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Allosteric binding behaviour of a 1,3–*alternate* thiacalix[4]arene–based receptor by fluorescent signal†

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A novel heteroditopic thiacalix[4]arene receptor **L** possessing 1,3-*alternate* conformation, which contains two pyrene moieties attached to the lower rim via urea linkages together with a crown ether moiety appended at the opposite side of the thiacalix[4]arene cavity, has been synthesized. The complexation behaviour of receptor **L** was studied by means of fluorescence spectra and ^{1}H NMR titration experiments in the presence of K^+ ions and a variety of other anions. The results suggested that receptor **L** can complex efficiently via the urea cavity or the crown ether moiety, and a positive/negative allosteric effect operating in receptor **L** was observed.

Introduction

A number of excellent receptors based on the use of three–dimensional calix[n]arenes have been designed,[1] and there are capable of selectively recognizing cations, anions or neutral molecules. In particular, thiacalix[4]arenes[2] which contain bridging sulfur atoms, have been successfully utilized as potential building blocks or molecular scaffolds. It has been noted that such thiacalix[4]arene systems can induce favourable host–guest interactions with metal cations of biological and environmental importance via allosteric regulation[3] Anions also exist in various locations everywhere biological systems (e.g., DNA and enzyme substrates), and play Moreover, anions play an important role in the fields of medicine and catalysis. It is thus important that anion selective sensors[4] are developed and fully investigated. However, the situation is not as simple as for metal cation sensors because anions can possess different types of structures, *viz* spherical (F^-, Cl^-, Br^-, I^-), Y-shaped (AcO^-, $PhCOO^-$) and tetrahedral ($H_2PO_4^-$).[5] Anion receptors[6] based on calixarenes are relatively new in the aria of supramolecular chemistry. Furthermore, it is noteworthy that calixarene urea derivatives, in which the anion complexes exclusively through hydrogen bonding, are quite efficient for anion recognition.

In 1996, Reinhoudt and co–workers[7] reported that calix[4]arene based systems could act as bifunctional receptors to solubilize NaX salts (X = C1, Br) in chloroform via an allosteric effect of calixarene framework. Following this report, a number of neutral bifunctional receptors were developed which were capable of the simultaneous complexation of hydrophilic anions and cations.[8] There has also been recent interest in simultaneous binding of cationic and anionic guest species by ditopic receptors, and this is a rapidly developing field for ion pair recognition in environmental and biological systems.[9]

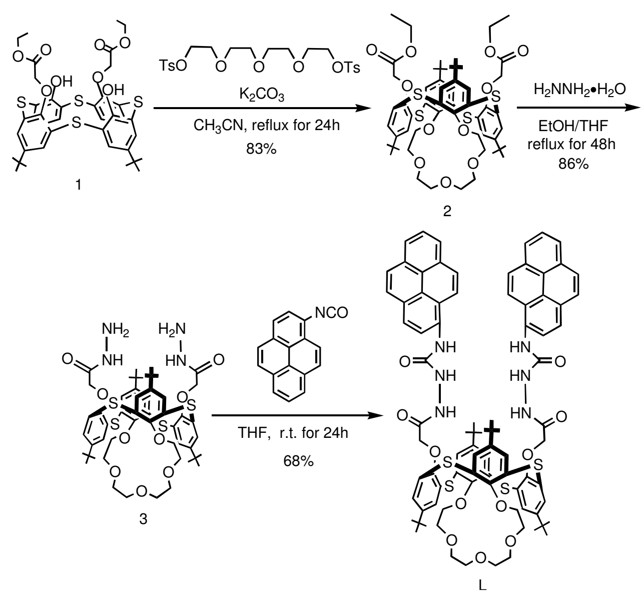
It has been known that the 1,3–*alternate* conformation of calix[4]arene can provide the two excellent binding sites for guest molecules when the appropriate functionalization has been achieved.[1h] Kumar[10] and co–workers have reported a that heteroditopic receptor bearing a thiacalix[4]arene in the 1,3–*alternate* conformation, which possesses two urea linked pyrene moieties and a crown–ether moiety at the opposite sides of the thiacalix[4]arene cavity. This compound is an interasting ratiometric fluorescent chemosensor for the F^- ion and the CN^- ion utilizing different modes via the two urea moieties in THF. However, investigations concerning the appearance of an allosteric effect in such an individual binding system based on a thiacalix[4]arene together with alkali metal cations and anions has not yet been reported.

