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Coordination Metallacycles of an Achiral Dendron Self-Assemble via Metal−Metal Interaction To Form Luminescent Superhelical Fibers

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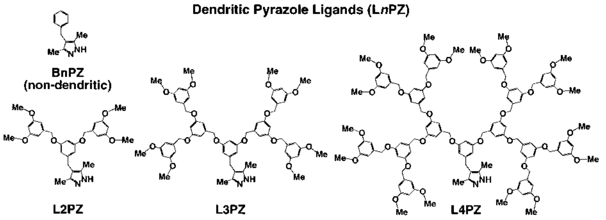
Hierarchical self-assembly of dendritic macromolecules via weak interactions such as H-bonding forces[1] has attracted great attention for the design of well-defined mesoscopic materials and also in relation to self-organization events in natural systems. For example, Percec and co-workers have reported that a carboxylic acid-anchored poly(benzyl ether) dendron having long alkyl chains at the periphery self-assembles via H-bonding and van der Waals interactions to form a cylindrical columnar assembly,[2] which can be regarded as a primary synthetic model of icosahedral viruses.[3] Recently, we have reported that a poly(benzyl ether) dendron anchoring a H-bonding dipeptide core self-assembles to form micrometer-scale fibers to induce efficient gelation of various organic solvents.[4]

Herein we report results of the first study on utilization of weak metal−metal interactions among group 11 metal ions[5] for hierarchical self-organization of dendritic macromolecules (Chart 1).[6] For this purpose, we chose pyrazole as the metal-ligating module, which is an exobidentate ligand capable of forming coordination metallacycles with Cu(I), Ag(I), and Au(I).[7,8] X-ray diffraction studies have suggested that they form in the solid-state long columnar assemblies involving a weak metal−metal interaction.[8d] More recently, pyrazoles having long alkyl chains, in the presence of Au(I), have been reported to form discotic liquid crystalline materials[9] via an edge-to-edge zigzag stacking of the metal pyrazolate coordination triangles.[9b]

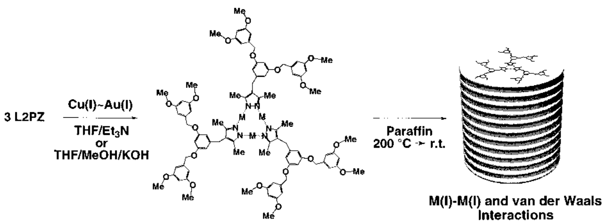
A series of pyrazole-anchored poly(benzyl ether) dendrons (L*n*PZ, Chart 1) with different generation numbers (*n* [number of alkoxybenzyl layers] = 2−4) were synthesized by the reaction of acetylacetone derivatives of the corresponding dendrons[10] with hydrazine.[11] Metal pyrazolate complexes of L*n*PZ with group 11 metal ions were prepared according to a literature method[7a,9a] with partial modification and unambiguously characterized.[11] For example, the IR spectrum of the Au(I) complex of L2PZ (KBr pellet) showed a vibrational band at 1517 cm^{-1} assignable to a metal-coordinated N=C bond[8d,9a,12] without any N−H stretching vibrational band at 3200−3000 cm^{-1}. ^{1}H NMR spectrum in CDCl$_3$ of L2PZ, upon coordination with Au(I), showed a slight downfield shift ($\Delta\delta = 0.03$ ppm) of the signal due to the pyrazole methyl groups.[11] In size-exclusion chromatography (SEC) of the complex, a single, sharp elution peak was observed at a higher molecular weight region than L2PZ.[11] Although the complexation of pyrazole with group 11 metal ions is known to form linear coordination polymers in the solid state,[13] the absence of any polydisperse character in the SEC profile, together with the simplicity of the ^{1}H NMR spectrum, indicates that the Au(I) complex adopts a uniformly sized, highly symmetric cyclic structure. MALDI-TOF-MS analysis showed a single peak centered at 2144, which corresponds to a trimer of Au(L2PZ) ([Au(L2PZ)]$_3$; [M + H$^+$] calcd 2144).[11] [Au(L2PZ)]$_3$ was highly robust toward protonolysis with water and inert to autoxidation in air. Although other metal complexes of L*n*PZ (*n* = 2−4) with Cu(I), Ag(I), and Au(I) all showed similar spectral profiles to those of [Au(L2PZ)]$_3$,[11] the complexes of Cu(I) and Ag(I) were rather susceptible to air and decomposed under SEC and MALDI-TOF-MS conditions.

