Optimizing Strategy for Enhancing the Stability and $^{99}$TcO$_4^-$ Sequestration of Poly(ionic liquids)@MOFs Composites

Cheng-Peng Li,$^\dagger$ Hai-Ruo Li,$^\dagger$ Jin-Yun Ai,$^\dagger$ Jing Chen,$^\dagger$ and Miao Du$^*,\dagger,\ddagger$

$^\dagger$College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecules, Tianjin Normal University, Tianjin 300387, China

$\ddagger$College of Material and Chemical Engineering, Zhengzhou University of Light Industry, Zhengzhou 450001, China
**Section S1. Experimental Section**

1. General Materials and Methods

Commercially available reagents were used directly. $^1$H NMR spectra were recorded on a Bruker AV 400 spectrometer, and the chemical shifts were reported in ppm with respect to reference standards (Figure S12). FT-IR spectra were taken on a Bruker AlPHA FT-IR spectrometer (with KBr pellets) in 4000–400 cm$^{-1}$. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer (Cu-Kα, λ = 1.5406 Å), operating at 40 kV and 100 mA, and the diffraction intensity data were obtained by the continuous scans in the 2θ/θ mode with scan speed of 2 s/step and step size of 0.02°. X-ray photoelectron spectroscopy (XPS) measurements were taken on a Thermo Scientific ESCALAB 250Xi spectrometer. The scanning transmission electron microscope (STEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on a Thermo Fisher Scientific Talos F200X scanning electron microscope, with the electron beam energy of 200 keV. N$_2$ sorption isotherms at 77 K were measured with Micromeritics ASAP 2020 HD88. The concentrations of TcO$_4^-$ in solution were measured on a UV-vis spectrometer (Varian Cary 6000i) by monitoring the characteristic absorption peak at 290 nm. The activity of $^{99}$TcO$_4^-$ was analyzed by a liquid scintillation counting (LSC) system (Perkin Elmer Quantulus 1220). The ReO$_4^-$ concentrations in solution were determined on a Perkin-Elmer Avio 200 inductively coupled plasma optical emission spectrometer (ICP-OES). Thermogravimetric analysis (TGA) plots were recorded on a TGA Q500 thermal analyzer in 25–800 °C at a heating rate of 10 °C/min under N$_2$ atmosphere.

**Safety Note.** Caution! $^{99}$Tc must be handled following the standard precautions and procedures, due to its significant health risks when inhaled or digested. All $^{99}$Tc studies were performed in a licensed laboratory dedicated to radiological investigation.

2. Synthesis and Characterization

**1-Vinyl-3-ethylimidazolium bromide (C$_2$).** A mixture of 1-vinylimidazole (4.71 g, 0.05 mmol), bromoethane (5 mL, 0.07 mmol), and acetone (20 mL) was heated at 60 °C under N$_2$ atmosphere for 48 h. After naturally cooled to room temperature, a white solid was obtained by adding ethyl ether, which was filtered and dissolved in the minimum amount of methanol. The white solid was obtained by evaporation under reduced pressure, which was washed by ethyl ether for several times and dried overnight under vacuum. Yield: 9.89 g (98%). $^1$H NMR (400 MHz, DMSO-$_d^6$): δ (ppm) 9.88 (s, 1H), 8.34 (s, 1H), 8.08 (s, 1H), 7.36 (dd, $J = 15.6$ and 8.8 Hz, 1H), 6.05 (dd, $J = 15.6$ and 2.4 Hz, 1H), 5.38 (dd, $J = 8.8$ and 2.4 Hz, 1H), 4.26 (q, $J = 8$ Hz, 2H), 1.42 (t, $J = 8$ Hz, 3H).

