Axial coordination changes the morphology of porphyrin assemblies in an organogel system†

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The gelation properties of a zinc porphyrin bearing peripheral urea groups (**1·Zn**) were evaluated in the absence and the presence of several diamines. In aromatic solvents such as benzene, toluene and *p*-xylene, **1·Zn** only provided the precipitate. In contrast, **1·Zn** with 0.5 and 1.0 equiv. of piperazine formed gels, and the gel with 0.5 equiv. of piperazine showed a unique physical property called 'thixotropy'. On the other hand, upon addition of similar diamines such as DABCO, ethylenediamine and *N*,*N*′-dimethylethylenediamine, **1·Zn** did not gelate these solvents. When the critical gelation concentration was plotted against the ratio of piperazine *versus* **1·Zn**, it afforded a minimum breakpoint at 0.5 equiv. and the critical concentration increased with further increase in the fraction of piperazine, indicating that the stable gel is formed from the **1·Zn** + piperazine 2 : 1 complex and the subsequent transformation to the 1 : 1 complex rather destabilizes the gel. Very interestingly, it was clearly shown by SEM and TEM observations that such structural changes of the unit complex induced by the ratio of piperazine *versus* **1·Zn** can lead to gradual morphological transitions: that is, spherical structure at 0 equiv., 1-D fibrous structure at 0.5 equiv. and 2-D sheet-like structure at 1.0 equiv. In addition, UV-VIS spectra revealed that **1·Zn** itself adopts a J-aggregation mode, whereas **1·Zn** + piperazine 2 : 1 and 1 : 1 complexes adopt an H-like aggregation mode. On the other hand, upon addition of 0.5 equiv. of other diamines, **1·Zn** + diamine complexes result in different morphologies other than the 1-D fibrous structure. To explore a reasonable rationale for these results, we conducted computational studies. As a result, we found that the complex symmetry of the unit complex plays an important role in determining the final ordered structure.

Introduction

Organogels are thermo-reversible soft materials composed of three-dimensional (3-D) networks created by the spontaneous assembly of low molecular mass molecules. In the field of supramolecular chemistry, they can be recognized as specific systems in which nano- and micro-scale geometrical superstructures such as one-dimensional (1-D) fibrous, two-dimensional (2-D) sheet-like and 3-D ribbon-like and helical structures are created according to their specific self-assembling manners.[1–5] The fact implies that the superstructure of molecular assemblies thus created strongly reflects the shape of each molecular unit, because they basically are constructed by assembling molecular units *via* various non-covalent interactions. Therefore, to clarify a correlation relationship between the molecular shape and the aggregation mode would enable us to explore new potential applications of nano- and micro-scale objects in chemistry and material sciences. Recently, we found that introduction of hydrogen-bond-forming groups into peripheral meso-phenyl groups or a metal ion into a porphyrin ring can tune the aggregation mode of porphyrin rings in organogel systems; for example, J-aggregated **1** and **2** create 2-D sheet-like structures, whereas H-aggregated **1·Cu** and **3** create 1-D fibrous structures.[6,7] Furthermore, if one can reversibly change the unit structure of gelator molecules, their gelation properties and morphologies would become reversibly controllable. As far as we are aware, there are few successful examples.[2–5] Especially, examples in which the gelation properties are drastically affected by additives have scarcely been reported.[5] We thus approached a new strategy for controlling metalloporphyrin-based superstructures by addition of diamine ligands which can act as axial ligands. It is well-known that metalloporphyrins self-assemble with coordinative molecules to create geometrical complexes and their shapes largely depend on the kind and the amount of coordinal molecules added.[8–12] It occurred to us that the skilful use of such axial ligands in organogel systems would allow us to control gelation properties and gel morphology by a change in the aggregation mode of porphyrin–diamine complexes. With this idea in mind, we used Zn(II) complexes of **1** (**1·Zn**) and several diamine molecules and evaluated whether diamine molecules can play an important role in controlling the porphyrin-based superstructures.

Results and discussion

Gelation properties

The gelation abilities of **1·Zn** in the absence and the presence of several diamines were tested for three aromatic solvents by the

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Table 1 Gelation properties of **1·Zn** in the absence and the presence of diamines[a]

Diamine (the stoichiometry for **1·Zn**)	Benzene	Toluene	*p*-Xylene
None	P	P	P
Piperazine (0.5 equiv.)	G (3.0)	G (3.0)	G (2.0)
Piperazine (1.0 equiv.)	G (30)	G (20)	G (10)
DABCO (0.5 or 1.0 equiv.)	PG	PG	PG
Other diamines[b] (0.5 or 1.0 equiv.)	P	P	P

[a] G, PG and P denote gelation, partial gelation and precipitate, respectively. The critical gelation concentration (g dm^{-3}) is shown in parenthesis. P and PG are at [gelator] = 30 g dm^{-3}. [b] Ethylenediamine and *N*,*N*′-dimethylethylenediamine.

