

*Supporting information*

**Fabrication of O-enriched HyperCross-Linked Polymers and Their Adsorption of Aniline from Aqueous Solution**

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## 1. Experimental section

### 1.1 Material

Initial material macroporous low crosslinked chloromethylated polystyrene (CMPS) were purchased from Nankai University Chemical Factory (Tianjin, China). Its cross-linking degree was 6 wt.% and chlorine content was 4.88 mmol/g. Other pore parameters were shown in Table 1. The anhydrous catalysts  $\text{FeCl}_3$  and  $\text{K}_2\text{CO}_3$ , 2,2'-dihydroxybiphenyl (DBP), 1,5-dihydroxynaphthalene (NP), phenol (PH), formaldehyde dimethyl acetal (FDA), cyanuric chloride (CC),  $\alpha,\alpha'$ -dichloro-p-xylene (DCX), and 4,4'-bis(chloromethyl)-1,1'-diphenyl (BCMBP) were all purchased from Shanghai Aladdin Reagent Co. Ltd (Shanghai, China). 1,2-dichloroethane (DCE), o-dichlorobenzene (o-DCB), N,N-Dimethylformamide (DMF) and aniline were purchased from Xilong Chemicals. these agents were analytical pure agents without further purification before use.

### 1.2 Preparation of intermediate polymers

The synthetic procedure of the intermediate polymers PS@DBP was as follows: 20 g CMPS was swelled in 120 mL N,N-Dimethylformamide (DMF) overnight, then 5 g anhydrous  $\text{K}_2\text{CO}_3$  and 18 g 2,2'-dihydroxybiphenyl (DBP) were quickly added and the mixture were stirred under  $\text{N}_2$  atmosphere and at room temperature for 30 min. It was fully dissolved and reacted at 368K for 24 h. The light white microspheres were obtained by filtration and washed thoroughly with absolute ethanol, methanol, 1 M HCl, and distilled water. The product was further purified in a Soxhlet extractor with water and ethanol solution for 24 h to remove the impurities. Then the product was collected after drying under vacuum at 60°C for 24 h. The other polymers are constructed by the same method.

### 1.3 Preparation of PS@DBP-FDA

10 g dried PS@DBP resin was swollen in 100 mL o-dichlorobenzene (o-DCB) overnight. After quickly adding 4 g anhydrous FeCl<sub>3</sub>, 15 mL formaldehyde dimethyl acetal (FDA) and stirred for 30 min. The reaction was slowly heat up to 353K and retained for 24h. The dark brown microspheres were obtained by filtration and washed thoroughly with o-DCB, absolute ethanol, methanol, 1 M HCl, and distilled water. The product was further purified in a Soxhlet extractor with water and ethanol solution for 24 h to remove the catalyst. Then the product was collected after drying under vacuum at 60°C for 24 h. The other polymers are synthesized by the same method.

#### *1.4 Characterization*

The pore structure of the resin was determined by a nitrogen adsorption-desorption isotherm (77 K) using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer (Micromeritics Instrument Corporation, USA). Prior to measurement, a degassing process was carried out for 300 min at a nitrogen purge and degassing pretreatment temperature of 363 K. The BET surface area ( $S_{BET}$ ) was calculated by the BET model including  $P/P_0=0.05-0.30$ , and the total pore volume was calculated ( $V_{total}$ ) at  $P/P_0=0.99$ . The micropore area ( $S_{micro}$ ) and micropore volume ( $V_{micro}$ ) were determined by the Barrett-Joyner-Halenda (BJH) model, while the pore size distribution (PSD) was calculated by the non-local density functional theory (NLDFT) model. The Fourier transform infrared spectroscopy (FT-IR) of resins was subjected to measurement by KBr disk method using Nicolet 510P Fourier transform infrared spectroscopy (Thermo Nicolet Corporation, USA) in the range of 500-4000 cm<sup>-1</sup>. Its resolution is 1.0 cm<sup>-1</sup>. The chlorine content of the resins was measured according to the Volhard method<sup>1</sup>. The contact angles (CA) of the resins were measured by JC 2000D1 contact angle measuring instrument (Zhongchen, Shanghai).

