Synthesis of cyclic bis- and trismelamine derivatives and their complexation properties with barbiturates

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Cyclic bis- and trismelamine derivatives were prepared from cyanuric chloride by stepwise substitutions with appropriate amines. The complexation abilities of these melamine derivatives with barbituric acid derivatives were evaluated by UV-vis spectroscopy and ^{1}H NMR. The structure was also confirmed by X-ray crystallography. Both the acyclic and the cyclic bismelamine derivatives formed a 1 : 1 complex *via* six hydrogen bonds with barbituric acid derivatives. van't Hoff analyses on the complexation of the bismelamines with the barbituric acid derivative revealed that the complexation of the cyclic bismelamine was entropically favored and enthalpically less favored process than those of the acyclic bismelamine. X-Ray crystallographic analysis and ^{1}H NMR studies revealed that the cyclic trismelamine bound one barbituric acid derivative into the cavity *via* six hydrogen bonds by two melamine moieties and another barbituric acid *via* three hydrogen bonds by the residual melamine moiety.

Introduction

The molecular recognition of neutral target substances *via* hydrogen bonds has been attracting considerable attention in the last two decades.[1] Barbituric acids were attractive guest molecules because of medicinal use as sedatives and anticonvulsants.[2] Barbituric acid derivatives have two sets of hydrogen bonding acceptor-donor–acceptor arrays in the molecule. To associate barbituric acid derivatives, two types of functionality were usually employed as a recognition site of host molecules, *i.e.* diamidopyridine and melamine groups. These two functionalities consist of a complementary hydrogen bond donor–acceptor–donor array for barbiturate.

Hamilton *et al.* reported that complexation of cyclic and acyclic receptors bearing two diamidopyridine units linked through an isophthaloyl spacer with barbituric acids *via* six hydrogen bonds in apolar organic solvents such as chloroform and dichloromethane.[3] Similar binding motifs bearing redox active,[4] chiral[5] metal ligand,[6] and chromophore[7] moieties have also been reported as barbiturate and cyanurate receptors. The diamidopyridine group was applied to construct more sophisticated materials such as supramolecular polymers.[8]

Melamine (2,4,6-triamino-1,3,5-*s*-triazine) derivatives are easily prepared from 2,4,6-trichloro-1,3,5-*s*-triazine (cyanuric chloride) by stepwise substitutions with appropriate amines and widely applied to supramolecular chemistry.[9] Complex structures of melamine derivatives and barbituric acids or isocyanurates were systematically investigated by Whitesides and co-workers. They prepared supramolecular structures such as linear and crinkled tapes and a rosette.[10] Reinhoudt and Timmerman extended the rosette complexes by use of bismelamines based on a calix[4]arene scaffold to give double rosette assemblies, $(\text{bismelamine})_3\cdot(\text{barbiturate})_6$.[11] We have also reported that receptors bearing a melamine moiety showed strong binding ability for imides such as flavin derivatives, barbituric acids, and thymine derivatives *via* multiple hydrogen bonds.[12] Melamine–baribituric acid complexation is also applied to supramolecular materials such as organogel,[13] supramolecular membranes,[14] and liquid crystals.[15] Meanwhile, cyclic melamine derivatives have been scarcely reported[16] although cyclic bis diamidopyridine derivatives have been prepared and evaluated at an early stage of the study.[3,17] Cyclic melamine derivatives form isolated binding pockets to complex with guest barbiturates and are applicable to analytical usages. Löwik and Lowe reported the synthesis of cyclic trismelamine derivatives by stepwise substitution and preliminary complexation properties of these derivatives with cyanuric acid and carbohydrates.[16b,c] Herein, we report the synthesis and complexation properties of less explored cyclic bis- and trismelamine derivatives **1**–**4**. A barbiturate derivative bearing an anthryl group (**5b**) was also prepared and was used as a probe for a complexation study. The complexation properties of cyclic bis- and trismelamine derivatives and barbiturates were studied by UV-vis, ^{1}H NMR spectroscopy, and X-ray crystallography.

Results and discussion

Design and synthesis of cyclic bis- and trismelamine derivatives

The prepared cyclic melamine derivatives are listed in Scheme 1. A *m*-xylylene spacer was employed to connect two melamine units because the corresponding acyclic bismelamine **1** showed strong complexation with barbituric acid derivatives *via* six hydrogen bonds in chloroform.[10f,18] Cyclic bismelamine derivatives **2** and **3** were cyclized with different types of spacer, *i.e.* an alkyl spacer and a bisphenol-A based spacer, respectively. Hamilton and co-worker reported a cyclic bisamidopyridine derivative in which *m*-phenylene and bisphenol-A were used as spacers.[3d] Cyclic

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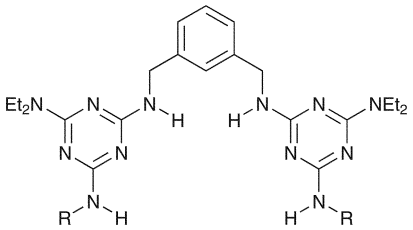
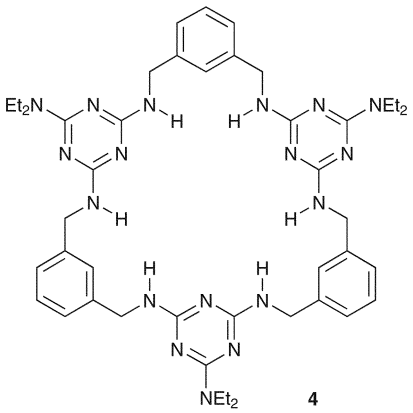
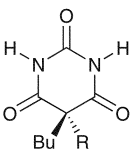


1: R = Bu
2: R = -(CH$_2$)$_{12}$-

3: R = -(H$_2$C)$_3$O- -O(CH$_2$)$_3$-

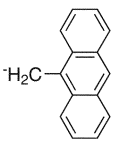


4



5a: R = Bu

5b: R =



Scheme 1

trismelamine derivative **4** has D_{3h} symmetry and three melamine units were connected *via m*-xylylene spacers. The acyclic and cyclic bismelamine derivatives and the cyclic trismelamine derivative were prepared from cyanuric chloride by stepwise substitutions with appropriate amines in the presence of a base as shown in below.

Preparation of the cyclic bismelamine derivatives (**2** and **3**) is illustrated in Fig. 1. *m*-Xylylenediamine was reacted with 2-diethylamino-4,6-dichloro-1,3,5-*s*-triazine (**6**) in the presence of sodium carbonate in dichloromethane to gave **7** in 84% yield. Cyclization of **7** and 1,12-diaminododecane in dilute conditions in 1,4-dioxane yielded cyclic bismelamine receptor **2** in 50% yield. The lower spacer of **3** was prepared from 1,3-dibromopropane and bisphenol-A in three steps,[19] and cyclization with **7** yielded cyclic bismelamine receptor **3** in 43%.

