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Supramolecular Chemistry of Acyclic Oligopyrroles

Hiromitsu Maeda*[a,b]

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Acyclic π-conjugated oligopyrrole derivatives, though not extensively studied, often have more advantages as anion receptors and metal-coordination ligands than their cyclic counterparts. This is due to the formation of versatile complexes and supramolecular assemblies, although they do require conformational changes by guest binding. Of the linear oligopyrroles, oligomeric derivatives of dipyrrins bridged by π-conjugated spacers behave as building subunits and form coordination oligomers and discrete coordination nanorings. In contrast, pyrrole oligomers with hydrogen-bond-acceptor site(s) have yielded unique morphologies as supramolecular assemblies and micro- and nanometer-scale structures by means of hydrogen-bonding interactions. Furthermore, a new class of acyclic anion receptors, namely, BF_2 complexes of dipyrrolyl diketones, has been shown to interact with anions by means of the pyrrole NH group and bridging CH interactions. Inversion of the pyrrole rings was found to be essential to capture anions by using these binding sites. Aryl substitution of the receptors as π-extended derivatives has enabled the formation of assemblies such as supramolecular organogels that can be controlled by the addition of anions.

Introduction

Pyrrole, a π-conjugated aromatic heterocyclic molecule, is a constituent of the structural skeleton of several biotic dyes such as heme and chlorophyll.[1] Pyrrole exhibits a "duality" of its nitrogen moiety, as it can behave as both a hydrogen-bonding acceptor, or a metal-coordination ligand, due to the N site (Figure 1a) and a hydrogen-bonding donor due to the NH site (Figure 1b). The π-planes of the pyrrole unit also enable effective interactions that yield stacking assemblies (Figure 1c). Therefore, pyrrole rings can act as potential building subunits to form supramolecular nanoscale structures. In general, well-defined micro- and nanometer-sized architectures fabricated by self-assembled organic molecules have attracted considerable attention due to their ability to act as potential functional materials by using noncovalent interactions such as metal coordination, hydrogen-bonding, van der Waals interactions, and so on.[2] For example, amphiphilic hexa-*peri*-hexabenzocoronenes self-assemble to form π-electronic discrete nanotubular objects.[3] In contrast to such soft materials, larger tube- and pipe-like structures have also been assembled by the organization and crystallization of small organic molecules.[4] Of the self-assembled oligomeric systems based on low molecular weight π-conjugated molecules, the gel materials − especially those susceptible to the influence of external stimuli − are of interest and play a crucial role as potential soft materials.[5,6] Supramolecular gels consist of nanoscale fibers, tubes, and sheets formed by organized molecular assemblies. In contrast to physical stimuli, structural modification of supramolecular organogels under chemical control is very attractive as a large variety of potential additives are available.[7]

[a] Department of Bioscience and Biotechnology, Faculty of Science and Engineering, Ritsumeikan University,
Kusatsu 525-8577, Japan
Fax: +81-77-561-2659
E-mail: maedahir@se.ritsumei.ac.jp
[b] Department of Materials Molecular Science, Institute for Molecular Science (IMS),
Okazaki, 444-8787, Japan

Hiromitsu Maeda was born in 1976 in Kadoma (Osaka), Japan. He received his PhD in 2004 from Kyoto University under the guidance of Prof. Hiroyuki Furuta (Kyushu University) and Prof. Atsuhiro Osuka; he focused on the synthesis and exploration of porphyrin analogs including N-confused porphyrins. He was selected as a Research Fellow of the Japan Society for the Promotion of Science (JSPS) in 2001–2004. During the autumn of 2001, as a visiting fellow, he worked in the laboratory of Prof. Jonathan L. Sessler, Department of Chemistry and Biochemistry, the University of Texas at Austin. In 2004, he started an academic career at the Department of Bioscience and Biotechnology, Faculty of Science and Engineering, Ritsumeikan University as a lecturer, and in 2005 he became an Associate Professor. Since 2006, he has also served as a visiting Associate Professor at the Department of Materials Molecular Science, Institute for Molecular Science (IMS). He was awarded the IUPAC Prize for Young Chemists in 2005.

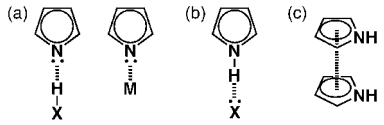

Figure 1. Possible interactions of pyrrole as (a) a hydrogen-bonding acceptor and a metal-coordination site, (b) a hydrogen-bonding donor, and (c) a π-plane. The structures with "aromatic circles" are used to represent various types of pyrrole units.

Metal coordination enables organic ligands to form versatile discrete or infinite architectures, such as wire structures and nanospace materials, with potential applications in catalysis, optics, and biosensing.[8] However, metal-coordinated self-assemblies have thus far been limited to crystalline systems, which make possible, for example, the encapsulation of gas molecules in nanospaces. Recently, nanoscale morphologies based on coordination polymers were reported to exist as spherical and fibrous structures.[9,10] Discrete coordination macrocycles and cages have also been explored as isolated spaces to bind specific molecules and ions in solution. With regard to coordinating ligands, dipyrrins (dipyrromethenes), as partial structures of bile pigments consisting of two pyrroles with an sp^2 *meso* position, are essential π-conjugated bidentate monoanionic ligands for metal ions in natural and artificial systems.[11–13] Multitopic dipyrrin derivatives are promising scaffolds for self-assemblies and would provide neutral coordination oligomers, which, in combination with various spacer units, could be used to fabricate supramolecular structures and fine-tuned nanoscale morphologies by means of bridging metal cations. For example, Cohen et al. showed infinite coordination networks based on dipyrrin derivatives in the solid state (Figure 2a).[12] Lindsey et al. reported dipyrrin metal complexes as bridging units for energy transfer systems consisting of porphyrins (Figure 2b).[13] Apart from these studies, the author has also attempted to form coordination oligomers to yield nanoscale spherical architectures and discrete coordination macrocycles by using dimeric dipyrrin derivatives.[14–16]

In natural systems, the double helix of DNA is constructed by complementary hydrogen-bonding between the base pairs, and the high-dimensional structures of proteins are maintained by means of noncovalent interactions between subunits such as amides.[17] Nonetheless, hydrogen-bonding interactions are useful to form various molecular assemblies and supramolecular structures in artificial systems.[18] Of the various ditopic interaction units, the set consisting of a pyrrole NH and a hydrogen-bonding acceptor on the same plane would exhibit double hydrogen-bonding interactions that are appropriate for self-organization. Therefore, self-assembled supramolecular chains of acyclic pyrrole derivatives with carbonyl groups at the α-positions have been observed in the solid state as well as in solution.[19,20] For example, bis(ethoxycarbonyl)-substituted terpyrrole and the ferrocene-bridging pyrrole dimer form 1D chains by using N–H···O=C interactions in the solid state (Figure 3a,b).[20a,20c] Recently, bis(iminopyrrole)benzenes

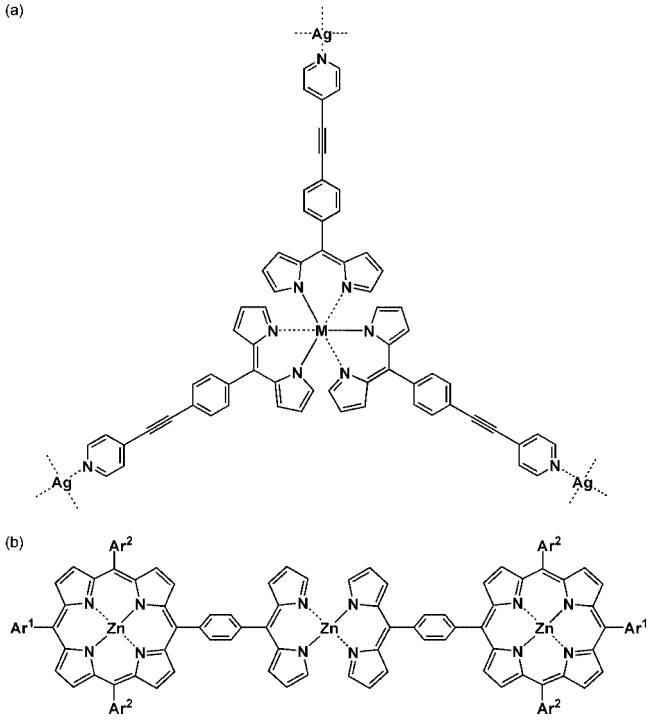

Figure 2. Metal-coordination assemblies of dipyrrin derivatives.

