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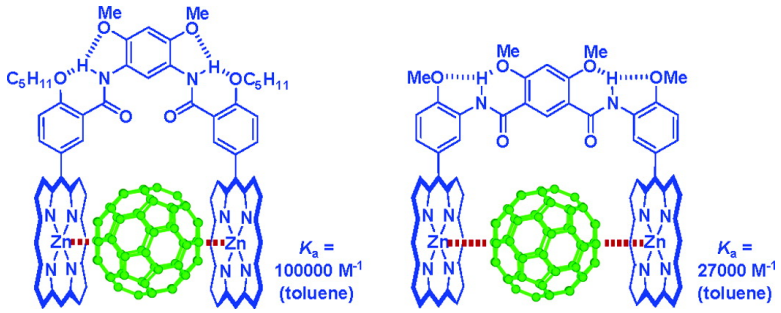

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Hydrogen-Bonding-Driven Preorganized Zinc Porphyrin Receptors for Efficient Complexation of C_{60}, C_{70}, and C_{60} Derivatives

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Abstract: This paper describes the self-assembly of a new class of foldamer-based molecular tweezers, whose rigid folded conformations are stabilized by intramolecular hydrogen bonding. Two zinc porphyrin units are introduced to the ends of molecular tweezers Zn_2**1** and Zn_2**2**, while three zinc porphyrin units are incorporated to the S-shaped bi-tweezers Zn_3**3**, which may be regarded as a combination of two Zn_2**1** molecules. Due to the preorganized U-shaped feature, Zn_2**1** and Zn_2**2** are able to strongly complex C_{60}, C_{70}, and C_{60} derivative **25** in chloroform or toluene in a 1:1 binding stoichiometry, whereas Zn_3**3**, which possesses two tweezer units, complexes the guests in a 1:2 stoichiometry. More stable complex Zn_3**3·24** is formed between Zn_3**3** and **24**, a linear molecule bearing two C_{60} moieties at the ends, as a result of the cooperative interaction of two binding sites. Chiral induction is observed for all the three receptors upon complexation with C_{60}-incoporated chiral phenylalanine derivative **29**, although the complexation of **29** by the folding receptors is pronouncedly weaker than that of C_{60} and **25** due to increased steric hindrance. The driving force for the formation of the complexes is the well established $\pi-\pi$ stacking between the zinc porphyrin and fullerene units. The ^{1}H and ^{13}C NMR, UV−vis, fluorescent, and circular dichroism spectroscopy have been used to investigate the complexing behavior of the folding receptors and the fullerene guests. The association constants of the corresponding complexes in toluene and chloroform (if possible) have been evaluated with the UV−vis and fluorescent titration experiments.

Introduction

Efficient recognition of the synthetic receptor for a special molecule or ion requires high structural and binding-site complementarity between the receptor and the guest. For spherical guests, macrocyclic receptors are usually of high efficiency because the recognition sites in these receptors are pre-organized in the cavity to favorably surround a specific guest.[1] Another class of efficient receptors for spherical guests are rigid, covalently bonded molecular tweezers, which are able to employ their two "jaws" to closely hold a binding site-matching "prey".[2] Nevertheless, the synthesis of both kinds of receptors are usually of low efficiency or time consuming.[3] Moreover, the structural modifications for achievement of a site-tailored recognition are frequently difficult.

Fullerenes and their derivatives are a class of attractive spherical molecules that have been applied extensively in discrete research areas. After the first reports of the cocrystallization of C_{60} or C_{70} with the porphyrin unit, the search for highly efficient porphyrin receptors has become intensified.[4] A number of bisporphyrin[5] and multiporphyrin receptors[6] have been developed and the resulting porphyryn−fullerene assemblies have brought forward many interesting photophysical,

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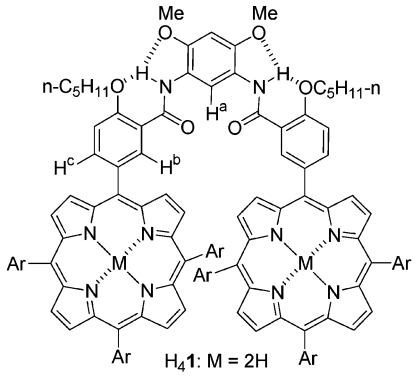
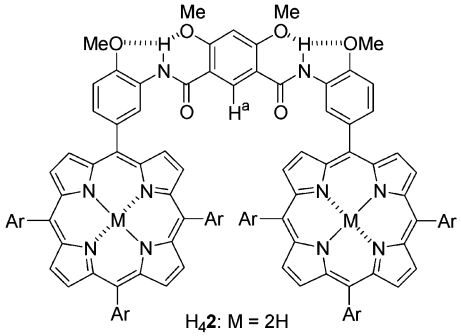
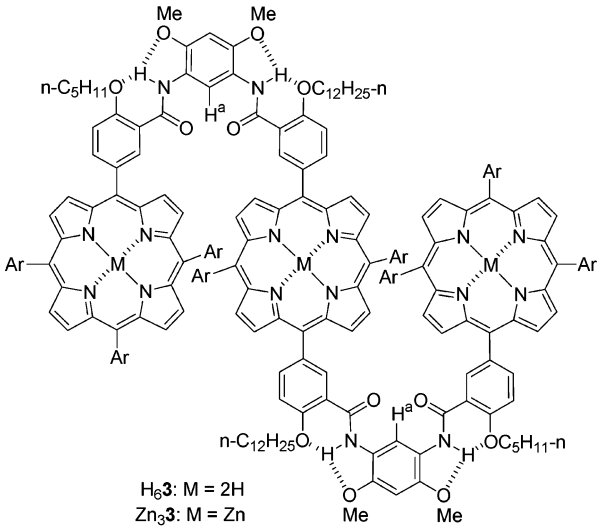
10.1021/ja056509h CCC: $30.25

photochemical, and/or electrochemical properties.[7] In the past decade, foldamers, linear molecules that are driven by noncovalent forces to adopt well-established secondary structures, have received increasing attention.[8] Because of its strength and directionality, hydrogen bonding is an ideal driving force for the construction of foldamers. A number of foldamers with rigid and predictable conformations have been developed based on rationally designed aromatic amide oligomers.[9−16] Some of the foldamers have been reported as new receptors for recognition of saccharides[14a,14d] or alkylammoniums[14e] or encapsulation of water.[15a] Example of foldamers that can promote oxidation of pyridine has also been described.[15b] We envisioned that introduction of additional binding units to rationally designed folding scaffolds would lead to new generation of tailored receptors with robust recognition ability. In this paper, we report the self-assembly of such a class of hydrogen-bonding-driven porphyrin-appended folding receptors, which exhibit remarkably high binding affinity for C_{60}, C_{70}, and C_{60} derivatives in chloroform and toluene.[17−19]







Results and Discussion

Three porphyrin foldamer receptors Zn_2**1**, Zn_2**2**, and Zn_3**3** have been designed, which were based on the recent observations that intramolecular three-centered hydrogen bonding[20] can induce linear anthranilamide oligomers to adopt rigid zig-zag or straight conformation.[14c,21] Both Zn_2**1** and Zn_2**2** were incorporated with two porphyrin units. It was expected that, due to the existence of the intramolecular hydrogen bonding, the porphyrin units in both compounds would be arranged roughly parallel to each other to produce two noncovalently bonded molecular tweezers. Compound Zn_3**3** might be regarded as combination of two molecules of Zn_2**1**.

