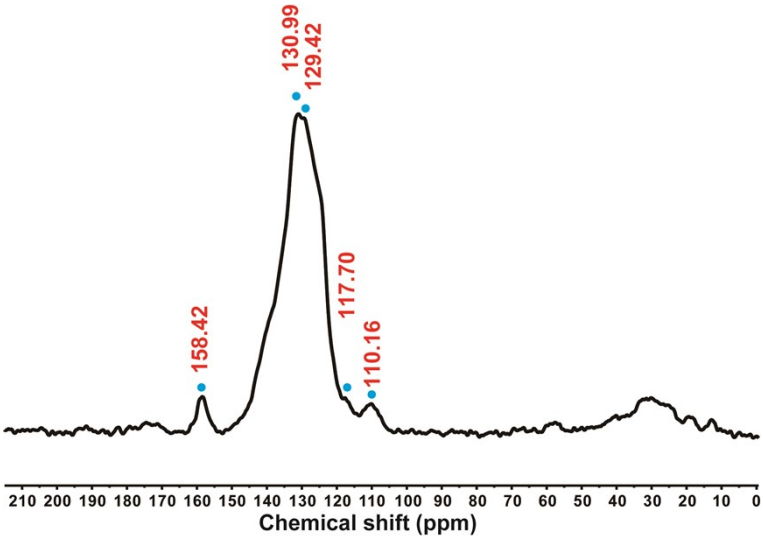


Fig. S2 The solid-state ^{13}C NMR spectrum of PY-SE-COF.

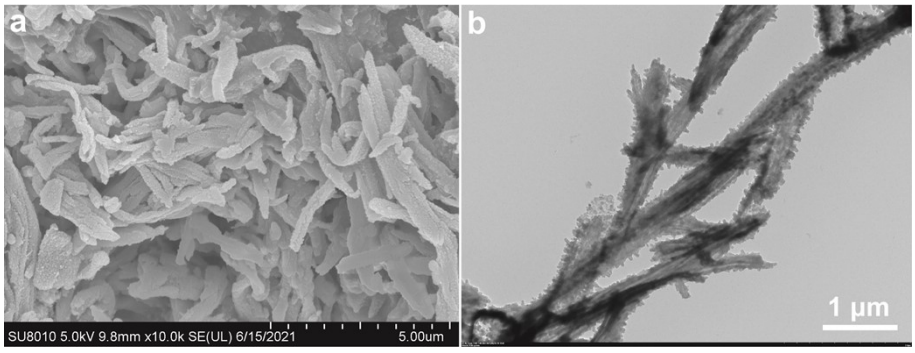


Fig. S3 The SEM (a) and TEM (b) morphology of PY-SE-COF.

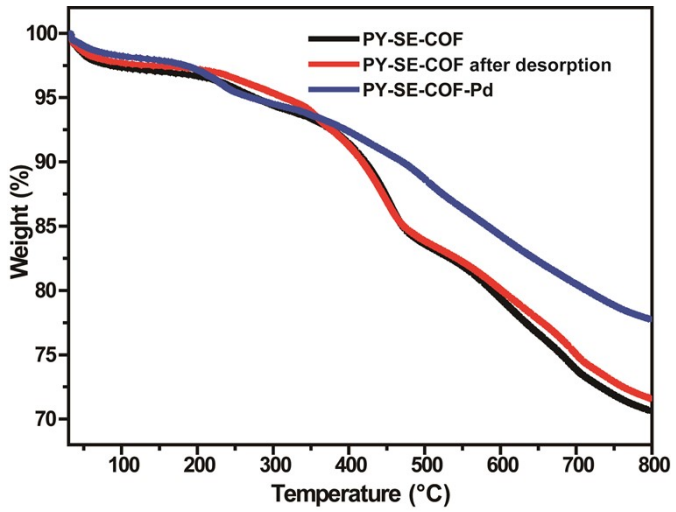


Fig. S4 The TGA curves of PY-SE-COF (black line), PY-SE-COF-Pd (blue line) and PY-SE-COF after desorption of Pd^{2+}.

