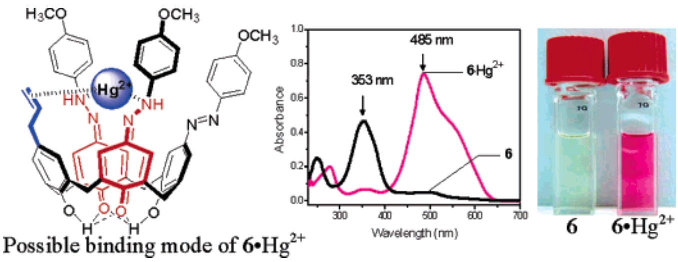
Synthesis of Upper-Rim Allyl- and *p*-Methoxyphenylazocalix[4]arenes and Their Efficiencies in Chromogenic Sensing of Hg^{2+} Ion

I-Ting Ho,† Gene-Hsiang Lee,‡ and Wen-Sheng Chung*,†

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050, Republic of China and Instrument Center, National Taiwan University, Taipei, Taiwan 106, Republic of China

wschung@cc.nctu.edu.tw

Received November 4, 2006



A series of upper-rim *p*-allyl and *p*-methoxyphenylazocalix[4]arenes (**6**, **8**, **9a**,**b**, and **10a**,**b**) were synthesized and shown to exhibit substantial color changes upon complexation with Hg^{2+} ion. Both the upper-rim *p*-allyl- and *p*-methoxyphenylazo groups on calix[4]arenes are proven to be key components in the recognition of Hg^{2+} ion. Job's plots revealed 1:1 binding stoichiometry for all these *p*-allyl- and *p*-arylazo-coupled calix[4]arenes with Hg^{2+} ions and Benesi−Hilderbrand plots were used for determination of their association constants. Our results also demonstrated that two *p*-methoxyphenylazo groups prefer to bind Hg^{2+} in a *distal* orientation rather than a *proximal* one, and if there are three *p*-methoxyphenylazo groups, the third flanking *p*-methoxyphenylazo group plays a role in disturbing the binding of the two distal diazo groups. Furthermore, it should be noted that triazocalix[4]arenes (**6**, **9a**, and **9b**) responded to all 14 metal ions without showing much preference among the eight transition-metal ions screened in this work (Cr^{3+}, Ni^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+}, Hg^{+}, Hg^{2+}, and Pb^{2+}).

Introduction

One of the keys in designing a useful chemosensor is to effectively convert molecular recognitions into optical or electrochemical signals. In this aspect, azo compounds are widely used in chromoionophores because they have been shown to exhibit substantial color changes upon complexation with metal ions.[1] Vögtle and co-workers were one of the first to couple the 4-(4-nitrophenyl)azo group with a crown ether and found that it exhibited a large hypsochromic shift when bound with Ba^{2+} ion.[1a] Recently, a 4-(4-nitrophenyl)azobenzene-based chemosensor, which can be used under physiological pH conditions, was reported for colorimetric detection of Cu^{2+} ion.[1b] Moreover, a series of 4-(4-nitrophenyl)azo-coupled calix[4]arenes and calix[4]crowns were found to be useful chromogenic sensors for various cations[1d,e,g−k] and anions,[1f,l] which in most cases exhibited large bathochromic shifts in the UV−vis spectra upon complexation with ions.

In spite of the 4-(4-nitrophenyl)azo group being frequently been used in calixarene-based chromoionophores, it is usually considered to be only a chromogenic center and not a metal-

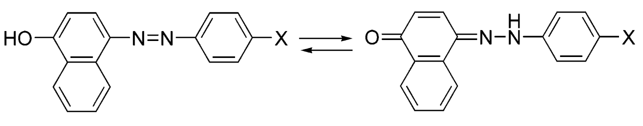
---

[1] For 4-(4-nitrophenyl)azo coupled chemosensors, see: (a) Löhr, H. G.; Vögtle, F. *Acc. Chem. Res.* **1985**, *18*, 65 and references therein. (b) Gunnlaugsson, T.; Leonard, J. P.; Murray, N. S. *Org. Lett.* **2004**, *6*, 1557. (c) Gordon, J. L. M.; Böhmer, V.; Vogt, W. *Tetrahedron Lett.* **1995**, *36*, 2445. (d) van der Veen, N. J.; Egberink, R. J. M.; Engbersen, J. F. J.; van Veggel, F. J. C. M.; Reinhoudt, D. N. *Chem. Commun.* **1999**, 681. (e) van der Veen, N. J.; Rozniecka, E.; Woldering, L. A.; Chudy, M.; Huskens, J.; van Veggel, F. J. C. M.; Reinhoudt, D. N. *Chem. Eur. J.* **2001**, *7*, 4878. (f) Lee, D. H.; Lee, K. H.; Hong, J.-I. *Org. Lett.* **2001**, *3*, 5. (g) Kim, J. S.; Shon, O. J.; Lee, J. K.; Lee, S. H.; Kim, J. Y.; Park, K.-M.; Lee, S.-S. *J. Org. Chem.* **2002**, *67*, 1372. (h) Kim, J. Y.; Kim, G.; Kim, C. R.; Lee, S. H.; Lee, J. H.; Kim, J. S. *J. Org. Chem.* **2003**, *68*, 1933. (i) Lee, S. H.; Kim, J. Y.; Ko, J.; Lee, J. Y.; Kim, J. S. *J. Org. Chem.* **2004**, *69*, 2902. (j) Kim, S. K.; Kim, S. H.; Kim, H. J.; Lee, S. H.; Lee, S. W.; Ko, J.; Bartsch, R. A.; Kim, J. S. *Inorg. Chem.* **2005**, *44*, 7866. (k) Liu, C. J.; Lin, J. T.; Wang, S. H.; Jiang, J. C.; Lin, L.-G. *Sens. Actuators, B* **2005**, *108*, 521. (l) Chen, C.-F.; Chen, Q.-Y. *New J. Chem.* **2006**, *30*, 143.

† National Chiao Tung University.
‡ National Taiwan University.

10.1021/jo062280s CCC: $37.00

SCHEME 1. Azophenol to Quinone−Hydrazone Tautomerism[4]

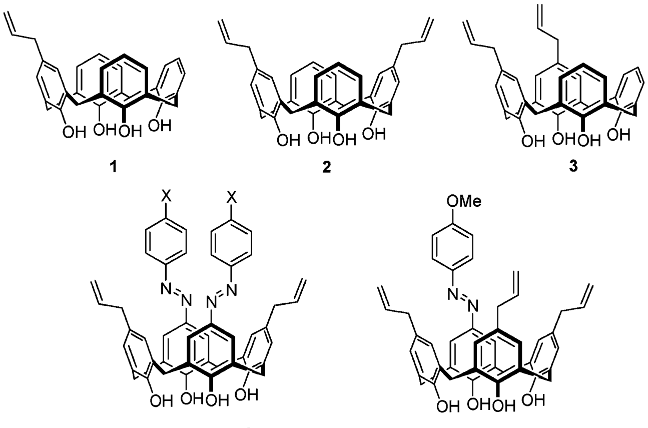


X = OCH_3, CH_3, H, Cl, NO_2

chelating site; therefore, lower-rim modification of calix[4]arene is usually required to endow it with metal-chelating ability. The perception changed completely when Nomura[2a,b] and Shinkai[2c] independently disclosed that *p*-(phenylazo)calix[4]- and -[6]-arenes, without any lower-rim substituent, were able to bind heavy metal ions such as Ag^+, Hg^+, and Hg^{2+}. More experimental results accumulated and supported that upper-rim azocalix[4]arenes can bind transition-metal ions effectively.[2d,f,g] Recently, we also reported that 5,17-bisallyl-11,23-bis-(*p*-methoxyphenyl)azocalix[4]arene (**7a**, vide infra), without lower-rim modification, is a highly sensitive chromogenic sensor for mercury ion (Hg^{2+}).[3] Why *two distal* (face-to-face) *p*-methoxyphenylazo groups bind Hg^{2+} ion so well may be because the methoxy groups help to donate electrons toward the azo group through resonance, which reinforces formation of hydrazone through azophenol to quinone−hydrazone tautomerization. Such a tautomerism (Scheme 1) has been known[4] to be highly favored in polar solvents.

