Tetrahedron 66 (2010) 4057–4062

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Chiral eighteen-component three-dimensional supramolecular entities stabilized by the hydrogen bonding and coordination interactions

Shi-Gui Chen [a], Yong-Chun Fu [b], Gui-Tao Wang [a], Guang-Yu Li [a], Yuguo Ma [c,*], Xi-Kui Jiang [a], Zhan-Ting Li [a,*]

[a] State Key Laboratory of Bioorganic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China
[b] Shangqiu Technician College, 9 Guilin Lu, Shangqiu 476000, China
[c] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

ARTICLE INFO

Article history:
Received 12 February 2010
Received in revised form 30 March 2010
Accepted 2 April 2010
Available online 7 April 2010

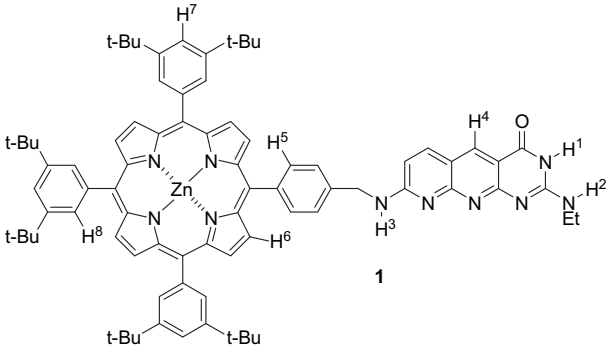
Keywords::
Supramolecular chirality
Hydrogen bonding
Coordination interaction
Porphyrin
Bipyridyl

ABSTRACT

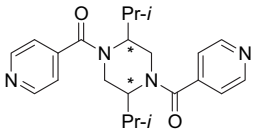
A new class of chiral eighteen-component three-dimensional supramolecular entities has been assembled in toluene and chloroform from twelve zinc porphyrin-appended 2-(ethylamino)- pyrimido[4,5-*b*][1,8]naphthyridin-4(3*H*)-one monomers and six chiral bipyridyl compounds. The heterocyclic segments form two C_6-symmetric cyclic hexamers, which are stabilized by a well-established DDA–AAD hydrogen bonding motif, while the six chiral bispyridine ligands are coordinated to the corresponding zinc porphyrin units to give the two-layered architectures. The structures have been characterized by the ^{1}H NMR, UV–vis and circular dichroism experiments, which also reveals that, when the concentration of the monomers is high enough, the chiral supramolecular entity can be formed exclusively.

1. Introduction

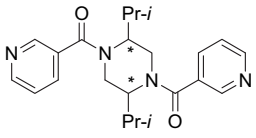
Over the past decade, the self-assembly of hydrogen bonding-driven three-dimensional ordered architectures has received considerable interest.[1–9] One unique feature of this kind of dynamic aggregates is that chiral transfer and amplification can be achieved from simple chiral molecular blocks to the whole supramolecular entities.[6–9] For example, Reinhoudt et al. have used three calix[4]arene-linked dimelamines and six chiral 5,5-diethylbarbituric acid derivatives to assemble chiral nine-component capsular entities via forming two hydrogen bonded rosette motifs from the complementary heterocyclic units.[6,10] However, the self-assembly of chiral supramolecular systems from even more molecular components has been a great challenge.[11] We previously reported that an arylamide foldamer, appended with six zinc porphyrins from outside the backbone, complexed six chiral C_{60}-bearing histidine ligands to generate a chiral propeller-like helicate.[12] The key for the selective formation of this seven-component chiral aggregate was that the rigid foldamer backbone enabled the appended zinc porphyrins to adopt a roughly uniform arrangement and thus to maximize the chiral amplifcation.[13–15] Considering that several stable C_6-symmetric planar hydrogen bonding motifs have been established based on the complementary AAD–DDA (A and D:



1



2 (*R*,*R* and *S*,*S*)



3 (*R*,*R* and *S*,*S*)

* Corresponding authors. Tel.: +86 21 54925122; fax: +86 21 64166128; e-mail addresses: ygma@pku.edu.cn (Y. Ma), ztli@mail.sioc.ac.cn (Z.-T. Li).