Chart 1

Dendritic Pyrazole Ligands (L*n*PZ)



Example of Coordination of L*n*PZ (*n* = 2) with Group 11 Metal Ions and Their Self-Assembly



Coordination Metallacycle of L2PZ and M(I)

When a paraffin suspension of [Au(L2PZ)]$_3$ was once heated at 200 °C and allowed to cool to room temperature, it gradually became turbid to give a white fibrous precipitate, as observed by optical microscopy. Polarized microscopy of the precipitate showed a strong birefringence, indicating that the fibers are crystalline with a regular arrangement of the building blocks. Quite unexpectedly, the fibers at a closer look were helical, although precursor [Au(L2PZ)]$_3$ is devoid of any chiral centers. Figure 1b shows a SEM picture of the fiber, which is not single-stranded but a bundle of several loosely twisted elementary fibrils (∼0.2 μm in diameter) with a helical pitch of approximately 2.5 μm. According to NMR and SEC profiles, the fibers were soluble in CDCl$_3$ via dissociation into the individual metallacycles,

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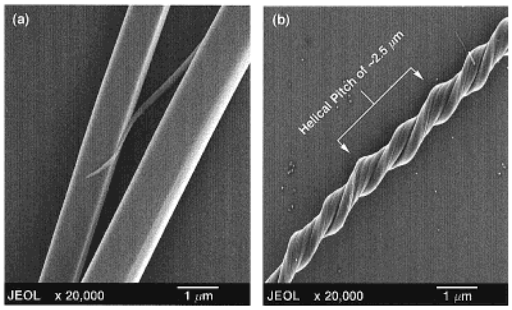

Figure 1. Scanning electron micrographs (SEM) of self-organized structures formed upon heating paraffin suspensions of pyrazolate complexes of (a) 4-benzyl-3,5-dimethylpyrazole (BnPZ) and (b) L2PZ with [Au(SMe$_2$)]Cl at 200 °C, followed by cooling to room temperature.

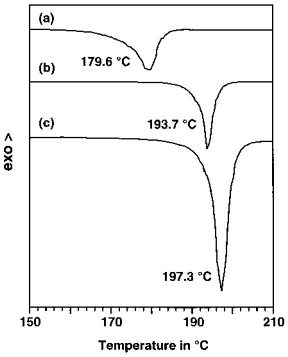

Figure 2. Differential scanning calorimetry (DSC) profiles of self-organized pyrazolate complexes of L2PZ with (a) [Cu(MeCN)]PF$_6$, (b) AgPF$_6$, and (c) [Au(SMe$_2$)]Cl.

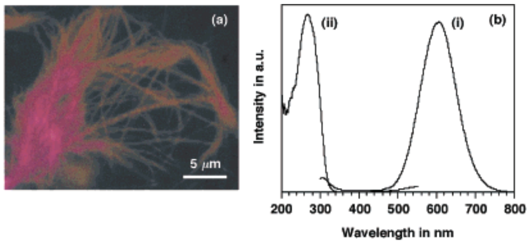

Figure 3. Luminescence profiles of a self-organized pyrazolate complex of L2PZ with [Cu(MeCN)]PF$_6$. (a) Fluorescence microscope image upon excitation at 336 nm. (b) (i) Emission ($\lambda_{\mathrm{ext}} = 280$ nm) and (ii) excitation spectra ($\lambda_{\mathrm{obsd}} = 605$ nm) of its Nujiol sample.

indicating that they are formed by the physical assembly of [Au(L2PZ)]$_3$ without ring opening to give linear polymeric structures. Likewise, superhelical fibers were formed from dendritic pyrazolate complexes of L2PZ with Cu(I) and Ag(I).

