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Chromogenic Receptors: Versatility of the Colorimetric Recognizing Behavior

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Abstract. This article briefly reviews our recent achievement in developing synthetic chromogenic receptors which are characterized by combining "recognition" and "optical sensing" functions; synthesis of several kinds of azomethine-derived calixarenes is described, as well as some colorimetric recognizing behavior for chemically or biologically significant guests ranging from cations to chiral amine derivatives.

Key words: chromogenic receptor, indoaniline, indophenol, calixarene, cation, chiral recognition, chiral amine, amino acid.

1. Introduction

Bio-inspired materials will no doubt be a key part of constructing advanced molecular devices [1], defined as an organized and integrated chemical system, because the required function and regulation processes are often seen in biological systems such as enzymes or receptors in protein, protein aggregates, allosteric regulation, the restoration of the genetic code, neurotransmission processes, intercellular recognition and cell adhesion, and immunology [2]. In order to develop molecular devices that have similar or superior functions in comparison to biological entities, the key material should be a tailored intelligent molecular architecture with an antenna, information-transmittance, and signaling segments, the combined action of which is essential in the system. Synthetic chromogenic receptors [3] that give rise to specific optical responses on selective complexation with guest species allow us to study the methodology of the above-mentioned system, which is due to the fact that the molecular recognition event can be monitored in real-time as molecular information. On another front, it would help to clarify uncertainties about complementary interaction that governs molecular recognition events. This review describes our development of synthetic chromogenic receptors, and thus a simple monitoring system for biologically and/or chemically important species is discussed.

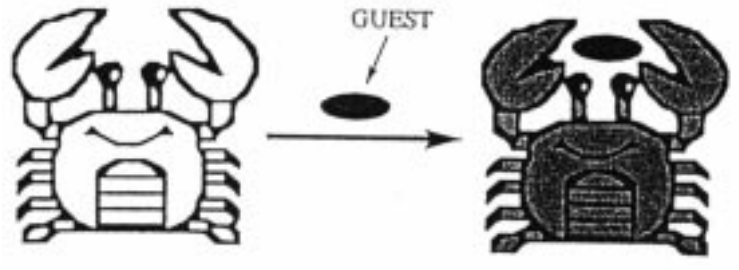


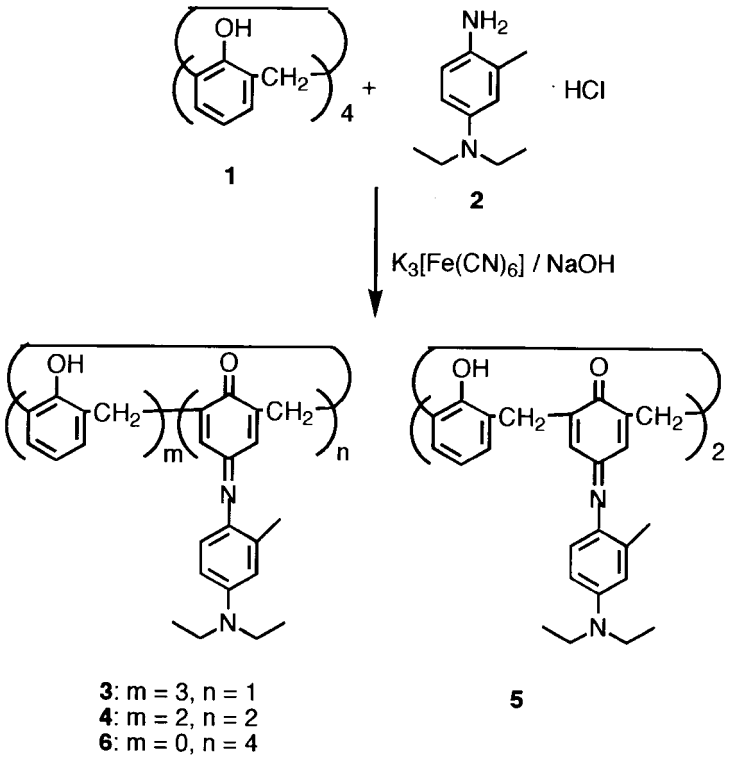
Figure 1. Simplified representation of a chromogenic receptor [3].

2. Indoaniline-Derived Calixarenes [4–6]

Calixarenes [7] are cyclic oligomers of varying ring size derived from *para*-substituted phenols and formaldehyde. The scope for chemical modification both at the phenolic OH groups (lower rim) or at the aromatic nuclei (upper rim) has allowed them to function as hosts for ions or small molecules. Therefore, if one could introduce an appropriate optical sensory group into a calixarene bearing a pre-organized guest-binding site, an encapsulated species would cause a physical change in the opto-functional site which can be monitored by using spectroscopy. An indoaniline-type chromophore was chosen as a promising optical sensory group for use in the requisite strategy. This choice was made because not only can it be introduced into the calixarene platform with synthetic ease, but its optical properties can also be significantly perturbed by chemical stimuli. In the latter case, we found that the quinone carbonyl group of indoaniline-type ligands interacts with divalent metal ions to cause a pronounced color change [8]. Thus, the combined use of the chromophore constrained within a calixarene receptor framework would be of interest in the design of chromogenic receptors; the inclusion of a positively charged species in the cavity would then, it was thought, cause a significant electrostatic perturbation of the chromophore. This chapter describes the cation recognition properties of several new types of indoaniline-derived calixarene derivatives.

