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Calix[4]arenes containing thiourea and amide moieties: neutral receptors towards α,ω-dicarboxylate anions

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Two-armed neutral anion receptors (**4**, **5**), were prepared and examined for their anion-binding ability using UV-vis, fluorescence and ^{1}H NMR spectra in DMSO. The results of non-linear curve fitting indicate that **4** or **5** form 1 : 1 stoichiometric complexes with dicarboxylate anions by multiple hydrogen bonding interactions and the sensitivity for recognition of dicarboxylate depends on the chain length of these dicarboxylate anions. Receptors **4** and **5** have no binding ability with acetate, dihydrogen phosphate and the halogen (Cl^-, Br^-, I^-) anions. This demonstrates that receptors **4** or **5** could be used as chemical sensors for some special dicarboxylate anions.

Introduction

Selective binding of anions is an important aspect of anion detection and anion transport.[1] Dicarboxylates are critical components of numerous metabolic processes[2] including, for instance, the citric acid and glyoxylate cycles.[2a] They also play an important role in the generation of high-energy phosphate bonds and in the biosynthesis of important intermediates.[2b] To develop the artificial receptors for on line and real time detection of biologically and environmentally important anions, the synthesized receptors have attracted increasing attention in supramolecular chemistry and several elegant receptor systems for selective binding anions have been reported.[3] But to the best of our knowledge, the neutral receptors of calix[4]arene containing amide groups and thiourea groups for dicarboxylate anions have seldom been reported.

In the design of a suitable ditopic receptor for α,ω-dicarboxylate anions in biology and the environment, the following parameters must be taken into account: the number of binding sites forming the binding subunits, the distance separating the two sites from each other within a binding subunit and the pH values of the solvent. So neutral receptors containing amide, urea/thiourea units with a strong hydrogen-bond donor capability, which can interact with anionic species effectively by hydrogen bonding, have become the focus.[4] As we know, calix[4]arenes are one of the most important supramolecular building blocks because of their capability of being modified at both the upper and lower rims. The functionalized calix[4]arenes can show some specific and excellent properties. Our strategy for the synthesis of (large) neutral receptor molecules is attaching amide and thiourea units to calix[4]arenes at the lower rim, which can offer a suitable distance between the two binding sites and form enough strong hydrogen bonding to recognize dicarboxylate under neutral conditions. In this paper, we report the synthesis and binding properties of **4** and **5** containing two amide groups and two thiourea groups. The binding ability of receptors **4** and **5** has been evidenced by UV-vis absorption and fluorescent emission spectra.

Results and discussion

Synthesis

The synthesis of calix[4]arene derivatives **4** and **5** is outlined in Scheme 1. Compound **3** was synthesized through the method proposed by Beer and co-workers.[5] The condensation reactions between the calix[4]arenes **3** and *p*-nitrophenylisothiocyanate or 1-naphthylisothiocyanate were performed in dry $CHCl_3$ at room temperature for 15 min or 4 h in the presence of triethylamine, both giving a good yield. The difunctionalized calix[4]arene **5** is soluble in chloroform, methanol, ethanol, acetone and DMSO, but **4** is only soluble in DMSO. Both **4** and **5** were characterized by IR, ^{1}H NMR, MS and elemental analysis.

UV-vis spectra

The UV-vis spectrum is used extensively to study a coordination system with a spectral change, which is a convenient method to determine the associate constants of the supramolecular complex.[6] The recognition properties of receptors **4** and **5** with various anions such as malonate, succinate, glutarate, adipate, acetate, dihydrogen phosphate and the halogen (Cl^-, Br^-, I^-) anions were monitored by UV-vis spectra. In each case the counter cation was tetrabutylammonium.