The X-ray photoelectron spectroscopy (XPS) of the samples was investigated on a Thermo ESCALAB 250Xi (ThermoFisher-VG Scientific, China) spectrometer with an Al K-alpha source. The morphology of the polymers was detected by using a field emission scanning electron microscope (FESEM, FEI Verios 460) operated at 10 kV. The concentration of phenol in aqueous solution was determined using a UV-2450 spectrophotometer.

### *1.5 Adsorption isotherm and adsorption kinetics*

0.05 g dry resins were accurately weighed and added to a dry 100 mL erlenmeyer flask with 50 mL adsorbate aniline solution with its initial concentration at 100.9, 202.2, 303.2, 404.3, and 506.4 mg/L respectively. In a constant temperature oscillator at a certain temperature (298, 308, and 318 K), the conical flask was fixed and shaken at a constant speed for 4 hours to balance the adsorption of the resin on the adsorbate. The equilibrium concentration of aniline solution was measured at the maximum adsorption wavelength (aniline:  $\lambda_{\max} = 280$  nm), then calculate the equilibrium adsorption capacity of the resin on the adsorbate  $q_e$  (mg/g) according to the equation  $q_e = (C_0 - C_e)V/W$  (Eq.1)

Where  $q_e$  is the equilibrium capacity (mg/g),  $C_e$  and  $C_0$  are the equilibrium and initial concentration (mg/L),  $V$  is the solution volume (L), and  $W$  is the resin mass (g). The adsorption isotherms of aniline for each resin at a certain temperature were plotted with  $C_e$  as the abscissa and  $q_e$  as the ordinate.

The kinetic adsorption was similar to the equilibrium adsorption. 0.5 g dry resins were accurately weighed and added to a dry 250 mL erlenmeyer flask with 50 mL adsorbate aniline solution with its initial concentration at 506.4 mg/L. After reaching equilibrium through oscillation, the concentration of aniline  $C_t$  (mg/L) at the contact time ( $t$ ) was measured, and the capacity  $q_t$  (mg/g) was calculated. The adsorption

kinetics curve of resin to aniline was plotted with  $t$  as the horizontal coordinate and  $q_t$  as the vertical coordinate.