2.1. Synthesis and structure

Condensing calix[4]arene **1** [9] with 4-diethylamino-2-methylaniline hydrochloride **2** under alkaline conditions in the presence of $K_3[Fe(CN)_6]$ as an oxidizing agent afforded four types of indoaniline-derived calix[4]arenes **3**, **4**, **5**, and **6** after chromatography (Scheme 1). These structures were identified by observed analytical data. In this case, bis(indoaniline)-derived analogues **4** and **5** are regioisomers, the assignments of which were carefully conducted using NMR spectroscopy [6]. Table I summarizes the results of the condensing reaction of **1** with **2**, implying that the number of indoaniline-type chromophores incorporated with the calix[4]arene increased as the [**2**]:[**1**] molar ratio and reaction time increased.



Scheme 1.

An X-ray structure for indoaniline-derived calix[4]arene affords some useful insights with regard to a better understanding of the conformation. After several trials, the crystal structure for **3** has been determined. As illustrated in Figure 2, the ORTEP diagram of **3** exhibits the calix with a cone conformation in the solid state. Note that a unique intramolecular hydrogen bonding network involving the carbonyl oxygen of indoaniline is observed. These results suggested that the quinone carbonyl group as an acceptor of the indoaniline chromophore can easily be subject to an electrostatic interaction that takes place on the lower rim of the calixarene and that functionalization of the lower rim will produce a new type of chromogenic receptor.

2.2. COLORIMETRIC RECOGNITION FOR ALKALI AND ALKALINE EARTH METAL IONS

Our strategy to expand the investigation of the colorimetric recognition is to choose target guests going from simple species to more complicated ones. Metal ions are one of simplest species yet they are the most important ones in biology and/or chemistry. Accordingly, the development of molecular sensors for the detection of metal ions in aqueous and nonaqueous media continues to be the focus of research

Table I. Synthesis of indoaniline-derived calix[4]arene[a]

Run	Molar ratio			Yield/%			
	[**2**]/[**1**]	[ox][b]/[**1**]	RT/min[c]	**3**	**4**	**5**	**6**
1	4	8	120	50	11.5	8	Trace
2	16	32	10	2	25	35	Trace
3	16	32	240	–	3	1	37.5

[a] The procedure is similar to that described in Ref. 10.
[b] $K_3[Fe(CN)_6]$.
[c] Reaction time.

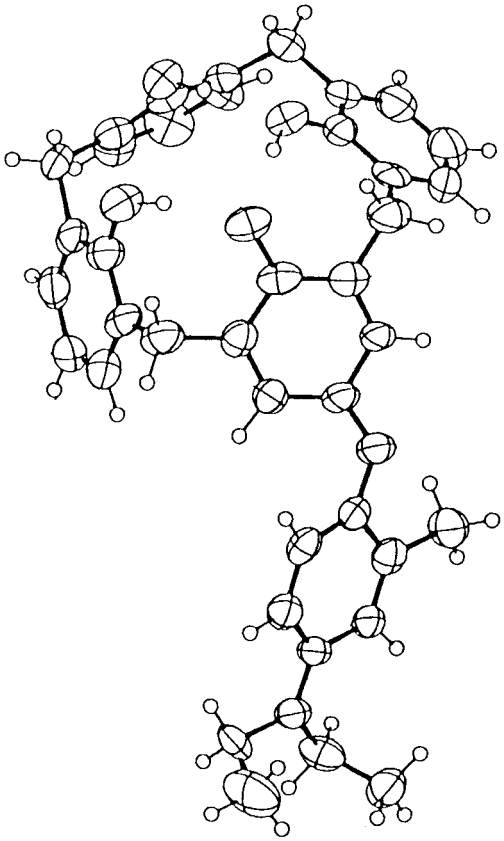
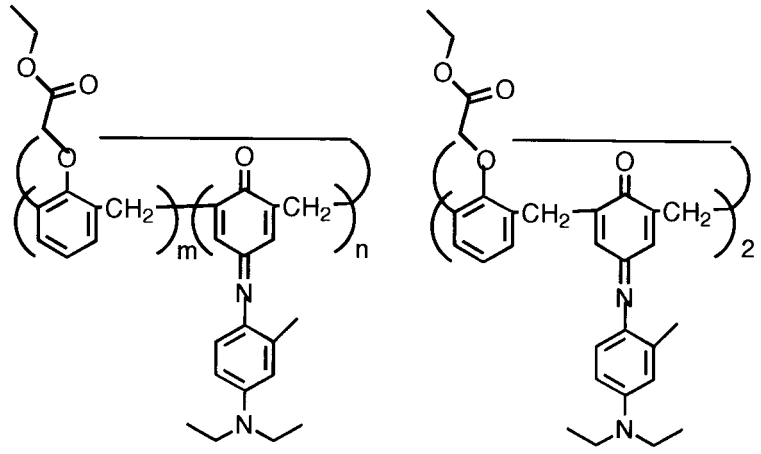
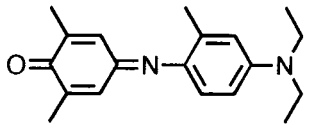


Figure 2. X-ray crystallographic structure of **3**.



7: m = 3, n = 1
9: m = 2, n = 2

8



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Scheme 2.

[11]. As an initial project to test the indoaniline-derived calixarene's utility as a chromogenic receptor, we tested the colorimetric recognition behavior for Na^+, K^+, Mg^{2+}, Ca^{2+} contained in human blood plasma [12].

With the aim of developing the desired receptor, an anchoring functional group oriented in such a way that it delineates a suitable binding site is required: we decided to append ethyl acetate groups on the lower rim of the calix[4]arene platform because of the synthetic ease as well as its well-known function as an anchoring group [13]. In this way, the ethoxycarbonylmethylations were achieved with ethyl-bromoacetate in the presence of NaH to give the corresponding desired analogues **7**–**9**, respectively (Scheme 2).