On the basis of the above, we independently designed a heterodimeric system[11] based on a thiacalix[4]arene having two different side arms, which were typically two urea linked pyrene moieties and a crown ether moiety at the opposite sides of thiacalix[4]arene cavity. We hypothesized that such a heterodimeric system, whereby complexation control is achieved on the opposing side arms with anions and K^+ ions, can exhibit an effective positive and negative allosteric effect. In this article, we report the synthesis and complexation studies of a novel heteroditopic receptor based on a thiacalix[4]arene in the 1,3–*alternate* conformation, which contains two urea linked pyrene moieties and a crown ether moiety at the opposite sides of the thiacalix[4]arene cavity. In our complexation studies, we investigated the fluorescent properties of this heteroditopic receptor and the selective fluorescent behaviour toward targeting K^+ ions and various other anions by using the intensity ratio of the monomer to excimer emission (I_M/I_E) of the pyrene moiety.

Results and discussions

Synthesis

O-Alkylation of *distal*–**1** was carried out with 1.5 equiv. of tetraethyleneglycol ditosylate in the presence of an equivalent of K_2CO_3 according to the reported procedure, and afforded the desired 1,3–*alternate*–**2** in 83 % yield.[12] The hydrazinolysis of 1,3–*alternate*–**2** was carried out with a large excess of hydrazine hydrate, and afforded the desired 1,3–*alternate*–**3** in 86 % yield. The condensation of 1,3–*alternate*–**3** with 2.2 equivalents of 1–pyreneisocyanate[13] in THF furnished the receptor **L** in 68 % yield (Scheme 1). The ^{1}H NMR spectrum of receptor **L** in $CDCl_3$–DMSO (10:1, v/v) exhibits the characteristics of a 1,3-*alternate* canformation such as two singlets (18H each) for the *tert*-butyl protons at δ 1.29 and 1.40 ppm, one singlet (4H) for O*CH$_2$*CO protons, two singlets (4H each) for aromatic protons and two singlets (2H each) for four urea NH protons. Dilution experiments at different concentrations of receptor **L** indicated that the excimer emission resulted from the intramolecular excimer, rather than the intermolecular excimer (Fig. S7). Moreover, the concentration dependence of the ^{1}H NMR chemical shifts of the ureido protons in receptor **L** was not observed (Fig. S8). This result suggests that receptor **L** has a strong intramolecular hydrogen bond between the two ureas linking the pyrene moieties. Upon addition of Cl^- ion (0–30 μM) to the solution of receptor **L** (1.0 μM), Fig. 1 reveals how the excimer emission of the pyrene unit (486 nm) decreased, whilst the monomer emission of the pyrene unit (392 nm) increased due to the complexation of the Cl^- ion by receptor **L** inducing 'conformational unstacking' of the two pyrene ureas thereby quenching any intramolecular $\pi-\pi$ interactions. Meanwhile, a discernible isoemissive point was observed at 460 nm. A Job's plot



Scheme 1 Synthesis of receptor **L**.

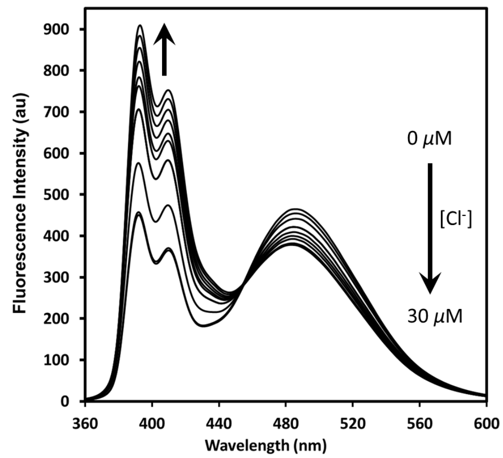


Fig. 1 Fluorescence spectral changes of receptor **L** (1.0 μM) upon addition of increasing concentrations of Cl^- ion as the tetrabutylammonium (TBA) salt in CH_2Cl_2–DMSO (10:1, v/v). λ_{ex} = 343 nm.

