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ORIGINAL PAPER

Synthesis of novel calix[6]-1,4-crown-based netty polymer and its excellent adsorption capabilities for aniline derivatives

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Abstract By introducing four ester groups on *p-tert*-butylcalix[6]-1,4-crown-4 and then ammonolysis with ethanolamine, *p-tert*-butylcalix[6]-1,4-crown-4 amido derivative with four terminal hydroxyl groups (**4**) was obtained in good yield. Further by reacting compound **4** with 1,1,1-tris(tosylatemethyl)propane (**6**) in NaH/THF system, the novel netty calix[6]-1,4-crown-based polymer **7** was prepared in "4+3" condensation mode. The structure of polymer **7** was confirmed by elemental analysis, IR and ^{1}H NMR spectra. The loose pores and cross-linked netty architecture were observed for polymer **7** in its SEM images. The M_n of polymer **7** was 39,816 which indicated an average of approximately 23 calixarene units in each polymer molecule. Polymer **7** exhibited outstanding adsorption abilities for series of aniline derivatives (aniline, *o*-phenylenediamine, *m*-phenylenediamine, *p*-phenylenediamine, *o*-nitroaniline, *m*-nitroaniline and *p*-nitroaniline). The adsorption percentages for these aniline derivatives were above 90 %. The saturation adsorption capacities for aniline and *p*-nitroaniline were as high as 2.30 and 2.22 mmol/g, respectively. The adsorption abilities of polymer **7** kept stable at pH 6–10 and it could be re-used after desorption of 10 % HCl. The high adsorption abilities of polymer **7** for aniline derivatives were not just because of π–π stack action of the phenyl groups and the hydrogen bond action, but also due to the stable conformation of calix[6]arene skeleton and big cavity, which were favorable for adsorption of aniline derivatives.

Keywords Calix[6]crown · Polymer · Synthesis · Adsorption · Aniline

Introduction

In the past few decades, calixarenes have been considered as excellent building blocks to construct interesting receptors for ions and biomolecules [1]. With the extensive and in-depth studies of all kinds of calixarene derivatives, more and more attentions have been paid to calixarene-based polymers. These polymers are usually easily processed into materials as effective extraction agents for toxic heavy metal cations or polluted organic molecules in water [2–4]. To prepare calixarenes-based polymers, one common practice is by immobilization of calixarene units onto polymer matrix such as peptide resin [5], PEG [6], polystyrene [7], dextrans [8], polysilane [9], Merrifield resin [10], polyacrylate [11], and silica gel [12]. Another method is by copolymerization of calixarene with other active *bis*-functional monomers, such as bisphenol [13], styrene [14, 15], vinyl acetate [16], diisocyanate [17], poly(ethyleneglycol) [18], terephthaloyl dichloride [19], norbornene [20], dibromoxylene [21], and no tri-functional monomer has been studied so far. Compared with grafting method, the copolymerization method is more useful in preparation of calixarene-based polymers with greater amount of calixarene units in polymers, which are favorable for acquiring excellent recognition characteristics based on calixarene units. For example, lately, we prepared thiacalix[4]arene-based polymers with excellent absorption properties for metallic cations and aniline derivatives [22].

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Up to now, although the syntheses and excellent complexation properties of various calix[4]arene-based polymers have been achieved, the research works on macrocyclic calixarenes, such as calix[6]arene-based polymers are seldom reported [23–27]. Theoretically, to compare calix[4]-arene-based polymer having small cavity for absorption of metallic cations, calix[6]arene-based polymer possess bigger tri-dimensional cavity, which is in favor of binding guests with larger cubage, such as organic molecules. However, the flexible and unstable conformation of calix[6]arene is a barrier to produce materials with excellent complexation abilities. In order to eliminate the flexibility of calix[6]arene conformation, an effective method has been to construct bridging structures on calix[6]arene skeleton. We have reported some calix[6]-1,4-crowns with stable cone conformation [28], and further prepared "4+2" condensed calix[6]-1,4-crown-based polyamino polymers with excellent adsorption abilities for soft metallic cation, although no adsorption ability for organic molecules has yet been achieved [27]. In the present work, we prepared another novel calix[6]-1,4-crown-based netty polymer in "4+3" condensation and studied the adsorption abilities for organic aniline derivatives for the first time. The results show that this calix[6]-1,4-crown-based netty polymer possess excellent adsorption abilities for aniline derivatives as expected.