The optical response property of mono(indoaniline)-derived tris(ethyl acetate) derivative **7** was elucidated: the addition of 100 equiv. of Na^+, K^+, Mg^{2+}, and Ca^{2+} to a 99% EtOH solution of **7** showed cation-induced selective spectral change accompanying a high Na^+ preference (Figure 3). The understanding of the binding profile came from a continuous variation method [14] that was made from mixtures

of **7** and Na^+ in 99% EtOH under conditions of invariant total concentration. This approach suggested the formation of a 1 : 1 complex between **7** and Na^+, so that the association constant calculated using a Benesi–Hildebrand plot [15] is 2×10^3 dm^3 mol^{-1}. Although this value is higher than those of other cations by a factor of 7 or more, the solution upon complexation with Na^+ remained blue. Subsequently we could not detect an expected color change. Figure 3, however, indicated that **7** shows an extreme bathochromic shift ($\lambda_{complex}$: 701 nm) in the presence of Ca^{2+} in spite of the low complexation ability. This shift might be attributable to a significant ion-dipole interaction between the divalent cation and the quinone carbonyl group of **7**. It occurred to us to consider that a bis(indoaniline)-derived anologue possessing two quinone carbonyl groups has great promise of better affinity for the cation. Figure 4 shows a UV/Vis titration study performed by adding incremental amounts of $Ca(SCN)_2 \cdot 4H_2O$ to a 99% EtOH solution of **8**. Substantial change was observed: compound **8** is blue, the λ_{max} value of which is 609 nm (ϵ_{max} 35,000 dm^3 mol^{-1} cm^{-1}) in 99% EtOH; the stepwise addition of Ca^{2+} to compound **8** in the solution causes a large bathochromic shift with an increase in absorption intensity with isosbestic points at 460 and 630 nm, respectively. At a ratio of [Ca^{2+}] to [**8**] of 5 : 1, a new absorption band in the near-IR region at 724 nm was observed while the absorption band at 609 nm disappeared completely, the change reflecting the blue-to-green color change. The phenomenon related to the formation of a 1 : 1 complex between **8** and Ca^{2+} using a similar continuous variation method.

We tested to see if compound **8** acted as a chromogenic receptor. Figure 5 shows the spectral responses ($\Delta\lambda = \lambda(\text{complex}) - \lambda(\text{ligand})$) in the presence of ($10^2$ equiv.) or absence of metal salts. A large bathochromic shift of 110 nm was observed in the presence of Ca^{2+}. In contrast, addition of NaSCN, KSCN, or $Mg(ClO_4)_2$ caused only minor changes ranging from 12 to 40 nm in the absorption spectra suggesting that compound **8** exhibited a significant selectivity for Ca^{2+}. Alternatively, 1,2-bis-substituted analogue **9** was quite inefficient in the presence of those metal ions (*even on addition of* Ca^{2+}) as shown in Figure 5. The examination of CPK space-filling molecular models implies that **9** retains no cavity to encapsulate metal ions on the lower rim of the calix[4]arene segments. Thus, the lack of cation response of **9** is considered to be due to the unfavorable steric complementarity between **9** and the cations. The spectroscopic study, in this way, reveals a significant difference between **8** and **9**; it is intriguing that distal- *vs.* proximal-ethyl acetated derivatives provoke a drastic stereochemical difference of cation complexation ability. Furthermore, the cyclic indoaniline tetramer **6** shows an unfavorable complexation property with Ca^{2+}, which indicates that disposition of ethyl acetate groups is significantly important. This consideration is also supported by the fact that compound **10** shows no color change with alkali and alkaline earth metal ions in a control experiment. Recently, a calixarenequinone derivative possessing similar shape of cavity to that which exists in **8** has been reported with the aim of recognition of guest cations [16].

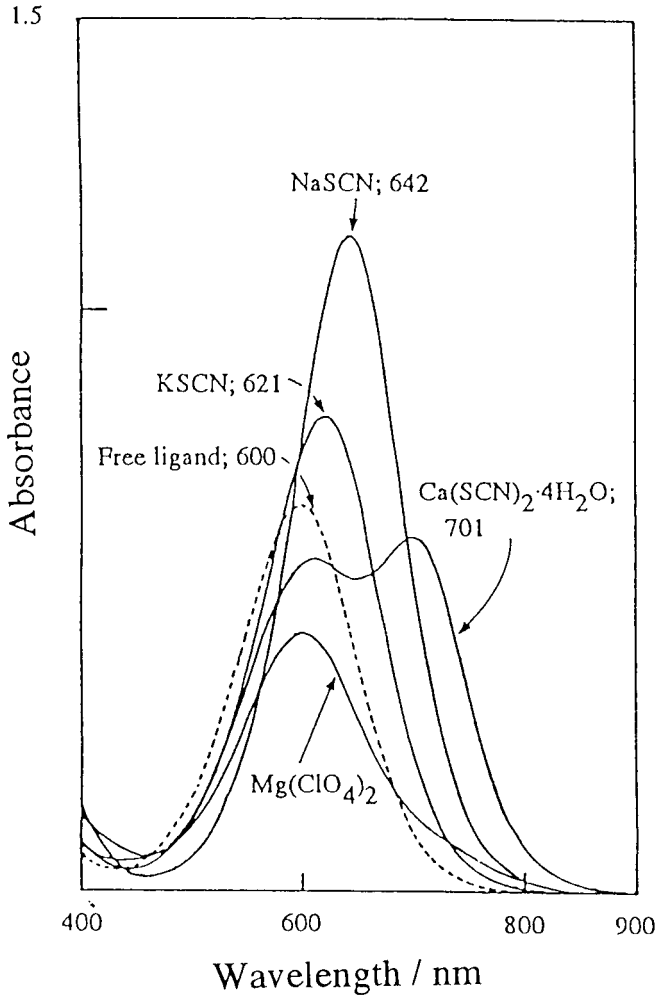


Figure 3. Influence of added NaSCN, KSCN, $Mg(ClO_4)_2$, and $Ca(SCN)_2{\cdot}4H_2O$ on the absorption spectra of **7** in 99% EtOH; [Metal salt]/[**7**] = 100; [**7**] = 4.0×10^{-5} mol dm^{-3}[3].