Löwik and Lowe reported the synthesis of trismelamine derivatives bearing piperidine or *m*-xylylene as spacers with stepwise substitution and finally intramolecular cyclization after deprotection of terminal residues. As shown in Fig. 2, we selected the preparation of **4** by intermolecular cyclization method. Two mono Boc-protected *m*-xylylenediamine units were introduced to 2-diethylamino-4,6-dichloro-1,3,5-*s*-triazine, followed by the deprotection of the Boc groups by TFA to give **9**. Two 2-diethylamino-4,6-dichloro-1,3,5-*s*-triazines were introduced to the diamine **9** to give **10**. The slow and simultaneous addition of **10** and *m*-xylylenediamine gave a facile and efficient cyclization to give **4** in a moderate yield.

Products were analyzed by ^{1}H NMR, elemental analysis, and electrospray ionization mass spectroscopy (ESI-MS). Proton NMR spectra of cyclic melamine derivatives **2**–**4** gave broad signals at 25 °C in $CDCl_3$, and the signals were slightly sharpened at 45 °C. However, ^{1}H NMR spectra of acyclic bismelamine **1** gave sharp signals at 25 °C indicating slow conformational change such as ring flipping of the macrocycles. A similar result was also reported by Löwik and Lowe.[16b]

Complexation of cyclic bis- and trismelamine derivatives with barbiturates

In general, it is difficult to determine the association constants for complexation of melamine derivatives and barbiturates without chromophore by UV-vis and fluorescent spectroscopies. A barbiturate bearing chromophore is quite useful for the study of complexation with receptors, however, only a limited number of examples have been reported previously. Prins *et al.* reported a barbiturate bearing a chromogenic donor–π-acceptor system with the bismelamine based on calix[4]arene skeleton.[20] De Cola and Vögtle reported a barbiturate bearing rhenium–bipyridine complex.[21] The anthryl group is a useful chromophore since UV-vis and fluorescence change during complexation is expected due to electronic perturbation of the large π-surface. We prepared a barbituric acid derivative (**5b**) bearing an anthryl

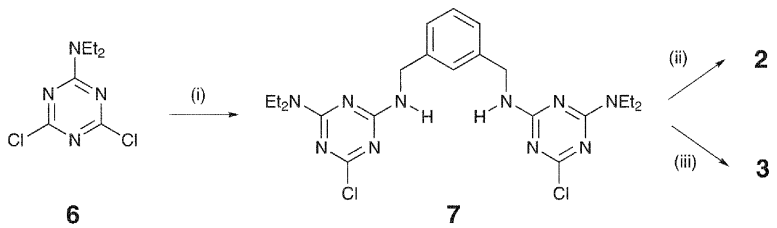


Fig. 1 Synthesis of **2** and **3**. (i) *m*-Xylylenediamine, K_2CO_3, 1,4-dioxane, rt, 84%; (ii) 1,12-diaminododecane, K_2CO_3, 1,4-dioxane, reflux, 50%; (iii), K_2CO_3, 1,4-dioxane, reflux, 43%.

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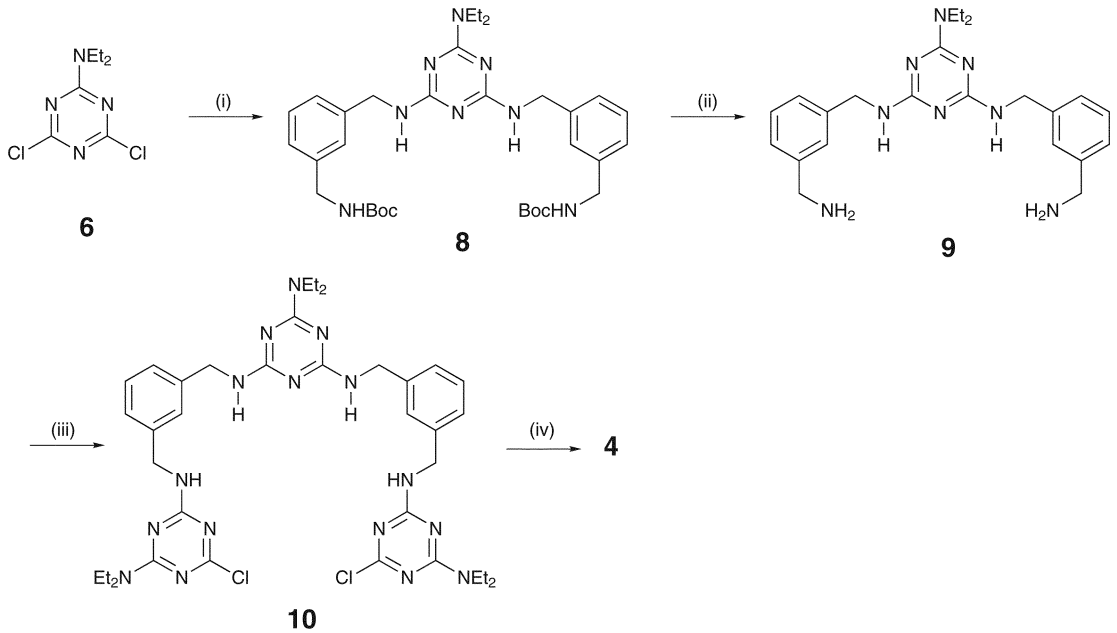

Fig. 2 Synthesis of **4**. (i) 3-*tert*-Butoxycarbonylaminomethylbenzylamine, K_2CO_3, 1,4-dioxane, reflux, 98%; (ii) TFA–H_2O, rt, 85%; (iii) 2,6-dichloro-4-diethylamino-1,3,5-*s*-triazine, K_2CO_3, 1,4-dioxane, rt, 75%; (iv) *m*-xylylenediamine, K_2CO_3, 1,4-dioxane, reflux, 15%.

group as a chromophore from diethyl butylmalonate and 9-chloromethylanthracene in two steps. The barbiturate **5b** shows well-resolved vibronic transitions of the anthryl group at 337, 353.5, 372.5, and 392.5 nm in $CHCl_3$. Strong emission is also observed at 399, 421.4, and 446 nm excited at 340 nm in $CHCl_3$. UV-vis spectroscopic titrations were carried out to determine the association constants for **5b** with **1–4**. Cyclic bis- and trismelamine derivatives showed remarkable spectral changes corresponding to the anthryl group through isosbestic points indicating 1 : 1 complexation as shown in Fig. 3.

