Hydrogen bonding self-assemblies with 1-D linear, dimeric and hexagonal nanostructures of *meso*-pyridyl-substituted dipyrromethanes†

Hiromitsu Maeda,*[a,b] Masahiro Hasegawa[a] and Atsushi Ueda[a]

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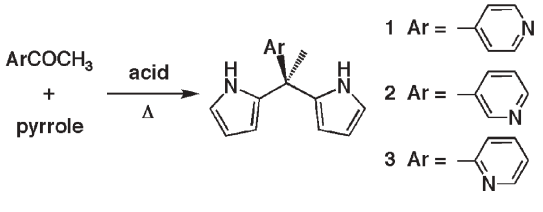
Dipyrromethanes with *meso*-pyridyl groups form various hydrogen bonding structures such as dimeric and hexagonal structures and infinite chains. The formation of the self-assembled structures and chains depends on the existence of *meso*-pyridyl nitrogen in the solid state.

Noncovalent interactions between molecules can result in the formation of versatile supramolecular nanostructures in the solid and solution state.[1] In natural systems, the double helix of DNA is constructed by complementary hydrogen bonding between base pairs, and the high-dimensional structures of proteins are maintained by means of noncovalent interactions between, for example, amide units.[2] With regard to π-conjugated moieties, a pyrrole N unit acts as an essential binding site in, for example, porphobilinogen deaminase, which is a key enzyme in the biosynthetic pathway of tetrapyrroles.[3] In artificial systems, pyrrolyl NH, which is incorporated in cyclic or acyclic oligomers, binds with various anions to form the host–guest complex.[4] Further, pyrrole derivatives with hydrogen bonding acceptor(s) can be used to construct supramolecular oligomers or infinite chains by self-assembly.[5] Among the various types of oligopyrroles in natural and artificial systems, dipyrromethane, which consists of two pyrrole units and one *meso* carbon, is a useful precursor for porphyrin and its analogues. At present, it is known that the NH site of pyrrole associates with another pyrrole plane by means of N–H···π interaction[6] in the solution and solid state.[7–9] In this communication, we report the hydrogen bonding interactions of dipyrromethanes with *o*-, *m*- and *p*-pyridyl substituents at the *meso* position. These dipyrromethanes exhibit various solid-state nanostructures, depending on the positions of pyridyl N, as a result of complementary hydrogen bonding with pyrrole NH and N/C–H···π interactions.

In accordance with the reported procedures,[10] pyridyl-substituted dipyrromethanes **1–3** were synthesised in 26, 51 and 10% yields from *p*-, *m*- and *o*-acetylpyridines, respectively. In the synthesis, pyrrole and EtOH were refluxed for *ca.* 4 days with CH_3SO_3H (Scheme 1). In comparison with derivative **3′**, which has hydrogen at the *meso* position instead of methyl group, dipyrromethanes **1–3** did not undergo oxidative transformation or decomposition because of the presence of the *meso*-alkyl substituent.

The self-assembled nanostructures of **1–3**, which are based on hydrogen bonding between pyrrole NH and pyridyl N, as well as **3′**, have been examined by X-ray single-crystal analyses; for these analyses, crystals are grown from CH_2Cl_2–hexane, as shown in Fig. 1.‡ *p*-Pyridyldipyrromethane **1** forms crinkled hydrogen bonding chains with an intermolecular N–H···N distance of 2.979(2) Å (Fig. 1(a)). On the other hand, *m*-pyridyl derivative **2** shows a dimeric structure, for which two interactions between pyrrole NH and pyridyl N are confirmed by an intermolecular N–H···N distance of 3.015(2) Å (Fig. 1(b)). In this dimer, two pyridyl planes form a slipped π–π stacking with a distance of 3.517 Å. In both cases (**1** and **2**), some of the pyrrole CH sites of one assembly interact with the pyrrole π-plane of the neighbouring assemblies by means of C–H···π interactions (Fig. 2). In the case of *p*-pyridyl **1**, an α-CH site with a 'free' NH unit interacts with the π-plane of the pyrrole ring with a 'busy' NH unit (C(–H)···π distance: 3.522(2) Å) to form 2-D grids based on N–H···N chains (Fig. 2(a)). Here, planes defined by five heavy atoms are used for estimating the distances. On the other hand, in *m*-pyridyl **2**, two types of interactions between pyrrole α-CH and the π-plane, for which the C(–H)···π distances are 3.542(2) and 3.845(2) Å, are observed in the assemblies consisting of N–H···N hydrogen bonding dimers (Fig. 2(b)). Interaction between free pyrrole NH and the π-plane is also suggested by a N(–H)···π distance of 3.445(2) Å (not indicated in Fig. 2(b)); in this interaction, the NH direction is slightly distorted from the perpendicular to the plane.

