

**Anionic COFs intercalated cationic MOFs composites: synergistic adsorption-reduction toward efficient precious metal recovery**

Zhihao Li<sup>a</sup>, Fenglei Liu<sup>a,\*</sup>

<sup>a</sup>School of Life and Environmental Sciences, Shaoxing University, Huancheng West Road 508, Shaoxing 312000, P. R. of China

**Table S1** Summary of pore parameters of all the adsorbent

Adsorbent	Specific surface area (m <sup>2</sup> /g)
TpPa-SO <sub>3</sub> H	243.3
MIL-101(Cr)-NH <sub>2</sub>	1139.8
TpPa-SO <sub>3</sub> H@MIL-101(Cr)-NH <sub>2</sub>	368.2

**Table S2** Isotherms model constants for adsorption of Au(III)/Pd(II) on TpPa-SO<sub>3</sub>H@MIL-101(Cr)-NH<sub>2</sub>.

Adsorbents	T (K)	Langmuir model <sup>[1]</sup>			Freundlich model <sup>[2]</sup>		
		Q <sub>max</sub> (mg/g)	b(L/g)	R <sup>2</sup>	K(mg <sup>1-n</sup> .L <sup>n</sup> .g <sup>-1</sup> )	1/n	R <sup>2</sup>
Au(III)	298	1659.6	1.32	0.99	1046.1	0.367	0.93
Pd(II)	298	400.5	0.72	0.97	188.7	0.357	0.98

<sup>[1]</sup> Langmuir equation:  $q_e = q_{\max} b C_e / (1+bC_e)$ ; <sup>[2]</sup> Freundlich equation:  $q_e = k C_e^{1/n}$

Where  $C_e$  (mg/L),  $Q_e$  (mg/g), and  $Q_{\max}$  (mg/g) represent the concentration of uranium in solution, the uranium adsorption capacity of the adsorbent, and the maximum uranium adsorption capacity at equilibrium, respectively.  $b$  and  $K$  are Langmuir and Freundlich isotherm adsorption constants, respectively.

**Table S3** Calculated thermodynamic parameters from the thermodynamic equations.

Metal ions	Temperature (K)	$\Delta G^\circ$ (kJ.mol <sup>-1</sup> )	$\Delta H^\circ$ (kJ.mol <sup>-1</sup> )	$\Delta S^\circ$ (J/mol <sup>-1</sup> .K <sup>-1</sup> )
Au(III)	298	-17.96	61.78	355.8
	313	-19.07		
	333	-20.63		
Pd(II)	298	-6.37	36.5	143.8
	313	-8.56		
	333	-11.48		

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ; \Delta G^\circ = -RT\ln K_c; K_c = q_e/C_e$$

Where  $K_c$  (L/mg) is calculated as  $q_e/C_e$ ,  $R$  (8.314 kJ/mol·K) represents the universal gas constant, and  $T$  (K) denotes the absolute temperature.

**Table S4** Comparison of Au(III)/Pd(II) elimination by TpPa-SO<sub>3</sub>H@MIL-101(Cr)-NH<sub>2</sub> and other adsorption materials.

Adsorbents	Adsorption capacity (mg/g)		Refs
	Au(III)	Pd(II)	
TpPa-SO <sub>3</sub> H@MIL-101(Cr)-NH <sub>2</sub>	1659.6	400.5	This work
Biochar	246.9	44.7	[10]
MOFs	77.4	88.7	[11]
Microgels	241.3	275.8	[12]
COFs	1913	-	[16]
Graphene oxide	1076.6	216.9	[26]
Chitosan	1322	1337	[31]

Cellulose	-	143.4	[32]
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**Table S5** Kinetics model constants for adsorption of Au(III)/Pd(II) on TpPa-SO<sub>3</sub>H@MIL-101(Cr)-NH<sub>2</sub>.