All of the stoichiometries of the complex formation were confirmed by Job's plots (Fig. 4) in $CHCl_3$. Receptors **3** and **4** showed maximum at mole fraction of 0.5 indicating that the receptors and the barbiturate **5b** form a 1 : 1 complex. The association constants were calculated from the changes of the absorbance at 400 nm by non-linear regressions. The results are summarized in Table 1. To determine the association constants of the receptors with barbiturate **5a**, competitive titration in the presence of **5b** was employed. As shown in Fig. 5, addition of **5a** in a solution of **5b** and **3** formed free **5b** through isosbestic points. The association constants were calculated by computer-aided regression using the association constants for **5b** described above, and the results were also summarized in Table 1. Cyclic bismelamine derivative **2** showed a gradual decrease of the association constants for **5** compared to that of **1** because of steric repulsion of the dodecyl group suggested by molecular mechanics calculations. Cyclic bismelamine **3**, in which bisphenol-A was used as a spacer, showed slightly higher but less pronounced association constants for **5** relative to that of the acyclic bismelamine **1**. Thermodynamic parameters for the complexation are informative. The thermodynamic parameters for the association of **3** with **5b** were determined by the van't Hoff analysis (T = 288–313 K) giving $\Delta H = -31.6$ kJ mol^{-1} and $\Delta S = -12.3$ J mol^{-1} K^{-1} ($T\Delta S$ at 298 K was -3.7 kJ mol^{-1}). The result indicates the association of **3** with **5b** is enthalpy driven. The average enthalpy change of six hydrogen bonds for complexation of **3** with **5b** is 5.27 kJ mol^{-1}. This value is compatible with the values for complexation of melamine–cyanuric acid derivatives (5.4 kJ mol^{-1}) and others.[22] The thermodynamic parameters for the association of acyclic host **1** with **5b** were also determined to be $\Delta H = -40.3$ kJ mol^{-1} and $\Delta S = -44.8$ J mol^{-1} K^{-1} ($T\Delta S$ at 298 K was -13.4 kJ mol^{-1}). These data showed acyclic host **1** formed a complex in a more enthalpically favored process than **3** due to the flexible host structure, however, the process is entropically disfavored. The result is consistent with the so-called macrocyclic effect.[23]

The cyclic trismelamine derivative **4** was expected to form a complex with barbiturate **5** with a potential of eight hydrogen bonds, *i.e.*, two sets of donor–acceptor–donor hydrogen bonds from two melamine units and two hydrogen bond donor of NHs from remaining melamine moiety. However the association constants of **4** with **5** are similar to that of **1** suggesting the participation of only six hydrogen bonds to form the complexes due to steric hindrance of the disubstituted groups at the 5,5-positions of **5** pointed out by Hamilton and co-workers.[1] Unfortunately, host–guest complexes were not observed in ESI-MS studies because of the difficulty of ionization of host–guest complexes in $CHCl_3$.

X-Ray crystal structure of the 4 and 5a complex

To evaluate the complex of **4** with barbiturates, single crystals suitable for X-ray analysis of the complex of **4** and **5a** were obtained by slow diffusion of cyclohexane into a $CHCl_3$ solution of **4** and **5a** in a 1 : 1 molar ratio. The proton NMR spectrum of the crystal dissolved in $CDCl_3$ revealed that the ratio of **4** and **5a** is 1 : 2 from the integrations of the corresponding peaks. X-Ray analysis of the complex (triclinic system, space group $P\bar{1}$) showed two 1 : 1 complexes of **4** and **5a** were connected with two other barbiturates **5a** to form a 2 : 4 complex as shown in Fig. 6.

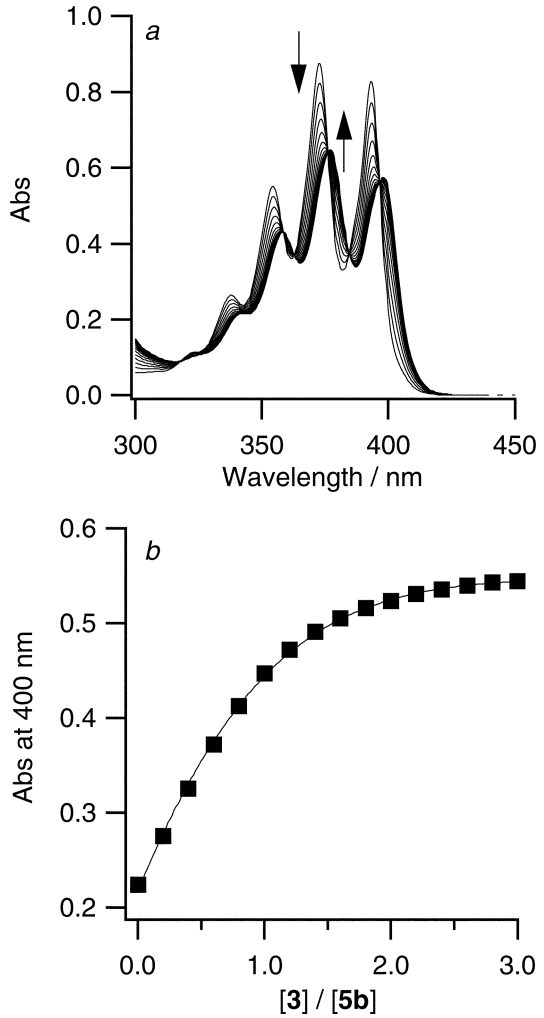

Fig. 3 (a): Spectral changes of **5b** upon addition of **3** in $CHCl_3$ at 298 K. [**5b**] = 1.0 × 10^{-4} mol dm^{-3}, [**3**] = 0–3.0 × 10^{-4} mol dm^{-3}. (b): Changes in the intensity of absorbance at 400 nm of **5b** upon addition of **3** in $CHCl_3$ at 298 K.

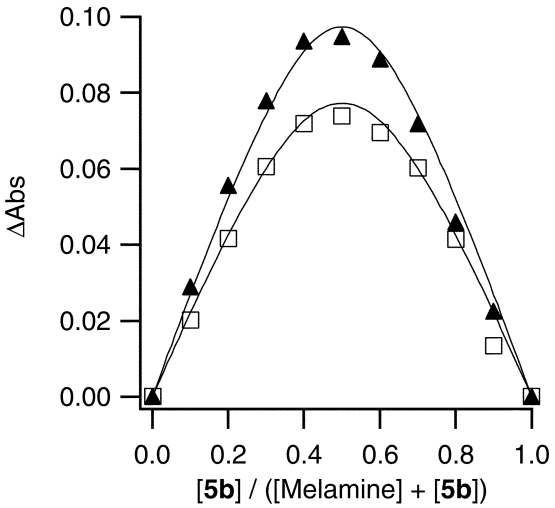

Fig. 4 Job's plots for complexation of **5b** with **3** (▲) and **4** (□). Determined by UV-vis spectroscopy. [**5b**] + [melamine] = 1.0 × 10^{-4} mol dm^{-3} in $CHCl_3$ at 298 K.