Fig. 1 shows the absorption spectra of interaction between **4** and adipate anion. With the addition of adipate anion to the solution of receptor **4** in DMSO (5.0×10^{-5} mol L^{-1}), the characteristic absorption peak of the host at 359 nm was increased gradually with a slight blue shift and a new peak at 487 nm was produced. At the same time, an isosbestic point was observed at 291 nm. The graph in the top right corner of Fig. 1 illustrates the absorbance change of receptor solution upon

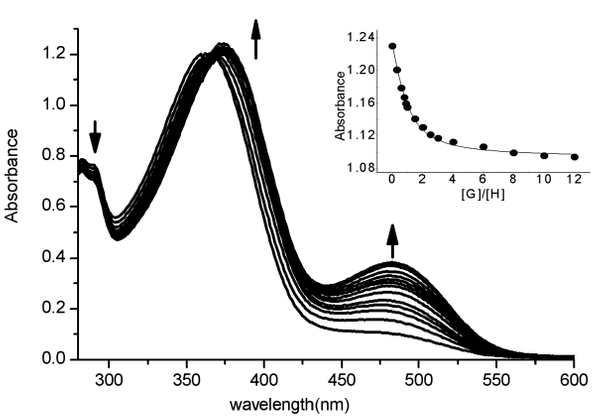

Fig. 1 UV-vis absorption spectra of receptor **4** (DMSO, 5.0×10^{-5} mol L^{-1}) upon the addition of various amounts of adipate anions in DMSO. Equivalent of adipate: 0, 0.3, 0.6, 0.8, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0, 4. 0, 6.0, 8.0, 10.0 and 12.0. The nonlinear fitting curve of change in absorbance at 359 nm with respect to the amount of adipate anion is shown in the inset.

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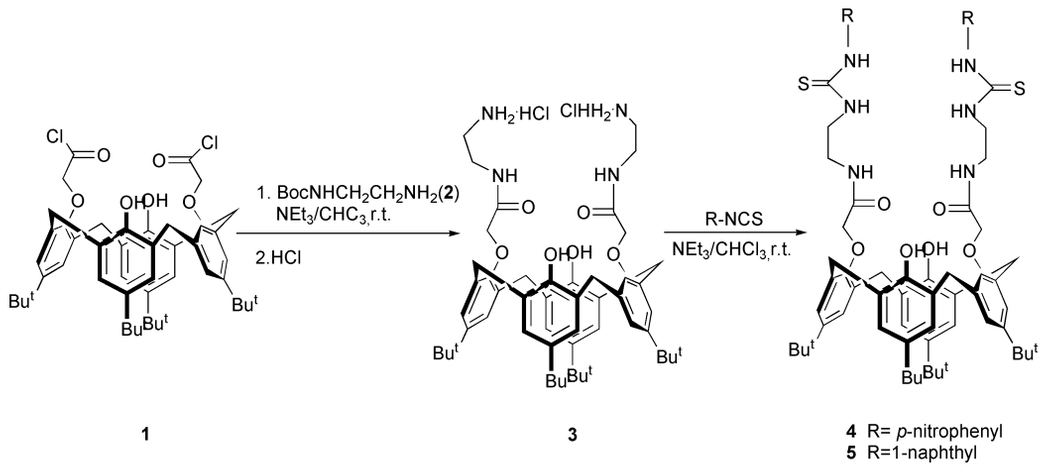


Scheme 1 Synthesis route of calix[4]arenes.

the addition of adipate at 359 nm. In particular, upon the gradual increase of the concentration of dicarboxylate anions (malonate, succinate, glutarate, adipate), the color of the solution of **4** changed from yellow to red, which could be observed by the naked eye. The color change is due to an obvious increase of absorption in the visible region at 487 nm. When a protic solvent such as methanol was added to the red solution of **4** and dicarboxylate anions in DMSO, the color of the solution changed to yellow. This phenomena illustrated that the addition of protic solvent destroyed the complexation of **4** with dicarboxylate anions, which demonstrated that the interactions between **4** and dicarboxylate were in essence hydrogen bonding interactions.