of the binding between receptor **L** and the Cl^- ion revealed a 1:1 stoichiometry (Fig. S9), whilst the association constant (K_a) for the complexation with Cl^- ion by receptor **L** was determined to be 3.54 × 10^4 M^{-1} by ^{1}H NMR titration experiments in $CDCl_3$–DMSO (10:1, v/v) (Fig. S11–S12). The fluorescent titration profile for receptor **L** with Cl^- ion demonstrated that the detection limit of Cl^- ion was 1.73 × 10^{-8} M (Fig. S13). As a result, receptor **L** can be regarded as being highly sensitive to Cl^- ion, especially given the large fluorescence dynamic range and the low detection limit of 1.73 × 10^{-8} M. Moreover, a fluorescence titration experiment of receptor **L** with K^+ ions was carried out by ^{1}H NMR titration experiments in $CDCl_3$–DMSO (10:1, v/v). The Job's plot binding between receptor **L** and K^+ ion revealed a 1:1 stoichiometry (Fig. S13), whilst the K_a value for the complexation with K^+ ion was determined to be 1.48 × 10^4 M^{-1} by ^{1}H NMR titration experiments in $CDCl_3$–DMSO (10:1, v/v) (Fig. S15–S17). Interestingly, upon addition of K^+ ions (0–10 μM) to a solution of the receptor **L**, it was observed, see Fig. S14, that the excimer emission of the pyrene unit (486 nm) decreased and

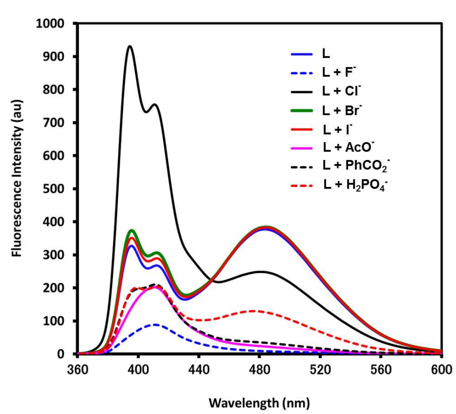


Fig. 2 Fluorescence spectral changes of receptor **L** (1.0 μM) upon addition of various tested anions (100 μM) in CH_2Cl_2–DMSO (10:1, v/v). λ_{ex} = 343 nm.

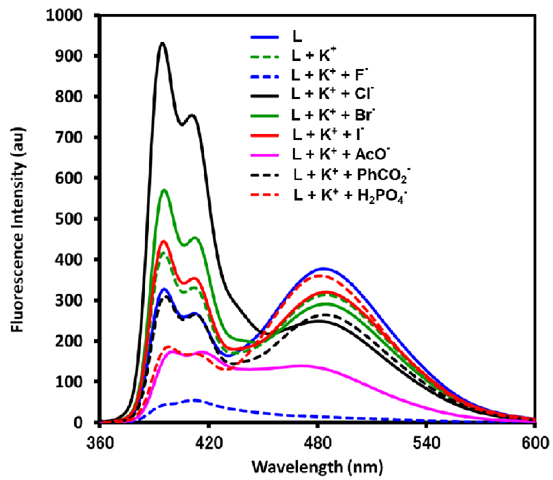


Fig. 3 Fluorescence spectral changes of receptor **L** • K^+ ([**L**] / [K^+] = 1:30, [**L**] = 1.0 μM) upon addition of various tested anions (100 μM) in CH_2Cl_2–DMSO (10:1, v/v). λ_{ex} = 343 nm.

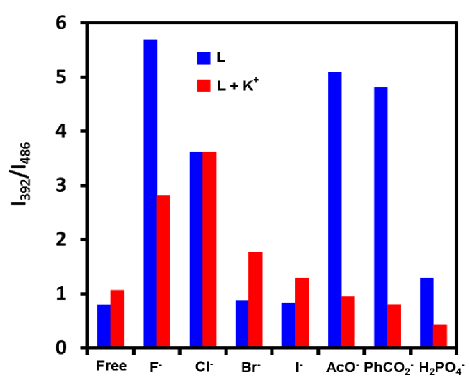


Fig. 4 Ratiometric signal changes of I_{M392}/I_{E486}: upon addition of 100 μM of various anions in receptor **L** (1.0 μM) (blue bar) and receptor **L** • K^+ ([**L**] / [K^+] = 1:30, [**L**] = 1.0 μM) (red bar) solution in CH_2Cl_2–DMSO (10:1, v/v) at 298 K. λ_{ex} = 343 nm.