Experimental

Materials and measurements

^{1}H NMR Spectra were recorded in $CDCl_3$ on a Bruker-ARX 500 instrument at room temperature, using TMS as an internal standard. Elemental analyses were performed at Carlo-Erba 1106 Elemental Analyzer. Osmometric molecular weight determinations were carried out by a Knauer vapour pressure osmometer at concentrations of ca. 10^{-3} M in $CHCl_3$ (37 °C). IR Spectra were recorded on Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. UV–Vis measurements were performed on a Varian UV–Vis instrument. All solvents were purified by standard procedures before use. All other chemicals, except specifically instructed, were analytically pure and used without further purification. All reactions were carried out under nitrogen atmosphere. Calix[6]-1,4-crown-4 tetraesters (**3**) and compound **6** were synthesized by appropriate methods given in literature [28].

Synthesis of calix[6]-1,4-crown-4 tetraamides (**4**)

Compound **3** (1.43 g, 1 mmol) and ethanolamine (0.6 g, 10 mmol) were refluxed in toluene–methanol (80 mL, V:V = 1:1) for 10 h. Then the solvent was removed under reduced pressure and the residue was treated with water to give crude product. After recrystallization from CH_2Cl_2/MeOH, compound **4** was obtained as white powder in 94 % yield. **4**: mp 273–275 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.87 [s, 36 H, $C(CH_3)_3$], 1.42 [s, 18 H, $C(CH_3)_3$], 2.51 (bs, 4 H, OH), 3.15 (s, 8 H, NCH_2), 3.42 (d, 4 H, $J = 15.0$ Hz, $ArCH_2Ar$), 3.49 (s, 4 H, OCH_2), 3.56 (m, 10 H, OCH_2 and $ArCH_2Ar$), 3.80 (bs, 8 H, CH_2O), 4.25 (d, 4 H, $J = 15.0$ Hz, OCH_2CO), 4.32 (d, 4 H, $J = 15.0$ Hz, OCH_2CO), 4.42 (d, 2 H, $J = 15.0$ Hz, $ArCH_2Ar$), 4.51 (d, 4 H, $J = 15.0$ Hz, $ArCH_2Ar$), 6.69, 6.93, 7.35 (s, each, 4 H, each, ArH), 7.85 (bs, 4 H, NHCO). ESI–MS *m/z* (%): 1491.4 (M^+, 100). Anal. Calcd. for $C_{88}H_{122}O_{16}N_4$: C 70.84, H 8.24, N 3.75; Found: C 70.86, H 8.28, N 3.73.

Synthesis of novel calix[6]-1,4-crown-4-based netty polymer (**7**)

Under nitrogen atmosphere, the mixture of compound **4** (0.75 g, 0.5 mmol) and NaH (0.15 g, 6.5 mmol) was stirred in 30 mL of dry THF for 30 min at room temperature. Then 5 mL THF solution of compound **6** (0.4 g, 0.67 mmol) was dropped in it. The solution was stirred and refluxed for 12 h until the materials utterly vanished under the monitor of TLC. After reaction, the excess NaH was eliminated by addition of a minimal quantity of methanol (CAUTION!). Then the solvent was removed under reduced pressure. The residue was treated with distilled water (50 mL) and extracted with $CHCl_3$ (50 mL). The organic layer was separated, dried with $MgSO_4$. After evaporating off the solvent to dryness, the powder was washed by a small amount of acetone to remove small molecules and it was dried in vacuum. An amount of 1.12 g of polymer **7** was obtained as light yellow powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.87–0.99 [m, 40 H, $C(CH_3)_3$ and $\underline{CH_3}CH_2$], 1.25–1.39 [m, 21 H, $C(CH_3)_3$ and CH_3CH_2], 3.16 (bs, 8 H, NCH_2), 3.27 (bs, 8 H, OCH_2), 3.41–4.48 (m, 40 H, $ArCH_2Ar$, OCH_2CO and OCH_2), 6.65–7.29 (m, 12 H, ArH), 8.13 (bs, 4 H, NHCO). IR (KBr) ν: 3,463 (NH), 1,645 (C=O) cm^{-1}; the elemental analysis, IR spectrum, SEM, and osmometric M_n of polymer **7** are shown in Table 1, Figs. 1 and 2, respectively.

