Electronic Supplementary Materials

Efficient Collection of Perrhenate Anion from Water Using Poly(pyridinium salts) via Pyrylium Mediated Transformation

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1. Materials and Methods

1.1 General

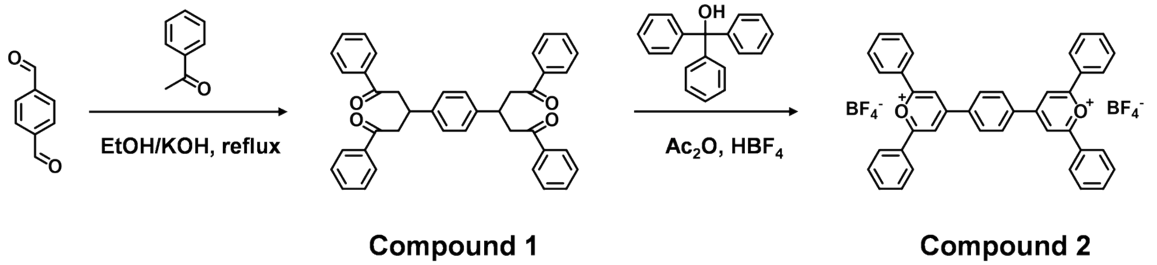
Acetophenone and terephthalaldehyde were purchased from Bidepharm. Triphenylmethanol and HBF_4 were purchased from Energy Chemical. The Re ICP standard solution (100 mg L^{-1} in 5% nitric acid) was purchased from Guobiao (Beijing) Testing & Certification Co., Ltd., China. Sodium perrhenate (99%) was purchased from Macklin, China. Sodium chloride, sodium sulfate, sodium hydroxide, potassium hydroxide, acetic anhydride and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd, China. The syringe filters (Nylon 66, 0.45 μm) were purchased from Jinlong company, China. ReO_4^- solutions were prepared by dissolving sodium perrhenate in distilled water. The pH values were adjusted by sodium hydroxide or hydrochloric acid.

1.2 Characterization Methods

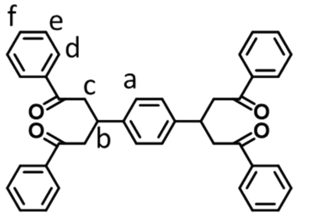
The structures of the model **compounds 3** and **PPS** synthesized in this manuscript were determined by NMR technique (Supplementary Fig. S1 and Supplementary Fig. S2). ^{13}C NMR spectra were recorded on Bruker ADVANCE 400 NMR Spectrometer in $CDCl_3$. Chemical shifts are expressed in ppm downfield from TMS at =0 ppm, and J values are shown in Hz. ^{13}C (100.5 MHz) cross-polarization magic-angle spinning (CP-MAS) NMR experiments were recorded on a Varian infinity plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO_2 rotor. Scanning electron microscopy (SEM) images was obtained from a MIRA3 LMH (TESCAN, Czech Republic) and elemental mapping images was collected by X MAX20 (Oxford, UK). The concentration of Re was detected by the inductively coupled plasma optical emission spectrometry (ICP-OES, 5100 Agilent Technologies, USA) and ICP-Mass spectrometer (NexION 2000, PerkinElmer, USA). Fourier transform infrared (FTIR) spectra were obtained by mixing samples with KBr to form pellets and collecting data with FTIR spectrometer (Nicolet IS10, Thermo scientific, USA). X-ray photoelectron spectroscopy (XPS) experiments were conducted on a Thermo ESCALAB Xi+ analyzer (Thermo Fisher Scientific Inc., USA) with Al Kα radiation ($h\nu$ =1486.6 eV) as the excitation source, and the binding energies were calibrated using the C1s peak at 284.80 eV. Thermal gravimetric analysis (TGA) was carried out using a NETZSCH STA449F3 Jupiter thermogravimetric analyzer at a heating rate of 10 K min^{-1} in Ar atmosphere (NETZSCH, Germany). The data of Zeta potential in water was detected by Malvern ZEN3600. Raman spectroscopy was carried out using a inVia Raman Microscope (RENISHAW, UK), and a 785 nm semiconductor laser was used as the excitation source. Gel permeation chromatography (GPC) was performed for **PPS-Cl** in DMF at 40 ^{o}C at a flow rate 1.0 mL/min with Agilent PL-GPC50 equipped with a differential detector and Agilent mixed-c columns.

