

Self-Assembly of Heteroleptic [Cu(dipyrrinato)(hfacac)] Complexes Directed by Fluorine–Fluorine Interactions

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Heteroleptic copper(II) complexes were synthesized from three different meso-substituted pyridyl- and quinoline-dipyrrinato ligands (3-pyrdpm, 3-quindpm, and 4-quindpm). Metal complexes were prepared with both acetylacetonate (acac) and hexafluoroacetylacetonate (hfacac) ancillary ligands. The complexes undergo a self-complementary self-assembly process upon crystallization to generate a range of solid-state topologies including one-dimensional coordination polymers and discrete hexameric rings. The self-assembly of these molecular aggregates is driven by metal–ligand bonding, but is also modulated by fluorine–fluorine interactions. Perfluorination of the spectator ligand tends to generate more compact structures, which is attributed to aggregation of the perfluoromethyl groups. The results presented here demonstrate that fluorine–fluorine contacts can be used to modulate supramolecular structures in the solid state.

Coordination polymers have received a great deal of attention in recent years because they hold promise for developing novel magnetic, electronic, and functionalized materials.¹ A large body of work has been reported that utilizes Cu(acac)₂ (acac = acetylacetonato) and Cu(hfacac)₂ (hfacac = hexafluoroacetoacetonato) bound to pyridine derivatives to form molecular complexes,^{2–4} discrete supramolecular structures,^{5,6} and coordination polymers.^{7–10} We have reported that a single acac ligand of Cu(acac)₂ can be

replaced with a dipyrromethene (dipyrrin) chelator, resulting in a square-planar copper complex that can subsequently take on an axial donor atom.¹¹ In this motif, a self-complementary self-assembly process occurs when a heteroatom donor group that can occupy the vacant axial position of a second complex is incorporated into the meso position of the dipyrrin ligand, resulting in a square-pyramidal copper(II) center and the formation of a supramolecular structure. Pyridine and thioether donor groups both have been found to form coordination polymers via this approach.^{11,12} Furthermore, some very unusual structures, including a complex that forms both a molecular hexagon and an antiparallel double-helix in the same crystalline framework, have been discovered;¹³ in this complex, the unusual topology is attributed to the effect of fluorine–fluorine interactions^{14,15} in the solid state. Herein, we confirm that the use of perfluorinated spectator ligands can be used to drive the formation of compact structures in the solid state, thereby directing the self-assembly of metal complexes.

The synthesis of the ligand 5-(3-pyridyl)dipyrromethene (3-pyrdpm) has previously been described.¹¹ To determine the effect of adding additional hydrophobic groups to the meso position of 3-pyrdpm and related dipyrrin ligands, two quinoline-dipyrrin compounds were synthesized. Quinoline-derived ligands have been previously shown to coordinate to Cu(acac)₂.¹⁶ Condensation of either 3-quinolinecarboxaldehyde or 4-quinolinecarboxaldehyde with pyrrole followed by oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) gave the heteroditopic ligand 5-(3-quinolyl)dipyrromethene (3-quindpm) or 5-(4-quinolyl)dipyrromethene (4-quindpm), respectively. Addition of copper(II) sources, such as Cu(acac)₂ or Cu(hfacac)₂·H₂O, to the oxidized

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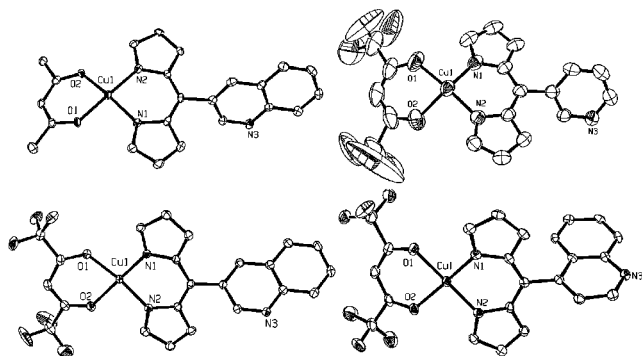
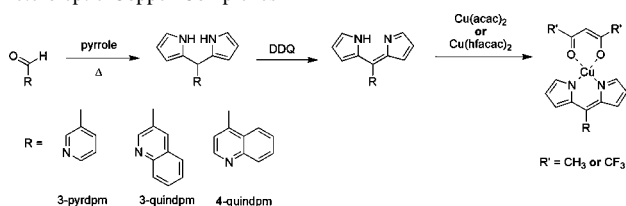