Even if one finds an efficient way to convert molecular recognitions into optical signals, a very difficult task remains in designing a useful ion sensor, namely, *achieving high selectivity*. To achieve high selectivity in a chemosensor relies on how one assembles all these ligands in a stereofashion so that they may function cooperatively and selectively. In this context, using calix[4]arene as the framework for metal-ion sensors has at least two advantages: (1) one can attach metal binding ligands on the upper rim of the calix[4]arene in various combinations such as mono-, bis- (including *distal* and *proximal* orientations), tri-, and tetra substitutions and (2) even in the cone conformation the calix[4]arene is flexible enough to accomplish better binding with guest ion. Since "two distal" *p*-methoxyphenylazo groups on the upper rims of calix[4]arenes form strong complexes with Hg^{2+} ion, we were curious to find out whether "two proximal" or "three" *p*-methoxyphenylazo groups are still effective (better or worse?) in metal-ion sensing. Furthermore, we wished to evaluate which of the two di-*p*-methoxyphenylazocalix[4]arenes, namely, proximal (17,23) or distal (11,23), is more effective toward metal-ion binding. Moreover, the binding efficiencies of the juxtaposed allyl- or thioacetoxypropyl group(s) in these upper-rim *p*-methoxyphenylazo-modified calix[4]arenes was also examined.

CHART 1



1 **2** **3**

7a X = OMe
7b X = H

11

Results and Discussion

Using a radical elongation method on the double bond (thioacetic acid in the presence of AIBN at 75 °C),[5] the 5-allyl- and 5,17-diallylcalix[4]arenes (**1**[6a] and **2**[6b]) were converted to the corresponding 5-thioacetoxypropyl- and 5,17-dithioacetoxypropylcalix[4]arenes **4** and **5** in 49% and 75% yield, respectively. The 5,11-diallycalix[4]arene **3** was prepared according to a literature[6b] procedure. Compounds **1**, **3**, **4**, and **5** were then followed by diazo coupling reactions to furnish the corresponding 5-allyl-11,17,23-triazocalix[4]arene **6**, 5,11-diallyl-17,23-diazocalix[4]arene **8**, 5-thioacetoxypropyl-11,17,23-triazocalix[4]arenes **9a**,**b**, and 5,17-dithioacetoxypropyl-11,23-diazocalix[4]arenes **10a**,**b** in 67−93% yields (Chart 1 and Scheme 2). ^1H NMR spectra of these azocalix[4]arenes **6** and **8**−**10** exhibit two broad peaks around δ 4.4−4.2 and 3.9−3.4 which are the signals of the methylene bridge protons of these calix[4]arenes and imply that they are more stable in cone conformations.[7] ^{13}C NMR signals of the methylene bridges of these azocalix[4]arenes **6** and **8**−**10** appeared around δ 32, providing additional evidence to support that they are in cone conformations.[7] The structures of all these calix[4]arenes were fully characterized by NMR (^1H and ^{13}C), MS, and HRMS (see Experimental Section), where compound **10a** was further confirmed by a single-crystal X-ray analysis to be in the cone conformation (Figure 1).

The absorption maxima (λ_{max}) and molar extinction coefficients of the chromogenic calix[4]arenes synthesized in this work are summarized in Table 1. As can be seen, these *p*-methoxyphenylazocalix[4]arenes have similar λ_{max}

---

(2) For some of the early examples reporting complexation between azocalix[4]arenes and metal ions, see: (a) Nomura, E.; Taniguchi, H.; Otsuji, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3797. (b) Nomura, E.; Taniguchi, H.; Tamura, S. *Chem. Lett.* **1989**, 1125. (c) Shimizu, H.; Iwamoto, K.; Fujimoto, K.; Shinkai, S. *Chem. Lett.* **1991**, 2147. (d) Deligöz, H.; Erdem, E. *Solvent Extr. Ion Exch.* **1997**, *15*, 811. (e) Kim, N. Y.; Chang, S.-K. *J. Org. Chem.* **1998**, *63*, 2362. (f) Ma, Q.; Ma, H.; Su, M.; Wang, Z.; Nie, L.; Liang, S. *Anal. Chim. Acta* **2001**, *439*, 73. (g) Roundhill, D. M.; Shen, J. Y. In *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrofield, J., Vicens, J., Eds.; Kluwer: Dordrecht, 2001; Chapter 22, pp 407−420. (h) Oueslati, F.; Dumazet-Bonnamour, I.; Lamartine, R. *New J. Chem.* **2003**, *27*, 644. (i) Dumazet-Bonnamour, I.; Halouani, H.; Oueslati, F.; Lamartine, R. *C. R. Chim.* **2005**, *8*, 881. (j) Rouis, A.; Mlika, R.; Dridi, C.; Davenas, J.; Ouada, H. B.; Halouani, H.; Bonnamour, I.; Jaffrezic, N. *Mater. Sci. Eng., C* **2006**, *26*, 247.

(3) Kao, T.-L.; Wang, C.-C.; Pan, Y.-T.; Shiao, Y.-J.; Yen, J.-Y.; Shu, C.-M.; Lee, G.-H.; Peng, S.-M.; Chung, W.-S. *J. Org. Chem.* **2005**, *70*, 2912.

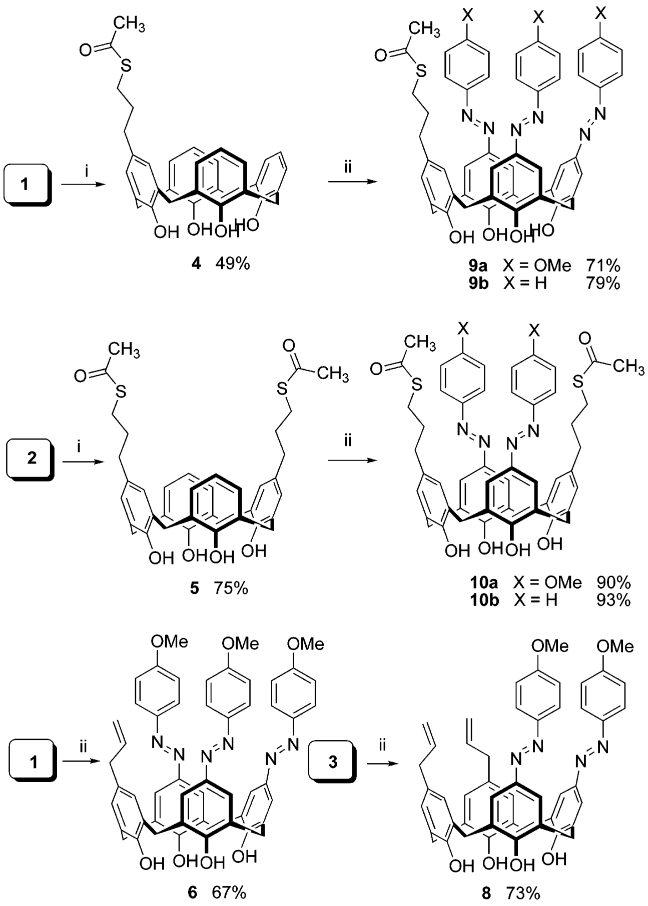
(4) For references of azophenol to quinone−hydrazone tautomerism, see: (a) Kishimoto, S.; Kitahara, S.; Manabe, O.; Hiyama, H. *J. Org. Chem.* **1978**, *43*, 3882. (b) Shinkai, S.; Araki, K.; Shibata, J.; Tsugawa, D.; Manabe, O. *Chem. Lett.* **1989**, 931. (c) Zazulak, W.; Chapoteau, E.; Czech, B. P.; Kumar, A. *J. Org. Chem.* **1992**, *57*, 6720. (d) Karci, F.; Sener, Í.; Deligöz, H. *Dyes Pigments* **2003**, *59*, 53. (e) Chawla, H. M.; Singh, S. P.; Sahu, S. N.; Upreti, S. *Tetrahedron* **2006**, *62*, 7854.

(5) Buskas, T.; Söderberg, E.; Konradsson, P.; Fraser-Reid, B. *J. Org. Chem.* **2000**, *65*, 958.

(6) (a) Gutsche, C. D.; Lin, L. G. *Tetrahedron* **1986**, *42*, 1633. (b) Shu, C.-M.; Yuan, T.-S.; Ku, M.-C.; Ho, Z.-C.; Liu, W.-C.; Tang, F.-S.; Lin, L.-G. *Tetrahedron* **1996**, *52*, 9805.

(7) (a) Jaime, C.; De Mendoza, J.; Prados, P.; Nieto, P. M.; Sanchez, C.; *J. Org. Chem.* **1991**, *56*, 3372−3376. (b) Magrans, J. O.; De Mendoza, J.; Pons, M.; Prados, P. *J. Org. Chem.* **1997**, *62*, 4518−4520.