Adsorption percentages of polymer **7**

According to a published method [27], 10 mg of polymer was added to 10 mL of water–ethanol (V:V = 8:2) solution

Table 1 Elemental analysis (%) and molecular weight of polymer **7**

	C (%) found (calcd.)	H (%) found (calcd.)	N (%) found (calcd.)	M_n
7	69.21 (69.34)	8.11 (8.04)	3.28 (3.37)	39,816

Table 2 Aniline derivatives adsorption percentages of polymer **7**

	AN	*o*-PA	*m*-PA	*p*-PA	*o*-NA	*m*-NA	*p*-NA
7	95.7	94.3	93.5	90.1	94.2	92.6	96.8
8[a]	65.5	70.2	72.9	86.8	84.5	88.9	94.2

AN aniline, *o-PA* *o*-phenylenediamine, *m-PA* *m*-phenylenediamine, *p-PA* *p*-phenylenediamine, *o-NA* *o*-nitroaniline, *m-NA* *m*-nitroaniline, *p-NA* *p*-nitroaniline

[a] **8** was an thiacalix[4]-based netty polymer obtained by reacting thiacalix[4]arene tetraesters with *tri*-(ethyleneimine), which possessed outstanding adsorption abilities [22]

of aniline compounds (1.0×10^{-3} mol/L). After stirring for 24 h at 25 °C, the mixture was filtered. The concentration of aniline compound after adsorption in filtrate was examined by UV spectra. The percentage of aniline compound adsorbed by polymer was calculated as follows:

$$E\,(\%) = (C_0 - C)/C \times 100$$

where E is the adsorption percentage of polymer, C_0 and C are the concentration of aniline compound before and after adsorption, respectively. Average of twice-independent experiments was carried out. Blank control experiment in the absence of the calixarene polymer showed that the change of concentration before and after stirring for 24 h at 25 °C was less than 1 %.

Saturated adsorption capacity of polymer 7

According to reported method [29], the approach of changing the volume of aniline derivatives was employed to examine the saturated adsorption capacity. The polymer **7** (10 mg) was added in sequences into solutions of aniline derivatives (1.0×10^{-3} mol/L), of which the volumes were 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 and 60 mL, respectively. Then the mixture was stirred for 24 h at 25 °C and filtered. The concentration in the filtrate was determined by UV spectra. The adsorption capacity was calculated as following:

$$Q = (C - C^{*})V/W$$

where Q is the adsorption capacity, C is the initial concentration before adsorption, C^{*} is the concentration after adsorption, V is the volume of solution and W is the mass of the polymer.

Adsorption percentages at different pH values

According to reported method [29], the polymer (10 mg) and solutions of aniline or *p*-nitroaniline (1×10^{-3} mol/L, 10 mL) at different pH values were mixed and stirred for 24 h at 25 °C. After filtration, the concentration of *p*-nitroaniline was examined by UV spectra and the adsorption percentage was counted.

Results and discussions

Synthesis and characterization

Scheme 1 shows the synthetic route of novel polymer **7**. Compound **3** was synthesized according to published method [28]. The ammonolysis of compound **3** with ethanolamine afforded compound **4** in high yield. Further, by condensating compound **4** with compound **6** in NaH/THF system, the novel polymer **7** was obtained in good yield. Since compounds **4** and **6** possessed four and three reactive groups, respectively, polymer **7** was a tri-dimensional netty "4+3" cross-linking polymer. It noteworthy, that this kind of "4+3" cross-linking polymer is reported for the first time in the field of a calixarene-based polymer. The structure of polymer **7** was confirmed by elemental analysis, IR spectra, ^{1}H NMR spectra, SEM images, and etc.