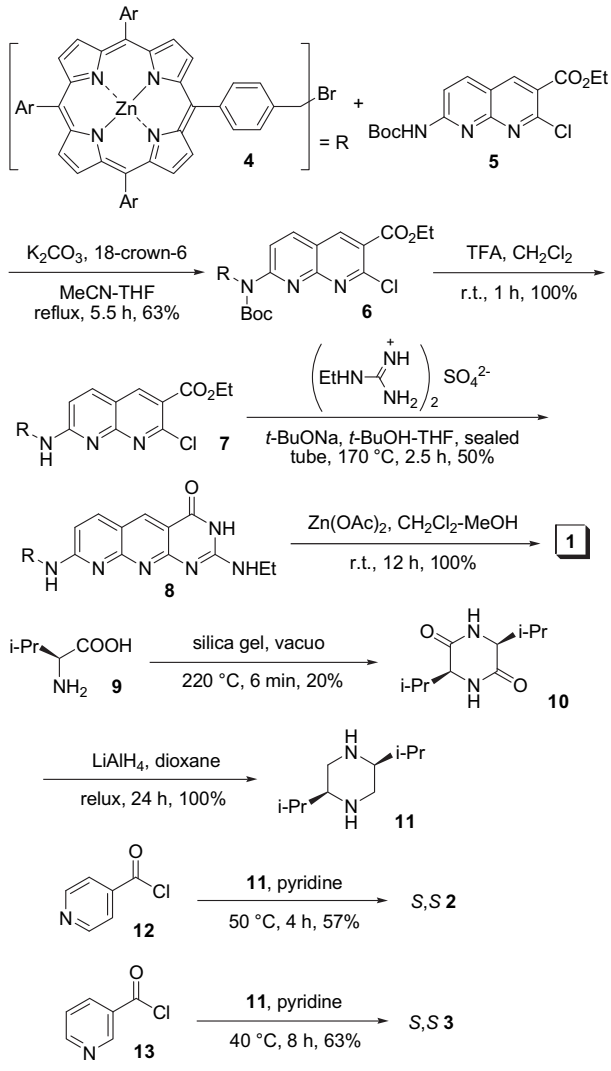
0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.04.009

acceptor and donor) motifs,[16–19] we became interested in attaching the zinc porphyrin unit to the monomeric heterocycles to build new supramolecular synthons for the multi-component chiral assembly. We herein report that one such molecule (**1**) interacts with chiral bispyridines **2** (*R*,*R* and *S*,*S*) and **3** (*R*,*R* and *S*,*S*) to produce a new class of chiral eighteen-component supramolecular entities, that are stabilized by thirty-six hydrogen bonds and twelve Zn–N(py) coordination bonds.

2. Results and discussion

The synthetic route of compound **1** is shown in Scheme 1. Thus, bromide **4**[20] was first reacted with heterocycle **5**[21,22] in refluxed actetonitrile and THF to give compound **6** in 63% yield. The latter was then treated with trifluoroacetic acid to afford compound **7** quantitatively, which was further reacted with ethyl guanidinium in *tert*-butanol and THF to produce compound **8** in 50% yield. Finally, **8** was treated with $Zn(OAc)_2$ to give compound **1**. The synthesis of *S*,*S* **2** and **3** are also provided in Scheme 1. The key intermediate *S*,*S* **11** was prepared according to the reported method.[23] The *R*,*R* isomers were prepared by using the same reactions.

Compound **1** was soluble in chloroform and toluene. Its signals in the downfield area of the ^{1}H NMR spectrum in chloroform-*d* were assigned based on the NOESY and COSY experiments (see the structure). The H-1–3 signals appeared at 14.33, 11.20, and 10.85 ppm (3 mM), which were very close to the related values of Zn-free **8** and porphyrin-free analogs,[21,22] indicating that the nitrogen atoms of the heterocyclic segment of **1** did not interact with its Zn porphyrin. Thus, this compound should also form a stable cyclic hexamer (Fig. 1), as reported for the prototype molecules.[17,21]



Scheme 1. The synthesis of compounds **1**–**3**.

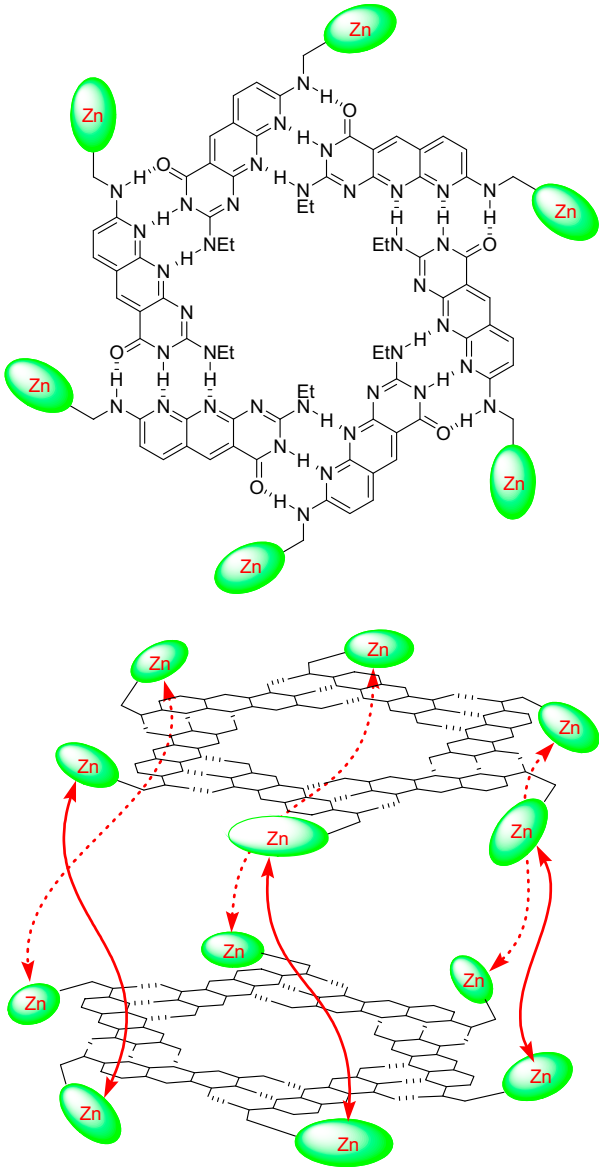
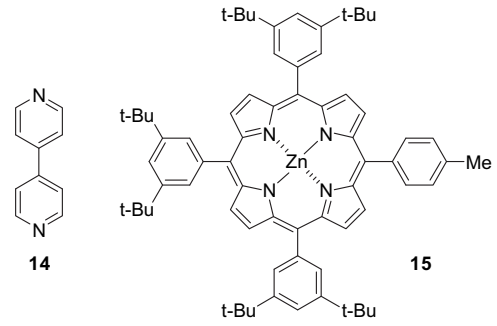