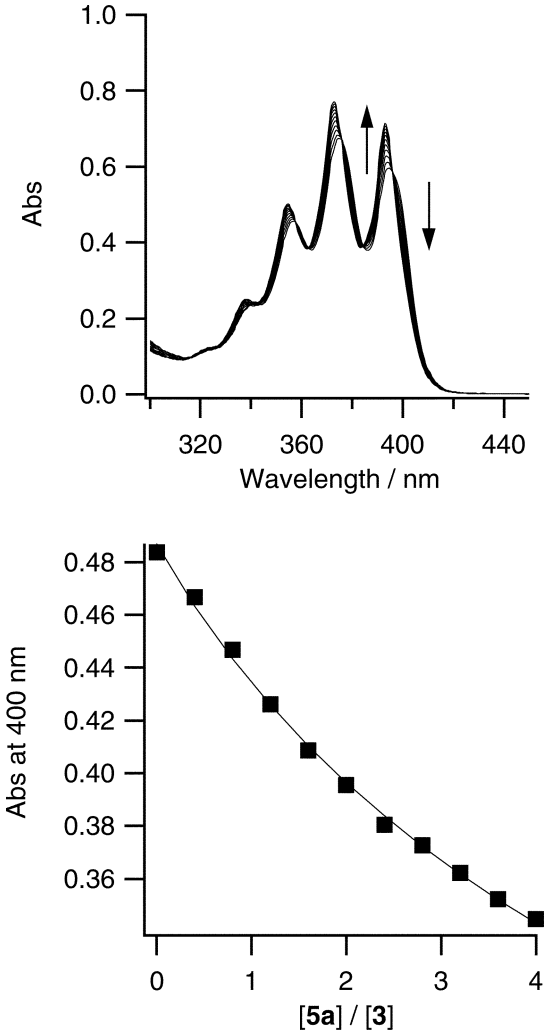

Fig. 5 Competitive titration of **3** upon addition of **5a** in the presence of **5b** in $CHCl_3$. [**3**] = [**5b**] = 1.0 × 10^{-4} mol dm^{-3}, [**5a**] = 0–4.0 × 10^{-4} mol dm^{-3} at 298 K. Inset: Changes in the intensity of absorbance at 400 nm upon addition of **5b**.

Table 1 Association constants for **5** with melamine derivatives in $CHCl_3$

	K_a/mol^{-1} dm^3	
Receptor	**5a**[a]	**5b**[b]
1	4.65 ± 0.19 × 10^4	5.00 ± 0.15 × 10^4
2	4.14 ± 0.23 × 10^3	1.37 ± 0.04 × 10^4
3	2.38 ± 0.10 × 10^4	1.29 ± 0.02 × 10^5
4	4.19 ± 0.19 × 10^4	4.35 ± 0.05 × 10^4

[a] Determined by the competitive titration method. [Receptor] = 1.0 × 10^{-4} mol dm^{-3}, [**5b**] = 1.0 × 10^{-4} mol dm^{-3}, [**5a**] = 0–3.0 × 10^{-4} mol dm^{-3} in $CHCl_3$, at 298 K. [b] Determined by UV-vis spectroscopy. [**5b**] = 1.0 × 10^{-4} mol dm^{-3}, [Receptor] = 0–3.0 × 10^{-4} mol dm^{-3} in $CHCl_3$, at 298 K.

Two melamine moieties bind one barbiturate *via* six hydrogen bonds and the other melamine moiety is oriented out of the cavity forming an intermolecular hydrogen bond to another barbiturate *via* three hydrogen bonds. The outer barbiturate dimerized with the adjacent barbiturate *via* two C=O···H–N hydrogen bonds with the same N···O distance of 2.920 Å. The interatomic N···O and N···N distances corresponding to

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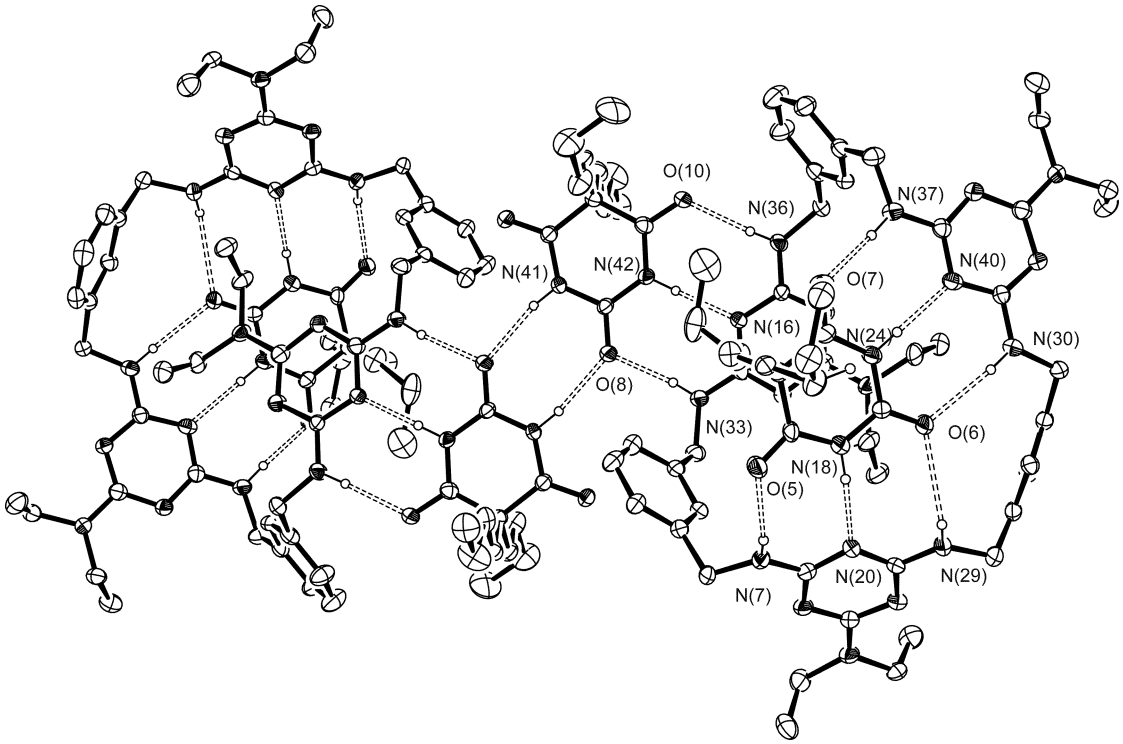

Fig. 6 An ORTEP drawing (30% probability ellipsoids) of the $(\mathbf{4}\cdot\mathbf{5a}_2)_2$ complex grown from slow vapor diffusion of cyclohexane. Hydrogen atoms except for NHs are omitted for clarity.

N–H · · · O and N–H · · · N bonds of **4** with internal **5a** are in the ranges 2.855–3.132 and 2.847–2.862 Å, respectively.

Hamilton *et al.* reported that the isophthaloyl spacer of bis(diamidopyridine) was positioned in the same plane as the pyridines with small deviations due to conjugation of the amide groups.[3d] However, in the solid structure of the complex of **4** and **5a**, the spacer xylylene group was bent relative to the plane of the triazine rings. The spacer phenylene ring was positioned out of the plane of the triazine ring to reduce steric hindrance by bending aside by about 61° and 63° with respect to the appended NH groups. This result is ascribed to more flexible structure of triazine-*m*-xylylene units than that of isophthaloyl amide.

