Supporting Information

Synthesis of porphyrin and calixarene-based porous organic polymers for the superfast adsorption of bisphenol A and cationic herbicides

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Experimental Section:

Characterization:

The FT-IR spectrum was performed on a Fourier transform infrared (FT-IR) spectrophotometer (Thermo Scientific Co., United States, Nicolet 6700) and the samples were prepared using a KBr pellet. The solid-state ^{13}C NMR was measured on a Bruker INOVA 400 MHz NMR spectrometer. The N_2 adsorption-desorption isotherms were performed on a Quantachorme Micromeritics ASAP 2020 instrument at 77 K to measure the Brunauer-Emmett-Teller (BET) surface areas of the samples. The powder X-ray diffraction (PXRD) of the samples was performed on an X'Pert-Pro MPD analyzer. The surface morphology of the samples is observed by the Scanning Electron Microscope (SEM, Merlin Compact, Japan) and the Transmission Electron Microscopy (TEM, FEI-Tecnai G2 F20, USA). The thermal stability of the samples is tested by thermogravimetric analysis (TGA, TG209F3, Germany) in the range of 30-700 ℃ with a heating rate of 10 ℃ min^{-1}.

Equations:

The adsorption kinetics were analyzed *via* the pseudo-first-order and pseudo-second-order kinetic models[1].

The pseudo-first-order kinetic model is:

$$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t \tag{S1}$$

The pseudo-second-order kinetic model is:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \tag{S2}$$

Where Q_e (mg g^{-1}) is the adsorption capacity in equilibrium; Q_t (mg g^{-1}) is the adsorption capacity in t (min); k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the constants of pseudo-first-order and pseudo-second-order models, respectively.

The adsorption capacity in equilibrium (Q_e, mg g^{-1}) is calculated according to the following equation:

$$Q_e = \frac{C_i - C_e}{m} V \tag{S3}$$

Where C_i and C_e (mg L^{-1}) are the initial and final concentrations of targeted pollutants, m (g) is the weight of the adsorbents, and V (L) is the volume of the targeted pollutants solutions.

Two adsorption isothermal models including the Freundlich model and the Langmuir model are adopted to fit the adsorption isotherms data[2].

The Freundlich model is:

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{S4}$$

The Langmuir model is:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (S5)$$

Where K_F and K_L are the constants of Freundlich and Langmuir models, respectively; 1/n is an empirical parameter of the Freundlich model; C_e (mg g^{-1}) is the concentration of pollutants in equilibrium.

The corresponding parameters are calculated according to the following equations[3]:

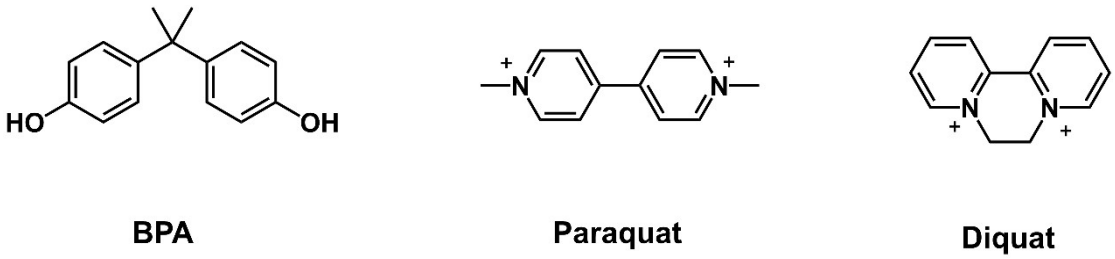
$$K^0 = \frac{Q_e}{C_e} \times c^0 \times M_A \quad (S6)$$

$$\Delta G = -RT \ln K^0 \quad (S7)$$

$$\ln K^0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (S8)$$

$$\Delta G = \Delta H - T\Delta S \quad (S9)$$

where K^0 is the thermodynamic distribution coefficient, c^0 (1 mol L^{-1}) is the standard concentration unit, and M_A (g mol^{-1}) is the molecular weights of the pollutants. ΔG (kJ mol^{-1}), ΔS (J mol^{-1} K^{-1}), and ΔH (kJ mol^{-1}) are the standard Gibbs free energy, entropy, and enthalpy changes, respectively. Moreover, T is the temperature and R (8.314 J mol^{-1} K^{-1}) is the universal gas constant.



BPA **Paraquat** **Diquat**

Fig. S1 The chemical structures of the target pollutants in this work.