Figure 1. Upper: the structure of the cyclic hexamer of compound **1**. Down: the tentative model for the two-layered supramolecular entities formed by two hexamers of **1** and six dipodal ligands, which are represented by the arrows. The chiral ligands induce the whole architectures to produce the supramolecular chirality.

The binding property of compounds **1**–**3**, and **14** was then investigated. The apparent association constants of its Zn porphyrin to the single pyridine unit of the dipodal ligands in toluene were determined by the UV–vis titration experiments to be 5.6×10^5, 4.3×10^5, and 2.3×10^6 M^{-1}, respectively,[12,24] which were substantially larger than the related values of the complexes of control compound **15** with the single pyridine units of the three ligands. These results showed that the binding of the zinc porphyrin of **1** to the two pyridines of these dipodal ligands were cooperative, which

provided the first evidence that two-layered supramolecular entities were formed from two hexamers of **1** and six dipodal ligands (Fig. 1), as observed for the linear zinc porphyrin oligomers and dipodal ligands.[25–27]



Another evidence for the eighteen-component assembled entities came from ^{1}H NMR titration experiments in chloroform-*d*. For example, upon addition of **14**, the H-3–8 signals of **1** shifted upfield or down-field notably, which displayed a turning point when ca. 0.5 equiv of **14** was added (Fig. 2). The result not only supported the 2:1 binding stoichiometry and the two-layered structure, but also implied that the excess ligand did not cause the formation of other supramolecular species. More solid evidence for the eighteen-component supramolecular entities came from the two-dimensional diffusion-ordered NMR (DOSY) experiments in chloroform-*d*.[28,29] The diffusion coefficients (*D*) of **1**, **1**/**14** (1:0.5), and **1**/**2** (1:0.5) were determined to be $6.1\times e^{-9}$, $2.6\times e^{-9}$, and $2.0\times e^{-9}$ m^2/s, respectively ([**1**]=4.8 mM). The values of the two mixtures were remarkably lower than that of **1**, supporting that the two mixtures formed the two-layered supramolecular entities that had an increased average size. The value of the **1**/**2** mixture was notably smaller than that of the **1**/**14** mixture, which was also consistent with the fact that **2** is longer than **14** and thus formed a larger supramolecule.

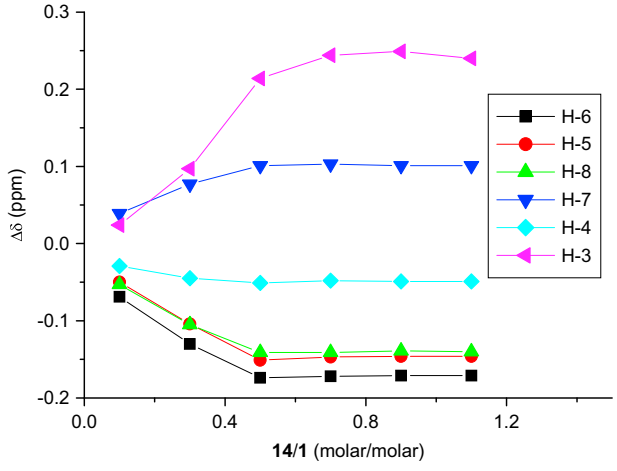


Figure 2. The change of the chemical shifts of partial signals of compound **1** (10 mM) in the ^{1}H NMR spectra in chloroform-*d* at 25 °C, upon addition of compound **14**.