NMR titration

To evaluate the formation of the complex in solution in more detail, ^{1}H NMR titration of **5a** with **4** was performed in $CDCl_3$. As shown in Fig. 7, all protons of the alkyl chain in **5a** showed an upfield shift upon the addition of **4**. The rate of the equilibrium for the complexation is faster than the NMR time scale. Binding isotherms of the titration for **5a** with **4** showed a good fit to higher order complexation such as host : guest = 1 : 2 model rather than the 1 : 1 model. Although all protons of the alkyl chain in **5a** also showed an upfield shift upon addition of **3**, binding isotherms agreed with a 1 : 1 stoichiometry in $CDCl_3$ as shown in Fig. 8. Association constants for **3** and **5a** were calculated from non-linear curve fitting to give $2.97 \pm 0.55 \times 10^4$ dm^3 mol^{-1} and the value is in good agreement with the value determined by UV-vis spectroscopy. A Job's plot determined by ^{1}H NMR showed a similar tendency, *i.e.* a maximum was observed at mole fractions of 0.5 and *ca.* 0.6 for **3** and **4** with **5a**, respectively as shown in Fig. 9. Dimerization of hosts was negligible since a dilution experiment in $CDCl_3$ by ^{1}H NMR spectroscopy gave virtually identical spectra in the experimental range (1.0×10^{-2}–6.25×10^{-4} mol dm^{-3}). These results suggested that the $\mathbf{4}\cdot(\mathbf{5a})_2$ complex is also formed in the solution state. The association constant (K_{12}) for $\mathbf{4}\cdot(\mathbf{5a})_2$ from $\mathbf{4}\cdot\mathbf{5a}$ and **5a** was estimated to be 2.4×10^2 dm^3 mol^{-1} by non-linear curve fitting of changes of chemical shift ($K_{11} = 4.19 \times 10^4$ dm^3 mol^{-1} was used for the calculation).

The conflict of the results from UV-vis titration and ^{1}H NMR titration can be explained by the difference of concentrations in the experiments. In dilute conditions (around 10^{-4} mol dm^{-3} for UV-vis titration), a 1 : 1 complex was predominantly formed and the formation of the 1 : 2 complex was negligible due to the relatively smaller K_{12}. However, a more concentrated condition (around 10^{-2} mol dm^{-3} for ^{1}H NMR titration) is sufficient for the formation of 1 : 2 or higher order complex. Löwik and Lowe reported that the similar trismelamine derivative forms a 1 : 1 complex with cyanuric acid ($K_a = 2.5 \times 10^4$ dm^3 mol^{-1}) *via* nine hydrogen bonds in $CDCl_3$.[16b]

Conclusion

The results presented herein show syntheses of novel and less explored cyclic bis- and trismelamine derivatives in which *m*-xylylene is used as a spacer group and complexation properties of the macrocycles with barbituric acid derivatives. The barbiturate **5b** bearing an anthryl moiety is a useful probe for the determination of the association constants for complexation. Van't Hoff analyses on the complexation of the bismelamine **1** and **3** with the barbituric acid derivative **5b** revealed that the complexation

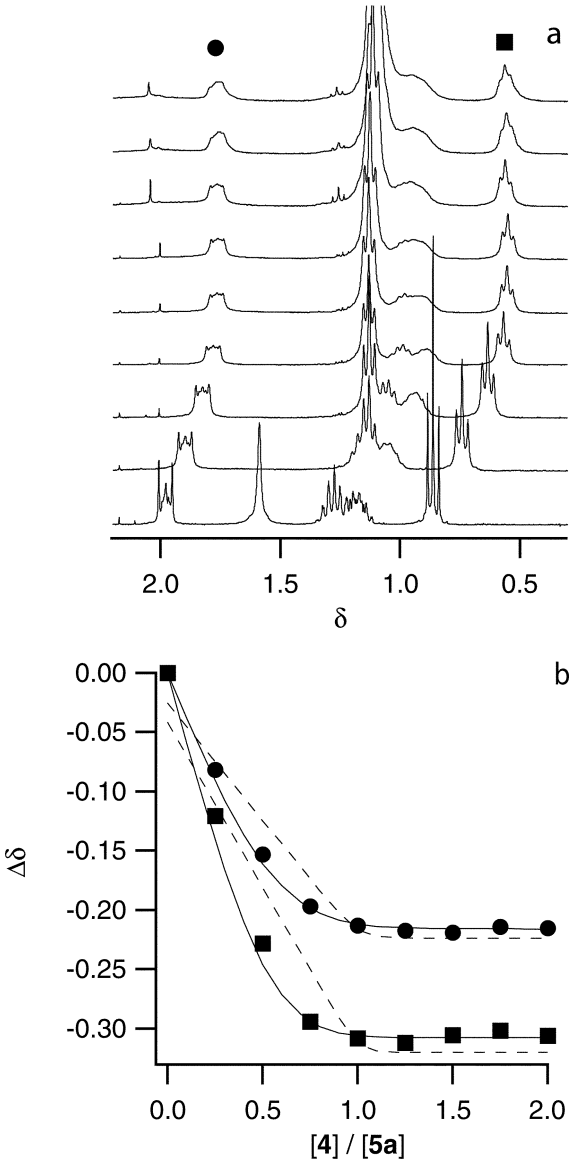

Fig. 7 The ^{1}H NMR titration of **5a** upon addition of **4** in $CDCl_3$ at 298 K. [**5a**] = 1.0×10^{-2} mol dm^{-3}, [**4**] = 0–2.0×10^{-2} mol dm^{-3} (from the bottom to the top). The solid and dashed lines indicate calculated binding isotherms based on host : guest = 1 : 2 and 1 : 1 models, respectively. Methyl and methylene protons of butyl groups of **5a** are represented by closed squares and circles, respectively.

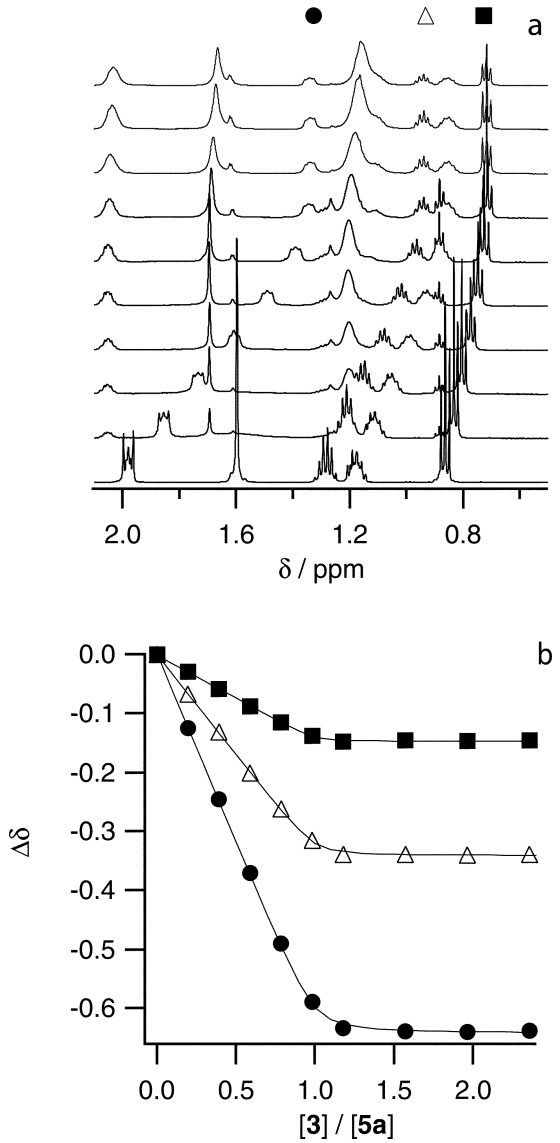

Fig. 8 The ^{1}H NMR titration of **5a** upon addition of **3** in $CDCl_3$ at 298 K. [**5a**] = 1.0×10^{-2} mol dm^{-3}, [**3**] = 0–2.4×10^{-2} mol dm^{-3} (from the bottom to the top). Methyl and methylene (C1 and C2) protons are represented by closed circles, open triangles, and closed squares, respectively.

of the cyclic bismelamine **3** with **5b** was entropically favored and enthalpically less favored process than those of the acyclic bismelamine **1**. In addition, we found that cyclic trismelamine, in which *m*-xylylene was used as a spacer, formed 2 : 4 complex with barbituric acids in both solution and the solid state. These cyclic bis- and trismelamine derivatives can be used as a new class of receptors for barbiturates and related compounds.