Upon addition of increasing amounts of dicarboxylate to the solution of **5** in DMSO (5.0×10^{-5} mol L^{-1}), the characteristic peaks at 260 nm and 289 nm of the host changed (Fig. 2). The peak (at 289 nm) decreased while the other (at 260 nm) increased, and a new absorption band appeared at 340 nm. Two clear isobestic points were observed at 280 nm and 310 nm. The graph in the top right corner of Fig. 2 illustrates the absorbance change of receptor solution upon the gradual increase in the concentration of adipate at 289 nm.The isobestic point in the UV-vis spectra indicates that there is a balance in the solution and the complex has been formed between the host and the guest. This can also be confirmed by the ^{1}H NMR data described in the following section.

Similar phenomena were observed when other α,ω-dicarboxylate anions (malonate, succinate, glutarate) were added to a solution of **4** or **5**. Therefore, no matter which dicarboxylate is added, receptors **4** or **5** can form complexes with anions through multiple hydrogen bonding. The new absorption is attributed to the formation of these complexes.

When adding acetate (AcO^-), dihydrogen phosphate ($H_2PO_4^-$) or the halogen (Cl^-, Br^-, I^-) anions respectively to a solution of **4** (or **5**) in DMSO, the UV-vis absorption spectra of **4** (or **5**) do not change, which demonstrates that the recognition interactions between **4** (or **5**) and the anions is not occurring.

The continuous variation methods were used to determine the stoichiometric ratios of the receptor **4** or **5** and the anion guests. The total concentration of host and adipate anion guest was constant (1.0×10^{-4} mol L^{-1}), with a continuously variable molar fraction of guest ([G]/([H] + [G])). Fig. 3 shows the Job plot of **4** with adipate anion (at 487 nm). The receptor–anion complex concentration approaches a maximum when the molar fraction of guest is 0.5, meaning that receptor **4** and adipate anion formed a 1 : 1 complex.[7] Using the same method, it was deduced that receptor **4** (or **5**) and other dicarboxylate anions (malonate, succinate, glutarate) also formed 1 : 1 complexes.

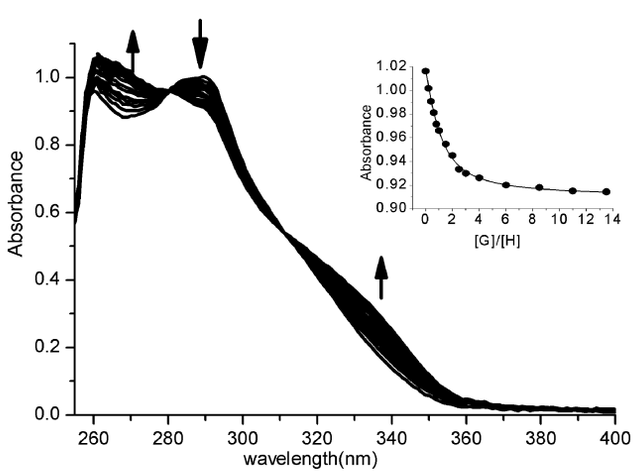


Fig. 2 UV-vis absorption spectra of receptor **5** (DMSO, 5.0×10^{-5} mol L^{-1}) upon the addition of various amounts of adipate anions in DMSO. Equivalent of adipate: 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, 3.0, 4. 0, 6.0, 8.5, 11.0 and 13.5. The nonlinear fitting curve of change in absorbance at 289 nm with respect to the amount of adipate anion was shown in the inset.

