Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 62 (2006) 11687–11696

Cholic acid-based high sensitivity fluorescent sensor for α,ω-dicarboxylate: an intramolecular excimer emission quenched by complexation

Shun-Ying Liu,[a,b] Yong-Bing He,[a] Wing Hong Chan[b,*] and Albert W. M. Lee[b]

[a]*Department of Chemistry, Wuhan University, Hubei, China*
[b]*Department of Chemistry and Central Laboratory of the Institute of Molecular Technology for Drug Discovery and Synthesis, Hong Kong Baptist University, Hong Kong, China*

Received 21 July 2006; revised 13 September 2006; accepted 14 September 2006
Available online 17 October 2006

Abstract—Fluorescent receptors (**1** and **2**) bearing two binding units on C3 and C24 and two signal display units on C7 and C12 of cholic acid, respectively, were designed and synthesized. Both **1** and **2** emit a much weaker fluorescence than that of the control compound **3** lacking of the binding units reflecting that a PET process originated from the C-3 thiourea group to the plural pyrenyl pendant groups is operative. Addition of terminal dicarboxylate anions to the CH_3CN solution of **1** or **2** enhances the PET process, which leads to a significant and highly sensitive fluorescence response, resulting in an almost complete quenching of the excimer emission of the signal units. To maximize the interaction of the host and the guest, carboxylates of more than five carbon chains could penetrate through the space between the two pyrenyl pendants of the host, triggering a considerable conformational change of the fluorophores. As a result, an enhancement of the monomer emission at the expense of the excimer emission will take place. The binding properties and mechanism of **1** and **2** to dicarboxylates in CH_3CN were manifested by the combined fluorescence, UV–vis, and ^1H NMR spectroscopic method.

1. Introduction

Anions play an important role in a wide range of chemical, environmental, and biological processes.[1] The quest for chemosensors capable of effecting the selective and sensitive binding and sensing of negatively charged species through visible, electrochemical, and optical responses has continued to attract considerable attention in scientific community.[2] Dicarboxylates are among the most attractive targets for the study of anion recognition and sensing because of their biological importance,[3] such as their critical roles in numerous metabolic processes.[4] Therefore, their sensitive detection is of great interest in a variety of areas in bioanalytical and biomedical researches.[4b,5] The optical methods, owing to their simplification of manipulation and sensitivity of transduction of binding behaviors, are extensively adopted in the investigation of molecular/ion recognition.[6] Numerous endeavors have been particularly devoted to the design and synthesis of ditopic anion receptors bearing optical signal display subunits (i.e., chromophore or fluorophore) as sensing probes for dicarboxylates.[7]

The structural complementary between receptors and terminal dicarboxylates ($^-OOC(CH_2)_nCOO^-$) plays a crucial role in the selective recognition processes.[8] To assemble selective artificial ditopic receptors for terminal dicarboxylates, based on cyclopolyammonium,[9] sapphyrin,[10] and calix[4]-arene,[11] some classical molecular skeletons were rationally designed and exquisitely synthesized. Charge neutral chemosensors, which are immune from cross pH interference are particularly attractive. Gunnlaugsson and Davis[12] reported a neutral fluorescent PET sensor for glutarate while He's group developed two fluorescent sensors for adipate.[13] Mei and Wu reported a sensor containing a naphthalene group as the signal unit for pimelate.[14] However, most of these chemosensors exhibit good selectivity only for dicarboxylates of a relatively short chain length ($n \leq 3$) and with moderate binding constants of $10^5\ M^{-1}$. It is very difficult to construct a suitable receptor for a long-chain terminal dicarboxylate using the classical molecular scaffolds such as polyazamacrocycles and calixarenes. To our best knowledge, there is no example of chemosensor, which can bind strongly with a long-chain terminal dicarboxylate ($n>5$). In this paper, we report the design and synthesis of two cholic acid-based fluorescent sensors, which are amenable to the sensitive detection of long-chain terminal dicarboxylates ($n=6$ and 8).

Pioneered by the seminal works of Davis and others, cholic acid has recently emerged as a promising natural material to

Keywords: Cholic acid; Fluorescence; UV–vis spectroscopy; Dicarboxylate; Chemosensor.
* Corresponding author. Tel.: +852 3411 7076; fax: +852 3411 7348; e-mail: whchan@hkbu.edu.hk

0040–4020/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2006.09.042

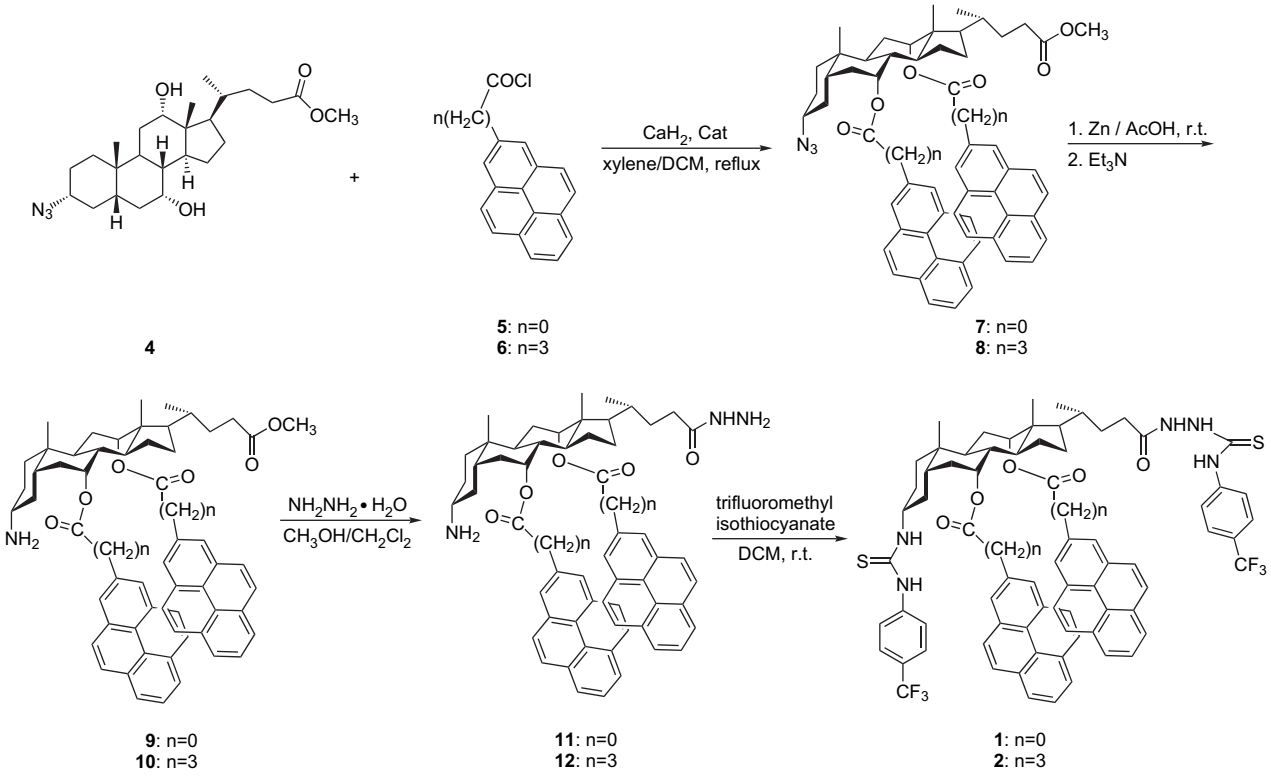
construct supramolecular systems for molecular recognition.[15] To achieve high affinity and selectivity to the 'host', the three axially oriented functionalities at the C3, C7, and C12 of cholic acid could be modified and assembled in such a way to confer cooperative binding interactions to a specific guest anion. Recently, by incorporation of two thiourea groups connected to an anthracene moiety at the C3 and C24 as the signal subunit, we have created a fluorescent ditopic receptor possessing binding capability to dicarboxylates even in aqueous media.[16] Our findings represent the first charge neutral chemosensor, which can be exploited for binding dicarboxylates in aqueous conditions. However, the fluorescent signal change of the sensor over a wide concentration range of the guest is only moderate. To further improve the sensitivity and selectivity of the sensor, we envisage that, if two pyrene moieties are introduced onto the C7 and C12 as signal display units and two thiourea receptive subunits were appended onto C3 and C24 of cholic acid, upon association with dicarboxylates, a distinct fluorescent response indicative of binding will be observed. The two pendent proximate pyrenyl groups can display not only a well-defined monomer emission at 370~430 nm but also an efficient excimer emission at around 480 nm.[17] To effectively interact with the host, the terminal dicarboxylates may penetrate through the space between the plural pyrenyl pendants reaching the two receptive sites at the two ends of the host. The binding event can trigger conformational changes of the pyrene-appended signal display units, which could upset the equilibrium between the monomer and the excimer emissions. Besides, the fluorescence of the system will be quenched by the formation of the complex via a PET (photo-induced electron transfer) mechanism. In addition, appending bulky pyrenyl groups to the C7 and C12 of cholic acid can also create a bigger steric hindrance and sharpen the selectivity of the sensor favoring the binding between the host and long-chain terminal dicarboxylates.

