

# Synthesis of $\beta$ -cyclodextrin-calix[4]arene coupling product and its adsorption of basic fuchsin and methylene blue from water

Xiaomei Zhang · Liang Shi · Guocai Xu ·  
Chaoyue Chen

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**Abstract** Two new  $\beta$ -CD-calix[4]arene coupling products **3,4** which contained one or two  $\beta$ -CD units in molecules were synthesized by ammonolysis of *p*-tert-butyl-25,27-dihydroxyl-26,28-di (ethoxy carbonyl methoxy) calix[4]arene **1** and mono-6-ethylenediamino-6-deoxy- $\beta$ -CD **2**, and their structures were confirmed by  $^1\text{H}$  NMR, IR and MS (Maldi-Tof). The probable mechanism for forming **3** was discussed also. Using water-insoluble coupling product **3** as an adsorbent, the influences of the adsorption capacities of **3** including initial concentration, temperature and pH onto basic fuchsin (BF) and methylene blue (MB) from aqueous solution were investigated. Results showed that the adsorption capability of **3** to BF was obviously higher than that to MB at similar adsorption conditions. The values of %sorption to BF were over 90 % in range of initial concentrations from 20 to 140 mg L $^{-1}$  whereas those to MB dropped rapidly from 92 to 58 %. The adsorptions of **3** to both BF and MB obeyed Freundlich adsorption isotherm well.

**Keywords**  $\beta$ -CD-calix[4]arene coupling product · Synthesis · Adsorption · Dye

## Introduction

Calixarenes and cyclodextrins (CDs) are two families of cavity-forming macrocyclic compounds which play major roles in supramolecular chemistry [1–5]. Due to their capability to form host–guest superstructures, calixarenes and

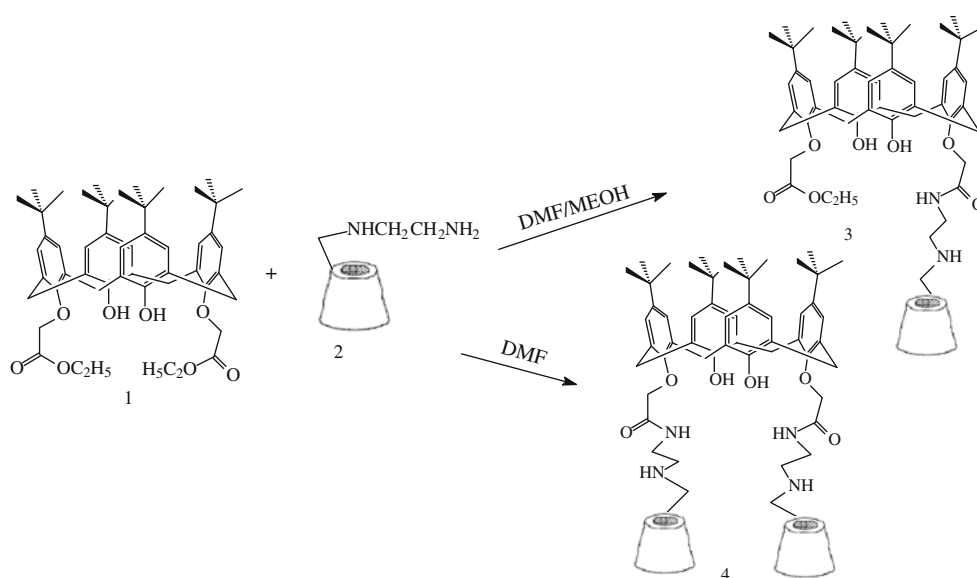
CDs turned out to be very attractive not only as molecular receptors but also as building blocks for the construction of supramolecular architectures [6]. Recently, promising synthetic materials calixarenes and CDs have got much interest because they are the most important platforms to prepare new macrocyclic hosts for the recognition of harmful organic pollutants [7–14], for example dyes, whereas dye pollution has become one of the biggest problems in the world in recent decades. For that reason, we were encouraged to couple these two different types of macrocycles to get new host molecules with dual or more cavities nearby in expectation of their enhanced inclusion properties coming from cooperative actions between  $\beta$ -CD and calix[4]arene cavities and/or between cavities and “linker”. Though there are many articles about synthesis of coupling products in literatures [15–24], very few of them dealt with the property investigations [21–24], especially with adsorption property. In our previous study, we successfully coupled mono-6-ethylenediamino-6-deoxy- $\beta$ -CD on to calix[4]arene derivative modified by formyl groups [20]. In this work, two new  $\beta$ -CD-calix[4]arene coupling products **3, 4** (see Scheme 1) were synthesized, and water-insoluble **3** was utilized to adsorb dyes basic fuchsin (BF) and methylene blue (MB) (see Fig. 1 for their chemical structures) from aqueous solution using the method introduced by Narjs Toumi’s [25]. The aim of this work was to investigate the inclusion property of **3** to guests with different structures.

