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Click synthesis and dye extraction properties of novel thiacalix[4]arene derivatives with triazolyl and hydrogen bonding groups

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ABSTRACT

Using a click reaction between alkynylthiacalix[4]arene and ethyl 2-azidoacetate followed by an ammonolysis with ethanolamine, leucinol and hydrazine hydrate, respectively, three novel thiacalix[4]arene derivatives **4**, **5** and **6** with triazolyl and hydrogen bonding groups (NH and OH) were synthesized in high yields. They exhibited excellent extraction capability for six anionic and cationic dyes. The flexible cavity, π-triazole rings and hydrogen bonding groups all play crucial roles in dye complexation.

1. Introduction

Dyes are widely used in various industries including textiles, leather, dyestuffs, papers, *etc.* Unfortunately, the wastewater from these industries represents a serious source of pollution [1,2]. In order to remove the dyes from wastewater, various types of conventional treatment processes including chemical coagulation, precipitation, extraction, adsorption, membrane filtration, photodegradation *etc.*, had been developed [3–7]. Among them, liquid–liquid extractions can provide a selective separation and recovery of dyes from the effluent mixtures. In the processes of liquid–liquid extraction, the extractants or carriers played the crucial roles. Recently, supramolecular chemistry has provided a much improved solution to search for molecular structures that could serve as building blocks for the production of sophisticated molecules by anchoring functional groups oriented in such a way that they provided a suitable binding site for the dyes of interest [8–10]. In particular, calixarene-based derivatives were paid much attention to as potential extractants owing to their highly efficient complexation for dyes lately. Calixarene-based derivatives and resins with highly removal ability of dyes were reported by Yilmaz [11–13], Memnon [14,15] and Diao [16], respectively. Data from previous research indicated that the size of cavity, the π–π and hydrogen bond interactions with the dye molecules were important for the inclusion of dyes, and the cavity of calix[4]arene was not favorable for the inclusion of commonly used dyes [11–16]. Compared to calix[4]arenes, thiacalix[4]arenes possess a more flexible cavity, which might be more amicable for size adjustment to match the dimension of the dyes of interest. However, no thiacalix[4]arene derivatives were reported to bind dyes up until now. In this paper, several novel thiacalix[4]arene derivatives with triazolyl and hydrogen bonding groups were designed and synthesized by a click reaction and their dye complexation properties were studied for the first time. The extraction experiments indicated they exhibited excellent extraction capability for all kinds of dyes, which might be attributed to the flexible cavity of thiacalix[4]arene, the π–π interactions between the triazole ring and the dyes, and the hydrogen bonding interactions between the NH or OH groups and the dyes.

2. Experimental

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 600 instrument at room temperature, using TMS as an internal standard. ESI-MS spectra were obtained from DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed using a Carlo-Erba 1106 Elemental Analyzer. IR spectra were recorded on a Perkin-Elmer 1605 FTIR spectrometer as KBr pellets. UV–vis measurements were performed on a Varian UV–vis instrument. Alkynylthiacalix[4]arene **2** and 25, 26, 27, 28-tetra(ethylacetyl-1*H*-1,2,3-triazolyl-methyloxy)thiacalix[4]arene **3** were prepared using literature methods [17,18]. The liquid–liquid extraction studies were performed following the classic

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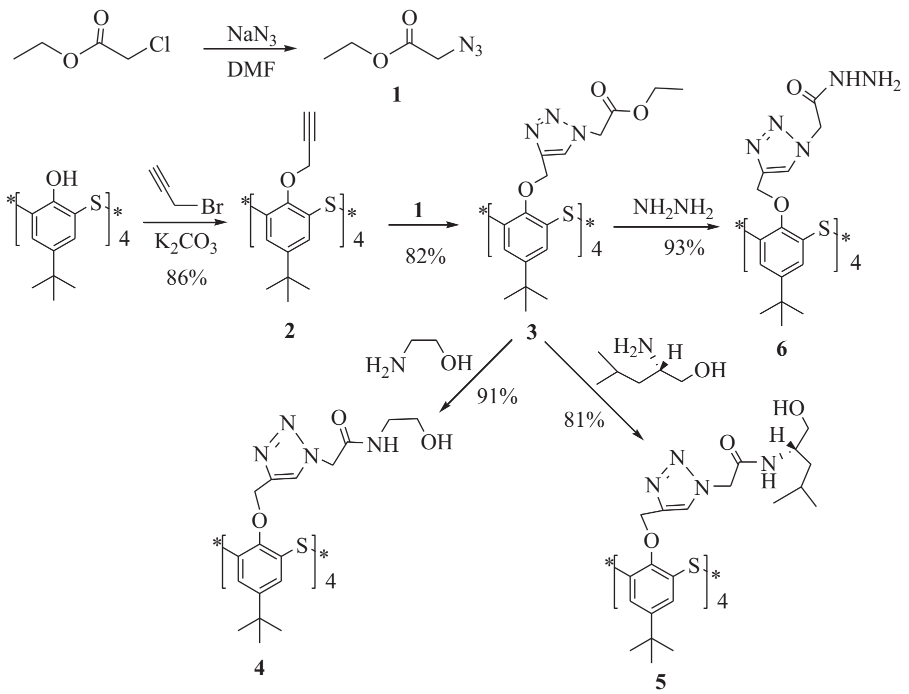