2. Experimental Section of Synthesis

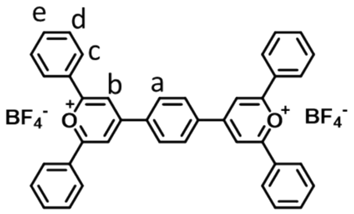
2.1 Synthesis of pyrylium salt



Scheme S1. Synthetic route of compound **2**.

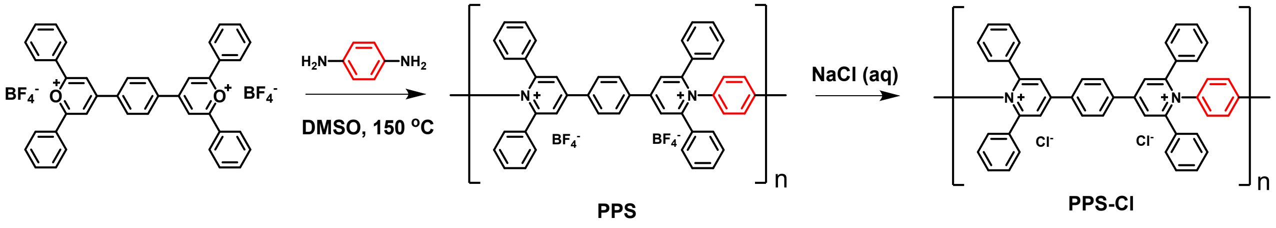


Compound 1[1]: Acetophenone (54.3 g, 0.45 mol) and terephthalaldehyde (10.0 g, 0.75 mol) were dissolved in 250 mL ethanol and heated to 65 ^{o}C, KOH (10.5 g, 0.19 mol) in 10 mL water was added dropwise over 30 min with vigorous stirring. Then the mixture was heated at reflux for 6 hours and pale precipitate was formed. The solid was filtered while hot, and was recrystallized in toluene to obtain the product as a white solid, 32.6 g, yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.92-7.90 (d, 8H, J=8 Hz, Ph-H^d), δ 7.54-7.50 (m, 4H, Ph-H^f), δ7.44-7.40 (m, 4H, Ph-H^e), δ7.19 (s, 4H, Ph-H^a), δ4.05-3.98 (m, 2H, H^b) δ3.46-3.28 (m, 8H, H^c).

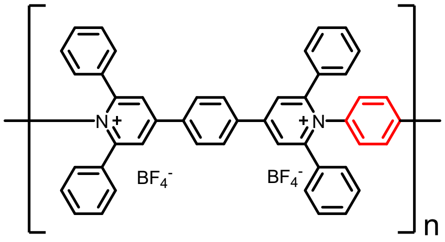


Compound 2[1]: Triphenylmethanol (7.8 g, 0.030 mol) were added to 100 mL of Ac_2O and the mixture was heated to 65 ^{o}C until clear. After cooling down to room temperature, 5.2 mL HBF_4 (48% wt in water) was added dropwise and compound **1** (7.2 g, 0.012 mol) was added portion-wise, then mixture was stirred at room temperature for overnight. Yellow precipitate was formed and collected by filtration, after washed with Ac_2O for three times, the product was obtained as a yellow solid, 5.8 g, yield 68%. ^{1}H NMR (400 MHz, d_6-DMSO) δ9.30 (s, 4H, H^b), δ8.63 (s, 4H, Ph-H^a), δ7.87-7.75 (m, 20H, Ph-$H^{c,d,e}$).