## Experimental

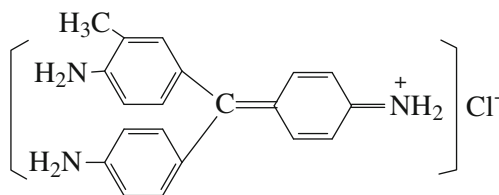
### Reagents

All the inorganic and organic reagents were analytical-grade. All aqueous solutions were prepared with

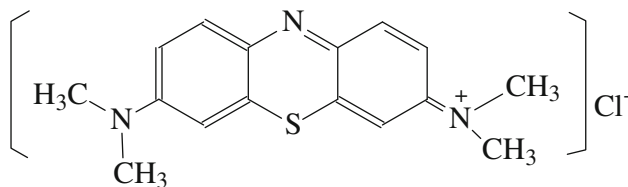
X. Zhang (✉) · L. Shi · G. Xu · C. Chen  
Anhui University of Science and Technology, Huainan,  
Anhui, China  
e-mail: xmzhang6289@yahoo.com.cn



**Scheme 1** Synthesis of  $\beta$ -CD-calix[4]arene coupling products **3**, **4**



Basic Fuchsin (BF)



Methylene Blue (MB)

**Fig. 1** The chemical structures of basic fuchsin and methylene blue

deionized water that had been passed through Ultrapure water system.

#### Instrumentation and analysis

FT-IR spectra were recorded on a Bruker VECTOR 33FT-IR spectrometer using KBr pellets.  $^1\text{H}$ NMR spectra were obtained from a Bruker Avance 400 NMR spectrometer in  $\text{DMSO-d}_6$  with TMS as internal standard. All the UV-Vis experiments were carried out using a Shimadzu UV-Vis 2550 recording spectrophotometer. The MALDI-TOF-MS spectra were recorded by a Voyager DESTRA spectrometer.

#### Synthesis of the calix[4]arene- $\beta$ -CD coupling products

The compounds *p*-tert-butyl calix[4]arene, *p*-tert-butyl-25,27-dihydroxyl-26,28-di(ethoxy carbonyl methoxyl) calix[4]arene **1** and mono-6-ethylenediamino-6-deoxy- $\beta$ -CD **2** were synthesized according to the literature procedure [26] and [14], respectively. Their spectroscopic data were conformed to those described.

#### Synthesis of compound **3**

A mixture of 0.12 g (0.15 mmol) of **1** in 20 mL DMF-MeOH(1:1, v/v) was stirred to homogeneous, then, 0.18 g (0.15 mmol) of **2** was added and the reaction mixture was stirred at 65–70 °C for 48 h. The solvents were removed under reduced pressure, and the residue was washed three times with deionized water. The dried filter cake was washed three times with dichloromethane and dried to give 0.22 g (77 %) of **3** as a light yellow powder, m.p.: 250 °C (decomposed).  $^1\text{H}$ NMR ( $\text{DMSO-d}_6$ )  $\delta$ : 6.80–7.15 (m, 8 H, ArH), 5.60–5.69 (m, 14 H, CD-OH), 4.82 (s, br. 11 H, 7 CD-H + 4 CA-H), 4.23–4.47 (m, 12 H, 6 CA-H + 6 OH), 3.34–3.82 (m, 50 H, CD-H + CA-H, overlap with DOH), 0.97–1.18 (m, 39 H, -CH<sub>3</sub>). IR ( $\nu/\text{cm}^{-1}$ ): 3392, 2954, 1746, 1660, 1483, 1030, 578. MS (Maldi-Tof)  $m/z$ (%): 2005.7 [ $\text{M}\cdot 3\text{H}_2\text{O}$ ]<sup>+</sup> (100 %, calcd. for  $\text{C}_{94}\text{H}_{138}\text{O}_{41}\text{N}_2\cdot 3\text{H}_2\text{O}$ ).

