

# Synthesis and photophysical properties of 2,2'-binaphthalene-based receptor bearing trimethylsilyl groups to improve the solubility

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Received: 3 November 2011 / Accepted: 1 March 2012 / Published online: 18 April 2012  
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**Abstract** Two trimethylsilyl groups were introduced at 5- and 5'-positions of 2,2'-binaphthalene to improve the solubility of 2,2'-binaphthalene-based receptors. The X-ray crystallographic analysis revealed the twisted structure of **2** in the solid state. The solubility of **2** was moderately improved by 3.1-fold comparing with mother skeleton **1**. As a practical example of **2**, receptor **8** bearing two aza-15-crown-5 moieties was prepared and the selective binding of **8** with Ba<sup>2+</sup> can be observed by the formation of sandwich-like complex, which shows no prevention of binding ability of the receptor by introduction of the bulky substituents.

**Keywords** 2,2'-Binaphthalene · Solubility · Trimethylsilyl group · Fluorescence sensor · UV-Vis spectroscopy

## Introduction

For the design of chemosensors, how to achieve the conversion of a recognition event into a signal is the crucial point in molecular recognition chemistry. Recently, various chemosensors, which can detect a binding event by changing UV-Vis and fluorescence spectra, have been widely developed, because high sensitivity and low-cost instrument used [1–3]. In the design of such receptors, fused aromatic

hydrocarbons, such as anthracene and pyrene, have widely been applied as a fluorescence signaling moieties. These structurally rigid fluorophores without a conjugation of recognition sites show no conformational and electronic change upon complexation in ground state, therefore, no or small UV-Vis spectral change can be observed.

During recent years, we have studied 2,2'-binaphthalene [4–10] and 2,2'-bianthracene-based receptors [11] bearing two recognition sites in each aromatic moieties for detection of cations and anions by both UV-Vis and fluorescence spectroscopy by the restriction of the free rotation of two naphthyl or anthryl groups with the cooperative binding of the guest by these recognition sites. For instance, we have designed 2,2'-binaphthalene bearing two aza-15-crown-5 ethers at 8- and 8'-positions via methylene spacer (receptor **3**, Scheme 1) for specific detection of Ba<sup>2+</sup> among the alkali and alkaline earth metal cations by both UV-Vis and fluorescence spectroscopies to form a sandwich-like complex by two azacrown moieties. However, the solubility of these receptors was not enough due to highly planar structure of naphthyl and anthryl moieties. To overcome the disadvantage of 2,2'-binaphthyl-based receptors, introduction of bulky substituents into the 2,2'-binaphthyl skeleton should be effective.

Trimethylsilyl group is one of the bulky substituents as structurally similar *t*-Bu group and easily introduced into an aryl group by substitution of halide group through lithiation, therefore, introduction of the trimethylsilyl group into a less soluble compound should lead the increasing solubility in organic solvent due to facile deaggregation in the solid state. For instance, Fmoc [12], phthalocyanines [13], and pentacene [14] bearing trimethylsilyl groups were reported to increase the solubility in common organic solvents. Moreover, introduction of silyl substituents on fluorescent moieties such as pyrene and

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anthracene enhances the fluorescence intensity due to  $\sigma$ - $\pi$  interaction of silicon atom and the fluorescence moieties [15, 16].

In this paper, we show the synthesis and photophysical properties of 2,2'-binaphthalene bearing two trimethylsilyl substituents on 5- and 5'-positions (**2**, Scheme 1). In addition, receptor **8** having two aza-15-crown-5 ethers was prepared as a practical example of **2**.

## Results and discussion

### Synthesis of 8,8'-dimethyl-5,5'-bis(trimethylsilyl)-2,2'-binaphthalene

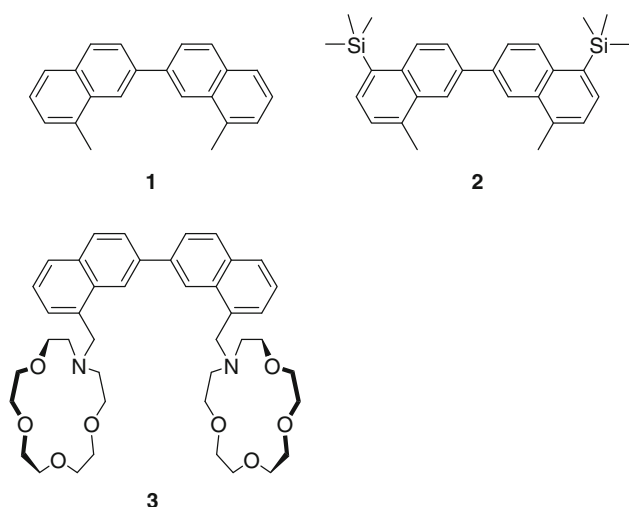
Synthesis of **2** is outlined in Scheme 2. 2-Chloro-8-methylnaphthalene (**4**) was reacted with bromine in the presence of iron and catalytic amount of iodine in tetrachloromethane to give **5** in 51 %. After lithiation of **5** by *n*-butyl lithium in THF, addition of trimethylsilyl chloride gave 2-chloro-8-methyl-5-trimethylsilylnaphthalene (**6**) in 86 %. It should be

