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Nanoscale Spherical Architectures Fabricated by Metal Coordination of Multiple Dipyrrin Moieties

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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.[1] Recently, nanoscale morphologies[2] based on coordination polymers have been reported to exist as spherical and fibrous structures.[3] Of the coordinating ligands, dipyrrins (dipyrromethenes), 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.[4−6] Therefore, dipyrrins are promising planar scaffoldings for self-assemblies and would give neutral coordination oligomers, which, in combination with various spacer units, could be used to fabricate fine-tuned nanoscale morphologies using bridging metal cations. In this communication, we report nanoarchitectures based on metal coordination of dipyrrin oligomers.

Dipyrrin "dimers" (**1**−**4**, Figure 1a) with various rigid phenylethynyl spacers were prepared by cross-coupling reactions.[6a] Sonogashira coupling of 4-bromobenzaldehyde and 1,4- and 1,3-diethynylbenzenes followed by condensation with pyrrole and a subsequent DDQ oxidation afforded dipyrrin derivatives **1** and **2** in 45 and 35% yields (from diethynylbenzene). By similar procedures involving reaction between 3-bromobenzaldehyde and the corresponding diethynylbenzenes, dimers **3** and **4** were also obtained in 8.7 and 20% yields, respectively. Structures of **1**−**4** were confirmed by ^{1}H NMR and FAB-MS.[7] For reference, dipyrrin **5** was also prepared (Figure 1b).

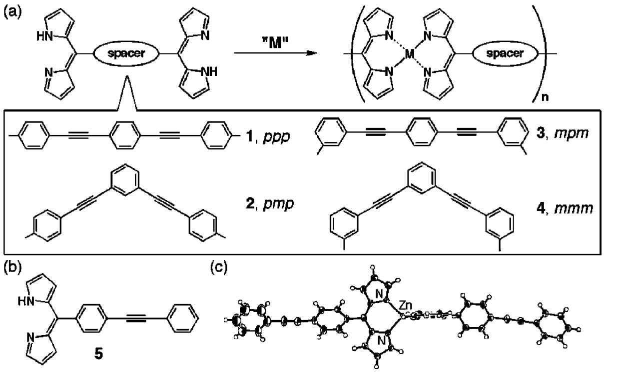

Figure 1. (a) Metal complexation of dipyrrin "dimers" **1**−**4**, (b) structure of dipyrrin **5**, and (c) X-ray single-crystal structure of **5·Zn^{II}** as one of the disordered conformations. Thermal ellipsoids are scaled to the 50% probability level.

Ditopic ligands **1**−**4** exhibit coordination behavior indicated by changes of solution color, and in some cases, precipitation occurs immediately upon addition of metal salts. Of the divalent metal cations, Zn^{II} is known to be a useful bridging metal between two dipyrrin units with tetrahedral geometry demonstrated by the X-ray structure of **5·Zn^{II}** (Figure 1c).[8,9] Therefore, dipyrrins **1**−**4** were treated with 1 equiv of $Zn(OAc)_2$ in THF to give oligomeric structures (Figure 1a). Metal coordination was confirmed by UV/vis spectral changes in THF solution (5×10^{-5} M) upon addition of 1 equiv of $Zn(OAc)_2$, where the band at 434 nm due to a free dipyrrin moiety disappeared with a concurrent emergence of a new band at 483−485 nm due to **1**−**4·Zn^{II}**. In contrast, 1 equiv of $ZnCl_2$ provided a mixture of metal complex and free ligand, possibly due to partial demetalation by HCl. In addition, ^{1}H NMR in THF-d_8 also exhibited the Zn^{II}-bridged oligomers of **2**−**4**, observed as another resonance of metal-free ligand moieties, by equimolar metal salt. Furthermore, MALDI-TOF-MS of rather rigid polymers **1,2·Zn^{II}** afforded no significant peaks, in contrast with that of **3,4·Zn^{II}**, showing the dimeric and trimeric [$n + n$] structures derived from fragmented oligomers.[10] In these cases and judging from the UV/vis spectra and X-ray analysis of **5·Zn^{II}**, Zn^{II} coordinated by dipyrrins does not suffer THF coordination, possibly because of its tetrahedral geometry.

Self-assembled nanoscale structures of coordination oligomers based on dipyrrin dimers were observed by scanning electron microscopy (SEM). Zn^{II} complexes of rod-like *ppp* **1** and crinkled *mmm* **4** give randomly shaped objects from THF, wherein **1·Zn^{II}** is less soluble and affords precipitates. In sharp contrast, Zn^{II}-coordinated oligomers of partially crinkled *pmp* **2** and *mpm* **3** give uniform nanosized spherical structures with a diameter ca. 0.3 μm from the same solvent with initial concentrations of ca. 10^{-3} M (Figure 2a,b). In the case of **2·Zn^{II}**, "trains" of spheres are also observed. Submicron-sized polymer particles are normally spherical for minimization of the interfacial free energy between the particle and the *solvents*. Further, dynamic light scattering (DLS) of **2·Zn^{II}** and **3·Zn^{II}** at 10^{-3} M in THF furnished an average diameter of their particles of ca. 0.1 μm, which suggests the formation of spherical structures in solution. The effects of temperature and concentration were also observed. On the other hand, metal-free dipyrrins **1**−**4** give amorphous objects from THF, which suggests that metal bridging between organic ligands as well as both *para* and *meta* linkages is required for well-defined nanoscale objects.