Figure 1. Structural diagrams of [Cu(3-quindpm)(acac)] (top left), [Cu(3-pyrdpm)(hfacac)] (top right), [Cu(3-quindpm)(hfacac)] (bottom left), and [Cu(4-quindpm)(hfacac)] (bottom right) with partial atom numbering schemes (ORTEP, 50% probability ellipsoids). Hydrogen atoms, solvent molecules, and axial ligands have been omitted for clarity.

Scheme 1. General Synthesis for Preparing Dipyrin Ligands and Heteroleptic Copper Complexes



ligands in situ produced the heteroleptic complexes [Cu(3-quindpm)(acac)], [Cu(4-quindpm)(acac)], [Cu(3-pyrdpm)(hfacac)], [Cu(3-quindpm)(hfacac)], and [Cu(4-quindpm)(hfacac)] in modest (14–38%) isolated yields (Scheme 1).

The heteroleptic copper complexes were fully characterized by infrared and electronic spectroscopy, as well as high-resolution mass spectrometry (see Supporting Information). Furthermore, most of the complexes were characterized in the solid state by single-crystal X-ray diffraction (Figure 1, Table S1). Attempts to crystallize [Cu(4-quindpm)(acac)] yielded only microcrystalline material not suitable for X-ray diffraction. All of the complexes are found to self-assemble in the solid state to form supramolecular structures (vide infra). The complexes display square-pyramidal coordination geometries with the acac and dipyrin chelates occupying the square plane and the pyridyl or quinoline nitrogen atoms from a neighboring complex occupying the apical site (Figure 1). Perfluorination of the spectator ligand results in small differences in the Cu–N_{dipyrin} and Cu–O bond lengths. The acac-derived complex has Cu–N_{dipyrin} bond distances of 1.97–1.98 Å and Cu–O bond distances of 1.94–1.96 Å, whereas the hfacac-derived complexes have shorter Cu–N_{dipyrin} bond distances of 1.94–1.96 Å and longer Cu–O bond distances of 1.98–2.00 Å.

The [Cu(3-quindpm)(acac)] complex assembles into one-dimensional zigzag polymer chains (Figure 2), in a manner essentially identical to that of the structurally related complex [Cu(3-pyrdpm)(acac)].¹¹ The polymer chains pack in a herringbone fashion (Figure S1), again very similar to the [Cu(3-pyrdpm)(acac)] counterpart. The chains of [Cu(3-quindpm)(acac)] are aligned along the crystallographic *a* axis with a Cu–N_{quin} bond distance of ~2.46 Å, slightly longer than that found in the [Cu(3-pyrdpm)(acac)] system

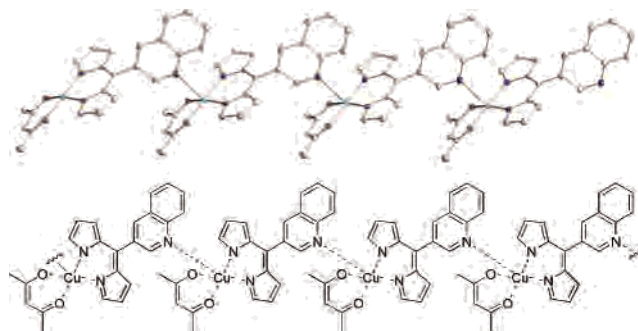


Figure 2. ORTEP representation (50% probability ellipsoids, top) and chemical drawing (bottom) representation of the coordination polymer formed by [Cu(3-quindpm)(acac)]. Hydrogen atoms have been omitted for clarity.