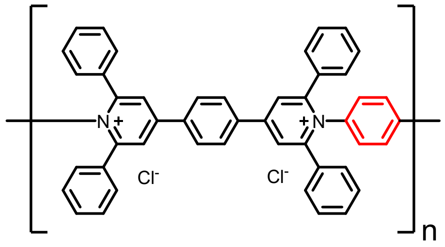
2.2 Synthesis of PPS-Cl



Scheme S2. Synthetic route of **PPS-Cl**.

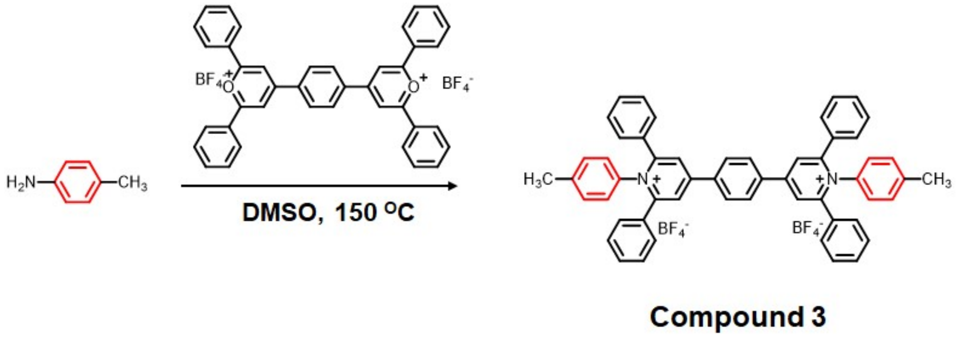


PPS: p-Phenylenediamine (1.08 g, 10 mmol, 1.0 equiv.) and compound **2** (7.14 g, 10 mmol, 1.0 equiv.) were dissolved in 100 mL DMSO in a 500 mL flask under N_2. The resulting mixture was stirred at 150 °C for 24 h. Then the polymer powder was obtained by pouring into deionized water and washed three times subsequently with deionized water, followed by drying in a vacuum freezing dryer. **PPS** (6.469 g, 70%) was obtained as an orange powder.

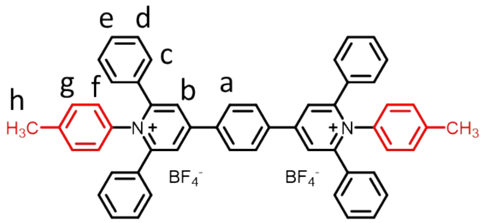


PPS-Cl: 1 g **PPS** was soaked three times with 2 M sodium chloride solution of 100 mL and stirred for 4 h. Then the solid was filtered off and washed with deionized water for three times, then **PPS-Cl** was obtained as an orange powder after drying under vacuum.

2.3 Synthesis of Model compound 3



Scheme S3. Synthetic route of model compound **3**.



Model compound 3: 4-Methylaniline (216 mg, 2 mmol) and compound **2** (714 mg, 1 mmol) were added to DMSO in a flask under N_2. The resulting mixture was heated at 120 °C for 24 h. Then the result solution was poured into methylene chloride and extracted with brine for three times. The organic layer was collected and the solvent was removed under reduced pressure. Then compound **3** (767 mg, 86%) was obtained as a yellow powder[2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.78 (s, 8H, H^b, Ph-H^a), δ7.50-7.48 (d, 8H, J=8 Hz, Ph-H^c), δ7.29-7.25 (m, 4H, Ph-H^e), δ7.23-7.21 (d, 8H, J=8 Hz, Ph-H^d), δ7.18-7.16 (d, 4H, J=8 Hz, Ph-H^f), δ6.86-6.84(d, 4H, J=8 Hz, Ph-H^h), δ2.14 (s, 6H, H^h).