The synthesis of Zn_2**1** is presented in Scheme 1. Compound **4**[22] was first alkylated to produce aldehyde **5**, which then reacted

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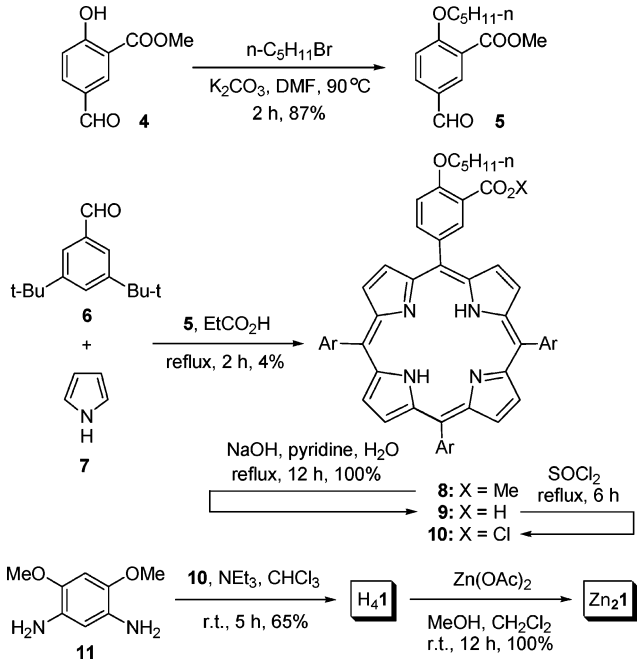
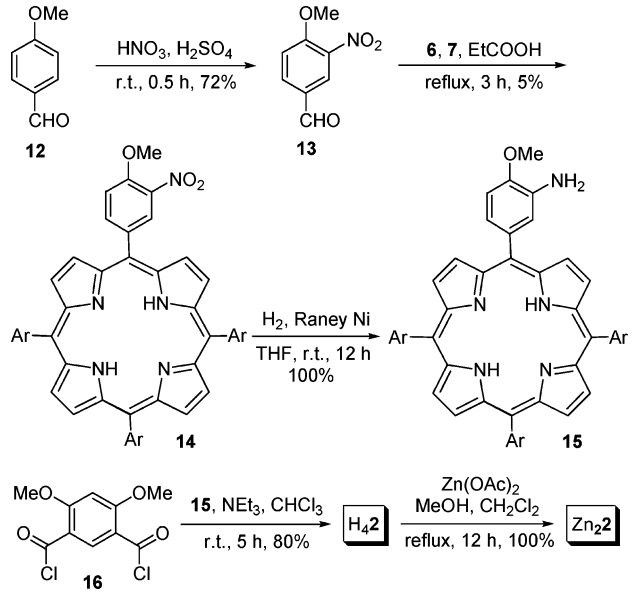
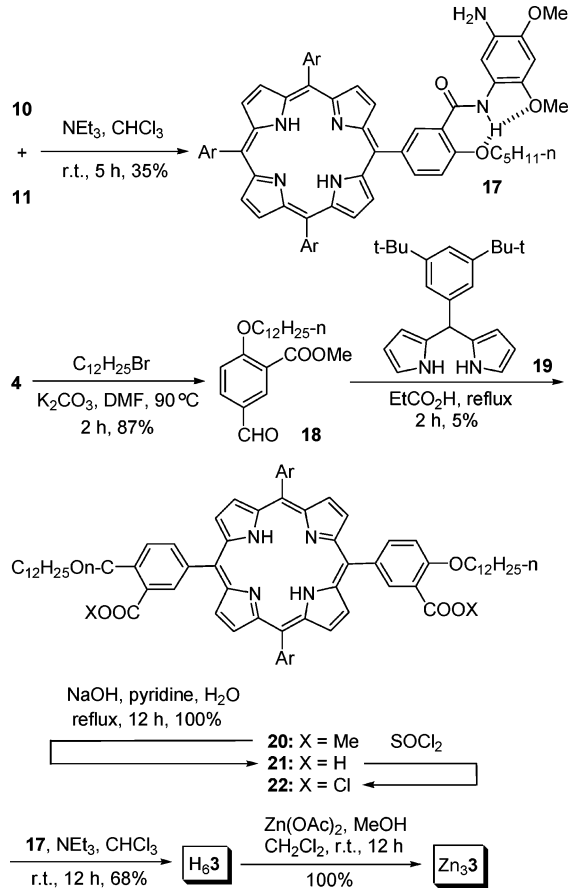
Scheme 1



Scheme 2



Scheme 3



with **6**[23] and pyrrole in refluxing propionic acid to afford porphyrin **8**.[24] The latter was then hydrolyzed with sodium hydroxide and further converted to acyl chloride **10** with thionyl chloride. Treatment of **10** with **11**[25] afforded H_4**1**, which then reacted with zinc acetate to give Zn_2**1** in quantitative yield. For the synthesis of Zn_2**2** (Scheme 2), compound **13**[26] was first prepared from nitration of **12** in concentrated sulfuric acid and then reacted with **6** and **7** in refluxing propionic acid to afford porphyrin **14**. This intermediate was reduced to amine **15** and then reacted with **16**[27] to yield compound H_4**2**, which was then treated with zinc acetate in methanol and dichloromethane to afford Zn_2**2** in high yield.

The synthetic route for Zn_3**3** is shown in Scheme 3. Porphyrin **17** was first prepared from the reaction of compounds **10** and **11** in chloroform, and then compound **18** was obtained by alkylation of **4** in hot DMF. Treatment of **18** with dipyrrole **19** in hot propionic acid produced porphyrin diester **20**. This intermediate was then hydrolyzed with sodium hydroxide and followed by treatment with thionyl chloride to afford **22**. The latter intermediate was further reacted with **17** in chloroform to yield porphyrin trimer H_6**3**. Finally, treatment of H_6**3** with zinc acetate produced Zn_3**3** quantitatively. Compounds Zn_2**1**, Zn_2**2**, and Zn_3**3** have been characterized by the ^{1}H, ^{13}C NMR,