Herein, we report the synthesis and structural characterization of two new charge neutral fluorescent sensors **1** and **2** bearing two signal subunits at C7 and C12 and two binding subunits at C3 and C24 of cholic acid, respectively. The binding abilities of **1** and **2** to dicarboxylates were demonstrated by fluorescence emission spectra, UV–vis spectra, and ^{1}H NMR method.

2. Results and discussion

2.1. Synthesis

Treatment of 1-pyrenyl acid or 1-pyrenebutyric acid with sulfuryl dichloride in benzene afforded the corresponding acid chlorides **5** and **6** in 100% yield, which could be directly used for the subsequent condensation reaction (Scheme 1). To overcome the high steric hindrance of introducing the plural pyrenyl moieties on the C7 and C12 of the cholic acid scaffold, we adopted the Maitra's protocol by reacting excess **5** or **6** with methyl 3-azidocholate (**4**)[15c] in a mixed solvent of dichloromethane and xylene (1:10) using CaH_2 as a base with a catalytic amount of benzyltriethylammonium chloride, giving rise to **7** and **8** in ca. 40% yield, respectively.[18] Reduction of **7** (or **8**) by zinc dust in acetic acid followed by hydrazidation with hydrazine yielded amine **11** (or **12**). Condensation reactions were performed between **11** (or **12**) and 4-trifluoromethylphenylisothiocyanate in dichloromethane and the target compounds **1** and **2** were



Scheme 1. Synthetic routes for receptors **1** and **2**.

obtained in ca. 30~50% over two steps. In order to investigate the effect of binding behaviors on the fluorescence of **1** and **2**, control compound **3** was synthesized from methyl 3α-acetyl-7α,12α-dihydroxy-5β-cholan-24-oate.[19]

2.2. Binding properties

As expected, when excited at 352 nm in CH_3CN, receptor **1** (1×10^{-5} M) displayed a monomer emission at 388 nm and an excimer emission at 488 nm, with an intensity ratio of monomer to excimer emission (I_M/I_E) as 2.42. Compared to sensor **1**, **2** (1×10^{-5} M) was excited in CH_3CN at a shorter wavelength (342 nm) and gave a monomer and an excimer emission at 375 and 475 nm, respectively, the ratio of I_M/I_E was found to be 0.21, which is substantially smaller than that of **1**. This indicated that, in comparison with **1**, the presence of the more flexible three carbon spacer in **2** between the pyrenyl groups and the C-7 and C-12 ester functionalities enables a tighter excimer formation arising from a stronger π–π stacking in receptor **2**. In both **1** and **2**, the intensity of ratio of monomer to excimer is barely changed in the concentration range of 10^{-7}–10^{-4} M, implicating that their excimer emissions result from an intramolecular excimer but not from an intermolecular excimer (Supplementary data).

To unravel the details of the interaction between the host and the guest, compound **3** lacking the thiourea groups on the C3 and C24 served as the control was synthesized. Compared with **1** and **2**, **3** can emit relatively stronger emissions and give a monomer emission at 388 nm and an excimer at 488 nm when excited at 352 nm. On this basis a higher I_M/I_E ratio of 0.84 was obtained for **3** compared with the value of 0.21 for **1**, it is quite likely that the quenching effect by the thiourea group is more pronounced to the excimer than that to the monomer (Fig. 1). Apparently, the thiourea groups not only affect the ratio of monomer to excimer emission but also quench the fluorescence of receptors **1** and **2**. This is conceivably attributable to the fact that the thiourea groups take part in the PET process in which an electron is transferred from a lone-pair electron of the sulfur atom to two excited pyrenyl units of **1** and **2**.[20] The quantum yield of **1**, **2** and **3** were assessed using pyrene as the standard and the results are tabulated in Table 1. The quantum yield of **3** was much higher than that of **1** and **2** with the order of $\Phi_3>\Phi_2>\Phi_1$. Due to the more proximal thiourea groups at the two pyrenyl units in receptor **1** than in receptor **2**, a more effective PET process was effectuated for **1**.

To obtain insight into the binding properties of **1** and **2** toward dicarboxylate anions, we first investigated the fluorescence change of the sensors upon addition of dicarboxylates in CH_3CN. With a gradual increase in the concentration of dicarboxylate anions, malonate, succinate, glutarate, adipate, suberate, and sebacate (all as tetrabutylammonium salts), the monomer emission of **1** (1×10^{-5} M) can be quenched ca. 50% and the excimer can be quenched as much as >90%. Comparing with our previously reported anthracene based carboxylate sensors,[16] the extent of quenching of the present systems caused by the guests is significantly enhanced. Potentially, sensors **1** and **2** would be more sensitive optical probes toward dicarboxylates. Typical fluorescence change of **1** and **2** modulated with different amounts of suberate in CH_3CN is showed in Figures 2 and 3, respectively. The inset of the graph shows the change of the fluorescence intensity of the monomer and excimer upon addition of suberate. Several interesting features of the plots are noteworthy. Firstly, both sensors are ratiometric, which are more superior systems in sensor design due to their ability to eliminate the sample matrix effect in the recognition process. Both sensors operate complementarily to each other. As the concentration of the guest increases, the I_M/I_E of **1** and **2** responds differently (i.e., the ratio of **1** decreases while that of **2** increases, Supplementary data). It is noteworthy that, when treated with different amounts of dicarboxylate anions, the excimer of receptor **2** at 475 nm (1×10^{-5} M in CH_3CN) had shown a more sensitive fluorescence response than that of receptor **1** and the excimer was almost completely quenched. The guest induced conformational change of sensor **2** was implicated at the moderate concentration of suberate as a slightly increase in the monomer peak was observed. Expansion of Figure 3 in the range of 400–450 nm allows the manifestation of an iso-emission point at around 421 nm (Supplementary data).