Previously, it was reported that the heterocyclic segment formed the stable cyclic hexamer in toluene even at the low concentration of 3.6×10^{-6} M.[21] It is thus reasonable to assume that, at remarkably higher concentrations ($\geq2.7\times10^{-5}$ M), compound **1** should also exist exclusively in the form of the hexamer in toluene. The circular dichroism (CD) spectra of the mixtures of compound **1** with chiral **2** and **3** were then recorded in toluene to investigate their supramolecular chirality. The results are provided in Figure 3a. It can be found that both pairs of chiral ligands induced the zinc porphyrin of **1** to form Cotton signals of mirror symmetry in the area of the Soret band of the zinc porphyrin. Control experiments showed that the dipodal ligands or their 1:2 mixtures with compound **15** of the identical concentrations did not exhibit any signal in the wavelength area. Thus, the above induced CD (ICD) signals should be attributed to the zinc porphyrin unit of **1** in the chiral eighteen-component supramolecular entity (Fig. 1). The ICD signal of the mixtures of ligand **2** was substantially stronger than that of the mixtures of ligand **3**, which might reflect that the chiral supramolecular entity formed by **2** was more compact or ordered than that of **3**. The chloroform solution of the mixtures also gave rise to similar ICD signals, although the strength was notably weaker due to the higher polarity of the solvent. As expected, reducing the temperature caused the signals to strengthen, while raising the temperature weakened the signals. Thus, compared with that at 10 °C, the molar absorptivity of the ICD signal of the mixture of **1** and *S*,*S* **2** recorded at 60 °C was decreased by ca. 50% as a result of the weakening of the two intermolecular interactions at higher temperatures. Adding polar methanol to the solution caused the ICD signals to weaken rapidly (Fig. 3b). When about 10% of methanol was added, the ICD signals vanished completely. These results again supported the formation of the chiral two-layered supramolecules in toluene, whose hydrogen bonded propeller-like hexamers were decomposed in the presence of methanol.

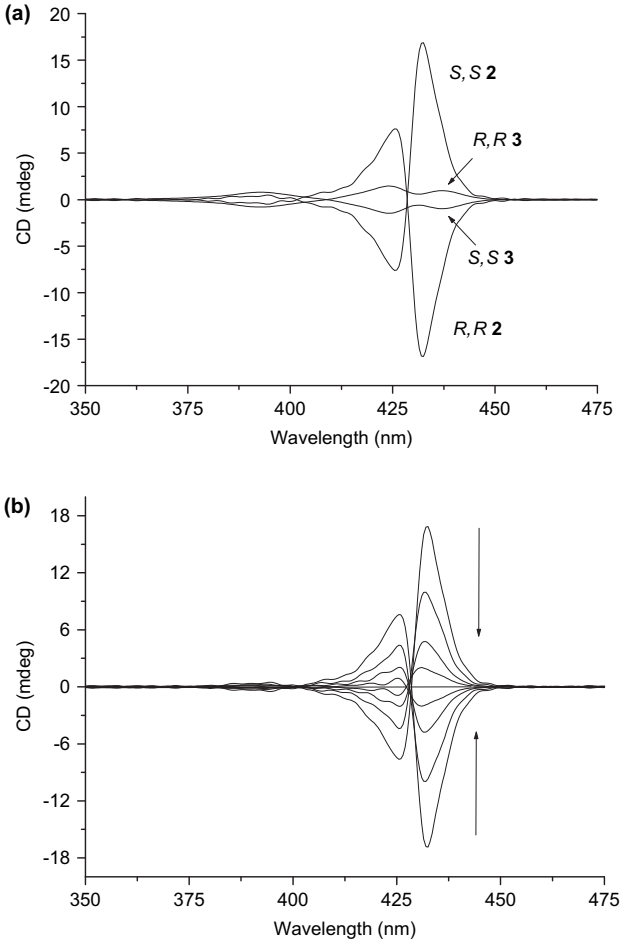


Figure 3. (a) Induced circular dichroism spectra of compound **1** (5.4×10^{-5} M) in the presence of chiral **2** (*R*,*R* and *S*,*S*) and **3** (*R*,*R* and *S*,*S*) in toluene at 25 °C ([**2**]=[**3**]=2.7×10^{-5} M). (b) ICD spectra of **1** (5.4×10^{-5} M) in toluene at 25 °C in the presence of *R*,*R* or *S*,*S* **2** (2.7×10^{-5} M), upon addition of 0%, 1%, 2%, 3%, and 10% of methanol (v%).

As expected, the strength of the ICD signal of the 2:1 mixture of compounds **1** and *S*,*S* **2** was increased with the increase of the

concentration (Fig. 4) at the early stage, implying that, within this concentration range, the multi-component architectures were formed in increasing yields. It can be found that, in the range of low concentrations, the peak shifted pronouncedly, which also indicated that other simple chiral entities existed. When the concentration of **1** was increased to 3×10^{-5} M, the molar absorptivity of this ICD signal stopped to increase (Inset, Fig. 4). This result suggested that, above this critical concentration, the two-layered supramolecular entity was generated exclusively. This low critical concentration again shows that the three-dimensional supramoleuclar entity is highly stable.