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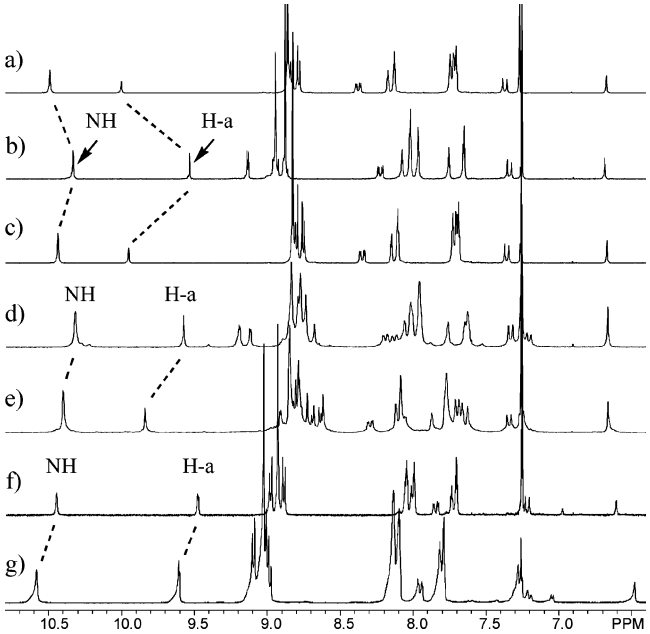

Figure 1. Partial ^{1}H NMR spectrum of (a) Zn_2**1** (4.0 mM) + C_{70} (1:1), (b) Zn_2**1** (4.0 mM), (c) Zn_2**1** (4.0 mM) + C_{60} (1:1), (d) Zn_4**3** (2.0 mM), (e) Zn_4**3** (2.0 mM) + C_{60} (1:2), (f) Zn_2**2** (4.0 mM), and (g) Zn_2**2** (4.0 mM) + C_{60} (1:1) in $CDCl_3$ at 25 °C.

and (HR) mass spectroscopy or microanalysis and are of good solubility in organic solvents such as chloroform and toluene.

Previous X-ray and spectroscopic investigations have revealed a rigid planar conformation for the diamide skeletons in Zn_2**1**, Zn_2**2**, and Zn_3**3** due to the intramolecular three-centered hydrogen bonding.[11a,14c,21] Molecular modeling (see Supporting Information) showed that the two porphyrin units in the folded Zn_2**1** and Zn_2**2** form a rigid tweezer, with a spatial separation of approximately 12 and 13 Å from the center of the porphyrin units. Such distances are very suitable to sandwich a C_{60} or C_{70} molecule.[28] Trimer Zn_3**3** may be considered a combination of two molecules of Zn_2**1** and the spatial separation between its neighboring porphyrin units should be comparable to that of Zn_2**1**. In principle, Zn_3**3** may exist in a S- or C-shaped conformation, depending on the orientation of the two peripheral porphyrin units relative to the central porphyrin unit. The S-shaped conformation should be of lower energy considering that it avoids any possible steric hindrance, which is expected from the two peripheral porphyrin units in the C-shaped conformation.

The ^{1}H NMR spectra of Zn_2**1**, Zn_4**3**, and Zn_2**2** in chloroform-*d* are shown in Figure 1. All three spectra are of high resolution, and the signals in the downfield area have been assigned based on the 2D-NOESY experiments. Although in principle Zn_4**3** has two sets of different amide protons, only one single signal is exhibited for the NH protons in its ^{1}H NMR spectrum. It can be found that the signal of the amide protons of all the three compounds appears in the downfield area (10.34, 10.33, and 10.23 ppm, respectively). This observation supports the formation of the intramolecular three-centered O···H−N hydrogen bonding in these compounds. Dilution of their solutions in chloroform-*d* did not produce important shifting of signals (<0.008 ppm from 10 to 0.2 mM) in the ^{1}H NMR spectrum.

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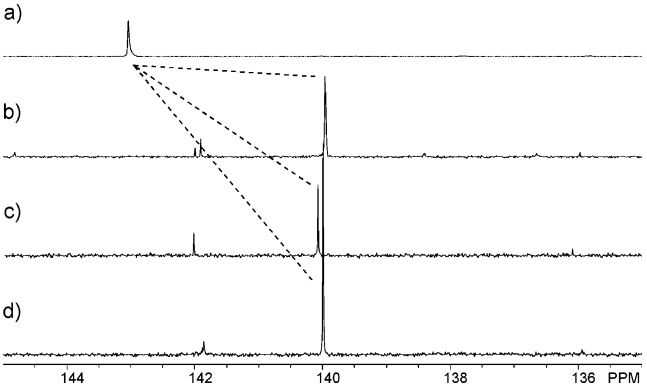


Figure 2. Partial ^{13}C NMR spectrum of (a) C_{60} (2.0 mM), (b) Zn_2**1** (2.0 mM) + C_{60} (1:1), (c) Zn_2**2** (2.0 mM) + C_{60} (1:1), and (d) Zn_3**3** (1.0 mM) + C_{60} (2.0 mM) in $CDCl_3$ containing 5% CS_2 at 25 °C.

Moreover, the UV−vis absorbance (Soret band) of all three compounds in chloroform observes Beer's law in the concentration range of less than 50 μM. These results show that the porphyrin units in these molecules do not significantly interact with each other both intramolecularly and intermolecularly.

Addition of 1 equiv of C_{60} to the solution of the three compounds in chloroform-*d* caused substantial change of several signals in their ^{1}H NMR spectrum.[29] For example, the signal of the amide proton of Zn_2**1** shifted from 10.34 to 10.44 ppm, while its H−a signal moved from 9.54 to 9.96 ppm (Figure 1c). These observations can be rationalized by considering that encapsulation of C_{60} within the porphyrin tweezer reduces the conformational flexibility of the porphyrins relative to the bisanthranilamide moiety[30] and consequently strengthens the intramolecular hydrogen bonding. This strengthened hydrogen bonding again increases the defielding effect of the C═O group to H−a.[10,31] Similar downfield shifting was also observed for both Zn_4**3** ($\Delta\delta$: 0.07 ppm for NH and 0.26 ppm for H−a) and Zn_2**2** ($\Delta\delta$: 0.13 ppm for both NH and H−a) (parts e and g of Figure 1). All the results suggest a strong interaction between the porphyrin tweezers and C_{60}. Similar downfield shifting was also observed when C_{60} was replaced with C_{70}. For example, when 1 equiv of C_{70} was added to the solution of Zn_2**1** in chloroform-*d*, the NH and H−a signals ($\Delta\delta$ 0.12 and 0.46 ppm, respectively) of Zn_2**1** moved downfield substantially (parts a and c of Figure 1). The values are even larger than those observed for Zn_2**1** induced by C_{60}, implying an even stronger interaction between the porphyrin receptor and C_{70} (vide infra).[5a,b]

Strong encapsulation of C_{60} by the porphyrin receptors was also supported by the ^{13}C NMR spectroscopy (Figure 2). The spectrum of the 1:1 solution of C_{60} and Zn_2**1**, Zn_2**2**, and Zn_3**3** in chloroform and carbon disulfide revealed significant upfield shifting ($\Delta\delta$: −3.01, −2.94, and −3.10 ppm, respectively) of the C_{60} signal relative to that of the free C_{60} (143.03 ppm).[32] This upfield shifting is obviously resulted from the shielding or ring current effect of the zinc porphyrin units of the receptors

(29) Both C_{60} and C_{70} are scarcely soluble in chloroform. Addition of the zinc porphyrin receptors substantially increases their solubility and the homogeneous phase, obtained after sonication, is stable at room temperature.
(30) The X-ray analysis reveals a torsion angle of 16° between the peripheral benzene and the central benzene in the solid state in the bisanthranilamide moiety, see ref 14c.
(31) The defielding of the encapsulated C_{60} might also be partially responsible for the large downfield shifting of the H−a signal.
(32) All the spectra were recorded in chloroform-*d* containing 10% (v/v) of carbon disulfide, in which the ^{13}C NMR spectrum of C_{60} could be recorded.