Regarding the nature of the guest–host interaction in the sensor systems, the key question was: how do dicarboxylates preorganize themselves in reaching the two binding sites of the host? Could they penetrate through or just move around the space between the pyrenyl pendent groups in the

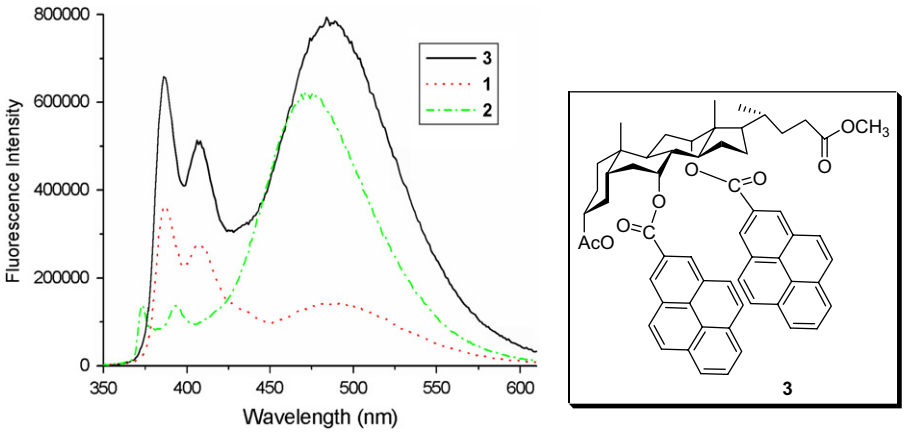


Figure 1. The fluorescence emission spectra of **1**, **2**, and **3** in CH_3CN (1×10^{-6} M) (**1** and **3** were excited at 352 nm, and **2** at 342 nm).

Table 1. Absorption and fluorescence spectral data of **1**, **2**, and **3** in CH_3CN

Sample	λ_{abs} (nm)	ε (10^4 M^{-1} cm^{-1})[a]	$\Phi_{313\ nm}$
Pyrene	231/240/262/272/306/319/334	3.83/6.95/2.15/4.05/1.02/2.53/4.15	0.530[b,d]
3	282/352/385	7.49/6.95/2.18	0.877[c,d]
2	235/242/265/276/313/327/343	11.1/14.9/7.09/10.3/3.09/5.49/6.97	0.699[c,d]
1	280/348/383	7.44/4.96/1.33	0.592[c,d]

[a] The concentration is 1×10^{-5} M.
[b] Quantum yield was detected in EtOH and used as the standard.
[c] Quantum yield was detected in CH_3CN.
[d] Quantum yield was determined with λ_{ex}=303 nm.

respective complexes? Treated with ca. 60 equiv of malonate and succinate anions (i.e., short chain dicarboxylates), the fluorescence response of **1** or **2** attained equilibrium, while with only ca. 15 equiv of other longer chain dicarboxylate anions an equilibrium could be observed. The excimer emission is more sensitive to the dicarboxylates than the monomer emission both in **1** and **2**. With the increase of the length of the dicarboxylate anion, the sensitivity of both **1** and **2** toward dicarboxylate increases. For long chain dicarboxylates, there is a significant fluorescence response even at the concentration at around 10^{-8} M (Supplementary data). Sensor **2** has a more sensitive response to the same dicarboxylate than **1** because of its two pyrenyl groups linked with flexible spacers, which lead to a stronger excimer emission. Introducing dicarboxylates and other anions such as AcO^-, Cl^-, Br^-, and I^- to the CH_3CN solution of **3**, there is no change observed in the fluorescence spectra. This indicated that the anions quenched the fluorescence intensity of pyrenyl groups only by coordinating with thiourea groups present in **1** and **2**.

After binding the dicarboxylate anion, the electron-donating power of either the aminothiourea or amidothiourea group in the hosts can be enhanced, which leads to a stronger PET process from the thiourea to the pyrenyl units (vide supra). This possibly contributes to the quenching of the monomer and excimer. At the same time, when the binding events occurred, the dicarboxylate anion would go through the C-7 and C-12 pendent groups of the cholic acid derivatives. Such type of interaction could destroy the π–π stack of the two pyrenyl units leading to the enhancement of the monomer emission at the expense of the excimer peak (vide supra). The observation appears to be consistent with this interaction model. When treated with 100 equiv of AcO^-, the monomer emission of **1** and **2** could be quenched ca. 50% as the extent of quench caused by dicarboxylates (except malonate and succinate) while both the excimer of **1** and **2** only could be quenched at about 50% (Supplementary data). Apparently, acetate due to its small size could not go through the space of the two pendent groups. This observation strongly supported that the long-chain dicarboxylates (n=3, 4, 6, 8) went through rather than passed around the two pyrenyl units, which also contributed to a great quenching of the excimer of **1** and **2** (i.e., from 50 to 90%). In response to the combined electronic and conformational change effects triggered by complex formation, an enhancing PET process from thiourea groups to the pyrenyl groups and a decrease of the π–π stack between the two pyrenyl groups take place. Accordingly, the excimer emission can be quenched significantly, which creates a highly sensitive fluorescence responsive system to dicarboxylates. While treated with 100 equiv of other anions, spherical anions such as Cl^-, Br^-, and I^-, only less than 10% quenching was observed in the fluorescence spectra of **1** and **2**.

Job plot[21] showed that both **1** and **2** formed 1:2 complexes with malonate and succinate (Fig. 4) and 1:1 complexes with other dicarboxylate anions (Supplementary data). This result is consistent with the phenomena observed in the fluorescence spectra (vide supra) and suggest that pyrenyl groups on C7 and C12 not only act as signal units but also play

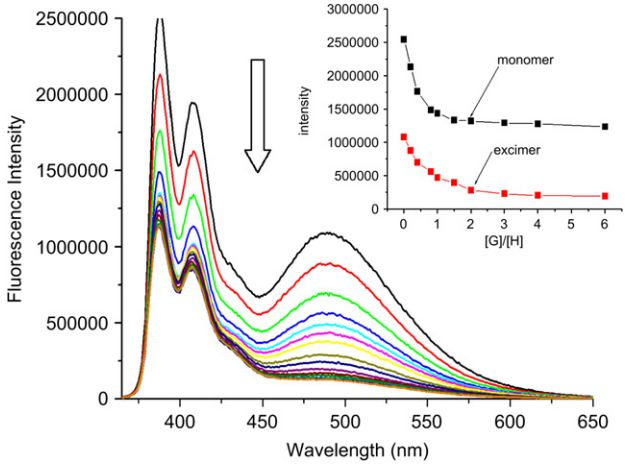


Figure 2. The fluorescence emission spectra of **1** (1×10^{-5} M) with suberate in CH_3CN, λ_{ex}=352 nm. Inset: the fluorescence intensity of **1** at 388 nm (monomer) and 488 nm (excimer) with different amounts of suberate.

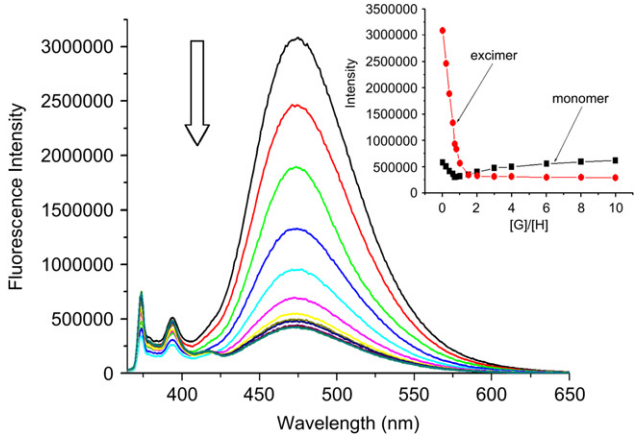


Figure 3. The fluorescence emission spectra of **2** (1×10^{-5} M) with suberate in CH_3CN, λ_{ex}=342 nm. Inset: the fluorescence intensity of **1** at 475 nm with different amounts of suberate.

