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Self-complementary bis-porphyrins

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Abstract—Self-complementary bis-porphyrins assembled to form the supramolecular dimers in chloroform and in gas phase.

Association of two or more copies of a self-complementary molecule gives rise to large and elaborate molecular architectures, showing interesting function unique to their assembled states.[1] Self-complementary molecules have been fruitfully used as building blocks for supramolecular architectures. Hydrogen bonds[2] and other polar interaction[3] are usually responsible for such self-association in organic media. Limited examples of self-assembling systems due to weak forces such as van der Waals and C–H/π interactions in organic media have been reported so far.[4,5]

Porphyrin is a versatile platform in the field of supramolecular chemistry.[6] Recent developments have seen the incorporation of the self-complementary porphyrins into supramolecular assemblies utilizing metal-coordination.[7] Here, we report new self-complementary bis-porphyrins **1**–**3** that assemble into dimers in organic media primarily by virtue of the weak molecular forces.[8] The bis-porphyrins have rigid clefts and find their complements in themselves (Fig. 1).

Bis-porphyrin **1** was prepared by the simple acylation of the corresponding 3-aminophenyltriphenylporphyrin[9] and pyridine-2, 6-dicarbonyldichloride.[10] Their ^{1}H NMR signals were concentration-dependent in chloroform-*d*, gradually moving upfield as the concentrations were increased. In particular, two broad multiplets of the pyridyl protons of **1** appeared at 4.25 and 5.14 ppm in the concentration of 15.2 mmol/L. These unexpected upfield shifts suggested that the pyridyl linkage stay on the porphyrin ring, forming supramolecular assemblies.

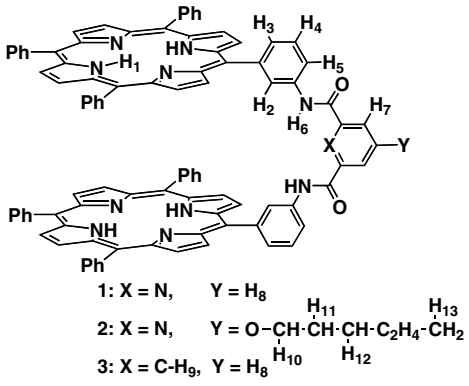

Figure 1. Bis-porphyrins **1**–**3**.

The ESI mass measurement of **1** taken in positive mode revealed the intense peaks at *m*/*z* 2782 and 1391 attributable to $[\mathbf{1}\cdot\mathbf{1}+H]^+$ and $[\mathbf{1}\cdot\mathbf{1}+2H]^{2+}$ (Fig. 2). The measured

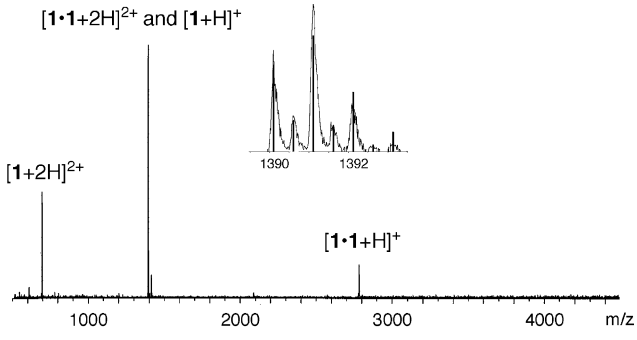

Figure 2. Mass spectrum of **1** in $CHCl_3$–CH_3OH (8:2). The inset shows the calculated (straight lines) and experimental isotope pattern (curve). The calculated isotope pattern is estimated on the basis of the composition of 30% $[\mathbf{1}\cdot\mathbf{1}+2H]^{2+}$ and 70% $[1+H]^+$.

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Table 1. Dimerization constants for **1**, **2** and **3** at 295 K in chloroform-d_1 and toluene-d_8

	K_D (M^{-1})	
	Chloroform-d_1	Toluene-d_8
1	310 ± 20	5400 ± 500
2	75 ± 1	830 ± 30
3	98 ± 2	—

isotope pattern for $[\mathbf{1}\cdot\mathbf{1}+2H]^{2+}$ matched the calculated abundance, confirming the elemental composition and the dicationic nature of the complex. These results revealed that a self-assembled dimer of **1** was formed in gas phase.