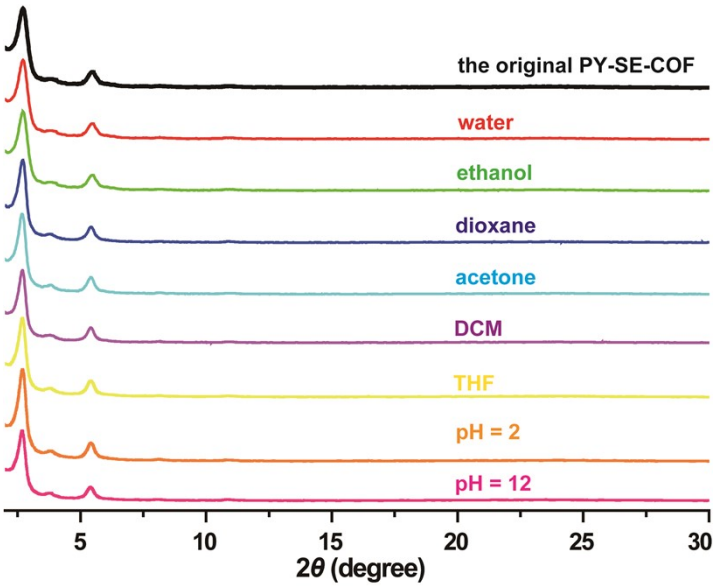


Fig. S5 The solvent and acid/base stability of PY-SE-COF.

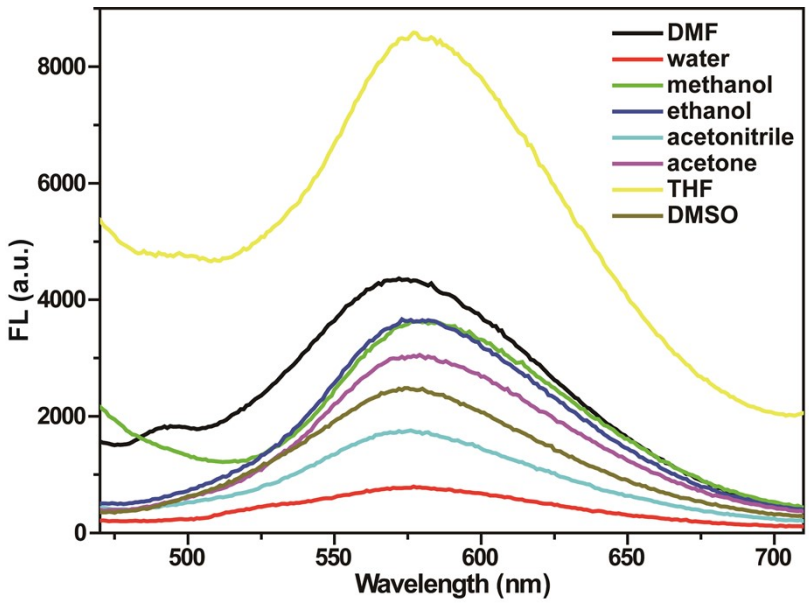


Fig. S6 The fluorescence intensity of PY-SE-COF in different solvent.

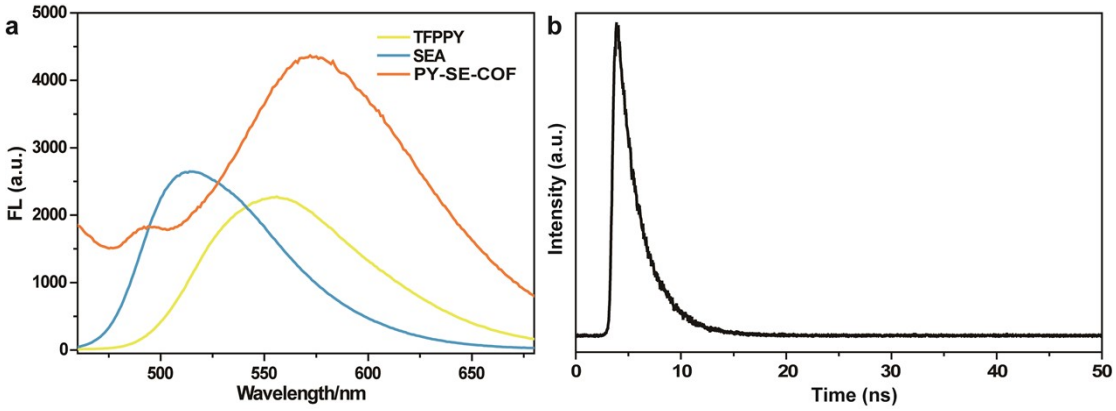


Fig. S7 (a) The emission peaks of TFPPY, SEA and PY-SE-COF in DMF; (b) the fluorescence decay curve of PY-SE-COF in DMF.