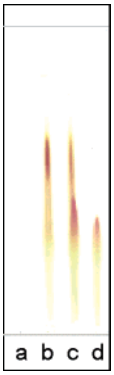


Figure 3. TLC (developed in iodine vapor) of (a) C_{60} (R_f = ca. 1.0, the spot is too pale to scan), (b) Zn_2**1** + C_{60} (1:1), (c) Zn_2**1** + C_{60} (2:1), and (d) Zn_2**1.** TLC condition: silica gel plate/CS_2−$CHCl_3$ (1:2).

upon strong encapsulation of the guest.[5a−c] Straight-phase thin-layer chromatography (TLC) analysis, which exhibited a new spot for the complexes, also indicated the formation of stable complexes between the receptors and C_{60} or C_{70}. As an example, Figure 3 provides the TLC result of the complexation of C_{60} by Zn_2**1**.

Upon addition of C_{60} to the solution of the receptors in toluene, the Soret band of the receptors in the UV−vis spectrum was shifted notably (from 423.6 nm to 427.2, 427.0, and 427.1 nm, respectively, for Zn_2**1**, Zn_2**1**, and Zn_3**3**). Replacement of C_{60} with C_{70} of the identical concentration caused even larger red shift. The results are consistent with the above ^{1}H and ^{13}C NMR observations, also suggesting strong electronic interaction between the porphyrin receptors and the fullerene guest.[5a] As examples, parts a and b of Figure 4 present the UV−vis spectra of Zn_2**1** in toluene in the presence of incremental amount of C_{60} and C_{70}. Job's plot analysis based on the UV−vis experiments, as shown in Figure 5, supported a 1:1 stoichiometry for complexes Zn_2**1**:C_{60} and Zn_2**2**:C_{60} and a 1:2 stoichiometry for complex Zn_3**3**:C_{60}, which exhibited a largest change of absorbance at the 1:1 and 1:2 ratio of the receptor and C_{60} when the total concentration of the two samples was kept unchanged.[33,34] The ^{1}H NMR spectra for [Zn_2**1**]:[C_{60}] = 1:0−1:3 in chloroform-*d* at 25 °C revealed a saturation of complexation-induced chemical shift change at [Zn_2**1**]:[C_{60}] = 1:0 (see Figure 1S in Supporting Information), also supporting the 1:1 stoichiometry of their complex. Figure 6 shows the proposed binding mode for the 1:1 and 1:2 complexes. Because C_{70} exhibits a stronger binding affinity than C_{60},[28a] it is reasonable to consider that its complexes with the porphyrin receptors should have similar binding mode.

The association constants (K_a) of complexes Zn_2**1**·C_{60} and Zn_2**2**·C_{60} in toluene were then evaluated by the UV−vis titration method. The absorption spectral change of the receptors induced by addition of C_{60} displayed a clear isosbestic point both at 429 nm (Figure 3a). On the basis of the change values of absorbance with [C_{60}], we estimated the K_a of the two complexes to be 1.0 (±0.1) × 10^5 and 2.7 (±0.2) × 10^4 M^{-1}, respectively.[35] Similar spectroscopic changes were also observed when incremental amount of C_{70} was added to the solution of Zn_2**1** and Zn_2**2** in toluene and the K_a of complexes Zn_2**1**·C_{70} and Zn_2**2**·C_{70} was determined to be 1.1 (±0.1) × 10^6 and 9.8 (±1.2) × 10^5 M^{-1}, respectively, by the same method. The association constant of Zn_2**1**·C_{70} and Zn_2**2**·C_{70} is pronouncedly greater than that of the corresponding C_{60} complexes. This is in accordance with the above ^{1}H NMR observation and implies that the complexation of C_{70} by the porphyrin receptors occurs mainly at its equatorial region rather than its poles.[5b] Such a binding mode can lead to greater $\pi-\pi$ contact area from the less curved region of C_{70} to the porphyrin units of the receptors.[28a]

The Job's plot study described above has established that receptor Zn_3**3** can complex two fullerene molecules. Also from the UV−vis titration experiments, we determined the apparent association constant K_a of the single porphyrin tweezer of Zn_3**3** with C_{60} and C_{70} in toluene to be 1.5 (±0.1) × 10^4 and 6.7 (±1.0) × 10^4 M^{-1}, respectively.[36] The association constant of the present complexes are pronouncedly higher than that of the complexes of C_{60} with the palladium-linked bisporphyrin "jaws", reported by Boyd and Reed et al.,[18] demonstrating that the intramolecular hydrogen bonding in the present receptors plays an important role in increasing the binding affinity of the new preorganized foldamer receptors toward fullerene guest.

In principle, incorporation of two C_{60} units into one guest molecule would double the binding site and should, in the absence of large steric hindrance, increase its binding affinity to receptor Zn_3**3**. On the basis of this consideration, C_{60} dimer **24** was designed and prepared from amine **23**, which could be produced conveniently from the reaction of C_{60}, glycine and dodecyl aldehyde in refluxing chlorobenzene.[37] For the sake of comparison, compound **25** was also prepared from the acylation of **23**. Introduction of the long aliphatic chains provides both 24 and **25** with good solubility in chloroform and toluene.

Mixing the same equivalents of Zn_3**3** with **24** in chloroform-*d* also led to significant change of the signals of both molecules in the ^{1}H NMR spectrum. Especially, the NH signal of the receptor moved downfield remarkably, as observed above for the complex of Zn_2**1** with C_{60} or C_{70}. Similar shifting was also observed in the ^{1}H NMR spectrum of the solution of Zn_2**1** with **25**. These results clearly showed that important interaction also occurs between Zn_2**1** and the new C_{60} derivatives. Quantitative binding behavior between Zn_3**3** and **24** and **25** was investigated in chloroform and toluene with the UV−vis titration method. The UV−vis spectra of Zn_3**3** in chloroform, obtained with addition of incremental amount of **24** and **25**, are provided in parts c and d of Figure 4. The data obtained upon addition of **24** to the solution of Zn_3**3** in chloroform were fit to a 1:1 binding mode, giving K_a = 1.8 (±0.2) × 10^7 M^{-1} for complex Zn_3**3**·24. The K_a of Zn_3**3**·24 in toluene is obviously beyond the limit of the UV−vis titration method,[28b] because the absorbance change was linearly dependent on the concentration of **24** when 0−1 equiv of **24** was added and became unchanged when more amount of **24** was added. By virtue of the analysis method described above for the complexes of Zn_3**3** and C_{60} or C_{70}, the

(33) Job, P. *Ann. Chim. Ser. 10* **1928**, *9*, 113.
(34) The ^{1}H NMR titration experiments in chloroform-*d* also revealed that the NH and H−a signals of Zn_2**1** shifted downfield with the addition of C_{60} and achieved the maximum values when 1 equiv of C_{60} was added. Further addition of C_{60} did not cause shifting of the signals, and the C_{60} added was not dissolved neither.
(35) Conners, K. A. *Binding Constants: The Measurement of Molecular Complex Stability* Wiley: New York, 1987.
(36) The apparent association constant may be regarded as the averaged value of the K_a of the discrete zinc porphyrin tweezers when the receptor contains more than one zinc porphyrin tweezers. For a recent example of the method, see: Li, W.-S.; Jiang, D.-L.; Suna, Y.; Aida, T. *J. Am. Chem. Soc.* **2005**, *127*, 7700.
(37) Herranz, M. A.; Illescas, B.; Martin, N.; Luo, C.; Guldi, D. M. *J. Org. Chem.* **2000**, *65*, 5728.