Interestingly, *o*-isomer **3** forms cyclic hexamers possessing hexagonal structures, each with a diagonal of 1.7 nm and height of 1.1 nm, by means of 'external' N–H···N interactions (3.050(4) Å) as well as 'internal' ones between NH and the neighbouring pyrrole π-planes (3.367(3) Å) (Fig. 1(c)). Molecules with *R* and *S* configurations, which are derived from unequivalent pyrrole moieties due to different types of interactions (N–H···N and N–H···π), are arranged in a cycle and interact with each other



Scheme 1 Synthesis of *meso*-pyridyl-substituted dipyrromethanes **1–3**.

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[a] *Department of Bioscience and Biotechnology, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, 525–8577, Japan. E-mail: maedahir@se.ritsumei.ac.jp*
[b] *Department of Materials Molecular Science, Institute for Molecular Science (IMS), Okazaki, 444–8787, Japan*

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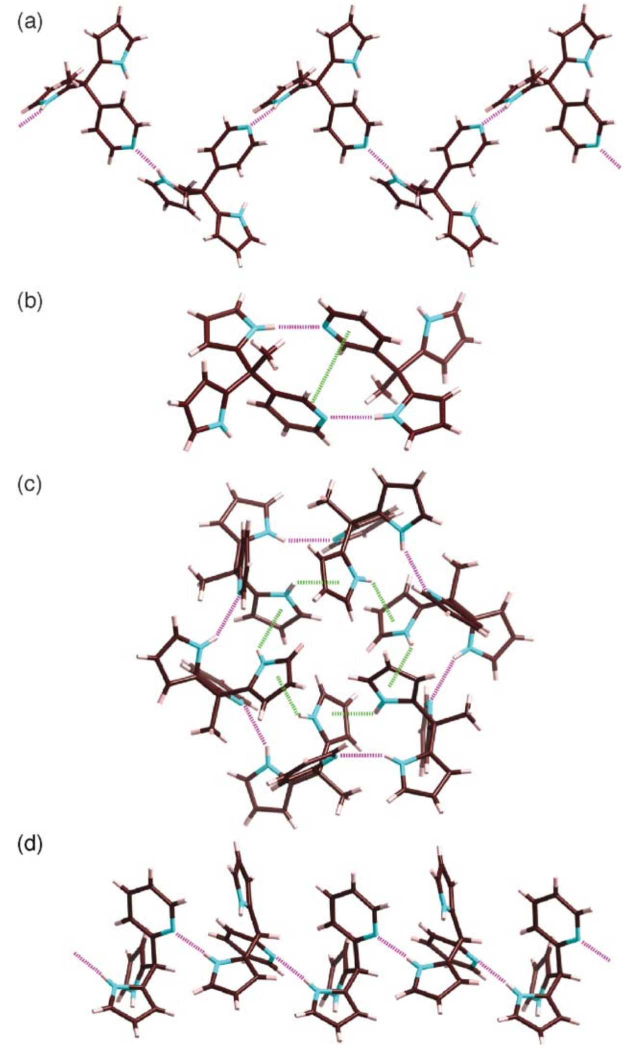

Fig. 1 Hydrogen bonding nanostructures of (a) **1** (infinite chain), (b) **2** (dimer), (c) **3** (cyclic hexamer) and (d) **3′** (infinite chain) in the solid state. The N–H···N and N–H···π (and π–π) interactions are indicated by magenta and yellow–green dotted lines, respectively. Atom colour code: brown, blue, pink and red refer to carbon, nitrogen, hydrogen and oxygen, respectively.