Figure S1 Contact angles of (a) CMPS; (b) PS@DBP; and (c) PS@DBP-FDA

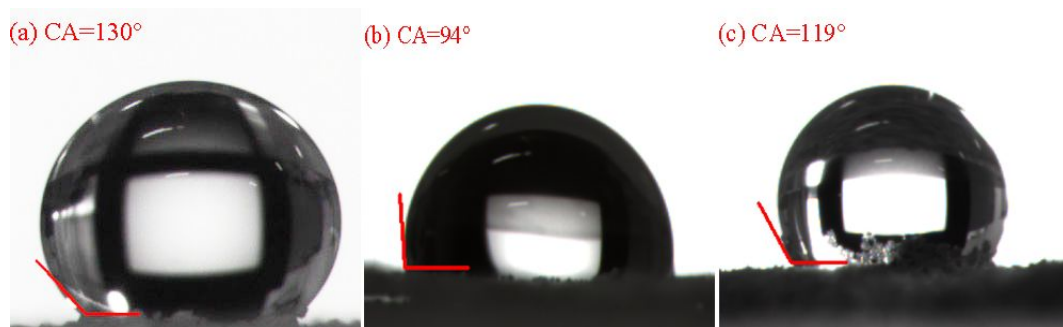


Figure S2 FT-IR spectra of the polymers

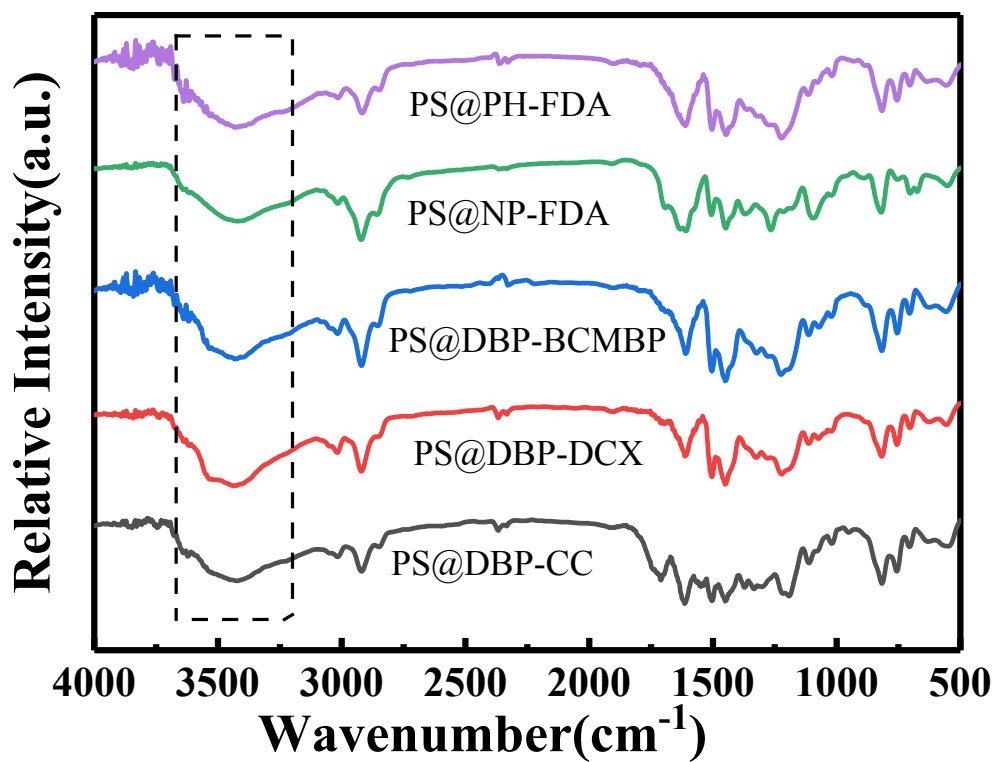


Figure S3 SEM images (a, d) CMPS, (b, e) PS@DBP, (c, f) PS@DBP-FDA and TEM images of the polymers (g) CMPS, (h) PS@DBP, (i) PS@DBP-FDA