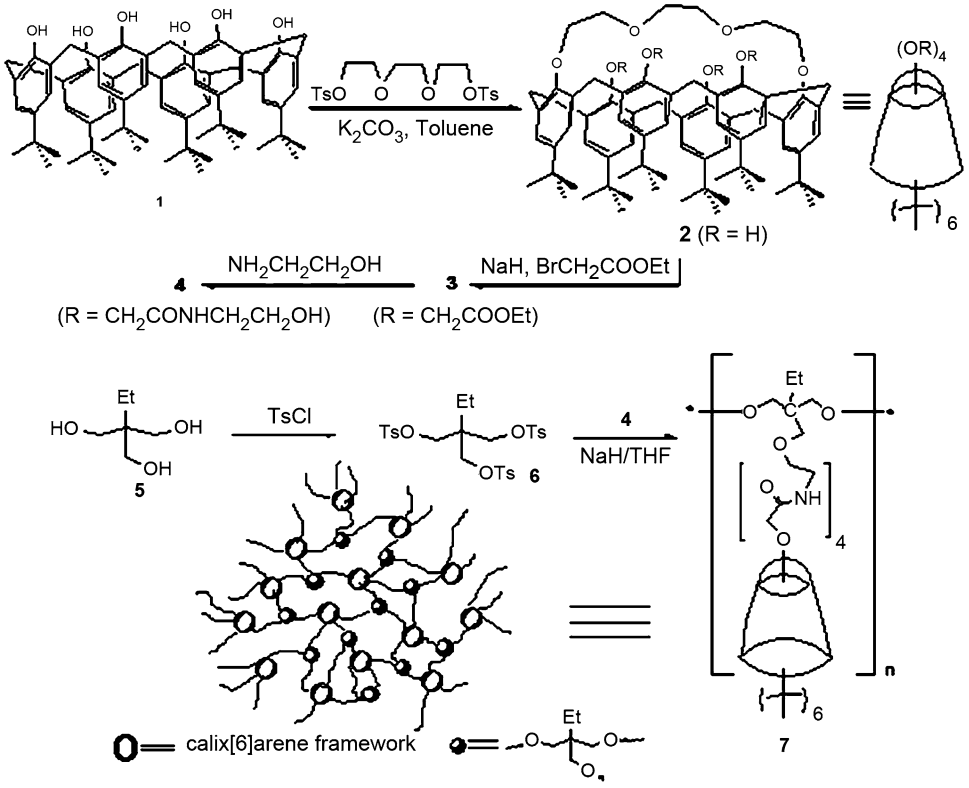
The elemental analysis data and molecular weight of polymer **7** are shown in Table 1. The molecular weight for polymers was determined by vapor pressure osmometric measurements. The M_n of polymer **7** was 39,816, which indicated an average of approximately 23 calixarene units in each polymer molecule.

The structure of polymer **7** was confirmed by IR spectra. Figure 1 shows the IR spectra of polymer **7** and compound **4**. In the IR spectra of polymer **7**, the C–OH characteristic absorption peak at 1,119 cm^{-1} disappeared completely and the strong absorption peak of ethyl groups at 775 cm^{-1} appeared. Also, the peak at 3,387 cm^{-1} for OH and NH groups of compound **4** shifted to 3,463 cm^{-1} for NH groups of polymer. These IR data certainly suggested that condensating reaction was accomplished completely. In this respect, the signals of ^{1}H NMR spectrum of polymer **7** were assigned to the suitable protons. Although it was difficult to determine the conformation due to the overlapped signals of ArCH$_2$Ar, OCH$_2$CO and OCH$_2$, it was reasonable to deduce polymer **7** with stable cone conformation for calix[6]-1,4-crown skeleton based on similar structural analysis of calix[6]-1,4-crown derivatives in literature [27, 28]. The surface structure of polymer **7** was also observed by scanning electron microscopy (SEM) as shown in Fig. 2. As expected, polymer **7** possessed loose pores and cross-linked netty architectures. This porous architecture and stable conformation of calix[6]arene were favorable for producing the binding abilities for guests.

Adsorption percentages of polymer 7

It has been widely reported that the binding abilities of calixarene derivatives are influenced by the size of macrocyclic cavity, the stability of conformation and the feature of the functional groups [5–22]. Polymer **7** possesses big and stable tri-dimensional cavity as well as multiple

Scheme 1 The synthetic route of polymer **7**



ester, ether and amido groups, which are favorable for binding big guests, such as amino organic compounds. Thus, the adsorption abilities of polymer **7** for a series of aniline derivatives, which are usual pollutants in water, have been investigated.