#### Synthesis of compound **4**

A mixture of 0.12 g (0.15 mmol) of **1** in 20 mL DMF was stirred to homogeneous, then, 0.35 g (0.30 mmol) of **2** was added and the reaction mixture was stirred at 65–70 °C for

48 h. The solvent was evaporated under reduced pressure, and the residue was washed three times with dichloromethane. The dried filter cake was treated using dialysis bag to remove water-soluble substances whose molecule were lower than 2,000 and then precipitated by addition of acetone to dialysis concentrate. The precipitate was filtered off, and dried to give 0.07 g (15 %) of product **4** as a yellowish powder, m.p.: 250 °C (decomposed).  $^1\text{H}$  NMR( $\text{D}_2\text{O}$ )  $\delta$ : 4.92 (m, br. CD-H + CA-H), 3.64–3.83 (m, CD-H), 3.43–3.51(m, CD-H + CA-H), 1.02–1.21(m,  $-\text{CH}_3$ ) IR( $\nu/\text{cm}^{-1}$ ): 3365, 2927, 1700, 1658, 1414, 1033, 578. MS (Maldi-Tof)  $m/z$ : 3104.2 [ $\text{MNa}$ ] $^+$  (100 %, calcd. for  $\text{C}_{136}\text{H}_{208}\text{O}_{74}\text{N}_4\text{Na}$ ).

### Adsorption studies

The adsorptions of dyes BF and MB onto water-insoluble  $\beta$ -CD-calix[4]arene coupling product **3** were carried out in aqueous solution at desired concentrations, temperatures and pHs. In general, 100 mg adsorbent coupling product **3** were added to 25 mL of BF or MB solution and shaken for 2 h. The initial concentrations of BF and MB solution were 20–140  $\text{mg L}^{-1}$ . The effects of temperature on adsorption capacity were tested within 10–35 °C, and the effects of pH on adsorption capacity were analyzed in the pH range from 2 to 12. The pH was adjusted using HCl or NaOH solution. After equilibrium was reached, the adsorbent was removed from dye solution by centrifugation. The adsorption values of dyes were estimated from the concentration change of dyes in solution after adsorption by spectrophotometer method at 543.0 nm for BF and at 665.0 nm for MB. The calibration curves were plotted between absorbance and concentration of the BF and MB solution, respectively. By the way, the pH values of all dye solutions after adsorption

were adjusted to  $5.8 \pm 0.1$  for BF and  $6.5 \pm 0.1$  for MB to exclude the influences of pH on BF and MB themselves. Each experiment was performed in twice under identical condition. The adsorption capacity was then calculated and expressed in adsorption quantity  $Q_e$  ( $\text{mg g}^{-1}$ ) or % sorption by (1) or (2):