'stable-to-inversion of a test tube' method (Table 1). **1·Zn** did not gelate all solvents tested herein with 30 g dm^{-3}. Interestingly, when each amine was added to **1·Zn**, **1·Zn** with 0.5 and 1.0 equiv. of piperazine acted as a good gelator for benzene, toluene and *p*-xylene, whereas **1·Zn** with other amines formed a partial gel (1,4-diazabicyclo[2.2.2]octane (DABCO)) or precipitates (ethylenediamine and *N*,*N*′-dimethylethylenediamine). Furthermore, we found that **1·Zn** + 0.5 equiv. of piperazine gel used herein shows a unique physical behaviour called '*thixotropy*' in aromatic solvents.[13] Generally, a low molecular-weight gel cannot regenerate its original gel state once it is converted from the gel state to the sol state by physical stimuli such as vibration. As shown in Fig. 1, on the other hand, **1·Zn** with 0.5 equiv. of piperazine gel again formed its original gel state when it was left at room temperature for a few seconds after its gel state had been collapsed by vibration. In contrast, **1·Zn** with 1.0 equiv. of piperazine gel did not show such behaviour, resulting in the precipitate after several minutes. This difference of physical properties is dependent on the added amount of piperazine and seems to determine the shape and morphology of these gels. Through these findings, we tried to seek a reasonable rationale as to why the gelation properties of **1·Zn** are drastically affected by added piperazine. We thus investigated the properties of **1·Zn** + diamine from the both sides of morphological observation and spectral analyses.

SEM and TEM observations

First of all, to have an insight into the morphology of the architectures formed by **1·Zn** and **1·Zn** + piperazine gels in benzene, we conducted SEM and TEM observations. Surprisingly, as seen from Fig. 2, the superstructures are remarkably changed depending upon the stoichiometry between piperazine and **1·Zn**. The precipitate of **1·Zn** gives a spherical structure with 0.1–5 μm diameter (Fig. 2a and 2d). When **1·Zn** and piperazine form the 2 : 1 complex, the resultant benzene gel creates a 1-D fibrous structure which develops into a highly 3-D network (Fig. 2b and 2e). Furthermore, the structure of 1 : 1 complex + benzene gel is transformed into a 2-D sheet-like structure (Fig. 2c and 2f). The more-magnified visual image (Fig. 2f) obtained from TEM observation shows the presence of a fine striped structure, indicating that a highly-ordered molecular array is constructed in this sheet-like structure. The fact supports the view that the physical properties of these gels are controllable by the amount of piperazine added.

We took SEM images of the aggregates of **1·Zn** + other diamine complexes in benzene. While all dried samples prepared from **1·Zn** + diamine 1 : 1 complexes commonly form the morphology based on the 2-D sheet-like structure (Fig. 2c and 3d–e), some dried samples prepared form 2 : 1 complexes afford new morphologies different from that of **1·Zn** + piperazine 2 : 1 complex which gives the 1-D fibrous structure: that is, the 2-D sheet-like structure for DABCO and the amorphous structure for ethylenediamine and *N*,*N*′-dimethylethylenediamine (Fig. 2b and 3a–c). In addition, FT-IR spectral data consistently support the morphological difference of 2 : 1 complexes dependent on the sort of diamine (Fig. 4b and 4d–f). In general, when hydrogen-bonding interactions among urea groups become stronger, IR absorption bands assignable to amide I and amide II appear at lower and higher wave number region, respectively. Amide I and amide II of each **1·Zn** + diamine 2 : 1 complex were observed at expected wave numbers; (piperazine) 1627 and 1580, (DABCO) 1628 and 1575, (ethylenediamine) 1630 and 1571, (*N*,*N*′-dimethylethylenediamine) 1631 and 1571 cm^{-1}. These data mean that the hydrogen-bonding interactions among urea groups in **1·Zn** + piperazine and DABCO 2 : 1 complexes are stronger than those in **1·Zn** + ethylenediamine and *N*,*N*′-dimethylethylenediamine 2 : 1 complexes, suggesting that former two complexes fabricate more ordered superstructures than latter two complexes. These results indicate that the morphological difference dependent on the sort of diamine reflects the gel properties of **1·Zn**.

Stoichiometry of complexes

Secondly, we investigated the correlation between the unit structure and the aggregation mode of **1·Zn** + piperazine complex in the gel phase in detail. To estimate the stochiometry of **1·Zn** + piperazine complexes in benzene gels, we evaluated whether the critical gelation concentrations (CGC) of **1·Zn** + piperazine complex in benzene gels are influenced by the concentration of piperazine

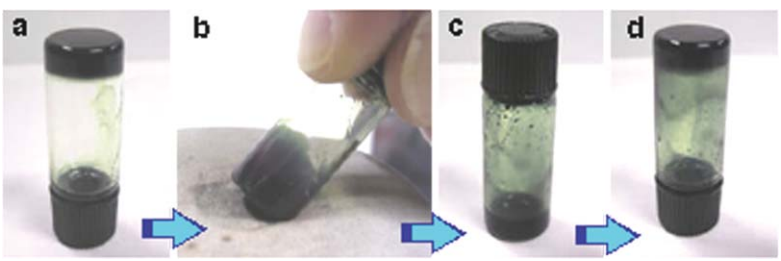

Fig. 1 Photographs showing the thixotropic behaviour of **1·Zn** + piperazine 2 : 1 complex + benzene gel; (a) the benzene gel, [**1·Zn**] = 10 g dm^{-3} (5.2 mM), [piperazine] = 0.5 equiv. for **1·Zn**, (b) shaking the gel with a vibrator, (c) leaving the gel for several seconds, (d) the regenerated gel state.