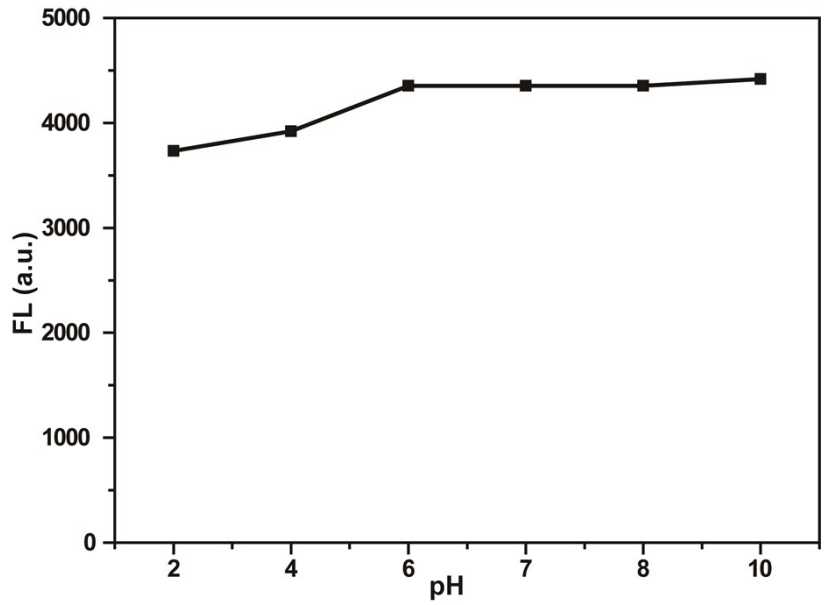


Fig. S8 The fluorescence intensity of PY-SE-COF under different pH.

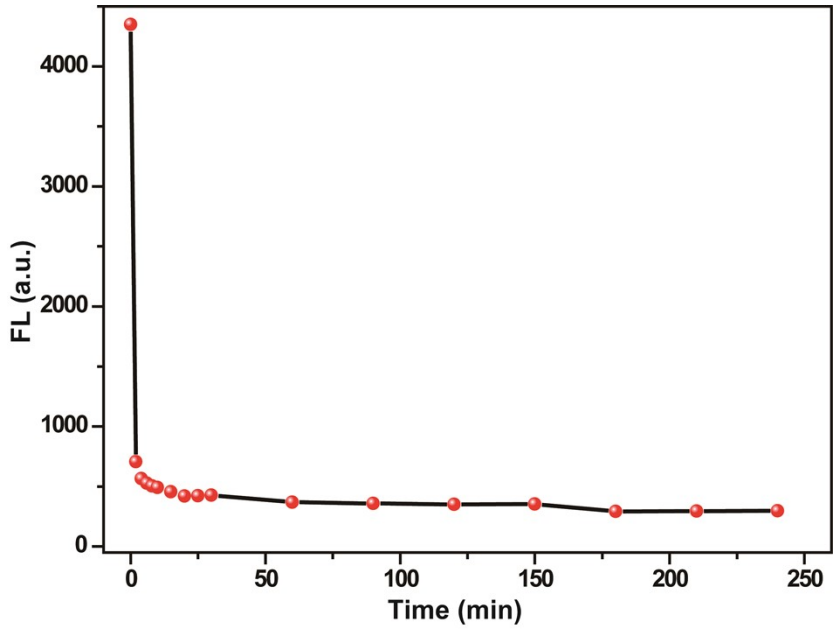


Fig. S9 The fluorescence intensity of PY-SE-COF after adding 200 μL of Pd^{2+} solution (1 mM) within 250 min.