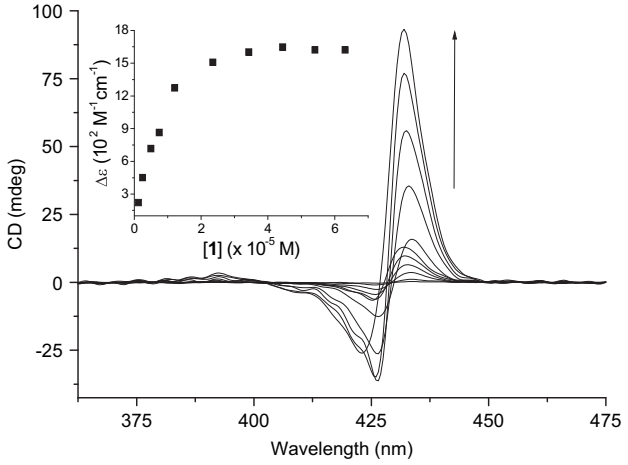


Figure 4. Induced circular dichroism spectra of the 2:1 mixture of compound **1** and *S*,*S* **2** in toluene at 25 °C at different concentrations ([**1**]=0.13–6.3×10^{-5} M). Inset: the plot of the CD molar absorptivity of **1** at 432 nm versus its concentration.

3. Conclusion

In summary, we have successfully assembled a new class of chiral eighteen-component three-dimensional supramolecular entities by making use of the cooperative interactions of the hydrogen bonding and coordination interaction as the driving forces. When the concentrations of the components are high enough, the chiral entities can be formed exclusively. This strategy may act as a new design rationale for the formation of chiral layer-styled supramolecular polymers. For this goal, we are synthesizing new chiral hexadentate ligands with their six binding sites alternately pointing to the opposite sides of the backbones. By appending two heterocyclic segments to the zinc porphyrin unit, new two-layered molecular containers may also be assembled from six monomers, which may also exhibit unique binding property.

4. Experimental section

4.1. General methods

All reactions were carried out under a dry nitrogen atmosphere. All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials were obtained from commercial suppliers and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm silica 60 coated on glass plates with F_{254} indicator. The ^{1}H and ^{13}C NMR spectra were recorded on 300, 400 or 500 MHz spectrometers in the indicated solvents. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards (^{1}H: chloroform: δ 7.26 ppm; DMSO: δ 2.49 ppm; ^{13}C: $CDCl_3$: 77.2 ppm). Elemental analysis was conducted at the SIOC analytical center. MALDI-FT spectra were obtained on a Voyager-DE STR or IonSpec 4.7 T FTMS spectrometer. UV–vis spectra were recorded on a CARY 100 spectrometer. Circular dichroism spectra were recorded on a JASCO 810 circular dichroism spectrometer.

*4.1.1. Compound **6**.* To a stirred solution of compound **5**[21] (0.37 g, 1.04 mmol), potassium carbonate (1.04 g, 7.2 mmol), and 18-crown-6 (56 mg, 0.21 mmol) in the mixture of acetonitrile (80 mL) and THF (60 mL) was added dropwise a solution of compound **4**[20] (1.08 g, 1.04 mmol) in THF (50 mL). The mixture was heated to reflux for 5.5 h and then cooled to room temperature. The solid was filtrated off and the filtrate concentrated in vacuo. The resulting residue was purified by column chromatography (AcOEt/petroleum ether 1:9) to give compound **6** as a purple solid (0.86 g, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.89–8.88 (m, 6H), 8.81 (d, *J*=4.9 Hz, 1H), 8.70 (s, 1H), 8.50 (d, *J*=9.1 Hz, 1H), 8.23 (d, *J*=9.1 Hz, 1H), 8.15 (d, *J*=7.9 Hz, 2H), 8.08–8.07 (m, 6H), 7.80–7.79 (m, 3H), 7.71 (d, *J*=7.9 Hz, 2H), 5.87 (s, 2H), 4.49 (q, *J*=7.09 Hz, 2H), 1.62 (s, 9H), 1.52 (s, 54H), 1.46 (t, *J*=7.09 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 159.3, 155.0, 154.2, 151.3, 150.4, 148.7, 141.5, 141.3, 141.1, 138.5, 137.8, 137.4, 134.4, 131.3, 129.8, 129.7, 125.5, 124.0, 122.1, 121.4, 121.3, 121.0, 120.0, 119.6, 119.5, 117.8, 111.8, 83.16, 62.19, 49.82, 35.04, 31.75, 28.23, 23.86, 14.21. MS (MALDI-TOF): *m*/*z* 1314 $[M+H]^+$. HRMS (MALDI-FT): calcd for $C_{85}H_{97}N_7O_4Cl$: 1314.7285 $[M+H]^+$. Found: 1314.7258.