Figure 2 shows DSC profiles of the pyrazolate complexes of L2PZ with (a) Cu(I), (b) Ag(I), and (c) Au(I). In every case, a clear endothermic peak was observed, which is assignable to the melting temperature of the self-organized structure (T_m), as a possible consequence of the breakdown of the weak metal−metal interaction. In principle, orbital mixing is more likely to occur for heavier elements in the same group of the periodic table. Accordingly, the assembly of the metal complex of L2PZ with Au(I) showed the highest T_m at 197.3 °C,[14] while those with Ag(I) and Cu(I) displayed lower T_m at 193.7 and 179.6 °C, respectively.

Fluorescence microscopy (Figure 3a) showed that the superhelical fibers from the metal complex of L2PZ with Cu(I) are highly luminescent. Upon excitation of the dendritic wedge at 280 nm, the fibers emitted an intense orange luminescence centered at 605 nm (Figure 3b (i)) with a negligibly weak fluorescence from the dendritic wedge at 305 nm.[11,15] The excitation spectrum of the fibers, monitored at 605 nm (ii), was similar to the absorption spectrum, suggesting an excitation energy transfer from the dendritic wedge as an antenna[16] to the interior metal ion cluster. Interestingly, when the fibers were dissolved in CH$_2$Cl$_2$ to allow dissociation into the individual metallacycles, such a characteristic luminescence at the visible region disappeared completely, while the fluorescence from the dendritic wedge became pronounced. Although the superhelical fibers containing Ag(I) ($\lambda_{\mathrm{em}} = 521$, 605 nm) and Au(I) ($\lambda_{\mathrm{em}} = 594$ nm) exhibited similar luminescence profiles, they involved a relatively strong fluorescence from the dendritic wedge.[11]

Higher generation L3PZ and L4PZ gave stable coordination triangles with Au(I),[11] which however gave only nonfibrous, glassy aggregates upon thermal treatment in paraffin. Use of Cu(I) or Ag(I) in place of Au(I) also resulted in the formation of glassy aggregates. All these aggregates were luminescent, although they were much less emissive than the superhelical fibers with lower generation L2PZ. Together with the fact that the glassy aggregates in DSC showed T_m though at much lower temperatures than the fibers with L2PZ,[11] they are not random aggregates but involve metal−metal interactions. In contrast, the metal complexes of a *nondendritic* 4-benzyl-3,5-dimethylpyrazole (BnPZ) formed highly luminescent but nonhelical, needle-like fibers (Figure 1a). Therefore, the formation of superhelical fibers likely requires a delicate balance between the steric and van der Waals interactions among the dendritic wedges. Formation of helical assemblies from achiral building blocks is very rare.[17,18] Although the origin of the helicity is not clear at present, a possibility for generating a chiral element in the self-organization event is a helically twisted edge-to-edge stacking, rather than a zigzag stacking, of the coordination triangles, which can reduce the steric repulsion among the dendritic wedges.

In conclusion, we demonstrated that medium-sized group 11 dendritic metallacycles without any chiral elements form micrometer-scale, luminescent superhelical fibers. The morphology of the aggregate was totally dependent on the size of the dendritic wedge. In view of materials science, the dendritic fiber containing Cu(I) is particularly interesting, since it involves a long-range interaction among the highly redox-active transition metal ions surrounded by the dendritic coat. Thus, use of metal−metal interactions as driving forces for self-organization of dendritic macromolecules provides a novel strategy for the fabrication of mesoscopic functional materials.

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Supporting Information Available: Synthesis and analytical data of L*n*PZ ($n = 2-4$) and their metal complexes with Cu(I)−Au(I), SEC profiles of BnPZ and L*n*PZ ($n = 2-4$) and their metal complexes with Au(I), MALDI-TOF-MS spectra of metal complexes of BnPZ and L*n*PZ ($n = 2-4$) with Au(I), DSC profiles of self-organized metal complexes of BnPZ and L*n*PZ ($n = 2-4$) with Cu(I), and selected luminescence spectra of self-organized metal complexes of BnPZ and L*n*PZ ($n = 2-4$) with Cu(I)−Au(I) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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