SCHEME 2. Synthetic Pathways for Chromoionophores 4−7 and 9−10[a]



[a] Reagents and conditions: (i) thioacetic acid, AIBN, 1,4-dioxane, reflux 24 h. (ii) *p*-OMe-aniline/acetone, $NaNO_2$/4 N HCl, pyridine, 0 °C, 3 h.

TABLE 1. λ_{max} and Corresponding Extinction Coefficient of Azocalix[4]arenes 6, 8, 9a,b, and 10a,b in a Methanol−Chloroform (v/v = 1/399) Cosolvent at 25 °C

compound	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})
6	353	66 000
7a[a]	359	51 000
8	355	51 000
9a	355	68 000
9b	338	54 000
10a	358	42 000
10b	348	43 000

[a] Data from ref 3.

(356 ± 2 nm) and those without *p*-substituted phenylazo groups have shorter λ_{max} (**9b**, 338 nm and **10b**, 348 nm). Although the molar extinction coefficients for tri(*p*-methoxyphenyl)azocalix[4]arenes **6** and **9a** are higher than those for di(*p*-methoxyphenyl)azocalix[4]arenes **8** and **10a**, they are not linearly proportional to the numbers of the azo groups. Next, we then investigated the affinities of these upper-rim allyl-, thioacetoxypropyl-, and *p*-methoxyphenylazo-coupled calix[4]arenes **6** and **8**−**10** for a series of groups 1A (Li^+, Na^+, K^+), 2A (Mg^{2+}, Ca^{2+}, Ba^{2+}), and transition-metal ions (Cr^{3+}, Ni^{2+}, Cu^{2+}, Ag^+, Cd^{2+}, Hg^+, Hg^{2+}, and Pb^{2+}) in a methanol−chloroform (v/v = 1/399) cosolvent. It was interesting to find that triazocalix[4]arenes (**6**, **9a**, and **9b**) responded to all 14 metal ions without showing much preference among the eight transition-metal ions screened. Using 5-allyl-11,17,23-tri(*p*-methoxyphenyl)azocalix[4]arene **6** as an example, we found that it complexed with not only the Groups 1A and 2A ions (Figure 2a) but also the eight transition-metal ions without showing much difference in their sensitivity (Figure 2b). By contrast, the *proximal* di-*p*-methoxyphenylazocalix[4]arene **8** was more selective toward transition-metal ions, especially Hg^{2+} and Hg^+ ions (Figure 3a and b).[8a] The latter observation is reminiscent of our previous report[3] in which the *distal* di(*p*-methoxyphenyl)azocalix[4]arene **7a** was found to be most sensitive toward Hg^{2+} ion among the 14 metal ions screened. Hg^{2+} is known to prefer a linear coordination;[8b] therefore, it forms a very strong complex with compound **7a**, which contains two sets of distal diazo and diallyl groups. Compound **6**, which contains three azo groups and an allyl, not only engages in a linear coordination by two azo groups, but also adopts different types of coordination, such as trigonal planar and pyramidal, by the three azo groups to bind various other metal ions.[8b] In order to have a direct comparison of the relative binding efficiencies of the newly synthesized azocalix[4]arenes (**6** and **8**−**10**) with **7a**, we used Hg^{2+} for detailed UV−vis titration studies.

Upon interacting with $Hg(ClO_4)_2$ all these azocalix[4]arene compounds (**6** and **8**−**10**) experienced a marked bathochromic shift in their λ_{max}. Taking **6** as an example, the absorption maximum at 353 nm gradually decreased in intensity with formation of a new absorption band near 485−550 nm (Figure 4a). Three isosbestic points at 264, 294, and 410 nm can be easily identified when difference absorption spectral analysis[9a] was used for the titration (Figure 4b). The spectral features in Figure 4 are consistent with a 1:1 binding ratio between calix[4]arene **6** and Hg^{2+} ion. Further support of the 1:1 binding ratio comes from a Job's plot experiment,[9b] where absorption of the complex at 485 nm was plotted against the molar fraction of **6** under the condition of an invariant total concentration. As a result, the concentration of complex **6**·Hg^{2+} approached a maximum when the molar fraction of [**6**]/([**6**] + [Hg^{2+}]) was about 0.5 (Figure 4c). The 1:1 association constants for all these azo-coupled calix[4]arenes with Hg^{2+} were determined on the basis of Benesi−Hilderbrand plots[10] (see Figures 4d and S1−S3). Finally, the bathochromic shifts and isosbestic points of all these azocalix[4]arenes in the presence of 5 equiv of $Hg(ClO_4)_2$ and their association constants K_as (M^{-1}) are summarized in Table 2. It is interesting to note that λ_{max} for the *distal* diazocalix[4]arenes (e.g., **7a** and **10a**) are further red shifted when compared with those obtained for triazocalix[4]arenes (e.g., **6** and **9a**). When bonding with Hg^{2+} ion, the tri-*p*-methoxyphenylazocalix[4]arenes showed a λ_{max} around 485 nm and a shoulder around 510 nm, which may come from the

---

[8] (a) The *proximal* di-*p*-methoxyphenylazocalix[4]arene **8** was also showing chromogenic response toward Ag^+ ion, however, with complex UV−vis absorption changes which did not allow accurate estimation of the binding constant. Furthermore, ^1H NMR titration of compound **8** with Ag^+ ion showed very little complexation-induced chemical shift changes (see Figures S13 and S14). (b) For a concise table that quantitatively expresses the frequency of occurrence of the various coordination numbers and geometries for the d-block elements and their ions, see: Venkartaraman, D.; Du, Y.; Wilson, S. R.; Hirsch, K. A.; Zhang, P.; Moore, J. S. *J. Chem. Educ.* **1997**, *74*, 915. (c) We thank one of the reviewers for suggesting this experiment which helps to explain the UV−vis changes of the triazocalix[4]arene **6**.

[9] (a) Difference absorption spectra analysis is a popular method used in biophysical and biochemical fields, see: Lyles, M. B.; Cameron, I. L. *Biophys. Chem.* **2002**, *96*, 53. (b) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.

[10] Benesi, H. A.; Hilderbrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

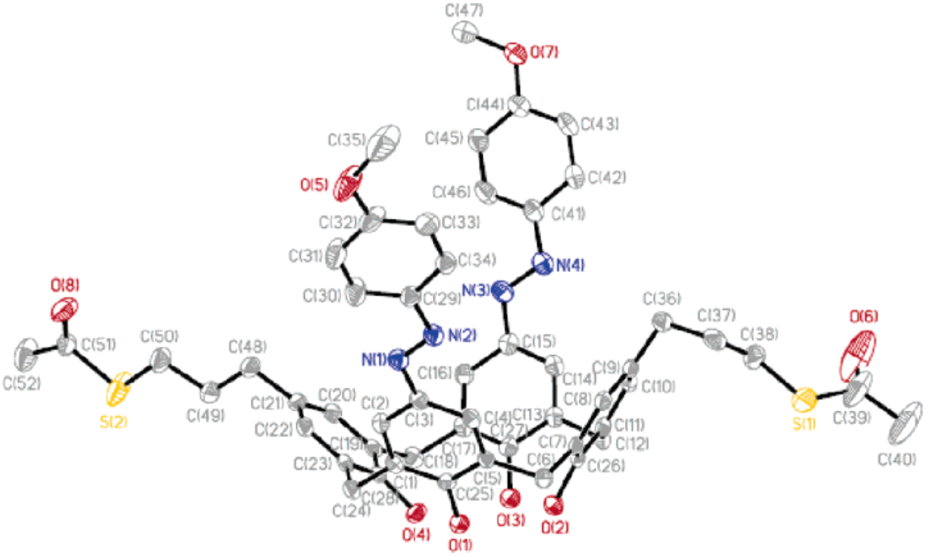


FIGURE 1. X-ray single-crystal structure of 5,17-dithioacetoxypropyl-11,23-di(*p*-methoxy-phenyl)azocalix[4]arene **10a**.