*4.1.2. Compound **7**.* Compound **6** (0.34 g, 0.26 mmol) was dissolved in the mixture of dichloromethane (16 mL) and trifluoroacetic acid (8 mL). After stirring at room temperature for 1 h, the solution was concentrated with a rotavapor. The resulting residue was dissolved in ethyl acetate (50 mL) and the solution was washed with saturated sodium bicarbonate solution (20 mL), water (20 mL), and brine (20 mL), and dried over sodium sulfate. Upon removal of the solvent under reduced pressure, compound **7** was obtained as a purple solid (0.31 g, 100%). The compound was further purified by recrystallization from methanol for analysis. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.90–8.89 (m, 6H), 8.84–8.83 (m, 2H), 8.53 (s, 1H), 8.22 (d, *J*=8.0 Hz, 2H), 8.08–8.05 (m, 6H), 7.91 (d, *J*=8.5 Hz, 1H), 7.80–7.79 (m, 3H), 7.74 (d, *J*=8.0 Hz, 2H), 6.86 (d, *J*=8.5 Hz, 1H), 5.73 (br, 1H), 5.21 (d, *J*=6.97 Hz, 2H), 4.46 (q, *J*=7.1 Hz, 2H), 1.56 (t, *J*=7.1 Hz, 3H), 1.52 (s, 54H), −2.72 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 160.7, 157.4, 151.3, 148.8, 141.8, 141.4, 141.3, 137.5, 134.8, 131.5, 129.9, 129.7, 126.0, 121.6, 121.5, 121.0, 120.3, 119.1, 115.5, 61.76, 45.51, 35.06, 31.76, 14.28. MS (MALDI-TOF): *m*/*z* 1214.5 $[M+H]^+$. HRMS (MALDI-FT): calcd for $C_{80}H_{89}ClN_7O_2$: 1214.6761 [M+H]. Found: 1214.6803.

*4.1.3. Compound **8**.* Bis(*N*-ethyl guanidinium) sulfate (62 mg, 0.23 mmol) and sodium *tert*-butoxide (39 mg, 0.41 mmol) were suspended in the mixture of tetrahydrofuran (3 mL) and *tert*-butanol (3 mL), and then the mixture was heated to reflux for half an hour. The resulting turbid solution was separated from the insoluble salts by pipette and then added to compound **7** (50 mg, 0.041 mmol). The mixture was then sealed into a glass tube, heated at 170 °C for 2.5 h and cooled to room temperature. The solvent was removed with a rotavapor, and the resulting residue was purified by column chromatography (CH_2Cl_2/CH_3OH 25:1) to give compound **8** as a purple solid (26 mg, 50%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 14.36 (s, 1H), 11.26 (s, 1H), 10.88 (s, 1H), 8.88–8.87 (m, 8H), 8.63 (s, 1H), 8.28 (d, *J*=6.3 Hz, 2H), 8.01–8.00 (m, 6H), 7.92 (d, *J*=6.3 Hz, 2H), 7.78 (d, *J*=8.7 Hz, 1H), 7.57 (s, 3H), 6.86 (d, *J*=8.7 Hz, 1H), 5.41 (s, 1H), 5.11 (s, 1H), 4.52 (d, *J*=38.4 Hz, 2H), 1.70 (s, 3H), 1.34 (s, 54H), −2.72 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.2, 162.8, 160.4, 154.6, 148.7, 141.6, 141.4, 141.3, 139.6, 138.4, 138.1, 135.1, 132.2, 131.4, 131.1, 130.5, 130.3, 129.8,

125.4, 121.4, 120.9, 119.4, 113.9, 110.1, 107.5, 46.66, 35.77, 35.08, 34.93, 31.80, 31.65, 16.96. MS (MALDI-TOF): m/z 1220.0 $[M+H]^+$. HRMS (MALDI-FT): calcd for $C_{81}H_{91}N_{10}O$ 1219.7372 $[M]^+$. Found: 1219.7374.

4.1.4. Compound ***1***. Compound **8** (30 mg, 0.027 mmol) was dissolved in the solution of zinc acetate in dichloromethane and methanol (4:1) (0.05 M, 5 mL) and stirred at room temperature for 12 h. After removing the solvents with a rotavapor, the resulting residue was dissolved in dichloromethane (20 mL). The solution was washed with water (10 mL) and brine (20 mL), and dried over sodium sulfate. Upon removal of the solvent under reduced pressure, compound **1** was obtained as a purple solid (33 mg, 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 14.35 (s, 1H), 11.23 (s, 1H), 10.85 (s, 1H), 8.93–8.92 (m, 8H), 8.64 (s, 1H), 8.24 (d, J=7.0 Hz, 2H), 7.98–7.97 (m, 6H), 7.89 (d, J=7.0 Hz, 2H), 7.74 (d, J=7.3 Hz, 1H), 7.58–7.57 (m, 3H), 6.87 (d, J=7.3 Hz, 1H), 5.36 (s, 1H), 5.12 (s, 1H), 4.42–4.40 (m, 2H), 1.68–1.64 (m, 3H), 1.27 (s, 54H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.2, 160.4, 154.5, 150.4, 150.1, 148.4, 142.0, 141.8, 139.5, 138.1, 134.9, 132.3, 132.1, 131.7, 129.6, 125.1, 122.4, 120.7, 120.4, 113.8, 110.1, 107.6, 46.59, 37.41, 35.03, 34.88, 31.96, 31.76, 16.90. MS (MALDI-FT): m/z 1281.7 $[M+H]^+$. HRMS (MALDI-FT): calcd for $C_{81}H_{89}N_{10}OZn$ 1281.6507 $[M]^+$. Found: 1281.6529.

