

## Supporting Information

### Macroporous Polymer Monoliths Fabricated by Using Metal-Organic Coordination Gel Template

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**Preparation of M-BTC coordination gels.** To prepare M-BTC coordination gels, 0.6 mmol iron nitrate nonahydrate (0.25 g) or cobaltous nitrate (0.18 g) and 0.4 mmol H<sub>3</sub>BTC were each dissolved in each 4 ml solvent (typically ethanol) containing 20 µL triethylamine (which is catalyst to deprotonate H<sub>3</sub>BTC without binding to metal ions). The metal and ligand solution were mixed together, then yellow-brown gels for Fe<sup>III</sup>-BTC coordination and mauve gels for Co<sup>III</sup>-BTC coordination were rapidly obtained in 2-5 min.

The M-BTC gel could also be constructed in the presence of organic polymer precursors. Either mixing this gel (in ethanol) with ethylene dimethacrylate (EDMA) and glycidylmethacrylate (GMA) (2:1:1, v/v) or directly conducting it in the mixture of ethanol, EDMA and GMA (2:1:1, v/v) could get the M-BTC gel in similar appearances (Fig. 1S). The obtained gel was relatively stable in such organic polymer precursors mixture if sealed and stored in a 4 °C refrigerator. But the polymerization would be occurred when this gel-polymer precursors mixture was UV irradiated (365nm) or thermally initiated in the presence of ca. 1 wt % azoisobutyronitrile (AIBN) initiator (with respect to the monomers).



**Fig. 1S** Fe-BTC and Co-BTC gels produced in organic polymer precursors

**Preparation of rigid macroporous polymer monoliths, macroporous membrane and the reference monolith.** The rigid macroporous polymer monolith was prepared by a facile molding protocol using M-BTC gel template. The polymer precursors consisted of 3.0 ml of coordination gel, 1.0 ml EDMA, 2.0 ml GMA and 25 mg AIBN. The mold, a stainless steel column (4.6 mm i.d.  $\times$  100 mm), was sealed at one end, filled with the pre-polymerization mixture and then sealed the other end. The polymerization was then triggered by heating in a water bath at a temperature of 60 °C. After polymerization, the seals were removed, the column was provided with fittings, attached to a HPLC pump, and then 0.25 M H<sub>2</sub>SO<sub>4</sub> aqueous solution, water, acetone and methanol were pumped through the monolith to remove the templates and any other soluble compounds which remained in the pores.

The macroporous P(GMA-co-EDMA) membrane was prepared by a similar method but using UV-irradiated polymerization. The polymer precursors was filled in a glass plate, and then irradiated by a 40 W UV365 lamp. After polymerization at 10 °C for 36 h, the Fe-BTC template was removed by washing with 1 M hydrochloric acid, leaving a P(GMA-co-EDMA) membrane with 2-5 um macropores. The porous membrane exhibited both softness and friability.

The reference monolith was prepared by the in-situ polymerization within a stainless-steel tube. A mixture of GMA (1.0 mL), EDMA (0.5 mL), dodecanol (0.5 mL), methanol (2.5 mL) and triethylamine (20  $\mu$ L) with AIBN (20 mg) was filled into a stainless-steel tube (50 mm  $\times$  4.6 mm i.d), sealed at both ends, and then allowed to proceed at 55 °C for 24 h. After the polymerization, the seals were removed and the column was provided with fittings, attached to the HPLC system. Tetrahydrofuran (THF) was pumped through the column at a flow-rate of 0.1 mL/min under 45 °C to remove the porogen and other soluble compounds present in the polymer rod.

**Monolithic HIC stationary phase.** HIC monolith was prepared by hydrolyzing the GMA epoxide moiety in the macroporous monolith with 0.25 M H<sub>2</sub>SO<sub>4</sub> aqueous solution at 70 °C. Then the HIC monolith was washed with deion water to neutral pH, followed by methanol and finally DI water.

**Separation of proteins on the prepared macroporous HIC monolith.** Separation of proteins was applied on the resulting HIC monolithic column with a Shimadzu Prominence 20A HPLC system. Mobile phase gradient was set as: (A) 2.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aqueous solution and (B) 0.1 M NaCl aqueous solution containing 2% 2-propanol (volume proportion), linear gradient from 100% A to 100% B within 5 min, flow-rate 3.0 mL/min. The proteins were detected at a UV wavelength 280 nm.