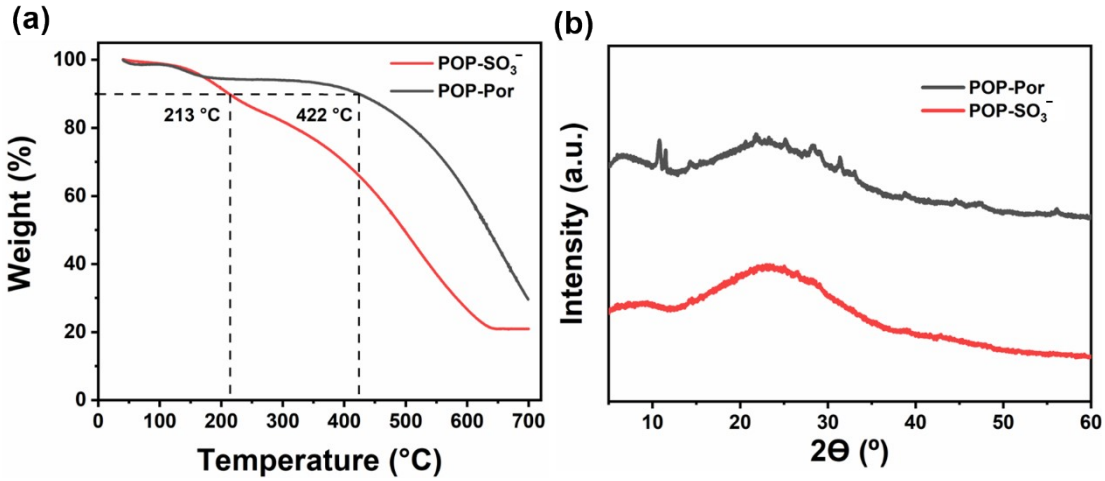


Fig. S2 The (a) TGA and (b) XRD curves of POP-Por and POP-SO_3^-.

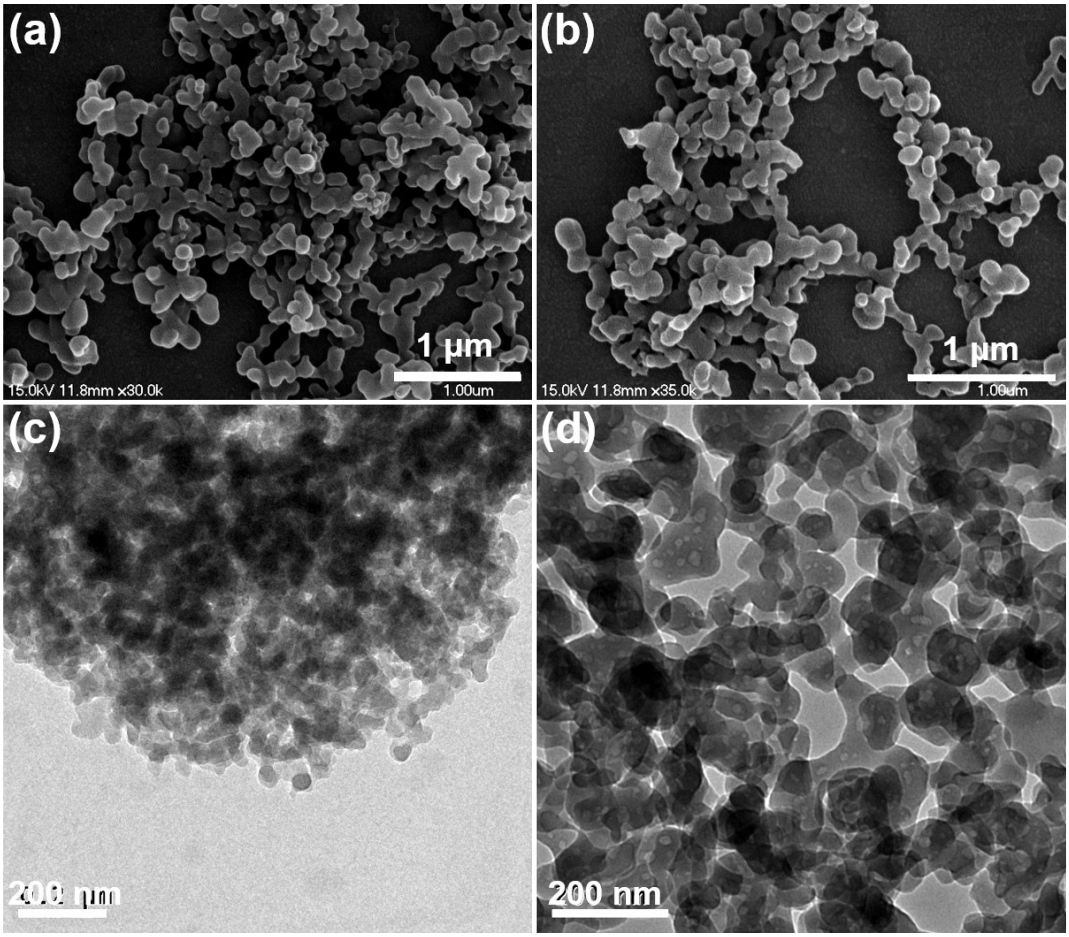


Fig. S3 The (a, b) SEM images and (c, d) TEM images of POP-Por and POP-SO_3^-.

