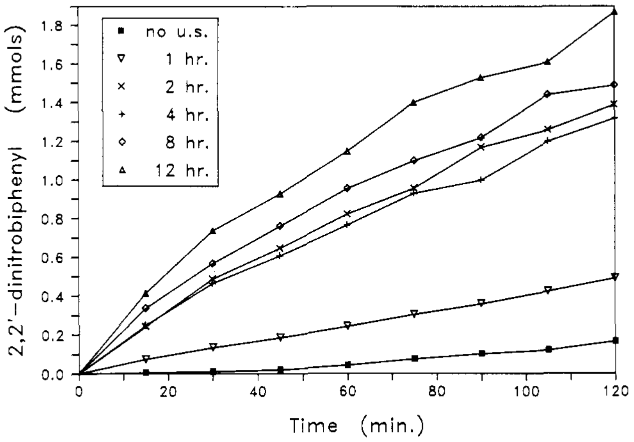
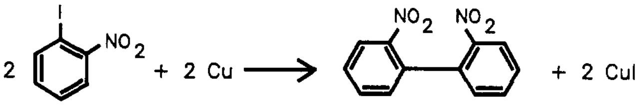


Figure 3. Initial rates of product formation in the Ullmann coupling reaction. The amount of 2-iodonitrobenzene is plotted against the length of ultrasonic pretreatment of Cu powder. Ultrasonic irradiation was done in dimethylformamide at 288 K with an acoustic intensity of $\approx$50 W/cm^2. Reactions were run at 373 K under Ar in dimethylformamide; 100% yield corresponds to 5.0 mmol.

conditions. Whether or not the surface deposition of carbon is important to the enhanced reactivity remains an open question. Further work is under way to clarify this matter.

The effects of ultrasound on the reactivity of Cu metal as a stoichiometric reagent have been documented in the literature in two cases: the Ullmann coupling[18] (where $C_6H_4(NO_2)$ is *o*-nitrophenyl)



and the reaction of Cu with salicylalaniline to form uncharacterized copper complexes.[20] In the former case, substantial rate enhancements (as large as 64-fold) are reported when the entire reaction mixture is irradiated with ultrasound. This synthetically important rate increase was postulated to arise from multiple possible effects, including particle size reduction and surface cleaning. In addition, ultrasound has been used to enhance[21,22] the reduction of Cu salts by alkali metals to form highly reactive copper dispersions.[23]

To determine the effect of ultrasound on the reactivity of the copper surface, we choose to use the Ullmann coupling reaction as a kinetic probe. To this end, we irradiated a slurry of the copper powder *in the absence of substrate* (2-iodonitrobenzene) and then examined the rate of coupling upon addition of substrate. As shown in Figure 3, we find substantial rate enhancements upon ultrasonic pretreatment of the Cu powder. The induction period observed in the absence of ultrasound complicate a quantitative comparison of rates. At early stages of the reaction, pretreatment of Cu powder with ultrasound can increase rates more than 50-fold, while at later stages the rate increase is 10-fold. The effectiveness of pretreatment demonstrates that ultrasound produces an irreversible change in the Cu powder (i.e., the removal of the oxide coating), even in the absence of substrate. Enhanced mass transport is *not* responsible for the sonochemical improvements.

In conclusion, ultrasonic irradiation of Cu powder removes the passivating oxide coating, induces significant surface damage, and enhances the reactivity of Cu powder. Interparticle collisions driven by shock waves are probably the causative event.

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Chemical Vapor Deposition of Copper and Copper Oxide Thin Films from Copper(I) *tert*-Butoxide

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The low-temperature deposition of thin-film materials from molecular transition-metal precursors is an area of rapidly growing interest.[1-4] We now describe the deposition of copper-containing films from copper(I) *tert*-butoxide tetramer, $[Cu(O\text{-}t\text{-}Bu)]_4$,[5] which was chosen because it is one of the more volatile molecular derivatives of copper known. These results are related to efforts directed toward the chemical vapor deposition of thin films of the

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new copper oxide based high-temperature superconductors.[6,7]

Films of metallic copper have previously been vapor deposited by evaporation from the bulk metal,[8] by thermal decomposition of copper(I) and copper(II) halides,[9] and by various techniques from 1,1,1-trifluoro-2,4-pentanedionato (tfa) or 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfa) complexes of copper(II). For example, thermal decomposition of $Cu(tfa)_2$ or $Cu(hfa)_2 \cdot H_2O$,[10] argon/hydrogen plasma enhanced deposition from $Cu(hfa)_2$,[11] photochemical decomposition of $Cu(hfa)_2 \cdot EtOH$ or $Cu(hfa)_2 \cdot 2EtOH$,[12] and laser photothermal decomposition of $Cu(hfa)_2$[13] all give metallic copper films. Some of these methods result in appreciable fluoride contaminants in the deposits; a volatile copper precursor free of halogen or halogen-containing ligands is accordingly of interest.