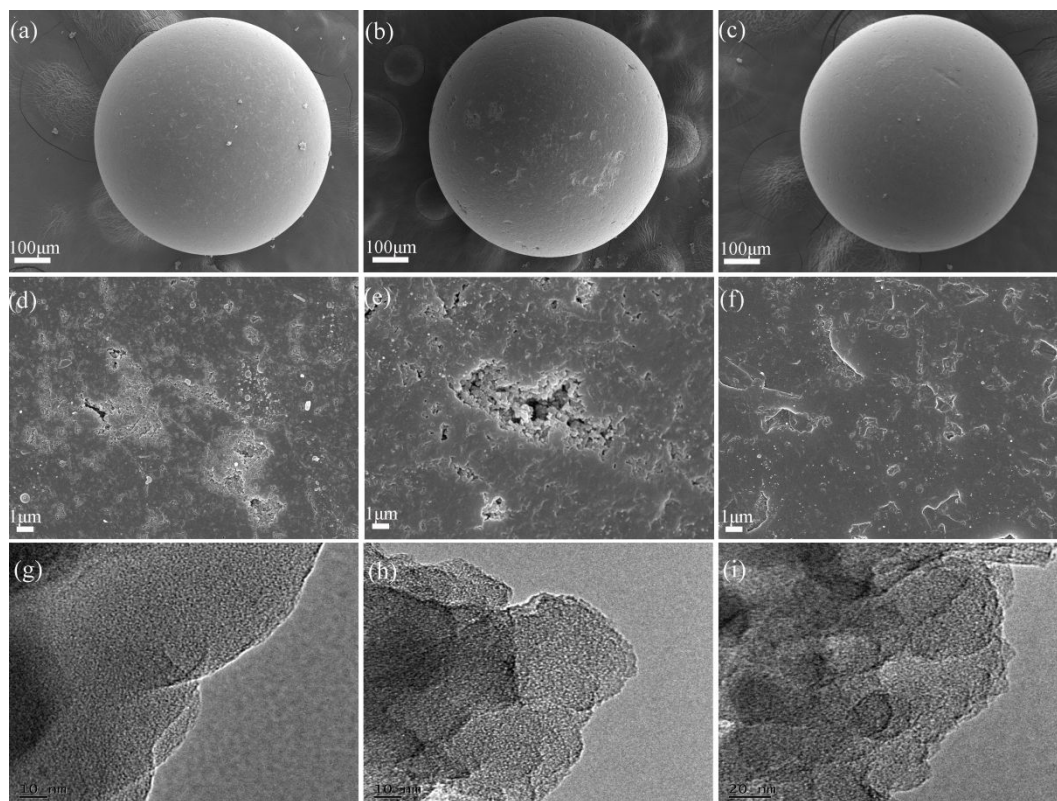




Figure S4 Vant-Hoff plotting of  $\ln(q_e/C_e)$  versus  $1/T$  (PS@DBP-FDA)

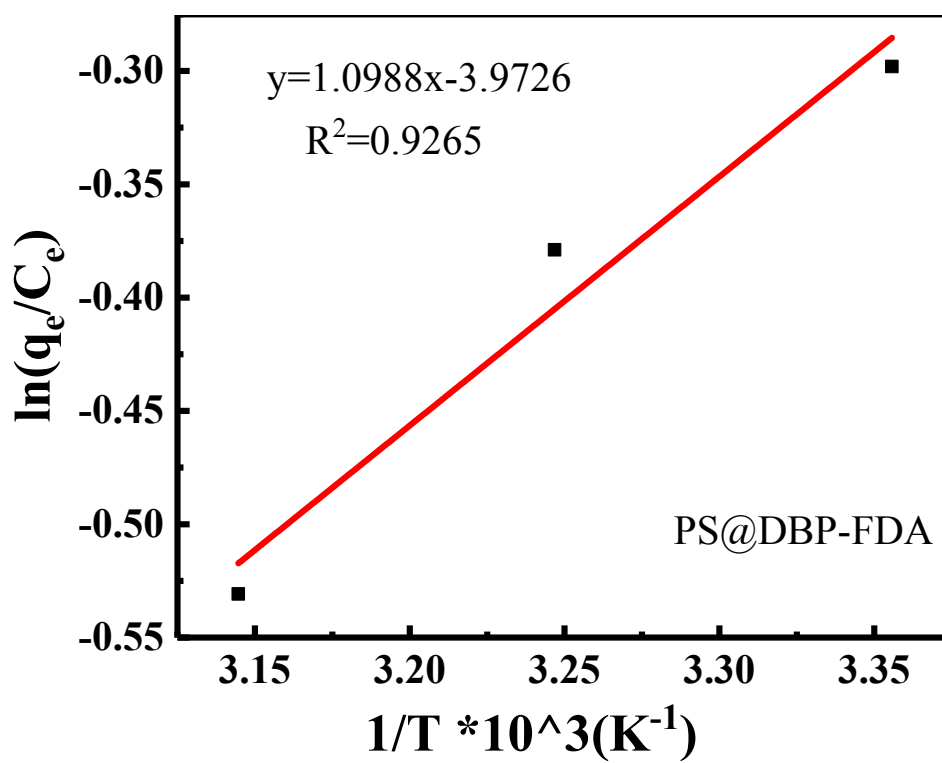


Figure S5 (a) Pseudo first order of the polymers, (b) pseudo second order of the polymers