Table 2 shows the adsorption results of polymer **7** for aniline derivatives. It was observed that polymer **7** exhibits excellent adsorption percentages for tested aniline derivatives. The adsorption percentages were beyond 90 % and were higher than that of polymer **8**. By comparing the structures of polymers **7** and **8**, it may be concluded that the high adsorption percentages of polymer **7** for aniline derivatives are not only due to π–π stack action of the phenyl groups and the hydrogen bond action in complexation, but also the stable conformation of calix[6]arene skeleton and bigger cavity, which are favorable for binding guests with larger cubage, such as organic molecules, as expected.

Saturated adsorption capacities of polymer 7

The saturated adsorption experiments of polymer **7** for aniline derivatives were investigated and the results are shown in Fig. 3. It could be seen that the saturation adsorption capacities of polymer **7** for aniline derivatives are as high as 1.8–2.3 mmol/g, which are higher than the saturation adsorption capacity (1.34 mmol/g) of polymer **8** for *p*-nitroaniline [22]. The highest saturation adsorption capacities for aniline and *p*-nitroaniline are found to be 2.30 and 2.22 mmol/g, respectively. Obviously, comparing with the structure of calix[4]arene-based polymer [22], these saturated adsorption results of polymer **7** also support the stable conformation of calix[6]arene skeleton and bigger cavity which are favorable for binding guests with larger cubage. To the best of our knowledge, the adsorption capacities of calix[6]arene-based polymer for noxious organic molecules are studied for the first time. This kind of polymer exhibits good applied prospective for the extraction of noxious organic molecules in polluted water.