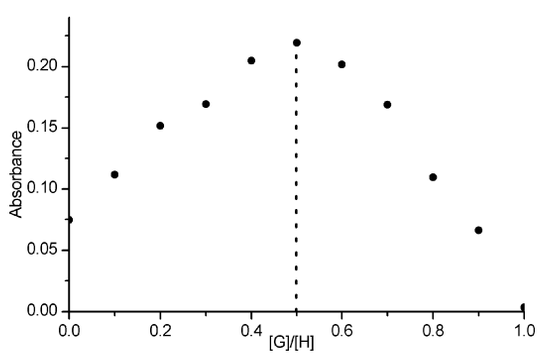
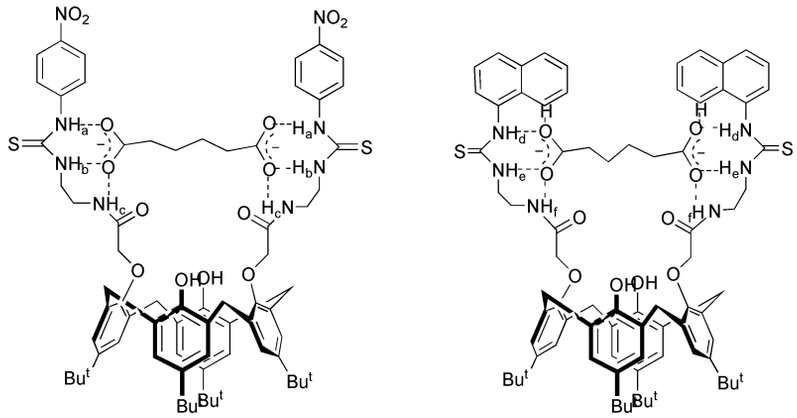


Fig. 3 Job plot of **4** with adipate anion. The total concentration of the host and guest is 1.0×10^{-4}mol L^{-1}.

Fluorescence spectra

The fluorescence spectra of receptor **5** were studied from a solution (5.0×10^{-5} mol L^{-1}) of **5** in DMSO in the absence and presence of various dicarboxylate, acetate, dihydrogen phosphate and halogen (Cl^-, Br^-, I^-) anions.

Fig. 4 shows the fluorescence spectra of **5** and its adipate anion complexes following excitation at 344 nm. With the addition of adipate anion, the fluorescence intensity of **5** was increased. In addition, new broad spectra having long-wavelength fluorescence emissions from ~410 nm to 600 nm were observed. Similar phenomena were also observed as other dicarboxylate anions were introduced to a solution of **5**. The anion-induced fluorescence enhancement might be due to the efficient fluorescent retrieval upon interaction between the



(a) (b)

Scheme 2 Possible binding models of **4** (a) and **5** (b) with adipate anions.

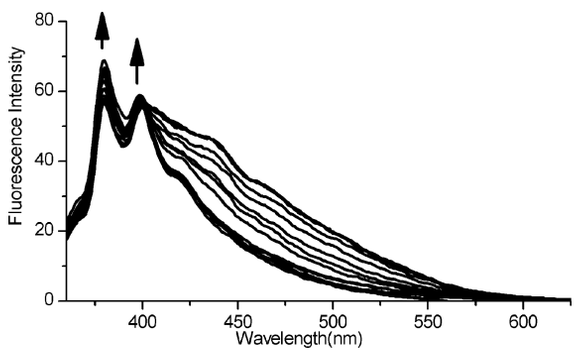


Fig. 4 Fluorescence spectra of receptor **5** (DMSO, 5.0×10^{-5} mol L^{-1}) upon the addition of various amounts of adipate anions in DMSO. Equivalent of adipate: 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.8, 2.8, 6.0, 7.0, 10.0, 18.0, 28.0 and 38.0, λ_{ex} = 344.0 nm.

anion guest and the receptor unit of **5**. In the absence of anion, the fluorescence intensity of receptor **5** was quenched by a PET (photo-induced electron transfer) process to some extent. As the anion was introduced into the solution of receptor **5**, the interaction between the receptor unit and anion could diminish the efficiency of the PET process.[8] Adding a great excess of Br^- and I^- did not cause significant fluorescence quenching of **5**, ruling out quenching by heavy atom effect, while acetate, dihydrogen phosphate and chloride did not cause any fluorescence change.