Metal ions	Pseudo-first-order parameters <sup>[1]</sup>			Pseudo-second-order parameters <sup>[2]</sup>		
	q <sub>e</sub> (mg/g)	k <sub>f</sub> (h <sup>-1</sup> )	R <sup>2</sup>	q <sub>e</sub> (mg/g)	k <sub>s</sub> (g/mg/h)	R <sup>2</sup>
Au(III)	586.2	127.6	0.649	587.3	0.031	0.98
Pd(II)	184.5	33.6	0.413	188.5	0.61	0.96

Metal ions	Intraparticle diffusion model <sup>[3]</sup>					
	k <sub>1</sub> (mg/g/h <sup>0.5</sup> )	R <sup>2</sup>	k <sub>2</sub> (mg/g/h <sup>0.5</sup> )	R <sup>2</sup>	k <sub>3</sub> (mg/g/h <sup>0.5</sup> )	R <sup>2</sup>
Au(III)	49.2	0.99	1.93	0.90	0.59	0.92
Pd(II)	42.3	0.98	4.65	0.86	0.71	0.96

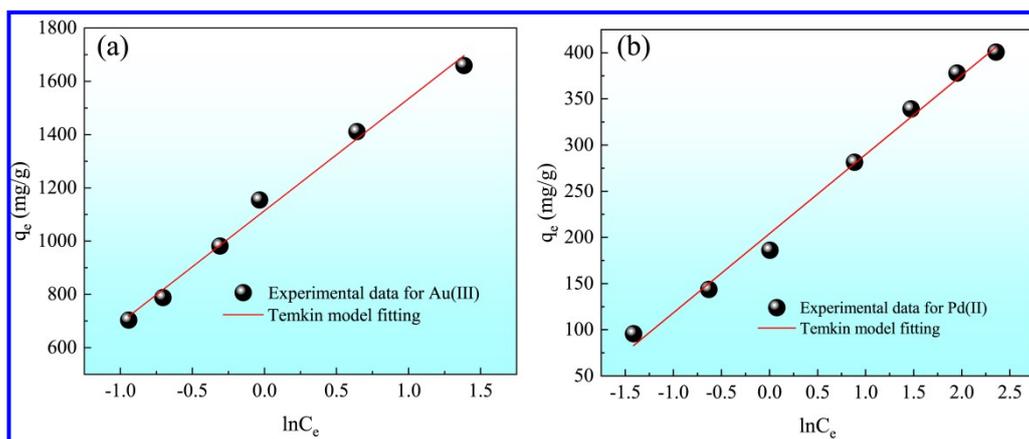
<sup>[1]</sup>Pseudo-first-order equation:  $q_t = q_e[1 - \exp(-kt)]$ ; <sup>[2]</sup> Pseudo-second-order equation:

$$q_t = \frac{q_e^2 k_s t}{1 + q_e k_s t}; \text{ } ^{[3]} \text{Intraparticle diffusion equation: } q_t = k_i t^{0.5} + C$$

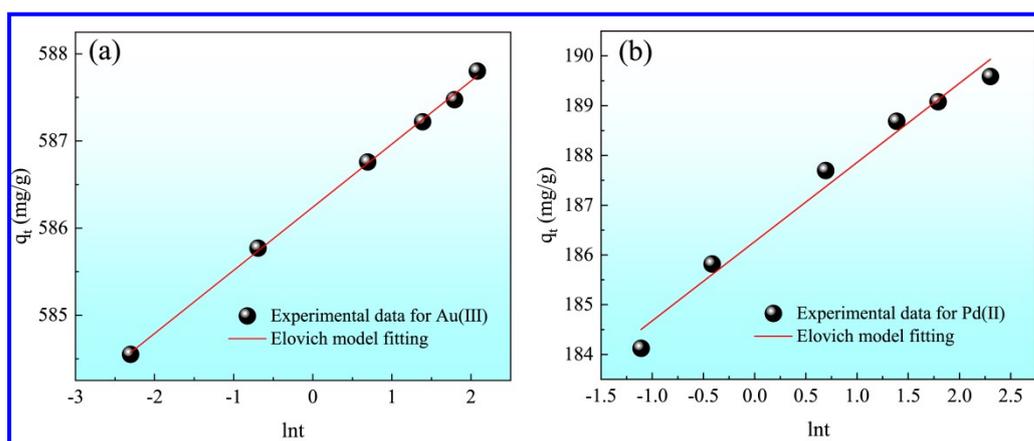
Where q<sub>e</sub> (mg/g) and q<sub>t</sub> (mg/g) represent the equilibrium adsorption capacity and the capacity at any given time *t*, respectively, while k<sub>f</sub> (h<sup>-1</sup>), k<sub>s</sub> (g/mg/h) and k<sub>i</sub>(mg/g/h<sup>0.5</sup>) denote the rate constants of the pseudo first-order, pseudo-second-order models and intraparticle diffusion.