**1-Vinyl-3-hexylimidazolium bromide (C$_4$).** A mixture of 1-vinylimidazole (4.71 g, 0.05 mol), 1-bromohexane (8.25 g, 0.05 mol), and methanol (50 mL) was heated at 65 °C under N$_2$ atmosphere for 72 h. After naturally cooled to room
temperature, the obtained white solid was washed with ethyl ether for several times and dried overnight at 50 °C under vacuum. Yield: 10.76 g (83%). 1H NMR (400 MHz, DMSO-\(d^6\)): \(\delta\) (ppm) 9.65 (s, 1H), 8.26 (s, 1H), 7.99 (s, 1H), 7.33 (dd, \(J = 15.6\) and 8.8 Hz, 1H), 6.00 (dd, \(J = 15.6\) and 2.4 Hz, 1H), 5.42 (dd, \(J = 8.4\) and 2.0 Hz, 1H), 4.21 (t, \(J = 7.2\) Hz, 2H), 1.85–1.79 (m, 2H), 1.27 (s, 6H), 0.87–0.84 (m, 3H).

1-Vinyl-3-dodecylimidazolium bromide (C\(_{12}\)). A mixture of 1-vinylimidazole (4.71 g, 0.05 mol), bromododecane (12.5 g, 0.05 mol), and ethanol (20 ml) was heated at 80 °C under N\(_2\) atmosphere for 48 h. Upon solvent distillation, the obtained white solid was washed with ethyl ether for several times and dried overnight at 60 °C under vacuum. Yield: 15.92 g (93%). 1H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 10.77 (s, 1H), 7.86 (s, 1H), 7.53 (s, 1H), 7.48 (dd, \(J = 15.6\) and 8.8 Hz, 1H), 5.96 (dd, \(J = 15.6\) and 2.8 Hz, 1H), 5.37 (dd, \(J = 8.8\) and 3.2 Hz, 1H), 4.38 (t, \(J = 7.2\) Hz, 2H), 1.94–1.88 (m, 2H), 1.30–1.21 (m, 18H), 0.84 (t, \(J = 6.8\) Hz, 3H).

3,3’-Divinyl-1,1’(1,2-ethanediyl)diimidazolium dibromide (bis-C\(_2\)). A mixture of 1-vinylimidazole (18.8 g, 0.2 mol), 1,2-dibromoethane (18.7 g, 0.1 mol), and acetonitrile (150 mL) was heated at 60 °C under N\(_2\) atmosphere for 48 h. After naturally cooling to room temperature, the obtained white solid was washed by ethyl ether for several times and dried overnight under vacuum. Yield: 26.93 g (72%). 1H NMR (400 MHz, DMSO-\(d^6\)): \(\delta\) (ppm) 9.62 (s, 1H), 8.27 (s, 1H), 7.89 (s, 1H), 7.35 (dd, \(J = 15.6\) and 8.8 Hz, 1H), 5.98 (dd, \(J = 15.6\) and 2.4 Hz, 1H), 5.44 (dd, \(J = 8.8\) and 2.4 Hz, 1H), 4.82 (s, 2H).

3,3’-Divinyl-1,1’(1,6-hexanediyl)diimidazolium dibromide (bis-C\(_6\)). A mixture of 1-vinylimidazole (4.71 g, 0.05 mol), 1,6-dibromohexane (6.10 g, 0.025 mol), and acetonitrile (10 mL) was kept in dark for 1 week at room temperature. The obtained white solid was washed with acetone for several times and dried overnight under vacuum. Yield: 7.63 g (71%). 1H NMR (400 MHz, DMSO-\(d^6\)): \(\delta\) (ppm) 9.68 (s, 2H), 8.25 (s, 2H), 7.99 (s, 2H), 7.33 (dd, \(J = 15.6\) and 8.8 Hz, 2H), 6.00 (dd, \(J = 15.6\) and 2.4 Hz, 2H), 5.43 (dd, \(J = 8.8\) and 2.0 Hz, 2H), 4.23 (t, \(J = 7.2\) Hz, 4H), 1.84 (s, 4H), 1.31 (s, 4H).

**MIL-101, UiO-66, and ZIF-8.** The MOFs were prepared and activated according to the literature procedures.\(^{1-3}\)

**Bis-PC\(_2\)(Br)@MIL-101.** A mixture of activated MIL-101 (2 g) and bis-C\(_2\) (1 g) in DMF (40 mL) was stirred at room temperature for 24 h. Then, 2,2’-azobis(isobutyronitrile) (AIBN, 250 mg) in DMF (5 mL) was added, which was heated to 80 °C under N\(_2\) atmosphere for 24 h. After that, additional DMF solution (5 mL) of AIBN (250 mg) was added, which was heated at 80 °C under N\(_2\) atmosphere for 48 h. The resultant green solid was washed with DMF and methanol for three times, and dried at 50 °C under vacuum.