noted that selective substitution of bromo groups at 5-position of **5** was achieved due to higher reactivity of bromo group than chloro group at 7-position. Homocoupling of **6** was successfully performed with  $\text{NiCl}_2$  in the presence of stoichiometric amount of zinc, triphenylphosphine, and catalytic amount of 2,2'-bipyridine in *N,N*-dimethylacetamide to give **2** in 43 % yield. The product was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, and elemental analysis. It should be noted that trimethylsilyl groups are stable during the course of the homocoupling reaction.

Single crystals of **2** were grown from EtOH and X-ray crystallographic analysis of **2** (Fig. 1) revealed that two naphthyl groups are placed in slightly twisted positions (the torsion angle of the two naphthyl groups is  $29.3^\circ$ ). This finding is different from the solid-state structures of biphenyl [17, 18] and 2,2'-binaphthyl-based receptors [4, 9, 19] in which two aryl groups are placed in the same plane. The CH- $\pi$  interactions [20] of trimethylsilyl group with the adjacent naphthyl moiety can be observed, therefore, the twisted structure may arise from packing force in the crystal. Two naphthyl groups of **2** adopt an anti-conformation in the solid state, however, may freely rotate in solution. High solubility of **2** in organic solvents is expected due to the crystal structure without  $\pi$ - $\pi$  stacking between adjacent 2,2'-binaphthyl moieties.

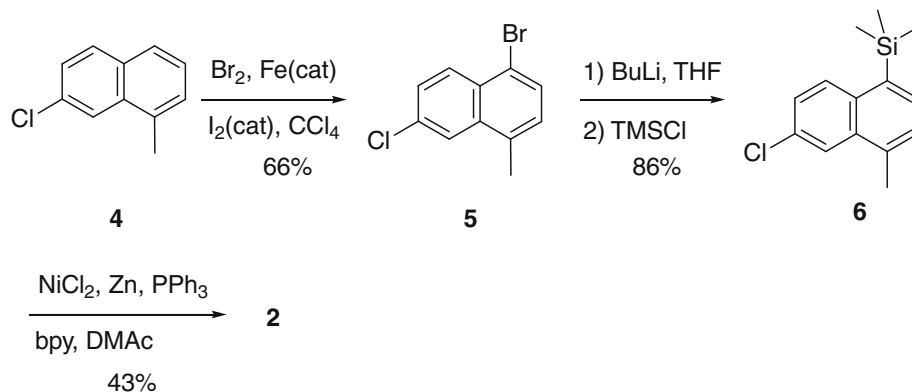
### Photophysical properties of **2**

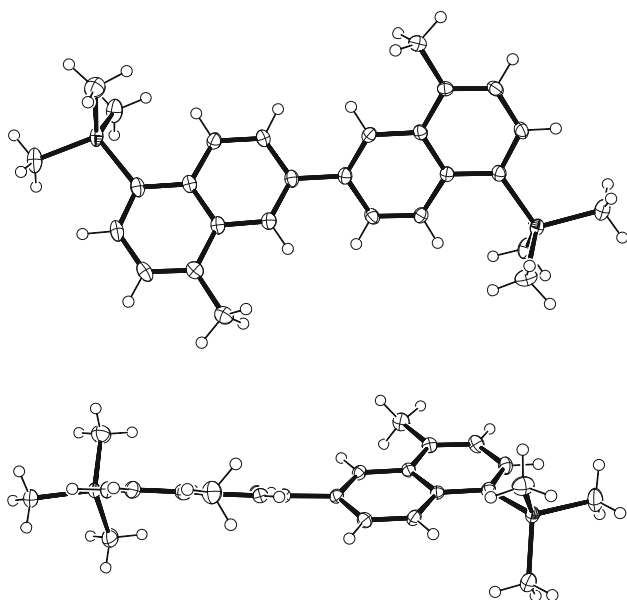
UV-Vis spectra of **2** and 8,8'-dimethyl-2,2'-binaphthalene (**1**) in MeCN are shown in Fig. 2. The absorbance at around 220 nm of **2** was enhanced by the introduction of trimethylsilyl groups into **1**. The absorbance maximum of **2** was observed at 265 nm, which shows bathochromic shift ( $\Delta\lambda = 3$  nm) compared to that of **1** (262 nm). A shoulder peak at around 320 nm, which are ascribed to the  $\pi$ - $\pi^*$  transition of 2,2'-binaphthalene, showed also slightly bathochromic shift indicating a weak  $\sigma$ - $\pi$  conjugation of trimethylsilyl group. Fluorescence maxima excited at 320 nm of **2** showed similarly red shift as depicted in Fig. 3; fluorescence maxima of **2** and **1** were observed at 365 and