^{1}H NMR study

^{1}H NMR spectroscopy has been widely used to investigate receptor–substrate interactions[9] and it can provide details of the interactions between the host and the guest. The bridged methylene of the parent ring in receptor **4** in the absence and presence of adipate both showed two double signals in DMSO-d_6. This indicates that the difunctionalised calix[4]arene **4** keeps a cone conformation after interacting with adipate anion in DMSO. The relative rigid conformation of receptor **4** will benefit the formation of the 1 : 1 complex between **4** and the dicarboxylate anion. ^{1}H NMR spectra of **4** in the absence and presence of adipate anion in DMSO-d_6 at room temperature were recorded. The NMR spectrum of **4** shows a small broad signal at δ 8.90 due to the H_c proton and two simplet signals at δ_H 10.05 (H_a) and δ_H 8.46 (H_b) which are due to the protons of the thiourea groups respectively. Upon addition of adipate anions, the signals of H_a, H_b and H_c disappear, which is similar to what Cho[10] has described in his work. The signal of the OH (ArOH) proton becomes broad and has a downfield shift with a change of 0.51 ppm. This further proves that the complex between **4** and adipate anion has been formed by multiple hydrogen bondings.

Compared to the receptor **4**, the signals of the NH protons of receptor **5** don't disappear but are shifted markedly downfield when adding the dicarboxylate into the solution of **5**. The signals of thiourea protons (H_d, H_e) and amide protons (H_f) were respectively shifted from 8.42 to 10.98, 9.61 to 12.19 and 8.72 to 8.99 ppm. At the same time, the signals of H_d and H_e become broader. The signal of OH proton (a broad signal at 8.54 ppm), which overlaps with the signals of the naphthalene ring in the absence of adipate, obviously has a downfield shift. Interestingly, the multiplet signals of the naphthalene ring at δ_H 7.31–7.91 are changed into two broad signals at δ_H 8.01, 7.81 and three double signals at δ_H 7.65 (J = 7.5 Hz), 7.50 (J = 6.6 Hz), 7.38 (J = 7.5 Hz) with a downfield shift. From this, we presume that the naphthalene proton also participates in the formation of hydrogen bonds. Possible structures for the complex between **4** and **5** with adipate are shown in Scheme 2 (a, b). Similar data were also obtained upon addition of other dicarboxylates to a solution of **4** or **5** in DMSO-d_6.

When adding acetate (AcO^-), dihydrogen phosphate ($H_2PO_4^-$) or the halogen (Cl^-, Br^-, I^-) anions respectively to solutions of **4** (or **5**) in DMSO-d_6, no changes are observed in the ^{1}H NMR spectra. This result is consistent with that of the UV-vis spectra and further proves that the recognition interactions between **4** (or **5**) and these anions have not happened.

Binding properties

In a supramolecular system, when the host molecule has a strong ultraviolet absorption but the guest molecule has no absorption in a same wavelength, we can calculate an association constant of a 1 : 1 stoichiometric complex by using the following equation:[11]

$$A = A_0 + \frac{A_{lim} - A_0}{2c_0}\{c_H + c_G + 1/K_{ass} - [(c_H + c_G + 1/K_{ass})^2 - 4\,c_H\,c_G]^{1/2}\}$$

Where A represents the ultraviolet absorbance; A_0 represents the absorbance of pure host; c_H and c_G are the corresponding concentration of host and anion guest; K_{ass} is the association constant (this equation also works in fluorescence titrations and A represents fluorescence intensity). The association constants and correlation coefficients (R) obtained by a non-linear least-square analysis of A *versus* c_H and c_G are tabulated in Table 1. The result of non-linear curve fitting confirms that a 1 : 1 stoichiometric complex has been formed between host and guest.[12] From Table 1, we can see that: (1) receptors **4** and **5** have a good selectivity for dicarboxylate anions, but the binding ability depends on the chain length of dicarboxylate anions; (2) receptors **4** and **5** have similar selectivity in the order of adipate > glutarate > succinate > malonate. This indicates that the cooperative action of thiourea and amide groups in binding

Table 1 Association constants K_{ass} (M^{-1}) of receptors **4** and **5** with dicarboxylate anions