2.3. URANYL ION RECOGNITION

In an effort to enhance the versatility of colorimetric recognition behavior through the molecular design based on the indoaniline-calixarene conjugate, we explore guest species which other chromoionophores (i.e., crown ether-derived dye molecules) hardly bind, and then have been fascinated by the unique binding property of calix[6]arene for uranyl ions (UO_2^{2+}) [17]. Thus, it is of interest to investigate if an indoaniline-derived calixarene shows a selective colorimetric recognition for UO_2^{2+}. In this section, we will briefly discuss this subject.

Condensing calix[6]arene **11** [9] with 1.2 equiv. of **2** under alkaline conditions in the presence of 2.4 equiv. of $K_3[Fe(CN)_6]$ at room temperature afforded

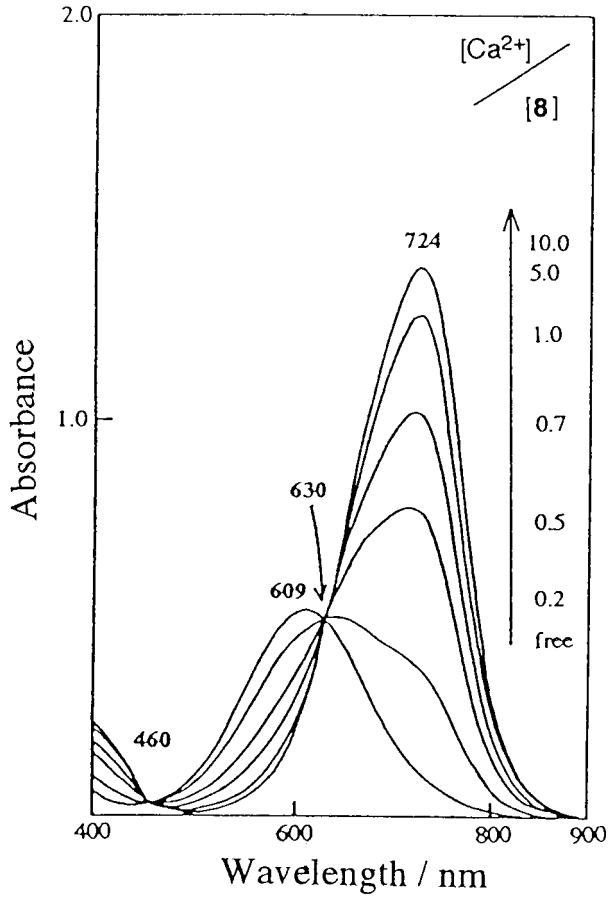


Figure 4. Spectral changes upon addition of $Ca(SCN)_2 \cdot 4H_2O$ to a solution of **8** in 99% EtOH; [**8**] = 1.5×10^{-5} mol dm^{-3}[3].

mono(indoaniline)-derived calix[6]arene **12** in 53% yield (Scheme 3). A titration study was performed to see if **12** would act as a chromogenic receptor for detection of UO_2^{2+}. Compound **12** has an absorption band at 628 nm in the presence of 10^3 equiv. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 99% EtOH at 25 °C. Interestingly, as shown in Figure 6, addition of UO_2^{2+} to the solution causes a large bathochromic shift with an increase in absorption intensity. In this case, the λ_{max} value in the stationary state is 687 nm, conferring a green coloration upon the solution. By following the increase in absorbance at 687 nm as a function of [UO_2^{2+}] : [**12**] molar ratio, the association constant could be established to be 8×10^4 dm^3 cm^{-1}. However, addition of other metal ions caused no or minor changes in the absorption spectra (Figure 7), implying that **12** exhibits a significant selectivity for UO_2^{2+}.

Proton NMR spectra can be used to gain an understanding of the coordination structure. While **12** in the presence of excess DBU in $CDCl_3$ at room temperature

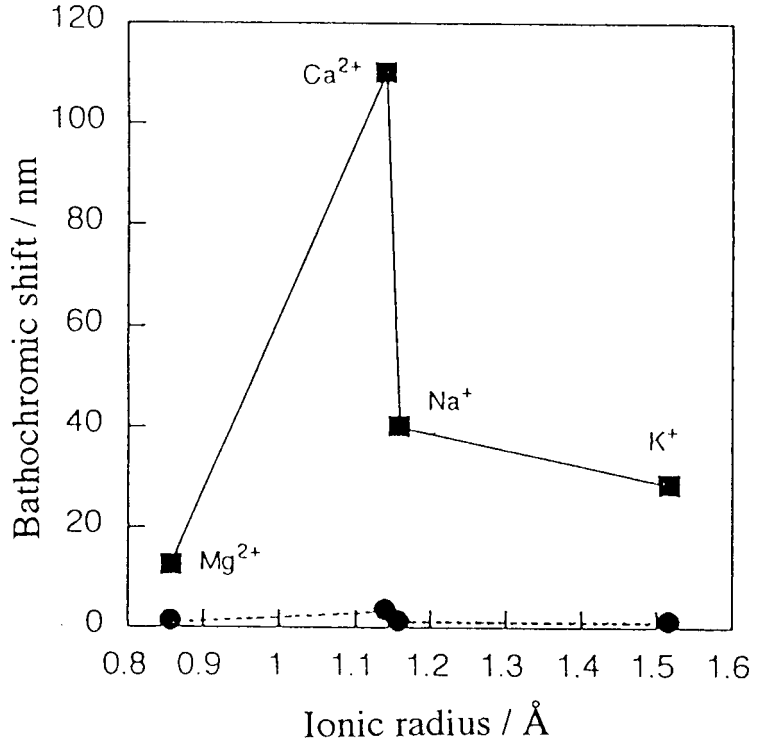
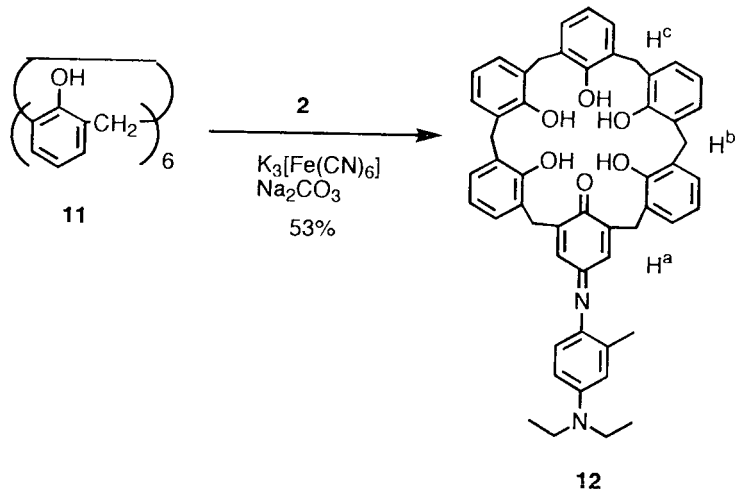