Plotting the chemical shifts changes on protons produced the hyperbolic curves. These data nicely fit a simple dimerization model and yield formation constants K_D for **1**, **2** and **3** in chloroform-d_1 and toluene-d_8 (Table 1).

While the structure of the assembled dimers remains to be determined, molecular mechanics calculation of the complex is informative. The calculation was carried out using MM3* as implemented in MacroModel V.6.5.[11] During the calculations, two plausible structures were found: one is structure A, in which the two molecules arranged in a self-complementary mode, the other is head-to-tail dimeric structure B (Fig. 3).

The complexation induced chemical shift changes of the protons are useful to determine which is predominant in solution (Table 2). In both structures, H_7, H_8, H_{10} and H_{11} have experienced the large shielding effect due to the anisotropic contribution of the porphyrin rings; however, the extent of the shielding effect in A is much larger than in B because one of the pyridyl linkers stays outside of the cleft in B. Our chemical shift simulation program[12] estimated the induced shift changes for H_7 and H_8 in the self-complementary form of A (Fig. 4,[13] $\Delta\delta$: 5.46 and 5.90 ppm). These values are close to those observed for H_7 and H_8 in **1**·**1**, suggesting that the self-assembled dimer should mainly adopt A form in solution. In contrast, the induced shift changes for H_7 and H_8 in **2**·**2** and **3**·**3** are slightly smaller than those for **1**·**1**. This result does not allow us to rule out the presence of structure B in **2**·**2** and **3**·**3**, which might be partly present in solution.

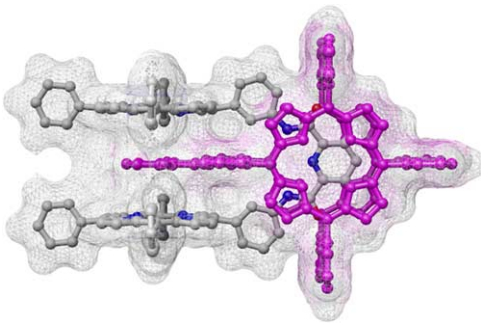

Figure 4. Calculated structure of self-assembled dimer **1**·**1**.

It is well known that amide functionality forms intermolecular hydrogen bonds between N–H and O=C groups in a head-to-tail fashion.[14] The intermolecular hydrogen bonds between the amide groups could drive the self-assembly; however, diphenyl 2,6-pyridinedicarboxyamide itself did not show any spectral changes in a variety of the concentrations in chloroform. This result ruled out the possibility of the formation of N–H···O=C hydrogen bonds in the assembled dimers.

To gain the detailed understanding of the self-assembling processes, the thermodynamic studies of the association of **1**–**3** were carried out. From the corresponding van't Hoff plots, the enthalpies and the entropies of the association for **1**, **2** and **3** were obtained (Table 3). These association events are enthalpically favored and entropy opposed. As expected, the favorable enthalpic contribution should be provided primarily by π–π stacking and van der Waals interactions of the pyridyl and phenyl linkers in the cleft of the two porphyrins (Fig. 4).

The hexyl chain brings the extra enthalpic gain (-1.3 kcal mol^{-1}), but large entropic loss

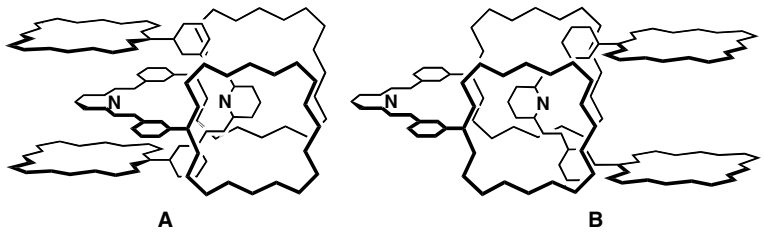

Figure 3. Plausible structures of the self-assembled dimers.