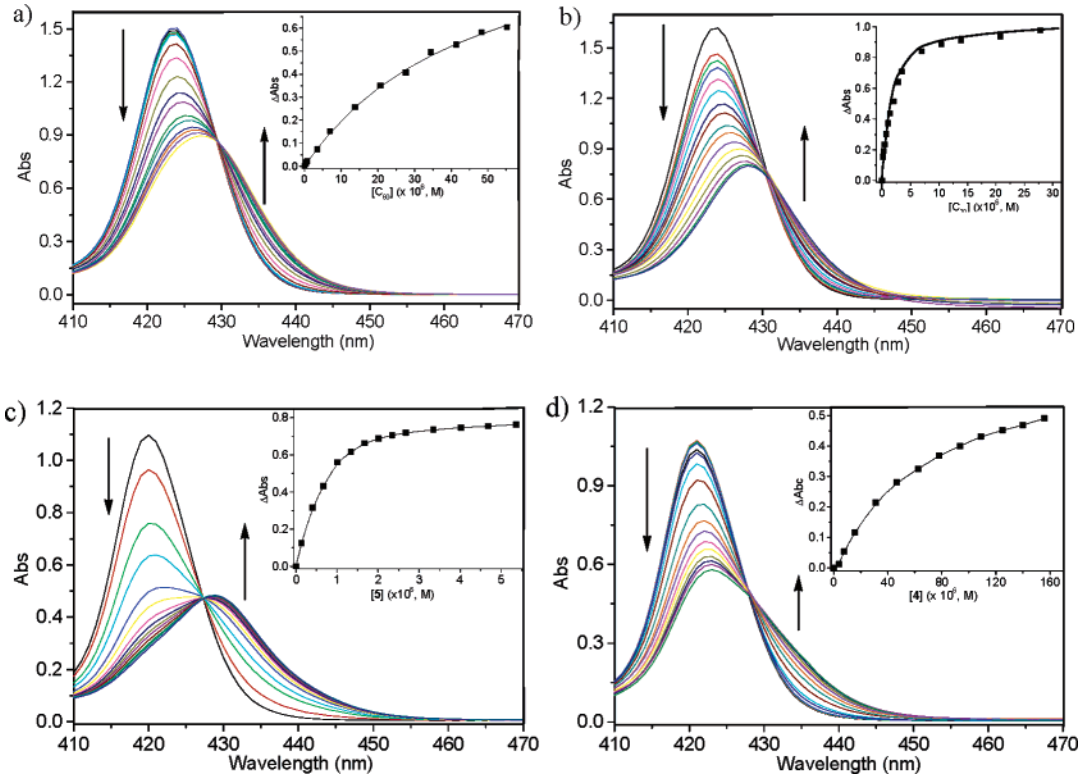


Figure 4. Absorption spectral changes of Zn_2**1** (1.5 μM) upon addition of (a) C_{60} and (b) C_{70} in toluene at 25 °C. Absorption spectral changes of Zn_3**3** (0.67 μM) upon on addition of (c) **24** and (d) **25**. All the spectra were recorded in chloroform at 25 °C (the absorbance of the fullerene unit had been subtracted from the spectra; inset, the plot of the absorbance change vs [C_{60}] or [C_{70}]).

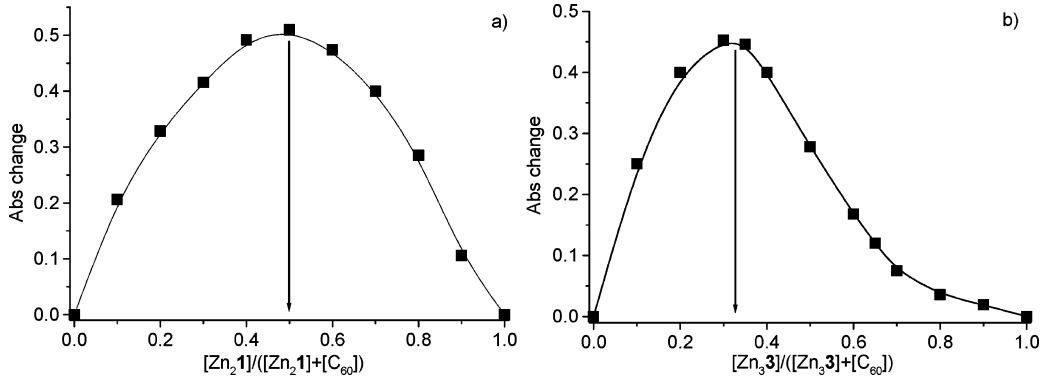


Figure 5. Job's plots: absorbance change of the Soret band at 428 nm of (a) Zn_2**1** vs [Zn_2**1**]/([Zn_2**1**] + [C_{60}]) and (b) Zn_3**3** vs [Zn_3**3**]/([Zn_3**3**] + [C_{60}]) in toluene at 25 °C (the overall concentration = 5.0×10^{-6} M).

apparent association constant K_a for the complex of the single tweezer of Zn_3**3** with **25** in chloroform and toluene was determined to be 1.3 ($\pm$0.1) $\times$ 10^4 and 8.6 ($\pm$0.8) $\times$ 10^4 M^{-1}, respectively. The stability of Zn_3**3**·24 is substantially higher than that of the complex of Zn_3**3** and **25** due to the doubling of its binding site (Figure 7). On the basis of the UV−vis titration, the K_a of complexes Zn_2**1**·25 and Zn_2**2**·25 in chloroform and toluene was also evaluated to be 1.6 ($\pm$0.2) $\times$ 10^4 and 6.0 ($\pm$1.0) $\times$ 10^4 M^{-1} and 7.9 ($\pm$1.2) $\times$ 10^3 and 1.2 ($\pm$0.1) $\times$ 10^4 M^{-1}, respectively. Compared to that of the complexes of C_{60}, the stability of the complexes of **25** is notably decreased as a result of the additional aliphatic moiety in **25**. To explore the influence of the solvent polarity on the binding affinity, the K_a of complex Zn_2**1**·25 in mixture of chloroform and methanol (9:1 v/v) was also evaluated, which gave rise to a value of 2.3 ($\pm$0.3) $\times$ 10^3 M^{-1}. The value is pronouncedly smaller than that of the complex obtained in chloroform, indicating that the addition of polar methanol would weaken the intramolecular hydrogen bonding of the receptor and consequently reduced its preorganization.