Figure 5. Influence of added NaSCN, KSCN, $Mg(ClO_4)_2$, and $Ca(SCN)_2 \cdot 4H_2O$ on the absorption spectra of **8** (■) and **9** (●) [3, 6].



Scheme 3.

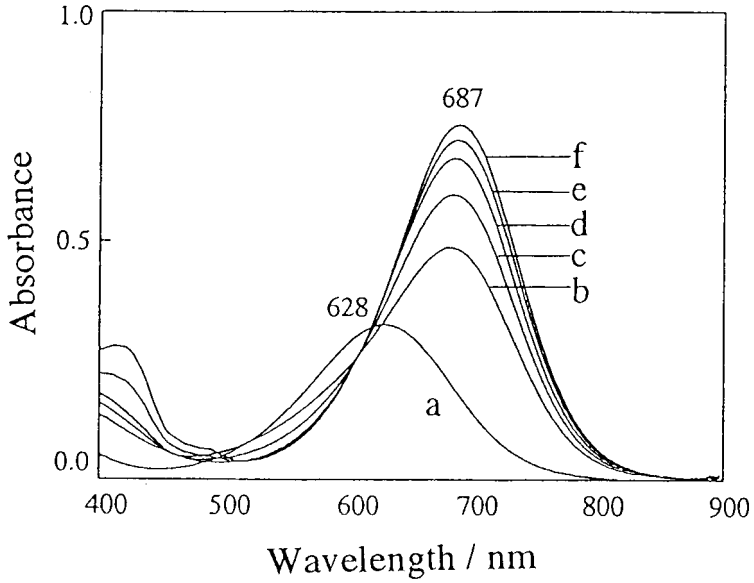


Figure 6. Spectral changes upon addition of $UO_2(CH_3CO_2)_2{\cdot}2H_2O$: (a) 0; (b) 5.0×10^{-5}; (c) 1.0×10^{-4}; (d) 2.0×10^{-4}; (e) 1.0×10^{-3}; (f) 2.0×10^{-3} mol dm^{-3}; to a 99% EtOH solution of **12** (2.0×10^{-5} mol dm^{-3}) in the presence of 10^3 equiv. of DBU.

displays a broad signal in the range of δ 3.6–4.0 ppm being attributable to $ArCH_2Ar$ of the calix[6]arene segments, upon interaction with UO_2^{2+}, the spectral pattern was found to be changed to three singlets in 1 : 1 : 1 ratio for the methylene protons (H^a, H^b, H^c: Scheme 3). These results pointed out that UO_2^{2+} upon complexation with **12** might cause the ligand to adopt an unusual pseudoplanar structure in which the UO_2^{2+} is six-coordinate. Indeed, the absence of an interaction between the calix[4]arene anologue **3** and UO_2^{2+} supports the premise that selectivity for UO_2^{2+} in the present case results from a good match between the rigid calix[6]arene skeleton and the coordination requirements of UO_2^{2+}.

3. Colorimetric Chiral Recognition [19]

One of the most pressing challenges in the design of a chromogenic receptor is to achieve naked eye-detectable discrimination between enantiomers [20]. A simple monitoring system that would allow real-time distinction between the right- and left-handed forms of a drug could have an immediate impact in the areas of analytical chemistry, physiology, and pharmacology [21]. Here, a new strategy, which is based on a bis(indophenol)-derived calix[4]crown, is presented.

Receptor **13a** (Figure 8) was synthesized from optically pure (*S*)-1,1′-bi-2-naphthol via a set of straightforward steps involving etherfication in the presence of a base, tosylation with tosyl chloride, a modified Williamson synthesis, and finally a condensation reaction with 4-amino-*m*-cresol under alkaline conditions in the