**Table S6.** The concentration of the metal ions e-waste leaching solution.

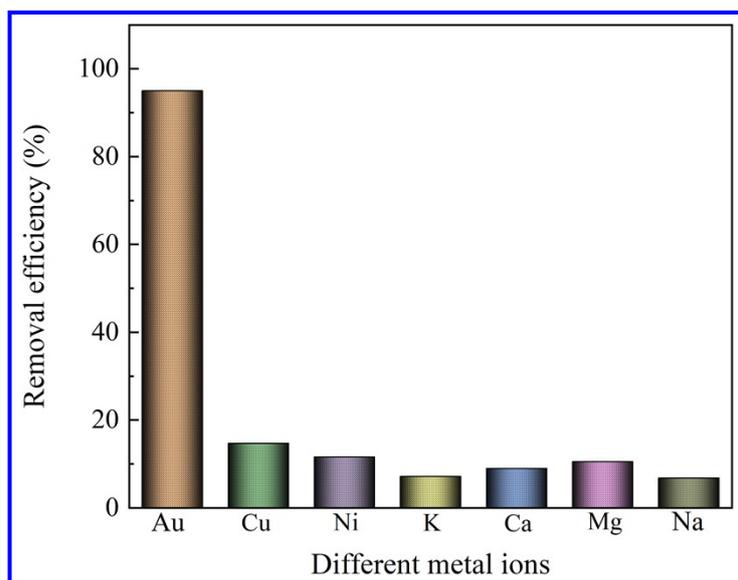
Metal ions	Au(III)	Ni(II)	Cu(II)	Zn(II)
Concentration (mg/L)	18.3	2670.7	7035.8	6.3



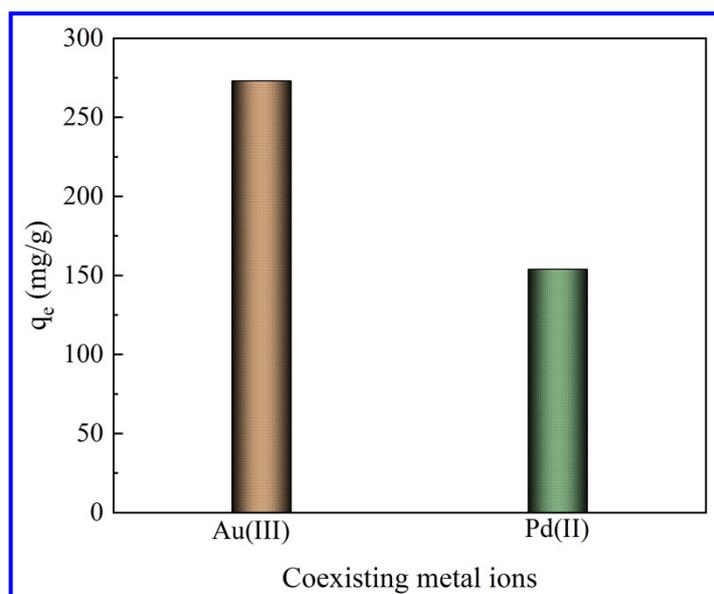
**Fig. S1.** Adsorption Isotherms fitting using Temkin for adsorption of Au(III) and Pd(II) on TpPa-SO<sub>3</sub>H@MIL-101(Cr)-NH<sub>2</sub> ( $C_{Au(III)}$ =10-160 ppm,  $C_{Pd(II)}$ = 5-60 ppm, pH = 2.0, m/V = 0.1 g/L).