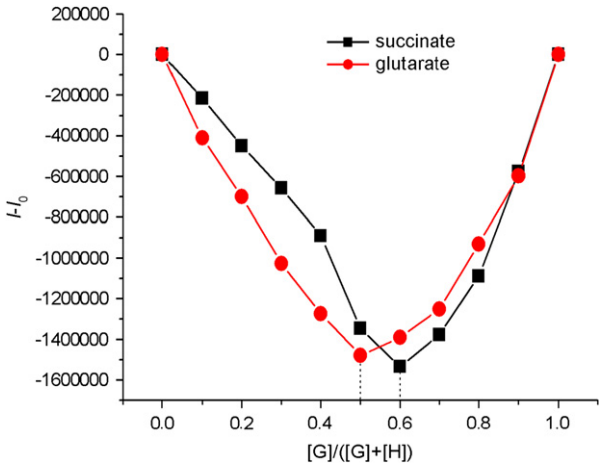


Figure 4. Job plot for the complexation of **2** with succinate and glutarate in CH_3CN (the total concentration is 1×10^{-5} M).

important roles in complexing with terminal dicarboxylate anions. Specifically, non-bonding repulsion between the host and malonate (or succinate) precludes the formation of a 1:1 complex by passing through the bulky pyrenyl pendants. We have reported for the first time that the flexible C17 side chain of cholic acid derivatives can be exploited to provide a binding unit onto the C24[22] and the resulting fluorescent sensor had demonstrated a fairly selective binding toward adipate,[16] which possesses a carbon chain of suitable length. With the help of the flexible binding arm on C17 and the steric constraint of the pendent groups on C7 and C12, **1** and **2** can show a selective recognition to some long-chain terminal dicarboxylate anions.

On the basis of the change in fluorescent intensity associated with the stepwise addition of guest dicarboxylates, the complex association constants (K_a) for 1:1 binding model were calculated using non-linear least-squares curve fitting[23] and are compiled in Table 2. Excellent relative coefficients (R>0.99) were obtained and demonstrated that **1** and **2** formed 1:1 complexes with long-chain terminal dicarboxylate anions (n=3, 4, 6, 8).[24] The association constants of **1** and **2** to sebacate are much larger than those of other dicarboxylates, suggesting that both **1** and **2** exhibit selective recognition to sebacate. For all 1:1 binding models, **1** presumably due to its more rigid structure has a slightly weaker binding ability to dicarboxylates than **2**.

For short chain dicarboxylates, the complex association constants (log K_a) and the stoichiometry for 1:2 binding model are calculated using the Benesi–Hildebrand equation[25] and are listed in Table 3. Both **1** and **2** gave the values of stoichiometry (n) with malonate and succinate close to 2, which corroborated well with the results obtained from the Job plot (vide supra).

To investigate the chiral discriminative power of the sensors, L-, D-glutamate, and *N*-acetyl-L-glutamate (used as tetrabutylammonium salts) were chosen to introduce into the CH_3CN solution of **1** and **2** (1×10^{-5} M). The corresponding association constants are determined and are given in Table 2. Within the experimental errors, the binding strength of the hosts and glutamate was found to be slightly greater than that of the hosts and glutarate. The possible H-bonding between the α-amino group of glutamate and the oxygen of the C-7/C-12 ester group of the host may contribute to the additional binding interaction. Interestingly, comparing the binding constants of the two antipodal forms of glutamate to the hosts, enantioselective factors exhibited by **1** and **2** to the guests were found to be 1.53 and 1.79, respectively. The ^{1}H NMR also showed that, under the chiral influence of the host **1**, the splitting of the two β-proton signals of glutamate centered at δ 2.08 and 2.18 was evident. Reciprocally, the C-7 and C-12 protons of **1** at δ 5.40 and 5.60 were split by the racemic glutamate (Supplementary data).

To substantiate the binding interaction between the dicarboxylates and the hosts, all titration experiments were performed in CH_3CN with UV–vis spectroscopic method. The typical spectra of **1** and **2** (1×10^{-5} M) with different amounts of suberate in CH_3CN are shown in Figures 5 and 6, respectively. Sensor **1** has two characteristic peaks at 280 and 348 nm, with addition of suberate, the intensity of both peaks was increased with a slight blue shift and a new absorption band appeared at around 308 nm. At the same time, in the first derivative of the UV titration curves, an isosbestic peak at 269 nm could be easily identified.

The free **2** gives a similar absorption with pyrene in CH_3CN. Adding suberate anion into the solution of **2**, the characteristic peak at 265 nm ascribed to the absorption of trifluoromethylphenyl ring was increased discernibly. A new absorption band appeared at the range of 283~323 nm and an isosbestic point at 276 nm could be observed in the first derivative of the corresponding UV-titration curves

Table 2. The association constants of **1** and **2** with dicarboxylates (1:1 binding model) in CH_3CN

Anion	**1**		**2**	
	K_a[a]	K_a[b]	K_a[a]	K_a[b]
Glutarate[c]	$(8.22\pm1.51)\times10^5$	$(1.08\pm0.09)\times10^6$	$(1.68\pm0.17)\times10^6$	$(1.60\pm0.11)\times10^5$
Adipate[c]	$(1.27\pm0.12)\times10^6$	$(1.29\pm0.14)\times10^6$	$(5.56\pm0.42)\times10^6$	$(1.87\pm0.14)\times10^7$
Suberate[c]	$(1.64\pm0.14)\times10^6$	$(1.03\pm0.06)\times10^6$	$(2.10\pm0.19)\times10^7$	$(3.19\pm0.10)\times10^7$
Sebacate[c]	$(2.27\pm0.23)\times10^7$	$(2.30\pm0.23)\times10^7$	$>10^{8d}$	$>10^{8d}$
L-Glutamate[c]	$(1.18\pm0.13)\times10^6$	$(2.21\pm0.13)\times10^6$	$(2.35\pm0.11)\times10^6$	$(2.03\pm0.22)\times10^6$
D-Glutamate[c]	$(1.81\pm0.11)\times10^6$	$(1.81\pm0.19)\times10^6$	$(4.21\pm0.23)\times10^6$	$(5.23\pm0.11)\times10^6$
N-Acetyl-L-glutamate[c]	$(1.29\pm0.19)\times10^6$	$(1.09\pm0.10)\times10^6$	$(1.63\pm0.21)\times10^6$	$(8.35\pm1.30)\times10^5$

[a] The values were calculated from the change of the fluorescence spectra.
[b] The values were calculated from the change of the UV–vis spectra.
[c] Anions were used as their tetrabutylammonium salts.
[d] The value is too large to calculate.

Table 3. The association constants of **1** and **2** with dicarboxylates (1:2 binding model) in CH_3CN

Anion	1				2			
	n[a]	log K_a[a]	n[b]	log K_a[b]	n[a]	log K_a[a]	n[b]	log K_a[b]
Manolate[c]	1.84	8.07±0.59	1.75	7.93±0.14	2.02	9.01±0.15	2.2	8.85±0.09
Succinate[c]	1.96	8.76±0.61	2.13	8.87±0.26	2.11	9.47±0.13	2.09	8.67±0.12

[a] The values were calculated from the change of the fluorescence spectra.
[b] The values were calculated from the change of the UV–vis spectra.
[c] Anions were used as their tetrabutylammonium salts.

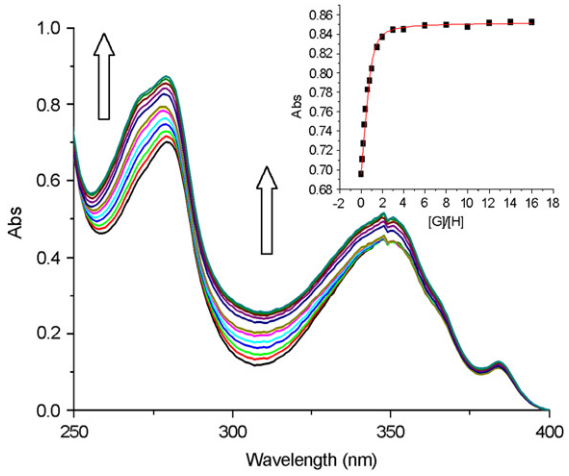


Figure 5. The absorption of **1** with different amounts of suberate in CH_3CN. Inset: the change of the absorption of **1** at 280 nm.