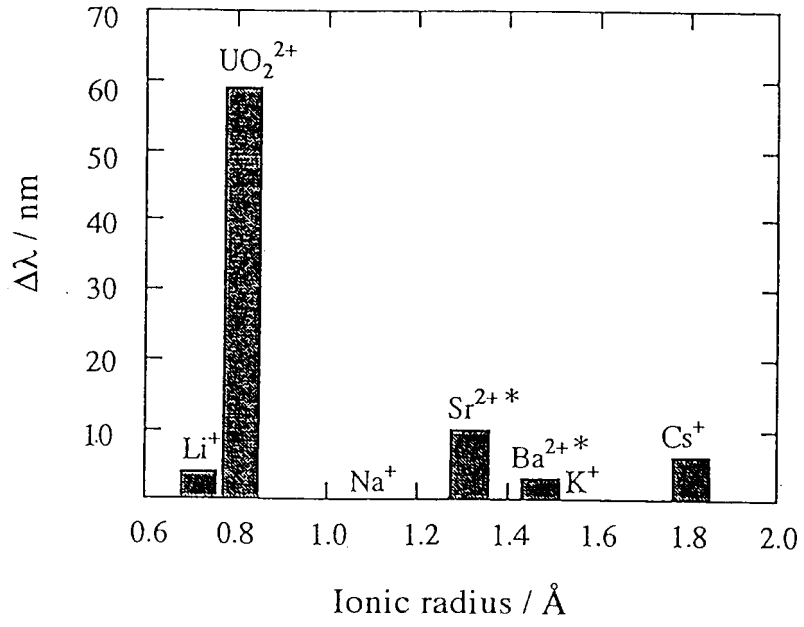


Figure 7. Spectral responses ($\Delta\lambda_{max} = \lambda_{max}$ (complex) $- \lambda_{max}$ (ligand)) of **12** in the presence (10^2 equiv.) or absence of several metal ions at 25 °C; [**12**] = 2.0×10^{-5} mol dm^{-3}; [DBU]/[**12**] = 10^3. In the case of addition of Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, the $\Delta\lambda_{max}$ could not be determined under these conditions owing to the formation of the salts. However, when 5 equiv. of these metal ions (except for Cu^{2+}) were added to a 99% EtOH solution of **12** in the presence of DBU (300 equiv. for Ni^{2+}, Zn^{2+}; 10^3 equiv. for Mg^{2+}, Ca^{2+}) caused almost no response; the ionic radius of U^{6+} is 0.66–0.87 Å [18]. Asterisks indicate spectral response after solid ($M(CH_3CO_2)_2 \cdot xH_2O$)-liquid (99% EtOH) two-phase solvent extraction.

presence of $K_3[Fe(CN)_6]$. The full assignments were conducted using satisfactory analytical data. It is noted that altering the length of ether-spacers in **13a** allows the position of the binaphthyl unit to be closer to an indophenol-OH site than the other, as evidenced by the chemical shifts of two indophenol-OH protons (δ 7.91 and δ 8.06 ppm) in the ^1H NMR spectrum. Thereby, on binding a chiral substrate to receptor **13a**, each of the chromophores in the receptor will be affected in different modes, and we reasoned that this might translate into a powerful chromogenic response.

Testing this hypothesis was quite simple: addition of (*R*)-phenylglycinol, (*R*)-**14**, as a putative response-inducing guest into a EtOH solution of **13a** at 25 °C immediately caused the solution to turn blue-violet in color, this phenomenon being reflected in the spectral shift (23 nm) of the band originally appearing at 515.5 nm and in the appearance of a new band at 652.5 nm (Figure 9). A Benesi–Hildebrand plot for a mixture of **13a** and (*R*)-**14** in EtOH at 25 °C was performed, and the plot was linear, supporting the 1 : 1 stoichiometry of the complex. The apparent association constant *K* was calculated as 66 ± 8.8 dm^3 mol^{-1}. Interestingly, when a similar experiment was carried out using the corresponding enantiomer,

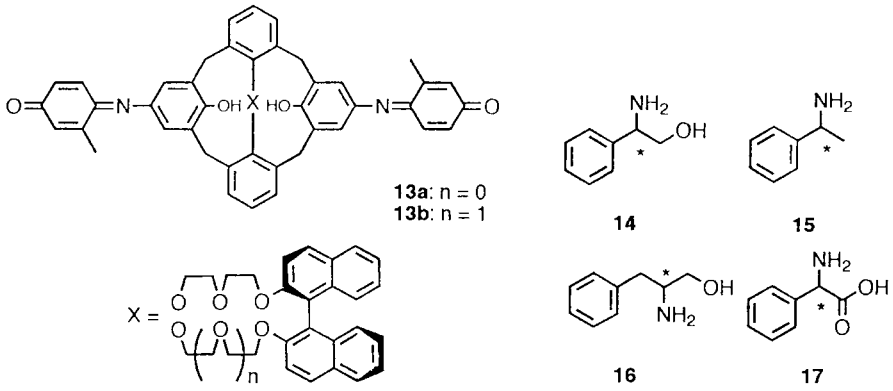


Figure 8. Structure of dual optical sensory system **13**, and guest amines and amino acid derivatives.

(*S*)-**14**, the color of the solution remains red with nearly no detectable change in the spectrum. From these results, naked eye distinction between enantiomers was successfully achieved. One can easily speculate that the enantioselectivity might result from the host-guest complexation ability. Indeed, the formation of a 1 : 1 complex between **13a** and (*R*)-**14** was confirmed by fast atom bombardment mass spectrometry (*m*-nitrobenzyl alcohol matrix) where Xe was used as the atom beam accelerated to 3.0 KeV, as indicated by the value of 1,181(**13a** + (*R*)-**14**). In an effort to understand the substrate-receptor interactions, congener **13b**, containing a large binaphthyl-derived crown ether unit, was studied. When this species was tested for (*R*)-**14**, a K value of 17 ± 12 dm^3 mol^{-1} was obtained, which is about a quarter of that of (**13a** + (*R*)-**14**). This finding suggests that the amine complexation process presumably involves the interaction with the crown oxygen and with the indophenolate. Furthermore, no selectivity for both enantiomers of phenylethylamine **15** was observed in the case of **13a**, also supporting the alcohol-OH group of the amine guest necessarily participates in the chiral recognition event, as the result of hydrogen-bonding interaction with the indophenolate. Figure 10 shows a possible structure for the complex of **13a** with a chiral amine. In order to exhibit enantioselective binding to the chiral amine, **13a** requires three recognition groups (ethylene oxygens, indophenolate oxygen, and binaphthyl group); the ethylene oxygens and the indophenolate oxygen stabilize the host-guest complex as well as restrict the rotation of the guest along the C*-NH_3^+ axis by ion-dipole and hydrogen-bonding interactions. The third recognition group, the binaphthyl group, acts as a minor steric-repulsive site for the (*R*)-isomer and as a major steric-repulsive site for the (*S*)-isomer.