**Fig. S2.** Adsorption kinetics data fitted by Elovich model ( $C_{Au(III)}$ =30 ppm,  $C_{Pd(II)}$ = 20 ppm, pH = 2.0, m/V = 0.05 g/L).

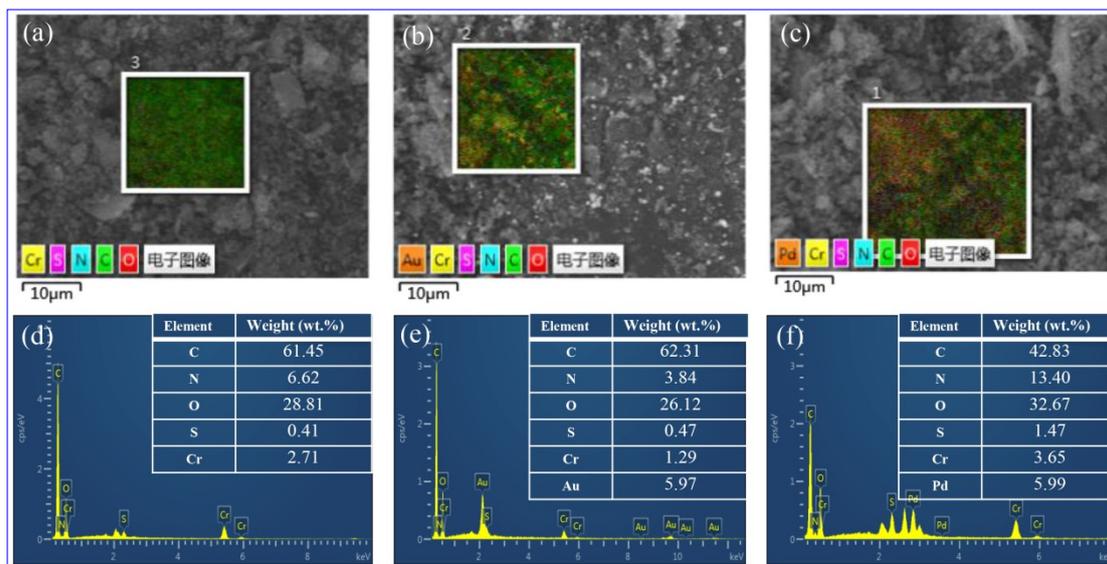


**Fig. S3.** Adsorption performance of TpPa-SO<sub>3</sub>H@MIL-101(Cr)-NH<sub>2</sub> toward metal ions in real laboratory waste solutions.



**Fig. S4.** Adsorption capacities of Au(III) and Pd(II) ions onto the

TpPa-SO<sub>3</sub>H@MIL-101(Cr)-NH<sub>2</sub> composite in a binary mixed solution system  
 (C<sub>Au(III)</sub>=30 ppm, C<sub>Pd(II)</sub>= 30 ppm, pH = 2.0, m/V = 0.1 g/L).



**Fig. S5.** The SEM-EDS images of TpPa-SO<sub>3</sub>H@MIL-101(Cr)-NH<sub>2</sub>(a,d), TpPa-SO<sub>3</sub>H@MIL-101(Cr)-NH<sub>2</sub>-Au(b,e) and TpPa-SO<sub>3</sub>H@MIL-101(Cr)-NH<sub>2</sub>-Pd(c,f).