(Supplementary data). In contrast, the characteristic peaks at 326 and 343 nm ascribed to the pyrenyl group seem to be intact. This strongly suggested that the pyrenyl groups in the ground state had not been involved in the interaction with dicarboxylates. According to the change of absorption during the titrations, the complex association constants are calculated and are listed in Tables 2 and 3. The values of the association constants are comparable with those obtained from the fluorescence titration experiments.

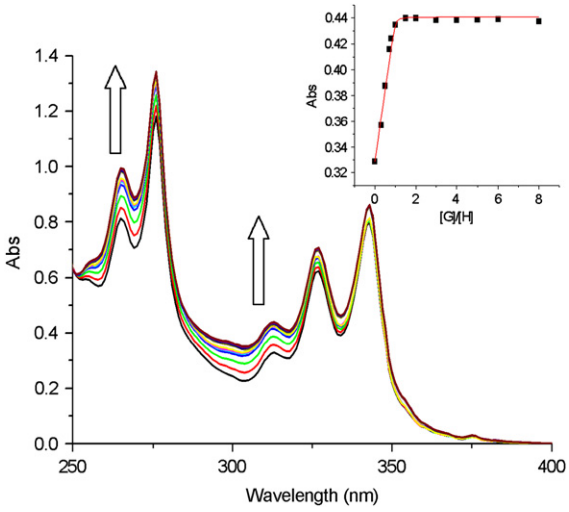


Figure 6. The absorption of **2** with different amounts of suberate in CH_3CN. Inset: the change of the absorption of **2** at 313 nm.

^{1}H NMR spectra also had been used to study the binding properties of **1** and **2** toward dicarboxylates. When **1** was treated with 1 equiv of adipate anion in DMSO-d_6, the intensity of the proton signals ascribed to the thiourea hydrogens diminished significantly and at least one of these protons recorded a downfield shift of 0.07 ppm, which is indicative of H-bonding interaction between the host and the guest (Supplementary data). The aromatic protons of the trifluoromethylphenyl ring of **1** underwent a clear upfield shift from 7.63 to 7.34 ppm after the thiourea groups were bound with the anion.

3. Conclusion

Charge neutral fluorescent chemosensors **1** and **2** for dicarboxylates have been rationally designed and synthesized. Both **1** and **2**, functionalized adequately at the C3, C7, C12, and C24 of cholic acid, showed high affinities to dicarboxylates resulting from multiple hydrogen bonding interactions. A significant fluorescence response of the sensors took place through an intramolecular excimer emission quenched by complexation. The preorganization of **1** and **2** permits two points binding with the guests on C3 and C24 receptive sites under the cooperation of bulky signal groups on C7 and C12 to produce highly selective affinities to long-chain terminal dicarboxylates. Sensors **1** and **2** exhibit high sensitive response to long-chain dicarboxylates (n=6 and 8) and the strong binding between the host and the guest rendered the detection of dicarboxylates possible even at the concentration of 10^{-8} M. Sensors **1** and **2** are promising fluorescent sensors for suberate and sebacate. The recognition characteristics of the novel hosts developed in this work are established unambiguously by the combined UV, fluorescence, and ^{1}H NMR spectroscopic methods. In addition, the moderate chiral recognition ability of the host was also demonstrated.

4. Experimental

4.1. General methods

Melting point was determined with a MEL-TEMPII melting-point apparatus (uncorrected). IR spectra were obtained on a Nicolet MAGNA-IR 550 spectrophotometer. ^{1}H NMR spectra were recorded in DMSO-d_6 or $CDCl_3$, with Me_4Si as the internal standard, on a JEOL EX270 spectrometer and ^{13}C NMR spectra on a Varian INOVA-400 FT NMR spectrometer. High-resolution mass spectra were recorded on a Bruker Autoflex mass spectrometer (MALDI-TOF) or Electrospray ionization high-resolution mass spectra on an API

Qstar Pulsari mass spectrometer (ESI-TOF). Infrared spectra were recorded on MAGNA-IR 550 spectrometer. Absorption spectra were recorded on a Hewlett Packard 8453 UV–vis spectrophotometer. Fluorescent emission spectra were collected on a Photon Technology International (PTI) at 293 K. CH_2Cl_2 and xylene were dried and distilled from CaH_2, and benzene was dried and distilled from Na freshly. THF was distilled under nitrogen in the presence of sodium chips using benzophenone ketyl as the indicator. All other commercially available reagents were used as received.

4.2. General procedure for the synthesis of 7 and 8

To a mixture solution of **4** (0.45 g, 1 mmol) in xylene/CH_2Cl_2 (10:1, 5 mL) were added calcium hydride (0.63 g, 15 mmol) and benzyltriethylammonium chloride (0.01 g, 0.04 mmol), and the mixture was refluxed for 10 min under a nitrogen atmosphere. To the refluxing solution was added a solution of freshly prepared 1-pyrenoyl chloride or 1-pyrenebutanoyl chloride (3 mmol) in xylene (10 mL) and refluxed for 24 h. The reaction mixture was filtered under reduced pressure, diluted with ethyl acetate, and washed with aq $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4, and volatiles were removed.

4.3. Methyl 3α-azide-7α,12α-dipyrenylcarbonyl-5β-cholan-24-oate (7)

The crude product was chromatographed on silica gel (230–400 mesh) eluting first with 25% ethyl acetate/petroleum ether (60–80 °C) and then with pure dichloromethane to give the pure product (0.33 g, 37%): mp 130 °C; IR (KBr, cm^{-1}): 3438, 2948, 2871, 2089, 1736, 1705, 1596, 1446, 1389, 1255, 1229, 1145, 1133, 849, 710; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (s, 3H), 0.96 (d, J=8.91 Hz, 3H), 1.11 (s, 3H), 3.03 (m, 1H), 3.52 (s, 3H), 5.48 (br, 1H), 5.70 (br, 1H), 7.58–8.61 (m, 16H), 9.16–9.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.2, 167.5, 167.0, 134.0, 133.9, 131.1, 131.0, 130.3, 130.2, 129.6, 129.4, 127.6, 127.4, 126.9, 126.1, 124.8, 124.6, 124.4, 124.1, 76.2, 71.5, 60.5, 51.4, 47.8, 45.6, 44.0, 41.5, 40.0, 38.7, 37.3, 35.4, 35.1, 34.8, 34.7, 31.7, 31.0, 30.7, 29.6, 29.0, 28.5, 27.4, 26.9, 25.9, 25.6, 24.5, 23.3, 22.8, 21.6, 17.9, 17.8, 17.2, 12.5; MALDI TOF HRMS: calcd for $C_{59}H_{57}N_3O_6$ $(M+H)^+$, 903.4247; found, 903.4218.