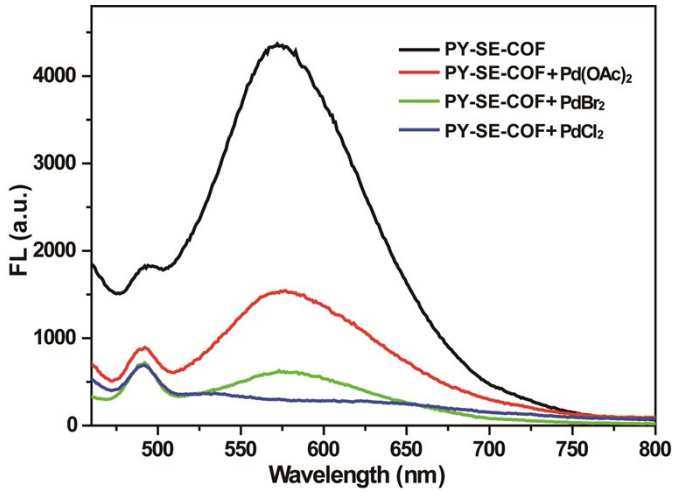


Fig. S10 The fluorescence spectra of PY-SE-COF after adding Pd(OAc), $PdBr_2$ and $PdCl_2$ with the concentration of 1 mM.

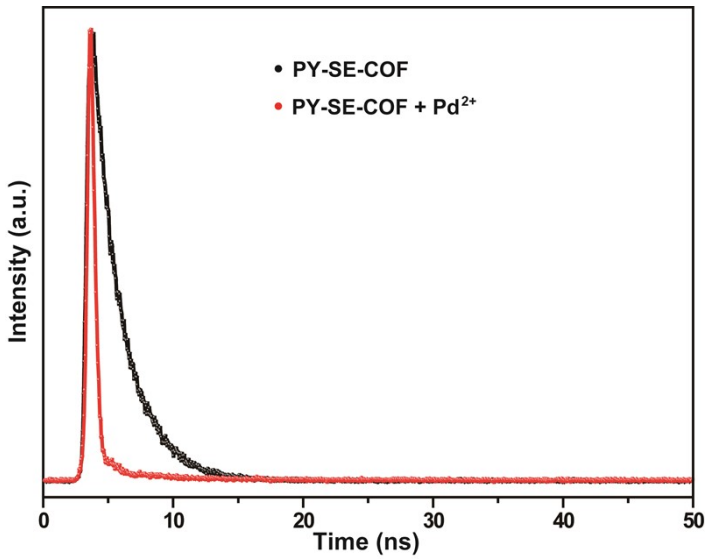


Fig. S11 The fluorescence lifetime of PY-SE-COF and PY-SE-COF with 200 μL of Pd^{2+} solution (1 mM).

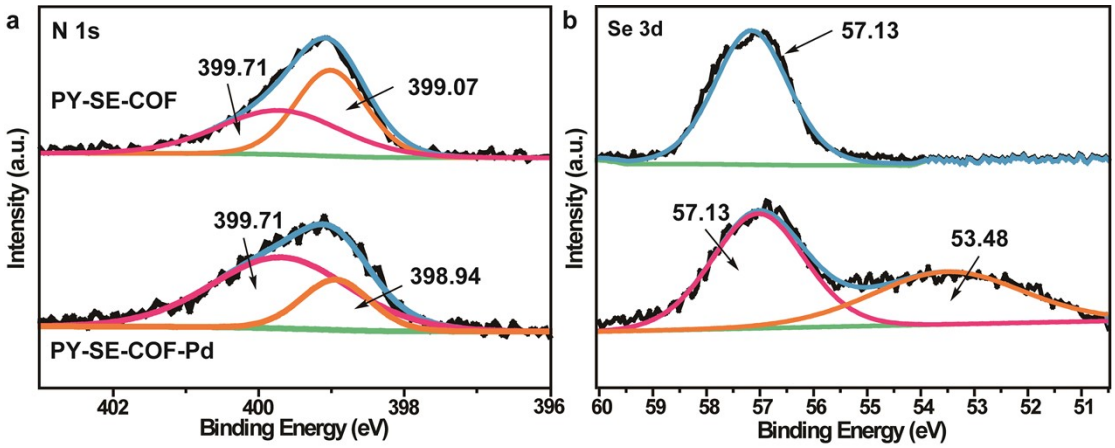


Fig. S12 The XPS spectra of N 1s (a) and Se 3d (b) in PY-SE-COF and PY-SE-COF-Pd. The N 1s spectra in PY-SE-COF can be divided into two peaks, which were 399.71 eV (-C≡N) and 399.07 eV (N in selenodiazole).[2] After addition of Pd^{2+}, the N 1s peak data were 399.91 eV and 398.04 eV, indicated that Pd^{2+} had interaction with N in selenodiazole. In the XPS spectrum of Se 3d, a new band at 53.48 eV was occurred, which might be resulted from the interaction between Se and Pd^{2+}.