Scheme 1. The synthetic routes for title compounds.

Pedersen's procedure [19]. A 10 mL of 2.0×10^{-5} mol/L aqueous solution of dye and 10 mL of 1.0×10^{-3} mol/L solution of carrier in CH_2Cl_2 were vigorously agitated in a stoppered glass tube with a mechanical shaker for 2 min. Then the mixture was stirred magnetically in a thermostated water-bath at 25 °C for 1 h, and was finally left standing for an additional 30 min. The concentration of the dyes remaining in the aqueous phase was subsequently determined by UV–vis analyses. Blank experiments showed that dye extraction were less than 2% in the absence of extractants. The percent extraction ($E\%$) was calculated as: $E\% = 100\ (A_0 - A)/A_0$. Where A_0 and A are initial and final concentrations of the dyes before and after the extraction, respectively. Each experiment was repeated three times. The dye concentration in the receiving phase was reported as the mean of the determination and the relative standard deviation from the mean was less than 5%.

Synthesis of novel thiacalix[4]arene derivatives with triazolyl and hydrogen bonding groups **4**, **5** and **6**: Under nitrogen atmosphere, a mixture of compound **3** (0.21 g, 0.15 mmol) and ethanolamine (0.2 g, 3.3 mmol) was refluxed in a 20 mL of EtOH/$CHCl_3$ (v:v = 1:1) solution for 10 h. After cooling, the solution was distilled under reduced pressure. The residue was recrystallized in MeOH/H_2O (v:v = 1:1) to afford **4** as a white solid (0.22 g, 91%). **4**: Mp: 208–211 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.98 (s, 36H, 12 × CH_3), 3.19 (d, 8H, J = 5.6 Hz, 4 × CH_2), 3.32 (s, 4H, 4 × OH), 3.46 (d, 8H, J = 5.6 Hz, 4 × CH_2), 4.97 (s, 8H, 4 × NCH_2CO), 5.08 (s, 8H, 4 × OCH_2), 7.47(s, 8H, 8 × ArH), 8.14 (s, 4H, 4 × CH═N), 8.33 (s, 4H, 4 × NH); IR (KBr, cm^{-1}): ν 3412 (NH), 1680 (C═O); MS m/z (%): 1471.7 (M+Na$^+$, 100). Anal. Calcd. for $C_{68}H_{88}N_{16}O_{12}S_4$: C 56.34, H 6.12, N 15.46; found C 56.38, H 6.16, N 15.41.

Using a similar procedure, compounds **5** and **6** were obtained by ammonolysis with leucinol and hydrazine hydrate in yields of 81% and 93%, respectively. **5**: Mp: 201–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (d, 24H, J = 6.8 Hz, 8 × CH_3), 1.04 (s, 36H, 12 × CH_3), 1.35–1.38 (m, 8H, 4 × CH_2), 1.51–1.69 (m, 4H, 4 × CH), 3.52–3.77 (m, 12H, 6 × CH_2), 4.04 (s, 4H, 4 × OH), 5.14 (s, 8H, 4 × NCH_2CO), 5.18 (s, 8H, 4 × OCH_2), 6.82 (d, 4H, J = 8.4 Hz, 4 × NH), 7.0 (s, 8H, 8 × CH═N), 7.16 (s, 4H, 4 × ArH); IR (KBr, cm^{-1}): ν 3380 (NH and OH), 1675 (C═O); MS m/z (%): 1696.8 (M+Na$^+$, 100). Anal. Calcd. for $C_{84}H_{120}N_{16}O_{12}S_4$: C 60.27, H 7.23, N 13.39; found C 60.21, H 7.28, N 13.33. **6**: Mp: 225–228 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (s, 36H, CH_3), 2.25 (bs, 8H, NH_2), 4.99 (s, 8H, NCH_2CO), 5.07 (s, 8H, OCH_2), 7.41 (s, 8H, ArH), 8.11 (s, 4H, CH═N), 8.26 (s, 4H, NH); IR (KBr, cm^{-1}): ν 3407 (NH), 1668 (C═O); MS m/z (%): 1355.2(M+Na$^+$, 100). Anal. Calcd. for $C_{60}H_{76}N_{20}O_8S_4$: C 54.04, H 5.73, N 21.02; found C 54.09, H 5.78, N 21.08.