monomer emission of pyrene unit (392 nm) increased. These changes were thought to arise because of the conformational change upon complexation of the K^+ ion with the crown-5 ring. Fig. 2 shows the fluorescence intensity changes of the monomer emission for receptor L in the presence of various anions. Upon the addition of Cl^- ion, the fluorescence intensity change was very large. However, no significant fluorescent intensity changes were observed upon the addition of either Br^- or I^- ions. On the other hand, upon addition of F^- ions the monomer and excimer emission exhibited a quenching due to the photoinduced electron transfer (PET) from F^- to the pyrene moieties.[14] Also, upon the addition of AcO^-, $PhCOO^-$ or $H_2PO_4^-$ ions, relatively little quenching was observed (Fig. S18). In comparison with the Cl^- ion, a much weaker response and different was given at the same concentration for the F^-, Br^-, I^-, AcO^-, $PhCOO^-$ or $H_2PO_4^-$ ions. The much larger response (and different) fluorescence intensities caused by the presence of the Cl^- ion for receptor **L**, suggests that receptor **L** has a much higher affinity and selectivity toward the Cl^- ion. Moreover, it was found that receptor **L** was capable of binding all of the anions tested, irrespective of their shape. The quantum yield of the free receptor **L** is Φ = 0.23, for both the monomer and excimer emission (392 and 486 nm). The quantum yield of the receptor **L**•Cl^- complex is Φ = 0.13 as a result of increased monomer emission. While, the quantum yields of the receptors **L**•Br^- and **L**•I^- (Φ = 0.20 and 0.22, respectively) are almost unchanged in comparison with the quantum yield of the free receptor **L**. In contrast, the quantum yields of the receptor **L** with F^-, AcO^-, $PhCOO^-$ or $H_2PO_4^-$ ions could not be measured due to quenching. Furthermore, the result of the fluorescence responses of the receptor **L**•K^+ to the various tested anions exhibited the appearance of an effective positive and negative allosteric effect between the receptor **L**•K^+ and the various anions. As shown in Fig. 3, upon addition of Br^- ions the fluorescence response was enhanced because of a positive allosteric effect via an ion-pair electrostatic interaction and a conformational change. However, upon the addition of Cl^- ions, the fluorescence response was almost the same in comparison to the case in the absence of K^+ ions. This was attributed to the two ureas linked pyrene moieties of receptor L •K^+ binding to the Cl^- ion by an ion-pair electrostatic interaction which induces the decomplexation of the K^+ ion from the crown-5 ring of receptor **L** via a conformational change of the thiacalix[4]crown-5. The quantum yield of the receptor **L** with K^+ ion was found to be Φ = 0.18. The quantum yield of receptor **L** with Cl^- and K^+ ions was Φ = 0.12, as a result of the increased monomer emission. The quantum yield of receptor **L** with Br^- and K^+ ions was Φ = 0.16, caused by increasing the monomer emission. These results suggested that the monomer emission was increased. Indeed, Fig. 4 shows the intensity ratio of the monomer to excimer emission (I_M/I_E) of receptor **L** which is 0.79. It can be seen that amongst all the anions tested, there are some different trends for I_M/I_E exhibited both in the absence or presence of K^+ ions. In the absence of K^+ ions, I_M/I_E on addition of F^-, AcO^- or $PhCOO^-$ ions revealed a dramatic increase of the order of 6.1~7.2-fold to 4.8~5.7. This is because the receptor **L** complexes strongly with each anion via two ureas linked pyrene moieties, resulting in a quenching of the excimer emission by PET from each anion to the pyrene moieties. On the other hand, in the presence of K^+ ions, I_M/I_E on addition of Cl^- ions was enhanced somewhat by *ca* 3.3 to 3.6 fold (I_M/I_E of receptor **L** •K^+ is 1.1), which was attributed to receptor **L** complexing strongly with the Cl^- ion via the two ureas linked pyrene moieties. Moreover, it was found that I_M/I_E on addition of Br^- ions increased in intensity by 1.7–1.8 fold in the presence of K^+ ions (*versus* the absence of K^+ ion) because the two ureas linked pyrene moieties of receptor **L**•K^+ bind Br^- ion by an effective positive allosteric effect (an ion-pair electrostatic interaction and a conformational change).