The complexing behavior of **24** by Zn_2**1** and Zn_2**2** was also investigated. Job's plot studies based on the UV−vis experiments revealed a 1:1 stoichiometry for their complexes in both chloroform and toluene (see Figure 2S in Supporting Information). The corresponding association constant in chloroform and toluene was evaluated to be 4.7 ($\pm$0.1) $\times$ 10^4 and 7.6 ($\pm$0.6) $\times$ 10^5 for Zn_2**1**·24 and 4.1 ($\pm$0.4) $\times$ 10^4 and 1.8 ($\pm$0.2) $\times$ 10^5 for Zn_2**2**·24, respectively. It can be found that the stability of Zn_2**1**·24 and Zn_2**2**·24 in toluene is significantly higher than that of the corresponding complexes Zn_2**1**·C_{60} and Zn_2**2**·C_{60} but substantially lower than that of Zn_3**3**·24 in chloroform of high polarity. This result reflects that the existence of the second C_{60} unit in **24** may promote the binding stability of Zn_2**1**·24

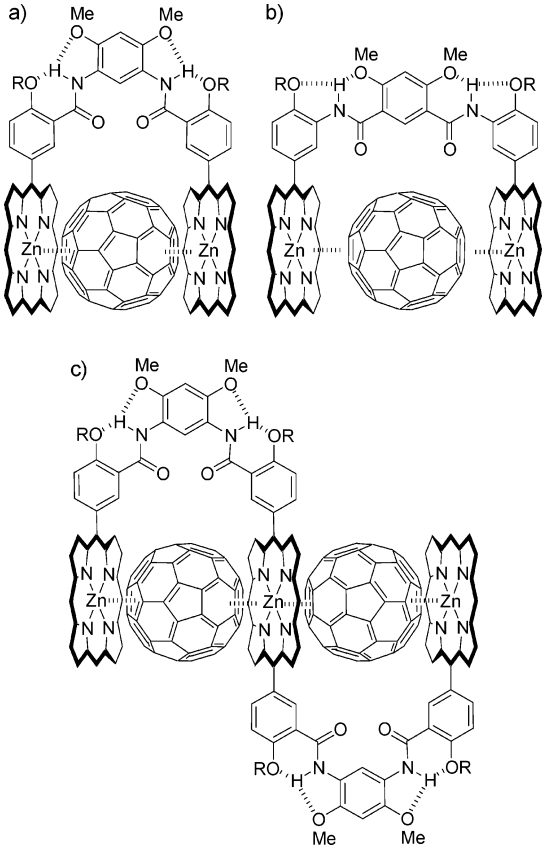


Figure 6. The binding mode for complexes (a) Zn_2**1**·C_{60}, (b) Zn_2**2**·C_{60}, and (c) Zn_3**3**·$2C_{60}$.

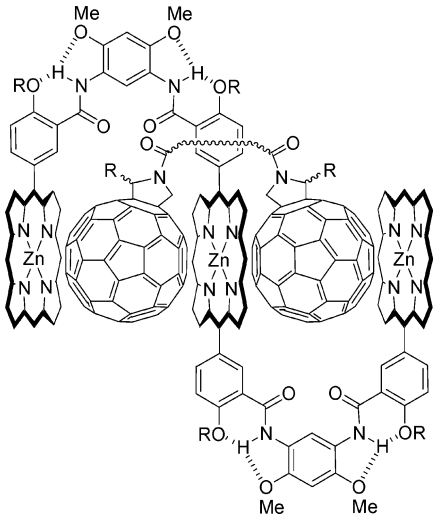


Figure 7. The proposed binding mode for complex Zn_3**3**·24.

and Zn_2**2**·24 by additional aromatic interaction with the porphyrin unit of the receptors, as shown in Figure 8 (with Zn_2**1** as example). Such additional interaction is obviously of low efficiency compared to that between C_{60} and the porphyrin units of a tweezer. The fact that three-component complexes $(Zn_2\mathbf{1})_2$·24 and $(Zn_2\mathbf{2})_2$·24 were not formed (in measurable amount) implies a large spatial repulsion might exist between the two large bisporphyrin molecules in such possible tricomponent complexes. Only one set of signals was displayed in the downfield area of the ^{1}H NMR spectrum of both complexes in

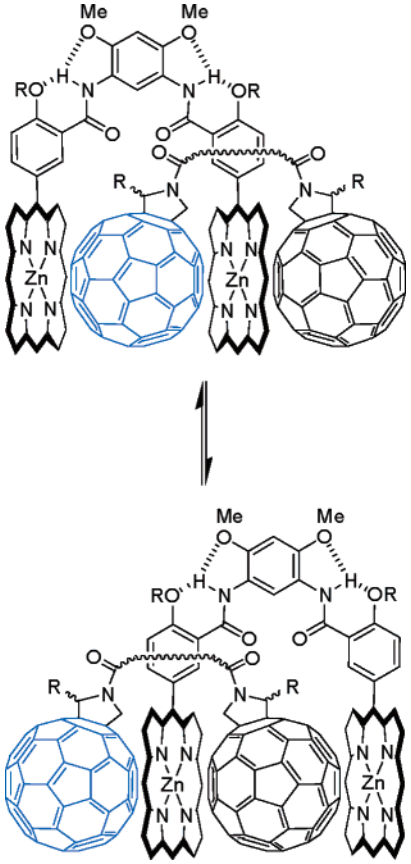


Figure 8. Dynamic exchanging process for complex Zn_2**1**·24.

chloroform-*d* and did not split even under reduced temperature. This observation indicates that the exchanging process for complexes Zn_2**1**·24, as shown in Figure 8, and Zn_2**2**·24 is quick on the ^{1}H NMR time scale.

Fluorescent studies revealed that the emission of the zinc porphyrin units of the receptors could be efficiently quenched by the fullerene guests. All the receptors exhibited typical emission bands of the zinc porphyrin units at ca. 606 and 643 nm upon excitation at the isosbestic point of their Soret band.[38] The quenching results of the first emission with fullerene receptors in toluene are provided in Table 1. It can be found that the quenching efficiency of Zn_3**3** by **24** is substantially higher than any other receptor-guest system. This result is consistent with the above UV−vis investigation, reflecting the remarkably increased complexing affinity between Zn_3**3** and **24** due to the doubling of their binding site. Figure 9 presents the fluorescent spectra of Zn_3**3** in toluene in the presence of increasing amount of **24**. The emission of the porphyrin units of Zn_3**3** could not be quenched completely even in the presence of excessive **24**,[19l] which may be rationalized by considering that the complexation is a dynamic process and there is always a small amount of free Zn_3**3** in the solution. On the basis of the change of the emission strength at 606 nm with [**24**], the K_a of complex Zn_3**3**·24 was evaluated to be 3.4 (±0.4) × 10^8 M^{-1}.[39] For the sake of comparison, the K_a of complex Zn_2**1**·25 in

(38) Solladié, N.; Walther, M. E.; Gross, M.; Duarte, T. M. F.; Bourgogne, C.; Nierengarten, J.-F. *Chem. Commun.* **2003**, 2412.
(39) (a) Hauke, F.; Swartz, A.; Guldi, D. M.; Hirsch, A. *J. Mater. Chem.* **2002**, *12*, 2088. (b) D′Souza, F.; Chitta, R.; Gadde, S.; Zandler, M. E.; McCarty, A. L.; Sandanayaka, A. S. D.; Araki, Y.; Ito, O. *Chem.−Eur. J.* **2005**, *11*, 4416. (c) Sessler, J. L.; Jayawickramarajah, J.; Gouloumis, A.; Torres, T.; Guldi, D. M.; Maldonado, S.; Stevenson, K. J. *Chem. Commun.* **2005**, 1892.