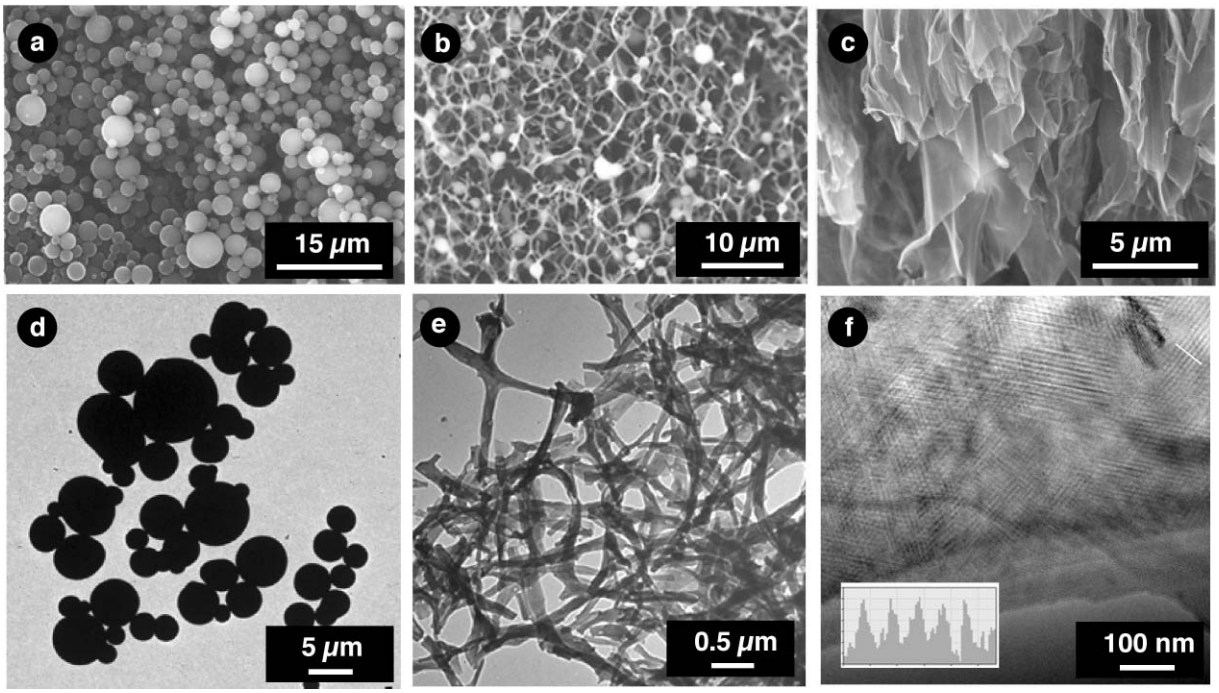

Fig. 2 SEM (a–c) and TEM (d–f) images of xerogels prepared from (a and d) the aggregate of **1·Zn** and **1·Zn** + piperazine (b and e) 2 : 1 and (c and f) 1 : 1 complexes gels in benzene; [**1·Zn**] = 10 g dm^{-3} (5.2 mM), [piperazine] = 0.5 or 1.0 equiv. for **1·Zn**. Inset shows cross-section analysis in the image of (f). White line in the image represents the place scanned.