Experimental

All reagents used were of analytical grade. Acetonitrile was dried and distilled over calcium hydride. Tetrahydrofuran was dried over Na–benzophenone. UV-vis spectra were recorded on Shimadzu UV-2200A, UV-2500PC and JASCO Ubest-560 spectrometers with thermal regulator (±0.5 °C). ^{1}H NMR spectra were measured on JEOL JNM α-500 (500 MHz), JEOL AL300 (300 MHz) and Varian GEMINI 200 (200 MHz) spectrometers. Electron spray ionization mass spectra (ESI-MS) were recorded on an Applied Biosystems/MDS-Sciex API-100 spectrometer. Column chromatography was performed by using Wakogel C-200 (silica gel, 70–250 μm, Wako Chemical Co. Ltd). Elemental analyses were performed at the Center of Instrumental Analysis of Gunma University.

Synthesis of receptors

The receptors were prepared according to the routes outlined in Figs. 1 and 2. Preparation of 2,4-dichloro-6-diethylamino-*s*-triazine (**6**) was carried out according to the literature procedures.[9a] 5,5-Dibutylbaributuric acid was prepared according to the literature.[24]

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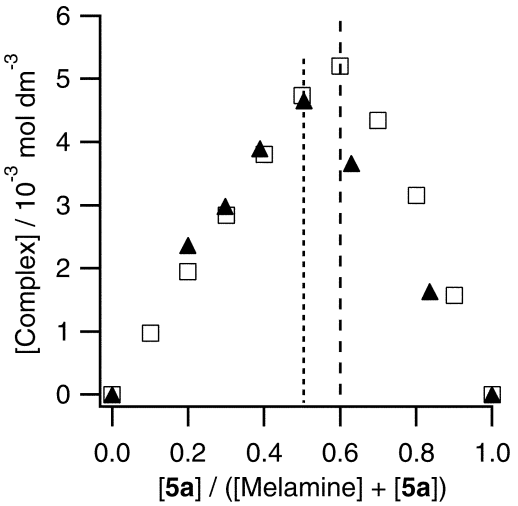

Fig. 9 Job's plots for complexation of **5a** with **3** (▲) and **4** (□) determined by 300 MHz ^{1}H NMR spectroscopy. [**5a**] + [melamine] = 1.0×10^{-2} mol dm^{-3} in $CDCl_3$ at 298 K.

1,3-Bis((2-chloro-4-diethylamino-1,3,5-*s*-triazin-6-yl)aminomethyl)benzene (7)

A mixture of **6** (5.00 g, 22.6 mmol), *m*-xylylenediamine (1.55 g, 11.3 mmol), and sodium carbonate (2.40 g, 22.6 mmol) in CH_2Cl_2 (50 ml) and water (50 ml) was stirred at 40 °C for 10 h. The resulting mixture was extracted with CH_2Cl_2 (30 ml × 3). The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by recrystallization from acetone to give the product (4.82 g, 84%) as a colorless powder; mp 153–154 °C (Found: C, 52.66; H, 6.05; N, 28.08. $C_{22}H_{30}Cl_2N_{10}$ requires C, 52.28; H, 5.98; N, 27.71%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.02–1.03 (12H, m, CH_3), 3.61–3.44 (8H, m, CH_2), 4.59 (4H, d, *J* 6.0, CH_2), 6.16 (2H, br s, NH), 7.18–7.27 (4H, m, C_6H_4).

1,3-Bis((2′-butylamino-4′-diethylamino-1′,3′,5′-*s*-triazin-6′-yl)aminomethyl)benzene (receptor 1)

A mixture of **7** (2.0 g, 3.45 mmol), butylamine (0.56 g, 7.59 mmol) and potassium carbonate (0.96 g, 6.95 mmol) in 1,4-dioxane (100 ml) was refluxed overnight under nitrogen atmosphere. After evaporation under reduced pressure, the residue was extracted with $CHCl_3$ (30 ml × 3) and water. The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography (5% MeOH–$CHCl_3$ as eluent) to give the product as a colorless powder (2.0 g, 88%); mp 91–93 °C (Found: C, 60.75; H, 8.56; N, 28.44. $C_{30}H_{50}N_{12}\cdot H_2O$ requires C, 60.37; H, 8.78; N, 28.16%); δ_H (300 MHz; $CDCl_3$; Me_4Si) 0.91 (6H, t, *J* 7.2, CH_3), 1.11 (12H, t, *J* 6.9, CH_3), 1.36 (4H, sextet, *J* 7.20, CH_2), 1.52 (4H, quintet, *J* 7.2, CH_2), 3.33 (4H, q, *J* 7.2, CH_2), 3.52 (8H, t, *J* 6.9, CH_2), 4.52 (4H, d, *J* 5.9, $C_6H_4CH_2$), 4.76 (2H, br s, NH), 5.18 (2H, br s, NH), 7.20–7.26 (4H, m, C_6H_4); *m*/*z* (ESI; positive ion mode) 579.4 (M + H^+. $C_{30}H_{51}N_{12}$ requires 579.44).

Receptor 2

Into a refluxed suspension of potassium carbonate (2.76 g, 20 mmol) in 1,4-dioxane (300 ml), **7** (5.05 g, 10.0 mmol) and 1,12-diaminododecane (2.00 g, 10.0 mmol) in chloroform were separately added over 2 d. The mixture was stirred for an additional 6 d, and then cooled and evaporated under reduced pressure. The residue was extracted with $CHCl_3$ (100 ml × 3)–H_2O. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The crude material was purified by column chromatography on silica gel (5% MeOH–$CHCl_3$ as eluent) to give the product (3.16 g, 50%) as colorless foam; mp 82–84 °C (Found: C, 64.20; H, 8.85; N, 26.48. $C_{34}H_{56}N_{12}$ requires C, 64.52; H, 8.92; N, 26.56%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.13 (12H, t, *J* 7.0, CH_3), 1.20–1.34 (16H, m, CH_2), 1.47–1.64 (4H, m, CH_2), 3.34 (4H, q, *J* 5.7, CH_2), 3.53 (8H, q, *J* 7.0, CH_2), 4.54 (4H, d, *J* 5.6, CH_2), 4.74 (2H, s, NH), 5.02 (2H, s, NH), 7.21–7.38 (4H, m, C_6H_4). *m*/*z* (ESI; positive ion mode) 633.5 (M + H^+. $C_{34}H_{57}N_{12}$ requires 633.48).