It is noteworthy that receptor **13a** is not limited in its utility to the simple chiral substrate **14**; it shows enantiomeric discrimination for phenylalaninol salts such as **16** as well as certain amino acid derivatives such as phenylglycine **17**. In the case of the latter, which is a physiologically more interesting substrate, the typical

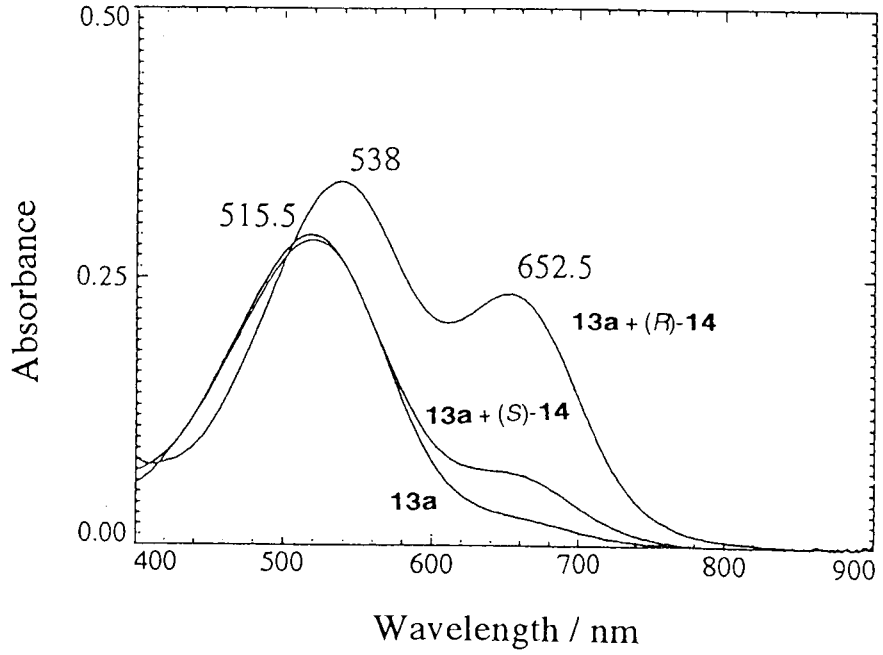


Figure 9. Spectral changes upon addition of 500 equiv. of phenylglycinol ((*R*)-**14**: (a); (*S*)-**14**: (b)) to an EtOH solution of **13a** (2.0×10^{-5} mol dm^{-3}).

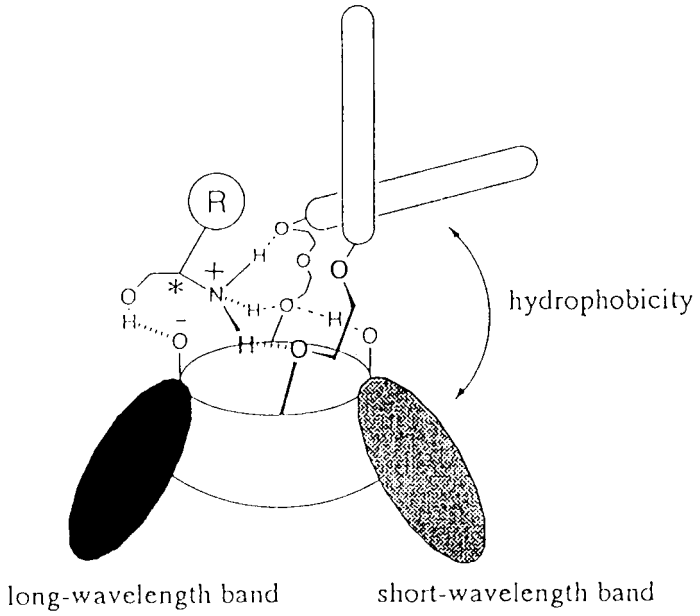


Figure 10. A possible structure for the complex of **13a** with a chiral amine.

absorption spectrum of **13a** was recorded, after a solid (**17**)-liquid (2.0×10^{-5} mol of **13a** in EtOH at 25 °C) two-phase solvent extraction process was carried out. While the addition of (*R*)-**17** caused only a 20 nm shift in the short-wavelength band with increasing absorbance, a substantial shift was observed in the visible region (from 500 to 600 nm), reflecting the red-to-reddish-violet color change under these conditions. On the other hand, when (*S*)-**17** was used, almost no discernible change in the absorption spectrum of **13a** was observed.

Taken together, these results lead us to the conclusion that **13a** is not only the first rationally designed colorimetric sensor for chiral recognition but also a paradigm of a new approach to achieve real-time visual distinction between enantiomers.

4. Conclusions

Naturally occurring proteins take advantage of α-amino acids as common building blocks, performing not only its structural diversity but also the modulation. As a result, numerous biological functions take place *in vivo*. This phenomenon leads us to consider molecular design for artificial receptors in which a slight structure-modification would induce a drastic change in the function. Bearing this in mind, in the former section, we investigated some colorometric recognition behavior for a family of indoaniline-derived calixarenes as chromogenic receptors. The latter is to target a molecular sensor for chiral recognition whose concept is simple but often most difficult in practice. In our strategy to obtain such a system, we have proposed a new molecular design, so-called "*dual optical sensory system*"; the practical system **13a** possessing a chiral receptor unit based on calixarene and two indophenol-type chromophores amplified the chiral recognition event for some examples of unsymmetrical guest amines to a discernible color change. In our laboratory, the design and synthesis of new types of chromogenic receptors in line with obtaining an insight from "*static*" molecular recognition to "*dynamic*" ones are under active study.