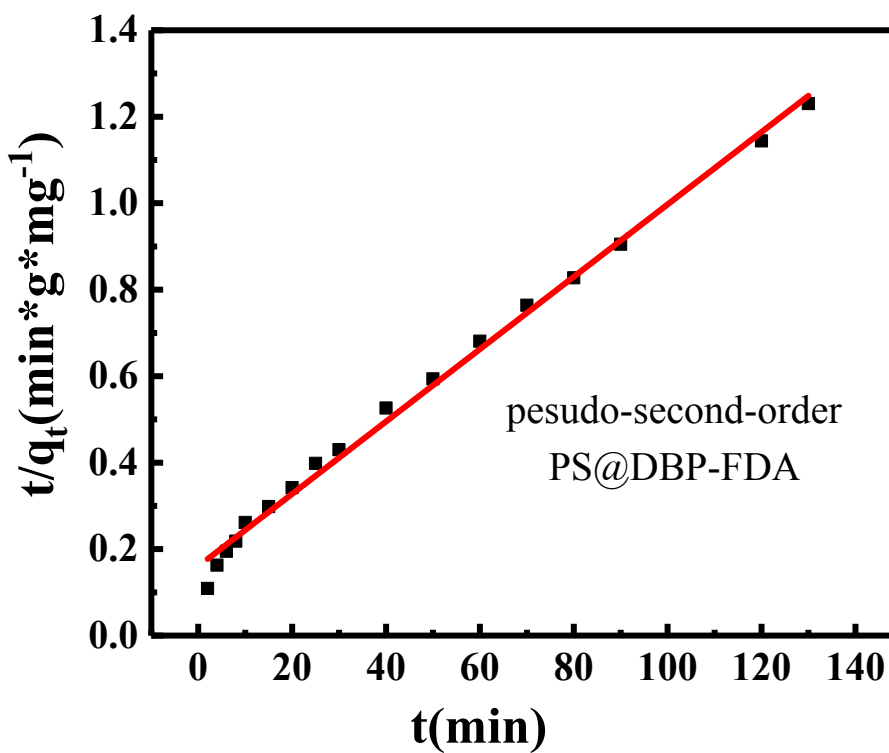
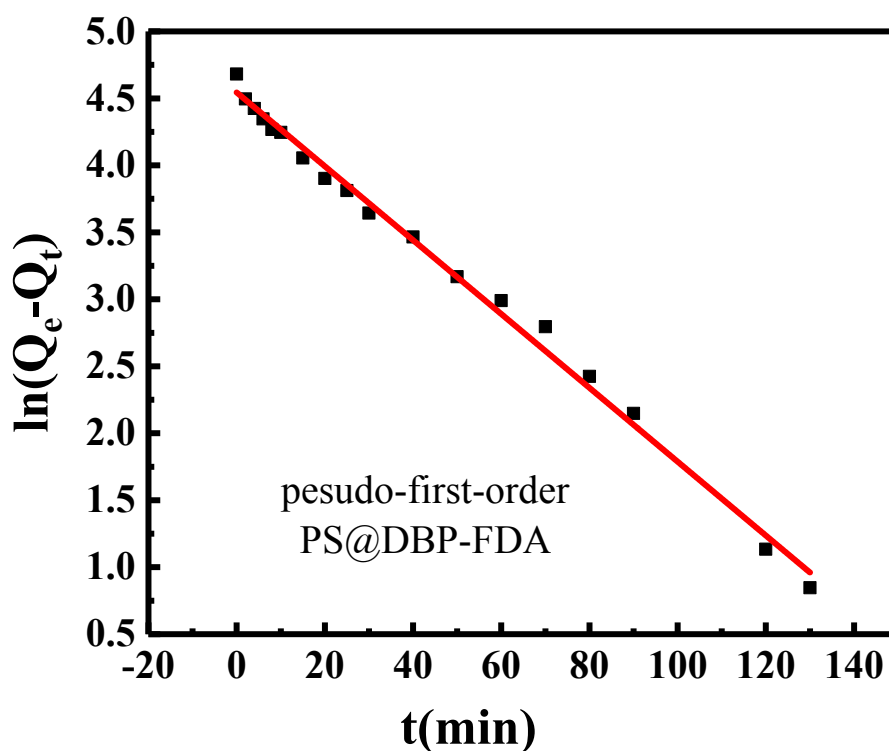


Figure S6 Effect of the amount of polymer on the adsorption of aniline on the polymer