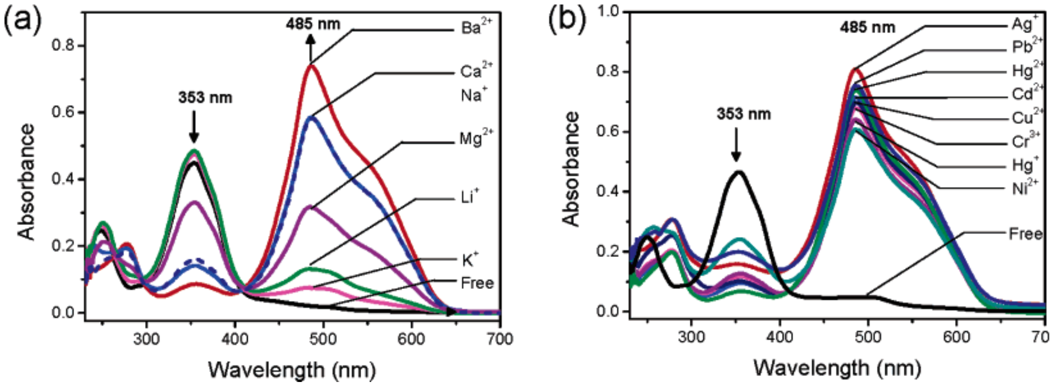


FIGURE 2. UV–vis spectra of 5-allyl-11,17,23-tri(*p*-methoxyphenyl)azocalix[4]arene **6** (7 μM) before (free) and after adding 9 equiv of various metal perchlorates in a methanol–chloroform (v/v = 1/399) cosolvent at 25 °C.

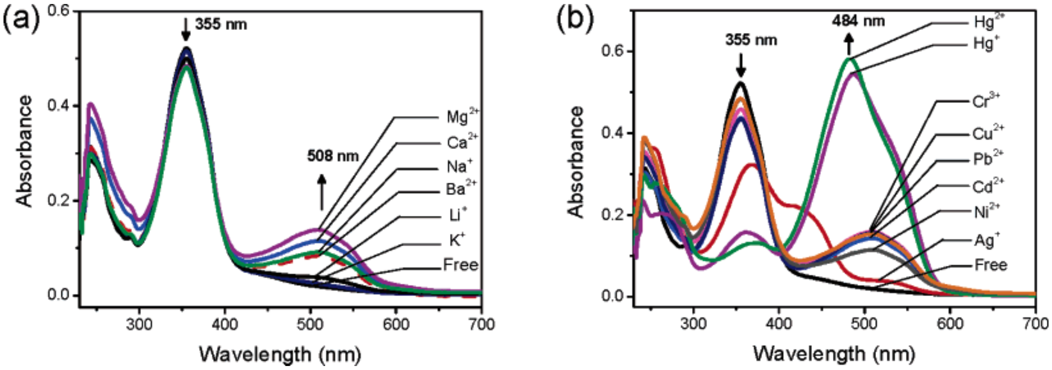


FIGURE 3. UV–vis spectra of 5,11-diallyl-17,23-di(*p*-methoxyphenyl)azocalix[4]arene **8** (10 μM) before and after adding 9 equiv of various metal perchlorates in a methanol–chloroform (v/v = 1/399) cosolvent at 25 °C: (a) Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, and Ba^{2+} and (b) Ag^+, Pb^{2+}, Hg^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Hg^+, and Ni^{2+} ions.

overlap of two absorption bands due to tautomerization of the *distal*[3] and the *proximal* diazo groups.

Since it is well known that these *p*-methoxyphenylazocalix[4]arenes (**6**–**10**) may behave like an acid–base indicator, we also inspected their UV–vis response with added acid.[8c] Previously we reported[3] that the UV–vis spectra of the "distal" diazocalix[4]arenes (e.g., **7a**) did not change much with added base when compared with the marked bathochromic shift with 1 equiv of added $Hg(ClO_4)_2$. Here we also found that the "distal" or "proximal" diazocalix[4]arenes (e.g., **7a**, **10a,b** and **8**) did not show significant response with 10 equiv of *p*-toluenesulfonic acid (*p*TSA), whereas large bathochromic shifts were observed with just 1 equiv of $Hg(ClO_4)_2$ (see Figures S17 and S18, Supporting Information). Interestingly, the UV–vis spectra of

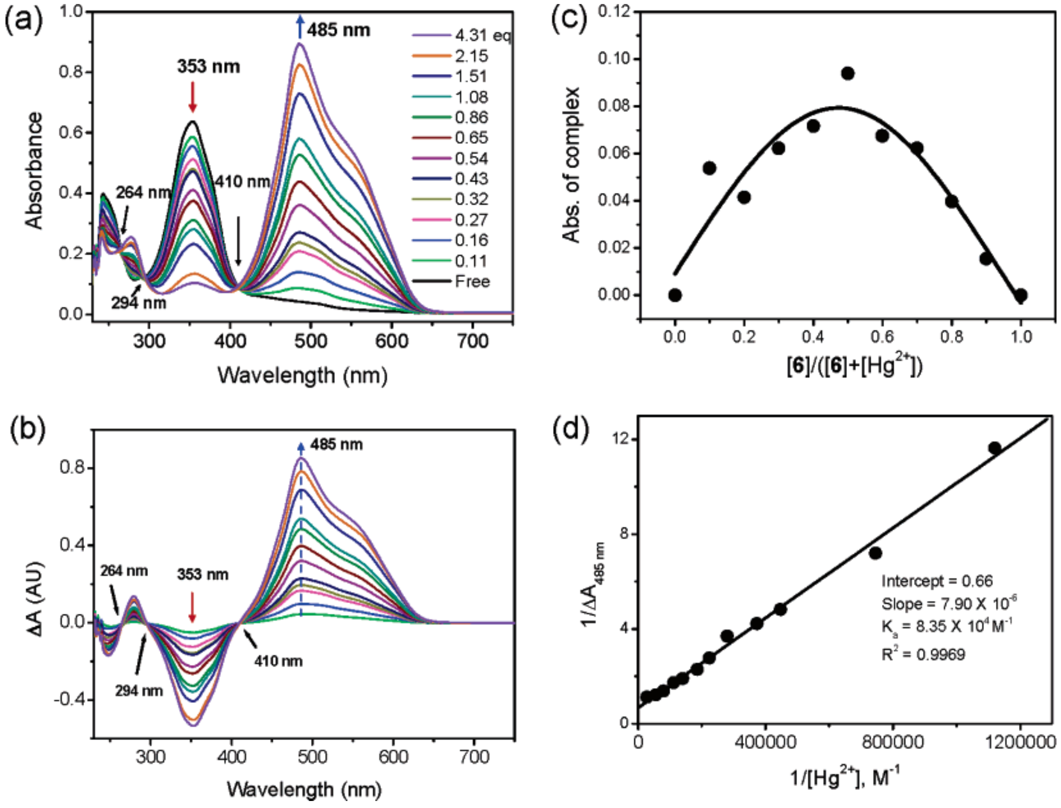


FIGURE 4. (a) UV−vis spectra of **6** (8 μM) upon titration with $Hg(ClO_4)_2$ in a methanol−chloroform (v/v = 1/399) cosolvent at 25 °C. (b) Difference absorption spectra of a. (c) Job's plot of a 1:1 complex of **6** and Hg^{2+} ion, where the absorption at 485 nm was plotted against the mole fraction of **6** at an invariant total concentration of 10 μM. (d) Benesi−Hilderbrand plot of **6** with $Hg(ClO_4)_2$ in the same cosolvent system.

TABLE 2. Association Constants (M^{-1}) of Ionophores 6, 7a,b, 8a,b, and 9a,b with $Hg(ClO_4)_2$ in a Methanol−Chloroform (v/v = 1/399) Cosolvent at 25 °C

compound	λ_{max} (nm)[b]	K_a (10^4 M^{-1})[c]	isosbestic point (nm)		
7a[a]	359 → 520	23.5	263	285	410
7b[a]	348 → 480	14.8	-	294	385
6	353 → 485	8.35	264	294	410
8	355 → 490	6.00	258	294	402
9a	355 → 489	3.05	265	294	410
9b	338 → 457	2.68	258	282	383
10a	358 → 512	2.09	260	286	410
10b	348 → 477	1.03	-	-	384

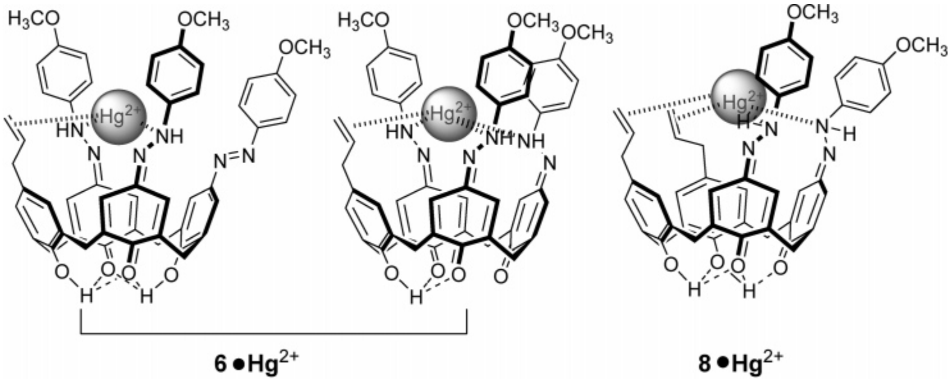
[a] Data from ref 3. [b] The arrows indicates a bathochromic shift of λ_{max}. [c] The error bar in the determination of association constant is estimated to be ±15% based on three independent experimental series.

triazocalix[4]arenes (**6** and **9a**,**b**) showed a similar response with 1 equiv of $Hg(ClO_4)_2$ or 10 equiv of *p*TSA. The latter observation seems to correlate with the nonselective responses of triazocalix[4]arenes (**6** and **9a**,**b**) with various other metal ions (see Figure 2).