3. Experimental Section of Sorption

3.1 Sorption isotherm investigations.

The sorption isotherm experiments of **PPS-Cl** were conducted in a water-bathing at 30 °C by ranging the initial concentrations of ReO_4^- from 10 to 500 ppm. **PPS-Cl** (5 mg) was added to 15 mL of ReO_4^- aqueous solution with different concentrations (V/m ratio is 3000 mL g^{-1}). After shaking at a rate of 120 rpm for 5 h, the mixture was separated with a membrane filter (0.45 μm). The concentrations of residual ReO_4^- in the filtrate were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and ICP-Mass spectrometer. Previous literature can be referred for the calculation of sorption capacity at equilibrium q_e (mg g^{-1}), and equation expression of the Langmuir isotherm model as well as the Freundlich isotherm model.[3]

3.2 Sorption kinetics investigations.

The sorption kinetics experiments of **PPS-Cl** were conducted by collecting samples at different times. **PPS-Cl** (20 mg) was added to 150 mL of ReO_4^- aqueous solution of 45 ppm in a 500 mL Erlenmeyer flask (V/m ratio is 7500 mL g^{-1}). The flask was shaken at a rate of 120 rpm in the water-bathing vibrator. Then 2 mL samples were removed from the mixture at increasing time intervals (0.5 min, 1 min, 2 min, 5 min, 10 min, 20 min, 30 min, 45 min, 60 min, 90 min, 120 min, 150 min, 180 min, 240 min, 300 min), followed by separation for further ICP-OES analysis. Previous literature can be referred for the calculation of removal efficiency (RE), and equation expression of pseudo-first-order model as well as pseudo-second-order model.[3]

3.3 Selectivity study.

Effect of competing ions SO_4^{2-} on the sorption properties of ReO_4^- was tested by adding different concentrations of Na_2SO_4. **PPS-Cl** (10 mg) was added to 10 mL ReO_4^- aqueous solution (40 ppm, 0.16 mM, V/m ratio is 1000 mL g^{-1}) with varying concentrations of SO_4^{2-} (1.6 mM, 16 mM, 160 mM, 800 mM). After shaking at a rate of 120 rpm for 8 h, the mixture was separated for ICP-OES analysis.

3.4 pH effect study.

Effect of pH on the sorption properties of ReO_4^- was tested by adjusting pH values from 1 to 12. 5 mg of **PPS-Cl** was added to 20 mL ReO_4^- aqueous solution with a concentration of 100 ppm (*V/m* ratio is 4000 mL g^{-1}). After shaking at a rate of 120 rpm for 20 h, the mixture was separated for ICP-OES analysis.

3.5 Reusability study.

After 50 mg **PPS-Cl** was adsorbed with 100 mL ReO_4^- solution of 45 ppm (*V/m* ratio is 2000 mL g^{-1}) at 30 °C for 12 h, **PPS-Re** was first regenerated by 1 M HCl solution of 20 mL at 60 °C for 5 h. Then the regenerated material was filtered and put into the next run after washing by distilled water for three times. **PPS-Cl** was reused for additional four times of adsorption-desorption tests.

3.6 Exchange experiments with simulated industrial water.

The simulated industrial water was prepared according to the chemical composition of copper leach solution from a certain copper smelting plant in southern China. A large excess of SO_4^{2-} (86770 mg L^{-1}) and As (3099 mg L^{-1}) were added into the Re-contained solution (36.5 mg L^{-1}) with pH 1.7. And 10 mg **PPS-Cl** was added in 10 mL simulated industrial water. After shaking at a rate of 120 rpm for 24 h, the mixture was separated for ICP-OES analysis.

