

## V-F Pyrrole-Based Molecular Assemblies and Supramolecular Structures

An important class of naked-eye sensors are synthetic receptors that permit anionic guest species to be seen by visual means or *via* changes in the electronic absorption or fluorescent spectral properties. Among the various artificial host molecules reported to date, pyrroles incorporated into macrocycles are particularly attractive because they behave as essential binding units due to the presence of polarized NH sites. Although less well studied, acyclic pyrrole derivatives often potentially have even more advantages. This is because they can form the complexes with anions via the synthetic attachment of additional recognition units such as amide NH, or simply because they are easily to make their macrocyclic systems.

On the other hand, metal ion 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. Recently, nanoscale morphologies based on coordination polymers have been reported to exist as spherical and fibrous structures. Of the coordinating ligands, dipyrrens (dipyrromethenes), consisting of two pyrroles with an  $sp^2$ -*meso* position, are essential  $\pi$ -conjugated *bidentate monoanionic* ligands for metal ions in natural and artificial systems. Therefore, dipyrrens are promising planar scaffoldings for self-assemblies and would give neutral coordination oligomers and, which, in combination with various spacer units, could be used to fabricate fine-tuned nanoscale morphologies using bridging metal cations.

From the above background, we are focusing on development of nanoarchitectures based on metal coordination of dipyrren oligomers as well as efficient anion binding systems of acyclic oligopyrroles.

### V-F-1 Dipyrrolyldiketone Difluoroboron Complexes: Novel Anion Sensors with C–H...X<sup>−</sup> Interactions

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1,3-Dipyrrolyl-1,3-propanediones, synthesized from pyrroles and malonyl chloride, form BF<sub>2</sub> complexes, a new class of naked-eye sensors for halide and oxoanions. Association mode with the interactions of both the pyrrolyl NH and bridging CH protons for anion was confirmed by <sup>1</sup>H NMR chemical shifts in CD<sub>2</sub>Cl<sub>2</sub> and supported by theoretical study. Binding constants ( $K_a$ ) were estimated at  $8.1 \times 10^4$ ,  $2.0 \times 10^3$ ,  $3.3 \times 10^2$ ,  $1.3 \times 10^4$ , and  $80 \text{ M}^{-1}$  for F<sup>−</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, H<sub>2</sub>PO<sub>4</sub><sup>−</sup>, and HSO<sub>4</sub><sup>−</sup> by UV/vis absorption spectral changes in CH<sub>2</sub>Cl<sub>2</sub>. Augmentation of  $K_a$  compared to dipyrrolylquinoxaline for H<sub>2</sub>PO<sub>4</sub><sup>−</sup> is much larger than those for other anions. F<sup>−</sup> quenches the emission almost completely, contrasted with other anions, detected by fluorescence spectrum as well as naked-eye. In the case of the chloride anion complex, the formation of Cl<sup>−</sup>-bridged 1-D networks, in which anion is associated with two BF<sub>2</sub> complexes, is observed in the solid state.

### V-F-2 CH...Anion Interaction in BF<sub>2</sub> Complexes of C<sub>3</sub>-Bridged Oligopyrroles

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Alkyl-substituted derivatives of 1,3-dipyrrolyl-1,3-propanedione BF<sub>2</sub> complexes, the efficient receptors for halide and oxoanions using bridging CH as well as

pyrrole NH, are reported. BF<sub>2</sub> complexes with only one pyrrole NH interaction site, which exhibit less affinities than the basic structures, bind anions tightly, inferred by UV/vis absorption spectral changes, compared to the derivatives with an alkyl group at the bridging carbon or two pyrrole nitrogen sites. Using <sup>1</sup>H NMR and theoretical studies for anion complexes of N-blocked and N-lacked receptors, bridging CH (and one  $\beta$ -CH in N-blocked) as well as pyrrole NH is found to interact with anions.