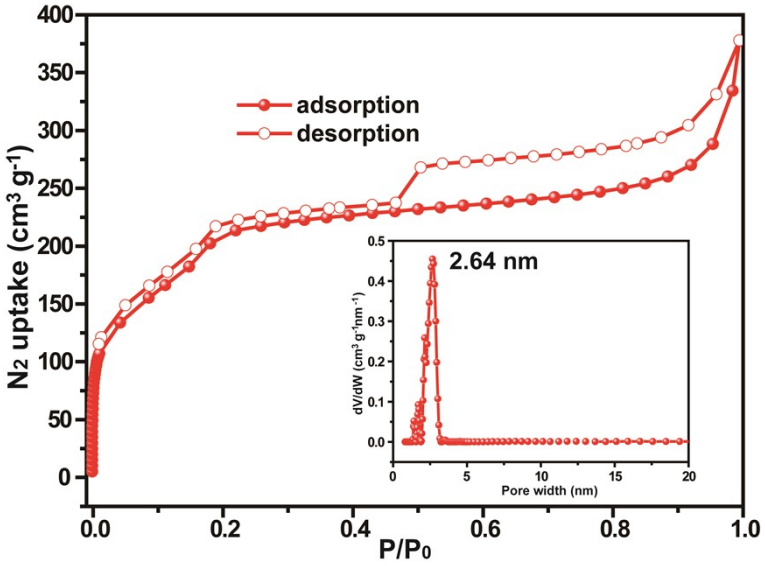


Fig. S13 The BET surface and pore size distribution of PY-SE-COF-Pd.

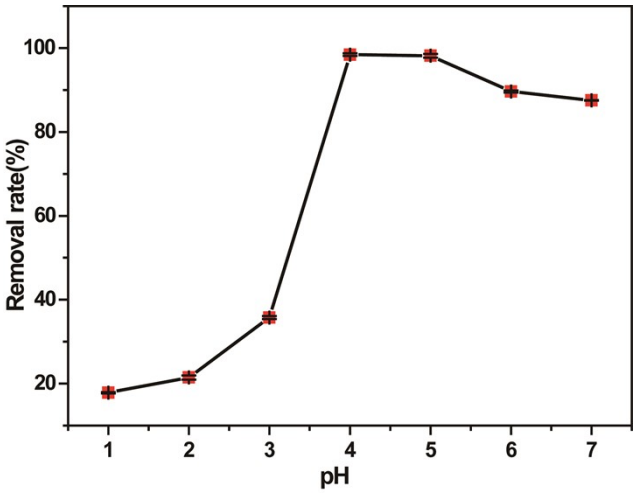


Fig. S14 The pH effects on the adsorption behavior of PY-SE-COF towards Pd^{2+}.

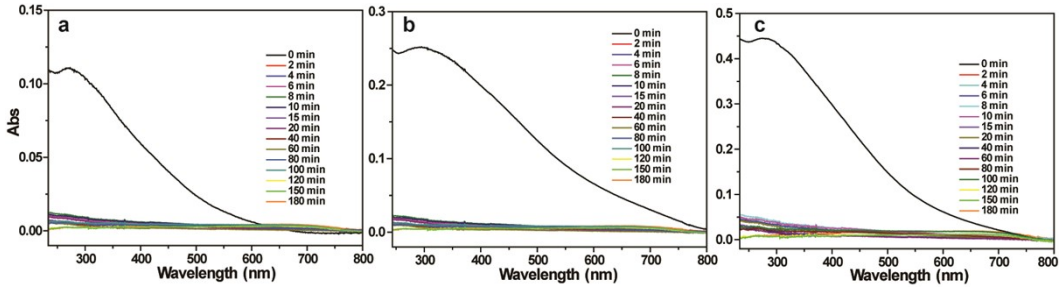
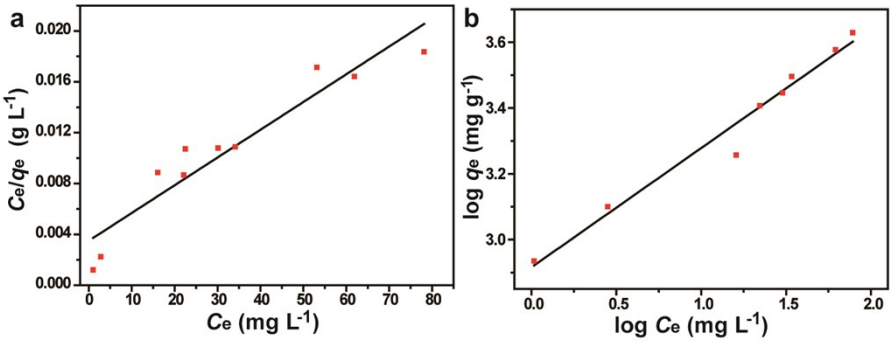