4.1.5. Compound R,R ***2***. Isonicotinic acid (0.22 mg, 1.8 mmol) was suspended in thionyl chloride (4.0 mL) and DMF (0.1 mL), heated under reflux for 1 h and then concentrated in vacuo. The resulting residue 12 was dissolved in pyridine (2.0 mL) and then the solution was added to a solution of **11**[23] (0.1 g, 0.59 mmol) in pyridine (2.0 mL). The mixture was stirred at 50 °C for 4 h and then concentrated under reduced pressure. The crude product was dissolved in dichloromethane (10 mL) and the solution washed with saturated sodium bicarbonate solution (5 mL), water (5 mL) and brine (5 mL), and dried over sodium sulfate. After removing the solvent, the resulting residue was purified by column chromatography (CH_2Cl_2/CH_3OH 50:1) to give compound *R,R* **2** as a white solid (0.13 g, 57%). $[\alpha]_D^{25}$ +148 (c 0.25, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (s, 4H), 7.34 (s, 4H), 4.38 (s, 2H), 3.59 (s, 2H), 3.13–3.10 (m, 2H), 1.94–1.91 (m, 2H), 0.92–0.87 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 150.3, 143.7, 120.6, 56.84, 44.31, 30.10, 19.30. MS (ESI): m/z 381 $[M+H]^+$. HRMS (ESI): calcd for $C_{22}H_{29}N_4O_2$ $[M+H]^+$: 380.2291. Found: 381.2285.

4.1.6. Compound S,S ***2***. Compound *S,S* **2** was prepared by using the same procedure and characterized by the ^{1}H NMR and MS methods. $[\alpha]_D^{25}$ −149 (c 0.24, CH_2Cl_2).

4.1.7. Compound R,R ***3***. Isonicotinic acid (0.22 g, 1.8 mmol) was suspended in thionyl chloride (4.0 mL) and DMF (0.1 mL). The mixture was heated to reflux for 1 h to give a light yellow solution, which was concentrated under reduced pressure to give compound **13**, which was then dissolved in pyridine (2.0 mL). To this solution was added dropwise a solution of compound **11** (96 mg, 0.59 mmol) in pyridine (2.0 mL). The mixture was stirred at 50 °C for 4 h and then concentrated in vacuo. The resulting residue was dissolved in dichloromethane (10 mL). The solution was washed with saturated sodium bicarbonate solution (5 mL), water (5 mL) and brine (5 mL), and dried over sodium sulfate. After removing the solvent with a rotavapor, the resulting residue was purified by column chromatography (CH_2Cl_2/MeOH 50:1) to give compound *R,R* **3** as a white solid (0.14 g, 63%). $[\alpha]_D^{25}$ +187 (c 0.54, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.72–8.68 (m, 4H), 7.81 (d, J=6.6 Hz, 2H), 7.43–7.40 (m, 2H), 4.36 (s, 2H), 8.75 (s, 2H), 3.12 (s, 2H), 1.98–1.90 (m, 2H), 0.90 (d, J=6.3 Hz, 6H), 0.86 (d, J=6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 150.9, 147.3, 134.5, 132.0, 123.7, 57.06, 44.57, 30.31, 19.41. MS (ESI): m/z 381 $[M+H]^+$. Anal. Calcd for $C_{22}H_{28}N_4O_2$: C, 69.45; H, 7.42; N, 14.73. Found: C, 69.02; H, 7.70; N, 14.64.

4.1.8. Compound S,S ***3***. Compound *S,S* **3** was prepared by using the same procedure and characterized by the ^{1}H NMR and MS methods. $[\alpha]_D^{25}$ −183 (c 0.54, CH_2Cl_2).

4.2. Typical procedures for the UV–vis titration and method for determining the apparent association constants[12,24]

Aliquots of a fixed solution of **2**, **3**, and **14** in toluene were added to a toluene solution of **1**, and the mixture was subjected to UV–vis spectroscopy at 25 °C. The spectrum was corrected with a dilution factor and background subtraction. The difference in absorbance (ΔA) of the receptor in the presence of the guest and absence of the guest was recorded and the data were plotted against [guest]. The UV–vis spectral change of the receptor upon titration with the guest clearly showed isobestic points, suggesting that each zinc porphyrin moiety in the receptor binds with a nitrogen ligand unit. The apparent association constants were derived by using the non-linear curve fitting based on the equation:

$$\Delta A = \Delta A_\infty \left((1 + K_{assoc}[G] + K_{assoc}[H]_0) - \left((1 + K_{assoc}[G] + K_{assoc}[H]_0)^2 - 4K_{assoc}^2[H]_0[G] \right)^{0.5} \right) \Big/ (2K_{assoc}[H]_0)$$

where $\Delta A = A - \Delta A_0$, $\Delta A_\infty - A_0$

$[G]$ is the pyridine concentration of ligands (2×[**2**], 2×[**3**] or 2×[**14**]).