were reported to form nanostructural morphologies such as zig–zag and straight chains depending on the isomers (Figure 3c).[20e] However, micro- and nanometer-scale materials based on acyclic pyrrole derivatives have not been reported. The 1,3-dipyrrolyl-1,3-propanedione derivatives (Figure 3d), which were first reported by Oddo et al. in the early 20th century,[21] would form dimension-controlled micro- and nanometer-scale structures based on the hydrogen-bonding interactions of N–H···O=C.[22] Furthermore, the positions of the N site in *meso*-pyridyl-substituted dipyrromethanes affect the structures of the molecular assemblies in the solid state (Figure 3e).[23]

Hydrogen-bonding interaction is also useful for association with specific guest species. Of the various "targets", the recognition of inorganic and biotic anions such as acetate, phosphate, and halide, which are ubiquitous in biology, is concerned with essential aspects such as the activity of enzymes, transport of hormones, protein synthesis, and DNA regulation.[24,25] As an example, the antibiotic ristocetin has been known to efficiently and selectively bind amino acid carboxylates.[26] To date, considerable efforts have been devoted to the development of artificial acetate and carboxylate receptors and carriers, and various binding motifs have been synthesized in these years.[27] Among the various artificial host molecules reported to date, macrocycles consisting of pyrroles are particularly attractive because they behave as essential binding units as a result of the presence of polarized NH sites, as seen in diprotonated sapphyrins[28] and calixpyrroles[29] (Figure 4a).

Although less extensively studied, acyclic pyrrole derivatives have potentially even greater advantages.[25e] This is because they can form complexes with anions by the syn-

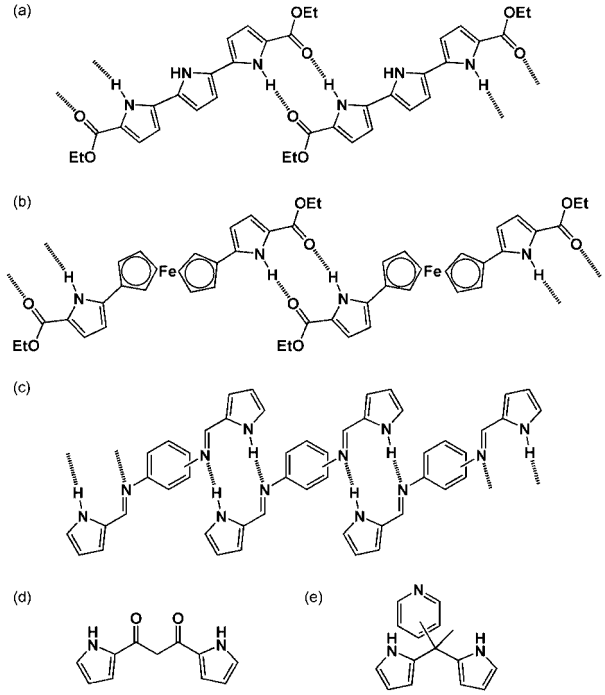

Figure 3. (a–c) Hydrogen-bonding assemblies of pyrrole derivatives and (d,e) structures of 1,3-dipyrrolyl-1,3-propanedione and *meso*-pyridyl-substituted dipyrromethanes.

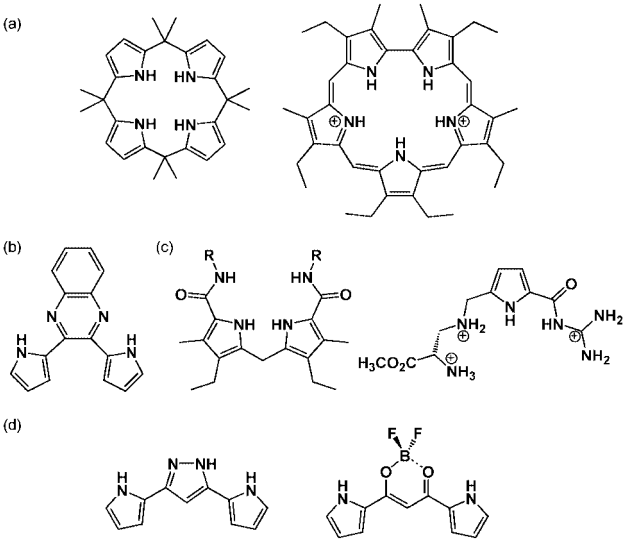

Figure 4. Representatives of (a) cyclic and (b–d) acyclic oligopyrrole-based anion receptors.

thetic attachment of additional recognition units such as amide NH, or simply because they easily form macrocyclic systems. As targets by conformational changes, receptors with linear geometries are required to fit with the volume and shape of the negatively charged species. Therefore, in these cases, the essential factors that determine the binding affinities for guest species would be the existence of temporal preorganization, the strength of the induced effect required to polarize the association site(s), and the steric and electrostatic repulsion by the peripheral substituents. Among the open-chain pyrrolyl anion receptors that have been reported to date are the dipyrrolylquinoxalines − fluorescent dyes that are directly connected to pyrrole rings (Figure 4b). These receptors undergo quenching of emission in the presence of certain anions.[30] The peripheral NH site(s) of N-confused porphyrins plays an essential role in binding anions.[31] Furthermore, amino acid bindings were achieved by using synthetic receptors, such as amide- and guanidiniocarbonyl-substituted pyrroles (Figure 4c) and pyrrole-based open-chain metal complexes.[32,33] A new set of acyclic oligopyrrole receptors based on 1,3-dipyrrolyl-1,3-propanediones (Figure 4d), dipyrrolyl-substituted pyrazoles,[34] and boron complexes,[35–39] have been synthesized; they act as the building units in [2+2] assemblies to form nano- and micrometer-scale architectures and also as efficient colorimetric and fluorescent anion sensors to form supramolecular assemblies.

π-Conjugated oligomers capable of guest binding are fascinating and potentially useful materials because of the possible solvent-free detection of analytes in the solid (i.e. film) state.[40] Apart from covalently-linked oligomers, supramolecular assemblies assisted by noncovalent π–π interactions can be considered as stacking oligomers. Porphyrins and related macrocycles are representatives of "extended" oligopyrroles; they can form self-assemblies by means of π–π stacking interactions.[1,6b,41]

Metal Coordination of Acyclic Oligopyrroles

Nanoscale Spherical Architectures Fabricated by Metal Coordination of Multiple Dipyrrin Moieties

Dipyrrin "dimers" (**1a**–**d**) with various rigid phenylethynyl spacers were prepared by the cross-coupling of bromobenzaldehydes with diethynylbenzenes, followed by condensation with pyrrole and subsequent DDQ oxidation. Dipyrrins **1a**–**d** were treated with $Zn(OAc)_2$ (1 equiv.) in THF to give oligomeric structures (Figure 5), as confirmed by the UV/Vis spectral changes in THF and ^1H NMR spectroscopy in $[D_8]$THF as well as trace peaks in the MALDI-TOF-MS.

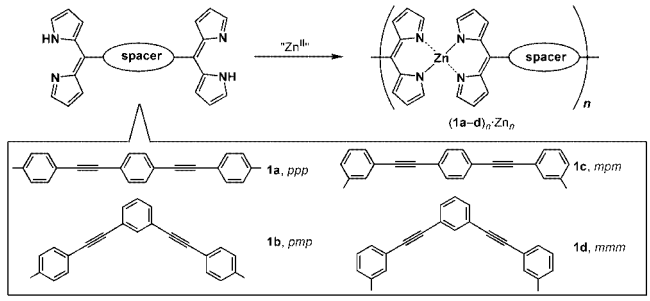

Figure 5. Metal complexation of dipyrrin "dimers" **1a**–**d**.