Scrutiny of the association constants of these upper-rim allyl-, thioacetoxypropyl-, and *p*-substituted phenylazocalix[4]arenes **6**−**10** (see Table 2) with Hg^{2+} ion allows us to rank the relative binding affinities of the metal coordinating ligands as well as realize their exquisite stereoarrangements in space. On the basis of the fact that the K_a of **6**·Hg^{2+} (8.35×10^4 M^{-1}) is larger than that of **8**·Hg^{2+} (6.00×10^4 M^{-1}), we concluded that 'three' *p*-methoxyphenylazo groups are better than *proximal* (namely, 17,23) di-*p*-methoxyphenylazo groups in their binding toward Hg^{2+} ion. However, it was puzzling to find that *distal* (namely, 11,23) di-*p*-methoxyphenyl-azocalix[4]arene **7a** ($K_a = 23.5 \times 10^4$ M^{-1}) was better than tri-*p*-methoxyphenylazocalix[4]arene **6** toward Hg^{2+} binding. We further noted that *distal* di-*p*-methoxyphenylazocalix[4]arene **7a** was better than *proximal* di-*p*-methoxyphenylazocalix[4]arene **8** toward Hg^{2+} binding. All these results seem to imply that *p*-methoxyphenylazo groups prefer to bind Hg^{2+} in a linear fashion (namely, distal) and the third flanking *p*-methoxyphenylazo group plays a role in disturbing the strong binding of the distal diazo groups. Alternatively, the relatively poor binding of the tri-*p*-methoxyphenyl-azocalix[4]arenes with Hg^{2+} may be because there is a mismatch of the lower-rim hydrogen bondings when the hosts undergo azophenol to quinone−hydrazone tautomerization (see Scheme 1 and Chart 2).

One should be aware that the above discussion had an assumption that none of the allyl groups participated in Hg^{2+} binding. This assumption came from a previous observation[3] that no chemical shift change was found for the juxtaposed allyl groups when Hg^{2+} was added to the upper-rim *p*-methoxyphenyl-azocalix[4]arenes **7a** and **7b**, despite that the signal intensities of the allyl protons decreased dramatically in the presence of 1 equiv of Hg^{2+} ion. However, one should be able to assess the binding ability of the *p*-allyl group(s) toward Hg^{2+} ion if they are modified to other functional group(s) while keeping the juxtaposed *p*-methoxyphenylazo groups intact. Comparing the association constants in Table 2, we can see that both di- and tri-*p*-methoxyphenylazocalix[4]arenes became worse in their binding toward Hg^{2+} when the juxtaposed *p*-allyl group(s) was/were replaced by thioacetoxypropyl group(s) (e.g., K_a (**7a**) > K_a (**10a**), K_a (**7b**) > K_a (**10b**) and K_a (**6**) > K_a (**9a**)). The latter results imply that both the *p*-allyl and the azo groups must have assisted each other in their binding toward Hg^{2+} ion and the

CHART 2. Possible Binding Modes for 6·Hg^{2+} and 8·Hg^{2+}



binding ability of the allyl group is stronger than that of thioacetoxypropyl group.

Association constants in Table 2 also revealed that *p*-methoxyphenylazocalix[4]arenes are better than phenylazocalix[4]arenes in their binding toward Hg^{2+}, e.g. K_a (**9a**) > K_a (**9b**) and K_a (**10a**) > K_a (**10b**). This is also consistent with a previous report[3] that K_a (**7a**) > K_a (**7b**) (cf. entries 1 and 2, Table 2). Finally, when the *p*-allyl group(s) is/are replaced by thioacetoxypropyl group(s), the triazocalix[4]arenes have stronger K_as than those of diazocalix[4]arenes, for example, K_a (**9a**,**b**) > K_a (**10a**,**b**). The latter results seem to imply that in the absence of *p*-allyl groups the binding toward Hg^{2+} is dominated by the *p*-methoxyphenylazo groups in the calix[4]arenes; therefore, "three" azo groups are better than "two" in their binding toward metal ions. By the same token, the "three" *p*-methoxyphenylazocalix[4]arenes lost their specificity toward Hg^{2+} sensing and became sensitive to many metal ions (see Figure 2b).

In order to gain insight into the structures of complex formation of these chromogenic ionophores, we carried out ^{1}H NMR titration experiments. Figure 5 shows the ^{1}H NMR spectra of **6** (5 mM) in methanol-d_4/CDCl$_3$ (v/v = 1:3) solution in the presence of different amounts of Hg^{2+} ion. A few important features were observed from the ^{1}H NMR spectra: (1) some variation in chemical shifts is experienced by protons on the *p*-methoxyphenyl azophenol groups, that is, protons H$_{34}$, H$_{36}$, H$_{41}$, H$_{43}$, H$_{48}$, and H$_{50}$ on the *p*-methoxyphenyl ends move 0.05 ppm downfield upon complexation with Hg^{2+} ion (see inset of Figure 5, δ 7.1−7.2 where a new signal appeared); (2) signal intensities of the protons on allyl groups (namely, H$_{29}$, H$_{30}$, and H$_{31}$) almost disappeared in the presence of 0.9 equiv of Hg^{2+} ion; (3) the vaguely seen broad singlets of the methylene bridges around δ 3.5−4.5 in free ligand **6** were upfield shifted to δ 2−4 upon complexation with Hg^{2+} and became sharp and complicated.

Previously, it was thought that the allyl groups were not involved in the binding of metal ions;[3] however, the new results described above support its involvement in binding. Direct evidence to support the allyl group's participation in Hg^{2+} binding came from the ^{1}H NMR titration of 5,17-diallylcalix[4]arene **2** with Hg(ClO$_4$)$_2$ (see Figure 6). One can see that the

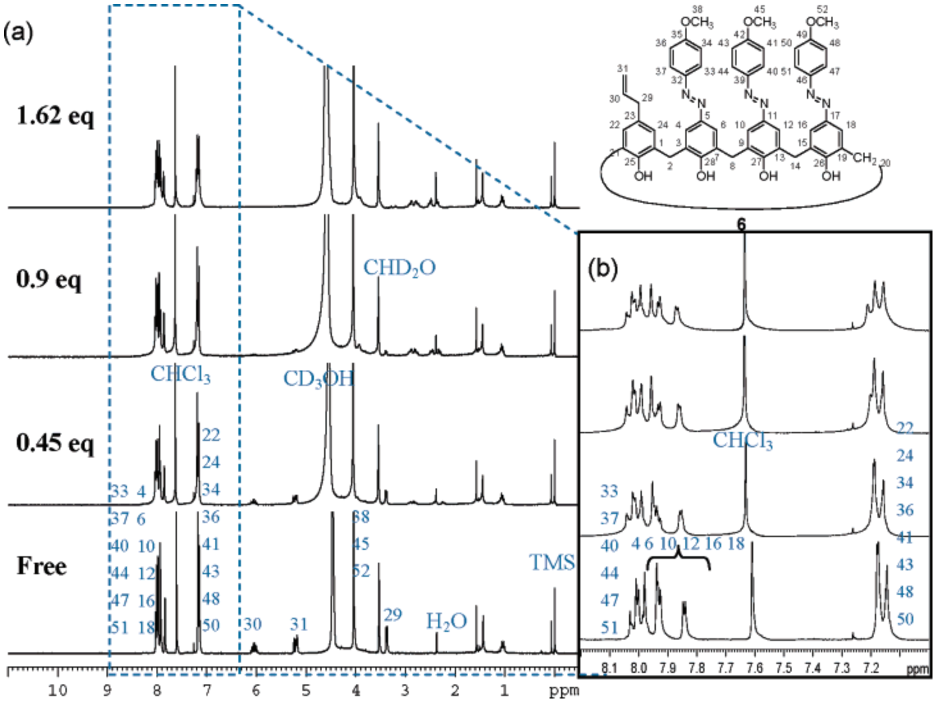


FIGURE 5. (a) ^{1}H NMR spectra of compound **6** (5 mM) in a methanol-d_4/CDCl$_3$ (v/v = 1:3) cosolvent in the presence of different amounts of Hg(ClO$_4$)$_2$. (b) The inset of spectra a in the δ 7.0−8.2 region.