**Bis-PC\(_2\)(Cl)@MIL-101.** Green solid was obtained by soaking the as-synthesized bis-PC\(_2\)(Br)@MIL-101 (1 g) in a
water solution of NaCl (1 M, 250 mL) for 3 days, which was dried overnight under vacuum.

**PCₙ(Cl)@MIL-101 (n = 2, 6, and 12) and bis-PCₜ(Cl)@MIL-101.** They were prepared by the similar procedure to that of bis-PC₂(Cl)@MIL-101, except bis-C₂ was replaced by C₂, C₆, C₁₂, and bis-C₆, respectively.

**PCₜ(Cl)/bis-PCₜ(Cl)@MIL-101.** It was prepared by the similar procedure to that of bis-PC₂(Cl)@MIL-101, except bis-C₂ was replaced by a mixture of C₂ and bis-C₂.

**Bis-PC₂(Cl)/bis-PC₂(Cl)@UiO-66 and bis-PC₂(Cl)@ZIF-8.** They were prepared by the similar procedure to that of bis-PC₂(Cl)@MIL-101, except MIL-101 was replaced by UiO-66 and ZIF-8, respectively.

### 3. Sorption Experiments

**General Equations.** In the batch sorption experiment, the removal percentage (%), sorption capacity at equilibrium, $q_e$ (mg g⁻¹), and distribution coefficient, $K_d$ (mL g⁻¹), were calculated by the following equations:

- **Removal percentage (%)**

  $$\text{Removal percentage} = \frac{c_0 - c_e}{c_0} \times 100\%$$  

- **$q_e$**

  $$q_e = \frac{c_0 - c_e}{m} \times V$$

- **$K_d$**

  $$K_d = \frac{c_0 - c_e}{c_e} \times \frac{V}{m}$$

  in which $c_0$ (mg g⁻¹) and $c_e$ (mg g⁻¹) are the initial and equilibrium concentrations of adsorbate, $V$ (mL) is the volume of solution, and $m$ (g) is the mass of sorbent.

**TcO₄⁻ Sorption Kinetics.** bis-PC₂(Cl)@MIL-101 (5 mg) was added into a water solution of TcO₄⁻ (5 mL, 26 ppm). The samples were collected after stirring for 30 s, 1 min, 2 min, 5 min, and 10 min, respectively. The activity of TcO₄⁻ was determined by LSC.

**ReO₄⁻ Sorption Data Fitting by Kinetics Models.** bis-PC₂(Cl)@MIL-101 (2 mg) was added to a water solution of ReO₄⁻ (5 mL, 50 ppm). The samples were collected after stirring for 30 s, 1 min, 2 min, 5 min, and 10 min, respectively. The concentrations of ReO₄⁻ remaining in water phase were determined by ICP-OES. The equation of linearized form of pseudo-second-order model is

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{q_e k_2 n_0}$$

where the measured $q_t$ is the uptake amount of ReO₄⁻ at $t$ min (mg g⁻¹), $q_e$ is the uptake amount of ReO₄⁻ at equilibrium (mg g⁻¹), and $k_2$ is the pseudo-second-order rate constant (g mg⁻¹ min⁻¹). The model parameter and correlation coefficient are listed in Table S1.
ReO₄⁻ Sorption Data Fitting by Isotherm Models. *bis*-PC₂(Cl)@MIL-101 (5 mg) was added to a water solution (5 mL) of ReO₄⁻ at a given concentration (10–1000 ppm). The solution was stirred for 30 min to ensure the equilibrium. The concentration of ReO₄⁻ remaining in water phase was determined by ICP-OES.