Self-assembled nanoscale structures of coordination oligomers (polymers) based on dipyrrin dimers were observed by using scanning electron microscopy (SEM), trans-

mission electron microscopy (TEM), and optical microscopy (OM). Zn^{II} complexes of the rod-like *ppp* **1a** and crinkled *mmm* **1d** give randomly shaped objects from THF, whereas coordination oligomer $\mathbf{1a}_n{\cdot}Zn_n$ is less soluble and forms precipitates. In sharp contrast, Zn^{II}-coordinated oligomers of the partially crinkled *pmp* **1b** and *mpm* **1c** give uniform nano-sized spherical structures with diameters of ca. 0.3 μm from the same solvent with initial concentrations of ca. 10^{-3} M. Submicron-sized polymer particles are normally spherical to minimize the interfacial free energy between the particle and the solvents. Further, dynamic light scattering (DLS) of $\mathbf{1b}_n{\cdot}Zn_n$ and $\mathbf{1c}_n{\cdot}Zn_n$ at 10^{-3} M in THF furnished the average diameter of their particles as ca. 0.1 μm, which suggests the formation of spherical structures in the solution. The effects of temperature, concentration, and solvent were also observed. Metal-free dipyrrins **1a**–**d** give amorphous objects from THF, which suggests that metal-bridging between organic ligands as well as both *para* and *meta* linkages are required for well-defined nanoscale objects. As shown in Figure 6, object formation requires several steps: (1) formation of coordination oligomers (primary), (2) stacking of the oligomers (secondary), (3) conversion into spheres (tertiary), and (4) assembly into larger objects without fusion and segmentation (quaternary).

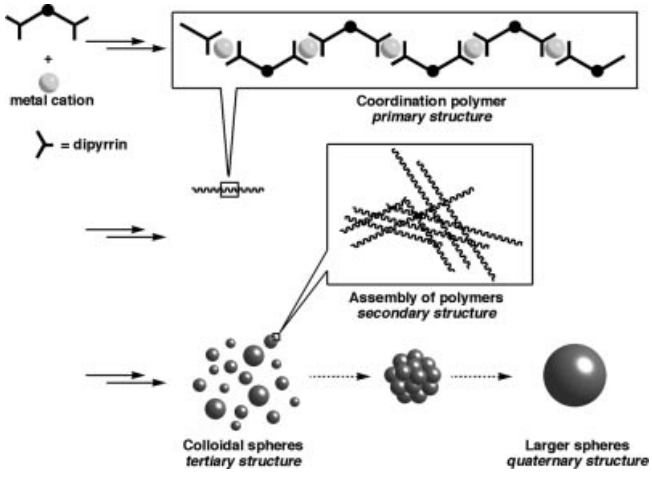

Figure 6. Formation pathway for particles from coordination oligomers (polymers).

In THF (5×10^{-5} M), the coordination oligomers $(\mathbf{1b}–\mathbf{d})_n{\cdot}Zn_n$ have emission maxima at 510–515 nm, which can be ascribed to the Zn^{II}–bis(dipyrrin) moieties. Conversely, in the solid state obtained by assembly from THF, $(\mathbf{1b}–\mathbf{d})_n{\cdot}Zn_n$ give fluorescent spherical objects with emission maxima at 532–543 nm. If other solvents such as CH_3CN are used, no emission is observed, possibly because of the aggregation of the nanoparticles. The addition of a 1:1 mixture of $Zn(OAc)_2$ and $Cu(OAc)_2$ to a THF solution of **1b** resulted in the quenching of the emission from the Zn^{II}–dipyrrin units. This is similar to the case of the single metal complex $\mathbf{1b}_n{\cdot}Cu_n$ and is possibly due to intramolecular energy transfer.[15]

Nanoscale Metal-Coordination Macrocycles Fabricated by "Dimeric" Dipyrrins

When $Zn(OAc)_2$ was added to a $CHCl_3$ solution of **1d** and pyrene (0.5 equiv.; length of ca. 9 Å), which was used as a template molecule with a size suitable for the cavity, and the mixture was heated at reflux for 2 d, the color of the solution slightly darkened. ESI-TOF-MS analyses of the complexes with added $AgClO_4$ (5 equiv.) as a cation source to associate the π-planes revealed the formation of Zn^{II} complexes of discrete [2+2]-type coordination macrocycles (Figure 7). Under these conditions, discrete higher homologs were not obtained. The UV/Vis absorption spectrum of $\mathbf{1d}_2{\cdot}Zn_2$ in $CHCl_3$ exhibits an absorption maximum (λ_{max}) at 486 nm, with a shoulder at ca. 465 nm, derived from the mixture of stereoisomers. Binuclear Zn^{II} complexes are expected to afford two chiral centers owing to the tetrahedral geometry of the Zn^{II} ion. In [2+2]-type complexes such as $\mathbf{1d}_2{\cdot}Zn_2$, two metal recognition sites (dipyrrin groups) are "strapped on" by phenylethynyl linkers; therefore, the Zn^{II} complexes are classified into three types of stereoisomers (two diastereomers), achiral (*meso*, *ΛΔ*) and chiral (*ΛΛ* and *ΔΔ*).

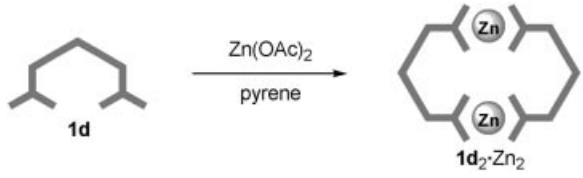

Figure 7. Formation of [2+2] coordination macrocycle $\mathbf{1d}_2{\cdot}Zn_2$.

The ^1H NMR spectrum of $\mathbf{1d}_2{\cdot}Zn_2$ in $CDCl_3$, which has two sets of signals with different integrations at a ratio of 4.6:1, revealed (1) the formation of [2+2] coordination macrocycles and (2) the existence of diastereomers derived from the cyclization. The formation of coordination nanorings is further suggested by the split chemical shifts in each dipyrrin β-CH signal of $\mathbf{1d}_2{\cdot}Zn_2$, ascribable to the relative "internal" and "external" protons derived from the cavity. Chiral HPLC analysis of $\mathbf{1d}_2{\cdot}Zn_2$ revealed that the major and minor fractions are achiral (*meso*) and chiral stereoisomers, respectively; this is also consistent with the existence of two types of diastereomers. Although tetrahedral dipyrrin-Zn^{II} moieties are achiral, covalent linkages of the *same* helicities produce "chiral rings", which would be the potential receptors for the chiral species. Such chirality that is observed in the minor isomers is a unique property derived from the distorted geometries of dipyrrin complexes as opposed to those of planar porphyrins.

From the equilibrium constants (K) between the chiral and *meso* isomers of $\mathbf{1d}_2{\cdot}Zn_2$, which were determined by analysis of the ^1H NMR spectra ($CDCl_3$) and the van't Hoff plots, the thermodynamic parameters (ΔH^0, ΔS^0) could be estimated as 0.75 kJ mol^{-1} and 15 J mol^{-1} K^{-1} for $\mathbf{1d}_2{\cdot}Zn_2$; this suggests that the chiral isomer is slightly more thermodynamically stable than the achiral one. In contrast, the rate constant (k) of the rotation of the dipyrrin moieties of $\mathbf{1d}_2{\cdot}Zn_2$ from the achiral to the chiral isomer was deter-

mined to be 0.5 s^{-1} at 20 °C by means of the spin-saturation transfer method. Such a slow transition between the stereoisomers is consistent with the results of HPLC analysis to yield the mixture of stereoisomers after resolution by HPLC. Exchanges between the achiral and chiral isomers (Figure 8a) would be achieved by a 90° rotation of one of the two dipyrrin–metal units, wherein one of the four β-CH passes through a nanoscale ring cavity, such as those in molecular motors or vehicles.