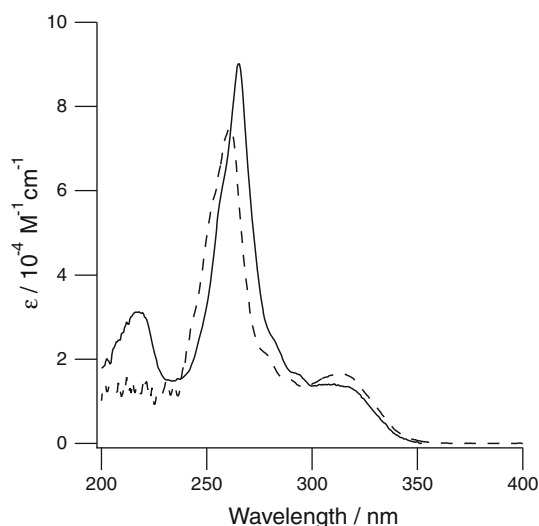
**Scheme 1** Molecular structures of 2,2'-binaphthalene derivatives

### Scheme 2 Synthesis of **2**





**Fig. 1** ORTEP drawings of **2** (50 % probability ellipsoids): *Top view* and *side view*

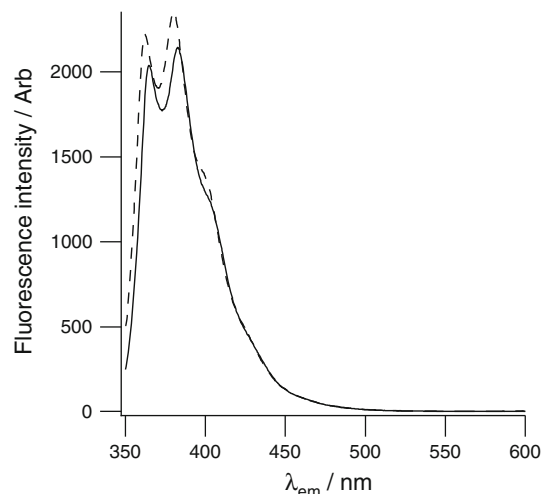


**Fig. 2** UV–Vis spectra of **1** (dashed line) and **2** (solid line) in MeCN at 298 K

362 nm, respectively. Fluorescence quantum yields of **2** and **1** were separately determined to be 0.40 and 0.36, respectively. These results indicate that introduction of TMS groups into 2,2'-binaphthyl group affects small perturbation of electronic properties of the 2,2'-binaphthyl moiety resulting no adverse photophysical properties to construct artificial fluororeceptors based on the 2,2'-binaphthalene skeleton bearing trimethylsilyl groups at 5- and 5'-positions.

#### Solubility of **2** in hexane

A solubility of **2** in hexane was estimated by means of UV–Vis spectroscopy. Aliquots of saturated solution of **2** in



**Fig. 3** Fluorescence spectra of **1** (dashed line) and **2** (solid line) in MeCN at 298 K.  $\lambda_{\text{ex}} = 320$  nm

hexane were added into acetonitrile and the UV–Vis spectra of the solutions were measured repeatedly. The saturated concentration of **2** in hexane was calculated from the absorbance at 320 nm and the molar extinction coefficient of **2** at 320 nm, which is separately determined, and the value was estimated to be  $0.077 \text{ mol dm}^{-3}$ . The saturated concentration of **1** in hexane was also elucidated to be  $0.025 \text{ mol dm}^{-3}$  by a similar method. These results revealed that the solubility of **2** in hexane was moderately improved by 3.1-fold compared to mother skeleton **1** by introduction of bulky trimethylsilyl substituents.

#### Synthesis of receptor **8** bearing two aza-15-crown-5 moieties

As a practical application of **2**, bis(trimethylsilyl) substituted 2,2'-binaphthalene bearing two aza-15-crown-5 moieties (**8**) was prepared as shown in Scheme 3 [21–27]. Bromination of **2** was conducted by *N*-bromosuccinimide (NBS) in the presence of catalytic amount of 2,2'-azodii-sobutyronitrile (AIBN) in  $\text{CCl}_4$  to give **7** in 58 %. The dibromo intermediate **7** was successfully reacted with monoaza-15-crown-5 in the presence of triethylamine in THF giving receptor **8** in 61 %. The product was characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, IR, and MS.