### V-F-3 BF<sub>2</sub> Complex of Fluorinated Dipyrrolyldiketone: A New Class of Efficient Receptor for Acetate Anions

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$\beta$ -Fluorinated derivative of 1,3-dipyrrolyl-1,3-propanedione BF<sub>2</sub> complex has been prepared from 3,4-difluoropyrrole and malonyl chloride followed by treatment with BF<sub>3</sub>·OEt<sub>2</sub>. Despite the simple, acyclic, and neutral structure,  $\beta$ -fluorinated receptor exhibits efficient 1:1 binding for anions in CH<sub>2</sub>Cl<sub>2</sub> using bridging CH and pyrrole NH as interaction sites. Binding constant ( $K_a$ ) for acetate (CH<sub>3</sub>CO<sub>2</sub><sup>−</sup>), associated more effectively compared to the anions like F<sup>−</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, H<sub>2</sub>PO<sub>4</sub><sup>−</sup>, and HSO<sub>4</sub><sup>−</sup>, is estimated as  $9.6 \times 10^5 \text{ M}^{-1}$ , *ca.* 9-times augmented in comparison with that of  $\beta$ -H derivative ( $1.1 \times 10^5 \text{ M}^{-1}$ ). UV/vis and fluorescence spectral changes of the receptors elucidate the effective recognition of an amino acid such as phenylalanine in anionic form, also supported by CD spectral changes with mirror images by L- and D-isomers. Furthermore, in the solid state, BF<sub>2</sub> complex of  $\beta$ -F receptor provides Cl<sup>−</sup>-bridged supramolecular networks, and, in sharp contrast, deprotonated “anionic” self-assembled structures by F<sup>−</sup> binding.

### V-F-4 Dipyrin-Porphyrin Hybrids: Potential $\pi$ -Conjugated Platform to Fabricate Coordination Oligomers

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Bis-dipyrin-appended porphyrin derivatives are synthesized and exhibited complexation at the two dipyrin sites with  $\text{BF}_2$  and  $\text{Rh}(\text{CO})_2$ . Treatment with  $\text{Zn}(\text{OAc})_2$  is found to show the MALDI-TOF-MS suggesting the formation of dimer (corresponding to  $2 \times$  dipyrin-porphyrin hybrid +  $2 \times \text{Zn}^{2+}$ ) as a major product and trimetric and tetrametric structures as traces, which infers that the dipyrin moieties behave as potential scaffolds for supramolecular coordination polymers.

### V-F-5 Nanoscale Spherical Architectures Fabricated by Metal Coordination of Multiple Dipyrin Moieties

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Phenylethynyl-bridged dipyrin “dimers” have been prepared by cross-coupling reactions of bromobenzaldehydes and diethynylbenzenes followed by condensation with pyrrole and a subsequent DDQ oxidation. The dipyrin dimers performed  $\text{Zn}^{\text{II}}$  complexation in THF, detected by UV/vis and  $^1\text{H}$  NMR spectral changes. The coordination oligomers, according to the spacer units, provided the submicrometer-scale colloidal spherical objects observed by DLS measurements in solution and SEM, TEM, and optical microscopy on the substrate. Using mixture of THF and water, unique morphologies, such as hemispheres and bell-shaped and “golf ball”-like architectures, were observed. The coordination oligomers have emission maxima at 510–515 nm in THF, which can be ascribed to the  $\text{Zn}^{\text{II}}$ -bisdipyrin moieties, and give fluorescent spherical objects with emission at 532–543 nm in the solid state by assembly from THF. In contrast, addition of a 1:1 mixture of  $\text{Zn}(\text{OAc})_2$  and  $\text{Cu}(\text{OAc})_2$  into a THF solution of dipyrin dimer resulted in quenching of emission from the  $\text{Zn}^{\text{II}}$ -dipyrin units similarly to the case of the single  $\text{Cu}^{\text{II}}$  complex possibly due to intramolecular energy transfer.