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, dipyrrins (dipyrromethenes), consisting of two pyrroles with an sp²-meso position, are essential π-conjugated bidentate monoanionic ligands for metal ions in natural and artificial systems. Therefore, dipyrrins are promising planar scaffolding 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 dipyrrin oligomers as well as efficient anion binding systems of acyclic oligopyrroles.

V-F-1 Dipyrrolyldiketone Difluoroboron Complexes: Novel Anion Sensors with C–H–X⁻ Interactions

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1,3-Dipyrrolyl-1,3-propanediones, synthesized from pyrroles and malonyl chloride, form BF₂ 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 ¹H NMR chemical shifts in CD₂Cl₂ and supported by theoretical study. Binding constants (Kₐ) were estimated at 8.1 × 10⁴, 2.0 × 10³, 3.3 × 10², 1.3 × 10², and 80 M⁻¹ for F⁻, Cl⁻, Br⁻, H₂PO₄⁻, and HSO₄⁻ by UV/vis absorption spectral changes in CH₂Cl₂. Augmentation of Kₐ compared to dipyrrolylquinone for H₂PO₄⁻ is much larger than those for other anions. F⁻ 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⁻-bridged 1-D networks, in which anion is associated with two BF₂ complexes, is observed in the solid state.

V-F-2 CH–Anion Interaction in BF₂ Complexes of C₃-Bridged Oligopyrroles

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Alkyl-substituted derivatives of 1,3-dipyrrolyl-1,3-propanedione BF₂ complexes, the efficient receptors for halide and oxoanions using bridging CH as well as pyrrole NH, are reported. BF₂ 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 pyrrolyl nitrogen sites. Using ¹H NMR and theoretical studies for anion complexes of N-blocked and N-lacked receptors, bridging CH (and one β-CH in N-blocked) as well as pyrrolyl NH is found to interact with anions.

V-F-3 BF₂ Complex of Fluorinated Dipyrrolyldiketone: A New Class of Efficient Receptor for Acetate Anions

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β-Fluorinated derivative of 1,3-dipyrrolyl-1,3-propanedione BF₂ complex has been prepared from 3,4-difluoropyrrole and malonyl chloride followed by treatment with BF₃·OEt₂. Despite the simple, acyclic, and neutral structure, β-fluorinated receptor exhibits efficient 1:1 binding for anions in CH₂Cl₂ using bridging CH and pyrrole NH as interaction sites. Binding constant (Kₐ) for acetate (CH₃CO₂⁻), associated more effectively compared to the anions like F⁻, Cl⁻, Br⁻, H₂PO₄⁻, and HSO₄⁻, is estimated as 9.6 × 10⁵ M⁻¹, ca. 9-times augmented in comparison with that of β-H derivative (1.1 × 10³ 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, BF₂ complex of β-F receptor provides Cl⁻-bridged supramolecular networks, and, in sharp contrast, deprotonated “anionic” self-assembled structures by F⁻ binding.
V-F-4 Dipyrrin-Porphyrin Hybrids: Potential π-Conjugated Platform to Fabricate Coordination Oligomers

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Bis-dipyrrin-appended porphyrin derivatives are synthesized and exhibited complexation at the two dipyrrin sites with BF₂ and Rh(CO)₂. Treatment with Zn(OAc)₂ is found to show the MALDI-TOF-MS suggesting the formation of dimer (corresponding to 2 × dipyrrin-porphyrin hybrid + 2 × Zn²⁺) as a major product and trimetric and tetrametric structures as traces, which infers that the dipyrrin moieties behave as potential scaffolds for supramolecular coordination polymers.

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

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Phenylethynyl-bridged dipyrrin “dimers” have been prepared by cross-coupling reactions of bromobenzaldehydes and diethynylbenzenes followed by condensation with pyrrole and a subsequent DDQ oxidation. The dipyrrin dimers performed Zn²⁺ complexation in THF, detected by UV/vis and ¹H 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 Zn²⁺-bisdipyrrin 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 Zn(OAc)₂ and Cu(OAc)₂ into a THF solution of dipyrrin dimer resulted in quenching of emission from the Zn²⁺-dipyrrin units similarly to the case of the single Cu²⁺ complex possibly due to intramolecular energy transfer.