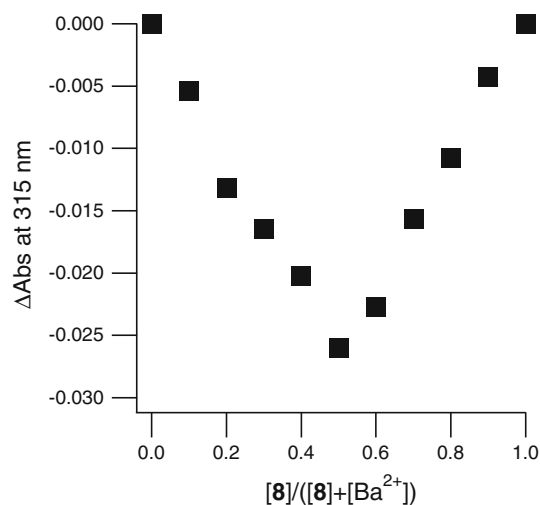
#### Recognition properties of **8** with alkaline earth metal ions

The recognition ability of **8** with alkaline earth metal ions was evaluated by means of UV–Vis and fluorescence spectroscopies in aqueous MeCN [2 %  $\text{H}_2\text{O}$  (v/v)] for application of analytical use. An UV–Vis titration of **8** with  $\text{Ba}(\text{ClO}_4)_2$  was shown in Fig. 4. A gradual decrease of

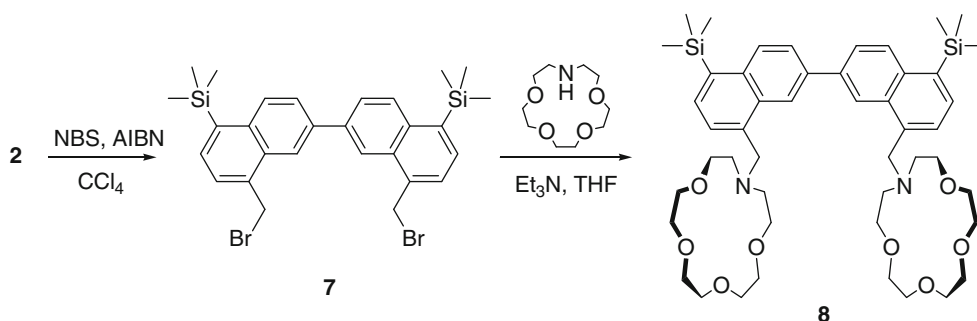
absorption at around 315 nm arising from 2,2'-binaphthyl skeleton with concomitant increase at 293 nm was observed upon the addition of  $\text{Ba}^{2+}$ . The presence of isosbestic points at 299 and 337 nm suggests that the equilibrium consists of two species, free **8** and  $\text{8}\cdot\text{Ba}^{2+}$  complex. The less significant spectral changes can be observed upon the addition of other alkaline earth metal cations such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$  to a solution of **8**. The stoichiometry of the complexation of **8** with  $\text{Ba}^{2+}$  was confirmed by Job's plot analysis. As shown in Fig. 5, the minimum for the complexation of **8** with  $\text{Ba}^{2+}$  at mole fraction 0.5 indicates 1:1 complex formation.

Receptor **8** shows weak fluorescence excited at 320 nm, which is one of the isosbestic points during the course of the titration with  $\text{Ba}^{2+}$  in the UV–Vis titration as described above, in 2 %  $\text{H}_2\text{O}$ – $\text{MeCN}$  (v/v) due to photo-induced electron transfer (PET) from the lone pair of nitrogen atoms in aza-15-crown-5 moieties [28, 29]. As shown in Fig. 6, the fluorescence intensity of **8** centered at 374 nm was greatly increased upon the addition of  $\text{Ba}^{2+}$ . However, the smaller or negligible increase of fluorescence intensity of **8** was observed upon the addition of other alkaline earth metal ions, such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$  [30–33]. These results indicate that receptor **8** forms intramolecular sandwich-like complex ( $\text{8}\cdot\text{Ba}^{2+}$  in Scheme 4) by two azacrown

moieties of **8** with  $\text{Ba}^{2+}$ . The formation of  $\text{8}\cdot\text{Ba}^{2+}$  causes decrease of UV–vis absorption at 315 nm by the conformational restriction [34–39] of the 2,2'-binaphthalene moiety by cooperative complexation of two aza-15-crown-5 moieties, and the enhancement of fluorescence intensity by the inhibition of PET processes [28, 29]. However,