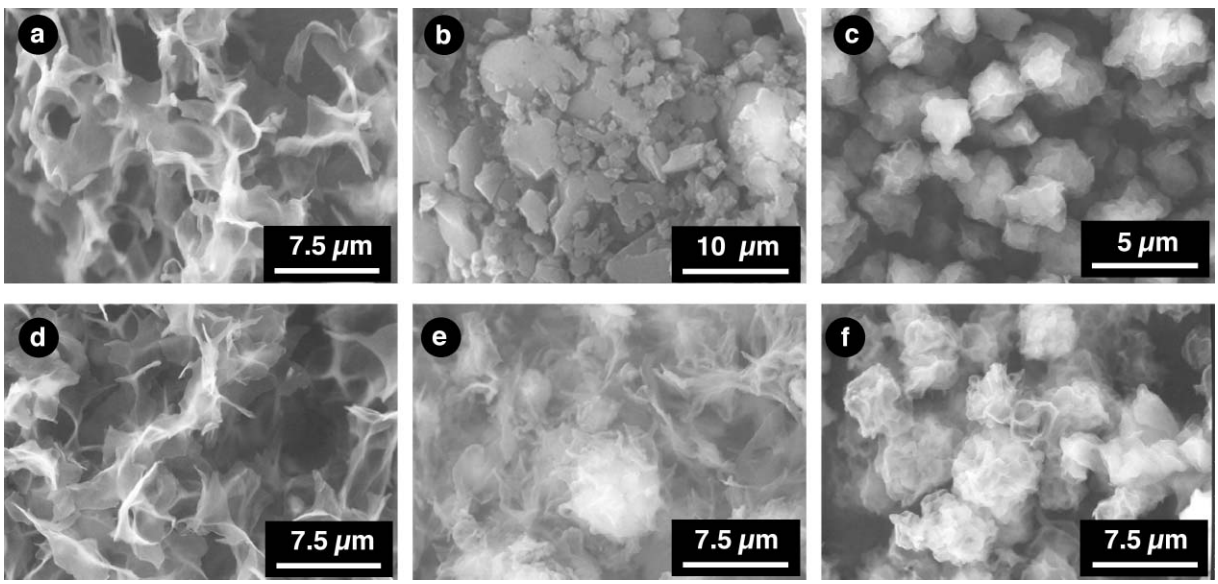

Fig. 3 SEM images of dried samples prepared from the aggregates of **1·Zn** + diamine (a–c) 2 : 1 and (d–f) 1 : 1 complexes in benzene; (a and d) DABCO, (b and e) ethylenediamine and (c and f) *N*,*N*′-dimethylethylenediamine, [**1·Zn**] = 10 g dm^{-3} (5.2 mM), [diamine] = 0.5 and 1.0 equiv. for **1·Zn**.

with respect to **1·Zn**. When less than 0.2 equiv. of piperazine is added, the mixture gives the precipitate, whereas when more than 0.2 equiv. of piperazine is added, **1·Zn** + piperazine complex is able to gelate benzene. A plot of CGC *versus* [piperazine]/[**1·Zn**] gives a minimum at [piperazine]/[**1·Zn**] = 0.5 and the CGC increases with the increase in [piperazine]/[**1·Zn**] (Fig. 5). This change indicates that the benzene gel is most stabilized when **1·Zn** and piperazine form the 2 : 1 complex originating from axial coordination to Zn(II), whereas it is gradually destabilized by transformation to the 1 : 1 complex with the increase in the added amount of piperazine.

Further evidence for the stoichiometry of these complexes was obtained from ^{1}H NMR spectra using **4·Zn** as a reference compound, because no useful information was obtained from **1·Zn** itself because of the serious peak broadening. The chemical shift of the β-proton in ^{1}H NMR titration of a benzene solution of **4·Zn** by piperazine showed that **4·Zn** and piperazine initially form a 2 : 1 **4·Zn**–piperazine complex, which is then transformed to a

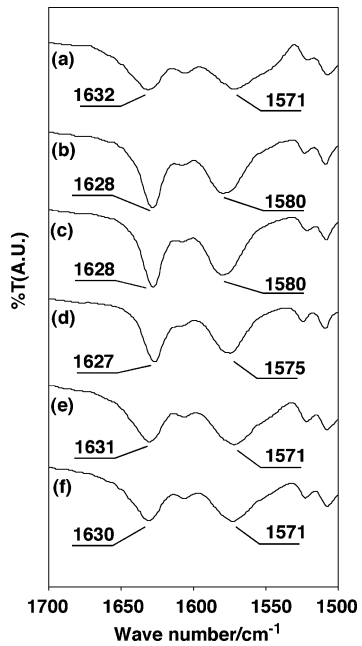

Fig. 4 FT-IR spectra of (a) the aggregate of **1·Zn** only, **1·Zn** + piperazine (b) 2 : 1 and (c) 1 : 1 complexes gels and the aggregates of **1·Zn** + (d) DABCO, (e) ethylenediamine and (f) *N*,*N*′-dimethylethylenediamine 2 : 1 complexes in benzene; [**1·Zn**] = 10 g dm^{-3} (5.2 mM), [piperazine] = 0.5 and 1.0 equiv. and [other diamine] = 0.5 equiv. for **1·Zn**.

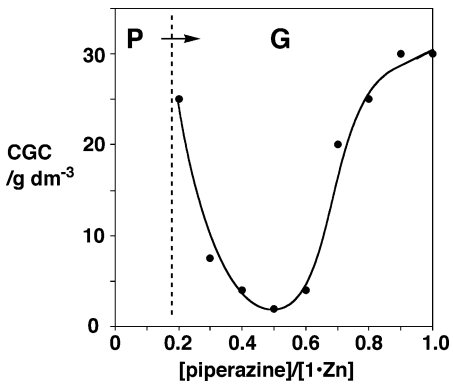

Fig. 5 A plot of CGC *versus* [piperazine]/[**1·Zn**] in benzene; G and P denote gelation and precipitate, respectively.