4. Characterization of compound 3 and PPS

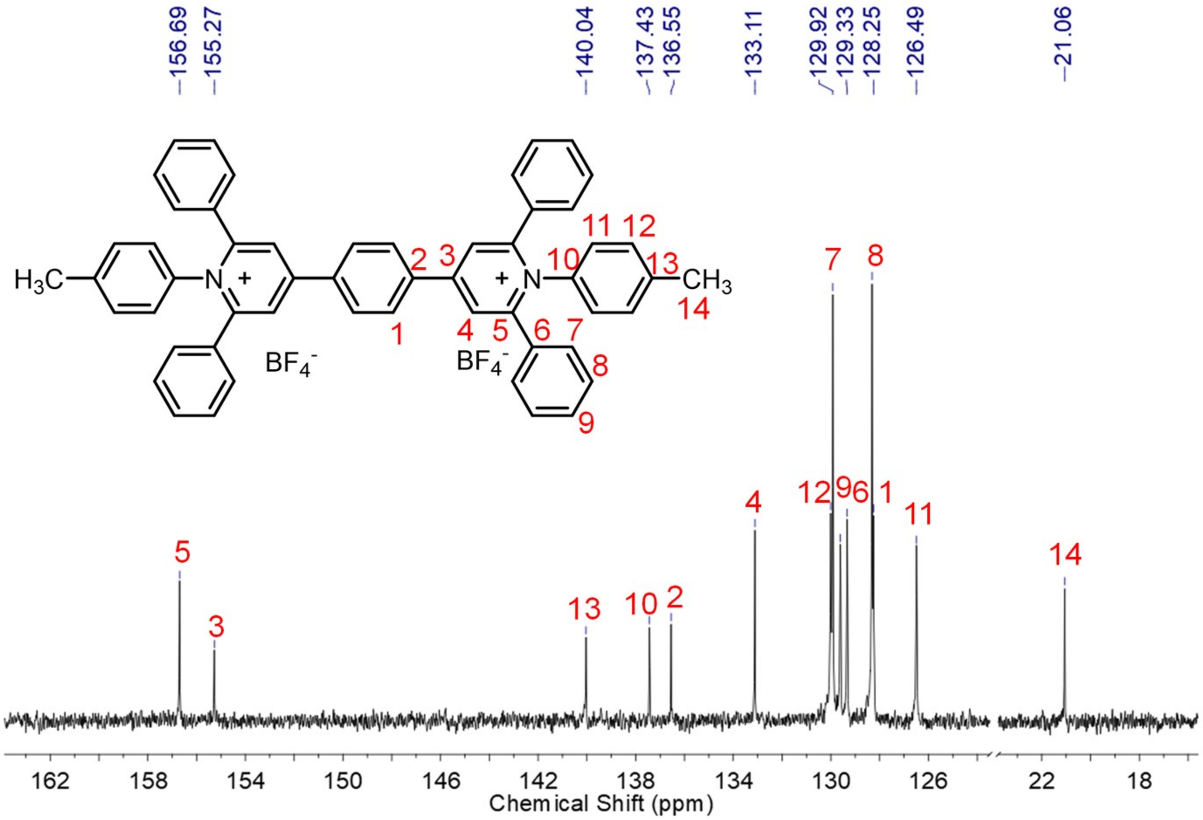


Fig. S1. ^{13}C NMR spectrum of model compound **3** in $CDCl_3$.

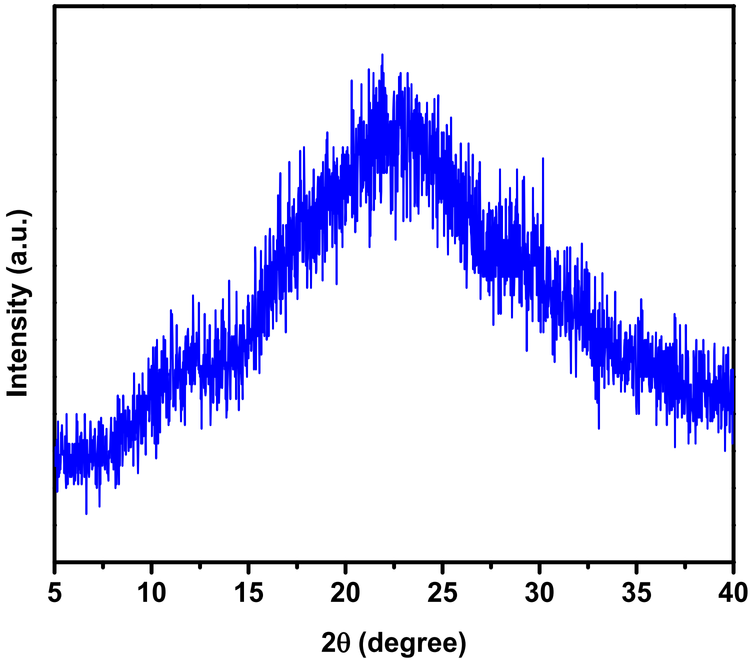


Fig. S2. PXRD data of **PPS-Cl**.