4.4. Methyl 3α-azide-7α,12α-di(1-pyrenebutanoyl)-5β-cholan-24-oate (8)

The crude product was chromatographed on silica gel (230–400 mesh) eluting first with 20% ethyl acetate/petroleum ether (60–80 °C) and then for the second time with pure dichloromethane to give the pure product (0.34 g, 35%): mp 90 °C; IR (KBr, cm^{-1}): 3442, 2953, 2865, 2089, 1727, 1638, 1456, 1384, 1251, 1182, 1094, 844, 716; ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.75 (s, 3H), 0.81 (d, 3H), 0.94 (s, 3H), 3.10–3.28 (m, 4H), 3.57 (s, 3H), 5.02 (br, 1H), 5.17 (br, 1H), 7.68–8.19 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.7, 173.1, 173.0, 135.8, 135.7, 131.6, 131.1, 130.2, 130.1, 129.0, 128.9, 128.6, 127.7, 127.6, 127.4, 127.0, 126.1, 125.3, 125.2, 125.1, 125.0, 124.9, 123.5, 123.4, 75.6, 71.0, 60.9, 51.7, 47.8, 45.4, 43.7, 41.5, 38.2, 35.4, 35.0, 34.7, 34.6, 34.5, 33.0, 32.8, 31.6, 31.2, 31.0, 29.0, 27.5, 27.1, 27.0, 26.8, 25.6, 23.3, 22.8, 17.9, 12.5; MALDI TOF HRMS: calcd for $C_{65}H_{69}N_3O_6$, 987.5186; found, 987.5204.

4.5. General procedure for the synthesis of 9 and 10

Activated zinc powder (0.65 mg, 10 mmol) was added to a solution of **7** or **8** (0.5 mmol) in glacial acetic acid (10 mL). The mixture was stirred vigorously for 24 h. Acetic acid was then completely removed under reduced pressure by adding toluene for several times. The residue, acetate ammonium salt of **9** or **10**, was dissolved by saturated sodium chloride solution (10 mL). Basification of the solution by excessive triethylamine and extraction of it by ethyl acetate gave amine **9** or **10** as the pure product. After drying by sodium sulfate and removal of organic solvent, compound **9** or **10** was obtained.

4.6. Methyl 3α-amino-7α,12α-dipyrenylcarbonyl-5β-cholan-24-oate (9)

Compound **9** was obtained as yellow foam (0.44 g, 99%): mp 122–124 °C; IR (KBr, cm^{-1}): 3437, 2949, 2912, 2876, 1735, 1704, 1632, 1607, 1456, 1446, 1389, 1255, 1231, 1193, 1145, 1133, 1086, 849, 721; ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.54 (s, 3H), 5.47 (br, 1H), 5.68 (br, 1H), 7.26–8.56 (m, 16H), 9.24–9.30 (m, 2H); MALDI TOF HRMS: calcd for $C_{59}H_{59}NO_6$ $(M+H)^+$, 878.4420; found, 878.4405.

4.7. Methyl 3α-amino-7α,12α-di(1-pyrenebutanoyl)-5β-cholan-24-oate (10)

Compound **10** was obtained as yellow foam (0.43 g, 90%): mp 100–104 °C; IR (KBr, cm^{-1}): 3436, 2948, 2914, 2876, 1735, 1705, 1632, 1607, 1457, 1448, 1389, 1255, 1231, 1197, 1140, 1132, 1086, 846, 725; ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.12–3.30 (m, 4H), 3.48 (s, 3H), 4.86 (br, 1H), 5.05 (br, 1H), 7.61–8.08 (m, 18H); MALDI TOF HRMS: calcd for $C_{65}H_{71}NO_6$ $(M+H)^+$, 962.5359; found, 962.5392.

4.8. General procedure for the synthesis of 11 and 12

The mixture of **9** or **10** (0.5 mmol) and hydrazine (1.0 mL, large excess) monohydrate in a mixture solution of methanol/CH_2Cl_2 (10 mL, 2:1) was stirred under nitrogen at ambient temperature for 48 h. Then organic solvent and the excess of hydrazine were removed under reduced pressure. The residue was poured into 30 mL cold water and stirred for 10 min. After filtration, the solid was washed with large amount of cold water and dried in vacuum at 60 °C. The product was obtained as a yellow solid.

4.9. 1-Hydrazide 3α-amino-7α,12α-dipyrenylcarbonyl-5β-cholan-24-oate (11)

Compound **11** was obtained as a yellow solid in a 76% yield (0.33 g) and need no further purification for the next reaction: mp>166 °C (decomposed); IR (KBr, cm^{-1}): 3430, 2921, 2876, 1702, 1625, 1389, 1250, 1231, 1194, 1145, 1133, 1086, 849, 705; ^{1}H NMR (270 MHz, $CDCl_3$): δ 3.72 (br, 4H), 5.46 (br, 1H), 5.67 (br, 1H), 6.55 (br, 1H), 7.60–8.55 (m, 16H), 9.24–9.30 (m, 2H); MALDI TOF

HRMS: calcd for $C_{58}H_{59}N_3O_5$ $(M+H)^+$, 878.4532; found, 878.4519.

4.10. 1-Hydrazide 3α-amino-7α,12α-di(1′-pyrenebutanoyl)-5β-cholan-24-oate (12)

Compound **12** was obtained as a yellow solid in a 80% yield (0.38 g) and need no further purification for the next reaction: mp>140 °C (decomposed); IR (KBr, cm^{-1}): 3418, 2933, 2864, 1722, 1645, 1622, 1456, 1379, 1249, 1183, 1143, 1016, 844, 705; ^1H NMR (270 MHz, $CDCl_3$): δ 3.26 (m, 4H), 3.70 (br, 4H), 4.97 (br, 1H), 5.14 (br, 1H), 6.35 (br, 1H), 7.72–8.19 (m, 18H); MALDI TOF HRMS: calcd for $C_{64}H_{71}N_3O_5$ $(M+H)^+$, 962.5471; found, 962.5495.

4.11. 1-[(4′-Trifluoromethylphenyl)thioureido]hydrazide 3α-[(4′-trifluoromethylphenyl)thioureido]-7α,12α-dipyrenylcarbonyl-5β-cholan-24-oate (1)

To a solution of **11** (0.26 g, 0.3 mmol) in dried CH_2Cl_2 (10 mL), 4-trifluoromethylphenylisocyanate (0.15 g, 0.7 mmol) was added and stirred at room temperature for 36 h under nitrogen. The reaction mixture was diluted with CH_2Cl_2. The organic solution was first washed by saturated brine and then dried by anhydrous sodium sulfate. Purification of the crude by preparative TLC plate (SiO_2) eluted by the solvent of ethyl acetate/dichloromethane (20:100) gave the pure product **1** as a yellow solid (0.20 g, 52%): mp 164–166 °C; IR (KBr, cm^{-1}): 3394, 2938, 2865, 1706, 1622, 1520, 1324, 1257, 1232, 1166, 1125, 1066, 850, 705; ^1H NMR (270 MHz, DMSO-d_6): δ 0.81 (d, J=8.1 Hz, 3H), 3.86 (m, 1H), 5.39 (br, 1H), 5.57 (br, H), 7.33–8.49 (m, 26H), 9.04–9.25 (m, 4H), 9.70 (br, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): 179.0, 170.1, 170.0, 148.5, 134.1, 133.6, 133.4, 133.2, 130.9, 130.5, 130.1, 130.0, 129.8, 129.7, 129.6, 128.3, 127.6, 127.3, 127.1, 1265.8, 126.7, 126.4, 125.2, 124.6, 124.0, 123.3, 123.0, 121.1, 116.6, 76.3, 72.2, 53.9, 47.9, 45.2, 43.6, 41.1, 40.1, 37.7, 35.4, 34.5, 34.1, 31.3, 30.1, 28.8, 26.8, 26.3, 25.3, 23.6, 22.8, 22.5, 20.3, 17.7, 17.0, 12.1; ESI TOF HRMS: calcd for $C_{74}H_{67}F_6N_5O_5S_2Na$ $(M+Na)^+$, 1306.4385; found, 1306.4436.