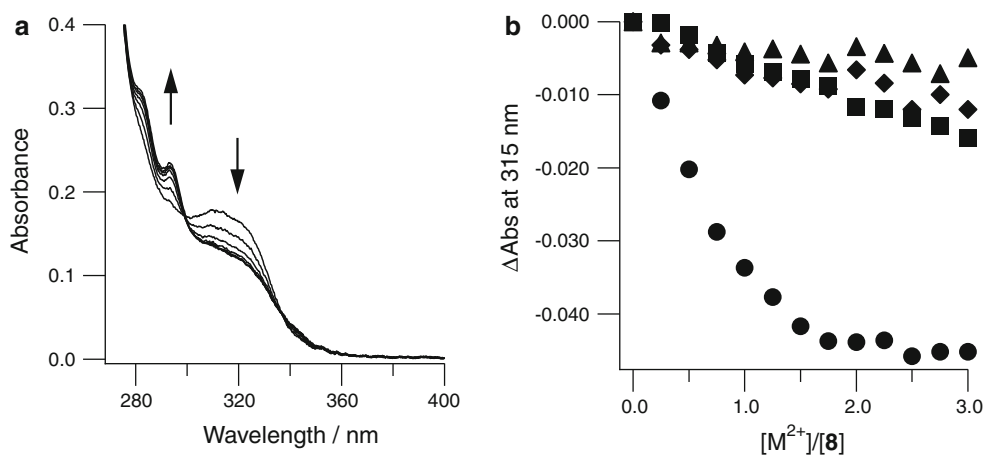


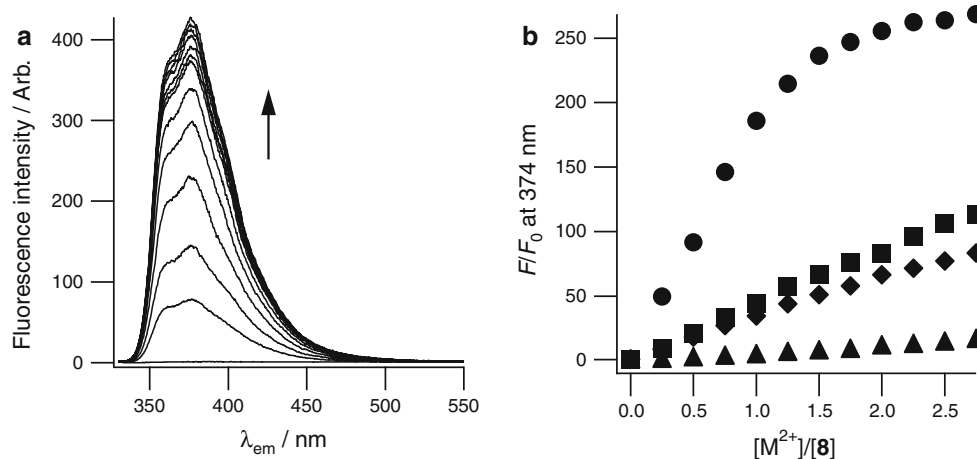
**Fig. 5** Job's plot for **8** with  $\text{Ba}^{2+}$  by UV–Vis spectroscopy in 2 %  $\text{H}_2\text{O}$ – $\text{MeCN}$  at 298 K.  $[\text{8}] + [\text{Ba}^{2+}] = 1.0 \times 10^{-5}$  M



**Scheme 3** Synthesis of **8**

**Fig. 4 a** UV–Vis spectral titration of **8** upon the addition of  $\text{Ba}(\text{ClO}_4)_2$  in 2 %  $\text{H}_2\text{O}$ – $\text{MeCN}$  at 298 K. **b** UV–Vis spectral changes of **8** at 315 nm upon the addition of  $\text{Mg}^{2+}$  (triangle),  $\text{Ca}^{2+}$  (diamond),  $\text{Sr}^{2+}$  (square), and  $\text{Ba}^{2+}$  (circle).  $[\text{8}] = 1.0 \times 10^{-5}$  M





**Fig. 6** **a** Fluorescence spectral titration of **8** upon the addition of  $\text{Ba}(\text{ClO}_4)_2$  in 2 %  $\text{H}_2\text{O}$ – $\text{MeCN}$  at 298 K. **b** Fluorescence spectral changes of **8** at 374 nm upon the addition of  $\text{Mg}^{2+}$  (triangle),  $\text{Ca}^{2+}$  (diamond),  $\text{Sr}^{2+}$  (square), and  $\text{Ba}^{2+}$  (circle).  $[\mathbf{8}] = 1.0 \times 10^{-5}$  M,  $\lambda_{\text{ex}} = 320$  nm

smaller spectral changes in both UV–Vis and fluorescence spectroscopies upon the addition of smaller alkaline earth metal cations were due to the formation of a complex in which one of the azacrown moieties is occupied with these metal cations ( $\mathbf{8}\text{-M}^{2+}$  in Scheme 4) as observed in receptor **3**. Therefore, the introduction of bulky trimethylsilyl substituent into 2,2′-binaphthalene does not prevent cooperative recognition of two binding sites at 8- and 8′-positions.