Table S1 GPC data for **PPS-Cl**

Polymer	Mn	Mw	Mw/Mn
PPS-Cl	19618	30822	1.57

5. Sorption investigations

Table S2 Sorption isotherm of **PPS-Cl** with excess of ReO_4^-

Material	C_0 (ReO_4^-) (ppm)	V/m (mL g^{-1})	Sorption Capacity (mg ReO_4^-/g sorbent)
PPS-Cl	900	3000	596.0

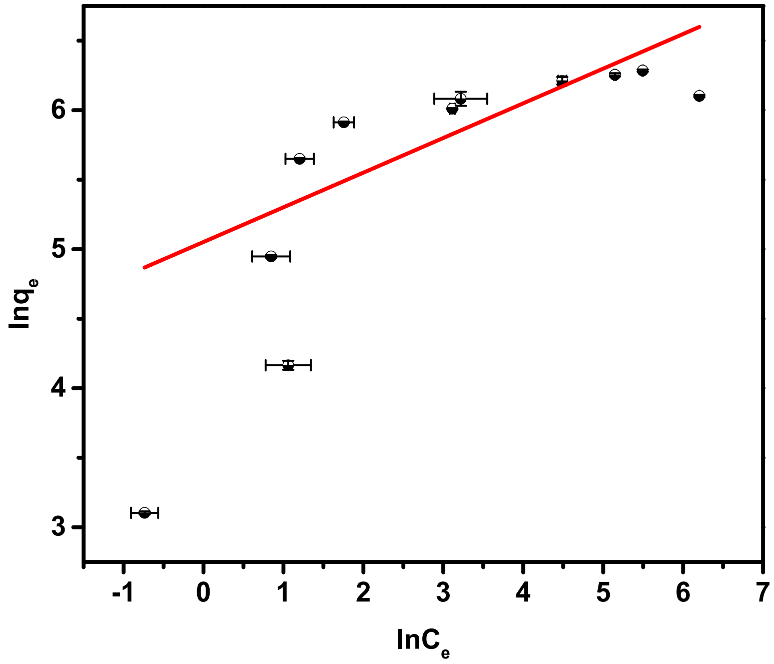


Fig. S3. Adsorption isotherm of **PPS-Cl** for ReO_4^-, fitting with linear form of Freundlich equation.

Table S3 Parameters of Fitting with Isotherm Models.

Isotherm model	Parameters
Langmuir	$K_L = 0.192$ L mg^{-1} $q_m = 543.48$ mg g^{-1} $R^2 = 0.994$
Freundlich	$K_F = 156.343$ (mg g^{-1}) (L mg^{-1})$^{4.01}$ $n = 4.01$ $R^2 = 0.410$

Table S4 Parameters of Fitting with Kinetic Models.

Kinetics model	Parameters
Pseudo-first-order	$k_1 = 0.00484$ min^{-1} $R^2 = 0.4520$
Pseudo-second-order	$k_2 = 2.9 \times 10^{-4}$ g mg^{-1} min^{-1} $R^2 = 0.994$