4.12. 1-[(4′-Trifluoromethylphenyl)thioureido]hydrazide 3α-[(4′-trifluoromethylphenyl)thioureido]-7α,12α-di(1′-pyrenebutanoyl)-5β-cholan-24-oate (2)

To a solution of **12** (0.29 g, 0.3 mmol) in dried CH_2Cl_2 (10 mL), 4-trifluoromethylphenylisocyanate (0.15 g, 0.7 mmol) was added and stirred at room temperature for 36 h under nitrogen. The reaction mixture was diluted with CH_2Cl_2. The organic solution was first washed by saturated brine and then dried by anhydrous sodium sulfate. Purification of the crude by preparative TLC plate (SiO_2) eluted by the solvent of ethyl acetate/dichloromethane (10:100) gave the pure product **2** as a yellow solid (0.20 g, 29%): mp 138–140 °C; IR (KBr, cm^{-1}): 3430, 3274, 2953, 2865, 1720, 1617, 1549, 1524, 1324, 1249, 1165, 1122, 1067, 850, 724; ^1H NMR (400 MHz, $CDCl_3$): δ 0.69 (s, 3H), 0.78 (d, J=4.1 Hz, 3H), 0.96 (s, 3H), 3.0–3.26 (m, 4H), 4.00 (br, 1H), 5.06 (br, 1H), 5.19 (br, 1H), 6.49 (br, 1H), 6.61 (br, 1H), 7.00 (br, 1H), 7.48–8.24 (m, 18H), 8.87 (br, 1H), 9.82 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 182.9, 178.9, 172.6, 172.3, 170.5, 140.9, 139.6, 136.5, 135.0, 134.8, 133.0, 131.2, 131.1, 131.0, 129.9, 129.8, 128.5, 127.7, 127.6, 127.3, 127.2, 127.0, 126.8, 126.7, 126.5, 126.1, 126.0, 125.2, 125.0, 124.9, 124.8, 124.7, 124.5, 124.3, 122.8, 116.9, 76.7, 75.4, 55.1, 47.3, 45.2, 43.4, 41.2, 37.9, 35.6, 35.2, 34.6, 34.5, 34.1, 32.3, 31.5, 31.1, 29.7, 29.0, 27.5, 27.2, 26.4, 25.4, 22.9, 22.6, 17.6, 12.2; MALDI TOF HRMS: calcd for $C_{80}H_{79}F_6N_5O_5S_2$ $(M+H)^+$, 1368.5505; found, 1368.5400.

4.13. Methyl 3α-acetyl-7α,12α-dipyrenylcarbonyl-5β-cholan-24-oate (3)

To a mixture solution of methyl 3α-acetyl-7α,12α-dihydroxy-5β-cholan-24-oate (0.46 g, 1 mmol) in xylene/CH_2Cl_2 (10:1, 5 mL) were added calcium hydride (0.63 g, 15 mmol) and benzyltriethylammonium chloride (0.01 g, 0.04 mmol), and the mixture was refluxed for 10 min under a nitrogen atmosphere. To the refluxing solution was added a solution of freshly prepared 1-pyrenoyl chloride (0.79 g, 3 mmol) in xylene (10 mL) and refluxed for 24 h. The reaction mixture was filtered under reduced pressure, diluted with ethyl acetate, and washed with aq $NaHCO_3$. The organic layer was dried over anhydrous Na_2SO_4, and volatiles were removed. The crude product was chromatographed on silica gel (230–400 mesh) eluting first with 10% ethyl acetate/petroleum ether (60–80 °C) and then for the second time with pure dichloromethane to give the pure product (0.25 g, 26%): mp 114–116 °C; IR (KBr, cm^{-1}): 3446, 3042, 2932, 2873, 1735, 1705, 1559, 1449, 1393, 1254, 1231, 1145, 1133, 1087, 1045, 848, 712; ^1H NMR (270 MHz, $CDCl_3$): δ 0.85 (s, 3H), 1.01 (d, J=6.48 Hz, 3H), 1.11 (s, 3H), 3.54 (s, 3H), 4.55 (m, 1H), 5.47 (br, 1H), 5.72 (br, 1H), 7.26–8.53 (m, 16H), 9.20–9.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 174.4, 170.4, 168.2, 168.0, 167.5, 133.9, 133.7, 133.5, 130.9, 130.8, 130.7, 130.2, 130.0, 129.5, 129.4, 129.2, 129.1, 128.9, 128.7, 127.6, 127.4, 127.2, 127.1, 127.0, 126.9, 126.8, 126.4, 126.3, 126.2, 126.0, 125.9, 125.4, 125.0, 124.8, 124.6, 124.4, 124.1, 123.7, 74.8, 74.3, 73.5, 72.0, 71.8, 68.2, 51.4, 47.9, 47.8, 46.7, 45.6, 44.0, 41.2, 41.0, 38.7, 34.8, 34.7, 34.6, 31.6, 31.5, 31.0, 30.7, 29.7, 28.2, 27.2, 26.9, 26.7, 25.9, 25.8, 23.2, 22.5, 22.4, 21.1, 17.8, 12.4; MALDI TOF HRMS: calcd for $C_{61}H_{60}O_8Na$ $(M+Na)^+$, 943.418; found, 943.4147.

4.14. Binding experiments

All dicarboxylate anions were obtained from the respective dicarboxylic acid treated with 2.0 equiv of tetrabutylammonium hydroxide in CH_3OH and dried in vacuum at 60 °C for over night. The structures of these guest anions were verified by ^1H NMR.

All the host compounds **1**, **2**, and **3** were prepared as $2\sim5\times10^{-4}$ mol/L stock solutions in acetonitrile. All anions used in this report were in the form of tetrabutylammonium salt. They were prepared to approximate 0.01 mol/L and $2\sim5\times10^{-3}$ mol/L of stock solutions in acetonitrile. The work solutions were prepared by adding different volumes of anion stock solution to a series of test tubes followed by dilution to 5 mL by acetonitrile. Then, the same amount of stock solution of the host compound was added into each of the test tube. After shaking for several minutes, the work solutions could be measured immediately.

Association constants (1:1) of **1** and **2** with anions are calculated by non-linear least square curve fitting using the following equation in origin 7.0:

$$X = X_0 + 0.5\Delta\varepsilon\left\{c_H + c_G + 1/K_{ass} - \left[(c_H + c_G + 1/K_{ass})^2 - 4c_H c_G\right]^{1/2}\right\}$$

Association constants (1:2) of **1** and **2** with anions are calculated by Benesi–Hildebrand equation and linearly fitted in origin 7.0:

$$\log[(X - X_0)/(X_\infty - X)] = n\log[G] + \log K_a$$

X_0: fluorescent intensity or absorption of host without anions; X: fluorescent intensity or absorption reaching a limitation by adding excessive anions; c_H: concentration of host molecule; c_G: concentration of anions added.

Acknowledgements

The financial support of the work by grants from the University Grants Committee of the Hong Kong Special Administrative Region, China (AoE/P-10/01), and from the Hong Kong Baptist University (FRG/04-05/II-18) is acknowledged.

Supplementary data

Synthesis and characterization spectra of **1** and **2**, the fluorometric titration experiment and the ^{1}H NMR study, the fluorescence intensity of **1** and **2** with different concentration in CH_3CN, Job plot of **1** and **2** with dicarboxylates. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.09.042.