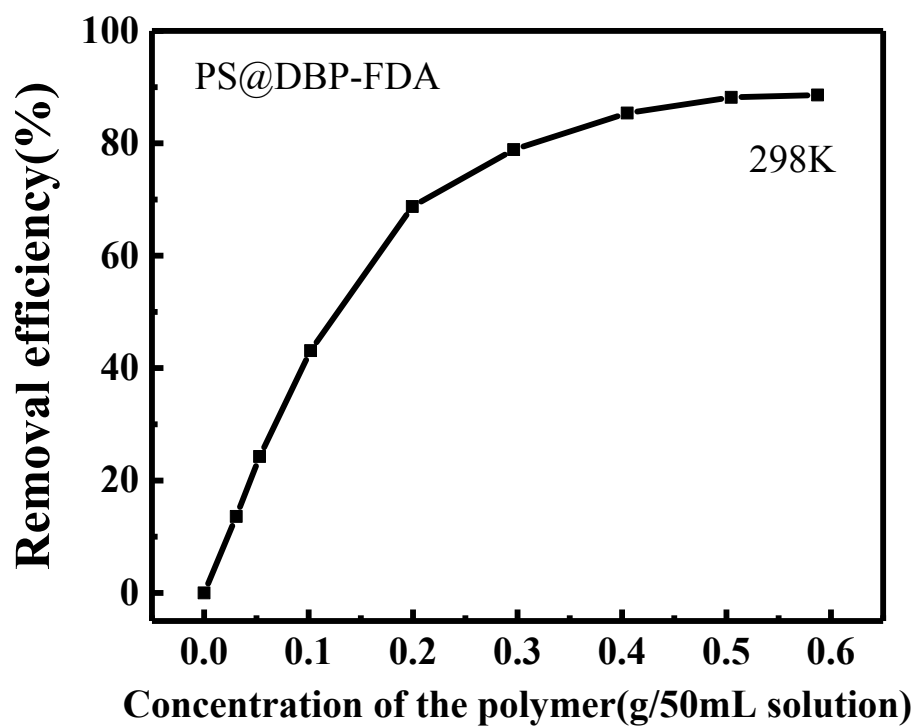


Figure S7 The recycling times of aniline adsorption on PS@DBP-FDA

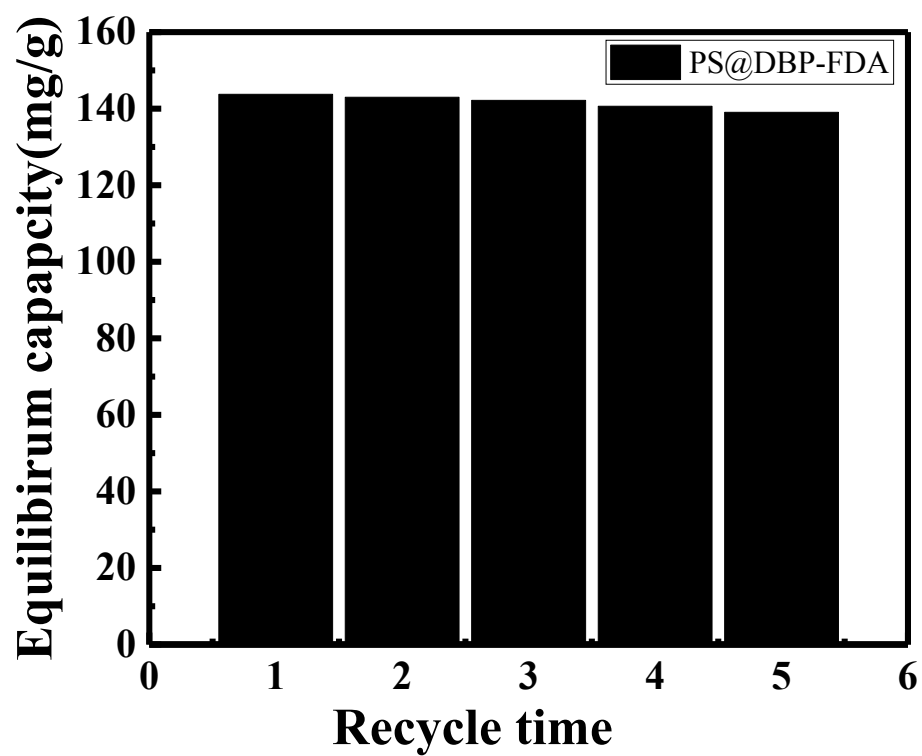


Figure S8 Adsorption of different amines by PS@DBP-FDA

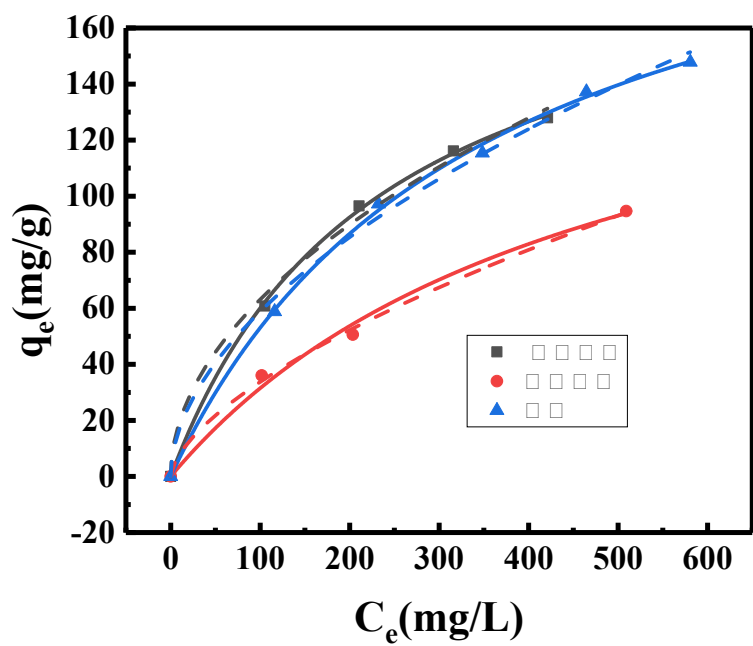


Figure S9 XPS spectra survey of PS@DBP-FDA before and after adsorption of aniline;