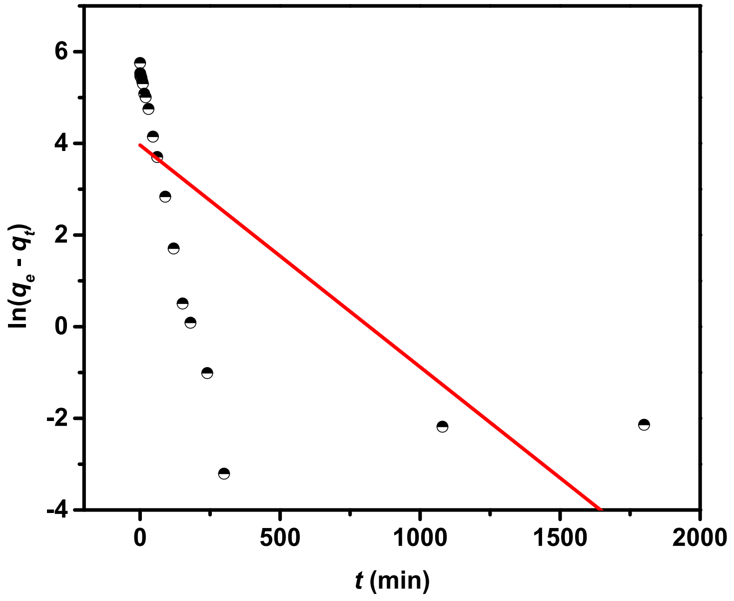


Fig. S4. Adsorption kinetics of **PPS-Cl** for ReO_4^-, fitting with pseudo-first-order linear equation.

Table S5 Comparison of selectivity for ReO_4^- in excess SO_4^{2-} solution over various cationic materials.

Name of sorbents	C_0 for ReO_4^-	m/V (mL g^{-1})	Removal efficiency/ Molar ratio of SO_4^{2-} : ReO_4^-	Ref
SCU-CPN-1	0.15 mM	1000	64%/6000:1	4
PQA-Py-Cl	0.15 mM	1000	75.7%/6000:1	5
PQA-*p*NH_2Py-Cl	0.15 mM	1000	70.6%/6000:1	5
PQA-*p*$N(Me)_2$Py-Cl	0.15 mM	1000	83.4%/6000:1	5
CPN-tpm	0.16 mM	1000	49.1%/5000:1	3
iCON	0.1 mM	1000	>30%/1000:1	6
ImPOP-1	0.1 mM	500	72.9%/1000:1	7
VBCOP	0.29 mM		50%/100:1	8
PPS-Cl	0.16 mM	1000	**89.5%**/5000:1	**This work**

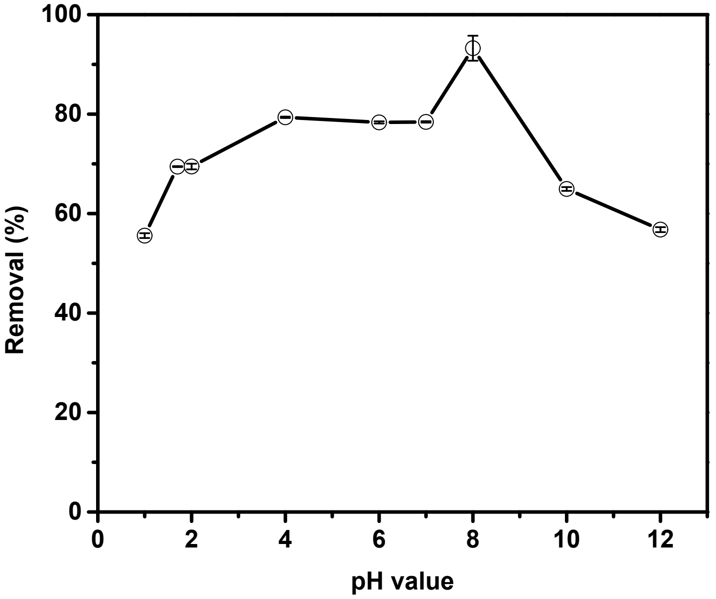


Fig. S5. Effect of different pH on the sorption properties of ReO_4^- by **PPS-Cl**.