N-1-(3-Bromopropyl)phthalimide

A mixture of 1,3-dibromopropane (32.0 g, 158 mmol) and potassium phthalimide (14.7 g, 79.4 mmol) in DMF (100 ml) was stirred under nitrogen atmosphere at 80 °C overnight. After 200 ml of water was added, the mixture was extracted with $CHCl_3$ (100 ml × 3) and the combined organic layer was washed with water (100 ml × 3), dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel ($CHCl_3$: hexane = 1 : 1 as eluent) to give the product as a white powder (5.25 g, 25%); mp 72–73 °C; δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.24 (2H, quintet, *J* 6.8, CH_2), 3.39 (2H, t, *J* 6.8, $BrCH_2$), 3.81 (2H, t, *J* 6.8, NCH_2), 7.69–7.71 (2H, m, Ar), 7.81–7.84 (2H, m, Ar).

2,2-Di(4-(3-phthalimido-1-propyloxy)phenyl)-propane

A mixture of *N*-1-(3-bromopropyl)phthalimide (3.13 g, 11.7 mmol), bisphenol-A (1.33 g, 5.83 mmol) and potassium carbonate (3.23 g, 23.4 mmol) in DMF (40 ml) was stirred under nitrogen atmosphere at 80 °C for 1 d. The mixture was extracted with $CHCl_3$ (200 ml)–2 N HCl and the organic layer was washed with water (100 ml × 3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude material was purified by column chromatography ($CHCl_3$ as an eluent) to give 1.89 g (54%) of the product as viscous oil; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.60 (6H, s, CH_3), 2.16 (4H, quintet, *J* 6.6, CH_2), 3.90 (4H, t, *J* 7.0, CH_2), 4.00 (4H, t, *J* 7.0, CH_2), 6.70 (4H, d, *J* 8.6, Ar), 7.07 (4H, d, *J* 8.6, Ar), 7.69–7.73 (4H, m, Ar), 7.82–7.86 (4H, m, Ar).

2,2-Di(4-(3-amino-1-propyloxy)phenyl)propane

Into a solution of 2,2-di(4-(3-phthalimino-1-propyloxy)phenyl)-propane (1.89 g, 3.14 mmol) in EtOH (60 ml) was added hydrazine monohydrate (2 ml) and the mixture was refluxed under nitrogen atmosphere overnight. After evaporation, the residue was extracted with $CHCl_3$ (100 ml × 3)–diluted aqueous NaOH (100 ml). The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure to give 0.92 g (85%) of the product as pale yellow oil; δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.52 (4H, br s, NH_2), 1.63 (6H, s, CH_3), 1.89 (4H, quintet, *J* 6.4, CH_2), 2.90 (4H, t, *J* 6.4, CH_2), 4.02 (4H, t, *J* 6.4, CH_2), 6.79 (4H, d, *J* 8.8, C_6H_4), 7.12 (4H, d, *J* 8.8, C_6H_4).

Receptor 3

Into a refluxing suspension of potassium carbonate (1.93 g, 14.0 mmol) in 1,4-dioxane (200 ml), **7** (3.54 g, 7.0 mmol) and 2,2-di(4-(3-amino-1-propyloxy)phenyl)propane (2.40 g, 7.0 mmol) in 1,4-dioxane were separately added over 6 d. The mixture was stirred for an additional 2 d, then cooled and evaporated under reduced pressure. The residue was extracted with $CHCl_3$ (100 ml × 3)–H_2O. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The crude material was purified by column chromatography on silica gel (5% MeOH–$CHCl_3$ followed by 10% MeOH–$CHCl_3$ as eluent) to give the product (2.42 g, 43%) as a white foam; mp 106–108 °C (Found: C, 64.40; H, 7.40; N, 20.57. $C_{43}H_{58}N_{12}O_2 \cdot 1.5H_2O$ requires C, 64.39; H, 7.67; N, 20.96%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.11 (12H, t, *J* 7.0, CH_3), 1.66 (6H, s, $C(CH_3)_2$), 2.01 (4H, q, *J* 5.7, CH_2), 3.57–3.45 (12H, m, CH_2), 4.01 (4H, d, *J* 5.8, CH_2), 4.50 (4H, d, *J* 5.7, CH_2), 5.1 (4H, br s, NH), 6.78 (4H, d, *J* 8.8, C_6H_4), 7.08 (4H, d, *J*, 8.7, C_6H_4), 7.20 (4H, s, C_6H_4); *m/z* (ESI; positive ion mode) 775.5 ($M + H^+$. $C_{43}H_{59}N_{12}O_2$ requires 775.49).

4,6-Bis(3-*tert*-butylcarbonylaminomethylphenylmethylamino)-2-diethylamino-1,3,5-*s*-triazine (8)

A mixture of **6** (1.64 g, 7.4 mmol), 3-*tert*-butoxycarbonylaminomethylbenzylamine (3.50 g, 14.8 mmol), and potassium carbonate (2.05 g, 14.8 mmol) in 1,4-dioxane (100 ml) was refluxed for 2 d. After addition of water (100 ml), the mixture was evaporated under reduced pressure. The residue was extracted with $CHCl_3$ (100 ml × 3), and the combined organic layer was dried over anhydrous sodium sulfate. After evaporation, the residue was purified by column chromatography on silica gel (10% MeOH–$CHCl_3$ as eluent) to give the product as viscous foam (4.50 g, 98%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.02–1.21 (6H, m, CH_3), 1.46 (18H, s, CH_3 of *t*-Bu), 3.48–3.61 (4H, m, CH_2), 4.30 (4H, d, *J* 5.8, CH_2), 4.57 (4H, d, *J* 5.9, CH_2), 4.83 (2H, br s, NH), 5.56 (2H, br s, NH), 7.22–7.27 (8H, m, C_6H_4).

4,6-Bis(3-aminomethylphenylmethylamino)-2-diethylamino-1,3,5-*s*-triazine (9)

A mixture of **8** (4.60 g, 7.5 mmol) in trifluoroacetic acid (50 ml)–H_2O (20 ml) was stirred at rt overnight. After evaporation under reduced pressure, the residue was extracted with $CHCl_3$ (100 ml × 3)–H_2O and the combined organic layer was dried over anhydrous sodium sulfate. Evaporation under reduced pressure to give the product (2.7 g, 85%) as a yellow oil; δ_H (200 MHz; $CDCl_3$; Me_4Si) 1.15 (6H, t, *J* 7.0, CH_3), 1.6 (4H, br s, NH_2), 3.57 (4H, q, *J* 7.0, CH_2), 3.88 (4H, s, CH_2), 4.62 (4H, d, *J* 5.9, CH_2), 5.21 (2H, br s, NH), 7.28 (8H, m, C_6H_4).

4,6-Bis((2′-chloro-4′-diethylamino-1′,3′,5′-*s*-triazin-6′-yl)aminomethylphenylmethylamino)-2-diethylamino-1,3,5-*s*-triazine (10)

A mixture of **6** (1.92 g, 8.7 mmol), **9** (1.83 g, 4.35 mmol), and potassium carbonate (1.4 g, 10.1 mmol) in 1,4-dioxane (100 ml)–H_2O (50 ml) was refluxed overnight. After evaporation under reduced pressure, the residue was extracted with $CHCl_3$ (100 ml × 3)–H_2O (50 ml) and the combined organic layer was dried over anhydrous sodium sulfate. The mixture was evaporated under reduced pressure, the residue was chromatographed on silica gel ($CHCl_3$: AcOEt = 20 : 3 followed by AcOEt) to give the product as a viscous foam (2.56 g, 75%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 0.93–1.21 (18H, m, CH_3), 3.38–3.61 (12H, m, CH_2), 4.48–4.62 (8H, m, CH_2), 5.05–5.29 (2H, br s, NH), 6.60–6.77 (2H, br s, NH), 7.11–7.29 (8H, m, C_6H_4).