Table 1. Fluorescent Quenching Data of Receptors Zn_2**1**, Zn_2**2**, and Zn_3**3** by the Fullerene Guests in Toluene at 25 °C

		I^b ($[I_0 - I]/I_0$)[c]				(M)[d]			
	I_0[a]	C_{60}	C_{70}	**24**	**25**	$[C_{60}]$	$[C_{70}]$	[**24**]	[**25**]
Zn_2**1**	262	252 (0.04)	165 (0.24)	179 (0.32)	230 (0.12)	3.7×10^{-5}	3.1×10^{-6}	1.5×10^{-6}	8.0×10^{-6}
Zn_2**2**	248	235 (0.03)	199 (0.24)	225 (0.12)	238 (0.04)	3.1×10^{-5}	2.8×10^{-6}	9.1×10^{-6}	3.4×10^{-5}
Zn_3**3**	221	212 (0.04)	165 (0.25)	10 (0.95)	195 (0.04)	3.8×10^{-5}	2.8×10^{-6}	2.8×10^{-7}	8.6×10^{-6}

[a] Values of pure receptors at [porphyrin] = 2.0×10^{-6} M. [b] Values when 1 equiv of fullerene guest ([fullerene] = 2.0×10^{-6} M) was added. [c] Quenching efficiency. [d] Guest concentration at $[I_0 - I]/I_0 = 0.5$.

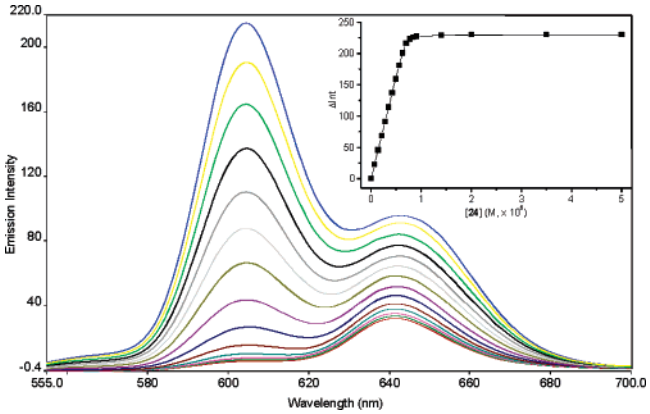
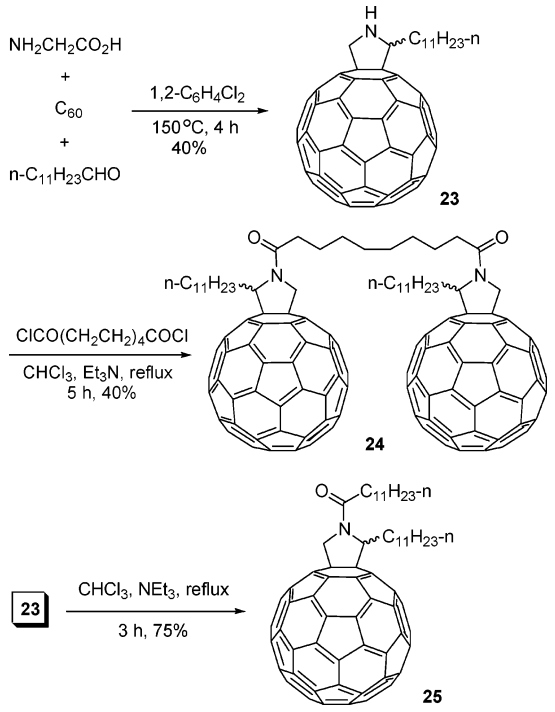


Figure 9. Fluorescence spectral changes of Zn_3**3** (7.0×10^{-7} M) upon addition of **24** ($0-5.0 \times 10^{-6}$ M) in toluene at 25 °C. Excitation wavelength = 429 nm at the isosbestic point of the UV−vis spectra. Inset: the plot of change emission intensity at 606 nm vs [**24**].

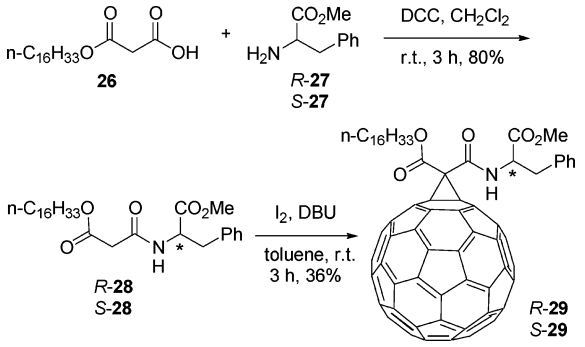
chloroform and the apparent K_a of complexes of Zn_3**3** with C_{60} and C_{70} in toluene were also evaluated by the fluorescent titration method, which afforded a value of 1.8 (±0.1) × 10^4, 1.4 (±0.2) × 10^{-4}, and 7.4 (±1.1) × 10^{-4} M^{-1}, respectively. These results are in good accordance with those estimated from the UV−vis titration method.

Given the strong complexing feature between the foldamer-based porphyrin tweezers and the fullerene guests, the possibility of supramolecular chiral induction through complexation of the foldamer receptors toward chiral C_{60} derivative **29** was explored.[40,41] The synthesis of **29** is shown in Scheme 5. Briefly, treatment of **26** with **27** in chloroform in the presence of DCC afforded **28**, which reacted with C_{60} in hot toluene to give **29**. The K_a of complexes Zn_2**1**·29 and Zn_2**2**·29 in chloroform was evaluated to be 3.2 (±0.3) × 10^3 and 1.5 (±0.2) × 10^3 M^{-1}, while the apparent K_a of the complex of the single tweezer of Zn_3**3** with **29** was determined to be 2.6 (±0.3) × 10^3 M^{-1}. The values are notably lower than that of the corresponding complexes of **25**, which can be attributed to the increased size of the aliphatic moiety of **29** relative to that of **25**. Adding *R*-**29** or *S*-**29** to the solution of the porphyrin receptors in chloroform led to the generation of induced circular dichroism (CD) of mirror image, as shown in Figure 10 (the CD spectrum of the C_{60} guest had been subtracted). The spectral modes of the complexes of Zn_2**1** and Zn_2**2** are comparable, reflecting a similar pattern of chiral induction. In contrast, Zn_3**3** displays a strong Cotton effect in region of the porphyrin Soret band. The results may be ascribed to the different orientation of the two chiral guest molecules, relative to each other, in the three-component

Scheme 4



Scheme 5



complexes, which lead to a different orientation of the three poprhyrin chromophores in Zn_3**3**. Although the relative strength is significantly varied, the Cotton effects between 500 and 650 nm of all the porphyrin receptors do not shift significantly.