$$Q_e = V(C_0 - C_e)/W \quad (1)$$

$$\text{Sorption \%} = 100(C_0 - C_e)/C_0 \quad (2)$$

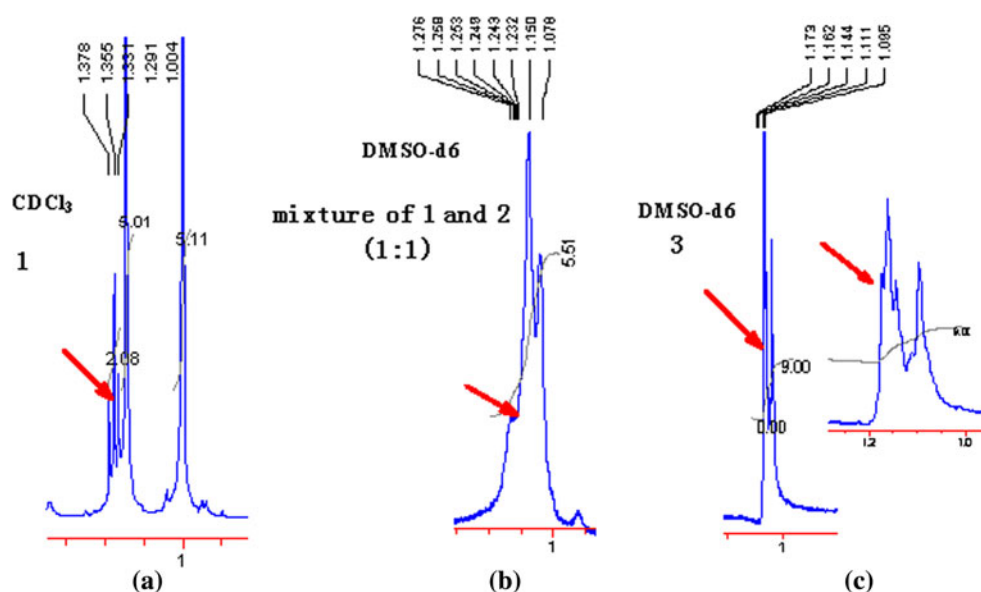
where  $C_0$  is the initial concentration( $\text{mg L}^{-1}$ ),  $C_e$  the equilibrium concentration( $\text{mg L}^{-1}$ );  $V$  is the volume of the solution used (L); and  $W$  is the weight of adsorbent used (g).

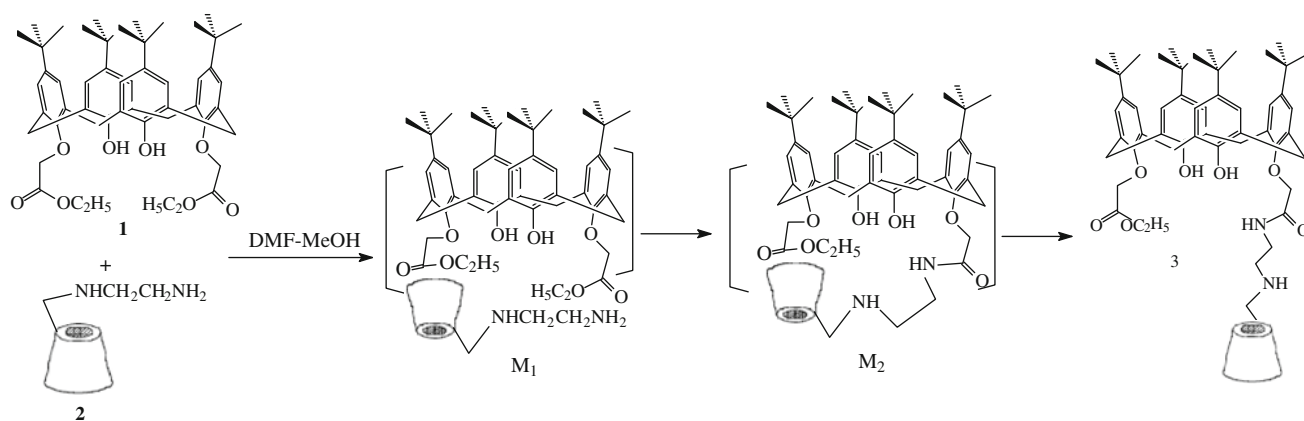
## Results and discussion

### Synthesis and characterization of $\beta$ -CD-calix[4]arene coupling products

Water-insoluble coupling product **3** with one  $\beta$ -CD unit in yield over 70 % was obtained by using DMF- $\text{CH}_3\text{OH}$  (1:1, v/v) as reaction solvent even at 1:1 stoichiometric ratio of the starting material. Increasing the dosage of **2** over **1** from 4 to ten-folds, did only **3** be got as a major product. As we know,  $\beta$ -CD includes a guest molecule in aqueous solution in axial mode more easily than in organic solvent in equatorial mode, additionally with a less stability in organic solvent [4]. In order to obtain the evidences of interaction between **1** and **2**, methyl protons in ester moiety of compound **1** and **3** were chosen as observation objects by using  $^1\text{H}$  NMR (see Fig. 2) because the chemical shifts of protons signals in compound **1** and **2** overlapped greatly