## Conclusion

In summary, we have synthesized 8,8′-dimethyl-5,5′-bis(trimethylsilyl)-2,2′-binaphthalene **2** as a new scaffold to construct chromo- and fluororeceptors. X-ray crystallographic analysis revealed the structure of **2** unambiguously. The solubility of **2** is moderately improved by introduction of two bulky substituents, trimethylsilyl groups, into 2,2′-binaphthalene. As a practical example of **2**, receptor **8** was prepared and the selective binding of **8** with  $\text{Ba}^{2+}$  can be observed by formation of a sandwich-like complex, which shows no prevention of the binding ability of the receptor by introduction of such bulky substituents. We believe that the present 5,5′-bis(trimethylsilyl)-2,2′-binaphthalene scaffold is quite useful for the construction of various types of receptors by functionalization of 8- and 8′-positions. Further studies along this line are in progress in our laboratory.

## Experimental

### General methods

All reagents used were of analytical grade. Tetrahydrofuran was dried over  $\text{Na}$ /benzophenone. NMR spectra were

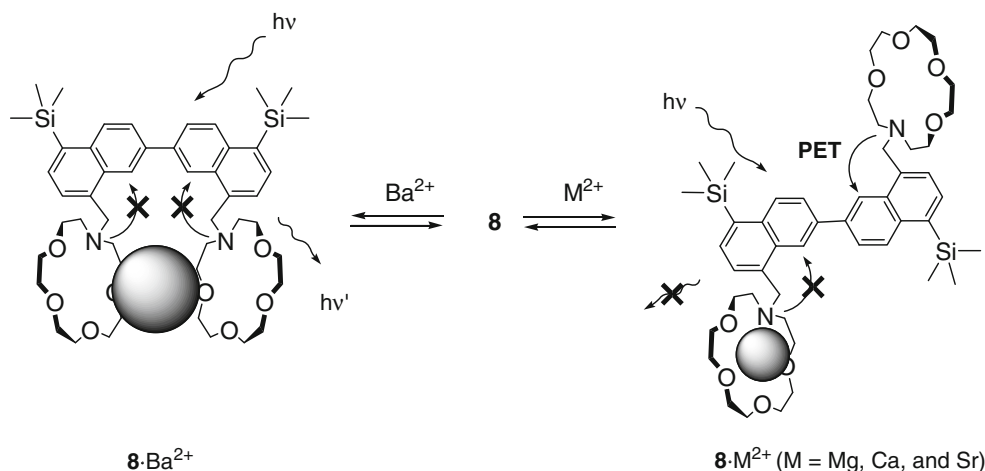
measured on an ECA500 (500 MHz) spectrometers using tetramethylsilane or residual solvent as an internal standard. UV–Vis spectra were recorded on a Shimadzu UV-2500PC spectrometer with thermal regulator ( $\pm 0.5$  °C). Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrometer. Melting points were determined with a Yanagimoto micro melting point apparatus MP-J3 and are uncorrected.

### Synthesis of 5-bromo-2-chloro-8-methylnaphthalene

Into a mixture of 2-chloro-8-methylnaphthalene [40] (4.50 g, 25 mmol), iron powder (10 mg, cat.), and iodine (10 mg, cat.) in tetrachloromethane (5 mL), was added bromine (0.15 mL, 6.0 mmol) in tetrachloromethane (3 mL) at  $-7$  °C. After the mixture was stirred for 4 h, the resulting mixture was washed with aqueous 2 M NaOH, and the organic layer was evaporated under reduced pressure. The residue was recrystallized from hexane to give the product as white solids. Yield 4.2 g, 66 %. Mp.  $45.2$ – $46.4$  °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d, 1H,  $J = 8.9$  Hz), 7.95 (s, 1H), 7.64 (d, 1H,  $J = 7.5$  Hz), 7.59 (d, 1H,  $J = 8.9$  Hz), 7.17 (d, 1H,  $J = 7.4$  Hz), 2.61 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  134.5, 133.7, 132.7, 130.2, 129.8, 129.5, 128.0, 127.7, 123.6, 120.5, 19.2. Anal. calcd for  $\text{C}_{11}\text{H}_8\text{BrCl}$ : C 51.70, H 3.16; found: C 51.49, H 3.21.