To study the removal thermodynamics of ReO₄⁻ by *bis*-PC₂(Cl)@MIL-101, the Langmuir and Freundlich sorption models were used (Table S2). In the Langmuir model, the sorption of ReO₄⁻ was assumed on a homogenous surface of sorbent, following a monolayer sorption process. No interaction occurs between ReO₄⁻ and sorbent, suggesting homogenous binding site and equivalent sorption energy. The equation of the Langmuir model is

\[
\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m} \tag{5}
\]

in which \(c_e\) is the equilibrium concentration of Re in ReO₄⁻ (mg g⁻¹), \(q_e\) and \(q_m\) are the equilibrium and maximum Re sorption amount (mg g⁻¹), and \(k_L\) is the constant indirectly related to the sorption amount and sorption energy (L mg⁻¹), characterizing the affinity of ReO₄⁻ with sorbent. The fitting line was obtained by plotting \(c_e q_e\) against \(c_e\), and \(q_m\) and \(k_L\) can be calculated from the slope and intercept.

As for the Freundlich sorption model, it is based on a heterogeneous surface, suggesting different binding energies between ReO₄⁻ and the surface sites of sorbent. The equation of the Freundlich model is

\[
\ln q_e = \ln k_F + \frac{1}{n} \ln c_e \tag{6}
\]

in which \(c_e\) and \(q_e\) are the equilibrium concentration of Re in ReO₄⁻ (mg g⁻¹) and equilibrium Re sorption amount (mg g⁻¹), and \(k_F\) and \(n\) are the Freundlich constants related to the sorption amount and sorption intensity, characterizing the affinity of ReO₄⁻ with sorbent.

ReO₄⁻ Sorption by Various Sorbents. In each sample, 5 mg of sorbent (UiO-66, *bis*-PC₂(Cl)@UiO-66, ZIF-8, *bis*-PC₂(Cl)@ZIF-8, MIL-101, PC₂(Cl)@MIL-101, PC₂(Cl)/*bis*-PC₂(Cl)@MIL-101, or *bis*-PC₂(Cl)@MIL-101) was added into a water solution of ReO₄⁻ (5 mL, 200 ppm). The sample was stirred and collected after different time intervals. The concentrations of ReO₄⁻ remaining in water phase were determined by ICP-OES.

ReO₄⁻ Sorption by PC₂(Cl)@MIL-101, PC₂(Cl)/*bis*-PC₂(Cl)@MIL-101, and *bis*-PC₂(Cl)@MIL-101 under Different Concentrations. In each case, 5 mg of sorbent was added into a water solution (5 mL) of ReO₄⁻ at a given concentration (50–3000 ppm). The sample was stirred for 30 min to ensure the equilibrium. The concentrations of ReO₄⁻ remaining in water phase were determined by ICP-OES.

Stability. Stability was studied by immersing *bis*-PC₂(Cl)@MIL-101 into 2 M, 3 M, 4 M, and 6 M HNO₃ or NaOH
solutions with different pH values for one week at room temperature. The solid was separated for PXRD test.

**Effect of pH Value.** The effect of pH value on ReO$_4^-$ sorption was performed in the solutions of pH = 0–13. *bis*-PC$_2$(Cl)@MIL-101 (5 mg) was added into a water solution of ReO$_4^-$ (5 mL, 50 ppm). The sample was stirred for 30 min to ensure the equilibrium. The concentrations of ReO$_4^-$ remaining in water phase were determined by ICP-OES.

**ReO$_4^-$ Sorption in HNO$_3$ System.** In a batch experiment, a water solution (1 mL) containing 463 ppm ReO$_4^-$ and 3 M HNO$_3$ (mole ratio of NO$_3^-$: ReO$_4^-$ = 1619) was mixed with *bis*-PC$_2$(Cl)@MIL-101 (1 mg, 10 mg, 30 mg, 50 mg, 75 mg, or 100 mg). The sample was stirred for 30 min to ensure the equilibrium. The concentrations of ReO$_4^-$ remaining in water phase were determined by ICP-OES.

**Recyclability.** In the first cycle, *bis*-PC$_2$(Cl)@MIL-101 (50 mg) was immersed in a water solution of ReO$_4^-$ (50 mL, 180 ppm) for 30 min and the concentration of ReO$_4^-$ remaining in water phase was determined by ICP-OES. After that, the ReO$_4^-$ sorbed material was stirred in NaCl water solution (100 mL, 5 mol L$^{-1}$) by heating at 60 °C, and the solid was collected by centrifugation. Such recovered material was then subject to the next cycling test.