Interestingly, mixtures of THF and H_2O (2:1, v/v), where the Zn^{II} complexes are insoluble and precipitate, afforded hemispheres for the oligomers **2,3·Zn^{II}**, bell-shaped objects for **3·Zn^{II}** (Figure 2c), and spheres with "craters" for **4·Zn^{II}**. These features suggest that the nanospheres are colloidal and "fragile".[11] Further, 1:1 THF/H_2O solutions of **4·Zn^{II}** provided nanoscale "golf balls" as well as

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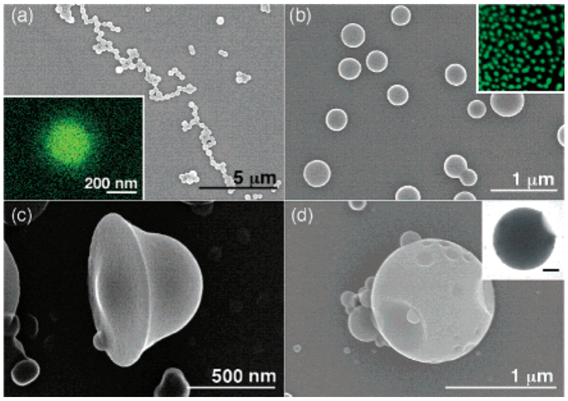

Figure 2. SEM of (a) **2·Zn**$^{\mathbf{II}}$ from THF (8×10^{-4} M; inset: Zn mapping by HRTEM-EDX), (b) **3·Zn**$^{\mathbf{II}}$ from THF (3×10^{-3} M; inset: fluorescence micrograph with 25 μm sides of each square), (c) **3·Zn**$^{\mathbf{II}}$ from THF/H_2O (2:1, 1.5×10^{-3} M), and (d) **4·Zn**$^{\mathbf{II}}$ from THF/H_2O (1:1, 1.5×10^{-3} M; inset: TEM with 200 nm bar).

objects-with-dents (Figure 2d). In contrast, using CH_3CN, which also affords precipitates, oligomers of **1−4·Zn**$^{\mathbf{II}}$ form bunches of the smaller spherical objects with ca. 100 nm diameters. In these solvent systems and similarly to protein foldings, object formation requires several steps: (i) formation of coordination oligomers (primary), (ii) stacking of the oligomers (secondary), (iii) conversion into spheres (tertiary), and (iv) assembly into larger objects without *fusion* (in CH_3CN) and segmentation (in THF/H_2O) (quaternary). X-ray analysis of **5·Zn**$^{\mathbf{II}}$, as a reference monomer, elucidates ordered π-planes (average distances between phenylethynyl units = 3.62 and 3.25 Å) and a CH−π interaction of phenylethynyl and dipyrrin moieties[9] to give structure information at subnanoscale level. In step (iii), diameters of spheres are augmented on the substrate compared to in solution. One of the formation mechanisms of the dents, in the final step, could be the release of residual solvents from the particles.[11,12] Furthermore, "denaturation" by sonication of CH_3CN solutions separated some assemblies into individual spherical objects. From the crystal packing of **5·Zn**$^{\mathbf{II}}$, ca. 10^5−10^6 dipyrrin units are estimated to be contained possibly with some solvent molecules in a sphere with a diameter of 100 nm.

The spherical nanostructures of coordination oligomers **2−4·Zn**$^{\mathbf{II}}$ obtained from THF or CH_3CN were also observed by transmission electron microscopy (TEM) and optical microscopy (OM). TEM also supports the formation of "dents" on the spheres in THF/H_2O solution (inset of Figure 2d). HRTEM-EDX of both **2·Zn**$^{\mathbf{II}}$ (from THF, inset of Figure 2a) and **4·Zn**$^{\mathbf{II}}$ (from CH_3CN) provided zinc mapping (8.63 keV derived from Zn−K level) to suggest that Zn is contained in the core. Further, AFM of **2·Zn**$^{\mathbf{II}}$ from THF suggests the heights of 70−80 nm and widths of ca. 500 nm for the hemispheres mounted on a silicon substrate.

In THF (5×10^{-5} M), the coordination oligomers **2−4·Zn**$^{\mathbf{II}}$ have emission maxima at 510−515 nm, which can be ascribed to the Zn^{II}−bisdipyrrin moieties. On the other hand, in the solid state by assembly from THF, **2−4·Zn**$^{\mathbf{II}}$ give fluorescent spherical objects (inset of Figure 2b) and emission maxima at 532−543 nm. If other solvents, such as CH_3CN, are used, no emission was observed possibly because of the aggregation of the nanoparticles.

Preliminary investigation of other metal cations (Co^{II}, Ni^{II}, Cu^{II}) gave similar spherical objects. Addition of a 1:1 mixture of $Zn(OAc)_2$ and $Cu(OAc)_2$ into a THF solution of **2** resulted in quenching of emission from the Zn^{II}−dipyrrin units similarly to the case of the single metal complex **2·Cu**$^{\mathbf{II}}$, possibly due to intramolecular energy transfer. In contrast to nanoscale quantum dots consisting of inorganic compounds (e.g., CdS), particles derived from Zn^{II}-bridged dipyrrin oligomers show emission even at the submicron scale.

Spherical nanoarchitectures fabricated from various metal cations and dipyrrin-based ligands could provide functional materials. Dimension control by solvents,[13] metal cations, and peripheral substituents will afford well-defined versatile shapes of nanoscale objects. Further construction and application of our current system are now being investigated.

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Supporting Information Available: Synthetic procedures for dipyrrin dimers **1−4**, NMR, MS (MALDI), DLS, SEM, TEM, OM, AFM, and solid-state FL of **1−4·Zn**$^{\mathbf{II}}$, and CIF file for the X-ray structural analysis of **5·Zn**$^{\mathbf{II}}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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