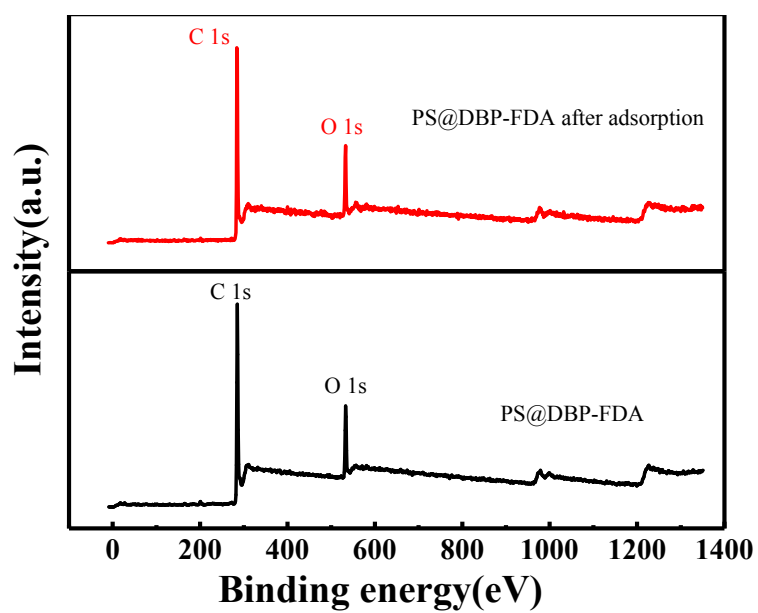


Figure S10 Possible interaction between aniline and the polymers

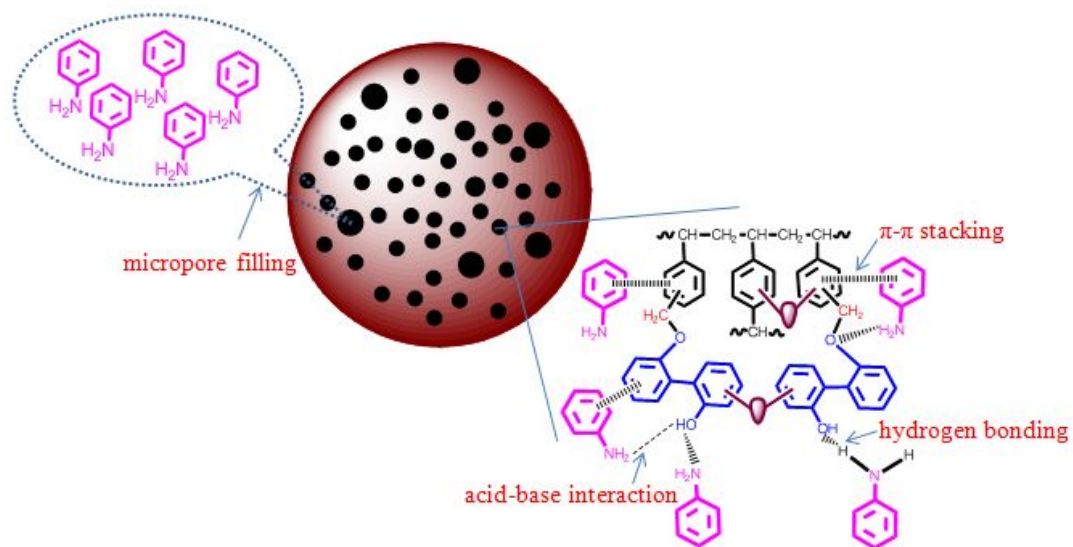


Table S1 Correlated parameters of the equilibrium data for the adsorption of aniline on the polymers according to the Langmuir and Freundlich model

	Langmuir model			Freundlich model		
	$K_L$	$q_m/$	$R^2$	$K_F$	$n$	$R^2$
	/(L/mg)	(mg/g)		/(mg/g)((L/mg) <sup>1/n</sup> )		
CMPS 298 K	$7.38 \times 10^{-4}$	87.9	0.9926	0.14	1.21	0.9961
PS@DBP 298 K	$1.76 \times 10^{-3}$	105.8	0.9962	0.75	1.48	0.9960
PS@DBP-FDA 298 K	$4.94 \times 10^{-3}$	223.7	0.9987	6.91	1.94	0.9913
298 K	$4.94 \times 10^{-3}$	223.7	0.9987	6.91	1.94	0.9913
308 K	$8.51 \times 10^{-3}$	148.9	0.9921	10.62	2.49	0.9934
318 K	$8.72 \times 10^{-3}$	126.5	0.9968	9.89	2.59	0.9955



Table S2 The adsorption thermodynamic parameters of PS@DBP-FDA

Temperature (K)	$\Delta G$ (kJ·mol <sup>-1</sup> )	$\Delta H$ (kJ·mol <sup>-1</sup> )	$\Delta S$ (J·(mol·K) <sup>-1</sup> )
298 K	1.626	-21.04	-76.06
308 K	2.389	-21.04	-76.06
318 K	3.147	-21.04	-76.06