$[Cu(O\text{-}t\text{-}Bu)]_4$, which is a white air-sensitive solid, is introduced into a Pyrex vacuum system via a break-seal ampule after the system has been baked out and evacuated to a base pressure of 10^{-8} Torr. The precursor sublimes slowly at a pressure of 10^{-5} Torr from a reservoir that is heated to 100 °C by an oil bath. The precursor travels via 5-cm diameter glass tubing into the deposition zone, which is maintained at a constant temperature of 400 °C by a tube furnace. The glass tubing leading to the deposition chamber is warmed to 100 °C with heating tape to prevent the precursor from condensing before reaching the hot zone.

Chemical vapor deposition (CVD) from $[Cu(O\text{-}t\text{-}Bu)]_4$ yields thin films of copper metal on a variety of substrates, including borosilicate glass, silicon, KBr, quartz, aluminium, and graphite. No appreciable differences in the film morphology as a function of substrate were noted. The films are approximately 1.5 μm thick and are polycrystalline; they exhibit sharp X-ray powder diffraction profiles characteristic of bulk copper. Auger analysis confirms the presence of copper, indicates that the films contain approximately 5% oxygen, and shows that carbon is essentially absent (<1%). Scanning electron microscopy (SEM) indicates that the films are uniform and featureless. Mass spectrometric analysis of the gaseous byproducts exiting the hot zone reveals that *tert*-butyl alcohol is the only species present. This suggests a decomposition mechanism involving cleavage of the Cu–O bonds to produce *tert*-butoxy radicals, which subsequently abstract hydrogen atoms from surface-bound hydroxyl groups on the surrounding glass chamber.

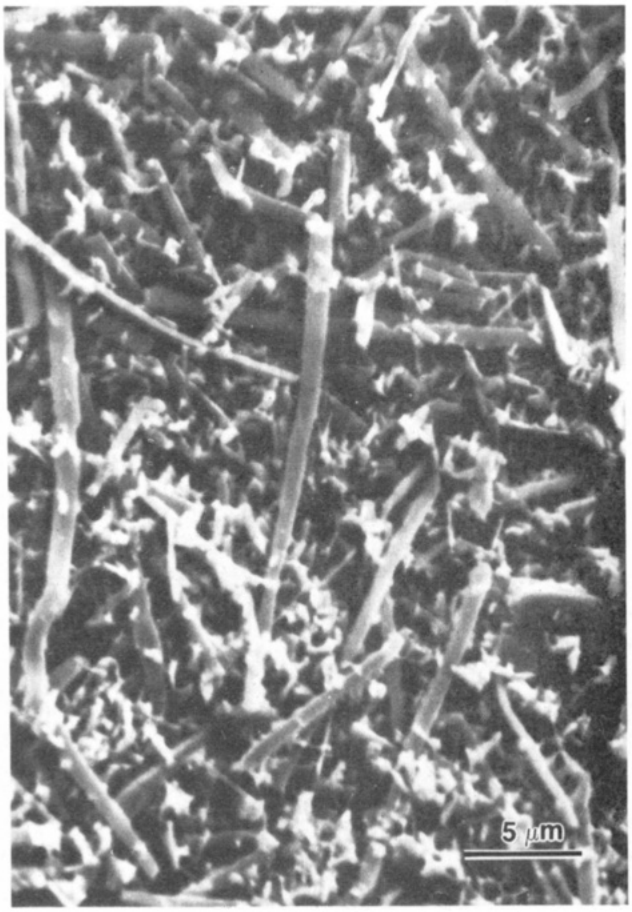

Figure 1. Scanning electron micrograph of Cu_2O deposit at 15 kV showing whisker formation.

These results establish that metallic films can be deposited from a molecular alkoxide precursor;[14] we have previously shown that metallic palladium and platinum thin films may be grown by CVD from organometallic precursors such as the allyl compounds $Pd(C_3H_5)_2$ and $Pt(C_3H_5)_2$.[2,3]