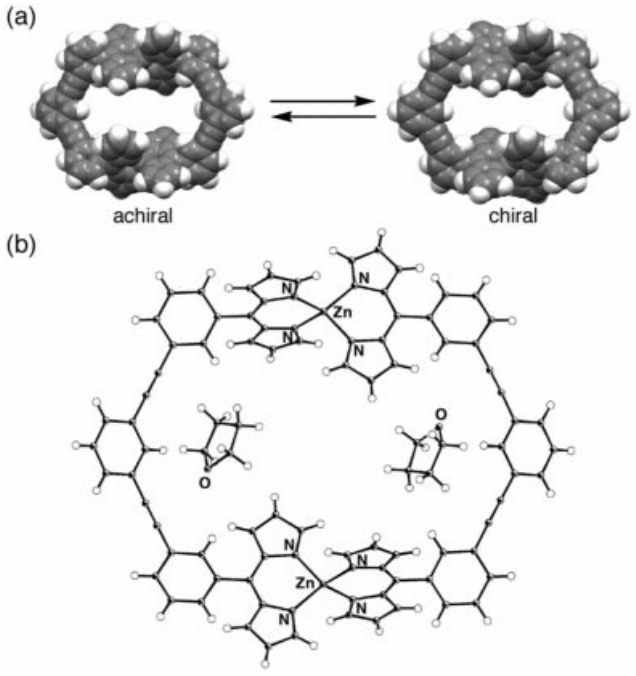

Figure 8. (a) Transition between two stereoisomers and (b) ORTEP drawing (50% probability ellipsoids) of **1d**$_2$·Zn_2 (achiral isomer).

The solid-state structure of the *meso* diastereomer of **1d**$_2$·Zn_2, which is the major stereoisomer, was revealed by X-ray diffraction analysis of a single crystal that was obtained from the mixture of the two diastereomers. The analysis showed a distorted hexagonal cavity with a diagonal of 1.6 nm (Figure 8b). In a nanoscale cavity, two THF molecules used as the solvent are encapsulated. Moreover, intermolecular donor–donor and acceptor–acceptor-type CH–π interactions are also observed. The nanorings are stacked with those in the other layers and are "connected" with those in the same layer to yield the molecular "bricks" in the solid state.[16]

Hydrogen-Bonding Assembly of Acyclic Oligopyrroles

Micro- and Nanometer-Scale Porous, Fibrous, and Sheet Architectures Fabricated from Supramolecular Assemblies of Dipyrrolyl Diketones

Various 1,3-dipyrrolyl-1,3-propanediones (**2a**–**e**, **3a**–**d**, **4a**–**d**; Figure 9a) were synthesized in modest yields from pyrroles and malonyl chloride derivatives in CH_2Cl_2.[21] In solution, dipyrrolyl diketones exist in equilibrium with their

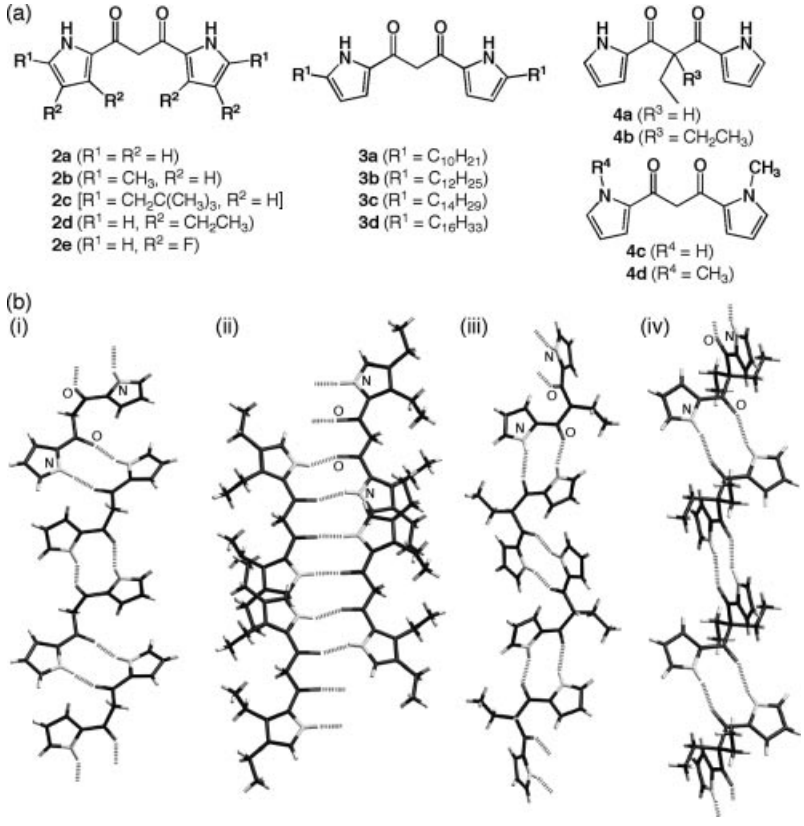

Figure 9. (a) Dipyrrolyl diketone derivatives **2**–**4** and (b) hydrogen-bonding chains of (i) **2a**, (ii) **2d**, (iii) **4a**, and (iv) **4b**.

enol tautomers. Single-crystal X-ray analyses of dipyrrolyl diketones elucidate that the keto forms are more stable in the solid state. Further, unsubstituted **2a**, β-ethyl-substituted **2d**, and bridging-C-alkyl **4a** and **4b** form 1D intermolecular hydrogen-bonding assemblies by using the NH and CO moieties at the edges of each molecule (Figure 9b). Of these diketones, β-ethyl **2d** has a rather planar geometry that affords the hydrogen-bonding arrays. In contrast, the *N*-methyl-substituted derivative (**4d**) exhibits a packing diagram without any hydrogen-bonding interactions in the solid state.

Various self-organizations of diketones observed in the X-ray structures make possible the fabrication of micro- and nanometer-sized objects that are identifiable by SEM. From CH_2Cl_2, the objects were rapidly fabricated by evaporation of the solvent. In contrast to unsubstituted **2a** and methyl-substituted diketone **2b**, which possess rather crystalline flower-like and plate morphologies, respectively, neopentyl-substituted derivative **2c** exhibits hexagonal tubes with pores of diagonal widths of 0.5–4 μm and lengths of 10–20 μm, when the same solvent is used (Figure 10a). Smaller objects are also grown within some of the porous spaces (inset of Figure 10a). Similarly, β-ethyl-substituted **2d** forms tube structures with rectangle- and parallelogram-shaped pores with diagonals of 1–4 μm (Figure 10b); whereas β-fluorinated **2e** forms fibers with widths of 0.1–0.3 μm (Figure 10c). Further, derivatives with long alkyl chains, such as hexadecyl substituents (**3d**), exhibit assemblies of thin-layered stacking sheets from CH_2Cl_2 (Figure 10d). Alternatively, micro- and nanometer-scale objects such as sheets of alkyl-substituted derivatives **3a**–**d** are constructed in the solvent from *n*-hexane. The TEM and OM images have also illustrated similar tubes, sheets, and fibers of the diketones. Polymorphs from CH_2Cl_2, in which the diketone derivatives are soluble as monomers, are fabricated during rapid evaporation of the solvent on the substrate to produce microcrystals (hexagonal and parallelogram tubes) or regularly ordered assemblies (fibers and sheets). Adequate alkyl chains or substituents are effective in the fabrication of micro- and nanometer-scale polymorphs controlled by van der Waals interactions. The morphologies can be correlated with and explained by X-ray diffraction (XRD) analyses to show the existence of well-organized 2D lamellar multilayer structures in the cases of **3a**–**d**.[22]

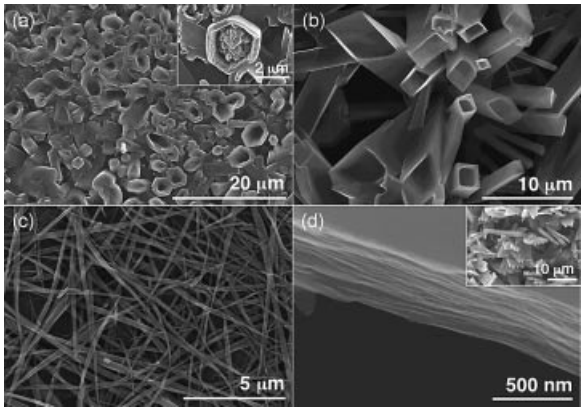

Figure 10. SEM images of (a) **2c** and hexagonal pore (inset), (b) **2d**, (c) **2e**, and (d) **3d** and assemblies of nanosheets (inset). The samples are prepared by casting of the CH_2Cl_2 solution on a silicon substrate.