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References

1. J.-M. Lehn: *Angew. Chem. Int. Ed. Engl.* **27**, 89 (1988); J.-M. Lehn: From Molecular Recognition towards Information and Signal Processing at the Supramolecular Level, in H.J. Schneider and H. Dürr (Eds.), *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, pp. 1–28. VCH, Weinheim (1991).
2. As an excellent account: B. Albert, D. Bray, J. Lewis, M. Raff, K. Roberts, and J.D. Watson: *Molecular Biology of the Cell*, Garland Publishing Inc., New York (1983).
3. Y. Kubo: *Yuki Gosei Kagaku Kyokai Shi* **55**, 506 (1997).
4. Y. Kubo, S. Hamaguchi, K. Kotani, and K. Yoshida: *Tetrahedron Lett.* **32**, 7419 (1991).
5. Y. Kubo, S. Hamaguchi, A. Niimi, K. Yoshida, and S. Tokita: *J. Chem. Soc., Chem. Commun.* 305 (1993).
6. Y. Kubo, S. Tokita, Y. Kojima, Y.T. Osano, and T. Matsuzaki: *J. Org. Chem.* **61**, 3758 (1996).
7. (a) C.D. Gutsche: in J.F. Stoddart (Ed.), *Calixarene, Monographs in Supramolecular Chemistry*, The Royal Society of Chemistry, Cambridge (1989); (b) in J. Vicens and V. Böhmer (Eds.), *Calixarenes: A Versatile Class of Macrocyclic Compounds*, Kluwer, Dordrecht (1991). Recent reviews see: (c) S. Shinkai: Calixarenes as the Third Supramolecular Host, in G.W. Gokel (Ed.), *Advances in Supramolecular Chemistry*, Vol. 3, pp. 97–130, JAI Press Inc., Greenwich (1993); (d) M. Takeshita and S. Shinkai: *Bull. Chem. Soc. Jpn.* **68**, 1088 (1995); (e) V. Böhmer: *Angew. Chem., Int. Ed. Engl.* **34**, 713 (1995).
8. Y. Kubo, K. Sasaki, H. Kataoka, and K. Yoshida: *J. Chem. Soc., Perkin Trans. 1* 1469 (1989).
9. C.D. Gutsche and L.-G. Lin *Tetrahedron*, **42**, 1633 (1986).
10. G.H. Brown, J. Figueras, R.J. Gledhill, C.J. Kibler, F.C. McCrossen, S.M. Parmerter, P.W. Vittum, and A. Weissberger: *J. Am. Chem. Soc.* **79**, 2929 (1957).
11. A.W. Czanik (Ed.): *Fluorescence Chemosensors for Ion and Molecule Recognition*, ACS Symposium Series 538, American Chemical Society, Washington, DC (1992); R.A. Bissell, A.P. de Silva, H.Q.N. Gunaratne, P.L.M. Lynch, G.E.M. Maguire, C.P. McCoy, and K.R.A.S. Sandanayake: *Top. Cur. Chem.* **168**, 223 (1993); T. Hayashita and M. Takagi: Chromoionophores Based on Crown Ethers and Related Structures, in G.W. Gokel (Ed.), *Comprehensive Supramolecular Chemistry*, Vol. 1, pp. 635–669, Pergamon Press, New York (1996).
12. A.L. Lehninger: *Principles of Biochemistry*, pp. 705–707, Worth Publisher Inc., New York (1982).
13. T. Arimori, M. Kubota, T. Matsuda, O. Manabe, and S. Shinkai: *Bull. Chem. Soc. Jpn.* **62**, 1674 (1989).
14. K. Ueno: *Neumon Chelate Kagaku*, pp. 56–60, Nankodo, Tokyo (1969).
15. H.A. Benesi and J.H. Hildebrand: *J. Am. Chem. Soc.* **71**, 2703 (1949).
16. P.D. Beer, Z. Chen, and P.A. Gale: *Tetrahedron* **50**, 931 (1994).
17. S. Shinkai, H. Koreishi, K. Ueda, T. Arimura, and O. Manabe: *J. Am. Chem. Soc.* **109**, 6371 (1987); S. Shinkai, Y. Shirahama, H. Satoh, O. Manabe, T. Arimura, K. Fujimoto, and T. Matsuda: *J. Chem. Soc., Perkin Trans. 2* 1167 (1987); T. Nagasaki and S. Shinkai: *J. Chem. Soc., Perkin Trans. 2* 1067 (1991); K. Araki, N. Hashimoto, H. Otsuka, T. Nagasaki, and S. Shinkai: *Chem. Lett.* 829 (1993).
18. Kagaku Binran II: *The Chem. Soc. Jpn.*, pp 717. Maruzen, Tokyo (1984).
19. Y. Kubo, S. Maeda, S. Tokita, and M. Kubo: *Nature* **382**, 522 (1996).
20. F. Vögtle and P. Knops: *Angew. Chem., Int. Ed. Engl.* **30**, 958 (1991) and references cited therein; K. Naemura, Y. Tobe, and T. Kaneda: *Coord. Chem. Rev.* **148**, 199 (1996).
21. Recently, excellent optical sensors for chiral recognition have been reported: T.D. James, K.R.A.S. Sandanayake, and S. Shinkai: *Nature* **374**, 345 (1995); K. Bodenhöfer, A. Hierlemann, J. Seemann, B. Kappenhoefer, and G. Göpel: *Nature* **387**, 577 (1997).