Table 2. Complexation induced ^{1}H chemical shift changes[a] (ppm) in chloroform-d_1 estimated by non-linear curve fitting analyses

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}	H_{11}	H_{12}	H_{13}
1	−0.80	−0.28	−0.27	−0.25	−0.59	−2.10	−5.09	−5.69					
2	−0.10	+0.14	−0.21	−0.37	−0.64	−0.66	−2.84			−3.29	−2.02	−1.18	−0.07
3	−0.11	−0.60	−0.47	−1.13	−1.49	−0.86	−2.98	−3.99	−0.81				

[a] − Sign denotes upfield shift.

Table 3. Thermodynamic data for the dimerization in chloroform-*d*

	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
1	-3.8 ± 0.1	-1.7 ± 0.2
2	-5.1 ± 0.1	-9.1 ± 0.5
3	-3.3 ± 0.1	-2.0 ± 0.4

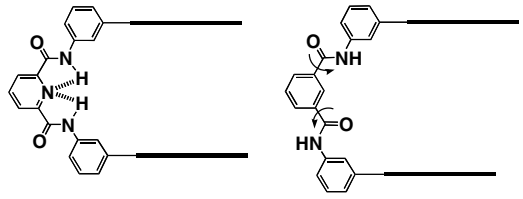

Figure 5. Preferential conformations of individual subunits **1** and **3**.

(-7.4 cal mol^{-1} K^{-1}) clearly indicating a compensation effect. The self-assembling event forces the hexyl chain into the cleft. This arrangement of the hexyl chain provides extra enthalpic benefit through a multitude of van der Waals contacts within the cleft, but has to pay the entropic cost (-7.4 cal mol^{-1} K^{-1}) due to the loss of the rotational freedom. As a result, this negative entropic contribution reduces the free energy of the dimerization.

The pyridyl group is more advantageous than the phenyl as a linker. The nitrogen of the pyridine ring causes the hydrogen bonds to the amide N–H protons,[15] which fix the conformational freedom around the pyridine ring while such hydrogen bonds are absent in the benzenedicarboxyamide subunit (Fig. 5). The more preorganized **1** receives a little enthalpic and entropic gains ($\Delta\Delta H$: -0.5 kcal/mol, $\Delta\Delta S$: 0.3 cal mol^{-1} K^{-1}) for the dimerization.[16]

When compared to the general dimer formation processes,[4,17] these cases have much smaller entropy changes. One plausible explanation can be given in terms of the desolvation of the bis-porphyrins. The planar porphyrin ring has large and flat contact area on which solvent molecules can be arranged due to noncovalent interactions. The association liberates some of the solvents. The small entropic changes should be a consequence of the desolvation during the process.[5]

In summary, we have demonstrated that the bis-porphyrin clefts undergo a self-association due to their self-complementary nature. The π–π stacking interaction and desolvation should be major driving forces for the self-association. The self-association might offer a useful alternative for the construction of the supramolecular architectures.

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10. Spectroscopic data for bisporphyrins **1**, **2** and **3** are provided. Their NMR spectra are concentration dependent. **1**: ^{1}H NMR (500 MHz, 10 mM, $CDCl_3$): 8.78 (m, 8H), 8.73 (d, 4H, $J = 4.9$ Hz), 8.70 (d, 4H, $J = 4.9$ Hz), 8.45 (s, 2H), 8.36 (brs, 2H), 8.22 (d, 2H, $J = 7.3$ Hz), 8.16–8.13 (m, 6H), 8.07 (d, 4H, $J = 7.3$ Hz), 7.79 (d, 2H, $J = 8.0$ Hz), 7.71 (d, 2H, $J = 8.0$ Hz), 7.70–7.48 (m, 18H), 7.47 (t, 2H, $J = 8.0$ Hz), 5.43 (brs, 2H), 4.59 (brs, 1H), -3.32 (brs, 4H) ppm; ^{13}C NMR (125 MHz, 10 mM, $CDCl_3$): 159.4, 145.4, 142.8, 142.1, 142.0, 135.6, 135.5, 134.6, 134.5, 131.2, 127.6, 127.0, 126.6, 125.7, 122.2, 120.3, 120.0, 119.0, 118.9 ppm; IR (KBr): 3375, 3314, 1689, 1532 cm^{-1} ; UV–vis ($CHCl_3$): 418.5, 515.5, 550.5, 590.0, 645.5 nm; ESI-MS: *m/z* 1392.0 $[\mathbf{1}+H]^+$, 2782.0 $[\mathbf{1}\cdot\mathbf{1}+H]^+$; FAB-MS: *m/z* 1391 $[\mathbf{1}+H]^+$.
2: ^{1}H NMR (500 MHz, 10 mM, $CDCl_3$): 9.51 (s, 2H), 8.85 (d, 4H, $J = 4.6$ Hz), 8.83 (d, 4H, $J = 4.6$ Hz), 8.78 (d, 4H, $J = 4.6$ Hz), 8.74 (d, 4H, $J = 4.6$ Hz), 8.66 (s, 2H), 8.25 (d,