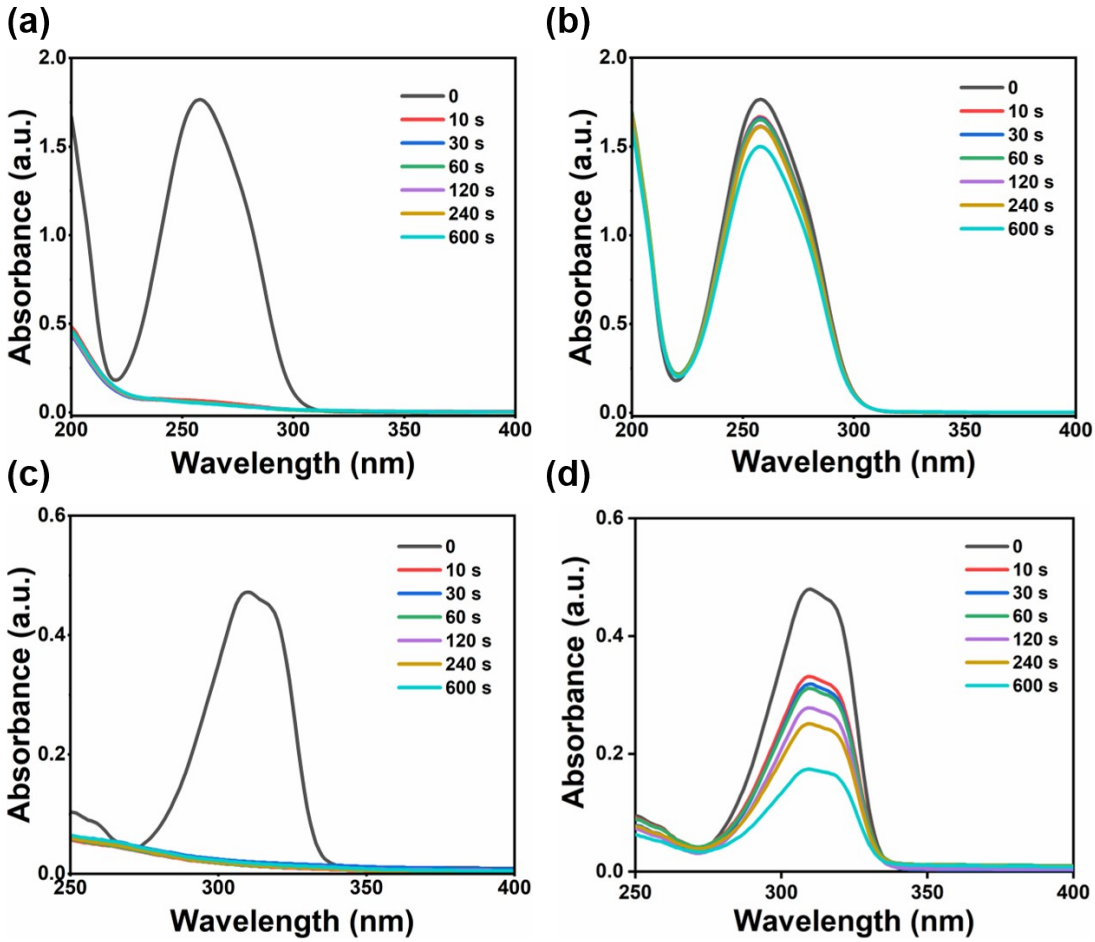


Fig. S4 The changes of UV-vis spectra of (a, b) paraquat with the addition of POP-SO_3-50% and POP-SO_3-10%; (c, d) diquat with the addition of POP-SO_3-50% (50% dosage of chlorosulfonic acid) and POP-SO_3-10% (10% dosage of chlorosulfonic acid).