References and notes

1. (a) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609–1646; (b) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516; (c) Best, M. D.; Tobey, S. L.; Anslyn, E. V. *Coord. Chem. Rev.* **2003**, *240*, 3–15; (d) *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., García-España, E., Eds.; Wiley-VCH: New York, NY, 1997.
2. (a) Shin-ichi, S.; Masaaki, M.; Koichiro, N.; Yoshito, T. *J. Org. Chem.* **2000**, *65*, 275–289; (b) Sessler, J. L.; Davis, J. M. *Acc. Chem. Res.* **2001**, *34*, 989–997; (c) Amendola, V.; Fabbrizzi, L.; Monzani, E. *Chem.—Eur. J.* **2004**, *10*, 76–82; (d) Kristln, B. J. *Acc. Chem. Res.* **2005**, *38*, 671–678; (e) Myiaji, H.; Kim, K. H.; Sim, E. K.; Lee, C. K.; Cho, W. S.; Sessler, J. L.; Lee, C. H. *J. Am. Chem. Soc.* **2005**, *127*, 12510–12512; (f) Sessler, J. L.; Cho, W.-S.; Gross, D. E.; Shriver, D. E.; Lynch, V. M.; Marquez, M. *J. Org. Chem.* **2005**, *70*, 5982–5986; (g) Chmielewski, M. J.; Jurczak, J. *Chem.—Eur. J.* **2005**, *11*, 6080–6094; (h) Juewen, L.; Yi, L. *Angew. Chem., Int. Ed.* **2006**, *45*, 90–94; (i) Massimiliano, T.; Salvatore, S.; Andrew, P. W.; Francisco, M. R. *J. Org. Chem.* **2006**, *71*, 744–753; (j) Nieto, S.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Chem.—Eur. J.* **2006**, *12*, 2244–2251.
3. Voet, D.; Voet, J. G. *Biochemistry*, 2nd ed.; Wiley: New York, NY, 1995.
4. (a) Nohta, H.; Sonoda, J.; Yoshida, H.; Satozono, H.; Ishida, J.; Yamaguchi, M. *J. Chromatogr., A* **2003**, *1010*, 37–44; (b) Miao, H.; Rubakhin, S. S.; Sweedler, J. V. *Anal. Chem.* **2005**, *77*, 7190–7194.
5. (a) Cordek, J.; Wang, X.; Tan, W. *Anal. Chem.* **1999**, *71*, 1529–1533; (b) Rossi, S.; Kyne, G. M.; Turner, D. L.; Wells, N. J.; Kilburn, J. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4233–4236.
6. (a) Fabbrizzi, L.; Licchelli, M.; Rabaioli, M. G.; Taglietai, A. *Coord. Chem. Rev.* **2000**, *205*, 85–108; (b) Amendola, V.; Boiocchi, M.; Fabbrizzi, L.; Palchetti, A. *Chem.—Eur. J.* **2005**, *11*, 5648–5660; (c) Qing, G.-Y.; He, Y.-B.; Zhao, Y.; Hu, C.-G.; Liu, S.-Y.; Yang, X. *Eur. J. Org. Chem.* **2006**, 1574–1580.
7. (a) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419–4476; (b) Pu, L. *Chem. Rev.* **2004**, *104*, 1687–1716; (c) Vázquez, M.; Fabbrizzi, L.; Taglietti, A.; Pedrido, R. M.; González-Noya, A. M.; Bermejo, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1962–1965; (d) Gunnlaugsson, T.; Kruger, P. E.; Jensen, P.; Tierney, J. *J. Org. Chem.* **2005**, *70*, 10875–10878; (e) Peng, X.; Wu, Y.; Tian, M.; Han, K. *J. Org. Chem.* **2005**, *70*, 10524–10531; (f) Ragusa, A.; Rossi, S.; Hayes, J. M.; Stein, M.; Kilburn, J. D. *Chem.–Eur. J.* **2005**, *11*, 5674–5688.
8. Hosseini, M. W.; Lehn, J.-M. *Helv. Chim. Acta* **1986**, *69*, 587–603.
9. (a) Lara, K. O.; Godoy-Alcántar, C.; Rivera, I. L.; Eliseev, A. V.; Yatsimirsky, A. K. *J. Phys. Org. Chem.* **2001**, *14*, 453–462; (b) Boiocchi, M.; Bonizzoni, M.; Fabbrizzi, L.; Piovani, G.; Taglietti, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 3847–3852; (c) Bonizzoni, M.; Fabbrizzi, L.; Piovani, G.; Taglietti, A. *Tetrahedron* **2004**, *60*, 11159–11162.
10. Král, V.; Andrievsky, A.; Sessler, J. L. *J. Am. Chem. Soc.* **1995**, *117*, 2953–2954.
11. Liu, S.-Y.; He, Y.-B.; Wu, J.-L.; Wei, L.-H.; Qin, H.-J.; Meng, L.-Z.; Hu, L. *Org. Biomol. Chem.* **2004**, *2*, 1582–1586.
12. Gunnlaugsson, T.; Davis, A. P. *Org. Lett.* **2002**, *4*, 2449–2452.
13. (a) Zeng, Z.-Y.; He, Y.-B.; Wu, J.-L.; Wei, L.-H.; Liu, X.; Meng, L.-Z.; Yang, X. *Eur. J. Org. Chem.* **2004**, 2888–2893; (b) Wu, J.-L.; He, Y.-B.; Zeng, Z.-Y.; Wei, L.-H.; Meng, Z.; Yang, T.-X. *Tetrahedron* **2004**, *60*, 4309–4314.
14. Mei, M.; Wu, S. *New J. Chem.* **2001**, *25*, 471–475.
15. (a) Davis, A. P.; Joos, J. B. *Coord. Chem. Rev.* **2003**, *240*, 143–156; (b) Lawless, L. J.; Blackburn, A. G.; Ayling, A. J.; Pérez-Payán, M.; Davis, A. P. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1329–1341; (c) Vijayalakshmi, N.; Maitra, U. *Org. Lett.* **2005**, *7*, 2727–2730; (d) Sisson, A. L.; Clare, J. P.; Davis, A. P. *Chem. Commun.* **2005**, 5263–5265.
16. Liu, S.-Y.; Fang, L.; He, Y.-B.; Chan, W.-H.; Yeung, K.-T.; Cheng, Y.-K.; Yang, R.-H. *Org. Lett.* **2005**, *7*, 5825–5828.
17. (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970; (b) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587–614; (c) Seiichi, N.; Yuichi, K.; Norio, T. *J. Am. Chem. Soc.* **1999**, *121*, 9463–9464; (d) Akimitsu, O.; Keiichiro, K.; Isao, S. *J. Am. Chem. Soc.* **2004**, *126*, 4820–4827; (e) Vyacheslav, V. F.; Erik, B. P. *J. Am. Chem. Soc.* **2005**, *127*, 14849–14858.
18. Potluri, V. K.; Maitra, U. *J. Org. Chem.* **2000**, *65*, 7764–7769.
19. Davis, A. P.; Pérez, P. M. N. *Synlett* **1999**, 991–993.
20. Lee, S. H.; Kim, S. H.; Kim, S. K.; Jung, J. H.; Kim, J. S. *J. Org. Chem.* **2005**, *70*, 9288–9295.

21. (a) Job, A. *Ann. De Chim. (Paris)* **1928**, *9*, 133–157; (b) Nishizawa, S.; Kato, R.; Hayashita, T.; Teramae, N. *Anal. Sci.* **1998**, *14*, 595–597.
22. Fang, L.; Chan, W.-H.; He, Y.-B.; Kwong, D. W. J.; Lee, A. W. M. *J. Org. Chem.* **2005**, *70*, 7640–7646.
23. Valeur, B.; Pouget, J.; Bourson, J. *J. Phys. Chem.* **1992**, *96*, 6545–6549.
24. (a) Bernard, V. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH: Weinheim, Germany, 2002; (b) Wu, F. Y.; Li, Z.; Wen, Z. C.; Zhou, N.; Zhao, Y. F.; Jiang, Y. B. *Org. Lett.* **2002**, *4*, 3203–3205.
25. (a) Pocker, Y.; Ciula, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4728–4753; (b) Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552–4557.