Receptor 4

Into a refluxed suspension of potassium carbonate (0.21 g, 1.52 mmol) in 1,4-dioxane, **10** (0.79 g, 1.00 mmol) and *m*-xylylenediamine (0.13 ml, 0.98 mmol) in 1,4-dioxane (80 ml) were added dropwise separately over 1 d and the mixture was refluxed 2 d. After evaporation under reduced pressure, the residue was extracted with $CHCl_3$ (50 ml × 4)–H_2O (50 ml) and the combined organic layer was dried over potassium carbonate. After the mixture was evaporated under reduced pressure, the residue was chromatographed on silica gel ($CHCl_3$: AcOEt = 2 : 1 followed by 1 : 1) and recrystallized from acetonitrile to give the product as white solid (142 g, 17%); mp 130–133 °C (Found C, 62.26; H, 7.08; N, 28.61. $C_{45}H_{60}N_{18} \cdot H_2O$ requires C, 62.05; H, 7.17; N, 28.94%); δ_H (300 MHz; $CDCl_3$; Me_4Si) 1.09 (18H, t, *J* 7.2, CH_3), 3.49 (12H, q, *J* 7.2, CH_2), 4.51 (12H, d, *J* 5.9, $NHCH_2$), 5.11 (6H, br s, NH), 7.09–7.38 (12H, m, C_6H_4); *m/z* (ESI; positive ion mode) 853.5 ($M + H^+$. $C_{45}H_{61}N_{18}$ requires 853.53).

Diethyl 2-(9-anthrylmethyl)-2-butylmalonate

Into a suspension of sodium hydride (140 mg, 5.83 mmol) in 20 ml of THF, diethyl butylmalonate (1.38 g, 6.38 mmol) in THF was dropwise at rt under nitrogen atmosphere. After stirring for 30 min, a THF solution of 9-chloromethylanthracene (1.20 g, 5.30 mmol) was added dropwise and the resulting mixture was refluxed under nitrogen atmosphere overnight. The reaction mixture was quenched by addition of water, and the mixture was evaporated under reduced pressure. After the residue was extracted with $CHCl_3$ (100 ml × 3)–3 N HCl, the combined organic layer was washed with brine, and dried over anhydrous sodium sulfate. Chloroform was evaporated under reduced pressure and the residue was chromatographed on silica gel (hexane : $CHCl_3$ = 2 : 1 as eluent) to give diethyl 2-(9-anthrylmethyl)-2-butylmalonate as a pale yellow oil (1.99 g, 92%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 0.86 (3H, t, *J* 7.0, CH_3 of butyl), 0.95 (6H, t, *J* 7.0, CH_3 of ethyl), 1.23–1.56 (4H, m, CH_2), 1.86 (2H, t, *J* 9.0, CH_2Pr), 3.90–3.73 (4H, m, CH_2 of ethyl), 4.39 (2H, s, CH_2Anth), 7.50–7.20 (4H, m, 2-, 3-, 6-, and 7-H of anthryl), 7.95–7.99 (2H, m, 4- and 5-H of anthryl), 8.30–8.36 (3H, m, 1-, 8-, and 10-H of anthryl).

5-(9-Anthrylmethyl)-5-butyl-barbituric acid (5a)

Into a solution of urea (0.42 g, 7.01 mmol) in ethanol (10 ml), sodium (0.25 g, 10.7 mmol) was added and the mixture was stirred for 30 min under nitrogen atmosphere at rt, followed by diethyl 2-(9-anthrylmethyl)-2-butylmalonate (0.45 g, 1.10 mmol) in ethanol dropwise over 30 min. After the mixture was refluxed for 12 h, 3 N HCl was added and the mixture was evaporated under reduced pressure. The residue was recrystallized from toluene to give **5a**

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as pale yellow needles (0.04 g, 10%); mp 267–268 °C (Found: C, 73.96; H, 5.92; N, 7.24%. $C_{23}H_{22}N_2O_3$ requires C, 73.78; H, 5.92; N, 7.48%); δ_H (200 MHz; $CDCl_3$; Me_4Si) 0.92 (3H, t, *J* 7.0, CH_3 of butyl), 1.10–1.48 (4H, m, CH_2), 2.41–2.50 (2H, m, CH_2Pr), 4.93 (2H, s, CH_2Anth), 7.42–7.49 (4H, m, 2-, 3-, 6-, and 7-H of anthryl), 7.94–7.99 (2H, m, 4- and 5-H of anthryl), 8.19–8.24 (2H, m, 1- and 8-H of anthryl), 8.39 (1H, s, 10-H of anthryl).

Titration method

Into a solution of **5a** (1.0×10^{-4} mol dm^{-3}) in $CHCl_3$, aliquots of a stock solution (0.01 mol dm^{-3}) of the receptor in $CHCl_3$ were added and UV-vis spectra were recorded. Association constants were determined by the non-linear least-squares method following absorbance at 400 nm. All measurements were carried out in at least duplicate using independent samples.

Single-crystal X-ray crystallographic study

Single crystals of $(\mathbf{4})_2\cdot(\mathbf{5a})_4$ were obtained by slow vapor diffusion of cyclohexane into a chloroform solution of a 1 : 1 mixture of **4** and **5a**. A colorless prismatic crystal having approximate dimensions of 0.20 × 0.20 × 0.25 mm was mounted in a glass capillary. Intensity data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with graphite monochromated Mo-Kα ($\lambda = 0.71070$ Å) radiation at 113 K. Data were collected and processed using the CrystalClear program (Rigaku). The structure was solved by direct methods using the SIR97 program[25] and expanded using Fourier techniques using DIRDIF94 program.[26] The structure was refined using the program SHELXL-97.[27] All hydrogen atoms were located in calculated positions. Crystal structural data for $(\mathbf{4})_2\cdot(\mathbf{5a})_4$ [$(\mathbf{4})\cdot(\mathbf{5a})_2$]: $C_{69}H_{100}N_{22}O_6$, $M = 1333.69$, triclinic, space group $P\bar{1}$, $a = 14.995(2)$, $b = 15.949(2)$, $c = 17.6433(4)$ Å, $\alpha = 69.348(10)$, $\beta = 71.33(1)$, $\gamma = 88.86(1)°$, $V = 3692.2(8)$ Å^3, $Z = 2$, $D_c = 1.200$ g cm^{-3}, $T = 233$ K, $\mu = 0.80$ cm^{-1}, $R_1 = 0.0836$ for 5059 $F_0 > 4\sigma F_0$ and 0.1391 for all 15745 reflections, $wR_2 = 0.2366$, $GOF = 0.831$.†

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