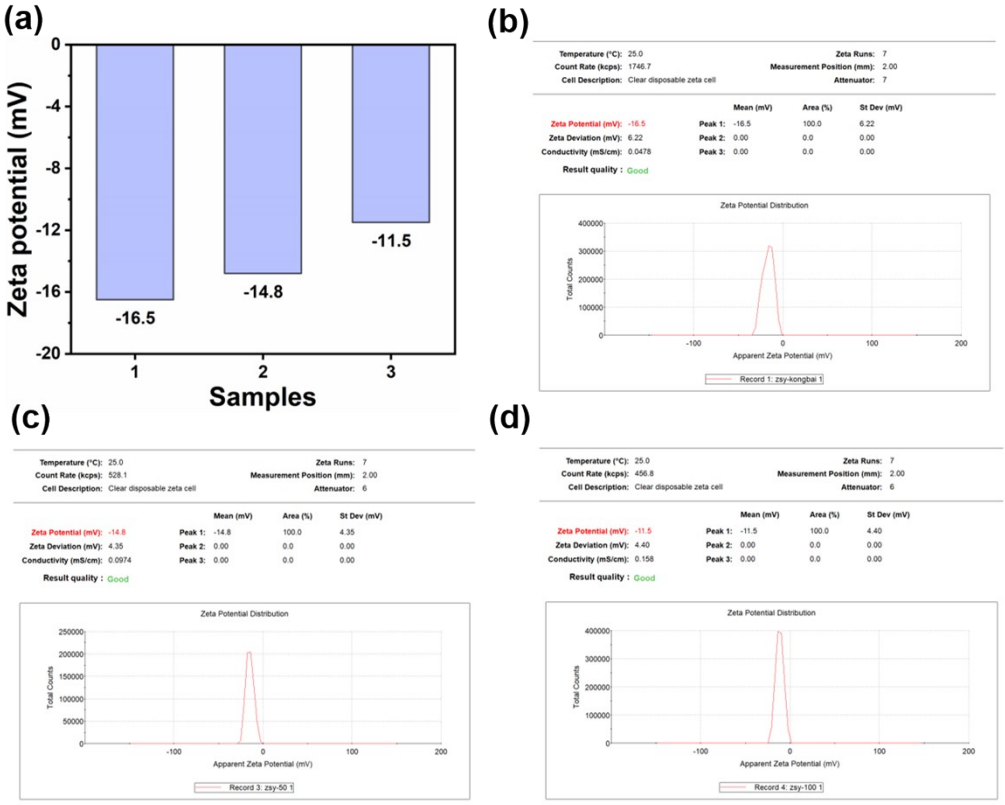


Fig. S5 (a) The zeta potentials of POP-SO_3^- before and after the adsorption of paraquat under neutral conditions. Sample 1: POP-SO_3^- itself; sample 2: POP-SO_3^- after adsorption of paraquat (50 ppm); sample 3: POP-SO_3^- after adsorption of paraquat (100 ppm); (b, c, d) the corresponding primary data.

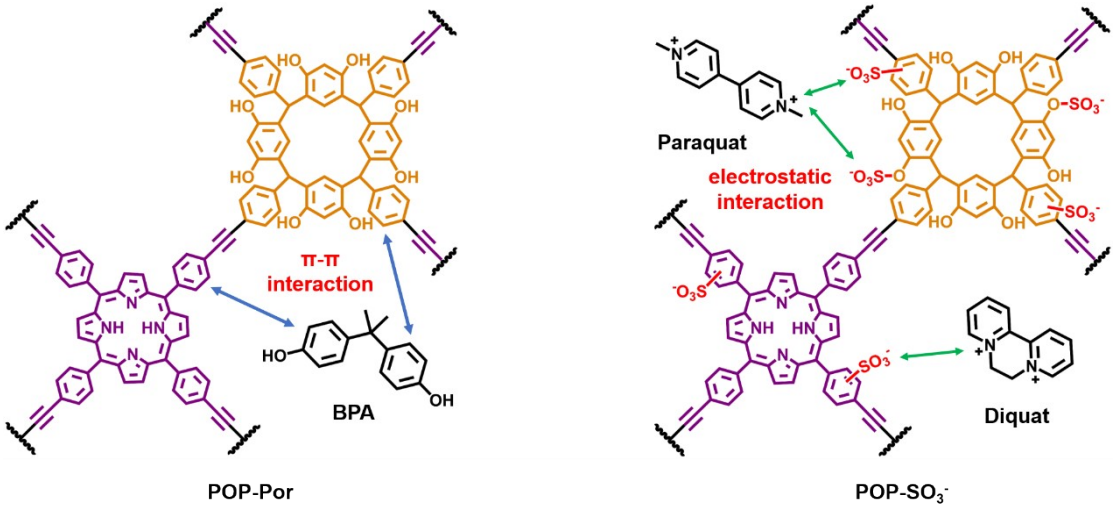


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Fig. S6 The schematic illustration of the binding sites of BPA, paraquat and diquat with POP-Por and POP-SO_3^-.

References:

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[2] I.X. Garcia-Zubiri, G. Gonzalez-Gaitano, J.R. Isasi, Sorption models in cyclodextrin polymers: Langmuir, Freundlich, and a dual-mode approach, J. Colloid Interface Sci., 337 (2009) 11-18.

[3] M. Goswami, P. Phukan, Enhanced adsorption of cationic dyes using sulfonic acid modified activated carbon, J. Environ. Chem. Eng., 5 (2017) 3508-3517.