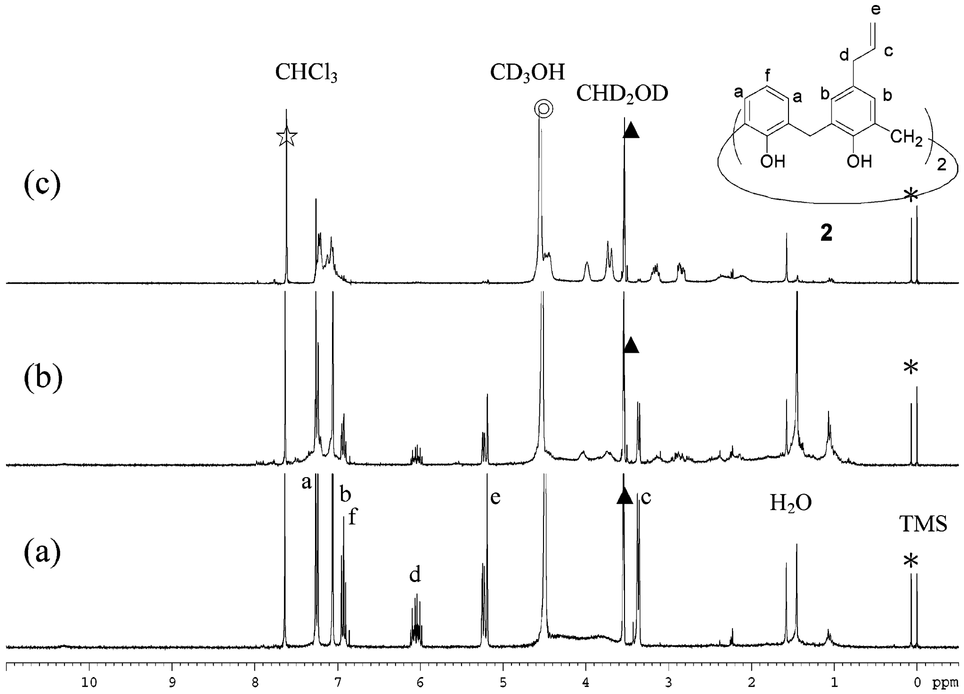


FIGURE 6. (a) ^{1}H NMR spectra of compound **2** (5 mM) in a methanol-d_4/CDCl$_3$ (v/v = 1:3) cosolvent in the presence of different amounts of Hg(ClO$_4$)$_2$: (b) 5.0 and (c) 10 mM.

effects of Hg^{2+} ion on the proton signals of the 5,17-diallylcalix[4]arene **2** are very similar to those with 5,17-diallyl-11,23-di-(*p*-methoxyphenyl)azocalix[4]arene **7a**^{3} and **6** (cf. Figure 5). More strong evidence for Hg^{2+} complexation with **6** and **8** came from their FAB-MS or ESI-MS, which showed mass peaks (M + Hg^{2+} + CH$_3$O) of the alkoxymercuration complexes (see Figures S19 and S20). This is reminiscent of the fact that oxymercuraton and aminomercuration reactions on olefins are well documented in the literature.[11] Furthermore, there are many ion-selective electrodes for soft metal ions which involve cation−π interactions from the alkenyl or alkynyl bonds.[12] Thus, it is believed that changes in the chemical shifts and signal intensities of **6** and **7a** with Hg^{2+} ion are due to coordination of the Hg^{2+} ion by the upper-rim juxtaposed allyl and azo groups.

One issue remains to be explained: is there any evidence that the thioacetoxypropyl groups do not interact with the Hg^{2+} ion? In synthesizing the thioacetoxypropyl groups on the upper rim of calix[4]arenes we actually expected that S of the carbonyl group in thioacetoxypropyl should coordinate to Hg^{2+}; however, we were surprised to find that the association constants of **9a**,**b** and **10a**,**b** toward Hg^{2+} were smaller than those of corresponding allyl-calix[4]arenes (such as **6**, **7**, and **8**). ^{1}H NMR titration spectra of compound **10a** with various amounts of Hg(ClO$_4$)$_2$ showed that there was no chemical shift change in the spectra; however, the moment we added Hg(ClO$_4$)$_2$ into the NMR tube, some precipitates formed (see Figure S12). Note that the spectra were taken after the precipitate was filtered out; otherwise, it would disturb the sharpness and quality of the spectra. It should also be noted that we did not "observe" such a precipitation *by the naked eye* in the UV−vis titration experiments of **9a**,**b** and **10a**,**b** by Hg^{2+}. The precipitation explains why there is an abnormal behavior of the binding constants of **9a,b** toward Hg^{2+} as compared with **10a**,**b**.

FIGURE 7. Colors of (a) **6** (10 μM) in a methanol−chloroform (v/v = 1/399) cosolvent at 25 °C and (b) **6** after adding 5 equiv of Hg(ClO$_4$)$_2$.

Summary and Conclusions

The series of upper-rim *p*-allyl- and *p*-methoxyphenylazocalix[4]arenes studied here (compounds **6** and **8**−**10**) was readily synthesized and shown to exhibit substantial color changes upon complexation with Hg^{2+} ion (see Figure 7). Both the upper-rim *p*-allyl- and *p*-methoxyphenylazo groups on calix[4]arenes are key components in the recognition of Hg^{2+} ion. Our results

---

(11) (a) Traylor, T. G.; Baker, A. W. *J. Am. Chem. Soc.* **1963**, *85*, 2746. (b) Btrown, H. C.; Geoghegan, P. J., Jr. *J. Org. Chem.* **1970**, *35*, 1844. (c) Bach, R. D.; Richter, R. F. *J. Org. Chem.* **1973**, *38*, 3442. (d) Griffith, R. C.; Gentile, R. J.; Davidson, T. A.; Scott, F. L. *J. Org. Chem.* **1979**, *44*, 3580. (e) Chatt, J. *Chem. Rev.* **1950,** *50*, 7−43.

(12) (a) Ma, J. C.; Dougherty, D. A. *Chem. Rev.* **1997**, *97*, 1303. (b) Yajima, S.; Yoshioka, N.; Tanaka, M.; Kimura, K. *Electroanalysis* **2003**, *15*, 1319. (c) Dong, H.; Zheng, H.; Lin, L.; Ye, B. *Sens. Actuator B* **2006**, *115*, 303.

show that the binding ability of various *p*-methoxyphenylazocalix[4]arenes toward Hg^{2+} ion follow the order 5,17-diallyl-11,23-di-*p*-methoxyphenylazo- **7a** > mono-allyl-tri-*p*-methoxyphenylazo- **6** > 5,11-diallyl-17,23-di-*p*-methoxyphenylazo- **8** > 5-thioacetylpropyl-11,17,23-tri-*p*-methoxyphenylazo- **9a** > 5,-17-dithioacetylpropyl-11,23-di-*p*-methoxyphenylazo- **10a** ≈ tri-allyl-mono-*p*-methoxyphenylazocalix[4]arene[3] **11**. The results imply that *p*-methoxyphenylazo groups prefer to bind Hg^{2+} in a *distal* orientation rather than a *proximal* one and the third flanking *p*-methoxyphenylazo group plays a role in disturbing the binding of the two *distal* diazo groups (see Chart 2), which is due in part to the mismatch of lower-rim hydrogen bonds. Thus, "three" metal chelating groups do not warrant a better binding efficiency than "two" toward a linear coordinating metal ion (such as Hg^{2+}); furthermore, they may lose the metal-ion specificity due to various coordination modes.

Experimental Section

The syntheses of 5-monoallylcalix[4]arene **1**,[6a] 5,17-bisallylcalix[4]arene **2**,[6b] and 5,11-bisallylcalix[4]arene **3**[6b] have been reported by Lin et al., and we followed their procedures for the preparation.