$[H] = [1]$

Acknowledgements

We thank NSFC (No. 20732007), Ministry of Science and Technology of China (2007CB-808001), Chinese Academy of Sciences (KJCX2-YW-H13) and Science and Technology Commission of Shanghai Municipality (09XD1405300) for financial support.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.04.009.

References and notes

1. MacGillivray, L. R.; Atwood, J. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 1018–1033.
2. Zimmerman, S. C.; Corbin, P. S. *Struct. Bond.* **2000**, *96*, 63–94.
3. Davis, J. T.; Spada, G. P. *Chem. Soc. Rev.* **2007**, *36*, 296–313.
4. Sessler, J. L.; Lawrence, C. M.; Jayawickramarajah, J. *Chem. Soc. Rev.* **2007**, *36*, 314–325.
5. Rebek, J., Jr. *Acc. Chem. Res.* **2009**, *42*, 1660–1668.
6. Vazquez-Campos, S.; Crego-Calama, M.; Reinhoudt, D. N. *Supramol. Chem.* **2007**, *19*, 95–106.
7. Palmans, A. R. A.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 8948–8968.
8. Hembury, G. A.; Borovkov, V. V.; Inoue, Y. *Chem. Rev.* **2008**, *108*, 1–73.
9. Kumaki, J.; Sakuraiy, S.-i.; Yashima, E. *Chem. Soc. Rev.* **2009**, *38*, 737–746.
10. Prins, L. J.; De Jong, F.; Timmerman, P.; Reinhoudt, D. N. *Nature* **2000**, *408*, 181–184.
11. Feiters, M. C.; Nolte, R. J. M. *Adv. Supramol. Chem.* **2000**, *6*, 41–156.
12. Hou, J.-L.; Yi, H.-P.; Shao, X.-B.; Li, C.; Wu, Z.-Q.; Jiang, X.-K.; Wu, L.-Z.; Tung, C.-H.; Li, Z.-T. *Angew. Chem., Int. Ed.* **2006**, *45*, 796–800.
13. Yi, H.-P.; Li, C.; Hou, J.-L.; Jiang, X.-K.; Li, Z.-T. *Tetrahedron* **2005**, *61*, 7974–7980.
14. Yi, H.-P.; Wu, J.; Ding, K.-L.; Jiang, X.-K.; Li, Z.-T. *J. Org. Chem.* **2007**, *72*, 870–877.
15. Yan, Y.; Qin, B.; Shu, Y.; Chen, X.; Yip, Y. K.; Zhang, D.; Su, H.; Zeng, H. *Org. Lett.* **2009**, *11*, 1201–1204.
16. Marsh, A.; Silvestri, M.; Lehn, J.-M. *Chem. Commun.* **1996**, 1527–1528.
17. Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1998**, *120*, 9092–9093.

18. Fenniri, H.; Mathivanan, P.; Vidale, K. L.; Sherman, D. M.; Hallenga, K.; Wood, K. V.; Stowell, J. G. *J. Am. Chem. Soc.* **2001**, *123*, 3854–3855.
19. Yang, Y.; Xue, M.; Xiang, J.-F.; Chen, C.-F. *J. Am. Chem. Soc.* **2009**, *131*, 12657–12663.
20. Salom-Roig, X. J.; Chambron, J.-C.; Goze, C.; Heitz, V.; Sauvage, J.-P. *Eur. J. Org. Chem.* **2002**, 3276–3280.
21. Ma, Y.; Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2002**, *124*, 13757–13769.
22. Jin, S.; Ma, Y.; Zimmerman, S. C.; Cheng, S. Z. D. *Chem. Mater.* **2004**, *16*, 2975–2977.
23. Soai, K.; Hayashi, H.; Shinozaki, A.; Umebayashi, H.; Yamada, Y. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3450–3452.
24. Li, W.-S.; Jiang, D.-L.; Suna, Y.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 7700–7702.
25. Wilson, G. S.; Anderson, H. L. *Chem. Commun.* **1999**, 1539–1540.
26. Camara-Campos, A.; Hunter, C. A.; Tomas, S. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 3034–3038.
27. Hunter, C. A.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 7488–7499.
28. Zhu, Y.-Y.; Li, C.; Li, G.-Y.; Jiang, X.-K.; Li, Z.-T. *J. Org. Chem.* **2008**, *73*, 1745–1751.
29. Wu, J.; Hou, J.-L.; Li, C.; Wu, Z.-Q.; Jiang, X.-K.; Li, Z.-T.; Yu, Y.-H. *J. Org. Chem.* **2007**, *72*, 2897–2905.