Anion	Receptor **4**		Receptor **5**		Receptor **5**	
	$K_{ass}(M^{-1})^b$	*R*	$K_{ass}(M^{-1})^b$	*R*	$K_{ass}(M^{-1})^c$	*R*
Adipate[a]	$(4.64 \pm 0.34^d) \times 10^4$	0.9981	$(3.43 \pm 0.20^d) \times 10^4$	0.9989	$(3.18 \pm 0.33^d) \times 10^4$	0.9929
Glutarate[a]	$(6.38 \pm 0.44^d) \times 10^3$	0.9977	$(1.69 \pm 0.19^d) \times 10^4$	0.9938	$(8.31 \pm 0.67^d) \times 10^3$	0.9977
Succinate[a]	$(4.05 \pm 0.33^d) \times 10^3$	0.9974	$(1.50 \pm 0.21^d) \times 10^3$	0.9955	$(4.35 \pm 0.20^d) \times 10^3$	0.9933
Malonate[a]	$(3.02 \pm 0.40^d) \times 10^3$	0.9971	$(1.20 \pm 0.11^d) \times 10^3$	0.9959	$(3.35 \pm 0.20^d) \times 10^3$	0.9924

[a] The anions were used as their tetrabutylammonium salts. [b] The data were calculated from UV-vis titrations in DMSO. [c] The data were calculated from fluorescence titrations in DMSO. [d] All error values were obtained by the results of non-linear curve fitting.

anions by multiple hydrogen bonding is an important factor for an efficient recognition. The incorporation of multiple NH into the receptors strengthens the interactions between the host and the guest. In receptor **4**, the electron-withdrawing effect of nitro groups enhances the acidity of the protons in thiourea groups, as the naphthalene protons in receptor **5**, taking part in the formation of multiple hydrogen bonding. All these factors improve the binding ability of the hosts to dicarboxylate anions. The results contained in Table 1 confirm that receptors **4** and **5** are better selective receptors for dicarboxylate anions than those of known receptor systems.[3d,e] Both receptors **4** and **5** have no binding ability with acetate, dihydrogen phosphate and the halogen (Cl^-, Br^-, I^-) anions.

Conclusions

Calix[4]arenes **4** and **5** containing thiourea and amide moieties were synthesized in high yields. Compounds **4** and **5** can form 1 : 1 complexes with dicarboxylate anions by multiple hydrogen bonding interactions. The result of non-linear curve fitting confirms that both **4** and **5** have a good sensitivity for recognition of dicarboxylates and the sensitivity depends on the chain length of the dicarboxylate anions. The results indicate that receptors **4** and **5** have no the recognition ability for AcO^-, Cl^-, Br^-, I^- and $H_2PO_4^-$. It is clear that the cooperative actions of thiourea and amides in binding anions by multiple hydrogen bonding and the relative stable conformation of the hosts play an important role in the selective anion recognition. There is an observable colour change by the naked eye in the recognition of **4** and dicarboxylate, which is promising for use as optical chemosensors for dicarboxylate anions.

Experimental

General

Melting points were determined with a Reichert 7905 melting-point apparatus (uncorrected). IR spectra were obtained on a Nicolet 670 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded in DMSO-d_6, with Me_4Si as internal standard, on a Varian Mercury VX-300 MHz spectrometer. Mass spectra were recorded on a ZAB-HF-3F mass spectrometer. Elemental analysis was determined with a Carlo-Erba 1106 instrument. The UV-vis spectra were performed with a TU-1901 spectrophotomer. Fluorescence spectra were obtained on a Shimadzu RF-5301 spectrometer. $CHCl_3$ and Et_3N were dried and distilled from CaH_2. Toluene was dried and distilled from Na. Potassium carbonate was baked at 500 °C. All other commercially available reagents were used without further purification. Compounds **1**, **2**, **3** were synthesized respectively according to the literature.[13,14,5]