General Procedures for the Upper-Rim Sulfanylacetylation of the Allylcalix[4]arenes **1** and **3** To Give Compounds **4** and **5**. Compound **1** or **3** (0.50 g, 1.08 or 0.99 mmol) was dissolved in dry 1,4-dioxane (10 mL), and then thioacetic acid (2 and 4 equiv for **1** and **3**, respectively) and AIBN (2,2′-azobisisobutyronitrile, 0.1 equiv) were added under nitrogen. Before reacting at 75 °C, the solution was thoroughly purged with N_2 for 20 min. After refluxing for 24 h, the reaction was quenched with cyclohexene, and then the solvent was removed under vacuum to give the crude product. Column chromatography on silica gel eluting with hexane and ethyl acetate gave white solid compounds **6** and **8** in 49% and 75% yield, respectively.

Data for 5-[3-(Acetylsulfanyl)propyl]-25,26,27,28-tetrahydroxycalix[4]arene 4. The solid was eluted with hexane/ethyl acetate (v/v = 10/1) and gave 0.32 g (49%) of a white powder, mp 244−246 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 10.18 (s, 4H), 7.04 (d, *J* = 7.6 Hz, 6H), 6.84 (s, 2H), 6.78−6.65 (m, 3H), 4.40−4.10 (bs, 4H), 3.70−3.40 (bs, 4H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.46(t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 1.87−1.70 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8 (C_q), 148.7 (C_q), 146.8 (C_q), 134.7 (C_q), 128.9 (CH), 128.9 (CH), 128.8 (CH), 128.2 (C_q), 128.2 (C_q), 128.1 (C_q), 122.2 (CH), 33.9 (CH_2), 31.7 (CH_2), 31.7 (CH_2), 31.0 (CH_2), 30.6 (CH_3), 28.6 (CH_2); IR (KBr pellet, cm^{-1}) 3192, 2943, 1691, 1467, 1452, 753; FAB-MS *m*/*z* 541 ($M + H^+$); HRMS *m*/*z* calcd for $C_{38}H_{40}O_6S_2$ 656.2266, found 656.2279.

Data for 5,17-Bis[3-(acetylsulfanyl)propyl]-25,26,27,28-tetrahydroxycalix[4]arene 5. The solid was eluted with hexane/ethyl acetate (v/v = 6/1) and gave 0.49 g (75%) of a white powder, mp 141−143 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 10.17 (s, 4H), 7.04 (d, *J* = 7.6 Hz, 4H), 6.84 (s, 4H), 6.72 (t, *J* = 7.6 Hz, 2H), 4.40−4.10 (bd, 4H), 3.65−3.35 (bd, 4H), 2.83 (t, *J* = 7.2 Hz, 4H), 2.46-(t, *J* = 7.2 Hz, 4H), 2.30 (s, 6H), 1.90−1.70 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8 (C_q), 148.8 (C_q), 146.9 (C_q), 134.7 (C_q), 128.9 (CH), 128.8 (CH), 128.2 (C_q), 128.1 (C_q), 122.2 (CH), 33.9 (CH_2), 31.7 (CH_2), 31.0 (CH_2), 30.6 (CH_3), 28.6 (CH_2); IR (KBr pellet, cm^{-1}) 3189, 2936, 1689, 1480, 1455, 1132, 753; FAB-MS *m*/*z* 657 ($M + H^+$); HRMS *m*/*z* calcd for $C_{33}H_{32}O_5S$ 540.1970, found 540.1970.

General Procedures for the Synthesis of Allyl- and Acetylsulfanyl- arylazo-25,26,27,28-tetrahydroxycalix[4]arenes 6, 8, 9a,b, and 10a,b. To an ice cold solution of 2.6 mmol of *p*-substituted aniline in 5 mL of acetone was added a solution of 0.27 g (3.88 mmol) of $NaNO_2$ in 5 mL of 4 N HCl, and this was stirred for 30 s. The combined solution was then added to another ice cold solution of 0.20 g (0.43 mmol) of monoallyl-, 1,2-diallyl-, mono-acetylsulfanyl-, or mono-acetylsulfanylcalix[4]arenes (1, 3, 4, or 5) in 10 mL of pyridine to produce a colored solution. The reaction mixture was stirred at 0 °C for 3 h and then treated with 50 mL of 4 N HCl to give a colored precipitate. The solid residue was purified by column chromatography with hexane and ethylacetate as eluent and gave the corresponding bisarylazo or triarylazo products in 67−93% yields.

Data for 5-Allyl-11,17,23-tri(*p*-methoxyphenyl)azo-tetrahydroxycalix[4]arene, 6. The solid product was eluted with hexane/ethyl acetate (v/v = 2/1) and gave 0.25 g (67%) of a yellow powder, mp 252−254 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 10.27 (bs, 4H), 7.90−7.80 (m, 6H), 7.80−7.70 (m, 4H), 7.66 (d, *J* = 2.2 Hz, 2H), 7.05−6.90 (m, 8H), 5.95−5.75 (m, 1H), 5.10−5.00 (m, 2H), 4.45−4.20 (bm, 4H), 3.85 (s, 9H), 3.90−3.55 (m, 4H), 3.19 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6 (C_q), 161.6 (C_q), 151.0 (C_q), 150.9 (C_q), 147.7 (C_q), 147.6 (C_q), 147.0 (C_q), 146.9 (C_q), 146.7 (C_q), 137.4 (CH), 134.1 (C_q), 129.5 (CH), 128.7 (C_q), 128.3 (C_q), 128.1 (C_q), 127.5 (C_q), 124.4 (CH), 124.3 (CH), 124.2 (CH), 123.9 (CH), 123.4 (CH),115.7 (CH_2), 114.1 (CH), 55.5 (CH_3), 39.2 (CH_2), 31.9 (CH_2), 31.8 (CH_2); IR (KBr pellet, cm^{-1}) 3181, 2929, 1600, 1583, 1502, 1454, 1252, 1146, 836; FAB-MS *m*/*z* 867 ($M + H^+$); HRMS *m*/*z* calcd for $C_{52}H_{46}N_6O_7$ 866.3428, found 866.3415.

Data for 5,11-Diallyl-17,23-di(*p*-methoxyphenyl)azo-tetrahydroxycalix[4]arene, 8. The solid product was eluted with hexane/ethyl acetate (v/v = 2/1) and gave 0.20 g (73%) of a yellow powder, mp 245−246 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 10.24 (bs, 4H), 7.84 (d, *J* = 8.8 Hz, 4H), 7.73 (d, *J* = 2.2 Hz, 2H), 7.65 (d, *J* = 2.2 Hz, 2H), 7.10−6.92 (m, 6H), 6.90−6.85 (bd, 2H), 5.91−5.80 (m, 2H), 5.06−5.01 (m, 4H), 4.40−4.15 (br m, 4H), 3.86 (s, 6H), 3.90−3.40 (br m, 4H), 3.19 (d, *J* = 6.5 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6 (C_q), 151.1 (C_q), 147.6 (C_q), 147.0 (C_q), 146.8 (C_q), 137.5 (CH), 133.8 (C_q), 129.2 (CH), 128.9 (C_q), 128.2 (C_q), 128.1 (C_q), 127.4 (C_q), 124.3 (CH), 124.0 (CH), 123.4 (CH), 115.7 (CH_2), 114.1 (CH), 55.5 (CH_3), 39.2 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 31.7 (CH_2); IR (KBr pellet, cm^{-1}) 3185, 2929, 1601, 1583, 1502, 1457, 1253, 1147, 837; FAB-MS *m*/*z* 773 ($M + H^+$); HRMS *m*/*z* calcd for $C_{48}H_{44}N_4O_6$ 772.3261, found 772.3271.

Data for 5-[3-(Acetylsulfanyl)propyl]-11,17,23-tri(*p*-methoxyphenyl)azo-tetrahydroxycalix[4]arene, 9a. The solid product was eluted with hexane/ethyl acetate (v/v = 2/1) and gave 0.25 g (71%) of a yellow powder, mp 266−268 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 10.27 (bs, 4H), 8.00−7.80 (m, 6H), 7.80−7.76 (m, 4H), 7.70−7.65 (m, 2H), 7.10−6.90 (m, 8H), 4.50−4.20 (m, 4H), 3.87 (s, 9H), 4.00−3.60 (m, 4H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 1.86−1.76 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8 (C_q), 161.7 (C_q), 161.6 (C_q), 151.0 (C_q), 150.9 (C_q), 147.7 (C_q), 147.7 (C_q), 147.0 (C_q), 146.6 (C_q), 135.3 (C_q), 129.3 (CH), 128.8 (C_q), 128.4 (C_q), 128.1 (C_q), 127.5 (C_q), 124.4 (CH), 124.4 (CH), 124.2 (CH), 123.9 (CH), 123.4 (CH), 114.1 (CH), 55.5 (CH_3), 33.8 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 31.0 (CH_2), 30.6 (CH_3), 28.5 (CH_2); IR (KBr pellet, cm^{-1}) 3176, 2929, 1688, 1600, 1583, 1502, 1453, 1252, 1146, 837; FAB-MS *m*/*z* 943 ($M + H^+$); HRMS *m*/*z* calcd for $C_{54}H_{50}N_6O_8S$ 942.3411, found 942.3389.