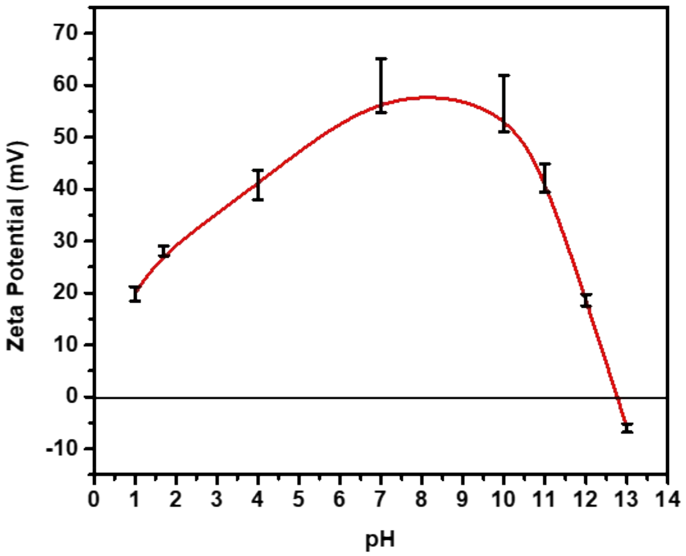


Fig. S6. Zeta potential of **PPS-Cl** as a function of pH.

6. Sorption investigations

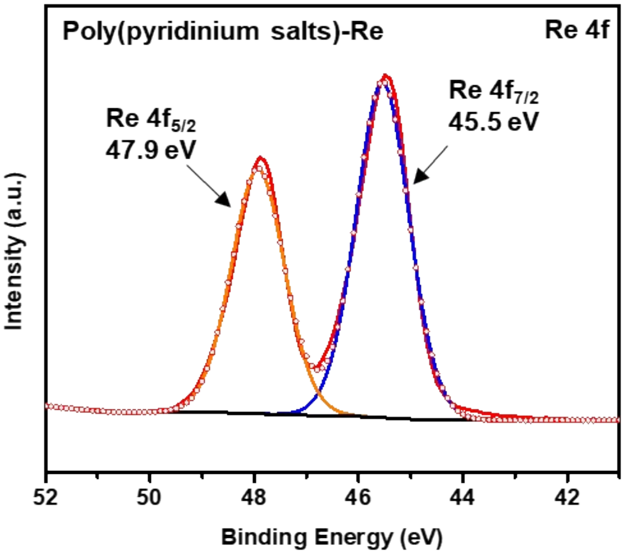


Fig. S7. XPS analysis of Re 4f from ReO_4^- sorbed **PPS**.

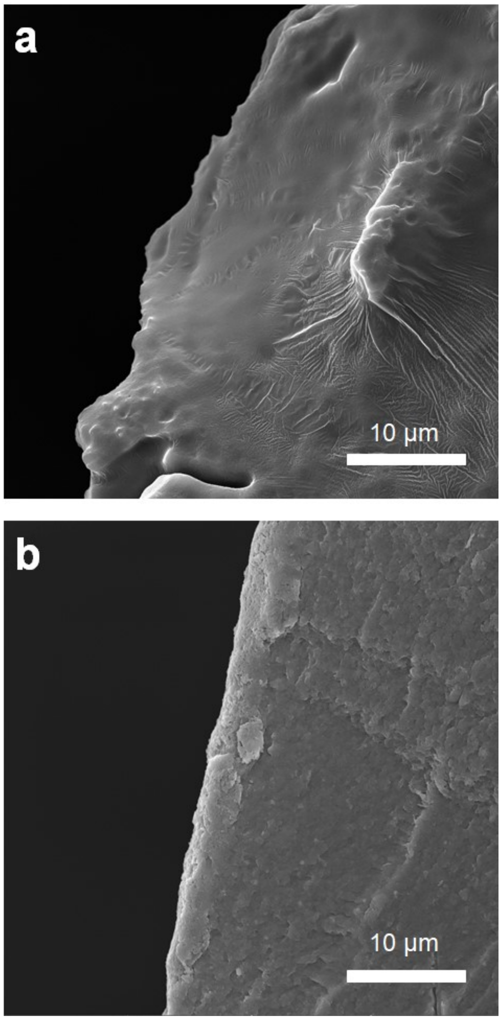


Fig. S8. SEM image of a) **PPS-Cl** and b)**PPS-Re**.

References

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