Electronic Supplementary Information

Spherical covalent organic frameworks as advanced adsorbents for preconcentration and separation of phenolic endocrine disruptors followed by high performance liquid chromatography

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Synthesis of TpPa-1: A pyrex tube (o.d. × i.d. = $10 \times 8 \text{ mm}^2$ and length 18 cm) is charged with Tp (63 mg, 0.3 mmol), Paraphenylenediamine (Pa-1) (48 mg, 0.45 mmol), 1.5 mL of mesitylene, 1.5 mL of dioxane, 0.5 mL of 3 M aqueous acetic acid. This mixture was sonicated for 10 minutes in order to get a homogenous dispersion. The tube was then flash frozen at 77 K (liquid N₂ bath) and degassed by three freeze-pump-thaw cycles. The tube was sealed off and then heated at 120 °C for 3 days. A red colored precipitate formed was collected by centrifugation and washed with anhydrous acetone. The powder collected was then solvent exchanged with anhydrous acetone 5-6 times and then dried at 180 °C under vacuum for 24 hours to give a deep red colored powder of TpPa-1.

Synthesis of TpPa-2: The synthesis of TpPa-2 was carried out by utilizing the same protocol with a mixture of Tp (63 mg, 0.3 mmol), 2,5-dimethylparaphenylenediamine (Pa-2), (61 mg, 0.45 mmol), 1.5 mL of mesitylene, 1.5 ml of dioxane, 0.5 mL of 3 M aqueous acetic acid. The reaction mixture was heated at 120 °C for 3 days and after the reaction the red coloured solid at the bottom of the tube was isolated by centrifugation, and washed with acetone. The powder collected was then solvent exchanged with anhydrous acetone 5-6 times and then dried at 180 °C under vacuum for 24 hours to give a deep red colored powder of TpPa-2.

Reference

S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2012, 134, 19524-19527.



Fig. S1 The adsorption equilibrium experiment of Commercial adsorbents (A), TpPa-1 (B), and TpPa-2 (C) to four endocrine disruptors.