Hydrogen-Bonding Self-Assemblies with 1D Linear, Dimeric, and Hexagonal Nanostructures of *meso*-Pyridyl-Substituted Dipyrromethanes

The self-assembled nanostructures of pyridyl-substituted dipyrromethanes **5a**–**c** (Figure 11a) obtained by hydrogen-bonding between the pyrrole NH and pyridyl N were examined by single-crystal X-ray analyses; for these analyses, the crystals were grown from CH_2Cl_2/hexane. *p*-Pyridyl **5a** and *m*-pyridyldipyrromethane **5b** form crinkled hydrogen-bonding chains and a dimeric structure, respectively. *o*-Isomer **5c**, however, exhibited cyclic hexamers possessing hexagonal structures, each with a diagonal of 1.7 nm and a height of 1.1 nm, by means of the external N–H···N interactions as well as internal ones between NH and the neighboring pyrrole π-planes (Figure 11b). Moreover, columnar wires consisting of stacked cyclic hexamers were observed along the *c* axis. Furthermore, in sharp contrast to *meso*-quaternary **5c**, *meso*-tertiary derivative **5c′** formed crinkled 1D chains similar to **5a**, which implies that the substituents at the *meso* position also significantly affect the morphologies of the nanostructures. Although cyclic oligomers of pyrrole are the most stable species, also supported by density functional theory (DFT) calculations, and utilize all the NH sites during hydrogen-bonding, cyclic hexamers have not been fabricated or observed thus far. ^{1}H NMR spectroscopic and DLS measurements indicate that dipyrromethanes **5a**–**c** 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.[23]

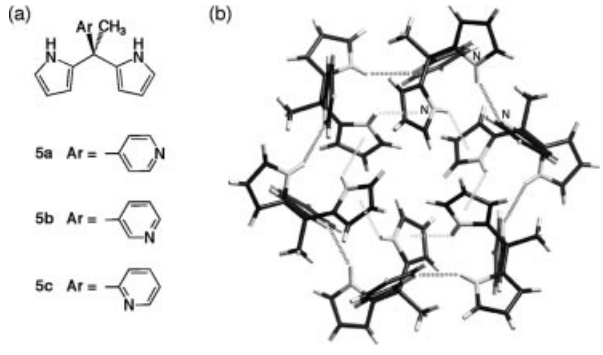

Figure 11. (a) *meso*-Pyridyl-substituted dipyrromethanes **5a**–**c** and (b) hydrogen-bonding cyclic hexamer of **5c** in the solid state.

Supramolecular Chemistry of Anion Binding

Dipyrrolylpyrazoles as Anion Receptors in the Protonated Form and Efficient Building Blocks for Organized Structures

Pyrazole can interact electrostatically or through hydrogen bonds with anionic or polar substrates in partly or fully protonated forms. Therefore, the combination of pyrrole and pyrazole groups within a single molecule could yield an essential role for binding various guest species. In accordance with the first example reported by Oddo in 1912,[21a] dipyrrolylpyrazoles (*dpp*, **6a**–**e**; Figure 12a) were synthesized by the condensation of excess hydrazine monohydrate with the corresponding 1,3-dipyrrol-2-yl-1,3-propanediones (**2a**–**c**, **3d**, **2e**)[22,35,37] in refluxing AcOH for 3–4 d. *N*-methyl-substituted **7a**–**c** were obtained similarly from diketone **4d** (for **7a**) or from methylation of **6a** and **6e** (for **7b** and **7c**, respectively). The 1:1 anion binding of pyrazole-N-blocked derivatives (**7b** and **7c**) was observed through their UV/Vis and ^{1}H NMR spectral changes [e.g., binding constants (K_a) of **7b** and **7c** for $CH_3CO_2^-$ in CH_2Cl_2 are 1600 and 28000 M^{-1}, respectively]. The anion binding ability of the pyrrole NH sites drove us to further investigate the details of *dpp* as a new class of π-conjugated systems. In contrast to N-protected *dpp*, the planar [2+2] binding structures of N-free *dpp* with TFA were elucidated by X-ray analyses of the **6a**$_2$·TFA_2, **6b**$_2$·TFA_2, and **6e**$_2$·TFA_2 complexes (Figure 12b). Of the anion binding complexes,[25,26] only a few examples of discrete aggregates consisting of multiple host and guest species have been reported.[42,43]

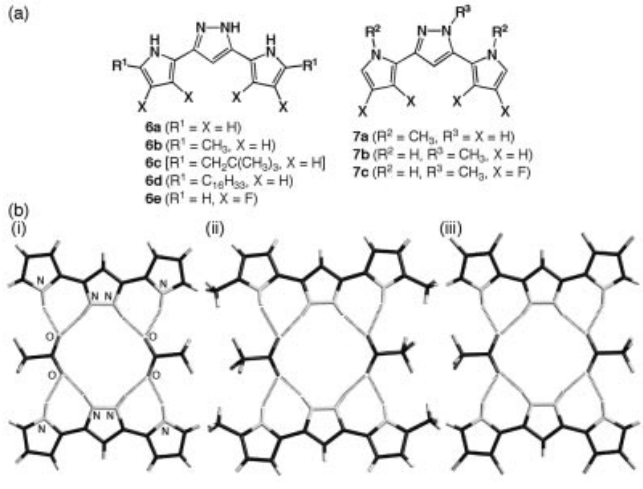

Figure 12. (a) Dipyrrolylpyrazoles **6a**–**e** and **7a**–**c** and (b) [2+2] assemblies of (i) **6a**$_2$·TFA_2, (ii) **6b**$_2$·TFA_2, and (iii) **6e**$_2$·TFA_2.

By casting the TFA complexes of *dpp* in CH_2Cl_2 on a silicon substrate, organized structures could be observed by SEM analysis. In sharp contrast to unsubstituted **6a**$_2$·TFA_2 and α-methyl **6b**$_2$·TFA_2 that yield crystalline objects, TFA complexes **6c**$_2$·TFA_2 and **6d**$_2$·TFA_2 with neopentyl and $C_{16}H_{33}$ chains provided petal-like objects with widths of ca. 500 nm and assembled sheet structures with thickness <100 nm. Further, β-fluorinated **6e**$_2$·TFA_2 exhibits rod-like morphologies with widths of ca. 100–200 nm, as well as small amounts of microcrystals. TFA complexes of N-blocked **7a** and **7b** as well as those of anion-free **6b**–**d** show only random and amorphous structures. From this we can infer that the role of TFA as the bridging moieties between the *dpp* planes makes the formation of nano- and micrometer-scale objects possible. Complexation with an acid would provide the planar geometry of *dpp*, which is required for the formation of nano- and micrometer-scale morphologies with the use of intermolecular interactions such as π–π stacking, as observed in the X-ray structures of **6a**$_2$·TFA_2, **6b**$_2$·TFA_2, and **6e**$_2$·TFA_2.[34]

Boron Complexes of Dipyrrolyl Diketones as a New Class of Acyclic Anion Receptors with C–H···X$^-$ Interactions