to form an achiral assembly. In comparison with the pyrrole units, the *meso*-pyridyl rings are located at the axial positions. Moreover, columnar 'wires' consisting of stacked cyclic hexamers are observed along the *c*-axis (Fig. 3). On the basis of the observations of the solid-state structures of **1–3**, the positions of pyridyl N are considered crucial to determine the geometries of the supramolecular assemblies as well as the 'stability' observed in the melting points (181.1–186.2, 156.4–163.4 and 147.6–151.8 °C for **1–3**, respectively). Preliminary differential scanning calorimetry (DSC) measurements suggest that new solid states are formed after the melting of crystals from the solvents. Furthermore, in sharp contrast to *meso*-quaternary **3**, *meso*-tertiary **3′** forms crinkled 1-D chains, similar to **1**, with N–H···N distances of 2.9317(18) and 2.9345(18) Å (Fig. 1(d)). This implies that the substituents at the *meso* position also significantly affect the morphologies of nanostructures.

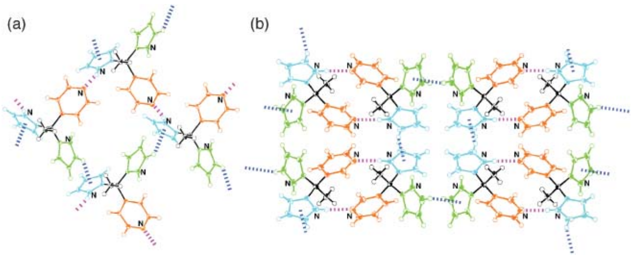

Fig. 2 Supplementary C–H···π interactions, represented by blue dotted lines, between assemblies consisting of N–H···N hydrogen bonding (magenta dotted lines) in (a) **1** and (b) **2**. The two types of pyrrole rings are represented by blue and yellow–green colors.

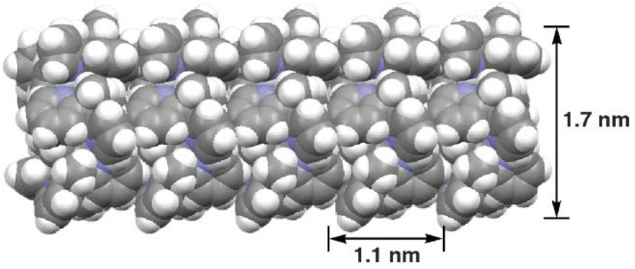

Fig. 3 Columnar structures consisting of stacked cyclic hexamers of **3**.

Pyrrole assemblies based on N–H···π interactions have been investigated by the X-ray single-crystal analysis of solid pyrrole and FT-IR analysis of the solution. These investigations suggest the formation of a 1-D chain and T-shaped dimer in solid pyrrole and the solution, respectively.[7,8] DFT calculation (B3LYP/6-31G(d,p) level) of the pyrrole cyclic hexamer, which is carried out as part of an extended study of the cyclic trimer and tetramer,[8] suggests the existence of stability in the 'monomer' at 5.89 kcal $\mathrm{mol^{-1}}$ per pyrrole unit.[11] At this level of calculation, the theoretical studies of the cyclic trimer, tetramer, pentamer and heptamer afforded stabilities at 5.09, 5.37, 5.13 and 5.71 kcal $\mathrm{mol^{-1}}$, respectively, suggesting that hexameric geometry is more preferable. Although cyclic oligomers are the most stable species and they utilize all the NH sites during hydrogen bonding, cyclic hexamers have not been fabricated and observed thus far.

In contrast to the assemblies present in the solid state, the monomeric forms of **1–3** are present in the solution state at 3×10^{-3} M, as revealed by the ^{1}H NMR spectra of **1–3** in $CDCl_3$ at various temperatures. The signals of pyrrole NH at 7.83, 7.85 and 9.06 ppm for **1–3** at 20 °C show no significant downfield shifts (8.00, 8.00 and 9.24 ppm, respectively, at −50 °C) suggesting the existence of only weak interactions at the NH sites in the solution state, in contrast to the anion binding of the protonated species.§ The results of dynamic light scattering (DLS) measurements of **1–3** in $CHCl_3$ (3×10^{-3} M) are consistent with the results of NMR analysis. The above observations indicate that pyridyl-substituted dipyrromethanes **1–3** exist as monomers in the solution state and form hydrogen bonding assemblies in the solid state as a result of multiple weak interactions such as van der Waals interactions.