To obtain further more detailed information about the presence of a positive or negative allosteric effect between the receptor **L** •K^+ and Br^- or Cl^- ions, ^1H NMR titration experiments in $CDCl_3$–DMSO (10:1, v/v) were conducted. When only K^+ ions was added, we observed a large downfield shift of not only the crown–ether bridge protons, but also all the

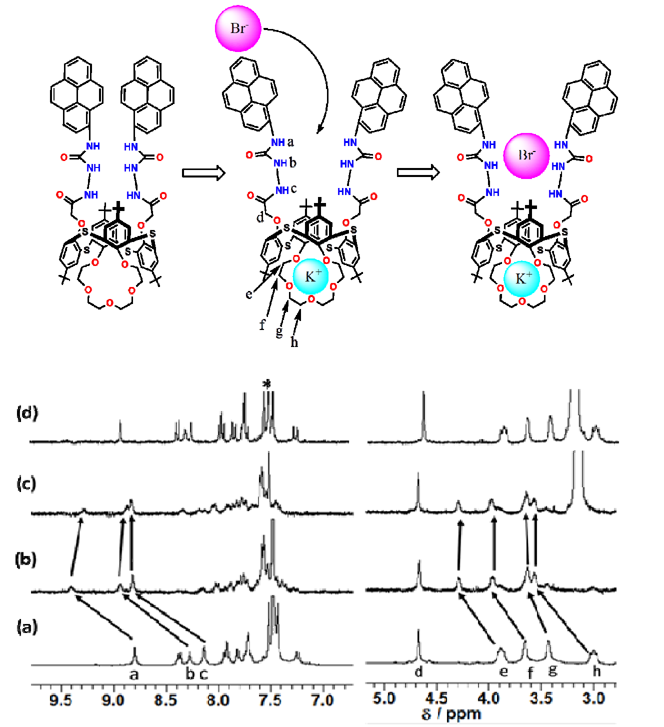


Fig. 5 Proposed positive allosteric behaviour of receptor **L** with Br^- and K^+ ions. Partial ^1H NMR spectra of **L**/guest (H/G = 1:1); a) free **L**; b) **L**⊃KSO_3CF_3; c) Bu_4NBr⊂ [**L**⊃K^+]; d) **L**⊃Bu_4NBr. Solvent: $CDCl_3$–DMSO (10:1, v/v). 300 MHz at 298 K. *Denotes the solvent peak.

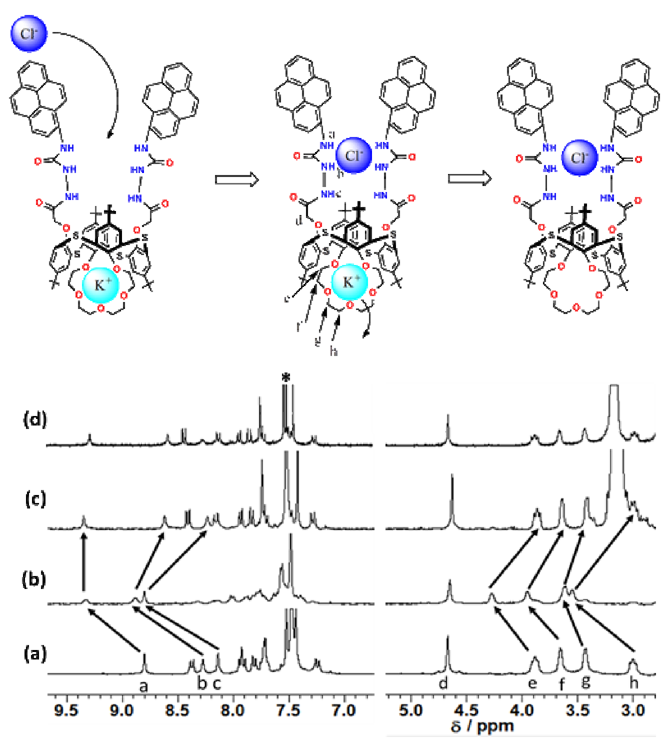


Fig. 6 Proposed negative allosteric behaviour of **L** with Cl^- and K^+ ions. Partial ^1H NMR spectra of **L**/guest (H/G = 1:1); a) free **L** ; b) **L**⊃KSO_3CF_3 ; c) Bu_4NCl⊂[**L**⊃K^+]; d) **L**⊃Bu_4NCl. Solvent: $CDCl_3$–DMSO (10:1, v/v). 300 MHz at 298 K. *Denotes the solvent peak.