5,11,17,23-Tetra-4-*tert*-butyl-25,27-bis(*p*-nitrophenylthio-ureido-ethene-aminocarbonylmethoxy)-26,28-dihydroxycalix[4]-arene (4). To a solution of *p*-nitrophenylisothiocyanate (0.10 g, 0.56 mmol) and triethylamine (1.0 mL, 7.18 mmol) in dry $CHCl_3$ (10 mL), **3** (0.23 g, 0.25 mmol) in dry $CHCl_3$ (10 mL) was added at room temperature. After stirring at room temperature for 15 min, the precipitate was filtered off, the solid was washed by $CHCl_3$ and dried *in vacuo* to obtain **4** (0.27 g) as a yellow powder in 91% yield; mp > 200 °C. Found: C, 65.29; H, 6.81; N, 9.18. Calc. for $C_{66}H_{80}N_8O_{10}S_2$: C, 65.53; H, 6.68; N, 9.27%; IR (KBr, cm^{-1}): 3529, 3341 (NH, OH), 1664 (s, C=O), 1543 (s, NO_2), 1332 (C=S); ^{1}H NMR (DMSO-d_6): δ_H 1.12 (s, 18H, Bu^t), 1.14 (s, 18H, Bu^t), 3.47 (d, *J* = 13.5 Hz, 4H, $ArCH_2Ar$), 3.61 (s, 4H, $CNCH_2$), 3.71 (s, 4H, CH_2NCO), 4.15 (d, *J* = 13.5 Hz, 4H, $ArCH_2Ar$), 4.54 (s, 4H, OCH_2CO), 7.08 (s, 4H, ArH), 7.15 (s, 4H, ArH), 7.68 (d, *J* = 10.8 Hz, 4H, ArH), 8.10 (d, 4H, *J* = 10.8 Hz, ArH), 8.27 (s, 2H, ArOH) 8.45 (s, 2H, NHCS), 8.90 (s, 2H, CONH), 10.06 (s, 2H, ArNH); MS (*m*/*z*): 1208 (M^+, 20%), 611 (15), 555 (8), 337(10), 175 (100).

5,11,17,23-Tetra-4-*tert*-butyl-25,27-bis(1′-naphthylthioureido-ethene-aminocarbonylmethoxy)-26,28-dihydroxycalix[4]arene (5). To a solution of 1-naphthylisothiocyanate (0.09 g, 0.50 mmol) and triethylamine (1.0 mL, 7.18 mmol) in dry $CHCl_3$ (10 mL), **3** (0.23 g, 0.25 mmol) in dry $CHCl_3$ (10 mL) was added at room temperature. After stirring for 4 h, the solvent and excessive triethylamine were evaporated under reduced pressure. Acetone was poured into the residue and stirred for 10 min. After filtration, the solvent was removed under reduced pressure, and the residue was recrystallized from ethanol and petroleum ether (60–90 °C) to obtain **5** (0.19 g) as a white powder in 62% yield; mp > 200 °C. Found: C, 72.65; H, 7.23; N, 6.82. Calc. for $C_{74}H_{86}N_6O_6S_2$.: C, 72.86; H, 7.12; N, 6.89%; IR (KBr, cm^{-1}): 3418, 3293 (NH, OH), 1673 (s, C=O), 1398 (C=S); ^{1}H NMR (DMSO-d_6): δ_H 1.10 (s, 18H, Bu^t), 1.17 (s, 18H, Bu^t), 3.42 (d, *J* = 13.5Hz, 4H, $ArCH_2Ar$), 3.46 (s, 4H, $SCNCH_2$), 3.61 (s, 4H, CH_2NCO), 4.15 (d, *J* = 13.5Hz, 4H, $ArCH_2Ar$), 4.38 (s, 4H, OCH_2CO), 7.14 (s, 8H, ArH), 7.31–7.91(m, 16H, H-naph and ArOH;), 8.42 (s, 2H, NHCS), 8.72 (s, 2H, CONH), 9.61(s, 2H, NH-naph); MS (*m*/*z*): 1218 (M^+, 20%), 611(10), 555 (8), 337 (10), 229 (15), 175 (100).

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