**Digestion of bis-PC$_2$@MIL-101@Re.** *bis*-PC$_2$@MIL-101@Re (30 mg) was completely digested by NaOH aqueous solution (4 M, 5 mL). The insoluble *bis*-PC$_2$ solid was collected by centrifugation, washing with water and methanol for several times, and drying overnight at 65 °C in vacuum.

**Sorption in Simulated Waste System.** A simulated Hanford Low Activity Waste (LAW) melter recycle stream was prepared, in which TcO$_4^-$ was replaced by ReO$_4^-$ . In a batch experiment, *bis*-PC$_2$(Cl)@MIL-101 (20 mg) was added into the simulated waste (5 mL). The sample was stirred for 5 min, and the concentration of ReO$_4^-$ remaining in water phase was determined by ICP-OES.
Figure S1. FT-IR spectra of (a) PC$_2$@MIL-101, (b) PC$_6$@MIL-101, (c) PC$_{12}$@MIL-101, and (d) bis-PC$_6$@MIL-101.
Figure S2. PXRD patterns of (a) PC$_2$@MIL-101, (b) PC$_6$@MIL-101, (c) PC$_{12}$@MIL-101, and (d) bis-PC$_6$@MIL-101.
Figure S3. Pore size distributions for MIL-101, bis-PC₂(Br)@MIL-101, bis-PC₂(Cl)@MIL-101, and bis-PC₂@MIL-101@Re.

Figure S4. Re 4f XPS spectra of bis-PC₂@MIL-101@Re and bis-PC₂(Cl)@MIL-101.
Figure S5. STEM and EDS mapping images of MIL-101, PC$_2$(Br)@MIL-101, and PC$_2$(Cl)@MIL-101.
**Figure S6.** STEM and EDS mapping images of MIL-101, PC₂(Br)/bis-PC₂(Br)@MIL-101, and PC₂(Cl)/bis-PC₂(Cl)@MIL-101.
Figure S7. STEM and EDS mapping images of MIL-101, bis-PC$_2$(Br)@MIL-101, and bis-PC$_2$(Cl)@MIL-101.
Figure S8. TGA plots of MIL-101 and bis-PC$_2$(Cl)@MIL-101.
Figure S9. Sorption kinetics of TeO$_4^-$ and ReO$_4^-$ by bis-PC$_2$(Cl)@MIL-101.
Figure S10. Pseudo-second-order kinetic plot for ReO$_4^-$ sorption by $\textit{bis}$-PC$_2$(Cl)@MIL-101 in water.
**Figure S11.** Column-chromatographic sorption for ReO$_4^-$.
Stationary phase: $bis$-$PC_2$(Cl)@MIL-101 (100 mg); mobile phase: ReO$_4^-$ solution (188 ppm, 2 mL).
Figure S12. STEM and EDS mapping images for the digested product of $bis\text{-}PC_2@MIL-101\text{-}Re$. 
Figure S13. (a) PXRD patterns and (b) FT-IR spectra of \textit{bis-PC}_2(\textit{Cl})@\textit{MIL}-101 after different cycles of ReO_4^- sorption.
Figure S14. $^1\text{H}$ NMR spectra of (a) C$_2$, (b) C$_6$, (c) C$_{12}$, (d) bis-PC$_2$, and (e) bis-PC$_6$. 
Table S1. Model parameters and correlation coefficient for ReO$_4^-$ (50 ppm, 5mL) sorption kinetics by \textit{bis}-PC$_2$(Cl)@MIL-101 (2 mg).

| Sorbent         | $k_2$ (g mg$^{-1}$ min$^{-1}$) | $q_e$ (mg g$^{-1}$) | $R^2$  |
|-----------------|-------------------------------|---------------------|-------|
| \textit{bis}-PC$_2$(Cl)@MIL-101 | 22.03                         | 116.13              | > 0.9999 |
Table S2. Fitting results of ReO$_4^-$ sorption by bis-PC$_2$(Cl)@MIL-101 based on the Langmuir and Freundlich models.