3. Results and discussion

The synthetic route is shown in Scheme 1. Alkynylthiacalix[4]arene **2** and its triazolyl derivative **3** were prepared by a click reaction according to the literature procedures [17,18]. Then by ammonolysis of compound **3** with ethanolamine, leucinol and hydrazine hydrate, the target novel thiacalix[4]arene derivatives **4**, **5** and **6** were obtained in yields of 80%–93%, respectively. The structures of compounds **4**, **5** and **6** were characterized by elemental analysis, IR, ESI-MS, and NMR spectroscopy. Their IR spectra showed the corresponding amide groups (NHC═O) instead of ester groups (OC═O). Their ESI-MS spectra exhibited the corresponding molecular base peaks (M+Na$^+$). In their ^{1}H NMR spectra, one singlet for the *tert*-butyl groups, one singlet for the aromatic protons, indicated **4**, **5** and **6** were in the cone or 1,3-alternate conformation. The analysis of structures of compounds **4**–**6** suggested they possessed a flexible cavity, four π-triazole rings and several NH and OH groups, which were favorable for binding dyes. Thus, six normal dyes were chosen to test their extraction ability by liquid–liquid extraction. The results are shown in Table 1.

Previously, it was reported that the cavity of calix[4]arene was not favorable for inclusion of dyes [11–16]. However, from Table 1, it could be seen that compound **2** showed a certain level of extraction ability for dyes, which could be attributed to its flexible cavity for dye complexation as expected. Moreover, the extraction percentage of compound **3** was higher than that of compound **2**, increased from 30% to 60%. These results suggested the π-triazole rings in compound **3** produced more favorable interactions for dye complexation. Further, after bridging with NH and OH groups, the

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Table 1
Extraction percentages of six dyes with compounds **2**, **3**, **4**, **5** and **6**.[a]

Compound	OG	BP	VB	CV	NR	MB
2	26.8	19.7	21.7	16.6	25.6	23.4
3	56.2	49.8	38.9	44.6	50.1	43.6
4	91.4	90.6	74.7	88.6	88.7	86.3
5	93.8	88.1	79.7	84.3	80.1	88.3
6	91.3	86.5	82.6	88.8	82.9	79.8

[a] The pH 7 in aqueous solution were adjusted by HAc or ammonia. OG, BP, VB, CV, NR and MB were the abbreviation of Orange G sodium salt, Brilliant ponceau 5R, Victoria blue B, Crystal violet, Neutral red and Methylene blue, respectively.

extraction percentages of compounds **4**, **5** and **6** were greatly improved to 80% and some were as high as 90%. By comparing the structures of compounds **2**, **3** and **4**–**6**, it could be deduced that the hydrogen bonding groups (NH and OH) in compounds **4**–**6** improved the extraction ability greatly. On the other hand, the different structures of dyes, such as anionic dyes and cationic dyes, had little influence on extraction percentages. All these results suggested the flexible cavity of thiacalix[4]arene, π-triazole rings and hydrogen bonding groups all played crucial roles in binding dyes.

4. Conclusion

In summary, using a click reaction between alkynylthiacalix[4]arene and ethyl 2-azidoacetate followed by an ammonolysis with ethanolamine, leucinol and hydrazine hydrate, respectively, three novel thiacalix[4]arene derivatives **4**, **5** and **6** with triazolyl groups and hydrogen bonding groups (NH and OH) were synthesized in high yields. They exhibited excellent extraction capability for six anionic and cationic dyes. The flexible cavity, π-triazole rings and hydrogen bonding groups all play crucial roles in dye complexation. The in-depth studies for binding dyes by liquid membrane transportion and adsorption, which are important for practical applications, will be reported in future work.

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