NH protons, which is due to the conformational change on complexation of the K^+ ion by the crown-5 ring (Figures 5a and 5b). Figure 5 shows that when Br^- ions were added to the solution of [**L**⊃KSO_3CF_3] (Fig. 5c), resultant upper field shifts were induced of 0.09 ppm (δ = 9.40 to 9.31 ppm) for the NH_a protons and 0.04 ppm (δ = 8.89 to 8.85 ppm) for the NH_b protons, whilst the chemical shifts of the crown-ether bridge protons did not change. These results suggested that the formation of a heterogeneous dinuclear complex Br^-⊂[**L**⊃K^+] had occurred, and we propose a positive allosteric effect of receptor **L** toward Br^- ions in the presence of K^+ ion as shown in Figure 4. On the other hand, Figure 6 reveals that when Cl^- ions were added to a solution of [**L**⊃KSO_3CF_3] (Fig. 6c), the addition induced upper field shifts of 0.22 ppm (δ = 8.89 to 8.67 ppm) for the NH_b protons and 0.55 ppm (δ = 8.80 to 8.25 ppm) for the NH_c protons, whilst upper field shifts for crown-ether bridge protons were observed. Interestingly, when Cl^- ions were added to a solution of [**L**⊃KSO_3CF_3] (Figure 6c), the chemical shifts for crown-ether bridge protons most closely match chemical shifts of the free crown-ether bridge protons (Figures 6c and 6d). These results suggested that the two ureas linked pyrene moieties of receptor **L**·K^+ bind Cl^- ions by an ion-pair electrostatic interaction, which induces the decomplexation of the K^+ ion from the crown-5 ring of receptor **L** by a conformational change of the thiacalix[4]crown-5. A negative allosteric effect of receptor **L** towards Cl^- ions in the presence of K^+ ions, as shown in Figure 6, is proposed.

Conclusion

In summary, a novel heteroditopic receptor **L** based on a thiacalix[4]arene in the 1,3-*alternate* conformation, which contains two ureas linked pyrene moieties and crown ether moiety at the opposite sides of a thiacalix[4]arene cavity, has been synthesized. The binding of K^+ ions and various anions at the crown-**5** ring moiety and the two ureas linked pyrene moieties, respectively, was investigated by using fluorescence and ^1H NMR titration experiments. It was found that receptor **L** was able to bind all of the anions tested, irrespective of their shape. The appearance of positive and negative allosteric effects in receptor **L** was also investigated by ^1H NMR and fluorescence titration experiments. Interestingly, the formation of a heterogeneous dinuclear complex of receptor **L** with Br^- and K^+ ions by a positive allosteric effect could be observed. On the other hand, when the two ureas linking pyrene moieties of receptor **L** •K^+ bind Cl^- ion, this induces the decomplexation of the K^+ ion from the crown-5 ring by a negative allosteric effect.

Experimental Section

General : Unless otherwise stated, all reagents used were purchased from commercial sources and used without further purification. Compounds **1**[17] and **2**[14] were prepared following the reported procedures. All solvents used were dried and distilled by the usual procedures prior to use.

All melting points (Yanagimoto MP-S1) are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Nippon Denshi JEOL FT-300 NMR spectrometer and Varian-400MR-vnmrs400 with $SiMe_4$ as an internal reference: *J*-values are given in Hz. IR spectra were measured for samples as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrophotometer. Mass spectra were obtained with a Nippon Denshi JMS-HX110A Ultrahigh Performance mass spectrometer at 75 eV by using a direct-inlet system. UV-vis spectra were recorded using a Shimadzu UV-3150UV-vis-NIR spectrophotometer. Fluorescence spectroscopic studies of compounds in solution were performed in a semimicro fluorescence cell (Hellma®, 104F-QS, 10 × 4 mm, 1400 μL) with a Varian Cary Eclipse spectrophotometer. Fluorescence quantum yields were recorded in solution (Hamamatsu Photonics K. K. Quantaurus-QY A10094) using the integrated sphere absolute PL quantum yield measurement method.Elemental analyses were performed by a Yanaco MT-5.The elemental analysis, MS, and emission spectra were measured.