Data for 5-[3-(Acetylsulfanyl)propyl]-11,17,23-tri(*p*-phenyl)-azo-tetrahydroxycalix[4]arene 9b. The solid product was eluted with hexane/ethyl acetate (v/v = 1/1) and gave 0.25 g (79%) of a yellow powder, mp 270−271 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 10.26 (s, 4H), 7.90−7.75 (m, 10H), 7.71 (s, 2H), 7.60−7.35 (m, 9H), 6.97 (s, 2H), 4.50−4.20 (m, 4H), 3.95−3.50 (m, 4H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.48 (t, *J* = 7.7 Hz, 2H), 2.27 (s, 3H), 1.90−1.70 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ195.8 (C_q), 152.7 (C_q), 152.6 (C_q), 151.6 (C_q), 151.5 (C_q), 147.6 (C_q), 147.6 (C_q), 146.6 (C_q), 135.4 (C_q), 130.5 (CH), 130.4 (CH), 129.3 (CH), 129.0 (CH), 128.9 (C_q), 128.4 (C_q), 128.1 (C_q), 127.5 (C_q), 124.5 (CH), 124.3 (CH), 123.8 (CH), 122.6 (CH), 122.5 (CH), 33.8 (CH_2), 31.8 (CH_2), 31.7 (CH_2), 31.0 (CH_2), 30.6 (CH_3), 28.5 (CH_2); IR (KBr pellet, cm^{-1}) 3181, 2925, 1688, 1592, 1472, 1455, 1274, 766, 689; FAB-MS *m*/*z* 853 (M + H$^+$); HRMS *m*/*z* calcd for $C_{51}H_{44}N_6O_5S$ 852.3094, found 852.3106.

Data for 5,17-Di[3-(acetylsulfanyl)propyl]-11,23-di(*p*-methoxyphenyl)azo-tetrahydroxycalix[4]arene 10a. The solid product was eluted with hexane/ethyl acetate (v/v = 2/1) and gave 0.25 g (90%) of a yellow powder, mp 240−242 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.22 (s, 4H), 7.83 (d, J = 8.9 Hz, 4H), 7.64 (s, 4H), 7.00−6.90 (m, 8H), 4.29 (d, J = 13.6 Hz, 4H), 3.63 (d, J = 13.6 Hz, 4H), 3.87 (s, 6H), 2.84 (t, J = 7.2 Hz, 4H), 2.50 (t, J = 7.6 Hz, 4H), 2.30 (s, 6H), 1.90−1.70 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.9 (C_q), 161.6 (C_q), 151.2 (C_q), 147.6 (C_q), 147.1 (C_q), 146.7 (C_q), 135.2 (C_q), 129.2 (CH), 128.6 (C_q), 127.7 (C_q), 124.3 (CH), 123.6 (CH), 114.1 (CH), 55.5 (CH_3), 33.9 (CH_2), 31.8 (CH_2), 31.1 (CH_2), 30.6 (CH_3), 28.5 (CH_2); IR (KBr pellet, cm^{-1}) 3186, 2931, 1689, 1600, 1583, 1502, 1455, 1251, 1147, 837; FAB-MS *m*/*z* 925 (M + H$^+$); HRMS *m*/*z* calcd for $C_{52}H_{52}N_4O_8S_2$ 924.3227, found 924.3232.

*X-ray Crystal Data for Compound **10a***. $C_{52}H_{52}Cl_3N_4O_8S_2$, M = 1031.45, triclinic, a = 12.7090(5) Å, b = 13.4048(5) Å, c = 16.4736(6) Å, α = 67.770(1)°, β = 70.213(1)°, γ = 74.126(1)°, V = 2410.16(16) Å^3, space group *P*-1, Z = 2, calcd density 1.421 Mg m^{-3}, crystal dimensions (mm^3) 0.36 × 0.27 × 0.10, T = 150(1) K, λ (Mo Kα) = 0.71073 Å, μ = 0.337 mm^{-1}, 31 834 reflections collected, 11 046 independent (R_{int} = 0.0387), 632 parameter refined on F^2, R_1 = 0.1059, $wR2[F^2]$ = 0.2048 (all data), GOF on F^2 1.126, $\Delta\rho_{max}$ = 0.701 e Å^{-3}. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 625918. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: data_request@ccdc.cam.ac.uk, or fax: +44−1223-336033].

Data for 5,17-Di[3-(acetylsulfanyl)propyl]-11,23-di(*p*-methoxyphenyl)azo-tetrahydroxycalix[4]arene 10b. The solid product was eluted with hexane/ethyl acetate (v/v = 2/1) and gave 0.25 g (93%) of a yellow powder, mp 276−278 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.22 (s, 4H), 7.81 (d, J = 7.2 Hz, 4H), 7.68 (s, 4H), 7.55−7.35 (m, 6H), 6.97 (s, 4H), 4.30 (d, J = 13.1 Hz, 4H), 3.64 (d, J = 13.1 Hz, 4H), 2.83 (t, J = 7.2 Hz, 4H), 2.51 (t, J = 7.6 Hz, 4H), 2.29 (s, 6H), 1.86−1.70 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.9 (C_q), 152.8 (C_q), 151.7 (C_q), 147.5 (C_q), 146.7 (C_q), 135.3 (C_q), 130.4 (CH), 129.3 (CH), 129.0 (CH), 128.7 (C_q), 127.6 (C_q), 124.0 (CH), 122.5 (CH), 33.8 (CH_2), 31.8 (CH_2), 31.1 (CH_2), 30.6 (CH_3), 28.5 (CH_2); IR (KBr pellet, cm^{-1}) 3187, 2932, 1688, 1590, 1472, 1456, 1275, 1135, 693; FAB-MS *m*/*z* 865 (M + H$^+$); HRMS *m*/*z* calcd for $C_{50}H_{48}N_4O_6S_2$ 864.3015, found 864.3019.

General Procedures for the UV−vis Experiments. Because of the poor solubility of metal perchlorates in chloroform, all UV−vis experiments reported in this work were carried out in methanol−chloroform (v/v =1/399) cosolvent unless otherwise specified. UV−vis spectra were recorded on a HP-8453 spectrophotometer with a diode array detector, and the resolution was set at 1 nm. The complexes were mixed and kept stirring for at least 20 min before measurements. During the measurements the temperature of the quartz sample cell and chamber was kept at 25 °C.

Stability Constants of Metal Complexes. The stability constants K_a of a 1:1 complex of **6**, **8**, **9a**, **9b, 10a**, and **10b** with Hg^{2+} were determined from the following Benesi−Hilderbrand equation[10]

$$1/\Delta A = 1/\Delta A_{sat} + 1/(\Delta A_{sat}K_a[Hg^{2+}]) \qquad (1)$$

where ΔA is the absorption difference between the apparent metal complex and the free ionophores and ΔA_{sat} is the absorption difference at saturation. The association constant K_a values were evaluated graphically by plotting $1/\Delta A$ against $1/[Hg^{2+}]$. In this study the concentration of the ionophores was kept constant (8 μM for **6** and **9a**,**b** and 10 μM for **8** and **10a**,**b**) and the concentration of Hg^{2+} ions was kept in the range [Hg^{2+}]/[ionophores] = 0.1−4.0. All plots gave a straight line, and the K_a values were obtained from the slopes and intercepts of this line (see Supporting Information).

Acknowledgment. We thank the ATU program of the Ministry of Education and National Science Council of the Republic of China for financial support.

Supporting Information Available: UV−vis titration spectra, Job's plots, and Benesi−Hilderbrand plots of **8**, **9a**, and **10a** with various transition-metal ions and *p*TSA (acid); ^{1}H NMR spectra of compounds **4**−**6**, **8**, **9a**,**b**, and **10a**,**b** and the titration spectra of **10a** with $Hg(ClO_4)_2$ and **8** with $AgClO_4$; IR and MS spectra of **6**·$Hg(ClO_4)_2$ and **8**·$Hg(ClO_4)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

JO062280S