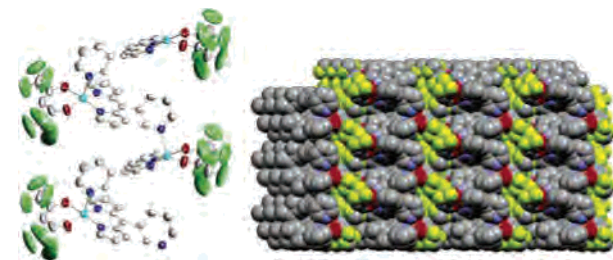


Figure 3. ORTEP representation (50% probability ellipsoids, left) and packing diagram (slightly off-set from crystallographic *a* axis, right) of [Cu(3-pyrdpm)(hfacac)]. Hydrogen atoms and solvent molecules have been omitted for clarity.

(~2.31 Å). The comparison of [Cu(3-pyrdpm)(acac)] and [Cu(3-quindpm)(acac)] suggests that moderate alterations at the meso position have little effect on these supramolecular structures.

We have previously shown that fluorinated ancillary ligands alter the packing of the heteroleptic complexes.¹³ To further explore these effects, [Cu(3-pyrdpm)(hfacac)] was prepared and crystallized (Figure 3). The topology of the [Cu(3-pyrdpm)(hfacac)] polymer is helical, which is distinct from the zigzag morphology of the unfluorinated counterpart.¹¹ The chains are aligned along the crystallographic *b* axis, and the Cu–N_{pyridyl} bond distance is 2.28 Å. The perfluoromethyl groups from the ancillary hfacac ligand are directed toward the outside of the helical structure, so that they are oriented toward perfluoromethyl groups of neighboring polymer chains. The complex aggregates such that each perfluoromethyl group interacts with four neighboring hfacac groups of adjacent chains with F–F distances of 2.9–3.5 Å. Examination of the chain packing clearly shows layers of alternating fluorinated and unfluorinated regions (Figure 3).

[Cu(3-quindpm)(hfacac)] was crystallized and found to form a one-dimensional coordination polymer with the chains aligned along the crystallographic *b* axis and Cu–N_{quin} bond distances of 2.35 Å (Figure 4). Like [Cu(3-pyrdpm)(hfacac)], the polymer displays a helical topology. The complex aggregates such that the perfluoromethyl groups interact with three neighboring perfluoromethyl groups of adjacent hfacac groups with F–F distances of 2.8–3.6 Å (Figure S2). As in [Cu(3-pyrdpm)(hfacac)], layers of alternating fluorinated and unfluorinated regions can be observed in the packing of the polymers (Figure 4). Comparison of [Cu(3-pyrdpm)(hfacac)]

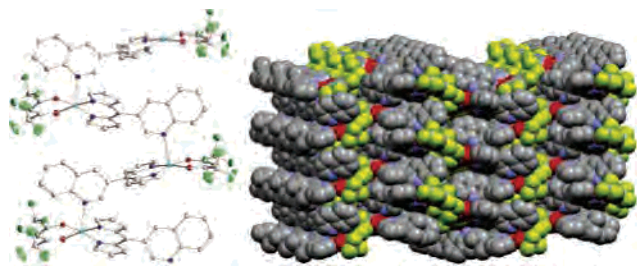


Figure 4. ORTEP representation (50% probability ellipsoids, left) and packing diagram (slightly off-set from crystallographic *a* axis, right) of [Cu(3-quindpm)(hfacac)]. Hydrogen atoms and solvent molecules have been omitted for clarity.

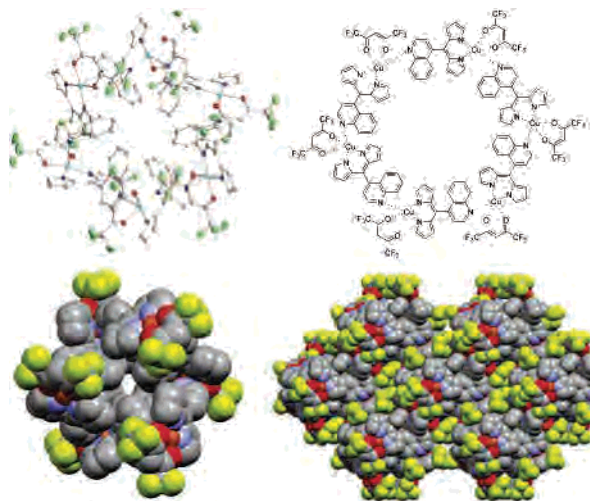


Figure 5. ORTEP representation (50% probability ellipsoids, top left), chemical (top right), space-filling (lower left), and packing diagrams (parallel to the crystallographic *c* axis, lower right) of the hexamer formed by [Cu(4-quindpm)(hfacac)]. Hydrogen atoms and solvent molecules have been omitted for clarity.