Synthesis of compound 3

Compound **2** (1.0g, 0.95mmol) was put into a round-bottom flask and ethanol (120 mL), THF (120 mL) and hydrazine hydrate (14 mL, large excess) were added and the system was refluxed for 48 h. After cooling, the solvents and excess hydrazine were removed under reduced pressure to give the crude product as a white solid. The residue was triturated sequentially with water and methanol and the product collected by filtration. Compound **3** was obtained 0.84g (86 %) as a white solid. M.p. 216–218 ℃. IR: υ_{max} (KBr)/cm^{-1}: 3421, 2961, 1670, 1438, 1263, 1091, 1019 and 801. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (18H, s, *t*Bu× 2), 1.37 (18H, s, *t*Bu × 2), 3.00 (4H, t, *J* = 9.1 Hz, OCH_2 × 2), 3.39 (4H, br, OCH_2 × 2), 3.48 (4H, broad s, NH_2 × 2), 3.60 (4H, broad s, OCH_2 × 2), 3.96 (4H, t, *J* = 9.1 Hz, OCH_2 × 2), 4.55 (4H, s, OCH_2CO × 2), 7.35 (4H, s, Ar–*H* × 2), 7.41 (4H, s, Ar–*H* × 2) and 7.54 (2H, s, N*H* × 2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.5 (CH_3), 33.5 ($C(CH_3)_3$), 64.9 (OCH_2), 67.4 (OCH_2), 69.2 (OCH_2), 70.5 (OCH_2), 72.6 (OCH_2), 126.2 (ArC), 126.4 (ArC), 126.5 (ArC), 126.7 (ArC), 146.5 (ArC), 146.7 (ArC), 153.6 (ArC), 155.4 (ArC) and 167.6 (CO) ppm. FABMS: *m/z*: 1023.38 (M^+). $C_{52}H_{70}N_4O_9S_4$ (1023.39): calcd C 61.03, H 6.89, N 5.47. Found: C 61.11, H 6.98, N 5.34.

Synthesis of receptor L

To compound **3** (150 mg, 0.195 mmol) in THF (10 mL), was added pyrenyl isocyanate (104 mg, 0.429 mmol) and the mixture was stirred at room temperature for 24 h under argon. The resulting precipitate was collected by filtration, washed with CH_3CN to give receptor **L** as a white solid. Recrystallization from $CHCl_3$–CH_3CN (1:1) gave receptor **L** (200 mg, 68 %) as pale-green solid. M.p. 221–223 ℃. IR: υ_{max} (KBr)/cm^{-1}: 3309, 2954, 2903, 1666, 1531, 1439, 1268, 1211, 1151, 1091, 842 and 755. ^{1}H NMR (300 MHz, $CDCl_3$–DMSO, 10:1): δ = 1.29 (18H, s, *t*Bu × 2), 1.40 (18H, s, *t*Bu × 2), 3.00 (4H, t, *J* = 9.1 Hz, OCH_2 × 2), 3.44 (4H, broad s, OCH_2 × 2), 3.66 (4H, s, OCH_2 × 2), 3.89 (4H, t, *J* = 9.1 Hz, OCH_2 × 2), 4.68 (4H, s, OCH_2CO × 2), 7.20 (2H, d, *J* = 8.1 Hz, pyrene-*H* × 2), 7.44 (4H, s, Ar–*H* × 2), 7.52 (4H, s, Ar–*H* × 2), 7.65–7.72. (10H, m, pyrene-*H* × 2), 7.79 (2H, d, *J* = 8.1 Hz, pyrene-*H* × 2), 7.90 (2H, t, *J* = 8.1 Hz, pyrene-*H* × 2), 8.15 (2H, s, N*H* × 2), 8.26 (2H, s, N*H* × 2), 8.39 (2H, d, *J* = 8.1 Hz, pyrene-*H* × 2) and 8.79 (2H, s, N*H* × 2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.9 (CH_3), 31.2 (CH_3), 34.3 ($C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 66.0 (OCH_2), 68.7 (OCH_2), 68.8 (OCH_2), 71.4 (OCH_2), 73.4 (OCH_2), 120.4 (ArC), 120.8 (ArC), 122.3 (ArC), 123.9 (ArC), 124.1 (ArC), 124.3 (ArC), 124.5 (ArC), 125.3 (ArC), 125.5 (ArC), 126.4 (ArC), 126.5 (ArC), 126.7 (ArC), 127.0 (ArC), 127.3 (ArC), 128.0 (ArC), 130.2 (ArC), 130.8 (ArC), 131.5 (ArC), 142.3 (ArC), 147.2 (ArC), 148.2 (ArC), 151.6 (ArC), 154.9 (ArC), 155.5 (ArC), 155.9 (CO) and 167.5 (CO) ppm. FABMS: *m/z*: 1509.61 (M^+). $C_{86}H_{88}N_6O_{11}S_4$ (1508.54): calcd C 68.41, H 5.87, N 5.57. Found: C 68.61, H 5.78, N 5.45.