### Synthesis of 2-chloro-8-methyl-5-trimethylsilylnaphthalene

Into a solution of 5-bromo-2-chloro-8-methylnaphthalene (3.3 g, 13 mmol) in THF (15 mL) at  $-70$  °C, butyllithium in hexane (8.6 mL, 14.3 mmol) was slowly added via syringe under argon atmosphere. After the mixture was stirred for 1.5 h, trimethylsilyl chloride (0.26 mL) was



**Scheme 4** Proposed structures of the complexes

slowly added into the mixture. The resulting mixture was stirred for 1.5 h, and then the reaction was quenched by addition of aqueous ammonium chloride. The mixture was extracted with ether (50 mL  $\times$  2) and the combined organic layer was dried over anhydrous sodium sulfate. After the solvent was evaporated under reduced pressure, the residue was chromatographed on silica gel (ether:hexane = 1:9) to give the product as colorless oil. Yield 2.79 g (86 %).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d, 1H,  $J$  = 8.9 Hz), 8.04 (d, 1H,  $J$  = 2.3 Hz), 7.59 (d, 1H,  $J$  = 6.9 Hz), 7.48 (dd, 1H,  $J_1$  = 8.9,  $J_2$  = 2.3 Hz), 7.32 (d, 1H,  $J$  = 6.9 Hz), 2.67 (s, 3H,  $\text{CH}_3$ ), 0.47 (s, 9H,  $\text{SiCH}_3$ ).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  136.2, 135.2, 135.1, 133.7, 132.3, 131.1, 130.2, 126.9, 126.0, 124.0, 19.5, 0.2. Anal. calcd for  $\text{C}_{14}\text{H}_{17}\text{ClSi}$ : C 67.58, H 6.89; found: C 66.46, H 6.77.

#### Synthesis of 8,8'-dimethyl-5,5'-bis(trimethylsilyl)-2,2'-binaphthalene (**2**)

After a mixture of anhydrous  $\text{NiCl}_2$  (52 mg, 0.40 mmol), triphenylphosphine (530 mg, 2 mmol), zinc powder (260 mg, 4.0 mmol), and 2,2'-bipyridine (63 mg, 0.40 mmol) in *N,N*-dimethylacetamide (DMAc, 6 mL) was stirred under argon atmosphere at 60 °C for 30 min, a solution of 2-chloro-8-methyl-3-trimethylsilylnaphthalene (1.0 g, 4.0 mmol) in DMAc (3 mL) was added into the mixture. The resulting mixture was stirred at 70 °C for 2 h. After the mixture was quenched with water, the mixture was filtered through Celite pad and washed with ether. The filtrate was extracted with ether, and the combined organic layer was washed with water, followed by dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel (benzene : hexane = 1 : 9 as eluents) to give the product as colorless solids. Yield 0.37 g, 43 %.

Mp. 189.6–191.0 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (d, 2H,  $J$  = 1.8 Hz), 8.24 (d, 2H,  $J$  = 8.6 Hz), 7.93 (dd, 2H,  $J_1$  = 8.6,  $J_2$  = 1.8 Hz), 7.60 (d, 2H,  $J$  = 6.9 Hz), 7.34 (d, 2H,  $J$  = 6.9 Hz), 2.74 (s, 6H), 0.49 (s, 18H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 136.2, 136.1, 136.0, 133.2, 133.0, 129.3, 126.6, 125.2, 123.4, 19.8, 0.33.  $^{29}\text{Si}$  NMR (99 MHz)  $\delta$  -4.3. Anal. calcd for  $\text{C}_{28}\text{H}_{34}\text{Si}_2$ : C 78.81, H 8.03; found: C 78.44, H 8.08.

#### Synthesis of 8,8'-bis(bromomethyl)-5,5'-bis(trimethylsilyl)-2,2'-binaphthalene

A mixture of 8,8'-dimethyl-5,5'-bis(trimethylsilyl)-2,2'-binaphthalene (0.30 g, 0.70 mmol), NBS (0.30 g, 1.6 mmol), and AIBN (10 mg, cat.) in tetrachloromethane (18 mL) was refluxed under argon atmosphere for 4 h. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel ( $\text{CHCl}_3$ :hexane = 1:4) to give the product as colorless solids. Yield 0.24 g, 58 %. Mp. 262.1–264.0 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.58 (d, 2H,  $J$  = 1.9 Hz), 8.30 (d, 2H,  $J$  = 8.7 Hz), 8.00 (dd, 2H,  $J_1$  = 8.7,  $J_2$  = 1.9 Hz), 7.65 (d, 2H,  $J$  = 6.7 Hz), 7.55 (d, 2H,  $J$  = 6.7 Hz), 5.04 (s, 4H), 0.52 (s, 18H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.7, 138.3, 136.8, 134.8, 132.9, 131.2, 129.7, 127.3, 125.6, 123.3, 32.0, 0.25. Anal. calcd for  $\text{C}_{28}\text{H}_{32}\text{Br}_2\text{Si}_2 \cdot \text{H}_2\text{O}$ : C 55.81, H 5.69; found: C 56.19, H 5.36.