| Sorbent                  | Langmuir model | Freundlich model |
|--------------------------|----------------|------------------|
|                          | $q_m$ (mg g$^{-1}$) | $k_L$ (L mg$^{-1}$) | $R^2$ | $k_F$ (L$^n$/mol$^{n-1}$ g) | $n$ | $R^2$ |
| bis-PC$_2$(Cl)@MIL-101   | 269.57         | 0.87             | $>0.99$ | 145.11 | 9.27 | 0.86  |
Table S3. ReO$_4^-$ sorption performances of polyILs@MOFs composites and corresponding MOFs (sorbent: 5 mg; ReO$_4^-$: 200 ppm, 5 mL).

| Sorbent                        | Removal (%) | $K_d$ (mL g$^{-1}$) | $k_2$ (g mg$^{-1}$ min$^{-1}$) |
|--------------------------------|-------------|----------------------|---------------------------------|
| UiO-66                         | 7.08        | 76.1                 | 0.14                            |
| $bis$-PC$_2$(Cl)@UiO-66         | 49.98       | $1.01 \times 10^3$  | 0.24                            |
| ZIF-8                          | 0.53        | 5.28                 | 0.12                            |
| $bis$-PC$_2$(Cl)@ZIF-8          | 95.94       | $2.36 \times 10^4$  | 1.23                            |
| MIL-101                        | 53.49       | $1.15 \times 10^3$  | 0.05                            |
| PC$_2$(Cl)@MIL-101             | 64.98       | $1.86 \times 10^3$  | 0.06                            |
| PC$_2$(Cl)/$bis$-PC$_2$(Cl)@MIL-101 | 79.03   | $3.77 \times 10^3$  | 0.08                            |
| $bis$-PC$_2$(Cl)@MIL-101        | **99.86**   | **7.38 \times 10^5**| **4.35**                        |
| PC$_6$(Cl)@MIL-101             | 59.25       | $1.45 \times 10^3$  | 0.06                            |
| PC$_{12}$(Cl)@MIL-101          | 56.58       | $1.30 \times 10^3$  | 0.06                            |
| $bis$-PC$_6$(Cl)@MIL-101        | 72.46       | $2.63 \times 10^3$  | 0.31                            |
Table S4. Removal performances of PC$_2$(Cl)@MIL-101, PC$_2$(Cl)/bis-PC$_2$(Cl)@MIL-101, and bis-PC$_2$(Cl)@MIL-101 from the ReO$_4^-$ solutions (5 mL) at different concentrations (50 to 3000 ppm).

| Concentration (ppm) | PC$_2$(Cl)@MIL-101 | PC$_2$(Cl)/bis-PC$_2$(Cl)@MIL-101 | bis-PC$_2$(Cl)@MIL-101 |
|---------------------|---------------------|----------------------------------|-----------------------|
| 50                  | 1.00                | 1.00                             | 1.00                  |
| 75                  | 1.00                | 1.03                             | 1.03                  |
| 100                 | 1.00                | 1.09                             | 1.10                  |
| 150                 | 1.00                | 1.23                             | 1.27                  |
| 200                 | 1.00                | 1.21                             | 1.49                  |
| 250                 | 1.00                | 1.34                             | 1.59                  |
| 300                 | 1.00                | 1.40                             | 1.99                  |
| 1000                | 1.00                | 1.41                             | 3.64                  |
| 2000                | 1.00                | 1.87                             | 4.89                  |
| 3000                | 1.00                | 2.95                             | 8.51                  |
Table S5. Composition of simulated Hanford LAW melter recycle stream.

| Anion     | Concentration (mol L⁻¹) | Anion: TcO₄⁻ (mole ratio) |
|-----------|-------------------------|---------------------------|
| ReO₄⁻     | 1.94 × 10⁻⁴             | 1.0                       |
| NO₃⁻      | 6.07 × 10⁻²              | 314                       |
| Cl⁻       | 6.39 × 10⁻²              | 330                       |
| NO₂⁻      | 1.69 × 10⁻¹              | 873                       |
| SO₄²⁻     | 6.64 × 10⁻⁶              | 0.343                     |
| CO₃²⁻     | 4.30 × 10⁻⁵              | 0.222                     |
**Section S4. References**

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