2H, $J = 6.7$ Hz), 8.17–8.14 (m, 10H), 7.85 (d, 2H, $J = 7.6$ Hz), 7.79 (d, 2H, $J = 7.6$ Hz), 7.72–7.54 (m, 18H), 7.45 (t, 2H, $J = 7.6$ Hz), 6.87 (brs, 2H), 2.86 (brs, 2H), 1.14 (m, 2H), 1.04–0.98 (m, 4H), 0.91 (m, 2H), 0.80 (t, 3H, $J = 7.3$ Hz), −2.88 (brs, 4H); ^{13}C NMR (125 MHz, 10 mM, $CDCl_3$): 167.0, 161.0, 149.8, 143.0, 142.2, 142.0, 135.6, 134.6, 134.5, 131.2, 127.7, 127.6, 127.1, 126.64, 126.57, 126.4, 120.25, 120.16, 119.5, 119.0, 110.7, 68.3, 31.2, 28.0, 25.0, 22.3, 13.9; IR (KBr): 3373, 3314, 1691, 1530 cm^{-1}; UV–vis ($CHCl_3$): 418.5, 516.0, 551.0, 590.0, 646.0 nm; ESI-MS: *m*/*z* 1491.9 [**2**+H]$^+$, 2982.5 [**2**·**2**+H]$^+$; FAB-MS: *m*/*z* 1491 [**2**+H]$^+$.

3:^{1}H NMR (500 MHz, 10 mM, $CDCl_3$): 8.88 (d, 4H, $J = 4.6$ Hz), 8.80 (d, 4H, $J = 4.6$ Hz), 8.69 (d, 4H, $J = 4.6$ Hz), 8.62 (d, 4H, $J = 4.6$ Hz), 8.25 (d, 2H, $J = 6.4$ Hz), 8.21 (d, 2H, $J = 6.4$ Hz), 8.12 (s, 1H), 8.10 (d, 4H, $J = 6.7$ Hz), 8.04 (s, 2H), 7.81–7.74 (m, 14H), 7.62 (t, 4H, $J = 7.3$ Hz), 7.54 (t, 4H, $J = 7.3$ Hz), 7.44 (d, 2H, $J = 7.6$ Hz), 7.23–7.18 (m, 6H), 6.59 (brs, 2H), 5.55 (brs, 1H), −2.87 (brs, 4H); ^{13}C NMR(125 MHz, 10 mM, $CDCl_3$): 164.6, 142.7, 142.1, 141.8, 135.8, 134.6, 134.5, 134.4, 134.2, 134.1, 130.9, 129.0, 127.9, 127.8, 127.5, 127.1, 126.71, 126.67, 126.6, 126.53, 126.45, 124.6, 120.4, 120.1, 119.6, 118.9; IR (KBr): 3419, 3315, 1675, 1540 cm^{-1}; UV–vis ($CHCl_3$): 418.5, 515.5, 551.0, 590.0, 646.0 nm; ESI-MS: *m*/*z* 1390.8 [**3**+H]$^+$, 2085.6 [**3**·**3**+H]$^+$; FAB-MS: *m*/*z* 1390 [**3**+H]$^+$.

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