Table S3 Fitted parameters for the kinetics adsorption data of aniline on the polymers by pseudo-first-order rate and pseudo-second-order rate equations at 298 K.

	Peudo-first-order			Peudo-second-order		
	$K_1 /$ ( $\text{min}^{-1}$ )	$q_m$ ( $\text{mg/g}$ )	$R^2$	$k_2 /$ ( $\text{g}/(\text{mg}\cdot\text{min})$ )	$q_{\text{cal}} /$ ( $\text{mg/g}$ )	$R^2$
PS@DBP-HC	0.02757	94.09	0.9939	$4.37 \times 10^{-4}$	119.47	0.994
P						1

Table S4 Correlated parameters of the equilibrium data for the adsorption of polymer PS@DBP-FDA on the different amines at 298 K according to the Langmuir and Freundlich model

	Langmuir model			Freundlich model		
	$K_L$ (L/mg)	$q_m$ (mg/g)	$R^2$	$K_F$ (mg/g)((L/mg) <sup>1/n</sup> )	$n$	$R^2$
aniline	4.94×10 <sup>-3</sup>	223.7	0.9987	6.91	1.94	0.9913
PPD	2.09×10 <sup>-3</sup>	182.1	0.9899	1.49	1.49	0.9946
MPD	4.26×10 <sup>-3</sup>	200.9	0.9992	4.35	1.76	0.9886

## References

- (1)Caldwell, J. R.; Moyer, H. V., Determination of chloride: A modification of the Volhard method. *Ind. Eng. Chem. Analy. Edit.* **1935**, 7, (1), 38-39.