**Fig. 2**  $^1\text{H}$  NMR signals of methyl protons (of ethoxy moiety) in **1** and **3**





**Scheme 2** Probable mechanism for forming **3**

in range of  $\delta$  3.0–4.8 ppm. Due to very low solubility of **1** in DMSO, methyl protons signals in compound **1** were taken in  $\text{CDCl}_3$  (see Fig. 2a). Fortunately, we noticed the solubility of **1** in DMSO was enhanced greatly at the present of compound **2** when measuring  $^1\text{H}$  NMR signals of the physical mixture of **1** and **2** at ratio of 1:1 (see Fig. 2b), and peak shapes of methyl protons signals in mixture and compound **3** was very different (see Fig. 2b, c), which meant that there should be interactions between **1** and **2**.

We inferred that the failure of introducing two  $\beta$ -CD units into **1** in DMF- $\text{CH}_3\text{OH}$  might be attributed to the shielding effect of  $\beta$ -CD cavity (seen Scheme 2), or, at the beginning of the reaction, one of ethoxy carbonyl of **1** included **2** on secondary face in equatorial mode ( $M_1$ ), and the amidogen in **2** underwent ammonolysis with another free ethoxy carbonyl nearby ( $M_2$ ). The ethoxy carbonyl did not be delivered till the reaction mixture was taken into aftertreatment step, which consequently prevented further reaction of ethoxy carbonyl of calix[4]arene moiety with the other **2**.

However, water-soluble product **4** with two  $\beta$ -CD units in yield of 15 % was obtained in DMF even at 2:1 stoichiometric ratio of reactants, and the result could act as an evidence to support the probable mechanism for forming **3** because DMF was a less polar solvent than DMF- $\text{CH}_3\text{OH}$ , in which  $\beta$ -CD did not include the guest easily. Low yield of **4** was due to much loss in purification by dialysis.

The coupling of **2** onto **1** at 1:1 stoichiometric ratio was proven by  $^1\text{H}$  NMR by appearance of proton signals of both calix[4]arene and  $\beta$ -CD units. Eight aromatic protons at 6.80–7.15 ppm and the tert-butyl groups at 1.0–1.2 ppm indicated the presence of the calix[4]arene unit. The  $\beta$ -CD unit was confirmed by the presence of the H2–H6 protons at 3.34–3.82 ppm and the 14 protons of secondary –OH groups at 5.60–5.69 ppm. The structure of compound **3** was additionally confirmed by IR spectroscopy by appearance of a new band for the amide carbonyl (–CONH–) at  $1,660\text{ cm}^{-1}$ , and existence of the band for

the ethoxy carbonyl (– $\text{COOC}_2\text{H}_5$ ) at  $1,746\text{ cm}^{-1}$ , which indicated only one ethoxy carbonyl in compound **1** was ammonolysed. In addition, the MS (Maldi-Tof) of  $m/z$  2005.7 (100 %) clearly confirmed the compound **3** with a molecular formula of  $[\text{M}\cdot 3\text{H}_2\text{O}]$ .

The structure of **4** was confirmed by MS (Maldi-Tof) with a base peak  $m/z$  3104.2 attributed to  $[\text{M} + \text{Na}]^+$ . The fact that there were no obvious signals of aromatic protons in  $^1\text{H}$  NMR spectrum could attribute to the very low ratio of them in molecule.