1 : 1 complex with the increase in the ratio of [piperazine]/[**4·Zn**] with the same concentration of [**1·Zn**] (5.2 mM) as observed for other spectral and microscopic analyses (Fig. 6). This view was judged from ^{1}H NMR titration datum of porphyrin derivative + diamine complex reported by Anderson *et al.*[11] In addition, the FT-IR spectra showed that the addition of piperazine does not give any damage on the hydrogen-bonding network among intramolecular urea-to-urea groups in **1·Zn** [amide I and amide II: (0 equiv.) 1632 and 1571, (0.5 equiv.) 1628 and 1580, (1.0 equiv.) 1628 and 1580 cm^{-1}] (Fig. 4a–c). These spectral results consistently support the view that **1·Zn** and piperazine form 2 : 1 and 1 : 1 complexes owing to axial coordination in the gel phase. Judging from both results of these data and SEM observations, the gradual transformation of the unit component induced by axial coordination can successfully result in the dimensional control of porphyrin-based superstructures. In addition, considering from

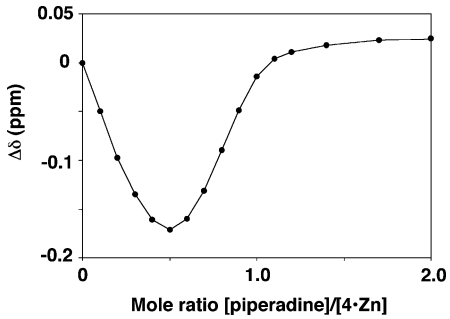

Fig. 6 ^{1}H NMR titration of piperazine into the benzene solution of **4·Zn**. $\Delta\delta$ is the change in chemical shift of the β-proton.

the fact that the added diamine does not directly affect the hydrogen-bonding network among the urea groups in the gel phase of **1·Zn**, we assume that **4·Zn** without urea groups can be used as a model compound of **1·Zn** in order to gain information about the formation of the complex in a solution phase.

UV-VIS absorption spectroscopic analyses

UV-VIS absorption measurements of **1·Zn** in the absence and the presence of piperazine were carried out to obtain an insight into the aggregation mode. The UV-VIS absorption spectrum of a homogeneous solution of reference compound **4·Zn** gave a Soret band at 425.5 nm in benzene. In the aggregate of **1·Zn** in benzene, it shifted to longer wavelength (441.0 nm), indicating that it assembles into a J-aggregate (Fig. 7a and 8a). Upon the addition of piperazine to the benzene solution of **4·Zn**, the Soret

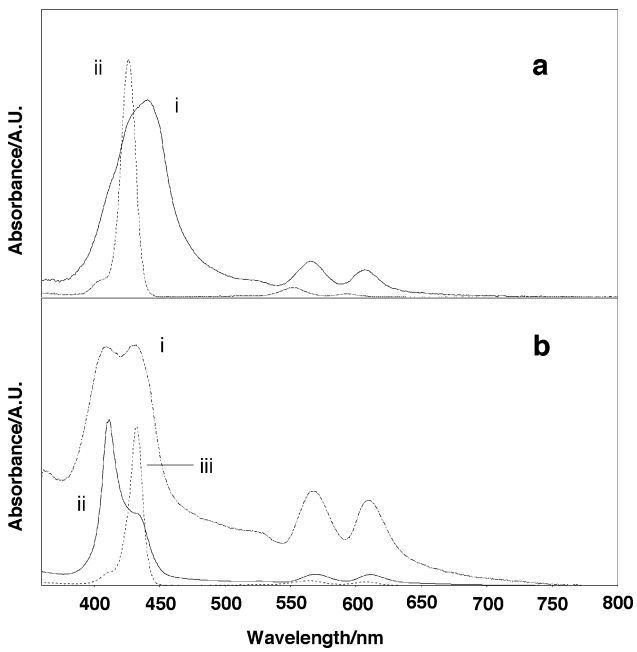

Fig. 7 UV-VIS absorption spectra of (a) the aggregate (i, 5.2 mM) of **1·Zn** and the solution (ii, 1.5 × 1^{-6} M) of **4·Zn** and (b) **1·Zn** + piperazine 2 : 1 (i, 5.2 mM) and 1 : 1 (ii, 5.2 mM) complex gels and the solution of **4·Zn** + piperazine 1 : 1 complex (iii, 1.5 × 1^{-6} M) in benzene at 25 °C. The saturated spectrum obtained from the titration of piperazine into the benzene solution of **4·Zn** was adopted as the spectrum of **4·Zn** + piperazine 1 : 1 complex (refer to the ESI).