The addition of an excess amount of BF_3·OEt_2 in CH_2Cl_2 to dipyrrolyl diketones **2a**, **2c**, **2e**, and **2d** gives rise to strongly emissive boron difluoride (BF_2) complexes (**8a**–**d**, Figure 13a) in modest yields.[35–38] Ester-appended **8e** was obtained by a similar procedure with the use of ethoxycarbonyl-substituted β-diethylpyrrole as the starting material. "Blocked" derivatives **9a**–**c** were also synthesized from **4d**, **4c**, and **4a**, respectively.[36] The anion binding properties of the BF_2 complexes (Figure 13b) were examined by UV/Vis absorption spectral changes upon the addition of anions (Cl^-, Br^-, $CH_3CO_2^-$, $H_2PO_4^-$, and HSO_4^-) as tetrabutylammonium salts in CH_2Cl_2. The binding constants (K_a) of **8b**–**e** are summarized in Table 1; enhanced values are obtained for β-F derivative **8c**. The receptors in **8b**–**d** bind $CH_3CO_2^-$ more efficiently than the other anions. In contrast to the K_a values of **8d**, which are larger than those of α-neopentyl-substituted **8b**, the Cl^- binding constant of ester-appended **8e** is 170 M^{-1}, which is less than that of **8d** and **8b**; this is also seen for other anions such as Br^- and $CH_3CO_2^-$. Here, the electron-withdrawing α-carbonyl moieties are electrostatically and sterically hindering, and they do not act as "enhancers" that polarizes the pyrrole NH, as seen in β-fluorinated **8c**. NH···X$^-$ and bridging CH···X$^-$ interactions[44,45] are suggested by the ^{1}H NMR chemical shifts of **8a**–**d** in CD_2Cl_2. For example, upon the addition of $CH_3CO_2^-$ to **8c** (2×10^{-3} M) at –50 °C, both the NH and CH peaks (at δ = 9.02 and 6.65 ppm, respectively) disappear and new signals appear in the downfield region at 12.09 and 8.23 ppm, respectively. Similar downfield shifts upon the addition of $CH_3CO_2^-$ are also observed in **8b** (3×10^{-3} M). The Cl^- anion also shifts the signals of **8c** (2×10^{-3} M) to 11.82 (NH) and 8.31 (CH) ppm at –50 °C. Furthermore, the discrete resonances of the two species − anion complex and free receptor − suggest that the equilibrium between these forms is too slow on the NMR timescale, possibly due to the requirement of pyrrole inversions to bind the anions.

Table 1. Anion binding constants (K_a, M^{-1}) of **8b–e** upon the addition of anions as tetrabutylammonium salts in CH_2Cl_2. The values in the parentheses are the ratios to the K_a of **8b**.

Anion	K_a of **8b**	K_a of **8c**	K_a of **8d**	K_a of **8e**
Cl^-	2000	26000 (13)	6800 (3.4)	170 (0.09)
Br^-	330	1700 (5.2)	1200 (3.6)	20 (0.06)
$CH_3CO_2^-$	110000	960000 (8.7)	210000 (1.9)	9100 (0.08)
$H_2PO_4^-$	13000	190000 (15)	91000 (7.0)	29000 (2.2)
HSO_4^-	80	1100 (14)	1200 (15)	490 (6.1)

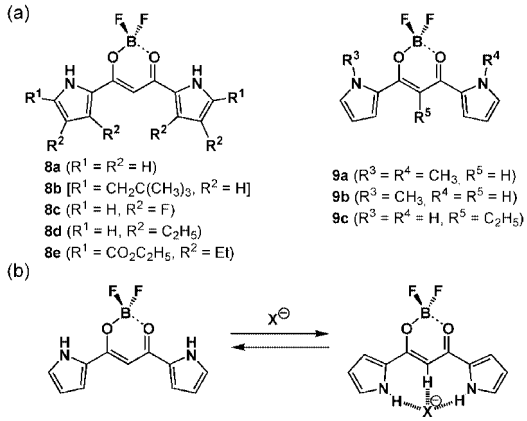

Figure 13. (a) BF_2 complexes of dipyrrolyl diketones **8a–e** and **9a–c** and (b) anion binding mode.

The above observations that the anion binding behaviors of these acyclic receptors cannot always be correlated with the electronic effects of the peripheral substituents can be explained by DFT calculations at the B3LYP/6-31G(d,p) level. Consistent with the experimental results, molecular simulations for receptors **8a–e** suggest that the most stable conformations of the free receptors with intramolecular interactions between pyrrole NH and oxygen atoms are not suitable for anion recognition; therefore, pyrrole inversions are required to bind the anions (Figure 14). The relative energies of the "preorganized" structures of **8a–e** compared to each stable conformation are estimated as 9.08, 8.96, 15.04, 4.98, and 1.18 kcal mol^{-1}, respectively, which suggests that the β-ethyl-substituted receptors, especially **8e**, show stronger preferred preorganized geometries than **8a–c**. However, ester-substituted **8e** exhibits lower K_a values than **8d** and comparable values to those of **8b**. This is possibly because of the electrostatic repulsion between the carbonyl oxygen atom and the anions and to the steric effects and the intramolecular interactions between the ester CO and pyrrole NH moieties, which may cancel the positive factor speculated by DFT.

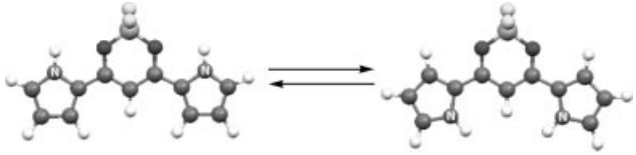

Figure 14. Optimized most stable (left) and preorganized (right) conformations of **8a**.

Furthermore, fully N-blocked derivative **9a** does not exhibit binding even for F^- in CH_2Cl_2, which indicates that the bridging CH moiety in this acyclic system is not able to associate with the anions in solution and, furthermore, that the NH moieties are more essential as interaction sites for the association with the anion than the bridging CH moieties. In this system, when *one* NH site is available for association, the question arises as to which of the interaction sites − the other NH group or the bridging CH unit − is more important in a supporting role for providing efficient binding. To answer this question, the substituent effects at the NH and bridging CH sites were investigated in detail. The K_a values of partially N- and C-blocked receptors **9b** and **9c** for $H_2PO_4^-$ and Cl^- were estimated as 1400 and 240 M^{-1}, respectively, for **9b** and 250 and <10 M^{-1}, respectively, for **9c**. The association constants of **9b** for Cl^- and $H_2PO_4^-$ are ca. 1/10, which is smaller than that of **8b**, and the C-blocked derivative **9c** exhibits much smaller K_a values for Cl^- and $H_2PO_4^-$ than it does for **8b**. The above observations suggested that, for Cl^- and $H_2PO_4^-$, multiple NH and CH interaction units are required.[36]

Single-crystal X-ray diffraction analyses of receptors **8a–c**, **8e**, **9b**, and **9c** revealed that the pyrrole nitrogen atoms face opposite sides of the molecule, which is possibly due to the intramolecular N–H···O interactions in the solid state (Figure 15a–c, e–g). Through intermolecular N–H···F hydrogen bonds, complicated 3D networks are formed. In contrast, *N*-alkyl-substituted **9a** shows 1D chains due to C–H···F interactions (Figure 15d). Further, ester-substituted **8e** forms a crinkled supramolecular assembly through ditopic N–H···O=C hydrogen-bonding (Figure 15g). Derivatives **8a** and **8c** show slipped π–π stacking structures wherein the core six-membered rings (diketone–boron moieties) are sandwiched between the two pyrrole rings of the neighboring molecules.

The interaction between the anions and the receptor was also studied by performing X-ray structural analysis of the Cl^- complex of **8a** with the use of a 1:1 mixture of the receptor and Bu_4NCl. In the solid state, the CH proton and one of the two pyrrole NH protons are associated with the Cl^- anion. The other NH proton turns to the opposite side and binds to another Cl^- anion to form an anion-bridging 1D hydrogen bonded infinite chain (Figure 16a). In contrast to **8a**, receptor **8c** utilizes only the NH interaction site to form the supramolecular 1D chains bridged by Cl^-, possibly due to the more polarized NH group relative to those of the β-H derivative (Figure 16b). In sharp contrast to Cl^- binding,

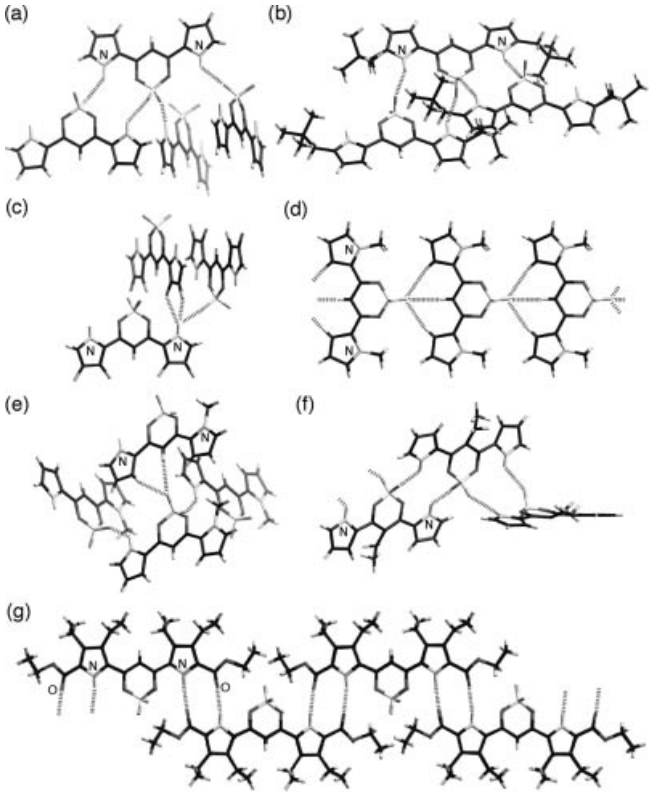

Figure 15. Molecular assemblies of (a) **8a**, (b) **8b**, (c) **8c**, (d) **9a**, (e) **9b**, (f) **9c**, and (g) **8e** in the solid state.