#### Synthesis of 8,8'-bis(1-aza-4,7,10,13-tetraoxacyclopentadecylmethyl)-5,5'-bis(trimethylsilyl)-2,2'-binaphthalene

A solution of 8,8'-bis(bromomethyl)-5,5'-bis(trimethylsilyl)-2,2'-binaphthalene (115 mg, 0.20 mmol), 1-aza-4,7,10,13-tetraoxacyclopentadecane (104 mg, 0.47 mmol), triethylamine (72 mg, 0.71 mmol) in THF (25 mL) was



refluxed for 17 h under argon atmosphere. The mixture was washed with saturated aqueous potassium carbonate, and the organic layer was evaporated under reduced pressure. The residue was chromatographed on alumina (chloroform as an eluent), followed by on silica gel (AcOEt) to give the product as colorless solids. Yield 86 mg, 51 %. Mp. 156.7–157.5 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.75 (d, 2H,  $J = 1.7$  Hz), 8.23 (d, 2H,  $J = 8.6$  Hz), 7.99 (dd, 2H,  $J_1 = 8.6$ ,  $J_2 = 1.7$  Hz), 7.62 (d, 2H,  $J = 6.9$  Hz), 7.48 (d, 2H,  $J = 6.9$  Hz), 4.18 (s, 4H), 3.69 (t, 8H,  $J = 6.0$  Hz), 3.59–3.62 (m, 24H), 2.91 (t, 8H,  $J = 6.0$  Hz), 0.50 (s, 18H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  137.7, 137.5, 137.0, 136.4, 132.8, 132.8, 129.2, 126.9, 125.1, 124.0, 71.0, 70.5, 70.2, 70.1, 59.9, 54.8, 0.31. Anal. calcd for  $\text{C}_{48}\text{H}_{72}\text{N}_2\text{O}_8 \cdot \text{Si}_2 \cdot 0.5\text{H}_2\text{O}$ : C 66.25, H 8.46, N 3.22; found: C 66.37, H 8.17, N 3.25.

### X-ray structure of **2**

The crystals of **2** for X-ray measurement were obtained by recrystallization from EtOH. Data collection was carried out at 123 K on a Rigaku RAXIS-IV++ imaging plate area detector with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.70860$  Å). The structure was solved by direct method (SHELXS-97 [41]) and refined full-matrix least-squares techniques. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in fixed positions. Crystal data:  $\text{C}_{28}\text{H}_{34}\text{Si}_2$ ,  $M = 426.73$ , orthorhombic,  $a = 12.8816(5)$ ,  $b = 18.2229(8)$ ,  $c = 21.2699(10)$  Å,  $V = 4992.9(4)$  Å<sup>3</sup>,  $T = 123$  K, space group  $Pbca$  (no. 61),  $Z = 8$ ,  $\mu(\text{Mo-K}\alpha) = 2.3$  cm<sup>-1</sup>, 29,877 reflections measured, 4,640 unique ( $R_{\text{int}} = 0.0344$ ). The structure was refined on  $F^2$  to  $R_1 = 0.0620$ ,  $wR_2 = 0.1139$  (all data) and  $\text{GOF} = 1.298$  for 279 parameters. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 851962. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44(0)-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk].

### Measurement of solubility of **1** and **2** in hexane

Saturated hexane solutions of **1** and **2** were prepared at r.t. and filtered. Into a 3 mL of acetonitrile in UV cell, aliquots of saturated solution of **1** or **2** were added and the UV–Vis spectrum of the solution was measured. The process was repeated and the saturated concentrations of **1** and **2** were calculated from the slope of added volume against absorbance at 320 nm and separately determined molar extinction coefficients of **1** ( $\epsilon = 1.51 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) and **2**

( $1.26 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>) in acetonitrile to give 0.025 and 0.077 M, respectively.

### Spectral titrations

All guest cations are commercially available as perchlorate salts and were dried over  $\text{P}_4\text{O}_{10}$  under reduced pressure for 1 day prior to use. All titration experiments were carried out with 3 mL of a receptor solution in a quartz cell at  $25 \pm 0.5$  °C, and UV–Vis and fluorescence spectra were recorded upon the addition of aliquots of the stock solution of appropriate guest cations with a microsyringe.

**Acknowledgments** This work was supported in part by a Grant-in-Aid for Scientific Research (C) from Japan Society for the Promotion of Science, The Salt Science Research Foundation, Nos. 1006 and 1104, and a research grant from The Mazda Foundation.

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