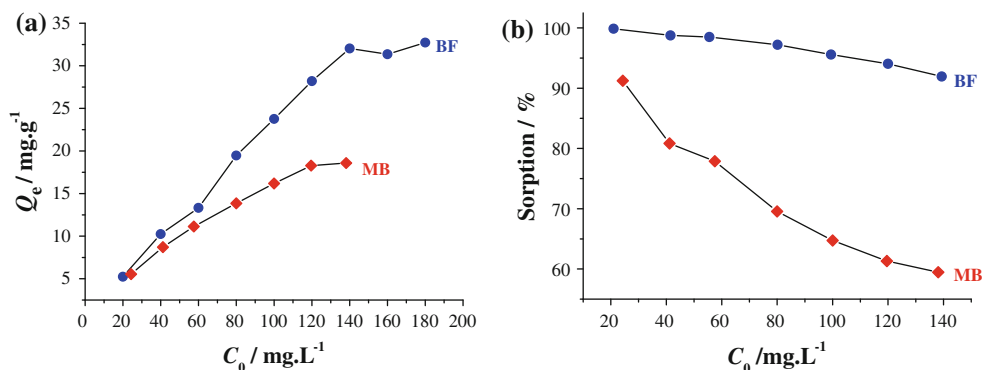
#### Adsorption of BF and MB on to $\beta$ -CD-calix[4] coupling product **3**

BF and MB are widely used dyes with the structures of three aromatic rings arranged in “trefoil” and “linearity” respectively, which may exhibit different behaviours towards adsorbent. Water-insoluble coupling product **3** was applied to adsorb BF and MB from aqueous solution to evaluate its inclusion and adsorption properties.

#### Effect of initial concentration

Effects of initial concentration ( $C_0$ ) of BF and MB on adsorption quantity  $Q_e$  and %sorption of product **3** were shown in Fig. 3. As shown in the figure, the values of  $Q_e$  to BF were higher than those to MB (Fig. 3a) at same  $C_0$ , especially at  $C_0$  over  $80\text{ mg L}^{-1}$ , and the changing trends of %sorption to BF and MB were obviously different (Fig. 3b). The %sorption to BF were over 90 % in range of tested  $C_0$  and the residual concentration of BF could reach to only  $0.029\text{ mg L}^{-1}$  with %sorption 99.9 when  $C_0$  was  $20\text{ mg L}^{-1}$ . But, the %sorption to MB dropped rapidly from 92 to 58 % with the increase of  $C_0$  from 20 to  $140\text{ mg L}^{-1}$ . The discrepancy could be explained by the stereostructure of  $\beta$ -CD-calix[4]arene coupling product **3** who with a special “ear” shape would include “trefoil” BF with three “antennae” more easily than “linearity” MB;

**Fig. 3** **a** Effect of  $C_0$  on  $Q_e$ .  
**b** Effect of  $C_0$  on %sorption.  
 Test conditions: sorbent dose 100 mg, contact time 2 h, 20 °C, pH 5.8 for BF, pH 6.5 for MB

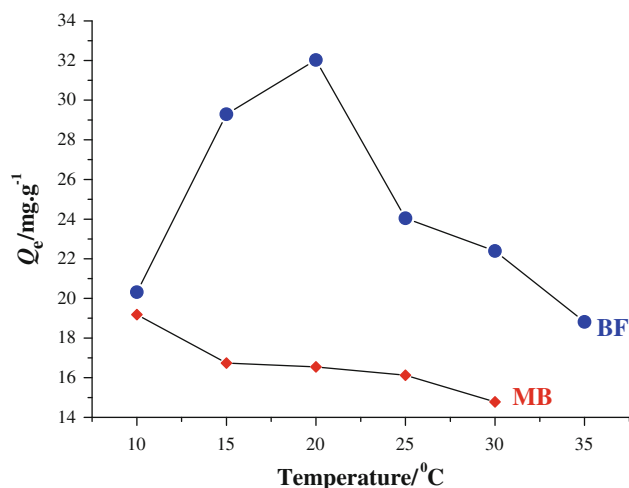


thus, the number of sorption sites in **3** for BF were more than those for MB.

Considering the potential application of our studies, initial concentrations of BF and MB for further investigations were chosen to be 140 and 100 mg L<sup>-1</sup>, respectively.