crystallization of a 1:1 mixture of **8c** with Bu_4NF from THF/hexane provides a self-assembly of the anionic form of **8c** by deprotonation of a pyrrole NH (Figure 16c). Furthermore, the single crystals obtained from CH_2Cl_2 or CH_2ClCH_2Cl, which are possible Cl^- sources, provides Cl^--bridging supramolecular chains that are identical to the structure shown in Figure 16b by anion exchange.

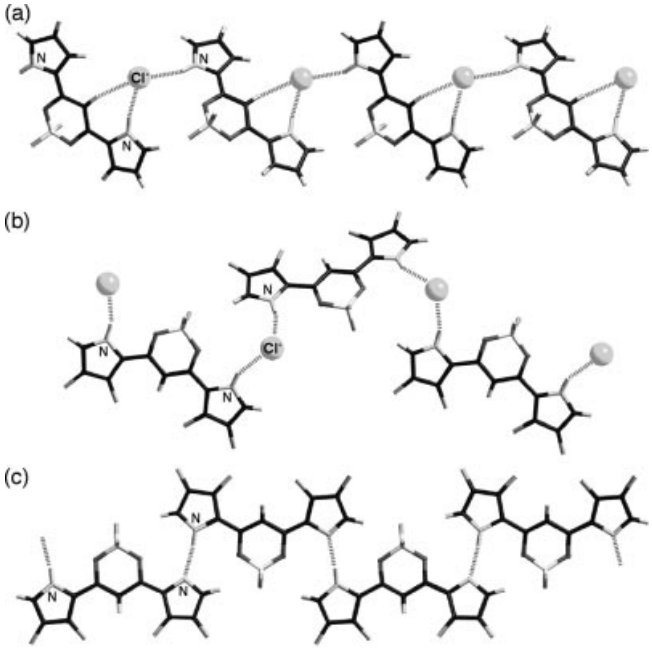

Figure 16. (a,b) Anion-bridging infinite chains of **8a**·Cl^- and **8c**·Cl^- and (c) assembly of the anionic form of **8c** in the solid state. Tetrabutylammonium cations are omitted for clarity.

Aryl-Substituted C_3-Bridged Oligopyrroles as Anion Receptors for the Formation of Supramolecular Organogels

Aryl-substituted derivatives of BF_2 complexes **10a**–**c** (Figure 17a) were obtained from the corresponding α-aryl-substituted diketones by treatment with BF_3·OEt_2. The absorption maxima (λ_{max}) of **10a** and **10b** in CH_2Cl_2 appear at 500 and 480 nm, respectively, which are redshifted relative to **8a** (432 nm), **8b** (457 nm), **8c** (421 nm), **8d** (452 nm), and **8e** (464 nm). Conversely, λ_{max} for **10c** appears at 456 nm, which is blueshifted by 44 and 24 nm relative to **10a** and **10b**, respectively, as a result of the distortion of the aryl rings. The gaps between the HOMO and LUMO of these receptors are related to these electronic absorption bands. Single-crystal X-ray diffraction analyses reveal that **10a** and **10b** form a dimeric structure through the N–H···F and *o*-C–H···F interactions (Figure 17b), whereas such assemblies are not formed for **10c**. Thus, the weak interaction of *o*-CH should play the role of a ligand for the anions in solution. Similar to the slipped π–π stacking structures of **8a** and **8c**, the stacking assemblies are observed in the crystals of aryl-substituted **10a** and **10b** (Figure 17c), wherein the slightly distorted aryl rings produce less-effective stacking.

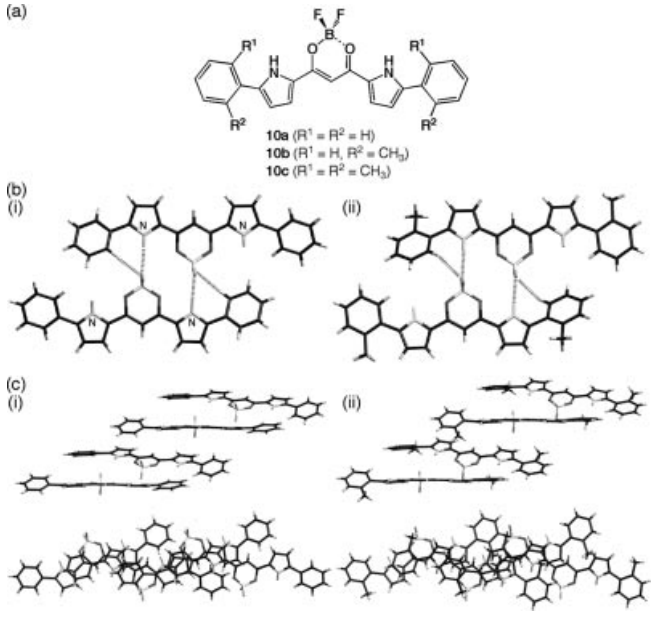

Figure 17. (a) Aryl-substituted derivatives **10a**–**c**, (b) single-crystal X-ray structures of (i) **10a** and (ii) **10b**, and (c) stacking structures (side and top views) of (i) **10a** and (ii) **10b** in the solid state.

The anion affinities of aryl-substituted receptors **10a**–**c** were estimated from the changes in the UV/Vis absorption spectra in the presence of increasing concentrations of the respective anions (Table 2). Relative to α-alkyl-substituted **8b**, α-phenyl **10a** shows augmented K_a values, especially for

Cl^- (ca. 15 hold enhancement) possibly due to its spherical structure. In contrast, doubly *o*-C-blocked **10b** exhibits K_a values less than that of **10a** and comparable to that of **8b**, whereas totally *o*-C-blocked **10c** shows K_a values (ca. 1/2) lower than that of **8b**. This is possibly due to steric hindrance and electrostatic repulsion of the anions by the π-plane.

Table 2. Anion binding constants (K_a, M^{-1}) of **10a–c** upon the addition of anions as tetrabutylammonium salts in CH_2Cl_2. The values in the parentheses are the ratios to the K_a of **8b**.

Anion	K_a of **10a**	K_a of **10b**	K_a of **10c**
Cl^-	30000 (15)	2500 (1.3)	1000 (0.50)
Br^-	2800 (8.5)	300 (0.91)	150 (0.50)
$CH_3CO_2^-$	210000 (1.9)	150000 (1.4)	7100 (0.65)
$H_2PO_4^-$	72000 (5.5)	8000 (0.62)	1400 (0.11)
HSO_4^-	540 (6.8)	35 (0.44)	14 (0.18)

^1H NMR spectral changes of **10a–c** by the addition of anions provided valuable insights into (1) the binding behaviors of the *o*-CH units as well as those of the pyrrole NH and bridging CH moieties and (2) the possible binding modes. Upon the addition of 1.5 equiv. of Cl^- to a CD_2Cl_2 solution of **10a** (1×10^{-3} M) at 20 °C, the signals due to **10a** at 7.68 (*o*-CH), 9.73 (pyrrole NH), and 6.23 (bridging CH) ppm decreased in intensity with the concurrent appearance of new signals at 8.19, 12.27, and 9.04 ppm. The peak derived from the *o*-CH group of the Cl^- complex (**10a**·Cl^-) with the integration of 4 H in the downfield region suggests the following: (1) an interaction between the *o*-CH group and the anion and (2) a rather rapid exchange (free rotation) between the anion-binding *o*-CH group and the "anion-free" *o*-CH group at this temperature. Further, the signals of receptor **10a** and complex **10a**·Cl^- can be observed independently, which is also seen in the case of derivatives such as **8b**, **8c**, **10b**, and **10c**, suggesting that a slow exchange takes place between these species on the NMR timescale. Rate constants *k* for the F^-, Cl^-, and Br^- binding of **10a** with the use of tetrabutylammonium salts in CH_2Cl_2 at 25 °C were estimated to be 7.2×10^4, 13.0×10^4, and 6.0×10^4 $M^{-1}s^{-1}$, respectively, by stopped-flow measurements.[46] Whereas the order of *k* ($Cl^- > Br^-$) is consistent with that of the binding constants (K_a), the more associated F^- (240000 M^{-1}) exhibits an intermediate value between those of Cl^- and Br^-; this suggests that thermodynamic stability is not always correlated with the kinetic properties.