Fig. S15 UV-vis spectra of the residual Pd^{2+} after Pd^{2+} adsorption (the original concentration of Pd^{2+}: a. 0.1 mM; b. 0.2 mM; c. 0.4 mM, at pH 5) on PY-SE-COF at different times.



c

Adsorbents	Langmuir parameters		Freundlich parameters	
	q_{max} (mg/g)	b (L/mg)	K_f ($mg^{1-1/n}L^{1/n}/g$)	n
PY-SE-COF	4578.6	0.062	823.5	2.758

Fig. S16 The linear fitting curves of (a) Langmuir adsorption model and (b) Freundlich adsorption

model. (c) The corresponding adsorption constant.

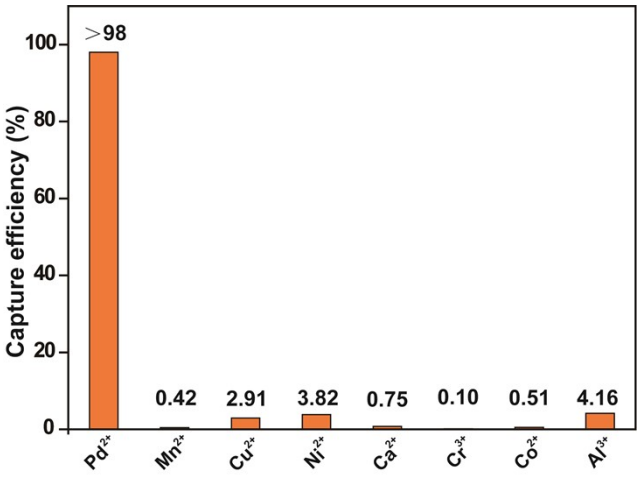


Fig. S17 Capture efficiency of different metal ions deduced from three parallel experiments.

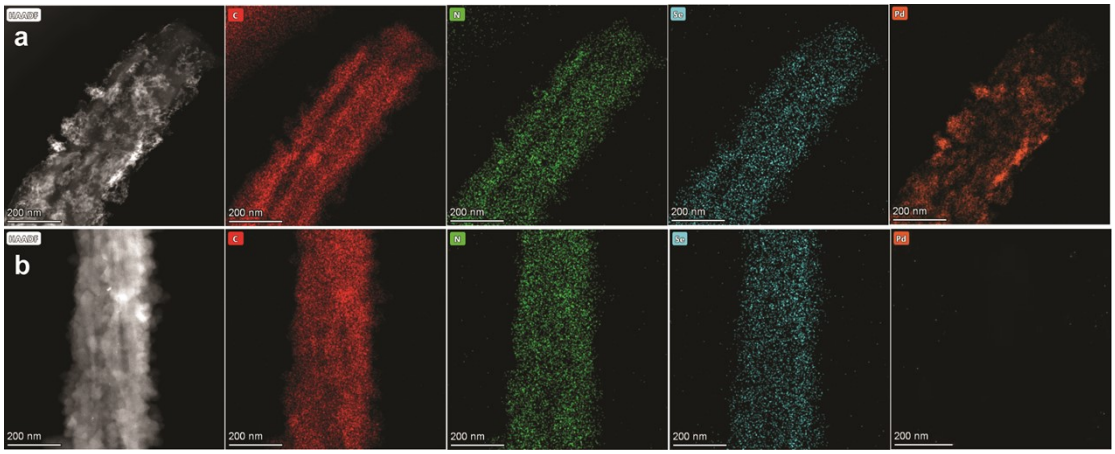


Fig. S18 The elemental mapping of (a) PY-SE-COF-Pd and (b) the regenerated PY-SE-COF.