and [Cu(3-quindpm)(hfacac)] to [Cu(3-pyrdpm)(acac)] and [Cu(3-quindpm)(acac)] clearly shows that addition of fluorinated groups has a strong influence on supramolecular structure. The hfacac ligands result in helical instead of zigzag arrangement; in contrast, the additional aromatic surface of 3-quindpm versus 3-pyrdpm has comparatively little effect on changing the polymer topology.

The most significant effect of fluorination is found in the complex [Cu(4-quindpm)(hfacac)]. Instead of a one-dimensional coordination polymer as found with [Cu(4-pyrdpm)(acac)],¹¹ the compound crystallizes as a discrete hexameric ring (Figure 5). Again, this parallels the chemistry found with the pyridyl analogue, where [Cu(4-pyrdpm)(hfacac)] forms six-membered rings and double-helical polymers in a single crystalline lattice.¹³ In [Cu(4-pyrdpm)(hfacac)], the copper(II) centers in the hexamer are essentially coplanar; however, in [Cu(4-quindpm)(hfacac)], the ring is twisted in on itself, and the copper(II) ions take on a cyclohexane-like “chair” conformation (Figure S3). The Cu–N_{quin} bond lengths range from 2.37 to 2.48 Å, significantly longer than the Cu–N_{pyr} distance in the hexamer reported previously.¹³ The benzo groups of the quinoline groups are directed toward the center

of the ring, and the perfluoromethyl groups are pointed outward from the complex (Figure 5). This creates a supramolecular structure with a hydrophobic core and a fluorinated periphery. The hexamers pack such that the perfluoromethyl groups contact two perfluoromethyl groups of nearby hexamers with F–F distances of 2.9–3.6 Å. In contrast to [Cu(4-pyrdpm)(hfacac)], no open channels or pores are present in the structure of [Cu(4-quindpm)(hfacac)].

In summary, we have synthesized a variety of polymeric and supramolecular topologies by using self-complementary, self-assembling heteroleptic copper(II) complexes. We have probed the effects of modifying the donor group in the meso position of the heteroleptic dipyrin ligand by examining both pyridyl and quinolyl derivatives. The results show that the hydrophobic and steric properties of the quinoline-derived ligands have little effect on the overall morphology of the solid-state structures. Heteroleptic complexes of the formulation [Cu(dpm)(acac)] where dpm is 4-pyrdpm, 3-pyrdpm, and 3-quindpm all form simple, one-dimensional zigzag polymers.¹¹ In contrast, the introduction of the perfluorinated spectator ligand hfacac is found to have a large influence on the resulting supramolecular structure. Complexes of the general composition [Cu(dpm)(hfacac)] generate compact, helical coordination polymers when dpm is 3-pyrdpm or 3-quindpm. Furthermore, hfacac complexes with 4-pyrdpm¹³ and 4-quindpm produce discrete six-membered rings that display perfluoromethyl groups at their periphery. By modifying the dipyrin and acac ligands in a stepwise fashion, we have established some guidelines by which these supramolecular structures can be devised and manipulated. The use of fluorine–fluorine interactions as a way to influence solid-state self-assembly might prove useful in fine-tuning the structure of crystalline materials. Efforts to explore this strategy in coordination polymers and metal–organic frameworks based on related ligand systems are underway.

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Supporting Information Available: Experimental details for all syntheses, spectroscopic studies, and X-ray structures. X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. CIF files have also been deposited with the Cambridge Crystallographic Data Centre (CCDC) and can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. [Fax: (+44)1223-336-033. Internet: <http://www.ccdc.cam.ac.uk>]. Refer to CCDC reference numbers 267094, 267095, 267096, and 267097.

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