Conclusion

In summary, we have described the self-assembly of a new class of molecular tweezers whose rigid skeletons are constructed based on the intramolecular hydrogen-bonding-driven aromatic amide foldamers. The new zinc porphyrin-based, well-ordered tweezers represent new efficient nonring receptors for complexation of fullerene and fullerene-derived molecules. Because of their preorganized rigid conformation, the new folding receptors exhibit a fullerene-binding ability that can be

(40) A chiral porphyrin-C_{60} triad had been reported, see: Kessinger, R.; Thilgen, C.; Mordasini, T.; Diederich, F. *Helv. Chim. Acta* **2000**, *83*, 3069.
(41) (a) Huang, S.; Nakanishi, S.; Berova, N. *Chirality* **2000**, *12*, 237. (b) Pescitelli, G.; Gabriel, S.; Wang, Y.; Fleischhauer, J.; Woody, R. W.; Berova, N. *J. Am. Chem. Soc.* **2003**, *125*, 7613.

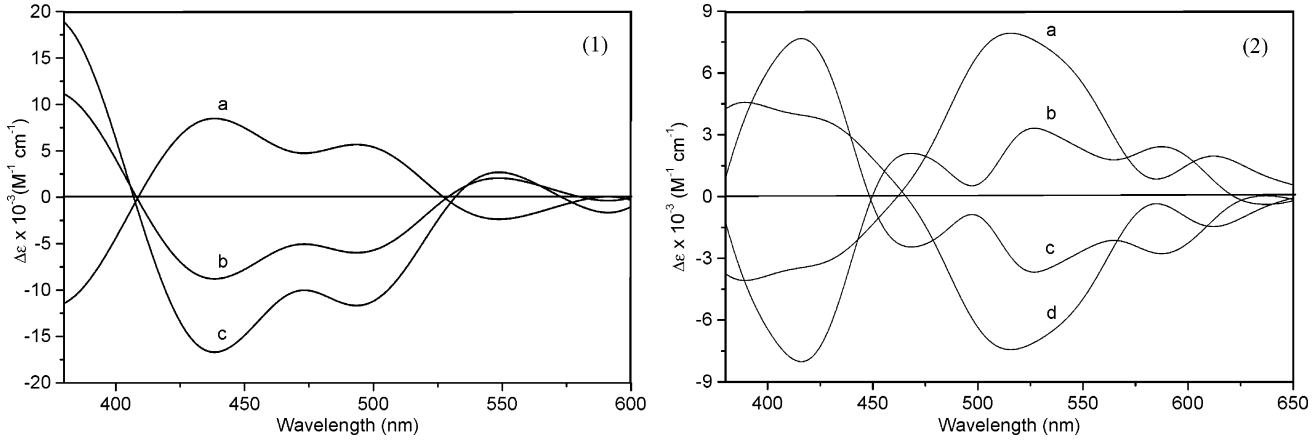


Figure 10. The induced CD spectra in chloroform at 25 °C. (1) Zn_2**1** (3.3×10^{-4} M) in the presence of *S*-**29** (3.3×10^{-3} M) (a), *R*-**29** (3.3×10^{-3} M) (b), and *R*-**29** (6.6×10^{-3} M) (c); (2) Zn_2**2** (3.3×10^{-4} M) in the presence of *S*-**29** (3.3×10^{-3} M) (a) and *R*-**29** (3.3×10^{-3} M) (d) and Zn_3**3** (2.3×10^{-4} M) in the presence of *S*-**29** (3.3×10^{-3} M) (b) and *R*-**29** (3.3×10^{-3} M) (c).

Table 2. Summary of the Association Constants of the New Porphyrin−Fullerene Complexes Determined by the UV−Vis Titration Method

complex	K_a (M^{-1})	solvent	complex	K_a (M^{-1})	solvent
Zn_2**1**·C_{60}	1.0×10^5	toluene	Zn_2**1**·C_{70}	1.1×10^6	toluene
Zn_2**2**·C_{60}	2.7×10^4	toluene	Zn_2**2**·C_{70}	9.8×10^5	toluene
Zn_3**3**·C_{60}[b]	$1.5\ 10^4$	toluene	Zn_3**3**·C_{70}[b]	6.7×10^4	toluene
Zn_3**3**·C_{60}[b,c]	1.4×10^4	toluene	Zn_3**3**·C_{70}[b,c]	7.4×10^4	toluene
Zn_2**1**·**24**	7.6×10^5	toluene	Zn_2**1**·**24**	4.7×10^4	chloroform
Zn_2**2**·**24**	1.8×10^5	toluene	Zn_2**2**·**24**	4.1×10^4	chloroform
Zn_3**3**·**24**	1.8×10^7	chloroform	Zn_3**3**·**24**[c]	3.4×10^8	toluene
Zn_2**1**·**25**	6.0×10^4	toluene	Zn_2**1**·**25**	1.6×10^4	chloroform
Zn_2**1**·**25**	2.3×10^3	chloroform[d]	Zn_2**1**·**25**[c]	1.8×10^4	chloroform
Zn_2**2**·**25**	1.2×10^4	toluene	Zn_2**2**·**25**	7.9×10^3	chloroform
Zn_3**3**·**25**[b]	8.6×10^4	toluene	Zn_3**3**·**25**[b]	1.3×10^4	chloroform
Zn_2**1**·**29**	3.2×10^3	chloroform	Zn_2**2**·**29**	1.5×10^3	chloroform
Zn_3**3**·**29**[b]	2.6×10^3	chloroform			

[a] The association constants are typically averages of two experiments at 25 °C. [b] Apparent association constant, representing the average binding ability of the single tweezer of the receptor to the fullerene guest. [c] Determined by the fluorescent titration method. [d] With 10% (v) of methanol.

comparable to the cyclic bisporphyrin receptors.[5a] The association constants of the new complexes are summarized in Table 2. The results well demonstrate the great potential of hydrogen bonding-induced foldamers or related well-ordered rigid architectures as building blocks or scaffolds for developing new synthetic receptors, which opens new possibility in molecular recognition and self-assembly.

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Supporting Information Available: Detailed experimental procedures and characterization of the intermediates and target molecules, examples of the ^{1}H NMR, UV−vis and fluorescent titration spectra, methods for evaluating the association constants and binding stoichiometry, energy-minimized conformation of the receptors, and complete ref 11a. This material is available free of charge via the Internet at http://pubs.acs.org.

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