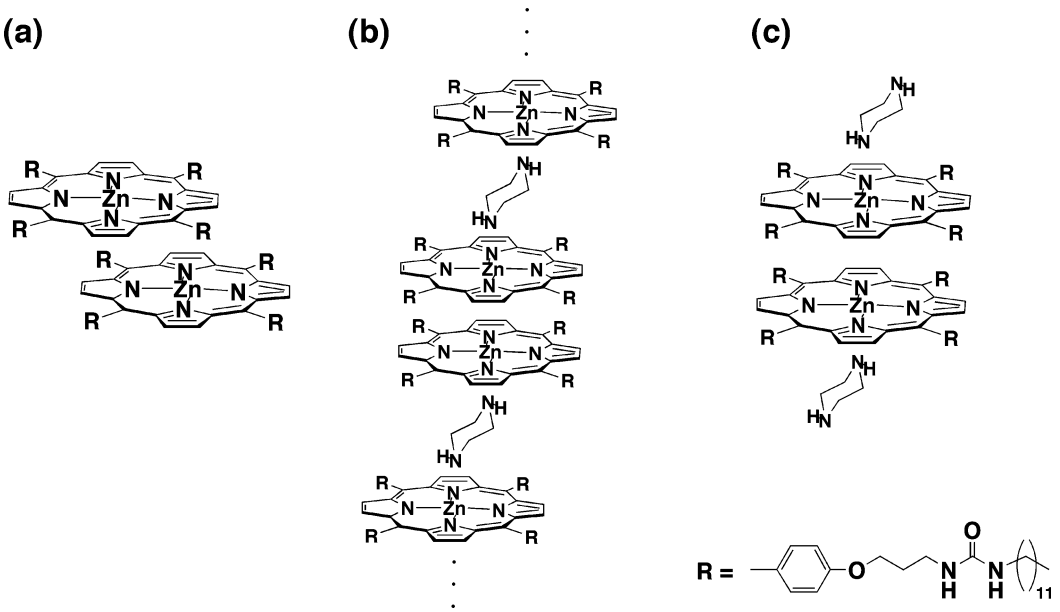

Fig. 8 Schematic representations of aggregation modes of (a) **1·Zn** only, **1·Zn** + piperazine (b) 2 : 1 and (c) 1 : 1 complexes in the aggregates.

band of **4·Zn** + piperazine 1 : 1 complex was observed at 432.0 nm (Fig. 7b). In the **1·Zn** + piperazine 1 : 1 complex + benzene gel, on the other hand, the new Soret band was observed at 411.0 nm with the Soret band attributable to the complex monomer (432.0 nm). These results imply that porphyrin rings in 1 : 1 complexes adopt an H-like aggregation mode in the gel phase, as shown in Fig. 8c.[14] On the other hand, the Soret band for **1·Zn** + piperazine 2 : 1 complex + benzene gel also appeared at the shorter wavelength (409.5 nm). Critically speaking, this peak should be compared to the Soret band of homogeneous solution of **4·Zn** + piperazine 2 : 1 complex. However, its spectral data could not be obtained because of its absence in the concentration region of UV-VIS absorption measurements. Therefore, we compared our data with the UV-VIS absorption spectral data of porphyrin derivative + diamine complex reported by Hunter *et al.* When they formed a sandwich-shaped complex, the Soret band of the complex appeared at a longer wavelength than that of the porphyrin derivative itself.[15] Judging from these data, one may regard that the Soret band obtained herein (409.5 nm) stems from the formation of an H-like aggregated stacking created by 2 : 1 complexes, but not from the formation of 2 : 1 complex (Fig. 8b).

Computational studies on the influence of diamines

As mentioned above, it is now apparent from SEM observations and FT-IR spectra that the aggregates of **1·Zn** + diamine 2 : 1 complexes provide different morphologies depending on the sort of diamine. To explore a reasonable rationale for this result, we conducted computational studies for 2 : 1 complexes of reference compound 5,10,15,20-*tetrakis*-(4-methoxyphenyl)porphine zinc and diamine.[16] These energy-minimized structures are shown in Fig. 9. It is seen from Fig. 9 that two porphyrin rings in complexes with piperazine or DABCO are nearly in parallel, whereas those in complexes with ethylenediamine or *N*,*N*′-dimethylethylenediamine are largely tilted, so that their structures lose symmetry: that is, the diamine structure remarkably influences the complex symmetry. This finding is complementary with SEM observation, suggesting that these results imply that complex symmetry is one of indispensable prerequisites to construct ordered superstructures.

Furthermore, we also found the difference between two symmetrical complexes composed of piperazine or DABCO which create 1-D fibrous or 2-D sheet-like structure, respectively. In the former, piperazine coordinates to zinc porphyrin with adopting a chair conformation. Accordingly, one can recognize from the side view of the complex that two porphyrin rings in the complex shift to some extent in the parallel direction: in other words, two porphyrin rings are not overlapped precisely (Fig. 9a). In contrast, those in the complex containing DABCO are precisely overlapped because of the symmetrical structure (Fig. 9b). One may regard, therefore, that this slight structural difference would lead to the large difference in the hydrogen-bond pattern determining their structural dimension, as shown in possible aggregation modes illustrated in Fig. 10.

The schematic representation of hydrogen-bonding pattern formed in the H-like aggregated porphyrin column is mentioned in Fig. 10. Generally, the hydrogen-bond-forming urea-to-urea distance is 0.43–0.46 nm.[17] However, in an energy-minimized structure, the nearest urea-to-urea distance in the complex is longer than the distance suitable to formation of hydrogen-bonds. Therefore, we assume an aggregation mode depicted in Fig. 10: that is, **1·Zn** + piperazine or DABCO 2 : 1 complex creates H-like aggregated columns driven by π–π stacking and hydrogen-bonding interactions. Then, it is reasonable to propose the interdigitated hydrogen-bonding network among these columns, adjusting the urea-to-urea distance by rotation of porphyrin rings in the complex. Herein, we again assume that there is some difference in the growth mechanism of the hydrogen-bonding networks constructed from two complexes: that is, as shown in Fig. 10(i), in the case of the H-like aggregated porphyrin column created from the piperazine complex, the column has some distortion in the axial direction because the complex features the lower symmetrical