Aryl substitution at the pyrrole α-positions in systems **10a–c** enables various substituents to be introduced in this new class of acyclic anion receptors for further applications and actually yields derivatives with alkoxy chains of various lengths at the aryl rings (**11a–d**, Figure 18a). X-ray analysis of **11a** shows one trimeric and two tetrameric stacking structures, which exhibit various slipped assemblies in the solid state (Figure 18b). Furthermore, X-ray analysis of anion complex **11a**·Cl^-, with a pentacoordinate geometry, suggests the formation of π-stacking and an electrostatically mediated columnar structure consisting of two **11a**·Cl^- planes and a layer of two tetrabutylammonium cations (Figure 18c).

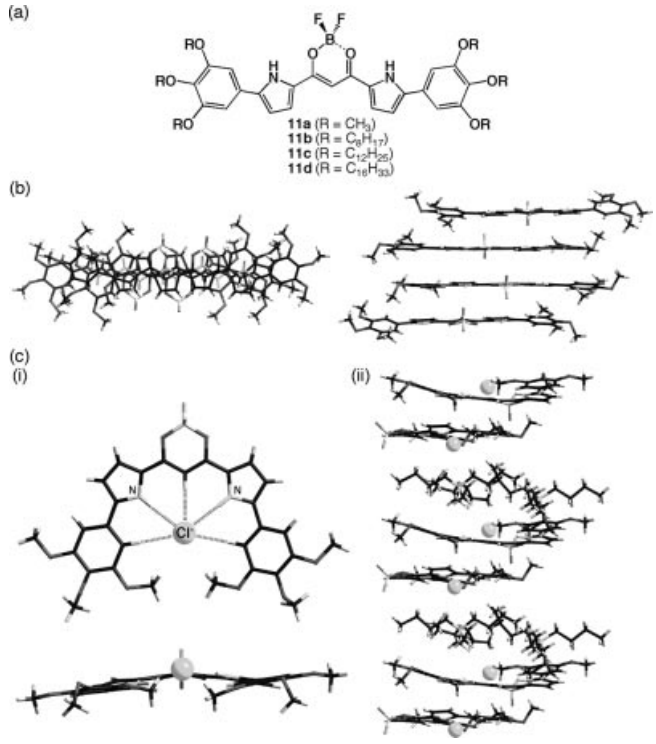

Figure 18. (a) BF_2 complexes **11a–d** with 3,4,5-trialkoxy-substituted aryl rings, (b) one of the stacking structures (top and side views) of **11a** in the solid state, and (c) (i) single-crystal X-ray structure (top and side views) of Cl^- complex of **11a** (one of the two conformations) and (ii) columnar structure. Solvents are omitted for clarity.

Hexadecyloxy-substituted **11d** forms a transparent emissive gel in hydrocarbon solvents such as octane (10 mg mL^{-1}). Upon heating above 27.5 °C, a sol–gel transition ($T_{sol-gel}$) occurs for the red organogel of **11d** in octane, which gives a solution that returns to the gel state upon cooling below $T_{sol-gel}$, whereas the octadecyloxy- and dodecyloxy-substituted derivatives **11b** and **11c** exhibit a $T_{sol-gel}$ at –8.5 and 4.5 °C, respectively. The split bands of gel **11d** at 525 nm, with shoulders at ca. 470 and 555 nm, are possibly derived from the slipped *H*- and *J*-aggregated modes. Fluorescence emission from the organogel is detected at 654 nm (λ_{ex} = 470 nm), which is redshifted relative to that (λ_{em} = 533 nm, λ_{ex} = 493 nm) of a dilute octane solution (1×10^{-5} M). Supramolecular organogel formation is achieved for the ordered structures on the basis of the noncovalent interactions between the π-conjugated moieties and their substituents; this is supported by atomic force microscopy (AFM), SEM, and XRD observations. The *d*-value of ca. 3.62 nm (001) estimated by XRD presumably corresponds to the distance between the stacking wires of **11d**. Although further details are required, the possible molecular level stacking structures, as suggested by X-ray analysis of the receptors as well as the molecular modeling of **11d**, can be correlated with the excitonic coupling between the chromophores.

The addition of Cl^- (10 equiv.) as its tetrabutylammonium salt (solid Bu_4NCl) to the octane gel of **11d** at 20 °C

produced gradual decomposition of the gelatinous state in ca. 2 h to yield an orange-colored and highly emissive solution. The absorption maximum and the corresponding fluorescence emission of the concentrated octane solution (10 mg mL^{-1}) including Cl^- were observed at 524 and 574 nm (λ_{ex} = 470 nm), respectively. This suggests that receptor **11d** is soluble as a "monomeric" anion complex in the octane solution. The addition of Br^- partially transformed the gel into a solution in 2–3 d under similar conditions, whereas $CH_3CO_2^-$ performs this transition in ca. 3 h. The slow gel collapse by these anions can be correlated with the pyrrole ring inversion to the π-stacking structure required for anion binding; this is a unique property of these acyclic receptors. The rapid change to the solution state induced by F^- (0.75 h) can be correlated to the peculiar binding behavior of F^- to NH site(s) without pyrrole ring inversions if they are not required. In contrast to the activities of anions such as F^-, Cl^-, and Br^-, the addition of Bu_4NPh_4B induces no transition to the solution state even after heating; this supports the assumption that anions, not tetrabutylammonium cations, are responsible for the transformation of the organogel to the solution state. Whereas the correlation with the rate constants, *k*, of the anion binding processes of **10a** in solution is observed in the cases of Cl^- and Br^-, the fast transition to solution caused by F^- is explained by the specific affinity of this anion to an NH site, as mentioned above. Supramolecular assemblies such as organogels amplify the rigidity of the stable conformations of monomers by means of π–π stacking; therefore, the organized structures controlled by the anion identity contrast the dynamic conformational changes of each molecule in the solution state.[39]

Conclusions

In this microreview, the author has demonstrated the recent progress in the supramolecular chemistry of acyclic oligopyrroles by using metal coordination, hydrogen-bonding, and other interactions such as π–π stacking, with a focus on the works of his group in the past three years. For example, bis(dipyrrin)-based ligands can induce coordination oligomers to form spherical nanoarchitectures and discrete [2+2] coordination macrocycles depending on the complexing conditions, whereas hydrogen-bonding interactions enable pyrrole oligomers to yield supramolecular assemblies and micro- and nanometer-scale structures. Furthermore, the boron complexes of dipyrrolyl diketones were shown to interact with anions through interactions by means of both pyrrole NH and bridging CH interactions with ring inversions of pyrroles from the stable geometries to capture the anions. Aryl-substituted π-extended receptors form assemblies such as supramolecular organogels as a result of the stacking structures, which can be controlled by the addition of anions. Acyclic oligopyrrole systems have the advantages of exhibiting dynamic conformation changes and, more essentially, they can be incorporated into various macromolecules and complexes as building subunits by means of covalent and noncovalent interactions. At present, the author is attempting to synthesize pyrrole-based π-conjugated molecules that form covalent-linked oligomers, supramolecular assemblies, and nanoscale materials, whose conformations and structures can be modulated by external chemical and physical stimuli.

Acknowledgments

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