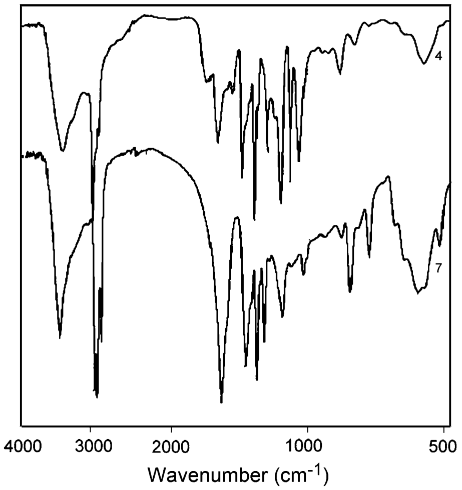


Fig. 1 IR spectra of polymer **7** and compound **4**

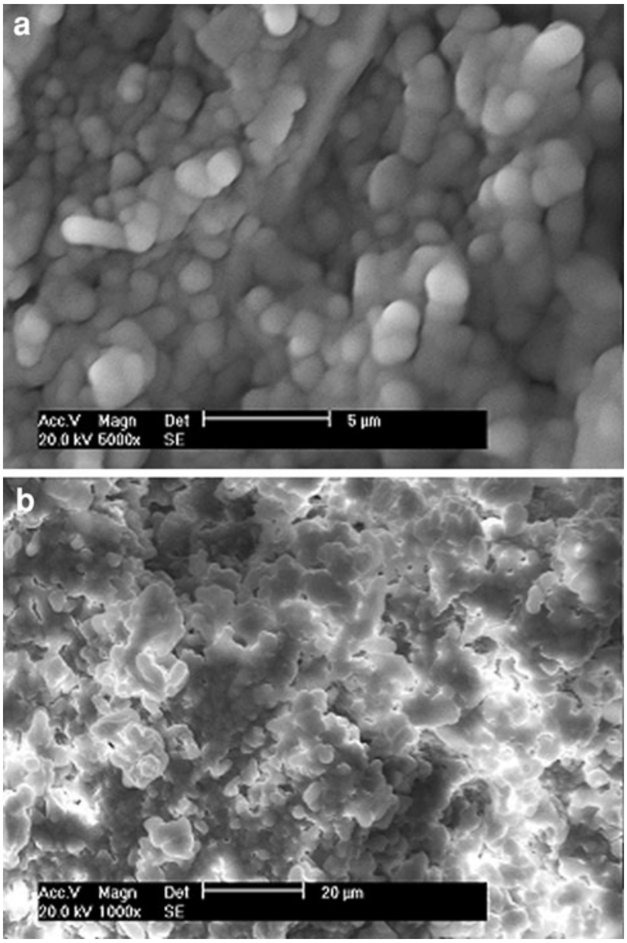


Fig. 2 SEM images of polymer **7**

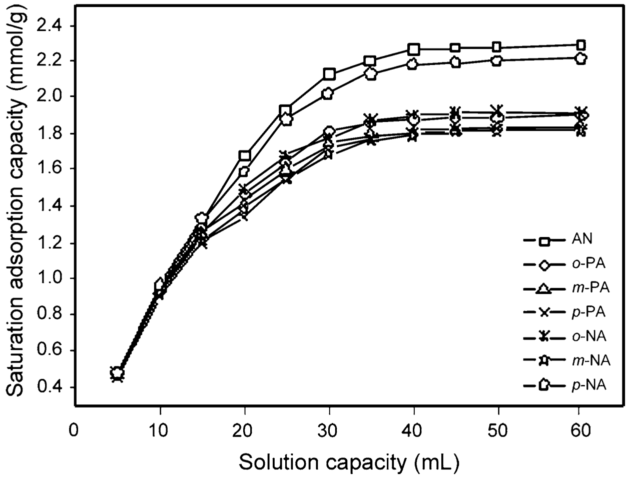


Fig. 3 Saturated adsorption curves of polymer **7** for aniline derivatives

The influence of pH values on adsorption percentages

The polymer **7** which has shown the highest adsorption abilities for aniline and *p*-nitroaniline has been tested for its adsorption capacity towards aniline and *p*-nitroaniline at different pH values and the results are shown in Fig. 4. Due to the protonation of aniline derivatives under acidic condition, the range of pH values was selected between pH 6–10. It can be seen that the adsorption percentages of polymer **7** are almost stable between pH 6–10. These results are good indications that the structure of polymer **7** remains stable at pH 6–10. Under basic condition, the adsorption percentages are decreased a little gradually, which might be attributed to the influence of increasing amount of NaOH for adjusting pH values. These adsorption results at different pH values suggest that polymer **7** possesses good application performance in wide range of pH values.

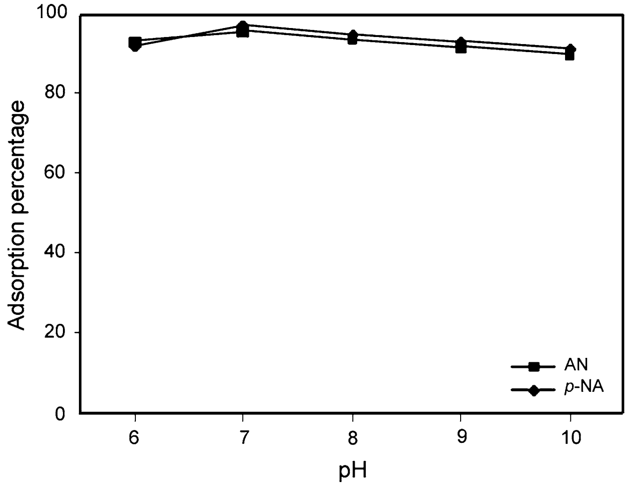


Fig. 4 The effect of pH values on adsorption percentages

The reusability of polymer **7** after desorption

Due to the reusing property as an important feature of a sorbent, the reused property of polymer **7** was evaluated. After adsorption of aniline, the polymer **7** was desorbed by 10 % HCl, washed adequately by distilled water and dried by vacuum. Then the polymer was reused for aniline adsorption again. The five times' adsorption percentages were measured and the results were 95.7, 93.8, 89.1, 86.5 and 82.4 %, respectively, which indicated that polymer **7** has good reused property.

Conclusion

This paper has described the synthesis of the first example of "4+3" condensated calix[6]-1,4-crown-based polymer **7** with porous and netty architecture. The adsorption experiments have shown that this polymer possesses excellent adsorption abilities for a series of aniline derivatives. The saturation adsorption capacities for aniline and *p*-nitroaniline have been found to be as high as 2.30 and 2.22 mmol/g, respectively. The adsorption abilities of polymer **7** remain stable at pH 6–10 and it could be reused after desorption. The big cavity and stable conformation of calix[6]arene skeleton of polymer **7** has played a crucial role in binding aniline derivatives.

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