In summary, dipyrromethanes with *meso*-pyridyl groups form unique self-assembled structures by means of N–H···N and N/C–H···π hydrogen bonding in the solid state. Because of the interesting morphologies of these assemblies, the introduction of functional substituents at the *meso* position, instead of, for example, the methyl group of **3**, would provide novel wires with hexagonal cut planes. Further investigations to fabricate nanoscale materials are in progress.

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Notes and references

‡ *Crystal data* for **1** (from CH_2Cl_2–hexane): $C_{15}H_{15}N_3$, $M_w = 237.30$, monoclinic, $P2_1/c$ (no. 14), $a = 9.510(4)$, $b = 10.572(6)$, $c = 12.645(5)$ Å, $\beta = 109.05(1)°$, $V = 1201.8(10)$ Å^3, $T = 123(1)$ K, $Z = 4$, $D_c = 1.312$ g cm^{-3}, μ(Mo-Kα) = 0.080 mm^{-1}, 11536 reflections measured, 2744 unique ($R_{int} = 0.0267$). $R_1 = 0.0410$, $wR_2 = 0.0979$, GOF = 1.066 ($I > 2\sigma(I)$). CCDC 637498. *Crystal data* for **2** (from CH_2Cl_2–hexane): $C_{15}H_{15}N_3$, $M_w = 237.30$, orthorhombic, *Pccn* (no. 148), $a = 27.092(7)$, $b = 14.512(6)$, $c = 6.1410(18)$ Å, $V = 2414.3(13)$ Å^3, $T = 123(1)$ K, $Z = 8$, $D_c = 1.306$ g cm^{-3}, μ(Mo-Kα) = 0.080 mm^{-1}, 21485 reflections measured, 2751 unique ($R_{int} = 0.0269$). $R_1 = 0.0525$, $wR_2 = 0.1434$, GOF = 1.043 ($I > 2\sigma(I)$). CCDC 637499. *Crystal data* for **3** (from CH_2Cl_2–hexane): $C_{15}H_{15}N_3$, $M_w = 237.30$, rhombohedral, $R\bar{3}$ (no. 148), $a = 27.653(8)$, $c = 8.536(3)$ Å, $V = 5653(3)$ Å^3, $T = 123(2)$ K, $Z = 18$, $D_c = 1.255$ g cm^{-3}, μ(Mo-Kα) = 0.077 mm^{-1}, 17891 reflections measured, 2862 unique ($R_{int} = 0.1308$). $R_1 = 0.0597$, $wR_2 = 0.1200$, GOF = 1.036 ($I > 2\sigma(I)$). CCDC 637500. *Crystal data* for **3′** (from CH_2Cl_2–hexane): $C_{14}H_{13}N_3$, $M_w = 223.27$, triclinic, $P\bar{1}$ (no. 2), $a = 9.1012(12)$, $b = 9.7702(13)$, $c = 13.9971(19)$ Å, $\alpha = 90.305(2)$, $\beta = 105.415(2)$, $\gamma = 107.982(2)°$, $V = 1136.1(3)$ Å^3, $T = 90(2)$ K, $Z = 4$, $D_c = 1.305$ g cm^{-3}, μ(Mo-Kα) = 0.080 mm^{-1}, 6819 reflections measured, 4828 unique ($R_{int} = 0.0175$). $R_1 = 0.0427$, $wR_2 = 0.1027$, GOF = 1.036 ($I > 2\sigma(I)$). CCDC 637501. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703236f

§ Protonation at pyridyl N would give the "*umpolung*" interaction site as hydrogen bonding donor NH. Upon the addition of 1 equiv. of TFA to $CDCl_3$ solutions of **1–3** at 50 °C, pyrrole NH appear at 7.99, 8.05, and 9.15 ppm, respectively, possibly due to the association of anion (trifluoroacetate). At −60 °C, these NH signals shift downfield to 8.94, 8.99 and 9.97 ppm, contrasting with the neutral **1–3**. The downfield shifts of **3** and **3**·H$^+$ compared to **1** and **2** are derived from the induction effect of the *o*-pyridyl moiety.

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