Depositions from $[Cu(O\text{-}t\text{-}Bu)]_4$ were also conducted at 400 °C and 10^{-5} Torr after dosing the walls of the vacuum chamber with small amounts of water. Under these conditions, water slowly desorbs from the reactor walls during CVD, and instead of a metallic film, we observed the formation of a reddish-yellow deposit on borosilicate glass, stainless steel, aluminium, copper, and silicon. This material gives sharp X-ray diffraction peaks at the proper *d* spacings and intensities for copper(I) oxide, Cu_2O. The Auger and XPS spectra[14] confirm the composition of the deposit and establish the absence of carbon, copper metal, and copper(II) oxide, CuO. SEM images of the deposits reveal the presence of Cu_2O whiskers that are 0.5–0.75 μm thick and up to 35 μm long (Figure 1). The whiskers are brittle and can be easily removed from the substrate. Mass spectrometric analysis of the gaseous products formed during the deposition again indicate the presence of only *tert*-butyl alcohol. If the depositions are conducted in the presence of D_2O, the mass spectrum of the evolved *tert*-

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butyl alcohol changes. The peaks at 31 and 59 mass units, which are the most intense peaks in the spectrum of unlabeled *tert*-butyl alcohol, decrease in intensity; correspondingly, the peaks at 32 and 60 mass units increase in intensity.[15] The mass 31 and 59 species have been ascribed to the hydroxyl-containing ions CH_2OH^+ and $C_3H_6OH^+$, respectively,[16] and therefore the D_2O experiment clearly suggests that *tert*-butyl alcohol specifically labeled at the hydroxyl site is formed. Although we cannot at present rule out the possibility that H/D exchange with D_2O occurs *after* the formation of unlabeled *tert*-butyl alcohol during CVD, the data are most consistent with a mechanism involving direct hydrolysis of $[Cu(O\text{-}t\text{-}Bu)]_4$.[19] This study represents the first chemical vapor deposition of pure copper(I) oxide, although a chemical vapor transport method has been reported previously.[17]

Further work will be directed toward the use of carrier gases such as hydrogen and oxygen, which would respectively reduce the level of contaminants in the copper film and promote the formation of CuO. Depositions conducted in the presence of $H_2{}^{18}O$ are being investigated to determine unambiguously the source of oxygen in the Cu_2O deposits.

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(15) Relative to the $m/e = 41$ base peak ($I = 100$), the peaks at 31, 32, 59, and 60 mass units have relative intensities of 67, 0, 198, and 7, respectively, when the depositions are conducted in the presence of H_2O, and 20, 4, 55, and 14 when the depositions are conducted in the presence of D_2O. Other mass peaks have the same relative intensities in both spectra.

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Hydrogen-Bond Directed Cocrystallization as a Tool for Designing Acentric Organic Solids

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One of the dilemmas facing chemists trying to make useful organic nonlinear optical materials is that they have exquisite control over designing individual molecules but practically no control over designing molecular packing patterns in solid-state materials. Since even-order nonlinear optical properties (such as second harmonic generation) occur only in acentric materials[1] and since the magnitude of the effect depends strongly on relative orientations of molecular and crystallographic axes,[2] progress in this field requires that new useful solid-state design tools be developed. Despite notable advances in understanding the molecular basis of organic crystal growth processes,[3] there are still no general synthetic tools available for controlling the structures of molecular aggregates or crystals. We have shown previously how hydrogen-bond interactions in organic compounds can be used to direct formation of aggregate structures with predictable connectivity patterns and, in some cases, with predictable symmetry.[4] In this paper we demonstrate how these concepts can be applied to the design and preparation of acentric organic cocrystals, exemplified by the structure of a 1:1 cocrystalline complex of 4-aminobenzoic acid (4-ABA) and 3,5-dinitrobenzoic acid (3,5-DNBA), I.

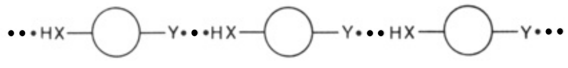
Figure 1. Photograph of a typical crystal of I (approximately 0.5 cm along the longest edge). On the right is a schematic diagram of the crystal showing Miller index assignments of the prominent faces.

Any single hydrogen bond is inherently acentric when the hydrogen atom is covalently bonded to one electronegative atom, X, and associated with another atom, Y ($X \neq Y$):

$$-Y\cdots HX$$

1

If the donor, XH, and acceptor, Y, groups are on the same molecule and positioned so that hydrogen-bonded chains form, these chains will necessarily be acentric, as shown:



2

Acentric one-dimensional aggregates such as this are the common packing patterns for nitroanilines and isographic analogues.[4c] Two-dimensional acentric aggregates, of which squaric acid is a prototype,[5] can be designed in a similar fashion with multiple donor and acceptor sites, as shown in **3**.

The same principles of molecular organization can be applied to the design of cocrystals. For example, if Y and HX are on different molecules an intermolecular bond of the type $-Y\cdots HX-$ will lead to a heterodimer. Likewise, two different carboxylic acids substituted with Y and HX

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