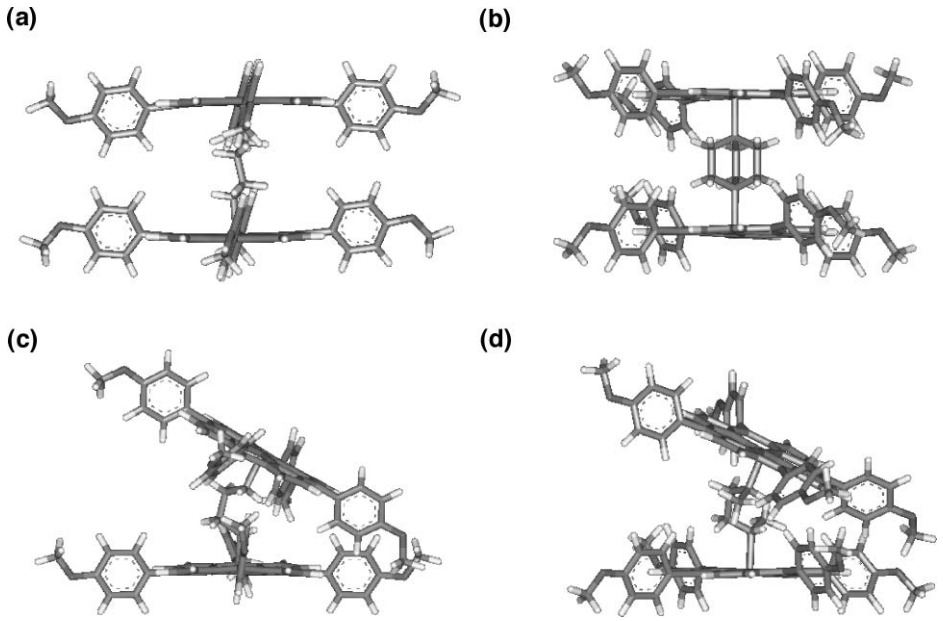

Fig. 9 Side views of the energy-minimized structures of 5,10,15,20-*tetrakis*-(4-methoxyphenyl)porphine zinc + diamine 2 : 1 comlexes with Discover 3/Insight II 98; (a) piperazine, (b) DABCO, (c) ethylenediamine and (d) *N*,*N*′-dimethylethylenediamine.

structure in the porphyrin rings. The columnar distortion should arise from the subtle disorder of urea groups arrangement along the column, which hampers the columns from assembling into the 2-D direction. On the other hand, as shown in Fig. 10(ii), the higher symmetrical structure in the DABCO complex creates the better ordered porphyrin column. Then, the peripheral urea groups can be appropriately pre-organized along the column to form the more energetically stable hydrogen-bonding network. As a result, the complex can effectively assemble into the 2-D direction.

Conclusion

In conclusion, we demonstrated that novel architectures of porphyrin assemblies can be designed utilizing metal–ligand interaction with diamines acting as axial ligands, and the superstructure fabricated from the complex creates an organogel showing a thixotropic behaviour. In this study, it has become clear that the unit components, which are affected by the sort and the stoichiometry of added diamine, remarkably influence the gelation properties, physical properties and morphologies. Especially, addition of piperazine induces remarkable changes in the formation and transformation of the complex. We believe, therefore, that this kind of molecular recognition in the gel system will be applicable to drug delivery systems, collection of waste materials and pollutants, recovery of precious bio-active compounds, *etc.*

Experimental

Equipment

^{1}H NMR spectra were measured on a Bruker DMX 600 spectrometer. *J* values are given in Hz. IR spectra were obtained using a Shimadzu FT-IR 8700 spectrometer. Mass spectral data were obtained using a Perseptive Voyager RP MALDI TOF mass spectrometer. UV-VIS absorption spectra were measured on a Shimadzu UV-2500PC spectrophotometer.

SEM measurements

The gel prepared in a sample tube was frozen by liquid. The sample was evaporated by a vacuum pump under reduced pressure for 1 d at room temperature. The obtained sample was shielded with platin. The accelerating voltage of the transmission electron microscope was 25 kV and the beam current was 10 μA.

TEM measurements

A piece of the gel was placed in a carbon-coated copper grid. The sample was dried by a vacuum pump under reduced pressure for 1 d at room temperature. The accelerating voltage of the transmission electron microscope was 120 kV and the beam current was 65 A.

Materials

5,10,15,20-*tetrakis*-[4-[3-(3-*N*-Dodecylureido)propoxy]phenyl]-porphine zinc (**1·Zn**) and 5,10,15,20-*tetrakis*-[4-[2-ethylhexoxy]-phenyl]porphyrin were prepared according to the literature reported previously and identified by FT-IR and ^{1}H NMR spectral evidence and elemental analysis.[7,18]

Synthesis of 5,10,15,20-*tetrakis*-[4-[2-ethylhexoxy]phenyl]porphine zinc (4·Zn)

To a solution of 5,10,15,20-*tetrakis*-[4-[2-ethylhexoxy]phenyl]-porphyrin (100 mg, 0.147 mmol) in 20 mL of chloroform–methanol = 3 : 1 (*v*/*v*) was added zinc acetate dihydrate (321 mg, 1.47 mmol) and the mixture was warmed at room temperature for