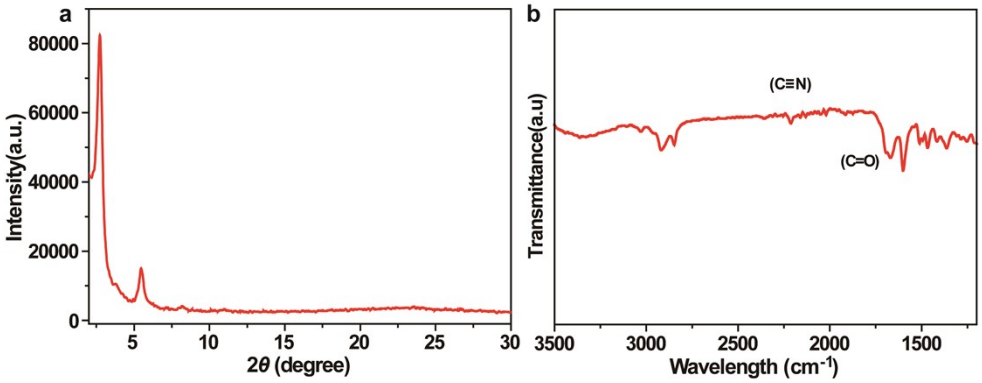


Fig. S19 The PXRD pattern and FT-IR spectrum of PY-SE-COF after 10 adsorption-desorption

cycles.

Lattice parameters a = 32.993677 Å b = 32.857069 Å c = 3.603397 Å α = 90° β = 90° γ = 90°			
Atom	x	y	z
H1	1.477344	-1.21173	-0.5
H2	1.591922	-1.21631	-0.5
H3	1.593845	-1.21418	-0.5
H4	1.602229	-1.1218	-0.5
H5	1.586818	-1.04813	-0.5
H6	1.452305	-1.08692	-0.5
H7	1.468227	-1.1606	-0.5
H8	1.577274	-0.9964	-0.5
H9	1.561308	-0.92298	-0.5
H10	1.552236	-0.87158	-0.5
H11	1.402031	-0.83692	-0.5
H12	1.417916	-0.91073	-0.5
H13	1.527233	-0.74663	-0.5
H14	1.412564	-0.74235	-0.5
H15	1.410597	-0.74455	-0.5
H16	1.551998	-0.67172	-0.5
H17	1.536547	-0.5982	-0.5
H18	1.402034	-0.63699	-0.5
H19	1.417956	-0.71067	-0.5
H20	1.392483	-0.58556	-0.5
H21	1.457348	-0.38006	-0.5
H22	1.401797	-0.43713	-0.5
H23	1.546495	-0.5787	-0.5
H24	1.602046	-0.52163	-0.5
H25	1.611195	-0.37301	-0.5
H26	1.386256	-0.44819	-0.5
H27	1.307726	-0.42988	-0.5
H28	1.26783	-0.56085	-0.5
H29	1.34636	-0.57915	-0.5
H30	1.617457	-0.51043	-0.5
H31	1.696496	-0.52882	-0.5

H32	1.736013	-0.39791	-0.5
H33	1.657245	-0.37999	-0.5
H34	1.601809	-0.32177	-0.5
H35	1.586358	-0.24824	-0.5
H36	1.451845	-0.28704	-0.5
H37	1.467767	-0.36072	-0.5
H38	1.771196	-0.50391	-0.5
H39	1.764878	-0.38973	-0.5
H40	1.766949	-0.38783	-0.5
H41	1.81779	-0.51047	-0.5
H42	1.89632	-0.52878	-0.5
H43	1.936381	-0.398	-0.5
H44	1.85707	-0.37995	-0.5
H45	1.942477	-0.53523	-0.5
H46	2.021517	-0.55362	-0.5
H47	2.067768	-0.56028	-0.5
H48	2.146261	-0.57855	-0.5
H49	2.186113	-0.44784	-0.5
H50	2.107619	-0.42958	-0.5
H51	2.234516	-0.45385	-0.5
H52	2.239061	-0.56863	-0.5
H53	2.23699	-0.57052	-0.5
H54	1.533393	-0.79739	-0.5
C1	1.510686	-1.22084	-0.5
C2	1.544162	-1.18746	-0.5
C3	1.535728	-1.14572	-0.5
C4	1.585765	-1.19586	-0.5
C5	1.568891	-1.11269	-0.5
C6	1.560763	-1.07091	-0.5
C7	1.518854	-1.06255	-0.5
C8	1.485684	-1.09588	-0.5
C9	1.494117	-1.13762	-0.5
C10	1.510726	-1.02077	-0.5
C11	1.543896	-0.98743	-0.5
C12	1.535455	-0.946	-0.5
C13	1.493851	-0.9376	-0.5
C14	1.460681	-0.97093	-0.5
C15	1.468809	-1.01271	-0.5
C16	1.485418	-0.89586	-0.5
C17	1.518893	-0.86248	-0.5
C18	1.468849	-0.81264	-0.5
C19	1.435373	-0.84602	-0.5
C20	1.443807	-0.88776	-0.5