#### Effect of temperature

Effects of temperature on  $Q_e$  were tested within 10–35 °C. As shown in Fig. 4,  $Q_e$  to BF was more sensitive to temperature than that to MB. The maximum  $Q_e$  32.0 mg g<sup>-1</sup> to BF appeared at 20 °C whereas  $Q_e$  to MB decreased with the increase of temperature though values of  $Q_e$  to BF and to MB were almost the same at 10 °C. We inferred that low diffusion velocity of dye molecules at low temperature resulted in low  $Q_e$  to both dyes; but to BF, its big molecular volume would impede interactions between BF and sorption sites. Diffusion velocity increased when temperature rose and average kinetic energy of BF could be high enough to overcome steric hindrance. However, high temperature could result in desorption of dye molecules

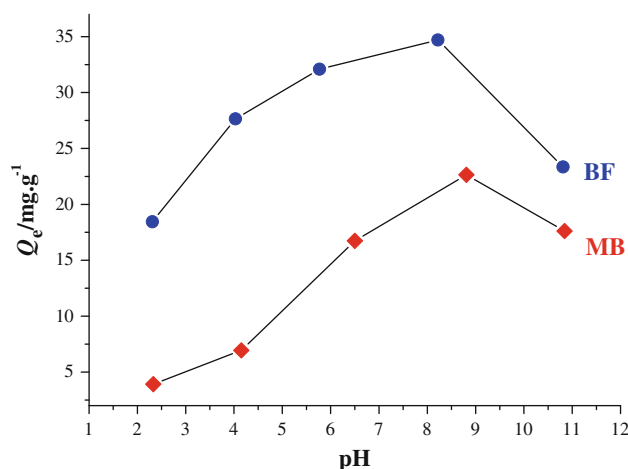


**Fig. 4** Effect of temperature on  $Q_e$ . Test conditions: sorbent dose 100 mg, contact time 2 h,  $C_0$  140 mg L<sup>-1</sup> for BF and 100 mg L<sup>-1</sup> for MB; pH 5.8 for BF, pH 6.5 for MB

from sorption sites, which caused  $Q_e$  depression. Comparisons of  $Q_e$  changing with temperature to BF and MB, we supposed that matching steric shape between sorption sites and adsorbate was one of most important factors for adsorption process, and it coincided with the essential of supramolecular chemistry [4].

#### Effect of pH

The change in the pH of solution will affect the degree of ionization of dye molecules present in the solution as well as the surface charge of the sorbent. Figure 5 showed the influences of the solution pH on  $Q_e$  within pH 2–12. As shown in Fig. 5, the changing trend of  $Q_e$  to both dyes with pH appeared similar, and both maximum  $Q_e$  (34.7 mg g<sup>-1</sup> to BF, 22.4 mg g<sup>-1</sup> to MB) were at near pH 9. It may be explained that protonated sorption sites on coupling product **3** would produce repellent to protonated BF and MB in acidic solution for there were all containing amidogens or substituted amidogens in the molecules. With the increase of pH, the extent of protonation of both product **3** and dyes



**Fig. 5** Effect of pH on  $Q_e$ . Test conditions: sorbent dose 100 mg, contact time 2 h, 20 °C,  $C_0$  140 mg L<sup>-1</sup> for BF and 100 mg L<sup>-1</sup> for MB

decreased, which lowered the repellent and increased interactions between dye molecule and sorption sites. At more high pH, some of hydroxy groups on  $\beta$ -CD moiety of **3** were deprotonated and the density of electron cloud of groups containing nitrogen in BF and MB increased, which could cause some repellent actions between sorption sites and with dyes also. Our results agreed with the report by Chen [8]. The effects of pH on sorption of dyes on to  $\beta$ -CD-calix[4] coupling product **3** seemed to be a phenomenon governed mainly by electrostatic action.