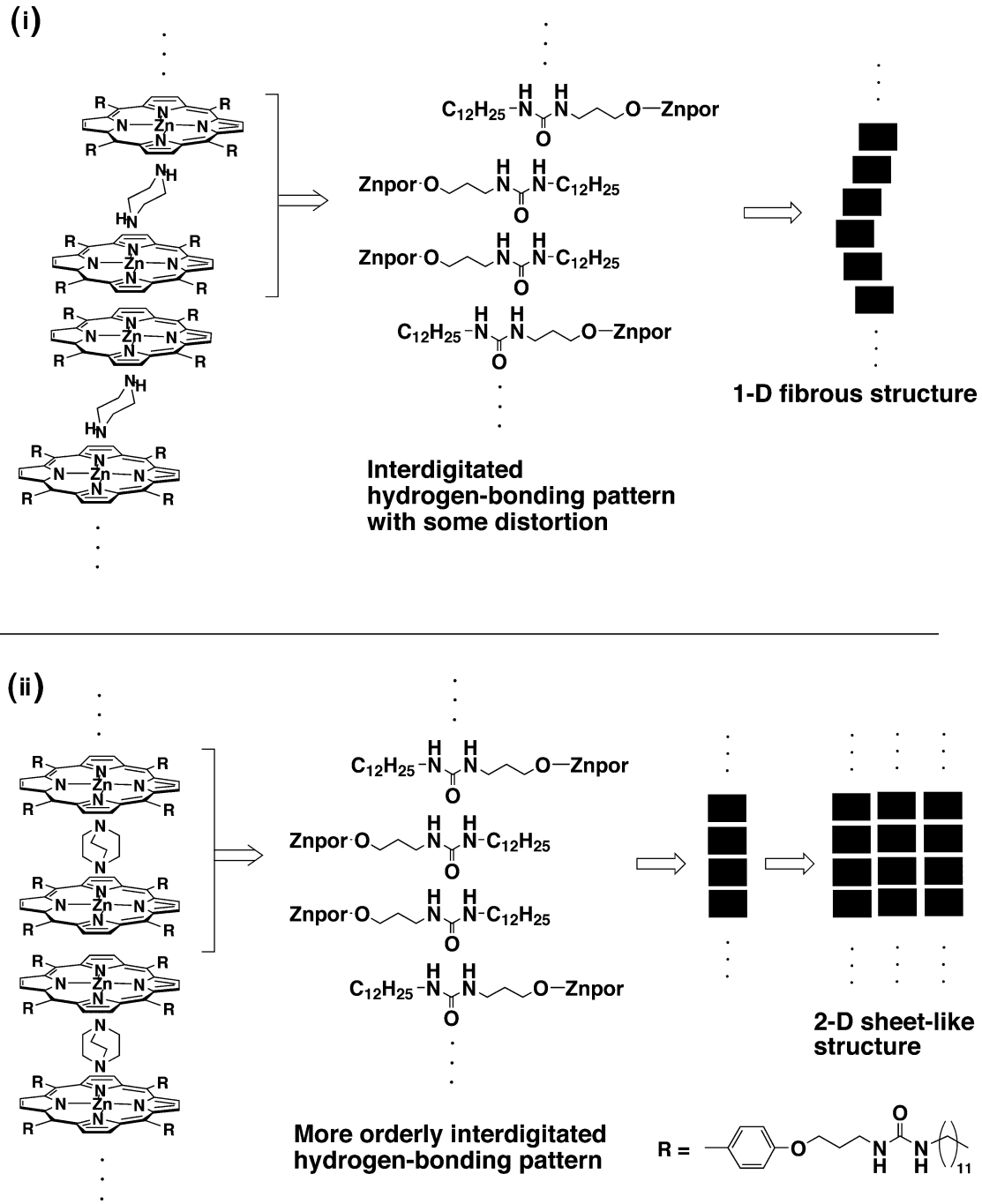

Fig. 10 Proposed mechanisms for different aggregation modes between **1·Zn** + piperazine (i) and DABCO (ii) 2 : 1 complexes. The middle figures represent the interdigitated hydrogen-bonding pattern forming among H-like aggregated complex columns. The right figures represent an axial distortion of an H-like aggregated complex column.

2 h. The solution was evaporated under reduced pressure. The solid residue was purified through chromatography [silica gel, $CHCl_3$] to give **4·Zn** in 90% (93 mg); mp 180–182 °C; δ_H(600 MHz; $CDCl_3$; Me_4Si) 0.72–1.39 (m, 2-ethylhexyl, 56 H), 1.52–1.55 (m, C*H*, 4 H), 3.64 (d, OC*H*, $J = 5.5$, 8H), 6.96 (d, Ph–*H*, $J = 8.6$, 8 H), 7.95 (d, Ph–*H*, $J = 8.5$, 8 H), 8.86 (s, β-pyrrole, 8H); IR ν_{max}/cm^{-1} 1243 (OC), 2858 (CH), 2923 (CH); MS [dithranol] *m/z*: 1091.4 [M + H]$^+$; Anal. calcd for $C_{76}H_{92}N_4O_4Zn$: C, 76.65; H, 7.79; N, 4.70. Found: C, 76.52; H, 7.76; N, 4.82%.

Acknowledgements

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