Determination of the Association Constants

The association constants were determined by using ^{1}H NMR titration experiments in a constant concentration of host receptor (4 × 10^{-3} M) and by varying the guest concentration (0–8.0 × 10^{-3} M). The ^{1}H NMR chemical shift of the urea protons (NH) signal was used as a probe. The association constant (K_a) for the complexes of receptor **L** were calculated by nonlinear curve–fitting analysis of the observed chemical shifts of the NH protons according to the literature procedure.[18]

^{1}H NMR Titration Experiments

A solution of Bu_4NX (X = F, Cl, Br, I, AcO, PhCOO, H_2PO_4) in CD_3CN (4 × 10^{-3} M) was added to a $CDCl_3$–DMSO (10:1, v/v) solution of receptor **L** in the absence or presence of KSO_3CF_3 in an NMR tube. ^{1}H NMR spectra were recorded after addition of the reactants and the temperature of the NMR probe was kept constant at 27 °C. The ^{1}H NMR data of the most-representative complexes are given below:

receptor **L**⊃K^+: ^{1}H NMR (300 MHz, $CHCl_3$–DMSO–CH_3CN, 10:1:1, v/v): δ = 3.55 (4H, br, OCH_2 × 2), 3.61 (4H, br, OCH_2 × 2), 3.96 (4H, br, OCH_2 × 2), 4.28 (4H, br, OCH_2 × 2), 4.68 (4H, s, OCH_2O × 2), 8.80 (2H, br, NH_c × 2), 8.89 (2H, br, NH_b × 2) and 9.40 (2H, br, NH_a × 2) ppm.

receptor **L**⊃Cl^-: ^{1}H NMR (300 MHz, $CHCl_3$–DMSO–CH_3CN, 10:1:1, v/v): δ = 3.00 (4H, br, OCH_2 × 2), 3.44 (4H, br, OCH_2 × 2), 3.66 (4H, br, OCH_2 × 2), 3.89 (4H, br, OCH_2 × 2), 4.68 (4H, s, OCH_2O × 2), 8.25 (2H, br, NH_c × 2), 8.65 (2H, br, NH_b × 2) and 9.38 (2H, br, NH_a × 2) ppm.

Cl^-⊂[receptor **L**⊃K^+]: ^{1}H NMR (300 MHz, $CHCl_3$–DMSO–CH_3CN, 10:1:1, v/v): δ = 3.00 (4H, br, OCH_2 × 2), 3.44 (4H, br, OCH_2 × 2), 3.66 (4H, br, OCH_2 × 2), 3.89 (4H, br, OCH_2 × 2), 4.68 (4H, s, OCH_2O × 2), 8.25 (2H, br, NH_c × 2), 8.67 (2H, br, NH_b × 2) and 9.40 (2H, br, NH_a × 2) ppm.

receptor **L**⊃Br^-: ^{1}H NMR (300 MHz, $CHCl_3$–DMSO–CH_3CN, 10:1:1, v/v): δ = 3.00 (4H, br, OCH_2 × 2), 3.44 (4H, br, OCH_2

× 2), 3.66 (4H, br, OCH_2 × 2), 3.89 (4H, br, OCH_2 × 2), 4.68 (4H, s, OCH_2O × 2), 8.23 (2H, br, NH_c × 2), 8.29 (2H, br, NH_b × 2) and 8.90 (2H, br, NH_a × 2)

Br^-⊂[receptor **L**⊃K^+]: ^{1}H NMR (300 MHz, $CHCl_3$–DMSO–CH_3CN, 10:1:1, v/v): δ = 3.00 (4H, br, OCH_2 × 2), 3.44 (4H, br, OCH_2 × 2), 3.66 (4H, br, OCH_2 × 2), 3.89 (4H, br, OCH_2 × 2), 4.68 (4H, s, OCH_2O × 2), 8.80 (2H, br, NH_c × 2), 8.85 (2H, br, NH_b × 2) and 9.31 (2H, br, NH_a × 2)

Supporting information : ^{1}H/^{13}C NMR spectra of **2, 3** and **L**. Moreover, detailed fluorescence and ^{1}H NMR titration spectra data.

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†Electronic Supplementary Information (ESI) available: Details of the ^{1}H/^{13}C NMR spectra, fluorescence spectra, Job's plot and ratiometric signal changes of I_{M392}/I_{E485}; see DOI: 10.1039/b000000x/

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