C21	1.460415	-0.7709	-0.5
C22	1.493891	-0.73753	-0.5
C23	1.418804	-0.76281	-0.5
C24	1.48545	-0.6961	-0.5
C25	1.51862	-0.66276	-0.5
C26	1.510492	-0.62098	-0.5
C27	1.468583	-0.61262	-0.5
C28	1.435413	-0.64595	-0.5
C29	1.443846	-0.68769	-0.5
C30	1.460448	-0.57114	-0.5
C31	1.493617	-0.53781	-0.5
C32	1.485184	-0.49607	-0.5
C33	1.44358	-0.48766	-0.5
C34	1.41041	-0.521	-0.5
C35	1.418538	-0.56278	-0.5
C36	1.518659	-0.46269	-0.5
C37	1.510226	-0.42095	-0.5
C38	1.468615	-0.41286	-0.5
C39	1.435139	-0.44623	-0.5
C40	1.535228	-0.54591	-0.5
C41	1.568704	-0.51253	-0.5
C42	1.560263	-0.4711	-0.5
C43	1.593739	-0.43772	-0.5
C44	1.585305	-0.39598	-0.5
C45	1.543702	-0.38758	-0.5
C46	1.3688	-0.5129	-0.5
C47	1.53526	-0.34615	-0.5
C48	1.635342	-0.44613	-0.5
C49	1.360366	-0.47116	-0.5
C50	1.318763	-0.46276	-0.5
C51	1.285287	-0.49613	-0.5
C52	1.29372	-0.53787	-0.5
C53	1.335324	-0.54628	-0.5
C54	1.643477	-0.4876	-0.5
C55	1.685386	-0.49596	-0.5
C56	1.718556	-0.46263	-0.5
C57	1.710123	-0.42089	-0.5
C58	1.668512	-0.41279	-0.5
C59	1.56843	-0.31281	-0.5
C60	1.560303	-0.27103	-0.5
C61	1.518393	-0.26267	-0.5
C62	1.485223	-0.296	-0.5
C63	1.493657	-0.33774	-0.5

C64	1.76016	-0.47103	-0.5
C65	1.793635	-0.43766	-0.5
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C67	1.785202	-0.39592	-0.5
C68	1.84368	-0.48749	-0.5
C69	1.885283	-0.4959	-0.5
C70	1.918453	-0.46256	-0.5
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C73	1.960362	-0.47093	-0.5
C74	1.968497	-0.5124	-0.5
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C76	2.043577	-0.48743	-0.5
C77	2.035143	-0.44569	-0.5
C78	1.993532	-0.43759	-0.5
C79	2.08518	-0.49583	-0.5
C80	2.093621	-0.53727	-0.5
C81	2.135225	-0.54567	-0.5
C82	2.1687	-0.5123	-0.5
C83	2.160259	-0.47086	-0.5
C84	2.118656	-0.46246	-0.5
C85	2.210304	-0.5207	-0.5
C86	2.243473	-0.48736	-0.5
C87	2.218737	-0.56244	-0.5
C88	1.385635	-0.79614	-0.5
C89	1.618935	-1.16253	-0.5
C90	1.818678	-0.36254	-0.5
C91	2.185262	-0.59581	-0.5
C92	1.508608	-0.82157	-0.5
N1	1.416711	-0.9719	-0.5
N2	1.430317	-1.0391	-0.5
N3	2.061729	-0.40707	-0.5
N4	1.994609	-0.39381	-0.5
N5	1.851847	-0.32921	-0.5
N6	1.352159	-0.82952	-0.5
N7	1.652411	-1.12915	-0.5
N8	2.152092	-0.62915	-0.5
Se1	1.398277	-1.0141	-0.5
Se2	2.036886	-0.37485	-0.5

Table S1. Atomistic coordinates for PY-SE-COF optimized by Forcite method.

4. References

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