#### Freundlich isotherm

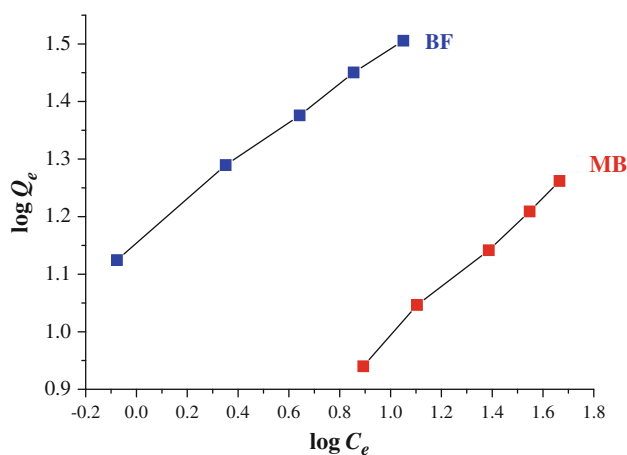
Freundlich isotherm is an empirical equation used to describe heterogeneous adsorption systems [27]. The linear form of Freundlich equation can be represented as follow:

$$\log Q_e = \log k + 1/n \log C_e \quad (3)$$

where  $Q_e$  is the equilibrium adsorption capacity of dyes on the adsorbent ( $\text{mg g}^{-1}$ ),  $C_e$  the equilibrium dyes concentration in solution ( $\text{mg L}^{-1}$ ),  $k$  is Freundlich constant ( $\text{L g}^{-1}$ ) and  $n$  is another Freundlich constant which demonstrates the favorability the Freundlich isotherm model [28].

The values of  $k$  and  $1/n$  were determined from the slope and intercept of the linear plot of  $\log Q_e$  versus  $\log C_e$  (Fig. 6). The isotherm parameters were shown in Table 1. The high values of correlation coefficients,  $R^2$  ( $>0.99$ ) for coupling product **3** on both dyes, indicated that the equilibrium data were fitted by Freundlich equation. Thus, the adsorptions of **3** to both BF and MB obeyed the Freundlich adsorption isotherm.

The  $n$  value of sorption intensity ( $1 < n < 10$ ) indicates that sorption is favorable [29]. The corresponding value of  $n$  for the sorption of BF and MB on product **3** was 2.97 and



**Fig. 6** Freundlich isotherm of **3** to BF and MB (20 °C). Test conditions: sorbent dose 100 mg, contact time 2 h, pH 5.8 for BF, pH 6.5 for MB

**Table 1** The constants of Freundlich adsorption isotherm

Freundlich isotherm model (20 °C)	Parameters	BF	MB
$\log Q_e = \log K + 1/n \log C_e$	$n$	2.967	2.475
	$K$ ( $\text{L g}^{-1}$ )	14.41	3.86
	$R$	0.998	0.998

2.47, respectively, which meant that the sorption was favorable.

#### Preliminary explanation for adsorption capability of **3** to dyes

The removal of BF and MB from aqueous solution using water-insoluble coupling product **3** is a solid-liquid adsorption process basically. It is difficult to investigate the inclusion phenomena between **3** and BF or MB by using  $^1\text{H}$  NMR titration because compound **3** can be dissolved only in DMF or DMSO. Moreover, protons signals of **3** in  $^1\text{H}$  NMR display widening peaks and overlap greatly due to high molecular weight of **3**. However,  $\beta$ -CD section in **3** should play a key role in the process of removing BF or MB from aqueous solution, for at similar adsorption conditions, no any removal effect had been detected while **3** was replaced with water-insoluble **1**. Though the adsorption capability of **3** to BF was obviously higher than that to MB, we have found some inverse results when  $\beta$ -CD section was coupled to other calix[4]arene derivatives in our unfinished work. So, we supposed that the stereostructure of **3** who was with a special “ear” shape constructed by  $\beta$ -CD section and the other groups at low rim in calix[4]arene section would contain “trefoil” BF with three “antennae” more easily than “linearity” MB.

#### Conclusion

Two new  $\beta$ -CD-calix[4]arene coupling products which contained one or two  $\beta$ -CD units in molecule were synthesized successfully by using different reaction solvents. Water-insoluble coupling product **3** was utilized to adsorb dyes BF and MB from aqueous solution. The adsorption capability of **3** to BF was obviously higher than that to MB at similar adsorption conditions and the results could be explained by the stereostructure of **3** who with a special “ear” shape would include “trefoil” BF with three “antennae” more easily than “linearity” MB; which caused the number of sorption sites in **3** for BF were more than those for MB. It is believed that molecular designing for novel efficient adsorbents for inclusion of harmful organic molecules may benefit from our results.

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